

The SCF-LCAO-MO Method and Extensions

11-1 *Ab Initio* Calculations

A rigorous variational calculation on a system involves the following steps:

1. Write down the hamiltonian operator \hat{H} for the system.
2. Select some mathematical functional form ψ as the trial wavefunction. This form should have variable parameters.
3. Minimize

$$\bar{E} = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (11-1)$$

with respect to variations in the parameters.

The simple and extended Hückel methods are not rigorous variational calculations. Although they both make use of the secular determinant technique from linear variation theory, no hamiltonian operators are ever written out explicitly and the integrations in H_{ij} are not performed. These are *semiempirical* methods because they combine the theoretical form with parameters fitted from experimental data.

The term *ab initio* (“from the beginning”) is used to describe calculations in which no use is made of experimental data. In an *ab initio* variational method, all three steps listed above are explicitly performed. In this chapter we describe a certain kind of *ab initio* calculation called the self-consistent field (SCF) method. This is one of the most commonly encountered types of *ab initio* calculation for atoms or molecules. We also describe a few popular methods for proceeding beyond the SCF level of approximation.

The SCF method and extensions to it are mathematically and physically considerably more complicated than the one-electron methods already discussed. Thus, one normally does not perform such calculations with pencil and paper, but rather with complicated computer programs. Therefore, in this chapter we are not concerned with how one does such calculations because, in most cases, they are done by acquiring a program written by a group of specialists. Rather we are concerned with a description of the mathematical and physical underpinnings of the method. Because the method is simultaneously complicated and rigorously defined, a special jargon has developed. Terms like “Hartree–Fock,” or “correlation energy” have specific meanings and are pervasive in the literature. Hence, a good deal of emphasis in this chapter is put on defining some of these important terms.

11-2 The Molecular Hamiltonian

In practice, one usually does not use the complete hamiltonian for an isolated molecular system. The complete hamiltonian includes nuclear and electronic kinetic energy operators, electrostatic interactions between all charged particles, and interactions between all magnetic moments due to spin and orbital motions of nuclei and electrons. Also an accounting for the fact that a moving particle experiences a change in mass due to relativistic effects is included in the complete hamiltonian. The resulting hamiltonian is much too complicated to work with. Usually, relativistic mass effects are ignored, the Born–Oppenheimer approximation is made (to remove nuclear kinetic energy operators), and all magnetic interactions are ignored (except in special cases where we are interested in spin coupling). The resulting hamiltonian for the electronic energy is, in atomic units,

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{\mu=1}^N \sum_{i=1}^n Z_{\mu} / r_{\mu i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 1 / r_{ij} \quad (11-2)$$

where i and j are indices for the n electrons and μ is an index for the N nuclei. The nuclear repulsion energy V_{nn} is

$$V_{nn} = \sum_{\mu=1}^{N-1} \sum_{v=\mu+1}^N Z_{\mu} Z_v / r_{\mu v} \quad (11-3)$$

In choosing this hamiltonian, we are in effect electing to seek an energy of an idealized nonexistent system—a nonrelativistic system with clamped nuclei and no magnetic moments. If we wish to make a very accurate comparison of our computed results with experimentally measured energies, it is necessary to modify either the experimental or the theoretical numbers to compensate for the omissions in \hat{H} .

11-3 The Form of the Wavefunction

The wavefunction for an SCF calculation is one or more antisymmetrized products of one-electron spin-orbitals. We have already seen (Chapter 5) that a convenient way to produce an antisymmetrized product is to use a Slater determinant. Therefore, we take the trial function ψ to be made up of Slater determinants containing spin-orbitals ϕ . If we are dealing with an atom, then the ϕ 's are atomic spin-orbitals. For a molecule, they are molecular spin-orbitals.

In our discussion of many-electron atoms (Chapter 5), we noted that certain atoms in their ground states are fairly well described by assigning two electrons, one of each spin, to each AO, starting with the lowest-energy AO and working up until all the electrons are assigned. If the last electron completes the filling of all the AOs having a given principal quantum number, n , we have a *closed shell* atomic system. Examples are He($1s^2$) and Ne($1s^2 2s^2 2p^6$). Atoms wherein the last electron completes the filling of all AOs having a given l quantum number are said to have a *closed subshell*. An example is Be($1s^2 2s^2$). Both types of system tend to be well approximated by a single determinantal wavefunction if the highest filled level is not too close in energy to the

lowest empty level. (Beryllium is the least successfully treated of these three at this level of approximation because the 2s level is fairly close in energy to the 2p level.) A similar situation holds for molecules; that is, the wavefunctions of many molecules in their ground states are well represented by single determinantal wavefunctions with electrons of paired spins occupying identical MOs. Such molecules are said to be *closed-shell systems*. We can represent a trial wavefunction for a $2n$ -electron closed-shell system as

$$\psi_{\text{closed shell}} = |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)\cdots\phi_n(2n-1)\bar{\phi}_n(2n)| \quad (11-4)$$

where we have used the shorthand form for a Slater determinant described in Chapter 5. *For the present, we restrict our discussion to closed-shell single-determinantal wavefunctions.*

11-4 The Nature of the Basis Set

Some functional form must be chosen for the MOs ϕ . The usual choice is to approximate ϕ as a linear combination of “atomic orbitals” (LCAO), these AOs being located on the nuclei. The detailed nature of these AOs, as well as the number to be placed on each nucleus, is still open to choice. We consider these choices later. For now, we simply recognize that we are working within the familiar LCAO-MO level of approximation. If we represent the basis AOs by χ , we have, for the i th MO,

$$\phi_i = \sum_j c_{ji} \chi_j \quad (11-5)$$

where the constants c_{ji} are as yet undetermined.

11-5 The LCAO-MO-SCF Equation

Having a hamiltonian and a trial wavefunction, we are now in a position to use the linear variation method. The detailed derivation of the resulting equations is complicated and notationally clumsy, and it has been relegated to Appendix 7. Here we discuss the results of the derivation.

For our restricted case of a closed-shell single-determinantal wavefunction, the variation method leads to

$$\hat{F}\phi_i = \epsilon_i \phi_i \quad (11-6)$$

These equations are sometimes called the Hartree–Fock equations, and \hat{F} is often called the *Fock operator*. The detailed formula for \hat{F} is (from Appendix 7)

$$\hat{F}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\mu} Z_{\mu}/r_{\mu 1} + \sum_{j=1}^n (2\hat{J}_j - \hat{K}_j) \quad (11-7)$$

The symbols \hat{J}_j and \hat{K}_j stand for operators related to the $1/r_{ij}$ operators in \hat{H} . \hat{J}_j is called a *coulomb operator* because it leads to energy terms corresponding to charge cloud repulsions. It is possible to write \hat{J}_j explicitly:

$$\hat{J}_j = \int \phi_j^*(2) (1/r_{12}) \phi_j(2) d\tau(2) \quad (11-8)$$

\hat{K}_j leads ultimately to the production of exchange integrals, and so it is called an *exchange operator*. It is written explicitly in conjunction with a function on which it is operating, viz.

$$\hat{K}_j \phi_i(1) = \int \phi_j^*(2) (1/r_{12}) \phi_i(2) d\tau(2) \phi_j(1) \quad (11-9)$$

Notice that an index exchange has been performed. It is not difficult to see that the expression (see Appendix 9 for bra-ket notation)

$$\langle \phi_i | \hat{F} | \phi_i \rangle = \epsilon_i \quad (11-10)$$

will lead to integrals such as

$$\langle \phi_i | \hat{J}_j | \phi_i \rangle = \langle \phi_i(1) \phi_j(2) | 1/r_{12} | \phi_i(1) \phi_j(2) \rangle = J_{ij} \quad (11-11)$$

$$\langle \phi_i | \hat{K}_j | \phi_i \rangle = \langle \phi_i(1) \phi_j(2) | 1/r_{12} | \phi_i(2) \phi_j(1) \rangle = K_{ij} \quad (11-12)$$

which are formally the same as the coulomb and exchange terms encountered in Chapter 5 in connection with the helium atom. Notice that, if the spins associated with spin-orbitals ϕ_i and ϕ_j differ, K_{ij} must vanish. This arises because integrations over space and spin coordinates of electron 1 (or 2) in Eq. (11-12) lead to integration over two different (and orthogonal) spin functions. On the other hand, J_{ij} is not affected by such spin agreement or disagreement.

It would appear from Eq. (11-6) that the MOs ϕ are eigenfunctions of the Fock operator and that the Fock operator is, in effect, the hamiltonian operator. There is an important qualitative difference between \hat{F} and \hat{H} , however. *The Fock operator is itself a function of the MOs ϕ* . Since the summation index j in Eq. (11-7) includes i , the operators \hat{J}_i and \hat{K}_i must be known in order to write down \hat{F} , but \hat{J}_i and \hat{K}_i involve ϕ_i , and ϕ_i is an eigenfunction of \hat{F} . Hence, we need \hat{F} to find ϕ_i , and we need ϕ_i to know \hat{F} . To circumvent this problem, an iterative approach is used. One makes an initial guess at the MOs ϕ . (One could use a semiempirical method to produce this starting set.) Then these MOs are used to construct an operator \hat{F} , which is used to solve for the new MOs ϕ' . These are then used to construct a new Fock operator, which is in turn used to find new MOs, which are used for a new \hat{F} , etc., until at last no significant change is detected in two successive steps of this procedure. At this point, the ϕ 's produced by \hat{F} are the same as the ϕ 's that produce the coulomb-and-exchange fields in \hat{F} . The solutions are said to be self-consistent, and the method is referred to as the self-consistent-field (SCF) method.

11-6 Interpretation of the LCAO-MO-SCF Eigenvalues

The physical meaning of an eigenvalue ϵ_i is best understood by expanding the integral

$$\epsilon_i = \langle \phi_i | \hat{F} | \phi_i \rangle \quad (11-13)$$

with \hat{F} given by Eq. (11-7). We obtain

$$\epsilon_i = \langle \phi_i | -\frac{1}{2} \nabla_1^2 | \phi_i \rangle - \sum_{\mu} \langle \phi_i | Z_{\mu} / r_{\mu 1} | \phi_i \rangle + \sum_{j=1}^n (2J_{ij} - K_{ij}) \quad (11-14)$$

It is common practice to combine the first two terms of Eq. (11-14), which depend only on the nature of ϕ_i , into a single expectation value of the one-electron part of the hamiltonian, symbolized H_{ii} . Thus,

$$\epsilon_i = H_{ii} + \sum_{j=1}^n (2J_{ij} - K_{ij}) \quad (11-15)$$

The quantity H_{ii} is the average kinetic plus nuclear-electronic attraction energy for the electron in ϕ_i .

The sum of coulomb and exchange integrals in Eq. (11-15) contains all the electronic interaction energy. Observe that the index j runs over all the occupied MOs. For a particular value of j , say $j = k \neq i$, this gives $2J_{ij} - K_{ij}$ as an interaction energy. This means that an electron in ϕ_i , experiences an interaction energy with the *two* electrons in ϕ_k of

$$2 \langle \phi_i(1)\phi_k(2) | 1/r_{12} | \phi_i(1)\phi_k(2) \rangle - \langle \phi_i(1)\phi_k(2) | 1/r_{12} | \phi_k(1)\phi_i(2) \rangle \quad (11-16)$$

The first part is the classical repulsion between the electron having an orbital charge cloud given by $|\phi_i|^2$ and the two electrons having charge cloud $|\phi_k|^2$. The second part is the exchange term which, as we saw in Chapter 5, arises from the antisymmetric nature of the wavefunction. It enters (11-16) only once because the electron in ϕ_i , agrees in spin with only one of the two electrons in ϕ_k , [Equation (11-15) applies because we have restricted our discussion to closed-shell systems.]

The summation over $2J_{ij} - K_{ij}$ includes the case $j = i$. Here we get $2J_{ii} - K_{ii}$. However, examination of Eqs. (11-11) and (11-12) shows that $J_{ii} = K_{ii}$, and so we are left with J_{ii} . This corresponds to the repulsion between the electron in ϕ_i (the energy of which we are calculating) and the other electron in ϕ_i . Because these electrons must occur with opposite spin, there is no exchange energy for this interaction.

In brief, then, the quantity ϵ_i , often referred to as an *orbital energy* or a *one-electron energy*, is to be interpreted as the energy of an electron in ϕ_i , resulting from its kinetic energy, its energy of attraction for the nuclei, and its repulsion and exchange energies due to all the other electrons in their charge clouds $|\phi_j|^2$.

11-7 The SCF Total Electronic Energy

It is natural to suppose that the total electronic energy is merely the sum of the one-electron energies, but this is not the case in SCF theory. Consider a two-electron system. The energy of electron 1 includes its kinetic and nuclear attraction energies and its repulsion and exchange energies for electron 2. The energy of electron 2 includes its kinetic and nuclear attraction energies and its repulsion and exchange energies for electron 1. If we sum these, we have accounted properly for kinetic and nuclear attraction energies, but we have included the interelectronic interactions *twice* as much as they actually occur. (The energy of repulsion, say, between two charged particles, 1 and 2, is given by the repulsion of 1 for 2 or of 2 for 1, but not by the sum of these.) Therefore, if we sum one-electron energies, we get the total electronic energy plus an extra measure

of electron repulsion and exchange energy. We can correct this by subtracting this extra measure away. Thus, for our closed-shell system

$$E_{\text{elec}} = \sum_{i=1}^n \left[2\epsilon_i - \sum_{j=1}^n (2J_{ij} - K_{ij}) \right] \quad (11-17)$$

where the summation is over the *occupied orbitals*. Comparing Eq. (11-17) with (11-18) makes it evident that we can also write

$$E_{\text{elec}} = \sum_{i=1}^n \left[2H_{ii} + \sum_{j=1}^n (2J_{ij} - K_{ij}) \right] \quad (11-18)$$

or

$$E_{\text{elec}} = \sum_{i=1}^n (\epsilon_i + H_{ii}) \quad (11-19)$$

To obtain the *total* (electronic plus nuclear) energy, we add the internuclear repulsion energy for the N nuclei:

$$E_{\text{tot}} = E_{\text{elec}} + V_{\text{nn}} \quad (11-20)$$

$$V_{\text{nn}} = \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^N \frac{Z_{\mu} Z_{\nu}}{r_{\mu\nu}} \quad (11-21)$$

11-8 Basis Sets

A great deal of research effort has gone into devising and comparing basis sets for *ab initio* calculations. There are essentially two important criteria:

1. We want a basis set that is capable of describing the actual wavefunction well enough to give chemically useful results.
2. We want a basis set that leads to integrals F_{ij} and S_{ij} that we can evaluate reasonably accurately and quickly on a computer.

Many types of basis set have been examined and two of these have come to dominate the area of *ab initio* molecular calculations. These two, which we refer to as the gaussian and the Slater-type-orbital (STO) basis sets, are actually very similar in many important respects.

Let us consider the STO basis set first. The essence of this basis choice is to place on each nucleus one or more STOs. The number of STOs on a nucleus and the orbital exponent of each STO remain to be chosen. Generally, the larger the number of STOs and/or the greater the care taken in selecting orbital exponents, the more accurate the final wavefunction and energy will be.

At the least sophisticated end of the spectrum of choices is the *minimal basis set of STOs*, which we encountered in Chapter 7. This includes only those STOs that correspond to occupied AOs in the separated atom limit. If we choose a minimal basis set,

then we must still decide how to evaluate the orbital exponents in the STOs. One way is to use Slater's rules, which are actually most appropriate for isolated atoms. Another way is to vary the orbital exponents until the energy of the molecular system is minimized. This amounts to performing a nonlinear variational calculation along with the linear variational calculation. For molecules of more than a few atoms, this procedure consumes much computer time, for reasons we will describe shortly, but for small molecules (two or three first-row atoms plus a few hydrogens) it is possible to accomplish this task. From this, one discovers what orbital exponent best suits an STO in a molecular environment. This leads us to the third way of choosing orbital exponents—choose the values that were found best for each type of atom in nonlinear variational calculations in smaller molecules.

One may improve the basis by adding additional STOs to various nuclei. Suppose, for example, each carbon 2p AO were represented as a linear combination of two p-type STOs, each having a different orbital exponent. An example of the basic principle involved is indicated in Fig. 11-1. If we treat these functions independently and do a linear variational calculation, they will both be mixed into the final wavefunction to some degree. If the *linear* coefficient for the “inner” STO is much larger, it means that the p-type charge cloud around this atom in the molecule is calculated to be fairly contracted around the nucleus. To describe a more diffuse charge cloud, the wavefunction would contain quite a lot of the “outer” STO, and not so much of the “inner” STO.

Thus, we have a linear variation procedure that, in effect, allows for AO expansion and contraction. It is akin to optimizing an orbital exponent, but it does not require nonlinear variation. Of course, one still has to choose the values of the “larger ζ ” and “smaller ζ ” of Fig. 11-1. This is normally done by optimizing the fit to very accurate atomic wavefunctions or by a nonlinear variation on atoms. A basis set in which every minimal basis AO is represented by an “inner-outer” pair of STOs is often referred to as a “double-zeta” basis set.

A further kind of extension is frequently made. In addition to the above types of STO, one includes STOs with symmetries different from those present in the minimal basis. This has the effect of allowing charge to be shifted in or out of bond regions in new ways. For example, one could add p-type STOs on hydrogen nuclei. By mixing this with the s-type STOs there, one can describe a skewed charge distribution in the regions of the protons. We have already seen (Chapter 7) that a hydrogen atom in a uniform

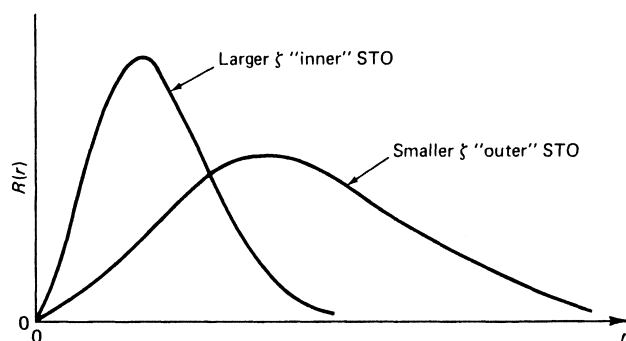


Figure 11-1 ► Radial functions $R(r) = r \exp(-\zeta r)$ for 2p-type STOs. The larger ζ value gives an STO more contracted around the nucleus. Hence, it is sometimes called the “inner” STO.

electric field is polarized in a way that is reasonably well described by an s-p linear combination. Since the hydrogen atom in a molecule experiences an electric field due to the remainder of the molecule, it is not surprising that such p functions are indeed mixed into the wavefunction by the variational procedure if we provide them in the basis set. Similarly, d-type STOs may be added to atoms that, in the minimal basis set, carried only s- and p-type STOs. Functions of this nature are often called *polarization functions* because they allow charge polarization to occur within the molecule as a result of the internally generated electric field.

It should be evident that one could go on indefinitely, adding more and more STOs to the basis, even placing some of them in bonds, rather than on nuclei. This is not normally done because the computing task goes up enormously as we add more basis functions. In fact, the number of integrals to be calculated eventually increases as N^4 , where N is the number of basis functions. The evaluation of integrals can be a logistic bottleneck in *ab initio* calculations, and for this reason nonlinear variations (of orbital exponents) are impractical for any but smaller molecules. Each new orbital exponent value requires re-evaluation of all the integrals involving that orbital. In essence, a change of orbital exponent is a change of basis set. In linear variations, the basis functions are mixed together but they do not change. Once all the integrals between various basis functions have been evaluated, they are usable for the remainder of the calculation.

The STO basis would probably be the standard choice if it were not for the fact that the many integrals encountered in calculating F_{ij} elements are extremely time consuming to evaluate, even on a computer. This problem has led to the development of an alternative basis set class that is based on gaussian-type functions. Gaussian functions include an exponential term of the form $\exp(-\alpha r^2)$. The radial dependence of such a function is compared to that for a hydrogenlike 1s function (which is identical to a 1s STO) in Fig. 11-2. There are two obvious problems connected with using gaussian functions as basis functions:

1. They do not have cusps at $r = 0$ as s-type hydrogen-like AOs do.
2. They decay faster at larger r than do hydrogen-like AOs.

Both of these deficiencies are relevant in molecules because, at $r = 0$ (on a nucleus) and at $r = \infty$, the molecular potential is like that in an atom, so similar cusp and asymptotic behavior are expected for molecular and atomic wavefunctions. Balanced against these deficiencies is an advantage: gaussian functions have mathematical properties that make it extremely easy to compute the integrals they produce in F_{ij} . This has led to a practice of replacing each STO in a basis set by a *number* of gaussian functions.

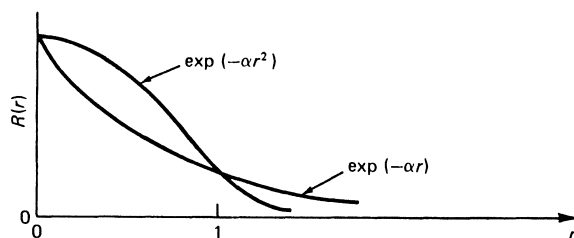


Figure 11-2 ► Radial dependence of hydrogen-like and gaussian functions.

By choosing several values of α in $\exp(-\alpha r^2)$, one can create a set of “primitive” gaussian functions ranging from very compact to very diffuse, and then take a linear combination of these to build up an approximation to the radial part of an STO function. Multiplication by the standard θ and ϕ dependences (spherical harmonics) generates p, d, etc. functions. Once this approximation is optimized, the linear combination of gaussian functions is “frozen,” being treated thereafter as a single function insofar as the subsequent molecular variational calculation is concerned. This linear combination of primitive gaussian functions is called a *contracted gaussian function*.

Once we have a contracted gaussian function corresponding to each STO, we can go through the same hierarchy of approximations as before—minimal basis set, double- ζ basis set, double- ζ plus polarization functions—now using contracted gaussian functions in place of STOs. Typically, *ab initio* calculations on systems involving only light elements, e.g., H–Ne, involve anywhere from 1 to 15 primitive gaussian functions for each contracted gaussian function. Basis sets for heavier elements, however, can contain more than 30 primitive gaussians for each contracted gaussian.

We have already described a certain amount of quantum-chemical jargon. Some of the basis set descriptions that one commonly encounters in the modern literature are as follows:

- DZP [double- ζ gaussian basis with polarization]
- STO-3G [each STO approximated as a linear combination of three gaussian primitives]
- 6-31G [each inner shell STO represented by a sum of six gaussians and each valence shell STO split into inner and outer parts (i.e., double- ζ) described by three and one gaussian primitives, respectively]
- 6-31G* [the 6-31G basis set augmented with six d-type gaussian primitives on each heavy ($Z > 2$) atom, to permit polarization]
- 6-31G** [same as 6-31G* but with a set of gaussian p-type functions on H and He atoms. Good for systems where hydrogen is a bridging atom, as in diborane or in hydrogen bonds]
- 6-31+G* [the 6-31G* basis set augmented with a set of diffuse s- and p-type gaussian functions on each heavy atom, to permit representation of diffuse electronic distribution, as in anions]
- cc-pVnZ, $n = D, T, Q, 5$ [correlation consistent polarized valence n - ζ gaussian basis sets. The inner shell STOs are described by single contracted gaussian functions while the valence STOs are described by n contracted gaussian functions, $n = D$ for double- ζ , $n = T$ for triple- ζ , etc. Both the number and angular momentum symmetry type of the polarization functions are increased with each successive correlation consistent basis set in a systematic manner. For example, the cc-pVDZ basis set has a set of 5 d-type gaussian primitive functions on each heavy atom, while the cc-pVTZ basis set has 2 sets of d-type gaussian functions and one set of 7 f-type gaussian primitives. These families of basis sets are designed to converge the total energy to the complete basis set limit for the SCF method and its extensions.]

- aug-cc-pVnZ [cc-pVnZ basis sets augmented with one set of diffuse primitive gaussian functions for each angular momentum symmetry present in the cc-pVnZ basis set, to provide an accurate description of anions and weak interactions, e.g., van der Waals forces and hydrogen bonding.]

11-9 The Hartree–Fock Limit

It should be apparent that different choices of basis set will produce different SCF wavefunctions and energies. Suppose that we do an SCF calculation on some molecule, using a minimal basis set and obtain a total electronic energy E_1 . If we now choose a double- ζ basis and do a new SCF calculation, we will obtain an energy E_2 that normally will be lower than E_1 . (If one happens to choose the first basis wisely and the second unwisely, it is possible to find E_2 higher than E_1 . We assume here that each improvement to the basis extends the mathematical flexibility while including the capabilities of all preceding bases.) If we now add polarization functions and repeat the SCF procedure, we will find E_3 to be lower than E_2 . We can continue in this way, adding new functions in bonds and elsewhere, always increasing the capabilities of our basis set, but always requiring that the basis describe MOs in a single determinantal wavefunction. The electronic energy will decrease with each basis set improvement, but eventually this decrease will become very slight for any improvement; that is, the energy will approach a limiting value as the basis set approaches mathematical completeness. This limiting energy value is the lowest that can be achieved for a single determinantal wavefunction. It is called the *Hartree–Fock energy*. The MOs that correspond to this limit are called Hartree–Fock orbitals (HF orbitals), and the determinant is called the HF wavefunction.

Sometimes the term *restricted Hartree–Fock* (RHF) is used to emphasize that the wavefunction is restricted to be a single determinantal function for a configuration wherein electrons of α spin occupy the same space orbitals as do the electrons of β spin. When this restriction is relaxed, and different orbitals are allowed for electrons with different spins, we have an *unrestricted Hartree–Fock* (UHF) calculation. This refinement is most likely to be important when the numbers of α - and β -spin electrons differ. We encountered this concept in Section 8-13, where we noted that the unpaired electron in a radical causes spin polarization of other electrons, possibly leading to negative spin density.

11-10 Correlation Energy

The Hartree–Fock energy is not as low as the true energy of the system. The mathematical reason for this is that our requirement that ψ be a single determinant is restrictive and we can introduce additional mathematical flexibility by allowing ψ to contain many determinants. Such additional flexibility leads to further energy lowering.

There is a corresponding *physical* reason for the HF energy being too high. It is connected with the independence of the electrons in a single determinantal wavefunction. To understand this, consider the four-electron wavefunction

$$\psi = |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)| \quad (11-22)$$

Recall from Chapter 5 that the numbers in parentheses stand for the spatial coordinates of an electron; that is, $\phi_1(1)$ really means $\phi_1(x_1, y_1, z_1)\alpha(1)$ or $\phi_1(r_1, \theta_1, \phi_1)\alpha(1)$.¹ In other words, if we pick values of r , θ , and ϕ for each of the four electrons and insert them into Eq. (11-22) we will be able to evaluate each function and we will obtain a determinant of numbers which can be evaluated to give a numerical value for ψ and ψ^2 . The latter number (times $d\nu$) can be taken as the probability for finding one electron in the volume element around r_1, θ_1 , and ϕ_1 , another electron simultaneously in $d\nu_2$ at r_2, θ_2 , and ϕ_2 , etc. The important point to notice is that the effect on ψ^2 of a particular choice of r_1, θ_1 , and ϕ_1 , is not dependent on choices of r, θ, ϕ for other electrons because the form of the wavefunction is *products of functions of independent coordinates*. Physically, this corresponds to saying that the probability for finding an electron in $d\nu_1$, at some instant is not influenced by the presence or absence of another electron in some nearby element $d\nu_2$, at the same instant. This is consistent with the fact that the Fock operator \hat{F} [Eq. (11-7)] treats each electron as though it were moving in the *time-averaged* potential field due to the other electrons.

Because electrons repel each other, there is a tendency for them to keep out of each other's way. That is, in reality, their motions are *correlated*. The HF energy is higher than the true energy because the HF wavefunction is formally incapable of describing correlated motion. The energy difference between the HF and the "exact" (for a simplified nonrelativistic hamiltonian) energy for a system is referred to as the *correlation energy*.

11-11 Koopmans' Theorem

Despite the fact that the total electronic energy is not given by the sum of SCF one-electron energies, it is still possible to relate the ϵ_i 's to physical measurements. If certain assumptions are made, it is possible to equate orbital energies with molecular ionization energies or electron affinities. This identification is related to a theorem due to Koopmans.

Koopmans [1] proved² that the wavefunction obtained by removing one electron from ϕ_k , or adding one electron to the virtual (i.e., unoccupied) MO ϕ_j in a Hartree–Fock wavefunction is stable with respect to any subsequent variation in ϕ_k , or ϕ_j . Notice that this ignores the question of subsequent variation of all of the MOs ϕ with unchanged occupations. It is not necessarily true that they remain optimized, since the potential they experience is changed by addition or removal of an electron. Nevertheless, Koopmans' theorem suggests a model. It suggests that we approximate the wavefunction for a positive ion by removing an electron from one of the occupied HF MOs for a neutral molecule without reoptimizing any of the MOs. Let us do this and compare the electronic energies for the two wavefunctions.

For the neutral molecule, which we assume is a closed-shell system,

$$E = \sum_i \left[2H_{ii} + \sum_j (2J_{ij} - K_{ij}) \right] \quad (11-23)$$

¹Note that ϕ_1 in parentheses represents a coordinate of electron 1, whereas ϕ_1 outside the parentheses represents an MO.

²See also Smith and Day [2].

For the cation, produced by removing an electron from ϕ_k ,

$$E_k^+ = \sum_{i \neq k} \left[2H_{ii} + \sum_{j \neq k} (2J_{ij} - K_{ij}) \right] + H_{kk} + \sum_{i \neq k} (2J_{ik} - K_{ik}) \quad (11-24)$$

The first sum in Eq. (11-24) gives the total electronic energy due to all but the unpaired electron in ϕ_k . H_{kk} gives the kinetic and nuclear attraction energies for the unpaired electron and the final sum gives the repulsion and exchange energy between this electron and all the others. Now we note that the last sum is exactly equal to the void produced in the first sum due to the restriction $j \neq k$. Therefore, we can combine these by removing the index restriction and deleting the last sum. This gives

$$E_k^+ = \sum_{i \neq k} \left[2H_{ii} + \sum_j (2J_{ij} - K_{ij}) \right] + H_{kk} \quad (11-25)$$

To compare this with E of (11-23) we should remove the remaining index restriction. We do this by allowing i to equal k in the sum and simultaneously subtracting the new terms thus produced:

$$E_k^+ = \sum_i \left[2H_{ii} + \sum_j (2J_{ij} - K_{ij}) \right] - H_{kk} - \sum_j (2J_{kj} - K_{kj}) \quad (11-26)$$

But, by virtue of Eqs. (11-15) and (11-23), this is

$$E_k^+ = E - \epsilon_k \quad (11-27)$$

Hence, the ionization energy I_k^0 , for ionization from the ϕ_k is

$$I_k^0 = E_k^+ - E = -\epsilon_k \quad (11-28)$$

This illustrates that, within the context of this simplified *model*, the negative of the orbital energies for occupied HF MOs are to be interpreted as ionization energies.

Another way to see the relation between I_k^0 and $-\epsilon_k$, is to recognize that the physical interactions lost upon removal of an electron from ϕ_k , are precisely those that constitute ϵ_k , [See Eq. (11-15).]

A similar result holds for orbital energies of unoccupied HF MOs and electron affinities. (However, this is less successful in practice; see Problem 11-3.)

In actuality, the relation (11-28) is only approximately obeyed. One reason for this has to do with our assumption that doubly occupied SCF MOs produced by a variational procedure on the neutral molecule will be suitable for the doubly occupied MOs of the cation as well. These MOs minimize the energy of the neutral molecule but give an energy for the cation that is higher than what would be produced by an independent variational calculation. For this mathematical reason, we expect the Koopmans' theorem prediction for the ionization energy to be higher than the value predicted by taking the difference between separate SCF calculations on the molecule and cation (which we will symbolize Δ SCF). The corresponding *physical* argument is that use of Eq. (11-28) views ionization as removal of an electron without any reorganization of the remaining

TABLE 11-1 ► Ionization Energies (in electron volts) of Water as Measured Experimentally and as Predicted from SCF Calculations

Cation state	Observed ^a	SCF (near HF limit) ^b	
		Koopmans	Δ SCF
2B_2	12.62	13.79	11.08
2A_1	14.74	15.86	13.34
2B_2	18.51	19.47	17.61

^aFrom Potts and Price [3].^bFrom Dunning et al. [4].

electronic charge. This neglects a process that stabilizes the cation and lowers the ionization energy. Whichever argument we choose, we have here a reason for expecting $-\epsilon$ to be an *overestimate* of the value obtained by independent calculations, Δ SCF.

Another error results from the neglect of change in correlation energy. We have seen that the total SCF energy for the molecule is too high because the single determinantal form of the wavefunction cannot allow for correlated electronic motion. The SCF energy for the cation is too high for the same reason, but the error is different for the two cases because there are fewer electrons in the cation. We expect the neutral molecule to have the greater correlation energy (since it has more electrons)³ so that proper inclusion of this feature would lower the energy of the neutral molecule more than the cation, making the true I_k^0 larger than that obtained by neglect of correlation. Hence, this leads us expect Δ SCF to *underestimate* I_k^0 . Since $-\epsilon$ overestimates Δ SCF, and Δ SCF underestimates the ionization energy, we can expect some cancellation of errors in using Eq. (11-28).

An illustration of these relations is provided in Table 11-1, where observed *vertical* ionization energies (i.e., no nuclear relaxation), the appropriate values of $-\epsilon$, and the values of Δ SCF are compared.

11-12 Configuration Interaction

There are several techniques for going beyond the SCF method and thereby including some effects of electron correlation. Some extremely accurate calculations on small atoms and molecules, making explicit use of interparticle coordinates, were described in Section 7-8. There is one general technique, however, that has traditionally been used for including effects of correlation in many-electron systems. This technique is called *configuration interaction* (CI).

The mathematical idea of CI is quite obvious. Recall that we restricted our SCF wavefunction to be a single determinant for a closed-shell system. To go beyond the optimum (restricted Hartree–Fock) level, then, we allow the wavefunction to be a linear

³This reasoning is rather naive. Significant correlation energy contribution can result from a small energy-level separation between filled and empty MOs (rather than from merely the number of electrons), but production of a cation should normally increase this gap and lead to reduced correlation.

combination of determinants. Suppose we choose two determinants D_1 and D_2 , each corresponding to a different orbital occupation scheme (i.e., different configurations). Then we can let

$$\psi = c_1 D_1 + c_2 D_2 \quad (11-29)$$

and minimize E as a function of the linear mixing coefficients c_1 and c_2 .

If we go through the mathematical formalism and express \bar{E} as $\langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$, expand this as integrals over D_1 and D_2 , and require $\partial \bar{E} / \partial c_i = 0$, we obtain the same sort of 2×2 determinantal equation that we find when minimizing an MO energy as a function of mixing of two AOs. That is, we obtain

$$\begin{vmatrix} H_{11} - \bar{E} S_{11} & H_{12} - \bar{E} S_{12} \\ H_{21} - \bar{E} S_{21} & H_{22} - \bar{E} S_{22} \end{vmatrix} = 0 \quad (11-30)$$

where now

$$H_{ij} = \langle D_i | \hat{H} | D_j \rangle \quad (11-31)$$

$$S_{ij} = \langle D_i | D_j \rangle \quad (11-32)$$

We see that, whereas before we might have had two AOs interacting to form two MOs, here we have two configurations (i.e., two determinantal functions) interacting to form two approximate wavefunctions. Our example involves only two configurations, but there is no limit to the number of configurations that can be mixed in this way.

Since each configuration D contains products of MOs, each of which is typically a sum of AOs, the integrals H_{ij} and S_{ij} can result in very large numbers of integrals over basis functions when they are expanded. This is the sort of situation where a computer is essential, and CI on atoms and molecules, while still expensive compared to SCF, have become routine on modern computers.

Our purpose in this chapter is not to describe how to carry out a CI calculation, but rather to convey what a CI calculation is and what its predictive capabilities are. Therefore, we will not concern ourselves with the mathematical complexities of evaluating H_{ij} and S_{ij} .⁴ But we will consider one practical aspect of CI calculations, namely, how one goes about choosing which configurations should be mixed together, and which ones may be safely ignored.

We begin by considering the H_2 molecule. The LCAO-MO-SCF method expresses the ground state wavefunction for H_2 as

$$\psi(1, 2) = \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(2)\alpha(2) \\ 1\sigma_g(1)\beta(1) & 1\sigma_g(2)\beta(2) \end{vmatrix} \quad (11-33)$$

that is, as the configuration $1\sigma_g^2$. The SCF procedure mixes the AO basis functions together in the optimum way to produce the $1\sigma_g$ MO.

We have noted at several points in this book that, if one begins with a basis set of n linearly independent functions, one ultimately arrives at n independent MOs. Hence, the $1\sigma_g$ MO of Eq. (11-33) is but one of several MOs produced by the SCF procedure.

⁴In most actual calculations, the D 's are orthonormal, and $S_{ij} = \delta_{ij}$.

It is called an *occupied* MO because it is occupied with electrons in this configuration. All the other MOs in this case are *unoccupied* or *virtual* MOs. The virtual MOs of H_2 have symmetry properties related to the molecular hamiltonian, just as does the occupied MO. Thus, we can refer to $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $1\pi_g$, etc., virtual MOs of H_2 . Which of these virtual MOs are produced by an SCF calculation depends on the number and nature of the AO basis set provided at the outset. If no π -type AOs are provided, no π -type MOs will be produced. If only a minimal basis ($1s_a$ and $1s_b$) is provided, $1\sigma_u$ will be the only virtual MO produced.

It is important to distinguish between the physical content of occupied versus virtual SCF MOs. The SCF procedure finds the set of *occupied* MOs for a system leading to the lowest SCF electronic energy. The virtual orbitals are the residue of this process. The virtual MOs span that part of the basis set function space that the SCF procedure found *least* suitable for describing ψ . The subspace is sometimes referred to as the *orthogonal complement* of the occupied orbital subspace. (Note that this situation differs from that pertaining to Hückel-type calculations, where MOs and energy levels are calculated without regard for electron occupancy. Only after the variational procedure are electrons added.)

Our concern with virtual MOs is due to the fact that they provide a ready means for constructing new configurations to mix with our $1\sigma_g^2$ configuration for H_2 . Thus, using some of the above-mentioned virtual MOs, we could write determinantal functions corresponding to the excited configurations $1\sigma_g 1\sigma_u$, $1\sigma_g 2\sigma_g$, $1\sigma_g 2\sigma_u$, $1\sigma_g 1\pi_u$, etc.⁵ These are commonly referred to as *singly excited* configurations because one electron has been promoted from a ground-state-occupied MO to a virtual MO. (This is *not* meant to imply that the orbital energy difference is equal to the expected spectroscopic energy of the transition.) It is also possible to construct *doubly excited* configurations, such as $1\sigma_u^2$, $1\sigma_u 2\sigma_g$, $2\sigma_g^2$, $1\sigma_u 2\sigma_u$, $1\sigma_u 1\pi_u$, etc. For systems having more electrons, one can write determinants corresponding to triple, quadruple, etc., excitations. If one has a reasonably large number, say 50, of virtual orbitals and, say, 10 electrons to distribute among them, then there is an enormous number of possible configurations. A major step in doing a CI calculation is deciding which configurations might be important in affecting the results and ought therefore to be included.

We can gain insight into this problem by considering our minimal basis set H_2 problem in more detail. We have

$$1\sigma_g = N_g(1s_A + 1s_B) \quad (11-34)$$

$$1\sigma_u = N_u(1s_A - 1s_B) \quad (11-35)$$

where N_g and N_u are normalization constants. The spatial part of the ground configuration is

$$\psi_{\text{space}} = 1\sigma_g(1)1\sigma_g(2) \quad (11-36)$$

⁵As was shown in Chapter 5, the symmetry requirements of the wavefunction require that each of these open shell configurations be expressed as a linear combination of two 2×2 determinants; for example, $1\sigma_g 2\sigma_u$ stands for the combination

$$\left(1/\sqrt{2}\right) \{ |1\sigma_g(1)2\bar{\sigma}_u(2)| \pm |1\bar{\sigma}_g(1)2\sigma_u(2)| \}$$

which expands to

$$\psi_{\text{space}} = N_g^2 [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)]$$

If both electrons are near nucleus A , the first term is quite large. This may be rephrased to say that ψ^2 gives a sizable probability for finding both electrons near nucleus A . The second term gives a similar likelihood for finding both electrons near B . These two terms are referred to as *ionic* terms because they become large whenever the instantaneous electronic dispositions correspond to $H_A^-H_B^+$ and $H_A^+H_B^-$, respectively. The last two terms cause ψ^2 to be sizable whenever an electron is near each nucleus. Hence, these are called *covalent terms*, and their presence means that ψ contains significant “covalent character.” In fact, because all four terms have the same coefficient, the configuration $1\sigma_g^2$ is said to have 50% covalent and 50% ionic character.

Is this bad? It turns out to be no problem at all when the nuclei are close together. Indeed, in the united-atom (helium) limit, the ionic-covalent distinction vanishes. But at large internuclear separations it is very inaccurate to describe H_2 as 50% ionic. In reality, H_2 dissociates to two neutral ground state H atoms—that is, 100% “covalent,” with an electron near each nucleus. In short, the SCF-MO description does not properly describe the molecule as it dissociates. This means that the calculation of \bar{E} versus R_{AB} for H_2 will deviate from experiment more and more as R_{AB} increases. This defect in the SCF treatment of H_2 occurs for many other molecular species also.

Can we correct this defect through use of CI? We ask the question this way: “What configuration could we mix with $1\sigma_g^2$ in order to make the mixture of covalent and ionic character variable?” Since $1\sigma_g^2$ expands to give us covalent and ionic terms of the *same* sign, we need an additional configuration that will give them with *opposite* sign. Then admixture of the two configurations will affect the two kinds of term differently. The configuration that will accomplish this is $1\sigma_u^2$:

$$1\sigma_u(1)1\sigma_u(2) = N_u^2 [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) - 1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)] \quad (11-37)$$

Mixing these two configurations together gives

$$\begin{aligned} \psi(c_1/c_2) &= c_1 1\sigma_g(1)1\sigma_g(2) + c_2 1\sigma_u(1)1\sigma_u(2) \\ &= (c_1 N_g^2 + c_2 N_u^2) [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)] \\ &\quad + (c_1 N_g^2 - c_2 N_u^2) [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] \quad (11-38) \end{aligned}$$

If c_1/c_2 is readjusted at each value of R_{AB} to minimize \bar{E} , it is evident that the relative weights of covalent and ionic character in Eq. (11-38) will change to suit the circumstances. Actual calculations on this system show that, as R_{AB} gets large, c_1/c_2 approaches a value such that $c_1 N_g^2 + c_2 N_u^2$ approaches zero, so that the ionic component of ψ vanishes.

This example illustrates that CI of this sort has an associated physical picture. It suggests that, in any CI calculation involving the dissociation (or extensive stretching) of a covalent bond, important configurations are likely to include double excitations into the antibonding virtual “mates” of occupied bonding MOs.

What about other configurations for H_2 ? What will $1\sigma_g 2\sigma_g$ do for the calculation, assuming now an extended basis set has produced a $2\sigma_g$ MO? Suppose we take as our trial function

$$\psi = c_1 1\sigma_g^2 + c_2 1\sigma_g 2\sigma_g \quad (11-39)$$

where the configurations are understood to stand for determinants. If the $1\sigma_g$ MO has been produced by an SCF calculation on the ground state, and $2\sigma_g$ is a virtual MO from that SCF calculation, then it is possible to show that the CI energy minimum occurs when c_2 in Eq. (11-39) is zero. In other words, these determinants will not mix when they are combined in this way. An equivalent statement is that the mixing element $H_{12} = \langle 1\sigma_g^2 | \hat{H} | 1\sigma_g 2\sigma_g \rangle$ vanishes. Hence, the CI determinant (11-33) is already in diagonal form, and no variational mixing will occur. This is an example of *Brillouin's theorem*, which may be stated as follows:

EXAMPLE 11-1 If D_1 is an optimized single determinantal function and D_j is a determinant corresponding to any single excitation out of an orbital ϕ_j occupied in D_1 and into the virtual subspace (orthogonal complement) of D_1 , then no improvement in energy is possible by taking $\psi = c_1 D_1 + c_2 D_j$.

The proof of Brillouin's theorem is very simple. We start with a basis set that spans a function space. An SCF calculation is performed, which produces the best single-determinantal wavefunction we can possibly get within this function space. This is D_1 . D_j differs from D_1 in only one orbital, which means they differ in only one row. A general property of determinants is that, if two of them differ in only one row or column, any linear combination of the two can be written as a single determinant (see Problem 11-4). This means that any combination $c_1 D_1 + c_2 D_j$ is still expressible as a single determinant. Since D_j makes no use of functions outside our original basis set, $c_1 D_1 + c_2 D_j$ is a single determinant within our original function space. However, D_1 is already known to be the single determinant within this function space that gives the lowest energy, and $c_1 D_1 + c_2 D_j$ cannot do better. QED.

A doubly excited configuration differs from D_1 in two rows, and mixing such a configuration with D_1 produces a result that cannot be expressed as a single determinant.

Because of Brillouin's theorem, one might decide to omit all single excitations from CI calculations. But it is important to recognize that singly excited configurations can affect the results of CI calculations *in the presence of doubly excited configurations*. This comes about because nonzero mixing elements can occur between singly and doubly excited configurations in the CI determinant. To illustrate, let ψ_0 be an SCF single determinant, ψ_1 be a singly excited configuration, and ψ_2 be a "double." Then the CI determinant could be, assuming orthogonal determinants,

$$\begin{vmatrix} H_{00} - E & 0 & H_{02} \\ 0 & H_{11} - E & H_{12} \\ H_{02} & H_{12} & H_{22} - E \end{vmatrix} = 0 \quad (11-40)$$

The zeros result from Brillouin's theorem. However, H_{12} does not necessarily vanish, and solution of this 3×3 determinantal equation leads to a wavefunction of the form

$$\psi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 \quad (11-41)$$

with c_1 not zero. ψ_1 comes in on the coattails of ψ_2 and is referred to as a second-order correction. This is not a guarantee that it will be unimportant, however. (See Example 7-4 for similar behavior in a different context.)

Another rule that is useful for recognizing configurations that may be omitted is the rather obvious one that each configuration must share the same set of eigenvalues for operators commuting with the hamiltonian. That is, if ψ is to be associated with a particular symmetry, angular momentum, spin angular momentum, etc., then each configuration in ψ must have that same symmetry, angular momentum, etc. This means that, for the ground state of H_2 , $1\sigma_g^2$ will not mix with $1\sigma_g1\sigma_u$ because the latter has overall u symmetry. $1\sigma_u2\sigma_u$ could contribute, but the symmetrized combination corresponding to the *singlet* state ($|1\sigma_u2\bar{\sigma}_u| - |1\bar{\sigma}_u2\sigma_u|$) must be used rather than the (positive) triplet state combination. The configuration $1\sigma_u1\pi_u$ will not contribute because it has the wrong total angular momentum.

Even with the aid of all these rules, a calculation on a molecule such as N_2 or O_2 using a reasonably extended basis set gives rise to an enormous number of possible configurations. Additional rules of thumb have been found to help choose the major configurations. It has been found, for example, that triply or higher excited configurations are usually of lesser importance than doubly excited configurations. [Since the hamiltonian contains only one- and two-electron operators, interaction elements must vanish between the ground-state configuration and all triply or higher-excited configurations. But, like singly excited configurations, these can, in principle, come in on the coattails of doubly (or other) excited configurations.] In addition, a study of the energy change in some process involving primarily the valence electrons (e.g., stretching N_2) really does not require calculation of the correlation energy of the 1s electrons since they are fairly unaffected by the change. Any correlation energy for these electrons tends to cancel itself when initial and final state energies are subtracted. Therefore, in a CI calculation of such a process, it is reasonable to omit configurations corresponding to excitation of a 1s electron unless high accuracy is desired.

The acronym CID refers to a CI calculation in which only all doubly excited configurations are included. Inclusion of all singly and doubly excited configurations is referred to as a CISD calculation. *Full* CI (FCI) means all excited configurations have been included, and this is the limit that gives all of the correlation energy within the chosen basis set. The combination of full CI and a complete basis gives the exact energy (generally nonrelativistic and within the Born–Oppenheimer approximation).

11-13 Size Consistency and the Møller–Plesset and Coupled Cluster Treatments of Correlation

Whenever certain parts of a well-defined procedure are omitted, as when full CI is truncated to CID or CISD, one must consider whether systematic errors are introduced. This is indeed the case in the above example. Suppose CID calculations are made for the energy of N_2 as a function of internuclear distance. At short distances, we treat the

system as a 14-electron molecule, including configurations in which 12 of the electrons are in their HF-occupied MOs. At very large distances we have two nitrogen atoms, which we normally treat as having twice the energy of one atom. Now CID on atom A includes the HF configuration, D_0^A , as well as doubly excited configurations in which five of the seven electrons are in their HF-occupied AOs. Let D_2^A represent this class of configuration. Then $\psi^A = c_0 D_0^A + c_2 D_2^A$. Atom B has a similar CID wavefunction: $\psi^B = c_0 D_0^B + c_2 D_2^B$. The wavefunction for the overall, noninteracting system is the antisymmetrized product of these wavefunctions. It will contain terms like $D_0^A D_0^B$, $D_0^A D_2^B$, and $D_2^A D_2^B$. There are no terms present corresponding to a single excitation at each atom, $D_1^A D_1^B$, and such terms *would* be present in a CID treatment of the combined system. Also, there is a class of terms present corresponding to *four* promoted electrons, $D_2^A D_2^B$, and these terms would *not* be present in a CID treatment of the combined system. The dilemma is that, if we treat the system as a single 14-electron “molecule,” which is appropriate at small R , we mix in different terms than if we treat it as two separate atoms, which is appropriate at large R . If we choose some fairly large R value to redefine N_2 as two separate atoms, we change the nature of the CI in a discontinuous way at an arbitrary point. This feature of truncated CI is called the problem of *size consistency*; CID and CISD methods are not size consistent. Doing separate calculations on each of two separated atoms and combining the energies yields a different result from doing a calculation on one system made up of two separated atoms.

A correlation method that is size consistent has been developed by Pople and co-workers.⁶ It is based on perturbation theory that was introduced many years ago by Møller and Plesset.⁷ This approach divides the process of treating correlation into a series of corrections to an unperturbed starting point. If one chooses to do such a calculation to, say, third order (MP3, standing for Møller–Plesset to third order), then the set of configurations to be included is determined by the perturbation formulas.⁸ It does not require further decision by the person doing the calculation and can be wholly managed by a computer program. Møller–Plesset perturbation theory is different from standard CI in at least two important respects: It is size consistent, and it is not variationally bound. One cannot assume, therefore, that going to higher and higher orders of perturbation will cause the calculated energy to approach closer and closer to the true energy from above.

Because of the way MP theory defines the unperturbed system, the starting point energy (MP0) is the sum of HF one-electron energies. The first-order correction to the energy (MP1) brings in the appropriate electronic coulomb and exchange integrals, giving the correct HF energy. MP2 brings in contributions wherein doubly excited configurations “interact with” (i.e., occur in the same integral with) the ground configuration. MP3 adds contributions due to doubly excited configurations interacting with each other. MP4 brings in interactions involving also single, double, triple, and quadruple excitations. The selection of interaction terms by the perturbation formalism is what produces size consistency, but it leaves out certain terms at each level that would be included in a variational calculation.

In coupled cluster (CC) approaches, which are also size consistent and generally not variationally bound, instead of including all configurations to a particular order as

⁶See Binkley and Pople [5].

⁷See Møller and Plesset [6].

⁸Perturbation theory is presented in Chapter 12. The present discussion avoids mathematical details.

in MP theory, each class of excited configurations is included to *infinite* order. This is accomplished via an exponential excitation operator,

$$\Psi_{CC} = e^{\hat{T}} \psi_0 = \left[1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \right] \psi_0 \quad (11-42)$$

where ψ_0 is the HF determinant for an N -electron system, and $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N$. \hat{T}_1 produces singly excited determinants, \hat{T}_2 doubly excited ones, and so on. Because of the exponential nature of the excitation operator, each class of excitations is included to all orders, e.g., terms in \hat{T}_2 would include products of double excitations (\hat{T}_2^2) that would be considered a subset of the possible quadruple excitations in CI. This is what makes CC theory size consistent. Usually coupled cluster theory is truncated to include just \hat{T}_1 and \hat{T}_2 , i.e., CCSD. One of the most accurate post-HF methods has been shown to be the CCSD(T) method, in which a CCSD calculation is followed by a contribution due to triple excitations (\hat{T}_3) via perturbation theory.

11-14 Multideterminant Methods

Up to this point, the methods that have been presented for describing electron correlation effects have been constructed with the single determinant SCF wavefunction as a starting point. For most molecules near their equilibrium geometries, this is a very good zeroth-order approximation, but as we saw earlier for the H_2 molecule, as covalent bonds are stretched towards dissociation multiple determinants are required for even a qualitative description. This puts much stronger demands on these so-called single reference methods, and their accuracy can be much degraded or even unphysical in these regions. In a multiconfigurational SCF (MCSCF) calculation one writes the wavefunction as a linear combination of determinants exactly as in a CI calculation, and the energy is minimized as a function of the linear CI coefficients. However, in an MCSCF calculation one also *simultaneously* optimizes the MO coefficients of the orbitals that are used to construct the determinants, using methods analogous to SCF theory. Because this greatly adds to the complexity of the calculation, the number of determinants used in MCSCF is generally much smaller than in a standard HF-based CI calculation. In the simplest case, only the additional determinants that allow for a qualitative treatment of the process under study are included, e.g., one would include only the determinants corresponding to excitations of bonding electrons into their respective antibonding orbitals when stretching the triple bond of N_2 . This procedure results in a set of MCSCF molecular orbitals (some strongly occupied, some weakly occupied) that smoothly changes in character from equilibrium to dissociation.

In multireference CISD (MRCISD) calculations, the wavefunction is written as

$$\psi = \sum_i c_i \psi_i + \sum_s c_s \psi_s + \sum_d c_d \psi_d \quad (11-43)$$

where $\sum_i c_i \psi_i$ is the set of MCSCF *reference* determinants, ψ_s are new determinants formed by single excitations into the virtual orbitals relative to all of the reference determinants, and ψ_d are doubly excited determinants. An MRCISD calculation of this type can yield a very balanced and accurate description of a molecule's potential energy surface, but often at a relatively steep cost in terms of computational requirements.

11-15 Density Functional Theory Methods

The wavefunction ψ for an n -electron molecule is a function of $3n$ spatial coordinates and n spin coordinates. From ψ we can produce the molecule's spin-free electron density function, $\rho(1)$, by integrating $\psi^*\psi$ over all of the spin coordinates and all the the space coordinates except those for one of the electrons:⁹

$$\rho(1) = \int |\psi(1, 2, \dots, N)|^2 d\omega_1 d\tau_2 \dots d\tau_n \quad (11-44)$$

which is a function of only the three spatial coordinates.¹⁰ We have seen that, in the early days of quantum chemistry, a major challenge was the evaluation of integrals over the interelectronic-repulsion term in the hamiltonian, as well as dealing with the related problem of electron correlation. Several methods were devised that attempted to approximate these quantities from the density function $\rho(1)$, with moderate success. However, the continuing progress in computer speed and the development of sophisticated *ab initio* methods gradually shifted attention away from approaches using the density function.

In 1964, proof by Hohenberg and Kohn [7] of a connection between the ground state energy, E_0 , for a system and ρ_0 , the ground state density function,¹¹ sparked new interest in finding a rigorous way to go from knowledge of the attractively simple three-dimensional density function to a value for E_0 .

Recall that, for a system having n electrons and N nuclei, the hamiltonian operator for the electronic energy is

$$H = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^n \sum_{\alpha=1}^N \frac{-Z_\alpha}{r_{i\alpha}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{r_{ij}} \quad (11-45)$$

The first and last terms can be written down immediately if we know how many electrons are present, but the middle term depends on $\sum_{\alpha=1}^N \frac{-Z_\alpha}{r_{i\alpha}}$, which is a function of nuclear charges and locations. This quantity is called the *external potential*, symbolized $v_{ext}(\vec{r})$, because it results from the presence of fields produced by particles not included in the group of electrons.

Hohenberg and Kohn were able to prove that there is a uniqueness relation between ρ_0 and the external potential: No two external potentials could give the same ρ_0 . This raises the possibility that one could work backwards from ρ_0 to find $v_{ext}(\vec{r})$ and then E_0 . The following route comes first to mind: Integrate ρ_0 to get the number of electrons n . Figure out $v_{ext}(\vec{r})$ from ρ_0 . This would allow one to write down the hamiltonian operator. Then, using *ab initio* methods, one could get to an accurate E_0 and ψ_0 , and from ψ_0 one could calculate T_0 , V_{ne_0} , V_{ee_0} , and all the other properties of interest for the system.

Two problems exist with this scenario. First, there is no generally applicable procedure known for getting from ρ_0 to $v_{ext}(\vec{r})$. We can posit that $v_{ext}(\vec{r})$ is a *functional* of ρ_0 , which we symbolize $v_{ext}[\rho_0]$, but we don't know what the functional relationship is. Second, even if we could get back to the hamiltonian operator, it would simply

⁹Because ψ is antisymmetric for exchange of electrons, the density function is independent of our choice as to which electron's coordinates should be spared from integration.

¹⁰Recall that ω is the spin coordinate and τ is the coordinate for space *and* spin. $d\tau = dv d\omega$.

¹¹We henceforth suppress the electron index in ρ .

land us back on square one: We would still have to solve the whole problem in the traditional way. Nevertheless, the hopes raised by this uniqueness theorem have led to the current goal of density functional theory, which is to find a procedure that takes us from ρ to E in a rigorous way that avoids the complexities of landing on square one and proceeding using standard *ab initio* methods. [8]

A subsequent relation proved by Hohenberg and Kohn [7] indicated a way to proceed. They proved that an *approximate* density function, $\rho_{0,approx}$, when subjected to the (unknown) procedure that relates the exact ρ_0 to the exact E_0 , must yield an energy higher than the exact E_0 : $E_{0,approx} \geq E_0$, so a variational bound exists. Note that the unknown process referred to here is one that assumes $v_{ext}(\vec{r})$ to be the same for the analysis of ρ_0 and $\rho_{0,approx}$, which means that the same nuclear framework applies in both cases.

If a procedure were known for finding E from ρ , then the existence of a variational bound would allow a variational procedure analogous to what we have applied earlier. One would start with a trial ρ , calculate its energy, and vary ρ to locate the ρ that gives the lowest energy.

The barrier to proceeding is the lack of a way to get E from ρ . Hence, the development of approximate functionals that relate the energy to the electron density is an extremely active area of current research and probably will be for some time to come.

In analogy to wavefunction methods, the functional that connects E to ρ , $E[\rho]$, can be separated into an electronic kinetic energy contribution, $T[\rho]$, a contribution due to nuclear-electron attractions, $E_{ne}[\rho]$, and the electron-electron repulsions, $E_{ee}[\rho]$. The latter term can be further decomposed into Coulomb and exchange terms, $J[\rho]$ and $K[\rho]$. Both the nuclear-electron attraction and the interelectronic Coulomb terms can be easily written in terms of the density using their classical expressions as in wavefunction methods. For an accurate treatment of the electronic kinetic energy term, however, one must differentiate a wavefunction,¹² and this has led to the practice first proposed by Kohn and Sham [9] of expressing the density in terms of one-electron orbitals ϕ (constructed numerically or from a basis set of Slater or gaussian functions). These orbitals serve two purposes. They allow us to calculate a value of the kinetic energy within a single Slater determinant framework similar to Hartree–Fock theory,

$$T_S = \sum_{i=1}^n \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \quad (11-46)$$

and to obtain the electron density, defined in terms of these Kohn–Sham orbitals as

$$\rho_s = \sum_i^n |\phi_i|^2 \quad (11-47)$$

The final DFT energy expression is then written as

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (11-48)$$

where the *exchange correlation* functional $E_{xc}[\rho]$ contains the difference between the exact kinetic energy and T_S , the nonclassical (exchange) part of electron-electron repulsions, $K[\rho]$, and correlation contributions to both $K[\rho]$ and $J[\rho]$. The Kohn–Sham

¹²As far as we know, we must differentiate a wavefunction to get kinetic energy. If there is a functional that permits us to obtain kinetic energy directly from the density function, we might avoid having to use orbitals.

orbitals are eigenfunctions of an effective one-electron hamiltonian that is nearly identical in form to the Fock operator in the SCF equations. In the Kohn–Sham case, however, the HF exchange operators are replaced by the functional derivative of the exchange correlation energy. Assuming the existence of $E_{xc}[\rho]$ and an initial guess for the electron density, one then solves the Kohn–Sham eigenvalue equations for the orbitals, which can then be used to define a new electron density and effective hamiltonian. These iterations continue until the density is converged to within a specified threshold.

The exact form of $E_{xc}[\rho]$ is not currently known, however, and a rapidly growing list of approximate exchange correlation functionals have appeared in the literature. Because these are all estimates of a part of the overall energy, the total energy finally calculated is not an upper bound to the true energy. Also, DFT is not size-consistent.

Generally, most existing exchange correlation functionals are split into a pure exchange and correlation contribution, $E_x[\rho]$ and $E_c[\rho]$ and the current functional nomenclature often reflects this with two-part acronyms, e.g., the BLYP DFT method uses an exchange functional from Becke (B) [10] and a correlation functional by Lee, Yang, and Parr (LYP) [11]. In principle, the exchange contribution could be calculated exactly (for a single determinant) in the same manner as T_S , but this is generally not done since this disturbs the balance between $E_x[\rho]$ and $E_c[\rho]$. In hybrid DFT, a percentage of this exact exchange is included in $E_{xc}[\rho]$.

The great benefit of present day DFT methods is computational cost. With the exchange correlation functionals commonly used, the computational effort is similar to a SCF calculation, but since $E_{xc}[\rho]$ implicitly includes some amount of electron correlation, the accuracy of DFT (depending on the chosen functional) is often similar to that obtained with MP2 or better. The great weakness of DFT at the present time, however, is the inability to systematically improve upon $E_{xc}[\rho]$ and converge towards the exact Born–Oppenheimer energy like one might conceptually do in a wavefunction-based CI or CC calculation, e.g., SCF, CCSD, CCSDT, CCSDTQ, etc. with sequences of correlation consistent basis sets.

One of the simplest DFT methods is the local density approximation (LDA), which assumes the density behaves locally like a uniform electron gas. Generally this does not lead to an accurate description of molecular properties, but if one makes $E_x[\rho]$ and $E_c[\rho]$ depend also on the gradient of the density, yielding gradient corrected DFT or the generalized gradient approximation (GGA), the results are much more accurate. Finally, the definition of $E_{xc}[\rho]$ also lends itself to semiempirical contributions. One such parameterization that has been very successful is the B3LYP hybrid DFT method, which includes 20% exact exchange and involves three semiempirical parameters that were obtained by fits to experimental thermochemical data (heats of formation, etc.) of small molecules [12].

11-16 Examples of *Ab Initio* Calculations

Self-consistent-field and correlated calculations have now been made for a very large number of systems. The best way to judge the capabilities of these methods is to survey some of the results.¹³

¹³For extensive surveys, see Schaefer [13], Hefre et al. [14], and Raghavachari [15].

Table 11-2 provides information on energies for a number of atoms in their ground states. Self-consistent-field energies are presented for three levels of basis set complexity. In the STO single- ζ level, a minimal basis set of one STO per occupied AO is used, and the energy is minimized with respect to independent variation of every orbital exponent ζ . The STO double- ζ basis set is similar except that there are two STOs for each AO, the only restriction being that the STOs have the same spherical harmonics as the AOs to which they correspond.

The Hartree–Fock energies are estimated by extrapolating from more extensive basis sets, and represent the limit achievable for the SCF approach using a complete basis set. We can make the following observations:

1. The improvement in energy obtained when one goes from a single- ζ to a double- ζ STO basis set is substantial, especially for atoms of higher Z .
2. The agreement between the optimized double- ζ data and the HF energies is quite good. Even for neon, the error is only about 10^{-2} a.u. (0.27 eV). Thus, for atoms, the double- ζ basis is capable of almost exhausting the energy capabilities of a single-configuration wavefunction.
3. The disagreement between HF and “exact” energies (i.e., the correlation energy) grows progressively larger down the list. For neon it is almost 0.4 a.u. (10 eV), which is an unacceptable error in chemical measurements.

One might think that the magnitude of the correlation energy in these examples would make SCF calculations on heavy atoms useless for quantitative purposes, but this

TABLE 11-2 ► Ground-State Energies (in atomic units) for Atoms, as Computed by the SCF Method and from Experiment

Atom	STO				Correlation ^c energy
	Single ζ^a	Double ζ^a	Hartree–Fock ^a	Exact ^b	
He	−2.8476563	−2.8616726	−2.8616799	−2.9037	−0.0420
Li	−7.4184820	−7.4327213	−7.4327256	−7.4774	−0.0447
Be	−14.556740	−14.572369	−14.573021	−14.6663	−0.0933
B	−24.498369	−24.527920	−24.529057	−24.6519	−0.1228
C	−37.622389	−37.686749	−37.688612	−37.8420	−0.1534
N	−54.268900	−54.397951	−54.400924	−54.5849	−0.1840
O	−74.540363	−74.804323	−74.809370	−75.0607	−0.2513
F	−98.942113	−99.401309	−99.409300	−99.7224	−0.3131
Ne	−127.81218	−128.53511	−128.54705	−128.925	−0.378
Ar	−525.76525	−526.81511	−526.81739	−527.542	−0.725

^aFrom Roetti and Clementi [16].

^b“Exact” equals experimental with relativistic correction but without correction for Lamb shift. See Veillard and Clementi [17].

^cCorrelation energy is “exact” minus HF energy.

is not the case. Most frequently we are not concerned with the value of the *total* energy of a system so much as with *energy changes* (e.g., in spectroscopy or in reactions) or else with other properties such as transition moments (for spectroscopic intensities) or, in molecular systems, dipole moments.

Let us, therefore, see how well SCF calculations can predict atomic ionization energies. We have already indicated (Section 11-11) that there are two ways we can get ionization energies from SCF calculations. The first, and simplest, is to take the various $-\epsilon_i$, as suggested by Koopmans' theorem. Table 11-3 shows that this gives only rough agreement with experimental values for neon. Another way is to do separate SCF calculations for each excited state produced by removal of an electron from an orbital (i.e., for each "hole state") and equate the ionization energies to the energy differences between these and the neutral ground state (Δ SCF). This second method requires much more effort. As Table 11-3 indicates, however, the extra effort leads to great improvement in agreement between theoretical and experimental values. We conclude that SCF calculations on atoms and ions give quantitatively useful data on ionization energies, even for ionization out of deep-lying levels. The Koopmans' theorem approach is less accurate, although still qualitatively useful.

A related problem is the calculation of energies of excited states of atoms. Weiss [19] has reported calculations on some of the excited states of carbon, and his results are summarized in Fig. 11-3. Inspection of this figure reveals that near-HF calculations only roughly reproduce the energy spectrum, but CI (with four or five configurations) brings about marked improvement. Weiss has omitted configurations involving excitations of 1s electrons, and so these results ignore correlation energy for the inner-shell electrons. The agreement suggests that these electrons experience almost no change in correlation for transitions among these states. Weiss has also calculated oscillator strengths¹⁴ associated with atomic transitions and he finds that CI is necessary before reasonable agreement with experiment is achieved.

TABLE 11-3 ► Ionization Energies of Neon^a

Ion configuration	Ionization potential (a.u.)		
	Koopmans	Δ SCF	Experiment
1s2s ² 2p ⁶	32.7723	31.9214	31.98
1s ² 2s2p ⁶	1.9303	1.8123	1.7815
1s ² 2s ² 2p ⁵	0.8503	0.7293	0.7937

^aFrom Bagus [18]. The basis set includes 5 s-type and 12 p-type STOs (4 of each m quantum number). ζ 's were varied as well as linear coefficients. The neutral ground state gives $E = -128.547$ a.u. (compare Table 11-2).

¹⁴The oscillator strength is a measure of the probability (i.e., intensity) of a transition. For a transition between states a and b in a $2n$ -electron system it is commonly given by the formula

$$\frac{2}{3} (E_b - E_a) \left| \int \psi_a^* \left\{ \sum_{i=1}^{2n} r_i \right\} \psi_b d\tau \right|^2$$

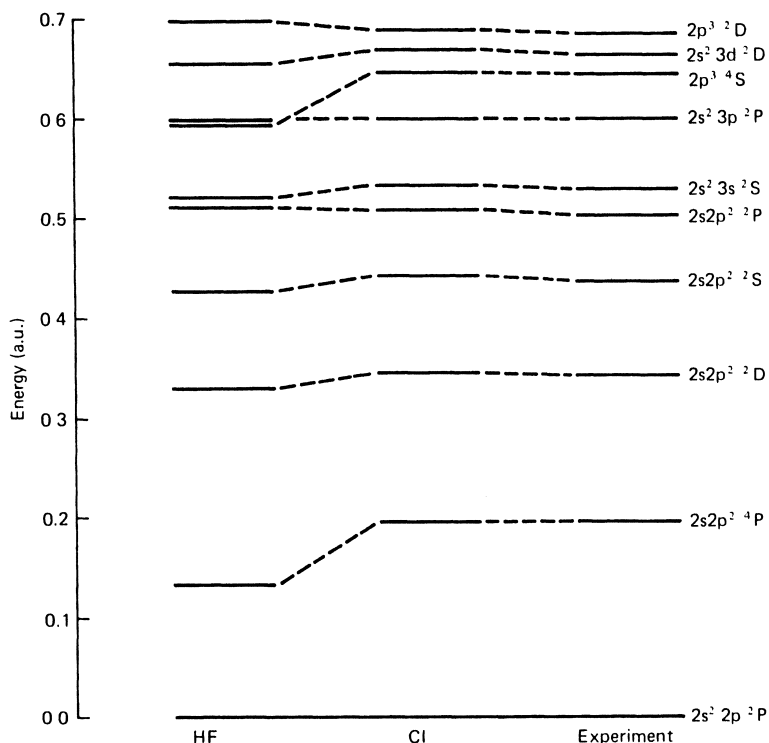


Figure 11-3 ▶ Transition energies in the C^+ ion as calculated by HF, CI, and as measured. (From Weiss [19].) Ionization from the ground state of C^+ occurs at 0.8958 a.u.

In brief, then, the evidence indicates that reasonably accurate atomic ionization energies can be obtained by high-quality SCF calculations on the neutral and ionized species (Δ SCF, not $-\epsilon$), but that transition energies and intensities require CI sufficient to account for much of the valence electron correlation.

Before we leave the subject of atoms, it should be pointed out that, for any atom, the expectation value \bar{T} of the kinetic energy operator is equal to $-\bar{E}$ if the wavefunction has been optimized with respect to a scale factor in the coordinates r_1, r_2 , etc. This relation, called the *virial relation*, is proved in Appendix 8. It is necessarily satisfied for any level of calculation that cannot be improved by replacing every r_i in ψ by ηr_i and allowing η to vary. Since the single- and double- ζ STO solutions have already been optimized with respect to such scale parameters, they satisfy the virial relation. Thus, for the beryllium atom, the single- ζ STO value for \bar{E} is (Table 11-2) -14.556740 a.u., and so we know that $\bar{T} = +14.556740$ a.u. and $\bar{V} = -29.113480$ a.u. for this wavefunction (since $\bar{E} = \bar{T} + \bar{V}$). For the double- ζ wavefunction $\bar{T} = +14.572369$ a.u., etc. The Hartree–Fock wavefunction is, by definition, the lowest-energy solution achievable within a restricted (single determinantal¹⁵) wavefunction form. Use of a scale factor does not affect the wavefunction form. Hence, no further lowering of \bar{E} below the HF level is possible in this way, and the HF energies \bar{E} , \bar{T} , and \bar{V} must satisfy the virial relation also. Finally, the exact energies are the lowest achievable for

¹⁵For open-shell systems, more than one determinant may be needed to satisfy symmetry requirements. This is still considered a HF wavefunction.

any wavefunction. Again, scaling cannot lower the energy further, so these energies also satisfy the virial relation.

We turn next to *ab initio* calculations on molecules. First, let us compare HF and exact energies for molecules as we did for atoms and see how large the errors due to correlation are. The results are not too different from those for atoms having the same number of electrons, as shown in Table 11-4; that is, the correlation energies for molecules having ten electrons (CH₄, NH₃, H₂O, HF) are about the same as that for neon, whereas that for the 18-electron molecule H₂O₂ is more like the correlation energy for argon. But this is only a very rough rule of thumb. We have already indicated that the correlation energy in a molecule varies with bond length, a factor not present in atomic problems. In order to get a more meaningful idea of the capabilities of *ab initio* calculations on molecules, we must look more closely at specific examples.

A calculation on the OH radical, reported by Cade and Huo [21], provides a good example of the capabilities of the extended basis set LCAO-MO-SCF technique on a small molecule. Their final wavefunction for the ground state at an internuclear separation $R = 1.8342$ a.u. is presented in Table 11-5. A minimal basis set of STOs for OH would include 1s, 2s, 2p_x, 2p_y, and 2p_z STOs on oxygen and a single 1s AO on hydrogen. Cade and Huo chose a much more extensive basis. Oxygen is the site for two 1s, two 2s, one 3s, four 2p, one 4f, eight 2p_π, two 3d_π, and four 4f_π STOs. On hydrogen, there are two 1s, one 2s, one 2p_σ, two 2p_π, and two 3d_π STOs. (The π-type basis functions are indicated in Table 11-5 for only one of the two directions perpendicular to the O–H axis.) The orbital exponents for all of these STOs have been optimized, and the resulting wavefunction is of “near-Hartree–Fock” quality. The optimized ζ values appear in Table 11-5. The STO labeled $\sigma 2p'_0$ is located on oxygen and has the formula

$$\sigma 2p'_0 = (2.13528)^{5/2} \pi^{-1/2} r \exp(-2.13528r) \cos \theta \quad (11-49)$$

TABLE 11-4 ► Estimated Hartree–Fock and Correlation Energies for Selected Molecules^a and Atoms^b

Molecule or atom	E (HF) (a.u.)	<i>E</i> (correlation) (a.u.)	Molecule or atom	E (HF) (a.u.)	<i>E</i> (correlation) (a.u.)
H ₂	−1.132	−0.043	Ne	−128.547	−0.378
He	−2.862	−0.042	CO	−112.796	−0.520
BH ₃	−26.403	−0.195	N ₂	−108.994	−0.540
O(¹ D)	−74.729	−0.262	Si(¹ D)	−288.815	−0.505
CH ₄	−40.219	−0.291	B ₂ H ₆	−52.835	−0.429
NH ₃	−56.225	−0.334	S(¹ D)	−397.452	−0.606
H ₂ O	−76.067	−0.364	H ₂ O ₂	−150.861	−0.688
HF	−100.074	−0.373	Ar	−526.817	−0.725

^aFrom Ermler and Kern [20].

^bSee Table 11-2.

TABLE 11-5 ▶ Near Hartree–Fock Wavefunction for the OH Molecule in Its Ground-State Configuration ($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3$) at $R = 1.8342$ a.u.^a

χ_σ	$C_{1\sigma}$	$C_{2\sigma}$	$C_{3\sigma}$	χ_π	$C_{1\pi}$
$\sigma 1s_o$ ($\zeta = 7.01681$)	0.94291	-0.25489	0.07625	$\pi 2p_o$ ($\zeta = 1.26589$)	0.37429
$\sigma 1s_o'$ (12.38502)	0.09313	0.00358	-0.00153	$\pi 2p_o'$ (2.11537)	0.46339
$\sigma 2s_o$ (1.71794)	-0.00162	0.46526	-0.20040	$\pi 2p_o''$ (3.75295)	0.23526
$\sigma 2s_o'$ (2.86331)	0.00418	0.55854	-0.18328	$\pi 2p_o'''$ (8.41140)	0.01023
$\sigma 3s_o$ (8.64649)	-0.03826	-0.02643	0.00550	$\pi 3d_o$ (1.91317)	0.02871
$\sigma 2p_o$ (1.28508)	-0.00055	0.05179	0.30153	$\pi 4f_o$ (2.19941)	0.00506
$\sigma 2p_o'$ (2.13528)	-0.00056	-0.07538	0.37791	$\pi 2p_H$ (1.76991)	0.02442
$\sigma 2p_o''$ (3.75959)	0.00115	0.01874	0.18390	$\pi 3d_H$ (3.32513)	0.00282
$\sigma 2p_o'''$ (8.22819)	0.00059	0.00229	0.00952		
$\sigma 3d_o$ (1.63646)	-0.00047	0.02437	0.04676		
$\sigma 3d_o'$ (2.82405)	0.00016	0.00845	0.01595		
$\sigma 4f_o$ (2.26641)	-0.00013	0.00882	0.01232		
$\sigma 1s_H$ (1.31368)	0.00150	-0.04651	0.21061		
$\sigma 1s_H'$ (2.43850)	-0.00034	0.09413	0.05113		
$\sigma 2s_H$ (2.30030)	0.00000	0.07654	0.04539		
$\sigma 2p_H$ (2.8052)	0.00018	0.01182	0.00999		

^aFrom Cade and Huo [21].

There are three σ -type MOs and two π -type MOs to accommodate the nine electrons of this radical. One π -type MO is

$$\begin{aligned} \phi 1\pi_y = & 0.37429\pi 2p_{oy} + 0.46339\pi 2p'_{oy} + 0.23526\pi 2p''_{oy} \\ & + 0.01023\pi 2p'''_{oy} + 0.02871\pi 3d_{oy} + 0.00506\pi 4f_{oy} \\ & + 0.02442\pi 2p_{Hy} + 0.00282\pi 3d_{Hy} \end{aligned} \quad (11-50)$$

and the other occupied π -type MO would be the same except with x instead of y . (The z axis is coincident with the internuclear axis.) It is evident that writing out the complete wavefunction given in Table 11-5 would result in a very cumbersome expression. It is a nontrivial problem to relate an accurate but bulky wavefunction such as this to the kinds of simple conceptual schemes chemists like to use. One solution is to have a computer produce contour diagrams of the MOs. Such plots for the valence MOs 2σ , 3σ , and 1π of Table 11-5 are presented in Fig. 11-4.

Cade and Huo [21] carried out similar calculations for OH at 13 other internuclear distances and also for the united atom (fluorine) and the separated atoms in the states with which the Hartree–Fock wavefunction correlates. Some of their data are reproduced in Table 11-6. A plot of the electronic-plus-nuclear repulsion energies is given in Fig. 11-5 along with the experimentally derived curve. It is evident that the near HF curve climbs too steeply on the right, leading to too “tight” a potential well for nuclear motion and too small an equilibrium internuclear separation. This comes about because, as mentioned earlier, the HF solution dissociates to an incorrect mixture of states, some

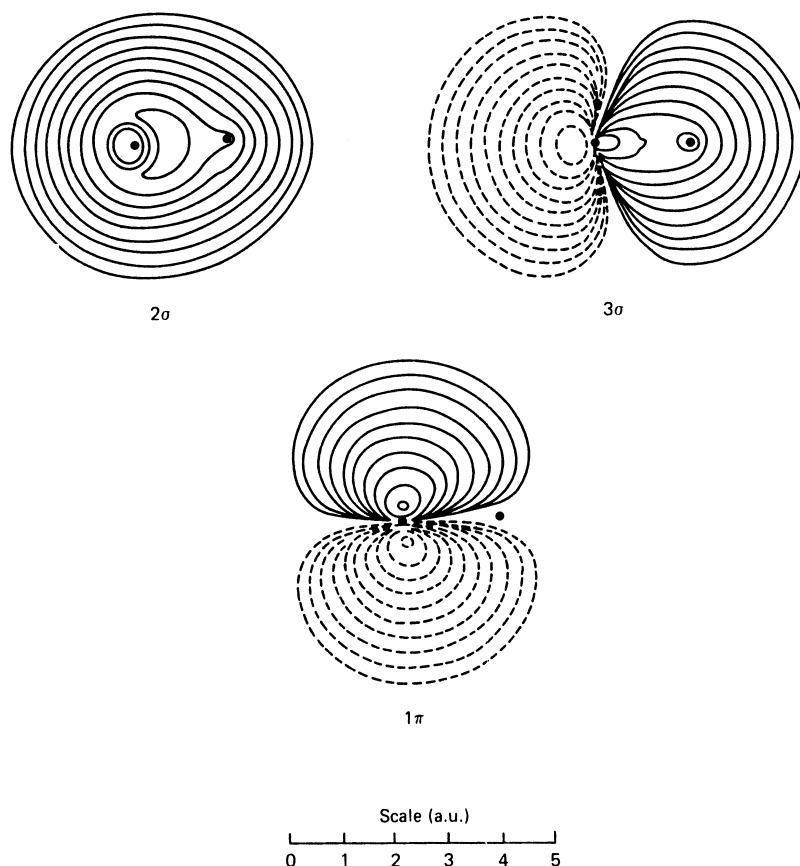


Figure 11-4 ► Contour plots of HF valence orbitals for OH as given in Table 11-5. (From Stevens et al. [22].)

TABLE 11-6 ► Spectroscopic Parameters and Dipole Moment for OH from Theoretical Curves and from Experiment^a

Wavefunction	Dipole moment (debyes)	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (cm^{-1})
SCF	1.780	1.795	8.831	4062.6	165.09	0.661
CI	1.655	1.838	4.702	3723.6	83.15	0.628
Experimental	$1.66 \pm .01$	1.834	4.63	3735.2	82.81	0.714

^aFrom Stevens et al. [22].

of which are ionic. It is possible to use the HF curve of Fig. 11-5 to derive theoretical values for molecular constants that can be compared to spectroscopic data. The results are displayed in Table 11-6, and they reflect the inaccuracy in the HF energy curve. Included there are the SCF and experimental values for the molecular dipole moment.

We turn now to the behavior of \bar{V}/\bar{T} for the HF wavefunctions of Cade and Huo at various internuclear separations. The data appear in Table 11-7. Observe that the

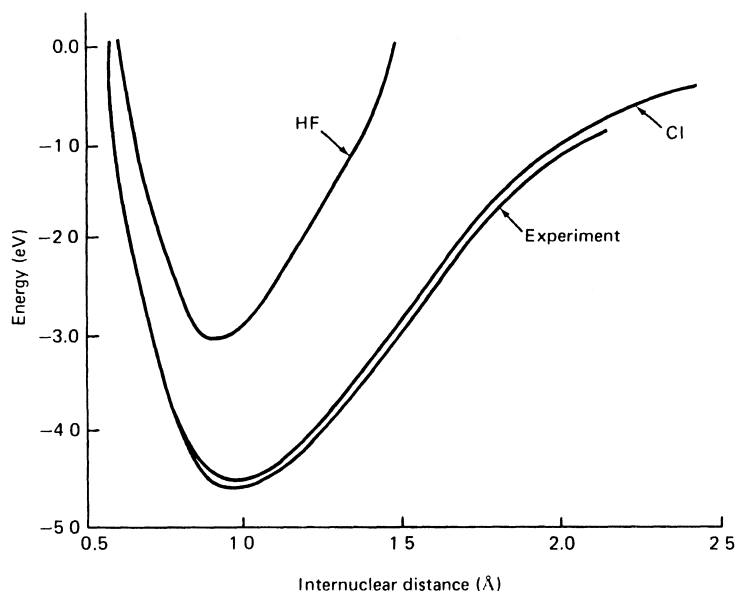


Figure 11-5 ► Theoretical and experimental energy curves for OH (from Stevens et al. [22].)

value of -2.00000 for \bar{V}/\bar{T} occurs at three values of R : 0 , ∞ , and the point where \bar{E} is a minimum. At $R=0$ and ∞ , we are dealing with one or two atoms, for which we have already seen the HF solution should give $\bar{V}/\bar{T} = -2$. At intermediate R we have a diatomic molecule, for which the virial relation is (see Appendix 8)

$$2\bar{T} + \bar{V} + R \frac{\partial \bar{E}}{\partial R} = 0 \quad (11-51)$$

There are three cases to consider. If $\partial \bar{E}/\partial R = 0$, then $\bar{V}/\bar{T} = -2$. This will occur at the minimum of the potential energy curve (and also at any subsidiary maxima or minima). If $\partial \bar{E}/\partial R$ is negative, then, since $\bar{V}/\bar{T} = -2 - (R/\bar{T})(\partial \bar{E}/\partial R)$ and \bar{T} is

TABLE 11-7 ► HF Total Energies and \bar{V}/\bar{T} for OH as a Function of Internuclear Distance^a

R (a.u.)	E (a.u.)	\bar{V}/\bar{T}	R (a.u.)	E (a.u.)	\bar{V}/\bar{T}
0	-99.40933	-2.00000	1.90	-75.41837	-2.00129
1.40	-75.34382	-1.99076	2.00	-75.41140	-2.00225
1.50	-75.38378	-1.99398	2.10	-75.40163	-2.00300
1.60	-75.40696	-1.99651	2.25	-75.38372	-2.00380
1.70	-75.41829	-1.99850	2.40	-75.36367	-2.00433
1.75	-75.42065	-1.99933	2.60	-75.33582	-2.00474
1.795	-75.42127	-2.00000	2.80	-75.30822	-2.00492
1.8342	-75.42083	-2.00052	∞	-75.30939	-2.00000

^aFrom Cade and Huo [21].

positive, \bar{V}/\bar{T} will be algebraically higher than -2 (e.g., -1.98). If $\partial\bar{E}/\partial R$ is positive, \bar{V}/\bar{T} will be lower than -2 . Thus, the values of \bar{V}/\bar{T} in Table 11-7 reflect the slope of a line tangent to the potential energy curve at each R value.

As mentioned earlier, it is possible to at least partly include the effects of electron correlation by allowing determinants corresponding to other configurations to mix into the wavefunction. Such calculations have been performed for the OH radical by several groups, and the results of Stevens et al. [22] are included in Table 11-6 and Fig. 11-5. These data come from intermixing 14 configurations. It is evident that the inclusion of correlation through CI has markedly improved the agreement with experiment.

Many diatomic molecules have been treated at a comparable and higher level, and it is clear that *ab initio* calculations including electron correlation are capable of giving quite accurate molecular data. In cases in which the diatomic system is experimentally elusive, such calculations may be the best source of data available. A further example of this is provided in Table 11-8, in which are listed dipole moments for ground and some excited states of diatomic molecules. The dipole moments computed from near-HF wavefunctions contain substantial errors. It can be seen that CI greatly improves dipole moments. It has been observed that inclusion of singly excited configurations is very important in obtaining an accurate dipole moment.

As a general rule, CID correlates electron motion and therefore has a significant energy-lowering effect but has little effect on the one-electron distribution or related properties, like dipole moment. Inclusion of singly excited configurations (CISD) allows the one-electron distribution to shift in response to the change in calculated interelectronic repulsion. For example, the value of the ground-state dipole moment of CO (entry 4 of Table 11-8) is calculated at the CID level to be $-0.20D$ and at the CISD level to be $+0.12D$. Thus CID may be a suitable level of computational effort if the interest is in energy, but CISD is better if the interest is in one-electron properties.

TABLE 11-8 ► Calculated and Experimental Dipole Moments of Diatomic Molecules (in Debyes)

Molecule and polarity	State	HF at R_e^a	CI at R_e^a	Experiment	Reference
Li ⁺ H ⁻	X ¹ Σ ⁺	6.002	5.86	5.83	[23]
C ⁺ N ⁻	X ² Σ ⁺	2.301	1.465	1.45 ± 0.08	[24]
C ⁻ N ⁺	B ² Σ ⁺	—	0.958	1.15 ± 0.08	[24]
C ⁻ O ⁺	X ¹ Σ ⁺	-0.274	0.12	0.112 ± 0.005	[23]
C ⁺ O ⁻	A ³ Π	2.34	1.43	1.37	[25]
C ⁻ S ⁺	X ¹ Σ ⁺	1.56	2.03	1.97	[23]
C ⁻ S ⁺	A ¹ Π	-0.09	0.63	0.63 ± 0.04	[26]
C ⁻ H ⁺	X ² Π	1.570	1.53	1.46 ± 0.06	[27]
O ⁻ H ⁺	X ² Π	1.780	1.655	1.66 ± 0.01	[27]
F ⁻ H ⁺	X ¹ Σ	1.942	1.805	1.797	[27]
N ⁻ H ⁺	X ³ Σ ⁻	1.627	1.537	Unknown	[27]

^aExperimental R_e Value used.

Highly accurate properties can be obtained with more sophisticated electron correlation methods, such as CCSD(T) or MRCISD.

Other examples of the use of *ab initio* methods on small molecules are shown in Table 11-9, which displays some calculated properties for the electronic ground states of H₂ and N₂ as a function of method with the cc-pVTZ basis set. In the case of H₂, the SCF bond length and harmonic frequency are both slightly too large compared to experiment, but the dissociation energy is underestimated by more than 30 kcal/mole due to the lack of electron correlation. For this two-electron system, the CISD and CCSD methods are equivalent to a FCI and exhibit marked improvement compared to SCF. The remaining deviations from experiment at this level of theory can be attributed to the use of the finite cc-pVTZ basis set. The MP methods show systematic improvement with each order of perturbation theory, but even a fourth-order treatment of single and double excitations results in non-negligible errors compared to FCI for this simple system. The B3LYP hybrid density functional method is observed to yield very reliable properties in this case.

As might be expected due to its triple bond, the N₂ molecule is considerably more challenging for *ab initio* methods. With the cc-pVTZ basis set, the SCF dissociation energy is smaller than experiment by nearly a factor of 2. Appreciable differences are now observed between the CISD and CCSD results, with the latter being somewhat closer to experiment. In addition, triple excitations, as measured by the difference between CCSD and CCSD(T), are relatively important for N₂, raising the dissociation energy by nearly 9 kcal/mole. In contrast to the H₂ case, the results for N₂ using perturbation theory (MP2, MP3, MP4) display a disturbing oscillatory behavior. This type of result with MP methods has been the subject of several previous studies.¹⁶

TABLE 11-9 ► Calculated Equilibrium Bond Lengths, Harmonic Vibrational Frequencies, and Equilibrium Dissociation Energies for the Ground States of H₂ and N₂ with the cc-pVTZ Basis Set Compared to Experiment

	H ₂			N ₂		
	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal/mole)	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal/mole)
SCF	0.734	4587	83.7	1.067	2732	120.4
CISD	0.743	4409	108.4	1.089	2509	193.1
MP2	0.737	4526	103.6	1.114	2195	228.7
MP3	0.739	4476	107.1	1.090	2532	206.0
MP4	0.741	4441	108.0	1.113	2192	221.2
CCSD	0.743	4409	108.4	1.097	2424	207.7
CCSD(T)				1.104	2346	216.5
B3LYP	0.743	4419	110.3	1.092	2449	229.6
Expt. [28]	0.741	4403	109.5	1.098	2359	228.4

¹⁶See Dunning and Peterson [29] and references therein.

Lastly, it is again the case that the B3LYP method yields relatively accurate results for this molecule and appears to be comparable in quality to MP2.

The results shown in Table 11-10 explore the choice of basis set with the CCSD and CCSD(T) methods for the H₂ and N₂ molecules, respectively. A large dependence on basis set is observed in each case. The use of a minimal basis set, STO-3G, leads to large errors since it provides very few virtual orbitals for electron correlation. Just a double- ζ basis set, either 6-31G** or cc-pVDZ, is observed to be a great improvement. The systematic convergence of the correlation consistent basis sets is readily observed in these results. One should note that increasing the size of the basis set from cc-pVTZ to cc-pV5Z in N₂ results in an increase in D_e by nearly 9 kcal/mole. This implies that the highly accurate result for D_e shown in Table 11-9 for the MP2 level of theory with the cc-pVTZ basis set was clearly fortuitous. From these results it should be obvious that errors due to basis set incompleteness can often rival those due to inadequate electron correlation.

As shown above, the hybrid DFT method B3LYP can be competitive in accuracy to more computationally expensive methods, such as CCSD(T). In fact, recent benchmark calculations [30] have shown that for the calculation of thermochemical quantities like enthalpies of formation, B3LYP exhibits average errors of only 1–5 kcal/mol. While these are still more than a factor of two larger than the accuracy obtainable with coupled cluster methods, the much lower computational cost of B3LYP makes it a very attractive alternative. The accuracy of equilibrium bond lengths and harmonic vibrational frequencies calculated by B3LYP have also been shown to be very satisfactory. The accurate calculation of some molecular properties, however, is still a great challenge to hybrid DFT methods. In particular, reaction activation energies are often too small and van der Waals interactions can be qualitatively incorrect. Correcting these deficiencies is the goal of many second generation hybrid DFT functionals.¹⁷

We have seen that inclusion of electron correlation often improves the \bar{E} versus R curve because it allows for variable ionic-covalent character in the wavefunction.

TABLE 11-10 ► Dependence on Basis Set Choice for the CCSD and CCSD(T) Properties of H₂ and N₂, respectively

	H ₂ /CCSD			N ₂ /CCSD(T)		
	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal/mole)	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal/mole)
STO-3G	0.735	5002	128.1	1.190	2145	147.8
6-31G**	0.738	4504	105.9	1.120	2342	201.6
cc-pVDZ	0.761	4383	103.6	1.119	2339	200.6
cc-pVTZ	0.743	4409	108.4	1.104	2346	216.5
cc-pVQZ	0.742	4403	109.1	1.100	2356	222.9
cc-pV5Z	0.742	4405	109.3	1.099	2360	225.1
Expt. [28]	0.741	4403	109.5	1.098	2359	228.4

¹⁷See, for instance, Zhao et al. [31] and Xu et al. [32].

However, there are some diatomic molecules that maintain a high degree of ionic character even when the nuclei are quite widely separated. NaCl is an example. For such systems, the Hartree–Fock energy curve is quite nearly parallel to the exact energy curve throughout the minimum energy region (i.e., the correlation energy is almost constant) and the theoretical values of spectroscopic constants agree quite well with experimental values. (*In vacuo*, an electron ultimately transfers from Cl[−] to Na⁺, and the experimental curve leads to neutral dissociation products, whereas the HF curve does not. This theoretical error affects the curve only at large R , however, and so has little effect on spectroscopic constants.) Schaefer [13] has reviewed this situation.

Of course, *ab initio* calculations have been performed on molecular systems much larger than the molecules referred to above. However, as one moves to molecules having four or more nuclei, one encounters a new difficulty: Integrals now appear that have the form

$$\langle ab | cd \rangle \equiv \langle \chi_a(1)\chi_b(2) | 1/r_{12} | \chi_c(1)\chi_d(2) \rangle \quad (11-52)$$

where χ_a is a basis function located on nucleus a , etc. Such integrals have basis functions on four different nuclei and are referred to as four-center integrals. If the basis functions χ are STOs, such integrals are relatively slow to evaluate on a computer. If they are gaussian functions, the computation is much faster, and this is the main reason for using gaussian basis functions. But the number of such integrals becomes enormous for a reasonable basis set and a medium sized molecule. In fact, the number of such integrals grows as the fourth power of the number of basis functions. Thus, replacing each STO by, say, three gaussian functions, will lead to 3⁴ times as many integrals to evaluate. Even though such integrals can be evaluated very rapidly, we eventually come to molecules of such a size that the sheer number of integrals makes for a substantial computing effort. The efficient calculation of molecular integrals continues to be an active research area, however, and new techniques have now diminished the importance of this bottleneck with reasonably sized gaussian basis sets on systems up to hundreds of atoms.

Modern quantum chemical programs have made high-quality calculations on reasonably large molecules tractable, but one is always balancing the level of accuracy against the computer time needed to achieve it. While a Hartree–Fock calculation on benzene with a cc-pVTZ basis set (264 contracted gaussian functions) might require just 4 minutes to complete on a given computer, inclusion of electron correlation at the MP2, CCSD, and CCSD(T) levels would require an additional 0.1, 4.3, and 11 times 4 minutes, respectively.

Numerous calculations have been reported for barriers to internal rotation in various molecules. The theoretical barriers agree best with experiment for molecules having threefold symmetry in the rotor. Self-consistent-field values are compared with experimental barrier values in Table 11-11. In every case, the theoretical energy curve predicts the correct stable conformation and even does reasonably well at predicting barrier height. The disagreement between different computed values of the barrier for the same molecule reflects differences in basis sets and, sometimes, differences in choices for bond length and angle made by different workers. The evidence to date suggests that *ab initio* calculations approaching the HF limit will ordinarily be within 20% of the experimental barrier. Even this level of accuracy is useful because experimental measurements of barriers in transient molecules or for excited molecules are often very rough, ambiguous, or nonexistent. Given the favorable cost and relative accuracy of

TABLE 11-11 ► Internal Rotation Barriers from Experiment and as Calculated by the LCAO-MO-SCF Method

Molecule	Barrier (kcal/mole)		
	SCF	Experiment	Reference
CH ₃ -CH ₃	2.58	2.88	[33]
	2.88	—	[34]
CH ₃ -NH ₂	1.12	1.98	[35]
	2.02	—	[34]
CH ₃ -OH	1.59	1.07	[34]
CH ₃ -CH ₂ F	2.59	3.33	[33]
CH ₃ -N=O	1.05	1.10	[36]
CH ₃ -CH=CH ₂	1.25	1.99	[37]
<i>cis</i> -CH ₃ -CH=CFH	1.07	1.06	[37]
<i>trans</i> -CH ₃ -CH=CFH	1.34	2.20	[37]
CH ₃ -CH=O	1.09	1.16	[38]

DFT approaches compared to HF, even higher quality results might be expected with the use of methods such as B3LYP; hence, DFT is often now the method of choice for calculations on medium to large organic molecules.

A large number of *ab initio* calculations have been made on clusters of molecules. Many of these have sought to delineate the distance and angle dependence of the hydrogen bond strength between molecules like water or hydrogen fluoride. Xantheas et al. [39] have reported large basis set MP2 calculations on small water clusters, (H₂O)_n, where *n* ranged from 2–6. These calculations predict that there are four distinct isomers of the water hexamer (*n* = 6) whose relative energies lie within ~1 kcal/mole of each other. These kinds of results are of great usefulness in defining new effective interaction potentials involving water that can be used in large-scale molecular simulations of solvation phenomena. Re et al. [40] have calculated the structures and relative energies of sulfuric acid solvated by 1–5 water molecules using the B3LYP method to provide a fundamental understanding of acid ionization. In addition to investigating the interaction of water with both the *cis* and *trans* conformers of H₂SO₄, they found that just five water molecules were sufficient to make dissociation into HSO₄⁻ and H₃O⁺ energetically favorable. The field of materials science is also benefitting from *ab initio* calculations, and studies of metal clusters and their absorbates are currently areas of high interest.

A great deal of attention has been given to the calculation by *ab initio* methods of energy surfaces for chemical reactions. For many years, such efforts were limited to reactions, such as D + H₂ → HD + H, which involve only a small number of electrons and nuclei. Much more complicated systems are now being explored.

In setting out to perform such a calculation, one likes to have some idea of whether the correlation energy of the system will change significantly with nuclear configuration. If it does not, then a Hartree–Fock or MCSCF calculation will parallel the true energy surface. If the correlation energy does change, it is necessary to include some treatment of electron correlation in the calculation.

As a rough rule of thumb, one expects the correlation energy to change least when the reactants, the intermediate or transition state complex, and the products are all closed-shell systems, hence all approximately equally well described by a single-determinantal wavefunction. Some calculations on S_N2 and radical reactions are summarized in Table 11-12. It can be seen that the S_N2 reactions, which do involve closed-shell systems in the three stages mentioned above, are fairly insensitive to the inclusion of CI, whereas the radical reactions undergo extensive change of correlation energy.

The determination of the potential energy surface for the unimolecular rearrangement $\text{HOCl} \rightleftharpoons \text{HClO}$ by Peterson et al. [43] provides an example of a very accurate and exhaustive calculation on a fairly small molecule. Because there are only three nuclei, there are only three structural variables to explore, so the number of calculations needed to map out the surface is not too large. (Note that, with three geometric variables, the energy "surface" is really a four-dimensional hypersurface.) These authors were also interested in the reactions occurring on this surface, i.e., $\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$ and $\text{Cl} + \text{OH} \rightarrow \text{ClO} + \text{H}$, which required a global representation of the surface that was constructed from over 1500 individual energies. Since the full energy surface involves bond breaking processes, MCSCF and MRCISD methods were utilized. Accurate relative energetics between HOCl, HClO, and the various dissociation asymptotes were obtained by carrying out calculations with a series of three correlation consistent basis sets at each geometry. This produced an approximate complete basis set (CBS) MRCISD energy surface. At the MRCISD CBS limit, HOCl was found to be more stable than HClO by 53.7 kcal/mole and the barrier for $\text{HOCl} \rightarrow \text{HClO}$ was predicted to be 73.5 kcal/mole above the HOCl minimum.

After determining an analytical representation of this surface from the individual energies, these authors carried out calculations of the full anharmonic vibrational spectrum of HOCl and HClO by solving the Schrödinger equation for nuclear motion. The HClO molecule has not yet been experimentally observed, but these calculations predict that the lowest three vibrational levels of this species lie below its dissociation threshold, so it should be detectable.

TABLE 11-12 ► Reaction Barrier Energies for Reactions as Calculated by *ab Initio* Methods

Reactant	Transition	Product	Reaction type	Reaction barrier (kcal/mole)		Reference
				SCF	CI (no.config.)	
$\text{H}^- + \text{CH}_4$	$(\text{CH}_5)^-$	$\text{CH}_4 + \text{H}^-$	S_N2	59.3	55.2(6271)	[41]
$\text{F}^- + \text{CH}_3\text{F}$	$(\text{FCH}_3\text{F})^-$	$\text{CH}_3\text{F} + \text{F}^-$	S_N2	5.9	5.9(26910)	[41]
$\text{H}^\bullet + \text{CH}_4$	CH_5^\bullet	$\text{CH}_3^\bullet + \text{H}_2$	Radical abstraction (axial)	35.2	18 (692)	[42]
$\text{H}^\bullet + \text{CH}_4$	CH_5^\bullet	$\text{CH}_4 + \text{H}^\bullet$	Radical exchange (inversion)	63.7	41.7(692)	[42]

The decisions regarding basis set and level of correlation can be daunting and in the past this sometimes discouraged nonspecialists from taking advantage of *ab initio* methods. However, there are now a wide range of programs that are available, which have made *ab initio* calculations amenable to theoreticians and experimentalists alike. The best known of these is undoubtedly the GAUSSIAN series of programs originally developed by the group of J.A. Pople. In this and other programs, one can conveniently choose from a large variety of available basis sets and methods to carry out energy evaluations or geometry optimizations and harmonic frequency calculations. These programs have brought about a revolution in the way that chemical research is done.

For small molecules ($\sim 1\text{--}5$ nonhydrogen atoms) *ab initio* methods are sometimes more precise and reliable than experiment, especially for unstable systems. The saga of the energy difference between ground and excited CH_2 is one of the best known of these experimental–theoretical confrontations.¹⁸

In summary, *ab initio* calculations provide useful data on bond lengths and angles, molecular conformation and internal rotation barriers, for ground and excited states of molecules. They are also very useful for calculating accurate thermochemistry, ionization energies, oscillator strengths, dipole moments (as well as other one-electron properties) and excitation energies. If one has access to large blocks of computer time, *ab initio* calculations can reveal the nature of energy surfaces pertaining to chemical reactions or molecular associations, as in fluids. The accuracy of the calculation and the magnitude of the system are limited ultimately by computer speed and capacity.

11-17 Approximate SCF-MO Methods

At the beginning of this chapter it was stated that *ab initio* calculations require exact calculation of all integrals contributing to the elements of the Fock matrix, but we have seen that, as we encounter systems with more and more electrons and nuclei, the number of three- and four-center two-electron integrals becomes enormous, driving the cost of the calculation out of the reach of most researchers. This has led to efforts to find sensible and systematic simplifications to the LCAO-MO-SCF method—simplifications that remain within the general theoretical SCF framework but shorten computation of the Fock matrix.

Since many of the multicenter two-electron integrals in a typical molecule have very small values, the obvious solution to the difficulty is to ignore such integrals. But we wish to ignore them without having to calculate them to see which ones are small since, after all, the reason for ignoring them is to avoid having to calculate them. Furthermore, we want the selection process to be linked in a simple way to considerations of basis set. That is, when we neglect certain integrals, we are in effect omitting certain interactions between basis set functions, which is equivalent to omitting some of our basis functions part of the time. It is essential that we know exactly what is involved here, or we may obtain strange results such as, for example, different energies for the same molecule when oriented in different ways with respect to Cartesian coordinates.

A number of variants of a systematic approach meeting the above criteria have been developed by Pople and co-workers, and these are now widely used. The approximations

¹⁸See Goddard [44] and Schaefer [45].

are based on the idea of *neglect of differential overlap* between atomic orbitals in molecules.

Differential overlap dS between two AOs, χ_a and χ_b , is the product of these functions in the differential volume element dv :

$$dS = \chi_a(1)\chi_b(1)dv \quad (11-53)$$

The only way for the differential overlap to be zero in dv is for χ_a or χ_b , or both, to be identically zero in dv . Zero differential overlap (ZDO) between χ_a and χ_b in *all* volume elements requires that χ_a and χ_b can never be finite in the same region, that is, the functions do not “touch.” It is easy to see that, if there is ZDO between χ_a and χ_b (understood to apply in all dv), then the familiar overlap integral S must vanish too. The converse is not true, however. S is zero for any two *orthogonal* functions even if they touch. An example is provided by an s and a p function on the same center.

It is a much stronger statement to say that χ_a and χ_b have ZDO than it is to say they are orthogonal. Indeed, it is easy to think of examples of orthogonal AOs but impossible to think of any pair of AOs separated by a finite or zero distance and having ZDO. Because AOs decay exponentially, there is always some interpenetration.

The attractive feature of the ZDO approximation is that it causes all three- and four-center integrals to vanish. Thus, in a basis set of AOs χ having ZDO, the integral $\langle \chi_a(1)\chi_b(2) | 1/r_{12} | \chi_c(1)\chi_d(2) \rangle$ will vanish unless $a \equiv c$ and $b \equiv d$. This arises from the fact that, if $a \neq c$, $\chi_a^*(1)\chi_c(1)$ is identically zero, and this forces the integrand to vanish everywhere, regardless of the value of $(1/r_{12})\chi_b^*(2)\chi_d(2)$.

It is not within the scope of this book to give a detailed description or critique of the numerous computational methods based on ZDO assumptions. An excellent monograph [46] on this subject including program listings is available. Some of the acronyms for these methods are listed in Table 11-13. In general, these methods have been popular because they are relatively cheap to use and because they predict certain properties (bond length, bond angle, energy surfaces, electron spin resonance hyperfine splittings, molecular charge distributions, dipole moments, heats of formation) reasonably well. However, they generally do make use of some parameters evaluated from experimental data, and some methods are biased toward good predictions of some properties, while other methods are better for other properties. For a given type of problem, one must exercise judgment in choosing a method.

As an example of the sort of chemical system that becomes accessible to study using such methods, we cite the valence-electron CNDO/2 calculations of Maggiora [56] on free base, magnesium, and aquomagnesium porphines. Such calculations enable us to examine the geometry of the complex (i.e., is the metal ion in or out of the molecular plane, and how is the water molecule oriented?), the effects of the metal ion on ionization energies, spectra, and orbital energy level spacings, and the detailed nature of charge distribution in the system.

Use of a combination of methods is often convenient. Novoa and Whangbo [57] studied theoretically the relative stabilities of di- and triamides in various hydrogen-bonded and nonhydrogen-bonded conformations, in both the absence and presence of solvent (CH_2Cl_2) molecules. There are many structural parameters to optimize in each of the conformations, and so high-level *ab initio* calculations for energy minimization of each class of structure would be prohibitively expensive. Instead, AM1 was used to determine the optimum geometry for each configuration, and then *ab initio* calculations

TABLE 11-13 ► Acronyms for Common Approximate SCF Methods

Acronym	Description
CNDO/1	Complete neglect of differential overlap. Parametrization Scheme no. 1 (Pople and Segal [47]).
CNDO/2	Parametrization scheme no. 2. Considered superior to CNDO/1 (Pople and Segal [48]).
CNDO/BW	Similar to above with parameters selected to give improved molecular structures and force constants. (See Pulfer and Whitehead [49] and references therein.)
INDO	Intermediate neglect of differential overlap. Differs from CNDO in that ZDO is not assumed between AOs on the same center in evaluating one-center integrals. This method is superior to CNDO methods for properties, such as hyperfine splitting, or singlet-triplet splittings, which are sensitive to electron exchange (Pople et al. [50]).
MINDO/3	Modified INDO, parameter scheme no. 3. Designed to give accurate heats of formation (Bingham et al. [51] and also Dewar [52]).
NDDO	Neglect of diatomic differential overlap. Assumes ZDO only between AOs on different atoms (Pople et al. [53]).
MNDO	Modified neglect of diatomic overlap. A semiempirically parametrized version of NDDO. Yields accurate heats of formation and many other molecular properties, but fails to successfully account for hydrogen bonding (Dewar and Thiel [54]).
AM1	“Austin Model 1.” A more recent parametrization of NDDO that overcomes the weakness of MNDO in that it successfully treats hydrogen bonding. (Dewar et al. [55].)

(e.g., 6-31G** with MP2) were done for a few near-optimum geometries for each conformation to check the AM1 results.

Additional helpful information on standard programs available at *ab initio* and semiempirical levels—where to get them, how to use them, what they have been used for—is available in the very well-written reference handbook by Clark [58].

11-17.A Problems

- 11-1.** Use the data in Table 11-3 to calculate the theoretical transition energies for Ne^+ when 1s and 2s electrons are excited into the 2p level. The experimental values are $2p \leftarrow 2s$, 0.989 a.u.; $2p \leftarrow 1s$, 31.19 a.u.
- 11-2.** Use the data in Table 11-1 to estimate separately the errors in ionization energies for the three states due to
- omission of electron correlation.
 - failure to allow electronic relaxation.
- 11-3.** In Section 11-11, it is argued that neglect of electron correlation and electronic relaxation in setting $I_k^0 = -\epsilon_k$ causes errors of opposite sign that partly cancel.

Would this also occur when Koopmans' theorem is used to predict electron affinities? Why?

11-4. Demonstrate that, if

$$D_1 = \begin{vmatrix} a & c \\ b & d \end{vmatrix} \text{ and } D_2 = \begin{vmatrix} a & e \\ b & f \end{vmatrix} \text{ then } D_1 + \lambda D_2 = \begin{vmatrix} a & c + \lambda e \\ b & d + \lambda f \end{vmatrix}$$

11-5. A singly excited configuration ψ_1 differs by one orbital from the ground state ψ_0 and also by one orbital from certain doubly excited configurations ψ_2 . Brillouin's theorem gives $\langle \psi_0 | \hat{H} | \psi_1 \rangle = 0$, but not $\langle \psi_1 | \hat{H} | \psi_2 \rangle = 0$. Where does the attempted proof to show that $\langle \psi_1 | \hat{H} | \psi_2 \rangle = 0$ break down?

11-6. Show that, if $\psi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n$, and if ψ is to be an eigenfunction of \hat{A} with eigenvalue a_1 , then it is necessary that all the ψ_i ($i = 0, \dots, n$) also be eigenfunctions of \hat{A} with eigenvalues a_1 .

11-7. How many distinct four-center coulomb and exchange integrals result when one has four nuclei, each being the site of five basis functions? Make no assumptions about symmetry or basis function equivalence or electron spin.

11-8. For a homonuclear diatomic molecule, which of the following singly excited configurations would be prevented for reasons of symmetry from contributing to a CI wavefunction for which the main "starting configuration" is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4$?

- $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^3 1\pi_g$ (i.e., $1\pi_u \rightarrow 1\pi_g$)
- $2\sigma_g \rightarrow 3\sigma_g$
- $2\sigma_g \rightarrow 1\pi_g$
- $1\sigma_g \rightarrow 3\sigma_g$

11-9. Write down the hamiltonian operator for electrons in the water molecule. Use summation signs with explicit index ranges. Use atomic units.

11-10. An SCF calculation on ground state H_2 at $R = 1.40$ a.u. using a minimal basis set gives a σ_g and a σ_u MO having energies

$$\epsilon_{\sigma_g} = -0.619 \text{ a.u.} \quad \epsilon_{\sigma_u} = +0.401 \text{ a.u.}$$

The nonvanishing two-electron integrals over these MOs are

$$\iint \sigma_g(1)\sigma_g(2)(1/r_{12})\sigma_g(1)\sigma_g(2)dv(1)dv(2) = 0.566 \text{ a.u.}$$

$$\iint \sigma_g(1)\sigma_u(2)(1/r_{12})\sigma_g(1)\sigma_u(2)dv(1)dv(2) = 0.558 \text{ a.u.}$$

$$\iint \sigma_g(1)\sigma_u(2)(1/r_{12})\sigma_g(2)\sigma_u(1)dv(1)dv(2) = 0.140 \text{ a.u.}$$

$$\iint \sigma_u(1)\sigma_u(2)(1/r_{12})\sigma_u(1)\sigma_u(2)dv(1)dv(2) = 0.582 \text{ a.u.}$$

- Write down the Slater determinant for the ground state of H_2 .
- Calculate the SCF electronic energy for H_2 at $R = 1.40$ a.u.

- c) Calculate the total (electronic plus nuclear repulsion) energy for H₂.
- d) What is the bond energy for H₂ predicted by this calculation, assuming that the minimum total energy occurs at $R = 1.40$ a.u.?
- e) Estimate the (vertical) ionization energy for H₂.
- f) What is the value of the kinetic-plus-nuclear-attraction energy for one electron in ground-state H₂ according to this calculation?

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