Chapter 2
Theoretical Methods

2.1 Introduction

Computational quantum chemistry has become an invaluable tool for the elucidation of the structure and energy of chemical systems. The basic premise involves con-

sidering individual molecules as a group of particles that can be treated using the equations of quantum mechanics (which treat particles like waves). Its value was given the ultimate accolade in 1998 when the Nobel Prize in Chemistry was awarded to "John A. Pople for his development of computational methods for use in quantum chemistry" and "Walter Kohn for his development of the density functional theory".

In practice, any natural system interacts with its environment to some extent and so any complete solution is effectively infinite and clearly intractable. Fortunately, it is possible to simplify most systems by limiting them to some natural boundary. For the chemist, and in particular the organic chemist, this boundary falls naturally at the molecular level. The natural boundary in this case is a consequence of the large difference between the strength of covalent bonds and intermolecular forces.[†] As a result, chemical systems which involve either individual molecules or a small number of interacting molecules (a chemical reaction) can be readily treated using quantum mechanical techniques. The systems that have been examined in this work (saturated hydrocarbon cage compounds) all fall into the category of well-bounded covalent molecules and are thus well-suited to study by the computational techniques outlined in this chapter.

However, it turns out that the resulting equations are insoluble for all but the very simplest systems, i.e. exact solutions are available for systems of only one or two particles.[1] To solve the resulting equations for all other systems requires the use of various approximations, and in most cases the use of computers to calculate the solution. The so-called *ab initio* methods[‡] achieve this using only the laws of quantum mechanics, along with the fundamental constants of nature, e.g. the speed of light and Planck's constant, and various rigorously defined mathematical approximations.[§] The methods known as semi-empirical use a number of empirically derived parameters for each of the atoms, which are determined by fitting calculated results to experimental data. This

[†] This is obviously not the case in all situations. Solvation has the effect of blurring the boundary between a discrete molecule and its environment. However, rather than attempting to treat the entire system as one large quantum system, ways are being developed to treat the boundary and apply the effects of the environment as a continuum or other non-quantum system.

[‡] The term "ab initio" was first used in this context by Emeritus Professor David Craig of the Australian National University.[6]

[§] Density functional methods (see Section 2.7 on page 71) are often considered a rather special category of *ab initio* calculation because they either use some parameters which are not truly fundamental or the design of functionals is not truly rigorous because the 'true' form of the functional is not known with the result that terms included in the functional are often chosen for empirical reasons.

enables more drastic simplification of the quantum mechanical equations but in doing so introduces both some degree of prejudice towards the systems used in the parametrization, and an incompleteness or inflexibility in the treatment that has been found in practise to sometimes lead to poor results outside the 'test set' used for the parametrization.

Because the complexity and the size of the problem, and as a result, the time to compute a solution, increases rapidly with the size of the system, increasing levels of approximation are required to treat ever larger systems. However, the steady advance in computer technology, which is well described by Moore's Law,[†] has meant that ever larger molecules can be investigated by the methods described hereafter.

This chapter presents a brief overview of the theoretical methods used in this thesis. More detailed discussions of these and other methods can be found elsewhere.[1–4]

2.2 Basic Concepts

2.2.1 The Schrödinger Equation

The state of almost any system can be described by the time-independent Schrödinger equation,[5] which is most simply written as,

$$\boldsymbol{H}\Psi = E\Psi \tag{2-1}$$

where $\boldsymbol{H}$ is the Hamiltonian, a differential operator representing the total energy (described below), Ψ is the wavefunction and E is the total energy of the system. The Hamiltonian operator ($\boldsymbol{H}$) can be divided into two components, corresponding to the kinetic and potential energy, i.e.

$$\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V} \tag{2-2}$$

where $\boldsymbol{T}$ and $\boldsymbol{V}$ are the kinetic and potential energy operators, respectively.

For a molecular system, the Hamiltonian operator can be written in atomic units as

[†] Moore's Law is named after one of the founders of the computer-chip-making giant Intel and states that computer processing power will double every 6–12 months.

follows,[3]

$$H = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} - \sum_{a=1}^{N_n} \frac{\nabla_a^2}{2M_a} - \sum_{i=1}^{N_e}\sum_{a=1}^{N_n} \frac{Z_a}{r_{ia}} + \sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{r_{ij}} + \sum_{a=1}^{N_n}\sum_{b>a}^{N_n} \frac{Z_a Z_b}{r_{ab}} \qquad (2\text{-}3)$$

where i and j represent the ith and jth electrons, a and b are the ath and bth nuclei, M_a is the mass of the ath nucleus relative to that of an electron, Z_a is the charge on nucleus a, and r_{xy} is the distance between the particles x and y. The first two terms represent the kinetic energy of the electrons and nuclei, respectively, while the remainder represent the potential energy.

2.2.2 The Born–Oppenheimer Approximation

The complexity of Equation 2-3, and hence the difficulty of determining a solution, can be reduced somewhat by employing a simple approximation, known as the Born–Oppenheimer (or adiabatic) approximation.[7] Since the nuclei are much heavier than the electrons, it is reasonable to suggest that the electrons can adjust rapidly to any change of the nuclear configuration, i.e. we assume that the electronic distribution depends on the instantaneous positions of the nuclei and not on their velocities. This allows separation of the Hamiltonian (Equation 2-3) into nuclear and electronic components, which allows calculation of the energy (an effective electronic energy) at fixed nuclear configurations. The electronic Hamiltonian is shown in Equation 2-4 below,

$$H = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} - \sum_{i=1}^{N_e}\sum_{a=1}^{N_n} \frac{Z_a}{r_{ia}} + \sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{r_{ij}} \qquad (2\text{-}4)$$

The hypersurface describing the variation of energy with nuclear position for a given electronic state is known as the potential energy surface (PES).

Although the Born–Oppenheimer approximation allows for considerable simplification, the resulting equations still have no analytic solutions except for one-electron systems (e.g. H_2^+). In order to make these methods applicable to systems of chemical interest, approximations for treating the electron many-body problem must also be included.

2.2.3 Orbitals and the Basis Set Expansion

2.2.3.1 The Molecular Orbital Approximation

The essence of the molecular orbital approach is to further simplify the Schrödinger equation (Equation 2-1) by assuming that the motion of each electron is independent. Although this does not give an accurate description of the electron it serves as a useful approximation and the correlation of motions between electrons can be dealt with in other ways (as will be seen later). The wavefunction of the system can then be expressed as a product of one-electron wavefunctions, referred to as spin-orbitals. Each spin-orbital χ, is the product of a spatial function (ψ), which is dependent on the position of the electron (and whose square gives the probability distribution of the electron in space), and a spin function, indicating the spin state of the electron.

Because electrons are fermions the total electronic wavefunction must be antisymmetric (change sign) with respect to interchange of any two electron coordinates. A simple product of spin-orbitals is not adequate. The Pauli exclusion principle, which states that no two electrons can have all quantum numbers equal, is a direct consequence of the antisymmetry requirement. A wavefunction that does have the antisymmetry requirement and which obeys the Pauli principle can be formed from the determinant of the n-electron spin-orbital matrix,

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix} \tag{2-5}$$

where $\chi_i(j)$ indicates electron j occupying the spin orbital χ_i and the prefactor is a normalization constant. Expansion leads to a sum of products of spin orbitals. This expression is commonly referred to as a Slater determinant.[8]

2.2.3.2 Basis Set Expansions

In practice, the spatial component of a spin-orbital is expanded in terms of a finite set of one-electron basis functions (ϕ_μ) which are usually atom centered. The molecular

orbitals can now be written as,

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu \tag{2-6}$$

where $c_{\mu i}$ are the molecular orbital expansion coefficients, which represent the contributions from each of the basis functions to the molecular orbital. When the atomic orbitals of the substituent atoms are used as basis functions, the method is known as a linear combination of atomic orbitals (LCAO).

2.2.4 The Variational Theorem

The variational theorem[1–4] states that the energy (E_{approx}) of an approximate wavefunction (Ψ_{approx}) is an upper bound to the exact energy (E_{exact}), i.e.

$$E_{approx} = \frac{\int \Psi^*_{approx} \mathbf{H} \Psi_{approx}\, d\tau}{\int \Psi^*_{approx} \Psi_{approx}\, d\tau} \geq E_{exact} \tag{2-7}$$

This allows an iterative approach to optimizing the molecular orbital coefficients ($c_{\mu i}$) in order to obtain the minimum total energy. This will give the best wavefunction possible within the constraints of the approximations used. Methods that calculate the energy utilizing Equation 2-7 are said to be variational.

2.3 Single-Determinant Methods

2.3.1 Hartree–Fock (HF) Theory

Applying the variational theorem (Equation 2-7) to an approximate N-electron wavefunction formed by the methods described above gives the Roothaan–Hall equations,[9]

$$\sum_{\mu=1}^{N} c_{\mu i}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0 \tag{2-8}$$

where $F_{\mu\nu}$ is the Fock matrix, ε_i is the energy of the molecular orbital ψ_i and $S_{\mu\nu}$ is the overlap matrix. Since the Fock matrix $F_{\mu\nu}$ is itself dependent on the orbital coefficients $c_{\mu i}$, these equations are not linear and must be solved iteratively until convergence of the energy and the orbital coefficients is achieved.

This approach was first proposed by Hartree[10] and Fock[11] and is referred to as Hartree–Fock (HF) theory. Because the molecular orbitals are derived from their own effective potential, this technique is also often referred to as self-consistent-field (SCF) theory (although it is one of many procedures that make use of such an iterative approach to achieving self-consistency in the electronic probability distribution).

If the Roothaan–Hall equations are formulated in such a way that each spatial molecular orbital should contain two electrons, one of α and one of β spin, the resulting wavefunction is known as a restricted Hartree–Fock (RHF) solution. This procedure works well for most ground-state molecules where the electronic configuration is well-described as a closed-shell singlet state. The majority of the calculations conducted in this work fall into this category. It has been necessary to consider open-shell states in a number of cases.[†] The Roothaan–Hall equations can be reformulated to remove the restriction that all spatial molecular orbitals be doubly-occupied. The most direct way of doing this, known as the unrestricted Hartree–Fock (UHF) method, defines two sets of Roothaan–Hall equations (the Pople–Nesbet equations[12]), one describing the α-electrons and one for the β-electrons. Allowing the spatial components of the spin-orbitals to vary, including those that are doubly-occupied, makes it possible for unpaired spins to interact differently with the α- and β-electrons in the 'doubly-occupied' orbitals, even though this is 'unphysical'. When this occurs, the resulting wavefunction is no longer an eigenfunction of $\langle S^2 \rangle$ (the expectation value of the spin-squared operator) because it is effectively including contributions from other high-lying spin states of the molecule. The added flexibility in the density distribution of the electron can also be seen as a weak form of electron correlation (see Section 2.3.2 on page 58). There is another formulation known as restricted open-shell Hartree–Fock (ROHF) which we have not used in this work but which is well described elsewhere.[1–4]

There are two fundamental limitations to the Hartree–Fock method. In the first place, it ignores relativistic effects, but since these effects are only important for heavier atoms (e.g transition metals), they need not concern us here. The second, more serious limitation, is its neglect of electron correlation. Methods for including electron correla-

[†] Examination of the electronic structure of the experimentally unknown, structurally-imposed planar-tetracoordinate carbon indicates a pair of low-lying non-degenerate orbitals which suggests an open-shell (or diradical) configuration might be preferred in some cases.

tion are discussed below.

2.3.2 Electron Correlation

As has been seen, the HF equations replace the real electron–electron interaction with an average interaction in which each electron 'sees' only the 'field' generated by the other electrons. This does not account for direct interactions between pairs of electrons. This pair-wise electron interaction is termed electron correlation and is often separated into Coulomb and Fermi correlation terms, which correspond to opposite-spin and like-spin correlating terms, respectively. Although the contribution of electron correlation to the total energy is relatively small, it often plays an important part in chemical processes. There are many ways of dealing with electron correlation and a number of these will be described below.

2.3.2.1 Full Configuration Interaction (FCI)

The solution to the Hartree–Fock equations for an N-basis function system is a set of N spin orbitals (χ_i). For an n-electron molecule/system only the lowest n of these orbitals are occupied, the remainder being referred to as virtual orbitals. This occupation scheme, or configuration, is only one of a set of $N!/((N–n)!n!)$ possible configurations. Other configurations can be obtained by exciting electrons from occupied to virtual orbitals. If a single electron is promoted, a singly-excited configuration results, if two electrons are promoted this gives rise to a doubly-excited configuration. These excitations are usually abbreviated as singles (S), doubles (D), triples (T) etc.

In order to improve the Hartree–Fock wavefunction, the full configuration interaction (FCI) method adds variationally determined amounts of all possible configurations to the Hartree–Fock wavefunction,

$$\Psi_{\mathrm{FCI}} = \Psi_0 + \sum_{i>0} a_i \Psi_i \tag{2-9}$$

where Ψ_0 represents the Hartree–Fock wavefunction, Ψ_i ($i > 0$) represent the various other configurations of this wavefunction and a_i is the amplitude of the configuration. This wavefunction represents the most accurate that is possible within the limits of the basis set used. The FCI wavefunction is variational and size-consistent. In the limit of

an infinite basis set, the FCI method gives the exact solution to the time-independent Schrödinger equation. However, in practice, the computational cost of this method makes it practical for treatment of only relatively small systems and even then with only modest basis sets.[13] The limitation on basis set size is perhaps the most critical factor here because an adequate treatment of electron correlation requires considerable flexibility in the electron density distribution that can only be gained from employing a reasonably large basis set (this is certainly the case when the gaussian-type[†] functions generally employed in calculations today are used (see Section 2.5 on page 66)).

2.3.2.2 Truncated CI Methods (CI and QCI)

The main contribution to the cost of computing an FCI solution is the immense number of configurations involved (this number rises factorially with the number of electrons and the number of basis functions). One obvious method of reducing the cost of including electron correlation this way is not to include all possible configurations. This results in methods such as CIS (single excitations) (which only gives improvement to the wavefunctions for excited states because all matrix elements between the HF wavefunction and singly-excited determinants are zero), CID (double excitations), CISD (single and double excitations), etc. These methods are, however, not size consistent (nor size extensive).[‡]

The quadratic configuration interaction (QCI) family of methods was introduced to overcome the problem of size consistency.[14] These methods achieve size consistency by adding various terms to the CISD wavefunction. The resulting QCISD wavefunction contains contributions from single and double, as well as some quadruple excitations. Although this method is size consistent, it is not variational.

The QCISD wavefunction does not consider triple excitations, which can be important in some systems. The direct inclusion of triples (QCISDT) would make the calcula-

[†] There has been much discussion as to the applicability of gaussian-type functions compared with Slater-type functions (which have the correct form for hydrogenic orbitals). Recent work suggests that gaussians (which allow for much simpler integral evaluation) may even be superior in molecular systems.

[‡] Size consistency and extensivity require that relative errors increase more or less in proportion with the size of the system. This is particularly important when comparisons between systems of various sizes are required. Size consistency refers to the problem of differing results from calculations on a pair of non-interacting systems (at say 100 Å separation) are treated individually and as a whole. Size extensivity implies that a method scales properly with the number of particles.[1–4]

tion prohibitively expensive for larger systems. Hence, in the QCISD(T) method, the triple excitations are included in an approximate, and much cheaper, perturbative treatment.

2.3.2.3 Couple Cluster Methods (CC)

The methods known as couple-cluster (CC) methods[15] take an approach to treating electron correlation which does not explicitly deal with configuration interaction. In these methods, the HF wavefunction is corrected using a coupled cluster scheme (or cluster operator, **T**) which in practise needs to be truncated.[1–4] The couple-cluster methods are based on an exponential wavefunction ansatz; the exact, non-relativistic ground-state molecular wavefunction, Ψ_{exact}, is written as,

$$\Psi_{exact} = \exp(\mathbf{T})\Psi_{HF} \tag{2-10}$$

where Ψ_{HF} is the normalized Hartree–Fock wavefunction, and exp(**T**) is written as a Taylor-series expansion,

$$\exp(\mathbf{T}) = 1 + \mathbf{T} + \frac{\mathbf{T}^2}{2!} + \frac{\mathbf{T}^3}{3!} + \ldots = \sum_{k=0}^{\infty} \frac{\mathbf{T}^k}{k!} \tag{2-11}$$

and the cluster operator (**T**) is the sum of the *n*-particle excitation operators ($\mathbf{T}_n$),

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \ldots + \mathbf{T}_n \tag{2-12}$$

where $n = 1, 2, 3 \ldots N$ (and N is the total number of electrons in the system). These excitation operators (T) act on the HF reference wavefunction (Ψ_{HF}) to generate all *n*th excited Slater determinants (Φ). For example,

$$\mathbf{T}_1\Psi_{HF} = \sum_{i}^{occ}\sum_{a}^{vir} t_i^a \Phi_i^a \tag{2-13}$$

$$\mathbf{T}_2\Psi_{HF} = \sum_{i<j}^{occ}\sum_{a<b}^{vir} t_{ij}^{ab} \Phi_{ij}^{ab} \tag{2-14}$$

where the expansion coefficients t are referred to as amplitudes, i and j are indices for the occupied orbitals and a and b are indices for the virtual orbitals.

The resulting methods, like both the QCI and MP methods (see Section 2.3.2.4 on page 61), are size extensive. The truncations in most common usage are couple-cluster doubles (CCD), where $\mathbf{T} = \mathbf{T}_2$, and couple-cluster singles doubles (CCSD), where $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2$. Larger expansions can only be used on relatively small systems. Accurate treatment of electron correlation has been found to require the inclusion of triple excitations. CCSD includes some contribution for triples but a full treatment of the triples (CCSDT) is found to be too computationally time consuming on most systems of chemical interest and so a perturbative correction is generally employed. This method, referred to as CCSD(T), is found to be an excellent approximation to the full CI wavefunction.

CCSD and CCSD(T) methods include a few extra terms over the corresponding QCI methods, QCISD and QCISD(T), and are therefore more complete. They require comparable amounts of computer time to generate solutions, and give similar results (except for a few cases where QCI is found to give an inferior result). For this reason, the CC methods should generally be preferred over QCI calculations.

2.3.2.4 Many Body Perturbation Theory (MBPT)

Perturbation theory provides another method of accounting for electron correlation, the most common form in use being Møller–Plesset (MP) perturbation theory.[16,17] The notion employed in many-body perturbation theory is that the correct solution should be in some sense close to a known solution. As its name implies, perturbation theory is concerned with finding the change in the energy that occurs as the result of a slight perturbation of the system. In Møller–Plesset (MP) perturbation theory, this is achieved by writing the Hamiltonian as a sum of the Hartree–Fock Hamiltonian ($\boldsymbol{H}_0$) and a perturbation ($\boldsymbol{H}'$),

$$\boldsymbol{H}(\lambda) = \boldsymbol{H}_0 + \lambda \boldsymbol{H}' \tag{2-15}$$

where λ is a dimensionless expansion parameter. The perturbed Schrödinger equation is then written,

$$\boldsymbol{H}(\lambda)\Psi = E(\lambda)\Psi \tag{2-16}$$

According to Rayleigh–Schrödinger perturbation theory,[1–4] the wavefunction and

energy can be expanded as a Taylor series,

$$\Psi(\lambda) = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots \tag{2-17}$$

$$E(\lambda) = \Psi^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \tag{2-18}$$

With λ set to one, these expressions are truncated to various levels (e.g. second-order truncation in the energy expression includes terms to $\lambda^2 E^{(2)}$), giving the MPn series.

The expression for the second-order energy correction, which is the first contribution to the correlation energy, involves a sum over doubly-excited determinants and can be written explicitly as,

$$E(\mathrm{MP2}) = \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{vir}} \frac{[\langle \psi_i \psi_j | \psi_a \psi_b \rangle - \langle \psi_i \psi_j | \psi_b \psi_a \rangle]^2}{\varepsilon_i + \varepsilon_\mathrm{j} - \varepsilon_\mathrm{a} - \varepsilon_\mathrm{b}} \tag{2-19}$$

where i and j are indices for the occupied molecular orbitals, a and b are indices for the virtual molecular orbitals, ψ_n are the molecular orbitals, and ε_n are the expectation values of the Fock operator ($\boldsymbol{F}$) in the MO basis.

$$\varepsilon_n = \langle \psi_n | \boldsymbol{F}_n | \psi_n \rangle \tag{2-20}$$

The MP2 energy typically includes about 80–90% of the correlation energy and is the most economical way of computing electron correlation. The third order term in the energy also only contains terms from doubly-excited determinants. Qualitatively, the MP2 contribution can be taken to describe the correlation between electron pairs while the MP3 contribution describes the interaction between pairs.[1]

The main problem with the MP methods is the assumption that the perturbation is small. If the underlying HF solution is poor then the correction terms are large. This in turn requires the inclusion of a greater number of terms to achieve the desired level of accuracy. Further, convergence (through inclusion of further terms in the expansion) is generally found to oscillate somewhat, such that the MP2 energy slightly overestimates the correction, MP3 leads to an underestimate of the correction and so on (Figure 2-1).

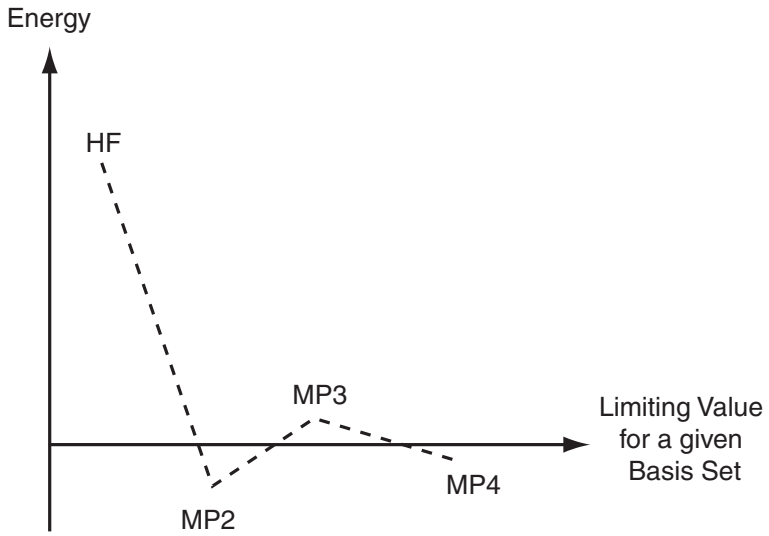


Figure 2-1. MP convergence on the energy typically oscillates to some degree.

MP methods have also been extended to apply to UHF and ROHF wavefunctions and are called UMP*n* and ROMP*n* (or simply RMP*n*). UMP*n* is generally expected to give a higher energy than the corresponding ROMP*n* result. However, which of the two is more accurate depends on the system being considered. Also, for various reasons UMP methods are simpler to implement than ROMP and the availability of ROMP gradients is limited to very few packages. In this work we have only used the UMP2 method.

In considering the MP*n* methods as a way of treating the problem of including electron correlation, the MP*n* methods have an advantage over CI methods in that they are size consistent. However, they are not variational.

2.3.2.5 The Frozen-Core Approximation (FC)

The frozen-core approximation is a specific case of a more general treatment based on the idea of forming a correlation window. In such treatments orbitals that are not expected to have a large effect on electron correlation are removed from the correlation treatment. Although the chemical core orbitals contribute significantly to the total energy, they rarely have much effect on chemical processes, which generally involve effects in the valence orbitals. The frozen-core approximation removes from the correlation treatment, the chemical core orbitals (none for hydrogen, 1*s* for the first-row

atoms, 2*s* and 2*p* for the second-row atoms, etc.). This has proven to save significant time in computations without greatly affecting the accuracy of results such as relative energy calculations and is applicable to all electron correlation treatments.

2.4 Multireference Methods

Multireference or multiconfigurational self-consistent-field (MCSCF) methods are especially well-suited to problems like the dissociation of a bond.[1,18,19] In these methods, a CI window is defined which leads to a list of determinants or configuration state functions (CSFs). As in the case of CI, the coefficients of the determinants are optimized. However, the MOs used in constructing the determinants are also included in the optimization. Allowing this orbital relaxation does not recover much of the electron correlation and it is normal to use a relatively small number of determinants in the window or active space (Figure 2-2).[†] The energy lowering introduced by adding this extra flexibility to the wavefunction so that a better qualitative description is possible is usually referred to as non-dynamic (or sometimes static) electron correlation. This type of correlation is the result of allowing for near-degeneracy or partial occupancy of the MOs. The rest of the correlation energy is termed dynamic. An MCSCF wavefunction that includes the minimal number of determinants to allow for the correct qualitative description recovers only the static correlation. In the extreme case, where the active space includes all MOs, the MCSCF wavefunction is equivalent to full CI and all the dynamic correlation is also recovered.

2.4.1 Active Space Considerations

The major problem involved in using MCSCF techniques is defining the active space. This problem has a number of facets. Firstly, a decision needs to be made about which configurations to include in the MCSCF procedure. The most common MCSCF technique in use at present is known as the complete-active-space self-consistent-field (CASSCF) method. Unlike restricted active space (RAS) methods, CASSCF includes in the SCF procedure all the proper symmetry-adapted configurations resulting from all

[†] It is worth noting that the traditional definition of correlation energy defines the RHF solution as the reference and all techniques that lower the energy in some way as accounting for electron correlation to some degree.

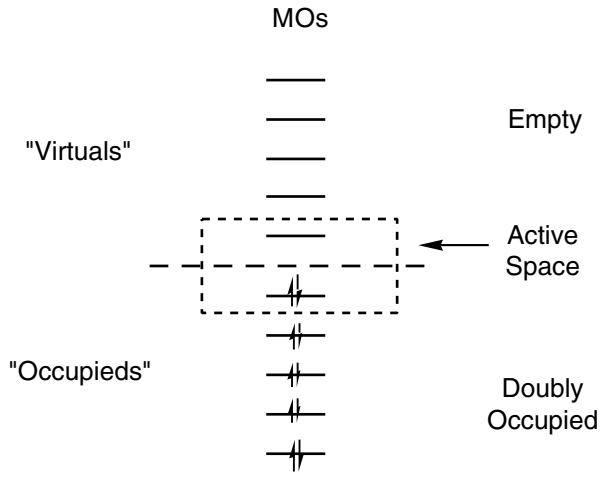


Figure 2-2. MCSCF techniques define an active space and determinants resulting from excitations within this space are then included in the SCF procedure.

excitations within the active space. Secondly, based on the problem at hand, one needs to decide which MOs (both doubly-occupied and empty) are to be included in the active space.[18] Deciding how many orbitals, and which orbitals, to include is not always straightforward. In order to reduce the time required to compute solutions the active space is generally chosen to be as small as possible and still give a qualitatively correct description of the region of a molecule that is being considered. For example, a simple C–C bond cleavage may be well-described by a [2,2]-CASSCF (which includes two electrons in two orbitals). However, an inappropriate selection of active space can lead to an unbalanced description and caution must be used to select the appropriate active space. One solution is to include all valence electrons (and the corresponding set of orbitals) in the active space. However, the factorial rise in the number of configurations generated from the full CI within the active space limits [*n*,*m*]-CASSCF to about 12 or 14 electrons/orbitals.

2.4.2 Including Dynamic Correlation

Because MCSCF only recovers a small proportion of the electron correlation, it is usually necessary to account for the dynamic electron correlation through either multi-reference configuration interaction (MRCI), which includes all single and double excitations from all reference configurations (i.e. MRCISD), or a perturbative treatment such

as second-order complete active space perturbation theory (CASPT2), which is one of a number of implementations of many-body perturbation theory as applied to MCSCF. MRCI calculations are often corrected for a contribution from the quadruples using a multireference equivalent of the Davidson correction.[20] This Davidson-corrected MRCI is usually written MRCI+Q and has the advantage of size extensivity.

2.5 Basis Sets

As described earlier, molecular orbitals are usually described as a linear combination of known atomic-centered functions. This approach of breaking an unknown function into a set of known functions is an approximation because the basis set is inevitably incomplete. Increasing the size and/or scope of a basis set until it approaches complete ness allows for a systematic improvement in the resulting solution (which may however be incorrect due to other approximations made in the method).

Typically, basis functions are atom-centered although this need not be true. Two types of atom-centered functions are commonly used. Slater-type orbitals[21] (STOs) are characterized by an $\exp(-\zeta r)$ radial dependence. STOs are the exact solutions to the hydrogen atom problem and therefore provide a good description of atomic wavefunctions, and importantly, they reproduce the correct behavior at the nucleus, where a cusp should exist. However, gaussian-type orbitals (GTOs), which are characterized by an $\exp(-\zeta r^2)$ radial dependence,[22] are by far the most commonly used basis functions. This is a consequence of the cost of calculating the two-electron integrals, which is much less for GTOs than for STOs. It is expected that more GTOs than STOs will be needed to properly describe a given wavefunction, both because of the incorrect behavior at the nucleus and because GTOs are expected to fall-off too rapidly at long distances from the nucleus. However, the greater efficiency of integral evaluation makes them the basis functions of choice. In order to improve the properties of an individual basis function, gaussian-type basis functions are often expressed as a linear combination of primitive gaussian functions,

$$\phi_\mu = \sum_i d_{\mu i} g_i \tag{2-21}$$

where the coefficients ($d_{\mu i}$) and the exponents (ζ) for each of the primitive gaussians (g_i)

are chosen so as to better represent a true atomic orbital. This type of basis function (ϕ_μ), known as a contracted gaussian, is used exclusively in this work and represents a mechanism for improving the form of the basis functions without increasing the number of basis functions. Keeping the total number of basis functions to a minimum is crucial because the time to compute a given system usually rises rapidly (in some cases to the seventh power) with the number of basis functions.

2.5.1 Split-Valence and Mixed Basis Sets

Selecting a set of basis functions for use in describing the molecular orbitals (Equation 2-6) generally involves some degree of chemical intuition. To start with, it is recognized that hydrogen and helium have no core electrons while atoms in the first row have clearly defined core and valence electrons.

Split-valence basis sets make use of a contraction scheme like that described in Equation 2-21, and the notion of core and valence electrons, to divide up the primitives into two components. By reducing the number of basis functions used to describe the core (by grouping primitives as a single function), this scheme allows more basis functions, and therefore flexibility, to be given to the chemically important valence orbitals while keeping the total number of basis functions to a minimum. Double-split-valence or valence-double-zeta (VDZ) basis sets have one basis function per core orbital and two basis functions per valence orbital, while triple-split-valence or valence-triple-zeta (VTZ) basis sets have one basis function for each core orbital and three basis functions per valence orbital. Increasing the number of functions used to describe the valence electron distribution allows, to some extent, for radial electron correlation. Common examples of VDZ basis sets are 6-31G[23] and cc-pVDZ,[24] while 6-311G[25] is a well-known example of a VTZ basis set.

Another method for reducing the total number of basis functions required in a particular calculation relies on using more basis functions per atom in the chemically important or difficult-to-describe region of the system. In these so-called mixed basis sets one might use a 6-311G type basis for atoms in the important region while a 6-31G basis is used for atoms in less important regions of the molecule. For large systems this can lead to a significant reduction in the number of basis functions for a given calcula-

tion.[†] Mixed basis sets must be used with caution because they may, if not properly used, bias a calculation and/or create artefacts.

2.5.2 Polarization and Diffuse Functions

The basic VDZ and VTZ basis sets discussed above (6-31G and 6-311G) do not allow for polarization of the electron distribution around the nucleus. The electron distribution can be polarized by interactions with other atoms. In order that the basis set is flexible enough to accurately describe any charge polarization, so-called polarization functions are employed. Polarization functions are higher angular momentum functions, which can combine with other functions in the basis set to allow charge polarization. These functions also have the effect of allowing for angular electron correlation (i.e. they allow for non-spherical distributions of the electrons about a nucleus). Basis functions of high angular momentum are very important in correlation treatments.

Diffuse functions are used to properly describe the outlying regions of the molecule. These functions are low angular momentum functions (*s* and *p*) with low exponents (ζ), i.e. they extend further away from the nucleus. Diffuse functions are generally needed to properly describe species with loosely bound electrons such as anions or species containing lone pairs.

2.5.3 Pople Basis Sets

The Pople basis sets used in this work have a straightforward nomenclature scheme. The notation 6-31G means that 6 primitive gaussians are used for each core orbital and two functions containing three and one primitives are used for each of the valence orbitals. In similar fashion 6-311G means that 6 primitive gaussians are used for each core orbital and three functions containing three, one and one primitives are used for each of the valence orbitals. Most Pople basis sets start with 6-31G or 6-311G and then extend them by adding diffuse (+) and/or polarization functions. Details of the nomenclature

[†] As an example, the 6-311+G(2d,p) basis with spherical polarization functions gives for dimethanospiro[2.2]octaplane ($C_{21}H_{24}$) (**2-1**) a basis set of 765 functions. However, the mixed basis set which we have termed 6-311+G(2d,p)(red), in which 6-311+G(2d,p) is used on the central atom and 6-311+G(d,p) is used on the four β-carbon atoms and 6-31G(d) is used elsewhere, affords a good approximation to the full 6-311+G(2d,p) basis for the alkaplanes but includes 'only' 415 basis functions.

are best explained through a number of examples:

6-31G(d)[23]	As for 6-31G described above with the addition of *d*-functions on heavy atoms (i.e. non-hydrogen atoms).
6-311G(d,p)[25]	The 6-311G basis with addition of *d*-functions on heavy atoms and *p*-functions on hydrogen.
6-311+G(2d,p)[25,26]	As above with the addition of diffuse (*s*- and *p*-) functions on heavy atoms and replacing the single set of *d*-functions with two well-spaced sets of *d*-functions (one set closer in and the other further out from the nucleus than the single set in 6-311G(d,p)).
6-311++G(3df,2p)[25,26]	The 6-311G basis with the addition of diffuse (*s*- and *p*-) functions on all atoms, three sets of *d*-functions and one set of *f*-functions on heavy atoms, and two sets of *p*-functions on hydrogen.

These basis sets are relatively small (compared with the correlation-consistent basis sets described below) and provide considerable flexibility in the choice of basis set size. They have also been used extensively so their performance in a wide variety of molecular situations is well-known. For these reasons, we have used these basis sets almost exclusively.

2.5.4 Correlation-Consistent Basis Sets

The correlation-consistent basis sets[24] were designed with the aim of recovering the correlation energy of the valence electrons. In essence, a step up in quality, for example, from double-zeta (DZ) to triple-zeta (TZ), involves adding one set of functions to each of the types already represented plus one set of the next higher orbital angular momentum. The smallest correlation-consistent basis set is referred to as correlation-consistent polarized valence-double-zeta (cc-pVDZ), the next is cc-pVTZ and so on. The number of contracted functions for first row atoms/hydrogen used in each of these basis sets is [3s,2p,1d/2s,1p] and [4s,3p,2d,1f/3s,2p,1d]. These basis sets can also be augmented by the addition of diffuse functions (aug-). In this case, one extra set of functions with the same angular momentum as those functions already represented is added but a small value is used for the exponent (ζ). For example, the aug-cc-pVQZ (or sim-

ply AVQZ) basis represents a [6s,5p,4d,3f,2g/5s,4p,3d,2f] basis. Similarly, the aug-cc-pV5Z (or simply AV5Z) basis represents a [7s,6p,5d,4f,3g,2h/6s,5p,4d,3f,2g] basis. We have used these basis sets where very large basis sets which approached the basis set limit were desired.

2.6 Hierarchy of *Ab Initio* Methods

The relationship between basis set and electron correlation level is summarized in the Pople diagram[3] shown in Figure 2-3.

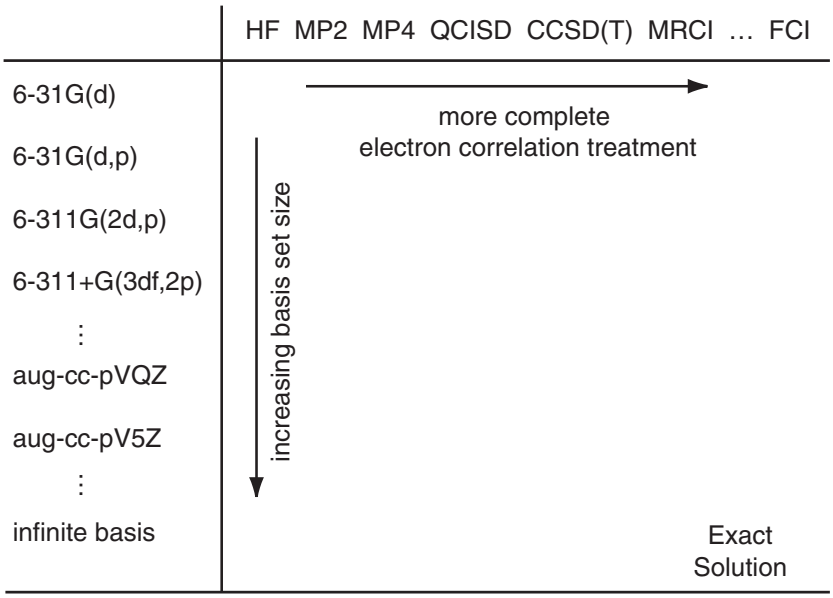


Figure 2-3. Pople diagram illustrating the progression of *ab initio* methods to the exact solution to the time-independent Schrödinger equation (under the Born–Oppenheimer approximation).

At the top of Figure 2-3 are various treatments of electron correlation, with Hartree–Fock, which includes no electron correlation, at the far left. Successively more accurate treatments of electron correlation are shown from left to right until FCI, which takes into account all the electron correlation within the limits of the basis set used, is reached. Going downwards, the basis sets become successively larger until an infinite basis set is reached. As we go down the diagonal of the figure, the calculations become more accurate until the exact solution to the non-relativistic Schrödinger equation is reached at the bottom right-hand corner. Since the increased accuracy also results in a

greater computational cost (often increasing in dramatic fashion), a balance must be struck between the desired accuracy and computational cost.

2.7 Density Functional Theory

2.7.1 Kohn–Sham Theory

The density functional theory (DFT) approach to solving the time-independent electronic Schrödinger equation rests on the proof by Hohenberg and Kohn[27] which showed that the ground-state electronic energy is determined completely by the electron density (ρ) with a one-to-one correspondence. Unfortunately this proof does not give any clues as to the functional form of this correspondence between energy and density.

By comparing with the equations of wave mechanics (and assuming the Born–Oppenheimer approximation), it is clear that the functional can be divided into three parts, a term for kinetic energy ($E^{T}[\rho]$), one for the Coulombic attraction between nuclei and electrons ($E^{V}[\rho]$), and one for interactions between electrons, which in turn can be readily divided (with reference to HF theory) into Coulomb ($E^{J}[\rho]$) and exchange ($E^{K}[\rho]$) terms (with correlation implicitly assumed in all terms).

$$E[\rho] = E^{T}[\rho] + E^{V}[\rho] + E^{J}[\rho] + E^{K}[\rho] \tag{2-22}$$

The use of DFT theory in computational quantum chemistry has been facilitated by a reformulation (by Kohn and Sham[28]) of the problem of determining the functional form of the relationship between the energy and density. In this reformulation, Kohn and Sham introduced an orbital approach by writing the approximate density ($\rho(r)$) in terms of a set of auxiliary one-electron functions (Equation 2-23).

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left|\psi_i(\mathbf{r})\right|^2 \tag{2-23}$$

Further, the kinetic energy is calculated under the assumption of non-interacting electrons ($E^{Ts}[\rho]$) (a similar approach to that used in HF theory). Equation 2-22 can

then be rewritten in the more customary form,

$$E[\rho] = E^{Ts}[\rho] + E^{V}[\rho] + E^{J}[\rho] + E^{XC}[\rho] \quad (2\text{-}24)$$

where $E^{XC}[\rho]$ is called the exchange–correlation term and by definition includes all contributions not accounted for in the first three terms. If the density is expressed as in Equation 2-23 (and in practice the one-electron functions are rewritten as a linear combination of atomic-centered orbitals), then the functional connection between the density and the energy for the first three terms of Equation 2-24 is known and the problem is reduced to finding the functional form for $E^{XC}[\rho]$. If the exact form for this term could be deduced, then an exact solution to the energy would result. Unfortunately, the exact form is not known, and what is worse, no means for systematically improving the functional is evident. As a result, all trial functionals must be compared with experimental results in order to determine their accuracy. It is in this sense that many people do not consider DFT implementations truly *ab initio*.

2.7.2 Functionals

The exchange–correlation term ($E^{XC}[\rho]$) is usually divided into separate exchange ($E^{X}[\rho]$) and correlation ($E^{C}[\rho]$) terms, although there is no requirement to proceed in this manner. As a first approximation, it has then been assumed that the density can be treated locally as a uniform electron gas. This leads to what is called the local density (LDA) or local spin density (LSDA) approximation. The resulting expressions for E^{X} and E^{C} are usually referred to as Slater or simply S (because of the similarity of the expression for the exchange term with that proposed by Slater[29] in his Xα method) and VWN (after Vosko, Wilks and Nusair[30] for their analytic interpolation formula for the correlation energy of a uniform electron gas), respectively. The LSDA approximation, although quite simple, performs remarkably well (even though it gives relatively large errors in the exchange and correlation energies) and is generally considered to do as well as HF theory.

Improvements over the LSDA approach have come from including dependency on not only the density but also the gradient of the density in the exchange and correlation terms. Becke[31] has proposed such a correction to the LSDA exchange term. The corrected exchange term is usually referred to as Becke or simply B. One of the most pop-

ular gradient-corrected functionals for the correlation term is that proposed by Lee, Yang and Parr[32] and is referred to as LYP. This functional is derived from fitting four parameters to data for the helium atom. The resulting gradient-corrected DFT method (B-LYP) has proven very popular.

Further improvements in the functional result from application of what is called the adiabatic connection formula (ACF).[1] This leads to methods that are termed hybrid methods because they use a suitable combination of both the exact exchange (of a system of non-interacting electrons, i.e. the HF exchange) and a functional exchange term. The most widely used hybrid method is a three-parameter method[33] and is referred to as B3-LYP,

$$E^{\mathrm{XC}}_{\mathrm{B3-LYP}} = \left[(1-a)E^{\mathrm{X}}_{\mathrm{S}} + aE^{\mathrm{X}}_{\mathrm{HF}}\right] + bE^{\mathrm{X}}_{\Delta\mathrm{B}} + cE^{\mathrm{C}}_{\mathrm{LYP}} \qquad (2\text{-}25)$$

where ΔB refers to Becke's gradient correction to the LSDA exchange and the other terms are as detailed above. The three parameters a, b and c are fitted to experimental data.[†] This method has been found to give remarkably good results in many situations (often in good agreement with CCSD(T)) and is the DFT method used exclusively in this work. However, like all functionals, its performance is only really known for systems similar to those for which it has been tested thoroughly. As a method for exploring the structure and energies of novel molecular systems (where no experimental data are available), it is clearly inferior to methods which can be systematically improved, or at the very least it needs to be tested in such cases against high-level calculations on model systems.

If confidence can be gained in the performance of a particular functional, DFT can be a very powerful technique because the computational cost (in terms of compute time) of even the hybrid methods is considerably less than any other method that allows for electron correlation.

[†] Although there are a number of parameters in both the Becke three-parameter model and the LYP correlation functional which are fitted to experimental data, these methods are not usually referred to as semi-empirical. For a discussion of the semi-empirical methods used in this work see Section 2.8 on page 74.

2.8 Semi-empirical Procedures

Unlike molecular mechanics[1] (MM) or force-field methods, which treat molecules as a classical system of particles whose interaction is described by a parametric force field equation, the so-called semi-empirical methods[1] are based on a quantum mechanical description of the molecule. The central assumption taken in the semi-empirical methods[34] is the zero differential overlap (ZDO) approximation. This approximation sets to zero all products of basis functions which depend on the same electron coordinates when located on different atoms.† The result of this is that the overlap matrix becomes a unit matrix, one-electron integrals involving three centers are set to zero, and the most numerous two-electron integrals, i.e. all three- and four-center two-electron integrals, are neglected. The remaining integrals are then replaced with parameters. It is this parametrization (usually done by comparing with experimental results) which leads to the name semi-empirical. The various semi-empirical methods differ as to how many integrals are neglected and how the parametrization is done. To further simplify the problem, all core electrons are accounted for by reducing the nuclear charge, so only valence electrons are considered. And finally, a minimum basis set (of *s* and *p* Slater-type functions) is employed.

The most common semi-empirical methods in use at present (and used in this work) are the methods referred to as Austin model 1[35] (AM1), and modified neglect of diatomic overlap, parametric method 3[36] (PM3).‡

For our purposes, these methods have been used in place of MM methods to find starting geometries for novel saturated hydrocarbon cage compounds because they were found to give superior geometries at the central quaternary carbon atom; MM methods were found to predict pyramidalization and loss of symmetry at the central carbon atom while AM1 and PM3 gave geometries of correct symmetry (for closed-shell species) with errors in the bond angles within the accepted limits for these methods (3.5° and 4.0°, respectively).[1] Energies from these calculations have not been considered.

† Note that it is the product of basis functions and not the integral over these products that is set to zero.

‡ A good overview of currently available semi-empirical methods along with some indication of their deficiencies is available elsewhere.[1]

2.9 Potential Energy Surfaces

As a consequence of the Born–Oppenheimer approximation, a chemical system is viewed as a set of nuclei moving on a potential energy surface which is (at each point in space) a solution to the electronic Schrödinger equation.

2.9.1 Geometry Optimization

For almost all computational problems, it is impractical to calculate the entire potential energy surface (PES). It is often more convenient to locate points of interest on the surface, which are usually stationary points. These points are characterized by all the derivatives with respect to the $3N-6$ (for a non-linear molecule) internal coordinates being equal to zero, i.e.

$$\frac{\partial E}{\partial r_i} = 0 \qquad \text{where } i = 1, 2, 3 \ldots 3N-6. \tag{2-26}$$

There are two types of stationary points that of most interest to chemists. The first are local minima, corresponding to equilibrium structures. The second are first-order saddle points, which correspond to transition structures. The two types of stationary points can be distinguished by examining the eigenvalues of the Hessian, or force-constant matrix, formed by the second derivatives of the energy with respect to the coordinates,

$$\frac{\partial^2 E}{\partial r_i \partial r_j} \qquad \text{where } i, j = 1, 2, 3 \ldots 3N-6. \tag{2-27}$$

Equilibrium structures are characterized by having no negative eigenvalues of the Hessian, while first-order saddle points have one negative eigenvalue.

Efficient geometry optimization techniques,[1,37,38] for both minima and saddle points, are implemented into the GAUSSIAN 98 system of programs.[39] These allow stationary points to be located in a relatively straightforward manner for methods that have readily available analytic first derivatives (HF, B3-LYP, MP2, QCISD, etc.). These techniques employ either an approximate second-derivative matrix (which is updated using information from the first derivatives and nuclear displacements) or no second-derivative matrix. As a consequence, true minima must be verified by calculation of the second

derivatives at the optimized geometry, i.e. where the first derivatives are all zero (to some level of accuracy). The HF, B3-LYP and MP2 methods are among those implemented in GAUSSIAN 98 which allow ready optimization and characterization of the resulting stationary points.

2.9.2 Normal Mode Analysis

Vibrational frequencies can be calculated by diagonalization of the force constant matrix (Equation 2-27), calculated by analytic or numerical second derivatives. The resulting values are known as normal-mode frequencies. An equilibrium structure is characterized by all frequencies being real while a first-order saddle point or transition structure has one imaginary frequency.

The harmonic approximation used in the calculation of normal mode frequencies leads to systematic errors; the calculated frequencies are usually larger than experimentally determined frequencies because of anharmonic contributions to the observed frequencies and inadequacies in the calculations.[40,41] Consequently, the calculated frequencies are often scaled to take into account the effects of the neglect of anharmonicity, incomplete electron correlation and basis set deficiencies. Scaling factors for many methods and basis sets (which have been determined by comparison with a wide range of experimental data) are available.[40]

2.9.3 Zero-Point Energies

Because nuclei are not a set of classical particles but form a quantum system, the true energies of a system of nuclei at any given point on the PES require a correction which takes into account the zero-point vibrational energy associated with that geometry. When determining or comparing results from MO calculations with experiment (for example heats of formation), it is necessary to add to the calculated energies a correction for this zero-point energy. The zero-point vibrational energy (ZPVE) is given by

$$\mathrm{ZPVE} = \frac{1}{2}h\sum_i \nu_i \qquad (2\text{-}28)$$

where ν_i are the scaled vibrational frequencies in appropriate units. It should be noted

that the optimum scaling factors for frequencies and zero-point energies often differ.[40]

2.10 Molecular Properties

2.10.1 Symmetry

Although symmetry is not strictly a molecular property it is indeed a geometric property of many molecular systems. We have found in this work that the use of molecular symmetry wherever possible has been of tremendous advantage. Because many computational algorithms are able to make use of molecular symmetry (for example this leads to block diagonalization of the overlap matrix), this can significantly reduce the time needed for calculations on a system. In principle, compute time is reduced by a factor of two for each order of symmetry (so D_2 symmetry reduces the computational cost by a factor of eight). In practice, sparse matrix techniques and other algorithmic improvements give better savings in compute time for molecules with little or no symmetry so the gain from making use of symmetry is somewhat less but it can still be quite considerable for high symmetry structures like dimethanospiro[2.2]octaplane (**2-1**).[†]

2.10.2 Strain Energies

The concept of strain is inexact. However, it is extremely useful conceptually.[42] It generally refers to the increase in energy of a molecule that results from structural deviations from the 'norm'. The effects of strain are generally discussed in terms of bond angle and bond length distortions, torsional effects, non-bonded interactions and so on. All of these effects refer to structural variation that can be seen to raise the energy of a molecule. The main problem with a rigorous definition of strain is that a reference point must be chosen. The usual definition of strain in hydrocarbon systems takes the molecules methane, ethane, propane, isobutane and neopentane to be strain-free. Essentially this defines the reference energy for methane and primary through to quaternary carbon centers. This definition can be extended to include further compounds (for example ole-

[†] The calculation of the numerical force constants for dimethanospiro[2.2]binonaplane (**2-3**) (see Section 2.11 on page 80) provides one example of the savings possible from the use of symmetry. If the D_{2h} symmetry of the molecule had not been used to reduce the number of gradients needed to calculate the numerical second derivatives (by double-differencing), then 294 gradients would have been required (instead of only 59) and the time to complete the calculation would have been almost six times greater, or 18 months!

fins) by defining further reference compounds (in the case of simple olefins one would need to include propene and 2-methylpropene).

Such a definition of strain for saturated hydrocarbons, in which the strain energy is given relative to the simple hydrocarbons (listed above), leads to a direct method for the calculation of strain energies (*SE*).[43] This involves writing a homodesmic reaction in which the target molecule is broken down into the unstrained hydrocarbons. For example,

$$\text{spiropentane} + 6\ \text{ethane} \longrightarrow \text{neopentane} + 4\ \text{propane} \qquad (2\text{-}29)$$

The associated total strain energy (*SE*) of spiropentane is the negative of the enthalpy ($-\Delta H^{\text{homod}}$) of the resulting reaction (Equation 2-29). Such a reaction is termed homodesmic because the number of primary, secondary, tertiary and quaternary carbon atoms and the number of bonds between atoms of the same hybridization on each side of the reaction are balanced. The aim in such a scheme is to maximize the cancellation of errors in the calculation of the enthalpy change. In order to obtain a true reaction enthalpy, the calculated energies are corrected for the ZPVE (as described above). The resulting entropies at 0 K are corrected to 298 K using the formula,

$$\Delta H(T) = H_{\text{trans}}(T) + H_{\text{rot}}(T) + \Delta H_{\text{vib}}(T) + RT \qquad (2\text{-}30)$$

where,
$$H_{\text{trans}}(T) = \frac{3}{2}RT \qquad \textbf{(2-31)}$$

$$H_{\text{rot}}(T) = \frac{3}{2}RT \quad \text{(RT for linear molecules)} \qquad \textbf{(2-32)}$$

$$\Delta H_{\text{vib}}(T) = Nh\sum_i \frac{\nu_i}{(e^{h\nu_i/kT} - 1)} \qquad \textbf{(2-33)}$$

assuming ideal gas behavior (*N* is Avogadro's number and *h* is Planck's constant). As with calculation of the ZPVE, scaled, calculated frequencies are used to calculate $\Delta H_{\text{vib}}(T)$, but a scale factor appropriate for reproducing temperature corrections is used.

Strain energies calculated in this way represent the total strain energy (*SE*) of a molecule. In this work we have found it useful in some cases to calculate strain energies

that are more localized to a certain region of a molecule by deducting the strain energy inherent in the remainder of the molecule. Such schemes are explained in detail where used.

2.10.3 Heats of Formation

Heats of formation allow for the relative energies of molecules to be compared in an absolute sense. They also allow for comparison between calculation and experiment. The method used for the calculation of heats of formation in this work is based on that of Schulman and Disch.[43] The heat of formation is determined from the calculated enthalpy of the same homodesmic reactions used to calculate the total strain energy (e.g. Equation 2-29) together with the experimental heats of formation of the unstrained hydrocarbons used to balance the homodesmic reactions. Again using the example of spiropentane, the expression for the calculated heat of formation (at 298 K) can be written,

$$\Delta H_f^{calc}(\text{spiro}) = SE^{calc} + \Delta H_f^{exp}(\text{neo}) + 4\Delta H_f^{exp}(\text{pro}) - 6\Delta H_f^{exp}(\text{eth}) \qquad (2\text{-}34)$$

where SE^{calc}, the total strain energy, is calculated as described above, and the labels neo, pro and eth refer to neopentane, propane and ethane, respectively.

2.10.4 Proton Affinities

Knowledge of the energetics of the reaction in which a molecule attracts a proton has many applications in chemistry. Very strong bases can be used in reactions as proton sinks or to remove a proton from a molecule to enable further reactivity. One way of expressing this property is as a gas-phase proton affinity (*PA*). Gas-phase proton affinities (*PA*) can be determined as the negative of the enthalpy of the protonation reaction,[44]

$$B_{(g)} + H^+_{(g)} \longrightarrow BH^+_{(g)} \qquad (2\text{-}35)$$

where B is the target molecule. As with other calculations of enthalpy changes, the *ab initio* total energies need to be corrected for ZPVE and to 298 K. The resulting calculated *PA*s can be compared with tabulations of experimentally determined gas-phase proton affinities.

2.10.5 Ionization Energies

The first adiabatic ionization energy (*IE*) indicates the ease or difficulty of removing a single electron from a molecule. Knowledge of the strength with which electrons are bound to a molecule is important in designing systems where electron transfer is facilitated. Adiabatic ionization energies are calculated as the negative of the enthalpy change in the following reaction,

$$B_{(g)} \longrightarrow B^{+}_{(g)} \qquad (2\text{-}36)$$

where B is the molecule in question. If B is a ground-state closed-shell system then B^+ will be an open-shell doublet state and will need to be treated with a method suitable for dealing with open-shell systems. In our calculations of ionization energies we have used the UMP2 method. Correction of the energy difference for ZPVE and to 298 K allows for comparison against experimentally determined *IE*s.

2.11 Computational Resources

2.11.1 Software

The main software package used for the *ab initio* calculations in this work was GAUSSIAN 98.[39] The SPARTAN system of programs[45] was used extensively for visualization purposes and for initial structure design studies. This initial design stage usually involved making use of SPARTAN's semi-empirical algorithms (in almost all cases AM1 was preferred). Calculations employing higher-level correlated techniques (CCSD(T), MRCI, etc.) were carried out using the MOLPRO system of programs.[46] One of the two numerical MP2 second derivatives reported here was calculated using GAMESS.[47]

2.11.2 Hardware

The majority of calculations in this work were performed using the Fujitsu VP-2200, VPP-300, SUN E4500 and SGI PowerChallenge of the Australian National University Supercomputing Facility (ANUSF) and various IBM RS/6000 workstations situated at the Research School of Chemistry, Australian National University. A large proportion of the B3-LYP calculations were run on the IBM SP systems at the Maui High Performance Computing Center (MHPCC).

2.11.3 Resource Usage

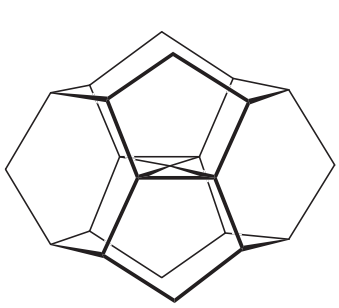
In the discussion so far, we have alluded on occasion to the cost in terms of computer time required to generate solutions for the various methods. Generating solutions can become computationally very expensive either for very high-level correlated methods (like CCSDT), or when the number of basis functions employed becomes large, either through use of a large basis set or when large systems (with many atoms) are being examined. For large systems (like, for example, the spiroalkaplanes (**2-2**)) even methods which we have indicated as being relatively cheap, like MP2, can become computationally expensive. As a result, whether or not a method can be used, or a system can be studied, often depends on the efficient implementation of a method on a particular computer platform. The algorithms used, and the implementation of those algorithms, on each computer platform, can have a major effect on what problems can be attempted with any given hardware. To the pure theoretician the matter of implementation may seem a trivial matter of writing computer code. In practise this is anything but simple. The task of implementation is complicated in part because their may not be a unique way of defining a method (e.g. perturbation methods applied to MCSCF). Further complications arise from the need or desire to tune or optimize the code to get maximum performance from the available hardware. Thus the rapid pace of hardware development acts as both a boon and a bane; the increased performance of new generations of computer technology allow much larger problems to be examined but the introduction of new hardware designs makes carefully-tuned codes rapidly obsolete.

A further problem that becomes obvious as larger systems are considered is that Moore's Law (see Section 2.1 on page 51) only predicts a doubling of processing speed for each year or so, while the computational cost of most methods increases with a much higher power. For example, the compute time to solve MP2 gradients formally increases with the order ON^4, where O is the number of occupied orbitals and N is the number of basis functions, while a CCSD(T) energy calculation scales as O^3V^4, where V represents the number of virtual orbitals.[48] This means that the size of systems being examined with these correlated techniques can only increase gradually from year-to-year.

The introduction of linear scaling techniques for HF and DFT methods, such as those based on the use of fast multipole methods (FMM), promises some relief from the

tyranny of exponential scaling in compute times. However, these methods all appear to introduce considerable up-front cost and the break-even point is usually somewhere beyond 50 atoms.[†] Further, DFT is the only method to date which includes electron correlation and which can be treated with these techniques. This suggests a bright future for DFT, especially if a means of systematically improving functionals can be derived.

Attempts to study relatively large systems (in this work molecules as large as 25 carbon atoms and 24 hydrogens have been considered in detail using correlated *ab initio* techniques) involve considerable effort in choosing the most efficient algorithms and maximizing usage of the available compute time. As an example, even the modest increase in molecular size from spiro[2.2]octaplane ($C_{21}H_{24}$) (**2-2**) to dimethanospiro[2.2]binonaplane ($C_{25}H_{24}$) (**2-3**), an increase of exactly four carbon atoms, leads to an increase in the compute time for an MP2/6-31G(d) gradient calculation (see Section 2.12 on page 84) in C_1 symmetry using GAUSSIAN 98[39] (which we find to be the most efficient package for single-processor MP2 calculations) of about 100%, i.e. a doubling of the compute time. This equates to an extra 5 days of compute time on an RS/6000 processor or 15 hours on a single VPP-300 processor.



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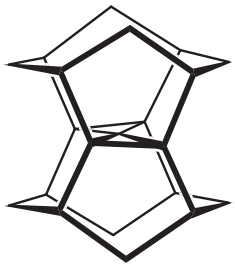
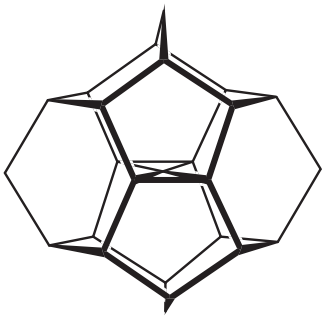


2-2



2-3

The full ramifications of such large compute times can be seen when one considers the time required to compute the MP2 second derivatives for dimethanospiro[2.2]octaplane (**2-1**) and dimethanospiro[2.2]binonaplane (**2-3**). These calculations were done numerically (using a double differencing method) rather than analytically for two reasons. Firstly, the analytic second derivatives can not be restarted during the calculation

[†] This is quite variable and actually depends on the three-dimensional shape of a system. The initial set-up cost for such linear-scaling calculations is least for linear systems (like all-*E*-dodecahexaene), greater for planar systems (for example a graphite fragment) and greatest for globular systems (like the alkaplanes or proteins).

so a power failure or forced 'down-time' would mean restarting the computation from the beginning. Secondly, the amount of storage space required for integrals and to do the transformation would be on the order of 60 GB. Although most modern computer architectures (64-bit platforms) can handle files of this size, there are no packages that we know of that allow such large file storage (the limit in GAUSSIAN 98[39] appears to be 20 GB which is a limitation in the algorithms for storing and retrieving data). The numerical second derivatives for dimethanospiro[2.2]binonaplane (**2-3**) took 1800 CPU hours (60 steps at 30 hours/step) on a single VPP-300 processor using GAUSSIAN 98. This equates to 75 days of compute time and required 3 months to complete! The time to complete such a calculation on an RS/6000 is staggering (over 1 year). Clearly, such time-consuming calculations can only be accomplished in limited numbers. The second derivatives for dimethanospiro[2.2]octaplane (**2-1**) were computed in parallel over 128 nodes on a CRAY-T3E using the GAMESS package.[47] This calculation required 30,000 node-hours to compute but because it was running over 128 nodes the total time to completion was around 10 days. The power of parallel execution becomes immediately obvious. Parallel computers represent a challenge to traditional software packages like GAUSSIAN 98[39] which were originally designed and optimized for single-processor execution. Parallel computers, and the soon-to-be massively parallel systems, will offer further relief from the scaling problems inherent in treating electron correlation (other than by DFT). However, suitable algorithms for methods beyond MP2 are still in development.

Another aspect of performance that is critical is the algorithms used to implement a given method and how well this implementation is tuned to particular hardware. One example from the current study that illustrates this quite dramatically is a comparison between the times required to compute a B3-LYP/AV5Z energy for methane (T_d symmetry) using GAUSSIAN 98[39] and the CCSD(T)/AV5Z energy for the same structure with MOLPRO.[46] Considering that CCSD(T) is known to scale formally as O^3V^4 (where O and V represent the number of occupieds and virtuals)[48] while B3-LYP should only scale as N^4 (in the worst case) (where N is the number of basis functions), it is surprising to find that the two calculations (which each use 447 basis functions) required roughly equal compute time of 4 hours on a single SGI PowerChallenge R10000 processor. Similarly, a CCSD(T)/AVTZ energy (total basis functions is reduced to 138) for

this same structure calculated using MOLPRO and GAUSSIAN 98[39] required 2 and 44 minutes, respectively (GAUSSIAN 98 is not making good use of symmetry, but even allowing for this MOLPRO performs remarkably well). As systems get larger and total compute time becomes very large (as seen above) these differences in the implementation can have drastic effects on the type of calculations that can be accomplished. Well-designed algorithms can allow calculations on today's computer hardware that otherwise could not be accomplished for years to come.

One final example of the CPU times required for calculations on molecules like the alkaplanes is in order. In this case we have chosen to examine the time to complete calculations of the cheapest method available to us which still includes the effects of correlation. A GAUSSIAN 98 UB3-LYP/6-31G(d) energy and gradient calculation (a single step in an optimization) with no symmetry on dimethanospiro[2.2]octaplane ($C_{23}H_{24}$) (**2-1**) requires 3 node-days (or 18 hours over 4 nodes) on a SUN Enterprise 4500 (an SMP machine with 400 MHz UltraSPARC II processors). But for structures with high symmetry (D_2), the time for this calculation is reduced to only 10 node-hours. Since typical optimizations to locate a local minimum will require at least six steps (and frequently more), it is clear that even the least-demanding calculations (in terms of compute time) are problematic when no symmetry is present. Further, optimizations to locate transition structures (which are frequently of low symmetry and often require the use of second derivatives to aid in the search) are clearly prohibitive for molecules of this size at this time.

The most extensively used code in this work has been the GAUSSIAN 98 package.[39] GAUSSIAN has been developed over many years since the early days of its inception in the research laboratories of John Pople at Carnegie–Mellon University. This package has proven to have the most efficient implementations for all HF, DFT and MP2 calculations for systems of the type examined in this work and for use on the non-parallel hardware platforms, where we have had most compute time. In particular, the GAUSSIAN implementation of algorithms for MP2 energies and gradients on the Fujitsu VPP-300 is very efficient both in terms of I/O bandwidth usage and CPU time.

2.12 Notation and Abbreviations

Throughout this work standard notation for describing a particular method will be

used. There are two types of notation used to describe the details of a computational level. In general, this requires specification of the method and basis set used.

Method / Basis

This notation is used when geometries are being considered, or when the energy and geometry have been computed at the same level. When energies have been calculated at a geometry optimized at a different level of theory (generally a lower level), the following notation is used,

EnergyMethod / EnergyBasis // GeometryMethod / GeometryBasis

The abbreviations used for the various methods throughout this work are listed below.

HF	Hartree–Fock theory
B3-LYP	Becke's three parameter density functional model (B3), incorporating the Lee, Yang and Parr (LYP) correction to the correlation energy
MP2	second order Møller–Plesset perturbation theory
CCSD(T)	couple cluster singles doubles with a perturbative correction for triples
[*n*,*m*]-CAS	a complete-active-space self-consistent-field calculation using *n* electrons in *m* orbitals
[*n*,*m*]-CASPT2	the many-body perturbation algorithm as applied to a complete-active-space self-consistent-field calculation using *n* electrons in *m* orbitals (this refers specifically to the method implemented in MOLPRO)[46]
MRCI+Q	multireference configuration interaction including a multireference Davidson correction

A prefix "U" indicates that the underlying wavefunction is of the UHF type for open-shell systems. All open-shell systems in this work treated with the HF, B3-LYP, MP2 and CCSD(T) methods fall into this category unless otherwise noted. The abbreviations "(fc)" or "(full)" written after a method (e.g. CCSD(T)(full)) indicates whether or not the frozen-core approximation has been used.

2.13 Units

All bond lengths are given in Ångstrom and all angles in degrees. All relative energies are in kJ mol^{-1}. Where quoted, total energies are reported in Hartree.

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