CH107 Assignment 4

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1 Many Electron Atoms

Consider a helium atom with 2 electrons. We seek to find solutions to TISE for this atom.

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m_N}\nabla_N^2}_{\hat{T}_N} + \underbrace{\frac{-\hbar^2}{2m_e}\nabla_1^2 + \frac{-\hbar^2}{2m_e}\nabla_2^2}_{\hat{T}_1+\hat{T}_2} - \frac{1}{4\pi\epsilon_0}\left[\frac{Z_N e^2}{r_1} + \frac{Z_N e^2}{r_2} - \frac{e^2}{r_{12}}\right] \equiv \hat{H}_N + \hat{H}_e = \hat{H}_N + \hat{H}_1 + \hat{H}_2 + \frac{Qe^2}{r_{12}}$$

We approximate the 2 e^- wavefunction to be the product of wavefunctions of the 2 electrons as $\psi_e = \psi_{1e}(r_1, \theta_1, \phi_1) \cdot \psi_{2e}(r_2, \theta_2, \phi_2)$. We find that this equation cannot be solved analytically due to the potential arising out of repulsion between electrons, so we resort to numerical methods. Every electron experiences *net nuclear attraction* which is attraction by the nucleus counteracted by repulsion from other electrons, which leads us to concept of **shielding**. Manipulating the equation by getting rid of $\sum_{ij} \frac{Qe^2}{r_{ij}}$ and replacing Z with Z_{eff}, can can solve the TISE.

Spin is the manifestation of 2 angular momentum states intrinsic to an electron. Spin angular momenta

$$|S| = \hbar\sqrt{s(s+1)}, \text{ and } S_z = m_s\hbar \text{ where } m_s = s, s-1\ldots, -s \ (2s+1 \text{ values})$$

Here s is the spin quantum number, which is 1/2 for an e^-. Thus there are 2 spin states of an electron - α (spin up) and β (spin down). We now incorporate spin into each 1 e^- wavefunction and give rise to **spin orbitals**. Each atomic orbital is now doubly degenerate and has both *spatial* and *spin* coordinates with new quantum number m_s.

For a 2e^- system , there are 4 spin functions

$$\alpha(1)\alpha(2);\ \beta(1)\beta(2);\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right];\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

where the first 3 are *symmetric* and the last is *anti-symmetric*. The Pauli principle :

> **The complete wavefunction of a system of identical fermions must be anti-symmetric with respect to interchange of all coordinates (spatial and spin) of any 2 particles**.

This implies that one of spatial or spin functions is symmetric, and other must be anti-symmetric.

Slater Determinants are a way to represent many e^- wavefunctions as a linear combination of various spatial and spin states. A many electronic wavefunction can be written as a slater determinant or a linear combination of them. This forms the complete wavefunction. For an excited helium atom, it has a singlet and a triplet state. The singlet state has one possible anti-symmetric spin function and a symmetric spatial function. The triplet state has 3 possible symmetric spin functions.