

B3.1

Quantum structural methods for atoms and molecules

Jack Simons

B3.1.1 What does quantum chemistry try to do?

Electronic structure theory describes the motions of the electrons and produces energy surfaces and wavefunctions. The shapes and geometries of molecules, their electronic, vibrational and rotational energy levels, as well as the interactions of these states with electromagnetic fields lie within the realm of quantum structure theory.

B3.1.1.1 *The underlying theoretical basis—the Born–Oppenheimer model*

In the Born–Oppenheimer [1] model, it is assumed that the electrons move so quickly that they can adjust their motions essentially instantaneously with respect to any movements of the heavier and slower atomic nuclei. In typical molecules, the valence electrons orbit about the nuclei about once every 10^{-15} s (the inner-shell electrons move even faster), while the bonds vibrate every 10^{-14} s, and the molecule rotates approximately every 10^{-12} s. So, for typical molecules, the fundamental assumption of the Born–Oppenheimer model is valid, but for loosely held (e.g. Rydberg) electrons and in cases where nuclear motion is strongly coupled to electronic motions (e.g. when Jahn–Teller effects are present) it is expected to break down.

This separation-of-time-scales assumption allows the electrons to be described by electronic wavefunctions that smoothly ‘ride’ the molecule’s atomic framework. These electronic functions are found by solving a Schrödinger equation whose Hamiltonian \hat{H}_e contains the kinetic energy T_e of the electrons, the Coulomb repulsions among all the molecule’s electrons V_{ee} , the Coulomb attractions V_{en} among the electrons and all of the molecule’s nuclei, treated with these nuclei held clamped, and the Coulomb repulsions V_{nn} among all of these nuclei, but it does not contain the kinetic energy T_N of all the nuclei. That is, this Hamiltonian keeps the nuclei held fixed in space. The electronic wavefunctions ψ_k and energies E_k that result

$$\hat{H}_e \psi_k = E_k \psi_k$$

thus depend on the locations $\{Q_i\}$ at which the nuclei are sitting. That is, the E_k and ψ_k are parametric functions of the coordinates of the nuclei, and, of course, the wavefunctions ψ_k depend on the coordinates of all of the electrons.

These electronic energies’ dependence on the positions of the atomic centres cause them to be referred to as electronic energy surfaces such as that depicted below in figure B3.1.1 for a diatomic molecule. For nonlinear polyatomic molecules having N atoms, the energy surfaces depend on $3N - 6$ internal coordinates and thus can be very difficult to visualize. In figure B3.1.2, a ‘slice’ through such a surface is shown as a function of two of the $3N - 6$ internal coordinates.

The Born–Oppenheimer theory is soundly based in that it can be derived from a Schrödinger equation describing the kinetic energies of all electrons and of all N nuclei plus the Coulomb potential energies of

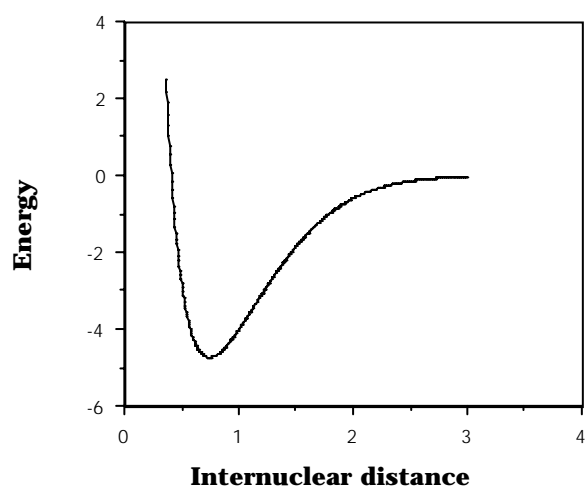


Figure B3.1.1. Energy as a function of internuclear distance for a typical bound diatomic molecule or ion.

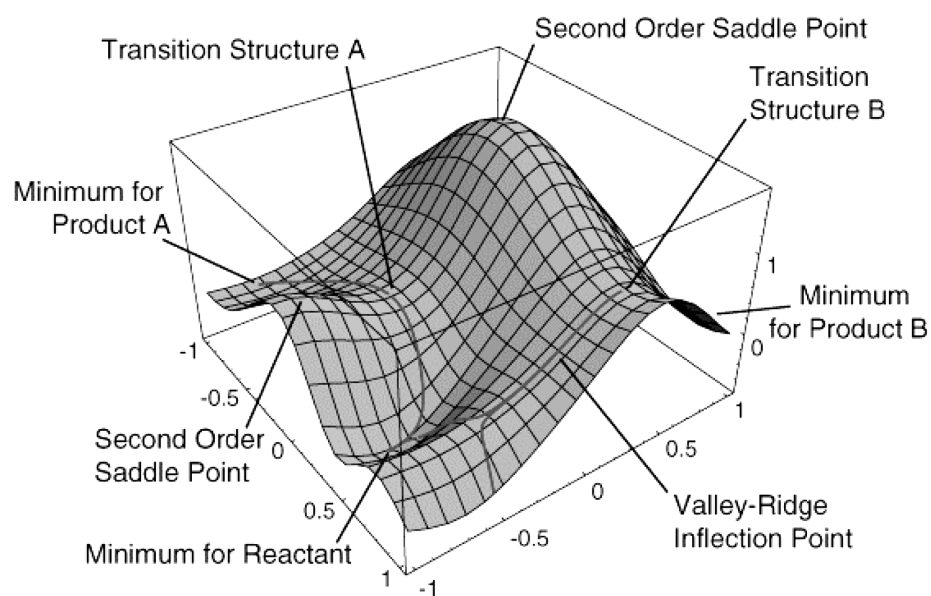


Figure B3.1.2. Two-dimensional slice through a $(3N - 6)$ -dimensional energy surface of a polyatomic molecule or ion. After [2].

interaction among all electrons and nuclei. By expanding the wavefunction Ψ that is an eigenfunction of this full Schrödinger equation in the complete set of functions $\{\psi_k\}$ and then neglecting all terms that involve derivatives of any ψ_k with respect to the nuclear positions $\{Q_i\}$, one can separate variables such that:

- (1) the electronic wavefunctions and energies obey

$$\hat{H}_e \psi_k = E_k \psi_k$$

- (2) the nuclear motion (i.e. vibration/rotation) wavefunctions obey

$$(\hat{T}_N + E_k) \chi_{k,L} = E_{k,L} \chi_{k,L}$$

where T_N is the kinetic energy operator for movement of all nuclei.

Each and every electronic energy state, labelled k , has a set, labelled L , of vibration/rotation energy levels $E_{k,L}$ and wavefunctions $\chi_{k,L}$.

B3.1.1.2 Non-Born–Oppenheimer corrections—radiationless transitions

Because the Born–Oppenheimer model is obtained from the full Schrödinger equation by making approximations, it is not exact. Thus, in certain circumstances it becomes necessary to correct the predictions of the Born–Oppenheimer theory (i.e. by including the effects of the neglected coupling terms using perturbation theory). For example, when developing a theoretical model to interpret the rate at which electrons are ejected from rotationally/vibrationally hot NH^- ions, we had to consider [3] coupling between:

- (1) $^2\Pi$ NH^- in its $v = 1$ vibrational level and in a high rotational level (e.g. $J > 30$) prepared by laser excitation of vibrationally ‘cold’ NH^- in $v = 0$ having high J (due to natural Boltzmann populations), see figure B3.1.3; and
- (2) $^3\Sigma^-$ NH neutral plus an ejected electron in which the NH is in its $v = 0$ vibrational level (no higher level is energetically accessible) and in various rotational levels (labelled N).

Because NH has an electron affinity of 0.4 eV, the total energies of the above two states can be equal only if the kinetic energy KE carried away by the ejected electron obeys

$$KE = E_{\text{vib/rot}}(\text{NH}^- (v = 1, J)) - E_{\text{vib/rot}}(\text{NH} (v = 0, N)) - 0.4 \text{ eV}.$$

In the absence of any coupling terms, no electron detachment would occur. It is only by the anion converting some of its vibration/rotation energy and angular momentum into electronic energy that the electron that occupies a bound N_{2p} orbital in NH^- can gain enough energy to be ejected.

My own research efforts [4] have, for many years, involved taking into account such non-Born–Oppenheimer couplings, especially in cases where vibration/rotation energy transferred to electronic motions causes electron detachment, as in the NH^- case detailed above. Professor Yngve Öhrn has been active [5] in attempting to avoid using the Born–Oppenheimer approximation and, instead, treating the dynamical motions of the nuclei and electrons simultaneously. Professor David Yarkony has contributed much [6] to the recent treatment of non-Born–Oppenheimer effects and to the inclusion of spin–orbit coupling in such studies.

B3.1.1.3 What is learned from an electronic structure calculation?

The knowledge gained via structure theory is great. The electronic energies $E_k(Q)$ allow one to determine [7] the geometries and relative energies of various isomers that a molecule can assume by finding those geometries $\{Q_i\}$ at which the energy surface E_k has minima $\partial E_k / \partial Q_i = 0$, with all directions having positive curvature (this is monitored by considering the so-called Hessian matrix $H_{i,j} = \partial^2 E_k / \partial Q_i \partial Q_j$: if none of its

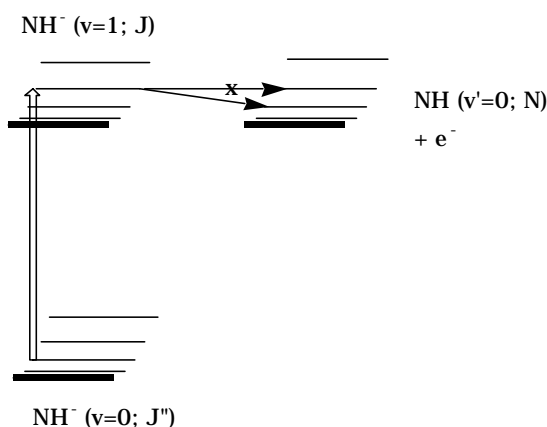


Figure B3.1.3. Energies of NH^- and of NH pertinent to the autodetachment of $v = 1, J$ levels of NH^- formed by laser excitation of $v = 0, J''\text{NH}^-$.

eigenvalues are negative, all directions have positive curvature). Such geometries describe stable isomers, and the energy at each such isomer geometry gives the relative energy of that isomer. Professor Berny Schlegel [8] has been one of the leading figures in using gradient and Hessian information to locate stable structures and transition states. Professor Peter Pulay [9] has done as much as anyone to develop the theory that allows us to compute gradients and Hessians for most commonly used electronic structure methods.

There may be other geometries on the E_k energy surface at which all 'slopes' vanish $\partial E_k / \partial Q_i = 0$, but at which not all directions possess positive curvature. If the Hessian matrix has only one negative eigenvalue, there is only one direction leading downhill away from the point $\{Q_i\}$ of zero force; all the remaining directions lead uphill from this point. Such a geometry describes that of a *transition state*, and its energy plays a central role in determining the rates of reactions which pass through this transition state. The energy surface shown in figure B3.1.2 displays such transition states, and it also shows a second-order saddle point (i.e. a point where the gradient vanishes and the Hessian has two directions of negative curvature).

At any geometry $\{Q_i\}$, the gradient vector having components $\partial E_k / \partial Q_i$ provides the forces ($F_i = -\partial E_k / \partial Q_i$) along each of the coordinates Q_i . These forces are used in molecular dynamics simulations which solve the Newton $F = ma$ equations and in molecular mechanics studies which are aimed at locating those geometries where the F vector vanishes (i.e. the stable isomers and transition states discussed above).

Also produced in electronic structure simulations are the electronic wavefunctions $\{\psi_k\}$ and energies $\{E_k\}$ of each of the electronic states. The separation in energies can be used to make predictions on the spectroscopy of the system. The wavefunctions can be used to evaluate the properties of the system that depend on the spatial distribution of the electrons. For example, the z component of the dipole moment [10] of a molecule μ_z can be computed by integrating the probability density for finding an electron at position r multiplied by the z coordinate of the electron and the electron's charge e : $\mu_z = \int e \psi_k^* \psi_k z \, d\mathbf{r}$. The average kinetic energy of an electron can also be computed by carrying out such an average-value integral: $\int \psi_k^* (-\hbar^2 / 2m_e \nabla^2) \psi_k \, d\mathbf{r}$. The rules for computing the average value of any physical observable are developed and illustrated in popular undergraduate text books on physical chemistry [11] and in graduate-level texts [12].

Not only can electronic wavefunctions tell us about the average values of all the physical properties for any particular state (i.e. ψ_k above), but they also allow us to tell us how a specific 'perturbation' (e.g. an electric field in the Stark effect, a magnetic field in the Zeeman effect and light's electromagnetic fields in spectroscopy) can alter the specific state of interest. For example, the perturbation arising from the electric field of a photon interacting with the electrons in a molecule is given within the so-called electric dipole

approximation [12] by:

$$\hat{H}_{\text{pert}} = \sum_j e^2 \mathbf{r}_j \cdot \mathbf{E}(t)$$

where \mathbf{E} is the electric field vector of the light, which depends on time t in an oscillatory manner, and \mathbf{r}_j gives the spatial coordinates of the j th electron. This perturbation, \hat{H}_{pert} can induce transitions to other states $\psi_{k'}$, with probabilities that are proportional to the square of the integral:

$$\int \psi_{k'}^* \hat{H}_{\text{pert}} \psi_k \, d\mathbf{r}.$$

So, if this integral were to vanish, transitions between ψ_k and $\psi_{k'}$ would not occur, and would be referred to as ‘forbidden’. Whether such integrals vanish or not often is determined by symmetry. For example, if ψ_k were of odd symmetry under a plane of symmetry σ_v of the molecule, while $\psi_{k'}$ were even under σ_v , then the integral would vanish unless one or more of the three Cartesian components of the dot product $\mathbf{r}_j \cdot \mathbf{E}$ were odd under σ_v . The general idea is that for the integral not to vanish, the direct product of the symmetries of ψ_k and of $\psi_{k'}$ must match the symmetry of at least one of the symmetry components present in \hat{H}_{pert} . Professor Poul Jørgensen [13] has been involved in developing such so-called response theories for perturbations that may be time dependent (e.g. as in the interaction of light’s electromagnetic radiation).

B3.1.1.4 Summary

In summary, computational *ab initio* quantum chemistry attempts to solve the electronic Schrödinger equation for the $E_k(\mathbf{R})$ energy surfaces and wavefunctions $\psi_k(\mathbf{r}; \mathbf{R})$ on a ‘grid’ of values for the ‘clamped’ nuclear positions. Because the Schrödinger equation produces wavefunctions, it has a great deal of predictive power. Wavefunctions contain all the information needed to compute dipole moments, polarizability, etc and transition properties such as the electric dipole transition strengths among states. They also permit the evaluation of system responses with respect to external perturbations such as geometrical distortions [9], which provides information on vibrational frequencies and reaction paths.

B3.1.2 Why is it so difficult to calculate electronic energies and wavefunctions with reasonable accuracy?

As a scientific tool, *ab initio* quantum chemistry is not yet as accurate as modern laser spectroscopic measurements, for example. Moreover, it is difficult to estimate the accuracies with which various methods predict bond energies and lengths, excitation energies and the like. In the opinion of the author, chemists who rely on the results of quantum chemistry calculations must better understand what underlies the concepts and methods of this field. Only by so doing will they be able to judge for themselves the value of given quantum chemistry data to their own research. There exist a variety of sources of further information on the ‘jargon’, underlying theory, methodologies, and current strengths and weaknesses of *ab initio* quantum chemistry. In 1996, Head-Gordon [14] produced a nice overview entitled ‘Quantum chemistry and molecular processes’, Schaefer *et al* [15] offered a very good discussion in 1995; Simons [16] offered a somewhat earlier perspective in 1991. The present chapter includes many of the ideas contained in these and other earlier descriptions of this field’s impacts, but also attempts to extend the perspective to include more recent developments.

Returning now to the issue of the accuracy of various electronic structure predictions, it is natural to ask why it is so difficult to achieve reasonable accuracy (i.e. ca. 1 kcal mol⁻¹ in computed bond energies or activation energies) even with the most sophisticated and computer-resource-intensive quantum chemistry calculations. The reasons include the following.

(A) *Many-body problems with R^{-1} potentials are notoriously difficult.* It is well known that the Coulomb potential falls off so slowly with distance that mathematical difficulties can arise. The $4\pi R^2$ dependence

of the integration volume element, combined with the R^{-1} dependence of the potential, produce ill-defined interaction integrals unless attractive and repulsive interactions are properly combined. The classical or quantum treatment of ionic melts [17], many-body gravitational dynamics [18] and Madelung sums [19] for ionic crystals are all plagued by such difficulties.

- (B) *The electrons require quantal treatment and they are indistinguishable.* The electron's small mass produces local de Broglie wavelengths that are long compared to atomic 'sizes', thus necessitating quantum treatment. Their indistinguishability requires that permutational symmetry be imposed on solutions of the Schrödinger equation.
- (C) *All mean-field models of electronic structure require large corrections.* Essentially all *ab initio* quantum chemistry approaches introduce a 'mean field' potential V_{mf} that embodies the average interactions among the N electrons. The difference between the mean-field potential and the true Coulombic potential is termed [20] the '*fluctuation potential*'. The solutions $\{\Psi_k, E_k\}$ to the true electronic Schrödinger equation are then approximated in terms of solutions $\{\Psi_k^0, E_k^0\}$ to the model Schrödinger equation in which V_{mf} is used. Improvements to the solutions of the model problem are made using perturbation theory or the variational method. Such approaches are expected to work when the difference between the starting model and the final goal is small in some sense.

The most elementary mean-field models of electronic structure introduce a potential that an electron at \mathbf{r}_1 would experience if it were interacting with a *spatially averaged* electrostatic charge density arising from the $N - 1$ remaining electrons:

$$V_{\text{mf}}(\mathbf{r}_1) = \int \rho_{N-1}(\mathbf{r}') \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}'|} d\mathbf{r}'.$$

Here $\rho_{N-1}(\mathbf{r}')$ represents the probability density for finding the $N - 1$ electrons at \mathbf{r}' , and $e^2/|\mathbf{r}_1 - \mathbf{r}'|$ is the mutual Coulomb repulsion between electron density at \mathbf{r}_1 and \mathbf{r}' .

The magnitude and 'shape' of such a mean-field potential is shown below [21] in figure B3.1.4 for the two 1s electrons of a beryllium atom. The Be nucleus is at the origin, and one electron is held fixed 0.13 Å from the nucleus, the maximum of the 1s orbital's radial probability density. The Coulomb potential experienced by the second electron is then a function of the second electron's position along the x -axis (connecting the Be nucleus and the first electron) and its distance perpendicular to the x -axis. For simplicity, this second electron is arbitrarily constrained to lie on the x -axis. Along this direction, the Coulomb potential is singular, and hence the overall interactions are very large.

On the ordinate, two quantities are plotted: (i) the mean-field potential between the second electron and the other 1s electron computed, via the self-consistent field (SCF) process (described later), as the interaction of the second electron with a spherical $|1s|^2$ charge density centred on the Be nucleus; and (ii) the fluctuation potential (F) of this average (mean-field) interaction.

As a function of the inter-electron distance, the fluctuation potential decays to zero more rapidly than does the mean-field potential. However, the magnitude of F is quite large and remains so over an appreciable range of inter-electron distances. The corrections to the mean-field picture are therefore quite large when measured in kcal mol⁻¹. For example, the differences (called pair correlation energies) ΔE between the true (state-of-the-art quantum chemical calculation as discussed later) energies of the interaction among the four electrons in the Be atom and the mean-field estimates of these interactions are given in table B3.1.1 in electronvolts (1 eV = 23.06 kcal mol⁻¹).

Another example of the difficulty is offered in figure B3.1.5. Here we display on the ordinate, for helium's ¹S (1s²) state, the probability of finding an electron whose distance from the He nucleus is 0.13 Å (the peak of the 1s orbital's density) and whose angular coordinate relative to that of the other electron is plotted on the abscissa. The He nucleus is at the origin and the second electron also has a radial coordinate of 0.13 Å. As the relative angular coordinate varies away from 0°, the electrons move apart; near 0°, the electrons approach

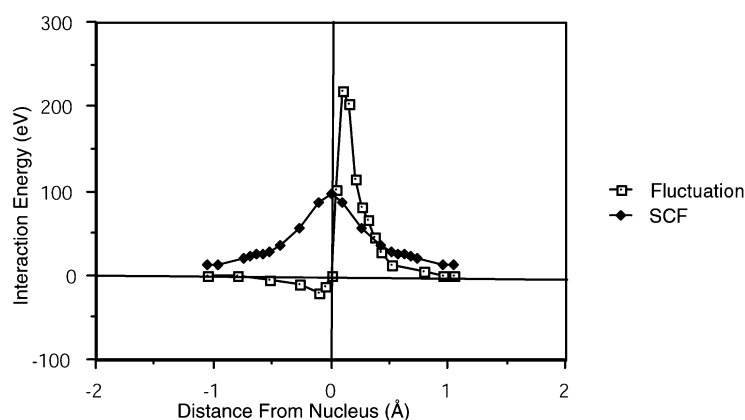


Figure B3.1.4. Fluctuation and mean-field SCF potentials for a 2s electron in Be.

Table B3.1.1. Pair correlation energies for the four electrons in Be.

Orbital pair	$1\alpha 1s\beta$	$1\alpha 2s\alpha$	$1\alpha 2s\beta$	$1s\beta 2s\alpha$	$1s\beta 2s\beta$	$2s\alpha 2s\beta$
ΔE (eV)	1.126	0.022	0.058	0.058	0.022	1.234

one another. Since both electrons have opposite spin in this state, their mutual Coulomb repulsion alone acts to keep them apart.

What figure B3.1.5 shows is that, for a highly accurate wavefunction (one constructed using so-called Hylleraas functions [23] that depend explicitly on the coordinates of the two electrons as well as on their interparticle distance coordinate), one finds a ‘cusp’ in the probability density for finding one electron in the neighbourhood of another electron with the same spin. The probability plot for the Hylleraas function is the lower bold curve in figure B3.1.5. The line above the Hylleraas plot was extracted from a configuration interaction wavefunction for He obtained using a rather large atomic orbital (AO) basis set [22]. Even for such a sophisticated wavefunction (of the type used in many state-of-the-art *ab initio* calculations), the cusp in the relative probability distribution is, clearly, not well represented. Finally, the Hartree–Fock (HF) probability, which is not even displayed above, would, if plotted, be flat as a function of the angle shown above and thus clearly very much in error.

B3.1.2.1 Summary

The above evidence shows why an *ab initio* solution of the Schrödinger equation is a very demanding task if high accuracy is desired. The HF potential takes care of ‘most’ of the interactions among the N electrons (which interact via long-range Coulomb forces and whose dynamics requires the application of quantum physics and permutational symmetry). However, the residual fluctuation potential is large enough to cause significant corrections to the HF picture. The reality is that electrons in atoms and molecules undergo dynamical motions in which their Coulomb repulsions cause them to ‘avoid’ one another at every instant of time, not only in the average-repulsion manner that the mean-field models embody. The inclusion of instantaneous spatial correlations (usually called *dynamical correlations*) among electrons is necessary to achieve a more accurate description of the atomic and molecular electronic structure.

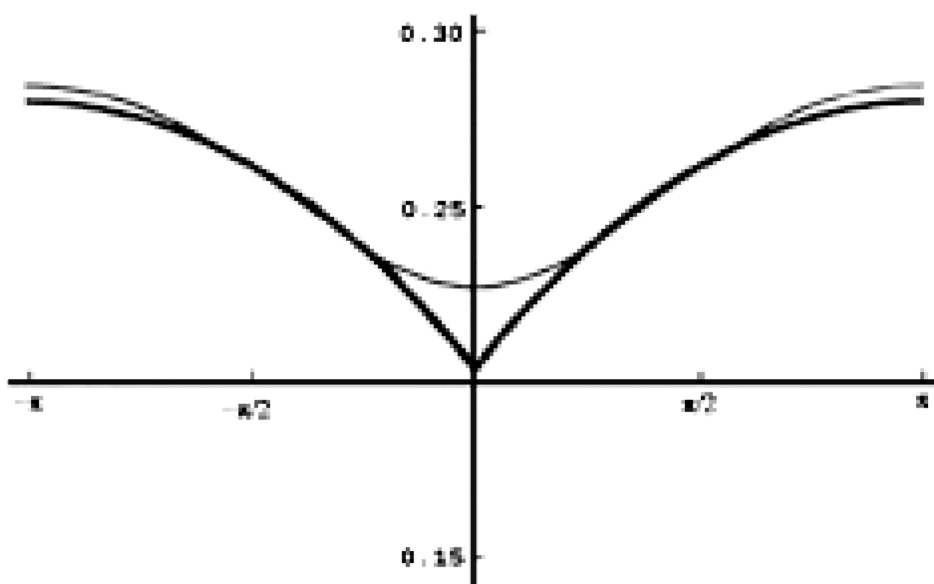


Figure B3.1.5. Probability (as a function of angle) for finding the second electron in He when both electrons are located at the maximum in the 1s orbital's probability density. The bottom line is that obtained using a Hylleraas-type function, and the other related to a highly-correlated multiconfigurational wavefunction. After [22].

B3.1.3 What are the essential concepts of *ab initio* quantum chemistry?

The mean-field potential and the need to improve it to achieve reasonably accurate solutions to the true electronic Schrödinger equation introduce three constructs that characterize essentially all *ab initio* quantum chemical methods: *orbitals*, *configurations* and *electron correlation*.

B3.1.3.1 Orbitals and configurations—what are they (really)?

(a) How the mean-field model leads to orbitals and configurations

The mean-field potentials that have proven most useful are all one-electron additive: $V_{\text{mf}}(\mathbf{r}) = \sum_j V_{\text{mf}}(\mathbf{r}_j)$. Since the electronic kinetic energy $\hat{T} = \sum_j \hat{T}_j$ operator is also one-electron additive, so is the mean-field Hamiltonian $\hat{H}^0 = \hat{T} + \hat{V}_{\text{mf}}$. The additivity of \hat{H}^0 implies that the mean-field energies $\{E_k^0\}$ are additive and the wavefunctions $\{\Psi_k^0\}$ can be formed in terms of products of functions $\{\phi_k\}$ of the coordinates of the individual electrons.

Thus, it is the *ansatz* that V_{mf} is separable that leads to the concept of *orbitals*, which are the one-electron functions $\{\phi_j\}$ found by solving the one-electron Schrödinger equations: $(\hat{T}_1 + \hat{V}_{\text{mf}}(\mathbf{r}_1))\phi_j(\mathbf{r}_1) = \varepsilon_j\phi_j(\mathbf{r}_1)$; the eigenvalues $\{\varepsilon_j\}$ are called *orbital energies*.

Given the complete set of solutions to this one-electron equation, a complete set of N -electron mean-field wavefunctions can be written. Each Ψ_k^0 is constructed by forming a product of N orbitals chosen from the set of $\{\phi_j\}$, allowing each orbital in the list to be a function of the coordinates of one of the N electrons (e.g. $\Psi_k^0 = |\phi_{k1}(\mathbf{r}_1)\phi_{k2}(\mathbf{r}_2)\phi_{k3}(\mathbf{r}_3) \dots \phi_{kN-1}(\mathbf{r}_{N-1})\phi_{kN}(\mathbf{r}_N)|$, as above). The corresponding mean-field energy is evaluated as the sum over those orbitals that appear in Ψ_k^0 : $E_k^0 = \sum_{j=1,N} \varepsilon_{kj}$.

Because of the indistinguishability of the N electrons, the antisymmetric component of any such orbital product must be formed to obtain the proper mean-field wavefunction. To do so, one applies the so-called antisymmetrizer operator [24] $\hat{A} = \sum_P (-1)^P \hat{P}$, where the permutation operator \hat{P} runs over all $N!$ permutations of the N electrons. Application of \hat{A} to a product function does not alter the occupancy of the functions $\{\phi_{kj}\}$ in Ψ_k^0 , it simply scrambles the order which the electrons occupy the $\{\phi_{kj}\}$ and it causes the resultant function (which is often denoted $|\phi_{k1}(\mathbf{r}_1)\phi_{k2}(\mathbf{r}_2)\phi_{k3}(\mathbf{r}_3)\dots\phi_{kN-1}(\mathbf{r}_{N-1})\phi_{kN}(\mathbf{r}_N)|$ and called a Slater determinant) to obey the Pauli exclusion principle.

Because the electrons also possess intrinsic spin, the one-electron functions $\{\phi_j\}$ used in this construction are taken to be eigenfunctions of $(\hat{T}_1 + \hat{V}_{\text{mf}}(\mathbf{r}_1))$ multiplied by either an α or β spin function. This set of functions is called the set of mean-field *spin orbitals*.

By choosing to place N electrons into N specific spin orbitals, one specifies a *configuration*. By making other choices of which $N\phi_j$ to occupy, one describes other configurations. Just as the one-electron mean-field Schrödinger equation has a complete set of spin-orbital solutions $\{\phi_j$ and $\varepsilon_j\}$, the N -electron mean-field Schrödinger equation has a complete set of antisymmetric N -electron Slater determinants. When these determinants are combined to generate functions that are eigenfunctions of the total S^2 and S_z and eigenfunctions of the molecule's point group symmetry (or \hat{L}^2 and \hat{L}_z for atoms), one has what are called *configuration state functions* (CSFs) Ψ_k^0 whose mean-field energies are also given by $E_k^0 = \sum_{j=1,N} \varepsilon_{kj}$.

(b) The self-consistent mean-field (SCF) potential

The one-electron additivity of the mean-field Hamiltonian \hat{H}^0 gives rise to the concept of spin orbitals for *any* additive $\hat{V}_{\text{mf}}(\mathbf{r})$. In fact, there is no *single* mean-field potential; different scientists have put forth different suggestions for \hat{V}_{mf} over the years. Each gives rise to spin orbitals and configurations that are specific to the particular \hat{V}_{mf} . However, if the difference between any particular mean-field model and the full electronic Hamiltonian is fully treated, corrections to all mean-field results should converge to the same set of exact states. In practice, one is never able to treat *all* corrections to any mean-field model. Thus, it is important to seek particular mean-field potentials for which the corrections are as small and straightforward to treat as possible.

In the most commonly employed mean-field models [25] of electronic structure theory, the configuration specified for study plays a central role in defining the mean-field potential. For example, the mean-field Coulomb potential felt by a $2p_x$ orbital's electron at a point \mathbf{r} in the $1s^2 2s^2 2p_x 2p_y$ configuration description of the carbon atom is:

$$\hat{V}_{\text{mf}}(\mathbf{r}) = 2 \int |1s(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + 2 \int |2s(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + \int |2p_y(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}'.$$

The above mean-field potential is used to find the $2p_x$ orbital of the carbon atom, which is then used to define the mean-field potential experienced by, for example, an electron in the $2s$ orbital:

$$\begin{aligned} \hat{V}_{\text{mf}}(\mathbf{r}) = & 2 \int |1s(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + \int |2s(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + \int |2p_y(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' \\ & + \int |2p_x(\mathbf{r}')|^2 e^2 / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}'. \end{aligned}$$

Notice that the orbitals occupied in the configuration under study appear in the mean-field potential. However, it is \hat{V}_{mf} that, through the one-electron Schrödinger equation, determines the orbitals. For these reasons, the solution of these equations must be carried out in a so-called SCF manner. One begins with an approximate description of the orbitals in Ψ_k^0 . These orbitals then define \hat{V}_{mf} , and the equations $(\hat{T}_1 + \hat{V}_{\text{mf}}(\mathbf{r}_1))\phi_j(\mathbf{r}_1) = \varepsilon_j \phi_j(\mathbf{r}_1)$ are solved for 'new' spin orbitals. These orbitals are then be used to define

an improved \hat{V}_{mf} , which gives another set of solutions to $(\hat{T}_1 + \hat{V}_{\text{mf}}(\mathbf{r}_1))\phi_j(\mathbf{r}_1) = \varepsilon_j\phi_j(\mathbf{r}_1)$. This iterative process is continued until the orbitals used to define \hat{V}_{mf} are identical to those that result as solutions of $(\hat{T}_1 + \hat{V}_{\text{mf}}(\mathbf{r}_1))\phi_j(\mathbf{r}_1) = \varepsilon_j\phi_j(\mathbf{r}_1)$. When this condition is reached, one has achieved ‘self-consistency’.

B3.1.3.2 What is electron correlation?

By expressing the mean-field interaction of an electron at \mathbf{r} with the $N - 1$ other electrons in terms of a probability density $\rho_{N-1}(\mathbf{r}')$ that is independent of the fact that another electron resides at \mathbf{r} , the mean-field models ignore spatial *correlations* among the electrons. In reality, as shown in figure B3.1.5, the conditional probability density for finding one of $N - 1$ electrons at \mathbf{r}' , given that one electron is at \mathbf{r} depends on \mathbf{r}' . The absence of a spatial correlation is a direct consequence of the spin-orbital *product nature* of the mean-field wavefunctions $\{\Psi_k^0\}$.

To improve upon the mean-field picture of electronic structure, one must move beyond the single-configuration approximation. It is essential to do so to achieve higher accuracy, but it is also important to do so to achieve a *conceptually* correct view of the chemical electronic structure. Although the picture of configurations in which N electrons occupy N spin orbitals may be familiar and useful for systematizing the electronic states of atoms and molecules, these constructs are approximations to the true states of the system. They were introduced when the mean-field approximation was made, and neither orbitals nor configurations can be claimed to describe the proper eigenstates $\{\Psi_k, E_k\}$. It is thus inconsistent to insist that the carbon atom be thought of as $1s^22s^22p^2$ while insisting on a description of this atom accurate to ± 1 kcal mol⁻¹.

B3.1.3.3 Summary

The SCF mean-field potential takes care of ‘most’ of the interactions among the N electrons. However, for all mean-field potentials proposed to date, the residual or fluctuation potential is large enough to require significant corrections to the mean-field picture. This, in turn, necessitates the use of more sophisticated and computationally taxing techniques (e.g., high-order perturbation theory or large variational expansion spaces) to reach the desired chemical accuracy.

For electronic structures of atoms and molecules, the SCF model requires quite substantial corrections to bring its predictions in line with experimental fact. Electrons in atoms and molecules undergo dynamical motions in which their Coulomb repulsions cause them to ‘avoid’ one another at every instant of time, not only in the average-repulsion manner of mean-field models. The inclusion of *dynamical correlations* among electrons is necessary to achieve a more accurate description of atomic and molecular electronic structure. No single spin-orbital product wavefunction is capable of treating electron correlation to *any* extent; its product nature renders it incapable of doing so.

B3.1.4 How to introduce electron correlation via configuration mixing

B3.1.4.1 The multi-configuration wavefunction

In most of the commonly used *ab initio* quantum chemical methods [26], one forms a set of configurations by placing N electrons into spin orbitals in a manner that produces the spatial, spin and angular momentum symmetry of the electronic state of interest. The correct wavefunction Ψ is then written as a linear combination of the mean-field configuration functions $\{\Psi_k\}$: $\Psi = \sum_k C_k \Psi_k^0$. For example, to describe the ground ¹S state of the Be atom, the $1s^22s^2$ configuration is augmented by including other configurations such as $1s^23s^2$, $1s^22p^2$, $1s^23p^2$, $1s^22s3s$, $3s^22s^2$, $2p^22s^2$, etc, all of which have overall ¹S spin and angular momentum symmetry. The various methods of electronic structure theory differ primarily in how they determine the $\{C_k\}$ expansion coefficients and how they extract the energy E corresponding to this Ψ .

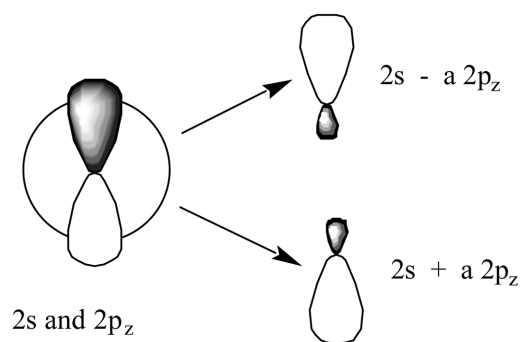


Figure B3.1.6. Polarized orbital pairs involving 2s and 2p_z orbitals.

B3.1.4.2 The physical meaning of mixing in 'excited' configurations

When considering the ground ¹S state of the Be atom, the following four antisymmetrized spin-orbital products are found to have the largest C_k amplitudes:

$$\Psi \cong C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|].$$

The fact that the latter three terms possess the same amplitude C₂ is a result of the requirement that a state of ¹S symmetry is desired. It can be shown [27] that this function is equivalent to

$$\begin{aligned} \Psi \cong & \frac{1}{6} C_1 |1s\alpha 1s\beta \{ [(2s - a2p_x)\alpha(2s + a2p_x)\beta - (2s - a2p_x)\beta(2s + a2p_x)\alpha] \\ & + [(2s - a2p_y)\alpha(2s + a2p_y)\beta - (2s - a2p_y)\beta(2s + a2p_y)\alpha] \\ & + [(2s - a2p_z)\alpha(2s + a2p_z)\beta - (2s - a2p_z)\beta(2s + a2p_z)\alpha] \} | \end{aligned}$$

where $a = \sqrt{3C_2/C_1}$.

Here two electrons occupy the 1s orbital (with opposite, α and β spins) while the other electron pair resides in 2s – 2p polarized orbitals in a manner that instantaneously correlates their motions. These *polarized orbital pairs* (2s ± a2p_{x,y or z}) are formed by combining the 2s orbital with the 2p_{x,y or z} orbital in a ratio determined by C₂/C₁. This way of viewing an electron pair correlation forms the basis of the generalized valence bond (GVB) method that Professor Bill Goddard [28] pioneered.

This ratio C₂/C₁ can be shown to be proportional to the magnitude of the coupling $\langle 1s^2 2s^2 | \hat{H} | 1s^2 2p^2 \rangle$ between the two configurations involved and inversely proportional to the energy difference ($\langle 1s^2 2s^2 | \hat{H} | 1s^2 2s^2 \rangle - \langle 1s^2 2p^2 | \hat{H} | 1s^2 2p^2 \rangle$) between these configurations. In general, configurations that have similar Hamiltonian expectation values and that are coupled strongly give rise to strongly mixed (i.e. with large |C₂/C₁| ratios) polarized orbital pairs.

A set of polarized orbital pairs is described pictorially in figure B3.1.6. In each of the three equivalent terms in the above wavefunction, one of the valence electrons moves in a 2s + a2p orbital polarized in one direction while the other valence electron moves in the 2s – a2p orbital polarized in the opposite direction. For example, the first term (2s – a2p_x)α(2s + a2p_x)β – (2s – a2p_x)β(2s + a2p_x)α describes one electron occupying a 2s – a2p_x polarized orbital while the other electron occupies the 2s + a2p_x orbital. The electrons thus reduce their Coulomb repulsion by occupying *different* regions of space; in the SCF picture 1s²2s², both electrons reside in the same 2s region of space. In this particular example, the electrons undergo *angular correlation* to 'avoid' one another.

Let us consider another example. In describing the π² electron pair of an olefin, it is important to mix in 'doubly excited' configurations of the form (π*)². The physical importance of such configurations can again

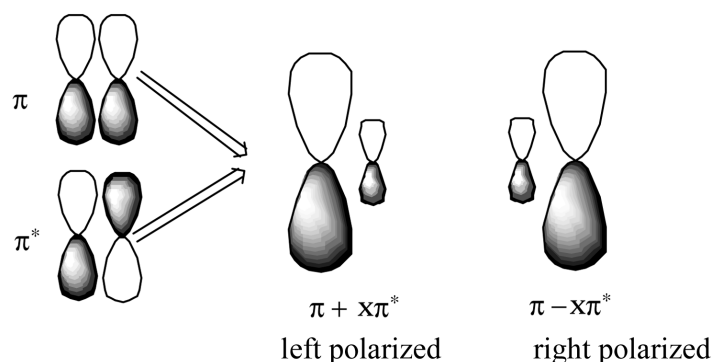


Figure B3.1.7. Left- and right-polarized orbital pairs involving π and π^* orbitals.

be made clear by using the identity

$$C_1|\dots\phi\alpha\phi\beta\dots\rangle - C_2|\dots\phi'\alpha\phi'\beta\dots\rangle = C_1/2\{|\dots(\phi - x\phi')\alpha(\phi + x\phi')\beta\dots\rangle - |\dots(\phi - x\phi')\beta(\phi + x\phi')\alpha\dots\rangle\}$$

where $x = (C_2/C_1)^{1/2}$.

In this example, the two non-orthogonal ‘polarized orbital pairs’ involve mixing the π and π^* orbitals to produce two left–right polarized orbitals as depicted in figure B3.1.7. Here one says that the π^2 electron pair undergoes left–right correlation when the $(\pi^*)^2$ configuration is introduced.

B3.1.4.3 Are polarized orbital pairs hybrid orbitals?

It should be stressed that these polarized orbital pairs are *not* the same as hybrid orbitals. The latter are used to describe directed bonding, but polarized orbital *pairs* are each a ‘mixture’ of two mean-field orbitals with amplitude $x = (C_2/C_1)^{1/2}$ and with a *single electron* in each, thereby allowing the electrons to be spatially correlated and to ‘avoid’ one another. In addition, polarized orbital pairs are *not generally orthogonal* to one another; hybrid orbital sets are.

B3.1.4.4 Relationship to the generalized valence bond picture

In these examples, the analysis allows one to *interpret* the combination of pairs of configurations that differ from one another by a ‘double excitation’ from one orbital (ϕ) to another (ϕ') as equivalent to a singlet coupling of two polarized orbitals ($\phi - a\phi'$) and ($\phi + a\phi'$). As mentioned earlier, this picture is closely related to the GVB model that Goddard [28] and Goddard and Harding [29] developed. In the simplest embodiment of the GVB model, each electron pair in the atom or molecule is correlated by mixing in a configuration in which that pair is ‘doubly excited’ to a correlating orbital. The direct product of all such pair correlations generates the simplest GVB-type wavefunction.

In most *ab initio* quantum chemical methods, the correlation calculation is actually carried out by forming a linear combination of the mean-field configuration state functions and determining the $\{C_k\}$ amplitudes by some procedure. The identities discussed in some detail above are then introduced merely to permit one to interpret the presence of configurations that are ‘doubly excited’ relative to the dominant mean-field configuration in terms of polarized orbital pairs.

B3.1.4.5 Summary

The dynamical interactions among electrons give rise to instantaneous spatial correlations that must be handled to arrive at an accurate picture of the atomic and molecular structure. The single-configuration picture provided by the mean-field model is a useful starting point, but it is *incapable* of describing electron correlations. Therefore, improvements are needed. The use of doubly-excited configurations is a mechanism by which Ψ can place electron *pairs*, which in the mean-field picture occupy the same orbital, into different regions of space thereby lowering their mutual Coulombic repulsions. Such electron correlation effects are referred to as *dynamical electron correlation*; they are extremely important to include if one expects to achieve chemically meaningful accuracy.

B3.1.5 The single-configuration picture and the HF approximation

Given a set of N -electron space- and spin-symmetry-adapted configuration state functions $\{\Phi_J\}$ in terms of which Ψ is to be expanded as $\Psi = \sum_J C_J \Phi_J$, two primary questions arise: (1) how to determine the $\{C_J\}$ coefficients and the energy E and (2) how to find the ‘best’ spin orbitals $\{\phi_j\}$? Let us first consider the case where a single configuration is used so only the question of determining the spin orbitals exists.

B3.1.5.1 The single-determinant wavefunction

(a) The canonical SCF equations

The simplest trial function employed in *ab initio* quantum chemistry is the single Slater determinant function in which N spin orbitals are occupied by N electrons:

$$\Psi = |\phi_1 \phi_2 \phi_3 \dots \phi_N|.$$

For such a function, variational optimization of the spin orbitals to make the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ stationary produces [30] the canonical HF equations

$$\hat{F} \phi_i = \varepsilon_i \phi_i$$

where the so-called Fock operator \hat{F} is given by

$$\hat{F} \phi_i = \hat{h} \phi_i + \sum_{j(\text{occupied})} [\hat{J}_j - \hat{K}_j] \phi_i.$$

The Coulomb (\hat{J}_j) and exchange (\hat{K}_j) operators are defined by the relations

$$\hat{J}_j \phi_i = \int \phi_j^*(r') \phi_j(r') / |r - r'| d\tau' \phi_i(r)$$

and

$$\hat{K}_j \phi_i = \int \phi_j^*(r') \phi_i(r') / |r - r'| d\tau' \phi_j(r)$$

the symbol \hat{h} denotes the sum of the electronic kinetic energy, and electron–nuclear Coulomb attraction operators. The $d\tau$ implies integration over the spin variables associated with the ϕ_j (and, for the exchange operator, ϕ_i), as a result of which the exchange integral vanishes unless the spin function of ϕ_j is the same as that of ϕ_i ; the Coulomb integral is non-vanishing no matter what the spin functions of ϕ_j and ϕ_i .

(b) *The equations have orbital solutions for occupied and unoccupied orbitals*

The HF [31] equations $\hat{F}\phi_i = \varepsilon_i\phi_i$ possess solutions for the spin orbitals in Ψ (the *occupied* spin orbitals) as well as for orbitals not occupied in Ψ (the *virtual* spin orbitals) because the \hat{F} operator is Hermitian. Only the ϕ_i occupied in Ψ appear in the Coulomb and exchange potentials of the Fock operator.

(c) *The spin-impurity problem*

As formulated above, the HF equations yield orbitals that do not guarantee that Ψ has proper spin symmetry. To illustrate, consider an open-shell system such as the lithium atom. If $1s\alpha$, $1s\beta$, and $2s\alpha$ spin orbitals are chosen to appear in Ψ , the Fock operator will be

$$\hat{F} = \hat{h} + \hat{J}_{1s\alpha} + \hat{J}_{1s\beta} + \hat{J}_{2s\alpha} - [\hat{K}_{1s\alpha} + \hat{K}_{1s\beta} + \hat{K}_{2s\alpha}].$$

Acting on an α spin orbital $\phi_{k\alpha}$ with F and carrying out the spin integrations, one obtains

$$\hat{F}\phi_{k\alpha} = \hat{h}\phi_{k\alpha} + (2\hat{J}_{1s} + \hat{J}_{2s})\phi_{k\alpha} - (\hat{K}_{1s} + \hat{K}_{2s})\phi_{k\alpha}.$$

In contrast, when acting on a β spin orbital, one obtains

$$\hat{F}\phi_{k\beta} = \hat{h}\phi_{k\beta} + (2\hat{J}_{1s} + \hat{J}_{2s})\phi_{k\beta} - (\hat{K}_{1s})\phi_{k\beta}.$$

Spin orbitals of α and β type do *not* experience the same exchange potential in this model because Ψ contains two α spin orbitals and only one β spin orbital. A consequence is that the optimal $1s\alpha$ and $1s\beta$ spin orbitals, which are themselves solutions of $\hat{F}\phi_i = \varepsilon_i\phi_i$, do not have identical orbital energies (i.e. $\varepsilon_{1s\alpha} \neq \varepsilon_{1s\beta}$) and are not spatially identical. This resultant spin polarization of the orbitals gives rise to *spin impurities* in Ψ . The determinant $|1s\alpha 1s'\beta 2s\alpha|$ is not a pure doublet spin eigenfunction, although it is an S_z eigenfunction with $M_s = 1/2$; it contains both $S = 1/2$ and $S = 3/2$ components. If the $1s\alpha$ and $1s'\beta$ spin orbitals were spatially identical, then $|1s\alpha 1s'\beta 2s\alpha|$ would be a pure spin eigenfunction with $S = 1/2$.

The above single-determinant wavefunction is referred to as being of the unrestricted Hartree–Fock (UHF) type because no restrictions are placed on the spatial nature of the orbitals in Ψ . In general, UHF wavefunctions are not of pure spin symmetry for any open-shell system or for closed-shell systems far from their equilibrium geometries (e.g. for H_2 or N_2 at long bond lengths). These are significant drawbacks of methods based on a UHF starting point. Such a UHF treatment forms the basis of the widely used and highly successful Gaussian 70 through Gaussian-9X series of electronic structure computer codes [32] which derive from Pople [32] and co-workers.

To overcome some of the problems inherent in the UHF method, it is possible to derive SCF equations based on minimizing the energy of a wavefunction formed by spin projecting a single Slater determinant starting function (e.g. using $\{|1s\alpha 2s\beta| - |1s\beta 2s\alpha|\}/2^{1/2}$ for the singlet excited state of He rather than $|1s\alpha 2s\beta|$). It is also possible for a trial wavefunction of the form $|1s\alpha 1s\beta 2s\alpha|$ to constrain the $1s\alpha$ and $1s\beta$ orbitals to have exactly the same spatial form. In both cases, one then is able to carry out what are called restricted Hartree–Fock (RHF) calculations.

B3.1.5.2 *The linear combinations of atomic orbitals to form molecular orbitals expansion of the spin orbitals*

The HF equations must be solved iteratively because the J_i and K_i operators in F depend on the orbitals ϕ_i for which solutions are sought. Typical iterative schemes begin with a ‘guess’ for those ϕ_i that appear in Ψ , which then allows \hat{F} to be formed. Solutions to $\hat{F}\phi_i = \varepsilon_i\phi_i$ are then found, and those ϕ_i which possess the space and spin symmetry of the occupied orbitals of Ψ and which have the proper energies and nodal character are used to generate a new \hat{F} operator (i.e. new \hat{J}_i and \hat{K}_i operators). This iterative HF SCF process

is continued until the ϕ_i and ε_i do not vary significantly from one iteration to the next, at which time one says that the process has converged.

In practice, solution of $\hat{F}\phi_i = \varepsilon_i\phi_i$ as an integro-differential equation can be carried out only for atoms [34] and linear molecules [35] for which the angular parts of the ϕ_i can be exactly separated from the radial because of axial- or full-rotation group symmetry (e.g. $\phi_i = Y_{l,m}(\theta, \phi)R_{n,l}(r)$ for an atom and $\phi_i = \exp(im\phi)R_{n,l,m}(\rho, z)$ for a linear molecule).

In the procedures most commonly applied to nonlinear molecules, the ϕ_i are expanded in a *basis* χ_μ according to the linear combinations of AOs to form molecular orbitals (LCAO–MO) [36] procedure:

$$\phi_i = \sum_{\mu} C_{\mu,i} \chi_{\mu}.$$

This reduces $\hat{F}\phi_i = \varepsilon_i\phi_i$ to a matrix eigenvalue-type equation:

$$\sum_{\nu} F_{\mu,\nu} C_{\nu,i} = \varepsilon_i \sum_{\nu} S_{\mu,\nu} C_{\nu,i}$$

where $S_{\mu,\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$ is the overlap matrix among the AOs and

$$F_{\mu,\nu} = \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle + \sum_{\delta,\kappa} [\gamma_{\delta,\kappa} \langle \chi_{\mu} \chi_{\delta} | \hat{g} | \chi_{\nu} \chi_{\kappa} \rangle - \gamma_{\delta,\kappa}^{\text{ex}} \langle \chi_{\mu} \chi_{\delta} | \hat{g} | \chi_{\kappa} \chi_{\nu} \rangle]$$

is the matrix representation of the Fock operator in the AO basis. Here and elsewhere, the symbol \hat{g} is used to represent the electron–electron Coulomb potential $e^2/|\mathbf{r} - \mathbf{r}'|$.

The charge- and exchange-density matrix elements in the AO basis are:

$$\gamma_{\delta,\kappa} = \sum_{i(\text{occupied})} C_{\delta,i} C_{\kappa,i}$$

and

$$\gamma_{\delta,\kappa}^{\text{ex}} = \sum_{i(\text{occupied and same spin})} C_{\delta,i} C_{\kappa,i}$$

where the sum in $\gamma_{\delta,\kappa}^{\text{ex}}$ runs over those occupied spin orbitals whose m_s value is equal to that for which the Fock matrix is being formed (for a closed-shell species, $\gamma_{\delta,\kappa}^{\text{ex}} = 1/2\gamma_{\delta,\kappa}$).

It should be noted that by moving to a matrix problem, one does not remove the need for an iterative solution; the $F_{\mu,\nu}$ matrix elements depend on the $C_{\nu,i}$ LCAO–MO coefficients which are, in turn, solutions of the so-called Roothaan [30] matrix HF equations: $\sum_{\nu} F_{\mu,\nu} C_{\nu,i} = \varepsilon_i \sum_{\nu} S_{\mu,\nu} C_{\nu,i}$. One should also note that, just as $\hat{F}\phi_i = \varepsilon_i\phi_i$ possesses a complete set of eigenfunctions, the matrix $F_{\mu,\nu}$, whose dimension M is equal to the number of atomic basis orbitals, has M eigenvalues ε_i and M eigenvectors whose elements are the $C_{\nu,i}$. Thus, there are *occupied and virtual* MOs each of which is described in the LCAO–MO form with the $C_{\nu,i}$ coefficients obtained via solution of $\sum_{\nu} F_{\mu,\nu} C_{\nu,i} = \varepsilon_i \sum_{\nu} S_{\mu,\nu} C_{\nu,i}$.

B3.1.5.3 AO basis sets

(a) Slater-type orbitals and Gaussian-type orbitals

The basis orbitals commonly used in the LCAO–MO process fall into two primary classes:

- (1) Slater-type orbitals (STOs) $\chi_{n,l,m}(r, \theta, \phi) = N_{n,l,m,\zeta} Y_{l,m}(\theta, \phi) r^{n-1} \exp(-\zeta r)$, are characterized by the quantum numbers n , l and m and the exponent (which characterizes the ‘size’) ζ . The symbol $N_{n,l,m,\zeta}$ denotes the normalization constant.

- (2) Cartesian Gaussian-type orbitals (GTOs) $\chi_{a,b,c}(r, \theta, \phi) = N'_{a,b,c,\alpha} x^a y^b z^c \exp(-\alpha r^2)$, are characterized by the quantum numbers a , b and c , which detail the angular shape and direction of the orbital, and the exponent α which governs the radial 'size'.

For both types of orbitals, the coordinates r , θ and ϕ refer to the position of the electron relative to a set of axes attached to the centre on which the basis orbital is located. Although STOs have the proper 'cusp' behaviour near the nuclei, they are used primarily for atomic- and linear-molecule calculations because the multi-centre integrals which arise in polyatomic-molecule calculations cannot efficiently be performed when STOs are employed. In contrast, such integrals can routinely be done when GTOs are used. This fundamental advantage of GTOs has led to the dominance of these functions in molecular quantum chemistry.

To overcome the primary weakness of GTO functions (i.e. their radial derivatives vanish at the nucleus whereas the derivatives of STOs are non-zero), it is common to combine two, three, or more GTOs, with combination coefficients which are fixed and *not* treated as LCAO–MO parameters, into new functions called *contracted* GTOs or CGTOs. Typically, a series of tight, medium, and loose GTOs are multiplied by *contraction coefficients* and summed to produce a CGTO, which approximates the proper 'cusp' at the nuclear centre.

Although most calculations on molecules are now performed using Gaussian orbitals (STOs are still commonly employed in atomic calculations), it should be noted that other basis sets can be used as long as they span enough of the region of space (radial and angular) where significant electron density resides. In fact, it is possible to use plane wave orbitals [37] of the form $\chi(r, \theta, \phi) = N \exp[i(k_x r \sin \theta \cos \phi + k_y r \sin \theta \sin \phi + k_z r \cos \theta)]$, where N is a normalization constant and k_x , k_y and k_z are the quantum numbers detailing the momenta of the orbital along the x , y and z Cartesian directions. The advantage to using such 'simple' orbitals is that the integrals one must perform are much easier to handle with such functions; the disadvantage is that one must use many such functions to accurately describe sharply peaked charge distributions of, for example, inner-shell core orbitals.

(b) Basis set libraries

Much effort has been devoted to developing sets of STO or GTO basis orbitals for main-group elements and the lighter transition metals. This ongoing effort is aimed at providing standard basis set libraries which:

- (1) yield predictable chemical accuracy in the resultant energies;
- (2) are cost effective to use in practical calculations;
- (3) are relatively transferable so that a given atom's basis is flexible enough to be used for that atom in various bonding environments.

The fundamental core and valence basis. In constructing an AO basis, one can choose from among several classes of functions. First, the size and nature of the primary core and valence basis must be specified. Within this category, the following choices are common.

- (1) A *minimal basis* in which the number of STO or CGTO orbitals is equal to the number of core and valence AOs in the atom.
- (2) A *double-zeta* (DZ) basis in which twice as many STOs or CGTOs are used as there are core and valence AOs. The use of more basis functions is motivated by a desire to provide additional variational flexibility so the LCAO–MO process can generate MOs of variable diffuseness as the local electronegativity of the atom varies.
- (3) A *triple-zeta* (TZ) basis in which three times as many STOs or CGTOs are used as the number of core and valence AOs (and, yes, there now are quadruple-zeta (QZ) and higher-zeta basis sets appearing in the literature).

- (4) Dunning and Dunning and Hay [38] developed CGTO bases which range from approximately DZ to substantially beyond QZ quality. These bases involve contractions of primitive uncontracted GTO bases which Huzinaga [39] had earlier optimized. These Dunning bases are commonly denoted as follows for first-row atoms: (10s,6p/5s,4p), which means that 10 s-type primitive GTOs have been contracted to produce five separate s-type CGTOs and that six primitive p-type GTOs were contracted into four separate p-type CGTOs in each of the x , y and z directions.
- (5) Even-tempered basis sets [40] consist of GTOs in which the orbital exponents α_k belonging to series of orbitals consist of geometrical progressions: $\alpha_k = a\beta^k$, where a and β characterize the particular set of GTOs.
- (6) STO-3G bases [41] were employed some years ago, but have recently become less popular. These bases are constructed by least-squares fitting GTOs to STOs which have been optimized for various electronic states of the atom. When three GTOs are employed to fit each STO, a STO-3G basis is formed.
- (7) 4-31G, 5-31G and 6-31G bases [42] employ a single CGTO of contraction length 4, 5, or 6 to describe the core orbital. The valence space is described at the DZ level with the first CGTO constructed from three primitive GTOs and the second CGTO built from a single primitive GTO.
- (8) More recently, the Dunning group has focused on developing basis sets that are optimal not for use in SCF-level calculations on atoms and molecules, but that have been optimized for use in correlated calculations. These so-called correlation-consistent bases [43] are now widely used because more and more *ab initio* calculations are being performed at a correlated level.
- (9) Atomic natural orbital (ANO) basis sets [44] are formed by contracting Gaussian functions so as to reproduce the natural orbitals obtained from correlated (usually using a configuration interaction with single and double excitation (CISD) level wavefunction) calculations on atoms.

Optimization of the *orbital exponents* (ζ s or α s) and the GTO-to-CGTO *contraction coefficients* for the kind of bases described above have undergone explosive growth in recent years. As a result, it is not possible to provide a single or even a few literature references from which one can obtain the most up-to-date bases. However, the theory group at the Pacific Northwest National Laboratories (PNNL) offer a webpage [45] from which one can find (and even download in a form prepared for input to any of several commonly used electronic structure codes) a wide variety of Gaussian atomic basis sets.

Polarization functions. One usually enhances any core and valence functions with a set of so-called polarization functions. They are functions of one higher angular momentum than appears in the atom's valence orbital space (e.g. d-functions for C, N and O and p-functions for H), and they have exponents (ζ or α) which cause their radial sizes to be similar to the sizes of the valence orbitals (i.e. the polarization p orbitals of the H atom are similar in size to the 1s orbital). Thus, they are *not* orbitals which describe the atom's valence orbital with one higher l value; such higher- l valence orbitals would be radially more diffuse.

The primary purpose of the polarization functions is to give additional angular flexibility to the LCAO-MO process in forming the valence MOs. This is illustrated below in figure B3.1.8 where polarization d_π orbitals are seen to contribute to formation of the bonding π orbital of a carbonyl group by allowing polarization of the carbon atom's p_π orbital toward the right and of the oxygen atom's p_π orbital toward the left.

The polarization functions are essential in strained ring compounds because they provide the angular flexibility needed to direct the electron density into the regions between the bonded atoms.

Functions with higher l values and with 'sizes' like those of lower- l valence orbitals are also used to introduce additional angular correlation by permitting angularly polarized orbital pairs to be formed. Optimal polarization functions for first- and second-row atoms have been tabulated and are included in the PNNL Gaussian orbital web site data base [45].

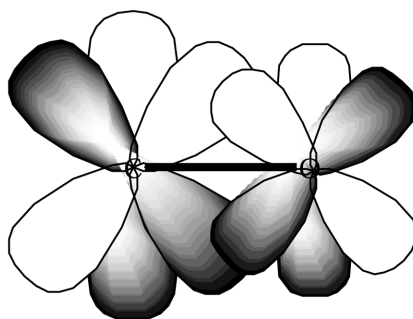


Figure B3.1.8. The role of d-polarization functions in the π bond between C and O.

Diffuse functions. When dealing with anions or Rydberg states, one must further *augment* the basis set by adding so-called diffuse basis orbitals. The valence and polarization functions described above do not provide enough radial flexibility to adequately describe either of these cases. Once again, the PNNL web site data base [45] offers a good source for obtaining diffuse functions appropriate to a variety of atoms.

Once one has specified an AO basis for each atom in the molecule, the LCAO–MO procedure can be used to determine the $C_{v,i}$ coefficients that describe the occupied and virtual orbitals. It is important to keep in mind that the basis orbitals are *not* themselves the SCF orbitals of the isolated atoms; even the proper AOs are combinations (with atomic values for the $C_{v,i}$ coefficients) of the basis functions. The LCAO–MO–SCF process itself determines the magnitudes and signs of the $C_{v,i}$; alternations in the signs of these coefficients allow radial nodes to form.

B3.1.5.4 The physical meaning of orbital energies

The HF–SCF equations $\hat{F}\phi_i = \varepsilon_i\phi_i$ imply that ε_i can be written as

$$\varepsilon_i = \langle \phi_i | \hat{F} | \phi_i \rangle = \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{j(\text{occupied})} \langle \phi_i | \hat{J}_j - \hat{K}_j | \phi_i \rangle = \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{j(\text{occupied})} [J_{i,j} - K_{i,j}].$$

Thus ε_i is the average value of the kinetic energy plus the Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin orbitals occupied in Ψ of the Coulomb minus exchange interactions.

If ϕ_i is an occupied spin orbital, the term $[J_{i,i} - K_{i,i}]$ disappears and the latter sum represents the Coulomb minus exchange interaction of ϕ_i with all of the $N - 1$ *other* occupied spin orbitals. If ϕ_i is a virtual spin orbital, this cancellation does not occur, and one obtains the Coulomb minus exchange interaction of ϕ_i with all N of the occupied spin orbitals.

Hence the orbital energies of *occupied* orbitals pertain to interactions appropriate to a total of N electrons, while the orbital energies of *virtual* orbitals pertain to a system with $N + 1$ electrons. This usually makes SCF virtual orbitals not very good for use in subsequent correlation calculations or for use in interpreting electronic excitation processes. To correlate a pair of electrons that occupy a valence orbital requires double excitations into a virtual orbital of similar size; the SCF virtual orbitals are too diffuse. For this reason, significant effort has been devoted to developing methods that produce so-called ‘improved virtual orbitals’ (IVOs) [46] that are of more utility in performing correlated calculations.

(a) Koopmans’ theorem

Let us consider a model of the vertical (i.e. at fixed molecular geometry) detachment or attachment of an electron to an N -electron molecule.

- (1) In this model, *both* the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
- (2) The HF orbitals of the parent molecule are used to describe both species. It is said that such a model neglects ‘*orbital relaxation*’ (i.e. the reoptimization of the spin orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows (ϕ_k represents the particular spin orbital that is added or removed):

- (1) For electron detachment

$$E^{N-1} - E^N = -\varepsilon_k.$$

- (2) For electron attachment

$$E^N - E^{N+1} = -\varepsilon_k.$$

So, within the limitations of the single-determinant, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as *Koopmans’ theorem* [47]; it is used extensively in quantum chemical calculations as a means for estimating IPs and EAs and often yields results that are qualitatively correct (i.e., ± 0.5 eV).

(b) Orbital energies and the total energy

The total SCF electronic energy can be written as

$$E = \sum_{i(\text{occupied})} \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i>j(\text{occupied})} [J_{i,j} - K_{i,j}]$$

and the sum of the orbital energies of the occupied spin orbitals is given by

$$\sum_{i(\text{occupied})} \varepsilon_i = \sum_{i(\text{occupied})} \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i,j(\text{occupied})} [J_{i,j} - K_{i,j}].$$

These two expressions differ in a very important way; the sum of occupied orbital energies double counts the Coulomb minus exchange interaction energies. Thus, within the HF approximation, the sum of the occupied orbital energies is *not* equal to the total energy.

B3.1.5.5 Solving the Roothaan SCF equations

Before moving on to discuss methods that go beyond the single-configuration mean-field model, it is important to examine some of the computational effort that goes into carrying out an SCF calculation.

Once atomic basis sets have been chosen for each atom, the *one- and two-electron integrals* appearing in $F_{\mu,v}$ must be evaluated. There are numerous, highly-efficient computer codes [48] which allow such integrals to be computed for s, p, d, f and even g, h and i basis functions. After executing one of these ‘*integral packages*’ for a basis with a total of P functions, one has available (usually on the computer’s hard disk) of the order of $P^2/2$ one-electron ($\langle \chi_\mu | \hat{h} | \chi_\nu \rangle$ and $\langle \chi_\mu | \chi_\nu \rangle$) and $P^4/8$ two-electron ($\langle \chi_\mu \chi_\delta | \hat{g} | \chi_\nu \chi_\epsilon \rangle$) integrals. When treating extremely large AO basis sets (e.g. 1000 or more basis functions), modern computer programs [49] calculate the requisite integrals, but never store them on the disk. Instead, their contributions to $F_{\mu,v}$ are accumulated ‘on the fly’ after which the integrals are discarded. Recently, much progress has been made towards achieving an evaluation of the non-vanishing (i.e. numerically significant) integrals [48] as well as solving the subsequent SCF equations in a manner whose effort *scales linearly* [50] with the number of basis functions for large P .

After the requisite integrals are available or are being computed on the fly, to begin the SCF process one must input into the computer routine which computes $F_{\mu,v}$ the *initial 'guesses'* for the $C_{v,i}$ values corresponding to the occupied orbitals. These initial guesses are typically made as follows.

- (1) If one has available the $C_{v,i}$ values for the system from a calculation performed at a nearby geometry, one can use these $C_{v,i}$ values.
- (2) If one has $C_{v,i}$ values appropriate to fragments of the system (e.g. for C and O atoms if the CO molecule is under study or for CH₂ and O if H₂CO is being studied), one can use these.
- (3) If one has no other information available, one can carry out one iteration of the SCF process in which the two-electron contributions to $F_{\mu,v}$ are ignored (i.e. take $F_{\mu,v} = \langle \chi_\mu | h | \chi_v \rangle$) and use the resultant solutions to $\sum_v F_{\mu,v} C_{v,i} = \varepsilon_i \sum_v S_{\mu,v} C_{v,i}$ as initial guesses.

Once the initial guesses have been made for the $C_{v,i}$ of the occupied orbitals, the full $F_{\mu,v}$ matrix is formed and new ε_i and $C_{v,i}$ values are obtained by solving $\sum_v F_{\mu,v} C_{v,i} = \varepsilon_i \sum_v S_{\mu,v} C_{v,i}$. These new orbitals are then used to form a new $F_{\mu,v}$ matrix from which new ε_i and $C_{v,i}$ are obtained. This iterative process is carried on until the ε_i and $C_{v,i}$ do not vary (within specified tolerances) from iteration to iteration, at which time the SCF process has reached self-consistency.

B3.1.6 Methods for treating electron correlation

B3.1.6.1 An overview of various approaches

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

$$\Psi = \sum_I C_I \Phi_I$$

where Φ_I is a spin- and space-symmetry-adapted CSF consisting of determinants $|\phi_{I1}\phi_{I2}\phi_{I3}\dots\phi_{IN}|$ (see [14, 16, 26]). In all such wavefunctions there are two kinds of parameters that need to be determined—the C_I and the LCAO–MO coefficients describing the ϕ_{Ik} . The most commonly employed methods used to determine these parameters include the following.

(a) The multiconfigurational self-consistent field method

In this approach [51], the expectation value $\langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$ is treated variationally and made stationary with respect to variations in the C_I and $C_{v,i}$ coefficients. The energy functional is a quadratic function of the C_I coefficients, and so one can express the stationary conditions for these variables in the secular form

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

However, E is a quartic function of the $C_{v,i}$ s because $H_{I,J}$ involves two-electron integrals $\langle \phi_i \phi_j | \hat{g} | \phi_k \phi_l \rangle$ that depend quartically on these coefficients.

It is well known that minimization of the function (E) of several nonlinear parameters (the $C_{v,i}$) is a difficult task that can suffer from poor convergence and may locate local rather than global minima. In a multiconfigurational self-consistent field (MCSCF) wavefunction containing many CSFs, the energy is only weakly dependent on the orbitals that appear in CSFs with small C_I values; in contrast, E is strongly dependent on those orbitals that appear in the CSFs with larger C_I values. One is therefore faced with minimizing a function of many variables that depends strongly on several of the variables and weakly on many others.

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 thousand) chosen to describe *essential correlations* (i.e. configuration crossings,

near degeneracies, proper dissociation, etc, all of which are often termed *non-dynamical correlations*) and important dynamical correlations (those electron-pair correlations of angular, radial, left–right, etc nature that are important when low-lying ‘virtual’ orbitals are present).

(b) The configuration interaction method

In this approach [52], the LCAO–MO coefficients are determined first via a single-configuration SCF calculation or an MCSCF calculation using a small number of CSFs. The C_I coefficients are subsequently determined by making the expectation value $\langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$ stationary.

The CI wavefunction is most commonly constructed from CSFs of Φ_J that include:

- (1) all of the CSFs in the SCF or MCSCF wavefunction used to generate the molecular orbitals ϕ_i . These are referred to as the ‘reference’ CSFs;
- (2) CSFs 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 are denoted S (singly), D (doubly), SD (singly and doubly), SDT (singly, doubly, and triply) excited.

The orbitals from which electrons are removed can be restricted to focus attention on the correlations among certain orbitals. For example, if the excitations from the core electrons are excluded, one computes the total energy that contains no core correlation energy. 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 5000 to 50 000 CSFs are routine, and functions with one to several billion CSFs are within the realm of practicality [53].

The need for such large CSF expansions should not be surprising considering (i) that each electron pair requires *at least* two CSFs to form polarized orbital pairs, (ii) there are of the order of $N(N - 1)/2 = X$ electron pairs for N electrons, hence (iii) the number of terms in the CI wavefunction scales as 2^X . For a molecule containing ten electrons, there could be $2^{45} = 3.5 \times 10^{13}$ terms in the CI expansion. This may be an overestimate of the number of CSFs needed, but it demonstrates how rapidly the number of CSFs can grow with the number of electrons.

The $H_{I,J}$ matrices are, in practice, evaluated in terms of one- and two-electron integrals over the MOs using the Slater–Condon rules [54] or their equivalent. Prior to forming the $H_{I,J}$ matrix elements, the one- and two-electron integrals, which can be computed only for the atomic (e.g. STO or GTO) basis, must be transformed [55] to the MO basis. This transformation step requires computer resources proportional to the fifth power of the number of basis functions, and thus is one of the more troublesome steps in most configuration interaction calculations.

For large CI calculations, the full $H_{I,J}$ matrix is *not* formed and stored in the computer’s memory or on disk; rather, ‘direct CI’ methods [56] identify and compute non-zero $H_{I,J}$ and immediately add up contributions to the sum $\sum_J H_{I,J} C_J$. Iterative methods [57], in which approximate values for the C_J coefficients are refined through sequential application of $\sum_J H_{I,J}$ to the preceding estimate of the C_J vector, are employed to solve these large eigenvalue problems.

(c) The Møller–Plesset perturbation method

This method [58] uses the single-configuration SCF process to determine a set of orbitals $\{\phi_i\}$. Then, using an unperturbed Hamiltonian equal to the sum of the N electrons’ Fock operators $\hat{H}^0 = \sum_{i=1,N} \hat{F}(i)$, perturbation theory is used to determine the C_I amplitudes for the CSFs. The MPPT procedure [59] is a special case of many-body perturbation theory (MBPT) in which the UHF Fock operator is used to define \hat{H}^0 . The amplitude for the *reference* CSF is taken as unity and the other CSFs’ amplitudes are determined by the Rayleigh–Schrödinger perturbation using $\hat{H} - \hat{H}^0$ as the perturbation.

In the MPPT/MBPT method, once the reference CSF is chosen and the SCF orbitals belonging to this CSF are determined, the wavefunction Ψ and energy E are determined in an order-by-order manner. The perturbation equations *determine* what CSFs to include and their particular order. This is one of the primary strengths of this technique; it does not require one to make further choices, in contrast to the MCSCF and CI treatments where one needs to choose which CSFs to include.

For example, the first-order wavefunction correction Ψ^1 is

$$\Psi^1 = - \sum_{i < j, m < n} [\langle i, j | \hat{g} | m, n \rangle - \langle i, j | \hat{g} | n, m \rangle] [\varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]^{-1} | \Phi_{i,j}^{m,n} \rangle$$

where the SCF orbital energies are denoted ε_k and $\Phi_{i,j}^{m,n}$ represents a CSF that is *doubly excited* (ϕ_i and ϕ_j are replaced by ϕ_m and ϕ_n) relative to Φ . Only doubly-excited CSFs contribute to the *first-order wavefunction*; the fact that the contributions from singly-excited configurations vanish in Φ^1 is known as the *Brillouin theorem* [60].

The energy E is given through second order as

$$E = E_{\text{SCF}} - \sum_{i < j, m < n} |\langle i, j | \hat{g} | m, n \rangle - \langle i, j | \hat{g} | n, m \rangle|^2 / [\varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j].$$

Both Ψ and E are expressed in terms of two-electron integrals $\langle i, j | \hat{g} | m, n \rangle$ coupling the virtual spin orbitals ϕ_m and ϕ_n to the spin orbitals from which the electrons were excited ϕ_i and ϕ_j as well as the orbital energy differences $[\varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]$ accompanying such excitations. Clearly, the major contributions to the correlation energy are made by double excitations into virtual orbitals $\phi_m \phi_n$ with large $\langle i, j | \hat{g} | m, n \rangle$ integrals and small orbital energy gaps $[\varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]$. In higher-order corrections, contributions from CSFs that are singly, triply, etc excited relative to Φ appear, and additional contributions from the doubly-excited CSFs also enter.

(d) The coupled-cluster method

In the coupled-cluster (CC) method [61], one expresses the wavefunction in a somewhat different manner:

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

where Φ is a single CSF (usually the UHF determinant) used in the SCF process to generate a set of spin orbitals. The operator \hat{T} is expressed in terms of operators that achieve spin-orbital excitations as follows:

$$T = \sum_{i,m} t_i^m \hat{m}^+ \hat{i} + \sum_{i,j}^{m,n} t_{i,j}^{m,n} \hat{m}^+ \hat{n}^+ \hat{j} \hat{i} + \dots$$

where the combination of operators $\hat{m}^+ \hat{i}$ denotes the *creation* of an electron in the virtual spin orbital ϕ_m and the *removal* of an electron from the occupied spin orbital ϕ_i to generate a single excitation. The operation $\hat{m}^+ \hat{n}^+ \hat{j} \hat{i}$ therefore represents a double excitation from $\phi_i \phi_j$ to $\phi_m \phi_n$.

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

$$\exp(-T)\hat{H}\exp(T)\Phi = E\Phi$$

against CSFs which are single, double, etc, excitations relative to Φ :

$$\begin{aligned} \langle \Phi_i^m | \hat{H} + [\widehat{H}, \widehat{T}] + \frac{1}{2} [[\widehat{H}, \widehat{T}], T] + \frac{1}{6} [[[\widehat{H}, \widehat{T}], T], T] + \frac{1}{24} [[[[\widehat{H}, \widehat{T}], T], T], T] | \Phi \rangle &= 0 \\ \langle \Phi_{i,j}^{m,n} | \hat{H} + [\widehat{H}, \widehat{T}] + \frac{1}{2} [[\widehat{H}, \widehat{T}], T] + \frac{1}{6} [[[\widehat{H}, \widehat{T}], T], T] + \frac{1}{24} [[[[\widehat{H}, \widehat{T}], T], T], T] | \Phi \rangle &= 0 \\ \langle \Phi_{i,j,k}^{m,n,p} | \hat{H} + [\widehat{H}, \widehat{T}] + \frac{1}{2} [[\widehat{H}, \widehat{T}], T] + \frac{1}{6} [[[\widehat{H}, \widehat{T}], T], T] + \frac{1}{24} [[[[\widehat{H}, \widehat{T}], T], T], T] | \Phi \rangle &= 0 \end{aligned}$$

and so on for higher-order excited CSFs.

It can be shown [62] that the expansion of the exponential operators truncates exactly at the fourth power in T . As a result, the exact CC equations are *quartic equations* for the t_i^m , $t_{i,j}^{m,n}$, etc amplitudes. The matrix elements appearing in the CC equations can be expressed in terms of one- and two-electron integrals over the spin orbitals including those occupied in Φ and the virtual orbitals not in Φ .

These quartic equations are solved in an iterative manner and, as such, are susceptible to convergence difficulties. In any such iterative process, it is important to start with an approximation reasonably close to the final result. In CC theory, this is often achieved by neglecting all of the terms that are nonlinear in the t amplitudes (because the t s are assumed to be less than unity in magnitude) and ignoring factors that couple different doubly-excited CSFs (i.e. the sum over i' , j' , m' and n'). This gives t amplitudes that are equal to the amplitudes of the first-order MPPT/MBPT wavefunction:

$$t_{i,j}^{m,n} = -\langle i, j | \hat{g} | m, n \rangle' / [\varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j].$$

As Bartlett [63] and Pople have both demonstrated [64], there is a 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.

(e) Density functional theories

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 wavefunction more configurations whose amplitudes they each determine in their own way. This can lead to a very large number of CSFs in the correlated wavefunction and, as a result, a need for extraordinary computer resources.

The density functional approaches are different [65]. Here one solves a set of orbital-level equations

$$\left[-\hbar^2/2m_e \nabla^2 - \sum_A Z_A e^2/|\mathbf{r} - \mathbf{R}_A| + \int \rho(\mathbf{r}') e^2/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + U(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i$$

in which the orbitals $\{\phi_i\}$ 'feel' potentials due to the nuclear centres (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 density functional theory (DFT) calculations are carried out, let us examine the origins underlying this theory.

The so-called Hohenberg–Kohn [66] 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

$$\hat{H} = \sum_j \left\{ -\hbar^2/2m_e \nabla_j^2 + V(r_j) + \frac{1}{2} \sum_{k \neq j} e^2/r_{j,k} \right\}$$

and, because \hat{H} determines the ground-state energy and wavefunction 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 \hat{H} and \hat{H}' , respectively, to solve for a ground state produce E_0 , $\Psi(\mathbf{r})$ and E'_0 , $\Psi'(\mathbf{r})$ that have the same one-electron density: $\int |\Psi|^2 dr_2 dr_3 \dots dr_N = \rho(\mathbf{r}) = \int |\Psi'|^2 dr_2 dr_3 \dots dr_N$.
- (c) If we think of Ψ' as trial variational wavefunction for the Hamiltonian \hat{H} , we know that

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \int \rho(\mathbf{r}) [V(\mathbf{r}) - V'(\mathbf{r})] d^3r = E'_0 + \int \rho(\mathbf{r}) [V(\mathbf{r}) - V'(\mathbf{r})] d^3r.$$

(d) Similarly, taking Ψ 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 \hat{H} , and therefore Ψ and E_0 . Furthermore, because Ψ determines all the 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 ρ ?

The main difficulty with DFTs 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* ρ (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 $(-\hbar^2/2m_e)\nabla^2$ 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

$$E = (\hbar^2/8m_e L^2)(n_x^2 + n_y^2 + n_z^2)$$

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 and 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 $E = (\hbar^2/2m_e L^2)R^2$ is one-eighth the volume of the sphere of radius R :

$$\Phi(E) = \frac{1}{8}(4\pi/3)R^3 = (\pi/6)(8m_e L^2 E / \hbar^2)^{3/2}.$$

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

$$g(E) = d\Phi/dE = (\pi/4)(8m_e L^2 / \hbar^2)^{3/2} E^{1/2}.$$

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

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

The total number of electrons N can be expressed as

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

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 a molecule is approximated using the above type 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:

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

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:

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

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 ρ) which depends only on $\rho(\mathbf{r})$ at the 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 the exchange energy and the correlation energy; moreover, the kinetic energy is treated only in the approximate manner described.

In the book by Parr and Yang [67], 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*:

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

with $C_x = (3/4)(3/\pi)^{1/3} = 0.7386$ in atomic units. Adding this exchange energy to the Thomas–Fermi total energy $E_{0,\text{TF}}[\rho]$ 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 $E_{\text{ex,Dirac}}$ are needed. One of the more commonly used so-called *gradient-corrected* approximations is that invented by Becke [68], and referred to as the Becke88 exchange functional:

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

where $x = \rho^{-4/3}|\nabla\rho|$, and γ 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 γ to equal 0.0042). A common gradient correction to the earlier $T[\rho]$ is called the Weizsacker correction and is given by

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

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 ρ . Kohn and Sham [69] (KS) introduced a set of so-called KS orbitals obeying the following equation:

$$\left\{ -(\hbar^2/2m_e)\nabla^2 + V(\mathbf{r}) + e^2/2 \int \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + U_{xc}(\mathbf{r}) \right\} \phi_j = \varepsilon_j \phi_j$$

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 $\{\phi_j\}$ could be used to compute the density ρ by simply adding up the orbital densities multiplied by orbital occupancies n_j :

$$\rho(\mathbf{r}) = \sum_j n_j |\phi_j(\mathbf{r})|^2.$$

Here $n_j = 0, 1$ or 2 is the occupation number of the orbital ϕ_j in the state being studied. The kinetic energy should be calculated as

$$T = \sum_j n_j \langle \phi_j(\mathbf{r}) | -(\hbar^2/2m_e)\nabla^2 | \phi_j(\mathbf{r}) \rangle.$$

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 *function* of the electron density ρ of the system, but only in two limiting cases—the high-density limit (large ρ) 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 ρ . Therefore, much work has been devoted to creating efficient and accurate interpolation formulae connecting the low- and high-density uniform electron gas expressions (see appendix E in [67] for further details). One such expression is

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

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 $\frac{4}{3}\pi r_s^3$ is equal to $1/\rho$; 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 [68]. 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 AO 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 $C_{j,a}$: $\phi_j = \sum_a C_{j,a} \chi_a$.
- (3) The density is computed as $\rho(\mathbf{r}) = \sum_j n_j |\phi_j(\mathbf{r})|^2$. Often, $\rho(\mathbf{r})$ is expanded in an AO basis, which need not be the same as the basis used for the ϕ_j , and the expansion coefficients of ρ are computed in terms of those of the ϕ_j . It is also common to use an AO 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 $\{-1/2\nabla^2 + V(\mathbf{r}) + e^2/2 \int \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + U_{xc}(\mathbf{r})\}$ whose 'new' eigenfunctions $\{\phi_j\}$ and eigenvalues $\{\varepsilon_j\}$ are found by solving the KS equations.
- (5) These new ϕ_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 ϕ_j used to determine the current iteration's ρ are the same ϕ_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

$$E[\rho] = \sum_j n_j \langle \phi_j(\mathbf{r}) | -(\hbar^2/2m_e)\nabla^2 | \phi_j(\mathbf{r}) \rangle + \int V(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + e^2/2 \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho].$$

In closing this section, it should once again be emphasized that this area is currently undergoing explosive growth and much scrutiny [70]. 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 DFTs 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 [71] with the basis set size than for conventional (MCSCF, CI, etc) methods, density functional methods offer great promise and are likely to contribute much to quantum chemistry in the next decade.

(f) *Efficient and widely distributed computer programs exist for carrying out electronic structure calculations*

The development of electronic structure theory has been ongoing since the 1940s. At first, only a few scientists had access to computers, and they began to develop numerical methods for solving the requisite equations (e.g. the HF equations for orbitals and orbital energies, the configuration interaction equations for electronic state energies and wavefunctions). By the late 1960s, several research groups had developed reasonably efficient computer codes (written primarily in Fortran with selected subroutines that needed to be written especially efficiently in machine language), and the explosive expansion of this discipline was underway. By the 1980s and through the 1990s, these electronic structure programs began to be used by practicing 'bench chemists' both because they became easier to use and because their efficiency and the computers' speed grew to the point where modest to large molecules could be studied.

Web page links [72] to many of the more widely used programs offer convenient access. At present, more electronic structure calculations are performed by non-theorists than by practicing theoretical chemists, largely because of the proliferation of such programs. This does not mean that all that needs to be done in electronic structure theory is done. The rates at which improvements are being made in the numerical algorithms used to solve the problems as well as at which new models are being created remain as high as ever. For example, Professor Rich Friesner [73] has developed and Professor Emily Carter [74] has implemented, for correlated methods, a highly efficient way to replace the list of two-electron integrals $(\phi_i\phi_j|1/r_{1,2}|\phi_k\phi_l)$, which number N^4 , where N is the number of AO basis functions, by a much smaller list $(\phi_i\phi_j|g)$ from which the original integrals can be rewritten as

$$(\phi_i\phi_j|1/r_{1,2}|\phi_k\phi_l) = \sum_g (\phi_i(g)\phi_j(g)) \int d\mathbf{r} \phi_k(\mathbf{r})\phi_l(\mathbf{r})/|\mathbf{r} - \mathbf{g}|.$$

This tool, which they call *pseudospectral methods*, promises to reduce the CPU, memory and disk storage requirements for many electronic structure calculations, thus permitting their application to much larger molecular systems. In addition to ongoing developments in the underlying theory and computer implementation, the range of phenomena and the kinds of physical properties that one needs electronic structure theory to address is growing rapidly. There is every reason to believe that this sub-discipline of theoretical chemistry is continuing to blossom.

B3.1.6.2 Computational requirements, strengths and weaknesses of various methods

(a) Computational steps

Essentially all of the techniques discussed above require the evaluation of one- and two-electron integrals over the N AO basis functions: $\langle \chi_a | \hat{f} | \chi_b \rangle$ and $\langle \chi_a \chi_b | \hat{g} | \chi_c \chi_d \rangle$. As mentioned earlier, there are of the order of $N^4/8$ such two-electron integrals that must be computed (and perhaps stored on disk); their computation and storage is a major consideration in performing conventional *ab initio* calculations. Much current research is being devoted to reducing the number of such integrals that must be evaluated using either the pseudo-spectral methods discussed earlier or methods that approximate integrals between product distributions (one such distribution is $\chi_a \chi_c$ and another is $\chi_b \chi_d$ when the integral $\langle \chi_a \chi_b | \hat{g} | \chi_c \chi_d \rangle$ is treated) whenever the distributions involve orbitals on sites that are distant from one another.

Another step that is common to most, if not all, approaches that compute orbitals of one form or another is the solution of matrix eigenvalue problems of the form

$$\sum_v F_{\mu,v} C_{v,i} = \varepsilon_i \sum_v S_{\mu,v} C_{v,i}.$$

The solution of any such eigenvalue problem requires a number of computer operations that scales as the dimension of the $F_{\mu,n}$ matrix to the third power. Since the indices on the $F_{\mu,n}$ matrix label AOs, this means that the task of finding all eigenvalues and eigenvectors scales as the cube of the number of AOs (N^3).

The DFT approaches involve basis expansions of orbitals $\phi_i = \sum_v C_{i,v} \chi_v$ and of the density ρ (or various fractional powers of ρ), which is a quadratic function of the orbitals ($\rho = \sum_i n_i |\phi_i|^2$). These steps require computational effort scaling only as N^2 , which is one of the most important advantages of these schemes. No cumbersome large CSF expansion and associated large secular eigenvalue problem arise, which is another advantage.

The more conventional quantum chemistry methods provide their working equations and energy expressions in terms of one- and two-electron integrals over the final MOs: $\langle \phi_i | \hat{f} | \phi_j \rangle$ and $\langle \phi_i \phi_j | \hat{g} | \phi_k \phi_l \rangle$. The MO-based integrals can only be evaluated by *transforming* the AO-based integrals [55]. Clearly, the N^5 scaling of the integral transformation process makes it an even more time-consuming step than the (N^4) atomic integral evaluation and a severe *bottleneck* to applying *ab initio* methods to larger systems. Much effort has been devoted to expressing the working equations of various correlated methods in a manner that does not involve the fully-transformed MO-based integrals.

Once the requisite one- and two-electron integrals are available in the MO 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 are to be determined.

The *number of configurations* (N_C) varies greatly among the methods and is an important factor to keep in mind. Under certain circumstances (e.g. when studying 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 a 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 $\sum_J H_{I,J} C_J = E C_I$ 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 H₂O might be distributed, in a manner that gives $M_S = 0$, among six valence orbitals (e.g. two lone-pair orbitals, two OH

σ -bonding orbitals and two OH σ^* -antibonding orbitals). The number of configurations thereby created is 225. If the same eight electrons were distributed among ten valence orbitals 44 100 configurations result; for 20 and 30 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.

(b) *Variational methods provide upper bounds to energies*

Methods that are based on making the functional $\langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$ stationary yield *upper bounds* to the lowest energy state having the symmetry of the CSFs in Ψ . The CI and MCSCF methods are of this type. They also provide approximate excited-state energies and wavefunctions in the form of other solutions of the secular equation [75] $\sum_J H_{I,J} C_J = E C_I$. Excited-state energies obtained in this manner obey the so-called *bracketing theorem*; that is, between any two approximate energies obtained in the variational calculation, there exists at least one true eigenvalue. 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.

(c) *Variational methods are not size-extensive*

Variational techniques suffer from a serious drawback, however: they are not necessarily *size extensive* [76]. The energy computed using these tools cannot be trusted to scale with the size of the system. For example, a calculation performed on two CH₃ 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 CH₃ species. Lack of size extensivity precludes these methods from use in extended systems (e.g. polymers and solids) where errors due to improper size scaling of the energy produce nonsensical results.

By carefully adjusting the variational wavefunction used, it is *possible* to circumvent size-extensivity problems for selected species. For example, the CI calculation on Be₂ using all $^1 \sum_g$ CSFs formed by placing the four valence electrons into the $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals 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 CAS-space MCSCF or CI calculations [77] are size extensive, but it is impractical to extend such an approach to larger systems.

(d) *Most perturbation and CC methods are size-extensive, but do not provide upper bounds and they assume that one CSF dominates*

In contrast to variational methods, perturbation theory and CC methods achieve their energies by projecting the Schrödinger equation against a reference function $\langle \Phi |$ to obtain [78] a *transition formula* $\langle \Phi | \hat{H} | \Psi \rangle$, rather than from an expectation value $\langle \Psi | \hat{H} | \Psi \rangle$. It can be shown that this difference allows non-variational techniques to yield size-extensive energies.

This can be seen by considering the second-order MPPT energy of two non-interacting Be atoms. The reference CSF is $\Phi = |1s_a^2 2s_a^2 1s_b^2 2s_b^2|$; as discussed earlier, only doubly-excited CSFs contribute to the correlation energy through second order. These ‘excitations’ can involve atom a, atom b, or both atoms. However, 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 to one- and two-electron integrals over orbitals on both atoms (e.g. $\langle 2s_a 2p_a | \hat{g} | 2s_b 2p_b \rangle$) that vanish if the atoms are far apart, so contributions due to such CSFs vanish. Hence, only CSFs that are excited on one or the other atom contribute to the energy. This, in turn, results in a second-order energy that is additive as required by any size-extensive method. In general, a method will be size extensive *if* its energy formula is additive *and* the equations that determine the C_J amplitudes are themselves separable. The MPPT/MBPT and CC methods possess these characteristics.

However, size-extensive methods have two serious weaknesses. 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). Moreover, they express the correct wavefunction in terms of corrections to a (presumed dominant) reference function which is usually taken to be a single CSF (although efforts have been made to extend the MPPT/MBPT and CC methods to allow for multiconfigurational reference functions, this is not yet standard practice). For situations in which two CSFs ‘cross’ along a reaction path, the single-dominant-CSF assumption breaks down, and these methods can have difficulty.

B3.1.7 There are methods that calculate energy differences rather than energies

In addition to the myriad of methods discussed above for treating the energies and wavefunctions as solutions to the electronic Schrödinger equation, there exists a family of tools that allow one to compute energy differences ‘directly’ rather than by first finding the energies of pairs of states and subsequently subtracting them. Various energy differences can be so computed: differences between two electronic states of the same molecule (i.e. electronic excitation energies ΔE), differences between energy states of a molecule and the cation or anion formed by removing or adding an electron (i.e. IPs and EAs).

Because of space limitations, we will not be able to elaborate much further on these methods. However, it is important to stress that:

- (1) these so-called *Greens function* or *propagator* methods [71] utilize essentially the same input information (e.g. AO basis sets) and perform many of the same computational steps (e.g. evaluation of one- and two-electron integrals, formation of a set of mean-field MOs, transformation of integrals to the MO basis, etc) as do the other techniques discussed earlier;
- (2) these methods are now rather routinely used when ΔE , IP, or EA information is sought. In fact, the 1998 version of the Gaussian program includes an electron propagator option.

The basic ideas underlying most, if not all, of the energy-difference methods follow

- (1) One forms a *reference wavefunction* Ψ (this can be of the SCF, MPn, CC, etc variety); the energy differences are computed relative to the energy of this function.
- (2) One expresses the *final-state wavefunction* Ψ' (i.e. describing the excited, cation, or anion state) in terms of an operator Ω acting on the reference Ψ : $\Psi' = \Omega\Psi$. Clearly, the Ω operator must be one that removes or adds an electron when one is attempting to compute IPs or EAs, respectively.
- (3) One writes equations which Ψ and Ψ' are expected to obey. For example, in the early development of these methods [80], the Schrödinger equation itself was assumed to be obeyed, so $\hat{H}\Psi = E\Psi$ and $\hat{H}'\Psi' = E'\Psi'$ are the two equations (note that, in the IP and EA cases, the latter equation, and the associated Hamiltonian \hat{H}' , refer to one fewer and one more electrons than does the reference equation $\hat{H}\Psi = E\Psi$).
- (4) One combines $\Omega\Psi = \Psi'$ with the equations that Ψ and Ψ' obey to obtain an equation that Ω must obey. In the above example, one: (a) uses $\Omega\Psi = \Psi'$ in the Schrödinger equation for Ψ' , (b) allows Ω to act from the left on the Schrödinger equation for Ψ and (c) subtracts the resulting two equations to achieve $(\hat{H}'\hat{\Omega} - \hat{\Omega}\hat{H})\Psi = (E' - E)\Omega\Psi$ or, in commutator form $[\hat{H}', \hat{\Omega}]\Psi = \Delta E\hat{\Omega}\Psi$. By expressing the Hamiltonian in the second-quantization form, only one \hat{H} appears in this final so-called *equation of motion* (EOM) $[\hat{H}, \hat{\Omega}]\Psi = \Delta E\hat{\Omega}\Psi$ (i.e. in the second-quantized form, \hat{H}' and \hat{H} are one and the same).
- (5) One can, for example, express Ψ in terms of a superposition of configurations $\Psi = \sum_J C_J \Phi_J$ whose amplitudes C_J have been determined from an MCSCF, CI or MPn calculation and express Ω in terms of second-quantization operators $\{O_K\}$ that cause single-, double-, etc, level excitations (for the IP (EA) cases, Ω is given in terms of operators that remove (add), remove and singly excite (add and singly excite) electrons): $\Omega = \sum_K D_K \hat{O}_K$.

- (6) Substituting the expansions for Ψ and for $\hat{\Omega}$ into the EOM $[H, \hat{\Omega}]\Psi = \Delta E \hat{\Omega}\Psi$, and then projecting the resulting equation on the left against a set of functions (e.g. $\{\hat{O}_{K'}|\Psi\rangle\}$ or $\{\hat{O}_{K'}|\Phi_0\rangle\}$, where Φ_0 is the dominant component of Ψ), gives a matrix eigenvalue–eigenvector equation:

$$\sum_K \langle \hat{O}_{K'}\Psi | [\hat{H}, \hat{O}_K]\Psi \rangle D_K = \Delta E \sum_K \langle \hat{O}_{K'}\Psi | \hat{O}_K \Psi \rangle \hat{D}_K$$

to be solved for the \hat{D}_K operator coefficients and the excitation energies ΔE . Such are the working equations of the EOM (or Greens function or propagator) methods.

In recent years, these methods have been greatly expanded and have reached a degree of reliability where they now offer some of the most accurate tools for studying excited and ionized states. In particular, the use of time-dependent variational principles have allowed the much more rigorous development of equations for energy differences and nonlinear response properties [81]. In addition, the extension of the EOM theory to include coupled-cluster reference functions [82] now allows one to compute excitation and ionization energies using some of the most accurate *ab initio* tools.

B3.1.8 Summary of *ab initio* methods

At this time, it may not be 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-, CC- or CAS-based MCSCF are preferred. Moreover, many chemical reactions and bond-breaking events require two or more ‘essential’ electronic configurations. For them, single-configuration-based methods such as conventional CC and MBTP/MPPT should be used only with caution; MCSCF or CI calculations are preferred. Very large molecules, in which thousands of AO basis functions are required, may be impossible to treat by methods whose effort scales as N^4 or higher; density functional methods would be the only choice then.

For all calculations, the choice of AO basis set must be made carefully, keeping in mind the N^4 scaling of the 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 a dynamic correlation increases rapidly. For example, many 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 (the latter being to find all eigenvalues and vectors), a dependence as strong as $n_e^6 N^6$ 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 100–5000 CSFs are routinely performed and calculations using even several billion CSFs are possible [53].

Some of the most significant advances that have been made recently in expanding the applicability of the *ab initio* methods to larger systems are based on recognizing that many of the two-electron integrals and one- and two-electron density matrix elements arising in the pertinent working equations vanish if expressed in terms of localized (atomic or molecular) orbitals. For example, in a polymer consisting of P monomer units (or a crystal composed of P unit cells), the integrals and density matrix elements indexed by monomer units far distant from one another are negligible. Thus, if a method whose effort scales as the k th power of the number of AOs (N) per monomer (or unit cell) is applied to a system having P units, the effort should

Table B3.1.2. Properties of commonly used methods.

Method	Variational/size extensive	Computational scaling
HF	Yes/Yes	N^4 integrals; N^3 eigenvalues; P^1
GVB	Yes/Yes	N^4 integrals N^4 (per electron pair) GVB equations
DFT	No/Yes	N^3 eigenvalues; N^2 integrals; P^1 N^3 orbital orthogonalization; P^1
MP2	No/Yes	N^5 ; P^2
CI	Yes/No	N^5 transformed integrals; N_C^2 to solve for <i>one</i> CI energy and eigenvector
CISD	Yes/No	N^5 transformed integrals; $n^2 N^4$ to solve for one CI energy and eigenvector
CAS-MCSCF	Yes/Yes	N^5 transformed integrals; N_C^2 to solve for CI energy; many iterations also needed
CCS	No/Yes	N^4
CCSD	No/Yes	N^6
CCSDT	No/Yes	N^8
CCSD(T)	No/Yes	N^7

N is the number of atomic basis functions, which usually is proportional to the number of electrons n . N_C is the number of configurations; in CI calculations, N_C is usually at least as large as the number of electrons squared times the number of orbitals squared $n_e^2 N^2$; in MCSCF calculations, N_C is usually much smaller than $n_e^2 N^2$. P is explained in section B3.1.8.

not scale as $(PN)^k$ but, hopefully, as PN^k . Indeed, for the DFT ($k = 3$), SCF ($k = 4$) and MP2 ($k = 5$) methods, specialized techniques [50] have allowed for the implementation of codes scaling linearly (or nearly so for MP2) with the system ‘size’ P (i.e. the number of units).

Other methods, most of which can be viewed as derivatives of the techniques introduced above, have been and are still being developed; stimulated by the explosive growth in computer power and changes in computer architecture realized in recent years. All indications are that this growth pattern will continue; so *ab initio* quantum chemistry is likely to have an even larger impact on future chemistry research and education (through new insights and concepts). For many of the most commonly employed *ab initio* quantum chemistry tools, the computational efforts, as characterized by how they scale with the system size P (i.e. the number of units), with basis set size N and with the number of electronic configurations N_C , as well their variational nature and size extensivity are summarized in table B3.1.2.

Figure B3.1.9 [83] displays the errors (in picometres compared to experimental findings) in the equilibrium bond lengths for a series of 28 molecules obtained at the HF, MP2-4, CCSD, CCSD(T), and CISD levels of theory using three polarized correlation-consistent basis sets (valence DZ through to QZ).

Clearly, the HF method, independent of basis, systematically underestimates the bond lengths over a broad percentage range. The CISD method is neither systematic nor narrowly distributed in its errors, but the MP2 and MP4 (but not MP3) methods are reasonably accurate and have narrow error distributions if valence TZ or QZ bases are used. The CCSD(T), but not the CCSD, method can be quite reliable if valence TZ or QZ bases are used.

In closing this section and this chapter, I wish to remind the reader that my discussion has been limited to *ab initio* techniques; that is, to methods that begin with the electronic Schrödinger equation attempt to solve it without explicitly introducing any experimental data or any numerical results from another calculation. There exists a whole family of alternative approaches called *semi-empirical methods* [84] in which (a) overlaps between pairs of orbitals distant from one another are neglected, (b) many of the two-electron

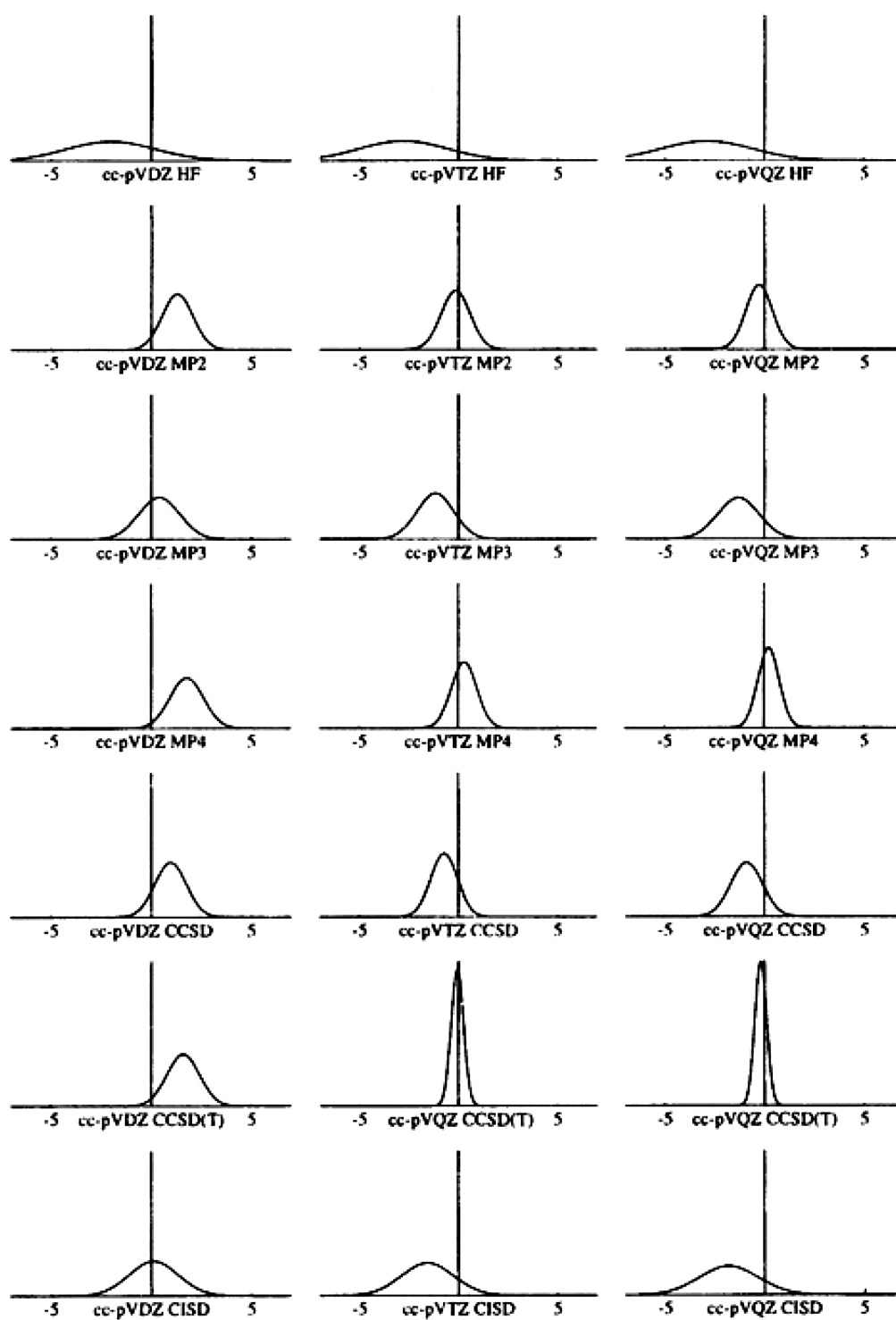


Figure B3.1.9. Distribution in errors (picometres) in calculated bond lengths for 28 test molecules.

integrals appearing in *ab initio* methods are neglected (because they are ‘small’ in some sense) and (c) certain combinations of one- and two-electron integrals that can be (approximately) related to orbital energies of a constituent atom are not computed explicitly but are replaced by experimental data (or data from an *ab initio* calculation) on that atom. Interested readers in these approaches to electronic structure are referred to the articles given in [84].

References

- [1] Born M and Oppenheimer J R 1927 *Ann. Phys., Lpz* **84** 457
It was then used within early quantum chemistry in the following references:
Kolos W and Wolniewicz L 1968 Improved theoretical ground-state energy of the hydrogen molecule *J. Chem. Phys.* **49** 404–10
Pack R T and Hirschfelder J O 1968 Separation of rotational coordinates from the *N*-electron diatomic Schrödinger equation *J. Chem. Phys.* **49** 4009
Pack R T and Hirschfelder J O 1970 Energy corrections to the Born–Oppenheimer approximation. The best adiabatic approximation *J. Chem. Phys.* **52** 521–34
- [2] Schlegel H B 1995 *Modern Electronic Structure Theory* ed D R Yarkony (Singapore: World Scientific) ch 8
- [3] Chalasinski G, Kendall R A, Taylor H and Simons J 1988 Propensity rules for vibration–rotation induced electron detachment of diatomic anions: application to $\text{NH}^- \rightarrow \text{NH} + e^-$ *J. Phys. Chem.* **92** 3086–91
- [4] Early treatments of molecules in which non-Born–Oppenheimer terms were included were made in:
Kolos W and Wolniewicz L 1963 Nonadiabatic theory for diatomic molecules and its application to the hydrogen molecule *Rev. Mod. Phys.* **35** 473–83
Kolos W and Wolniewicz L 1964 *J. Chem. Phys.* **41** 3663
Kolos W and Wolniewicz L 1964 *J. Chem. Phys.* **41** 3674
Kolos W and Wolniewicz L 1965 Potential energy curves for the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, and $C^1\Pi_u$ states of the hydrogen molecule *J. Chem. Phys.* **43** 2429–41
Some of the work my students and I have done in this area can be found in:
Simons J 1981 Propensity rules for vibration-induced electron detachment of anions *J. Am. Chem. Soc.* **103** 3971–6
Acharya P K, Kendall R A and Simons J 1984 Vibration-induced electron detachment in molecular anions *J. Am. Chem. Soc.* **106** 3402–7
Acharya P K, Kendall R A and Simons J 1985 Associative electron detachment: $\text{O}^- + \text{H} \rightarrow \text{OH} + e^-$ *J. Chem. Phys.* **83** 3888–93
O’Neal D and Simons J 1989 Vibration-induced electron detachment in acetaldehydeenolate anion *J. Phys. Chem.* **93** 58–61
Simons J 1989 Modified rotationally adiabatic model for rotational autoionization of dipole-bound molecular anion *J. Chem. Phys.* **91** 6858–68
- [5] Ohrn Y 2000 The Quantum Theory Project at the University of Florida webpage <http://www.qtp.ufl.edu/~ohrn/>
- [6] Yarkony D 2000 webpage <http://jhuniverse.jhu.edu/~chem/yarkony.html>
For a good recent overview of some of his work, see:
Yarkony D R 1995 Electronic structure aspects of nonadiabatic processes in polyatomic systems *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 642–721
- [7] Simons J 1983 *Energetic Principles of Chemical Reactions* (Boston, MA: Jones and Bartlett)
- [8] Schlegel B 2000 webpage <http://www.science.wayne.edu/~chem/schlegel.html>
For a good recent overview see:
Schlegel H B 1995 Geometry optimization on potential energy surfaces *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 459–500
Strategies for ‘walking’ on potential energy surfaces are overviewed by
Schlegel H B 1987 Optimization of equilibrium geometries and transition structures *Adv. Chem. Phys.* **67** 249–86
My own coworkers and I have also contributed to finding transition states, in particular. See, for example:
Simons J, Jørgensen P, Taylor H and Ozment J 1983 Walking on potential energy surfaces *J. Phys. Chem.* **87** 2745–53
Nichols J A, Taylor H, Schmidt P P and Simons J 1990 Walking on potential energy surfaces *J. Chem. Phys.* **92** 340–6
Simons J and Nichols J 1990 Strategies for walking on potential energy surfaces using local quadratic approximations *Int. J. Quant. Chem. S* **24** 263–76
- [9] Pulay P 1995 Analytical derivative techniques and the calculation of vibrational spectra *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 1191–240
Much of the early work is described in:
Pulay P 1977 Direct use of the gradient for investigating molecular energy surfaces *Modern Theoretical Chemistry* vol 4, ed H F III Schaefer (New York: Plenum) pp 53–185
One of the earliest applications to molecular structure is given in:

- Thomsen K and Swanstrøm P 1973 Calculation of molecular one-electron properties using coupled Hartree–Fock methods I. Computational scheme *Mol. Phys.* **26** 735–50
- More recent contributions are summarized in:
- Jørgensen P and Simons J (eds) 1986 *Geometrical Derivatives of Energy Surfaces and Molecular Properties* (Boston, MA: Reidel)
- Pulay P 1987 Analytical derivative methods in quantum chemistry *Advances in Chemical Physics* vol LXIX, ed K P Lawley (New York: Wiley–Interscience) pp 241–86
- Helgaker T and Jørgensen P 1988 Analytical calculation of geometrical derivatives in molecular electronic structure theory *Adv. Quantum Chem.* **19** 183–245
- [10] The dipole moment is discussed in:
- Karplus M and Porter R N 1970 *Atoms and Molecules* (New York: Benjamin)
- [11] Atkins P W 1992 *The Elements of Physical Chemistry* (New York: Freeman)
- Berry R S, Rice S A and Ross J 1980 *Physical Chemistry* (New York: Wiley)
- and also webpage www.whfreeman.com/chem/index.html
- [12] Levine I N 1991 *Quantum Chemistry* 4th edn (Englewood Cliffs, NJ: Prentice-Hall)
- McQuarrie D A 1983 *Quantum Chemistry* (Mill Valley, CA: University Science)
- Simons J and Nichols J 1997 *Quantum Mechanics in Chemistry* (New York: Oxford University Press)
- Atkins P W and Friedman R S 1997 *Molecular Quantum Mechanics* 3rd edn (Oxford: Oxford University Press)
- Szabo A and Ostlund N S 1989 *Modern Quantum Chemistry* 1st edn (revised) (New York: McGraw-Hill)
- and also webpage <http://www.emsl.pnl.gov:2080/docs/tms/quantummechanics/>
- [13] For a good recent overview, see:
- Olsen J and Jørgensen P 1995 Time-dependent response theory with applications to self-consistent field and multiconfigurational self-consistent field wave functions *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 857–990
- An earlier introduction of molecular properties in terms of wavefunctions and energies and their responses to externally applied fields is given in:
- Jørgensen P and Simons J 1981 *Second Quantization-Based Methods in Quantum Chemistry* (New York: Academic)
- Jørgensen P and Simons J (eds) 1986 *Geometrical Derivatives of Energy Surfaces and Molecular Properties* (Boston, MA: Reidel)
- Amos R D 1987 Molecular property derivatives *Advances in Chemical Physics* vol LXVII, ed K P Lawley, pp 99–153
- [14] Head-Gordon M 1996 Quantum chemistry and molecular processes *J. Phys. Chem.* **100** 13 213–25
- [15] Schaefer H F III, Thomas J R, Yamaguchi Y, DeLeeuw B J and Vacek G 1995 The chemical applicability of standard methods in *ab initio* molecular quantum mechanics *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 3–54
- Schaefer F 2000 webpage <http://zopyros.ccqc.uga.edu/>
- [16] Simons J 1991 An experimental chemist's guide to *ab initio* quantum chemistry *J. Phys. Chem.* **95** 1017–29
- [17] Levy H A and Danford M D 1964 *Molten Salt Chemistry* ed M Blander (New York: Interscience)
- Bredig M A 1969 *Molten Salts* ed G M Mamantov (New York: Dekker)
- [18] See, for example:
- Synge J L and Griffith B A 1949 *Principles of Mechanics* (New York: McGraw-Hill)
- [19] Berry R S, Rice S A and Ross J 1980 *Physical Chemistry* (New York: Wiley) section 11.9
- [20] One of the earliest uses of this term was offered by:
- Sinanoglu O 1961 Many-electron theory of atoms and molecules *Proc. US Natl Acad. Sci.* **47** 1217–26
- [21] Sinanoglu O 1962 Many-electron theory of atoms and molecules I. Shells, electron pairs vs many-electron correlations *J. Chem. Phys.* **36** 706–17
- [22] Helgaker T, Jørgensen P and Olsen J 1999 *Electronic Structure Theory* (New York: Wiley)
- [23] Hylleraas E A 1963 Reminiscences from early quantum mechanics of two-electron atoms *Rev. Mod. Phys.* **35** 421–31
- [24] Pilar F L 1968 *Elementary Quantum Chemistry* (New York: McGraw-Hill) section 11.5
- [25] Löwdin P O 1959 Correlation problem in many-electron quantum mechanics *Adv. Chem. Phys.* **2** 207–32
- [26] Excellent early overviews of many of these methods are included in:
- Schaefer H F III (ed) 1977 *Modern Theoretical Chemistry* vol 3 (New York: Plenum)
- Schaefer H F III (ed) 1977 *Modern Theoretical Chemistry* vol 4 (New York: Plenum)
- Lawley K P (ed) 1987 *Advances in Chemical Physics* vol LXVII (New York: Wiley–Interscience)
- Lawley K P (ed) 1987 *Advances in Chemical Physics* vol LXIX (New York: Wiley–Interscience)
- Yarkony D R (ed) 1995 *Modern Electronic Structure Theory* (Singapore: World Scientific)
- [27] Simons J 1983 *Energetic Principles of Chemical Reactions* (Boston, MA: Jones and Bartlett) p 129
- [28] Goddard W A III 2000 webpage <http://www.caltech.edu/~chemistry/Faculties/Goddard.html>
- When most quantum chemists were pursuing improvements in the molecular orbital method, he returned to the valence bond theory and developed the so-called GVB methods that allow electron correlation to be included within a valence bond framework
- [29] See, for example:
- Goddard W A III and Harding L B 1978 The description of chemical bonding from *ab initio* calculation *Ann. Rev. Phys. Chem.* **29** 363–96

- [30] The classic papers in which the SCF equations for closed- and open-shell systems are treated are:
Roothaan C C J 1951 New developments in molecular orbital theory *Rev. Mod. Phys.* **23** 69–89
Roothaan C C J 1960 Self-consistent field theory for open shells of electronic systems *Rev. Mod. Phys.* **32** 179–85
- [31] The original works by the Hartree father and son team appear in:
Hartree D R 1928 The wave mechanics of an atom with a non-Coulomb central field. Part III. Term values and intensities in series in optical spectra *Proc. Camb. Phil. Soc.* **24** 426–37
Hartree D R, Hartree W and Swirles B 1940 Self-consistent field including exchange and superposition of configurations with some results for oxygen *Phil. Trans. R. Soc. A* **238** 229–47
The work of Fock is given in:
Fock V 1930 *Z. Phys.* **61** 126
- [32] Frisch M J *et al* 1995 *Gaussian 94* Revision A.1 (Pittsburgh, PA: Gaussian)
- [33] Pople J 2000 webpage <http://www.chem.nwu.edu/brochure/pople.html>
Pople made many developments leading to the suite of Gaussian computer codes that now constitute the most widely used electronic structure computer programs
- [34] Froese-Fischer C 1970 A multi-configuration Hartree–Fock program *Comput. Phys. Commun.* **1** 151–66
- [35] McCullough E A Jr 1975 The partial-wave self-consistent method for diatomic molecules computational formalism and results for small molecules *J. Chem. Phys.* **62** 3991–9
Christiansen P A and McCullough E A Jr 1977 Numerical Hartree–Fock calculations for N₂, FH, and CO comparison with optimized LCAO results *J. Chem. Phys.* **67** 1877–82
- [36] Mulliken Prof. R S University of Chicago. He is the person who came up with the phrase ‘molecular orbital’ and the concepts behind it
- [37] Jordan Prof. K 2000 webpage <http://www.chem.pitt.edu/~jordan/index.html>
Jordan compared the use of plane wave and conventional Gaussian basis orbitals within density functional calculations in:
Nachtigall P, Jordan K D, Smith A and Jönsson H 1996 Investigation of the reliability of density functional methods reaction and activation energies for Si–Si bond cleavage and H₂ elimination from silanes *J. Chem. Phys.* **104** 148–58
- [38] Dunning T H Jr 1970 Gaussian basis functions for use in molecular calculations I. Contraction of (9s 5p) atomic basis sets for the first-row atoms *J. Chem. Phys.* **53** 2823–33
Dunning T H Jr and Hay P J 1977 Gaussian basis sets for molecular calculations *Methods of Electronic Structure Theory* vol 3, ed H F III Schaefer (New York: Plenum) pp 1–27
- [39] Huzinaga S 1965 Gaussian-type functions for polyatomic system I. *J. Chem. Phys.* **42** 1293–1302
- [40] Schmidt M W and Ruedenberg K 1979 Effective convergence to complete orbital bases and to the atomic Hartree–Fock limit through systematic sequences of Gaussian primitives *J. Chem. Phys.* **71** 3951–62
- [41] Hehre W J, Stewart R F and Pople J A 1969 Self-consistent molecular-orbital method I. Use of Gaussian expansions of Slater-type atomic orbitals *J. Chem. Phys.* **51** 2657–64
- [42] Ditchfield R, Hehre W J and Pople J A 1971 Self-consistent molecular-orbital methods IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules *J. Chem. Phys.* **54** 724–8
Hehre W J, Ditchfield R and Pople J A 1972 Self-consistent molecular-orbital methods XII. Further extension of Gaussian-type basis sets for use in molecular orbital studies of organic molecules *J. Chem. Phys.* **56** 2257–61
Hariharan P C and Pople J A 1973 The influence of polarization functions on molecular orbital hydrogenation energies *Theoret. Chim. Acta.* **28** 213–22
Krishnan R, Binkley J S, Seeger R and Pople J A 1980 Self-consistent molecular orbital methods XX. A basis set for correlated wave functions *J. Chem. Phys.* **72** 650–4
- [43] Helgaker T and Taylor P R 1995 Gaussian basis sets and molecular integrals *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) section 5.4, pp 725–856
- [44] Helgaker T and Taylor P R 1995 Gaussian basis sets and molecular integrals *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) section 5.3, pp 725–856
- [45] Pacific Northwest National Laboratories 2000 webpage www.emsl.pnl.gov:2080/forms/basisform.html
- [46] Hunt W J and Goddard W A III 1969 Excited states of H₂O using improved virtual orbitals *Chem. Phys. Lett.* **3** 414–18
- [47] von Koopmans T 1934 Über die zuordnung von wellenfunktionen und eigenwerten zu den einzelnen elektronen eines atoms *Physica* **1** 104–13
- [48] Some of the integral packages and the techniques used to evaluate the integrals are described in:
Csizmadia I G, Harrison M C, Moscovitz J W and Sutcliffe B T 1966 Commentationes. Non-empirical LCAO–MO–SCF–CI calculations on organic molecules with Gaussian type functions. Part I. Introductory review and mathematical formalism *Theoret. Chim. Acta* **6** 191–216
Clementi E and Davis D R 1967 Electronic structure of large molecular systems *J. Comp. Phys.* **1** 223–44
Rothenberg S, Kollman P, Schwartz M E, Hays E F and Allen L C 1970 Mole. A system for quantum chemistry I. General description *Int. J. Quantum Chem.* **S 3** 715–25
Hehre W J, Lathan W A, Ditchfield R, Newton M D and Pople J A 1971 *Program No 236* (Bloomington, IN: Quantum Chemistry Program Exchange)
Dupuis M, Rys J and King H F 1976 Evaluation of molecular integrals over Gaussian basis functions *J. Chem. Phys.* **65** 111–16

- McMurchie L E and Davidson E R 1978 One- and two-electron integrals over Cartesian Gaussian functions *J. Comp. Phys.* **26** 218–31
- Gill P M W 1994 Molecular integrals over Gaussian basis functions *Adv. Quantum Chem.* **25** 141–205
- [49] This concept of 'direct' calculations in which integrals are not stored but used 'on the fly' is discussed in:
Almlöf J, Faegri K and Korsell K 1982 Principles for a direct SCF approach to LCAO–MO *ab initio* calculations *J. Comput. Chem.* **3** 385–99
- A good recent overview of direct methods is given by:
Almlöf J 1995 Direct methods in electronic structure theory *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 110–51
- [50] Strain M C, Scuseria G E and Frisch M J 1996 Linear scaling for the electronic quantum coulomb problem *Science* **271** 51–3
White C A, Johnson B G, Gill P M W and Head-Gordon M 1994 The fast multipole method *Chem. Phys. Lett.* **230** 8–16
White C A, Johnson B G, Gill P M W and Head-Gordon M 1996 Linear scaling density functional calculations via the continuous fast multipole method *Chem. Phys. Lett.* **253** 268–78
Saebo S and Pulay P 1993 Local treatment of electron correlation *Ann. Rev. Phys. Chem.* **44** 213–36
- [51] Werner H-J 1987 Matrix-formulated direct multiconfiguration self-consistent field and multiconfiguration reference configuration-interaction methods *Advances in Chemical Physics* vol LXIX, ed K P Lawley (New York: Wiley–Interscience) pp 1–62
Shepard R 1987 The multiconfiguration self-consistent field method *Advances in Chemical Physics* vol LXIX, ed K P Lawley (New York: Wiley–Interscience) pp 63–200
- describe several of the advances that have been made in the MCSCF method, especially with respect to enhancing its rate and range of convergence
- Wahl A C and Das G 1977 The multiconfiguration self-consistent field method *Modern Theoretical Chemistry* vol 3, ed H F III Schaefer (New York: Plenum) pp 51–78
- covers the 'earlier' history on this topic
- Bobrowicz F W and Goddard W A III 1977 The self-consistent field equations for generalized valence bond and open-shell Hartree–Fock wave functions *Modern Theoretical Chemistry* vol 3, ed H F III Schaefer (New York: Plenum) pp 97–127
- provide, in *Modern Theoretical Chemistry* vol 3, an overview of the GVB approach, which can be viewed as a specific kind of MCSCF calculation
- See also:
- Dalgaard E and Jørgensen P 1978 Optimization of orbitals for multiconfigurational reference states *J. Chem. Phys.* **69** 3833–44
- Jensen H J Aa, Jørgensen P and Ågren H 1987 Efficient optimization of large scale MCSCF wave functions with a restricted step algorithm *J. Chem. Phys.* **87** 451–66
- Lengsfeld B H III and Liu B 1981 A second order MCSCF method for large CI expansions *J. Chem. Phys.* **75** 478–80
- [52] An early article on this method is:
Boys S F 1950 Electronic wave functions II. A calculation for the ground state of the beryllium atom *Proc. R. Soc. A* **201** 125–37
Shavitt I 1977 The method of configuration interaction *Modern Theoretical Chemistry* vol 3, ed H F III Schaefer (New York: Plenum) pp 189–275
- Ross B O and Siegbahn P E M 1977 The direct configuration interaction method from molecular integrals *Modern Theoretical Chemistry* vol 3, ed H F III Schaefer (New York: Plenum) pp 277–318
- give excellent overviews of the CI method
- For a nice overview of recent work, see:
Schaefer H F III, Thomas J R, Yamaguchi Y, Deleuw B J and Vacek G 1995 The chemical applicability of standard methods in *ab initio* molecular quantum mechanics *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 3–54
- [53] Olsen J, Roos B, Jørgensen P and Jensen H J Aa 1988 Determinant based configuration interaction algorithms for complete and restricted configuration interaction spaces *J. Chem. Phys.* **89** 2185–92
- Olsen J, Jørgensen P and Simons J 1990 Passing the one-billion limit in full configuration-interaction (Fci) calculations *Chem. Phys. Lett.* **169** 463–72
- [54] The so-called Slater–Condon rules express the matrix elements of any one-electron (F) plus two-electron (G) additive operator between pairs of antisymmetrized spin–orbital products that have been arranged (by permuting spin–orbital ordering) to be in so-called maximal coincidence. Once in this order, the matrix elements between two such Slater determinants (labelled $| \rangle$ and $|' \rangle$) are summarized as follows:

(i) if $| \rangle$ and $|' \rangle$ are identical, then

$$\langle |F + G| \rangle = \sum_i \langle \phi_i | f | \phi_i \rangle + \sum_{i>j} [\langle \phi_i \phi_j | g | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | g | \phi_j \phi_i \rangle]$$

where the sums over i and j run over all spin orbitals in $| \rangle$;

(ii) if $| \rangle$ and $|' \rangle$ differ by a single spin–orbital mismatch ($\phi_p \neq \phi'_p$),

$$\langle |F + G| \rangle = \langle \phi_p | f | \phi'_p \rangle + \sum_j [\langle \phi_p \phi_j | g | \phi'_p \phi_j \rangle - \langle \phi_p \phi_j | g | \phi_j \phi'_p \rangle]$$

where the sum over j runs over all spin orbitals in $| \rangle$ except ϕ_p ;

(iii) if $|j\rangle$ and $|j'\rangle$ differ by two spin orbitals ($\phi_p \neq \phi'_p$ and $\phi_q \neq \phi'_q$),

$$\langle |F + G| \rangle = \langle \phi_p \phi_q | g | \phi'_p \phi'_q \rangle - \langle \phi_p \phi_q | g | \phi'_q \phi'_p \rangle$$

(note that the F contribution vanishes in this case);

(iv) if $|j\rangle$ and $|j'\rangle$ differ by three or more spin orbitals, then

$$\langle |F + G| \rangle = 0$$

- [55] Nesbet R K 1963 Computer programs for electronic wave-function calculations *Rev. Mod. Phys.* **35** 552–7
It would seem that the process of evaluating all N^4 of the $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$, 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 N^5 by first performing a transformation of the $\langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$ to an intermediate array $\langle \chi_a \chi_b | g | \chi_c \phi_l \rangle = \sum_d C_{d,l} \langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$ which requires N^5 multiplications and additions. The list $\langle \chi_a \chi_b | g | \chi_c \phi_l \rangle$ is then transformed to a second-level transformed array $\langle \chi_a \chi_b | g | \phi_k \phi_l \rangle = \sum_c C_{c,k} \langle \chi_a \chi_b | g | \chi_c \phi_l \rangle$, which requires another N^5 operations. This sequential transformation is repeated four times until the final $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ array is in hand
- [56] For early perspectives, see, for example:
Nesbet, R K 1965 Algorithm for diagonalization of large matrices *J. Chem. Phys.* **43** 311–12
Davidson E R 1976 The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices *J. Comput. Phys.* **17** 87–94
Roos B O and Siegbahn P E M 1977 The direct configuration interaction method from molecular integrals *Modern Theoretical Chemistry* vol 3, ed H F III Schaefer (New York: Plenum) pp 277–318
Roos B 1972 A new method for large-scale CI calculations *Chem. Phys. Lett.* **15** 153–9
For a good review, see:
Saunders V R and Van Lenthe J H 1983 The direct CI method a detailed analysis *Mol. Phys.* **48** 923–54
- [57] Davidson E 2000 webpage <http://php.indiana.edu/~davidson/>
Professor Davidson has contributed as much as anyone both to the development of the fundamentals of electronic structure theory and its applications to many perplexing problems in molecular structure and spectroscopy
- [58] The essential features of the MPPT/MBPT approach are described in the following articles:
Pople J A, Krishnan R, Schlegel H B and Binkley J S 1978 Electron correlation theories and their application to the study of simple reaction potential surface *Int. J. Quantum Chem.* **14** 545–60
Bartlett R J and Silver D M 1975 Many-body perturbation theory applied to electron pair correlation energies I. Closed-shell first-row diatomic hydrides *J. Chem. Phys.* **62** 3258–68
Krishnan R and Pople J A 1978 Approximate fourth-order perturbation theory of the electron correlation energy *Int. J. Quantum Chem.* **14** 91–100
- [59] Kelly H P 1963 Correlation effects in atoms *Phys. Rev.* **131** 684–99
Møller C and Plesset M S 1934 Note on an approximation treatment for many electron systems *Phys. Rev.* **46** 618–22
- [60] Szabo A and Ostlund N S 1989 *Modern Quantum Chemistry* 1st edn (revised) (New York: McGraw-Hill) p 128
- [61] The early work in chemistry on this method is described in:
Cizek J 1966 On the correlation problem in atomic and molecular systems. Calculation of wave function components in Ursell-type expansion using quantum-field theoretical methods *J. Chem. Phys.* **45** 4256–66
Paldus J, Cizek J and Shavitt I 1972 Correlation problems in atomic and molecular systems IV. Extended coupled-pair many-electron theory and its application to the BH_3 molecule *Phys. Rev. A* **5** 50–67
Bartlett R J and Purvis G D 1978 Many-body perturbation theory coupled-pair many-electron theory and the importance of quadruple excitations for the correlation problem *Int. J. Quantum Chem.* **14** 561–81
Purvis G D III and Bartlett R J 1982 A full coupled-cluster singles and doubles model. The inclusion of disconnected triples *J. Chem. Phys.* **76** 1910
- [62] Jørgensen P and Simons J 1981 *Second Quantization Based Methods in Quantum Chemistry* (New York: Academic) ch 4
- [63] Bartlett R 2000 webpage <http://www.qtp.ufl.edu/~bartlett>
Professor Bartlett brought the CC method, developed earlier by others, into the mainstream of electronic structure theory. For a nice overview of his work on the CC method see:
Bartlett R J 1995 Coupled-cluster theory: an overview of recent developments *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 1047–131
- [64] Bartlett R J and Purvis G D 1978 Many-body perturbation theory coupled-pair many-electron theory and the importance of quadruple excitations for the correlation problem *Int. J. Quantum Chem.* **14** 561–81
Pople J A, Krishnan R, Schlegel H B and Binkley J S 1978 Electron correlation theories and their application to the study of simple reaction potential surfaces *Int. J. Quantum Chem.* **14** 545–60
- [65] Parr B 2000 webpage <http://net.chem.unc.edu/faculty/rgp/cfrgp01.html>
Professor Parr was among the first to push the density functional theory of Hohenberg and Kohn to bring it into the mainstream of electronic structure theory. For a good overview, see the book:
Parr R G and Yang W 1989 *Density Functional Theory of Atoms and Molecules* (New York: Oxford University Press)
- [66] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas *Phys. Rev. B* **136** 864–72

- [67] The Hohenberg–Kohn theorem and the basis of much of density functional theory are treated: Parr R G and Yang W 1989 *Density-Functional Theory of Atoms and Molecules* (New York: Oxford University Press)
The original paper relating to this theory is [66]
- [68] Professor Axel Becke of Queens University, Belfast has been very actively involved in developing and improving exchange–correlation energy functionals. For a good recent overview, see:
Becke A D 1995 Exchange–correlation approximations in density–functional theory *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 1022–46
Becke A D 1983 Numerical Hartree–Fock–Slater calculations on diatomic molecules *J. Chem. Phys.* **76** 6037–45
- [69] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects *Phys. Rev. A* **140** 1133–8
- [70] Many of the various density functional approaches that are under active development can be found in:
Jones R O 1987 Molecular calculations with the density functional formalism *Advances in Chemical Physics* vol LXVII, ed K P Lawley (New York: Wiley–Interscience) pp 413–37
Dunlap B I 1987 Symmetry and degeneracy in $X\alpha$ and density functional theory *Advances in Chemical Physics* vol LXIX, ed K P Lawley (New York: Wiley–Interscience) pp 287–318
Dahl J P and Avery J (eds) 1984 *Local Density Approximations in Quantum Chemistry Solid State Physics* (New York: Plenum)
Parr R G 1983 Density functional theory *Ann. Rev. Phys. Chem.* **34** 631–56
Salahub D R, Lampson S H and Messmer R P 1982 Is there correlation in $X\alpha$ analysis of Hartree–Fock and LCAO $X\alpha$ calculations for O_3 *Chem. Phys. Lett.* **85** 430–3
Ziegler T, Rauk A and Baerends E J 1977 On the calculation of multiplet energies by the Hartree–Fock–Slater method *Theor. Chim. Acta* **43** 261–71
Becke A D 1983 Numerical Hartree–Fock–Slater calculations on diatomic molecules *J. Chem. Phys.* **76** 6037–45
Case D A 1982 Electronic structure calculation using the $X\alpha$ method *Ann. Rev. Phys. Chem.* **33** 151–71
Labanowski J K and Andzelm J W (eds) 1991 *Density Functional Methods in Chemistry* (New York: Springer)
For a recent critical evaluation of situations where current DFT approaches experience difficulties, see:
Davidson E R 1998 How robust is present-day DFT? *Int. J. Quantum Chem.* **69** 241–5
- [71] This is because no four-indexed two-electron integral like expressions enter into the integrals needed to compute the energy. All such integrals involve $\rho(\mathbf{r})$ or the product $\rho(\mathbf{r})\rho(\mathbf{r}')$; because ρ is itself expanded in a basis (say of M functions), even the term $\rho(\mathbf{r})\rho(\mathbf{r}')$ scales no worse than M^2 . The solution of the KS equations for the KS orbitals ϕ_i involves solving a matrix eigenvalue problem; this is expected to scale as M^3 . However, as discussed in section B3.1.8, the scalings of the DFT, SCF, and MP2 methods have been reduced even further
- [72] Pacific Northwest National Laboratories is developing a suite of programs called NWChem
Pacific Northwest National Laboratories 2000 webpage <http://www.emsl.pnl.gov:2080/>
The MacroModel program of Professor C Still, Columbia University
webpage <http://www.cc.columbia.edu/~chempub/mmod/mmod.html>
The Gaussian suite of programs webpage <http://www.gaussian.com>
The GAMESS program webpage <http://www.msg.ameslab.gov/GAMESS/GAMESS.html>
The HyperChem programs of Hypercube, Inc webpage <http://www.hyper.com>
The CAChe software packages from Oxford Molecular webpage <http://www.oxmol.com/getinfo/eduf>
The MOPAC program of CambridgeSoft webpage <http://www.camsoft.com>
The Amber program of Professor Peter Kollman, University of California, San Francisco
webpage <http://www.amber.ucsf.edu/amber/amber.html>
The CHARMM program webpage charmm-bbs-request@emperor.harvard.edu
The programs of MSI, Inc webpage <http://www.msi.com/info/index.html>
The COLUMBUS program webpage shavitt@mps.ohio-state.edu
The CADPAC program of Dr Roger Amos webpage <http://www.cray.com/PUBLIC/DAS/files/CHEMISTRY/CADPAC.txt>
The programs of Wavefunction, Inc webpage <http://wavefun.com/>
The ACES II program of Professor Rod Bartlett webpage <http://www.qtp.ufl.edu/Aces2/>
The MOLCAS program of Professor Bjorn Roos webpage teobor@garm.teokem.lu.se
A nice compendium of various softwares is given in the appendix of reviews in:
Lipkowitz K B and Boyd D B (eds) 1996 *Computational Chemistry* vol 7 (New York: VCH)
- [73] Friesner R 2000 webpage <http://www.columbia.edu/cu/chemistry/faculty/raf.html>
Professor Friesner built on earlier developments of:
Beebe N H F and Linderberg J 1977 Simplifications in the generation and transformation of two-electron integrals in molecular calculations *Int. J. Quantum Chem.* **12** 683–705
Feyereisen M, Fitzgerald G and Komornicki A 1993 Use of approximate integrals in *ab initio* theory an application in MP2 energy calculations *Chem. Phys. Lett.* **208** 359–63
to develop the pseudospectral methods that he and others now widely use. See:
Friesner R A 1987 Solution of the Hartree–Fock equations for polyatomic molecules by a pseudospectral method *J. Chem. Phys.* **86** 3522–31
- [74] Carter E 2000 webpage <http://www.chem.ucla.edu/dept/Faculty/carter.html>

- For an overview of Professor Carter's group's work using pseudospectral methods, see:
Martinez T J and Carter E A 1995 Pseudospectral methods applied to the electron correlation problem *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 1132–65
- [75] Hylleraas E A and Undheim B 1930 *Z. Phys.* **65** 759
MacDonald J K L 1933 Successive approximations by the Rayleigh–Ritz variation method *Phys. Rev.* **43** 830–3
- [76] Pople J A 1973 Theoretical models for chemistry *Energy, Structure, and Reactivity* ed D W Smith and W B McRae (New York: Wiley) p 51–67
- [77] Roos B O, Taylor P R and Siegbahn P E M 1980 A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach *Chem. Phys.* **48** 157–73
Roos B O 1987 The complete active space self-consistent field method and its applications in electronic structure calculations *Adv. Chem. Phys.* **69** 399–445
- [78] Kelly H P 1963 Correlation effects in atoms *Phys. Rev.* **131** 684–99
- [79] Good early overviews of the electron propagator (that is used to obtain IP and EA data) and of the polarization propagator are given in:
Jørgensen P and Simons J 1981 *Second Quantization Based Methods in Quantum Chemistry* (New York: Academic)
The very early efforts on these methods are introduced in:
Linderberg J and Öhrn Y 1973 *Propagator Methods in Quantum Chemistry* (New York: Academic)
More recent summaries include:
Cederbaum L S and Domcke W 1977 Theoretical aspects of ionization potentials and photoelectron spectroscopy a Green's function approach *Adv. Chem. Phys.* **36** 205–344
Oddershede J 1987 Propagator methods *Adv. Chem. Phys.* **69** 201–39
Ortiz J V 1997 The electron propagator picture of molecular electronic structure *Computational Chemistry: Reviews of Current Trends* vol 2, ed J Leszczynski (Singapore: World Scientific) pp 1–61
- [80] The introduction of EOMs for energy differences and for operators that connect two states appears first in the nuclear physics literature; see for example:
Rowe D J 1968 Equation-of-motion method and the extended shell model *Rev. Mod. Phys.* **40** 153–66
I applied these ideas to excitation energies in atoms and molecules in 1971; see equation (2.1)–(2.6) in:
Simons J 1971 Direct calculation of first- and second-order density matrices. The higher RPA method *J. Chem. Phys.* **55** 1218–30
In 1973, the EOM method was then extended to treat IP and EA cases:
Simons J 1973 Theory of electron affinities of small molecules *J. Chem. Phys.* **58** 4899–907
In a subsequent treatment from the time-dependent response point of view, connection with the Greens function methods was made:
Simons J 1972 Energy-shift theory of low-lying excited electronic states of molecules *J. Chem. Phys.* **57** 3787–92
A more recent overview of much of the EOM, Greens function, and propagator field is given in:
Oddershede J 1987 Propagator methods *Adv. Chem. Phys.* **69** 201–39
- [81] Olsen J and Jørgensen P 1995 Time-dependent response theory with applications to self-consistent field and multiconfigurational self-consistent field wave functions *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 857–990
- [82] A good overview of the recent status is given in:
Bartlett R J 1995 Coupled-cluster theory: an overview of recent developments *Modern Electronic Structure Theory* vol 2, ed D R Yarkony (Singapore: World Scientific) pp 1047–131
- [83] Helgaker T, Gauss J, Jørgensen P and Olsen J 1997 The prediction of molecular equilibrium structures by the standard electronic wave functions *J. Chem. Phys.* **106** 6430–40
for a listing and for further details on this study
- [84] Two review papers that introduce and compare the myriad of semi-empirical methods:
Stewart J J P 1991 Semiempirical molecular orbital methods *Reviews in Computational Chemistry* vol 1, ed K B Lipkowitz and D B Boyd (New York: VCH) pp 45–81
Zerner M C 1991 Semiempirical molecular orbital methods *Reviews in Computational Chemistry* vol 2, ed K B Lipkowitz and D B Boyd (New York: VCH) 313–65
A very recent overview, including efforts to interface semi-empirical electronic structure with molecular mechanics treatments of some degrees of freedom is given by:
Thiel W 1996 Perspectives on semiempirical molecular orbital theory *New Methods in Computational Quantum Mechanics (Adv. Chem. Phys. XCIII)* ed I Prigogine I and S A Rice (New York: Wiley) pp 703–57
Earlier texts dealing with semi-empirical methods include:
Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
Murrell J N, Kettle S F A and Tedder J M 1965 *Valence Theory* 2nd edn (London: Wiley)