Chapter 2. Theoretical Background

A qualitative overview of the basic aspects of quantum chemistry and computational methods is provided in this chapter. It is intended to give an introduction without excessive detail to the approximations and methods of computational chemistry applied throughout the thesis. These methods are neither exact nor perfect. However, qualitative or approximate computations can give useful insight into chemistry if the researcher understands what they do or do not predict.

2.1. Introduction

The energy and electronic properties of a stationary state of a molecule can be obtained by solving the time-independent Schrödinger equation.[1] This is an eigenvalue equation that cannot be solved exactly, except for simple cases:

$$\hat{H}\,\Psi = \varepsilon\,\Psi \tag{2.1}$$

where $\hat{H}$ is a Hermitian operator called the Hamiltonian operator, Ψ is the exact wave function of the system and ε is the energy of the stationary states, with the lowest energy state being the ground state.

The Hamiltonian operator considers all possible contributions to the total energy of the system arising from the kinetic energy of electrons and nuclei, the attractive potential energy between the electrons and nuclei, and the interelectronic and internuclear repulsive potential energy. The adiabatic or Born-Oppenheimer[2] approximation is one of the most important approximations used to simplify the mathematical expression of the Hamiltonian operator. Since the electron mass is much less than that of the nuclei, the motions of the nuclei are negligible compared to those of the electrons. Hence, the nuclear kinetic term in the Hamiltonian operator can be neglected, and the internuclear repulsion term can be treated as a constant. In other words, we can consider the electrons in a molecule to be moving in a field of fixed nuclei.

The variational method[3] is based on the variational principle and is an important approach for finding approximate solutions to eigenvalue equations. The variational principle states that, given a normalized wavefunction, Ψ, that satisfies the appropriate boundary conditions, the expectation value of the Hamiltonian is an upper bound to the exact ground state energy, ε_0.

$$<\Psi|\hat{H}|\Psi> \geq \varepsilon_0 \tag{2.2}$$

The more accurate the wave function employed, the lower the energy obtained. The variational method uses a normalized trial function Ψ which can be written as a function of a set of parameters and the coordinates of the system; through differentiation the parameters are varied to minimize the energy.

2.2. The many-electron wavefunction

Molecular orbital theory is an approach to molecular quantum mechanics that assigns individual electrons to spin-orbitals to approximate the full wavefunction. The complete wavefunction for a single electron is the product of a molecular orbital (MO) and a spin function. The MOs, $\phi(x,y,z)$, are functions of the Cartesian coordinates x, y, z, while the spin functions, $\alpha(\xi)$ or $\beta(\xi)$, depend on the spin coordinates, ξ. This product, $\phi(x,y,z)\ \alpha(\xi)$ or $\phi(x,y,z)\ \beta(\xi)$, is called a spin-orbital, $\chi(x,y,z,\xi)$.[4]

Since electrons are fermions, the many-electron wavefunction has to be antisymmetric with respect to the interchange of any two of them, that is:

$$\Psi(1,\ldots,i,\ldots,j,\ldots,N) = -\Psi(1,\ldots,j,\ldots,i,\ldots,N) \tag{2.3}$$

The representation of an N-electron wavefunction as a Slater determinant[3,5] satisfies the antisymmetry requirement and also allows for the fact that electrons are indistinguishable:

$$\Psi(1,2,\ldots,N) = (N!)^{-1/2} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix} \tag{2.4}$$

The factor $(N!)^{-1/2}$ is a normalization factor. In this representation N electrons occupy N spin-orbitals without specifying which electron is in which orbital; rows are labelled by electrons and columns are labelled by spin-orbitals. Interchanging the coordinates of two electrons corresponds to interchanging two rows of the Slater determinant, which changes its sign. This representation of the many-electron wavefunction is the simplest MO approximation to the solution of the Schrödinger equation. Within the single Slater determinant description, the motion of electrons with parallel spins is partially correlated (the probability of finding two electrons with parallel spins at the same point in space is zero) but the motion of electrons with opposite spins is not.

2.3. Basis set expansions

A basis set in a vector space is a set of vectors (basis functions) linearly independent, which are able to generate all the vectors of the vector space. The wavefunctions used in quantum chemistry are vectors of an infinite-dimensional complex vector space: the Hilbert space. A complete basis set for this vector space should contain an infinite number of basis functions, but this is impossible from a computational point of view.

Practical applications of molecular orbital theory require that the individual MOs be expressed as a linear combination of a finite set of one-electron functions known as basis functions, φ:

$$\phi_i = \sum_{\mu=1}^{M} c_{\mu i}\varphi_\mu \qquad i = 1, 2, \ldots, M \tag{2.5}$$

where the $c_{\mu i}$ are the MO expansion coefficients. The larger and more complete the set of basis functions the more flexible the description of the orbitals since fewer restrictions are imposed on the location of the electrons in space.

Two types of basis functions have received widespread use: Slater-type (STO)[6] and Gaussian-type (GTO)[7] orbitals. STOs provide a reasonable representation of atomic orbitals but the evaluation of the two-electron integrals is very time consuming. The behaviour of the Gaussians near and far from the nucleus is incorrect. Thus, many more

GTOs than STOs are needed to approximate the orbitals to the same degree of accuracy, but as a consequence of the Gaussian product theorem the computation of integrals is relatively fast. In practice, linear combinations of Gaussians are used to represent the basis functions, which are called contracted basis functions.

When one basis function per atomic orbital is used the basis set is said to be minimum. If two basis functions are used (per atomic orbital) the basis set is called double-zeta; there are other variants. Additional Gaussians can also be added to extend the accuracy of the basis set. For example, polarization functions, those with higher angular momentum than are needed by the atom in its electronic ground state (*p* and higher on hydrogen; *d* and higher on heavy atoms) are added to account for distortion of the atomic orbitals in the molecular environment, giving the wavefunction more flexibility to change shape. Diffuse functions may also be added to account for large electronic clouds in systems where electrons are relatively far from the nucleus, such as molecules with lone pairs, anions, systems in their excited states, and when describing interactions at long distances in systems with van der Waals interactions. These diffuse functions are primitives with small exponents, thus describing the shape of the wavefunction far from the nucleus. The selection of the basis set is a difficult computational problem and is the focus of many research papers.[8]

2.3.1. ***Basis set notation***

Most calculations undertaken today are performed by choosing an existing segmented GTO basis set. A popular family of basis sets, commonly referred to as the Pople basis sets, are indicated by the notation 6-31G. This notation indicates that each atomic core orbital is described by a single contraction of six GTO primitives, and each valence shell orbital is described by two contractions (basis functions), one with three primitives and the other with one primitive, allowing for more flexibility in the description of the valence electrons. This notation identifies a double-zeta basis set, and is very popular when treating organic systems of considerable size. Another Pople basis set is 6-311G, a triple-zeta basis set that will be frequently used in the following chapters.

The Pople basis set notations described above can be modified by adding polarization functions, *e.g.*, 6-311G(d,p): *d* primitives are added to atoms other than hydrogen and *p* primitives are added to hydrogen as well. Another modification in this notation accounts for the inclusion of diffuse functions, *e.g.*, 6-311++G(d,p): a single plus sign indicates that diffuse functions are added to atoms other than hydrogen and a second plus implies that these functions are used for all atoms.

2.3.2. ***Basis set superposition error***

An artificial lowering of the interaction energy of weakly or strongly bound systems, such as dimers, systems with hydrogen bonding interactions, reactant or product complexes, and transition states, is encountered when the basis set used to optimize these systems is not big enough. It is an additional contribution to the inaccuracy of calculations when using a finite basis set. This phenomenon was discovered in 1968,[9] and five years later[10] received the name: basis set superposition error (BSSE).[11]

This phenomenon is easier to understand through an example: to calculate the dimerization energy of a certain molecule with a given basis set, it is possible to subtract the energy of the two infinitely separated monomers from the energy of the dimer, but this procedure involves an inconsistency. When the energy of a monomer is computed, only the basis set functions on its atoms are used to describe each electronic spatial orbital. On the other hand the electrons in the dimer have associated orbitals composed of linear combinations of the basis set functions for twice the number of atoms. The basis set for the dimer is larger than that of either monomer, and this enlargement of the basis results in a non-physical lowering of the energy of the dissociated dimer relative to the separated monomers. The BSSE would vanish in the limit of a complete set on each monomer.

No completely reliable scheme for either eliminating or estimating the BSSE has been given but the approach usually taken to estimate this effect is the counterpoise (CP) method.[12] In this procedure the energies of the “monomeric units” are computed by using the full basis set of the “dimer”. A basis set for each nucleus of the “monomer” is used as

well as the same basis set functions centred at the points in space that would correspond to the equilibrium positions of the other nuclei in the "dimer". In the original procedure the "monomeric units" (*e.g.*, the reactants) upon forming the "dimer" or "intermolecular complex" (*e.g.*, the TS) are not further optimized, *i.e.*, the "monomers" are frozen in their supermolecular geometries.

Estimates of the effects of the BSSE by the CP method have been found to be misleading for hydrogen bonded dimers, since they do not provide quantitative information about the basis set deficiencies.[13] Furthermore, it has been shown that the use of large enough basis sets so that the CP correction is small does not guarantee accurate results and that for smaller basis sets the inclusion of this correction does not systematically improve the accuracy of the calculations.[14] The CP procedure provides only a crude estimate and not an upper bound on the error.[15] Despite these criticisms and the fact that other methods for correcting the BSSE have been discussed in the literature,[16] the CP correction continues to be the most widely used method for this purpose.[17]

2.4. The Hartree-Fock approximation

The Hartree-Fock (HF) approximation,[4,18] which is equivalent to the MO approximation, has played an important role in elucidating modern chemistry. It usually constitutes the first step towards more accurate approximations. It is an independent particle model based on the variational method, which assumes that electrons are non-interacting. The essence of the HF approximation is to replace the complicated many-electron problem, that cannot be solved exactly, by a one-electron problem in which the electronic repulsion is treated in an average way.

The HF equations are eigenvalue non-linear integro-differential equations:

$$\hat{F}\chi_i = \varepsilon_i \chi_i \qquad i= 1,2,\ldots,N \tag{2.6}$$

where $\hat{F}$ is an effective one-electron operator, called the HF Hamiltonian operator defined by:

$$\hat{F} = \hat{H}^{core} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{2.7}$$

In equation (2.7), $\hat{H}^{core}$ is the core or one-electron Hamiltonian operator representing the energy of a single electron in a field of bare nuclei, $\hat{J}$ is the Coulomb operator describing the repulsion energy between two charge distributions, and $\hat{K}$ is the exchange operator arising from the antisymmetric nature of the determinantal wavefunction; it does not have a simple classical interpretation. The second term in equation (2.7) represents the average potential experienced by one electron due to the presence of the other (N-1) electrons.

The operators $\hat{J}$ and $\hat{K}$ are functions of the spin-orbitals, and since $\hat{F}$ itself depends on Coulomb and exchange operators, it also depends on the spin-orbitals which have to be found by applying the variational method. Hence these equations must be solved iteratively by a procedure called the self-consistent-field (SCF) method. An initial guess of the spin-orbitals is made, the average field seen by each electron is calculated and the eigenvalue equation (2.6) for a new set of spin-orbitals is solved. Using the new spin-orbitals, one can obtain new fields and repeat the procedure until self-consistency is reached (*i.e.*, until the fields no longer change and the spin-orbitals used to construct the HF operator are the same as its eigenfunctions).

The solution of the HF eigenvalue problem yields a set of orthonormal HF spin-orbitals $\{\chi_i\}$ with orbital energies $\{\varepsilon_i\}$. The N spin-orbitals with the lowest energies are called occupied spin-orbitals; the remaining members of the set are called virtual or unoccupied spin-orbitals. The Slater determinant formed from the occupied spin-orbitals is the HF ground-state wavefunction, Φ_0, and is the best possible variational approximation to the ground state of the system from the single determinant form.

2.5. The Roothaan-Hall method

The HF equations can only be solved exactly for atoms. No practical procedures are presently available to obtain numerical solutions for molecules. The representation of the HF orbitals as a linear combination of basis functions and the application of the

variational principle lead to a set of algebraic equations, derived by Roothaan and Hall,[4,19] that increase the applicability of the HF method.

The Roothaan-Hall (RH) equations for a closed-shell system (*i.e.*, a system where all electrons are spin paired) are:

$$\sum_{\nu=1}^{M}\left(F_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) c_{\nu i} = 0 \qquad \mu = 1, \ldots, M;\ i = 1, \ldots, N \tag{2.8}$$

Here, ε_i is the one-electron energy of the MO ϕ_i, the $c_{\nu i}$ are the MO expansion coefficients, the $S_{\mu\nu}$ are the overlap matrix elements indicating the overlap between the orbitals, and the $F_{\mu\nu}$ are the elements of the HF matrix:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\sigma}^{M} P_{\lambda\sigma}\left[(\mu\nu \mid \lambda\sigma) - \frac{1}{2}(\mu\lambda \mid \nu\sigma)\right] \tag{2.9}$$

The $H_{\mu\nu}$ are the elements of a matrix representing the energy of a single electron in a field of bare nuclei, $(\mu\nu|\lambda\sigma)$ and $(\mu\lambda|\nu\sigma)$ represent the Coulomb and exchange two-electron integrals respectively, and $P_{\lambda\sigma}$ are the elements of the one-electron density matrix. These equations also must be solved iteratively by the SCF procedure. As the basis set approaches completeness the spin-orbitals obtained in the RH method approach the exact HF spin-orbitals.

The above method, called restricted HF (RHF), is applied only to closed-shell system. For open-shell systems, in which electrons are not completely assigned to orbitals in pairs, the RH equations need modification. The most reasonable procedure is to assign different spatial orbitals to the α and β electrons, resulting in two sets of MOs defined by two sets of coefficients. Hence, two different Fock matrices are generated. This generalization of the RH equations is called the spin-unrestricted HF (UHF) method. Another variant to treat open-shell systems is called the spin-restricted open-shell calculation (ROHF).

2.5.1. ***Spin contamination***

In UHF calculations there are two complete sets of orbitals that use the same set of basis functions but different MO coefficients. These calculations can be performed very efficiently but have the disadvantage that the wavefunctions generated are no longer eigenfunctions of the total spin $\langle S^2 \rangle$ and an error called spin contamination, can be introduced into the calculation.[20]

The solutions to the UHF equations may not be pure spin states, but instead are often contaminated by higher spin states. Spin contaminated wavefunctions have lower total energies associated with them; unrestricted wavefunctions have lower energies than the corresponding restricted wavefunctions. A high spin contamination can affect the geometry, the population analysis, and significantly affects the spin density. Furthermore, spin contamination can slow down the convergence of Møller-Plesset (MP) calculations (*vide infra*). Calculations of transition states and high-spin transition metal complexes tend to be particularly affected by this phenomenon. Values of $\langle S^2 \rangle$ greater than 0.75 (for radicals) show spin contamination, but as derived from experience, when the difference is less than 10%, *i.e.*, $\langle S^2 \rangle$<0.82, spin contamination is negligible.

Spin contamination is often detected in unrestricted MP (UMP2, UMP3, UMP4) and UHF calculations. It is less common to find spin contamination in unrestricted density functional theory (DFT) calculations, and it has little effect on configuration interaction (CI) and coupled cluster (CC) calculations (these methods are described below). Unrestricted calculations often incorporate a spin annihilation step that removes a large percentage of spin contamination from the wavefunction, but does not prevent it.

In an ROHF procedure the orbitals are separated into two classes: doubly and singly occupied orbitals. The doubly occupied orbitals are treated under the RHF formalism while the orbitals with unpaired electrons are treated separately with more complex expressions. In ROHF calculations there is no spin contamination but they require

additional CPU time. ROHF computations give good total energies and wavefunctions, however, they do not include spin polarization and hence are not useful for some purposes.

An approach to obtaining reliable wavefunctions in cases of spin contamination is to run an unrestricted calculation and then to project out the spin contamination after the wavefunction has been obtained (PUHF, PMP2).[21] Spin projection nearly always improves *ab initio* results (except in cases of very high spin contamination) but seriously affects the accuracy of DFT calculations.

If spin contamination is small, unrestricted methods can be used preferably with spin-annihilated wavefunctions and spin projected energies. When spin contamination becomes significant, spin-restricted open-shell or highly correlated methods should be used.

2.5.2. ***Symmetry breaking***

The symmetry breaking or 'symmetry dilemma', as named by Löwdin,[22] is an artefact caused by the inadequate approximate solution of the electronic Schrödinger equation (due to oversimplified forms assumed for the wavefuction). Apparently, this phenomenon results from a dominance of the orbital localization effect over the resonance effect and leads to different solutions for the ground electronic state of certain chemical species corresponding to equilibrium geometries that are not connected on the same potential energy surface. An example of such a case is the NO_3 radical[23] which will be discussed in Chapter 6, but this problem can also be encountered in closed-shell systems. It is usually confronted in systems of high nuclear symmetry, although completely unsymmetrical molecules can also have geometries at which there is more than one optimal wavefunction of a limited functional form with the same energy. In such cases the potential energy surface will incorrectly display a cusp, and the calculated wavefunction will be discontinuous.[24]

The benzene molecule has D_{6h} ground-state symmetry, but calculations performed a few years ago indicated the existence of single determinants associated with the D_{3h} symmetry, which has a considerably lower energy than the corresponding determinants of symmetry D_{6h}.[25] More examples of this phenomenon can be found in solid state theory.

Imposition of symmetry conditions constitutes a reduction in flexibility in the wavefunction: a variational constraint. Consequently, even though the exact wavefunction may possess certain symmetry properties, in practical calculations a variationally better result can be achieved, *i.e.*, a lower energy, by not constraining the calculation to display these properties.[26]

The Jahn-Teller (JT) effect[27] is a consequence of the degeneracy of states in a symmetric molecule. It is encountered when two or more electronic states that coincide (degenerate) or are relatively close in energy (pseudo-degenerate) become sufficiently strongly mixed when the nuclei are displaced from their initial reference configuration. The potential energy surface has a double cone structure for small displacements from the high-symmetry point. As a result of this interaction between states the symmetric system becomes distorted to a lower symmetry structure. The simplest example of a JT unstable state involves a ^2E state of a molecule with D_{3h} symmetry. If the highest occupied MOs are degenerate and partially occupied, such as for the CH_3O radical, the highest symmetric structure C_{3v} will distort to a C_s structure because of the JT effect. Another example is the JT distortion ($T_d \rightarrow C_{2v}$) in the methane radical cation, $CH_4^{+\cdot}$.[28]

It should be clear that the symmetry breaking phenomenon and the JT effect are consequences of two different situations, although these topics could lead to some confusion.

2.6. The correlation energy

Electron motion is correlated, *i.e.*, the motion of every electron depends on the motion of its neighbours. HF theory describes this incompletely, considering only some correlation of the motions of electrons with the same spin ("exchange hole"). This is a consequence

of the single-determinant representation of the many-electron wavefunction and leads to calculated (HF) energies which are above the exact values, and also to a number of qualitative deficiencies in the description of electronic structures.

The SCF or HF approximation implies that an electron of the system interacts with the other electrons according to their average location. In reality, however, the electronic motion occurs according to the electrons' actual placement. The Coulomb repulsion between electrons becomes sufficiently reduced only when a correlated motion of the electronic system takes place. This aspect of the electron motion is not contained in the independent-electron or SCF approximation.[29] What is missing is the correlation hole every electron carries along to prevent other electrons from coming too close, and thus reducing their mutual Coulomb repulsion. This correlation hole can be seen as a combination of the Coulomb hole, that keeps two electrons apart due to coulombic interactions, and the Fermi hole, that prevents electrons of the same spin from being in the same point of space. The Fermi hole is a purely quantum mechanical phenomenon and is not related to the charge of electrons.

The difference between the exact N-electron wavefunction and its HF counterpart is related to the correlation aspect of the electron motion. Löwdin gave the most often used definition of the correlation energy:[30]

> *"The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration."*

There are a variety of procedures for improving upon the HF approximation, which are classified as post-HF or post-SCF methods. Some of these methods are discussed in the following sections.[31]

If electron correlation is viewed as an inadequacy of the single configuration HF approximation, two different effects can be identified. The first is the influence of other

configurations that are low-lying in energy and that mix strongly with the HF configuration. These give rise to non-dynamical correlation, which can usually be dealt with by multiconfigurational SCF techniques (*vide infra*). This effect is very important when dealing with open-shell systems like excited states, radicals or transition metals. The second effect (dynamical correlation) arises from the interelectronic repulsion, described by the term (r_{ij}^{-1}) in the Hamiltonian operator, and gives rise to dynamical correlation. This term (r_{ij}^{-1}) is singular as $r_{ij} \rightarrow 0$, but mathematical studies of the properties of exact wavefunctions show that they must contain cusps in r_{ij} to cancel this singularity. Thus, the cusp behaviour must be described to properly treat dynamical electron correlation. Methods such as MP, CI and CC (*vide infra*) are frequently used for this purpose, among others. There is no sharp dividing line between non-dynamical and dynamical correlation, and methods for treating one will undoubtedly account in some part for the other.

2.6.1. ***Configuration interaction***

The configuration interaction (CI) method[32,33] is conceptually the simplest procedure to account for correlation energy. The exact wavefunction Ψ is represented as a linear combination of N-electron trial functions (Slater determinants) often referred to as "configurations", "configuration state functions", or simply "configuration functions" (CFs):

$$\Psi = \sum_{R} c_R \Phi_R + \sum_{S} c_S \Phi_S \tag{2.10}$$

where c_R and c_S are the variational parameters and Φ_R denotes the so-called reference CFs, *i.e.*, those CFs that are dominant from the point of view of the energy criterion. Φ_S denotes the CFs obtained from the reference CFs by replacing one or more of the occupied spin-orbitals by virtual spin-orbitals, and the collective indexes R, S indicate the orbital structure of the individual CF.

In most cases the first sum in (2.10) contains just one term, and the expansion is called "single-reference CI" or simply "CI". In this case the reference function is usually the HF-SCF wavefunction and the CI expansion can be expressed as:

$$\Psi_0 = c_0\Phi_0 + \sum_{s>0} c_s\Phi_s \tag{2.11}$$

Only those CFs of the same symmetry and multiplicity as the reference configuration will have nonzero coefficients in the CI expansion. They are called spin- and space-adapted configurations.

When all possible CFs are included in the CI expansion and no further approximations are made, the CI procedure is called "full CI". The full CI method represents the most complete non-relativistic treatment possible for a molecular system within a certain basis set, but it is impractical except for very small systems. There are various approximations to the full CI calculation where different subsets of all possible CFs are selected. For example, CIS includes only single excitations (but the inclusion of only single excitations does not improve upon the ground state HF energy and wave function, as stated by Brillouin's theorem), CID includes only double excitations and CISD includes single and doubles, *etc*.

The most important criteria for an accurate electron correlation theory are the properties of size-consistency and size-extensivity.[34,35] A size-consistent method[36] is one in which the energy obtained for two fragments at sufficiently large separation is equal to the sum of the energies of those fragments computed separately. This property is of primary importance for correctly describing the energetics of a system relative to its separated parts. A method is size-extensive[37] if the energy is a linear function of the number of electrons. This property is very important if systems with different numbers of atoms are to be compared. Size-extensivity is a more general concept than size-consistency. While a full CI expansion is size-consistent and size-extensive, limited CI expansions are not. Improvements in the theory have been considered to account for this.

The multiconfiguration self-consistent field method (MCSCF) is another CI variant in which a truncated CI expansion is used and both the expansion coefficients and the spin orbitals are determined variationally. This simultaneous optimization makes MCSCF computationally demanding, but accurate results can be obtained with the inclusion of

even a relatively small number of configurations. The complete active-space self-consistent field (CASSCF)[38] method is a special form of the MCSCF method in which the orbital space is divided into three subspaces: inactive, virtual and active orbitals. The active electrons are those that are not in the doubly occupied inactive orbital set. Within the active subspace a full CI treatment is performed.

When the first sum in the expansion (2.10) contains more than one term the CI procedure is called multi-reference CI (MR-CI).[32,39] In this method the set of reference configurations is usually determined through a previous CI calculation. All the single and double excitations from the reference configurations, often singly or doubly excited with respect to Φ_0, are included in the CI expansion. Therefore, the final MR-CI wavefunction will include determinants which are triply and quadruply excited from Φ_0. This method is computationally very expensive.

CI techniques can be classified into two categories, those that start from the SCF approximation and those that bypass the SCF level. Moreover, they can be intended just to improve ground-state wavefunctions or to complete excited-states wavefunctions.

2.6.2. ***Møller-Plesset perturbation theory***

A different systematic procedure for finding the correlation energy that is not variational (*i.e.*, it does not give an upper bound to the exact energy), is perturbation theory (PT). In this approach, the total (perturbed) Hamiltonian of the system is divided in two parts: the unperturbed (zero-order) Hamiltonian, $\hat{H}_0$, which has known eigenfunctions and eigenvalues, and the perturbation, λV, where λ is a dimensionless parameter determining the order of the expansion in the perturbation.

The appropriate solutions to the Schrödinger equation may be expanded in powers of λ:

$$\Psi_\lambda = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\,\Psi^{(2)} + \ldots + \lambda^n\,\Psi^{(n)} \tag{2.12}$$

$$\varepsilon_\lambda = \varepsilon^{(0)} + \lambda\varepsilon^{(1)} + \lambda^2\,\varepsilon^{(2)} + \ldots + \lambda^n\,\varepsilon^{(n)} \tag{2.13}$$

If $\hat{H}_0$ is chosen wisely, the perturbation is small and the perturbation expansion, *i.e.*, the sum of the 1st, 2nd, …, nth order energies, converges quickly. When the HF Hamiltonian is chosen as the zero-order Hamiltonian the procedure is called Møller-Plesset perturbation theory. It is the most economical multi-determinant method and furthermore, is size-extensive.

The Møller-Plesset (MP) energy to first order is the HF energy. The inclusion of the second-order energy correction is designated MP2 and gives the simplest approximate expression for the correlation energy. When third- and fourth-order energy corrections are included the procedures are then referred to as MP3 and MP4, and so on. The results of increasing the order of the MP calculation vary depending on the nature of the chemical system; monotonic, oscillating and diverging convergence can be found.

2.6.3. ***Coupled cluster theory***

The foundations of coupled cluster (CC) theory in the context of quantum chemistry were laid by Čížek[40] in the late 1960s, but it was not until the late 1970s that practical implementations started to take place. CC calculations are similar to CI calculations in that the wavefunction is a linear combination of many determinants, but the way of choosing the determinants in a CC procedure is more complex.

The simplest practical application of the CC approach is to include only double excitations, CCD; single excitations can also be added, CCSD. There have been a variety of approaches to incorporate the effects of triplets.[41] The direct inclusion of triplets, CCSDT, is not practical for large systems. The approach used in this thesis includes the effects of triplets in a perturbative way, CCSD(T).[35,42] This method is probably the most commonly used triples correction, and is empirically observed to be the best behaved.

CC is the most accurate approach so far to treat electronic correlation. These methods are size-consistent, size-extensive and variational (as long as the excitations are included

successively, *i.e.*, CCSD is variational, but CCD is not). A full CC calculation is equivalent to a full CI calculation.

2.6.4. ***Density functional theory***

An alternative to the HF based methods that has been growing in popularity over the past decade is density functional theory (DFT). [32,43] It can be used to do calculations on large systems in significantly less time than the methods previously discussed. Even though DFT is primarily a theory of electronic ground state structure, a variant called time-dependent DFT (TD-DFT) has proved to be successful in the calculation of excited states.[44] So far its application has been restricted to single-reference systems, although various ways to develop DFT for multi-reference systems has been discussed.[45]

Hohenberg and Kohn[46] proved that the ground state energy of an electronic system and all other ground-state electronic properties are uniquely determined by the electron probability density, ρ, although the exact functional (a function of a function) dependence of the energy on density, $E[\rho]$, remains unknown. In addition, for any trial density the energy obtained is an upper bound to the exact energy of the ground state. These are the basic principles behind DFT.

Kohn and Sham,[47] solving equations analogous to the HF equations, obtained an expression for the exact ground-state electronic energy. This energy is expressed in terms of the kinetic energy of the electrons, the attractive potential energy between electrons and nuclei, the Coulomb interaction between the total charge distribution, and the exchange-correlation energy of the system (E_{xc}).

The exchange-correlation energy is also a functional of the density and takes into account all non-classical electron-electron interactions. If E_{xc} is ignored, the physical content of the theory becomes identical to that of the HF approximation. It is the only term for which an exact expression is not known. The main source of error in DFT arises from this functional.

Since DFT depends on an adequate knowledge of $E_{xc}[\rho]$, functionals are constantly being developed, but there is no known systematic way to improve upon a calculation, *i.e.*, a lower energy by a certain DFT method does not guarantee that such a functional leads to more accurate molecular properties. Some functionals are developed from fundamental quantum mechanics, while some are developed by parameterizing functions to best reproduce experimental results. Thus, there are in essence *ab initio* and semi-empirical versions of DFT. The simplest approximation, based only on the electron density, was achieved by making use of the exchange correlation energy per particle of a uniform interacting electron gas. This method is named: local spin density approximation (LSDA).[47]

A more complex generation of functionals uses the electron density and its gradient. Several gradient-corrected (or non-local) exchange and correlation functionals were developed and are known collectively as generalized gradient approximations (GGAs).[48] The most popular correlation functionals include those of Perdew (P86),[49] Lee, Yang and Parr (LYP),[50] and Perdew and Wang (PW91).[51] The exchange functionals more widely used are those derived by Perdew and Wang (PW86)[52] and Becke (B or B88).[53]

A new class of hybrid HF/GGA theories was developed, with precision surpassing that of pure GGAs.[54] These hybrid methods combine functionals from other methods with parts of a HF calculation, usually the exchange integrals. The hybrid functionals developed by Becke can be expressed as a linear combination of HF, LSDA and Becke's gradient-corrected exchange (B or B88) contributions, together with LSDA and gradient-corrected correlation functionals such as: P86, LYP or PW91. A very popular DFT method is named B3LYP. This method combines the B3 hybrid exchange functional (that contains 20% of HF exchange) with the correlation functional LYP. The first exchange functional to be suggested was the Becke half-and-half (BH&H),[55] which includes 50% HF exchange. B3LYP and BH&HLYP will be the functionals used in some chapters of the thesis.

2.7. Semi-empirical methods

The main difficulty in the solution of the RH equations is the evaluation of the two-electron integrals. The bigger the molecular system, the greater the number of integrals to solve. Based on the way computational methods deal with this problem they are classified into *ab initio* and semi-empirical methods. In *ab initio* methods, the integrals are solved for all the electrons of the system and all necessary quantities are computed accurately from the very beginning. On the other hand, semi-empirical methods[32,56] usually employ a minimal basis set for the valence electrons, neglect some of the two-electron integrals and determine the others directly from experimental data, from the corresponding analytical formulae, or from suitable parametric expressions.

Semi-empirical methods were first developed for conjugated π-electron systems, ignoring the σ electrons. The most famous and simplest π-electron theory is Hückel[57] molecular orbital (HMO) theory where all two-electron integrals are set to zero and the π-electron Hamiltonian is written as a sum of one-electron terms; thus electronic repulsions are treated very poorly.

The Pariser-Parr-Pople (PPP) method[58] is a much more substantial π-electron procedure where the inter-electronic repulsions are included in the π-electron Hamiltonian. It was the first SCF scheme for molecular calculations. Some of the two-electron integrals are neglected through the zero differential overlap (ZDO) approximation:

$$(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\, \delta_{\lambda\sigma}\, (\mu\mu|\lambda\lambda) \tag{2.14}$$

that is, all three- and four-centre two-electron integrals are neglected. For atomic orbitals centred on atoms that are not bonded together, the Hamiltonian matrix elements are set to zero, and for those centred on bonded atoms the matrix elements are taken to be empirical parameters.

Extended Hückel theory[59] is the first semi-empirical method where all the valence electrons are considered, but the two-electron repulsion integrals are neglected, among

other simplifications. Since 1965 a variety of SCF semi-empirical procedures were developed. They are generalizations of the PPP method where the ZDO approximation is applied to all the valence electrons at three different levels: CNDO, INDO and NDDO.

In the complete neglect of differential overlap (CNDO) methods,[60] the two-electron integrals (on one and two centres) that involve different atomic orbitals (AOs) centred on the same atom are neglected, and the remaining integrals are assumed to depend only on the atoms to which the AOs belong and not on the actual forms of these AOs.

In the methods based on the intermediate neglect of differential overlap (INDO) approximation,[61,62] one-centre repulsion integrals between AOs on the same atom are not neglected, and thus some exchange integrals enter the expressions for the matrix elements. As in CNDO, parameters are chosen in INDO to give as close agreement as possible to the results of minimal basis set HF-SCF calculations. Other methods (*vide infra*) were developed later with the aim of reproducing not the HF-SCF wavefunctions but rather four gas phase molecular properties, namely molecular geometries, enthalpies of formation, dipole moments and ionization energies.[63,64,65]

A variant of the INDO scheme is the Zerner's INDO method (ZINDO) that will be explained in Section 7.4.1. Another variant, SINDO1 (symmetrically orthogonalized INDO)[66] was designed for the prediction of the binding energies and geometries of compounds containing elements of the 1st and 2nd rows, as well as 3rd row transition metals.

A much less severe approximation than INDO is the neglect of diatomic differential overlap (NDDO), in which none of the one-centre integrals are neglected. The two-centre integrals $(\mu\nu|\lambda\sigma)$, where μ and ν are different orbitals on one atom, and λ and σ are different orbitals on another atom, neglected as well in the INDO methods, are also retained. The most popular NDDO methods currently used are AM1[63] (Austin method 1) and PM3 (parametric method 3). Both are improved versions of the MNDO[65] (modified neglect of differential overlap) method (also based on the NDDO approximation) where

the core-core repulsion function is represented by a more flexible function with several additional adjustable parameters, reducing the overestimated nonbonding repulsions in MNDO. Depending on the nature of the system and information desired, either AM1 or PM3 will usually give the most accurate results obtainable for organic molecules with semi-empirical methods.

Other more recently developed semi-empirical methods are: Feske-Hall (designed for the description of inorganic metal-ligand systems), TNDO (typed neglect of differential overlap, specially parameterized to reproduce NMR chemical shifts) and SAM1 (semi-*ab initio* method 1, that uses a parameterization to estimate correlation effects; this method gives results slightly more accurate than with AM1 or PM3.[67]

The Gaussian methods (G1, G2 and G3) are unique types of computations.[68] These are compound methods that combine the results of several *ab initio* calculations, carried out at relatively low levels of theory, to approximate the result of a single, high level calculation that is too expensive to be practical. These methods arose from the observation that certain *ab initio* methods tend to show a systematic error in the prediction of ground state energies of organic molecules.

Semi-empirical methods continue to be developed because there is always room for improvement of the parameterization scheme and the use of experimental data. They are very practical methods for describing electronic effects in large molecules.

2.8. Geometry optimizations

A potential energy hypersurface (PEH) describes the energy of a molecule with respect to its nuclear coordinates. Stationary points are places on the PEH with a zero gradient vector (the first derivative of the energy with respect to nuclear coordinates). If all the eigenvalues of the Hessian matrix (the second derivative of the energy with respect to nuclear coordinates) are positive, the stationary point is a minimum. If there is one, and only one, negative curvature, the stationary point is a transition state (TS). Points with more than one negative curvature do exist, but are not important in chemistry. Because

vibrational frequencies are basically the square roots of the curvatures, a minimum has all real frequencies, and a saddle point (of first order) has one imaginary vibrational frequency.

All geometry optimizations[69] require an initial guess for which the SCF equations are solved and the energy gradient is calculated. The gradient indicates the direction along the PEH in which the energy decreases most rapidly from the current point as well as the steepness of that slope. The structure is then varied along the energy gradient, and the process is repeated until the gradient of each nuclear coordinate is zero or, in practice, below a pre-set threshold. At this point the geometry has converged and a stationary point has been obtained that can be characterized by a frequency analysis.

There are many different optimization algorithms for finding the set of coordinates corresponding to the minimum energy of a stationary point. Some of these methods are: simplex, Fletcher-Powell, quasi-Newton (Berny algorithm), steepest decent, scaled steepest decent, GDIIS (geometric direct inversion of the iterative subspace), EF (eigenvector following), DFP (Davidson-Fletcher-Powell) and Newton-Raphson.[70]

To find a TS structure, the Hessian matrix has to be computed. The nuclei are moved in a manner that increases the energy in directions corresponding to negative values of the Hessian and decreases energy where there are positive values of the Hessian. A transition structure is a maximum on the reaction pathway and a minimum in all the other coordinates. TSs are more difficult to describe and find than equilibrium geometries.

To verify that the desired TS has been optimized, the frequencies must be calculated. The vibrational mode associated with the negative frequency should describe the motion toward reactants in one direction and products in the other direction. If after visualizing this vibrational mode it is still not clear whether the TS is correct, an intrinsic reaction coordinate (IRC)[71] calculation should be performed; sometimes artefacts of the method employed could lead to erroneous conclusions.

TSs have been computationally determined for many years. Experimentally, it has only recently become possible to examine reaction mechanisms directly using femtosecond pulsed laser spectroscopy.[72] This technique cannot yet be applied to all the compounds that are computationally accessible, and furthermore, they yield vibrational information rather than an actual geometry for the TS.

Usually after a geometry has been optimized at a certain level of theory, the energy of the molecular system is calculated at a higher level that includes more electronic correlation. Computations that do not involve geometry optimization are called single-point calculations.

2.8.1. ***Notation***

The conventional notation, used in this thesis, to describe a particular method or level of theory is as follows:

method 1 / basis set 1 // method 2 / basis set 2

This notation means that after a geometry optimization has been carried out using method 2 with basis set 2, a single point energy calculation is performed using method 1 with basis set 1. Method 1 generally accounts for more electronic correlation energy than method 2; basis set 1 is usually larger than basis set 2, but could also be the same. For example, the notation:

CCSD(T)/6-311G(d,p)//BH&HLYP/6-311G(d,p)

describes a CCSD(T) single-point calculation, using a geometry optimized at the BH&HLYP level, with the 6-311G(d,p) basis set.

2.9. References

1. Schrödinger, E. *Ann. Physik* **1926**, *79*, 361.

2. Born, O.; Oppenheimer, J.R. *Ann. Physik* **1927**, *84*, 457.

3. Szabo, A.; Ostlund, N.S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Dover, New York, 1989.

4. Hehre, W.J.; Radom, L.; Schleyer, P.v.R.; Pople, J.A. *Ab Initio Molecular Orbital Theory*; Wiley, New York, 1986.

5. Slater, J.C. *Phys. Rev.* **1929**, *34*, 1293; **1930**, *35*, 509.

6. Slater, J.C. *Phys. Rev.* **1930**, *36*, 57.

7. Boys, S.F. *Proc. R. Soc. London* **1950**, *A200*, 542.

8. (a) Davidson, E.R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681; Feller, D. (b) Davidson, E.R. in *Reviews in Computational Chemistry*, K.B. Lipkowitz and D.B. Boyd, Eds., Vol. 1, VCH, New York, p. 1, 1990.

9. Kestner, N.R. *J. Chem. Phys.* **1968**, *48*, 252.

10. Liu, B.; McLean, A.D. *J. Chem. Phys.* **1973**, *59*, 4557.

11. (a) Davidson, E.R. *Chem. Phys. Lett.* **1994**, *217*, 48. (b) *ibid.* **1995**, *241*, 146. (c) Kestner, N.R.; Combariza, J.E. in *Reviews in Computational Chemistry*, Volume 13, Lipkowitz, K.B. and Boyd, D.B., Editors, Wiley-VCH, New York, p. 99, 1999.

12. (a) Boys, S.F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. (b) Liu, B.; McLean, A.D. *J. Chem. Phys.* **1989**, *91*, 2348. (c) Handy, N.C.; Pople, J.A.; Shavitt, I. *J. Phys. Chem.* **1996**, *100*, 6007 (This paper gives a biographical synopsis on Boys's work).

13. Frisch, M.J.; Del Bene, J.E.; Binkley, J.S.; Schaefer III, H.F. *J. Chem. Phys.* **1986**, *84*, 2279.

14. Schwenke, D.W.; Truhlar, D.G. *J. Chem. Phys.* **1985**, *82*, 2418.

15. Frisch, Æ.; Frisch, M.J. *Gaussian 98 User's Reference*, Gaussian, Inc., p. 235, 1998.

16. For example, see: (a) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 1884. (b) Surjan, P.R.; Mayer, I.; Lukovitz, I. *Chem. Phys. Lett.* **1983**, *119*, 538. (c) Famulari, A.; Specchio, R.; Sironi, M.; Raimondi, M. *J. Chem. Phys.* **1998**, *108*, 3296. (d) Mayer, I.; Valiron, P. *J. Chem. Phys.* **1998**, *109*, 3360.

17. For example, see: (a) Petterson, L.; Wahlgren, U. *Chem. Phys.*, **1982**, *69*, 185. (b) Bolis, G.; Clementi, E.; Wertz, D.N., Scheraga, H.A.; Tosi, C. *J. Am. Chem. Soc.*, **1983**, *105*, 355. (c) Vargas, R.; Garza, J.; Dixon, D.A.; Hay, B.P. *J. Am. Chem. Soc.*, **2000**, *122*, 4750. (d) Simon, S.; Bertran, J.; Sodupe, M. *J. Phys. Chem. A* **2001**, *105*, 4359. (e) Vargas, R.; Garza, J.; Friesner, R.A.; Stern, H.; Hay, B.P.; Dixon, D.A. *J. Phys. Chem. A* **2001**, *105*, 4963. (f) Alagona, G.; Ghio, C.; Monti, S. *Int. J. Quantum Chem.* **2001**, *83*, 128.

18. (a) Hartree, D.R. *Cambridge Phil. Soc.* **1928**, *24*, 89. (b) Fock, V. *Z. Physik* **1930**, *61*, 126.

19. (a) Roothaan, C.C.J. *Rev. Mod. Phys.* **1951**, *23*, 69. (b) Hall, G.G. *Proc. R. Soc. London* **1951**, *A205*, 541.

20. (a) Schlegel, H.B. *Encycl. Comput. Chem.* **1998**, *4*, 2665. (b) Bally, T.; Borden, W.T. in *Reviews in Computational Chemistry*, Volume 13, Lipkowitz, K.B. and Boyd, D.B., Editors, Wiley-VCH, New York, p. 1 in *Reviews in Computational Chemistry*, Volume 13, Lipkowitz, K.B. and Boyd, D.B., Editors, Wiley-VCH, New York, p. 1, 1999.

21. Schlegel, H.B. *J. Chem. Phys.* **1986**, *84*, 4530.

22. (a) Löwdin, P.-O. *Rev. Mod. Phys.* **1963**, *35*, 496. (b) Löwdin, P.-O. *Adv. Chem. Phys.* **1969**, *14*, 283.

23. Eisfeld, W.; Morokuma, K. *J. Chem. Phys.* **2000**, *113*, 5587.

24. Davidson, E.R.; Borden, W.T. *J. Phys. Chem.* **1983**, *87*, 4783.

25. Pauncz, R.; de Heer, J.; Löwdin, P.O. *J. Chem. Phys.* **1962**, *36*, 2247.

26. Taylor, P.R. in *European Summerschool in Quantum Chemistry*, Book I, B.O. Roos and P.-O. Widmark, Eds., Lund University, Sweden, p. 147, 2000.

27. (a) Jahn, H.A.; Teller, E. *Proc. R. Soc. London A*, **1937**, *161*, 220. (b) Bersuker, I.B. *Chem. Rev.* **2001**, *101*, 1067.

28. Boyd, R.J.; Darvesh, K.V.; Fricker, P.D. *J. Chem. Phys.* **1991**, *94*, 8083.

29. Fulde, P. *Electron Correlations in Molecules and Solids*, Springer-Verlag, 1995.

30. Löwdin, P.O. *Adv. Chem. Phys.* **1959**, *2*, 207.

31. (a) Raghavachari, K.; Anderson, J.B. *J. Phys. Chem.* **1996**, *100*, 12960. (b) Taylor, P.R. in *European Summerschool in Quantum Chemistry*, Book III, B.O. Roos and P.-O. Widmark, Eds., Lund University, Sweden, p. 651, 2000.

32. Atkins, P.W.; Friedman, R.S. *Molecular Quantum Mechanics*, 3rd edition, Oxford University Press, 1997.

33. Schaefer III, H.F. (Ed.) *Methods of Electronic Structure Theory*, Plenum Press, 1977.

34. Young, D.C. *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems*, John Wiley & Sons, New York, 2001.

35. Taylor, P.R. in *European Summerschool in Quantum Chemistry*, Book II, B.O. Roos and P.-O. Widmark, Eds., Lund University, Sweden, p. 365, 2000.

36. Pople, J.A.; Binkley, J.S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *11*, 1.

37. Bartlett, R.J.; Purvis, G.D. *Int. J. Quantum Chem.* **1978**, *14*, 561.

38. Roos, B.O. *Int. J. Quantum Chem.*: *Quantum Chem. Symp.* **1980**, *14*, 175.

39. (a) Buenker, R.J.; Peyerimoff, S.D. *Theor. Chim. Acta* **1968**, *12*, 183. (b) Buenker, R.J.; Peyerimoff, S.D. *Theor. Chim. Acta* **1975**, *39*, 217. (c) Peyerimoff, S.D.; Buenker, R.J. *Adv. Quantum Chem.* **1975**, *9*, 69.

40. Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256.

41. (a) Pople, J.A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (b) Noga, J.; Bartlett, R.J. *J. Chem. Phys.* **1987**, *86*, 7041 (and references therein). (c) Bartlett, R.J. *J. Phys. Chem.* **1989**, *93*, 1697. (d) Bartlett, R.J. in *Modern Electronic Structure Theory*, Part II, Vol. 2, D.R. Yarkony, Ed., World Scientific Publishing, Singapore, 1995.

42. Raghavachari, K.; Trucks, G.W.; Pople, J.A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

43. (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (b) Kohn, W.; Becke, A.D.; Parr, R.G. *J. Phys. Chem.* **1996**, *100*, 12974.

44. (a) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454. (b) Casida, M.E.; Jamorski, C.; Casida, K.C.; Salahub, D.R. *J. Chem. Phys.* **1998**, *108*, 4439. (c) Stratmann, R.E.; Scuseria, G.E.; Frisch, M.J. *J. Chem. Phys.* **1998**, *109*, 8218.

45. Gräfenstein, J.; Cremer, D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2091.

46. Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *B136*, 864.

47. Kohn, W.; Sham, L.J. *Phys. Rev. A* **1965**, *140*, 1133.

48. Parr, R.G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.

49. (a) Perdew, J.P. *Phys. Rev. B* **1986**, *33*, 8822. (b) *ibid.* **1986**, *34*, 7406.

50. Lee, C; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785.

51. Perdew, J.P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

52. Perdew, J.P.; Wang, Y. *Phys. Rev. B* **1986**, *33*, 8800.

53. Becke, A.D. *Phys. Rev. A* **1988**, *38*, 3098.

54. (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) *ibid.* **1996**, *104*, 1040.

55. Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 1372.

56. (a) Thiel, W. in *Advances in Chemical Physics*, I. Prigogine and S.A. Rice, Eds., Vol. XCIII, Wiley, New York, p. 703, 1996. (b) Jug, K.; Neumann, F. *Encycl. Comput. Chem.* **1998**, *1*, 507. (c) Stewart, J.J.P. *Encycl. Comput. Chem.* **1998**, *2*, 1513. (d) *ibid.* **1998**, *3*, 2000.

57. Hückel, E.P. *Z. Physik* **1931**, *70*, 204.

58. (a) Pariser, R.; Parr, R.G. *J. Chem. Phys.* **1953**, *21*, 466, 767. (b) Pople, J.A. *Trans. Faraday Soc.* **1953**, *49*, 1475.

59. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

60. (a) Pople, J.A.; Santry, D.F.; Segal, G.A. *J. Chem. Phys.* **1965**, *43*, S129. (b) Pople, J.A.; Segal, G.A. *J. Chem. Phys.* **1965**, *43*, S136. (c) *ibid.* **1966**, *44*, 3289. (d) Del Bene, J.; Jaffé, H.H. *J. Chem. Phys.* **1968**, *48*, 1807, 4050.

61. (a) Pople, J.A.; Beveridge, D.L.; Dobosh, P.A. *J. Chem. Phys.* **1967**, *47*, 2026. (b) Nanda, D.N.; Jug, K., *Theor. Chim. Acta* **1980**, *57*, 95. (c) Jug, K.; Iffert, R.; Schulz, J. *Int. J. Quantum Chem.* **1987**, *32*, 265.

62. (a) Ridley, J.; Zerner, M.C. *Theor. Chim. Acta* **1973**, *32*, 111. (b) *ibid.* **1976**, *42*, 223. (c) Bacon, A.D.; Zerner, M.C. *Theor. Chim. Acta* **1979**, *53*, 21. (d) Zerner, M.C.; Loew, G.H.; Kirchner, R.F.; Mueller-Westerhoff, U.T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

63. (a) Dewar, M.J.S.; Zoebisch, E.; Healy, E.F.; Stewart, J.P.P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Holder, A.J. *Encycl. Comput. Chem.* **1998**, *1*, 8.

64. (a) Stewart, J.J.P. *J. Comp. Chem.* **1989**, *10*, 209, 221. (b) Stewart, J.J.P. *Encycl. Comput. Chem.* **1998**, *3*, 2080.

65. (a) Dewar, M.J.S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Thiel, W. *Encycl. Comput. Chem.* **1998**, *3*, 1599, 1604.

66. Jug, K.; Bredow, T. *Encycl. Comput. Chem.* **1998**, *4*, 2599.

67. Holder, A.J. *Encycl. Comput. Chem.* **1998**, *4*, 2542.

68. (a) Curtiss. L.A.; Raghavachari, K. *Encycl. Comput. Chem.* **1998**, *2*, 1104.

69. Foresman, J.B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd dition, Gaussian, Inc., 1996.

70. (a) Hehre, W.J. *Practical Strategies for Electronic Structure Calculations*, Wavefunction Inc., Irvine, 1995. (b) Schlegel, H.B. *Encycl. Comput. Chem.* **1998**, *2*, 1136. (c) Schlick, T. *Encycl. Comput. Chem.* **1998**, *2*, 1143.

71. (a) González, C.; Schlegel, H.B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) González, C.; Schlegel, H.B. *J. Phys. Chem.* **1990**, *94*, 5523.

72. Zewail, A.H. *J. Phys. Chem. A* **2000**, *104*, 5660.