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Overview of Molecular Modelling and *Ab initio* Molecular Orbital Methods Suitable for Use with Energetic Materials

H. Dorsett and A. White

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ABSTRACT

This is a review of molecular modelling techniques which may be applied to studies of energetic materials. It focusses on *ab initio* ('first-principles') molecular orbital calculations, since these methods offer the greatest accuracy. Since *ab initio* calculations are very computer-intensive, approximate MO methods are also discussed, which offer reasonably accurate predictions with reduced calculation times. These approximate methods include density functional theory and 'layered' techniques which combine different levels of theoretical sophistication into one calculation.

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Executive Summary

Qualifying energetic materials (EM) and formulations for military use is a tedious, expensive and hazardous process. It may be possible to replace much of the redundant empirical testing of EM, either in service or under consideration, by computer simulation. Therefore, accurate theoretical models of EM performance and stability can

- Accelerate research and development of new materials with improved performance and handling characteristics
- Reduce maintenance costs for energetic materials in service and
- Reduce risk to personnel testing, handling or using energetic materials.

Many relevant characteristics of energetic materials - for instance, the performance and sensitivity of explosives, or the stability and signatures of propellants – are controlled by their chemical properties. These characteristics depend upon properties such as molecular structures and reaction energies that can be predicted with computational chemistry techniques which focus on molecular modelling.

All molecular modelling techniques can be classified under three general categories: *ab initio* electronic structure calculations, semi-empirical methods, and molecular mechanics. *Ab initio* or 'first principles' electronic structure methods are based upon quantum mechanics and therefore provide the most accurate and consistent predictions for chemical systems. However *ab initio* methods are extremely computer-intensive. Semi-empirical methods are also founded upon quantum mechanics, but speed computation by replacing some explicit calculations with approximations based upon experimental data. Molecular mechanics techniques are purely empirical methods based upon the principles of classical physics, and as such are computationally fast. Molecular mechanics methods completely neglect explicit treatment of electronic structure, and are therefore severely limited in scope; however, they often provide the only means with which to study very large chemical systems (*e.g.*, polymers or solutions) or non-homogeneous mixtures like those typically used in conventional explosives, pyrotechnics or propellants formulations.

Ab initio methods are capable of high accuracy predictions over a wide range of systems. Rapid advances in computer technology are making *ab initio* methods increasingly more practical for use with realistic chemical systems. Similarly, computationally 'cheaper' techniques such as density functional calculations and 'layered' methods such as ONIOM, are continually being refined. These methods show

promise of providing consistent and accurate chemical predictions for complicated systems requiring explicit treatment of electronic structure, such as energetic molecules that contain azides or nitrogen oxides.

This document describes the theoretical basis of molecular modelling techniques which may be applied to energetic materials. A subsequent publication will describe in detail the application of electronic structure methods to the study of energetic materials.

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1. Introduction

Computational chemistry may be defined as the application of mathematical and theoretical principles to the solution of chemical problems. Molecular modelling, a subset of computational chemistry, concentrates on predicting the behaviour of individual molecules within a chemical system. The most accurate molecular models use *ab initio* or 'first principles' electronic structure methods, based upon the principles of quantum mechanics, and are generally very computer-intensive. However, due to advances in computer storage capacity and processor performance, molecular modelling has been a rapidly evolving and expanding field, to the point that it is now possible to solve relevant problems in an acceptable amount of time.

The types of predictions possible for molecules and reactions include [1]:

- Heats of formation
- Bond and reaction energies
- Molecular energies and structures (thermochemical stability)
- Energies and structures of transition states (activation energies)
- Reaction pathways, kinetics and mechanisms
- Charge distribution in molecules (reactive sites)
- Substituent effects
- Electron affinities and ionisation potentials
- Vibrational frequencies (IR and Raman spectra)
- Electronic transitions (UV/Visible spectra)
- Magnetic shielding effects (NMR spectra)

Prediction of these properties has many applications in energetic materials research, including studies of synthesis pathways, reaction products, initiation mechanisms, and exhaust plume signature. This report presents a review of computational chemistry techniques, focussing on electronic structure methods. Electronic structure methods, particularly *ab initio* calculations, are capable of consistent predictions with high accuracy (± 20 kJ/mol)[1] over a wide range of systems - a critical prerequisite for the successful modelling of energetic materials.

An example of the application of molecular modelling to energetic materials is calculation of the detonation properties of a new explosive FOX-7 (1,1-diamino-2,2-dinitroethylene). The ideal detonation properties of any explosive formulation can be calculated from the principles of chemical thermodynamics using only the heats of formation of the ingredients as input. The experimental heat of formation of FOX-7 is

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[1] The unit 'kJ/mol' is a convenient scale for discussing molecular energies. For instance, bonds within molecules typically have energies of a few hundred kJ/mol; bonds between molecules (e.g., hydrogen bonds) have energies of tens of kJ/mol; and bonds between atoms of inert gases (*e.g.*, He, Ne, Ar) have energies no more than a few kJ/mol.

-134 kJ/mol [2], and the calculated heat of formation using the PM-3 semi-empirical method is -53 kJ/mol. Estimates of the velocity of detonation (VoD) and Chapman-Jouguet detonation pressure ($P_{C\text{-}J}$) for FOX-7 calculated with the CHEETAH thermochemical code [3] are presented in Table 1.1. In this case, it is clear that the PM-3 heat of formation is accurate enough to yield values of VoD and $P_{C\text{-}J}$ that are very close to those estimated from the experimental heat of formation. Heats of formation calculated with *ab initio* methods are nearly identical to the experimental value.

Table 1.1 FOX-7 detonation parameters estimated with CHEETAH.

ΔH_f	CHEETAH v(1.39)		CHEETAH v1.41	
	VoD	$P_{C\text{-}J}$	VoD	$P_{C\text{-}J}$
-53 kJ/mol	9130 m/s	37.1 GPa	9040 m/s	36.0 GPa
-134 kJ/mol	9090 m/s	36.6 GPa	8870 m/s	34.0 GPa

Ab initio, semi-empirical and molecular mechanics methods have been used extensively to study the chemistry of energetic materials in explosives, propellants and pyrotechnics. A comprehensive review of published studies is beyond the scope of this paper, but will be summarised in a subsequent technical report [4].

2. Survey of Computational Chemistry Methods

All molecular modelling techniques can be classified under three major categories: *ab initio* electronic structure calculations, semi-empirical methods and molecular mechanics. General characteristics for each method are summarised in Table 2.1.

2.1 *Ab initio* electronic structure methods

Of the three, *ab initio* molecular orbital methods are the most accurate and consistent because they provide the best mathematical approximation to the actual system. The term *ab initio* implies that the computations are based solely on the laws of quantum mechanics, the masses and charges of electrons and atomic nuclei, and the values of fundamental physical constants, such as the speed of light (c = 2.998×10^{8} m/s) or Planck's constant (h = 6.626×10^{-34} J·s), and contain no approximations. 'Molecular orbital' methods solve Schrödinger's equation for the chemical system using a 'basis set' of functions that satisfy a series of rigorous mathematical approximations. *Ab initio* concepts are outlined in Chapter 3.

Ab initio molecular orbital calculations are specified by a 'model chemistry.' The model chemistry includes the choice of method and basis set, the general structure and electronic state of the molecular system under study (*e.g.*, charge and spin states), and the treatment of electron spin[2]. Molecular properties can be assessed from a user-specified input (single-point energy calculation or SPE), or the molecule can be allowed to relax to a minimum energy configuration (geometry optimisation).

Table 2.1. Synopsis of molecular modelling techniques.

Method	*Advantages*	*Disadvantages*	*Best for*
Ab initio • Uses quantum physics • Mathematically rigorous: no empirical parameters	• Useful for a broad range of systems • Does not depend on experimental data • Calculates transition states and excited states	• Computationally expensive	• Small systems (tens of atoms) • Electronic transitions • Systems without experimental data • Systems requiring high accuracy.
Semi-empirical • Uses quantum physics • Uses experimental parameters • Uses extensive approximations	• Less demanding computationally than *ab initio* methods. • Calculates transition states and excited states.	• Requires *ab initio* or experimental data for parameters. • Less rigorous than *ab initio* methods.	• Medium-sized systems (hundreds of atoms). • Electronic transitions.
Molecular Mechanics • Uses classical physics • Relies on force field with embedded empirical parameters.	• Computationally 'cheap:' fast and useful with limited computer resources. • Can be used for large molecules like enzymes.	• Does not calculate electronic properties • Requires *ab initio* or experimental data for parameters • Commercial software applicable to a limited range of molecules	• Large systems (thousands of atoms) • Systems or processes that do not involve bond breaking.

Ab initio molecular orbital computations can provide accurate quantitative predictions of chemical properties for a wide range of molecular systems. However, they place a considerable demand on computer resources. The choice of theoretical method and basis set determine the duration of the calculation; thus, a sophisticated method and a

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[2] Electrons may be assigned singly (unrestricted) or in pairs of opposite spin (restricted) to the molecular orbitals that make up the total wavefunction of the system.

large basis set will provide more accurate results, but will also require more computer resources. Hence timely calculations on large molecules ($n \sim$ 10-30 atoms[3]) may only be possible using the basic theory (*i.e.*, Hartree Fock approximation) with minimal basis sets, whereas calculations on chemical reactions between simple diatomic molecules can be performed with state-of the-art model chemistries. For very large systems ($n \sim$ 50 atoms or more), timely results are only possible with less sophisticated models, like those described in sections 2.2 and 2.3 below.

2.2 Semi-empirical methods

Semi-empirical methods increase the speed of computation by using approximations of *ab initio* techniques (*e.g.*, by limiting choices of molecular orbitals or considering only valence electrons) which have been fitted to experimental data (for instance, structures and formation energies of organic molecules). Until recently, the size of many energetic molecules placed them beyond the scope of *ab initio* calculations, so preliminary theoretical studies were performed using semi-empirical techniques [3-11]. However, semi-empirical methods have been calibrated to typical organic or biological systems and tend to be inaccurate for problems involving hydrogen-bonding, chemical transitions or nitrated compounds [5,7,12,13].

Several semi-empirical methods are available and appear in commercially available computational chemistry software packages such as HyperChem [14] and Chem3D [15]. Some of the more common semi-empirical methods can be grouped according to their treatment of electron-electron interactions [14].

2.2.1 The extended Hückel method

Extended Hückel calculations neglect all electron-electron interactions, making them computationally fast but not very accurate. The model provides a qualitative estimate of the shapes and relative energies of molecular orbitals, and approximates the spatial distribution of electron density. Extended Hückel models are good for chemical visualisation and can be applied to 'frontier orbital' treatments of chemical reactivity.

2.2.2 Neglect of differential overlap (NDO)

NDO models neglect some but not all of the electron-electron interactions. The Hartree-Fock Self-Consistent Field (HF-SCF) method (*see* section 3.2) is used to solve the Schrödinger equation with various approximations:

- *Complete NDO (CNDO)* – the product of two atomic orbitals on different atoms is set equal to zero everywhere. In this case, repulsion between electrons in different orbitals depends only upon the nature of the atoms involved, and not

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[3] Obviously, n is constantly increasing as computing power is improved.

on the particular orbitals. Because CNDO neglects almost all description of electron exchange properties, it does not differentiate between states that have the same electronic configuration, but different values of electron spin.

- *Intermediate NDO (INDO)* - differential overlap between orbitals on the same atom are taken into account in the description of electron-electron repulsion, but differential overlap between orbitals on different atoms is neglected.
- *Modified INDO, version 3 (MINDO/3)* - reparameterised version of INDO optimised to predict good enthalpies of formation and reasonable molecular geometries for a range of chemical systems, in particular, sulphur-containing compounds, carbocations, and polynitro organic compounds [16].
- *Zerner's INDO methods (ZINDO/1 and ZINDO/S)* - Michael Zerner's (University of Florida) versions of INDO developed for use with molecular systems containing transition metals. ZINDO/1 is optimised to predict molecular geometries and ZINDO/S is optimised to predict UV spectra.

2.2.3 Neglect of diatomic differential overlap (NDDO)

NDDO methods build upon the INDO model by including the overlap density between two orbitals on one atom interacting with the overlap density between two orbitals on the same or another atom.

- *Modified NDO (MNDO)* - a method introduced to correct some of the problems associated with MINDO/3 [14]. MNDO does not work well for sterically crowded molecules, four-membered rings, hydrogen bonding, hypervalent compounds, nitro groups and peroxides. In general, MNDO overestimates activation barriers to chemical reactions [15].
- *Austin Method, version 1 (AM1)* - a reparameterised version of MNDO which includes changes in nuclear repulsion terms [15]. Although more accurate than MNDO, AM1 does not handle phosphorus-oxygen bonds, nitro compounds and peroxide bonds [14].
- *Parameterisation Model, version 3 (PM3)* - a second reparameterisation of MNDO, functionally similar to AM1, but with some significant improvements. PM3 is a recently developed semi-empirical method that may contain as yet undiscovered defects [15].

2.3 Molecular mechanics

Molecular mechanics (MM) is often the only feasible means with which to model very large and non-symmetric chemical systems such as proteins or polymers. Molecular mechanics is a purely empirical method that neglects explicit treatment of electrons, relying instead upon the laws of classical physics to predict the chemical properties of molecules. As a result, MM calculations cannot deal with problems such as bond breaking or formation, where electronic or quantum effects dominate. Furthermore, MM models are wholly system-dependent; MM energy predictions tend to be meaningless as absolute quantities, and are generally useful only for comparative studies. Despite these shortcomings, MM bridges the gap between quantum and continuum mechanics, and has been used quite extensively to study 'mesoscopic' effects in energetic materials. Applications include modelling reaction and dissociation on classical potential energy surfaces [17-20], studies of equilibrium crystal properties (*e.g.*, density, packing, specific heats) [21-27], dynamic investigations of shock interactions with crystals and defects [28,29], and simulating detonation in molecular crystals [30-33].

The basic assumptions of typical molecular mechanics methods are listed below.

- Each atom (i.e., electrons and nucleus) is represented as one particle with a characteristic mass.
- A chemical bond is represented as a 'spring,' with a characteristic force constant determined by the potential energy of interaction between the two participating atoms. Potential energy functions can describe in*tra*molecular bond stretching, bending and torsion, or in*ter*molecular phenomena such as electrostatic interactions or van der Waals forces.
- The potential energy functions rely on empirically derived parameters obtained from experiments or from other calculations.

Current molecular mechanics models are characterised by the set of potential energy functions used to describe the chemical forces. These force fields depend upon:

- Atomic displacements (*i.e.*, bond lengths);
- Atom types, that is, the characteristics of an element within a specific chemical context (*e.g.*, a carbonyl carbon *versus* a methyl carbon); and
- One or more parameter sets relating atom types and bond characteristics to empirical data.

Examples of MM force fields in common use are:

- *AMBER (Assisted Model Building with Energy Refinement)* - primarily designed for the study of biomolecules such as proteins and nucleotides [34].
- *CHARMM (Chemistry at HARvard Molecular Mechanics)* - primarily designed for biological and pharmaceutical study, but has also been applied to micelles and self-assembling macromolecules [35].

- *MMx (MM2, MM3, etc)* - optimised for structural and thermodynamic studies of small non-polar molecules [14]. MMx force fields include third- and fourth-order corrections to standard quadratic fits for the potential energy surfaces of bonds and bond angles, thus allowing for non-harmonic effects in molecular vibrations. The various MMx versions differ primarily in their parameterisations. The higher versions tend to be more modern and address deficiencies in their predecessors. However, for the newer versions such as MM4, parameters may not be available for all classes of molecules.
- *OPLS (Optimised Potentials for Liquid Simulations)* - optimised for reproducing the physical properties of biomolecules in liquid solutions [14].

The authors are not aware of any published study discussing the use of AMBER, CHARMM, MM*x* or OPLS with energetic materials. Since these packages are optimised for biochemistry and pharmaceutical applications, it is unlikely that they will accurately reproduce the behaviour of energetic materials without further modification. However, it is likely they can be use for limited applications with only slight modification.

Basic techniques of molecular dynamics are described in texts such as Rapaport [36] and Haile [37], and a general review of molecular mechanics applications in several areas of chemistry is given by Rappé [38].

2.4 Hybrid methods

It is worth mentioning here recently developed hybrid methods which combine high-level quantum mechanical calculations on a small part of a system with a lower-level method on the rest of the system. Thus for large clusters or macromolecules, accurate calculations can be carried out on the area of interest without ignoring or making unnecessary assumptions about the remainder of the system.

Three methods have been developed and extensively used by Morokuma *et al.* at Emory University (Atlanta, GA). These methods and their applications are likely to receive increasing attention in the next few years:

- *Integrated Molecular Orbital + Molecular Mechanics (IMOMM)* - a two-layer method in which a high level MO calculation is combined with molecular mechanics [39]. For example, the IMOMM method has been used to investigate organometallic-catalysed polymerisation reactions [40,41].
- *Integrated Molecular Orbital + Molecular Orbital (IMOMO)* - a two-layer method which combines high level and low-level MO calculations [42,43]. This method can be used for calculating bond dissociation energies of large molecules [44].
- *"Our own N-layered Integrated molecular Orbital molecular Mechanics (ONIOM) method"* - a technique that has largely superseded IMOMM and IMOMO, which are

in fact, subsets of ONIOM. ONIOM is a three-level general method, allowing the combination of any high-level method with any low- or 'medium'-level method [45]. ONIOM has been applied to calculations of bond breaking in fullerenes [46].

3. *Ab initio* Molecular Orbital Theory

What follows is a brief description of the fundamental concepts that underlie the algorithms of typical off-the-shelf *ab initio* molecular orbital software. More comprehensive discussion of molecular orbital theory may be found in selected references [12,13,16,47-49].

3.1 The physico-chemical model

The basis of electronic structure methods is the assumption that all chemistry can be described in terms of the interactions between electronic charges within molecules. Hence, chemical bonds can be loosely defined as a redistribution of electronic charge that stabilises the molecule with respect to a collection of its (isolated) constituent atoms.

Relative stabilities are expressed in terms of the total energy of the system, which is defined by a differential equation,

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}}, \qquad (3.1.1)$$

where H is the Hamiltonian operator representing the sum of kinetic ($\hat{\mathrm{T}}$) and potential ($\hat{\mathrm{V}}$) energies. In quantum mechanical systems, the kinetic energy of a particle is

$$\hat{\mathrm{T}} = \frac{-\hbar^2}{2m}\nabla^2, \qquad (3.1.2)$$

where m is the mass of the particle, $\hbar$ is Planck's constant ($\hbar$ = 1.055×10^{-34} J·s), and

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \qquad (3.1.3)$$

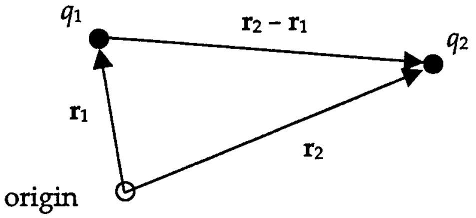

Figure 3.1 Vector diagram of pairwise electronic charge interactions.

For electrostatic systems, the potential energy is generally expressed in terms of pairwise interactions between charged particles (see Fig. 3.1):

$$\hat{\mathrm{V}} = \frac{q_1 q_2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{3.1.4}$$

where ε_0 is the permittivity of free space ($\varepsilon_0 = 8.854\times10^{-12}$ C^2/N·m^2), and $|\mathbf{r}_2 - \mathbf{r}_1|$ is the distance between charges q_1 and q_2.

3.1.1 The molecular Hamiltonian

Under the basic assumption of electronic structure methods, a molecule is a collection of charged quantum particles. The molecular Hamiltonian has the form of Eq. 3.1.1 above, however the kinetic energy is now a summation over all the particles in the molecule,

$$\hat{\mathrm{T}} = \frac{-\hbar^2}{2m} \sum_i \frac{1}{m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right), \tag{3.1.5}$$

and the potential energy is the Coulomb interaction between each pair of charged particles (electron-nucleus attraction, nucleus-nucleus repulsion, and electron-electron repulsion):

$$\hat{\mathrm{V}} = \frac{1}{4\pi\varepsilon_0} \sum_j \sum_{k<j} \frac{q_j q_k}{|\mathbf{r}_k - \mathbf{r}_j|}, \tag{3.1.6}$$

For electrons, $q = -e$ ($e = 1.602\times10^{-19}$ C), and for nuclei of atomic number Z, $q = +Ze$.

3.2 Hartree-Fock theory

3.2.1 The Schrödinger equation

The quantum mechanical description of chemical bonds is given by a space- and time-dependent probability distribution: the molecular wavefunction, $\Psi_{mol}(t)$. The molecular wavefunction is defined by the Schrödinger equation

$$\hat{\mathrm{H}}_{mol} \Psi_{mol}(t) = i\hbar \frac{\partial \Psi_{mol}(t)}{\partial t}. \tag{3.2.1}$$

If the potential energy operator is time-independent, then the solution obtained by separation of variables, leads to the molecular wavefunction

$$\Psi_{mol}(t) = \psi_{mol} e^{-iE_{mol}t/\hbar}, \qquad (3.2.2)$$

where ψ_{mol} satisfies the time-independent Schrödinger equation

$$\hat{\mathrm{H}}_{mol}\,\psi_{mol} = E_{mol}\psi_{mol}, \qquad (3.2.3)$$

and E_{mol} is the total energy of the molecule. Solutions of the time-independent Schrödinger equation represent various stationary states of the molecule (corresponding to stable or meta-stable electronic configurations). The set of wavefunctions ψ which satisfy Eq. 3.2.3 are its eigenfunctions, and the energies of the molecule, E_{mol}, in each stationary state are its eigenvalues. The stationary state with the lowest energy is called the 'ground state.'

3.2.2 Antisymmetry and electron spin

Standard electronic structure methods assume that the molecular wavefunction describing several electrons can be written as a product of single-electron wavefunctions called 'orbitals'; that is, for a molecule containing *n* electrons,

$$\psi_{mol}(1,2,\ldots n) = \psi(1)\psi(2)\ldots\psi(n). \qquad (3.2.4)$$

Electrons possess an intrinsic angular momentum or 'spin' with a value of ±½. A half-integer spin quantum number implies that electrons are antisymmetric with respect to exchange - in other words, a wavefunction describing a pair of electrons *i* and *j* must change sign when the electrons are interchanged:

$$\psi(i,j) = -\psi(j,i). \qquad (3.2.5)$$

The simplest antisymmetric combination of molecular orbitals (MOs) is a matrix determinant. A HF wavefunction is constructed by assigning electrons to molecular orbitals $\phi(\mathbf{r})$ in pairs of opposite spin, and then forming a determinant using two spin functions α and β, where

$$\alpha(\uparrow) = 1 \qquad \alpha(\downarrow) = 0 \qquad (3.2.6)$$

$$\beta(\uparrow) = 0 \qquad \beta(\downarrow) = 1. \qquad (3.2.7)$$

For two electrons *i* and *j*, the total wavefunction takes the form:

$$\psi(i,j) = \phi(\mathbf{r})\begin{vmatrix} \alpha(i) & \beta(i) \\ \alpha(j) & \beta(j) \end{vmatrix} \qquad (3.2.8)$$

with a determinant

$$\psi(i,j)=\frac{\phi(\mathbf{r})}{\sqrt{2}}\left[\alpha(i)\beta(j)-\beta(i)\alpha(j)\right] \qquad (3.2.9)$$

which satisfies the antisymmetrisation condition of Eq. 3.2.4. For a molecule containing n electrons, the wavefunction is referred to as a 'Slater determinant,' and takes the form:

$$\Psi_{mol}=\frac{1}{\sqrt{n!}}\begin{vmatrix}\phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) & \cdots & \phi_{n/2}(1)\alpha(1) & \phi_{n/2}(1)\beta(1)\\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) & \cdots & \phi_{n/2}(2)\alpha(2) & \phi_{n/2}(2)\beta(2)\\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots\\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \phi_2(n)\alpha(n) & \phi_2(n)\beta(n) & \cdots & \phi_{n/2}(n)\alpha(n) & \phi_{n/2}(n)\beta(n)\end{vmatrix} \qquad (3.2.10)$$

3.2.3 *Ab initio* essentials

For systems of more than two interacting particles, the Schrödinger equation cannot be solved exactly.[4] Therefore, all *ab initio* calculations for many-body systems (*e.g.*, molecules) involve some level of approximation and indeed, some level of empirical parameterisation.[5] Nevertheless, *ab initio* methods for molecular calculations must satisfy a set of stringent criteria:

1. Solutions must be well defined and specified by both the structure and the electronic states of the molecule.
2. The potential energy of the molecule must vary smoothly and continuously with respect to displacements of the atomic nuclei.
3. The model must contain no bias (*e.g.*, assuming a chemical bond exists between two atoms.)
4. The model must be 'size-consistent' - that is, solutions and their associated errors must scale in proportion to the size of the molecule.[6]
5. The model must be 'variational' - that is, approximate solutions must provide an upper bound to the 'true' energy of the system. Consequently, the approximate solution having the lowest energy represents the closest fit to the true wavefunction, within the constraints of the method.

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[4] This is true for any system, quantum or classical, since current permutation operators (e.g., the Levi-Civita symbol, ε_{ijk}) can only account for pairwise (two-particle) relationships [13].

[5] Indeed, *ab initio* electronic structure calculations could be considered the 'ultimate' semi-empirical approximation! It is perhaps more consistent to describe *ab initio* methods as 'universal,' that is, the a set of wavefunctions are optimised for a particular method using empirical data from a set of atoms and molecules, and it is then assumed that these wavefunctions may be applied to calculations involving all atoms and molecules.

[6] Size-consistency allows direct comparison between molecules of different sizes, and is therefore an important consideration for studies of chemical reactions.

3.2.4 Approximations

3.2.4.1 *Non-relativistic solutions*

Typical *ab initio* electronic structure methods are time-independent, solving only the spatial wavefunction, $\psi(\mathbf{r})$. This approximation is reasonable for most chemical systems, but breaks down in calculations involving large atoms (late transition metals, lanthanides, *etc.*), whose inner-shell electrons have velocities approaching the speed of light.

3.2.4.2 *Born-Oppenheimer approximation*

Electrons in molecules are much lighter than nuclei, and therefore generally have much higher velocities. Hence, under most circumstances, one can assume that electrons respond instantaneously to nuclear displacements. In practice, this means that the molecular Hamiltonian can be written assuming the nuclear positions are fixed (i.e., neglecting nuclear kinetic energy terms):

$$\hat{\mathrm{H}}_{mol} = \hat{\mathrm{T}}_{elec} + V = \frac{-\hbar^2}{2m_e}\sum_{i}^{electrons}\nabla_i^2 + \frac{1}{4\pi\varepsilon_0}\sum_j\sum_{k>j}\frac{q_j q_k}{\left|\mathbf{r}_k - \mathbf{r}_j\right|}. \qquad (3.2.11)$$

Most *ab initio* calculations solve only the electronic part of the molecular wavefunction, and therefore cannot account for systems where the electronic states are strongly coupled to nuclear vibrations.

3.2.4.3 *Single particle approximation*

As mentioned in Section 3.2.2, standard electronic structure methods approximate the total wavefunction of a many-electron system as the product of single-electron wavefunctions (Eq. 3.2.4). This is the essence of Hartree-Fock (HF) theory, which describes each electron in a molecule as moving in the average electric field generated by the other electrons and nuclei. As a single-particle theory, HF theory systematically overestimates molecular energies because it neglects the correlated motion of electrons resulting from Coulomb interactions.

3.2.4.4 *Linear combinations of atomic orbitals (LCAO)*

Although there is no exact analytical solution to the time-independent molecular Schrödinger equation (Eq. 3.2.3) for systems containing more than one electron, approximate solutions can be obtained using standard numerical techniques. The approach of all *ab initio* techniques is to build the total wavefunction from a 'basis' set of mathematical functions capable of reproducing critical properties of the system. An individual molecular orbital may then be expressed as

$$\phi_i(\mathbf{r}) = \sum_{\mu=i}^{N} c_{\mu i}\chi_\mu(\mathbf{r}), \tag{3.2.12}$$

where $\chi_\mu(\mathbf{r})$ are the basis functions, and the coefficients $c_{\mu i}$ are adjustable parameters. For a molecular wavefunction, the electronic orbitals of the constituent atoms form a natural set of basis functions. These atomic orbitals can in turn be represented by different types of mathematical functions. A highly accurate set of atomic orbitals (Slater-type orbitals or STOs) are based on hydrogenic wavefunctions having the form

$$\chi_{STO}(\mathbf{r}) \sim Ce^{-\alpha r}. \tag{3.2.13}$$

Exponential functions are not well suited to numerical manipulation, so most electronic structure calculations approximate STOs with a linear combination of gaussian-type functions,

$$\chi_{STO}(\mathbf{r}) \sim \chi_\mu = \sum_\nu d_{\mu\nu}e^{-\alpha_\nu r^2}, \tag{3.2.14}$$

where $d_{\mu\nu}$ and α_ν are adjustable parameters. As can be seen from Fig. 3.2, gaussian-type functions provide reasonable approximations of STOs, except at very small or very large electron-nucleus separations.

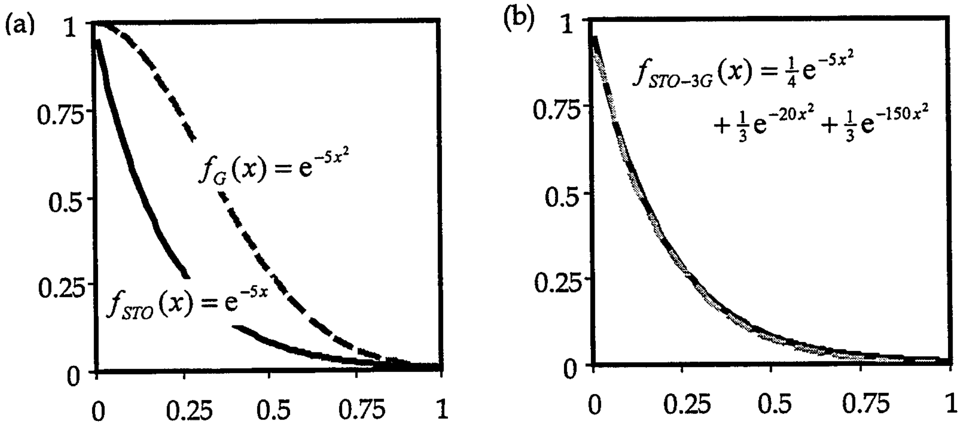

Figure 3.2 (a) Comparison of exponential and gaussian functions. (b) Comparison of the same exponential function and a sum of three gaussians.

Linear combinations of 'primitive' gaussian functions are referred to as 'contracted' gaussians. Standard *ab initio* software packages like *Gaussian98* [50] offer a choice of basis sets containing contracted gaussians optimised to reproduce the chemistry of a large range of molecular systems. A more detailed discussion of molecular basis sets is provided in section 3.3.

3.2.5 The variational principle and Roothan-Hall equations.

The sections above describe a method for constructing a determinantal wavefunction from a set of LCAO-MOs. It remains now to define a method to determine the MO expansion coefficients $c_{\mu i}$ (Eq. 3.2.11) which optimise the molecular wavefunction for a particular system. The variational nature of the model (Section 3.2.3) guarantees that the energy eigenvalue solution for any approximate wavefunction is always greater than the energy obtained using the exact wavefunction. It follows that the set of coefficients which minimise the energy of the resultant wavefunction will give the best approximation to the exact wavefunction from a chosen basis set.

The variational constraint leads to a set of algebraic equations (Roothan-Hall) for $c_{\mu i}$, expressed in matrix form as

$$\mathbf{FC} = \mathbf{SC}\varepsilon \qquad (3.2.15)$$

where

- **C** is the matrix of MO expansion coefficients;
- **F** is the Fock matrix, which is the sum of a term representing the energy of a single electron in the field of the bare atomic nuclei and a term describing electron-electron repulsion within an averaged field of electron density;
- **S** is a matrix describing the overlap of molecular orbitals; and
- ε is a diagonal matrix containing the one-electron energies of each molecular orbital χ_μ.

Since the terms within the Fock matrix **F** depend upon the electron density, which in turn, depends upon molecular wavefunction defined by the matrix of MO expansion coefficients **C**, the Roothan-Hall equations are nonlinear, and must be solved by an iterative procedure termed the 'self-consistent field' (SCF) method. Upon convergence of the SCF method, the minimum-energy MOs produce the electric field which generate the same orbitals (hence, the self-consistency).

3.3 Basis Sets

In general, a basis set is an assortment of mathematical functions used to solve a differential equation. In quantum chemical calculations, the term 'basis set' is applied to a collection of contracted gaussians representing atomic orbitals, which are optimised to reproduce the desired chemical properties of a system.

Standard *ab initio* software packages generally provide a choice of basis sets that vary both in size and in their description of the electrons in different atomic orbitals. Larger basis sets include more and a greater range of basis functions. Therefore, larger basis sets can better refine the approximation to the 'true' molecular wavefunction[7], but require correspondingly more computer resources. Alternatively, accurate wavefunctions may be obtained from different treatments of electrons in atoms. For instance, molecules containing large atoms (Z > 30) are often modelled using basis sets incorporating approximate treatments of inner-shell electrons which account for relativistic phenomena.

'Minimal' basis sets contain the minimum number of AO basis functions needed to describe each atom (*e.g.*, 1s for H and He; 1s, 2s, $2p_x$, $2p_y$, $2p_z$ for Li to Ne). An example of a minimal basis set is STO-3G, which uses three gaussian-type functions (3G) per basis function to approximate the atomic Slater-type orbitals (*see* Fig. 3.2b). Although minimal basis sets are not recommended for consistent and accurate predictions of molecular energies, their simple structure provides a good tool for visualising qualitative aspects of chemical bonding. Improvements on minimal basis sets are described below and illustrated in Fig. 3.3.

3.3.1 Split valence basis sets

In split valence basis sets, additional basis functions (one contracted gaussian plus some primitive gaussians) are allocated to each valence atomic orbital. The resultant linear combination allows the atomic orbitals to adjust independently for a given molecular environment. Split valence basis sets are characterised by the number of functions assigned to valence orbitals. 'Double zeta' basis sets use two basis functions to describe valence electrons, 'triple zeta' use three functions, and so forth. Basis sets developed by Pople and coworkers [51] are denoted by the number of gaussian functions used to describe inner and outer shell electrons. Thus '6-21G' describes an inner shell atomic orbital with a contracted gaussian composed of six primitive gaussians, an inner valence shell with a contracted gaussian composed of two primitives, and an outer valence shell with one primitive. Other split-valence sets include 3-21G, 4-31G, and 6-311G.

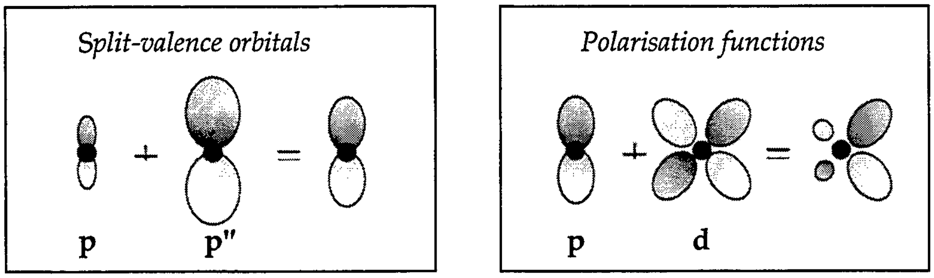

Figure 3.3. Basis set improvements.

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[7] It must be emphasised that although MOs are used to obtain values for physical 'observables' (e.g., molecular heats of formation, electronic dipole moments), they are strictly mathematical constructs (indeed, they are solutions to the Hartree-Fock approximation as opposed to the true many-body electronic Hamiltonian), and do not themselves contain any physical meaning.

3.3.2 Polarised basis sets

Polarisation functions can be added to basis sets to allow for non-uniform displacement of charge away from atomic nuclei, thereby improving descriptions of chemical bonding. Polarisation functions describe orbitals of higher angular momentum quantum number than those required for the isolated atom (*e.g.*, *p*-type functions for H and He, and *d*-type functions for atoms with $Z > 2$), and are added to the valence electron shells. For example, the 6-31G(d) basis set is constructed by adding six *d*-type gaussian primitives to the 6-31G description of each non-hydrogen atom. The 6-31G(d,p) is identical to 6-31G(d) for heavy atoms, but adds a set of gaussian *p*-type functions to hydrogen and helium atoms. The addition of *p*-orbitals to hydrogen is particularly important in systems where hydrogen is a bridging atom.

3.3.3 Diffuse basis sets

Species with significant electron density far removed from the nuclear centres (*e.g.*, anions, lone pairs and excited states) require diffuse functions to account for the outermost weakly bound electrons. Diffuse basis sets are recommended for calculations of electron affinities, proton affinities, inversion barriers and bond angles in anions. The addition of diffuse *s*- and *p*-type gaussian functions to non-hydrogen atoms is denoted by a plus sign - as in '3-21+G.' Further addition of diffuse functions to both hydrogen and larger atoms is indicated by a double plus[8].

3.3.4 High angular momentum basis sets

Basis sets with multiple polarisation functions are now practical for many systems and, although not generally required for Hartree-Fock calculations, are useful for describing the interactions between electrons in electron correlation methods (see section 3.4). Examples of high angular momentum basis sets include:

- 6-31G(2d) - two *d*-functions are added to heavy atoms;
- 6-311G(2df, pd) - besides the (311) valence functions, two *d* functions and one *f* function are added to heavy atoms, and *p* and *d* functions to hydrogen;
- 6-311G(3df, 2df, p) - three *d* functions and one f function are added to atoms with $Z > 11$, two *d* functions and one *f* function to first-row atoms (Li to Ne) and one *p* function to hydrogens.

High angular momentum basis sets augmented with diffuse functions represent the most sophisticated basis sets available. As is discussed in Section 4.3.3 below, energetic molecules have a complicated electronic structure due to the presence of nitro groups. Therefore, the most accurate *ab initio* studies of energetic materials would be produced by reasonably sophisticated polarised split-valence basis sets augmented with high angular momentum and diffuse atomic orbitals. However, the size of the optimum basis set, especially when used with electron correlation methods (discussed in

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[8] Diffuse functions on hydrogen atoms seldom make a difference in accuracy [1].

Section 3.3 below) will ultimately be determined by the size of the energetic molecule, the amount computing power available, and the time allotted for the studies. For example, conformational studies of RDX (1,3,5 trinitro-1,3,5-triazacyclohexane) range from rudimentary HF/STO-3G calculations performed in 1991 [52] to more sophisticated investigations in 1997 using B3LYP density functional theory and 6-311G(d,p) [53].

3.4 Electron correlation

Hartree-Fock theory is a single-particle approximation, and therefore cannot adequately treat the correlated motion of electrons that occurs due to electron-electron interactions. Neglect of electron correlation has been blamed for systematic HF errors such as underestimated bond lengths and overestimated vibrational frequencies. Calculations added to HF-SCF theory to remedy these errors are termed 'electron correlation' or 'post-HF' methods. There are three general types of electron correlation treatments: configuration-interaction (CI) methods, Møller-Plesset (MP) perturbation theory, and density functional theory (DFT).

3.4.1 Configuration-interaction

A HF wavefunction of a molecule has one determinant; therefore, it can only describe only one electronic configuration in a molecule. This approximation is so restrictive that HF theory cannot predict dissociation of the simplest molecule, the hydrogen dimer, into its neutral atomic components. However, correct dissociation behaviour is restored when extra configurations, corresponding to electronically excited states, are added to the wavefunction. Configuration-interaction methods incorporate excited state configurations into the wavefunction by constructing new determinants from the original HF determinant. New determinants are created by replacing one or more occupied orbitals with unoccupied (virtual) orbitals of higher energy. The number of replacements within the determinants designates the level of CI. For instance, single substitution (CIS) switches one pair of occupied and virtual orbitals,

$$\begin{aligned}\psi_{HF} &= \left|\phi_{1,}\ldots\phi_{j},\ldots\phi_{HOMO},\phi_{LUMO},\ldots\phi_{i},\ldots\phi_{n}\right| \rightarrow \\ &\qquad \psi_{CIS} = \left|\phi_{1,}\ldots\phi_{i},\ldots\phi_{HOMO},\phi_{LUMO},\ldots\phi_{j},\ldots\phi_{n}\right| \qquad (3.4.1)\end{aligned}$$

and is equivalent to a one-electron excitation. Higher-order calculations include CID (double substitutions), which generates determinants where two orbital pairs are switched; CISD, which adds singly and double-substituted determinants; and CISD(T), with single, double and triple excitations. The theoretical limit of this expansion - a full CI calculation - forms the molecular wavefunction as a linear combination of the HF determinant and all possible substituted determinants:

$$\psi_{full\text{-}CI} = a_0 \psi_{HF} + \sum_{n>0} a_n \psi_{S,D,T,\ldots} \qquad (3.4.2)$$

where the coefficients a_i are determined by minimising the energy of the total wavefunction. Full CI provides the most complete non-relativistic treatment possible for a molecular system; however, it is extremely computer-intensive, and generally untenable for all but the simplest molecules described by small basis sets.

3.4.2 Møller-Plesset perturbation

For typical molecules, most of the ground-state energy originates from one-electron HF contributions. Møller-Plesset perturbation theory assumes that the effects of electron correlation are minor, and can be described by small corrections (perturbations) to the HF solution. Essentially, MP methods assume the true molecular Hamiltonian (3.2.3) can be divided into two parts:

$$\hat{H}_{mol} = \hat{H}_{one-e} + \lambda \hat{P}_{many-e} \qquad (3.4.3)$$

where $\hat{H}_{one-e}$ denotes single-electron energy contributions that can be solved exactly by HF-SCF, and $\hat{P}_{many-e}$ represents contributions due to electron correlation. The coefficient λ is used to generate power series expansions of the energy and the molecular wavefunction:

$$E_{mol} = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots \qquad (3.4.4)$$

$$\psi_{mol} = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \lambda^3 \psi^{(3)} + \ldots \qquad (3.4.5)$$

These series are then substituted back into the molecular Schrödinger equation with the modified Hamiltonian (3.4.3), and each term is evaluated in turn. The first two energy terms constitute the HF energy

$$E_{HF} = E^{(0)} + E^{(1)}, \qquad (3.4.6)$$

and are used to evaluate $\psi^{(1)}$, which is composed of a linear combination of substituted determinants

$$\psi^{(1)} = \sum_{n} b_n \psi_{S,D,T,\ldots}, \qquad (3.4.7)$$

with coefficients b_i that are inversely proportional to the difference in energy between the ground state and the associated excited states. That is, substituted wavefunctions close in energy to the ground state make larger contributions to the perturbation expansion. The first-order correction to the wavefunction, $\psi^{(1)}$, is then used to calculate the second-order correction to the total energy $E^{(2)}$, and so on, back and forth, until the desired order of correction is achieved. Møller-Plesset theory is designated by the order of the perturbative corrections. Since the second-order energy term $E^{(2)}$ is the first-order correction to the HF energy, the designation begins at MP2, and continues with MP3, MP4, MP5, and so forth.

3.4.3 Density-functional theory

DFT theory models electron correlation as a functional[9] of the electron density, ρ. The functional employed by current DFT methods partitions the electronic energy via the Kohn-Sham equations [54,55] into several terms

$$E = E^{T} + E^{V} + E^{J} + E^{XC} \qquad (3.4.8)$$

where E^T is the kinetic energy term (arising from the motion of the electrons), E^V is the potential energy term that includes nuclear-electron and nuclear-nuclear interactions, E^J is the electron-electron repulsion term and E^{XC} is the electron correlation term. All terms except nuclear-nuclear repulsions are functions of the electron density. The terms E^T + E^V + E^J represent the classical energy of the electron distribution, while E^{XC} represents both the quantum mechanical exchange energy, which accounts for electron spin[10], and the dynamic correlation energy due to the concerted motion of individual electrons. Pure DFT methods calculate E^{XC} by pairing an exchange functional with a correlation functional and so are designated by the choice of combination. For example, BLYP combines Becke's gradient-corrected exchange functional with the gradient-corrected correlation functional of Lee, Yang and Parr [56].

DFT calculations fall into three general categories: local density approximations (LDA), generalised gradient approximations (GGA), and 'hybrid' combinations of DFT and Hartree-Fock terms. LDA exchange and correlation functionals only contain terms related to electron density[11] - an approach that works for some bulk materials, but fails to accurately predict properties in isolated molecules. GGA ('nonlocal') functionals contain terms that depend upon both the electron density and the density gradients[12].

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[9] A *functional* is a function defined by another function, that is, a function of a function.

[10] The quantum-mechanical exchange energy is accounted for in HF theory by generating antisymmetric determinental wavefuntions, as discussed in section 2.2.2. Thus, Coulomb "self-interaction" energy can be considered a type of electron correlation already included in HF theory.

[11] An example of a local functional is the 'Slater' functional:

$$E^{XC}_{LDA} = -\tfrac{3}{2}\left(\tfrac{3}{4\pi}\right)^{1/3} \int_{v} \rho^{4/3} d\vec{\mathbf{r}}$$

where ρ, the electron density, is a function of $\vec{\mathbf{r}}$. This local functional reproduces the properties of a uniform electron gas. Note: this is *not* the same as Slater determinants discussed in the previous footnote.

[12] Gradients represent spatial changes of a function as can be quite large. For example, the electronic density within a metal might be quite uniform, and thus be well modelled by the Slater functional in footnote 6, yet display large gradients at the metal surface. Large gradients

The gradient-corrected density functional method BLYP is capable of predicting intramolecular bond dissociation energies to within a few kJ/mol [57]. However, the generalised gradient approximation severely underestimates activation barriers for some reactions due to neglect of Coulomb 'self-interaction' of the electrons [58]. This problem is remedied with hybrid methods that combine Hartree-Fock self-interaction corrections with density functional exchange and correlation. Examples of hybrid methods are B3LYP and B3PW91, where B3 denotes Becke's three-parameter hybrid functional [59], while 'PW91' and 'LYP' are gradient-corrected correlation functionals of Perdew and Wang [60] and, as above, Lee, Yang and Parr.

3.4.4 Caveats for post-HF methods

Although post-SCF treatments should improve upon Hartree-Fock theory, each of these techniques violates at least one of the fundamental criteria that define *ab initio* methodology. Truncated CI calculations (*i.e.*, anything less than full configuration interaction) are not size-consistent, so comparative CI studies should include added corrections[13]. MP perturbation theory is not a variational technique, and as such does not provide an upper bound to the true molecular energy[14]. Finally, DFT contains a bias: the exact functional dependence of E^{XC} upon the electron density is unknown and must be approximated by assuming that ρ has certain properties (e.g., it behaves like a uniform electron gas). Excited-state DFT calculations, which require the application of linear response theory, has so far been limited to *atomic* systems[15]. These caveats serve as a reminder that although *ab initio* methods are capable of yielding predictions close to experimental results, many of the approximations that make quantum chemical computations feasible are wholly nonphysical. Hence, even the most sophisticated *ab initio* software packages should not be treated simply as 'black boxes.'

Given these considerations, the results of any MO calculation on energetic materials are subject to scrutiny. Nevertheless, one can assume with a high level of confidence that DFT/6-31G(d) will yield bond lengths accurate to ±0.01Å, and the molecular vibrational frequencies to within ±100 cm^{-1}. However, DFT predictions of chemical reaction energies should be treated as qualitatively correct at best. For quantitative

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also exist across interfaces of p- and n- type semiconductors, and govern gating and switching of electric current in transistors.

[13] One method , quadratic configuration interaction (QCI), restores size consistency by adding terms, with corrections available up to quadruply excited states: QCISD, QCISD(T) and QCISD(TQ). Coupled cluster methods correct for size-consistency by accounting for simultaneous substitutions in different molecules - a technique useful for modelling chemical reactions. Coupled-cluster calculations (CCD, CCSD) are useful when electron correlation makes a major contribution to electron-pair bonds and so cannot be reasonably described by perturbation methods [61].

[14] The second-order term (MP2) is always negative and often overcorrects for electron correlation.

[15] In other words, DFT should *not* be used to calculate excited states of molecules with existing commercial software [53].

accuracy (± 40 kJ/mol), a recommended procedure is to optimise the molecular structure using DFT with a high-level split-valence polarised basis set, then recalculate the structural energy with MP4 and the same or a slightly less sophisticated split-valence polarised basis set.

3.5 Open-shell calculations and spin contamination

In addition to the considerations above, input to molecular orbital calculations must specify the treatment of electron spin - that is, whether the molecule will be described using an 'open-shell' or 'closed-shell' model. Most molecules have singlet electronic ground states (zero total electron spin): they contain an even number of electrons which can be assigned to orbitals in pairs of opposite spin. HF models that pair electrons in this way are referred to as 'spin-restricted closed-shell' calculations, and are adequate for treating most types of chemical systems. However, there are several cases which require explicit consideration of unpaired electrons, and are better described by open-shell unrestricted models that generate separate MOs for spin-up (α) and spin-down (β) electrons. Spin-unrestricted calculations are used for:

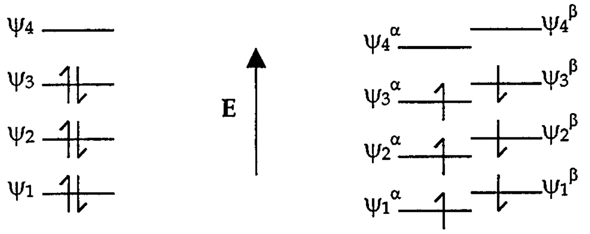

Figure 3.4. Electron assignments for closed-shell and open-shell calculations.

- Molecules with odd numbers of electrons (*e.g.*, some ions and radicals);
- Excited states;
- Molecules with triplet or higher-spin ground states (e.g., O_2);
- Processes that separate electron pairs (e.g., dissociation); and
- Delocalised orbitals for resonant systems.

Spin-unrestricted wavefunctions are not eigenfunctions of the spin operator ($\hat{S}^2$), and therefore suffer from intermixing between spin states. In most open-shell systems, spin contamination is negligible; however, for molecules where the unpaired electrons are delocalised, contamination can be quite significant, especially from the next-higher spin state. Unrestricted calculations of nitric oxide, a diatomic molecule with one unpaired electron and a doublet ($^2\pi$) ground state, display extreme spin contamination when small basis sets (STO-3G or 3-21G) are used[16]. Spin contamination can also be expected in calculations of energetic materials containing nitro (-NO_2) groups involving excited states or radical producing reactions.

The detrimental effects of spin contamination can be appreciable, although the degree of spin contamination decreases with increasing basis set size. Spin contamination has been blamed for poor predictions of molecular geometries [62] and vibrational frequencies [63]. The effects of spin contamination are particularly acute when occupied and unoccupied orbitals are nearly degenerate. This can happen, for instance, when a bond is stretched to the limit of dissociation, and the separation between bonding and antibonding orbitals approaches zero, generating a wavefunction that contains an equal mixture of singlet and triplet states. Another example is ethylene torsion, where the π and π^* orbitals become equivalent by symmetry at the transition state for rotation about the double bond [64].

It is more desirable to remove spin contamination than to ignore it, however, spin annihilation is beyond the scope of simpler post-HF methods. Open-shell HF wavefunctions effectively introduce some electron correlation, because the use of different orbitals for each electron allows α and β electrons to be spatially further apart. Hence, simpler correlation corrections (MP2 and CIS) do not generally improve spin-contaminated HF wavefunctions [65]. Suggested spin annihilation methods include high levels of electron correlation, spin-projected energy corrections, or the use of various forms of restricted open-shell wavefunctions. *Gaussian 98* automatically incorporates annihilation of one spin contaminant into its UHF calculations. Density functional methods also appear to reduce spin contamination. Baker, Scheiner and Andzelm [66] observed that 'pure' unrestricted Kohn-Sham wavefunctions display significantly less spin contamination than their HF counterparts, and concluded that spin contamination arises primarily from the use of Slater determinants in HF theory. Therefore, if spin contamination is a consideration in density functional calculations, hybrid methods that include HF exchange should be avoided.

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[16] An obvious manifestation of spin contamination is an overestimate of spin-squared expectation values. For a spin eigenfunction $\phi(\alpha,\beta)$, $\hat{S}^2\,\phi(\alpha,\beta) = s(s+1)\phi(\alpha,\beta)$, where s is the total spin. For pure doublet states ($s = ½$), $<\hat{S}^2> = ½\,(½ + 1) = 0.75$. As-mentioned unrestricted HF calculations of nitric oxide yield values of $<\hat{S}^2>$ ranging from 1.0 to 1.45.

4. Accuracy *versus* Efficiency for *Ab initio* Methods

4.1 Error reduction

4.1.1 Methods

The standard MO treatment for most closed-shell molecules is a spin-restricted Hartree-Fock self-consistent field calculation. HF-SCF calculations generally yield accurate molecular structures but are less successful at predicting molecular energies. Depending upon the system and the choice of basis set, HF energies typically fall anywhere within 200 kJ/mol of experimental values, although errors can be as large as 700 kJ/mol. The main source of error in HF calculations is neglect of electron correlation, which results in systematic overestimates of molecular energies. To account for electron correlation, calculations are added to HF results, including perturbation treatments (*e.g.*, MP2 and MP4), multiconfiguration methods (*e.g.*, CISD, CCSD and CASSCF[17]), and density functional theory (*e.g.*, BLYP, and B3PW91). Perturbation methods and density functional theory (DFT) are typically accurate to within 40 kJ/mol, while the results of multiconfiguration treatments are even better, falling within 5-8 kJ/mol of experiment. Since multiconfiguration calculations are extremely expensive for even moderately sized molecules, perturbation treatments and DFT tend to be the methods of choice for treating electron correlation.

4.1.2 Basis sets

In general, *ab initio* MO studies on complex unknown systems should begin with calculations using small basis sets, both to obtain a timely qualitative assessment of molecular properties, and to determine the computational cost of the higher-order calculations. However, minimal basis sets like STO-3G should only be used when the size of the molecule is beyond the scope of available computer resources for even small split-valence sets like 3-21G. Quantitative accuracy improves with the size of basis sets, since larger basis sets contain more adjustable parameters and are thus better able to approximate true molecular wavefunctions. Polarisation functions improve the accuracy of fundamental basis sets (*e.g.*, changing 6-31G to 6-31G(d)), although the ultimate gain is limited[18]. Diffuse functions (*e.g.*, changing 6-31G to 6-31+G) will improve results under certain circumstances. For general use, the smallest standard basis set recommended by developers of *Gaussian 98* is 6-31G(d) [51].

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[17] CASSCF is the acronym for 'complete active-space self-consistent field' calculations. CASSCF is a 'full' configuration-interaction calculation over a limited number of electrons. That is, CI determinants are constructed for specific molecular orbitals, usually those containing valence electrons [51].

[18] That is, for a given property, calculations performed with the 6-311+G(d,p) may be just as accurate as those using 6-311++G(3df,3pd), in which case 6-311+G(d,p) defines the 'basis set limit.'

4.2 Resource usage

Given the limits of computer memory and speed, the size of the chemical system generally determines the maximum size of the basis set used with MO methods. For instance, a moderately sized energetic molecule, 1,3,3-trinitroazetidine (TNAZ), contains 49 pairs of electrons. The 6-31G(d) basis set assigns 203 basis functions to the molecule, 49 of which are occupied, and the remaining 154, unoccupied or 'virtual' orbitals. To estimate memory requirements (in 8-byte words), *Gaussian 98* references [51] suggest using

$$M + 2N_B^2 \qquad (4.1.1)$$

where N_B is the number of basis sets used in the calculation and the value of M depends upon the method of calculation (typically around 4-6 MW).

Table 4.1 Resource usage by method and basis set

Method	CPU	Memory	Disk
SCF	N^4	N^2	N^4
MP2	ON^4	N^2	N^4
MP4/QCISD(T)	O^3V^4	N^2	N^4

N = total number of basis functions
O = total number of occupied orbitals
V = total number of virtual orbitals

According to Eq. 4.1.1, a Hartree-Fock SCF single-point energy calculation using the 6-31G(d) basis set (denoted 'HF/6-31G(d)') requires approximately 4.3 MW (34 MB) worth of memory. On a SGI Origin 2000[19], the recorded CPU time for this calculation is 19 minutes. From the guidelines listed in Table 4.1, a calculation using a larger basis set will require significantly more memory and CPU time. For instance, a HF/aug-cc-pVTZ[20] SPE, which assigns 609 basis functions to TNAZ, would require at least 40MB of memory, and take over a day to run[21]. Electron correlation treatments are also expensive: a MP2/6-31G(d) SPE would take roughly 16 hours to run, while MP4 or QCISD(T)/6-31G(d) would take a year and a half. Clearly, sophisticated post-HF calculations, such as CI and MP2 coupled with correlation-consistent basis sets, are only feasible for smaller molecules displaying unusual electronic properties.

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[19] This calculation was run with the standard default options of Gaussian98. The default mode imposes modest convergence criteria sufficient for 0.5 kJ/mol accuracy in the SCF energy and three decimal place accuracy in quantities derived from the electron densities (e.g. electrostatic potentials and derived charges). All calculations were performed under the IRIX 6.4 operating system using one 185MHz CPU optimised for floating-point arithmetic.

[20] This is the acronym for Dunning's correlation-consistent polarised valence triple-zeta basis set [67] augmented by diffuse functions. 'Correlation-consistent' refers to optimisation of the basis sets with electron-correlated atomic calculations.

[21] Recorded CPU time for single RHF/aug-cc-pVTZ energy calculation on the SGI Origin 2000: 4 days, 17 hours, 41 min and 16.7 sec.

Density functional methods avoid the computational expense of other post-HF methods by approximating the effects of electron correlation. DFT calculation times formally scale as the third power of the number of electrons in the system, N_e^3, whereas computational times for MP4 or QCISD(T) scale as N_e^5. In practical terms, this means that DFT treatments of electron correlation in TNAZ should only take four times as long as a HF calculation[22]. Given its demonstrated accuracy for predicting molecular energies and activation barriers, the enormous amount of time saved by using DFT makes it an attractive method for studying the ground state properties and reactions of larger energetic molecules like RDX or HMX.

4.3 High-accuracy/low-cost model chemistries

Several procedures have been developed to accurately predict[23] thermochemical quantities such as atomisation energies, ionisation potentials, electron affinities and proton affinities, at relatively low computational cost. These procedures fall into two general categories: compound methods, and complete basis set (CBS) models

4.3.1 Compound methods

Compound methods such as Gaussian-1 [68] and Gaussian-2 [69] ('G1' and 'G2') attempt to approximate a single high-level calculation by a combination of several low-level calculations. For example, the procedure for a G1 calculation is as follows:

1. Optimise the molecular structure using HF/6-31G(d) and determine the vibrational zero-point energy (ZPE)[24].
2. Reoptimise the molecular structure using full (all-electron) MP2/6-31G(d). Perform all subsequent calculations using this geometry.
3. Compute a base-level energy (E_{base}) at MP4/6-311G(d,p).
4. Compute the energy correction ΔE^+ obtained by including diffuse functions (MP4/6-311+G(d,p)): $\Delta E^+ = E_{base+diff} - E_{base}$.
5. Compute the energy correction ΔE^{2df} obtained by including higher polarisation functions on atoms with $Z > 2$ (MP4/6-311G(2df,p): $\Delta E^{2df} = E_{base+2df} - E_{base}$.
6. Compute the energy correction for residual electron correlation effects (to counteract the known deficiencies of truncating perturbation theory to fourth order) using QCISD(T)/6-311G(d,p): $\Delta E^{QCI} = E_{QCISD(T)} - E_{base}$.

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[22] Actual test time for single B3LYP/6-31G(d) energy calculation on the SGI Origin 2000: 34 min 18 sec.

[23] In some cases, predictions lie within 1% of experimental values.

[24] The ZPE is generally corrected by a scale factor which accounts for known deficiencies in the harmonic approximation of intramolecular potential energy surfaces. For HF/6-31G(d), the scale factor is 0.8929.

7. Estimate a higher-level correction of the remaining correlation energy between spin-paired electrons using the formula $\Delta E^{HLC} = -0.00019n_\alpha + -0.00595n_\beta$, where n_α is the number of spin-up electrons and n_β is the number of spin-down electrons in the molecule.

The resulting G1 energy, $E^{G1} = E_{base} + \Delta E^{+} + \Delta E^{2df} + \Delta E^{QCI} + \Delta E^{HLC} + ZPE$, is essentially an approximation to the energy of a much more computationally intensive calculation, QCISD(T)/6-311+G(2df,p).

The G2 procedure includes a couple of corrections to the G1 energy, and, for molecules containing first- and second-row atoms, is reported to predict properties to within an average absolute deviation of 6.7 kJ/mol of experimental results. A modified version of G2 known as G2(MP2) uses second-order instead of fourth-order perturbation theory, providing nearly the same accuracy as full G2 at substantially lower computational cost [1].

G1 and G2 methods have been used to study the smaller energetic molecules, nitromethane (H_3C-NO_2) [70, 71] and nitramide (H_2N-NO_2) [72]. For nitromethane, heats of formation and gas-phase acidities calculated with G1 and G2 show very good agreement with experiment (see Table 4.2), despite the tendency for MP2 to overestimate N-O bonds lengths.[25] As expected, the G2 predictions are slightly better than those of G1.

Table 4.2 Comparison of G1 and G2 predictions of nitromethane chemistry: heats of formation and gas phase acidities.

	$\Delta_f H^0_{298}$ (kJ/mol)	$\Delta_{acid} H^0$ (kJ/mol)
G1	-87.6	1500
G2	-64.6	1486
Expt	-74.8 ± 1.0	1491 ± 12

4.3.2 Complete basis set methods

The largest errors in MO thermochemical calculations result from the deficiencies of small (finite) basis sets. With perturbative methods (MP2, MP4, etc.), it is generally observed that successive contributions to the calculated energies decrease with the order of the expansion, so that the sum converges to an asymptote representing the best attainable energy for a particular basis. The convergence properties are easily approximated if the MP2 correlation energy for a many-electron system is rewritten as

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[25] Chemical bonds predicted by MP2 are typically too long because MP2 exaggerates the loss of electron density within the bonding region. In an extreme case, MP2/4-31G calculations of H_2N-NO_2 predict a N-N bond length of 2.106 Å, as compared to the experimental value of 1.86 Å [73].

a sum of electron pair energies in a particular series known as a 'pair natural orbital' (PNO) expansion. Complete basis set (CBS) methods use the known asymptotic convergence of PNO expansions to extrapolate the energy of a complete basis set[26] from calculations using finite basis sets: as the size of the basis set increases, the level of applied theory decreases. Hence, CBS models typically include a HF calculation with a very large basis set, an MP2 calculation with a smaller basis set, and one or more higher-level calculations with a medium- to modest-sized basis.

Two typical CBS model chemistries are CBS-4 and CBS-Q. CBS-4 yields results similar to other high-accuracy methods with substantially less computational cost; however, it is noteworthy that the optimised geometry is obtained using a rudimentary calculation, HF/3-21G(d). CBS-Q generally achieves better accuracies than G2, and is also less expensive computationally. CBS-4 and CBS-Q are only capable of handling systems composed of first- and second row atoms. More detail on these methods is given in [1].

4.3.3 Caveats for energetic materials

Care should be taken when using compound methods to model energetic molecules containing nitro groups. The electronic structures of nitrogen oxides display strong correlation effects because the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) have similar energies, allowing them to 'mix.' Thus, an accurate quantum chemical model of nitrogen oxides requires not only a description of the occupied electron orbitals up to the HOMO, but also a description of the LUMO – in technical jargon, this model is termed a 'multiconfigurational' treatment. Any model of nitro compounds that relies predominantly on single-configuration methods (*e.g.*, HF, MP2, MP4) is subject to error. For instance, the use of MP2 predictions with small basis sets grossly overestimate O-N and N-N bond distances in nitrogen oxides, and fail to predict the correct dissociation of nitromethane [74]. Such errors can corrupt the results of highly parameterised procedures like G1, G2 and CBS-Q, which rely on MP2/6-31G(d) geometry optimisations [1]. These errors may be avoided by the use of other procedures such as, for instance, CBS-RAD (complete basis set approximation for radicals), which uses a high-level configuration-interaction method, QCISD/6-31G(d), to determine geometries and zero-point energies, followed by coupled-cluster methods for high-accuracy calculations [75]. To date, there has been no reported use of CBS-RAD for studies of energetic materials.

5. Conclusions

Electronic structure calculations provide useful estimates of the energetic properties of chemical systems, including preferred molecular structures, spectroscopic features and probable reaction paths. This review of some current electronic structure calculations

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[26] A complete basis set contains an arbitrary number of terms, and can therefore generate the 'true' molecular wavefunction.

has concentrated on discussion of *ab initio* techniques, as these are the most accurate and, in principle, 'universal' methods. Rapid advances in computer technology are making computationally expensive *ab initio* methods increasingly more practical for use with realistic chemical systems. In particular, 'cheaper' methods such as density functional calculations and 'layered' models such as ONIOM are continually being refined, and show promise of providing consistent and accurate chemical predictions for most complex systems. Energetic materials, which often contain azide or nitro groups that require sophisticated treatments of electronic structure, fall into this category. A subsequent publication [4] will describe the application of electronic structure methods to estimates of the chemical properties of energetic materials.

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H.Dorsett and A. White

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This is a review of molecular modelling techniques which may be applied to studies of energetic materials. It focusses on *ab initio* ('first-principles') molecular orbital calculations, since these methods offer the greatest accuracy. Since *ab initio* calculations are very computer-intensive, approximate MO methods are also discussed, which offer reasonably accurate predictions with reduced calculation times. These approximate methods include density functional theory and 'layered' techniques which combine different levels of theoretical sophistication into one calculation.