Physics 441

addition of angular momentum:

$\vec{S}_1$ total $\vec{S}$?

$\vec{S}_2$

classically: $\vec{S}_T = \vec{S}_1 + \vec{S}_2$

However: $[S_x, S_y] = i\hbar S_z$

$[S^2, S_x] = 0$

raising and lowering operator for S_z:

$S_\pm = S_x \pm i S_y$

$S_z |sm\rangle = \hbar m |sm\rangle$

$S^2 |sm\rangle = \hbar^2 s(s+1) |sm\rangle$

$\uparrow$

$s = 0, \frac{1}{2}, 1, \frac{3}{2} \ldots$

for quantum addition of angular momentum, consider 2 sets of operators. $\vec{S}_1, \vec{S}_2$

$[S_{x1}, S_{y1}] = i\hbar S_{z1}$

$[S_{x2}, S_{y2}] = i\hbar S_{z2}$

$[S_{x1}, S_{y2}] = 0$

$\vec{S}_T = \vec{S}_1 + \vec{S}_2$

operators

commutation relationships for the total spin $\vec{S}$:

$[S_x, S_y] = [S_{x1} + S_{x2}, S_{y1} + S_{y2}]$

$= [S_{x1}, S_{y1}] + [S_{x2}, S_{y2}]$

cross terms are zero

$[S_x, S_y] = i\hbar (S_{z1} + S_{z2})$

$[S_x, S_y] = i\hbar S_z$ ✓

but what are the eigenvalues?

suppose 2 particles with spin $\frac{1}{2}$:

all possible states:

	s_1 m_1	s_2 m_2
1	$\lvert \frac{1}{2}\ \frac{1}{2}\rangle$	$\lvert \frac{1}{2}\ \frac{1}{2}\rangle$
2.	$\lvert \frac{1}{2}\ \frac{1}{2}\rangle$	$\lvert \frac{1}{2}\ -\frac{1}{2}\rangle$
3.	$\lvert \frac{1}{2}\ -\frac{1}{2}\rangle$	$\lvert \frac{1}{2}\ \frac{1}{2}\rangle$
4	$\lvert \frac{1}{2}\ -\frac{1}{2}\rangle$	$\lvert \frac{1}{2}\ -\frac{1}{2}\rangle$

4 compatible observables:

$S_1^2, S_{z1}, S_2^2, S_{z2}$

act on state 1 with S_z.

$S_z \left(|\tfrac{1}{2}\tfrac{1}{2}\rangle |\tfrac{1}{2}\tfrac{1}{2}\rangle \right) = (S_{z1} + S_{z2}) |\tfrac{1}{2}\tfrac{1}{2}\rangle |\tfrac{1}{2}\tfrac{1}{2}\rangle$

Note: S_{z1} acts only on first ket, essentially acting as an identity on the second ket

$= \left(S_{z1} |\tfrac{1}{2}\tfrac{1}{2}\rangle\right) |\tfrac{1}{2}\tfrac{1}{2}\rangle + |\tfrac{1}{2}\tfrac{1}{2}\rangle \left(S_{z2} |\tfrac{1}{2}\tfrac{1}{2}\rangle\right)$

$= \left(\tfrac{\hbar}{2} |\tfrac{1}{2}\tfrac{1}{2}\rangle\right) |\tfrac{1}{2}\tfrac{1}{2}\rangle + |\tfrac{1}{2}\tfrac{1}{2}\rangle \left(\tfrac{\hbar}{2} |\tfrac{1}{2}\tfrac{1}{2}\rangle\right)$

$= \hbar |\tfrac{1}{2}\tfrac{1}{2}\rangle |\tfrac{1}{2}\tfrac{1}{2}\rangle$

a.k.a. the eigenvalues just add

How about $S^2 |\tfrac{1}{2}\tfrac{1}{2}\rangle |\tfrac{1}{2}\tfrac{1}{2}\rangle$?

$\rightarrow S^2 |sm\rangle = \sum_{m_1 m_2} C_{m_1 m_2} |s_1 m_1\rangle |s_2 m_2\rangle$

Symmetries

there is a correspondance, in classical mechanics, between symmetries and conserved quantities

consider: $\mathcal{L}(q_i, \dot{q}_i, t)$

with operators: $\bar{q}_1 = f_1(q_i, t, \epsilon)$

$\vdots$

$\bar{q}_n = f_n(q_i, t, \epsilon)$

$\bar{t} = g(q_i, t, \epsilon)$

$\bar{q}_k = q_k + \epsilon \frac{\partial f_k}{\partial t} + O(\epsilon^2)$

$\bar{t} = t + \epsilon \frac{\partial g}{\partial t} + O(\epsilon^2)$

A.K.A. symmetric if q_i is time-independant. We get the result:

$0 = \frac{d}{dt}\left(\hat{H} q_i\right) = \frac{dE}{dt}$

$\Rightarrow$ Energy is constant (conserved)

In quantum mechanics:

say we have $|\psi\rangle$ and operator:

$$S|\psi\rangle \equiv |\psi_s\rangle$$

$$\uparrow$$

unitary: $SS^{+} = S^{+}S = 1$

such that:

$$\langle \psi_s | H | \psi_s \rangle = \langle \psi | H | \psi \rangle$$

we call S a symmetry of H:

$$\langle \psi_s | H | \psi_s \rangle = \langle \psi | S^{+} | H | S | \psi \rangle$$

$$S^{+} H S = H$$

$$S S^{+} H S = S H$$

$$\boxed{HS = SH} \quad \text{symmetric}$$

Def: any operator that commutes with H is said to be a symmetry of H

Note: symmetries form a group G:

$$S_1 \circ S_2 \in G$$

proof: $S_1 S_2 H = S_1 H S_2 = H S_1 S_2$

$\therefore (S_1 S_2)$ is a symmetry of H, so it exists in G

consider $S = e^{i\alpha G}$ where G is a unitary generator, e.g.:

$P_x = -i\hbar \frac{\partial}{\partial x}$ generator of x translations

L_x generator of z-axis rotations

and $[G, H] = 0$

consider the path:

$$\begin{tikzcd} {} \arrow[r, "S_2"] & {} \arrow[d, "S_1^{-1}"] \\ {} \arrow[u, "S_1"] & {} \arrow[l, "S_2^{-1}"] \end{tikzcd}$$

$$S_1 = e^{i\alpha G_1}$$

$$S_2 = e^{i\beta G_2}$$

$$S_1 S_2 S_1^{-1} S_2^{-1} = e^{i\alpha G_1} e^{i\beta G_2} e^{-i\alpha G_1} e^{-i\beta G_2}$$

take the taylor expansion:

$$= \left(1 + i\alpha G_1 - \tfrac{1}{2}\alpha^2 G_1^2\right)\left(1 + i\beta G_2 - \tfrac{1}{2}\beta^2 G_2^2\right)$$

$$\left(1 - i\alpha G_1 - \tfrac{1}{2}\alpha^2 G_1^2\right)\left(1 - i\beta G_2 - \tfrac{1}{2}\beta^2 G_2^2\right)$$

$$= 1 + \alpha\beta [G_1, G_2] + \text{cubic terms}$$

so if G_1 and G_2 commute, the transformation is just the identity and you end up where you start

note: rotation generators in 3D space don't commute

$$[L_x, L_y] = i\hbar L_z$$

but $[P_x, P_y] = 0$

suppose we have a constant vector field (space-independant)

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = V_x \hat{x} + V_y \hat{y} + V_z \hat{z}$$

small rotation by angle α about z-axis:

$$V_x' = V_x - \alpha V_y$$

$$V_y' = V_y + \alpha V_x$$

$$V_z' = V_z$$

our rotation matrix is thus:

$$\vec{V}' = \begin{bmatrix} 1 & -\alpha & 0 \\ \alpha & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \vec{V}$$

in the basis:

$$e_1 = \begin{bmatrix} 1 \\ i \\ 0 \end{bmatrix} \quad e_2 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \quad e_3 = \begin{bmatrix} 1 \\ -i \\ 0 \end{bmatrix}$$

this rotation matrix takes the form:

$$\vec{V}' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \vec{V}$$

which is just the S_z matrix for spin 1

result: a general rotation of a vector field can be written as:

$$e^{i \frac{\vec{\alpha}}{\hbar}(\vec{L} + \vec{S})}$$

$\vec{L}$: external DOF$_L$, $\vec{S}$: internal DOF$_S$

we call this a representation of the group of rotations about an axis

Perturbation Theory

suppose $\hat{H} = H_0 + H_1$

H_0: analytically solvable

H_1: perturbation

we know the spectrum of H_0:

$$H_0|n_0\rangle = E_0|n_0\rangle$$

additionally, we can control H_1:

$$H = H_0 + \lambda H_1$$

where H_1 is small compared to H_0

assume the energies can be expanded:

$$E_n = E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} \dots \text{ and}$$

$$|n\rangle = |n_0\rangle + \lambda|n_1\rangle + \lambda^2|n_2\rangle \dots$$

so we get:

$$(H_0 + \lambda H_1)(|n_0\rangle + \lambda|n_1\rangle + \lambda^2|n_2\rangle \dots)$$

$$= (E_0 + \lambda E_1 + \lambda^2 E_2 \dots)(|n_0\rangle + \lambda|n_1\rangle \dots)$$

combine like powers of λ:

$$H_0|n_0\rangle + \lambda(H_1|n_0\rangle + H_0|n_1\rangle) + \lambda^2(H_0|n_2\rangle + H_1|n_1\rangle) \dots = E_{n0}|n_0\rangle + \lambda(E_0|n_1\rangle + E_1|n_0\rangle) + \lambda^2(E_0|n_2\rangle + E_1|n_1\rangle + E_2|n_0\rangle)$$

equating like powers of λ:

$$H_0|n_0\rangle = E_0|n_0\rangle$$

$$H_1|n_0\rangle + H_0|n_1\rangle = E_0|n_1\rangle + E_1|n_0\rangle$$

$$H_0|n_2\rangle + H_1|n_1\rangle = E_0|n_2\rangle + E_1|n_1\rangle + E_2|n_0\rangle$$

AKA collecting terms of the same order

by assumption, we know how to solve the zeroeth-order eq.

$$H_0|n_0\rangle = E_0|n_0\rangle$$

first order eq.

$$H_1|n_0\rangle + H_0|n_1\rangle = E_0|n_1\rangle + E_1|n_0\rangle$$

multiply by $\langle n_0|$:

$$\langle n_0|H_1|n_0\rangle + \underbrace{\langle n_0|H_0|n_1\rangle}_{E_0\langle n_0|n_1\rangle} = E_0\underbrace{\langle n_0|n_1\rangle}_{0} + E_1\underbrace{\langle n_0|n_0\rangle}_{1}$$

$$\langle n_0|H_1|n_0\rangle + \underbrace{E_0\langle n_0|n_1\rangle}_{0} = E_1$$

$$\boxed{E_{n1} = \langle n_0|H_1|n_0\rangle}$$

i.e. the first-order correction to the energies (eigenvalues) of $|n\rangle$ when acted on by our perturbed hamiltonian

The second-order correction is:

$$\boxed{E_{n2} = \langle n_0|H_1|n_1\rangle}$$

Degeneracy

$$H_0|a_0\rangle = E_0|a_0\rangle$$

$$H_0|b_0\rangle = E_0|b_0\rangle$$

2-fold degeneracy

eigenstates can be written

$$\alpha|a_0\rangle + \beta|b_0\rangle + \underbrace{\lambda|\Psi_1\rangle}_{\text{perturbation}}$$

$$(E_0 - H_0)|\Psi_1\rangle = (H_1 - E_1)(\alpha|a_0\rangle + \beta|b_0\rangle)$$

multiply by $\langle a_0|$

1. $\underbrace{\langle a_0|E_0 - H_0|\Psi_1\rangle}_{0} = \alpha\langle a_0|H_1 - E_1|a_0\rangle + \beta\langle a_0|H_1 - E_1|b_0\rangle$

multiply by $\langle b_0|$: $\langle a_0|E_1|b_0\rangle = 0$

2. $\underbrace{\langle b_0|E_0 - H_0|\Psi_1\rangle}_{0} = \alpha\langle b_0|H_1 - E_1|a_0\rangle + \beta\langle b_0|H_1 - E_1|b_0\rangle$

1. $0 = \alpha(\langle a_0|H_1|a_0\rangle - E_1) + \beta\langle a_0|H_1|b_0\rangle$
2. $0 = \beta(\langle b_0|H_1|b_0\rangle - E_1) + \alpha\langle a_0|H_1|b_0\rangle$

$$\begin{bmatrix} \langle a_0|H_1|a_0\rangle - E_1 & \langle a_0|H_1|b_0\rangle \\ \langle a_0|H_1|b_0\rangle & \langle b_0|H_1|b_0\rangle - E_1 \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$(M - E_1 \cdot I)\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad \text{so}$$

$$\det(M - E_1) = 0$$

<u>Example</u>: particle on a ring

$$|n\rangle = \Psi_n = \frac{1}{\sqrt{2\pi}} e^{in\varphi} \qquad n = \pm 1, \pm 2, \pm 3$$

where $\pm n$ share the same eigenvalues

from above equations: $|a_0\rangle = |n\rangle \quad |b_0\rangle = |-n\rangle$

$$M = \begin{bmatrix} \langle n|H_1|n\rangle & \langle n|H_1|-n\rangle \\ \langle -n|H_1|n\rangle & \langle -n|H_1|-n\rangle \end{bmatrix}$$

$$H_0 = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial\varphi^2} \qquad H_1 = V_0\cos(2\varphi) \qquad E_{0n} = \frac{\hbar^2 n^2}{2m}$$

$$M = \begin{bmatrix} 0 & V_0 \\ V_0 & 0 \end{bmatrix}$$

How to find zeroes in M:

① H_0 has even parity: $PH_0P = H_0$

H_1 has odd parity: $PH_1P = -H_1$

$0 = \langle \text{even}_i | H_1 | \text{even}_j \rangle = \langle \text{odd}_i | H_1 | \text{odd}_j \rangle$

note: all diagonal elements automatically vanish

② suppose $[\Omega, H_0] = 0$ and $[\Omega, H_1] = 0$

$H_0 |\omega\alpha\rangle = \alpha|\omega\alpha\rangle \quad H_1|lm\rangle = l|lm\rangle$

$\Omega|\omega\alpha\rangle = \omega|\omega\alpha\rangle \quad \Omega|lm\rangle = m|lm\rangle$

$\langle \omega\alpha | H_1 | lm \rangle = 0$ if $\alpha \neq m$

Stark Effect

H_e in external electric field

$$\hat{H} = \underbrace{\frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}}_{H_0 \text{ (even)}} + \underbrace{e E_{ext} \cdot z}_{H_1 \text{ (odd)}}$$

$E_{0n} \approx -\frac{1}{n^2}$ degeneracy is n^2

consider $n = 2$:

4 possible states: $|2\,0\,0\rangle$ even

$|2\,1\,0\rangle$, $|2\,1\,1\rangle$, $|2\,1\,-1\rangle$ odd

so our matrix M is:

$$\begin{array}{c|cccc} & |2\,0\,0\rangle & |2\,1\,0\rangle & |2\,1\,1\rangle & |2\,1\,-1\rangle \\ \hline \langle 2\,0\,0| & 0 & & 0 & 0 \\ \langle 2\,1\,0| & & 0 & 0 & 0 \\ \langle 2\,1\,1| & 0 & 0 & 0 & 0 \\ \langle 2\,1\,-1| & 0 & 0 & 0 & 0 \end{array}$$

Fine Structure

$$E_n = -\frac{1}{n^2}\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

$$E_n = -\frac{1}{n^2}\frac{mc^2}{2}\underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)}_{\alpha}^2$$

$$E_n = -\frac{1}{2}\left(\frac{1}{n^2}\right)(mc^2\alpha^2)$$

note: α is called the fine structure constant

relativistic correction to KE:

$$T = \sqrt{(mc^2)^2 + (pc)^2} - mc^2$$

$$T = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} - mc^2$$

$$\sqrt{1+x} = 1 + \frac{x}{2} - \frac{x^2}{8}\ldots$$

for small x

$$T = mc^2\left(1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \ldots\right) - mc^2$$

$$T = \underbrace{\frac{p^2}{2m}}_{H_0} - \underbrace{\frac{p^4}{8m^3c^2}}_{H_1} \ldots$$

$$\hat{H}_0 = \frac{p^2}{2m} + V(r)$$

$$\hat{H}_1 = -\frac{p^4}{8m^3c^2}$$

we have eigenstates of H_0:

$|nlm\rangle \quad n = 1, 2, 3 \ldots \quad 0 \le l \le n-1$

$-l \le m \le l$

$H_0|nlm\rangle = E_n|nlm\rangle$

$E_{n1} = \langle nlm | H_1 | nlm \rangle$

$$H_1 = \frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2$$

$$\frac{p^2}{2m} = H_0 - V(r)$$

if Ω is a hermitian operator

$\langle \Psi | \Omega^2 | \Psi \rangle = (\Omega \langle \Psi |)(\Omega \langle \Psi |)$

we know that $\frac{p^2}{2m}$ is hermitian

$(H_0 - V(r))|nlm\rangle = (E_n - V(r))|nlm\rangle$

$E_{n1} = \langle nlm | (E_n - V(r))^2 | nlm \rangle$

$= \langle nlm | E_n^2 - 2E_nV(r) + V(r)^2 | nlm \rangle$

$= \frac{1}{2mc^2}\langle nlm | \left(-\frac{1}{2}\left(\frac{1}{n^2}\right)(mc^2\alpha^2)\right)^2 +$

$\frac{1}{n^2}(mc^2\alpha^2)\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{r} +$

$\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{r^2} | nlm \rangle$

we know that:

$\langle nlm | \frac{1}{r} | nlm \rangle = \frac{1}{n^2 a_0}$ bohr radius

$\langle nlm | \frac{1}{r^2} | nlm \rangle = \frac{1}{(l+\frac{1}{2})n^3a^2}$

$$\boxed{E_{n1} = \frac{-E_n^2}{2mc^2}\left(\frac{4n}{(l+\frac{1}{2})} - 3\right)}$$

Spin-Orbit Coupling

magnetic moment of electron

$$\vec{\mu} = \frac{e\overbrace{g}^{\approx 2}}{2m}\vec{S}$$

$$\hat{H} = \vec{\mu} \cdot \vec{B}$$

electron experiences $\vec{B}$ due to orbiting proton

$$\vec{B} = \frac{\mu_0}{4\pi} I \frac{\vec{dl} \times \vec{r}}{r^3} = \frac{1}{4\pi\varepsilon_0 c^2}\left(\frac{e}{m}\right)\frac{m\vec{v} \times \vec{r}}{r^3}$$

$$\vec{B} = \frac{1}{4\pi\varepsilon_0}\left(\frac{e}{mc^2}\right)\frac{\vec{L}}{r^3}$$

$$\vec{B} = \frac{1}{4\pi\varepsilon_0}\left(\frac{e}{mc^2}\right)\left(\frac{1}{r^3}\right)\vec{L}$$

$$\hat{H}_1 = \vec{\mu}\cdot\vec{B}$$

$$H_1 = \left(\frac{eg}{2m}\right)\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{e}{mc^2}\right)\left(\frac{1}{r^3}\right)\vec{S}\cdot\vec{L}$$

$g \approx 2$, but we didn't account for the rotating frame of the electron, which gives us a $\frac{1}{2}$, so:

$$H_1 = \frac{1}{8\pi\varepsilon_0}\left(\frac{e^2}{m^2c^2}\right)\left(\frac{1}{r^3}\right)\vec{S}\cdot\vec{L}$$

So our wave functions are now parameterized by s and m_s as well:

$$\psi(r,\theta,\varphi) = |n\, l\, m\, s\, m_s\rangle$$

$$\vec{L}\cdot\vec{S} = \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z$$

So it's not a scalar, but rather a sum of operators

consider the total angular momentum:

$$\vec{J} = \vec{L} + \vec{S}$$

$$\left[\vec{L}\cdot\vec{S},\, L^2\right] = 0$$

$$\left[\vec{L}\cdot\vec{S},\, S^2\right] = 0$$

$$\left[\vec{L}\cdot\vec{S},\, J_{x,y,z}\right] = 0$$

$$J^2 = (\vec{L}+\vec{S})^2 = L^2 + 2\vec{L}\cdot\vec{S} + S^2$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

so swap out $\{l\ m\ s\ m_s\}$ with

$\{l\ s\ j\ m_j\}$

$$\vec{L}\cdot\vec{S}\,|n\,l\,s\,j\,m_j\rangle = \frac{1}{2}\left(J^2 - L^2 - S^2\right)|n\,l\,s\,j\,m_j\rangle$$

$$\vec{L}\cdot\vec{S}\,|\psi\rangle = \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)|\psi\rangle$$

$$H_1 = \frac{1}{8\pi\varepsilon_0}\left(\frac{e^2}{m^2c^2}\right)\left(\frac{1}{r^3}\right)\left(\frac{\hbar^2}{2}\right)\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$$\langle\psi_0|H_1|\psi_0\rangle =$$

$$\frac{1}{8\pi\varepsilon_0}\left(\frac{e^2}{m^2c^2}\right)\left(\frac{\hbar^2}{2}\right)\left[j(j+1) - l(l+1) - s(s+1)\right]\langle\psi_0|\frac{1}{r^3}|\psi_0\rangle$$

we know:

$$\langle\psi_0|\frac{1}{r^3}|\psi_0\rangle = \left[l(l+\tfrac{1}{2})(l+1)a^3n^3\right]^{-1}$$

also:

$$E_n = -\frac{1}{n^2}\frac{mc^2}{2}\alpha^2 \quad \text{AND} \quad a = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m}$$

so:

$$\langle\psi_0|H_1|\psi_0\rangle = E_n^2\left(\frac{n}{mc^2}\right)\left[\frac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}\right]$$

$$s = \tfrac{1}{2} \quad \text{so} \quad s(s+1) = \tfrac{3}{4}$$

now combine spin-orbit coupling and the stark effect:

$$\langle H_{TOTAL}\rangle = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{l+\frac{1}{2}} + \frac{2n\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}{l(l+\frac{1}{2})(l+1)}\right]$$

but we know: $j = l \pm \frac{1}{2}$ but both give the same answer, so:

$$\langle H_T\rangle = \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$$

Hyperfine Splitting

spin-spin interaction between the proton and the electron

$$\vec{\mu}_p = \frac{g_p e}{2m_p}\vec{S}_p \qquad \vec{\mu}_e = \frac{g_e e}{2m_e}\vec{S}_e = \frac{e}{m_e}\vec{S}_e$$

$$g_p = 5.6 \qquad g_e = 2.0$$

$$H = \vec{\mu}_e\cdot\vec{B}_p$$

$$H_{ep} = \frac{g_p e^2}{2m_e m_p}\left[\frac{\mu_0}{4\pi}\left(\frac{3(\vec{S}_p\cdot\hat{r})(\vec{S}_e\cdot\hat{r}) - \vec{S}_p\vec{S}_e}{r^3}\right) + \frac{2}{3}\vec{S}_p\vec{S}_e\,\delta^3(\vec{r})\right]$$

displacement vector between proton and electron

consider the ground state ψ_0 s.t. $n=1$, $l=0$

$$E_{11} = \langle\psi_0|H_{ep}|\psi_0\rangle$$

since the $\frac{1}{r^3}$ term is spherically symmetric, it averages to zero in the integral

$$E_{11} = \frac{g_p e^2}{2m_e m_p}\left(\frac{2}{3}\vec{S}_p\vec{S}_e\right)\underbrace{\psi_0(0)^2}_{\text{due to } \delta^3(\vec{r}) = 1 \text{ iff } \vec{r}=0}$$

$$\psi_0(0)^2 = \frac{1}{\pi a^3}$$

$$\vec{S}_p\vec{S}_e = -\frac{3}{4}\hbar^2 \text{ for } S_T = 0$$

$$\frac{1}{4}\hbar^2 \text{ for } S_T = 1$$

$$\langle H_{ep}\rangle = \alpha^4 m_e c^2\left(\frac{m_e}{m_p}\right)\left(\frac{4}{3}\hbar^6 g_p\right)\begin{cases}\frac{1}{4} & (+)\\ -\frac{3}{4} & (-)\end{cases}$$

Zeeman Effect

$$H_z = -(\vec{\mu}_L + \vec{\mu}_s)\cdot \vec{B}_{ext}$$

$$H_z = -\left(\frac{-e}{2m_e}\vec{L} - \frac{e}{m_e}\vec{S}\right)\cdot \vec{B}_{ext}$$

$$H_z = \frac{e}{2m}\left(\vec{L} + 2\vec{S}\right)\cdot \vec{B}_{ext}$$

weak field: $E_{zeeman} \ll E_{fine}$

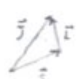
intermediate: $E_z \approx E_f$

strong field: $E_z \gg E_f$

<u>weak field:</u> $|n\, l\, s\, j\, m_j\rangle$

commuting operators: H_0, L^2, S^2, J^2, J_z

remember: $\vec{J} = \vec{L} + \vec{S}$



Energy correction for zeeman perturbation:

$$E_{z1} = \langle \psi_0 | \vec{L} + 2\vec{S} | \psi_0\rangle \left(\frac{e}{2m}\cdot \vec{B}_{ext}\right)$$

$$\vec{L} + 2\vec{S} = \vec{J} + \vec{S}$$

geometrically: $\langle \vec{S}\rangle = \langle \vec{J}\rangle\left(\frac{\vec{S}\cdot\vec{J}}{J^2}\right)$

so: $\langle \vec{J} + \vec{S}\rangle = \langle \vec{J}\left(1 + \frac{\vec{S}\cdot\vec{J}}{J^2}\right)\rangle$

$$= \langle \vec{J}\rangle \underbrace{\left(1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}\right)}$$

this comes from:

$$(\vec{J} - \vec{S})^2 = \vec{S}^2 - 2\vec{S}\cdot\vec{J} + \vec{J}^2 = \vec{L}^2$$

$$\vec{S}\cdot\vec{J} = \frac{1}{2}\left(\vec{J}^2 + \vec{S}^2 - \vec{L}^2\right)$$

now let's choose our coordinate system s.t. $\vec{B}_{ext} = B\hat{z}$

then $\langle \vec{J}\rangle \cdot \vec{B}_{ext} = \langle J_z\rangle B$

$$\langle J_z\rangle = \hbar m_j$$

so we get:

$$\boxed{E_{z1} = \frac{\hbar e B}{2m}\left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}\right] m_j}$$

since E_{z1} depends on m_j, we're now removed all degeneracies from the energy spectra of Hydrogen

<u>strong field:</u> since H_z is now the leading effect, $\vec{L} + 2\vec{S}$ no longer commutes with J

$\therefore$ we need a different basis (i.e. new quantum numbers to represent ψ with)

$$[\vec{L} + \vec{S}, \vec{L}^2] = 0$$

$$[\vec{L} + \vec{S}, \vec{S}^2] = 0$$

so $\psi = |n\, l\, m_l\, s\, m_s\rangle$

$$\langle \psi | H_z | \psi\rangle = \frac{eB}{2m}(m_l + 2m_s)$$

because $H_z = (\vec{L} + 2\vec{S})\cdot B\hat{z}$

$$H_z = (L_z + 2S_z)$$

Variational Principle

For any $|\psi\rangle$: $\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$

proof: $\langle\psi|\psi\rangle = 1$ $\quad H|n\rangle = E_n|n\rangle$

$$|\psi\rangle = \sum c_n |n\rangle$$

so: $\langle\psi|H|\psi\rangle = \sum c_n \langle\psi|H|n\rangle$

$$= \sum c_n E_n \langle\psi|n\rangle$$

$$\langle\psi| = \sum \langle m| c_m^*$$

$$\langle\psi|H|\psi\rangle = \sum_n\sum_m c_m^* c_n \underbrace{\langle m|n\rangle}_{\delta_{mn}} E_n$$

$$\langle\psi|H|\psi\rangle = \sum_n c_n^2 E_n$$

$$\sum_n c_n^2 E_n \geq \sum_n c_n^2 E_0 \leftarrow \text{ground state}$$

$$\boxed{\langle\psi|H|\psi\rangle \geq E_0}$$

consider the harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$$

ψ has one parameter: a

by minimizing $\langle\psi|H|\psi\rangle$ with respect to our choice of a, we get the best upper bound on the ground state energy

we end up getting:

$$\langle\psi|H|\psi\rangle = \frac{\hbar^2 a}{2m} + \frac{m\omega^2}{8a}$$

$$\frac{d}{da}\langle H\rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8a^2} = 0$$

$$a = \frac{m\omega}{2\hbar}$$

$$\langle H \rangle = \frac{\hbar^2 a}{2m} + \frac{m\omega^2}{8a}$$

$\langle H \rangle$ is minimized at $a = \frac{m\omega}{2\hbar}$

$$\langle H \rangle_{min} = \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{8}\left(\frac{2\hbar}{m\omega}\right)$$

$$\langle H \rangle_{min} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} \geq E_0$$

$$E_0 \leq \frac{1}{2}\hbar\omega$$

because we guessed the right $|\psi\rangle$, our bound is actually the correct value for E_0

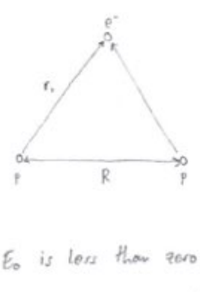
if we had guessed $\psi \sim e^{-ax^4}$, we would've gotten:

$$E_0 \leq 0.58\,\hbar\omega$$

which is pretty good

H_2^+ molecule

1 electron, 2 protons



if E_0 is less than zero, then this molecule can exist (if it was greater, the molecule couldn't hold itself together)

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

for our guess of $|\psi\rangle$, let's choose the ground state of hydrogen plus the ground state of another hydrogen

$$\psi_0 = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \leftarrow \text{bohr radius}$$

$$|\psi\rangle = A\left[\psi_0(r_1) + \psi_0(r_2)\right]$$

this guess is called "linear combination of atomic orbitals"

$$\langle \psi | \psi \rangle = 1$$

$$1 = A^2 \int \underbrace{\psi_0(r_1)^2}_{1} + \underbrace{\psi_0(r_2)^2}_{1} + 2\psi_0(r_1)\psi_0(r_2)$$

$$1 = A^2\left(2 + 2\int \psi_0(r_1)\psi_0(r_2)\, d^3\vec{r}\right)$$

$$1 = A^2\left[2 + 2e^{-R/a}\left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right)\right]$$

$A^2 = 2(1+I)$ where I is that mess

Time-dep. perturbation

$$H = H_0 + H'(t)$$

H_0: solvable and time independent

$H'(t)$: perturbation

$$H_0|n\rangle = E_n|n\rangle$$

$$i\hbar\frac{\partial\psi}{\partial t} = (H_0 + H')\psi$$

$$\psi = \sum c_n(t)|n\rangle$$

$|n\rangle$: stationary states of H_0

stationary states are time-periodic:

$$|n\rangle = e^{-iE_nt/\hbar}|n\rangle$$

$$\psi = \sum a_n(t) e^{-iE_nt/\hbar}|n\rangle$$

$a_n(t)$ depends entirely on H'

$$i\hbar\frac{\partial}{\partial t}\sum a_n(t) e^{-iE_nt/\hbar}|n\rangle =$$

$$(H_0 + H')\sum a_n(t) e^{-iE_nt/\hbar}|n\rangle$$

$$i\hbar\sum\left(\frac{da_n}{dt}e^{-iE_nt/\hbar} - \frac{iE_n}{\hbar}a_n e^{-iE_nt/\hbar}\right)|n\rangle =$$

$$\underbrace{H_0\sum a_n e^{-iE_nt/\hbar}|n\rangle}_{\sum E_n a_n e^{-iE_nt/\hbar}|n\rangle} + H'\sum a_n e^{-iE_nt/\hbar}|n\rangle$$

which cancels with the second term on the RHS

so we got:

$$i\hbar\sum\frac{da_n}{dt}e^{-iE_nt/\hbar}|n\rangle = \sum a_n e^{-iE_nt/\hbar}H'|n\rangle$$

$$\frac{da_m}{dt} = -\frac{i}{\hbar}\sum_n a_n e^{i(E_m - E_n)t/\hbar}\underbrace{\langle m|H'|n\rangle}_{H'_{mn}}$$

expand a_n in powers of H':

$$a_n = a_{n0} + a_{n1} + a_{n2} \ldots$$

0^{th} order: $\frac{da_{m0}}{dt} = 0$

1^{st} order: $\frac{da_{m1}}{dt} = -\frac{i}{\hbar}\sum a_{n0} e^{-i\omega t/\hbar} H'_{mn}$

this times this is first order

2^{nd} order: $\frac{da_{m2}}{dt} = -\frac{i}{\hbar}\sum a_{n1} e^{-i(E_m - E_n)t/\hbar} H'_{mn}$

At $t = 0$, turn on the perturbation:

assume ψ is in a stationary state:

only $a_{k0} \neq 0$, $\psi = |k\rangle$

what is the probability that ψ moves to some other state

$$\frac{da_m}{dt} = \frac{-i}{\hbar}\sum_n a_n e^{i(E_m - E_k)t/\hbar} H'_{mk}$$

by normalization: $a_{k0} = 1$

$$\frac{da_m}{dt} = \frac{-i}{\hbar} e^{i(E_m - E_k)t/\hbar} H'_{mk}$$

$$\boxed{a_m(t) = -\frac{i}{\hbar}\int_0^t e^{i(E_m - E_k)t'/\hbar} H'_{mk}(t')\,dt'}$$

in the same way, you can get higher order coefficients $a_m(t)$ by plugging in lower ones:

$$a_{m_2}(t) = \frac{-i}{\hbar}\sum_n \int_0^t a_{n_1}(t') e^{i(E_m - E_n)t'/\hbar} H'_{mn}(t')\,dt'$$

and so on...

Periodic Perturbations

assume H is periodic:

$$H' = Ve^{-i\omega t} + V^{+}e^{i\omega t}$$

$\uparrow$ because H is hermitian

$$H_{mk} = \langle m | H' | k \rangle$$

$$= \langle m|V|k\rangle e^{-i\omega t} + \langle m|V^{+}|k\rangle e^{i\omega t}$$

$$= V_{mk}e^{-i\omega t} + V_{mk}^{*}e^{i\omega t}$$

$$a_m(t) = \frac{-i}{\hbar}\int_0^t e^{i(E_m - E_k)t'/\hbar}\left(V_{mk}e^{-i\omega t'} + V_{mk}^{*}e^{i\omega t'}\right)dt'$$

call $E_m - E_k$ ω_{mk} (the natural period of the stationary state)

$$a_m(t) = \frac{\left(e^{i(\omega_{mk} - \omega)t} - 1\right)}{\hbar(\omega_{mk} - \omega)} V_{mk} - \frac{\left(e^{i(\omega_{mk} + \omega)t} - 1\right)}{\hbar(\omega_{mk} + \omega)} V_{mk}^{*}$$

if $\omega_{mk} \approx \omega$, term 1 >> term 2, so we can neglect term 2

assume $\omega \approx \omega_{mk}$:

$$a_m(t) = \frac{-i}{\hbar}\,\frac{e^{i(\omega_{mk} - \omega)t} - 1}{(\omega_{mk} - \omega)}$$

remember:

$a_m(t)^2$ is the probability of finding ψ in the state $|m\rangle$

$$a_m(t)^2 = \frac{|V_{mk}|^2}{\hbar^2}\left(\frac{\sin^2\left(\frac{\omega_{mk} - \omega}{2}t\right)}{(\omega_{mk} - \omega)^2}\right)$$

study the expression:

$$F = \frac{\sin^2\left[\frac{1}{2}(\omega_{mk} - \omega)t\right]}{\left[\frac{1}{2}(\omega_{mk} - \omega)\right]^2 t}$$

for $\omega_{mk} \neq \omega$

$F \to 0$ as $t \to \infty$

this sounds like a delta function;

we want to show that

$$\lim_{t\to\infty} F = \delta(\omega_{mk} - \omega)$$

call $\frac{1}{2}(\omega_{mk} - \omega)t = x$

integrate both sides w.r.t. ω:

$$F = \frac{\sin^2 x}{\frac{x^2}{t}}$$

$$d\omega = -\frac{t}{2}dx$$

$$\int_{-\infty}^{\infty} F\,d\omega = 2\underbrace{\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\,dx}_{\text{this is just } \pi}$$

$$\int_{-\infty}^{\infty} F\,d\omega = 2\pi$$

so we get

$$\lim_{t\to\infty} a_m^2 = \frac{V_{mk}^2}{\hbar^2}\left(2\pi\,\delta(\omega_{mk} - \omega)\right)\lim_{t\to\infty} t$$

so $P(a_m) \to \infty$ as $t \to \infty$?

define transition rate R as:

$$R = \frac{P(a_m)}{t} \quad \text{probability per time}$$

$$R = \frac{V_{mk}^2}{\hbar^2}\left(2\pi\,\delta(\omega_{mk} - \omega)\right)$$

"Fermi golden rule"

E and M

$$\vec{E} = -\nabla\varphi - \frac{\partial A}{\partial t}$$

$$\vec{B} = \nabla \times A$$

$$\varphi = \varphi - \frac{d\chi}{dt}$$

$$A = A + \nabla\chi$$

$\vec{E}$ and $\vec{B}$ stay the same

$$E = -\nabla\left(\varphi - \frac{d\chi}{dt}\right) - \frac{d}{dt}\left(A + \nabla\chi\right) \checkmark$$

$$B = \nabla \times (\varphi + \nabla\chi) \checkmark$$

maxwell in a vacuum:

$$\nabla \cdot E = 0 \qquad \nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \cdot B = 0 \qquad \nabla \times B = -\frac{1}{c^2}\frac{\partial E}{\partial t}$$

in the coulomb gauge:

$$-\nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial A^2}{\partial t^2} = 0$$

$$\vec{A} = \vec{A_0}\cos\left(\vec{k}\cdot\vec{r} - \omega t\right) \quad k^2 = \frac{\omega^2}{c^2}$$

insist: $\Psi = e^{ie\chi/\hbar}\psi$

$$H = \frac{1}{2m}\left(-i\hbar\vec{\nabla} - e\vec{A}\right)^2 + e\varphi$$

"minimal coupling"

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

$$i\hbar \frac{\partial}{\partial t}\left(e^{ie\chi/\hbar} \psi\right) = \frac{1}{2m}\left[\left(-i\hbar \vec{\nabla} - e(A + \nabla \chi)\right)^2 + e\left(\varphi - \frac{\partial \chi}{\partial t}\right)\right] e^{ie\chi/\hbar} \psi$$

$$L.H.S. = i\hbar\left(\frac{ie}{\hbar}\frac{\partial \chi}{\partial t}\psi + \frac{\partial \psi}{\partial t}\right) e^{ie\chi/\hbar}$$

$$R.H.S. = e^{ie\chi/\hbar}\left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{\hbar}{i}\frac{ie}{\hbar}\nabla\chi - e\left(A + \nabla\chi\right)\right)^2 + e\left(\varphi - \frac{\partial \chi}{\partial t}\right)\right]\psi$$

doing the algebra, we recover the original schrodinger equation

our new hamiltonian is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{\frac{e}{m}\frac{\hbar}{i}\vec{A}\cdot\nabla}_{H'} + \underbrace{\frac{e^2}{2m}\vec{A}^2}_{\text{ignore bc higher order}}$$

$$\vec{A} = \vec{A}_0 \cos(\vec{k}\cdot\vec{r} - \omega t)$$

$$k^2 = \frac{\omega^2}{c^2} \qquad \vec{A}_0 \cdot \vec{k} = 0$$

remember in the coulomb gauge:

$$\varphi = 0$$
$$\nabla \cdot A = 0$$

$$\vec{A} = \frac{1}{2}\vec{A}_0\left(e^{i(kr - \omega t)} + \underbrace{e^{-i(kr - \omega t)}}_{\text{this refers to transitions in the opposite direction, so we can ignore it}}\right)$$

$$\vec{E} = \frac{\partial A}{\partial t} = -\frac{1}{2} i \omega \vec{A}_0 e^{i(kr - \omega t)}$$

$$H' = \frac{e}{m}\frac{\hbar}{i}\vec{A}\cdot\vec{\nabla}$$

$$H' = \frac{e}{m}\frac{\hbar}{i} e^{ikr} e^{-i\omega t}\left(\frac{\vec{A}\cdot\vec{\nabla}}{2}\right)$$

$$\frac{\hbar}{i}\vec{\nabla} = \vec{p}$$

$$H' = \frac{e}{2m} e^{ikr} e^{-i\omega t} \vec{A}_0 \cdot \vec{p}$$

recall from periodic perturbation theory:

$$H' = V e^{-i\omega t}$$

so $V = \frac{e}{2m} e^{ikr} \vec{A}_0 \cdot \vec{p}$

$$V_{if} = \langle \text{final} | V | \text{initial} \rangle$$

and the fermi-golden rule says:

$$R = \frac{V_{if}^2}{\hbar^2} 2\pi\, \delta(\omega_{if} - \omega)$$

$$\omega_{if} = \frac{E_f - E_i}{\hbar}$$

$$V_{fi} = \frac{e}{2m}\langle f | e^{ikr} \vec{A}_0 \cdot \vec{p} | i \rangle$$

in the hydrogen atom:

$$\langle r \rangle \simeq a^0 \text{ (bohr radius)}$$
$$\langle p \rangle \simeq \frac{\hbar}{a}$$

$$e^{ikr} = 1 + ikr - \frac{1}{2}(kr)^2 \ldots$$

dipole approximation

the wavelength of the radiation is much bigger than the size of the atom, so we can ignore all kr terms

$$e^{ikr} \simeq 1$$

in the dipole approximation:

$$V_{fi} = \frac{e}{2m}\vec{A}_0 \cdot \langle f | \vec{p} | i \rangle$$

trick:

$$\left[\vec{r}, H_0\right] = \left[\vec{r}, \frac{p^2}{2m} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right]$$

$$\left[\vec{r}, H_0\right] = \frac{i\hbar}{m}\vec{p}$$

$$\vec{p} = \frac{m}{i\hbar}\left[\vec{r}, H_0\right]$$

$$V_{fi} = \frac{e}{2m}\left(\frac{m}{i\hbar}\right)\vec{A}_0 \cdot \langle f | [r, H_0] | i \rangle$$

$$V_{fi} = \frac{e}{2i\hbar}\vec{A}_0 \cdot \langle f | \vec{r} H_0 - H_0 \vec{r} | i \rangle$$

$$V_{fi} = \frac{e}{2i\hbar}(E_i - E_f)\vec{A}_0 \cdot \langle f | \vec{r} | i \rangle$$

$$\text{but } \frac{E_i - E_f}{\hbar} = -\omega_{fi}$$

$$V_{fi} = e\omega_{fi}\left(\frac{i}{2}\right)\vec{A}_0 \cdot \langle f | \vec{r} | i \rangle$$

$$-\frac{i\omega \vec{A}_0}{2} = \vec{E}_0$$

$$V_{fi} = -e\vec{E}_0 \quad \langle f | \vec{r} | i \rangle$$

$$\langle f | \vec{r} | i \rangle = \vec{d}$$

$$V_{fi} = -e\left(\vec{E}_0 \cdot \vec{d}\right)$$

we want R_{if} averaged over all polarizations and integrated over all frequencies

$$R_{if}\Big|_{avg} = \frac{2\pi}{\hbar^2}\int_{-\infty}^{\infty} V_{if}^2\, \delta(\omega_{if} - \omega)\, d\omega$$

$$V_{fi}^2 = e^2\left|\vec{E}_0 \cdot \vec{d}\right|^2$$

$\vec{E}_0$ is our polarization vector

$$\left|\vec{E}_0 \cdot \vec{d}\right|^2 = |d|^2 |E_0|^2 \sin^2\theta \cos^2\varphi$$

$$\text{average} = \frac{1}{4\pi}\int_0^{\pi}\sin^2\theta\, d\theta \int_0^{2\pi}\cos^2\varphi\, d\varphi$$
$$= \frac{1}{3}$$

$$V_{fi}^2 = \frac{1}{3}e^2 |d|^2 |E_0|^2$$

$$|E_0|^2 = \frac{2\rho(\omega)}{\varepsilon_0} \leftarrow \text{energy density}$$

the transition rate is therefore

$$R = \frac{\pi}{3\varepsilon_0\hbar^2}\rho(\omega_{if})\left|\vec{d}\right|^2$$

energy density of the EM radiation per unit frequency

3 types of transition: rate

① absorption B_{if}

② stimulated emission B_{fi}

③ spontaneous emission A

N_f = number of particles in final state

$$\frac{dN_f}{dt} = -AN_f - B_{fi}\,\rho(\omega_{if})N_f + B_{if}\,\rho(\omega_{if})N_i$$

in thermal equilibrium:

$$\frac{dN_f}{dt} = 0$$

$$\rho(\omega_{if})\left(B_{if}N_i - B_{fi}N_f\right) = AN_f$$

in thermal equilibrium however, the emitted radiation follows a blackbody spectrum:

$$\rho(\omega_{if}) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/kT}-1}$$

so $\frac{N_f}{N_i} = e^{-\hbar\omega_{if}/kT}$

$$\rho(\omega_{if}) = \frac{AN_f}{B_{if}N_i - B_{fi}N_f} = \frac{A}{B_{if}\frac{N_i}{N_f} - B_{fi}}$$

$$\rho(\omega_{if}) = \frac{A}{B_{if}\,e^{-\hbar\omega_{if}/kT} - B_{fi}}$$

but $B_{if} = B_{fi}$, so

$$\boxed{A = B_{if}\frac{\hbar\omega^3}{\pi^2 c^3}}$$ the rate of spontaneous emission

but we know

$$B_{if} = \frac{\pi}{3\varepsilon_0\hbar^2}\rho(\omega_{if})|\vec{d}|^2$$

so:

$$\boxed{A = \frac{\omega_{if}^3}{3\varepsilon_0\pi c^3\hbar}|\vec{d}|^2}$$

Quantum Computing

new notation:

V, W (2 vector spaces)

$|v\rangle \in V$

$|w\rangle \in W$

$|v\rangle \otimes |w\rangle \in V \otimes W$

tensor product

it's a linear operator:

$(\alpha|v_1\rangle + \beta|v_2\rangle) \otimes |w\rangle =$

$\alpha|v_1\rangle \otimes |w\rangle + \beta|v_2\rangle \otimes |w\rangle$

and vice versa

basis: $|e_i\rangle$ $i = 1, \dots, \dim(V)$ is our basis on V

$|f_j\rangle$ $j = 1 \dots \dim(W)$ is our basis on W

$|e_i\rangle \otimes |f_j\rangle$ is our basis on $V \otimes W$

So the dimension of $V \otimes W$ is:

$$\dim(V \otimes W) = \dim(V)\dim(W)$$

suppose A is an operator on V and B is an operator on W:

$$(A \otimes B)(|v\rangle \otimes |w\rangle) = A|v\rangle \otimes B|w\rangle$$

$$(A_1 \otimes B_1)(A_2 \otimes B_2) = A_1A_2 \otimes B_1B_2$$

normal matrix multiplication

example: $\left.\begin{matrix}V\\W\end{matrix}\right\}$ spin space for $s = \frac{1}{2}$

V, W: $|\tfrac{1}{2}\,\tfrac{1}{2}\rangle = |\tfrac{1}{2}\rangle = |\uparrow\rangle = |0\rangle$

$|\tfrac{1}{2}\,{-\tfrac{1}{2}}\rangle = |{-\tfrac{1}{2}}\rangle = |\downarrow\rangle = |1\rangle$

Basis on $V \otimes W$:

$|0\rangle \otimes |0\rangle = |00\rangle$

$|0\rangle \otimes |1\rangle = |01\rangle$

$|1\rangle \otimes |0\rangle = |10\rangle$

$|1\rangle \otimes |1\rangle = |11\rangle$

note: $V \otimes W$ is four dimensional

EPR Paradox

$$|EPR\rangle = \frac{1}{\sqrt{2}}\left(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle\right)$$

this is a 2 particle state:

suppose you seperate particle 1 and 2 and move them far away from each other

The 2 particle state is a superposition of $|01\rangle$ and $|10\rangle$:

If we measure particle 1 to be $|0\rangle$, then the other group will definitely measure particle 2 to be 1.

→ How do we explain this long distance correlation between measurements?

for each 1 particle state, the projection operator is:

$$P_z^0 = |0\rangle\langle 0|$$

$$P_z^1 = |1\rangle\langle 1|$$

$$P_{zz}^{00} = \langle EPR|\left(|0\rangle\langle 0| \otimes |0\rangle\langle 0|\right)|EPR\rangle$$

↖ probability that both particles are in the zero state

$$P_{zz}^{00} = 0 \qquad P_{zz}^{10} = \frac{1}{2}$$

$$P_{zz}^{01} = \frac{1}{2} \qquad P_{zz}^{11} = 0$$

how about P_x ?

$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ this has eigenvectors:

$\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ eigenvalue 1

$\frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$ eigenvalue -1

so $P_x^0 = \frac{1}{2}(|0\rangle + |1\rangle)(\langle 0| + \langle 1|)$

$P_x^1 = \frac{1}{2}(|0\rangle - |1\rangle)(\langle 0| - \langle 1|)$

$$P_{xx}^{nm} = P_x^n \otimes P_x^m$$

we can also measure two different directions:

$$P_{zx}^{nm} = P_z^n \otimes P_x^m$$

Teleportation

this is a quantum algorithm

$$|\Psi\rangle = \begin{bmatrix} a \\ b \end{bmatrix} = a|0\rangle + b|1\rangle$$

we don't know what this state is. If we did measure it, it would collapse and wouldn't be useful any more.

Take this single particle state and tensor it with the two-particle EPR state, with the second particle very far away:

$$|\Psi\rangle \otimes |EPR\rangle = \frac{1}{\sqrt{2}}\left(a|001\rangle - a|010\rangle + b|101\rangle - b|110\rangle\right)$$

① C_0 operation (this only acts on Ψ and the first particle in EPR; it can't affect the far away particle)

$$C_0 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$C_0|00\rangle = |00\rangle$$

$$C_0|01\rangle = |01\rangle$$

$$C_0|10\rangle = |11\rangle$$

$$C_0|11\rangle = |10\rangle$$

$$C_0\left(|\Psi\rangle \otimes |EPR\rangle\right) = \frac{1}{\sqrt{2}}\left(a|001\rangle - a|010\rangle + b|111\rangle - b|100\rangle\right)$$

② act on the first particle Ψ with the Hadamard gate:

$$H_0 = \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

$$H_0|0\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$$

$$H_0|1\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$$

* to act on the three part state, our real operator is $H_0 \otimes I \otimes I$ ← identity *

$$H_0 C_0\left(|\Psi\rangle \otimes |EPR\rangle\right) = \frac{1}{2}\left(a|001\rangle + a|101\rangle - a|010\rangle - a|110\rangle + b|011\rangle - b|111\rangle - b|000\rangle + b|100\rangle\right)$$

Entanglement

any state that cannot be factored into

$$|\text{particle } 1\rangle \otimes |\text{particle } 2\rangle$$

is called an entangled state

$|EPR\rangle$ is entangled because

$\frac{1}{\sqrt{2}}\left(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle\right)$ cannot be further reduced

on the other hand, the state:

$$\frac{1}{\sqrt{2}}\left(|0\rangle \otimes |1\rangle + |1\rangle \otimes |1\rangle\right)$$

can be factored into:

$$\frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right) \otimes |1\rangle$$

No clone theorem

theorem: there's no such thing as a "quantum copier" s.t.

$$|\psi\rangle|x\rangle \to |\psi\rangle|\psi\rangle$$

proof by contradiction:

$*\ |\psi_1\rangle|x\rangle \to |\psi_1\rangle|\psi_1\rangle$

$*\ |\psi_2\rangle|x\rangle \to |\psi_2\rangle|\psi_2\rangle$

now feed in a linear combination:

we should get (if the copier is good):

$$(\alpha|\psi_1\rangle + \beta|\psi_2\rangle)|x\rangle \to (\alpha|\psi_1\rangle + \beta|\psi_2\rangle)(\alpha|\psi_1\rangle + \beta|\psi_2\rangle)$$

but according to * and the linearity of operators:

$$(\alpha|\psi_1\rangle + \beta|\psi_2\rangle)|x\rangle = \alpha|\psi_1\rangle|\psi_1\rangle + \beta|\psi_2\rangle|\psi_2\rangle$$

so you can't clone a state without destroying the original state

Complexity

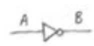
computational complexity is the time it takes to solve a problem as a function of the size of the problem (n)

polynomial: $t \sim O(n^c)$

NP: $t \sim O(e^n)$ but polynomial to verify

exponential: $t \sim O(e^n)$ and exponential to verify

classical gates:

NOT 

A	B
0	1
1	0

AND 

A	B	C
0	0	0
0	1	0
1	0	0
1	1	1

etc, you know what gates are

Notes: ① classical gates are often irreversible

② gates can be cascaded

Quantum Gates

quantum computation:

1. unitary transformations (Schrodinger evolution, preservation of probabilities, reversible)
2. measurements (irreversible)

unitary transformations are done by quantum gates:

1 bit: $x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ $z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ ...

there's infinitely many 2x2 matrices, so there's infinitely many 1 bit (particle) operators

2 bit gates: these are 4x4 matrices

ex: $C_{not} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$

for C_{not}, iff first bit is high, second bit is flipped

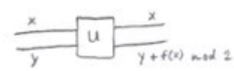
Deuch's Algorithm

$f(x): 0,1 \to 0,1$

→ goal is to check whether $f(0) = f(1)$

on a classical computer, we would need to call $f(x)$ twice, once for each input.

on a quantum computer, we only need to call $f(x)$ once

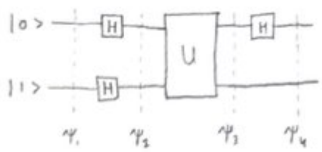


say $f(0) = 1$, $f(1) = 0$

x	y	x	y + f(x)
0	0	0	1
0	1	0	0
1	0	1	0
1	1	1	1

what matrix accomplishes this?

$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$ clearly, this is unitary the algorithm is the following:



$\boxed{H}$ is the hadamar gate: $\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$

$\psi_1 = |0\,1\rangle$ (actually $|0\rangle \otimes |1\rangle$)

$\psi_2 = \frac{1}{2}\left(|00\rangle + |10\rangle - |01\rangle - |11\rangle\right)$

$\psi_3 = \frac{1}{2}\left(|0\,f(0)\rangle + |1\,f(1)\rangle + |0\,\overline{f(0)}\rangle - |1\,\overline{f(1)}\rangle\right)$

$\psi_4 = \frac{1}{2\sqrt{2}}\Big(|0\,f(0)\rangle + |1\,f(0)\rangle + |0\,f(1)\rangle - |1\,f(1)\rangle$

$- |0\,\overline{f(0)}\rangle - |1\,\overline{f(0)}\rangle - |0\,\overline{f(1)}\rangle + |1\,\overline{f(1)}\rangle\Big)$

combine like terms for ψ_4:

$\psi_4 = \frac{1}{2\sqrt{2}}\Big[|0\,(f(0) + f(1) - \overline{f(0)} - \overline{f(1)})\rangle +$

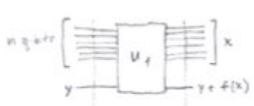
$|1\,(f(0) - f(1) - \overline{f(0)} + \overline{f(1)})\rangle\Big]$

Grover Search

n bits, 2^n possibilities

① $f(x) = \begin{cases} 0 & \text{if } x \neq a \\ 1 & \text{if } x = a \end{cases}$

x and a are n-bit numbers (i.e. we're searching for the x that is the same as a



② $|x\rangle_n|y\rangle \quad |x\rangle_n|y + f(x)\rangle$

start with evaluating:

$U_f\left(|x\rangle_n H|1\rangle\right)$

$U_f\left(|x\rangle_n \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)\right)$

$\frac{1}{\sqrt{2}}\left(|x\rangle_n|f(x)\rangle - |x\rangle_n|\overline{f(x)}\rangle\right)$

rewrite this:

$(-1)^{f(x)}|x\rangle_n H|1\rangle$

define a unitary operation:

$V|x\rangle_n = (-1)^{f(x)}|x\rangle_n$

③ $V|x\rangle_n = \begin{cases} |x\rangle_n & \text{for } x \neq a \\ -|a\rangle & \text{for } x = a \end{cases}$

now suppose ψ is some arbitrary state (maybe a superposition of a bunch of binary numbers)

④ $V|\psi\rangle = |\psi\rangle - 2|a\rangle\langle a|\psi\rangle$

we know this is true because

$|\psi\rangle = \sum c_x|x\rangle_n$

where our basis is:

$e_1 = \overbrace{000\ldots000}^{n\text{-long}}$

$e_2 = 000\ldots001$

$\vdots$

$e_{2^n} = 111\ldots111$

we can rewrite:

$V = 1 - 2|a\rangle\langle a|$

⑤ apply a hadamar gate to a $|0\rangle$ on every input. Notate this:

$|\varphi\rangle = H^n|0\rangle_n$

$|\varphi\rangle = (H|0\rangle_1) \otimes (H|0\rangle_2) \otimes (H|0\rangle_3) \ldots (H|0\rangle_n)$

→ $|\varphi\rangle$ is the superposition of all n-bit binary numbers, with equal weighting

⑥ define: $W = 2|\varphi\rangle\langle\varphi| - 1$

Now, put it all together:

what is $WV|\varphi\rangle$?

we can rewrite $|\varphi\rangle$ as:

$|\varphi\rangle = |a_\perp\rangle + \frac{1}{2^{n/2}}|a\rangle$

superposition of all numbers that aren't a (i.e orthogonal to $|a\rangle$)

$V|\varphi\rangle = V|a_\perp\rangle + 2^{-n/2}V|a\rangle$

$V|\varphi\rangle = |a_\perp\rangle - 2^{-n/2}|a\rangle$

$\left[V|\varphi\rangle = |\varphi\rangle - \frac{2}{2^{n/2}}|a\rangle\right]$

$WV|\varphi\rangle = W|\varphi\rangle - \frac{2}{2^{n/2}}W|a\rangle$

$= \big(2|\varphi\rangle\underbrace{\langle\varphi|\varphi\rangle}_{\text{one}} - |\varphi\rangle\big) -$

$\frac{2}{2^{n/2}}\left(2|\varphi\rangle\langle\varphi|a\rangle - |a\rangle\right)$

we know: $\langle\varphi|a\rangle = \frac{1}{2^{n/2}}$

$WV|\varphi\rangle = |\varphi\rangle - \frac{4}{2^n}|\varphi\rangle + \frac{2}{2^{n/2}}|a\rangle$

$\boxed{WV|\varphi\rangle = |a_\perp\rangle + \frac{3}{2^{n/2}}|a\rangle}$

so the operation WV increased the amount of $|a\rangle$ in $|\varphi\rangle$ by three.

By repeatedly applying WV, we linearly increase the probability that when $|\varphi\rangle$ is measured, we get $|a\rangle$

Note: if you apply it too many times, you'll overshoot and start lowering the probability of getting $|a\rangle$

Hidden Variables

$|EPR\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

rewrite in matrix notation:

$|EPR\rangle = \frac{1}{\sqrt{2}}\left(\begin{bmatrix}1\\0\end{bmatrix}\otimes\begin{bmatrix}0\\1\end{bmatrix} - \begin{bmatrix}0\\1\end{bmatrix}\otimes\begin{bmatrix}1\\0\end{bmatrix}\right)$

send to 2 detectors, measuring on arbitrary axis $\hat{a}$ and $\hat{b}$, respectively

$P(\hat{a},\hat{b})$ is the expectation value of the EPR state of measurement along $\hat{a}$ and $\hat{b}$ at locations A and B

$P(\hat{a},\hat{b}) = \langle EPR|\sigma_a \otimes \sigma_b|EPR\rangle$

$P(\hat{a},\hat{a}) = -1$ (because one is up and one is down, so the product of their eigenvalues is always negative)

$\sigma_a = \sigma_z$

$\sigma_b = \cos\alpha\,\sigma_z + \sin\alpha\,\sigma_x$

$\sigma_b = c\begin{bmatrix}1&0\\0&-1\end{bmatrix} + s\begin{bmatrix}0&1\\1&0\end{bmatrix}$

$\sigma_b = \begin{bmatrix}c&s\\s&-c\end{bmatrix}$

$P(\hat{a},\hat{b}) = \langle EPR|\begin{bmatrix}1&0\\0&-1\end{bmatrix}\otimes\begin{bmatrix}c&s\\s&-c\end{bmatrix}|EPR\rangle$

$c\text{-ket} = \left(\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix}\otimes\begin{bmatrix}c&s\\s&-c\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix}\right.$
$\left. - \begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix}\otimes\begin{bmatrix}c&s\\s&-c\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix}\right)\frac{1}{\sqrt{2}}$

$= \left(\begin{bmatrix}1\\0\end{bmatrix}\otimes\begin{bmatrix}s\\-c\end{bmatrix} - \begin{bmatrix}0\\-1\end{bmatrix}\otimes\begin{bmatrix}c\\s\end{bmatrix}\right)\frac{1}{\sqrt{2}}$

$c\text{-ket} = \frac{1}{\sqrt{2}}\begin{bmatrix}s\\-c\\0\\0\end{bmatrix} + \frac{1}{\sqrt{2}}\begin{bmatrix}0\\0\\c\\s\end{bmatrix}$

$= \frac{1}{\sqrt{2}}\begin{bmatrix}s\\-c\\c\\s\end{bmatrix}$

$\langle EPR| = \frac{1}{\sqrt{2}}\begin{bmatrix}0&1&-1&0\end{bmatrix}$

$\text{bra-}c\text{-ket}: \frac{1}{2}(-c-c)$

$\left[P(\hat{a},\hat{b}) = -\cos\alpha\right]$

now suppose there is some hidden variable λ

$$* \begin{cases} A(\hat{a},\lambda) = \pm 1 \\ B(\hat{b},\lambda) = \pm 1 \end{cases}$$

λ has some probability distribution

$P(\hat{a},\hat{b}) = \int \rho(\lambda)\, A(\hat{a},\lambda)\, B(\hat{b},\lambda)\, d\lambda$

if you set $\hat{a} = \hat{b}$:

$A(\hat{a},\lambda) = -B(\hat{a},\lambda)$

$P(a,b) - P(a,c) = -\int \rho(\lambda)\left[A(a,\lambda)A(b,\lambda) - A(a,\lambda)A(b,\lambda)\right]d\lambda$

$= -\int \rho(\lambda)\left[1 - A(b,\lambda)A(c,\lambda)\right]A(a,\lambda)A(b,\lambda)\,d\lambda$

$\leq 1 + \int \rho(\lambda)\, A(b,\lambda)\, B(c,\lambda)\, d\lambda$

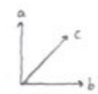
$\leq 1 + P(b,c)$

putting it all together:

$$\boxed{|P(a,b) - P(a,c)| \leq 1 + P(b,c)}$$

this is a bell inequality, it must be true if you think that probability can be explained by some hidden variable

consider:



$P(a,b) = 0$

$P(a,c) = \frac{1}{\sqrt{2}}$

$P(b,c) = \frac{-1}{\sqrt{2}}$

$\frac{1}{\sqrt{2}} \leq 1 - \frac{1}{\sqrt{2}}$

$1 \leq \sqrt{2} - 1$

$2 \leq \sqrt{2}$ X clearly, the experimental results disagree with any hidden variable theory

WKB Approximation

AKA: semi-classical approximation

can be used to approximate energies, bound states, and tunelling rates for arbitrary potentials

assume the wave function has the form:

$$\psi = A e^{i\varphi(x)/\hbar}$$

expand $\varphi(x)$ in powers of $\hbar$:

$$\varphi(x) = \varphi_0(x) + \hbar\varphi_1(x) + \hbar^2\varphi_2(x) \ldots$$

the WKB APPROXIMATION is to take only the first two terms

plug into schroedinger:

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi = E\psi$$

$$\left[\frac{i}{\hbar}\varphi'' - \frac{(\varphi')^2}{\hbar^2} + \frac{2m}{\hbar^2}(E - V(x))\right]e^{i\varphi(x)/\hbar} = 0$$

$$i\hbar\varphi'' - \varphi'^2 + 2m(E - V(x)) = 0$$

now apply approximation:

$$i\hbar(\varphi_0'' + \hbar\varphi_1'') - (\varphi_0' + \hbar\varphi_1')^2 + 2m(E - V(x)) = 0$$

group terms by order in $\hbar$:

0^{th} order: $-\varphi_0'^2 + 2m(E - V(x)) = 0$

1^{st} order: $i\hbar\varphi_0'' - 2\hbar\varphi_0'\varphi_1' = 0$

can't take 2^{nd} order because we didn't include them in the original approximation

call: $p(x) = (2m(E - V(x)))^{1/2}$

$$\varphi_0 = \int_{x_0}^{x} p(x')\,dx'$$

$$\varphi_1 = C + i\ln\sqrt{p(x)}$$

plug into wave function:

$$\psi(x) = A e^{\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx' + i(C + i\ln\sqrt{p(x)})}$$

$$A' = Ae^{iC}$$

$$\psi(x) = A'\frac{1}{\sqrt{p(x)}}\, e^{\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'}$$

we can express the normalization as:

$$A' = \psi(x_0)\sqrt{p(x_0)}$$

$$\boxed{\psi(x) = \psi(x_0)\sqrt{\frac{p(x_0)}{p(x)}}\, e^{\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'}}$$

note: $\sqrt{\frac{p(x_0)}{p(x_0)}}$ is the classical probability density

Applications

$$V(x) = \begin{cases} \infty & x < 0 \mid x > a \\ f(x) & 0 < x < a \end{cases}$$

$$\psi(x) = A\sin\left[\frac{1}{\hbar}\int_0^x p(x')dx'\right] + B\cos\left[\frac{1}{\hbar}\int_0^x p(x')dx'\right]$$

$\psi(0) = 0$ so $B = 0$

similarly, the argument of A must be $n\pi$

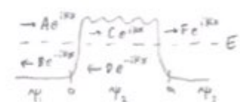
$$\frac{1}{\hbar}\int_0^a p(x')dx' = n\pi$$

suppose $f(x) = 0$ (infinite square well)

then $p(x) = \sqrt{2mE}$

$$\frac{1}{\hbar}a\sqrt{2mE} = n\pi$$

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

tunneling: 

$$V(x) = \begin{cases} 0 & x > a \mid x < 0 \\ f(x) & 0 < x < a \end{cases}$$

$$\psi_2 = C\exp\left[\frac{1}{\hbar}\int_0^x p(x')dx'\right] + D\exp\left[\frac{1}{\hbar}\int_0^x p(x')dx'\right]$$

etc.

continuity conditions:

$\psi|_0$: $A + B = C + D$

$\psi'|_0$: $ik(A - B) = \frac{1}{\hbar}p(0)(C - D)$

$\psi|_a$: $Ce^{\gamma} + De^{\gamma} = F$

$\psi'|_a$: $\frac{1}{\hbar}p(a)(Ce^{\gamma} - De^{\gamma}) = ikF$

after some sketchy approximations:

$$\left|\frac{F}{A}\right|^2 \approx e^{-2\gamma} = e^{-\frac{2}{\hbar}\int_0^a p(x)dx}$$

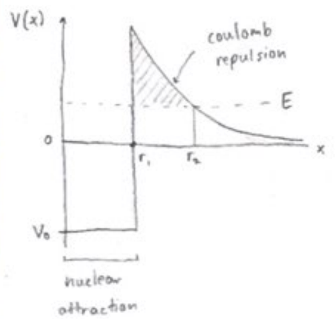
Decay

alpha decay:

$(Z+2)$ charge nucleus

$(Z+2) \rightarrow Z + \alpha_{2P\,2N}$

imagine this as a bound state between Z and α



so the probability of alpha decay is the probability that the particle tunnels through the shaded region, from r_1 to r_2

tunneling rate $T = e^{-2\gamma}$

$$\gamma = \frac{1}{\hbar}\int_{r_1}^{r_2} p(x)\,dx$$

recall: $p(x) = (2m(E - V(x)))^{1/2}$

$$V(x) = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(2e)}{r}$$

the solution to this integral is:

$$\frac{\sqrt{2mE}}{\hbar}\left[r_2\left(\frac{\pi}{2} - \sin^{-1}\sqrt{\frac{r_1}{r_2}}\right) - \sqrt{r_1 r_2 - r_1^2}\right]$$

for $r_1 << r_2$:

$$\gamma = \frac{\sqrt{2mE}}{\hbar}\left(\frac{\pi}{2}r_2 - 2\sqrt{r_1 r_2}\right)$$

$$V(r_2) = E = \frac{2Ze^2}{4\pi\varepsilon_0}\frac{1}{r_2}$$

$$r_2 = \frac{2Ze^2}{4\pi\varepsilon_0}\frac{1}{E}$$

$$\gamma = K_1\frac{Z}{\sqrt{E}} - K_2\sqrt{Zr_1}$$

lifetime $\tau = \frac{1}{T} = e^{2\gamma}$

$$\tau = e^{2K_1\frac{Z}{\sqrt{E}} - 2K_2\sqrt{Zr_1}}$$

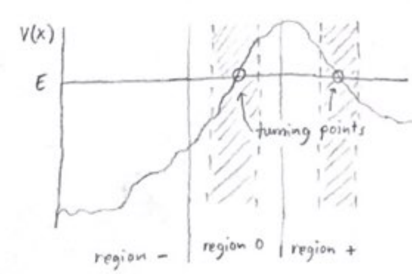
$$\boxed{\ln\tau = 2K_1\frac{Z}{\sqrt{E}} - 2K_2\sqrt{Zr_1}}$$

$$K_1 = \frac{\sqrt{2m}}{\hbar}\frac{\pi}{2}\frac{2e^2}{4\pi\varepsilon_0}$$

$$K_2 = \frac{4m}{\hbar}\sqrt{\frac{e^2}{4\pi\varepsilon_0}}$$

Connection Formulas

WKB breaks down at classical turning points because $\frac{1}{p} \rightarrow \infty$



suppose WKB works everywhere except the shaded regions. Also suppose that $V(x)$ can be linearly approximated in region 0.

region 0: $V(x) = E + V'x$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_0 + V'x\,\psi_0 + E\psi_0 = E\psi_0 x$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi_0}{dx^2} = V'x\,\psi_0$$

substitute variables: $B^3 = \frac{2mV'}{\hbar^2}$

$Bx = y$

$$\frac{d^2\psi_0}{dy} = y\,\psi_0$$

the solutions to this are called Airy's functions

the general solution is:

$$\psi_0 = A_0\,Ai(y) + B_0\,Bi(y)$$

Airy's A function   Airy's B function

$y << 0$:

$$Ai = \frac{1}{\sqrt{\pi}(-y)^{1/4}}\sin\left(\frac{2}{3}(-y)^{3/2} + \frac{\pi}{4}\right)$$

$$Bi = \frac{1}{\sqrt{\pi}(-y)^{1/4}}\cos\left(\frac{2}{3}(-y)^{3/2} + \frac{\pi}{4}\right)$$

$y >> 0$:

$$Ai = \frac{1}{2\sqrt{\pi}\,y^{1/4}}e^{-\frac{2}{3}y^{3/2}}$$

$$Bi = \frac{1}{2\sqrt{\pi}\,y^{1/4}}e^{\frac{2}{3}y^{3/2}}$$

Now look at WKB solutions for region − and region +:

$$\psi_{WKB} \approx \frac{1}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar}\int p(x)\,dx}$$

$$p(x) = \sqrt{2m(E - V(x))}$$

$$p(x) = \sqrt{2m(E - E - V'x)}$$

$$p(x) = \sqrt{-x}\,\sqrt{\frac{2mV'}{\hbar^2}}\,\hbar$$

$$p(x) = \sqrt{-x}\,\hbar\,\beta^{3/2}$$

$$\frac{i}{\hbar}\int \sqrt{-x}\,\hbar\,\beta^{3/2}\,dx = i\beta^{3/2}\frac{2}{3}(-x)^{3/2}$$

$$\left[\psi_- = C\frac{1}{(-x\beta)^{1/4}} e^{i\frac{2}{3}\beta^{3/2}(-x)^{3/2}} + D\frac{1}{(-x\beta)^{1/4}} e^{-i\frac{2}{3}\beta^{3/2}(-x)^{3/2}}\right]$$

note: x is strictly negative in region −

ψ_+ is analogous:

$$\left[\psi_+ = F\frac{1}{(x\beta)^{1/4}} e^{-\frac{2}{3}\beta^{3/2}x^{3/2}} + (\text{non-normalizable exponential})\right]$$

now glue ψ_- and ψ_+ to ψ_0

$$\psi_0 = A_0\,A_i(y) + B_0\,B_i(y)$$

functional dependance is the same!

compare coefficients:

$$B_0 = 0 \qquad \frac{A_0}{2\sqrt{\pi}} = F$$

$$C = -iFe^{i\pi/4}$$

$$D = iFe^{-i\pi/4}$$

we find:

$$\psi_- = \frac{F}{\sqrt{p(x)}}\sin\left(\int p(x)\,dx + \frac{\pi}{4}\right)$$

note:

for 2 infinite walls: $\frac{1}{\hbar}\int p(x)\,dx = n\pi$

for 1 infinite wall: $\frac{1}{\hbar}\int p(x)\,dx = \left(n - \frac{1}{4}\right)\pi$

(since ψ_- must disappear at the wall, and ψ_- has as the argument of a sin: $\int p(x)\,dx + \frac{\pi}{4}$)

analagously, for zero infinite walls:

$$\boxed{\int p(x)\,dx = \left(n - \frac{1}{2}\right)\pi}$$

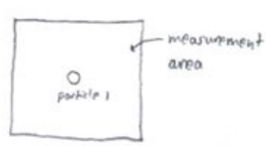
for small n, this greatly improves the approximation

3D Scattering

scattering experiments help to figure out the interaction potentials of various particles

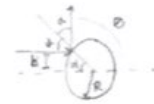
we'll scatter particles off of a central potential $V(r)$ (2-body reduced mass)

scattering cross-section:



throw particles at P1 and measure how they land on the measurement area.

classical example: hard sphere



b is the impact parameter

θ is the scattering angle

$$\sin\alpha = \frac{b}{R}$$

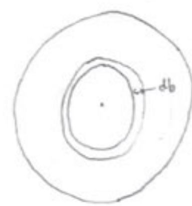
$$\alpha = \frac{1}{2}(\pi - \theta)$$

$$b = R\sin\alpha$$

$$b = R\sin\left(\frac{\pi}{2} - \frac{\theta}{2}\right)$$

$$b = R\cos\left(\frac{\theta}{2}\right)$$

calculate scattering cross-section:



σ = scattering cross-section

$$d\sigma = b\,db\,d\varphi$$

$$db = -\frac{1}{2}R\sin\left(\frac{\theta}{2}\right)d\theta$$

σ can't be negative though, so take $|db|$

$$d\sigma = \frac{1}{2}R^2\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right)d\theta\,d\varphi$$

quantum scattering:

assume incoming plane wave of particles

incoming wave function >> scattering center

uniform distribution in $\perp$ direction, so this automatically averages over all impact parameters

assume that $V(r) = 0$ for $r > R$

scattered particles obey the schrodinger equation for the free particle

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$(\nabla^2 + k^2)\psi_{sc} = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

solutions to this are the spherical bessel functions

$$\psi_{sc} = \sum_{lm} c_{lm} Y_l^m(\theta, \varphi)\left(j_l(k_r) + n_l(k_r)\right)$$

spherical bessel — spherical neuman

at large r:

$$h_l(x) = j_l(x) + n_l(x)$$

$$j_l(k_r) = \frac{1}{k_r}\sin\left(k_r - \frac{l\pi}{2}\right)$$

$$n_l(k_r) = \frac{-1}{k_r}\cos\left(k_r - \frac{l\pi}{2}\right)$$

say: $\psi = e^{ikz} + f(\theta,\varphi)\frac{e^{ikr}}{r}$

$$(\nabla^2 + k^2)\psi = \frac{2mV}{\hbar^2}\psi$$

$$(\nabla^2 + k^2)\left(-\frac{e^{ikr}}{4\pi r}\right) = \delta^3(\vec{r})$$

$$\frac{d\sigma}{d\Omega} = |f(\theta,\varphi)|^2$$

$$\psi(r) = e^{ikz}\left[-\frac{m}{2\pi\hbar^2}\int e^{-ik(\hat{r}-\hat{z})\vec{r}_0} V(r_0)\, d^3r_0\right]\frac{e^{ikr}}{r}$$

$$f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int e^{-ik(\hat{r}-\hat{z})r_0} V(r_0)\, d^3r_0$$

2 simplifying cases:

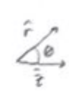
1. small k (big wavelength, low energy)

$$f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int V(r_0)\, d^3r_0$$

$\frac{d\sigma}{d\Omega} = |f|^2$ is independant of θ, φ

2. $V(\vec{r})$ is spherically symmetric

$$V(\vec{r}) = V(r)$$



$\hat{r}\cdot\hat{z} = \cos\theta$

Yukawa Potential

$$V(r) = \beta\frac{e^{-\mu r}}{r}$$

$$f(\theta) = -\frac{2m}{\hbar^2 K}\int_0^\infty r V(r)\sin(Kr)\, dr$$

$$f(\theta) = -\frac{2m\beta}{\hbar^2 K}\int_0^\infty e^{-\mu r}\sin(Kr)\, dr$$

$$K = 2k\sin(\theta/2)$$

$$f(\theta) = -\frac{2m\beta}{\hbar^2 2k\sin\left(\frac{\theta}{2}\right)}\int_0^\infty \frac{e^{-\mu r}}{2i}\left(e^{i2kr\sin\left(\frac{\theta}{2}\right)} - e^{-i2kr\sin\left(\frac{\theta}{2}\right)}\right)dr$$

this reduces to:

$$f(\theta) = \frac{2m\beta}{\hbar^2\left(\mu^2 + \left(2kr\sin\left(\frac{\theta}{2}\right)\right)^2\right)}$$

coulomb potential:

$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

evidently:

$$\beta = \frac{q_1 q_2}{4\pi\varepsilon_0}$$

$$\mu = 0$$

$$f(\theta) = \frac{q_1 q_2}{16\pi\varepsilon_0 E\sin^2\left(\frac{\theta}{2}\right)}$$

Path Integrals

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

$$\Psi(t) = e^{-i\hat{H}t/\hbar}\,\Psi(0)$$

this is one solution to the schroedinger equation, up to some multiplicative constant $\Psi(0)$

call $e^{i\hat{H}t/\hbar}$ the time-evolution operator

$$U(x', x, t) = \langle x' | e^{-i\hat{H}t/\hbar} | x \rangle$$

evaluate over small t step:

$$\partial t = \frac{t}{n+1}$$

$$e^{-i\hat{H}t/\hbar} = \prod_{n+1} e^{-i\hat{H}\partial t/\hbar}$$

$$\lambda = \frac{i\,\partial t}{\hbar}$$

$$e^{-i\hat{H}t/\hbar} = \prod_{n+1} e^{-\lambda \hat{H}}$$

$$e^{-\lambda H} = e^{-\lambda \hat{p}^2/2m}\, e^{-\lambda V(x)} + \mathcal{O}(\partial t^2)$$

$$U(x', x, t) = \langle x' | e^{-\lambda \hat{p}^2/2m}\, e^{-\lambda V(x)} \cdots e^{-\lambda \hat{p}^2/2m}\, e^{-\lambda V(x)} | x \rangle$$

$$\mathbb{I} = \int |x_n\rangle\langle x_n|\, dx \qquad \mathbb{I} = \int |x_1\rangle\langle x_1|\, dx_1$$

propagate from x_1 to x_2, from x_2 to x_3 ... etc.

at each point, we get:

$$\langle x_n | e^{-\lambda \hat{p}^2/2m}\, e^{-\lambda V(x)} | x_{n-1} \rangle$$

$$\int |p\rangle\langle p|\, dp$$

$$\langle x_n | e^{-\lambda \hat{p}^2/2m} | p \rangle \langle p | e^{-\lambda V(x)} | x_{n-1} \rangle$$

$$\hat{p}|p\rangle = p|p\rangle$$

$$\int e^{-\lambda p^2/2m}\, e^{-\lambda V(x_{n-1})} \langle x_n | p \rangle \langle p | x_{n-1} \rangle\, dp$$

$$\langle x_n | p \rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipx_n/\hbar}$$

$$\langle p | x_{n-1} \rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{-ipx_{n-1}/\hbar}$$

$$\frac{1}{2\pi\hbar}\, e^{-\lambda V(x_{n-1})} \int_0^\infty e^{-\lambda p^2/2m}\, e^{ip(x_n - x_{n-1})/\hbar}\, dp$$

completing the square and doing the integral, we get:

$$f(x_n, x_{n-1}) = \frac{e^{-\lambda V(x_{n-1})}}{2\pi\hbar} \sqrt{\frac{2m\pi}{\lambda}}\; e^{-i(x_n - x_{n-1})^2 2m / 4\pi\hbar^2 \lambda}$$

we can plug this back into our equation for U

$$U = \int dx_n \cdots \int dx_1 \left[f(x_n, x_{n-1}) \cdots f(x_2, x_1) \right]$$

the $(x_n - x_{n-1})$ terms can be written:

$$e^{\frac{i}{\hbar} \partial t \frac{m}{2} \underbrace{\left(\frac{x_n - x_{n-1}}{\partial t}\right)^2}_{\dot{x}}}$$

$$e^{\frac{i\partial t}{\hbar}\left(\frac{1}{2} m \dot{x}^2\right)}$$

$$U = \int \cdots \int e^{\frac{i}{\hbar} \partial t \left[\frac{m}{2} \sum_n \dot{x}_n^2 - V(x_n) \right]}$$

call $\lim_{n \to \infty} \int dx_n \cdots \int dx_1 = \int Dx$

$$U = \int e^{\frac{i}{\hbar} \int \mathcal{L}\, dt}\, Dx$$

$$\boxed{U = \int e^{\frac{i}{\hbar} S[x(t)]}\, Dx}$$

where $U(x', x, t)$ is the probability of propagating from x to x' in time t

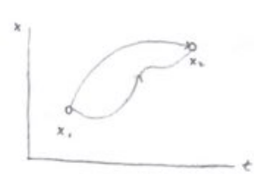
Applications

Electromagnetic field:

$$H = \frac{1}{2m}\left(\vec{p}^{\,2} - e\vec{A}\right)^2 + e\varphi$$

$$\mathcal{L} = \frac{1}{2} m \dot{\vec{r}}^{\,2} + e\dot{\vec{r}}\vec{A} - e\varphi$$

look at two paths:



take the contribution due to $\vec{B}$ field:

$$S = \int_{P_1} e\dot{\vec{r}}\vec{A}\, dt - \int_{P_2} e\dot{\vec{r}}\vec{A}\, dt$$

$$S = e\left[\int_{P_1} \vec{A}\, d\vec{r} - \int_{P_2} \vec{A}\, d\vec{r} \right]$$

but this is a closed loop $(P_1 + P_2 = C)$

$$S = e \int_C \vec{A}\, dr$$

the action (due only to the magnetic field) is:

$$S = e \int_c \vec{A}\, dr$$

$$S = e \int_A \nabla \times \vec{A}\, dA$$

surface enclosed by P_1 and P_2

$$S = e \underbrace{\int_A B\, dA}_{\text{this is just the magnetic flux}}$$

$$\int_A B\, dA = \Phi$$

$$S = e\,\Phi$$

so our phase shift is:

$$\boxed{\Delta\varphi = \frac{e\,\Phi}{\hbar}}$$

this is called the Aharonov-Bohm effect

Magnetic monopoles:

assume that a point like monopole exists ($\nabla \cdot B \neq 0$)

enclose it in a "gaussian surface" and take a path around the surface

$$\vec{B} = \frac{g}{4\pi} \frac{1}{r^2} \hat{r}$$

$$\nabla\varphi = \frac{e}{\hbar} \Phi$$

Summary sheets

Useful formulas:

$$S_- |s\ m\rangle = \hbar\sqrt{s(s+1) - m(m-1)}\ |s\ m-1\rangle$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Derivation of perturbation theory:

$$H = H_0 + H'$$

known H_0 s.t. $H_0|\psi_{n0}\rangle = E_{n0}|\psi_{n0}\rangle$

and $\langle \psi_{n0}|\psi_{m0}\rangle = \delta_{nm}$

note: H_0 unperturbed hamiltonian

ψ_{n0} the n^{th} eigenstate of H_0

E_{n0} the n^{th} eigenvalue of H_0

our goal is to find solutions to:

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

note: H perturbed hamiltonian

ψ_n the n^{th} eigenstate of H

E_n the n^{th} eigenvalue of H

now suppose that we can write ψ_n and E_n as power series:

$$\psi_n = \psi_{n0} + \psi_{n1} + \psi_{n2} \ldots$$

ψ_{n0} the n^{th} eigenstate of H_0

ψ_{n1} the 1^{st} order correction to the n^{th} eigenstate of H_0 ...

similarly

$$E_n = E_{n0} + E_{n1} + E_{n2}$$

plug back into $H|\psi_n\rangle = E_n|\psi_n\rangle$

$$(H_0 + H')\left(|\psi_{n0}\rangle + |\psi_{n1}\rangle + |\psi_{n2}\rangle\right) =$$

$$(E_{n0} + E_{n1} + E_{n2})\left(|\psi_{n0}\rangle + |\psi_{n1}\rangle\right)$$

$$H_0\psi_{n0} + H'\psi_{n0} + H_0\psi_{n1} + H'\psi_{n1}$$

$$+ H_0\psi_{n2} + H'\psi_{n2} = E_{n0}\psi_{n0} + E_{n0}\psi_{n1}$$

$$+ E_{n1}\psi_{n0} + E_{n1}\psi_{n1} + E_{n2}\psi_{n0} + E_{n2}\psi_{n1}$$

assume H' has order 1 and H_0 has order 0: collect by order:

zero order: $H_0\psi_{n0} = E_{n0}\psi_{n0}$ ✓

first order:

$$H'\psi_{n0} + H_0\psi_{n1} = E_{n0}\psi_{n1} + E_{n1}\psi_{n0}\ ;$$

take inner product with ψ_{n0}:

$$\langle\psi_{n0}|H'|\psi_{n0}\rangle + \langle\psi_{n0}|H_0|\psi_{n1}\rangle$$

$$= E_{n0}\langle\psi_{n0}|\psi_{n1}\rangle + E_{n1}\underbrace{\langle\psi_{n0}|\psi_{n0}\rangle}_{\text{one}}$$

second term:

$$\langle\psi_{n0}|H_0|\psi_{n1}\rangle = \langle H_0\psi_{n0}|\psi_{n1}\rangle$$

$$= E_{n0}\langle\psi_{n0}|\psi_{n1}\rangle$$

this cancels with the third term:

$$\boxed{\langle\psi_{n0}|H'|\psi_{n0}\rangle = E_{n1}}$$

correction to ψ_{n0}

$$H'\psi_{n0} + H_0\psi_{n1} = E_{n0}\psi_{n1} + E_{n1}\psi_{n0}$$

$$(H' - E_{n1})\psi_{n0} = -(H_0 - E_{n0})\psi_{n1}$$

but all terms except ψ_{n1} are known

we can express ψ_{n1} as a linear combination of ψ_{m0}'s

$$\psi_{n1} = \sum c_m \psi_{m0}$$

$$H'\psi_{n0} - E_{n1}\psi_{n0} = -\sum c_m(H_0\psi_{m0} - E_{n0}\psi_{m0})$$

$$H'\psi_{n0} - E_{n1}\psi_{n0} = -\sum c_m(E_{m0} - E_{n0})\psi_{m0}$$

take inner product with ψ_{k0}

$$\langle\psi_{k0}|H'|\psi_{n0}\rangle - E_{n1}\langle\psi_{k0}|\psi_{n0}\rangle =$$

$$-\sum c_m(E_{m0} - E_{n0})\langle\psi_{k0}|\psi_{m0}\rangle$$

the L.H.S. is clearly zero because (for $k=n$)

$$\langle\psi_{n0}|H'|\psi_{n0}\rangle = E_{n1}$$

so we know that $c_{m=n}$ must be zero

→ for $k \neq n$, $\langle\psi_{k0}|\psi_{m0}\rangle = \delta_{km}$

$$\langle\psi_{k0}|H'|\psi_{n0}\rangle = -\sum_m c_m(E_{m0} - E_{n0})\delta_{km}$$

$$\langle\psi_{m0}|H'|\psi_{n0}\rangle = -c_m(E_{m0} - E_{n0})$$

$$\boxed{c_m = \frac{\langle\psi_{m0}|H'|\psi_{n0}\rangle}{E_{n0} - E_{m0}}}$$

Degenerate perturbation theory:

H_0 unperturbed, solvable hamiltonian

H' perturbation

H perturbed hamiltonian

consider two-fold degeneracy:

$$H_0 |\psi_{na}\rangle = E_{n0} |\psi_{na}\rangle$$

$$H_0 |\psi_{nb}\rangle = E_{n0} |\psi_{nb}\rangle$$

because H_0 is hermitian:

$$\langle \psi_{na} | \psi_{nb} \rangle = 0$$

first-order equation from non-degenerate perturbation theory:

$$* \quad H'\psi_{n0} + H_0 \psi_{n1} = E_{n0}\psi_{n1} + E_{n1}\psi_{n0}$$

but this time, it's not clear what state to use for ψ_{n0}. The only condition is that $H_0 \psi_{n0} = E_{n0}\psi_{n0}$. For now, use some generic linear combination of ψ_{na} and ψ_{nb}:

$$\psi_{n0} = \alpha \psi_{na} + \beta \psi_{nb}$$

$$H_0 \psi_{n0} = \alpha H_0 \psi_{na} + \beta H_0 \psi_{nb}$$

$$= E_{n0}(\alpha \psi_{na} + \beta \psi_{nb}) \checkmark$$

plug into $*$:

$$H'(\alpha \psi_{na} + \beta \psi_{nb}) + H_0 \psi_{n1} =$$

$$E_{n1}(\alpha \psi_{na} + \beta \psi_{nb}) + E_{n0}\psi_{n1}$$

take the inner product with ψ_{na}:

$$\alpha \langle \psi_{na}|H'|\psi_{na}\rangle + \beta \langle \psi_{na}|H'|\psi_{nb}\rangle$$

$$= \alpha E_{n1} \langle \psi_{na}|\psi_{na}\rangle + \beta E_{n1} \langle \psi_{na}|\psi_{nb}\rangle$$

$$+ E_{n0} \langle \psi_{na}|\psi_{n1}\rangle - \langle \psi_{na}|H_0|\psi_{n1}\rangle$$

last term:

$$\langle \psi_{na}|H_0|\psi_{n1}\rangle = \langle H_0 \psi_{na}|\psi_{n1}\rangle$$

$$= E_{n0} \langle \psi_{na}|\psi_{n1}\rangle$$

which cancels with the second-to-last term. Additionally:

$$\beta E_{n1} \langle \psi_{na}|\psi_{nb}\rangle = \beta E_{n1}(0) = 0$$

and: $\alpha E_{n1} \langle \psi_{na}|\psi_{na}\rangle = \alpha E_{n1}$

So we get:

$$\boxed{\alpha \langle \psi_{na}|H'|\psi_{na}\rangle + \beta \langle \psi_{na}|H'|\psi_{nb}\rangle = \alpha E_1}$$

but this is only one equation and we still have two unknowns: α and β

To get another equation, take the inner product with ψ_{nb}:

$$\alpha \langle \psi_{nb}|H'|\psi_{na}\rangle + \beta \langle \psi_{nb}|H'|\psi_{nb}\rangle$$

$$+ \langle \psi_{nb}|H_0|\psi_{n1}\rangle = \alpha E_1 \langle \psi_{nb}|\psi_{na}\rangle$$

$$+ \beta E_{n1} \langle \psi_{nb}|\psi_{nb}\rangle + E_{n0} \langle \psi_{nb}|\psi_{n1}\rangle$$

same logic as above, we get:

$$\boxed{\alpha \langle \psi_{nb}|H'|\psi_{na}\rangle + \beta \langle \psi_{nb}|H'|\psi_{nb}\rangle = \beta E_1}$$

write this in matrix notation:

$$W = \begin{bmatrix} \langle \psi_{na}|H'|\psi_{na}\rangle & \langle \psi_{na}|H'|\psi_{nb}\rangle \\ \langle \psi_{nb}|H'|\psi_{na}\rangle & \langle \psi_{nb}|H'|\psi_{nb}\rangle \end{bmatrix}$$

$$W \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E_{n1} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

so the energy corrections are the eigenvalues of our matrix W, and our "good" states are the eigenvectors of W

Tricks for finding zeroes in W:

A s.t. $[H_0, A]$ and $[H', A] = 0$

$\psi_a = |E_{n0}, \lambda_a\rangle \quad \psi_b = |E_{n0}, \lambda_b\rangle$

$H_0 \psi_a = E_{n0}\psi_a \quad H_0 \psi_b = E_{n0}\psi_b$

$A\psi_a = \lambda_a \psi_a \quad A\psi_b = \lambda_b \psi_b$

$\rightarrow \langle \psi_a | [A, H'] | \psi_b \rangle = 0$

$\langle \psi_a | AH' | \psi_b \rangle - \langle \psi_a | H'A | \psi_b \rangle = 0$

$\langle A\psi_a | H' | \psi_b \rangle - \lambda_b \langle \psi_a | H' | \psi_b \rangle = 0$

$(\lambda_a - \lambda_b) W_{ab} = 0$ and

$$\boxed{\text{if } \lambda_a \neq \lambda_b, \ W_{ab} = 0}$$

also. $W_{ab} = \int \psi_a^* H' \psi_b \, dx$

$$\boxed{\text{if } \psi_a^* H' \psi_b \text{ is odd, then } W_{ab} = 0}$$

Time-Dependant Perturbation Theory

original hamiltonian:

$$H_0 \Psi_{n0} = E_{n0} \Psi_{n0} \qquad \langle \Psi_{m0} | \Psi_{n0} \rangle = \delta_{nm}$$

so any $\Psi(t)$ can be written:

$$\Psi(t) = \sum_n c_n(t) \Psi_{n0} e^{-iE_{n0}t/\hbar}$$

use the schroedinger equation to find $c(t)$:

$$\hat{H}\Psi(t) = i\hbar \frac{\partial \Psi}{\partial t}$$

but consider a small, time-dependant perturbation:

$$\hat{H} = H_0 + H'(t)$$

$$(H_0 + H')\Psi = i\hbar \sum_n \frac{\partial}{\partial t}\left[c_n(t)\Psi_{n0} e^{-iE_{n0}t/\hbar}\right]$$

$$\underline{\sum_n c_n H_0 \Psi_{n0} e^{-iE_n t/\hbar}} + \sum_n c_n H' \Psi_{n0} e^{-iE_n t/\hbar} =$$

$$i\hbar \sum_n \frac{\partial c_n}{\partial t} \Psi_{n0} e^{-iE_{n0}t/\hbar} + \underline{i\hbar \sum_n c_n \Psi_{n0}\left(\frac{-iE_n}{\hbar}\right) e^{-iE_n t/\hbar}}$$

clearly, the two underlined terms cancel

$$\sum_n c_n H' \Psi_{n0} e^{-iE_n t/\hbar} = i\hbar \sum_n \frac{\partial c_n}{\partial t} \Psi_{n0} e^{-iE_n t/\hbar}$$

take inner product with $\langle \Psi_{m0}|$

$$\sum_n c_n \langle \Psi_m | H' | \Psi_n \rangle e^{-iE_n t/\hbar} = i\hbar \sum_n \frac{\partial c_n}{\partial t} \langle \Psi_m | \Psi_n \rangle e^{-iE_n t/\hbar}$$

$$\boxed{\sum_n c_n \langle \Psi_m | H' | \Psi_n \rangle e^{-iE_n t/\hbar} = i\hbar \frac{\partial c_m}{\partial t} e^{-iE_m t/\hbar}}$$

this is a system of n coupled, first-order differential equations

For a 2-state system, this reduces to:

$$\frac{\partial c_a}{\partial t} = -\frac{i}{\hbar} \langle \Psi_a | H' | \Psi_b \rangle e^{-i\omega_0 t} c_b(t)$$

$$\frac{\partial c_b}{\partial t} = -\frac{i}{\hbar} \langle \Psi_b | H' | \Psi_a \rangle e^{i\omega_0 t} c_a(t)$$

where $\omega_0 = \dfrac{E_b - E_a}{\hbar}$

and we assume:

$$\langle \Psi_a | H' | \Psi_a \rangle = \langle \Psi_b | H' | \Psi_b \rangle = 0$$

and, to first order (assuming $c_{b0} = 0$ and $c_{a0} = 1$):

$$\frac{dc_a}{dt} = 0$$

$$① \quad \frac{dc_b}{dt} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t}$$

Sinusoidal Perturbations

$$H'(r,t) = V(r)\cos(\omega t)$$

$$H'_{ab} = V_{ab}\cos(\omega t)$$

plugging this into eq. ①, we find:

$$c_b(t) \approx -\frac{i}{\hbar} V_{ba} \frac{\sin\left[\frac{(\omega_0 - \omega)t}{2}\right]}{(\omega_0 - \omega)} e^{i(\omega_0 - \omega)t/2}$$

probability of transition from Ψ_a to Ψ_b is:

$$\boxed{P_{a\to b}(t) = |c_b|^2 = \frac{V_{ba}^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}}$$

in the special case of EM waves:

$$H' = -qE_0 r\cos(\omega t)$$

(the wave is polarized along $\hat{r}$)

so $V(r) = -qE_0 r$

$$V_{ab} = -qE_0 \langle \Psi_a | r | \Psi_b \rangle$$

call $\vec{p} = q\langle \Psi_a | \vec{r} | \Psi_b \rangle$

$$P_{a\to b}(t) = \left(\frac{|\vec{p}|E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0 - \omega)t/\hbar]}{(\omega_0 - \omega)^2}$$

same probability for absorbtion $(a \to b)$ and stimulated ommission $(b \to a)$

For a bath of radiation, distributed according to $\rho(\omega)$, with $u = \frac{\varepsilon_0}{2}E_0^2$:

$$P_{a\to b}(t) = \frac{2}{\varepsilon_0 \hbar^2} |\vec{p}|^2 \int_0^\infty \rho(\omega) \frac{\sin^2[(\omega_0 - \omega)t/\hbar]}{(\omega_0 - \omega)^2} d\omega$$

$$P_{b\to a}(t) = \frac{\pi}{\varepsilon_0 \hbar^2} |\vec{p}|^2 \rho(\omega_0) t$$

transition rate $R = \dfrac{dP}{dt}$

$$R_{b\to a} = \frac{\pi}{\varepsilon_0 \hbar^2} |\vec{p}|^2 \rho(\omega_0)$$

do a spherical average over all incident vectors $\vec{p}$:

$$\boxed{R_{b\to a} = \frac{\pi}{3\varepsilon_0 \hbar^2} |\vec{p}|^2 \rho(\omega_0)}$$

"Fermi's golden rule"

spontaneous emmission rate:

$$\boxed{A = \frac{\omega_0^3 |\vec{p}|^2}{3\pi\varepsilon_0 \hbar c^3}}$$

Relativistic correction

$$H = T + u$$

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2$$

relativistic momentum:

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}$$

doing some math, we get:

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

$$T = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right]$$

$$\sqrt{1+\left(\frac{p}{mc}\right)^2} = 1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \ldots$$

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \ldots$$

so we get:

$$H = \frac{p^2}{2m} + V(x) + \left(-\frac{p^4}{8m^3c^2}\right)$$

so our perturbation is:

$$\left[\; H' = -\frac{p^4}{8m^3c^2} \;\right]$$

the correction to the energy is:

$$E_{n1} = \langle \psi_{n0} | H' | \psi_{n0} \rangle$$

$$E_{n1} = -\frac{1}{8m^3c^2} \langle \psi_{n0} | p^4 | \psi_{n0} \rangle$$

but we know:

$$p^2\psi = 2m(E_{n0} - V)\psi$$

$$p^4 = 4m^2(E_{n0}^2 - 2E_{n0}V + V^2)$$

$$E_{n1} = -\frac{1}{2mc^2}\left(E_{n0}^2 + 2E_{n0}\langle V\rangle + \langle V^2\rangle\right)$$

for hydrogen: $V = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$

$$E_{n1} = -\frac{1}{2mc^2}\left(E_{n0}^2 - \frac{E e^2}{2\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right)$$

but we know:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$$

$$a\ (\text{bohr radius}) = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+\frac{1}{2})n^3a^2}$$

subbing this in, we get:

$$\boxed{E_{n1} = -\frac{E_{n0}^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right)}$$

Spin addition

$$|S\ M\rangle$$

$$|1\ 1\rangle = \uparrow\uparrow$$

$$|1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$$

$$|1\ {-1}\rangle = \downarrow\downarrow$$

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

$$S^2|s\ m\rangle = \hbar^2 s(s+1)|s\ m\rangle$$

$$S_z|s\ m\rangle = \hbar m|s\ m\rangle$$

Energy corrections

note: $\alpha = \left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2$

spin-orbit: $E_{so} = \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$

$$E_n = -\frac{1}{n^2}\frac{mc^2}{2}\alpha$$

H_2 energy levels with fine structure:

$$E_{nj} = -\frac{13.6\text{ eV}}{n^2}\left(1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right)$$

Weak-field zeeman correction:

$$E_z = \underbrace{\left(\frac{e\hbar}{2m}\right)}_{\mu_B}\left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right]B_{ext}m_j$$

strong-field zeeman

$$E_{nm_lm_s} = -\frac{13.6}{n^2} + \mu_B B_{ext}(m_l + 2m_s)$$

$$E_{fs} = \frac{13.6}{n^3}\alpha^2\left[\frac{3}{4n} - \left(\frac{l(l+1) - m_lm_s}{l(l+1/2)(l+1)}\right)\right]$$

spin-spin (hyperfine):

$$E_{hf} = \frac{4\hbar^4 g_p}{3m_pm_e^2c^2a^4}\begin{cases}\frac{1}{4} & \text{triplet}\\ -\frac{3}{4} & \text{singlet}\end{cases}$$

Variational Principle

H s.t. $H\psi_n = E_n\psi_n$

arbitrary ψ: $\psi = \sum c_n\psi_n$

$$\langle\psi|H|\psi\rangle = \sum_m\sum_n (c_m\psi_m)^* H c_n\psi_n$$

$$= \sum\sum E_n c_m^* c_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{mn}}$$

$$= \sum_n E_n|c_n|^2$$

$\langle\psi|H|\psi\rangle \geq E_0\sum|c_n|^2$ b/c the ground state is the smallest energy

$$\boxed{\langle\psi|H|\psi\rangle \geq E_{gs}}$$

for a gaussian trial function: $\psi = Ae^{-bx^2}$

$$A = \left(\frac{2b}{\pi}\right)^{1/4} \qquad \langle T\rangle = \frac{\hbar^2 b}{2m}$$

lifetime of an excited state:

$$\tau = \frac{1}{A}$$

selection rules:

$$(m'-m)\langle n'l'm'|z|nlm\rangle = 0$$

$$(m'-m)\langle n'l'm'|x|nlm\rangle =$$

$$i\langle n'l'm'|y|nlm\rangle$$

$$(m'-m)^2\langle n'l'm'|x|nlm\rangle =$$

$$\langle n'l'm'|x|nlm\rangle$$

so if $m'-m \neq \pm 1$

$$\langle n'l'm'|x|nlm\rangle = 0$$

also: $\Delta l = \pm 1$

$\Delta m = \pm 1, 0$

Quantum Computing

$$EPR = \frac{1}{\sqrt{2}}\left(|01\rangle - |10\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left(|0\rangle\otimes|1\rangle - |1\rangle\otimes|0\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left(\begin{bmatrix}1\\0\end{bmatrix}\otimes\begin{bmatrix}0\\1\end{bmatrix} - \begin{bmatrix}0\\1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix}\right)$$

$$= \frac{1}{\sqrt{2}}\begin{bmatrix}0\\1\\-1\\0\end{bmatrix}$$

$$H = \frac{1}{\sqrt{2}}\begin{bmatrix}1 & 1\\1 & -1\end{bmatrix}$$

WKB Approximation

write the schroedinger equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi$$

in the form:

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p(x)^2}{\hbar^2}\psi$$

$$p(x) = \sqrt{2m\left(E - V(x)\right)}$$

note: this is the classical momentum

assume our wave function is:

$$\psi(x) = A(x)e^{i\varphi(x)}$$

$$\frac{d^2\psi}{\partial x^2} = \left[A'' + 2iA'\varphi' + iA\varphi'' - A\varphi'^2\right]e^{i\varphi}$$

$$A'' + 2iA'\varphi' + iA\varphi'' - A\varphi'^2 = -\frac{p^2}{\hbar^2}A$$

take real and imaginary parts:

1. $A'' - A\varphi'^2 = -\frac{p^2}{\hbar^2}A$
2. $2iA'\varphi' + iA\varphi'' = 0$

can be written:

1. $A'' = A\left[\varphi'(x)^2 - \frac{p(x)^2}{\hbar^2}\right]$
2. $(A^2\varphi')' = 0$

we can solve the second one to get:

$$A = \frac{C}{\sqrt{\varphi'}}$$

now, for equation one, we make an approximation:

$$A'' \ll A\varphi'^2 \quad \text{and} \quad A'' \ll -\frac{p^2}{\hbar^2}A$$

so eq. 1 becomes:

$$\varphi' = \frac{p}{\hbar}$$

$$\varphi(x) = \frac{1}{\hbar}\int p(x)\,dx$$

and our full wave function is:

$$\boxed{\psi(x) = \frac{C}{\sqrt{p(x)}}e^{\pm\frac{i}{\hbar}\int p(x)dx}}$$

tunneling probability:

$$\psi(x) = \frac{C}{\sqrt{p(x)}}e^{\frac{1}{\hbar}\int p(x)\,dx}$$

note: the exponent is now real because $p(x)$ is imaginary in the tunneling region

$$T = e^{-2\gamma} \qquad \gamma = \frac{1}{\hbar}\int_0^a p(x)\,dx$$

connection formulas:

2 vertical walls: $\int_0^a p(x)\,dx = n\pi\hbar$

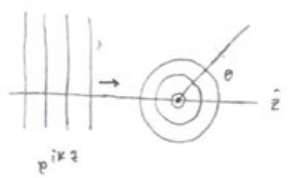
1 vertical wall: $\int_0^a p(x)\,dx = \left(n-\frac{1}{4}\right)\pi\hbar$

0 vertical walls: $\int_0^a p(x)\,dx = \left(n-\frac{1}{2}\right)\pi\hbar$

Scattering

the goal is to look for solutions of the schroedinger equation of the form:

$$\psi(r,\theta) = A\left[e^{ikz} + f(\theta)\frac{e^{ikr}}{r}\right] \quad (\text{big } r)$$



the differential scattering cross-section:

$$D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2$$

partial wave analysis:

$$\boxed{\psi = e^{ikz} + k\sum_{l=0}^{\infty} i^{l+1}(2l+1)\, a_l\, h_l^{(1)}(kr)\, P_l(\cos\theta)}$$

$h_l^{(1)}(kr)$ is the l^{th} hankel function of the first kind

$P_l(\cos\theta)$ is the l^{th} legendre polynomial

a_l is the l^{th} partial-wave amplitude

$$\sigma = 4\pi \sum (2l+1)|a_l|^2$$

Integral form of schroedinger:

$$\boxed{\psi(\vec{r}) = \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2}\int \frac{e^{ik|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} V(\vec{r}_0)\,\psi(\vec{r}_0)\, d^3r_0}$$

$\psi_0(\vec{r})$ is a solution to the free particle

assuming $V(\vec{r}_0)$ is localized around $\vec{r}_0 = 0$, and we want to know $\psi(\vec{r})$ for $\vec{r}$ far away from the origin:

$$\psi(r) = Ae^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{i\vec{k}\cdot\vec{r}_0} V(\vec{r}_0)\,\psi(\vec{r}_0)\, d^3r_0$$

$$\vec{k} = k\hat{r}$$

by comparison with the first equation:

$$f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int e^{-i\vec{k}\cdot\vec{r}_0} V(\vec{r}_0)\,\psi(\vec{r}_0)\, d^3r_0$$

Born approximation:

$$\psi(r_0) = \psi_0(r_0)$$

free particle solution

$$\psi(r_0) = Ae^{i\vec{k}'\cdot\vec{r}_0} \qquad k' = k\hat{z}$$

$$\boxed{f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int e^{i(\vec{k}-\vec{k}')\cdot r_0} V(\vec{r}_0)\, d^3r_0}$$

for low-energy scattering (small θ): $f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int V(\vec{r}_0)\, d^3r_0$

for a spherically symmetric potential: $f(\theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty r\, V(r)\sin(qr)\, dr$

$$q = 2k\sin\left(\frac{\theta}{2}\right)$$