CH 107 Week 4 - Summary

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This week, we discussed the Quantum Mechanics of Multielectronic Species. We started with the simplest example of such a compound: The Helium Atom
The Hamiltonian for the Helium Atom is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{1}$$

Due to the presence of the interelectronic repulsion potential ($\frac{e^2}{4\pi\epsilon_0 r_{12}}$), the Schrödinger Equation for the Helium Atom cannot be solved exactly.
We therefore developed the Orbital Approximation, which neglects interelectronic repulsion.

$$\psi(\vec{r}_1, \vec{r}_2, ...) = \psi_1(\vec{r_1})\psi_2(\vec{r_2})... \tag{2}$$

Here, $\vec{r}_1, \vec{r}_2...$ represent the positions of the electrons. However, it turns out that this approximation is a very bad one, and we cannot ignore interelectronic repulsion.
Therefore, we introduced the concept of Shielding, where the electrons partially shield the Nuclear Charge from one another. Therefore the Atomic Number Z must be replaced by an Effective Atomic Number $Z_{eff} = Z - \sigma$, where σ is the screening constant, which can be found numerically by the Variational Method or by Perturbation Theory.
We then talked about electronic spin and how it was discovered in the Stern-Gerlach Experiment. The presence of spin gives rise to a new Quantum Number m_s which can be $+\frac{1}{2}$ or $-\frac{1}{2}$. The presence of Spin gives rise to Spin orbitals containing Spatial as well as Spin parts, which causes each Atomic orbital to become doubly degenarate.
Therefore, we must write

$$\psi(\vec{r}, \omega) = \psi(\vec{r})\alpha(\omega) \tag{3}$$

or

$$\psi(\vec{r}, \omega) = \psi(\vec{r})\beta(\omega) \tag{4}$$

We then the discussed the sixth Postulate of Quantum Mechanics: The complete Wave Function of a collection of Fermions (such as electrons) must be antisymmetric with respect to exchange of the positions of 2 particles. That is,

$$\boxed{\Psi(1,2) = -\Psi(2,1)} \tag{5}$$

This naturally leads to Pauli's Exclusion Principle, which states that no two electrons can have the same values for all four Quantum Numbers (n, l, m and m_s).
To incorporate this Postulate into our treatment of multielectronic species, we devoloped the Slater Determinant.

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) & \dots & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) & \dots & \phi_n(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(n)\alpha(n) & \phi_2(n)\beta(n) & \dots & \phi_n(n)\beta(n) \end{vmatrix} \tag{6}$$

This Determinant naturally incorporates the antisymmetric property we desire, and if two rows or columns of the determinant are equal, it becomes 0, incorporatinf Pauli's Exclusion Principle.
We then analyzed the excited States of the Helium Atom using the Slater determinant and found two Excited States: A Singlet state and a Triplet state.