CH 107 Week 4 – Home Assignment

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This week, we discussed the Quantum Mechanics of Multi-electronic Atoms. We started with the simplest example – The Helium Atom, a 3-particle system.
The Hamiltonian operator for the Helium Atom contained the KE and PE terms for e_1 and e_2 (with Nucleus) as expected but also had an additional inter-electronic repulsion term due to which the Schrodinger Equation for the Helium Atom cannot be solved exactly. (We are also assuming that the nucleus is "STATIC.") Consequently, Hamiltonian is no longer spherically symmetric; hence, numerical methods must be used to solve TISE.
We, therefore, brought up the Orbital Approximation (for N electrons), under which we can write an N-electron wave function as a product of 1-electron wave functions. (Also, Total Energy = Sum of Orbital Energies). To solve for 1-electron orbital energies, we neglect the electronic repulsion (Energy of He-atom under the Orbital Approximation).

But as it turned out, the assumption of no inter-electronic interaction is flawed since those terms are small and must be addressed. And therefore, we need to solve it using other methods, such as Variational Method and Perturbation Theory, by replacing Atomic Number Z with Z_{eff} using Electronic Shielding.

Then, we talked about the intrinsic angular momentum of the electron – "SPIN", which was discovered by the Stern-Gerlach Experiment. This spin angular momentum was also quantized, giving rise to a new quantum number m_s with only two values, $+1/2$ and $-1/2$. For convenience, we defined spin angular momentum operators analogous to orbital angular momentum. We label the two possible spin states as "spin-up" (α) and "spin-down" (β). The Spin $S(\omega)$ has an unknown internal "Non-Classical" coordinate.
The presence of Spin gives rise to Spin Orbitals containing both Spatial as well as Spin parts, which causes each Atomic Orbital to become doubly degenerate.
We then talked about the Indistinguishability of two electrons and the Acceptable 2-electron Spin Wavefunctions involving the Exchange Operator. Then we discussed the 6^{th} postulate in Quantum Mechanics, which states, "The Complete Wavefunction of a system of identical fermions must be anti-symmetric with respect to the interchange of the coordinates of any two particles". This is also known as Pauli's principle, which can be derived (Postulate?) using relativistic QM; it is, though, not valid for bosons.

To include the 6^{th} postulate in multi-electronic atoms, we developed the Slater Determinant, which implies that the electrons should be of opposite spin in the same spatial orbital. This naturally leads to Pauli's Exclusion Principle. This Determinant inherently incorporates the Anti-Symmetric property that we desire. Also, suppose there is more than one electron with the same 'Complete' wavefunction. In that case, the Determinant reduces to Zero, thus implying that no more than two electrons can occupy a Spatial Orbital.
We then analyzed the excited states of the Helium Atom and found two Excited States: A Singlet and a Triplet State.