

## CHAPTER 2

# Theory (Energies and Potential Energy Surfaces)

## Theoretical Methods

### 1. Introduction

Gas phase chemistry is fertile ground for the interface of theory and experiment. Because intermolecular forces that are prevalent in condensed phases are of minimal importance in the gas phase, the focus is on the molecule or molecules that are directly reacting. Although some special considerations are necessary when the system of interest has a net charge (see below), theory has a special role to play in gas phase chemistry.

Because of recent advances in both theoretical and computational methodology and in computational hardware, theoretical chemistry can make quantitative predictions of molecular structures, relative isomer energies, reaction energetics, branching ratios, and the details of potential energy surfaces. Several methods have been developed that are frequently able to predict heats of formation, ionization energies, and electron affinities for small main group compounds with an accuracy of 4–8 kJ mol<sup>-1</sup>. This means that related properties, like isomerization energies, can be predicted with similar accuracy. New methods have also been developed that facilitate the prediction of such important properties as spin-orbit coupling matrix elements, often with an accuracy of just a few cm<sup>-1</sup>. Barrier heights are generally more difficult to predict accurately, because transition states are generally characterized by partially broken bonds that require sophisticated wave functions for an accurate description. This is especially important for the prediction of kinetics properties such as rate constants, which vary exponentially with activation energy. Nonetheless, it is possible to bring very accurate methods to bear in the detailed analysis of potential energy surfaces, and subsequently the dynamics, for small molecules.

### 2. Theoretical Methods

#### 2.1 Overview

The ultimate goal in electronic structure theory is to solve the Schrödinger equation,  $\hat{H}\Psi = E\Psi$ , where  $\hat{H}$  is the  $N$ -electron Hamiltonian,  $\Psi$  is the  $N$ -electron wave function, and  $E$  is the eigenvalue (energy) for the system. Unfortunately, this equation is exactly solvable only for very simple systems, such as the H atom. For more complex chemical systems, one is reduced to making approximations, either to the wave function or to the Hamiltonian. If the exact Hamiltonian is retained and only the wave function approximated, the corresponding approximate methods fall into the general category of “variational” methods. These methods are governed by the Variational Principle, which shows that the exact energy is a lower bound to the variational energy. This is a very powerful theorem, because it ensures that the approximate energy can never fall below the exact energy. Therefore, one can systematically improve the energy by improving the wave function, ultimately culminating in the exact energy and exact wave function.

Alternatively, one can approximate the Hamiltonian in such a manner that the corresponding approximate Schrödinger equation is exactly solvable. Then, both the wave function and the energy can be systematically improved using many body perturbation theory (MBPT). Using perturbation theory, the exact energy is not a lower bound (i.e., no Variational Principle), but the usual implementation of MBPT, using Rayleigh–Schrödinger perturbation theory, is “size-consistent.” This means that the energy of the whole system is equal to the sum of the energies of its component pieces, as those pieces are moved to very large separations ( $I$ ). Variational methods are not generally size-consistent, although certain implementations are, as discussed below. In principle, MBPT also leads to the exact energy and wave function if carried to a sufficiently high order, but this depends on the convergence of the perturbation series.

A third method for systematically approaching the exact solution of the Schrödinger equation is the cluster expansion, in which the exact wave function is expressed as  $e^T\Phi_0$ , where  $T$  is the sum of 1-, 2-, ... electron excitation operators and  $\Phi_0$  is the zeroth-order wave function. The cluster expansion, which is size-consistent, has emerged as a very powerful technique for obtaining highly accurate energy quantities, and it appears to converge much more quickly than do the traditional perturbation expansions.

For all three of the methods discussed above—variational, perturbation theory, cluster expansion—the wave function can be expressed as a linear combination of determinants:

$$\Psi = \sum_i a_i D_i \quad (1)$$

where  $D_i$  is a determinantal wave function:

$$D_i = |\psi_1 \psi_2 \cdots \psi_n| \quad (2)$$

and  $\psi_i$  is a molecular spin orbital,  $\psi_i = \phi_i \sigma_i$ , a product of a space function (molecular orbital)  $\phi_i$  and a spin function  $\sigma_i$ . The molecular orbitals in turn are expanded in an atomic basis,  $\chi_\mu$ :

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} \quad (3)$$

Because each method, taken to its limit, can in principle approach the exact wave function for a given atomic orbital basis  $\chi_\mu$ , the choice of this atomic basis plays a central role in electronic structure theory.

## 2.2 Atomic Basis Sets

In the early days of applied electronic structure theory, the most common basis set type was the exponential form:

$$\chi_\mu = r^\zeta e^{-\zeta r} Y_\ell^m(\theta, \phi) \quad (4)$$

where  $r$  is the distance of the electron from the nucleus,  $\ell$  is the angular momentum quantum number,  $\zeta$  is the orbital exponent that is sometimes taken to be an effective nuclear charge, and  $Y_\ell^m(\theta, \phi)$  are the spherical harmonics that describe the angular behavior. These ‘‘Slater-type orbitals’’ (STOs), named after their creator (2), were very popular until people started to seriously consider nonempirical calculations on polyatomic molecules. Nearly all semiempirical methods that were developed in the 1950s through the 1980s are based on STO basis sets. The great advantage of STOs is that they have approximately the correct shape, especially reproducing the ‘‘cusp’’ at the nucleus that is so important for accurately predicting properties related to NMR and ESR spectroscopy. The major difficulty associated

with Slater-type orbitals as basis functions is that the required two-electron integrals over these atomic functions do not generally have closed analytical forms. In particular, integrals of the type:

$$(\mu\nu|\lambda\sigma) = \iint \chi_\mu(1)\chi_\nu(1)[1/r_{12}]\chi_\lambda(2)\chi_\sigma(2) dV_1 dV_2 \quad (5)$$

in which the four atomic orbitals are centered on three or four different nuclei have no closed form. Because the number of these integrals increases as  $n^4$ , where  $n$  is the number of atomic basis functions, the computation of these integrals can become very demanding. Therefore, following a suggestion made by Boys (3), quantum chemists began constructing basis sets using Gaussian type orbitals (GTOs) instead. GTOs have the general form:

$$\chi_\mu = x^a y^b z^c e^{-\alpha r^2} \quad (6)$$

where  $a$ ,  $b$ ,  $c$  are integers that determine the type of ‘‘Cartesian Gaussian’’ one has specified. For example,  $a=1$ ,  $b=c=0$  represents a  $p_x$  orbital. The size (radial extent) of the Gaussian is determined by the exponent  $\alpha$ . The advantage of GTOs is that the product of two Gaussians is itself a Gaussian, only centered at a different point in space. So, the integrals in Eqn. (5) have a closed analytic form and are therefore much easier to evaluate. There are always trade-offs in making such decisions, and the downside of GTOs is that their shape is much different from the STOs in several respects. Gaussians do not reproduce the cusp at the nucleus and therefore cannot accurately represent properties that depend on the electron density near the nucleus. GTOs also fall off too rapidly with distance from the nucleus, so they do not adequately represent the valence region. Consequently, one must use more GTOs than STOs in the atomic basis in order to attain equivalent accuracy.

There are several common basis set types:

*Minimal basis sets (MBS):* These are the simplest possible basis sets, which contain only those atomic orbitals that are required to describe each atom in the molecule. Examples are a  $1s$  orbital for H;  $1s, 2s, 2p$  for C;  $1s, 2s, 2p, 3s, 3p$  for Si.

*Double zeta (DZ) basis sets:* These basis sets contain two atomic orbitals of each type; that is, exactly double the minimal basis set. For example, a double zeta basis set on C would contain  $1s, 1s', 2s, 2s', 2p, 2p'$ . The two orbitals of each type have the same shape, but different sizes determined by the exponent  $\alpha$  in Eqn. (6). One can imagine larger basis sets called triple zeta, quadruple zeta, etc.

*Split valence (SV) basis sets:* Because much of chemistry is determined by the valence electrons, a commonly used, compact type of basis set uses a

minimal basis set for inner shells and a double zeta or triple zeta basis set for the valence shell.

*Polarized basis sets:* All of the basis sets described above are essentially atomic in nature; that is, they are designed to improve the descriptions of the individual atoms in a molecule. However, they do not contain the flexibility required to describe the manner in which atomic electron densities are modified when the atoms are bound in a molecule. A simple example is  $H_2$ . The H atom is well described by a spherical  $s$  orbital. However, in  $H_2$ , the electron density needs to be decidedly non-spherical with a preferred polarization along the bond direction. This is best accomplished by mixing some  $p$  character into the basis set. So, a polarized double zeta (DZP) basis set for H would include a set of  $p$  functions in addition to the  $1s$  orbital. Likewise, a set of  $d$  polarization functions would be added to C or to Si.

*Diffuse functions:* There are several situations in which one needs to include diffuse functions (orbitals with a larger than usual radial extent) in the basis set. The most obvious case is the description of anions (see *Theory (Energies and Potential Energy Surfaces): Anions*). The “extra” electron in a mono-anion most commonly enters a previously unoccupied antibonding orbital. Such orbitals are, by their very nature, more diffuse than most occupied bonding and non-bonding orbitals. They therefore require more diffuse basis functions with smaller values of the exponents  $\alpha$ .

Several groups have expended considerable effort toward the development of basis sets. Given the space limitations, this summary will focus on two general basis set types that are arguably the most popular among current users. The first of these are collectively referred to as the “Pople basis sets,” because they were developed by the Pople group over several years, beginning with the initial emergence of systematic Gaussian basis sets. The simplest Pople basis sets are the minimal basis sets (MBS) STO-NG (4, 5) in which a STO is simulated as an expansion of  $N$  Gaussians. Surveys of the performance of STO-NG suggested that  $N=3$  is the best balance of accuracy and efficiency. So, each basis function (atomic orbital) is expanded in three Gaussians. Such an expansion is referred to as a “contraction.” Most of the other Pople basis sets are some variation of the split valence basis sets  $N$ -M1G or  $N$ -M11G (6–11). Here,  $N$  refers to the number of contracted Gaussians used for the MBS description of inner shells. That is, inner shells are treated using a MBS NG basis. The valence space is split into two or three subspaces. The innermost valence subspace is represented by a contraction of  $M$  Gaussians. The outer one or two valence subspaces are represented by single (uncontracted) Gaussians. The most commonly used

implementations of these basis sets are 3-21G, 6-31G and 6-311G. These basis sets are frequently augmented by polarization and/or diffuse functions. A typical example is 6-311++G(3df,2p). The ++ means a set of diffuse  $s$  and  $p$  orbitals is added to all heavy atoms (first +) and a set of diffuse  $s$  functions is added to all hydrogen atoms (second +). The 3df,2p means three sets of  $d$  and one set of  $f$  polarization functions are added to each heavy atom and two sets of  $p$  functions are added to each H. To save computer time,  $s$  and  $p$  orbitals in the Pople basis sets share common exponents. Most of the Pople basis sets are available for the first four rows of the main group elements in the periodic table.

The second popular group of basis sets are those developed more recently by Dunning and coworkers specifically for use with correlated wave functions that go beyond the simple orbital approximation. These systematic basis sets are referred to as correlation consistent (cc) polarized valence  $N$ -zeta (cc-pVNZ) or augmented (aug)-cc-pVNZ, where  $N$  ranges from 2 (cc-pVDZ) to 6 (cc-pv6Z) and “aug” refers to the addition of diffuse functions. Especially for  $N>3$ , these basis sets tend to become very large, because the number of diffuse and polarization functions grows with  $N$ . The basis sets with  $N=2,3$  are commonly used with the correlated methods discussed below, because those with larger  $N$  are very computationally demanding. These basis sets are currently available for the first three rows of main group elements.

### 2.3 Single-reference Methods

The simplest methods in electronic structure theory are those for which a single electronic configuration (i.e., one term in the expansion in Eqn. (1)) is adequate for a qualitatively correct description of the system of interest. In such cases, several methods of increasing sophistication are appropriate. The simplest of these is Hartree–Fock (HF) theory. For closed shell species, the restricted Hartree–Fock (RHF) wave function is a single determinant:

$$\Psi_{\text{rhf}} = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_N \bar{\phi}_N| \quad (7)$$

where the bar means  $\beta$  spin. For open shells, one has two choices. One choice is the restricted open shell HF (ROHF) method, in which all electrons are paired except those in the open subshells. The ROHF wave function for the high-spin case is:

$$\Psi_{\text{rohff}} = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_N \bar{\phi}_N \phi_{N+1} \phi_{N+2} \cdots| \quad (8)$$

For low-spin open shells, one would have a linear combination of determinants in order for the

wave function to be spin correct. The alternative unrestricted HF (UHF) method employs separate sets of orbitals for  $\alpha$  and  $\beta$  electrons. The UHF wave function is:

$$\Psi_{\text{uhf}} = \left| \phi_1^\alpha \phi_2^\alpha \cdots \phi_p^\alpha \bar{\phi}_{p+1}^\beta \bar{\phi}_{p+2}^\beta \cdots \bar{\phi}_{p+q}^\beta \right| \quad (9)$$

where  $\phi_i^\alpha$  and  $\phi_i^\beta$  are separate orbitals for the different spins.  $\Psi_{\text{uhf}}$  is variationally preferable, because it is expected to yield lower energies, and the formulation and coding of this method and related correlated methods are simpler. On the other hand,  $\Psi_{\text{uhf}}$  is not spin correct, and the ‘‘spin contamination’’ (the deviation from the correct spin multiplicity) can frequently be severe.  $\Psi_{\text{rohf}}$  is spin correct, but correlation methods based on the ROHF method can be more complicated to implement. In general, the cost of HF calculations is on the order of  $N^4$ , where  $N$  is the size of the basis set.

If one systematically improves the atomic basis set, eventually, one reaches the complete basis set (CBS) limit. This corresponds to the exact Hartree–Fock solution. Because Hartree–Fock uses an independent particle wave function (Eqns. (7)–(9)), the instantaneous correlation between electrons is not accounted for and electrons generally approach each other too closely. This results in an overestimation of the electron–electron repulsion. The difference between the correct Hartree–Fock energy and the exact nonrelativistic energy is referred to as the correlation energy or the correlation error,  $E_{\text{corr}}$ . Starting from a Hartree–Fock wave function, several techniques can be used to recover some fraction of  $E_{\text{corr}}$ . The simplest such approach is generally referred to variously as many body perturbation theory (MBPT) (12) and Moller–Plesset (MP) (13) perturbation theory. Perturbation theory provides correlation corrections by adding first ( $E_1$ ), second ( $E_2$ ), third ( $E_3$ ), etc., corrections to the HF energy. In general, the convergence of the perturbation expansion depends on the perturbation being small. For HF theory  $E_1=0$ , so the first nonzero correction is  $E_2$ , referred to as MP2 or MBPT2. MP2 energies and analytic gradients (first derivatives of the energy) have been derived and coded for RHF, UHF, and ROHF, and these methods are available in several popular electronic structure programs. Because MP2 is size-consistent and scales as  $N^5$ , this is the most widely used correlation method. As the order of perturbation theory increases, the cost increases as well. For example, full MP4 including triple excitations scales as  $N^7$ . Unfortunately, there is mounting evidence that the perturbation series does not converge, with MP3 frequently giving worse results than MP2 and MP4 often no better (and sometimes worse) than MP2 (14). Most troubling, the convergence problems appear to worsen as the basis set is

improved, especially with the addition of diffuse functions. Nonetheless, second-order perturbation theory is a very popular, and frequently reliable method for recovering much of the correlation energy. Several electronic structure codes have analytic MP2 gradients and some have analytic Hessians (energy second derivatives), so it is straightforward to probe potential energy surfaces using this approach.

An alternative to perturbation theory is configuration interaction (CI). Löwdin showed that if one constructs the wave function by starting with a reference function (e.g., the Hartree–Fock wave function), and then adding all possible single, double, ... replacements of electrons in occupied orbitals into unoccupied orbitals, one obtains the exact wave function for the chosen atomic orbital basis:

$$\Psi = \Psi_0 + \sum_{i \rightarrow a} C_i^a \Phi_i^a + \sum_{ij \rightarrow ab} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{ijk \rightarrow abc} C_{ijk}^{abc} \Phi_{ijk}^{abc} \cdots \quad (10)$$

In Eqn. (10),  $i, j, k$  refer to occupied orbitals and  $a, b, c$  refer to virtual (unoccupied) orbitals. If all possible configurations are included, the method is referred to as Full CI (FCI). This level of theory is extremely time- and resource-consuming, so it is realistically applicable only to small molecules. The most common implementation of CI truncates Eqn. (10) at single and double excitations and is called CISD. This level of theory, which scales as  $\sim N^7$ , is based on linear variation theory, so one can obtain several roots (ground and excited electronic states), each of which is an upper bound to the corresponding exact electronic state. However, the method is computationally demanding, and because excited states frequently exhibit significant configurational mixing, the use of Hartree–Fock orbitals as a basis can lead to slow convergence of the CI expansion in Eqn. (10). For ground states, because CISD includes only single and double excitations, the accuracy is expected to be similar to that of MP2 or MP3. Although CISD is variational, because it is a truncated version of Full CI, it is not size-consistent.

The third alternative to perturbation theory and variational methods is the cluster expansion, usually called coupled cluster theory (CC), in which the wave function is written as:

$$\Psi = e^T \Phi_0 \quad (11)$$

where  $\Phi_0$  is most commonly taken to be the Hartree–Fock wave function, and

$$T = T_1 + T_2 + T_3 \cdots + T_N \quad (12)$$

$T_m$  is an  $m$ -electron excitation operator:

$$\begin{aligned} T_1 &= \sum_i t^{(i)} \\ T_2 &= \sum_{i<j} t^{(ij)} \\ T_3 &= \sum_{i<j<k} t^{(ijk)} \\ &\vdots \end{aligned} \quad (13)$$

such that, for example,

$$\sum_i t^{(i)} \Psi_0 = \sum_r^{\text{occ}} \sum_a^{\text{virt}} d_r^a \Phi_r^a \quad (14)$$

and similarly for higher order excitation operators. Because  $e^T$  is an exponential operator, it may be expanded as the series

$$e^T = 1 + T + 1/2T^2 + \dots \quad (15)$$

This means that the quadratic and higher order terms in Eqn. (15) contain cross-terms (“unlinked” clusters) between  $m$ -electron and  $n$ -electron excitations (e.g.,  $t^{(m)}t^{(n)}$ ). As for CI, the coupled cluster expansion is generally truncated for computational tractability, leading to CCSD (coupled cluster with singles and doubles), CCSDT, etc. However, unlike truncated CI expansions, truncated coupled cluster expansions are size-consistent, because of the inclusion of the unlinked clusters. Triple excitations are frequently necessary to attain chemical accuracy for prediction of relative energies. Because the full CCSDT solutions are often too computationally demanding, a compromise approach is to estimate the effects of triple excitation using perturbation theory. This CCSD(T) method (15, 16) seems to lose very little in accuracy compared with CCSDT, so it has become the most commonly used method when high accuracy is desired and single configuration methods are appropriate.

Although it does not obviously fit into the hierarchy of methods discussed above, most modern implementations of density functional theory (DFT) do incorporate some level of electron correlation. In principle, DFT is an exact theory, based on a theorem by Hohenberg and Kohn (17) that the ground state electronic energy is completely determined by the density. This is very appealing, because the density  $\rho(x, y, z)$  is a function of only three variables, whereas the wave function is a function of  $3n$  variables, where  $n$  is the number of electrons. The difficulty is that the exact density is unknown, and the functional relation between the energy and the density is unknown. Consequently, the aim of density functional theory is to find appropriate energy “functionals”; that is, functions of the type  $E[\rho(x, y, z)]$  that closely approximate the exact energy. In most current implementations, DFT formally closely resembles Hartree–Fock theory.

Although in DFT one thinks in terms of the density rather than the wave function, in practice the method is formulated in terms of a wave function in order to obtain the density. The wave function is expressed as a single determinant of Kohn–Sham orbitals (18) that are determined iteratively in a self-consistent manner, just as the HF orbitals are obtained using a SCF procedure. The HF orbitals are determined by the Fock operator:

$$\hat{F} = \hat{h} + \sum_i (2\hat{J}_i - \hat{K}_i) \quad (16)$$

where  $\hat{h} = \hat{T} + \hat{V}_{\text{en}}$  is the sum of the kinetic energy and electron–nuclear attraction potential energy operators, and  $\hat{J}$  and  $\hat{K}$  are the local Coulomb and nonlocal exchange operators, respectively (1). In DFT the kinetic energy and exchange operators are replaced by functionals. In particular, the complex nonlocal exchange operator is generally replaced by a local functional that is intended to incorporate both exchange and correlation effects. In most implementations these functionals are determined by fitting some number of parameters to experimental data, usually thermodynamic quantities. In this sense, most DFT implementations are semiempirical methods. There are many functionals currently available in most electronic structure packages (19). It is difficult to choose one as the best, because different functionals appear to perform best for different properties. Nonetheless, the most popular functional appears to be B3LYP (20). The great appeal of DFT is that, whereas it scales as  $\sim N^4$ , it often performs at the level of second-order perturbation methods that scale as  $\sim N^5$ .

## 2.4 Multireference Methods

It is frequently the case that a system of interest cannot be adequately described by a single electronic configuration (e.g., single Lewis structure). In such instances the methods described in the preceding section are not reliable, and one must use a multi-configuration (MC) or multireference (MR) wave function. Examples of situations for which a multi-configuration description is often necessary are diradicals, transition states for chemical reactions, excited states, and unsaturated transition metal compounds. All such species have near degeneracies because of low-lying electronic states; it is these near degeneracies that are responsible for the need for MC wave functions.

The most common starting point for MC calculations is called the multiconfiguration self-consistent field (MCSCF) method. This method is similar to the CI method discussed above, in the sense that the wave function is a linear combination of configurations as in Eqn. (10). However, whereas the only optimized variational parameters in a CI calculation

are the CI coefficients, in a MCSCF calculation, both the CI coefficients and the molecular orbitals themselves (i.e., the LCAO coefficients) are optimized. This means the MCSCF orbitals are optimized for the set of configurations in the CI expansion, not for just one configuration.

A systematic method for formulating a MCSCF calculation is to construct a fully optimized reaction space (FORS) (21) or complete active space SCF (CASSCF) (22) wave function. In this approach, the full space of orbitals, defined by the number of atomic basis functions  $N$ , is divided into three subspaces: core, active, and virtual. The core consists of those orbitals whose electron occupation numbers are fixed at 2. These orbitals appear as doubly occupied in every configuration (determinant) of the overall wave function. The orbitals in the virtual space are always vacant, so they never appear as occupied in any configurations. The orbitals in the active space can appear in various configurations with occupancies of 0, 1, or 2. Because each configuration is weighted by a variationally determined CI coefficient (see Eqn. (10)), the occupation numbers for orbitals in the active space are generally not integers. Indeed, one useful measure of the importance of configurational mixing is how significantly these occupation numbers deviate from the integer values they would have in a Hartree–Fock wave function. Ideally, the “active space” in a MCSCF calculation would consist of all valence electrons, and all valence orbitals and their corresponding antibonding orbitals. For example, a full valence active space for ethane would consist of 14 electrons and 14 orbitals, denoted CASSCF (14,14), whereas that for methanol would be CASSCF (14,12) because one normally does not include antibonding orbitals for lone pairs (23). The configurations included in the corresponding CASSCF wave function are obtained from a full CI within the complete active space. However, CASSCF calculations, and especially higher order methods that build on CASSCF wave functions, become computationally intractable when the size of the active space exceeds 16 or 18 orbitals, so it is common practice to design the active space on the basis of the chemistry one is attempting to describe. For example, if one is describing the dissociation of ethane into two methyl groups the necessary active space is two electrons in two orbitals, CASSCF (2,2), whereas one needs a CASSCF (6,6) wave function for a correct description of the dissociation of  $N_2$ . A recent review discusses in detail methods for choosing active spaces (23). A difficulty arises when one is examining a complex reaction mechanism in which different segments of the mechanism require chemically different active spaces. One choice is to design a composite active space that incorporates the spaces needed for all segments; however, this may be computationally intractable. A common solution to

this dilemma is to solve the problem in two steps. First, one defines an active space that is appropriate for a part of the potential energy surface (PES) of interest, and optimizes the geometries for the relevant stationary points in that section of the PES. Once this has been accomplished for all sections of interest on the PES, final energies can be computed for these optimized geometries using an expanded active space and one of the electron correlation methods discussed below.

The CASSCF wave function provides a correct zeroth-order description of a particular molecule or chemical process, and is important when a single reference description is inappropriate. As is true for Hartree–Fock, one still needs to add electron correlation corrections, sometimes called “dynamic correlation,” to obtain accurate energies. This is accomplished using approaches that are similar to those described previously for Hartree–Fock (i.e., perturbation theory, CI, coupled cluster), with the important difference that these methods are more complicated and more computationally demanding than are their single reference counterparts. The potential advantage of the multireference approach is that it is possible that the perturbation, CI, or cluster expansion will exhibit improved convergence because the MR wave function is more accurate than the single reference one. At this point, there are not sufficient data to adequately assess this speculation. Most implementations of multireference perturbation theory (MRPT) are limited to second order. The most popular of these methods is CASPT2 (complete active space second-order perturbation theory) (24) developed by Roos and co-workers, although the MRMP2 (multireference, Moller–Plesset) (25, 26) and MCQDPT (multireference quasi-degenerate perturbation theory) (27) methods are also used frequently. The latter approach has the particular advantage that it can treat multiple electronic states. A third-order method, CASPT3 (28), is also available. As is the case for single reference methods, perturbation theory is the most efficient MR approach. However, unlike the single reference method, the multireference perturbation methods are not strictly size-consistent.

The most commonly used alternative to MRPT is multireference (MR) CI (29–31). The most common implementation of MRCI includes all single and double excitations from the MCSCF reference function. If the single and double replacements occur only from the MCSCF active space, this is often referred to as second-order CI (SOC) (32), whereas if these excitations emanate from the entire valence space, it is called MR(SD) CI (29–31). In general, such calculations are limited computationally to (14,14) active spaces. Considerable effort has been expended in the development of multireference coupled cluster methods (33), but such methods are not yet available in general electronic structure codes. However,

coupled cluster calculations can be performed on excited states using the equations of motion (EOM) method (34–36). The EOM-CC approach allows one to obtain excitation energies directly, rather than by calculating excited state energies and then calculating energy differences. All three methods, MRPT, MRCI, and EOM-CC, are very computationally demanding and analytic energy derivatives for these methods are not readily available. Nonetheless, they are the methods of choice for accurate predictions for excited states and complex species in their ground states.

### 3. Predictions of Thermodynamic Properties

Despite the improvements in computational software and hardware, the most accurate of the methods discussed in the previous section are still only applicable to small molecules. In order to predict accurate properties, methods have been developed that make use of additivity and extrapolation/interpolation relations. The most well known and popular of these methods are the Gn methods developed by Pople and coworkers (37) (“Gn,” where  $n = 1, 2, 3$ ). The basic premise of these methods is that if one starts with a sufficiently reliable level of theory, for example, MP2 with a double zeta plus polarization basis set, then subsequent improvements in (a) the basis set and (b) the level of theory are additive to a good approximation. The G1, G2, and G3 methods are increasingly sophisticated, but they all work roughly as follows. One starts with a baseline level of theory, such as MP2 with the 6-311G(d) basis set, and determines molecular geometries and vibrational frequencies at this level. In some of the methods HF is used to calculate the frequencies. One then:

(i) calculates the energy at a higher level of theory, usually CCSD(T) or an analogue of this method called quadratic CI (QCI) with the same basis set;

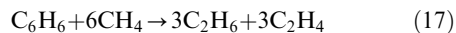
(ii) calculates the energy at the baseline level of theory with one or more improved basis sets, such as 6-311G(2d,p);

(iii) assumes that each improvement is additive in order to extrapolate to the energy at the highest level of theory and the composite largest basis set;

(iv) determines a “higher level correction,” using experimental data on heats of formation, ionization energies, and electron affinities, which accounts for remaining deficiencies in the basis set and level of theory.

There are many variations of this approach, for example, based on effective core potentials and including relativistic effects for heavier elements, with the basic criterion being predictive capability with chemical accuracy of  $\leq 8 \text{ kJ mol}^{-1}$ . The limitations of the Gn methods are that they are still computationally limited to molecules of moderate size (less than 10 heavy atoms) and there are

systematic errors as the size of the molecule increases (38). These difficulties can be diminished to some degree by making use of isodesmic or homodesmic reactions. In an isodesmic reaction, the formal bond types are conserved. For example, the reaction (Eqn. (17)):



is isodesmic, because the numbers of C—C, C=C and C—H bonds are conserved. If one performs a Gn calculation on each species in Eqn. (17), the error is minimized and the accuracy of the predictions is improved (38). The Gn methods are all single reference models. Recently, multireference analogues called MRGn have been developed, and initial tests of this suite of methods are promising.

Several other methods have been developed with a philosophy that is similar to that of the Gn methods. The bond additivity correction (BAC) methods (39) preceded the Gn methods and are most commonly applied with second- and fourth-order perturbation theory. Truhlar and co-workers have developed alternatives to the Gn methods called MC (multi-coefficient) methods (40). Several authors have developed methods for systematically extrapolating to the complete basis set limit (41). These are then applied to various levels of theory, most commonly MP2, CCSD(T) and DFT. Morokuma and co-workers have developed an increasingly popular suite of methods that are collectively called the ONIOM method (42). The basic idea of this method is that one wishes to calculate the energy of some target molecule (say molecule X) that is too large for the desired level of theory (method A). One then designs a smaller compound x that is a model for compound X and performs calculations on x using both method A and a simpler method B. Finally, a calculation is performed on X using method B and estimates the result of method A on X by assuming additivity:

$$A(X) = A(x) + B(X) - B(x) \quad (18)$$

### 4. Predictions of Potential Energy Surfaces

The prediction of potential energy surfaces (PES) and minimum energy reaction paths (MEP) is more complicated, and therefore more demanding, than the prediction of thermodynamic properties. Thermodynamic properties are usually calculated at potential energy minima, where molecular structures and chemical bonds are well defined and intact. A primary reason for studying a PES is to predict quantities related to kinetics and dynamics. Because the calculation of a rate constant, for example, involves relative energies in exponents, very accurate relative energies are very important. Probing a PES or MEP, especially in transition state regions or in

regions of a PES that are far from stationary points, results in bonds that are not well defined. Consequently, methods that include electron correlation corrections are necessary, certainly for the accurate prediction of energies and often for the prediction of geometries. It is also frequently the case that single reference methods are inadequate for extensive probing of potential energy surfaces, again because structures far from minima are not generally well described by single Lewis structures. Such species frequently have low-lying excited states that lead to near degeneracies and therefore to the need for a multireference description.

A detailed description of tools and strategies for exploring potential energy surfaces is beyond the scope of this chapter. Briefly, except for very small molecules, the availability of analytic energy gradients is critical, and analytic second derivatives (hessians) make the process much more tractable. Numerical hessians can be especially problematic for MCSCF wave functions, because it is not uncommon to encounter root flipping (dropping to a lower electronic state) when the structure is distorted so that it has no symmetry. This occurs because it is difficult to converge SCF methods to states that are not the lowest state of a given symmetry. In ion chemistry, the existence of loosely bound ion-dipole intermediates in the entrance or exit channel of an ion-molecule reaction is not unusual. This makes exploration of the minimum energy path particularly useful, because such intermediates are easily identified by walking along the MEP in each direction, starting from a transition state. A particularly effective method for tracking a MEP is the second-order algorithm developed by Gonzalez and Schlegel (43).

## 5. Summary and Outlook

The tools that have been, and continue to be, developed for exploring with high accuracy the properties and potential energy surfaces will broaden the types and sizes of ionic species that will be accessible using modern computational techniques. In addition to the methods discussed in this article, dramatic improvements continue to be made in the development of practical methods for treating relativistic effects (44–46), clearly of great importance if one is concerned with the chemistry of heavy elements. Beautiful new experiments, spectroscopic experiments using synchrotron radiation, provide highly detailed information about multiple electronic states and spin-orbit coupling within electronic states, all as a function of vibrational and even rotational quantum number (47). New, more reliable methods for calculating these effects (48) result in very exciting symbiosis between theory and experiment. Likewise, the development of new tools for predicting and analyzing nonadiabatic interactions and conical

intersections (49) is essential if one is to investigate the interactions of multiple electronic states. All of these new developments will enhance the interactions between theory and experiment.

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M. S. Gordon  
Iowa State University, Ames, Iowa, USA

## Anions

There are several very useful literature sources for values of atomic or molecular electron affinities (EAs).

(i) For atoms, the early reviews of Hotop and Lineberger (1), and the more recent review by Andersen *et al.* (2) remain excellent sources.

(ii) For molecules, there are several sources (3–7) that span many years, some of which are accessible on the web.

In this Chapter, we denote electron charge by  $-q$ , with its magnitude being  $q = 4.802 \times 10^{-10}$