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

$$\langle\psi|\phi\rangle = \int \psi^*\phi\ \mathrm{d}x$$

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:

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

$$\langle s, m'|\hat{S_\pm}|s,m\rangle = \sqrt{s(s+1) - m(m\pm1)}\hbar\delta_{m',m\pm1}$$

Variational Method

$$\langle E\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|psi\rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq E_1$$

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

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

for central potentials, Born Approximation becomes

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

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

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

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

Time-Independent Perturbations in Time-Dependent Perturbation Theory

$$p_{mk} = \frac{2|H'_{mk}|^2}{\hbar^2} f(t, \omega_{mk})$$

where

$$f(t, \omega_{mk}) = \frac{2sin^2(\omega_{mk}t/2)}{\omega_{mk}^2}$$

for constant perturbation, take integral between energy range of transition probability (with energy density) to obtain Fermi's Golden Rule:

$$R = \frac{2\pi}{\hbar}|H'_{mk}|^2 \rho(E)$$

which is transitions per unit time