Unlike hydrogenic atoms, the wavefunctions satisfying Schrödinger's equation for multi-electron atoms cannot be solved analytically. Instead, various techniques are used for giving approximate solutions to the wave functions.

**First Approximation**

The wavefunctions of multi-electron atoms can be considered, as a first approximation, to be built up of components, where the combined wavefunction for an atom with k electrons is of the form:

\[
\Psi = \Psi(1) \Psi(2) ... \Psi(k)
\]

Here, \(\Psi(1), \Psi(2), \ldots, \Psi(k)\) represent wave functions for the first, second, up to k\textsuperscript{th} electrons. Each \(\Psi(i)\) is considered to be in the form of a wave function for the single electron of the hydrogenic atom subject to the Pauli Exclusion Principle and after making adjustments to account for shielding and penetration.

The Pauli Exclusion Principle allows at most two electrons in any one orbital. This is explained by postulating an additional quantum number for electron spin, \(m_s\), which can have values of +1/2 or -1/2. The Dirac theory of quantum mechanics, applied to electron orbitals, more naturally explains this spin magnetic quantum number because the theory goes beyond the assumptions of the Schrödinger equation by also accounting for the relativistic behavior of orbiting electrons.

Shielding occurs because other electrons that are closer to the nucleus shield an electron from the attractive force of the nucleus. Adjusting the hydrogenic orbitals can be done by reducing the value of Z to \(Z_{\text{eff}}\). The amount of the reduction depends on which inner orbitals are occupied and how much the orbital being calculated is able to penetrate the shielding. As the amount of shielding increases, \(Z_{\text{eff}}\) becomes smaller, and the energy levels of the orbital increase. Conversely, as the amount of penetration increases, the shielding is reduced, \(Z_{\text{eff}}\) becomes bigger, and the energy level of the orbital decreases.

For example, when the 1s orbital is fully occupied by two electrons, the third electron could occupy any of 2s or 2p orbitals, which would have the same energy level in a hydrogenic atom. However, as illustrated in the diagrams below, the 2s orbital concentrates more of its probability near the nucleus than the 2p orbital does. As a result, the 2s orbital penetrates the 1s orbital shielding more than the 2p orbital does. Hence, a third electron will occupy the 2s orbital where it has a slightly lower energy than in the 2p orbital.

The values of \(Z_{\text{eff}}\) can be calculated by various techniques. Slater's rule is a relatively simple ad hoc method of estimating \(Z_{\text{eff}}\) for values of \(n\) up to 4, that is for electrons in the s, p, d, or f orbitals.

**Contributors and Attributions**

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