17.1: Orbitals, Configurations, and the Mean-Field Potential

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

$$V_{mf}(\mathbf{r}) = \sum_j V_{mf}(\mathbf{r}_j)$$

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 operator is one-electron additive

$$T = \sum_j T_j$$

the mean-field Hamiltonian

$$H^0 = T + V_{mf}$$

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 $\{\phi k\}$ 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 $\{\phi_j\}$. These orbitals are found by solving the one-electron Schrödinger equations:

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

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

Because each of the electrons also possesses intrinsic spin, the one-electron functions $\{\phi_j\}$ 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 Ψ_k^0 is constructed by forming an antisymmetrized product of N spin-orbitals chosen from the set of $\{\phi_j\}$, allowing each spin-orbital in the list to be a function of the coordinates of one of the N electrons (e.g,

$$\Psi_k^0 = \left|\phi_{k1}(\mathbf{r}_1)\phi_{k2}(\mathbf{r}_2)\phi_{k3}(\mathbf{r}_3)\ldots\phi_{k(N-1)}(\mathbf{r}_{N-1})\phi_{kN}(\mathbf{r}_N)\right|,$$

as above). The corresponding mean field energy is evaluated as the sum over those spin-orbitals that appear in Ψ_k^0:

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

By choosing to place N electrons into specific spin-orbitals, one has specified a **configuration**. By making other choices of which N ϕ_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) Ψ_k^0 and energies E_k^0.