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Balanced Basis Sets
In the Calculation of Potential Energy Curves
For Diatomic Molecules

by

V. J. BARCLAY, B. Sc. (Hons.)

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Ottawa-Carleton Chemistry Institute

Carleton University
Ottawa, Ontario
January 12th, 1990

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Abstract

"Balanced" basis sets, which describe the internuclear region as well as the nuclear region, are examined in the context of an *ab initio* selection-extrapolation configuration-interaction method (MRD-CI). The sets are balanced by adding bond functions (BF's), which are *s*, *p* and *d*-type orbitals at the bond mid-point, to atomic-centred molecular basis sets, which have double and triple sets of valence-shell orbitals (DZ and TZ) and one or two sets of polarization functions (PF's).

Potential energy curves and spectroscopic constants were calculated for the ground states of the hydrides H_2 , OH, NaH, MgH, AlH, SiH, PH, SH, HCl, and for the ionized species OH^+ and OH^{++} , and for the $A^3\Sigma_u$, $w^3\Delta_u$ and $B^3\Pi_g$ excited states of N_2 . The basis sets containing bond functions gave curves and constants superior to the DZP and (where calculated) TZPP results, and of quality similar to large basis set calculations in the literature. The single and double ionization potentials of OH, and the term energies of the N_2 excited states had error at the atomic asymptotes for *all* basis sets.

The dissociation energies of the ground states of ten first-row diatomics (C_2 , N_2 , O_2 , F_2 , CN, CO, CF, NO, NF, and FO) were studied using balanced basis sets. A correlation was found to exist between the actual bond order of a species, and the number and kinds of orbitals which comprise the optimum BF. For MRD-CI diatomic calculations, the following BF's should be added to a DZP basis set (*sp*) (for a bond order of 1); 2(*sp*) (B. O. 1.5); (*spd*) (B. O. 2); 3(*sp*) (B. O. 2.5); 2(*spd*) (B. O. 3). The prescribed BF basis method was tested on the 26 second-row congeners Si_2 , P_2 , S_2 , Cl_2 , SiP, SiS, SiCl, PS, PCl, and ClS, and mixed-row congeners SiN, SiO, SiF, PO, PF, SF, SiC, PN, SO, ClF, CP, CS, CCl, NS, NCl, and ClO. An average error of 6% and a maximum error of 10% relative to known experimental D_e 's was found; compared to an average error of 18% for TZPP calculations, this enabled the prediction of several dissociation energies for poorly-known species.

The balanced basis set / MRD-CI method yielded a positive D_e for ground state Cr_2 , in contrast to the SCF D_e which is unbound by ≈ 20 eV. The noise present in the calculated curve was attributed to an extremely restricted CI space.

The basis set superposition error (BSSE) was discussed relative to molecular basis set incompleteness (MBSI). The counterpoise-corrected curve for a DZP+BF basis was shown to be physically unreasonable, and the use of counterpoise corrections for covalent curves is not recommended.

Based on the results of calculations reported in this thesis, the addition of bond functions to the basis sets of diatomic molecules is recommended as an efficient means of improving the molecular description.

Keywords

Topics:

potential energy curve — diatomic molecules — bond function (BF) — polarization function (PF) — balanced basis set — bond order — basis set superposition error (BSSE) — molecular basis set incompleteness (MBSI) — dissociation energy — spectroscopic constants — Multiple Reference Single and Double Excitation Configuration Interaction (MRD-CI) —

Molecules (Ground State):

H_2 — OH — OH^+ — OH^{+2} — NaH — MgH — AlH — SiH — PH — SH — HCl — C_2 — N_2 — O_2 — F_2 — CN — CO — CF — NO — NF — FO — Si_2 — P_2 — S_2 — Cl_2 — SiP — SiS — SiCl — PS — PCl — ClS — SiN — SiO — SiF — PO — PF — SF — SiC — PN — SO — ClF — CP — CS — CCl — NS — NCl — ClO — Cr_2

Molecules (Excited State):

$\text{N}_2(A^3\Sigma_u)$ — $\text{N}_2(w^3\Delta_u)$ — $\text{N}_2(B^3\Pi_g)$

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Readers' Guide

This thesis was designed in modular fashion. The page numbering is specific to each Chapter, and within each chapter is obeyed the sequence: all written text, followed by all pertinent references, followed by all tables, and lastly, all figures. There is thus some repetition in the text and references, but it was felt this would make each "story" clearer within a particular chapter. A reader interested in only a particular chapter would thus be able to excerpt it more easily.

The reader may find Appendix A, which lists variables and constants used, and some conversion factors for the units used, a helpful reference.

Table of Contents

Abstract	i
Keywords	iii
Acknowledgements	iv
Reader's Guide	vii
Table of Contents	viii
List of Tables	xiii
List of Figures	xvi
1 Introduction	1-1
1.1 Fundamental Equations	1-4
1.2 Approximations to the Exact Solution	1-5
1.2.1 <i>Basis Set Formulation</i>	1-5
1.2.2 <i>Inclusion of Electron Correlation</i>	1-8
1.3 Experimental Determination of Dissociation Energies	1-11
1.3.1 <i>Spectroscopic Method of Determining D_0</i>	1-12
1.3.2 <i>Thermochemical Determination of D_0</i>	1-12
1.4 Spectroscopic constants	1-13
1.5 References	1-14
2 Methods	2-1
2.1 Introduction	2-1
2.2 Basis Sets	2-2
2.2.1 <i>Atom-Centred Basis Sets</i>	2-2
2.2.2 <i>Optimization of Polarization Exponents</i>	2-3
2.2.3 <i>Bond Functions</i>	2-4
2.3 Symmetry Considerations	2-4

2.4	Construction of the LCAO's	2-5
2.5	Freezing Orbitals	2-5
2.6	Selection-Extrapolation Technique	2-6
2.6.1	Reference Configurations	2-8
2.6.2	Davidson Correction and Variations	2-9
2.7	Dipole Moment	2-9
2.8	Obtaining the Relative Energies	2-10
2.9	Counterpoise Correction Method	2-10
2.10	Potential Energy Curve Function	2-11
2.11	References	2-12
3	Dihydrogen	3-1
3.1	Introduction	3-1
3.2	Results and Discussion	3-3
3.2.1	BF's vs. PF's: Minimum Energy	3-3
3.2.2	BF's vs. PF's: Difference Curves	3-4
3.3	References	3-9
4	The Single and Double Ionization Potentials of Hydroxyl	4-1
4.1	Introduction	4-1
4.2	Results and Discussion	4-2
4.2.1	OH	4-3
4.2.2	OH ⁺	4-5
4.2.3	OH ²⁺	4-6
4.2.4	Ionization Potentials	4-7
4.2.5	Effect of Ghost Orbitals	4-9
4.3	References	4-12
5	Diatomic Hydrides of the Second Row:	5-1
5.1	Introduction	5-1
5.2	Results and Discussion	5-3

5.2.1	<i>Second-Row Atoms</i>	5-3
5.2.2	<i>Second-Row Hydrides</i>	5-4
5.2.3	<i>Individual Hydrides: Results and Comparison</i>	5-5
5.2.4	<i>Core freezing</i>	5-15
5.2.5	<i>Results of the DZP and BF1 basis sets</i>	5-16
5.2.6	<i>Results of the TZPP and BF2 basis sets</i>	5-17
5.2.7	<i>Dipole Moments</i>	5-17
5.2.8	<i>Concluding Remarks</i>	5-18
5.3	<i>References</i>	5-19
6	Three Excited States of Dinitrogen:	6-1
6.1	<i>Introduction</i>	6-1
6.2	<i>Results</i>	6-3
6.2.1	<i>Absolute and Excitation Energies of the Atoms</i>	6-3
6.2.2	<i>Dissociation Energies</i>	6-4
6.2.3	<i>MO Energy Levels</i>	6-5
6.2.4	<i>Term Energies</i>	6-6
6.2.5	<i>Potential Curve of the $B^3\Pi_g$ State</i>	6-7
6.2.6	<i>Morse Function and Spectroscopic Parameters</i>	6-8
6.2.7	<i>Comparison with Other Work</i>	6-9
6.2.8	<i>BSSE or MBSI? Counterpoise Correction</i>	6-10
6.3	<i>References</i>	6-11
7	Diatomics of the First and Second Row	7-1
7.1	<i>Introduction</i>	7-1
7.2	<i>Results and Discussion: Background Details</i>	7-2
7.2.1	<i>C_2 and its Congeners Si_2 and SiC</i>	7-4
7.2.2	<i>CN and its Congeners SiP, SiN and CP</i>	7-11
7.2.3	<i>CO and its Congeners SiS, SiO and CS</i>	7-13
7.2.4	<i>CF and its Congeners $SiCl$, SiF and CCl</i>	7-22
7.2.5	<i>N_2 and its Congeners P_2 and PN</i>	7-27

7.2.6	<i>NO and its Congeners PS, PO, and NS</i>	7-31
7.2.7	<i>NF and its Congeners PCl, PF and NCl</i>	7-37
7.2.8	<i>O₂ and its Congeners S₂ and SO</i>	7-42
7.2.9	<i>FO and its Congeners SCl, SF and ClO</i>	7-46
7.2.10	<i>F₂ and its Congeners Cl₂ and ClF</i>	7-51
7.3	Results and Discussion: Overall Patterns	7-56
7.4	References	7-64
8	The Dissociation Energy of Dichromium	8-1
8.1	Introduction	8-1
8.2	Background	8-3
8.3	Methods	8-7
8.3.1	<i>Atoms</i>	8-7
8.3.2	<i>Dimer</i>	8-9
8.4	Results and Discussion	8-10
8.4.1	<i>Atomic Calculations</i>	8-10
8.4.2	<i>Molecular Calculations: Basis Set Explorations</i>	8-10
8.4.3	<i>BSSE Corrections</i>	8-16
8.4.4	<i>Potential Energy Curves and Spectroscopic Constants for Cr₂</i>	8-17
8.5	References	8-21
9	Concluding Remarks	9-1
9.1	Summary	9-1
9.2	Asymptotic Error	9-4
9.3	Relevance to Other Work	9-4
9.4	BF's Used to Create a Reaction Surface	9-6
9.5	BSSE vs. MBSI	9-8
9.6	References	9-11
A	Variables, Constants and Units Used	A-1
A.1	Variables and Constants Used	A-1

A.2 Energy Conversion Factors	A-3
B Listings of Some Short Programs Used	B-1
B.1 VBVIBE: Numerov-Cookey Vibrotational Levels	B-1
B.2 VBGMF-FIT: Non-Linear Least Squares Fitter for GMF-5	B-9
B.3 VBEVJFIT5: Fitter for Spectroscopic Equation	B-25
B.4 VBLOTPE: Plotter for Potential Energy Curve	B-27
B.5 VBPARAB: Determination of Parabolic Minimum	B-31
C Sample Worksheet and Datafile	C-1
C.1 Sample Worksheet for Si ₂	C-1
C.2 Sample Datafile: Si ₂	C-2
D Comparative Timings	D-1
D.1 Comparative Timings: BF's vs. PF's for H ₂	D-1

List of Tables

2	Methods	2-1
2.1	Optimization of the Polarization Exponents of N_2	2-14
2.2	Cartesian Orbitals in D_{2h} Symmetry	2-15
3	Dihydrogen	3-1
3.1	Hydrogen Basis Set	3-12
3.2	Absolute Energy of H_2 at R_e : Basis Set Variation	3-13
3.3	"Best" BF Curve for H_2	3-14
3.4	"Best" PF Curve for H_2	3-15
3.5	Morse Parameters for PF and BF Curves for H_2	3-16
3.6	Vibrotational Levels for BF and PF Curves	3-17
3.7	Calculated Spectroscopic Constants for BF and PF Curves	3-18
4	The Single and Double Ionization Potentials of Hydroxyl	4-1
4.1	The Absolute Energies of $O(^3P)$, $H(^2S)$, and $O(^4S)$	4-15
4.2	Molecular and Spectroscopic Constants of OH and OH^+	4-16
4.3	Effect of "Ghost Orbitals" on the O Atom Energy	4-17
5	Diatomic Hydrides of the Second Row	5-1
5.1	TZPP Basis Sets for Second-Row Atoms	5-24
5.1.a	Sodium, Magnesium, and Aluminum	5-24
5.1.b	Silicon and Phosphorus	5-25
5.1.c	Sulfur and Chlorine	5-26
5.2	Atomic Energies for DZP and TZPP Basis Sets	5-27
5.3	Calculated Properties for Ground State NaH	5-28
5.4	Calculated Properties for Ground State MgH	5-29
5.5	Calculated Properties for Ground State AlH	5-30
5.6	Calculated Properties for Ground State SiH	5-31

5.7	Calculated Properties for Ground State PH	5-32
5.8	Calculated Properties for Ground State SH	5-33
5.9	Calculated Properties for Ground State HCl	5-34
5.10	TZPP and TZPP+BF Well Depths of Second-Row Hydrides	5-35
5.11	Average Absolute Deviation of DZP and DZP+BF Values	5-36
5.12	Calculated Dipole Moments of the Second-Row Hydrides	5-37
6	Three Excited States of Dinitrogen:	6-1
6.1	Absolute Energies of 4S and 2D States of Nitrogen Atom	6-13
6.2	Dissociation and Term Energies of $N_2(A^3\Sigma_u^+)$	6-14
6.3	Dissociation and Term Energies of $N_2(B^3\Pi_g)$	6-15
6.4	Dissociation and Term Energies of $N_2(w^3\Delta_u)$	6-16
6.5	BF and CC Potential Energy Curves for $N_2(B^3\Pi_g)$	6-17
6.6	Morse Curve Fits for $N_2(B^3\Pi_g)$: F-CI, CC and RKR	6-18
6.7	Spectroscopic Constants for $N_2(B^3\Pi_g)$: F-CI, E(CC) and RKR	6-19
6.8	Summary of Calculations on Three Excited States of N_2	6-20
7	Diatomics of the First and Second Row	7-1
7.1	Ground State Atomic Energies of C, N, O, F, Si, P, S and Cl	7-76
7.2	Energies of C_2 and its Congeners Si_2 and SiC	7-77
7.3	Summary of Previous Work on C_2	7-79
7.4	Energies of CN and its Congeners SiP, SiN and CP	7-81
7.5	Energies of CO and its Congeners SiS, SiO and CS	7-83
7.6	Energies of CF and its Congeners SiCl, SiF and CCl	7-85
7.7	Energies of N_2 and its Congeners P_2 and PN	7-87
7.8	Summary of Previous Work on N_2	7-88
7.9	Energies of NO and its Congeners PS, PO, and NS	7-89
7.10	Energies of NF and its Congeners PCl, PF and NCl	7-91
7.11	Energies of O_2 and its Congeners S_2 and SO	7-93
7.12	Summary of Previous Work on O_2	7-95

7.13	Energies of FO and its Congeners SCl, SF and ClO	7-97
7.14	Energies of F ₂ and its Congeners Cl ₂ and ClF	7-99
7.15	Summary of Previous Work on F ₂	7-101
7.16	Summary of States and Equilibrium Bond Lengths Used	7-103
7.17	Reference Dissociation Energies vs. DZP Results	7-104
7.18	Reference Dissociation Energies vs. Optimum BF Results	7-105
7.19	Reference Dissociation Energies vs. Prescribed BF	7-106
7.20	Reference Dissociation Energies vs. TZPP Results	7-107
7.21	Proposed Dissociation Energies for Selected Diatomics	7-108
8	The Dissociation Energy of Dichromium	8-1
8.1	Summary of Previous Work on Cr ₂	8-24
8.2	Basis Set for Chromium	8-28
8.3	Calculated Energies of Chromium Atom	8-29
8.4	Calculated Dissociation Energies of Cr ₂	8-30
8.4.a	<i>DZ Calculations</i>	8-30
8.4.b	<i>DZ* Calculations</i>	8-31
8.5	Counterpoise-corrected Dissociation Energies	8-32
8.6	Potential Energy Curve: MO's and NO's	8-33
8.7	More Potential Energy Curves: Main and Threshold Variations	8-34
8.8	Molecular and Spectroscopic Constants for Cr ₂ Curves	8-35

List of Figures

3	Dihydrogen	3-1
3.1	Absolute Energy of H_2 vs. the Number of Extra Orbitals	3-19
3.2	Energy Difference Between PF and BF Curves and the Exact H_2 Curve	3-20
4	The Single and Double Ionization Potentials of Hydroxyl	4-1
4.1	Computed Potential Energy Curves for OH, OH^+ and OH^{2+}	4-18
5	Diatomic Hydrides of the Second Row	5-1
5.1	Ground State Potential Energy Curves for NaH	5-38
5.2	Ground State Potential Energy Curves for MgH	5-39
5.3	Ground State Potential Energy Curves for AlH	5-40
5.4	Ground State Potential Energy Curves for SiH	5-41
5.5	Ground State Potential Energy Curves for PH	5-42
5.6	Ground State Potential Energy Curves for SH	5-43
5.7	Ground State Potential Energy Curves for HCl	5-44
6	Three Excited States of Dinitrogen:	6-1
6.1	Effect of Bond Functions on Valence and Low-Lying Virtual MO's	6-21
6.2	RKR and DZP + BF Curves of $N_2(X^1\Sigma_g^+)$ and $N_2(B^3\Pi_g)$	6-22
6.3	RKR, DZP + BF, and Counterpoise-corrected Curves of $N_2(B^3\Pi_g)$	6-23
8	The Dissociation Energy of Dichromium	8-1
8.1	Variation of Cr_2 Potential Energy Curve with Treatment	8-36

Chapter 1

Introduction

There is something fascinating about science. One gets such wholesale returns of conjecture out of such a trifling investment of fact.

-Mark Twain

Although he intended to be sardonic, Mark Twain could easily have been speaking about the very fundamentals of quantum chemistry. *Ab initio* methods, as the name suggests, start "at the beginning," with nothing more than the electronic and nuclear charges, and the nuclear masses of some given atoms—and from these few facts, are able to "conjecture" a great deal about a molecule made from these atoms—everything from its bond length to bond strength to dipole moment to the electronic spectrum. It is a breathtakingly simple premise, but in practice as Davidson notes, the truly *ab initio* calculation is rare. Most methods are what he calls "calibrated *ab initio*" methods, which are built on experience with related atoms or molecules.[1]

In his book, *Introduction to Theoretical Chemistry*, Kutzelnigg provides a fascinating overview of the growth of the field of quantum chemistry since its inception in the 1920's, when Schrödinger formulated the wave equation

$$H\Psi = E\Psi \quad (1.1)$$

and Dirac proclaimed that the entirety of chemistry was contained in the basic equations of quantum mechanics.[†] Kutzelnigg roughly divides the development of quantum chemistry into three phases. In the first phase, ca. 1927–35, theorists showed how the rules of valence theory were connected to quantum mechanics. Good calculations on He and H₂ appeared, but numerical approximate solutions to the many-body equation for larger systems were too onerous and complex to do in this pre-computer age.[2]

[†] Even prior to this time, Kutzelnigg points out, chemists were grappling with ideas of molecules and atoms, and electromagnetism and chemical bonds, sometimes at loggerheads with their physicist counterparts.

The second phase was a time of relative quiescence, when "the problems which could be solved through thinking had been exhausted, and for those which had to be solved through computation, the time was not ripe." [2] The outstanding developments in this phase were Hückel's theory of π -electron systems and a broadening, by Mulliken, of the understanding of the chemical bond.

The third phase, the phase of "the quantitative model of the chemical bond," [1] began around 1950, and has been characterized by increasingly diverse and demanding applications of quantum chemical theory. Since about 1955 computer technology has made such advances that numerical approximations of quantitative accuracy could be made, and most molecular properties such as dissociation energy, dipole moment, fundamental frequency, equilibrium bond length, ionization potential *etc.* can be calculated to within chemical accuracy for small systems.

During this third and current phase, most of the advances in the *ab initio* technique used in this thesis were made. Although Hartree was calculating atomic energies in the 1930s, using a method where the electronic charge in the occupied orbitals is approximated as an "averaged cloud" of negative charge, the standardized Hartree-Fock method was worked out by Roothaan in 1951. Further progress in *ab initio* techniques was then made on two fronts: (i) formulation of the basis set, *i.e.*, the functions which are used to approximate Ψ in the Schrödinger wave equation, and (ii) the inclusion of electron correlation. These are discussed in more detail in Section 1.2.

In his general introduction to the 1984 Faraday Symposium, Davidson pointed out three important criteria for an approximate *ab initio* method to be considered successful. The method should be: [1][†]

- (i) computationally tractable for systems of chemical interest;
- (ii) conceptually simple, for explaining and comparing results obtained, and for accurately predicting outcomes; and
- (iii) widely applicable to well-known and unknown systems, as well as polyatomic systems.

Bond function basis sets used in conjunction with the MRD-CI method (to be discussed in detail later) which was used in this thesis may be considered to meet every one of these criteria to a degree better than or equal to other methods currently in use. This thesis

[†] To these should be appended, of course, a requirement that the method give accurate results!

demonstrates points (i) and (ii) explicitly.

Without attempting to be all-inclusive, this introductory section will outline the essential equations with which a theoretical calculation concerns itself, and will then consider some approximations to a solution which are encountered in the literature. How calculated quantities relate to experimentally-known values will be outlined, and some commonly used experimental techniques will be briefly discussed, since experimental quantities are so important in judging the quality of a calculation.

The remainder of the thesis consists of studying the specifics of the bond-function/MRD-CI method in a variety of applications. The basis set augmentation is studied with regard to the concept of "balance," i.e., achieving as good a level of the molecular description as an atomic description.† In Chapter 2, the MRD-CI method used to study basis set balance is considered in detail. In Chapter 3, a bond function basis set is used to replicate a very simple system for which the absolute energy is known to a high degree of accuracy. The calculation of accurate ionization potentials of a simple first-row hydride is explored in Chapter 4. The scope of hydrides studied is expanded to the ground states of the second-row hydrides in Chapter 5. Chapter 6 considers how this method can be applied to the case of excited states of a first-row molecule. The answer to this question suggested a trend with respect to molecular bond order, and Chapter 7, which may be considered the heart of this thesis, investigates the bond order-bond function phenomenon. Chapter 8 reports a study of a very difficult CI calculation to which the bond function method has been applied with some success. Chapter 9 concludes with general remarks on bond functions in the context of other basis set explorations; the problem of incompleteness; and the extension of balanced basis sets to the third Davidson criterion.

For ease of handling and reading, this thesis is modularized. The background sections relevant to the molecules studied at the end of each chapter are reported there, instead of in this Introduction. As well, the references for each chapter are included in that chapter, and the page numbering is also specific to each chapter.

† This usage of "balance" is to be distinguished from the atom-atom basis set "formal" and "physical" "balance" referred to by Mulliken.[3] The question of balance is also discussed by Smith.[4]

1.1 Fundamental Equations

Quantum chemistry is based on the assumption that the chemical bond can be described by the laws of quantum mechanics. The Schrödinger wave equation can thus be solved to give eigenvalues which will correspond to the quantized energy levels available to that system. The full non-relativistic Hamiltonian operator for a diatomic molecule with n electrons can be written:[†]

$$H(\mathbf{R}_a, \mathbf{R}_b, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = T_a + T_b + \sum_{i=1}^n T_i + \frac{1}{4\pi\epsilon_0} \left\{ - \sum_{i=1}^n \frac{Z_a e^2}{|\mathbf{R}_a - \mathbf{r}_i|} - \sum_{i=1}^n \frac{Z_b e^2}{|\mathbf{R}_b - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j}^n \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_a Z_b e^2}{|\mathbf{R}_b - \mathbf{R}_a|} \right\} \quad (1.2)$$

where the first two terms on the RHS are the kinetic energies of the nuclei, and the third term is the kinetic energy of the electrons:

$$T_a = -\frac{\hbar^2}{2M_a} \nabla_a^2; \quad T_i = -\frac{\hbar^2}{2m} \nabla_i^2 \quad (1.3)$$

The fourth and fifth terms are the Coulombic attractions of the i -th electron and the nuclei, the sixth term is the electron-electron repulsion and the last term is the nuclear-nuclear repulsion.

The Born-Oppenheimer approximation allows the separation of electronic and nuclear motion, by "clamping" the nuclei in a given position R so that they are at rest while the electrons move. The Born-Oppenheimer approximation is ordinarily a very good assumption since the electrons have a very much smaller mass than the nuclei, and so for a given time interval the electrons move about a great deal but the nuclei barely stir. The Schrödinger wave equation is rewritten:

$$H\Phi = (T_a + T_b + H_R)\Phi = E\Phi \quad (1.4)$$

where the electronic Hamiltonian H_R may then be written in atomic units as:

$$H_R = \sum_{i=1}^n T_i - \sum_{i=1}^n \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} - \sum_{i=1}^n \frac{Z_b}{|\mathbf{R}_b - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_a Z_b}{R} \quad (1.5)$$

[†] The reader should note that variables are defined according to the list in Appendix A.

where the kinetic energy operators for the nuclei are gone, and the last term on the RHS is now a constant at a given $R = |\mathbf{R}_a - \mathbf{R}_b|$.

The full molecular wavefunction Φ is assumed to be able to be written as a product of the electronic wavefunction Ψ_R and the nuclear wavefunction $\chi(\mathbf{R})$:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{R}) = \Psi_R(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \chi(\mathbf{R}) \quad (1.6)$$

so that the Schrödinger wave equation may be expressed as:

$$(T_a + T_b) \Psi_R \chi(\mathbf{R}) + E_R \Psi_R \chi(\mathbf{R}) = E \Psi_R \chi(\mathbf{R}). \quad (1.7)$$

Dividing out Ψ_R on both sides, one can obtain the effective Schrödinger equation for the motion of the nuclei, in which the electronic energy E_R is the potential energy operator:

$$(T_a + T_b + E_R) \chi(\mathbf{R}) = E \chi(\mathbf{R}). \quad (1.8)$$

The eigenvalue equation

$$H_R \Psi_R = E_R \Psi_R \quad (1.9)$$

is then solved by *ab initio* techniques such as the one used in the current work, MRD-CI, to determine the electronic energy for a wavefunction Ψ_R which has been constructed from basis sets of the kind explored in this thesis. For the remainder of the discussion, it will be understood that the electronic wavefunction is solved for at a fixed R value, and the subscript R will be dropped.

1.2 Approximations to the Exact Solution

The ability to calculate accurate potential energy curves for diatomics and polyatomics remains an important goal of theoretical chemistry. Although improved algorithms for rapid evaluation of integrals and fast solution of eigenvalue equations are available, and significant advances have been made in the hardware available for such computations, it is nonetheless desirable—and for larger species, necessary—to work with as small and efficient a basis set and configuration space as possible.

1.2.1 Basis Set Formulation

The selection of functions used to build the overall wavefunction is important because even today the calculation of two-centre integrals remains a time-consuming step. It is now

well recognized that all basis sets suffer from basis set incompleteness or truncation error to some degree, since they are of finite size. The aim in developing a good basis set is thus to construct the most flexible and "infinite-seeming" basis set from as few functions as possible. Boys' suggestion to use Gaussian-type orbitals (GTO's) instead of Slater-type orbitals (STO's) in constructing the wavefunction, simplified and speeded up calculations considerably.[2] A Cartesian Gaussian function with quantum numbers (l, m, n) centred on an atomic nucleus at r_a may be represented as:[5]

$$\psi(l, m, n, \zeta) = (x - x_a)^l (y - y_a)^m (z - z_a)^n \exp\{-\zeta_a(r - r_a)^2\} \quad (1.10)$$

The coefficients c_i of linear combinations of N_c Gaussian functions can be held in fixed ratio (contracted GTO's), and this permits greater descriptive flexibility while saving computational resources:

$$\psi = \sum_{i=1}^{N_c} c_i \psi_i. \quad (1.11)$$

The electronic wavefunctions for the carbon atom which has the occupation $1s^2 2s^2 2p^2$ would thus be written as a product of the orbitals:

$$\psi_C = \psi_{1s}\alpha(1)\psi_{1s}\beta(2)\psi_{2s}\alpha(3)\psi_{2s}\beta(4)\psi_{2p}\alpha(5)\psi_{2p}\alpha(6) \quad (1.12)$$

where the terms $\alpha(i)$ and $\beta(i)$ are taken as spin eigenfunctions of the i -th electron, and the Pauli principle, that no two electrons can have the same full set of quantum numbers, is obeyed. The electrons are indistinguishable, however, so the most compact way of denoting the electron permutations possible is by a matrix determinant. In Equation (1.9) the eigenfunction of the Hamiltonian operator may be expressed as a Slater determinant:[6]

$$\Psi(1, 2, \dots, n) = A \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \dots & \psi_{n/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & & \dots & \\ \dots & & \dots & & \\ \psi_1(n)\alpha(n) & \dots & & \dots & \psi_{n/2}(n)\beta(n) \end{vmatrix} \quad (1.13)$$

The orbitals are roughly divisible into "core" and "valence" orbitals. The former kind are doubly occupied and describe the region closest to the nucleus, and are thus affected by little other than the nuclear field. The valence orbitals (the $2s$ and $2p$ orbitals of carbon, for example) contain those paired or singular electrons in the outermost orbitals which are most involved in forming the chemical bond, and it is these orbitals which can change so drastically when the atoms combine to form molecules.

Early quantum chemical calculations had begun by using a "minimal" or "single-zeta" basis set of orbitals for a given species. For example, for a carbon atom two *s*-type orbitals and one set of three *p*-type orbitals would constitute a minimal basis, as would be the case for all first-row atoms. By comparing calculated and observed quantities, it was soon realized that at least double the number of such orbitals should be used (e.g., four *s* orbitals and two sets of *p* orbitals for carbon and similar first-row atoms). Doubling the minimal basis set is a "double zeta" basis set; tripling the minimal set (6 *s* orbitals, 3 sets of *p* orbitals in the example considered here) is a "triple zeta" basis set and so forth.

Comparison with experimental values showed further that not just the *number*, but also the *kind* of basis set function could be changed. Orbitals with a higher angular momentum number *l* than the highest valence orbital (e.g. *d* orbitals for first-row species), termed "polarization" functions, were useful in lowering (stabilizing) the molecular and atomic energies and in improving the dipole moment. Polarization functions represent a distortion of the shape of the atomic orbitals from that adopted in the atom to a shape in which the charge density is shifted away from the nucleus. When the wavefunction is displaced away from the nuclear centre the derivative with respect to the displacement ∂x may be written as:[5]

$$\frac{\partial \psi(l, m, n, \zeta)}{\partial x_a} = l\psi(l-1, m, n, \zeta) - 2\zeta\psi(l+1, m, n, \zeta) \quad (1.14)$$

which contains a wavefunction with a higher angular momentum number, $\psi(l+1, m, n, \zeta)$. Thus, polarization functions are effective in describing the molecule because they mimic a movement of the function away from the nuclear centre.

This movement of the function can in fact be done in a more straightforward way, and experimentation with basis sets has shown that the addition of non-atomic centred basis functions can lead to an improved wavefunction. This idea has been investigated by a few groups, in addition to this group of Wright and co-workers.[7][8] The use of additional gaussian lobes located in the middle of chemical bonds was proposed by Preuss and later Whitten a generation ago.[9][10] Several authors applied the suggestion to a variety of systems at the SCF level [11][12][13][14][15][16][17][18] An observation typical of these reports was given by Rothenberg and Schaefer: "bond functions provide a reasonable alternative to the more conventional type of polarization functions." [15] Burton experimented at the CI level with placing "probe functions" at different locations between the two nuclei and away

from them.[19] Buenker and Peyerimhoff and coworkers tend to use bond functions located nearly invariably at the bond midpoint in many published calculations.[20] Recently, Almlöf and coworkers have investigated "floating" GTO's, which are non-nuclear-centred orbitals whose positions are optimized using a second-order convergent SCF scheme.[21][5][22][23] Most recently of all, Martin, François and Gijbels have explored the issues of bond function accuracy and basis set unsaturation.[24][25][26]

Changing the number and kinds of properly-optimized atomic-centred orbitals will give dissociation energies which increase nearly monotonically to the correct value. However, adding more functions not located on either atomic centre—if the atomic centre is incompletely described—will not lead to such convergence for the dissociation energy; and "overshot" D_e may appear. Where, how many, and what kinds of extra-nuclear functions should then be added to reasonably supplement a standard atomic-centred basis set? The simplest position, that of the bond mid-point, has been adopted throughout this thesis, and it is the composition of that function fixed at the mid-bond point which is systematically explored in the current work.† The premise of this thesis is that bond functions lower the energy in a *bona fide* way because they are able to describe a region of increased electron density. It is therefore expected that a correlation should exist between the simple concept of molecular bond order, which is proportional to the intermolecular charge density, and the optimum composition of the bond function. The work contained in this thesis shows that this is so.

1.2.2 Inclusion of Electron Correlation

The electronic energy may be, to a first approximation, described by a negative charge cloud averaged out through the occupied orbitals in what is termed a self-consistent field (SCF) description. This does not entirely account for the mutual repulsion of electrons, and this leads to the second major problem with which to contend, the inclusion of electron correlation in the approximate solution. A number of different approaches exist in the literature, some of which are touched on briefly here, since reference will be made to other calculations.

Generally speaking, the commonest means of accounting for instantaneous electron

† Another simple scheme would be, for example, to weight the position according to the nuclear charge. In either case, generalization to the polyatomic case is still unclear.

repulsion is to include electronically excited configurations. Brillouin's theorem holds for closed-shell systems (on which the earliest *ab initio* work tended to focus), so double excitations account for most of the correlation energy, with single and higher excitations having coefficients an order of magnitude smaller than those of the doubles. By contrast, the single excitations are often as important as the doubles for open-shell systems, and higher excitations cannot be ignored.[‡]

An early modification of the SCF method to include some correlation was the extension of the scheme to use multiple configurations and not just the ground state configuration (MC-SCF). More recently, the CAS-SCF method has been devised. The complete active space SCF (CAS-SCF) method partitions the occupied orbital space into "inactive" and "active" orbitals. Configurations for the SCF stage of calculation are generated such that the "inactive" orbitals always remain doubly occupied and the remaining electrons are distributed among the "active" orbitals in all possible ways conserving space and spin symmetry. The orbitals thus created are not biased towards any one particular configuration.

Another approach is to focus solely on obtaining relative energies, irrespective of the absolute energy of a system. The pseudopotential method makes use of the fact that the core orbitals described in Section 1.2.1 (and eventually 2.5) are essentially invariant. An effective valence Hamiltonian operator is thus constructed which contains one-electron operators which model the potential energy of a given atom and its surrounding core electrons. This method is still technically *ab initio*, since the pseudopotential operators are determined from *ab initio* atomic calculations and are transferred to the molecular environment. Since potential curves are concerned with the relative and not absolute energy, the pseudopotential method often allows one to calculate large molecules with surprisingly small inaccuracies.

Davidson divides the remaining approaches used to account for electron correlation into valence bond-type treatments, where the electrons are treated in pairs, and multiple configurations-type methods, where the total electronic wavefunction which will be denoted

[‡] Nor can the spin symmetry be ignored. A single excitation from a closed shell $\phi_1(1)\alpha(1)\phi_1(2)\beta(2)$ gives two unpaired electrons with two singlet spin functions, $\phi_1(1)\alpha(1)\phi_2(2)\beta(2)$ and $\phi_1(2)\alpha(2)\phi_2(1)\beta(1)$. A double excitation from a four- or more-electron system can give four unpaired electrons. Since the total spin number must add up to zero, there are six permutations of the $\alpha\alpha\beta\beta$ spin system.

as Ψ , is expressed as a combination of many (N) possible states ψ_i of the same symmetry and multiplicity:

$$\Psi = \sum_{i=1}^N c_i \psi_i. \quad (1.15)$$

Thus, the ground state of the carbon atom, although *mainly* $1s^2 2s^2 2p_x^1 2p_y^1$ would have a Ψ_{tot} which also included small contributions from, say, $1s^2 3s^2 2p_x^1 2p_y^1$ and $1s^2 2p_x^1 2p_y^1 2p_z^2$, to name a couple of possible configurations of the same symmetry type and multiplicity. This is known as "configuration interaction" (CI).

As the basis sets described in the preceding section increase in size, there are numerous configurations which can be generated. For the relatively small case of a carbon atom with a double zeta-polarization (DZP) basis set ($4s2p1d$ GTO's) in C_{2v} symmetry, counting the configurations formed from *only the single and double excitations of the ground state*, there are 185 configurations. A $6s3p2d$ basis set under similar restrictions gives rise to 629 configurations—and these CI spaces do not even include triple and quadruple excitations as a "full" CI calculation would.

Timing constraints have forced the development of several approximations to overcome the unwieldy proportions of a rigorous CI expansion:

- (a) Consideration of only singly- and doubly-excited configurations of the ground state and reference configurations, with an estimation of the effect of triple and quadruple excitations on the energy to a high degree of accuracy by the Davidson correction[27] or variations thereof. (See Section 2.6.2)
- (b) Single and double excitations of *only* the ground state configuration (a single reference CI) is often not a sufficient description of the molecule. For example, the nitrogen molecule as it is stretched goes from a completely closed-shell occupation to a quasi-dissociated species which has six open shells (since the nitrogen atom with a ground state configuration of $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ has three open shells). The ground state and additional important configurations from which single and double excitations may be generated make up what is called a "multiple reference" set of configurations. As will be seen in later chapters, for some systems, the selection of the reference set can have a profound effect on the energy. The use of multiple reference configurations increases the size of the CI space (*e.g.*, the DZP case of carbon with eight reference configurations has a singles and doubles CI space of 700 configurations) but it is necessary for non-full-CI

calculations, especially to ensure correct dissociative behaviour.

- (c) Even considering only single and double excitations (SD-CI) can push the CI expansion to unworkable dimensions, so some methods turn to second-order perturbation theory in the selection of important configurations. For example, in the MRD-CI method used in this work, each configuration generated can be tested against the set of reference configurations, to determine whether it lowers the overall energy of that test secular equation. The accuracy achievable with such a method is estimated to be to within 1 kcal/mole of the absolute "full CI" energy for that particular basis.[28][29] The MRD-CI method will be discussed in greater detail in Chapter 2.
- (d) Perturbation theory can also be used in the "contracted-CI" scheme. In this method, configurations with the same internal parts are grouped together and their relative weights are frozen, not unlike the concept of basis set contraction. The first-order value of the energy is highly inaccurate, but by freezing certain CI coefficients at their first-order value the ratio is sufficiently well-represented at this level that the number of variational parameters can be drastically reduced without sacrificing accuracy in the final CI result.

1.3 Experimental Determination of Dissociation Energies

Although the research reported in this thesis did not include laboratory experiments in the usual sense, an important part of it depends on the comparison of calculated *ab initio* dissociation energies with experimentally-known values, so it is important to understand how experimentalists assign a value to the binding energy, and what sources of error exist for such a number. It should be noted that many of the quantities determined experimentally for the species of interest in this thesis were recently or are still poorly known. Many of the species studied herein are transient molecules such as radicals which can only be generated at low pressures and in low concentrations, so that a high-sensitivity technique, such as infrared diode laser spectroscopy, is essential. The last two decades have seen at least an order of magnitude increase in the resolution available now over conventional grating spectrophotometers. The dissociation energy D_0 is commonly determined experimentally in one or both of two ways: spectroscopically, using a Birge-Spöner extrapolation, or by mass spectrometric methods. The notation ' D_0 ' refers to the energy difference between the

$v = 0$ level and the asymptotic limits of the atoms. The *complete* well-depth, the difference from the energy minimum to the asymptote, also includes the zero-point energy (ZPE) and is represented by ' D_e :'

$$D_e = \frac{1}{2}\omega_e + D_0 \quad (1.15a)$$

1.3.1 Spectroscopic Method of Determining D_0

The Birge-Sponer extrapolation[30] is based on the fact that, for an anharmonic oscillator, the energy gap between successive vibrational levels must decrease to zero as the period goes to infinity. A plot of the energy gap ΔG_v vs. $(v + 1/2)$ can be extrapolated to find the point at which the curve crosses the abscissa (last vibrational level) and the area under the curve gives the dissociation energy. Usually only a small number of v levels have been experimentally determined, however, and the rate of convergence of the higher (unobserved) vibrational levels cannot always be reliably predicted from the lower levels' behaviour, due to perturbations from low-lying electronic states. The known levels of O_2 , for example, extend to $v = 25$ and cover about four-fifths of the well-depth. The observed levels converge in nearly linear fashion, but not so for the highest portion of the curve, and the Birge-Sponer extrapolation overestimates the D_0 .

1.3.2 Thermochemical Determination of D_0

The mass spectrometric method involves finding the equilibrium constant K_p for the dimer $\rightleftharpoons$ monomer reaction. In the second-law thermodynamic method, the standard enthalpy of dimerization is *assumed* to remain constant over the temperature range involved, and the dissociation energy is calculated from the slope

$$\frac{\partial \ln K_p}{\partial (1/T)} \quad (1.16)$$

The second-law method, where the reaction enthalpy ΔH_T^0 and the entropy difference ΔS_T^0 are derived from the variation of the equilibrium constant K_p with reciprocal temperature, should only be used where the temperature interval covered is fairly large.

In the third-law thermodynamic method, the value of the equilibrium constant is found at a single well-defined temperature, and that, with the absolute entropy calculated using statistical mechanics, produces a value for the dissociation energy. A molecule's mass, bond length and vibrational frequency must be known, to determine the vibrational, rotational,

and translational partition functions. The electronic function may differ substantially from unity if there are a large number of low-lying electronic states. The atomization energy was calculated from the reaction enthalpies ΔH_0^0 obtained by the third law method:

$$\Delta H_0^0 = -RT \ln K_p - T \Delta[(G_T^0 - H_0^0)/T] \quad (1.17)$$

where $(G_T^0 - H_0^0)/T$ is the free energy function calculated from statistical mechanical formulae.

1.4 Spectroscopic constants

Two conventions of notation are widespread. The first is that adopted by Huber and Herzberg, and used in this work:[31]

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \dots \quad (1.18)$$

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 \dots \quad (1.19)$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \dots \quad (1.20)$$

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots \quad (1.21)$$

The second convention, by Dunham, is based on a potential energy function of the form

$$V = hca_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots) \quad (1.22)$$

where

$$\xi = (r - r_e)/r_e,$$

$$a_0 = \omega_e^2/4B_e,$$

$$B_e = h/(8\pi^2 \mu R_e^2 c)$$

where R_e is the equilibrium bond length, μ is the reduced mass, and ω_e is the fundamental frequency of vibration. The energy levels are given by:

$$E(v, J) = \sum_{ij} (v + \frac{1}{2})^i (J(J+1))^j V_{ij} \quad (1.23)$$

and the coefficients Y_{ij} are the Dunham coefficients. A comparison of this equation with the first set of spectroscopic equations given shows that Y_{10} corresponds to ω_e , Y_{20} to $-\omega_e x_e$, and so forth.[31]

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Chapter 2

Methods

He who would do good to another must do it in Minute Particulars.
General Good is the plea of the scoundrel, hypocrite and flatterer;
For Art and Science cannot exist but in minutely organized Particulars.

William Blake,
Jerusalem

2.1 Introduction

Although the Schrödinger wave equation was formulated in the 1920's, it has only been in the last couple of decades, when theoretical chemists have debated the "Minute Particulars" of applying this equation to actual chemical systems, that its real predictive value has become apparent to experimental chemists. Section 1.2 of the preceding chapter outlined general approximations to the exact solution of the Schrödinger wave equation. This chapter discusses these issues more specifically, and relates them to the calculations which were carried out in the research described in this thesis. In brief, the method of calculation is a form of configuration interaction (CI) using molecular orbitals (MO's) generated using the self-consistent field (SCF) method, with orbitals created from a set of Gaussian-type orbitals (GTO's) known as the basis set. Following that, the data treatment of these absolute energies to obtain parameters for potential energy curves is described.

The CI selection-extrapolation method which will be described in some detail is known as the Multiple-Reference single and Double excitations Configuration Interaction (MRD-CI) method, as formulated and developed by Buenker and Peyerimhoff. Application of this technique to numerous systems has shown that MRD-CI can account for roughly 95 per cent of the total valence-shell correlation attainable with a given AO basis while still employing a relatively small number of reference configurations.[1]

2.2 Basis Sets

2.2.1 Atom-Centred Basis Sets

Exponents and coefficients are used to represent the mathematical functions which are integrated in the first stage of a calculation to create a spatial atomic orbital which may be spheroidal (s), bi-lobed (p), clover-leaved (d) or more complex in form (f , g , etc.).[†] As outlined in Chapter 1, the number of orbitals used to describe an atom varies widely. Factors influencing the choice of basis set are predominantly the computing resources available, the number of atoms in the species being studied, and the objective of the calculation, *e.g.*, whether qualitative or quantitative results are desired, and whether electronic or vibrational levels are of interest, *etc.*

The double-zeta (DZ) basis sets which were used for the calculations in the present work involving all first- and second-row atoms were built from "primitive," *i.e.*, uncontracted Gaussian-type orbitals published by Huzinaga in 1971.[2] The GTO's of inner-shell orbitals are routinely "contracted," or summed with fixed coefficients. One can obtain these coefficients from the SCF eigenvectors for the atom calculated with uncontracted orbitals. Contraction simply means that a few GTO's of a given angular momentum will always be used in a restricted ratio to one another in the SCF stage when a linear combination of atomic orbitals (LCAO's) is being variationally constructed. Determining one coefficient means the others in that particular contraction are immediately known, so a contracted set of orbitals is only as CPU-demanding as a single uncontracted counterpart, but gives a much better description of the inner cusp of the electronic wavefunction than a single Gaussian function alone.

The first-row DZ basis sets began with the (9s5p) basis sets of Huzinaga,[2] contracted to [4s2p] by Dunning and Hay.[3] To each of these was added a set of (6-component) Cartesian d orbitals, which were the "polarization functions" mentioned in Section 1.2.1. These orbital sets were given exponents of 0.75, 0.80, 0.85 and 0.90 for carbon, nitrogen, oxygen and fluorine, respectively, as suggested by Dunning and Hay based on SCF results.

The TZPP first-row basis sets began from [5s3p] contractions, also from Dunning and

[†] The integral packages used varied from CLEMEN (which handled only up to d functions) to PENGUIN (which gave correct energies but some incorrect properties) to HONDO.

Hay. The double-polarization functions' exponents were obtained in a fashion described in the following section.

The DZ basis sets for the second-row atoms were obtained from a $[6s4p]$ contraction published by McLean and Chandler[4] of the Huzinaga (12s8p) primitives.[2] Polarization exponents were determined by optimization of the (est.) full-CI energy of the atoms, and are given in Table 5.2. As with the first-row atoms, they vary monotonically on crossing the periodic row from Group I (Na, 0.1) to Group VII (Cl, 0.7).

Some difficulty was experienced in determining the most suitable atomic basis set for the chromium study. A flexible yet economical (14s9p5d) basis set reported by Wachters[5] was augmented by an extra diffuse d function of exponent 0.0912 as recommended by Hay.[6] The contraction scheme for the s and p orbitals followed that of Wachters' SCF-optimized contraction 1, namely, 62111111 and 5112 respectively.[5] The coefficients were re-determined in the current work from the SCF eigenvectors for the uncontracted atom, and are listed in Table 8.1. For the d orbitals, the "augmented (5d)" primitive orbitals were contracted to $[3d]$ by a 411 scheme whose coefficients are as given by Hay.[6] Since the d shell of the chromium atom is a valence shell, this is only a DZ-quality basis set; f orbitals are necessary as polarization functions.

2.2.2 Optimization of Polarization Exponents

How should the optimization be done: with respect to the atom or the molecule? With respect to absolute or relative energies? What sort of difference can one expect between the different types of optimization? Table 2.1 shows as an example the energies of the nitrogen (4S) atom and the ($X^1\Sigma_g^+$) molecule calculated using a TZPP basis set. A variety of polarization exponents are explored; each set however is constrained to a 2:5 ratio. Note that optimizing the polarization orbitals' (d) exponents with respect to the *lowest absolute molecular energy* gives a D_e of 8.912 eV, whereas optimizing the absolute *atomic energy* gives a D_e of 8.856 eV. The optimum D_e (which amounts to optimizing the *difference* between the atomic and molecular energies) of 8.98 eV is obtained with the highly compact d exponents of 1.0 and 2.5.

Optimization of polarization functions (PF's) in the current work was based on absolute atomic energy for three reasons: (i) literature optimizations for the DZP polarization functions had been carried out on the atoms,[3] albeit only at the SCF level; (ii) the atomic

calculations are simplest and demand the least computational resources; and most importantly, (iii) the polarization exponents do not have to be re-optimized for each new molecule. In the following section, it will be noted that the bond function (BF) is optimized at the molecular level. For BF basis sets, this means that deficiencies in the PF's can be overcome by the BF's, so the PF optimization is not so crucial. When comparing PF and BF results, however, it should be kept in mind that the slight differences in optimization can affect the well-depth obtained by about one-tenth of an electron volt.

According to what has been seen for N_2 , then, the double-polarization exponents were derived by multiplying the exponents of the single-polarization sets by 0.6 and 1.5, for both the first- and second-row elements.[7] This gave C($\zeta_{d1}=0.45$, $\zeta_{d2}=1.125$), N(0.48, 1.2), O(0.51, 1.275) and F(0.54, 1.35) and PF exponents for Na to Cl as noted in Table 5.2 (Chapter 5).

2.2.3 Bond Functions

The bond functions consisted of sets of s , p , d and f orbitals added in varying combinations to a centre of zero nuclear charge at the bond midpoint. When multiple sets were added, the ratio of the exponents was fixed to be 3:1 between the sets. A notation of "2(sp)" at "0.6, 1.8", for example, means that the following sets of functions were added: s (exponent $\zeta_s = 0.6$), p (0.6), s (1.8) and p (1.8). The estimated full CI energies (*vide infra*) using at least three different values for the sets of exponents constrained to the ratio 1:3 were calculated. A fit to a parabolic function predicted the optimum values of the set of exponents (which were subsequently confirmed or recalculated).[†]

2.3 Symmetry Considerations

The second stage of calculation took the integrals from the first stage and sorted them according to the rules of symmetry.[‡] Although the hetero- and homonuclear species were placed in the coordinate system to represent the molecule with maximum symmetry, by $C_{\infty v}$ and $D_{\infty h}$ symmetry respectively, due to program limitations the calculations were done in C_{2v} and D_{2h} symmetry. Table 2.2 shows the symmetry types of the Cartesian

[†] A parabolic optimization program is listed in Appendix B.

[‡] The name of the program used to do this is YELLOW; the variant YELLOG includes g orbital capability.

orbitals used for the D_{2h} group, and the numbered-symmetry convention which is followed in the MRD-CI set of programs. Note that in this symmetry, orbitals which are placed at the origin exactly are assigned to different types than the combined pairs of atomic orbitals shown in the top half of the Table. In C_{2v} symmetry, types 5-8 "collapse" into types 1-4, respectively, since the centre of inversion has been lost.

2.4 Construction of the LCAO's

The linear combinations of atomic orbitals (LCAO's) which were used to make the first approximations to molecular orbitals (MO's) were constructed by an SCF calculation from the ground state occupation.[†] The SCF method is well-described by Pople and Beveridge and the interested reader is referred to their book.[8] In a nutshell, the electronic charge is treated as an average cloud and linear combinations of the basis set functions are varied to determine the combination which yields the lowest energy, which is the SCF energy. The larger the basis set, the lower the energy drops until it reaches the Hartree-Fock (HF) energy, which is the limit of the "averaged-charge-density" approximation. This may still lie a few electron volts above the true energy, and configuration interaction (CI) is needed in order to account for the instantaneous repulsion.[9]

2.5 Freezing Orbitals

As stated in Chapter 1, the CI method used to recover the electron correlation energy involves generating numerous excited-state configurations. As the following section describes, there are very many singly- and doubly-excited configurations which can arise, since a reasonably large basis set will create many orbitals which increase the number of possible permutations of electrons-in-orbitals. A great deal of simplification occurred with the symmetry-sorting of the integrals in the second stage of these calculations, but prior to beginning the CI-segment of the calculation, it is sensible to *further* restrict the numbers of electrons and/or orbitals into which they may be excited. "Freezing the core" means the electron pairs in orbitals corresponding to the inner-shell occupation are retained in these orbitals (these orbitals had the lowest energy) and similarly, "excluding the *anti-core*" means

[†] The program which took the symmetry-sorted integrals and constructed the LCAO-MO's in the calculations reported here is called SCFYEL.

the highest-lying unoccupied orbitals were not allowed to be populated.[†] The CI is then carried out on the remainder of the electrons, which comprises the chemically-important valence shell.

Since hydrogen has no inner shell, no freezing was done. For other atoms of the first-row, two electrons, the [H₂] core, were constrained to remain in the lowest-lying occupied orbital while the highest-lying orbital of that symmetry, the "[He] anti-core," was not included as a "box" during occupation permutation. First-row diatomics had their [He₂] core and anti-core frozen, second row diatomics had the [Ne₂] core and anti-core frozen, and so forth. The calculations on chromium involved a frozen [Ar] and [Ar₂] core for the atom and molecule, respectively, but no anti-core was frozen.

2.6 Selection-Extrapolation Technique

Each of the diatomics studied in the current work—with one important exception—could have been the subject of a complete valence-shell single- and double-excitations CI (SD-CI), and, given considerable computational resources, a few of the species could even have been studied by full-CI methods, especially given the DZP-sized basis sets. However, full CI calculations quickly become impossibly large; with N orbitals and n_α , n_β the number of electrons with α and β spin, the number of determinants in the full CI is:

$$\binom{N}{n_\alpha} \binom{N}{n_\beta}. \quad (2.1)$$

For fifty orbitals, for $n_\alpha = n_\beta = 5$, the number of determinants is 4×10^{12} , which is reducible by symmetry to a size which is still of the order of 10^{11} . [10]

To calculate third-row diatomics such as Cr₂ or to add one more atom to the systems studied or to increase the size of basis sets used, one is faced with a molecule with several valence-shell electrons whose single- and double-excitation CI space becomes so large it is intractable using present-day technology. For example, Walch *et al.* estimate that for Cr₂ with a roughly DZP-size basis set, the size of the singles and doubles CI generated from a CAS-SCF calculation with 3088 configurations is of the order of 57 million in D_{2h} symmetry. [11]

[†] This stage of the calculation was performed by a program named STONEY.

However, most of the configurations generated contribute negligibly to the energy lowering. It is more efficient to use a reasonable method of selecting configurations which contribute most to the wavefunction, as has been done by Buenker and Peyerimhoff[12][1] and was recently suggested by Knowles and Handy.[10] The method of the former group, which is used in this thesis, then extrapolates from the energies calculated at given thresholds to a zero threshold answer. Numerous comparisons with benchmark full-CI calculations show that this extrapolation method yields an absolute energy within 1 kcal/mole or less of the exact solution.[13]

To begin with, all single and double excitations of the same symmetry of the valence-shell (non-frozen) electrons into the non-frozen virtual orbitals are generated from the ground-state occupation. Each newly-generated or "test" configuration is then included in a small preliminary secular equation, which is composed of the ground-state configuration and other reference configurations (*vide infra*).

The Hamiltonian matrix elements between Slater determinants constructed from an orthonormal one-electron basis had to be evaluated firstly in the test secular equation, and then, as will be seen shortly, for the large CI space consisting of all selected configurations. A wavefunction may be separated into a spin part and a spatial part; the spin part for a given multiplicity and number of open shells is invariant, and so products of two spin wavefunctions need not be remultiplied each time. The configuration-driven Table CI method was devised to take care of this spin part in an efficient manner.[14][†] In essence, a configuration-driven approach compares pairs of many-electron configurations *before* deciding which one- and two- electron integrals are required to compute the corresponding Hamiltonian matrix elements. The "look-up" nature of such an approach thus fully exploits the capabilities of configuration selection.

The energy lowering produced in the test secular equation is then used as an ordering parameter for the configuration's dominance in the overall wavefunction.[15] If the test configuration is found to lower the energy by more than a specified threshold amount, then it is retained, along with other test configurations which have been found to interact strongly with the given main configurations.[‡] In this way, the size of the CI space is easily

[†] The look-up table for the spin determinants of the wavefunctions is generated by a program called TABLE.

[‡] The configuration generator and selector program is called PARK.

controlled by adjusting the size of the threshold, T_1 , so that the over-all CI space consists of at most 6000 configurations, with the exception of Cr_2 to be discussed in Chapter 8. (For the atoms, the total number of single and double excitations never exceeded this range, so a zero threshold was always used.) Regardless of the effect on the energy, all single excitations are automatically included, to improve the description of the wavefunction used in calculation of the dipole moment.

The eigenvalue E_{T_1} is calculated using this subset of strongly-interacting configurations.[†] For a non-zero threshold, a second secular equation, comprised of mains which lowered the energy by an amount equal to the threshold amount plus the step-size, $T_1 + S \cdots T_2$, is constructed. The eigenvalue E_{T_2} found using this second smaller matrix is used, in conjunction with E_{T_1} , in a linear extrapolation to find the singles and doubles CI energy for the case where the threshold value is zero.[16]

2.6.1 Reference Configurations

The single and double excitations of only the ground state configuration are not enough to fully describe many molecules. For example, a double excitation of N_2 ($X^1\Sigma_g^+$) would have at most four open-shells and thus the quasi-dissociated configuration with six open-shells is impossible. It is therefore necessary to generate the singly- and doubly- excited configurations of *all* occupations important to the potential energy curve, called the reference set, in generating the test configurations and eventually the CI space.[17]

Consistency in the number of mains and size of CI space was the goal during the optimization of the BF exponents, and eventually, the construction of the potential energy curve. Those configurations which appeared in the final wavefunction with a c_i^2 contribution greater than x percent were specified as "main configurations." They were used to create a larger test secular equation in subsequent calculations. Except for the Cr_2 calculations, where the program was specifically modified for a large number of open shells, no configurations with more than five open shells could be specified as mains, although configurations with up to seven open shells could be generated in the testing phase.

In practice, the criterion for selection of the reference set varied slightly in the course of this work. The quantity x varied from 0.5% as a minimum recommendation in Ref. [18] in

[†] The program used to generate the Hamiltonian matrix elements was RUMPLE; the CI matrix diagonalization programs used were CONDOR or GRIZZLY (based on a faster diagonalization routine).

the calculations of the hydrides, to 0.2% in the calculations for Chapters 7 and 8. In cases where a low-lying excited state significantly perturbs the energy or electric dipole moment of the ground state, it is desirable to select for two roots. In a 2-root calculation, the energy lowering of not only the ground state but also the first excited state of the same symmetry and multiplicity, affects the number and kind of reference configurations chosen, and the number and kind of configurations selected to create the CI space.

2.6.2 Davidson Correction and Variations

Finally, the Davidson correction[19] gave an estimate of the CI energy as if quadruple excitations had been included as well (referred to as the "estimated full CI" or "F-CI (est.)" energy).[†] This is a broadly-used arithmetic correction to SD-CI calculations which estimates the contribution due to quadruple excitations, proposed by Langhoff and Davidson in 1974.[‡] The energy lowering to be expected from inclusion of quadruple excitations ΔE_Q is:[19]

$$\Delta F_Q = (1 - c_0^2)(E_0 - E_D), \quad (2.2)$$

where E_0 is the energy of the dominant configuration, E_D is the single- and double-excitation CI energy, and c_0 is the expansion coefficient of the dominant configuration in the CI wavefunction. Siegbahn suggested this could be modified to:[20]

$$\Delta E_Q = \frac{1 - c_0^2}{c_0^2}(E_0 - E_D). \quad (2.3)$$

For use in multi-reference calculations, the Davidson correction is modified to:

$$\Delta E_Q = (1 - \sum_{i=1}^{ref} c_i^2)(E_{ref} - E_{MRD-CI}) \quad (2.4)$$

where N is the number of reference configurations from which single and double excitations are made.

2.7 Dipole Moment

Once the wavefunction Ψ has been created, such properties as the dipole moment can be calculated:[21]

$$\mu = -2q \int \Psi R \Psi d\tau \quad (2.5)$$

[†] This was automatically done in the program which diagonalized the CI matrix, CONDOR or GRIZZLY.

[‡] This correction is so widely-used, in fact, that the original article was recently featured by *Current*

The dipole moment may be found at the SCF, partial, full, or corrected CI stage of the calculation.[†] Configuration interaction was shown to be an important tool in the calculation of an accurate dipole moment. In their classic paper on the dipole moment for CO, Grimaldi, Lecourt and Moser found that single excitations were three times as important and double excitations a hundred times more important in changing the energy,[22] whereas the single excitations had a dominant effect on the permanent dipole moment.

Bender and Davidson, in their calculation of the dipole moment of LiH found that single excitations were more important than double excitations in reducing the calculated value of μ to the experimental value.[23]

2.8 Obtaining the Relative Energies

Chapters 4-8 contain tables which summarize the absolute energies found for the atoms with DZP and/or TZPP basis sets. Other tables summarize the energies obtained for the molecules, using DZP, TZPP or DZP+BF basis sets, where 'BF' indicates various sets of bond functions, with optimum exponents for each given set.

The relative energies were obtained for a given molecule by taking the difference of the estimated full-CI energies of the atoms and the molecule. This approach is simpler than calculating the "supermolecule," because convergence for highly-stretched geometries can be slow. Previous checks of size consistency show that the absolute energies of two atoms differ very little (0.0004 hartree[24]) from the energy calculated for a highly-stretched (*e.g.* $R = 20$ bohr) molecule with or without bond functions, and so the simpler approach is justified.

2.9 Counterpoise Correction Method

The estimate of basis set superposition error (BSSE) was performed according to the function counterpoise method outlined by Boys and Bernardi.[25] These calculations were carried out in C_{2v} symmetry. They consisted of an atom situated at the origin, and a set of atomic functions situated where the second atom would be, except that in this case the nuclear charge of the second centre was zero. Where noted, a bond function was added to the basis set in the same manner as it was added to the molecule itself. The energies so

[†] The programs ROADRUN or BIGFOOT calculate the MRD-CI dipole moment.

obtained were used in lieu of the regular atomic energies, with care being taken to match the molecular and ghost orbital distances exactly.

2.10 Potential Energy Curve Function

In some cases, only the dissociation energies were of interest (*e.g.*, Chapter 7). For those cases where the electronic energy was found as a function of internuclear separation R , it was desirable to summarize the energies in compact form, from which molecular constants such as R_e and D_e are readily apparent. The energies $E(R)$ obtained were fit to a generalized Morse function (GMF).[†] Typically, a 5-parameter GMF was chosen and the parameters D_e , R_e , β_0 , λ_1 , and λ_2 were determined:[26]

$$E(R) = D_e \{1 - \exp[-\beta(R - R_e)]\}^2 - D_e, \quad (2.6)$$

where

$$\beta = \beta_0 [1 + \lambda_1(R - R_e) + \lambda_2(R - R_e)^2]. \quad (2.7)$$

The potential curve function could then be used to generate the curve for plotting[‡] or for solving for eigenvalues of nuclear motion.

The vibrational energy levels are determined by a numerical solution of the radial part of the nuclear Schrödinger equation using the Numerov-Cooley algorithm.[27] This procedure involves a predictor-corrector form of numerical integration of the wavefunction on both inner and outer branches of the potential energy curve (generated from the GMF5 function, in this case). The correction to the trial eigenvalue is determined by the *difference between the slopes* of the two curves and thus converges very quickly. If the wavefunction which is calculated by moving along the inner branch matches that calculated by moving along the outer branch when the functions are compared at R_e within a specified tolerance, then that is judged to be an eigenfunction.* To facilitate comparison with experimental

[†] The fitting program to do this is included in Appendix B; it is based on the MARQUARDT non-linear least-squares fitting algorithm.

[‡] See Appendix B for a sample plotting program.

* The program to calculate vibrational and rotational energy levels of a diatomic is included in Appendix B. The program, written by R. J. LeRoy (U. Waterloo) is based on an earlier program by R. N. Zare (Stanford).

data, these vibrotational levels may then be least-squares fit to spectroscopic equations such as outlined in Section 1.4 of Chapter 1.*

2.11 References

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* The program to fit the vibrational and rotational energy levels to a 5-parameter spectroscopic equation is included in Appendix B.

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Table 2.1

Optimization of the polarization exponents of N_2 . Energies of the nitrogen (4S) atom and the ($X^1\Sigma_g^+$) molecule calculated using a TZPP basis set.

Exponent (bohr ⁻²)	Atom or Molecule	Full CI (est.) (hartree)	Dissociation Energy (eV)
0.4, 1.0	A	-54.50289027	—
	M	-109.32881256	8.790
0.48, 1.2	A	-54.50382744	—
	M	-109.33309184	8.856
0.6, 1.5	A	-54.50352946	—
	M	-109.33456653	8.912
0.72, 1.8	A	-54.50219010	—
	M	-109.33314519	8.946
0.8, 2.0	A	-54.50089247	—
	M	-109.33116747	8.963
1.0, 2.5	A	-54.49645062	—
	M	-109.32290758	8.98
1.6, 4.0	A	-54.48121363	—
	M	-109.28844613	8.87

Table 2.2

Symmetry allocations of Cartesian orbitals in D_{2h} symmetry. Notation refers to a molecule situated along the principal axis, with atoms at A and $-A$ distances. The mid-point function is at the origin, and is denoted X .

	Abelian			Symmetry			Type	
	1	2	3	4	5	6	7	8
	A_g	B_{3u}	B_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{3g}	A_u
$s_{-A} + s_A$	1				1			
$p_{-A} + p_A$	1	1	1		1	1	1	
$d_{-A} + d_A$	3	1	1	1	3	1	1	1
$f_{-A} + f_A$	3	3	3	1	3	3	3	1
$g_{-A} + g_A$	6	3	3	3	6	3	3	3
s_X	1							
p_X		1	1		1			
d_X	3			1		1	1	
f_X		3	3		3			1
g_X	6			3		3	3	

Chapter 3

Dihydrogen

New opinions are always suspected, and usually opposed, without any other reason but because they are not already common.

John Locke,

Essay on the Human Understanding

3.1 Introduction

Of all molecules, dihydrogen is the simplest neutral species. Approximate solutions to the Schrödinger equation can be devised to such precision, and laboratory observations can be done with such accuracy, that it is possible "to confront basic theory with experiment."^[1] The dissociation energy D_0 of dihydrogen is well-known experimentally to be 36118.6 ± 0.5 cm^{-1} or 4.47817 eV.^{[2][3]} A very accurate calculated potential energy curve using the Born-Oppenheimer approximation was published nearly three decades ago^[4] and has since been further refined.^{[5][1][6][7][8]} The relativistic correction is calculated to be -0.5 cm^{-1} ; the correction for nuclear motion is about 5 cm^{-1} at R_e ;^[5] and the radiative correction is 0.2 cm^{-1} .^[1] The most recent highly-accurate calculation consists of a 249-term variational wavefunction in the region $0.2 \leq R \leq 4.8$ bohr and a 72-term function for $4.8 < R \leq 12.0$ bohr. The adiabatic D_0 was found to be $36117.590 \text{ cm}^{-1}$; the non-adiabatic value, $36118.088 \text{ cm}^{-1}$.^[8] This is a discrepancy of $0.5 \pm 0.5 \text{ cm}^{-1}$ or less than 15 parts in a million.[†]

After such outstanding success, the natural question is, why should anyone wish to recalculate a curve for hydrogen? The answer lies in the difficulty and expense of applying the same method used by Kolos and Wolniewicz to diatomics with a greater number of electrons, and in the outright impossibility of treating tri- and polyatomic molecules. In this

[†] To give some idea of the slowness of convergence of the exact solution with respect to the number of functions, the D_e is found to be 4.6698, 4.7415 and 4.7467 eV for wavefunctions of 5, 15, and 50 terms respectively.^[4]

respect, a highly-accurate curve serves as a benchmark against which more approximate—and more broadly applicable—methods may be judged.

Attempts to generate an accurate three-dimensional potential energy surface for H_3 are a case in point.[9][10][11][12] In addition to the increased complexity of a greater number of particles, the non-linear geometries mean that the integral transformation and the CI stages of the calculation must be carried out in lower symmetry, which is less efficient computationally. Integral evaluation for non-linear molecules is more easily but less accurately done with sets of contracted GTO's. To estimate the accuracy of the basis sets chosen, potential curves for the H_2 asymptote of the triatomic may be compared against the "benchmark" H_2 curves.[11][12] The difference curve (ΔE vs. R , where $\Delta E = E_{exact} - E_{calc}$) thereby constructed should be as flat as possible or at least monotonic, i.e., the error of the more approximate method should be slowly varying and predictable. The importance of having a very flat difference curve leads Siegbahn and Liu to write, "the variational calculation that yields the lowest total energy does not necessarily yield the best potential energy surface. In order to obtain the best possible results, short of an exact calculation, it is important to ensure that all points on the potential energy surface are calculated with nearly the same error." [11]

Since electron-electron repulsion does not occur, the exact energy of the hydrogen atom is known to be -0.5 hartree. Using the (9s) van Duijneveldt basis set[13] contracted to [4s] by Siegbahn and Liu[11], the atomic hydrogen energy is calculated to be -0.499998 hartree. The basis set incompleteness, which is the difference between the energy calculated using a particular basis set, and the true energy, is thus only 2 μ hartree for the atom, and dihydrogen thus provides a perfect test case of the most effective means of lowering *only* the molecular energy.

The conventional method of improving the capability of the basis sets to calculate the molecular energy is to add more functions to the atomic centres. The error in determining the absolute energy of the molecule is greater—in this case *much* greater—than that of the atoms (4 μ hartree here), so positioning more functions on the nuclei is an approach of questionable efficiency.

An alternative approach would be to add more functions to the region of expected greatest charge density, i.e., the bonding region.[14] In this chapter, calculations on H_2

with different basis sets containing polarization functions (PF's), bond functions (BF's) or a mixture of both, are presented. The systematic addition of PF's and BF's to the H_2 basis set at the equilibrium internuclear distance results in a lowering of the SD-CI energy which is examined in terms of computational efficiency (i.e., number of functions, since all calculations are performed in D_{2h} symmetry). Following this, potential energy curves using the "best" BF and the "best" PF basis sets are constructed for ground state H_2 . The difference curves for energies obtained using these basis sets and the essentially exact energies of Kolos *et al.*[8] are examined. The spectroscopic constants of the potential energy curves are determined, and compared against the "exact" constants.[8]

3.2 Results and Discussion

The sets of coefficients and exponents used to construct the GTO basis sets are shown in Table 3.1. The "core" $4s$ basis was obtained from Ref. [13]. The $3p$ PF's were obtained directly from Ref. [11], and the are not enumerated in Table 3.1. The remainder of the PF, and all of the BF exponents, were obtained by parabolic optimization; these values are noted explicitly in Table 3.1.

3.2.1 BF's vs. PF's: Minimum Energy

The calculated CI energies using all single and double excitations of the ground state configuration (SD-CI) at 1.40 bohr are shown in Table 3.2. The SD-CI energy of dihydrogen using the contracted van Duijneveldt $4s$ basis with neither BF's nor PF's is -1.154323 hartree, so another 0.02 hartree or 0.6 eV could be gained by basis set improvement. This is ten thousand times greater than the atomic basis set incompleteness. This "starting set" of orbitals was then augmented with a series of polarization functions, beginning with $1p$, and extending up to $3p2d1f$. The $1p$ exponent was determined by parabolic optimization to be 0.77, and the $2p$ exponents were held in a fixed ratio of 1:3 but similarly optimized. Since Cartesian Gaussian functions are used, with 6-component d functions, 10-component f , etc., the size of the $4s + PF$ basis sets ranges from 14 to 70 functions. The lowest absolute energy attained was -1.173973 hartree.

The same $4s$ atomic basis set was then augmented by a variety of bond functions, beginning with $1s$ (a total of 9 functions in the molecular basis set), and extending up to

$4s3p2d1f$ (43 functions total). The ratio of exponents for same- l -type functions was also held to be 1:3, as with the PF's.

Most noticeable is the general trend of energy lowering as the total number of functions is increased. Figure 3.1 illustrates the decrease in the absolute energy with respect to the number of functions which have been added to the $4s$ atomic basis set. Energy variations occur due to the type of extra functions added; for example, both the $4s + (spd)$ and $4s + (4s2p)$ basis sets have a total of 18 functions, yet the absolute energies differ by 0.2 millihartree. Although the points are scattered, it can be seen that the BF basis set points converge *more quickly* to the exact limit than the PF basis points.

The same trend at stretched geometries is observed for a subset of the basis sets shown in Table 3.2. At 3.0 bohr, the following energies were obtained:

$$4s1p \text{ (6 PF's)} = -1.052345 \text{ hartree}$$

$$4s + 2s1p \text{ (5 BF's)} = -1.053786 \text{ hartree}$$

$$4s3p \text{ (18 PF's)} = -1.055329 \text{ hartree}$$

$$4s + 4s3p1d \text{ (19 BF's)} = -1.055919 \text{ hartree}$$

and the BF basis sets are again approaching the exact energy of -1.057312 hartree more closely for a given number of functions.

Mixed basis sets containing both polarization and bond types of functions are also listed in the bottom third of Table 3.2, and these give an encouragingly low absolute energy.

3.2.2 BF's vs. PF's: Difference Curves

The next step was to construct potential energy curves for the two "best" basis sets representing BF's and PF's, to search for qualitative differences between these curves and the "exact" curve. The comparison may be made in two ways: by examining the shape of the difference curves, as suggested in the introduction, or by looking for agreement between the parameters determined for the two potential energy curves using some fitting function. The former method has the obvious advantage of ready interpretability, and the ease with which the areas of greatest discrepancy may be localized.

Figure 3.2 shows the qualitative difference in the BF and PF basis difference curves. This echoes the differences observable in the DZP and TZP curves and their BF counterparts

in Figures 1 and 2 of Ref. [12]. The strictly atomic-centred basis set shows much larger ΔE for $R < R_e$, and the slope is much steeper in this region for the PF difference curve than for the BF's. The BF curve, on the other hand, represents this region better. The strength of the BF's lies in their ability to delocalize electron density—this is especially important at small R distances. The BF curve does have a more pronounced and symmetrical "hill" in the region between 2 and 5 bohr than the PF curve. The size of the "hill" along the outer branch may be partially attributed to the fact that the BF's are optimized at R_e , and are not re-optimized as the atoms are stretched apart. In order for the overlap of the bond and molecular orbitals to be optimum at large R , the ζ_{BF} should decrease, so that the BF can grow larger, to accomodate the increasing size of the molecule.

Had time permitted, two other difference curves would be of interest. A difference curve for a PF basis set equal in size to the BF basis would give a clearer indication of the strengths of the BF's. As well, a difference curve obtained from a mixed basis would be enlightening to see if the such a basis "combined the best of both worlds," and gave a flattened difference curve along both inner and outer R branches.

Figure 3.2 is unfortunately an exception in this thesis because there are no "exact" calculations available for the remainder of the species studied herein and so no difference curves can be calculated. The latter treatment, that of comparing fitted parameters of the curves, will be encountered more often. It is more compact, and allows one to judge the "noise" inherent in the data sets, as indicated by the size of the root-mean-square (r.m.s.) deviation. Fitting the data set to the parameters in an equation is dependent on the size of the data set, the distribution of the points, and the domain covered by these points, so care must be taken to do the fits in the same fashion for all the curves.

The potential energy curves were found by subtracting twice the absolute energy of the separated atoms from the molecular energies reported in Tables 3.3 and 3.4. Then these points were fit over a variety of domains for the five-parameter generalized Morse function (see Equations (2.6–7)).

Table 3.5 shows the parameters and the r.m.s. deviations obtained for the fits. To obtain convergence of the parameters, the points at 0.2, 0.3 and 0.4 bohr which lie far above the asymptotic energy had to be excluded from all data sets. The parameters and their standard errors are shown for five different domains for the SD-CI and "exact" curves and

for three different domains for the reference energy curves. For the largest domain, 0.5—10.0 bohr, the r.m.s. deviation was largest, around 0.05 eV for all curves. The D_e could be determined to only three significant figures. Over this domain, the “exact” curve yielded a D_e of 4.76(2) eV. The D_e for the SD-CI curve calculated using bond functions in the basis set, noted as “BF SD-CI” in the Table, lies closest to this value, at 4.74(2) eV. The PF SD-CI value has a D_e of 4.72(2) eV. For the reference energy curves, the BF D_e is again better, at 3.92(2) eV and the PF D_e is 3.88(2) eV. In fact, over the largest domain, the best agreement with the exact curve for all the parameters is obtained with the BF basis set.

When the two short-distance points are discarded to fit the curves over the 0.7—10.0 bohr range, the r.m.s. deviations drop dramatically, to one-third of their former values. The D_e 's are determined to four places. The D_e 's for the exact curve and the BF curves change little from their former values, although they gain in precision. However, the PF D_e 's show a significant improvement. As implied in Figure 3.2, the PF curve lies a great deal higher than the exact curve when the internuclear separation is small. Thus, discarding the small- R points improves the D_e 's of the PF curves substantially. Over the range 0.7—10.0 bohr, the exact curve fit has a 4.766(7) eV well-depth. The closest SD-CI value is for the PF curve, at 4.755(7) eV, and the BF SD-CI well-depth is the next closest, at 4.743(7) eV. This is in agreement with the ordering one would expect from Table 3.2, where the best PF basis had a slightly larger well-depth. Of the reference energies, the curve constructed using a BF basis set again has the better D_e , at 3.94(1) eV whereas the reference energy curve has a D_e of 3.92 eV.

Shrinking the domain by discarding more small- R points and also the large- R points means an even better fit for all curves reported. The r.m.s. deviations for the “exact” and for the BF SD-CI curves are halved. The other curves show a less dramatic decrease in the deviation. Over the 1.0—7.0 bohr domain, the D_e in all cases decreases slightly from its value over the 0.7—10.0 bohr domain. The D_e from the PF SD-CI basis lies closest to that of the exact curve for the domain over which the most precise fit is obtained.

This is not the case for all parameters. The R_e of the BF SD-CI curve, for instance, coincides with that of the exact curve (although the PF SD-CI value agrees within the estimated uncertainty bounds as noted in the Table). Comparing the R_e 's for the largest domain (0.5—10.0 bohr) with the smaller domains shows, for every curve, one sees that R_e

increases slightly for fits over the smaller range. R_e changes significantly when the 0.8, 0.9 bohr points of the potential curve are discarded. These two points are very important in describing the shape of the inner branch of the curve and should thus not be excluded from the fit.

Similar to the case of R_e , the β_0 , λ_1 and λ_2 parameters for the BF SD-CI curve show the best agreement with those of the exact curve for the most precise fit. The parameters λ_1 and λ_2 are large in magnitude when the points cover a large region. These parameters, which are the coefficients for a Taylor expansion about R_e , indicate the extent of anharmonicity in the curves. As the size of the domain shrinks, the outer regions of the curve are less well-defined. The relative uncertainty of λ_1 and λ_2 increases as the domain shrinks.

To construct curves for determining vibrotational levels, the domains D and E were selected. Both curve segments were chosen to begin at 0.8 bohr, instead of 1.0 bohr because the inner turning point of the $v = 4$ level was estimated to lie some 2 to 3 eV above the minimum, at $R < 1.0$ bohr. For the $E(R)$ data for $0.8 \leq R \leq 4.4$ bohr, the PF values for D_e , β_0 , and λ_1 lie closer to the exact parameters, but R_e and λ_2 of the "best" BF lie closer. Increasing the outer R values to 0.7 bohr, to obtain better definition of the λ_1 and λ_2 parameters, brought the PF values into closer agreement. This is not so surprising, because from Table 3.2, the "best" PF basis set could be seen to have a lower absolute energy than the "best" BF basis. Nonetheless, the BF basis set performed well, performed, with only 60 per cent of the number of functions used by the PF basis set.

The GMF-5 parameters for the most precise fits for each set of data points (domains C, D, E) were used to construct potential energy curves from which vibrational and rotational energy levels were obtained using the Numerov-Cooley method.[15] (The weight of the hydrogen atom was taken to be 1.00794 a.m.u.[16]) The v -levels extended from 0 to 4, and the J -levels from 0 to 5 for each v -level, so a total of 30 levels were determined. The levels obtained are explicitly listed in Table 3.6, along with the experimental levels from Table V of Ref. [1]. Although vibrotational levels will be determined for potential energy curves in future chapters, v, J listings such as comprise Table 3.6 will not be given; fits to spectroscopic equations such as Equations (1.18-1.20) yield parameters such as those given in Table 3.7 which compactly summarize the data.

Huber and Herzberg tabulate for ω_e , $\omega_e x_e$, and $\omega_e y_e$ the values 4401.213, 121.336, and

0.8129 cm⁻¹, respectively.[17] They note these constants represent only the levels $v = 0 - 3$; the "true" ω_e (including the Dunham corrections) is 4403.2 cm⁻¹. The zero-point energy including the Y_{00} term of 8.93 cm⁻¹ is 2179.27 cm⁻¹. [17]

The energy levels from the "exact" curve have been obtained using the same fitting domain and v, J levels as for the BF and PF curves, so there is a slight discrepancy between the calculated levels reported in Ref. [8] and the levels reported for their curve here. The v, J levels of each curve were then fit to a 5-parameter spectroscopic equation, again using the non-linear least squares technique. These spectroscopic constants, for the potential curves fit to three different domains as in Table 3.5, are given in Table 3.7. The most striking thing about Table 3.7 is the great variability of the parameters according to the domain selected. Less variation in the parameters is seen for the curves with different basis sets, providing the domain is held constant. The potential curve fit over domain C (1.0—7.0 bohr) gives spectroscopic constants closest to those reported in Ref. [17]. This is because only the five bottom-most v levels were used to determine the experimental fit, so the smallest inner turning point would be *circa* (0.9 bohr, -1.09 hartree), based on a crude interpolation from Table 3.3 and 3.4. As noted previously, two more small- R points were specifically included, in order to describe the inner branch more fully. Potential curve fits over both domains D and E gave vibrotational energy levels which, when fit to equations (1.18-1.20), yielded spectroscopic constants for the BF and PF curves which agreed with those of the "exact" curve within one standard deviation. Moreover, the ω_e values for the two basis sets *bracketed* that of the exact curve:

$$\omega_e(BF) > \omega_e(exact) > \omega_e(PF)$$

Overall it may be seen that the BF basis set results gave marginally better results for the largest domain considered, whereas the PF basis set gave marginally better results for the truncated domain. The reason for this may be seen most clearly from Figure 3.2, where the average slope of the BF difference curve over the entire domain was less than that of the PF difference curve, but in the truncated domain the opposite was true.

With only three-fifths of the number of functions, the BF basis set performed nearly as well as the PF basis. A PF basis set which was closer in size, such as the (4s3p1d) set (58 functions) shown in Figure 3 of Ref. [12] has a ΔE of 1 to 2 millihartree throughout. Although H₂ is an exceptional case in that it has very little atomic basis set incompleteness,

and thus would have virtually no BSSE effects, there are some useful generalizations of this case which can be made with respect to the cases which will be encountered in the following chapters:

- (i) the addition of bond functions is generally a more efficient method of lowering the energy than the addition of higher angular momentum functions;
- (ii) the molecular basis set incompleteness (MBSI) is larger than the atomic basis set incompleteness;
- (iii) bond functions lessen the MBSI;
- (iv) mixed basis sets, consisting of BF's and PF's, are also a successful approach towards lowering the energy.

3.3 References

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Table 3.1

Exponents and contraction coefficients for the $4s + \text{PF}$ and BF basis sets for the hydrogen atom. Based on Refs. [13] and [11].

Orbital	Exponent	Coefficient
<i>s</i>	837.22	0.000112
<i>s</i>	123.524	0.000895
<i>s</i>	27.7042	0.004737
<i>s</i>	7.82599	0.019518
<i>s</i>	2.56504	0.065862
<i>s</i>	0.938258	0.178008
<i>s</i>	0.372145	1.0
<i>s</i>	0.155838	1.0
<i>s</i>	0.06618	1.0

Polarization Functions:

<i>p</i>	2.1175	1.0
<i>p</i>	0.77	1.0
<i>p</i>	0.28	1.0

<i>d</i>	1.89	1.0
<i>d</i>	0.63	1.0

<i>f</i>	0.8	1.0
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Bond Functions:

<i>s</i>	3.0	1.0
<i>s</i>	1.0	1.0
<i>s</i>	0.33	1.0
<i>s</i>	0.11	1.0

<i>p</i>	2.4	1.0
<i>p</i>	0.81	1.0
<i>p</i>	0.27	1.0

<i>d</i>	2.4	1.0
<i>d</i>	0.81	1.0

<i>f</i>	1.13	1.0
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Table 3.2

Calculated single-reference main single and double-excitations CI energy for the H₂ molecule at 1.4 bohr. All energies are in hartree. Numbers in parentheses refer to sequentially optimized exponents (first *s*, then *p*, *d*, *f*). "SL" refers to Ref. [11].

Basis Set	Number of functions	SDCI energy (hartree)
Starting 4s AO basis set:		
4s	8	-1.154322
Polarization functions added to 4s basis set:		
1p(0.77)	14	-1.168892
2p(1.32,0.44)	20	-1.171386
3p(SL)	26	-1.171830
3p1d(SL;1.0)	38	-1.173309
3p2d(SL;1.89,0.63)	50	-1.173752
3p1d1f(SL;1.0;1.0)	58	-1.173648
3p2d1f(SL;1.89,0.63;0.8)	70	-1.173973
Bond functions added to 4s AO basis:		
+ 1s(1.15)	9	-1.159388
+ 2s(1.2,0.4)	10	-1.160127
+ 1s1p(1.15,0.63)	12	-1.168408
+ 2s1p(1.2,0.4;0.57)	13	-1.169448
+ 2s2p(1.2,0.4;1.02,0.34)	16	-1.170712
+ 1s1p1d(1.15;0.63;0.6)	18	-1.170833
+ 4s2p(3,1,0.33,0.11;1,0.33)	18	-1.171042
+ 4s3p(3,1,0.33,0.11;2.43,0.81,0.27)	21	-1.171298
+ 4s2p1d(3,1,0.33,0.11;1,0.33;0.87)	24	-1.172621
+ 4s3p1d(3,1,0.33,0.11;2.43,0.81,0.27;0.87)	27	-1.172868
+ 2s2p2d(1.2,0.4;1.02,0.34;1.8,0.6)	28	-1.172776
+ 4s3p2d(3,1,0.33,0.11;2.4,0.81,0.27;2.4,0.81)	33	-1.173116
+ 4s3p2d1f(3,1,0.33,0.11;2.4,0.81,0.27;2.4,0.81;1.13)	43	-1.173637
Mixed basis (bond functions added to 4s3p AO polarization basis):		
+ 1s(1.4)	27	-1.172010
+ 2s(2.67,0.89)	28	-1.172106
+ 1s1p(1.4,0.93)	30	-1.172842
+ 2s2p(2.67,0.89;2.19,0.73)	34	-1.173103
+ 1s1p1d(1.4;0.93;0.8)	36	-1.173400
+ 3s3p(2.61,0.87,0.29;2.52,0.84,0.28)	38	-1.173127
+ 2s2p2d(2.67,0.89;2.19,0.73;2.01,0.67)	46	-1.173757
Mixed basis (bond functions added to 4s3p1d AO polarization basis):		
+ 3s3p2d(2.6,0.87,0.29;2.52,0.84,0.28;2.0,0.67)	62	-1.173917
Exact energy from Ref. [8]:		-1.174476

Table 3.3

Calculated SCF, 10 reference main, and multi-reference single and double-excitation CI energies as a function of internuclear distance for the H_2 molecule, using the $[4s] + BF(4s3p2d1f)$ basis set. The second-last column refers to the exact energy calculated by Ref. [8], and the last column represents the difference between the exact energy and the energies calculated using the "best" BF basis set. All energies are in hartree, except for ΔE (millihartree).

R	SCF Energy	Reference Energy	SD-CI Energy	$\%c_0^2$	$\Sigma\%c_i^2$	Exact Energy	ΔE
0.2	+2.239324	+2.238750	+2.1992810	99.16	99.19	+2.1978035	1.4775
0.3	+0.6603941	+0.6594815	+0.6207638	99.13	99.17	+0.619241	1.52200
0.4	-0.0794923	-0.08062518	-0.11873698	99.09	99.14	-0.1202302	1.49322
0.5	-0.4863871	-0.48781378	-0.52531990	99.05	99.11	-0.5266387	1.3188
0.6	-0.7298061	-0.73161694	-0.76850838	99.00	99.08	-0.7696353	1.12692
0.8	-0.9806468	-0.98358344	-1.01913872	98.87	99.03	-1.0200566	0.91788
0.9	-1.0442355	-1.04796184	-1.08275832	98.79	99.00	-1.0836432	0.88488
1.0	-1.0850156	-1.08971108	-1.12365978	98.70	98.98	-1.1245397	0.87992
1.1	-1.1103096	-1.11617594	-1.14917535	98.60	98.96	-1.1500573	0.88195
1.2	-1.1248723	-1.13211825	-1.16405964	98.48	98.96	-1.1649352	0.87556
1.3	-1.1318779	-1.14071256	-1.17148884	98.34	98.95	-1.1723471	0.85826
1.35	-1.1332538	-1.14295885	-1.17311610	98.27	98.96	-1.1739637	0.8476
1.4	-1.1334978	-1.14412160	-1.17363651	98.19	98.96	-1.1744757	0.83919
1.45	-1.1327823	-1.14437121	-1.17322385	98.10	98.96	-1.1740570	0.83315
1.5	-1.1312534	-1.14385125	-1.17202468	98.01	98.97	-1.1728550	0.83032
1.6	-1.1262345	-1.14097137	-1.16774812	97.80	98.99	-1.1685833	0.83518
1.8	-1.1108375	-1.13026760	-1.15418709	97.28	99.04	-1.1550687	0.88161
2.0	-1.0914803	-1.11606137	-1.13717794	96.60	99.10	-1.1381329	0.95496
2.2	-1.0704872	-1.10063968	-1.11910410	95.71	99.17	-1.1201321	1.02800
2.4	-1.0491743	-1.08534492	-1.10134052	94.55	99.25	-1.1024226	1.08208
2.6	-1.0282852	-1.07096349	-1.08468161	93.09	99.32	-1.0857912	1.10959
2.8	-1.0082312	-1.05793752	-1.06957439	91.27	99.40	-1.0706832	1.10881
3.0	-0.9892293	-1.04648800	-1.05624643	89.07	99.48	-1.0573262	1.07977
3.2	-0.9713806	-1.03668464	-1.04477560	86.51	99.56	-1.0457995	1.0239
3.4	-0.9547158	-1.02848892	-1.03513042	83.64	99.63	-1.0360752	0.94478
3.6	-0.9392228	-1.02178665	-1.02719553	80.52	99.69	-1.0280461	0.85037
3.8	-0.9248636	-1.01641600	-1.02080127	77.27	99.74	-1.0215495	0.74823
4.0	-0.9115852	-1.01219149	-1.01574413	74.01	99.79	-1.0163900	0.64587
4.4	-0.8880230	-1.00643281	-1.00879487	67.82	99.85	-1.0092561	0.46123
4.8	-0.8680204	-1.00252295	-1.00479479	62.54	99.84	-1.0051155	0.32071
5.2	-0.8510735	-1.00120437	-1.00257498	58.31	99.91	-1.0027964	0.22142
5.6	-0.8367231	-0.99978350	-1.00137026	55.06	99.88	-1.0015250	0.15474
6.0	-0.8245644	-0.99867364	-1.00072561	52.64	99.82	-1.0008355	0.10989
6.4	-0.8142483	-0.99798314	-1.00038297	50.87	99.78	-1.0004630	0.08003
6.8	-0.8054766	-0.99763819	-1.00020174	49.59	99.76	-1.0002611	0.05936
7.2	-0.7979967	-0.99751383	-1.00010624	48.67	99.75	-1.0001509	
7.6	-0.7915960	-0.99751543	-1.00005569	48.03	99.76	-1.0000900	
8.0	-0.7860960	-0.99758249	-1.00002880	47.58	99.77	-1.0000556	
8.5	-0.7802624	-0.99771583	-1.00001179	47.22	99.78	-1.0000322	
9.0	-0.7753667	-0.99788752	-1.00000412	47.01	99.80	-1.0000198	
9.5	-0.7712208	-0.99809308	-1.00000037	46.90	99.83	-1.0000129	
10.0	-0.7676761	-0.99832327	-0.99999862	46.85	99.86	-1.0000088	

Table 3.4

Potential energy curve for H_2 using "best" PF basis set from Table 3.2. Calculated SCF, 10-reference main secular equation, and multiple-reference single and double-excitation CI energies for the H_2 molecule at varying R , using the $[4s3p2d1f]$ basis set. See Table 3.3 for notation and units.

R	SCF Energy	Reference Energy	SD-CI Energy	$\%c_0^2$	$\Sigma\%c_i^2$	Exact Energy	ΔE
0.2	+2.2398770	+2.23945988	+2.19999595	99.16	99.18	+2.1978035	2.19245
0.3	+0.6609063	+0.66022260	+0.62141356	99.13	99.16	+0.6192418	2.17176
0.4	-0.0790303	-0.07990388	-0.11816841	99.10	99.13	-0.1202302	2.06179
0.5	-0.4859862	-0.48713903	-0.52484739	99.05	99.10	-0.5266387	1.79131
0.6	-0.7294965	-0.73100632	-0.76816574	99.00	99.07	-0.7696353	1.46956
0.8	-0.9805316	-0.98305081	-1.01906447	98.87	99.01	-1.0200566	0.99213
0.9	-1.0441995	-1.04743563	-1.08279459	98.79	98.98	-1.0836432	0.84861
1.0	-1.0850456	-1.08917516	-1.12379008	98.71	98.96	-1.1245397	0.74962
1.1	-1.1103877	-1.11560858	-1.14937889	98.60	98.94	-1.1500573	0.67841
1.2	-1.1249742	-1.13148977	-1.16430992	98.49	98.92	-1.1649352	0.62528
1.3	-1.1319820	-1.14000412	-1.17176304	98.35	98.92	-1.1723471	0.58406
1.35	-1.1333544	-1.14221119	-1.17339788	98.28	98.92	-1.1739637	0.56582
1.4	-1.1335937	-1.14333931	-1.17392547	98.20	98.92	-1.1744757	0.55023
1.45	-1.1328737	-1.14356118	-1.17352094	98.11	98.92	-1.1740570	0.53606
1.5	-1.1313411	-1.14302189	-1.17233167	98.02	98.93	-1.1728550	0.52333
1.6	-1.1263187	-1.14013063	-1.16808138	97.82	98.94	-1.1685833	0.50192
1.8	-1.1109281	-1.12949681	-1.15459471	97.31	99.00	-1.1550687	0.47399
2.0	-1.0915832	-1.11541343	-1.13767224	96.65	99.06	-1.1381329	0.46066
2.2	-1.0705950	-1.10012452	-1.11967579	95.78	99.13	-1.1201321	0.45631
2.4	-1.0492726	-1.08491886	-1.10196508	94.65	99.21	-1.1024226	0.45752
2.6	-1.0283613	-1.07064055	-1.08532904	93.22	99.29	-1.0857912	0.46216
2.8	-1.0082783	-1.05763853	-1.07021476	91.45	99.37	-1.0706832	0.46844
3.0	-0.9892458	-1.04614183	-1.05685323	89.31	99.45	-1.0573262	0.47297
3.2	-0.9713676	-1.03627298	-1.04532633	86.80	99.52	-1.0457995	0.47317
3.4	-0.9546758	-1.02803174	-1.03560747	83.98	99.59	-1.0360752	0.46773
3.6	-0.9391583	-1.02132177	-1.02759089	80.89	99.65	-1.0280461	0.45521
3.8	-0.9247767	-1.01598061	-1.02111234	77.68	99.71	-1.0215495	0.43716
4.0	-0.9114774	-1.01180563	-1.01597647	74.42	99.76	-1.0163900	0.41353
4.6	-0.8774417	-1.00422153	-1.00658482	65.39	99.86	-1.0068948	0.30998
5.0	-0.8589893	-1.00172516	-1.00354995	60.58	99.88	-1.0037852	0.23525
5.2	-0.8508487	-1.00092353	-1.00259437	58.56	99.89	-1.0027964	0.20203
5.6	-0.8364608	-0.99988053	-1.00137786	55.27	99.90	-1.0015250	0.14714
6.0	-0.8242709	-0.99930549	-1.00072872	52.81	99.90	-1.0008355	0.10678
6.4	-0.8139361	-0.99899113	-1.00038579	51.01	99.90	-1.0004630	0.07721
6.8	-0.8051603	-0.99881968	-1.00020552	49.71	99.90	-1.0002611	0.05558
7.2	-0.7976876	-0.99872501	-1.00011045	48.79	99.90	-1.0001509	
7.6	-0.7913002	-0.99867216	-1.00006083	48.14	99.90	-1.0000900	
8.0	-0.7858161	-0.9986432	-1.00003376	47.69	99.90	-1.0000556	
8.5	-0.7800041	-0.99862706	-1.00001703	47.33	99.90	-1.0000322	
9.0	-0.7751314	-0.99862377	-1.00000843	47.12	99.90	-1.0000198	
9.5	-0.7710098	-0.99862704	-1.00000432	47.00	99.90	-1.0000129	
10.0	-0.7674904	-0.99863288	-1.00000174	46.94	99.90	-1.0000088	

Table 3.5

Comparison of Morse parameters for PF and BF curves. Constants obtained from a non-linear least-squares fit to a five-parameter Morse function for the exact curve (Ref. [8]), and multiple-reference SD-CI and 10 reference-main energy curves obtained using both the "best" PF and BF basis sets. The standard error in each point is given in parentheses. The points were fit over different domains:

- A 0.5—10.0 bohr
 B 0.7—10.0 bohr
 C 1.0—7.0 bohr
 D 0.8—4.4 bohr
 E 0.8—7.0 bohr

Description	Range	D_e (eV)	R_e bohr	β_0 bohr ⁻¹	λ_1 bohr ⁻²	λ_2 bohr ⁻³	r.m.s. eV
Ref. [8] ("Exact")	A	4.76(2)	1.373(4)	1.06(1)	-0.123(6)	0.066(6)	0.049
	B	4.766(7)	1.399(3)	1.060(4)	-0.052(6)	0.033(2)	0.016
	C	4.742(5)	1.414(2)	1.029(4)	-0.001(6)	0.019(2)	0.009
	D	4.760(5)	1.398(2)	1.055(3)	-0.059(5)	0.040(2)	0.015
	E	4.763(6)	1.399(2)	1.058(3)	-0.052(5)	0.035(2)	0.017
PF Reference	A	3.88(2)	1.421(4)	1.05(1)	-0.120(6)	0.086(6)	0.041
	B	3.921(9)	1.433(3)	1.075(6)	-0.061(7)	0.050(4)	0.020
	C	3.912(8)	1.441(4)	1.062(7)	-0.03(1)	0.040(5)	0.015
BF Reference	A	3.92(2)	1.416(6)	1.06(1)	-0.117(6)	0.080(8)	0.050
	B	3.94(1)	1.433(6)	1.076(9)	-0.06(1)	0.045(7)	0.034
	C	3.93(1)	1.446(8)	1.06(1)	-0.02(2)	0.033(8)	0.026
PF SD-CI	A	4.72(2)	1.379(4)	1.05(1)	-0.126(6)	0.075(6)	0.048
	B	4.755(7)	1.399(2)	1.060(3)	-0.053(5)	0.036(2)	0.015
	C	4.735(6)	1.410(2)	1.035(5)	-0.012(7)	0.024(2)	0.011
	D	4.745(5)	1.399(2)	1.055(3)	-0.059(5)	0.041(2)	0.014
	E	4.748(6)	1.400(2)	1.059(3)	-0.052(5)	0.036(2)	0.016
BF SD-CI	A	4.74(2)	1.373(4)	1.06(1)	-0.121(6)	0.068(6)	0.048
	B	4.743(7)	1.398(3)	1.064(3)	-0.049(5)	0.034(2)	0.016
	C	4.719(4)	1.414(2)	1.033(3)	0.001(6)	0.020(2)	0.008
	D	4.737(6)	1.398(2)	1.058(3)	-0.056(5)	0.040(2)	0.014
	E	4.741(6)	1.399(2)	1.062(3)	-0.049(5)	0.035(2)	0.017

Table 3.6

Vibrational and rotational levels calculated for three potential curves using the Numerov-Cooley technique. The energy levels from the exact curve have been obtained using the same fitting methods as for the BF and PF curves, so there is a slight discrepancy between the calculated levels reported in Ref. [8] (denoted as "exact" in this Table) and the levels reported using their potential curve here. The potential curve parameters were obtained over the range 0.8–7.0 bohr, and the $E_{v,J}$ levels for $v = 0-4$ and $J = 0-5$ were used in the spectroscopic fit.

v	J	"exact"	BF SD-CI	PF SD-CI
$-\frac{1}{2}$	0	2236.48	2238.57	2233.97
0	0	0.00	0.00	0.00
0	1	118.84	118.87	118.72
0	2	355.46	355.57	355.12
0	3	707.80	708.03	707.13
0	4	1172.85	1173.23	1171.74
0	5	1746.70	1747.29	1745.04
1	0	4254.84	4259.38	4249.96
1	1	4367.60	4372.19	4362.60
1	2	4592.07	4596.77	4586.82
1	3	4926.23	4931.09	4920.62
1	4	5367.11	5372.18	5361.02
1	5	5910.86	5916.22	5904.19
2	0	8239.87	8249.32	8230.95
2	1	8346.59	8356.11	8337.55
2	2	8559.02	8568.67	8549.73
2	3	8875.18	8885.02	8865.53
2	4	9292.16	9302.27	9282.03
2	5	9806.21	9816.66	9795.52
3	0	11966.02	11980.52	11954.05
3	1	12066.61	12081.18	12054.52
3	2	12266.84	12281.56	12254.54
3	3	12564.86	12579.79	12552.23
3	4	12957.89	12973.11	12944.84
3	5	13442.34	13457.92	13428.78
4	0	15446.69	15466.14	15432.61
4	1	15540.57	15560.08	15526.42
4	2	15727.63	15747.27	15713.33
4	3	16006.37	16026.22	15991.85
4	4	16374.42	16394.54	16359.59
4	5	16828.50	16848.97	16813.29

Table 3.7

Comparison of spectroscopic constants for PF and BF multiple-reference single- and double-excitation CI curves. Constants obtained from a non-linear least-squares fit to a five-parameter spectroscopic equation for the exact curve (Ref. [8]), and SD-CI and 10-main reference energy curves obtained using both the "best" PF and BF basis sets. All quantities in cm^{-1} . Different ranges of points were used:

C 1.0—7.0 bohr

D 0.8—4.4 bohr

E 0.8—7.0 bohr

Description	Range	ZPE	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	r.m.s.
Ref. [8] ("Exact")	C	2171.58	4408(3)	123(2)	0.9(3)	58.9(1)	2.58(5)	4.1
	D	2228.22	4530(4)	149(2)	2.8(3)	59.9(1)	3.09(5)	3.9
	E	2236.48	4547(4)	148(2)	2.4(3)	59.9(1)	3.06(5)	3.8
BF SD-CI	C	2175.15	4414(4)	123(2)	0.9(3)	58.9(1)	2.58(5)	4.1
	D	2230.78	4535(4)	148(2)	2.7(3)	60.0(1)	3.08(5)	3.9
	E	2238.57	4551(4)	148(2)	2.4(3)	59.9(1)	3.06(5)	3.8
PF SD-CI	C	2182.59	4432(4)	128(2)	1.2(3)	59.2(1)	2.69(5)	4.0
	D	2226.31	4526(4)	149(2)	2.8(3)	59.9(1)	3.09(5)	3.9
	E	2233.97	4542(4)	148(2)	2.5(3)	59.8(1)	3.06(5)	3.8

Figure 3.1

Comparison of the convergence of the SD-CI energy for H_2 at 1.40 bohr as a function of the number of extra orbitals which had to be added to the atomic 4s AO basis. o : Bond functions added to basis; • : Polarization functions added to basis.

Figure 3.2

Energy difference (in millihartree) between the SD-CI energy for the H_2 molecule and the exact energy reported by Kolos, Szalewicz and Monkhorst. o : "Best" bond function basis set $[4s + BF(4s3p2d1f)]$ for a total of 43 functions; • : "Best" polarization function basis set $(4s3p2d1f)$ for a total of 70 functions.

Chapter 4

The Single and Double Ionization Potentials of Hydroxyl

Irrationally held truths may be more harmful than reasoned errors.

T. H. Huxley, *Science and Culture*,

xii. The Coming of Age of the Origin of the Species

4.1 Introduction

In the preceding chapter, it was seen that bond function (BF) and mixed basis sets could give results of accuracy better than that of same-sized polarization (PF) sets and of accuracy comparable to those of the much larger (i.e., more computationally expensive) PF basis sets. Given the success of the BF and mixed basis sets for dihydrogen in Chapter 3, the natural next step is to try adding BF's to the basis sets used to calculate different systems. Earlier work done by this group showed that BF's could be successfully added to DZP-quality atom-centred basis sets used in the calculation of the ground state first-row diatomics. The calculations were not much larger than DZP, but the accuracy was improved in all cases.[1] This is confirmed for OH in this chapter, and extended to the calculation of its mono- and di-cation.[2]

Although this is admittedly no breakthrough for OH or its ions, for which high-quality calculations already exist,[3][4][5][6][7] the balanced basis set method could be very useful in calculations of polyatomic systems, which demand economy and accuracy. Two well-known surfaces for the reaction

for example, show asymptotic errors of 0.6—0.4 eV for the OH well because the atom-centred basis sets were of necessity smaller than those described here for high-quality diatomic calculations, and thus did not have the flexibility to describe the inter-nuclear regions.[8][9]

Exploration into the ionization potential (IP) of a representative hydride such as OH was further prompted by a recent calculation of singly- and doubly-ionized hydrides by Pope

et al.[10] This work reported IP's of the neutral molecules (IP_1) consistently lower than the experimental values, whereas the IP's of the monocations (IP_2) were consistently high. The authors suggested that the error in IP calculations was "unlikely to reflect inadequacies in the calculations and points to excited vibrational states of the monocations being involved experimentally." [10] In a comment following the paper, Wright and Williams noted that before invoking experimental flaws to explain the discrepancy, the theoretical treatment itself could be the source of the disagreement. They argued that the error could either lie in the dissociation limits, which would change the position of the asymptotes relative to the correct values; or in the dissociation energies of the the neutral species and cation. For example, an erroneous D_e of the monocation would cause IP_1 to be too small and IP_2 to be too large. The numbers they used to back up this argument were a published curve for OH,[1] preliminary points for OH^+ , and only a schematic curve for OH^{2+} . [11] Since their data were obtained with basis sets containing bond functions, Hillier *et al.* suggested, in a reply to this comment, that such conclusions might not be valid due to the inclusion of BF's.[12]

In this chapter, it is shown how, using a basis set comparable in size to that of Ref. [10], the calculated IP_1 and IP_2 could be in error, regardless of the presence of BF's. The error in the calculation is shown to be caused by an inadequate atomic basis set, which yields an incorrect IP for oxygen.[2] Even large basis sets are unable to overcome this serious limitation in the atomic description.[6] Finally, it will be shown that adjusting for this discrepancy—a "reasoned error," in Huxley's words—leads to the correct ionization potentials.

4.2 Results and Discussion

Table 4.1 summarizes the atomic energies obtained using different basis sets. 'DZP' for oxygen in this Table refers to Dunning's $[4s2p]$ contraction[13] of Huzinaga's $(9s5p)$ set of primitive Gaussian orbitals[14], with an additional set of d orbitals of exponent 0.85. For hydrogen, the basis was a $[2s1p]$ contraction of $(4s1p)$ primitives, with molecule-optimized exponents. The TZP basis set was a $(9s5p1d) \rightarrow [5s3p1d]$ contraction from the same source, with exponents of 1.19 (atom) and 1.25 (ion). The cation draws in its charge density more than the neutral species, so its radius is slightly smaller, and the optimum exponent for its GTO is slightly larger, leading to a more compact orbital. The TZPP

exponents were held in a 1 : 2.5 ratio and optimized to 0.77 and 1.925 for the atom, and 0.8 and 2.0 for the ion. The TZP and TZPP basis sets for hydrogen were the same, using a $(5s1p) \rightarrow [3s1p]$ contraction in both cases.

The DZP ground state hydroxyl ($\text{OH}(^2\Pi_r)$) curve was obtained using the corresponding basis set and the MRD-CI method as outlined in Chapter 2. A GMF-5 fit of the (est.) full-CI points gave the usual five parameters, the dominant two of which (D_e and R_e) are listed in the fourth and fifth columns of Table 4.2. (See also Equation (2.6).) Vibrotational energy levels for $v = 0-4$ and $J = 0-5$ were found using the Numerov-Cooley technique, and then these levels were fit to the spectroscopic equation (1.18-1.20) for the four parameters ω_e , $\omega_e x_e$, B_e and α_e . The best-fit parameters of this equation, as well as the zero-point energy (ZPE), are given in the last five columns of Table 4.2. To this basis set was added a set of (sp) bond functions, whose exponents were optimized to be 0.73 at the experimental R_e .^[15] (This differs insignificantly from the 0.75 exponent obtained in Ref. [1], which reports a D_e of 4.582 eV from their curve.) These results are denoted as DZP+(sp) in Table 4.2.

Results for OH^+ ($^3\Sigma^-$), which were similarly obtained with DZP and DZP+(sp) basis sets and a bond function exponent of 0.74, are also listed in Table 4.2. For comparison, this Table also lists the molecular and spectroscopic constants for OH and OH^+ obtained with other methods.

4.2.1 OH

A double-zeta polarization (DZP) basis set gave a D_e of 4.235 eV, which is in error by nearly 0.4 eV, and an R_e of 1.848 bohr, which is in error by 0.015 bohr. The addition of a single set of (sp) bond functions to the modestly-sized DZP basis set caused an immediate improvement of over 0.3 eV, to give 4.577 eV, in the OH well-depth and 0.007 bohr, to give 1.841 bohr, in the R_e . (Expt. 4.58 eV; 1.833 bohr.)

It is not possible to go into detail about all the reported calculations, since OH is one of the most extensively studied radicals,[†] but a representative sample of results from other groups' work is included in Table 4.2.

As early as 1972, Bondybey *et al.* published a first-order CI (FO-CI) calculation on OH using a $[4s3p1d]$ STO basis on oxygen. The D_e and ω_e depicted a bond that was too

[†] In particular, the calculation of the radiative transition probabilities between the $X^2\Pi$ and $A^2\Sigma^+$ states is a sensitive indicator of the quality of the ground and excited state wavefunctions.

weak. The main source of error was judged to be in the first-order CI approximation.[16] Nearly simultaneously, Easson and Pryce reported a much more limited calculation. They used a minimal basis set and a CI space of only three dozen configurations in an effort to gain a qualitative picture of OH and its excited states. The (estimated) dissociation energy and fundamental frequency are surprisingly good, considering the severe restrictions of the calculation; however, Figure 10 in this reference shows the the ground state curve is anomalously pinched.[17]

Chu *et al.* used a basis set consisting of (6s4p3d1f) STO's on the oxygen atom and (4s3p2d) on the hydrogen atom. A multi-configuration SCF (MC-SCF) (see Section 1.2.2) calculation was performed, and then a limited 7311-configuration CI (consisting of mainly valence-shell excitations). Although the basis set was large, the CI was too restricted and the curve was too shallow, as evidenced by too small a D_e and ω_e . [18]

In their highly-accurate coupled electron pair approach (CEPA) calculations of the first- and second-row series of hydrides, Meyer and Rosmus also substantially underestimated the D_e at 4.38 eV, but the fundamental frequency and R_e are in excellent agreement. They also used a large basis set, consisting of [4s4p2d1f] GTO's on oxygen and [4s2p1d] on hydrogen.[5]

Rosmus and coworkers again used CEPA methods some eight years later, when they applied the self-consistent electron pair (SCEP) method in combination with 7-configuration MC-SCF, and CEPA, to obtain potential energy curves and dipole moment functions for OH, OH⁻ and OH⁺. The constants for the MCSCF-SCEP hydroxyl curve are in very good agreement with those from experiment; the SCEP-CEPA results are less so.[3]

Another study of the dipole moment function, reported by Langhoff *et al.*, compared a small-basis full-CI calculation with a large-basis multiple-reference single- and double excitation CI (MRSD-CI). The former calculation, with a [4s3p2d/2s1p] GTO basis set, had a shallower well-depth (4.395 eV) than the approximate CI calculation, with a set of [6s5p4d2f1g/4s3p2d] GTO's ($D_e = 4.59$ eV).[7][†] This implies that the error of approximating full-CI by MRSD-CI is less than the error of prematurely truncating the basis set to roughly TZPP quality (basis set incompleteness).

[†] These authors do not list other constants obtained from the large-basis curve for comparison.

4.2.2 OH⁺

As with the neutral species, addition of a single (*sp*) BF to the DZP basis set improved the D_e significantly but, contrary to the case of OH, R_e did not change drastically since it was not so much in error to begin with. To a first approximation, the ionization of OH removes an electron from a pair of electrons occupying a non-bonding $2p\pi$ orbital, which slightly lessens the repulsion, leading to a bond somewhat stronger than that in OH.

In a study following their work on diatomic hydrides, Rosmus and Meyer applied the pseudonatural orbital CI (PNO-CI) and CEPA methods to the ions of these hydrides. As with the neutral species, large basis sets were used and the CEPA results were in very good agreement with experiment.[4] (Calculated: 5.22 eV and 1.943 bohr; expt.: 5.28 eV and 1.945 bohr.)

Werner *et al.* report a SCEP-CEPA D_e value for the cation which agrees to within 0.2 eV. The MC-SCF D_e was not even reported for OH⁺ due to incorrect dissociation of the MC-SCF wavefunction into O⁺ + H.[3] A similar problem was noted by Rosmus and Meyer, in their calculation of the NH⁺ curve[4] and, as will be discussed below, it was encountered again in the present work.

A recent high-quality calculation on the ground and excited states of OH⁺ was reported by Saxon and Liu. They began with a (7s5p3d1f) STO basis on oxygen and a (5s2p1d) basis on hydrogen, constructed CAS-SCF MO's and then carried out a second-order CI (SO-CI) calculation. The D_e reported is for dissociation to the correct limits, which overestimates the experimental D_e since the calculation in fact approaches a different limit.[6]

The dissociation energies reported for OH⁺ in the present work are based on the dissociation limits to which the ion tended to go at large R , and not on the experimentally-known dissociation products. The ground state OH⁺ ion is of $^3\Sigma^-$ symmetry, which means that either dissociation limit is possible:

where the numbers at the far right are experimental values in eV showing how high above the neutral limit O(³P) + H(²S) these two ionic dissociation limits lie. Since the first limit

lies slightly lower than the second, the monocation dissociates to this limit. From the energies listed in Table 4.1, however, atomic/ionic calculations using a DZP basis do not give a correct ordering of these limits:

To understand the source of the 0.64 eV error in the calculations of the atomic IP, consider the initial and final multiplicities of the species involved in the following ionization:

Given that the largest source of error in *ab initio* calculations lies in the difficulty of accounting for the electron-electron repulsion, it stands to reason that those systems which do not place two electrons in the same orbitals (such as $\text{O}^+(^4S)$) will be better described (i.e., the calculated absolute energy will be closer to the true absolute energy, which is approached monotonically from above) than those which do (such as $\text{O}(^3P)$). Thus, the IP of atomic oxygen is too small.

Even the TZP and TZPP basis sets are deficient and incorrectly order the limits:

In fact, in the high-quality large basis set calculation by Saxon and Liu, the atomic IP was *still in error* by 0.389 eV, and the dissociation limits consequently remained reversed.[6]

If one were unaware of this discrepancy at the asymptotes for OH^+ , one would obtain D_e simply as the difference between the minimum in the ionic curve, and the experimental limit of $\text{O}(^3P) + \text{H}^+$. In the present work, the D_e would be over-estimated as 5.73 eV.

4.2.3 OH^{2+}

The potential curves are illustrated in Figure 4.1. The uppermost repulsive curve represents the $X^4\Sigma^-$ state of the doubly-charged ion, OH^{2+} . The OH^{2+} species is formed by the collision of high-speed OH^+ ions with neutral gas molecules M, in a "charge-stripping" reaction:

The OH^{2+} promptly dissociates to the unambiguous limits:

From Table 4.1, the DZP limit is found to lie 26.46 eV above the neutral atoms.

Points for $\text{OH}^{2+}(\text{}^4\text{S})$ calculated between 1.4 and 4.4 bohr were fit to a combined Coulombic-“anti-Morse” function, of the form:

$$E(R) = D_e \{1 + e^{-\beta x}\}^2 + \frac{a}{R} \quad (4.8)$$

Typical values obtained for these parameters were (energy in eV; length in bohr):

$$D_e = 3.62 \quad R_e = 1.614 \quad \beta = 1.555 \quad a = 1.00$$

In other words, a bound curve was superimposed on a Coulombic repulsive curve. There was little difference between the results with and without a bond function, as expected for a repulsive (non-bound) potential. Although the ground state electronic configuration

$$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$$

shows a bond order of one-half, which leads to a positive D_e , the shape of the curve, as can be seen from the value of the a parameter, is nearly purely charge-charge repulsion and so non-bonding character is dominant.

4.2.4 Ionization Potentials

The single adiabatic ionization potential IP_1 is the energy required to go from the $v = 0$ level of the neutral species to the $v = 0$ level of the cation:

$$\text{IP}_1 = D_e(\text{OH}) - \text{ZPE}(\text{OH}) + \text{IP}(\text{O}) - D_e(\text{OH}^+) + \text{ZPE}(\text{OH}^+). \quad (4.9)$$

For the DZP curves, this gives $\text{IP}_1 = 12.35$ eV. For the DZP+(*sp*) curve, IP_1 is nearly unchanged at 12.36 eV. The well-depths of the two curves have been changed by nearly the same amount (≈ 0.3 eV) by the addition of BF's to the basis sets, so one effect has cancelled the other. Pope *et al.* report a CAS-SCF IP_1 of 11.3 eV, which is improved by 1.0 eV upon extending their treatment to the CI level.[10] The experimental value is 13.0 eV.[19]

The double ionization potential, IP_2 , cannot be calculated in quite the same fashion, because the upper state is unbound. The absolute energy of OH^{2+} given as a function of R in equation (4.8) was calculated at the equilibrium bond length of the lower-lying OH^+ , and then the difference between this point and the energy of the $v = 0$ level of OH^+ was found. This is in effect the vertical distance between the OH^+ and OH^{2+} curves at $R_e(OH^+)$, less the ZPE. The DZP basis gave an IP_2 of 29.2 eV; the DZP+(*sp*) basis had an IP_2 of 29.3 eV. Pope *et al.* report a CAS-SCF IP_2 of 28.5 eV, which changed to 29.6 eV upon inclusion of CI.[10] The experimental value is 29.0 eV.[20]

The value for IP_2 is in much better agreement with experiment than that of IP_1 because not only are the curves well-described around $R_e(OH)$, but also the asymptotes happen to be in much better agreement (energetically, but not qualitatively) than they were for IP_1 . Experimentally, these should be the $OH^+ \rightarrow OH^{2+}$ asymptotes, which lie 13.62 eV apart:

Computationally, the $OH^+ \rightarrow OH^{2+}$ asymptotes turn out to involve different species, and lie some 13.55 eV apart:

So, although IP_2 is in good agreement, it is due to the fortuitous agreement of the experimental oxygen IP with the calculated hydrogen atomic IP—an agreement that would not always be so close for another hydride.

Two more points should be emphasized with respect to IP's. First of all, if the curves in Figure 4.1 were vertically adjusted so that the asymptotes agreed with experiment, IP_1 as well as IP_2 for the molecular species would be in excellent agreement. This is because the BF molecular curves replicate the D_e well, and even in the case of the DZP curves where the D_e is not so well replicated, the errors tend to cancel each other.

The second is that, as we have seen in Section 4.2.2, the difficulty in obtaining correct atomic IP's remains, even for very large basis sets, and does not show fast convergence. From Table 4.1 and Ref. [6], the error in the oxygen IP may be summarized as:

DZP	TZP	TZPP	(7s5p3d1f/5s3p1d)
0.71	0.67	0.56	0.38

Until theoretical calculations can overcome this problem, it seems presumptuous to point to experimental flaws as the reason for disagreement.

4.2.5 Effect of Ghost Orbitals

Extranuclear orbitals can be used as a qualitative "probe" of basis set incompleteness. That oxygen has a less-than-perfect atomic basis set is readily apparent in the difficulties encountered in this calculation[2] with the atomic IP. Another symptom of the atomic basis set incompleteness is the substantial energy lowering brought about by the presence of "ghost" orbitals, *i.e.*, orbitals situated at a nearby centre with zero charge. An incomplete atomic basis set leads to artificially lowered energies when ghost orbitals are in the vicinity, an effect which generally lessens in magnitude as increasingly larger atomic basis sets are used.

The lowering which occurs depends on the location and the size of the ghost orbitals. Predictably, for a given basis set, the "ghost" orbitals should coincide as much as possible with the atomic orbitals for the largest effect. Table 4.3 shows the effect of some (*sp*) ghost orbitals (corresponding to the BF's used in this study) on the calculated F-CI energy of the oxygen atom at three different distances, for six different sizes of orbitals. The left-most column shows the exponent ζ for the (*sp*) set. The second and third columns show the expectation values of r for the *s* and *p* orbitals (denoted $\langle r \rangle_s$ and $\langle r \rangle_p$), respectively, *i.e.*, that distance where an electron in an orbital would, on average, spend most of its time. Taking the radial part of a Gaussian-type orbital:

$$\psi = r^n e^{-\zeta r^2} \quad (4.12)$$

the expectation value for an orbital with angular momentum quantum number n , $\langle r \rangle_n$, may be expressed as:

$$\langle r \rangle_n = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^n e^{-\zeta r^2} r r^n e^{-\zeta r^2} r^2 \sin\theta dr d\theta d\phi \quad (4.13)$$

$$\langle r \rangle_n = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^{2n+3} e^{-2\zeta r^2} \sin\theta dr d\theta d\phi, \quad (4.14)$$

which was derived by Petsalakis to give:[25]

$$\langle r \rangle_s = \frac{2}{\sqrt{2\pi}\zeta} \quad (4.15)$$

$$\langle r \rangle_p = \frac{8}{3\sqrt{2\pi}\zeta} \quad (4.16)$$

$$\langle r \rangle_d = \frac{16}{5\sqrt{2\pi}\zeta} \quad (4.17)$$

The three right-most columns of Table 4.3 show the energy of the oxygen atom, calculated with the set of (*sp*) orbitals beside it at distances of 0.95, 1.9 and 4.0 bohr away. Going across the Table in horizontal fashion, and comparing $E(R)$ for a given exponent, one sees that when the exponent ζ is small (0.20) and the orbitals are diffuse, the energy lowering is small, ranging from 0.073 eV when the ghost orbitals are 0.95 bohr away from the atom, to 0.034 eV when the ghost orbitals are 4 bohr away.

When ζ is larger, the energy lowering is greater. The bottom-most row shows that when the (*sp*) set is quite compact, with $\zeta = 1.2$, the energy lowering at the distance of closest approach is larger, 0.33 eV. Conversely, a greater separation coupled with a more compact set of orbitals means considerably less overlap between the (*sp*) set and the orbitals of the oxygen atom, and so the energy is lowered by only 0.003 eV at 4 bohr. From this Table it is apparent that a small ζ gives rise to a large $\langle r \rangle$, and the energy lowering in the last column (farthest distance away) is greatest for a diffuse orbital, whose expectation value is roughly 4 bohr as well.

The greatest energy lowering is achieved *approximately* when the expectation value of the functions at the bond centre agrees with the distance R_{O-go} between the oxygen atom and the set of ghost orbitals ('go') but it must be borne in mind that this is in fact a simplification. The underlying assumption has been that the O—go distance of maximum overlap between the orbitals of oxygen and the ghost orbitals is roughly equivalent to the expectation value:

$$\langle \Psi_O | \Psi_{go} \rangle \simeq \langle r \rangle_{go} . \quad (4.18)$$

This is a reasonable first approximation. Looking at the vertical columns of the Table 4.3, it is seen that $E(R = 0.95)$ is lowest where $\langle r \rangle_s \simeq 0.95$ bohr and $E(R = 4.0)$ is lowest where $\langle r \rangle_s \simeq \langle r \rangle_p \simeq 4.0$ bohr. The lowest value of $E(R = 1.9)$ does not occur where

$\langle r \rangle_s$ and/or $\langle r \rangle_p \approx 1.9$ bohr, however, and this indicates where the approximation breaks down.

The stabilization of low-lying virtual MO's in order to overcome the molecular basis set incompleteness may be expressed in a similar fashion as maximizing the overlap of the BF orbitals with the bonding molecular orbitals (MO's), $\langle \Psi_{MO} | \Psi_{BF} \rangle$. Since the molecular orbitals are comparable in size to the atomic orbitals, the atomic and molecular forms of the BSI are closely linked. The optimum ζ 's would be similar but not necessarily identical for the two kinds of overlap. This is precisely what is seen in the OH case: the optimum (*sp*) exponent was 0.74 for OH at $R_e \approx 1.9$ bohr, whereas a parabolic interpolation of values from Table 4.3 indicates that the optimum ghost orbital exponent would be 0.83 at $R_{O-gs} = 0.95$ bohr.

It is deceptively easy to seize upon the artificial lowering brought about by ghost orbital calculations such as those tabulated in Table 4.3 as grounds for discarding entirely the approach of inserting functions in the internuclear region in molecular calculations. However, a very important distinction must be made between the two forms of BSI, and this is seen in connection with the use of non-nuclear functions:

The existence of atomic basis set incompleteness is shown by the artificial energy lowering that occurs when non-nuclear functions are added to the calculation; whereas artificially high molecular energies exist due to the molecular basis set incompleteness, and a reasonable distribution of non-nuclear functions is needed in order to counteract this error.

Consider the case where a "perfect" basis set is used. A perfect basis set would yield the true absolute energy of the atom. Placing an (*sp*) function in the vicinity would not further stabilize the atomic energy. This was practically the case with the hydrogen atom calculated in Chapter 3—the atomic basis set incompleteness (BSI) was $\approx 2 \mu\text{hartree}$ and so adding an additional set of functions some distance away from it would not be able to lower the energy any more than that.

Now consider what happens when this complete atomic basis set is used to build a molecule. The molecular orbitals are formed from linear combinations of the atomic orbitals. The molecular orbitals, which are concerned primarily with the internuclear region, are not modelled very well in comparison with the atom's orbitals, for the simple reason that the

functions used in their linear combination are *expanded (inefficiently) from points other than the main area of interest, i.e., the mid-nuclear region.*[†] Thus, when the molecular orbitals are formed, the (*sp*) function lying between two atoms—which cannot lower the atomic energy—helps to lower the artificially high molecular energy, as was observed in the case of H_2 , where the “perfect” atomic basis set resulted in a molecular basis set incompleteness of some 20 millihartree, or 10,000 times greater than the atomic BSI error. Qualitatively, the same case obtains for other molecules: the atomic BSI of a nuclear-centred basis set is *ipso facto* smaller than the molecular BSI. The problem gets more complex because the two kinds of error usually occur together. Although rare cases such as that of H_2 exist, which has no atomic BSI but substantial molecular BSI, there is no known molecule which has atomic but not molecular BSI.

In keeping with this Chapter's theme of “reasoned errors,” it is seen how non-nuclear orbitals are related to basis set incompleteness. How this incompleteness is interpreted, and most importantly, how one goes about compensating for it, in order to achieve the best potential energy curve for as economical a basis set as possible, is a matter of some discussion. Martin *et al.* have very recently argued that since the BSSE and the MBSI follow the same trend with respect to R , and since they tend to compensate for each other, it is self-defeating to correct for one effect and not the other.[26] Ghost orbitals act as a good “probe” of atomic basis set incompleteness, and, placed in the bonding region, they become a useful tool for decreasing the molecular basis set incompleteness. The approach taken in this thesis has been to acknowledge that *molecular and not just atomic* basis set incompleteness exists. A good calculation will therefore strike a balance between atomic and molecular descriptions.

4.3 References

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[†] An analogy is the difficulty one would experience in modelling a sphere centred at $R = 0$ if one were restricted to expanding functions only from $R = A$, where $A \neq 0$.

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Table 4.1

SCF, MRD-CI and estimated full-CI energies for the asymptotic limits of the potential energy curves. The CI space consisted of the complete set of all single and double excitations of the ground state occupation (as the single reference configuration). Energy in hartree; exponents in bohr⁻².

Species	Basis Set	Polarization	Energy		
		Exponent	SCF	MRD-CI	Est. Full-CI
O(³ P)	DZP	0.85	-74.8006	-74.9128	-74.9166
	TZP	1.19	-74.8019	-74.9356	-74.9397
	TZPP	0.77,1.925	-74.8020	-74.9479	-74.9528
H(² S)	DZP	1.0	-0.4976	—	—
	TZP	1.0	-0.4991	—	—
O ⁺ (⁴ S)	DZP	0.85	-74.3613	-74.4402	-74.4421
	TZP	1.25	-74.3624	-74.4617	-74.4639
	TZPP	0.8,2.0	-74.3631	-74.4703	-74.4729

Table 4.2

Molecular and spectroscopic constants for hydroxyl and its monocation.

Species	Calculation	Ref.	D_e (eV)	R_e (bohr)	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	B_e cm^{-1}	α_e cm^{-1}	ZPE cm^{-1}
OH($^2\Pi$)	DZP		4.235	1.848	3786	92.7	18.69	0.80	1870
	DZP+(<i>sp</i>)		4.577	1.841	3747	80.6	19.10	0.86	1853
	FO-Cl	[16]	4.26	1.841	3675	—	18.7	—	—
	minimal	[17]	4.3	—	3758	—	—	—	—
	MCSCF/Cl	[18]	4.43	1.811	3713	83.2	18.87	0.68	1847
	CEPA	[5]	4.34	1.835	3744	84.9	18.85	0.72	1850
	MCSCF-SCEP	[3]	4.53	1.837	3725	90	18.82	0.73	1840
	SCEP-CEPA	[3]	4.53	1.837	3735	86	0.72	—	1846
	F-Cl	[7]	4.266	1.855	3714	—	—	—	—
	MRSD-Cl	[7]	4.59	—	—	—	—	—	—
OH $^+$ ($^3\Sigma^-$)	expt.	[15]	4.62	1.833	3738	84.9	18.91	0.72	1848
	DZP		4.76	1.952	3167	82.2	16.90	0.81	1563
	DZP+(<i>sp</i>)		5.09	1.950	3151	74.9	16.87	0.75	1557
	PNO-Cl	[4]	—	1.933	3188	81.0	16.94	0.72	1574
	CEPA	[4]	5.22	1.943	3124	84.7	16.77	0.74	1541
	MCSCF-SCEP	[3]	—	1.948	3108	82	16.71	0.74	1534
	SCEP-CEPA	[3]	5.10	1.946	3121	82	0.74	1540	—
	Cl	[24]	5.31	1.952	3104	77.8	16.57	0.69	1533
	CASSCF-SOCI	[6]	5.358	1.948	3088	72.8	16.58	0.77	1526
	expt.	[15]	5.28	1.945	3113	78.5	16.79	0.75	1537

Table 4.3

Effect of "ghost" orbitals' position and exponent on the energy of the oxygen atom. With no additional orbitals present, the absolute energy is -74.916 564 hartree. The (*sp*) exponents are constrained so that $\zeta(s) = \zeta(p)$. Distances in bohr; energy in hartree; exponents in bohr⁻².

BF exponent	$\langle r \rangle_s$	$\langle r \rangle_p$	$E(R=0.95)$	$E(R=1.90)$	$E(R=4.00)$
0.05	3.57	4.76	—	—	-74.917 825
0.20	1.78	2.38	-74.919 229	-74.918 967	-74.917 819
0.50	1.12	1.50	-74.927 768	-74.921 551	-74.917 107
0.74	0.93	1.24	-74.930 707	-74.921 792	-74.916 857
0.95	0.82	1.09	-74.930 457	-74.921 305	-74.916 746
1.20	0.73	0.97	-74.928 575	—	-74.916 675

Figure 4.1

4-18

Computed potential energy curves for three species. ●: Bond function basis set; ○: Polarization function basis set.

Bottom: $\text{OH}(^2\Pi) \rightarrow \text{O}(^3P) + \text{H}(^2S)$.

Middle: $\text{OH}^+(^3\Sigma^-) \rightarrow \text{O}^+(^4S) + \text{H}(^2S)$; incorrect dissociation (see text).

Top: $\text{OH}^{2+}(^4\Sigma^-) \rightarrow \text{O}^+(^4S) + \text{H}^+$.

Chapter 5

Diatomic Hydrides of the Second Row:

NaH, MgH, AlH, SiH, PH, SH and HCl

Example is always more efficacious than precept.

Samuel Johnson,
Rasselas

5.1 Introduction

Accuracy in calculation of well depths for diatomic and polyatomic molecules has proven to be surprisingly difficult to attain in practice, and many calculations which report otherwise highly accurate diatomic properties such as the fundamental frequency (ω_e) fare much worse in the determination of well depth. The use of moderately large basis sets followed by large-scale CI calculations continues to underestimate the well depth by 0.25 eV or more in a potential well of depth 5 eV (5% error), even though spectroscopic parameters such as ω_e , or the ionization potentials may be calculated to within 1% or better.

The two main sources of error pinpointed in Chapter 1 are the difficulty of including higher-order correlations at the CI stage, and the basis set incompleteness. The former has been largely overcome by selection-extrapolation procedures such as the MRD-CI method used in this thesis, which comes within 1 kcal/mole of “benchmark” full-CI values for a wide range of molecules.[1] In this thesis, it is further demonstrated how the latter limitation can be overcome by judicious distribution of functions on *and between* the atomic nuclei.

The unifying theme of this thesis is that poor-quality potential curves, and in particular, the commonly underestimated D_e , arise from the use of exclusively nuclear-centered AO's to describe the molecule. The electron density in the molecule tends to be distributed more *away* from the nuclei, compared to the atomic case. Several diatomic molecules have been chosen as the “more efficacious” examples with which to prove this point. The nuclear-centred description inevitably biases the calculation in favour of the atoms and leads to

well depths which are too small. In conventional calculations, the well depth can only be improved by adding more and more orbitals of valence-shell-type (*e.g.*, progressing from double zeta (DZ) to triple zeta (TZ) quality), and of higher angular momentum (polarization functions, PF's). For example, a basis set containing double zeta single polarization (DZP) AO's followed by a reasonably large CI typically leads to *circa* 90% of the well depth for single bonds, whereas a triple zeta double polarization (TZPP) basis typically leads to 92-94% of the well depth. The process of adding additional AO's is slowly convergent to the correct D_e , as has been amply demonstrated for H_2 in Chapter 3.

The basis set exploration which comprises this thesis sets as a target the error limit of 0.1 eV for well depth, a figure which would lead to *ab initio* surfaces of useful accuracy. The first work on the hydrides by this group showed how the introduction of bond functions (BF's) located at the mid-bond position led to a systematic improvement in the dissociation energies of the first row hydrides BH, CH, NH, OH and HF.[2] For these hydrides, error limits of ± 0.1 eV in the well depth D_e were obtained using a basis set of DZP AO's and (*s,p*) bond functions. This basis set was considered to be well balanced, and was also used to construct potential surfaces for $O + H_2$ and $F + H_2$ [3] and $H + H_2$. [4] Extension of this same principle of basis set balance, applied to H_2 and H_3 , [4] led to the observation that larger TZPP AO basis sets necessitated the addition of *two* sets of (*s,p*) bond functions.

In the present chapter, these ideas are applied specifically to the calculation of potential curves for the second-row diatomic hydrides NaH through HCl.[5] It will be seen that the results for well depth and spectroscopic parameters are consistent with earlier work, in that the bond functions lead to an overall improvement in the quality of the results. In addition, the effects of the frozen core approximation (whether to use [He] or [Ne] cores for Group I-III[†] hydrides) is investigated. The results of these calculations are compared to the large basis CEPA calculations of the cross-table hydrides by Meyer and Rosmus[6] (hereinafter referred to as "MR"), to individual calculations on specific molecules, and to experimental values where they are accurately known.

[†] "Group" numbering here is according to the periodic table notation.

5.2 Results and Discussion

5.2.1 Second-Row Atoms

The method of calculation is similar in general to that described in Chapter 2, and in particular, to that described in Ref. [2] ("Paper I" of the series). In the present case the starting point was the GTO basis sets of Huzinaga.[7] For the second-row atoms, the DZ basis set was taken to be the $(12s8p) \rightarrow [6s4p]$ contraction reported by McLean and Chandler.[8] Polarization exponents were determined by optimization of the atomic energy at the CI stage, leading to the $[6s4p1d]$ DZP basis set. For the hydrogen atom, the DZP basis used was the scaled Dunning[9] $(4s1p) \rightarrow [2s1p]$ contraction used in Paper I, with polarization exponent 1.0.

The TZ basis was constructed by contracting the $(12s9p)$ basis to $[9s6p]$. The coefficients of contraction were established by means of an SCF calculation using the primitive (uncontracted) orbitals, and then the coefficients from the SCF stage combined the first four *s*-functions into a single contracted function and similarly for the first four *p*-functions; the remaining functions were left uncontracted. For reference, these TZ basis sets are given in Tables 5.1.a—5.1.c.

Polarization exponents were obtained in the following way: first, a ratio of 2.5 : 1 was assumed for the *d*-orbital exponents. Optimization of the estimated full-CI energy of the phosphorus atom using the TZPP basis gave values 0.23 and 0.575 for the two exponents, which are approximately in the ratio 0.60 and 1.50 relative to the optimum polarization exponent of 0.38 in the DZP basis. For simplicity, this ratio was assumed valid for the series, so that the remaining TZPP polarization exponents were obtained arithmetically from the optimized DZP exponent. These double polarization exponents are also given in Tables 5.1.a—5.1.c. The TZ hydrogen basis was scaled from the Dunning $(5s/3s)$ basis by the same factor 1.44 used for the DZP basis.[9] Polarization exponents of 1.0 and 0.3 completed the TZPP basis.

The DZP and TZPP energies of the ground state of each atomic species are reported in Table 5.2, which gives some indication of the success of the contraction scheme used for the heavy atoms. In this Table, the SCF energy is denoted as $E(\text{SCF})$, the MRD-CI energy as $E(\text{MRD-CI})$ and the estimated full CI energy as $E(\text{full CI})$. The sixth and seventh columns

of Table 5.2 refer to the size of CI space which was used (selected) from the total number of configurations (generated) in the extrapolation method (see Chapter 2).

The energy lowering obtained on going from a DZP basis set to TZPP ranged from a low of 0.01 hartree (P atom) to as high as 0.03 hartree (Cl atom). The atomic energies for both kinds of basis sets for the Group I—III atoms were obtained by freezing either the [He] core or the [Ne] core and their high-energy complements, which slightly affected the optimum polarization (and, as shall be seen later, bond function) exponents. Like the H atom calculated in Chapter 3, configuration interaction cannot be performed with Na with the [Ne] core frozen because only one electron can be excited; the appropriate energy is therefore the SCF energy. Since it will be shown that the [Ne] core approximation works well only for Si, P, S and Cl, and their hydrides, the TZPP results were all obtained with the frozen [He] core for Na, Mg and Al, but frozen [Ne] core for the rest.

5.2.2 Second-Row Hydrides

Bond function basis sets BF1 (smaller) and BF2 (larger) were then created for the molecules. First, to create the BF1 basis, one set of (*sp*) bond functions with equal exponents was added to the DZP basis and optimized at the CI stage for each hydride at the experimentally-determined equilibrium bond length. Then, to create the BF2 basis set, two sets of (*sp*) bond functions were added to the TZPP basis set. As with the PF's, the BF exponents were related in the splitting ratio 2.5:1. Optimization for PH gave the ratios 0.5 and 1.25 relative to the single BF exponent in the BF1 basis; the BF2 exponents for the remaining hydrides were thus determined arithmetically from the BF1 exponents. The explicit exponents used are given in the Tables for the individual molecules, Tables 5.3—5.9.

For NaH, Mg, MgH and Al with the [Ne] core, only two or three electrons can be excited, so no Davidson (quadruple excitation) correction[10] was applied, and the correct energy is simply an extrapolation of the SD-CI energy. For all other atoms and molecules, including those with the [He] core, the Davidson correction was used to give the estimated full-CI energy.

Potential curves were generated in the usual way, by subtracting the isolated atomic energies of Table 5.2 from the molecular energies. The appropriate atomic energies for basis sets BF1 and BF2 are taken from the DZP and TZPP basis sets, respectively, since the

bond functions do not contribute to the energy at infinite separation. Using basis sets DZP and BF1, the potential energy data were fitted by a 5-parameter generalized Morse function (GMF5 function)[83] to give the Morse parameters D_e , R_e , β_0 , λ_1 and λ_2 as per equation (2.6) over the ranges stated in the individual tables. Tables 5.3—5.9 give the properties calculated from the potential curves for the second-row hydrides, for basis sets DZP and BF1. The GMF5 fits are generally very good over the indicated range, with a root mean square (r.m.s.) deviation of 0.003 eV being typical for circa 15 data points. The same function was used in an identical fashion to fit the CEPA data of Meyer and Rosmus[6] ("MR") for comparison. In the following sections, the reader should bear in mind that MR used moderately large basis sets consisting of $[4s4p2d1f]$ (heavy atom) and $[4s2p1d]$ (hydrogen) GTO's: a total size of 45 functions, nearly double the size of the basis sets used in the current work (e.g., 25 functions in the BF1 basis).

The parameters obtained were used to construct the potential energy curve used in the Numerov-Cooley algorithm,[11] which solves the vibrotational Schrödinger equation for $E_{v,J}$. The energies for the thirty-six $v=0-5$, $J=0-5$ levels were then fit to the 5-parameter spectroscopic equation (Equations (1.18–1.20)). Because the domain of R and the number of v, J levels are rather large, this formula proved more accurate than the more commonly used 4-term expression which omits $\omega_e y_e$. Spectroscopic parameters are also given in these Tables 5.3—5.9, and it can be seen that the fitting formula has a precision of better than 1 cm^{-1} for a range of several thousand cm^{-1} . As noted in previous chapters, the values of the spectroscopic parameters depend on how many terms the fitting function has, and which $E_{v,J}$ levels are included in the fit. For that reason, the potential energy data of MR were again fitted in a fashion identical to the MRD-CI calculations. It should be noted that values reported from other calculations and experiments are directly reported, and are not re-fit, so there is a slight inconsistency in the comparisons.

In accordance with the best results observed in Tables 5.3—5.5, only the [He] core and its high-lying complement are frozen for NaH, MgH and AlH; the [Ne] core and its complement are frozen for the remainder of the molecules.

5.2.3 Individual Hydrides: Results and Comparison

5.2.3.1 NaH

Table 5.3 shows the calculated properties for NaH, with experimental values listed in

the last column. Clearly, freezing the [He] core yields results superior to the [Ne] core. Figure 5.1 shows the BF1, DZP and MR curves with some vibrotational levels drawn in.[†]

The potential energy curves of NaH are dominated by an avoided crossing between the covalent and ionic potentials of sodium hydride. This leads to a ground state curve which is very harmonic and an $A^1\Sigma^+$ curve which is extremely anharmonic.[12] The non-smooth $\Delta G(v + \frac{1}{2})$ behaviour arising from this avoided crossing makes an accurate Birge-Sponer extrapolation difficult for the experimentalists[14][15] and demands the theoretical model take the first excited state into account[16][17][18], especially with regard to the dipole moment. Experimentalists who have analyzed the emission spectrum of NaH ($X^1\Sigma^+$ as well as $A^1\Sigma^+$) up to a maximum $v = 8$ level report a fundamental frequency of 1171.4 cm^{-1} . [19] Analysis of the far infrared spectrum yielded a B_e of 4.903 and α_e of 0.137 cm^{-1} . [20]

Yang *et al.* extrapolated the known $A^1\Sigma^+$ state to the avoided crossing point, to estimate the D_e of the ground state to be $1.98 \pm 0.05 \text{ eV}$. [15] The D_e estimated by Ref. [21] of 2.36 eV clearly appears to be an overestimate.[‡]

Laser-excited fluorescence permitted observation as high as $v = 15$. From this spectrum, Giroud and Nedelec derived a larger fundamental frequency of 1176.1 cm^{-1} and a large D_e of $2.02(6) \text{ eV}$ from extrapolation.[14] Further work by that group on the $A^1\Sigma^+$ state permitted a very precise determination of D_e , to be $1.957(2) \text{ eV}$.

RKR curves have been published in a number of sources.[22][14][19] The most recent Rydberg-Klein-Rees (RKR) curve, whose values are shown in Table 5.3, assumes a dissociation energy of $1.971 \pm 0.062 \text{ eV}$ and an ω_e of 1171.75 cm^{-1} . [23] The most recent direct measurement of the dipole moment, $6.4 \pm 0.7 \text{ Debye}$ [24], has too large an error bar to be of any use in distinguishing between the "goodness" of the calculated dipole moments. The reference value chosen for Table 5.3 is 6.425 D , which is Zemke *et al.*'s calculated expectation value.[23]

As early as 1975, relatively accurate calculations on NaH appeared, beginning with a detailed look at the potential energy curves of six low-lying states of NaH, and the rovibrational levels of three of these. The values obtained by Sachs *et al.* are listed in Table

[†] The fitting program is given in Appendix B.

[‡] The drawbacks of the Hulbert-Hirschfelder potential function are discussed more fully in Ref. [83].

5.3 along with the contemporaneous results of Meyer and Rosmus' highly accurate CEPA calculations.[6] Although Sachs *et al.* performed 2-root multi-configuration self-consistent field (MCSCF) calculations with a large basis set (Na: (7s5p3d1f) and H: (4s2p1d) STO's), only two electrons were correlated. The dipole moment is overestimated by about 0.4 Debye (yet still within the error bars) and the D_e is underestimated by about 0.1 eV.[16]

Olson and Liu's (10s6p2d) (Na) and (5s2p1d) (H) STO core-valence CI (CVCI) calculation yielded a very accurate ω_e of 1171.8 cm⁻¹ and a slightly underestimated D_e of 1.92 ± 0.02 eV.[17] This method ignores all double excitations involving two core electrons, but includes single excitations from the core. Its relative success is a measure of the importance of including the core in a Group I species.

A recent very large basis set (Na: (8s6p4d2f); H: (4s3p2d) STO's) coupled-pair functional (CPF) calculation again underestimated the D_e to be 1.92 eV and underestimated ω_e slightly at 1163 cm⁻¹. The CPF method does not allow the diatomic to dissociate correctly and would be unsuitable for large- R points. The dipole moment was found to be 6.425 D[18], identical to Zemke *et al.*'s calculated expectation value of the dipole moment.[23]

At the fully numerical Hartree-Fock level, the energy at R_e is -162.393 50 hartree; and the dipole moment is 6.989 D.[25] This is 0.02 hartree lower than the SCF energy obtained in this work at the minimum of the curve, but is about 0.01 hartree higher than the CI energy obtained, which shows the importance of configuration interaction in stabilizing the molecule.

Two pseudopotential calculations have appeared very recently. One which uses an analytical pseudopotential form reported $R_e = 3.31$ bohr and $D_e = 1.42$ eV.[26] Although the form of the potential suggested is simple, it does not appear to adequately account for the electron correlation, and thus the molecule appears to have too short and too weak a bond. The second calculation confirms the [He]/[Ne] core problem observed in the current work, and has the most success when it includes a term for core polarization. The D_e , R_e , and ω_e , at 1.91 eV, 3.55 bohr, and 1162 cm⁻¹, are all in good agreement with experiment.[27]

5.2.3.2 MgH

Table 5.4 lists the calculated properties of MgH; again, it is clear that the BF1 basis is superior to the DZP, and the [He] core and anti-core freezing is preferable to the [Ne]

core freezing. Figure 5.2, of the curves constructed using the BF1, DZP and MR basis sets, shows the rather shallow, wide MgH potential.

The magnesium hydride radical is an astrophysically important species, observed in the atmospheres of the sun, late-type stars and the stellar populations in other galaxies.[28] In order to unravel its spectrum as well as to model the singlet/triplet Mg-H₂ reactivity,[29] it has been studied experimentally and theoretically a great deal. Although MgH has been known for about a century and is of such interest to astronomers, its D_e has been a matter of controversy for years.[30] Huber and Herzberg report a D_0^0 of 1.34 eV (D_e is thus 1.43 eV), based on mass spectrometry measurements made in 1937.[80]

Balfour and Cartwright discovered a new $B'^2\Sigma^+$ state[31][32] which correlates diabatically to $\text{Mg}(^1S) + \text{H}(^2S)$. There is thus an avoided crossing between the $X^2\Sigma^+$ state, which dissociates to these atomic products, and this state. As with NaH, this avoided crossing makes a Birge-Sponer extrapolation unreliable,[33] with the D_e decreasing as more v, J levels were observed.[34] The high-resolution emission spectrum of MgH showed that earlier extrapolations, which had agreed quite well with the mass spectrometric value, were too long, and gave too large a well-depth. D_0 from a short extrapolation is 1.27 ± 0.03 eV.[34] Jenč and Brandt using the reduced potential curve (RPC) method on the RKR data for MgH, confirm the lower limit for D_e reported in Ref. [34], of 1.362 eV.[30] The reference spectroscopic constants given in Table 5.4 are obtained from very recent infrared diode laser work.[35]

MgH and other second-row hydrides provided an early subject for computation, for the SCF calculations with minimal Slater-type basis sets of Cade and Huo. For magnesium hydride, they found quite good results, with $R_e = 3.259$ bohr and $D_e = 1.15$ eV.[36] Chan and Davidson used a $16\sigma 8\pi 6\delta 2\phi$ STO basis set and by means of natural orbitals they selected 1045 configurations. They estimated a dissociation energy D_0 of 2.0 ± 0.2 eV.[37]

Meyer and Rosmus compared the results of their CEPA calculations to Gaydon's compilation.[6][84] They recommended that the experimental value of $D_0 = 2.0 \pm 0.5$ eV be changed to 1.23 eV (giving a D_e of 1.34 eV), with an estimated error of 0.05 eV. In the majority of hydrides those authors studied, the CEPA D_e underestimated the experimental value, but for BeH, the first-row analogue of MgH, CEPA over-estimated, and it was thus not unexpected that this value was less than that calculated by CEPA.

Sink *et al.*, upon learning of Balfour and Cartwright's discovery of the new $B' \ ^2\Sigma^+$ state,[31] conducted a cursory investigation into the low-lying electronic states of MgH.[38] Those authors used an extended STO basis set ($20\sigma 10\pi 2\delta$) and froze all but three electrons for the full one-root single-, double-, and triple-excitations CI (SDT-CI) calculation. They calculated spectroscopic constants but no dissociation energy.[38]

Saxon, Kirby and Liu calculated SCF energies using a ($12s9p4d1f$) extended STO basis set and then performed SDT-CI using MCSCF-created MO's. They over-estimated the D_e at 1.385 eV. They attributed the error to the exclusion of core effects. Once they adjusted for core-valence correlation and core relaxation the D_e improved, to 1.34 eV, and R_e remained unchanged at 3.294 bohr.[39] The valence electrons were restricted to three, and no high-lying root was taken into account, which may explain the disagreement between their calculated dipole moment of 1.400 D and the Meyer and Rosmus value of 1.236 D.[6] The μ determined by the current calculation is 1.2043 D.

A very recent pseudopotential calculation underscored the necessity of inclusion of core effects. Fuentealba *et al.* report a D_e of 1.24 eV, an ω_e of 1354 cm^{-1} and an R_e of 3.27 bohr.[27] While the agreement with experiment is not as good as the analogous calculations on NaH using that method, it is apparent that a core-polarization term for pseudopotential calculations—or, in terms of CI, an expansion of the CI space by “thawing” the [Ne] core freezing—is necessary for small-valence species such as MgH.

5.2.3.3 AlH

Table 5.5 shows the values calculated for aluminum monohydride, and Figure 5.3 shows the BFI potential energy curve with the $J = 0$ and 5 levels drawn in for the $v = 0$ to 5 manifold, along with the DZP and MR potential energy curves. Compared with the preceding hydrides, AlH is much more strongly bound, as evidenced by its short bond length and a well-depth which is greater by a third. The experimental values in the rightmost column consist of the most recent dissociation energy determination, evaluated by observation of the radiative lifetimes of the $A \rightarrow X$ transition[40] and spectroscopic constants from Zeeman and Ritter's RKR curve which ranged from $v = 0$ to $v = 4$, covering about the bottom one-third of the ground state curve.[41] No dipole moment is yet known experimentally for AlH.

Early calculations only went as far as the SCF level (to give $D_e = 2.39\text{ eV}$) which

dissociated incorrectly[42] or neglected polarization functions, such as Ref. [43], which found $D_e = 2.91$ eV for a DZ + (*sp*) basis and $D_e = 2.36$ eV for a TZ-quality basis, once a ΔE_{corr} term was taken into account.

After such a dearth of activity in AlH calculations, it has fortunately been coming to the forefront again. Table 5.5 reports results in very good agreement with experiment from a couple of very recent very high quality calculations. Matos *et al.* used a large basis set (H: [8s4p2d] and Al: [12s7p4d1f]) in a CASSCF calculation and reported an accurate ω_e of 1678.6 cm^{-1} but a not-so-accurate dissociation energy of 3.112 eV.[44]

Bauschlicher and Langhoff's "benchmark" calculations on AlH used a [7s5p2d/1s3p] GTO basis set, constructed CASSCF MO's, and then performed full CI on the four valence electrons. Against this were compared a variety of second-order CI (SO-CI) results obtained with a larger [8s7p5d2f/4s3p2d] ANO basis set. The authors omitted the Davidson correction, noting that it tended to "overshoot the importance of higher excitations when only four electrons are involved." [45] It is quite remarkable that not only are the large basis SO-CI results in all respects better than the F-CI results, but even the BF1 basis with a smaller core yields a better D_e and R_e . This emphasizes the fact that the error due to incomplete CI expansion—once a major hurdle in *ab initio* calculations—has now been superseded in importance by the error due to molecular basis set incompleteness (MBSI).

A recent calculation using a moderate-sized basis set found a dipole moment as low as 0.064 D; again, though, polarization functions were not used, and four electrons at most were correlated. The author concluded that core-core and core-valence correlation could have a significant effect on the dipole moment.[46]

5.2.3.4 SiH

Silylidyne, SiH, has prompted numerous recent calculations[47][48][49] and experimental measurements.[50][51][52][53][54] There has been such widespread interest in this species due to its role as an intermediate in silicon reactions of tremendous importance to the semiconductor manufacturing industry. Experimental measurements predicted conflicting dissociation energies of 3.31 eV[55], 3.59 eV[56] and 2.98 ± 0.03 eV.[51] A very recent IR emission spectrum of 192 rovibrational levels gives the most accurate RKR curve for SiH to date,[52] which is reported in the rightmost column of Table 5.6. The results obtained in the present work are listed in Table 5.6 and the BF1, DZP, and VR curves are illustrated

2

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in Figure 5.4. Preliminary calculations indicated that SiH with its five electrons was not as sensitive to core freezing as the Group I—III hydrides, so only [Ne] core/anticore frozen results are reported for the remainder of the second-row series.

Recent theoretical work by Lewerenz *et al.* with a moderately-large basis set (Si: [7s5p2d1f] and H: [3s1p1d] GTO's) gave $\omega_e = 2015 \text{ cm}^{-1}$ and $D_e = 3.05 \text{ eV}$ using the MRD-CI method.[48] Using CAS-CI with a large basis set (Si: [10s7p4d1f] and H: [7s4p1d] GTO's) Larsson obtained an ω_e of 2057.8 cm^{-1} and a D_e of 3.128 eV .[49] Both of these calculations, as well as Meyer and Rosmus' value of $D_e = 3.09 \text{ eV}$, lend more credence to the upper dissociation limit recommended by Verma[55] so it is this value for D_e which is listed in Table 5.6.

The above calculations found $\mu = 0.124$, [48] 0.123 , [49] and 0.141 , [6] all in Debye. Allen and Schaefer, for a DZP GTO basis set with the SD-CI method, found $\mu = 0.167 \text{ D}$, and with a TZPP basis, 0.077 D . [47] It is somewhat surprising that the TZPP value is "worse" than the DZP value, compared to what more accurate calculations (Refs. [48] [49] and [6]) predict. Note that the calculation did not take into account the next lowest-lying root, so it appears that the DZP dipole moment may have been so close due to a fortuitous cancellation of errors. The TZPP value shows the dipole moment is not converged with respect to basis set completeness.

Pettersson and Langhoff studied dipole moments of five-valence-electron hydrides with the SD-CI and CPF methods. They used (8s6p3d2f) STO's on Si and (4s3p2d) STO's on H. They determined the dipole moment to be 0.160 D (SD-CI) and 0.118 D (CPF). The authors reported a polarity of Si^-H^+ opposite to that found for Ge^+H^- and Sn^+H^- , but in agreement with that of C^-H^+ . [57]

5.2.3.5 PH

Not many curves have been calculated for phosphinidene (PH), although with the discovery of interstellar phosphorus-containing compounds (see Chapter 7), and the general growth of interest in second-row hydrides, this situation will no doubt change.

Table 5.7 shows the BF1 results are in excellent agreement with those of MR and experiment, except for the D_e , where both MR and BF1 underestimate it significantly. Figure 5.5 shows the BF1, DZP and MR curves for PH.

Experimentally, PH has been extensively studied. A very recent RKR curve has been

deduced from FT-IR spectroscopy over the $v = 0$ to 5 levels (covering $\approx 50\%$ of the well-depth), the spectroscopic constants from which are given as the right-most column in Table 5.7. These spectroscopic constants supplant earlier values derived from a study of a much lower region of v, J levels.[59][60][61][62][63][64] A matter which is still of great controversy is the D_e . Rostas *et al.* use a rather long Birge-Sponer extrapolation to predict a D_e of 3.89 ± 0.58 eV,[59] although the authors add the disclaimer that "the true dissociation energies are probably 10 to 15% smaller as usual for hydrides" (and thus, the size of the error bar given). Huber and Herzberg list Meyer and Rosmus' recommended value of 3.17 eV, and this is the value used in the right-most column of Table 5.7.[80][6] The dipole moment at R_e is not known experimentally. Meyer and Rosmus calculate it to be 0.481 D[6].

Besides MR, two calculations of note are reported by Bruna *et al.*, and by Senekowitsch *et al.* The former calculations added an (*s*) BF to a moderately large basis set which included diffuse Rydberg functions. The MRD-CI method was then used to calculate several states of PH. The results are very comparable to those obtained here.[65]

The latter calculation employed the MCSCF-CI method with a [10*s*8*p*4*d*1*f*/6*s*3*p*1*d*] GTO basis set. The results obtained are listed in Table 5.7 for comparison. The claim of these authors, that "the present MCSCF-CI wavefunctions are so far the most accurate obtained for PH"[66] can only be made by the narrowest of margins; in fact, the most striking difference between the present results and those of the other calculations lies in the fundamental frequency, which is *more accurately determined here* than by either Ref. [65] or Ref. [66]. However, Senekowitsch *et al.* estimate the μ to be 0.403 D[66] and this is closer to the MR value than the dipole moment obtained here. (The problems of obtaining an accurate dipole moment peculiar to the MRD-CI method relevant to the hydrides' moments will be discussed in a separate section.)

Lastly, it may be noted that as a prelude to a study of the P_2H_2 and P_2H_4 isomers, Nguyen used a 6-31G** basis set, and with the MP2 method, found $\omega_e = 2485$ cm⁻¹.[58] Such a small basis set was necessary in order to model the larger polyatomic systems, which is yet another reason why improvements on the DZP-quality basis sets need to be developed, even though much larger basis sets are available for the diatomics and give more reasonable results.

5.2.3.6 SH

Although the OH radical is well-known, comparatively little has been written about its second-row analogue SH. The $A^2\Sigma^+ - X^2\Pi_i$ transition has been the subject of some studies, such as that by Senekowitsch *et al.*[67] and Pathak and Palmer.[68] It is only these two lowest valence states which are in fact bound.[69] The dissociation energy tabulated in Huber and Herzberg is extrapolated from the vibrational levels of the $A^2\Sigma^+$ state dissociating to the $^1D + ^2S$ limit,[80] and is essentially in agreement with that recommended by Meyer and Rosmus.[6] Analysis of the $A - X$ emission spectrum by Pathak and Palmer led to the spectroscopic parameters[68] which are used as reference values in Table 5.8. The dipole moment was experimentally determined by electron resonance to be 0.758 D.[70]

Besides the theoretical work by Meyer and Rosmus, four other *ab initio* calculations on ground state SH have appeared recently, two of which use the MRD-CI method to calculate a variety of electronic states.

Martin's theoretical study of the reaction

is pertinent to the current work because it illustrates why medium- to small-sized basis sets are important in an age when a hundred orbitals used to calculate a single diatomic is not unheard of. A basis-set study of the bond energy of SH is tabulated, which ranges from $[4s3p/2s]$ (to give 2.64 eV) to $[6s4p2d1f/3s2p1d]$ (to give a D_e of 3.64 eV). The SH asymptote is taken as an indication of the sort of accuracy expected for the height and location of the barrier on the $\text{H} + \text{HS}$ potential energy surface. With a DZP quality basis set (which was used to generate the surface), D_e was found to be 3.37 eV, R_e to be 2.554 bohr, and ω_e to be 2597 cm^{-1} . These are somewhat worse than the DZP results obtained in this work, and quite a bit worse than the BF1 results in Table 5.8. The largest basis set (which was used to check a suspiciously high barrier height) gave, in addition to the improved D_e , an R_e of 2.544 bohr, and ω_e of 2631 cm^{-1} , all values which are comparable in accuracy to the BF1 values, but obtained with one-third as many functions.[71]

The results obtained by Hirst and Guest in a DZP-quality MRD-CI calculation are listed in Table 5.8 along with those obtained in this calculation using DZP and BF1 basis sets. (Figure 5.6 shows a plot of the BF1 curve and some v, J levels, as well as the DZP and

MR potential energy curves.) The D_e obtained by those authors is intermediate between the DZP and BF1 D_e 's but R_e appears to be poorer than either the DZP or BF1 results here.[72]

Five years later, Bruna and Hirsch used a moderately large basis set of some 56 functions, which included an s orbital located at the bond mid-point. A multiple-root MRD-CI calculation yielded an estimated full-CI energy of -398.2402 hartree, somewhat lower than the minimum of -398.2347 hartree obtained in this calculation by the BF1 basis set, which had only 25 functions. The molecular constants they calculated are listed in Table 5.8, and are generally closer to the reference values than the MR constants. In particular, the D_e is second only to the BF1 D_e in how well it agrees with experiment, and the R_e value is in excellent agreement too. The permanent dipole moment was found to be 0.812 D at $R = 2.551$ bohr.[69]

Senekowitsch *et al.* studied the potential energy curves and electric dipole moment functions of SH and its cationic and anionic forms using the SCEP-CEPA (self-consistent electron pair approach with coupled electron pair approximation) technique with a large basis (S: [10s9p4p1f] and H: [6s3p1d] GTO's). The minimum energy of the ground state lies at -398.2842 hartree, the lowest energy obtained so far. The ω_e is slightly underestimated at 2695 cm^{-1} .

5.2.3.7 HCl

Hydrogen chloride is well-known experimentally[80] because its completely-filled electron shell means relative stability and ease of interpretation.[73] The D_e reference value is obtained directly from the heats of formation;[80] the spectroscopic parameters are obtained from an analysis of the 1-0 and 2-0 bands of HCl by Rank *et al.*[74] A molecular beam electric resonance experiment of some low-lying v, J levels of HCl produced the reference μ of 1.0933(5).[75]

The results of the current calculation are summarized in Table 5.9 and are, for fits to the BF1, DZP and MR data, plotted in Figure 5.7. HCl has been the subject of two investigations by this group, in which bond functions added to a molecule of bond order 1 were first tested.[76][77] The calculations reported here for the sake of completeness of the second-row series are in fact replications with results virtually identical to the original

work.[†] Table 5.9 shows that the DZP basis set is clearly inferior to a DZP basis with a single set of (*sp*) bond functions added. The BF1 basis shows a D_e in nearly perfect agreement with the reference value, certainly more so than the MR D_e , but the R_e is as usual slightly overestimated, and the fundamental frequency is in error by about 1%. The latter disagreement is probably exacerbated by the fact that the experimental values stem from a vibrational analysis done over only the lowest 3 *v*-levels.

The same fitting done to MR data gives an ω_e in much closer agreement, but an R_e larger than that of BF1. The electric dipole moment obtained by MR is much closer to the experimental value as well.

Nearly simultaneous with the CEPA study of the diatomic hydrides by MR, Ahlrichs *et al.* published PNO-CI (pair natural-orbital) and CEPA-CI calculations on the (stable) polyatomic second-row hydrides, one of which was HCl. In that study they used a basis set consisting of [6s4p2d1f] (Cl) and [3s1p] (H) GTO's, and obtained a D_e of 4.43 eV, and a fundamental frequency of 2977.2 cm⁻¹. [78] As with MR results, the spectroscopic constants are well-determined, but the curve is too shallow and the calculation is limited to the region close to R_e , since the wavefunction is not flexible enough for dissociation.

Some five years later, Hirst and Guest calculated a potential curve for HCl using MRD-CI techniques. They found the D_e of HCl at 4.23 eV was underestimated significantly, but the fundamental frequency was in error by only 10 cm⁻¹ or one third of one percent. [79]

In 1982, Bettendorff *et al.* published a clarification of the HCl electronic spectrum, in which they began with a basis set quite similar to the DZP one used here, but added several diffuse functions in order to provide an adequate description of the Rydberg states. For the ground state, they found $D_e = 4.46$ eV and $\omega_e = 2961$ cm⁻¹. [73] The BF1 D_e looks very good in comparison with these values, although the ω_e has ≈ 30 cm⁻¹ disagreement.

5.2.4 Core freezing

The effect of core freezing was studied only for basis set BF1, but the conclusions derived from this basis set are expected to be general. In Tables 5.3—5.5 (NaH, MgH and AlH), it was seen by comparison of the results in columns 3 and 4 that differences of up to 0.17 eV (NaH) arose in D_e , according to whether the [He] or [Ne] core and its complement

[†] Different *v*, *J* levels used in the fit to the spectroscopic equation are the source of the discrepancy.

were frozen, with the frozen [He] core being more accurate. Freezing the [Ne] core would leave only n valence electrons available for excitation in the CI stage, *versus* $(n + 8)$ for a [He] core description, so the CI space is necessarily much smaller in the former case. The discrepancy is largest for NaH, where n is only 2, decreases for MgH and AlH (0.07 eV), and is quite small for SiH (~ 0.03 eV) where n is five. It was therefore deemed appropriate to freeze the [Ne] core and its complement for Si, P, S, Cl and their monohydrides, but freezing the [He] core and its complement was more suitable for Na, Mg, Al and their corresponding monohydrides. The DZP, TZPP and BF2 results are based on this prescription. A similar conclusion relative to the CEPA method was reached by MR, based on their analysis of the inter-shell correlation energy.[6]

5.2.5 Results of the DZP and BF1 basis sets

The polarization exponents for the DZP basis set form a fairly smoothly ascending series. The same can be said for the bond function exponents. Compared to the "best" experimental values of D_e , it can be seen in Tables 5.3—5.9 that the DZP basis consistently underestimates the dissociation energy (87% of D_e for NaH, 86% for MgH, *etc.*), for an average underestimate of 9% (or 0.28 eV). Freezing the [He] core (and anti-core) for NaH—AlH and [Ne] otherwise, basis set BF1 gives much better results, the average absolute error being reduced to 1.5%. Compared to the best recommended values for D_e (obtained by using good experimental numbers where available or the extrapolated CEPA values of MR otherwise), basis set BF1 agrees with experiment to within a maximum deviation of 0.11 eV, with the average deviation being only 0.04 eV. Therefore, the same type of basis set which proved optimum for the first-row hydrides also gives very good results for the second row, and is essentially within the desired goal of 0.1 eV for the D_e .

The quality of the curves may also be deduced from a comparison of spectroscopic properties such as ω_e , $\omega_e x_e$, *etc.*. Since the MR values are very accurate for all properties except D_e , and since by design the v, J levels fit were identical to those used for DZP and BF1, these values are in fact better reference standards than some experimental and/or calculated values which may have been fit over much different v, J levels.

Considering DZP and BF1 basis sets, respectively, average deviations from MR are given in Table 5.11. This Table shows that the average (absolute) deviation of the R_e from the fitted MR value is reduced from 0.016 to 0.012 bohr when bond functions are added

to the DZP basis to form BF1, and the deviation in ω_e is reduced from 28 to 22 cm^{-1} , to name but two instances. In fact, *all* properties listed in the Table show improvement. In general, therefore, for the second-row hydrides, *the addition of (s,p) bond functions to the DZP basis set leads to systematic improvement of the potential curve and its derived properties.*

5.2.6 Results of the TZPP and BF2 basis sets

No potential curves were generated for these basis sets, for which only a single point was calculated at the experimental R_e . Table 5.10 gives the bond function exponents for basis set BF2, and the well depths for both the TZPP and BF2 basis sets. In the case of the well depths, the average deviation from accurate reference values is 0.14 eV for the TZPP basis sets and 0.05 eV for BF2. This is consistent with the improvement observed in the quality of the H_3 potential surface as the TZPP basis set was augmented by two sets of (*sp*) bond functions.[4] It should be noted, however, that BF2 substantially overestimates D_e for SH (by 0.11 eV) and even more so for HCl (by 0.17 eV), the latter being outside the desired tolerance altogether. It appears that basis set BF2 may not in fact be "balanced", i.e., the description of the internuclear region has been improved to a greater extent than the TZPP basis sets have been able to improve the atomic energies. A need for additional basis set experimentation is indicated here, and possibly use of a better TZPP—possibly even QZPP—atomic basis set as a starting point, to which the two sets of (*sp*) functions could be added.

If the TZ atomic basis sets as given in Table 5.1 are retained, then some further experimentation with the BF would be in order, to improve the atom/molecule balance. The experimentation carried out in Chapter 3 suggests that possible bond function basis sets which may be superior are TZPP plus a single set of (*s, p*) bond functions, with individually-optimized exponents for the *s*- and *p*-type functions, or a ($2s, 1p$) bond function basis which includes more of the lower angular momentum bond functions.

5.2.7 Dipole Moments

Table 5.12 summarizes the results obtained for the dipole moments for the ground states of all the hydrides. The dipole moment was calculated as described in section 2.7, for the DZ, DZP and BF1 basis (with [He] frozen for NaH, MgH and AlH). The strongest trend

observable in the Table is that, for each column, the calculated dipole moment increases on going from NaH to HCl. This is as expected from the general trend of electronegativities as the periodic row is traversed.

Few experimental dipole moments are well-known, but of those which are, the MR values lie closest, with the exception of NaH, where MR is still in excellent agreement. In the subsections pertaining to the individual species, dipole moments were reported by other calculations; in general, these were in closer agreement to MR than the results of the present calculations.

The dipole moments calculated for wavefunctions whose basis sets did not include polarization functions (DZ basis) showed poorer agreement throughout than either DZP or BF1 basis sets, with the exception of AlH. Furthermore, the DZP values are seen to agree as often with the MR values as the BF1 values do. As discussed in Section 1.2.1, BF's and PF's are both effective in mimicking the displacement of the charge density away from the nucleus. However, due to the central location of the BF, it can only act to "pull" charge from one nucleus towards the centre, and so *on average* bond functions are neither help nor hindrance in the matter of describing the charge polarization.

The primary source of error in these calculations, however, lies not with the basis set formulation, but more with the method used to construct the CI wavefunction. The selection criterion is based on the *energy lowering*, as described in Chapter 2. This would mean some configurations are excluded which affect the energy very little, but which have a large effect in determining the charge distribution, such as the whole class of single excitations, as briefly discussed in Section 2.7. One strategy would be to carry out selection with not only energy lowering but also effect on dipole moment as the governing criteria.[81] Alternatively, the extrapolation procedure used to determine the energy could be employed to obtain an "extrapolated density matrix" which could then be used to calculate a variety of properties such as the dipole moment.[82]

5.2.8 Concluding Remarks

In straightforward SD-CI or full-CI calculations, basis sets which contain only nuclear-centered AO's underestimate the depth of a potential energy well, even for large basis full-CI calculations, as we have seen for example for AlH.[45] The consistently underestimated well depths for the diatomic hydrides NaH through HCl in the present calculations, using both

DZP and TZPP basis sets, is thus not surprising. It was demonstrated for both the smaller basis set BF1 and the larger basis set BF2 that adding mid-bond functions to the basis sets permits a better description of the internuclear region, leading to improved well depths. In each case there appears to be a *basis set-dependent* optimum balance point between nuclear-centered functions and bond functions, leading to an optimum description of the potential curve. Future chapters will explore another dimension to the determination of the optimum basis set composition, namely, the relation of BF size to the bond order of the species studied. Basis set BF1, which was shown to be optimum previously for the first-row hydrides,[2] has also been found to be optimum for the second-row hydrides. This is a very significant result, since it may then be *possible to prescribe optimum basis sets independent of any "calibration," and dependent only on the size of the atomic basis, and the bond order of the molecule*. Basis set BF2 was less thoroughly explored, but also, its addition to larger atomic-centred basis sets led to a notable improvement in D_e relative to the TZPP basis set. More extensive calculations appear to be necessary to define an optimally balanced BF basis set containing nuclear-centered AO's of TZPP-quality or greater.

The spectroscopic parameters derived from the potential curves generated from the DZP and BF1 basis sets were compared for all second-row species with the accurate values obtained by Meyer and Rosmus from very large basis CEPA-CI calculations,[6] as well as with calculations reported for the individual species. Overall, it was seen that basis set BF1 provided much better agreement, not only for well depth but also for the internuclear distance and the spectroscopic constants derived from the potential curve.

The overall conclusions of this study are clear: bond functions represent an important missing factor in traditional AO basis sets, and where accurate properties are desired while maintaining modest-sized basis sets, their inclusion is worthwhile.

5.3 References

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Table 5.1.a

Exponents and contraction coefficients for the TZPP basis sets for the sodium, magnesium and aluminum atoms. Based on Ref. [8]. Contraction is 4, 1, 1, etc. for both *s* and *p* sets.

Na			Mg			Al		
Orb.	Exponent	Coefficient	Orb.	Exponent	Coefficient	Orb.	Exponent	Coefficient
<i>s</i>	36166.42	0.0003912	<i>s</i>	43866.5	0.0003807	<i>s</i>	54866.49	0.0003529
<i>s</i>	5372.58	0.0030615	<i>s</i>	6605.37	0.0029270	<i>s</i>	8211.77	0.0027442
<i>s</i>	1213.21	0.0160102	<i>s</i>	1513.26	0.0149405	<i>s</i>	1866.18	0.0141584
<i>s</i>	339.62	0.0641950	<i>s</i>	432.317	0.0585871	<i>s</i>	531.129	0.0557315
<i>s</i>	109.55	1.0	<i>s</i>	142.149	1.0	<i>s</i>	175.118	1.0
<i>s</i>	38.777	1.0	<i>s</i>	51.398	1.0	<i>s</i>	64.0055	1.0
<i>s</i>	14.576	1.0	<i>s</i>	19.920	1.0	<i>s</i>	25.2925	1.0
<i>s</i>	5.2699	1.0	<i>s</i>	8.0247	1.0	<i>s</i>	10.5349	1.0
<i>s</i>	1.8278	1.0	<i>s</i>	2.5082	1.0	<i>s</i>	3.2067	1.0
<i>s</i>	0.6199	1.0	<i>s</i>	0.8715	1.0	<i>s</i>	1.1526	1.0
<i>s</i>	0.0572	1.0	<i>s</i>	0.1082	1.0	<i>s</i>	0.1767	1.0
<i>s</i>	0.0240	1.0	<i>s</i>	0.0401	1.0	<i>s</i>	0.0652	1.0
<i>p</i>	144.645	0.0053634	<i>p</i>	193.854	0.0047943	<i>p</i>	259.284	0.0040522
<i>p</i>	33.907	0.0384522	<i>p</i>	45.442	0.0351271	<i>p</i>	61.0769	0.0304384
<i>p</i>	10.629	0.1492650	<i>p</i>	14.186	0.1432897	<i>p</i>	19.3032	0.1267618
<i>p</i>	3.8239	0.3275765	<i>p</i>	5.0575	0.3346510	<i>p</i>	7.0109	0.3122443
<i>p</i>	1.4443	1.0	<i>p</i>	1.8886	1.0	<i>p</i>	2.6739	1.0
<i>p</i>	0.5526	1.0	<i>p</i>	0.7227	1.0	<i>p</i>	1.0366	1.0
<i>p</i>	0.1887	1.0	<i>p</i>	0.2364	1.0	<i>p</i>	0.3168	1.0
<i>p</i>	0.0465	1.0	<i>p</i>	0.0934	1.0	<i>p</i>	0.1143	1.0
<i>p</i>	0.0163	1.0	<i>p</i>	0.0348	1.0	<i>p</i>	0.0414	1.0
<i>d</i>	0.066	1.0	<i>d</i>	0.12	1.0	<i>d</i>	0.13	1.0
<i>d</i>	0.165	1.0	<i>d</i>	0.3	1.0	<i>d</i>	0.325	1.0

Table 5.1.b

Exponents and contraction coefficients for the TZPP basis sets for the silicon and phosphorous atoms. Based on Ref. [8]. Contraction is 4, 1, 1, *etc.* for both *s* and *p* sets.

Si			P		
Orbital	Exponent	Coefficient	Orbital	Exponent	Coefficient
<i>s</i>	69379.23	0.0003175	<i>s</i>	77492.4	0.0003291
<i>s</i>	10354.94	0.0024857	<i>s</i>	11605.8	0.0025518
<i>s</i>	2333.88	0.0130303	<i>s</i>	2645.96	0.0131300
<i>s</i>	657.14	0.0522608	<i>s</i>	753.98	0.0518978
<i>s</i>	214.30	1.0	<i>s</i>	248.75	1.0
<i>s</i>	77.629	1.0	<i>s</i>	91.157	1.0
<i>s</i>	30.631	1.0	<i>s</i>	36.226	1.0
<i>s</i>	12.801	1.0	<i>s</i>	15.211	1.0
<i>s</i>	3.9269	1.0	<i>s</i>	4.7138	1.0
<i>s</i>	1.4523	1.0	<i>s</i>	1.7827	1.0
<i>s</i>	0.2562	1.0	<i>s</i>	0.3425	1.0
<i>s</i>	0.0943	1.0	<i>s</i>	0.1246	1.0
<i>p</i>	335.48	0.0035551	<i>p</i>	384.84	0.0037127
<i>p</i>	78.900	0.0273860	<i>p</i>	90.552	0.0285867
<i>p</i>	24.988	0.1166338	<i>p</i>	28.806	0.1211404
<i>p</i>	9.2197	0.2933742	<i>p</i>	10.688	0.3014862
<i>p</i>	3.6211	1.0	<i>p</i>	4.2521	1.0
<i>p</i>	1.4513	1.0	<i>p</i>	1.7405	1.0
<i>p</i>	0.5050	1.0	<i>p</i>	0.5979	1.0
<i>p</i>	0.1863	1.0	<i>p</i>	0.2292	1.0
<i>p</i>	0.0654	1.0	<i>p</i>	0.0838	1.0
<i>d</i>	0.15	1.0	<i>d</i>	0.23	1.0
<i>d</i>	0.375	1.0	<i>d</i>	0.575	1.0

Table 5.1.c

Exponents and contraction coefficients for the TZPP basis sets for the sulfur and chlorine atoms. Based on Ref. [8]. Contraction is 4, 1, 1, etc. for both *s* and *p* sets.

S			Cl		
Orbital	Exponent	Coefficient	Orbital	Exponent	Coefficient
<i>s</i>	93413.4	.0003065	<i>s</i>	105818.8	0.0003055
<i>s</i>	13961.7	.0023915	<i>s</i>	15872.0	0.0023651
<i>s</i>	3169.9	.0123581	<i>s</i>	3619.7	0.0121892
<i>s</i>	902.46	.0490393	<i>s</i>	1030.8	0.0484137
<i>s</i>	297.16	1.0	<i>s</i>	339.91	1.0
<i>s</i>	108.702	1.0	<i>s</i>	124.538	1.0
<i>s</i>	43.155	1.0	<i>s</i>	49.514	1.0
<i>s</i>	18.108	1.0	<i>s</i>	20.806	1.0
<i>s</i>	5.5705	1.0	<i>s</i>	6.4648	1.0
<i>s</i>	2.1427	1.0	<i>s</i>	2.5254	1.0
<i>s</i>	0.4340	1.0	<i>s</i>	0.5378	1.0
<i>s</i>	0.1570	1.0	<i>s</i>	0.1935	1.0
<i>p</i>	495.04	.0031156	<i>p</i>	689.78	0.0025757
<i>p</i>	117.22	.0241931	<i>p</i>	139.85	0.0236093
<i>p</i>	37.507	.1058262	<i>p</i>	44.795	0.1010589
<i>p</i>	13.910	.2824443	<i>p</i>	16.612	0.2786668
<i>p</i>	5.5045	1.0	<i>p</i>	6.5995	1.0
<i>p</i>	2.2433	1.0	<i>p</i>	2.7141	1.0
<i>p</i>	.7762	1.0	<i>p</i>	0.9528	1.0
<i>p</i>	.2919	1.0	<i>p</i>	0.3580	1.0
<i>p</i>	0.1029	1.0	<i>p</i>	0.1250	1.0
<i>d</i>	0.29	1.0	<i>d</i>	0.42	1.0
<i>d</i>	0.725	1.0	<i>d</i>	1.05	1.0

Table 5.2

Atomic energies for DZP and TZPP basis sets. All energies in hartree.^a For definitions, see text.

Atom	Basis Set	Frozen Core	Polarization Exponent(s)	E(SCF)	SAF's Gen.	SAF's Sel.	E(MRD-CI)	full CI (est.)
H	DZP	—	1.00	-0.49763	—	—	—	—
	TZPP	—	1.00,0.30	-0.49921	—	—	—	—
Na	DZP	He	0.11	-161.84606	1941	1941	-161.92998	-161.93117
	DZP	Ne	0.13 ^b	-161.84579	—	—	—	—
	TZPP	He	0.165,0.066	-161.85420	3531	3531	-161.98348	-161.98546
Mg	DZP	He	0.20	-199.60669	8401	2142	-199.72337	-199.72486
	DZP	Ne	0.164	-199.60526	41	41	-199.63858	—
	TZPP	He	0.30,0.12	-199.60956	16533	3443	-199.76704	-199.76993
Al	DZP	He	0.21	-241.86747	23132	4781	-242.01411	-242.01705
	DZP	Ne	0.196	-241.86746	97	97	-241.91775	—
	TZPP	He	0.325,0.13	-241.87142	23481	4209	-242.04109	-242.04784
Si	DZP	Ne	0.25	-288.82875	637	637	-288.89791	-288.89893
	TZPP	Ne	0.375,0.15	-288.84883	2294	2294	-288.92443	-288.92601
P	DZP	Ne	0.38	-340.70721	763	763	-340.78986	-340.79238
	TZPP	Ne	0.575,0.23	-340.71227	2601	2601	-340.80495	-340.80851
S	DZP	Ne	0.48	-397.49075	416	416	-397.59540	-397.60067
	TZPP	Ne	0.725,0.29	-397.49892	3157	3157	-397.62159	-397.62787
Cl	DZP	Ne	0.70	-459.46382	409	409	-459.58936	-459.59501
	TZPP	Ne	1.05,0.42	-459.47432	1271	1271	-459.62523	-459.63378

^a 1 hartree = 27.2116 eV; 1 eV = 8065.48 cm⁻¹.

^b The optimum *d* exponent obtained by extrapolation of the optimum *d* exponents of the other second row atoms.

Table 5.3

Calculated properties for the $X^1\Sigma^+$ state NaH. Parameters D_e , R_e , β_0 , λ_1 , λ_2 , are from a generalized 5-parameter Morse fit. Parameters ω_e , $\omega_e x_e$, $\omega_e y_e$, B_e and α_e are from a five-parameter spectroscopic fit using levels $J = 0$ to 5 for each of the v levels 0 to 5 inclusive. The dipole moment is calculated at the experimental R_e .

Property	DZP basis [He] core	BF1 basis [He] core	BF1 basis [Ne] core	MR	Ref. [16]	Reference Value
Range (bohr)	2.6–6.0	2.6–6.0	2.6–6.0	2.8–5.0	2.0–6.0	
pol. expt.	0.11	0.11	0.13 ^a			
B.F. expt.	—	0.26	0.20			
D_e (eV)	1.6874	1.8920	1.7162	1.9238	1.878	1.957(2) ^b
R_e (bohr)	3.6017	3.5613	3.6235	3.5732	3.609	3.566 ^c
β_0 (bohr ⁻¹)	0.6101	0.6150	0.6151	0.5949	—	—
λ_1 (bohr ⁻²)	0.0130	0.0212	0.0206	0.0079	—	—
λ_2 (bohr ⁻³)	0.0221	0.0169	0.0160	0.0165	—	—
r.m.s. ^d (eV)	0.0009	0.0031	0.0003	0.0002	—	—
ω_e (cm ⁻¹)	1124.6	1200.3	1143.2	1170.9	1183.17	1171.750 ^e
$\omega_e x_e$ (cm ⁻¹)	17.71	18.18	18.40	18.22	21.23	19.7405 ^e
$\omega_e y_e$ (cm ⁻¹)	0.011	-0.027	-0.031	0.037	—	0.19225 ^e
B_e (cm ⁻¹)	4.811	4.919	4.751	4.884	4.748	4.903 ^e
α_e (cm ⁻¹)	0.136	0.129	0.131	0.131	0.126	0.137 ^e
r.m.s. ^f (cm ⁻¹)	0.23	0.14	0.14	0.17	—	
μ (D)	-6.4226 ^g	-6.3996	—	-6.470	-6.796	-6.425 ^h

^a Obtained by extrapolation of optimum d exponents for other atoms.

^b Ref. [13]

^c Ref. [23].

^d The root mean square deviation of a fit to a five-parameter generalized Morse function, as in Ref. [83].

^e Ref. [20].

^f The root mean square deviation of a non-linear least-squares fit to a 5-parameter spectroscopic equation.

^g DZ basis: -6.2822 D.

^h Ref. [24].

Table 5.4Calculated properties for the $X\ ^2\Sigma^+$ state of MgH. See also Table 5.3.

Property	DZP basis [He] core	BF1 basis [He] core	BF1 basis [Ne] core	MR ^a	Ref. [39]	Reference Value
Range (bohr)	2.5–4.5	2.5–4.5	2.5–4.5	2.5–4.5		
pol. expt.	0.20	0.20	0.164			
B.F. expt.	—	0.23	0.26	—		
D_e (eV)	1.1680	1.3420	1.2739	1.3610	1.385	1.362 ^b
R_e (bohr)	3.2807	3.2928	3.3000	3.2665	3.294	3.271 ^b
β_0 (bohr ⁻¹)	0.9735	0.9154	0.9336	0.9029	—	—
λ_1 (bohr ⁻²)	0.1376	0.1323	0.1251	0.1069	—	—
λ_2 (bohr ⁻³)	0.0437	0.0488	0.0441	0.0440	—	—
r.m.s. (eV)	0.0032	0.0036	0.0037	0.0004	—	—
ω_e (cm ⁻¹)	1486.1	1499.8	1489.9	1490.6	1484	1495.263 ^c
$\omega_e x_e$ (cm ⁻¹)	29.21	24.61	27.44	26.90	30.99	31.641 ^c
$\omega_e y_e$ (cm ⁻¹)	-1.753	-1.331	-1.374	-1.076	0.391	—
B_e (cm ⁻¹)	5.860	5.796	5.774	5.881	5.7177	5.8248 ^c
α_e (cm ⁻¹)	0.240	0.199	0.215	0.211	0.1453	0.1750 ^c
r.m.s. (cm ⁻¹)	0.62	0.43	0.46	0.38	—	—
μ (D)	-1.1249 ^d	-1.2043	—	-1.236	-1.400	—

^a Digits of point at 3.1 bohr in Table XII of Ref. [6] are transposed.^b Ref. [34], confirmed by Ref. [40]. Ref. [35] reports 3.2689 bohr.^c Ref. [35].^d DZ basis: $\mu = -1.0643$ D.

Table 5.5

Calculated properties for the $X^1\Sigma^+$ state of AlH. See also Table 5.3.

Property	DZP basis [He] core	BF1 basis [He] core	BF1 basis [Ne] core	MR	Ref. [44]	Ref. SO-Cl	[45] F-Cl	Reference Value
Range (bohr)	2.3-5.0	2.3-5.0	2.3-5.0	2.3-4.3				
pol. expt.	0.21	0.21	0.196					
B.F. expt.	—	0.27	0.27	—				
D_e (eV)	2.9433	3.1786	3.2461	3.1302	3.112	3.162	3.072	3.16 ± 0.01^a
R_e (bohr)	3.1248	3.1212	3.1329	3.1085	3.122	3.124	3.135	3.115^b
β_0 (bohr ⁻¹)	0.6934	0.6851	0.6648	0.6771	—	—	—	—
λ_1 (bohr ⁻²)	-0.0031	-0.0094	-0.0215	-0.0308	—	—	—	—
λ_2 (bohr ⁻²)	0.0225	0.0177	0.0215	0.0114	—	—	—	—
r.m.s. (eV)	0.0025	0.0040	0.0061	0.0005	—	—	—	—
ω_e (cm ⁻¹)	1683.0	1727.9	1694.7	1694.6	1678.6	1686	1672	1682.56^b
$\omega_e x_e$ (cm ⁻¹)	26.91	27.27	26.53	30.81	29.22	—	—	29.09^b
$\omega_e y_e$ (cm ⁻¹)	0.146	0.133	0.206	0.205	0.24	—	—	$(0.239)^c$
B_e (cm ⁻¹)	6.349	6.362	6.316	6.410	6.360	—	—	6.3907^b
α_e (cm ⁻¹)	0.172	0.167	0.168	0.186	0.184	—	—	0.1858^b
r.m.s. (cm ⁻¹)	0.27	0.21	0.28	0.19	—	—	—	—
μ (D)	-0.2251 ^d	-0.2342	—	-0.098	-0.119	-0.102	-0.101	—

^a Ref. [40].^b Ref. [41].^c Ref. [41], value for $\omega_0 y_0$.^d DZ basis: $\mu = -0.1798$ D.

Table 5.6

Calculated properties of the $X^2\Pi_r$ state of SiH. See also Table 5.3.

Property	DZP basis ^a [Ne] core	BF1 basis ^a [Ne] core	MR	Ref. [49]	Reference Value
Range (bohr)	2.2-4.0	2.2-4.0	2.2-4.0		
pol. expt.	0.25	0.25			
B.F. expt.	—	0.35	—		
D_e (eV)	2.8933	3.1364	3.0895	3.13	3.19 ^b
R_e (bohr)	2.9019	2.8953	2.8850	2.872	2.872
β_0 (bohr ⁻¹)	0.8303	0.8142	0.8187	—	—
λ_1 (bohr ⁻²)	0.0228	0.0098	0.0078	—	—
λ_2 (bohr ⁻³)	0.0277	0.0251	0.0263	—	—
r.m.s. (eV)	0.0007	0.0012	0.0002	—	—
ω_e (cm ⁻¹)	1997.3	2038.3	2034.3	2057.8	2042.5229 ^c
$\omega_e x_e$ (cm ⁻¹)	34.24	35.04	35.56	37.8	36.0552 ^c
$\omega_e y_e$ (cm ⁻¹)	-0.033	0.055	0.070	—	0.1254 ^c
B_e (cm ⁻¹)	7.357	7.388	7.442	7.505	7.503898 ^c
α_e (cm ⁻¹)	0.212	0.211	0.216	0.218	0.21575 ^d
r.m.s. (cm ⁻¹)	0.25	0.25	0.27	—	—
μ (D)	0.3163 ^e	0.3067	0.141	0.123	—

^a Basis set in Ref. [8] had to be modified, to have coefficients -0.93, 1.47 for contraction of second p -orbital.

^b Ref. [84].

^c Ref. [52].

^d Ref. [50].

^e DZ basis: $\mu = 0.4063$ D.

Table 5.7

Calculated properties of the $X^3\Sigma^-$ state of PH. See also Table 5.3.

Property	DZP basis [Ne] core	BF1 basis [Ne] core	MR	Ref. [66]	Reference Value
Range (bohr)	2.1-4.0	2.1-4.0	2.0-3.5		
pol. expt.	0.38	0.38			
B.F. expt.	—	0.53	—		
D_e (eV)	2.8089	3.0527	3.0433	3.05	3.17 ^a
R_e (bohr)	2.7138	2.7081	2.6944	2.689	2.686 ^b
β_0 (bohr ⁻¹)	0.9864	0.9583	0.9617	—	—
λ_1 (bohr ⁻²)	0.0580	0.0412	0.0389	—	—
λ_2 (bohr ⁻³)	0.0346	0.0318	0.0308	—	—
r.m.s. (eV)	0.0041	0.0029	0.0002	—	—
ω_e (cm ⁻¹)	2331.6	2362.1	2366.8	2379	2363.779 ^c
$\omega_e x_e$ (cm ⁻¹)	43.71	43.79	44.71	42	43.911 ^c
$\omega_e y_e$ (cm ⁻¹)	-0.377	-0.203	-0.188	—	0.1068 ^c
B_e (cm ⁻¹)	8.393	8.424	8.509	8.524	8.53899 ^c
α_e (cm ⁻¹)	0.263	0.258	0.264	0.253	—
r.m.s. (cm ⁻¹)	0.23	0.24	0.23	—	—
μ (D)	0.5789 ^d	0.5919	0.481	0.431	—

^a Ref. [6], recommended value.^b Ref. [80].^c Ref. [85].^d DZ basis: $\mu = 0.8445$ D.

Table 5.8Calculated properties of the $X^2\Pi_i$ state of SH. See also Table 5.3.

Property	DZP basis [Ne] core	BF1 basis [Ne] core	MR	Ref. [69]	Ref. [72]	Reference Value
Range (bohr)	2.0–4.5	2.0–4.5	2.0–3.5			
pol. expt.	0.48	0.48				
B.F. expt.	—	0.64	—			
D_e (eV)	3.4086	3.7127	3.5464	3.62	3.50	3.71 ^a
R_e (bohr)	2.5544	2.5489	2.5407	2.535	2.557	2.5339 ^b
β_0 (bohr ⁻¹)	1.0331	0.9947	1.0079	—	—	—
λ_1 (bohr ⁻²)	0.0495	0.0300	0.0340	—	—	—
λ_2 (bohr ⁻³)	0.0270	0.0294	0.0380	—	—	—
r.m.s. (eV)	0.0034	0.0026	0.0005	—	—	—
ω_e (cm ⁻¹)	2629.0	2702.5	2676.7	2739	2715	2711.6 ^c
$\omega_e x_e$ (cm ⁻¹)	51.79	50.22	49.47	55.1	55.8	59.9 ^c
$\omega_e y_e$ (cm ⁻¹)	-0.292	-0.099	-0.135	—	—	—
B_e (cm ⁻¹)	9.454	9.494	9.561	9.59	9.42	9.461 ^c
α_e (cm ⁻¹)	0.292	0.285	0.293	0.29	0.22	0.270 ^c
r.m.s. (cm ⁻¹)	0.16	0.23	0.32	—	—	—
μ (D)	0.9832 ^d	0.9964	0.810	0.812 ^e	—	0.758 ^f

^a Ref. [6], recommended value.^b As in Ref. [67].^c Ref. [68].^d DZ basis: $\mu = 1.2455$ D.^e Calculated at 2.551 bohr.^f Ref. [70].

Table 5.9

Calculated properties for $X^1\Sigma^+$ state of HCl. See also Table 5.3.

Property	DZP basis [Ne] core	BF1 basis [Ne] core	MR	Reference Value
Range (bohr)	1.8-3.6	1.8-3.6	1.9-3.4	
pol. expt.	0.70	0.70		
B.F. expt.	—	0.84	—	
D_e (eV)	4.2619	4.6199	4.4268	4.6175 ^a
R_e (bohr)	2.4129	2.4122	2.4142	2.4085 ^a
β_0 (bohr ⁻¹)	1.0427	0.9993	1.0051	—
λ_1 (bohr ⁻²)	0.0193	0.0029	0.0092	—
λ_2 (bohr ⁻³)	0.0327	0.0358	0.0372	—
r.m.s. (eV)	0.0029	0.0012	0.0005	—
ω_e (cm ⁻¹)	3031.7	3025.6	2979.0	2990.9463 ^b
$\omega_e x_e$ (cm ⁻¹)	57.21	54.45	53.7	52.8185 ^b
$\omega_e y_e$ (cm ⁻¹)	-0.002	0.150	0.100	0.2244 ^b
B_e (cm ⁻¹)	10.566	10.571	10.555	10.593416 ^b
α_e (cm ⁻¹)	0.321	0.310	0.312	0.307181 ^b
r.m.s. (cm ⁻¹)	0.30	0.39	0.38	—
μ (D)	1.3787 ^c	1.3897	1.136	1.0933(5) ^d

^a Ref. [80].^b Ref. [74].^c DZ basis: $\mu = 1.7094$ D.^d Ref. [75].

Table 5.10

Geometry, bond function exponents and well depth for TZPP and BF2 basis sets, compared to experimental values.[†] Both TZPP and BF2 calculations use [He] for NaH, MgH, and AlH, and [Ne] core and anti-core freezing for SiH, PH, SH, and HCl.

Molecule	Geometry (bohr)	Bond function exponents	Dissociation Energy(eV)		
			TZPP	BF2	Expt.
NaH	3.566	0.40, 0.16	1.882	1.971	1.95
MgH	3.269	0.35, 0.14	1.325	1.362	1.362
AlH	3.110	0.425, 0.17	3.078	3.174	3.16
SiH	2.872	0.22, 0.22	3.027	3.188	3.19
PH	2.687	0.85, 0.34	2.927	3.131	3.17
SH	2.534	1.0, 0.40	3.535	3.817	3.71
HCl	2.4085	1.15, 0.46	4.429	4.793	4.6175

[†] See Tables 5.3-5.9 for references to experimental work.

Table 5.11

Average absolute deviation between MR values and the DZP and BF1 values for the second-row monohydrides NaH–HCl. For D_e and R_e , experimental values were used, where known to be accurate. Both DZP and BF1 calculations use [He] for NaH, MgH, and AlH, and [Ne] core and anti-core freezing for SiH, PH, SH, and HCl.

Property	Average Deviation	
	DZP	BF1
D_e	0.28	0.04
$R_e(\text{bohr})$	0.016	0.012
$\omega_e(\text{cm}^{-1})$	28	22
$\omega_e x_e(\text{cm}^{-1})$	2.4	1.3
$\omega_e y_e(\text{cm}^{-1})$	0.18	0.07
$B_e(\text{cm}^{-1})$	0.08	0.05
$\alpha_e(\text{cm}^{-1})$	0.009	0.008

Table 5.12

Dipole moments for the second-row diatomic hydrides, calculated using DZ, DZP, and BF1 quality basis sets. All calculations use [He] for NaH, MgH, and AlH, and [Ne] core and anti-core freezing for SiH, PH, SH, and HCl. For comparison, dipole moments obtained by MR and (where available) known by experiment, are listed. All values in Debye.^a

Molecule	DZ	DZP	BF1	MR	expt.
NaH	-6.2822	-6.4226	-6.3996	-6.470	-6.425
MgH	-1.0643	-1.1249	-1.2043	-1.236	—
AlH	0.1798	0.2251	0.2342	-0.098	—
SiH	0.4063	0.3163	0.3067	0.141	—
PH	0.8445	0.5789	0.5919	0.481	—
SH	1.2455	0.9832	0.9964	0.810	0.758
HCl	1.7094	1.3787	1.3897	1.136	1.0933

^a 1 D = 0.39345 a.u.

Figure 5.1

Calculated potential energy curves of the $X^1\Sigma^+$ state of NaH, showing the $v = 0$ to 5 vibrational levels, with the $J = 0$ and 5 rotational levels drawn for each v . The solid curve is for the BF1 basis, [He] core, as tabulated in Table 5.3. The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5.2

Calculated potential energy curves of the $X^2\Sigma^+$ state of MgH. The solid curve is for the BF1 basis, [He] core, as tabulated in Table 5.4, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5 3

Calculated potential energy curves of the $X^1\Sigma^+$ state of AlH. The solid curve is for the BF1 basis, [He] core, as tabulated in Table 5.5, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5.4

Calculated potential energy curves of the $X^2\Pi_r$ state of SiH. The solid curve is for the BF1 basis, [Ne] core, as tabulated in Table 5.6, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5.5

Calculated potential energy curves of the $X^3\Sigma^-$ state of PH. The solid curve is for the BF1 basis, [Ne] core, as tabulated in Table 5.7, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5.6

Calculated potential energy curves of the $X^2\Pi_1^+$ state of SH. The solid curve is for the BF1 basis, [Ne] core, as tabulated in Table 5.8, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Figure 5.7

Calculated potential energy curves of the $X^1\Sigma^+$ state of HCl. The solid curve is for the BF1 basis, [Ne] core, as tabulated in Table 5.9, and the $v = 0$ to 5 vibrational levels are shown, with the $J = 0, 5$ rotational levels drawn for each v . The dotted curve is for the DZP basis set; the broken curve is for a fit to MR data.

Chapter 6

Three Excited States of Dinitrogen:

As the births of living creatures are at first ill-shapen, so are all innovations, which are the births of time.

Francis Bacon,
Essays. Of Innovation

6.1 Introduction

In the preceding three chapters the use of bond functions in hydrogen-containing diatomics has been discussed. In each case where atomic basis sets were of DZP quality, the addition of a set of (*sp*) bond functions resulted in a dramatic improvement. One might generalize that the (*sp*) bond function will result in a similar improvement when the bonding is no longer between hydrogen and another more complex atom. In a study of the ground state of dinitrogen, $N_2\ X^1\Sigma_g^+$, this was found not to be the case: although an (*sp*) set resulted in a stabilization of the molecular energy, a much larger bond function basis set, consisting of *two* sets of (*spd*) orbitals, was found to be optimum.[8]

The difference in the hydrides and dinitrogen results could be interpreted in one of two ways:

- (i) a computational artefact, basis set superposition error (BSSE);
- (ii) a genuinely chemical effect, such as molecular basis set incompleteness (MBSI).

If it is related to option (i), then the optimum BF composition for any state of nitrogen would be related to the fact that the basis set for nitrogen is particularly deficient and so many orbitals must be used to overcome the atomic basis set incompleteness. This would bolster the claim that bond function effectiveness is merely a computational artefact, and that the energy lowering is due to basis set superposition error.[14] In such a case, another

calculation with the identical nitrogen atomic basis sets, *e.g.*, an excited state of nitrogen with a smaller bond order, would require the *same* bond function be added.

On the other hand, the optimum BF composition could be related not primarily to computational artefact, but to something of a more chemical nature. A very striking difference between the ground states of the hydrides and dinitrogen is, of course, that the former have a bond order of 1 whereas N_2 ($X^1\Sigma_g^+$) has a much greater bond order of 3. Such an interpretation focusses on the molecular basis set incompleteness, and would predict that cases such as the less-strongly-bound excited states of nitrogen would need *fewer* bond functions to describe the mid-bond region, since to a first approximation, the charge density is lower for a bond order of 2 than 3. In this Chapter, the "ill-shapen" innovation of BF becomes clearer in form as a pattern for BF composition appears.

The low-lying excited states of nitrogen are of intrinsic chemical interest as well because of the crucial role they play in atmospheric phenomena such as auroras and afterglows. The complexity of the observed spectrum of N_2 may be understood by considering the large number of valence molecular orbital configurations that can be created from the approach of two nitrogen atoms in their three lowest (4S , 2D , 2P) states. Freezing four electrons in the lowest-energy $1\sigma_g$ and $1\sigma_u$ cores allows the remaining ten electrons to be distributed in all possible ways among the six valence MO's, $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$. These intra-valence-shell permutations give rise to 96 electronic states of $^1\Sigma_g^+$ symmetry, 100 of $^3\Sigma_u^+$ symmetry, 164 of $^3\Pi_g$, *etc.* (These are the dimensions of the valence CI calculation for the corresponding states.)[12] The states arising from single orbital replacements of the ground state alone are:

$$A^3\Sigma_u^+, B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, a'^1\Sigma_u^-, a^1\Pi_g, w^1\Delta_u, C^3\Pi_u, b^1\Pi_u, b'^1\Sigma_u^+.$$

The potential energy curves for these states are close in energy, and have similar shapes and term energies.[12] Of these states, this chapter singles out the first three, to test the BSSE *vs.* MBSI interpretations of bond function effectiveness. The (dipole-allowed) infrared $W^3\Delta_u \rightarrow B^3\Pi_g$ [4], the (forbidden) ultraviolet $W^3\Delta_u \rightarrow X^1\Sigma_g^+$ [5] and recently, the (forbidden) near-infrared $W^3\Delta_u \rightarrow A^3\Sigma_u^+$ [6] transitions have all been observed. The electronic configurations for the three excited states involve predominantly π_u and σ_g bonding MO excitations into the antibonding π_g MO:

$$A^3\Sigma_u^+ : 1\pi_u^3 3\sigma_g^2 1\pi_g^1;$$

$$B^3\Pi_g : 1\pi_u^4 3\sigma_g^1 1\pi_g^1;$$

$$W^3\Delta_u : 1\pi_u^3 3\sigma_g^2 1\pi_g^1.$$

The $B^3\Pi_g$ state has been particularly difficult to interpret spectroscopically because of the close proximity of other states such as the $B^3\Sigma_u^-$ and $W^3\Delta_u$ states.[†] Intrasytem cascading has been observed, where consecutive transitions of $B \rightarrow W \rightarrow B$ to successively lower vibrational levels, occurs. The $W \rightarrow B \rightarrow A$ radiative cascade has also been reported.[1] For spectroscopists, investigation and identification of the $W - B$ lines have been especially difficult in the spectral range where the first positive system $B^3\Pi_g - A^3\Sigma_u^+$ and the recently studied $B^3\Sigma_u^- - B^3\Pi_g$ system are intense.[9]

However, recent high-resolution Fourier transform spectrometry work has enabled high- v level analysis of the $W - B$ electronic transitions,[2] and the molecular constants of the $B^3\Pi_g$ state, for vibrational levels up to $v = 12$, which is the last level prior to dissociation to two $N(^4S)$ atoms, are now well-established.

The existence of the $W^3\Delta_u$ state was first postulated by Mulliken in 1957.[1] It has since been found that the cross-section for $X - W$ excitation by impact is large, and results in the largest excitation rate by electron collisions of the N_2 states under auroral conditions.[1]

The calculation of the radiative lifetimes of the $B - W$ transition has been a matter of some controversy, but recent *ab initio* work has determined the lifetimes to an estimated accuracy of fifteen percent.[7] The prediction of accurate transition probabilities and radiative lifetimes depends very much on the electronic transition moment function, which in turn depends on accurate *ab initio* electronic wavefunctions.

6.2 Results

6.2.1 Absolute and Excitation Energies of the Atoms

Table 6.1 shows the energies calculated for the nitrogen atom in its 4S and 2D states, using a DZP-quality basis set[13] as well as a TZPP [5s3p2d] basis set,[15] for the SD-CI eigenvalue energies, and after the Davidson correction[16] has been applied. The atoms were calculated with the lowest occupied and highest virtual orbitals frozen, i.e, they were excluded from being changed during the generation of configurations for the CI space.

[†] The energy separation between the W and B state $v = 0$ levels, for example, is only 74 cm^{-1} . [1]

The atomic excitation energies for the $^4S \rightarrow ^2D$ transition are shown in this Table to be 2.705 eV (DZP basis) and 2.604 eV (TZPP basis). These are in significant disagreement with the experimental value of 2.383 eV.[19] This is reminiscent of the case studied in Chapter 4, where the ionization potential of the oxygen atom was difficult to recover with DZP or TZPP or even larger basis sets, leading to problems with the dissociation limits and hence the molecular ionization potentials. Here, the problem of an over-estimated atomic excitation energy will lead to an incorrect term energy for species whose asymptotic limits differ, *e.g.*, for transitions such as $A \rightarrow B$, but not for interstate transitions which have the identical asymptote, such as $W \rightarrow B$.

6.2.2 Dissociation Energies

Tables 6.2, 6.3, and 6.4 summarize the results of systematically augmenting a DZP-quality basis set with varying sets of bond functions, as well as results using a TZPP [5s3p2d] basis set.[15] The atoms were maintained as distance of 2.4314 bohr and 2.2915 bohr apart, corresponding to the experimental R_e for the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states, respectively. The R_e of the A state is within 0.01 bohr of the equilibrium bond length of the $W^3\Delta_u$ state.

The SCF MO's were constructed using the ground state occupation, and the selection threshold and step-size were 20 μ hartree. This gave typically 3000 configurations for the $A^3\Sigma_u^+$ and $W^3\Delta_u$ states, and 5000 configurations for the $B^3\Pi_g$ state CI space. Two roots were selected for in both kinds of calculation. Smaller selection thresholds gave variations of up to 0.15 eV in the total energy. The criterion for inclusion as a reference configuration was that the configuration contribute 0.5% or more to the c_i^2 CI wavefunction.[17] This rule was relaxed in the case of two 6 open-shell configurations which could not be included in the A/W calculations, due to program limitations. Such a criterion gave 6 reference configurations for the A and W states, and 14 configurations for the $B^3\Pi_g$ state.

Looking first of all at the MRD-CI energies in Tables 6.2-4 one sees that the contribution due to quadruple excitations which is estimated by the Davidson correction[28] (the difference between $E(\text{MRD-CI})$ and $E(\text{F-CI})$) is about 0.4 eV. Since the lowering is dependent on the c_i^2 contribution and the absolute energy, which are roughly comparable for all states considered, the quadruple excitations correction is roughly constant for each species and each kind of basis set. The dissociation energies reported in Tables 6.2-6.4 were obtained by subtracting the energies of the separated atoms (DZP or TZPP; at the

SD-CI/MRD-CI or (est.) F-CI level, as the case may be) from the calculated molecular energy. The energies of the isolated atoms could be used because the bond function does not contribute as $R \rightarrow \infty$.

In Table 6.2, the D_e of the $A^3\Sigma_u^+$ state is seriously underestimated with a DZP basis (2.63 eV vs. 3.68 eV, expt.); in fact, the D_e is underestimated by 0.9–1.0 eV for all three states. Changing to the TZPP basis set improves the D_e by only around 0.2 eV for the A and W states, and in the case of the B state, there is no noticeable improvement; expanding the nuclear basis to TZPP brings little improvement for this state (2.80 eV). The same may be said for the $B^3\Pi_g$ state, with $D_e = 4.01$ eV (DZP) and 4.04 eV (TZPP) (4.90 eV, expt.). The $W^3\Delta_u$ state also has $D_e = 3.98$ eV (DZP) and 4.10 eV (TZPP) (4.87 eV, expt.). On average, the DZP basis set recovers only 78% of the D_e for these three doubly-bound states and the TZPP recovers only 81%.

Addition of a single (sp) bond function causes an immediate improvement, bringing the calculated D_e to an average 87% of the experimental D_e .

When a set of (spd) bond functions is added, the D_e further improves, to 3.33 (90%), 4.69 (96%) and 4.71 (97%) eV for the $A^3\Sigma_u^+$, $B^3\Pi_g$, and $W^3\Delta_u$ states respectively. Removing the constraint that the exponents of this set be equivalent ($\zeta_s \neq \zeta_p \neq \zeta_d$) leads to the greatest agreement of all basis sets tried, with D_e 's which are 92, 96 and 98 percent of the experimental values.

Using a BF composition which was found to be optimum for the ground state does not, however, produce good agreement with the experimental D_e 's. From Tables 6.2–4 it may be seen that two sets of (spd) bond functions consistently overestimated the D_e , at 103%, 107% and 106% for the $A^3\Sigma_u^+$, $B^3\Pi_g$ and $W^3\Delta_u$ cases. With respect to the issues discussed in the introduction to this chapter, this sensitivity to bond order lends credence to the second interpretation, namely, that BF's *act primarily to overcome the molecular basis set incompleteness*.

6.2.3 MO Energy Levels

As bond functions are added to the set of atomic orbitals, the distribution and arrangement of the molecular orbitals (MO's) created changes. The SCF MO's of the $N_2(X^1\Sigma_g^+)$, were used in the present calculations for building configurations at the CI stage. The energy

levels of the MO's for the valence region are shown in Figure 6.1 for a bond distance of 2.29 bohr; the energetically very high- and very low-lying MO's had to be excluded from the diagram for obvious reasons. Ignoring the columns of BF-basis MO's and focussing solely on the DZP and TZPP nuclear-centred sets, one can qualitatively understand what progressing to larger and larger atomic-centred basis sets does: the TZPP column shows a greater density than the DZP column of low-lying virtual MO's which may be populated during the configuration interaction stage. The addition of any set of bond functions causes little change in the energy of the occupied MO's, which lie below zero hartree. The BF effects are thus most pronounced at the CI and not SCF level of calculation.

The π_g orbitals, which lie very slightly above zero, are also relatively unaffected by the addition of few or many bond functions. On going from the DZP to DZP+(sp) orbitals' column, one sees that a single set of (sp) bond functions introduces new virtual MO's at 3.1, 3.6 and 4.9 hartree, and shifts energetically-close virtual MO's somewhat. Additional relatively low-lying virtual orbitals are introduced when a set of d orbitals is added and mixes in with the π_g^* orbitals and others higher up the manifold, as in the next column over. Two sets of (spd) orbitals added to a DZP basis result in *exactly the same total number* of virtual MO's as the TZPP basis does, but note the extreme difference in these two columns: the TZPP MO's are less evenly distributed over this energy range, and there appear to be fewer of them. In fact, there are more energetically very high-lying MO's (not shown in Figure 6.1) created by the TZPP basis than by the DZP+2(spd) basis. Qualitatively, the efficiency of bond functions may be understood as the *creation of a greater number of energetically accessible virtual MO's*, which are able to interact at the CI stage more strongly than the very high-lying MO's.

6.2.4 Term Energies

Tables 6.2-6.4 also show the term energies. (T_0'' does not appear in Table 6.2 because the $A^3\Sigma_u^+$ state dissociates to two 4S atoms.) The excitation energies denoted T_0 are quite similar, with a spread of at most 0.5 eV for the DZP, no BF basis set. The reasonable agreement of term energies is to be expected, through a cancellation of errors (underestimate in the ground and upper state well-depths). The best of the T_0' term energies are when the basis set is DZP+2(spd) for the upper state, which also relates to the "optimum" cancellation of errors, since the ground state by definition of T_0' is DZP+2(spd) as well.

For the final column of term energies, T_0'' , when the T_0' are adjusted for the incorrect atomic excitation energy, the DZP+(s, p, d ,) basis set gives the best results. What this means is that the DZP+(s, p, d) basis set is overall the best for the molecular description; when it seems less than optimum, the fault actually lies with the poorer atomic description.

The left-most sets of columns in Tables 6.2–4 give the term energies between the excited state and the ground state where the ground state basis set uses the same BF as the excited state (denoted T_0); where the ground state basis is held fixed at a BF of 2(spd) (denoted T_0'); and, finally, for the $B^3\Pi_g$ and $W^3\Delta_u$ states, where the asymptote is corrected for the somewhat over-estimated atomic excitation energy mentioned in Table 6.1 above (denoted T_0'').

The term energy T_0 calculated for the same basis set for the ground state is not reported for every case because no (s, p, d) BF or TZPP atomic basis set results were reported in Ref. [8]. The former BF composition refers to sequential and separate optimization of the bond function: first the s orbital was optimized, then the p and finally the d . This was done to increase the flexibility of the bond function.

6.2.5 Potential Curve of the $B^3\Pi_g$ State

Comparison of the term and dissociation energies which are reported in Tables 6.2–6.4 shows that the (s, p, d) bond function composition is in all cases optimum. Calculation of the curves for the $A^3\Sigma_u^+$, $B^3\Pi_g$ and $W^3\Delta_u$ excited states was begun with this basis. The A and W curves presented some difficulty; even at $R \simeq R_e$, two six-open-shell main configurations should have been specified in the multiple reference, but due to program limitations, could not be. Preliminary results for very small sections of these curves showed that such an omission led to significant underestimation of the fundamental frequency.

The potential curves obtained at the MRD-CI and (est.) full-CI levels of treatment are reported for the $B^3\Pi_g$ state in Table 6.5. The right-most column refers to the counterpoise correction of Boys and Bernardi[21] applied to this calculation. The counterpoise-corrected energy was found by subtracting the energies of the atom-and-ghost orbitals, where the ghost orbitals included the bond function and the set of orbitals for the second nitrogen atom (a nuclear charge of zero was maintained in both cases):

$$E_{N_2,B}(CC) = E(N_2, B) - E(N_S - BF - X_N) - E(N_D - BF - X_N) \quad (6.1)$$

The point-counterpoise correction is often suggested as the means to overcome the artefact of BSSE. That this is clearly an overestimate of the possible BSSE in the case of bond functions is demonstrated by the fact that the E(CC) potential curve rises *above* the dissociation limit, as the right-most column shows.

6.2.6 Morse Function and Spectroscopic Parameters

Table 6.6 gives the parameters of the fits of generalized Morse function for the (est.) F-CI and E(CC) curves from Table 6.5, and the RKR curve from Ref. [18]. The five-parameter fits are to the function given in Eq. (2.6–2.7) of Chapter 2. The right-most column gives the root mean square deviation for the non-linear least-squares fit. Although the calculated curves have very little noise in their points, as evidenced by the small r.m.s. deviation, the RKR data had about 20 times *less* noise, and could be fitted to a 7-parameter generalized Morse function (GMF7). The seven-parameter fit includes cubic and quartic correction terms to the GMF5:

$$V = D_e(y^2 + \sum_{n=3}^{\infty} a_n y^n) - D_e, \quad (6.2)$$

where

$$y = 1 - e^{-\beta(R-R_e)}$$

and

$$\beta = \beta_0[1 + \lambda_1(R - R_e) + \lambda_2(R - R_e)^2].$$

The analytic specifications for potential energy curves were used in the Numerov-Cooley numerical generation of the vibrotational levels, $J = 0 - 6$ for each of the $v = 0 - 12$ levels. A non-linear least-squares fit to the five-parameter spectroscopic equation (Eq. (1.18–1.20)) was done, to determine values for ω_e , $\omega_e x_e$, $\omega_e y_e$, B_e and α_e . These are listed in Table 6.7 for the same three curves given in Table 6.6. The spectroscopic constants were obtained in the same fashion for each curve, to eliminate the disagreement that can occur from merely fitting different numbers of v, J levels or from fitting to higher terms in the spectroscopic equation. The parameters derived here for the RKR curve, for instance, are in close but not exact agreement with those reported by Lofthus and Krupenie ($\omega_e = 1733.39$, $\omega_e x_e = 14.122$, $\omega_e y_e = -0.00226 \text{ cm}^{-1}$) who used a different v, J level assortment and included $\omega_e z_e$ in the fit.[18] The greatest disagreement for the F-CI spectroscopic constants with the experimental value is the 31 cm^{-1} (1.8%) disagreement for ω_e .

The potential energy curve for the $B^3\Pi_g$ state calculated with the DZP+(s, p, d) basis set with exponents $\zeta_s = \zeta_p = 0.56$ and $\zeta_d = 0.72$ is shown (denoted by triangles) in Figure 6.2, along with the RKR curves for that state and the $X^1\Sigma_g^+$ state. The calculated curve is very similar in shape to the RKR curve for the $B^3\Pi_g$ state, but it is displaced upwards somewhat due to the asymptotic problem.

In Figure 6.3 the atomic splitting is corrected for. The asymptotic shift has the effect of "pinning" the RKR and F-CI curves to the same energy zero. (Both are shown as solid lines.) There is some discrepancy between the shapes of the calculated and experimental curves, which is evident in the too-small D_e and the too-large R_e values in Table 6.6. Also, the fundamental frequency of the F-C curve in Table 6.7 is in some 30 cm^{-1} disagreement. Although the DZP+(s, p, d) basis set is an excellent first approximation—far better than a DZP or TZPP curve, judging from the D_e 's—there are still some improvements which need to be made. The asymptotic problems suggest that the next step up in basis set enhancement would be a significantly larger and more flexible atomic description. From then on, a new exploration with the optimum BF composition, similar to the exploration carried out here, would have to be done. The dihydrogen results from Chapter 3 suggest that, as the number of atomic-centred orbitals increases, so does the number of functions that can be added at the mid-bond point for balance.

The uppermost curve in Figure 6.3 is the counterpoise-corrected curve of the $B^3\Pi_g$ state (denoted by triangles). From Table 6.6 the D_e is seen to be grossly underestimated; it is even smaller than that for the DZP basis alone. The behaviour near dissociation is qualitatively incorrect, since the potential energy curve exhibits a maximum before it approaches zero at large R values.

6.2.7 Comparison with Other Work

Table 6.8 shows the results of some other calculations with different methods for comparison, beginning with a CAS-SCF study published in 1980,[11] where the results are markedly better than Hartree-Fock SCF calculations, but worse than the CI results shown in Table 6.8. Although Ermler *et al.* did not report molecular constants for the (5s4p3d) STO basis set calculation of numerous valence-excited state curves given in that work, the energies tend to lie a couple of eV above the MC-CI values. This is likely due to the use of a single reference configuration, and not multiple reference configurations from which the

SD-CI space was generated.[12]

Verner *et al.* recently reported high-quality calculations for five low-lying excited states of N_2 , including the three states which are of interest in this chapter. They used a basis set consisting of (11s7p3d1f) GTO functions contracted to [8s5p3d1f], formed the molecular orbitals by multi-configuration SCF (MC-SCF) means, and then carried out extensive configuration interaction (CI) using multiple reference configurations, which they denote as MC-CI. Their results are summarized in Table 6.8. For the dissociation energies, they consistently underestimated the dissociation energies at 3.30, 4.38, and 4.55 eV for the $A^3\Sigma_u^+$, $B^3\Pi_g$, and $W^3\Delta_u$ states respectively, even with a large atomic-centred basis set and extensive CI.[7] From Tables 6.2, 6.3 and 6.4, the comparable D_e 's found for the DZP + (s,p,d) basis sets were 3.38, 4.69, and 4.77 eV. The experimental values listed are 3.68, 4.90, and 4.87 eV.

6.2.8 BSSE or MBSI? Counterpoise Correction

Now consider the two kinds of errors mentioned in Chapter 1 and the methods proposed to correct for them. On the one hand there is the basis set superposition error (BSSE), with the counterpoise correction or variations thereof. On the other hand there is the molecular basis set incompleteness (MBSI), with the calibrated addition of BF's to a basis set to counteract that.

A distinction must first be drawn between the BSSE and the counterpoise correction (CC). The BSSE is the unavoidable error caused by the mutual enlargement of the basis sets of each system component (atom, or in the case of van der Waals' species, monomer) by the presence of the orbitals of the other system components. The counterpoise correction is the method proposed in 1970 by Boys and Bernardi to quantify the BSSE for small van der Waals-bound species.[21] As noted by several authors, the counterpoise correction gives an imperfect representation of the BSSE.[24][25][26][27] Increasing the size of the basis set does not necessarily reduce the size of the correction to be made.[24][25] Nor does a systematic improvement in accuracy occur for the application of the CC to smaller calculations.[24] The CC overestimates the BSSE in some cases, even without the presence of BF's or other orbitals which will be taken into account more than once using the CC method.[26][27] However, one cannot assume that the CC represents an upper bound to the BSSE, because for smaller basis sets an underestimate of the error was found. The counterpoise correction

is unsatisfactory in this author's eyes because it provides a rather erratic "correction" which in the case of BF's is obviously an overcorrection, and the corrected calculation, as is seen clearly in results presented here, is of poorer quality than an uncorrected, even leading to incorrect dissociative behaviour.

Now consider the alternative interpretation. The addition of BF's may be viewed as a kind of correction for the MBSI, and unlike the counterpoise correction it can immediately be seen to lead to an improvement in the quality of the curve, and furthermore, that this correction can be used to set the bounds for unknown quantities. The case *against* BSSE and *for* MBSI has already been made. In Chapters 3, 4 and 5, and in other work published by this group[22][23], it has been shown that bond functions enable the calculation of ground state species to within 0.1 eV. This chapter has shown their success in the calculation of valence excited state species, to within 0.3 eV. In contrast, the counterpoise-corrected curves are giving poor results—worse even than DZP, no BF. The observations of this group have been recently confirmed by another group.[29]

The improvement gained through the use of BF's cannot be attributed solely to the BSSE exaggeration, or, as argued in the introduction, we would not see a bond-order-related phenomenon. This will be explored in further detail in the following chapter, where the argument for a strong correlation between bond order and BF composition is presented.

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Table 6.1

SD-CI and estimated full-CI energies for the 4S and 2D states of the nitrogen atom. Absolute energies in hartree; excitation energies in eV; exponents in bohr $^{-2}$.

Species	Basis Set	Polarization	Absolute		Excitation
		Exponent	SD-CI	Full-CI (est.)	Energy ^a
4S	DZP	0.80	-54.48213	-54.48489	0.0
	TZPP	1.8846,0.5582	-54.50101	-54.50472	0.0
2D	DZP	0.80	-54.38400	-54.38550	2.705
	TZPP	1.8846,0.5582	-54.40600	-54.40904	2.604

^a For $^4S \rightarrow ^2D$ excitation, for identical basis sets on each atom. (Experimentally, this is 2.383 eV.[19])

Table 6.2

Dissociation and term energies for the $A^3\Sigma_u^+$ state of N_2 at $R_e = 2.4314$ bohr, as a function of basis set composition. All energies are in eV.^a

Basis Set	B.F. Exponent	No. of Functions	Dissociation-Energy		Term Energy ^b	
			MRD-CI	full CI (est.)	T_0	T'_0
DZP	—	32	2.277	2.627	5.667	7.277
DZP+(<i>sp</i>)	0.56	36	2.631	3.002	5.852	6.902
DZP+(<i>spd</i>)	1.0	42	2.939	3.333	5.886	6.574
DZP+(<i>s, p, d</i>)	0.56, 0.56, 0.8	42	2.981	3.376	— ^c	6.531
DZP+2(<i>spd</i>)	0.4, 1.2	52	3.377	3.801	5.999	5.999
DZP+3(<i>spd</i>)	0.4, 1.0, 2.5	62	3.554	3.992	6.042	5.912
TZPP	—	52	2.388	2.801	— ^c	5.996
Expt. (Ref. [18])	—	—	3.6806		6.1688	

^a 1 hartree = 27.2116 eV, 1 bohr = 0.529177 Å.

^b T_0 is the difference between the excited state minimum and ground state minimum using the same basis set; T'_0 is the difference between the excited state minimum using the stated basis set and the ground state minimum using the optimum DZP+2(*spd*) basis set.

^c This basis set not used in the study of the ground state in Ref. [8].

Table 6.3

Dissociation and term energies for the $B^3\Pi$, state of N_2 at $R_e = 2.2915$ bohr, as a function of basis set composition. Same units and format as Table 6.2.

Basis Set	B.F. Exponent	No. of Functions	Dissociation-Energy		Term Energy		
			MRD-CI	full CI (est.)	T_0	T'_0	T''_0^a
DZP	—	32	3.630	4.012	7.004	8.596	8.275
DZP+(<i>sp</i>)	0.56	36	3.953	4.357	7.219	8.252	7.931
DZP+(<i>spd</i>)	1.2	42	4.263	4.687	7.250	7.922	7.601
DZP+(<i>s, p, d</i>)	0.56,0.56,0.72	42	4.22	4.69	—	7.92	7.60
DZP+2(<i>spd</i>)	0.5,1.5	52	4.729	5.245	7.402	7.402	7.081
DZP+3(<i>spd</i>)	0.4,1.0,2.5	62	4.873	5.358	7.398	7.251	6.930
TZPP	—	52	3.683	4.044	7.381	—	—
Expt. (Ref. [18])	—	—	4.8967		7.3531		

^a Asymptotes shifted, to correct for $^4S \rightarrow ^2D$ splitting.

Table 6.4

Dissociation and term energies for the $W^3\Delta_u$ state of N_2 at $R_e \simeq R = 2.4314$ bohr, as a function of basis set composition. Same units and format as Table 6.2.

Basis Set	B.F.	No. of Functions	Dissociation-Energy		Term Energy		
	Exponent		MRD-CI	full CI (est.)	T_0	T_0^*	$T_0'^*$
DZP	—	32	3.607	3.980	7.023	8.613	8.292
DZP+(<i>sp</i>)	0.56	36	3.979	4.375	7.187	8.218	7.897
DZP+(<i>spd</i>)	1.0	42	4.292	4.711	7.210	7.881	7.560
DZP+(<i>s, p, d</i>)	0.56, 0.56, 0.8	42	4.354	4.774	—	7.818	7.497
DZP+2(<i>spd</i>)	0.4, 1.2	52	4.713	5.155	7.456	7.454	7.133
DZP+3(<i>spd</i>)	0.4, 1.0, 2.5	62	4.883	5.339	7.403	7.253	6.392
TZPP	—	52	3.720	4.104	7.307	—	—
Expt. (Ref. [18])	—	—	4.8733		7.3622		

* Asymptotes shifted, to correct for $^4S \rightarrow ^2D$ splitting.

Table 6.5

Potential energy curve for the $B^3\Pi_g$ state of N_2 , calculated using a DZP + (s, p, d) basis set with exponents $\zeta_s = \zeta_p = 0.56$; $\zeta_d = 0.72$. Energies are in eV relative to separated atoms; distance is in bohr.

<i>R</i>	E(SCF)	No. Mains	Sel./Gen. ^a	E(MRD-CI)	$\sum_i c_i^2$	E(F-CI)	E(CC) ^b
1.9	+2.014	14	4378/112297	-0.991	.9356	-1.343	-0.412
2.0	+0.371	14	4273/112297	-2.654	.9338	-3.012	-2.103
2.1	-0.599	14	4193/112297	-3.624	.9326	-3.991	-3.109
2.2	-1.082	14	4175/112297	-4.118	.9309	-4.498	-3.644
2.3	-1.218	14	4241/112297	-4.285	.9284	-4.685	-3.859
2.4	-1.109	14	4321/112297	-4.213	.9259	-4.634	-3.851
2.5	-0.829	14	4414/112297	-3.990	.9228	-4.438	-3.673
2.6	-0.435	14	4428/112297	343	.9198	-4.116	-3.381
2.7	+0.026	14	4417/112297	3.242	.9159	-3.750	-3.044
2.8	+0.517	14	4252/112297	-2.824	.9118	-3.369	-2.693
2.9	+1.011	14	4135/112297	-2.398	.9077	-2.980	-2.331
3.0	+1.473	16	4094/131204	-1.964	.9035	-2.579	-1.957
3.2	+1.734	20	3740/160790	-1.287	.9140	-1.787	-1.219
3.5	+2.089	15	3484/120629	-0.576	.9147	-1.041	-0.542
4.0	+2.278	16	2918/128117	+0.065	.9248	-0.297	+0.097

^a Number of configurations selected / total number generated.

^b "Corrected" for BSSE using counterpoise method; see text.

Table 6.6

Generalized Morse function fits to F-Cl and RKR curves for the $B^3\Pi_g$ state of N_2 . The numbers in parentheses refer to the standard deviation in the last place; e.g., 4.690(3) eV means a parameter standard deviation error of 0.003 eV. "CC" refers to counterpoise-corrected data. The range of fit also included the energy zero at 20.0 bohr.

Potential Curve	Range (bohr)	D_e (eV)	R_e (bohr)	β_0 (bohr ⁻¹)	λ_1 (bohr ⁻¹)	λ_2 (bohr ⁻²)	r.m.s. (eV)
F-Cl ^a	1.9—3.0	4.690(3)	2.3224(8)	1.493(6)	0.097(5)	0.07(1)	0.0057
E(CC) ^a	1.9—3.0	3.872(4)	2.338(1)	1.589(8)	0.152(5)	0.12(2)	0.0059
RKR ^b	1.88—3.24	4.8969(2)	2.2915(4)	1.4886(4)	-0.05(1)	0.020(2)	0.00022

^a Five-parameter fit.

^b Seven-parameter fit, which was needed for the more accurate RKR data. See Eq. (6.2). The sixth and seventh parameters are: 0.20(2) bohr⁻³ and 0.045(8) bohr⁻⁴.

Table 6.7

Fits of five-parameter spectroscopic functions (see text) for the RKR, F-CI, and E(CC) curves of the $B^3\Pi_g$ state of N_2 . Notation as in Table 6.6. All units are in cm^{-1} .

Potential Curve	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	Z.P.E.	r.m.s.
F-CI	1703.43(9)	14.39(5)	-0.015(5)	1.605(4)	0.021(1)	858.2	0.14
E(CC)	1648.1(1)	13.98(6)	-0.060(7)	1.588(6)	0.022(2)	821.1	0.18
RKR	1734.75(2)	14.438(3)	-0.0108(2)	1.633(1)	0.0181(1)	863.5	0.093

Table 6.8

Summary of molecular and spectroscopic constants for the $A^3\Sigma_g^+$, $B^3\Pi_g$, and $W^3\Delta_u$ excited states of N_2 , as calculated in this and other work.

State	Method	Ref.	$E(R_e)$ hartree	D_e eV	R_e Å	B_e cm^{-1}	α_e cm^{-1}	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	$T_e(A)^a$ cm^{-1}
$A^3\Sigma_g^+$	MC-CI	[7]	-109.148 961	3.30	1.294	1.438	0.0179	1442.2	13.6	0.0
	CASSCF	[11]		2.43	1.309	1.405	0.0195	1385.9	15.15	0.0
	SD-CI	[12]	-109.073 738		1.278					0.0
	This work	[3]	-109.093 845	3.376	(1.287) ^b					0.0
	Expt.	[10]		3.70	1.287	1.455	0.0182	1460.6	13.8	0.0
$B^3\Pi_g$	MC-CI	[7]	-109.095 841	4.38	1.216	1.627	0.0182	1730.4	14.5	1.45
	CASSCF	[11]		3.39	1.230	1.592	0.0179	1679.6	14.39	2.66
	SD-CI	[12]	-109.018 159		1.213					1.51
	This work	[3]	-109.042 743	4.69	1.229	1.605	0.021	1703.4	14.4	1.39
	Expt.	[9]		4.90	1.2124	1.6379	0.01813	1733.98	14.39	1.17
$W^3\Delta_u$	MC-CI	[7]	-109.102 218	4.55	1.285	1.457	0.0166	1497.1	12.1	1.27
	SD-CI	[12]	-109.026 602		1.274					1.28
	This work	[3]	-109.045 830	4.77	(1.287) ^b					1.31
	Expt.	[2]		4.87	1.2797	1.4703	0.0171	1506.54	12.57	1.19

^a The difference between the minimum of the $A^3\Sigma_g^+$ state and the minimum of the state of interest.

^b The molecular calculation was fixed at this distance.

Figure 6.1

The energies of SCF MO's constructed for the ground-state occupation at 2.29 bohr using basis sets which range from DZP to DZP + BF[3(*spd*)] to TZPP. The addition of more bond functions adds more low-lying virtual MO's.

Figure 6.2

Solid lines, RKR curves for the $X^1\Sigma_g^+$ and $B^3\Pi_g$ states of N_2 . Triangles, F-CI curve calculated using a DZP + BF(s, p, d) basis with $\zeta_s = \zeta_p = 0.56$ and $\zeta_d = 0.72$.

Figure 6.3

Potential energy curves for the $B^3\Pi_u$ excited states of N_2 . Bottom line: RKR curve. Middle line: DZP + BF(s, p, d) as in Figure 6.2. Triangles: same basis set, with counterpoise correction applied. All curves are plotted relative to a $4S + 2D$ asymptote of 0.00 eV.

Chapter 7

Diatomics of the First and Second Row

Science is nothing but trained and organized common sense, differing from the latter only as a veteran may differ from a raw recruit: and its methods differ from those of common sense only as far as the guardsman's cut and thrust differ from the manner in which a savage wields his club.

T. H. Huxley,

Collected Essays iv. The Method of Zadiq

7.1 Introduction

Modelling the dynamics of chemical reactions using potential energy surfaces remains an important goal of theoretical chemistry. To be suitable for the creation of such accurate surfaces, a computational method must not only yield accurate dissociation energies, but it must do so in an economical fashion. As discussed in the previous chapters, most *ab initio* methods presently used strive for an accurate well depth (D_e) using nuclear-centred basis sets containing increasingly larger numbers of high-angular momentum orbitals as polarization functions (PF's).[1] Although for SD-CI or full CI-type applications, the D_e is known to be always underestimated,[†] this approach is expensive and converges slowly with the number of functions. The approach investigated by this thesis locates additional low-angular momentum functions away from the nuclei, at the bond mid-point.[2] While this method has proven economical, a serious barrier to widespread use has been that one cannot say *a priori* how many, or what kind of bond functions (BF's) are needed to give an accurate D_e for an unknown system. Work reported in the preceding chapters[3][4] has suggested that the larger the bond order of a diatomic, the greater the number of bond functions that must be added to a DZP-quality basis set in order to obtain a D_e as close as possible to the experimentally-measured D_e . The current chapter is crucial to broadening the application of BF's, because it solidifies what has formerly been a qualitative understanding of the BF

[†] The same cannot of course be said for CEPA, CPF or DFT applications.

composition, in order to develop rules for basis set augmentation according to the bond order of the molecule.

Up to this point, much insight has been gained by focussing on a single system, but now the perspective broadens to an entire class of molecules, in order to show the existence of a pattern. This chapter examines, in a "trained and organized" manner, the ground states of all diatomics which can be constructed from C, N, O, F, Si, P, S, and Cl.[†] These hetero- and homonuclear diatomics vary in bond order from 1 to 3. The atomic-centred functions of a widely-used small basis set[6] are systematically augmented with bond functions (BF's) which range in composition from (*sp*) to 2(*spd*), to determine the basis set which yields a dissociation energy closest to the experimental D_e .

A strong correlation will be shown to exist between the bond order and the number of BF's required in the optimum basis set, as was suspected in light of earlier investigations.[7][8][5][9] It is indeed possible to predict the optimum composition of the BF which should be added to a DZP-quality basis set for a case in which only the bond order is known. Based on the generalization of bond order and BF composition, the D_e 's for thirty-six diatomic molecules are found to have an average relative error of $\pm 6\%$, and a maximum relative error of 10%.

7.2 Results and Discussion: Background Details

The questions, "does a pattern exist? and if so, what is that pattern?", when asked of most first-row species AB ($A = \text{C, N, O, or F}$ and $B = \text{C, N, O, or F}$), entail little more than the comparison of calculated values against well-known, widely-tabulated experimental values.[‡] However, the inclusion of second-row congeners CD ($C = \text{Si, P, S, or Cl}$ and $D = \text{Si, P, S, or Cl}$) and the "mixed" congeners AC meant that the approach to discussion in this chapter had to be adjusted accordingly. For one thing, each set of four congeners (or three, in the case of the homonuclear-type series) was interesting in its own right as a subset possessing stronger similarities than two neighbours or two isoelectronic species of the same row. (For example, NO and NS have greater commonality than the first-row neighbours NO and NF, or the isoelectronic NO and CF.) Typically, members of a congener subset

[†] With the exception of N_2 , whose prototypical study appeared in Ref. [5].

[‡] The radical FO is a notable exception; the experimental R_e , for example, has only been known since 1985.

had the same ground state term symbol—and for those cases which didn't (*e.g.*, the C₂ and CN subsets), the reasons why this was so provided a fascinating glimpse into inter-row MO stability.

Secondly, there were species for which the spectroscopic constants were not tabulated and were only recently reported (*e.g.* SCl and PCl) or the *D_e* was not well-known (*e.g.* PO and NS) or the species had simply not been observed experimentally (*e.g.*, SiC, SiP). A brief description of the source and method of obtaining the reference values—and whether this was substantiated by experiment or theory, and whether further confirmation could be found—gave an indication of how reliable the reference values were.

Thirdly, approaches to calculating these species varied widely, ranging from a multitude of treatments of the well-known first-row species which were often the subject of "benchmark" calculations, to reports which were of uneven quality or virtually non-existent (*e.g.*, SiCl). Of great interest to the prescribed BF / MRD-CI method reported here, is, naturally, how well the present work compares to other calculations on the same systems, especially with larger atomic-centred basis sets.

Fourthly, each species was of interest in its own right. Apart from successful emulation of chemical reactions, the first- and second-row diatomics are intriguing to astrophysicists, geologists and chemists for the widely-differing roles they play in the earth's atmosphere, industrial processes, interstellar dust clouds, and/or chemical laser systems.

These factors led to the separation of the discussion section in 10 subsections, according to the first-row species: the subset of C₂ and its congeners; the set of CN and its congeners; and so forth, up to the F₂ subset. In these subsections, experimental and other theoretical results pertinent to the specific molecules are summarized. After considering each member of each subset individually and in some detail, some general observations are made on the first- and second-row species and on the overall pattern of the results obtained.

The reader is therefore strongly advised to advance first to the section towards the end of this Chapter, entitled "Results: Overall Patterns," which places what is otherwise a myriad of minutiae into a broader perspective. The reader can then refer to the pertinent sections on the subsets (immediately following) as needed.

7.2.1 C₂ and its Congeners Si₂ and SiC

C₂, SiC and Si₂ all possess different low-lying states arising from several possible electron configurations:

$$\dots\pi_u^4\sigma_g^0 \longrightarrow {}^1\Sigma_g^+$$

$$\dots\pi_u^3\sigma_g^1 \longrightarrow {}^3\Pi_u, {}^1\Pi_u$$

$$\dots\pi_u^2\sigma_g^2 \longrightarrow {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+.$$

Although the ground states are all different, making this a unique subset of the ten which will be considered in this Chapter, they are in every case representative of a bond order of 2. The results of calculations in the present work for these three molecules are summarized in Table 7.2. In each case, the optimum BF composition was a single set of (*spd*) orbitals.

7.2.1.1 C₂

C₂ is known to occur in terrestrial sources, such as hydrocarbon flames, in carbon arc emission, on the boundary layer of high-speed planetary entry vehicles; and in several astrophysical sources, such as the heads of comets and the atmospheres of certain kinds of stars.

Diatomic carbon presents a fascinating story of an original symmetry assignment being overturned in favour of another. Mulliken's original molecular orbital analysis predicted the lowest ${}^1\Sigma_g^+$ state was some 0.8 eV above the lowest ${}^3\Pi_u$ state[10] but Ballik and Ramsay were able to experimentally prove that the ${}^1\Sigma_g^+$ state in fact lay *below* the triplet state.[11] They studied perturbations in the rotational levels of the three lowest vibrational levels of the ${}^3\Sigma_g^-$ state. They deduced these perturbations were related to the perturbations of equal but opposite magnitude in the fourth and fifth levels of the ${}^1\Sigma_g^+$ state; hence it was established that the singlet state lay some 610 cm⁻¹ *below* the triplet state.[11] (Singlet and triplet states are able to perturb each other through the phenomenon of spin-orbit coupling.)

The currently-accepted values for the molecular constants of C₂ are listed at the top of the Table. Ballik and Ramsay, in their re-investigation of the Phillips (${}^1\Pi_u - {}^1\Sigma_g^+$) band system, determined the spectroscopic constants ω_e and $\omega_e x_e$ to be 1854.71 and 13.34 cm⁻¹,

respectively.[11] Marenin and Johnson corrected these values for high- J -level deviation, to 1854.783 and 13.389 cm^{-1} . [12] Read and Vanderslice published a small RKR curve for the ground state.[13]

The D_0 of C_2 was determined by thermochemical methods (second-law) to be 6.25 ± 0.2 eV.[10] From a mass spectrometric study, Kordis and Gingerich reported $D_0^0 = 6.2 \pm 0.1$ eV.[14] So many calculations have been carried out on C_2 , ground and excited states, and its anionic and cationic forms as well, that for clarity of presentation, several results have been summarized in Table 7.3. In general, these calculations are able to pinpoint the $^1\Sigma_g^+$ state as the ground state, which has the electronic occupation

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4.$$

but the important contribution from a second configuration,

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 1\pi_u^4,$$

due to the near-degeneracy of the $2\sigma_u$ and $3\sigma_g$ orbitals, is noted.

Since C_2 has a bond order of 2, the optimum basis set predicted† in the present work contains an (*spd*) BF. The D_e is in error by 0.01 eV. An MRD-CI calculation by Zeitz *et al.* which adds double the number of BF's to approximately the same size of atomic basis set gives a lower absolute energy, as noted in Table 7.3.[15] The D_e obtained by Zeitz *et al.* is not noted but, judging from present results, 2(*spd*) likely overestimates the D_e . Dupuis and Liu, with a large STO basis set including f functions, obtain a D_e which is next closest to the experimental value, with an error of 0.07 eV.[16]

7.2.1.2 Si_2

A veritable rash of studies on Si_2 have been appearing in the recent literature. This is due not only to the growing importance of silicon in various technologies, but also due to the desire to gain insight into the relative stabilities of the σ and π bonding orbitals of the Group IV A diatomics. The ease of $s \rightarrow p$ electron promotion, giving rise to orbital hybridization, is very important in Group IV A chemistry. In the case of Si_2 , it changes the energy of the $4\sigma_u$ orbital to the point that $4\sigma_u$, $5\sigma_g$ and $2\pi_u$ are nearly equivalent. It has

† Section 7.3 which discusses the overall pattern of observations explains fully what is meant by the "predicted optiruum" or "prescribed" BF basis set, and how such a prescription was arrived at.

been established that the ground state of Si_2 is a ${}^3\Sigma_g^-$ state, with occupation $\sigma_g^2\pi_u^2$. This is in marked contrast to the ground states of its first-row congener C_2 ($X^1\Sigma_g^+$) and mixed congener SiC ($X^3\Pi$). Experimentally, two main systems corresponding to $n^3\Sigma_u^- - X^3\Sigma_g^-$ and $n^3\Pi_g - D^3\Pi_u$ have been observed.[17][18]

Theoretical calculations show that the ${}^3\Sigma_g^-$ and ${}^3\Pi_u$ states of Si_2 are only a few hundred wavenumbers apart in energy, and even the ${}^1\Sigma_g^+$ state lies at most an eV above that:

$$E(X^3\Sigma_g^-) < E({}^3\Pi_u) < E({}^1\Sigma_g^+).$$

The vibrational levels of the two lowest-lying states are closely interwoven, and give rise to electronic transitions which can be detected in the infrared absorption region. Although this work is concerned with the ground, and not excited, states of the first- and second-row diatomics, a small part of this discussion will in the case of Si_2 deal with the nearly-degenerate second state, since the correct prediction of the order of the low-lying electronic states of Si_2 is a sensitive indicator of the quality of a calculation.

Si_2 is also an interesting example of a molecule whose excited states have a slightly shorter bond length, since the shorter distance means greater π overlap:

$$R_e(X^3\Sigma_g^-) > R_e({}^3\Pi_u) > R_e({}^1\Sigma_g^+).$$

From the absorption spectrum, Verma and Warsop found the bond length of Si_2 to be 2.246 Å or 4.2443 bohr, and the spectroscopic constants ω_e and $\omega_e x_e$ to be 510.98 and 2.02 cm^{-1} , respectively. From a Birge-Sponer extrapolation of the ground state, they report a D_e of 3.97 eV. However, the Birge-Sponer extrapolation of the H state, which has a much shallower curve, gives a D_0 of 3.21 eV, which they report as a D_0 of 3.0 with a conservative error estimate of ± 0.2 eV.[17] This is in good agreement with the dissociation energy D_0 derived from thermochemical data,[18] so the reference D_e in this work is 3.24 eV.

An early high-quality investigation into Si_2 appeared in 1980, where the ordering of the states of several isovalent species was compared by Bruna *et al.* The MRD-CI method was used with a [6s4p1d] GTO basis set, so the calculations are very comparable to the DZP results reported in this work. The absolute energy at the extrapolated MRD-CI limit was -577.8821 hartree, 0.001 hartree lower than that of the ${}^3\Pi_u$ state. The minimum of the ground state curve was at 2.29 Å and the fundamental frequency was found to be 494

cm^{-1} . [19] In a subsequent study, a set of (*spd*) bond functions was added to that basis, and a D_e of 3.08 eV was found. [20]

The pseudopotential method has been applied a few times to the Si_2 problem. (See Ref. [21] for references to prior work.) Contrary to CI calculations, which had some problems predicting the ground state of Si_2 , pseudopotential calculations quickly determined the ground state to be $^3\Sigma_g^-$. Moskowitz *et al.* used all-electron and effective potentials, and took care of correlation effects using the generalized valence bond (GVB) approximation. Although a binding energy of only 0.8 eV was found, they were able to deduce that the stability of the ground state is due to the tendency of silicon to prefer s^2p^2 hybridization, rather than the tetrahedral sp^3 form. [22]

A recent investigation by Dunlap and Mei using the $X\alpha$ method predicted that the $^3\Pi_u$ state lay 0.02 eV above the ground state, and the $^1\Sigma_g^+$ state 0.65 eV above that. The R_e was found to be 4.31 bohr, ω_e to be 470 cm^{-1} and D_e to be 3.21 eV, once adjusted according to Jörg *et al.* [23] [21]

Nearly coincident with this report, Northrup *et al.* reported pseudopotential local-spin-density (LSD) calculations which significantly overestimated the D_e , at 4.29 eV. They observed that as the atomic nuclei were moved closer together, the π -state eigenvalues decreased, to the point where it became energetically favourable to transfer an electron in the σ MO to the π MO, thus creating a $^3\Pi_u$ ground state. [24]

The last $X\alpha$ report to be dealt with here investigated the use of bond-centered basis functions in the Si_2 system. Jörg *et al.* looked at a variety of different basis sets and forms of the pseudopotential, but did not especially recommend one particular form. The results were comparable in quality to CI calculations, and they concluded that the bond-centered functions exerted only a minor effect and were unnecessary for $X\alpha$ applications. [23]

An extensive look at second-row homonuclear diatomics using a very large [8s6p3d2f] STO basis set was reported by McLean *et al.* At the SCF, SD-CI and SDQ-CI levels of treatment, the $^3\Sigma_g^-$ state was consistently the state of lowest energy. They looked at the $\langle 3s|3s \rangle$ overlap of Si_2 and found that it was higher at 3.9 bohr (appropriate to the $4\sigma_g^2 4\sigma_u^2 2\pi_u^4$ configuration) than at 4.2 bohr (appropriate to the $4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^2$ configuration). The basis set was so good that even the D_e at the SCF level, at 1.97 eV, is quite reasonable. The calculated R_e was 2.251 or 2.255 Å and the dissociation energy was found

to be 2.84 or 2.90 eV, depending on whether the Davidson or Siegbahn form of the quadruple excitations correction was used. The SDQ(Siegbahn correction) fundamental frequency was 514 cm^{-1} . They concluded that their results were essentially similar to those of Bruna *et al.*[25]

Not surprisingly, the HF-CI results from Shim *et al.*'s calculation report a larger R_e (by about 0.08 bohr) and smaller D_e (by 0.3 eV) than McLean *et al.* This is because the former authors performed a smaller CI with a smaller basis set than what the latter authors used. A Mulliken population analysis showed that the overlap populations due to the bonding σ orbitals were cancelled out by contributions from the antibonding σ orbitals, and that the total overlap population was mainly due to contributions from the π and not σ valence MO's.[26]

Rohlfing and Martin studied the C_2 , SiC and Si_2 series by the Møller-Plesset, CASSCF and externally-contracted CI method in order to accurately predict the fundamental frequency of SiC. They began with a [7s6p2d] basis set. In each case, the bond distance was overestimated and the well-depth and fundamental frequency underestimated. The MP4(SDTQ) calculations gave 2.272 Å , 494 cm^{-1} , and 2.81 eV for R_e , ω_e , and D_e , respectively. The CCI+Q calculations gave 2.292 Å , 482 cm^{-1} , and 2.76 eV, and the CASSCF calculations with a large active space gave 2.286 Å , 494 cm^{-1} , and 2.82 eV for the same quantities.[27]

Raghavachari studied Si_2 as part of a series on semiconductor clusters. Using a 6-31G* basis set, with the coupled-cluster double excitation fourth-order singles' + triples' contribution (CCD+ST(4)) method, the two triplet states were actually found to be reversed, i.e., the ground state was $^3\Pi_u$. On going to larger basis sets, such as [6s5p3d1f] with an MP4 treatment, the $^3\Sigma_g^-$ state was favoured, by 0.6 kcal/mol. The binding energy of the ground state was 3.06 eV, and the fundamental frequency was 507 cm^{-1} . [28]

To try and sort out the two triplet states of Si_2 , Lüthi and McLean carried out comparative calculations on the well-known C_2 species, and transferred the error adjustments from the C_2 to the Si_2 spectrum to finally conclude that the $T_e(^3\Pi_u) = 180 \pm 200\text{ cm}^{-1}$, an estimate which they hoped "can guide spectroscopists to observations which will close the issue." Their second-order CI calculation, which employed basis sets consisting of [8s6p3d2f] STO's, found a T_e of 520 cm^{-1} by direct calculation. For the ground state, R_e

is calculated to be 4.307 bohr, and ω_e and $\omega_e x_e$ to be 504 and 2.15 cm^{-1} , respectively.[29]

Bauschlicher and Langhoff in fact suggested the adjustment made by Lüthi and McLean to the $^3\Sigma - ^3\Pi$ splitting was far too large, since it was based on the C_2 spectrum which has splittings an order of magnitude greater. The gap between the triplet states was predicted by them to be some $440 \pm 100 \text{ cm}^{-1}$ according to the highest-quality large-scale *ab initio* calculation to date. They investigated a series of basis sets, with the largest consisting of [6s5p3d2f1g] GTO's—a total of 148 Cartesian orbitals! Multi-reference CI with an empirical correction for quadruple excitations yielded $R_e = 2.267 \text{ \AA}$, $D_e = 3.25 \text{ eV}$ and $\omega_e = 496 \text{ cm}^{-1}$. This D_e is in unarguably excellent agreement with experiment (0.01 eV disagreement) but for a smaller basis set, consisting of [5s4p2d1f] GTO's, or roughly *half* the number of Cartesian orbitals, they reported $R_e = 2.275 \text{ \AA}$, $D_e = 3.10 \text{ eV}$, and $\omega_e = 492 \text{ cm}^{-1}$; clearly the convergence toward the experimental values is painfully slow.[30]

The assignment of the peaks of the photoelectron spectrum of Si_2 was aided by the extensive *ab initio* calculations done on this system. Very recently, Nimlos *et al.* were able to settle the issue when they concluded from experiment that the T_e for $\text{Si}_2(^3\Pi_u)$ was $430 \pm 120 \text{ cm}^{-1}$. Comparing other theoretical studies with their own calculation (included in the experimental report) they pointed out the need for a large-sized basis set for an accurate determination of T_e . [31]

Since an error was made in assigning the ground state configuration, Table 7.2 lists data for the lowest $^1\Sigma$ state. A $^3\Sigma$ calculation with the DZP basis gave an energy some 0.64 eV lower; therefore, as a temporary measure, the D_e 's in the rightmost column of Table 7.2 have been adjusted by this amount, assumed to be constant over the range of basis sets studied. The best basis set is DZP + (*spd*), with an adjusted D_e of 3.21 eV, in one per cent error with the reference value.

7.2.1.3 SiC

Unlike C_2 and Si_2 , no spectrum has yet been conclusively assigned to SiC, although a mass spectrometric study by Verhaegen *et al.* report a D_0^0 for it of 4.64 eV.[32] This may be overestimated, however, and the reference D_e used in this work will be 4.4 eV, as suggested by Bauschlicher and Langhoff.[30] SiC is believed to exist in interstellar space and to be an important component in carbon stars. Experimental groups headed by Bondybey and by Smalley have tried, without success, to vapourize silicon carbide rods with a laser, in order

to record the SiC spectrum.[27] A possible reason for the difficulty in its detection could be its very small dipole derivative.[30]

The ground state of SiC is believed to be of $^3\Pi$ symmetry, unlike C_2 ($X^1\Sigma_g^+$) which has the π^4 configuration, and Si_2 ($X^3\Sigma_g^-$), which has the $\pi^2\sigma^2$ configuration. The $^3\Pi$ corresponds to a $(\pi^3\sigma^1)$ ground state occupation and it is mid-way in length between the short-bond π^4 and long-bond σ^2 occupations.

An MRD-CI calculation was carried out by Bruna *et al.* with a $[4s2p1d]$ C/ $[6s4p1d]$ Si basis set—this is nearly directly comparable to the DZP-basis MRD-CI results reported in this thesis. For the $^3\Pi$ ground state, they obtained an extrapolated absolute energy of -326.7816 hartree. The R_e was determined to be 1.75 Å and the fundamental frequency, 914 cm^{-1} . Six low-lying states are reported in that study of diatomics with 8 valence electrons.[19] A subsequent related calculation added a set of (*spd*) BF's, and produced a D_e of 4.30 eV.[20]

Two high-quality calculations on SiC have recently appeared with an aim to predict precisely enough the fundamental frequency, as an aid for spectroscopic observation. To obtain accuracy, both groups use large basis sets and as large a CI space as possible, and they simultaneously consider the congeners C_2 and Si_2 with the same treatments as a means of estimating the error in their predicted spectroscopic constants.

Rohlfing and Martin used a basis set consisting of $[5s4p2d]$ GTO's on C and $[7s6p2d]$ on Si. They compared the MP4(SDTQ) treatment with CAS-SCF contracted-CI. For the former, they obtained an R_e of 1.701 Å, spectroscopic constants ω_e and $\omega_e x_e$ of 917 and 10.4 cm^{-1} , and a D_e of 3.50 eV. The CCI+Q(Dav.) calculations yielded quite different results, with an R_e of 1.746 Å, spectroscopic constants ω_e and $\omega_e x_e$ of 936 and 6.6 cm^{-1} , and a D_e of 4.18 eV. By considering the typical errors incurred in analogous calculations on C_2 and Si_2 , they concluded that the fundamental frequency should be 975 ± 10 cm^{-1} . [27] A similar analysis shows that the well-depths for C_2 and Si_2 obtained by the CCI+Q method are consistently too low; adjusting for this error in the SiC results gives a D_e of 4.64 eV, slightly lower than that predicted by Huber and Herzberg.[18]

Bauschlicher and Langhoff present the largest calculations to date on SiC and its congeners, with a $[5s4p2d1f]$ set of GTO's for Si and a $[4s3p2d1f]$ set on C. From MRCI+Q calculations they obtained $R_e = 1.741$ Å, $\omega_e = 925$ cm^{-1} and $D_e = 4.28$ eV. Using the

same adjustment procedure, they suggest a "true" value of the fundamental frequency of $962 \pm 10 \text{ cm}^{-1}$. Their best estimate of the D_e is 4.4 eV.[30]

Table 7.2 summarizes the results of calculations in the present work for SiC($X^3\Pi$) for a bond distance ($R = 3.439 \text{ bohr}$) slightly greater than what is now believed to be the equilibrium bond length for that state ($R_e = 3.29 \text{ bohr}$ [30]). A TZPP calculation at the latter bond length resulted in a 0.051 eV drop in the energy, so the D_e 's in Table 7.2 have been adjusted to account for this fact. The optimum basis set (DZP + (spd)) gave an adjusted D_e of 4.31 eV, which is in two per cent error with the predicted well depth. The dipole moment was 1.452 D (+SiC-) with this basis set.

7.2.2 CN and its Congeners SiP, SiN and CP

Unique to this and the previous subsection, not all congeners have the same ground state symmetry. The σ -type orbital has a slightly greater stability than the π -type orbital in the purely second-row species SiP, and so the doubly-occupied σ orbital is more energetically favourable than the fully occupied π orbital, and so SiP has the ground state symmetry $X^2\Pi_i$, whereas the opposite obtains for CN, SiN and CP, and so the other members in the subset have the symmetry $X^2\Sigma^+$.

The calculations for this subset are summarized in Table 7.4. This subset, with its bond order of 2.5, required a BF as large as that used for cases of bond order 3. In every case, with the exception of SiN, whose D_e is not known, two sets of (spd) functions were the optimum composition of the BF. However, as the calculations in Table 7.4 show, the prescribed BF results were in far better agreement than even the TZPP basis set results.

7.2.2.1 CN

CN is an important radical in combustion processes, astrophysical processes, and in cyanide photochemistry.[33] The ground state configuration of CN has a fully occupied π MO and a singly-occupied σ^* MO:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4.$$

The tabulated values of molecular constants are: $R_e = 2.2144 \text{ bohr}$, $D_0 = 7.76 \text{ eV}$. With spectroscopic constants of 2068.7 and 13.14 cm^{-1} for ω_e and $\omega_e x_e$, respectively, this

gives a reference D_e of 7.88 eV, which Huber and Herzberg note could be as much as 0.1 eV smaller. The permanent dipole moment is listed as 1.45 D for polarity (+CN-).[18]

An extensive calculation of the excited states of CN by Schaefer and Heil reported a D_e of 6.178 eV, and the R_e is significantly underestimated, at 2.34 bohr.[34] Das *et al.* used the MC-SCF technique and obtained a better well depth for the ground state, of 7.011 eV, and a much-improved R_e of 2.20 bohr.[35] A recent and more accurate study of the electronic spectrum of CN has been reported by Bruna *et al.*, but no D_e is given.[36] The present calculation reports the best D_e for the BF composed of two sets of (*spd*) functions, which gave $D_e = 7.787$ eV. The BF basis prescribed for a bond order of 2.5, gave a dissociation energy of 7.38 eV, which is in about six per cent error with the experimental value.

Green reports a dipole moment of 1.465 D from a small CI calculation.[37] The dipole moment found by Das *et al.* was 1.48 D[35]; and by Bruna *et al.*, 1.47—1.70 D, with the better value resulting from the use of natural orbitals.[36] The μ found here using the prescribed BF basis, of 1.67 D, is bracketed by these (calculated) literature values.

7.2.2.2 SiP

As mentioned above, the SiP radical stands out in this subset because it possesses as $X^2\Pi_i$ ($\sigma^2\pi^3$)-occupied ground state, whereas the others possess a ($\sigma^1\pi^4$) ground state configuration.[36] SiP is not well-known experimentally; Huber and Herzberg tabulate no molecular constants except for an estimated D_0 of 3.73 eV.[18] The bond length is estimated by Bruna *et al.* from an MRD-CI study of the excited states of SiP to be 3.98 bohr. This group also reports a dipole moment of 0.76—0.89 D for (+SiP-).[36]

The present calculation (after adjustment—see Table 7.4) suggests the tabulated well depth is too large. The largest BF basis, DZP + 2(*spd*), gives a D_e of 3.57 eV. The prescribed BF basis, which has only three sets of (*sp*) functions added to a DZP atomic basis, yields a D_e of 3.17 eV. This is possibly an underestimate, however, judging from the results for the first-row congener CN.

7.2.2.3 SiN

The ground state occupation of SiN, like that of CN, is $\sigma^2\sigma^1\pi^4$, and the term symbol is $X^2\Sigma^+$. The tabulated molecular constants are 1.5719 Å for the equilibrium bond length; and 1151.36 and 6.47 cm^{-1} for the fundamental and anharmonic frequencies respectively.[18] No value for the dissociation energy is given. By the approximate relationship

terminated by high-resolution spectroscopy to be 1336.99 and 6.911 cm^{-1} , respectively.[110] The equilibrium bond length was found to be 1.49086 Å or 2.8173 bohr.[111]

The mass spectrometric determination of the dissociation energy reported by Gingerich in 1969 substantiated an earlier long Birge-Sponer extrapolation. Noting a slight pressure dependence in the second-law method, more weight was given to the enthalpy derived from third-law methods, and a D_0^0 of $6.3_6 \pm 0.2$ eV was reported.[112] Using the spectroscopic constants to correct for the ZPE, D_e is 6.4₄ eV. This value has been updated by Coquart and Prudhomme to 6.20 eV, which shall be used as the reference value in this work.[113]

The molecular beam electric resonance spectrum of PN over the first three vibrational levels gave an electric dipole moment function of:

$$\mu_v = 2.7511 - 0.0086(v + 1/2).$$

Raymonda and Klemperer predict a polarity of (+PN-) for this species.[114]

An early SCF calculation of several electronic states of PN was reported by Gottscho *et al.*[115] The electronic spectrum was amplified and refined in 1983 by Grein and Kapur, who used the MRD-CI method and DZPP + Rydberg basis sets to establish the T_e 's and spectroscopic constants. For the ground state, they found a D_e of 5.49 eV, an R_e of 1.488 Å and fundamental frequency of 1400 cm^{-1} . [133]

PN has been included in some recent "method survey" calculations. For example, Pyykkö *et al.* tested a fully numerical Hartree-Fock method on several second-row diatomics. For PN they obtained an absolute energy of -395.18864 hartree and a dipole moment of 3.28 D.[117] Peterson and Woods tested the fourth-order Møller-Plesset single, double and quadruple excitations (MP4SDQ) method on PN, and obtained an absolute energy of -395.5343 hartree and a fundamental frequency of 1333.6 cm^{-1} . [68] These absolute energies compare to the lowest SCF energy of -395.1647 and (est.) F-CI energy of -395.5059 hartree obtained with the DZP + 2(*spd*) basis set in the present work.

The optimum BF basis set, with two sets of (*spd*) orbitals (identical to other species in the subset) led to a well depth of 6.23 eV, which is in disagreement with the reference D_e by only one-half of one per cent. The dipole moment found for this molecule with this basis set was 2.777 D (+PN-).

to treatment. The literature on CO is so extensive that this background section must exclude much of it, but a few representative calculations will be reported.

The tabulated R_e is 2.13222 bohr, and Huber and Herzberg list a D_0 of 11.09₂ eV based on predissociation of the $B^1\Sigma^+$ state. They note that an uncertainty of ± 0.017 eV arises from the uncertainty as to which combination of 3P component states arises at the dissociation limit.[18] The (two leading) spectroscopic constants are $\omega_e = 2169.814$ and $\omega_e x_e = 13.288 \text{ cm}^{-1}$. [38] Using these to find the ZPE, the D_e is thus known to be 11.22₆ (reference value here) or 11.24₃ eV. A published RKR curve[39] which extends over about 60% of the well-depth can be fit to a 5-parameter generalized Morse function to give: $D_e = 11.26(6)$ eV, $R_e = 2.13208(3)$ bohr, $\beta_0 = 1.215(3)$, $\lambda_1 = -0.028(2) \text{ bohr}^{-1}$, and $\lambda_2 = 0.0217(8) \text{ bohr}^{-2}$.

The electric dipole moment of the CO molecule was measured by molecular beam resonance spectroscopy to be 0.1222 D.[40] The sign of μ , originally deduced from a microwave experiment, corresponded to (-CO+).

Whether this was actually the polarity of CO has been a matter of some discussion since early *ab initio* calculations at the Hartree-Fock level, reinforced by arguments that oxygen was more electronegative than carbon, indicated the polarity should be (+CO-). Grimaldi *et al.* reported μ from a near-Hartree-Fock calculation to be +0.15 D (+CO-) but when the treatment was extended to the configuration-interaction level, the dipole moment acquired the correct sign, -0.17 D (-CO+). They noted that the change in μ came from second-order contributions to $\langle z \rangle$, since the first-order contribution is zero. Predominantly singly-substituted configurations contributed.[41]

Table 7.5 shows that the optimum basis set for CO, with a BF consisting of a single set of (*spd*) functions, had a D_e of 11.182 eV, an error of some 0.04 eV. Considering the relatively high bond order (3), a larger BF was predicted. Two sets of (*spd*) functions, however, yield a D_e which is in error by 0.4 eV, or four per cent. The dipole moment calculated using the predicted optimum basis set is 0.0625 D (-CO+).

CO was the "benchmark" diatomic chosen by Diercksen *et al.* when they compared two methods of calculating first-order properties for truncated CI functions. Dipole moments of 0.125 and 0.141 D for CO at R_e were determined at the single- and double-excitations level, respectively.[42]

An in-depth look at several singlet and triplet states of CO was undertaken by Cooper and Langhoff, who used a basis set consisting of (26 σ 12 π 10 δ) STO's. The CI extrapolation technique was similar to the MRD-CI method used in this work. They reported a D_e of 10.86 eV (an error of 0.4 eV as well, just like the results obtained here using the 2(*spd*) basis set), an R_e of 1.133 Å and spectroscopic constants $\omega_e = 2183.8$ and $\omega_e x_e = 12.2$ cm⁻¹. The dipole moment at the experimental R_e was -0.049 D. (This reference discusses some other earlier dipole calculations.)[43]

A comparison of many-body perturbation theory and coupled-cluster theory with respect to accuracy of the computed dipole moment found that coupled cluster double excitation (CCD) gave results (ranging from 0.08 to 0.17 D, depending on the inclusion of single, double, triple, quadruple excitations) generally better than the MP4 results (between 0.10 and 0.24 D).[44] A similar theme was echoed by Kellö *et al.* who found an absolute energy of -113.145275 hartree (MBPT(4)) and a range of from -113.12 up to -113.142522 hartree (CCSD + various corrections) at the experimental R_e . The dipole moment in Debye was -0.224 (MBPT(4)) and between -0.069 and -0.175 (CCSD). The CASSCF values, although in error, were superior to the HF values in terms of energy lowering and sign of dipole moment.[45] An analysis of the changes in polarity of the C-O bond over R shows that, with increasing bond distance, the SCF wavefunction has increasing contributions from the (+CO-) configuration. Electron correlation effects also become increasingly important in the polarity description of negative ions.[45]

Ahlrichs *et al.* investigated the convergence of absolute energy, D_e , and R_e as more and higher polarization functions were added. With a [6s4p2d1f] basis set, D_e was found to be 10.10 eV (SD-CI treatment) or 10.67 eV (CPF treatment). With a very large [6s4p3d2f1g] basis set (142 Cartesian Gaussian functions), the D_e was 10.84 eV (coupled pair functional (CPF) treatment only), which again, is an error of the same magnitude as that in the present calculation. Corresponding R_e values were 2.115 or 2.131 (smaller basis set) and 2.129 bohr (large). The absolute energy in the latter case was -113.16979 hartree. Clearly the convergence with respect to basis set size is slow.[46]

The error in the D_e of the predicted optimum BF basis set, 0.4 eV, is rather large, relative to the small discrepancy seen for the ground states of the other first-row diatomics. However, this is the same size of error encountered in the very large basis set calculation, which contained nearly *three times the number of orbitals* as the present work.

7.2.3.2 SiS

SiS is the second-row congener of CO, and its ground state has a bond order of 3 as well. The ground state orbital occupation is:

$$1\sigma^2 \dots 8\sigma^2 9\sigma^2 1\pi^4 2\pi^4 3\pi^4$$

It is of astrophysical interest[47] and has been moderately well-studied. (See Ref. [48] for brief review.) Huber and Herzberg list the value of R_e at 3.64589 bohr, and estimate the experimental D_e to be 6.47 eV.[18] Recently, however, a Birge-Sponer extrapolation of the $E^1\Sigma^+$ state, which dissociates to two (3P) atoms like the $X^1\Sigma^+$ state, estimated the dissociation energy to be $51460 \pm 1000 \text{ cm}^{-1}$ ($6.38 \pm 0.12 \text{ eV}$).[49] It is this value which will be referred to in the current work.

An RKR curve has been published for the $v = 0$ to 18 levels of SiS.[50] When these are least-squares-fit to a 3-parameter Morse function, the following parameter values are obtained: $D_e = 6.37(6) \text{ eV}$; $R_e = 3.6452(4) \text{ bohr}$; and $\beta = 0.826(5) \text{ bohr}^{-1}$; with a root mean square deviation of 0.0023 eV. (Not enough high- v data were available to permit a 4- or 5-parameter fit; for the same reason, the dissociation energy from the RKR curve may not be very accurate.)

The dipole moment was found from Stark effect measurements at 1040 K to be 1.74 ± 0.07 Debye.[MC65] By convention, the structure $(\text{IV})^+(\text{VI})^-$ is regarded as having positive polarity. Although CO and CS have negative dipole moments, SiS as well as SiO is expected to have a positive dipole moment.[51]

One of the first *ab initio* calculations on SiS tested the core pseudopotential valence electron method on CO, SiS, SiO, and CS. The basis sets used (STO-3G and STO-6G) were too small to give reliable results.[52] Guest and Wilson included SiS in a series of small molecules in an investigation into the importance of triple and quadruple excitations in MBPT calculations. At the experimental R_e , the absolute energy is -686.715353 hartree. Of this, 12 millihartree lowering is due to triple excitations. Quadruple excitations increase the energy by 6 millihartree. The authors estimate the triple-excitation energy component is quite large because SiS is a multiply-bonded molecule.[53] Soon after appeared a rather ambitious study of the low-lying electronic states of SiS using a double-zeta STO basis. Robbe *et al.* obtain an absolute energy of -686.55 hartree close to R_e but D_e is not

calculated.[54] The prediction of the electronic levels by Robbe *et al.* was very helpful in an extensive deperturbation of the $A^1\Pi-X^1\Sigma^+$ spectrum by Harris *et al.*[55] In 1984, a CIPSI calculation on SiS using a DZP basis set gave an absolute energy of -686.691 and a dipole moment of 2.02 Debye.[47]

The most recent theoretical work has been a large-scale multi-reference CI calculation of the potential energy curve and the dipole moment function, using sets of $[6s5p2d]$ and $[7s6p3d1f]$ atomic-centred GTO's.[48] Li *et al.* report a D_e of 5.68 eV and an R_e of 3.671 bohr for the former basis, and a D_e of 6.06 eV, R_e of 3.647 bohr for the latter. For the larger basis set, a dipole moment of 1.57 D at the calculated minimum is found. Clearly these authors are reaching a point of diminishing returns: they are not only doing a complete (i.e., non-extrapolated and very expensive) single- and double-excitations CI on this system, but in their biggest calculations they have added a set of $1s1p1d1f$ orbitals at each atomic centre, for a total of 106 (Cartesian) orbitals!

Their absolute MR-CI energies at the minima were -686.69007 and -686.724575 hartree respectively (parabolic interpolation, this work). By comparison, the DZP energy reported here is -686.710999 hartree, so it is possible the starting basis sets of [48] are not fully optimized. The absolute energy found using the "best" basis set in this work (DZP+2(*spd*)) was -686.754733 hartree.

Another very recent study of SiS investigates different levels of perturbation treatment in the MBPT method. At the experimental bond length, they report an absolute MBPT(4) energy of -686.74698 hartree for a $[7s5p2d]$ basis set derived, as in the current work, from that of McLean and Chandler.[56] The absolute energy is nearly as low as that found in the current work. (No D_e is reported.) Lima and Canuto note that the MBPT(4) is considered to be the "state of the art" level in perturbation calculations, but gloomily conclude that "inclusion of *f* functions may be the next important step, and/or going beyond the fourth-order scheme may be necessary."

By contrast, the present work found a dissociation energy of 6.53 eV using the prescribed BF basis set of DZP + 2(*spd*); this was also the optimum BF basis for this species. This is in less than three per cent disagreement with the reference value of 6.38 eV.

7.2.3.3 SiO

The excited states of the diatomic silicon monoxide, SiO, have been the subject of

numerous experiments. It is of interest astrophysically, and it has also been studied as a boundary layer species which forms on the surface of spacecraft fitted with siliceous heat shields.[57]

The dominant ground state configuration is

$$1\sigma^2 \dots 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4.$$

The most comprehensive article on the deconvolution of the perturbed spectrum of SiO is Ref. [58]. Huber and Herzberg list an R_e of 2.85299 bohr and a D_0^0 of 8.26 eV,[18] which stems from a mass-spectrometric measurement with an estimated error of ± 0.13 eV.[59] A thermochemical determination gives a D_0^0 of 8.27 ± 0.09 eV.[60] With $\omega_e = 1241.557$ and $\omega_e x_e = 5.966$ cm^{-1} , [18] this gives a D_e of 8.35 eV, which agrees with the value tabulated by Pedley and Marshall in 1983, of 8.33 eV,[61] which will be the reference value of this work. The RKR curve published by Nair *et al.*[50] was fit to a 4-parameter GMF to find $D_e = 8.1(8)$ eV, $R_e = 2.8537(4)$ bohr, $\beta_0 = 1.00(5)$ bohr^{-1} , and $\lambda_1 = -0.01(3)$ bohr^{-2} with an r.m.s. deviation of 0.0026 eV. More recent RKR curves and dipole moment matrix elements for isotopes of SiO have been published by Tipping and Chackerian.[62]

The electric dipole of silicon monoxide was measured over the four lowest-lying v levels by molecular electric beam resonance spectra, and fitted by vibrational number to obtain the equilibrium μ of 3.0882 D.[63] Although this seems surprisingly large compared to the dipole moment of the first-row congener, CO, Field *et al.* note that as the orbitals on an atom become larger, the π and π' orbitals become increasingly localized on the electronegative and electropositive atoms, thus increasing the polarity. They note that replacing the smaller atom ($\text{CO} \rightarrow \text{SiO}$) should have a more dramatic effect than replacing the larger atom ($\text{CO} \rightarrow \text{CS}$),[58] and this has indeed been found to be the case.[64]

Two in-depth theoretical papers on SiO appeared in 1979. Using an STO basis set of (approximately) $[7s5p2d1f]$ on Si and $[5s4p2d1f]$ on O and a CI selection-extrapolation procedure similar to that used in the current study, with 20 and 100 μ hartree, the D_e was found to be 8.10 eV for an SCF-CI and 8.15 eV for an MCSCF-CI calculation.[57] (No absolute energies are reported.) Their spectroscopic constant ω_e , 1247.9 cm^{-1} , is in excellent agreement with experiment. The value of μ at 2.854 bohr is 3.099 D (SCF-CI) and 2.966 D (MCSCF-CI).[57]

The second group reported an SCF-CI calculation using 20 σ -type and 10 π -type STO's.

An absolute energy of -363.837 hartree was obtained at 2.9 bohr, after a CI limited to roughly 150 configurations. The ω_e was found to be 1365 cm^{-1} and the permanent dipole moment, 3.02 D.[65]

A many-body perturbation theory (MBPT) calculation with a [5s3p] GTO basis set on O and a [7s4p] set on Si reports an absolute molecular energy of -364.115834 hartree. Of this, 12 millihartree lowering is due to the inclusion of triple excitations in the wavefunction description, and a 4 mhartree increase in the energy is due to quadruple excitations.[53]

Snyder and Raghavachari looked at the dimerization of SiO using Møller-Plesset techniques with at most 6-31G basis sets with additional valence-shell or polarization functions. The lowest absolute energy obtained is -364.103 hartree.[66]

A CIPSI calculation with a basis set of DZP quality reports an absolute energy of -364.083 hartree at the experimental D_e and a dipole moment of 3.00 D.[47]

A high-quality MC-SCF-CI calculation by Werner *et al.* reported a minimum energy of -364.11398 hartree, a μ of 2.993 D, an R_e of 2.8629 bohr, and a fundamental frequency of 1241.7 cm^{-1} . [67]

Peterson and Woods applied the MP4SDQ method to first- and second-row diatomics, including SiO. They report an absolute energy of -364.193 hartree and a slightly underestimated ω_e of 1222.6 cm^{-1} . [68]

As a prelude to determining molecular constants for the protonated species HOSi^+ , Botschwina and Rosmus reported highly accurate CEPA results for SiO of $R_e = 2.8708$ bohr, and a fundamental frequency of 1240.7 cm^{-1} . The minimum absolute energy was -364.15812 hartree; no D_e was reported, but μ was -3.058 D.[69]

Only the last two reported absolute energies are lower than that obtained with the best predicted BF basis set (DZP + (*spd*), for a bond order of 2), of -364.138 hartree. More importantly, none of the reported dissociation energies—even for the large STO basis sets containing *f* functions—agrees as well as that obtained in this study, using a relatively economical basis set. The calculated D_e by the prescribed BF method was 8.35 eV, in nearly perfect agreement with the reference value of 8.33 eV. The dipole moment using this basis set was found to be 3.051 D (+SiO⁻), in excellent agreement with the reference value as well.

7.2.3.4 CS

The ground state configuration of CS is

$$1\sigma^2 \dots 6\sigma^2 7\sigma^2 1\pi^4 2\pi^4.$$

The experimental bond length of 2.900619 bohr for this molecule is known to high precision,[18] but the value of D_0^0 has excited some controversy. Hildenbrand obtained a dissociation energy for CS of 7.20 ± 0.09 eV based on a thermochemical study of the gaseous equilibrium:[59]

A new value obtained for the heat of formation of the CS radical, however, implied that D_0^0 should be 8.76 eV,[70] which is suspiciously large. Fits of the RKR curve[50] to generalized Morse functions are just as contradictory: for a 3-parameter GMF, D_e was found to be 7.69(5) eV, $R_e = 2.9009(4)$ bohr, $\beta = 0.986(4)$ bohr⁻¹ and the r.m.s. deviation was 0.0041 eV. For a 4-parameter GMF, however, the D_e is 8.5(5) eV, $R_e = 2.9006(4)$ bohr, $\beta_0 = 0.94(3)$ bohr⁻¹, $\lambda_1 = -0.03(2)$ bohr⁻² and the r.m.s. deviation was 0.0038 eV. The fit is worse for the more R-dependent parameters, because the known R values do not cover a wide range. Based on a short extrapolation of the vibrational levels in $A^1\Sigma^+$, assuming products in the 3P_2 state, Fell *et al.* propose a D_0^0 of $7.35_5 \pm 0.01$ eV.[71] Using the Dunham coefficients from Ref. [72], the D_e is found to be $7.43_4 \pm 0.01$ eV (not the 7.51₃ eV given by Piñeiro *et al.*, who seem to have neglected to halve Y_{10} [51]), and this will be the reference value used in this work.

The high-resolution IR spectrum of CS was analyzed by Yamada and Hirota, to give $\omega_e = 1285.139$ and $\omega_e x_e = 6.486$ cm⁻¹. [73]

Measurements of the Stark effect of the $J = 0 \rightarrow 1$ transition indicate $\mu_{v=0}$ is 1.958(5) D and $\mu_{v=1}$ is 1.94(1) D[74]; Green extrapolates these to the $v = -1/2$ level to estimate $\mu_e = 1.97$ D.[64] A dipole moment function fit over a range of R to a Padé approximant is given in Ref. [51] Using the molecular Zeeman effect on three isotopic species, it was shown that the sign of the electric dipole moment is (-CS+).[75] A very limited CI calculation, involving only excitations into the valence shell, confirmed that single excitations were more important than double excitations, and that the change going from the RHF μ to the CI μ was qualitatively similar to that observed for CO.[64] In that study it was also

concluded that the core should not be frozen, since this only gave a $\mu = 2.10$ D, inferior to that obtained from a no-frozen-core CI ($\mu = 2.03$ D) but this interpretation overlooks the possible error due to the very restricted basis set and CI excitations. The core has been frozen in the present work, for example, and the dipole moment with the predicted best basis set, at 1.98 D, is in excellent agreement with Green's value.

The assignment of the electronic spectrum of CS has, like the D_0^0 , also been the subject of dispute, and was the motivation behind two *ab initio* calculations. Bruna *et al.* report an early MRD-CI calculation of the vertical electronic spectrum of CS for which they used a variety of basis sets, including ones that closely parallel the DZP basis used here, and a DZ+BF(*sp*) (note: no polarization functions) basis set. The SCF energy values for the ground state are -435.31537 and -435.30781 hartree, respectively.[76] The current SCF energies calculated are -435.327915 and -435.332153 hartree for DZP and DZP+BF(*sp*) basis sets. Adding Rydberg functions to their DZ+BF(*sp*) basis and performing a 3 reference-main CI, Bruna *et al.* report a ground state energy of -435.46351 hartree and a dipole moment of 2.023 D.[76] No dissociation energies are reported. By contrast, the DZP + (*sp*) F-CI energy in this work was significantly lower, at -435.620 hartree, indicating the strong role of the polarization functions in obtaining correlation energy.

Robbe and Schamps investigated several low-lying electronic states of CS as well, but they also do not report a well-depth. Their DZ basis yielded a CI dipole moment of 2.35 D.[77] The absolute energy close to R_e (at 2.8 and 3.0 bohr) is -435.41 hartree, lying well above the values found in the current study.

An absolute energy which is close to that reported here was obtained by Guest and Wilson, who report an MBPT (with triple and quadruple excitations) calculated energy of -435.608583 hartree. Their basis set is [5*s3p1d*] on the carbon and [7*s4p1d*] on sulfur.[53] A recent calculation of spectroscopic quality has been reported by Botschwina and Sebald, who employ a basis set of nearly QZPP quality ([7*s4p2d*] on C; [10*s7p2d*] on S for a total of 74 GTO's) to predict CS as a means of scaling quantities found for HCS⁺. The CI-SD D_e calculated at the experimental R_e is 7.27 eV; the CEPA-1 D_e is greatly overestimated at 8.13 eV but excellent agreement with experimental spectroscopic constants for the small R range close to R_e is found. They report $\mu = 1.945$ and 1.974 D for CI-SD and CEPA-1 values respectively.[78]

As with the CEPA-1 calculation, the D_e obtained by the best predicted basis set—which has 2(*spd*) BF's—is overestimated. In light of its congener CO whose “predicted best basis” D_e was found to be 0.4 eV too large, it is perhaps not surprising that the D_e for CS is also 0.4 eV too large. In fact, in both instances the BF added should consist of only *one* set of (*spd*) functions, not two. Nonetheless, the well depth found using the prescribed BF basis was in less than six per cent disagreement with the reference value (7.84 eV compared to 7.43 eV) and is the best calculated value so far. The electric dipole moment at R_e was determined to be 1.979 D (-CS+).

7.2.4 CF and its Congeners SiCl, SiF and CCl

The results from this subset, which has a bond order of 2.5, were mixed. To begin with, only one well depth is known with any degree of certainty, namely, the CF D_e . None of these species have a very large optimum BF, considering the relatively high bond order. This is in contrast with the CN subset, where for the same bond order of 2.5, the optimum BF was as large as for the N_2 subset. Nonetheless, the prescribed BF method gave better results than atomic-centred basis sets of comparable size. The calculations are summarized in Table 7.6.

7.2.4.1 CF

In processes which utilize fluorocarbon compounds as a source of fluorine atoms during plasma etching of semiconductor chips, the simplest fluorocarbon, the radical CF, has been observed.[79] The ground state occupation ($X^2\Pi_r$ symmetry) is:

$$1\sigma^2 \dots 5\sigma^2 1\pi^4 2\pi^1,$$

and thus the bond order is 2.5.

The earliest determination of the dissociation energy was made by Andrews and Barrow, who concluded D_e must be 4.8 eV on the basis of a linear (*i.e.*, including only ω_e and $\omega_e x_e$ terms) Birge-Sponer extrapolation.[80] Porter *et al.*, in their investigation of the emission spectrum up to the $v = 9$ level of CF, refined this by inclusion of the $\omega_e y_e$ and $\omega_e z_e$ terms to conclude that D_e was 5.50 ± 0.10 eV.[81] This is nonetheless a very long extrapolation, from levels extending only over the bottom one-third of the potential curve, so the “best” value to date for the well-depth of CF is that derived from a molecular effusion study of

the gaseous equilibrium

This second-law determination indicated that CF was slightly more stable than previously thought, with $D_0^0 = 5.67 \pm 0.10$ eV.[82] The reference D_e for this work shall be taken as 5.75 eV. The high-resolution spectroscopic constants reported by Gondal *et al.* are 1307.99 and 11.07 cm^{-1} for ω_e and $\omega_e x_e$, respectively.[83]

The permanent electric dipole moment was measured experimentally by Carrington and Howard. A static electric field was applied and the splitting of the rotational lines as a function of field strength was observed with a microwave spectrometer, and then was carefully calibrated against the precisely known values of the Stark splitting in the NO molecule. They reported $\mu = 0.65 \pm 0.05$ D, with a presumed polarity of (+CF-).[84] Saito *et al.* repeated the dipole measurement several years later using a OCS as an internal standard, and obtained 0.645 ± 0.014 D,[85] which is the reference value used in this work.

There are a few *ab initio* calculations on CF in the literature. In 1972 Hall and Richards reported SCF results for the ground and low-lying states of CF, calculated using an (5s4p2d) STO basis set. They obtained an R_e of 2.34 bohr and an ω_e of 1480 cm^{-1} . At the experimental R_e , the absolute energy was -137.21409 hartree. This led to a D_e of roughly 2.5 eV.[86] Dunning *et al.* used a comparable basis set of (5s3p1d) STO's but improved the SCF method by allowing multiple configurations (up to 6, close to the dissociation limit) to be used. This led to marked improvements: $R_e = 2.419$ bohr, $D_e = 4.00$ eV, and $\omega_e = 1312 \text{ cm}^{-1}$. [87] Hess and Buenker chose a basis set consisting of [4s3p2d] on C and [7s5p2d] on F. In constructing molecular orbitals they used the SCF-LCAO's of the ground state ion CF^+ . The CI was carried out using the same MRD-CI method as this report's calculations used. The extrapolated CI energy at the experimental R_e was -137.515532 and the estimated full-CI energy was -137.550225 hartree. They obtain a D_e of 4.98 eV, an R_e of 2.419(4) bohr, and an ω_e of $1300(40) \text{ cm}^{-1}$. The discrepancy between the calculated and experimental D_e is questionably large, especially in comparison with a parallel study of CCl, and they argue that the experimental data should be re-examined. (Here they used Porter *et al.*'s D_e of 5.5(1); apparently they were not aware of Hildenbrand's thermochemically-determined D_e of 5.67 eV.)[88] A possible source of error in their calculations could be the use of different-quality basis sets for atoms which belong in the same periodic row.

Theoretical predictions for μ at the experimental R_e have been 0.81 D[86], 0.36 D[87], and 0.49(1) D[88]. but in all cases the reverse polarity, namely, (-CF+) is predicted. The fact that every calculation has predicted this polarity means that the sign reversal is likely not caused by calculation artefact, as one might suspect if results from only one method were reported.

The surprising polarity of this molecule has been discussed in the literature at some length.[87] [89][85] Saykally *et al.* estimated that the unpaired electron spends approximately 18% of its time on the F atom, which they argued implies a substantial degree of double bond character. Hyperfine structure indicates a high degree of delocalization of the $2\pi^*$ orbital over both atoms.[89] Dunning *et al.* have shown that the 2π bonding orbitals are also very delocalized. The C $2s$ (3σ) orbitals, which contain the lone pair, are depicted as significantly rotated away from the F atom. Thus, there is a high degree of polarization of the 3σ C electrons. Back donation of this electron density through the π bonding to the F atom counteracts the expected C-F polarity and creates the dipole moment observed.[87] Saykally *et al.* note that the case of CO is similar: instead of the highly polar molecule one would expect on the basis of the assigned electronegativities, the 5σ electrons localized primarily on the C atom cancel the bond polarity and create a very small dipole moment.[89]

The current calculations, shown in Table 7.6, also agree with the (-CF+) polarity assignment; a dipole moment of 0.669 D was found using the prescribed BF basis set DZP + 3(*sp*). This basis set yielded a D_e of 5.83, which is in less than two per cent disagreement with the reference value of 5.75 eV. The optimum BF (consisting of 2(*sp*)) led to a D_e of 5.70 eV.

7.2.4.2 SiCl

To the best of this author's knowledge, there is no experimental determination of the dissociation energy of silicon monochloride ($X^2\Pi$). There are no known theoretical studies. Rai *et al.* have determined a rotational constant B_e of 0.2561(1) cm^{-1} which leads to an equilibrium bond length of 3.889 bohr.[90] The spectroscopic constants ω_e and $\omega_e x_e$ are 535.60 and 2.16₈ cm^{-1} , respectively.[18] The spin splitting in the ground state is 206.6 cm^{-1} . [18] From the approximate relationship, $D_e \approx \omega_e^2/4\omega_e x_e$, the reference D_e is estimated to be 4.1 eV.

In the current case, with results summarized in Table 7.6, the prescribed BF method gave a D_e of 4.45 eV for the DZP + 3(*sp*) basis set. Judging from its first-row congeners, CF, this is likely a slight overestimate, but it should give a more reliable indication than the D_e from the approximation above, or the D_e from either atomic-centred basis set. The actual D_e is predicted to lie between 4.2 and 4.7 eV.

7.2.4.3 SiF

Silicon monofluoride is a molecule of astrophysical interest and it could be of use in chemical laser development. It is also a by-product of the plasma etching technique of semi-conductor chips.[91] The main configuration of the ground state, $X^2\Pi_r$, is:

$$1\sigma^2 \dots 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi^1.$$

Its equilibrium bond length is 3.0256 bohr[18] and a mass-spectrometric determination of the atomization energy reports $D_0 = 5.62 \pm 0.13$ eV (third-law determination) and $D_e = 5.5 \pm 0.4$ eV (second-law determination).[92] The reference value, $D_0 + \text{ZPE}$, is thus 5.67 eV.

The earliest theoretical studies on it were conducted by O'Hare, whose near-Hartree-Fock treatment gave an absolute energy of -388.41765 hartree at the experimental R_e and a permanent dipole moment of -1.201 D. (In light of known dipole moments calculated at the HF limit, however, a dipole of 0.5 D was proposed.)[93] The first CI calculation on SiF was reported a few years later, using a minimal basis set of STO's. The D_e was calculated to be 2.91 eV.[94]

Robbe also used the full-valence CI (FV-CI) technique, but enlarged the STO basis set to DZP quality. The absolute CI energy close to R_e was -388.41929 hartree. The dipole moment was calculated to be 1.07 D for (+SiF-).[95]

Karna and Grein investigated the low-lying electronic states of SiF and SiF⁺ using the MRD-CI method, which is the same one used here. The GTO basis set used was [6s4p2 π^*] on Si and [5s3p1d] on F, plus two sets of diffuse *s* and *p* orbitals. The CI energy was found to be -388.6385 hartree and the D_e was in excellent agreement with experiment, at 5.59 eV. The computed ω_e of 846.0 cm⁻¹ compared favourably with the known value of 857.31 cm⁻¹. The electric dipole moment was 1.126 D.[91]

The prescribed BF method of the present work shows a D_e which overshoots the reference value considerably. The optimum BF composition is a single set of (*sp*) orbitals, which

gives a D_e of 5.83 eV—also an overshoot, which is suspicious since the (*sp*) BF is good for bond orders of 1, but should not overshoot for species of bond order 2.5! The prescribed BF well depth, of 6.05 eV, is in nearly seven per cent disagreement with the reference value. The dipole moment calculated with this basis is 0.765 D (+SiF-).

7.2.4.4 CCl

Current interest in carbon monochloride arises from its relation to chlorocarbon photochemistry and its possible role in plasma etching.[96] The ground state of CCl is of $^2\Pi$ symmetry:

$$1\sigma^2 \dots 7\sigma^2 1\pi^4 2\pi^4 1\pi^{*1}.$$

States of $^2\Pi$ symmetry exhibit zero-field splitting due to spin-orbit effects but incorporating this term into the Hamiltonian to solve for splitting of the order of 100 cm^{-1} and less[88] is beyond the scope of this work.

The calculations in this work were carried out assuming $R_e = 3.1086 \text{ bohr}$ [18]; the latest accurate determination of R_e is $3.10871(30) \text{ bohr}$ [97] but the error from this source is negligible.

Miller and Palmer estimated the CCl D_0 to be $3.34 \pm 0.17 \text{ eV}$ from chemiluminescence in diffusion flames.[98] Using recently-determined spectroscopic constants (for the level of accuracy needed here, either Yamada *et al.*'s values of $\omega_e = 876.746$ and $\omega_e x_e = 5.3300 \text{ cm}^{-1}$ [97] may be taken or the more recent but less precise values of 874 and 6.5 cm^{-1} of Mélen *et al.*[99]) the experimental D_e is found to be $3.39(17) \text{ eV}$, and this will be the reference value for this work.

The earliest *ab initio* calculation on CCl was a minimal STO basis set full-valence CI study. Not surprisingly, such restrictions in basis and CI treatment resulted in errors of 0.26 bohr in the R_e , and 250 cm^{-1} in ω_e . The D_e was computed to be 2.91 eV.[94]

Hess and Buenker reported potential curves and dipole moments and zero-field splittings for CCl and its first-row analogue, CF. For a basis set consisting of $[5s4p1d]$ on C and $[6s5p1d]$ on Cl with a set of (*sp*) functions at the mid-bond position, they obtained a D_e of 3.51 eV and a dipole moment of $1.25 \pm 0.01 \text{ D}$.[88] This calculation is most similar to the one reported here, since it uses the MRD-CI method. The SCF configuration specified, however, is that of the Σ -symmetry ion CCl^+ . The absolute extrapolated-CI energy is -497.514294 and the estimated full-CI energy is -497.54912^o hartree.[88]

Larsson *et al.*, in their CAS-SCF/C-CI study of the $A^2\Delta-X^2\Pi$ predissociation, used a basis set composed of $[6s5p2d1f]$ GTO's on Cl and $[4s2p2d]$ on C. At the C-CI level, they also found a D_0 greater than experiment (3.44 eV).[100]

Pettersson and Siegbahn studied the effect of $3d$ shell back-bonding on the binding of CCl, using a $[7s5p3d1f]/[5s4p2d1f]$ GTO basis set, at the CAS-SCF and contracted CI (C-CI) level. The best active space scheme gave both R_e and D_e significantly overestimated at 3.140 bohr and 3.64 eV; and μ was found to be 1.422 D. At the C-CI level, R_e improved dramatically, to 3.1095 bohr but the agreement between the calculated and experimental D_e worsened. ($D_e(\text{calc}) = 4.0$ eV).[101] The fact that purely nuclear-centred basis sets, including even the DZP-quality calculation reported in the current work, overestimates D_e , casts great doubt on the validity of the experimental D_e . The dissociation energy predicted in the current study is 4.30 eV, using a basis whose BF consisted of three sets of (sp) orbitals. Since, for the first-row congener CF, this overestimated the D_e , the D_e for CCl is predicted to lie in the range 4.0 to 4.3 eV. The dipole moment was found to be 1.520 D for the polarity ($-\text{CCl}^+$).

7.2.5 N_2 and its Congeners P_2 and PN

The nitrogen and/or phosphorus diatomics were predictably all closed-shell species with a bond order of three. Table 7.7 summarizes the results for calculations on this subset; in each case, the optimum BF composition was found to be $2(sp d)$, which is congruent with their relatively large bond order.

7.2.5.1 N_2

The ground state occupation of N_2 is of $^1\Sigma_g^+$ symmetry:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4.$$

N_2 is an example of a molecule which is very well-known (see Ref. [102] for a comprehensive review) yet whose ground state is extremely difficult to calculate. The difficulty of calculating N_2 is perhaps best illustrated by the fact that the Hartree-Fock limit still lies nearly 5 eV above the absolute molecular energy. A method must clearly go beyond the SCF treatment in order to yield an appropriate well-depth.

The status of dinitrogen as a "benchmark" molecule is evident in the large number of articles (only a portion of which is surveyed here) which select N_2 as a subject against

which to try new methods and techniques. In fact, as mentioned in the introduction to this Chapter, N_2 served as a "test case" for basis set augmentation by Wright and Buenker, who found a BF composition of $2(sp d)$ was optimum, giving them an error of only 0.05 eV.[103] Table 7.8 summarizes the results of other calculations on N_2 . It is quite noticeable, from this Table, that the results which come closest to the experimental R_e involve addition of BF's to the basis set.[104]

7.2.5.2 P_2

The ground state occupation of the P_2 ($X^1\Sigma_g^+$) molecule is:

$$1\sigma_g^2 \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^4.$$

Huber and Herzberg list the dissociation energy D_0^0 of P_2 as 5.033 eV. This is based on the accurately known curve of the $C^1\Sigma_u^+$ state, which dissociates to 4S and 2D . A Knudsen effusion mass spectrometric study of P_2 yields a D_0^0 of 5.06 ± 0.07 eV and 5.10 ± 0.02 eV by the second and third law methods respectively, with a recommended value of 5.08 ± 0.05 eV, thereby confirming the spectroscopic value.[105]

The emission spectrum of diphosphorus required some analysis of additional perturbing influences; the most accurate values to date are given by Brion *et al.* as $\omega_e \approx 780.765$ and $\omega_e x_e = 2.835 \text{ cm}^{-1}$. [106] Using these values to compute the ZPE, the complete well-depth D_e is found to be 5.081 eV. The equilibrium bond length is 3.5780 bohr.[18]

In the present work, the optimum BF was also the predicted optimum BF ($2(sp d)$, since P_2 has a bond order of 3) and it gave a D_e of 4.89 eV, in 0.2 eV disagreement with the experimental value.

A recent calculation focussed on Group VA homonuclear diatomics as a means of illustrating an *ab initio* model potential approach. The Coulomb and exchange core operators J_c and K_c are represented by model potentials in such a case. This should be viewed as an improvement over SCF-, but certainly not CI-level calculations. Their most extensive calculation yielded a D_e of 1.47 eV, $\omega_e = 905 \text{ cm}^{-1}$ and $R_e = 3.519$ bohr.[107]

Two high-quality *ab initio* calculations on P_2 have appeared relatively recently. CI calculations which included all single and double excitations of the ground state occupation were reported by McLean *et al.* for most of the homonuclear diatomics of the second row. They used a very large basis set, consisting of (8s6p3d2f) STO's. The SCF energy obtained

was -681.499323 hartree; the CI(SD) energy was -681.767060 at a computed minimum of 3.545 bohr. The main configuration contributes to some 93% of this wavefunction, compared to around 84% in the current work. Two corrections are compared for the estimation of quadruple excitations: the Siegbahn correction gives a D_e of 4.29 eV, whereas the Langhoff correction (used in this work) gives a D_e of 4.15 eV. (It was in fact generally observed that the Siegbahn correction gave a lower relative error in the well-depth overall.) The error of 0.79 eV in the best D_e estimate for P_2 reflected the 0.72 eV error observed in parallel calculations on N_2 . [25]

In a study undertaken to compare the stability of P_4 with P_2 and P_8 , Ahlrichs *et al.* reported basis saturation problems, with basis sets ranging from $[6s4p1d]$ to $[6s4p3d2f1g]$. The coupled pair functional approach (CPF) with the largest basis differed from the experimental R_e by only 0.004 bohr, and gave an absolute energy of -681.73051 hartree, but the binding energy was still 0.55 eV too small. The difficulty of comparing the energy of a $^1\Sigma_g$ molecule with two 4S_u atoms—the same problem as encountered for N_2 , of course—is absent in P_4 vs. $2P_2$ or P_8 vs. $2P_4$ comparisons [108]

Given the 0.9 eV error of McLean *et al.* and the 0.55 eV error of Ahlrichs *et al.*—both of whom used very large atomic-centred basis sets—it is obvious that a basis set constructed by analogy with N_2 would give better energetic results, with the added advantage that the calculation would be smaller. The addition of a $2(sp d)$ BF to the DZP basis, as shown in Table 7.7, gave the best D_e , of 4.89 eV, which is in only four per cent disagreement with the reference value.

7.2.5.3 PN

$PN(X^1\Sigma^+)$ does not differ in its ground state symmetry from N_2 or P_2 :

$$1\sigma^2 \dots 7\sigma^2 2\pi^4,$$

PN has been known spectroscopically since 1933, and it has excited new interest of late because it was the first astronomically detected phosphorus-containing compound. [109] The observed relative abundance of PN was $10^2 - 10^4$ times greater than what was expected, so much re-thinking of interstellar phosphorus chemistry has begun.

Rotational transitions in a few vibrational states have been measured by a high-temperature microwave spectrometer. The spectroscopic constants ω_e and $\omega_e x_e$ were de-

terminated by high-resolution spectroscopy to be 1336.99 and 6.911 cm^{-1} , respectively.[110] The equilibrium bond length was found to be 1.49086 Å or 2.8173 bohr.[111]

The mass spectrometric determination of the dissociation energy reported by Gingerich in 1969 substantiated an earlier long Birge-Sponer extrapolation. Noting a slight pressure dependence in the second-law method, more weight was given to the enthalpy derived from third-law methods, and a D_0^0 of $6.3_6 \pm 0.2$ eV was reported.[112] Using the spectroscopic constants to correct for the ZPE, D_e is 6.4₄ eV. This value has been updated by Coquart and Prudhomme to 6.20 eV, which shall be used as the reference value in this work.[113]

The molecular beam electric resonance spectrum of PN over the first three vibrational levels gave an electric dipole moment function of:

$$\mu_v = 2.7511 - 0.0086(v + 1/2).$$

Raymonda and Klemperer predict a polarity of (+PN-) for this species.[114]

An early SCF calculation of several electronic states of PN was reported by Gottscho *et al.*[115] The electronic spectrum was amplified and refined in 1983 by Grein and Kapur, who used the MRD-CI method and DZPP + Rydberg basis sets to establish the T_e 's and spectroscopic constants. For the ground state, they found a D_e of 5.49 eV, an R_e of 1.488 Å and fundamental frequency of 1400 cm^{-1} . [133]

PN has been included in some recent "method survey" calculations. For example, Pyykkö *et al.* tested a fully numerical H̄artree-Fock method on several second-row diatomics. For PN they obtained an absolute energy of -395.18864 hartree and a dipole moment of 3.28 D.[117] Peterson and Woods tested the fourth-order Møller-Plesset single, double and quadruple excitations (MP4SDQ) method on PN, and obtained an absolute energy of -395.5343 hartree and a fundamental frequency of 1333.6 cm^{-1} . [68] These absolute energies compare to the lowest SCF energy of -395.1647 and (est.) F-CI energy of -395.5059 hartree obtained with the DZP + 2(*spd*) basis set in the present work.

The optimum BF basis set, with two sets of (*spd*) orbitals (identical to other species in the subset) led to a well depth of 6.23 eV, which is in disagreement with the reference D_e by only one-half of one per cent. The dipole moment found for this molecule with this basis set was 2.777 D (+PN-).

7.2.6 NO and its Congeners PS, PO, and NS

Table 7.9 summarizes the results of calculations in the present work for the molecules NO, PS, PO, and NS. These species are not all well-known, and the pattern for the BF composition of these diatomics with bond order 2.5 is inconclusive.

7.2.6.1 NO

Nitric oxide, NO, is an important radical in atmospheric chemistry. The ground state occupation corresponds to $^2\Pi_r$ symmetry:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1.$$

An extensive review of the NO spectrum exists[118] and its experimental values have been well-known for a relatively long time. Its equilibrium bond length is 2.17464 bohr, the spectroscopic constants ω_e and $\omega_e x_e$ are 1904.20₄ and 14.075 cm⁻¹, respectively, and the $^2\Pi_{3/2}$ state lies 119.82 cm⁻¹ above the $^2\Pi_{1/2}$ state. The dissociation energy D_0^0 has been determined very precisely to be 6.496₈ eV from the breaking-off point in the $C \rightarrow A$ 0-0 band emitted during radiative recombination of N and O atoms in a process known as inverse predissociation. Thus, the reference D_e in this work is 6.614₄ eV. The electric dipole moment in the $v = 0$ level $\mu(v = 0)$ is 0.15872 D, from Stark effect measurements.[18]

Many *ab initio* calculations have been carried out on this challenging open-shell system, and the reader is referred to Ref. [119] for a summary of calculations done prior to 1982 on the ground and some excited states of NO.

The optimum BF found in the current study for this molecule with a bond order of 2.5 was 3(*sp*). The calculated D_e was in 0.26 eV, or 4% error.

In 1982, Grein and Kapur studied several low-lying states of NO using a [5s3p1d] basis set augmented by a set of diffuse (*sp*) Rydberg orbitals on each atomic centre. Grein and Kapur used the MRD-CI method, as in this work, but a rather large threshold of 40 μ hartree was chosen, to keep the CI space at less than 6000 configurations. The minimum absolute energy was -129.5067 hartree. The equilibrium bond length was determined to be 0.01 Å too long, at 1.163 Å and D_e was significantly underestimated at 5.85 eV. The spectroscopic constants ω_e and $\omega_e x_e$ were found to be 2014.8 and 26.34 cm⁻¹, respectively.[119]

Using the same (MRD-CI) method but a better basis set and larger CI space, another group calculated a series of potential curves in order to predict radiative lifetimes of excited

states. De Vivie and Peyerimhoff began with a $[7s5p2d]$ set of GTO's, to which a set of (sp) Rydberg orbitals were added at each atom. The threshold was chosen so that the CI space was 12000—16000 configurations in size. Only term energies are reported relative to the $X^2\Pi$ state, so the absolute and dissociation energies cannot be compared with values from this work. They reported an R_e of 1.159 Å and a fundamental frequency of 1836 cm^{-1} . The permanent dipole moment was -0.218 D.[120] No dissociation energy was reported.

Langhoff *et al.* published a "benchmark" full-CI calculation on NO using a $[4s2p1d]$ GTO basis set. From a full-CI treatment they obtained an R_e of 2.220 bohr, a fundamental frequency of 1914 cm^{-1} and a dissociation energy of 5.754 eV. The absolute energy at 2.2 bohr was -129.479325 hartree.[121] Although the fundamental frequency is in fortuitously good agreement, R_e , μ and the absolute energy are worse than in the calculation with the larger basis set and the approximated CI. Clearly this calculation which is unarguably complete in its CI treatment suffers from an incomplete AO basis.

The following year, the same group took a basis set consisting of $(13s8p6d4f2g)$ primitive GTO's, and contracted this to $[4s3p2d1f]$ by obtaining natural orbitals from an SDCI calculation on the atomic states; this is known as an atomic natural orbital (ANO) basis set. An 11-electron MR-CI calculation using orbitals from an 11-electron CASSCF gave an absolute energy of -129.714400 hartree at 2.20 bohr and a permanent electric dipole moment of 0.220 D. The fundamental frequency is 1838 $\text{cm}^{-1}\dagger$ and the equilibrium bond length is 2.190 bohr. By comparison, their coupled pair functional calculation yielded a dipole moment of 0.310 D, ω_e of 1853 cm^{-1} and an R_e of 2.181 bohr. This curve was generated in order to predict the transition moment function of the $X^2\Pi \leftarrow A^2\Sigma^+$ system.[122] Again, no dissociation energy was reported.

The present calculation, summarized in Table 7.9, showed that a BF consisting of three sets of (sp) orbitals was optimum for the case of NO, giving a well depth of 6.35 eV (relative error: four percent). This was also the BF prescribed for a bond order of 2.5. The dipole moment with this basis set was found to be 0.049 D.

[†] The poor disagreement of ω_e with the experimental value for the two calculations considered here with the largest basis sets is likely due to the way in which ω_e was calculated. Both groups reported ω_e and not $\omega_e x_e$, which suggests that a fit of the vibrational levels to the spectroscopic equation was not carried out, but instead a more approximate method for obtaining the fundamental frequency was used.

7.2.6.2 PS

Although its congeners NO and PO have been extensively studied, the PS radical is not so well-known. Due to the resurgence of interest in phosphorus-containing compounds in astrophysical investigations (*e.g.*, see PN), these compounds, including PS, will likely be attracting more attention, as astrophysicists seek to gain a deeper insight into the components of the universe. It is predicted that the PS radical should be abundant in the regions of low-temperature oxygen-rich stars.[123]

The ground state of PS has the following configuration:

$$1\sigma^2 1\sigma^{*2} \dots 4\sigma^2 5\sigma^2 2\pi^2 3\pi^4 4\pi^{*1},$$

which is denoted by the term symbol $X^2\Pi_r$.

Kawaguchi *et al.* recently observed a high-resolution spectrum of PS, and determined the equilibrium bond length to be 1.89752 Å (3.5858 bohr) and the spectroscopic constants ω_e and $\omega_e x_e$ to be 739.45 and 2.79 cm⁻¹. [123] The constants are in good agreement with those determined a decade earlier by Jenouvrier and Pascat, who obtained 739.45 and 2.98 cm⁻¹ from an analysis of the emission spectrum of the $B^2\Pi-X^2\Pi$ band. The splitting between the $\Pi_{1/2}$ and $\Pi_{3/2}$ terms is 321.93 cm⁻¹. [124]

The D_e obtained by Jenouvrier and Pascat from a Birge-Sponer extrapolation is 4.57 eV, in good agreement with the mass spectrometric value $D_0 = 4.54$ eV ($D_e = 4.59$ eV) as tabulated.[18]

The calculations in this work (summarized in Table 7.9) were carried out at 1.9007 Å, the tabulated R_e [18] which was obtained in preliminary work by Narasimham and Balasubramanian,[125] after they were able to reassign the (originally incorrect) vibrational levels of the PS spectrum,[126] but this does not alter the results significantly.

The present work holds some ambiguity: although PS has a bond order of 2.5 and not 3, the optimum BF is large, at 2(*spd*), which gives 4.50 eV. This is *still an underestimate* of the experimental value, even though the “notorious” N₂ D_e was overestimated with such a BF. This is much larger than the optimum BF of its first-row congener NO, 3(*sp*). A 3(*sp*) composition yields a D_e of only 3.95 eV, in error by nearly 14%. This suggests a re-examination of the experimental D_e is in order.

This suggestion is further supported by large atomic-centred basis set calculations which

converge well above the experimental D_e . Ahlrichs *et al.* underestimate the D_e by 0.55 eV, even with a $3d2f1g$ basis set.[108] An extensive study of the electronic states of PS by Karna *et al.* Their MRD-CI calculation began with a $[6s5p2d] + \text{Rydberg } (4s4p3d)$ basis set and also significantly underestimated the D_e by 1.2 eV.[127] They remark that the discrepancy is likely due to the lack of f and g functions in the basis set.[127] It is highly suspicious, however, that the former calculations, with some 53 additional polarization functions on each atom still obtain a D_e one-half of an eV too small.

7.2.6.3 PO

The PO radical is the most fundamental oxide of phosphorus. Now that phosphorus has been detected in interstellar space, there are predictions of relative abundances and (heretofore unsuccessful) attempts made to observe the PO species. The ground state of $X^2\Pi$ symmetry has the occupation:

$$\dots 7\sigma^2 2\pi^4 3\pi^1.$$

The spectroscopic constants ω_e and $\omega_e x_e$ of the $X^2\Pi$ ground state (as well as for a few deperturbed excited states) have been accurately and with consistency determined by Verma and Singhal to be 1233.34 and 6.56 cm^{-1} . [128] Singh and Rai published an RKR curve from $v = 0$ to 9 from which they estimated a D_0 of 5.4 eV.[129] Several Birge-Sponer extrapolations have tended to overestimate the well-depth, as well as a Knudsen cell determination in 1972 in which the atomization energies of PO when reacting with Y, Gd and Sn was calculated by the second- and third-law methods to be 6.15 ± 0.08 eV.[130] The reference value for D_e for this work will be based on Verma and Singhal's estimate of 5.5 eV.[128]

The dipole moment for PO was not measured until very recently, due to the difficulty in producing a sufficient number of the short-lived species in an electric field. Predictably, at 1.88 ± 0.07 D, $\mu(\text{PO})$ is much greater than $\mu(\text{NO})$, which is 0.16 D.[131]

Nearly simultaneously in 1973 there appeared two *ab initio* CI studies on low-lying valence states of PO. Roche and Lefebvre-Brion used a double-zeta STO basis set, with a $3d$ orbitals on P included, and carried out a restricted (131-configuration) CI. They obtained an absolute energy of -415.39545 hartree, and ω_e of 1043 cm^{-1} and an R_e of 1.536 Å. The term splitting was found to be 208 cm^{-1} , and the dissociation energy is about 3.1 eV.[132]

Tseng and Grein used a minimal STO basis set (with no 3d on P) and performed a full-valence CI calculation (218 configurations). With a smaller basis set, the absolute energy was poorer: -414.4982 hartree at a near-minimum of 3.015 bohr. The atoms were also poorly described, so the well-depth obtained, 2.59 eV, is comparable to Roche and Lefebvre-Brion's. The R_e was found to be 1.64 Å and ω_e and $\omega_e x_e$ were 939 and 7.06 cm⁻¹.

A decade later, advances in the programs and computing power enabled a much higher quality calculation to be carried out. A set of [6s4p2d] GTO's was placed on the P atom and [5s3p1d] GTO's on the O atom; to this was added an additional set of diffuse (*sp*) orbitals on each atom. (They noted the second set of *d* orbitals was necessary to obtain a good R_e value.) The MRD-CI method gave a total energy of -415.8561 hartree, increased the D_e to 4.99 eV, gave an R_e of 1.491 Å and the spectroscopic constants were much improved at 1239.9 and 8.46 cm⁻¹. [116] Kanata *et al.* quote a value for μ of 2.13 D from Grein. [131]

The most recent calculation on PO used third-order Møller-Plesset and CI techniques, in a study of gaseous oxides and their anions. With a 6-31G* basis set, the MP3 absolute energy was -415.83464 hartree and the CISD was -415.81634 hartree. The D_e 's were 4.70 eV (MP3) and 4.29 eV (CISD) and the fundamental frequency was 1406 cm⁻¹ (method unspecified). The dipole moment was 2.76 D. [134] This calculation is of generally lower quality than the preceding study because Lohr sought to generalize results to larger molecular systems, which cannot have as elaborate basis sets and CI treatments as a diatomic typically can.

In the present work, the value of the reference D_e of 5.5 eV is supported. In contrast to the *ab initio* work reported above, which routinely underestimated the well depth by a large margin, the prescribed BF method gives a slightly overestimated D_e of 5.64 eV (a disagreement of three per cent with the reference value). Table 7.9 shows that the optimum BF is in fact 2(*sp*), with a dissociation energy of 5.51 eV. The dipole moment calculated with the prescribed BF basis set is 2.117 D (+PO-).

7.2.6.4 NS

The ground state of NS is of $^2\Pi_r$ symmetry and has the following orbital occupation:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 \dots 2\pi^4 3\pi^1.$$

The $^2\Pi_{3/2}$ state lies higher than the $^2\Pi_{1/2}$ state by 223.15 cm⁻¹, [135] which is why the subscript *r* is appended to the term symbol, to denote a "regular" ordering of multiplets.

Nitrogen sulfide has been known to spectroscopists for over fifty years (for example, see Ref. [126] and references therein), but its thermochemical properties such as the dissociation energy are not precisely known, due to the unstable nature of this radical. O'Hare adjusted the linear Birge-Sponer extrapolation to give a D_0^0 of 4.8 ± 0.25 eV,[136] and this is the value tabulated by Huber and Herzberg.[18] The reference D_e for this work is therefore taken to be 5.1(3) eV.

Jenouvrier and Pascat reported a study of several bands of electronic transitions in NS, from which they deduced the spectroscopic constants ω_e and $\omega_e x_e$ to be 1219.14 and 7.28 and an equilibrium bond length of 1.4955 Å for the $X^2\Pi_{1/2}$ state.[135] A more recent high-resolution infrared diode laser determination gives a value of 1218.80 cm^{-1} averaged over $\Pi_{1/2}$ and $\Pi_{3/2}$ levels. The equilibrium bond length was found to be 1.49403(4) Å.[137] High-resolution techniques have also improved the determination of rotational, fine structure and hyperfine parameters.[138][139][140]

The electric dipole moment of NS was derived from measurements of spectra observed in a Stark modulated microwave spectrometer to be 1.81 ± 0.02 D.[141] This prompted a re-examination of the initial determination obtained from Stark splitting in gas phase electron resonance spectra, and an earlier measurement was corrected to 1.86 ± 0.03 D.[142]

An early *ab initio* calculation was reported by O'Hare, who used a $(23\sigma 12\pi)$ STO basis set in a Hartree-Fock calculation and obtained an absolute energy of -451.932861 hartree, a D_e of 0.75 eV, and a dipole moment of 1.732 D.[136]

Bialski and Grein used a minimal basis set of STO's and limited the CI to the valence shell in their calculation of several low-lying electronic states of NS. They obtained an ω_e of 1250 cm^{-1} , an R_e of 1.70 Å, and a D_e of 2.07 eV—an improvement over the HF calculations, but still in poor agreement with experiment, due to the very restricted nature of the basis set and CI space.[94]

The most recent calculation on NS also examined several electronic states. Lie *et al.* used a DZP GTO basis set, to which a $2(sp)$ bond function and very diffuse (sp) Rydberg orbitals were added. The MRD-CI method was used, and so their calculations are very nearly comparable to the DZP+BF2(sp) results reported in this work, with three important exceptions. Firstly, the SCF occupation chosen by Lie *et al.* to generate the MO's was of

$^4\Sigma^-$ symmetry:

$$1\sigma^2 \dots 5\sigma^2 6\sigma^2 7\sigma^1 2\pi^4 3\pi_x^1 3\pi_y^1,$$

which treats the π orbitals equally and dissociates easily to the ground state atoms. Since more than the ground state was being calculated, more mains were input than the current calculation. Lastly, the threshold at 30 μ hartree was substantially higher than the threshold selected in the current work. The dissociation energy for the $X^2\Pi$ state is not given, but they do report a fundamental frequency of 1043 cm^{-1} and an R_e of 1.513 Å.[143]

The prescribed BF basis set in the current work (see Table 7.9) also underestimated the D_e at 4.54 eV, which is in eleven per cent disagreement with the reference value, and suggests that it be re-evaluated experimentally. The dipole moment with the DZP + 3(*sp*) basis set was found to be 1.752 D (-NS+).

7.2.7 NF and its Congeners PCl, PF and NCl

The members of this subset, with bond order two throughout, all have an optimum BF composition of a single set of (*spd*), with the exception of PCl, whose dissociation energy is only approximated. The results of calculations using a variety of augmented basis sets are summarized in Table 7.10.

7.2.7.1 NF

The fluoroimidogen radical, NF, has the ground state ($X^3\Sigma^-$) configuration:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^2.$$

It is of interest in chemical laser applications; for example, the reaction:

produces electronically excited NF and vibrationally hot HF—both products being observable by their chemiluminescence.[144]

NF is isoelectronic with O_2 and has similar low-lying electronic states. In 1966 Douglas and Jones were able to identify and analyze the emission spectrum of the (spin-forbidden) $b^1\Sigma^+ \longrightarrow X^3\Sigma^-$ transition. They found R_e to be 1.3173 Å and the spectroscopic constants ω_e and $\omega_e x_e$ to be 1141.37 and 8.99 cm^{-1} respectively.[145] A more recent high-resolution

infrared diode laser study confirms these values.[146] The value of R_e used, 2.48873 bohr, from Huber and Herzberg's compilation, differs slightly.

The dissociation energy of NF is not so firmly known. Huber and Herzberg list the D_0^0 value as 3.5 eV, which stems from O'Hare and Wahl's estimate, based on spectroscopic and thermochemical data.[18][147] A recent study on the reaction of F atoms with HNCO reports $D_0^0 \leq 3.61$ eV.[148] Taking into account the ZPE, the D_e lies between 3.57 and 3.68 eV, so the reference value used in this work will be 3.63(6) eV.

The earliest calculation on NF was reported in 1967. Sahni compared calculated (LCAO-MO) electronic states of known species with the calculated results for the hitherto unknown species. A bond length of 2.44 bohr was predicted for this molecule, and some computed ionization energies in that study proved useful to experimentalists trying to observe NF. More detailed early *ab initio* work on NF was reported by O'Hare and Wahl, who carried out SCF calculations of near-Hartree-Fock quality using an STO basis set consisting of 21 σ -type functions and 11 π -type functions. The bond energy of the second-row fluoride PF was found to be larger than that of the first-row, NF. The absolute energy at the experimental R_e was -153.83526 hartree, and the dissociation energy was 0.7 eV. The permanent dipole was found to be -0.41 D, where the negative end of the dipole was at the F atom.[147]

Two years later, the first CI calculation on NF was reported, using a minimal STO basis set. The D_e improved to 2.28 eV, although the absolute energy, at -153.2906 hartree, was in fact lower than the near-HF value. The fundamental frequency was found to be 1265 cm^{-1} and the R_e was severely overestimated, at 1.382 Å.[149] Banyard and Ellis reported similar results, from a valence-CI treatment of a minimal STO basis set— R_e and ω_e were significantly overestimated, and the absolute energy at the minimum was only -153.2928 hartree.[150]

A recent calculation which was undertaken to evaluate the line-strengths of spin-forbidden transitions in NF was reported by Havriliak and Yarkony, who used [5s4p1d] GTO basis sets in an MCSCF-CI calculation averaged over a few low-lying electronic states. They report an absolute energy around -153.903 hartree close to the minimum, and a dipole moment opposite in sign to that resulting from an SCF calculation: $\mu = 0.2\text{--}0.5$ D (close to R_e) corresponding to ($\cdot$ NF+).

The most comprehensive calculation to date known to this author was undertaken by Bettendorff and Peyerimhoff, who used the MRD-CI method to investigate several excited states. Their basis set consisted of $[5s3p2d]$ GTO's augmented by a single (sp) set of bond functions and two s and two p Rydberg-type orbitals, the latter useful in the calculation of excited states. They found the absolute energy (est. F-CI) to lie at -154.20337 hartree, a significant drop from the best SCF calculation. R_e is much more reasonable, at 2.487 bohr, $\omega_e = 1138.5 \text{ cm}^{-1}$ and the D_e is 3.03 eV, estimated at the full-CI level. As with the other extended-basis CI treatment, the dipole moment was found to be opposite in sign from that predicted by near-Hartree-Fock calculations; it is 0.081 D (-NF+).[151]

The present calculation, summarized in Table 7.10, resulted in a dissociation energy of 3.52 eV for the prescribed BF basis set of DZP + (spd), which was also the optimum basis set. This is in only three per cent error with the experimental D_e . The dipole moment found with this basis set was 0.0176 D (-NF+).

7.2.7.2 PCI

The radical chlorophosphinidene, PCI, was little studied[18] until two reports of high-resolution work appeared in 1985. It had been first observed in the absorption following the flash photolysis of PCl_3 in 1967 and a fundamental frequency of 577 cm^{-1} was assigned.[152] A decade later, visible and near-IR emission spectra of two band systems were reported. The spectroscopic constants were more precisely determined to be $\omega_e = 552.3$ and $\omega_e x_e = 2.24 \text{ cm}^{-1}$. From the very approximate relationship $D_e \approx \omega_e^2 / 4\omega_e x_e$ a value of 33980 cm^{-1} or 4.2 eV for the well-depth was deduced.[153] (For comparison, the relationship predicts a D_e of 4.49 eV for NF, overestimating the experimental D_e of 3.63 eV by some twenty per cent. On the other hand, for CO, the prediction is within three per cent of the experimental value.) The results from present calculations (summarized in Table 7.10) suggest a limiting value of 3.6 eV.

More recently, Minowa *et al.* have reported rotational molecular constants derived from the microwave spectrum of PCI ($X^3\Sigma^-$).[154] Kanamori *et al.* observed the vibration-rotation spectrum of PCI by infrared diode laser spectroscopy. From the latter study, the equilibrium bond length was found to be 2.014609 Å or 3.80706 bohr, and the spectroscopic constants $\omega_e = 551.384$ and $\omega_e x_e = 2.226 \text{ cm}^{-1}$. [155]

An *ab initio* study which used a 6-31G* basis in a Moller-Plesset second-order (MP2)

perturbation theory treatment reported a bond length of 2.037 Å and a fundamental frequency of 568 cm⁻¹. The absolute energy, at the MP4 level, was -800.42904 hartree. The dipole moment was 1.38 D for (+PCl-) polarity.[156] Minowa *et al.* note that, for chlorine-containing diatomics, the spin density on the chlorine is smaller when the electronegativity difference between the two atoms is greater. They explain this fact by back-donation of electron density to compensate for ionicity of the bond.

The results tabulated in Table 7.10 were mistakenly calculated at an estimated R_e of 3.3 bohr, and not at the recently-determined R_e of 3.80706 bohr. A DZP + 2(*spd*) basis set calculation showed that the energy at the experimental D_e was 0.081 eV lower, so the D_e values in the right-most column of Table 7.10 were adjusted accordingly. As noted above, the prescribed BF basis set predicts a substantially smaller well depth -3.18 eV. It is expected that the actual D_e will lie in the range 3 to 3.4 eV.

7.2.7.3 PF

Fluorophosphinidene, PF, is a poorly-known species, despite the important role it plays in fluorination of compounds which contain phosphorous. The ground state occupation of this radical is:

$$1\sigma^2 \dots 7\sigma^2 3\pi_x^1 3\pi_y^1.$$

Its spectrum was first reported in 1962, when it was resorted to after attempts to record the spectrum of NF failed. The X³Σ⁻ ground state was found to have a bond length of 1.5896 Å or 3.004 bohr and spectroscopic constants $\omega_e = 846.75$ and $\omega_e x_e = 4.489$ cm⁻¹. [157] Later reports concerned the electronic spectrum [158] and rotational transitions of PF (because both nuclei possess spin $\frac{1}{2}$, the three spin components of each rotational level show further hyperfine splitting). [159][160] The dissociation energy for PF has not yet been experimentally determined, although it is expected to be larger than that of NF. [147]

As early as 1971 an *ab initio* calculation on PF was reported by O'Hare and Wahl, who computed near-Hartree-Fock level wavefunctions at the experimental R_e . They estimated the experimental D_e would be about 4.5 ± 0.3 eV; from an absolute energy of -440.22237 hartree, they found the Hartree-Fock binding energy to be 2.6 eV. The dipole moment was calculated to be -1.17 D $\pm$ 20% (corresponding to (+PF-)). [147] Using the same level of treatment over varying R distances two years later, the fundamental frequency was found to be 901 cm⁻¹ and the calculated R_e was 1.58 Å. In light of previous computational

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experience with other fluorides, the predicted D_0^0 for PF was refined to 4.65 ± 0.2 eV, and the predicted dipole moment was 0.6 D.[93] (These estimates will be the reference values in this work.)

The most recent *ab initio* calculation of PF was reported by Nguyen, who used a split-valence plus polarization 6-31 G* basis set in a second-order Møller-Plesset perturbation theory calculation (MP2). A bond length of 1.620 Å and a vibrational frequency of 874 cm^{-1} and a dipole moment of 1.48 (+PF-) were obtained. At the MP4 level of treatment, the absolute energy was calculated to be -440.42714 hartree.[156]

The present calculation (see Table 7.10) yielded a dissociation energy of 4.61 eV with the prescribed BF basis; this also gave the best agreement in the Table. The relative error is only one per cent, compared to the reference value. The dipole moment was found to be 1.053 D (+PF-) with this basis set.

7.2.7.4 NCl

The configuration of NCl in the ground electronic state is:

$$1\sigma^2 \dots 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^2.$$

The tabulated value for the bond distance of NCl is 1.6144 Å (with some doubt). Colin and Jones report spectroscopic constants of $\omega_e = 827.0$, $\omega_e x_e = 5.1 \text{ cm}^{-1}$, [161] which give a D_e of 4.2 eV by the approximate relation $D_e \approx \omega_e^2 / 4\omega_e x_e$. However, the more reasonable estimated D_e value of 2.9 eV suggested by Bettendorff and Peyerimhoff (*vide infra*)[162] will be used as the reference D_e in this work. Yamada *et al.* have recently reported the microwave spectrum of the NCl ($X^3\Sigma^-$) radical.[†] They note the spin density of three diatomic chlorides follows the trend:

$$\text{CCl} < \text{NCl} < \text{OCl},$$

which reflects the effect of back donation, since it increases with electronegativity difference.[163]

As an illustration of a simplified method to estimate the correlation energy, Lievin and Metz considered the ground and two low-lying states of NCl. Their best level of

[†] In Ref. [163] it is noted that a high-resolution IR spectrum is forthcoming, but this has unfortunately not been located by this author.

approximation yields $R_e = 3.12$ bohr, $\omega_e = 781 \text{ cm}^{-1}$, and a D_e of 2.14 eV, which they denote as a lower limit of the true well-depth.[164]

Recent high-quality *ab initio* potential energy curves have been published for the ground and excited states of NCl. Bettendorff and Peyerimhoff used a basis set consisting of $[6s4p2d]\text{Cl}/[5s3p2d]\text{N}$ GTO's with one set of (*sp*) BF's added and a (*2s1p1d*) set of Rydberg orbitals. The CI treatment was the MRD-CI method as used in the current study, with a larger number of mains and a bigger CI space. The absolute energy at 3.0 bohr, which is close to the experimental R_e , was -514.1856 hartree (est. full-CI). The calculated minimum was in surprisingly large error, at 1.647 Å as opposed to 1.6144 Å from experiment. The fundamental frequency was found to be 803 cm^{-1} and the D_e to be 2.75 eV. Based on previous experience, they estimate the true D_e to be 2.9 eV, which will be the reference value of this work.[162]

The dissociation energy found in the present work (see Table 7.10) supports the prediction made by Bettendorff and Peyerimhoff. The D_e with the prescribed BF basis set was found to be 2.85 eV, within two per cent of the value recommended by that group. The dipole moment with this basis set was found to be 1.001 D for the polarity ($-\text{NCl}^+$).

7.2.8 O_2 and its Congeners S_2 and SO

The results of calculations on the members of this subset, summarized in Table 7.11, show that the optimum BF's were 2(*sp*) for both homonuclear species, and one set of (*spd*) for sulfur monoxide. The single set of (*spd*), which was predicted for these molecules with a bond order of 2, gave slight overestimates of the homonuclear well depths, but the relative error was still small, at 5% (O_2) and 8.2% (S_2).

7.2.8.1 O_2

The ground state configuration of $\text{O}_2(X^3\Sigma_g^-)$ is:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2.$$

Being a molecule of such importance to the earth's atmosphere and to most life-forms on earth as well, it is no wonder that O_2 has prompted a great deal of experimental and theoretical interest. The experimental work has been collected and reviewed by Krupenie. The dissociation energy D_0 , obtained from the convergence of the $B \leftarrow X$ bands, is 5.1156

eV. The equilibrium bond length is 1.20752 Å or 2.28188 bohr. With $\omega_e = 1580.19_3$ and $\omega_e x_e = 11.98_1 \text{ cm}^{-1}$ a reference dissociation energy D_e of 5.213₃ eV may be deduced.[165]

Dioxygen, with a Hartree-Fock bond energy less than 2 eV, presented a considerable challenge to early *ab initio* methods. As the accompanying table summarizing several calculations on O₂ shows (Table 7.12), progress has been made by (i) increasing the size of the basis set, (ii) extending the method to include CI wavefunctions, and (iii) proceeding from single- to multi-reference CI-generation techniques.

Included in this Table are the prescribed BF results, which give a D_e of 5.47 eV. The optimum BF was 2(*sp*), which gave a well depth of 5.27 eV, in error by one per cent.

7.2.8.2 S₂

The ground state electronic configuration of S₂ is:

$$1\sigma_g^2 \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^4 2\pi_g^2.$$

S₂ is of interest spectroscopically because its electronic spectrum is not well-established yet, and it may allow some insight to be gained for its first-row relative O₂. Also, lasing has been observed in two electronic systems.[166]

The equilibrium bond length of S₂ is 1.8892 Å or 3.57007 bohr and the spectroscopic constants ω_e and $\omega_e x_e$ are tabulated as 725.65 and 2.844 cm⁻¹, respectively.[18] Due to extrapolation problems with spectroscopic data, the dissociation energy of S₂ was a matter of some controversy: it could have been 3.3, 3.6 or 4.4 eV.[167] Budininkas *et al.* carried out a Knudsen-effusion experiment which measured the equilibrium constant of the dimerization reaction

and from the third-law equation determined D_0 to be 4.4 ± 0.1 eV.[167] Confirmation of this value came from a photoionization experiment conducted by Berkowitz and Chupka at nearly the same time. This involves the reaction:

From this a D_0 of 4.379 ± 0.008 eV was concluded.[168] Huber and Herzberg list a spectroscopic value of 35240.2 cm⁻¹ based on the predissociation limit in the $B^3\Sigma_u^-$ state, assuming dissociation into $^3P_2 + ^3P_1$. Thus, the reference D_e is 4.4142 eV.

The first high-quality *ab initio* calculation on the ground and low-lying excited states of S_2 appeared in 1979. Swope *et al.* used a $[6s4p1d]$ GTO basis set in a single-reference SD-CI calculation. This gave an absolute energy of -795.24914 hartree at the experimental R_e , which led to a D_e of 66.5 kcal/mole. The calculated R_e was 1.900 Å and the fundamental frequency was found to be 760 cm^{-1} .

The following year, Saxon and Liu published calculations on some excited states of S_2 as well. They began with a $(9s8p3d)$ STO basis set, generated MO's by a 5-configuration MCSCF calculation, and followed this with a limited CI. Generally, the results were poorer than for Swope *et al.*, with an R_e of 1.947 Å, and a fundamental frequency of 600 cm^{-1} . The well-depth was found to be 3.72 eV and the anharmonicity constant, 2.98 cm^{-1} .

Theodorakopoulos *et al.* explored a variety of basis sets in their MRD-CI calculation of S_2 . Using a $[6s4p1d1f]$ GTO basis they obtained a well-depth of 3.53 eV at the F-CI level. The absolute energy was -795.35928 hartree, the calculated R_e was 1.914 Å and the fundamental frequency was 742 cm^{-1} . [169][†]

Hess *et al.* similarly used the MRD-CI method in their calculations of the zero-field splitting of S_2 ($X^3\Sigma_g^-$). The basis set was of double-zeta quality, with an (*sp*) bond function included. This gave an absolute energy of -795.1518 hartree at the experimental R_e , a calculated R_e of 1.94 Å and a fundamental frequency of 701 cm^{-1} . [170]

A recent calculation by McLean *et al.* used an $[8s6p3d2f]$ STO basis set and carried out single-reference SD-CI, then corrected for quadruple excitations, to give an absolute energy of -795.455637 (Davidson correction) and -795.461431 (Siegbahn correction) hartree at 3.6 bohr. The R_e was very close to experiment, at 1.891 (SDQ-D) and 1.895 (SDQ-S) Å. The dissociation energy at 3.70 (SDQ-D) and 3.82 (SDQ-S) eV still needed improvement. [25]

The results of the present calculations, summarized in Table 7.11, show the optimum BF basis, with two sets of (*sp*) orbitals, gives a D_e of 4.12 eV. This is a slightly different set than the BF prescribed for diatomics with a bond order of two, which is (*spd*). The latter basis gave a well depth of 4.48 eV, which is overestimated by about eight per cent. Nonetheless, this basis set is preferable to the atomic-centred sets, which resulted in an error (underestimate) of twice the size.

[†] Note the absolute energy in Table 5 of this paper is -795, not -975 hartree.

7.2.8.3 SO

The sulfur monoxide radical SO is an important intermediate in reactions involving sulfur- and oxygen-containing molecules. It has also been observed in interstellar space. Its most stable electronic occupation consists of:

$$1\sigma^2 2\sigma^2 \dots 6\sigma^2 7\sigma^2 2\pi^4 3\pi^2,$$

which gives rise to a ground state symmetry of $^3\Sigma^-$.

The equilibrium bond length is tabulated as 1.481087 Å [18] although Ref. [171] notes that this should be revised to 1.48101 Å to account for the contribution of electron mass to the effective mass of vibration ("electron slipping effect"). The dissociation energy of SO was determined through mass-spectrometric studies of the vaporization of the sulfides of calcium, strontium and barium, which confirmed a spectroscopic value of 5.36 ± 0.01 eV. [172]

Kawaguchi *et al.* recently used laser magnetic resonance spectroscopy to determine the fundamental frequency ω_e and the anharmonicity constant $\omega_e x_e$ to be 1150.710(11) and 6.3505(51) cm^{-1} , respectively. [171] (Note that these are slightly larger than the values tabulated in Huber and Herzberg. [18]) Using these values to calculate the ZPE, the reference D_e is 5.43 ± 0.01 eV.

Measurements of the Stark effect on the microwave spectrum of SO led Powell and Lide to conclude that the permanent dipole moment of SO is 1.55 ± 0.02 D. [173]

The first calculation of sulfur monoxide which presented excited states as well as the ground state used the pseudopotential method, and aimed for a qualitative ordering of the states, instead of a quantitative description. A bond length of 1.64 Å was obtained, and a dissociation energy of 3.51 eV. [174]

Soon afterwards, Swope *et al.* undertook a similar investigation into the excited valence states, using SCF-constructed MO's and single-reference SD-CI, in analogy to other work on S_2 and O_2 . The basis set consisted of $[6s4p1d]$ GTO's for S and $[4s2p1d]$ for O. They obtained an R_e of 1.499 Å, an ω_e of 1200 cm^{-1} and a dipole moment of 1.95 D—clearly an improvement over the pseudopotential results. [175]

Theodorakopoulos *et al.* studied the calculated properties of the SO molecule as a function of basis set size and composition. Basis set (ii) was composed of $[4s2p1d1f]$ GTO's

on O and $[6s4p1d1f]$ on S. An MRD-CI calculation with Davidson correction yielded an absolute energy of -472.7245 hartree, a fundamental frequency of 1383 cm^{-1} , an R_e of $1.517\text{ \AA}$ and a D_e of 4.35 eV . When a set of (sp) bond functions was added to this basis, the D_e improved to 4.59 eV . (No additional properties were calculated for the BF basis).[169]

A very recent calculation on SO considers it in light of developing a general contraction technique for the atomic natural orbital method, in which the contraction coefficients for a basis set are determined from the natural orbitals obtained from an atomic CI calculation. A set of $(20s13p6d/13s8p6d)$ primitive Gaussians gave an absolute energy of -472.74529 hartree and a D_e of 4.03 eV . Contraction of these orbitals into a $[6s5p3d/5s4p3d]$ set increased the absolute energy to -472.73902 hartree but decreased the D_e by only about 0.1 eV , to 3.91 eV .

The present work reports the best value for the well depth of these studies, with 5.28 eV for the prescribed (and optimum) BF basis of $DZP + (spd)$. This is a relative error of only three per cent, compared to the experimental value. The dipole moment was found to be $1.924D (+SO^-)$ with this basis.

7.2.9 FO and its Congeners SCl, SF and ClO

FO, with a bond order of 1.5, was found to have an optimum BF composition of $2(sp)$. This was intermediate to the optimum BF's for bond orders of 1 and 2, so $2(sp)$ was settled on as the prescribed BF. As results for the FO congeners in Table 7.13 show, the optimum composition in fact varies between a single (sp) and three sets of (sp)—ignoring the anomalous instance of SCl. However, the prescribed BF basis sets give a small relative error and a BF of $2(sp)$ is recommended for other species with a bond order of 1.5.

7.2.9.1 FO

The oxygen monofluoride radical $FO\ (^2\Pi_i)$ exists in a ground state configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^3.$$

It proved to be an elusive species for many years, although other Group VI–VII diatomics such as ClO and SF were extensively studied. The difficulties in detection were not due to a short lifetime but instead were related to its very small dipole moment and its highly predissociated electronic spectrum.[176]

Early observations of FO were made using matrix isolation techniques which showed a fundamental frequency of about 1030 cm^{-1} , leading to an estimation of about 56 kcal/mole (2.4 eV) for the dissociation energy.[177][178] Andrews and Raymond predicted partial double-bond character for this radical, noting that fluorine is well-known for its ability to attract electron density in σ bonds and to release it in π bonds, possibly resulting in such a "balance of charge density that the atoms in OF remain approximately neutral." [178]

Observation of FO in the gas phase, created by reacting ozone with fluorine atoms, soon followed.[179][180] From appearance potentials for FO^+ , Clyne and Watson estimated the D_0^0 to be $2.25 \pm 0.15\text{ eV}$. [179] It was not until 1979, however, that the infrared absorption of gas-phase FO was observed. McKellar applied the technique of laser magnetic resonance (lmr), in which molecular transitions are brought into resonance with fixed laser frequencies by means of the Zeeman effect. The bond length was reported to be $1.35789(25)\text{ \AA}$ or 2.566 bohr.[181] High resolution vibrational/rotational spectra of the 1-0 band,[182] the 2-0 band[176] and for v levels up to 9[183] have been reported. The equilibrium bond length is now established to be $1.35412\text{ \AA}$ (2.55892 bohr).[176] and the spectroscopic constants $\omega_e = 1052.994$ and $\omega_e x_e = 9.900\text{ cm}^{-1}$ (using 5 vibrational parameters in the fit).[183] In this work, the reference D_e for FO is 2.31(15) eV, using these values and the mass spectrometric measurement from Ref. [179].

A high-quality *ab initio* calculation on FO was carried out to determine its potential energy curve and dipole moment as a function of internuclear distance. A set of DZP GTO's, as well as a very large basis set consisting of $[6s4p2d1f]$ GTO's were used. (Results from an $(8s5p4d2f)\text{O}/(8s6p4d2f)\text{F}$ set of STO's were only obtained at the CASSCF level, which were inferior to those of even the DZP basis at the CI level.) A CASSCF procedure was used to determine the molecular orbitals, and then externally contracted CI and multi-reference CI calculations were performed. The dissociation energy was found to be 1.79 eV (DZP) and 2.01 eV (large GTO basis). At 2.6 bohr (close to experimental R_e) the absolute energies were found to be -174.49520 (DZP), -174.63228 (large GTO) hartree at the MRCI stage. The dipole moments at this distance were -0.03175 (DZP) and -0.01407 (large GTO) Debye, with (+OF-) polarity.[184]

In 1983 McKellar reported the direct measurement of the permanent dipole moment of the FO $X^2\Pi_{3/2}$ state. The saturated absorption laser magnetic spectrum was taken in the presence of an electric field (Stark effect). The dipole moment $\mu(v=0) = 0.0043(4)\text{D}$

and $\mu(v=1) = 0.0267(9)$ D was found to be very small but changing relatively quickly over vibrational level. In fact, McKellar noted that ground state μ must be the smallest ever observed for a heteronuclear diatomic, with a magnitude only 5 times larger than the HD molecule's "forbidden" dipole moment![185] A linear extrapolation of $\mu(v = -1/2)$ gives an estimated equilibrium dipole moment of -0.0069 D.

The present calculation, with its optimum/ prescribed basis set of DZP + 2(sp), gave an erroneously large dipole moment of 0.150 D (+OF-). The dissociation energy, at 2.34 eV, though, is in excellent agreement with experiment, differing by only 1.3%. (See Table 7.13.)

7.2.9.2 SCl

The sulfur monochloride radical is relatively unknown and, to the best of this author's knowledge, has not been theoretically studied. Donovan *et al.* first report a transient diffuse spectrum which they attributed to the presence of SCl. A rough estimate of the bond energy of SCl is 3.6 eV.[186] Willner formed SCl by photolysis of SCl_2 in a Ne matrix, and determined a vibrational frequency of 574 cm^{-1} (which, since it is for a matrix-isolated species, is similar but not identical to the gas-phase frequency) and predicted a bond order around 1.2. Compared with the isoelectronic species S_2^- and Cl_2^+ , this was somewhat weaker. Willner attributes this weaker bond in the heteronuclear species to the fact that the free electrons are less delocalized than they are in the symmetric species.[187] A recent infrared diode laser spectroscopic study led to an estimate of the equilibrium bond length of 3.73155 bohr.[188]

Table 7.13 summarizes results of the present calculations on SCl. When these calculations were begun, the experimental R_e was not known and a value of 3.6 bohr was assumed. The DZP + 2(sp) basis set calculations show that the energy is lowered by 0.061 eV at the proper R_e . Thus, the values in the rightmost column have been adjusted for this amount; it does not affect the overall message. In every instance, the well depth is *underestimated* compared to the reference value. The reference value is highly suspect, considering that sulfur monochloride has a small bond order of 1.5. The prescribed BF basis yields a dissociation energy of 2.81 eV, and it would be surprising if the actual minimum of the potential energy curve were to lie at greater than 3 eV.

7.2.9.3 SF

Although SF_6 plays an important role in high temperature work such as electron scavenging in plasmas and acting as a source of F atoms for chemical lasers, the radical SF has not been thoroughly studied.[189] The free radical sulfur monofluoride was not detected spectroscopically until 1969, when Carrington *et al.* reported constants from the electron resonance spectra and confirmed the inverted $^2\Pi$ ground state. The equilibrium bond length of 1.599(2) Å (3.0217 bohr) was derived.[190] (This study uses the tabulated value of 3.02465 bohr.[18]) From a study of the Stark splitting in the gas phase electron resonance spectra, the same group determined the electric dipole moment of SF to be 0.87 ± 0.05 . [142] Amano and Hirota reported a more precise value of 0.794 ± 0.012 D,[191] which is referred to in this work.

In a study of SF_6 reactions in a heated Knudsen cell, Hildenbrand obtained the heats of reaction for several processes, and from this deduced that the D_0^0 of SF was 3.51(5) eV.[189] This conclusion was based on a third-law determination which assumed a value for ω_e of 900 cm^{-1} . Second-law determinations were in good agreement but had large uncertainties associated with them.[189] The precision of the work done in this particular study may in fact be the 0.05 eV uncertainty Hildenbrand quoted, but as a reasonable indication of the "firmness" of the D_0 , the uncertainty is likely underestimated, since the bond energy depends so strongly on the accurate knowledge of other quantities *not* known to 0.05 eV. Huber and Herzberg list a lower value, however, $D_0^0 \leq 3.3$ eV, which is based on predissociation observed in the $A_1 \leftarrow X_1$ bands. The reference value for D_e used in this work will thus be 3.4 eV.

The only theoretical study of SF known to this author consists of an SCF curve. At the experimental R_e the absolute energy was computed to be -496.96701 hartree, and μ was 1.395 D for (+SF-) polarity.[93] No dissociation energy was reported.

Table 7.13 lists an optimum basis set composition for SF of DZP + (*sp*), which gives $D_e = 3.35$ eV. This is narrowly the better energy; the prescribed BF basis set of DZP + 2(*sp*) gives $D_e = 3.46$ eV, which is in two per cent disagreement with the reference value of 3.4 eV. The dipole moment from the prescribed basis set is 1.100 D.

7.2.9.4 ClO

Chlorine atoms may be an important sink for ozone via the reactions:[192]

and thus, accurate measurement of the stratospheric abundance of chlorine monoxide is a critical test of the models which have been put forth to describe the depletion of the atmospheric ozone layer by chlorofluorocarbons.[193] To measure the abundance, the band strengths of the transitions must be well-known, and this has been a proving-ground for theoretical calculations of the transition dipole moment.[194][192][195]

The ground state occupation of ClO is:

so its $^2\Pi$ ground state is an inverted spin doublet, with the $^2\Pi_{3/2}$ level being the lowest-lying electronic state. It is unusual among diatomics in that its absorption spectrum was well-known as early as 1950 and v levels have been observed nearly up to the dissociation limit. D_0^0 is thus known to a high degree of precision. An early value based on the absorption spectrum of flash photolysis of a $\text{Cl}_2\text{—O}_2$ mixture was 2.746(1) eV[196]; this was superseded in 1976 by a short extrapolation of a Birge-Sponer plot for the $A^2\Pi_i$ state (dissociating to the same limit) which gave $D_0^0 = 2.7504(4)$ eV.[197] Correcting for the zero-point energy (ZPE) which is found from $\omega_e = 853.724$ and $\omega_e x_e = 5.58 \text{ cm}^{-1}$ [198], one obtains a reference experimental D_e of 2.8032(4) eV.

Microwave measurements of the rotational spectra indicate that ClO has an equilibrium bond length of 2.96617 bohr.[199] The electric dipole moment was measured by the Stark effect splitting to be 1.239 ± 0.010 D.[200]

An early *ab initio* calculation using 47 STO's and an 825-configuration MCSCF wavefunction constructed according to the optimized valence configuration (OVC) scheme plus CI limited to 3600 configurations. A dipole moment at the experimental R_e of 1.232 D, and a D_e of 2.75 eV—unusually good results—were obtained.[201]

Lievin and Metz predict a D_e of 2.54 eV and an ω_e of 952 cm^{-1} for ClO using a simplified method to calculate the molecular correlation energy.[164]

A more recent theoretical study of the potential energy and dipole moment curves of ClO compared the multi-reference (MR) CI, contracted (C) CI and coupled pair functional (CPF) methods, and did not compare quite so well with experiment. The basis sets ranged from $(32\sigma 18\pi 8\delta 3\phi)$ STO's to $[7s5p3d1f/6s4p2d1f]$ GTO's, and between 9 and 13 electrons (i.e., without or with the Cl(3s) and O(2s) electrons) were correlated. The best results were for a CCI(9 electron) calculation corrected for quadruple excitations by the Davidson correction, as in the current work. This yielded an R_e of 3.004 bohr, ω_e of 845 cm^{-1} , and a D_e of 2.58 eV. The dipole moment however is best for the CCI(13 electron) + Q treatment: $\mu_0 = 1.275$ and $\mu_1 = 1.252$ D, compared to $\mu_0 = 1.2980(12)$ and $\mu_1 = 1.2779(19)$ D from experiment. Pettersson *et al.* note that the polarity of the (+ClO-) bond is poorly described at the SCF level since the electron affinity of the oxygen is poorly described. Charge transfer, which places the unpaired electron mainly on the chlorine atom, is necessary and occurs via the π orbitals, and some of this back donation of charge occurs into the 3d orbitals of the chlorine.[195]

The present calculation (refer to Table 7.13) found a D_e of 2.61 eV using the prescribed BF for a bond order of 1.5 (two sets of (*sp*) added to a DZP-quality basis), which is a seven per cent discrepancy with the reference value. The optimum BF composition was actually a little larger than this BF—three sets of (*sp*) gave a well depth of 2.76 eV. The prescribed BF basis resulted in a calculated permanent dipole moment of 1.107 D (+ClO-).

7.2.10 F₂ and its Congeners Cl₂ and ClF

Table 7.14 summarizes the results of the present calculations for F₂, Cl₂, and ClF, which all have a bond order of one. In each case, the optimum BF composition was the smallest one studied here, a single set of (*sp*) functions. It was remarkably successful in the case of the hydrides (Chapter 5) and now, except for F₂, it proves successful again.

7.2.10.1 F₂

Difluorine, and its positive and negative ions, has been attracting interest lately because of the role it plays in rare-gas-halogen laser systems. The ground state configuration of $X^1\Sigma_g^+$ symmetry is:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4.$$

The value used in this work as the experimental R_e was the tabulated value of 1.41193 Å (2.66816 bohr),[18] and not the R_e 's reported from a couple of earlier Raman studies of 1.4168 Å[202] and 1.4131 Å[203]. The electronic spectrum of F_2 has been known and studied since 1924 by numerous groups but the most recent and comprehensive report is an absorption spectrum analysis by Colbourn *et al.* up to the $v = 22$ level. Since the energy of the last level is 12830 cm^{-1} , this is a lower bound for D_0 , and the authors concluded that the D_0 must be $12920 \pm 50\text{ cm}^{-1}$ ($1.602 \pm 0.006\text{ eV}$). An RKR curve is given in that report[†] and the vibrational constants ω_e and $\omega_e x_e$ were determined to be 916.64 and 11.236 cm^{-1} for a fit of the vibrational levels from 0 to 8.[241] The reference value for D_e will be 1.658 eV.

As with the other first-row homonuclear diatomics, a great deal of attention has been paid to calculations on F_2 , and to facilitate comparisons between the values calculated in this work and the literature, Table 7.15, summarizing other work, is given. The well depth of F_2 has been notably difficult to calculate accurately. It has many electrons to correlate, and the curve is quite shallow. The bottom-most entry in Table 7.15 quotes the prescribed BF basis value from the present work, with a D_e of 1.82 eV. (See also Table 7.14.) This leads to the largest discrepancy with experiment of all of the well-measured diatomics in this Chapter, with a relative error of nearly ten per cent. This is still much smaller than the DZP and TZPP results. A BF composed of a single (*s*) orbital may well be optimum.

7.2.10.2 Cl_2

The spectrum of Cl_2 has been much studied and much discussed, and its electronic spectrum has been receiving much attention lately.[205][206] The ($X^1\Sigma_g^+$) ground state of Cl_2 has the following electronic configuration:

$$1\sigma_g^2 \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^4 2\pi_g^4.$$

The equilibrium bond length is 1.987₉ Å or 3.756₆ bohr.[18] Experimentalists were able to record the ground state vibrational spectrum up to the dissociation limit, but due to poor resolution some of the observed lines were incorrectly assigned. Douglas and Hoy settled the matter with a high-resolution resonance fluorescence study, from which they obtained a D_0 of 19997.28 cm^{-1} or 2.47936₇ eV. They published an RKR curve extending

[†] Up to 13294 cm^{-1} —clearly indicative of the breakdown in the method for high v .

to $v = 40$ and reported 559.7507 and 2.69427 cm^{-1} for spectroscopic constants ω_e and $\omega_e x_e$, respectively (a 14-parameter fit to the Dunham equation).[207] The reference D_e for this work is thus 2.5139₈ eV.

The first high-quality calculation of the ground and excited states of Cl_2 appeared in 1981. Peyerimhoff and Buenker used a $[5s4p2d]$ basis set, augmented by a an (sp) bond function and a set of (sp) Rydberg orbitals. Since they used the MRD-CI method, the difference between their results and the BF(sp) results here are attributable to the basis set difference and the larger number of mains (15) in their test secular equation, and the larger number of roots (4) whose energy lowering determined selection. At the experimental R_e the absolute full-CI (est.) energy was -919.2760 hartree. The calculated R_e was 2.020 Å and the fundamental frequency was 552 cm^{-1} , in excellent agreement with experiment. The D_e was similarly quite accurate, at 2.4⁹ eV.[206]

In a study of second-row homonuclear diatomics at the basis set limit, McLean *et al.* used a basis set consisting of $(8s6p3d2f)$ STO's, and then performed a single-reference SD-CI calculation with the SCF-generated molecular orbitals. They compared the Davidson and Siegbahn corrections for quadruple excitations. At the SD-CI level, the potential minimum occurred at 1.984 Å, where the absolute energy was -919.385102 hartree. At 3.7 bohr, the absolute energies corrected for quadruple excitations were -919.4293 (Davidson correction) and -919.4353 (Siegbahn) hartree. The calculated R_e values were 1.997 Å (SDQ-D) and 2.000 Å (SDQ-S); the dissociation energies were found to be 1.92 eV (SDQ-D) and 2.03 eV (SDQ-D). They concluded the Siegbahn correction was slightly more effective than the Davidson, but in either case the estimates were effective at improving the depth and shape of the curve. Correcting for quadruples invariably increased the predicted bond length, however.[25]

Perhaps the best contrast with the calculations in this thesis is given by a study into the effect of higher polarization basis sets, which used basis sets as large as $[7s4p3d2f1g]$ (called "A" here) and $[7s5p2d1f1g]$ ("B"). Becherer and Ahlrichs used single-reference SD-CI and coupled pair functional (CPF) methods. The B basis gave the lower absolute energy: -919.3485 (SD-CI level) and -919.3975 (CPF), whereas A gave -919.2815 (SD-CI) and -919.3323 (CPF) hartree. This indicates the slightly better treatment of the occupied and valence orbitals with basis set B. The higher polarization functions gave a definite advantage, however, in the calculation of the well-depth: basis set A gave 1.56 eV (SD-

CI) and 2.40 eV (CPF) whereas B only gave 1.43 eV (SD-CI) and 2.24 eV (CPF). At the SD-CI level, both sets slightly underestimated the R_e and at the CPF level, both sets slightly overestimated it (B: 3.793 bohr; A: 3.778 bohr compared to the experimental value of 3.760). The SD-CI R_e did not show a convergence toward the experimental value as the basis sets grew ever larger, but the CPF results showed a clear trend to convergence as more polarization functions were added.[208]

With respect to the dissociation energy of chlorine, the present method of prescribed BF's gave stellar results. With a bond order of one, a BF comprised of a single set of (*sp*) functions was recommended for Cl_2 . The optimum BF was indeed this basis set; the D_e was found to be 2.49 eV, with disagrees one per cent with the experimental value. Larger BF's skewed the atom/molecule balance, and resulted in an overestimate of the dissociation energy, as Table 7.14 clearly shows.

7.2.10.3 ClF

The ground state of ClF is $X^1\Sigma^+$, and its ground-state occupation is:

$$1\sigma^2 \dots 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^4.$$

Like other interhalogen compounds, it is increasingly used in organic syntheses as a fluorinating agent, and it is also of interest in chemical laser applications.

Although the dissociation energies of the homonuclear halogens such as Cl_2 and F_2 are known to a high degree of accuracy, the dissociation energy of ClF has been a matter of some debate. Dibeler *et al.* conducted a photoionization/mass- spectrometric study of dissociative ionization reactions and concluded that the D_0^0 of ClF was 2.53 ± 0.04 eV.[209] Nordine measured the gas phase reaction

to determine the equilibrium constant. From the value determined for the heat of reaction, a D_0^0 of 60.35 kcal/mole (2.62 eV) was derived.[210]

To resolve this discrepancy and others, Coxon studied the trends of the halogen species. While unable to unequivocally assign the dissociation energy, he could suggest where to place odds. The problem lies in correctly identifying the dissociation products of the converging $^3\Pi \longrightarrow ^1\Sigma^+$ transition, products which differ by 478 cm^{-1} :

By analogy with the diabatic dissociation products of BrF and IF, Coxon points out that the fluorine should dissociate to a $^2P_{3/2}$ state, i.e., the lower D_0 should obtain.[211] Coxon was also able to re-fit the vibrational data to give spectroscopic constants ω_e and $\omega_e x_e$ of 786.15(3) and 6.16(2) cm^{-1} , respectively.[211] Thus, a reference value of 2.606₆ eV for D_e will be used in this work.

Pettersson *et al.* calculated ClF as a fragment of the larger ClF₃ species and determined the binding energy for the reaction:

Both diatomic fragments, as seen in this subsection, have been remarkably difficult to calculate accurately. Pettersson *et al.* concluded the improvement in binding energy came at the CI level from the unlinked clusters contributions, and that more f functions would be needed in the basis set to approach the experimental value.[212]

Two years later, Scharf and Ahlrichs also tackled the ClF₃ species, and examined the effects of various basis set extensions. They went to the extreme of a large basis set—[6s4p3d2f1g] on F and [6s6p3d2f1g] on Cl—in a coupled pair functional calculation and obtained an R_e of 1.631 Å and a D_e of 2.45 eV. The best calculation of μ had to omit the 1g orbitals, and the dipole moment obtained was 0.85 D.[213]

Pettersson and Siegbahn examined the effect of 3d back-bonding on the binding energies and dipole moments of chlorine-containing molecules such as ClF in an effort to understand why their earlier results (*vide supra*) were not in such good agreement with experiment. In this calculation they used a basis set consisting of [9s5p3d1f] GTO's on the Cl atom and [5s4p2d1f] on the F atom. The best CAS-SCF results (for 15202 configurations) gave an R_e of 3.085 bohr, a dipole moment of 0.932 D, and a D_e of 2.45 eV. Then the CAS-SCF orbitals were used to carry out a multi-reference contracted CI (MR-CCI) calculation, which, after the Davidson correction gave excellent agreement with experiment: the bond length was found to be 3.075 bohr, the dipole moment was 0.885 D, (used as the reference μ in this work) and D_e was 2.533 eV. They concluded that the F $2p\pi \rightarrow$ Cl 3d excitations were of crucial importance in obtaining a good binding energy and dipole moment for the ClF species, especially at the CAS-SCF stage where the 3d shell *must* be included in the active space.[101]

Kucharski *et al.* recently reported calculations at the MBPT(4) level on the interhalogen series, using effective potentials to describe the core. The valence shells for both F and Cl were described with a $[4s4p2d]$ basis set. At the SCF level, the dipole moment was 1.2172 D, but the MBPT(4) correlation decreased this by some 0.3289 D, to give a total μ of 0.8883 D.[214]

Table 7.14 shows that, again, a BF composition of (*sp*) was optimum for this diatomic with bond order 1. The D_e was calculated to within one per cent of the experimental value. The success of the prescribed BF method for both ClF and Cl₂ make the trifluorochloride reaction mentioned above a tempting prospect, and a suitable candidate for examining the effect of BF's in a polyatomic. The dipole was found to be 1.176 D (+ClF-) for this basis set.

7.3 Results and Discussion: Overall Patterns

Tables 7.16 to 7.20 summarize some attributes and results of calculations of the first- and second-row diatomics to make several useful generalizations more prominent. In these Tables, the bond order is given in boldface type, and the reference values for D_e and R_e are given in regular font, with uncertain values being denoted by parentheses. The results of calculations are given in slanted font, with those values which had to be adjusted (see the relevant sections) being denoted by parentheses.

Table 7.16 gives the ground states and equilibrium bond lengths used in the basis set explorations which constitute Tables 7.2, 7.4, 7.5, 7.6, 7.7, 7.9, 7.10, 7.11, 7.13, and 7.14, as noted throughout the background section. (These Tables will be referred to as the "Results Tables" in the following discussion.) Generally speaking, the ground states of the second-row and mixed congeners are the same as those of the first-row species. Notable exceptions are the C₂ group, and the CN group, where the presence of the Si atom lends near-degeneracy to the valence π and σ orbitals. The bond order, however, is identical for the members of each subset, and it is clearly noted to the left of each subset listed.

The previous discussions of first-row diatomics and their second-row counterparts have shown in a piecemeal fashion what is evident at a glance from Table 7.16: the bond lengths are typically larger for the second-row species and the fundamental frequencies (not shown here) are typically lower. There is a smaller energy separation between states as a result

of the less contracted charge distributions in the second-row species. The dipole moments of mixed diatomics (one first-row and one second-row atom) were seen in the background sections to be typically larger than the dipole moments of the purely first-row or purely second-row species, since the electronegativity difference is large, on going from the members of one row in the periodic table to the next.

Table 7.16 shows that some of the R_e values are not precisely known for molecules such as SiC, SiP (which have not been observed experimentally), and SiCl. It also demonstrates that the R_e 's of the members of a subset always follow the pattern:

$$\text{second-row} > \text{mixed} > \text{first-row}.$$

These R_e values were used to calculate the dissociation energies. Potential energy curves calculated using the estimated full-CI energy typically over-estimate the equilibrium bond length by 0.02 bohr or less compared to the experimental value.[217] One can thus assume that the D_e found using the experimental bond length is a few thousandths of an eV less[†] than what the D_e would be if a potential energy curve using that basis were calculated, and the true minimum of that curve found. For the discrepancy between calculation and experiment, the underestimate error is diminished or conversely, the overestimate error is increased.

Tables 7.17—7.20 show the reference (experimental, or, when lacking, theoretical) dissociation energies of these species. Again, a general trend with respect to the well-depths may be observed for the members of a subset:

$$\text{second-row} < \text{mixed} < \text{first-row}.$$

This correlates well with the R_e trend, but not exactly, as in the case of O₂ (5.21 eV), S₂ (4.14) and SO (5.43) where the mixed congener in fact has the strongest bond, not the first-row diatomic.

The reference energies reported in parentheses are not known to a good level of confidence, as far as could be surmised from the background literature review. Some of the reference D_e 's in parentheses appear to be quite plausible (*e.g.*, those for SiC and NCl) but some other values are crude estimates (*e.g.* SiCl and PCl, both of which are estimated from the $\omega_e^2/4\omega_e x_e \approx D_e$ relationship) and two appear to suffer from experimental error of some sort (CCl and SCl).

[†] Assuming the R_e is correct, of course.

Table 7.17 shows first of all the DZP results. These are in nearly uniformly poor agreement, exhibiting 10 to 30 per cent discrepancy with the reference values. The D_e of a ground state calculated using a strictly DZP basis set (using a variational method) should never exceed the true value, but this happens in the case of CCl and so the D_e should clearly be redetermined.[‡] Arguing from the well-depth trend alone, one would expect the purely second-row species to have a smaller D_e than their mixed-row congeners:

$$D_e(\text{CCl}) > D_e(\text{SiCl}),$$

$$D_e(\text{PF}), D_e(\text{NCl}) > D_e(\text{PCl}),$$

and

$$D_e(\text{SF}), D_e(\text{ClO}) > D_e(\text{SCl}).$$

Taking the DZP results into account as qualitative indicators of the probable trend of well depths, however, one would revise these predictions. The DZP results show that the well-depths of the second-row diatomics PCl and SCl are in fact *greater* than the D_e of their mixed congeners ClO and NCl. Accounting for possible exceptions (to a trend which is not absolute to begin with), the revised and more reliable D_e predictions are:

$$D_e(\text{CCl}) > D_e(\text{SiCl}),$$

$$D_e(\text{PF}) > D_e(\text{PCl}),$$

and

$$D_e(\text{SF}) > D_e(\text{SCl}).$$

The very qualitative nature of the DZP calculations is borne out by the large relative errors associated with the D_e 's which were calculated at the (est.) full-CI level. The relative error appears to be greatest for the F_2 subset, with an average relative error for the subset of 26%, and diminishes to only as small as about nine percent, excepting the pathological case of CCl, which it overestimates very slightly. The average relative error of these DZP results for the first-row diatomics alone is 17%. The average relative error of the DZP results for the all the diatomics in Table 7.17 is 20%; without the species whose D_e values are rather uncertain, the average relative error is nearly the same, at 19%. Discarding

[‡] Other calculations discussed in the CCl background section also reported large negative relative errors.

the dubious values has little effect on the average relative error because ignoring, say, the huge discrepancy found for SCl (nearly fifty percent) also means ignoring the excellent "agreement" of the DZP result with the mistakenly-low CCl experimental D_e .

The next stage in this investigation involved the addition of a variety of BF's to the DZP basis set. The effect of BF's has been shown[4] to lie in their ability to create low-lying virtual MO's which lower the energy almost exclusively at the CI stage. In the D_{2h} or C_{2v} symmetry used in these calculations, the p BF's are seen to mix in with π_u valence and virtual MO's; and the d BF's mix in with the π_g MO's. Table 7.18 collects the optimum BF results for the molecules which may be found in the Results Tables. This involved comparing the calculated D_e 's to the reference D_e , and selecting that basis set result which came closest to the reference value. The basis set giving the best result was designated the optimum basis set; its composition and the D_e it yielded are given in Table 7.18.

The addition of BF's has been criticized by Bauschlicher as the deliberate creation of basis set superposition error (BSSE) in incomplete basis sets.[215] One would thus not expect the effect of additional functions to be related to anything other than the relative unsaturation of the atomic basis sets used. Hence, basis sets for molecules containing fluorine, whose DZP basis is known to be highly unsaturated,[†] should require more BF's than, say, basis sets for non-fluorinated molecules. Table 7.18 shows several instances where this is not the case (*e.g.*, ClF, SF, FO and F_2 all require a smaller BF than than, say, C_2 , CO, PN, SiS, ...). Pointing only to the artefacts caused by atomic basis set incompleteness ignores the error present in the description of the interatomic region, where electron density increases when bonding orbitals are occupied when the molecule is formed. In this respect, BF's act to overcome the error of molecular basis set incompleteness (MBSI). According to this view, the number of BF's needed to describe the bonding region should be related to the populations of the bonding orbitals, *i.e.*, the probability density at the bond midpoint.

Table 7.18 confirms the MBSI interpretation and illustrates this chapter's central theme, namely, that bond order correlates with the optimum bond function composition. The correlation is strong but not perfect. From the first-row species in this Table, which compares known experimental D_e 's with the calculated D_e at the experimental R_e , and lists the op-

[†] "Counterpoise corrected" calculations show a much greater effect for ghost orbitals placed close to the F atom, than for ghost orbitals placed close to C, N, or O atoms, and this is a qualitative indication of basis set unsaturation.

timum BF composition for each individual case, rules for adding bond functions to a DZP basis based on knowing only the bond order of a given species can be formulated.

From the first-row results were seen patterns which turned out also to agree with what was seen for precisely-known second- and mixed-row species, and the discussion which follows considers *all* the well-known species in Table 7.18. Conclusions regarding the optimum basis set composition (the construction of the "prescription") which were originally made based on experience with first-row diatomics only,[245] are broadened to include the second- and mixed-row diatomics.

From Table 7.18, it is clear that diatomics with a bond order of one, such as the F_2 subset, favour a single set of (*sp*) bond functions added to a DZP basis; this confirms what had been observed earlier in Chapter 5 for the second-row hydrides and in Chapter 4 for the hydroxyl calculation. Species with a bond order of two largely exhibit (*spd*) as the optimum BF for the DZP basis set, as evident from the C_2 subset and the NF subset.[†] This confirms the observation in Chapter 6, in which the excited states of N_2 with a bond order of 2 also required a single set of (*spd*) orbitals. The homonuclear diatomics O_2 and S_2 favoured a smaller BF, consisting of two sets of (*sp*) functions, although the mixed congener SO requires one set of (*spd*). The O_2 subset was in dramatic contrast to the other homonuclear subsets which show a very strong bond-order trend and intra-subset-consistency. A more refined calculation which included low-lying roots would be necessary to clarify whether this is a true anomaly of the O_2 subset.

Diatomics with a bond order of three generally needed *two* sets of (*spd*) orbitals in their optimum basis set, as shown by SiS, SiO and the entire N_2 subset. This was not a perfect rule; the CO and CS species preferred a single set of (*spd*) orbitals, but it is plain that for a diatomic of bond order 3, the D_e is bracketed by one and two (*spd*) BF's added to DZP basis sets.

The optimum BF composition was more ambiguous for fractional bond orders of 1.5 and 2.5. As a rule of thumb, one would expect the 1.5 bond order case to require a larger optimum bond function than the case of bond order 1, but a smaller BF than the case of bond order 2. A similar rule would apply to molecules with a bond order of 2.5.

Looking at the FO subset (bond order 1.5), the optimum BF's of the members are

[†] Excepting the D_e of PCl, which appears to be overestimated, as discussed above.

evenly spread between one and three sets of (*sp*) orbitals. Incidentally, the molecule with the largest D_e , SF, needed the smallest BF, which is exactly opposite to what one would expect if the BF's were only artificially depressing the energy. A "middle" sort of composition of 2(*sp*) was chosen as the prescribed BF for molecules with a bond order of 1.5.

A similar "middle" position was chosen for the species with bond order of 2.5. This group had the greatest spread of optimum compositions, even after the values with uncertain D_e 's such as CCl, SiCl, SiF, PO and NS were put aside. Carbon monofluoride needed only two (*sp*) sets to recover its experimental D_e ; NO needed 3 sets, and CN and CP, most disquietingly, needed as many as 2(*spd*).[†] Three sets of (*sp*) orbitals were chosen as the prescribed BF.

To summarize, the optimum BF's for a DZP-quality basis set according to bond order are predicted to be:

(1) An (*sp*) bond function added to a DZP-quality basis gives the closest D_e for a bond order of one. Any more bond functions added will definitely result in an overestimated D_e .

(2) For a bond order of $1\frac{1}{2}$, the experimental D_e is bracketed by the values calculated using (*sp*) and 2(*sp*) BF's.

(3) For a bond order of 2, the optimum BF composition appears to be one set of (*spd*).

(4) A bond order of $2\frac{1}{2}$ requires anywhere from 2(*sp*) to 2(*spd*). The optimum BF composition would be 3(*sp*).

(5) A bond order of 3 requires between 3(*sp*) and 2(*spd*), with 2(*spd*) being the recommended composition.

Now, the interesting question becomes, how well do these prescribed augmented basis sets compare? Table 7.19 shows the reference D_e 's vs. the D_e 's calculated using the prescribed BF basis set. The effect is startling: the average relative error of the first-row species is 3.5%—only *one-fifth* the corresponding error in the DZP results. The average relative error of all species in the Table is only 6%—less than *one-third* the DZP overall relative error. Moreover, the average of all species whose D_e 's are known to some degree of confidence is 3.5%, which indicates some predictive ability of the prescribed BF method.

[†] PS had an anomalously large D_e , as indicated by this and other calculations. (Please see relevant subsection.)

The largest relative error is 9.6%, for fluorine; the largest absolute error overall is 0.5 eV, for the cyanogen radical. This is in direct contrast to the DZP results, where the largest relative error is 33% (for chlorine), a few D_e 's are in error by over 1 eV, and the largest absolute error overall is 1.5 eV (for nitrogen). With respect to the accurate calculation of well depths, the prescribed BF method is undeniably successful.

The exceptions to the general rules above regarding bond order and BF composition are explicable in terms of (a) bonding between atoms whose valence shell energies differ greatly; and (b) discrepancies in recovery of correlation energy of the atom *vs.* molecule.

In the case of the CF subset, the bond order is only nominally $2\frac{1}{2}$. The large energetic gap between the valence shells of the atoms means that not much AO-mixing will occur. The highest-occupied bonding MO will strongly resemble the fluorine valence MO and the lowest unoccupied anti-bonding MO, that of the C atom. The electron density will tend to remain localized on the fluorine atom, instead of contributing to the molecular description. Thus, CF with its bond order of 2.5 does not need as many BF's to describe the inter-atomic region, as do NO or CN. It has a smaller D_e than the other diatomics of bond order 2.5, whose atoms are not so energetically disparate in the valence-shell region.

The D_e is more difficult to recover fully when the atoms are very well-correlated and the molecule is not, as, for example, in the case of the N_2 subset. With its high multiplicity due to one electron per p orbital, the nitrogen or phosphorous atom (4S) has a good treatment of the correlation energy in the SCF-CI calculation, but the nitrogen molecule and its congeners ($X^1\Sigma_g^+$) do not. The absolute molecular energy is thus significantly underestimated, although the addition of BF's will improve the correlation energy by the creation of many low-lying virtual MO's, as was seen in Chapter 6. Due to the extreme discrepancy in the ability to correlate the atoms and molecule, in addition to the large bond order, the N_2 subset required the most BF's of all the precisely-known diatomics considered here.

An objection which could be raised to the DZP *vs.* prescribed optimum BF comparison in Table 7.19 is that the latter basis sets contain more functions. To ensure a fairer comparison, the TZPP results have also been tabulated, and are summarized in Table 7.20. A TZPP basis set contains as many basis functions as a DZP + 2(*spd*) basis set. The TZPP

basis sets are superior to the DZP, but clearly do not give as good well-depths as the DZP + BF basis sets. The average relative error of the first-row species is 15%, still *four times* the corresponding error of the BF results. The average relative error of all species in Table 7.20 is nearly as large as the DZP error, 18%, and the average of all species whose D_e 's are known to some degree of confidence is 19%.

Thus, the BF basis sets are seen to *compare very favourably to nuclear-centred basis sets of the same size or slightly larger*. The second objection which is often raised is that obtaining a good D_e employing BF basis sets does not guarantee good description of the diatomic over the whole potential curve. This is possible, but given the results from Chapter 5, where curves for the hydrides using DZP and BF basis sets were calculated, and the BF basis sets were markedly superior for each hydride, it is unlikely that BF basis sets used to calculate potential energy curves for the diatomics in the current chapter would yield worse results than the DZP curves. It is even unlikely that the TZPP basis sets would give as good molecular constants as the BF constants. Unfortunately, the generation and full comparison of such curves is beyond the scope of this work.

Assuming a margin of error of 6% for the optimum BF results, the predictive capability of this method may be tested. The dissociation energies of those species with parenthesized D_e 's were re-examined using the ground states of symmetry and bond lengths as shown in Table 7.16. The reference dissociation energies[†] are given in the second column of Table 7.21. The predicted dissociation energies—i.e., calculated with the prescribed BF method—are given in the third column. The fourth column gives the predicted range assuming $\pm 6\%$ of the prescribed BF D_e . An asterisk in the last column on the right denotes species whose postulated dissociation energies do not lie within the 6% range. These species merit further investigation: either the equilibrium geometry and state specifications are incorrect (unlikely) or the well depth needs to be determined or closely re-examined. A dagger in this right-most column denotes reference D_e 's which lie more than ten per cent away from the D_e calculated with the prescribed BF basis set. These species in particular merit further attention. The most questionable D_e 's are reported for the molecules SiP, CCl, PS, NS, PCl, and SCl. Two postulated D_e 's (for SiC and PO) lie within the fairly broad range of the prescribed BF D_e 's, and it is recommended their values be accepted.

[†] Not always experimental; for example, the D_e 's for SiCl, PCl, and SCl were obtained using an approximation.

7.4 References

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Table 7.1

Ground state atomic energies of C, N, O, F, Si, P, S, and Cl, calculated using basis sets from Ref. [6] and [56]. All energies in hartree.^a For the first-row atoms, the [He] core and anti-core orbitals were frozen; for the second-row atoms, the [Ne] core and anti-core orbitals were frozen. All calculations run with zero threshold, i.e., no extrapolation. For definitions, see text.

Atom	Exponent	SCF Energy	No. Mains	CI Space	Eigenvalue Energy	Total %c _i ²	Full CI (est.)
DZP							
C(³ P)	0.75	-37.684625	8	700	-37.760242	98.29	-37.760853
N(⁴ S)	0.80	-54.394407	4	926	-54.483050	97.58	-54.484697
O(³ P)	0.85	-74.800581	5	2328	-74.914965	97.58	-74.916984
F(² S)	0.90	-99.394325	4	2244	-99.528013	97.61	-99.530456
Si(³ P) ^b	0.25	-288.84441	9	739	-288.91367	98.24	-288.91410
P(⁴ S)	0.38	-340.70721	3	763	-340.78986		-340.79238
S(³ P)	0.48	-397.49075	2	416	-397.59540		-397.60067
Cl(² S)	0.70	-459.46382	1	409	-459.58936		-459.59501
TZPP							
C	0.45,1.125	-37.685246	7	2755	-37.773066	97.47	-37.774442
N	0.48,1.2	-54.395191	4	4128	-54.501350	97.19	-54.503830
O	0.51,1.275	-74.801993	2	3053	-74.945782	96.60	-74.950460
F	0.54,1.35	-99.397186	2	7916	-99.576590	96.92	-99.581744
Si	0.375,0.15	-288.84883	7	2294	-288.92443		-288.92601
P	0.575,0.23	-340.71227	3	2601	-340.80495		-340.80851
S	0.725,0.29	-397.49892	2	3157	-397.62159		-397.62787
Cl	1.05,0.42	-459.47432	1	1271	-459.62523		-459.63378

^a 1 hartree = 27.2116 eV; 1 eV = 8065.48 cm⁻¹.

^b The energies are different than those reported in Table 5.1 because a different integrals routine used for this set of calculations accepted the coefficients given by Ref. [56].

Table 7.2 Energies of C_2 , Si_2 and SiC .
Calculations on C_2 and its congeners with a variety of basis sets. Energies in hartree except where noted; R_e in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total $\%c_2^2$	Est. F-CI Energy	D_e (eV)
C_2 $X^1\Sigma_g^+$ $R_e = 2.3480_4$ B.O. = 2 $D_e = 6.32(1)$ eV ^a									
DZP	—	-75.389594	16	5813/16811	0.5	-75.719342	92.75	-75.731770	5.716
DZP+(sp)	0.4	-75.392077	16	4571/23681	1.0	-75.729595	92.89	-75.742261	6.002
DZP+2(sp)	0.4,1.2	-75.394105	16	5019/31801	1.0	-75.737536	92.89	-75.750627	6.229
DZP+3(sp)	0.2,0.6,1.8	-75.394136	18	4294/47273	1.5	-75.737101	93.09	-75.749718	6.205
DZP+(spd)	0.4	-75.392504	18	5583/41038	1.0	-75.741457	92.97	-75.754466	6.334
DZP+2(spd)	0.3,0.9	-75.394910	14	6329/59060	1.0	-75.748914	92.32	-75.764633	6.610
TZPP	—	-75.395997	13	5877/55753	1.0	-75.743620	92.08	-75.759604	5.734
Si_2 $^1\Sigma_g^+$ $R_e = 4.244_4$ B.O. = 2 $D_e = 3.24$ eV ^c									
DZP	—	-577.657896	21	5918/23976	0.5	-577.890069	90.18	-577.902698	(2.668)
DZP ^d	—	-577.657896	11	3157/32283	1.0	-577.913292	90.45	-577.926242	2.668
DZP+(sp)	0.4	-577.661192	22	4694/33871	1.0	-577.899974	90.39	-577.912931	(2.947)
DZP+2(sp)	0.3,0.9	-577.661825	22	5034/45472	1.0	-577.902830	90.34	-577.916058	(3.032)
DZP+3(sp)	0.07,0.21,0.63	-577.662777	24	5744/66767	1.0	-577.902955	90.14	-577.916645	(3.048)
DZP+(spd)	0.4	-577.661872	22	5473/51178	1.0	-577.906589	90.22	-577.922549	(3.208)
DZP+2(spd)	0.25,0.75	-577.662666	22	5203/88794	1.5	-577.912883	89.90	-577.927852	(3.353)
TZPP ^e	—	-577.774020	8	5651/129806	1.5	-577.930519	88.81	-577.948025	2.612

^a Ref. [10]; [14].

^b The ground state is $X^3\Sigma_g^-$; due to time limitations, the D_e values are adjusted by 0.64 eV.

^c Ref. [17].

^d Calculation for the correct state, $X^3\Sigma_g^-$. Other calculations adjusted by 0.641 eV.

^e Correct state.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-CI Energy	D_e (eV)	μ (Debye)
SiC $X^3\Pi$	$R_e = 3.439^f$	B.O. = 2	$D_e = 4.4$	eV ^g						
DZP	—	-326.595092	11	6170/42700	1.0	-326.797684	91.17	-326.810995	(3.75)	1.4334
DZP+(sp)	0.6	-326.600947	11	5286/60163	2.0	-326.809014	91.38	-326.822448	(4.06)	1.4450
DZP+2(sp)	0.2,0.6	-326.602605	11	4503/80640	4.0	-326.812127	91.60	-326.825351	(4.14)	1.4465
DZP+3(sp)	0.09,0.27,0.81	-326.603154	12	4373/119394	5.0	-326.813042	91.59	-326.826620	(4.18)	1.4701
DZP+(spd)	0.47	-326.653993	11	4728/90309	4.0	-326.815972	91.56	-326.829648	(4.26)	1.4519
DZP+2(spd)	0.2,0.6	-326.604086	12	5027/180643	5.0	-326.824384	91.56	-326.838518	(4.50)	1.5014
TZPP	—	-326.604600	12	4959/226835	5.0	-326.821280	91.22	-326.835959	(3.74)	1.5298
TZPP ^h	—	-326.612466	12	4864/226835	5.0	-326.823752	91.51	-326.837828	3.74	1.3654

^f R_e should be 3.29 bohr. Values adjusted by 0.051 eV

^g Ref. [30]. Estimated from calculations.

^h At the R_e distance of 3.29. Other D_e 's adjusted by 0.051 eV.

Table 7.3 Summary of previous work on C_2 ($X^1\Sigma_g^+$).

Reference	Year	Basis Set: ^a	Absolute energy (hartree)	D_e (eV)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Method/Comments
[18][12]	1979	—	—	6.32	1.2425 ₃	1854.78	13.39	Experimental values.
[220]	1977	(4s2p1d) S	-75.5446	—	1.42	—	—	CI, 1000 singly- and doubly- excited configurations (small).
		(4s2p1d) G	-75.7206	—	1.46	—	—	
[15]	1978	[5s3p2d]+	-75.75589	—	1.25	1880	—	MRD-CI
		BF (sp) G						
		[5s3p1d]+ BF 2(sp d) G						
[221]	1979	(5s3p2d) S	-75.606937	5.55	1.26	1788.6	13.6	MCSCF and limited CI; $^3\Pi$ more stable than ground state.
[16]	1980	(7s5p3d1f) S	-75.76648 ^b	6.25	1.239	1897	12.85	SD-CI+Q, single reference configuration.
[222]	1982	—	—	6.2	1.25	1870	—	numerical Hartree-Fock-Slater method. Functions are distributed over 2D space. Convergence with respect to mesh size.
[223]	1983	[5s3p2d]+ BF(sp)+Ry(sp) G	-75.75233	—	1.249	1860	—	MRD-CI, 33 reference configurations.
[21]	1983	[9s5p1d] G ^c	—	5.41	1.38	1390	—	LCAO-X α .
[1]	1985	6-311+(sp3df) G	—	6.07-6.53	—	—	—	Coupled-cluster double excitation, with singles and triples

^a G = Gaussian-type orbitals, S = Slater-type orbitals, A = atomic natural orbitals.^b At 2.35 bohr.^c Plus a "fitting basis set" for the density functional calculation.

[224]	1985	(4s3p2d) S	—	5.91	1.247	1871	11.5	taken into account by CCD (6.07) and MP4 (6.53) methods.
	1987	[5s3p2d1f] G	—	6.15	—	—	—	Homonuclear diatomics used to test a momentum-space representation of the chemical bond.
[225]	1987	[5s3p2d1f] G	—	6.15	—	—	—	Extended valence MCSCF; with only a few hundred configurations.
	1987	[5s3p2d1f] G	—	6.15	—	—	—	Test of method for all first-row homonuclear diatomics.
[226]	1987	[8s6p3d] G	—	6.06	1.252	1835.5	14.9	CAS-SCF 8 electrons/10 orbitals
	1987	[8s6p3d] G	—	5.94	1.246	1870.6	15.8	contracted CI
[227]	1987	—	-75.4066	—	1.243	—	—	numerical Hartree-Fock
	1987	[4s3p2d1f] A	-75.750837 ^d	—	1.255	1778	—	MRCI + Q
[30]	1987	[5s4p3d2f1g] A	—	—	1.250	1785	—	MRCI + Q
	1987	[5s4p1d] + Ry(sp) G	-75.6768	—	1.2847	—	—	multiconfigurational electron propagator study of C ₂ and C ₂ ⁻ .
[228]	1987	[5s4p1d] + Ry(sp) G	-75.6768	—	1.2847	—	—	multiconfigurational electron propagator study of C ₂ and C ₂ ⁻ .
	1987	[5s4p1d] + Ry(sp) G	-75.6768	—	1.2847	—	—	multiconfigurational electron propagator study of C ₂ and C ₂ ⁻ .
This work	1988	[4s2p1d] + BF(sp) G	-75.754466	6.33	—	—	—	MRD-CI with bond functions
	1988	[4s2p1d] + BF(sp) G	-75.754466	6.33	—	—	—	MRD-CI with bond functions

^d The authors do not specify which basis set gives this energy.

Table 7.4 Energies of CN, SiP, SiN, and CP.

Calculations on CN and its congeners with a variety of basis sets. Energies in hartree except where noted; R_e in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolat.d CI Energy	Total % c^2	Est. F-CI Energy	D_e (eV)	μ (Debye)
CN $X^2\Sigma^+$ $R_e=2.2144$ B.O. = $2.5 D_e = 7.8_a$ eV ^a $\mu = 1.45$ D ^b										
DZP	—	-92.200334	9	3960/38869	2.0	-92.476588	92.57	-92.492827	6.729	1.5007
DZP+(sp)	0.5	-92.204848	11	4986/70523	2.0	-92.490701	93.00	-92.505886	7.084	1.5868
DZP+2(sp)	0.5,1.5	-92.207846	11	4007/94687	5.0	-92.500246	93.15	-92.515530	7.347	1.6472
DZP+3(sp)	0.2,0.66,2.0	-92.209366	11	3296/122415	10.0	-92.501735	93.29	-92.516784	7.381	1.6698
DZP+(spd)	1.1	-92.206884	9	3563/82092	7.0	-92.498686	92.78	-92.515096	7.335	1.6382
DZP+2(spd)	0.4,1.2	-92.208932	11	3928/183309	10.0	-92.515307	93.13	-92.531701	7.787	1.6515
TZPP	—	-92.211648	11	4145/183309	10.0	-92.511304	93.03	-92.527597	6.784	1.6515
SiP $X^2\Pi_1$ $R_e = 3.98^d$ B.O. = $2.5 D_e = (3.7)$ eV $\mu = 0.89$ D ^d										
DZP	—	-629.566274	7	5127/42145	1.0	-629.780392	90.15	-629.796936	(2.689)	
DZP+(sp)	0.6	-692.571519	9	6286/65446	1.0	-629.796532	90.47	-629.813057	(3.128)	
DZP+2(sp)	0.3,0.9	-629.572242	9	7087/87613	1.0	-629.799343	90.46	-629.816103	(3.211)	
DZP+3(sp)	0.2,0.6,1.8	-629.572835	9	5140/113014	2.5	-629.798466	90.67	-629.814741	(3.174)	
DZP+(spd)	0.5	-629.572381	7	5755/89260	2.0	-629.804591	90.19	-629.822816	(3.394)	
DZP+2(spd)	0.3,0.9	-629.574384	7	5002/153865	4.0	-629.810899	90.24	-629.820459	(3.574)	
DZP+2(spd) ^e	0.3,0.9	-629.602753	5	4430/122793	5.0	-629.817792	89.46	-629.837825	3.574	0.8684
TZPP ^f	—	-629.610617	7	5129/358628	5.0	-629.816139	89.34	-629.835256	2.741	1.0657

^a Ref. [18]^b Ref. [TD68]^c Calculations for $2\Sigma^+$ state at $R = 3.6$ bohr. Adjusted for state and bond length in final column.^d Ref. [36]; calculated.^e Calculated for the correct state, $X^2\Pi$, at the R_e of 3.98 bohr. Other calculations adjusted by 0.228 eV.^f Correct state and R_e .

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total $\%c^2$	Est. F-CI Energy	D_e (eV)	μ (Debye)
SiN $X^2\Sigma^+$	$R_e=2.9705^a$	B.O. =	2.5	$\mu = 2.33$	Γ^d					
DZP		-343.259618	13	6771/54381	1.0	-343.512369	91.52	-343.528584	3.532	2.2707
DZP+(sp)	0.8	-343.273734	11	5485/60905	2.0	-343.529269	91.43	-343.546828	4.028	2.2618
DZP+2(sp)	0.3,0.9	-343.275001	11	3804/81475	6.0	-343.532548	91.76	-343.549614	4.104	2.1812
DZP+3(sp)	0.1,0.3,0.9	-343.276445	13	4289/132897	6.0	-343.532925	91.54	-343.550805	4.136	2.3072
DZP+(spd)	0.5	-343.274733	11	4429/91427	5.0	-343.537917	91.68	-343.555646	4.268	2.2941
DZP+2(spd)	0.26,0.78	-343.278122	11	4389/157283	8.0	-343.548700	91.56	-343.567508	4.591	2.2515
TZPP	—	-343.273489	11	4193/199010	8.0	-343.541570	91.25	-343.561312	3.578	2.2792
CP $X^2\Sigma^+$	$R_e = 2.952$	B.O. =	2.5	$D_e = 5.36$	eV ^a					
DZP	—	-378.455445	11	4327/43331	2.0	-378.701956	91.47	-378.717617	4.470	0.8198
DZP+(sp)	0.8	-378.462404	11	3778/60905	4.0	-378.714525	91.63	-378.730349	4.820	0.8161
DZP+2(sp)	0.3,0.9	-378.463897	11	4349/81475	4.0	-378.719943	91.61	-378.736145	4.977	0.8399
DZP+3(sp)	0.1,0.3,0.9	-378.465369	13	5908/132897	3.0	-378.722667	91.47	-378.739199	5.060	0.8142
DZP+(spd)	0.5	-378.461957	9	5275/82092	3.0	-378.724537	91.01	-378.742986	5.163	0.8007
DZP+2(spd)	0.3,0.9	-378.466572	11	3907/183309	8.0	-378.736185	91.52	-378.753709	5.455	0.8788
TZPP	—	-378.467511	9	4329/179106	8.0	-378.729011	90.65	-378.748686	4.510	0.8444

Table 7.5 Energies of CO, SiS, SiO, and CS.

Calculations on CO and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-Cl Energy	D_e (eV)	μ (Debye)
CO $X^1\Sigma^+$ $R_e=2.13222$ B.O. = $3 D_e = 11.22_6$ eV ^a $\mu = 0.1222$ D ^b										
DZP	---	-112.759069	6	2239/16870	2.0	-113.036156	92.95	-113.053298	10.217	0.1246
DZP+(sp)	0.5	-112.763115	6	3604/23662	1.0	-113.052405	92.87	-113.070624	10.688	0.1143
DZP+2(sp)	0.6,1.8	-112.767578	6	4310/31602	1.0	-113.068116	92.87	-113.087151	11.138	0.0855
DZP+3(sp)	0.2,0.6,1.8	-112.769338	4	3910/33457	2.0	-113.068083	92.47	-113.088673	11.179	0.0970
DZP+(spd)	1.0	-112.766926	6	3955/35372	1.5	-113.069664	92.90	-113.088769	11.182	0.0734
DZP+2(spd)	0.6,1.8	-112.769139	4	4667/49771	2.5	-113.083900	92.52	-113.105769	11.645	0.0625
TZPP	---	-112.773106	6	4711/60646	2.5	-113.089160	92.74	-113.109727	10.472	0.0486
SiS $X^1\Sigma^+$ $R_e=3.64589^a$ B.O. = $3 D_e = 6.4_2$ eV ^c $\mu = 1.74(7)$ D ^d										
DZP	---	-686.492729	4	2679/13807	1.0	-686.690375	89.57	-686.710999	5.34	
DZP+(sp)	0.6	-686.482111	4	3261/19405	1.0	-686.708025	89.49	-686.729998	5.86	
DZP+2(sp)	0.3,0.9	-686.483298	6	3896/25955	1.0	-686.712715	89.47	-686.735106	5.996	
DZP+3(sp)	0.1,0.3,0.9	-686.485411	6	4505/70766	1.0	-686.714576	89.37	-686.737335	6.056	
DZP+(spd)	0.6	-686.483639	4	4211/29001	1.0	-686.720151	89.43	-686.743379	6.221	
DZP+2(spd)	0.3,0.9	-686.487489	4	5287/49771	1.5	-686.730640	89.37	-686.754733	6.530	
TZPP	---	-686.494681	4	5030/77965	1.5	-686.727741	88.99	-686.751959	5.390	1.8209

^a Ref. [18].^b Ref. [40].^c Ref. [49].^d Ref. [MC65].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total % c_i^2	Est. F-CI Energy	D_e (eV)	μ (Debye)
SiO $X^1\Sigma^+$ $R_e=2.85299^a$ B.O. = 3 $D_e = 8.35(9)$ eV b $\mu = 3.0882$ D f										
DZP	—	-363.807288	8	3540/19790	1.0	-364.068481	91.69	-364.088042	6.992	2.3609
DZP+(sp)	0.8	-363.825394	8	4205/27824	1.0	-364.095447	91.75	-364.115650	7.744	2.9554
DZP+2(sp)	0.3,0.9	-363.827768	8	4077/37234	1.5	-364.100924	91.80	-364.121263	7.896	2.9338
DZP+3(sp)	0.1,0.3,0.9	-363.830465	8	4659/48020	1.5	-364.103197	91.60	-364.124376	7.981	3.1331
DZP+(spd)	0.64	-363.826820	8	4307/41682	1.5	-364.106592	91.79	-364.127515	8.066	3.0297
DZP+2(spd)	0.3,0.9	-363.830377	6	5431/60646	2.0	-364.115254	91.33	-364.138044	8.353	3.0511
TZPP	—	-363.825560	6	5126/76705	2.0	-364.116671	91.22	-364.140644	7.189	3.0630
CS $X^1\Sigma^+$ $R_e=2.90062^a$ B.O. = 3 $D_e = 7.43(1)$ eV b $\mu = 1.97$ D h										
DZP	—	-435.327915	4	3484/13807	1.0	-435.581602	90.44	-435.602388	6.554	1.8516
DZP+(sp)	0.8	-435.332153	4	4148/19405	1.0	-435.597585	90.38	-435.619659	7.024	1.8180
DZP+2(sp)	0.34,1.02	-435.335197	4	4118/25955	1.5	-435.604893	90.40	-435.627297	7.23	1.8944
DZP+3(sp)	0.1,0.3,0.9	-435.338644	4	4352/33457	2.0	-435.608831	90.36	-435.631411	7.344	1.8960
DZP+(spd)	0.8	-435.332904	4	4219/29001	1.5	-435.609042	90.41	-435.632067	7.362	1.7992
DZP+2(spd)	0.3,0.9	-435.339230	4	5012/49771	2.5	-435.625152	90.21	-435.649635	7.841	1.9794
TZPP	—	-435.343733	6	3723/133959	5.0	-435.621626	90.46	-435.644137	6.580	1.8708

^a Ref. [60].

^f Ref. [63].

^g Ref. [71].

^h Ref. [64].

Table 7.6 Energies of CF, SiCl, SiF, and CCl.

Calculations on CF and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-Cl Energy	D _e (eV)	μ (Debye)
CF $X^2\Pi_r$, $R_e=2.4034^a$ B.O. = 2.5 $D_e = 5.75$ eV ^b $\mu = 0.645(14)$ D ^c										
DZP	—	-137.202903	3	4347/18219	1.0	-137.459598	92.99	-137.476667	5.044	0.6793
DZP+(sp)	0.9	-137.205486	3	4397/25674	3.0	-137.474667	93.09	-137.492817	5.483	0.6733
DZP+2(sp)	0.6,1.8	-137.207069	3	5000/34407	4.0	-137.482411	93.12	-137.500896	5.703	0.6800
DZP+3(sp)	0.2,0.6,1.8	-137.208251	3	5549/44418	6.0	-137.486585	93.09	-137.505360	5.825	0.6686
DZP+(spd)	0.8	-137.206755	3	4384/38687	6.0	-137.491122	93.17	-137.510097	5.954	0.6695
DZP+2(spd)	0.3,0.9	-137.209761	3	4466/66773	12.0	-137.502505	93.17	-137.522058	6.279	0.6791
TZPP	—	-137.211325	3	3979/66773	12.0	-137.521233	93.12	-137.542102	5.059	0.6796
SiCl $X^2\Pi_r$, $R_e=3.889^d$ B.O. = 2.5										
DZP	—	-748.413157	6	4671/39321	1.0	-748.623556	91.70	-748.639670	3.553	
DZP+(sp)	0.5	-748.423207	6	5335/55498	1.5	-748.643977	91.55	-748.661246	4.140	
DZP+2(sp)	0.3,0.9	-748.424571	6	5735/74581	2.5	-748.650809	91.45	-748.668772	4.345	
DZP+3(sp)	0.1,0.3,0.9	-748.426330	5	6067/86162	4.0	-748.653196	90.96	-748.672786	4.454	
DZP+(spd)	0.4	-748.424605	6	5344/84462	4.0	-748.656243	91.38	-748.674803	4.509	
DZP+2(spd)	0.3,0.9	-748.426397	6	6099/146825	5.0	-748.667844	91.20	-748.687742	4.861	
TZPP	—	-748.435245	5	5966/319168	5.0	-748.673795	90.73	-748.694098	3.655	0.8731

^a Ref. [18].^b Ref. [82].^c Ref. [85].^d Ref. [90].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-CI Energy	D _e (eV)	μ (Debye)
SiF X ² Π_r R _e =3.0256 ^a B.O. = 2.5 D _e = 5.67 eV ^c μ = 1.126 D ^f										
DZP	—	-388.379444	4	4875/27732	1.0	-388.616141	93.20	-388.630958	5.072	1.0328
DZP+(sp)	0.7	-388.397010	4	5552/39115	1.5	-388.643242	93.24	-388.658610	5.925	0.9656
DZP+2(sp)	0.3,0.9	-388.398067	5	5497/68559	3.0	-388.647530	93.35	-388.662754	5.938	0.8900
DZP+3(sp)	0.1,0.3,0.9	-388.401209	4	5406/67737	4.0	-388.650250	92.89	-388.667021	6.054	0.7653
DZP+(spd)	0.65	-388.397567	4	4963/59279	5.0	-388.653954	93.34	-388.669759	6.128	0.9382
DZP+2(spd)	0.2,0.6	-388.400290	4	4995/102662	10.0	-388.662257	93.31	-388.678724	6.372	0.8299
TZPP	—	-388.397604	5	4331/169918	10.0	-388.686456	93.55	-388.703848	5.336	0.8487
CCl X ² Π_r R _e =3.10871 ^g B.O. = 2.5 D _e = 3.39(17) eV ^h										
DZP	—	-497.227086	6	4393/72170	1.0	-497.464389	91.63	-497.482542	3.447	1.4090
DZP+(sp)	0.8	-497.229672	4	4676/56116	2.0	-497.477725	91.19	-497.498851	3.891	1.4204
DZP+2(sp)	0.3,0.9	-497.233085	3	3701/34407	8.0	-497.486401	90.95	-497.508990	4.167	1.4721
DZP+3(sp)	0.1,0.3,0.9	-497.235236	4	4578/98178	8.0	-497.490903	90.88	-497.513858	4.299	1.5201
DZP+(spd)	0.5	-497.232162	4	4451/85364	5.0	-497.490939	91.06	-497.512314	4.284	1.5162
DZP+2(spd)	0.3,0.9	-497.235841	3	4451/66773	10.0	-497.508109	90.68	-497.533145	4.824	1.5485
TZPP	—	-497.243001	3	3948/170137	10.0	-497.511007	90.58	-497.534824	3.445	1.3637

^c Ref. [92].

^f Ref. [91], calculated.

^g Ref. [YNH89]. The calculations in the present work were carried out at 3.1086 bohr.

^h Ref. [98].

Table 7.7 Energies of P₂ and PN.

Calculations on P₂ and its congener with a variety of basis sets. Energies in hartree except where noted; distance in bohr. This table is a companion to Table 2 in Ref. [103].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μh)	Extrapolated CI Energy	Total %c ²	Eat. F-CI Energy	D _e (eV)	μ ^d (Debye)
P ₂ X ¹ Σ ⁺	R _e =3.5780 ^b	B.O. =	3	D _e =	5.081	eV ^a				
DZP	—	-681.462986	8	3079/20723	1.0	-681.706081	90.30	-681.724102	3.79	
DZP+(sp)	0.6	-681.464997	6	3622/20259	1.0	-681.719227	89.79	-681.740092	4.23	
DZP+2(sp)	0.3,0.9	-681.466154	8	3996/39919	1.0	-681.724504	90.11	-681.744464	4.35	
DZP+3(sp)	0.1,0.3,0.9	-681.469309	7	4486/35275	1.0	-681.725289	89.51	-681.747400	4.43	
DZP+(spd)	0.5	-681.466363	7	4278/30548	1.0	-681.732273	89.70	-681.754525	4.62	
DZP+2(spd)	0.3,0.9	-681.470894	8	3940/52883	2.0	-681.741378	89.62	-681.764499	4.89	
TZPP	—	-681.478296	8	4202/100910	2.0	-681.736901	89.51	-681.758674	3.855	
PN X ¹ Σ ⁺	R _e =2.81733 ^a	B.O. =	3	D _e =	6.44	eV ^c	μ = 2.75	D ^d		
DZP	—	-395.150169	4	4075/13807	1.0	-395.438070	90.53	-395.460253	4.985	2.6091
DZP+(sp)	0.8	-395.158991	6	5079/28003	1.0	-395.458424	90.89	-395.479916	5.520	2.6487
DZP+2(sp)	0.35,1.05	-395.161054	4	4710/25955	1.5	-395.464851	90.60	-395.488334	5.749	2.6710
DZP+3(sp)	0.14,0.42,1.26	-395.163463	6	5487/48547	1.5	-395.466456	90.43	-395.490668	5.812	2.7290
DZP+(spd)	0.72	-395.159743	6	5302/42005	1.5	-395.469932	90.98	-395.492006	5.849	2.6895
DZP+2(spd)	0.33,0.99	-395.164658	4	5314/49771	3.0	-395.480872	90.52	-395.505949	6.230	2.7766
TZPP	—	-395.165541	4	3978/63066	5.0	-395.473840	90.37	-395.498996	5.079	2.7645

^a Applicable only to PN.

^b Ref. [18].

^c Ref. [112].

^d Ref. [114].

Table 7.8 Summary of previous work on N_2 ($X^1\Sigma_g^+$).

Reference	Year	Basis Set ^a	Absolute energy (hartree)	D_e (eV)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Method/Comments
[18]	1979	—	—	9.905	1.09768 ₆	2358.57	14.324	Tabulated experimental values from Huber and Herzberg.
[229]	1974	(11s7p) G ^b	-109.0920	7.9	—	—	—	limited CI; investigated contribution of quadruple excitations.
[230]	1975	(9s5p1d) G	-109.28106	—	1.100	2417	13.5	CEPA-CI
[104]	1977	[5s3p]+ BF 2(sp) G [5s3p2d]	-109.2440 -109.3580	9.98 9.33	—	—	—	MRD-CI
[53]	1980	[5s3p1d] G	-109.306096	—	—	—	—	MBPT(4)+triple and quadruple excitations
[222]	1982	—	—	9.6	1.09	2380	—	numerical Hartree-Fock-Slater method. Functions are distributed over 2D space. Convergence with respect to mesh size.
[231]	1983	[5s4p2d] G [6s5p2d1f] G	-109.338473 -109.365826	9.09 9.46	1.102 1.101	2332 2345	14.7	Externally contracted CI
[103]	1984	[4s2p1d]+BF2(sp _d) G	-109.3358	9.96	—	—	—	MRD-CI
[1]	1985	6-311+(sp3df) G	—	9.50-9.67 ^a	—	—	—	Coupled-cluster double excitation, with singles and triples

^a G = Gaussian-type orbitals, S = Slater-type orbitals, A = atomic natural orbitals.

^b Contracted and distributed off the atomic centres as described in Ref. [229].

^a A basis set consisting of [7s6p4d2f] GTO's improved the D_e by only ≈ 0.1 eV.

taken into account by CCD (9.50) and MP4 (9.67) methods.									
[46]	1985	[6s4p3d2f] G [6s4p3d2f1g] G	-109.344932 -109.383950	8.45 9.23	— —	— —	— —	— —	CI(SD), single reference Coupled Pair Functional (CPF)
[224]	1985	(4s3p2d) S	—	9.09	1.099	2385	13.7	—	Homonuclear diatomics used to test a momentum-space representation of the chemical bond.
[225]	1987	[5s4p2d1f] G	—	9.41	—	—	—	—	Extended valence MCSCF; with only a few hundred configurations. Test of r.ethod for all first- row homonuclear diatomics. MP4(SDTQ)
[107]	1987	—	—	5.09	1.068	2729	—	—	Core Model Potential— models Coulomb and exchange core operators J_c and K_c .
[232]	1987	[4s3p1d]	-109.31176	8.778	1.1128	2288	14.2	—	Multi-reference coupled cluster method.
[121]	1987	[4s2p1d]	-109.150642 ^c	8.750	1.123	2333	—	—	Full-CI "benchmark" calculation. Found triple excitations very important in multiple bonds. CASSCF orbitals, MRCI-FCI
[233]	1987	[4s2p1d] [8s5p2d] G	-109.150632 ^c -109.41081	8.743 —	1.123 1.0972	2334 2365.6	— 16.41	—	Møller-Plesset many-body perturbation theory (4th order) with single,

^c At 2.10 bohr.

Table 7.9 Energies of NO, PS, PO, and NS.

Calculations on NO and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-CI Energy	D_e (eV)	μ (Debye)
NO $X^2\Pi_r$ $R_e=2.17464^a$ B.O. = 2.5 $D_e = 6.6144$ eV ^a $\mu_0 = 0.15872$ D ^a										
DZP	—	-129.268359	5	4709/51998	2.0	-129.582653	92.82	-129.601044	5.425	0.0619
DZP+(sp)	0.6	-129.270426	5	4520/74256	5.0	-129.596895	93.00	-129.615668	5.823	0.0473
DZP+2(sp)	0.7,2.1	-129.275900	5	4691/100484	6.0	-129.612684	93.03	-129.632110	6.270	0.0270
DZP+3(sp)	0.23,0.7,2.1	-129.278007	5	4279/130682	10.0	-129.615609	93.11	-129.634988	6.349	0.0488
DZP+(spd)	0.8	-129.273504	5	4075/113149	10.0	-129.614825	93.08	-129.634440	6.334	0.0272
DZP+2(spd)	0.7,2.1	-129.277792	5	4162/197794	12.0	-129.637087	93.12	-129.657820	6.970	0.0531
TZPP	—	-129.279076	5	5009/197794	12.0	-129.637487	92.98	-129.658776	5.560	0.0918
PS $X^2\Pi_r$ $R_e=3.5858^b$ B.O. = 2.5 $D_e = 4.57$ eV ^c										
DZP	—	-738.249963	4	5635/43483	1.0	-738.492293	89.71	-738.514403	3.30	
DZP+(sp)	0.6	-738.253525	4	6238/61926	1.5	-738.507678	89.70	-738.531026	3.75	
DZP+2(sp)	0.3,0.9	-738.255272	4	6165/83635	2.5	-738.511866	89.73	-738.535491	3.88	
DZP+3(sp)	0.1,0.3,0.9	-738.258014	4	5749/108610	5.0	-738.513808	89.58	-738.538120	3.95	
DZP+(spd)	0.6	-738.255534	5	5004/94183	5.0	-738.521155	89.84	-738.545352	4.14	
DZP+2(spd)	0.3,0.9	-738.260923	4	5489/164245	6.0	-738.533084	89.69	-738.558510	4.50	
TZPP	—	-738.269021	4	4195/254357	12.0	-738.530455	89.42	-738.555755	3.248	0.8286

^a Ref. [18].^b Ref. [123]. Calculations in this work carried out at 3.5922; difference insignificant.^c Ref. [124].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-CI Energy	D_e (eV)	μ (Debye)
PO $X^3\Pi_r$ $R_e = 2.7890^a$ B.O. = 2.5 $D_e = (5.5) \text{ eV}^d$ $\mu = 1.88(7) \text{ D}^e$										
DZP	—	-415.579819	5	5795/26617	1.0	-415.858125	91.15	-415.880871	4.667	2.1306
DZP+(sp)	0.8	-415.593825	6	5938/50471	2.0	-415.882267	91.40	-415.904863	5.313	2.2558
DZP+2(sp)	0.4,1.2	-415.595427	4	4429/40924	8.0	-415.886783	91.28	-415.910536	5.474	2.2359
DZP+3(sp)	0.14,0.42,1.26	-415.599709	5	4929/65839	10.0	-415.892746	91.29	-415.916758	5.644	2.1168
DZP+(spd)	0.66	-415.594675	5	5167/65684	8.0	-415.894980	91.41	-415.918661	5.695	2.3391
DZP+2(spd)	0.4,1.2	-415.599407	4	5410/79438	10.0	-415.906935	91.22	-415.932348	6.068	2.2996
TZPP	—	-415.599318	4	5515/100703	10.0	-415.911353	91.05	-415.937814	4.867	2.1896
NS $X^3\Pi_r$ $R_e = 2.8232^f$ B.O. = 2.5 $D_e = 5.1(3) \text{ eV}^g$ $\mu = 1.81(2) \text{ D}^h$										
DZP	—	-451.907252	5	6703/45412	1.0	-452.197693	90.81	-452.220119	3.667	1.8563
DZP+(sp)	0.8	-451.913874	5	6436/64680	2.0	-452.216130	90.87	-452.239464	4.193	1.8525
DZP+2(sp)	0.33,1.0	-451.917578	6	4416/104536	8.0	-452.223258	91.33	-452.245280	4.351	1.8235
DZP+3(sp)	0.16,0.48,1.44	-451.919247	5	4554/75431	10.0	-452.228628	91.09	-452.252081	4.537	1.7521
DZP+(spd)	0.76	-451.914764	6	4605/141603	8.0	-452.229239	91.25	-452.252350	4.544	1.8315
DZP+2(spd)	0.3,0.9	-451.921599	4	4477/79348	12.0	-452.245609	90.86	-452.271466	5.06	1.8515
TZPP	—	-451.925239	6	4356/261331	12.0	-452.246546	91.18	-452.270266	3.771	1.7024

^d Ref. [126].^e Ref. [131].^f Ref. [137].^g Ref. [136].^h Ref. [141].

Table 7.10 Energies of NF, PCl, PF, and NCl.

Calculations on NF and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total $\%c^2$	Est. F-Cl Energy	D_e (eV)	μ (Debye)
NF $X^3\Sigma^-$ $R_e=2.48873^a$ B.O. = $2 D_e = 3.63(6)$ eV ^b $\mu = 0.081$ D ^c										
DZP	—	-153.811971	5	4221/44367	5.0	-154.092053	93.14	-154.10631	2.598	0.0420
DZP+(sp)	0.8	-153.814130	5	4146/63452	10.0	-154.107087	93.32	-154.126035	3.017	0.0267
DZP+2(sp)	0.5,1.5	-153.815621	5	4741/85947	10.0	-154.114503	93.32	-154.133885	3.231	0.0286
DZP+3(sp)	0.2,0.6,1.8	-153.816748	4	3574/94237	20.0	-154.117932	93.35	-154.137688	3.334	0.0107
DZP+(spd)	0.8	-153.815059	5	3257/97195	20.0	-154.125071	93.55	-154.144487	3.519	0.0176
DZP+2(spd)	0.7,2.1	-153.817037	5	3300/170481	20.0	-154.137373	93.64	-154.157183	3.865	0.0025
TZPP	—	-153.818566	6	4501/237968	15.0	-154.158616	93.60	-154.179435	2.536	0.0190
PCl $X^3\Sigma^-$ $R_e=3.80706^d$ B.O. = $2 D_e = (4.2)$ eV ^e $\mu = (1.38)$ D ^f										
DZP	—	-800.219023	5	5794/34252	2.0	-800.446137	91.21	-800.465333	(2.20)	
DZP+(sp)	0.6	-800.227161	4	4679/48844	8.0	-800.466232	91.26	-800.486355	(2.77)	
DZP+2(sp)	0.3,0.9	-800.229221	3	4905/66020	10.0	-800.472570	91.01	-800.494078	(2.98)	
DZP+3(sp)	0.2,0.6,1.8	-800.230296	2	4313/66195	12.0	-800.475592	91.07	-800.497083	(3.06)	
DZP+(spd)	0.5	-800.229354	5	4153/74749	12.0	-800.480400	91.30	-800.501496	(3.18)	
DZP+2(spd)	0.3,0.9	-800.233174	3	4087/130850	15.0	-800.496052	91.21	-800.158603	(3.65)	
DZP+2(spd) ^g	0.3,0.9	-800.240620	3	4007/130850	15.0	-800.499576	91.22	-800.521566	3.65	0.4767
TZPP ^g	—	-800.249675	2	4323/158210	12.0	-800.506336	90.40	-800.530489	2.400	0.7023

^a Ref. [16].^b Ref. [146],[147].^c Ref. [151].^d Ref. [155]. These calculations were carried out at 3.6 bohr, so the D_e values in the last column are adjusted.^e Ref. [153].^f Ref. [156]. Calculation.^g Calculated at the proper R_e of 3.80706 bohr. Other D_e 's adjusted by 0.081 eV.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ₂	Est. F-CI Energy	D _e (eV)	μ (Debye)
PF X ³ Σ^- R _e = 3.004, ^a B.O. = 2 D _e = (4.65) eV ⁱ μ = (0.6) D [*]										
DZP	—	-440.185690	3	6348/34048	1.0	-440.437902	92.48	-440.456070	3.626	1.0894
DZP+(sp)	0.7	-440.198632	3	4719/48598	8.0	-440.460912	92.70	-440.479277	4.257	1.0823
DZP+2(sp)	0.4,1.2	-440.199132	3	4869/65732	10.0	-440.463510	92.43	-440.483232	4.365	1.0040
DZP+3(sp)	0.13,0.39,1.17	-440.202287	3	5307/85450	10.0	-440.470060	92.78	-440.488687	4.513	0.7810
DZP+(spd)	0.64	-440.199200	3	5021/74452	12.0	-440.473433	92.83	-440.492331	4.612	1.0526
DZP+2(spdp)	0.2,0.6	-440.202605	2	5419/101040	14.0	-440.483388	92.59	-440.503891	4.93	0.8166
TZPP	—	-440.202597	2	4894/128014	14.0	-440.508516	92.56	-440.530784	3.824	0.9367
NCl X ³ Σ^- R _e =(3.0508) ^a B.O. = 2 D _e = 2.9 eV ⁱ										
DZP	—	-513.868908	6	4658/60289	4.0	-514.129318	91.93	-514.149022	1.886	0.9817
DZF+(sp)	0.8	-513.872283	6	4072/80500	8.0	-514.146066	92.05	-514.166611	2.365	0.9896
DZP+2(sp)	0.37,1.11	-513.875452	6	3190/117433	16.0	-514.156296	92.12	-514.177281	2.655	0.9899
DZP+3(sp)	0.1,0.3,0.9	-513.877394	4	4080/69426	16.0	-514.155714	91.49	-514.179214	2.708	0.9989
DZP+(spdp)	0.64	-513.873714	6	4263/132745	10.0	-514.162676	92.00	-514.184584	2.854	1.0016
DZP+2(spdp)	0.3,0.9	-513.878173	3	4798/75116	12.0	-514.174909	91.05	-514.201464	3.313	1.0352
TZPP	—	-513.884903	3	4644/95460	12.0	-514.179840	90.83	-514.206653	1.879	0.9132

^a Ref. [157].^{*} Ref. [93]. Calculation.ⁱ Ref. [162]. Calculation.

Table 7.11 Energies of O_2 , S_2 and SO .Calculations on O_2 and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %C ²	Eat. F-CI Energy	D_e (eV)
O_2 $X^3\Sigma^-_g$	$R_e=2.28188$	B.O. =	2	D_e =	5.2133 eV ^a				
DZP	—	-149.634962	8	6053/58999	1.0	-149.980049	93.44	-149.997241	4.443
DZP+(sp)	0.8	-149.636686	8	5288/85650	3.0	-149.995667	93.52	-150.013697	4.891
DZP+2(sp)	0.6,1.8	-149.640165	8	5265/117215	5.0	-150.008844	93.51	-150.027669	5.271
DZP+3(sp)	0.2,0.6,1.8	-149.642917	7	5943/117457	6.0	-1 ¹ 1.011986	92.99	-150.033277	5.423
DZP+(spd)	0.8	-149.637897	7	5742/101750	5.0	-150.014834	93.26	-150.035149	5.474
DZP+2(spd)	0.7,2.1	-149.642510	8	5002/235807	10.0	-150.035976	93.63	-150.055975	6.041
TZPP	—	-149.643499	6	4903/174790	15.0	-150.042139	93.27	-150.064429	4.45
S_2 $X^3\Sigma^-_g$	$R_e=3.57008$	B.O. =	2	D_e =	4.4142 eV ^a				
DZP	—	-795.047152	8	5803/30334	1.0	-795.306340	90.56	-795.327899	3.44
DZP+(sp)	0.7	-795.050841	7	5591/68844	2.0	-795.324013	90.85	-795.345530	3.92
DZP+2(sp)	0.3,0.9	-795.053676	6	6353/87486	2.5	-795.329934	90.59	-795.352581	4.12
DZP+3(sp)	0.07,0.21,0.63	-795.055623	4	6833/68539	4.0	-795.332305	89.69	-795.358580	4.28
DZP+(spd)	0.6	-795.054478	7	5210/59463	5.0	-795.340777	90.19	-795.366120	4.48
DZP+2(spd)	0.3,0.9	-795.059844	6	5883/174440	6.0	-795.354131	90.42	-795.378952	4.83
TZPP	—	-795.067810	6	6501/277054	6.0	-795.356393	89.90	-795.382138	3.439

^a Ref. [18].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total %c ²	Est. F-CI Energy	D_e (eV)	μ (Debye)
SO $X^3\Sigma^-$	$R_e=2.79885^a$	B.O. =	2	$D_e = 5.43(1)$	eV ^b					
$\mu = 1.55(2)$ D ^c										
DZP	—	-472.351686	6	4507/88872	8.0	-472.647734	91.20	-472.668602	4.108	1.9022
DZP+(sp)	0.8	-472.362167	6	3942/128275	15.0	-472.670294	92.12	-472.691617	4.734	1.9033
DZP+2(sp)	0.34,1.02	-472.365474	4	4220/103670	15.0	-472.678195	91.67	-472.701906	5.014	1.8381
DZP+3(sp)	0.14,0.42,1.26	-472.368531	4	4822/135293	15.0	-472.680705	91.01	-472.707559	5.168	1.7834
DZP+(spd)	0.67	-472.363234	6	4469/197631	15.0	-472.688964	92.08	-472.711624	5.284	1.924
DZP+2(spdl)	0.5,1.5	-472.368632	4	4375/205524	15.0	-472.702148	91.56	-472.727979	5.723	1.8741
TZPP	—	-472.371942	4	4996/262009	15.0	-472.709491	91.38	-472.736484	4.304	1.7704

^b Ref. [172].^c Ref. [173].

Table 7.12 Summary of previous work on O_2 ($X^1\Sigma_g^+$).

Reference	Year	Basis Set ^a	Absolute energy (hartree)	D_e (eV)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Method/Comments
[163]	1972	—	—	5.115 ₆	1.20752	1580.19 ₃	11.98 ₁	Experimental values (review).
[234]	1971	[4s2p1d] S	-149.79443	4.72	1.220	1614	15.80	Iterative natural orbitals (INO), first-order CI
[235]	1975	[4s2p1d] G	-149.78030	4.876	1.238	1692.7	—	Generalized valence-bond CI
[236]	1976	(5s3p1d)+ 2 Ry(sp) S	—	—	1.22	1656.2	9.5	Single-reference first- order (FO) CI
[237]	1977	(5s3p2d) S	-149.876857	4.957	1.236	1498.8	9.87	6-configuration MC-SCF, then FO-CI.
[238]	1977	[3s2p1d]	-149.73506	4.99	1.224	1583.8	12.87	Multi-reference, FO-CI
[222]	1982	—	—	7.1	1.20	1620	—	numerical Hartree-Fock-Slater method. Functions are distributed over 2D space. Convergence with respect to mesh size.
[1]	19856-311+(sp3df) G	—	—	5.00-5.16	—	—	—	Coupled-cluster double excitation, with singles and triples taken into account by CCD (5.00) and MP4 (5.16) methods.
[239]	1983	[4s3p2d] G	—	5.56	1.17 ₁	1581	12.3	MCSCF, then multi-reference many-body perturbation theory.
[240]	1984	[4s2p1d] G	—	5.668	1.21 ₉	1664.0	11.19	Effective valence shell Hamiltonian;

^a G = Gaussian-type orbitals, S = Slater-type orbitals, A = atomic natural orbitals.

quasi-degenerate MBPT.									
[224]	1985	(4s3p2d) S	—	6.77	1.210	1564	10.5	Homonuclear diatomics used to test a momentum-space representation of the chemical bond.	
[225]	1987	[5s4p2d1f] G	—	5.31	—	—	—	Extended valence MCSCF; with only a few hundred configurations.	
[121]	1987	[4s2p1d] G	—	4.637	1.227	1600	—	Full-CI "benchmark" calculation. Found triple excitations very important in multiple bonds. CASSCF orbitals, MRCI-FCI	
This work	1988	[4s2p1d]+ BF(sp _d) G	-150.027669	5.271	—	—	—	MRD-CI with bond functions.	

Table 7.13 Energies of FO, SCl, SF, and ClO.

Calculations on FO and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total $\%c_1^2$	Est. F-Cl Energy	D_e (eV)	μ (Debye)
FO $X^2\Pi$, $R_e = 2.55892^a$ B.O. = 1.5 $D_e = 2.31$ eV ^b $\mu = 0.0069$ D ^c										
DZP	—	-174.169622	5	5094/38692	2.0	-174.489515	93.18	-174.508630	1.665	0.1584
DZP+(sp)	0.8	-174.172788	5	4778/55500	5.0	-174.506814	93.33	-174.526509	2.152	0.1616
DZP+2(sp)	0.6,1.8	-174.173860	5	4603/75336	8.0	-174.513338	93.38	-174.533306	2.337	0.1509
DZP+3(sp)	0.2,0.6,1.8	-174.175189	5	5386/98200	8.0	-174.516775	93.31	-174.537215	2.443	0.1178
DZP+(spd)	0.8	-174.173173	5	4581/85552	10.0	-174.526949	93.24	-174.543763	2.757	0.1413
DZP+2(spd)	0.7,2.1	-174.175501	5	4529/150764	12.0	-174.540221	93.47	-174.561756	3.111	0.1234
TZPP	—	-174.177270	5	4444/150764	15.0	-174.568484	93.55	-174.591250	1.607	0.1902
SCl $X^2\Pi$, $R_e = 3.73155^d$ B.O. = 1.5 $D_e = (3.6)$ eV ^e										
DZP	—	-856.988084	3	5416/24894	1.0	-857.241719	90.95	-857.263743	(1.91)	
DZP+(sp)	0.6	-856.996287	3	5794/35526	2.5	-857.263531	90.83	-857.287093	(2.55)	
DZP+2(sp)	0.3,0.9	-856.998758	3	6317/48046	3.5	-857.271960	90.65	-857.296607	(2.81)	
DZP+3(sp)	0.1,0.3,0.9	-856.999744	3	6757/62454	5.0	-857.274130	90.51	-857.299378	(2.88)	
DZP+(spd)	0.6	-856.998348	5	5732/25426	5.0	-857.278932	90.54	-857.304820	(3.03)	
DZP+2(spd)	0.3,0.9	-857.003090	2	5857/44282	8.0	-857.294220	90.29	-857.321878	(3.495)	
DZP+2(spd) ^f	0.3,0.9	-857.006613	2	5788/44282	8.0	-857.296612	90.25	-857.324104	3.495	0.1339
TZPP ^f	—	-857.016945	2	5530/69158	8.0	-857.306048	89.75	-857.335119	1.999	0.2327

^a Ref. [176].^b Ref. [179].^c Ref. [185]. Extrapolated.^d Ref. [188]. These calculations were carried out at 3.6 bohr and the D_e values have been adjusted.^e Ref. [186].^f Calculated at the proper R_e , 3.73155 bohr. Other D_e 's adjusted by 0.061 eV.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total % c_i^2	Est. F-CI Energy	D_e (eV)	μ (Debye)
SF $X^2\Pi$, $R_e = 3.02465^\circ$ B.O. = 1.5 $D_e = 3.4^\circ$ $\mu = 0.794(12)$ D $^\circ$										
DZP	—	-496.930755	3	5107/45511	1.0	-497.210707	91.97	-497.232125	2.748	1.1595
DZP+(sp)	0.8	-496.940341	3	5868/65387	2.0	-497.231998	91.98	-497.254320	3.352	1.1579
DZP+2(sp)	0.5,1.5	-496.940929	3	4367/88859	8.0	-497.235950	92.12	-497.258179	3.457	1.0995
DZP+3(sp)	0.17,0.51,1.53	-496.943038	3	6138/115927	6.0	-497.240387	91.70	-497.264586	3.632	0.8956
DZP+(spd)	0.65	-496.941486	3	5853/100889	6.0	-497.248234	92.01	-497.271691	3.825	1.1197
DZP+2(spd)	0.2,0.6	-496.944363	2	6694/44282	10.0	-497.255888	91.74	-497.281183	4.083	0.9345
TZPP	—	-496.947729	3	5433/226165	10.0	-497.284850	91.90	-497.311295	2.767	1.0263
ClO $X^2\Pi$, $R_e = 2.96617^\circ$ B.O. = 1.5 $D_e = 2.8032(4)$ eV $^\circ$ $\mu = 1.239(10)$ D $^\circ$										
DZP	—	-534.265729	4	6317/27394	1.0	-534.558240	91.70	-534.580999	1.878	1.3456
DZP+(sp)	0.8	-534.271506	4	5584/39160	4.0	-534.577175	91.82	-534.600678	2.413	1.2302
DZP+2(sp)	0.32,0.96	-534.274536	4	4305/53026	10.0	-534.584077	91.85	-534.607946	2.611	1.1066
DZP+3(sp)	0.2,0.6,1.8	-534.275197	4	4731/68992	10.0	-534.588773	91.69	-534.613520	2.763	1.0261
DZP+(spd)	0.71	-534.272643	4	4620/60108	10.0	-534.595789	91.95	-534.620347	2.948	1.1665
DZP+2(spd)	0.3,0.9	-534.277126	4	4857/105514	15.0	-534.609726	91.74	-534.635887	3.371	1.0879
TZPP	—	-534.282456	6	4364/476681	15.0	-534.623714	91.89	-534.649071	1.764	0.9808

* Ref. [191].

^ Ref. [199].

^ Ref. [197].

^ Ref. [200].

Table 7.14 Energies of F_2 , Cl_2 and ClF .Calculations on F_2 and its congeners with a variety of basis sets. Energies in hartree except where noted; distance in bohr.

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μh)	Extrapolated CI Energy	Total $\%c_1^2$	Est. F-Cl Energy	D_e (eV)
F_2 $X^1\Sigma_g^+$	$R_e=2.66816^a$	B.O. =	1	$D_e = 1.658$	eV ^b				
DZP	—	-198.734575	5	4795/19321	0.3	-199.091631	93.85	-199.108490	1.294
DZP+(sp)	0.8	-198.738741	6	4772/36298	0.5	-199.110028	93.92	-199.127604	1.815
DZP+2(sp)	0.7,2.1	-198.739312	6	4375/49742	1.0	-199.114705	93.93	-199.132540	1.949
DZP+3(sp)	0.2,0.6,1.8	-198.740100	6	5231/65284	1.0	-199.117002	93.63	-199.136490	2.057
DZP+(spd)	0.8	-198.739013	6	5046/56681	1.0	-199.132130	93.95	-199.150923	2.449
DZP+2(spd)	0.7,2.1	-198.741043	3	5439/21463	2.0	-199.140032	93.41	-199.162109	2.754
TZPP	—	-198.742463	5	5632/77246	2.0	-199.166096	93.77	-199.208874	1.23
Cl_2 $X^1\Sigma_g^+$	$R_e = 3.7566^a$	B.O. =	1	$D_e = 2.51398$	eV ^c				
DZP	—	-918.954066	2	2984/2984	0.0	-919.229291	91.42	-919.251663	1.68
DZP+(sp)	0.5	-918.968567	4	2896/24510	1.0	-919.259049	91.51	-919.281564	2.49
DZP+2(sp)	0.25,0.75	-918.968831	2	3431/5652	1.0	-919.266444	90.73	-919.292811	2.80
DZP+3(sp)	0.3,0.9,2.7	-918.969165	4	3923/43662	1.0	-919.271753	91.07	-919.297041	2.91
DZP+(spd)	0.5	-918.969546	6	3841/28005	1.0	-919.274117	91.25	-919.298605	2.95
DZP+2(spd)	0.3,0.9	-918.971020	3	5585/11092	1.0	-919.289027	90.31	-919.318557	3.50
TZPP	—	-918.983147	5	6114/121865	1.0	-919.306202	90.39	-919.334688	1.827

^a Ref. [18].^b Ref. [204].^c Ref. [207].

Basis Set	B.F. Exponent	SCF Energy	No. Mains	Selected/ Generated	T (μ h)	Extrapolated CI Energy	Total % c_i^2	Est. F-CI Energy	D_e (eV)	μ (Debye)
CIF $X^1\Sigma^+$ $R_e = 3.07707^a$ B.O. = 1 $D_e = 2.6066$ eV ^d $\mu = 0.885^e$										
DZP	—	-558.871051	3	3253/20739	1.0	-559.178729	92.32	-559.200386	2.039	1.2213
DZP+(sp)	0.8	-558.878151	5	4557/70055	1.0	-559.201061	92.62	-559.222137	2.631	1.1760
DZP+2(sp)	0.24,0.72	-558.880082	3	4627/40395	2.0	-559.205542	91.98	-559.229707	2.837	1.0215
DZP+3(sp)	0.24,0.72,2.16	-558.880435	3	5151/52659	2.0	-559.210059	91.77	-559.235991	3.008	1.0161
DZP+(spd)	0.72	-558.879086	2	5139/12586	2.0	-559.216661	91.97	-559.242548	3.186	1.1669
DZP+2(spd)	0.24,0.72	-558.881536	2	-588/21900	10.0	-559.227823	91.63	-559.255703	3.544	1.0186
TZPP	—	-558.887137	5	3601/245677	10.0	-559.260698	92.24	-559.286875	1.942	1.0509

^d Ref. [211]^e Ref. [101].

Table 7.15 Summary of previous work on F_2 ($X^1\Sigma_g^+$).

Reference	Year	Basis Set ^a	Absolute energy (hartree)	D_e (eV)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Method/Comments
[241]	1975	—	—	1.602	1.41193	916.64	11.236	Tabulated experimental values from absorption spectrum.
[242]	1972	(9σ5π) S	-198.98092 ^b	1.67	1.41	942	—	Optimized valence configuration (OVC) method.
			-198.88526 ^b	1.82	1.40	986	—	6-configuration MCSCF.
[230]	1975	[9s5p1d] G	-199.15400	—	1.411	945	14.0	CEPA
[222]	1982	—	—	3.3	1.38	1060	—	numerical Hartree-Fock-Slater method. Functions are distributed over 2D space. Convergence with respect to mesh size.
[243]	1984	[6s4p2d1f] G	-199.293170	1.591	1.420	—	—	Multi-reference SD-CI (280076 CSF's).
[1]	1985-311+(sp3df) G	—	—	1.46-1.56 ^c	—	—	—	Coupled-cluster double excitation, with singles and triples taken into account by CCD (1.46) and MP4 (1.56) methods.
[224]	1985	(4s3p2d) S	—	3.15	1.390	1073	7.1	Homonuclear diatomics used to test a momentum-space representation of the chemical bond.
[225]	1987	[5s3p2d1f] G	—	1.77	—	—	—	Extended valence MCSCF; with only a few hundred configurations.

^a G = Gaussian-type orbitals, S = Slater-type orbitals, A = atomic natural orbitals.^b At 2.68 bohr.^c A basis set of [7s6p4d2f] improved the D_e by only ≈ 0.1 eV.

[244]	1987	$[3s2p1d]$ G	—	1.91	1.423	894	—	Generalized valence bond (GVB)-CI.
[232]	1987	$[4s3p1d]$ G	-199.18832 ^d	1.221	1.4350	842	15.3	Linearized couple cluster method, with multiple reference configurations.
[227]	1987	—	-198.7741	—	1.412	—	—	Numerical Hartree-Fock
This work	1988	$[4s2p1d]+$ BF(sp) G	-199.127604	1.82	—	—	—	MRD-CI with bond functions

^d At 2.7 bohr.

Table 7.16

Summary of the bond orders (boldface type), ground states and equilibrium bond lengths (in bohr) used in calculating diatomics of the first- and second-row.

2	C₂	$X^1\Sigma_g^+$	2.34804	2.5	CN	$X^2\Sigma^+$	2.2144	3	CO	$X^1\Sigma^+$	2.132222	2.5	CF	$X^2\Pi$,	2.4034
	Si₂	$X^3\Sigma_g^-$	4.2444		SiP	$X^2\Pi_i$	3.98		SiS	$X^1\Sigma^+$	3.64589		SiCl	$X^2\Pi$,	3.889
	SiC	$X^3\Pi$	3.29		SiN	$X^2\Sigma^+$	2.9705		SiO	$X^1\Sigma^+$	2.85299		SiF	$X^2\Pi$,	3.0256
3	N₂	$X^1\Sigma_g^+$	2.07435	2.5	NO	$X^2\Pi_r$	2.17464	2	NF	$X^3\Sigma^-$	2.48873				
	P₂	$X^1\Sigma_g^+$	3.5780		PS	$X^2\Pi_r$	3.5858		PCl	$X^3\Sigma^-$	3.80706				
	PN	$X^1\Sigma^+$	2.81733		PO	$X^2\Pi_r$	2.7890		PF	$X^3\Sigma^-$	3.0041				
					NS	$X^2\Pi_r$	2.82329		NCl	$X^3\Sigma^-$	3.0508				
2	O₂	$X^3\Sigma_g^-$	2.28188	1.5	FO	$X^2\Pi_i$	2.55892								
	S₂	$X^3\Sigma_g^-$	3.57008		SCl	$X^2\Pi_i$	3.73155								
	SO	$X^3\Sigma^-$	2.79885		ClO	$X^2\Pi_i$	2.96617								
1	F₂	$X^1\Sigma_g^+$	2.66816												
	Cl₂	$X^1\Sigma_g^+$	3.7566												
	ClF	$X^1\Sigma^+$	3.07707												

Table 7.17

Bond orders (boldface) and dissociation energies (in eV) of diatomics of the first- and second-row: experimental *vs.* DZP (slanted typeface) results. Uncertain experimental values, and adjusted calculated values given in parentheses.

2	C ₂	6.32	5.72	2.5	CN	7.88	6.73	3	CO	11.23	10.22	2.5	CF	5.75	5.04
	Si ₂	3.24	(2.67)		SiP	(3.7)	(2.69)		SiS	6.38	5.34		SiCl	(4.1)	3.55
	SiC	(4.4)	(3.75)		SiN	(6.4)	3.53		SiO	8.33	6.99		SiF	(5.67)	5.07
3					CP	5.36	4.47		CS	7.43	6.55		CCl	(3.4)	3.45
	N ₂	9.91	8.35	2.5	NO	6.61	5.43	2	NF	3.63	2.60				
	P ₂	5.08	3.79		PS	4.57	(3.30)		PCl	(4.2)	(2.20)				
2	PN	6.20	4.99		PO	(5.5)	4.67		PF	(4.65)	3.63				
					NS	(5.1)	3.67		NCI	(2.9)	1.89				
	O ₂	5.21	4.44	1.5	FO	2.31	1.67								
1	S ₂	4.14	3.44		SCI	(3.6)	(1.91)								
	SO	5.43	4.11		CIO	2.80	1.88								
					SF	3.4	2.75								
1	F ₂	1.66	1.29												
	Cl ₂	2.51	1.68												
	ClF	2.61	2.04												

Table 7.19

Bond orders (boldface) and dissociation energies (in eV) of diatomics of the first- and second-row: experimental ^a. DZ + prescribed BF (slanted type) results.

2 (spd)	C ₂	6.32	6.33	2.5 3(sp)	CN	7.88	7.38	3 2(sp)	CO	11.23	11.65	2.5 3(sp)	CF	5.75	5.83
	Si ₂	3.24	(3.21)		SiP	(3.7)	(3.17)		SiS	6.38	6.53		SiCl	(4.1)	4.45
	SiC	(4.4)	(4.26)		SiN	(6.4)	4.14		SiO	8.33	8.35		SiF	(5.67)	6.05
					CP	5.36	5.06		CS	7.43	7.84		CCl	(3.4)	4.30
3 2(sp)	N ₂	9.91	9.96	2.5 3(sp)	NO	6.61	6.35	2 (spd)	NF	3.63	3.52				
	P ₂	5.08	4.89		PS	4.57	(3.95)		PCl	(4.2)	(3.18)				
	PN	6.2	6.23		PO	(5.5)	5.64		PF	4.65	4.61				
					NS	(5.1)	4.54		NCI	2.9	2.85				
2 (spd)	O ₂	5.21	5.47	1.5 2(sp)	FO	2.31	2.34								
	S ₂	4.14	4.48		SCI	(3.6)	(2.81)								
	SO	5.43	5.28		ClO	2.80	2.61								
1 (sp)	F ₂	1.66	1.82		SF	3.4	3.46								
	Cl ₂	2.51	2.49												
	ClF	2.61	2.63												

Table 7.21

Proposed dissociation energies for selected diatomics. Calculations carried out as noted in Table 7.16 using optimum BF basis set according to bond order. All energies in eV.

Molecule	Reference D_e	Calculated D_e	Predicted Range	Recheck
SiC	(4.4)	4.26	4.00—4.52	
SiP	(3.7)	3.17	2.98—3.36	*†
SiCl	(4.1)	4.45	4.18—4.72	*
SiF	(5.67)	6.05	5.69—6.41	*
CCl	(3.4)	4.30	4.04—4.56	*†
PS	4.57	3.95	3.71—4.19	*†
PO	(5.5)	5.64	5.30—5.98	
NS	(5.1)	4.54	4.27—4.81	*†
PCl	(4.2)	3.18	2.99—4.47	*†
SCl	(3.6)	2.81	2.64—2.98	*†

Chapter 8

The Dissociation Energy of Dichromium

The gem cannot be polished without friction, nor man perfected without trials.

(Chinese proverb)

8.1 Introduction

In principle the exact non-relativistic Born-Oppenheimer energy for a given molecule can be calculated by using an infinite basis set, and all possible excitations in a configuration interaction calculation. In practice, as the previous chapters show, full CI calculations with very large basis sets have been done for the diatomics of only the first or at most the second row.[†] For systems greater than this in size, as Chapter 2 noted, progress in quantum chemistry calculations has proceeded along two different fronts: the improvement of the techniques used to limit the CI space to the most strongly-contributing configurations, and other means of estimating the correlation energy; and the gradual eradication of the error caused by basis set incompleteness.

To push at the very frontiers is to gain a deeper understanding of the strengths and weaknesses of various *ab initio* approaches, and the relative importance of these two types of improvement. The calculation of the binding energy of dichromium—that famous “bête noire” of quantum chemistry[1]—is a case in point. This Chapter begins with a survey of nearly two decades of theoretical and experimental attempts to determine the binding energy and the potential energy curve for Cr_2 . Partial success in this difficult case has led and can lead to more insight than complete success for simpler systems. Then, the challenge presented by dichromium is taken up, and the results of calculations on it using the bond function/MRD-CI approach are presented and discussed.

[†] And even for these cases, the freezing discussed in Section 2.5 is crucial.

What makes dichromium such a challenge to *ab initio* methods? The short answer is, its size and complexity. Most *ab initio* calculations are concerned with first- and/or second-row atoms. The chromium atom, lying in the 3*d* period, will have as *minimum* basis requirement, 4*s*2*p*1*d* orbitals—almost double the number of minimum functions needed to describe a chlorine atom. Six valence electrons from each atom mean that a total of twelve electrons must be correlated in Cr₂. There are many low-lying states of dichromium, so significant mixing between other state configurations will occur. To top it all off, the atoms have very high multiplicity (⁷*S*) whereas Cr₂ (*X*¹Σ_g⁺) is closed-shell with a bond order of 6. The ability to recover the correlation error is strongly dependent on the multiplicity of the species; it is greatest when the electrons are distributed one to each orbital, so the Cr atom in this case has a significant advantage over the molecular form.

These factors all serve to make dichromium a most interesting source of “friction” against which to polish the bond function / MRD-CI approach. The huge configuration space which threatens to arise from so many orbitals with so many electrons and so many highly-contributing reference configurations, must be kept to a tractable size.[†] Clearly, selection/extrapolation techniques which were merely “economical” or “efficient” for smaller species, are now *sine qua non* for dichromium calculations. This Chapter will further show that some parameters which, on the basis of past experience, had been taken for granted, now become important considerations in setting up a perturbation-type of calculation.

Complementary to the bond function theme, Cr₂ also presents the largest bond order studied, yet paradoxically, has one of the smallest binding energies. The results from Chapter 7 indicate that a DZ basis set for a species with a bond order as high as that of dichromium will need *more* than 2 sets of (*spd*) orbitals (seen for cases of bond order three), and this is borne out in the first phase of the investigation. Results of multiple-reference extrapolated-CI calculations on dichromium at the equilibrium bond length are reported using basis sets which begin as strictly double-zeta. As in the preceding Chapter, where the phenomenon of bond order/bond function composition is explored, the Cr basis set is systematically augmented by polarization functions and/or a variety of bond functions. The best binding energy is obtained using a basis set consisting of [8*s*4*p*2*d*] + BF 2(*spd*), *f*.

[†] One recent estimate of configuration-interaction carried out on a CAS-SCF calculation using a roughly DZP-quality basis set projected a CI space of 57 million configurations.[2]

Then, in the second phase of the calculations, two types of estimates of the superposition error are discussed. The counterpoise correction is not a true indicator of the atomic basis set incompleteness; it is an overestimate in the case of BF's; and most importantly, it ignores the error due to molecular basis set incompleteness. Even the "worst case" correction shows that the use of BF's substantially improves the recovery of the D_e .

In the third phase of the calculations, the optimum basis set is used to generate a small portion of the Cr_2 curve. This curve appears to be highly sensitive to truncations in the CI approximation, and various levels of treatment (*e.g.*, number of reference configurations and size of selection threshold) will be explored. Thus, the increased focus on the finer points of the CI methodology used is a marked change from the former chapters, but a necessary one, for this complex and challenging diatomic.

8.2 Background

The binding energy for dichromium has proven to be a matter of controversy not just for theoretical chemists, but also for the experimentalists.[3] Table 8.1 outlines chronologically the developments of this work; two good recent reviews are [1] and [4]. As briefly described in Chapter 1, the D_e may be found experimentally using the second- and third-law methods. The nature of the errors inherent in the experimental determination have been discussed in Ref. [4]. The second-law method involves obtaining the enthalpies of sublimation and association from the Clausius-Clapeyron relationship. The third-law method, on the other hand, is based on statistical thermodynamics. It requires accurate knowledge of molecular parameters such as the equilibrium bond length and vibrational frequencies of the ground state as well as low-lying electronic states (which contain a non-negligible population at the high temperatures at which the experiments are performed).

As early as 1966, Kant and Strauss analyzed Knudsen cell-mass spectrometer data on Cr_2 . [3] They reported $D_e = 1.56 \pm 0.30$ eV using the third-law method, and $D_e = 1.78 \pm 0.35$ eV using the second-law method. Quite recently, Goodgame and Goddard have re-evaluated the D_e [5] using up-to-date R_e and ω_e values and have adjusted the third-law value to 2.0 ± 0.3 eV. Very recently, however, Hilpert and Ruthardt report a large discrepancy in their second- and third-law analysis of Knudsen cell-mass spectrometer data. [6] Similar to Ref. [3], their second-law value is a few tenths of an eV larger than the third-law value.

They are able to reconcile the difference by taking low-lying electronic states of Cr_2 into account.[6] They report $D_e = 1.47 \pm 0.06$ eV. Morse notes that since the error in the third-law binding energies is most often due to an underestimation of the number of lower-lying excited states, the D_e is typically an overestimate.[4] It is thus possible that the D_e is somewhat smaller than 1.47 eV.

The bond energy is surprisingly weak, considering that Cr_2 has twelve valence electrons, all in bonding MO's. Goodgame and Goddard also point out the strong anti-ferromagnetic effects which are induced as one atom with 6 "spins up" encounters another atom with 6 opposite spins. These stabilizing influences in the molecule are offset against the unusual stability of an atom of septet multiplicity. Also, the optimum bonding distance of the $4s-4s$ molecular orbital is significantly larger than the $3d-3d$ overlap length, so the former does not contribute substantially to the strength of a short bond.

The earliest calculations on Cr_2 were extended Hückel-type calculations.[7][9][8] They yielded positive D_e 's and "reasonable" bond lengths.[†] An early SCF calculation [10] showed an unbound dimer. The SCF is based on a single configuration which does not dissociate properly as the bond stretches. An MCSCF calculation around the same time, restricted by the antisymmetric product of strongly orthogonal geminals (APSG) method, yielded a D_e of 1.48 eV.[11] The A13G method permits a multiconfigurational wavefunction which will dissociate to the atoms in a weighted average of all the atomic states arising from the $4s^1 3d^5$ configuration, an asymptote which lies some 3 eV above the 7S atomic limit.

A more extensive MCSCF calculation, however, gave a very shallow potential energy curve with a large R_e . [12] The eigenvalue contribution of the ground state configuration was unusually low, at 10%. The MCSCF method is a more sophisticated method than extended Hückel theory, so a deterioration in results as the method improved could only be explained by a fortuitous cancellation of errors in the earlier cases. There was serious consideration given to the idea that Cr_2 might be a weakly bound antiferromagnetic dimer.

Such an hypothesis was first advanced by Goodgame and Goddard in 1981, on the basis of their calculations. They had used the generalized valence bond (GVB) method with corrections for van der Waals terms to find a $D_e = 0.35$ eV and an $R_e = 3.06$ Å.[13] With semi-empirical corrections for the atomic "self-Coulomb energy" the GVB method

[†] However, Ref. [7] predicted a $^3\Sigma_g^+$ ground state.

produces a double minimum at 1.61 and 3.06 Å with D_e of 1.86 and 0.3 eV, respectively.[5]

More discussion has appeared in the literature on ways of improving the methods of recovering the correlation energy than on ways of overcoming basis set deficiencies. Most standard basis sets are based upon the 14s9p5d GTO basis set developed by Wachters in 1970.[14] The best contraction, [8s4p2d], lowers the energy of the 5D atom by about 0.03 hartree, compared to the primitive (uncontracted) orbital case. Both the orbital exponents and contraction coefficients are optimized with respect to the 5D atom. The energy is comparable to that obtained by Huzinaga's (14s11p5d) GTO basis set.[15] In 1977 Hay argued that a successful basis set should be flexible enough to describe, not just the ground state atom, but also the excited electronic states of the atom. Diffuse 3d functions were added, and the contraction coefficients were re-optimized for the 7S atom. Some preliminary calculations on CrCO showed the importance of these functions in the molecular environment, as well as in the atom.[16]

Along the same lines of basis set improvement, a few years later McLean and Liu pointed out that a double-zeta basis set without polarization functions was an inadequate starting point, especially for any species containing a high- Z species such as chromium.[17] They obtained an energy lowering of 0.93 eV at the SCF stage, although the molecule remained unbound by about 20 eV at R_e . Salahub[1] dismisses the projected contribution of f orbitals to the D_e , "... since it [would imply] a binding energy contribution of f and g functions which surpasses that of the s and d orbitals." Two comments apply to this statement; the most obvious is that the lowering achieved by the f and g orbitals should be taken in the context of 1 eV out of a total of twenty or so eV by which the molecular minimum must be lowered, in order to observe binding, and not in the context of 1.5 eV, the experimental dissociation energy. In general, proponents of the local spin density approach remain quite skeptical about the inclusion of PFs in their basis sets.[†] The distinction must be emphasized between the mathematical function which is used to create the orbital and the electron which occupies that orbital in the ground state. For example, the LCAO σ_g orbital could be composed of g as well as s functions in its linear expansion. In this sense, the functions—which do not necessarily have to emulate H atom orbitals in their form—act only as a basis set for linear combinations. A given function *modelled* on the H atom d orbital, for instance, should not be interpreted as acting as a discrete molecular

[†] See, for example, Ref. [18].

entity, separate from the s and p orbitals. It would be fallacious to argue, in a similar vein to the statement made about *ab initio* work on Cr_2 , that because the N_2 energy dropped dramatically on adding polarization functions, it was due to the presence of d -shell binding. The polarization functions have only acted to increase the flexibility of the MO's created at the SCF stage, which effects some energetic lowering. Their greatest contribution is seen at the CI stage, when the greater number of virtual MO's enhances the CI description.

Some entries in Table 8.1[13][12][19][5] report a strikingly different bond length than that obtained (with remarkable reproducibility) in the gas-phase.[20][21] The much longer bonds were thought to correspond to a weakly bound antiferromagnetically coupled dimer. [13][22] Moskovits *et al.* suggest that these results (from fairly sophisticated theoretical treatments), along with the results of recent matrix isolation experiments, may indicate the presence of a double-minimum ground state potential.[23] This would agree with predictions made for the similar case of Mo_2 . [22][†] The bonding in the shallow outer well ($\omega_e \approx 80\text{--}100\text{ cm}^{-1}$ [24][23]) is attributed to $4s$ orbital overlap which becomes repulsive at shorter bond distances. The inner, deeper minimum would then be mainly due to overlap of the $3d$ orbitals. The most recent work by Goodgame and Goddard predicts an inner minimum of 1.86 eV at a distance of 1.6 Å and an outer minimum of 0.3 eV at 3.0 Å, with a barrier to conversion of 0.4 eV.[5]

The molecular vibrations of Cr_2 seem quite sensitive to the molecular environment. Comparing the gas-phase results[20] with matrix isolation studies of the dimer imbedded in argon[24] and xenon[23] matrices, the vibrational frequency is found to decrease by roughly $30\text{--}40\text{ cm}^{-1}$.

The local-spin density approach has proven useful in the description of the anti-ferromagnetism of bulk chromium[18] so this method has been applied to Cr_2 . [25][26][27][18] Table 8.1 illustrates some LSD results using different forms of the potential. The earliest such work on Cr_2 [25] reported binding only for the $^{13}\Sigma_g^+$ configuration (with a D_e of 0.2 eV) although the authors write it is unlikely to be the experimental ground state. They proposed that $^{11}\Sigma_u^+$ (unbound by 0.02 eV) or $^5\Sigma_g^+$ (by 1.9 eV) could be the true species observed.

[†] In this paper, however, the authors maintain that Cr_2 exists only in long-bond form, since the $3d$ overlaps are not strong enough at smaller R to overcome various repulsive interactions.

It is now agreed that the ground state of Cr_2 is of singlet multiplicity.[†] The problems with Ref. [25] stem from the $X\alpha$ approximation. It is recognized[18] that this approximation overestimates the exchange contribution, relative to the correlation, and does not give reliable results for R_e or D_e . [19][18] The R_e 's calculated using other forms of the LSD approach appear to be very close to the experimental value, but the D_e 's are almost uniformly overestimated. Baykara *et al.* note that while the charge density is of $D_{\infty h}$ symmetry, the spin density is actually $C_{\infty v}$ symmetry. The potential curves obtained differ markedly, depending on whether they are calculated with high or lower symmetry constraints. (The lower symmetry means that the antiferromagnetic configuration is allowed.) [18]

A comparison of the two extremes of bonding in Cr_2 arises by considering the orbital occupation. The orbital occupation for a short-bond model[28] reports:

$$\sigma_g^{1.78} \sigma_g^{1.92} \pi_u^{3.62} \delta_g^{3.20} \delta_u^{0.80} \sigma_u^{0.22} \pi_g^{0.38} \sigma_u^{0.08} \quad (8.1)$$

to give a bond order of 4.52. The orbital occupation for a long-bond model[12] reports:

$$\sigma_g^{1.65} \sigma_g^{1.08} \pi_u^{2.14} \delta_g^{2.04} \delta_u^{1.96} \sigma_u^{0.35} \pi_g^{1.86} \sigma_u^{0.92} \quad (8.2)$$

where the anti-bonding orbitals have a significantly greater occupation, to give a bond order of only 0.91.

In their investigation of the $A \leftarrow X$ transition, Riley *et al.* remark that the values of ω_e and $\omega_e x_e$ cannot be accurately determined without measurement of additional vibrational levels. For example, the value for ω_e could range from 472.7 to 493.3 cm^{-1} , and the value of $\omega_e x_e$ could lie between 10.2 and 20.5 cm^{-1} , depending whether a Morse potential is assumed, or an expansion in powers of $(R - R_e)$ is used. [21]

Riley *et al.* postulate that the spectrum they observe in their two-colour resonance-enhanced ionization experiment may be due to the transition from an $A^1\Sigma_u^+$ state with a double minimum to the ground state which is quite regular in appearance. It would, however, be possible to observe the *same energy gaps as were observed if the ground state, and not the excited state, contained the double minimum.* This is clearly a case where calculations of the X and A state curves need to be done, and fortunately a basis set has been found which will give a ground state with reasonable binding energy.

[†] Efremov *et al.* unequivocally established the observed transition as $^1\Sigma \rightarrow ^1\Sigma$; only confirmation of the identity of the species producing the spectrum was required. [43]

8.3 Methods

8.3.1 Atoms

The atomic energies for the chromium atom using different basis sets were calculated in a straightforward way. The (14s9p5d) GTO basis set reported in Ref. [14] was augmented by an extra diffuse *d* function of exponent 0.0912 as recommended by Ref. [16]. (The *d* functions consist of 6-component Cartesian orbitals.) The uncontracted SCF energy for the Cr (7S) atom was found to be -1043.334656 hartree. This is only 0.59 eV above the recently-reported numerical Hartree-Fock value of -1043.35641 hartree.[29] The contraction scheme for the *s* and *p* orbitals followed that of Ref. [14]'s contraction 1, namely, 62111111 and 5112 respectively. For the *d* orbitals, the "augmented (5d)" primitive orbitals were contracted to [3d] by a 411 scheme whose coefficients are as given by Hay. [16] The SCF energy of the chromium atom basis set upon contraction to [8s4p3d] was thereby found to be -1043.292704 hartree. Hay reports an energy of -1043.328709 hartree for the same basis, using a spatially unrestricted Hartree-Fock program, which differs from the current value by 0.98 eV. (As a means of comparison, the SCF energy obtained by Wachters and the spatially-unrestricted energy obtained by Hay for identical unaugmented 5d-type basis sets differ by 0.88 eV.)

The argon core was frozen, i.e., the electron pairs in orbitals corresponding to ground-state argon were retained in these orbitals, so that a configuration-interaction (CI) calculation was done using only the 6 remaining valence electrons. All single and double excitations with *S* symmetry and septet multiplicity were then generated from the ground-state configuration, to form a total singles and doubles CI space of 583. The ground state occupation accounted for 97.3% of the total wavefunction. The lowest CI eigenvalue was -1043.343711 hartree, and the Davidson estimate [30] of the CI energy with quadruple excitations included was -1043.345095 hartree. Thus, configuration-interaction resulted in an energy lowering of 1.43 eV from the SCF energy.

The [8s4p2d] basis set used in this work followed the same contraction as the [3d] basis, except that the diffuse *d* orbital ($\alpha = 0.0912$) was omitted. This yielded an SCF energy of -1043.25717 hartree. The CI space consisted of 277 symmetry-adapted configurations, and the estimated full-CI energy was -1043.296628 hartree. The [2d] $\rightarrow$ [3d] change thus

destabilizes the SCF energy by 0.96 eV, and the CI energy by 1.32 eV. By comparison, Hay reports a difference of 1.0 eV between the [2*d*] and [3*d*] types of contraction.[16]

Then sets of 10-component Cartesian *f* functions were added to the [2*d*] and [3*d*] basis sets obtained above. The diffuse *f* orbitals ($\alpha = 0.1$) did not lower the atomic energies as significantly as the more contracted ($\alpha = 1.0$) polarization exponents. The results for all atomic calculations are summarized in Table 8.3.

8.3.2 Dimer

As with the atomic calculations, the molecular calculations were also carried out in D_{2h} symmetry. The nuclear centres were separated by a distance of 3.1725 bohr, corresponding to the experimental bond length[20] for the first section of the calculations, and for the second half, *R* was varied from 2.9 to 3.5 bohr. Bond functions, i.e., atomic orbitals centred at a "nucleus" of zero charge, were added to the bond midpoint.

The SCF energy was calculated with a ground state occupation of

$$4s\sigma_g^2 3d\sigma_g^2 3d\pi_{xu}^2 3d\pi_{yu}^2 3d\delta_{xyg}^2 3d\delta_{x^2-y^2g}^2. \quad (8.3)$$

Interestingly enough, an SCF occupation with a $3d\delta_{xyu}^2$ pair instead of a $3d\delta_{xyg}^2$ pair yielded an SCF energy which was 0.2 hartree lower still. However, the CI energy calculated with MO's constructed from the latter case was about 0.1 hartree higher than that obtained using MO's from the former case.

The calculation of a short portion of the Cr_2 curve close to the R_e required a slightly different approach than that used to study basis set effects only at R_e . Although previous work on simpler diatomics showed the mains required at R_e were sufficient at bond lengths $R \leq R_e$, [31][32] this is not the case for Cr_2 . The c_i^2 contributions naturally change drastically as *R* grows larger than R_e since the $\text{Cr} \dots \text{Cr}$ moiety close to dissociation has 12 open shells, and even at *R* slightly larger than R_e , mains with substantial open-shell character are required. A very restricted portion of the curve, from 2.9 to 3.5 bohr, was considered. For optimum smoothness of the curve, it is preferable to use the same set of reference configurations throughout, which meant adding four, and eventually as many as 17, more mains to the set used for the optimum basis ($\text{DZ} + 2(\text{spd}), f$). Furthermore, for one curve, a set of natural orbitals (NO's) was generated from the original set of MO's and an estimated full-CI energy was obtained using these NO's in an analogous manner.

The energies obtained as R varied were then least-squares-fit to a 3-parameter Morse curve. Some energy levels were determined for this curve, and these values were then least-squares-fit to a 2 parameter spectroscopic equation to obtain ω_e and $\omega_e x_e$.

8.4 Results and Discussion

8.4.1 Atomic Calculations

Table 8.2 gives the exponents and coefficients of the atomic $[8s4p3d]$ basis set used in this work. Omission of the last d function with exponent 0.0912 gives the $[8s4p2d]$ basis set.

Table 8.3 shows the results of the atomic calculations. Comparing the $[8s4p3d]$ (from now on, 'DZ*') atomic energy with the $[8s4p2d]$ ('DZ') results, it is seen that the third d function acts to lower the atomic energy by 1.32 eV at the estimated full CI level, so that the sum of the two atoms is lowered a total of 2.64 eV. This lowering is fairly constant, for DZ *vs.* DZ* basis sets, even when f functions are added to either basis set to act as polarization functions ('PF's) as recommended by McLean and Liu.[17]

Table 8.3 also shows that the change which occurs upon addition of polarization functions to the atoms depends strongly on the choice of exponent. For both the DZ and DZ* cases, a set of compact f orbitals lowers the atomic energy by 0.7 and 0.6 eV, respectively. A set of diffuse f orbitals lowers the atoms in both the DZ and DZ* cases less than 0.1 eV. For either choice of exponent, the DZ case has a slightly greater lowering brought on by adding the f function, than in the DZ* case. The effect is predictably small, since the third d set, which is a valence-shell-type of orbital, does not act in the same fashion as a polarization function.

8.4.2 Molecular Calculations: Basis Set Explorations

This initial phase of the Cr_2 calculations assumes the error lies predominantly in the basis set truncation. More explicitly, a balance is sought between atomic and molecular descriptions, since the basis set size is quite restrictive, and the discussion in this section focusses on how to achieve that balance. The results of these calculations are summarized in Table 8.4(a) for basis sets which start with DZ, and in Table 8.4(b) for basis sets beginning with the DZ* atomic-centred orbitals.

8.4.2.1 DZ vs. DZ*

In the preceding section, it was seen that the extra d function lowered the sum of the two atoms by 2.6 eV. This has been an atom-biased improvement, however, because the atom has benefitted more from this basis set change than has the molecule. Table 8.4(b) shows that the D_e of the DZ* molecule is -3.91 eV, which is worse than the D_e of the DZ molecule, shown in Table 8.4(a) as -2.73 eV.

Nor does the presence of polarization functions in the molecule affect the conclusions one can draw about the presence of that third d function. Although going from DZP to DZ*P lowered the absolute atomic energy by 1.2 (f exponent, $\zeta_f = 0.1$) and 1.3 eV ($\zeta_f = 1.0$), the D_e was improved by only half as much, 0.7 and 0.6 eV, respectively. In all cases the DZ* basis set represents an improvement mainly for the atom and less so for the molecule.

8.4.2.2 DZ vs. DZP

Unlike the unequivocally atom-biased improvement of the third d set, Table 8.4(a) shows that the addition of polarization functions to a basis set may be *either* an atom- or a molecule-biased improvement, depending on the PF's compactness. The compact PF lowers the sum of the absolute energies of the atoms by 1.46 eV and yet the D_e is improved by only 0.5 eV, to a value of -2.26 eV. The diffuse PF has improved the atoms by a much smaller extent, 0.11 eV, so the improvement of the D_e by 0.26 eV (to give -2.47 eV) has, by contrast, been a molecule-biased basis set improvement. Both nuclear-centered basis sets show that the molecule is unbound with respect to the separated atoms. This is true even though a large number of reference configurations (up to 43) have been used to improve the CI treatment, and is consistent with previous *ab initio* results. The relatively small improvement in D_e on addition of f -functions (20 additional AO's, 0.5 eV improvement) shows the slow trend toward bonding with added nuclear-centered polarization functions. Since the CI space generated in D_{2h} symmetry also grows from 392,000 to 841,000 on addition of f -functions, the size of the calculation is growing rapidly. Additional calculations using the DZ* and DZ*P basis sets generated even larger CI spaces but gave even more negative dissociation energies, an indication that the atom was being more stabilized than the molecule by the extra atom-centred functions.

These are in fact the best binding energies obtained by any of the atom-centred basis

sets. A total of twenty more (Cartesian) orbitals has been added to the basis set, yet the improvement has been small, in comparison to the greater complexity of the calculation. Along the same lines, McLean and Liu reported an SCF-level improvement in energy of a very small amount when they extended the chromium basis set to include *g* functions.[17] If the problem of Cr_2 is viewed as more than just a question of CI space truncation error, i.e., if it is seen as a question of overcoming the basis set incompleteness, then it is apparent why conventional methods have not yielded satisfactory results. The addition of PF's is not the most efficient way to satisfy the basis set incompleteness for third row and higher elements.

8.4.2.3 DZ* vs. DZ*P

Table 8.4(b) shows that the conclusions regarding the addition of PF's to a DZ* basis set are similar to those made for the DZ case. The compact PF's have lowered the sum of the atomic energies fairly dramatically, by 1.25 eV. The D_e , however, is improved by somewhat less, about 1 eV, to a value of -2.89 eV; again, it is an atom-biased improvement. Previously, it was seen that the diffuse PF's had little effect on the atoms, causing a drop of 0.16 eV in the sum of the atomic energies. The D_e is, in contrast, improved by about 0.8 eV, to a value of -3.07 eV. As with the DZ case, the diffuse *f* function is a molecule-biased improvement whereas the compact *f* function is an atom-biased improvement.

8.4.2.4 DZ vs. DZ+BF's

The sum of the separated atoms is assumed to be identical, within the error for size consistency (about 0.0004 hartree[33]), since as the nuclei are pulled apart, the overlap of the central orbitals with those of the separating atoms goes to zero. Bond functions are thus a *purely molecule-biased improvement* to any basis set.

When no BF's are added to the basis set, the DZ molecular energy lies *above* the sum of the estimated full-CI energies of the atoms, by 2.73 eV. The addition of sets of (*spd*) bond functions improved the results. A single set of bond functions (BF's) with exponent 0.4, when added to the DZ basis, changed D_e from -2.73 eV to -1.43 eV. Comparing the DZ results with the DZ + 2(*spd*) results in Table 8.4(a), it is seen that the addition of bond functions brings about a dramatic improvement in the molecular description: a 1.6 eV lowering for the more compact (1.0, 0.4) set, and a 3.5 eV lowering for the more diffuse (0.1, 0.4) set, to give a positive binding energy. A BF composition of 2(*spd*) added to a

DZP basis set had been found optimum for the N_2 case, which has a bond order of three. From first principles Cr_2 is known to have a bond order of six, although it has been argued that at short bond lengths the overlap of the 4s orbitals is negligible and the bond order is closer to five.[28] At any rate, given that the bond order is greater than three and that the basis set is also of double-zeta quality, it comes as no surprise that the D_e is somewhat underestimated with a BF of two sets of (*spd*) orbitals. *It is consistent with previous trends which link BF composition with bond order.* More BF's were needed for Cr_2 , and so the addition of a set of *f* orbitals, as well as of another set of (*spd*) orbitals was investigated.

Three sets of (*spd*) BF's gave an additional improvement, to +1.11 eV. This basis set contains 64 nuclear AO's and 30 BF's. Even better is the 2(*spd*)1*f* set of BF's (also 30 BF's) which gave the largest D_e value reported here, +1.23 eV.

Table 8.4(a) shows the effect of adding a BF of 2(*spd*) + *f*. To examine the influence of ζ_f , the (*spd*) sets were restricted to the 'best' exponents, as seen from the 2(*spd*) exercise, i.e., 0.1 and 0.4. A mid-range value of 0.4 for the *f* exponent seems especially good, and the D_e grows to its "best ever" value of 1.23 eV. When the *f* set is very diffuse (0.1), then the D_e is 0.70 eV.

A comparison of the 2(*spd*) BF and the 2(*spd*) + *f* BF shows that the SCF energies differ very little, since the *f* set does not mix in significantly with the occupied orbitals. The effect of the *f* orbitals is most strongly felt at the CI stage, where the *f* set can mix in with the δ_g^* molecular orbital. When the *f* set has a mid-range exponent ($\zeta = 0.4$), it is a worthwhile addition to the basis set. When the *f* exponent is very diffuse, the D_e in fact deteriorates very slightly, compared to a simple 2(*spd*) BF. (The est. F-CI results are opposite to the effect observed at the SCF level, where the more diffuse exponent yields a greater energetic lowering.)

A BF comprised of three sets of (*spd*) functions improved the D_e by 3.8 eV, compared to the no-BF case. The third set of (*spd*) functions represents the addition of some ten more BF's to the 2(*spd*) basis set. The third set (which is quite compact, with $\zeta = 1.0$) has a small effect, compared to that observed with the first two sets of (diffuse) BF's. This likely indicates the basis set is nearing saturation, especially in the more compact range of exponent.

An interesting question is, does the effect of adding more bond functions depend a

great deal on the nature of the orbitals added? (The size of the exponent has been seen to cause a shift in the D_e by as much as half an eV.) For Cartesian orbitals, a BF composed of two sets of (spd) functions and a set of f orbitals has as many functions as a BF of $3(sp)$. From Table 8.4(a) it is seen that the D_e for the $3(sp)$ BF is 1.11 eV; for the $2(sp) + f$ BF it is 1.23 eV ($\zeta_f = 0.4$) or 0.70 eV ($\zeta_f = 0.1$). Thus, adding an f set can have a greater or lesser effect on the D_e than adding a set of (spd) functions, depending on whether the ζ_f is diffuse or not. *Both the size and the composition of the orbitals of the bond function seem to play a role in improving the molecular description.*

8.4.2.5 DZ^* vs. $DZ^* + \text{BF's}$

Table 8.4(b) shows the D_e 's obtained by adding a variety of BF's to the DZ^* basis set. Along the same lines as the DZ case, the molecular energy of the DZ^* basis set with no BF's lies well above the atomic asymptote, by 3.91 eV. When a BF of $2(sp)$ was added, the compact set increased the D_e by 1.57 eV (to give -2.34 eV), whereas the diffuse set increased the D_e by 2 eV (to -1.88 eV). Adding 20 BF's did not lower the absolute energy of the molecule as much as adding 20 PF's (2 sets of f orbitals) but since the atomic energy is unchanged, D_e improves.

8.4.2.6 $DZ + 2(sp)$ vs. $DZ^* + 2(sp)$

The section comparing DZ with DZ^* results without BF's showed clearly that balancing the atomic and molecular description was important: the D_e was improved by 1.2 eV by using a basis set which was not optimized so strongly for the atoms. When compact BF's are added to the basis sets, the DZ case has a D_e of -1.13 eV, and the DZ^* case, a D_e of -2.34 eV. Although the BF's have improved the D_e 's relative to the non-BF basis sets, the DZ vs. DZ^* improvement with BF's still stands at 1.2 eV, even with BF's added.

This is not the case with the more diffuse set of BF's: here it is seen that the $DZ + 2(sp)$ basis has a D_e of 0.78 eV, whereas its DZ^* analogue has a D_e of only -1.88 eV. This is a difference of 2.7 eV when the diffuse BF's are used. The improvement in the D_e is thus due to *more* than the addition of the third d function. The BF's have a smaller incremental effect when they are added to a larger beginning AO basis set. This result is consistent with earlier work which showed that an (sp) BF was optimum for a DZP basis for H_2 , but that on increasing the atomic basis to TZPP quality, the optimum BF had also increased in size to $2(sp)$. [31]

8.4.2.7 DZP vs. DZP +2(sp) + d

Understanding the effects due to basis set changes when both PF's and BF's are present becomes a little more complex, because the compactness of both the polarization and bond function exponents must be taken into account, and the total number of orbitals becomes a restriction.

In all four cases of BF 2(sp) + d reported in Table 8.4(a), the two (sp) exponents have been maintained as fairly diffuse, at 0.1 and 0.4. Only the PF (f) and BF (d) exponents have been varied. Table 8.4(a) shows that the BF generally improves the D_e by 2 to 2.5 eV. It appears that whether the PF is diffuse or not, the more diffuse d BF is better. The "best case" is a compact PF and a diffuse d BF.

8.4.2.8 DZ*P vs. DZ*P +2(s)

The investigation of adding BF's to a DZ*P basis set was severely hampered by the large number (96) of AO functions already present. From Table 8.4(b), adding two s BF's is seen to have a small effect (0.1 eV) when the PF is compact, regardless of the compactness of the BF. When the PF is diffuse, then a less diffuse BF seems preferable, and the two s functions can lower the D_e by as much as 0.5 eV. This lowering may seem quite remarkable, given that there are over 90 atom-centred functions and only 2 functions which are located in the mid-bond region. The dramatic improvement in the D_e for a basis set which is considered to be very good for the atom emphasizes the need to consider the molecular basis set incompleteness.

From the results discussed in detail in Sections 8.4.2.1 to 8.4.2.8, it is evident that further improvements will result from 3-point optimization of the BF exponents. Also, a larger number of BF's should be used to achieve a balanced description for the DZF nuclear basis; a rough figure would be approximately two (valence + polarization) AO's to one bond function, but this also depends on the nature of the multiple bonding situation. Finally, it is worth noting that the Davidson correction increases D_e by up to 1 eV, because of the relatively incomplete CI wave function (total c_i^2 values around 88%). This places a larger emphasis on the validity of this correction than is desirable; however, this is known to be part of the difficulty in achieving an adequate treatment for the Cr₂ problem. An

alternative starting point for the SCF with more open-shell character, or use of natural orbitals, may help to overcome this problem.

The dissociation energy of Cr_2 is shown to be sensitive not only to the extent of the CI calculation, as has been discussed in the literature,[1] but also to the specific composition of the basis set. Systematic inclusion of bond functions into the Cr_2 basis set, plus use of a large multireference CI calculation, shows that dissociation energies become positive and binding can result. Using a DZ nuclear basis set and $2(sp\bar{d}), 1f$ bond functions resulted in $D_e = +1.23$ eV. Further basis set optimization would be expected to increase D_e slightly, providing a basis set which would be a good starting point for construction of the Cr_2 potential curve. Similar trends were noted for the DZP basis set, although not enough bond functions could be added in this case due to program limitations.

8.4.3 BSSE Corrections

The utility and validity of the counterpoise correction, which is the most commonly-used method to estimate the basis set superposition error (BSSE)[34] have been recently questioned.[35][36][37] For a homonuclear diatomic, it is certainly an overestimate.[38] To say that BF's work only through BSSE is to ignore the real lowering effects of BF's. For example, a hydrogen basis set yields an atomic energy for hydrogen which lies only 2 μ hartree above its true energy. An estimate of the BSSE thus can show a lowering of 4 μ hartree at most. Yet when the BF's are added to the basis set, the molecular energy can be lowered by nearly 20 millihartree.[39]

For a basis set such as chromium's, which is known to be incomplete for the atom, it is impossible to sort out exactly which lowering of the absolute molecular energy is due to BSSE artefact and which is a genuine improvement in the molecular description.[40]

Nonetheless it is of interest to consider the sensitivity of these results to possible basis set superposition effects, as measured by the "counterpoise correction," since the Cr basis set is far from complete. For a subset of the basis set results reported in Tables 8.3, 8.4(a) and 8.4(b), Table 8.5 shows Δ , the difference between the atomic energy when only the atomic-centred AO's for Cr are used; and the atomic energy when a set of ghost orbitals is located at the second Cr centre as well as (where indicated) a set of BF's is located at the bond midpoint.

$$\Delta = E_{\text{Cr}} - E_{\text{Cr}-X_{\text{BF}}-X_{\text{Cr}}} \quad (8.4)$$

Although whether to correct potential curves for such effects by using all orbitals or "virtinals only" is a matter of current debate in the literature—or whether the "correction" should be made at all, as Ref. [40] and Chapter 9 in this work argues—for the present purpose we apply the standard all-orbitals Boys-Bernardi function counterpoise correction[34] to the molecular full-CI (est.) energy, i.e.,

$$D'_e = E_{Cr_2} - 2E_{Cr-X_{BF}-X_{Cr}} \quad (8.5)$$

This is labelled Correction I in Table 8.5.

In the case of bond functions this clearly leads to an overcorrection,[38] since a set of orbitals which must be shared equally between the atoms is counted twice. A more reasonable correction, labelled Correction II in Table 8.5, avoids grossly overestimating the lowering due to the BF.

$$D''_e = E_{Cr_2} - E_{Cr-X_{BF}-X_{Cr}} - E_{Cr-X_{Cr}}, \quad (8.6)$$

although the validity of this correction is still questionable.

Comparing the results for the DZ atomic-centred set to the results for the "best" basis set which adds a 2(*spd*), *f* BF to the same set, it is seen that the regular or uncorrected D_e 's differ by 3.9 eV. The Δ of the DZ basis is 0.2 eV whereas the Δ for the DZ+BF basis set is 1.5 eV, not surprising since the BF is much closer and the overlap with the nuclear-centred AO's is correspondingly greater.

If the BF's succeeded only due to superposition error, little or no difference between the corrected D_e 's of the DZ and "best" basis sets would be expected. However, it is seen that Correction I—the "worst case," an overestimate—*still* reveals an improvement of 1.4 eV in the D_e on going from a DZ to a DZ+BF basis set. A more reasonable "correction" for the BSSE (which is arguably a correction at all, as Chapter 9 discusses in more detail) for the best basis set (Corr. II) means the molecule is unbound by 0.5 eV but this is still a significant improvement over the (uncorrected) DZ value of -2.7 eV or the (uncorrected) DZP D_e of -2.3 eV. Martin *et al.* concur with the inclination of this group, not to counterpoise-correct, when BF's are used for a non-van der Waals' species.[40]

8.4.4 Potential Energy Curves and Spectroscopic Constants for Cr_2

To illustrate the effectiveness of the BF-optimization approach to obtain not only an improved D_e but also a reasonable curve shape, a small portion of the curve was studied, and

the results of these preliminary calculations are reported. As indicated in the Introduction, what was a simple extension of basis set exploration to potential curve generation in previous Chapters, did not prove to be a simple undertaking. Re-examination of the selection-extrapolation technique led to modifications, to handle increases in the number of open-shells specifiable as main configurations; in the size of test secular equation; and in the size of CI space which could be diagonalized.

8.4.4.1 Use of Natural Orbitals

To improve the Σc_i^2 natural orbitals (NO's) were generated and used to obtain the (est.)full-CI energies used to construct the curve given in Table 8.6, which shows values obtained using both MO's and NO's for reference.

Table 8.6 shows that the SCF energies (determined from a ground state occupation) led to a minimum at an R less than R_e , in fact, even smaller than 2.9 bohr. This emphasizes the poor description of the molecular state by a single configuration. Due to program limitations the main configurations used in the selection scheme were restricted in total number and in degree of excitation (a maximum of four open shells possible in this version, although some 6 and 8 open shell configurations contributed more than 1 per cent to the total wavefunction). The noise in the points in Table 8.6 is attributable to these restrictions, and not to the use of BF's, as may be seen by calculating the same portion of the curve with only an atomic-centred basis.

Increasing the number of mains, to accomodate those required at different geometries, influenced the energy calculated at the experimental R_e more than expected, based on previous experience with first- and second-row species (1.18 eV for 38M2R calculation *vs.* 1.23 eV in Table 8.4(a) for 34M2R) and the use of NO's has lowered it slightly (1.25 eV, again with 38M2R) so an estimate of the noise inherent in the calculation would be 0.07 eV. A 3-parameter Morse fit of the NO's' energies gave $D_e = 1.30 \pm 0.03$ eV, $R_e = 3.19 \pm 0.02$ bohr and $\beta = 1.58 \pm 0.16$ bohr⁻¹. The root mean square deviation of these points was 0.04 eV. By comparison, the curve from the energies determined using MO's was less noisy, with an r.m.s. deviation of 0.03 eV but the parameters showed less agreement with the experimental values. The well-depth is 1.18 ± 0.02 eV, $R_e = 3.23 \pm 0.02$ bohr, and $\beta = 1.51 \pm 0.11$ bohr⁻¹. The Schrödinger equation was then solved for the five lowest vibrational energy levels using the Numerov-Cooley algorithm,[41] using 51.9961

a.m.u. for the chromium atom mass.[42] Levels $v = 0-4$ were fit to a two-parameter spectroscopic equation to obtain (for the NO's case) $\omega_e = 490 \text{ cm}^{-1}$ and $\omega_e x_e = 6 \text{ cm}^{-1}$. The potential curve constructed from MO's energies alone gave $\omega_e = 450 \text{ cm}^{-1}$ and $\omega_e x_e = 5 \text{ cm}^{-1}$. Although both curves are not without noise, the spectroscopic constants are in good agreement with experiment (470 and 9 cm^{-1}),[44] and represent the best *ab initio* constants to date. (See Table 6 in Ref. [6].)

8.4.4.2 Mains and CI Space Dependence

Further attempts made to refine the curve centred around increasing the maximum number of open shells the configurations could have; and increasing the size of the CI space. The former is necessary because, as noted in the Background section, Cr_2 dissociation involves a closed-shell hextuple bond, creating a 12-open-shell supermolecule. Even at small R distances, open-shell mains contributed substantially (*e.g.*, the 6- and 8- open-shell contributions of about one per cent for the first curve). As noted in Chapter 2, a single multi-open-shell main configuration can mean many symmetry-adapted functions (SAF's) are added to the test secular equation[†] so the size of the test secular equation grows. The CI space should also be expanded, to accommodate the increasing number of configurations.

An unexpected sensitivity to the level of CI treatment in these respects was found. Table 8.7 summarizes four curves constructed with slight variations in treatment; in each case the calculation used the MO's created at the SCF stage to generate configurations. Table 8.8 summarizes the Morse parameters and spectroscopic constants obtained from least-squares fits of the data for these curves and the 38-main curves using MO's and NO's from the previous subsection.

To begin with, the inclusion of a second root in the selection criteria favoured the addition of a dozen new configurations to the set of main reference configurations,[‡] including three 6-open-shell configurations,* and the calculation was carried out at a slightly lower threshold. Increasing the number of mains led to a dramatic shift in the dissociation energy and the fundamental frequency, leading to a discouraging 200 cm^{-1} error in the latter. This is the lowest-lying curve in Figure 8.1.

[†] For example, a 4-open-shell singlet represents two SAF's; and 8-open-shell singlet gives 12 SAF's.

[‡] This required some revision to the PARK program, to work with a larger test secular equation.

* The TABLE, PARK and RUMPLE programs required modification to handle the 6- and 8-open-shell configurations, and the single and double excitations generated therefrom.

Secondly, the effect of adding in three more highly open-shell configurations was tested. These configurations did not contribute significantly to the ground state wavefunction, and contributed only somewhat to the higher-lying root, but as Table 8.8 shows, a 53-main 2-root calculation using the same threshold as the previous 50-main calculation ($8 \mu\text{hartree}$) shifted the D_e significantly upwards and decreased the fundamental frequency, so that it was within 100 cm^{-1} of the experimental value. This is the highest-lying curve in Figure 8.1.

Table 8.7 shows that the size of the generated CI space was now well above 3 million. Of this, only 10–12,000 configurations were being selected to form the actual CI space. The sum of the energy lowerings created by those test configurations which were discarded from the extrapolation CI space (summed individually, so this is just an estimate of the size of the extrapolations) was 70–90 millihartree, or over 2 eV, so the selection threshold T was decreased to $5 \mu\text{hartree}$. This resulted in a CI size of about 16,000 and a sum of energy lowerings from discarded configurations of 50–80 millihartree. The curve changed, to give a well depth of about 1.3 eV. Figure 8.1 shows this curve lies close to the 50-main curve. An extra fine grid was chosen close to the experimental R_e to examine the noise level. As with the other curves, the noise affected the precision of the fit, and depending on which range of R values was chosen, the ω_e could change by 20 cm^{-1} .

It should be emphasized that for each curve, the *same* set of mains was used throughout. The noise was attributed to the extremely restricted CI space; a threshold size of $5 \mu\text{hartree}$ was leading to a selection of only *one-half of one percent* of the generated configurations. Compare this to the largest of all the previous calculations, which had about 5000 selected configurations out of 350,000 or less generated configurations (1.4% or greater, ratio of actual CI space to total available). The size of this CI space was increased, and the last set of points in Table 8.7 shows a small region of the curve calculated with $T=2\mu\text{hartree}$, leading to about 28,000 selected configurations, or nearly one percent of the number of generated configurations.[†] When the CI space increased, two new mains appeared to contribute more to the ground state wavefunction, so these were added to the set of reference configurations. The sum of energy lowerings for the discarded configurations dropped to 30 to 40 millihartree—still over 1 eV. These points are not plotted, but it is easy to see that they would lead to a substantially larger D_e and a flatter curve (lower ω_e).

[†] This also involved some program revisions to PARK, RUMPLE and GRIZZLY.

Overall, Table 8.8 shows a relatively wide variance in D_e over curves calculated with the same basis set, compared to the level of accuracy and precision observed for calculations reported in previous chapters, but this variation is understandable. The range of D_e , 1.1--1.6 eV, is large compared to the goal of absolute uncertainty in the D_e of 0.1 eV, but this appears to be due to restrictions in CI treatment.

Dichromium has proven to be yet again a difficult species to tackle. What first appeared to be solely a problem of molecular basis set incompleteness showed secondary effects due to the CI methodology. Truncation errors in the CI space which had been smoothly varying and on the order of 0.1 eV in previous chapters were larger and quite unpredictable in the current case.

It appears that further calculations are necessary to determine convergence with respect to size of extrapolation space, and to the number of main reference configurations. One means of lessening the noise over the range of the curve would be to ensure that not only the set of reference configurations remains constant (as is currently done) but also the entire set of selected configurations; these "merged CI space" calculations are underway.

Compared to other *ab initio* results discussed in Section 8.2, the fact that binding is observed using a method which is easily extended from first- and second-row species is remarkable. Problems due to lack of convergence in the level of CI treatment cast doubt on the quantitative accuracy of the basis set explorations carried out in the first part of this investigation. However, this does not by any means rule out the validity of the selection-extrapolation procedure. This excursion into a "frontier" calculation has brought to the forefront the sometimes-thorny problems of accounting for electron correlation. It does indicate the importance of maintaining as large a set of reference configurations and CI space as possible, in order to include higher-order excitations. Most importantly, the conclusions made regarding achievement of balance for both atomic and molecular descriptions in the basis set remain unchanged.

8.5 References

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Table 8.1

Summary of previous work on Cr_2 . C = calculation; E = experiment. For other notations, please see text.

Reference	Year	C/E	$D_e(\text{eV})$	$R_e(\text{\AA})$	$\omega_e(\text{cm}^{-1})$	Method/Comments
[3]	1966	E	$1.56 \pm .30$ $1.78 \pm .35$			Third Law Second Law
[7]	1972	C	2.6	1.90	300	Extended Hückel. Predict $^3\Sigma_g^+$ ground state.
[43]	1974	E	1.71			Flash photolysis of $\text{Cr}(\text{CO})_6$ $^1\Sigma \leftarrow ^1\Sigma$ transition assigned to observed spectrum Not sure whether species is Cr_2 , CrO_2 or CrC_2 .
[8]	1976	C	1.05 ± 0.10			Modified Hückel.
[9]	1977	C	2.65	1.8		Extended Hückel.
[25]	1979	C	0.2	3.66	55	LSD. Predict $^3\Sigma_g^+$ ground state or $^1\Sigma_g^+$ as next most likely ground state.
[10]	1980	C		1.56	750	SCF
[11]	1980	C	1.48	1.9		APSG-MCSCF. $[6s3p2d]$ GTO basis set. SCF unbound by 27 eV at 1.9 Å. Atoms are not purely 7S .
[13],[22]	1981	C	0.35	3.06	110	6000-configuration GVB with VdW terms. RHF unbound

by ≈ 20 eV. Suggests D_e of [3] is incorrect due to errors in partition function. Suggests R_e of [43] is incorrect due to assignment errors. Ref. [22] discards double min. hypothesis, contrary to that found for Mo_2 .

[12] 1982 C 0.14 3.14 92 3196 - configuration MCSCF. $c_0^2 = 0.106!$
 [8s6p3d]+(spd) GTOs. Propose "antiferromagnetic" model.
 APSG-MCSCF.
 "internal space" CI.

[24] 1982 E 427.5 $\omega_e x_e = 15.75 \text{ cm}^{-1}$. Resonance Raman
 78 in argon matrix. $\Delta G_{1/2} = 396 \text{ cm}^{-1}$
 Postulate double minimum.

[44] 1982 E 1.68 ± 0.01 Resonant 2-photon ionization in molecular beam.
 Removed doubts on [43] cast by [13].

[19] 1983 C 1.01 2.75 110 $X\alpha$ method. Double minimum found.

[28] 1983 C 1.73 396 GMO method—does not dissociate properly.
 [5s4p3d] + (spd) GTOs.

[21] 1983 E 1.6788 472.7 – 493.3 2-colour resonance-enhanced ionization spectroscopy.
 $\omega_e x_e = 10.2 - 20.5 \text{ cm}^{-1}$
 $\Delta G_{1/2} = 452.34 \pm 0.04$, $B_e = 0.2303$, $\alpha_e = 0.0039$ (all in cm^{-1})
 Suggest double minimum in $A^1\Sigma_u^+$ state, but not X state.

[20] 1983 E 1.6788 ≈ 470 Gas-phase. Fluorescence excitation spectrum. $\omega_e x_e \approx 9 \text{ cm}^{-1}$
 $\Delta G_{1/2} = 452.34 \pm 0.02$, $B_e = 0.2303$, $\alpha_e = 0.0038$ (all in cm^{-1})

[46]	1986	C	3.0	Density functional theory	LDA
			0.9	DFT	Langreth-Mehl gradient correction
			1.7	DFT	Semi-empirical gradient correction
[6]	1987	E	1.47 ± 0.06	Knudsen effusion cell	Second- and third-law methods.

Table 8 2

Exponents and contraction coefficients for the $8s4p3d$ basis set for the chromium atom. Based on Refs. [14] and [16]

Orbital	Exponent	Coefficient
<i>s</i>	236658.0	0.00058
<i>s</i>	35364.0	0.00453
<i>s</i>	8058.3100	0.02340
<i>s</i>	2294.230	0.09360
<i>s</i>	756.1180	0.29323
<i>s</i>	277.0000	0.67294
<i>s</i>	110.179	0.67001
<i>s</i>	46.37100	0.36029
<i>s</i>	14.82150	1.0
<i>s</i>	6.13262	1.0
<i>s</i>	1.62959	1.0
<i>s</i>	0.641177	1.0
<i>s</i>	0.099511	1.0
<i>s</i>	0.037588	1.0
<i>p</i>	1478.770	0.00327
<i>p</i>	351.4900	0.02637
<i>p</i>	111.160	0.12210
<i>p</i>	43.15670	0.35557
<i>p</i>	17.77750	0.61343
<i>p</i>	7.661280	1.0
<i>p</i>	3.077650	1.0
<i>p</i>	1.266190	0.70654
<i>p</i>	0.493534	0.34994
<i>d</i>	34.02210	0.02936
<i>d</i>	9.431610	0.15844
<i>d</i>	3.159180	0.42747
<i>d</i>	1.079950	0.59446
<i>d</i>	0.346582	1.0
<i>d</i>	0.091200	1.0

4

OF/DE

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Table 8.3

Calculated energies of the chromium atom, in the ground (7S) case. In all cases only one main configuration was used, $[\text{Ar}]4s^13d^5$. All energies are in hartree, relative to -1043.0 hartree. (1 hartree = 27.2116 eV.)

Basis Set	Notation	PF Exponent	SCF Energy	CI Space	Eigenvalue Energy	Total % c_i^2	Full CI (est.)
8s4p2d	DZ	—	-0.257437	277	-0.296120	98.7	-0.296628
8s4p2d1f	DZP	0.1	-0.258734	670	-0.298107	98.6	-0.298654
8s4p2d1f	DZP	1.0	-0.260617	670	-0.322397	98.3	-0.323439
8s4p3d	DZ*	—	-0.292704	583	-0.343711	97.3	-0.345095
8s4p3d1f	DZ*P	0.1	-0.293929	976	-0.346538	97.1	-0.348074
8s4p3d1f	DZ*P	1.0	-0.294721	976	-0.366068	97.2	-0.368054

Table 8.4 (a).

Results of calculations with the DZ (i.e., $8s4p2d$) basis set. PF = polarization functions (f orbitals, where used); BF = bond functions. All energies in hartree, relative to -2085.0 hartree, except for threshold, which is in μ hartree, and D_e , which is in eV. 1 hartree = 27.2116 eV.

PF Exponent	BF	BF Exponent(s)	SCF Energy	No. Mains	Reference Energy	Sel. Thresh.	Selected/ Generated	Extrapolated Energy	Total c_f^2	est. F-Cl Energy	D_e
—	—	—	-0.650120	31	-1.167384	10	7228/392448	-1.459108	88.37	-1.493043	-2.73
—	(spd), (spd)	0.1,0.4	-0.793927	34	-1.234489	10	9037/1005601	-1.580061	87.87	-1.621981	+0.78
—	(spd), (spd)	1.0,0.4	-0.691733	43	-1.207113	12	6843/1261490	-1.519195	89.62	-1.551578	-1.13
—	(spd), (spd), (spd)	0.1,0.4,1.0	-0.803173	31	-1.241726	20	5710/1222716	-1.594124	88.63	-1.634195	+1.11
—	(spd), (spd), f	0.1,0.4,0.4	-0.796344	34	-1.234683	10	10263/1374566	-1.595391	88.01	-1.638628	+1.23
—	(spd), (spd), f	0.1,0.4,0.1	-0.801089	36	-1.223710	12	9003/1469156	-1.575910	87.79	-1.618915	+0.70
1.0	—	—	-0.678869	29	-1.184782	10	7046/841537	-1.526592	89.14	-1.563723	-2.26
1.0	(sp), (sp), d	0.1,0.4,0.4	-0.735830	21	-1.188000	10	10045/911844	-1.581587	86.68	-1.634012	-0.35
1.0	(sp), (sp), d	0.1,0.4,0.1	-0.800347	35	-1.243563	20	6234/1550888	-1.613519	88.99	-1.654268	+0.20
0.1	—	—	-0.685698	35	-1.120828	10	7390/949169	-1.462556	87.08	-1.506707	-2.47
0.1	(sp), (sp), d	0.1,0.4,0.4	-0.748328	32	-1.164038	12	8822/1355480	-1.537532	86.86	-1.586621	-0.29
0.1	(sp), (sp), d	0.1,0.4,0.1	-0.789004	36	-1.197959	12	8483/1561705	-1.551903	87.44	-1.596369	-0.03

Table 8.4 (b).

Results of calculations with DZ* (i.e., 8s4p3d) basis set. See Table 4(a) for notation and units.

PF Exponent	BF	BF Exponent(s)	SCF Energy	No. Mains	Reference Energy	Sel. Thresh.	Selected/ Generated	Extrapolated Energy	Total c_i^2	est. F-CI Energy	D_e
—	—	—	-0.757645	37	-1.170309	15	5841/765705	-1.506249	88.02	-1.546510	-3.91
—	—	—*	-0.757668	43	-1.189464	10	7180/1074077	-1.522024	87.69	-1.562679	-3.47
—	(spd), (spd)	0.1,0.4	-0.802914	36	-1.214154	10	9987/1491889	-1.575370	87.39	-1.620923	-1.88
—	(spd), (spd)	0.4,1.0	-0.804322	36	-1.193395	35	4584/1465971	-1.561929	88.49	-1.604349	-2.34
—	(spd), (spd), p	0.1,0.4,1.0	-0.809132	27	-1.200750	20	3831/1083788	-1.562686	87.98	-1.606209	-2.29
1.0	—	—	-0.788437	31	-1.163131	10	9854/1132066	-1.575397	86.81	-1.629788	-2.89
1.0	s, s	0.4,1.0	-0.792494	20	-1.132205	15	7698/800631	-1.572386	85.4	-1.636482	-2.71
1.0	s, s	0.1,0.4	-0.791319	30	-1.167503	10	10065/1190361	-1.581547	86.80	-1.636192	-2.72
0.1	—	—	-0.774018	34	-1.179794	15	6913/1450448	-1.537755	87.31	-1.583180	-3.07
0.1	s, s	0.4,1.0	-0.785633	38	-1.202089	10	9304/1571655	-1.557056	87.53	-1.601330	-2.58
0.1	s, s	0.1,0.4	-0.775355	36	-1.188708	10	9119/1555190	-1.545584	87.23	-1.591147	-2.86

* Run with 10 open-shell version of programs; four 6-open-shell configurations are included as mains.

Table 8.5

Counterpoise-corrected dissociation energies. The atomic energies for basis sets containing ghost orbitals as noted yield the full-CI (estd.) energies in hartree, relative to -1043.0 hartree. The dissociation energies and Δ are in eV.

Basis Set	BF Exponents	Full CI (estd.)	Δ^a	D'_e Correction I ^b	D''_e Correction II ^c	D_e Regular
DZ	—	-0.304545	0.22	-3.16	—	-2.73
DZ+2(sp) d	0.1,0.4	-0.345559	1.33	-1.88	-0.77	+0.78
DZ+3(sp) d	0.1,0.4,1.0	-0.349593	1.44	-1.77	-0.55	+1.11
DZ+2(sp) d, f	0.1,0.4,0.4	-0.351034	1.48	-1.73	-0.47	+1.23
DZP	—	-0.373224	0.14	-2.54	—	-2.26
DZ*	—	-0.348179	0.08	-3.64	—	-3.47
DZ*P	—	-0.373224	0.14	-3.17	—	-2.89

$$^a \Delta = E_{Cr} - E_{Cr-X_{BF}-X_{Cr}} \text{ or } \Delta = E_{Cr} - E_{Cr-X_{Cr}}$$

$$^b D'_e = E_{Cr_2} - 2E_{Cr-X_{BF}-X_{Cr}}$$

$$^c D''_e = E_{Cr_2} - E_{Cr-X_{BF}-X_{Cr}} - E_{Cr-X_{Cr}}$$

$$^d D_e = E_{Cr_2} - 2E_{Cr}$$

Table 8.6

MRD-CI and full CI (estd.) energies for Cr_2 ($X^1\Sigma_g^+$) showing the characteristics of 38-Main 2-root calculations using both molecular and natural orbitals using a $\text{DZ} + 2(\text{spd})$, f basis set. (See text.) The number of SAF's generated is 1,456,356. Selection is done with a 10.0 μ hartree threshold. Energies (in hartree except for $E(R)$) are relative to -2085.0 hartree for the molecule.

R (bohr)	Molecular				Orbitals				Natural				Orbitals	
	SCF Energy	No. SAF's Selected	MRD-CI Energy	Total %c _i ²	F-CI Energy (est.)	-E(R) (eV)	No. SAF's Selected	MRD-CI Energy	Total %c _i ²	F-CI Energy (est.)	-E(R) (eV)			
2.9	-0.850108	11099	-1.571520	87.41	-1.619411	0.712	6922	-1.600247	91.53	-1.623783	0.831			
3.0	-0.835597	9857	-1.590225	89.14	-1.627910	0.943	7082	-1.611585	90.96	-1.637906	1.215			
3.1	-0.814513	10169	-1.596337	88.69	-1.636213	1.169	7245	-1.609493	90.33	-1.638198	1.223			
3.1725	-0.796396	10138	-1.595079	88.27	-1.636758	1.184	7397	-1.608061	89.81	-1.639013	1.245			
3.3	-0.760541	10260	-1.590174	87.42	-1.635762	1.157	7556	-1.605127	88.66	-1.641386	1.310			
3.4	-0.730213	10347	-1.583214	86.47	-1.632990	1.081	7587	-1.596536	87.62	-1.637235	1.197			
3.5	-0.698767	10481	-1.577043	85.24	-1.632579	1.070	7715	-1.587245	86.32	-1.633478	1.094			

Table 8.7

Calculated energies of the dichromium molecule, in the ground state ($X^1\Sigma_g^+$) for a small portion of the curve for a variety of thresholds and mains. The basis set used in every case was the "best" DZ + BF basis. All energies are in hartree, relative to -2085.0 hartree, except $E(R)$, which is in eV. (1 hartree = 27.2116 eV.)

R	SCF Energy	Ref. Energy	No. Sel.	Ext. Energy	Total	Full CI (est.)	$E(R)$
50 M, T=8 μ h, Gen.=2,229,557							
2.9	-0.850108	-1.242574	11544	-1.583673	89.11	-1.620824	0.750
3.0	-0.835597	-1.262648	11832	-1.600481	89.17	-1.637056	1.192
3.1	-0.814513	-1.263603	11749	-1.604248	88.86	-1.642189	1.331
3.1725	-0.796356	-1.260719	11697	-1.603839	88.57	-1.643072	1.355
3.3	-0.760541	-1.250926	11789	-1.598891	87.81	-1.641318	1.308
3.4	-0.730213	-1.240520	11578	-1.588752	87.06	-1.633877	1.105
3.5	-0.698767	-1.228811	11273	-1.578933	86.04	-1.627984	0.945
53 M, T=8 μ h, Gen.=3,109,722							
2.9	-0.850108	-1.244908	11661	-1.584138	89.20	-1.620798	0.749
3.0	-0.835597	-1.268217	11594	-1.595202	89.51	-1.629503	0.986
3.1	-0.814513	-1.270420	11686	-1.598112	89.25	-1.633333	1.090
3.1725	-0.796356	-1.268519	11587	-1.597809	89.01	-1.634007	1.109
3.3	-0.760541	-1.260770	11495	-1.593575	88.45	-1.632072	1.056
3.4	-0.730213	-1.252323	11078	-1.585723	87.90	-1.626250	0.898
3.5	-0.698767	-1.242805	10308	-1.579020	87.18	-1.622481	0.795
53 M, T=5 μ h, Gen.=3,109,722							
2.9	-0.850108	-1.244908	16297	-1.586878	88.89	-1.624881	0.860
3.0	-0.835597	-1.268217	15726	-1.601200	89.09	-1.637516	1.204
3.1	-0.814513	-1.270420	15971	-1.604129	88.81	-1.641487	1.312
3.14	-0.804741	-1.269654	16158	-1.603371	88.70	-1.641095	1.302
3.1725	-0.796365	-1.268519	16255	-1.602898	88.60	-1.641037	1.300
3.22	-0.783495	-1.266169	16105	-1.602671	88.41	-1.641682	1.318
3.26	-0.772195	-1.263663	15969	-1.601850	88.24	-1.641653	1.317
3.3	-0.760541	-1.260770	15806	-1.598386	88.06	-1.638755	1.238
3.4	-0.730213	-1.252323	15387	-1.591631	87.52	-1.634138	1.112
3.5	-0.698767	-1.242805	14285	-1.584138	86.80	-1.629506	0.986
55 M, T=2 μ h, Gen.=3,129,960							
3.14	-0.804741	-1.274176	28080	-1.612334	88.51	-1.651195	1.576
3.1725	-0.796356	-1.272947	28060	-1.611974	88.39	-1.651328	1.580
3.22	-0.783495	-1.270435	28338	-1.611366	88.18	-1.651669	1.589
3.26	-0.772195	-1.267765	28118	-1.609937	88.00	-1.651001	1.571

Table 8.8

Summary of molecular and spectroscopic constants for the $X^1\Sigma_g^+$ state of Cr_2 , according to variations in level of CI treatment. Fits of points from Tables 8.6 and 8.7.

No. Mains	Threshold (μh)	D_e (eV)	R_e (bohr)	β (bohr $^{-1}$)	ω_e cm $^{-1}$	$\omega_e x_e$ cm $^{-1}$
38	10	1.18(2)	3.23(2)	1.5(1)	450	5
38	10 ^a	1.30(3)	3.19(2)	1.6(2)	490	6
50	8	1.36(2)	3.143(7)	2.12(7)	673	10
53	8	1.10(2)	3.131(8)	1.97(9)	565	9
53	5	1.33(1)	3.142(6)	1.93(6)	606	9
53	5 ^b	1.32(1)	3.14(1)	1.9(1)	588	9

^a Using natural orbitals.

^b Smaller range: 3.0—3.4 bohr.

Figure 8.1

Variations in the calculation of $\text{Cr}_2 (X\Sigma_g^+)$ led to curves which differed significantly, depending on number of mains and size of selection threshold. Top curve: 53 main configurations; $T = 8 \mu$ hartree gave w_e of 565 cm^{-1} . Middle curve: 53 main configurations; $T = 5 \mu$ hartree gave w_e of $588\text{--}606 \text{ cm}^{-1}$. Bottom curve (o): 50 main configurations; $T = 8 \mu$ hartree gave w_e of 673 cm^{-1} .

Chapter 9

Concluding Remarks

Apart from the unknowns,
Everything is obvious.

J. P. Hogan,
Giant Star

9.1 Summary

Chapter 1 outlined how electronic structure calculations are set up with orbitals described as linear combinations of basis functions derived predominantly from an atomic model, and how these orbitals are used to form configurations which are then linearly combined to create the wavefunction.

To ensure sufficient flexibility, one must use more and more basis functions and configurations, as has been seen throughout. The basis sets and CI space grow so large that one is quickly forced to make approximations to the “complete” treatment, and this is where the truncation errors appear. Since the error in neither basis set nor CI truncations forms a closed analytical expression, approximations to overcome that error must be tested inductively, i.e., in a case-by-case manner.

Chapter 2 discussed one means of overcoming the CI space limitation, while incurring a minimum amount of truncation error, namely, the approximate method of selection-extrapolation. Numerous groups have shown that this is in fact an excellent approximation for the level of molecular complexity treated here.[1]

The remainder of the thesis looked at the problem of overcoming basis set incompleteness, and tested the practicability of the simple yet controversial addition of bond functions. One objective of this thesis was to see how well bond function (BF) basis sets compared to

extended atomic-centred basis set calculations of similar and much larger sizes for molecular properties such as the bond length, fundamental frequency, dipole moment and, most importantly, the dissociation energy. In keeping with the inductive frame of testing approximations, several small- and medium-sized diatomic systems, and finally, one large and very challenging diatomic system, were studied.

Bond functions have been shown to improve results throughout, for a variety of diatomic cases. Chapter 3 showed that, for a simple two-electron diatomic, the addition of bond functions to a purely atomic-centred basis resulted in greater energy lowering per function added, than when only polarization functions were added to such a basis. A BF basis less than two-thirds the size of a PF basis gave a curve which showed less deviation at small R and greater deviation at large R from the exact curve, compared to the PF basis. It was concluded that mixed BF/PF basis sets should be used. This case demonstrated a vital point about the need for BF's because the atomic basis set was virtually perfect, yet molecular basis set incompleteness was undeniably present. In other words, the two types of incompleteness are not one and the same.[2]

In Chapter 4, the potential energy curves of the neutral, and singly- and doubly- ionized species of a first-row hydride OH were improved when bond functions were added. The term energies did not improve significantly, because for both atomic-centred and balanced basis sets, the errors tended to cancel. The most serious discrepancy, that of incorrect dissociation limits, was due to deficiencies in the purely atomic description, and are known to still occur for very large basis sets with no BF's.[3]

In Chapter 5, bond functions were tested on the ground state curves of the second-row hydrides, and were shown to give outstanding agreement with high-quality CEPA calculations.[4] The BF basis sets performed much better than comparably-sized atomic-centred basis sets, with the exception of dipole moment calculations where the BF results did not differ significantly. The BF basis sets on average gave better well depths, although slightly poorer fundamental frequencies and equilibrium bond lengths[5] than the large and very large atomic-centred basis sets of other calculations reported on the hydrides.[6] This agreed with previous calculations on some other systems by this group.[7][8][9]

Chapter 6 showed that bond functions could be used to improve significantly the molecular constants of valence excited states of a first-row homonuclear diatomic, providing the

bond order of the state were taken into account when deciding the composition of the bond function. The error in the term energies was shown to be due to the error in the atomic excitation energies—again, an asymptotic problem related to the atomic basis set.[10]

A second objective of this thesis was to go beyond mere application of BF's, and to formulate some rules for their use. A pattern was sought for the addition of BF's to a typical basis set, so that the optimum economical basis set could be prescribed for an unknown system based only on simple chemical principles. Chapter 7 extended the concept of bond order/bond function composition in a survey of the dissociation energies of the ground states of thirty-six diatomics of the first- and second-row. A systematic study showed that a pattern of optimum basis set composition indeed existed with respect to bond order, and that this pattern extended over a wide range of cases.[11] This was a timely contribution to the BF methodology, because it provided a crucial demonstration that BF's could be added to the basis set of a diatomic in an *a priori* fashion. It was shown that the use of a bond function constructed in a manner prescribed solely by consideration of bond order would yield a D_e within, on average, six per cent of the experimental value. Using the prescribed BF method, the average relative error in the well depth was shrunk to one-third its size for comparable atom-centred basis sets. On these grounds, the dissociation energies of some poorly-known species were predicted. This aspect of the investigation has clearly reached a successful methodological conclusion which gives the experimentalist food for thought as well.

Lastly, in Chapter 8, the well depth of a transition metal dimer with a high bond order and an intimidatingly large correlation energy "gap" was studied using bond functions. Tackling one of the most difficult diatomic cases, that of Cr_2 , underscored the importance of overcoming the CI truncation error which is easily enough done for small and medium-sized diatomics, but can present a problem for large species, even with the availability of MRD-CI techniques. Even so, the explorations on Cr_2 may be judged a qualitative success. A balanced basis set gave a positive dissociation energy, and the composition of the BF was, for such a high bond order, greater than the optimum BF size used on any other diatomic with a double zeta basis set, even though the actual binding energy of dichromium (a bond order of six) was smaller than that of F_2 , with a bond order of one. Preliminary results showed noise was present in the calculated curve, due to the (comparatively) extremely restricted CI space available.

9.2 Asymptotic Error

The major errors in these calculations were attributable to asymptotic problems, i.e., deficiencies in the atomic description which led to incorrect atomic ionization potentials (Chapter 4) and atomic excitation energies (Chapter 6). A good atomic description is a necessary condition for a truly balanced description, although as the H_2 calculations in Chapter 3 showed, even an excellent atomic description is not a *sufficient* condition. Use of a larger basis set would lead to some improvement, although with obvious drawbacks. A new advance in basis set development, which uses non-segmented[†] atomic natural orbitals developed at the CI level[12][13] may be more successful at recovering the correlation energy and it would be interesting to merge this concept with the use of BF's. Dunning proposes "correlation consistent" basis sets which have been optimized at the CI and not SCF level, as equally good basis sets[14]. In either case, since the atomic fragments are better described, yet with more compact basis sets, the basis set superposition error is decreased,[15] and the energy lowering which would occur upon addition of BF's would be unequivocally attributable to overcoming the molecular basis set incompleteness, as was nicely illustrated for the H_2 case in Chapter 3.

9.3 Relevance to Other Work

The basis set explorations which constitute this thesis may be seen as part of a progression in the general understanding of optimizing the wavefunction description. The thrust of *ab initio* calculations has been to move from simple atoms to more complex atoms, and from atoms to simple molecules and eventually, more complex molecules. Basis set development occurs in tandem with this progression, as quantum chemists are challenged by each new type of problem that emerges. The simplest (minimal) atomic basis sets were first extended in the valence shell in order to improve the atomic energies; then they were extended with polarization functions to improve the energies of simple diatomics; and now, attention is being focussed on the best means to describe the molecular orbitals, in order to improve the energies of more difficult diatomics.

Comparison with traditional purely atomic-centred basis set calculations has occurred

[†] "Segmented" means that a given primitive orbital contributes to only one contracted function.

throughout this thesis and will not be dealt with again here. Some attention has been paid in the literature to the distribution of basis set functions away from the nuclei,[16] especially since interest has been growing in speeding up the convergence of well depths with respect to basis set size. In this thesis, and in the work reported by other *ab initio* researchers, the emphasis is changing now, away from the *type* of functions (*s*, *p*, *d*, and higher angular momentum functions) and towards the *placement* of these functions.

The notion of distributing the basis set functions can be placed in the context of variational optimization of the parameters of the wavefunction description. Linear optimization in electronic structure calculations is not a new concept: the coefficients of linear combinations of atomic orbitals are variationally optimized to build molecular orbitals, and then the coefficients of a linear combination built from configurations of these molecular orbitals are also variationally optimized in a straightforward manner to give the lowest absolute energy.

The optimization of the configuration space may continue to be treated within the linear expansion framework, with a variety of approximations currently in use which nearly replicate full CI calculations. However, recent attempts to diminish the size of the basis set truncation error show that the optimization of the basis set occurs more efficiently when a parameter of the calculation is changed, such as allowing the atomic orbitals to "move" to positions where the lowest absolute energy is achieved. This is the idea behind the use of non-nuclear-centred functions, such as the bond functions studied in this thesis. As noted in the Introduction, many calculations carried out by the groups of Buenker and of Peyerimhoff routinely add a few functions at the bond mid-point. Work which explores the BF methodology itself has been reported by this group,[7][8][17] and very recently, by Martin, François, and Gijbels.[18][19][20][21]

The BF approach may be thought of as intermediate to the floating GTO's and the completely atomic-centred extremes, and so the advantages and disadvantages may be weighed relative to one another. Balanced basis sets, which contain valence, polarization and bond function orbitals are like a first step in allowing the functions to "float." Most of the orbitals of a balanced basis set are restricted to remain on the atomic centres, and for the orbitals which are allowed to move off-centre, their movement is restricted to a single location, namely, the bond mid-point.

At the other extreme in exploring the notion of placement is the work on "floating" GTO's.[22] The difference between the bond function and the floating GTO method is that full variational optimization with respect to orbital location occurs for the latter method.[†]

Like the BF basis sets, a smaller number of functions are needed in a floating basis than an atom-centred basis set to attain the same quality of potential energy curve. However, a full variational optimization of the placement of the non-nuclear orbitals would be as expensive as a conventional geometry optimization of the same number of centres. This would be especially prohibitive in the application intended for the BF basis sets, namely, the modelling of potential energy surfaces for chemical reactions since the placement would have to be re-optimized at each geometry.

Considering economy of the total number of basis set functions and the total time which must be spent doing multi-variable non-linear optimization, of the three possibilities, the BF basis sets remain the most promising.

9.4 BF's Used to Create a Reaction Surface

Computational advances permit the use of large and very large basis sets in calculations on small systems (the archetypal diatom AB) where highly-accurate "static" molecular properties are desired. Small- or moderately-sized basis sets such as the ones typically used here are of interest primarily because they represent the first step in constructing a potential energy surface which can be used to model, for example, the $A + BC \rightarrow AB + C$ reaction, which is not tractable with large basis sets. Therefore, particular emphasis has been placed on obtaining an accurate dissociation energy and shape of the curve (*i.e.*, the fundamental frequency) while maintaining an economical size.

Although such a goal has been achieved, this does not mean the use of BF basis sets in the creation of such surfaces is entirely problem-free; for example, the thorny question of where to locate the BF's in a triatomic remains. One could place a single BF in the middle of three atoms, or three BF's between the three atoms taken pairwise. In the limit, as $R_{AB}, R_{BC} \rightarrow 0$, the BF's become functions located on the united atom, and their exponents would be finite, like regular AO's. As the atoms pull apart, however, the BF's

[†] Also, the BF calculations proceeded beyond the Hartree-Fock level, at which point the floating basis set calculations currently stop.

must become more diffuse in order to maintain maximum overlap with the AO's, as was seen in Chapter 4. Therefore, one suggestion has been to optimize the BF exponents at various geometries.[23][†]

Consider a different guiding principle behind the location of BF's, which is a generalization of the BF-according-to-bond-order pattern to the $A + BC$ potential energy surface. Even if AB and BC have the same bond order, at some regions on that surface the bond order is changing, and to maintain consistency with the prescription, the composition of that BF should also vary.

The differences become apparent in the case where A collinearly approaches the " B end" of BC . A strictly "geometric" interpretation of the BF placement would not only place BF's between the A and B and the B and C pairs, but also *between the A and C pair*. Even the suggested BF re-optimization would not be helpful at the point where $R_{AB} \approx R_{BC}$ because the $A-C$ BF would coincide with the B centre and artificially lower the energy. In the simple bond order model, however, a physically more reasonable situation obtains: since A and C are not nearest neighbours, the bond order is zero and *no BF should be placed between A and C* , which would avoid superimposing the BF orbitals on the B atom when the $A-B$ and $B-C$ lengths are equivalent.

On the other hand, when A approaches BC perpendicularly, the overlap between valence shell orbitals for each pair becomes significant, and the bond order between each species would have to be taken into account. Application of BF's to the creation of a three-dimensional surface would be complicated by having to provide enough flexibility to ensure a smooth switching between collinear surfaces created with two BF's and non-collinear three-BF surfaces which would have a range of "transient bond orders."

There would also be some difficulty in artificial lowering caused by the three BF's approaching too closely as the atoms drew together. One could place a single BF in the middle of the three non-collinear atoms, but if a bond-order pattern is followed, this would still have to "split" into two BF sets for the collinear case, and one would still have to contend with discontinuities caused by using different finite basis sets.

[†] This would increase the computational workload, but it would be safe to assume a smoothly-varying function for $\zeta(R)$ which could be interpolated. This would still be less optimization than a floating basis calculation, and be more tractable than an extended-basis triatomic calculation.

9.5 BSSE vs. MBSI

Overall, the BF calculations may be judged a resounding success. This good agreement cannot be due solely to the computational artefact of basis set superposition error, as Chapter 3 showed.[2] It cannot be due to fortuitous cancellation of error in a particular kind of basis set: the effect has been shown using van Duijneveldt[24] (QZ), Dunning and Hay[25] (DZ and TZ), McLean and Chandler (DZ),[26] and Wachters / Hay[27][28] (DZ) basis sets. It cannot be an artefact dependent on the approximate method used to compute the correlation energy; this work uses MRD-CI techniques, but equally good effects have been observed using Møller-Plesset techniques.[18][19][20] Nor can it be an artefact dependent on the kind of diatomic species studied, because improvement has been shown for neutral and ionized ground states, and for excited states, for a variety of symmetries and multiplicities.

When molecules are formed, the shapes of the atomic orbitals, in particular the valence orbitals, undergo considerable deformations in the charge distribution. The error in the basis set truncation, which can be quite substantial for atomic calculations, is thus even greater for molecular species, leading to incorrect molecular properties in, for example, the dissociation energy and dipole moment. The molecular basis set incompleteness (MBSI) refers to the inadequacies of the truncated basis set in describing these deformations in the charge distribution. This error is reduced by using extensive basis sets, or, as discussed above, in a more efficient manner, by spatially distributing these basis sets.

The secondary error caused by truncated basis sets is known as the basis set superposition error (BSSE).[29] An example of the misleading nature of the BSSE is the "false dipole" created when a set of atomic orbitals with zero charge is placed close to an atom, or the false minima that appear in the repulsive SCF interaction potentials between rare-gas atoms.[30] The BSSE was identified as a source of error in calculations on weakly- or non-bonded systems (for example, Ref. [31]) and the literature consists primarily of studies of van der Waals species (in particular, dimers), which are mainly tractable only at the SCF level, due to their size and complexity. Nonetheless, reluctance to use bond functions stems mainly from concern about the BSSE problem,[18] and so interest has grown in the search for an unequivocal procedure which would totally eliminate the BSSE for all systems, regardless of geometry and basis set.[32] The most obvious solution to the BSSE

problem—to work with very large basis sets—would also help eradicate the molecular basis set incompleteness (MBSI), but this is not feasible beyond a certain limit.

The function counterpoise method touched on briefly in preceding Chapters, proposed to correct for the BSSE,[29] is itself a matter of some debate. Some authors recommend it be used as originally proposed, with the correction being calculated without removing the occupied orbitals of the partner “ghost” atom.[33][30][31][15] This has been observed to lead to overcorrection which becomes markedly apparent when ΔE is small, or when minimal basis sets are used.[32] Other authors argue that the Pauli principle prevents one atom from using the occupied orbitals of the other atom, and so the ghost atom should be made from only the unoccupied or “virtual” orbitals.[32] The difference is significant: the virtuals-only method at the SCF level yields only 10–50 per cent of the total-basis correction.[33]

Which orbitals to use in the counterpoise correction is not clear, and neither is how to extend the correction to larger species. Comparable to the question of BF placement in a triatomic, Wells and Wilson point out that the function counterpoise method is not easily generalizable to the many-body case. They distinguish between the “pairwise additive function counterpoise” (PAFC) method, which approximates the BSSE of a many-body system as a sum of Boys-Bernardi function counterpoise corrections between pairs of bodies, and the “site-site function counterpoise” (SSFC) method, which mixes in the interactions of *all* other orbitals in the cluster.[34] Martin *et al.* have newly proposed a third type of correction, the “successive reaction counterpoise” (SRCP) method, where the polyatomic formation can be written as a sequence of binary reactions. For the species in each reaction, a counterpoise term may be written, and when these are summed, the SRCP correction is known for the polyatom.[18] The PAFC method will lead to an overcorrection for the BSSE, and the SSRC method, while giving a smaller BSSE, could also be argued by the virtuals-only proponents to be overcorrecting as well.[34] The SRCP method yields the largest BSSE term of all three.[18] Since three-body, four-body, and many-body effects are significantly smaller than two-body effects, and since the counterpoise correction is an approximation to begin with, the distinctions are small.[34]

The controversy arising over whether “all-orbitals” or “virtuals-only” is the more appropriate correction scheme, and the strong non-additivity effects seen for the polyatomic cases, indicate that none of these schemes is satisfactory. To account for atomic basis set unsatu-

ration, one should first saturate the polarization component of the atomic basis set,[19] and then, look beyond a "separated parts" arithmetic adjustment. A method recently proposed for dimer-dimer interactions at the Hartree-Fock level proposed by Mayer and co-workers excludes BSSE from the beginning by the use of a "chemical Hamiltonian approach".[35][36] This modified Hamiltonian decomposes the SCF Hamiltonian into a "physical" part and terms which cause the BSSE-type delocalizations, and then it calculates the conventional energy expectation value; thus, no additional ghost-atom calculations are necessary. It is not clear whether this approach can be translated to the CI level because the whole point of this stage of the calculation is to account for excitations of the electron into many different orbitals, many of which are not localized on the originating monomer (atom).

Another indictment against the use of the counterpoise correction method comes from an investigation by Schwenke and Truhlar of the HF-HF dimer at the Hartree-Fock level using a very wide variety of basis sets. They found, in accordance with what has been reported in this thesis, that the counterpoise-corrected interaction energy is not more reliably accurate than the uncorrected energies. They could not always decrease the size of the counterpoise correction by increasing the size of the basis set, which indicates that the correction was not strictly alleviating only the BSSE (which is caused by an unsaturated basis set). A "virtuals-only" approach did not improve matters. One useful thing about "corrections" in general is that, even if not exact, they should give an indication of the error estimate ϵ . Schwenke and Truhlar found that this also did not apply: the fact that the counterpoise correction was smaller than some small value ϵ did not mean that the calculated interaction energy was accurate to within ϵ . [37]

Martin, François and Gijbels also pointed out the serious deficiencies in counterpoise correction methods, in their examination of the BSSE at the correlated energy level for covalently-bound species. They concluded that there was no good reason for dismissing bond function basis sets as prone to BSSE, or for advocating that counterpoise-adjusted BF calculations are more appropriate than the non-adjusted BF calculations:[18]

The most powerful argument supporting this conclusion is and remains the excellent agreement between calculated and experimental values using this approximation, since in the end, that is what quantum chemistry is all about.

Why is the counterpoise correction not a correction? Why is the accuracy not pre-

```

53 301 CONTINUE
54 C WRITE(IOUT,3)(XI(I),YI(I),I=1,N)
55 C
56 NPT=(XI(N)-XI(1))/XH+1.00001D0
57 N=NPT-1
58 RVAL=XI(1)-XH
59 DO 30 IX=1,NPT
60 RVAL=RVAL+XH
61 R(IX)=RVAL
62 RINT(1)=RVAL
63 CALL INTERP(RINT,PINT)
64 X WRITE(IJUNK,201) RINT(1),PINT(1)
65 X 201 FORMAT(2F10.6)
66 30 UU(IX)=PINT(1)
67 C
68 DO 120 JJ=1,NQ
69 NROT=JJ-1
70 DO 94 K=1,NPT
71 RVAL=R(K)
72 94 U(K)=UU(K)*UNITS1+NROT*(NROT+1)/RVAL/RVAL
73 DO 95 K=1,N
74 MID=K
75 IF(U(K).LT.U(K+1)) GO TO 96
76 95 CONTINUE
77 96 DO 110 NV=1,NVIBL
78 NVIB=NV-1
79 IF(JJ-2) 50,60,70
80 50 ETRIAL=EVJR(NV)*UNITS1
81 GO TO 99
82 60 ETRIAL=(EVJR(NV)+NROT*(NROT+1)*DEKTR(NV))*UNITS1
83 GO TO 99
84 70 DEL=(EROT(NV,NROT)-EROT(NV,1))*(JJ+1)/NROT
85 ETRIAL=(EVJR(NV)+DEL/CONV)*UNITS1
86 99 DO 100 J=2,MID
87 IL=J
88 IF((ETRIAL.LE.U(J-1)).AND.(ETRIAL.GT.U(J))) GO TO 101
89 100 CONTINUE
90 101 DO 105 J=MID,N
91 C
92 C
93 C
94 C
95 IT=J
96 IF((ETRIAL.LE.U(J+1)).AND.(ETRIAL.GT.U(J))) GO TO 106
97 105 CONTINUE
98 106 ILOW=IDINT((R(IL)-R(1))/XH)
99 ITOP=IDINT((R(IT)-R(1))/XH)
100 SLPTOP=DABS((U(IT+1)-U(IT))/(R(IT+1)-R(IT)))
101 SLPLOW=DABS((U(IL-1)-U(IL))/(R(IL)-R(IL-1)))
102 INAX=ITOP+IDINT(9.655D0*SLPTOP**(-1.D0/3.D0)/XH)
103 IMIN=ILOW-IDINT(9.655D0*SLPLOW**(-1.D0/3.D0)/XH)
104 IF(IMIN.LT.1)IMIN=1

```

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APPENDIX A.1

Definition of variables, constants and units used.^a

$\text{\AA}$	=	$1 \times 10^{-10} \text{ m}$
a.u. (energy)	=	27.2116 eV ... see Table A.2 following
a.u. (length)	=	$0.529177 \times 10^{-10} \text{ m}$
a.u. (time)	=	$2.41888 \times 10^{-17} \text{ sec}$
a.m.u. (mass)	=	$1.66056 \times 10^{-27} \text{ kg}$
a.u. (charge-distance)	=	2.5416 Debye
h	=	$6.626176 \times 10^{-34} \text{ J s}$ (Planck's constant)
$\hbar$	=	$\frac{h}{2\pi}$
ψ	=	electronic wavefunction for a single electronic configuration
Ψ	=	total electronic wavefunction (sum of states)
Ψ_R	=	Ψ , with the subscript to emphasize the Born-Oppenheimer approximation
χ	=	wavefunction for nuclear motion
Φ	=	total wavefunction, including nuclear and electronic components
$\mathbf{r}$	=	electronic coordinates in three-dimensional space, usually (x, y, z) or (r, θ, ϕ)
t	=	time
H	=	Hamiltonian operator, a sum of the kinetic and potential energy operators
M_a	=	nuclear mass of atom a
Z_a	=	nuclear charge of atom a
∇	=	three-dimensional first-order derivative, $(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z})$
∇^2	=	three-dimensional second-order derivative, $(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
V	=	potential energy operator
T	=	kinetic energy operator
p , or $\mathbf{p}$	=	momentum (one- and three-dimensional, respectively)
π	=	3.141592654....
$\mathbf{R}$	=	nuclear coordinates in three-dimensional space
E	=	energy
μ	=	permanent electric dipole moment of diatomic (Debye or esu-cm)

^a Based in part on P. W. Atkins, *Physical Chemistry* 2nd. ed.

ω_e	=	harmonic, or fundamental, frequency of diatomic
$\omega_e x_e$	=	anharmonic frequency
B_e	=	rotational constant
R_e	=	equilibrium bond distance
α_e or α	=	vibrotational coupling constant
D_e	=	dissociation energy
ZPE	=	zero-point energy (i.e., energy when $v = J = 0$)
D_0	=	also called dissociation energy; $D_e = D_0 + \text{ZPE}$
$\beta_0, \lambda_1, \lambda_2$	=	length-dependent parameters in the 5-parameter generalized Morse function. (See Section 2.2.1)
ζ	=	exponent in Gaussian-type orbitals
v	=	vibrational level
J	=	rotational level
$\alpha(i), \beta(i)$	=	spin eigenfunction of the i -th electron

APPENDIX A.2

Energy conversion factors. To convert from the unit at the beginning of a row, multiply by the number in the appropriate column.

	eV	erg	kcal/mole	cm ⁻¹	kJ/mole	hartree	K
eV	1	1.60210×10^{-12}	23.0609	8.065479×10^3	96.48452	3.67502×10^{-2}	1.16046×10^4
erg	6.24181×10^{11}	1	1.43942×10^{13}	5.03448×10^{15}	6.02257×10^{13}	2.29388×10^{10}	7.2433×10^{15}
kcal/mole	4.33634×10^{-2}	6.94725×10^{-14}	1	349.755	4.18402	1.59362×10^{-3}	503.21
cm ⁻¹	1.239852×10^{-4}	1.98630×10^{-16}	2.85911×10^{-3}	1	1.19626×10^{-2}	4.55633×10^{-6}	1.4388
kJ/mole	1.03644×10^{-2}	1.66042×10^{-14}	0.23900	83.5935	1	3.8088×10^{-4}	120.274
a.u.	27.2116	4.35943×10^{-11}	6.27503×10^2	2.19474×10^5	2625.49	1	3.1578×10^5
K	8.6173×10^{-5}	1.3806×10^{-16}	1.9872×10^{-3}	0.069502	8.3143×10^{-3}	3.1668×10^{-6}	1

APPENDIX B.1 Short Program Listings

VBVIBE

```

1      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
2      COMMON/ONE/XI(200),YI(200),N
3      COMMON/CTRL/IN,IOUT
4      COMMON/BACKK/ILOW,ITOP
5      COMMON/XSCHR/NI,NS,MAXIT
6      DIMENSION U(4001),P(4001),EVJR(30),DEKTR(30),R(4001)
7      1 ,UU(4001),EROT(25,50)
8      DIMENSION RINT(1),PINT(1)
9  C    SOLUTION OF VIBRATION-ROTATION WAVE EQUATION USING THE
10 C    NUMEROV-COOLEY METHOD.  PROGRAM OBTAINED FROM DAVID BISHOP
11 C    OCTOBER, 1982.  THE POTENTIAL FUNCTION IN THIS VERSION
12 C    IS INPUT AS A GENERALIZED MORSE FUNCTION.
13 C    DATA INPUT:
14 C      1.  # OF POINTS ON CURVE, # V-LEVELS, # J-LEVELS PER V.
15 C      2.  REDUCED MASS (ATOMIC UNITS), R-INCREMENT FOR INTERPOLATION.
16 C      3.  ESTIMATES OF V-LEVELS (THIS VERSION)
17 C      4.  DE (EV), RE(BOHR)
18 C      5.  BETAO,P4,P5 (ATOMIC UNITS)
19 C      6.  STARTING R-VALUE, R-INCREMENT FOR MORSE FUNCTION
20      PRINT*,'SET FILE ON UNIT 20 TO RECEIVE V,R,E DATA'
21      IN=6
22      IOUT=6
23      NI=1
24      NS=33
25      MAXIT=100
26      CONV=219474.6156
27      20 READ(IN,1,END=200) N,NVIBL,NQ
28      READ(IN,2) UNITS1,XH
29      READ(IN,10)(EVJR(I),I=1,NVIBL)
30      WRITE(IOUT,4) N,NVIBL,NQ,UNITS1,XH
31      WRITE(IOUT,5)
32      WRITE(IOUT,6)(I,EVJR(I),I=1,NVIBL)
33      WRITE(IOUT,7)
34      READ(IN,21) DE,RE
35      21 FORMAT(2F12.6)
36      READ(IN,35) BETAO,P4,P5
37      35 FORMAT(3F12.6)
38      READ(IN,21)RMIN,DEL1
39      WRITE(IOUT,23) DE,RE,BETAO,P4,P5
40      23 FORMAT(1X,'DE = ',F12.6,2X,'RE = ',F11.6,/,1X,'BETAO = ',
41      1 F11.6,2X,'P4 = ',F11.7,2X,'P5 = ',F11.7,/)
42      DO 300 I=1,N
43      U(I)=0.
44      300 P(I)=0.DO
45      RVAL=RMIN
46      DO 301 I=1,N
47      RVAL=RVAL+DEL1
48      XI(I)=RVAL
49      DEL=RVAL-RE
50      BETA=BETAO*(1.DO+P4*DEL + P5*DEL**2)
51      YI(I)=DE*(1.DO-DEXP(-BETA*DEL))**2 - DE
52      YI(I)=YI(I)/27.2116

```

```

53 301 CONTINUE
54 C WRITE(IOUT,3)(XI(I),YI(I),I=1,N)
55 C
56 NPT=(XI(N)-XI(1))/XH+1.00001D0
57 N=NPT-1
58 RVAL=XI(1)-XH
59 DO 30 IX=1,NPT
60 RVAL=RVAL+XH
61 R(IX)=RVAL
62 RINT(1)=RVAL
63 CALL INTERP(RINT,PINT)
64 X WRITE(IJUNK,201) RINT(1),PINT(1)
65 X 201 FORMAT(2F10.5)
66 30 UU(IX)=PINT(1)
67 C
68 DO 120 JJ=1,NQ
69 NROT=JJ-1
70 DO 94 K=1,NPT
71 RVAL=R(K)
72 94 U(K)=UU(K)*UNITS1+NROT*(NROT+1)/RVAL/RVAL
73 DO 95 K=1,N
74 MID=K
75 IF(U(K).LT.U(K+1)) GO TO 96
76 95 CONTINUE
77 96 DO 110 NV=1,NVIBL
78 NVIB=NV-1
79 IF(JJ-2) 50,60,70
80 50 ETRIAL=EVJR(NV)*UNITS1
81 GO TO 99
82 60 ETRIAL=(EVJR(NV)+NROT*(NROT+1)*DEDKTR(NV))*UNITS1
83 GO TO 99
84 70 DEL=(EROT(NV,NROT)-EROT(NV,1))*(JJ+1)/NROT
85 ETRIAL=(EVJR(NV)+DEL/CONV)*UNITS1
86 99 DO 100 J=2,MID
87 IL=J
88 IF((ETRIAL.LE.U(J-1)).AND.(ETRIAL.GT.U(J))) GO TO 101
89 100 CONTINUE
90 101 DO 105 J=MID,N
91 C
92 C
93 C
94 C
95 IT=J
96 IF((ETRIAL.LE.U(J+1)).AND.(ETRIAL.GT.U(J))) GO TO 106
97 105 CONTINUE
98 106 ILOW=IDINT((R(IL)-R(1))/XH)
99 ITOP=IDINT((R(IT)-R(1))/XH)
100 SLPTOP=DABS((U(IT+1)-U(IT))/(R(IT+1)-R(IT)))
101 SLPLOW=DABS((U(IL-1)-U(IL))/(R(IL)-R(IL-1)))
102 IMAX=ITOP+IDINT(9.655D0*SLPTOP**(-1.D0/3.D0)/XH)
103 IMIN=ILOW-IDINT(9.655D0*SLPLOW**(-1.D0/3.D0)/XH)
104 IF(IMIN.LT.1)IMIN=1

```

```

105      IF(IMAX.GT.NPT)IMAX=NPT
106      XMIN=R(1)
107      XMAX=R(NPT)
108      CALL VIBWFN(U,P,ETRIAL,XMIN,XMAX,XH,NPT,NVIB,IMIN,IMAX,BVSUM)
109      IF(NVIB.LT.0) GO TO 115
110      ETRIAL=ETRIAL/UNITS1
111 C     WRITE(11)IMIN,IMAX,ETRIAL,(P(I),I=IMIN,IMAX)
112      BVSUM=BVSUM/UNITS1
113      IF(NVIB.EQ.0.AND.NROT.EQ.0) THEN
114          ESAVE=ETRIAL*CONV
115          EEV1=ETRIAL*27.2116
116          ZPE=(DE+EEV1)*8065.48
117          WRITE(IOUT,*) ' ZERO POINT ENERGY = ',ZPE
118          WRITE(IOUT,*) ' '
119      WRITE(IOUT,11)
120      ENDIF
121      DELTAE=ETRIAL*CONV-ESAVE
122      EROT(NV,JJ)=DELTAE
123      IF(JJ.GT.1) GO TO 111
124      EVJR(NV)=ETRIAL
125      DEDKTR(NV)=BVSUM
126      EEV=ETRIAL*27.2116
127 111  WRITE(IOUT,12)NVIB,NROT,ETRIAL,EEV,BVSUM,DELTAE
128 110  WRITE(20,17)NVIB,NROT,DELTAE
129 17   FORMAT(I,',',I,',',F10.3)
130      GO TO 120
131 115  NVIBL=NV-1
132      IF(NVIBL.LT.1) GO TO 20
133 120  WRITE(IOUT,13)
134      GO TO 20
135 C
136      1 FORMAT(16I5)
137      2 FORMAT(2F20.8)
138 C    3 FORMAT(F12.6,F12.6)
139      4 FORMAT(5X,'# OF POINTS =',I5/5X,'# OF VIBRATIONAL LEVELS =',
140          1 I5/5X,'# OF ROTATIONAL LEVELS =',I5/5X,'2*MU =',F13.5/5X,
141          2 'SPACING =',F7.3/)
142      5 FORMAT(2X,'GUESSED EIGENVALUES'//)
143      6 FORMAT(2X,I5,F12.5)
144      7 FORMAT(/2X,'INPUT POTENTIAL ENERGY CURVE'//)
145 C    8 FORMAT(F15.5,4F27.10)
146 C    9 FORMAT('1',2X,'INTERPOLATED POTENTIAL ENERGY CURVE'//)
147      10 FORMAT(8F10.5)
148      11 FORMAT(/2X,'NV,NJ,E(AU),E(EV),B,DELTAE(CM-1)',//)
149      12 FORMAT(2I4,F12.7,F12.6,E14.7,F12.3)
150      13 FORMAT(/)
151 C    14 FORMAT(4(F7.3,F13.9))
152 C    22 FORMAT(4F20.8)
153 200  STOP
154      END
155      SUBROUTINE VIBWFN(U,P,ETRIAL,XMIN,XMAX,H,N,NV,IMIN,IMAX,BVSUM)
156      IMPLICIT REAL*8(A-H,O-Z)

```

```
157      COMMON/CNTRL/IN,IOUT
158      COMMON/BACKK/ILOW,ITOP
159      COMMON/XSCHR/NI,NS,MAXIT
160      DIMENSION U(1),P(1)
161      EPS=1.D-10
162      H2=H*H
163      H2BY12=H2/12.DO
164      DO 1 I1=1,MAXIT
165      UMIN2=U(IMAX-1)-ETRIAL
166      UMIN1=U(IMAX)-ETRIAL
167      IF(UMIN2.GT.0.0D0.AND.UMIN1.GT.0.0D0) GO TO 3
168      WRITE(IOUT,621) U(IMAX-1),ETRIAL
169 621 FORMAT(' VIBWFN IS FAILING WITH U(IMAX-1)=',D20.10,' AND
170 1 ETRIAL =',D20.10)
171      WRITE(IOUT,620) U(IMAX),ETRIAL
172 620 FORMAT(' VIBWFN IS FAILING WITH U(IMAX)=',D20.10,' AND
173 1 ETRIAL=',D20.10)
174      NV=-1
175      RETURN
176 3 TO=DSQRT(UMIN1)
177      T1=DSQRT(UMIN2)
178      P(IMAX)=1.0D-30
179      PM=1.D-30*DSQRT(TO/T1)*DEXP((TO+T1)*H*0.5D0)
180      P(IMAX-1)=PM
181      Y1=(1.D0-H2BY12*UMIN1)*1.0D-30
182      Y2=(1.D0-H2BY12*UMIN2)*PM
183      Y3=2.0D0*Y2-Y1+PM*UMIN2*H2
184      SUMP2I=1.0D-60+PM*PM
185      IRUN=IMAX-1
186 4 IRUN=IRUN-1
187      UMIN2=U(IRUN)-ETRIAL
188      PMM=PM
189      PM=Y3/(1.0D0-H2BY12*UMIN2)
190      IF(PM.LT.PMM)GO TO 5
191      P(IRUN)=PM
192      SUMP2I=SUMP2I+PM*PM
193      Y1=Y2
194      Y2=Y3
195      Y3=2.D0*Y2-Y1+H2*UMIN2*PM
196      GO TO 4
197 5 MARK=IRUN+1
198      PMIN=PMM
199      YMPL1=Y1/PMIN
200      SUMP2I=SUMP2I/PMIN/PMIN
201      PMM=1.D-30
202      IF(NV/2*2.NE.NV)PMM=-1.D-30
203      P(IMIN)=PMM
204      UMIN1=U(IMIN)-ETRIAL
205      UMIN2=U(IMIN+1)-ETRIAL
206      TO=DSQRT(UMIN1)
207      T1=DSQRT(UMIN2)
208      PM=PMM*DSQRT(TO/T1)*DEXP((TO+T1)*H*0.5D0)
```

```

209      P(IMIN+1)=PM
210      Y1=(1.DO-H2BY12*UMINE1)*PM
211      Y2=(1.DO-H2BY12*UMINE2)*PM
212      Y3=2.DO*Y2-Y1+PM*UMINE2*H2
213      SUMP20=1.D-60+PM*PM
214      IT=IMIN+2
215      DO 8 I8=IT,MARK
216      UMINE2=U(I8)-ETRIAL
217      PM=Y3/(1.DO-H2BY12*UMINE2)
218      P(I8)=PM
219      Y1=Y2
220      Y2=Y3
221      Y3=2.DO*Y2-Y1+H2*UMINE2*PM
222      SUMP20=SUMP20+PM*PM
223      8 CONTINUE
224      PMOUT=PM
225      SUMP20=SUMP20/PMOUT/PMOUT
226      YMIN1=Y1/PMOUT
227      YM=Y2/PMOUT
228      DE=((2.DO*YM-YMIN1-YMPL1)/H2+(U(MARK)-ETRIAL))/(SUMP2I
229      1 +SUMP20 -1.DO)
230      ENEW=ETRIAL + DE
231      CONV=DABS(DE/ENEW)
232      C      IF(NI.EQ.1)WRITE(IOUT,655)ITOP,ILOW,IMIN,IMAX, MARK,DE
233      C 655 FORMAT(' ITOP=',I4,' ILOW=',I3,' IMIN=',I3,' IMAX=',I4,
234      C      1 ' MARK=',I4,' DE=',D15.7)
235      IF(CONV.LE.EPS) GO TO 14
236      ETRIAL=ENEW
237      IF(PMOUT.LE.0.DO) GO TO 500
238      X=1.5DO*DLOG(PMOUT*1.D30)
239      IMIN=ILOW-IDINT(DFLOAT(ILOW-IMIN)*(X*X)**(-1.DO/3.DO))*10
240      500 IF(PMIN.LE.0.DO)GO TO 550
241      X=1.5DO*DLOG(PMIN*1.D30)
242      IMAX=ITOP+IDINT(DFLOAT(IMAX-ITOP)*(X*X)**(-1.DO/3.DO))*10
243      550 IF(IMAX.GT.N)IMAX=N
244      IF(IMIN.LT.1)IMIN=1
245      1 CONTINUE
246      WRITE(IOUT,650)MAXIT
247      650 FORMAT(' CONVERGENCE NOT ATTAINED EVEN AFTER',I4,' ITERATIONS')
248      RETURN
249      14 ETRIAL=ENEW
250      NODE=0
251      SN=DSQRT(H*(SUMP2I+SUMP20-1.DO))
252      P IOUT=1.DO/(PMOUT*SN)
253      PMIN=1.DO/PMIN/SN
254      R=XMIN+IMIN*H
255      SI=P(IMIN)*PMOUT/R
256      BVSUM=SI*SI
257      IT=IMIN+1
258      DO 15 I15=IT,MARK
259      P(I15)=P(I15)*PMOUT
260      SJ=SI

```



```
261      SI=P(I15)/R
262      BVSUM=BVSUM+SI*SI
263      IF(SI)18,23,20
264      18 IF(SJ)15,15,23
265      20 IF(SJ)23,15,15
266      23 NODE=NODE+1
267      15 R=R+H
268 C      IF(NS.EQ.33)WRITE(IOUT,651)NV,NODE
269 C 651 FORMAT(' THE NODE COUNT FOR NV=',I4,'IS',I4)
270      IT=MARK+1
271      DO 16 I16=IT,IMAX
272      P(I16)=P(I16)*PMIN
273      SI=P(I16)/R
274      BVSUM=BVSUM+SI*SI
275      16 R=R+H
276      BVSUM=BVSUM*4
277      RETURN
278      END
279      SUBROUTINE INTERP(P,V)
280      IMPLICIT REAL*8(A-H,O-Z)
281      DIMENSION P(1),V(1)
282      COMMON/ONE/XI(200),YI(200),N
283      DIMENSION XJ(200),YJ(200),NUMB(200)
284 C
285 C      SUBROUTINE FOR SHROG SYSTEM VERSION 1.1 73/05/01 1212.
286 C
287 C      INTERPOLATION PROGRAM (BY SUCCESSIVE RANGES)
288 C
289 C      THE METHOD OF LAGRANGE IS USED. THE ABSCISSAE ARE GENERATED PRIOR
290 C      TO ENTRY AND PLACED IN THE P ARRAY M IS THE NUMBVER OF POINTS
291 C      TO BE FOUND BY INTERPOLATION. V CONTAINS THE INTIERPOLATED
292 C      ORDINATES THE FIRST OF WHICH IS AT V(LX). THE ORDINATE FOR
293 C      ANY POINT CLOSER THAN .01*RH TO AN IAPUT POINT IS TAKEN AS THAT
294 C      FOR THE INPUT POINT. NUSED IS THE UNMBER OF POINTS USED FOR EACH
295 C      INTERPOLATED POINT. NUSED MUST BE EVEN AND LESS THAN OR EQUAL TO
296 C      8. NUSED = 8 IS SUGGESTED. ANY POINT FARTHER THAN
297 C      NUSED/2 POINTS FROM EITHER END IS FOUND FROM THE NUSED/2 POINTS
298 C      ON EACH SIDE.
299 C
300      M=1
301      LX=1
302      RH=0.01D0
303      NUSED=8
304      NIK=N
305      DO 8 I=1,NIK
306      8 XJ(I)=XI(I)
307      MF=LX+M-1
308      MSTA=LX
309      MUST=NUSED/2
310      NS=MUST+1
311      NF=NIK-NS+1
312      NFP=NF+1
```

```
313      DO 16 I=NS,NFP
314 16   NUMB(I)=0
315      IF(NF.LT.NS)GO TO 27
316      DO 25 J=LX,MF
317      DO 23 I=NS,NF
318      IF(P(J).GT.XJ(I))GO TO 23
319      NUMB(I)=NUMB(I)+1
320      GO TO 25
321 23   CONTINUE
322      NUMB(NFP)=NUMB(NFP)+1
323 25   CONTINUE
324      GO TO 28
325 27   NUMB(NFP)=M
326 28   DO 73 L=NS,NFP
327      IF(NUMB(L).LE.0)GO TO 73
328      M=NUMB(L)
329      NSTA=L-NUST
330      NFIN=NSTA+NUSED-1
331      DO 35 I=NSTA,NFIN
332      XJ(I)=XI(I)
333 35   YJ(I)=YI(I)
334      NSTA1=NSTA+1
335      XSCALE=(XJ(NFIN)-XJ(NSTA))/1.D1
336      YMAX=YJ(NSTA)
337      YMIN=YJ(NSTA)
338      DO 43 I=NSTA1,NFIN
339      IF(YJ(I).GT.YMAX)YMAX=YJ(I)
340      IF(YJ(I).LT.YMIN) YMIN=YJ(I)
341 43   CONTINUE
342      YSCALE=YMAX-YMIN
343      DO 47 I=NSTA,NFIN
344      XJ(I)=XJ(I)/XSCALE
345 *7   YJ(I)=(YJ(I)-YMIN)/YSCALE+.5D0
346      XN=RH/XSCALE
347      MFIN=NSTA+M-1
348      MTA=NSTA
349      EPSIL=.01D0*XN
350      DO 71 II=MTA,MFIN
351      P(II)=P(II)/XSCALE
352      V(II)=0.D0
353      PNUM=1.D0
354      DO 68 I=NSTA,NFIN
355      XNUM=P(II)-XJ(I)
356      IF(DABS(XN*M).GT.EPSIL) GO TO 61
357      V(II)=YJ(I)
358      GO TO 70
359 61   PNUM=PNUM*XNUM
360      PDEN=1.D0
361      DO 66 J=NSTA,NFIN
362      IF(I.EQ.J)GO TO 66
363      PDEN=(XJ(J)-XJ(J))*PDEN
364 66   CONTINUE
```

```
365      DEN=PDEN*XNUM
366      68 V(II)=YJ(I)/DEN+V(II)
367      V(II)=V(II)*PNUM
368      70 V(II)=(V(II)-.5D0)*YSCALE+YMIN
369      71 P(II)=P(II)*XSCALE
370      MSTA=MSTA+M
371      73 CONTINUE
372      M=MSTA-LX
373      RETURN
374      END
```

```

1  C  PROGRAM TO DO GMF5, GMF4 OR GMF3 FIT TO DIATOMIC MOLECULE
2      IMPLICIT REAL*8 (A-H,O-Z)
3      CHARACTER*4 TITLE(10)
4      DIMENSION R(100),E(100),IPAR(5),PARM(5),W(100),COV(5,5)
5      DIMENSION W1(100),W2(400),W3(100,100),W4(400)
6      IMAX=100
7      IFLAG=0
8      WRITE(6,*) ' *** Generalized Morse Function Fitter ***'
9      WRITE(6,*) ' '
10     WRITE(6,*) ' If you have set unit 10 for ',
11     1 'potential vs. R data, type 0; else, another number'
12     READ(5,*) IANS
13     IF(IANS.NE.0) STOP 999
14     WRITE(6,*) ' Are there extra lines at the beginning ',
15     1 'of the file on unit 10? (type 0,1,2, etc. ',
16     2 'corresponding to the number of extra lines)'
17     READ(5,*) ILINE
18     DO 110 I=1,ILINE
19         READ(10)
20     110 CONTINUE
21     WRITE(6,*) 'Please characterize the file briefly ',
22     1 '(40 characters or less)'
23     READ(5,97) (TITLE(K),K=1,10)
24     97  FORMAT(10A4)
25  C  Determine the number of parameters.
26     101 WRITE(6,*) ' How many parameters? (3, 4 or 5)'
27     READ(5,*) N
28     IF(N.NE.3 .AND. N.NE.5 .AND. N.NE.4) THEN
29         WRITE(6,*) ' Error in no. parameters specification',N
30         IFLAG=IFLAG+1
31         IF(IFLAG.LE.1) GO TO 101
32         STOP 1001
33     ENDIF
34  C  Set the parameter weights to 1.0
35     DO 30 I=1,N
36         IPAR(I)=1
37     30 CONTINUE
38     IF(N.EQ.5) THEN
39         WRITE(6,*) 'Input guesses for De, Re, Bo, L1, L2'
40     ELSEIF(N.EQ.4) THEN
41         WRITE(6,*) 'Input guesses for De, Re, Bo, L1'
42     ELSE
43         WRITE(6,*) 'Input guesses for De, Re, Bo'
44     ENDIF
45     READ(5,15) (PARM(I), I=1,N)
46     15  FORMAT(5F12.6)
47     PRINT*, ' Input the asymptotic value '
48     READ(5,15) EO
49     WRITE(6,15) EO
50     DO 17 I=1,100
51         W(I)=1.0
52         READ(10,18,END=19) R(I),E(I)

```

```

53      E(I)=E(I)-E0
54      WRITE(6,18) R(I),E(I)
55      17 CONTINUE
56      18 FORMAT(F12.5,F16.8)
57      WRITE(6,*) ' More than 100 points on data file '
58      STOP 100
59      19 NPT=I-1
60      WRITE(6,*) NPT,' points read on unit 10 '
61      CALL MARQ(NPT,N,IMAX,R,E,PARM,IPAR,W,W1,W2,W3,W4,COV)
62      WRITE(6,98) (TITLE(K),K=1,10)
63      98  FORMAT(2X,10A4)
64      STOP
65      END
66      SUBROUTINE DERNUM(N,PARM,NPT,R,E)
67      IMPLICIT REAL*8 (A-H,O-Z)
68      DIMENSION PARM(1),R(1),E(1)
69      DO 10 I=1,NPT
70          X=R(I)-PARM(2)
71          IF(N.EQ.3) THEN
72              TERM2=PARM(3)
73          ELSE IF(N.EQ.4) THEN
74              TERM2=PARM(3)*(1.+(PARM(4)*X))
75          ELSE
76              TERM2=PARM(3)*(1.+(PARM(4)*X)+(PARM(5)*(X**2)))
77          ENDIF
78          TERM=DEXP(-TERM2*X)
79          E(I)=(PARM(1)*((1.-TERM)**2))-PARM(1)
80      10 CONTINUE
81      RETURN
82      END
83 C      PURPOSE                                SOLD0030
84 C      MATRIX INVERSION AND SOLUTION OF LINEAR EQUATIONS    SOLD0040
85 C      SOURCE LANGUAGE                                SOLD0090
86 C      IBM SYSTEM 360 FORTRAN IV (DOUBLE PRECISION)        SOLD0100
87 C                                                        SOLD0110
88 C                                                        SOLD0140
89 C      CALLING SEQUENCE                                SOLD0150
90 C      CALL SOLVD (X,IX,M,N,PREC,DET,TEST)                SOLD0160
91 C                                                        SOLD0170
92 C      ON ENTRY                                          SOLD0180
93 C          X      - A TWO DIMENSION ARRAY CONTAINING THE MATRIX AND    SOLD0190
94 C                   OPTIONALLY SOME RIGHT HAND SIDES                SOLD0200
95 C          IX     - THE FIRST DIMENSION OF X                      SOLD0210
96 C          M      - THE NO. OF ROWS IN THE MATRIX                SOLD0220
97 C          N      - THE NO. OF COLUMNS IN THE MATRIX            SOLD0230
98 C                   N = M + (NO. OF RIGHT HAND SIDES)              SOLD0240
99 C          PREC   - A PARAMETER USED IN TESTING FOR SINGULAR MATRIX.    SOLD0250
100 C                   MATRIX IS SINGULAR IF ANY PIVOT IS SMALLER THAN    SOLD0260
101 C                   PREC * (MATRIX NORM). PREC GE 0, IF 0 THEN IS      SOLD0270
102 C                   ASSUMED TO BE .5D-14                            SOLDC280
103 C                                                        SOLD0290
104 C      ON RETURN                                          SOLD0300

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105	C	X - THE INVERSE MATRIX HAS REPLACED THE ORIGINAL	SOLD0310
106	C	AND THE RIGHT HAND SIDES (IF ANY) HAVE BEEN REPLACED BY	SOLD0320
107	C	THEIR CORRESPONDING SOLUTIONS	SOLD0330
108	C	DET - THE DETERMINANT	SOLD0340
109	C	TEST - =0 IF INVERSE AND SOLUTIONS ARE CALCULATED O.K.	SOLD0350
110	C	NE 0 IF MATRIX IS SINGULAR, IN WHICH CASE NO INVERSE	SOLD0360
111	C	OR SOLUTIONS HAVE BEEN FOUND	SOLD0370
112	C		SOLD0380
113		SUBROUTINE SOLVD(X,IX,M1,M,PREC1,DET,TEST)	
114	C		SOLD0400
115		IMPLICIT DOUBLE PRECISION (A-H,O-Z)	
116		INTEGER I1(255),I2(255)	SOLD0410
117		DIMENSION X(IX,2)	SOLD0420
118		EQUIVALENCE (BIG,TEMP,PIV)	SOLD0430
119		M=M1	
120		PREC=PREC1	
121		GO TO 4	
122		ENTRY INVERT(X,IX,M,DET,TEST)	
123		M=M	
124		PREC=0.0	
125		4 DET=1.	
126		TEMP = PREC	SOLD0450
127		IF (TEMP .EQ. 0.00) TEMP = 0.5E-10	SOLD0460
128		TEST=0.0	SOLD0470
129		DO 1 I = 1,M	SOLD0480
130		I2(I) = 0	SOLD0490
131		DO 1 J = 1,M	SOLD0500
132		1 TEST = TEST + X(I,J) * X(I,J)	SOLD0510
133		TEST = TEMP * DSQRT(TEST) / M	SOLD0520
134		DO 9 K=1,M	
135		BIG=0.0	SOLD0540
136		DO 3 I = 1,M	SOLD0550
137		IF (I2(I) .NE. 0) GO TO 3	SOLD0560
138		DO 2 J = 1,M	SOLD0570
139		IF (I2(J) .NE. 0) GO TO 2	SOLD0580
140		T=ABS(X(I,J))	SOLD0590
141		IF (T .LE. BIG) GO TO 2	SOLD0600
142		BIG = T	SOLD0610
143		IROW = I	SOLD0620
144		JCOL = J	SOLD0630
145		2 CONTINUE	SOLD0640
146		3 CONTINUE	SOLD0650
147		IF (BIG .LE. TEST) RETURN	SOLD0660
148		I1(K) = JCOL	SOLD0670
149		I2(JCOL) = IROW	SOLD0680
150		IF (JCOL .EQ. IROW) GO TO 6	SOLD0690
151		DO 5 J = 1,M	SOLD0700
152		TEMP = X(IROW,J)	SOLD0710
153		X(IROW,J) = X(JCOL,J)	SOLD0720
154		5 X(JCOL,J) = TEMP	SOLD0730
155		DET = -DET	SOLD0740
156		6 DET = DET * X(JCOL,JCOL)	SOLD0750

157	PIV = 1.E0/X(JCOL,JCOL)	SOLD0760
158	DO 7 J = 1,N	SOLD0770
159	IF (J .NE. JCOL) X(JCOL,J) = PIV * X(JCOL,J)	SOLD0780
160	7 CONTINUE	SOLD0790
161	X(JCOL,JCOL) = PIV	SOLD0800
162	DO 9 I = 1,M	SOLD0810
163	IF (I .EQ. JCOL) GO TO 9	SOLD0820
164	PIV = -X(I,JCOL)	SOLD0830
165	DO 8 J = 1,N	SOLD0840
166	IF (J .NE. JCOL) X(I,J) = X(I,J) + PIV * X(JCOL,J)	SOLD0850
167	8 CONTINUE	SOLD0860
168	X(I,JCOL) = PIV * X(JCOL,JCOL)	SOLD0870
169	9 CONTINUE	SOLD0880
170	DO 11 K = 1,M	SOLD0890
171	I = M+1 - K	SOLD0900
172	JCOL = I1(I)	SOLD0910
173	IROW = I2(JCOL)	SOLD0920
174	IF (IROW .EQ. JCOL) GO TO 11	SOLD0930
175	DO 10 I = 1,M	SOLD0940
176	TEMP = X(I,IROW)	SOLD0950
177	X(I,IROW) = X(I,JCOL)	SOLD0960
178	10 X(I,JCOL) = TEMP	SOLD0970
179	11 CONTINUE	SOLD0980
180	TEST=0.0	SOLD0990
181	RETURN	SOLD1000
182	END	SOLD1010
183	SUBROUTINE MARQ(M,N,IMAX,X,Y,A,IPAR,W,W1,W2,W3,W4,COV)	
184	IMPLICIT REAL*8(A-H,O-Z)	
185	DIMENSION X(1),Y(1),IPAR(1),A(1),W(1),W1(1),	
186	1 W2(1),W3(1,1),W4(1),YCOMP(300),STDEVA(300),COV(M,M),	
187	2 DELTA(300)	
188	REAL*8 RCONST(6)	
189	INTEGER ICONST(3)	
190	PRINT 4	
191	PRINT 3,(A(I),I=1,N)	
192	PRINT 1	
193	PRINT 3,(X(I),I=1,M)	
194	1 FORMAT(1X,'INITIAL Y-VALUES:')	
195	PRINT 2	
196	2 FORMAT(1X,'INITIAL FUNCTION VALUES:')	
197	PRINT 3,(Y(I),I=1,M)	
198	4 FORMAT(1X,'GUESSES AT PARAMETERS:')	
199	C	
200	C*** PRINT DATA	
201	C	
202	C	
203	C*** SET UP MRQRDT CONSTANTS	
204	C	
205	NDRIV=0	
206	ICONST(1)=1	
207	ICONST(2)=IMAX	
208	ICONST(3)=0	

```
209      RCONST(1)=.01
210      RCONST(2)=5.
211      RCONST(3)=1.D-6
212      RCONST(4)=.707
213      RCONST(5)=2.
214      RCONST(6)=0.
215 C
216      EXTERNAL DERNUM
217 C
218      CALL MRQRDT(DERNUM,N,X,Y,YCOMP,W,N,IPAR,A,STDEVA,COV,N,
219      1 SUM,ICONST,RCONST,DELTA,IEND,W1,W2,W3,N,W4,NDRIV)
220 C
221      IF(IEND.EQ.1)GO TO 100
222      IF(IEND.EQ.-1)GO TO 101
223      IF(IEND.EQ.-2)GO TO 102
224      IF(IEND.EQ.-3)GO TO 103
225 C
226 C      CALL MRQCNF(AMIN,AMAX,TTEST,FTEST,1,108,1)
227 C      THE CALL TO MRQCNF HAS BEEN REMOVED, SINCE THE CP6 VERSION
228 C      OF MRQRDT HAS HAD THE ENTRY POINT REMOVED. J. WRIGHT.
229 C
230 C***  OUTPUT THE RESULTS
231 C
232      PRINT 6
233      6 FORMAT(1X,'COMPUTED FUNCTION VALUES')
234      PRINT 3,(YCOMP(I),I=1,N)
235      3 FORMAT(1X,6E12.6)
236      PRINT 7
237      7 FORMAT(1X,'FINAL PARAMETER VALUES')
238      PRINT 3,(A(I),I=1,N)
239      PRINT 10
240      10 FORMAT(1X,'PARAMETER ERRORS')
241      PRINT 3,(STDEVA(I),I=1,N)
242      PRINT 8,SUM
243      8 FORMAT(1X,'SUM OF SQUARES = ',E12.6)
244      APOINT=M
245      RMSDEV=DSQRT(SUM/APOINT)
246      PRINT 9,RMSDEV
247      9 FORMAT(' RMS DEVIATION = ',E11.6)
248      DEL=0.0
249      DO 12 I=1,M
250      DEL2=DABS(YCOMP(I)-Y(I))
251      IF(DEL2.GT.DEL) DEL=DEL2
252      12 CONTINUE
253      PRINT 13,DEL
254      13 FORMAT(' MAX DEVIATION = ',E11.6)
255      GO TO 104
256      100 PRINT 200
257      200 FORMAT(' IMAX IS TOO SMALL')
258      GO TO 104
259      101 PRINT 201
260      201 FORMAT('CONVERGENCE TROUBLE IN MRQRDT(IEND=-1).USE FULL MRQRDT VN.
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261      1')
262      GO TO 104
263 102 PRINT 202
264 202 FORMAT('USE FULL MRQDRT VERSION.(IEND=-2)')
265      GO TO 104
266 103 PRINT 203
267 203 FORMAT(' TOO FEW DATA PTS. OR TOO MANY EQNS. ')
268 104 RETURN
269      END
270 C
271 C
272 C      ***BEWARE***
273 C
274 C
275 C      THIS IS A MODIFIED VERSION OF MRQDRT DESIGNED TO OBTAIN
276 C      DERIVATIVES NUMERICALLY, IF DESIRED.
277 C      THE FOLLOWING COMMENT CARDS SHOULD BE READ IN CONJUNCTION WITH
278 C      THE EXPLANATORY NOTE ON THE MODIFICATIONS. THIS NOTE CAN BE
279 C      OBTAINED FROM THE S.P.L. PROGRAM LIBRARIAN.
280 C      ***DATE:4/1/72.***
281 C
282 C
283 C      MRQDRT / GENERAL MINIMIZATION ROUTINE
284 C
285 C      AUTHOR / DATE
286 C      A.VELD / COMPUTATION CENTRE, NRC / FEBRUARY 1968
287 C
288 C      SOURCE LANGUAGE
289 C      IBM SYSTEM 360 FORTRAN IV
290 C
291 C      PURPOSE
292 C      1. TO CALCULATE THE LEAST SQUARES STATISTICS FOR A GIVEN MODEL AND
293 C          SET OF DATA
294 C      2. TO SOLVE A SYSTEM OF NON-LINEAR EQUATIONS
295 C
296 C      REFERENCES
297 C      SEE NRC PROGRAMMERS MANUAL, PROGRAM LIBRARY CHAPTER
298 C
299 C      ACCURACY---DOUBLE PRECISION
300 C
301 C      CALLING SEQUENCE
302 C          THERE ARE TWO ENTRIES DEPENDING UPON THE OPERATIONS DESIRED.
303 C          A MORE DESCRIPTIVE LIST IS GIVEN IN THE PROGRAMMER'S MANUAL.
304 C
305 C      1. CALL MRQDRT(DERIV,M,X,Y,YCOMP,W,N,IPAR,A,STDEVA,COV,N1,SUM,
306 C          1 ICONST,RCONST,DELTA,IEND,W1,W2,W3,ND,W4)
307 C
308 C          DERIV -NAME OF A USER SUPPLIED SUBROUTINE USED IN EVALUATING
309 C          FUNCTIONS OR FUNCTIONAL DERIVATIVES W.R.T. THE A(I) SET.
310 C          M      -NUMBER OF DATA POINTS
311 C          X,Y,W -USER'S DATA
312 C          N      -THE TOTAL NO. OF A(I) PARAMETERS INCLUDING THOSE NOT
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313 C      ENTERING THE REGRESSION.
314 C      IPAR -AN ARRAY SPECIFYING WHICH PARAMETERS ARE TO ENTER THE
315 C      MINIMIZATION. IPAR(I)=1, YES, IPAR(I)=0, NO FOR THE
316 C      I TH PARAMETER
317 C      A      -INITIAL ESTIMATES TO THE PARAMETERS. FINAL ESTIMATES
318 C      RETURNED VIA THIS ARRAY.
319 C      STDEVA-ESTIMATED STANDARD ERROR OF THE A(I) PARAMETERS.
320 C      COV      -CORRELATION MATRIX OF THE A(I) PARAMETERS.
321 C      N1      -FIRST DIMENSION OF COV (N.LE.N1).
322 C      SUM      -FINAL SUM OF SQUARES.
323 C      ICONST-AN INTEGER ARRAY CONTAINING ITERATION PARAMETERS.
324 C      ICONST(1)=1 IMPLIES NO WEIGHTS, W MAY BE ANY NAME AS IT IS
325 C      NOT REFERENCED.
326 C      =0 IMPLIES WEIGHTS ARE EMPLOYED.
327 C      ICONST(2)=MAXIMUM NO. OF FUNCTION EVALUATIONS
328 C      ICONST(3)=0 IF NO INTERMEDIATE OUTPUT.
329 C      =IDS IF THIS OUTPUT IS DESIRED. USUALLY IDS=3.
330 C      THIS OUTPUT IS SELF EXPLANATORY.
331 C      RCONST-A REAL ARRAY CONTAINING ITERATION PARAMETERS.
332 C      FOR FURTHER INFORMATION CONSULT PROGRAMMERS MANUAL
333 C      THE FOLLOWING VALUES ARE FOR THE AVERAGE SYSTEM.
334 C      RCONST(1)=0.01D0
335 C      RCONST(2)=10.0D0
336 C      RCONST(3)=CONVERGENCE TEST ON THE SUM OF SQUARES GE.1.0D-15
337 C      RCONST(4)=0.707D0 (ANGLE OF 45 DEGREES)
338 C      RCONST(5)=2.0D0
339 C      RCONST(6)=0.0D0
340 C      DELTA -CORRECTION VECTOR FOR A(I) OF DIMENSION N1
341 C      IEND -SWITCH INDICATING TYPE OF ENDING.
342 C      IEND=0 CONVERGENCE OCCURRED
343 C      IEND=1 CONVERGENCE WITHIN ICONST(2) FUNCTION EVALUATIONS
344 C      HAS NOT OCCURRED
345 C      IEND.LT.0 OTHER ERRORS. SEE INTERMEDIATE OUTPUT
346 C      W1      -WORK AREA OF DIMENSION M
347 C      W2      -WORK AREA OF DIMENSION N1
348 C      W3      -WORK AREA OF DIMENSION (ND,MAX(N+1,M))
349 C      W4      -WORK AREA OF DIMENSION N1
350 C
351 C      2. CALL MRQCNF(AMIN,AMAX,TTEST,FTEST,ISW,IPRINT,JMAX)
352 C
353 C      THIS ENTRY CALCULATES A VARIETY OF CONFIDENCE REGIONS.
354 C      SEE PROGRAMMERS MANUAL FOR A FULL DESCRIPTION.
355 C
356 C      USER SUPPLIED SUBPROGRAMS
357 C      THE USER SUPPLIED ROUTINE DERIV (SUBSTITUTE USERS NAME IF IT
358 C      IS DIFFERENT) CALCULATES FUNCTION VALUES AND DERIVATIVES. THIS
359 C      ROUTINE IS CALLED BY THE MRQDRT ROUTINE. PROGRAM SET-UP IS AS
360 C      FOLLOWS.
361 C
362 C      SUBROUTINE DERIV(N,IPAR,A,M,X,F,DF,N1,ISW)
363 C      REAL*8 A(2),X(2),F(2),DF(N1,2),IPAR(2)
364 C

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365 C      IF ISW=1 CALCULATE THE FUNCTION VALUES F
366 C      IF ISW=0 CALCULATE THE DERIVATIVES DF W.R.T. THE A(I) SET.
367 C
368 C      FOR THE SOLUTION OF A SYSTEM OF NON-LINEAR EQUATIONS,
369 C          G(K,A)=C(K)  K=1,2,...,N
370 C      WHERE G(K,A) IS THE K TH FUNCTION, SUBSTITUTE C FOR Y AND G(K,A)
371 C      FOR F(X(K),A) TO OBTAIN THE MINIMIZATION.
372 C
373 C      NOTE: THE SUBROUTINE MRQRDT HAS BEEN MODIFIED TO BE
374 C      COMPATIBLE WITH THE CP6 FORTRAN COMPILER. THE ENTRY
375 C      POINT HAS BEEN DELETED SO THAT MRQCNF IS ENTERED DIRECTLY
376 C      NOW. THEREFORE THERE IS ONLY ONE CALL TO MARQUARDT NOW,
377 C      AND NO SECOND CALL TO MRQCNF. THE FTEST AND TTEST
378 C      STATISTICS HAVE BEEN INACTIVATED--THEY ARE NOT NORMALLY
379 C      USED ANYWAY.
380 C-----
381 C
382 C      SUBROUTINE MRQRDT(FDERIV      ,M,X,Y,YCOMP,W,N,IPAR,AZERO,STDEVA,
383 C      1ASTAR,N1,SUMOLD,ICONST,RCONST,DELTA,IE,DELT,ABAR,D,ND,A1,NDRIV)
384 C
385 C      IMPLICIT REAL*8(A-H,O-Z)
386 C
387 C      DIMENSION X(M),Y(M),YCOMP(M),W(M),AZERO(N),STDEVA(N),ASTAR(N1,N),
388 C      1          RCONST(6),DELTA(N),IPAR(N),ICONST(3),DELT(M),ABAR(N),
389 C      2          D(ND,1),A1(N)
390 C      DIMENSION AMIN(5),AMAX(5)
391 C
392 C      REAL*8 LMBDN,NU,K,KDIV,LMBD1,LMBDMN/0.5D-16/,LMBDMX/1.0D70/
393 C
394 C      INTEGER*4 R
395 C
396 C      LOGICAL IWT
397 C
398 C      DATA LMAX/50/,PREC/0.0D0/
399 C
400 C      WRITE(108,2006) M
401 C2006 FORMAT(' ENTER MRQRDT, M=' I5)
402 C      IE=0
403 C      R=0
404 C      IWT=ICONST(1).NE.1
405 C      IMAX=ICONST(2)
406 C      IPRINT=ICONST(3)
407 C      IPRNT=IPRINT
408 C      LMBDN=RCONST(1)
409 C      COSMAX=RCONST(4)
410 C
411 C      CALCULATE THE INITIAL SUM OF SQUARES
412 C
413 C
414 C
415 C      6001 CALL FDERIV(N,AZERO,M,X,YCOMP,IPAR,ASTAR,N1,1)
416 C      6002 ISW1=1

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```

417 C
418 C
419     100 R=R+1
420         IF(R.GT.IMAX)GO TO 450
421         SUM1=0.0D0
422         DO 101 L=1,M
423             X1=(Y(L)-YCOMP(L))*2
424             IF(IWT)X1=X1+W(L)
425     101 SUM1=SUM1+X1
426         IF(ISW1.LT.1) GO TO 250
427         SUMOLD=SUM1
428         I1=0
429         K=1.0D0
430 C
431 C             PRINT OUT THE INITIAL PARAMETERS AND ITERATION CONSTANTS
432 C
433         IF(IPRINT.NE.0)WRITE(IPRINT,3009)
434     3009 FORMAT('1')
435         IF(IPRINT.NE.0)WRITE(IPRINT,3000)I1,LMBDM,COSMAX,SUMOLD,K,
436     1         (IPAR(J),AZERO(J),J=1,M)
437     3000 FORMAT ('0', I2, '   Q = ',D10.3, '   COS(B'') = ',F6.3,
438     1         '   SUM OF SQUARES = ',D12.5, '   1/K**D = ',D10.3 /
439     2         4(I5,D13.5))
440 C
441         IF(IMAX.EQ.1)RETURN
442         ISW1=-1
443         NU=RCNST(2)
444         CONV=RCNST(3)
445         KDIV=RCNST(5)
446         III=0
447 C
448 C             WRITE OUT THE STATISTICS FOR THE R TH ITERATION
449 C
450     110 IF(IPRINT.NE.0)WRITE(IPRINT,3001)R,SUMOLD
451     3001 FORMAT('0',82X,'NOFEV=',I4,' SUM OF SQUARES=',D12.5)
452         K=1.0D0
453 C
454 C             SET UP THE MATRIX SYSTEM WITHOUT HAVING DETERMINED LAMBDA
455 C
456 C
457 C
458         IF(NDRIV.GT.0)GO TO 5001
459 C*** CALCULATE THE DERIVATIVE MATRIX
460         DO 5005 I=1,M
461             EPS=1.D-5
462             STEP=DABS(EPS*AZERO(I))
463             IF(STEP.LT.1.D-5)STEP=1.D-5
464             AZERO(I)=AZERO(I)+STEP
465             CALL FDERIV(M,AZERO,M,X,DELTY,IPAR,D.WD,0)
466             DO 5004 J=1,M
467     5004 D(I,J)=(DELTY(J)-YCOMP(J))/STEP
468 C         WRITE(108,1055)(D(I,J),J=1,M)

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469 C8055 FORMAT('DERIV...',6E9.3)
476 5005 AZERO(I)=AZERO(I)-STEP
471 GO TO 5002
472 5001 CALL FDERIV(N,AZERO,M,X,YCOMP,IPAR,D,ND,0)
473 C
474 C
475 5002 DO 111 L=1,M
476 111 DELTY(L)=Y(L)-YCOMP(L)
477 X5=0.0D0
478 N2=0
479 DO 120 I=1,N
480 IF(IPAR(I).NE.1) GO TO 120
481 N2=N2+1
482 X4=0.0D0
483 DO 121 L=1,M
484 YCOMP(L)=D(I,L)
485 IF(IWT)YCOMP(L)=YCOMP(L)+W(L)
486 121 X4=X4+DELTY(L)*YCOMP(L)
487 J1=N2
488 DO 122 J=I,N
489 IF(IPAR(J).NE.1)GO TO 122
490 X1=0.0D0
491 DO 123 L=1,M
492 123 X1=X1+YCOMP(L)*D(J,L)
493 ASTAR(N2,J1)=X1
494 J1=J1+1
495 122 CONTINUE
496 STDEVA(N2)=DSQRT(ASTAR(N2,N2))
497 ASTAR(N2,N2)=1.0D0
498 X4=X4/STDEVA(N2)
499 'BAR(N2)=X4
500 A5=X5+X4*X4
501 120 CONTINUE
502 NP1=N2+1
503 IF (N2.EQ.1)GO TO 126
504 J1=N2-1
505 DO 125 I=1,J1
506 X1=STDEVA(I)
507 IP1=I+1
508 DO 125 J=IP1,N2
509 125 ASTAR(I,J)=ASTAR(I,J)/(X1*STDEVA(J))
510 C
511 C SET UP CONVERGENCE CRITERIA
512 C
513 126 IF(M-N2)130,131,131
514 130 IE=-3
515 IF(IPRINT.NE.0)WRITE('PRINT,3013)
516 3013 FORMAT('O M.L.T.N I AG THE PROBLEM INDETERMINATE')
517 GO TO 460
518 131 CONV1=CONV*(SUMOLD+RCONST(6))
519 200 LMBD1=LMBD' NU
520 IF(LMBD1.L1...BDMN)GO TO 269

```

```
521 C
522 C          STEP 1.
523 C
524      I1=1
525      210 DO 211 I=1,N2
526          D(I,I)=1.0D0+LMBD1
527          D(I,NP1)=ABAR(I)
528          IF(I.EQ.N2)GO TO 211
529          IP1=I+1
530          DO 212 J=IP1,N2
531              D(J,I)=ASTAR(I,J)
532      212 D(I,J)=ASTAR(I,J)
533      211 CONTINUE
534 C
535      CALL SOLVD (D,ND,N2,NP1,PREC,DET,TEST)
536      IF(TEST.NE.0.0D0)GO TO 350
537 C
538      COS1=0.0D0
539       $\lambda$ 1=0.0D0
540      DO 220 I=1,N2
541          X2=D(I,NP1)
542          DELTA(I)=X2/STDEVA(I)
543          COS1=COS1+X2*ABAR(I)
544      220 X1=X1+X2*X2
545          COS1=COS1/DSQRT(X1*X5)
546      225 I2=0
547          DO 230 I=1,N
548              IF(IPAR(I)-1)231,232,231
549      231 A1(I)=AZERO(I)
550              GO TO 230
551      232 I2=I2+1
552              A1(I)=AZERO(I)+K*DELTA(I2)
553      230 CONTINUE
554 C
555 C
556 C
557      7001 CALL FDERIV(N,A1,M,X,YCOMP,IPAR,ASTAR,N1,1)
558      7002 GO TO 100
559 C
560 C
561      250 IF(IPRINT.NE.0)WRITE(IPRINT,3000)I1,LMBD1,COS1,SUM1,K,
562          1      (IPAR(I),A1(I),I=1,N)
563 C
564 C          TEST FOR CONVERGENCE
565 C
566          IF(SUM1.LE.SUMOLD.OR.DABS(SUM1-SUMOLD).LE.CONV1)GO TO 400
567          IF(I1.EQ.2)GO TO 280
568          IF(I1.EQ.3)GO TO 300
569 C
570      269 LMBD1=LMBDN
571      270 I1=2
572          GO TO 210
```

```
573 C
574 C          STEP 2.
575 C
576 C          TRY LAMBDA=LAMBDA(R)*N**S AS LONG AS ALPHA GT ALPHAO
577 C
578 C      280 IF(COS1-COSMAX)281,281,282
579 C      281 LMBD1=LMBD1*NU
580 C          GO TO 270
581 C      282 K=1.0D0
582 C          I1=3
583 C          J=1
584 C      290 K=K/KDI'
585 C
586 C          STEP 3.
587 C
588 C          EVALUATE S(DELTA/K**J)
589 C
590 C          GO TO 225
591 C      300 J=J+1
592 C          IF(J.LE.LMAX)GO TO 290
593 C          IE=-1
594 C          GO TO 460
595 C
596 C          MATRIX WOULD NOT INVERT, INCREASE LAMBDA
597 C
598 C      350 LMBDN=LMBDN*NU
599 C          IF(LMBDN.LE.LMBDMX)GO TO 200
600 C          IE=-2
601 C          GO TO 460
602 C
603 C          TEST FOR CONVERGENCE
604 C
605 C      400 DO 401 J=1,N
606 C      401 AZERO(J)=A1(J)
607 C          LMBDN=LMBD1
608 C      WRITE(108,4000) SUM1,SUMOLD,CONV1
609 C      C4000 FORMAT('SUM1=',E13.5,'SUMOLD=',E12.5,'CONV1=',E12.5)
610 C          IF(DABS(SUM1-SUMOLD)-CONV1)410,410,411
611 C      411 SUMOLD=SUM1
612 C          GO TO 110
613 C      410 IE=0
614 C          GO TO 460
615 C      450 IE=1
616 C      460 CONTINUE
617 C
618 C-----
619 C
620 C          ENTRY POINT WHICH CALCULATES THE VARIOUS CONFIDENCE LIMITS
621 C
622 C-----
623 C
624 C          ENTRY MRQCNF(ANIN,AMAX,TTEST,FTEST,ISW,IPRNT,JMAX)
```

```
625      ISW=1
626      JMAX=1
627      TTEST=0.
628      FTEST=0.
629 C
630 C
631 C      WRITE(108,2007) M
632 C2007 FORMAT(1X,'M=',I5)
633 C      WRITE(108,2560) III
634 C2560 FORMAT(1X,'III=',I8)
635      IF(III.NE.0)GO TO 600
636      III=1
637      X3=0.0
638 C      WRITE(108,2001)
639 C2001 FORMAT(' VALUES OF M,N2,SUMOLD')
640 C      WRITE(108,2005) M,N2,SUMOLD
641 C2005 FORMAT(2I5,E13.5)
642      IF(M.GT.N2)X3=DSQRT(SUMOLD/(M-N2))
643      IF(N2.EQ.1)GO TO 502
644      I1=N2-1
645      DO 500 I=1,I1
646      IP1=I+1
647      DO 500 J=IP1,N2
648      500 ASTAR(J,I)=ASTAR(I,J)
649 C
650      502 CALL SOLVD (ASTAR,N1,N2,N2,PREC,DET,TEST)
651      I1=N2+1
652      I=N
653 C
654      501 IF(IPAR(I)-1)510,511,510
655      510 STDEVA(I)=0.0D0
656      DELTA(I)=0.0D0
657      GO TO 512
658      511 I1=I1-1
659      DELTA(I)=DELTA(I1)
660      A111=DABS(ASTAR(I1,I1))
661      ABAR(I1)=DSQRT(A111)
662      STDEVA(I)=X3*ABAR(I1)/STDEVA(I1)
663      512 X1=ABAR(I1)
664      J1=N2+1
665      J=N
666 C
667      520 IF(IPAR(I).EQ.1.AND.IPAR(J).EQ.1)GO TO 525
668      X2=0.0D0
669      GO TO 530
670      525 J1=J1-1
671      X2=ASTAR(I1,J1)/(X1*ABAR(J1))
672      530 ASTAR(I,J)=X2
673      J=J-1
674      IF(J.GE.1)GO TO 520
675      I=I-1
676      IF(I.GE.1)GO TO 501
```



```
677 C
678     DO 540 I=1,N
679     DO 540 J=I,N
680     540 ASTAR(J,I)=ASTAR(I,J)
681 C
682     IF(ISW.NE.1)GO TO 600
683     IF(IPRNT.EQ.0)GO TO 581
684     WRITE(IPRNT,3010)
685     3010 FORMAT('1 I ',11X,'A(I)',15X,'STANDARD ERROR',11X,
686     1      'LAST CORRECTION')
687     DO 541 I=1,N
688 C     IF(IPAR(I).EQ.1)WRITE(3,3014) I,AZERO(I),STDEVA(I),DELTA(I)
689     IF(IPAR(I).EQ.1)WRITE(IPRNT,3014) I,AZERO(I),STDEVA(I),DELTA(I)
690 C     IF(IPAR(I).NE.1)WRITE(3,3014) I,AZERO(I)
691     IF(IPAR(I).NE.1)WRITE(IPRNT,3014) I,AZERO(I)
692     3014 FORMAT('0',I4,3D25.15)
693     541 CONTINUE
694     WRITE(IPRNT,3011)
695     3011 FORMAT('0 CORRELATION MATRIX')
696     DO 550 I=1,N
697     550 WRITE(IPRNT,3003)(ASTAR(I,J),J=1,I)
698     3003 FORMAT('0',10F13.9)
699     IF(.NOT.IWT)WRITE(IPRNT,3004)
700     3004 FORMAT('0',20X,'OBSERVED',22X,'ESTIMATED',20X,'DIFFERENCE'/)
701     IF(IWT)WRITE(IPRNT,3012)
702     3012 FORMAT('0',20X,'OBSERVED',22X,'ESTIMATED',20X,'DIFFERENCE',21X,
703     1      'WEIGHTS'/)
704     DO 560 L=1,M
705     K=Y(L)-YCOMP(L)
706     IF(.NOT.IWT)WRITE(IPRNT,3005)L,Y(L),YCOMP(L),K
707     IF(IWT)WRITE(IPRNT,3005)L,Y(L),YCOMP(L),K,W(L)
708     3005 FORMAT(' ',I5,4D30.15)
709     560 CONTINUE
710     581 RETURN
711 C
712     600 IF(ISW-3)601,610,620
713     601 X1=TTEST
714     GO TO 611
715     610 X1=DSQRT(N2*FTEST)
716     611 DO 612 I=1,N
717     X2=X1*STDEVA(I)
718     AMIN(I)=AZERO(I)-X2
719     612 AMAX(I)=AZERO(I)+X2
720     SCRIT=SUMOLD
721     GO TO 800
722 C
723     620 SCRIT=SUMOLD*(1.0D0+N2*FTEST/(M-N2))
724     DO 630 I=1,N
725     X2=AZERO(I)
726     IF(IPAR(I).EQ.1)GO TO 640
727     AMIN(I)=X2
728     AMAX(I)=X2
```

```
729      GO TO 630
730 C
731      640 X3=TTEST*STDEVA(I)
732      X1=X3
733      641 ISW1=0
734      PO=0.0D0
735      PHIO=SUMOLD
736      P1=1.0D0
737      DO 650 J=1,JMAX
738      AZERO(I)=X2+P1*X1
739 C
740 C
741      8001 CALL FDERIV(N,AZERO,M,X,DELT,IPAR,ASTAR,M1,1)
742      8002 PHI1=0.0D0
743 C
744 C
745      DO 651 L=1,M
746      X4=(Y(L)-DELT(L))*2
747      IF(IWT)X4=X4*W(L)
748      651 PHI1=PHI1+X4
749      IF(ISW1)660,660,670
750      660 IF(PHI1-SCRIT)661,661,662
751      661 P2=2.0D0*P1
752      GO TO 680
753      662 ISW1=2
754 C
755      670 IF(DABS(P1-PO).LT.1.0D-2*DABS(PO))GO TO 690
756      P2=PO+(SCRIT-PHI0)*(P1-PO)/(PHI1-PHI0)
757 C
758      680 PO=P1
759      P1=P2
760 C
761      650 PHIO=PHI1
762      AZERO(I)=X2
763 C
764      690 IF(X1)691,691,692
765      692 AMAX(I)=AZERO(I)
766      X1=-X3
767      GO TO 641
768      691 AMIN(I)=AZERO(I)
769      630 AZERO(I)=X2
770 C
771 C      OUTPUT THE RESULTS IF DESIRED
772 C
773      800 IF(IPRNT.EQ.0)GO TO 850
774      WRITE(IPRNT,3008)ISW,TTEST,FTEST,M,M2,SCRIT
775      3008 FORMAT('1CONFIDENCE LIMIT CALCULATIONS USING TECHNIQUE NUMBER',
776      1      I3/' T(M-N)=' ,D22.15,' F(M,M-N)=' ,D22.15,' FOR',I5,' POINTS',
777      2      ' USING',I5,' PARAMETERS'/'OS**2 CRITICAL=' ,D22.15/'OPARA',
778      3      8X,'LOWER A',16X,'A',16X,'UPPER A'//)
779      DO 801 I=1,M
780      IF(IPAR(I)-1)802,803,802
```

```
781 C
782   802 WRITE (IPRNT,3007)I,AZERO(I)
783   3007 FORMAT(' ',I5,20X,D20.10)
784       GO TO 801
785   803 X1=AZERO(I)-AMIN(I)
786       X2=AMAX(I)-AZERO(I)
787       WRITE(IPRNT,3008)I,AMIN(I),AZERO(I),AMAX(I),X1,X2
788   3008 FORMAT(' ',I5,5D20.10)
789   801 CONTINUE
790 C
791   850 RETURN
792       END
```

```

1 C  PROGRAM FOR EVJ FIT USING:
2 C  EVJ = WE*(V+.5) - WEKE*(V+.5)**2 + WEYE*(V+.5)**3 + BE*J*(J+1)
3 C      -ALPHA*(V+.5)*J*(J+1)
4 C Set unit 10 for read-in of v,j, Evj cards. (No end card req.)
5     IMPLICIT REAL*8 (A-H,O-Z)
6     DIMENSION X(2,300),EVJ(300),PARM(5),IPAR(5),WORK(1000),
7     1 W(1000),W1(1000),W2(1000),W3(300,300),W4(1000),TITLE(20),
8     2 COV(1000)
9     N=5
10    IMAX=100
11    WRITE(6,*) 'Input title (max. 20 chars.)'
12    READ(5,99) (TITLE(I),I=1,20)
13    99 FORMAT(20A4)
14    WRITE(6,*) 'Input zero-point energy (in cm-1)'
15    READ(5,*) ZPE
16    WRITE(6,*) ' ZPE = ',ZPE
17    WRITE(6,99) (TITLE(I),I=1,20)
18    DO 17 J=1,M
19    READ(10,20,END=18) X(1,J),X(2,J),EVJ(J)
20    20 FORMAT(3F)
21    EVJ(J)=EVJ(J)+ZPE
22  17 CONTINUE
23  18 M=J-1
24    WRITE(6,*) ' Input guesses for parameters we, weke, weye',
25    1 ' Be, alphae'
26    READ(5,21) (PARM(I),I=1,M)
27    21 FORMAT(5F)
28    DO 3 I=1,M
29    3 IPAR(I)=1
30    WRITE(6,100)
31    100 FORMAT(' INPUT VALUES ARE : ',/)
32    WRITE(6,101)
33    101 FORMAT('      V      J      EVJ      ',/)
34    DO 4 I=1,M
35    W(I)=1.0
36    WRITE(6,102) X(1,I),X(2,I),EVJ(I)
37    4 CONTINUE
38    102 FORMAT(3X,F4.1,6X,F4.1,F10.1)
39    CALL MARQ(M,M,IMAX,X,EVJ,PARM,IPAR,W,W1,W2,W3,W4,COV)
40    STOP
41    END
42    SUBROUTINE DERNUM(M,PARM,M,X,EVJ)
43    IMPLICIT REAL*8 (A-H,O-Z)
44    REAL*8 J
45    DIMENSION X(2,1),PARM(1),EVJ(1)
46    DO 1 I=1,M
47    V=X(1,I)
48    J=X(2,I)
49    EVJ(I)=PARM(1)*(V+0.5) - PARM(2)*(V+0.5)**2
50    1 + PARM(4)*J*(J+1) - PARM(5)*(V+0.5)*J*(J+1)
51    2 + PARM(3)*(V+0.5)**3
52    1 CONTINUE

```

October 12, 1989

VBEVJFIT5

Page B-26

53 RETURN
54 END

```

1 C      PLOT WITH DISSPLA package.                                VBP00010
2 C n.b. use DISFI EXEC.                                          VBP00020
3 C      plot of potential energy curve, with lowest v-levels.    VBP00030
4      DIMENSION RR(100), EE(100),EVIB(2),RVIB(2),PC(5), SC(5)    VBP00040
5      COMMON DY(1000)                                           VBP00050
6 C Data for MgH molecule.                                         VBP00060
7 C      Pot. Curve:      D-e      R-e      beta      1-1      1-2    VBP00070
8      DATA(SC(L),L=1,5)/1499.8,24.61,-1.331,5.796,0.199/
9      DATA(PC(L),L=1,5)/1.3420,3.2928,0.9154,0.1323,0.0488 /
10 C      Spec. Const.:      w-e      w-ex-e w-ey-e B-e alpha-e    VBP00100
11 C Data for AlH curve:
12 C      DATA(PC(L),L=1,5)/3.1786,3.1212,0.6851,-0.0094,0.0177 /
13 C      DATA(SC(L),L=1,5)/1727.9,27.27,0.133,6.362,0.167 /
14 C DADData for SiH molecule:
15 C      DATA(PC(L),L=1,5)/3.1364,2.8953,0.8142,0.0098,0.0251 /
16 C      DATA(SC(L),L=1,5)/2038.3,35.04,0.055,7.388,0.211 /
17 C Data for PH molecule:
18 C      DATA(PC(L),L=1,5)/3.0527,2.7081,0.9583,0.0412,0.0318 /
19 C      DATA(SC(L),L=1,5)/2362.1,43.79,-0.203,8.424,0.258 /
20 C Data for SH molecule:
21 C      DATA(PC(L),L=1,5)/3.7127,2.5489,0.9947,0.0300,0.0294 /
22 C      DATA(SC(L),L=1,5)/2702.5,50.22,-0.099,9.494,0.285 /
23 C Data for HCl molecule
24 C      DATA(PC(L),L=1,5)/4.6199,2.4122,0.9993,0.0029,0.0358 /
25 C      DATA(SC(L),L=1,5)/3025.6,54.45,0.150,10.571,0.310 /
26      NPTS=100                                                    VBP00120
27      EVTOCH=8065.48                                             VBP00130
28      NVIB=6                                                      VBP00140
29      NROT=6                                                      VBP00140
30      XLEN=6.0D0                                                  VBP00150
31      YLEN=8.0D0                                                  VBP00160
32      XDIV=6.0D0                                                  VBP00170
33      YDIV=8.0D0                                                  VBP00180
34 C      ...to decide where to start & end domain,
35 C      solve for real roots at -0.2 eV.
36      CALL RROOTS(PC,-0.2,REND,RSTART)
37      WRITE(6,*) ' ROOTS FOR -0.2 EV ',RSTART,REND
38      DO 77 J=1,1000
39      DY(J)=0.2                                                    VBP00190
40      77 CONTINUE                                                VBP00200
41      CALL BCOMMON(5000)                                          VBP00210
42 C      Generate the energies, beginning at R-start.            VBP00220
43      RINC=(REND-RSTART)/100.                                     VBP00230
44      RR(1)=RSTART - RINC                                         VBP00240
45      RMIN=RSTART                                                  VBP00250
46      RMAX=REND                                                    VBP00260
47 C      Use the GMF-5 function to construct curve.             VBP00270
48      DO 100 I =1,NPTS                                           VBP00280
49      RR(I)=RSTART+FLOAT(I)*RINC                                  VBP00290
50      XX=RR(I)-PC(2)                                              VBP00300
51      BETA=PC(3)*(1.0+PC(4)*XX+PC(5)*XX*XX)                     VBP00310
52      EE(I)=PC(1)* ( 1.0-EXP(-BETA*XX))*2 - PC(1)               VBP00320

```

53	C	WRITE(6,*) RR(I), EE(I)	VBP00340
54	100	CONTINUE	VBP00350
55		EMAX=MAX(EE(1),EE(100))	VBP00360
56		EMIN=-PC(1)	VBP00370
57		RDON= ABS(RMIN-RMAX)/12.0	VBP00380
58		RMIN= (RMIN-RDON)	VBP00390
59		RMAX= (RMAX+RDON)	VBP00400
60		WRITE(6,*) 'The R-domain goes from ',RMIN,' to ',RMAX	VBP00410
61		WRITE(6,*) ' Accept = 0; reject = other no. '	VBP00420
62		READ(5,*) IANS	VBP00430
63		IF (IANS.NE.0) THEN	VBP00440
64		WRITE(6,*) 'Please respecify Rmin and Rmax.'	VBP00450
65		READ(5,*) RMIN,RMAX	VBP00460
66		ENDIF	VBP00470
67		EDON= (EMIN-EMAX)/12.0	VBP00480
68		EMIN= (EMIN-EDON)	VBP00490
69		EMAX= (EMAX+EDON)	VBP00500
70		WRITE(6,*) 'The E-range goes from ',EMIN,' to ',EMAX	VBP00510
71		WRITE(6,*) ' Accept = 0; reject = other no. '	VBP00520
72		READ(5,*) IANS	VBP00530
73		IF (IANS.NE.0) THEN	VBP00540
74		WRITE(6,*) 'Please respecify Emin and Emax.'	VBP00550
75		READ(5,*) EMIN,EMAX	VBP00560
76		ENDIF	VBP00570
77		WRITE(6,*) 'RMIN, RMAX = ',RMIN,RMAX	VBP00580
78		WRITE(6,*) 'EMIN, EMAX = ',EMIN,EMAX	VBP00590
79		DELX=ABS(RMIN-RMAX)/XDIV	VBP00600
80		DELY=ABS(EMIN-EMAX)/YDIV	VBP00610
81		WRITE(6,*) 'DELX and DELY = ',DELX,DELY	VBP00620
82		WRITE(6,*) ' Accept = 0; reject = other no. '	VBP00630
83		READ(5,*) IANS	VBP00640
84		IF (IANS.NE.0) THEN	VBP00650
85		WRITE(6,*) 'Please respecify delx and dely.'	VBP00660
86		READ(5,*) DELX,DELY	VBP00670
87		ENDIF	VBP00680
88		WRITE(6,*) 'DELX and DELY = ',DELX,DELY	VBP00690
89	C	... recalculate the RMAX and EMAX values, now that	VBP00700
90	C	DELX and DELY are known	VBP00710
91		RMAX=RMIN+XDIV*DELX	VBP00720
92		EMAX=EMIN+YDIV*DELY	VBP00730
93		WRITE(6,*) 'RMIN,RMAX = ',RMIN,RMAX	VBP00740
94		WRITE(6,*) 'EMIN,EMAX = ',EMIN,EMAX	VBP00750
95		CALL ANYDEV	VBP00760
96		CALL PAGE(8.5,11.)	VBP00770
97		CALL NOBRDR	VBP00780
98		CALL AREA2D(XLEN,YLEN)	VBP00790
99		CALL SIMPLX	VBP00800
100		CALL HEIGHT(0.16)	VBP00810
101		CALL MX1ALF('STANDARD','/')	VBP00820
102		CALL MX2ALF('L/CSTD','%')	VBP00830
103		CALL MX3ALF('INSTR','*')	VBP00840
104		CALL MX4ALF('GREEK','&')	VBP00850

```

105      CALL XREVTX
106      CALL XNAME('R% (BOHR)',9)
107      CALL YREVTX
108      CALL YNAME('ENERGY (%E/V)',13)
109      CALL GRAF(RMIN,DELX,RMAX,EMIN,DELY,EMAX)
110      CALL THKCRV(.008)
111      CALL CURVE(RR,EE,NPTS,0)
112 C      Now, we want to calculate the energies of the lowest NVIB
113 C      vibrational levels, and find the outer and inner turning
114 C      points, so that a line can be drawn corresponding to that
115 C      particular v-level. (Finding the turning points of the
116 C      GMF-5 function is done in the subroutine called RROOTS.)
117      CALL THKCRV(.004)
118      DO 200 IV=1,NVIB
119          V= FLOAT(IV-1) + 0.5
120          DO 200 IJ= NROT,NROT+1
121 C              ...only want (NROT-1)-th level drawn
122              XJ=FLOAT((IJ-1)*IJ)
123              ELEV=SC(1)*V - SC(2)*V*V + SC(3)*V*V*V
124              1      +SC(4)*XJ - SC(5)*V*XJ
125              EVIB(1)=-PC(1)+ELEV/EVTOCH
126              CALL RROOTS(PC,EVIB(1),RVIB(1),RVIB(2))
127              EVIB(2)=EVIB(1)
128 C              Check to see that the points are within the region of
129 C              the graph.
130              IF(RVIB(1).GT.RMIN .AND. RVIB(1).LT.RMAX .AND.
131              1      RVIB(2).GT.RMIN .AND. RVIB(2).LT.RMAX .AND.
132              2      EVIB(1).GT.EMIN .AND. EVIB(1).LT.EMAX ) THEN
133                  CALL CURVE(RVIB,EVIB,2,0)
134              ENDIF
135 200      CONTINUE
136      CALL ENDPL(0)
137      CALL DONEPL
138      END
139      SUBROUTINE RROOTS(PC,V1,ROOT1,ROOT2)
140 C      This subroutine calculates the R value from a given Energy.
141 C      assuming that the function is a 5-parameter generalized
142 C      Morse function. For the analytical roots, (5 of which exist)
143 C      only two are real, and these are the turning points of
144 C      the 5-parameter curve.
145 C      -VJB 10.10.89
146      IMPLICIT REAL*4(A-H, O-Z)
147      REAL*4 L1,L2,PC(5)
148      DE=PC(1)
149      RE=PC(2)
150      BO=PC(3)
151      L1=PC(4)
152      L2=PC(5)
153      IROOT=1
154 C      Now the GMF-5 is solved for x, where x=R-Re
155 C      V=De(1-exp(-beta*x))**2 -De
156 C      where beta = b0(1+l1*x+l2*x*x)

```

VBP00860
 VBP00870
 VBP00880
 VBP00890
 VBP00900
 VBP00910
 VBP00920
 VBP00930
 VBP00940
 VBP00950
 VBP00960
 VBP00910
 VBP00980
 VBP00990
 VBP01000
 VBP01010
 VBP01020
 VBP01030
 VBP01060
 VBP01070
 VBP01080
 VBP01090
 VBP01100
 VBP01110
 VBP01120
 VBP01130
 VBP01140
 VBP01150
 VBP01160
 VBP01170
 VBP01180
 VBP01190
 VBP01200
 VBP01210
 VBP01220
 VBP01230
 VBP01240
 VBP01250
 VBP01260
 VBP01270
 VBP01280
 VBP01290
 VBP01300
 VBP01310
 VBP01320
 VBP01330
 VBP01340


```
157 C          and then the values of R are found by adding Re.          VBP01350
158 C                                                  VBP01360
159      TN= -(-DE+SQRT(DE*(DE+V1)))/DE          VBP01370
160      TN=ALOG(TN)          VBP01380
161      TP= ( DE+SQRT(DE*(DE+V1)))/DE          VBP01390
162      TP=ALOG(TP)          VBP01400
163      RECIP6 =1.0/6.0          VBP01410
164 C                                                  VBP01420
165 100      F1 =      L1/(6.0*L2*L2) - TN/(2.0*B0*L2) - (L1/(3.0*L2))**3          VBP01430
166      F2 = (4.0*L2*B0*B0 -L1*L1*B0*B0 - 18.0*L1*L2*B0*TN          VBP01440
167      2  + 27.0*TN*TN*L2*L2 + 4.0*TN*(L1**3)*B0 )          VBP01450
168      F2 = RECIP6 * F2**(1./2.) /(SQRT(3.0)*L2*L2*B0)          VBP01460
169      F3 = (F1+F2)**(1./3.)          VBP01470
170 C          ...fortvs didn't like finding the cubic root of -ve no.          VBP01480
171      F4 = -ABS(F1-F2)**(1./3.)          VBP01490
172      ROOT = F3+F4 -L1/(3.*L2)          VBP01500
173 C                                                  VBP01510
174      IF(IROOT.EQ.1) ROOT1=ROOT+RE          VBP01520
175      TN=TP          VBP01530
176      IROOT=IROOT+1          VBP01540
177      IF(IROOT.EQ.2)      GO TO 100          VBP01550
178      ROOT2=ROOT+RF          VBP01560
179      RETURN          VBP01570
180      END          VBP01580
```

1	WRITE(6,11)	PAR00010
2	11 FORMAT(' INPUT NUMBER OF CASES')	PAR00020
3	READ(5,*) NCASE	PAR00030
4	DO 10 I=1,NCASE	PAR00050
5	WRITE(6,1)	PAR00080
6	1 FORMAT(' INPUT X1,X2,X3')	PAR00070
7	READ(5,*) X1,X2,X3	PAR00080
8	WRITE(6,3)	PAR00100
9	3 FORMAT(' INPUT Y1,Y2,Y3')	PAR00110
10	READ(5,*) Y1,Y2,Y3	PAR00120
11	$C = (1. / (X2 - X3)) * ((Y1 - Y2) / (X1 - X2) - (Y1 - Y3) / (X1 - X3))$	PAR00130
12	$B = ((Y1 - Y3) / (X1 - X3)) - C * (X1 + X3)$	PAR00140
13	$A = Y1 - B * X1 - C * X1 ** 2$	PAR00150
14	$X = -B / (2. * C)$	PAR00160
15	$Y = A + B * X + C * X ** 2$	PAR00170
16	WRITE(6,4)X1,Y1	PAR00180
17	WRITE(6,4)X2,Y2	PAR00190
18	WRITE(6,4)X3,Y3	PAR00200
19	WRITE(6,5) X,Y	PAR00210
20	WRITE(6,14)A,B,C	PAR00220
21	14 FORMAT(' A + BX + CX*X', 'A=',E12.5, ' B=',E12.5, ' C=',E12.5)	PAR00230
22	4 FORMAT(2F10.5)	PAR00240
23	5 FORMAT(/, ' XMIN=',F10.6,2X, 'YMIN=',F10.6)	PAR00250
24	10 CONTINUE	PAR00260
25	END	PAR00270

APPENDIX C. Sample Worksheet

Worksheet for Si_2 ($X^3\Sigma_g^-$) molecule with a (9s6p2d) data set, showing D_{2h} symmetry allocations of Cartesian orbitals. (Refer also to Table 2.2.) Notation refers to the Si_2 molecule situated along the principal axis, with Si atoms at A and $-A$ distances. The ground state occupation of Si_2 is $[\text{Ne}]_2 1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 1\pi_u^1 1\pi_u^1$. Arrows ($\uparrow$) refer to unpaired electrons.

			Abelian		Symmetry		Type		
	1	2	3	4	5	6	7	8	Row
	A_g	B_{3u}	B_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{3g}	A_u	
$9(s_{-A} + s_A)$	9				9				<i>A</i>
$6(p_{-A} + p_A)$	6	6	6		6	6	6		<i>B</i>
$2(d_{-A} + d_A)$	6	2	2	2	6	2	2	2	<i>C</i>
Total Unfrozen Orbs. $A + B + C$	21	8	8	2	21	8	8	2	<i>D</i>
SCF occ. pairs	5	1, $\uparrow$	1, $\uparrow$	0	4	1	1	0	<i>E</i>
Freeze core pairs	3	1	1	0	3	1	1	0	<i>F</i>
Freeze anti-core orbs.	3	1	1	0	3	1	1	0	<i>G</i>
Tot. Orbs. after Freezing $D - (F + G)$	15	6	6	2	15	6	6	2	<i>H</i>
PARK Renumbering for Orbitals	1-15	16-21	22-27	28-29	30-44	45-50	51-56	57-58	<i>I</i>
Valence occ. pairs $E - F$	2	$\uparrow$	$\uparrow$		1				

Therefore, the ground state occupation for the CI section of the calculation (PARK notation; increasing order with open shells first) would be 16 22 1 2 30.

1	HONDO SI2					
2	SI2	MOLECULE, TZPP		BASIS		
3	0	0	0			
4	C1					
5	0	1	0			
6	SI	14.0	0.0		0.0	2.1222
7	1	S	4			
8	1	69379.23		0.0003175		
9	2	10354.94		0.0024857		
10	3	2337.88		0.0130303		
11	4	657.14		0.0522608		
12	2	S	1			
13	1	214.30		1.0		
14	3	S	1			
15	1	77.629		1.0		
16	4	S	1			
17	1	30.631		1.0		
18	5	S	1			
19	3	12.801		1.0		
20	6	S	1			
21	1	3.9269		1.0		
22	7	S	1			
23	1	1.4523		1.0		
24	8	S	1			
25	1	0.2562		1.0		
26	9	S	1			
27	1	0.0943		1.0		
28	10	P	4			
29	1	335.48		0.0035551		
30	2	78.900		0.0273860		
31	3	24.988		0.1166338		
32	4	9.2197		0.2933742		
33	11	P	1			
34	1	3.6211		1.0		
35	12	P	1			
36	2	1.4513		1.0		
37	13	P	1			
38	1	0.5050		1.0		
39	14	P	1			
40	1	0.1863		1.0		
41	15	P	1			
42	1	0.0654		1.0		
43	16	D	1			
44	1	0.15		1.0		
45	17	D	1			
46	1	0.375		1.0		
47						
48	SI	14.0	0.0		0.0	-2.1222
49	1	S	4			
50	1	69379.23		0.0003175		

51	2	10354.94	0.0024857
52	3	2333.88	0.0130303
53	4	857.14	0.0522608
54	2	S 1	
55	1	214.30	1.0
56	3	S 1	
57	1	77.629	1.0
58	4	S 1	
59	1	30.631	1.0
60	5	S 1	
61	3	12.801	1.0
62	6	S 1	
63	1	3.9269	1.0
64	7	S 1	
65	1	1.4523	1.0
66	8	S 1	
67	1	0.2562	1.0
68	9	S 1	
69	1	0.0943	1.0
70	10	P 4	
71	1	335.48	0.0035551
72	2	78.900	0.0273860
73	3	24.988	0.1166338
74	4	9.2197	0.2933742
75	11	P 1	
76	1	3.6211	1.0
77	12	P 1	
78	2	1.4513	1.0
79	13	P 1	
80	1	0.5050	1.0
81	14	P 1	
82	1	0.1863	1.0
83	15	P 1	
84	1	0.0654	1.0
85	16	D 1	
86	1	0.15	1.0
87	17	D 1	
88	1	0.375	1.0
89			
90			
91			
92	YELLOG DATA		
93			
94	SCFYEL SI2		
95	1		
96	1	70	1 0
97	4	2	2 0 4 1 1 0
98	1 11	1 1 1 1 1	1 1 1 11 1 11 1 11 1 11
99	STONEY SI2		
100	1	1	1 1

APPENDIX D.1

Comparative calculation times for BF- and PF-containing basis sets. Refer also to Tables 3.1 and 3.2. These calculations were done on a Sun 386i/250 workstation. The CPU times are given in seconds. The names in italics refer to the MRD-CI program used.

	BF Basis Set	PF Basis Set
Basis set functions	<i>4s</i> + BF(<i>4s3p1d</i>)	<i>4s3p</i>
Number of functions	27	26
Size of SD-CI matrix	109	80
SD-CI energy (hartree)	-1.172868	-1.171830
Integral evaluation (<i>hondo</i>)	67	56
Symmetry transformation (<i>yellow</i>)	12	9
LCAO-MO's creation (<i>scfyel</i>)	12	6
Core/anti-core freezing (<i>stonej</i>)	12	6
Configuration generator (<i>parkeu</i>)	0.4	0.3
CI matrix calculation (<i>rumple</i>)	2	1
CI matrix diagonalization (<i>condor</i>)	22	22

END

2002/9 1

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