Physics Background

Time-Independent Schrödinger Wave Equation

Hydrogen Atom: Bound Electron, Discrete Binding Energy E_n

$\psi(x, y, z)$ probability wave function of electron

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2}(E_n - V)\psi = 0$$

where

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \qquad \text{and} \qquad E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} = \frac{E_1}{n^2}$$

Solution Space

Solve using
1) rotation invariance (spherical coordinates) and
2) separation of variables.

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

where

$$\Phi(\phi) = Ae^{im_l\phi},$$

$$\frac{1}{\sin(\theta)}\frac{d}{d\theta}\Big(\sin(\theta)\frac{d\Theta}{d\theta}\Big) \;+\; \Big[l(l+1) - \frac{m_l^2}{\sin^2(\theta)}\Big]\Theta = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\Big(r^2\frac{dR}{dr}\Big) + \Big[\frac{2m}{\hbar^2}\Big(\frac{e^2}{4\pi\epsilon_0 r} + E_n\Big) - \frac{l(l+1)}{r^2}\Big]R = 0$$

Quantum Numbers

$$\psi_{n,l,m_l} = R_{n,l}\ \Theta_{l,m_l}\ \Phi_{m_l}$$

Principal Quantum Number $= n = 1, 2, 3, \ldots$

Orbital Quantum Number $= l = 0, 1, 2, 3, \ldots n - 1$

Magnetic Quantum Number $= m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$

Linear Algebra/Representation Theory of $SO(3)$

E_n is binding energy in original differential equation.
Total energy is determined by n and l.

Orbital quantum number l corresponds to the magnitude L of the electron's angular momentum $\mathbf{L}$:

$$\mathbf{L}^2\psi = l(l+1)\psi.$$

(Representation theory: highest weight)

Magnetic quantum numbers correspond to eigenvalues (weights) for projection in z-direction,

$$\mathbf{L}_z\psi = m_l\hbar\psi.$$

Thus, l determines an $l+1$ dimensional space.
m_l determines a one-dimensional eigenspace under $\mathbf{L}_z$.

Coupling of Angular Momentum States

If two electrons are combined into one system, multiply wave functions.

$$\Phi_{m_{l_1}}(\phi) \cdot \Phi_{m_{l_2}}(\phi) = A_1 e^{i m_{l_1} \phi} A_2 e^{i m_{l_2} \phi} = A_3 \Phi_{m_{l_1}+m_{l_2}}(\phi)$$

$$\Theta_{l_1, m_{l_1}}(\theta) \cdot \Theta_{l_2, m_{l_2}}(\theta) = \sum_i C(l_1, l_2, m_{l_1}, m_{l_2}, l_i)\ \Theta_{l_i, m_{l_1}+m_{l_2}}(\theta)$$

$C(l_1, l_2, m_{l_1}, m_{l_2}, l_i)$ is called a Clebsch-Gordan coefficient.

Restriction on m_{l_i}: $-l_1 - l_2 \leq m_{l_1} + m_{l_2} \leq l_1 + l_2$

Restriction on l_i: $|l_1 - l_2| \leq l_i \leq l_1 + l_2$

(Think $\sin(l_1\theta) \cdot \sin(l_2\theta) = \frac{1}{2}(\cos((l_1 - l_2)\theta) - \cos((l_1 + l_2)\theta)))$

Clebsch-Gordan Sum

Wigner (1931): Closed formula for Clebsch-Gordan coeffcients C

Reformulate the interesting part, the summation

m, n nonnegative integers. $0 \leq k \leq \min(m, n)$

$$0 \leq i \leq m, \qquad 0 \leq j \leq n, \qquad 0 \leq i + j - k \leq m + n - 2k$$

$$c_{m,n,k}(i,j) = \sum_{s=0}^{k} (-1)^s \binom{i+j-k}{i-s} \binom{m-s}{k-s} \binom{n-k+s}{s}$$