

Section 6 More Quantitative Aspects of Electronic Structure Calculations.

Chapter 17

Electrons interact via pairwise Coulomb forces; within the "orbital picture" these interactions are modelled by less difficult to treat "averaged" potentials. The difference between the true Coulombic interactions and the averaged potential is not small, so to achieve reasonable (ca. 1 kcal/mol) chemical accuracy, high-order corrections to the orbital picture are needed.

The discipline of computational *ab initio* quantum chemistry is aimed at determining the electronic energies and wavefunctions 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 is too difficult to solve 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 that allow quantitative predictions to be made.

Essentially all *ab initio* quantum chemistry methods use, as a starting point from which improvements are made, a picture in which the electrons interact via a one-electron additive potential. These so-called **mean-field** potentials $V_{\text{mf}}(\mathbf{r}) = \sum_j V_{\text{mf}}(\mathbf{r}_j)$ provide descriptions of atomic and molecular structure that are approximate. Their predictions must be improved to achieve reasonably accurate solutions to the true electronic Schrödinger equation. In so doing, three constructs that characterize essentially all *ab initio* quantum chemical methods are employed: **orbitals, configurations, and electron correlation.**

Since the electronic kinetic energy $T = \sum_j T_j$ operator is one-electron additive, the mean-field Hamiltonian $H^0 = T + V_{\text{mf}}$ is also of this form. The additivity of H^0 implies that the mean-field wavefunctions $\{\psi_k^0\}$ can be formed in terms of products of functions $\{\psi_k\}$ of the coordinates of the individual electrons, and that the corresponding energies $\{E_k^0\}$ are additive. Thus, it is the ansatz that V_{mf} is separable that leads to the concept of

orbitals, which are the one-electron functions $\{ \psi_j \}$. These orbitals are found by solving the one-electron Schrödinger equations:

$$(T_1 + V_{mf}(\mathbf{r}_1)) \psi_j(\mathbf{r}_1) = \epsilon_j \psi_j(\mathbf{r}_1);$$

the eigenvalues $\{ \epsilon_j \}$ are called **orbital energies**.

Because each of the electrons also possesses intrinsic spin, the one-electron functions $\{ \psi_j \}$ used in this construction are taken to be eigenfunctions of $(T_1 + V_{mf}(\mathbf{r}_1))$ multiplied by either α or β . This set of functions is called the set of mean-field **spin-orbitals**.

Given the complete set of solutions to this one-electron equation, a complete set of N-electron mean-field wavefunctions can be written down. Each Φ_k is constructed by forming an antisymmetrized product of N spin-orbitals chosen from the set of $\{ \psi_j \}$, allowing each spin-orbital in the list to be a function of the coordinates of one of the N electrons (e.g,

$$\Phi_k = | \psi_{k1}(\mathbf{r}_1) \psi_{k2}(\mathbf{r}_2) \psi_{k3}(\mathbf{r}_3) \dots \psi_{kN-1}(\mathbf{r}_{N-1}) \psi_{kN}(\mathbf{r}_N) |,$$

as above). The corresponding mean field energy is evaluated as the sum over those spin-orbitals that appear in Φ_k :

$$E_k^0 = \sum_{j=1,N} \epsilon_j.$$

By choosing to place N electrons into specific spin-orbitals, one has specified a **configuration**. By making other choices of which N ψ_j to occupy, one describes other configurations. Just as the one-electron mean-field Schrödinger equation has a complete set of spin-orbital solutions $\{ \psi_j \text{ and } \psi_j \}$, the N-electron mean-field Schrödinger equation has a complete set of N-electron configuration state functions (CSFs) Φ_k and energies E_k^0 .

II. Electron Correlation Requires Moving Beyond a Mean-Field Model

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 be told that 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 $1s^2 2s^2 2p^2$, $1s^2 2s^2 3p^2$, $1s^2 2s^2 3d^2$, $2s^2 3s^2 2p^2$ (and any other configurations whose angular momenta can be coupled to produce $L=1$ and $S=1$).

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 describe the proper eigenstates $\{ \psi_k, E_k \}$. 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 wavefunction is capable of treating electron correlation to any extent; its product nature renders it incapable of doing so.

III. Moving from Qualitative to Quantitative Models

The preceding Chapters introduced, in a qualitative manner, many of the concepts which are used in applying quantum mechanics to electronic structures of atoms and molecules. Atomic, bonding, non-bonding, antibonding, Rydberg, hybrid, and delocalized orbitals and the configurations formed by occupying these orbitals were discussed. Spin and spatial symmetry as well as permutational symmetry were treated, and properly symmetry-adapted configuration state functions were formed. The Slater-Condon rules were shown to provide expressions for Hamiltonian matrix elements (and those involving any one- or two-electron operator) over such CSFs in terms of integrals over the orbitals occupied in the CSFs. Orbital, configuration, and state correlation diagrams were introduced to allow one to follow the evolution of electronic structures throughout a 'reaction path'.

Section 6 addresses the quantitative and computational implementation of many of the above ideas. It is not designed to address all of the state-of-the-art methods which have been, and are still being, developed to calculate orbitals and state wavefunctions. The rapid growth in computer hardware and software power and the evolution of new computer architectures makes it difficult, if not impossible, to present an up-to-date overview of the techniques that are presently at the cutting edge in computational chemistry. Nevertheless, this Section attempts to describe the essential elements of several of the more powerful and commonly used methods; it is likely that many of these elements will persist in the next

generation of computational chemistry techniques although the details of their implementation will evolve considerably. The text by Szabo and Ostlund provides excellent insights into many of the theoretical methods treated in this Section.

IV. Atomic Units

The electronic Hamiltonian is expressed, in this Section, in so-called atomic units (aus)

$$H_e = \sum_j \left\{ -\frac{1}{2} \nabla_j^2 - \sum_a \frac{Z_a}{r_{j,a}} \right\} + \sum_{j < k} \frac{1}{r_{j,k}} .$$

These units are introduced to remove all \hbar , e , and m_e factors from the equations.

To effect this unit transformation, one notes that the kinetic energy operator scales as r_j^{-2} whereas the coulombic potentials scale as r_j^{-1} and as $r_{j,k}^{-1}$. So, if each of the distances appearing in the cartesian coordinates of the electrons and nuclei were expressed as a unit of length a_0 multiplied by a dimensionless length factor, the kinetic energy

operator would involve terms of the form

$(-\hbar^2/2(a_0)^2 m_e) \nabla_j^2$, and the coulombic potentials would appear as

$Z_a e^2/(a_0) r_{j,a}$ and $e^2/(a_0) r_{j,k}$. A factor of e^2/a_0 (which has units of energy since a_0 has units of length) can then be removed from the coulombic and kinetic energies, after which the kinetic energy terms appear as $(-\hbar^2/2(e^2 a_0) m_e) \nabla_j^2$ and the potential energies appear as $Z_a/r_{j,a}$ and $1/r_{j,k}$. Then, choosing $a_0 = \hbar^2/e^2 m_e$ changes the kinetic energy terms into $-1/2 \nabla_j^2$; as a result, the entire electronic Hamiltonian takes the form given above in which no e^2 , m_e , or \hbar^2 factors appear. The value of the so-called Bohr radius $a_0 = \hbar^2/e^2 m_e$ is 0.529 Å, and the so-called Hartree energy unit e^2/a_0 , which factors out of H_e , is 27.21 eV or 627.51 kcal/mol.