The Central Field Approximation for many-electron atoms

In the analysis of the hydrogen atom the potential function:

$$V(r) = \frac{e^2}{4\pi\varepsilon_0 r}$$

was inserted in the Schrödinger equation. Since this potential is independent of the angular coordinated θ and ϕ, the method of *separation of variables* could be followed, resulting in wave functions depending on 3 quantum numbers. Later an additional variable was added (spin) that was not expressed in terms of spatial coordinates. The wave function was expressed as:

$$\Psi_{nlm_lsm_s} = \psi_{nlm_lsm_s}(\vec{r})e^{\frac{-iE_nt}{\hbar}}$$

An important result of the nature of the differential equation for the radial coordinate (purely Coulombic potential) is that the energy depends only on the quantum number n.

In a multi-electron atom the potential can be written as:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{|\vec{r}_i|} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

The first term represents the attraction of the positively charged nucleus to all electrons; the second term represents the repulsion between the electrons with Z(Z-1)/2 contributions. This term in the potential is *not centrally directed*.

The Schrödinger equation for such a many-electron system reads:

$$-\frac{\hbar^2}{2m}(\nabla_1{}^2 + \dots + \nabla_Z{}^2)\psi + V\psi = E\psi$$

and is a function of 3Z spatial coordinates.

If the electron-electron repulsion can be regarded as negligibly small, the electrons can be decoupled from each other; each electron can be considered then as moving in its own central Coulomb potential. The problem can be treated with a separation of variables for each electron.

In a better approximation each electron can be considered to undergo some net attractive force to the nucleus, which is partially screened. Then each electron experiences a net potential $V_c(r)$ with the limiting behaviour:

$$V_c(r) \rightarrow \begin{cases} -\dfrac{Ze^2}{4\pi\varepsilon_0 r} & \text{for} \quad r \rightarrow 0 \\ -\dfrac{e^2}{4\pi\varepsilon_0 r} & \text{for} \quad r \rightarrow \infty \end{cases}$$

An effective *screened nuclear charge* can be introduced by writing:

$$V_c(r) = -\frac{Z_{eff}(r)e^2}{4\pi\varepsilon_0 r}$$

In this *Central Field Approximation* the function $V_c(r)$ can be considered as centrally directed. Note that each electron undergoes a different potential.

The Schrödinger equation can be solved by writing a product wave function:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\dots\psi_Z(\vec{r}_Z)$$

If the potential energy is written as the sum over all contributions:

$$V = \sum_{i=1}^{Z} V_c(r_i)$$

and the eigen energy is expressed as:

$$E = \sum_{i=1}^{Z} E_i$$

This procedure yields Z different differential equations, one for each electron and having a different $V_c(r_i)$ term:

$$-\frac{\hbar^2}{2m}(\nabla_i^{\ 2})\psi_i + V_c(r_i)\psi_i = E_i\psi_i$$

Each of these independent equations yields a solution:

$$\psi_\alpha(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta, \phi)(up \ \text{ or } \ down)$$

Now the crucial issue is that the potential function in the differential equation is *not exactly Coulombic*, i.e. does not depend exactly on *1/r*. The radial dependence scales like:

$$\boldsymbol{\frac{Z_{eff}(r)}{r}}$$

The radial part of the Schrödinger equation can be written, after separating off the angular part:

$$-\frac{\hbar^2}{2mr}\frac{d^2}{dr^2}rR_{nl} + \left[\frac{Z_{eff}(r)}{r} + \frac{\hbar^2 l(l+1)}{2mr^2}\right]R_{nl} = E_{nl}R_{nl}$$

This equation does not depend on the quantum number m_l for symmetry reasons. However, the resulting energy does depend on *l*, as well as *n*. For a certain value of *l* and for a certain Z_{eff} the equation can be solved. here lies the origin of the *l*-dependence of the energy levels of the one-electron orbitals in the many-electron atom.