

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 14: The multi-electron atom: structure meets properties

References

1. Levine, *Physical Chemistry*, Sections 18.5–8

Key Concepts

- Concepts/tools you have used before such as the Pauli exclusion principle, Hund's rule, and the Aufbau principle all come from the quantum mechanical structure of the atom.
- For the excited helium atom, where one of the 1s electron is promoted to the 2s orbital,
 1. $\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)$, which is antisymmetric and lower in energy
 2. $\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)$, which is symmetric and higher in energy
- Since the lower energy spatial part is antisymmetric, the spin part of the total wave function must be symmetric. This ensures that the total wave function is antisymmetric. This leaves us with 3 possible spin states:

$$\alpha(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

$$\alpha(1)\beta(2) + \alpha(2)\beta(1)$$

- Since there are 3 possible spin states leading to a total of 3 equivalent wave functions, this excited state is called a triplet and given the term symbol 3S . This indicates a multiplicity of 3 and a total angular momentum of 0 (or that the solution is *s*-type.)
- In general, the total wave functions, Ψ are going to lead to what we have seen in previous chemistry classes and have called shells (*n*), subshells (*l* and *m_l*). This leads to understanding of the size and/or radii of the ground state of atoms.
- The total energy, *E*, leads to an understanding of the ionization energies and other spectroscopic properties of multi-electron atoms.
- We can make our model of the multi-electron atom a bit more quantitative if we include effective nuclear charge. This parameter takes into account the shielding of the positive nuclear charge by inner shell electrons.
- This is the beginnings of what are called variational methods. Using this technique, a solution is assumed in the form of a combination of hydrogen wave functions. Then using parameters such as effective *Z*, the energy is minimized using the Schrödinger Equation leading to solutions for the multi-electron atom.
- The screening of core electrons is imperfect due to the radial distribution of electrons in shells with *n* > 1. For example, 4s electrons are most likely found at a somewhat large distance from the nucleus, but the solutions also predicts that there is a finite probability that the electrons in 4s penetrate close to the nucleus.