CHAPTER OVERVIEW

25: Many-Electron Atoms

When two or more electrons are present in a system, the TISEq equation cannot be solved analytically. Thus for the vast majority of chemical applications, we must rely on approximate methods. We will explore some of these approximations in this and further chapter, starting from the many-electron atoms (all atoms other than hydrogen). It is important to stress that because of the nature of approximations, this is still a very active field of scientific research, and improved methods are developed every year.

The electronic Hamiltonian for a many-electron atom can be written as:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j} \frac{1}{r_{ij}}, \tag{10.1}$$

where Z is the nuclear charge, m_e and e are respectively the mass and charge of an electron, $\mathbf{r}_i$ and ∇_i^2 are the spatial coordinates and the Laplacian of each electron, $r_i = |\mathbf{r}_i|$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two electrons (all other symbols have been explained in previous chapters). The TISEq is easily written using Equation 22.3.1.