

Modern Theoretical Chemistry. Vol. 4

*Applications of*  
*Electronic*  
*Structure*  
*Theory*

*Edited by*  
*Henry F. Schaefer III*

*Applications of*  
***Electronic***  
***Structure***  
***Theory***

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## *Preface*

These two volumes deal with the quantum theory of the electronic structure of molecules. Implicit in the term *ab initio* is the notion that approximate solutions of Schrödinger's equation are sought "from the beginning," i.e., without recourse to experimental data. From a more pragmatic viewpoint, the distinguishing feature of *ab initio* theory is usually the fact that no approximations are involved in the evaluation of the required molecular integrals. Consistent with current activity in the field, the first of these two volumes contains chapters dealing with methods *per se*, while the second concerns the application of these methods to problems of chemical interest. In a sense, the motivation for these volumes has been the spectacular recent success of *ab initio* theory in resolving important chemical questions. However, these applications have only become possible through the less visible but equally important efforts of those developing new theoretical and computational methods and models.

*Henry F. Schaefer*

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# A Priori Geometry Predictions

J. A. Pople

## 1. Introduction

Early quantum mechanical computations on the electronic structure of molecules were generally concerned with the determination of a wave function for a single assumed nuclear geometry (usually an experimentally determined equilibrium structure). As techniques have improved, however, it has increasingly become possible to make explorations of potential surfaces (total energies for heavy nuclei in the Born–Oppenheimer approximation) and hence to use theory directly to locate the minima in such surfaces and the corresponding equilibrium structural parameters. Such explorations can either be carried out partially, that is assuming some parameters and varying others (as in the study of “rigid” internal rotation with fixed bond lengths and angles) or, more desirably, by complete minimization of the energy with respect to all variables. Given the quantum mechanical procedure, the latter leads to *a priori* predictions of structure making no appeal to experimental data other than using the values of fundamental constants. Theoretical structures of this sort have been used for two main purposes. The first is to assess how well experimentally known structures are reproduced at a given level of theory and hence evaluate the limitations of the theory in a systematic manner. Second, the theory has been increasingly used to investigate structures of molecules for which experimental data are insufficient. Many such predictions have been made and there is an increasing number of examples of subsequent experimental verification.

In this chapter most attention will be devoted to structural prediction at the Hartree–Fock level, that is using a single-determinant molecular orbital wave function with a basis-set expansion. Most of the applications carried out to date have been at this level. If the basis set is sufficiently large the results

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should be independent of detail and characteristic of a geometry at the Hartree-Fock limit. However, for basis sets of limited size, as is presently necessary for large molecules, the predicted structures will depend on the basis used. Under these circumstances it is desirable to select a well-defined small basis set and then use it systematically for extensive exploration. This is the concept of a "theoretical model chemistry" in which a uniform level of approximation is used throughout.<sup>(1)</sup> It is a valuable approach in that it permits discussion of relative structural features and general trends even though absolute agreement with experimental data is lacking. We shall review some Hartree-Fock model chemistries of this type. Probably the most widely used models are those including a minimal basis of Slater-type orbitals.<sup>(2)</sup>

For some small molecules, geometrical studies have been carried out with sufficiently large basis sets for the Hartree-Fock limiting structure to be well established. These show a number of systematic deviations from experimental data. To correct these it is necessary to go beyond single-determinant wave functions and investigate modifications of equilibrium geometry due to corrections for the correlation of the motion of electrons with different spin. This involves configuration interaction or some other equivalent higher level of approximation. If carried out to sufficient extent, such treatments should generally lead to highly accurate structural predictions since the remaining relativistic energy corrections are mostly associated with inner-shell electrons and, hence, are likely to be largely independent of nuclear positions. The number of structural studies of polyatomic molecules using correlated wave functions is still relatively small, but some interesting trends are already becoming evident. These will be reviewed in the latter part of this chapter.

## **2. Equilibrium Geometries by Hartree-Fock Theory**

### **2.1. Restricted and Unrestricted Hartree-Fock Theories**

The fundamental feature of Hartree-Fock theory is the use of a single-determinant wave function  $\Psi$  which is formed from a set of occupied spin-orbitals  $\chi_1, \chi_2, \dots, \chi_n$

$$\Psi = A \det\{\chi_1(1)\chi_2(2)\cdots\chi_n(n)\} \quad (1)$$

where  $n$  is the number of electrons,  $A$  is a normalization constant, and the diagonal element product of the determinant is specified explicitly in Eq. (1). The spin-orbitals are, in general, one-electron functions in the space of the Cartesian and spin coordinates. Before proceeding to the discussion of geometry predictions using Hartree-Fock theory it is desirable to identify constraints which are sometimes imposed on the spin-orbitals. These con-

straints are of some importance since the self-consistent, or Hartree-Fock, orbitals  $\chi_i$  are derived by variation to minimize the energy expectation,

$$E = \int \cdots \int \Psi^* \mathcal{H} \Psi d\tau_1 \cdots d\tau_n \quad (2)$$

$\mathcal{H}$  being the total Hamiltonian. Imposition of constraints must raise (or possibly leave unchanged) the value of the energy (2) for any nuclear arrangement.

In a completely unconstrained Hartree-Fock theory no limitations are placed on the functions  $\chi_i$  other than orthonormality, which may be imposed without restriction of the full wave function  $\Psi$ . This version of the theory is rarely used. A common assumption is to use products of ordinary molecular orbitals  $\psi$  (functions of only the Cartesian coordinates  $x$ ,  $y$ , and  $z$ ) and spin functions  $\alpha$  and  $\beta$ . The spin-orbitals are then

$$\psi_i^\alpha \alpha, \quad \psi_i^\beta \beta, \quad i = 1, 2, \dots \quad (3)$$

If the molecular orbitals  $\psi_i^\alpha$  associated with  $\alpha$  spin are varied, completely independently of those associated with  $\beta$  spin ( $\psi_i^\beta$ ), the method is described as "spin-unrestricted Hartree-Fock" (SUHF or UHF) or sometimes as "different orbitals for different spins." If, on the other hand, the molecular orbitals for the  $\alpha$  set are constrained to be identical with the  $\beta$  set where both are occupied, they are then described as "doubly or singly occupied" and the corresponding theory is "spin-restricted Hartree-Fock" (SRHF or RHF). In some situations the additional flexibility in UHF theory does not lead to any energy lowering relative to RHF, but for most systems with unpaired electrons there is such a difference.

The relation between RHF and UHF theories is of some importance in geometry predictions for the following reason. It can be shown that RHF wave functions are strictly eigenfunctions of the total spin operator  $\mathbf{S}^2$  and so correspond to pure singlet, doublet, triplet, etc., electronic states. UHF functions, on the other hand, are not always eigenfunctions of  $\mathbf{S}^2$  and may lead to "contaminated" wave functions where a primarily double wave function, for example, may also have some quartet character. If this contamination becomes large, the search for a minimum, corresponding to a doublet state, may produce a structure partly characteristic of a neighboring higher-multiplicity quartet state.

Another constraint that is sometimes imposed is the requirement that the molecular orbitals  $\psi_i$  belong to irreducible representations of the point group of the nuclear framework. Again, this restriction does not necessarily raise the energy, but if it does, the constraint is undesirable since small distortions which break the symmetry would lead to discontinuity in the potential surface.

In practice, the molecular orbitals are normally expanded as linear combinations of a set of basis functions  $\varphi_\mu(x, y, z)$ . For UHF theory,

$$\begin{aligned}\psi_i^\alpha &= \sum_\mu c_{\mu i}^\alpha \varphi_\mu \\ \psi_i^\beta &= \sum_\mu c_{\mu i}^\beta \varphi_\mu\end{aligned}\quad (4)$$

In RHF theory, the  $c^\alpha$  and  $c^\beta$  matrices are constrained to be identical. Algebraic equations for RHF coefficients, if the orbitals are doubly occupied (or empty), were given by Roothaan.<sup>(3)</sup> The corresponding UHF equations are due to Pople and Nesbet.<sup>(4)</sup> The RHF equations with both doubly and singly occupied orbitals are rather more complicated, but several algebraic procedures are available.<sup>(5-8)</sup> Once the optimized self-consistent energy is obtained, as a function of geometrical parameters, the subsequent minimization to locate the potential surface minimum can be carried out by any of a wide range of general optimization techniques.<sup>(9)</sup>

## 2.2. Basis Sets for Hartree-Fock Studies

In published Hartree-Fock calculations a wide variety of basis sets  $\varphi_\mu$  are used. Since certain features of predicted structures depend on the nature of the basis set, some survey of the bases commonly used is desirable.

The earliest wave function computations were generally based on the use of Slater-type functions<sup>(2)</sup> as approximations to atomic orbitals. These are functions with exponential radial parts such as

$$\begin{aligned}\varphi_{1s} &= (\zeta_1^3/\pi)^{1/2} \exp(-\zeta_1 r) \\ \varphi_{2s} &= (\zeta_2^5/3\pi)^{1/2} r \exp(-\zeta_2 r) \\ \varphi_{2p} &= (\zeta_2^5/\pi)(x, y, z) \exp(-\zeta_2 r)\end{aligned}\quad (5)$$

and similar forms for  $3s, 3p, 3d, \dots$ . If the Slater-type functions correspond just to those shells which are populated (or partly populated) in the atomic ground states, the basis is described as *minimal* (e.g.,  $1s$  only for hydrogen,  $1s, 2s, 2p$  for carbon, etc.).

The direct use of the Slater-type basis functions (5) leads to difficult two-electron repulsion integrals. Such integrals can be evaluated by methods such as the Gaussian transform technique proposed by Shavitt and Karplus.<sup>(10)</sup> A number of structural studies have been made by such methods. However, it turns out that a more efficient procedure, leading to equivalent results, uses the replacement of Slater-type functions with linear combinations of Gaussian functions obtained by least-squares fitting.<sup>(11-14)</sup> All integrals can then be explicitly evaluated. In the fits proposed by Hehre, Stewart, and Pople,<sup>(4)</sup> each Slater-type function  $\varphi_\mu$  is replaced by a linear combination of  $K$  Gaussian