8.1: Potential Energy and the Hamiltonian

The potential energy of a poly electronic atom is all electrostatic in nature. There are attractive forces between electrons and the nucleus and repulsive forces between the electrons themselves. For simplicity, we will consider the helium atom first, which has a nucleus with a charge of +2 electron charges and two electrons with -1 charges each.

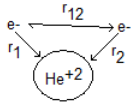

Figure 8.1.1

The Hamiltonian for this system will have kinetic energy terms for both electrons and three terms to describe the potential energy in the system. The attractive forces will lead to negative contributions to the potential energy and the repulsive (electron-electron) force will contribute a positive value to the potential energy. In atomic units, this yields

$$\hat{H} = \hat{T}_1 + \hat{T}_1 - \frac{2}{r_1} - \frac{2}{r_2} + -\frac{1}{r_{12}}$$

The $-\frac{1}{r_{12}}$ (electron-electron repulsion term) makes the problem unseparable into terms that relate only to a single electron. This creates a three body problem, which cannot be solved analytically.

The Orbital Approximation

The way we deal with this problem is to simply ignore the electron-electron repulsion term in the solution, and treat it phenomenologically after the fact. This is known as the **orbital approximation**, as it allows for the separation of the Hamiltonian into two terms, one of which deals in electron 1 and the other in electron 2.

$$\begin{aligned} \hat{H}_{tot} &= \hat{T}_1 - \frac{2}{r_1} + \hat{T}_2 - \frac{2}{r_2} \\ &= \hat{H}_1 + \hat{H}_2 \end{aligned}$$

This is also the approximation that allows us to write electronic configurations for polyelectronic atoms. In the electronic configuration, we assume that each electron has a hydrogen-like wavefunction.