Basics

Linear superposition of eigenstates:

$$|\psi, t\rangle = \sum_i c_i(t) |u_i\rangle$$

$$\Psi(\vec{r}, t) = \sum_i c_i(t) u_i(\vec{r})$$

Probability of getting result:

$$P(A_i) = |c_i(t)|^2$$

Identity operator in a basis, i:

$$\hat{I} = \sum_i |i\rangle \langle i|$$

Expectation value of observable:

$$\langle \hat{A} \rangle = \langle \psi, t | \hat{A} | \psi, t \rangle$$

Uncertainty relations:

$$\Delta \hat{A}_t \equiv (\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2)^{\frac{1}{2}}$$

$$\Delta \hat{A}_t \Delta \hat{B}_t \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$$

Schrödinger equation:

$$\hat{H}\psi = i\hbar \frac{\partial}{\partial t} \psi$$

Braket $\leftrightarrow$ Function notation

$$\langle \psi | \phi \rangle = \int \psi^* \phi \; dx$$

Angular Momentum & Spin

Angular Momentum Operators:

$$\hat{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle$$

$$\hat{L}_z^2 |l, m\rangle = m\hbar |l, m\rangle$$

Spherical Polars:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \left(\frac{\partial^2}{\partial\phi^2} \right) \right]$$

$$\hat{L}z = -i\hbar \frac{\partial}{\partial\phi}$$

Quantum Numbers

$$l = 0, 1, 2, 3...n$$

$$m_l = l, l-1, ..., -l$$

$$m_l \text{ degeneracy} = (2l+1)$$

$$s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, ...$$

$$m_s = s, s-1, ..., -s$$

$$m_s \text{ degeneracy} = (2s+1)$$

$$j = l+s, l+s-1, ..., |l-s+1|, |l-s|$$

Russel Saunders notation labels terms $n^{(2s+1)}l_j$

Total angular momentum:

$$\underline{\hat{J}} \equiv \underline{\hat{L}} + \underline{\hat{S}}$$

$$[\hat{J}_i, \hat{J}_j] = i\hbar \varepsilon_{ijk} \hat{J}_k$$

coupled basis $|l, m_l, s, m_s\rangle$
uncoupled basis $|l, s, j, m_j\rangle$

Matrix Elements:

$$\langle s, m' | \hat{S}_z | s, m \rangle = m\hbar \delta_{m', m}$$

$$\langle s, m' | \hat{S}_\pm | s, m \rangle = \sqrt{s(s+1) - m(m \pm 1)} \hbar \delta_{m', m \pm 1}$$

Atoms

General multi-electron Hamiltonian:

$$\hat{H} = \sum_{i=1}^{N} \left\{ \frac{\hat{p}_i^2}{2m} - \frac{Ze^2}{(4\pi\epsilon_0)r_i} \right\} + \sum_{i>j=1}^{N} \frac{e^2}{(4\pi\epsilon_0)r_{ij}}$$

Hydrogen fine structure:

$$\Delta_{nj} = E_n^{(0)} \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right)$$

2-Electron wavefunctions:

$$\chi_{1,1} = \alpha_1 \alpha_2$$

$$\chi_{1,0} = \tfrac{1}{\sqrt{2}} \{ \alpha_1 \beta_2 + \beta_1 \alpha_2 \}$$

$$\chi_{1,-1} = \beta_1 \beta_2$$

$$\chi_{0,0} = \tfrac{1}{\sqrt{2}} \{ \alpha_1 \beta_2 - \beta_1 \alpha_2 \}$$

Scattering

Born Approximation

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^2} L^6 |\langle \vec{k'} | \hat{V} | \vec{k} \rangle|^2$$

where matrix element $V_{\vec{k'}\vec{k}}$ is given by

$$\langle \vec{k'} | \hat{V} | \vec{k} \rangle = \frac{1}{L^3} \int V(\vec{r}) \exp(-i\vec{q} \cdot \vec{r}) d^3 r$$

for central potentials, Born Approximation becomes

$$\frac{d\sigma}{d\omega} = \frac{4m^2}{\hbar^4 K^2} \left| \int_0^\infty rV(r) \sin(Kr) dr \right|^2$$

where K is the wave-vector transfer, $K = 2k\sin\frac{\theta}{2}$

Perturbation Theory

Time-Independent Non-Degenerate:

- let $H = H_o + \lambda H'$
- expand E_n and $|n\rangle$ in orders of lambda
- compare λ's
- act with arbitrary vector $|k\rangle$

$$E_n^{(1)} = \langle n^{(0)}|\hat{H}'|n^{(0)}\rangle \equiv H'_{nn}$$

$$|n^{(1)}\rangle = \sum_{k \neq n} \frac{H'_{kn}}{(E_n^{(0)} - E_k^{(0)})} |k^{(0)}\rangle$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{(E_n^{(0)} - E_m^{(0)})}$$

Degeneracy

- linear superposition of the g degenerate substates is also an eigenstate with the same eigenvalue as substates, i.e

$$|E^{(0)}\rangle = \sum_{n=1}^{g} b_n |E_n^{(0)}\rangle$$

- same procedure as Time-Independent, then take $k \leq g$ for the arbitrary state, leads to $g \times g$ matrix which must have 0 determinant for non-zero solutions

$$\sum_{n=1}^{g}(H'_{kn} - E^{(1)}\delta_{kn})b_n = 0, \qquad k = 1, ..., g$$

$$\det(H'_{kn} - E^{(1)}\delta_{kn}) = 0$$

Time-Dependent

General solution to TDSE

$$|\psi, t\rangle = \sum_n c_n^{(0)} e^{-E_n^{(0)}t/\hbar} |n^{(0)}\rangle$$

$$i\hbar \frac{\partial}{\partial t} |\psi, t\rangle = H_o |\psi, t\rangle$$

- time-dependent perturbation implies c_n coefficients are time-dependent
- sub general solution into TDSE and take scalar product with general state $\langle m^{(0)}|$ to obtain differential equation for coefficients

$$\dot{c_m} = (i\hbar)^{-1} \sum_n H'_{mn} e^{i\omega_{mn}t}$$

- Expand coefficients and Hamiltonian with λ as before, compare orders of λ
- Integrate differential equation for $\dot{c_m}^{(1)}$

$$c_m^{(1)}(t) = c_m^{(1)}(t_0) + (i\hbar)^{-1} \sum_n \int_{t_0}^{t} H'_{mn} e^{i\omega_{mn}t'} dt'$$

- when system is known to initially be in eigenstate k at $t = 0$ get transition probability

$$p_{mk}(t) \approx \left| c_m^{(1)}(t) \right|^2 = \frac{1}{\hbar^2} \left| \int_{t_0}^{t} H'_{mk} e^{i\omega_{mn}t'} dt' \right|^2$$