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Relative Stability of Hydrogen Rings

by

C. A. Di Labio, B.Sc.

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

Department of Chemistry

Carleton University

Ottawa, Ontario

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Abstract

Hydrogen rings in the D_{nh} point groups are studied using the MRD-CI and GAUSSIAN-90 package programs. These rings include H_3^+ , H_4 , H_5^+ , H_6 , H_7^+ , and H_8 . One other conformation of H_8 is examined: the cubic species having O_h symmetry. Absolute energies and equilibrium internuclear distances are reported and compared with other inorganic rings. All rings, with the exception of H_3^+ , are unstable with respect to their dissociation products. Molecules having $4n + 2$ electrons follow the general trend of being relatively stable. These are the H_5^+ , H_6 , and H_7^+ rings. Molecules not having $4n + 2$ electrons (H_4 , H_5^+ , and both H_8 species) are highly unstable. The utility of Hückel molecular orbital theory and the $4n + 2$ rule, as applied to these systems, is examined through the analysis of predictions made by HMO and the thermochemistry of the hydrogen rings. Earlier works predicting that the square H_4 species violates Hund's multiplicity rule are reviewed. It is found that H_4 does not violate this rule and a restatement of Hund's rule for molecules is offered.

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Common Abbreviations

- AO** -Atomic orbital.
BO -Bond order.
CAS -Complete active space.
CC -Coupled-cluster.
CI -Configuration interaction.
CI-SD -Configuation interaction with single and double excitations.
D_e -Dissociation energy.
DZ, DZP, TZ -Double-zeta, double-zeta plus polarization, triple zeta.
EA -Electron affinity.
E_(corr) -Correlation energy.
E_(min) -Minimum energy.
FCI -Full configuration interaction.
GTO -Gaussian-type orbital.
HMO -Hückel molecular orbital theory.
HOMO -Highest occupied molecular orbital.
LCAO -Linear combination of atomic orbitals.
MO -Molecular orbital.
MP2, MP4 -Moller-Plesset perturbation theory, second and fourth order.
MPPT -Moller-Plesset perturbation theory.
MRD-CI, MR-CI, MR-CI(+Q) -multi-reference, single and double configuration interaction. +Q refers to the inclusion of Davidson correction.
ω_e -Harmonic vibrational frequency.
PA -Proton affinity.
PT -Perturbation theory.
R_e -Equilibrium internuclear distance.
RSPT -Rayleigh-Schrödinger perturbation theory.
SALC -Symmetry adapted linear combination of atomic orbitals.
SCF -Self-consistent field.

Chapter 1

Introduction

Ab initio methods are powerful tools used for predicting the properties like equilibrium geometries, vibrational frequencies, and thermochemical stabilities of species not yet experimentally observed because of their low stability or a lack of appropriate methods for synthesis.

In the past few years, there has been a surge of interest in the detection and characterization of small molecular clusters. Metal clusters, like $\text{Li}_{(n)}$, $\text{Be}_{(n)}$ and others, have attracted considerable attention on account of their interest as models for crystals, point defects, and chemisorption. Other non-metallic clusters, such as rings of N_4 , N_6 , and N_8 are of considerable interest owing to the fact that these may be metastable and of potential use as novel, high energy fuels for rockets. Octaazacubane has been predicted to be metastable. In other words, it has a local energy minimum on its potential energy surface that lies above its dissociation products. This species has not yet been observed experimentally [1].

One of the earlier works in exploring the possible existence of new ring compounds was that of J.S. Wright [2]. Here it was proposed that inorganic analogs of the hydrocarbon rings (cyclopropenyl cation, cyclopentadienyl anion,

benzene), formed by replacing the (CH) groups with isoelectronic groups like nitrogen or O^+ , may also be stable. While the $4n + 2$ rule derived from the Hückel molecular orbital theory was originally applied exclusively to π -orbital systems, HMO theory can be applied to s-orbitals and the philosophy in this publication was that by following the $4n + 2$ rule, new inorganic rings may be found. A publication later that year, by the same author [3], saw the discussion of a wide variety of stable or metastable ring compounds such as cyclic ozone, hexaazabenzene and other species. Since then, more detailed analyses of the geometries and relative stabilities of these rings have appeared and have corroborated speculations made by Wright.

Many results currently available on $X_{(n)}$ species stem from recent *ab initio* calculations. In fact, clusters of Li, Be, B, C, N, and O as well as Na, Mg, Al, Si, P, and S have been reported [4]. Therefore, given the interest in X_n ring systems, it is surprising that no one has studied the properties of hydrogen rings systems other than H_3 , H_4 , and H_6 using a systematic, theoretical approach.

The goal of this work is to investigate these hydrogen ring systems and to provide a high quality, detailed study of the properties of various hydrogen rings (H_n , $n = 3$ to 8). The species chosen to be studied are analogs of the well known $C_3H_3^+$, C_4H_4 , $C_5H_5^-$, and C_6H_6 . Charged species include H_3^+ , H_5^+ , H_5^- , and H_7^+ . Neutral rings examined are H_4 , H_6 , and H_8 . Properties of these systems are determined while keeping their geometries in their respective D_{nh} point groups using highly correlated MR-CI and MP4 wavefunctions with relatively large basis sets. To evaluate the dissociation energies of the rings, their components, H^- , H_2^+ , and H_2 were likewise studied. The octaazacubane analogue, H_8 in O_h symmetry

was also investigated.

Lithium rings are known to be quite stable [5],[6],[7],[8]. Since Li and H both have just one valence electron, the electronic structure and thermochemical stability of both series will be compared. The comparison will be extended to include other inorganic rings reported in the literature (for example [9],[10],[11],[8]).

The interactions occurring in the hydrogen ring systems will be discussed in terms of atomic overlap, internuclear distances, and stability of dissociation products. Patterns occurring in the relative stability and total binding energies will be compared with predictions made by Hückel molecular orbital theory and the $4n + 2$ rule. Finally, the possible breakdown of Hund's multiplicity rule by H_4 will be briefly discussed.

Chapter 2

Theoretical Background

2.1 Self-Consistent Field Theory

By starting from first principles and treating molecular states as solutions to the Schrödinger equation,

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

the electronic energies and wavefunctions of molecules can be obtained. One attempts to solve this equation by treating the species as a collection of positive nuclei and negative electrons moving under the influence of a Coulombic potential. The full Schrödinger equation has never been solved exactly for anything but simple models and so approximate methods are used.

The total Hamiltonian for a diatomic molecule with n electrons is given by:

$$H = T_a + T_b + \sum_{i=1}^n T_i + \frac{1}{4\pi\epsilon_0} \left\{ - \sum_{i=1}^n \frac{Z_a e^2}{|R_a - r_i|} - \sum_{i=1}^n \frac{Z_b e^2}{|R_b - r_i|} + \sum_{i \neq j}^n \frac{e^2}{|r_i - r_j|} + \frac{Z_a Z_b e^2}{|R_b - R_a|} \right\} \quad (2.2)$$

where the kinetic energy terms of the nuclei and electrons are defined by:

$$T_a = -\frac{\hbar^2 \nabla_a^2}{8\pi^2 M_a} \quad \text{and} \quad T_i = -\frac{\hbar^2 \nabla_i^2}{8\pi^2 m_e}, \quad (2.3)$$

respectively, R_a and R_b are the distances of nuclei a and b from the origin, respectively and r_i is the distance from the origin of electron i . The charges of the nuclei are represented by Z_a and Z_b . For a polyatomic molecule, the expression for $\hat{H}$ is modified by including the electron-nuclear attraction and nuclear-nuclear repulsion terms associated with all centers.

The essential approximation made in *ab initio* quantum chemistry is the Born-Oppenheimer approximation, in which the nuclear motion is assumed to take place on much longer time scales than the electrons, typically on the order of 10^3 to 10^5 slower than the latter [12]. The approximation is then implemented by fixing the geometry and formulating the equation with nuclear energy parameters held constant. The electronic Hamiltonian may then be written as:

$$\hat{H}^{el} = \sum_{i=1}^n T_i + \sum_{i=1}^n \frac{Z_a}{|R_a - r_i|} - \sum_{i=1}^n \frac{Z_b}{|R_b - r_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} + \frac{Z_a Z_b}{R} \quad (2.4)$$

where R is the distance between nuclei.

The eigenvalue equation

$$\hat{H}^{el} \Psi^{el} = E^{el} \Psi^{el} \quad (2.5)$$

can be solved to determine the electronic energies and wavefunctions. It is important to note that, within the Born-Oppenheimer approximation, the electronic energy term E^{el} at the same time represents the potential energy $V(R)$ in which the nuclei move.

The SCF approximation assumes one Slater determinant (D_k) to be the solution to the Schrödinger equation, the elements of the determinant being MOs generated by linear combinations of atomic orbitals (ψ_i) (LCAOs), i.e.:

$$\psi^{MO} = \sum_{i=1}^n c_i \psi_i . \quad (2.6)$$

This procedure treats the electronic charges as an average cloud. Linear combinations of the basis functions are varied to yield the lowest total energy. This energy is often referred to as the Self-Consistent Field (SCF) energy. The Hartree-Fock limit is the energy obtained with a basis set of infinite size.

2.2 Configuration Interaction

In the configuration interaction (CI) method, the best possible wavefunctions are obtained through linear combinations of Slater determinants (D_k) generated by using the occupied and virtual MOs from the SCF step. That is, the expansion

$$\Psi^{CI} = \sum_{k=1}^m c_k D_k \quad (2.7)$$

comprises the final correlated wavefunction. As the m terms making up the Ψ^{CI} solution can range in the millions [13], a limited number of configurations are taken, corresponding to a given selection threshold for energy calculations. In this study, the multireference single and double excitation method (MRD-CI) [14], [15], [16], [17] is employed. The so-called estimated full-CI energy (FCI) is obtained by applying a generalized Langhoff-Davidson correction [18], [19] to

the extrapolated MRD-CI energy. This correction takes into account the energy lowering expected from quadruple excitations and is given by:

$$\Delta E_Q = (1 - c_o^2)(E_o - E_D) \quad (2.8)$$

where c_o is the coefficient of the dominant configuration, E_o is the energy of the dominant configuration, and E_D is the single- and double excitation CI (CI-SD) energy.

2.3 Perturbation Theory

Configuration interaction is a widely accepted procedure for going beyond the Hartree-Fock level of theory. However, unless all excitations are taken into account in the SD-CI matrix the method is not size consistent. This can cause problems, particularly when studying molecules with large internuclear separations.

The use of perturbation theory (PT) ensures size consistency but does not have the advantage of CI methods in that it is not variational so that the predicted eigenvalue may lie below the exact energy. A further disadvantage is that only one state can be studied at one time whereas CI methods can study several states of the same symmetry simultaneously.

In PT, the total hamiltonian is expressed as the sum of two parts: the zeroth-order part, H_o , which has known eigenfunctions and eigenvalues and a perturbational part, V , which is associated with small changes of the eigenvalues of H_o . (Due to this fact, PT can totally fail if applied to a system where a strong mixing of states occurs. In this case, the perturbational part of the hamiltonian is too large.) The exact energy is the infinite sum of contributions which contain

eigenvalues of H_0 and matrix elements of the perturbation between the eigenfunctions of H_0 . Terms that involve n matrix elements constitute the n -th order perturbation energy. In Rayleigh-Schrödinger perturbation theory (RSPT), the zeroth-order hamiltonian is chosen to be the same as the Hartree-Fock hamiltonian (see above). This particular method was used by Møller and Plesset and is quite often referred to as MP2T. Energies arrived at using RSPT are generally denoted MP2, MP3, MP4, etc. with the integer indicating the order of perturbation energy.

2.3.1 Rayleigh-Schrödinger Perturbation Theory

RSPT begins as a conventional eigenvalue problem with the hamiltonian expressed in two parts:

$$\hat{H}\Psi = (H_0 + V)\Psi = E\Psi. \quad (2.9)$$

The eigenvalues and eigenfunctions of the operator H_0 are known since they are the results of a standard HF procedure.

$$\hat{H}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \quad (2.10)$$

If the perturbation, V , is small values for the zeroth-order solutions, $\Psi^{(0)}$ and $E^{(0)}$ are expected to be close to the exact Ψ and E quantities, respectively.

By the introduction of an ordering parameter, λ , the eigenvalues and eigenfunctions of $\hat{H}$ can be significantly improved.

$$\hat{H} = H_0 + \lambda V \quad (2.11)$$

The exact eigenvalues and eigenfunctions can then be expanded in a Taylor series in λ :

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots + \lambda^n E^{(n)}$$

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots + \lambda^n \Psi^{(n)} \quad (2.12)$$

The value $E^{(n)}$ is the n^{th} -order energy. The $E^{(n)}$ expressions are then expressed in terms of the zeroth-order energies of the matrix elements of the perturbation between the unperturbed wavefunctions.

The eigenfunctions of the Taylor expansion are then operated on by the perturbation operator giving the following set of equations:

$$H_0 \Psi^{(0)} = E^{(0)} \Psi^{(0)}$$

$$H_0 \Psi^{(1)} + V \Psi^{(0)} = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi^{(0)} \quad (2.13)$$

$$H_0 \Psi^{(2)} + V \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)} \quad (2.14)$$

By multiplying these by $\Psi^{(0)}$ and using the fact that $\Psi^{(0)}$ and $\Psi^{(1)}$ are orthogonal, the energies of order 0, 1, and 2 can be expressed as:

$$E^{(0)} = \langle \Psi^{(0)} | H_0 | \Psi^{(0)} \rangle$$

$$E^{(1)} = \langle \Psi^{(0)} | V | \Psi^{(0)} \rangle \quad (2.15)$$

$$E^{(2)} = \langle \Psi^{(0)} | V | \Psi^{(1)} \rangle$$

Solving for $E^{(2)}$ above yields the MP2 energy of the system. The MP4 energy for a system can be determined by solving the following:

$$E^{(4)} = \langle \Psi^{(0)} | V | \Psi^{(3)} \rangle . \quad (2.16)$$

Chapter 3

Method of Calculation

One of the most common types of functions used in *ab initio* studies are referred to as Gaussian-type orbitals (GTOs). In Cartesian coordinates, these have the basic form:

$$\phi(l, m, n, \xi) = (x - x_a)^l (y - y_a)^m (z - z_a)^n e^{-\xi_a(r-r_a)^2} \quad (3.1)$$

where the function is centered on a nucleus and represents an orbital with an amplitude that is dependent on the distance from the nucleus. The quantum numbers for the orbital are represented by l , m , and n . When the sum of all three quantum numbers is zero, the Gaussian represents an s-orbital.

Basis sets are built up with these types of functions. A double-zeta (DZ) basis set is composed of several of these with each physical atomic orbital being approximately represented by two "contracted" functions.

The smallest basis set used to study the series of hydrogen rings is referred to as 311+G* [20], [21]. This set, basis A, describes the hydrogen atom with a three component s-orbital, a p-type polarization function with exponent 0.75 and a semidiffuse function with exponent 0.0360. Therefore, basis set A is composed

of 6s1p primitive functions which are contracted to 4s1p (simplified 6s1p/4s1p).

The larger basis set B was adapted from van Duijneveldt's 9s/5s set [22]. A semidiffuse s-function (exponent 0.0360) and two p-type functions (0.938258 and 0.0618) were added to the set making basis B of the type 10s2p/6s2p.

Both basis sets, while not being very large, give the correct properties for the systems studied. In particular, addition of the diffuse s-type function (0.0360) was necessary for an accurate prediction of the electron affinity of the H atom at the correlated level. The basis sets are shown in Tables 6.1 and 6.2.

Basis A was used in conjunction with the GAUSSIAN-90 [23] package of programs. A Z-matrix input specifying the type of calculation (eg. SCF, MP2, etc) and the 311+G* basis set is read by the program. The optimized internuclear distances and minimum energies are provided in the output file. The features of the local potential energy surface is used by the program for the evaluation of the harmonic vibrational frequencies.

Basis set B was used by the MRD-CI [16], [17], [14], [15] package program. Energy calculations proceed in two steps: first, determining the SCF wavefunction and eigenvalue then using the corresponding SCF molecular orbitals (MOs) to determine the configuration interaction wavefunction and energy. In calculating the SCF energy, the program sorts the integrals of the basis into symmetry types. The orbitals for all molecules made up of an even number of atoms were separated into the irreducible representations of the D_{2h} abelian point group. Those molecules with an odd number of atoms were calculated in the C_{2v} abelian point group. The SCF energy of a given molecule at a fixed geometry is then calculated.

In determining the CI energy, the assumption that core orbitals do not

participate in bonding is often made. However, as the hydrogen atom has only one electron, this assumption was not made here. Therefore, these calculations are referred to as all electron calculations.

The number of reference configurations used throughout this work was kept at one (with the exception of the H_4 molecule, where the ϵ_u^2 occupation in D_{4h} is described by two components in D_{2h} symmetry). The main, or SCF configuration for each molecule contributed over 90% to the wavefunction. All single and double excitations from the main were used to form the final CI wavefunction.

Several configurations were required to accurately determine the energies of the first four states of the H_4 molecule. The SCF calculation was performed for the open-shell, $a_{1g}^2 \epsilon_u^1 \epsilon_u^1$ wavefunction. The MRD-CI calculations, based on this wavefunction, were then performed for the ${}^3A_{2g}$, ${}^1B_{1g}$, ${}^1B_{2g}$, and ${}^1A_{1g}$ states. The first two required the use of 11 and 7 reference configurations, respectively. A total of 26 mains were used for ${}^1B_{2g}$ and ${}^1A_{1g}$. These states, both being of the totally symmetric irreducible representation of the D_{2h} point group, were calculated simultaneously and represent the first two roots of the CI energy for that representation.

Since single and double excitations from the multireference set of mains generate a relatively large number of configurations (9500-13165), only those excited state configurations contributing more than 1 nanohartree were selected to form the final CI wavefunction.

Further study of the energy separation between the two lower states (${}^3A_{2g}$ and ${}^1B_{1g}$) of H_4 was done with a larger basis set C. The s-functions in this set were the same as those used in basis B. However, the original two p-orbitals of

basis B were replaced by three uncontracted p-orbitals (2.292, 0.838, and 0.292) and a d-orbital (1.057) [24] which were taken from Dunning [25]. Therefore, basis set C corresponds to 10s3p1d/6s3p1d.

The corresponding single-point energies determined from the MRD-CI calculations were fitted with a parabola to determine the equilibrium geometries (R_{min}). A final MRD-CI calculation was carried out at that point, giving the final tabulated absolute energy values (E_{min}).

The MRD-CI package was also used to investigate the reasons why earlier studies erroneously predicted that square H_4 violates Hund's multiplicity rules. Basis sets of uncontracted 4s, 5s, 10s, 2slp, and 4slp functions, taken from Huzinaga [26], were used at the equilibrium geometries obtained with MRD-CI using basis B. The absolute energies determined for the $^3A_{2g}$ and $^1B_{1g}$ states of square H_4 were compared with the corresponding results obtained with basis sets B and C.

Chapter 4

Results and Discussion

4.1 One and Two Electron Systems: H^- , H_2^+ , H_2 , and H_3^+

The absolute energies and internuclear distances determined for these systems are collected in Table 6.3. Dissociation energies and vibrational frequencies are listed in Tables 6.8 and 6.9, respectively.

At the SCF level, the hydrogen atom is seen to have a negative electron affinity. In other words, at this level of theory, H^- is higher lying than the H atom. The introduction of correlation, however, shows that H does indeed stabilize with electron attachment. Single and double excitation CI, which is equivalent to full CI, gives an $\text{EA} = 0.545 \text{ eV}$. A recommended value of 0.755 eV [27] represents an error of 30% in the present results. This is not uncommon for theoretical calculations of electron affinities and reflects the omission of diffuse atomic orbitals of p and d character in the hydrogen basis set.

The largest single contribution to the EA for the H atom comes from the addition of a diffuse s-function with exponent of 0.036 [23]. This feature clearly indicates the increased size of the 1s orbital after a second electron is attached to

the atom. H^- has an ionic radius of 2.91 bohr [28].

The simplest molecular system studied here is H_2^+ . Results are quite abundant as this cation contains only one electron, making theoretical calculations of its properties extremely simple. In fact, if the atomic basis set is sufficiently large, the HF (SCF) solution will essentially represent the exact solution for this molecular ion.

Experimental data for H_2^+ has been cataloged by Huber and Herzberg (HH) [29]. For the ground state of H_2^+ , HH report an equilibrium internuclear distance (R_e) of 1.988 bohr (1.052 Å) and a dissociation energy (D_e), including zero-point vibrational energy, of 2.793 eV. Also given is the harmonic vibrational frequency (ω_e) of 2321.7 cm^{-1} . The results of this study agree quite well with these experimental values. The E and R_e listed for H_2^+ in Table 6.3 are the SCF results from the two different procedures (programs) used here. The internuclear distance and dissociation energy are within 1.6% of those reported by HH.

The ground state for this molecule arises from the electronic configuration σ_g^1 and corresponds to $X^2\Sigma_g^+$. This state arises from the single ionization of the $X^1\Sigma_g^+$ state of H_2 . The theoretical ionization potential (IP) (with zero-point energy taken into account) lies at 15.426 eV. The loss of a bonding electron upon ionization justifies the larger R_e and smaller ω_e and D_e values when compared with those of neutral H_2 (see below).

The H_2 molecule is, needless to say, also extremely well known. With an experimental internuclear distance of 1.401 bohr, $D_e = 4.7477$ eV and vibration frequency of 4401 cm^{-1} [29], excellent agreement is seen in many theoretical studies, in particular, the early but rigorous work of Kolos and Wolniewicz [30]. These

authors calculate a dissociation energy for H_2 equal to the experimentally determined value.

A simple CI-SD (single and double excitation relative to one reference configuration) calculation represents for H_2 the full CI (FCI) solution. Since the correlation energy of H_2 of a given AO basis set can be calculated exactly, the quality of a given *ab initio* study merely reflects the basis set quality.

The CI-SD results give an internuclear distance of 1.402 bohr, in excellent agreement with HH. Less but still acceptable agreement is seen in the dissociation energy of H_2 . A value of 4.605 eV is determined here for the $H_2 \rightarrow 2 H$ process.

Since the largest system being studied is H_8 , it is important to keep the basis sets as small as possible so that the computations are of manageable proportions. In fact, technical problems (limitations in disk space) were encountered when attempting to study H_7^+ using the MRD-CI method. However, the above results serve to show that, while the basis sets used here are relatively small, they are effective in determining the properties of the systems under investigation. This is demonstrated by the small discrepancies between calculated and experimentally determined properties for H_2^+ and H_2 .

Ground state H_2 , with a $X\ ^1\Sigma_g^+$ ($1\sigma_g^2$) structure, shows the shortest R_e and highest ω_e among neutral homonuclear diatomics. Its dissociation energy is also relatively high, reflecting the strength of the sigma bond.

The first excited state, $1^3\Sigma_u^+$ ($1\sigma_g\ 1\sigma_u$), is of valence character but repulsive, that is, unbound with respect to two H atoms. Its dissociation products, $H(^2S) + H(^2S)$, are the same as those of the ground state. This state lies 11.37 eV vertically above the ground state of H_2 [29].

All other excited states of H_2 are of Rydberg character. These Rydberg states consist of an ionic H_2^+ core ($^2\Sigma_g^+$) plus an orbiting electron in a diffuse molecular orbital. This feature is responsible for the similar values of R_e and ω_e for the Rydberg states of H_2 and those of ground state H_2^+ . The lowest-lying Rydberg state of H_2 lies approximately 12.5 eV above the ground state.

The reaction $H_2 (X^1\Sigma_g^+) + e^-$ does not stabilize the system: the H_2^- species lies above the neutral, generating what is known as a resonant state. This feature implies that the electronic configuration $1\sigma_g^2 1\sigma_u^1$ of H_2^- is unbound. In contrast, the isoelectronic He_2^+ species has a bound ground state ($X^2\Sigma_u^+ (1\sigma_g^2 1\sigma_u^1)$) by about 2.365 eV [29]. This simple example demonstrates that the stability of a given diatomic molecule is not only governed by its electronic configuration but also by its overall charge.

The first ring studied in the series, H_3^+ , has an interesting history. The first experimental evidence of the existence of this, the lightest polyatomic molecule, was given in 1912 from mass spectroscopy studies carried out by Thomson [31]. Before its rediscovery at the beginning of the last decade, all of the properties of this system were determined from theoretical studies. It is for this reason that H_3^+ has been referred to as the triumph of theoretical chemists. In 1980, Oka and Geballe [32] performed the first definitive experimental characterization of this triatomic. Recently, Maillard et al. [33] detected H_3^+ in the northern and southern ionospheres of Jupiter. The importance of H_3^+ in interstellar chemistry, for protonation reactions of the type $AB + H_3^+ \rightarrow ABH^+ + H_2$, has also been long recognized. In order for the above reaction to proceed, the proton affinity of AB should be higher than that of H_2 (4.62 eV MRD-CI(+Q)). According to compiled

data on proton affinities [28], most of the atomic and molecular species have PA (proton affinities) above 5.0 eV, compared to 4.61 eV for H_2 .

A summary of properties from selected theoretical works published after 1964 is presented in Table 6.4, together with experimental data. The remarkably good agreement among the various studies indicates the relatively simple electronic structure of H_3^+ .

The symmetry-adapted linear combinations (SALCs) for atomic orbitals for this ring (restricted to 1s orbital per atom) are:

$$\begin{aligned} o_{a_1'} &= \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \\ o_{e'}^X &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \quad o_{e'}^Y = \frac{1}{\sqrt{2}}(s_2 - s_3) \end{aligned} \quad (4.1)$$

Due to the high symmetry of this system, these SALCs also represent the true molecular orbitals for H_3^+ . The ground state electronic configuration for this molecule is $a_1'^2$, corresponding the 1A_g state.

Comparison of the SCF and MRD-CI energies shows that correlation lowers the total energy for this system by about 1.1 eV. This stabilization is almost equivalent to the contribution correlation makes to the H_2 system. Also interesting is the small difference in the calculated proton affinity (PA) of H_2 at the various levels of theory. Only 0.09 eV separates the PA of H_2 at the SCF and full CI levels (H_3^+ has only 2 electrons). This makes sense in that, when PA is calculated, the energy difference between H_3^+ and H_2 is taken. Since H_2 has all the correlation energy in both systems, E_{corr} cancels, leaving the proton affinity to be simply the SCF energy difference. Furthermore, this indicates the lack of

electronic rearrangement that is required for bonding to occur between H_2 and the proton.

The formation of H_3^+ can be thought to proceed through the approach of H^+ along a line perpendicular to a H_2 molecule. At intermediate distances, the interaction between them is simply the polarization of the molecular electron density by the positive charge of the approaching proton. When the proton is close to its equilibrium position, the electrons become tightly bound within the ring and the polarizability is reduced relative to H_2 [34]. The two electrons now occupy the low energy a_1' MO generated by the linear combination of the 1s hydrogen atomic orbitals. The short bond distance in H_3^+ is also important in understanding why the molecule is so stable. Since the atomic radius of the H (1s) atom is 1 bohr and the atom-to-ring-center distance is 0.95 bohr, the overlap among all three 1s orbitals in the center of the ring is quite large. This feature indicates a higher electron density in the center of the ring rather than between the atoms, as is clearly illustrated in Figure 7.1. Finally, this molecule obeys the $4n + 2$ rule and appears to validate the prediction of stability in ring compounds with $4n + 2$ electrons. The calculated energy for the reaction $H_3^+ \rightarrow H_2 + H^+$ demonstrates the stability of the ring; this value is 4.621 eV.

The neutral H_3 ring will not be discussed in detail here. However, it is worth mentioning that despite having an unbound ground state, several low-lying excited states are of Rydberg character and are bound. In other words, these Rydberg states have a planar H_3^+ -core with an electron orbiting in a diffuse MO [29],[35].

Since lithium is isoelectronic with hydrogen (and are equivalent in Hückel

molecular orbital theory), comparisons between the properties of $H_{(n)}$ and $Li_{(n)}$ compounds could prove useful. The discussion below focuses on lithium systems but other inorganic rings will also be included.

Lithium has a much lower ionization potential than hydrogen, about 5.39 eV versus 13.65 eV for the latter [36]. This is due to both the shielding of the nuclear charge by the filled 1s orbital as well as the diffuse nature of the Li 2s orbital ($\langle r \rangle = 3.88$ bohr). An electron affinity of 0.618 eV for Li [27] is slightly less than that of H.

The Li_2^+ cation is markedly different from its hydrogen counterpart, H_2^+ . While Li_2 has a dissociation energy of about 1.04 eV, the ionized molecule (Li_2^+) has a bond strength of about 1.44 eV [29]. In other words, in going from H_2 to H_2^+ , the dissociation energy of the molecule formed decreases. On the other hand, ionization of Li_2 results in a more strongly bound molecule.

While H_2^- is an unstable species, Li_2^- is bound. Electron attachment to Li_2 leads to the $X^2\Pi_u (\sigma_g^2 \pi_u^1)$ state of Li_2^- . This corresponds to adding the electron to the virtual, bonding π_u orbital. With this previously unoccupied orbital now becoming singly occupied, the properties of this system change in an unexpected manner. There is an increase in the bond distance and a drop in the dissociation energy to 0.9 eV [29].

These results for the diatomic species already suggest that $H_{(n)}$ and $Li_{(n)}$ rings may differ significantly. The main reason for the different behavior lies in the existence of low-lying valence p-orbitals in the lithium atom.

The Li_3^+ ion, like H_3^+ , has its absolute minimum in D_{3h} symmetry. This Li ring is bound relative to $Li_2^+ + Li$ by about 1.66 eV [5]. This stabilization energy

is comparable to the dissociation energy of Li_2 in the same way as the energetics for the process $\text{H}_2 + \text{H}^+$ compares with the dissociation energy of the hydrogen molecule. The bond lengths in Li_3^+ increase over that of Li_2 , to about 5.65 bohr. Relatively speaking, this increase corresponds to a distance about 10% larger than in Li_2 , close to the 15% increase calculated for the H_2/H_3^+ pair.

Like H_3 , the ground state for equilateral Li_3 is also unstable. However, a distortion in Li_3 (D_{3h}), due to Jahn-Teller effects, forms a bound species in C_{2v} symmetry. The Li_3 ground state (valence) configuration $a_{1g}^2 e_u^1$ in D_{3h} correlates with $a_1^2 a_1^1$ and $a_1^2 b_2^1$ in C_{2v} . In these cases, the a_1 and b_1 MOs acquire some bonding character from interactions with in-plane p-orbitals. Similar stability and behavior is also observed for other group 1A rings [8].

It is interesting to compare the above to Be_3^{2+} . The Be_2 ($X^1\Sigma_g^+$) molecule is only slightly bound, having an $R_e = 4.63$ bohr and a $D_e = 98$ meV. However, the Be_3^{2+} molecule, having four valence electrons (corresponding to a molecular structure of $(a_1')^2 (e')^2$) and being doubly charged, is locally bound but still metastable relative to Be_2^+ and Be^+ [37],[38].

Roa, Khanna and Jena [39] performed a study in which the properties of clusters of three and four Li, Be, Mg, and C atoms were calculated. They find that the closed shell Be_3 and Mg_3 clusters (having electronic configurations $(a_1')^2 (e')^4$) both have minima in D_{3h} symmetry and have internuclear distances smaller than their diatomic counterparts. The C_3 molecule, on the other hand, is a linear molecule with equal bond lengths at its lowest energy.

An analysis of the structure of B_3 (electronic configuration) carried out by Marinelli and Pellegatti [40] indicates that the D_{3h} isomer molecule is extremely

stable. They report that $B_2 + B$ stabilizes by 8.3 eV by forming the D_{3h} ring and that the B-B equilibrium distance is very close to that of the diatomic. An analysis of the occupied orbitals in B_3 shows that the e' MOs actually have contributions from 2s and in-plane 2p atomic orbitals, just as in group 1A metals. Thus, the reason why B_3 is so stable comes from the strong, in plane s-p hybridization. The same results were observed by Martin et al. [11]. An example of the in-plane orbitals' involvement in ring bonding is illustrated in Figure 7.2.

The N_3^+ molecule is bound and has a linear ground state. A secondary minimum in D_{3h} symmetry [2] is also bound.

Neutral N_3 , like C_3 , exhibits a linear ground state [11]

4.2 The Four Electron System: H_4

The next molecule in this series is H_4 . Four hydrogen atoms can be arranged in space in many different ways. Some of the isomers that have been studied in the past are square (D_{4h}), rectangular (D_{2h}), tetrahedral (T_d), rhombic (D_{2h}), and T-shaped (C_{2v}). Of all of these, H_4 is only stable in the T-shaped configuration, that is, only this conformation lies lower in energy than two ground state H_2 molecules. However, the bonding in this configuration corresponds to a weakly bound van der Waals complex.

Prior investigations carried out on the $(H_2)_2$ complex were done by Schneider et al. [41] and Magnasco [42]. The former authors studied the T-shaped conformation at the MP2/[4s2p] level. They reported a shallow potential minimum, of nearly 3 meV (0.068 kcal/mole), at an intermolecular separation of 6.73 bohr. These results reproduce experiments to within 2% [29].

All other H_4 isomers are unstable, that is, either unbound (with at least one imaginary frequency) or metastable (all frequencies are real but with the local minimum lying above products).

The square (D_{4h}) arrangement has attracted considerable interest due to the possibility of this H_4 structure being a transition state for the bimolecular exchange reaction. Another reason why the D_{4h} conformation has received recent attention lies in the fact that H_4 , as well as related molecules like cyclobutadiene, may violate Hund's multiplicity rules.

The process $H_2 + D_2 \rightarrow 2 HD$ has been studied by several authors [3],[43],[44]. It has been shown that the square (D_{4h}) transition structure lies energetically far above the equidistant linear conformation. The energetics of the latter agrees well with the experimental observations reported for this reaction. Specifically, experimental results indicate that the energy required for the exchange reaction is about 42 kcal/mole [45]. On the other hand, *ab initio* studies place linear, equidistant H_4 at 43 - 45 kcal/mole [3],[46] relative to reactants. Furthermore, this barrier height is significantly lower than other possible structures (including rhombic, tetrahedral, rectangular, and kite shaped), all of which range in energy between 110 and 190 kcal/mole [46]. However, the linear structure cannot be a transition state for the H_2 - D_2 exchange. Since there is no low-lying structure predicted by *ab initio* calculations for this reaction, the $H_2 + D_2$ reaction is now thought to proceed via an atomic exchange mechanism.

For H_4 in the D_{4h} point group, the symmetry-adapted linear combinations of atomic orbitals (SALCs) consist of two non-degenerate and one degenerate pairs of molecular orbitals. Due to the high symmetry, the MOs are the same as the SALCs

(each SALC belongs to a different irreducible representation). The lowest-lying MO, the totally symmetric a_{1g} , is doubly occupied and of bonding character. The other non-degenerate MO is the antibonding b_{1g} MO and is unoccupied. The e_u MOs form the degenerate pair and are non-bonding. The remaining two electrons of the H_4 system are distributed in this pair, generating four possible electronic states. The SALCs for H_4 are shown below:

$$\begin{aligned} \phi_{a_{1g}} &= \frac{1}{2}(s_1 + s_2 + s_3 + s_4) \\ \phi_{b_{1g}} &= \frac{1}{2}(s_1 - s_2 + s_3 - s_4) \\ \phi_{e_u}^X &= \frac{1}{\sqrt{2}}(s_1 - s_3), \quad \phi_{e_u}^Y = \frac{1}{\sqrt{2}}(s_2 - s_4) \end{aligned} \quad (4.2)$$

In order to determine the symmetry of the electronic states generated by the global configuration e_u^2 , the following approach taken by Voter and Goddard [48] has been adapted here to apply to the H_4 molecule.

By using 4.2, the forms of the four molecular orbitals for H_4 without inclusion of spin functions, can be written as follows:

$$\begin{aligned} \Psi^1 &= \phi_2 \phi_3 - \phi_3 \phi_2 \\ \Psi^2 &= \phi_2 \phi_3 + \phi_3 \phi_2 \\ \Psi^3 &= \phi_2^2 - \phi_3^2 \end{aligned} \quad (4.3)$$

$$\Psi^4 = \phi_2^2 + \phi_3^2$$

where ϕ_2 and ϕ_3 represent $\phi_{e_u}^X$ and $\phi_{e_u}^Y$, respectively. The $\phi_{a_{1g}}$ MO is not included in these representations as it is common to all four functions.

By denoting ϕ_2 and ϕ_3 by X and Y and including spin, the states which are formed from 4.3 can be described by:

$$\begin{aligned} &^3(XY - YX) \\ &^1(XX - YY) \\ &^1(XY + YX) \\ &^1(XX + YY) \end{aligned} \tag{4.4}$$

The state representations for the global electronic configuration $(a_{1g})^2 (e_u)^2$ are then determined, through the application of the appropriate symmetry operations [49] in D_{4h} on (3) to be $^3A_{2g}$, $^1B_{1g}$, $^1B_{2g}$, and $^1A_{1g}$.

Wilson and Goddard (WG) [44] followed the dissociation of all four states of the square H_4 molecule along a rectangular path. The two lowest states, $^3A_{2g}$ and $^1B_{1g}$ are reported to lie nearly 3 eV below $^1B_{2g}$ and $^1A_{1g}$ and correlate with two H_2 molecules as follows:

$$^3A_{2g} \longrightarrow {}^3\Sigma_u^+ + X {}^1\Sigma_g^+$$

$$^1B_{1g} \longrightarrow X {}^1\Sigma_g^+ + X {}^1\Sigma_g^+$$

Thus only ${}^1B_{1g}$ correlates to two ground state H_2 molecules. The higher-lying states, ${}^1B_{2g}$ and ${}^1A_{1g}$ both correlate to singly excited states of H_2 , namely:

WG used a minimal Slater basis set and configuration interaction. They found ${}^3A_{2g}$ to be the lowest lying state at the SCF level over the range of geometries investigated ($R_c(H-H) = 1 - 3$ bohr). Lying slightly above that, by about 0.6 eV, was the ${}^1B_{1g}$ state. Inclusion of correlation reversed their stabilities, making ${}^1B_{1g}$ the lowest state on the D_{4h} surface with the triplet state lying about 0.6 eV higher. *These findings indicate that of the states that are generated from the occupation of the degenerate MOs of H_4 , the state with the lowest multiplicity, ${}^1B_{1g}$, lies lower in energy than the higher multiplicity state, ${}^3A_{2g}$.* The barrier height for the four-centered exchange reaction with a square transition structure was reported to be 6.42 eV (148 kcal/mole), relative to two ground state hydrogen molecules. These authors further noted that the ${}^1B_{1g}$ state was unstable with respect to kite-shaped distortions and concluded that this could not be the transition structure for the exchange reaction.

Similar studies were performed by Rubinstein and Shavitt (RS) [46] and Silver and Stevens [43].

RS employed a method similar to that of WG, except that the basis set was expanded to double-zeta (DZ) quality (ie. each H atom was described by two s-orbital type functions). With this larger basis, they found results which were in agreement with the earlier study. For example, the ${}^1B_{1g}$ state was still found to

be lowest at the CI level, lying about 0.35 eV lower than the triplet state. This singlet lay 6.2 eV (142 kcal/mole) above two ground state H_2 molecules. Bond distances in the two states decreased only slightly compared to those computed by WG.

Silver and Stevens also used a double-zeta basis set in their full CI calculations. Their results were slightly better than those of RS since all single and double excitation configurations were included (hence, *full* CI). The basis set was expanded with polarization functions *only* at $R_e(H-H) = 2.0$ and 2.4 bohr. This was done in order to estimate the effect on the barrier height. This DZP basis showed that, at 2.0 bohr, the $^3A_{2g}$ state was lower in energy than the $^1B_{1g}$. At 2.4 bohr, a reverse order of stabilization was found. These authors failed to comment on the causes of this reversal of relative energies and to further explore the surface with the larger basis set.

A more recent study on H_4 was carried out by Janoschek and Kalcher (JK) [50]. They applied the CAS(4,4)-CI(SD+Q)/[5s2p] method (comparable to our own) on the $^1B_{1g}$ state of H_4 . The results were a molecule with an internuclear separation of 2.44 bohr, lying about 149 kcal/mole (6.47 eV) above two ground state H_2 molecules. While their computed relative energy was similar to ours, JK find an internuclear distance about 0.13 bohr larger. Although basis set details were not given by these authors, the error is most likely due to the lack of a diffuse s-function in their basis. CAS vibrational frequencies were also reported. These are: 6087i (b_{1g}), 1139i (e_u), 914 (b_{1g}), 1347 (b_{2g}), and 1409 (a_{1g}) cm^{-1} . Here, the *i* symbol denotes imaginary or negative frequencies that indicate that along the b_{1g} (rectangular) and the degenerate e_u (trapezoidal) modes of vibration, the H_4

molecule proceeds to its products in a down-hill, barrierless process.

Comparisons of the results of the above studies with those of this work are summarized in Table 6.5.

In all prior studies, the lowest-lying state on the H_4 D_{4h} surface was predicted to be $^1B_{1g}$. This finding led many to believe that square planar H_4 violates Hund's rule. Discussion of this apparent breakdown is presented in Section 4.2.1.

The results of the present calculations on the four lowest states of H_4 are summarized in Table 6.6. Immediately noticed is that the $^3A_{2g}$ state has the lowest absolute energy, with its minimum $R_e(H-H)$ at 2.18 bohr. This state lies almost 0.15 eV below the $^1B_{1g}$ state, making it the ground state on the D_{4h} surface. This is seen to be true at both the SCF [44] and MRD-CI(+Q) levels of computation. The other singlet states, $^1A_{1g}$ and $^1B_{2g}$, lie around 2 eV higher than the triplet. The H_4 species in its triplet state lies 6.304 eV (145 kcal/mole) above two ground state H_2 molecules. This quantity is in good agreement with previous works and confirms the findings of Rubinstein and Shavitt that inclusion of polarization functions in the basis set does not significantly lower this barrier height.

Also of interest are the equilibrium geometries of the two lowest states. As can be seen from Table 6.6, the present results (using the 10s2p/6s2p basis) show the internuclear separations of the $^3A_{2g}$ and the $^1B_{1g}$ states to be significantly shorter than in previous works. Compared to WG, distances reported here are nearly 0.3 bohr shorter.

It has long been common knowledge that inclusion of polarization functions is vital to the proper description of the properties of ring systems. This fact is

verified by these results. However, it is also demonstrated here that, by including polarization functions in the basis set, the proper ordering of the triplet and lowest singlet is determined. Further testing of the singlet-triplet separation was done using the larger basis set C (10s3p1d/6s3p1d). To avoid biasing the results, the parent SCF molecular orbital for each state, that is a triplet SCF-MO for $^3A_{2g}$ and a singlet SCF-MO for the $^1B_{1g}$ state, were used. A selection threshold of zero was used in the CI calculations. The results showed that the triplet state is indeed lowest-lying with a triplet-singlet splitting of about 0.2 eV. The importance of polarization functions in correctly predicting the lowest state on the D_{4h} surface was not realized by Silver and Stevens.

Since, in this work, only the lowest state on each D_{nh} surface is considered, the discussion will continue for the $^3A_{2g}$ state. Results for equilibrium geometries and absolute energies are collected in Table 6.3.

From Table 6.3, it can be seen that H_4 has the largest internuclear separation of all other hydrogen molecules studied up to this point. With two electrons in the non-bonding e_u MO, the remaining two that occupy the a_{1g} MO are responsible for stabilizing this molecule. This bonding MO is shown in Figure 7.3. This orbital has minimal overlap between atoms, as well as low density at the ring center. It is quite easy to see from this picture why no bonding arises. With the H-H distance in square H_4 being more than twice the radius of 1s H, very little overlap between adjacent atomic orbitals exists.

However, there is indeed some degree of bonding character here. From Table 6.6, it is seen that, H_4 is bound with respect to 4 hydrogen atoms ($H_4 \rightarrow 4 H$, $\Delta E = 2.9$ eV). The reaction energies collected in Table 6.8 show this species lies over

6 eV higher than 2 H₂ molecules. However, dissociation to this limit cannot occur because, as shown earlier, the ³A_{2g} state does not correlate with two ground state hydrogen molecules (see above). Decomposition to H₂ + 2 H is symmetry allowed and releases 1.7 eV.

The vibration frequencies for this molecule are shown in Table 6.9. For the bound modes, little difference is seen between the SCF and MP2 frequencies for the bound (positive frequency) modes. At both the SCF and MP2 levels, the degenerate, trapezoidal *E_u* mode is unbound (imaginary frequency). This indicates the vibration which is responsible for lowering the energy of the system and characterizes the path of dissociation to H₂ and 2 H atoms. The difference between the magnitude of this frequency at the SCF and MP2 levels (2515i cm⁻¹ vs 1654i cm⁻¹) can be attributed to the differences in energy separation of H₄ and the dissociation products. At the SCF level, the reaction H₄ → H₂ + 2 H releases about 2.67 eV. At the MP2 level, this energy drops by nearly 0.7 eV, to 1.97 eV. The steepness of the surface along the dissociation path is quite different at the two levels of theory and, therefore, so is the frequency that characterizes the dissociation. This vibration is illustrated in Figure 7.4. The totally symmetric, ring breathing, *A_{1g}* mode has the largest magnitude of all the vibrations, at 2025 cm⁻¹. This mode is associated with H-H stretching and its magnitude indicates the degree to which "diatomic" H₂ character is retained in the H₄ ring structure. Comparisons with the harmonic vibrational frequency of H₂ and the totally symmetric vibration of H₃⁺ (4532 and 3498 cm⁻¹, respectively) indicate that the reduction of the magnitude of this vibration may continue with increasing ring size. Indeed, it is seen that the totally symmetric vibration decreases in magnitude along the series

At this point, it is of interest to compare the stabilization of H_4 with that of isoelectronic Li_4 .

The theoretical results reported for Li_4 isomers are quite varied *but are in agreement that Li_4 is stable (bound)*. Cardelino et al. [51] find the rhombic D_{2d} species to be bound and the most stable. This prediction agrees with the findings of Flad et al. [5]. On the other hand, Richtsmeier's group finds the square configuration D_{4h} to be lowest in energy [8]. However, the most recent publication on lithium clusters [52] reports that the rhombic Li_4 isomer lies 0.3 eV below the square. Averaging over all theoretical data, the binding energy per atom (atomization energy) lies in the range of 0.71 ± 0.07 eV.

Comparing Li_4 and H_4 (both species being antiaromatic according to the $4n + 2$ rule), the complete atomization energy to 4 Li or 4 H is endothermic in both cases. However, Li_4 is bound with respect to 2 Li_2 molecules in the ground state. Dissociation to this limit requires about 1 eV. A similar trend is followed for all group 1A four-atom clusters [8],[6],[5]. It is therefore seen that the $4n + 2$ rule fails in its prediction that Li_4 should be unbound.

Also interesting is the Li_2H_2 molecule. Even calculations at the SCF level show this molecule to be stable [51] in D_{2h} symmetry. The hydrogen and lithium atoms occupy alternating positions at the points of a rhombus and are separated by a distance of 0.42 bohr. Dissociation to Li_2 and H_2 is reported to require 1.19 eV. At correlated levels, this energy increases to more than 4.0 eV. In a similar study by Kato et al. [53], it was found that there is a strong tendency for charge to accumulate around the H atom indicating that the bonding in this system is

highly ionic as in diatomic $\text{Li}^6+\text{H}^{6-}$ [29].

With even shorter atomic separation than the triatomic rings, the tetrahedral conformations of Be_4 and Mg_4 clusters are stable [10],[11],[54]. The C_4 compound behaves like Li_4 , that is, the most stable isomer is a rhombic, D_{2h} structure [39].

The group of Lauderdale, Stanton, and Bartlett have recently investigated various conformations of N_4 . Tetrahedral N_4 (T_d) is locally bound (metastable) even though it lies more than 7.5 eV above 2 N_2 molecules. Rectangular N_4 (D_{2d}) is less stable than tetrahedral N_4 [1].

Interestingly, the N_4^{2-} dianion has been reported to be metastable in D_{4h} symmetry [9]. Even though the extra two electrons are unbound with respect to electron detachment, this unusual species is stable toward geometrical distortions.

4.2.1 A Discussion of the Breakdown of Hund's Rule

Hund's multiplicity rules are empirical rules developed by the spectroscopist Frederick Hund. These say that for electronic states arising from a common electronic configuration [55]:

1. The state with the largest spin angular momentum, S , is the most stable, and stability decreases with decreasing S .
2. For states with the same value of S the state with the largest orbital angular momentum, L , is the most stable.
3. If the states have the same value of S and L , then, for a subshell that is less than half-filled, the state with the smallest value of J , total angular momentum ($S + L$), is the most stable; for a subshell that is more than half-filled, the state

with the largest value of J is the most stable.

Hund's rules were originally developed for application to atoms. However, these multiplicity rules were later extended to molecules without justification. The version applicable to molecular systems with states arising from the same electronic configuration would be:

1. The state with the largest value of S should be the most stable, with stability decreasing with decreasing S .
2. For states with the same value of S , the state with the largest value of M_L should be the most stable.

Raftery, Scott, and Richards [47] pointed out the lack of justification for the applying Hund's rules to linear molecules. On the basis of total energies estimated within a monodeterminant approximation, they provide more useful criteria for predicting relative stabilities. They also show that the extended Hund's rules fail for certain configurations.

Hund's rules have traditionally been explained by the fact that, in higher multiplicity states, electrons are kept further apart in space because each electron occupies a different orbital. As a result, their total interelectronic repulsion is smaller than that of the lower multiplicity state. Consequently, the higher multiplicity state lies lower in energy than its low multiplicity counterpart.

Early works by Katriel [56],[57], on the He isoelectronic sequence have shown that this simple assumption is wrong. His works show that the average distance between electrons in the He atom is higher in the 3P ($1s^12s^1$) state than in the 1P

($1s^1 2s^1$) state. However, with the nuclear charge reduced to zero and increased to large numbers (≈ 200), the probability of finding the electrons further apart is highest in the singlet state.

This type of analysis was extended by Colpa and Brown [58],[59] to the lowest $^1\Pi_u$ and $^3\Pi_u$ states of the H_2 ($1s^1 2p^1$) molecule. these authors discovered that electron-electron repulsion is highest in the triplet state over all geometries studied. However, the triplet state lies lower in energy due to the contribution of other energy components, such as nucleus-electron attraction. Similar results were found for the 1E_g and 3E_g states of square planar H_4 for internuclear distances of 1.5, 2.0, and 2.5 bohr [59].

More recently, a series of papers by Darvesh et al. [60],[61],[62] re-examined the theoretical foundations of Hund's rules. Various CI energy components (including electron-electron repulsion (V_{ee}), electron-nuclear attraction (V_{ne}), kinetic energy (T_e), and nuclear repulsion (V_{nn})) of molecular species such as CH_2 (1B_1 , 3B_1), LiH ($a^3\Sigma^+$, $A^1\Sigma^+$), BH ($a^3\Pi$, $A^1\Pi$) were studied over a large range of geometries. In all cases, the triplet state of each molecule is more stable than its singlet counterpart. However it was found that, at their respective minima, V_{ee} is higher in the triplet state, contradicting the old interpretation of Hund's rules. The authors also point out that the ΔV_{ee} ($V_{ee}^{singlet} - V_{ee}^{triplet}$) term varies as a function of internuclear distance. This feature causes a breakdown in the original interpretation of the rule because it indicates that the electrons in the higher multiplicity state are in fact closer together in space when compared to the lower multiplicity state.

In all of the above examples, the singlet-triplet pairs studied showed the

triplet is energetically lower-lying than the singlet. In some cases, the electronic repulsion is higher for the triplet state than, forcing a re-evaluation of the origin of Hund's rules. However, it must be kept in mind that the breakdown in the interpretation of the rules does not mean that a violation in Hund's rules occurs for these cases.

There are examples of genuine breakdowns in Hund's rules for molecules. For instance, previous works on H_4 [44],[46] square have found that that lowest-lying state on the D_{4h} surface is the $^1B_{1g}$ state with the $^3A_{2g}$ state lying slightly higher in energy. This led several authors to seek an explanation for the breakdown of the multiplicity rule.

Kollmar and Staemmler (KS) [63] studied a series of molecules, including C_4H_4 and H_4 . They explicitly state that they know of no experimental evidence for the breakdown of Hund's rule in any of the molecules they study. However, they list several examples of *theoretical works* that show singlet states lying lower in energy than triplets arising from the same electronic configuration.

KS justify the violation of Hund's rule due to a phenomenon they refer to as spin-polarization. In essence, spin polarization is the effect of an unpaired electron polarizing lower-lying, filled orbitals in such a way as to cause electrons with the same spin to be closer together in space. By including into the wavefunction different orbitals for different spin, this effect can be examined. The authors analyzed two geometries for H_4 , 2.0 and 2.4 bohr. Various basis sets ranging in quality from triple-zeta (TZ) to TZP were employed with CI. The smallest basis predicts the $^1B_{1g}$ state to lie considerably lower in energy than $^3A_{2g}$ at both distances. Use of the largest basis lowers the energy of the triplet below that of

the singlet at 2.0 bohr. At 2.4 bohr this is not the case and the singlet remains lower in energy. KS attributed this to a reduction in spin polarization by the increase in the size of the basis set. They concluded that Hund's rule is violated by the H_4 molecule. Similar anomalies were reported for all other species studied in that work.

Gallup [64] also sought to explain the breakdown in Hund's rules and found that, for a breakdown in Hund's rule to occur, certain conditions are required. The system must have four-fold symmetry and single excitations in the CI representation must also make important contributions to the energy lowering. He further points out that Brillouin's theorem prevents single excitations from contributing at the first order level for closed-shell RHF wavefunctions but this does not apply to open shell RHF wavefunctions. In looking at this wavefunction for H_4 , he observes that the $^1B_{1g}$ spin coupling will have a large effect on the CI energy in the second order: the corresponding energy lowering for the $^3A_{2g}$ will only be 75% that of the singlet state. A criterion for violation to occur was that the exchange integral needed to be small. Using Huzinaga's 4s GTO basis set, Gallup showed that H_4 did indeed violate Hund's rule due to abnormally low values of the exchange integral and not because of abnormally high CI stabilizations.

Basis set effects upon the energy difference between the triplet and singlet states (at their respective minima) has also been examined in this work. The results were obtained with various uncontracted Gaussian basis sets, which include a 4s, 5s, 10s, 2slp, and 4slp taken from Huzinaga [26]. The 4s set of functions is the same as that used by Gallup.

The MRD-CI(+Q) for ΔE results with the basis sets from above, together

with results from basis B and C are shown in Figure 7.5 and Table 6.7.

The smallest basis (4s) set gives results very similar to those of the earlier studies on H_4 , with an energy separation (ΔE) of 0.26 eV (singlet lies lower). The equilibrium internuclear distances are similar to those calculated by Silver and Stevens [43], being 2.31 and 2.42 bohr for $^3A_{2g}$ and $^1B_{1g}$, respectively. As the number of s primitives increases, the total energies of both states are lowered. The use of the 10s basis almost uniformly reduces the energies of both states by 0.12 eV. In both cases, relatively larger nuclear separations are found. The energy splitting remains more or less constant at about 0.26 eV. By using the basis with only 2 s AOs and including a polarization function (DZ+P), the absolute energies of both states increase by about 0.8 eV but *the triplet is now lower than the singlet by about 0.13 eV*. At the same time, a large decrease in the ring size is observed for triplet H_4 with a smaller decrease for the singlet. With further increasing in the basis set size, lower absolute energies are obtained but the triplet remains lower than the singlet. With the use of basis set C, a ΔE of -0.209 eV is obtained and the corresponding internuclear distances are considerably shorter than those predicted with the 4s basis set.

Hence, these results clearly show that the use of basis sets containing only s functions are not adequate for describing the splitting that occurs between the $^3A_{2g}$ and the $^1B_{1g}$ states of H_4 . Further, it is seen that p-orbitals are not only necessary for the accurate determination of equilibrium geometries but also for energy splitting.

Given the above results, qualification of Hund's rule is necessary. Is Hund's rule violated if the highest multiplicity state has a minimum that is lowest only

over a small range of geometries? Or must the entire potential energy curve (surface) lie lowest?

Both the $^3A_{2g}$ and $^1B_{1g}$ states were followed along the D_{4h} surface over a geometry range of $R(H-H) = 1.2$ to 4.0 bohr. These MRD-CI(+Q) results, using basis B, are shown in Figure 7.6. The $^3A_{2g}$ state has a minimum that is lower in energy than the $^1B_{1g}$ state. As can be seen, both states approach the common limit of -2.00 hartree as the molecule is symmetrically stretched. This dissociation limit corresponds to the energy of four isolated hydrogen atoms. The same asymptote limit will be approached for the similar states of any D_{4h} molecule. Furthermore, in the united atom case, the triplet corresponds to an open shell Be atom and the singlet to the closed shell, ground state atom (this is not directly obvious from the figure). Again, in all cases and for all molecules of this type, the triplet will correlate to an electronically excited atom, higher in energy than the singlet. Therefore, at some point along the D_{4h} surface, as R is reduced *the triplet state must be higher in energy than the corresponding singlet state*.

One must also consider the effects of configuration interaction upon the triplet-singlet splitting. Hund's rule states that atoms with equivalent electronic configurations will have that state with the highest multiplicity lying lowest. By including CI, the wavefunctions are linear combinations of the most important configurations. Thus, the actual electronic structure of the two states might change so that they are no longer equivalent.

Summarizing the above discussion, in the case of H_4 it has been seen that at their respective minima the $^3A_{2g}$ state does indeed lie lower than the $^1B_{1g}$ state. Since a triplet arising from the same configuration as a singlet will always

correlate, in the united atom case, to an energetically higher limit and due to mixing of configurations, *Hund's multiplicity rule clearly cannot apply over an entire potential surface*. A more restricted but logical approach would be to apply Hund's rule to the states in question when they are at their respective minima. In this respect, the $^3A_{2g}$ and $^1B_{1g}$ states of H_4 do not violate Hund's rule.

4.3 Five Center Molecules

Much less is known about the H_5^+ molecular ion. To our knowledge, there have been no studies on the pentagonal conformation of this species. A couple of works have been published on charged hydrogen clusters ($H_{(n)}^+$ n =odd) involving a H_3^+ core interacting with H_2 molecules [65],[52]. Both theoretical studies were performed at the TZP CISD level of calculation and find a minimum for H_5^+ in C_{2v} symmetry. Association of a hydrogen molecule with the H_3^+ ring is stable by about 0.33 eV. The H_2 unit is bonded perpendicularly to planar H_3^+ at a distance of 2.45 bohr. The interaction with the charged molecule stretches the H_2 unit slightly, to 1.45 bohr. Accordingly, the corresponding H-H vibration frequency in this C_{2v} conformation of H_5^+ is reduced to about 4150 cm^{-1} . The H_3^+ unit is also somewhat distorted, with H-H lengths of 1.84 and 1.53 bohr. The weak bonding of this $H_2 - H_3^+$ complex is reflected by a stretching frequency of only 520 cm^{-1} [52].

In the case of the ring species, addition of a proton to the unbound $^3A_{2g}$ state of H_4 gives rise the unstable pentagonal H_5^+ ion. With four valence electrons, H_5^+ is considered to be antiaromatic. As in the case of H_4 , H_5^+ has a fully occupied, totally symmetric a_1' MO. However, the additional bonding center in H_5^+ lowers

the non-bonding, doubly-degenerate MOs of H_4 to bonding, degenerate e'_1 MOs in H_5^+ . Also lowered in energy is the non-degenerate, anti-bonding b_{2g} MO of H_4 . This forms part of a degenerate, anti-bonding pair of e''_2 symmetry. The composition of these SALCs are shown below.

$$\begin{aligned}
 \phi_{a'_1} &= \frac{1}{\sqrt{5}}(s_1 + s_2 + s_3 + s_4 + s_5) \\
 \phi_{e'_1}^X &= \sqrt{\frac{2}{5}}(s_1 + s_2 \cos \omega + s_3 \cos 2\omega + s_4 \cos 2\omega + s_5 \cos \omega) \\
 \phi_{e'_1}^Y &= \sqrt{\frac{2}{5}}(s_2 \sin \omega + s_3 \sin 2\omega - s_4 \sin 2\omega - s_5 \sin \omega) \\
 \phi_{e''_2}^X &= \sqrt{\frac{2}{5}}(s_1 + s_2 \cos 2\omega + s_3 \cos \omega + s_4 \cos \omega + s_5 \cos 2\omega) \\
 \phi_{e''_2}^Y &= \sqrt{\frac{2}{5}}(s_2 \sin 2\omega - s_3 \sin \omega + s_4 \sin \omega - s_5 \sin 2\omega)
 \end{aligned} \tag{4.5}$$

The angle ω , in this case, is $\frac{2\pi}{5}$ or 72° .

As in H_4 , due to the high symmetry of the molecule, these SALCs represent the true MOs for the H_5^+ system. The global electronic configuration for the latter is $(a'_1)^2 (e'_1)^2$.

Since the triplet state of square H_4 is the lowest lying state on the D_{4h} surface, the triplet state of H_5^+ is examined here. The corresponding lowest singlet state dissociates to H_3^+ and H_2 . In the ${}^3A'_1$ state, H_5^+ lies well above the $H_3^+ + H_2$ (in ground states) limit, by about 5.2 eV. However, this reaction is spin forbidden. Similar to H_4 , this molecule must decompose to form two hydrogen atoms, making the other component of dissociation H_3^+ . This process releases an energy of only 0.55 eV.

At equilibrium, the H_5^+ molecule has a H-H separation of 2.049 bohr (MRD-

CI(+Q)). This value represents a decrease in internuclear separation of about 5% relative to H_4 . This shortening comes from two effects: a change to the new conformation (pentagon) increases the H-H distance and the presence of a charge contracts the ring. Also important is the stabilization of the non-bonding MOs of H_4 to the slightly bonding MOs of H_5^+ . This too will favor ring contraction.

The calculated SCF frequencies for H_5^+ show that 2 modes destabilize this species. These are the doubly degenerate E_2' and E_1' vibrations. Inclusion of correlation effects at the MP2 level leads to only one imaginary frequency, the E_2' mode. The small magnitude of this vibration (-252 cm^{-1}) indicates the flatness of the surface along that motion. With this large decrease in the $\omega(E_2')$ in going from SCF to MP2, further testing of this vibrational path was done. By using the displacements of the atoms as predicted by MP2, the MRD-CI method was used in order to determine if this vibration mode becomes bound at a higher level of theory. The results show that, as the distortion due to the vibration increases, the energy of the molecule lowers indicating that the dissociation of H_5^+ proceeds downhill along the E_2' mode with no potential barrier.

As stated above, the bond lengths in this molecule are not much shorter than in the more unstable H_4 . At 2.05 bohr, the H-H distances are still too large for significant overlap between adjacent atoms. There is more overlap at the molecular center as is evident in Figure 7.7. This indicates that there is a higher degree of delocalization occurring here.

With the addition of the proton to H_4 , and subsequent change in geometry, the nodal planes are shifted and the non-bonding orbitals of H_4 become bonding in the pentagonal molecule. This will, in itself, create a more stable system relative

to H_4 because of the bonding that occurs with the occupation of the degenerate MOs. As is expected, adding the proton creates more nuclear repulsion because of the decrease in internuclear distances but with the shorter geometries comes more electron-electron repulsion.

Addition of two electrons to H_5^+ formally creates the aromatic H_5^- system. Only one conformation for H_5^- is known to be stable. From theoretical calculations [66], this species has a global minimum in $D_{\infty h}$ symmetry. With two hydrogen molecules on either side of a hydride ion, linear H_5^- is bound in a very shallow potential of 6.7 meV. Such weak stability arises from ion-induced dipole interactions. Hiroa et al. [66] suggest that this anionic species might be detectable at very low temperatures and pressures. This feature suggests that H_5^- may play a minor role in interstellar chemistry but its existence would be difficult to prove. This anion, together with H_6 and H_7^+ are examples of "aromatic" rings according to the $4n + 2$ rule (see discussion below).

The SALCs for H_5^- are identical to those for the five-center cation. And like H_5^+ , these represent the true MOs for the negatively charged system.

Addition of a hydride ion to the square H_4 molecule generates the H_5^- anion in D_{5h} symmetry. The degenerate MOs are now fully occupied giving this system an electronic configuration of $(a'_1)^2 (e'_1)^4$. Both of these MOs are bonding. However, the energy gain from this full occupation of bonding orbitals is not large enough to stabilize the system. The lowest state for this molecule, $^1A'_1$, still lies 1.8 eV about the ground products $2 H_2 + H^-$.

Correlation in this system is extremely important. Since hydrogen has a negative electronic affinity at the SCF level (from Table 6.3, $EA(H) = 0.355$ eV),

proper description of the energy separation between the H_5^- molecule and its dissociation products, $2 H_2 + H^-$, can only be achieved by inclusion of correlation effects. This feature is seen in the large difference in dissociation energies at the SCF and correlated levels of theory (Table 6.8). Specifically, at the SCF level and MRD-CI(+Q) levels, the calculated dissociation energies for H_5^- are -2.456 and -1.803 eV, respectively.

It is interesting to note the relatively short bond distances in H_5^- of only 2.124 bohr. With full occupation of all bonding orbitals, however, this must balance the increased electronic repulsion of the negative charge. By adding two electrons to H_5^+ to generate H_5^- , the corresponding increase in internuclear distance is less than 0.1 bohr.

The highest vibration frequency of H_5^- , 1862 cm^{-1} , has A'_1 symmetry and corresponds to H-H stretching. This property of the ring follows the trend of decreased breathing frequencies but is almost the same as that of H_5^+ . The mode which lowers the energy for H_5^- is larger than that of H_4 even though the dissociation products for H_4 lie relatively lower than those for H_5^- . This vibration, characterized by a rather large 1803 cm^{-1} is illustrated in Figure 7.4. It is important to note that the E'_2 mode for H_5^- is not the same type of vibration that characterizes the decomposition of H_5^+ . This too is illustrated in Figure 7.4.

Apparently, neither theoretical nor experimental data are available for charged, group 1A rings in D_{5h} symmetry. However, theoretical data is available for the corresponding neutral ring systems [8]. In general, there exists in M_5 (D_{5h}) a slight decrease in the atomization energy over that of the smaller M_4 (D_{4h}) compounds. Like the four-centered systems, M_5 clusters are not minima in D_{5h} . The

lowest energy structure has D_{3h} symmetry and has an average increase in binding energy per atom of 0.4 eV more than their planar counterparts. These structures correspond to trigonal pyramidal clusters.

These D_{5h} compounds have shorter M-M distances relative to the M_3 and M_4 clusters. The triangular portions of the D_{3h} (M_5) compounds have bond lengths between 0.1 and 0.2 bohr shorter than in the triatomics. Moreover, the atoms lying above and below the plane exhibit larger distances ($\approx 125\%$ larger than in plane M-M bonds).

A theoretical study of the reaction between N_3^- and N_2 [67] has shown that the pentazole anion, N_5^- , is metastable in D_{5h} symmetry. The electronic configuration of this molecule corresponds to $....(a_1'')^2(e_1'')^4$. This species lies only 0.32 eV above its dissociation products and is trapped in a potential barrier of about 0.23 eV. Nguyen et al. also suggest that N_5^- may be isolated in solution and act as a ligand in sandwich compounds.

4.4 The Benzene Analog: H_6

The H_6 ring has been the focus of interest in the reaction of 3 H_2 molecules forming a six-centered transition state. An early calculation by Wright [2] at the SZ-SCF-MO level of theory determined this transition state at 3.9 eV above three ground state H_2 molecules. The more sophisticated DZP-FCI study of Seel, Bagus, and Ladik [68] report an internuclear distance of 2.06 bohr and an absolute energy of -3.2394 hartree. Finally, a more detailed, 4s3p2d1f basis, CI(+Q) study of H_6 by Taylor et al. [54] gave a $R_{(H-H)} = 1.8652$ bohr and an $E_{min} = -3.4166$ hartree. The height of the transition state was found to be 2.884 eV, much lower

than expected. These authors also reported the following vibrational frequencies: 3038i (B_{2u}), 1122 (B_{1u}), 1326 (E_{2u}), 1484 (A_{2u}), 1574 and 1908 (E_{2g}), 1936 (A_{1g}), and 1978 (E_{1u}) cm^{-1} . The B_{2u} mode represents the in-plane dissociation of the molecule into 3 H_2 molecules.

The H_6 species in D_{6h} symmetry has 2 non-degenerate MOs and 2 sets of degenerate MOs. Just as for H_4 , H_6 has its lowest lying MO of a_{1g} (totally symmetric) character. Lying above this are the degenerate e_{1u} MOs. From simple Hückel molecular orbital theory, these are slightly more bonding in nature than the occupied, e'_1 MOs of H_5^+ and H_5^- . The antibonding molecular orbitals have e_{2g} and b_{1u} symmetry. The SALCs for H_6 are:

$$\begin{aligned}
 \phi_{a_{1g}} &= \frac{1}{\sqrt{6}}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6) \\
 \phi_{e_{1u}}^X &= \frac{1}{\sqrt{12}}(2s_1 + s_2 - s_3 - 2s_4 - s_5 + s_6) \\
 \phi_{e_{1u}}^Y &= \frac{1}{2}(s_2 + s_3 - s_5 - s_6) \\
 \phi_{e_{2g}}^X &= \frac{1}{\sqrt{12}}(2s_1 - s_2 - s_3 + 2s_4 - s_5 - s_6) \\
 \phi_{e_{2g}}^Y &= \frac{1}{2}(s_2 - s_3 + s_5 - s_6) \\
 \phi_{b_{1u}} &= \frac{1}{\sqrt{6}}(s_1 - s_2 + s_3 - s_4 + s_5 - s_6)
 \end{aligned} \tag{4.6}$$

With the first three molecular orbitals of H_6 being fully occupied, this molecule has an electronic configuration of $(a_{1g})^2 (e_{1u})^4$ and is expected to obey the $4n + 2$ rule.

The approach of 3 H_2 molecules to form hexagonal H_6 is endothermic by 3.05 eV. This value is in good agreement with those of Taylor et al. given the

much larger basis set used in their study. The unstable H_4 molecule in the triplet state can be combined with molecular hydrogen to form H_6 . In this case, an energy lowering of 3.35 eV occurs. Neutralization of the H_5^+ molecule with H^- represents another way of generating H_6 in D_{6h} symmetry. This reaction is very exothermic, releasing an energy of 12.94 eV. This is very close to the ionization potential of hydrogen, taking into account the calculated electron affinity of the atom. Similarly, addition of a proton to H_5^- is even more exoergic, giving off 16.42 eV.

Distances between centers in H_6 are smaller than those of the more stable H_5^+ molecule. At the MRD-CI(+Q) level, the H-H distance is predicted to be 1.86 bohr. This is especially interesting since the charge in H_5^+ has a "shrinking" effect on the ring. Regardless of this fact, the H-H distance in H_6 is almost 10% less than in H_5^+ . Again, this result agrees with the findings of Taylor et al.

The large frequency of the energy lowering B_{2u} mode of H_6 characterizes the steepness of the surface on the way down to dissociation. This frequency, calculated to be $2643i\text{ cm}^{-1}$ constitutes the highest imaginary frequency of all the molecules studied so far. This makes sense in that H_6 lies higher in energy relative to its dissociation product than any of the other molecules. The SCF vibrational frequencies predicted for this system are in good agreement with the correlated MP2 frequencies.

An unusual feature of H_6 is the magnitude of the totally symmetric vibrational mode. While the other H_n rings show a decrease in this breathing mode as n increases, H_6 does not follow the general trend. The A_{1g} mode has a frequency of about 2000 cm^{-1} , almost the same as for H_4 and nearly 160 cm^{-1} larger than that

of H_5^- . This finding indicates that the charge delocalization in H_6 is significant.

Also interesting is the magnitude of the correlation energy in H_6 . From Table 6.3, the MRD-CI(+Q) correlation energy is 3.827 eV. Similarly, $E_{(corr)}$ for H_2 is 0.999 eV. Comparison of the two values indicates that H_6 has 0.83 eV more correlation energy than three isolated H_2 molecules. This result also indicates that in this ring less H_2 character exists since the greater degree of correlation means that the electron cloud of H_6 is delocalized relative to H_2 .

Now that the internuclear distances are below 2 bohr, an increase in electron density between the nuclei is also observed (see Figure 7.8). Overlap in the ring center increases slightly over the H_4 and H_5 species, but the hydrogen-to-ring-center distances remain above 1.0 bohr.

Richtsmeier et al. [8] studied hexamers of alkali metals. These D_{6h} species have a slightly higher atomization energy than their smaller ring counterparts and internuclear distances are consequently shorter. Values of 0.82 eV/atom and 5.04 bohr, respectively, have been reported. The hexagonal Li_6 molecule has also been studied by Förner and Seel (FS) using a DZP basis and the coupled-cluster (DZP-CC) method [69]. These authors find slightly different results, with the molecule being most stable at an atomic equidistance of 5.59 bohr. The atomization energy found with this method is reported to be 0.46 eV. According to FS, their results indicated that the 2s electrons are able to form a pseudoaromatic bond system which stabilizes the ring.

In general, M_6 clusters prefer octahedral (O_h) conformations at equilibrium (rather than D_{6h}). The octahedral Li_6 cluster has almost 1 eV/atom of binding energy with a metal-metal distance of 5.47 bohr in this conformation. The

spin-coupled calculations of Tornaghi et al. [70] showed a rather large deviation from the above results, reporting 0.41 eV/atom. Furthermore, they found a D_{3h} structure (a large equilateral triangle composed of four small equilaterals) to be the lowest on the potential surface. The binding energy here was found to be 0.47 eV. Förner and Seel also pointed out the preference of Li_6 to have other than D_{6h} conformations. While they reported this molecule to be stable in equidistant, hexagonal form, they found the O_h structure to be more stable. FS also pointed out that p-orbitals in the atomic basis set are essential for obtaining reliable results and that the number of s functions is not very important.

For N_6 (D_{6h}) a high stability is expected since the azo-compound is isoelectronic with benzene. Lauderdale et al. [1] indicated that, at the SCF level, the N_6 ring is energetically lower-lying than 3 N_2 molecules. However, upon inclusion of correlation, this ring is no longer a minimum on the potential surface. With an out-of-plane vibration stabilizing system, N_6 is predicted to be stable in a boat-like structure. A recent study, performed at the 6-31G/MP4 level, indicates that the energetically lowest-lying conformation of N_6 is a twisted open-chain C_2 structure [71]. This isomeric form of N_6 is predicted to be thermodynamically unstable by nearly 8.2 eV.

4.5 The H_7^+ Molecular Ion

The next ring in the series is H_7^+ . As for H_5^+ , no ring conformation for this system, to our knowledge, has been studied but rather 2 hydrogen molecules bound to a central H_3^+ , again in C_{2v} symmetry [52]. The H_2 units are bound perpendicularly to the central H_3^+ . The addition of H_2 to H_3^+ to form H_5^+ in C_{2v} symmetry releases

about 0.33 eV. However, adding a second H_2 molecule to form H_7^+ (C_{2v}) apports only 0.16 eV of stabilization. Both diatomic units lie further away from the central ring (2.93 bohr) when compared to H_5^+ but with bond lengths of 1.43 bohr, slightly closer to their isolated equilibrium geometries of 1.40 bohr. The H_3^+ unit of H_7^+ is considerably more distorted than that in H_5^+ , with two sides of length 1.79 bohr and the third one at 1.65 bohr (the distance between the H atoms to which the H_2 molecules are attached). Accordingly, the H-H vibration frequency of both H_2 units, at 4465 cm^{-1} , is very nearly that of isolated H_2 and the H_2 - H_3^+ frequency is lowered to 481 cm^{-1} . Interestingly enough, Farizon et al. report the existence of clusters up to H_{13}^+ ($H_3^+(H_2)_5$).

The planar H_7^+ (D_{7h}) cation has six valence electrons and is isoelectronic with H_6 . According to the $4n + 2$ rule, H_7^+ is expected to show aromatic character. Based on the relatively low destabilization of H_6 with respect to 3 H_2 molecules, the H_7^+ ion may be stable relative to $3 H_2 + H^+$.

Adding a proton to the H_6 (D_{6h}) ring can generate H_7^+ with D_{7h} symmetry in the $^1A'_1$ state. The highest occupied molecular orbital (HOMO) of H_6 will be stabilized due to the addition of a bonding center. The SALCs for H_7^+ consist of a single, non-degenerate MO and three pairs of doubly degenerate MOs. These are shown below.

$$\begin{aligned} \phi_{e'_1} &= \frac{1}{\sqrt{7}}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7) \\ \phi_{e'_1}^X &= \sqrt{\frac{2}{7}}(s_1 + s_2 \cos \omega + s_3 \cos 2\omega + s_4 \cos 3\omega + s_5 \cos 3\omega + s_6 \cos 2\omega + s_7 \cos \omega) \\ \phi_{e'_1}^Y &= \sqrt{\frac{2}{7}}(s_2 \sin \omega + s_3 \sin 2\omega + s_4 \sin 3\omega - s_5 \sin 3\omega - s_6 \sin 2\omega - s_7 \sin \omega) \end{aligned}$$

$$\begin{aligned}
\phi_{e'_2}^X &= \sqrt{\frac{2}{7}}(s_1 + s_2 \cos 2\omega + s_3 \cos 3\omega + s_4 \cos \omega + s_5 \cos \omega + s_6 \cos 3\omega + s_7 \cos 2\omega) \\
\phi_{e'_2}^Y &= \sqrt{\frac{2}{7}}(s_2 \sin 2\omega - s_3 \sin 3\omega - s_4 \sin \omega + s_5 \sin \omega + s_6 \sin 3\omega - s_7 \sin 2\omega) \quad (4.7) \\
\phi_{e'_3}^X &= \sqrt{\frac{2}{7}}(s_1 + s_2 \cos 3\omega + s_3 \cos \omega + s_4 \cos 2\omega + s_5 \cos 2\omega + s_6 \cos \omega + s_7 \cos 3\omega) \\
\phi_{e'_3}^Y &= \sqrt{\frac{2}{7}}(s_2 \sin 3\omega - s_3 \sin \omega + s_4 \sin 2\omega - s_5 \sin 2\omega + s_6 \sin \omega - s_7 \sin 3\omega)
\end{aligned}$$

The angle ω is $\frac{2\pi}{7}$ or about 51.43° . The electronic configuration of the H_7^+ ring is $(a'_1)^2 (e'_1)^4$.

The internuclear distance for this molecule is the shortest among all unstable rings. At 1.78 bohr, H_7^+ has an H-H separation not very much larger than H_3^+ . The absolute energy decreases substantially: the protonation reaction $H_6 + H^+ \rightarrow H_7^+$ yields almost 6.4 eV. Furthermore, dihydrogenation of the nearly stable H_5^+ system is exothermic by 3.9 eV. The H_7^+ cation is the only species studied here (other than H_3^+) that is stable relative to hydrogen molecules. Dissociation of the molecule to $3 H_2 + H^+$ requires about 3.4 eV of energy. However, the lower energy products for H_7^+ exist. Formation of H_3^+ and $2 H_2$ releases about 1.22 eV.

The SCF vibrational frequencies of H_7^+ are in good agreement with those calculated at the MP2 level. As it has also been seen for other rings, the largest difference occurs for the imaginary frequency. The degenerate e'_1 mode describes the dissociation path into H_3^+ into $2 H_2$ and has an SCF magnitude of $1975i \text{ cm}^{-1}$. This frequency drops to $1397i \text{ cm}^{-1}$ at the MP2 level. The totally symmetric vibrational, $\nu(A'_1) = 1891 \text{ cm}^{-1}$ (MP2), mode follows the pattern of decreasing magnitude with increasing ring size.

Examination of the $\Psi_{a'_1}^2$ density distribution (Figure 7.8) gives the expected

results: a shortening in the H-H distance increases the overlap between adjacent hydrogens atoms. However, this increase is not substantial and is estimated to be only a few per cent higher than in the H_6 molecule. The overlap at the ring center is reduced below that of H_6 since the H-to-ring-center distance in the cation is larger in this case.

Little or no data is available for inorganic analogues of the H_7^+ ring. A pentagonal bipyramidal, neutral Li cluster, examined by Tornaghi et al. [70], has a binding energy of only 0.1 eV/atom.

4.6 Cubic and Planar H_8

The largest $H_{(n)}$ molecule considered in this study is H_8 . We only know of only one other theoretical work in which planar H_8 (D_{8h}) has been studied. The recent publication by Kucharski, Balková, Szalay, and Bartlett [72] investigates various planar conformations of H_8 to evaluate the capability of a newly developed multireference coupled-cluster method. By fixing the H-H distance at 2.0 bohr, they calculate a DZ FCI energy for the $^1A_{1g}$ state on the D_{8h} surface to be -4.308 037 hartree. This absolute energy is reduced at the DZP-CAS-CI level to -4.363 101 hartree. The improved coupled-cluster method gave similar results. It is further seen that, as the molecule becomes more distorted in D_{2h} symmetry, the total energy drops significantly. This occurs because the molecule is approaching its dissociation limit (4 H_2 molecules).

Two structures were investigated for H_8 , a planar, D_{8h} configuration in the $^3A_{2g}$ state, and a cubic structure (O_h symmetry) having a ground state $^1A_{1g}$.

The molecular orbitals for the planar molecule are similar to those of H_4 .

The H_8 species has a totally symmetric bonding MO of a_{1g} symmetry and a corresponding antibonding MO of b_{2g} symmetry. H_8 also has a degenerate pair of non-bonding orbitals (e_{2g} symmetry). In addition to these, the molecule has a bonding pair of degenerate orbitals of e_{1u} symmetry and a nonbonding degenerate pair of e_{3u} symmetry. The forms of these MOs are shown below, in order of greatest to least stability.

$$\begin{aligned}
 \phi_{a_{1g}} &= \frac{1}{\sqrt{8}}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_8) \\
 \phi_{e_{1u}}^X &= \frac{1}{\sqrt{8}}(\sqrt{2}s_1 + s_2 - s_4 - \sqrt{2}s_5 - s_6 + s_8) \\
 \phi_{e_{1u}}^Y &= \frac{1}{\sqrt{8}}(s_2 + \sqrt{2}s_3 + s_4 - s_6 - \sqrt{2}s_7 - s_8) \\
 \phi_{e_{2g}}^X &= \frac{1}{2}(s_1 - s_3 + s_5 - s_7) \\
 \phi_{e_{2g}}^Y &= \frac{1}{2}(s_2 - s_4 + s_6 - s_8) \\
 \phi_{e_{3u}}^X &= \frac{1}{\sqrt{8}}(\sqrt{2}s_1 - s_2 + s_4 - \sqrt{2}s_5 + s_6 - s_8) \\
 \phi_{e_{3u}}^Y &= \frac{1}{\sqrt{8}}(s_2 - \sqrt{2}s_3 + s_4 - s_6 + \sqrt{2}s_7 - s_8) \\
 \phi_{b_{2g}} &= \frac{1}{\sqrt{8}}(s_1 - s_2 + s_3 - s_4 + s_5 - s_6 + s_7 - s_8)
 \end{aligned} \tag{4.8}$$

The electronic configuration for planar H_8 then corresponds to $(a_{1g})^2 (e_{1u})^4 (e_{2g})^2$. From the previous discussion on H_4 , it was seen that the $^1B_{1g}$ state of that molecule correlates directly with two ground state hydrogen molecules. With the similarities between the electronic configurations of H_4 and H_8 , it was recognized that the singlet state of the latter would similarly dissociate to four hydrogen molecule in the ground state. It is for this reason that the $^3A_{2g}$ of planar H_8 is investigated.

The SALC representing the totally symmetric molecular orbital for cubic H_8

is the same as that of the octagonal H_8 species. However, the similarities between the two end here. Cubic H_8 has a triply-degenerate, fully occupied MO of t_{2g} symmetry lying above the a_{1g} MO. The corresponding anti-bonding MOs are of t_{1u} and a_{2u} symmetry. The non-degenerate anti-bonding MO of cubic H_8 has the same structure as that of planar H_8 . The SALCs for cubic H_8 are shown below.

$$\begin{aligned}
 o_{a_{1g}} &= \frac{1}{\sqrt{8}}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_8) \\
 o_{t_{2g}}^Y &= \frac{1}{\sqrt{40}}(s_1 - s_2 + 3s_3 - 3s_4 + 3s_5 - 3s_6 + s_7 - s_8) \\
 o_{t_{2g}}^Z &= \frac{1}{\sqrt{40}}(3s_1 - 3s_2 - s_3 + s_4 - s_5 + s_6 + 3s_7 - 3s_8) \\
 o_{t_{2g}}^X &= \frac{1}{\sqrt{8}}(s_1 + s_2 - s_3 - s_4 - s_5 - s_6 + s_7 + s_8) \\
 o_{t_{1u}}^X &= \frac{1}{\sqrt{40}}(s_1 + s_2 + 3s_3 + 3s_4 - 3s_5 - 3s_6 - 3s_7 - s_8) \\
 o_{t_{1u}}^Y &= \frac{1}{\sqrt{40}}(3s_1 + 3s_2 - s_3 - s_4 + s_5 + s_6 - 3s_7 - 3s_8) \\
 o_{t_{1u}}^Z &= \frac{1}{\sqrt{8}}(s_1 - s_2 - s_3 + s_4 + s_5 - s_6 - s_7 + s_8) \\
 o_{a_{2u}} &= \frac{1}{\sqrt{8}}(s_1 - s_2 + s_3 - s_4 + s_5 - s_6 + s_7 - s_8)
 \end{aligned} \tag{4.9}$$

Full occupation of the lowest-lying MOs with eight electrons results in the configuration of $(a_{1g})^2 (t_{2g})^6$, corresponding to a ${}^1A_{1g}$ ground state.

Bringing together 2 H_4 rings in the ${}^3A_{2g}$ state to form cubic H_8 allows the pairing of the non-bonding e_2 electrons in each tetratomic fragment. By allowing the H-H distances in each ring to optimize independently, a stationary point on the surface is found at the cubic arrangement. In other words, the cubic arrangement of 2 H_4 rings is energetically preferred to any other structure. The interaction between the two rings lowers the total energy of the system relative to 2 H_4

molecules by 5.09 eV. The reaction $4 \text{ H}_2 \rightarrow \text{H}_8$ (O_h) is even more unfavourable than this, requiring about 7.57 eV. The hydrogen separation in this molecule is only slightly reduced below that of H_4 . At the MP4 level, $R(\text{H-H})$ for cubic H_8 is predicted to be 2.136 bohr.

This compound has two unbound vibrational modes which lower the energy of the system: triply degenerate T_{2u} (-2198 cm^{-1}) and the doubly degenerate E_u (-645 cm^{-1}) (MP2). The SCF predicted frequency for the T_{2u} mode is higher than that predicted at the MP2 level. However, the doubly-degenerate mode is higher at the lower level of theory. These results do not follow the trend of lower imaginary frequencies at higher levels of theory as seen throughout this work. This feature is difficult to explain due to the complex nature of the E_u vibration. This mode, shown in Figure 7.4, represents a rotation of the two H_4 units of the cube in opposite directions with a small degree of puckering in each ring. The large magnitude of the T_{2u} vibration reflects the 7.58 eV height between cubic H_8 and the 4 H_2 products.

The $^3A_{2g}$ state of planar H_8 can be formed by combining 3 $\text{H}_2 + 2 \text{ H}$. This process is energetically unfavourable by 2.79 eV. While the triplet state is 7.36 eV above 4 H_2 molecules, the H_8 ring cannot approach this molecular limit because of symmetry restrictions. The sideways addition of 2 H_4 molecules is quite favourable, releasing almost 5.3 eV. Addition of a hydrogen molecule to H_6 is endoergic by 4.36 eV, indicating rather well the differences in relative stability between the two molecules.

The hydrogen-hydrogen separation in planar H_8 is significantly shorter than in cubic H_8 . At 1.95 bohr, some atomic orbital overlap between adjacent centers

is possible in planar H_8 but not much is seen in the $\Psi_{a_1g}^2$ picture (see Figure 7.10).

The vibrational frequencies determined for this species give rather curious results. As can be seen from Table 6.9, there is a significant change in both the magnitudes of vibrations and the ordering of the modes of vibration at the SCF and MP2 levels. This property generally indicates an extreme rearrangement in the electronic structure of a species upon inclusion of correlation. However, examination of Table 6.8 indicates this not to be the case since the SCF and correlated dissociation energies differ by ≈ 1 eV. No explanation for this phenomenon can be provided.

At the SCF level, the E_{3u} mode has a large imaginary frequency of nearly -3800 cm^{-1} . The MP2 results are much different, showing the B_{2u} vibration to be unbound with a frequency of -533 cm^{-1} . This relatively low number does not reflect well the 2.8 eV incline of the potential energy surface to the $3 H_2 + 2 H$ (ground state) products. This B_{2u} mode corresponds to a ring puckering and it is not clear how this type of vibration can lead to the dissociation products of planar H_8 .

A comparison of the correlation energies of the cube and the planar H_8 species provides some interesting results. From Table 6.3, the correlation energy of the O_h isomer is determined to be $E_{corr} = 5.922$ eV. This value is substantially higher than in the D_{8h} species, with an $E_{corr} = 4.933$ eV, indicating that the degree of electron delocalization is larger for the cube. Both H_8 species are more delocalized relative to $2 H_4$ products ($2E_{corr}(H_4) = 3.748$ eV). The following series summarizes this relationship:

$$E_{corr}(H_8cube) > E_{corr}(H_8ring) > 2 E_{corr}(H_4) \approx 4 E_{corr}(H_2) \quad (4.10)$$

corresponding to (MP4) correlation energies of:

$$5.92eV > 4.93eV > 3.75eV \approx 3.83eV \quad (4.11)$$

There are no known studies of other inorganic D_{8h} systems. However, results of theoretical studies on cubic species are quite abundant. In particular, several investigations of octaazacube, or cubane, (N_8 in O_h symmetry) have been performed. This species has an electronic structure corresponding to $....(a_{2u})^2 (t_{2u})^6 (t_{1u})^6 (t_{2g})^6$. Engelke and Stine [73] addressed the question of cubane's stability using SCF-MP4 methods. These authors discovered that the molecule is metastable, even at the lowest level of theory. They report an N-N internuclear separation of 2.77 bohr (RHF/4-31G*), about 35 % larger than the experimental equilibrium geometry of diatomic N_2 . Also reported is an activation barrier of about 7 eV for N_8 decomposing into 4 N_2 ground state molecules. At the MP4/4-31g* level, this reaction is exothermic by nearly 23 eV making cubic N_8 a potentially useful component of high energy density fuels.

Lauderdale et al. also carried out *ab initio* results for octaazacubane ($N_8 O_h$) [1]. Their study, performed at the CCSD/TZ2P level, corroborate the findings of Engelke and Stine.

4.7 Hückel Theory

Simple Hückel molecular orbital theory is generally applied to p_π -orbitals in systems like benzene. For the molecular orbitals that lie within the molecular plane a localized description is possible. In other words, for the bonding centers in the molecule, there are an equivalent number of electrons and neighbouring atoms. Therefore, in-plane bonding in these types of ringed molecules are of sigma (σ) character.

For the out-of-plane p_z atomic orbitals only a delocalized description can be used to describe the bonding between them. That is, each atomic center has one (p_z) electron but two neighbouring atoms with which it must bond. In HMO theory, these p_z AOs are used as the basis set for a delocalized molecular orbital treatment. The energy of the MO is then determined on a scale relative to the AOs. The energy gain associated with the occupation of these MOs is referred to as the delocalization energy and is generally described as a stabilization force in π -molecules.

Hückel molecular orbital theory has shown itself to be extremely useful in predicting the relative stability of organic molecules [55]. By applying HMO theory to the hydrogen ring systems, the role played by electron delocalization in stabilizing $H_{(n)}$ species can be evaluated.

A summary of the predicted relative stabilities of the Hückel molecular orbital theory, along with the corresponding calculated relative energies, are shown in Tables 6.10 and 6.11.

4.7.1 Two Centered Systems

In simple HMO theory, both H_2^+ and H_2 have the same Hückel matrix:

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \quad (4.12)$$

where the eigenvalues are:

$$\varepsilon_B = \alpha + \beta \quad \text{and} \quad \varepsilon_A = \alpha - \beta \quad (4.13)$$

Here, ε_B and ε_A are the energies of the bonding and antibonding MOs, respectively. From these, the diatomic binding energies (ΔE) can be determined. One finds that, for H_2^+ , $\Delta E = \alpha + \beta - \alpha = \beta$, whereas for H_2 , $\Delta E = 2(\alpha + \beta) - 2\alpha = 2\beta$. These expressions show that the binding energy of H_2 is expected to be exactly twice that of H_2^+ . Data calculated at a higher level of theory as well as experimental results indicate that this is not the case, with ΔE values of 4.605 eV for H_2 and of 2.748 eV for H_2^+ (see previous section). Since $\Delta E(\text{H}_2) \approx 1.68 \Delta E(\text{H}_2^+)$, however, the oversimplistic Hückel model roughly reproduces the relative stabilities of H_2 and H_2^+ .

4.7.2 Three Centered Bonds

The Hückel matrix for equilateral triangular H_3^+ (or similar $\text{X}_{(3)}$ species) is given by:

$$H = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$$

$$(4.14)$$

with solutions:

$$\varepsilon_B = \alpha + 2\beta, \quad \varepsilon_A = \alpha - \beta, \quad \text{and} \quad \varepsilon_A = \alpha - \beta \quad (4.15)$$

This model leads to a binding energy of $\Delta E = 2(\alpha + 2\beta) - 2\alpha$ with respect to the total dissociation of H_3^+ into $2 H + H^+$. For the series H_2^+ , H_2 , and H_3^+ , the atomization energy amounts to β , 2β , and 4β , respectively. Therefore, the stability of H_3^+ relative to $H_2 + H^+$ should be comparable to that of H_2 relative to $2 H$. Using our MRD-CI(+Q) results from Table 6.3, the corresponding ΔE values are 0.101, 0.169, and 0.339 hartree. There is quite excellent agreement between these values and predictions made using HMO theory, especially when one considers the differences in bond lengths in the three compounds.

These HMO predictions for H_2^+ , H_2 , and H_3^+ must be taken with caution. For instance, the unbound H_3 ring has the same Hückel matrix as H_3^+ . This theoretical model predicts H_3 to be stable with an atomization energy of 3β . Therefore, it is clear that predictions made by simple HMO, even for the simplest systems, show that using this method gives inconsistent results.

4.7.3 Antiaromatic, Four Electron Systems

As the first example of "antiaromatic" $H_{(n)}$ rings, the $4n + 2$ prediction of the instability of H_4 agrees with the calculated data. Solution of the Hückel matrix gives a total atomization energy of 4β but zero stability relative to $2 H_2$. The prediction of H_4 being unbound compared with two molecules of hydrogen is indeed correct. However, this model implies that the overall binding energy of

H_4 is the same as in H_3^+ , which is incorrect and again points out the limited application of the Hückel approximation.

From the present results, the H_5^+ ring shows an extraordinarily high relative stability, despite the fact that, having 4 electrons, it is antiaromatic according to the $4n + 2$ rule. The Hückel eigenvalues give a binding energy of 5.236β relative to $4 H + H^+$. This stabilization energy is 1.236β larger than that predicted for H_4 . The relative ΔE computed at the MRD-CI(+Q) level for the total atomization of H_5^+ is 8.63 eV, over three times larger than for H_4 . Furthermore, the HMO model predicts H_5^+ to be unstable by 0.764β compared to $H_3^+ + H_2$ and stable by 1.236β relative to $H_3^+ + 2 H$ products. The former prediction is correct according to the MRD-CI(+Q) calculated dissociation energy of -5.151 eV. However, H_5^+ is *unstable* relative to $H_3^+ + 2 H$ by 0.546 eV.

4.7.4 Aromatic, Six electron Systems

With the bonding e'_1 molecular orbitals being fully occupied, H_5^- is structurally analogous to the stable cyclopentadienyl ion, $C_5H_5^-$. The solution of the Hückel matrix for H_5^- gives a total binding energy of 6.472β relative to $4 H + H^-$. On the other hand, the stability with respect to $2 H_2 + H^-$ is predicted to be 2.472β . While showing a much higher relative stability compared to H_4 , this anionic species is still quite unstable. Its complete atomization energy is calculated to be 7.41 eV (MRD-CI(+Q)), 1.25 eV less than that of H_5^+ .

According to the Hückel model, the H_6 ring (analogous to benzene) should be bound by 8β with respect to 6 H atoms. The MRD-CI(+Q) calculations show agreement with this prediction, evaluating this quantity as 10.76 eV. In

contrast, Hückel molecular orbital theory incorrectly predicts a binding energy of 2β relative to 3 H_2 . This quantity is calculated to be -3.05 eV (MRD-CI(+Q)).

Cyclic H_7^+ is expected to be stable by about 9β with respect to $6 \text{ H} + \text{H}^+$. The total binding energy is found to be 17.06 eV (MP4). The stability relative to $3 \text{ H}_2 + \text{H}^+$, predicted to be almost 3β , is seen to be correct. Compared to this limit, H_7^+ is stable by 3.37 eV . Once again though, the HMO theory is seen to fail when determining stability relative to $2 \text{ H}_2 + \text{H}_3^+$. In this respect, HMO theory says H_7^+ should be bound by nearly 1β . In actuality, the MP4 calculations of this work place H_7^+ at 1.374 eV above this dissociation limit.

4.7.5 The Antiaromatic H_8 Species

As the second example of an "antiaromatic" ring, H_8 (D_{8h}) is predicted to be the most unstable (relative to H_2 components) of all the $\text{H}_{(n)}$ rings studied. Predicted by HMO theory to have the highest atomization (9.657β), more sophisticated calculations show this is not the case. However, comparisons of the atomization energy with those of the other neutral rings indicates that H_8 has the highest binding energy per atom. Also predicted by HMO is a slight stability of 1.657β relative to 4 H_2 molecules and a larger 3.657β compared to 3 H_2 and 2 H atoms. Both are incorrect as is shown by the calculated values of -7.36 eV and -2.797 eV , respectively.

Predictions of atomization and delocalization energies, made by Hückel molecular orbital theory are listed in Tables 6.10 and 6.11, respectively, together with those calculated quantities. Plots of these data are shown in Figures 7.11 and 7.12.

4.7.6 Bond Order

The bond order (BO) of a chemical system can be determined by taking the product of the coefficients of the atomic orbitals between given bonding centers and weighting them by the number of electrons occupying the corresponding MO.

The bond order of the H-H bond in the ring systems has been calculated using the appropriate SALCs. These are presented in Table 6.12.

As is expected, H_3^+ has the highest bond order (0.667). In fact, all the molecules obeying the $4n + 2$ rule have relatively high bond orders. The H_5^- , H_6 , and H_7^+ molecules have BOs in the range of 0.642 to 0.677. Of the antiaromatic species, planar H_8 has the highest BO. Comparable to the $4n + 2$ molecules, this species has a bond order of 0.604. The cubic H_8 has the lowest BO of all the molecules studied (0.455). The antiaromatic H_4 and H_5^+ species have similar bond orders of 0.500 and 0.524, respectively.

Also listed in Table 6.12 are the internuclear distances of the species. From this collection of data, it is difficult to deduce a correlation between the BOs and $R(H-H)$ values. However, by correcting for the effect of charges on the appropriate systems, a clear relationship between the two is observed. This correction for charge was made by adjusting internuclear distances by 10% (adding 10% for positively charged molecules and subtracting 10% for negatively charged species). This approximate factor was determined by placing a negative charge at the center of the H_3^+ molecule. The system was allowed to re-optimize and, at the MP2 level, the new H_3^+ internuclear distances were found to be roughly 10% larger. These values are also presented in Table 6.12. A plot of bond orders and corrected distances for the hydrogen rings (and cube) is shown in Figure 7.13.

The plot reveals an excellent correlation between BO and $R(\text{H-H})$. With increasing bond order, there is a corresponding decrease in internuclear distance. Only the H_3^+ molecule deviates from this general trend.

Despite the rather poor agreement between the energetic properties of hydrogen rings predicted by the HMO theory and the corresponding *ab initio* results, the bond order analysis indicates a strong relationship between bond order and internuclear distances among the various $\text{H}_{(n)}$ species.

4.7.7 Summary

It has been shown here that caution must be taken when applying HMO theory to predict the relative stability of hydrogen rings. While a reasonable agreement among the total binding energies of H_2^+ , H_2 , and H_3^+ is obtained, HMO wrongly predicts H_3 (D_{3h}) to be bound by 33. However, it is well known that H_3 is only slightly stable relative to three hydrogen atoms. Furthermore, while it can be said that Hückel MO theory can be applied to s- or p-orbitals, the resulting molecular orbitals formed from either set of AOs are not the same. Using p_z atomic orbitals generate an MO that is asymmetric about the molecular plane. Moreover, molecules forming these types of out-of-plane MOs (benzene, etc) have a rigid sigma frame, arising from the occupation of bonding in-plane MOs already in place. In other words, while these well known and stable hydrocarbon rings seem to exhibit stability by forming delocalized molecular orbitals, this stability is gained over and above the stability of the in-plane sigma bonding. In the case of hydrogen rings, only delocalized MOs form since each atom has only one electron.

Despite these arguments, certain trends in energetics are noted in the rings.

For the neutral $H_{(n)}$, the trend for increasing atomization energy with increasing n predicted by HMO is roughly obeyed. The charged species show a similar trend with the exception of H_3^+ . Comparing delocalization energies, even though all species except H_3^+ and H_7^+ are unstable in this regard, reveals the trend of aromatic species being less unstable.

Analysis of the bond order of the hydrogen rings reveals a strong relationship between that quantity and internuclear distances corrected for charge.

4.8 Thermochemistry

Additional calculations were carried out to include other systems in the $H_{(n)}$ ($n = 1$ to 8) series (such as H_3 , H_4^+ , H_5 , and H_6^+). Since this study mainly deals with selected rings, the properties of these species (for example, absolute energies, equilibrium geometries) will not be discussed in detail. The absolute energies of these rings are considered only for the calculation of energies of reactions. The energetics of various processes are presented in Table 6.13.

4.8.1 Protonation Reactions

The addition of a proton to a given $H_{(n)}$ ($n=1$ to 6) systems in D_{nh} symmetry ($n=1$ to 6) is invariably an exothermic reaction. In fact, the proton affinity of the neutral rings increases with the number of atoms (n). For example, protonation of H_3 ($(a'_1)^2 (e')^1$) to form H_4^+ ($((a_{1g})^2 (e_u)^1)$) releases an energy of about 4.47 eV. The same reaction involving the larger H_6 ring ($((a_{1g})^2 (e_{1u})^4)$) produces H_7^+ ($((a'_1)^2 (e'_1)^4)$), with an exothermicity of 6.38 eV of energy. This stabilization caused by protonation is easy to explain: by increasing the size of the ring and thereby going from

D_{nh} to $D_{(n+1)h}$ symmetry, the corresponding highest occupied molecular orbital species stabilize. In fact, all molecular orbitals, except the lowest, are stabilized. Consequently, the absolute energy of the $H_{(n+1)}$ product is lower than that of the neutral reactant. Therefore, the following relationship should always hold:

$$E_{H_{n+1}^+} < E_{H_n} \quad (4.16)$$

The degree of stability per atom achieved via protonation decreases with increasing ring size (n), indicating that, perhaps, some asymptotic limit is being approached. This, too, is explainable by the same argument as above.

Consider a circle with radius 2β centered on a point α . Using this circle, the energy of the Hückel molecular orbitals of any planar, cyclic species can be derived by drawing the molecule, point down, within the circle. This is illustrated in Figure 7.14 for a triatomic ring. It is easily seen that, as the D_{nh} group becomes of higher and higher order, the energy of the various MOs become lower but, also with increasing n , the degree of stabilization becomes less. The asymptotic limit is approached as the molecular shape approaches that of a circle ($n \rightarrow \infty$).

The energy released by protonation of larger neutral $H_{(n)}$ rings will eventually approach some limiting value. This is implied by the results of Bagus et al. [68] who have shown that the SCF energy per electron approaches a limiting value for the series H_6 , H_{10} , H_{14} , H_{22} , and H_{30} . Therefore, as the number of atoms in the protonated species increases ($n \rightarrow \infty$), the proton affinity per atom in the ring will approach zero. This trend is shown in Figure 7.15.

Also of interest is the discrepancy between the values of the proton affinities calculated at the SCF and correlated levels. Since a proton has no electron the

correlation energy belongs solely to the neutral molecule being protonated. For example, from Table 6.3, the correlation energy of H_2 is 0.999 eV. The correlation energy of H_3^+ amounts to 1.102 eV. One can see that the E_{corr} belongs almost entirely to H_2 . This should be true for all such processes with only minor differences between SCF and correlated protonation energies. What is seen, however, is a trend of increasing differences between two levels of theory with increasing ring size. For example, the protonation of the H atom to form H_2^+ has a difference in the predicted energy of reaction of 0.01 eV. For H_6 , the difference in protonation energy predicted by the SCF and MP4 calculations increases slightly to 0.27 eV. Larger differences imply that some sort of re-arrangement is occurring during the process. However, from the above discussion, no significant re-arrangement is required for the addition of a proton. What is in fact happening is, with increasing n (electrons), the ability to calculate all of the correlation energy of a given system is reduced. This is a common result and this trend was noted by Seel, Bagus, and Ladik [68] in their study of large (H_6 , H_8 , H_{14} , and H_{30}) hydrogen ring systems.

4.8.2 Dihydrogenation

The thermochemistry of selected dihydrogenation reactions ($H_n + H_2 \rightarrow H_{n+2}$) are shown in Table 6.13.

The most striking feature arising from the data is the following: *products with 2 (H_3^+) or 6 electrons (H_6, H_7^+) have positive energies of reaction.* In other words, parent H_n systems with 0 (H^+) or 4 electrons (H_4, H_5^+) stabilize through dihydrogenation. For reactants with $4n + 2$ electrons, the dihydrogenation process creates a product that does not have $4n + 2$ electrons and the processes are

endothermic. The stabilization that occurs upon forming products with 2 or 6 electrons is illustrated in the following examples: $H_4 + H_2 \rightarrow H_6$, $\Delta E = 4.518$ eV, $H_5^+ + H_2 \rightarrow H_7^+$, $\Delta E = 2.863$ eV. Conversely, the formation of the H_4 and H_5^+ reactants above, through dihydrogenation, destabilizes the systems by 6.288 and 5.150 eV, respectively.

So, while the predictions made by HMO theory about the absolute stabilities are generally incorrect, the series of dihydrogenation reactions discussed here affords some credibility to the $4n + 2$ rule. This is illustrated in Figure 7.16.

It is more difficult to make predictions based on this even smaller series of reactions. However, by simple extension of the ideas outlined in the previous section, it is believed that the degree of stability achieved by forming molecules obeying the $4n + 2$ rule by dihydrogenation will decrease with increasing n but remain positive. On the other hand, the degree of instability will also decrease for molecules formed without $4n + 2$ electrons but remain negative. In other words, for reactions involving large systems: $H_n + H_2 \rightarrow H_{n+2}$, product has $4n + 2$ electrons, $\Delta E > 0$, but small. Similarly, $H_n + H_2 \rightarrow H_{n+2}$, product has $4n$ electrons, $\Delta E < 0$, but small.

There is a curious difference between the energies for dihydrogenation reactions at different levels of theory. One immediately notices a large energy difference when H_2 is reacted with an open-shelled molecule to form a closed-shell ring. For example, at the SCF level, the reaction $H_5^+ + H_2 \rightarrow H_7^+$ is predicted to release 2.863 eV. However, inclusion of correlation increases this reaction energy by more than 1 eV, to 3.866 eV. This in itself is not unusual since by going from an open- to a closed-shell electronic structure requires significant re-arrangement

of the electron cloud in the reactant ring. However, what is interesting is the small energy differences for closed-shell reactants forming open-shell products. A similar degree of re-arrangement must occur but, energetically speaking, it is much less visible. The energies predicted at the SCF and correlated levels for the process forming H_8 from H_6 differ by only 0.23 eV.

4.8.3 Neutralization Reactions

Neutralization reactions of the type $H_n^+ + H^- \rightarrow H_{n+1}$ are highly exothermic (see Table 6.13). However, in the five cases studied here, the reactions can be categorized into two groups: those forming a molecule with $4n + 2$ ($n = 0.1$) electrons and those not doing so. It can be seen that more energy is released when an anti-aromatic cation is neutralized to form an aromatic product (or simply a molecule with $4n + 2$ electrons). For example, the neutralization reactions forming H_2 and H_6 are exothermic by about 17.6 and 14.3 eV of energy, respectively. For the processes forming antiaromatic products like H_4 and H_8 , the reaction energies are much smaller: these neutralizations release about 6.8 and 6.9 eV, respectively.

For the formation of an aromatic ring through the addition of a hydride, the reactant species must be antiaromatic. In the case of H_7^+ being neutralized to form H_8 , the reactant has half-filled, slightly bonding MOs. The addition of another bonding center (H^-) lowers the HOMOs of H_7^+ which stabilizes the system. More energy is released when these orbitals are completely filled with the two electrons of the hydride ion. The same process occurs for an aromatic reactant. In this case, however, the HOMO for these types of rings are already completely filled. Addition of a hydride lowers the MOs, releasing energy but the added electrons

occupy non-bonding (in the case of $\text{H}_3^+ + \text{H}^- \rightarrow \text{H}_4$) or only slightly bonding ($\text{H}_2^+ + \text{H}^- \rightarrow \text{H}_3$) orbitals. This explains the difference between neutralization energies of the two types of molecules.

The degree of stabilization of the MOs decreases with increasing n and therefore a generally lower neutralization energy will be yielded with increasing ring size. This trend should apply to both types of reactions.

4.8.4 Altering Nodal Structure

The three reactions displayed at the bottom of table 4.5 are unique: all $\text{H}_5^?$ products ($q = -1, 0, +1$) belong to the D_{3h} point group but the total number of electrons is different. The H_4 square molecule is the smallest ring studied here having electrons in non-bonding orbitals. By adding another H center to the ring, the effects of shifting the nodes can be examined. The stability of molecules in D_{3h} symmetry can be evaluated on this basis. These results are illustrated in the relative energy diagram shown in Figure 7.17.

Addition of another bonding center to H_4 in the form of H^+ , H, or H^- is an exothermic process in all cases. The highest energy release corresponds to the protonation reaction. The liberation of 5.77 eV can be attributed to the shifting of the non-bonding MOs in H_4 to the bonding MOs in H_5^+ . The reaction of H_4 with a hydrogen atom to form H_5 stabilizes the system to a lesser degree. This stability comes from the energy lowering of the non-bonding MOs of H_4 and the occupation of the added H electron to these lowered MOs. Similarly for the $\text{H}_4 + \text{H}^-$ reaction, molecular orbitals are lowered in energy and are now fully occupied.

Chapter 5

Conclusions

The results of this work indicate that all hydrogen rings with four or more centers are invariably unstable. In all these species, the hydrogen atom is forced to become divalent, a state which is rarely seen but does exist in molecules like B_2H_6 and Be_2H_4 . In both of these bridged molecules, electron deficient covalent bonding occurs. For diborane, the B atom hybridizes to sp^3 and these AOs are oriented in space so that both boron hybrid orbitals can simultaneously overlap with the hydrogen 1s orbitals. This also occurs for the beryllium compound. Most of the hydrogen ring compounds have distances about twice the radius of the 1s hydrogen orbital and, hence, simultaneous overlap of the 1s orbitals between adjacent 1s orbitals (atoms) does not occur.

Application of Hückel molecular orbital theory predicts all hydrogen rings except H_4 to be stable. Since the HMO model does not take Pauli's principle into account (that is it cannot distinguish between singlet and triplet states), the relative energies of the systems may be compared to the stability predictions made by the $4n + 2$ rule without taking into account symmetry the restrictions of dissociation.

In this case, the relative stability of the rings compared to their energetically lowest products shows a pattern following the $4n + 2$ rule. The "antiaromatic" H_4 , H_3^+ , and H_8 systems lie 6.33, 5.08, and 7.36 eV above their products, respectively. On the other hand, the "aromatic" H_5^- , H_6 , and H_7^+ molecules are relatively more stable, lying 1.62, 3.00, and 1.22 eV above products, respectively. However, the stabilizing effects of charge cannot be discounted. All positively charged species, including H_3^+ , can be considered to be more stable due to the imbalance of charge. More specifically, cationic rings can be thought of as positive centers attracted to a central cloud of electrons. The H_5^+ molecule also fits into this scheme if it is considered to dissociate to its symmetry allowed limit of H_3^+ and 2 H atoms.

The relative stability of H_7^- mainly arises from its relatively high lying products, one of which is the H^- anion, and through the full occupation of bonding orbitals. In other words, bringing together two H_2 and a H^- requires a given (relatively small) amount of energy. This situation is slightly alleviated by the electrons occupying bonding molecular orbitals. In fact, the orbital energies of H_7^- lie substantially higher in energy than those of "antiaromatic" H_4 .

HMO theory also fails when applied to systems topologically similar to the hydrocarbon rings. Hexaazabenzene (the $6-\pi$, nitrogen analog of benzene), is expected to be quite stable. However, theoretical calculations indicate the most likely conformation for this molecule to be a "boat"-like structure. By the same token, N_4^{2-} should be unstable according to HMO theory but is seen to be metastable with large positive frequencies.

Lithium rings are known to have absolute minima on their potential energy surfaces near or at the D_{nh} geometries. While Li ($1s^2 2s$) is isoelectronic with

hydrogen, other interactions are suspected to be occurring which makes them bound relative to their components. Since first row atoms are known to undergo hybridization easily, in-plane p-orbitals may aid in the stability of these molecules. This type of interaction is seen to occur in the very stable B_3 (D_{3h}) molecule.

The values of the totally symmetrical vibrational modes indicate that H-H stretching show a steady, decreasing trend for all hydrogen rings, with the exception of H_6 . This indicates that the H_2 subunits of the molecule retain more identity upon forming the ring. This finding is somewhat contradictory since it would indicate that H_6 has the degree of instability of one of the antiaromatic molecules.

It is suggested here that Hund's rules should only be applied to the absolute minima of the D_{4h} SCF surface. By applying the rule to CI surfaces, the general precept that the rule only be applied to two states of the same configuration is being violated. Moreover, since any system in D_{4h} symmetry will experience a crossing in the singlet and triplet curves at least twice over a large geometry range, the rule should only be applied to the absolute minimum that occurs on the surface. It was shown here that the lowest lying state on the D_{4h} surface, at the SCF level, is the $^3A_{2g}$ state indicating that H_1 does not violate Hund's rule after all.

The results of this work have filled a visible void in the knowledge that has accumulated over the years on ring systems. As such, the findings of this thesis have recently been published [74].

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Chapter 6

Tables

Table 6.1: Basis set A, 311+G* (6s1p/4s1p) used with the GAUSSIAN-90* program.

<i>Function</i>	<i>Exponent</i>	<i>Coefficient</i>
s	33.865000	0.025494
	5.094790	0.190373
	1.158790	0.852161
	0.325840	1.000000
	0.102741	1.000000
	0.036000	1.000000
p	0.750000	1.000000

* Ref. [23].

Table 6.2: Basis set B (10s2p/6s2p) used with the MRD-CI* package program.

<i>Function</i>	<i>Exponent</i>	<i>Coefficient</i>
s	837.219740	0.000112
	123.524314	0.000895
	27.704222	0.004737
	7.825986	0.019518
	2.565036	0.065862
	0.938258	1.000000
	0.372145	1.000000
	0.155838	1.000000
	0.066180	1.000000
	0.036000	1.000000
p	0.938258	1.000000
	0.066180	1.000000

* Refs. [16],[17],[14],[15].

Table 6.3: Total energy of hydrogen rings at optimized geometries for SCF and MP4 calculations (basis A) and MRCI(+Q) (basis B) (All distances in bohr, energies in hartree).

<i>Species</i>	<i>State</i>	<i>Group</i>	<i>SCF</i>		<i>MP4</i>		<i>MR-CI (+Q)^a</i>	
			<i>R</i>	<i>E</i>	<i>R</i>	<i>E</i>	<i>R</i>	<i>E</i>
H	² S	<i>O_h</i>	—	-0.499 818	—	-0.499 818 ^b	—	-0.499 998 ^b
H ⁺	¹ S	<i>O_h</i>	—	-0.486 963	—	-0.512 850	—	-0.520 010
H ₂ ⁺	² Σ _g ⁺	<i>D_{∞h}</i>	1.9827	-0.601 180	—	—	1.9752	-0.600 969 ^b
H ₂	¹ Σ _g ⁺	<i>D_{∞h}</i>	1.3897	-1.132 507	1.4021	-1.167 707	1.4016	-1.169 224
H ₃ ⁺	¹ A ₁ ⁺	<i>D_{3h}</i>	1.6428	-1.298 530	1.6561	-1.336 377	1.6490	-1.339 044
H ₄	³ A _{2g}	<i>D_{4h}</i>	2.1521	-2.033 938	2.1726	-2.102 795	2.1867	-2.106 770
H ₅ ⁺	³ A ₁ ⁺	<i>D_{5h}</i>	2.0373	-2.241 760	2.0521	-2.317 294	2.0492	-2.318 967
H ₅ ⁺	¹ A ₁ ⁺	<i>D_{5h}</i>	2.1318	-2.661 713	2.1184	-2.788 919	2.1240	-2.792 183
H ₆	¹ A _{1g}	<i>D_{6h}</i>	1.8593	-3.254 946	1.8608	-3.392 753	1.8596	-3.395 583
H ₇ ⁺	¹ A ₁ ⁺	<i>D_{7h}</i>	1.7680	-3.479 486	1.7792	-3.627 079	—	—
H ₈	¹ A _{1g}	<i>O_h</i>	2.1361	-4.174 935	2.1401	-4.392 582	—	—
H ₈	³ A _{2g}	<i>D_{8h}</i>	1.9182	-4.219 053	1.9541	-4.400 331	—	—

^a All calculations were performed with 1 reference configuration (MRCI=SDCI) except for H₄, which required from 7 to 23, depending on the particular electronic state. In all cases except H₄ the contribution of the dominant reference configuration exceeded 93%.

^b SCF energy.

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Table 6.4: Comparisons of selected theoretical and experimental results on H_3^+ (D_{3h}).

Ref	Method	$R_{(H-H)}$ (bohr)	Energy (au.)	$\nu_1^\dagger$ cm^{-1}	$\nu_2^\ddagger$ cm^{-1}
[75]	DZP STO CI	1.6575	-1.332 640	3354	2790
[76]	15 term corr. GF	1.6495	-1.341 176	3272	2735
[77]	GLF SZ SCC	1.6405	-1.342 030	—	—
[78]	81 CGTO PNO-CI	1.6525	-1.341 880	3332	—
[79]	10s4p2d FCI	1.6504	-1.343 400	—	2521
[80]	GF Random walk	1.6500	-1.343 760	—	—
[32]	Experiment	1.6500	—	3177	2521

† Totally symmetric (breathing) mode. ‡ Asymmetric stretching.

Table 6.5: Comparisons of selected theoretical and experimental results on H_4 (D_{4h}).

Ref.	Method	State	$R(\text{H-H})$ (bohr)	Energy (a.u.)	E_{rel}^a (eV)
[44]	Min STO. CI	$^1\text{B}_{1g}$	2.60	-2.060 000	6.42
		$^3\text{A}_{2g}$	2.54	-2.037 000	7.10
[46]	DZ CI	$^1\text{B}_{1g}$	2.47	-2.075 000	6.20
		$^3\text{A}_{2g}$	2.38	-2.062 000	6.55
[43]	DZ FCI	$^1\text{B}_{1g}$	2.437	-2.078 490	6.16
		$^3\text{A}_{2g}$	2.340	-2.068 270	6.44
[81]	3-1G SCF-MO-CI	$^1\text{B}_{1g}$	2.2	-1.969 700	9.96
		—	—	—	—
[50]	5s2p CAS(4.4)-CISD(+Q)	$^1\text{B}_{1g}$	2.438	—	6.47
		—	—	—	—
This Work	10s2p/6s2p MRD-CI(+Q)	$^3\text{A}_{2g}$	2.181	-2.106 770	6.034
		$^1\text{B}_{1g}$	2.312	-2.099 790	6.456

^a relative to two H_2 molecules.

Table 6.6: Absolute and relative energies for the four electronic states of H_4 arising from the $a_{1g}^2 e_u^2$ configuration. The equilibrium internuclear distance is also given.

State	MR-CI			MR-CI(+Q)		
	R (bohr)	E (hartree)	E_{rel}^a (eV)	R (bohr)	E (hartree)	E_{rel}^a (eV)
$^3A_{2g}$	2.1814	-2.10434	6.370	2.1867	-2.10677	6.304
$^1B_{1g}$	2.3117	-2.09979	6.494	2.3135	-2.10121	6.456
$^1A_{1g}$	2.2403	-2.02393	8.558	2.2396	-2.02594	8.504
$^1B_{2g}$	2.0532	-2.00987	8.669	2.0488	-2.02207	8.609

^a Relative to 2 molecules of H_2 in the ground electronic state.

Table 6.7: Total energies (hartree) and energy differences (eV) for the $^3A_{2g}$ and $^1B_{1g}$ states of H_4 using various basis sets.

Basis set	State	R(H-H) (bohr)	E(MRD-CI(+Q))	$\Delta E_{(T-S)}$ (eV)
4s	$^3A_{2g}$	2.309	-2.067 864	
	$^1B_{1g}$	2.421	-2.077 334	0.258
5s	$^3A_{2g}$	2.304	-2.068 717	
	$^1B_{1g}$	2.422	-2.078 494	0.266
10s	$^3A_{2g}$	2.317	-2.072 203	
	$^1B_{1g}$	2.435	-2.081 646	0.257
2s1p	$^3A_{2g}$	2.239	-2.040 864	-0.129
	$^1B_{1g}$	2.414	-2.036 115	
4s1p	$^3A_{2g}$	2.186	-2.100 313	-0.103
	$^1B_{1g}$	2.320	-2.096 527	
B	$^3A_{2g}$	2.181	-2.106 770	-0.152
	$^1B_{1g}$	2.312	-2.101 210	
C	$^3A_{2g}$	2.187	-2.119 850	-0.209
	$^1B_{1g}$	2.314	-2.112 179	

Table 6.8: Energy difference (eV) for indicated reactions. Reactants in D_{nh} ring electronic state; products in ground electronic states.

<i>Reaction</i>	<i>SCF</i> ^a	<i>MP2</i> ^a	<i>MP4</i> ^a	<i>MRCI (+Q)</i> ^b	<i>Expt.</i>
$H^- \rightarrow H + e^-$	< 0	0.158	0.355	0.545	0.755 ^c
$H_2^+ \rightarrow H + H^+$	2.758	—	—	2.748	2.793
$H_2 \rightarrow H + H$	3.616	4.371	4.573	4.605	4.748 ^d
$H_3^+ \rightarrow H_2 + H^+$	4.518	4.587	4.590	4.621	4.608 ^e
$H_4 \rightarrow 2H + H_2$	-2.672	-1.969	-1.756	-1.699	—
$H_4 \rightarrow 2H_2$	-6.288	-6.341	-6.330	-6.304	—
^f $H_5^+ \rightarrow H_2 + H_3^+$	-5.150	-5.111	-5.083	-5.151	—
$H_5^- \rightarrow 2H_2 + H^-$	-2.456	-1.617	-1.615	-1.803	—
$H_6 \rightarrow 3H_2$	-3.880	-3.041	-3.003	-3.050	-2.923 ^g
$H_7^+ \rightarrow 2H_2 + H_3^+$	-2.287	-1.317	-1.374	—	—
$H_8 (O_h) \rightarrow 4H_2$	-9.663	-7.577	-7.572	—	—
$H_8 (D_{8h}) \rightarrow 4H_2$	-8.462	-7.407	-7.360	—	—

^a Basis A.

^b Basis B.

^c Ref. [82]

^d Ref. [30]

^e Ref. [83]

^f Note: this dissociation is symmetry forbidden. ^g Ref. [84]

Table 6.9: Harmonic vibration frequencies (cm^{-1}) for hydrogen species.

<i>Species</i>		ν_{SCF}				ν_{MP2}			
H_2		4595				4532			
H_3^+	E'	2859	A'	3539		E'	2797	A'	3498
H_4	E_u	2515 <i>i</i>	B_{2u}	1160		E_u	1654 <i>i</i>	B_{2u}	1181
	B_{1g}	1457	B_{2g}	1858		B_{1g}	1467	B_{2g}	1861
	A_{1g}	2018				A_{1g}	2025		
H_5^+	E'_2	1166 <i>i</i>	E'_1	1035 <i>i</i>		E'_2	252 <i>i</i>	E''_2	855
	E''_2	796	E'_2	1618		E'_1	955	E'_2	1790
	A'_1	1912				A'_1	1904		
H_5^-	E'_2	2099 <i>i</i>	E'_1	1401		E'_2	1803 <i>i</i>	E'_1	1446
	E''_2	1442	E'_2	1572		E''_2	1506	E'_2	1546
	A'_1	1844				A'_1	1862		
H_6	B_{2u}	3231 <i>i</i>	B_{1u}	707		B_{2u}	2643 <i>i</i>	B_{1u}	713
	E_{2u}	1245	B_{2g}	1284		E_{2u}	1267	B_{2g}	1196
	E_{2g}	1636	A_{1g}	1994		E_{2g}	1556	A_{1g}	2002
	E_{1u}	2153	E_{2g}	2300		E_{1u}	2163	E_{2g}	2297
H_7^+	E'_1	1975 <i>i</i>	E''_3	311		E'_1	1397 <i>i</i>	E''_3	309
	E''_2	796	E'_3	1223		E''_2	831	E'_3	1190
	E'_2	1443	A'_1	1801		E'_3	1626	A'_1	1794
	E'_2	2168	E'_3	2729		E'_2	2159	E'_3	2702
H_8 (O_h)	T_{2u}	2742 <i>i</i>	E_u	331 <i>i</i>		T_{2u}	2198 <i>i</i>	E_u	645 <i>i</i>
	A_{2u}	836	T_{2g}	1348		A_{2u}	926	T_{2g}	1312
	T_{2g}	1826	T_{1u}	1842		T_{2g}	1738	T_{1u}	1891
	A_{1g}	2072	E_g	2152		A_{1g}	2098	E_g	2125
H_8 (D_{8h})	E_{3u}	3820 <i>i</i>	E_{2u}	533		B_{2u}	533 <i>i</i>	E_{2u}	563
	E_{2g}	582	E_{3u}	953		E_{2g}	593	E_{3g}	1100
	E_{3g}	1105	B_{2u}	1196		E_{1u}	1105	B_{1g}	1165
	B_{2g}	1226	A_{1g}	1400		A_{1g}	1399	E_{3u}	1466
	E_{1u}	1440	E_{2g}	1702		E_{2g}	1749	E_{3u}	2034
	B_{1g}	1939				B_{2g}	2070		

Table 6.10: Atomization Energies (hartree) of H_n rings.^a

Species	HMO	E
H_2	2β	-0.167 7
H_3^+	4β	-0.336 4
H_4	4β	-0.102 8
H_5^+	5.236β	-0.317 3
H_5^-	6.472β	-0.788 9
H_6	8β	-0.392 8
H_7^+	8.988β	-0.627 1
H_8	9.657β	-0.400 3

^a For uniformity, the MP4 results are tabulated.Table 6.11: Binding Energy Relative to H_2 (Delocalization Energy)^a.

Species	HMO	E
H_3^+	2β	-0.168 7
H_4	0	+0.232 6
H_5^+	1.236β	+0.018 1
H_5^-	2.472β	+0.059 3
H_6	2β	+0.110 4
H_7^+	2.988β	-0.124 0
H_8	1.657β	+0.270 5

^a For uniformity, the MP4 results are tabulated. Energies in hartrees.

Table 6.12: Bond orders and equilibrium geometries (corrected for charge) of hydrogen species.

<i>Species</i>	<i>Bond Order</i>	<i>R_{corr}</i>
H ₃ ⁺	0.667	1.814
H ₄	0.500	2.187
H ₅ ⁺	0.524	2.254
H ₅ ⁻	0.647	1.912
H ₆	0.667	1.860
H ₇ ⁺	0.642	1.957
H ₈	0.604	2.140
H ₈ (<i>O_h</i>)	0.500	1.954

Table 6.13: Thermochemistry of Selected Reactions. ΔE in eV.

Reaction	Product	E_{SCF}	ΔE	Level
$H + H^+$	H_2^+	2.758	2.748	MRD-CI
$H_2 + H^+$	H_3^+	4.518	4.605	MRD-CI
$H_3 + H^+$	H_4^+	4.439	4.473	MP2
$H_4 + H^+$	H_5^+	5.655	5.774	MRD-CI
$H_5 + H^+$	H_6^+	6.025	6.240	MP4
$H_6 + H^+$	H_7^+	6.111	6.376	MP4
$H^+ + H_2$	H_3^+	4.518	4.621	MRD-CI
$H_3^+ + H_2$	H_5^+	-5.150	-5.151	MRD-CI
$H_5^+ + H_2$	H_7^+	2.863	3.866	MP4
$H_2 + H_2$	H_4	-6.288	-6.304	MRD-CI
$H_4 + H_2$	H_6	2.408	3.254	MRD-CI
$H_6 + H_2$	H_8	-4.582	-4.357	MP4
$H^+ + H^-$	H_2	17.566	17.666	MRD-CI
$H_3^+ + H^-$	H_4	6.761	6.741	MRD-CI
$H_5^+ + H^-$	H_6	14.319	15.146	MRD-CI
$H_7^+ + H^-$	H_8	6.874	7.086	MP4
$H_4 + H^+$	H_5^+	5.655	5.837	MRD-CI
$H_4 + H$	H_5	1.741	2.561	MP4
$H_4 + H^-$	H_5^-	2.832	4.715	MRD-CI

Figure 7.1: Electron density distribution for the Ψ_{1g} molecular orbital of H_3^+ .

Figure 7.2: Representation of hybridization of in-plane orbitals occurring in X_3 molecules.

Figure 7.3: Electron density distribution for the $\Psi_{\sigma_{11}}$ molecular orbital of H_4 .

Figure 7.4: Unbound vibrational modes of selected hydrogen species calculated at the MP2 level.

Figure 7.5: Basis set dependence of energy splitting of ${}^3A_{2g}$ and ${}^1B_{1g}$ states of H_4 .

Figure 7.6: Potential energy curves for the $^3A_{2g}$ and $^1B_{1g}$ states of H_4 on the D_{4h} surface.

Figure 7.7: Electron density distribution for the Ψ_0 molecular orbital of H_3^+ .

Figure 7.8: Electron density distribution for the $\Psi_{1,0}$ molecular orbital of H_6 .

Figure 7.9: Electron density distribution for the Ψ_4 molecular orbital of H_7^+ .

Figure 7.10: Electron density distribution for the Ψ_6 molecular orbital of H_8 .

Figure 7.11: Total predicted ($\times$) and calculated (Δ) binding energies (atomization energy) for hydrogen rings.

Figure 7.12: Predicted ($\times$) and calculated (Δ) delocalization energies of hydrogen rings.

Bond Order vs. Corrected Bond Distance

Figure 7.13: Plot of bond order ($\diamond$) versus corrected internuclear distance (R_{corr}) (in bohr) for various hydrogen species.

Figure 7.14: Diagram illustrating how the Hückel delocalized molecular energies of an X_3 can be determined.

Proton Affinity per Atom vs. Number of Atoms with fitting

Figure 7.15: Fitted plot of proton affinity versus number of bonding centers in selected hydrogen rings.

Figure 7.16: Plot of energy release versus product formed from dihydrogenation reactions for various hydrogen rings.

Figure 7.17: Relative energy diagram correlating Π_5^q ($q=-1,0,+1$) with species of H_4 and H .

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