# FEATURE ARTICLE

## An Experimental Chemist's Guide to ab Initio Quantum Chemistry

**Jack Simons**

*Chemistry Department, University of Utah, Salt Lake City, Utah 84112 (Received: October 5, 1990)*

This article is not intended to provide a cutting edge, state-of-the-art review of ab initio quantum chemistry. Nor does it offer a shopping list of estimates for the accuracies of its various approaches. Unfortunately, quantum chemistry is not mature or reliable enough to make such an evaluation generally possible. Rather, this article introduces the essential *concepts* of quantum chemistry and the *computational features* that differ among commonly used methods. It is intended as a guide for those who are not conversant with the jargon of ab initio quantum chemistry but who are interested in making use of these tools. In sections I–IV, readers are provided overviews of (i) the *objectives* and *terminology* of the field, (ii) the reasons underlying the often disappointing accuracy of present methods, (iii) and the meaning of *orbitals, configurations, and electron correlation*. The content of sections V and VI is intended to serve as reference material in which the computational tools of ab initio quantum chemistry are overviewed. In these sections, the Hartree–Fock (HF), configuration interaction (CI), multiconfigurational self-consistent field (MCSCF), Møller–Plesset perturbation theory (MPPT), coupled-cluster (CC), and density functional methods such as $X_\alpha$ are introduced. The *strengths and weaknesses* of these methods as well as the *computational steps* involved in their implementation are briefly discussed.

## I. What Does ab Initio Quantum Chemistry Try To Do?

The trends in chemical and physical properties of the elements described beautifully in the periodic table and the ability of early spectroscopists to fit atomic line spectra by simple mathematical formulas and to interpret atomic electronic states in terms of empirical quantum numbers provide compelling evidence that *some* relatively simple framework must exist for understanding the electronic structures of all atoms. The great predictive power of the concept of atomic valence further suggests that molecular electronic structure should be understandable in terms of those of the constituent atoms. This point of view lies at the heart of modern chemistry.

Much of ab initio quantum chemistry attempts to make more quantitative these aspects of chemists' views of the periodic table and of atomic valence and structure. By starting from "first principles" and treating atomic and molecular states as solutions of the Schrödinger equation, quantum chemistry seeks to determine *what underlies* the empirical quantum numbers, screening, quantum defects, the aufbau principle, and the concept of valence used by spectroscopists and chemists, in some cases, even prior to the advent of quantum mechanics.

The discipline of computational ab initio quantum chemistry is aimed at determining the electronic energies and wave functions of atoms, molecules, radicals, ions, solids, and all other chemical species. The phrase ab initio implies that one attempts to solve the Schrödinger equation from first principles, treating the molecule as a collection of positive nuclei and negative electrons moving under the influence of Coulombic potentials and not using any prior knowledge about this species' chemical behavior.

To make practical use of such a point of view requires that approximations be introduced; the full Schrödinger equation has never been solved exactly for any but simple model problems. These approximations take the form of physical concepts (e.g., orbitals, configurations, quantum numbers, term symbols, energy surfaces, selection rules, etc.) that provide useful means of organizing and interpreting experimental data and computational methods[1] (e.g., HF, CI, MCSCF, CC, MPPT, and $X_\alpha$) that allow

quantitative predictions to be made.

The full Schrödinger equation for a molecule $H\psi = E\psi$ involves a Hamiltonian $H$ containing the kinetic energies $\{T_j, j = 1, 2, 3, ..., N; T_a, a = 1, 2, ..., M\}$ of each of the $N$ electrons and $M$ nuclei (of charges $Z_a e$, $a = 1, 2, 3, ..., M$) as well as the mutual Coulombic interactions among all of these particles $\{e^2/r_{ij}, i, j = 1, 2, 3, ..., N; Z_a Z_b e^2/R_{ab}, a, b = 1, 2, 3, ..., M; -Z_a e^2/r_{ja}, j = 1, 2, 3, ..., N, a = 1, 2, 3, ..., M\}$. As stated above, such a Schrödinger equation has never been solved exactly for more than two-particle systems.

The essential approximation made in ab initio quantum chemistry is called the Born–Oppenheimer approximation,[2] in which the motions of the (heavy) nuclei are assumed to take place on much longer time scales than the Bohr orbit time scales of the electrons. To implement this approximation:

1. One first solves the so-called *electronic* Schrödinger equation in which the *nuclei are held fixed* (at a geometry denoted **R**). That is, the nuclear translational, vibrational, and rotational kinetic energy ($T_a$) factors are ignored in formulating this equation.

2. One then uses the energies $E_k(\mathbf{R})$ and wave functions $\psi_k(r;\mathbf{R})$ of this equation as a basis to express the full wave function $\psi = \sum_k \chi_k(\mathbf{R}) \psi_k(r;\mathbf{R})$.

3. The $\{\chi_k(\mathbf{R})\}$ are determined by insisting that this $\psi$ wave function obey the full $N$-electron, $M$-nuclei Schrödinger equation. This results in a set of "coupled channel" equations for the $\{\chi_k(\mathbf{R})\}$. If terms in the equations that involve coupling between pairs of electronic states are ignored, the so-called Born–Oppenheimer picture is obtained. The "nonadiabatic" or "non-Born–Oppenheimer" terms ignored can be treated[3] (perturbatively or otherwise) as corrections to the Born–Oppenheimer picture of electronic–vibrational–rotational eigenstates.

4. In the Born–Oppenheimer picture, the equations for the $\{\chi_k(\mathbf{R})\}$ functions are the vibration-rotation Schrödinger equations in which the potential energy is the electronic energy $E_k(\mathbf{R})$ for the state under study.

(1) Excellent overviews of many of these methods are included in: Schaefer, H. F., III Ed. *Modern Theoretical Chemistry*; Plenum Press: New York, 1977; Vols. 3 and 4. Lawley, K. P., Ed. *Advances in Chemical Physics*; Wiley-Interscience: New York, 1987; Vols. LXVII and LXIX. Within this article, these two key references will be denoted MTC, Vols. 3 and 4, and ACP, Vols. 67 and 69, respectively.

(2) This approximation was introduced by Born and Oppenheimer in: *Ann. Phys.* **1927**, *84*, 457. It was then used within early quantum chemistry in the following references: Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1968**, *49*, 404. Pack, R. T.; Hirschfelder, J. O. *J. Chem. Phys.* **1968**, *49*, 4009. *Ibid.* **1970**, *52*, 528.

(3) Early treatments of molecules in which non-Born–Oppenheimer terms were treated were made in: Wolniewicz, L.; Kolos, W. *Rev. Mod. Phys.* **1963**, *35*, 473; *J. Chem. Phys.* **1964**, *41*, 3663, 3674; **1965**, *43*, 2429.

In summary, computational ab initio quantum chemistry attempts to solve the electronic Schrödinger equation for the $E_k(\mathbf{R})$ energy surfaces and wave functions $\psi_k(r;\mathbf{R})$ on a "grid" of values of the "clamped" nuclear positions. Because the Schrödinger equation produces wave functions, it has a great deal of predictive power. Wave functions contain all information needed[4] to compute dipole moments, polarizability, and transition properties such as electric dipole transition strengths among states. They also permit evaluation of system responses with respect to external perturbations such as geometrical distortions,[5] which provides information on vibrational frequencies and reaction paths.

## II. Why Is It So Difficult To Calculate Electronic Energies and Wave Functions with Reasonable Accuracy?

As a scientific tool, ab initio quantum chemistry is not yet very accurate when compared to modern laser spectroscopic measurements, for example. Moreover, it is difficult to estimate the accuracies with which various methods will predict bond energies and lengths, excitation energies, and the like. Chemists who rely on 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 quantum chemistry data to their own research.

It is, of course, natural to ask why it is so difficult to achieve reasonable accuracy (i.e., ca. 1 kcal/mol in computed bond energies or activation energies) with quantum chemistry calculations. After all, many chemists can "guess" bond energies more accurately than even state-of-the-art ab initio computer codes can calculate them. 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 volume element, combined with the $R^{-1}$ dependence of the potential, produces ill-defined interaction integrals unless attractive and repulsive interactions are properly combined. The classical or quantum treatment of ionic melts,[6] many-body gravitational dynamics,[7] and Madelung sums[8] 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. Solving the Schrödinger equation provides information on more than the ground state.* A theory that can provide wave functions and hence many properties of all electronic states should be expected to present serious computational challenges.

*D. All mean-field models of electronic structue require large corrections.* Essentially all ab initio quantum chemistry approaches introduce a "mean-field" potential $V_{mf}$ that embodies the average
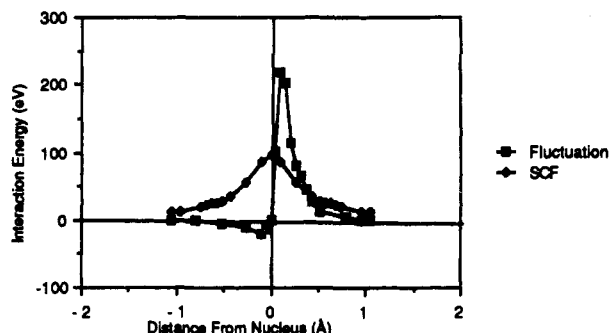


**Figure 1.** Fluctuation and mean-field SCF potentials for a 1s electron in Be.

| Orb. Pair | 1sα1sβ | 1sα2sα | 1sα2sβ | 1sβ2sα | 1sβ2sβ | 2sα2sβ |
|---|---|---|---|---|---|---|
| ΔE in eV | 1.126 | 0.022 | 0.058 | 0.058 | 0.022 | 1.234 |

**Figure 2.** Pair correlation energies for the four electrons in Be.

interactions among the $N$ electrons. The difference between the mean-field potential and the true Coulombic potential is termed[9] the "fluctuation potential".

The solutions $\{\psi_k, E_k\}$ to the true electronic Schrödinger equation are then approximated in terms of solutions $\{\psi^0_k, E^0_k\}$ 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 $r_1$ would experience if it were interacting with a spatially averaged electrostatic charge density arising from the $N - 1$ remaining electrons:

$$V_{mf}(r_1) = \int \rho_{N-1}(r')e^2/|r_1 - r'|\, dr'$$

Here $\rho_{N-1}(r')$ represents the probability density for finding the $N - 1$ electrons at $r'$, and $e^2/|r_1 - r'|$ is the mutual Coulomb repulsion between electron density at $r_1$ and $r'$.

The magnitude and "shape" of such a mean-field potential is shown[10] in Figure 1 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, in the graph shown in Figure 1, 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, there are two quantities 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 centered on the Be nucleus, and (ii) the fluctuation potential ($F$) of this average (mean-field) interaction.

As a function of the interelectron 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 interelectron distances. The corrections to the mean-field picture are therefore quite large when measured in kcal/mol. For example, the differences $\Delta E$ between the true (state-of-the-art quantum chemical calculation as discussed later) energies of interaction among the four electrons in the Be atom and the mean-field estimates of these interactions

(4) A treatment of molecular properties in terms of wave functions and energies and their responses to externally applied fields is given in: Jørgensen, P.; Simons, J. *Second Quantization-Based Methods in Quantum Chemistry*; Academic Press: New York, 1981. *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jørgensen, P., Simons, J., Eds.; D. Reidel: Dordrecht, Holland, 1986. Also see the chapter by: Amos, R. *Adv. Chem. Phys.* **1987**, *67*, 99.

(5) Much of the early work is described in: Pulay, P. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed. Plenum Press: New York, 1977; Vol. 4, p 153. One of the earliest applications to molecular structure is given in: Thomsen, K.; Swanstrøm, P. *Mol. Phys.* **1973**, *26*, 735. More recent contributions are summarized in: *Geometrical Derivatives of Energy Surfaces and Molecular Properties*: Jørgensen, P., Simons, J., Eds.; D. Reidel: Dordrecht, Holland, 1986. Pulay, P. *Adv. Chem. Phys.* **1987**, *69*, 241. Helgaker, T.; Jørgensen, P. *Adv. Quantum Chem.* **1988**, *19*, 183. Strategies for "walking" on potential energy surfaces are overviewed by: Schlegel, H. B. *Adv. Chem. Phys.* **1987**, *67*, 249.

(6) Levy, H. A.; Danford, M. D. In *Molten Salt Chemistry*; Blander, M., Ed.; Interscience: New York, 1964. Bredig, M. A. In *Molten Salts*: Mamantov, G. M., Ed.; Marcel Dekker: New York, 1969.

(7) See, for example: Synge, J. L.; Griffith, B. A. *Principles of Mechanics*; McGraw-Hill: New York, 1949.

(8) Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*; Wiley: New York, 1980; Section 11.9.

(9) Sinanoglu, O. *Proc. Nat. Acad. Sci. U.S.A.* **1961**, *47*, 1217.
(10) Sinanoglu, O. *J. Chem. Phys.* **1962**, *36*, 706.

are given in Figure 2 in electronvolts (1 eV = 23.06 kcal/mol). The mean-field interaction energy between the two 2s orbitals of $1s^2 2s^2$ Be is

$$\int |2s(r)|^2 |2s(r')|^2 e^2/|r - r'| \, dr \, dr' = 5.95 \text{ eV}$$

The corrections to the mean-field model (e.g., 1.234 eV compared to 5.95 eV for the two 2s electrons of Be) are therefore quite substantial.

*E. Summary.* The above evidence shows why an ab initio solution of the Schrödinger equation is a very demanding task if high accuracy is desired. However, chemical intuition based "guessing" cannot be trusted when faced with novel bonding situations, strained or unstable species, or many excited or ionized states; it is in these circumstances that the ab initio approach has most to offer, even if its ultimate accuracy is, to date, severely limited by the strength of the fluctuation potential (even for the "best" mean-field models that have yet been created).

## III. What Are the Essential Concepts of ab Initio Quantum Chemistry?

The mean-field potential and the need to improve it to achieve a 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.

*A. Orbitals and Configurations: What Are They (Really)?* *1. How the mean-field model leads to orbitals and configurations:* The mean-field potentials that have proven most useful are all one-electron additive: $V_{mf}(r) = \sum_j V_{mf}(r_j)$. Since the electronic kinetic energy $T = \sum_j T_j$ operator is also one-electron additive, the mean-field Hamiltonian $H^0 = T + V_{mf}$ is of this form. The additivity of $H^0$ implies that the mean-field energies ($E^0_k$) are additive and the wave functions $\{\psi^0_k\}$ 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 $\{\phi_j\}$. These orbitals are found by solving the one-electron Schrödinger equations: $(T_1 + V_{mf}(r_1))\phi_j(r_1) = \epsilon_j \phi_j(r_1)$; the eigenvalues $\{\epsilon_j\}$ are called *orbital energies*.

Given the complete set of solutions to this one-electron equation, a complete set[11] of $N$-electron mean-field wave functions can be written down. Each $\psi^0_k$ 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., $\psi^0_k = |\phi_{k1}(r_1)\phi_{k2}(r_2)\phi_{k3}(r_3) \ldots \phi_{kN-1}(r_{N-1})\phi_{kN}(r_N)|$, as above). The corresponding mean field energy is evaluated as the sum over those orbitals that appear in $\psi^0_k$: $E^0_k = \sum_{j=1,N} \epsilon_{kj}$.

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 wave function. To do so, one applies the so-called antisymmetrizer operator $A = \sum_P (-1)^P P$, where the permutation operator $P$ runs over all $N!$ permutations of the $N$ electrons. Application of $A$ to a product function does not alter the occupancy of the functions $\{\phi_{kj}\}$ in $\psi^0_k$; it simply scrambles the order that the electrons occupy the $\{\phi_{kj}\}$.

Because each of the electrons also possesses intrinsic spin, the one-electron functions $\{\phi_j\}$ used in this construction are taken to be eigenfunctions of $(T_1 + V_{mf}(r_1))$ multiplied by either $\alpha$ or $\beta$. This set of functions is called the set of mean-field *spin-orbitals*.

By choosing to place $N$ electrons into specific spin-orbitals, one has specified 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 $\epsilon_j\}$, the $N$-electron mean-field Schrödinger equation has a complete set of $N$-electron *configuration state functions* (CSFs) $\psi^0_k$ and energies $E^0_k$.

*2. The self-consistent mean-field (SCF) potential:* The one-electron additivity of the mean-field Hamiltonian $H^0$ gives rise

to the ab initio concept of spin-orbitals for any additive $V_{mf}(r)$. In fact, there is no *single* mean-field potential; different scientists have put forth different suggestions for $V_{mf}$ over the years. Each such suggestion gives rise to spin-orbitals and configurations that are specific to the particular $V_{mf}$. 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 of the full $H$.

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[12] of electronic structure theory, the configuration specified for study (e.g., the $1s^2 2s^2 2p^4$ description of the oxygen atom) 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 $r$ in the $1s^2 2s^2 2p_x 2p_y$ configuration description of the carbon atom is

$$V_{mf}(r) = 2\int |1s(r')|^2 e^2/|r - r'| \, dr' +$$
$$2\int |2s(r')|^2 e^2/|r - r'| \, dr' + \int |2p_y(r')|^2 e^2/|r - r'| \, dr'$$

Here the density $\rho_{N-1}(r')$ is the sum of the charge densities of the orbitals occupied by the five other electrons $2|1s(r')|^2 + 2|2s(r')|^2 + |2p_y(r')|^2$.

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:

$$V_{mf}(r) = 2\int |1s(r')|^2 e^2/|r - r'| \, dr' + \int |2s(r')|^2 e^2/|r - r'| \, dr'$$
$$+ \int |2p_y(r')|^2 e^2/|r - r'| \, dr' + \int |2p_x(r')|^2 e^2/|r - r'| \, dr'$$

Notice that the orbitals occupied in the configuration under study appear in the mean-field potential. However, it is $V_{mf}$ 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 *self-consistent field* (SCF) manner. One begins with an approximate description of the orbitals in $\psi^0_k$. These orbitals then define $V_{mf}$, and the equations $(T_1 + V_{mf}(r_1))\phi_j(r_1) = \epsilon_j \phi_j(r_1)$ are solved for "new" spin-orbitals. These orbitals are then be used to define an improved $V_{mf}$, which gives another set of solutions to $(T_1 + V_{mf}(r_1))\phi_j(r_1) = \epsilon_j \phi_j(r_1)$. This iterative process is continued until the orbitals used to define $V_{mf}$ are identical with those that result as solutions of $(T_1 + V_{mf}(r_1))\phi_j(r_1) = \epsilon_j \phi_j(r_1)$. When this condition is reached, one has achieved "self-consistency".

*B. What Is Electron Correlation?* By expressing the mean-field interaction of an electron at $r$ with the $N - 1$ other electrons in terms of a probability density $\rho_{N-1}(r')$ that is independent of the fact that another electron resides at $r$, the mean-field models ignore spatial *correlations* among the electrons. In reality, the conditional probability density for finding one of the $N - 1$ electrons at $r'$, given that one electron is at $r$, depends on $r$; the electrons "avoid" one another because of their like charge. The absence of spatial correlation is a direct consequence of the spin-orbital *product nature* of the mean-field wave functions $\{\psi^0_k\}$.

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 chemical electronic structure. However, it is very disconcerting to most of us to be told the the familiar $1s^2 2s^2 2p^2$ description of the carbon atom is inadequate and that instead one must think of the $^3P$ ground state of this atom as a "mixture" of $1s^2 2s^2 2p^2$, $1s^2 2s^2 3p^2$, $1s^2 2s^2 3d^2$, and $2s^2 3s^2 2p^2$ (and any other configurations whose angular momenta can be coupled to produce $L = 1$ and $S = 1$).

(11) Löwdin, P. O. *Adv. Chem. Phys.* **1959**, *2*, 207.

(12) Hartree, D. R. *Proc. Camb. Philos. Soc.* **1928**, *24*, 89, 111, 426. Hartree, D. R.; Hartree, W.; Swirles, B. *Philos. Trans. Roy. Soc. London* **1939**, *A238*. Fock, V. *Z. Phys.* **1930**, *61*, 126. Slater, J. C. *Rev. Mod. Phys.* **1930**, *35*, 210.

Although the picture of configurations in which $N$ electrons occupy $N$ spin–orbitals may be very familiar and useful for systematizing 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 would be inconsistent to insist that the carbon atom be thought of as $1s^2 2s^2 2p^2$ while insisting that the ab initio quantum chemistry description of this atom yield electronic excitation energies accurate to $\pm 1$ kcal/mol.

*C. 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 into 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 instantaneous spatial correlations among electrons is necessary to achieve a more accurate description of atomic and molecular electronic structure. *No* single spin–orbital product wave function is capable of treating electron correlation to *any* extent; its product nature renders it incapable of doing so.

It is now time to examine how one moves beyond the single-configuration approximation and how the resulting more complicated wave function can be interpreted in terms of dynamical interactions among the $N$ electrons.

## IV. How To Introduce Electron Correlation via Configuration Mixing

*A. The Multiconfiguration Wave Function.* In most of the commonly used ab initio quantum chemical methods,[1] one forms a set of configurations by placing $N$ electrons into spin–orbitals of the atom or molecule under study in a manner that produces the spatial, spin, and angular momentum symmetry of the electronic state of interest. This set of functions is then used to achieve a more accurate and dynamically correct description of the electronic structure of that state.

In particular, the correct wave function $\psi$ is written as a linear combination of the mean-field wave functions $\{\psi^0_k\}$: $\psi = \sum_k C_k \psi^0_k$. For example, to describe the ground $^1S$ state of the Be atom, the $1s^2 2s^2$ configuration is augmented by including other configurations such as $1s^2 3s^2$, $1s^2 2p^2$, $1s^2 3p^2$, $1s^2 2s 3s$, $3s^2 2s^2$, $2p^2 2s^2$, 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 $\psi$.

*B. Physical Meaning of Mixing in "Excited" Configurations.* When performing ab initio calculations on the ground $^1S$ state of the Be atom, the following four antisymmetrized spin–orbital products are found to have the largest $C_k$ amplitudes:

$$\psi = C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|]$$

The fact that the latter three antisymmetrized products possess the same amplitude $C_2$ is a result of the requirement that a state of $^1S$ symmetry is desired. It can be shown[13] that this function is equivalent to

$$\psi = \tfrac{1}{6} C_1 |1s^2 \{[(2s - a2p_x)\alpha(2s + a2p_x)\beta - \\ (2s - a2p_x)\beta(2s + a2p_x)\alpha] + \\ [(2s - a2p_y)\alpha(2s + a2p_y)\beta - (2s - a2p_y)\beta(2s + a2p_y)\alpha] + \\ [(2s - a2p_z)\alpha(2s + a2p_z)\beta - (2s - a2p_z)\beta(2s + a2p_z)\alpha]\}$$

where $a = (3C_2/C_1)^{1/2}$.

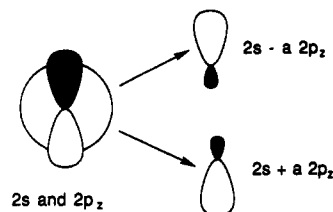(13) Simons, J. *Energetic Principles of Chemical Reactions*; Jones and Bartlett: Boston, 1983; p 129.



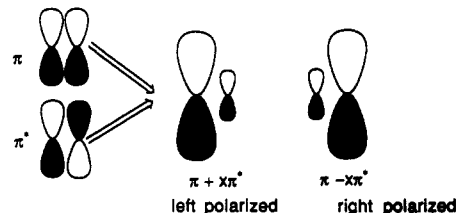**Figure 3.** Polarized orbital pairs involving 2s and $2p_z$ orbitals.



**Figure 4.** Left and right polarized orbital pairs involving $\pi$ and $\pi^*$ orbitals.

Here two electrons occupy the 1s orbital (with opposite, $\alpha$ and $\beta$ spins) while the other pair resides in 2s–2p polarized orbitals in a manner that instantaneously correlates their motions. These *polarized orbital pairs* $(2s \pm a2p_{x,y,\text{or } z})$ are formed by combining the 2s orbital with the $2p_{x,y,\text{ or } z}$ orbital in a ratio determined by $C_2/C_1$.

This ratio can be shown[14] to be proportional to the magnitude of the coupling $\langle 1s^2 2s^2 | H | 1s^2 2p^2 \rangle$ between the two configurations involved and inversely proportional to the energy difference $[\langle 1s^2 2s^2 | H | 1s^2 2s^2 \rangle - \langle 1s^2 2p^2 | H | 1s^2 2p^2 \rangle]$ 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 $|C_2/C_1|$ ratios) polarized orbital pairs.

A set of polarized orbital pairs is described pictorially in Figure 3. It still remains to ascribe sound physical meaning to these polarized orbital pairs and, hence, to explain how mixing the $1s^2 2s^2$ and $1s^2 2p^2$ configurations achieves a better description of the ground state of Be.

In each of the three equivalent terms in the above wave function, 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 $[(2s - a2p_x)\alpha(2s + a2p_x)\beta - (2s - a2p_x)\beta(2s + a2p_x)\alpha]$ describes one electron occupying a $2s - a2p_x$ polarized orbital while the other electron occupies the $2s + a2p_x$ orbital.

In this picture, the electrons reduce their mutual Coulomb repulsion by occupying *different* regions of space; in the SCF picture $1s^2 2s^2$, both electrons reside in the same 2s region of space.

(14) 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 (labeled $|\rangle$ 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 ($\phi_p \neq \phi'_p$), then

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

where the sum over $j$ runs over all spin–orbitals in $|\rangle$ except $\phi_p$. (iii) If $|\rangle$ and $|'\rangle$ differ by two spin–orbitals ($\phi_p \neq \phi'_p$ and $\phi_q \neq \phi'_q$), then

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

(note that the $F$ contribution vanishes in this case). (iv) if $|\rangle$ and $|'\rangle$ differ by three or more spin orbitals, then

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

Virtually all practicing quantum chemists have these rules committed to memory.

In this particular example, the electrons undergo *angular correlation* to "avoid" one another.

Let us consider another example. In describing the $\pi^2$ electron pair of an olefin, ab initio calculations indicate it is important to mix in "doubly excited" configurations of the form $(\pi^*)^2$. The physical importance of such configurations can again be made clear by using the identity introduced above:

$$C_1|...\phi\alpha\phi\beta...| - C_2|...\phi'\alpha\phi'\beta...| =$$
$$C_1/2\{|...(\phi - a\phi')\alpha(\phi + a\phi')\beta...| - |...(\phi - a\phi')\beta(\phi + a\phi')\alpha...|\}$$

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

In this example, the two nonorthogonal "polarized orbital pairs" involve mixing the $\pi$ and $\pi^*$ orbitals to produce two left–right polarized orbitals as depicted in Figure 4. Here one says that the $\pi^2$ electron pair undergoes left–right correlation when the $(\pi^*)^2$ configuration is introduced. In the alkaline-earth-metal atom case, the polarized orbital pairs give rise to $(ns \pm anp)$ angular correlation. Use of an $(n + 1)s^2$ configuration for the alkaline-earth-metal calculation would contribute radial correlation involving $(ns \pm a(n + 1)s)$ orbital pairs.

*C. 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, and each hybrid is occupied, in the mean-field picture, by two electrons. In contrast, polarized orbital *pairs* are sets of two orbitals, each being a "mixture" of two mean-field orbitals with amplitude $a = (C_2/C_1)^{1/2}$. A *single electron* residues in each of these orbitals, 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.

*D. 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 $(\phi)$ to another $(\phi')$ as equivalent to a singlet coupling of two polarized orbitals $(\phi - a\phi')$ and $(\phi + a\phi')$. This picture is closely related to the generalized valence bond (GVB) model that Goddard and his co-workers have developed.[15]

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 wave function. In the GVB approach, these electron correlations can be specified either in terms of double excitations involving CSFs formed from orthonormal spin orbitals or in terms of explicitly nonorthogonal GVB orbitals as shown above. The latter is more convenient for imagining how electrons undergo correlated motions, but the former is how GVB calculations are carried out on a computer.

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.

*E. Summary.* The dynamical interactions among electrons give rise to instantaneous spatial correlations that must be handled to arrive at an accurate picture of 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 often needed.

The use of doubly excited configurations is a mechanism by which $\psi$ can place electron *pairs*, which in the mean-field picture occupy the same orbital, into different regions of space (i.e., each one into a different member of the polarized orbital *pair*) 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.

*F. Transition to Treatment of Methodology.* In the next two sections, various ab initio quantum chemistry methods for determining the $\{C_k\}$ expansion coefficients and for computing the energy $E$ are detailed. All of these methods use as a starting point a set of mean-field configuration state functions. In particular, *combinations* of antisymmetrized spin–orbital products that are eigenfunctions of those operators that commute with the $N$-electron Hamiltonian $H$ are used to so expand $\psi$.

For polyatomic molecules, these symmetry operators include point-group symmetry operators (which act on *all* $N$ electrons) and the spin angular momentum operators $(S^2$ and $S_z)$ of *all* of the electrons taken as a whole (in the absence of spin–orbit coupling).

For linear molecules, the $N$-electron operators $L_z$, $S^2$, and $S_z$ commute with $H$. For atoms, the corresponding operators are $L^2$, $L_z$, $S^2$, and $S_z$ (again, in the absence of spin–orbit coupling).

To construct $N$-electron functions that are eigenfunctions of the spatial symmetry or orbital angular momentum operators as well as the spin angular momentum operators, one has to "couple" the symmetry or angular momentum properties of the individual spin–orbitals used to construct the $N$-electrons functions. This coupling involves forming direct product symmetries in the case of polyatomic molecules that belong to finite point groups; it involves vector coupling orbital and spin angular momenta in the case of atoms; and it involves vector coupling spin angular momenta and axis coupling orbital angular momenta when treating linear molecules.

## V. The Single-Configuration Picture and the Hartree–Fock Approximation

Given a set of $N$-electron symmetry adapted configuration state functions $(\Phi_j)$ in terms of which $\psi$ is to be expanded as $\psi = \sum_j C_j \Phi_j$, attention can be turned to determining the $\{C_j\}$ and $E$. Before doing so, it is important to discuss in more detail the task of finding the "best" spin–orbitals $\{\phi_j\}$ for cases in which a self-consistent field (SCF) mean-field potential is used. This is important because such mean fields are employed in the vast majority of ab initio calculations, including those that subsequently move on to treat electron correlation.

*A. The Single-Determinant Wave Function. 1. 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 and only one configuration is included:

$$\psi = |\phi_1 \phi_2 \phi_3 ... \phi_N|$$

For such a function, variational optimization of the spin–orbitals to make the expectation value $\langle \psi|H|\psi \rangle$ stationary produces[16] the *canonical Hartree–Fock equations*:

$$F\phi_i = \epsilon_i \phi_i$$

where the so-called Fock operator $F$ is given by

$$F\phi_i = h\phi_i + \sum_{j(\text{occupied})} [J_j - K_j]\phi_i$$

The Coulomb $(J_j)$ and exchange $(K_j)$ operators are defined by the relations

$$J_j\phi_i = \int \phi^*_j(r')\phi_j(r')1/|r - r'| \, d\tau \, \phi_i(r)$$

$$K_j\phi_i = \int \phi^*_j(r')\phi_i(r')1/|r - r'| \, d\tau' \, \phi_j(r)$$

the symbol $h$ denotes the electronic kinetic energy and electron-nuclear Coulomb attraction operators. The $d\tau$ implies integration over the spin variables associated with the $\phi_j$ (and, for the exchange

(15) See, for example: Goddard, W. A.; Harding, L. B. *Annu. Rev. Phys. Chem.* **1978**, *29*, 363.

(16) Classic papers in which the SCF equations for closed- and open-shell systems are treated: Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69; **1960**, *32*, 179.

operator, $\phi_j$), as a result of which the exchange integral vanishes unless the spin function of $\phi_j$ is the same as that of $\phi_i$; the Coulomb integral is nonvanishing no matter what the spin functions of $\phi_j$ and $\phi_i$. These are the spin-orbital level equations of the SCF mean-field model.

*2. The equations have orbital solutions for occupied and unoccupied orbitals*: The Hartree–Fock equations $F\phi_i = \epsilon_i \phi_i$ possess solutions for the spin-orbitals in $\psi$ (the *occupied* spin-orbitals) as well as for orbitals not occupied in $\psi$ (the *virtual* or unoccupied spin-orbitals). The $F$ operator is hermitian, so it possesses a complete set of orthonormal eigenfunctions; only those that are in $\psi$ appear in the Coulomb and exchange potentials of the Fock operator.

*3. The spin-impurity problem*: As formulated above, the Hartree–Fock (HF) equations yield orbitals that do not guarantee that $\psi$ has proper spin symmetry. To illustrate, consider the equations for an open-shell system such as the lithium atom. If $1s\alpha$, $1s\beta$, and $2s\alpha$ spin-orbitals are chosen to appear in $\psi$, the Fock operator will be

$$F = h + J_{1s\alpha} + J_{1s\beta} + J_{2s\alpha} - [K_{1s\alpha} + K_{1s\beta} + K_{2s\alpha}]$$

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

$$F\phi_{k\alpha} = h\phi_{k\alpha} + (2J_{1s} + J_{2s})\phi_{k\alpha} - (K_{1s} + K_{2s})\phi_{k\alpha}$$

In contrast, when acting on a $\beta$ spin-orbital, one obtains

$$F\phi_{k\beta} = h\phi_{k\beta} + (2J_{1s} + J_{2s})\phi_{k\beta} - (K_{1s})\phi_{k\beta}$$

Spin-orbitals of $\alpha$ and $\beta$ type do *not* experience the same exchange potential in this model because $\psi$ contains two $\alpha$ spin-orbitals and only one $\beta$ spin-orbital. A consequence is that the optimal $1s\alpha$ and $1s\beta$ spin-orbitals, which are themselves solutions of $F\phi_i = \epsilon_i \phi_i$, do not have identical orbital energies (i.e., $\epsilon_{1s\alpha} \neq \epsilon_{1s\beta}$) and are not spatially identical. This resultant spin polarization of the orbitals gives rise to spin impurities in $\psi$. 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 wave function 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 $\psi$. In general, UHF wave functions are not of pure spin symmetry for any open-shell system; this is a significant drawback of methods based on a UHF mean-field 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[17] that derive from Pople and co-workers.

*B. LCAO-MO 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 $\phi_i$, for which solutions are sought. Typical iterative schemes begin with a guess for those $\phi_i$ that appear in $\psi$, which then allows $F$ to be formed. Solutions to $F\phi_i = \epsilon_i \phi_i$ are then found, and those $\phi_i$ that possess the space and spin symmetry of the occupied orbitals of $\psi$ and have the proper energies and nodal character are used to generate a new $F$ operator (i.e., new $J_i$ and $K_i$ operators). This iterative Hartree–Fock *self-consistent field* (SCF) process is continued until the $\phi_i$ and $\epsilon_i$ do not vary significantly from one iteration to the next, at which time one says that the process has converged.

In practice, solution of $F\phi_i = \epsilon_i \phi_i$ as an integrodifferential equation can be carried out only for atoms[18] and linear molecules[19]

for which the angular parts of the $\phi_i$ can be exactly separated from the radial because of the axial- or full-rotation group symmetry (e.g., $\phi_i = Y_{l,m} R_{n,l}(r)$ for an atom and $\phi_i = \exp(im\phi)R_{n,l,m}(r,\theta)$ for a linear molecule).

In the procedures most commonly applied to nonlinear molecules, the $\phi_i$ are expanded in a *basis* of functions $\chi_\mu$ according to the linear combinations of atomic orbitals to form molecular orbitals (LCAO-MO) procedure:

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

This reduces $F\phi_i = \epsilon_i \phi_i$ to a matrix eigenvalue-type equation:

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

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

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

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

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

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

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

where the sum in $\gamma_{\delta,\kappa}{}^{ex}$ 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, $\gamma_{\delta,\kappa}{}^{ex} = {}^1/_2\gamma_{\delta,\kappa}$).

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 matrix Hartree–Fock equations $\sum_\nu F_{\mu,\nu} C_{\nu,i} = \epsilon_i S_{\mu,\nu} C_{\nu,i}$. One should also note that, just as $F\phi_i = \epsilon_i \phi_j$ possesses a complete set of eigenfunctions, the matrix $F_{\mu,\nu}$, whose dimension $M$ is equal to the number of atomic basis orbitals used in the LCAO-MO expansion, has $M$ eigenvalues $\epsilon_i$ and $M$ eigenvectors whose elements are the $C_{\nu,i}$. Thus, there are occupied and virtual molecular orbitals (MOs) each of which is described in the LCAO-MO form with $C_{\nu,i}$ coefficients obtained via solution of $\sum_\nu F_{\mu,\nu} C_{\nu,i} = \epsilon_i \sum_\nu S_{\mu,\nu} C_{\nu,i}$.

*C. Atomic Orbital Basis Sets. 1. STOs and GTOs*: The basis orbitals commonly used in the LCAO-MO process fall into two classes:

1. Slater-type orbitals $\chi_{n,l,m}(r,\theta,\phi) = N_{n,l,m,\zeta} Y_{l,m}(\theta,\phi) r^{n-1} e^{-\zeta r}$ characterized by quantum numbers $n$, $l$, and $m$ and exponents (which characterize the "size" of the basis function) $\zeta$. The symbol $N_{n,l,m,\zeta}$ denotes the normalization constant.

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

For both types of orbitals, the coordinates $r$, $\theta$, and $\phi$ refer to the position of the electron relative to a set of axes attached to the center on which the basis orbital is located. Although Slater-type orbitals (STOs) have the proper "cusp" behavior near nuclei, they are used primarily for atomic and linear molecule calculations because the multicenter integrals that arise in polyatomic-molecule calculations can not efficiently be performed when STOs are employed. In contrast, such integrals can routinely be done when Gaussian-type orbitals (GTOs) are used. This fundamental advantage of GTOs has lead 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 nonzero), it is common to combine two, three, or more GTOs, with combination coefficients that are fixed and *not* treated as LCAO-MO parameters, into new functions called *contracted* GTOs or CGTOs. Typically, a series of light, medium, and loose

(17) See, for example: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohling, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whitehead, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.
(18) Froese-Fischer, C. *Comput. Phys. Commun.* **1970**, *1*, 152.
(19) McCullough, E. A. *J. Chem. Phys.* **1975**, *62*, 3991. Christiansen, P. A.; McCullough, E. A. *J. Chem. Phys.* **1977**, *67*, 1877.

GTOs are multiplied by contraction coefficients and summed to produce a CGTO that appears to possess the proper "cusp" at the nuclear center.

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

*a. The fundamental core and valence basis*: In constructing an atomic orbital basis, one must 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 atomic orbitals in the atom.

2. A *double-ζ* (DZ) basis in which twice as many STOs or CGTOs are used as there are core and valence atomic orbitals. The use of more basis functions is motivated by a desire to provide additional variational flexibility so the LCAO-MO process can generate molecular orbitals of variable diffuseness as the local electronegativity of the atom varies.

3. A *triple-ζ* (TZ) basis in which 3 times as many STOs or CGTOs are used as the number of core and valence atomic orbitals.

4. Dunning has developed[20] CGTO bases that range from approximately DZ to substantially beyond TZ quality. These bases involve contractions of primitive GTO bases that Huzinaga had earlier optimized.[21] 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 5 separate s-type CGTOs and that 6 primitive p-type GTO's were contracted into 4 separate p-type CGTOs in each of the *x*, *y*, and *z* directions.

5. Even-tempered basis sets[22] consist of GTOs in which the orbital exponents $\alpha_k$ belonging to series of orbitals consist of geometrical progressions: $\alpha_k = a\beta^k$, where $a$ and $\beta$ characterize the particular set of GTOs.

6. STO-3G bases[23] were employed some years ago but are less popular recently. These bases are constructed by least-squares fitting GTOs to STOs that 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[24] 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.

The values of the orbital exponents (ζ's or α's) and the GTO-to-CGTO contraction coefficients needed to implement a particular basis of the kind described above have been tabulated in several journal articles[25] and in computer data bases.

*b. Polarization functions*: In addition to core and valence functions, one usually adds a set of so-called *polarization functions* to the basis. They are functions of one higher angular momentum than appears in the atom's valence orbital space (e.g., d functions
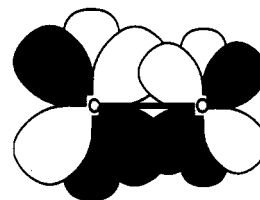


**Figure 5.** Role of d-polarization functions in the π bond between C and O.

for C, N, and O and p functions for H). These polarization functions have exponents (ζ or α) that 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 that describe the atom's valence orbital with one higher *l* value; such higher *l* valence orbitals would be radially more diffuse and would require STOs or GTOs with smaller exponents.

The primary purpose of polarization functions is to give additional angular flexibility to the LCAO-MO process in forming the valence molecular orbitals. This is illustrated in Figure 5, where polarization $d_\pi$ orbitals are seen to contribute to formation of the bonding π orbital of a carbonyl group by allowing polarization of the carbon atom's $p_\pi$ orbital toward the right and of the oxygen atom's $p_\pi$ orbital toward the left. Polarization functions are essential in strained ring compounds because they provide the angular flexibility needed to direct the electron density into regions between 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 polarized orbital pairs involving higher angular correlations to be formed. Optimal polarization functions for first- and second-row atoms have been tabulated.[26]

*c. Diffuse functions*: When dealing with anions or Rydberg states, one must 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. Energy-optimized diffuse functions appropriate to anions of most lighter main-group elements have been tabulated in the literature and in data bases.[25]

Once one has specified an atomic orbital basis for each atom in the molecule, the LCAO-MO procedure can be used to determine the $C_{\nu,i}$ 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 atomic orbitals are combinations (with atomic values for the $C_{\nu,i}$ coefficients) of the basis functions. The LCAO-MO-SCF process itself determines the magnitudes and signs of the $C_{\nu,i}$; alternations in the signs of these coefficients allow nodes to form.

For example, in a minimal-basis treatment of the carbon atom, the 2s atomic orbital is formed by combining the two CGTOs with opposite sign to achieve the radial node; the more diffuse s-type basis function will have a larger $C_{i,\nu}$ coefficient in the 2s atomic orbital. The 1s atomic orbital is formed by combining the same two CGTOs but with the same sign (and hence no radial node) and with the less diffuse basis function having a larger $C_{\nu,i}$ coefficient.

*D. Physical Meaning of Orbital Energies.* The HF-SCF equations $F\phi_i = \epsilon_i\phi_i$ imply that $\epsilon_i$ can be written as

$$\epsilon_i = \langle\phi_i|F|\phi_i\rangle = \langle\phi_i|h|\phi_i\rangle + \sum_{j(\text{occupied})} \langle\phi_i|J_j - K_j|\phi_i\rangle =$$

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

Thus $\epsilon_i$ is the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in $\phi_i$ plus the sum over all of the spin-orbitals occuped in $\psi$ of Coulomb minus exchange interactions between $\phi_i$ and these occupied spin-orbitals.

(20) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; H. F. Schaefer, III, Ed.; Plenum Press: New York, 1977.
(21) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(22) Schmidt, M. W.; Ruedenberg, K. *J. Chem. Phys.* **1979**, *17*, 3961.
(23) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(24) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta. (Berlin)* **1973**, *28*, 213. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(25) In particular, in the data base contained in: Poirer, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian Basis Sets: A. Compendium for Ab initio Molecular Orbital Calculations*; Elsevier Science: New York, 1985.

(26) Roos, B.; Siegbahn, P. *Theor. Chim. Acta (Berlin)* **1970**, *17*, 199. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

If $\phi_i$ 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 $\phi_i$ with all of the $N - 1$ *other* occupied spin–orbitals. If $\phi_i$ is a virtual spin–orbital, this cancellation does not occur, and one obtains the Coulomb minus exchange interaction of $\phi_i$ 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. It is this fact that makes SCF virtual orbitals not usually 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.

*1. Koopmans' theorem:* Let us consider a mdoel 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 Hartree–Fock orbitals of the parent molecule are used to describe both the parent and the species generated by electron addition or removal. 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 simplified model, the energy difference between the daughter and the parent species can be written as follows ($\phi_k$ represents the particular spin–orbital that is added or removed):

1. For electron detachment:

$$E^{N-1} - E^N = -\epsilon_k$$

2. For electron attachment:

$$E^N - E^{N+1} = -\epsilon_k$$

So, within the limitations of the single-determinant, frozen-orbital model set forth, 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;[27] it is used extensively in quantum chemical calculations as a means of estimating IPs and EAs and often yields results that are qualitative correct (i.e., ±0.5 eV).

*2. Orbital energies and the total energy:* The total SCF electronic energy can be written as

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

For this same system, the sum of the orbital energies of the occupied spin–orbitals is given by

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

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 Hartree–Fock approximation, the sum of the occupied orbital energies is *not* equal to the total energy. This means that as one attempts to develop a qualitative picture of the energies of configurations along a reaction path, one must be careful not to equate the sum of orbital energies with the total configurational energy; the former is higher than the latter by an amount equal to the sum of the Coulomb minus exchange interactions.

*E. Solving the Roothaan SCF Equations.* Before moving on to discuss methods that go beyond the uncorrelated, single-configuration, mean-field method, it is important to examine some of the computational effort that goes into carrying out an SCF calculation. Such a calculation may represent the final product in certain cases; in others, it is the starting point for further treatment of electron correlation. In any event, it is important to see what is involved.

The matrix SCF equations $\sum_\nu F_{\mu,\nu} C_{\nu,i} = \epsilon_i \sum_\nu S_{\mu,\nu} C_{\nu,i}$ are solved for the occupied and virtual orbitals' energies $\epsilon_i$ and $C_{\nu,i}$ values even though only the occupied orbitals' $C_{\nu,i}$ coefficients enter into the Fock operator:

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

Once atomic basis sets have been chosen for each atom, the *one- and two-electron integrals* appearing in $F_{\mu,\nu}$ must be evaluated. Doing so is a time-consuming process, but there are numerous highly efficient computer codes[28] that allow such integrals to be computed for s, p, d, and 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 ($\langle \chi_\mu | h | \chi_\nu \rangle$ and $\langle \chi_\mu | \chi_\nu \rangle$) and $P^4/8$ two-electron ($\langle \chi_\mu \chi_\delta | g | \chi_\nu \chi_\kappa \rangle$) integrals. When treating extremely large atomic orbital basis sets (e.g., 200 or more basis functions), modern computer programs[29] calculate the requisite integrals but never store them on the disk. Instead, their contributions to $F_{\mu,\nu}$ are accumulated "on the fly", after which the integrals are discarded.

To begin the SCF process, one must input to the computer routine that computes $F_{\mu,\nu}$ *initial guesses* for the $C_{\nu,i}$ values corresponding to the occupied orbitals. These initial guesses are typically made as follows:

1. If one has available $C_{\nu,i}$ values for the system from a calculation performed at a nearby geometry, one can use these $C_{\nu,i}$ values.

2. If one has $C_{\nu,i}$ values appropriate to fragments of the system (e.g., for C and O atoms if the CO molecule is under study or for $CH_2$ and O if $H_2CO$ 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 $F_{\mu,\nu}$ are ignored (i.e., take $F_{\mu,\nu} = \langle \chi_\mu | h | \chi_\nu \rangle$) and use the resultant solutions to $\sum_\nu F_{\mu,\nu} C_{\nu,i} = \epsilon_i \sum_\nu S_{\mu,\nu} C_{\nu,i}$ as initial guesses for the $C_{\nu,i}$.

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

## VI. Methods for Treating Electron Correlation

*A. Overview of Various Approaches.* There are numerous procedures currently in use for determining the "best" wave function of the form

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

where $\Phi_I$ is a spin- and space-symmetry-adapted CSF consisting of determinants $|\phi_{I1} \phi_{I2} \phi_{I3}...\phi_{IN}|$. Excellent overviews of many of these methods are included in ref 1.

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

*1. The multiconfigurational self-consistent field (MCSCF) method,*[30] in which the expectation value $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ is

(27) Koopmans, T. *Physica* 1933, *1*, 104.

(28) Some of the integral packages and the techniques used to evaluate the integrals are described in: Csizmadia, I. G.; Harrison, M. C.; Moscowitz, J. W.; Sutcliffe, B. T. *Theor. Chim. Acta* 1966, *6*, 191. Clementi, E.; Davis, D. R. *J. Comput. Phys.* 1966, *1*, 223. Rothenberg, S.; Kollman, P.; Schwartz, M. E.; Hays, E. F.; Allen, L. C. *Int. J. Quantum Chem.* 1970, *S3*, 715. Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. Prog. No. 236, Quantum Chem. Prog. Exchange, Bloomington, IN. Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* 1976, *65*, 111. McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* 1978, *26*, 218.

(29) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* 1982, *3*, 385.

treated variationally and *simultaneously* made stationary with respect to variations in the $C_I$ and $C_{\nu,i}$ coefficients.

The energy functional is a quadratic function of the CI coefficients, and so one can express the stationary conditions for these variables in the secular form:

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

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

It is well-known that minimization of a function ($E$) of several nonlinear parameters (the $C_{\nu,i}$) is a difficult task that can suffer from poor convergence and may locate local rather than global minima. In an MCSCF wave function 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 hundred) chosen to describe essential correlations (i.e., configuration crossings, proper dissociation) and important dynamical correlations (those electron-pair correlations of angular, radial, left–right, etc., nature that arise when low-lying "virtual" orbitals are present).

*2. The configuration interaction (CI) method,*[31] in which 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 $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ stationary. In this process, the optimizations of the orbitals and of the CSF amplitudes are done in separate steps.

In the CI method, one usually attempts to realize a high-level treatment of electron correlation. The CI wave function is most commonly constructed from CSFs $\Phi_J$ that include the following:

1. All of the CSFs in the SCF or MCSCF wave function used to generate the molecular orbitals $\phi_i$. These CSFs 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 wave functions limited to include contributions through various levels of excitation are denoted S (singly excited), D (doubly), SD (singly and doubly), SDT (singly, doubly, and triply), and so on.

The orbitals from which electrons are removed can be restricted to focus attention on correlations among certain orbitals. For example, if excitations out of core electrons are excluded, one computes a total energy that contains no 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 wave functions including 5000–50 000 CSFs are routine, and functions with one to *several million* CSFs are within the realm of practicality.[32]

The need for such large CSF expansions should not come as a surprise considering (i) that each electron pair requires *at least*

two CSFs to form polarized orbital pairs and (ii) that there are of the order of $N(N-1)/2 = X$ electron pairs in an atom or molecule containing $N$ electrons, hence (iii) the number of terms in the CI wave function scales as $2^X$. For a molecule containing 10 electrons, there would be $2^{55} = 3.6 \times 10^{16}$ terms in the CI expansion. This may be an over estimate 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 molecular orbitals. 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[33] identify and compute nonzero $H_{I,J}$ and immediately add up contributions to the sum $\sum_J H_{I,J} C_J$. Iterative methods,[33] 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.

*3. The Møller–Plesset perturbation (MPPT) method*[34] uses the single-configuration SCF process (usually the UHF implementation) to determine a set of orbitals $\{\phi_i\}$. Then, using an unperturbed Hamiltonian equal to the sum of Fock operators for each of the $N$ electrons $H^0 = \sum_{i=1,N} F(i)$, perturbation theory is used to determine the $C_I$ amplitudes for the CSFs. The MPPT procedure[35] is a special case of many-body perturbation theory (MBBT) in which the UHF Fock operator is used to define $H^0$.

The amplitude for the *reference* CSF is taken as unity and the other CSFs' amplitudes are determined by Rayleigh–Schrödinger perturbation using $H - H^0$ 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 wave function $\Psi$ and energy $E$ are determined in an order-by-order manner. The perturbation equations *determine* what CSFs to include through any particular order. This is one of the primary strengths of this technique; it does not require one to make further (potentially arbitrary) choices, in contrast to the MCSCF and CI treatments where one needs to choose which CSFs to include or exclude.

For example, the first-order wave function correction $\Psi^1$ is

$$\Psi^1 = -\sum_{i<j,m<n} [\langle i,j|g|m,n\rangle - \langle i,j|g|n,m\rangle][\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]^{-1} |\Phi_{i,j}^{m,n}\rangle$$

where the SCF orbital energies are denoted $\epsilon_k$ and $\Phi_{i,j}^{m,n}$ represents a CSF that is *doubly excited* ($\phi_i$ and $\phi_j$ are replaced by $\phi_m$ and $\phi_n$) relative to $\Phi$. Only doubly excited CSFs contribute to the *first-order wave function*.

The energy $E$ is given through second order as

$$E = E_{\text{SCF}} - \sum_{i<j,m<n} |\langle i,j|g|m,n\rangle - \langle i,j|g|n,m\rangle|^2 / [\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]$$

Both $\Psi$ and $E$ are expressed in terms of two-electron integrals $\langle i,j|g|m,n\rangle$ coupling the virtual spin–orbitals to the spin–orbitals from which electrons were excited as well as the orbital energy differences $[\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]$ accompanying such excitations. Clearly, major contributions to the correlation energy are made by double excitations into virtual orbitals $\phi_m \phi_n$ with large $\langle i,j|g|m,n\rangle$ integrals and small orbital energy gaps $[\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]$.

(30) The articles by Werner, H.-J.; Shepard, R. in ACP Vol. 69 (see ref 1) provide up to date reviews of the status of this approach. The article by Wahl, A. C.; Das, G. in MTC Vol. 3 covers the "earlier" history on this topic. Bobrowicz, F. W.; Goddard, W. A. III provide, in MTC Vol. 3, an overview of the GVB approach, which can be viewed as a specific kind of MCSCF calculation. In addition to the references mentioned earlier in ACP and MTC, the following papers describe several of the advances that have been made in the MCSCF method, especially with respect to enhancing its rate and range of convergence: Dalgaard, E.; Jørgensen, P. *J. Chem. Phys.* **1978**, *69*, 3833. Jensen, H. J. A.; Jørgensen, P.; Ågren, H. *J. Chem. Phys.* **1987**, *87*, 457. Lengsfield, B. H., III; Liu, B. *J. Chem. Phys.* **1981**, *75*, 478.

(31) Boys, S. F. *Proc. Roy. Soc. London* **1950**, *A201*, 125. Also, the articles by: Shavitt, I.; Ross, B. O.; Siegbahn, P. E. M. in MTC, Vol. 3 give excellent overviews of the CI method.

(32) See, for example: Olsen, J.; Roos, B.; Jørgensen, P.; Jensen, H. J. A. *J. Chem. Phys.* **1988**, *89*, 2185. Olsen, J.; Jørgensen, P.; Simons, J. *Chem. Phys. Lett.* **1990**, *169*, 463.

(33) See, for example: Nesbet, R. K. *J. Chem. Phys.* **1965**, *43*, 311. Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87. For more modern applications of these "large-matrix" methods as related to the development of the "direct CI" technique, see: Roos, B. O.; Siegbahn, P. E. M. In *Modern Theoretical Chemistry*, Vol. 3, Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 7. Roos, B. *Chem. Phys. Lett.* **1972**, *15*, 153. For a good review, see: Saunders, V. R.; Van Lenthe, J. H. *Mol. Phys.* **1983**, *48*, 923.

(34) The essential features of the MPPT/MBPT approach are described in the following articles: Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545. Bartlett, R. J.; Silver, D. M. *J. Chem. Phys.* **1975**, *62*, 3258. Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(35) Kelly, H. P. *Phys. Rev.* **1963**, *131*, 684. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

In higher order corrections, contributions from CSFs that are singly, triply, etc., excited relative to $\Phi$ appear, and additional contributions from the doubly excited CSFs also enter. It is relatively common to carry MPPT/MBPT calculations through to third or fourth order in the energy. The GAUSSIAN-8X series of programs,[17] which have been used in thousands of important chemical studies, calculate $E$ in this manner.

*4. The coupled-cluster (CC) method*[36] expresses the wave function in a somewhat different manner:

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

where $\Phi$ is a single CSF (usually the UHF determinant) that is used in the SCF process to generate a set of spin–orbitals. The operator $T$ generates, when acting on $\Phi$, single, double, etc., excitations (in which one, two, etc., of the occupied spin–orbitals in $\Phi$ have been replaced by virtual spin–orbitals).

$T$ is expressed in terms of operators that effect such spin–orbital removals and additions as follows:

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

where the combination of operators $m^+i$ denotes *creation* of an electron in virtual spin–orbital $\phi_m$ and *removal* of an electron from occupied spin–orbital $\phi_i$ to generate a single excitation. The operation $m^+n^+ji$ 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

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

against CSFs that are single, double, etc., excitations relative to $\Phi$:

$$\langle\Phi_i^m|H + [H,T] + \tfrac{1}{2}[[H,T],T] + \tfrac{1}{6}[[[H,T],T],T] +$$
$$\tfrac{1}{24}[[[[H,T],T],T],T]|\Phi\rangle = 0$$

$$\langle\Phi_{i,j}^{m,n}|H + [H,T] + \tfrac{1}{2}[[H,T],T] + \tfrac{1}{6}[[[H,T],T],T] +$$
$$\tfrac{1}{24}[[[[H,T],T],T],T]|\Phi\rangle = 0$$

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

and so on for higher order excited CSFs. It can be shown[37] that the expansion of the exponential operators truncates exactly at the fourth power.

As a result, the exact CC equations are *quartic equations* for the $t_i^m$, $t_{i,j}^{m,n}$, etc., amplitudes. Although it is a rather formidable task, all of the matrix elements appearing in the CC equations have been expressed in terms of one- and two-electron integrals over the spin–orbitals including those in $\Phi$ itself and the "virtual" orbitals not in $\Phi$.

These quartic equations are solved in an iterative manner and are susceptible to convergence difficulties similar to those that arise in MCSCF calculations. 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 $i',j',m',n'$). This gives $t$ amplitudes that are equal to the amplitudes of the first-order MPPT/MBPT wave function:

$$t_{i,j}^{m,n} = -\langle i,j|g|m,n\rangle'/[\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]$$

where the prime on $\langle i,j|g|m,n\rangle'$ indicates the combination of integrals $\langle i,j|g|m,n\rangle - \langle i,j|g|n,m\rangle$. As Bartlett and Pople have both demonstrated,[38] 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.

*5. The density functional or $X_\alpha$ methods*[39] provide alternatives to the conventional approaches. The family of approaches that often are referred to as $X_\alpha$-type methods is realizing a renewed importance and popularity in quantum chemistry; a density functional module is rumored likely to appear in the next version of GAUSSIAN 9X. Therefore, a brief overview is in order.

The CI, MCSCF, MPPT/MBPT, and CC methods move beyond the single-configuration picture in a rather straightforward manner; they add to the expansion of the wave function more configurations whose amplitudes they each determine in their own way. This can lead to a very large number of CSFs in the correlated wave function, and, as a result, a large need for computer resources.

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

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

in which the orbitals $\{\phi_i\}$ "feel" potentials due to the nuclear centers (labeled $A$ and having charges $Z_A$), due to Coulombic interaction with the *total* electron density $\rho(\mathbf{r'})$, and due to a so-called correlation-exchange potential, which will be denoted $U_{X_\alpha}(\mathbf{r'})$. The particular electronic state for which the calculation is being performed is specified by forming a corresponding density $\rho(\mathbf{r'})$.

This potential $U_{X_\alpha}(\mathbf{r'})$ must remove the "self-interaction" of the electron in $\phi_i(\mathbf{r})$ that is incorrectly included in $\int\rho(\mathbf{r'})e^2/|\mathbf{r} - \mathbf{r'}|\,d\mathbf{r'}\,\phi_i(\mathbf{r})$. The self-interaction is included in this integral because $\rho(\mathbf{r'})$ represents the *total* electron density at $\mathbf{r'}$, including that due to the electron in $\phi_i$. To compensate for this incorrect evaluation of the electron–electron interactions, $U_{X_\alpha}$ must include terms that remove the self-interactions.

The fundamental theory that underlies the density functional methods dates to work of Hohenberg and Kohn,[40] who showed that the *ground-state* energy $E_0$ of an $N$-electron system can be expressed as a *functional* (not necessarily a function) of the electron density $\rho(\mathbf{r})$ of that system. A great deal of work has subsequently been devoted to (i) finding a functional relationship for $E_0[\rho]$ in terms of $\rho(\mathbf{r})$ and (ii) finding computational schemes to compute $\rho(\mathbf{r})$ and then $E_0$ in an efficient manner.

Researchers studying the idealized "uniform electron gas" found that the exchange and correlation energy (per electron) for this system could be written exactly as a *function* of the electron density $\rho$ of the system: $E_{exchange} = W(\rho)$. This motivated workers to suggest that this exact result could be used to define, for each point in $\mathbf{r}$ space, a correlation-exchange potential $W(\mathbf{r}) = W(\rho(\mathbf{r}))$ and that $W(\mathbf{r})$ could be used to generate the exchange energy by integrating over all points $\mathbf{r}$:

$$E_{exchange} = \int \rho(\mathbf{r}) \, W(\rho(\mathbf{r})) \, d\mathbf{r}$$

These studies of the uniform electron gas influenced early work by Slater and co-workers,[41] who focused on single-configuration

(36) The early work in chemistry on this method is described in: Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256. Paldus, J.; Cizek, J.; Shavitt, I. *Phys. Rev.* **1972**, *A5*, 50. Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561. Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(37) This is demonstrated in: Jørgensen, P.; Simons, J. *Second Quantization Based Methods in Quantum Chemistry*, Academic Press: New York, 1981; Chapter 4.

(38) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545.

(39) For excellent overviews of the history and more recent developments in this area, see, for example: Jones, R. O. *Adv. Chem. Phys.* **1987**, *67*, 413. Dunlap, B. I. *Adv. Chem. Phys.* **1987**, *69*, 287. Dahl, J. P., Avery, J., Eds. *Local Density Approximations in Quantum Chemistry and Solid State Physics*; Plenum: New York, 1984. Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631. Salahub, D. R.; Lampson, S. H.; Messmer, R. P. *Chem. Phys. Lett.* **1982**, *85*, 430. Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta (Berlin)* **1977**, *43*, 261. Becke, A. *J. Chem. Phys.* **1983**, *76*, 6037. Case, D. A. *Annu. Rev. Phys. Chem.* **1982**, *33*, 151.

(40) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.

descriptions where the electron density is straightforwardly evaluated in terms of the orbitals $\{\phi_j\}$:

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

Here $n_j = 0$, 1, or 2 is the occupation number of the orbital $\phi_j$ in the state being studied. Combining the single-configuration ansatz with the approximation that the exchange contributions to $E_0[\rho]$ be represented by the "uniform electron gas" (ueg) value

$$W_{\text{ueg}}(\mathbf{r}) = -\tfrac{9}{4}\rho(\mathbf{r})(3\rho(\mathbf{r})/8\pi)^{1/3}$$

Slater arrived at an orbital-level equation for the $\{\phi_j\}$ that define $\rho$:

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

where

$$U_{\text{ueg}}(\mathbf{r}) = -\tfrac{9}{2}(3\rho(\mathbf{r})/8\pi)^{1/3}$$

However, Slater found the uniform electron gas estimate of the exchange function overestimated the magnitude of the exchange energy when compared to results of ab initio calculations. He therefore introduced an empirical scaling of the expression for $U_{\text{ueg}}(\mathbf{r})$ and proposed that

$$U_{\text{X}_\alpha}(\mathbf{r}) = -9\alpha/2(3\rho(\mathbf{r})/8\pi)^{1/3}$$

be used in its place. Slater named the scaling parameter $\alpha$, which is the origin of the name of the $\text{X}_\alpha$ procedure (the X denoting exchange).

Although Slater's work emphasized a single-configuration picture of electronic structure where the evaluation of $\rho(\mathbf{r})$ as a sum $\sum_j n_j|\phi_j(\mathbf{r})|^2$ is straightforward, the fundamental theory behind density functional methods applies to exact energies if an exact $E_0[\rho]$ functional and an exact density $\rho(\mathbf{r})$ are used.

Within the $\text{X}_\alpha$ modification of the local uniform gas density functional (sometimes called the local density approximation (LDA)) $U_{\text{X}_\alpha}(\mathbf{r}) = -9\alpha/2(3\rho(\mathbf{r})/8\pi)^{1/3}$, it has empirically been found that using a value of $\alpha$ near $^2/_3$ produces orbital and total energies that most closely reproduce high-quality ab initio and experimental values. Moreover, Kohn and Sham[42] have shown that the value $\alpha = ^2/_3$ can be derived from a variational theory as the optimal value.

Most of the early applications of density functional methods solved equations of the form

$$\left[-\hbar^2/2m_e\nabla^2 - \sum_A Z_A e^2/|\mathbf{r} - \mathbf{R}_A| + \right.$$
$$\left. \int \rho(\mathbf{r}')e^2/|\mathbf{r} - \mathbf{r}'|\ d\mathbf{r}' + U_{\text{X}_\alpha}(\mathbf{r})\right]\phi_i = \epsilon_i\phi_i$$

in terms of functions expressed as "scattered waves" defined locally in spherical regions of space surrounding each atom in the molecule or solid. In this so-called *muffin tin* view, the volume of space available to electrons in the molecule is divided into atom-centered spheres, regions lying outside such atom-centered spheres yet inside a so-called "outer sphere" surrounding the molecule, and a region lying beyond the outer sphere. In the atom-centered regions and within the outer sphere, the orbital-level equations are easily solved (the angular and radial parts separate because the potential is assumed to be spherically averaged and thus angle independent). These scattered-wave solutions are then matched at the boundaries among the atom-centered spheres and the outer sphere.

The muffin-tin potential approach was shown to suffer when applied to molecules of low symmetry. Therefore, it became more common to not introduce the local muffin-tin potentials but simply

to solve the density functional orbital equations using atomic basis sets such as those utilized in conventional ab initio quantum chemistry. The individual orbitals $\phi_j(\mathbf{r})$ can easily be expanded in terms of the atomic orbital basis as in the LCAO-MO expansion; it is also straightforward to express $\rho(\mathbf{r}) = \sum_j n_j|\phi_j(\mathbf{r})|^2$ or even the multiconfigurational analogue $\rho(\mathbf{r}) = \sum_{i,j}\gamma_{ij}\phi_i^*(\mathbf{r})\ \phi_j(\mathbf{r})$, in like fashion. However, to express the $U_{\text{ueg}}(\mathbf{r}) = -\tfrac{9}{2}(3\rho(\mathbf{r})/8\pi)^{1/3}$ in terms of an atomic orbital basis requires considerably more effort; several approaches to this problem exist and are in common use.

In the simplest version of density functional theory, the total energy $E$ is computed as

$$E = \sum_j n_j\epsilon_j$$

where $\epsilon_j$ are the orbital energies obtained from the $\text{X}_\alpha$-like equations. Although the sum-of-orbital-energies does not correctly represent the total energy in the CI, MCSCF, MPPT/MBPT, or CC approaches, it can be shown that it is reasonably correct for these methods. A more accurate alternative is to compute $E$ as

$$E = \sum_j n_j\langle\phi_j| - \hbar^2/2m_e\nabla^2|\phi_j\rangle - \int \rho(\mathbf{r})Z_A e^2/|\mathbf{r} - \mathbf{R}_A|\ d\mathbf{r} +$$
$$\tfrac{1}{2}\int \rho(\mathbf{r})\ \rho(\mathbf{r}')e^2/|\mathbf{r} - \mathbf{r}'|\ d\mathbf{r}\ d\mathbf{r}' - \int \tfrac{9}{4}\rho(\mathbf{r})(3\rho(\mathbf{r})/8\pi)^{1/3}\ d\mathbf{r}$$

Once the orbitals are found by solving the above equations, the kinetic energy integrals, the electron–nuclear attraction integral, and the Coulomb integral can be evaluated by using conventional ab initio basis set tools. As stated above, the exchange correlation integral is more difficult to treat because $[\rho(\mathbf{r})]^{1/3}$ appears; $\rho(\mathbf{r})$ is easily expanded in a basis, but $[\rho(\mathbf{r})]^{1/3}$ requires a separate expansion.

Various density functional approaches are under active development and thus appear in the literature in many forms; ref 39 describes many of the historically important developments as well as several of the more recent advances. Because the computational effort involved in these approaches scales much less strongly with basis set size than for conventional (SCF, MCSCF, CI, etc.) methods, density functional methods offer great promise and are likely to contribute much to quantum chemistry in the next decade.

*B. Computational Requirements, Strengths, and Weaknesses of Various Methods. 1. Computational steps*: Essentially all of the above techniques require the evaluation of one- and two-electron integrals over the $N$ atomic *orbital basis* functions: $\langle\chi_a|f|\chi_b\rangle$ and $\langle\chi_a\chi_b|g|\chi_c\chi_d\rangle$. As mentioned earlier, there are of the order of $N^4/8$ such integrals that must be computed (and perhaps stored on disk); their computation and storage are a major consideration in performing conventional ab initio calculations.

The density functional approaches, because they involve basis expansions of orbitals $\phi_i = \sum_\nu C_{i,\nu}\chi_\nu$ and of the density $\rho$, which is a quadratic function of the orbitals ($\rho = \sum_i n_i|\phi_i|^2$), require computational effort scaling only as $N^2$. This is one of the most important advantages of these schemes. Moreover, wave functions that must be characterized by two or more dominant electronic configurations (e.g., as in Woodward–Hoffmann-forbidden reactions) are treated within density functional approaches by specifying a density that properly embodies the multiconfigurational nature of the state. No cumbersome large CSF expansion and associated large secular eigenvalue problem arise. This is another advantage of density functional methods.

The conventional quantum chemistry methods provide their working equations and energy expressions in terms of one- and two-electron integrals over the final *molecular orbitals*: $\langle\phi_i|f|\phi_j\rangle$ and $\langle\phi_i\phi_j|g|\phi_k\phi_l\rangle$. The MO-based integrals can only be evaluated by *transforming* the AO-based integrals[43] as follows:

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

$$\langle\phi_i|f|\phi_j\rangle = \sum_{a,b}C_{a,i}C_{b,j}\langle\chi_a|f|\chi_b\rangle$$

(41) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4. Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.
(42) Kohn, W.; Sham, L. *J. Phys. Rev.* **1965**, *B13*, 4274.

It is possible to perform the full transformation of the two-electron integral list in a time that scales as $4N^5$. 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.

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

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

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

So-called *complete-active-space* (CAS) methods form *all* CSFs that can be created by distributing $N$ valence electrons among $P$ valence orbitals. For example, the eight non-core electrons of $H_2O$ might be distributed, in a manner that gives $M_S = 0$, among six valence orbitals (e.g., two lone-pair orbitals, two OH $\sigma$-bonding orbitals, and two OH $\sigma^*$-antibonding orbitals). The number of configurations thereby created is 225. If the same 8 electrons were distributed among 10 valence orbitals 44 100 configurations results; 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 by using a few valence orbitals. The primary advantage of CAS configurations is discussed in section VI.B.3.

*2. Variational methods provide upper bounds to energies*: Methods that are based on making the energy functional $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ stationary yield *upper bounds* to the lowest energy state having the symmetry of the CSFs in $\Psi$. The CI and MCSCF methods are of this type. They also provide approximate excited-state energies and wave functions in the form of other solutions of the secular equation[44] $\sum_J H_{I,J} C_J = EC_I$.

Excited-state energies obtained in this manner "bracket" the true energies of the given symmetry; that is, between any two approximate energies obtained in the variational calculation, there exists at least one true eigenvalue. This characteristic is commonly referred to[45] as the "bracketing theorem". 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.

*3. Variational methods are not size-extensive*: However, all variational techniques suffer from at least one serious drawback; they are not necessarily *size-extensive*.[46] The energy computed by using these tools can not be trusted to scale with the size of the system. For example, a calculation performed on two $CH_3$ species at large separation may not yield an energy equal to twice the energy obtained by performing the *same* kind of calculation on a single $CH_3$ species. Lack of size-extensivity precludes these methods from use in extended systems (e.g., solids) where errors due to improper size scaling of the energy produce nonsensical results.

By carefully adjusting the variational wave function used, it is *possible* to circumvent size-extensivity problems for selected species. For example, CI calculation on $Be_2$ using *all* $^1\Sigma_g$ 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[47] are size extensive; this is one of the primary benefits of CAS CSFs.

Unfortunately, it is impractical to extend such an approach to larger systems. The Be example shows that if the "monomer" (Be atom) requires $K$-fold excited CSFs relative to its dominant CSF (Be requires doubly excited CSFs), a size-extensive variational calculation on the "dimer" ($Be_2$) requires $2K$-fold excited CSFs. A size-extensive variational calculation on a species containing $M$ monomers therefore requires $M \times K$-fold excited CSFs; for $Be_6$ 12-fold excited CSFs are needed.

*4. 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 coupled-cluster methods achieve their energies by projecting the Schrödinger equation against a reference function $\langle \Phi |$ to obtain[48] a *transition formula* $\langle \Phi | H | \Psi \rangle$, rather than from an expectation value $\langle \Psi | H | \Psi \rangle$. It can be shown that this difference allows nonvariational techniques to yield size-extensive energies.

This can be seen by considering the second-order MPPT energy of two noninteracting 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; these integrals (e.g., $\langle 2s_a 2p_a | g | 2s_b 2p_b \rangle$) 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 weakness. Their energies do *not* provide upper bounds to the true energies of the system (because their energy functional is not of the expectation-value form for which the upper bound property has been proven). Moreover, they express the correct wave function in terms of corrections to a (presumed dominant) reference function that is usually taken to be a single CSF (although efforts are being made to extend the MPPT/MBPT and CC methods to allow for multiconfigurational reference functions). For situations such as Woodward–Hoffmann-forbidden reactions in which two CSFs "cross" along a reaction path, the single-dominant-CSF assumption breaks down, and these methods have difficulty.

(43) Nesbet, R. K. *Rev. Mod. Phys.* **1963**, *35*, 552. 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.
(44) See the discussions of the CI and MCSCF methods in MTC and ACP in ref 1.
(45) Hylleraas, E. A.; Undheim, B. *Z. Phys.* **1930**, *65*, 759. MacDonald, J. K. L. *Phys. Rev.* **1933**, *43*, 830.

(46) Pople, J. A. In *Energy, Structure, and Reactivity*; Smith, D. W., McRae, W. B., Eds.; Wiley: New York, 1973; p 51.
(47) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. Also, see the article by B. O. Roos in ACP for an overview of this approach.[1]
(48) Kelly, H. P. *Phys. Rev.* **1963**, *131*, 684.

## VII. Summary

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

For all calculations, the choice of atomic orbital basis set must be made carefully, keeping in mind the $N^4$ scaling of the one- and two-electron integral evaluation step and the $N^5$ scaling of the two-electron integral transformation step. Of course, basis functions that describe the essence of the states to be studied are essential (e.g., Rydberg or anion states require diffuse functions, and strained rings require polarization functions).

As larger atomic basis sets are employed, the size of the CSF list used to treat dynamic correlation increases rapidly. For example, most of the above methods use singly and doubly excited CSFs for this purpose. For large basis sets, the number of such CSFs, $N_C$, scales as the number of electrons squared $n_e^2$ times the number of basis functions squared $N^2$. Since the effort needed to solve the CI secular problem varies as $N_C^2$ or $N_C^3$, a dependence as strong as $N^4$ to $N^6$ can result. To handle such large CSF spaces, all of the multiconfigurational techniques mentioned in this paper have been developed to the extent that calculations involving of the order of 100–5000 CSFs are routinely performed and calculations using 10 000, 100 000, and even several million CSFs are practical. A benchmark CI calculation involving one billion determinants[49] demonstrates the computational tractability of such large CSF expansion methods.

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

(49) Olsen, J.; Jørgensen, P.; Simons, J. *Chem. Phys. Lett.* 1990, *169*, 463.

# ARTICLES

# Electron Excitation Energy Transfer from Highly Excited Cs Atoms Forming High Rydberg State Atoms and Molecules

**Jörgen Lundin and Leif Holmlid\***

*Department of Physical Chemistry GU, University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden (Received: November 15, 1989; In Final Form: August 20, 1990)*
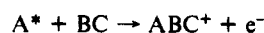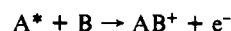
The reactions of excited Cs atoms with various gases have been studied in a quadrupole mass spectrometer ion source. The excited atoms are formed in a thermionic converter (TIC) plasma and are sampled into the ion source as a molecular beam. Direct field ionization of the excited states from the plasma at field strengths up to 600 V/cm in the ion source gives ions $Cs^+$, $Cs^{2+}$, and $H_2^+$. The intensity of the doubly ionized Cs is often larger than that of singly ionized Cs, and it is believed to be formed from $Cs^{2*}$. The doubly excited Cs is found to transfer its excitation energy to gas molecules M in the ion source, as $Cs^{2*} + M \rightarrow Cs^*$ (or Cs) $+ M^*$. The excited molecules are field ionized to $M^+$ or dissociate to smaller ions. Charge-exchange reactions are excluded, especially due to the low electron affinity of Cs. The variation of the positive current of $M^+$ is studied as a function of gas pressure between $10^{-6}$ and $10^{-4}$ mbar. During inlet of some gases, e.g. $CO_2$, almost *all* mass peaks vary linearly with pressure, which is interpreted as excitation transfer from the Rydberg states of $CO_2$ to other atoms and molecules. The initial excitation-transfer cross sections are estimated to be 4000–10 000 $Å^2$, corresponding approximately to $n = 10$ for $Cs^{2*}$.

## 1. Introduction

Reactions of Rydberg atoms have been studied by a number of research groups. Such processes may have the form of charge transfer[1-3]

$$A^* + X \rightarrow A^+ + X^-$$

$$A^* + B \rightarrow A^+ + B + e^-$$
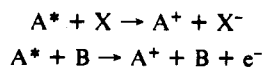
or associative ionization[3,4]

$$A^* + B \rightarrow AB^+ + e^-$$

$$A^* + BC \rightarrow ABC^+ + e^-$$

For some processes very large cross sections of the order of $10^3$–$10^4$ $Å^2$ have been reported.[2,3] Since processes with such large cross