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Lecture 13: Spin & its implication for the multi-electron atom

References

1. Levine, *Physical Chemistry*, Sections 18.5–18.7

Key Concepts

- The Schrödinger Equation yielded solutions for the orbitals of the hydrogen atom in the form

$$\psi_{nlm} \;=\; R_{nl}\Theta_{lm}\Phi_m$$

- In order to complete the picture, we need to add the intrinsic electron spin to the wave function.
- Electron spin is a result of relativistic effects and cannot be obtained from the Schrödinger Equation . It is additional component, which we can call σ and we need to add to the ψ's derived from the Schrödinger Equation .

$$\psi_{nlm_lm_s} \;=\; R_{nl}\Theta_{lm}\Phi_m\sigma_{m_s}$$

- In order to include spin, we need to introduce a new quantum number, m_s that characterizes the electron spin. For an electron, $m_s = \pm\frac{1}{2}$. In order to make the bookkeeping a bit simpler we introduce two new spin wave functions, α and β which represents the two possible spin states.
- Now, the wave function has the following form:

$$\psi = (\text{Spatial Part}) \times (\text{Spin Part}) = (R\Theta\Phi) \times (\alpha \text{ or } \beta)$$

- If we now want to consider atoms with more than one electron, the picture gets very complicated. For example, with the addition of one extra electron (He) we get several new terms in the Schrödinger Equation to account for the additional electron-nucleus interaction as well as an electron-electron repulsion term.
- Analytical solutions for the Schrödinger Equation for atoms with more than one electron do not exist. In order to formulate solutions approximations needs to be made and numerical methods used to solve the resulting mathematics.
- The orbital approximation allows us to write the total wave function of our multi-electron atom in terms of the one-electron solutions of the Schrödinger Equation for hydrogen (hydrogen orbitals). If the total wave function for He isΨ_{He} we can write is as:

$$\Psi_{He}(r_1, r_2) = \psi_H(r_1)\psi_H(r_2)$$

where ψ_H are one electron wave functions (or hydrogen-like orbitals). This allows us to use known solutions (ψ_H) in order to explain more complicated atoms (Ψ).

- The Pauli exclusion principle as stated in general chemistry goes something like this: "Two electrons cannot have the same set of four quantum numbers."
  - This is a result of the requirement that the total wave function must be antisymmetric with respect to the exchange of two electrons. This means that if you exchange the location or occupancy of two electrons, the wave function has the same form, but opposite sign:

$$\Psi(1, 2) = -\Psi(2, 1)$$

– For the ground state of He, the spatial part of the wave function is always symmetric: $\psi_{1s}(1)\psi_{1s}(2)$. Therefore the spin part must be antisymmetric.

– We can construct the total wave function using Slater determinants. The two electrons are both in the $1s$ orbital but can have spin wave functions of either α or β:

$$\Psi_{He} = \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(1)\beta(1) \\ \psi_{1s}(2)\alpha(2) & \psi_{1s}(2)\beta(2) \end{vmatrix} = \psi_{1s}(1)\alpha(1)\psi_{1s}(2)\beta(2) - \psi_{1s}(2)\alpha(2)\psi_{1s}(1)\beta(1)$$

$$\Psi_{He} = \psi_{1s}(1)\psi_{1s}(2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

The determinant contains all possible combinations of spatial and spin wave functions for the two electrons. The form of Ψ when using the determinant notation is antisymmetric as can be seen above.

– The determinant form has two useful properties:

1. If you exchange two rows, the sign of the determinant flips.
2. If two rows or columns are identical, the determinant and thus Ψ is equal to zero.

– Therefore we have arrived at two important parts of the Pauli principle: no two electrons can have the same 4 quantum numbers (the determinant will be zero) which leads to only two electrons (of opposite spin) can occupy a single orbital.