# Chapter 19

*Corrections to the mean-field model are needed to describe the instantaneous Coulombic interactions among the electrons. This is achieved by including more than one Slater determinant in the wavefunction.*

Much of the development of the previous chapter pertains to the use of a single Slater determinant trial wavefunction. As presented, it relates to what has been called the unrestricted Hartree-Fock (UHF) theory in which each spin-orbital $\phi_i$ has its own orbital energy $\varepsilon_i$ and LCAO-MO coefficients $C_{\nu,i}$ ; there may be different $C_{\nu,i}$ for $\alpha$ spin-orbitals than for $\beta$ spin-orbitals. Such a wavefunction suffers from the spin contamination difficulty detailed earlier.

To allow for a properly spin- and space- symmetry adapted trial wavefunction and to permit $\Psi$ to contain more than a single CSF, methods which are more flexible than the single-determinant HF procedure are needed. In particular, it may be necessary to use a combination of determinants to describe such a proper symmetry function. Moreover, as emphasized earlier, whenever two or more CSFs have similar energies (i.e., Hamiltonian expectation values) and can couple strongly through the Hamiltonian (e.g., at avoided crossings in configuration correlation diagrams), the wavefunction must be described in a multiconfigurational manner to permit the wavefunction to evolve smoothly from reactants to products. Also, whenever dynamical electron correlation effects are to be treated, a multiconfigurational $\Psi$ must be used; in this case, CSFs that are doubly excited relative to one or more of the essential CSFs (i.e., the dominant CSFs that are included in the so-called reference wavefunction) are included to permit polarized-orbital-pair formation.

Multiconfigurational functions are needed not only to account for electron correlation but also to permit orbital readjustments to occur. For example, if a set of SCF orbitals is employed in forming a multi-CSF wavefunction, the variational condition that the energy is stationary with respect to variations in the LCAO-MO coefficients is no longer obeyed (i.e., the SCF energy functional is stationary when SCF orbitals are employed, but the MC-energy functional is generally not stationary if SCF orbitals are employed). For such reasons, it is important to include CSFs that are singly excited relative to the dominant CSFs in the reference wavefunction.

That singly excited CSFs allow for orbital relaxation can be seen as follows. Consider a wavefunction consisting of one CSF $|\phi_1\ldots\phi_i\ldots\phi_N|$ to which singly excited CSFs of the form $|\phi_1\ldots\phi_m\ldots\phi_N|$ have been added with coefficients $C_{i,m}$:

$$\Psi = \Sigma_m C_{i,m} |\phi_1\ldots\phi_m\ldots\phi_N| + |\phi_1\ldots\phi_i\ldots\phi_N|.$$

All of these determinants have all of their columns equal except the $i^{th}$ column; therefore, they can be combined into a single new determinant:

$$\Psi = |\varphi_1 \ldots \varphi_i' \ldots \varphi_N|,$$

where the relaxed orbital $\varphi_i'$ is given by

$$\varphi_i' = \varphi_i + \Sigma_m C_{i,m} \varphi_m.$$

The sum of CSFs that are singly excited in the $i^{th}$ spin-orbital with respect to $|\varphi_1 \ldots \varphi_i \ldots \varphi_N|$ is therefore seen to allow the spin-orbital $\varphi_i$ to relax into the new spin-orbital $\varphi_i'$. It is in this sense that singly excited CSFs allow for orbital reoptimization.

In summary, doubly excited CSFs are often employed to permit polarized orbital pair formation and hence to allow for electron correlations. Singly excited CSFs are included to permit orbital relaxation (i.e., orbital reoptimization) to occur.

## I. Different Methods

There are numerous procedures currently in use for determining the 'best' wavefunction of the form:

$$\Psi = \Sigma_I C_I \Phi_I,$$

where $\Phi_I$ is a spin-and space- symmetry adapted CSF consisting of determinants of the form $| \varphi_{I1} \varphi_{I2} \varphi_{I3} \ldots \varphi_{IN} |$. Excellent overviews of many of these methods are included in <u>Modern Theoretical Chemistry</u> Vols. 3 and 4, H. F. Schaefer, III Ed., Plenum Press, New York (1977) and in <u>Advances in Chemical Physics</u>, Vols. LXVII and LXIX, K. P. Lawley, Ed., Wiley-Interscience, New York (1987). Within the present Chapter, these two key references will be denoted MTC, Vols. 3 and 4, and ACP, Vols. 67 and 69, respectively.

In all such trial wavefunctions, there are two fundamentally different kinds of parameters that need to be determined- the CI coefficients $C_I$ and the LCAO-MO coefficients describing the $\varphi_{Ik}$. The most commonly employed methods used to determine these parameters include:

1. The **multiconfigurational self-consistent field** ( MCSCF) method in which the expectation value $< \Psi | H | \Psi > / < \Psi | \Psi >$ is treated variationally and simultaneously made stationary with respect to variations in the $C_I$ and $C_{\nu,i}$ coefficients subject to the constraints that the spin-orbitals and the full N-electron wavefunction remain normalized:

$< \phi_i | \phi_j > = \delta_{i,j} = \Sigma_{\nu,\mu} C_{\nu,i} \; S_{\nu,\mu} C_{\mu,i}$ , and

$\Sigma_I C^2{}_I = 1.$

The articles by H.-J. Werner and by R. Shepard in ACP Vol. 69 provide up to date reviews of the status of this approach. The article by A. C. Wahl and G. Das in MTC Vol. 3 covers the 'earlier' history on this topic. F. W. Bobrowicz and W. A. Goddard, III provide, in MTC Vol. 3, an overview of the GVB approach, which, as discussed in Chapter 12, can be viewed as a specific kind of MCSCF calculation.

2. The **configuration interaction** (CI) method in which the LCAO-MO coefficients are determined first (and independently) via either a single-configuration SCF calculation or an MCSCF calculation using a small number of CSFs. The CI coefficients are subsequently determined by making the expectation value $< \Psi | H | \Psi > / < \Psi | \Psi >$ stationary with respect to variations in the $C_I$ only. In this process, the optimizations of the orbitals and of the CSF amplitudes are done in separate steps. The articles by I. Shavitt and by B. O. Ross and P. E. M. Siegbahn in MTC, Vol. 3 give excellent early overviews of the CI method.

3. The **Møller-Plesset perturbation method** (MPPT) uses the single-configuration SCF process (usually the UHF implementation) to first determine a set of LCAO-MO coefficients and, hence, a set of orbitals that obey $F\phi_i = \varepsilon_i \phi_i$ . Then, using an unperturbed Hamiltonian equal to the sum of these Fock operators for each of the N electrons $H^0 = \Sigma_{i=1,N} F(i)$, perturbation theory (see Appendix D for an introduction to time-independent perturbation theory) is used to determine the $C_I$ amplitudes for the CSFs. The MPPT procedure is also referred to as the many-body perturbation theory (MBPT) method. The two names arose because two different schools of physics and chemistry developed them for somewhat different applications. Later, workers realized that they were identical in their working equations when the UHF $H^0$ is employed as the unperturbed Hamiltonian. In this text, we will therefore refer to this approach as MPPT/MBPT.

The amplitude for the so-called reference CSF used in the SCF process is taken as unity and the other CSFs' amplitudes are determined, relative to this one, by Rayleigh-Schrödinger perturbation theory using the full N-electron Hamiltonian minus the sum of Fock operators $H-H^0$ as the perturbation. The Slater-Condon rules are used for evaluating matrix elements of $(H-H^0)$ among these CSFs. The essential features of the MPPT/MBPT approach are described in the following articles: J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. 14, 545 (1978); R. J. Bartlett and D. M. Silver, J. Chem. Phys. 62, 3258 (1975); R. Krishnan and J. A. Pople, Int. J. Quantum Chem. 14, 91 (1978).

4. The **Coupled-Cluster method** expresses the CI part of the wavefunction in a somewhat different manner (the early work in chemistry on this method is described in J. Cizek, J. Chem. Phys. 45, 4256 (1966); J. Paldus, J. Cizek, and I. Shavitt, Phys. Rev. A5, 50 (1972); R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14, 561 (1978); G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 76, 1910 (1982)):

$$\Psi = \exp(T)\, \Phi,$$

where $\Phi$ is a single CSF (usually the UHF single determinant) which has been used to independently determine a set of spin-orbitals and LCAO-MO coefficients via the SCF process. The operator T generates, when acting on $\Phi$, single, double, etc. 'excitations' (i.e., CSFs in which one, two, etc. of the occupied spin-orbitals in $\Phi$ have been replaced by virtual spin-orbitals). T is commonly expressed in terms of operators that effect such spin-orbital removals and additions as follows:

$$T = \Sigma_{i,m}\, t_i^m\, m^+\, i + \Sigma_{i,j,m,n}\, t_{i,j}^{m,n}\, m^+\, n^+\, j\, i + ...,$$

where the operator $m^+$ is used to denote creation of an electron in virtual spin-orbital $\varphi_m$ and the operator j is used to denote removal of an electron from occupied spin-orbital $\varphi_j$ .

The $t_i^m$ , $t_{i,j}^{m,n}$, etc. amplitudes, which play the role of the CI coefficients in CC theory, are determined through the set of equations generated by projecting the Schrödinger equation in the form

$$\exp(-T)\, H \exp(T)\, \Phi = E\, \Phi$$

against CSFs which are single, double, etc. excitations relative to $\Phi$. For example, for double excitations $\Phi_{i,j}{}^{m,n}$ the equations read:

$$< \Phi_{i,j}{}^{m,n} \mid \exp(-T)\ H \exp(T) \mid \Phi > \ = E < \Phi_{i,j}{}^{m,n} \mid \Phi > = 0;$$

zero is obtained on the right hand side because the excited CSFs $|\Phi_{i,j}{}^{m,n}>$ are orthogonal to the reference function $|\Phi>$. The elements on the left hand side of the CC equations can be expressed, as described below, in terms of one- and two-electron integrals over the spin-orbitals used in forming the reference and excited CSFs.

## A. Integral Transformations

All of the above methods require the evaluation of one- and two-electron integrals over the N atomic orbital basis: $<\chi_a|f|\chi_b>$ and $<\chi_a\chi_b|g|\chi_c\chi_d>$. Eventually, all of these methods provide their working equations and energy expressions in terms of one- and two-electron integrals over the N final molecular orbitals: $<\phi_i|f|\phi_j>$ and $<\phi_i\phi_j|g|\phi_k\phi_l>$. The mo-based integrals can only be evaluated by transforming the AO-based integrals as follows:

$$<\phi_i\phi_j|g|\phi_k\phi_l> = \Sigma_{a,b,c,d}\, C_{a,i}C_{b,j}C_{c,k}C_{d,l} <\chi_a\chi_b|g|\chi_c\chi_d>,$$

and

$$<\phi_i|f|\phi_j> = \Sigma_{a,b}\, C_{a,i}C_{b,j} <\chi_a|f|\chi_b>.$$

It would seem that the process of evaluating all $N^4$ of the $<\phi_i\phi_j|g|\phi_k\phi_l>$, each of which requires $N^4$ additions and multiplications, would require computer time proportional to $N^8$. However, it is possible to perform the full transformation of the two-electron integral list in a time that scales as $\mathbf{N^5}$. This is done by first performing a transformation of the $<\chi_a\chi_b|g|\chi_c\chi_d>$ to an intermediate array labeled $<\chi_a\chi_b|g|\chi_c\phi_l>$ as follows:

$$<\chi_a\chi_b|g|\chi_c\phi_l> = \Sigma_d\, C_{d,l}<\chi_a\chi_b|g|\chi_c\chi_d>.$$

This partial transformation requires $N^5$ multiplications and additions. The list $<\chi_a\chi_b|g|\chi_c\phi_l>$ is then transformed to a second-level transformed array $<\chi_a\chi_b|g|\phi_k\phi_l>$:

$$<\chi_a\chi_b|g|\phi_k\phi_l> = \Sigma_c C_{c,k}<\chi_a\chi_b|g|\chi_c\phi_l>,$$

which requires another $N^5$ operations. This sequential, one-index-at-a-time transformation is repeated four times until the final $<\phi_i\phi_j|g|\phi_k\phi_l>$ array is in hand. The entire transformation done this way requires $\mathbf{4N^5}$ multiplications and additions.

Once the requisite one- and two-electron integrals are available in the molecular orbital basis, the multiconfigurational wavefunction and energy calculation can begin. These transformations consume a large fraction of the computer time used in most such calculations, and represent a severe bottleneck to progress in applying ab initio electronic structure methods to larger systems.

## B. Configuration List Choices

Once the requisite one- and two-electron integrals are available in the molecular orbital basis, the multiconfigurational wavefunction and energy calculation can begin. Each of these methods has its own approach to describing the configurations $\{\Phi_J\}$ included in the calculation and how the $\{C_J\}$ amplitudes and the total energy E is to be determined.

The number of configurations ($N_C$) varies greatly among the methods and is an important factor to keep in mind when planning to carry out an *ab initio* calculation. Under certain circumstances (e.g., when studying Woodward-Hoffmann forbidden reactions where an avoided crossing of two configurations produces an activation barrier), it may be essential to use more than one electronic configuration. Sometimes, one configuration (e.g., the SCF model) is adequate to capture the qualitative essence of the electronic structure. In all cases, many configurations will be needed if highly accurate treatment of electron-electron correlations are desired.

The value of $N_C$ determines how much computer time and memory is needed to solve the $N_C$-dimensional $\Sigma_J H_{I,J} C_J = E C_I$ secular problem in the CI and MCSCF methods. Solution of these matrix eigenvalue equations requires computer time that scales as $N_C^2$ (if few eigenvalues are computed) to $N_C^3$ (if most eigenvalues are obtained).

So-called complete-active-space (CAS) methods form all CSFs that can be created by distributing N valence electrons among P valence orbitals. For example, the eight non-core electrons of $H_2O$ might be distributed, in a manner that gives $M_S = 0$, among six valence orbitals (e.g., two lone-pair orbitals, two OH $\sigma$ bonding orbitals, and two OH $\sigma^*$ antibonding orbitals). The number of configurations thereby created is 225 . If the same eight electrons were distributed among ten valence orbitals 44,100 configurations results;

for twenty and thirty valence orbitals, 23,474,025 and 751,034,025 configurations arise, respectively. Clearly, practical considerations dictate that CAS-based approaches be limited to situations in which a few electrons are to be correlated using a few valence orbitals. The primary advantage of CAS configurations is discussed below in Sec. II. C.

## II. Strengths and Weaknesses of Various Methods

### A. Variational Methods Such as MCSCF, SCF, and CI Produce Energies that are Upper Bounds, but These Energies are not Size-Extensive

Methods that are based on making the energy functional $< \Psi | H | \Psi > / < \Psi | \Psi >$ stationary (i.e., variational methods) yield upper bounds to the lowest energy of the symmetry which characterizes the CSFs which comprise $\Psi$. These methods also can provide approximate excited-state energies and wavefunctions (e. g., in the form of other solutions of the secular equation $\Sigma_J H_{I,J} C_J = E C_I$ that arises in the CI and MCSCF methods). Excited-state energies obtained in this manner can be shown to 'bracket' the true energies of the given symmetry in that between any two approximate energies obtained in the variational calculation, there exists at least one true eigenvalue. This characteristic is commonly referred to as the 'bracketing theorem' (E. A. Hylleraas and B. Undheim, Z. Phys. 65, 759 (1930); J. K. L. MacDonald, Phys. Rev. 43, 830 (1933)). These are strong attributes of the variational methods, as is the long and rich history of developments of analytical and computational tools for efficiently implementing such methods (see the discussions of the CI and MCSCF methods in MTC and ACP).

However, all variational techniques suffer from at least one serious drawback; they are not **size-extensive** (J. A. Pople, pg. 51 in Energy, Structure, and Reactivity, D. W. Smith and W. B. McRae, Eds., Wiley, New York (1973)). This means that the energy computed using these tools can not be trusted to scale with the size of the system. For example, a calculation performed on two $CH_3$ species at large separation may not yield an energy equal to twice the energy obtained by performing the same kind of calculation on a single $CH_3$ species. Lack of size-extensivity precludes these methods from use in extended systems (e.g., solids) where errors due to improper scaling of the energy with the number of molecules produce nonsensical results.

By carefully adjusting the kind of variational wavefunction used, it is possible to circumvent size-extensivity problems for selected species. For example, a CI calculation on $Be_2$ using all $^1\Sigma_g$ CSFs that can be formed by placing the four valence electrons into the orbitals $2\sigma_g$, $2\sigma_u$ , $3\sigma_g$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ can yield an energy equal to twice that of the Be atom described by CSFs in which the two valence electrons of the Be atom are placed into the 2s and 2p orbitals in all ways consistent with a $^1S$ symmetry. Such special choices of configurations give rise to what are called complete-active-space (CAS) MCSCF or CI calculations (see the article by B. O. Roos in ACP for an overview of this approach).

Let us consider an example to understand why the CAS choice of configurations works. The $^1S$ ground state of the Be atom is known to form a wavefunction that is a strong mixture of CSFs that arise from the $2s^2$ and $2p^2$ configurations:

$$\Psi_{Be} = C_1 |1s^2\, 2s^2| + C_2 |1s^2\, 2p^2|,$$

where the latter CSF is a short-hand representation for the proper spin- and space-symmetry adapted CSF

$$|1s^2\, 2p^2| = 1/\surd 3\, [\, |1s\alpha 1s\beta 2p_0\alpha 2p_0\beta| - |1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta|$$

$$- |1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta|\, ].$$

The reason the CAS process works is that the $Be_2$ CAS wavefunction has the flexibility to dissociate into the product of two CAS Be wavefunctions:

$$\Psi = \Psi_{Bea} \Psi_{Beb}$$

$$= \{C_1 |1s^2\, 2s^2| + C_2 |1s^2\, 2p^2|\}_a \{C_1 |1s^2\, 2s^2| + C_2 |1s^2\, 2p^2|\}_b,$$

where the subscripts a and b label the two Be atoms, because the four electron CAS function distributes the four electrons in all ways among the $2s_a$, $2s_b$, $2p_a$, and $2p_b$ orbitals. In contrast, if the $Be_2$ calculation had been carried out using only the following CSFs : $|1\sigma^2_g\, 1\sigma^2_u\, 2\sigma^2_g\, 2\sigma^2_u|$ and all single and double excitations relative to this (dominant) CSF, which is a very common type of CI procedure to follow, the $Be_2$ wavefunction would not have contained the particular CSFs $|1s^2\, 2p^2|_a\, |1s^2\, 2p^2|_b$ because these CSFs are four-fold excited relative to the $|1\sigma^2_g\, 1\sigma^2_u\, 2\sigma^2_g\, 2\sigma^2_u|$ 'reference' CSF.

In general, one finds that if the 'monomer' uses CSFs that are K-fold excited relative to its dominant CSF to achieve an accurate description of its electron correlation, a size-extensive variational calculation on the 'dimer' will require the inclusion of CSFs that are 2K-fold excited relative to the dimer's dominant CSF. To perform a size-extensive variational calculation on a species containing M monomers therefore requires the inclusion of CSFs that are MxK-fold excited relative to the M-mer's dominant CSF.

### B. Non-Variational Methods Such as MPPT/MBPT and CC do not Produce Upper Bounds, but Yield Size-Extensive Energies

In contrast to variational methods, perturbation theory and coupled-cluster methods achieve their energies from a '<u>transition formula</u>' $< \Phi | H | \Psi >$ rather than from an expectation value $< \Psi | H | \Psi >$. It can be shown (H. P. Kelly, Phys. Rev. <u>131</u>, 684 (1963)) that this difference allows non-variational techniques to yield size-extensive energies. This can be seen in the MPPT/MBPT case by considering the energy of two non-interacting Be atoms. The reference CSF is $\Phi = | 1s_a^2\ 2s_a^2\ 1s_b^2\ 2s_b^2 |$; the Slater-Condon rules limit the CSFs in $\Psi$ which can contribute to

$$E = < \Phi | H | \Psi > = < \Phi | H | \Sigma_J C_J \Phi_J >,$$

to be $\Phi$ itself and those CSFs that are singly or doubly excited relative to $\Phi$. These 'excitations' can involve atom a, atom b, or both atoms. However, any CSFs that involve excitations on both atoms ( e.g., $| 1s_a^2\ 2s_a\ 2p_a\ 1s_b^2\ 2s_b\ 2p_b |$ ) give rise, via the SC rules, to one- and two- electron integrals over orbitals on both atoms; these integrals ( e.g., $< 2s_a\ 2p_a | g | 2s_b\ 2p_b >$ ) vanish if the atoms are far apart, as a result of which the contributions due to such CSFs vanish in our consideration of size-extensivity. Thus, only CSFs that are excited on one or the other atom contribute to the energy:

$$E = < \Phi_a \Phi_b | H | \Sigma_{Ja} C_{Ja} \Phi_{Ja} \Phi_b + \Sigma_{Jb} C_{Jb} \Phi_a \Phi_{Jb} >,$$

where $\Phi_a$ and $\Phi_b$ as well as $\Phi^*_{Ja}$ and $\Phi^*_{Jb}$ are used to denote the a and b parts of the reference and excited CSFs, respectively.

This expression, once the SC rules are used to reduce it to one- and two- electron integrals, is of the additive form required of any size-extensive method:

$$E = < \Phi_a | H | \Sigma_{Ja} C_{Ja} \Phi_{Ja} > + < \Phi_b | H | \Sigma_{Jb} C_{Jb} \Phi_{Jb} >,$$

and will yield a size-extensive energy if the equations used to determine the $C_{Ja}$ and $C_{Jb}$ amplitudes are themselves separable. In MPPT/MBPT, these amplitudes are expressed, in first order, as:

$$C_{Ja} = < \Phi_a \Phi_b \mid H \mid \Phi^*_{Ja} \Phi_b >/[ E^0_a + E^0_b - E^*_{Ja} - E^0_b]$$

(and analogously for $C_{Jb}$). Again using the SC rules, this expression reduces to one that involves only atom a:

$$C_{Ja} = < \Phi_a \mid H \mid \Phi^*_{Ja} >/[ E^0_a - E^*_{Ja} ].$$

The additivity of E and the separability of the equations determining the $C_J$ coefficients make the MPPT/MBPT energy size-extensive. This property can also be demonstrated for the Coupled-Cluster energy (see the references given above in Chapter 19. I.4). However, size-extensive methods have at least one serious weakness; their energies do not provide upper bounds to the true energies of the system (because their energy functional is not of the expectation-value form for which the upper bound property has been proven).

## C. Which Method is Best?

At this time, it may not possible to say which method is preferred for applications where all are practical. Nor is it possible to assess, in a way that is applicable to most chemical species, the accuracies with which various methods predict bond lengths and energies or other properties. However, there are reasons to recommend some methods over others in specific cases. For example, certain applications require a size-extensive energy (e.g., extended systems that consist of a large or macroscopic number of units or studies of weak intermolecular interactions), so MBPT/MPPT or CC or CAS-based MCSCF are preferred. Moreover, certain chemical reactions (e.g., Woodward-Hoffmann forbidden reactions) and certain bond-breaking events require two or more 'essential' electronic configurations. For them, single-configuration-based methods such as conventional CC and MBTP/MPPT should not be used; MCSCF or CI calculations would be better. Very large molecules, in which thousands of atomic orbital basis functions are required, may be impossible to treat by methods whose effort scales as $N^4$ or higher; density functional methods would be better to use then.

For all calculations, the choice of atomic orbital basis set must be made carefully, keeping in mind the $N^4$ scaling of the one- and two-electron integral evaluation step and the

$N^5$ scaling of the two-electron integral transformation step. Of course, basis functions that describe the essence of the states to be studied are essential (e.g., Rydberg or anion states require diffuse functions, and strained rings require polarization functions).

As larger atomic basis sets are employed, the size of the CSF list used to treat dynamic correlation increases rapidly. For example, most of the above methods use singly and doubly excited CSFs for this purpose. For large basis sets, the number of such CSFs, $N_C$, scales as the number of electrons squared, $n_e^2$, times the number of basis functions squared, $N^2$ . Since the effort needed to solve the CI secular problem varies as $N_C^2$ or $N_C^3$, a dependence as strong as $N^4$ to $N^6$ can result. To handle such large CSF spaces, all of the multiconfigurational techniques mentioned in this paper have been developed to the extent that calculations involving of the order of 100 to 5,000 CSFs are routinely performed and calculations using 10,000, 100,000, and even several million CSFs are practical.

Other methods, most of which can be viewed as derivatives of the techniques introduced above, have been and are still being developed. This ongoing process has been, in large part, stimulated by the explosive growth in computer power and change in computer architecture that has been realized in recent years. All indications are that this growth pattern will continue, so *ab initio* quantum chemistry will likely have an even larger impact on future chemistry research and education (through new insights and concepts).

## III. Further Details on Implementing Multiconfigurational Methods

### A. The MCSCF Method

The simultaneous optimization of the LCAO-MO and CI coefficients performed within an MCSCF calculation is a quite formidable task. The variational energy functional is a quadratic function of the CI coefficients, and so one can express the stationary conditions for these variables in the secular form:

$$\Sigma_J H_{I,J} C_J = E C_I .$$

However, E is a quartic function of the $C_{\nu,i}$ coefficients because each matrix element $< \Phi_I | H | \Phi_J >$ involves one- and two-electron integrals over the mos $\phi_i$ , and the two-electron integrals depend quartically on the $C_{\nu,i}$ coefficients. The stationary conditions with respect to these $C_{\nu,i}$ parameters must be solved iteratively because of this quartic dependence.

It is well known that minimization of a function (E) of several non-linear parameters (the $C_{\nu,i}$) is a difficult task that can suffer from poor convergence and may locate local rather than global minima. In an MCSCF wavefunction containing many CSFs, the energy is only weakly dependent on the orbitals that are weakly occupied (i.e., those that appear in CSFs with small $C_I$ values); in contrast, E is strongly dependent on the $C_{\nu,i}$ coefficients of those orbitals that appear in the CSFs with larger $C_I$ values. One is therefore faced with minimizing a function of many variables (there may be as many $C_{\nu,i}$ as the square of the number of orbital basis functions) that depends strongly on several of the variables and weakly on many others. This is a very difficult job.

For these reasons, in the MCSCF method, the number of CSFs is usually kept to a small to moderate number (e.g., a few to several hundred) chosen to describe essential correlations (i.e., configuration crossings, proper dissociation) and important dynamical correlations (those electron-pair correlations of angular, radial, left-right, etc. nature that arise when low-lying 'virtual' orbitals are present). In such a compact wavefunction, only spin-orbitals with reasonably large occupations (e.g., as characterized by the diagonal elements of the one-particle density matrix $\gamma_{i,j}$) appear. As a result, the energy functional is expressed in terms of variables on which it is strongly dependent, in which case the non-linear optimization process is less likely to be pathological.

Such a compact MCSCF wavefunction is designed to provide a good description of the set of strongly occupied spin-orbitals and of the CI amplitudes for CSFs in which only these spin-orbitals appear. It, of course, provides no information about the spin-orbitals that are not used to form the CSFs on which the MCSCF calculation is based. As a result, the MCSCF energy is invariant to a unitary transformation among these 'virtual' orbitals.

In addition to the references mentioned earlier in ACP and MTC, the following papers describe several of the advances that have been made in the MCSCF method, especially with respect to enhancing its rate and range of convergence: E. Dalgaard and P. Jørgensen, J. Chem. Phys. 69, 3833 (1978); H. J. Aa. Jensen, P. Jørgensen, and H. Ågren, J. Chem. Phys. 87, 457 (1987); B. H. Lengsfield, III and B. Liu, J. Chem. Phys. 75, 478 (1981).

## B. The Configuration Interaction Method

In the CI method, one usually attempts to realize a high-level treatment of electron correlation. A set of orthonormal molecular orbitals are first obtained from an SCF or MCSCF calculation (usually involving a small to moderate list of CSFs). The LCAO-MO coefficients of these orbitals are no longer considered as variational parameters in the subsequent CI calculation; only the $C_I$ coefficients are to be further optimized.

The CI wavefunction

$$\Psi = \Sigma_J C_J \Phi_J$$

is most commonly constructed from CSFs $\Phi_J$ that include:

1. All of the CSFs in the SCF (in which case only a single CSF is included) or MCSCF wavefunction that was used to generate the molecular orbitals $\phi_i$ . This set of CSFs are referred to as spanning the 'reference space' of the subsequent CI calculation, and the particular combination of these CSFs used in this orbital optimization (i.e., the SCF or MCSCF wavefunction) is called the reference function.

2. CSFs that are generated by carrying out single, double, triple, etc. level 'excitations' (i.e., orbital replacements ) relative to reference CSFs. CI wavefunctions limited to include contributions through various levels of excitation (e.g., single, double, etc. ) are denoted S (singly excited), D (doubly), SD ( singly and doubly), SDT (singly, doubly, and triply), and so on.

The orbitals from which electrons are removed and those into which electrons are excited can be restricted to focus attention on correlations among certain orbitals. For example, if excitations out of core electrons are excluded, one computes a total energy that contains no correlation corrections for these core orbitals. Often it is possible to so limit the nature of the orbital excitations to focus on the energetic quantities of interest (e.g., the CC bond breaking in ethane requires correlation of the $\sigma_{CC}$ orbital but the 1s Carbon core orbitals and the CH bond orbitals may be treated in a non-correlated manner).

Clearly, the number of CSFs included in the CI calculation can be far in excess of the number considered in typical MCSCF calculations; CI wavefunctions including 5,000 to 50,000 CSFs are routinely used, and functions with one to several million CSFs are within the realm of practicality (see, for example, J. Olsen, B. Roos, Poul Jørgensen, and H. J. Aa. Jensen, J. Chem. Phys. 89, 2185 (1988) and J. Olsen, P. Jørgensen, and J. Simons, Chem. Phys. Letters 169, 463 (1990)).

The need for such large CSF expansions should not come as a surprise once one considers that (i) each electron pair requires at least two CSFs (let us say it requires P of them, on average, a dominant one and P-1 others which are doubly excited) to form polarized orbital pairs, (ii) there are of the order of N(N-1)/2 = X electron pairs in an atom or molecule containing N electrons, and (iii) that the number of terms in the CI wavefunction scales as $P^X$. So, for an $H_2O$ molecule containing ten electrons, there would be $P^{55}$ terms in the CI expansion. This is 3.6 $\times 10^{16}$ terms if P=2 and 1.7 $\times 10^{26}$ terms if P=3. Undoubtedly, this is an over estimate of the number of CSFs needed to describe electron correlation in $H_2O$, but it demonstrates how rapidly the number of CSFs can grow with the number of electrons in the system.

The $H_{I,J}$ matrices that arise in CI calculations are evaluated in terms of one- and two- electron integrals over the molecular orbitals using the equivalent of the Slater-Condon rules. For large CI calculations, the full $H_{I,J}$ matrix is not actually evaluated and stored in the computer's memory (or on its disk); rather, so-called 'direct CI' methods (see the article by Roos and Siegbahn in MTC) are used to compute and immediately sum contributions to the sum $\Sigma_J H_{I,J} C_J$ in terms of integrals, density matrix elements, and approximate values of the $C_J$ amplitudes. Iterative methods (see, for example, E. R. Davidson, J. Comput. Phys. 17, 87 (1975)), in which approximate values for the $C_J$ coefficients and energy E are refined through sequential application of $\Sigma_J H_{I,J}$ to the preceding estimate of the $C_J$ vector, are employed to solve these large CI matrix eigenvalue problems.

## C. The MPPT/MBPT Method

In the MPPT/MBPT method, once the reference CSF is chosen and the SCF orbitals belonging to this CSF are determined, the wavefunction $\Psi$ and energy E are determined in an order-by-order manner. This is one of the primary strengths of the MPPT/MBPT technique; it does not require one to make further (potentially arbitrary) choices once the basis set and dominant (SCF) configuration are specified. In contrast to the MCSCF and CI treatments, one need not make choices of CSFs to include in or exclude from $\Psi$. The MPPT/MBPT perturbation equations determine what CSFs must be included through any particular order.

For example, the first-order wavefunction correction $\Psi^1$
(i.e., $\Psi = \Phi + \Psi^1$ through first order) is given by:

$$\Psi^1 = - \Sigma_{i<j,m<n} < \Phi_{i,j}{}^{m,n} \,|\, H - H^0 \,|\, \Phi > [\ \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j\ ]^{-1} \,|\, \Phi_{i,j}{}^{m,n} >$$

$$= - \Sigma_{i<j,m<n} [< i,j\ |g|\ m,n > - < i,j\ |g|\ n,m >][\ \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j\ ]^{-1} \,|\, \Phi_{i,j}{}^{m,n} >$$

where the SCF orbital energies are denoted $\varepsilon_k$ and $\Phi_{i,j}{}^{m,n}$ represents a CSF that is doubly excited relative to $\Phi$. Thus, only doubly excited CSFs contribute to the first-order wavefunction; as a result, the energy E is given through second order as:

$$E = < \Phi \mid H^0 \mid \Phi> + < \Phi \mid H - H^0 \mid \Phi> + < \Phi \mid H - H^0 \mid \Psi^1 >$$

$$= < \Phi \mid H \mid \Phi> - \Sigma_{i<j,m<n} |< \Phi_{i,j}{}^{m,n} \mid H - H^0 \mid \Phi >|^2 / [\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \,]$$

$$= E_{SCF} - \Sigma_{i<j,m<n} \mid < i,j \mid g \mid m,n > - < i,j \mid g \mid n,m > |^2 / [\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]$$

$$= E^0 + E^1 + E^2.$$

These contributions have been expressed, using the SC rules, in terms of the two-electron integrals $< i,j \mid g \mid m,n >$ coupling the excited spin-orbitals to the spin-orbitals from which electrons were excited as well as the orbital energy differences $[\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \,]$ accompanying such excitations. In this form, it becomes clear that major contributions to the correlation energy of the pair of occupied orbitals $\phi_i\ \phi_j$ are made by double excitations into virtual orbitals $\phi_m\ \phi_n$ that have large coupling (i..e., large $< i,j \mid g \mid m,n >$ integrals) and small orbital energy gaps, $[\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \,]$.

In higher order corrections to the wavefunction and to the energy, contributions from CSFs that are singly, triply, etc. excited relative to $\Phi$ appear, and additional contributions from the doubly excited CSFs also enter. It is relatively common to carry MPPT/MBPT calculations (see the references given above in Chapter 19.I.3 where the contributions of the Pople and Bartlett groups to the development of MPPT/MBPT are documented) through to third order in the energy (whose evaluation can be shown to require only $\Psi^0$ and $\Psi^1$). The entire GAUSSIAN-8X series of programs, which have been used in thousands of important chemical studies, calculate E through third order in this manner.

In addition to being size-extensive and not requiring one to specify input beyond the basis set and the dominant CSF, the MPPT/MBPT approach is able to include the effect of all CSFs (that contribute to any given order) without having to find any eigenvalues of a matrix. This is an important advantage because matrix eigenvalue determination, which is necessary in MCSCF and CI calculations, requires computer time in proportion to the third power of the dimension of the $H_{I,J}$ matrix. Despite all of these advantages, it is important to remember the primary disadvantages of the MPPT/MBPT approach; its energy is not an upper bound to the true energy and it may not be able to treat cases for which two or more

CSFs have equal or nearly equal amplitudes because it obtains the amplitudes of all but the dominant CSF from perturbation theory formulas that assume the perturbation is 'small'.

## D. The Coupled-Cluster Method

The implementation of the CC method begins much as in the MPPT/MBPT case; one selects a reference CSF that is used in the SCF process to generate a set of spin-orbitals to be used in the subsequent correlated calculation. The set of working equations of the CC technique given above in Chapter 19.I.4 can be written explicitly by introducing the form of the so-called cluster operator T,

$$T = \Sigma_{i,m} t_i^m m^+ i + \Sigma_{i,j,m,n} t_{i,j}^{m,n} m^+ n^+ j i + ...,$$

where the combination of operators $m^+ i$ denotes creation of an electron in virtual spin-orbital $\varphi_m$ and removal of an electron from occupied spin-orbital $\varphi_i$ to generate a single excitation. The operation $m^+ n^+ j i$ therefore represents a double excitation from $\varphi_i \varphi_j$ to $\varphi_m \varphi_n$. Expressing the cluster operator T in terms of the amplitudes $t_i^m$ , $t_{i,j}^{m,n}$ , etc. for singly, doubly, etc. excited CSFs, and expanding the exponential operators in exp(-T) H exp(T) one obtains:

$$< \Phi_i^m | H + [H,T] + 1/2 [[H,T],T] + 1/6 [[[H,T],T],T] + 1/24 [[[[H,T],T],T],T] | \Phi > = 0;$$

$$< \Phi_{i,j}^{m,n} | H + [H,T] + 1/2 [[H,T],T] + 1/6 [[[H,T],T],T] + 1/24 [[[[H,T],T],T],T] | \Phi > = 0;$$

$$< \Phi_{i,j,k}^{m,n,p} | H + [H,T] + 1/2 [[H,T],T] + 1/6 [[[H,T],T],T] + 1/24 [[[[H,T],T],T],T] | \Phi > = 0,$$

and so on for higher order excited CSFs. It can be shown, because of the one- and two-electron operator nature of H, that the expansion of the exponential operators truncates exactly at the fourth power; that is terms such as [[[[[H,T],T],T],T],T] and higher commutators vanish identically (this is demonstrated in Chapter 4 of Second Quantization Based Methods in Quantum Chemistry, P. Jørgensen and J. Simons, Academic Press, New York (1981).

As a result, the exact CC equations are quartic equations for the $t_i^m$ , $t_{i,j}^{m,n}$ , etc. amplitudes. Although it is a rather formidable task to evaluate all of the commutator matrix elements appearing in the above CC equations, it can be and has been done (the references given above to Purvis and Bartlett are especially relevant in this context). The result is to express each such matrix element, via the Slater-Condon rules, in terms of one- and two-electron integrals over the spin-orbitals used in determining Φ, including those in Φ itself and the 'virtual' orbitals not in Φ.

In general, these quartic equations must then be solved in an iterative manner and are susceptible to convergence difficulties that are similar to those that arise in MCSCF-type calculations. In any such iterative process, it is important to start with an approximation (to the t amplitudes, in this case) which is reasonably close to the final converged result. Such an approximation is often achieved, for example, by neglecting all of the terms that are non-linear in the t amplitudes (because these amplitudes are assumed to be less than unity in magnitude). This leads, for the CC working equations obtained by projecting onto the doubly excited CSFs, to:

$$< i,j \mid g \mid m,n >' + [\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \,]\, t_{i,j}^{m,n} +$$

$$\Sigma_{i',j',m',n'} < \Phi_{i,j}^{m,n} \mid H - H^0 \mid \Phi_{i',j'}^{m',n'} > t_{i',j'}^{m',n'} = 0 \,,$$

where the notation $< i,j \mid g \mid m,n >'$ is used to denote the two-electron integral difference $< i,j \mid g \mid m,n > - < i,j \mid g \mid n,m >$. If, in addition, the factors that couple different doubly excited CSFs are ignored (i.e., the sum over i',j',m',n') , the equations for the t amplitudes reduce to the equations for the CSF amplitudes of the first-order MPPT/MBPT wavefunction:

$$t_{i,j}^{m,n} = - < i,j \mid g \mid m,n >' / [\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \,] \,.$$

As Bartlett and Pople have both demonstrated, there is, in fact, close relationship between the MPPT/MBPT and CC methods when the CC equations are solved iteratively starting with such an MPPT/MBPT-like initial 'guess' for these double-excitation amplitudes.

The CC method, as presented here, suffers from the same drawbacks as the MPPT/MBPT approach; its energy is not an upper bound and it may not be able to accurately describe wavefunctions which have two or more CSFs with approximately equal amplitude. Moreover, solution of the non-linear CC equations may be difficult and slowly (if at all) convergent. It has the same advantages as the MPPT/MBPT method; its energy is size-extensive, it requires no large matrix eigenvalue solution, and its energy and wavefunction are determined once one specifies the basis and the dominant CSF.

## E. Density Functional Methods

These approaches provide alternatives to the conventional tools of quantum chemistry. The CI, MCSCF, MPPT/MBPT, and CC methods move beyond the single-configuration picture by adding to the wave function more configurations whose amplitudes they each determine in their own way. This can lead to a very large number of CSFs in the correlated wave function, and, as a result, a need for extraordinary computer resources.

The density functional approaches are different. Here one solves a set of orbital-level equations

$$[ - \hbar^2/2m_e \nabla^2 - \Sigma_A Z_A e^2/|\mathbf{r}-\mathbf{R}_A| + \int \rho(\mathbf{r}')e^2/|\mathbf{r}-\mathbf{r}'|\mathbf{dr}'$$

$$+ U(\mathbf{r})] \varphi_i = \varepsilon_i \varphi_i$$

in which the orbitals $\{\varphi_i\}$ 'feel' potentials due to the nuclear centers (having charges $Z_A$), Coulombic interaction with the *total* electron density $\rho(\mathbf{r}')$, and a so-called *exchange-correlation* potential denoted $U(\mathbf{r}')$. The particular electronic state for which the calculation is being performed is specified by forming a corresponding density $\rho(\mathbf{r}')$. Before going further in describing how DFT calculations are carried out, let us examine the origins underlying this theory.

The so-called Hohenberg-Kohn theorem states that the *ground-state* electron density $\rho(\mathbf{r})$ describing an N-electron system uniquely determines the potential $V(\mathbf{r})$ in the Hamiltonian

$$H = \Sigma_j \{-\hbar^2/2m_e \nabla_j^2 + V(r_j) + e^2/2 \, \Sigma_{k\neq j} 1/r_{j,k} \},$$

and, because H determines the ground-state energy and wave function of the system, the ground-state density $\rho(\mathbf{r})$ determines the ground-state properties of the system. The proof of this theorem proceeds as follows:

a. $\rho(\mathbf{r})$ determines N because $\int \rho(\mathbf{r})\, d^3r = N$.

b. Assume that there are two distinct potentials (aside from an additive constant that simply shifts the zero of total energy) $V(\mathbf{r})$ and $V'(\mathbf{r})$ which, when used in H and H', respectively, to solve for a ground state produce $E_0$, $\Psi(r)$ and $E_0'$, $\Psi'(r)$ that have the same one-electron density: $\int |\Psi|^2\, dr_2\, dr_3 \ldots dr_N = \rho(\mathbf{r}) = \int |\Psi'|^2\, dr_2\, dr_3 \ldots dr_N$.

c. If we think of $\Psi'$ as trial variational wave function for the Hamiltonian H, we know that

$E_0 < \langle\Psi'|H|\Psi'\rangle = \langle\Psi'|H'|\Psi'\rangle + \int \rho(\mathbf{r})\, [V(\mathbf{r}) - V'(\mathbf{r})]\, d^3r = E_0' + \int \rho(\mathbf{r})\, [V(\mathbf{r}) - V'(\mathbf{r})]\, d^3r$.

d. Similarly, taking $\Psi$ as a trial function for the H' Hamiltonian, one finds that

$E_0' < E_0 + \int \rho(\mathbf{r})\, [V'(\mathbf{r}) - V(\mathbf{r})]\, d^3r$.

e. Adding the equations in c and d gives

$E_0 + E_0' < E_0 + E_0'$,

a clear contradiction.

Hence, there cannot be two distinct potentials V and V' that give the same ground-state $\rho(\mathbf{r})$. So, the ground-state density $\rho(\mathbf{r})$ uniquely determines N and V, and thus H, and therefore $\Psi$ and $E_0$. Furthermore, because $\Psi$ determines all properties of the ground state, then $\rho(\mathbf{r})$, in principle, determines all such properties. This means that even the kinetic energy and the electron-electron interaction energy of the ground-state are determined by $\rho(\mathbf{r})$. It is easy to see that $\int \rho(\mathbf{r})\, V(\mathbf{r})\, d^3r = V[\rho]$ gives the average value of the electron-nuclear (plus any additional one-electron additive potential) interaction in terms of the ground-state density $\rho(\mathbf{r})$, but how are the kinetic energy $T[\rho]$ and the electron-electron interaction $V_{ee}[\rho]$ energy expressed in terms of $\rho$?

The main difficulty with DFT is that the Hohenberg-Kohn theorem shows that the ground-state values of T, $V_{ee}$, V, etc. are all unique functionals of the ground-state $\rho$ (i.e., that they can, in principle, be determined once ρ is given), but it does not tell us what these functional relations are.

To see how it might make sense that a property such as the kinetic energy, whose operator $-\hbar^2/2m_e\ \ {}^2$ involves derivatives, can be related to the electron density, consider a simple system of N non-interacting electrons moving in a three-dimensional cubic "box" potential. The energy states of such electrons are known to be

$$E = (h^2/2m_eL^2)\,(n_x^2 + n_y^2 + n_z^2),$$

where L is the length of the box along the three axes, and $n_x$, $n_y$, and $n_z$ are the quantum numbers describing the state. We can view $n_x^2 + n_y^2 + n_z^2 = R^2$ as defining the squared radius of a sphere in three dimensions, and we realize that the density of quantum states in this space is one state per unit volume in the $n_x$, $n_y$, $n_z$ space. Because $n_x$, $n_y$, and $n_z$ must be positive integers, the volume covering all states with energy less than or equal to a specified energy $E = (h^2/2m_eL^2)\,R^2$ is 1/8 the volume of the sphere of radius R:

$$\Phi(E) = 1/8\,(4\pi/3)\,R^3 = (\pi/6)\,(8m_eL^2E/h^2)^{3/2}\,.$$

Since there is one state per unit of such volume, Φ(E) is also the number of states with energy less than or equal to E, and is called the <u>integrated density of states</u>. The number of states g(E) dE with energy between E and E+dE, the <u>density of states</u>, is the derivative of Φ:

$$g(E) = d\Phi/dE = (\pi/4)\,(8m_eL^2/h^2)^{3/2}\,E^{1/2}\,.$$

If we calculate the total energy for N electrons, with the states having energies up to the so-called <u>Fermi energy</u> (i.e., the energy of the highest occupied molecular orbital HOMO) doubly occupied, we obtain the ground-state energy:

$$E_0 = 2\int_0^{E_F} g(E)E\,dE = (8\pi/5)\,(2m_e/h^2)^{3/2}\,L^3\,E_F^{5/2}.$$

The total number of electrons N can be expressed as

$$N = 2\int_0^{E_F} g(E)dE = (8\pi/3)\,(2m_e/h^2)^{3/2}\,L^3\,E_F^{3/2},$$

which can be solved for $E_F$ in terms of N to then express $E_0$ in terms of N instead of $E_F$:

$$E_0 = (3h^2/10m_e)\,(3/8\pi)^{2/3}\,L^3\,(N/L^3)^{5/3}\,.$$

This gives the total energy, which is also the kinetic energy in this case because the potential energy is zero within the "box", in terms of the electron density $\rho\,(x,y,z) = (N/L^3)$. It therefore may be plausible to express kinetic energies in terms of electron densities $\rho(\mathbf{r})$, but it is by no means clear how to do so for "real" atoms and molecules with electron-nuclear and electron-electron interactions operative.

In one of the earliest DFT models, the Thomas-Fermi theory, the kinetic energy of an atom or molecule is approximated using the above kind of treatment on a "local" level. That is, for each volume element in $\mathbf{r}$ space, one assumes the expression given above to be valid, and then one integrates over all $\mathbf{r}$ to compute the total kinetic energy:

$$T_{TF}[\rho] = \int (3h^2/10m_e)\,(3/8\pi)^{2/3}\,[\rho(\mathbf{r})]^{5/3}\,d^3r = C_F \int [\rho(\mathbf{r})]^{5/3}\,d^3r\,,$$

where the last equality simply defines the $C_F$ constant (which is 2.8712 in atomic units). Ignoring the correlation and exchange contributions to the total energy, this T is combined with the electron-nuclear V and Coulombic electron-electron potential energies to give the Thomas-Fermi total energy:

$$E_{0,TF}\,[\rho] = C_F \int [\rho(\mathbf{r})]^{5/3}\,d^3r + \int V(\mathbf{r})\,\rho(\mathbf{r})\,d^3r + e^2/2 \int \rho(\mathbf{r})\,\rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}|\;d^3r\,d^3r',$$

This expression is an example of how $E_0$ is given as a local density functional approximation (LDA). The term local means that the energy is given as a functional (i.e., a function of $\rho$) which depends only on $\rho(\mathbf{r})$ at points in space but not on $\rho(\mathbf{r})$ at more than one point in space.

Unfortunately, the Thomas-Fermi energy functional does not produce results that are of sufficiently high accuracy to be of great use in chemistry. What is missing in this theory are a. the exchange energy and b. the correlation energy; moreover, the kinetic energy is treated only in the approximate manner described.

In the book by Parr and Yang, it is shown how Dirac was able to address the exchange energy for the 'uniform electron gas' (N Coulomb interacting electrons moving in a uniform positive background charge whose magnitude balances the charge of the N electrons). If the exact expression for the exchange energy of the uniform electron gas is applied on a local level, one obtains the commonly used Dirac local density approximation to the exchange energy:

$$E_{ex,Dirac}[\rho] = - C_x \int [\rho(\mathbf{r})]^{4/3}\, d^3r,$$

with $C_x = (3/4)\,(3/\pi)^{1/3} = 0.7386$ in atomic units. Adding this exchange energy to the Thomas-Fermi total energy $E_{0,TF}\,[\rho]$ gives the so-called Thomas-Fermi-Dirac (TFD) energy functional.

Because electron densities vary rather strongly spatially near the nuclei, corrections to the above approximations to $T[\rho]$ and $E_{ex.Dirac}$ are needed. One of the more commonly used so-called gradient-corrected approximations is that invented by Becke, and referred to as the Becke88 exchange functional:

$$E_{ex}(\text{Becke88}) = E_{ex,Dirac}[\rho] -\gamma \int x^2 \rho^{4/3} (1+6\,\gamma\, x \sinh^{-1}(x))^{-1}\, \mathbf{dr},$$

where $x = \rho^{-4/3}\, |\ \ \rho|$, and $\gamma$ is a parameter chosen so that the above exchange energy can best reproduce the known exchange energies of specific electronic states of the inert gas atoms (Becke finds $\gamma$ to equal 0.0042). A common gradient correction to the earlier $T[\rho]$ is called the Weizsacker correction and is given by

$$\delta T_{Weizsacker} = (1/72)(\hbar/m_e) \int |\ \ \rho(\mathbf{r})|^2/\rho(\mathbf{r})\, d\mathbf{r}.$$

Although the above discussion suggests how one might compute the ground-state energy once the ground-state density $\rho(\mathbf{r})$ is given, one still needs to know how to obtain

$\rho$. Kohn and Sham (KS) introduced a set of so-called KS orbitals obeying the following equation:

$$\{-1/2\ {}^{2} + V(\mathbf{r}) + e^{2}/2 \int \rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}|\ \mathbf{dr'} + U_{xc}(\mathbf{r})\}\varphi_j = \varepsilon_j\, \varphi_j\,,$$

where the so-called exchange-correlation potential $U_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$ could be obtained by functional differentiation if the exchange-correlation energy functional $E_{xc}[\rho]$ were known. KS also showed that the KS orbitals $\{\varphi_j\}$ could be used to compute the density $\rho$ by simply adding up the orbital densities multiplied by orbital occupancies $n_j$ :

$$\rho(\mathbf{r}) = \Sigma_j\, n_j\, |\varphi_j(\mathbf{r})|^2.$$

(here $n_j$ =0,1, or 2 is the occupation number of the orbital $\varphi_j$ in the state being studied) and that the kinetic energy should be calculated as

$$T = \Sigma_j\, n_j <\varphi_j(\mathbf{r})|-1/2\ {}^{2}\ |\varphi_j(\mathbf{r})>.$$

The same investigations of the idealized 'uniform electron gas' that identified the Dirac exchange functional, found that the correlation energy (per electron) could also be written exactly as a <u>function</u> of the electron density $\rho$ of the system, but only in two limiting cases- the high-density limit (large $\rho$) and the low-density limit. There still exists no exact expression for the correlation energy even for the uniform electron gas that is valid at arbitrary values of $\rho$. Therefore, much work has been devoted to creating efficient and accurate interpolation formulas connecting the low- and high- density uniform electron gas expressions. One such expression is

$$E_C[\rho] = \int \rho(\mathbf{r})\, \varepsilon_c(\rho)\, \mathbf{dr},$$

where

$$\varepsilon_c(\rho) = A/2\{\ln(x/X) + 2b/Q \tan^{-1}(Q/(2x+b)) - bx_0/X_0\ [\ln((x-x_0)^2/X)$$

$+2(b+2x_0)/Q \tan^{-1}(Q/(2x+b))]$

is the correlation energy per electron. Here $x = r_s^{1/2}$ , $X=x^2 +bx+c$, $X_0 =x_0^{\ 2} +bx_0+c$ and $Q=(4c - b^2)^{1/2}$, A = 0.0621814, $x_0$= -0.409286, b = 13.0720, and c = 42.7198. The parameter $r_s$ is how the density ρ enters since $4/3\ \pi r_s^{\ 3}$ is equal to 1/ρ; that is, $r_s$ is the radius of a sphere whose volume is the effective volume occupied by one electron. A reasonable approximation to the full $E_{xc}[\rho]$ would contain the Dirac (and perhaps gradient corrected) exchange functional plus the above $E_C[\rho]$, but there are many alternative approximations to the exchange-correlation energy functional. Currently, many workers are doing their best to “cook up” functionals for the correlation and exchange energies, but no one has yet invented functionals that are so reliable that most workers agree to use them.

To summarize, in implementing any DFT, one usually proceeds as follows:

1. An atomic orbital basis is chosen in terms of which the KS orbitals are to be expanded.
2. Some initial guess is made for the LCAO-KS expansion coefficients $C_{jj,a}$: $\varphi_j = \Sigma_a C_{j,a} \chi_a$.
3. The density is computed as $\rho(\mathbf{r}) = \Sigma_j n_j |\varphi_j(\mathbf{r})|^2$ . Often, $\rho(\mathbf{r})$ is expanded in an atomic orbital basis, which need not be the same as the basis used for the $\varphi_j$, and the expansion coefficients of ρ are computed in terms of those of the $\varphi_j$ . It is also common to use an atomic orbital basis to expand $\rho^{1/3}(\mathbf{r})$ which, together with ρ, is needed to evaluate the exchange-correlation functional’s contribution to $E_0$.
4. The current iteration’s density is used in the KS equations to determine the Hamiltonian $\{-1/2\ \ {}^2 + V(\mathbf{r}) + e^2/2 \int \rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}|\ \ \mathbf{dr'} + U_{xc}(\mathbf{r})\ \}$whose “new” eigenfunctions $\{\varphi_j\}$ and eigenvalues $\{\varepsilon_j\}$ are found by solving the KS equations.
5. These new $\varphi_j$ are used to compute a new density, which, in turn, is used to solve a new set of KS equations. This process is continued until convergence is reached (i.e., until the $\varphi_j$ used to determine the current iteration’s ρ are the same $\varphi_j$ that arise as solutions on the next iteration.
6. Once the converged $\rho(\mathbf{r})$ is determined, the energy can be computed using the earlier expression

$$E\,[\rho] = \Sigma_j\, n_j \,\langle\varphi_j(\mathbf{r})| -1/2 \quad {}^2\, |\varphi_j(\mathbf{r})\rangle + \int V(\mathbf{r})\, \rho(\mathbf{r})\, \mathbf{dr} + e^2/2 \int \rho(\mathbf{r})\rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}|\mathbf{dr}\ \mathbf{dr'} + E_{xc}[\rho].$$

In closing this section, it should once again be emphasized that this area is currently undergoing explosive growth and much scrutiny. As a result, it is nearly certain that many of the specific functionals discussed above will be replaced in the near future by improved and more rigorously justified versions. It is also likely that extensions of DFT to excited states (many workers are actively pursuing this) will be placed on more solid ground and made applicable to molecular systems. Because the computational effort involved in these approaches scales much less strongly with basis set size than for conventional (SCF, MCSCF, CI, etc.) methods, density functional methods offer great promise and are likely to contribute much to quantum chemistry in the next decade.