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**Stability of the Ground and Excited
States of Diatomic Neutral and
Multiply Charged Molecules**

by

Marcin Kolbuszewski, M.Sc.

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

Department of Chemistry

Carleton University
Ottawa, Ontario
November 9, 1993

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Abstract

This work is devoted to the theoretical study of bonding in neutral and multiply charged heteronuclear diatomic molecules.

An effect of significant strengthening of the bond upon double excitation of the $2\sigma_u^2 \rightarrow \text{bonding molecular orbital}$ type was observed previously for a series of homonuclear diatomics. Using BeC and its positive ions as prototypes it is shown in this thesis that significant bond shortening and strengthening can also be observed in heteronuclear molecules. Strongly bound doubly excited states are present in BeC and BeC^{2+} . In these systems the maximum occupation of π orbitals corresponds to the strongest bonds, irrespective of the nature of the molecular orbitals and term energy of the strongly bound state. Potential curves and spectroscopic constants are given for the low-lying states of BeC, BeC^+ , and BeC^{2+} . The contribution to the total (CI) wave function for each state is analyzed in terms of the contributions from the important configurations.

In the second part of the thesis, the main conditions for stability of a diatomic dication are reviewed and applied to examine the stability of several molecules. BeF^{3+} , MgN^{2+} , MgF^{2+} , and AlF^{2+} dications are predicted and shown to be new thermodynamically stable ions. The stability is explained in terms of polarization of a neutral atom by a dication of the metal and an avoided crossing between repulsive and attractive potential curves. Thermodynamically unstable BeC^{2+} and MgC^{2+} diatomic dications are shown to have several metastable electronic states. The importance of strongly bonding configurations in the stability of multiply charged diatomic and the possible ways of increasing bonding interaction in the attractive channel are discussed. The BF^{2+} dication is characterized by an unusually strong bond.

The criteria of thermodynamic stability of multiply charged molecules are discussed and stability is predicted for the currently unknown diatomic dications SiN^{2+} ,

SiO^{2+} , SiF^{2+} , MgCl^{2+} , several noble gas species, and transition metal compounds. Based on the findings of this work, general arguments are given for the existence of novel compounds in condensed and gas phases. The differences between the energy content of stable and metastable dications are discussed. The neutralization of the positive charge of a multiply charged ion does not necessarily lead to the loss of high energy content.

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Preface

The general approach to the solution of problems of a chemical nature used in this thesis can be described as a "theoretical experiment". In general it consists of performing the calculations on the chemical entities, using established methods, instead of performing the experimental determination of the same properties. The limitations and advantages of such an approach are discussed and the applicability of the methods is verified on some systems where the accurate results are already known.

Some of the results included in this thesis were published elsewhere. The strongly bound doubly excited states of BeC were discussed in reference [1]. The thermodynamic stability of BeF^{2+} was established in reference [2].

Chapters 3 and 4 are essentially independent and can be read separately, however some aspects of the results presented in Chapter 3 motivated the work reported in Chapter 4.

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Chapter 1

Introduction

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known... the difficulty is only that the *exact*¹ application of these laws leads to equations much too complicated to be soluble.

P.A.M. Dirac

The correctness of Dirac's opinion is clear in modern quantum chemistry. Exact application, in our case of the Schrödinger equation, leads to equations that cannot be solved accurately for more than a one-electron system. Quantum chemistry is a science which depends upon introducing rational approximations and subsequent solution of the approximate problems. The solution is then approximate but the limitations of the answers obtained are generally known. For example, a graduate textbook by Szabo and Ostlund [3] explains the modern approaches to the calculation of the electronic structure and properties of molecules.

In the standard approach to solve the Schrödinger equation $H\Psi = E\Psi$, the Born-Oppenheimer approximation is invoked. The motion of nuclei (which are heavier than electrons) is much slower than that of electrons. Therefore, for a fixed geometrical arrangement of nuclei the electronic wavefunction (depending only on electron coordinates) is written as a linear combination of Slater determinants:

$$\Psi = \sum a_j \Psi_j \tag{1.1}$$

¹emphasis MK

where Slater determinants Ψ_j contain molecular orbitals ψ_i :

$$\Psi_j = \det|\psi_1\psi_2 \dots \psi_n| \quad (1.2)$$

and a molecular orbital ψ_i is written as a linear combination of basis functions:

$$\psi_i = \sum c_{ki} \phi_k \quad (1.3)$$

The overall quality of the electronic wavefunction depends on the choice of basis functions ϕ_k and the extent of the electron correlation treatment, determined by the length of the expansion in equation 1.1 and the method of determining the coefficients a_j .

From a practical point of view a compromise has to be made, as large basis set calculations involving long expansions in equation 1.1 are computationally expensive and quickly become prohibitive. Infinite basis sets and complete correlation of the electron motion would give the exact solution of the non-relativistic Schrödinger equation, however the solution would require an infinite time. The compromise is to use a basis set and a level of treatment that is tractable with current computational resources and gives consistent (and correct) answers [4].

The chemical literature shows many examples of extreme treatments. Very accurate calculations using small basis sets seem to mostly be reference points for testing new theoretical methods. A series of Full Configuration Interaction (F-CI)² calculations, by Handy and co-workers [5][6] and Bauschlicher *et. al.* [7][8], using small but realistic basis sets, provides such a reference point for a variety of systems and properties, including term energies, ionization potentials, and electron affinities. At the other end of the spectrum there are low-level treatments with very large basis sets, that were also used as benchmarks for basis set quality (testing the convergence of total energies to the Hartree-Fock limit). The total available computational resources enable one to perform high quality calculations on a small system or less accurate calculations on larger molecules. The majority of calculations giving insight into the

²See Appendix A for explanation of abbreviations, symbols and units used in the thesis

properties and behaviour of molecules involve some kind of balance between the size of the basis set and the level of treatment.

A good level of balance between the basis set size and the level of electron correlation treatment was proposed by Pople as a G-1 level of theory[9][10]. G-1 theory corresponds to the calculations using a 6-311+G(2df,p) basis set[11] and the treatment of electron correlation at the Quadratic Configuration Interaction with Single Double and Triple excitations (QCISD(T)) level. 6-311+G(2df,p) denotes the basis set composed of the split valence triple-zeta basis set augmented with one set of diffuse, 2 sets of polarization *d*, and 1 set of polarization *f* functions on heavy atoms and supplemented by a set of *p* polarization functions on hydrogen. Computational treatment at this level is able to reproduce the atomization energies to within 0.15 eV, for molecules composed of the first and second row atoms. A concept of “balanced basis sets” [12][13][14] is also an attempt to balance the level of treatment, the size of the nuclear-centered basis set and extra-nuclear functions (bond functions). Barclay and Wright showed that when appropriate bond functions are used in conjunction with small to moderate nuclear-centered basis sets, very accurate potential energy curves of diatomic molecules can be obtained with relatively little computational expense. The theoretical level of treatment corresponds to the MultiReference singles and Doubles Configuration Interaction (MRD-CI).

As a result of the capabilities of *ab initio* calculations, these methods are widely used as an instrument in studying various problems in chemistry and molecular physics. In some instances, the quantum-chemical methods have distinct advantages over experiments for the determination of the same measurable property[15]. One of the most important advantages is the possibility of studying molecular systems that are not accessible to experimental determinations because of their lack of stability, danger in manipulation, difficulty of preparation, etc. This is due to the fact that in the theoretical study, an atom, a molecule or any physical system in general is characterized by the number, charges and locations of the constituent nuclei and total number of electrons. It is thus possible to study with generally the same accuracy, neutral molecules, excited states, positively or negatively charged ions, and transition

states for chemical reactions. The results of *ab initio* calculations can also give quantitative information about the electronic structure of the object of study, information that cannot be derived directly from the experiment. The same quantum-chemical methods can be applied to study the energetic processes corresponding to the spectral range from ultraviolet (UV) to far-infrared (IR), covering energies from inner-shell ionization (hundreds of thousands of cm^{-1}) to rotational spectra (fractions of cm^{-1}). This gives *ab initio* quantum chemical methods an energy range on the order of 10^6 .

There are several examples in the chemical literature, where theoretical methods were able to predict results of experiments performed afterwards or to resolve the ambiguities that arose during the interpretation of these experiments. A recent example is the observation of several new bands in B_2 by Brazier and Carrick [16]. The transition energies and character of the involved states were predicted by Bruna and Wright [17][18] and Bauschlicher and Langhoff [19].

Currently, a great deal is known about the properties of diatomic molecules. Huber and Herzberg [20] provide both background and tabulation of experimental and theoretical results. A book by Mulliken and Ermler [21] gives a very good insight into the quantitative nature of a chemical bond. However, our knowledge of bonding in the excited state and in the multiply charged molecules is far behind our understanding of ground-state chemistry.

This thesis presents the results of theoretical work on the relationship between the electronic structure and properties of diatomic molecules. The goal of the study is to increase the understanding of bonding processes in small molecules, using established *ab initio* procedures instead of performing actual experimental determination of properties.

The introductory section, without aspiring to be complete or definitive, outlines the current standing of mathematical methods in the study of chemical problems. Relatively little attention will be devoted to the detailed discussion of mathematical methods used in this work. The approach of the thesis is to use the established and accepted theoretical procedures to study a chemical problem.

The organization of the core material of the thesis is as follows. The computa-

tional procedures used in this work are described in Chapter 2. Chapter 3 presents current knowledge about strong bonding in the excited state in homonuclear diatomic molecules and extends the concept to the heteronuclear case. Strongly bound excited states of BeC and BeC^{2+} are reported. The criteria for stability of diatomic doubly charged cation are discussed in Chapter 4 and thermodynamic stability of BeF^{2+} , MgN^{2+} , MgF^{2+} , and AlF^{2+} is predicted. Chapter 5 discusses some aspects of the stability of multiply charged ions for spectroscopy, synthetic chemistry of novel compounds and energy storage.

Chapter 2

Methods

2.1 *Ab initio* calculations

2.1.1 Basis set

In modern *ab initio* chemistry, the accuracy of calculated potential energy surfaces for ground and excited states of molecules depends on the level of treatment and on the atomic-orbital basis set [15][22]. With the current advances in *ab initio* theory and the speed of computers the emphasis is more on the quality of the basis set.

As most of the basis sets published in the literature were optimized in ground state atomic and sometimes molecular calculations, special care must be taken to include basis functions necessary to describe the excited states. The molecules of interest for this thesis contain Be, B, C, N, O, F, Mg, and Al atoms and require basis sets that would be reasonably close to the Hartree-Fock limit, yet small enough to allow for addition of polarization and diffuse functions. Calculated atomic excitation and ionization energies should have an error as small as possible, with the value of 0.15 eV being described as “an error that can normally be tolerated” [22]. The value of 0.15 eV is also the largest error obtained at the G-1 level of theory by Pople and coworkers [9].

A very complete discussion of the basis sets necessary for excited state calculations was given by Bruna and Peyerimhoff [15]. To summarize, a basis set for excited-state calculations must contain appropriate functions for the the description of core orbitals, valence orbitals, and spectroscopic orbitals (describing negative ion or

Rydberg states). For the atoms of third row, additional correlation functions should be present in the basis to allow for appropriate correlation (in the Configuration Interaction (CI) sense) of valence electrons [15][23]. Negative ion and polarization functions should be added to the valence part of the basis for molecules that are expected to exhibit significant charge transfer or polarization effects

The basis sets used in this study were constructed systematically by starting from the $10s6p$ primitive sets of Huzinaga [24]. This set was contracted according to Dunning [25] yielding the $5s4p$ set. This valence triple zeta basis was systematically augmented with negative ion s and p functions as recommended by Dunning [26]. To allow for proper description of polarization two sets of d (six-component) and one set of f (ten-component) functions were added [27]. Thus the total basis set for B, C, N, O, and F atoms can be denoted as $6s5p2d1f$ for a total of 43 functions. The beryllium basis set was obtained in a similar way, with the exception of the $5p/3p$ [26] contraction instead of the $6p/4p$ as used for other atoms. The exponents of diffuse and polarization functions were optimized in the atomic calculations [28] to give good agreement of the atomic excitation energies with the experimental data [29]. The magnesium and aluminum basis sets were derived from the $12s9p$ primitives of Huzinaga, contracted to $6s5p$ by McLean and Chandler [30]. This valence basis set was augmented with two d polarization functions [12] and s, p semi-diffuse functions [28]. Diffuse functions on the electropositive atom are necessary to describe the possible back-transfer of charge from the electronegative partner in the excited state and to account for the possible Rydberg [15] character of the excited state.

2.1.2 Electron correlation

To study potential energy surfaces it is necessary to use theoretical methods giving a balanced description for all states at various conformations. A proper and consistent description of the potential well and geometries close to the dissociation limits must be obtained. Only theoretical methods that account for electron correlation and are size-consistent can be used. A method is size-consistent if the results obtained for a system of infinitely separated molecules equals the sum of the results obtained for

each molecule calculated separately. The Hartree-Fock method is size consistent for closed shell systems: the energy of two helium atoms at a very long distance is equal to the sum of He atomic energies. The Singles and Doubles Configuration Interaction (SDCI) method is not size consistent. Very clear arguments were given by Szabo and Ostlund [3].

The approach used in this work is of the multi-reference configuration interaction type. MRD-CI [31][32][33][34] wavefunctions are constructed by generating all spin and symmetry allowed single and double excitations from a list of reference configurations. Each of the reference configurations corresponds to a particular occupation of the Self Consistent Field (SCF) molecular orbitals (MO's), and the choice of reference configurations is based on an energetic criterion. A particular configuration is used as a reference configuration if it contributes more than a predetermined value to the final CI wavefunction i.e. its a_j^2 coefficient from equation 1.1 is larger than the predetermined value (usually 0.002 to 0.005 [35]). Single and double excitations from such a reference list generate CI spaces that are too large to be diagonalized with the available computational resources and selection of the most important generated configurations is performed.

Consider the reference list consisting of m configurations. An excited configuration is included in the final CI wavefunction if the CI energy of the matrix composed of m reference configurations and the tested configuration ($m + 1$ by $m + 1$ matrix) is lower than the CI energy of the reference list (m by m matrix) by a predetermined selection threshold T . The procedure is automatic in the sense of keeping in the final CI wavefunctions only the energetically important configurations. In principle, this procedure also gives a degree of size consistency because it includes the most important triple and quadruple excitations [3] (a double excitation from a reference configuration that is singly or doubly excited produces triple and quadruple excitations). Only the energetically most important higher excitations are included in the final CI.

The results of the diagonalization are then extrapolated to the selection threshold $T = 0$ and subsequently are corrected for higher order excitations, not included

in the multi-reference treatment, using a generalized Langhoff-Davidson correction [36][37]. The energies are obtained at the estimated F-CI level, while the wave functions are MRD-CI wavefunctions composed of up to 18,000 (in the implementation used for this work) of the most important configurations. Extensive testing of the method shows a good consistency for estimating the F-CI limit. An average deviation of the total estimated F-CI energies (denoted as MRD-CI(+Q)) from the known F-CI values of 0.92 kcal/mole was obtained in 66 test calculations [38].

2.2 Fitting potential curves

In order to calculate the spectroscopic parameters of the molecular state, the calculated MRD-CI(+Q) energy values have to be represented in a continuous form. The calculations in this thesis concern excited states of diatomic molecules, where the potentials are not necessarily calculated accurately at extended geometries. For such a potential, local fitting functions, usually a non-linear least squares polynomial in the internuclear distance coordinate, are used to fit the calculated potential data. On several occasions, non-linear smoothing splines under tension [39] were fitted to calculated data.

The dissociation energy, D_e , is given by a difference between the fitted minimum energy and true computed energy at “infinite” separation (usually 20.0 or 50.0 bohr). If the energy of molecule at “infinite” separation was not available, then the energy of the molecule was replaced with the sum of atomic energies in appropriate electronic states.

Potential energy curves were fitted for approximately 1/4 to 1/2 of the well depth for bound potentials. Metastable curves (with a local maximum located between a local and a global minimum) were fitted with a spline function for a whole range of calculated geometries starting at the repulsive wall, up to the unperturbed behaviour close to dissociation.

The reduced masses of diatomics were calculated using the masses of the most abundant stable isotopes reported in reference [40]. Rotation-vibration levels were calculated using the Numerov method for bound states and assuming Airy boundary

conditions for metastable states [41]. The LEVEL and BOUND programs of LeRoy [41] were used in calculations on metastable states. Calculated rotation-vibration levels were fitted to a four-parameter expression using the convention of Huber and Herzberg. Thus the energy of an $E_{v,J}$ level, relative to the minimum of the potential energy curve is given by:

$$E_{v,J} = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + B_e J(J+1) - \alpha_e(v + \frac{1}{2})J(J+1) \quad (2.1)$$

This choice of parameters allows direct comparison with the reference [20].

2.3 Radiative properties

In some instances, radiative properties were calculated using a procedure described by Chabalowski [42]. The transition moments between two electronic states are calculated using the length form of the dipole moment operator $\mathbf{P} = \sum e \mathbf{r}$:

$$T_\mu(R) = \int \Psi_2(\mathbf{r}, R) \mathbf{P} \Psi_1(\mathbf{r}, R) d\mathbf{r} \quad (2.2)$$

Due to the fact that *ab initio* packages are performing calculations in irreducible representations of a given point group, it is necessary to consider the degeneracy of the calculated transition moment when converting the computed values to the total transition moment squared. The total transition moment squared $\sum R_{e'e''}^2$ equals $K R_{e'e''}^2$ where K is a factor considering the spatial degeneracy and spin multiplicity of the involved states.

The Franck-Condon factors $q_{v'v''}$ which are related to the intensity distribution due to geometric changes upon the excitation, are given by:

$$q_{v'v''} = \left| \int \Psi_{vib}^{v''} \Psi_{vib}^{v'} dR \right|^2 \quad (2.3)$$

with v'' and v' denoting the vibrational levels of the lower and upper electronic state. The band strength $S_{v'v''}$ is defined as:

$$S_{v'v''} = K \left| \int \Psi_{vib}^{v''} T_\mu(R) \Psi_{vib}^{v'} dR \right|^2 \quad (2.4)$$

with K taking into account the total degeneracy of the upper and lower states. For instance, $K = 4$ for the $^2\Sigma - ^2\Pi$ transitions and $K = 2$ for the $^2\Sigma - ^2\Sigma$ transitions. $T_\mu(R)$ is a polynomial fit to the calculated transition moment values. The absorption oscillator strength is given by:

$$f_{v'v''} = \frac{2}{3} \frac{\Delta E_{v'v''} S_{v'v''}}{(2 - \delta_{0,\Lambda''})(2S'' + 1)} \quad (2.5)$$

where Λ'' is the total angular momentum of the absorbing state, $(2S'' + 1)$ its spin multiplicity, and $E_{v'v''}$ is given in atomic units. The Einstein coefficients for spontaneous emission are obtained from:

$$A_{v'v''} = k \frac{\Delta E_{v'v''}^3 S_{v'v''}}{(2 - \delta_{0,\Lambda'}) (2S' + 1)} \quad (2.6)$$

where $k = 2.1419 \times 10^{10}$ and ΔE is in atomic units, giving $A_{v'v''}$ in s^{-1} units. The radiative lifetimes of excited states are represented by the sum:

$$\tau_{v'}^{-1} = \sum_{v''=0} A_{v'v''} \quad (2.7)$$

2.4 Evaluation of the basis set and correlation treatment

The dissociation energy and spectroscopic constants of the BeF molecule were calculated using the methods described in this chapter. High quality theoretical calculations are available for this molecule and the spectroscopic properties were investigated experimentally. This gives us a possibility of comparing the results obtained at the level of treatment used throughout the thesis with the accurately known properties.

The potential energy curve of the ground state of BeF was calculated using the $6s5p2d1f(F)/6s4p2d1f(Be)$ basis set and the MRD-CI method. The level of computations on BeF can be denoted as MRD-CI/ $6s5p2d1f$. This notation will be used in the following discussion and comparisons with other work. The SCF molecular orbitals correspond to the ground state $X^2\Sigma^+$. At the CI level the $1,2\sigma$ MO's were kept doubly occupied (frozen [He] cores) and the two highest lying MO's were discarded.

Table 2.1: Spectroscopic parameters of the ground state of BeF.

Parameter	This work	ref. [44]	ref. [43]	ref. [20]
Be basis	GTO ^a 6s4p2d1f	STO ^b 6s6p5d2f	GTO 6s4p1d	
F basis	GTO 6s5p2d1f	STO 6s5p4d2f	GTO 8s6p3d1f	
CI treatment	MRD-CI	SDCI	MR-CI	
D_e (eV)	5.62 ^c	5.94	5.82	5.85±0.10
R_e (bohr)	2.584	2.576	2.587	2.571
ω_e (cm ⁻¹)	1270.7	1250	1272.5	1247.4
$\omega_e x_e$ (cm ⁻¹)	9.57	—	9.52	9.12
B_e (cm ⁻¹)	1.478	—	1.472	1.489

^a GTO = Gaussian Type Orbitals

^b STO = Slater Type Orbitals

^c D_e was computed as the difference of energies at $R = 2.584$ and $R = 20.0$ bohr
 $D_e = 5.868$ eV when formula (5) from ref. [44] is used

The reference list included 23 reference configurations. The diagonalized space was on the order of 8000 configurations. The MRD-CI(+Q) energies were calculated for 20 internuclear geometries from 1.8 to 20.0 bohr. The resulting parameters of the potential energy curve of the $X^2\Sigma^+$ state of BeF are given in Table 2.1. This table also shows the results obtained by other authors. The level of treatment used by Ornellas [43] and Bauschlicher [44] is also given in the table.

The SDCI treatment used in reference [44] is sufficient to describe the ground state of BeF. Additional reference configurations used by Ornellas and in this work only slightly improve the quality of the calculations i.e. the ground state of BeF is essentially a single reference problem at short Be-F distances. The differences between this work and other theoretical treatments are small, with the largest discrepancies obtained for D_e , clearly dependent on the basis set size. The value of ω_e is 1.8 % larger than the experimental, but very similar to the MR-CI value obtained with a larger basis set.

The parameters given in Table 2.1 clearly show good quality of the basis set used to describe a polarized system. The analogous 6s5p2d1f and 6s4p2d1f basis sets will be used in this work. We can estimate that the errors in the calculated properties of the diatomic molecules will be generally of the same order, less than 5%

for D_e , 0.02 bohr for R_e and $20\text{-}30\text{ cm}^{-1}$ for ω_e .

Chapter 3

Strongly-bound states of diatomic molecules

3.1 Strongly bound doubly excited states of homonuclear diatomics

The dissociation energy of most chemical bonds falls in the range 1-10 eV. Examples of strong bonds in diatomic molecules can be found in the compilation of Huber and Herzberg [20]. For example, the dissociation energy D_0 of the dinitrogen molecule is 9.759 eV and for carbon monoxide $D_0 = 11.09$ eV, whereas bonding in the Li_2 molecule ($D_0 = 1.05$ eV) is weak. Strong bonds correspond to the picture of high occupation of bonding orbitals and high bond orders in the simple molecular orbital theory.

In the excited state the situation is somewhat complicated. The potential energy curve (PEC) of the electronic state of interest may exhibit interactions with other curves and the electron configuration of the state may change drastically with the internuclear coordinate. As a result of these interactions the dissociation energy of the state may not be a good measure of the bond strength. *Local* properties of the chemical bond are better descriptors in such a case. The equilibrium distance of the given state, the vibration frequency, and diabatic dissociation energy ¹ [45] are other useful measures of the local bond strength. Thus, a state that has a short equilibrium geometry R_e (relative to the ground state) and a large harmonic vibration frequency

¹The diabatic dissociation energy, D'_e , corresponds to the hypothetical situation where the state is not crossed by other states dissociating to lower limits

ω_e (relative to the ground state) will be called a *strongly-bound* (SB) state.

The origin of the "local" bond strength may vary from one system to another. The natural way of increasing the bond strength is to ionize a molecule by removing an antibonding electron. For example, the dioxygen molecule O_2 in its ground state has $D_0 = 5.115$ eV, $R_e = 2.28$ bohr, and $\omega_e = 1580.19$ cm^{-1} , while O_2^+ shows a stronger bond with $D_0 = 6.663$ eV, $R_e = 2.11$ bohr, and $\omega_e = 1904.7$ cm^{-1} [20]. Ionization of the antibonding electron results in an increase of the formal bond order by 1/2. An analogous change takes place when an antibonding electron is excited into a non-bonding i.e. Rydberg orbital. Using dioxygen as an example, the $f^1\Sigma_u^+$ state has ($R_e = 2.10$ bohr, $\omega_e = 1927$ cm^{-1}), a bond shortening of 0.18 bohr and increase in ω_e by a factor of 4/3.

In a series of papers, Bruna and Wright [17][45][46] showed that multiple excitations from an antibonding molecular orbital to a *bonding* MO, increasing the formal bond order by a maximum of two, result in a significant increase in the strength of the bond. They refer to the electronic states generated by such an excitation as *strongly-bound multiply excited states*. The problem with their properties is that the density of the electronic states is significantly larger for multiply-excited states. A state of expected properties may interact with other states of the same symmetry and repulsive nature. This interaction may effectively mask the effect of strong bonding. Such is the case in the $E^1\Sigma^+$ state of C_2 [46], generated by a $2\sigma_u^2 \rightarrow 3\sigma_g^2$ excitation from the ground-state configuration. The formal configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$, (abbreviated to $\dots \sigma_g^2 \pi_u^4 \sigma_g^2$)², for a formally quadruple bond. However, the bond length of this state is similar to the ground state and there is no significant change in the ω_e value. The explanation lies in the low weight of the strongly bonding configuration in the total wavefunction and contributions from the repulsive configurations.

In some cases the effect is very pronounced, especially in the case of the double excitation $2\sigma_u^2 \rightarrow 1\pi_u^2$. In neutral B_2 , the ground state $X^3\Sigma_g^-$ is characterized by the electron configuration $\dots 2\sigma_g^2 2\sigma_u^2 1\pi_u^2$. The double excitation $2\sigma_u^2 \rightarrow 1\pi_u^2$ leads to the

²For brevity, the molecular orbitals of a homonuclear diatomic will be denoted as $\sigma_g \sigma_u \sigma_g \pi_u \pi_g$, except for the cases where full numbering is necessary. For a heteronuclear diatomic, notation $\sigma^2 \sigma^2 \pi^2$ corresponds to the configuration $3\sigma^2 4\sigma^2 1\pi^2$

electron configuration $\sigma_g^2\pi_u^4$. This configuration, generating a state of $^1\Sigma_g^+$ symmetry, is triply bound. As a result the $3^1\Sigma_g^+$ state, characterized by significant contribution of the *strongly-bonding* configuration $\sigma_g^2\pi_u^4$, shows bond shortening of 0.36 bohr and a 60% increase in ω_e (from 1058 to 1749 cm^{-1}) with respect to the ground state [45]. For this type of situation Bruna and Wright proposed the name *strongly-bound doubly excited state* (SBDES) [45].

The increase was even more drastic in B_2^+ , where the ground state $X^2\Sigma_g^+$, with configuration $\sigma_g^2\sigma_u^2\sigma_g$, has $R_e = 4.015$ bohr and $\omega_e = 423$ cm^{-1} . The triply-excited state $2^2\Pi_u$, with configuration $\sigma_g^2\pi_u^3$, has $R_e = 2.695$ bohr, $\omega_e = 1401$ cm^{-1} , a bond shortening of over 30% and an increase in the vibration frequency by over a factor of 3 [17].

The bond-strengthening effect has also been observed in the B_2^{2+} molecule [47]. The $2\sigma_u^2 \rightarrow 1\pi_u^2$ excitation results in the creation of the metastable state $1^3\Sigma_g^-$, compared to the purely repulsive potential of the ground state $X^1\Sigma_g^+$ ($\sigma_g^2\sigma_u^2$). In this case antibonding $\rightarrow$ bonding MO excitation results in a *qualitative* change in the properties of the electronic state. Figure 3.1, reproduced from the reference [47] illustrates the changes in the character of the potential energy curves. This figure is also useful in introducing the specific nomenclature for the potential energy curves. The ground state curve is repulsive, with two separated B^+ ions being the lowest point on the curve. The PEC for the $1^3\Sigma_g^-$ state is metastable (quasi-bound), with the local minimum trapped behind the potential barrier. The total energy at the local minimum is higher than that of the dissociation limit. A state will be called *bound* if the energy of the molecule in this electronic state is lower than the dissociation limit appropriate for that state. Finally, a molecule will be considered *thermodynamically stable* if its total energy is lower than the total energy of all possible dissociation products. This includes the situation where the dissociation into the lowest products is forbidden by spin or spatial symmetry [48]. Examples of (thermodynamically) stable and bound states are provided by the ground and first excited states of O_2 respectively: $X^3\Sigma_g^-$ and $a^1\Delta_g$ [20].

The strongly-bound states of B_2 , B_2^+ and B_2^{2+} described previously correlate

Figure 3.1: MRD-CI potential energy curves for selected low-lying states of Σ character of B_2^{2+} .

diabatically with the two $s \rightarrow p$ excited boron atoms. For the $3^1\Sigma_g^+$ state of B_2 , two boron atoms in the sp^2 configuration combine to form the molecular configuration $\sigma_g^2\pi_u^4$. In B_2^+ , the configuration $\sigma_g^2\pi_u^3$ correlates diabatically with sp^2 and sp configurations of B and B^+ [17]. The molecular configuration $\sigma_g^2\pi_u^2$ in the $3^3\Sigma_g^-$ state of the B_2^{2+} molecule is equivalent to the sp configuration of two B^+ ions.

In the diatomic molecules formed from the atoms of the XII-XIVth groups, the $2\sigma_g$ and $2\sigma_u$ MO's are linear combinations of $2s$ atomic orbitals (AO). Therefore, the $s \rightarrow p$ atomic excitation of one of the atoms corresponds to the excitation from the $2\sigma_g$ or $2\sigma_u$ orbitals in the molecule. Two $s \rightarrow p$ excited atoms correlate with the molecular states having a doubly depopulated $2\sigma_g$ and/or $2\sigma_u$ MO. There are three possible double excitations from the $2\sigma_g$ and $2\sigma_u$ MO's. The double excitations from the σ_g^2 and $\sigma_g\sigma_u$ configurations require more energy than the $\sigma_u^2 \rightarrow \text{bonding MO}$ excitation leading to the SBDES.

Consider the $2\sigma_u^2 \rightarrow \text{bonding MO}^2$ excitation. Two bonding molecular orbitals, $3\sigma_g$ and $1\pi_u$, may be populated in a diatomic molecule with up to eight electrons. There are three possible double excitations from the $2\sigma_u$ orbital, namely $2\sigma_u^2 \rightarrow 1\pi_u^2$, $2\sigma_u^2 \rightarrow 1\pi_u 3\sigma_g$, and $2\sigma_u^2 \rightarrow 3\sigma_g^2$. Such excitations are possible for molecules with four to eight valence electrons. Therefore SBDES may exist in the following molecules of the second period, in order of increasing number of valence electrons: (4) Be_2 , BeB^+ , B_2^{2+} ; (5) BeB , BeC^+ , B_2^+ , BC^{2+} ; (6) BeB^- , BeC , BeN^+ ... Other possible combinations include third row and mixed second-third row molecules.

Several of these molecules have been studied in detail and SBDES were shown to exist in B_2 and B_2^+ [17][45][49], B_2^{2+} [47], C_2 , C_2^+ and C_2^{2+} [46], N_2^+ [50], and Al_2^+ [51]. So far this effect has been observed in homonuclear diatomic molecules and its existence suggested in a series of polyatomic beryllium hydrides [52].

3.2 Strongly bound doubly excited states of heteronuclear diatomics

The extension of the idea to heteronuclear molecules is straightforward. The best candidates for the SBDES effect are heteronuclear molecules that are isoelectronic

or isovalent with the homonuclear molecules known to have SBDES. As the increase of bond strength was shown to be most pronounced in diboron and its cations, the molecules of choice would be isoelectronic BeC and its ions. For similar heteronuclear molecules some data are available for LiN [53] and BC^+ [54]. Interesting theoretical results on BeN were reported by Ornellas [55]. The authors predict several excited states to have bond lengths shorter than the ground state but do not discuss the significance of their results. A very recent study of the BeC molecule by Borin and Ornellas [56] reports accurate potential energy curves for 13 low-lying electronic states. The authors observe bond shortening in one of the electronic states ($^3\Pi$) but do not relate the change of the electronic structure with the properties of the PEC.

The expected problems with the existence of SBDES in heteronuclear molecules have been described in the literature [17]. Due to the symmetry lowering from $D_{\infty h}$ to $C_{\infty v}$, the number of electronic states of a given symmetry increases, because of the removal of the center of inversion. For example, the electronic states that belong to Π_g and Π_u symmetry in $D_{\infty h}$, become Π in $C_{\infty v}$. This creates a situation of increased mixing between the strongly-bonding and repulsive configuration, already encountered in the C_2 molecule.

In order to resolve the question of the existence of SBDES in heteronuclear diatomics, the search will begin with the BeC, BeC^+ , and BeC^{2+} molecules. For the neutral molecule, the ground state is expected to be $^3\Sigma^-$ which is characterized by the configuration $\sigma^2\sigma^2\pi^2$. The expected strongly-bound state should be characterized by the configuration $\sigma^2\pi^4$ in the $^1\Sigma^+$ state. A bond strengthening is also expected upon the single excitation into the π orbital, generating the $\sigma^2\sigma^1\pi^3$ configurations in the $^1\Pi$ and $^3\Pi$ states. In BeC^{2+} , the double excitation $\sigma^2 \rightarrow \pi^2$ is expected to create metastable states of $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ symmetry. For the dication, the question of correlation of the molecular configuration with the atomic dissociation limits is essential for the qualitative properties of the curves and will be discussed thoroughly in Section 4.1.

Doubly-excited states of the B_2^{2+} molecule are particularly interesting because of the previously mentioned *qualitative* change in the properties of the electronic

Table 3.1: Atomic basis sets for Be and C atoms.

Type	Be exponent	reference	C exponent	reference
s	0.025	[28]	0.034	[26]
p	0.025	[28]	0.034	[26]
d	0.3	[28]	1.097	[27]
d	0.05	[28]	0.318	[27]
f	0.26	[28]	0.761	[27]

state. Based on the isoelectronic analogy of BeC^{2+} and B_2^{2+} , the change in electron configuration of BeC^{2+} from $\dots 3\sigma^2 4\sigma^2$ to $\dots 3\sigma^2 1\pi^2$ should result in similar changes in the properties of the potential energy curves.

The results of the atomic calculations on Be and C atoms are given in Section 3.3. The molecules BeC , BeC^+ , and BeC^{2+} are discussed in Sections 3.4, 3.5, and 3.6, respectively.

3.3 Beryllium and carbon atoms

A systematic description of the atomic basis set used in this work was presented in Section 2.1.1. Table 3.1 lists the exponents of the diffuse and polarization functions that were added to the valence $5s4p$ basis set [25] together with the references to their origin.

It was shown previously that the MRD-CI method in conjunction with the $6s4p2d1f/6s5p2d1f$ basis set reproduces well the properties of the BeF molecule. The additional test of the quality of the basis set comes from the results of the calculations on excitation energies of the neutral atom and its ion and the ionization potentials. Excited states of diatomic molecules may correlate with the atoms in their ground or excited states. As mentioned previously, for the creation of a SBDES both atoms should be $s \rightarrow p$ excited. Thus the separation between the electronic states corresponding to the $s^n p^m - s^{n-1} p^{m+1}$ configurations of the atoms is important in the qualitative and quantitative ordering of the dissociation levels.

All entries in Table 3.3 were obtained at the MRD-CI(+Q) level, with the

Table 3.2: Excitation energies (in eV) of Be and Be⁺.

Species	Configuration	State	This work ^{a)}	Expt. ^{b)}
Be	2s ²	¹ S _g	0.00	0.00
Be	2s2p	³ P _u	2.74	2.73
Be	2s2p	¹ P _u	5.37	5.28
Be	2s3s	³ S _g	6.46	6.46
Be	2s3s	¹ S _g	6.83	6.78
Be	2s3p	³ P _u	7.48	7.29
Be	2s3p	¹ P _u	7.74	7.46
Be ⁺	2s	² S _g	9.29 (0.00)	9.32 (0.00)
Be ⁺	2p	² P _u	13.28 (3.99)	13.28 (3.96)
Be ⁺⁺	1s ²	¹ S _g	27.41 (18.12)	27.53 (18.21)

^{a)} Relative to SD-CI energy of Be = -14.61823 E_H,

SCF energy of Be⁺ = -14.27697 E_H,

^{b)} Values taken from C.E. Moore, *Atomic Energy Levels*

(National Bureau of Standards, Washington, D.C., 1971)

excitation disallowed from the 1s AO. For the beryllium species from Table 3.2, the results correspond to the SD-CI calculation on the Be atom, and SCF for Be⁺ and Be²⁺ ions. The tables are organized as follows: term energies of each species are given relative to the ground state of the neutral atom. For the ions, the values in parentheses are the term energies with respect to the ground state of the ion. Thus the term energy of the ground state of the ion is actually the first ionization potential of the atom. All experimental values are taken from the compilation by Moore, *Atomic Energy Levels* National Bureau of Standards, Washington, D.C., 1971. Only the electronic states that are relevant to the topic of the thesis are considered.

The ground state of the Be atom is ¹S_g, arising from the configuration 2s². The ground state AO's were used for all excited state calculations. The calculated term energies of triplet states are closer to the experimental values than the calculated terms of singlet states. This includes four Rydberg states occupying 3s and 3p AO's. The beryllium basis set does not explicitly contain Rydberg functions. However, semi-diffuse functions, with exponents of $\alpha_s = 0.025$, $\alpha_p = 0.025$, and $\alpha_d = 0.05$, provide enough flexibility to reproduce the energies of Rydberg orbitals to within 0.3

Table 3.3: Excitation energies (in eV) of C and C⁺.

Species	Configuration	State	This work ^{a)}	Expt. ^{b)}
C	2s ² 2p ²	³ P _g	0.00	0.00
C	2s ² 2p ²	¹ D _g	1.33	1.26
C	2s ² 2p ²	¹ S _g	2.72	2.68
C	2s2p ³	⁵ S _u	4.15	4.18
C	2s ² 2p3s	³ P _u	7.49	7.48
C ⁺	2s ² 2p	² P _u	11.19 (0.00)	11.26 (0.00)
C ⁺	2s2p ²	⁴ P _g	16.47 (5.28)	16.59 (5.33)

^{a)}Relative to MRD-CI (+Q) energy of C = -37.78501 E_H.

^{b)} Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

eV. The $s - p$ splitting in beryllium is important for the creation of the SBDES, and these values are in error by 0.01 and 0.09 eV, for the ¹S_g-³P_u and ¹S_g-¹P_u excitations.

The results of the calculations on the C atom are given in Table 3.3. For the atomic calculations, ground state (high multiplicity) SCF-MO's were used for the CI calculations on all excited states. The CI description of the ground state is better than that of the low-spin excited state, and consequently, the term energies of low-spin states are consistently over-estimated. The energies of high spin states are calculated with generally smaller errors. Energies of both singlet states of neutral C are overestimated, and the energy of the third excited state, ⁵S, is underestimated.

With the exception of the Rydberg states, all term energies of neutral Be and C are calculated to within 0.09 eV and the ionization potentials are correct to within 0.12 eV. Atomic calculations on Be and C atoms show that the 6s5p2d1f basis set and the MRD-CI level of treatment are adequate for the description of ground and excited states of both atoms.

Table 3.4: Minima of SCF potential energy curves from important single configurations.

Configuration	State (eV)	R_e (a.u.)	Approx. bond order ^{a)}
$\sigma^2\sigma\sigma\pi^2$	$^5\Sigma^-$	3.10	1.5
$\sigma^2\sigma^2\sigma\pi$	$^3\Pi$	3.37	0.5
$\sigma^2\sigma^2\pi^2$	$^3\Sigma^-$	3.35	1.0
$\sigma^2\sigma\pi^3$	$^3\Pi$	2.80	2.0
$\sigma^2\sigma^2\sigma^2$	$^1\Sigma^+$	—	0.0
$\sigma^2\pi^4$	$^1\Sigma^+$	2.66	3.0

^{a)} See text for scheme used to obtain bond order

3.4 BeC

3.4.1 Results and discussion

SCF potential energy curves

BeC is a ten-electron molecule, with the [He] cores in both atoms not participating in the bonding. The molecular states studied arise from different occupation of valence 3,4,5 σ and 1,2 π orbitals by six valence electrons. SCF calculations were performed for the most important configurations in order to understand the contribution of particular electron configuration on the properties of an electronic state. Potential energy curves were calculated for the states listed in Table 3.4.

The corresponding curves are plotted in Figure 3.2. For all electron configurations from the table, the highest possible multiplicity was used. For example, the configuration $\sigma^2\sigma^2\pi^2$ generates not only a $^3\Sigma^-$ state but also $^1\Sigma^+$ and $^1\Delta$. Only the triplet state is considered at the SCF level because the restricted open shell Hartree-Fock (ROHF) procedure is not able to properly construct molecular orbitals in two singlet cases.

Convergence difficulties were observed for several geometries for the $\sigma^2\sigma^2\pi^2$ and $\sigma^2\sigma\pi^3$ configurations. Inspection of Figure 3.2 reveals an unusual flatness of the first curve and an abrupt change in the slope of the second. Such convergence problems, arising from the mixing of 4 σ and 5 σ (...4 σ^2 5 σ 1 π^2 mixing with ...4 σ 5 σ^2 1 π^2) at the

Figure 3.2: Restricted open-shell SCF potential energy curves for various electronic configurations of BeC.

SCF level, have already been observed in the BC molecule by Hirsch and Buenker [54]. They obtained two slightly different SCF potential energy curves for BC, depending on the starting choice of the MO's in the SCF procedure. A curve with a shorter minimum was obtained when the density matrix from the previously calculated shorter geometry was used as a starting point for the SCF procedure. This approach favours the $\dots 4\sigma^2 5\sigma \dots$ occupation. A longer minimum resulted when the density matrix input was taken from the previously calculated longer geometry ($\dots 4\sigma 5\sigma^2 \dots$). Subsequent CI calculations were giving very close results regardless of the SCF-MO's used.

The first observation is that the equilibrium geometries are shorter for the curves with higher occupation of the π MO. The correlation can be improved considering the formal bond orders in analogy to the neutral B_2 [1]. The formal correspondence of MO's between BeC and B_2 is as follows: $3\sigma = 2\sigma_g$, $4\sigma = 2\sigma_u$, $5\sigma = 3\sigma_g$, $1\pi = 1\pi_u$. In B_2 , the MO's $2\sigma_g$ and $1\pi_u$ are bonding (bond order of 0.5 per electron), $2\sigma_u$ is antibonding (bond order of -0.5), and $3\sigma_g$ is non-bonding (bond order of 0) [21]. The formal bond orders resulting from those assignments are given in the Table 3.4. Now the correlation of the bond distance with the bond order is improved. At the SCF level the $^5\Sigma^-$ state is the ground state, and the double excitation $\sigma\sigma \rightarrow \pi^2$ leads to the strongly bound state, with the shortening of the bond by 0.44 bohr. At this level of calculation the electron configuration $\sigma^2\pi^4$ generates a *strongly-bound doubly excited state* $^1\Sigma^+$. In order to quantitatively assess the effects of mixing with other configurations generating states of $^1\Sigma^+$ symmetry, MRD-CI calculations were performed.

MRD-CI potential energy curves

The molecular orbitals with $\sigma^2\sigma\sigma\pi^2$ occupation in the $^5\Sigma^-$ state were used in order to avoid the convergence problems occurring in the triplet calculations. Also, quintet calculations allow for the optimization of the 5σ molecular orbital. The 2π MO (π^*) is left unoccupied and is not optimized at the SCF level. The excitation from the [He] core of both Be and C atoms ($1,2\sigma$ MO's) were disallowed and the corresponding

Table 3.5: Correlation diagram for low lying states of BeC.

Channel	C	Be	This work (eV)	Expt. ^{a)} (eV)	States
I	3P_g	1S_g	0.00	0.00	$^3\Sigma^-, ^3\Pi$
II	1D_g	1S_g	1.33	1.26	$^1\Sigma^+, ^1\Pi, ^1\Delta$
III	1S_g	1S_g	2.72	2.68	$^1\Sigma^+$
IV	3P_g	3P_u	2.74	2.73	$(^{1,3,5})\Sigma^+, \Sigma^-(2), \Pi(2), \Delta$
V	1D_g	3P_u	4.07	3.99	$^3\Sigma^+(2), ^3\Sigma^-, ^3\Pi(3), ^3\Delta(2), ^3\Phi$
VI	5S_u	1S_g	4.15	4.18	$^5\Sigma^-$
A ^{b)}	3P_g	3P_g	—	7.40	$(^{1,3,5})\Sigma^+(2), \Sigma^-, \Pi(2), \Delta$

^{a)} Values taken from C.E. Moore, *Atomic Energy Levels*

(National Bureau of Standards, Washington, D.C., 1949)

^{b)} 3P_g state of Be atom corresponds to electron configuration $2p^2$.

high-lying (anti-core) MO's were discarded. From 21 to 48 reference configurations (depending on the spin and symmetry of the state of interest) were used to distribute 6 electrons in 79 molecular orbitals (43 AO's (C) + 39 AO's (Be) - 2 (frozen core) - 2 (discarded anticore) = 79 MO's). The MRD-CI generated spaces were up to ,500,000 determinants and subsequent selection with respect to the thresho'd varying from 4 to 5 μ hartree led to the diagonalized spaces of 10000 to 18000. The energies of up to 5 states with the same spin and symmetry were calculated for 12 to 17 internuclear distances varying from 2.4 to 5.0 bohr. The total number of electronic states studied is 25. The correspondence of the electronic states in the true group $C_{\infty v}$ with the calculated roots in C_{2v} is as follows: Σ^+ and Δ states belong to A_1 , Π states to B_1 and B_2 , and Σ^- and Δ to A_2 . Up to 9 lowest roots of A_1 and A_2 symmetry were calculated, in order to account for five $^1\Sigma^+$ and three $^1\Delta$ states of BeC. Five roots in the B_1 representation of C_{2v} are equivalent to five Π states in $C_{\infty v}$.

Table 3.5 shows a correlation diagram for the low-lying states of BeC. The first three dissociation channels combine three terms of the ground state configuration s^2p^1 of the carbon atom with the s^2 configuration of the Be atom. At short distances, these terms generate the following configurations: $\sigma^2\sigma^2\pi^2$, $\sigma^2\sigma^2\sigma\pi$, and $\sigma^2\sigma^2\sigma^2$. The fourth channel combines the singly-excited Be atom with the ground state of carbon.

This channel introduces two important configurations, $\sigma^2\sigma\pi^3$ and $\sigma^2\sigma\sigma\pi^2$. The single occupation of both 4 and 5 σ orbitals will play an important role in many of the states of BeC. Lack of this occupation was a reason for the convergence problems mentioned in the previous section. A strongly-bonding configuration $\sigma^2\pi^4$ combines the $s^2 \rightarrow p^2$ excited beryllium with the ground state of C, 7.40 eV above the lowest channel. For comparison, the lowest channel correlating with SBDES in B₂ lies at 8.20 eV [17] and is equivalent to the $s \rightarrow p$ excitation of both B atoms. In BeC, the lowest channel with both atoms $s \rightarrow p$ excited lies at 6.91 eV, combining the 5S_u term of the C atom with 3P_u of Be. It does not lead however to the singlet state.

The summarized data on the low-lying electronic states of BeC are given in Tables 3.6, 3.7, and 3.8. The spectroscopic parameters for each state are given in Table 3.6. These include the internuclear distance, dissociation energy, term energy, vibration frequency and dipole moment. The dominant electron configurations at three Be-C distances are given in the next two Tables 3.7 and 3.8³. Corresponding potential energy curves are plotted in Figures 3.3 and 3.4. Energies are relative to the ground state potential minimum. Atomic dissociation channels I-VI are shown at the right of the figure. In Figure 3.3 the heavy line indicates the ground state $X^3\Sigma^-$ and excited states of $^1\Sigma^+$ symmetry. The states of $^1\Pi$, $^3\Pi$, and $^5\Pi$ symmetry in Figure 3.4 are indicated with dashed, solid and long-dashed lines respectively.

Ground state configuration. The discussion of the properties of the electronic states follows the electronic structure of the state. The ground state $X^3\Sigma^-$ is characterized by two important configurations $\sigma^2\sigma\sigma\pi^2$ and $\sigma^2\sigma^2\pi^2$. The four-open shell configuration dominates at short geometries, while the two open shell configuration is able to correlate properly with the lowest dissociation limit. Single and double excitations from these two configurations generate three manifolds of states: "ground state manifold", singly excited, and doubly excited states. One of two main configurations characterizing the ground state, $\sigma^2\sigma^2\pi^2$, generates states of $^3\Sigma^-$, $^1\Sigma^+$, and $^1\Delta$ symmetry. All three states have very similar parameters of potential energy curves with $R_e = 3.20$ for all three states and the ω_e value around 900 cm⁻¹. The

³The notation $70\sigma^2\sigma\sigma\pi^2$ implies the square of the CI coefficient of the configuration $3\sigma^24\sigma5\sigma1\pi^2$ is 0.70

Table 3.6: Spectroscopic parameters of the low-lying states of BeC.

State	R_e (bohr)	D_e (eV)	T_e (eV)	ω_e (cm ⁻¹)	μ^a (Debye)
X ³ Σ^-	3.20	2.04	0.00 ^{b)}	905	1.45
1 ⁵ Σ^-	3.10	4.47	0.28	978	0.40
1 ¹ Δ	3.20	2.27	1.10	904	1.97
1 ³ $\Pi^{c)d)$	3.40	0.92	1.12	—	1.10
1 ¹ Π	3.36	1.97	1.40	818	1.30
1 ¹ Σ^+	3.20	1.81	1.56	907	2.28
2 ³ $\Pi^{c)d)$	2.95	3.17	1.61	—	3.92
2 ³ Σ^-	3.11	3.10	1.68	976	1.92
1 ³ Δ	3.13	2.77	2.01	964	—
1 ¹ Σ^-	3.19	2.33	2.44	849	1.50
1 ³ Σ^+	3.17	2.05	2.73	885	—
2 ¹ Π	2.91	2.03	2.76	1103	2.92
3 ³ Σ^-	3.02	1.69	3.10	976	3.72
2 ¹ Δ	3.01	1.32	3.46	1031	3.82
3 ³ $\Pi^{c)}$	4.02	1.26	3.52	—	0.39
2 ¹ Σ^+	2.94	0.96	3.80	852	—
1 ⁵ Π	3.33	0.87	3.91	707	2.27
4 ³ Π	3.40	2.05	4.06	—	—
2 ³ Δ	3.82	1.98	4.14	571	1.56
3 ¹ $\Pi^{c)}$	3.80	0.58	4.21	1089	1.40
2 ³ Σ^+	3.65	0.44	4.35	673	—
3 ¹ $\Sigma^{+c)d)}$	3.27	—	4.40	1294	—
4 ¹ $\Sigma^{+c)d)}$	3.25	—	5.00	2144	—

^{a)} All dipole moment values at 3.2 bohr.

^{b)} MRDCI+Q energy: -52.478118 E_H .

^{c)} Local minima for several states are: 1³ Π , 2.79; 3³ Π , 3.02, 3¹ Π , 2.98; 3¹ Σ^+ , 2.87.

^{d)} Dipole moment for selected states and geometries: (1³ Π , 3.88D (2.8)), (2³ Π , 2.89D (2.8)), (3¹ Σ^+ , 3.81D (2.8), -2.98D (3.4)), (4¹ Σ^+ , -4.98D (2.8), 3.84D (3.4)).

Table 3.7: Most important configurations of electronic states of BeC at three inter-nuclear distances (in bohr).

State	R = 2.8	R = 3.6	R = 5.0
$X^3\Sigma^-$	$70\sigma^2\sigma\sigma\pi^2$, $20\sigma^2\sigma^2\pi^2$	$54\sigma^2\sigma\sigma\pi^2$, $36\sigma^2\sigma^2\pi^2$	$79\sigma^2\sigma^2\pi^2$
$1^5\Sigma^-$	$94\sigma^2\sigma\sigma\pi^2$	$93\sigma^2\sigma\sigma\pi^2$	$89\sigma^2\sigma\sigma\pi^2$
$1^1\Delta$	$51\sigma^2\sigma\sigma\pi^2$, $34\sigma^2\sigma^2\pi^2$	$46\sigma^2\sigma\sigma\pi^2$, $8\sigma^2\sigma^2\pi\pi^*$, $34\sigma^2\sigma^2\pi^2$	$80\sigma^2\sigma^2\pi^2$
$1^3\Pi$	$64\sigma^2\sigma\pi^3$, $18\sigma^2\sigma\pi^2\pi^*$	$88\sigma^2\sigma^2\sigma\pi$	$67\sigma^2\sigma^2\sigma\pi$
$1^1\Pi$	$83\sigma^2\sigma^2\sigma\pi$, $9\sigma^2\sigma\pi^3$	$88\sigma^2\sigma^2\sigma\pi$, $3\sigma^2\sigma\pi^3$	$61\sigma^2\sigma^2\sigma\pi$, $23\sigma^2\sigma\sigma^2\pi$
$1^1\Sigma^+$	$37\sigma^2\sigma^2\pi^2$, $34\sigma^2\sigma\sigma\pi^2$, $7\sigma^2\pi^4$	$44\sigma^2\sigma^2\pi^2$, $25\sigma^2\sigma\sigma\pi^2$, $14\sigma^2\sigma^2\pi\pi^*$	$64\sigma^2\sigma^2\pi^2$
$2^3\Pi$	$83\sigma^2\sigma^2\sigma\pi$	$47\sigma^2\sigma\pi^3$, $28\sigma^2\sigma\pi^2\pi^*$	$53\sigma^2\sigma\sigma^2\pi$
$2^3\Sigma^-$	$58\sigma^2\sigma\sigma\pi^2$, $24\sigma^2\sigma^2\pi^2$	$72\sigma^2\sigma\sigma\pi^2$, $11\sigma^2\sigma^2\pi^2$	$85\sigma^2\sigma\sigma\pi^2$
$1^3\Delta$	$92\sigma^2\sigma\sigma\pi^2$	$87\sigma^2\sigma\sigma\pi^2$	$67\sigma^2\sigma\sigma\pi^2$, $14\sigma^2\sigma\sigma\pi\pi^*$
$1^1\Sigma^-$	$90\sigma^2\sigma\sigma\pi^2$	$82\sigma^2\sigma\sigma\pi^2$	—
$1^3\Sigma^+$	$88\sigma^2\sigma\sigma\pi^2$	$87\sigma^2\sigma\sigma\pi^2$	$30\sigma^2\sigma\sigma\pi^2$, $33\sigma^2\sigma\sigma\pi\pi^*$, $15\sigma^2\sigma^2\pi\pi^*$
$2^1\Pi$	$61\sigma^2\sigma\pi^3$, $14\sigma^2\sigma\pi^2\pi^*$	$37\sigma^2\sigma\pi^3$, $25\sigma^2\sigma^0\sigma\pi^3$, $18\sigma^2\sigma\pi^2\pi^*$	$50\sigma^2\sigma\pi^2\pi^*$, $21\sigma^2\sigma\pi^3$
$3^3\Sigma^-$	$55\sigma^2\sigma\sigma\pi^2$, $23\sigma^2\sigma^2\pi^2$	$40\sigma^2\sigma\sigma\pi^2$, $38\sigma^2\sigma^2\pi\pi^*$	$20\sigma^2\sigma\sigma\pi^2$, $30\sigma^2\sigma\sigma\pi\pi^*$, $25\sigma^2\sigma^2\pi\pi^*$
$2^1\Delta$	$40\sigma^2\sigma\sigma\pi^2$, $20\sigma^2\sigma^2\pi\pi^*$, $30\sigma^2\sigma^2\pi^2$	$46\sigma^2\sigma^2\pi\pi^*$, $37\sigma^2\sigma\sigma\pi^2$	—
$3^3\Pi$	$71\sigma^2\sigma^0\sigma\pi^3$	$58\sigma^2\sigma\sigma^2\pi$	$56\sigma^2\sigma\pi^2\pi^*$, $16\sigma^2\sigma\pi^3$
$2^1\Sigma^+$	$37\sigma^2\pi^4$, $35\sigma^2\sigma\sigma\pi^2$	$50\sigma^2\sigma^2\sigma^2$	$50\sigma^2\sigma^2\sigma^2$, $11\sigma^2\sigma^2\sigma\sigma$

Table 3.8: Most important configurations of electronic states of BeC at three internuclear distances (in bohr), continued.

State	R = 2.8	R = 3.6	R = 5.0
$1^5\Pi$	$92\sigma^2\sigma\pi^2\pi^*$	$89\sigma^2\sigma\pi^2\pi^*$	$87\sigma^2\sigma\pi^2\pi^*$
$4^3\Pi$	—	$44\sigma^2\sigma^0\sigma\pi^3$, $28\sigma^2\sigma\pi^2\pi^*$	$61\sigma^2\sigma\pi^2\pi^*$,
$2^3\Delta$	$80\sigma^2\sigma^2\pi\pi^*$, $5\sigma^2\sigma\sigma\pi\pi^*$	$80\sigma^2\sigma^2\pi\pi^*$, $5\sigma^2\sigma\sigma\pi\pi^*$	$30\sigma^2\sigma^2\pi\pi^*$, $32\sigma^2\sigma\sigma\pi\pi^*$, $20\sigma^2\sigma\sigma\pi^2$
$3^1\Pi$	$67\sigma^2\sigma^0\pi^3$	$40\sigma^2\sigma^0\pi^3$, $14\sigma^2\sigma\pi^2\pi^*$	$38\sigma^2\sigma\sigma^2\pi$, $11\sigma^2\sigma\pi^2\pi^*$
$2^3\Sigma^+$	$73\sigma^2\sigma^2\pi\pi^*$, $11\sigma^2\pi^3\pi^*$	$76\sigma^2\sigma^2\pi\pi^*$	$40\sigma^2\sigma\sigma\pi^2$, $22\sigma^2\sigma^2\pi\pi^*$, $20\sigma^2\sigma\sigma\pi\pi^*$
$3^1\Sigma^+$	$22\sigma^2\pi^4$, $20\sigma^2\sigma^2\pi^2$, $16\sigma^2\sigma\sigma\pi^2$, $16\sigma^2\sigma\sigma\pi\pi^*$	$20\sigma^2\sigma^2\sigma^2$, $32\sigma^2\sigma\sigma\pi^2$, $27\sigma^2\sigma^2\pi\pi^*$	$40\sigma^2\sigma^2\pi\pi^*$, $10\sigma^2\sigma^2\pi^2$, $15\sigma^2\sigma\sigma\pi\pi^*$
$4^1\Sigma^+$	$70\sigma^2\sigma^2\sigma^2$	$37\sigma^2\pi^4$, $35\sigma^2\pi^3\pi^*$	$44\sigma^2\sigma^0\sigma^2\pi^2$, $12\sigma^2\sigma\sigma\pi^2$

Figure 3.3: MRD-CI potential energy curves for selected electronic states of BeC.

lowest lying excited state is $^5\Sigma^-$. Due to its correlation with the fourth channel it has a large D_e of 4.5 eV. Several other states contain significant weight of the ground state configurations. The $1^1\Delta$, $2^3\Sigma^-$, $1^3\Delta$, $1^1\Sigma^-$, $1^3\Sigma^+$, $3^3\Sigma^-$, and $2^1\Delta$ states have regular, Morse-like potential energy curves (see Figure 3.3). Spectroscopic parameters are falling into the narrow range of R_e varying from 3.1 to 3.2 bohr and ω_e from 850 to 1050 cm^{-1} .

Singly excited states. Singly excited states arise from the following excitations: $\sigma \rightarrow \pi$, $\sigma \rightarrow \sigma$, and $\pi \rightarrow \sigma$. The excitation from the two open-shell configurations describing the ground state overlap with the excitations from the four open-shell configuration and lead to the single and triple occupation of π orbitals ($\sigma^2\sigma\pi^3$ and $\sigma^2\sigma^2\sigma\pi$ configurations). Single and triple occupation of the π orbitals creates states of Π symmetry. The $\pi \rightarrow \pi^*$ excitation also leads to high-lying states of Π symmetry.

Potential energy curves for singlet and triplet states of Π symmetry are shown in Figure 3.4. Among triplet states, the lower lying $1^3\Pi$, with $T_e = 1.12$ eV, exhibits a sharp avoided crossing with the $2^3\Pi$ state. The electron configuration of the lower state changes from $\sigma^2\sigma\pi^3$ before the crossing to $\sigma^2\sigma^2\sigma\pi$ after the crossing, while the reverse is true for the second state. Significant changes in the dipole moment values for both states can be seen in the Table 3.6. The $\dots\pi^3$ configuration has $\mu = 3.88$ D at 2.8 bohr while the $\dots\pi$ has $\mu = 0.89$ D. At 3.2 bohr (equilibrium geometry of the ground state, after the avoided crossing), the change in the configuration is expressed in the change of the dipole moment ($\mu = 1.10$ D for the $1^3\Pi$, single π occupation; $\mu = 3.92$ D for the $2^3\Pi$, triple π occupation). Both states are connected to the ground state by single electron replacement $\sigma \rightarrow \pi$ and $\pi \rightarrow \sigma$.

The explanation of the sharp avoided crossing lies in the similarity of BeC to B_2 [1]. In B_2 , corresponding states $1^3\Pi_g$ and $1^3\Pi_u$ have g and u symmetry and cannot interact. In BeC, the 4σ and 1π molecular orbitals of BeC are of predominantly $2p_C$ character and have approximate u symmetry, and the 5σ located on the Be atom has approximate g symmetry. To illustrate, the contour plots of molecular orbitals of BeC in the $^5\Sigma^-$ state are shown in Figure 3.5. The configuration $\sigma^2\sigma\pi^3$ has approximate g symmetry and $\sigma^2\sigma^2\sigma\pi$ has u symmetry. The configurations are almost orthogonal

Figure 3.4: MRD-CI potential energy curves for states of Π symmetry of BeC.

Figure 3.5: Contour maps for MO's in BeC ($R = 3.20$ bohr), generated using the configuration $3\sigma^2 4\sigma 5\sigma 1\pi^2$ in the $^5\Sigma^-$ electronic state.

and do not interact.

The second, third and fourth $^3\Pi$ states exhibit two more avoided crossings. The sign and values of the dipole moments for the third state, combined with the weight of electronic configuration, give more information about the nature of the molecular orbitals. The dipole moment of the third state before the crossing at 3.4 bohr arises from the $\sigma^2\sigma^0\sigma^1\pi^3$ configuration and equals 2.32 D. After the crossing, where the 5σ MO is doubly occupied ($\sigma^2\sigma^1\sigma^2\pi^1$) the dipole moment is inversely oriented; $\mu = -3.9$ D. This situation corresponds to the Be^-C^+ polarity of the molecule.

The values of the dipole moment are not very accurate in the case of strong orbital mixing. Hirsch and Buenker [54] showed that significant differences in the dipole moment values for the $X^4\Sigma^-$ state of BC are obtained when switching from the regular CI calculations to the CI based on the natural orbitals (NO). For some geometries the differences were up to 50 % but the polarity of the molecule was always properly assigned.

Multireference calculations based on the MultiConfiguration SCF (MCSCF) molecular orbitals are preferable in the calculations of one-electron properties, but MCSCF is currently not implemented in the MRD-CI package. Thus the calculated values of the dipole moment for BeC have to be considered carefully. However, current calculations are qualitatively and at least semi-quantitatively correct. A test calculation of the dipole moment of the ground state of BeC at 3.20 bohr, using $^3\Sigma^-$ MOs and subsequent CI treatment gave the μ value of 1.95 compared to 1.43 Debye for the calculations starting from the $^5\Sigma^-$ MOs. The NO treatment was not used because of the additional computational effort needed. Also, the choice of the CI wavefunctions for the NO procedure is not obvious: Should the natural orbitals be based on the $^3\Sigma^-$ or $^5\Sigma^-$ CI wavefunction? What should the starting SCF-MO's be - $^3\Sigma^-$ or $^5\Sigma^-$?

The states of singlet symmetry follow the same pattern as the triplet states. The geometry of the avoided crossing between the first and second state is shorter than in the triplet case and longer for the $3^1\Pi - 4^1\Pi$ than in the triplet.

Doubly excited states. SBDES arise from the $4\sigma^2 \rightarrow 1\pi^2$ excitation. Due to

the large weight of the four open-shell configuration in the ground state, the excitation $\sigma\sigma \rightarrow \pi^2$ also generates SBDES. The excitation $1\pi^2 \rightarrow 5\sigma^2$ generates a repulsive configuration $\sigma^2\sigma^2\sigma^2$. Figure 3.3 shows the potential energy curves for the $^1\Sigma^+$ states of BeC. All four states of $^1\Sigma^+$ symmetry have contributions from the strongly-bonding configuration $\sigma^2\pi^4$, as seen in Tables 3.7 and 3.8. The contribution is very small for the lowest state, but is as high as 0.37 for the second state at 2.8 bohr. The potential energy curve for the $1^1\Sigma^+$ state is very similar to those of other states belonging to the “ground state manifold”. The PEC of the second, third and fourth states of $^1\Sigma^+$ symmetry are irregular because of the avoided crossings between them. The SB configuration is present in the second and third state at short geometries and in the fourth state after the avoided crossing located at 3.2 bohr (5 eV above $X^3\Sigma^-$ minimum). The repulsive configuration $\sigma^2\sigma^2\sigma^2$ contributes to all four states, the $4^1\Sigma^+$ at short R and to the second state at long distances. As a result of the avoided crossings the shape of the $3^1\Sigma^+$ curve is irregular, but the vibrational analysis performed for the local minimum at 2.87 bohr, with shortening of 0.33 bohr with respect to the ground state, shows the increase in the bond strength. The vibration frequency equals 1294 cm^{-1} , which is a 43 % increase from the ground state value. The PEC of the highest calculated state is very anharmonic and the large value of ω_e is a result of the avoided crossing.

The changes in the dipole moment values are larger for the $^1\Sigma^+$ states than for Π states and are caused by larger changes in the occupation of π orbital. For example, quadruple occupation in the $3^1\Sigma^+$ state corresponds to the dipole moment of 3.98 Debye at 2.8 bohr. At the same distance the $4^1\Sigma^+$ state with nil occupation of the π MO has the dipole moment of -4.98 D. To compare, the dipole moment of the $1^5\Sigma^-$ state is only 0.40 D. This implies that the double occupation of π orbitals (carbon $2p_x, 2p_y$) transfers as much electron density on the C atom as the occupation of 4,5 σ on the beryllium atom. Transfer of the 5σ electron onto the 1π orbital increases the dipole moment to 3.88 D (for the $1^3\Pi$ state). For quadruple occupation of the π MO in the $^1\Sigma^+$ state, the dipole moment is unchanged at 3.81 D. However, the weight of the $\dots\pi^3$ configuration in the $^3\Pi$ state is 64 %, compared with 22 % weight of the π^4

configuration in the $3^1\Sigma^+$ state. Despite the mixing, the dipole moment remains very high. This proves that the BeC bond is strongly polarized. Additional arguments come from the discussion of the dipole moment of the $4^1\Sigma^+$ state. Nil occupation of the π orbital and the double occupation of the 5σ MO ($\mu = -4.98$ D) at 2.8 bohr shows very strong Be^-C^+ polarization of this state.

The extent of the charge transfer can be assessed semi-quantitatively. The dipole moment of 3.81 Debye is equivalent to the dipole moment created by two charges of $\pm 0.55e$ separated by 2.8 bohr. The partial charges of 0.55e coincide with the results of the Mulliken population analysis of various configurations of BeC at 3.2 bohr shown in Table 3.9. It was shown [57] that the Mulliken population analysis may be unreliable for compounds with electropositive atoms. Despite its deficiencies, the population analysis provides a qualitative description of charge shifts. Both results show that the charge transfer in the excited BeC can be similar to the transfer in the ground state of BeF where the partial charges were calculated to be ± 0.47 [58].

These drastic changes in the dipole moment indicate that ionic effects are important in the description of the Be-C bond. The results of one electron density analysis of CBe_2 , C_2Be and C_2Be_2 [59] indicate that charge transfer from Be to C is causing the stability of non-linear isomers and that there is little covalent bonding in this family of molecules. Theoretical results on CBe_2 in the solid state [60] indicate that the bonding in CBe_2 is highly ionic with contributions from covalent interactions.

To summarize, the SBDES exist in BeC. The strongly polarized SBDES of BeC, $3^1\Sigma^+$, shows a bond shortening of 0.33 bohr and increase in ω_e by 43 %. The dipole moment at the distance of 2.8 bohr amounts to 3.81 D, caused by the 22% weight of the SB configuration $\sigma^2\pi^4$. Several other states show significant but smaller shortening of the bond.

3.4.2 Comparison to other systems

The study of the excited states of BeC was undertaken because of the expected similarities with B_2 . The previous discussion was pointing to significant differences resulting from the polarity of the bond. In many aspects, however, BeC and B_2 are

Table 3.9: Mulliken population analysis of BeC at $R_e = 3.20$ bohr using 6-31+G(d) basis set.

Configuration	State	Be charge	C charge
$\sigma^2\sigma\sigma\pi^2$	$^5\Sigma^-$	+0.25	-0.25
$\sigma^2\sigma^2\pi^2$	$^3\Sigma^-$	+0.25	0.25
$\sigma^2\sigma\pi^3$	$^3\Pi$	+0.35	-0.35
$\sigma^2\pi^4$	$^1\Sigma^+$	+0.55	-0.55

Table 3.10: Comparison of several electronic states of BeC and B_2 .

B_2				BeC			
State	R_e (bohr)	ω_e (cm $^{-1}$)	T_e (eV)	State	R_e (bohr)	ω_e (cm $^{-1}$)	T_e (eV)
$X^3\Sigma_g^-$	3.014	1064	0.00	$X^3\Sigma^-$	3.20	905	0.00
$1^5\Sigma_u^-$	2.878	1277	0.14	$1^5\Sigma^-$	3.10	978	0.28
$1^3\Pi_u$	3.277	848	0.43	$1^3\Pi$	3.40	—	1.12
$1^1\Pi_u$	3.366	738	1.22	$1^1\Pi$	3.36	818	1.40
$1^1\Sigma_g^+$	3.082	859	0.91	$1^1\Sigma^+$	3.20	907	1.56
$1^3\Pi_g$	2.795	1459	2.04	$2^3\Pi$	2.95	—	1.61
$1^1\Pi_g$	2.802	1270	3.19	$2^1\Pi$	2.91	1103	2.03
$2^1\Sigma_g^+$	3.402	997	1.40	$2^1\Sigma^+$	2.94	852	3.80
$3^1\Sigma_g^+$	2.676	1720	4.88	$3^1\Sigma^+$	2.87	1294	4.40

quite similar. The explanation of the sharpness of the avoided crossing between the $^3\Pi$ states lies in the retention of the g and u character in the molecular orbitals. Also, the properties of molecular states are quite similar.

The spectroscopic parameters of several electronic states of BeC and B_2 are listed in Table 3.10. In order to obtain consistency of comparisons, all entries for B_2 are taken from the work by Hachey *et. al.* [61]. Their results are in good agreement with other works on the B_2 molecule [17][19]. The MRD-CI approach is used in references [17] and [61] while computations in reference [19] are based on another multi-reference scheme. The order of the states of B_2 in Table 3.10 follows term energies of BeC states with two exceptions. The relative changes of equilibrium geometries in B_2 are very similar to those in BeC. For example, both singlet and triplet Π_u states of B_2 have longer R_e , in line with the $1^1\Pi$ and $1^3\Pi$ state of BeC. The

agreement is also seen for the states characterized by the increased bond strength. The $1^1\Pi_g$, $1^3\Pi_g$, and $3^1\Sigma_g^+$ states of B_2 correspond to the $2^1\Pi$, $2^3\Pi$, and $3^1\Sigma^+$ states of BeC.

Other molecules for which some results are available are LiN [53], BC^+ [54], MgC [62], LiP and NaP [63]. The ground state of LiN is $^3\Sigma^-$ and the $^3\Pi$ state is low-lying and shows a stronger bond ($R_e = 1.70 \text{ \AA}$ vs. $1.85 \text{ \AA}$, $\omega_e = 833 \text{ cm}^{-1}$ vs. 657 cm^{-1}). A bond shortening upon the $\sigma^2 \rightarrow \pi^2$ excitation has been recently observed in LiP and NaP [63]. The ground state $X^3\Sigma^-$ of LiP has $R = 2.342 \text{ \AA}$ at the QCISD/6-311+G(2df) level while the $^1\Sigma^+$ state ($\sigma^2\pi^4$ configuration) shows a shorter bond with $R = 2.072 \text{ \AA}$. The $^5\Sigma^-$ state is unbound and the $^3\Sigma^-$ and $^3\Pi$ state have very small spin contaminations. However, the spin contamination was large for the $^2\Pi$ state of BeP [63], consistently with the large weight of the three open shell configuration observed in BeN [55].

In BC^+ , the ordering of three lowest electronic states is identical to BeC. The ground state $X^3\Sigma^-$ of BC^+ has similar electronic structure, with 46 % weight of the two open-shell and 42 % weight of the four open-shell configuration. The first excited state $1^5\Sigma^-$ lies 0.08 eV above the ground state (0.28 eV for BeC). The ground state of MgC was calculated to be $^3\Sigma^-$ [62].

Knowledge about ten-electron molecules arises mostly from theoretical calculations. However, diboron has been observed in mass spectrometry [64] and electronic spectra of several bands have been assigned [16]. To the best of my knowledge there are no reports of observation of BeC. In order to assist future experiments, Wright and Kolbuszewski predicted the main features of the electron absorption spectrum [1].

Comparison with a recent study on BeC

A recent study by Borin and Ornellas (hereafter B&O) reports the potential energy curves, spectroscopic constants and dipole moments for 13 low-lying states of BeC [56]. The authors used a $7s6p3d1f(C)/8s5p2d1f(Be)$ basis set composed of 98 contracted Gaussian functions. The SCF energy in the $^3\Sigma^-$ state at the distance of 3.5 bohr

reported by B&O equals $-52.27018 E_H$, 0.68 mhartree lower than the present value of $-52.26950 E_H$. The CI calculations of Borin and Ornellas were done using the MELD codes [65], a multireference single and double excitation CI with perturbative selection of configurations. The natural orbitals derived from the $^3\Sigma^-$ SCF calculations and subsequent SDCI calculation on the $X^3\Sigma^-$ state were used as a one-particle basis.

The equilibrium distances of the 13 electronic states reported by B&O are within 0.05 bohr of the present calculations. The term energies agree to within 0.1 eV and the ordering of the electronic states is the same with the exception of the $1^1\Sigma^+$ state. The differences in the ω_e values are on the order of 5%. The calculated dipole moments are more sensitive to the level of treatment [66]. The CI calculations based on the natural orbitals are more accurate than CI based on the SCF molecular orbitals. The agreement between B&O and this work is still good, with the largest errors occurring for the ground state. At 3.2 bohr B&O report $\mu = 1.71$ D, 0.38 D larger than 1.43 D from Table 3.6. The 4σ - 5σ mixing in the ground state is expressed as the linear combination of the $\sigma^2\sigma^2\pi^2$ and $\sigma^2\sigma^0\sigma^2\pi^2$ configurations as B&O use the $^3\Sigma^-$ MO's. In this work the ground state has significant contributions from the $\sigma^2\sigma\sigma\pi^2$ configuration.

The differences in the dissociation energies are larger. For the electronic states correlating with channels I, II, and III, B&O report D_e values 0.1 to 0.3 eV larger than those in Table 3.6. The differences are 0.5 to 0.6 eV for the states correlating with channel IV.

B&O use the energy of the molecule at 30.0 bohr as the dissociation energy of the electronic state, while in this work the sum of the energies of the atoms in the appropriate states is used. As a result B&O overestimate the energy of channel II by 0.06 eV and the energy of channel IV by 0.3 eV, whereas present data in Table 3.5 are correct to within 0.01 eV for channel IV. Thus the differences in the dissociation energies of the channel IV states are reduced to less than 0.3 eV, after the overestimation of the atomic limits is taken into account.

The remaining difference (for example the D_e of the $1^3\Pi$ state is calculated to be 1.16 eV by B&O and 0.92 eV in this thesis) can be attributed to the larger (more

flexible) basis set used by B&O, and the natural orbitals treatment. The absolute energy of BeC in the $X^3\Sigma^-$ state at 3.20 bohr is -52.478118 E_H in this work and Borin and Ornellas report -52.469082 E_H . However, they do not extrapolate the calculated eigenvalues to the zero selection threshold and do not apply the Davidson correction. The corresponding calculated eigenvalue in this work is -52.451919 E_H , 18 mhartree higher than that of B&O.

The authors observe the significant weight of the strongly-bonding configuration $\sigma^2\pi^4$ in the $1^1\Sigma^+$ state at short geometries, but they report only the lowest $1^1\Sigma^+$ state and do not discuss the importance of this configuration in the excited states of BeC. Overall, Borin and Ornellas provide a slightly better (numerically) description of the low-lying electronic states of BeC. However, their results are in the agreement with this chapter and reference [1].

3.4.3 Strong bonding: Covalent or Ionic ?

The analysis of the ionicity of the excited states of BeC leads to a question whether the increase in the bond strength is caused by the increase in the occupation of the covalently bonding MO or by the change in the nature of the bond from polarized covalent to ionic. In order to address this question consider two strongly ionic molecules BeO and LiO. In BeO [67], the ground state $X^1\Sigma^+$ characterized by the configuration $\sigma^2\sigma^2\pi^4$ has a dipole moment $\mu = 4.372$ D at 1.35 Å. The first excited singlet state $A^1\Pi$, with triple occupation of the π MO ($\sigma^2\sigma^2\pi^3$) has: a) longer R_e of 1.479 Å vs. 1.369 Å, b) smaller ω_e of 1129 cm^{-1} vs. 1471 cm^{-1} , c) smaller dipole moment of 0.111 D at 1.35 Å vs. 4.372 D.

In BeO, an eight valence electron molecule, all formally bonding MOs are already occupied and any excitation leads to weaker bonds. However, the relation between the structure and the strength of the bond remains essentially the same. Maximum occupation of π orbitals corresponds to the stronger bond, irrespective of the nature of the molecular orbital.

In even more ionic LiO [68], the ground state is $^2\Pi$ ($\sigma^2\sigma^2\pi^3$) and the first excited state $^2\Sigma^+$ ($\sigma^2\sigma\pi^4$) has a shorter equilibrium distance (3.02 bohr vs. 3.20

bohr for the ground state) and larger vibration frequency ω_e of 824 cm^{-1} , compared to 772 cm^{-1} for the ground state. In both molecules the more ionic state has more π electrons and a stronger bond. Another molecule, namely BN [69] shows the strongest bonding in the excited $^1\Sigma^+$ state ($\sigma^2\sigma^2\pi^4$). The ground state of BN is $^3\Pi$, with triple occupation of the π MO ($\sigma^2\sigma^2\sigma\pi^3$).

The calculations presented above indicate that the excited states of BeC exhibit larger mixing in the excited state than both B_2 and more ionic molecules. The "dilution" effect is strong but even low weights of strongly bonding configurations on the order of 20 % increase the local bond strength. In general the strong-bonding configurations correspond to the maximum occupation of π orbitals, in homo- and heteronuclear molecules.

The results obtained for BeC and examples from the literature show that the strong-bonding in diatomics with up to 8 valence electrons depends of the occupation of π orbitals. *Electronic states with dominant configurations characterized by maximum occupation of π (bonding) orbitals have the shortest bond length and the highest vibration frequencies, irrespective of the energetic location of the state and constituent atoms.*

3.5 BeC⁺

In the previous section it was shown that the BeC molecule, similarly to B_2 , shows strong bonding in the excited states. For homonuclear molecules the increase in the bond strength was the most pronounced in B_2^+ . In the present section, we consider whether the heteronuclear monocation BeC⁺, which is isoelectronic with B_2^+ , also shows strong bonding in its excited states.

Computational details

The calculations were performed using the $6s5p2d1f(C)/6s4p2d1f(Be)$ basis set described previously. The molecular orbitals correspond to the $\sigma^2\sigma\pi^2$ configuration in the $^4\Sigma^-$ state. The [He] core was frozen on both Be and C atoms (1,2 σ MO's) and the two highest-lying orbitals (38,39 σ MO's) were discarded in the CI calculations,

so that five electrons were distributed in 79 molecular orbitals. The length of the reference list varied from 17 to 41 configurations and the selection threshold varied from 2.0 to 4.0 μ hartree. The generated CI spaces ranged from 150,000 to 250,000 configurations and diagonalized matrices were on the order of 10,000 to 15,000. Up to five roots were extracted in C_{2v} symmetry. The correspondence of calculated roots to the molecular states in the $C_{\infty v}$ point group is the same as in the neutral BeC. MRD-CI(+Q) energies were calculated for 14 geometries varying from 2.4 to 6.0 bohr. At the geometry of 2.8 bohr, 9 roots were calculated in the A_1 representation, in order to establish the structure of the 6 lowest $^2\Sigma^+$ and three lowest $^2\Delta$ states.

Potential energy curves

Table 3.11 lists the term energies, equilibrium distances, vibration frequencies and dominant configurations of 18 low-lying states of the BeC^+ molecule. The corresponding potential energy curves are plotted on three figures for the sake of clarity. The ground state is plotted in all three figures, the $^2\Sigma^+$, $^2\Delta$ and $^2\Sigma^-$ states are shown in Figure 3.6, and the $^2\Pi$ and all quartet states are shown in Figures 3.7 and 3.8 respectively.

The $X^4\Sigma^-$ ground state of the BeC^+ molecule, characterized by the configuration $\sigma^2\sigma\pi^2$, has a Morse-like potential energy curve. The equilibrium distance of this state is 3.0 bohr and vibration frequency $\omega_e = 1131 \text{ cm}^{-1}$. A different situation occurs in B_2^+ where the ground state $X^2\Sigma_g^+$, with configuration $\sigma_g^2\sigma_u^2\sigma_g$ has no π electrons. This state is weakly bound, with $R_e = 4.015$ bohr and $\omega_e = 415 \text{ cm}^{-1}$.

As the ground state of B_2^+ has a formal bond order of 0.5, any excitation of the $\sigma \rightarrow \pi_u$ type from the $\sigma_g^2\sigma_u^2\sigma_g$ configuration results in a state with shorter equilibrium distance, by up to 1.3 bohr. For example, the $\sigma_g\sigma_u \rightarrow \pi_u^2$ excitation leads to the $^4\Sigma_u^-$ state, a strongly bound doubly excited state with $R_e = 2.927$ bohr. Such a drastic bond shortening is unlikely in BeC^+ as the $X^4\Sigma^-$ ground state of the heteronuclear molecule *already corresponds* to the $^4\Sigma_u^-$ SBDES of the homonuclear species and is strongly bound.

The difference between the ground state configurations of B_2^+ and BeC^+ can be

Table 3.11: Spectroscopic parameters of the low-lying states of BeC⁺.

State	R_e (bohr)	D_e (eV)	T_e (eV)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	configuration ^{a)}
X ⁴ Σ^-	3.00	2.61	0.00 ^{b)}	1130.7	9.5	93 $\sigma^2\sigma\pi^2$
1 ² Π	3.50	2.10	0.51	676.7	8.3	78 $\sigma^2\sigma^2\pi$
1 ² Δ	3.01	2.29	1.65	1105.9	10.0	90 $\sigma^2\sigma\pi^2$
1 ⁴ Π	3.78	0.71	1.90	427.4	10.7	86 $\sigma^2\sigma\sigma\pi$
1 ² Σ^-	3.03	0.54	2.07	927.9	22.1	88 $\sigma^2\sigma\pi^2$
1 ² Σ^+	4.11	1.86	2.08	583.0	—	85 $\sigma^2\sigma\pi^2$
2 ² Σ^+	3.32	1.97	2.54	1523.4	54.3	86 $\sigma^2\sigma^2\sigma$
2 ² Π	3.52	1.14	2.80	—	—	86 $\sigma^2\sigma\sigma\pi$
3 ² Π	2.98	0.91	3.59	—	—	65 $\sigma^2\pi^3$
2 ⁴ Σ^-	3.58	2.71	3.89	578.4	-1.9	75 $\sigma^2\sigma^0\sigma\pi^2$
2 ² Σ^-	3.38	2.55	4.05	867.4	6.9	70 $\sigma^2\sigma^0\sigma\pi^2$
4 ² Π	3.26	—	4.10	—	—	—
1 ⁴ Δ	3.80	1.84	4.76	529.2	3.8	90 $\sigma^2\sigma\pi\pi^*$
1 ⁴ Σ^+	3.84	1.78	4.82	516.8	2.6	90 $\sigma^2\sigma\pi\pi^*$
2 ² Δ	3.79	0.51	5.05	395.3	5.4	73 $\sigma^2\sigma^0\sigma\pi^2$
3 ² Σ^-	3.76	0.40	5.16	590.3	-1.1	—
3 ² Σ^+	4.62	1.00	5.64	376.3	—	—
2 ⁴ Π	4.01	0.11	6.48	296.5	15.0	66 $\sigma^2\pi^2\pi^*$

^{a)} Dominant electronic configuration at $R = 3.0$ bohr.^{b)} Relative to MRD-CI(+Q) energy of -52.157810 E_H

Table 3.12: Correlation diagram for low lying states of BeC^+ and B_2^+ .

The lowest-lying dissociation channels of BeC^+					
CHANNEL	Be	C	TW ^{a)} (eV)	Expt. ^{b)} (eV)	States
I	$\text{Be}^+ \ ^2S_g (s)$	$\text{C} \ ^3P_g (s^2p^2)$	0.00	0.00	$^2,4\Sigma^-, \Pi$
II	$\text{Be}^+ \ ^2S_g (s)$	$\text{C} \ ^1D_g (s^2p^2)$	1.33	1.26	$^2\Sigma^+, \Pi, \Delta$
III	$\text{Be} \ ^1S_g (s^2)$	$\text{C}^+ \ ^2P_u (s^2p)$	1.90	1.94	$^2\Sigma^+, \Pi$
IV	$\text{Be}^+ \ ^2S_g (s)$	$\text{C} \ ^1S_g (s^2p^2)$	2.72	2.68	$^2\Sigma^+$
V	$\text{Be}^+ \ ^2P_u (p)$	$\text{C} \ ^3P_g (s^2p^2)$	3.99	3.96	$^2,4\Sigma^+, \Sigma^-(2), \Pi(2), \Delta$
...					
X	$\text{Be}^+ \ ^2P_u (p)$	$\text{C} \ ^5S_u (sp^3)$	8.14	8.14	quartet, sextet states
Three lowest-lying dissociation channels of B_2^+					
I	$\text{B}^+ \ ^1S_g (s^2)$	$\text{B} \ ^2P_u (s^2p)$		0.00	$^2\Sigma_{g,u}^+, \Pi_{g,u}$
II	$\text{B}^+ \ ^1S_g (s^2)$	$\text{B} \ ^4P_g (sp^2)$		3.57	$^4\Sigma_{g,u}^-, \Pi_{g,u}$
III	$\text{B}^+ \ ^3P_u (sp)$	$\text{B} \ ^2P_u (s^2p)$		4.63	doublet, quartet states

^{a)} This work^{b)} Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

explained considering the electronic structure of atomic fragments of both molecules. To allow for direct comparison the correlation diagram for low-lying electronic states of BeC^+ and B_2^+ (taken from reference. [17]) is shown in Table 3.12.

The $X^2\Sigma_g^+$ ground state of B_2^+ arises from the ground states of B and B^+ in the s^2 and s^2p configurations, respectively. The $1^4\Sigma_u^-$ state correlates with channel II which consists of the $s \rightarrow p$ excited boron atom and the ground state of B^+ ion, 3.57 eV above the ground state dissociation limit I. The $1^4\Sigma_u^-$ state of the homonuclear molecule is low lying with $T_e = 1.41$ eV. In the heteronuclear molecule the ordering of the dissociation limits is inverted. The $X^4\Sigma^-$ state correlates with the lowest dissociation channel I, while the $^2\Sigma^+$ state correlates with the excited term of the carbon atom and the ground state of Be, 1.26 eV higher in energy. The relative stabilization of the quartet state relative to the doublet causes the $1^2\Sigma^+$ state to lie 2.08 eV higher.

There are three excited doublet electronic states of BeC^+ generated by the

molecular configuration $\sigma^2\sigma\pi^2$: $1^2\Delta$, $1^2\Sigma^-$, and $1^2\Sigma^+$. The first two of these states have regular Morse-like potential energy curves, with equilibrium distances within 0.03 bohr of the ground state. The potential energy curves of these states, plotted in Figure 3.6 are stacked vertically as was the case with the ground state configuration of BeC. The vibration frequencies for these states do not vary significantly from the ground state value. The dissociation energy of the $X^4\Sigma^-$ state is 2.61 eV and the dissociation energy of the $1^2\Sigma^-$ state is 0.54 eV, consistent with the average 2 eV stabilization of the high spin configuration, observed for many diatomic molecules [20].

The two lowest lying $^2\Sigma^+$ states show an avoided intersection at approximately 3.3 bohr. The lower state, $1^2\Sigma^+$, is characterized by the $\sigma^2\sigma\pi^2$ configuration before the intersection and assumes $\sigma^2\sigma^2\sigma$ character at longer Be-C distances. This configuration corresponds to the Be + C⁺ limit. A local minimum of the $1^2\Sigma^+$ state is located at 3.0 bohr, unchanged relative to the ground state, as expected from the electron configuration. The estimated depth of the local minimum is only 0.08 eV and the vibration frequency was not calculated. The true minimum of the $1^2\Sigma^+$ state is located at 4.11 bohr and the harmonic vibration frequency is small at 583 cm⁻¹. The dissociation energies for the two lowest $^2\Sigma^+$ states are 1.86 and 1.97 eV, comparable with 1.97 eV for the ground state of B₂⁺ [17]. For the configuration $\sigma^2\sigma\pi^2$ in the $^2\Sigma^+$ state the diabatic dissociation energy amounts to approximately 2.25 eV, from the local minimum at 3.0 bohr to the dissociation channel III, only 0.04 eV lower than the D_e of the $1^2\Delta$ state with the same configuration.

In both B₂⁺ and BeC⁺, the lowest $^2\Sigma^+$ states are (relatively) weakly bound, while the $^4\Sigma^-$ states have stronger bonds. The changes in the bond strength are better represented in the equilibrium distances and vibration frequencies than in the dissociation energies of the concerned states. The change in the bond length of 1.11 bohr in BeC⁺ is very similar to that in B₂⁺, where the R_e of the $1^4\Sigma_u^-$ state is 2.927 bohr and $\omega_e = 1173$ cm⁻¹. The bond shortens by 1.088 bohr and the vibration frequency increases 2.6 times in B₂²⁺ and 2 times in BeC⁺. Concluding, the electronic states of homo- and heteronuclear molecules discussed above, connected by the $\pi^2 \leftrightarrow \sigma\sigma$

excitation, have very similar properties, but their ordering on the energy scale is different.

Although the mechanism explaining the relative bond strength in both molecules (occupation of the $\pi_{(u)}$ MO) is essentially the same, the name of SBDES is not strictly correct for BeC^+ . In the original paper [45], Bruna and Wright used the name SBDES for the *double excitation from the σ_u orbital of the ground state*. In BeC^+ the strong bond was observed in the ground state that is described by the electron configuration analogous to the strongly bound doubly excited state of the homonuclear B_2^+ . The underlying relation between the electron configuration and properties of the electronic state is unchanged. Population of the π MO, while depopulating the σ MO leads to a very significant increase in the bond strength.

In B_2^+ , the strongest bond was found in the $2^2\Pi_u$ state, arising from the triple excitation $\sigma_u^2\sigma_g \rightarrow \pi_u^3$ from the ground state. The analogous configuration of BeC^+ , $\sigma^2\pi^3$, is generated by a single excitation $4\sigma \rightarrow \pi$ from the ground state. The potential energy curves for the five lowest $^2\Pi$ states are shown in Figure 3.7. As discussed before, the Π_g and Π_u states become Π in $C_{\infty v}$ symmetry, and as a result three avoided crossings can be seen on the figure. There are two avoided crossings between the 2,3 and $4^2\Pi$ states. The singly excited configuration $\sigma^2\pi^3$ contributes to the second state at $R < 2.9$ bohr, to the third state at $R = 2.9\text{--}3.4$ bohr and finally to the $4^2\Pi$ state after 3.4 bohr. The R_e of the diabatic curve for the $\sigma^2\pi^3$ configuration would be slightly shorter than the tabulated R_e value of 2.98 bohr for the $3^2\Pi$ state (see Figure 3.7). This state, characterized by high occupation of the π MO, *has the shortest R_e among all states of BeC^+* . The vibration frequency of 1533 cm^{-1} for the $4^2\Pi$ state reflects the avoided crossing at 3.5 bohr. The potential is very anharmonic as indicated by the $\omega_e x_e$ value approximately 5 times larger than for other potentials listed in Table 3.11.

The discussion of quartet states is simplified by the fact that only the ground and the $1^4\Pi$ states are low lying, correlating with channel I. The $1^4\Pi$ state ($\sigma^2\sigma\sigma\pi$) has only one π electron hence it is not strongly bound. The remaining quartet states arise from the excitation into the 5σ and π^* MO and the bond length increases with

Figure 3.6: MRD-CI potential energy curves for the $^2\Sigma^+$, $^2\Sigma^-$ and $^2\Delta$ states of BeC^+

Figure 3.7: MRD-CI potential energy curves for the 2Π states of BeC^+

Figure 3.8: MRD-CI potential energy curves for the quartet states of BeC^+

respect to the ground state. Interestingly, the $4\sigma \rightarrow 5\sigma$ excitation, leads to the $2^4\Sigma^-$ state, with R_e longer than that of the $2^2\Sigma^+$ state. Also the potential of the $2^4\Sigma^-$ state is significantly wider than the potential of the $2^2\Sigma^-$ state (see Figures 3.6 and 3.8). The ω_e values differ by 300 cm^{-1} between those two states.

Character of the molecular orbitals

Comparison of bonding in the $1^4\Pi$ and $1^2\Pi$ states of BeC^+ gives some additional insight into the nature of the 4σ and 5σ MO's. The doublet and quartet states are described by the dominant configurations $\sigma^2\sigma^2\pi$ and $\sigma^2\sigma\sigma\pi$. The $4\sigma \rightarrow 5\sigma$ promotion, i.e. from $4\sigma^2$ to $4\sigma 5\sigma$, causes the bond to lengthen by 0.28 bohr, the dissociation energy to decrease by 1.4 eV and ω_e to decrease from 676 to 427 cm^{-1} . This change suggests that the 4σ MO acquired some bonding character - in clear opposition to B_2^+ . The differences in the equilibrium distances between the $X^4\Sigma^-$ and $2^4\Sigma^-$ states (+0.58 bohr), $1^2\Delta$ and $2^2\Delta$ (+0.79 bohr) indicate loss of bonding character when depopulating the 4σ MO. Also the $4\sigma \rightarrow 1\pi$ excitation, which connects the $X^4\Sigma^-$ and $3^2\Pi$ states, shortens the bond by only 0.05 bohr. In B_2^+ the $2\sigma_u \rightarrow 1\pi_u$ excitation, connecting the $1^4\Sigma_u^-$ and $3^2\Pi_u$ states shortens the bond by 0.22 bohr, from 2.927 to 2.695 bohr. The $2\sigma_u$ is antibonding in B_2^+ while the 4σ MO is almost as bonding as the 1π MO in BeC^+ .

The contour plots of the MO's and an analogy with B_2 were used to explain the character of the molecular orbitals of the neutral BeC molecule. An alternative approach is convenient for BeC^+ . The energy of the bonding MO is lower than that of the interacting atomic orbitals, therefore the increase in energy of the MO with internuclear distance indicates bonding character. The energies of the antibonding MO's decrease at larger distances and those of the non-bonding remain more or less constant. The energies of 3,4 and 5 σ and 1,2 π MO's in the $^4\Sigma^-$ state at two Be-C distances are given in Table 3.13.

Inspection of the table shows that the 3,4 σ and 1π MO's are bonding and the 5 σ and 2 π (π^*) are essentially non-bonding. The fact that the 4σ MO has become bonding in BeC^+ is due to the large lowering of the energy of the 2s orbitals in

Table 3.13: Energies of the SCF molecular orbitals of BeC^+ at 3.0 and 6.0 bohr in the $^4\Sigma^-$ state.

	R = 3.0 bohr		R = 6.0 bohr	
Orbital	E (eV)	E (eV)		character
3σ	-26.8	-23.7		bonding
4σ	-21.2	-18.1		bonding
5σ	-13.7	-14.1		non-bonding
1π	-18.0	-16.0		bonding
2π	-10.8	-10.4		non-bonding

Be^+ compared to Be so that it can effectively overlap with the $2s$ and $2p$ orbitals of the carbon atom. All low-lying electronic states are doubly populating the 3σ MO and any distribution of three electrons on the remaining MO's allows for the overall bonding character of all configurations. This explains the absence of repulsive potential energy curves in BeC^+ .

The "true" strongly bound doubly excited state of BeC^+ has to arise from the double excitation from the antibonding molecular orbital. SBDES is not an appropriate term, but the strongest bond in BeC^+ may be expected to arise from the $\sigma\pi^4$ configuration in the $^2\Sigma^+$ state. This state, generated by a $3\sigma 4\sigma \rightarrow \pi^2$ excitation, has a formal bond order of 2.5, which is similar to the $\sigma^2\pi^3$ configuration. The strongly bound state must be high lying, due to the correlation of the $\sigma\pi^4$ configuration with $\text{Be}^+ + \text{C}$ or $\text{Be} + \text{C}^+$ both $s \rightarrow p$ excited. Such a state was not observed in the calculations. Furthermore, the $\sigma\pi^4$ configuration never contributed more than 0.005, as measured by the a_j^2 coefficient, to the final CI wavefunction for six lowest $^2\Sigma^+$ states in the single point calculation at the distance of 2.8 bohr. In the presence of strong mixing, even low weight of the given configuration in the low-lying state would suggest the importance of the configuration for the higher-lying state. For example, in BeC the SB configuration $\sigma^2\pi^4$, characterizing the $3^1\Sigma^+$ state, contributed several percent to the wavefunction of the lowest $^1\Sigma^+$ state. We can conclude that the true SBDES of BeC^+ is very high lying and as such must be perturbed by the higher lying $^2\Sigma^+$ states.

The results of the present calculations show that the maximum occupation of the π molecular orbitals leads to the strongest bonds as measured by the local parameters R_e and ω_e . The lack of the SBDES in the strict sense of the term is a result of different correlation of the molecular states with the atomic dissociation limits.

Ionization potentials of BeC

When a gas phase synthesis of BeC has been achieved, the ionization potential data should be of value in interpreting the photoionization spectrum and observing BeC^+ . The main features of the photoelectron spectrum of BeC are reported to assist the experimental observation of the BeC^+ molecule. The ground state of BeC^+ , $X^4\Sigma^-$, is connected to the ground state of BeC, $X^3\Sigma^-$, by a single excitation $4\sigma \rightarrow \infty$ and to the first excited state, $1^5\Sigma^-$, by the $5\sigma \rightarrow \infty$ ionization. The decrease in R_e by 0.2 bohr upon the ionization is indicative of the net gain in bonding character. The polarization of C by Be^+ is a bonding effect not present in BeC. The Franck-Condon Factors (FCF) should be favourable for this process, with the $\Delta R_e = 0.2$ bohr and $\Delta\omega_e = 226 \text{ cm}^{-1}$. The one-electron connection between the electronic states should make the detection of BeC^+ molecule possible by means of conventional one-photon ionization. The adiabatic ionization potential for this process equals 8.71 eV.

The next low-energy ionization connects the $X^3\Sigma^-$ state with the $1^2\Pi$ state of BeC^+ by a $\pi \rightarrow \infty$ ionization from the two open shell configuration of BeC. This is also a one-photon process accompanied by an increase in R_e by 0.30 and 0.40 bohr and a decrease in ω_e by 40%. A wider progression of vibrational bands is expected as a result. The adiabatic ionization potential amounts to 9.32 eV.

The last two ionizations considered connect the $1^3\Pi$ state of BeC ($\sigma^2\sigma^2\sigma\pi$) with the ground and $1^2\Pi$ states of BeC^+ . The first process is a double excitation $\sigma\sigma \rightarrow \pi, \infty$ and would require multiphoton methods for study. The direct ionization of the 4σ electron from the $1^3\Pi$ leads to the $1^2\Pi$ state of BeC^+ with the adiabatic IP of 8.00 eV and favourable Franck-Condon Factors ($\Delta R_e = 0.1$ bohr). It can be concluded that the properties of the electronic states of BeC^+ are favorable for the observation of the photo-electron spectrum and also that BeC^+ should be observable

in the one-photon ionization experiments at around 9 eV.

3.6 BeC²⁺

It will be shown in the Section 4.1 that the diatomic dications (+2 charged ions) have distinct properties from the neutral and singly charged molecules. Most of dications reported in the literature are metastable (see Figure 3.1 in Section 3.1 and Section 4.1) meaning that the dissociation products are lying lower (energetically) than the local minimum of the molecule. The spin, symmetry and relative energies of the dissociation products strongly influence the behaviour of the curves at short geometries. In this section, however, the relative stability of the ground and excited states of the BeC²⁺ molecules will be analyzed in a limited manner. Only the short range properties of the electronic states of the dication will be discussed, based on the previously established strong-bonding criteria. The population of σ and π orbitals is sufficient to rationalize the bond lengths in the electronic states of BeC²⁺. The complete discussion of the molecular properties, including the long-range behaviour and time-dependent properties will be given in the next chapter, after basic consideration of stability of dications.

Potential energy curves

Potential energy curves were calculated for 18 electronic states of BeC²⁺ using the 83 AO basis set used in the BeC and BeC⁺ calculations. The SCF-MO's correspond to the $\sigma^2\pi^2$ configuration in the $^3\Sigma^-$ electronic state. As previously, [He] cores were frozen in the CI calculations and two highest lying σ MO's were discarded. Four electrons were distributed on 79 MO's using 5 to 67 reference configurations. Single and double excitations from these lists generated CI spaces varying from 27172 to 115171 configurations depending on the symmetry. The diagonalized CI spaces were on the order of 10000, and were selected using a threshold varying from 1.0 to 5.0 μ hartree. Up to six of the lowest eigenvalues were computed in the C_{2v} point group. The MRD-CI(+Q) energy values were calculated for 20 distances from 2.4 to 15.0 bohr.

Table 3.14: Spectroscopic parameters of the metastable states of BeC^{2+} .

Parameter	$X^1\Sigma^+$	$1^3\Pi$	$1^3\Sigma^-$	$1^1\Delta$	$1^5\Sigma^-$
T_e (eV)	3.28	3.38	5.39	6.75	8.95
R_e (bohr)	3.86	3.53	3.41	3.38	3.97
D_e (eV)	-3.28	-3.38	-1.43	-2.79	-3.67
D_{eff} (eV)	0.61	0.75	1.65	1.31	0.35
ω_e (cm^{-1})	560	697	673	694	403
$\omega_e x_e$ (cm^{-1})	5.2	12.3	8.5	8.2	3.2
B_e (cm^{-1})	0.806	0.959	1.005	1.029	0.755
α_e (cm^{-1})	0.022	0.023	0.017	0.019	0.023
configuration	$30\sigma^2\sigma^2,$ $40\sigma^2\sigma\sigma$	$54\sigma^2\sigma\pi,$ $34\sigma^20\sigma\pi$	$92\sigma^2\pi^2$	$92\sigma^2\pi^2$	$78\sigma\sigma\pi^2,$ $16\sigma0\sigma\pi^2$

The potential energy curves of 18 electronic states of BeC^{2+} are shown in Figures 3.9 (singlet states) and 3.10 (triplet states). Most of the potential curves in the figures are repulsive. However, five electronic states have local minima at short geometries around 3.5 bohr. The absolute minima at infinite internuclear separation (shown with solid lines at the right of the figures) correspond to the dissociation of the molecule. The local minima are separated from the dissociation limit by potential barriers. The $X^1\Sigma^+$, $1^3\Pi$, $1^3\Sigma^-$, $1^1\Delta$, and $1^5\Sigma^-$ states are *metastable*. This unusual shape of the potential energy curve, not seen in BeC and BeC^+ , is a characteristic feature of diatomic multiply charged ions and will be discussed in the next chapter.

Five metastable electronic states have potential wells deep enough to hold several vibrational levels. The spectroscopic parameters were calculated for these states. The standard Numerov method with Airy boundary conditions, implemented in the program LEVEL, [41] was used to derive the parameters. Therefore, the values given in Table 3.14 take into account the possibility of small perturbations in the ro-vibrational levels caused by tunneling through the barrier. This aspect of the calculations will be discussed in the next chapter. Table 3.14 also shows the dominant electron configurations at $R = 3.8$ bohr.

 Figure 3.9: MRD-CI potential energy curves for the singlet states of BeC^{2+}

Figure 3.10: MKD-CI potential energy curves for the triplet states of BeC^{2+}

Ground state

The ground state of the BeC^{2+} molecule is $X^1\Sigma^+$. Unlike the unbound homonuclear analog B_2^{2+} , this state has a local minimum at 3.86 bohr. The electron configuration⁴ $30\sigma^2\sigma^2 + 40\sigma^2\sigma\sigma$ has sufficient bonding character to change the character of the curve from purely repulsive in B_2^{2+} to quasi-bound in BeC^{2+} . The change in the properties of the ground state of BeC^{2+} relative to B_2^{2+} is due to the differences in the character of the molecular orbitals between the homo- and heteronuclear molecules.

Consider the composition of the $3,4,5\sigma$ and 1π molecular orbitals of BeC^{2+} at the internuclear distance of 3.8 bohr. The 3σ MO corresponds to the $2s_C$ AO. The 4σ is a bonding combination of the $2s_C$, $2p_C$ and $2s_{Be}$ atomic orbitals, polarized towards the carbon atom. The 5σ MO is an essentially non-bonding MO localized on Be atom and the 1π MO is predominantly the $2p_C$ orbital with small overlap with the $2p$ orbital of Be. Therefore the $\sigma^2\sigma^2$ configuration is polarized and bonding. This occupation puts 2 electrons on the $2s_C$ orbital; the remaining 2 electrons are polarized towards the C atom along the bond axis. The structure of the molecule can be described as $\text{Be}^{(1+\delta)+} \text{C}^{(1-\delta)+}$ where $0 < \delta < 1$. Clearly the excitation from the 4σ MO to the 1π MO will partially transfer electron density onto the p orbitals of the carbon atom. The structure of the molecule in the electronic state corresponding to the single and double population of the π molecular orbital will approach $\text{Be}^{2+} + \text{C}$.

Singly excited states

Single excitation $4\sigma \rightarrow 1\pi$ and $5\sigma \rightarrow 1\pi$ leads to two states $^1\Pi$ and $^3\Pi$ characterized by two configurations $\sigma^2\sigma^1\pi^1$ and $\sigma^2\sigma^0\sigma^1\pi^1$. The triplet state has a metastable local minimum at 3.53 bohr. The local minimum depth as measured from the bottom of the well to the transition state is 0.75 eV. The single excitation populating the 1π MO leads to the significant bond shortening of 0.33 bohr. The vibration frequency increases accordingly from 560 for the $X^1\Sigma^+$ state to 697 cm^{-1} for the $1^3\Pi$. The $1^1\Pi$ state does not have a local minimum, but the bonding character is expressed in the flattening of the curve around 3-4 bohr.

⁴See page 27 for notation

Doubly excited states

Double excitations from the 4σ and 5σ molecular orbital ($\sigma^2 \rightarrow \pi^2$ or $\sigma\sigma \rightarrow \pi^2$) generate strongly bonding configurations. The configuration $\sigma^2\pi^2$ generates three electronic states $^1\Sigma^+$, $^1\Delta$, and $^3\Sigma^-$. All three states have local minima in the potential curves. The $^1\Delta$ and $^3\Sigma^-$ states are described by a formally bonding configuration $\sigma^2\pi^2$. The equilibrium distances for these two states are 3.38 and 3.41 bohr and the vibration frequencies are 673 and 694 cm^{-1} respectively. Upon double excitation from the ground state configuration the bond shortens by up to 0.48 bohr and the vibration frequency increases by 24%. The $2^1\Sigma^+$ state is perturbed by the $3^1\Sigma^+$ state and will be discussed later on.

A very limited scope of the discussion, using only the composition of the wavefunction near the potential minima, is sufficient to explain the bond lengths and vibration frequencies of the metastable electronic states of BeC^{2+} . Single and double excitations from the σ molecular orbitals increase the occupation of the π orbital from 0 to 2. The equilibrium distances of the excited states are up to 0.5 bohr shorter than the ground state. The results obtained for BeC^{2+} corroborate the previous findings that in the heteronuclear molecules the *strongest bonds correspond to maximum occupation of the π molecular orbital*. These results allow for a generalization of the findings on the BeC^{q+} family and other molecules having SBDES.

3.7 Strong bonding in the excited state

The phenomenon of strong bonding in the excited state, originally established for homonuclear diatomic molecules, is clearly retained in a polarized heteronuclear molecule. The analysis of bonding in terms of contributions from dominant electronic configuration works remarkably well in the heteronuclear case, despite strong mixing in the excited state. For all three species, BeC , BeC^+ and BeC^{2+} , the shortest bonds and largest vibration frequencies were seen for the states with the maximum occupation of the bonding orbitals. For increasingly ionic bonds, the nature of the MO's changes. In particular the π_u bonding MO becomes localized on the more electronegative atom, but its *maximum occupation ensures the strongest bonding effect for*

the molecules ranging from four electron covalent Be_2 to clearly ionic eight electron BeO .

The discussion of the properties of the BeC^{2+} molecule was based on the analysis of the electronic configuration of the molecule at short distance. The character and occupation of the molecular orbitals and SBDES effect were used to explain the relative stability of the electronic states of BeC^{2+} . The discussion of the properties was analogous to that of neutral and monpositive ion and the robustness of the SBDES effect was confirmed. The strength of the bond was indicated by the equilibrium distance and vibration frequency. However, the correlation of the electronic state of the molecule with the configuration of the dissociation product was totally neglected. Several avoided crossings between the potential energy curves were observed in Figures 3.9 and 3.10. No explanation was given for the reasons of the avoided intersections. In order to better understand the character of bonding in BeC^{2+} , the rules explaining the stability of a diatomic multiply charged ion will be discussed in the next chapter and applied to complete the discussion of BeC^{2+} .

Chapter 4

Thermodynamically stable dications

4.1 Bonding in dications

The energy of the electrostatic interaction between two charges is given by the Coulomb law $E = q_1 q_2 / r$. The repulsion between two positive charges, amounting to 14.4 eV at 1 Å separation, may dominate over any bonding effect present in the diatomic molecule. However, at the distance of 6 Å the repulsion is only 2.4 eV and it is not surprising that a larger molecule, like $\text{CH}_2\text{CCCCCH}_2^+$ [70] is stable, just because of the spatial separation of charges. However, the results obtained for the BeC^{2+} molecule are far from being unique. Metastability in dications has been observed for several small molecules. For example, diatomics formed from the first row atoms, including He_2^+ [71], N_2^+ [72], NO^{2+} [73], and NeN^{2+} [74] have been observed. The experimental methods include double charge transfer [75], charge stripping mass spectrometry [76], and photoelectron-photoelectron coincidence spectroscopy [77]. Among others, He_2^+ [78][79], B_2^+ [47], F_2^+ [80], CF^{2+} [81][82], CO^{2+} [83], NF^{2+} [84][85], and NNe^{2+} [86] molecules have been investigated theoretically at various levels of theory.

The first systematic study of bonding in dications by Bates and Carson [87] points out to two possible situations, corresponding to the *attractive* ($\text{Y}^{2+} + \text{X}$) and *repulsive* ($\text{X}^+ + \text{Y}^+$) dissociation limits. In the first case, the polarization of X by Y^{2+} leads to attractive interactions. In the other case the Coulomb repulsion is present and for some molecules ordinary valence bonding may exist. Bond-

ing interactions may lead to metastable potential curves. Thus the qualitative behaviour of the potential energy curves depends on the energetics of the dissociation products. The energy difference between the attractive and repulsive asymptotes $\Delta E = E(X^+ + Y^+) - E(X + Y^{2+}) = IP_1(X) - IP_2(Y)$ is the single most important property of the diatomic dication.

These purely theoretical ideas were extended and verified by experiment and calculations by several authors. Generalization of these ideas produced two widely-accepted models of bonding in dications, each of them covering a wide range of molecular systems.

4.1.1 Model based on the avoided crossing

One of the models is based on an avoided crossing between the states correlating with dissociation asymptotes of repulsive ($X^+ + Y^+$) and attractive ($X + Y^{2+}$) character and has been successfully applied to a variety of dications [88][89][90]. The possibility of the avoided crossing between the repulsive and attractive curves was proposed by Dorman [91]. In this model asymptotic behavior of the system is considered. The $X^+ + Y^+$ curve is repulsive due to the Coulomb repulsion of two monocations ($V = e^2/r$) and $X + Y^{2+}$ is attractive due to the interaction of the (+2) charge with the induced dipole moment. The molecular configurations corresponding to the $X + Y^{2+}$ and $X^+ + Y^+$ will be referred to as “attractive” and “repulsive” configurations, respectively. The term repulsive may be misleading because, as was shown for F_2^{2+} [80], there may exist a net attractive interaction between two monpositive ions. Alternatively, the terms “ionic” ($X + Y^{2+}$) and “covalent” ($X^+ + Y^+$) may be used. If both states have the same symmetry, they interact and an avoided crossing may occur [91]. The extension of the simple avoided crossing model includes the diabatic coupling between two electronic states. A schematic plot of two interacting curves is shown in Figure 4.1.

As a result of the interaction, the stability of the lower-lying state increases and it may become metastable. The main parameter describing the interaction of attractive and repulsive curves is the energy difference between attractive and repulsive

$$\Delta = IE[A^+] - IP[B]$$

Figure 4.1: Avoided crossing model of Radom and Gill

channels: $\Delta = IP_2(Y) - IP_1(X)$. Here $IP_n(X)$ stands for the n -th ionization potential of the atom X . The sign of the Δ is opposite to the convention used by Bates and Carson [87]. Following Radom and Gill, a positive sign of Δ will correspond to the situation where the repulsive asymptote lies lower than the attractive one. The details are discussed thoroughly in references [48][88][89]. This approach describes nicely the systems in which the avoided crossing occurs at relatively long distances ($R \geq 5-6$ bohr) as it neglects a possible formation of a covalent bond between X^+ and Y^+ . The virtue of this model is that it only requires the ionization potentials of the atoms and polarizability of the atom X to make useful predictions about the potential curves.

The Avoided Crossing Diabatic Coupling and Polarization (ACDCP) model of Gill and Radom in its original formulation applies to the ground states of all ions. Bruna and Wright [47] extended the idea based on the ACDCP model to the excited states. The lowest-lying repulsive and attractive channel, separated by Δ in energy may not necessarily generate the states of the same spin and symmetry. In such a case, Δ' will denote the actual energy difference between the repulsive and attractive dissociation channels for the states of the same symmetry. As shown in reference [47], the differences between Δ and Δ' can be significant.

In this approach three main conditions must be fulfilled for a given state to be metastable. First, the attractive and repulsive channels must generate electronic states of the same symmetry. Second, the attractive channel must correspond to the bonding configurations. Third, for the interaction to be truly effective, the separation Δ (Δ') between the channels, should not exceed 15 eV [92][93]. If all three conditions are met, the metastability will depend on the actual values of Δ and electronic structure of the upper state (weakly vs strongly bonding). The same arguments were shown to apply to triply charged molecular ions [28][92]. The only important aspect neglected in the ACDCP model is the possibility of covalent bond formation.

4.1.2 Model based on the formation of covalent bond

There is no reason why a regular covalent bond could not be formed between two positively charged atomic ions. In this situation a model established by Hurley and Maslen [94] becomes useful. It predicts the shape of a potential energy curve for a dication as a sum of the Coulomb repulsion and a scaled potential of the isoelectronic neutral molecule [94], according to the formula 4.1

$$V_{2+}(r) = 1/r + t^2 V_0(tr) \quad (4.1)$$

where V_{2+} stands for the potential energy of a dication, V_0 for the potential for the neutral isoelectronic molecule, r for the internuclear distance (all expressed in atomic units) and t is a scaling parameter depending on the atomic numbers of the constituent atoms. The expression $t = (Z+1)/Z$, where Z is the atomic number of the constituent atom, accounts for the more compact charge distribution in the dication compared to the neutral molecule.

Figure 4.2, reproduced from reference [80], shows the calculated potential curve for F_2^{2+} with the e^2/r term removed and the unscaled potential for the O_2 molecule. It is clear that the dication curve subtracted from the Coulomb repulsion curve produces the scaled O_2 potential. The model was successfully applied to O_2^{2+} and N_2^{2+} and the properties were predicted for several other molecules, including F_2^{2+} [94].

The electron configuration of the system consists of three main components corresponding to one "covalent", and two "ionic" structures $X^+ + Y^+$, $X + Y^{2+}$, $X^{2+} + Y$ [83]. Both a valence bond treatment of He_2^{2+} [78], and CI calculations [79] indicate that the bonding interaction between He^+ and He^+ , with the σ_g^2 configuration, is the main component responsible for the observed metastability of the molecule. The valence bond treatment of the CO^{2+} molecule [83] considers explicitly the components of the bond by analyzing the contributions of three possible structures ($C^+ + O^+$, $C^{2+} + O$, and $C + O^{2+}$) and assigning occupation numbers to atomic orbitals in various electronic states of the system.

An *ab initio* study of the F_2^{2+} [80] molecule in the $X^3\Sigma_g^-$ (ground) state points to the similarities between F_2^{2+} and the isoelectronic O_2 . The comparison of the

FIG. 3. The dotted line shows the MR-CI potential curve of F_2^{2+} with the Coulomb repulsion term removed, and the solid line shows the MR-CI potential of isoelectronic O_2 in a corresponding basis (this work). There is a geometric difference because the additional nuclear charge of the fluorine produces a more compact electron charge distribution. Allowing for this, the fact that the two potentials are so similar suggests that the oddly shaped dication potential (Fig. 2) is composed of an ordinary chemical binding potential overlayed on a Coulomb repulsion of the constituent ions.

Figure 4.2: Bonding in homonuclear diatomic dications: F_2^{2+}

components of the CI wavefunctions of both systems reveals very similar electronic structures. The drastic changes in the dominant configurations upon the change of geometry from the local minimum through the transition state to the repulsive part of the curve are attributed to the bond breaking, not curve crossing.

For low values of Δ , on the order of several eV, the configuration corresponding to the attractive asymptote contributes significantly to the wavefunction at the local minimum. For large values of Δ the interpretation based on bond breaking is more attractive. However, the separation of channels remains important.

Consider the Δ values for B_2^{2+} and BeC^{2+} dications. The value of 16.94 eV (B_2^{2+}) is very close to that of F_2^{2+} (17.55 eV). Covalent bonding between two B^+ ions is a good description of the interaction in the metastable states as in F_2^{3+} . Bruna and Wright [47] did not observe significant contributions of the electron configurations corresponding to the $B^{2+} + B$ channel in the MRD-CI wavefunctions. However, for BeC^{2+} Δ is significantly smaller (only 6.94 eV) and the ACDCP model should be applicable. A very similar Δ value of 6.96 eV characterizes the CF^{2+} dication and Koch and Frenking attribute the $C^{2+} + F$ structure to the potential minimum in their theoretical study [81]. Senekowitsch and co-workers arrived at the same conclusion [82]. Bearing this in mind we can turn our attention to the description of the BeC^{2+} molecule within the ACDCP framework.

4.1.3 Avoided crossings between the potential curves of BeC^{2+}

The correlation of electronic states of the molecule with the atomic dissociation limits is essential for understanding of bonding in the diatomic dications. The review given above allows us to consider and analyze the correlation of the metastable states of BeC^{2+} with repulsive and attractive asymptotes.

To illustrate the avoided crossing of the potential curves in BeC^{2+} consider the formation of the molecule in the $^1\Delta$ state. Table 4.1 shows possible low lying dissociation channels of BeC^{2+} . The $^1\Delta$ states are the only case in which the attractive channel leads to the second state of given symmetry; i.e the $1^1\Delta$ correlates with the

Table 4.1: Correlation diagram for low lying states of BeC^{2+} .

CHANNEL	Be	C	This work (eV)	Expt. ^{a)} (eV)	States
I	$\text{Be}^+ 2S_g$	$\text{C}^+ 2P_u$	0.00	0.00	$1,3\Sigma^+, \Pi$
II ^{b)}	$\text{Be}^+ 2P_u$	$\text{C}^+ 2P_u$	3.96	3.99	$1,3\Sigma^+(2), \Sigma^-, \Pi(2), \Delta$
III	$\text{Be}^+ 2S_g$	$\text{C}^+ 4P_g$	5.28	5.33	$3,5\Sigma^-, \Pi$
A	$\text{Be}^{2+} 1S_g$	$\text{C} 3P_g$	6.90	6.95	$3\Sigma^-, 3\Pi$
B ^{b)}	$\text{Be}^{2+} 1S_g$	$\text{C} 1D_g$	8.24	8.21	$1\Sigma^+, \Pi, \Delta$
IV	$\text{Be}^+ 2P_u$	$\text{C}^+ 4P_g$	—	9.29	
V	$\text{Be}^+ 2S_g$	$\text{C}^+ 2D_g$	—	9.29	

^{a)} Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

^{b)} See text for emphasis of channels **II** and **B**

repulsive channel **II** and the $2^2\Delta$ with the attractive channel **B**. The Δ' separation between the dissociation limits amounts to 4.22 eV. The potential energy curves for two lowest $1^1\Delta$ states are plotted in Figure 4.3. The dashed line represents the e^2/r Coulomb repulsion, originating in the channel **II**. The changes in the composition of the electronic states with internuclear distance are shown at the bottom of Figure 4.3. The thick and thin solid lines indicate the weights of the $\sigma^2\pi^2$ and $\sigma^2\pi\pi^*$ configurations in the $1^1\Delta$ state, the dashed lines represent the weights of the same configurations in the $2^1\Delta$ state.

At 12.0 bohr the PEC of the $1^1\Delta$ state is repulsive and overlaps with the e^2/r Coulomb repulsion curve. The dominant configuration is $\sigma^2\pi\pi^*$. In the dissociation limit this configuration corresponds to the $2p$ and $2s^2p$ occupations on Be^+ and C^+ ions. The σ MO corresponds to $2s_C$, π to $2p_C$ and π^* to $2p_{Be}$. The $1^1\Delta$ state has a $\text{Be}^+ + \text{C}^+$ structure. At the same distance the $2^1\Delta$ state is described by the $\sigma^2\pi^2$ configuration corresponding to the $\text{Be}^{2+} + \text{C}$ structure.

The interaction occurs at the distance of 6 to 8 bohr. For example, at the internuclear distance of 7.0 bohr the lower state is described by the $27\sigma^2\pi^2 + 63\sigma^2\pi\pi^*$ linear combination and the upper state has a 27% contribution from the $\sigma^2\pi\pi^*$ configuration. The wavefunction of the lower state acquires the character of the upper state and vice versa. The potential energy curve of the lower state deviates from the

Figure 4.3: MRD-CI potential energy curves for the $1^2\Delta$ and $2^2\Delta$ states of BeC^{2+} .

e^2/r curve as a result of the increasing weight of bonding configuration. At the distance of 6.0 bohr the change in the electron configuration is complete. The physical description corresponds to the transfer of the electron density from the $2p$ orbital of beryllium onto the $2p$ orbital of carbon. At the local minimum of the PEC, the $1^1\Delta$ state is described by the $\sigma^2\pi^2$ configuration and the $2^1\Delta$ by $\sigma^2\pi\pi^*$. The $\sigma^2\pi^2$ configuration has significant $\text{Be}^{2+} + \text{C}$ character. To summarize, the structure of the $1^1\Delta$ state changes from $\text{Be}^+ + \text{C}^+$ at large R to $\text{Be}^{2+} + \text{C}$ at short R . The reverse is true for the $2^1\Delta$ state. The interaction of two lowest $^1\Delta$ states has a form of genuine avoided crossing and the ACDGP model is applicable.

The avoided crossing described above is perturbed for other states. The dissociation limit of the lowest metastable state $X^1\Sigma^+$ is separated from the attractive asymptote **B** by two additional states correlating with the repulsive asymptotes. In the triplet manifold, the attractive channel corresponds to the $5^1\Pi$, $5^3\Pi$, and $3^3\Sigma^-$ states. The changes in the electronic configuration of the metastable states of BeC^{2+} are shown in Table 4.2. The electron configuration responsible for the metastability of the state is shown with the bold font in the table. At the distance of 12.0 bohr, the $3^3\Sigma^-$ state is described by the $\sigma^2\pi^2$ configuration ($\text{Be}^{2+} + \text{C}$), while the $1^3\Sigma^-$ state has a dominant configuration $\sigma^2\pi\pi^*$. The configuration corresponding to channel A at extended geometries is the main configuration of the lowest $^3\Sigma^-$ state at short distance. A similar propagation occurs for the $^3\Pi$ states. The configuration $\sigma^2\sigma\pi$ corresponds to the $5^3\Pi$ state at $R = 12.0$ bohr and to the $1^3\Pi$ state at the local minimum of the curve. Only two lowest potential curves of $^3\Pi$ symmetry are shown in the Figure 3.10 for the sake of clarity. However, the change of the electron configuration of the five electronic states over the distance of approximately 10.0 bohr implies the existence of at least four avoided crossings between the potential curves. This creates a situation of very strong mixing in the manifold of the intermediate states. For example, at the internuclear distance of 8.0 bohr seven electron configurations contribute more than 0.04, as measured by the a_j^2 in equation 1.1, to the final CI wavefunction of the $2^3\Pi$ state.

The density of the $^1\Sigma^+$ electronic states is also high. Inspection of the Figure

Table 4.2: Most important configurations of selected electronic states of BeC^{2+} at three internuclear distances (in bohr).

State	3.8	5.0	12.0
$X^1\Sigma^+$	30 $\sigma^2\sigma^2 + 40\sigma^2\sigma\sigma$	$20\sigma^2\sigma\sigma + 44\sigma^20\sigma\sigma$	$94\sigma^2\sigma\sigma$
$2^1\Sigma^+$	$80\sigma^2\pi^2$	$15\sigma^20\sigma^2 + 40\sigma^2\sigma0\sigma$	$89\sigma^2\sigma0\sigma$
$3^1\Sigma^+$	$20\sigma^2\sigma^2 + 48\sigma^20\sigma^2$	$60\sigma^2\pi^2 + 16\sigma^2\pi\pi^*$	$86\sigma^2\pi\pi^*$
$1^1\Delta$	92 $\sigma^2\pi^2$	88 $\sigma^2\pi^2$	$86\sigma^2\pi\pi^*$
$2^1\Delta$	$80\sigma^2\pi\pi^*$	$80\sigma^2\pi\pi^*$	92 $\sigma^2\pi^2$
$1^3\Sigma^-$	92 $\sigma^2\pi^2$	91 $\sigma^2\pi^2$	$90\sigma^2\pi\pi^*$
$2^3\Sigma^-$	$54\sigma^2\pi\pi^* + 26\sigma\sigma\pi^2$	$75\sigma^2\pi\pi^* + 9\sigma\sigma\pi^2$	$90\sigma0\sigma\pi^2$
$3^3\Sigma^-$	$44\sigma\sigma\pi^2 + 31\sigma0\sigma\pi^2$	$70\sigma\sigma\pi^2$	93 $\sigma^2\pi^2$ —
$1^3\Pi$	54 $\sigma^2\sigma\pi + 34\sigma^20\sigma\pi$	53 $\sigma^2\sigma\pi + 26\sigma^20\sigma\pi$	$89\sigma^20\sigma\pi$
$2^3\Pi$	$33\sigma^2\sigma\pi + 38\sigma^20\sigma\pi$	$31\sigma^2\sigma\pi + 52\sigma^20\sigma\pi$	$89\sigma^2\sigma\pi$
$3^3\Pi$	$28\sigma^2\sigma\pi^* + 29\sigma^20\sigma\pi^*$	$54\sigma^20\sigma\pi + 33\sigma\sigma\sigma\pi$	$90\sigma\sigma\sigma\pi$
$4^3\Pi$	$26\sigma\sigma\sigma + 20\sigma\sigma^2\pi$	$46\sigma^200\sigma\pi + 25\sigma\sigma0\pi$	$86\sigma^200\sigma\pi$
$5^3\Pi$	$24\sigma\pi^3 + 20\sigma\sigma\sigma\pi$	—	90 $\sigma^2\sigma\pi$
$1^5\Sigma^-$	78 $\sigma\sigma\pi^2 + 16\sigma0\sigma\pi^2$	47 $\sigma\sigma\pi^2 + 30\sigma0\sigma\pi^2$	$88\sigma0\sigma\pi^2$
$2^5\Sigma^-$	$16\sigma\sigma\pi^2 + 68\sigma0\sigma\pi^2$	$40\sigma\sigma\pi^2 + 33\sigma00\sigma\pi^2$	95 $\sigma\sigma\pi^2$

^a Boldface indicates main bonding configurations.

3.9 reveals an avoided crossing between the $2^1\Sigma^+$ and $3^1\Sigma^+$ states around 4.0 bohr, $3^1\Sigma^+$ and $4^1\Sigma^+$ at around 6.0 bohr, $2^1\Sigma^+$ and $3^1\Sigma^+$ at around 7.0 bohr. The $1^5\Sigma^-$ state is also metastable as a result of the avoided intersection with the $2^5\Sigma^-$ state. The change of the electron configuration from $\sigma\sigma\pi^2$ to $\sigma\sigma^0\sigma\pi^2$ occurs at the distance of about 5 bohr.

Stability of the electronic states of BeC^{2+}

The occurrence of metastability in BeC^{2+} was rationalized as a result of the avoided crossing between the diabatic curves of repulsive and attractive character, within the ACDGP framework. The metastable electronic states $1^3\Sigma^-$, $1^1\Delta$, and $1^5\Sigma^-$ of BeC^{2+} are characterized by relatively single configurations in the region of the potential well. Significant mixing occurs in the $1^1\Sigma^+$ and $1^3\Pi$ states. The SBDES effect provides a simple and efficient way of relating the bond lengths and vibration frequencies to those single configurations. The strong bonding rules apply to the diabatic curves

of the dication and avoided crossing rules combined with the SBDES provide a way of predicting the relative stability of the excited states of the metastable dication. To illustrate, recall the three conditions for metastability given in page 64. The strongest bonds in the attractive channel are related to the occupation of π molecular orbital the same way as in the neutral and monpositive diatomics, i.e. *the higher the occupation of the π MO, the shorter the bond and the higher the harmonic frequency.*

The five electronic states given in Table 3.6 are metastable and consequently the dissociation energies are negative. The D_e value of -1.43 eV is the largest (least negative) for the $^3\Sigma^-$ state, reflecting the strongest bond caused by the $\sigma^2\pi^2$ configuration and the lowest Δ' value of 2.96 eV. The energy difference between the local maximum of the state at 8 bohr to the channel II is 3.08 eV. The relative energy of the state with respect to the lowest dissociation channel is significantly larger. The minimum of the curve lies 5.39 eV from the minimum of the curve and the transition state lies 7.04 eV above the channel I products. Therefore BeC^{2+} is thermodynamically unstable in all five quasi-bound states.

How stable is the molecule in the vibrational levels trapped behind the potential barrier? Generally a metastable molecule can decay via tunneling through the barrier and by radiative decay. Only the former mechanism is possible for the ground state $X^1\Sigma^+$. In a simple approximation [95], assuming a parabolic shape of the barrier, the coefficient of transmission is proportional to the exponent of the negative barrier width ($\Delta R_{v'}^*$), barrier height (D_{eff}), reduced mass (μ) and vibrational energy $E_{v'}$:

$$\kappa_t = \exp\{-(\pi^2/h) \Delta R_{v'}^* [2\mu(D_{eff} - E_{v'})]^{1/2}\} \quad (4.2)$$

Using the values $D_{eff} = 0.61$ eV, $E_{v'} = 0.034$ eV, $\Delta R_{v'}^* = 3.5$ bohr, $\mu = 5.146833$ amu, which describe the $v = 0$ level of BeC^{2+} in the $X^1\Sigma^+$ state, we obtain an approximate value of the transmission coefficient on the order of $\exp(-3 \times 10^{12})$, corresponding to an essentially infinite lifetime.

The more quantitative calculations of the tunneling lifetimes for low vibrational levels of the $X^1\Sigma^+$ state were performed using program LEVEL of LeRoy [41]. The calculated tunneling lifetimes vary from 10^{23} years for $v = 0$ to about a week for $v =$

3. Compare these values with the tunneling lifetimes of low lying vibrational levels of the metastable ground state of BeH^{2+} [96]. The lifetimes of the $v = 0$ and $v = 1$ levels are reported as "stable" and 60000 years, in spite of the small mass of BeH^{2+} and low barrier to dissociation $D_{eff} = 0.72$ eV. The practical consequence of the very long tunneling lifetimes is that the BeC^{2+} is *kinetically stable* under non-perturbed conditions.

The tunneling lifetimes for the higher lying metastable states are expected to be even longer, due to the larger well depth and wider potential barrier. In this situation, the higher states may decay radiatively or predissociate. Predissociation is a possibility for two out of five metastable states that are crossed by the repulsive curves in the outer wall of the potential well. The $1^3\Sigma^-$ state is crossed by the $1^3\Sigma^+$ at around 4.8 bohr and the $1^1\Delta$ by the $2^1\Sigma^+$ and $2^1\Pi$ at around 5.0 bohr. The quantitative aspects are not discussed here, but the lowest lying vibrational levels of the quasi-bound state should not be affected (see Figures 3.9 and 3.10).

The possible allowed radiative processes include bound-bound emission from the $1^3\Sigma^-$ to $1^3\Pi$ and bound-continuum emission $1^1\Delta - 1^1\Pi$. Although both emissions are allowed by the selection rules, they are expected to be weak. The Franck-Condon Factors are favourable for the detection of the transitions within the triplet states ($\Delta R = 0.08$ bohr), but the electronic structure of both states can be approximated by $\text{Be}^{2+} + \text{C}$. The emission from the $3\Sigma^-$ to the 3Π state involves the $1\pi - 4\sigma$ molecular orbitals. As both MO's have significant $2p_C$ character, the transition is comparable to the $p - p$ atomic transition which is forbidden in the isolated atom. Similar effects are expected in the $1\Delta - 1\Pi$ system. To qualitatively confirm that, the transition moments between the $3\Sigma^-$ and 3Π states were calculated for R varying from 2.4 to 6.0 bohr. The application of the methods described in the Section 2.3 leads to the radiative lifetime of the $v = 0$ level of the $1^3\Sigma^-$ state on the order of 0.1 millisecond. This property of the $3\Sigma^- - 3\Pi$ band may lead to difficulties in the observation of the emission from the triplet state. On the other hand the lifetime of the $1^3\Sigma^-$ state is long enough for the mass-spectrometric detection at the microsecond scale. The same arguments should apply to the $1^1\Delta$ state.

4.1.4 Conclusions

BeC^{2+} has five quasi-bound states in which the occupation of the π molecular orbitals varies from 0 to 2. The geometries of the local minima and vibration frequencies are related to the occupation of the π molecular orbital and the Δ' value. The R_e decrease by up to 0.5 bohr, upon the increase in the number of π electrons from 0 to 2. The vibration frequencies increase by up to 24 % upon the increase of the occupation of the 1π MO. The $1^1\Delta$ and $1^3\Sigma^-$ electronic states are *strongly-bound doubly excited states* (SBDES).

The dissociation energies are negative, meaning that the minimum of the diabatic “ionic” curve lies above the dissociation limit of the lower “covalent” curve. The lowest value of Δ' of 2.96 eV occurs for the $3\Sigma^-$ states. The dissociation energy of the $1^3\Sigma^-$ state of -1.43 eV implies that the energy lowering in the attractive channel amounts to $2.96 - 1.43 = 1.53$ eV, very close to the D_{eff} of 1.65 eV. The energy of the attractive interaction in channel A is approximately 50 % of the Δ' value.

Consider now the hypothetical situation of the molecule where the stabilization arising from the attractive asymptote is larger than Δ (Δ'). Obviously, in the case of negative Δ values, any stabilization in the attractive channel is larger than Δ' . The lowest lying dissociation asymptote corresponds to the attractive channel, and the charge-induced dipole interaction *will* occur. In the absence of destabilizing effects, the molecule will be bound and *thermodynamically stable*. This behaviour is shown by a small group of molecules, predominantly noble-gas dications. For example, HeBe^{2+} is bound, due to the fact that the attractive channel $\text{Be}^{2+} + \text{He}$ lies 6.0 eV below the repulsive one ($\text{He}^+ + \text{Be}^+$).

Consequently, an interesting question arises, as to whether it is possible to form a diatomic dication that is thermodynamically stable but does not contain noble gas atoms. Alternatively, the question could be modified: “Is it possible for a diatomic dication, dissociating into two monocationic ions, to be thermodynamically stable?”. A positive answer to that question requires the diabatic dissociation energy of the attractive state to be larger than Δ' .

Table 4.3: Δ values (eV) for dications of the second period.

	Li	Be	B	C	N	O	F	Ne
Li	70.3	12.8	19.8	19.0	24.2	29.7	29.6	35.6
Be		8.9	9.9	7.0	3.7	4.6	0.8	<i>-3.4</i>
B			16.9	13.9	10.6	11.5	7.7	3.6
C				13.1	9.9	10.8	7.0	2.8
N					15.1	16.0	12.2	8.0
O						21.5	17.7	13.6
F							17.6	13.4
Ne								19.4

Table 4.4: Δ values (eV) for dications of the third period.

	Na	Mg	Al	Si	P	S	Cl	Ar
Na	42.2	9.9	13.7	11.2	14.6	18.2	18.7	22.5
Mg		7.4	9.1	6.9	4.6	4.7	<u>2.1</u>	<u>-0.7</u>
Al			12.8	10.4	8.3	8.5	5.9	3.1
Si				8.2	5.9	6.0	3.4	<u>0.6</u>
P					9.2	9.4	6.8	4.0
S						13.0	10.4	7.6
Cl							10.8	8.1
Ar								11.9

4.2 Absolute stability of diatomic dications

The discussion from the previous section and reference [2] suggests the use of Δ as a predictor of thermodynamic stability. The Δ values for diatomic dications composed of second-row, third-row, and second-third row atoms are shown in Tables 4.3, 4.4, and 4.5. The boldface indicates the dications studied in this work, the italicized entries show the dications that were shown to be thermodynamically stable, and underlined entries indicate the dications predicted to be thermodynamically stable. Hydrides and helides of second and third period are not enumerated but there are studies in the literature showing metastability and stability of both classes of compounds [97][98][99].

Inspection of these tables reveals several “areas” of low values of Δ . Several

Table 4.5: Δ values (eV) for dications of the second-third period.

	Na	Mg	Al	Si	P	S	Cl	Ar
Li	41.9	9.7	13.4	11.0	14.3	17.9	18.4	22.2
Be	13.1	5.7	9.5	7.0	7.7	7.9	5.2	2.5
B	20.0	6.7	10.5	8.1	11.4	14.8	12.2	9.4
C	19.2	3.8	7.6	5.1	8.5	12.1	11.4	8.6
N	24.5	0.5	4.3	<u>1.8</u>	5.2	8.8	9.3	13.1
O	30.0	1.4	5.2	<u>2.7</u>	6.1	9.7	10.2	14.0
F	29.8	-2.4	1.4	<u>-1.1</u>	<u>2.3</u>	5.9	6.4	10.2
Ne	25.7	<u>-6.5</u>	<u>-2.7</u>	<u>-5.2</u>	<u>-1.8</u>	<u>1.8</u>	<u>2.3</u>	6.1

noble-gas containing molecules with negative Δ 's (BeNe^{2+} , HeBe^{2+} [97], SiNe^{2+} [100]) were shown to be bound and stable in their ground states and as such are excluded from further discussion. The third-period — neon dications are mostly unstudied but negative values of Δ suggest thermodynamic stability. If the energy lowering arising from the bonding effects in the attractive channel is larger than Δ , a molecule will be stable. Even if there is no covalent bond formation in the upper channel, charge-induced polarization effects will be present.

Analysis of the above tables leads to an interesting observation: only 15 out of 136 diatomics listed in the tables have Δ larger than 20 eV. Only one of the large Δ dications (O_2^{2+}) does not contain alkali metals. However, the O_2^{2+} molecule is metastable despite the very high $\Delta = 21.5$ eV. More than 50% of (+2) ions from the tables have $\Delta \leq 10$ eV. One may therefore expect that metastability should be (and actually is) a very common phenomenon.

For a diatomic dication to be thermodynamically stable, the diabatic dissociation energy D'_e must be larger than Δ . The strongest known bond has D_0 of 11.09 eV for carbon monoxide. Thus all diatomics with Δ larger than 11 eV can probably be excluded. The lowest values of Δ correspond to the MgX^{2+} and XF^{2+} diatomics from Table 4.5. The explanation lies in the properties of Mg and F. Magnesium is very easy to doubly ionize with $\text{IP}_1 = 7.646$ eV and $\text{IP}_2 = 15.035$ eV, while F is difficult ($\text{IP}_1 = 17.422$) [40].

How large is the *minimal* expected strength of the interactions in the attractive

channel of a diatomic dication? In a series of papers Koch, Frenking and collaborators discussed the nature of the bond formation in charged, noble-gas containing molecules [48][97]. One of the conclusions of this work was that the interaction of the point charge with the charge-induced dipole is a good approximation for the description of the bond. An estimate of the size of the charge-induced dipole moment interaction may be obtained by truncating the multipole expansion for the electrostatic interaction at the first leading term [101], $E_{ind} = -0.5\alpha q^2 r^{-4}$. Here α is the static polarizability, q is the charge and r is the distance. For the BeNe^{2+} molecule, using the recommended [40] value of $\alpha=0.396 \text{ \AA}^3$ and $r = 3.06 \text{ bohr}$ [97], the E_{ind} is estimated to be 1.66 eV. Koch *et. al.* found that actual dissociation energies are 30 to 50 % smaller than E_{ind} for noble gas compounds.

Table 4.6 lists Δ and E_{ind} values for several ions characterized by low Δ values. The noble gas containing dications are excluded from this list and the reasonable threshold of $\Delta \leq 3 \text{ eV}$ was chosen, as the electrostatic attraction is unlikely to exceed this value. Note that the fact of possible formation of the covalent bond in the attractive channel is neglected, but that this effect will usually further increase the stability of the dication. An interaction distance of 3.0 bohr was chosen for dications from Table 4.3, 4.0 bohr for those from Table 4.5 and 4.5 bohr for the molecules from Table 4.4. To my knowledge only BeF^{2+} [2], AlF^{2+} [102], and PF^{2+} [100][103] dications from Table 4.6 were studied. The BeF^{2+} and PF^{2+} species are *stable* and bound by 1.09 [2] and 4.81 eV [100] respectively, and reference [102] reports only the equilibrium distance of AlF^{2+} . The energetics of the remaining species MgN^{2+} , MgO^{2+} , MgF^{2+} , AlF^{2+} , SiN^{2+} , SiO^{2+} , and SiF^{2+} are generally unknown.

No study except our (reference [2]) undertook the *systematic search for the thermodynamic stability* of highly charged species. BeF^{2+} is the only non-noble gas species composed of second period atoms that has a low Δ of only 0.79 eV and the stabilizing interaction E_{ind} of 2.53 eV, so this dication is a very good candidate for thermodynamic stability. This *prototype* molecule will be studied in detail in Section 4.4, including the detailed analysis of the origin of the bond, electron configuration, parameters of the potential energy curves, and radiative properties. The results on

Table 4.6: Δ and E_{ind} values (eV) for several diatomic dications.

Molecule	Δ	E_{ind}
BeF ²⁺	0.79	2.53
MgC ²⁺	3.78	2.38
MgN ²⁺	0.51	1.58
MgO ²⁺	1.42	1.15
MgF ²⁺	-2.39	0.80
MgCl ²⁺	2.07	1.95
AlF ²⁺	1.41	0.80
SiN ²⁺	1.82	1.58
SiO ²⁺	2.73	1.15
SiF ²⁺	-1.08	0.80
PF ²⁺	2.31	0.80

the MgC²⁺, MgN²⁺, MgO²⁺, and MgF²⁺ molecules using the extended GTO basis set and the MRD-CI method are reported in Sections 4.5-4.9.

As pointed out in the literature, preparation of dications from the stable precursors is relatively simple, by means of electron impact double ionization. Thus the single most promising molecule is MgO²⁺, but neutral precursors for MgF²⁺ and BeF²⁺ have also been synthesized [104]. Ionization of SiO₂ and MgF₂ may lead to SiO²⁺ and MgF²⁺, among other products. Generation of dications in three-body collisions, as proposed by Bates and Carson [87] is more complicated. MgN²⁺ may not be easy to synthesize, but its low value of Δ makes it an interesting subject of study. MgC²⁺ is unlikely to be thermodynamically stable but its similarity with BeC²⁺ and existence of SBDES can be explored.

4.3 Atomic calculations

The proper calculation of ionization potentials is necessary to reproduce the experimental ordering of the dissociation channels for the mono- and dications. For example in MgN²⁺ the experimental value of Δ is only 0.5 eV. If the error in the ionization potential calculations is large, the relative change in the Δ value may be large. Such a large change may show up as the improperly calculated geometries of the transition

Table 4.7: Atomic basis sets used in the diatomic calculations.

Atom	Valence		Polarization		Diffuse functions
Be	10s5p/5s3p ^{a)} ^{b)}		2d1f	[27]	sp [28]
Mg	12s9p/6s5p	[30]	2d	[12]	sp [28]
C	10s6p/5s4p	[25]	2d1f	[27]	sp [26]
N	10s6p/5s4p	[25]	2d1f	[27]	sp [26]
O	10s6p/5s4p	[25]	2d1f	[27]	sp [26]
F	10s6p/5s4p	[25]	2d1f	[27]	sp [26]

^{a)} 10s/5s contraction from reference [25]^{b)} 5p/3p contraction from reference [26]

state and avoided crossing. As an example, a dication with $\Delta = 1/50$ hartree (0.54 eV) will show the avoided crossing at the distance of 50 bohr [88], while an absolute error of 0.27 eV (calculated $\Delta = 0.27$ eV) may increase the computed geometry of the avoided crossing geometry to 100 bohr.

Atomic basis sets for Be, Mg, C, N, O, and F atoms are listed in Table 4.7, together with references to their origin. The results of the atomic calculations will be used to correlate the configuration of the atoms with the molecular states using the Wigner-Witmer rules [20]. The carbon and fluorine atom basis sets used in the MgX^{2+} calculations are identical to those used in the BeC and BeF²⁺ calculations. The nitrogen and oxygen atom basis sets are derived by analogy which ensures the same level of treatment of all members of the series. The magnesium basis set corresponds to the 12s9p/6s5p contraction by McLean and Chandler [30] augmented with *s*, *p* diffuse and 2*d* polarization functions with exponents $\alpha_s = 0.02$, $\alpha_p = 0.015$, and $\alpha_d = (0.3, 0.12)$. The magnesium basis set is smaller than used for Be previously, but the basis set should be sufficient to properly describe the (+2) ion of the metal.

The results of calculations on atomic excitation energies and ionization potentials are given in Tables 4.8, 4.9, 4.10, and 4.11 in the tables were obtained at the MRD-CI(+Q) level. The tables are organized as follows: term energies of each species are given relative to the ground state of the neutral atom. For the ions, the values in parentheses are the term energies with respect to the ground state of the ion. Thus the term energy of the ground state of the ion is actually the first ionization poten-

Table 4.8: Excitation energies (in eV) of Mg and Mg⁺.

Species	Configuration	State	This work ^{a)} (eV)	Expt. ^{b)} (eV)
Mg	[Ne]3s ²	¹ S _g	0.00	0.00
Mg	[Ne]3s3p	³ P _u	2.66	2.71
Mg ⁺	[Ne]3s	² S _g	7.55 (0.00)	7.65 (0.00)
Mg ⁺	[Ne]3p	² P _u	11.87 (4.33)	12.07 (4.42)
Mg ⁺⁺	[Ne]	¹ S _g	22.37 (14.82)	22.68 (15.03)

^{a)} Relative to MRD-CI (+Q) energy of Mg = -199.75719845 E_H.

^{b)} Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

tial of the atom. All experimental values are taken from the compilation by Moore, *Atomic Energy Levels* National Bureau of Standards, Washington, D.C., 1971. Only the electronic states that are relevant to the topic of the thesis are considered.

The discussion of the results of calculations on the excitation energies is simplified by the same nature of errors in the calculations. For the atomic calculations, ground state (high multiplicity) MO's were used for the CI calculations on all excited states. The CI description of the ground state is better than that of the low-spin excited state, and consequently, the term energies of low-spin states are consistently over-estimated. Energies of high spin states are calculated with generally smaller errors. For example, for the N atom the term energies of the ²D_u and ²P_u states are overestimated by 0.11 and 0.09 eV, while for the magnesium atom the energy of the ³P_u term is underestimated by 0.05 eV. The calculated ionization potentials have larger errors. For example, for MgN²⁺ the experimental value of Δ = 0.5 eV. The energy of the lowest repulsive channel is underestimated at the MRD-CI(+Q) level by 0.23 eV and the energy of the lowest attractive channel is underestimated by 0.31 eV. As a results of the cancelation of errors, the difference between the experimental and calculated Δ is only 0.08 eV.

The results of atomic calculations on the N, O, F, and Mg atoms indicate the good quality of *ab initio* treatment as well as the adequacy of the basis set for the excited state calculations. Generally the errors are below 0.15 eV. Thus, the predictions of thermodynamic stability to follow should generally be reliable to within

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Table 4.9: Excitation energies (in eV) of N and N⁺.

Species	Configuration	State	This work ^{a)} (eV)	Expt. ^{b)} (eV)
N	2s ² 2p ³	⁴ S _u	0.00	0.00
N	2s ² 2p ³	² D _u	2.49	2.38
N	2s ² 2p ³	² P _u	3.67	3.58
N ⁺	2s ² 2p ²	³ P _g	14.40 (0.00)	14.53 (0.00)
N ⁺	2s ² 2p ²	¹ D _g	16.37 (1.97)	16.43 (1.90)
N ⁺	2s ² 2p ²	¹ S _g	18.54 (4.14)	18.58 (4.05)

^{a)}Relative to MRD-CI (+Q) energy of N = -54.52056 E_H.^{b)}Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)Table 4.10: Excitation energies (in eV) of O and O⁺.

Species	Configuration	State	This work ^{a)} (eV)	Expt. ^{b)} (eV)
O	2s ² 2p ⁴	³ P _g	0.00	0.00
O	2s ² 2p ⁴	¹ D _g	2.01	1.97
O	2s ² 2p ⁴	¹ S _g	4.12	4.19
O ⁺	2s ² 2p ³	⁴ S _u	13.33 (0.00)	13.62 (0.00)
O ⁺	2s ² 2p ³	² D _u	16.79 (3.46)	16.94 (3.32)
O ⁺	2s ² 2p ³	² P _u	18.49 (5.16)	18.64 (5.02)

^{a)}Relative to MRD-CI (+Q) energy of O = -74.98274 E_H.^{b)}Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)Table 4.11: Excitation energies (in eV) of F and F⁺.

Species	Configuration	State	This work ^{a)} (eV)	Expt. ^{b)} (eV)
F	2s ² 2p ⁵	² P _u	0.00	0.00
F ⁺	2s ² 2p ⁴	³ P _g	17.18 (0.00)	17.43 (0.00)
F ⁺	2s ² 2p ⁴	¹ D _g	19.80 (2.62)	20.02 (2.59)
F ⁺	2s ² 2p ³	¹ S _g	22.78 (5.60)	23.00 (5.57)

^{a)}Relative to MRD-CI (+Q) energy of F = -99.62734 E_H.^{b)}Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

Table 4.12: Low-lying dissociation channels of BeF^{2+} .

	Conf.	Term		Conf.	Term		Expt. ^{a)}	CI ^{b)}	El. states
Be^+	$2s^1$	2S_g	F^+	$2p^4$	3P_g	I	0.00	0.00	$1^2\Sigma^-, X^2\Pi, 1^4\Sigma^-, 1^4\Pi$
Be^{2+}	$1s^2$	1S_g	F	$2p^5$	2P_u	A	0.79	0.94	$A^2\Sigma^+, 2^2\Pi$
Be^+	$2s^1$	2S_g	F^+	$2p^4$	1D_g	II	2.59	2.62	$2^2\Sigma^+, 3^2\Pi, 1^2\Delta$
Be^+	$2p^1$	2P_u	F^+	$2p^4$	3P_g	III	3.96	3.99	$3^2\Sigma^+, 2,3^2\Sigma^-, 4,5^2\Pi$ $2^2\Delta, 1^4\Sigma^+, 2,3^4\Sigma^-, 2,3^4\Pi$
Be^+	$2s^1$	2S_g	F^+	$2p^4$	1S_g	IV	5.57	5.60	$4^2\Sigma^+$

^{a)} Values (eV) taken from reference.[29]

^{b)} In eV, relative to the MRD-CI(+Q) energy of Be^+ and F^+ of $-113.27496 E_H$.

this (or better) uncertainty.

4.4 BeF^{2+}

The MRD-CI method, described in section 2.1.2, was used to study the BeF^{2+} molecule. The molecular orbitals of the ground state $X^2\Pi$ were used for the CI expansion. Excitations from the two lowest σ MO's were disallowed and the high-lying counterpart MO's were discarded, leaving 7 electrons to populate 79 MO's. Thirty six reference configurations for the two lowest $^2\Pi$ states and 24 reference configurations for the $1,2\ ^2\Sigma^+$ states were used. The selection threshold of $5.0\ \mu\text{hartree}$ led to selected spaces on the order of 10,000, selected from the generated space of 867,123 ($^2\Pi$) and 610,113 ($^2\Sigma^+$).

Calculations were carried out at 40 internuclear geometries spanning the range from 2.0 to 50.0 bohr with additional calculations at 1000.0 bohr to establish the dissociation limits for the channels of interest. In this case the calculated energies corresponding to repulsive channels were lowered by $0.001 E_H$, corresponding to the remaining Coulomb repulsion at 1000 bohr.

4.1.1 Dissociation limits and electronic states

Information about the dissociation channels of BeF^{2+} is summarized in Table 4.12. The lowest dissociation channel corresponds to the Be^+ and F^+ in their ground

states (channel I). The next channel A is *attractive* and correlates the ground states of Be^{2+} and F. The experimental separation between channels I and A is 0.79 eV and the *ab initio* value overestimates the separation by 0.15 eV. Entries in Table 4.12 result from the atomic calculations on Be, F and their ions, given in Tables 3.2 and 4.11. Energies of Be^+ and Be^{2+} ions are calculated at the SCF level and the 0.15 eV error is the result of the "frozen core" approximation. The remaining channels are in error by less than 0.04 eV.

The lowest channel I combines the 2S_g state of Be^+ ($2s^1$) with the ground state of F^+ ($^3P_g, 2s^2p^4$). The corresponding molecular configurations are (neglecting the frozen core) $\sigma^2\sigma^2\sigma\pi^2$ and $\sigma^2\sigma\sigma\pi^3$. The electronic states are $^2,4\Sigma^-$ and $^2,4\Pi$ respectively. Channel A combines ground states of doubly ionized beryllium ($\text{Be}^{2+}, ^1S_g, 1s^2$) and neutral fluorine ($\text{F}, ^2P_u, 2s^2p^5$). These atomic states generate $\sigma^2\sigma^2\pi^3$ and $\sigma^2\sigma\pi^4$ molecular configurations in the $^2\Pi$ and $^2\Sigma^+$ states. The two configurations equivalent to $^2\Pi$ states correlating with channels I and A may interact at extended geometries in the form of genuine avoided crossing between the "ionic-like" ($\sigma^2\sigma^2\pi^3$) and "covalent-like" $\sigma^2\sigma\sigma\pi^3$ configurations. The three main conditions for metastability of diatomic dication system, described in section 4.1, are thus fulfilled for the $X^2\Pi$ state [92]. The lowest state of $^1\Sigma^+$ symmetry correlates with the $\text{Be}^{2+} + \text{F}$ asymptote (dissociation limit A).

The higher lying channels II, III, and IV correspond to the excited states of Be^+ and F^+ . The electronic states correlating with these limits are expected to be repulsive and their potential energy curves should closely follow the Coulomb repulsion potential e^2/r . The potential curves for 21 electronic states listed in Table 4.12 are shown in Figure 4.4. Many of the curves are overlapping and cannot be labelled because of the congestion on the plot. All but two potential curves are repulsive. The expanded view of two lowest states near the minimum (encircled area from Figure 4.4) is shown in Figure 4.5. The spectroscopic parameters of the $X^2\Pi$ and $A^2\Sigma^+$ states are listed in Table 4.13.

4.4.2 Bound states of BeF^{2+}

The potential energy curves for two lowest states of $^2\Pi$ symmetry show an interesting avoided intersection. At distances shorter than 25 bohr the potential energy curve of the lower state has a Morse-like shape. The minimum of the potential energy of the $X^2\Pi$ state at 3.09 bohr lies 1.08 eV below the dissociation channel I and the BeF^{2+} molecule is *thermodynamically stable*. At the distances of 5 to 25 bohr the potential is flat, but at an extended geometry of around 25 bohr it becomes repulsive. At infinite separation this curve dissociates to channel I.

The potential of the $2^2\Pi$ state is repulsive for $R \leq 25$ bohr and becomes flat afterwards. The electronic structures at short distances correspond to $\sigma^2\sigma^2\pi^3$ for the bound curve and $\sigma^2\sigma\sigma\pi^3$ for the repulsive one. These electron configurations correspond to the $\text{Be}^{2+} + \text{F}$ and $\text{Be}^+ + \text{F}^+$ structures respectively. After the avoided crossing the $X^2\Pi$ state is described by the $\sigma^2\sigma\sigma\pi^3$ configurations and the $2^2\Pi$ by $\sigma^2\sigma^2\pi^3$.

The interaction between the attractive and repulsive states has the form of a genuine avoided crossing, unlike in diatomic molecules with larger repulsive-attractive separation. In most of the diatomic dications, the upper attractive state is separated from the lower repulsive state by several other repulsive curves. Also, the wavefunction in the region of the transition state is strongly mixed with important configurations corresponding not only to the two initial states but also the manifold in between. A very clear example of such mixing is given by the $^3\Pi$ states of BeC^{2+} discussed previously.

The $A^2\Sigma^+$ state, with ionic configuration $\sigma^2\sigma\pi^4$ is also bound with the minimum at 3.23 bohr. The minimum of the curve lies 0.45 eV below its dissociation limit and 0.49 eV above channel I. The $A^2\Sigma^+$ dissociates to the lowest attractive channel and does not show interaction with the higher lying states of the same symmetry.

The spectroscopic constants for the two low-lying states are shown in Table 4.13, together with constants for isoelectronic LiO . The standard integration method of Numerov-Cooley can be used for the low lying vibrational levels of the ground state. For the v levels lying above the channel I, tunneling through the potential

Figure 4.4: MRD-CI potential energy curves for low-lying states of BeF^{2+} .

Figure 4.5: Minima of two lowest-lying states of BeF^{2+}

Table 4.13: Spectroscopic parameters of the bound states of BeF^{2+} and LiO .

Species	BeF^{2+}		LiO^a	
Parameter	$X^2\Pi$	$A^2\Sigma^+$	$X^2\Pi$	$A^2\Sigma^+$
T_e (eV)	0.00	1.59	0.00	0.29
R_e (bohr)	3.09	3.23	3.20	3.02
D_e (eV)	1.08	0.45	3.59	—
D_{eff} (eV)	2.07	—	—	—
ω_e (cm^{-1})	717	497	852	867
k (dynes/cm)	1.85×10^5	0.89×10^5	2.09×10^5	2.16×10^5
$\omega_e x_e$ (cm^{-1})	9.7	14.0	12.5	6.7
B_e (cm^{-1})	1.04	0.94	1.20	1.35
α_e (cm^{-1})	0.019	0.029	0.015	0.019

^a Values taken from reference.[20]

barrier is still a possibility. However, the discussion of tunneling in the $X^1\Sigma^+$ state of BeC^{2+} suggests extremely small transmission coefficients. Both bound states are not perturbed by higher lying states, and this fact is reflected in the low value of $\omega_e x_e$.

The two bound states of BeF^{2+} differ significantly in their dissociation energies. Both electronic configurations $\sigma^2\sigma^2\pi^3$ and $\sigma^2\sigma\pi^4$ correspond to the limit of $\text{Be}^{2+} + \text{F}$, with the unpaired electron along the axis of the molecule in the $A^2\Sigma^+$ state and perpendicular on fluorine atom in the case of $X^2\Pi$. In this case the σ_{2p} orbital is doubly occupied. This increases the electron density along the bond axis and allows for better polarization of fluorine by the beryllium ion. The effect is reflected in the two-fold change in the harmonic force constants, given in Table 4.13. Figure 4.6 shows a schematic drawing of these two situations. Interestingly, in isoelectronic LiO , which has an ionic structure Li^+O^- , the $A^2\Sigma^+$ state has equilibrium distance shorter than the ground state $X^2\Pi$ by 0.17[105] or 0.22 bohr[68], as would be expected from the π bonding rules. Since Li^+ is isoelectronic with Be^{2+} and O^- is isoelectronic with F , the electron configurations of LiO are analogous to those in BeF^{2+} . In both LiO and BeF^{2+} the $^2\Pi$ state lies lower than $^2\Sigma^+$. Partridge *et. al.* [106] suggest that two σ electrons in the Π state are closer to the Li^+ ion and experience stronger attraction, compared to one σ electron in the $^2\Sigma^+$ state.

The energy of the charge-induced dipole interaction of 2.24 eV at 3.09 bohr

Figure 4.6: Occupation of p orbitals in the electronic states of BeF^{2+}

corresponds well to the calculated energy difference between the potential minimum and the $\text{Be}^{2+} + \text{F}$ limit of 2.02 eV. E_{ind} is an overestimate of the interaction energy and the actual D_e , in line with the findings of Frenking *et. al.* on noble gas compounds [97].

The strength of the bond in BeF^{2+} is comparable with other molecules in which charge-induced polarization is responsible for the bonding. For example BeHe^{2+} has $D_e = 0.87$ eV [48] and BeNe^{2+} $D_e = 1.25$ eV [97]. In BeC^{2+} , calculated in the previous section, the D_{eff} values vary from 0.33 to 1.69 eV depending on the electronic state. In all three cases stable (HeBe^{2+} , BeNe^{2+}) or metastable (BeC^{2+}) minima correspond to a $\text{Be}^{2+} + \text{X}$ structure with little or no π bonding.

Seven-electron diatomics can be formed combining the atoms having 0 and 7, 1 and 6, 2 and 5, 3 and 4 valence electrons, for example HeF , LiO , BeN , and BC . Due to the low multiplicity of the atoms and ions with 0,1,6 and 7 valence electrons, the resulting molecule has low multiplicity (doublet) and high occupation of the π MO. In this case $\sigma^2\sigma^2\pi^3$ and $\sigma^2\sigma\pi^4$ configurations are competing for the ground

state. For LiO, $X^2\Pi$ is a ground state and $1^2\Sigma^+$ lies only 0.32 eV above [68]. $^2\Sigma^+$ with its ... π^4 occupation becomes the ground state only in the case of heavier alkali oxides as demonstrated by Goddard and coworkers [68]. Goddard attributes the change in the ordering of the states to the balance between the Pauli repulsion forces, favoring the $^2\Sigma^+$ state and quadrupole interactions, favoring the $^2\Pi$ state. If one of the atoms has higher multiplicity in the ground state (2+5 and 3+4 combinations), the resulting configurations are $\sigma^2\sigma^2\sigma\pi^2$, $\sigma^2\sigma^2\sigma^2\pi$ and $\sigma^2\sigma^2\pi^3$. The first of these three configuration corresponds to the electronic state $^4\Sigma^-$, being the ground state of BeN, BC and BN^+ molecules. The higher multiplicity states are more covalent, although molecules such as BeN are still strongly polarized [55].

4.4.3 Radiative properties

The $X^2\Pi - A^2\Sigma^+$ band system has an electric-dipole allowed transition near 1.6 eV. Since the minimum of the upper state is shifted by only 0.14 bohr with respect to the ground state, the Franck-Condon factors should be favorable. Table 4.14 shows radiative data for low-lying vibrational levels of the X-A system. For each v'' level, the first line in the block gives the transition energy, second the Franck-Condon factor, the next line gives Einstein coefficients, and the last line gives the oscillator strength. The fluorescence lifetime of each v' level is given in the last line of the table.

The FCF's are nearly diagonal, at least for low v levels, with the maximum intensities spreading over several levels for higher v . Despite the fact that the transition $X^2\Pi - A^2\Sigma^+$ is electric dipole-allowed, the calculated transition moment values are rather small, varying from -0.03 to 0.01 in the spectroscopic region. Due to the nature of both states, differing only in orientation of the unpaired electron on one of the 2p orbitals of the F atom, the transition is equivalent to 2p-2p in the isolated atom, which is electric-dipole forbidden [20]. This results in low values of the Einstein coefficients and oscillator strengths. A similar situation occurs in LiO where O^- ion, isoelectronic with F atom, can assume two orientations with respect to the Li^+ ion. The transition moments between the X and A states are approximately two times larger, so the oscillator strengths are roughly four times larger for X - A band in LiO.

Table 4.14: Radiative data for the $X^2\Pi-A^2\Sigma^+$ system of BeF^{2+} .

v''^a	$v''^b = 0$	$v' = 1$	$v' = 2$	$v' = 3$	$v' = 4$	
0	12705	13176	13621	14042	14822	ν (cm^{-1})
	0.706E 0	0.242E 0	0.456E-1	0.560E-2	0.361E-3	$q_{v',v''}^c$
	0.618E 2	0.172E 3	0.129E 3	0.544E 2	0.158E 2	$A_{v',v''}^d$
	0.287E-6	0.743E-6	0.522E-6	0.207E-6	0.568E-7	$f_{v',v''}^e$
1	12007	12478	12923	13344	13744	
	0.231E 0	0.254E 0	0.341E 0	0.136E 0	0.322E-1	
	0.401E 2	0.197E 2	0.124E 3	0.195E 3	0.148E 3	
	0.208E-6	0.951E-7	0.557E-6	0.825E-6	0.589E-6	
2	11327	11797	12243	12664	13064	
	0.533E-1	0.313E 0	0.258E-1	0.267E 0	0.221E 0	
	0.178E 2	0.645E 2	0.177E 2	0.604E 2	0.158E 3	
	0.104E-6	0.348E-6	0.886E-7	0.282E-6	0.695E-6	
3	10664	11135	11580	12001	12401	
	0.830E-2	0.144E 0	0.237E 0	0.178E-1	0.107E 0	
	0.371E 1	0.473E 2	0.558E 2	0.299E 2	0.311E 2	
	0.245E-7	0.286E-6	0.312E-6	0.155E-6	0.151E-6	
4	10017	10488	10930	11355	11754	
	0.109E-2	0.375E-1	0.224E 0	0.903E-1	0.101E 0	
	0.297E 0	0.164E 2	0.758E 2	0.243E 2	0.468E 2	
	0.222E-8	0.111E-6	0.475E-6	0.141E-6	0.254E-6	
5	9386	9856	10301	10722	11123	
	0.113E-3	0.735E-2	0.941E-1	0.228E 0	0.287E-2	
	0.597E-1	0.273E 1	0.425 2	0.795E 2	0.739E 0	
	0.508E-9	0.211E-7	0.300E-6	0.518E-6	0.440E-8	
	8.1	3.1	2.2	1.8	1.6	τ^f (ms)

^a v'' indicates vibrational levels of $X^2\Pi$ ^b v' indicates vibrational levels of $A^2\Sigma^+$ ^c Franck-Condon Factors^d Einstein coefficients (s^{-1})^e Oscillator strength^f Fluorescence lifetime of v'' level (ms). The series of Einstein coefficients was summed over 20 v'' levels and is converged.

(See ref [68] for details).

One of the consequences of the small oscillator strengths and Einstein coefficients is that the observation of the A-X band will be difficult. However, long lifetimes for both bound states of BeF^{2+} should facilitate the mass spectrometric detection of the thermodynamically stable dication. The possible ways of formation of BeF^{2+} were discussed by Kolbuszewski and Wright [2]. One of the proposed mechanisms is ionization of BeF^+ according to $\text{BeF}^+ \rightarrow \text{BeF}^{2+} + e^-$. BeF^+ was observed above 15 eV in the reaction $\text{BeF}_2 + e^- \rightarrow \text{BeF}^+ + \text{F} + 2e^-$ [104].

4.5 Magnesium containing dications of the second period

The following four sections describe the calculations on the series of low Δ dications. In the series MgX^{2+} , where $\text{X}=\text{C}, \text{N}, \text{O},$ and F , the separation of the attractive and repulsive asymptotes decreases from 3.78 eV for MgC^{2+} to -2.39 eV for MgF^{2+} . The stabilization in the attractive channel in MgC^{2+} is unlikely to exceed 3.78 eV and MgC^{2+} should be metastable. This molecule is isovalent with BeC^{2+} and similar electronic structures are expected. The attractive channel lies below the repulsive one for MgF^{2+} and it is predicted to be bound and stable. The $\text{Mg}^{2+} - \text{F}$ distance should be larger than $\text{Be}^{2+} - \text{F}$ distance by more than 0.6 bohr, which is the difference between the ionic radii of Mg^{2+} and Be^{2+} in solid state [40]. On the other hand MgN^{2+} and MgO^{2+} should exhibit the behaviour of BeF^{2+} , i.e. that of the thermodynamically stable ground state dissociating to $\text{Mg}^+ + \text{N}(\text{O})^+$.

The sections 4.6 to 4.9 are organized as follows: the correlation of the electronic states with the dissociation limits using the Wigner-Witmer rules [20] is given first for each molecule. The properties of the metastable and bound states are tabulated and the corresponding potential curves are shown in figures. In these figures, the zero of the energy scale corresponds to the lowest dissociation channel and the negative energies of the potential curves correspond to the thermodynamic stability of the state. This choice of zero in the energy scale facilitates the discussion of the metastable molecules, where the lowest energy corresponds to the lowest dissociation channel.

Table 4.15: Details of the MRD-CI treatment of MgX^{2+} species, $X = \text{C, N, O, and F}$

	MgC^{2+}	MgN^{2+}	MgO^{2+}	MgF^{2+}
SCF-MO's	$^3\Sigma^-$	$^4\Sigma^-$	$^5\Sigma^-$	$^2\Sigma^+$
length of reference list	10-32	5-25	9-29	8-21
generated space ($\times 10^6$)	1.1-4.3	0.8-5.0	0.9-23	1.4-4.7
selection threshold (μE_H)	1.5-3.0	5.0-8.0	5.0-6.0	5.0-8.0
selected space ($\times 10^3$)	8-12	8-13	7-12	9-11
maximum number of roots	5	4	4	3
total energy of the ground state at $R = 1000.0$ bohr (E_H)	-236.853399	-253.468769	-273.970713	-298.561634

Application of the same convention to the thermodynamically stable dications leads to the negative term energies of the thermodynamically stable states. The conversion from this energy scale to the true term energy is very simple. The energy difference between the ground state and the lowest dissociation limit ($-T_e$ of the ground state) must be added to all tabulated term energies. The same convention is used in all tables. The discussion of the results, comparison with other molecular systems and significance of the results will be given in the section 4.11.

The calculation on MgX^{2+} series were performed using the $7s6p2d$ (Mg) and $6s5p2d1f$ (electronegative atoms) basis set and the MRD-CI package. The details of the multireference treatment of all four molecules are summarized in Table 4.15. The four lowest σ orbitals and the lowest π orbital will be omitted in the notation of the electron configuration. The character of the MO's in MgX^{2+} compounds is as follows: $1\sigma = 1s_{\text{Mg}}$, $2\sigma = 1s_X$, $3\sigma = 2s_{\text{Mg}}$, $4\sigma = 2p_{z(\text{Mg})}$, $5\sigma = 2s_X$, $6\sigma = 2p_{z(X)}$, $7\sigma = 3s_{\text{Mg}}$, $1\pi = 2p_{x,y(\text{Mg})}$, and $2\pi = 2p_{x,y(X)}$. Only the occupation of 5σ , 6σ , 7σ and 2π is important in the molecules of interest. These orbitals will be denoted as $\sigma\sigma\sigma\pi$. However, an improvement of 0.07 eV in the calculated dissociation energy of MgH was observed when the valence and $n=2$ electrons of Mg were correlated [12]. Therefore, the $2s2p$ electrons of magnesium were included in the reference lists in the MRD-CI calculations.

In the CI calculations the [He] core were frozen on both atoms, allowing for the

Table 4.16: Correlation diagram for low lying states of MgC^{2+} .

CHANNEL	Mg	C	This work (eV)	Expt. ^{a)} (eV)	States
I	$\text{Mg}^+ \ ^2S_g$	$\text{C}^+ \ ^2P_u$	0.00	0.00	$^1,^3\Sigma^+, \Pi$
A	$\text{Mg}^{2+} \ ^1S_g$	$\text{C} \ ^3P_g$	3.63	3.77	$^3\Sigma^-, \Pi$
II	$\text{Mg}^+ \ ^2P_u$	$\text{C}^+ \ ^2P_u$	4.33	4.42	$^1,^3\Sigma^+(2), \Sigma^-,$ $\Pi(2), \Delta$
B	$\text{Mg}^{2+} \ ^1S_g$	$\text{C} \ ^1D_g$	4.96	5.03	$^1\Sigma^+, \Pi, \Delta$

a) Values taken from C.E. Moore, *Atomic Energy Levels*

(National Bureau of Standards, Washington, D.C., 1971)

correlation of the $2s, 2p$ shell of the magnesium atom as well as valence electrons. The total treatment included 12 (for MgC^{2+}) to 15 (for MgF^{2+}) electrons that were distributed over 76 orbitals. The weight of the reference configurations in the MRD-CI wavefunctions varied from 92 to 97%, depending on symmetry, spin, root number and internuclear distance.

4.6 MgC^{2+}

Information about the dissociation channels of MgC^{2+} is summarized in Table 4.16. Channel I combines the ground states of Mg^+ and C^+ in the $3s^1$ and $2s^2p$ configurations. Channel A corresponds to the $\text{Mg}^{2+} + \text{C}$ in their respective ground states. The separation of 3.77 eV between the channels is smaller than in the case of BeC^{2+} where the separation is 6.95 eV. The only electronic state common to channels A and I is $^3\Pi$. The next attractive channel (B) leads to the $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states. This limit is separated from channel A by the repulsive asymptote II leading to 12 singlet and triplet states. The lowest $^3\Sigma^-$ electronic state correlates directly with channel A. We may then expect avoided crossings in the $^1\Pi$, $^1\Delta$, $^1\Sigma$, and $^3\Pi$ states and also that the $^3\Sigma^-$ state should be bound.

Figure 4.7 shows potential energy curves for 11 electronic states of MgC^{2+} . The local minimum of the ground state, $X^3\Pi$, lies 2.02 eV above channel I and the molecule is effectively bound by 1.07 eV. MgC^{2+} is not thermodynamically stable. The bond distance in this state is 4.38 bohr, second shortest of all states of MgC^{2+} . This state

Table 4.17: Spectroscopic parameters of the metastable states of MgC^{2+} .

Parameter	$X^3\Pi$	$1^1\Sigma^+$	$1^3\Sigma^-$	$1^1\Pi$	$1^1\Delta$
T_e (eV)	2.02	2.39	3.27	3.34	4.64
R_e (bohr)	4.38	4.60	4.36	4.94	4.44
D_e (eV)	-2.02	-2.39	0.47	-3.34	-0.31
D_{eff} (eV)	1.07	0.82	0.47	0.15	0.41
ω_e (cm^{-1})	457	371	351	151	312
$\omega_e x_e$ (cm^{-1})	22.2	-0.5	12.8	-17.0	6.8
B_e (cm^{-1})	0.393	0.356	0.398	0.329	0.392
α_e (cm^{-1})	0.006	0.004	0.009	0.010	0.010

undergoes an avoided crossing with the $2^3\Pi$ state at 8-9 bohr. The situation of direct unperturbed crossing is similar to the avoided crossing in the $1^1\Delta$ states of BeC^{2+} . The minimum of the lowest excited state $1^1\Sigma^+$ lies 0.37 eV above the minimum of the ground state. The singlet state is bound by 0.82 eV and its equilibrium distance is 0.22 bohr longer than the ground state value. The vibration frequency decreases from 457 cm^{-1} to 371 cm^{-1} . The ordering of the 3Π and $1^1\Sigma^+$ was different in BeC^{2+} where the singlet was the ground state.

The lowest attractive channels of 3Π and $1^1\Sigma^+$ symmetry lie 3.77 and 5.03 eV above the dissociation limits for the $X^3\Pi$ and $1^1\Sigma^+$ states. Attractive channels A and B combine the s^2p^2 configuration of the C atom in the $3P_g$ and $1D_g$ terms with the ground state of Mg^{2+} . The relative strength of the bond depends on both Δ' and occupation of the π molecular orbital. The ground state has one π (formally 2π) electron while the $1^1\Sigma^+$ state has none. The 3Π state shows a shorter bond, larger potential barrier and larger vibration frequency (ω_e) than the $1^1\Sigma^+$ state. The third metastable state correlating with channel I, namely the $1^1\Pi$ undergoes avoided crossings with other $1^1\Pi$ states. The first crossing can be observed at $R = 6-8$ bohr. The local minimum occurs at a large distance of 4.94 bohr and the barrier is very low at 0.15 eV.

The $1^3\Sigma^-$ state is an interesting example of the bound potential curve arising directly from the attractive channel. The depth of the potential is only 0.47 eV at 4.36 bohr. The last metastable state of MgC^{2+} , $1^1\Delta$, is also weakly bound and undergoes

Figure 4.7: MRD-CI potential energy curves for low-lying states of MgC^{2+}

an avoided crossing with the $2^1\Delta$ state at long internuclear distance (not shown in the Figure 4.7). The energy separation between channels II and B is only 0.61 eV (MRD-CI(+Q) value of 0.63 eV) and the avoided crossing occurs at the distance of approximately 35 bohr.

The tunneling lifetimes are essentially infinite for all bound states except for the $1^1\Pi$ state. The lifetimes of three lowest v levels are 1.5×10^6 , 500 and 0.2 seconds and reflect the very low and narrow barrier to dissociation of 0.15 eV. The tunneling effect is sufficiently pronounced to perturb the vibrational levels and cause a negative value of $\omega_e x_e$.

The main difference between BeC^{2+} and MgC^{2+} is that of different ordering in the dissociation channels. The first attractive channel lies at 3.77 eV compared to 6.95 eV in BeC^{2+} , this difference reflecting the easier ionization of magnesium. The first attractive channel is the second overall in MgC^{2+} and the fourth overall in BeC^{2+} . The $1^3\Sigma^-$ state becomes bound in MgC^{2+} , while in the second period analog this state is metastable.

4.7 MgN^{2+}

The correlation of the atomic fragments with the electronic states of MgN^{2+} is shown in Table 4.18. The MgN^{2+} molecule has more low-lying attractive channels than MgC^{2+} . Three out of five dissociation limits correspond to the doubly ionized magnesium and neutral nitrogen. The lowest quartet term of atomic nitrogen combined with closed shell Mg^{2+} (channel A) leads to the low lying $^4\Sigma^-$ state. The lowest channel, I, correlates doublet and triplet ionic terms and produces doublet and quartet states in the repulsive channel. It is the interaction of the two lowest $^4\Sigma^-$ states that may lead to the thermodynamic stability of MgN^{2+} . Inspection of Table 4.9 reveals that two doublet terms of neutral nitrogen, 2D_u and 2P_u , are low lying at 2.38 and 3.58 eV relative to 4S_u . The singlet (Mg^{2+}) + doublet (N) atomic terms lead to $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ states, which arise from channels B and C. The presence of the repulsive channel II, 1.90 eV above channel I and only 0.98 and 2.18 eV below channels B and C, creates repulsive-attractive interactions within the doublet states.

Table 4.18: Correlation diagram for low lying states of MgN^{2+} .

CHANNEL	Mg	N	This work (eV)	Expt. ^{a)} (eV)	States
I	$\text{Mg}^+ \ ^2S_g$	$\text{N}^+ \ ^3P_g$	0.00	0.00	$^2,4\Sigma^-, \Pi$
A	$\text{Mg}^{2+} \ ^1S_g$	$\text{N} \ ^4S_u$	0.42	0.50	$^4\Sigma^-$
II	$\text{Mg}^+ \ ^2P_u$	$\text{N}^+ \ ^1D_g$	1.97	1.90	$^2\Sigma^+, \Pi, \Delta$
B	$\text{Mg}^{2+} \ ^1S_g$	$\text{N} \ ^2D_u$	2.91	2.88	$^2\Sigma^-, \Pi, \Delta$
C	$\text{Mg}^{2+} \ ^1S_g$	$\text{N} \ ^2P_u$	4.09	4.08	$^2\Sigma^+, \Pi$

a) Values taken from C.E. Moore, *Atomic Energy Levels*
(National Bureau of Standards, Washington, D.C., 1971)

Table 4.19: Spectroscopic parameters of the stable and metastable states of MgN^{2+} .

Parameter	$X^4\Sigma^-$	$1^2\Pi$	$1^2\Sigma^-$	$1^2\Delta$	$1^2\Sigma^+$
T_e (eV)	-0.49	1.36	1.95	2.08	3.30
R_e (bohr)	4.18	4.29	4.52	4.23	4.31
D_e (eV)	0.49	-1.36	-1.95	-0.11	-1.33
D_{eff} (eV)	0.82	1.37	0.84	0.85	0.84
ω_e (cm^{-1})	371	391	334	374	330
$\omega_e x_e$ (cm^{-1})	4.7	3.2	10.9	6.9	3.4
B_e (cm^{-1})	0.391	0.391	0.342	0.382	0.373
α_e (cm^{-1})	0.006	0.004	0.005	0.007	0.006
$1/\Delta'_{exp}$	54.4	9.5	9.5	27.8	12.5
$1/\Delta'_{MRD-CI}$	64.8	9.4	9.4	28.9	12.8
R_{TS}	≥ 50	8.6	9.1	—	11.9

The potential energy curves of Σ character, corresponding to calculated eigenvalues and eigenstates of A_1 and A_2 symmetry, are shown in Figure 4.8. The potential curves of Π states are shown in Figure 4.9. Spectroscopic parameters of the bound potentials are given in Table 4.19. The ground state of MgN^{2+} is $X^4\Sigma^-$. The minimum of the curve, at 4.18, bohr lies 0.49 eV below channel I products, therefore MgN^{2+} is *thermodynamically stable*. The $2^4\Sigma^-$ state is repulsive at the distances shown on the figure. However, at the distance of approximately 60 bohr the energy of the repulsive state decreases to 0.42 eV above channel I, and the avoided crossing with the flat potential of the $X^4\Sigma^-$ state occurs. The ground state acquires repulsive character and the potential curve decays hyperbolically to channel I. The $2^4\Sigma^-$ state becomes flat and dissociates to channel A. The electron configurations of both states are (neglecting all $n=1$ electrons and $2sp$ electrons of magnesium) $\dots\sigma^2\sigma\pi^2$ and $\dots\sigma^20\sigma\pi^2$. The complete configuration of the lowest state is $1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^26\sigma1\pi^42\pi^2$. The 6σ MO is essentially $2p_N$ while the 7σ is predominantly $3s_{Mg}$. The composition of the molecular orbitals at short distances confirms the ionic character of the lower state and covalent character of the upper state.

The vibration frequencies of all bound states of MgN^{2+} are similar at around $360 \pm 30 \text{ cm}^{-1}$. The equilibrium distances of those states are also similar at 4.35 ± 0.17 bohr. The differences in strength of the electrostatic interactions are less pronounced than in the second period dications. The larger effective barrier for the $1^2\Pi$ state may be attributed to double occupation of the $2p_\sigma$ orbital of the N atom, allowing for better polarization in this state. Similar arguments were used for BeF^{2+} .

Although five electronic states of MgN^{2+} have short distance minima in their potential energy curves, only three avoided crossings occur at distances shorter than the 15 bohr shown in the figures. The avoided intersection in the $2^2\Sigma^-$ states occurs at 9 bohr, in the $2^2\Sigma^+$ states at 12 bohr (see Figure 4.8) and in the $2^2\Pi$ states at 9 bohr, shown in Figure 4.9.

The ACDGP model in its simplest form considers only the avoided crossing [88] between the attractive and repulsive curves. The transition state geometry is

Figure 4.8: MRD-CI potential energy curves for low-lying states of MgN^{2+}

Figure 4.9: MRD-CI potential energy curves for low-lying states of Π symmetry of MgN^{2+}

given as $R_{TS} = \Delta^{-1}$, where R_{TS} and Δ are in atomic units. The physical description corresponds to the distance at which the e^2/r repulsion is equal to the energy of the attractive channel relative to the repulsive channel. This model is correct in the limit of small Δ and the repulsive curve strictly following the Coulomb law.

Compare the actual transition state geometries in the electronic states of MgN^{2+} with the prediction of the simple model. The values of $1/\Delta'$, derived from experimental data and MRD-CI calculations, and the geometries of the local maxima of the curves are given at the bottom of Table 4.19. The differences between the computed transition state geometries and the R_{TS} calculated from the simple model are small. The 1 bohr errors are similar to those obtained by Radom and Gill [88]. The 10 bohr difference between the $1/\Delta'_{exp}$ and $1/\Delta'_{MRD-CI}$ values arose from the 0.08 eV, (less than 2 kcal/mole) error in the Δ'_{MRD-CI} value. This shows extreme sensitivity of computed transition state geometries to the accuracy of calculated ionization potentials.

4.8 MgO^{2+}

The discussion of bound states in MgO^{2+} is straightforward because of only one possible avoided crossing, that occurs between the $X^3\Sigma^-$ and $2^3\Sigma^-$ states. The four lowest dissociation channels are listed in Table 4.20. There is only one symmetry in the table where the repulsive asymptote lies below the attractive one, namely $^3\Sigma^-$. The Δ' value of 1.41 eV for the $^3\Sigma^-$ states is low. For all other states the attractive limit lies below the repulsive one or the states correlate only with the repulsive asymptotes. The $^5\Sigma^-$ state correlates with repulsive channel I, the $^3\Pi$ state with channel A, and the $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states with channel B.

The ground state of MgO^{2+} has a local minimum at $R = 4.11$ bohr, lying *only 0.08 eV above* its dissociation products and hence MgO^{2+} is metastable. The remaining four states with potential minima at short distances are bound. The depths of minima in the $X^3\Sigma^-$ and $1^1\Delta$ states are 1.36 and 1.32 eV. The $1^3\Pi$, $1^1\Sigma^+$ and $1^1\Pi$ states have well depths around 0.4 eV. The dominant electron configurations of the bound states are given in the bottom part of the Table 4.21. The deeper potentials

Figure 4.10: MRD-CI potential energy curves for low-lying states of MgO^{2+}

Table 4.20: Correlation diagram for low lying states of MgO^{2+} .

CHANNEL	Mg	O	This work (eV)	Expt. ^{a)} (eV)	States
I	$\text{Mg}^+ \ ^2S_g$	$\text{O}^+ \ ^4S_u$	0.00	0.00	$^3\Sigma^-$
A	$\text{Mg}^{2+} \ ^1S_g$	$\text{O} \ ^3P_g$	1.49	1.41	$^3\Sigma^-, \Pi$
B	$\text{Mg}^{2+} \ ^1S_g$	$\text{O} \ ^1D_g$	3.50	3.38	$^1\Sigma^+, \Pi, \Delta$
II	$\text{Mg}^+ \ ^2S_g$	$\text{O}^+ \ ^2D_u$	4.12	4.19	$^1,^3\Sigma^-, \Pi, \Delta$

a) Values taken from C.E. Moore, *Atomic Energy Levels*

(National Bureau of Standards, Washington, D.C., 1971)

Table 4.21: Spectroscopic parameters of the metastable and bound states of MgO^{2+} .

Parameter	$X^3\Sigma^-$	$1^3\Pi$	$1^1\Delta$	$1^1\Sigma^+$	$1^1\Pi$
T_e (eV)	0.08	1.12	2.18	3.04	3.10
R_e (bohr)	4.11	4.10	4.05	4.09	4.33
D_e (eV)	-0.08	0.37	1.32	0.44	0.40
D_{eff} (eV)	1.36	0.37	1.32	0.44	0.40
ω_e (cm^{-1})	396	291	384	333	276
$\omega_e x_e$ (cm^{-1})	3.8	8.5	-1.3	2.5	6.7
B_e (cm^{-1})	0.372	0.369	0.380	0.380	0.344
α_e (cm^{-1})	0.005	0.010	0.005	0.010	0.008
Dominant configuration	$\sigma^2\sigma^2\pi^2$	$\sigma^2\sigma\pi^3$	$\sigma^2\sigma^2\pi^2$	$\sigma^2\sigma^2\pi^2$	$\sigma^2\sigma\pi^3$
				$\sigma^2\pi^4$	

correspond to the $\sigma^2\sigma^2\pi^2$ configuration, while the shallower potentials have dominant configurations with three or four π electrons. The $\sigma^2\sigma^2\pi^2$ occupation locates two electrons on the 2s orbital of the oxygen atom, two electrons on the 2p orbital *along* the axis of the molecule and two electrons perpendicularly on the $2p_{x,y}$ AO. The transfer of one or two electrons from the bond axis into the π orbital decreases the polarizability of the oxygen atom. The $1^1\Sigma^+$ state shows contributions from the most polarizable configuration $\sigma^2\sigma^2\pi^2$ and the least polarizable $\sigma^2\pi^4$. The bond lengths are similar for all states and the highest vibration frequencies, around 400 cm^{-1} , correspond to the most polarizable orientation of the O atom. The lowest frequencies, below 300 cm^{-1} are found for the least polarizable orientation. The $1^1\Sigma^+$ state has contributions from both configurations and the vibration frequency ω_e is 333 cm^{-1} .

Table 4.22: Correlation diagram for low lying states of MgF^{2+} .

CHANNEL	Mg	F	This work (eV)	Expt. ^{a)} (eV)	States
A	$\text{Mg}^{2+} \ ^1S_g$	$\text{F} \ ^2P_u$	0.00	0.00	$^2\Sigma^+, \Pi$
I	$\text{Mg}^+ \ ^2S_g$	$\text{F}^+ \ ^3P_g$	2.36	2.40	$^2,4\Sigma^-, \Pi$
II	$\text{Mg}^+ \ ^2S_g$	$\text{F}^+ \ ^1D_g$	4.98	4.99	$^2\Sigma^+, \Pi, \Delta$

a) Values taken from C.E. Moore, *Atomic Energy Levels*

(National Bureau of Standards, Washington, D.C., 1971)

Table 4.23: Spectroscopic parameters of the $X^2\Pi$ state of MgF^{2+} .

Parameter	$X^2\Pi$
T_e (eV)	-0.79
R_e (bohr)	3.98
D_e (eV)	0.79
D_{eff} (eV)	0.79
ω_e (cm^{-1})	365
$\omega_e x_e$ (cm^{-1})	5.2
B_e (cm^{-1})	0.397
α (cm^{-1})	0.007

4.9 MgF^{2+}

The dication of magnesium fluoride is isovalent with BeF^{2+} . Magnesium is easier to ionize than beryllium and the lowest dissociation channel (A) is attractive, 2.39 eV *below* the first repulsive channel (I), whereas in BeF^{2+} attractive channel A lies 0.79 eV *above* the repulsive channel (I). The next (formally) attractive channel involves the lowest Rydberg state of F at 12.5 eV. This channel has a $\text{Be}^{2+} + \text{F}^+$ character with a surrounding Rydberg electron, and is repulsive. The only electronic states arising from the attractive channel are $^2\Pi$ and $^2\Sigma^+$.

Potential energy curves for the 9 lowest electronic states of MgF^{2+} correlating with channels A, I, and II are shown in Figure 4.11. All curves except for the $X^2\Pi$ and $A^2\Sigma^+$ states are repulsive. The parameters of the only bound state of MgF^{2+} are given in Table 4.23. The lowest potential energy curve is bound and as the molecule dissociates to the attractive limit, MgF^{2+} is *thermodynamically stable* by 0.79 eV,

Figure 4.11: MRD-CI potential energy curves for low-lying states of MgF^{2+}

with the equilibrium bond distance $R_e = 3.98$ bohr. The potential curve of the $A^2\Sigma^+$ state is essentially flat, with a very shallow minimum of about 0.05 eV around 4.5 bohr.

The bond is weaker in MgF^{2+} than in BeF^{2+} because of an increase in internuclear distance that leads to a decrease in E_{ind} by a factor of $(3.98/3.09)^4 = 2.75$. The ratio of effective barriers in BeF^{2+} and MgF^{2+} is 2.63. This is another confirmation of the electrostatic bonding interactions (proportional to r^{-4}) in strongly ionic dications. The properties of MgF^{2+} are remarkably similar to BeF^{2+} with the exception of the order of dissociation limits.

4.10 Low lying electronic states of BF^{2+} and AlF^{2+}

All the molecules discussed above were characterized by relatively weak bonds (the largest $D_{eff} = 2.09$ eV) despite being described by the formally strongly bonding configurations! The best example is the $1^2\Sigma^+$ state of MgF^{2+} , with the $\sigma^2\sigma\pi^4$ configuration and only 0.05 eV stabilization. The following section shortly reviews the electronic structure of the electrostatically bound, thermodynamically stable dications and resolves the contradictions with the conclusions given in Section 3.7. The possibility of significant increase in the bond strength by means of non-electrostatic interactions is discussed and MRD-CI results on two *strongly-bound* dications BF^{2+} and AlF^{2+} are given.

General arguments

The results from previous sections show that the BeF^{2+} , MgN^{2+} , and MgF^{2+} dications are thermodynamically stable, and that BeC^{2+} , MgC^{2+} , and MgO^{2+} are kinetically stable, detectable species. The local minimum of the potential energy curve corresponds to the $metal^{2+}$ - neutral electronegative atom structure. The interaction between the ion and the neutral atom was shown to be primarily electrostatic with small indication of covalent contributions in BeC^{2+} and MgC^{2+} . In these two molecules stronger bonds (shorter R_e , larger ω_e) were present in the electronic states

with more π electrons, in the following order of increasing bond strength: $\sigma^2\sigma^2$, $\sigma^2\sigma\pi$, and $\sigma^2\pi^2$. In the remaining dications, which were studied, larger occupation of π molecular orbital led to weaker bonds. The localization of the molecular orbital on the electronegative center is responsible for the above property. In BeC^{2+} and MgC^{2+} , the π molecular orbital is predominantly the $2p$ orbital of carbon atom but still shows positive overlap with the $2p$ orbitals of Be. For comparison see the contour plot of the 1π molecular orbital in BeC, shown in Figure 3.5. The π MO is more localized on the electronegative atom in the remaining dications of the series. The orientation of the doubly occupied $2p$ orbital, with respect to the bond axis, determines the effective polarizability of the neutral atom in the molecule. The bond lengths decrease from 4.38 bohr (MgC^{2+}) to 3.98 bohr (MgF^{2+}), in line with the reduction of atomic radii from 1.72 bohr (C) to 1.36 bohr (F).

The strength of the bond in BeF^{2+} depends on the orientation of the unpaired electron on the fluorine atom with respect to the axis of the molecule, as shown in Figure 4.6. The bond in the $^2\Sigma^+$ state is very weak as indicated by a low value of D_e of 0.45 eV. Can the strength of this bond be *significantly* increased?

Consider now the addition of one electron to the BeF^{2+} molecule in the $^2\Sigma^+$ state. BeF^+ is known to be strongly bound and ionic, with $D_e = 5.83$ eV and $\mu = 3.024$ au (7.68 D) at 2.5 bohr [43]. The estimate of the dipole moment for the purely ionic configuration Be^{2+}F^- gives 10.66 Debye. The bond in BeF^+ is strongly ionic with the covalent component contributing to the decrease of the dipole moment. The increase in the dissociation energy, by a factor of 13 (from 0.45 to 5.83 eV), is a result of the change in the nature of the bond from (weak) electrostatic to (strong) ionic.

The replacement of the Be^{2+} ion by B^{2+} is equivalent to the addition of one electron along the axis of the bond into the system. Now the additional electron is not located on the F atom (Be^{2+}F^-) but on the $2s$ orbital of B^{2+} . The single electron on the $2s$ orbital can effectively overlap with the singly occupied $2p_\sigma$ orbital of fluorine, creating a σ bond between B^{2+} and F. This leads to a synergistic effect of shortening of the interatomic distance due to the formation of the covalent bond, which increases the electrostatic interactions between the (+2) charge and neutral

atom. The same arguments apply to the MgF^{2+} - AlF^{2+} pair. Possible donation of π electrons from F to B is also a bonding effect, as observed in CF^{2+} which has a remarkably short C-F bond ($R_e = 2.183$ bohr) due to the sum of bonding effects.

Senekowitsch *et. al.* state that the wavefunction of the $\text{X}^2\Sigma^+$ and $\text{A}^2\Pi$ states resembles a doubly charged C^{2+} ion interacting with neutral F at short distances. We have calculated the Mulliken charges of the ground state of CF^{2+} at $R=2.137$ bohr, equilibrium distance given in reference [82], using the GAMESS package [107] and the double-zeta polarization basis of Dunning [26]. The charge is $+1.44e$ on carbon and $+0.56e$ on fluorine, as the latter donates π electrons. A lesser π donation is expected in BF^{2+} because of the larger difference of electronegativities of the B and F compared to C and F.

The only study of the BF^{2+} and AlF^{2+} dications is due to O'Keefe [102] who calculated fluoride (F^-) affinities for a variety of molecules using Hartree-Fock method and 6-31G* basis set. The equilibrium distances for BF^{2+} and AlF^{2+} given in reference [102] are 2.22 and 2.95 bohr respectively.

BF^{2+}

The MRD-CI calculations were performed on the $^1\Sigma^+$ and $^3\Pi$ states of BF^{2+} and AlF^{2+} . The boron basis set corresponds to $6s5p2d1f$, derived analogically to the C...F basis sets. The aluminum basis set corresponds to the $12s9p/6s5p$ contraction by McLean and Chandler [30] augmented with s, p diffuse and $2d$ polarization functions with exponents $\alpha_s = 0.031$, $\alpha_p = 0.025$, and $\alpha_d = (0.6, 0.20)$ [12]. The [He] cores were frozen in BF^{2+} and [Ne] core was frozen for Al in the CI calculations. The MRD-CI(+Q) potential curves for the lowest $^1\Sigma^+$ and $^3\Pi$ states of both molecules are shown in Figure 4.12.

The parameters of the potential curves for low lying states of BF^{2+} and AlF^{2+} are given in Table 4.24. The potential curve of the $^1\Sigma^+$ state of BF^{2+} has a local minimum 5.98 eV deep, located at 2.25 bohr. The $^1\Sigma^+$ state is bound with respect to its own dissociation limit by 1.29 eV, but the minimum of the potential lies 1.30 eV above the lowest dissociation products. The Δ value for BF^{2+} is 7.73 eV and

Figure 4.12: MRD-CI potential energy curves for the $1^1\Sigma^+$ and $1^3\Pi$ states of BF^{2+} and AlF^{2+}

Table 4.24: Spectroscopic parameters of the $^1\Sigma^+$ and $^3\Pi$ states of BF^{2+} and AlF^{2+}

Species	BF^{2+}		AlF^{2+}	
Parameter	$X^3\Pi$	$1^1\Sigma^+$	$X^1\Sigma^+$	$1^3\Pi$
T_e^a (eV)	4.62	1.30	-1.70	0.93
R_e (bohr)	2.95	2.25	2.98	3.86
D_e (eV)	-4.62	1.29	3.25	-0.93
D_{eff} (eV)	0.67	5.98	3.25	0.62
ω_e (cm^{-1})	668	1811	1064	364
$\omega_e x_e$ (cm^{-1})	8.2	14.8	46.5	15.7
B_e (cm^{-1})	1.01	1.70	0.467	0.444
α_e (cm^{-1})	0.023	0.017	-0.042	0.033

^{a)} Relative to the MRD-CI(+Q) energy of -123.291461 E_H for BF^{2+} and -340.700870 E_H for AlF^{2+}

the molecule is *thermodynamically unstable despite the very strong bond*. The well depth, D_{eff} , of 5.98 eV is possibly an example of *the strongest local bond in a diatomic dication*. The bond is only 0.14 Å longer than the O-O distance in O_2^{2+} , which is the shortest bond among second period atoms.

The contour plots of the molecular orbitals were generated in order to interpret the σ bond between B^{2+} and F and the π donor properties of the F atom. The contour plots of the 3,4, and 5 σ and 1 π molecular orbitals of BF^{2+} derived from the $\sigma^2\sigma^2\pi^4$ configuration are shown in Figure 4.13. The 3 σ MO is predominantly a $2s_F$ AO polarized towards the boron atom. The electron density is partially transferred to the area between the nuclei and 3 σ MO has bonding character. The 4 σ is a $2p_{zF}$ with contributions from the 2s of boron; the 5 σ has predominant sp character on the boron atom. The 1 π orbital has mostly the $2p_{x,y}$ character from fluorine, partially delocalized towards boron. At the CI level the ground state is described by a single configuration $\sigma^2\sigma^2\pi^4$ which corresponds to the partial donation of the 2s electron of B^{2+} to the fluorine atom, and to partial back-transfer of charge via π orbitals. All three effects contribute to the bond hence the large 5.98 eV deep well.

The $X^3\Pi$ state with the $3\sigma^24\sigma^25\sigma1\pi^3$ configuration has a longer and weaker bond. The $\pi \rightarrow 5\sigma$ electron replacement from the strongly bonding configuration leads to single occupation of the nonbonding 5 σ MO and more B^+-F^+ character.

The bond length R_e for this state is 2.95 bohr, 0.70 bohr longer than in the more strongly bound $1^1\Sigma^+$ state and the barrier to dissociation decreases drastically from 5.98 to 0.67 eV.

The Mulliken populations obtained for BF^{2+} in the $1^1\Sigma^+$ state, using the GAMESS package [107] and the DZP basis of Dunning [26], attribute charges of +1.77e to boron atom and +0.23e to the fluorine atom. The transfer of charge is less pronounced than in CF^{2+} . Alternatively, one can compare the dipole moment of a (+2) charge located at $R=2.25$ bohr with the *ab initio* dipole moment computed at the same distance. The dipole moment of a (+2) charge at $R = 2.25$ bohr amounts to 4.50 au while that of two (+1) charges, one located at origin, the other at 2.25 bohr is 2.25 au. The dipole moment derived from the MRD-CI wavefunction of the $1^1\Sigma^+$ state at 2.25 bohr is 4.72 au, confirming the B^{2+}F structure of BF^{2+} . In CF^{2+} , the MR-CI dipole moment at $R=2.1$ bohr amounts to approx 6.5 D (read from the Figure 3 in reference [82]) in the center of mass coordinate system and around 10.6 D (4.2 au) after the F atom is translated to the origin. The theoretical value corresponding to the (+2) charge at 2.1 bohr is 4.2 au, confirming the $\text{B}(\text{C})^{2+} - \text{F}$ structure of both diatomic dications.

The $5\sigma \rightarrow 1\pi$ excitation from the ground state configuration results in a very pronounced change in the overall bonding character of the electronic state. The differences are significantly larger here than in the other eight electron molecules LiF , BeO , or CN^+ , where the differences in R_e values between the states with $\sigma^2\sigma^2\pi^4$ and $\sigma^2\sigma^2\sigma\pi^3$ configurations are smaller than 0.2 bohr. A similar relation also holds for CF^{2+} where the bond in the $2^2\Sigma^+$ state ($\sigma^2\sigma^2\sigma\pi^4$) is shorter and stronger than in the $2^2\Pi$ state ($\sigma^2\sigma^2\sigma^2\pi^3$). We also see that the removal of the 5σ electron from the $2^2\Sigma^+$ state ($\sigma^2\sigma^2\sigma\pi^4$) of CF^{2+} leads to a stronger bond in BF^{2+} or metastability of the isovalent trication CF^{3+} [28]. The strong bond in the $1^1\Sigma^+$ state of BF^{2+} is consistent with the findings on strong bonding in the 4-8 electron diatomic i.e. *larger occupation of the π molecular orbital leads to stronger bonds* in the diatomic with the significant π overlap.

Figure 4.13: Contour maps for MO's in BF_2^+ ($R = 2.25$ bohr), generated using the configuration $3\sigma^2 4\sigma^2 1\pi^4$ in the $^1\Sigma^+$ electronic state.

AlF²⁺

The results obtained for AlF²⁺ are qualitatively similar. The barrier to dissociation in the X¹Σ⁺ state of AlF²⁺ is smaller than that of BF²⁺ and amounts to 3.25 eV, but the lower value of $\Delta = 1.41$ eV causes the AlF²⁺ to be *thermodynamically stable* by 1.70 eV. The equilibrium distance of this state is 2.98 bohr. The $1\pi \rightarrow 5\sigma$ excitation leads to the 1³Π state, characterized by a shorter and weaker bond. The barrier to dissociation is 0.62 eV and the interatomic distance increases to 3.86 bohr. This state undergoes an avoided crossing at extended geometries, correlating with Al⁺ and F⁺. The D_e is -0.92 eV and the computed $\Delta = 1.55$ eV. The ground state of AlF²⁺ correlates with Al²⁺ + F, 1.41 eV above Al⁺ + F⁺. The bond is significantly weaker in AlF²⁺ than in BF²⁺ because of an increase in the internuclear distance, which decreases the electrostatic component of the bond and reduction of the π donation from fluorine.

4.11 Stability of dications

It was shown in the previous sections that the BeF²⁺, MgN²⁺, MgF²⁺, and AlF²⁺ dications are thermodynamically stable. The minima of all four molecules are described by single-electron configurations corresponding to the metal²⁺ - neutral fluorine structures. The Δ values vary from -2.39 eV for MgF²⁺ to +1.41 eV for AlF²⁺ and the interactions between the (+2) ion of the metal and the neutral atom are essentially electrostatic. The very deep potential well in the ¹Σ⁺ state of BF²⁺ is a result of contributions from charge induced polarization plus σ , and π bonding. The results obtained for these four new thermodynamically stable dications will be related to other theoretical studies of multiply charged molecules.

4.11.1 Electrostatic interactions in the diatomic dications

Pure electrostatic interactions are common in dications. The HeBe²⁺, NeBe²⁺, and ArBe²⁺ molecules were studied at the MP4/6-311G(2df,2pd) level by Frenking and coworkers [97]. All three dications are bound and stable by 0.87, 1.24 and 2.93 eV with respect to the Be²⁺ + noble gas dissociation limit. The bond originates from the

electrostatic interaction of the +2 charge with charge-induced dipole moments. The CNe^{2+} molecule is also described by the C^{2+}Ne structure at the metastable minimum [108]. The minimum of the ground state lies 1.94 eV above the dissociation limit and the barrier to dissociation computed at the MCSCF/5s4p2d level amounts to 1.62 eV. The authors note that Hurley's procedure [94] does not describe properly CNe^{2+} . The well depth of 5 eV at a bond distance of 2.1 bohr given in reference [74] is clearly too large as a result of assigning the strong bond of boron fluoride to the dication.

Several other dications have predominantly electrostatic bonds. SiHe^{2+} has $R_e = 4.85$ bohr while, SiNe^{2+} has a somewhat stronger bond with $D_e = 0.37$ eV [100] and $R_e = 4.40$ bohr. The bond length in BeMg^{2+} was predicted to be 4.82 bohr by Pyykko [109].

4.11.2 Strong bonds in the diatomic dications

Covalent contributions to bonding in heteronuclear dications were observed in many molecules. The comparison of bonding between the isoelectronic series was the main motivation of several studies. Radom and coworkers [84] and Pyykko [109] studied 14-electron molecules isoelectronic with N_2 . Isovalent 22-electron molecules of second-third period [100] and multiple bonds in XAr^{n+} molecules where $\text{X}=\text{B}, \text{C}, \text{N}$ and $n = 1, 2, 3$ [110] were also studied by Radom and coworkers.

The 14-electron molecules vary from van der Waals molecules, like BeNe , through strongly bound CF^+ to esoteric species like Ne_2^{6+} . Some of the species are dications and O_2^{2+} , NF^{2+} , and CNe^{2+} are metastable. The O_2^{2+} molecule has the shortest bond among all second-period diatomic molecules with an R_e of 1.98 bohr. While O_2^{2+} is thermodynamically unstable by 3.66 eV at the correlated level, the height of the barrier is quite large at 3.6 eV. Hurley's model is appropriate for the description of O_2^{2+} [111] as the molecule is described by the covalent triple " N_2 " bond. The bond in NF^{2+} is slightly longer at 2.08 bohr but still very short, and the D_e is only -0.41 eV while the $D_{eff} = 4.60$ eV. Radom and coworkers attribute the strength of the bond to the lack of antibonding 2π electrons [84].

Strong bonds were also observed in 22-electron dications [100][103]. Dissociation

barriers were calculated to be 3.47 and 3.48 eV for SO^{2+} and NCl^{2+} , respectively. The S-O bond in SO^{2+} at 2.64 bohr is the shortest bond between the second and third period atoms.

The bond becomes very strong in PF^{2+} . Fragmentation to $\text{P}^+ + \text{F}^+$ products requires 4.81 eV, making PF^{2+} another *thermodynamically stable* dication. The low value of Δ (2.31 eV) for PF^{2+} suggests the P^{2+}F structure of the molecule at the minimum with π donation from fluorine. This structure was also confirmed by calculations in reference [103]. This diatomic combines both necessary condition for stability of a dication i.e. low value of Δ coincides with the strong bond described by the $\sigma^2\sigma^2\sigma^2\pi^4$ configuration.

The wealth of data available from literature and the results of this work indicate that many (+2) charged diatomics are stable (at least kinetically) species that have strong bonds. The extreme values of shortest R_e and largest D_{eff} are $R_e = 1.99$ bohr for O_2^{2+} [84], $R_e = 2.64$ bohr for SO^{2+} [100], $D_{eff} = 5.98$ eV for BF^{2+} (this work), and $D_{eff} = 4.90$ eV for CF^{2+} [82].

4.11.3 Diatomic highly charged species

Metastability in (+3) and higher charged diatomics is less common than in dications. The significant increase in the Coulomb repulsion, from 14.4 to 28.8 eV at 1 Å, for the interaction of a (+2) with a (+1) ion, requires very strong local bonds to overcome the destabilizing effect. Most trications of the second and third period have large Δ , around 10 or more eV. Ionic structures of trications are thus less common and most bonds in tri- and higher charged cations have significant covalent components. Several molecules were found to be metastable.

The potential curves for the $^3\Phi$ states of VHe^{3+} were calculated by Pyykko [112]. The region from the local minimum of the curve at around 4.0 bohr to the avoided crossing at 13 bohr follows very closely the potential obtained from the expression for E_{ind} , confirming the V^{3+}He structure of the molecule. The other “ionic” molecule is PNe^{3+} , corresponding to P^{3+}Ne [100]. The bond length in PNe^{3+} is 3.62 bohr, the Δ of 8.62 eV is relatively low and the local minimum is 1.34 eV deep. The calculated

dissociation energy of -6.27 eV implies that the local minimum of the curve lies ($\Delta - D_e$) 2.35 eV below the $P^{3+} + Ne$ limit. The $E_{ind} = 1.90$ eV at 3.62 bohr which is in good agreement with the implicit 2.35 eV stabilization and 1.34 eV deep well.

Other trications from the 22 electron series of Radom [100] are OCl^{3+} , SF^{3+} and NAr^{3+} . All three cations have short bonds, with R_e of the local minima at 2.73, 2.71, and 2.90 bohr. OCl^{3+} and NAr^{3+} are relatively weakly bound, $D_{eff} = 0.33$ eV and 0.23 eV respectively, but SF^{3+} has a 2.11 eV (local) bond. All four trications are metastable. The D_e values vary from -6.27 to -12.26 eV.

The π bonding was observed in XAr^{3+} series [110]. The bond lengths for $X = B, C$, and N at the CASSCF/6-311G(2df) level are around 3 bohr and the metastable wells are 0.23 to 0.67 eV deep. The Mulliken population assigns the charges of +1.5e on each of the atoms, indicating a π donor bond from argon.

4.11.4 Polyatomic multiply charged cations

Several mechanism explain the stability of polyatomic multiply charged cations. Generally, a polarizable species or a σ or π donor can coordinate to the metastable or stable multiply charged atom or diatomic. The positive charge remains concentrated on one of the centers of the molecule and the attractive interactions, whether covalent or of electrostatic origin, stabilize the molecule.

Several dications were considered theoretically as acceptors in the complex. The complexes of CH_2^{2+} with F, OH, NH_2, CH_3, Cl , and SH π donors were studied by Radom and coworkers [113]. Note that the CH_2^{2+} molecule is unbound in the ground state and very short bonds to carbon were observed as a result of the interaction of the π electrons of the donor with the formally unoccupied p orbital of carbon. The C-F bond length in HCF^{2+} is 2.13 bohr and the C-Cl bond length in $HCCl^{2+}$ is 2.75 bohr at the MP3/6-311G** level.

The complexes of CH_2^{2+} with small molecules were discussed in reference [114]. For example, $CH_2NH_3^{2+}$ is unstable by 1.21 eV with respect to fragmentation to $CH_2^+ + NH_3^+$, but the dissociation is prohibited by a 3.08 eV barrier. Several similar complexes were also reported.

The properties of CH_2^{2+} as a σ and π acceptor have been investigated by Frenking *et. al.* [115] in complexes with closed shell molecules. The carbon atom in the CH_2^{2+} dication is sp hybridized and the dication is linear. The donation of the lone pair from the donor to one of the p orbitals of carbon leads to rehybridization of C from sp to sp^2 . The complexes $\text{CH}_2\text{FH}^{2+}$, $\text{CH}_2\text{OH}_2^{2+}$, $\text{CH}_2\text{NH}_3^{2+}$ are Y shaped. Note that diatomic CF^{2+} can be interpreted as the strong complex of the π acceptor C^{2+} with the π donor F.

The other option is to delocalize the positive charge or to increase the distance between the charged centers in a molecule. The Coulomb repulsion between the charges decreases as e^2/r upon spatial separation and as $\sum (k/n)^2 r_{ab}^{-1}$ upon delocalization of charge k on n centers located at the distances r_{ab} . For example, the total repulsion between two (+1) charges separated by 1 Å equals 14.4 eV while the repulsion between six (+1/3) charges located on the corners of a hexagon of the same size is 3.14 eV larger! The stabilization by delocalization *must be accompanied by an increase in the size of the system*. However, the existence of resonant structures should in general lead to contraction of the bonds and the bond lengthening may not be observable.

A large group of experimentally observed stable organic carbocations has been reviewed by Prakash [116]. These species can be loosely divided into the structures characterized by spatial separation of charges and by delocalized ring structures. Both classes of molecules are already stabilized by a relatively rigid framework of carbon-carbon bonds. For example in 1,4-diisopropylbenzene dication, reported in reference [116] the (+1) charges are separated by about 5.7 Å by two C-C bonds and a phenyl group. At this distance the repulsion between the charges is only 2.5 eV.

Aromatic carbocations have also been observed. Cyclobutadiene(+2) and its derivatives are aromatic. The (+2) charge can also be delocalized over larger spaces. In the [16]annulene dication, the charge is spread over 16 carbon atoms (structure 48) while in C_{60}^{2+} 20 equatorial atoms become equivalent [117].

Boyd *et. al.* [118] and Boldyrev and Simons [98] studied the multiple protonation of stable hydrides HF, H_2O , H_2S , and HCl. H_4O^{2+} and H_4S^{2+} are tetrahedral,

with the total (+2) charge distributed over four H centers. Metastable H_3F^{2+} and H_3Cl^{2+} are planar and pyramidal, respectively. H_4Cl^{3+} is nearly metastable since the potential barrier to dissociation is slightly smaller than the ZPE correction. The authors predict H_4I^{3+} to be metastable based on the size of I atom compared to Cl.

Another delocalization option is formation of an inorganic ring. $\text{S}_3\text{N}_2^{2+}$ in a pentagonal (+2) charged ring structure is metastable [119], with the relatively small local barrier to dissociation to SNS^+ and NS^+ of 0.85 eV. A stable salt of this dication, $[\text{S}_3\text{N}_2^{2+} (\text{AsF}_6^-)_2]$ has been synthesized [120] despite relatively high-lying local minimum ($D_e = -4.13$ eV).

The metastable diatomic dications can be stabilized by increasing the electron density *between* the ions. The metastable ground state of Be_2^{2+} is described by the σ_g^2 configuration. The single "H₂-like" bond provides efficient screening of the (+1) charge of the Be^+ ions. The insertion of the H atoms into the Be-Be bond in Be_2^{2+} , leads to bridged structures $\text{BeH}_n\text{Be}^{2+}$ [121]. The single electron of each hydrogen atom participates in a one-electron three-center bond. The three-center MO has π (bonding) character and the Be-Be distances are 3.92 bohr in BeHBe^{2+} , 3.74 bohr in $\text{BeH}_2\text{Be}^{2+}$, and 3.65 bohr in $\text{BeH}_3\text{Be}^{2+}$. For comparison, the R_e in Be_2^{2+} equals 4.02 bohr and the bond shortens by 0.37 bohr upon the creation of three " π -like" bonds.

The metastability of polyatomic cations is very common. The large number of degrees of freedom allows for a better accommodation of the positive charge on the molecule by a multitude of specific mechanisms. A rigid framework of covalent bonds existing in the larger molecules is also a stabilizing effect.

Chapter 5

Concluding remarks

The results of this work and vast amount of available data from the literature allow for the generalization of the findings on multiply charged molecules. The focus of the next sections will be on predicting the thermodynamic stability of the positively charged di- and polyatomic species. Section 5.2 will be devoted to the implications of stability of charged molecules for energy storage and the possibility of existence of unusual molecular structures based on (meta)stable diatomic dications. Several arguments, already given in previous chapters may be repeated here for completeness.

5.1 Predicting thermodynamic stability of multiply charged ions

5.1.1 Diatomic dications

Most of the diatomic dications are kinetically stable. The existence of the metastable potential minimum can be explained using the ACDCP or covalent bonding model of Hurley. The tunneling lifetimes of the quasi-bound vibrational levels are usually large because of the large mass of the molecule and the width of the potential barrier. Thermodynamic stability is less common, but several molecules were reported in the literature and in this thesis. All thermodynamically stable dications have low values of Δ and stability is restricted to heteronuclear molecules.

There are two possible orders in the dissociation limits, corresponding to negative and positive values of Δ . When Δ is negative, the asymptotic structure $X^{2+} + Y$ is preserved at short X-Y distances. Polarization of Y by X^{2+} leads to electrostatic

bonds where XY^{2+} lies lower than $X^{2+} + Y$ on the energy scale and the molecule is thermodynamically stable. Additional bonding effects (formation of the covalent bond, charge transfer, coordinative bond) only increase the strength of the bond. All negative Δ dications are or are predicted to be thermodynamically stable.

The molecules dissociating to $X^+ + Y^+$ have positive Δ . These systems can be divided into homo- and heteronuclear molecules. At the local minimum the electronic structure of the homonuclear dication is that of a covalent bond between X^+ and X^+ (Hurley's model). The potential of the dication is represented as a difference of the e^2/r repulsion and scaled potential of the isoelectronic neutral species. The C-O bond in CO is the strongest bond among two atoms with $D_0 = 11.11$ eV at $R_e = 2.13$ bohr [20]. However, at the same distance e^2/r amounts to 12.77 eV and the subtraction of the CO potential from e^2/r leads to a metastable well. The scaling of the potential according to formula 4.1 increases the depth of the subtracted potential and shifts its minimum towards shorter R . Assuming $t = 1.125$ in formula 4.1 [94], the R_e of the dications shortens to 1.89 bohr and the depth of the scaled potential is 14.1 eV. At a distance of 1.89 bohr, the e^2/r repulsion increases to 14.4 eV and the homonuclear diatomic dication can not be thermodynamically stable. However, the bond between two monocations is strong enough to cause metastability of most homonuclear diatomic dications.

The attractive channel lies above the repulsive one in most heteronuclear diatomic dications. The molecule will be thermodynamically stable if the minimum of the diabatic curve corresponding to the attractive channel lies below the lowest possible dissociation limit, i.e $D'_e \leq \Delta$. A reliable predictor for thermodynamic stability depends on the estimation of the bonding interactions in the attractive channel. The charge induced polarization will always occur but the expression $E_{ind} = -1/2\alpha q^2 r^{-4}$ overestimates the true interaction energy. This expression applies only to such cases where charges are well separated, since the polarizability of the partially charged atom is generally unknown.

Additional bonding effects may occur between X^{x+} and Y^{y+} where $x+y=2$. For x larger than (+2), the bond has an additional ionic component while for $1 < x < 2$

and $0 < y < 1$ a covalent polarized bond may form in both attractive and repulsive channels. The adiabatic electron wavefunction will have contributions from both $X^{2+} + Y$ and $X^+ + Y^+$ components and such is the case in CO^{2+} [83].

The *a priori* estimation of the bonding interactions requires reliable estimation of charge transfer at short distances, which is generally difficult. Estimation of bonding in both channels in the case of partial charges of the ions is also a difficult task.

The ACDCP and Hurley's models are qualitatively and quantitatively correct for the limiting cases of purely ionic (ACDCP) and purely covalent (Hurley) molecules. The covalent bonding model has been recently extended[122] by explicitly considering induction effects in the repulsive channel, i.e. polarization of X^+ by X^+ . Also, the validity of the model has been demonstrated for excited states of homonuclear diatomic dication. The ACDCP model is more general than Hurley's in that it can predict the transition state geometries for covalent dications. However the formation of the bond in both channels is neglected and Senekowitsch and coworkers suggest that unphysically large [122] diabatic coupling between two electrostatic potentials is responsible for the strong interactions between the "attractive" and "repulsive" states at short distances. The ACDCP model can not predict the depths and locations of the potential minima for large Δ cases due to the neglect of the abovementioned bond formation. For intermediate species, which cover most of chemistry, it is difficult to estimate the bonding in a reliable and consistent way. In particular, it is difficult to determine the limiting value of Δ , separating the "ionic" (ACDCP) from "covalent" (Hurley) bonding. It is clear, however, that all the dications studied in this thesis, with Δ up to 8 eV, are the ACDCP cases. The value of Δ indicates the extent of "ionic" effects but the *ab initio* calculations are the best methods to establish stability and structure of a diatomic dication. However, it can be concluded that the low value or negative value of Δ is a necessary condition for thermodynamic stability of a diatomic dication. This necessary condition seems to have priority over the strength of the bonding effects in the attractive channel.

So far the thermodynamic stability of diatomic dication has been established

for several dications of second and third period. The summary is given in Table 5.1, together with the qualitative predictions of new stable species.

The value of Δ does not exceed 3 eV for the above list of molecules. It is thus quite likely, although not certain, that the only remaining candidates for thermodynamic stability are the unstudied dications from Table 4.6, i.e. SiN^{2+} , SiO^{2+} , SiF^{2+} , MgCl^{2+} , and the neon-third period atom diatomics (last row from Table 4.5). These molecules are currently being investigated. The less explored area comprises the transition metal and fourth period compounds. The "low Δ " rule suggests that the thermodynamic stability should be common among these species because of the decreasing ionization potentials.

5.1.2 Diatomic multiply charged ions

Following the arguments from the previous section, a diatomic trication with negative Δ should be stable. There are no negative values of Δ among second and third row species, but yttrium, zirconium and several lanthanides and actinides have $\text{IP}_3 \leq 24.59$ eV, which is the first ionization potential of helium. Consequently, the lowest dissociation channel has attractive character for YHe^{3+} and ZrHe^{3+} and these species should be thermodynamically stable.

The thermodynamic stability of the covalent trications formed by a chemical bond between a (+2) and a (+1) ion can be excluded based on the twofold increase in the Coulomb repulsion, but no possibility of increasing the bonding interactions compared to carbon monoxide (CO). Hence, the only possible candidates for absolute stability are low Δ species and among second and third row trications only AlHe^{3+} , PHe^{3+} , SiHe^{3+} , AlNe^{3+} and PNe^{3+} have Δ smaller than 10 eV. However, helium and neon atoms are not particularly polarizable and E_{ind} values for (+3)-He interaction at $R = 3.0$ bohr is 2.09 eV and for the polarization of the neon atom by a (+3) charge at $R=4.0$ bohr, $E_{\text{ind}} = 1.28$ eV. Electrostatic attraction can not overcome the Δ difference and the minima of the potential curves will lie above the $\text{X}^{2+} + \text{Ne}^+$ products. The thermodynamic stability of a diatomic trication is even more restricted than in the (+2) charged species.

Table 5.1: Known and predicted thermodynamically stable diatomic dications of second and third period.

Noble gas species			
Molecule	Δ (eV)	$D_e^{a)}$ (eV)	reference
BeNe ²⁺	< 0	1.24	[97]
MgNe ²⁺	< 0	stable	
AlNe ²⁺	< 0	stable	
SiNe ²⁺	< 0	0.37	[100]
NeP ²⁺	< 0	stable	
NeS ²⁺	1.77	possibly stable	
NeCl ²⁺	2.25	possibly stable	
BeAr ²⁺	2.45	0.48	[97]
MgAr ²⁺	< 0	stable	
SiAr ²⁺	0.59	possibly stable	
Non-noble gas species			
Molecule	Δ (eV)	$D_e^{a)}$ (eV)	reference
BeF ²⁺	0.79	1.08	This work
MgN ²⁺	0.51	0.49	This work
MgO ²⁺	1.42	-0.08 ^{b)}	This work
MgF ²⁺	< 0	0.79	This work
MgCl ²⁺	2.07	possibly stable	
AlF ²⁺	1.41	1.70	This work
SiN ²⁺	1.82	possibly stable	
SiO ²⁺	2.73	possibly stable	
SiF ²⁺	< 0	stable	
PF ²⁺	2.31	4.81	[100]

^{a)} Reported dissociation energy for known species,
qualitative prediction for unknown

^{b)} stable within the conservative
error estimate of current calculations of 0.15 eV

Table 5.2: Possible dissociation products for XYZ^{2+} dication.

3 atoms	molecule + atom	
$X^+ + Y^+ + Z$	$XY + Z^{2+}$	(I)
$X + Y^+ + Z^+$	$XZ + Y^{2+}$	(I)
$X^+ + Y + Z^+$	$YZ + X^{2+}$	(I)
$X^{2+} + Y + Z$	$XY^{2+} + Z$	(II)
$X + Y^{2+} + Z$	$XZ^{2+} + Y$	(II)
$X + Y + Z^{2+}$	$YZ^{2+} + X$	(II)
	$XY^+ + Z^+$	(III)
	$XZ^+ + Y^+$	(III)
	$YZ^+ + X^+$	(III)

5.1.3 Polyatomic molecules

The thermodynamic stability of a polyatomic dication is a distinct possibility. The potential surface for a XYZ^{2+} molecule is significantly more complicated than the surface for a diatomic dication system that can be fragmented in only 3 possible ways ($X^+ + Y^+$, $X^{2+} + Y$, and $X + Y^{2+}$; very high lying channels like $X^{3+} + Y^-$ are excluded). One of the goals of the thesis was the search for thermodynamic stability in charged species hence the discussion will be limited to those features of the XYZ^{2+} hypersurface that is relevant to this topic.

A triatomic dication XYZ^{2+} is thermodynamically stable when its total energy is lower than the total energy of any of the possible dissociation products. Table 5.2 shows all possible fragments. The dissociation channel consisting of three atoms (ions) *always* lies higher than the molecule + atom channel, because XY is always more stable than $X + Y$ (at least van der Waals interaction) and XY^+ always lies lower than $X + Y^+$ or $X^+ + Y$ (charge induced polarization). Finally, XY^{2+} lies either below $X^+ + Y^+$, $X^{2+} + Y$, and $X + Y^{2+}$ when XY^{2+} is thermodynamically stable or above $X^+ + Y^+$ when it is not. In this case XY^{2+} dissociates towards lower X^+ and Y^+ and the combinations $XZ^+ + Y$ and $YZ^+ + X$ lie lower than $X^+ + Y^+ + Z$.

We can concentrate now on the molecule + atom fragmentation. These dis-

sociation limits can be divided into three possible structures: neutral diatomic + atomic dication (**I**), diatomic dication + neutral atom (**II**), and diatomic monocation + atomic monocation (**III**).

Consider now the energy of each of nine possible combinations given in Table 5.2 relative to the ground state of three separated atoms $X + Y + Z$, neglecting the correlation of the spin and symmetry of the electronic states. The lowest energy of each of the structures **I**, **II**, and **III** are given by:

$$\text{I} \quad A = \min(\text{IP}_{1,2}(Z) - D_e(XY), \text{IP}_{1,2}(Y) - D_e(XZ), \text{IP}_{1,2}(X) - D_e(YZ))$$

$$\text{II} \quad B = \min(\text{IP}_{1,2}(XY) - D_e(XY), \text{IP}_{1,2}(XZ) - D_e(XZ), \text{IP}_{1,2}(YZ) - D_e(YZ))$$

$$\text{III} \quad C = \min(\text{IP}_1(Z) + \text{IP}_1(XY) - D_e(XY), \text{IP}_1(Y) + \text{IP}_1(XZ) - D_e(XZ), \text{IP}_1(X) + \text{IP}_1(YZ) - D_e(YZ))$$

The values of A , B , and C depend only on the ionization potentials of atoms, available from reference [29], dissociation energies of the neutral diatomics, generally available from reference [20], and ionization potentials of diatomics. These values are known for a variety of molecules but are not as available as the previous parameters.

If A is smaller than B and C , the lowest dissociation limit is a $(+2)$ ion of the atom and a neutral molecule. A bonding interaction will occur between the $(+2)$ ion and a polarizable neutral molecule in analogy to the diatomic dication with negative Δ . Thermodynamic stability of XYZ^{2+} is essentially guaranteed.

A similar interaction is expected for molecules in which B is smaller than A and C . The XYZ^{2+} is expected now to be thermodynamically stable as a complex of X^{2+} with Z . For example, He_2C^{2+} is thermodynamically stable [97] and HeBeNe^{2+} is bound with respect to $\text{BeNe}^{2+} + \text{He}$ by 0.8 eV at the SCF level [28].

The third most common case corresponds to the dissociation into the singly charged atom and molecule. An example related to the species studied in this thesis is BeF_2^{2+} , dissociating into $\text{BeF}^+ + \text{F}^+$ which lies 20.91 eV above $\text{Be} + \text{F} + \text{F}$. $\text{BeF}_2^{2+} + \text{F}$ lies 25.66 eV above $\text{Be} + \text{F} + \text{F}$. Now, BeF_2^{2+} may be thermodynamically stable if the fluorine affinity of BeF^{2+} is greater than 4.75 eV. The energy difference between the two dissociation limits $\Delta E = E(\text{BeF}_2^{2+}) + E(\text{F}) - (E(\text{BeF}^+) + E(\text{F})) = \text{IP}(\text{BeF}^+)$

- $IP(F)$ is an equivalent of Radom's Δ for a diatomic molecule. The low value of the ΔE (or A or B being lower than C) *seems to be a necessary condition for the thermodynamic stability of the (+2) charged triatomic*. The structures ($X^{2+}YZ$ or $XY^{2+}Z$) are more likely to be thermodynamically stable than the separated charges X^+Y^+Z or X^+YZ^+ .

Generally, the extent of charge transfer between three atoms is even more difficult to predict reliably than in diatomics and theoretical methods are very useful in the investigations of these systems.

The fragmentation of the larger polyatomics may be considered in analogy to the arguments shown for triatomics, i.e. the most important dissociation products of a pentaatomic molecule are a diatomic and a triatomic. However, the number of possibilities increases exponentially and complete correlation of all isomers with all dissociation products quickly becomes impractical. Appropriate use of "chemical knowledge" becomes essential in distinguishing the important and unimportant fragmentation channels.

5.2 High Energy Density Materials and unusual molecular structures

5.2.1 Energy content of diatomic dications

Several authors pointed to the possible application of metastable dications as energy reservoirs [111][79][98]. The amount of kinetic energy that can be released from a diatomic dication can be as high as 9 eV, the dissociation energy D_e of He_2^{2+} [79]. The amount of electronic energy stored in the double ionization of any species is limited by the value of 75 eV, $IP_1 + IP_2$ for helium, which is the highest double ionization potential for any atom. It was proposed that the large amount of kinetic energy ($XY^{2+} \rightarrow X^+ + Y^+$) can be released by exciting the quasi-bound vibrational level above the potential barrier [79]. The ionization energy ($XY^{2+} + 2e \rightarrow XY$) can be released by transferring electrons from neighbouring atoms or ions [98].

Following a study of energetics of the reaction of He_2^{2+} dication with small ions and molecules by Nicolaides [79], consider the theoretical amount of energy stored

in the four-atom system composed of two helium and two hydrogen atoms. On the thermodynamical scale the zero corresponds to two helium atoms and a hydrogen molecule. The creation of the $\text{He}_2^{2+} + 2\text{H}^-$ requires $2 \times \text{IP}_1(\text{He}) - D_0(\text{He}_2^{2+}) + D_0(\text{H}_2) - 2 \times \text{EA}(\text{H})$ for a total of 61.2 eV. Thus the reaction $\text{He}_2^{2+} + 2\text{H}^- \rightarrow 2\text{He} + \text{H}_2$ is exothermic by 1411 kcal/mole, e.g. 590 MJ/kg. This value is *47 times larger* than the 12.56 MJ/kg released in the benchmark reaction $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ (liquid hydrogen - liquid oxygen) [123].

The charged species can not be stored in high concentration due to the internal Coulomb repulsion between the ions. If positively charged ions could be stored we would already have a “perfect” energy reservoir, for example in the form of Be^{2+} ions. Neutralization of Be^{2+} to form Be releases 27.5 eV (295 MJ/kg), approximately 25 times more than the liquid hydrogen - liquid oxygen system. However, stabilization of the Be^{2+} ion by neutralization of the charge causes the Be^{2+} compounds to become stable solids with no energy content, for example BeO.

To illustrate the energetics of (and the differences between) atomic and molecular dications consider the formation of solid BeO and a hypothetical analog He_2O . BeO is a white crystalline substance, and obviously not a high energy content material. Formation of solid BeO according to the Haber-Born process requires several steps. Energy gain or loss with respect to solid beryllium and gaseous O_2 will be given in parentheses. All energy values are taken from reference [40] unless otherwise indicated. Solid BeO is formed by vaporizing solid Be (+3.36 eV), dissociating O_2 ($1/2 \times 5.16$ eV), ionizing $\text{Be} \rightarrow \text{Be}^{2+}$ (+9.32 eV, +18.211 eV), associating two electrons to one oxygen atom, (-1.46 eV for the $\text{O} \rightarrow \text{O}^-$, +9.1 eV for $\text{O}^- \rightarrow \text{O}^{2-}$). Be^{2+} and O^{2-} lie 41.11 eV above the zero of the thermochemical scale. The fact that BeO is stable implies that the lattice energy is larger than 41.11 eV.

In a simple electrostatic model the total lattice energy is approximated by the Madelung energy U [124]:

$$U = 0.9Mq_1q_2r^{-1} \quad (5.1)$$

where M is the Madelung constant, q_1 and q_2 are the charges of the ions, r is the

smallest distance between two ions of opposite charges, and 0.9 is the value of the Born parameter, accounting for Pauli repulsion at short distance, as proposed by Kittel [124].

Several assumptions have to be made: Crystalline BeO is hexagonal and the value of the Madelung constant depends on the details of the lattice parameters. We will use a Madelung constant of 1.55, similar to 1.4985 and 1.64132 characterizing hexagonal ZnO and ZnS. The sum of ionic radii of Be^{2+} (0.35 Å) and O^{2-} (1.32 Å) [40] will be used as r . The Madelung energy for BeO obtained from equation 5.1 is 48.11 eV. The heat of formation of BeO is estimated to be 7 eV per molecule, which is close to the experimental value of 6.32 eV [40].

We have just proven an obvious fact that BeO is a stable solid(!), but we can now use the same method to discuss the stabilization in the ionic $\text{He}_2^{2+} \text{O}^{2-}$ system. Separated He_2^{2+} and O^{2-} lie 68.3 eV above $2\text{He} + 1/2\text{O}_2$. We will use the same hexagonal crystalline structure for the hypothetical He_2O with $M=1.55$. The reasonable choice of the distance between the ions is the sum of the O^{2-} radius of 2.49 bohr and the radius of 0.75 bohr, which is slightly more than $1/2 R_e$ of He_2^{2+} . The Madelung energy is now 46.9 eV and the hypothetical solid lies 21.4 eV above $2\text{He} + 1/2\text{O}_2$.

This result has to be interpreted in two ways. The first is that the $\text{He}_2^{2+}\text{O}^{2-}$ is not a stable system and decays to $2\text{He} + 1/2\text{O}_2$. However, the importance of this result is that *there is still an enormous amount of energy stored in the neutral system*, while the metal analog BeO, of the same charge and mass, is stable. Note that the distance between the He_2^{2+} and O^{2-} was chosen to be as small as possible, which maximizes the Madelung energy. Consequently larger separation of charges decreases the electrostatic stabilization of the crystal and the energy content increases.

The question whether the “remaining” 20 or more eV can be stabilized is open and of interest to experimentalists and theoreticians. The most obvious, intensively studied solution is that of trapping the active energetic species in light, rigid, nonpolarizable and nonreactive matrices... but the discussion of this topic is well beyond the scope of this work.

Thermodynamically stable dications are *less likely* to have high energy content

because of two complementary reasons. The amount of kinetic energy is by definition negative and the thermodynamically stable dications contain at least one easy to ionize atom. For example the thermodynamically stable BeF^{2+} lies approximately 26 eV above $\text{Be} + 1/2\text{F}_2$, while the lattice energies for (+2) (-2) ionic crystals are on the order of 30 to 40 eV. Thus, the metastable dications like He_2^{2+} or F_2^{2+} are more suitable for the energy storage, but generally will be more difficult to trap than the thermodynamically stable ones.

The smaller energy content and larger stability of thermodynamically stable dications may lead to several groups of novel compounds. One such group implicitly proposed above are the salts of thermodynamically stable dications with negative ions. The successful synthesis of $[\text{S}_3\text{N}_2^{2+}][(\text{AsF}_6^-)_2]$ [120] confirms that a polyatomic cation with larger than (+1) charge can be stable in the condensed phase. The natural suggestion is that the thermodynamically stable dication can remain in the molecular form in the crystal and occupy a single site like a large atom with a (+2) charge. The other group discussed below are the Rydberg states of small molecules.

5.2.2 Rydberg states of charged species

Rydberg molecules are molecular species which are unstable in the ground electronic state but have a series of bound excited states of Rydberg (atomic) character [125], for example H_3 , NeH , FH_2 . Many molecules that are bound in their ground electronic states (for example HF) have bound excited states of Rydberg character, that can also be described by a singly ionized core ("parent") with an electron occupying the Rydberg atom-like orbital. In several systems a neutral Rydberg molecule can attach another electron to create a generally metastable double-Rydberg molecular anion [126].

The existence of the bound parent core is a prerequisite for the existence of Rydberg states. Metastable and thermodynamically stable dications fulfill this requirement. This suggests the existence of Rydberg states of positively singly charged ions that have (meta)stable dications. For example, the $2s_{\text{Be}} \rightarrow ns_{\text{Be}}$ excitation from the ground state of bound BeNe^{2+} should lead to Rydberg states of the monopositive

ion as BeNe^{2+} is relatively well bound.

The best parents for Rydberg states are the species with completely filled $n = 1, 2, 3$ shells, e.g. 2 electron (H_3^+), 10 electron (NeH^+), 18 electron (ArH^+) etc. When the parent molecule is not a closed species, one or more of the valence orbitals is unoccupied and the excitation from the ground state configuration leads to both (repulsive) valence and (bound) Rydberg excited states that generally interact and the bound potentials become perturbed. Hence, the best parents for the Rydberg states of the monocations are the 2, 10 etc electron dications. For example, several of the lowest diabatic Rydberg states of He_2^+ were analyzed by Metropoulos [127]. Significant contribution of Rydberg character were also seen in the excited states of Be_2^+ [50]. Rydberg states of the ethane monocation C_2H_6^+ were also discussed by Richartz *et. al.* [128]

Double-Rydberg neutral species may exist under similar conditions. When the (+2) charged parent is valence saturated, both electrons may occupy the Rydberg orbitals. The energy of the double excitation of the (*valence orbital*)² $\rightarrow$ (*Rydberg orbital*)² is larger than the ionization potential for the ejection of the electron from the valence orbital. Hence, the double Rydberg state of the neutral molecule will lie higher than the singly ionized molecule. However, the possible structure of the molecule is that of a bound and stable core and two surrounding Rydberg electrons. The stability of this double Rydberg state depends on the stability of the Rydberg electrons with respect to autodetachment. The arguments from reference [126] imply that some of these states could be long-lived and experimentally detectable. Also, there is no apparent reason why these arguments should not hold for the Rydberg states with the underlying metastable or stable (+3) charged core, i.e double Rydberg states of monocations.

5.3 Summary

Several important points emerge from this study.

- Several new molecules BeC , BeC^+ , BeC^{2+} , BeF^{2+} , MgC^{2+} , MgN^{2+} , MgO^{2+} , MgF^{2+} , BF^{2+} , and AlF^{2+} have been characterized. Most of the species are new and the reported parameters should be helpful in the experimental determinations.
- The phenomenon of strongly bound doubly excited states (SBDES), established for the homonuclear diatomic with 4 to 8 valence electrons, is also observed in polarized heteronuclear diatomics BeC and BeC^{2+} .
- The strongest bonds among all covalent and polarized species corresponds to the highest occupation of the π molecular orbitals. This was shown for BeC , BeC^{2+} , MgC^{2+} , BF^{2+} , and AlF^{2+} .
- The strongest bonds in the predominantly electrostatic complexes correspond to the most polarizable orientation of the neutral atom. This was shown in BeF^{2+} , MgN^{2+} , MgO^{2+} , and MgF^{2+} .
- BeF^{2+} , MgN^{2+} , MgF^{2+} , and AlF^{2+} are predicted to be new thermodynamically stable diatomic dications.
- The 6 eV deep potential well in the PEC of the $1^1\Sigma^+$ state of BF^{2+} is the strongest bond known for any dication. This caused by a synergistic combination of bonding effects: polarization of neutral species by a (+2) charge, σ and π bonding.
- The ACDGP treatment of multiply charged diatomics is more general than Hurley's model. The Hurley model gives accurate potential curves for homonuclear dications. The ACDGP model is quantitatively correct for highly ionic dications, and gives a reasonable description of the molecules with large degree of covalency.

- The neutralization of the positive charge of a multiply charged ion *does not necessarily lead to the loss of high energy content.*
- Arguments were given for the existence of novel crystalline compounds in condensed and gas phases. Thermodynamically stable dications may form crystals with stable molecular anions. The double Rydberg states of neutral molecules may be observable.

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Appendix A

Symbols, units and abbreviations

A.1 Commonly used abbreviations

ACDCP	Avoided Crossing with Diabatic Coupling and Polarization
AO	Atomic Orbital
CASSCF	Complete Active Space Self Consistent Field
CI	Configuration Interaction
F-CI	Full Configuration Interaction
$IP_n(X)$	n-th Ionization Potential of atom X
MCSCF	MultiConfiguration Self Consistent Field
MO	Molecular Orbital
MP2	Second order Moller-Plesset perturbation theory
MP3	Third order Moller-Plesset perturbation theory
MP4	Fourth order Moller-Plesset perturbation theory
MR-CI	MultiReference Configuration Interaction
MRD-CI	MultiReference singles and Doubles Configuration Interaction
MRD-CI(+Q)	MultiReference singles and Doubles Configuration Interaction energy corrected with generalized Davidson correction
NO	Natural Orbital
PEC	Potential Energy Curve
ROHF	Restricted Open shell Hartree Fock
SB	Strongly Bonding
SBDES	Strongly Bound Doubly Excited States
SCF	Self Consistent Field
SDCI	Singles and Doubles Configuration Interaction
STO	Slater Type Orbital
T	Selection Threshold

A.2 Variables, constants and conversion factors

1 Å	=	1×10^{-10} m
1 bohr	=	0.529177 Å
1 hartree	=	27.2116 eV
1 eV	=	23.06 kcal/mole
1 kcal/mole	=	4.184 kJ/mole
1 eV	=	8065.48 cm^{-1}
T_e		term energy
E_{ind}		energy of the charge induced dipole moment interaction
D_{eff}		effective dissociation energy, barrier height
R_{TS}		location of Transition State
μ		dipole moment or reduced mass
Δ		energy difference between the lowest attractive and the lowest repulsive channels in ACDCP model
Δ'		energy difference between the attractive and repulsive channels of the same symmetry in ACDCP model
R_e		equilibrium bond distance
D_e		dissociation energy
ZPE		Zero Point Energy
D_0		$D_e - \text{ZPE}$
$E_{v,j}$		energy of the v, J level of a diatomic
ω_e		harmonic frequency of a diatomic
$\omega_e x_e$		anharmonic frequency
B_e		rotational constant
α_e		vibrotational coupling constant
α		static polarizability
v		vibrational level
J		rotational level
$q_{v'v''}$		Franck-Condon Factor
$S_{v'v''}$		band strength
$f_{v'v''}$		absorption oscillator strength
$A_{v'v''}$		Einstein coefficient of spontaneous emission
τ		lifetime
q		charge
r		internuclear distance
H		Hamilton operator
Ψ		electronic wavefunction
ϕ		basis set function
a_j		CI coefficient

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