7.1: The LCAO-MO Expansion and the Orbital-Level Schrödinger Equation

In the simplest picture of chemical bonding, the valence molecular orbitals ϕ_i are constructed as linear combinations of valence atomic orbitals χ_μ according to the LCAOMO formula:

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

The core electrons are not explicitly included in such a treatment, although their effects are felt through an electrostatic potential V that has the following properties:

1. V contains contributions from all of the nuclei in the molecule exerting coulombic attractions on the electron, as well as coulombic repulsions and exchange interactions exerted by the other electrons on this electron;
2. As a result of the (assumed) cancellation of attractions from distant nuclei and repulsions from the electron clouds (i.e., the core, lone-pair, and valence orbitals) that surround these distant nuclei, the effect of V on any particular mo ϕ_i depends primarily on the atomic charges and local bond polarities of the atoms over which ϕ_i is delocalized.

As a result of these assumptions, qualitative molecular orbital models can be developed in which one assumes that each mo fi obeys a one-electron Schrödinger equation

$$h\phi_i = \varepsilon_i\phi_i.$$

Here the orbital-level hamiltonian h contains the kinetic energy of motion of the electron and the potential V mentioned above:

$$\left[\frac{-\hbar^2}{2m_e\nabla^2}\right]\phi_i = \varepsilon_i\phi_i.$$

Expanding the mo ϕ_i in the LCAO-MO manner, substituting this expansion into the above Schrödinger equation, multiplying on the left by χ_ν^*, and integrating over the coordinates of the electron generates the following orbital-level eigenvalue problem:

$$\sum_\mu \langle\chi_\nu|\frac{-\hbar^2}{2m_e}\nabla^2 + V|\chi_\mu\rangle C_{i\mu} = \varepsilon\sum_\mu\langle\chi_\nu|\chi_\mu\rangle C_{i\mu}.$$

If the constituent atomic orbitals $\{\chi_\mu\}$ have been orthonormalized as discussed earlier in this chapter, the overlap integrals $\langle\chi_\nu|\chi_\mu\rangle$ reduce to $\delta_{\mu,\nu}$.