7.2: Determining the Effective Potential

In the most elementary models of orbital structure, the quantities that explicitly define the potential V are not computed from first principles as they are in so-called ab initio methods. Rather, either experimental data or results of **ab initio** calculations are used to determine the parameters in terms of which V is expressed. The resulting empirical or semi-empirical methods discussed below differ in the sophistication used to include electron-electron interactions as well as in the manner experimental data or ab initio computational results are used to specify V.

If experimental data is used to parameterize a semi-empirical model, then the model should not be extended beyond the level at which it has been parameterized. For example, experimental bond energies, excitation energies, and ionization energies may be used to determine molecular orbital energies which, in turn, are summed to compute total energies. In such a parameterization it would be incorrect to subsequently use these molecular orbitals to form a wavefunction, as in Sections 3 and 6, that goes beyond the simple 'product of orbitals' description. To do so would be inconsistent because the more sophisticated wavefunction would duplicate what using the experimental data (which already contains mother nature's electronic correlations) to determine the parameters had accomplished.

Alternatively, if results of **ab initio** theory at the single-configuration orbital-product wavefunction level are used to define the parameters of a semi-empirical model, it would then be proper to use the semi-empirical orbitals in a subsequent higher-level treatment of electronic structure as done in Section 6.