

Electron-Correlation Methods

16.1 Correlation Energy

The four sources of error in ab initio molecular electronic calculations are (1) neglect of or incomplete treatment of electron correlation, (2) incompleteness of the basis set, (3) relativistic effects, and (4) deviations from the Born–Oppenheimer approximation. Deviations from the Born–Oppenheimer approximation are usually negligible for ground-state molecules. Relativistic effects will be discussed in Section 16.11. In calculations on molecules without heavy atoms, (1) and (2) are the main sources of error.

Almost all computational methods expand the MOs in a basis set of one-electron functions. The basis set has a finite number of members and hence is incomplete. The incompleteness of the basis set produces the **basis-set incompleteness** (or **truncation error**) (**BSIE** or **BSTE**).

The Hartree–Fock method, discussed in Chapter 15, neglects electron correlation. Chapter 16 discusses methods that include electron correlation. The main correlation methods are configuration interaction (**CI**, Section 16.2), Møller–Plesset (**MP**) perturbation theory (Section 16.3), the coupled cluster (**CC**) method (Section 16.4), and density functional theory (**DFT**, Section 16.5).

Correlation Energy

Recall from Eq. (11.16) that the molecular correlation energy is defined as the difference between the nonrelativistic true molecular energy and the restricted Hartree–Fock (HF) nonrelativistic energy calculated with a complete basis set: $E_{\text{corr}} \equiv E_{\text{nonrel}} - E_{\text{HF}}$. For a closed-shell state, the HF wave function is a single Slater determinant. For some open-shell states [such as some He excited states—Eqs. (10.44) and (10.45)], the HF wave function contains more than one determinant so that it is an eigenfunction of the appropriate spin and symmetry operators. Even though these open-shell HF wave functions may have more than one Slater determinant, as noted in Section 11.3, they contain only one configuration state function (**CSF**).

In Section 11.6 the existence of a nonzero E_{corr} was ascribed to the failure of the HF calculation to account for the instantaneous correlations between motions of electrons. This source of E_{corr} is called **dynamic correlation**.

There is a second reason why E_{HF} may differ from E_{nonrel} : In some situations, the single-Slater-determinant HF wave function (or the few-determinant CSF required for some open-shell states) is a poor representation of the system's state, thereby making E_{HF}

deviate very considerably from the true nonrelativistic E , and making E_{corr} substantial. This contribution to E_{corr} is called **static** (or **nondynamic** or **strong** or **near-degeneracy correlation**). For example, we saw in Section 13.11 that the MO single-determinant wave function for H_2 has equal probability for ionic terms with both electrons close to one atom and covalent terms with one electron on each atom. Since H_2 dissociates to two H atoms and not to ions, the single-determinant wave function is qualitatively wrong at large internuclear distances. At large internuclear distances in H_2 , the static correlation becomes substantial. In order to have a qualitatively correct wave function at large R , one must take a linear combination of the $1\sigma_g^2$ Slater determinant and the ${}^1\Sigma_g^+ 1\sigma_u^2$ Slater determinant [Eq. (13.95) with the right-hand side multiplied by the antisymmetric two-electron spin function]; the contribution of the $1\sigma_u^2$ determinant increases as R increases.

At large internuclear distances, the energy difference between the highest occupied MO (HOMO) $1\sigma_g$ in H_2 and the lowest unoccupied MO (LUMO) $1\sigma_u$ becomes small and goes to zero as $R \rightarrow \infty$. This near degeneracy of occupied and virtual orbitals is characteristic of systems with substantial static correlation. For example, for the ground state of the Be atom, the HF wave function is a single determinant corresponding to the electron configuration $1s^2 2s^2$. However, in Be the $2p$ AO is nearly degenerate with the $2s$ AO, and the static correlation is substantial. To have a qualitatively correct wave function, one must include a contribution from the ${}^1S$ CSF with orbital occupancy $1s^2 2p^2$. Another example is the ground electronic state of O_3 , which has only a small gap between the HOMO and the LUMO; O_3 has substantial biradical character (a resonance structure with an unpaired electron on each of the noncentral O atoms can be written) and a large contribution from static correlation. Other situations not involving covalent bond breaking where static correlation is important include molecules with double or triple bonds, transition-metal compounds, and the majority of excited electronic states.

To deal with static correlation, one replaces the single determinant (or single CSF) used in the HF method with a linear combination of the CSFs that make substantial contributions to the wave function. This gives a **multiconfiguration (MC)** wave function. Various MC methods are discussed in the following sections.

Properties of Methods

A quantum-chemistry approximation method is **variational** if the energy calculated by the method is never less than the true energy of the state being calculated. Since an SCF MO wave-function energy is equal to the variational integral (8.1), the SCF MO method is variational. Although being variational is a desirable property, we shall see that many of the calculation methods currently used (such as MP, CC, DFT) are not variational.

Two other desirable properties are size extensivity and size consistency. These terms have been used by various people to mean somewhat different things. The definitions given here are from I. Shavitt, *Mol. Phys.*, **94**, 3 (1998). A method is **size extensive** if the computed energy of a system composed of n noninteracting identical systems equals n times the energy of one subsystem computed by the same method, and the computed energy of a uniform system (such as the uniform electron gas of Section 16.5) is proportional to the size of the system. Size extensivity is desirable so as to make the energy scale properly as the number of particles in the system increases. A method is **size consistent** if the computed energy of a molecule dissociated into two or more infinitely separated parts and treated as a single system equals the sum of the computed energies of each part. Size extensivity and size consistency are related but not equivalent properties, and a method can have one property but not the other. Size consistency applies only at infinite separation of the parts, but size extensivity applies at all geometries.

CBS Extrapolation

A common procedure to reduce basis-set truncation error is to do a series of calculations using one method with two, three, or four increasingly larger basis sets and extrapolate the results to what one hopes is a value close to the complete-basis-set (**CBS**) limit. Examples are the extrapolation done with the formula (15.23) (Prob. 15.21) and with the formula (15.88) (Prob. 15.22) to estimate the CBS HF limit for H_2O . When a method such as CC that includes correlation is used, the extrapolation is commonly done in two steps. One first does HF calculations with a series of basis sets to estimate the CBS HF energy limit E_∞^{HF} . Then one does a series of CC calculations with the same series of basis sets and uses an empirical extrapolation formula to estimate the CBS correlation energy E_∞^{corr} . The estimate of the CBS molecular energy is then found as $E_\infty^{\text{HF}} + E_\infty^{\text{corr}}$. See the discussion after Eq. (16.31).

The basis sets most commonly used for CBS extrapolations are the correlation consistent (cc) basis sets such as cc-pVnZ and aug-cc-pVnZ (Section 15.4). For a review of basis sets, see F. Jensen, *WIREs Comput. Mol. Sci.* 2012, doi: 10.1002/wcms.1123.

Another method to reduce basis-set truncation error is the F12 method, which introduces interelectronic distances r_{ij} into the wave function. See Sections 16.3 and 16.4 for discussion.

Notation

A notation having the form Method/(Basis set) is used to specify the method and the basis set used in a calculation. For example, HF/6-31G* denotes an SCF MO calculation using the 6-31G* basis set. The letters HF denote any SCF MO calculation and do not imply that the Hartree–Fock limit has been reached. The notation CCSD(T)/CBS denotes a result found by extrapolation of CCSD(T) calculations to the CBS limit. (The CCSD(T) method is discussed in Section 16.4.) For high-level calculations, a geometry optimization may be too time consuming to do, so one sometimes does a single-point high-level energy calculation at the equilibrium geometry found from a lower-level calculation. The notation CCSD(T)/cc-pVQZ//HF/6-31G* denotes a single-point energy calculation done with the high-level CCSD(T) method and the cc-pVQZ basis set at the equilibrium geometry found by an HF/6-31G* geometry optimization.

Test Sets of Data

Many sets of experimental and high-level calculation data have been compiled for use in testing the performance of quantum-chemistry methods.

The **G3/05 test set** of accurately known experimental thermochemical data consists of 270 enthalpies of formation, 105 ionization energies, 63 electron affinities, 10 proton affinities, and 6 dimerization energies of H-bonded dimers [L. A. Curtiss et al., *J. Chem. Phys.*, **123**, 124107 (2005)]. Some medium-size molecules in the G3/05 set are naphthalene (C_{10}H_8), SF_6 , and $\text{C}_6\text{H}_{13}\text{Br}$. The G3/05 set does not include any transition-metal compounds. (Accurate thermochemical data for such compounds is sparse.) The G3/05 set (which contains 454 energy changes) is an expansion of the earlier test sets G2 (125 energy changes), G2/97 (301 energy changes), and G3/99 (376 energy changes).

Noncovalent interactions such as hydrogen bonding and dispersion (London) forces are important in determining the structures of biomolecules. The **S66 test set** was devised to test the accuracy of methods used in biomolecule calculations [J. Řezáč et al., *J. Chem. Theory Comput.*, **7**, 2427, 3466 (2011)]. S66 contains equilibrium binding energies of 66 noncovalently bound molecular complexes subdivided into three categories: hydrogen-bonded complexes (for example, the water dimer; the complex of water with N-methylacetamide), dispersion-dominated complexes (for example, the benzene dimer; the complex of uracil

with pentane), and complexes bound by a mix of dispersion and electrostatic interactions (for example, the complex of water and benzene). The energies were calculated using a high-level method that accurately estimates the CCSD(T)/CBS limit. The interaction energies were also calculated for eight nonequilibrium distances along the dissociation curve of each complex, and these energies comprise the S66x8 dataset. The S66 set is an improvement on an earlier set, the **S22** set. These and other sets can be found at www.begdb.com.

The GMTKN30 database (general main group thermochemistry, kinetics, and noncovalent interactions database) is a collection of 30 databases of experimental and high-level ab initio atomization energies, ionization potentials, electron affinities, reaction barrier heights, reaction energies, energy differences between conformers, isomerization energies, noncovalent interaction energies, . . . and contains 841 relative energy values [L. Goerigk and S. Grimme, *J. Chem. Theory Comput.*, **7**, 291 (2011); toc.uni-muenster.de/GMTKN/GMTKNmain.html].

16.2 Configuration Interaction

To overcome the deficiencies of the Hartree–Fock wave function (for example, improper behavior as internuclear distances go to infinity and very inaccurate dissociation energies), one can introduce configuration interaction (CI), thus going beyond the Hartree–Fock approximation. Recall (Section 11.3) that in a molecular CI calculation one begins with a set of basis functions χ_i , does an SCF MO calculation to find SCF occupied and virtual (unoccupied) MOs, uses these MOs to form **configuration (state) functions** (CSFs) Φ_i , writes the molecular wave function ψ as a linear combination $\sum_i b_i \Phi_i$ of the CSFs, and uses the variation method to find the b_i 's. The number of MOs produced equals the number of basis functions used. The type of MOs produced depends on the type of basis functions used. For example, if we include only s AOs in the basis set for a CI calculation on a linear molecule, we get only σ MOs, and no π , δ , . . . MOs.

Each CSF is a linear combination of one to a few Slater determinants, is an eigenfunction of the spin operators $\hat{S}^2$ and $\hat{S}_z$, and satisfies the spatial symmetry requirements of the molecule. Alternatively, the CI wave function can be expressed as the equivalent linear combination of Slater determinants. When this is done, the number of Slater determinants is typically 4 or 5 times the number of CSFs.

The configuration functions in a CI calculation are classified as **singly excited, doubly excited, triply excited**, . . . , according to whether 1, 2, 3, . . . electrons are excited from occupied to unoccupied (virtual) orbitals. For example, the H_2 configuration function $2^{-1/2}|\sigma_u^*1s\sigma_u^*1s|$ used in Eq. (13.95) is doubly excited (another term sometimes used is **doubly substituted**).

In the CI expansion $\psi = \sum_i b_i \Phi_i$, one includes only configuration functions that have the same symmetry properties (symmetry eigenvalues) as the state that is being approximated by the expansion. (This follows from Theorem 3 proved in Section 7.3.) For example, the ground state of H_2 is a $^1\Sigma_g^+$ state, and a CI calculation of the H_2 ground state would include only configuration functions that correspond to $^1\Sigma_g^+$ terms. A $\sigma_g\sigma_u$ electron configuration would have states of odd parity (u) and would not be included in ψ . A $\sigma_g\pi_g$ configuration would produce only Π terms (Table 13.3 in Section 13.8) and would not be included. For a π_g^2 or π_u^2 configuration, only the configuration function corresponding to the $^1\Sigma_g^+$ term (Table 13.3) would contribute to ψ .

The number of possible configuration functions with the proper symmetry increases extremely rapidly as the number of electrons and the number of basis functions increase. For n electrons and b basis functions, the number of configuration functions turns out to be roughly proportional to b^n . A CI calculation that includes all possible configuration

functions with proper symmetry is called a **full CI** calculation. Because of the huge number of configuration functions, full CI calculations are out of the question except for small molecules (small n) and rather small basis sets (small b).

In most calculations (for example, molecular dissociation, excitation of valence-shell electrons to produce excited electronic states), one is looking at energy changes in processes affecting primarily the valence-shell electrons, so one expects the correlation energies involving the inner-shell electrons to change only slightly. Hence one usually makes the approximation of including only configuration functions that involve excitation of valence-shell electrons. The omission of excitations of inner-shell (core) electrons is called the **frozen-core (FC) approximation**. The contribution of core excitations is not always small, but their contribution changes only slightly with changes in environment. Use of the frozen-core approximation does not disqualify a calculation from being called full CI, provided all possible excitations of valence-shell electrons are included. The notation FCI(FC) denotes a full-CI calculation with the frozen-core approximation, but use of the FC approximation is so common that people often omit the FC. The default option in *Gaussian 09* CI, MP, and CC calculations is to use the frozen-core approximation unless otherwise specified by the user.

For a molecule with n electrons and with spin quantum number $S = 0$, the number of CSFs in a full CI calculation (with spatial symmetry restrictions ignored) is (Wilson, page 199)

$$\frac{b!(b+1)!}{(\frac{1}{2}n)!(\frac{1}{2}n+1)!(b-\frac{1}{2}n)!(b-\frac{1}{2}n+1)!} \quad (16.1)$$

where b is the number of one-electron basis functions used to express the MOs. For a 6-31G** full CI calculation of the small molecule CH_3OH , $b = 15 + 15 + 4(5) = 50$. For $n = 18$ and $b = 50$, the number of CSFs given by (16.1) is 7.6×10^{17} , so a full CI 6-31G** calculation on CH_3OH is not possible. One might therefore try a full CI calculation with the minimal STO-3G basis set, which has $b = 5 + 5 + 4(1) = 14$ for CH_3OH . This gives a mere 1.0×10^6 CSFs. This calculation is feasible, since an FCI(FC) calculation with 65×10^9 determinants has been done on the C_2 molecule using a parallel supercomputer [Z. Gan and R. J. Harrison, Proceedings of the ACM/IEEE SC 2005 Conference, p. 22], but would be a waste of time. Experience shows that in order to get a substantial portion of the correlation energy, one must use a large basis set. For example, for H_2O , full CI calculations with a (relatively small) DZ basis set and 256473 CSFs gives an energy of -76.158 hartrees, compared with the Hartree–Fock limit of -76.068 hartrees and the true nonrelativistic energy of -76.438 hartrees (Table 16.1), so only a relatively small portion of the -0.370 -hartree correlation energy has been obtained. The SCF energy obtained with this DZ H_2O basis set is -76.010 hartrees, and the difference of -0.148 hartree between this SCF energy and the full-CI DZ energy is called the **basis-set correlation energy**. Even for a DZP basis set, a full CI calculation on H_2O gives only -76.257 hartrees, which is still quite far from -76.438 hartrees.

High-level correlation calculations may use basis sets that are triple zeta with two sets of polarization functions with different orbital exponents added on each atom; such a set is designated TZ2P. The correlation-consistent basis sets of Dunning and co-workers (Section 15.4) were especially designed for correlation calculations.

Since full CI calculations cannot be done for medium-size and large molecules, one must therefore decide which types of configuration functions are likely to make the largest contributions to ψ , and one includes only these. We expect the unexcited configuration function (the SCF MO wave function) to make the largest contribution. Which types of excited configurations make significant contributions to ψ ? To answer this question,

we consider the effects of instantaneous electron correlation as a perturbation on the Hartree–Fock wave function. One finds that the first-order correction to the unperturbed (Hartree–Fock) wave function of a closed-shell state contains only doubly excited configuration functions (for justification, see Section 16.3). Thus we expect the most important correction to the Hartree–Fock wave function to come from doubly excited configuration functions. Although singly excited configuration functions are less important than double excitations in affecting the wave function, it turns out (see I. Shavitt, in *Schaefer, Methods of Electronic Structure Theory*, page 255) that single excitations have a significant effect on one-electron properties. [A *one-electron property* is one calculated as $\langle \psi | \hat{B} | \psi \rangle$, where the operator $\hat{B}$ is a sum of terms, each of which involves only a single particle; an example is the dipole moment; Eqs. (14.19) and (14.20).] Therefore, one usually includes single excitations in a CI calculation, and the most common type of CI calculation (designated **CISD** or CI-SD or SD-CI) includes the singly and doubly excited configuration functions. CISD is an example of **limited CI**, which is anything less than a full CI calculation. (It turns out that the second-order correction to the Hartree–Fock function includes single, double, triple, and quadruple excitations.)

For calculations on a few 10-electron molecules, CISD gave about 94% of the basis-set correlation energy [R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983)]. This result might seem to be a cause for optimism about CISD, but CISD has serious drawbacks. Calculations on a simple model system [F. Sasaki, *Int. J. Quantum Chem. Symp.*, **11**, 125 (1977)] indicate that the percentage of the basis-set correlation energy obtained by CISD decreases as the size of the molecule increases. For molecules that consist of first-row atoms, CISD is estimated to give 82% to 90% of the basis-set correlation energy of 20-electron molecules, 68% to 78% of the correlation energy of 50-electron molecules, and 55% to 67% for 100-electron molecules (Prob. 16.2).

A related defect is that CISD calculations are neither size extensive nor size consistent (see the beginning of Chapter 16). These properties are important whenever calculations on molecules of substantially different sizes are to be compared, as, for example, in calculation of the energy change in the dissociation reaction $A \rightarrow B + C$.

To see that CISD is not size consistent, consider two infinitely separated helium atoms He_a and He_b . If we do a CISD calculation of He_a using a complete basis set, we get the exact energy E_a of He_a , since CISD is the same as full CI for this two-electron atom. The same applies for He_b . Now consider a complete-basis-set CISD calculation for the composite system of infinitely separated He_a and He_b . This composite system has four electrons, so a CISD calculation is not equivalent to a full CI calculation, and the CISD calculation will give an energy higher than the exact energy $E_a + E_b$ of the composite system. Therefore, CISD is not size consistent.

Full CI is size extensive and size consistent. SCF MO calculations are size extensive.

Because the CISD wave function is a variation function, the variation theorem assures us that the CISD energy cannot be less than the true energy. The CISD method is therefore variational.

Theory indicates that after double excitations, quadruple excitations are next in importance. Calculations on some 10-electron molecules found that CI with inclusion of single, double, triple, and quadruple excitations (CI-SDTQ) gave over 99% of the basis-set correlation energy (Harrison and Handy, op. cit.). For molecules containing only first-row atoms, CI-SDTQ is estimated to give the following percentages of the basis-set correlation energy: 98% to 99% for 20-electron molecules, 90% to 96% for 50-electron molecules, and 80% to 90% for 100-electron molecules (Sasaki, op. cit.). Provided we confine ourselves to molecules with no more than about 50 electrons, CI-SDTQ will come reasonably close to full CI and hence will be approximately size extensive. However, CI-SDTQ calculations with basis sets large enough to give good results for the correlation energy involve far too many CSFs to be practical.

An approximate formula due to Davidson [S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974)] is widely used to estimate the energy contribution ΔE_Q due to quadruple excitations:

$$\Delta E_Q \approx (1 - a_0^2)(E_{\text{CI-SD}} - E_{\text{SCF}}) \quad (16.2)$$

where a_0 is the coefficient of the SCF function Φ_0 in the normalized CI expansion $\psi = \sum_i a_i \Phi_i$, and $E_{\text{CI-SD}}$ and E_{SCF} are the CI-SD and SCF energies calculated with the basis set. For example, a DZ calculation on H_2O gave (in atomic units) at the equilibrium geometry $E_{\text{SCF}} = -76.009838$, $E_{\text{CI-SD}} = -76.150015$, and $a_0 = 0.97874$; from (16.2), we find $\Delta E_Q \approx -0.005897$, which, when added to $E_{\text{CI-SD}}$, gives -76.155912 ; this result is reasonably close to the CI-SDTQ DZ result of -76.157603 (the contribution of triple excitations is small). The Davidson formula becomes less accurate as the size of the molecule increases. Other formulas proposed for ΔE_Q give somewhat improved accuracy compared with the Davidson formula [see Section 2.1.3.1 of P. G. Szalay et al., *Chem. Rev.*, **112**, 108 (2012)]. (If static correlation is small, a_0 will be close to 1, indicating that a single CSF is a reasonably good representation of the state. If static correlation is substantial, a_0 will be substantially less than 1.)

Use of the Davidson correction reduces the size-consistency error. For example, CISD/DZP calculations on two H_2O molecules separated by 500 Å, a distance at which their interaction energy is utterly negligible, found that the CISD energy of this system exceeded twice the CISD energy of one H_2O molecule by 12.3 kcal/mol, which is the size-consistency error. The Davidson correction reduced this error to 3.8 kcal/mol [M. J. Frisch et al., *J. Chem. Phys.*, **84**, 2279 (1986)].

CISD calculations of molecular properties often do not give highly accurate results. For example, a comparison of molecular geometries calculated by several correlation methods found that the CISD method gave the poorest results of those correlation methods studied [T. Helgaker et al., *J. Chem. Phys.*, **106**, 6430 (1997)]. Highly accurate CI results require a CISDTQ calculation, which is generally impractical.

Table 16.1 on page 532 lists some calculations on H_2O that include electron correlation. The methods used in these calculations are discussed in Sections 16.2–16.7. All the calculations listed are nonrelativistic, fixed-nuclei calculations. The B3LYP/cc-pVTZ calculation gives an energy below the -76.438 true nonrelativistic energy. This is a density-functional calculation and is not variational. The lowest-energy variational calculation is the FN-DQMC calculation, which gives 97% of the correlation energy.

EXAMPLE

The He SCF MO calculation in Section 14.3 used a basis set of two STOs χ_1 and χ_2 . For the helium ground state treated with this basis set, (a) write down the configuration state functions (CSFs) that are present in the wave function in a full CI treatment, and (b) carry out a CI calculation that includes only doubly excited CSFs.

- (a) Since we used two basis functions, the SCF calculation yielded two SCF orbitals ϕ_1 and ϕ_2 . In the ground state of this two-electron atom, only ϕ_1 is occupied, and ϕ_2 is an unoccupied (virtual) orbital. We found $\phi_1 = 0.842\chi_1 + 0.183\chi_2$, but didn't bother to find ϕ_2 . Use of the root $\varepsilon_2 = 2.809$ [Eq. (14.54)] and the final F_{rs} 's of (14.53) in the Roothaan equation (14.34) with $r = 1$ gives $-3.690c_{12} - 3.290c_{22} = 0$, and $c_{12}/c_{22} = -0.892$. The normalization condition (14.48) rewritten for c_{22} gives $c_{22} = 1.816$; hence $c_{12} = -1.620$. The SCF orbitals are

$$\phi_1 = c_{11}\chi_1 + c_{21}\chi_2 = 0.842\chi_1 + 0.183\chi_2$$

$$\phi_2 = c_{12}\chi_1 + c_{22}\chi_2 = -1.620\chi_1 + 1.816\chi_2$$

TABLE 16.1 H₂O Calculations That Include Correlation^a

Reference ^b	Method ^c /Basis Set	Energy/ <i>E_h</i>	μ /D	θ	<i>R</i> _{OH} /Å
Harrison, Handy	CISD/DZ	−76.150			
Harrison, Handy	FCI/DZ	−76.158			
CCCBDB	MP2(FC)/6-31G*	−76.197	2.24	104.0°	0.969
CCCBDB	CISD(FC)/6-31G*	−76.198	2.24	104.2°	0.966
CCCBDB	MP2(full)/6-31G*	−76.199	2.24	104.0°	0.969
CCCBDB	CCSD(FC)/6-31G*	−76.206	2.25	103.9°	0.969
CCCBDB	MP4(FC)/6-31G*	−76.207	2.25	103.8°	0.970
CCCBDB	CCSD(T)(FC)/6-31G*	−76.208	2.25	103.8°	0.971
CCCBDB	MP2(FC)/6-31G**	−76.220	2.20	103.8°	0.961
CCCBDB	CISD(FC)/6-31G**	−76.221	2.19	104.2°	0.958
CCCBDB	MP2(FC)/cc-pVDZ	−76.229	2.10	101.9°	0.965
CCCBDB	CCSD(T)(FC)/cc-pVDZ	−76.241	2.10	101.9°	0.966
Scuseria, Schaefer	CISDTQ/DZP	−76.270	2.13	104.5°	0.963
Schaefer et al.	CISD/TZ2P	−76.312	1.94	104.9°	0.952
CCCBDB	CISD(FC)/cc-pVTZ	−76.314	2.03	104.2°	0.953
CCCBDB	MP2(FC)/6-31+G(3df,2p)	−76.318	2.02	104.5°	0.959
CCCBDB	MP2(FC)/cc-pVTZ	−76.319	2.04	103.5°	0.959
CCCBDB	CCSD(T)(FC)/cc-pVTZ	−76.332	2.04	103.6°	0.959
Cortez et al.	CCSD(T)(FC)/cc-pV6Z	−76.372		104.4°	0.958
Kim et al.	CISD(full)/(13s . . . 2d) ^d	−76.382		104.8°	0.952
Kim et al.	MP2(full)/(13s . . . 2d)	−76.391		104.2°	0.959
Kim et al.	CCSD(full)/(13s . . . 2d)	−76.396		104.4°	0.956
Kim et al.	CCSD(T)(full)/(13s . . . 2d)	−76.406		104.1°	0.959
Kim et al.	MP4(full)/(13s . . . 2d)	−76.407		104.1°	0.960
CCCBDB	B3LYP/6-31G*	−76.409	2.10	103.6°	0.969
CCCBDB	B3LYP/6-31G**	−76.420	2.04	103.7°	0.965
CCCBDB	B3LYP/cc-pVDZ	−76.421	1.94	102.7°	0.969
Lüchow et al.	MRCISD/aug-cc-pCV5Z	−76.427 ^e			
Gurtubay, Needs	FN-DQMC	−76.428 ^e			
CCCBDB	B3LYP/cc-pVTZ	−76.460	1.92	104.5°	0.961
<i>Nonrelativistic fixed-nuclei energy</i>		−76.438			
<i>Experimental values</i>		−76.480	1.85	104.5°	0.958

^aSee footnote a to Table 15.2 in Section 15.6.^bR. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theory Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.^d(13s . . . 2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.^eCalculated at a geometry close to the experimental geometry.

(Note that ϕ_2 has a node; ϕ_2 is an approximation to the $2s$ AO of helium.) The terms that arise from placing two electrons into these two s orbitals are a ^1S term with both electrons in ϕ_1 , a ^1S term with both electrons in ϕ_2 , a ^1S term with one electron in ϕ_1 and one in ϕ_2 , and a ^3S term with one electron in ϕ_1 and one in ϕ_2 . Since the ground state is ^1S , we include only the ^1S CSFs, which are [see Eqs. (10.41), (10.45), and (11.60)]:

$$\begin{aligned}\Phi_1 &= |\phi_1\bar{\phi}_1|, \quad \Phi_2 = |\phi_2\bar{\phi}_2| \\ \Phi_3 &= \frac{1}{2}[\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}\quad (16.3)$$

(b) The CSF Φ_2 is doubly substituted, and Φ_3 is singly substituted, so we include only Φ_2 in addition to Φ_1 . The variational function is $\psi = a_1\Phi_1 + a_2\Phi_2$, and the secular equation (11.18) is

$$\begin{vmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle - E & \langle \Phi_1 | \hat{H} | \Phi_2 \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle - E \end{vmatrix} = 0 \quad (16.4)$$

The orthogonality of the orbitals ϕ_1 and ϕ_2 (Section 14.3) ensures that $\langle \Phi_1 | \Phi_2 \rangle = 0$.

The function Φ_1 is the SCF wave function, so $\langle \Phi_1 | \hat{H} | \Phi_1 \rangle$ is equal to the SCF energy -2.862 hartrees calculated in the previous example: $\langle \Phi_1 | \hat{H} | \Phi_1 \rangle = -2.862$.

In evaluating the integrals in the secular determinant, we can omit the spin factors in the wave functions, since summation over these gives 1.

The He Hamiltonian (9.39) is $\hat{H} = \hat{H}^{\text{core}}(1) + \hat{H}^{\text{core}}(2) + 1/r_{12}$, and

$$\begin{aligned}\langle \Phi_2 | \hat{H} | \Phi_2 \rangle &= \langle \phi_2(1)\phi_2(2) | \hat{H}^{\text{core}}(1) + \hat{H}^{\text{core}}(2) + 1/r_{12} | \phi_2(1)\phi_2(2) \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_2 \rangle &= \langle \phi_2(1) | \hat{H}^{\text{core}}(1) | \phi_2(1) \rangle \langle \phi_2(2) | \phi_2(2) \rangle \\ &\quad + \langle \phi_2(2) | \hat{H}^{\text{core}}(2) | \phi_2(2) \rangle \langle \phi_2(1) | \phi_2(1) \rangle \\ &\quad + \langle \phi_2(1)\phi_2(2) | 1/r_{12} | \phi_2(1)\phi_2(2) \rangle\end{aligned}$$

where $\langle \phi_2(2) | \phi_2(2) \rangle = 1 = \langle \phi_1(1) | \phi_1(1) \rangle$. To evaluate the integrals over the orbitals ϕ_i in terms of integrals over the basis functions χ_r , we substitute the expansion $\phi_i = \sum_r c_{ri}\chi_r$ [Eq. (14.33)] into the integrals. We get

$$\langle \phi_i(1) | \hat{H}^{\text{core}}(1) | \phi_j(1) \rangle = \sum_r \sum_s c_{ri}^* c_{sj} \langle \chi_r(1) | \hat{H}^{\text{core}}(1) | \chi_s(1) \rangle = \sum_{r=1}^b \sum_{s=1}^b c_{ri}^* c_{sj} H_{rs}^{\text{core}} \quad (16.5)$$

$$\begin{aligned}\langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_k(1)\phi_l(2) \rangle &= \sum_r \sum_s \sum_t \sum_u c_{ri}^* c_{sj}^* c_{tk} c_{ul} \langle \chi_r(1)\chi_s(2) | 1/r_{12} | \chi_t(1)\chi_u(2) \rangle \\ \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_k(1)\phi_l(2) \rangle &= \sum_{r=1}^b \sum_{t=1}^b \sum_{s=1}^b \sum_{u=1}^b c_{ri}^* c_{tk} c_{sj}^* c_{ul} (rt|su)\end{aligned}\quad (16.6)$$

where the notation (14.39) is used. Using these equations, we find (Prob. 16.6)

$$\begin{aligned}\langle \Phi_2 | \hat{H} | \Phi_2 \rangle &= 2(c_{12}^2 H_{11}^{\text{core}} + 2c_{12}c_{22} H_{12}^{\text{core}} + c_{22}^2 H_{22}^{\text{core}}) + c_{12}^4 (11|11) \\ &\quad + 4c_{12}^3 c_{22} (11|12) + 2c_{12}^2 c_{22}^2 (11|22) + 4c_{12}^2 c_{22}^2 (12|12) \\ &\quad + 4c_{12}c_{22}^3 (12|22) + c_{22}^4 (22|22) \\ &= 3.226\end{aligned}$$

where the values of the integrals were taken from the example in Section 14.3. Similarly, we find (Prob. 16.6)

$$\begin{aligned}\langle \Phi_2 | \hat{H} | \Phi_1 \rangle &= \langle \Phi_1 | \hat{H} | \Phi_2 \rangle = c_{11}^2 c_{12}^2 (11|11) + 2(c_{11}^2 c_{12} c_{22} + c_{11} c_{12}^2 c_{21})(11|12) \\ &\quad + 2c_{11} c_{12} c_{21} c_{22} (11|22) \\ &\quad + (c_{11}^2 c_{22}^2 + 2c_{11} c_{21} c_{12} c_{22} + c_{12}^2 c_{21}^2)(12|12) \\ &\quad + 2(c_{11} c_{21} c_{22}^2 + c_{12} c_{22} c_{21}^2)(12|22) + c_{21}^2 c_{22}^2 (22|22) \\ &= 0.289_5\end{aligned}$$

The $\hat{H}^{\text{core}}$ integrals vanish for $\langle \Phi_2 | \hat{H} | \Phi_1 \rangle$ because of the orthogonality of ϕ_1 and ϕ_2 . The secular equation (16.4) is

$$\begin{vmatrix} -2.862 - E & 0.289_5 \\ 0.289_5 & 3.22_6 - E \end{vmatrix} = 0$$

$$E = -2.876, 3.24$$

The lower root gives

$$E = -2.876 \text{ hartrees} = -78.25 \text{ eV}$$

as compared with the SCF energy of -77.87 eV and the true energy of -79.00 eV . This CI calculation has recovered 34% of the correlation energy. The CI ground-state ψ is found to be (Prob. 16.5) $\psi = 0.9989\Phi_1 - 0.0474\Phi_2$.

One finds that inclusion of the singly excited CSF Φ_3 gives only a very slight further improvement (see *Jørgensen and Oddershede*, page 38). Significant further improvement requires redoing the SCF calculation with a larger basis set, which will generate more virtual orbitals so that many more CSFs can be included in the CI calculation.

In a CI calculation that uses SCF MOs, there are two major computational tasks. One task is to transform the known integrals over the AO basis functions χ_r into integrals over the SCF MOs ϕ_i using Eqs. (16.5) and (16.6). Calculation of the integrals $\langle \phi_i \phi_j | 1/r_{12} | \phi_k \phi_l \rangle$ from the $(rs|tu)$ integrals is especially time consuming. For a basis set of b functions $\chi_1, \dots, \chi_b$, there are b MOs ϕ_i and approximately $b^4/8$ different $\langle \phi_i \phi_j | 1/r_{12} | \phi_k \phi_l \rangle$ integrals to be computed [the factor $1/8$ arises from equalities similar to (14.47)], and there are b^4 terms in the sums on the right side of (16.6). Hence the number of computations is apparently about $b^8/8$. For 100 basis functions, $b^8/8$ is about 10^{15} . Fortunately, use of a clever procedure can reduce the number of computations to about b^5 (see *Hehre et al.*, Section 3.3.4). The second task is to solve the CI secular equation to find the lowest-energy eigenvalue and the corresponding set of expansion coefficients. In an SCF calculation that uses 500 basis functions, one must solve for the eigenvalues and eigenvectors of a matrix whose order is 500. This is readily done using standard matrix diagonalization methods (Section 8.6). In an accurate CI calculation, one might use 10^8 CSFs to expand the wave function, and one must find the lowest eigenvalue and corresponding eigenvector of a matrix whose order is 10^8 . Special techniques have been devised to find the lowest few eigenvalues and corresponding eigenvectors of a very large matrix (see I. Shavitt in *Schaefer, Methods of Electronic Structure Theory*, pp. 228–238); Davidson's method for doing this is widely used [see the references in J. H. van Lenthe and P. Pulay, *J. Comput. Chem.*, **11**, 1164 (1990)].

In a CI calculation with 10^8 CSFs, there are 10^{16} matrix elements H_{ij} between CSFs, which is too many to be stored in the internal memory of the computer. To avoid the problems of dealing with large matrices, Roos developed the **direct configuration interaction**

method in 1972 (see B. O. Roos and P. E. M. Siegbahn, in *Schaefer, Methods of Electronic Structure Theory*, Chapter 7). The direct CI method avoids explicit calculation of the integrals H_{ij} between CSFs and avoids the need to solve the secular equation (11.18). Instead, the CI expansion coefficients in (11.16) and the energy are calculated directly from the one- and two-electron integrals over the basis functions. The direct CI method (not to be confused with the direct SCF method of Section 15.16) allows CI calculations with more than 10^{10} CSFs.

The CI procedure just discussed calculates SCF occupied and virtual orbitals from the basis functions and uses these SCF MOs to form configuration state functions. The convergence rate of this procedure is very slow, and huge numbers of CSFs must be included for accurate results. A major reason for the very slow convergence is that the excited (virtual) SCF orbitals have much of their probability density at large distances from the nuclei, whereas the ground-state wave function has most of its probability density reasonably near the nuclei.

Actually, there is no necessity to use SCF MOs in a CI calculation. Any set of MOs calculated from the basis set will produce the same final wave function, provided a full CI calculation is carried out. Moreover, if the non-SCF MOs are well chosen, they can produce much faster convergence to the true wave function than is obtained with SCF MOs, thereby allowing substantially fewer CSFs to be included in ψ . Two approaches that use this idea are the use of localized orbitals, and the multiconfiguration SCF method.

The LC Method

The use of localized SCF MOs (Section 15.8) instead of canonical SCF MOs in an electron correlation calculation gives the **local correlation (LC)** method [S. Saebø and P. Pulay, *Annu. Rev. Phys. Chem.*, **44**, 213 (1993)]. Let Ψ_{ij}^{ab} denote the doubly substituted CSF in which electrons are moved from the localized occupied MOs i and j to the virtual MOs a and b . The two-electron integral $(ia|jb)$ will be small if the MOs i and a are in different regions of space or if j and b are in different regions. This allows many CSFs to be omitted from the calculation with very little loss in accuracy. CI calculations on 1,3-butadiene using the LC method showed speedups by factors of 20 to 40 [S. Saebø and P. Pulay, *Chem. Phys. Lett.*, **113**, 13 (1985)]. The LC method can be used not only with the CI method but also with other correlation methods.

The MCSCF Method

In the **multiconfiguration SCF (MCSCF)** method, one writes the molecular wave function as a linear combination of CSFs Φ_i and varies not only the expansion coefficients b_i in $\psi = \sum_i b_i \Phi_i$, but also the forms of the molecular orbitals in the CSFs. The MOs are varied by varying the expansion coefficients c_{ri} that relate the MOs ϕ_i to the basis functions χ_r . For example, if we were to do an MCSCF calculation for the He ground state using the basis functions χ_1 and χ_2 of (14.46) and including only the CSFs Φ_1 and Φ_2 of (16.3), we would write as the MCSCF wave function

$$\begin{aligned}\psi &= b_1 \Phi_1 + b_2 \Phi_2 = b_1 |\phi_1 \bar{\phi}_1| + b_2 |\phi_2 \bar{\phi}_2| \\ &= b_1 |(c_{11}\chi_1 + c_{21}\chi_2)(\overline{c_{11}\chi_1 + c_{21}\chi_2})| + b_2 |(c_{12}\chi_1 + c_{22}\chi_2)(\overline{c_{12}\chi_1 + c_{22}\chi_2})|\end{aligned}$$

and we would simultaneously vary the coefficients b_1 , b_2 , c_{11} , c_{21} , c_{12} , and c_{22} (subject to the conditions of orthonormality of ϕ_1 and ϕ_2 and normalization of ψ) to minimize the variational integral. The MCSCF values found for these six coefficients will differ from the corresponding values found in the SCF plus CI calculations we did, and the energy will be lower, since the c_{ri} 's will be optimal for the MCSCF ψ , rather than being optimal for the SCF ψ .

The optimum MCSCF orbitals can be found by an iterative process somewhat similar to the iterative process used to find SCF wave functions; see A. C. Wahl and G. Das, Chapter 3 in *Schaefer, Methods of Electronic Structure Theory*. By optimizing the orbitals, one can get good results with inclusion of relatively few CSFs. Because the orbitals are varied, the amount of calculation required in the MCSCF procedure is great, but advances in methods of computing MCSCF wave functions [R. Shepard, *Adv. Chem. Phys.*, **69**, 63 (1987)] have led to wide use of the MCSCF and related methods.

The most commonly used kind of MCSCF method is the **complete active space SCF (CASSCF or CAS)** method [B. O. Roos, *Adv. Chem. Phys.*, **69**, 399 (1987)]. Here, as usual, one writes the orbitals ϕ_i to be used in the CSFs as linear combinations of basis functions: $\phi_i = \sum_{r=1}^b c_{ri} \chi_r$. One divides the orbitals in the CSFs into inactive and **active orbitals**. The inactive orbitals are kept doubly occupied in all CSFs. The electrons not in the inactive orbitals are called **active electrons**. One writes the wave function as a linear combination of all CSFs Φ_i that can be formed by distributing the active electrons among the active orbitals in all possible ways and that have the same spin and symmetry eigenvalues as the state to be treated: $\psi = \sum_i b_i \Phi_i$. One then does an MCSCF calculation to find the optimum coefficients c_{ri} and b_i . A reasonable choice is to take the active orbitals as those MOs that arise from the valence orbitals of the atoms that form the molecule.

For example, the C_2 ground-state configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$$

The 2s and 2p carbon AOs give rise to the $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$, and $3\sigma_u$ MOs, where the last four are unoccupied in the ground state. One might thus take the inactive orbitals as the $1\sigma_g$ and $1\sigma_u$ MOs (giving eight active electrons) and the active orbitals as the $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$, and $3\sigma_u$ MOs (giving eight active orbitals). A CASSCF calculation on the C_2 ground electronic state used a basis set of 82 functions and took the inactive orbitals as $1\sigma_g$ and $1\sigma_u$ and the active orbitals as $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$, $3\sigma_u$, $4\sigma_g$, and $4\sigma_u$ [W. P. Kraemer and B. O. Roos, *Chem. Phys.*, **118**, 345 (1987)]. Distribution of the eight active electrons among the ten active orbitals gave a wave function consisting of 1900 CSFs. The electronic energy was calculated for several points in the neighborhood of R_e , and the calculated $U(R)$ curve was substituted into the Schrödinger equation for nuclear motion, which was solved numerically (Section 13.2) to find vibrational–rotational energy levels, from which spectroscopic constants were found. The results were (experimental values in parentheses): $R_e/\text{\AA} = 1.25$ (1.24), $D_e/\text{eV} = 6.06$ (6.3), $\tilde{\nu}_e/\text{cm}^{-1} = 1836$ (1855), and $\tilde{\nu}_e x_e/\text{cm}^{-1} = 14.9$ (13.4), where $\tilde{\nu}_e x_e \equiv \nu_e x_e/c$ [see Eq. (4.60)]. For comparison, the Hartree–Fock ψ gives $D_e = 0.8$ eV, $\tilde{\nu}_e/\text{cm}^{-1} = 1905$, $\tilde{\nu}_e x_e/\text{cm}^{-1} = 12.1$, and $R_e = 1.24$ \AA.

With modern computational techniques, very large MCSCF wave functions can be calculated. A CASSCF(12,14)/aug-cc-pV5Z calculation on Be_3 included 545857 CSFs [J. I. Amaro-Estrada et al., *J. Chem. Phys.*, **135**, 104311 (2011)]. The notation means that 12 active electrons were distributed among 14 active MOs. For large molecules, use of all the valence orbitals as active gives rise to too many CSFs to be handled, and so the number of active orbitals must be limited in such cases. Typically, up to about 15 active orbitals and 15 active electrons can be handled.

A CASSCF calculation uses far fewer CSFs than full CI, and its aim is not to recover a substantial portion of the correlation energy, but to find how the correlation energy changes with change in some process such as a change in geometry or a chemical reaction.

CASSCF calculations are “not for the faint hearted” (*Foresman and Frisch*, p. 229). The choice of active orbitals is often not obvious. Also, the SCF process in CASSCF sometimes converges to a function that is not the true energy minimum.

The MRCI Method

A widely used method that combines the MCSCF and conventional CI methods is the **multireference CI (MRCI) method**. In the conventional (or single-reference) CI method, one starts with the SCF wave function Φ_1 (which is called the **reference function**) and moves electrons out of occupied orbitals of Φ_1 into virtual SCF orbitals to produce CSFs $\Phi_2, \Phi_3, \dots$, and one writes the wave function as $\psi = \sum_i b_i \Phi_i$. One then varies the b_i 's to minimize the variational integral. Recall that for H_2 , although the Hartree–Fock function Φ_1 gives a reasonably good representation of the wave function in the region of R_e , in the limit as $R \rightarrow \infty$ we must take the variational function as a linear combination of two CSFs in order to get the proper dissociation behavior. For N_2 , which has a triple bond, one finds that a linear combination of 10 CSFs is needed to give proper behavior at large R . In the MRCI method, one first does an MCSCF calculation to produce a wave function that is a linear combination of several CSFs $\Phi_1, \Phi_2, \dots, \Phi_m$ with optimized orbitals and that has the proper behavior for all nuclear configurations. One then takes this MCSCF function and moves electrons out of occupied orbitals of the CSFs $\Phi_1, \Phi_2, \dots, \Phi_m$ (called the *reference CSFs*) into virtual orbitals to produce further CSFs $\Phi_{m+1}, \dots, \Phi_n$. Most commonly, one does a CISD calculation starting with the MCSCF function, giving an MR-CISD or MRSDCI calculation. One writes $\psi = \sum_{i=1}^n b_i \Phi_i$ and finds the optimum b_i 's. Typically, the reference CSFs will contain singly and doubly excited CSFs, and the final wave function will include single and double excitations from the reference CSFs. Thus, the final MRCI wave function will include some triple and quadruple excitations.

CASSCF wave functions are often used as the starting point for MRCI calculations. The calculations that determined the ordering of the lowest states of Si_2 and Al_2 (Section 13.7) were CASSCF MRCI calculations.

When a CASSCF wave function is used for a MRCISD calculation, the number of CSFs produced may be too many to deal with, so various methods are used to reduce the amount of computation needed. One widely used procedure is **internally contracted MRCI (icMRCI)** [H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, **89**, 5803 (1988)]. Here, the optimized MCSCF function is treated as a single reference function (with fixed coefficients) from which one generates doubly excited functions. Each excited function is a linear combination of many ordinary CSFs, with the coefficients within a given excited function being held fixed at the values for the MCSCF function. Thus, far fewer coefficients need to be calculated than in a conventional (uncontracted) MRCI calculation. (Singly excited functions are also included, but for technical reasons, these are not contracted but are treated as in uncontracted MRCI.) Experience has shown that the contracted MRCI wave function is almost as accurate as the uncontracted one.

MRCI methods that use localized orbitals have been developed; see D. Walter et al., *J. Chem. Phys.*, **118**, 8127 (2003); A. Venkatnathan et al., *ibid.*, **120**, 1693 (2004); T. S. Chwee et al., *J. Chem. Phys.*, **128**, 224106 (2008).

An extensive review of MCSCF and MRCI methods and applications is P. G. Szalay et al., *Chem. Rev.*, **112**, 108 (2012).

Status of the CI Method

Although calculation of SCF MO wave functions for closed-shell, small- and medium-size molecules is essentially a routine procedure, molecular CI calculations often present special problems. To obtain reliable results, one must use sound judgment in choosing the basis set, the configuration functions to be included, and the procedure to be used.

Because of slow convergence, lack of size consistency, and disappointing results of CISD calculations, CI calculations have lost their former dominance in correlation calculations, and several other correlation methods have been developed (Sections 16.3–16.7).

These correlation methods are much more efficient than CISD in giving accurate results for ground-state molecules at or near the equilibrium geometry. However, when it comes to dealing with geometries far from minima, as when dealing with complete potential-energy surfaces and chemical reactions, these methods do not perform so well, and multireference CI calculations (MRCI) are widely used to explore potential-energy surfaces and in studying chemical reactions (Section 16.14). “MRCI is perhaps the most widely applicable and commonly used method for modeling bond-breaking reactions and ground- and excited-state potential-energy surfaces in small molecules” [C. D. Sherrill and P. Piecuch, *J. Chem. Phys.*, **122**, 124104 (2005)].

The CI-Singles Method

The CI-singles (CIS) method (also called the Tamm–Dancoff approximation) is a computationally simple, often used procedure for treating excited states [J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. Frisch, *J. Phys. Chem.*, **96**, 135 (1992)].

CIS wave functions for the lowest several excited states of a molecule are calculated as follows. A fixed molecular geometry is chosen. This is typically the optimized ground-state geometry found using a basis set and method known to give accurate ground-state geometries (or it might be the experimental ground-state geometry). A basis set that includes diffuse functions is used to calculate a single-determinant SCF MO ground-state wave function Φ_0 at the chosen geometry. This calculation also yields a set of unoccupied (virtual) orbitals, whose number depends on the size of the basis set used. Let ψ_i^a denote a singly excited Slater determinant in which the occupied spin-orbital i in Φ_0 is replaced by the virtual spin-orbital a . One forms the CIS linear variation function $\psi_{\text{CIS}} = \sum_a \sum_i c_{ia} \psi_i^a$, where the sums go over all the occupied and all the virtual spin-orbitals and c_{ia} is a variational coefficient. The equations of the linear variation method (Sections 8.5 and 8.6) are used to find the lowest several roots of the secular equation (where the molecular electronic Hamiltonian used to evaluate the matrix elements corresponds to the chosen ground-state geometry) and to find the coefficients that go with each root. Each of these roots is an approximation to the energy of an excited electronic state at the fixed molecular geometry that was chosen for the calculation.

When an electronic transition occurs from the ground state to an excited state, the much greater mass of the nuclei than that of the electrons means that the excited state has the greatest probability to be produced in a geometry that is close to the equilibrium geometry of the ground electronic state (the Franck–Condon principle), even though this geometry is not likely to be the equilibrium geometry of the excited state.

The excited state is thus produced in a high vibrational level. Hence the observed maximum-intensity frequency ν_{max} in the electronic absorption spectrum corresponds to no change in geometry. The energy change $h\nu_{\text{max}}$ is called the **vertical excitation energy**. The CIS prediction of the vertical excitation energy is found by taking the difference between the excited state energy found as a root of the secular equation and the ground-state energy found from Φ_0 . CIS predictions of vertical excitation energies are semiquantitatively correct, but not of high accuracy. Errors run about 1 eV in a quantity whose range is typically 3 to 10 eV.

The CIS wave function is found by solving for the coefficients c_{ia} . Since analytic gradients of CIS energies are available, one can then optimize the geometry of each excited state and also calculate its vibrational frequencies. CIS excited-state geometries and vibrational frequencies are more accurate than CIS vertical excitation energies [J. F. Stanton et al., *J. Chem. Phys.*, **103**, 4160 (1995)].

Note that the form of a CIS wave function differs from that of an ordinary CI wave function. In an ordinary CI wave function, the reference function (the SCF wave function

for the state of interest) makes the largest contribution. In the CIS method for an excited state, the reference function is the SCF wave function for the ground state, and this reference function does not appear in the CIS wave function. (This makes the CIS wave function orthogonal to the ground-state wave function, which is desirable, so as to avoid having the variational calculation “collapse” to the ground state.) The CIS wave function includes only a modest amount of electron correlation.

Use of the Two-Electron Reduced Density Matrix

The MRCI method is widely used to deal with molecules with substantial static correlation, but can only be applied to relatively small molecules. (The CASPT2 method of Section 16.3 can treat static correlation in somewhat larger molecules.) Another approach is to avoid using a wave function and instead deal with the two-electron reduced density matrix.

The wave function ψ of an N -particle system is a function of the $3N$ spatial and N spin coordinates of the electrons: $\psi(q) = \psi(q_1, q_2, \dots, q_N)$, where q_1 denotes the three spatial coordinates and one spin coordinate of electron 1 and q denotes all the coordinates. The function $\psi(q)\psi^*(q') = \psi(q_1, q_2, \dots, q_N)\psi^*(q'_1, q'_2, \dots, q'_N)$ is called the N th-order density matrix of the system (although a more mathematically proper term would be density kernel). The primes do not denote differentiation but just a relabeling of coordinates; q'_1 stands for $x'_1, y'_1, z'_1, m'_{s1}$. Note that if we set $q' = q$, we get the ordinary probability density $\psi^*(q)\psi(q)$. If we integrate $\psi(q)\psi^*(q')$ over the spatial coordinates of electrons 3 to N and sum over the spin coordinates of electrons 3 to N and multiply by $N(N-1)$, we get the **two-electron reduced density matrix (2-RDM)**. Because the molecular Hamiltonian operator contains only one- and two-electron terms, one can show that the energy $E = \langle \psi | \hat{H} | \psi \rangle$ can be calculated from the 2-RDM (see *Pilar*, Section 10-5 for a proof).

The 2-RDM involves far fewer variables than does the wave function of a many-electron system. Hence in the 1950s it was proposed that, rather than searching for the wave function that minimizes the variational integral, one search for the 2-RDM that minimizes the energy. However, such a procedure gives an energy that is below the true ground-state energy. The problem is that one must impose conditions that ensure that the 2-RDM that is found in the search is one that could possibly arise from (or “represent”) an N -electron wave function. These so-called *N -representability* conditions were unknown in the 1950s, but in recent years work by Mazziotti and others has found several necessary N -representability conditions [see the references in D. A. Mazziotti, *Phys. Rev. A*, **85**, 062507 (2012)]. This has allowed an approximate 2-RDM and energy to be calculated for some rather large systems that have static correlation using two different procedures. An example is octacene ($C_{42}H_{24}$), which is much too large to treat using CASSCF. However, only a small DZ unpolarized basis set was used in this calculation, and the number of applications using the 2-RDM is rather small. For a detailed review, see D. A. Mazziotti, *Chem. Rev.*, **112**, 244 (2012).

16.3 Møller–Plesset (MP) Perturbation Theory

Physicists and chemists have developed various perturbation-theory methods to deal with systems of many interacting particles (nucleons in a nucleus, atoms in a solid, electrons in an atom or molecule), and these methods constitute **many-body perturbation theory (MBPT)**. In 1934, Møller and Plesset proposed a perturbation treatment of atoms and molecules in which the unperturbed wave function is the Hartree–Fock function. This form of MBPT is called **Møller–Plesset (MP) perturbation theory**. Actual molecular applications of MP perturbation theory (**MPPT**) began only in 1975 with the work

of Pople and co-workers and Bartlett and co-workers [R. J. Bartlett, *Ann. Rev. Phys. Chem.*, **32**, 359 (1981); *Hehre et al.*]. For a review of MPPT, see D. Cremer, *WIREs Comput. Mol. Sci.*, **1**, 509 (2011).

The treatment of this section will be restricted to closed-shell, ground-state molecules. Also, the development will use spin-orbitals u_i , rather than spatial orbitals ϕ_i . For spin-orbitals, the Hartree–Fock equations (14.25) and (14.26) for electron m in an n -electron molecule have the forms (*Szabo and Ostlund*, Section 3.1)

$$\hat{f}(m)u_i(m) = \varepsilon_i u_i(m) \quad (16.7)$$

$$\hat{f}(m) \equiv -\frac{1}{2}\nabla_m^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{m\alpha}} + \sum_{j=1}^n [\hat{j}_j(m) - \hat{k}_j(m)] \quad (16.8)$$

where $\hat{j}_j(m)$ and $\hat{k}_j(m)$ are defined by equations like (14.28) and (14.29) with spatial orbitals replaced by spin-orbitals and integrals over spatial coordinates of an electron replaced by integration over spatial coordinates and summation over the spin coordinate of that electron.

The MP unperturbed Hamiltonian is taken as the sum of the one-electron Fock operators $\hat{f}(m)$ in (16.7):

$$\hat{H}^0 \equiv \sum_{m=1}^n \hat{f}(m) \quad (16.9)$$

The ground-state Hartree–Fock wave function Φ_0 is the Slater determinant $|u_1 u_2 \cdots u_n|$ of spin-orbitals. This Slater determinant is an antisymmetrized product of the spin-orbitals [for example, see Eq. (10.36)] and, when expanded, is the sum of $n!$ terms, where each term involves a different permutation of the electrons among the spin-orbitals. Each term in the expansion of Φ_0 is an eigenfunction of the MP $\hat{H}^0$; for example, for a four-electron system, application of $\hat{H}^0$ to a typical term in the Φ_0 expansion gives

$$\begin{aligned} [\hat{f}(1) + \hat{f}(2) + \hat{f}(3) + \hat{f}(4)]u_1(3)u_2(2)u_3(4)u_4(1) \\ = (\varepsilon_4 + \varepsilon_2 + \varepsilon_1 + \varepsilon_3)u_1(3)u_2(2)u_3(4)u_4(1) \end{aligned}$$

where $\hat{f}(m)u_i(m) = \varepsilon_i u_i(m)$ [Eq. (16.7)] was used. Similarly, each other term in the expansion of $|u_1 u_2 u_3 u_4|$ is an eigenfunction of $\hat{H}^0$ with the same eigenvalue $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4$. Since Φ_0 is a linear combination of these $n!$ terms, Φ_0 is an eigenfunction of $\hat{H}^0$ with this eigenvalue:

$$\hat{H}^0 \Phi_0 = \left(\sum_{m=1}^n \varepsilon_m \right) \Phi_0 = E^{(0)} \Phi_0 \quad (16.10)$$

The eigenfunctions of the unperturbed Hamiltonian $\hat{H}^0$ are the zeroth-order (unperturbed) wave functions [Eq. (9.2)], so the Hartree–Fock ground-state function Φ_0 is one of the zeroth-order wave functions. What are the other eigenfunctions of $\hat{H}^0$? The Hermitian operator $\hat{f}(m)$ has a complete set of eigenfunctions, these eigenfunctions being all the possible spin-orbitals of the molecule. The n lowest-energy spin-orbitals are occupied, and there are an infinite number of unoccupied (virtual) orbitals. The operator $\hat{H}^0 \equiv \sum_{m=1}^n \hat{f}(m)$ is the sum of the operators $\hat{f}(m)$, and so the eigenfunctions of $\hat{H}^0$ are all possible products of any n of the spin-orbitals. However, the wave functions must be antisymmetric, so we must antisymmetrize these zeroth-order wave functions by forming Slater determinants. Thus, the zeroth-order wave functions are all possible Slater determinants formed using any n of the infinite number of possible spin-orbitals. (Of course, the n chosen spin-orbitals must all be different or the Slater determinant would vanish.)

The perturbation $\hat{H}'$ is the difference between the true molecular electronic Hamiltonian $\hat{H}$ and $\hat{H}^0$; $\hat{H}' = \hat{H} - \hat{H}^0$. Use of (15.10) for $\hat{H}$ and (16.9) and (16.8) for $\hat{H}^0$ gives (Prob. 16.9)

$$\hat{H}' = \hat{H} - \hat{H}^0 = \sum_l \sum_{m>l} \frac{1}{r_{lm}} - \sum_{m=1}^n \sum_{j=1}^n [\hat{j}_j(m) - \hat{k}_j(m)] \quad (16.11)$$

The perturbation $\hat{H}'$ is the difference between the true interelectronic repulsions and the Hartree–Fock interelectronic potential (which is an average potential).

The MP first-order correction $E_0^{(1)}$ to the ground-state energy is [Eq. (9.22)] $E_0^{(1)} = \langle \psi_0^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle$, since $\psi_0^{(0)} = \Phi_0$. The subscript 0 denotes the ground state. We have

$$E_0^{(0)} + E_0^{(1)} = \langle \psi_0^{(0)} | \hat{H}^0 | \psi_0^{(0)} \rangle + \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle = \langle \Phi_0 | \hat{H}^0 + \hat{H}' | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$

Since $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$ is the variational integral for the Hartree–Fock wave function Φ_0 , it equals the Hartree–Fock energy E_{HF} . Hence (recall the beginning of Section 9.4)

$$E_0^{(0)} + E_0^{(1)} = E_{\text{HF}}$$

Note from (16.10) that the zeroth-order (unperturbed) eigenfunction Φ_0 of $\hat{H}^0$ has the eigenvalue $\sum_{m=1}^n \epsilon_m$. Therefore, [Eq. (9.2)] $E_0^{(0)} = \sum_{m=1}^n \epsilon_m$.

To improve on the Hartree–Fock energy, we must find the second-order energy correction $E_0^{(2)}$. From (9.35),

$$E_0^{(2)} = \sum_{s \neq 0} \frac{|\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle|^2}{E_0^{(0)} - E_s^{(0)}} \quad (16.12)$$

We saw above that the unperturbed functions $\psi_s^{(0)}$ are all possible Slater determinants formed from n different spin-orbitals. Let $i, j, k, l, \dots$ denote the occupied spin-orbitals in the ground-state Hartree–Fock function Φ_0 , and let $a, b, c, d, \dots$ denote the unoccupied (virtual) spin-orbitals. Each unperturbed wave function can be classified by the number of virtual spin-orbitals it contains; this number is called the **excitation level**. Let Φ_i^a denote the singly excited determinant that differs from Φ_0 solely by replacement of the occupied spin-orbital u_i by the virtual spin-orbital u_a . Let Φ_{ij}^{ab} denote the doubly excited determinant formed from Φ_0 by replacement of u_i by u_a and u_j by u_b ; and so on.

Consider the matrix elements $\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle$ in (16.12), where Φ_0 is a closed-shell single determinant. One finds (*Szabo and Ostlund*, Section 6.5) that this integral vanishes for all singly excited $\psi_s^{(0)}$'s; that is, $\langle \Phi_i^a | \hat{H}' | \Phi_0 \rangle = 0$ for all i and a . Also, $\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle$ vanishes for all $\psi_s^{(0)}$'s whose excitation level is three or higher. This follows from the Condon–Slater rules (Table 11.3). Hence, we need consider only doubly excited $\psi_s^{(0)}$'s to find $E_0^{(2)}$. Also, the same reasoning applied to Eq. (9.27) shows that $\psi_0^{(1)}$, the first-order correction to the wave function, contains only doubly excited $\psi_s^{(0)}$'s.

The doubly excited function Φ_{ij}^{ab} is an eigenfunction of $\hat{H}^0 = \sum_m \hat{f}(m)$ with an eigenvalue that differs from the eigenvalue of Φ_0 solely by replacement of ϵ_i by ϵ_a and replacement of ϵ_j by ϵ_b . Hence in (16.12), $E_0^{(0)} - E_s^{(0)} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ for $\psi_s^{(0)} = \Phi_{ij}^{ab}$. Use of (16.11) for $\hat{H}'$ and of the Condon–Slater rules allows the integrals involving Φ_{ij}^{ab} to be evaluated; one finds (Prob. 16.10)

$$E_0^{(2)} = \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{i=j+1}^n \sum_{j=1}^{n-1} \frac{|\langle ab | r_{12}^{-1} | ij \rangle - \langle ab | r_{12}^{-1} | ji \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (16.13)$$

where n is the number of electrons and

$$\langle ab|r_{12}^{-1}|ij\rangle \equiv \iint u_a^*(1)u_b^*(2)r_{12}^{-1}u_i(1)u_j(2) d\tau_1 d\tau_2 \quad (16.14)$$

The integrals over spin-orbitals (which include a sum over spins) are readily evaluated in terms of electron-repulsion integrals. The sums over a, b, i , and j in (16.13) provide for the inclusion of all the doubly substituted $\psi_s^{(0)}$'s in (16.12).

Taking the molecular energy as $E^{(0)} + E^{(1)} + E^{(2)} = E_{\text{HF}} + E^{(2)}$ gives a calculation designated as **MP2** or MBPT(2), where the 2 indicates inclusion of energy corrections through second order.

Formulas for the MP energy corrections $E^{(3)}$, $E^{(4)}$, and so on, have also been derived [for example, see R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, **14**, 91 (1978)]. Since $\psi^{(1)}$, the first-order correction to the wave function, determines both $E^{(2)}$ and $E^{(3)}$ (Section 9.2), and since $\psi^{(1)}$ contains only doubly excited determinants, $E^{(3)}$ contains summations over only double substitutions. The MP $E^{(4)}$ involves summations over single, double, triple, and quadruple substitutions. MP calculations that include energy corrections through $E^{(3)}$ are designated **MP3**, and those that include corrections through $E^{(4)}$ are **MP4**.

To do an MP electron-correlation calculation, one first chooses a basis set and carries out an SCF MO calculation to obtain Φ_0 , E_{HF} , and virtual orbitals. One then evaluates $E^{(2)}$ (and perhaps higher corrections) by evaluating the integrals over spin-orbitals in (16.13) in terms of integrals over the basis functions. One ought to use a complete set of basis functions to expand the spin-orbitals. The SCF calculation will then produce the exact Hartree–Fock energy and will yield an infinite number of virtual orbitals. The first two sums in (16.13) will then contain an infinite number of terms. Of course, one always uses a finite, incomplete basis set, which yields a finite number of virtual orbitals, and the sums in (16.13) contain only a finite number of terms. One thus has a basis-set truncation error in addition to the error due to truncation of the MP perturbation energy at $E^{(2)}$ or $E^{(3)}$ or whatever.

In MP4 calculations, evaluation of the terms that involve triply substituted determinants is very time consuming, so these terms are sometimes neglected [even though their contribution to $E^{(4)}$ is not small], giving an approximation to MP4 that is designated MP4(SDQ), where SDQ indicates inclusion of single, double, and quadruple excitations. Evaluation of $E^{(5)}$ is extremely time consuming and so is almost never done except by specialists investigating the convergence of the series.

To save time in MP2, MP3, and MP4 computations, the **frozen-core (FC)** approximation is usually used. Here, terms involving excitations out of core orbitals are omitted.

MP3 calculations take a lot longer than MP2 calculations but provide little improvement over MP2 molecular properties and so are not often done (except as part of an MP4 calculation). A notable exception is the use of MP3 calculations in the MP2.5 and MP2.X methods (Section 16.8). By far, the most common MP level used is MP2; the next most common is MP4.

MP2 calculations are much faster than CI calculations, and most ab initio programs (Section 15.14) can perform MP calculations. Relative times for geometry-optimization calculations on CH_3OH using the 6-31G* basis set (38 basis functions) and the cc-pVTZ basis set (116 basis functions) are (cccbdb.nist.gov) 1 for HF/6-31G*, 1.4 for MP2(FC)/6-31G*, 26 for MP4(FC)/6-31G*, 19 for HF/cc-pVTZ, 46 for MP2(FC)/cc-pVTZ, and 1250 for MP4(FC)/cc-pVTZ, where FC means frozen core.

In addition to their computational efficiency, MP calculations truncated at any order can be shown to be size extensive (Szabo and Ostlund, Section 6.7.4). However, MP calculations are not variational and can produce an energy below the true energy. Currently, size extensivity is viewed as more important than being variational.

A study of the convergence of the frozen-core MP perturbation series for small atoms and molecules [J. Olsen et al., *J. Chem. Phys.*, **105**, 5082 (1996)] found that for the cc-pVDZ basis set, the series usually converged, but when the basis set was augmented with diffuse functions, the MP series often diverged. For example, for the Ne atom, the MP_n /aug-cc-pVDZ contributions for $n > 16$ increased in magnitude as n increased. (The high-order MP_n contributions were not calculated directly but were obtained as by-products of FCI calculations.) For the F^- ion, the divergence of the perturbation series affected the reliability of the MP_4 /aug-cc-pVDZ results. Large-basis-set MP calculations on small diatomic molecules showed the results “to be far from converged at MP_4 ,” with MP_4 errors in R_e and ν_e often larger than MP_2 errors [T. H. Dunning and K. A. Peterson, *J. Chem. Phys.*, **108**, 4761 (1998)]. For further examples of MP series divergence, see M. L. Leininger et al., *J. Chem. Phys.*, **112**, 9213 (2000). These studies raise doubts about the use of MP perturbation theory beyond MP_2 to calculate molecular properties. A mathematical analysis of when MP calculations converge or diverge is given in A. V. Sergeev and D. Z. Goodson, *J. Chem. Phys.*, **124**, 094111 (2006). Because of the convergence problems with the MP method, quantum chemists have largely stopped doing MP_4 calculations (except for the use of MP_4 calculations in the G3 method—Section 16.6), but the MP_2 method is still very widely used.

As with CI calculations, MP calculations with small basis sets are of little practical value, and MP calculations should use a 6-31G* or larger basis set for useful results. For DZP basis sets, MP_2 calculations on closed-shell molecules typically yield 85% to 95% of the basis-set correlation energy [R. J. Bartlett, *Ann. Rev. Phys. Chem.*, **32**, 359 (1981)] and substantially improve the accuracy of equilibrium-geometry and vibrational-frequency predictions.

Experience indicates that in most electron-correlation calculations, the basis-set truncation error is larger than the error due to truncation of the correlation treatment. For example, when one goes from a 6-31G* basis set to a TZ2P basis set, the errors in MP_2 -predicted equilibrium single-bond lengths are reduced by a factor of 2 or 3 [E. D. Simandiras et al., *J. Chem. Phys.*, **88**, 3187 (1988)], but when one goes from MP_2 /TZ2P to MP_3 /TZ2P calculations, no improvement in geometry accuracy is obtained [I. L. Alberts and N. C. Handy, *J. Chem. Phys.*, **89**, 2107 (1988)].

The energy gradient in MP_2 calculations is readily evaluated analytically [see P. Pulay, *Adv. Chem. Phys.*, **69**, 276 (1987)]. This allows MP_2 geometry optimization to be done easily and also permits calculation of MP_2 vibrational frequencies.

The *direct* and *semidirect* MP_2 methods, like the corresponding SCF methods (Section 15.16), speed up calculations on large molecules by recalculating all or some of the electron-repulsion integrals as needed, instead of storing them externally on disk and then retrieving them. A semidirect $MP_2(FC)$ /TZP geometry optimization of buckminsterfullerene, C_{60} , involved 1140 basis functions and found bond lengths of 1.446 and 1.406 Å [M. Häser, J. Almlöf, and G. E. Scuseria, *Chem. Phys. Lett.*, **181**, 497 (1991)], in agreement with the experimental values 1.45 and 1.40 Å.

A method to speed up MP_2 calculations on large molecules is the **local MP_2 (LMP2)** method of Saebø and Pulay [S. Saebø and P. Pulay, *Annu. Rev. Phys. Chem.*, **44**, 213 (1993)]. Here, instead of using canonical SCF MOs in the Hartree–Fock reference determinant Φ_0 , one transforms to localized MOs (Section 15.8). Also, instead of using the virtual orbitals found in the SCF calculation as the orbitals a and b in (16.13) to which electrons are excited, one uses atomic orbitals that are orthogonal to the localized occupied MOs. Also, in (16.13), one includes only unoccupied orbitals a and b that are in the neighborhood of the localized MOs i and j .

As noted in Section 15.16, calculation of 2-electron repulsion integrals in SCF MO calculations on large molecules can be speeded up by expanding products like $\phi_i(1)\phi_j(1)$

using an auxiliary basis set—the RI approximation. This same approximation is also used in the MP2 method, giving the **RI-MP2** method. [For a review of the RI approximation, see R. A. Kendall and H. A. Früchtel, *Theor. Chem. Acc.*, **97**, 158 (1997).] The RI-MP2 method is also called the **DF-MP2** method, where DF stands for **density fitting**, since it fits the one-electron density function $\phi_i(1)\phi_j(1)$ with a series.

The DF-MP2 method has been combined with the LMP2 method to give the **DF-LMP2** method [H. J. Werner et al., *J. Chem. Phys.*, **118**, 8149 (2003)]. The DF-LMP2 method is so efficient, that for large molecules, the preceding Hartree–Fock part of the calculation takes a lot longer than the MP2 part of the calculation.

For species involving open-shell ground states (for example, O_2 , NO_2 , and OH), one can base an MP calculation on the unrestricted SCF wave function (Section 15.3), giving calculations designated UMP2, UMP3, and so on. Unrestricted SCF wave functions are not eigenfunctions of $\hat{S}^2$, and this “spin contamination” can sometimes produce serious errors in UMP-calculated quantities [K. Wolinski and P. Pulay, *J. Chem. Phys.*, **90**, 3647 (1989)]. Alternatively, several versions of open-shell MP perturbation theory that are based on the ROHF wave function have been developed. It is not clear which of these ROHF MP methods is best [T. D. Crawford, H. F. Schaefer, and T. J. Lee, *J. Chem. Phys.*, **105**, 1060 (1996)].

Another limitation of MP calculations is that, although they work well near the equilibrium geometry, they do not work well at geometries far from equilibrium. For example, DZ calculations on H_2O showed that at the equilibrium geometry an MP2 calculation obtained 94% of the basis-set correlation energy, but at a geometry with the bonds at twice their equilibrium lengths an MP2 calculation obtained only 83% of the basis-set correlation energy [W. D. Laidig et al., *Chem. Phys. Lett.*, **113**, 151 (1985)]; also, the MP energy series at this stretched geometry converged erratically [N. C. Handy et al., *Theor. Chim. Acta*, **68**, 87 (1985)].

A third limitation is that MP calculations are not generally applicable to excited electronic states.

Because of these limitations, MP calculations have not made CI calculations obsolete, and multireference CI calculations are widely used for excited states and for geometries far from equilibrium.

Because of its computational efficiency and good results for molecular properties, the MP2 method is one of the two most commonly used methods for including correlation effects on molecular ground-state equilibrium properties. (The other widely used method is the density-functional method—Section 16.5.) Also, in perhaps the most accurate form of density-functional theory, the MP2 correlation energy (16.13) is multiplied by an empirical constant and added to the density functional energy to give improved results; see the discussion of double-hybrid functionals in Section 16.5.

Table 16.1 lists results of some MP calculations on H_2O .

The MP2-R12 and MP2-F12 Methods

Because we always use a finite, and hence, incomplete, basis set, Eq. (16.13) gives only an approximation to the MP2 quantity $E_0^{(2)}$. The aim of the MP2-R12 method is to essentially eliminate this basis-set-truncation error and give a value of $E_0^{(2)}$ that is close to the value that would be obtained with a complete basis set. The MP2-R12 method starts with the variation–perturbation inequality (9.38), where $\psi_g^{(0)}$ is the SCF MO wave function Φ_0 , and u (which can be any well-behaved function) is an approximation to the MP first-order ground-state wave-function correction $\psi^{(1)}$. In the MP2 method, the first-order correction to the wave function contains terms involving Slater determinants with two electrons excited from occupied to vacant orbitals. In the MP2-R12 method, the first-order correction to the wave function used as u in (9.38) contains additional terms of the form $c_{ij}r_{ij}\Phi_0$ for all pairs of electrons (this is a bit of an oversimplification),

where c_{ij} is a variational parameter, r_{ij} is the distance between electrons i and j , and Φ_0 is the unperturbed Hartree–Fock function. (When terms that involve r_{ij} are introduced into the wave function, one says the wave function is **explicitly correlated**.) Recall that inclusion of r_{12} in trial variation functions can give extremely accurate results for the He atom (Section 9.4). Whereas only two-electron integrals occur in the MP2 method, the inclusion of r_{ij} in the MP2-R12 method produces a very large number of three- and four-electron integrals containing factors like $r_{12}r_{34}/r_{23}$. These integrals are evaluated by using the resolution-of-the-identity method to express these integrals in terms of two-electron integrals and an auxiliary basis set. (Mathematically, this is not exactly the same as the use of the RI equation in density-fitting methods.) Since the auxiliary basis set is necessarily incomplete, the three- and four-electron integrals are being approximated, but with a proper basis set, the errors introduced are quite small. The variational parameters are evaluated so as to minimize the left side of (9.38), which gives the MP2-R12 value of $E_0^{(2)}$.

The MP2-R12 method cannot give a better result than would be given by the MP2 method with a complete basis set, and the hope was that introduction of the r_{ij} terms into the MP2 wave function would yield essentially the same result as would be obtained by MP2 with a complete basis set. Although MP2-R12 results are significantly improved compared with MP2 results with the same medium-size basis set, it turns out that MP2-R12 results still differ substantially from the complete-basis-set limit. The reason for this is that the form $c_{ij}r_{ij}\Phi_0$ linear in r_{ij} is not the optimum form to use. When r_{ij} is replaced in the wave function by $\exp(-\gamma r_{ij})$ where γ is a constant, results very close to the MP2 complete-basis-set limit are obtained with only a moderate-size basis set [A. J. May et al., *Phys. Chem. Chem. Phys.*, **7**, 2710 (2005)]. The value used for the constant γ has only a small effect on the results, and values in the range 0.8 to 2 have been used. Higher values work better in molecules with heavy elements. Also, using a smaller value for correlating a valence pair of electrons than for correlating core electrons works better. When any function other than the linear function r_{ij} is introduced into the MP2 wave function, the method is called **MP2-F12**, indicating that some function $f(r_{12})$ of interelectronic distances is being used. Tests of several functions found that the function $e^{-\gamma r_{ij}}$ worked best [D. P. Tew and W. Klopper, *J. Chem. Phys.*, **123**, 074101 (2005)]. This function is called a *Slater-type geminal* (STG) correlation factor.

The MP2-R12 and MP2-F12 methods have been combined with the DF-MP2 and LMP2 methods to give the DF-LMP2-R12 method [H.-J. Werner and F. R. Manby, *J. Chem. Phys.*, **124**, 054114 (2006)] and the **DF-LMP2-F12** method [F. R. Manby et al., *J. Chem. Phys.*, **124**, 094103 (2006)].

Since MP2-F12 is much better than MP2-R12, it has made MP2-R12 obsolete.

For reviews of explicitly correlated atomic and molecular wave function calculations, see C. Hättig et al., *Chem. Rev.*, **112**, 4 (2012); L. Kong et al., *Chem. Rev.*, **112**, 75 (2012); S. Ten-no and J. Noga, *WIREs Comput. Mol. Sci.*, **2**, 114 (2012).

The SCS-MP2 and SOS-MP2 Methods

Because of the orthogonality of the spin functions α and β , the integrals in the MP2 energy expression (16.13) and (16.14) will be zero unless either (1) the virtual spin-orbital u_a has the same spin function as the occupied spin-orbital u_i and u_b has the same spin function as u_j , or (2) u_a has the same spin function as u_j and u_b has the same spin function as u_i . Thus, if u_i and u_j both have spin function α , then u_a and u_b must both have spin function α ; if u_i and u_j both have spin function β , then u_a and u_b must both have spin function β ; if u_i and u_j have different spin functions, then u_a and u_b must have different spin functions. We can therefore divide the MP2 correlation energy (16.13) into a *same-spin* ($\alpha\alpha, \beta\beta$) component (also called a “triplet” component) and an *opposite-spin* ($\alpha\beta, \beta\alpha$) component (also called

a “singlet” component). We have $E^{(2)} = E_{\text{OS}}^{(2)} + E_{\text{SS}}^{(2)}$, where OS and SS indicate opposite spin and same spin. Calculations show that $E_{\text{OS}}^{(2)}$ is typically 3 or 4 times $E_{\text{SS}}^{(2)}$.

To improve the accuracy of MP2 calculations, Grimme proposed the **spin-component-scaled MP2 (SCS-MP2) method**, which takes $E^{(2)} = p_{\text{OS}}E_{\text{OS}}^{(2)} + p_{\text{SS}}E_{\text{SS}}^{(2)}$, where the empirical parameters p_{OS} and p_{SS} are given the values $p_{\text{OS}} = 1.2$ and $p_{\text{SS}} = 1/3$ [S. Grimme, *J. Chem. Phys.*, **118**, 9095 (2003)]. These values were found by a least-squares fit to a test set of reaction energies calculated by the QCISD(T) method (Section 16.4) with a large basis set. The SCS-MP2 method gives results for several properties such as atomization energies, bond lengths, and vibrational frequencies that are significantly improved over MP2 results at no additional computational cost.

The **scaled-opposite-spin MP2 (SOS-MP2) method** omits the $E_{\text{SS}}^{(2)}$ contribution entirely and takes $E^{(2)} = 1.3E_{\text{OS}}^{(2)}$ [Y. Jung et al., *J. Chem. Phys.*, **121**, 9793 (2004); *J. Comput. Chem.*, **28**, 1953 (2007)]. The SOS-MP2 method gives results slightly less accurate than the SCS-MP2 method, but is faster and can be applied to larger molecules than SCS-MP2. Of course, the use of empirical parameters makes the SCS-MP2 and SOS-MP2 methods no longer strictly ab initio methods.

Several other spin-component-scaled MP2 methods have been proposed, and spin-component scaling has also been applied to the CC method; see S. Grimme et al., *WIREs, Comput. Mol. Sci.*, **2**, 886 (2012) for a review.

The CASPT2 Method

The MP method applies perturbation theory to a zeroth-order wave function (reference function) that is a single Slater determinant. Instead of starting with an SCF wave function as the zeroth-order wave function, one can start with an MCSCF wave function (Section 16.2) as the zeroth-order function and apply perturbation theory to get a generalization of MP theory. The MCSCF function most commonly used for this purpose is a CASSCF wave function (Section 16.2). The choice of zeroth-order Hamiltonian is not unique, and the $\hat{H}_0$ used is more complicated than (16.9). Inclusion of energy corrections through $E^{(2)}$ gives the **CASPT2** (complete active space second-order perturbation theory) method [K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.*, **96**, 1218 (1992); K. Andersson and B. O. Roos in *Yarkony*, Part I, Chapter 2]. CASPT2 results, though quite good, are typically of lower quality than MRCI results, but CASPT2 involves significantly less computational effort than MRCI [M. L. Abrams and C. D. Sherrill, *J. Phys. Chem. A*, **107**, 5611 (2003)]. One can carry the perturbation treatment to higher orders, giving CASPT3, etc. However, multireference MP calculations are found to diverge more often than single-reference MP calculations [J. Olsen and M. P. Fülscher, *Chem. Phys. Lett.*, **326**, 225 (2000)].

An alternative choice is to take the unperturbed MCSCF wave function as the generalized valence-bond (GVB) wave function (Section 16.13).

16.4 The Coupled-Cluster Method

The **coupled-cluster (CC) method** for dealing with a system of interacting particles was introduced around 1958 by Coester and Kümmel in the context of studying the atomic nucleus. CC methods for molecular electronic calculations were developed by Čížek, Paldus, Sinanoglu, and Nesbet in the 1960s and by Pople and co-workers and Bartlett and co-workers in the 1970s. For reviews of the CC method, see R. J. Bartlett, *J. Phys. Chem.*, **93**, 1697 (1989); R. J. Bartlett in *Yarkony*, Part II, Chapter 16; T. J. Lee and G. E. Scuseria, in S. R. Langhoff (ed.), *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, Kluwer, 1995, pp. 47–108; T. Helgaker et al., *J. Phys. Org. Chem.*, **17**, 913 (2004).

The fundamental equation in CC theory is

$$\psi = e^{\hat{T}}\Phi_0 \quad (16.15)$$

where ψ is the exact nonrelativistic ground-state molecular electronic wave function, Φ_0 is the normalized ground-state Hartree–Fock wave function, the operator $e^{\hat{T}}$ is defined by the Taylor-series expansion

$$e^{\hat{T}} \equiv 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!} \quad (16.16)$$

and the **cluster operator** $\hat{T}$ (no connection with kinetic energy) is

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n \quad (16.17)$$

where n is the number of electrons in the molecule and the operators $\hat{T}_1, \hat{T}_2, \dots$ are defined below. Proof of (16.15) is omitted [see references in R. F. Bishop and H. G. Kümmler, *Physics Today*, March 1987, p. 52], but its plausibility will be shown below. The wave function ψ in (16.15) is not normalized (Prob. 16.15) but can be normalized at the end of the calculation.

The **one-particle excitation operator** $\hat{T}_1$ and the **two-particle excitation operator** $\hat{T}_2$ are defined by

$$\hat{T}_1\Phi_0 \equiv \sum_{a=n+1}^{\infty} \sum_{i=1}^n t_i^a \Phi_i^a, \quad \hat{T}_2\Phi_0 \equiv \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{j=i+1}^n \sum_{i=1}^{n-1} t_{ij}^{ab} \Phi_{ij}^{ab} \quad (16.18)$$

where Φ_i^a is a singly excited Slater determinant with the occupied spin-orbital u_i replaced by the virtual spin-orbital u_a , and t_i^a is a numerical coefficient whose value depends on i and a and will be determined by requiring that Eq. (16.15) be satisfied. The operator $\hat{T}_1$ converts the Slater determinant $|u_1 \cdots u_n| = \Phi_0$ into a linear combination of all possible singly excited Slater determinants. Φ_{ij}^{ab} is a Slater determinant with the occupied spin-orbitals u_i and u_j replaced by the virtual spin-orbitals u_a and u_b , respectively; t_{ij}^{ab} is a numerical coefficient. Similar definitions hold for $\hat{T}_3, \dots, \hat{T}_n$. Since no more than n electrons can be excited from the n -electron function Φ_0 , no operators beyond $\hat{T}_n$ appear in (16.17). The limits in (16.18) are chosen so as to include all possible single and double excitations without duplication of any excitation. By definition, when $\hat{T}_1$ or $\hat{T}_2$ or $\dots$ operates on a determinant containing both occupied and virtual spin-orbitals, the resulting sum contains only determinants with excitations from those spin-orbitals that are occupied in Φ_0 and not from virtual spin-orbitals. The function $\hat{T}_1^2\Phi_0 \equiv \hat{T}_1(\hat{T}_1\Phi_0)$ contains only doubly excited Slater determinants, and $\hat{T}_2^2\Phi_0$ contains only quadruply excited determinants. When $\hat{T}_1$ operates on a determinant containing only virtual spin-orbitals, the result is zero, by definition.

The effect of the $e^{\hat{T}}$ operator in (16.15) is to express ψ as a linear combination of Slater determinants that include Φ_0 and all possible excitations of electrons from occupied to virtual spin-orbitals. A full CI calculation also expresses ψ as a linear combination involving all possible excitations, and we know that a full CI calculation with a complete basis set gives the exact ψ . Hence, it is plausible that Eq. (16.15) is valid.

The mixing into the wave function of Slater determinants with electrons excited from occupied to virtual spin-orbitals allows electrons to keep away from one another and thereby provides for electron correlation.

In the CC method, one works with individual Slater determinants, rather than with CSFs, but each CSF is a linear combination of one or a few Slater determinants, and the CC and CI methods can each be formulated either in terms of individual Slater determinants or in terms of CSFs.

The aim of a CC calculation is to find the coefficients t_i^a , t_{ij}^{ab} , t_{ijk}^{abc} , ... for all $i, j, k, \dots$, and all $a, b, c, \dots$. Once these coefficients (called **amplitudes**) are found, the wave function ψ in (16.15) is known.

To apply the CC method, two approximations are made. First, instead of using a complete, and hence infinite, set of basis functions, one uses a finite basis set to express the spin-orbitals in the SCF MO wave function. One thus has available only a finite number of virtual orbitals to use in forming excited determinants. As usual, we have a basis-set truncation error. Second, instead of including all the operators $\hat{T}_1, \hat{T}_2, \dots, \hat{T}_n$, one approximates the operator $\hat{T}$ by including only some of these operators. Theory shows (Wilson, p. 222) that the most important contribution to $\hat{T}$ is made by $\hat{T}_2$. The approximation $\hat{T} \approx \hat{T}_2$ gives

$$\psi_{\text{CCD}} = e^{\hat{T}_2} \Phi_0$$

Inclusion of only $\hat{T}_2$ gives an approximate CC approach called the **coupled-cluster doubles (CCD) method**. Since $e^{\hat{T}_2} = 1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \dots$, the wave function ψ_{CCD} contains determinants with double substitutions, quadruple substitutions, hexuple substitutions, and so on. Recall (Section 16.2) that quadruple substitutions are next in importance after double substitutions in a CI wave function. The treatment of quadruple substitutions in the CCD method is only approximate. The CCD quadruple excitations are produced by the operator $\frac{1}{2}\hat{T}_2^2$, and so the coefficients of the quadruply substituted determinants are determined as products of the coefficients of the doubly substituted determinants [see Eq. (16.18)], rather than being determined independently, as in the CI-SDTQ method. The CCD approximation of the coefficients of the quadruply substituted determinants turns out to be pretty accurate.

We need equations to find the CCD amplitudes. Substitution of $\psi = e^{\hat{T}} \Phi_0$ [Eq. (16.15)] in the Schrödinger equation $\hat{H}\psi = E\psi$ gives

$$\hat{H}e^{\hat{T}} \Phi_0 = Ee^{\hat{T}} \Phi_0 \quad (16.19)$$

Multiplication by Φ_0^* and integration gives

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E \langle \Phi_0 | e^{\hat{T}} \Phi_0 \rangle \quad (16.20)$$

We have $e^{\hat{T}} \Phi_0 = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \dots) \Phi_0 = \Phi_0 + \hat{T} \Phi_0 + \frac{1}{2}\hat{T}^2 \Phi_0 + \dots$. Since [Eq. (16.17)] $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n$, the functions $\hat{T} \Phi_0$, $\frac{1}{2}\hat{T}^2 \Phi_0$, and so on, contain only Slater determinants with at least one occupied orbital replaced by a virtual orbital. Because of the orthogonality of the spin-orbitals, all such excited Slater determinants are orthogonal to Φ_0 , as can be seen by replacing $\sum_{i=1}^n \hat{f}_i$ with 1 in Table 11.3. Therefore, $\langle \Phi_0 | e^{\hat{T}} \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1$, and (16.20) becomes

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E \quad (16.21)$$

Multiplication of the Schrödinger equation (16.19) by Φ_{ij}^{ab*} and integration gives

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E \langle \Phi_{ij}^{ab} | e^{\hat{T}} \Phi_0 \rangle \quad (16.22)$$

Use of (16.21) to eliminate E from (16.22) gives

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle \langle \Phi_{ij}^{ab} | e^{\hat{T}} \Phi_0 \rangle \quad (16.23)$$

So far, the treatment is exact. We now invoke the CCD approximation $\hat{T} \approx \hat{T}_2$, and Eqs. (16.21) and (16.23) become

$$E_{\text{CCD}} = \langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle \quad (16.24)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle \langle \Phi_{ij}^{ab} | e^{\hat{T}_2} \Phi_0 \rangle \quad (16.25)$$

Since these equations are approximate, the exact energy E has been replaced by the CCD energy E_{CCD} . Also, the coefficients t_{ij}^{ab} (produced when $e^{\hat{T}_2}$ operates on Φ_0) in these equations are approximate. The first integral on the right side of (16.25) is

$$\begin{aligned}\langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \cdots) \Phi_0 \rangle \\ \langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} | \hat{T}_2 \Phi_0 \rangle + 0 = E_{\text{HF}} + \langle \Phi_0 | \hat{H} | \hat{T}_2 \Phi_0 \rangle\end{aligned}\quad (16.26)$$

where E_{HF} is the Hartree–Fock (or SCF) energy. The integral $\langle \Phi_0 | \hat{H} | \frac{1}{2} \hat{T}_2^2 \Phi_0 \rangle$ and similar integrals with higher powers of $\hat{T}_2$ vanish because $\hat{T}_2^2 \Phi_0$ contains only quadruply excited determinants. Hence, $\hat{T}_2^2 \Phi_0$ differs from Φ_0 by four spin-orbitals, and the Condon–Slater rules (Table 11.3) show that the matrix elements of $\hat{H}$ between Slater determinants differing by four spin-orbitals are zero. Similar use of the Condon–Slater rules gives for the integral on the left of (16.25) (Prob. 16.17)

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2) \Phi_0 \rangle \quad (16.27)$$

Also, use of the orthogonality of different Slater determinants gives (Prob. 16.17)

$$\langle \Phi_{ij}^{ab} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{T}_2 \Phi_0 \rangle \quad (16.28)$$

Use of (16.26) to (16.28) in (16.25) gives

$$\langle \Phi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2) \Phi_0 \rangle = (E_{\text{HF}} + \langle \Phi_0 | \hat{H} | \hat{T}_2 \Phi_0 \rangle) \langle \Phi_{ij}^{ab} | \hat{T}_2 \Phi_0 \rangle \quad (16.29)$$

$$i = 1, \dots, n-1; \quad j = i+1, \dots, n; \quad a = n+1, \dots; \quad b = a+1, \dots$$

Next, one uses the definition (16.18) of $\hat{T}_2$ to eliminate $\hat{T}_2$ from (16.29). $\hat{T}_2 \Phi_0$ is a multiple sum involving $t_{ij}^{ab} \Phi_{ij}^{ab}$, and $\hat{T}_2^2 \Phi_0 \equiv \hat{T}_2(\hat{T}_2 \Phi_0)$ is a multiple sum involving $t_{ij}^{ab} t_{kl}^{cd} \Phi_{ijkl}^{abcd}$. For each unknown amplitude t_{ij}^{ab} , there is one equation in (16.29), so the number of equations is equal to the number of unknowns. After replacing $\hat{T}_2 \Phi_0$ and $\hat{T}_2^2 \Phi_0$ by these multiple sums, one expresses the resulting integrals involving Slater determinants in terms of integrals over the spin-orbitals by using the Condon–Slater rules (Table 11.3). The integrals over spin-orbitals are then expressed in terms of integrals over the basis functions. The net result is a set of simultaneous nonlinear equations for the unknown amplitudes t_{ij}^{ab} , whose form is (see *Carsky and Urban*, pages 96–97)

$$\sum_{s=1}^m a_{rs} x_s + \sum_{t=2}^m \sum_{s=1}^{t-1} b_{rst} x_s x_t + c_r = 0, \quad r = 1, 2, \dots, m \quad (16.30)$$

where $x_1, x_2, \dots, x_m$ are the unknowns t_{ij}^{ab} , the quantities a_{rs} , b_{rst} , and c_r are constants that involve orbital energies and electron-repulsion integrals over the basis functions, and m is the number of unknown amplitudes t_{ij}^{ab} . The set of equations (16.30) is solved iteratively, starting with an initial estimate for the x 's found by neglecting many of the terms in (16.30). Once the x 's (that is, the t_{ij}^{ab} 's) are known, the wave function is known from $\psi_{\text{CCD}} = e^{\hat{T}_2} \Phi_0$ [the displayed equation before (16.19)] and the energy is found from (16.24).

The next step in improving the CCD method is to include the operator $\hat{T}_1$ and take $\hat{T} = \hat{T}_1 + \hat{T}_2$ in $e^{\hat{T}}$; this gives the **CC singles and doubles (CCSD) method**. With $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$, one obtains the **CC singles, doubles, and triples (CCSDT) method** [J. Noga and R. J. Bartlett, *J. Chem. Phys.*, **86**, 7041 (1987)]. CCSDT calculations give very accurate results for correlation energies and molecular properties but are very demanding computationally and are only feasible for small molecules. Several approximate forms of CCSDT have been developed. The most widely used such approximation is **CCSD(T)**, coupled cluster with inclusion of single and double excitations and perturbative inclusion of triple excitations.

Table 16.1 lists the results of some CC calculations on H₂O.

The CCD, CCSD, CCSD(T), and CCSDT methods are size extensive but not variational. Analytic gradients are available for these methods. Usually, the frozen-core (FC) approximation is used in CC calculations. Here, excitations of inner-shell electrons are omitted.

For open-shell ground states (for example, OH, O₂), one can base a CC calculation on either a UHF or an ROHF wave function. Spin contamination is less serious for UHF-based CC wave functions than for UHF-MP2 wave functions.

A few versions of CC theory have been developed for treating excited states. One such version, the equation-of-motion (EOM) CCSD, has given very good results for vertical excitation energies. Analytic gradients for the EOM-CCSD method are available, allowing calculation of geometries and vibrational frequencies of excited states. For details see R. J. Bartlett in *Yarkony*, Part II, Chapter 16, Section 9; A. I. Krylov, *Annu. Rev. Phys. Chem.*, **59**, 433 (2008). CC excited-state methods are reviewed in K. Sneskov and O. Christiansen, *WIREs Comput. Mol. Sci.*, **2**, 566 (2012).

Pople and co-workers developed the nonvariational **quadratic configuration-interaction (QCI) method**, which is intermediate between the CC and CI methods. The QCI method exists in the size-consistent forms QCISD, which is an approximation to CCSD, and QCISD(T). QCISD(T) has given excellent results for correlation energies in many calculations but occasionally fails dramatically [L. A. Curtiss et al., *Chem. Phys. Lett.*, **359**, 390 (2002)], so CCSD(T) calculations are currently much preferred to QCISD(T) calculations.

The exact basis-set correlation energy (Section 16.2) is obtained by full CI, by CC calculations with $\hat{T}$ not truncated, and by MP perturbation-theory carried to infinite order (provided the series converges, which isn't always true). Full CI calculations with DZP basis sets were done for the H₂O, HF, and BH molecules at their equilibrium geometries and at geometries where the bond lengths were stretched to $1.5R_e$ and to $2R_e$. By comparing the DZP energies obtained by a partial correlation method with the full CI energies for these molecules, one can judge the accuracy of the correlation method for calculating molecular energies. The average absolute energy errors (deviations from FCI) in millihartrees (one millihartree corresponds to 0.627 kcal/mol) for various methods at the equilibrium geometry (At R_e) and at all three geometries (All R) are as follows (R. J. Bartlett in *Yarkony*, Part II, Chapter 16):

Method	MP2	CISD	MP3	CISDT	CCD	CCSD	QCISD	MP4
At R_e	16.5	9.2	7.9	7.1	3.8	3.0	2.7	2.1
All R	27.8	22.0	22.9	16.7	12.8	7.1	6.4	5.9
Method	MP5	MP6	CCSD(T)	QCISD(T)	CCSDT	CISDTQ	CCSDTQ	
At R_e	1.3	0.5	0.5	0.4	0.3	0.2	0.01	
All R	5.1	1.4	1.2	0.8	0.8	1.1	0.03	

The very accurate CCSDTQ, CCSDT, CISDTQ, and MP6 methods are much too computationally demanding to be used regularly. The CCSD(T) method “is widely considered to be the most accurate practicable method at hand” [A. Hesselmann et al., *J. Chem. Phys.*, **122**, 014103 (2005)] and has often been called “the gold standard” for dealing with the ground state of a small or medium-size closed-shell molecule near its equilibrium geometry. CCSD(T) bond lengths are typically accurate to 0.003 Å, bond angles are accurate to 0.3°, vibrational frequencies are accurate to within 2%, and bond energies are accurate to within 2 kcal/mol.

Most of the methods used to improve the MP2 method (Section 16.3) have also been applied to the coupled-cluster method. Thus, the use of localized rather than canonical SCF MOs has given the LCCSD and LCCSD(T) methods (where the L is for local), which are much faster than the usual CC methods [M. Schütz and H.-J. Werner, *J. Chem. Phys.*, **114**, 661 (2001) and references cited therein]. An approximate version of LCCSD(T) called LCCSD(T0) has given “breathhtaking” speedups of factors of 1000 to 10^6 for large molecules over conventional CCSD(T) and has allowed a single-point LCCSD(T0)/cc-pVDZ calculation on indinavir, a 92-atom molecule with 865 basis functions in this basis set [M. Schütz, *J. Chem. Phys.*, **113**, 9986 (2000)] and on a certain enzyme-catalyzed reaction with 49 atoms treated quantum mechanically using 1294 basis functions (mainly the cc-pVTZ set) with the remaining atoms treated using molecular mechanics [F. Claeysens et al., *Angew. Chem. Int. Ed.*, **45**, 6856, (2006)]. This calculation gave a barrier height for the reaction in very good agreement with experiment.

A disadvantage of such local correlation methods is that the approximation of neglecting interactions between distant orbitals introduces small discontinuities into the molecule’s potential-energy surface, which might interfere with geometry optimization. A computationally efficient version of local CCSD that avoids such discontinuities has been developed [J. E. Subotnik et al., *J. Chem. Phys.*, **125**, 074116 (2006)].

As is done in the HF and MP methods, computation of electron-repulsion integrals in CC calculations can be speeded up by using the density-fitting (resolution-of-the-identity) method [M. Schütz and F. R. Manby, *Phys. Chem. Chem. Phys.*, **5**, 3349 (2003)].

As in the MP method, terms linear in interelectronic distances r_{ij} or containing $\exp(-\gamma r_{12})$ can be introduced into the CC wave function so as to reduce the basis-set truncation error, thereby giving the CCSD-R12, CCSD(T)-R12, and CCSD-F12 methods [J. Noga and P. Valiron, in *Computational Chemistry: Reviews of Current Trends*, Vol. 7, J. Leszczynski (Ed.), p. 131, World Scientific (2002); J. Noga et al., *J. Chem. Phys.*, **128**, 174103 (2008)]. The CCSD-F12 method gives CCSD energies close to the basis-set limit, but the substantial added computational cost in comparison to CCSD makes CCSD-F12 impractical. Therefore, several approximations to CCSD-F12 have been developed, one of which, CCSD(F12*), is nearly as accurate as CCSD-F12 but with only a small added computational cost [C. Hättig et al., *J. Chem. Phys.*, **132**, 231102 (2010)]. When the F12 method is used with CCSD(T) calculations, the triples energy contribution is not explicitly correlated. The version CCSD(T)-F12b was found to give good results [D. Feller et al., *J. Chem. Phys.*, **133**, 184102 (2010)].

Just as one can use spin-component scaling to improve the performance of MP2, one can multiply the contribution of the same-spin terms to the CCSD energy by an empirical parameter and multiply the contribution of the opposite-spin terms by another parameter. This gives the SCS-CCSD method [T. Takatani et al., *J. Chem. Phys.*, **128**, 124111 (2008)]. The same-spin and opposite-spin parameter values 1.13 and 1.27, respectively, were found by fitting a set of known reaction energies. SCS-CCSD performs quite well for intermolecular interactions.

Another way to reduce the basis-set truncation error is to use a formula that attempts to extrapolate incomplete-basis-set results to the complete basis set limit. One of many such approximate formulas is that due to Helgaker and co-workers [A. Halkier et al., *Chem. Phys. Lett.*, **286**, 243 (1998)]

$$E_n^{\text{corr}} = E_\infty^{\text{corr}} + A/n^3 \quad (16.31)$$

where E_n^{corr} is the correlation energy found from a CC calculation method [such as CCSD or CCSD(T)] using the cc-pVnZ basis set (or a related basis set such as aug-cc-pVnZ or cc-pCVnZ), A is a parameter, and E_∞^{corr} is the estimate of the correlation energy that would be found in the complete-basis-set (CBS) limit. (Note that $E_n^{\text{corr}} \equiv E_n - E_n^{\text{HF}}$,

where E_n and E_n^{HF} are the energies found by a CC method and by the Hartree–Fock method, respectively, with both calculations using the cc-pVnZ basis set.) Equation (16.31) needs to be combined with an extrapolation formula such as (15.23) for the estimated Hartree–Fock limit so as to obtain the estimated CBS limit for the total energy, according to $E_\infty = E_\infty^{\text{HF}} + E_\infty^{\text{corr}}$. Combining the results of cc-pVnZ and cc-pV($n - 1$)Z CC calculations to eliminate A , we get from (16.31) (Prob. 16.18)

$$E_\infty^{\text{corr}} = \frac{n^3 E_n^{\text{corr}} - (n - 1)^3 E_{n-1}^{\text{corr}}}{n^3 - (n - 1)^3} \quad (16.32)$$

which allows E_∞^{corr} to be estimated from calculations with two correlation-consistent basis sets. Use of the cc-pVDZ and cc-pVTZ pair in (16.32) is found to give much less accuracy than use of the cc-pVTZ and cc-pVQZ pair. A test of several proposed CBS extrapolation formulas did not find one single formula that is best in all circumstances [D. Feller et al., *J. Chem. Phys.*, **135**, 044102 (2011)].

Some people feel that separate extrapolation of HF and correlation energies is unnecessary and advocate simply extrapolating the total energy. For example, the following extrapolation formula was found to work well for CCSD(T)/aug-cc-pVnZ calculations with $n = 4$ and 5 [K. A. Peterson et al., *Theor. Chem. Acc.*, **131**, 1079 (2012)]:

$$E_n = E_\infty + B / (n + \frac{1}{2})^4$$

where E_n is the total CCSD(T) energy for the $n = 4$ or 5 basis set and E_∞ is the estimated CCSD(T) CBS limit. From the E_4 and E_5 values, one gets the constants B and E_∞ (Prob. 16.19).

To overcome the failures of the CCSD(T) method in dealing with bond-breaking and open-shell species, several multireference (MR) CC methods have been developed, but none of these methods is fully satisfactory. Reviews of MR CC methods noted that “even now the situation in the MRCC field is not satisfactory, since none of the MRCC methods is in a wide use” [D. I. Lyakh et al., *Chem. Rev.*, **112**, 182 (2012)] and a “generally accepted multireference CC theory is still lacking” (A. Kohn et al., *WIREs Comput. Mol. Sci.* 2012, doi: 10.1002/wcms.1120).

16.5 Density-Functional Theory

The electronic wave function of an n -electron molecule depends on $3n$ spatial and n spin coordinates. Since the Hamiltonian operator (15.10) contains only one- and two-electron spatial terms, one finds that the molecular energy can be written in terms of integrals involving only six spatial coordinates (*Pilar*, Section 10-5). In a sense, the wave function of a many-electron molecule contains more information than is needed and is lacking in direct physical significance. This has prompted the search for functions that involve fewer variables than the wave function and that can be used to calculate the energy and other properties.

The Hohenberg–Kohn Theorem

In 1964, Pierre Hohenberg and Walter Kohn proved that for molecules with a nondegenerate ground state, the ground-state molecular energy, wave function, and all other molecular electronic properties are uniquely determined by the ground-state electron probability density $\rho_0(x, y, z)$ (Section 14.1), a function of only three variables [P. Hohenberg and W. Kohn, *Phys. Rev.*, **136**, B864 (1964)]. (The zero subscript indicates the ground state.) One says that the ground-state electronic energy E_0 is a functional of ρ_0 and writes $E_0 = E_0[\rho_0]$, where the square brackets denote a functional relation. **Density-functional**

theory (DFT) attempts to calculate E_0 and other ground-state molecular properties from the ground-state electron density ρ_0 .

What is a functional? Recall that a *function* $f(x)$ is a rule that associates a number with each value of the variable x for which the function f is defined. For example, the function $f(x) = x^2 + 1$ associates the number 10 with the value 3 of x and associates a number with each other value of x . A **functional** $F[f]$ is a rule that associates a number with each function f . For example, the functional $F[f] = \int_{-\infty}^{\infty} f^*(x)f(x) dx$ associates a number, found by integration of $|f|^2$ over all space, with each quadratically integrable function $f(x)$. The variational integral $W[\phi] = \langle \phi | \hat{H} | \phi \rangle / \langle \phi | \phi \rangle$ is a functional of the variation function ϕ and gives a number for each well-behaved ϕ .

The proof of the Hohenberg–Kohn theorem is as follows. The ground-state electronic wave function ψ_0 of an n -electron molecule is an eigenfunction of the purely electronic Hamiltonian of Eq. (13.5), which, in atomic units, is

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^n v(\mathbf{r}_i) + \sum_j \sum_{i>j} \frac{1}{r_{ij}} \quad (16.33)$$

$$v(\mathbf{r}_i) = - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} \quad (16.34)$$

The quantity $v(\mathbf{r}_i)$, the potential energy of interaction between electron i and the nuclei, depends on the coordinates x_i, y_i, z_i of electron i and on the nuclear coordinates. Since the electronic Schrödinger equation is solved for fixed locations of the nuclei, the nuclear coordinates are not variables for the electronic Schrödinger equation. Thus, $v(\mathbf{r}_i)$ in the electronic Schrödinger equation is a function of only x_i, y_i, z_i , which we indicate by using the vector notation of Section 5.2. In DFT, $v(\mathbf{r}_i)$ is called the **external potential** acting on electron i , since it is produced by charges external to the system of electrons.

Once the external potential $v(\mathbf{r}_i)$ and the number of electrons n are specified, the electronic wave functions and allowed energies of the molecule are determined as the solutions of the electronic Schrödinger equation. Hohenberg and Kohn proved that for systems with a nondegenerate ground state, the ground-state electron probability density $\rho_0(\mathbf{r})$ determines the external potential (except for an arbitrary additive constant) and determines the number of electrons. Hence, the ground-state wave function and energy (and, for that matter, all excited-state wave functions and energies) are determined by the ground-state electron density.

To see that $\rho_0(\mathbf{r})$ determines the number of electrons, we integrate (14.5) over all space and use the normalization of ψ to get $\int \rho_0(\mathbf{r}) d\mathbf{r} = n$.

To see that $\rho_0(\mathbf{r})$ determines the external potential $v(\mathbf{r}_i)$, we suppose that this is false and that there are two external potentials v_a and v_b (differing by more than a constant) that each give rise to the same ground-state electron density ρ_0 . Let $\hat{H}_a$ and $\hat{H}_b$ be the n -electron Hamiltonians (16.33) corresponding to $v_a(\mathbf{r}_i)$ and $v_b(\mathbf{r}_i)$, where v_a and v_b are not necessarily given by (16.34); they can be any external potential. Let $\psi_{0,a}$ and $\psi_{0,b}$ and $E_{0,a}$ and $E_{0,b}$ be the normalized ground-state wave functions and energies for these Hamiltonians. [Note that even if $\hat{H}_a$ is a molecular electronic Hamiltonian with v_a given by (16.34), $v_b(\mathbf{r}_i)$ is not restricted to the form (16.34) but can be any function of $\mathbf{r}_i$.] $\psi_{0,a}$ and $\psi_{0,b}$ must be different functions, since they are eigenfunctions of Hamiltonians that differ by more than an additive constant (Prob. 16.22). If the ground state is nondegenerate, then there is only one normalized function—the exact ground-state wave function ψ_0 , that gives the exact ground state energy E_0 when used as a trial variation function. According to the variation theorem, use of any normalized well-behaved function that differs from ψ_0 will make the variational integral greater than E_0 (Prob. 8.14): that is, $\langle \phi | \hat{H} | \phi \rangle > E_0$ if $\phi \neq \psi_0$ and the

ground state is nondegenerate. Therefore, use of $\psi_{0,b}$ as a trial function with the Hamiltonian $\hat{H}_a$ gives

$$E_{0,a} < \langle \psi_{0,b} | \hat{H}_a | \psi_{0,b} \rangle = \langle \psi_{0,b} | \hat{H}_a + \hat{H}_b - \hat{H}_b | \psi_{0,b} \rangle = \langle \psi_{0,b} | \hat{H}_a - \hat{H}_b | \psi_{0,b} \rangle + \langle \psi_{0,b} | \hat{H}_b | \psi_{0,b} \rangle$$

The Hamiltonians $\hat{H}_a$ and $\hat{H}_b$ differ only in their external potentials v_a and v_b , so $\hat{H}_a - \hat{H}_b = \sum_{i=1}^n [v_a(\mathbf{r}_i) - v_b(\mathbf{r}_i)]$ and we have

$$E_{0,a} < \left\langle \psi_{0,b} \left| \sum_{i=1}^n [v_a(\mathbf{r}_i) - v_b(\mathbf{r}_i)] \right| \psi_{0,b} \right\rangle + E_{0,b}$$

The quantities $v_a(\mathbf{r}_i)$ and $v_b(\mathbf{r}_i)$ are one-electron operators, and using Eq. (14.8), we get

$$E_{0,a} < \int \rho_{0,b}(\mathbf{r}) [v_a(\mathbf{r}) - v_b(\mathbf{r})] d\mathbf{r} + E_{0,b}$$

where, since the integration is over $\psi_{0,b}$, we get the electron density $\rho_{0,b}$ corresponding to $\psi_{0,b}$. If we go through the same reasoning with a and b interchanged, we get

$$E_{0,b} < \int \rho_{0,a}(\mathbf{r}) [v_b(\mathbf{r}) - v_a(\mathbf{r})] d\mathbf{r} + E_{0,a}$$

By hypothesis, the two different wave functions give the same electron density: $\rho_{0,a} = \rho_{0,b}$. Putting $\rho_{0,a} = \rho_{0,b}$ and adding the last two inequalities, the two integrals cancel and we get $E_{0,a} + E_{0,b} < E_{0,b} + E_{0,a}$. This result is false, so our initial assumption that two different external potentials could produce the same ground-state electron density must be false. Hence, the ground-state electron probability density ρ_0 determines the external potential (to within an additive constant that simply affects the zero level of energy) and also determines the number of electrons. Therefore ρ_0 determines the molecular electronic Hamiltonian and so determines the ground-state wave function, energy, and other properties.

The ground-state electronic energy E_0 is thus a functional of the function $\rho_0(\mathbf{r})$, which we write as $E_0 = E_v[\rho_0]$, where the v subscript emphasizes the dependence of E_0 on the external potential $v(\mathbf{r})$, which differs for different molecules.

The purely electronic Hamiltonian (13.5) is the sum of electronic kinetic-energy terms, electron–nuclear attractions, and electron–electron repulsions. Taking the average of (13.5) for the ground state, we have $E = \bar{T} + \bar{V}_{Ne} + \bar{V}_{ee}$, where, for notational convenience, overbars instead of angular brackets have been used to denote averages. Each of the average values in this equation is a molecular property determined by the ground-state electronic wave function, which, in turn, is determined by $\rho_0(\mathbf{r})$. Therefore, each of these averages is a functional of ρ_0 :

$$E_0 = E_v[\rho_0] = \bar{T}[\rho_0] + \bar{V}_{Ne}[\rho_0] + \bar{V}_{ee}[\rho_0]$$

From (13.1), $\hat{V}_{Ne} = \sum_{i=1}^n v(\mathbf{r}_i)$, where $v(\mathbf{r}_i) = -\sum_{\alpha} Z_{\alpha}/\mathbf{r}_{i\alpha}$ in atomic units, so

$$\bar{V}_{Ne} = \left\langle \psi_0 \left| \sum_{i=1}^n v(\mathbf{r}_i) \right| \psi_0 \right\rangle = \int \rho_0(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \quad (16.35)$$

where (14.8) was used, and where $v(\mathbf{r})$ is the nuclear attraction potential-energy function (16.34) for an electron located at point $\mathbf{r}$. Thus $\bar{V}_{Ne}[\rho_0]$ is known, but the functionals $\bar{T}[\rho_0]$ and $\bar{V}_{ee}[\rho_0]$ are unknown. We have

$$E_0 = E_v[\rho_0] = \int \rho_0(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \bar{T}[\rho_0] + \bar{V}_{ee}[\rho_0] = \int \rho_0(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[\rho_0] \quad (16.36)$$

where the functional $F[\rho_0]$ defined by $F[\rho_0] \equiv \bar{T}[\rho_0] + \bar{V}_{ee}[\rho_0]$, is independent of the external potential. Equation (16.36) does not provide a practical way to calculate E_0 from ρ_0 , because the functional $F[\rho_0]$ is unknown.

The Hohenberg–Kohn Variational Theorem

To change (16.36) from a formal relation to a practical tool, we need a second theorem proven by Hohenberg and Kohn, and an approach developed by Kohn and Sham. Hohenberg and Kohn proved that for every trial density function $\rho_{\text{tr}}(\mathbf{r})$ that satisfies $\int \rho_{\text{tr}}(\mathbf{r}) d\mathbf{r} = n$ and $\rho_{\text{tr}}(\mathbf{r}) \geq 0$ for all $\mathbf{r}$, the following inequality holds: $E_0 \leq E_v[\rho_{\text{tr}}]$, where E_v is the energy functional in (16.36). Since $E_0 = E_v[\rho_0]$, where ρ_0 is the true ground-state electron density, *the true ground-state electron density minimizes the energy functional $E_v[\rho_{\text{tr}}]$* (just as the true normalized ground-state wave function minimizes the variational integral).

The proof of this Hohenberg–Kohn variational theorem is as follows. Let ρ_{tr} satisfy the above two conditions of integrating to n and being nonnegative. By the Hohenberg–Kohn theorem, ρ_{tr} determines the external potential v_{tr} , and this in turn determines the wave function ψ_{tr} that corresponds to the density ρ_{tr} . (Actually, this is only true if there exists an external potential v_{tr} that will give rise to an antisymmetric wave function that corresponds to ρ_{tr} . If this condition holds, ρ_{tr} is said to be *v-representable*. It turns out that not all ρ_{tr} 's are *v-representable*. This has not caused any practical difficulties in applications of DFT. Also, Levy has reformulated the Hohenberg–Kohn theorems in a way that eliminates the need for *v-representability*. See *Parr and Yang*, Sections 3.3, 3.4, and 7.3.) Let us use the wave function ψ_{tr} that corresponds to ρ_{tr} as a trial variation function for the molecule with Hamiltonian $\hat{H}$. The variation theorem gives

$$\langle \psi_{\text{tr}} | \hat{H} | \psi_{\text{tr}} \rangle = \left\langle \psi_{\text{tr}} \left| \hat{T} + \hat{V}_{ee} + \sum_{i=1}^n v(\mathbf{r}_i) \right| \psi_{\text{tr}} \right\rangle \geq E_0 = E_v[\rho_0]$$

Using the fact that the average kinetic and potential energies are functionals of the electron density, and using (16.35) with ψ_0 replaced by ψ_{tr} , this last equation becomes

$$\bar{T}[\rho_{\text{tr}}] + \bar{V}_{ee}[\rho_{\text{tr}}] + \int \rho_{\text{tr}} v(\mathbf{r}) d\mathbf{r} \geq E_v[\rho_0] \quad (16.37)$$

The functionals $\bar{T}$ and $\bar{V}_{ee}$ are the same in (16.36) and (16.37), although the functions ρ_0 and ρ_{tr} differ. The left side of (16.37) differs from the corresponding expression in (16.36) only by having ρ_0 replaced by ρ_{tr} . Use of (16.36) with ρ_0 replaced by ρ_{tr} in (16.37) gives $E_v[\rho_{\text{tr}}] \geq E_v[\rho_0]$, which proves that no trial electron density can give a lower ground-state energy than the true ground-state electron density.

Hohenberg and Kohn proved their theorems only for nondegenerate ground states. Subsequently, Levy proved the theorems for degenerate ground states (see *Parr and Yang*, Section 3.4).

The Kohn–Sham (KS) Method

If we know the ground-state electron density $\rho_0(\mathbf{r})$, the Hohenberg–Kohn theorem tells us that it is possible in principle to calculate all the ground-state molecular properties from ρ_0 without having to find the molecular wave function. [In the traditional quantum-mechanical approach, one first finds the wave function and then finds ρ by integration; Eq. (14.5).] The Hohenberg–Kohn theorem does not tell us *how* to calculate E_0 from ρ_0 [since the functional F in (16.36) is unknown], nor does it tell us how to find ρ_0 without first finding the wave function. A key step toward these goals was taken in 1965 when Kohn and Sham devised a practical method for finding ρ_0 and for finding E_0 from ρ_0 [W. Kohn and L. J. Sham, *Phys. Rev.*, **140**, A1133 (1965)]. Their method is capable, in principle, of yielding exact results, but because the equations of the Kohn–Sham (KS) method contain an unknown functional that must be approximated, the KS formulation of DFT yields approximate results.

Kohn and Sham considered a fictitious reference system (denoted by the subscript s and often called *the noninteracting system*) of n noninteracting electrons that each experience the same external potential-energy function $v_s(\mathbf{r}_i)$, where $v_s(\mathbf{r}_i)$ is such as to make the ground-state electron probability density $\rho_s(\mathbf{r})$ of the reference system equal to the exact

ground-state electron density $\rho_0(\mathbf{r})$ of the molecule we are interested in; $\rho_s(\mathbf{r}) = \rho_0(\mathbf{r})$. Since Hohenberg and Kohn proved that the ground-state probability-density function determines the external potential, once $\rho_s(\mathbf{r})$ is defined for the reference system, the external potential $v_s(\mathbf{r}_i)$ in the reference system is uniquely determined, although we might not know how to actually find it. The electrons do not interact with one another in the reference system, so the Hamiltonian of the reference system is

$$\hat{H}_s = \sum_{i=1}^n \left[-\frac{1}{2} \nabla_i^2 + v_s(\mathbf{r}_i) \right] \equiv \sum_{i=1}^n \hat{h}_i^{\text{KS}}, \quad \text{where} \quad \hat{h}_i^{\text{KS}} \equiv -\frac{1}{2} \nabla_i^2 + v_s(\mathbf{r}_i) \quad (16.38)$$

$\hat{h}_i^{\text{KS}}$ is the one-electron Kohn–Sham Hamiltonian. Use of a fictitious system of noninteracting electrons should not be too disturbing. Recall that we used a system of noninteracting electrons in the Section 9.3 perturbation treatment of the He atom. We can relate the fictitious Kohn–Sham reference system to the real molecule by writing the Hamiltonian $\hat{H}_\lambda \equiv \hat{T} + \sum_i v_\lambda(\mathbf{r}_i) + \lambda \hat{V}_{ee}$, where the parameter λ ranges from 0 (no interelectronic repulsions, which is the reference system) to 1 (the real molecule), and v_λ is defined as the external potential that will make the ground-state electron density of the system with Hamiltonian $\hat{H}_\lambda$ equal to that of the real molecule's ground state.

Since the reference system s consists of noninteracting particles, the results of Section 6.2 and the antisymmetry requirement show that the ground-state wave function $\psi_{s,0}$ of the reference system is the antisymmetrized product (Slater determinant) of the lowest-energy Kohn–Sham spin-orbitals u_i^{KS} of the reference system, where the spatial part $\theta_i^{\text{KS}}(\mathbf{r}_i)$ of each spin-orbital is an eigenfunction of the one-electron operator $\hat{h}_i^{\text{KS}}$:

$$\psi_{s,0} = |u_1^{\text{KS}} u_2^{\text{KS}} \cdots u_n^{\text{KS}}|, \quad u_i^{\text{KS}} = \theta_i^{\text{KS}}(\mathbf{r}_i) \sigma_i \quad (16.39)$$

$$\hat{h}_i^{\text{KS}} \theta_i^{\text{KS}} = \varepsilon_i^{\text{KS}} \theta_i^{\text{KS}} \quad (16.40)$$

where σ_i is a spin function (either α or β) and the $\varepsilon_i^{\text{KS}}$'s are Kohn–Sham orbital energies.

For a closed-shell ground state, the electrons are paired in the Kohn–Sham orbitals, with two electrons of opposite spin having the same spatial Kohn–Sham orbital (as in the RHF method).

Kohn and Sham rewrote the Hohenberg–Kohn equation (16.36) as follows. Let $\Delta \bar{T}$ be defined by

$$\Delta \bar{T}[\rho] \equiv \bar{T}[\rho] - \bar{T}_s[\rho] \quad (16.41)$$

where, for convenience, the zero subscript on ρ is omitted in this and many subsequent equations. $\Delta \bar{T}$ is the difference in the average ground-state electronic kinetic energy between the molecule and the reference system of noninteracting electrons with electron density equal to that in the molecule. Let

$$\Delta \bar{V}_{ee}[\rho] \equiv \bar{V}_{ee}[\rho] - \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (16.42)$$

where r_{12} is the distance between points x_1, y_1, z_1 and x_2, y_2, z_2 . The quantity $\frac{1}{2} \iint \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$ is the classical expression (in atomic units) for the electrostatic interelectronic repulsion energy if the electrons were smeared out into a continuous distribution of charge with electron density ρ . The charge dQ_1 in a tiny volume element $d\mathbf{r}_1$ of such a distribution is $dQ_1 = -e\rho(\mathbf{r}_1) d\mathbf{r}_1$ and the potential energy of repulsion between dQ_1 and the charge in the volume element $d\mathbf{r}_2$ located at $\mathbf{r}_2$ is $e^2 r_{12}^{-1} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$. Integration of this expression over $d\mathbf{r}_2$ gives the repulsion energy between dQ_1 and the charge distribution. Integration over $d\mathbf{r}_1$ and multiplication by $\frac{1}{2}$ then gives the total interelectronic repulsion energy for the continuous distribution, where the factor $\frac{1}{2}$ is needed

to prevent counting each repulsion twice, once as the repulsion between dQ_1 and dQ_2 and once as the repulsion between dQ_2 and dQ_1 .

With the definitions (16.41) and (16.42), Eq. (16.36) becomes

$$E_v[\rho] = \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + \bar{T}_s[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \Delta\bar{T}[\rho] + \Delta\bar{V}_{ee}[\rho]$$

The functionals $\Delta\bar{T}$ and $\Delta\bar{V}_{ee}$ are unknown. Defining the **exchange–correlation energy functional** $E_{xc}[\rho]$ by

$$E_{xc}[\rho] \equiv \Delta\bar{T}[\rho] + \Delta\bar{V}_{ee}[\rho] \quad (16.43)$$

we have

$$E_0 = E_v[\rho] = \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + \bar{T}_s[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho] \quad (16.44)$$

The motivation for the definitions (16.41), (16.42), and (16.43) is to express $E_v[\rho]$ in terms of three quantities, the first three terms on the right side of (16.44), that are easy to evaluate from ρ and that include the main contributions to the ground-state energy, plus a fourth quantity E_{xc} , which, though not easy to evaluate accurately, will be a relatively small term. The key to accurate KS DFT calculation of molecular properties is to get a good approximation to E_{xc} .

Before we can evaluate the terms in (16.44), we need to find the ground-state electron density. Recall that the fictitious system of noninteracting electrons is defined to have the same electron density as that in the ground state of the molecule: $\rho_s = \rho_0$. It is readily proved (see Prob. 16.28) that the electron probability density of an n -particle system whose wave function [Eq. (16.39)] is a Slater determinant of the spin-orbitals $u_i^{\text{KS}} = \theta_i^{\text{KS}}\sigma_i$ is given by $\sum_{i=1}^n |\theta_i^{\text{KS}}|^2$. Therefore,

$$\rho = \rho_s = \sum_{i=1}^n |\theta_i^{\text{KS}}|^2 \quad (16.45)$$

How do we evaluate the terms in (16.44)? Using (16.34), we have $\int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} = -\sum_{\alpha} Z_{\alpha} \int \rho(\mathbf{r}_1)r_{1\alpha}^{-1} d\mathbf{r}_1$, which is easily evaluated if $\rho(r)$ is known. The $\bar{T}_s$ term in (16.44) is the kinetic energy of the system of noninteracting electrons whose wave function ψ_s in (16.39) is equal to a Slater determinant of orthonormal Kohn–Sham spin-orbitals. We have $\bar{T}_s[\rho] = -\frac{1}{2} \langle \psi_s | \sum_i \nabla_i^2 | \psi_s \rangle$. The Slater–Condon rules [Table 11.3 and Eq. (11.78)] give $\bar{T}_s[\rho] = -\frac{1}{2} \sum_i \langle \theta_i^{\text{KS}}(1) | \nabla_1^2 | \theta_i^{\text{KS}}(1) \rangle$. Thus (16.44) becomes

$$E_0 = -\sum_{\alpha} Z_{\alpha} \int \frac{\rho(\mathbf{r}_1)}{r_{1\alpha}} d\mathbf{r}_1 - \frac{1}{2} \sum_{i=1}^n \langle \theta_i^{\text{KS}}(1) | \nabla_1^2 | \theta_i^{\text{KS}}(1) \rangle + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho] \quad (16.46)$$

We can therefore find E_0 from ρ if we can find the KS orbitals θ_i^{KS} and if we know what the functional E_{xc} is. The electronic energy including nuclear repulsion is found by adding the internuclear repulsion V_{NN} to (16.46).

The Kohn–Sham orbitals are found as follows. The Hohenberg–Kohn variational theorem tells us that we can find the ground-state energy by varying ρ (subject to the constraint $\int \rho d\mathbf{r} = n$) so as to minimize the functional $E_v[\rho]$. Equivalently, instead of varying ρ , we can vary the KS orbitals θ_i^{KS} , which determine ρ by (16.45). (In doing so, we must constrain the θ_i^{KS} 's to be orthonormal, since orthonormality was assumed when we evaluated $\bar{T}_s$.)

Just as one can show that the orthonormal orbitals that minimize the Hartree–Fock expression for the molecular energy satisfy the Fock equation (14.25), one can show that the Kohn–Sham orbitals that minimize the expression (16.46) for the molecular ground-state energy satisfy (for a proof, see *Parr and Yang*, Section 7.2):

$$\left[-\frac{1}{2}\nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + v_{xc}(1) \right] \theta_i^{\text{KS}}(1) = \epsilon_i^{\text{KS}} \theta_i^{\text{KS}}(1) \quad (16.47)$$

where the function $v_{xc}(1)$ is defined by (16.50). From (16.40) and (16.38), alternative ways to write (16.47) are

$$\left[-\frac{1}{2}\nabla_1^2 + v_s(1) \right] \theta_i^{\text{KS}}(1) = \epsilon_i^{\text{KS}} \theta_i^{\text{KS}}(1) \quad (16.48)$$

$$\hat{h}^{\text{KS}}(1) \theta_i^{\text{KS}}(1) = \epsilon_i^{\text{KS}} \theta_i^{\text{KS}}(1) \quad (16.49)$$

The **exchange–correlation potential** v_{xc} is found as the functional derivative $\delta E_{xc}/\delta \rho$ of the exchange–correlation energy E_{xc} :

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (16.50)$$

The precise definition of the functional derivative need not concern us (see *Parr and Yang*, Appendix A). The following formula allows one to find the **functional derivative** of many functionals that occur in DFT. For a functional defined by

$$F[\rho] = \int_e^f \int_c^d \int_a^b g(x, y, z, \rho, \rho_x, \rho_y, \rho_z) dx dy dz$$

where ρ is a function of x , y , and z that vanishes at the limits of the integral, and where $\rho_x \equiv (\partial \rho / \partial x)_{y,z}$ etc., the functional derivative can be shown to be given by

$$\frac{\delta F}{\delta \rho} = \frac{\partial g}{\partial \rho} - \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial \rho_x} \right) - \frac{\partial}{\partial y} \left(\frac{\partial g}{\partial \rho_y} \right) - \frac{\partial}{\partial z} \left(\frac{\partial g}{\partial \rho_z} \right) \quad (16.51)$$

Note from (16.51) that the units of $\delta F / \delta \rho$ are not the same as the units of F / ρ , since F and g have different units. One can show that

$$\delta(c_1 F_1 + c_2 F_2) / \delta \rho = c_1 \delta F_1 / \delta \rho + c_2 \delta F_2 / \delta \rho$$

where c_1 and c_2 are constants.

If $E_{xc}[\rho]$ is known, its functional derivative is readily found from (16.50) and (16.51), and so v_{xc} is known. The functional $E_{xc}[\rho]$ in (16.46) is a number. The functional derivative of $E_{xc}[\rho]$ is a function of ρ (see Prob. 16.23 for an example), and since ρ is a function of $\mathbf{r}$, v_{xc} is a function of $\mathbf{r}$, that is, of x , y , and z . Sometimes people write v_{xc} as $v_{xc}(\rho(\mathbf{r}))$. [In the Kohn–Sham eigenvalue equation (16.49), the variable is taken as $\mathbf{r}_1$ rather than as $\mathbf{r}$.] The functional derivative $\delta E_{xc}[\rho(\mathbf{r})] / \delta \rho(\mathbf{r})$ is a function of x , y , and z whose value at point (x, y, z) depends on how much $E_{xc}[\rho]$ changes when $\rho(x, y, z)$ changes by a tiny amount in a tiny region centered at (x, y, z) .

The one-electron Kohn–Sham operator $\hat{h}^{\text{KS}}(1)$ in (16.49) and (16.47) is the same as the Fock operator (16.8) in the Hartree–Fock equations except that the exchange operators $-\sum_{j=1}^n \hat{k}_j$ in the Fock operator are replaced by v_{xc} (Prob. 16.24), which handles the effects of both exchange (antisymmetry) and electron correlation.

There is only one problem in using the Kohn–Sham method to find ρ and E_0 . No one knows what the correct functional $E_{xc}[\rho]$ is. Therefore, both E_{xc} in the energy expression (16.46) and v_{xc} in (16.47) and (16.50) are unknown. Various approximations to E_{xc} will be discussed shortly.

The Kohn–Sham orbitals θ_i^{KS} are orbitals for the fictitious reference system of noninteracting electrons, so, strictly speaking, these orbitals have no physical significance other than in allowing the exact molecular ground-state ρ to be calculated from (16.45). The density-functional molecular wave function is not a Slater determinant of spin-orbitals. In fact, *there is no density-functional molecular wave function*. However, in practice, one finds that the occupied Kohn–Sham orbitals resemble molecular orbitals calculated by the Hartree–Fock method, and the Kohn–Sham orbitals can be used (just as Hartree–Fock MOs are used) in qualitative MO discussions of molecular properties and reactivities [see E. J. Baerends and O. V. Gritsenko, *J. Phys. Chem.*, **101**, 5383 (1997); Gritsenko et al., *J. Chem. Phys.*, **107**, 5007 (1997); R. Stowasser and R. Hoffmann, *J. Am. Chem. Soc.*, **121**, 3414 (1999)]. (Note that, strictly speaking, Hartree–Fock orbitals also have no physical reality, since they refer to a fictitious model system in which each electron experiences some sort of average field of the other electrons.)

For a closed-shell molecule, each Hartree–Fock occupied-orbital energy is a good approximation to the negative of the energy needed to remove an electron from that orbital (Koopmans’ theorem). However, this is not true for Kohn–Sham orbital energies. The one exception is ϵ_i^{KS} for the highest-occupied KS orbital, which can be proved to be equal to minus the molecular ionization energy. With the currently used approximations to E_{xc} , ionization energies calculated from KS highest-occupied-orbital energies agree poorly with experiment.

Various approximate functionals $E_{xc}[\rho]$ are used in molecular DFT calculations. To study the accuracy of an approximate $E_{xc}[\rho]$, one uses it in DFT calculations and compares calculated molecular properties with experimental ones. The lack of a systematic procedure for improving $E_{xc}[\rho]$ and hence improving calculated molecular properties is the main drawback of the DFT method.

In a “true” density-functional theory, one would deal with only the electron density (a function of three variables) and not with orbitals, and would search directly for the density that minimizes $E_v[\rho]$. Because the functional E_v is unknown, one instead uses the Kohn–Sham method, which calculates an orbital for each electron. Thus, the KS method represents something of a compromise with the original goals of DFT.

The exchange–correlation energy E_{xc} in (16.43) contains the following components: the *kinetic correlation energy* [the $\Delta\bar{T}$ term in (16.43), which is the difference in $\bar{T}$ for the real molecule and the reference system of noninteracting electrons—Eq. (16.41)], the *exchange energy* (which arises from the antisymmetry requirement), the *Coulombic correlation energy* (which is associated with interelectronic repulsions), and a *self-interaction correction* (SIC). The SIC arises from the fact that the classical charge-cloud electrostatic-repulsion expression $\frac{1}{2} \iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$ in (16.42) erroneously allows the portion of ρ in $d\mathbf{r}_1$ that comes from the smeared-out part of a particular electron to interact with the charge contributions of that same electron to ρ throughout space. In actuality, an electron does not interact with itself. (Note that for a one-electron molecule, there is no interelectronic repulsion, but the expression $\frac{1}{2} \iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$ erroneously gives an interelectronic repulsion.) The kinetic energy $\bar{T}_s$ of the reference system turns out to be close to $\bar{T}$ of the real molecule, and $\Delta\bar{T}/\bar{T}$ is small. However, the contribution of $\Delta\bar{T}$ to E_{xc} in (16.43) is not negligible.

The Local-Density Approximation (LDA)

Hohenberg and Kohn showed that if ρ varies extremely slowly with position, then $E_{xc}[\rho]$ is accurately given by

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r})\epsilon_{xc}(\rho) d\mathbf{r} \quad (16.52)$$

where the integral is over all space, $d\mathbf{r}$ stands for $dx dy dz$, and $\epsilon_{xc}(\rho)$ is the exchange plus correlation energy per electron in a homogeneous electron gas with electron density ρ .

Jellium is a hypothetical electrically neutral, infinite-volume system consisting of an infinite number of interacting electrons moving in a space throughout which positive charge is continuously and uniformly distributed. The number of electrons per unit volume in the jellium has a nonzero constant value ρ . The electrons in the jellium constitute a **homogeneous** (or **uniform**) **electron gas**. Taking the functional derivative of E_{xc}^{LDA} , we find [Eqs. (16.50) and (16.51)]

$$v_{xc}^{\text{LDA}} = \frac{\delta E_{xc}^{\text{LDA}}}{\delta \rho} = \varepsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \quad (16.53)$$

Kohn and Sham suggested the use of (16.52) and (16.53) as approximations to E_{xc} and v_{xc} in (16.46) and (16.47), a procedure that is called the **local density approximation** (LDA). One can show that ε_{xc} can be written as the sum of exchange and correlation parts:

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \quad (16.54)$$

where

$$\varepsilon_x(\rho) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} (\rho(\mathbf{r}))^{1/3} \quad (16.55)$$

The correlation part $\varepsilon_c(\rho)$ has been calculated, and the results have been expressed as a very complicated function $\varepsilon_c^{\text{VWN}}$ of ρ by Vosko, Wilk, and Nusair (VWN); see *Parr and Yang*, Appendix E; S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980). Thus

$$\varepsilon_c(\rho) = \varepsilon_c^{\text{VWN}}(\rho) \quad (16.56)$$

where $\varepsilon_c^{\text{VWN}}$ is a known function. From (16.50), (16.51), (16.52), (16.54), and (16.55), we get (Prob. 16.25)

$$v_{xc}^{\text{LDA}} = v_x^{\text{LDA}} + v_c^{\text{LDA}}, \quad v_x^{\text{LDA}} = -\left[(3/\pi)\rho(\mathbf{r}) \right]^{1/3}, \quad v_c^{\text{LDA}} = v_c^{\text{VWN}} \quad (16.57)$$

$$E_x^{\text{LDA}} \equiv \int \rho \varepsilon_x d\mathbf{r} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int [\rho(\mathbf{r})]^{4/3} d\mathbf{r} \quad (16.58)$$

The method for finding the LDA quantities ε_x and ε_c is as follows (for fuller details, see *Parr and Yang*, Appendix E). Consider a uniform electron gas (UEG) with $\rho(\mathbf{r}) = k$, where k is some constant value. As noted after (16.51), $v_{xc} = v_{xc}(\rho(\mathbf{r}))$, and since $\rho(\mathbf{r})$ is a constant for a particular UEG, v_{xc} is a constant for a particular UEG. (Of course v_{xc} will have different values for two UEGs with different electron densities.) In the Kohn–Sham equations (16.47) for the reference system that corresponds to the UEG, the constant v_{xc} can be omitted without affecting the eigenfunctions (Prob. 4.52). Also, for a UEG, the second term in brackets in (16.47) (the external potential) must be replaced by the attraction between electron 1 and the uniformly distributed positive charge. Since the UEG is electrically neutral, the positive charge density equals the electron density, and the second and third terms in brackets in (16.47) cancel. Thus, the term $-\frac{1}{2}\nabla_1^2$ is the only surviving term in $\hat{h}^{\text{KS}}$ for the UEG. The UEG KS orbitals can thus be taken as three-dimensional free-particle wave functions $Ae^{i(k_x x + k_y y + k_z z)}$ [recall (2.30)], where the value of A is chosen to give the desired electron density in (16.45). Because the UEG is electrically neutral in each region of space, the sum of the electrostatic repulsions between the smeared-out electrons [the third term on the right side of (16.46)], the attractions between the smeared-out electrons and the continuous positive charge distribution [the first term on the right of (16.46) modified to correspond to continuous positive charges], and the repulsions between parts of the positive charge distribution [analogous to the internuclear repulsion term to be added to (16.46)] adds

to zero. This leaves on the right side of the energy expression (16.46) only the E_{xc} term and the kinetic-energy term $\bar{T}_s$, which is readily evaluated from the known KS orbitals. Breaking E_{xc} into the sum of E_x and E_c [Eq. (16.59)], one evaluates E_x from (16.60) and the KS orbitals, with the result shown in (16.58). This leaves only E_c as unknown. One then does an accurate numerical solution of the UEG Schrödinger equation to find the energy for the particular density $\rho = k$. Combining this energy with the already calculated KS energy terms gives the unknown E_c for that ρ . Repetition of the entire procedure for many density values gives the UEG E_c as a function of ρ . From E_x and E_c , we find ε_x and ε_c .

The Functionals E_x and E_c

As an aid to developing approximate functionals for use in KS DFT, the functional E_{xc} is written as the sum of an **exchange-energy functional** E_x and a **correlation-energy functional** E_c :

$$E_{xc} = E_x + E_c \quad (16.59)$$

E_x is defined by the same formula used for the exchange energy in Hartree–Fock theory, except that the Hartree–Fock orbitals are replaced by the Kohn–Sham orbitals. The Hartree–Fock exchange energy of a closed-shell molecule is given by the terms in (14.22) that involve the exchange integrals K_{ij} . Replacing the Hartree–Fock orbitals by the Kohn–Sham orbitals in (14.24), we have for a closed-shell molecule

$$E_x = -\frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n \langle \theta_i^{\text{KS}}(1) \theta_j^{\text{KS}}(2) | 1/r_{12} | \theta_j^{\text{KS}}(1) \theta_i^{\text{KS}}(2) \rangle \quad (16.60)$$

where the factor of $\frac{1}{4}$ comes from the fact that in (14.22) we are summing over the orbitals, whereas in (16.60) we are summing over the electrons, which gives four times as many terms in the double sum in (16.60) (Prob. 16.26). Since, in practice, KS orbitals are found to rather closely resemble Hartree–Fock orbitals, the DFT exchange energy is close to the Hartree–Fock exchange energy. Now that E_x is defined, the correlation-energy functional E_c is defined as the difference between E_{xc} and E_x ; that is $E_c \equiv E_{xc} - E_x$, and (16.59) follows. When E_x is evaluated using the definition (16.60) and E_c is evaluated by one of the currently available models (such as the LDA), one obtains poor results for molecular properties. Thus, in practice it is best to model both E_x and E_c , because this leads to cancellation of errors and better results. One therefore uses the LDA (or one of its improved versions discussed later) to find both E_x and E_c . (For further discussion of why the known exact E_x expression is replaced by an approximate E_x expression, see V. N. Staroverov, Chapter 6 in *A Matter of Density*, N. Sukumar, ed., Wiley, 2013.)

Both E_x and E_c are negative, with $|E_x|$ being much larger than $|E_c|$. The definition of E_c in DFT differs from the definition (11.16) of the correlation energy in Hartree–Fock theory, but analysis and calculations show that these two quantities are nearly equal [E. K. U. Gross et al. in B. B. Laird et al. (eds.), *Chemical Applications of Density Functional Theory*, American Chemical Society, 1996, Chapter 3]. Starting with accurate electron densities from MRCI wave functions for Li_2 , N_2 , and F_2 , Gritsenko and co-workers used an iterative procedure to calculate KS orbitals and the KS quantities E_x and E_c for each of these molecules at three internuclear distances [O. V. Gritsenko et al., *J. Chem. Phys.*, **107**, 5007 (1997)]. The KS E_x and E_c values were found to be very close to the corresponding Hartree–Fock (HF) values E_x^{HF} and E_c^{HF} at the equilibrium internuclear distances, but agreement between these quantities decreased as the internuclear distances increased. For N_2 at R_e , values in hartrees for these quantities and for quantities in (16.41) are: $E_x = -13.114$, $E_x^{\text{HF}} = -13.008$; $E_c = -0.475$, $E_c^{\text{HF}} = -0.469$; $\Delta\bar{T} = 0.329$, $\bar{T} = 109.399$. The correlation kinetic energy $\Delta\bar{T}$ is a significant part of E_c .

The $X\alpha$ Method

The following approximation for E_{xc} gives the **$X\alpha$ method** (the X stands for exchange). Here, the correlation contribution to E_{xc} is omitted (it is substantially smaller in magnitude than the exchange contribution), and the exchange contribution is taken as

$$E_{xc} \approx E_x^{X\alpha} = -\frac{9}{8} \left(\frac{3}{\pi} \right)^{1/3} \alpha \int [\rho(\mathbf{r})]^{4/3} d\mathbf{r} \quad (16.61)$$

where α is an adjustable parameter; α values from $\frac{2}{3}$ to 1 have been used. Functional differentiation of (16.61) [Eqs. (16.50) and (16.51)] gives the $X\alpha$ exchange potential as $v_x^{X\alpha} = -(3\alpha/2)(3\rho/\pi)^{1/3}$. Note that with $\alpha = \frac{2}{3}$, the $X\alpha$ expression (16.61) for E_{xc} becomes equal to the exchange part (16.58) of the LDA E_{xc} expression. The $X\alpha$ method gives rather erratic results in molecular calculations and has been superseded by better approximations to E_{xc} . The $X\alpha$ method was developed by Slater prior to the work of Hohenberg, Kohn, and Sham, and was viewed by Slater as an approximation to the Hartree–Fock method. It is sometimes called the Hartree–Fock–Slater method. However, the $X\alpha$ method is best viewed as a special case of DFT.

Performing Kohn–Sham Density-Functional Calculations

How does one do a molecular density-functional calculation with E_{xc}^{LDA} (or some other functional)? One starts with an initial guess for ρ , which is usually found by superposing calculated electron densities of the individual atoms at the chosen molecular geometry. From the initial guess for $\rho(\mathbf{r})$, an initial estimate of $v_{xc}(\mathbf{r})$ is found from (16.53) and (16.57). This initial $v_{xc}(\mathbf{r})$ is used in the Kohn–Sham equations (16.47), which are solved for the initial estimate of the KS orbitals. In solving (16.47), the θ_i^{KS} 's are usually expanded in terms of a set of basis functions χ_r

$$\theta_i^{\text{KS}} = \sum_{r=1}^b c_{ri} \chi_r$$

to yield equations that resemble the Hartree–Fock–Roothaan equations (14.34) and (14.56), except that the Fock matrix elements $F_{rs} = \langle \chi_r | \hat{F} | \chi_s \rangle$ are replaced by the Kohn–Sham matrix elements $h_{rs}^{\text{KS}} = \langle \chi_r | \hat{h}^{\text{KS}} | \chi_s \rangle$, where $\hat{h}^{\text{KS}}$ is in (16.48) and (16.49). Thus, instead of (14.34), in KS DFT with a basis-set expansion of the orbitals, one solves the equations

$$\sum_{s=1}^b c_{si} (h_{rs}^{\text{KS}} - \varepsilon_i^{\text{KS}} S_{rs}) = 0, \quad r = 1, 2, \dots, b \quad (16.62)$$

The basis functions most commonly used in molecular KS DFT calculations are contracted Gaussians, but some DF programs use STOs or still other basis functions.

The KS equations can also be solved numerically, without using a basis-function expansion of the orbitals, but this choice is not often used.

The initially found θ_i^{KS} 's are used in (16.45) to get an improved electron density, which is then used to find an improved v_{xc} , which is then used in the KS equations (16.47) to find improved KS orbitals, and so on. The iterations continue until there is no further significant change in the density and the KS orbitals. KS DFT calculations involve iterations until self-consistency between the exchange–correlation potential v_{xc} and the KS orbitals θ_i^{KS} in (16.47) has been reached. They are thus a kind of SCF calculation.

Once the calculation has converged, the ground-state energy E_0 in (16.46) is found from the converged ρ and E_{xc}^{LDA} (or whatever functional is being used). The dipole moment can be calculated from ρ using (14.21), and other one-electron properties can be found from (14.8). Analytic gradients of the energy have been developed for KS DFT calculations, so the equilibrium geometry is readily found using one of the methods of Section 15.10.

Analytic second derivatives of the KS DFT energy are available, and DF vibrational frequencies are readily calculated.

One significant difference between KS DFT calculations and Hartree–Fock calculations arises from the fact that $v_{xc}^{\text{LDA}}(\mathbf{r})$ and versions of v_{xc} more accurate than the LDA are very complicated functions of the coordinates. This makes it impossible to analytically evaluate the integrals $\langle \chi_r | v_{xc} | \chi_s \rangle$, which occur in h_{rs}^{KS} . Instead, $\langle \chi_r | v_{xc} | \chi_s \rangle$ is evaluated numerically by evaluating the integrand at each point of a grid of points in the molecule and performing a summation. [A less-used alternative approach is to expand $v_{xc}(\mathbf{r})$ using an auxiliary set of basis functions (not the same set used to expand the orbitals), where the expansion coefficients are chosen to give a good least-squares fit to values of $v_{xc}(\mathbf{r})$ evaluated at a grid of points.] The numerical evaluation of the $\langle \chi_r | v_{xc} | \chi_s \rangle$ integrals is the most time-consuming step in a DFT calculation with Gaussian basis functions. If too few grid points are used, inaccurate results will be obtained. If very many grid points are used, the calculation time can become prohibitive. Many DFT programs give the user the power to choose the grid size. [See J. M. L. Martin et al., *Comput. Phys. Commun.*, **133**, 189 (2001).]

DF calculations that use a basis-set expansion of the KS orbitals involve the same Coulomb matrix elements J_{rs} [Eq. (15.79)] that occur in Hartree–Fock calculations. Such DF calculations can be speeded up and linear scaling obtained for large molecules by the same techniques used to speed up Hartree–Fock calculations, namely, direct and semidirect methods, neglect of integrals smaller than a threshold value, use of the RI method to evaluate electron repulsion integrals, the continuous fast multipole and quantum-chemical tree-code methods, the J -matrix engine. For details, see the references in Section 15.16. Also the conjugate-gradient density-matrix search method (Section 17.4) can be used to avoid diagonalizing the Kohn–Sham matrix.

Deviations of KS DF calculated results from the true values are due to use of approximate E_{xc} and v_{xc} expressions, and to basis-set inadequacies.

The programs *Gaussian*, GAMESS, Q-Chem, Jaguar, Turbomole, Molpro, NWChem, Spartan, ORCA, and HyperChem (Section 15.14) all contain KS DFT modules. Some programs that only do KS DFT calculations are ADF (www.scm.com) and deMon (www.demon-software.com).

The Local-Spin-Density Approximation (LSDA)

For open-shell molecules and molecular geometries near dissociation, the **local-spin-density approximation** (LSDA) gives better results than the LDA. Whereas in the LDA, electrons with opposite spins paired with each other have the same spatial KS orbital, the LSDA allows such electrons to have different spatial KS orbitals $\theta_{i\alpha}^{\text{KS}}$ and $\theta_{i\beta}^{\text{KS}}$. The LSDA is thus analogous to the UHF method (Section 15.3), which allows different spatial Hartree–Fock orbitals for electrons with different spins. The theorems of Hohenberg, Kohn, and Sham do not require using different orbitals for electrons with different spins (unless an external magnetic field is present), and if the exact functional $E_{xc}[\rho]$ were known, one would not do so. With the approximate E_{xc} functionals that are used in KS DFT calculations, it is advantageous to allow the possibility of different orbitals for electrons with different spins, so as to improve calculated properties of open-shell species and species with geometries near dissociation.

The generalization of density-functional theory that allows different orbitals for electrons with different spins is called **spin-density-functional theory** (Parr and Yang, Chapter 8). In spin-DFT, one deals separately with the electron density $\rho^\alpha(\mathbf{r})$ due to the spin- α electrons and the density $\rho^\beta(\mathbf{r})$ of the spin- β electrons, and functionals such as E_{xc} become functionals of these two quantities: $E_{xc} = E_{xc}[\rho^\alpha, \rho^\beta]$. One deals with separate Kohn–Sham eigenvalue equations for the spin- α orbitals and the spin- β orbitals, where these equations have $v_{xc}^\alpha = \delta E_{xc}[\rho^\alpha, \rho^\beta] / \delta \rho^\alpha$ and similarly for v_{xc}^β . For species like CH_3

or the O₂ triplet ground state, the number n^α of α electrons differs from the number of β electrons, so here $\rho^\alpha \neq \rho^\beta$, and spin-DFT will give different orbitals for electrons with different spins.

Gunnarsson and Lundqvist did an LSDA spin-DFT calculation of the H₂ molecule, expanding the occupied KS orbitals using the $1s_a$ and $1s_b$ AOs as basis functions. For internuclear separations up to 3.2 bohrs, they found the lowest energy KS orbitals to be $\theta_\alpha^{\text{KS}} = \theta_\beta^{\text{KS}} = N(1s_a + 1s_b)$. However, for internuclear separations greater than 3.2 bohrs, they found the lowest-energy KS orbitals to be $\theta_\alpha^{\text{KS}} = N(1s_a + c1s_b)$ and $\theta_\beta^{\text{KS}} = N(c1s_a + 1s_b)$, where $c < 1$ and c decreased to zero as the internuclear separation increased to infinity. Having the spin- α electron's KS orbital differ from that of the spin- β electron allowed the H₂ molecular energy versus internuclear separation curve to show the proper dissociation behavior, corresponding to dissociation to one hydrogen atom with a spin- α electron and a second H atom with a spin- β electron. [Recall that the RHF wave function of H₂ dissociates improperly. The UHF H₂ wave function shows proper dissociation (*Szabo and Ostlund*, Section 3.8.7).]

As in the UHF method, allowing differing KS orbitals for electrons with different spins can produce a wave function for the reference system s that is not an eigenfunction of $\hat{S}^2$, but this spin-contamination is less of a problem in KS DFT than in the UHF method.

For species with all electrons paired and molecular geometries in the region of the equilibrium geometry, we can expect that $\rho^\alpha = \rho^\beta$, and spin-DFT will reduce to the ordinary form of DFT.

Despite the fact that ρ in a molecule is not a slowly varying function of position, the LSDA works surprisingly well for calculating molecular equilibrium geometries, vibrational frequencies, and dipole moments, even for transition-metal compounds, where Hartree–Fock calculations often give poor results. However, calculated LSDA molecular atomization energies are very inaccurate. Accurate dissociation energies require functionals that go beyond LSDA.

Gradient-Corrected (GGA) Functionals

The LDA and LSDA are based on the uniform-electron-gas model, which is appropriate for a system where ρ varies slowly with position. The integrand in the expression (16.52) for E_{xc}^{LDA} is a function of only ρ , and the integrand in E_{xc}^{LSDA} is a function of only ρ^α and ρ^β . Functionals that go beyond the LSDA aim to correct the LSDA for the variation of electron density with position. A common way to do this is by including the gradients [Eq. (5.30)] of ρ^α and ρ^β in the integrand. Thus

$$E_{xc}^{\text{GGA}}[\rho^\alpha, \rho^\beta] = \int f(\rho^\alpha(\mathbf{r}), \rho^\beta(\mathbf{r}), \nabla\rho^\alpha(\mathbf{r}), \nabla\rho^\beta(\mathbf{r})) d\mathbf{r} \quad (16.63)$$

where f is some function of the spin densities and their gradients. The letters GGA stand for **generalized-gradient approximation**. The term **gradient-corrected functional** is also used. (The LDA functional is called a **local** functional because it involves only the value of ρ at the point $\mathbf{r}$. Gradient-corrected functionals are called **semilocal** because they involve the values of ρ at $\mathbf{r}$ and in an infinitesimal neighborhood of $\mathbf{r}$.) E_{xc}^{GGA} is usually split into exchange and correlation parts, which are modeled separately:

$$E_{xc}^{\text{GGA}} = E_x^{\text{GGA}} + E_c^{\text{GGA}} \quad (16.64)$$

Approximate gradient-corrected exchange and correlation energy functionals are developed using theoretical considerations such as the known behavior of the true (but unknown) functionals E_x and E_c in various limiting situations as a guide. Often some empiricism is thrown in by choosing the values of parameters in the functionals to give good performance for known values of various molecular properties.

Some commonly used GGA exchange functionals E_x are Perdew and Wang's 1986 functional (which contains no empirical parameters), designated PW86 or PWx86, Becke's 1988 functional, denoted B88, Bx88, Becke88, or B, and Perdew and Wang's 1991 exchange functional PWx91. The explicit form of the B88 exchange functional is

$$E_x^{\text{B88}} = E_x^{\text{LSDA}} - b \sum_{\sigma=\alpha,\beta} \int \frac{(\rho^\sigma)^{4/3} \chi_\sigma^2}{1 + 6b\chi_\sigma \ln[\chi_\sigma + (\chi_\sigma^2 + 1)^{1/2}]} d\mathbf{r} = E_x^{\text{LSDA}} + \Delta E_x^{\text{B88}}$$

where $\chi_\sigma \equiv |\nabla \rho^\sigma|/(\rho^\sigma)^{4/3}$, b is an empirical parameter whose value 0.0042 atomic units was determined by fitting known Hartree–Fock exchange energies (which are close to KS exchange energies) of several atoms, ΔE_x^{B88} is an abbreviation for the B88 gradient correction to E_x^{LSDA} , and [see (16.58) and Prob. 16.27]

$$E_x^{\text{LSDA}} = -\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} \int [(\rho^\alpha)^{4/3} + (\rho^\beta)^{4/3}] d\mathbf{r} \quad (16.65)$$

The PWx86 functional (which has no empirical parameters) and the B88 exchange functional work about equally well in predicting molecular properties.

Commonly used GGA correlation functionals E_c include the Lee–Yang–Parr (LYP) functional, the Perdew 1986 correlation functional (P86 or Pc86), and the Perdew–Wang 1991 parameter-free correlation functional (PW91 or PWC91).

The Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional has no empirical parameters [*Phys. Rev. Lett.*, **77**, 3865 (1996)] and is widely used in DFT calculations on solids.

Some E_x and E_c values in hartrees for the Ar atom are (A. D. Becke in *Yarkony*, Chapter 15): $E_x^{\text{HF}} = -30.19$, $E_x^{\text{LSDA}} = -27.86$, $E_x^{\text{B88}} = -30.15$; $E_c^{\text{HF}} = -0.722$, $E_c^{\text{LSDA}} = -1.431$, $E_c^{\text{PW91}} = -0.768$, where the Hartree–Fock (HF) values should be good estimates of the KS DFT values. These values may be compared with the total energy -527.54 hartrees for Ar, so the exchange and correlation energies are about 6% and 0.14%, respectively, of the total energy.

Any exchange functional can be combined with any correlation functional. For example, the notation BLYP/6-31G* denotes a DFT calculation done with the Becke 1988 exchange functional and the Lee–Yang–Parr correlation functional, with the KS orbitals expanded in a 6-31G* basis set. The letter S (which acknowledges Slater's $X\alpha$ method) denotes the LSDA exchange functional (16.65). VWN denotes the Vosko–Wilk–Nusair expression for the LSDA correlation functional. (Actually, these workers gave two different expressions for E_c^{LSDA} , which are sometimes referred to as VWN3 and VWN5.) Thus an LSDA calculation can be denoted by the letters LSDA or by SVWN.

Meta-GGA Functionals

The GGA density functionals of the form (16.63) depend on the ground-state electron probability density ρ and its first derivatives. One way to improve on GGA functionals is to go to functionals that also depend on the second derivatives of ρ and/or a quantity called the kinetic-energy density (which is defined below). Such functionals are called **meta-GGA** (mGGA) functionals and have the form

$$E_{xc}^{\text{MGGA}}[\rho^\alpha, \rho^\beta] = \int f(\rho^\alpha, \rho^\beta, \nabla \rho^\alpha, \nabla \rho^\beta, \nabla^2 \rho^\alpha, \nabla^2 \rho^\beta, \tau_\alpha, \tau_\beta) d\mathbf{r} \quad (16.66)$$

where the *Kohn–Sham kinetic-energy density* for the spin- α electrons is defined by

$$\tau_\alpha \equiv \frac{1}{2} \sum_i |\nabla \theta_{i\alpha}^{\text{KS}}|^2$$

where the $\theta_{i\alpha}^{\text{KS}}$'s are the Kohn–Sham orbitals for the spin- α electrons and the sum goes over the occupied orbitals. The reason for the name “kinetic-energy density” becomes clear if you look at Prob. 7.7(b). Most meta-GGA functionals omit $\nabla^2\rho^\alpha$ and $\nabla^2\rho^\beta$ from (16.66). The dependency of a meta-GGA functional on τ_α and τ_β can occur in the exchange part, in the correlation part, or in both parts of the functional.

Meta-GGA DFT calculations require a little more time than GGA calculations and can give better results than GGA calculations.

Becke's B95 meta-GGA correlation functional, containing two parameters whose values were fitted to atomic correlation energy data, is often used. The TPSS (Tau, Perdew, Staroverov, Scuseria) meta-GGA functional has given good results for many properties. A reparametrization of TPSS gave the oTPSS functional, where o is for optimized [L. Goerigk and S. Grimme, *J. Chem. Theory Comput.*, **6**, 107 (2010)].

Hybrid Functionals

Hybrid exchange–correlation functionals are widely used. A hybrid functional mixes together the formula (16.60) for E_x with GGA (or meta-GGA) E_x and E_c formulas and was first proposed by Becke. For example, the popular **B3LYP** (or Becke3LYP) hybrid GGA functional (where the 3 indicates a three-parameter functional) is defined by

$$\begin{aligned} E_{xc}^{\text{B3LYP}} &= (1 - a_0 - a_x)E_x^{\text{LSDA}} + a_0E_x^{\text{exact}} + a_xE_x^{\text{B88}} + (1 - a_c)E_c^{\text{VWN}} + a_cE_c^{\text{LYP}} \\ E_{xc}^{\text{B3LYP}} &= 0.08E_x^{\text{LSDA}} + 0.20E_x^{\text{exact}} + 0.72E_x^{\text{B88}} + 0.19E_c^{\text{VWN}} + 0.81E_c^{\text{LYP}} \quad (16.67) \\ E_{xc}^{\text{B3LYP}} &= 0.80E_x^{\text{LSDA}} + 0.20E_x^{\text{exact}} + 0.72\Delta E_x^{\text{B88}} + 0.19E_c^{\text{VWN}} + 0.81E_c^{\text{LYP}} \end{aligned}$$

In (16.67), E_x^{exact} (which is usually denoted E_x^{HF} , since it uses a Hartree–Fock definition of E_x) is given by (16.60); the parameter values $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$ were chosen to give good fits to experimental molecular atomization energies; and the relation $E_x^{\text{B88}} = E_x^{\text{LSDA}} + \Delta E_x^{\text{B88}}$ [the equation after (16.64)] was used. In the B3PW91 hybrid functional, E_c^{PW91} replaces E_c^{LYP} in (16.67), and the same a values are used. Becke's one-parameter hybrid meta-GGA functional B1B95 (also called B1B96) is $E_{xc}^{\text{B1B95}} = (1 - a_0)E_x^{\text{B88}} + E_c^{\text{B95}} + a_0E_x^{\text{exact}}$, where the empirical-parameter value $a_0 = 0.28$ was found by fitting atomization energies. One says that B1B95 contains 28% exact exchange.

Although Becke's name is associated with the widely used B3LYP functional, he did not actually propose it. Rather, he proposed the B3PW91 functional and chose the three parameters in it to fit experimental data [A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993)]. Other workers then replaced E_c^{PW91} with E_c^{LYP} and did not change the three parameter values, giving the B3LYP functional. They then programmed B3LYP into the *Gaussian* program. The enormous popularity of B3LYP is evidenced by the fact that Becke's paper has been cited over 45000 times.

As an improvement on the B3LYP, B3PW91, and B1B95 hybrid functionals, Becke [A. D. Becke, *J. Chem. Phys.*, **107**, 8554 (1997); H. L. Schmider and Becke, *J. Chem. Phys.*, **108**, 9624 (1998)] proposed the B97 hybrid GGA functional

$$E_{xc} = E_x^{\text{GGA}} + c_xE_x^{\text{exact}} + E_c^{\text{GGA}} \quad (16.68)$$

where c_x is a parameter and E_x^{GGA} and E_c^{GGA} are certain GGA functionals that contain three and six parameters, respectively. The values of the 10 parameters in E_{xc} were determined as the set that gave the best fit to experimental energy data in the G2 test set (Section 16.1). Using a numerical method to solve the Kohn–Sham equations (so as to avoid basis-set truncation error), Becke found that the functional (16.68) gave a mean absolute error (MAE) of only 1.8 kcal/mol for 55 atomization energies, a significant improvement over the functional B3PW91, which had an MAE of 2.4 kcal/mol for these energies. Revised versions of B97, called B97-1, B97-2, and B97-3 exist. [For the references, see Table 2

in Y. Zhao et al., *J. Chem. Theory Comput.*, **2**, 364 (2006).] B98 is a hybrid GGA exchange–correlation functional that is a revision of B97.

The PBE0 functional is a hybrid extension of PBE and includes 25% exact exchange.

Most density functionals give only fair accuracy for predicted activation energies (barrier heights) for chemical reactions. The BMK (Boese–Martin for kinetics) hybrid meta-GGA exchange–correlation functional uses 42% exact exchange and contains 16 parameters whose values were chosen to give good performance for barrier heights without significantly sacrificing performance on other properties [A. D. Boese and J. M. L. Martin, *J. Chem. Phys.*, **121**, 3405 (2004)].

To speed up density-functional calculations on large molecules, one can use the density fitting (RI) method (Section 16.3). Hybrid functionals have the disadvantage that when density fitting is used with hybrid functionals, the calculations are much slower than when a functional that does not include exact exchange is used.

GGA, meta-GGA, hybrid-GGA, and hybrid-meta-GGA functionals give not only good equilibrium geometries, vibrational frequencies, and dipole moments, but also generally accurate molecular atomization energies. For example, B3LYP/6-311+G(2d,p) calculations on the G2 data set gave an MAE of 3.1 kcal/mol (*Foresman and Frisch*, Chapter 7).

Double-Hybrid Functionals

Grimme proposed improving DFT energy results by using the MP2 second-order energy-correction formula, as follows [S. Grimme, *J. Chem. Phys.*, **124**, 034108 (2006)]. One first defines a hybrid-GGA DFT functional of the form

$$E_{xc}^{\text{hybrid-GGA}} = a_1 E_x^{\text{GGA}} + (1 - a_1) E_x^{\text{exact}} + a_2 E_c^{\text{GGA}} \quad (16.69)$$

and uses this functional to self-consistently solve for KS orbitals (both occupied and virtual) and orbital energies by the standard DFT approach. One then calculates an improved value of E_{xc} as

$$E_{xc} = E_{xc}^{\text{hybrid-GGA}} + (1 - a_2) E_c^{\text{KS-MP2}} \quad (16.70)$$

where $E_c^{\text{KS-MP2}}$ is calculated from the MP2 equation (16.13) using the KS orbitals and KS orbital energies. This improved E_{xc} is then used in (16.46) to calculate the ground-state energy E_0 . The two parameters a_1 and a_2 are chosen as values that give good fits to a chosen set of data. Grimme defined the B2-PLYP functional, also called B2PLYP (where the 2 indicates two parameters and the first P stands for perturbation), by taking E_x^{GGA} as the B88 exchange functional, taking E_c^{GGA} as the LYP correlation functional, and taking $a_1 = 0.47$, $a_2 = 0.73$. The mPW2-PLYP functional uses the modified Perdew–Wang functional for exchange and LYP for correlation, and has $a_1 = 0.45$, $a_2 = 0.75$. Since an MP2 energy calculation is required, this method requires significantly more time than a conventional DFT calculation, but the MP2 calculation can be speeded up by using the RI approximation (Section 16.3). Also, since the method is intermediate between DFT and MP2, to get good results a larger basis set is required than for DFT, but smaller than for MP2. Instead of the MP2 expression in (16.70), the SCS-MP2 energy can be used.

For the G3/05 test set (Section 16.1), mean absolute deviations from experiment are 2.5 kcal/mol for B2-PLYP and 2.1 kcal/mol for mPW2-PLYP, as compared with 4.4 kcal/mol for B3LYP [T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, **8**, 4398 (2006)]. In these calculations, the geometry was found from a B3LYP calculation with a VTZ2P basis set, and the single-point energy calculation was done using a polarized valence quadruple-zeta basis set.

B2PLYP and mPW2PLYP are called **double-hybrid density functionals (DHDFs)**, since they mix in not only some exact exchange but also some correlation calculated by the MP2 method.

According to Grimme, “DHDFs are currently by far the most accurate DFT methods available” [S. Grimme et al., *WIREs, Comput. Mol. Sci.*, **2**, 886 (2012)].

The preceding density functionals have been grouped into five categories, as follows.

1. The LDA expression for E_{xc} involves only $\rho(\mathbf{r})$.
2. GGA functionals involve both ρ and $\nabla\rho$.
3. Meta-GGA functionals involve ρ , $\nabla\rho$, and either $\nabla^2\rho$ or τ .
4. Hybrid functionals add exact exchange.
5. Double hybrid functionals add a dependence on the unoccupied KS orbitals.

These five categories of functionals correspond roughly to the five rungs on what Perdew called a Jacob’s ladder (Genesis 28:10–12) of successively more accurate functionals [J. Perdew and K. Schmidt, AIP Conf. Proc. **577**, 1 (2001); <http://dx.doi.org/10.1063/1.1390175>].

Dispersion Corrections

A major deficiency of most of the functionals discussed so far is their poor performance in dealing with intramolecular and intermolecular London dispersion interactions between nonbonded atoms. Such interactions are important in large molecules such as biomolecules. Several methods have been proposed to deal with this failing. For a review, see S. Grimme, *WIREs Comput. Mol. Sci.*, **1**, 211 (2011).

One approach is to simply add on to the energy a correction term for dispersion after the usual KS DFT energy calculation has been done. This procedure is called the **DFT-D** method. The simplest form of correction term is $E_{\text{disp}} = -\sum_{AB} (C_{AB}/R_{AB}^6) f(R_{AB})$ [see Eq. (14.103)] where the sum goes over all pairs of atoms A and B, C_{AB} is a constant, R_{AB} is the distance between A and B, and $f(R_{AB})$ is a damping function that makes E_{disp} go to zero as $R_{AB} \rightarrow 0$. In practice, more complicated forms of E_{disp} are used. The most successful of several DFT-D methods is the **DFT-D3** method; the 3 indicates the third version [S. Grimme et al., *J. Chem. Phys.*, **132**, 154104 (2010)]. DFT-D3 includes three empirically determined parameters in E_{disp} , calculates the C_{AB} coefficients theoretically, and also includes a $1/R_{AB}^8$ term. The values of the three parameters depend on which functional the dispersion correction is being used with. The DFT-D energy is $E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$.

A few highly parametrized functionals that do not include explicit allowance for dispersion do fairly well for nonbonded interactions. An example is the M06-2X functional.

Vydrov and Van Voorhis devised the two-parameter **VV10** correlation functional E_c^{VV10} that can be added to any existing E_{xc} functional that does not give significant binding in van der Waals complexes to produce a functional that provides for dispersion [O. A. Vydrov and T. Van Voorhis, *J. Chem. Phys.*, **133**, 244103 (2010)]. Tests of VV10 with various standard hybrid functionals found quite good performance for energies of non-covalent interactions (5 to 10% error) and for intramolecular and intermolecular distances in the complexes of the S22 and S66 test sets [W. Hujo and S. Grimme, *J. Chem. Theory Comput.*, doi: 10.1021/ct300813c and references cited therein]. The performance of VV10 was similar to that of DFT-D3. DFT-D3 is computationally much faster than VV10, but VV10 may be more generally applicable than DFT-D3.

Evaluation of Functionals

Hundreds of density functionals have been proposed. For listings and classifications of over 40 functionals, see N. E. Schultz et al., *J. Phys. Chem. A*, **109**, 11127 (2005); **109**, 4388 (2005); Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, **1**, 415 (2005). There is no correct answer to the question “Which is the best DFT functional?”, since functionals that give good results for organic compounds may give inferior results for inorganic compounds, and functionals that give good results for energy changes in reactions may give

inferior results for activation energies of reactions. Thus the best functional to use depends on the kinds of compounds being studied and on which properties are being calculated. During the period 1995–2010, the B3LYP functional was the most widely used by chemists, since it gives good results for a number of commonly studied properties. Functionals that surpass the performance of B3LYP have been developed and will see increasing use.

Zhao and Truhlar developed a set of meta-GGA exchange–correlation functionals that have the following percentages of exact (Hartree–Fock) exchange: 0% for M06-L, 27% for M06, 28% for M05, 54% for M06-2X, 56% for M05-2X, and 100% for M06-HF [Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, **120**, 215 (2008); *Acc. Chem. Res.*, **41**, 157 (2008)]. M06 stands for the University of Minnesota 2006 and L stands for “local,” indicating that no exact exchange is included. [For the functional $E_{xc} = (Y/100)E_x^{\text{exact}} + (1 - Y/100)E_x^{\text{DFT}} + E_c^{\text{DFT}}$, the percentage of exact exchange is Y .] These functionals each have about 35 parameters. Zhao and Truhlar tested the performance of 15 functionals for a variety of properties and found that M06-2X, BMK, and M05-2X gave the best performance for main-group thermochemistry and kinetics. For example, for 177 energy changes, some mean absolute errors (MAEs) are 1.3 kcal/mol for M06-2X as compared with 2.6 kcal/mol for B98 and 3.6 kcal/mol for B3LYP; for 76 chemical-reaction barrier heights, the MAEs are 1.2 kcal/mol for M06-2X as compared with 3.6 kcal/mol for B98 and 4.5 kcal/mol for B3LYP. (These tests used polarized triple-zeta basis sets.) M06-L and M06 gave the best performance for transition-metal thermochemistry. M06-2X, M05-2X, M06-HF, M06, and M06-L gave the best performance for noncovalent interactions such as hydrogen bonding. The absence of exact exchange in M06-L speeds up calculations and allows larger systems to be treated.

Goerigk and Grimme used the GMTKN30 database (Section 16.1) to test 47 functionals with the DFT-D3 dispersion correction added to most of them [L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, **13**, 6670 (2011)]. With a quadruple-zeta polarized basis set, they found the following weighted mean absolute energy errors in kcal/mol (given in parentheses) for functionals on the five rungs of Perdew’s Jacob’s ladder of functionals: LDA (12.0), GGA functionals (5.3), meta-GGA functionals (4.4), hybrid functionals (3.3), double-hybrid functionals (1.8). The popular B3LYP-D3 functional did worse than average for hybrid functionals with 3.8. MP2 results for comparison are MP2/CBS (3.6), SCS-MP2/CBS (2.9), and SOS-MP2/CBS (3.8). The best overall GGAs were B97-D3 (4.8) and revPBE-D3 (4.6). The best meta-GGA was oTPSS-D3 (3.8), and the best hybrids were M062X-D3 (2.2) (but this functional had SCF convergence problems as did other Minnesota functionals) and PW6B95 (2.8). The best double-hybrids were DSD-BLYP-D3 (1.5) and PWPB95-D3 (1.6).

Basis Sets

In the **wave-function-theory (WFT)** correlation methods of Sections 16.2–16.4, the adequacy of the basis set is crucial. Use of too small a basis set gives unreliable results, and for the highest accuracy, one attempts to extrapolate to the complete basis-set limit. In DFT, which is based on the electron density ρ , rather than on the wave function, the basis set plays a smaller role, and rather good results can often be obtained with a rather small basis set, such as a DZP set (for example, 6-31G*). Moreover, in DFT most properties calculated with TZP basis sets have converged. The Goerigk and Grimme study of the last paragraph found quite significant improvement in going from a DZP to a TZP basis set, but little further improvement in going to a QZP set for most functionals. In DFT, one finds that a Pople basis set usually gives significantly better results than a correlation-consistent (cc) basis set of similar size [A. D. Boese et al., *J. Chem. Phys.*, **119**, 3005 (2003)]. Whereas in WFT, the cc basis sets usually allow a smooth extrapolation to the complete-basis-set limit, DFT/cc calculations sometimes show irregular convergence to a limit.

Excited States

DFT was originally developed as a ground-state theory, but several DFT theories that can calculate properties of excited electronic states have been developed. The most widely used such theory is **linear response time-dependent DFT (LR-TDDFT)**. Here, one applies time-dependent perturbation theory to the ground electronic state of a molecule perturbed by a weak oscillating time-dependent spatially uniform electric field. The effect of the applied field on the ground-state electronic density ρ is found to depend on a sum whose terms involve the energy differences $E_j - E_0$ between the various excited electronic states j and the ground electronic state, where these energies are calculated at the same molecular geometry. (Thus we are dealing with *vertical* excitation energies; see the CIS discussion in Section 16.2.) By using certain mathematical techniques, one can solve for the quantity $E_j - E_0$ for individual excited electronic states. Moreover, one can also calculate the strength of the electronic absorption to state j , so the electronic absorption spectrum can be predicted. By repeating the TDDFT calculation at various molecular geometries, one can find $E_j - E_0$ at each of these geometries for state j . Use of DFT-calculated E_0 values at these geometries then gives the potential-energy surface (Section 15.10) for the excited state j . Methods to find excited-state energy gradients analytically in LR-TDDFT have been developed, which allows efficient location of the equilibrium geometry of an excited state. Note that LR-TDDFT calculates properties of an excited state by examining the response of the ground-state electron density to the applied field.

The results of LR-TDDFT for vertical electronic excitation energies are quite good, with typical errors lying in the range 0.1 to 0.5 eV for situations where the theory is applicable, which is much better than for the CIS method (Section 16.2), which gives errors of 1 to 2 eV. Moreover, excited-state equilibrium geometries and vibrational frequencies are accurately calculated. However, LR-TDDFT works well only for excitations of a single valence electron to a low-lying excited state, and fails for molecules involving long-chain conjugated π -electron systems and for excited states involving charge transfer. Whether future functionals will increase the applicability of LR-TDDFT is unclear.

A review of single-reference methods for large-molecule excited-state calculations noted that LR-TDDFT can treat systems with up to 200 to 300 first-row atoms and stated that LR-TDDFT “is the most prominent method for the calculation of excited states of medium-sized and large molecules” [A. Dreuw and M. Head-Gordon, *Chem. Rev.*, **105**, 4009 (2005)]. For more on TDDFT, see C. Ullrich, *Time-Dependent Density-Functional Theory*, Oxford, 2012.

The Past and Future of DFT

Hohenberg, Kohn, and Sham’s work was published in 1964 and 1965. [For a personal account, see P. C. Hohenberg, W. Kohn, and L. J. Sham, *Adv. Quantum Chem.*, **21**, 7 (1990).] Quickly thereafter, physicists applied KS DFT using the LSDA to study solids with considerable success, and DFT became the dominant method of doing quantum-mechanical calculations on solids. Chemists were rather slow to apply DFT to molecules because of numerical difficulties in doing reliable DFT molecular calculations, the lack of widely available molecular DFT computational programs, and perhaps partly in reaction to disappointment with the $X\alpha$ method, which had been overpraised by some of its practitioners. The numerical difficulties were largely solved around 1980, and LSDA DFT molecular calculations in the 1980s achieved good results for molecular geometries but failed to give accurate dissociation energies.

The next major advance in DFT was the introduction of gradient-corrected functionals in the mid-1980s, which Becke found to give accurate dissociation energies. Also in 1988, analytic gradients were implemented in DFT, greatly facilitating calculation of equilibrium geometries. The 1989 DFT book by Parr and Yang helped draw the attention of quantum

chemists to DFT. In 1993, provision for DF calculations was added to the popular program *Gaussian*. In the mid-1990s molecular DFT calculations experienced explosive growth.

DFT has the advantage of allowing for correlation effects to be included in a calculation that takes roughly the same time as a Hartree–Fock calculation, which does not include correlation. Whether KS DFT should be classified as an ab initio method is a matter of debate. If the true E_{xc} were known and used, then KS DFT would be an ab initio method. However, the true E_{xc} is unknown and must be replaced by a model E_{xc} , such as the LSDA or the LSDA with gradient corrections. Some people would consider that use of E_{xc}^{LSDA} disqualifies KS DFT as being an ab initio method, but others would not. Many of the gradient-corrected functionals contain empirical parameters, and in hybrid functionals, the mixing constant(s) are determined empirically. Use of functionals with empirically determined parameters clearly disqualifies a method as being ab initio, but the number of parameters used in these versions of DFT is far fewer than the number used in common semiempirical theories such as AM1 or PM3 (Section 17.4), which use different parameters for each kind of atom, which is not true in DFT. The KS DFT method is usually considered in a category by itself, distinct from ab initio methods such as HF, CI, MP, and CC.

Despite its successes, DFT is not a panacea. Some drawbacks and failings of DFT are the following.

The Hohenberg–Kohn–Sham theory is basically a ground-state theory. LR-TDDFT can only be applied to certain kinds of excited states. (One can use DFT to calculate the lowest state of each symmetry; for example, one can calculate the lowest singlet state and the lowest triplet state.)

Because approximate functionals are used, KS DFT is not variational and can yield an energy below the true ground-state energy. For example, a B3LYP/cc-pVTZ geometry optimization of H_2O gives an energy of -76.460 hartrees, compared with the true non-relativistic energy of -76.438 hartrees (Table 16.1). Calculations with gradient-corrected functionals are size-consistent.

The true E_{xc} contains a self-interaction correction that exactly cancels the self-interaction energy in $\frac{1}{2} \iint \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$, but most currently used functionals are not completely free of self-interaction. Because of the self-interaction error, most currently available functionals give very incorrect $U(R)$ curves at large internuclear distances for symmetrical radical ions such as H_2^+ , He_2^+ , and F_2^+ and overestimate the intermolecular interaction in some charge-transfer complexes [Y. Zhang and W. Yang, *J. Chem. Phys.*, **109**, 2604 (1998)].

Although KS DFT yields good results for most molecular properties, with the presently available functionals, KS DFT cannot match the accuracy that the ab initio CCSD(T) method can achieve. Of course, CCSD(T) is limited to dealing with rather small molecules, whereas DFT can handle large molecules.

With methods such as CC, CI, and MP, the way to achieve more accurate results is clear. One uses larger basis sets and goes to higher orders of correlation (CCSD, CCSDT, . . . ; CISD, CISDT, . . . ; MP2, MP3, . . . , provided the perturbation series converges), although how far one can go for a given size molecule is limited by currently available computing power. In KS DFT, there is no clear way to construct more accurate E_{xc} functionals. One must try out new functionals one by one to see whether they will give improved results.

Many of the currently used E_{xc} functionals fail for van der Waals molecules. For example, the BLYP, B3LYP, and BPW91 functionals predict no binding in He_2 and Ne_2 . However, the PBE functional works fairly well here [Y. Zhang et al., *J. Chem. Phys.*, **107**, 7921 (1997)]. Also, Adamo and Barone modified the parameters in the PW91 exchange functional to give the modified Perdew–Wang (mPW or MPW) exchange functional and found that the hybrid GGA one-parameter functional $E_{xc} = (1 - a)E_x^{\text{mPW91}} + aE_x^{\text{exact}} + E_c^{\text{PW91}}$ with $a = 0.25$ (called mPW1PW91) performs fairly well for He_2 and Ne_2 and works well

for bond lengths, atomization energies, and vibrational frequencies of ordinary molecules [C. Adamo and V. Barone, *J. Chem. Phys.*, **108**, 664 (1998)]. Moreover, the DFT-D3 method and the VV10 functional work well for dispersion interactions.

Most of the currently available KS DFT functionals give only fair results for activation energies of reactions. However, a study of many methods of calculating barrier heights found good results from a few functionals, including PWB6K, BMK, BB1K, and MPW1K [J. Zheng et al., *J. Chem. Theory Comput.*, **3**, 5691 (2007)], with mean absolute errors running $1\frac{1}{4}$ to 2 kcal/mol with modest-size basis sets. The functional BB1K (where K stands for kinetics) is the same as B1B95 (see above) except that the parameter a_0 was fitted to kinetics data to give $a_0 = 0.42$. MPW1K is the mPW1PW91 functional with the parameter a changed to 0.428. PWB6K is a six-parameter hybrid meta-GGA functional based on the PW91 exchange functional and the B95 correlation functional. It has six parameters because the parameters within the exchange and correlation functionals (along with the fraction of exact exchange) were adjusted to fit kinetics data.

Although many functionals give good results for molecular properties, currently available forms of these functionals are known to be significantly in error. DFT shows that the exact E_x , E_c , v_x , and v_c must satisfy certain conditions, and currently available functionals violate at least some of these conditions [see C. Filippi et al., in J. M. Seminario (ed.), *Recent Developments and Applications of Modern Density Functional Theory*, Elsevier, 1996, p. 295]. The Hohenberg–Kohn theorem applied to the reference system of noninteracting electrons assures us that the true ground-state electron density determines the external potential v_s in (16.48). Iterative methods have been devised that take a very accurate ground-state molecular electron density found from a high-level calculation (for example, CI) and use it to calculate v_s for the corresponding reference system. From v_s , we can use (16.47) and (16.48) to find $v_{xc}(\mathbf{r})$. The accurate v_{xc} found from an accurate ρ for a particular atom or molecule can then be compared with the v_{xc} 's found from currently used E_{xc} 's. The results show that many currently used v_{xc} 's are substantially in error [M. E. Mura, P. J. Knowles, and C. A. Reynolds, *J. Chem. Phys.*, **106**, 9659 (1997); E. J. Baerends et al., in B. B. Laird et al. (eds.) *Chemical Applications of Density-Functional Theory*, American Chemical Society, 1996, Chapter 2].

DFT is now the most common method used in quantum-chemistry calculations. Also, DFT has been used to give quantitative definitions of such chemical concepts as electronegativity, hardness and softness, and reactivity; see *Parr and Yang*, Chapters 5 and 10; W. Kohn, A. D. Becke, and R. G. Parr, *J. Phys. Chem.*, **100**, 12974 (1996); P. Geerlings et al., *Chem. Rev.*, **103**, 1793 (2003).

16.6 Composite Methods for Energy Calculations

A desirable goal is to compute a thermodynamic energy such as the molecular atomization energy or the enthalpy of formation, with chemical accuracy, which means an accuracy of 1 kcal/mol. Currently available functionals in DFT cannot do this. High-level methods such as CCSD(T), QCISD(T), and CISDTQ with large basis sets (such as aug-cc-pCV6Z), can do this but are much too costly to be feasible except for small molecules. The aim of the composite methods discussed in this section is to achieve 1 kcal/mol or better accuracy with a computational time that allows calculations on molecules containing several nonhydrogen atoms. These composite methods use a series of ab initio calculations and some of them also include empirical corrections. Composite methods are reviewed in K. A. Peterson et al., *Theor. Chem. Acc.*, **131**, 1079 (2012).

The **Gaussian-3 (G3) method** (so called because it is an improvement on its predecessors, the G1 and G2 methods) is designed to give a result close to what would be obtained by a QCISD(T)/G3large calculation in much less computer time than required by such a

calculation [L. A. Curtiss et al., *J. Chem. Phys.*, **109**, 7764 (1998); **114**, 9287 (2001)]. G3large is an improved version of the 6-311+G(3df,2p) basis set. In the G3 method, the zero-point energy is found by scaling the frequencies found in a HF/6-31G* frequency calculation with the factor 0.893. All subsequent calculations are done at the optimized geometry found in an MP2/6-31G* calculation. One then computes a base energy E^{base} from an MP4/6-31G* calculation. Various corrections to E^{base} are then found as differences between E^{base} and energies obtained from MP4/6-31+G(d), MP4/6-31G(2df,p), QCISD(T)/6-31G(d), and MP2/G3large single-point calculations. These corrections are added to E^{base} , and an empirical *higher-level correction* of $-An_{\text{pairs}} - Bn_{\text{unpaired}}$ hartrees is added to correct for basis-set incompleteness. Here, n_{pairs} is the number of valence electron pairs in the molecule and n_{unpaired} is the number of unpaired electrons; A and B are empirical parameters with $A = 0.0006386$, $B = 0.0002977$ for molecules, and $A = 0.0006219$, $B = 0.0001185$ for atoms. The various corrections to E^{base} allow for the effects of including diffuse basis functions, polarization basis functions, and higher levels of electron correlation.

G3//B3LYP (also called G3B3 or G3B) is a modification of G3 that uses geometries and zero-point vibrational energies found from B3LYP/6-31G* calculations instead of from MP2/6-31G* and HF/6-31G* calculations [A. G. Baboul, *J. Chem. Phys.*, **110**, 7650 (1999)]. G3//B3LYP is faster than G3 and just as accurate as G3.

G3X (where the X stands for extension) is an improvement of the G3 method. It uses B3LYP/6-31G(2df,p) geometries and zero-point energies and adds a g polarization function to the G3Large basis set for second- and third-row atoms [L. A. Curtiss et al., *J. Chem. Phys.*, **114**, 108 (2001)]. For the G3/05 test set, the mean absolute deviation of calculated values from experimental values is 1.01 kcal/mol for G3X and 1.13 kcal/mol for G3 [L. A. Curtiss et al., *J. Chem. Phys.*, **123**, 124107 (2005)].

G3S and G3SX are modifications of G3 and G3X, respectively, in which instead of using the additive higher-level correction, one multiplies each of the various parts of the Hartree–Fock and the correlation energies by an empirically determined scale factor (six such factors are used). These methods give similar performance to G3 and G3X, and have the advantage of being applicable to determining the potential-energy surface of reactions where the products have a different number of unpaired electrons than the reactants [L. A. Curtiss et al., *J. Chem. Phys.*, **112**, 1125 (2000)].

The MP4 calculations are the most time-consuming steps in the G3 and G3X methods and prevent their applicability to large molecules. The G3(MP2) and G3X(MP2) methods [L. A. Curtiss et al., *J. Chem. Phys.*, **110**, 4703 (1999); **114**, 108 (2001)] are modifications of G3 and G3X that replace MP4 calculations with MP2 calculations, thereby speeding up the calculations and allowing somewhat larger molecules to be treated. For the G3/99 test set, mean absolute deviations from experiment are 1.31 kcal/mol for G3(MP2), 1.19 kcal/mol for G3X(MP2), 1.07 kcal/mol for G3, and 0.95 kcal/mol for G3X.

The **G4 method** is an improvement on G3 and differs from G3 as follows: G4 uses an extrapolation procedure [Eq. (15.23)] to estimate the Hartree–Fock energy in the complete-basis-set limit; uses a larger basis set; replaces the QCISD(T) calculation by a CCSD(T) calculation; uses B3LYP/6-31G(2df,p) to find the equilibrium geometry and the zero-point energy; and includes two additional empirical parameters in the higher-level correction [L. A. Curtiss et al., *J. Chem. Phys.*, **126**, 084108 (2007)]. For the G3/05 test set, G4 has a mean absolute error of 0.83 kcal/mol, compared with 1.13 kcal/mol for G3. Relative computation times for benzene are 2 for G2, 1 for G3, and 3 for G4.

The **correlation-consistent composite approach (ccCA)** is based in part on the G3B method, but uses Dunning correlation-consistent basis sets instead of Pople basis sets, does extrapolations to the CBS limit, replaces the QCISD(T) calculation with a CCSD(T) calculation, includes a relativistic correction, and contains no empirical parameters [N. J. DeYonker et al., *J. Chem. Phys.*, **125**, 104111 (2006); *Mol. Phys.*, **107**,

1107 (2009)]. For the G3/99 test set the mean absolute deviations from experiment are 0.96 and 0.97 kcal/mol for the versions ccCA-P and ccCA-S4 (which differ in the extrapolation formulas used), compared with 1.16 and 0.95 kcal/mol for G3 and G3X, respectively. About 20 versions of ccCA exist, including a version for transition metal compounds, a multireference version, and RI versions,

The CBS-Q, CBS-QB3, CBS-q, and CBS-4 methods are varieties of **CBS** (complete basis set) composite methods devised for calculations on molecules containing the atoms H to Ar. These methods use procedures designed to extrapolate calculated energies to the complete-basis-set limit. Like G3, the CBS methods include several correlated calculations done at a geometry optimized at a lower level of theory. The highest-level calculation used is QCISD(T)/6-31+G[†] (the 6-31+G[†] basis set is a slightly improved version of 6-31G*) in the CBS-Q and CBS-QB3 methods, is QCISD(T)/6-31G in the CBS-q method, and is MP4(SDQ)/6-31G in the CBS-4 method. Like G3, the CBS methods contain empirical corrections. For details see J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, *J. Chem. Phys.*, **104**, 2598 (1996); J. A. Montgomery et al., *J. Chem. Phys.*, **110**, 2822 (1999).

The composite methods **W1**, **W2**, **W3**, and **W4** (where the W stands for the Weizmann Institute, where the methods were developed) use high-level coupled-cluster calculations to achieve extraordinary accuracy in thermochemical quantities [A. Karton et al., *J. Chem. Phys.*, **125**, 144108 (2006) and references cited therein]. W1 has one empirically determined parameter, but W2, W3, and W4 have no empirical parameters. W1 and W2 use CCSD(T) and CCSD calculations with correlation-consistent basis sets, do extrapolations to the complete basis-set limit, and include relativistic corrections. W3 and W4 include CCSDT and CCSDTQ calculations, and W4 includes a CCSDTQ5 calculation with a small basis set. For various test sets of small molecules, the mean absolute deviation from experimental atomization energies or heats of formation is 0.6 kcal/mol for W1, 0.5 kcal/mol for W2, 0.2 kcal/mol for W3, and 0.1 kcal/mol for W4. W4 also gives highly accurate bond distances, harmonic vibrational frequencies, vibrational anharmonicity constants, and dipole moments for small molecules [A. Karton and M. L. Martin, *J. Chem. Phys.*, **133**, 144102 (2010); arxiv.org/abs/1008.4163]. These methods are limited to small molecules.

To make W1 and W2 applicable to larger molecules, the F12 explicitly correlated method was used in the CCSD and MP2 calculations and the RI approximation was used in the HF, CCSD-F12, and MP2-F12 calculations, giving the **W1-F12** and **W2-F12** methods [A. Karton and J. M. L. Martin, *J. Chem. Phys.*, **136**, 124114 (2012)]. The use of the F12 method allows smaller basis sets to be used than in W1 and W2, thereby speeding up the calculation and reducing the storage requirements. For small molecules, W1-F12 and W2-F12 typical errors in gas-phase enthalpies of formation are about 0.2 kcal/mol. W1-F12 has been applied to medium-size molecules such as guanine (C₅H₅N₅O) and to tetracene (C₁₈H₁₂); W2-F12 has been applied to adenine (C₅H₅N₅) and anthracene (C₁₄H₁₀).

The **HEAT** (high accuracy extrapolated ab initio thermochemistry) method, which has no empirical parameters, uses CC calculations up to CCSDTQ, extrapolations to the CBS limit, corrections for vibrational anharmonicity, relativistic effects, and deviations from the Born–Oppenheimer approximation to achieve mean absolute deviation of 0.1 kcal/mol in atomization energies. The high level of calculations means the method can be used only with tetraatomic or smaller molecules. HEAT, like the other methods in this section, exists in several versions [A. Tajti et al., *J. Chem. Phys.*, **121**, 11599 (2004); J. Y. Bomble et al., *ibid.*, **125**, 064108 (2006)].

The composite methods of this section have uncovered significant errors in tabulated experimental thermodynamic data,

16.7 The Diffusion Quantum Monte Carlo Method

A **quantum Monte Carlo (QMC) method** uses a random process to solve the Schrödinger equation. Many QMC methods exist, but the **diffusion QMC (DQMC)** method is most commonly used for molecular calculations. Defining the imaginary time variable $\tau \equiv it/\hbar$, one finds (Prob. 16.32) that in the limit $\tau \rightarrow \infty$, the time-dependent state function Ψ (no matter what its form Ψ_0 is at $\tau = 0$, provided Ψ_0 includes some mixture of the ground state) becomes proportional to the ground-stationary-state wave function ψ_{gs} . Moreover, the equation for $\partial\Psi/\partial\tau$ has the same form as Fick's second law for the diffusion of a substance in a $3n$ -dimensional space (where n is the number of electrons) with an added term corresponding to the substance undergoing a first-order reaction (with a rate constant that can take on positive or negative values) as well as diffusing. One simulates the diffusion and reaction processes on a computer by starting with a large number of particles (called *walkers*) distributed in the regions near the nuclei. One chooses a step size $\Delta\tau$, and at each increment in τ , the particles undergo random changes in coordinates, where the probability for a particular size change Δx in each coordinate is taken to be proportional to the probability that a diffusing particle will suffer a displacement by Δx in a given direction in time $\Delta\tau$. Also, at each step $\Delta\tau$, each particle has a probability to either disappear or give birth to a second particle, corresponding to the first-order reaction term. Eventually, the distribution of walkers in $3n$ -dimensional space will be proportional to the ground-state wave function, provided proper allowance is made for the antisymmetry requirement for the wave function.

Because of the antisymmetry requirement, the ground-state wave function has nodal surfaces in $3n$ -dimensional space (see Prob. 16.33). To ensure that the walkers converge to the ground-state wave function, one must know the locations of these nodes and must eliminate any walker that crosses a nodal surface in the simulation. In the **fixed-node (FN)** DQMC method, the nodes are fixed at the locations of the nodes in a known approximate wave function for the system, such as is found from a large basis-set Hartree–Fock calculation. This approximation introduces some error, but FN-DQMC calculations are variational. In practice, the accuracy of FN-DQMC calculations is improved by a procedure called importance sampling. Here, instead of simulating the evolution of Ψ with τ , one simulates the evolution of f , where $f \equiv \Psi\psi_{tr}$, where ψ_{tr} is a known accurate trial variation function for the ground state. ψ_{tr} guides the random walkers to regions where $|\psi_{tr}|$ is large. ψ_{tr} typically has the form of a function of interelectronic coordinates r_{ij} multiplied by a linear combination of one or more Slater determinants of HF orbitals. (This ψ_{tr} can also be used to define the locations of the nodes.)

QMC calculations are especially well suited to be run on parallel computers. The Quantum Monte Carlo at Home project using the home computers of tens of thousands of volunteers to run FN-DQMC calculations (qmcathome.org) has calculated accurate interaction energies for the DNA base pairs adenine–thymine and guanine–cytosine. This project will be changing its focus to run quantum-mechanical calculations at home in such areas as protein–ligand interactions and development of new materials for batteries.

QMC methods have given very accurate results in some calculations on small systems, but the method can require very long calculation times, and no efficient method has yet been found to allow geometry optimization in a QMC calculation. (The FN-DQMC calculation on H_2O in Table 16.1 was done at the experimental geometry.) Currently, none of the widely used quantum-chemistry program packages include the DQMC method, and its use is restricted to specialists. For more on DQMC, see Probs. 16.32 and 16.33, and J. B. Anderson, *Int. Rev. Phys. Chem.*, **14**, 85 (1995); K. Raghavachari and J. B. Anderson, *J. Phys. Chem.*, **100**, 12960 (1996); A. Lüchow and J. B. Anderson, *Annu. Rev. Phys. Chem.*, **51**, 501 (2000); B. A. Austin et al., *Chem. Rev.*, **112**, 263 (2012).

16.8 Noncovalent Interactions

In the broadest sense, **noncovalent interactions** in chemistry include all interactions except covalent bonding and thus include such things as ionic bonding. In this section we will concentrate on hydrogen bonding and dispersion interactions, which are key to the structures of such biomolecules as proteins and DNA. The importance of hydrogen bonding in biomolecules has long been recognized, but only recently have calculations shown that dispersion interactions in biomolecules are of comparable magnitude to hydrogen bonding interactions.

Hydrogen bonding is important throughout chemistry and biochemistry, and for a method to give reliable results when applied to large biological molecules, it must treat hydrogen bonding properly.

Many gas-phase hydrogen-bonded dimers have been characterized spectroscopically. Examples include $(\text{H}_2\text{O})_2$, $(\text{HCl})_2$, $\text{HF}-\text{H}_2\text{O}$, and $\text{HF}-\text{HCN}$. For $(\text{H}_2\text{O})_2$, the structure (determined by molecular-beam microwave spectroscopy) is shown in **Fig. 16.1** [T. R. Dyke, et al., *J. Chem. Phys.*, **66**, 498 (1977)].

For H-bonded dimers, HF STO-3G, 3-21G, and 3-21G^(*) calculations give equilibrium-geometry separations between the heavy atoms that are usually substantially in error (errors of 0.1 to 0.5 Å); 6-31G* calculations give heavy-atom separations in pretty good agreement with experiment (Hehre et al., Table 6.32).

Suppose we want to calculate the dimerization energy of H_2O using the 3-21G basis set. The natural procedure would be to calculate the energy of the dimer $(\text{H}_2\text{O})_2$ at its 3-21G equilibrium geometry using a 3-21G basis set on each of the six atoms of $(\text{H}_2\text{O})_2$ and to calculate the energy of each H_2O monomer at its 3-21G equilibrium geometry using a 3-21G basis set on each of the three atoms of the monomer, and to take the dimerization energy as

$$\Delta\varepsilon = \varepsilon(\text{AB})_{\text{ab}}^{\text{d}} - \varepsilon(\text{A})_{\text{a}}^{\text{m}} - \varepsilon(\text{B})_{\text{b}}^{\text{m}} \quad (16.71)$$

Here A and B stand for the monomer molecules and AB for the dimer. In this case, $\text{A} = \text{H}_2\text{O}$, $\text{B} = \text{H}_2\text{O}$, and $\text{AB} = (\text{H}_2\text{O})_2$. The letters a, b, and ab symbolize the 3-21G basis set centered on the atoms of A, the 3-21G basis set centered on the atoms of B, and the 3-21G basis set centered on the atoms of AB, respectively. The letters d and m denote calculated dimer and monomer equilibrium geometries: $\varepsilon(\text{A})_{\text{a}}^{\text{m}}$ is the energy of monomer A at the A equilibrium geometry calculated with the a basis set, with a similar meaning for $\varepsilon(\text{B})_{\text{b}}^{\text{m}}$; and the quantity $\varepsilon(\text{AB})_{\text{ab}}^{\text{d}}$ is the energy of AB at the equilibrium geometry of AB calculated with the ab basis set. For $(\text{H}_2\text{O})_2$, $\varepsilon(\text{A})_{\text{a}}^{\text{m}} = \varepsilon(\text{B})_{\text{b}}^{\text{m}}$, but this is not true for a mixed dimer such as $\text{HF}-\text{H}_2\text{O}$.

However, this procedure involves an inconsistency. When the monomer energy $\varepsilon(\text{A})_{\text{a}}^{\text{m}}$ is calculated, the electrons of A have available to themselves only the 3-21G orbitals on the three atoms of A, whereas when $\varepsilon(\text{AB})_{\text{ab}}^{\text{d}}$ is calculated, the electrons of each H_2O molecule within the dimer have available not only the orbitals on their own nuclei, but also the orbitals on the nuclei of the other H_2O molecule. In effect, the dimer basis set is larger than that of each monomer, and this produces an artificial lowering of the dimer energy relative to that of the separated monomers. This artificial lowering is called the **basis-set superposition error (BSSE)**. The BSSE would vanish in the limit of using a complete set for each monomer. The most common procedure (due to Boys and Bernardi) to correct for the BSSE is to calculate the dimerization energy by adding the following **counterpoise (CP) correction** to $\Delta\varepsilon$ of (16.71):

$$\Delta\varepsilon_{\text{CP}} = \varepsilon(\text{A})_{\text{a}}^{\text{d}} - \varepsilon(\text{A})_{\text{ab}}^{\text{d}} + \varepsilon(\text{B})_{\text{b}}^{\text{d}} - \varepsilon(\text{B})_{\text{ab}}^{\text{d}} \quad (16.72)$$

where d indicates that each of the four quantities in (16.72) is calculated with the A or B atoms located at their calculated locations in the dimer, and $\varepsilon(\text{A})_{\text{ab}}^{\text{d}}$ is calculated with a

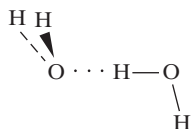


FIGURE 16.1 The water dimer.

basis set that consists of 3-21G orbitals on each nucleus of the monomer A and the appropriate 3-21G orbitals (called “ghost orbitals”) centered at the three points in space that would correspond to the equilibrium positions of the other three nuclei in the dimer. The CP procedure has been very controversial, but is now accepted by the majority of researchers as a good way to reduce the BSSE [G. Chalasiński and M. M. Szczesniak, *Chem. Rev.*, **94**, 1723 (1994); F. B. van Duijneveldt et al., *Chem. Rev.*, **94**, 1873; see also the references in A. Galano and J. R. Alvarez-Idaboy, *J. Comput. Chem.*, **27**, 1203 (2006)]. Because of the asymmetry of $(\text{H}_2\text{O})_2$, $\epsilon(\text{A})_{\text{ab}}^{\text{d}} \neq \epsilon(\text{B})_{\text{ab}}^{\text{d}}$.

From the temperature and pressure dependences of the thermal conductivity of water vapor, ΔH_{373}° for $2\text{H}_2\text{O}(g) \rightarrow (\text{H}_2\text{O})_2(g)$ has been found to be -3.6 ± 0.5 kcal/mol [L. A. Curtiss et al., *J. Chem. Phys.*, **71**, 2703 (1979)]. This ΔH_{373}° is found to correspond to an energy change involving nonvibrating, nonrotating, nontranslating species of $\Delta E_{\text{el}} = -5.0 \pm 0.7$ kcal/mol [E. M. Mas et al., *J. Chem. Phys.*, **113**, 6687 (2000)], where the theoretically calculated zero-point energy of the dimer is used to help find the electronic energy change ΔE_{el} .

MP2 calculations with large aug-cc-pVnZ basis sets yielded an estimate of 5.0 ± 0.1 kcal/mol for the dissociation energy D_e of the water dimer to two monomers in the CBS limit, and the effect of going to the MP4 level was found to be negligible [M. W. Feyereisen et al., *J. Phys. Chem.*, **100**, 2993 (1996)]. Essentially the same result was found by a method called symmetry-adapted perturbation theory (SAPT), which treats the interactions between the monomers as a perturbation [E. M. Mas and K. Szalewicz, *J. Chem. Phys.*, **104**, 7606 (1996)]. CCSD(T) calculations extrapolated to the CBS limit gave $D_e = 5.02 \pm 0.05$ kcal/mol [W. Klopper et al., *Phys. Chem. Chem. Phys.*, **22**, 2227 (2000)].

The theoretical results agreed with the experimental result, but it wasn't until 2011 that an accurate and direct measurement of the dimer dissociation energy was made. Measurements of velocities and translational energy distributions of monomers produced by dissociation were analyzed to give the dimer bond dissociation energy as $D_0 = 3.16 \pm 0.03$ kcal/mol [B. E. Rocher-Casterline et al., *J. Chem. Phys.*, **134**, 211101 (2011)]. Shank and others fitted a potential-energy surface (PES) for the dimer to 30000 CCSD(T)/aug-cc-pVTZ calculated points, thereby finding an accurate ZPE for the dimer, which together with the theoretically calculated D_e gave for the dimer $D_0 = 3.15 \pm 0.01$ kcal/mol [Y. Shank et al., *J. Chem. Phys.*, **130**, 144314 (2009)].

Density-functional studies of hydrogen-bonded dimers generally found good results with the B3LYP functional, provided large enough basis sets (valence triple zeta with polarization functions) were used [B. Paizs and S. Suhai, *J. Comput. Chem.*, **19**, 575 (1998)].

The performance of semiempirical methods for hydrogen bonding is discussed in Section 17.4.

In DNA, in addition to the hydrogen bonding between paired bases, one has $\pi \cdots \pi$ dispersion interactions between the aromatic rings of one base pair and the base pair stacked “above” it and the base pair stacked “below” it. Accurate calculations show that “the stacking of aromatic systems represents the leading stabilization energy contribution in biomacromolecules . . . Therefore stacking (dispersion) interactions predominantly determine the double helical structure of DNA” (K. E. Riley and P. Hobza, *Acc. Chem. Res.*, doi: 10.1021/ar300083h). Accurate stabilization energies for hydrogen bonding between base pairs and for stacking (dispersion) were obtained by CCSD(T)/CBS calculations and revealed the key role of stacking. “Without dispersion energy a double-helical structure would unwind” (Riley and Hobza, *ibid.*). Moreover, in proteins, dispersion interactions involving aromatic rings of amino acids are important, and “dispersion is the dominant contribution to attractive interactions involving aromatic amino acids within the hydrophobic core of a protein” (Riley and Hobza).

The reliability of MP2 and CCSD methods for calculating noncovalent interactions was tested using the S66 database (Section 16.1); corrections for BSSE were included [P. Hobza, *Acc. Chem. Res.*, **45**, 663 (2012)]. The following rms errors in kcal/mol were found for the best-performing methods: 0.08 for SCS(MI)-CCSD/CBS, 0.14 for MP2.X/6-31+G*, 0.25 for SCS-CCSD/CBS, 0.28 for MP2.5/6-31+G*, and 0.38 for SCS(MI)-MP2. For comparison, the poorly performing MP2/CBS method gave 0.69. The binding energies in the S66 set are mostly in the range 1.5 to 10 kcal/mol. The SCS(MI)-CCSD and SCS(MI)-MP2 methods are the SCS-CCSD and SCS-MP2 methods (Sections 16.4 and 16.3), with the two scaling parameters changed to values that work better for noncovalent interactions (MI stands for molecular interaction). The MP2.5 method calculates the binding energy $\Delta E(\text{MP2.5}/\text{bas-x})$ of a hydrogen-bonded or van der Waals complex using

$$\Delta E(\text{MP2.5}/\text{bas-x}) = \Delta E(\text{MP2}/\text{CBS}) + 0.5[\Delta E(\text{MP3}/\text{bas-x}) - \Delta E(\text{MP2}/\text{bas-x})]$$

Here $\Delta E(\text{MP2}/\text{CBS})$ is the binding energy found by MP2 calculations extrapolated to the CBS limit, and $\Delta E(\text{MP3}/\text{bas-x})$ is the MP3 binding energy found using a relatively small basis set (bas-x) such as 6-31+G*. If bas-x were a huge basis set that gave essentially the CBS limit, then the MP2.5 method would give the average of the MP2 and MP3 binding energies. By using a relatively small basis set for the MP3 calculation, one keeps the computation time low, allowing larger complexes to be treated. In the CBS limit for bas-x, the MP2.5 rms error is reduced to 0.16. The MP2.X method is an improvement on MP2.5 that replaces the 0.5 in the formula with an empirical parameter whose value depends on what bas-x is [K. E. Riley et al., *Phys. Chem. Chem. Phys.*, **13**, 21121 (2011)].

Rms errors in kcal/mol for the S22 test set for some density functionals that did well on this set are 0.31 for $\omega\text{B97X-D}$, 0.33 for B2PLYP-D3, and 0.34 for BLYP-D3 [L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, **13**, 6670 (2011)] as compared with 0.44 for B3LYP-D3.

16.9 NMR Shielding Constants

To calculate NMR chemical shielding (screening) constants, the applied magnetic field **B** is treated as a perturbation, and one solves a set of equations called coupled perturbed equations. For details of the theory, see D. B. Chesnut in K. B. Lipkowitz and D. B. Boyd, *Reviews in Computational Chemistry*, vol. 8, VCH, 1996, Chapter 5. Just as the electric field is minus the gradient of the electric potential, the magnetic induction **B** is given by $\mathbf{B} = \nabla \times \mathbf{A}$, where **A** is the magnetic vector potential. Many different choices for **A** give the same **B**. A particular choice defines the “gauge” of the vector potential. Several methods have been proposed to give calculated quantum-mechanical results that are independent of the choice of gauge. The most widely used of these is the *gauge-including atomic orbital* (GIAO) method, in which each basis AO includes an exponential factor that contains **B**.

Chemical shifts are reported in parts per million (ppm) and are the difference between screening constants in the molecule and that in a reference molecule such as tetramethylsilane (TMS) for proton and ^{13}C NMR spectra. The **chemical shift** δ_i of nucleus *i* is defined by

$$\delta_i \equiv 10^6(\sigma_{\text{ref}} - \sigma_i) = \sigma_{\text{ref}}^{\text{ppm}} - \sigma_i^{\text{ppm}} \quad (16.73)$$

where σ_i and σ_{ref} are the shielding constants for nucleus *i* and for the reference nucleus (usually the protons or ^{13}C in TMS). The ppm superscript denotes values in parts per million (which is how the output values in the *Gaussian* program appear). The shielding constant σ_i is actually a second-rank tensor (3 by 3 matrix) with the nine components $\sigma_i^{xx}, \sigma_i^{xy}, \dots, \sigma_i^{zz}$. In the liquid or gas phase, one observes the rotationally averaged value $(\sigma_i^{xx} + \sigma_i^{yy} + \sigma_i^{zz})/3$, which is the *isotropic* shielding constant.

For 14 small molecules, MAEs in ^{13}C shifts in ppm using the GIAO method with a QZ2P basis set and MP2/TZ2P geometries were as follows: 9 for HF, 14 for LSDA, 6.5 for BPW91, 8 for BLYP, 7 for B3PW91, and 1.6 for MP2 [J. R. Cheeseman et al., *J. Chem. Phys.*, **104**, 5497 (1996)]. Since the observed shifts cover a range of about 200 ppm, all these results are good. The QZ2P basis set is too large for use with large molecules. For a series of molecules with two to eight nonhydrogen atoms, average absolute errors in ^{13}C shifts in ppm using the GIAO method with B3LYP/6-31G* geometries were 9 for HF/6-31G*, 9 for HF/6-311+G(2d,p), and 4 for B3LYP/6-311+G(2d,p) (Cheeseman et al., op. cit.).

Many standard quantum-chemistry programs allow calculation of NMR shielding constants and spin–spin coupling constants.

Before calculating shielding constants σ_i , one first calculates an optimized molecular geometry. After the shielding constants in a molecule have been calculated, one averages those of nuclei interchangeable by nearly free rotation about a single bond (such as in a methyl group). One then uses the same method and basis set to calculate the shielding constant for the reference nucleus in a reference compound (such as tetramethylsilane) and subtracts to get the predicted chemical shifts. Large molecules may have several low-energy conformers, and one should suitably average the calculated shielding constants for such conformers. Solvent effects can be allowed for by using a dielectric continuum model such as the SCRF method (Section 15.17). Solvent effects in the commonly used solvent CDCl_3 are often small.

Hartree–Fock calculations of shielding constants are not reliable. DFT calculations are most commonly used to predict NMR chemical shifts. Unfortunately, the GIAO method can be used only with GGA and hybrid GGA functionals and not with meta-GGA or hybrid-meta GGA functionals; for these the CSGT (continuous set of gauge transformations) method (which requires a larger basis set for good results than the GIAO method) is used. MP2 calculations give better results than DFT calculations but are too time-consuming to use routinely on medium and large molecules. CCSD(T) calculations with large basis sets give accurate shielding constants but are only feasible for small molecules.

To improve the accuracy of calculated NMR shifts, an empirical correction to theoretically calculated results is often used. One takes a large set of compounds, computes ^{13}C (or proton) shielding constants in them using a particular method (such as B3LYP or MP2) and basis set, and plots the calculated $\sigma_{i,\text{calc}}^{\text{ppm}}$ values on the y axis versus the experimentally observed chemical shifts $\delta_{i,\text{exp}}$. The true shielding constants are given by (16.73) as $\sigma_i^{\text{ppm}} = -\delta_i + \sigma_{\text{ref}}^{\text{ppm}}$. If the calculation gave perfect accuracy, the plotted points would lie on a straight line with slope -1 and intercept $\sigma_{\text{ref}}^{\text{ppm}}$. In practice, if the calculation method is a sound one, the resulting points will lie quite close to a straight line, and the slope m of the least-squares regression line $\sigma_{\text{calc}}^{\text{ppm}} = m\delta_{\text{exp}} + b$ fitted to the data points will be close to -1 . Once the slope m and intercept b of this line are known, one can substitute σ_i values calculated with the same method that produced the data points for the line into the regression equation and solve for the predicted chemical shifts as $\delta_i = (\sigma_i - b)/m$. Tables of m and b for common density functionals with various basis sets and for MP2 with various basis sets can be found at cheshirenmr.info. This **empirical scaling** procedure typically reduces average errors in ^{13}C and proton chemical shifts by a factor of 3 and usually gives quite accurate results—typical errors of 0.1 ppm for proton shifts and 2 or 3 ppm for ^{13}C shifts, about 1% of the range of observed shifts and close to experimental precision.

Calculations of proton chemical shifts that used several common density functionals and basis sets on a test set of compounds together with linear scaling of the results recommended WP04/cc-pVDZ (rms error 0.115 ppm, $m = 1.020$, $b = 31.84$), WP04/6-31G** (rms error 0.12 ppm, $m = 1.033$, $b = 32.02$), B3LYP/6-31G** (rms error 0.13 ppm,

$m = 1.055, b = 31.84$) as giving the best ratio of accuracy/cost [R. Jain et al., *J. Org. Chem.*, **74**, 4018 (2009)]. WP04 is the B3LYP functional reparametrized to give good proton shielding constants in chloroform. (A similar reparametrization of B3LYP for ^{13}C shifts gave the WC04 functional.) The B3LYP/6-31G* optimized geometries were used. For the recommended methods, the calculations were done using the GIAO method and the SCRF method with chloroform as solvent. Surprisingly, it was found, contrary to previous recommendations of others, that going to triple-zeta basis sets did not improve the results.

A review of methods for calculating chemical shifts in organic compounds noted that “It seems as though every research group has its own preferred density functional for these calculations” and went on to recommend geometry optimization using B3LYP/6-31G* or B3LYP/6-31+G** followed by screening constant calculations using the PBE0, mPW1PW91, or B3LYP functional and the 6-311+G(2d,p) basis set, and then linearly scaling the results to get the chemical shifts [M. W. Lodewyk et al., *Chem. Rev.*, **112**, 1839 (2012)].

Calculation of NMR spin–spin coupling constants is more challenging than calculation of shielding constants but can be done with fair accuracy with DFT, thereby allowing the complete prediction of the NMR spectrum. For example, the ^1H and ^{13}C NMR spectra of several medium-size natural-product molecules were calculated with a fair degree of accuracy using such methods as B3LYP/6-31G**, and agreement with experiment was improved when the effect of solvent was allowed for by using the PCM method [A. Bagno et al., *Chem. Eur. J.*, **12**, 5514 (2006)]. A study that calculated proton–proton spin–spin coupling constants $J_{\text{H–H}}$ with many possible combinations of density functionals and basis sets recommended B3LYP/6-31G(d,p)u+1s[H] together with scaling as providing an economical way to calculate rather accurate values [T. Bally and P. R. Rablen, *J. Org. Chem.*, **76**, 4818 (2011)]. Here, 6-31G(d,p)u+1s[H] denotes the 6-31G** basis set modified by uncontracting the 1s basis functions (that is, allowing all the coefficients in each of them to vary) and adding four more s functions with large orbital exponents on each H atom. All calculations were done at the B3LYP/6-31G* optimized geometry. Four terms contribute to $J_{\text{H–H}}$, and it was found that the most accurate results with scaling were found if only the largest term, the Fermi contact term (which involves the electron density at the nucleus), is calculated and the calculated $J_{\text{H–H}}$ values are multiplied by the scaling factor 0.91. This gives $J_{\text{H–H}}$ values with an rms error of only 0.5 Hz. Similar accuracy is obtained using B3LYP/cc-pVTZ with the scaling factor 1.10, but calculations take much longer. Details for carrying out this procedure with the *Gaussian* program are given at cheshirenmr.info/Recommendations.htm#ballyccc.

One can use calculated NMR shielding constants and $J_{\text{H–H}}$ values to help assign the structure of a new compound by seeing which of several possible structures has a calculated spectrum in good agreement with the observed one.

16.10 Fragmentation Methods

To deal with large molecules that are currently out of reach of ab initio and density functional methods, a slew of methods have been developed that split a large molecule into fragments, treat the fragments one at a time (with allowance for interaction of each fragment with the rest of the molecule), and then use the results to calculate properties of the whole molecule. In addition to allowing for treatment of very large molecules, fragmentation methods allow for parallel computation to increase efficiency. A review article listed 20 fragmentation methods in a classification diagram [Figure 1 in M. S. Gordon et al., *Chem. Rev.*, **112**, 263 (2012)]. In detaching bonds to form the fragments, some methods add capping atoms (such as H) to detached bonds and other methods do

not add caps. The ESP (Section 15.7) produced by the rest of the molecule may be used in calculations on each fragment. The GAMESS program has several fragmentation methods available.

Applications of fragmentation methods include calculations on proteins, protein–ligand binding, solids, and nanomaterials, and study of chemical reactions. The above-cited review noted that fragmentation methods are underused, due perhaps to uncertainty as to their accuracy.

16.11 Relativistic Effects

For a nonrelativistic hydrogenlike atom, the root-mean-square speed of a $1s$ electron is $Zc/137$, where Z is the nuclear charge and c is the speed of light (Prob. 16.36). Hence, for atoms of high atomic number, the average speed of inner-shell electrons is a significant fraction of c , and relativistic corrections to inner-shell orbitals and orbital energies are substantial for high- Z atoms. The valence electrons in an atom or molecule are well shielded from the nuclei, and their average speeds are far less than the speed of light, even in heavy atoms. Hence, it was formerly believed that one need not worry about relativistic corrections in molecules containing high- Z atoms. It is now realized that relativistic effects on properties of molecules with heavy atoms can be quite substantial.

The average radius of a hydrogenlike atom is proportional to the Bohr radius a_0 , and a_0 is inversely proportional to the electron mass. Hence, the relativistic increase of mass with velocity shrinks the inner s orbitals in a heavy atom. To maintain their orthogonality to the inner s orbitals, the outer s orbitals are required to shrink also. The relativistic increase of mass also shrinks the p orbitals, but to a lesser extent than the s orbitals. Because of the relativistic shrinkage of the s and p orbitals, these orbitals screen the nucleus more effectively than in nonrelativistic atoms, and this produces an expansion of the d and f orbitals. Calculated relativistic contractions of the $6s$ orbital average radius in some atoms are 4% for $_{55}\text{Cs}$, 7% for $_{70}\text{Yb}$, 12% for $_{75}\text{Re}$, 18% for $_{79}\text{Au}$, and 12% for $_{86}\text{Rn}$ [P. Pyykkö, *Chem. Rev.*, **88**, 563 (1988)]. Because of relativistic contraction, the atomic radius of Fr is less than that of Cs, which lies above Fr in the periodic table.

The relativistic form of the one-electron Schrödinger equation is the Dirac equation. One can do relativistic Hartree–Fock calculations using the Dirac equation to modify the Fock operator, giving a type of calculation called **Dirac–Fock** (or Dirac–Hartree–Fock). Likewise, one can use a relativistic form of the Kohn–Sham equations (16.49) to do relativistic density-functional calculations. (Relativistic $X\alpha$ calculations are called Dirac–Slater or Dirac– $X\alpha$ calculations.)

All-electron Dirac–Fock relativistic calculations on molecules containing heavy atoms such as Au or U are very time-consuming. A commonly used approach is to do an all-electron atomic Dirac–Fock calculation on each type of atom in the molecule and use the result to derive a **relativistic effective core potential** (RECP) or pseudopotential (Section 15.16) for that atom. (Since the smallest parts of the relativistic effects are neglected in deriving RECPs, RECPs are sometimes called quasirelativistic ECPs.) One then does a molecular Hartree–Fock calculation in which only the valence electrons are treated explicitly. The valence electrons are treated nonrelativistically, and the effects of the core electrons are represented by adding the operator $\sum_{\alpha} \hat{U}_{\alpha}$ to the Fock operator $\hat{F}$, where $\hat{U}_{\alpha}$ is a relativistic ECP for atom α , and the sum goes over the atoms of the molecule. Here, it is assumed that the inner-shell AOs are not significantly changed on going from isolated atoms to the molecule. The results of the SCF calculation can be improved using CI or MP perturbation theory. MCSCF and MCSCF–CI calculations with RECPs are also done. RECPs can also be used in KS DFT calculations. RECPs for most elements of the periodic table are available at www.clarkson.edu/~pac/rep.html.

Another approach is to do a nonrelativistic calculation, using, for example, the Hartree–Fock method, and then use perturbation theory to correct for relativistic effects. For perturbation-theory formulations of relativistic Hartree–Fock calculations and relativistic KS DFT calculations, see W. Kutzelnigg, E. Ottschowski, and R. Franke, *J. Chem. Phys.*, **102**, 1740 (1995) and C. van Wüllen, *J. Chem. Phys.*, **103**, 3589 (1995); **105**, 5485 (1996).

Some examples of relativistic effects on molecular properties found from Hartree–Fock calculations with RECPs follow, where the numbers are listed in the following order: nonrelativistic-ECP calculated value, relativistic-ECP calculated value, experimental value (see P. Pyykkö, op. cit. for references). (Also listed in parentheses are calculated nonrelativistic, calculated relativistic, and experimental values, where the calculated values are from nonrelativistic KS DFT and relativistic perturbation-theory KS DFT calculations using the B88P86 functional and a contracted Gaussian basis set; see C. van Wüllen, op. cit.) Equilibrium bond lengths: 2.80, 2.73, 2.48 Å in Ag₂; 1.73, 1.71, 1.70 Å in SnH₄; 1.76, 1.51, 1.52 Å (1.73, 1.56, 1.52 Å) in AuH; 2.83, 2.48, 2.47 Å (2.77, 2.58, 2.47 Å) in Au₂; 2.81, 2.53, 2.50 Å in Hg₂²⁺; (2.10, 2.06, 2.06 Å) for the W–C length in W(CO)₆. Bond angle: 98.6°, 98.2°, 98° in PbCl₂. Dipole moments: 1.02, 0.92, 0.83 D for HBr, 0.71, 0.52, 0.45 D for HI. Harmonic vibrational wavenumber: 77, 163, 191 cm^{−1} (121, 165, 191 cm^{−1} for Au₂. Equilibrium dissociation energies: (52.3, 69.1, 77.4 kcal/mol) for AuH; (33.0, 47.1, 53.1 kcal/mol) for Au₂. Relativistic effects are substantial for these heavy-atom molecules.

Relativistic all-electron calculations on F₂, Cl₂, Br₂, I₂, and At₂ using various correlation methods found that the relativistic corrections were approximately independent of the level of theory used, except for At₂ [L. Visscher and K. G. Dyall, *J. Chem. Phys.*, **104**, 9040 (1996)]. For example, with a valence triple-zeta polarized basis set, the changes in D_e on going from a nonrelativistic to a relativistic calculation were −8, −7, −7, −7, −7 kcal/mol for Br₂ using the HF, MP2, CISD, CCSD, CCSD(T) methods, respectively; for I₂, these changes were −15, −13, −12.5, −13, −13 kcal/mol; for At₂, they were −30, −27, −24, −25, −24 kcal/mol.

Relativistic DFT calculations on the solids PbO, PbSO₄, and PbO₂ resulted in a standard emf for the lead storage cell of 2.13 V, quite close to the true value 2.11 V, whereas when relativistic effects were omitted, the calculation gave an emf of only 0.39 V [R. Ahuja et al., *Phys. Rev. Lett.*, **106**, 018301 (2011)].

Some reviews of relativistic quantum chemistry are N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.*, **1997**, 1; K. G. Dyall and K. Faegri, *Introduction to Relativistic Quantum Chemistry*, Oxford, 2007; T. Nakajima and K. Hirao, *Chem. Rev.*, **112**, 385 (2012); P. Pyykkö, *Annu. Rev. Phys. Chem.*, **63**, 45 (2012).

16.12 Valence-Bond Treatment of Polyatomic Molecules

The valence-bond treatment of polyatomic molecules is closely tied to chemical ideas of structure. One begins with the atoms that form the molecule and pairs up the unpaired electrons to form chemical bonds. There are usually several ways of pairing up (coupling) the electrons. Each pairing scheme gives a VB **structure**. A Heitler–London-type function Φ_i (called a **bond eigenfunction**) is written for each structure i , and the molecular wave function ψ is taken as a linear combination $\sum_i c_i \Phi_i$ of the bond eigenfunctions. The variation principle is then applied to determine the coefficients c_i . The VB wave function is said to be a **resonance hybrid** of the various structures.

The weight of each resonance structure in the wave function is sometimes taken as proportional to the square of its coefficient in the wave function. Because the bond eigenfunctions are not mutually orthogonal, the electron probability density is not equal to the weighted sum of the probability densities of the various structures, and the $|c_i|^2$ quantities are somewhat lacking in direct physical significance. There are several other ways of

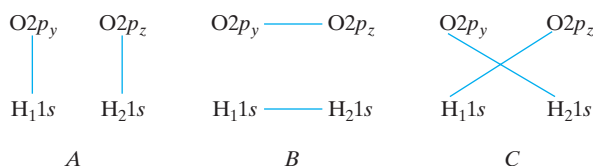


FIGURE 16.2 Ways of pairing valence AOs in H₂O.

assigning weights to VB structures. One procedure defines the *occupation number* n_i for the VB structure i as $n_i \equiv c_i^* \sum_j c_j S_{ij}$, where the sum goes over all the VB structures and $S_{ij} = \langle \Phi_i | \Phi_j \rangle$. The n_i 's add to 1 (Prob. 16.37).

Water

The oxygen-atom ground-state electron configuration is $1s^2 2s^2 2p^4$, with an unpaired electron in each of the AOs $2p_y$ and $2p_z$. We thus assume that these AOs along with the hydrogen $1s$ AOs will form electron-pair bonds. The three possible ways of pairing these four AOs to get covalent structures are shown in Fig. 16.2.

Let

$$s_1 \equiv \text{H}_1 1s, \quad s_2 \equiv \text{H}_2 1s, \quad p_y \equiv \text{O} 2p_y, \quad p_z \equiv \text{O} 2p_z$$

The normalized VB function corresponding to structure A is [see Eq. (13.119)]

$$\begin{aligned} \Phi_A = N | \cdots \widehat{p_y s_1} \widehat{p_z s_2} | &= N | \cdots p_y \overline{s_1} p_z \overline{s_2} | - N | \cdots \overline{p_y} s_1 p_z \overline{s_2} | \\ &\quad - N | \cdots p_y \overline{s_1} \overline{p_z} s_2 | + N | \cdots \overline{p_y} s_1 \overline{p_z} s_2 | \end{aligned} \quad (16.74)$$

where the signs are determined by the rule in Section 13.12. The dots stand for $\text{O} 1s \overline{\text{O} 1s} \text{O} 2s \overline{\text{O} 2s} \text{O} 2p_x \overline{\text{O} 2p_x}$. Similarly,

$$\Phi_B = N | \cdots \widehat{p_y p_z} \widehat{s_1 s_2} |, \quad \Phi_C = N | \cdots \widehat{p_y s_2} \widehat{p_z s_1} | \quad (16.75)$$

We then take as a trial variation function ψ , a linear combination of the bond eigenfunctions of structures A, B, and C. However, the functions Φ_A , Φ_B , and Φ_C are not linearly independent; we have (Prob. 16.38)

$$\Phi_C = -(\Phi_A + \Phi_B) \quad (16.76)$$

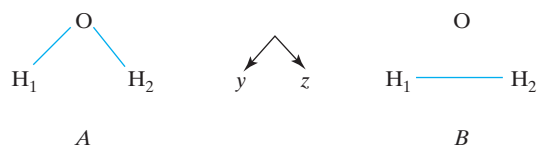
It is wasted effort to include all three structures; we shall drop structure C, taking $\psi = c_A \Phi_A + c_B \Phi_B$.

For a molecule with n valence AOs to be paired, where n is even, Rumer showed in 1932 that the following procedure gives the linearly independent covalent structures for singlet states: The n AOs are arranged in a ring, and lines are drawn between pairs of AOs; those structures where no lines cross are linearly independent. These are the **VB canonical covalent structures** of the molecule. Any structure with lines crossing is linearly dependent on the canonical structures and is omitted from the VB wave function. The number of ways of drawing $\frac{1}{2}n$ noncrossing lines between n points on a circle is

$$\frac{n!}{(\frac{1}{2}n)!(\frac{1}{2}n + 1)!} \quad (16.77)$$

[For a proof of (16.77), see J. Barriol, *Elements of Quantum Mechanics with Chemical Applications*, Barnes and Noble, 1971, pages 281–282.] H₂O has $4!/2!3! = 2$ canonical covalent structures, and these are A and B. (Actually, which structures are taken as the canonical ones is arbitrary, since the orbitals can be arranged in various ways on the ring.) To use Rumer's method when the number of orbitals to be paired is odd, we add a "phantom" orbital, whose contribution is subtracted at the end of the calculation.

FIGURE 16.3 Structures corresponding to the pairing schemes A and B of Fig. 16.2.



Rumer's procedure is easily justified. Let $\Phi(| \quad |)$, $\Phi(\square)$, and $\Phi(\times)$ be three bond eigenfunctions that involve any number of AOs, but that differ only in the way they pair up a certain subset of four AOs. Each of these functions corresponds to one of the three different ways of pairing these four AOs (see Fig. 16.2). By a slight extension of (16.76), it follows that

$$\Phi(\times) = -[\Phi(| \quad |) + \Phi(\square)] \quad (16.78)$$

Any pairing scheme involving lines that cross can be shown by repeated application of (16.78) to be a linear combination of structures with no lines crossing. (See Prob. 16.39).

The structures corresponding to the pairing schemes A and B for H_2O in Fig. 16.2 are shown in Fig. 16.3.

The separation between H_1 and H_2 is considerably greater than that between O and each hydrogen. The small overlap between the hydrogen $1s$ AOs makes structure A far more significant than structure B. Since the $2p_y$ and $2p_z$ AOs are at 90° to each other, the VB structure A predicts a bond angle of 90° , since this allows maximum overlap between the bonding oxygen and hydrogen AOs. The observed angle of $104\frac{1}{2}^\circ$ can be rationalized by considering electrostatic repulsions between the hydrogen atoms (ionic structures) and by allowing some mixing in (hybridization) of the $2s$ oxygen AO with the two bonding $2p$ AOs.

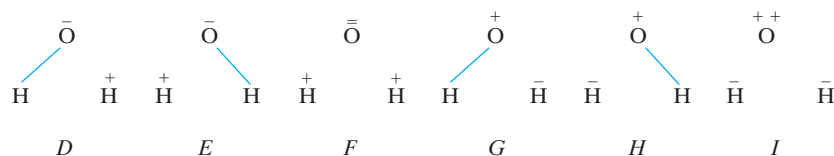
For H_2 the Heitler–London function was improved by inclusion of small contributions from ionic structures. Because of the considerable electronegativity difference between O and H, we expect ionic structures to be important in H_2O . Some ionic structures for H_2O are shown in Fig. 16.4. Because oxygen is much more electronegative than hydrogen, the contributions of G, H, and I are likely to be quite small. The point group $\mathcal{C}_{2v}$ has no degenerate symmetry species, and all the electronic wave functions of H_2O must be eigenfunctions of the $\hat{O}_{C_2}$ operator (see Section 15.2). The ground electronic state belongs to the totally symmetric symmetry species. Therefore, the coefficients of Φ_D and Φ_E in the wave function must be equal. In place of the terms $c_D\Phi_D + c_E\Phi_E$ in the VB wave function, we write $c_{DE}[N(\Phi_D + \Phi_E)]$, where the normalization constant is $N = (2 + 2\langle\Phi_D|\Phi_E\rangle)^{-1/2}$. The function $N(\Phi_D + \Phi_E)$ is called a VB **symmetry function** (or symmetry structure), whereas Φ_D and Φ_E are called **individual** VB functions. Thus, a reasonable variation function for H_2O is

$$c_A\Phi_A + c_B\Phi_B + c_{DE}[N(\Phi_D + \Phi_E)] + c_F\Phi_F \quad (16.79)$$

The ionic functions are written by analogy to the equation preceding (13.128); for example,

$$\Phi_D = |\cdots \widehat{p_y s_1 p_z p_z}| = |\cdots \overline{p_y s_1 p_z p_z}| - |\cdots \overline{p_y s_1 p_z p_z}|$$

FIGURE 16.4 Some ionic structures for H_2O .



The linear variation function (16.79) leads to a secular equation

$$\det(H_{ij} - ES_{ij}) = 0 \quad (16.80)$$

The AOs are expressed as STOs or as linear combinations of GTFs, and the matrix elements H_{ij} and overlap integrals between the functions $\Phi_A, \dots, \Phi_F$ are calculated. The lowest root of the secular equation gives an approximation to the ground-state energy (higher roots correspond to excited singlet states). Evaluation of the corresponding coefficients gives the VB ground-state wave function. The calculation can be done semiempirically using experimental data to evaluate some of the integrals. Calculation of the matrix elements is involved, and approximations are often made. For example, overlap integrals between different AOs (but *not* between different structures) are neglected and exchange integrals involving interchange of the coordinates of more than two electrons are neglected. Systematic procedures for evaluating the matrix elements have been developed.

Peterson and Pfeiffer did an ab initio all-electron VB calculation on H_2O [C. Peterson and G. V. Pfeiffer, *Theor. Chim. Acta*, **26**, 321 (1972)]. They included 10 covalent and 39 ionic VB structures in their wave function. The large number of structures arises because they considered structures arising from such oxygen configurations as $1s^2 2s 2p^5$ and $1s^2 2p^6$, as well as $1s^2 2s^2 2p^4$. The contribution of the ionic structures, as measured by the sum of their occupation numbers, was found to be 62%. The calculated energy and equilibrium geometry are -76.02 hartrees and $106.5^\circ, 0.968 \text{ \AA}$, which may be compared with the values in Table 15.2. They also did calculations on OH and O so as to calculate the first and second bond dissociation energies of H_2O . The calculated dissociation energies were not in good agreement with experiment.

Methane

The carbon-atom ground-state electron configuration $1s^2 2s^2 2p^2$ has two unpaired electrons and would seem to indicate a valence of 2. To get the well-known tetravalence of carbon, we assume that a $2s$ electron is promoted to the vacant $2p$ orbital, giving the configuration $1s^2 2s 2p^3$. If we then assume one bond is formed with the $2s$ electron and three bonds are formed with the $2p$ electrons, the bonds are not all equivalent as they are known to be. Hence Pauling proposed that the $2s$ and $2p$ functions be linearly combined to form **hybridized** sp^3 atomic orbitals of the form

$$b_i(\text{C}2s) + d_i(\text{C}2p_x) + e_i(\text{C}2p_y) + f_i(\text{C}2p_z), \quad i = 1, \dots, 4 \quad (16.81)$$

For maximum overlap we want each function to point to a vertex of a tetrahedron. From the discussion following Eq. (15.47), the constants d_i, e_i, f_i are proportional to the direction cosines in (15.57). Also, each orbital should have the same value of b_i so that the four hybrid orbitals will be equivalent. Thus the orbitals (16.76) are of the form (15.58) with $a = 0$ and $2a_1, 1t_{2x}, 1t_{2y}, 1t_{2z}$, replaced by $\text{C}2s, \text{C}2p_x, \text{C}2p_y, \text{C}2p_z$. If we impose the requirement that the hybrid AOs be orthonormal, we have

$$\begin{aligned} b^2 + c^2 &= 1, & b^2 - \frac{1}{3}c^2 &= 0 \\ c &= \frac{1}{2}\sqrt{3}, & b &= \frac{1}{2} \end{aligned}$$

The four equivalent sp^3 hybrid carbon AOs are then

$$\begin{aligned} \text{te}_1 &= \frac{1}{2}[\text{C}2s + \text{C}2p_x + \text{C}2p_y + \text{C}2p_z] \\ \text{te}_2 &= \frac{1}{2}[\text{C}2s + \text{C}2p_x - \text{C}2p_y - \text{C}2p_z] \\ \text{te}_3 &= \frac{1}{2}[\text{C}2s - \text{C}2p_x + \text{C}2p_y - \text{C}2p_z] \\ \text{te}_4 &= \frac{1}{2}[\text{C}2s - \text{C}2p_x - \text{C}2p_y + \text{C}2p_z] \end{aligned} \quad (16.82)$$

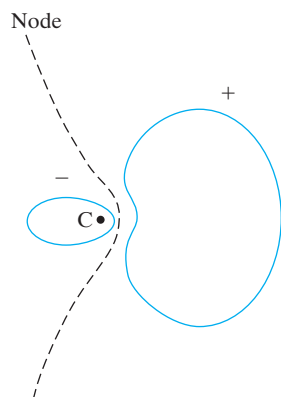


FIGURE 16.5 Carbon sp^3 hybrid orbital.

where “te” stands for tetrahedral. A typical sp^3 hybrid AO contour is shown in **Fig. 16.5**. (The three-dimensional shape is obtained by rotation about a horizontal axis through carbon.) Carbon sp^2 and sp hybrid AOs have similar shapes. [See I. Cohen and T. Bustard, *J. Chem. Educ.*, **43**, 187 (1966).]

There are many canonical covalent VB structures for methane, as well as ionic structures; however, chemical intuition suggests that the main contribution to the wave function is from the following covalent structure:

$$|C1s\overline{C1s}\ s_1\widehat{te}_1\ s_2\widehat{te}_2\ s_3\widehat{te}_3\ s_4\widehat{te}_4| \quad (16.83)$$

where $s_1 = H_11s$, and so on. The structure (16.83) is a linear combination of $2^4 = 16$ determinants. Taking the CH_4 VB wave function as the single covalent structure (16.83) or the H_2O VB wave function as the function corresponding to structure A in Fig. 16.3 gives what is called the **perfect pairing** approximation.

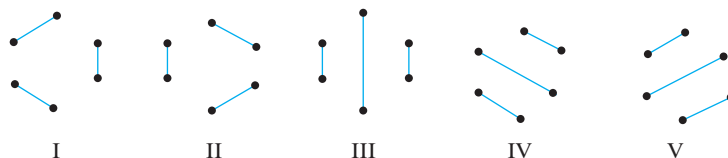
Raimondi, Campion, and Karplus did an ab initio all-electron VB calculation on CH_4 using a minimal AO basis set of STOs [M. Raimondi, W. Campion, and M. Karplus, *Mol. Phys.*, **34**, 1483 (1977)]. Their wave function is a linear combination of 104 symmetry functions (and is a linear combination of a much larger number of individual functions) and contained 4900 Slater determinants. Very surprisingly, the function with the largest coefficient in the wave function is not the perfect-pairing function (16.83), but is an ionic symmetry function with two covalent bonds and two ionic bonds. In this function, one of the sp^3 hybrid AOs on C has two electrons and the H atom it points to has no electrons, giving a C^-H^+ ionic bond, and a second sp^3 hybrid has no electrons and the H atom it points to has two electrons, giving a C^+H^- ionic bond. The perfect-pairing function, with four covalent bonds, has the second-highest coefficient. Two symmetry functions with three covalent bonds and one ionic bond (one symmetry function with a C^+H^- bond and one with a C^-H^+ bond) have coefficients almost as large as that of the perfect-pairing function. The perfect-pairing function has too little electron density in the overlap regions between atoms, and the great importance of the ionic structures is due to the fact that they increase the electron density in the overlap regions.

For ethylene the VB method uses sp^2 -hybridized carbon AOs to form the σ bonds by overlap with the $1s$ hydrogen AOs. This leaves a p orbital on each carbon to form the bond. The HCH bond angle is predicted to be 120° , in reasonable agreement with the observed value of 117° . For acetylene each carbon is sp hybridized.

Conjugated Molecules

Consider benzene. The σ bonds are formed by sp^2 carbon hybrid AOs and $1s$ hydrogen orbitals. This leaves a p orbital on each carbon to form π bonds. There are $6!/3!4! = 5$ canonical covalent structures for pairing the π orbitals, and these are shown in **Fig. 16.6**. Structures I and II are the Kekulé structures, and III, IV, and V are the Dewar structures. The VB Dewar structures of benzene are formal ways of pairing up electrons in AOs. Each VB Dewar structure is based on a regular-hexagonal arrangement of carbon atoms. Likewise, structures I and II correspond to a regular hexagon of carbons and differ from the hypothetical molecule cyclohexatriene with alternating bond lengths. Each VB resonance structure is based on the same internuclear distances, but a different electron-pairing scheme.

FIGURE 16.6 Canonical covalent structures for pairing the π orbitals in benzene.



The ground-state electronic wave function of C_6H_6 belongs to the totally symmetric symmetry species and is an eigenfunction of $\hat{O}_{C_6}$ with eigenvalue +1. The functions I and II combine with equal coefficients to form a single symmetry function, and the functions III, IV, and V combine to form a second symmetry function.

Benzene has six types of singly polar ionic structures. Four of the six types each have 12 associated individual structures, and the other two types each have 6 individual structures, giving a total of 60 individual singly polar ionic structures (see Prob. 16.40). Doubly and triply polar ionic structures also occur.

Recall that increasing the number of functions f_i in a linear variation function $\sum_i c_i f_i$ improves the variation function, that is, lowers the value of the variational integral. If we were to consider structure I only, then the energy obtained would be considerably higher than when several VB structures are considered. The difference between the energy for the individual structure I and that found when all VB structures are included is the **resonance energy** of benzene. One says that benzene is “stabilized by resonance,” but of course resonance is not a real phenomenon.

Such concepts as configuration interaction, resonance, hybridization, and exchange are not real physical phenomena, but only artifacts of the approximations used in the calculations. Similarly, the concept of orbitals is but an approximation, and, strictly speaking, orbitals do not exist.

Atomic Valence States

The **valence state** of an atom for a given molecular electronic state is the state in which the atom exists in the molecule. Since individual atoms do not really exist in molecules, the valence-state concept is an approximate one. The VB approximation constructs molecular wave functions from wave functions of the individual atoms. We use the VB wave function to define the valence state of an atom as the wave function obtained on removing all other atoms to infinity, while keeping the form of the molecular wave function invariant. This process is purely hypothetical, and the valence state is not in general a stationary atomic state.

A simple example is the H_2 ground state. The Heitler–London function is

$$N[|1s_a \overline{1s_b}| - |\overline{1s_a} 1s_b|]$$

Removal of hydrogen atom b leaves (at large internuclear separation, the normalization constant for each Slater determinant becomes $1/\sqrt{2}$)

$$2^{-1/2}1s_a - 2^{-1/2}\overline{1s_a}$$

The valence state is a hydrogen atom with a $1s$ spatial function and a 50% probability of having each of spin α or spin β . The valence-state ionization potential of hydrogen is thus 13.6 eV.

A less trivial example is H_2O . Although the H_2O ionic VB structures D and E are very important, it is traditional to ignore the ionic structures and find the oxygen valence state in H_2O from the perfect-pairing covalent function (16.74) corresponding to structure A. Removal of the H atoms from (16.74) gives

$$N[|\cdots 2p_y 2p_z| - |\cdots \overline{2p_y} 2p_z| - |\cdots 2p_y \overline{2p_z}| + |\cdots \overline{2p_y} \overline{2p_z}|] \quad (16.84)$$

Each determinant in (16.84) belongs to the oxygen configuration $1s^2 2s^2 2p^4$. This configuration gives the terms ^3P , ^1D , and ^1S (Table 11.2). The first and last determinants are eigenfunctions of $\hat{S}_z$ with eigenvalues $+1\hbar$ and $-1\hbar$, respectively; hence these two determinants must correspond to states of the ^3P term (which has $S = 1$). Analysis (which we omit) of the other two determinants shows each of them to be an equal mixture (coefficients $1/\sqrt{2}$) of states belonging to the ^1D and ^3P terms. Thus the valence state is a mixture of states of

the terms ^1D and ^3P and is not a stationary state of the atom. The valence-state wave function ψ_{vs} is not an eigenfunction of the atomic Hamiltonian. We can, however, calculate an average energy $\langle E_{vs} \rangle = \langle \psi_{vs} | \hat{H} | \psi_{vs} \rangle$. From $\psi_{vs} = N' [c_1 \psi(^3P) + c_2 \psi(^1D)]$, we have

$$\langle E_{vs} \rangle = |N'|^2 [c_1^2 E(^3P) + c_2^2 E(^1D)]$$

The preceding discussion gives

$$|c_1|^2 = 1^2 + (2^{-1/2})^2 + (2^{-1/2})^2 + 1^2 = 3, \quad |c_2|^2 = (2^{-1/2})^2 + (2^{-1/2})^2 = 1$$

We have $|N'|^2 = (|c_1|^2 + |c_2|^2)^{-1} = \frac{1}{4}$ and

$$\langle E_{vs} \rangle = \frac{3}{4}E(^3P) + \frac{1}{4}E(^1D)$$

$\langle E_{vs} \rangle$ can then be calculated from tables of atomic energy levels (Section 11.5).

If $2s$ hybridization is included in the $2p$ bonding oxygen orbitals of water, the oxygen valence state is found to be a linear combination involving terms of the configurations $1s^2 2s^2 2p^4$, $1s^2 2s 2p^5$, and $1s^2 2p^6$ (M. Kotani et al. in S. Flugge, ed., *Encyclopedia of Physics/Handbuch der Physik*, Springer, New York, 1961, Volume 37, pages 110–115). Hybridization gives a mixing of configurations in the valence state.

The valence state of carbon in CH_4 is important. Although the VB wave function of ground-state CH_4 is now known to have major contributions from ionic structures, the traditional way to find the C valence state is to start with the covalent perfect-pairing function (16.83). It is sometimes carelessly stated that the carbon sp^3 valence state corresponds to the ^5S term of the carbon atom $2s2p^3$ configuration. This is not correct. The $M_S = 2$ state of the $2s2p^3 \ ^5S_2$ level has one $2s$ and three $2p$ electrons, with all four of these electrons having spin α . It is true that we can use the procedure of Section 15.8 to form linear combinations of the $2s$ and $2p$ orbitals and thereby put each of the four outer electrons of the $^5S_2 \ M_S = 2$ state into an sp^3 hybrid AO without changing the wave function. However, each such hybrid AO would still have spin α . On the other hand, when we remove the hydrogen AOs from the CH_4 VB wave function (16.83), we are left with a linear combination of sixteen determinants in which each sp^3 hybrid AO has spin α in eight determinants and spin β in eight determinants. Thus the carbon valence state differs from the $2s2p^3 \ ^5S_2 \ M_S = 2$ state and in fact differs from the other states of this term. The valence state obtained on removal of the hydrogens from (16.83) turns out to be a mixture of states of the ^5S , ^3D , and ^1D terms of the $2s2p^3$ atomic configuration. [When other CH_4 VB structures besides (16.83) are included, we also get contributions from terms of the $2p^4$ and $2s^2 2p^2$ configurations to the C valence state.] The valence-state energy of carbon is well above the energy of the ground ^3P term of the $2s^2 2p^2$ configuration, but the energy gained by forming four bonds instead of two more than compensates for the energy needed to form the valence state.

Valence-state ionization potentials are used to estimate integrals in semiempirical calculations (Sections 17.2 and 17.3). The **valence-state ionization potential** for a $2p$ electron in an sp^3 -hybridized carbon atom is the energy difference between the valence state of sp^3 -hybridized C and the valence state of sp^2 -hybridized C^+ .

Status of the VB Method

The MO method puts electrons into orthogonal MOs. The VB method puts electrons into nonorthogonal AOs. This nonorthogonality makes VB calculations a huge computational task for a molecule with many electrons. To reduce the calculations, the σ electrons in a C_6H_6 ab initio VB calculation [J. M. Norbeck and G. A. Gallup, *J. Am. Chem. Soc.*, **96**, 3386 (1974)] were put into MOs, but even so this calculation did not optimize the molecular geometry, which is a simple task for an SCF MO calculation. The VB method allows for the change in the AOs that occurs on molecule formation by including ionic and other

resonance structures, thereby complicating the wave function. One finds quite large contributions from ionic structures even for such compounds as CH_4 and C_6H_6 . In contrast to the complicated VB wave function, a single-determinant SCF MO wave function usually furnishes a good description of the molecular ground electronic state in the region of the equilibrium geometry. The VB wave function does have the advantage of dissociating properly. For quantitative calculations, the MO method has greatly overshadowed the VB method, but there is still interest in generalizations of the VB method (see the next section).

Valence-bond theory has been used to describe the electronic structure of transition-metal complex ions, with such concepts as d^2sp^3 hybridization of the metal orbitals. However, the simple VB treatment of complex ions is not fully satisfactory and has been replaced by ligand-field theory, which is MO theory applied to species whose atoms have d (or f) electrons.

16.13 The GVB, VBSCF, and BOVB Methods

The classical VB method described in the last section uses AOs that are optimized for individual atoms. Several modern ab initio VB methods have been developed that use orbitals optimized for the molecule. Three such methods are described in this section.

The **generalized valence-bond (GVB) method** was developed in about 1970 by Goddard and co-workers [W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, **57**, 738 (1972); P. J. Hay, W. J. Hunt, and W. A. Goddard, *J. Am. Chem. Soc.*, **94**, 8293 (1972); W. A. Goddard, T. H. Dunning, W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973)].

The Heitler–London VB wave function for ground-state H_2 is [Eq. (13.100)] $1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)$ multiplied by a normalization constant and a spin function. The GVB ground-state H_2 wave function replaces this spatial function by $f(1)g(2) + f(2)g(1)$, where the functions f and g are found by minimization of the variational integral. To find f and g , one expands each of them in terms of a basis set of AOs and finds the expansion coefficients by iteratively solving one-electron equations that resemble the equations of the SCF MO method.

Clearly, the GVB method will give a lower energy than the simple VB wave function. The GVB method allows for the change in the AOs that occurs on molecule formation by solving variationally for f and g . In the VB method, this change is allowed for by adding to the wave function terms that correspond to ionic and other resonance structures. The GVB wave function is thus much simpler than a VB wave function with resonance structures and the calculations are simpler.

The GVB method gives a D_e of 4.12 eV for ground-state H_2 , as compared with 3.15 eV for the Heitler–London VB function, 3.78 eV for the Heitler–London–Wang function with an optimized orbital exponent, 4.03 eV for the Weinbaum function (13.109) that includes an ionic term, and 4.75 eV for the experimental value. At very large internuclear distance R , the GVB functions f and g approach the atomic orbitals $1s_a$ and $1s_b$. Thus, like the VB ψ (but unlike the MO ψ), the GVB wave function shows the correct behavior on dissociation. At intermediate distances, f is a linear combination of AOs that has its most important contribution from $1s_a$ but that has a significant contribution from $1s_b$ and lesser contributions from the other AOs (these contributions reflect the polarization of the $1s_a$ AO that occurs on molecule formation).

In the MO method, there is one orbital (an MO) for each electron pair. In the GVB method, there are two orbitals (f and g in the H_2 example) for each electron pair.

For CH_4 the VB wave function with resonance structures omitted is (16.83). For CH_4 the GVB wave function is

$$| \widehat{i_a i_b} \widehat{b_{1a} b_{1b}} \widehat{b_{2a} b_{2b}} \widehat{b_{3a} b_{3b}} \widehat{b_{4a} b_{4b}} | \quad (16.85)$$

The electrons are divided into pairs, and each pair is given two orbitals. In the VB method, the inner-shell orbitals i_a and i_b are each assumed to be $1s$ AOs on carbon, the bonding orbital b_{1a} is assumed to be an sp^3 -hybridized carbon AO pointing toward H_1 , and b_{1b} is assumed to be a $1s$ AO on hydrogen number 1. In the GVB method, no assumptions are made about the nature of the orbitals. One simply expands each of them in terms of the chosen basis set and solves the GVB equations until self-consistency is attained.

To simplify the calculation, the GVB method restricts orbitals in different pairs to be orthogonal to one another. (For example, b_{1a} and b_{2a} are assumed orthogonal, but b_{1a} and b_{1b} are not assumed orthogonal.) This should be a good assumption since Pauli repulsion between pairs keeps them well separated spatially. Moreover, a few test calculations have shown the orthogonality requirement to lead to little error.

For CH_4 one finds that i_a and i_b are essentially $C1s$ AOs; b_{1a} is an orbital centered mainly on C with some contribution from H_1 ; b_{1a} points toward H_1 and has a carbon AO hybridization of $sp^{2.1}$ (using a minimal basis set). The hybridization differs from the sp^3 hybridization of the VB wave function as a result of the contribution of $H_1 1s$ to b_{1a} . The orbital b_{1b} is found to be mainly an $H_1 1s$ AO with some contribution of carbon AOs mixed in, thereby polarizing the orbital toward C.

Since inner-shell electrons are little changed on molecule formation, one can simplify the GVB calculation by assuming each of i_a and i_b to be a $C1s$ AO, as is done in the VB wave function. This gives little loss in accuracy.

For C_2H_6 a GVB calculation with a minimal basis set gave a 3.1 kcal/mol rotational barrier, in good agreement with the 2.9 kcal/mol experimental value.

For C_2H_4 a GVB calculation gave a description of the double bond as composed of one σ and one π bond, in contrast to the energy-localized MOs (Section 15.9), which are two equivalent bent banana bonds.

For H_2O a GVB calculation produced an inner-shell pair on oxygen, two equivalent bonding pairs, and two equivalent lone pairs. With a DZP on oxygen basis set, an energy of -76.11 hartrees was obtained, which is below the Hartree–Fock limit of -76.07 hartrees (Table 15.2).

The GVB method (like the VB method) gives a description in terms of localized inner-shell, bonding, and lone pairs, whereas one must carry out a time-consuming special procedure to find localized MOs from canonical SCF MOs.

The GVB method is most applicable to molecules for which a single VB covalent structure is a good approximation.

The GVB method has been used to develop qualitative descriptions of chemical bonding; see W. A. Goddard and L. B. Harding, *Ann. Rev. Phys. Chem.*, **29**, 363 (1978).

The GVB method can be extended by writing the wave function as a linear combination of functions that correspond to different ways of coupling (combining) the electron spins to give a singlet state (just as is done in the VB method when the wave function is written as a linear combination of canonical covalent structures). This gives the *unrestricted* GVB wave function. A GVB wave function like (16.85) is sometimes called the GVB *perfect-pairing* (PP) wave function, to distinguish it from the unrestricted GVB wave function. The unmodified term GVB wave function usually refers to the GVB-PP wave function.

The **VBSCF** method [J. H. van Lenthe and G. G. Balint-Kurti, *J. Chem. Phys.*, **78**, 5699 (1983)] writes the molecular VB wave function as a linear combination of covalent and ionic VB structures and simultaneously optimizes the coefficients in the linear combination and the orbitals (which are expressed using a set of basis functions). The orbitals might be localized on individual atoms (as in the classical VB method of the last section) or they might be taken as semidelocalized (as in the GVB method).

The **breathing-orbital VB (BOVB)** method [P. C. Hiberty and S. Shaik, *Theor. Chem. Acc.*, **108**, 255 (2002) and references cited therein] differs in two ways from the VBSCF method. Each orbital in the BOVB method is always taken to be localized on an individual atom. The orbitals used in different structures are free to differ, so that each VB structure has its own set of optimized orbitals.

Although the VB method is not part of the standard arsenal of current quantum chemistry methods, its modern forms have their strong adherents, who point out that VB theory provides valuable conceptual insights and that the computational efficiency of VB methods is increasing. Some reviews of classical and modern valence-bond theory are: S. Shaik and P. C. Hiberty in K. B. Lipkowitz et al. (eds.), *Reviews in Computational Chemistry*, vol. 20, Chapter 1, 2004, Wiley-VCH; P. C. Hiberty and S. Shaik, *J. Comput. Chem.*, **28**, 137 (2007); A. Shurki, *Theor. Chem. Acc.*, **116**, 253 (2006); S. Shaik and P. C. Hiberty, *A Chemist's Guide to Valence Bond Theory*, Wiley, 2007; Shaik and Hiberty, *WIREs Comput. Mol. Sci.*, **1**, 18 (2011); W. Wu et al., *Chem. Rev.*, **111**, 7557 (2011); P. Su and W. Wu, *WIREs Comput. Mol. Sci.*, **3**, 56 (2013).

16.14 Chemical Reactions

The course of a chemical reaction is determined by the potential-energy function for nuclear motion $U(q_\alpha)$ (Section 13.1), where q_α indicates the coordinates of the N nuclei of the reactant molecules. To find the potential-energy surface (PES) $U(q_\alpha)$ (Section 15.10), we must solve the electronic Schrödinger equation at a very large number of nuclear configurations, which is a formidable task.

Once U is found, we look for the path of minimum potential energy on U connecting reactants and products. The point of maximum potential energy U on the minimum-energy path is called the **transition state**. This is a saddle point on the U surface, since it is a maximum point on a minimum-energy path. The transition state is not a stable molecule, and the transition from reactants to products is a smooth one. (However, in certain theories of reaction rates, it is convenient to ascribe properties such as entropy, free energy, and vibrational frequencies, to the transition state.) The energy difference between the transition state and the reactants (omitting zero-point vibrational energies) is called the **(classical) barrier height** for the forward reaction. For the reverse reaction, the surface U is the same as for the forward reaction.

When the U surface is known, it is possible (at least in principle) to calculate the reaction rate constant k as a function of temperature. Such calculations are extremely difficult. One must allow for quantum-mechanical tunneling through the barrier. Tunneling is important in reactions involving light species (e^- , H^+ , H , H_2), including reactions that transfer such species between heavy molecules. Moreover, there is significant probability for molecules to traverse the reaction surface on paths that deviate somewhat from the minimum-energy path. Thus one must perform averaging over the various possible paths. (In other words, we must consider different approaches of the reactant molecules, calculate the probability of reaction occurring for each approach, and then suitably average these probabilities.) The rate constant thus depends not only on the barrier height, but on the whole shape of the reaction potential-energy surface. For qualitative discussion we can use the fact that a large barrier height means a small rate constant, and a low barrier means a fast reaction.

By measuring the experimental rate constant k as a function of temperature, one can determine an experimental **activation energy** E_a , where $k = A \exp(-E_a/RT)$. The experimental quantity E_a differs slightly from the barrier height on the U surface. [See I. Shavitt, *J. Chem. Phys.*, **49**, 4048 (1968); M. Menzinger and R. Wolfgang, *Angew. Chem. Int. Ed. Engl.*, **8**, 438 (1969); Levine, *Physical Chemistry*, Section 22.4.]

To determine a complete reaction surface $U(q_\alpha)$, one needs to solve the electronic Schrödinger equation at about 10 points on the surface for each of the $3N - 6$ variables, so one needs about 10^{3N-6} calculations. For three-, four-, and five-atom systems, one needs 10^3 , 10^6 , and 10^9 calculations. Moreover, since the Hartree–Fock method does not usually correctly describe the process of molecular dissociation, we must include electron correlation to calculate a PES accurately.

Except for systems with very few atoms, accurate ab initio calculation of the complete potential-energy surface is out of the question. Instead, one aims to find the most important features of the surface. One attempts to locate the points on the surface where all the first derivatives $\partial U/\partial q_\alpha$ (the components of the gradient) are zero. These are called stationary points. A stationary point may be a local minimum, a local maximum, or a saddle point. To determine the nature of a stationary point, one evaluates the $(3N - 6)^2$ second derivatives $\partial^2 U/\partial q_\alpha \partial q_\beta$ (the components of the Hessian) at the point and uses these second derivatives to find the vibrational frequencies (Section 15.12) at the stationary point. At a local minimum, all the vibrational frequencies are real numbers. A transition state is a first-order saddle point and has one and only one imaginary vibrational frequency. A higher-order saddle point has two or more imaginary vibrational frequencies and is not a transition state. (Equivalently, since the eigenvalues of the Hessian matrix are proportional to the squares of the vibrational frequencies, the Hessian has all positive eigenvalues at a local minimum and has one negative eigenvalue at a transition state.)

Local minima correspond to reactants, products, or reaction intermediates. A **reaction intermediate** (which should not be confused with a transition state) is a product in one elementary step and a reactant in a subsequent elementary step of a multistep mechanism. A reaction intermediate lies at a minimum in U for all nuclear displacements. Reaction intermediates are often too short lived to allow spectroscopic determination of their structure. Hence, a very significant application of quantum chemistry is the determination of the structures and relative energies of reaction intermediates; for ab initio SCF MO results, see *Hehre et al.*, Section 7.3.

Finding transition states on a PES is much harder than finding local energy minima (Section 15.10). Analytical gradients of U facilitate finding transition states. Techniques to find transition states are discussed in H. B. Schlegel, *Adv. Chem. Phys.*, **67**, 250 (1987); H. B. Schlegel in J. Bertran and I. G. Csizmadia (eds.) *New Theoretical Concepts for Understanding Organic Reactions*, Kluwer, 1989, pp. 33–53; H. B. Schlegel in *Yarkony*, Part I, Chapter 8; *Leach*, Section 5.9.

After finding a transition state (first-order saddle point) on a PES, one must determine the nature of the reactants and products for this transition state by following the downhill paths from the saddle point to the reactants and to the products. (See the discussion below of the IRC.) Moreover, a lower-energy transition state for these reactants and products might exist elsewhere on the surface, so one must explore the surface so as to find the lowest-energy transition state between given sets of reactants and products.

An aid to finding the reactants and products for a given transition state is the fact that the atomic displacements in the normal vibrational mode that corresponds to the imaginary frequency tend to be in the directions of the reactants and products for this transition state. In the Spartan program, one can produce an animation of this mode.

The PES of a reaction with more than a few atoms may have many first-order saddle points. For example, calculations on the PES of the $\text{NH}_2 + \text{NO}$ reaction found 3 possible sets of products, 9 reaction intermediates, and 23 first-order saddle points [E. W.-G. Diau and S. C. Smith, *J. Chem. Phys.*, **106**, 9236 (1997)].

Knowledge of the minima, transition states, and barrier heights on a surface gives a good idea of the reaction mechanism.

Once the structure and vibrational frequencies of the transition state and the barrier height have been calculated, a rough estimate of the rate constant can be found using Eyring's transition-state (activated complex) theory (see any physical chemistry text). For more precise results, one must locate the minimum-energy path between reactants and products.

Although the location of the transition state is independent of the nuclear coordinates used as the variables in $U(q_\alpha)$, one finds that the location of the minimum-energy path depends on the choice of coordinates used. (For example, for H_2O , one possible choice is the $\text{O}-\text{H}_1$ and $\text{O}-\text{H}_2$ distances and the HOH angle, and another choice is the $\text{O}-\text{H}_1$, $\text{O}-\text{H}_2$, and H_1-H_2 distances.) The minimum-energy path (MEP) usually used is the **intrinsic reaction coordinate** (IRC), which is defined as the path that would be taken by a classical particle sliding downhill with infinitesimal velocity from the transition state to each of the minima [see Schlegel, *Adv. Chem. Phys.*, **67**, 250 (1987)]. The IRC turns out to correspond to the minimum-energy path (the path of steepest descent from the transition state) on a surface whose coordinates are the mass-weighted Cartesian coordinates $m_\alpha^{1/2}x_\alpha$, $m_\alpha^{1/2}y_\alpha$, $m_\alpha^{1/2}z_\alpha$ of the nuclei, where m_α is the mass of nucleus α . The IRC is also called the **reaction path**. However, the reaction path is not the actual path taken by reacting molecules moving according to classical mechanics, since the molecules have translational, rotational, and vibrational kinetic energy. Techniques to determine the IRC are discussed in the preceding references for finding transition states.

Once the reaction path and the force-constant matrix at points along the reaction path have been found, one can use improved versions of transition-state theory (TST) called *generalized transition-state theory* to calculate rate constants that are more accurate than those given by TST [see references cited in D. G. Truhlar, R. Steckler, and M. S. Gordon, *Chem. Rev.*, **87**, 217 (1987)] and can construct a reaction-path Hamiltonian and use it to study such things as vibrational-energy transfer during the reaction [W. H. Miller et al., *J. Chem. Phys.*, **72**, 99 (1981); W. H. Miller, *J. Phys. Chem.*, **87**, 3811 (1983)].

The *Gaussian* program contains many features designed to find transition states, follow reaction paths, and explore PESs. To locate a transition state, one can input a guessed transition-state structure that is intermediate between the structures of reactants and products of the elementary reaction and use the keyword `Opt=(TS,CalcFC)`. The TS tells *Gaussian* to use a search procedure that is appropriate to finding a first-order saddle point. The CalcFC tells *Gaussian* to accurately calculate the force constants (Hessian matrix elements) at the initial input geometry, rather than using the default procedure of estimating them (as is done in energy minimization—Section 15.10). Although using CalcFC increases the time needed for the calculation, it makes the transition-state search considerably more likely to succeed.

If a few guesses and `Opt=(TS,CalcFC)` don't succeed in locating a transition state, one can have *Gaussian* calculate an initial estimate of the transition-state structure from the structures of the reactants and products using a procedure called synchronous transit (ST) and then have *Gaussian* use this initial estimate as the starting point for the transition-state search. In this procedure, one uses the keyword `Opt=QST2` and one inputs the structures of the reactants and of the products. For details, see *Foresman and Frisch*, p. 46, and the *Gaussian* manual, which is available at the *Gaussian* website (www.gaussian.com).

The keyword IRC causes *Gaussian* to perform an IRC calculation. The input to such a job is the geometry of the transition state.

The keyword Scan allows one to use *Gaussian* to explore a PES. One specifies the variable(s) that will be scanned and the ranges of values they take on.

The most famous reaction surface is that for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$. The H_3 surface has been calculated to an extraordinary accuracy of 0.01 kcal/mol at 4067 points using

a highly accurate special extrapolation procedure applied to results of multireference CI aug-cc-pVTZ and aug-cc-pVQZ wave functions, and an analytical potential function has been very accurately fitted to these points [S. L. Mielke, B. Garrett, and K. A. Peterson, *J. Chem. Phys.*, **116**, 4142 (2002)]. From this surface, rate constants in very good agreement with experiment have been calculated [S. L. Mielke et al., *Phys. Rev. Lett.*, **91**, 063201 (2003)]. This surface is called the CCI (complete configuration interaction) surface, where CCI indicates it is extremely close to what would be found from a full-CI calculation with a complete basis set. The effect on the H_3 barrier height of the main correction to the Born–Oppenheimer approximation is calculated in S. L. Mielke, *J. Chem. Phys.*, **122**, 224313 (2005)].

Comparisons of ab initio HF calculations with calculations that include electron correlation indicate that for many reactions ab initio HF transition-state structures are reasonably accurate, but for certain classes of reactions, HF transition-state geometries are unreliable [F. Bernardi and M. A. Robb, *Adv. Chem. Phys.*, **67**, 155 (1987)]. HF calculations do not generally give accurate energy differences between points on potential-energy surfaces.

The IMOMO, IMOMM, and ONIOM Methods

Accurate calculation of reaction barrier heights usually requires inclusion of electron correlation and use of a substantial-size basis set, and is impractical for medium and large molecules. To deal with this problem, the IMOMO (integrated molecular orbital plus molecular orbital) method of Morokuma and co-workers allows one to estimate energy changes involving large molecules by combining high-level quantum-mechanical calculations on a related smaller system (the *model* system) with low-level calculations on the actual system (the *real* system) [S. Humbel, S. Sieber, and K. Morokuma, *J. Chem. Phys.*, **105**, 1959 (1996)]. The IMOMO energy of a system is taken as

$$E_{\text{IMOMO}} = E(\text{real, low}) + [E(\text{model, high}) - E(\text{model, low})]$$

Roughly speaking, the quantity in brackets gives an estimate of $E(\text{real, high}) - E(\text{real, low})$ so that E_{IMOMO} is an approximation to $E(\text{real, high})$. The low level might be HF, DFT, MP2, or a semiempirical MO method (Section 17.4). The high level might be MP2, MP4, CCSD(T), CASSCF, and so on. Note that “MO” in the name IMOMO is not synonymous with Hartree–Fock but includes such MO-based methods as MP and CC; DFT does not use MOs but does use Kohn–Sham orbitals.

As an example, suppose one wants to calculate the barrier height for the reaction $\text{Cl}_a^- + \text{H}_a\text{H}_b\text{C}_a(\text{Cl}_b)\text{C}_b\text{H}_3 \rightarrow \text{H}_2\text{C}(\text{Cl}_a)\text{CH}_3 + \text{Cl}_b^-$, where the subscripts help distinguish identical atoms. The model system can be taken as $\text{Cl}^- + \text{H}_a\text{H}_b\text{C}_a(\text{Cl})\text{H}_c$, in which an H atom (the *capping atom*) replaces the methyl group, so as to give a smaller system more easily treatable at a higher level. The methyl carbon in the real system that is replaced by the capping atom is called the *link atom*. The model system retains the atoms and bonds that are most directly involved in the reaction.

To optimize the reactants’ geometries or the transition-state geometry, one varies the bond distances, angles, and dihedral angles in the real and the model systems (subject to certain constraints) so as to either minimize E_{IMOMO} or to locate a first-order saddle point. IMOMO constrains corresponding bond distances, bond angles, and dihedral angles in the real and model systems to be the same. For example, the $\text{H}_a\text{C}_a\text{H}_b$ angles in the real and the model system are equal, and the $\text{H}_a\text{C}_a\text{C}_b$ angle in the real system equals the $\text{H}_a\text{C}_a\text{H}_c$ angle in the model system. Moreover, to avoid problems in geometry optimization, IMOMO takes the bond distance $\text{C}_a - \text{H}_c$ to the capping atom in the model system and the distance $\text{C}_a - \text{C}_b$ to the link atom in the real system to be frozen at standard values.

The method works rather well in finding barrier heights and produces large savings in computational time.

The IMOMM (integrated molecular orbital plus molecular mechanics) method resembles IMOMO, but the lower level used is the molecular-mechanics method (Section 17.5) and some details of the implementation differ from IMOMO [F. Maseras and K. Morokuma, *J. Comput. Chem.*, **16**, 1170 (1995)].

The IMOHC (integrated molecular orbital method with harmonic cap) method is a modification of IMOMO and IMOMM in which the bond distances to the link atom in the real system and the capping atom in the model system are not frozen but are allowed to vary in the optimization [J. C. Corchado and D. G. Truhlar, *J. Phys. Chem. A*, **102**, 1895 (1998)].

The ONIOM (our own n -layered integrated molecular orbital and molecular mechanics) method is an extension of IMOMO and IMOMM that performs calculations on n different systems using n levels of calculation. Each system and calculation level constitute a layer. The IMOMO and IMOMM methods are versions of ONIOM with $n = 2$. ONIOM3 is the three-layered version of ONIOM and uses a real system calculated at a low level, an intermediate model system calculated at a medium level, and a small model system calculated at a high level [M. Svensson et al., *J. Phys. Chem.*, **100**, 19357 (1996)].

Problems

Sec.	16.2	16.3	16.4	16.5	16.7	16.9
Probs.	16.1–16.8	16.9–16.14	16.15–16.20	16.21–16.31	16.32–16.33	16.34–16.35

Sec.	16.11	16.12	16.14
Probs.	16.36	16.37–16.44	16.45–16.46

- 16.1** Find the number of CSFs in a full CI calculation of CH_2SiHF using a 6-31G** basis set.
- 16.2** Let γ be the fraction of the basis-set correlation energy obtained by a CI-SD calculation on a molecule with n electrons. Sasaki showed that an approximate equation satisfied by γ is $\gamma^{-1} - 1 = \frac{1}{2}\beta\gamma n - \beta$, where β is a quantity whose value is typically 0.015 to 0.03 for molecules consisting of first-row atoms. For such molecules, use this equation to estimate the percent of the basis-set correlation energy obtained by CI-SD calculations for $n = 20, 50, 100$, and 200.
- 16.3** Frozen-core SCF/DZP and CI-SD/DZP calculations on H_2O at its equilibrium geometry gave energies of -76.040542 and -76.243772 hartrees. Application of the Davidson correction brought the energy to -76.254549 hartrees. Find the coefficient of Φ_0 in the normalized CI-SD wave function.
- 16.4** For a CI calculation of the H_2 ground electronic state, which of the following electron configurations will produce a CSF that will contribute to the wave function? (a) $(1\sigma_g)(2\sigma_g)$; (b) $(1\sigma_g)(2\sigma_u)$; (c) $(1\sigma_u)^2$; (d) $(1\pi_u)(1\pi_g)$; (e) $(1\pi_u)(3\sigma_u)$; (f) $(1\pi_u)^2$; (g) $(1\pi_u)(2\pi_u)$.
- 16.5** Verify the expression given for the CI ground-state wave function in the Section 16.2 example.
- 16.6** In the Section 16.2 CI example, verify the expressions given in terms of integrals over the basis functions for (a) $\langle \Phi_2 | \hat{H} | \Phi_2 \rangle$; (b) $\langle \Phi_2 | \hat{H} | \Phi_1 \rangle$.
- 16.7** For a CASSCF wave function in which the active orbitals are taken as those that arise from the $2s$ and $2p$ AOs, state the number of active electrons and the maximum number of electrons excited to virtual orbitals in the ground-state wave function for (a) C_2 ; (b) N_2 ; (c) O_2 ; (d) F_2 .
- 16.8** For a CASSCF(m, n) calculation, the number N of singlet CSFs (ignoring any symmetry restrictions) is

$$N = \frac{n!(n+1)!}{(\frac{1}{2}m)!(\frac{1}{2}m+1)!(n-\frac{1}{2}m)!(n-\frac{1}{2}m+1)!}$$

- (a) Calculate N for a CASSCF(6,6) calculation. (b) Calculate N for a CASSCF(14,14) calculation.

- 16.9** Verify (16.11) for the MP perturbation $\hat{H}'$.
- 16.10** To derive the MP $E_0^{(2)}$, we set $\psi_s^{(0)} = \Phi_{ij}^{ab}$ in (16.12); the sum over excited states $s \neq 0$ in (16.12) is replaced by a quadruple sum over i, j, a , and b that produces all possible determinants that contain two excited spin-orbitals and that represent different states. (a) For this quadruple sum, explain why we want the limits for i and j to be as in (16.13); explain why $\Phi_{ij}^{ab} = 0$ if $a = b$, and explain why we want the limits for a and b to be as in (16.13). (b) Use the Condon–Slater rules to evaluate $\langle \Phi_{ij}^{ab} | \hat{H}' | \Phi_0 \rangle$, and show that (16.13) follows.
- 16.11** True or false? A nonrelativistic MP2 calculation can give an energy that is less than the true nonrelativistic ground-state energy.
- 16.12** (a) Use MP2(FC)/6-31G* calculations to predict the geometry, vibrational frequencies, dipole moment, and atomization energy of CO_2 . Use 0.95 as the scale factor for the vibrational frequencies. Compare with HF/6-31G* and experimental results (Prob. 15.40). (Note that frozen core is the default in *Gaussian* MP calculations, so the keyword MP2 produces an FC calculation.) (b) Repeat (a) for H_2O .
- 16.13** For the HF molecule, find the predicted bond length, dipole moment, electronic energy including nuclear repulsion, and unscaled harmonic vibrational frequency using the following calculations. Also, if your program calculates these, give the predicted values of the thermodynamic quantities $U_{298}^\circ - U_0^\circ$ and S_{298}° . (a) MP2(FC)/6-31G*; (b) MP4(FC)/6-31G*. (You can do these using the WebMO Demo Server.) Compare with HF/6-31G* and experimental values. Note that frozen core is the default option in most programs and need not be specified. (Note that *Gaussian 09* uses a standard pressure of 1 atm, rather than the recommended 1 bar.)
- 16.14** Although ab initio HF calculations fail in predicting molecular atomization energies, one can still use HF energies to estimate energy changes for certain types of reactions. Recall that good barriers to internal rotation can usually be obtained from ab initio SCF MO calculations because of a near cancellation in correlation energies between different molecular conformations. As ethane goes from staggered to eclipsed, the number of chemical bonds of each type does not change. More generally, one might hope that a similar near cancellation of correlation energies might occur for an isodesmic chemical reaction; an **isodesmic reaction** (Greek *isos*, “equal”; *desm*, “bond”) is one in which the number of bonds of each type does not change [W. J. Hehre et al., *J. Am. Chem. Soc.*, **92**, 4796 (1970)]. For example, the isodesmic reaction $\text{CH}_2=\text{CHCH}_2\text{OH} + \text{CH}_2=\text{O} \rightarrow \text{CH}_2=\text{CHOH} + \text{CH}_3\text{CH}=\text{O}$ has seven CH bonds, one CC double bond, one CC single bond, one CO double bond, one CO single bond, and one OH bond on each side. A special kind of isodesmic reaction is a **bond-separation reaction**. Here, one starts with a molecule and converts it to products, each of which contains only one bond between nonhydrogen atoms. For example, starting with $\text{CH}_3-\text{CH}=\text{C}=\text{O}$, one would form the products CH_3-CH_3 , $\text{CH}_2=\text{CH}_2$, and $\text{CH}_2=\text{O}$, in which the C—C, C=C, and C=O bonds are separated from one another. To balance the reaction, one adds an appropriate number of hydride molecules (for example, CH_4 , NH_3 , H_2O) to the left side. The bond-separation reaction for CH_3CHCO is then $\text{CH}_3-\text{CH}=\text{C}=\text{O} + 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 + \text{CH}_2\text{O}$. The bond-separation reaction for benzene is $\text{C}_6\text{H}_6 + 6\text{CH}_4 \rightarrow 3\text{C}_2\text{H}_6 + 3\text{C}_2\text{H}_4$. (If the energy of a molecule could be represented as the sum of bond energies that were invariant from molecule to molecule, then the energy change for any isodesmic reaction would be zero. The energy change for a bond-separation reaction measures the interactions between the bonds in the molecule.) If an SCF MO calculation could fairly accurately predict the energy change for the bond-separation reaction of a large molecule, then we could use the known energies of the small product molecules like C_2H_6 to get a reasonably good estimate for the energy of the large molecule from an SCF calculation, without having to use expensive correlation methods. (a) Write the bond-separation reaction for cyclopropane. Do the same for CH_3CHO . (b) Do HF/6-31G* energy and vibrational frequency calculations on the molecules in the CH_3CHO bond-separation reaction. Scale the vibrational frequencies (Section 15.12) to find the zero-point energies. Find the ΔH_0° value predicted by the HF/6-31G* method for the gas-phase CH_3CHO bond-separation reaction. Compare with the experimental value of 11.5 kcal/mol.

- (c) Repeat (b) using MP2/6-31G* calculations. (Although isodesmic-reaction calculations work reasonably well for small molecules, the errors become too large when used with large molecules.)
- 16.15** Show that ψ in (16.15) satisfies $\langle \psi | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1$, and show that $\langle \psi | \psi \rangle \neq 1$. In what earlier chapter in this book does an equation like $\langle \psi | \Phi_0 \rangle = 1$ appear?
- 16.16** (a) Give an example of an uncharged molecule for which the CCSD(T)(full)/cc-pVQZ energy is the same as the CCSD(full)/cc-pVQZ energy. (b) Give an example of an uncharged molecule for which the CCSD(T)(FC)/cc-pVQZ is exactly the same as the CCSD(FC)/cc-pVQZ energy but the CCSD(full)/cc-pVQZ energy differs from the CCSD(T)(full)/cc-pVQZ energy. (c) Give an example of an uncharged molecule for which the CCSD energy in the CBS limit equals the exact nonrelativistic energy.
- 16.17** (a) Verify the CC equation (16.27). (b) Verify (16.28).
- 16.18** Verify the extrapolation equation (16.32).
- 16.19** For H₂O, CCSD(T)(FC) energies in hartrees at the optimized geometry for each basis set for the aug-cc-pVnZ basis sets are -76.363588 for $n = 4$, -76.370298 for $n = 5$, -76.372559 for $n = 6$, and -76.373672 for $n = 7$ [D. Feller and K. A. Peterson, *J. Chem. Phys.*, **131**, 154306 (2009)]. (The $n = 7$ basis set exists for only a few elements.) (a) Use the equation following (16.32) to derive a formula that expresses E_∞ in terms of E_n and E_{n-1} . (b) Use this formula with n and $n - 1$ being 5 and 4 to estimate the CCSD(T)(FC) CBS limit for H₂O. Repeat for the values 6 and 5 and then for 7 and 6. Your estimates will not be close to the true nonrelativistic energy -76.438 listed in Table 16.2 mainly because of the frozen-core approximation. A CCSD(T)(full)/aug-cc-pCV5Z calculation gives -76.432 hartrees [M. Cortez et al., *J. Chem. Theory Comput.*, **3**, 1267 (2007)].
- 16.20** For the HF molecule, run the following calculations to find the predicted bond length, (unscaled) harmonic vibrational frequency, dipole moment, and electronic energy including nuclear repulsion. Also, if your program calculates these, give the predicted values of the thermodynamic quantities $U_{298} - U_0^\circ$ and S_{298}° . (a) CCSD(FC)/6-31G*; (b) CCSD(T)(FC)/6-31G*. You can run these on the Internet using the WebMO Demo Server. Note that frozen core is the default option in most programs. (c) Compare your results with the MP2 and MP4 calculations of Prob. 16.13 and with HF/6-31G* and experimental values.
- 16.21** Which of the following are functionals? (a) $\int f(x) dx$; (b) $\int_0^1 f(x) dx$; (c) $\int_0^2 [f(x) + 1]^2 dx$; (d) $[f(x) + 1]^2$; (e) $df(x)/dx|_{x=0}$.
- 16.22** Let $\hat{H}_a$ and $\hat{H}_b$ be the operators obtained when $v(\mathbf{r}_i)$ in (16.33) is replaced by $v_a(\mathbf{r}_i)$ and $v_b(\mathbf{r}_i)$, respectively, where $v_a(\mathbf{r}_i)$ and $v_b(\mathbf{r}_i)$ differ by more than a constant. Prove that the ground-state wave functions $\psi_{0,a}$ and $\psi_{0,b}$ of these Hamiltonians must be different functions. *Hint:* Assume they are the same function, write the Schrödinger equations for $\hat{H}_a$ and $\hat{H}_b$, subtract one equation from the other, and show that this leads to $v_a(\mathbf{r}_i) - v_b(\mathbf{r}_i)$ equals a constant, thereby contradicting the given information and proving that the two wave functions cannot be equal.
- 16.23** (a) Find $\delta E_x^{X\alpha} / \delta \rho$, where $E_x^{X\alpha}$ is given by (16.61). (b) If $F[\rho] = \int \rho^{-1} \nabla \rho \cdot \nabla \rho dv$, where the integral is over all space, and ρ is a function of x , y , and z that vanishes at infinity, find $\delta F / \delta \rho$.
- 16.24** Verify that $\hat{h}^{\text{KS}}(1)$ in (16.49) is the same as the Fock operator (16.8) except that the exchange operators in the Fock operator are replaced by v_{xc} .
- 16.25** Verify Eqs. (16.57) and (16.58).
- 16.26** Verify (16.60) for E_x .
- 16.27** Verify that (16.65) for E_x^{LSDA} reduces to (16.58) for E_x^{LDA} if $\rho^\alpha = \rho^\beta$.
- 16.28** (a) For an n -electron molecule, show that the electron probability density is given by $\rho(\mathbf{r}) = n \langle \psi | \delta(\mathbf{r} - \mathbf{r}_1) | \psi \rangle = \langle \psi | \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{r}_i) | \psi \rangle$, where $\delta(\mathbf{r} - \mathbf{r}_i) = \delta(x - x_i) \delta(y - y_i) \delta(z - z_i)$ and δ is the Dirac delta function (Section 7.7). (b) Use the Condon-Slater rules to show that if ψ is a single Slater determinant of spin-orbitals $u_i = \theta_i \sigma_i$, then $\rho(\mathbf{r}) = \sum_{i=1}^n |\theta_i(r)|^2$.

- 16.29** (a) For CO₂, use SVWN/6-31G*, BLYP/6-31G*, and B3LYP/6-31G* calculations to predict the equilibrium geometry, vibrational frequencies, and atomization energy. Do not scale the vibrational frequencies. Compare the results and the computational times with HF/6-31G* calculations (Prob. 15.40). (b) Repeat (a) for H₂O.
- 16.30** Repeat Prob. 15.57 for HCOOH using B3LYP/6-31G* calculations.
- 16.31** Repeat Prob. 16.14(b) using B3LYP/6-31G* calculations.
- 16.32** (a) Problem 7.46 showed that if $\hat{H}$ is independent of time, Ψ as a function of time is given by (7.101), where the c_n 's are constants. Use (7.101) to explain why in the limit $\tau \rightarrow \infty$ (where $\tau \equiv it/\hbar$) we have $\Psi = c_{gs} \exp(-\tau E_{gs}) \psi_{gs}$, where ψ_{gs} is the ground-state wave function. For convenience, we shift the zero level of energy by subtracting the constant V_{ref} from $\hat{H}$, where V_{ref} is chosen as the best estimate we have of the ground-state energy E_{gs} . Explain why this shift gives $\Psi = c_{gs} \exp[-\tau(E_{gs} - V_{\text{ref}})] \psi_{gs}$. (Use of V_{ref} prevents Ψ from becoming very small or very large at large τ .) (b) Show that the time-dependent Schrödinger equation (7.97) for an n -electron molecule is $\partial\Psi/\partial\tau = \frac{1}{2}\sum_{i=1}^n \nabla_i^2 \Psi - (V - V_{\text{ref}})\Psi$. This equation has the same form as the equation $\partial C/\partial t = D \nabla^2 C - kC$ for a species undergoing both diffusion (with diffusion coefficient D) and a first-order chemical reaction with rate constant k , where C is the concentration, provided we replace the three-dimensional space of the diffusion equation with a $3n$ -dimensional "space" whose variables are the coordinates of the n electrons.
- 16.33** To properly apply the DQMC method, one must allow for the nodes produced by the antisymmetry requirement. (a) Consider a system of three electrons in a one-dimensional box, where we shall pretend that the interelectronic repulsions are small enough to be neglected. By analogy to the Li zeroth-order wave function (10.48), write down the ground-state wave function for this system. (b) Use orthogonality of the three different three-electron spin factors that multiply a , b , and c in Prob. 10.15 to show that each spatial factor that corresponds to a , b , or c is an eigenfunction of $\hat{H}$. Hence, in doing the DQMC computer simulation of the imaginary-time Schrödinger equation, we need deal with only one of the spatial factors, say, the one corresponding to a . For our system of electrons in a box, there are three spatial variables, the coordinates x_1 , x_2 , and x_3 of the three electrons, and the DQMC simulation is done in a three-dimensional space bounded by the sides of a cube, on which the wave function vanishes. Show that the spatial factor corresponding to a has a nodal surface defined by $x_2 = x_3$ and this is the only nodal surface within the cube. (*Hint*: Use a trigonometric identity for $\sin 2z$.) (c) Show that the nodal surface $x_2 = x_3$ is a plane that divides the cube into two regions of equal volume; that in one of these regions (the one with $x_3 > x_2$) the wave function is positive, and in the other region, the wave function is negative. Also show that for each point P in one region, there is a corresponding point (the one with the values of x_2 and x_3 interchanged) where the wave function has minus its value at P. In doing the DQMC simulation, one works entirely within one region and eliminates any walker that crosses the nodal surface. (Note that the concentration C in the diffusion equation must always be positive or zero.)
- 16.34** (a) For gas-phase CH₃CHO, optimize the geometry at the B3LYP/6-31G* level and then use the GIAO method with B3LYP/6-31G* to find the predicted proton and ¹³C isotropic shielding constants (in ppm). (In *Gaussian*, the keyword NMR or NMR=GIAO on the line that begins with a # sign produces a GIAO calculation.) If you are using the WebMO Demo Server, you will need to click on Raw output to see the shielding constants. (b) The TMS GIAO shielding constants for B3LYP/6-31G* are 189.78 ppm for ¹³C and 32.18 for the protons. Use the results of part (a) to find the predicted proton and ¹³C chemical shifts relative to TMS. (c) Look up at cheshirenmr.info the recommended linear scaling constants for the method of part (a) to get scaled chemical shift predictions. Compare these with the experimental results at riodb01.iastate.edu/sdbs. Ignore the effect of the solvent.
- 16.35** Repeat Prob. 16.34 using MP2/6-31+G(d,p) geometry optimization followed by a single-point NMR MP2/6-31+G(d,p) calculation.
- 16.36** Use the virial-theorem result (14.76) to show that $\langle v^2 \rangle^{1/2}/c = Ze^2/4\pi\epsilon_0\hbar c \approx Z/137$ for the ground-state H atom.
- 16.37** Prove that the sum of the VB occupation numbers n_i is 1.

- 16.38** Verify Eq. (16.76) for the H_2O covalent VB structures.
- 16.39** Consider the orbitals 1, 2, ..., 6 arranged in order on a circle. Use (16.78) repeatedly to show that the scheme with the pairings 1–5, 2–4, 3–6 can be expressed as a linear combination of structures with no lines crossing.
- 16.40** Draw an example of each of the six types of singly polar ionic benzene structures. Work out how many individual structures of each type exist.
- 16.41** For 1,3-butadiene: (a) How many canonical covalent VB structures are there for the π electrons? (b) Draw these structures. (c) Draw the 12 individual singly polar ionic structures for the π electrons.
- 16.42** (a) How many canonical covalent structures are there for the naphthalene π electrons? (b) Of these, how many are Kekulé structures (no long bonds)? (c) Considering only the Kekulé structures, which bonds in naphthalene does the resonance method predict to be the shortest?
- 16.43** The three equivalent sp^2 hybrid AOs of carbon point to the corners of an equilateral triangle. Derive expressions for them, assuming orthonormality.
- 16.44** The two equivalent sp hybrid carbon AOs make an angle of 180° with each other. Derive them.
- 16.45** Consider the reaction $\text{HCN} \rightarrow \text{CNH}$. (a) Find the HF/6-31G* equilibrium geometries of HCN and HNC. (Recall that 180° is not allowed as a Z-matrix bond angle.) (b) Find the HF/6-31G* transition-state structure for this reaction. *Hints:* We expect the transition-state (TS) structure to be roughly halfway between the reactant and product structures. Thus we expect a triangular TS with the CN distance somewhere between its values in the reactant and product, the HC distance somewhat longer than its values in the reactant, and the HN distance somewhat longer than its value in the product. Start with an initial guess for the TS structure. In *Gaussian*, one way to find a TS is to replace Opt by Opt(CalcFC,TS).
- 16.46** (a) For formic acid, HCOOH , find the two stable conformers at the HF/6-31G* level; check that each conformer is a local minimum. Then find the structure of the HF/6-31G* transition state between these conformers. (See also Prob. 16.45.) What is the HF/6-31G* barrier to internal rotation about the CO single bond (omit zero-point energies)? (b) Repeat for vinyl alcohol.