Griffiths Ch 2 Notes

2.1 - Stationary States

- We want to solve Schrödinger Eqn for a variety of potentials

$$\Rightarrow \quad i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad \text{where } \Psi(x,t) = \psi(x)\varphi(t)$$

- To solve Schrödinger Eqn:

$$\frac{\partial \Psi}{\partial t} = \psi \frac{\partial \varphi}{\partial t} \qquad \frac{\partial \Psi}{\partial x} = \frac{\partial \psi}{\partial x}\varphi$$

$$\Rightarrow \quad i\hbar \frac{\partial \varphi}{\partial t}\psi = \frac{-\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2}\varphi + V\psi\varphi$$

$$i\hbar \frac{1}{\varphi}\frac{\partial \varphi}{\partial t} = \frac{-\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2} + V$$

$$\rightarrow \text{① } E = i\hbar \frac{1}{\varphi}\frac{\partial \varphi}{\partial t}$$

$$\text{② } E = \frac{-\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2}$$

$>$ E is separation constant

- Solution of ① always yields $\varphi(t) = e^{-iEt/\hbar}$; we now call ② the time-independent Schrödinger Eqn, where we now must specify V to proceed
- Probability densities + expectation values constant in time due to $\psi^*\psi$ multiplication
- There is a different ψ for every allowable energy value E_i; therefore by the rules of linear algebra + differential equations, any linear combinations of solutions is also a solution

$$\Rightarrow \Psi(x,t) = \sum_n c_n \psi_n(x) \exp[-iE_n t/\hbar]$$

2.2 - Infinite Square Well

$$V(x) = \begin{cases} 0 & \text{if } 0 \le x \le a \\ \infty & \text{otherwise} \end{cases}$$

← These boundaries can be shifted at will

- Since $E \ge V$, outside the well we know $\psi(x) = 0$
  - ↳ we want only ψ w/in the well

2.2 (cont.)

$$\Rightarrow H\psi = E\psi$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + 0\right)\psi = E\psi$$

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

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-2mE}{\hbar^2}\psi$$

* let $k \equiv \sqrt{2mE}/\hbar$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\psi$$

$$\Rightarrow \psi(x) = A\sin(kx) + B\cos(kx) \leftarrow \underline{\text{easier to solve}}$$

$$= Ae^{ikx} + Be^{-ikx}$$

* To be normalizable, generally our boundary conditions are that both ψ and $\frac{\partial \psi}{\partial x}$ are continuous, but we can ignore the second condition when $V \to \infty$.

$$\Rightarrow \psi(0) = \psi(a) = 0$$

$$0 = A\overset{0}{\sin(kx)} + B\cos(kx)\Big|_{x=0}$$

$\hookrightarrow B = 0$

$$0 = A\sin(ka)$$

$$\hookrightarrow k_n = \frac{n\pi}{a} \rightarrow E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 n^2 \hbar^2}{2ma^2}$$

* Check normalization to solve for A

$$1 = \int_0^a \psi^*(x)\,\psi(x)\,dx$$

$$1 = |A|^2 \int_0^a \sin^2(kx)\,dx$$

$$1 = |A|^2 \frac{a}{2}$$

$$\hookrightarrow A = \sqrt{\frac{2}{a}}$$

* for an individual solution

$$C_n = \int \psi_n^*(x) f(x)\,dx, \quad f(x) = \sqrt{\frac{2}{a}}\sum_i c_i \sin\left(\frac{i\pi x}{a}\right)$$

5.2. The Particle in a Box

We now consider our first problem with a potential, albeit a rather artificial one:

$$\begin{aligned} V(x) &= 0, \qquad |x| < L/2 \\ &= \infty, \qquad |x| \geq L/2 \end{aligned} \tag{5.2.1}$$

This potential (Fig. 5.1a) is called the box since there is an infinite potential barrier in the way of a particle that tries to leave the region $|x| < L/2$. The eigenvalue equation in the X basis (which is the only viable choice) is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{5.2.2}$$

We begin by partitioning space into three regions I, II, and III (Fig. 5.1a). The solution ψ is called ψ_{I}, ψ_{II}, and ψ_{III} in regions I, II, and III, respectively.

Consider first region III, in which $V = \infty$. It is convenient to first consider the case where V is not infinite but equal to some V_0 which is greater than E. Now

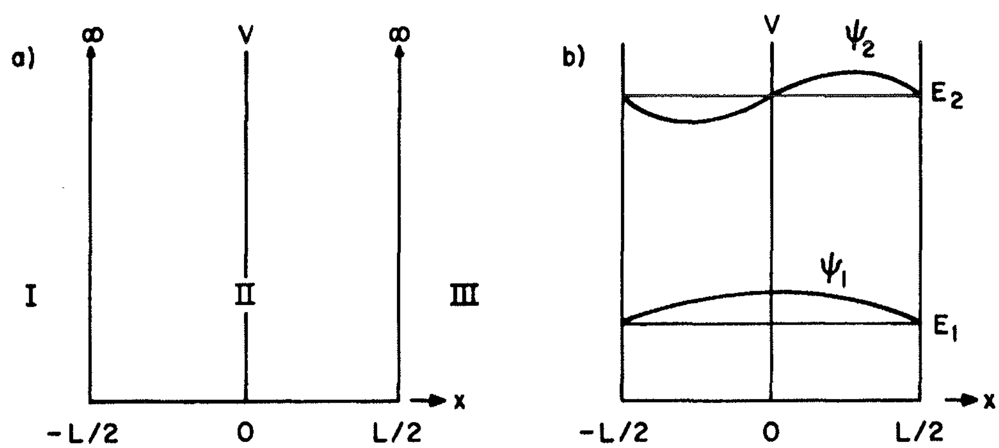


Figure 5.1. (a) The box potential. (b) The first two levels and wave functions in the box.

Eq. (5.2.2) becomes

$$\frac{d^2\psi_{\mathrm{III}}}{dx^2}-\frac{2m(V_0-E)}{\hbar^2}\,\psi_{\mathrm{III}}=0 \tag{5.2.3}$$

which is solved by

$$\psi_{\mathrm{III}}=A\,e^{-\kappa x}+B\,e^{\kappa x} \tag{5.2.4}$$

where $\kappa=[2m(V_0-E)/\hbar^2]^{1/2}$.

Although A and B are arbitrary coefficients from a mathematical standpoint, we must set $B=0$ on physical grounds since $B\,e^{\kappa x}$ blows up exponentially as $x\to\infty$ and such functions are not members of our Hilbert space. If we now let $V\to\infty$, we see that

$$\psi_{\mathrm{III}}\equiv 0$$

It can similarly be shown that $\psi_{\mathrm{I}}\equiv 0$. In region II, since $V=0$, the solutions are exactly those of a free particle:

$$\psi_{\mathrm{II}}=A\,\exp[i(2mE/\hbar^2)^{1/2}x]+B\,\exp[-i(2mE/\hbar^2)^{1/2}x] \tag{5.2.5}$$

$$=A\,e^{ikx}+B\,e^{-ikx},\qquad k=(2mE/\hbar^2)^{1/2} \tag{5.2.6}$$

It therefore appears that the energy eigenvalues are once again continuous as in the free-particle case. This is not so, for $\psi_{\mathrm{II}}(x)=\psi$ only in region II and not in all of space. We must require that ψ_{II} goes continuously into its counterparts ψ_{I} and ψ_{III} as we cross over to regions I and II, respectively. In other words we require that

$$\psi_{\mathrm{I}}(-L/2)=\psi_{\mathrm{II}}(-L/2)=0 \tag{5.2.7}$$

$$\psi_{\mathrm{III}}(+L/2)=\psi_{\mathrm{II}}(+L/2)=0 \tag{5.2.8}$$

(We make no such continuity demands on ψ' at the walls of the box since V jumps to infinity there.) These constraints applied to Eq. (5.2.6) take the form

$$A\,e^{-ikL/2}+B\,e^{ikL/2}=0 \tag{5.2.9a}$$

$$A\,e^{ikL/2}+B\,e^{-ikL/2}=0 \tag{5.2.9b}$$

or in matrix form

$$\begin{bmatrix} e^{-ikL/2} & e^{ikL/2} \\ e^{ikL/2} & e^{-ikL/2} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{5.2.10}$$

Such an equation has nontrivial solutions only if the determinant vanishes:

$$e^{-ikL} - e^{ikL} = -2i \sin(kL) = 0 \tag{5.2.11}$$

that is, only if

$$k = \frac{n\pi}{L}, \qquad n = 0, \pm 1, \pm 2, \ldots \tag{5.2.12}$$

To find the corresponding eigenfunctions, we go to Eqs. (5.2.9a) and (5.2.9b). Since only one of them is independent, we study just Eq. (5.2.9a), which says

$$A\, e^{-in\pi/2} + B\, e^{in\pi/2} = 0 \tag{5.2.13}$$

Multiplying by $e^{i\pi n/2}$, we get

$$A = -e^{in\pi} B \tag{5.2.14}$$

Since $e^{in\pi} = (-1)^n$, Eq. (5.2.6) generates two families of solutions (normalized to unity):

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \qquad n \text{ even} \tag{5.2.15}$$

$$= \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi x}{L}\right), \qquad n \text{ odd} \tag{5.2.16}$$

Notice that the case $n = 0$ is uninteresting since $\psi_0 \equiv 0$. Further, since $\psi_n = \psi_{-n}$ for n odd and $\psi_n = -\psi_{-n}$ for n even, and since eigenfunctions differing by an overall factor are not considered distinct, we may restrict ourselves to positive nonzero n. In summary, we have

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi x}{L}\right), \qquad n = 1, 3, 5, 7, \ldots \tag{5.2.17a}$$

$$= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \qquad n = 2, 4, 6, \ldots \tag{5.2.17b}$$

and from Eqs. (5.2.6) and (5.2.12),

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \tag{5.2.17c}$$

[It is tacitly understood in Eqs. (5.2.17a) and (5.2.17b) that $|x| < L/2$.]

2.3 – Harmonic Oscillator

$$V(x) = \frac{1}{2} m\omega^2 x^2$$

$$\Rightarrow \quad H\Psi = E\Psi$$

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right)\Psi = E\Psi$$

* Brute force method involves power series, but we can rewrite H in terms of ladder operators to more easily achieve solution

$\Rightarrow$ Ladder Operator Method:

$$H = \frac{-\hbar^2}{2m}\frac{\partial}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

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

$$= \hbar\omega\left(a_- a_+ - \frac{1}{2}\right)$$

where $a_\pm = \frac{1}{\sqrt{2m\hbar\omega}}\left(\mp ip + m\omega x\right)$

$$= \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)$$

$\Rightarrow$ Note: Applying a_- to the ground state Ψ_0 yields:

$$a_- \Psi_0 = 0$$

$$\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{\partial}{\partial x} + m\omega x\right)\Psi_0 = 0$$

$$\frac{\partial \Psi_0}{\partial x} = -\frac{m\omega x}{\hbar}\Psi_0$$

$$\int \frac{\partial \Psi_0}{\Psi_0} = -\frac{m\omega}{\hbar}\int x\,\partial x$$

$$\ln(\Psi_0) = \frac{-m\omega}{2\hbar}x^2 + C$$

$$\Psi_0 = \exp\left[\frac{-m\omega x^2}{2\hbar} + C\right]$$

$$= A\exp\left[-\frac{m\omega x^2}{2\hbar}\right]$$

* Normalization yields: $A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$

* Plugging into Schrödinger Eqn yields: $E_0 = \frac{\hbar\omega}{2}$

* Higher energy states generated by repeated application of raising operator

$$E_n = (n + 1/2)\hbar\omega$$

2.3 (cont.)

- Other facts about ladder operators include:

$$a_+ \psi_n = \sqrt{n+1}\, \psi_{n+1}$$
$$a_- \psi_n = \sqrt{n}\, \psi_n$$
$$\tilde{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(a_+ + a_-)$$
$$\tilde{p} = i\sqrt{\frac{\hbar m\omega}{2}}\,(a_+ - a_-)$$

* Normalization of previous solution requires multiplication by Gaussian to be normalizable

$$\Rightarrow \psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad H_n \text{ are Hermite polynomials}$$

2.4 – Free Particle

$V = 0$ for all x

- Our solution will be of the same form as infinite square well

$$\Rightarrow \psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

$$\Psi(x,t) = A\exp\left[i\left(kx - \frac{\hbar k^2}{2m}t\right)\right], \quad k = \pm\frac{\sqrt{2mE}}{\hbar} \quad \begin{cases} k>0, & \text{travels to right} \\ k<0, & \text{travels to left} \end{cases}$$

- The velocity of the above wave is:

$$V = \frac{\hbar |k|}{2m} = \sqrt{\frac{E}{2m}}$$

$$p = \hbar k$$

* But our above solution is not normalizable on its own; we must combine these waves into a wave packet

$$\Rightarrow \Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) \exp\left[i\left(kx - \frac{\hbar k^2}{2m}t\right)\right] dk$$

$$\hookrightarrow \phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx \quad \text{(via inverse Fourier Transform)}$$

$\Rightarrow$ But now our speeds don't match

$$V_{group} = \frac{d\omega}{dk}$$

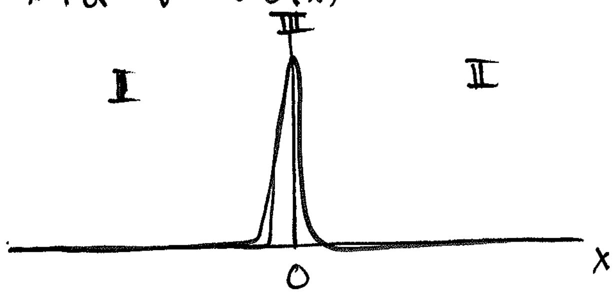
$$V_{phase} = \frac{\omega}{k}$$

2.5 - δ-Function Potential

- Potentials that do not go to infinity as $x \to \infty$ now allows to have both bound and scattered states

↳ $\begin{cases} E > V & \Rightarrow \text{scattering state} \\ E < V & \Rightarrow \text{bound state} \end{cases}$

* For $V = \alpha\delta(x)$



⇒ If $E < 0$ (Bound States)

* In region I:

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - \alpha\cancel{\delta(x)}^{0}\psi = E\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-2mE}{\hbar^2}\psi$$

$$\Rightarrow \psi(x) = \cancel{Ae^{-kx}}^{0} + Be^{kx}, \quad k = \frac{\sqrt{-2mE}}{\hbar}$$

$$= Be^{kx}$$

* In region II:

* By same work as above

$$\psi(x) = Fe^{-kx} + \cancel{Ge^{kx}}^{0}$$

$$= Fe^{-kx}$$

* Remembering our boundary conditions:

① $\psi(x)$ is continuous

② $\frac{d\psi}{dx}$ is continuous where $V(x) \neq \infty$

2.5 (cont.)

$$\Rightarrow \psi(x) = \begin{cases} Be^{kx} & x \le 0 \\ Be^{-kx} & x \ge 0 \end{cases}$$

* But we get no information about 2nd condition unless:

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

$$\frac{-\hbar^2}{2m}\frac{d\psi}{dx}\Big|_{-\epsilon}^{\epsilon} + \int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx = 0$$

$$\Delta\left(\frac{d\psi}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx$$

$$-2Bk = \frac{-2m\alpha}{\hbar^2}\psi(0)$$

$$\Rightarrow k = \frac{m\alpha}{\hbar^2}$$

$$E = \frac{-\hbar^2k^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}$$

* Normalization yields final form

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}\exp\left[-m\alpha|x|/\hbar^2\right], \quad E = \frac{-m\alpha^2}{2\hbar^2}$$

* Note: Only one bound state exists

$\Rightarrow$ If $E > 0$ (Scattering States)

* In region I:

$$H\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{-2mE}{\hbar^2}\psi$$

$$\hookrightarrow \psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

* In region II:

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}$$

2.5 (cont.)

* Application of boundary conditions yields:

① $\psi(x)$ is continuous

$$\Rightarrow \quad Ae^{ikx} + Be^{-ikx} = Fe^{ikx} + Ge^{-ikx} \Big|_{x=0}$$

$$A + B = F + G$$

② $\frac{d\psi}{dx}$ is continuous except where $V(x) = \infty$

$$\Rightarrow \quad \Delta\left(\frac{d\psi}{dx}\right) = ik(F - G - A + B) = \frac{-2m\alpha}{\hbar^2}(A+B)$$

$$\hookrightarrow \quad F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \beta = \frac{m\alpha}{\hbar^2 k}$$

⇒ Since we currently have an unsolvable system (2 eqns, 4+ unknowns) in a non-normalizable state, we rephrase the problem in terms of scattering w/ particles

↳ When combined w/ time dependent part of wavefunction:

$A \rightarrow$ Incoming wave

$B \rightarrow$ Reflected wave

$F \rightarrow$ Transmitted wave

$G \rightarrow \emptyset$

⇒ This now implies

$$B = \frac{i\beta}{1 - i\beta} A \qquad F = \frac{1}{1 - i\beta} A$$

where the reflection + transmission coefficients R & T are:

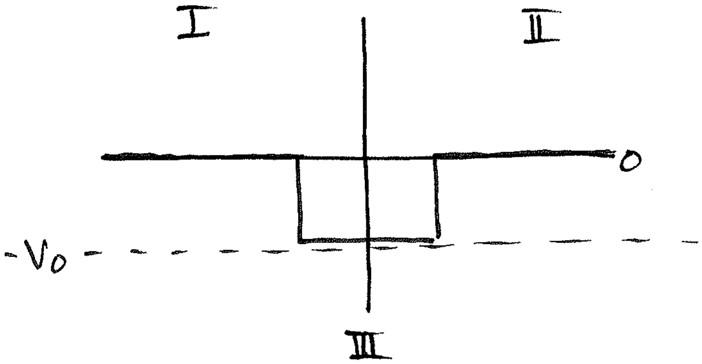
$$R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1+\beta^2}$$

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{1+\beta^2}$$

2.6 - Finite Square Well

$$V(x) = \begin{cases} 0, & |x| > a \\ -V_0, & -a < x < a \end{cases}$$

* Remember, we must consider both bound + unbound states



* For bound states $-V_0 < E < 0$ ($E < -V_0$ is not allowed)
  - In region I:

$$H\psi = E\psi$$

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

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi, \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

$$\Rightarrow \psi(x) = \cancelto{0}{Ae^{-\kappa x}} + Be^{\kappa x}$$

$$= Be^{\kappa x}$$

  - In region II:
    * Similarly to above

$$\psi(x) = Fe^{-\kappa x} + \cancelto{0}{Ge^{\kappa x}}$$

$$= Fe^{-\kappa x}$$

  - In region III:

$$H\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + -V_0\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{-(E+V_0)2m}{\hbar^2}\psi$$

2.6 (cont.)

$$\Rightarrow \psi(x) = Ce^{-ikx} + De^{ikx}, \qquad k = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$

$$= C\sin(kx) + D\cos(kx)$$

* Application of our boundary conditions + the fact that we have a symmetric potential informs us that solutions will either be even or odd.

$\Rightarrow$ Even Case:

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & x > a \\ D\cos(kx), & 0 < x < a \\ \psi(-x), & x < 0 \end{cases}$$

① $\psi(x)$ is continuous

$$Fe^{-\kappa a} = D\cos(ka)$$

② $\frac{d\psi}{dx}$ is continuous

$$-\kappa Fe^{-\kappa a} = -kD\sin(ka)$$

* Dividing ② by ① yields

$$+\kappa = +k\tan(ka)$$

↳ Redefining $z = ka$

$$z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$$

* Notice, $k^2 + \kappa^2 = \frac{2mV_0}{\hbar^2}$

↳ $\kappa a = \sqrt{z_0^2 - z^2}$

↳ $\tan(z) = \sqrt{\frac{z_0}{z^2} - 1}$

* If we examine the limiting cases

① Wide, deep well

$$E_n + V_0 \approx \frac{\pi^2 n^2 \hbar^2}{2m(2a)^2}$$

$\Rightarrow$ Approximates infinite square well, but w/ finite energy states

② Shallow, narrow well

$\Rightarrow$ Eventually results in only one bound state

2.6 (cont.)

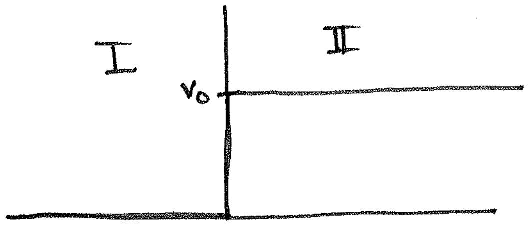
* For the scattering states $(E > 0)$
  - In region I:
    $$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$
    * From free-particle solution
  - In region II:
    $$\psi(x) = Fe^{ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$
    * From free-particle solution + scattering interpretation
  - In region III:
    $$\psi(x) = C\sin(lx) + D\cos(lx), \quad l = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$
    * From bound state solution
  - Applying our boundary conditions yield:
    * At $x = -a$
    $$Ae^{-ika} + Be^{ika} = -C\sin(la) + D\cos(la) \quad ①$$
    $$ik\left[Ae^{-ika} - Be^{ika}\right] = l\left[C\cos(la) + D\sin(la)\right] \quad ②$$
    * At $x = a$
    $$C\sin(la) + D\cos(la) = Fe^{ika} \quad ③$$
    $$l\left[C\cos(la) - D\sin(la)\right] = ikFe^{ika} \quad ④$$
  - Eliminating C & D yields:
    $$B = \frac{i\sin(2la)}{2kl}(l^2 - k^2)F$$
    $$F = \frac{\exp[-2ika]}{\cos(2la) - i\frac{k^2+l^2}{2kl}\sin(2la)} A$$

* Note: Perfect transmission occurs when
$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$$

Step Potential

$$V(x) = \begin{cases} 0 & x<0 \\ V_0 & x>0 \end{cases}$$

* Solutions will follow from free particle and finite well



* In region I:
  - ⇒ Free particle solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

* In region II:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V_0\psi = E\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m(V_0-E)}{\hbar^2}\psi$$

$$= Ce^{-\alpha x}, \quad \alpha = \frac{\sqrt{2m(V_0-E)}}{\hbar}$$

* Applying boundary conditions yields:

① ψ is continuous

$$\Rightarrow A+B=C$$

② $\frac{d\psi}{dx}$ is continuous

$$ik(A-B) = -\alpha C$$

⇒ Scattering states like in Finite Well

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0-E)}}$$ (skin depth, ie depth of tunnelling into barrier)

Hydrogen Atom / Central Potential

* First, we examine the Schrödinger Eqn in spherical coordinates:

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

where $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)$

$$\Rightarrow \frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\varphi^2}\right)\right] + V\psi = E\psi$$

* Assuming a solution of the form $\psi = R(r)\,Y(\theta,\varphi)$

$$\frac{-\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\varphi^2}\right)\right] + VRY = ERY$$

* We can separate the equations by multiplying by $\frac{-2mr^2}{\hbar^2 RY}$

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r)-E)\right] + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\theta^2}\right] = 0$$

* Using the separation constant $\ell(\ell+1)$, we see:

$\Rightarrow$ Radial Eqn: $\frac{1}{R}\left(\frac{d}{dr}\left[r^2\frac{dR}{dr}\right]\right) - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right) = \ell(\ell+1)$

Angular Eqn: $\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = -\ell(\ell+1)$

* Since there is no dependence of the angular equation on the potential, all problems in spherical coordinates will partly be composed of its solution

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\varphi^2}\right] = -\ell(\ell+1)$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\varphi^2} = -\ell(\ell+1)\sin^2\theta\,Y$$

* Again trying separation of variables, we assume $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$

$$\Rightarrow \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\Phi + \frac{\partial^2\Phi}{\partial\varphi^2}\Theta = -\ell(\ell+1)\sin^2\theta\,\Theta\Phi$$

$$\left(\frac{1}{\Theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\right] + \ell(\ell+1)\sin^2\theta\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = 0$$

* Using the separation constant m^2, we see:

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m^2$$

* from here it's easy to see that the solution to the Φ equation is:

$$\Phi = e^{im\varphi}$$

where m is allowed to be both positive and negative and the normalization constant is absorbed into the Θ equation.

* Applying the periodic boundary condition $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, we find

$$\exp[im\varphi] = \exp[im(\varphi + 2\pi)]$$

$$1 = \exp[im2\pi]$$

$$\Rightarrow m \in 0, \pm 1, \pm 2, \ldots$$

* The Θ equation has the known solution of the Legendre polynomials

$$\Rightarrow \Theta = A P_\ell^m(\cos\theta), \quad P_\ell^m = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$

$\Rightarrow$ Note: $\ell > 0$ and $|m| > \ell \rightarrow m \in [-\ell, \ell]$

* Multiplying the two equations together and normalizing, we obtain the <u>spherical harmonics</u>

$$Y_\ell^m(\theta, \varphi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, e^{im\varphi} P_\ell^m(\cos\theta)$$

$$\epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m < 0 \end{cases}$$

* Returning to the radial equation, we cannot proceed any further w/o specifying a potential after a few manipulations

$$\Rightarrow \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = \ell(\ell+1)R$$

* if we substitute $u(r) = rR(r) \Rightarrow R = \frac{u}{r}$

$$\hookrightarrow \frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

* Note: This is the 1-D Schrödinger Eqn if $V + \frac{\hbar^2}{2m}\frac{(\ell+1)\ell}{r^2} = V_{eff}$ where the extra term is called the centrifugal term, as it forces the particle further away from the origin.

The normalization condition now becomes $\int_0^\infty |u|^2 dr = 1$

ex. Spherical Well

$$V = \begin{cases} 0 & r \le a \\ \infty & r > a \end{cases}$$

* Similar to the square well, if $r > a$, $u(r) = 0$

$\hookrightarrow$ $$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = Eu$$

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}u = Eu$$

$$\frac{d^2u}{dr^2} + \frac{-\ell(\ell+1)}{r^2}u = \frac{-2mE}{\hbar^2}u$$

$$\frac{d^2u}{dr^2} + \frac{-\ell(\ell+1)}{r^2}u = -k^2u, \quad k = \frac{\sqrt{2mE}}{\hbar^2}$$

* In the case where $\ell = 0$, we get our familiar square well answers

$$\frac{d^2u}{dr^2} = -k^2u \iff u(r) = A\sin(kr) + B\cos(kr)$$

$$B \to 0 \text{ since } \frac{\cos(kr)}{r} \to \infty \text{ as } r \to 0$$

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad n \in \mathbb{Z}^+$$

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}}\frac{\sin(n\pi r/a)}{r}$$

* If $\ell \neq 0$, solving yields the spherical Bessel functions

$$E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2, \quad \beta_{n\ell} \text{ is } n^{th}\ 0 \text{ of } \ell^{th} \text{ spherical Bessel function}$$

$$\psi_{n\ell m} = A_{nj}\, j_\ell\!\left(\beta_{n\ell}\frac{r}{a}\right) Y_\ell^m(\theta, \varphi)$$

ex. Hydrogen Atom / Central Potential

$$V(r) = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = Eu$$

$$\frac{-\hbar^2}{2mE}\frac{d^2u}{dr^2} + \frac{1}{E}\left[\frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = u$$

* substituting $\kappa = \frac{\sqrt{-2mE}}{\hbar}$

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = u\left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]$$

* defining $p = \kappa r$, $p_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$

$$\frac{d^2u}{dp^2} = u\left[1 - \frac{p_0}{p} + \frac{\ell(\ell+1)}{p^2}\right]$$

* Examining the limits of the equation offers clues to its solution

↳ In the limit where $p \to \infty$

$$\frac{d^2u}{dp^2} = u \iff u = Ae^{-p} + \cancel{Be^{p}}^{\,0}$$

↳ $u(p) \sim Ae^{-p}$

↳ In the limit where $p \to 0$

$$\frac{d^2u}{dp^2} = \frac{\ell(\ell+1)}{p^2}u \iff u = Cp^{\ell+1} + \cancel{Dp^{-\ell}}^{\,0}$$

↳ $u(p) \sim Cp^{\ell+1}$

* We now rewrite our general solution as: $u(p) = p^{\ell+1}e^{-p}v(p)$ and resolve the differential equation

$$\Rightarrow \frac{du}{dp} = p^{\ell}e^{-p}\left[(\ell+1-p)v + p\frac{dv}{dp}\right]$$

$$\frac{d^2u}{dp^2} = p^{\ell}e^{-p}\left[\left(-2\ell-2+p+\frac{\ell(\ell+1)}{p}\right)v + 2(\ell+1-p)\frac{dv}{dp} + p\frac{d^2v}{dp^2}\right]$$

↳ Eliminating common terms, we see:

$$p\frac{d^2v}{dp^2} + 2(\ell+1-p)\frac{dv}{dp} + [p_0 - 2(\ell+1)]v = 0$$

* Assuming we can express the solution as a power series, $v(p) = \sum c_j p^j$ we find that:

$$\frac{dv}{dp} = \sum_{j=0} j c_j p^{j-1} = \sum_{j=0} (j+1) c_{j+1} p^j$$

$$\frac{d^2 v}{dp^2} = \sum_{j=0} j(j+1) c_{j+1} p^{j-1}$$

* Plugging these into the differential equation yields the recursion relation for c_j:

$$c_{j+1} = \frac{2(j+l+1) - p_0}{(j+1)(j+2l+2)} c_j$$

⇒ At large j our relationship approximates: $c_{j+1} = \frac{2}{j+1} c_j$

↳ Plugging this into our differential equation yields a solution of:

$$v(p) = c_0 \sum \frac{2^j}{j!} p^j = c_0 e^{2p} \Leftrightarrow U(p) = c_0 p^{l+1} e^p$$

Note: Since this blows up as $p \to \infty$, there must be a j_{max} such that:

$$c_{j_{max}+1} = 0$$

$$\hookrightarrow 2(j_{max} + l + 1) - p_0 = 0$$

if $n = j_{max} + l + 1$

$$p_0 = 2n \Leftrightarrow E = \frac{-\hbar^2 \kappa^2}{2m} = \frac{-me^4}{8\pi^2 \epsilon_0^2 \hbar^2 p_0^2}$$

$$\hookrightarrow E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} \qquad n \in 1,2,3\ldots$$

* Returning to our overall solution, we know that our solution has the form:

$$\psi_{nlm} = R_{nl}(r)\, Y_l^m(\theta,\varphi) \quad ; \quad R_{nl}(r) = \frac{1}{r} p^{l+1} e^{-p} v(p)$$

Note: The derived formulas above for $v(p)$ are those of the associated Laguerre polynomials: $L_{q-p}^{p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$; $L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$

6.1 - Non-degenerate Perturbation Theory

* Suppose for a system we have already solved

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

where we have obtained a complete set of orthonormal ψ_n^0 and their corresponding E_n^0 but we have perturbed the system slightly since then. How do we find the new ψ_n and E_n?

$\Rightarrow$ We want to solve $H\psi_n = E_n \psi_n$

$\hookrightarrow$ $H = H^0 + \lambda H'$

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

* Note: ψ_n^1 and E_n^1 are first order corrections to wavefunction / energy

$$\Rightarrow (H^0 + \lambda H')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots)$$

$$H^0 \psi_n^0 + \lambda (H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2 (H^0 \psi_n^2 + H' \psi_n^1) + \ldots$$
$$= E_n^0 \psi_n^0 + \lambda (E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2 (E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \ldots$$

* Now match orders of λ

$\Rightarrow$ λ^0: $H^0 \psi_n^0 = E_n^0 \psi_n^0$ (Unperturbed system)

λ^1: $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

λ^2: $H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^0 \psi_n^2$

* To determine E_n^1, take inner product w/ $\langle \psi_n^0 |$

$$\Rightarrow \langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n^0 | E_n^0 | \psi_n^1 \rangle + E_n^1 \overset{1}{\langle \psi_n^0 | \psi_n^0 \rangle}$$

$$\cancel{\langle \psi_n^0 | E_n^0 | \psi_n^1 \rangle} + \quad '' \quad = \quad \cancel{''} \quad ''$$

$$\Rightarrow E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

6.1 (cont.)

* To determine ψ_n^1, we first rewrite our equation

$$\Rightarrow (H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$$

* but $\psi_n^1 = \sum_{m \neq n}' c_m^{(n)} \psi_m^0$

$$\Rightarrow \sum_{m \neq n}' (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1)\psi_n^0$$

Now take inner product w/ $\langle \psi_l^0 |$

$$\sum_{m \neq n}' (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle$$

$$(E_l^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle$$

$$c_l^{(n)} = \frac{-\langle \psi_l^0 | H' | \psi_n^0 \rangle}{E_l^0 - E_n^0} \qquad l = m$$

$$\Rightarrow \psi_n^1 = \sum_{m \neq n}' \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$$

* Following a similar procedure for the 2^{nd} order corrections, we see:

$$E_n^2 = \sum_{m \neq n}' \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$

6.2 - Degenerate Perturbation Theory

* Note: If our energy levels in the formulas above are degenerate, the result goes to infinity unless $\langle m | H' | n \rangle = 0$ as well

ex. Two-fold Degeneracy

Given: $H^0 \psi_a^0 = E^0 \psi_a^0$, $H^0 \psi_b^0 = E^0 \psi_b^0$ $\quad \langle \psi_a^0 | \psi_b^0 \rangle = 0$

↳ Note: $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$ is also eigenstate w/ energy E^0

Typically, applying a perturbation H' will lift the degeneracy and allow us to write that state as a linear combination of ψ_a^0 and ψ_b^0, but we don't know the values of α and β a priori. Keeping them general, we attempt to solve: $H\psi = E\psi$

6.2 (cont.)

$$H\Psi = E\Psi \quad \text{where} \quad H = H^0 + \lambda H'$$
$$E = E^0 + \lambda E' + \lambda^2 E^2 + \dots$$
$$\Psi = \Psi^0 + \lambda\Psi' + \lambda^2\Psi^2 + \dots$$

Substituting in the expansions and collecting in powers of λ, we find:

$$H^0\Psi^0 + \lambda(H'\Psi^0 + H^0\Psi') + \dots = E^0\Psi^0 + \lambda(E'\Psi^0 + E^0\Psi') + \dots$$

* Ignoring terms $> \lambda^2$, we see

$$H'\Psi^0 + H^0\Psi' = E'\Psi^0 + E^0\Psi'$$

Taking the inner product with $\langle\Psi_a^0|$ yields:

$$\langle\Psi_a^0|H'\Psi^0\rangle + \langle\Psi_a^0|H_0\Psi'\rangle = E'\langle\Psi_a^0|\Psi^0\rangle + E_0\langle\Psi_a^0|\Psi'\rangle$$

$$\langle\Psi_a^0|H'\Psi^0\rangle + \cancel{E^0\langle\Psi_a^0|\Psi'\rangle} = E'\langle\Psi_a^0|\Psi^0\rangle + \cancel{E_0\langle\Psi_a^0|\Psi'\rangle}$$

$$\langle\Psi_a^0|H'\Psi^0\rangle = E'\langle\Psi_a^0|\Psi^0\rangle$$

Remembering $\Psi^0 = \alpha\Psi_a^0 + \beta\Psi_b^0$

$$\alpha\langle\Psi_a^0|H'|\Psi_a^0\rangle + \beta\langle\Psi_a^0|H'|\Psi_b^0\rangle = \alpha E'$$

which can be rewritten as:

$$\alpha W_{aa} + \beta W_{ab} = \alpha E', \quad W_{ij} = \langle\Psi_i^0|H'|\Psi_j^0\rangle$$

By a similar method, the inner product w/ $\langle\Psi_b^0|$ will yield:

$$\alpha W_{ba} + \beta W_{bb} = \beta E'$$

Notice that W_{ij} are the matrix elements of H' and should therefore be known.
More importantly, if we multiply the above equation by W_{ab} we see:

$$\alpha W_{ab}W_{ba} + \beta W_{ab}W_{bb} = \beta E' W_{ab}$$
$$\beta W_{ab} = \alpha E' - \alpha W_{aa} \quad \text{from above}$$

$$\Rightarrow \alpha W_{ab}W_{ba} + W_{bb}(\alpha E' - \alpha W_{aa}) = \beta E' W_{ab}$$
$$\alpha W_{ab}W_{ba} + W_{bb}\alpha E' - \alpha W_{bb}W_{aa} = E'(\alpha E' - \alpha W_{aa})$$
$$\alpha W_{ab}W_{ba} + \alpha W_{bb}E' - \alpha W_{bb}W_{aa} = \alpha(E')^2 - \alpha W_{aa}E'$$

$$0 = \alpha\left[(E')^2 + E'(W_{aa}+W_{bb}) + (-W_{ab}W_{ba} + W_{aa}W_{bb})\right]$$

* if $\alpha \neq 0$, then solving the quadratic eqn for E' yields

$$E' = \frac{(W_{aa}+W_{bb}) \pm \sqrt{(-W_{aa}-W_{bb})^2 + 4(W_{aa}W_{bb} - W_{ab}W_{ba})}}{2}$$

$$\boxed{E' = \frac{1}{2}\left[(W_{aa}+W_{bb}) \pm \sqrt{(W_{aa}-W_{bb})^2 + 4|W_{ab}|^2}\right]}$$

* Note: There is a proff in Griffiths which states that if you can find a Hermitian operator A that commutes with H and H', then use the simultaneous eigenfunctions of A and H to use non-degenerate perturbation theory.

ex. Higher-Order Degeneracies

To see how the above procedure generalizes, we can rewrite our equations above in matrix form

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E'\begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

From here, it is easy to see that the first order energy corrections are the eigenvalues of the perturbation matrix and the good eigenvectors are those of the same matrix.

In math terms, we are finding the basis in the degenerate subspace which diagonalizes the perturbation matrix.

WKB Approximation

* An equation solving technique for obtaining approximate solutions to TISE in 1-D
* A simplistic explanation follows: If we imagine a particle w/ energy E moving in a constant potential $V(x)$ where $E > V(x)$, then we know our solution to be:

$$\psi(x) = Ae^{\pm ikx} \; ; \quad k = \frac{1}{\hbar}\sqrt{2m(E-V)} \qquad \text{(Note: } \pm \text{ indicates direction of travel)}$$

$\Rightarrow$ Our solution is a oscillatory function w/ $\lambda = \frac{2\pi}{k}$ and amplitude A

If we now allow $V(x)$ to vary, but slowly in comparison to λ, we have a region over several full wavelengths where $V(x)$ is essentially constant. Thus, we can reasonably assume $\psi(x)$ stays sinusoidal in nature, with A and λ now varying w/ position.

In the situation where $E < V(x)$, our solution becomes, assuming $V \approx$ constant:

$$\psi(x) = Ae^{\pm \kappa x} \; ; \quad \kappa = \frac{1}{\hbar}\sqrt{2m(V-E)}$$

Again allowing $V(x)$ to vary; this time slowly with respect to $1/\kappa$, our solution will remain exponential in nature and A and κ will vary slowly with position.

Note: This will all fail at the "turning point" $E = V$. We will handle this later.

* We begin by examining the classical region, where $E > V$, which ensures $p(x)$ is real

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E(\psi) \iff \frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \; ; \quad p(x) = \sqrt{2m(E-V(x))}$$

In general, we know $\psi(x)$ has the form $\psi(x) = A(x)e^{i\varphi(x)}$

$$\hookrightarrow \quad \frac{d\psi}{dx} = (A' + iA\varphi')e^{i\varphi(x)}$$

$$\frac{d^2\psi}{dx^2} = \left[A'' + 2iA'\varphi' + iA\varphi'' - A(\varphi')^2\right]e^{i\varphi(x)}$$

This separates into two equations (one real, one imaginary) when substituted into Schrödingers equation, yielding:

$$A'' - A(\varphi')^2 = \frac{-p^2}{\hbar^2}A \iff A'' = A\left((\varphi')^2 - \frac{p^2}{\hbar^2}\right) \qquad \text{(Real)}$$

$$2A'\varphi' + A\varphi'' = 0 \iff (A^2\varphi')' = 0 \qquad \text{(Imaginary)}$$

The imaginary equation can be easily solved by:

$$A^2 \varphi' = C^2 \quad \Rightarrow \quad A = \frac{C}{\sqrt{\varphi'}}, \quad C \in \mathbb{R}$$

To solve the real equation, we assume A varies slowly (A'' is ignored) such that $A''/A \ll (\varphi')^2$ and $\frac{p^2}{\hbar^2}$. Thus, our real equation becomes:

$$(\varphi')^2 = \frac{p^2}{\hbar^2} \quad \Rightarrow \quad \frac{d\varphi}{dx} = \pm \frac{p}{\hbar}$$

Therefore: $\varphi(x) = \pm \frac{1}{\hbar} \int p(x)\,dx$

This results in our overall solution becoming:

$$\psi(x) = \frac{C}{\sqrt{p(x)}} \exp\left[\pm \frac{i}{\hbar} \int p(x)\,dx\right]$$ where C has absorbed constants from the real equation and may now be complex.

Note: The true solution is a linear combination of positive and negative exponentials

ex. Potential w/ 2 vertical walls

$$V(x) = \begin{cases} V(x) & 0 < x < a \\ 0 & \text{otherwise} \end{cases}$$

We know our solution has the form $\psi(x) = \frac{1}{\sqrt{p(x)}}\left[C_+ e^{i\varphi(x)} + C_- e^{-i\varphi(x)}\right]$

$$= \frac{1}{\sqrt{p(x)}}\left[C_1 \sin[\varphi(x)] + C_2 \cos[\varphi(x)]\right]$$

where $\varphi(x) = \frac{1}{\hbar}\int_0^x p(x')\,dx'$

Since our solution must go to 0 at $x=0$, and so does $\varphi(x)$, we automatically know $C_2 = 0$. Using our other 0 at $x = a$, since $\sin(\varphi(x)) = 0$, we know that $\varphi(a) = n\pi$, $n \in \mathbb{Z}^+$

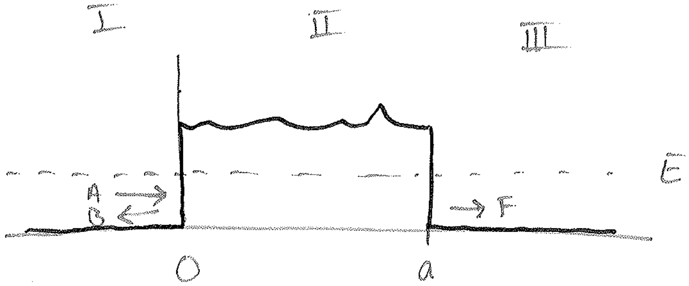
$$\hookrightarrow \int_0^a p(x)\,dx = n\pi\hbar$$

Note: For the infinite square well ($V=0$) we get $\sqrt{2mE}\,a = n\pi\hbar \Rightarrow E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$

* Now we examine the "nonclassical region" where $V(x) > E$. In this region, p is imaginary.

$$\hookrightarrow \psi(x) = \frac{C}{\sqrt{|p(x)|}} \exp\left[\pm \frac{1}{\hbar} \int |p(x)| dx\right]$$

ex. Rectangular barrier w/ uneven top



In section I : $\psi(x) = Ae^{ikx} + Be^{ikx}$, $k = \frac{1}{\hbar}\sqrt{2mE}$

III : $\psi(x) = Fe^{ikx}$; $T = |F|^2 / |A|^2$ (transmitted probability)

II : $\psi(x) = \frac{C}{\sqrt{|p(x)|}} \exp\left[\frac{1}{\hbar}\int_0^x |p(x')| dx'\right] + \frac{D}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_0^x |p(x')| dx'\right]$

Quantum Exam 2 Study Guide

Basics from Exam 1

$S_i = \frac{\hbar}{2}\sigma_i$, $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ $\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$ $\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

$[\sigma_x, \sigma_y] = \sigma_z$ * and cyclic permutations for other commutators

$|\alpha\rangle = \sum_i c_i |a_i\rangle$ or $A|\alpha\rangle = a_i|\alpha\rangle$ (definition of a ket)

$\tilde{A} = |\beta\rangle\langle\alpha|$ (definition of an operator)

$\sum_i \Lambda_i = \sum_i |a_i\rangle\langle a_i| = 1$ (Projection operator / Completeness relation)

* All observables are represented by Hermitian operators; $A = A^+$ is condition for Hermitivity
* Unitary operators satisfy $UU^+ = U^+U = \mathbb{I}$

$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$ (Schwartz Inequality)

$\langle\hat{A}\rangle = \langle\alpha|\hat{A}|\alpha\rangle$ (Definition of expectation value)

$\langle(\Delta\hat{A})^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$ (RMS or avg value)

$\Delta\hat{A} = \hat{A} - \langle A\rangle\mathbb{I}$ (Dispersion operator)

$\langle(\Delta\tilde{A})^2\rangle\langle(\Delta\tilde{B})^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$ (Uncertainty relation)

Continuous Basis / Spectra

* In a continuous basis, the completeness relation is now defined as:

$$\int_a^b |x'\rangle\langle x'|\, dx' = \tilde{\mathbb{I}}$$

* Orthogonality is now defined by Dirac δ-function
* All position operators $(\tilde{x}, \tilde{y}, \tilde{z})$ commute

Translation Operators

* Allow us to see how systems evolve in time

$$\tilde{T}(dx') = \mathbb{I} - \frac{i\,\tilde{p}\cdot d\tilde{x}}{\hbar} \qquad \text{(Infinitetesimal translation operator)}$$

⇒ Derived from the following conditions:

① Normalization unchanged ⇒ $\tilde{T}^{+}\tilde{T} = \mathbb{I}$

② Addition of successive translations ⇒ $T(dx'')T(dx') = T(dx'+dx'')$

③ Inverse is translation in opposite direction ⇒ $T^{-1}(dx) = T(-dx)$

④ Zero translation is identity operator ⇒ $T(0) = \mathbb{I}$

* Note: $[x_i, p_j] = i\hbar\,\delta_{ij}$

Wavefunctions

* We define the position space wavefunction as:

$$\psi_a(x') = \langle x'|a\rangle$$

$$\Rightarrow \langle\beta|\alpha\rangle = \int dx' \langle\beta|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx'\, \psi^*_\beta(x')\,\psi_\alpha(x')$$

$$\langle\beta|\hat{A}|\alpha\rangle = \int dx' \int dx'' \langle\beta|x''\rangle\langle x''|A|x'\rangle\langle x'|\alpha\rangle$$

⇒ write $\hat{A}$ in terms of position operator to solve

$$\langle\alpha|\alpha\rangle = \int dx' \langle\alpha|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx' |\psi_\alpha(x')|^2$$

$$= 1$$

⇒ Normalization condition + generator of PDF

* We define the momentum space wavefunction as:

$$\varphi_\alpha(p') = \langle p'|\alpha\rangle$$

⇒ Momentum eigenkets follow same rules as position eigenkets above

$$\langle x'|\tilde{p}|p'\rangle = -i\hbar\frac{\partial}{\partial x}\langle x'|p'\rangle \quad \Rightarrow \quad \tilde{p} = -i\hbar\frac{\partial}{\partial x} \qquad \langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp\left[\frac{ip'x'}{\hbar}\right]$$

Time Evolution

* Schrödinger Picture: state vectors evolve in time, eigenkets + operators constant.

* Heisenberg Picture: eigenkets/operators evolve in time, state vectors constant

$\Rightarrow$ Time translation operator must follow these properties

① Unitary

② $\lim_{\delta t \to 0} \tilde{U}(t_1 + \delta t, t_0) = \mathbb{I}$

③ Successive translations are also translations $\tilde{U}(t_2, t_1)\tilde{U}(t_1, t_0) = \tilde{U}(t_2, t_0)$

$$\Rightarrow \tilde{U}(t, t_0) = \mathbb{I} - i\Omega\delta t$$

* by dimensional analysis $[\Omega] = \frac{1}{t}$

$$\Rightarrow \Omega = \frac{H}{\hbar}$$

$$\rightarrow U(t, t_0) = \mathbb{I} - \frac{iHt}{\hbar}$$

* Heisenberg equations of motion:

$$i\hbar \frac{\partial A^{(H)}}{\partial t} = [A, H]$$

* Ehrenfest Theorem: $\frac{d\langle \vec{p}\rangle}{dt} = -\frac{\partial}{\partial x}\langle V(\vec{x})\rangle$

Simple Harmonic Oscillator

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

* To derive creation/annihilation operators

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

$$\Rightarrow \hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right) \quad \text{(annihilation operator)}$$

$$\hat{a}^+ = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right) \quad \text{(creation operator)}$$

$$\Rightarrow \hat{N} = \hat{a}^+\hat{a} \quad \text{(Number operator)}$$

$[a, a^+] = +1$ $\qquad [N, a] = -\hat{a}$

$[a^+, a] = -1$ $\qquad [N, a^+] = \hat{a}^+$

SHO (cont.)

* Acting these new operators on the energy eigenkets yields:

$$\tilde{a}|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$\tilde{a}^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$N|n\rangle = n|n\rangle$$

⇒ Hamiltonian can be rewritten as:

$$\frac{H}{\hbar\omega} = \frac{1}{2}\frac{p^2}{\sigma_p^2} + \frac{1}{2}\frac{x^2}{\sigma_x^2}\,; \qquad \sigma_p = \sqrt{m\hbar\omega} \qquad \sigma_x = \sqrt{\hbar/m\omega}$$

Important Derivations

* See sections on Translation Operators + Time Evolution for appropriate translation operators

* Derivation of momentum operator:

$$\left(\mathbb{I} - \frac{ip\Delta x}{\hbar}\right)|\alpha\rangle = \int dx'\, T(\Delta x')|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx'\, |x' + \Delta x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx'\, |x'\rangle\langle x' - \Delta x'|\alpha\rangle$$

* if we Taylor expand $\langle x' - \Delta x'|\alpha\rangle$

$$= \int dx'\, |x'\rangle\left(\langle x'|\alpha\rangle - \Delta x' \frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right)$$

$$= |\alpha\rangle - \int dx'\left(-\Delta x' \frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right)$$

$$-\frac{ip\Delta x}{\hbar} = -\int dx\left(-\Delta x' \frac{\partial}{\partial x'}\langle x'|\alpha\rangle\right.$$

$$\hat{p} = -i\hbar \int dx'\,|x'\rangle\langle x'|\alpha\rangle$$

$$\hat{p}|\alpha\rangle = -i\hbar \frac{\partial}{\partial x'}|\alpha\rangle$$

Derivations (cont.)

* Schrödinger Equation

$$\tilde{U}(t+\delta t, t_0) = U(t+\delta t, t)\tilde{U}(t,t_0)$$
$$= \left(\mathbb{I} - \frac{iH\delta t}{\hbar}\right)\tilde{U}(t,t_0)$$

$$\tilde{U}(t+\delta t, t_0) - U(t,t_0) = \frac{1}{i\hbar} H U(t,t_0)\delta t$$

* if $\delta t \to dt$
* Taylor expand ~~LHS~~ RHS around $t - \delta t$

$$U(t+dt, t_0) - U(t,t_0) = \cancel{U(t,t_0)} + \delta t \frac{\partial}{\partial t} U(t,t_0) - \cancel{U(t,t_0)}$$

$$\delta t \frac{\partial}{\partial t} U(t,t_0) = \frac{1}{i\hbar} H U(t,t_0)\delta t$$

$$i\hbar \frac{\partial}{\partial t} U(t,t_0) = H U(t,t_0) \checkmark$$

Other Important Equations

$$[\hat{x}, F(\hat{p})] = i\hbar \frac{\partial F}{\partial p}$$

$$[\hat{p}, G(\hat{x})] = -i\hbar \frac{\partial G}{\partial x}$$

$$[x_i, p_j] = -i\hbar \delta_{ij}$$

Quantum Exam 3 Study Guide

Basics from previous exams

$S_i = \frac{\hbar}{2}\sigma_i \Rightarrow \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

$[\sigma_i, \sigma_j] = \sigma_k$ (other relations result from cyclic permutations)

$|\alpha\rangle = \sum_i' c_i |a_i\rangle$ or $A|\alpha\rangle = a_i|\alpha\rangle$ (definition of a ket)

$\hat{A} = |a\rangle\langle b|$ (definition of an operator)

$\sum_i' \Lambda_i = \sum_i' |a_i\rangle\langle a_i| = 1$ (Projection operator / completeness relation)

*To get matrix elements:

$A \to \sum_{m,n}' |m\rangle \underbrace{\langle m|A|n\rangle}_{\text{matrix elements}} \langle n|$

$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$ (Schwartz Inequality)

$\langle\hat{A}\rangle = \langle\alpha|\hat{A}|\alpha\rangle$ (Expectation value)

$\langle(\Delta\hat{A})^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$ (RMS or avg value)

$\Rightarrow \Delta A = \hat{A} - \langle\hat{A}\rangle \mathbb{I}$ (Dispersion operator)

$\langle(\Delta A^2)\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$ (Uncertainty Relation)

$[x_i, x_j] = 0 = [p_i, p_j]$ (Position/Momentum operators, self commute)

* $[x_i, p_j] = i\hbar\delta_{ij}$ *

$\psi_a = \langle x'|\alpha\rangle$ (Definition of wavefunction)

$= \langle p'|\alpha\rangle$

$\langle x'|\hat{p}|p'\rangle = -i\hbar\frac{\partial}{\partial x}\langle x'|p'\rangle \qquad \langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp\left[\frac{ip'x'}{\hbar}\right]$

$\Rightarrow \hat{p} = -i\hbar\frac{\partial}{\partial x}$

Basics (cont.)

* Schrödinger Picture → state vectors time evolve; operators + eigenkets constant
* Heisenberg Picture → eigenkets + operators evolve; state vectors constant

$$\hat{U}(t, t_0) = \mathbb{I} - i\Omega \delta t$$
$$= \exp\left[\frac{-i\hat{H}t}{\hbar}\right]$$

⇒ Heisenberg equations of motion: $-i\hbar \frac{\partial A}{\partial t} = [A, H]$

$$[\hat{x}, F(\hat{p})] = i\hbar \frac{\partial F}{\partial p} \qquad [\hat{p}, G(\hat{x})] = -i\hbar \frac{\partial G}{\partial x}$$

Simple Harmonic Oscillator

$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$ ⇒ $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right)$ annihilation operator

↳ $E_n = (n + 1/2)\hbar\omega$ $\qquad \hat{a}^{+} = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$ creation operator

$\hat{N} = \hat{a}^{+}\hat{a}$ Number operator

$$\Rightarrow [a, \hat{a}^{+}] = 1 \qquad [N, \hat{a}] = -\hat{a}$$
$$[\hat{a}^{+}, \hat{a}] = -1 \qquad [N, \hat{a}^{+}] = \hat{a}^{+}$$

* We can rewrite position/momentum operators in terms of ladder operators as:

$$\hat{x} = \frac{\sigma_x}{\sqrt{2}}(\hat{a}^{+} + \hat{a}) \qquad \sigma_x = \sqrt{\hbar/m\omega}$$
$$\hat{p} = \frac{i\sigma_p}{\sqrt{2}}(\hat{a}^{+} + \hat{a}) \qquad \sigma_p = \sqrt{m\hbar\omega}$$

⇒ Uncertainty relation can be derived using these versions of $\hat{x}, \hat{p}$; result from expectation values of $\hat{x}^2, \hat{p}^2 \neq 0$

* To derive eigen function, apply annihilation operator to lowest state, switch to either position or momentum space + solve differential equation.

$$\Rightarrow U_0(x) = \frac{1}{\pi^{1/4}\sqrt{\sigma_x}} \exp[-x^2/2\sigma_x^2] \qquad \text{(position space)}$$
$$V_0(x) = \frac{1}{\pi^{1/4}\sqrt{\sigma_p}} \exp[-x^2/2\sigma_p^2] \qquad \text{(momentum space)}$$

SHO (cont.)

* Eigenfunctions can be generated from Hamiltonian by solving differential equation when written in position space using B.C. that eigenfunction must go to 0 at boundary + must be normalizable
  - $\Rightarrow$ Generates Hermite polynomials (hard to recognize normally) w/ inclusion of Gaussian necessary for normalizability

* Time evolution of SHO is handled via application of Heisenberg equations of motion, yielding

$$\frac{d\tilde{p}}{dt} = -m\omega^2 \tilde{x} \qquad \frac{d\tilde{x}}{dt} = \frac{\tilde{p}}{m}$$

$\Rightarrow$ after solving for $\tilde{p}(t)$ and $\tilde{x}(t)$, time evolution of operators can be written, but rewriting ↑ equations before solving yields:

$$\frac{d\hat{a}}{dt} = \sqrt{\frac{m\omega}{2\hbar}}\left(\frac{\partial\tilde{x}}{\partial t} + \frac{i}{m\omega}\frac{d\hat{p}}{dt}\right) = -i\omega\hat{a}$$

$$\frac{d\hat{a}^+}{dt} = i\omega\hat{a}^+$$

$\Rightarrow$ Solving above yields: $\tilde{a}(t) = \tilde{a}(0)e^{-i\omega t}$

$$\tilde{a}^+(t) = \tilde{a}^+(0)e^{i\omega t}$$

$$\tilde{x}(t) = \tilde{x}(0)\cos(\omega t) + \frac{\tilde{p}(0)}{m\omega}\sin(\omega t)$$

$$\tilde{p}(t) = -m\omega\tilde{x}(0)\sin(\omega t) + \tilde{p}(0)\cos(\omega t)$$

Guage Transformations

* Effectively amount to multiplying by a phase; only transformations that do not multiply everything uniformly will result in measurable difference

$$\Rightarrow H = \frac{p^2}{2m} + V(\tilde{x}) \qquad\qquad H = \frac{p^2}{2m} + V(\tilde{x}) + V_0$$

$$|\alpha, t_0; t\rangle = \exp[iH\Delta t/\hbar]|\alpha, t_0\rangle \qquad |\alpha, t_0; t\rangle = \exp[iV_0\Delta t/\hbar]|\alpha, t_0; t\rangle$$

Guage Transforms (cont.)

* Most applicable to E+M fields

$\Rightarrow$ Maxwells Eqns

$$\nabla \cdot B = 0 \quad \Rightarrow \quad B = \nabla \times A \quad \Rightarrow \quad A \to A + \nabla \lambda$$

$$\nabla \times E = \frac{-1}{c}\frac{\partial B}{\partial t} \quad \Rightarrow \quad E = -\nabla \varphi - \frac{\partial A}{\partial t} \quad \Rightarrow \quad \varphi \to \varphi - \frac{\partial \lambda}{\partial t}$$

Rotations

* Classically, rotation about the z-axis is given by:

$$R = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 - \delta\varphi^2/2 & -\delta\varphi & 0 \\ \delta\varphi & 1 - \delta\varphi^2/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$ * Taylor expanded for infinitesimal rotation

$\Rightarrow$ Infinitesimal Rotation operator:

$$\mathcal{D}(\hat{n}, \delta\varphi) = \mathbb{I} - \frac{i}{\hbar} \vec{J} \cdot \hat{n}\, \delta\varphi$$

$$\lim_{N \to \infty} \left(\mathbb{I} - \frac{i}{\hbar} J_z \frac{\varphi}{N} \right)^N = \exp\left[\frac{-i}{\hbar} J_z \varphi \right]$$ (finite Rotation operator)

* Rotation operator must satisfy the following:

① $\mathcal{D}(R)\mathbb{I} = \mathcal{D}(R)$

② $\mathcal{D}(R_1)\mathcal{D}(R_2) = \mathcal{D}(R_3)$

③ $\mathcal{D}(R)\mathcal{D}^{-1}(R) = \mathbb{I}$

④ $[\mathcal{D}(R_1)\mathcal{D}(R_2)]\mathcal{D}(R_3) = \mathcal{D}(R_1)[\mathcal{D}(R_2)\mathcal{D}(R_3)]$

* Expanding operators yields commutator relations

$$[\tilde{J}_x, \tilde{J}_y] = i\hbar \tilde{J}_z$$ (and cyclic permutations)

Quantum Final Exam Study Guide

* Basics from previous exams:

- Definition of a ket: $|\alpha\rangle = c_i |a_i\rangle$

$$a_i|\alpha\rangle = A|\alpha\rangle$$

- Definition of an operator: $\hat{A} = |a\rangle\langle b|$

- Projection Operator/Completeness Relation: $\sum_i \Lambda_i = \sum_i |a_i\rangle\langle a_i| = 1$

  * sum to integral if a_i is continuous basis set

- To get the matrix elements of an operator: $A \rightarrow \sum_{m,n} |m\rangle\langle m|A|n\rangle\langle n|$

- Schwartz Inequality: $\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$

- Expectation value: $\langle\hat{A}\rangle = \langle\alpha|A|\alpha\rangle$

- RMS / Avg value: $\langle(\Delta\hat{A})^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$

  $\hookrightarrow \Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle\mathbb{I}$ (Dispersion Operator)

- Uncertainty Relation: $\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$

- Important Commutation Relations include:

$$[x_i, x_j] = 0 = [p_i, p_j] \qquad S_i = \frac{\hbar}{2}\sigma_i \qquad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$[x_i, p_j] = i\hbar\delta_{ij} \qquad [\sigma_i, \sigma_j] = \sigma_k \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$[x, F(p)] = i\hbar\frac{\partial F}{\partial p}$$

$$[p, G(x)] = -i\hbar\frac{\partial G}{\partial x}$$

$$[A, H] = -i\hbar\frac{\partial A}{\partial t} \quad \text{(Heisenberg eqn of motion)}$$

- Two pictures: Schrödinger Picture → state vectors evolve in time, operators const.

  Heisenberg Picture → eigenkets + operators evolve; state vectors cons

Bases (cont.)

* For functions of continuous variables

  - Definition of wave function: $\psi_a(x') = \langle x'|a\rangle$

    $\varphi_b(p') = \langle p'|b\rangle$

$$\Rightarrow \langle\beta|\alpha\rangle = \int dx' \langle\beta|x'\rangle\langle x'|\alpha\rangle = \int dx' \, \psi_b^*(x')\, \psi_a(x')$$

$$= \int dp' \langle\beta|p'\rangle\langle p'|\alpha\rangle = \int dp' \, \varphi_b^*(p')\, \varphi_a(p')$$

$$\langle\beta|A|\alpha\rangle = \int dx'' \int dx' \langle\beta|x''\rangle\langle x''|A|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dp'' \int dp' \langle\beta|p''\rangle\langle p''|A|p'\rangle\langle p'|\alpha\rangle$$

$\rightarrow$ rewrite $\hat{A}$ in terms of x or p to solve

$$\langle\alpha|\alpha\rangle = \int dx' \langle\alpha|x'\rangle\langle x'|\alpha\rangle$$

$$= \int dx' \, |\psi_a(x')|^2$$

$$= 1$$

$\rightarrow$ Normalization condition + PDF generator

$$\Rightarrow \langle x'|\hat{p}|p'\rangle = i\hbar \frac{\partial}{\partial x}\langle x'|p'\rangle \quad \Rightarrow \hat{p} = i\hbar \frac{\partial}{\partial x}$$

$$\Rightarrow \langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{ip'x'}{\hbar}\right]$$

* Translation operators obey the following properties

  ① Unitary

Important Derivations

① Angular Momentum

*Remember that: J → Arbitrary angular momentum (often refers to total)

S → Spin angular momentum

L → Orbital angular momentum

Total Angular momentum operator: $\tilde{J}^2 = \tilde{J} \cdot \tilde{J}$

$$= J_x^2 + J_y^2 + J_z^2$$

Commutation Relations: $[\tilde{J}^2, \tilde{J}_z] = 0$ $\qquad [\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} J_k$

$$[\hat{J}^2, \hat{J}_y] = 0$$

$$[\hat{J}^2, \hat{J}_x] = 0$$

*Following our approach from SHO, we define ladder operators

$\Rightarrow J_\pm = J_x \pm i J_y$

↳ $[J^2, J_\pm] = 0$

$[J_z, J_\pm] = \hbar J_\pm$

$[J_+, J_-] = 2\hbar J_z$

$J_\pm^n |a,b\rangle = b \pm n\hbar\, |a, b \pm n\hbar\rangle$

*Since $\tilde{J}^2$ and $\tilde{J}_z$ commute, we might simultaneous eigenkets such

$\tilde{J}^2 |a,b\rangle = a$ and $\tilde{J}_z |a,b\rangle = b$

→ Relationship b/w $\tilde{J}^2$ and J_z implies max value for b

*Individually, $\langle a,b| J_- J_+ |a,b\rangle \geq 0$

$\langle a,b| J_+ J_- |a,b\rangle \geq 0$

$$\Rightarrow \langle a,b| J_+ J_- + J_- J_+ |a,b \geq 0$$

$$= \langle a,b| 2(J^2 - J_z^2) |a,b\rangle \geq 0$$

↳ $a \geq b^2$.

Derivations (cont)

* We can show that J_z is incremented in terms of $\hbar$ by:

$$J_z(J_\pm|a,b\rangle) = (J_\pm J_z + \hbar J_\pm)|a,b\rangle$$
$$= J_\pm(J_z + \hbar\mathbb{I})|a,b\rangle$$
$$= J_\pm(b+\hbar)|a,b\rangle$$
$$= (b+\hbar)(J_\pm|a,b\rangle)$$

* Note: Acting $J_\pm|a,b\rangle = c_\pm|a, b+\hbar\rangle$

Interpretation: $J_\pm$ increments eigenvalue of angular momentum

* To find extremum values, act raising/lowering operators on max/min states

$$J_+|a, b_{max}\rangle = 0$$
$$J_- J_+|a, b_{max}\rangle = 0$$
$$(J^2 - J_z^2 - \hbar J_z)|a, b_{max}\rangle = 0$$

* assuming a non-zero ket

$$a - b_{max}^2 - \hbar b_{max} = 0$$
$$a = b_{max}(b_{max}+\hbar)$$

* let $b_{max} = j\hbar$

$$a = j(j+1)\hbar^2$$

$\Rightarrow j(j+1)$ are eigenvalues of J^2

$$J_-|a, b_{min}\rangle = 0$$
$$J_+ J_-|a, b_{min}\rangle = 0$$
$$(J^2 - J_z^2 + \hbar J_z)|a, b_{min}\rangle = 0$$
$$\hookrightarrow a - b_{min}^2 + \hbar b_{min} = 0$$
$$a = b_{min}(b_{min} - \hbar)$$

$$b_{max}(b_{max} + h) = b_{min}(b_{min} - \hbar)$$
$$\Rightarrow b_{max} = -b_{min}$$

Derivations (cont.)

$\Rightarrow$ This implies $b_{max} = b_{min} + \hbar$

$\hookrightarrow J_+^n |a, b_{min}\rangle = J_+^n |a, -b_{max}\rangle$

$\Rightarrow b_{max} = \frac{n\hbar}{2}$; since $n \in \mathbb{Z}$, b must be an integer or ½-integer

* But what about $c_\pm$?

$\Rightarrow J_\pm |a,b\rangle = c_\pm |a, b \pm \hbar\rangle$

$\rightarrow$ Starting w/ J_+

$$\langle a,b| J_+^\dagger J_+ |a,b\rangle = |c_+|^2 \underbrace{\langle a, b+\hbar | a, b+\hbar\rangle}_{1}$$

$$\Rightarrow |c_+|^2 = \hbar^2[j(j+1)] - b^2 - \hbar b$$

*if $b = m\hbar$

$$|c_+|^2 = \hbar^2[j(j+1)] - m^2\hbar^2 - \hbar^2 m$$

$$c_+ = \hbar\sqrt{j(j+1) - m^2 - m}$$

$$= \hbar\sqrt{(j-m)(j+m+1)}$$

$\rightarrow$ Now w/ J_-

$$|c_-|^2 \underbrace{\langle a, b-\hbar | a, b-\hbar\rangle}_{1} = \langle a,b| J_-^\dagger J_- |a,b\rangle$$

$$= \hbar^2[j(j+1)] - b^2 + \hbar b$$

$$= \hbar^2[j(j+1)] - m^2\hbar^2 + \hbar^2 m$$

$$c_- = \hbar\sqrt{j(j+1) - m^2 + m}$$

$$= \hbar\sqrt{(j+m)(j-m-1)}$$

Derivations (cont.)

② Orbital Angular Momentum

* We define orbital angular momentum operator $\tilde{L}$ as:

$$\tilde{L} = \tilde{\vec{X}} \times \tilde{\vec{P}} \xrightarrow{\text{via cross-product}} \begin{aligned} \tilde{L}_x &= \tilde{y}\tilde{p}_z - \tilde{z}\tilde{p}_y \\ \tilde{L}_y &= \tilde{z}\tilde{p}_x - \tilde{x}\tilde{p}_z \\ \tilde{L}_z &= \hat{x}\tilde{p}_y - \tilde{y}\hat{p}_x \end{aligned}$$

$$\Rightarrow [\hat{L}_i, \tilde{L}_j] = i\hbar \tilde{L}_k$$

* Using the infinitesimal rotation operators, we can generate wavefunctions in position basis

$$\mathcal{D}(\delta\varphi, \hat{z})|x', y', z\rangle = (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi L_z)|x', y', z'\rangle$$
$$= (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi[xp_y - yp_x])|x', y', z'\rangle$$
$$= (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi[p_y x - p_x y])|x', y', z\rangle \quad b/c \ [x_i, p_j] = i\hbar\delta_{ij}$$

* But when distributed, these are translation operators

$$= |x' - y\delta\varphi, y' + x\delta\varphi, z'\rangle$$

* Note, this matches what we expect from applying rotation matrix on our position operator

* We define our wavefunction as:

$$\varphi(\vec{r}) = \langle x', y', z' | \varphi\rangle \ , \quad |\varphi\rangle = (\mathbb{I} - \tfrac{i}{\hbar}L_z\delta\varphi)|\alpha\rangle$$
$$= \langle r, \theta, \varphi | \varphi\rangle$$
$$= \langle r, \theta, \varphi | \mathbb{I} - \tfrac{i}{\hbar}L_z\delta\varphi|\alpha\rangle = \langle r, \theta, \varphi - \delta\varphi|\alpha\rangle$$

*Taylor expansion about $\delta\varphi = 0$ yields

$$= \langle r, \theta, \varphi|\alpha\rangle - \delta\varphi \frac{\partial}{\partial\varphi}\langle r, \theta, \varphi|\alpha\rangle$$

$$\Rightarrow -i\hbar\frac{\partial}{\partial\varphi}\langle r, \theta, \varphi|\alpha\rangle = \langle r, \theta, \varphi|\tilde{L}_z|\alpha\rangle$$

$$\hookrightarrow \ -i\hbar\frac{\partial}{\partial\varphi} = L_z$$

Derivations (cont.)

* To derive other operators in Cartesian system, apply infinitesimal rotation operator to cartesian vector, then convert to spherical using δx_i and form matching. Taylor expand $\langle r,\theta,\varphi | L_i | \alpha \rangle$ about $\delta\varphi_i = 0$ and derive form of operator

Results: $\tilde{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$

$\tilde{L}_x = -i\hbar\left(-\sin\varphi \frac{\partial}{\partial\theta} - \cot\theta\cos\varphi \frac{\partial}{\partial\varphi}\right)$

$\tilde{L}_y = -i\hbar\left(\cos\varphi \frac{\partial}{\partial\theta} - \cot\sin\varphi \frac{\partial}{\partial\varphi}\right)$

* To derive Spherical Harmonics, we focus on L_z component

$$\Rightarrow L_z|l,m\rangle = m\hbar|l,m\rangle$$

$$\langle\hat{n}|L_z|l,m\rangle = m\hbar\langle\hat{n}|l,m\rangle$$
$$= i\hbar\frac{\partial}{\partial\varphi} Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

* Solving the above differential equation by separation of variables yields

$$\Phi(\varphi) \propto e^{+im\varphi}$$

* If we define the orbital angular momentum operators as:

$$L_\pm = L_x \pm iL_y$$
$$= -i\hbar e^{\pm i\varphi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\frac{\partial}{\partial\varphi}\right)$$

then

$$L_+|l,l\rangle = 0$$

$$\langle\hat{n}|L_+|l,l\rangle = -i\hbar\, e^{i\varphi}\left(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\theta}\right) Y_l^l(\theta,\varphi)$$
$$= 0$$

* Solving the above differential equation via separation of variables + $\Phi = e^{im\varphi}$

$$\Rightarrow Y_l^l(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) = c_l e^{im\varphi}\sin^l(\theta)$$

Derivations (cont.)

* Normalization via

$$\langle l', m' | l, m\rangle = \langle l' m' | \theta, \varphi\rangle\langle\theta, \varphi | l, m\rangle$$
$$= \int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\theta)\, |Y_l^m|^2$$

$$\Rightarrow c_l = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)(2l)!}{4\pi}}$$

③ Spherical Harmonic + The Rotation Operator

$\Rightarrow$ We want: $|\hat{n}\rangle = \mathcal{D}(\alpha, \beta, \gamma)|\hat{z}\rangle$
$= \mathcal{D}(\varphi, \theta, \gamma)|\hat{z}\rangle$

$$\hookrightarrow \langle l', m' | \hat{n}\rangle = \sum_{l,m} \langle l', m' | \mathcal{D}(\varphi, \theta, \gamma) | l, m\rangle\langle l, m | \hat{z}\rangle$$

* $l = l'$ or total $\bar{L}$ changes

$$= \sum_{m} \langle l, m' | \mathcal{D}(\varphi, \theta, \gamma) | l, m\rangle\langle l, m | \hat{z}\rangle$$

$$= (Y_l^m)^*(\theta, \varphi)\,(Y_l^0)(\theta, \varphi)$$

$$=$$

$J_{\pm} = J_x \pm i J_y$

$$\Rightarrow J_- J_+ = (J_x - iJ_y)(J_x + iJ_y)$$
$$= J_x^2 - iJ_yJ_x + iJ_xJ_y - i^2 J_y$$
$$= J_x^2 + J_y^2 + i(J_xJ_y - J_yJ_x)$$
$$= J^2 - J_z^2 + i[J_x, J_y]$$
$$= J^2 - J_z^2 + i(i\hbar J_z)$$
$$= J^2 - J_z^2 - \hbar J_z$$

* To derive L_x operator form

$$\mathcal{D}(\delta\varphi, \hat{x})|x', y', z'\rangle = (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi L_x)|x', y', z'\rangle$$
$$= (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi[yp_z - zp_y])|x', y', z'\rangle$$
$$= (\mathbb{I} - \tfrac{i}{\hbar}\delta\varphi[p_z y - p_y z])|x', y', z'\rangle$$
$$= |x', y' - \delta\varphi z', z' + \delta\varphi y'\rangle$$

* In spherical: $x = r\sin\theta\cos\varphi \longrightarrow \delta x = r\cos\theta\,\delta\theta\cos\varphi + r\sin\theta\sin\varphi\,\delta\varphi$

$y = r\sin\theta\sin\varphi \longrightarrow \delta y = r\sin\theta\cos\varphi\,\delta\varphi + r\cos\theta\,\delta\theta\sin\varphi$

$z = r\cos\theta \longrightarrow \delta z = -r\sin\theta\,\delta\theta$

$$\Rightarrow y'\delta\varphi_x = r\sin\theta\sin\varphi\,\delta\varphi_x = -r\sin\theta\,\delta\theta$$
$$\hookrightarrow \delta\theta = -\sin\varphi\,\delta\varphi_x$$

$$\delta x = 0 = r\cos\theta\cos\varphi\,\delta\theta - r\sin\theta\sin\varphi\,\delta\varphi$$
$$\cos\theta\cos\varphi\,\delta\theta = \sin\theta\sin\varphi\,\delta\varphi$$
$$\cot\theta\cot\varphi\,\delta\theta = \delta\varphi$$
$$-\cot\theta\cos\varphi\,\delta\varphi_x = \delta\varphi$$

$$\Rightarrow |x', y' - \delta\varphi_x z', z' + \delta\varphi_x y'\rangle = |r, \theta + \delta\theta, \varphi - \delta\varphi\rangle$$
$$= |r, \theta + \sin\varphi\,\delta\varphi_x, \varphi - \cot\theta\cos\varphi\,\delta\varphi_x\rangle$$

* Now, Taylor expand about $\delta\varphi_x$

$$\langle r, \theta, \varphi|\mathbb{I} - \tfrac{i}{\hbar}L_x\delta\varphi_x|\alpha\rangle = \langle r, \theta + \sin\varphi\,\delta\varphi_x, \varphi - \cot\theta\cos\varphi\,\delta\varphi_x|\alpha\rangle$$

Quantum II Exam II Study Guide

Basics

$|\alpha\rangle = \sum_i' c_i |a_i\rangle$ or $A|\alpha\rangle = a_i|\alpha\rangle$ (Definition of a ket)

$A = |a\rangle\langle b|$ (Definition of an operator)

$\sum_i' \Lambda_i = \sum_i' |a_i\rangle\langle a_i| = 1$ (Projection operator / Completeness Relation)

* To get the matrix elements of an operator

$$A \rightarrow \sum_{m,n}' |m\rangle \underbrace{\langle m|A|n\rangle}_{\text{matrix element}} \langle n|$$

$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$ (Schwartz Inequality)

$\langle\alpha|A|\alpha\rangle = \langle A\rangle$ (Expectation Value)

$\langle(\Delta A)^2\rangle = \langle A^2\rangle - \langle A\rangle^2$ (RMS or Avg value)

$\Rightarrow \Delta A = A - \langle A\rangle \mathbb{I}$ (Dispersion Operator)

$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$ (Uncertainty Relation)

* Important Commutation Relations include:

$[x_i, x_j] = [p_i, p_j] = 0$

$[x_i, p_j] = i\hbar\delta_{ij}$

$[x, F(p)] = i\hbar\frac{\partial F}{\partial p}$

$[p, G(x)] = i\hbar\frac{\partial G}{\partial x}$

$[\sigma_i, \sigma_j] = \sigma_k$, $S_i = \frac{\hbar}{2}\sigma_i$

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

$[A, H] = -i\hbar\frac{\partial A}{\partial t}$ (Heisenberg Eqn of Motion)

* For functions of continuous variables:

$\psi_a(x') = \langle x'|a\rangle$

$\varphi_b(p') = \langle p'|b\rangle$

$\langle\beta|\alpha\rangle = \int dx' \psi_b^*(x')\psi_a(x')$

$= \int dp' \varphi_b^*(p')\varphi_a(p')$

$p = i\hbar\frac{\partial}{\partial x}$

$\langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp\left[\frac{i}{\hbar}p'x'\right]$

Basics (cont.)

* Remember, when discussing angular momentum:

$J \rightarrow$ Arbitrary Angular Momentum (often refers to total)

$L \rightarrow$ Orbital Angular Momentum

$S \rightarrow$ Spin Angular Momentum

* Important angular momentum formulas include:

$$J^2 = J \cdot J = J_x^2 + J_y^2 + J_z^2 \qquad J_\pm = J_x \pm i J_y$$

$$[J^2, J_i] = 0 \qquad [J^2, J_\pm] = 0$$

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k \qquad [J_z, J_\pm] = \hbar J_\pm$$

$$[J_+, J_-] = 2\hbar J_z$$

$\Rightarrow$ We often write simultaneous eigenkets of J^2, J_z as $|a, b\rangle$ such that:

$$J^2 |a, b\rangle = a|a, b\rangle \qquad J_\pm^n |a, b\rangle = b \pm n\hbar |a, b \pm n\hbar\rangle$$

$$J_z |a, b\rangle = b|a, b\rangle$$

$$J_\pm |a, b\rangle = \hbar\sqrt{(j \mp m)(j \pm m + 1)}\, |a, b \pm \hbar\rangle$$

* When adding angular momentum, it is often useful to use direct product notation

$$|S_1, S_{1,z}; S_2, S_{2,z}\rangle = |S_1, S_{1z}\rangle \otimes |S_2, S_{2z}\rangle$$

$\Rightarrow$ Our total system operators now become:

$$J = J_1 + J_2 = J_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes J_2$$

$$J^2 = (J_1 + J_2)\cdot(J_1 + J_2) = J_1^2 + J_2^2 + 2 J_1 \cdot J_2$$

$$= J_{1z} J_{2z} + \tfrac{1}{2}(J_{1+} J_{2-} + J_{1-} J_{2+})$$

* This flexibility allows us to use two sets of kets to describe the system

$$|j_1, j_2; m_1, m_2\rangle \Longleftrightarrow |j_1, j_2; j; m\rangle$$

$$[J_1^2, J_2^2] = 0 = [J_{1z}, J_{2z}] = [J_{1i}, J_{2k}]$$

36. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND d FUNCTIONS

Note: A square-root sign is to be understood over *every* coefficient, *e.g.*, for $-8/15$ read $-\sqrt{8/15}$.

Notation:

	J J ...	
	M M ...	
m_1 m_2		
m_1 m_2	Coefficients	
. .		

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$$

$$Y_2^2 = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{2i\phi}$$

$$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$$

$$d^\ell_{m,0} = \sqrt{\frac{4\pi}{2\ell+1}}\, Y_\ell^m\, e^{-im\phi}$$

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 J M\rangle = (-1)^{J-j_1-j_2}\langle j_2 j_1 m_2 m_1 | j_2 j_1 J M\rangle$$

1/2×1/2

m_1 m_2	$J=1$, $M=+1$
+1/2 +1/2	1

m_1 m_2	$J=1$, $M=0$	$J=0$, $M=0$
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

m_1 m_2	$J=1$, $M=-1$
−1/2 −1/2	1

1×1/2

m_1 m_2	$3/2$, $+3/2$
+1 +1/2	1

m_1 m_2	$3/2$, $+1/2$	$1/2$, $+1/2$
+1 −1/2	1/3	2/3
0 +1/2	2/3	−1/3

m_1 m_2	$3/2$, $-1/2$	$1/2$, $-1/2$
0 −1/2	2/3	1/3
−1 +1/2	1/3	−2/3

m_1 m_2	$3/2$, $-3/2$
−1 −1/2	1

2×1

m_1 m_2	3, $+3$
+2 +1	1

m_1 m_2	3, $+2$	2, $+2$
+2 0	1/3	2/3
+1 +1	2/3	−1/3

m_1 m_2	3, $+1$	2, $+1$	1, $+1$
+2 −1	1/15	1/3	3/5
+1 0	8/15	1/6	−3/10
0 +1	2/5	−1/2	1/10

m_1 m_2	3, 0	2, 0	1, 0
+1 −1	1/5	1/2	3/10
0 0	3/5	0	−2/5
−1 +1	1/5	−1/2	3/10

m_1 m_2	3, -1	2, -1	1, -1
0 −1	2/5	1/2	1/10
−1 0	8/15	−1/6	−3/10
−2 +1	1/15	−1/3	3/5

m_1 m_2	3, -2	2, -2
−1 −1	2/3	1/3
−2 0	1/3	−2/3

m_1 m_2	3, -3
−2 −1	1

1×1

m_1 m_2	2, $+2$
+1 +1	1

m_1 m_2	2, $+1$	1, $+1$
+1 0	1/2	1/2
0 +1	1/2	−1/2

m_1 m_2	2, 0	1, 0	0, 0
+1 −1	1/6	1/2	1/3
0 0	2/3	0	−1/3
−1 +1	1/6	−1/2	1/3

m_1 m_2	2, -1	1, -1
0 −1	1/2	1/2
−1 0	1/2	−1/2

m_1 m_2	2, -2
−1 −1	1

2×1/2

m_1 m_2	$5/2$, $+5/2$
+2 +1/2	1

m_1 m_2	$5/2$, $+3/2$	$3/2$, $+3/2$
+2 −1/2	1/5	4/5
+1 +1/2	4/5	−1/5

m_1 m_2	$5/2$, $+1/2$	$3/2$, $+1/2$
+1 −1/2	2/5	3/5
0 +1/2	3/5	−2/5

m_1 m_2	$5/2$, $-1/2$	$3/2$, $-1/2$
0 −1/2	3/5	2/5
−1 +1/2	2/5	−3/5

m_1 m_2	$5/2$, $-3/2$	$3/2$, $-3/2$
−1 −1/2	4/5	1/5
−2 +1/2	1/5	−4/5

m_1 m_2	$5/2$, $-5/2$
−2 −1/2	1

3/2×1/2

m_1 m_2	2, $+2$
+3/2 +1/2	1

m_1 m_2	2, $+1$	1, $+1$
+3/2 −1/2	1/4	3/4
+1/2 +1/2	3/4	−1/4

m_1 m_2	2, 0	1, 0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

m_1 m_2	2, -1	1, -1
−1/2 −1/2	3/4	1/4
−3/2 +1/2	1/4	−3/4

m_1 m_2	2, -2
−3/2 −1/2	1

3/2×1

m_1 m_2	$5/2$, $+5/2$
+3/2 +1	1

m_1 m_2	$5/2$, $+3/2$	$3/2$, $+3/2$
+3/2 0	2/5	3/5
+1/2 +1	3/5	−2/5

m_1 m_2	$5/2$, $+1/2$	$3/2$, $+1/2$	$1/2$, $+1/2$
+3/2 −1	1/10	2/5	1/2
+1/2 0	3/5	1/15	−1/3
−1/2 +1	3/10	−8/15	1/6

m_1 m_2	$5/2$, $-1/2$	$3/2$, $-1/2$	$1/2$, $-1/2$
+1/2 −1	3/10	8/15	1/6
−1/2 0	3/5	−1/15	−1/3
−3/2 +1	1/10	−2/5	1/2

m_1 m_2	$5/2$, $-3/2$	$3/2$, $-3/2$
−1/2 −1	3/5	2/5
−3/2 0	2/5	−3/5

m_1 m_2	$5/2$, $-5/2$
−3/2 −1	1

3/2×3/2

m_1 m_2	3, $+3$
+3/2 +3/2	1

m_1 m_2	3, $+2$	2, $+2$
+3/2 +1/2	1/2	1/2
+1/2 +3/2	1/2	−1/2

m_1 m_2	3, $+1$	2, $+1$	1, $+1$
+3/2 −1/2	1/5	1/2	3/10
+1/2 +1/2	3/5	0	−2/5
−1/2 +3/2	1/5	−1/2	3/10

m_1 m_2	3, 0	2, 0	1, 0	0, 0
+3/2 −3/2	1/20	1/4	9/20	1/4
+1/2 −1/2	9/20	1/4	−1/20	−1/4
−1/2 +1/2	9/20	−1/4	−1/20	1/4
−3/2 +3/2	1/20	−1/4	9/20	−1/4

m_1 m_2	3, -1	2, -1	1, -1
+1/2 −3/2	1/5	1/2	3/10
−1/2 −1/2	3/5	0	−2/5
−3/2 +1/2	1/5	−1/2	3/10

m_1 m_2	3, -2	2, -2
−1/2 −3/2	1/2	1/2
−3/2 −1/2	1/2	−1/2

m_1 m_2	3, -3
−3/2 −3/2	1

2×3/2

m_1 m_2	$7/2$, $+7/2$
+2 +3/2	1

m_1 m_2	$7/2$, $+5/2$	$5/2$, $+5/2$
+2 +1/2	3/7	4/7
+1 +3/2	4/7	−3/7

m_1 m_2	$7/2$, $+3/2$	$5/2$, $+3/2$	$3/2$, $+3/2$
+2 −1/2	1/7	16/35	2/5
+1 +1/2	4/7	1/35	−2/5
0 +3/2	2/7	−18/35	1/5

m_1 m_2	$7/2$, $+1/2$	$5/2$, $+1/2$	$3/2$, $+1/2$	$1/2$, $+1/2$
+2 −3/2	1/35	6/35	2/5	2/5
+1 −1/2	12/35	5/14	0	−3/10
0 +1/2	18/35	−3/35	−1/5	1/5
−1 +3/2	4/35	−27/70	2/5	−1/10

m_1 m_2	$7/2$, $-1/2$	$5/2$, $-1/2$	$3/2$, $-1/2$	$1/2$, $-1/2$
+1 −3/2	4/35	27/70	2/5	1/10
0 −1/2	18/35	3/35	−1/5	−1/5
−1 +1/2	12/35	−5/14	0	3/10
−2 +3/2	1/35	−6/35	2/5	−2/5

m_1 m_2	$7/2$, $-3/2$	$5/2$, $-3/2$	$3/2$, $-3/2$
0 −3/2	2/7	18/35	1/5
−1 −1/2	4/7	−1/35	−2/5
−2 +1/2	1/7	−16/35	2/5

m_1 m_2	$7/2$, $-5/2$	$5/2$, $-5/2$
−1 −3/2	4/7	3/7
−2 −1/2	3/7	−4/7

m_1 m_2	$7/2$, $-7/2$
−2 −3/2	1

2×2

m_1 m_2	4, $+4$
+2 +2	1

m_1 m_2	4, $+3$	3, $+3$
+2 +1	1/2	1/2
+1 +2	1/2	−1/2

m_1 m_2	4, $+2$	3, $+2$	2, $+2$
+2 0	3/14	1/2	2/7
+1 +1	4/7	0	−3/7
0 +2	3/14	−1/2	2/7

m_1 m_2	4, $+1$	3, $+1$	2, $+1$	1, $+1$
+2 −1	1/14	3/10	3/7	1/5
+1 0	3/7	1/5	−1/14	−3/10
0 +1	3/7	−1/5	−1/14	3/10
−1 +2	1/14	−3/10	3/7	−1/5

m_1 m_2	4, 0	3, 0	2, 0	1, 0	0, 0
+2 −2	1/70	1/10	2/7	2/5	1/5
+1 −1	8/35	2/5	1/14	−1/10	−1/5
0 0	18/35	0	−2/7	0	1/5
−1 +1	8/35	−2/5	1/14	1/10	−1/5
−2 +2	1/70	−1/10	2/7	−2/5	1/5

m_1 m_2	4, -1	3, -1	2, -1	1, -1
+1 −2	1/14	3/10	3/7	1/5
0 −1	3/7	1/5	−1/14	−3/10
−1 0	3/7	−1/5	−1/14	3/10
−2 +1	1/14	−3/10	3/7	−1/5

m_1 m_2	4, -2	3, -2	2, -2
0 −2	3/14	1/2	2/7
−1 −1	4/7	0	−3/7
−2 0	3/14	−1/2	2/7

m_1 m_2	4, -3	3, -3
−1 −2	1/2	1/2
−2 −1	1/2	−1/2

m_1 m_2	4, -4
−2 −2	1

$$d^j_{m',m} = (-1)^{m-m'} d^j_{m,m'} = d^j_{-m,-m'}$$

$$d^1_{0,0} = \cos\theta \qquad d^{1/2}_{1/2,1/2} = \cos\frac{\theta}{2} \qquad d^{1/2}_{1/2,-1/2} = -\sin\frac{\theta}{2}$$

$$d^1_{1,1} = \frac{1+\cos\theta}{2} \qquad d^1_{1,0} = -\frac{\sin\theta}{\sqrt{2}} \qquad d^1_{1,-1} = \frac{1-\cos\theta}{2}$$

$$d^{3/2}_{3/2,3/2} = \frac{1+\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{3/2,1/2} = -\sqrt{3}\frac{1+\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{3/2}_{3/2,-1/2} = \sqrt{3}\frac{1-\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{3/2,-3/2} = -\frac{1-\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{3/2}_{1/2,1/2} = \frac{3\cos\theta-1}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{1/2,-1/2} = -\frac{3\cos\theta+1}{2}\sin\frac{\theta}{2}$$

$$d^2_{2,2} = \left(\frac{1+\cos\theta}{2}\right)^2$$

$$d^2_{2,1} = -\frac{1+\cos\theta}{2}\sin\theta$$

$$d^2_{2,0} = \frac{\sqrt{6}}{4}\sin^2\theta$$

$$d^2_{2,-1} = -\frac{1-\cos\theta}{2}\sin\theta$$

$$d^2_{2,-2} = \left(\frac{1-\cos\theta}{2}\right)^2$$

$$d^2_{1,1} = \frac{1+\cos\theta}{2}(2\cos\theta-1)$$

$$d^2_{1,0} = -\sqrt{\frac{3}{2}}\sin\theta\cos\theta$$

$$d^2_{1,-1} = \frac{1-\cos\theta}{2}(2\cos\theta+1) \qquad d^2_{0,0} = \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

Figure 36.1: The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974).

Basics (cont.)

⇒ Use of the Clebsh-Gordon coefficients allows us to relate the two sets of kets (see attached table)

→ If calculating by hand, equate states of degenerecy 1 (ie max/min J) and use ladder operators

Tensor Operators

* For Cartesian tensors, we know they rotate as:

Rank 1 - $V_i' = R_{ij} V_j$

2 - $W = \tilde{R}' \tilde{R} V_i U_j$

* Remember we define our Rotation operator $R(\alpha, \beta, \gamma)$ as:

$$R(\alpha,\beta,\gamma)\,|j,m\rangle = \sum_{j'm'} |j',m'\rangle\langle j',m'|R(\alpha,\beta,\gamma)|j,m\rangle$$
$$= \mathcal{D}^{(j)}_{m,m'}\,|j',m'\rangle \quad \text{where } j=j' \text{ so } J=\text{const.}$$

⇒ Comparing this to our classical picture, we see:

$$\langle\alpha|V_i|\alpha\rangle \longrightarrow \langle\alpha|\mathcal{D}^{+}(R)\,V\,\mathcal{D}^{*}(R)|\alpha\rangle = \sum_{ij} R_i R_j \langle\alpha|V_j|\alpha\rangle$$
$$\text{where } \mathcal{D}(R) = \exp\left[\tfrac{i}{\hbar}(J\cdot\hat{n})\delta\varphi\right]$$

$$\hookrightarrow \sum_j R_{ij} V_j = \mathcal{D}^{+}(R)\,V_i\,\mathcal{D}(R)\,, \quad \mathcal{D}$$

* Applying our infinitesimal operator, we see

$$V_i' = V_i + \frac{\epsilon}{i\hbar}[V_i, J\cdot\hat{n}] = \sum_j R_{ij}(\hat{n},\epsilon)\,V_j$$

which allows us to deduce the commutation relation

$$[V_i, J_j] = i\,\epsilon_{ijk}\hbar\,V_k$$

Tensor Operators (cont.)

* A closer examination of rank two tensors reveals they can be decomposed as follows:

$$U_iV_j = \underbrace{\frac{U\cdot V}{3}\delta_{ij}}_{\text{scalar}} + \underbrace{\frac{U_iV_j - U_jV_i}{2}}_{\text{anti-symmetric tensor}} + \underbrace{\left(\frac{U_iV_j + U_jV_i}{2} - \frac{U\cdot V}{3}\delta_{ij}\right)}_{\text{traceless symmetric tensor}}$$

1 3 5

⇒ The circled #'s represent the number of independent per term, which happen to match the multiplicity of states for $l = 0, 1, 2$ respectively

↳ Replacing $\hat{n}$ by $\vec{V}$ in our definition of spherical tensors, we see:

$$T_q^{(k)} = Y_{l=k}^{m=q}(\vec{V})$$

ex. $Y_1^0 = T_0^{(1)} = \sqrt{\frac{3}{4}}\cos\theta = \sqrt{\frac{3}{4}}V_z$

$$Y_1^{\pm 1} = T_{\pm 1}^{(1)} = \sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\cos\theta = \sqrt{\frac{3}{2\pi}}V_x \pm iV_y$$

⇒ To derive transformation properties we return to our definition of the spherical harmonics

$$Y_l^m(\hat{n}) = \langle \hat{n} | l, m\rangle$$

* Remembering $|n'\rangle = \mathcal{D}(R)|n\rangle \Leftrightarrow \langle n'| = \langle n|\mathcal{D}(R^{-1})$, we our ang. mom. kets will transform as:

$$\mathcal{D}(R^{-1})|l,m\rangle = \sum_{m'} |l,m'\rangle\langle l,m'|\mathcal{D}(R^{-1})|l,m\rangle$$

$$= \sum_{m'} |l,m'\rangle \mathcal{D}_{mm'}^{(l)}(R^{-1})$$

* Applyin $\langle n|$ to both sides of the equation

$$\langle n|\mathcal{D}(R^{-1})|l,m\rangle = \sum_{m'} \langle n|l,m'\rangle \mathcal{D}_{mm'}^{(l)}(R^{-1})$$

$$\langle n'|l,m\rangle = \sum_{m'} Y_l^{m'}(n)\mathcal{D}_{mm'}^{(l)}(R^{-1})$$

$$Y_l^m(n') = \sum_{m'} Y_l^{m'}(n)\mathcal{D}_{mm'}^{(l)}(R^{-1})$$

⇒

Tensor Operators (cont.)

* Switching to operator formulations:

$$\mathcal{D}^{+}(R)\, Y_\ell^m(V)\, \mathcal{D}(R) = \sum_{m'} Y_\ell^{m'}(V) \left[\mathcal{D}^{(\ell)}_{mm'}(R)\right]^*$$

* And finally moving to tensor notation:

$$\mathcal{D}^{+}(R)\, T_q^{(k)}\, \mathcal{D}(R) = \sum_{q'} T_{q'}^{(k)} \left[\mathcal{D}^{(k)}_{qq'}(R)\right]^*$$

* Applying this equation to an infinitesimal rotation:

$$[J\cdot n, T_q^{(k)}] = \sum_{q'} T_{q'}^{(k)} \langle kq' | J\cdot n | kq \rangle$$

⇒ Evaluating the above in the z, and $\pm$ directions yields:

$$[J_z, T_q^{(k)}] = \hbar q\, T_q^{(k)}$$

$$[J_\pm, T_q^{(k)}] = \hbar \sqrt{(k \mp q)(k \pm q + 1)}\, T_{q\pm 1}^{(k)}$$

* We have a theorem that defines spherical tensors in terms of Cartesian tensors by:

$$T_q^{(k)} = \sum_{q_1} \sum_{q_2} \underbrace{\langle k_1 k_2; q_1 q_2 | k_1 k_2; kq \rangle}_{\text{CG Coefficient}}\, X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)}$$

← irreducible spherical tensors

⇒ To show the above transforms as a spherical tensor:

$$\mathcal{D}^{+}(R)\, T_q^{(k)}\, \mathcal{D}(R) = \sum_{q_1} \sum_{q_2} \langle k_1 k_2; q_1 q_2 | k_1 k_2; kq \rangle\, \mathcal{D}^{+}(R) X_{q_1}^{(k_1)} \mathcal{D}(R)\, \mathcal{D}^{+}(R) Z_{q_2}^{(k_2)} \mathcal{D}(R)$$

$$= \sum_{q_1} \sum_{q_2} \sum_{q_1'} \sum_{q_2'} \langle k_1 k_2; q_1 q_2 | k_1 k_2; kq \rangle\, X_{q_1'}^{(k_1)} \left[\mathcal{D}^{(k_1)}_{q_1 q_1'}(R)\right]^* Z_{q_2'}^{(k_2)} \left[\mathcal{D}^{(k_2)}_{q_2 q_2'}(R)\right]^*$$

* using $\mathcal{D}^{(j_1)}_{m_1 m_1'}(R)\, \mathcal{D}^{(j_2)}_{m_2 m_2'}(R) = \sum_j \sum_m \sum_{m'} \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle \langle j_1 j_2; m_1' m_2' | j_1 j_2; jm' \rangle\, \mathcal{D}^{(j)}_{mm'}(R)$

$$= \sum_{k''} \sum_{q_1} \sum_{q_2} \sum_{q_1'} \sum_{q_2'} \sum_{q''} \sum_{q'} \langle k_1 k_2; q_1 q_2 | k_1 k_2; kq \rangle \langle k_1 k_2; q_1 q_2 | k_1 k_2; k'' q' \rangle$$
$$\langle k_1 k_2; q_1 q_2 | k_1 k_2; k'', q'' \rangle \left[\mathcal{D}_{q' q''}(R)\right]^* X_{q_1'}^{k_1} Z_{q_2'}^{k_2}$$

$$= \sum_{q'} T_{q'}^{(k)} \left[\mathcal{D}^{(k)}_{qq'}(R)\right]^*$$

Tensor Operators (cont.)

* We determine the matrix elements of a spherical tensor via the Wigner-Eckart Theorem

⇒ Starting w/ $[J_\pm, T_q^{(k)}] = \hbar\sqrt{(k\mp q)(k\pm q+1)}\, T_{q\pm1}^{(k)}$

$$\langle \alpha', j' m' | [J_\pm, T_q^{(k)}] - \hbar\sqrt{(k\mp q)(k\pm q+1)} | \alpha, j, m\rangle = 0$$

⇒ Switching to $[J_z, T_q^{(k)}] = \hbar q\, T_q^{(k)}$

$$\langle \alpha', j', m' | J_z T_q^{(k)} - T_q^{(k)} J_z - \hbar q\, T_q^{(k)} | \alpha, j, m\rangle = 0$$

$$\langle \alpha', j', m' | m' T_q^{(k)} - T_q^{(k)} m - q\, T_q^{(k)} | \alpha, j, m\rangle = 0$$

⇒ $m' = m + q$ where q is angular momentum added to system by the spherical tensor

⇒ We apply the Wigner-Eckart Thm by noting $\langle \alpha', j' m' | T_q^{(k)} | \alpha, j, m\rangle$ can be written in terms of a CG coefficient and a reduced matrix element

$$\langle \alpha'; j', m' | T_q^{(k)} | \alpha; j, m\rangle = \langle j, k; m, q | j, k; j' m'\rangle \frac{1}{\sqrt{2j+1}} \langle \alpha', j' \| T_q^{(k)} | \alpha, j\rangle$$

* Our general approach is to calculate reduced matrix element in a simple case then use that # in our situation of interest

ex.

$$\langle 3,0 | T_0^{(2)} | 1,0\rangle = \langle 1,2; 0 0 | 1,2, 1,0\rangle \langle 3 \| T^{(2)} \| 1\rangle$$

$$\int Y_3^0(\theta,\varphi)\, Y_2^0(\theta,\varphi)\, Y_1^0(\theta,\varphi)\, d\Omega = \langle 1,2; 00 | 1,2; 1,0\rangle \langle 3 \| T^{(2)} \| 1\rangle$$

$$\Rightarrow \langle 3 \| T^{(2)} \| 1\rangle = \sqrt{\tfrac{3}{4\pi}}$$

Perturbation Theory

* We only consider time-independent, non-degenerate cases for this exam

* Perturbation theory is an approximation technique that allows us to solve non-idealized problems in quantum mechanics and other fields

* For a given Hamiltonian H, we write it as

$$H = H_0 + V \quad , \text{ where we know the solutions for } H_0 \text{ but not } V$$

$$H = E_1^{(0)} |1^{(0)}\rangle\langle 1^{(0)}| + E_2^{(0)} |2^{(0)}\rangle\langle 2^{(0)}| + \lambda V_{12} |1^{(0)}\rangle\langle 2^{(0)}| + \lambda V_{21} |2^{(0)}\rangle\langle 1^{(0)}|$$

$$\doteq \begin{bmatrix} E_1^{(0)} & \lambda V_{12} \\ \lambda V_{21} & E_2^{(0)} \end{bmatrix} ; \quad V_{21} = V_{12}, \quad V_{12}, V_{21} \in \mathbb{R} \text{ for Hermiticity}$$

$\Rightarrow$ Thru normal matrix methods we see:

$$E_1 = \tfrac{1}{2}(E_1 + E_2) + \sqrt{\tfrac{1}{4}(E_1 - E_2) + \lambda^2 V_{12}^2}$$

$$E_2 = \tfrac{1}{2}(E_1 + E_2) - \sqrt{\tfrac{1}{4}(E_1 - E_2) + \lambda^2 V_{12}^2}$$

* However, if we are unable to solve the problem exactly, we proceed as follows:

$\Rightarrow$ We know: $H_0 |n\rangle = E_n^{(0)} |n\rangle$

$$(H_0 + \lambda V)|n\rangle = E_n |n\rangle$$

$\Rightarrow$ Introducing $\Delta_n = E_n - E_n^{(0)}$

$$\hookrightarrow \quad E_n^{(0)} - H_0 |n\rangle = \lambda V - \Delta_n |n\rangle$$

$$\langle n^{(0)}| E_n^{(0)} - H_0 |n\rangle = \langle n^{(0)}| \lambda V - \Delta_n |n\rangle$$

$$0 = \langle n^{(0)}| \lambda V - \Delta_n |n\rangle$$

* Defining a projection operator $\varphi_n = \mathbb{I} - |n^{(0)}\rangle\langle n^{(0)}|$

$$= \sum_{k \neq n}' |k^{(0)}\rangle\langle k^{(0)}|$$

$$\Rightarrow |n\rangle = \frac{1}{E_n^{(0)} - H_0} \varphi_n (\lambda V - \Delta_n)|n\rangle$$

* but as $\lambda \to 0$, we must approach $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$

Perturbation Theory (cont.)

$\Rightarrow$ We ~~redefine~~ $|n\rangle$ as:

$$|n\rangle = c_n(\lambda)|n_0\rangle + \frac{1}{E_n^{(0)} - H_0}\varphi_n(\lambda V - \Delta_n)|n\rangle \; ; \; C_n(\lambda) = \langle n^0|n\rangle$$

*Note: We choose $\langle n^{(0)}|n\rangle = 1$, therefore we most always normalize $|n\rangle$ after solving for it

$$\hookrightarrow \boxed{|n\rangle = |n_0\rangle + \frac{1}{E_n^{(1)} - H_0}\varphi_n(\lambda V - \Delta_n)|n\rangle}$$

*We extract the value of Δ_n by multiplying both sides by $\langle n^{(0)}|$

$$\boxed{\Delta_n = \lambda\langle n^{(0)}|V|n\rangle}$$

* Expanding $|n\rangle$ and Δ_n as power series:

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots$$

$$\Delta_n = \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \ldots$$

* Substituting the above into the above boxed equations yields the corrections after matching in powers of λ:

$$\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$$

$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle \quad \Rightarrow \sum_{k\neq n}' \frac{|V_{nk}|^2}{(E_n^{(0)} - E_k^{(0)})^2}$$

$$|n^{(1)}\rangle = \frac{1}{E_n^{(0)} - H_0}\varphi_n|n^{(0)}\rangle$$

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

Quantum II Exam III Study Guide

Basics

$|\alpha\rangle = \sum_i' c_i |a_i\rangle$ and $A|\alpha\rangle = a_i|\alpha\rangle$ (Definition of a ket)

$A = |a\rangle\langle b|$ (Definition of an operator)

$\sum_i' \Lambda_i = \sum_i' |a_i\rangle\langle a_i| = 1$ (Projection Operator/Completeness Relation)

* To get the matrix elements of an operator:

$$A \rightarrow \sum_{mn}' |m\rangle\langle m|A|n\rangle\langle n|$$

$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$ (Schwartz Inequality)

$\langle\alpha|A|\alpha\rangle = \langle A\rangle$ (Expectation Value)

$\Delta A = A - \langle A\rangle \mathbb{I}$ (Dispersion Operator)

$\langle(\Delta A)^2\rangle = \langle A^2\rangle - \langle A\rangle^2$ (Avg value or RMS)

$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$ (Uncertainty Relation)

* Important commutation relations include:

$[x_i, x_j] = [p_i, p_j] = 0$

$[x_i, p_j] = i\hbar\delta_{ij}$

$[x, F(p)] = i\hbar \frac{\partial F}{\partial p}$

$[p, G(x)] = i\hbar \frac{\partial G}{\partial x}$

$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$; $\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$, $\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$; $S_i = \frac{\hbar}{2}\sigma_i$

$\hookrightarrow [\sigma_i, \sigma_j] = \sigma_k$

$[A, H] = -i\hbar \frac{\partial A}{\partial t}$ (Heisenberg Eqn of Motion)

* For functions of continuous variables

$\psi_a(x') = \langle x'|a\rangle$

$\phi_b(p') = \langle p'|b\rangle$

$\langle\beta|\alpha\rangle = \int dx'\, \psi_\beta^*(x')\psi_a(x')$

$= \int dp'\, \phi_\beta^*(p')\phi_a(p')$

$p = i\hbar\, \partial/\partial x$

$\langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{i}{\hbar}p'x'\right]$

Basics (cont.)

* Remember, for angular momentum:

  $J \rightarrow$ Arbitrary Angular Momentum (usually refers to total)

  $L \rightarrow$ Orbital Angular Momentum

  $S \rightarrow$ Spin Angular Momentum

* Important angular momentum formulas include:

$$J^2 = J \cdot J = J_x^2 + J_y^2 + J_z^2 \qquad J_\pm = J_x \pm i J_y$$

$$[J^2, J_i] = 0 \qquad [J^2, J_\pm] = 0 = [J_z, J_\pm]$$

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k \qquad [J_+, J_-] = 2\hbar J_z$$

$\Rightarrow$ We often write simultaneous eigenkets of J^2, J_z as $|a, b\rangle$ such that:

$$J^2 |a, b\rangle = a|a, b\rangle \qquad J_\pm |a, b\rangle = \hbar\sqrt{(j \mp m)(j \pm m+1)}\,|a, b+\hbar\rangle$$

$$J_z |a, b\rangle = b|a, b\rangle \qquad J_\pm^n |a, b\rangle = b \pm n\hbar\,|a, b+n\hbar\rangle$$

* When adding angular momentum, it is useful to use direct product notation:

$$|S_1, S_{1z}; S_2, S_{2z}\rangle = |S_1, S_{1z}\rangle \otimes |S_2, S_{2z}\rangle$$

$\Rightarrow$ Our total system operators now become:

$$J = J_1 + J_2 = J_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes J_2$$

$$J^2 = (J_1 + J_2) \cdot (J_1 + J_2) = J_1^2 + J_2^2 + 2 J_1 \cdot J_2$$

$$= J_{1z} + J_{2z} + \tfrac{1}{2}(J_{1+} J_{2-} + J_{1-} J_{2+})$$

* This flexibility allows us to use two sets of kets to describe the system:

$$|j_1, j_2; m_1, m_2\rangle \Longleftrightarrow |j_1, j_2; j, m\rangle$$

$$[J_1^2, J_2^2] = 0 = [J_{1z}, J_{2z}] = [J_{1i}, J_{2k}]$$

* Use of Clebsh-Gordon coefficients allows us to relate the two sets of kets to one another (see table)

  $\hookrightarrow$ If calculating by hand, equate states of degeneracy 1 (ie max or min J) and use ladder operators

Basics (cont.)

*Remember that we define tensor operators as follows:

$$T_q^{(k)} = Y_{\ell=k}^{m=q}(\vec{V}) \quad \text{where } \vec{V} \text{ is a normal cartesian vector}$$

ex. $Y_1^0 = T_0^{(1)} = \sqrt{\frac{3}{4}}\cos\Theta = \sqrt{\frac{3}{4}}\, V_z$

$$Y_1^{\pm 1} = T_{\pm 1}^{1} = \sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\cos\Theta = \sqrt{\frac{3}{2\pi}}\, V_x \pm iV_y$$

*Spherical Tensors / Tensor Operators have the following properties:

$$Y_\ell^m(\hat{n}) = \langle \hat{n} | \ell, m \rangle$$

$$Y_\ell^m(n') = \sum_{m'} Y_\ell^{m'}(n)\,\mathcal{D}_{mm'}^{(\ell)}(R^{-1}), \quad \text{where } R \text{ is the rotation operator}$$

$$\hookrightarrow \mathcal{D}_{mm'}^{(j)} |j',m'\rangle = \sum_{j',m'} |j',m'\rangle \langle j',m'| R(\alpha,\beta,\gamma) |j,m\rangle$$

⇒ The transformation properties are as follows:

$$\mathcal{D}^{+}(R)\, Y_\ell^m(\vec{v})\,\mathcal{D}(R) = \sum_{m'} Y_\ell^{m'}(V)\left[D_{mm'}^{(\ell)}(R)\right]^*$$

$$\mathcal{D}^{+}(R)\, T_q^{(k)}\,\mathcal{D}(R) = \sum_{q'} T_{q'}^{(k)}\left[D_{qq'}^{(k)}(R)\right]^*$$

⇒ The above properties yield the following commutators:

$$[J_z, T_q^{(k)}] = \hbar q\, T_q^{(k)}$$

$$[J_\pm, T_q^{(k)}] = \hbar\sqrt{(k\mp q)(k\pm q+1)}\; T_{q\pm 1}^{(k)}$$

⇒ The theorem that defines spherical tensors in terms of Cartesian tensors is:

$$T_q^{(k)} = \sum_{q_1}\sum_{q_2} \langle k_1 k_2; q_1 q_2 | k_1 k_2; k, q\rangle\, X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)} \quad \text{irreducable spherical tensors}$$

⇒ The matrix elements of a spherical tensor are given by the Wigner-Eckart Thm:

reduced matrix element

$$\langle \alpha'; j', m' | T_q^{(k)} | \alpha; j, m\rangle = \langle j, k; m, q | j, k; j', m'\rangle \frac{1}{\sqrt{2j+1}} \langle \alpha'; j' || T_q^{(k)} || \alpha, j\rangle$$

*for $m' = m + q$

<u>ex.</u> $\langle 3,0 | T_0^{(2)} | 1,0\rangle = \langle 1,2; 0,0 | 1,2; 1,0\rangle \langle 3 || T^{(2)} || 1\rangle$

$$\int Y_3^0(\theta,\varphi)\, Y_2^0(\theta,\varphi)\, Y_1^0(\theta,\varphi)\, d\Omega = \langle 1,2; 0 0 | 1,2; 1,0\rangle \langle 3 || T^{(2)} || 1\rangle$$

$$\hookrightarrow \langle 3 || T^{(2)} || 1\rangle = \sqrt{\frac{3}{4\pi}}$$

Bases (cont.)

* For time-independent, non-degenerate perturbation theory, the key eqn's are:

$$|n\rangle = |n^{(0)}\rangle + \frac{1}{E_n^{(0)} - H_0} \varphi_n (\lambda V - \Delta_n)|n\rangle$$

$$\Delta_n = \lambda \langle n^{(0)}|V|n\rangle$$

⇒ Expanding the above as power series, we find that:

$$\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$$

$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle$$

$$= \sum_{k\neq n}' \frac{|V_{nk}|^2}{(E_n^{(1)} - E_k^{(0)})}$$

$$|n^{(1)}\rangle = \frac{1}{E_n^{(0)} - H_0} \varphi_n |n^{(0)}\rangle$$

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

⇒ Remember, perturbation theory is simply an approximation schemes that cannot be easily solved exactly, but are close to a problem that can. Many problems can be easily solved by diagnolizing the Hamiltonian as normal.

Time-Independent Perturbation Theory (Degenerate Case)

* Put simply, we need to diagonalize the degenerate submatrix however we can

⇒ For our degenerate energies, our eigenkets become:

$$|l^{(0)}\rangle = \sum_{m\in D}' |m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle$$

⇒ To solve the eigenvalue eqn ($H = H_0 + V$)

$$(E - H_0 - V)|l\rangle = 0$$

↳ Isolate degenerate + non-degenerate states w/ projection operators:

$$\tilde{P}_0 = \sum_{k\in D}' |k^{(0)}\rangle\langle k^{(0)}| \qquad \tilde{P}_1 = \sum_{k\notin D}' |k^{(0)}\rangle\langle k^{(0)}| = \tilde{\mathbb{I}} - \tilde{P}_0$$

Degenerate Perturbation Theory (cont.)

$\Rightarrow$ Rewrite eigenvalue equation as:

$$(E - H_0 - \lambda V)P_0|\ell\rangle + (E - H_0 - \lambda V)P_1|\ell\rangle = 0$$

* Applying our projection operators to above yield:

① $(E - H_0 - \lambda V)P_0^2|\ell\rangle + (E - H_0 - \lambda V)P_0P_1|\ell\rangle = 0$

* using $P_0P_0 = P_0 \qquad P_0P_1 = 0$

$$(E - E_D^{(0)} - \lambda P_0V)P_0|\ell\rangle - \lambda P_0VP_1|\ell\rangle = 0$$

② $-\lambda P_1VP_0|\ell\rangle + (E - H_0 - \lambda P_1V)P_1|\ell\rangle = 0$

* Solving the above system of equations yields:

$$|\ell\rangle = \lambda[E - H_0 - \lambda P_1VP_1]^{-1} P_1VP_0|\ell\rangle$$

$$\hookrightarrow P_1|\ell\rangle = \tilde{P}_1 \frac{\lambda}{E - H_0 - \lambda P_1VP_1} P_1VP_0|\ell\rangle$$

* expanding $|\ell\rangle$ as a power series and $\frac{1}{E-H_0-\lambda P_1VP_1} \approx \frac{1}{E-H_0} + \frac{\lambda P_1VP_1}{(E-H_0)^2} + \dots$

$$\Rightarrow \boxed{P_1|\ell^{(1)}\rangle = \sum_{k \notin D} \frac{V_{k\ell}}{E_D^{(0)} - E_k^{(0)}} |k^{(0)}\rangle}$$

ex. Linear Stark Effect

* Our physical set-up is a hydrogen-like atom in a uniform $\vec{E}$-field

$\Rightarrow V = -ezE_0$; $n = N + \ell + 1$ where $n \in \mathbb{Z}^+$, $\ell \in [0, n-1]$, $N \in \{0, \mathbb{Z}^+\}$

$\hookrightarrow H|n\ell m\rangle = E_n|n\ell m\rangle$

$L^2|n\ell m\rangle = \ell(\ell+1)\hbar^2|n\ell m\rangle$

$L_z|n\ell m\rangle = m\hbar|n\ell m\rangle$

$\tilde{\Pi}|n\ell m\rangle = (-1)^\ell|n\ell m\rangle$ (Parity Operator)

* Remember, in terms of spherical tensors: $z = \hat{T}_0^{(1)}$

$\Rightarrow \langle n, \ell', m'|T_0^{(1)}|n\ell m\rangle \longrightarrow m = m'$ b/c no addition of z ang. mom

$\ell' \in [\ell+1, |\ell-1|]$

Degenerate Perturbation Theory (cont.)

* Notice that: $\Pi^{\dagger} z \Pi = -z$

$\hookrightarrow \langle odd | z | even \rangle = \langle odd | \Pi^{\dagger}\Pi z \Pi^{\dagger}\Pi | even \rangle$
$= \langle odd | z | even \rangle$

$\langle odd | z | odd \rangle = -\langle odd | z | odd \rangle$
$\langle even | z | even \rangle = -\langle even | z | even \rangle$ > must equal 0

* From this we see $l' = l \pm 1$ and that we can now write the interaction matrix

$\Rightarrow$ For $n=2$, $l = 0, 1$

$$V = \begin{bmatrix} 0 & \langle 2,0,0|V|2,1,0\rangle \\ \langle 2,1,0|V|2,0,0\rangle & 0 \end{bmatrix} = \begin{bmatrix} 0 & 3ea_0E_0 \\ 3ea_0E_0 & 0 \end{bmatrix}$$

$\hookrightarrow$ via diagonalization:

$|+\rangle = \frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle) \quad \Delta_+^{(1)} = 3e\,a_0E_0$

$|-\rangle = \frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle) \quad \Delta_-^{(1)} = -3ea_0E_0$

$\Rightarrow$ Further corrections to the hydrogen atom from perturbation theory include:

① "Relativistic Correction"

$E = \sqrt{(pc)^2 + m^2c^4}$

$T = \sqrt{(pc)^2 + m^2c^4} - m_ec^2$

$= mc^2\left(1 + \frac{pc^2}{m^2c^4}\right)^{1/2} - m_ec^2$

$\hookrightarrow T \approx \frac{p^2}{2m} - \frac{p^4}{8m_e^3c^2}$ ← becomes interaction term in perturbed Hamiltonian

$\Rightarrow H = \frac{p^2}{2m} - \frac{e^2}{r} - \frac{p^4}{8m_e^3c^2}$

* But notice $[L, p^2] = 0$, so we proceed via non-degenerate P.T b/c we are unable to break the degeneracy

Degenerate Perturbation Theory (cont.)

$$\Rightarrow \Delta_{n\ell}^{(1)} = \langle n\ell m | \frac{-p^4}{8m_e^3c^2} | n\ell m \rangle$$

$$* \text{but } \frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = \frac{p^4}{8m_e^3c^2} = \frac{1}{2mc^2}\left(H_0 + \frac{e^2}{r}\right)^2$$

$$= \left[\langle n\ell m | \frac{e^4}{r^2} | n\ell m \rangle + 2E_n^{(0)} \langle n\ell m | \frac{e^2}{r} | n\ell m \rangle + (E_n^{(0)})^2\right] \frac{1}{2mc^2}$$

$$= \frac{-1}{2} mc^2 \alpha^4 \left(\frac{-3}{4n^2} - \frac{1}{n^3(\ell+\frac{1}{2})}\right)$$

$$= \frac{-mc^2\alpha^2}{2n^2}\left(\alpha^2\left[\frac{-3}{4} + \frac{1}{n(\ell+\frac{1}{2})}\right]\right)$$

② Spin-Orbit Coupling

$$\vec{B} = \frac{-v}{c} \times E, \quad \vec{\mu} = \frac{e\vec{S}}{m_e c} \quad (\vec{S} = \text{spin vector})$$

$$H_{LS} = -\vec{\mu}\cdot\vec{B}$$
$$= \mu \cdot \left(\frac{v}{c} \times E\right)$$
$$= \frac{e\vec{S}}{m_e c}\cdot\left(\frac{v}{c} \times \frac{\vec{r}}{r}\frac{dV_c}{dr}\left(\frac{-1}{e}\right)\right) \quad * \text{Note } V_c \text{ is for central potential}$$
$$= \frac{eS}{m_e c}\cdot\left[\frac{p}{m_e c} \times \frac{\vec{r}}{r}\frac{dV}{dr}\left(\frac{-1}{e}\right)\right]$$
$$= \frac{1}{m_e^2c^2 r}\frac{dV_c}{dr}\vec{L}\cdot\vec{S}$$

*Note: We can rewrite $L\cdot S \Rightarrow J^2 = (L+S)^2$

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

*Introducing the spin-angular functions

$$\mathcal{Y}_\ell^{j=\ell\pm 1/2} = \frac{1}{\sqrt{2\ell+1}}\begin{bmatrix} \pm\sqrt{\ell \pm m + 1/2}\; Y_\ell^{m-1/2}(\theta,\varphi) \\ \sqrt{\ell \mp m + 1/2}\; Y_\ell^{m+1/2}(\theta,\varphi)\end{bmatrix} \quad * \text{Note: } m = m_\ell + m_s$$

$= (\ )Y_\ell^m \chi^+ + (\ )Y_\ell^m \chi^-$, where $\chi^\pm$ are spinor states

$$\Rightarrow \Delta_{n\ell}^{(1)} = \frac{1}{2m_e^2c^2}\left\langle \frac{1}{r}\frac{dV_c}{dr}\right\rangle_{n\ell} \frac{\hbar}{2}\begin{Bmatrix} \ell \\ -\ell+1 \end{Bmatrix} \begin{matrix}\text{for } j = \ell + 1/2 \\ = \ell - 1/2\end{matrix} \quad (\text{choose } |j)$$

where $\frac{1}{2}\int \mathcal{Y}^*(J^2 - L^2 - S^2)\mathcal{Y}\, d\Omega = \frac{\hbar^2}{2}[j(j+1) - \ell(\ell+1) - s(s+1)]\,(\ )$
is used in expectation value calculation

$$\Rightarrow \text{In H-atom: } V_c = \frac{e^2}{r} \Rightarrow \left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle = \left\langle \frac{e^2}{r^3}\right\rangle$$

(via hyper-confluent geometric functions)

$$= \frac{-2m_e^2e^2\alpha^2}{n\,\ell(\ell+1)(\ell+\frac{1}{2})\hbar^2} E_n^{(0)}$$

Time-Dependent Perturbation Theory

* Now we assume time-dependent $H = H_0 + V(t)$
  $\Rightarrow$ Normal time evolution operator $U(t, t_0) = \exp[\frac{-i}{\hbar} H t]$ only works when H is time-independent

$\Rightarrow$ We must develop the interaction picture

$$|\alpha\rangle = \sum_n c(0)|n\rangle \; ; \quad C(0) = \langle n|\alpha\rangle|_{t=0}$$

$$|\alpha, t_0=0; t\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar}|n\rangle \rightarrow c_n(t) \text{ only associated w/ } V$$

$\hookrightarrow c_n \rightarrow 0$ yields normal evolution

$$\Rightarrow |\alpha, t_0; t\rangle_I = e^{iH_0 t/\hbar}|\alpha, t_0; t\rangle_S$$ (time evolve only unperturbed Hamiltonian)

* Operators will transform as: $\tilde{A}_I = e^{iH_0 t/\hbar} A_S e^{-iH_0 t/\hbar}$

$$\Rightarrow i\hbar \frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = i\hbar \frac{\partial}{\partial t}\left(e^{iH_0 t/\hbar}|\alpha, t_0, t\rangle_S\right)$$

$$= i\hbar \frac{H_0}{-i\hbar} e^{iH_0 t/\hbar}|\alpha, t_0; t\rangle_S + i\hbar e^{iH_0 t/\hbar}\left(\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_S\right)$$

$$= \tilde{H}_0 e^{iH_0 t/\hbar}|\alpha, t_0; t\rangle_S + e^{iH_0 t/\hbar}[H_0 + V(t)]|\alpha, t_0, t\rangle_S$$

$$= e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} e^{iH_0 t/\hbar}|\alpha, t_0; t\rangle_S$$

$$i\hbar \frac{\partial}{\partial t}|\alpha, t_0; t\rangle = \tilde{V}_I(t)|\alpha, t_0; t\rangle_I$$

* we convert above equation to a # by multiplying both sides by $\langle n|$

$$\Rightarrow i\hbar \frac{\partial}{\partial t}\langle n|\alpha, t_0; t\rangle_I = \langle n| V_I(t)|\alpha, t_0; t\rangle_I$$

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_m \langle n|V_I(t)|m\rangle\langle m|\alpha, t_0, t\rangle_I$$

$$= \sum_m V_{nm} c_m(t) e^{i\omega_{nm} t}$$

* We now develop the above in terms of perturbation theory by expanding c_n such that:

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \ldots$$

Time-Dependent P.T. (cont.)

ex. Exact Solution to a 2-state problem

$$H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2|, \quad E_2 > E_1$$
$$V(t) = \gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1|$$
$$> H \doteq \begin{bmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & E_2 \end{bmatrix}$$

* this system generates the following differential equations

$$i\hbar \frac{d}{dt}(c_1(t)) = V_{12}(t)\, e^{-i(E_2 - E_1)t/\hbar} c_2(t)$$
$$i\hbar \frac{d}{dt}[c_2(t)] = V_{21}(t)\, e^{+i(E_2 - E_1)t/\hbar} c_1(t)$$

* Assume $c_1(0) = 1$, $c_2(0) = 0$

⇒ we solve this set of eqns by taking a derivative of one equation + substituting it into the other equation, which yields:

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega - \omega_{21})^2} \sin^2\left[\left(\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}\right)^{1/2} t\right]$$

$$|c_1(t)|^2 = 1 - |c_2(t)|^2$$

* But realistically, we want to develop an approximation for the above problem

$$\Rightarrow i\hbar \frac{dc_n^{(j)}}{dt} = \sum_m V_{nm} e^{i\omega_{nm} t} c_m^{(j-1)}(t)$$

* Now we proceed to develop a proper time evolution operator

$$|\alpha, t_0, t\rangle_I = U_I(t, t_0)|\alpha, t_0; t_0\rangle_I$$

⇒ taking the time derivative yields:

$$i\hbar \frac{d}{dt}\left(U(t,t_0)|\alpha, t_0; t_0\rangle_I\right) = V_I U_I(t, t_0)\, |\alpha, t_0; t_0\rangle_I$$

$$i\hbar \frac{d}{dt}(U(t,t_0)) = V_I U_I(t,t_0)$$

$$\hookrightarrow U_I(t,t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t') U_I(t', t_0')\, dt'$$

* but since most problems aren't directly integerable, we approximate by:

$$U_I(t,t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')dt' + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' V_I(t'') V_I(t') + \dots$$

Time-Dependent P.T (cont.)

ex. Infinite Perturbatron

$$c_n^{(0)} = \delta_{in}$$

$$c_n^{(1)}(t) = \frac{-i}{\hbar}\int_{t_0}^{t} e^{-i\omega_{ni}t'} V_{ni}(t')\,dt' \; ; \quad \omega_{ni} = \omega_n - \omega_i \, , \quad E = \hbar\omega$$

⇒ Our initial state becomes

$$|i,0;t\rangle_I \approx |i\rangle + \sum_n{}' c_n^{(1)}(t)|n\rangle \, , \qquad V = \begin{cases} 0 & t<0 \\ V & t \geq 0 \end{cases}$$

*To solve for probability:

$$P(i\to n) = |c_n^{(1)}(t)|^2$$

$$\hookrightarrow c_n^{(1)}(t) = \frac{V_{ni}}{E_n - E_i}\left(1 - e^{i\omega_{ni}t}\right)$$

$$P(i\to n) = \left|\frac{V_{ni}}{E_n - E_i}\right|^2 \left(2 - 2\cos(\omega_{ni}t)\right)$$

$$= \left|\frac{V_{ni}}{E_n - E_i}\right|^2 \sin^2\left(\frac{(E_n - E_i)t}{2\hbar}\right)$$

⇒ In the case where $E_n \approx E_i$, we see:

$$\sin\left(\frac{(E_n - E_i)t}{2\hbar}\right) \longrightarrow \frac{(E_n - E_i)t}{2\hbar}$$

$$P \approx \left|\frac{V_{ni}}{E_n - E_i}\right|^2 \frac{(E_n - E_i)^2 t^2}{4\hbar^2}$$

$$\approx \frac{|V_{ni}|^2 t^2}{4\hbar^2}$$

Quantum II Final Exam Study Guide

Basics

$|\alpha\rangle = \sum_i' c_i |a_i\rangle$ and $A|\alpha\rangle = a_i|\alpha\rangle$ (Definition of a ket)

$A = |a\rangle\langle b|$ (Definition of an operator)

$\sum_i' \Lambda_i = \sum_i' |a_i\rangle\langle a_i| = 1$ (Projection Operator/Completeness Relation)

*To get the matrix elements of an operator:

$$A \rightarrow \sum_{m,n}' |m\rangle\langle m|A|n\rangle\langle n|$$

$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$ (Schwartz Inequality)

$\langle A\rangle = \langle\alpha|A|\alpha\rangle$ (Expectation Value)

$\Delta A = A - \langle A\rangle \mathbb{I}$ (Dispersion Operator)

$\hookrightarrow \langle(\Delta A)^2\rangle = \langle A^2\rangle - \langle A\rangle^2$ (Avg value or RMS)

$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2$ (Uncertainty Relation)

*Important Commutation relations include:

$[x_i, x_j] = 0 = [p_i, p_j]$

$[x_i, p_j] = i\hbar\delta_{ij}$

$[x, F(p)] = i\hbar \frac{\partial F}{\partial p}$

$[p, G(x)] = i\hbar \frac{\partial G}{\partial x}$

$[\sigma_i, \sigma_j] = \sigma_k$ where:

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

$[A, H] = -i\hbar \frac{\partial A}{\partial t}$ (Heisenberg Eqn of Motion)

*For functions of a continuous variable:

$\psi_a(x') = \langle x'|a\rangle$

$\varphi_b(p') = \langle p'|b\rangle$

$\langle\beta|\alpha\rangle = \int dx'\, \psi_\beta^*(x')\, \psi_\alpha(x')$

$= \int dp'\, \varphi_\beta^*(p')\, \varphi_\alpha(p')$

$p = i\hbar \partial/\partial x$

$\langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{i}{\hbar} p' \cdot x'\right]$

Basics (cont.)

* Remember, for angular momentum:

  $J \rightarrow$ Arbitrary Angular Momentum (usually refers to total)

  $L \rightarrow$ Orbital Angular Momentum

  $S \rightarrow$ Spin Angular Momentum

* Important angular momentum formulas include:

$$J^2 = J \cdot J = J_x^2 + J_y^2 + J_z^2 \qquad J_\pm = J_x \pm i J_y$$

$$[J^2, J_i] = 0 \qquad [J^2, J_\pm] = 0 = [J_z, J_\pm]$$

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k \qquad [J_+, J_-] = 2\hbar J_z$$

$\Rightarrow$ We often write simultaneous eigenkets of J^2, J_z as $|a,b\rangle$ such that:

$$J^2 |a,b\rangle = a|a,b\rangle \qquad J_\pm |a,b\rangle = \sqrt{(j \pm m+1)(j \mp m)}\,\hbar\, |a, b+\hbar\rangle$$

$$J_z |a,b\rangle = b|a,b\rangle \qquad J_\pm^n |a,b\rangle = (b \pm n\hbar)|a, b \pm n\hbar\rangle$$

* When adding angular momentum, it is useful to use direct product notation:

$$|S_1, S_{1z}; S_2, S_{2z}\rangle = |S_1, S_{1z}\rangle \otimes |S_2, S_{2z}\rangle$$

$\Rightarrow$ Our total system operators now become:

$$J = J_1 + J_2 = J_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes J_2$$

$$J^2 = (J_1 + J_2) \cdot (J_1 - J_2) = J_1^2 + J_2^2 + 2 J_1 \cdot J_2$$

$$= J_{1z} + J_{2z} + \tfrac{1}{2}(J_{1+} J_{2-} + J_{1-} J_{2+})$$

* This flexibility allows us to use two sets of kets to describe the system:

$$|j_1, j_2; m_1, m_2\rangle \Longleftrightarrow |j_1, j_2; j, m\rangle$$

$$[J_1^2, J_2^2] = [J_{1z}, J_{2z}] = [J_{1i}, J_{2j}] = 0$$

* Use of the Clebsh - Gordon coefficients allow us to relate the two sets of kets to one another (see table)

  ↳ If calculating by hand, equate states of degeneracy 1 (ie max or min J) and use ladder operators

Tensor Operators

* For Cartesian Tensors, we know they rotate like:

Rank 1 → $V_i' = R_{ij} V_j$

2 → $W = \tilde{R}' \hat{R}\, V_i U_j$

* Remember, we defined our rotation operator $R(\alpha,\beta,\gamma)$ as:

$$R(\alpha,\beta,\gamma)|j,m\rangle = \sum_{j',m'} |j',m'\rangle\langle j',m'|R(\alpha,\beta,\gamma)|j,m\rangle$$
$$= \mathcal{D}^{(j)}_{mm'}|j',m'\rangle \quad \text{where } j=j' \text{ so } \vec{J} = \text{const.}$$

⇒ Comparing this to our classical picture, we see:

$$\langle\alpha|V_i|\alpha\rangle \to \langle\alpha|\mathcal{D}^{+}(R)\,V\,\mathcal{D}(R)|\alpha\rangle = \sum_{ji} R_i R_j \langle\alpha|V|\alpha\rangle$$
$$\text{where } \mathcal{D}(R) = \exp\left[\tfrac{i}{\hbar}(J\cdot\hat{n})\,\delta\varphi\right]$$

↳ $\sum R_{ij} V_j = \mathcal{D}^{+}(R)\, V_i\, \mathcal{D}(R)$

* Applying our infinitesimal operator, we see

$$V_i' = V_i + \frac{\epsilon}{i\hbar}[V_i, \vec{J}\cdot\hat{n}] = \sum_j R_{ij}(\hat{n},\epsilon)\, V_j$$

which allows us to deduce the commutation relation:

$$[V_i, J_j] = i\hbar\,\epsilon_{ijk} V_k$$

* A closer examination of rank two tensors reveals they can be decomposed as follows:

$$U_i V_j = \underbrace{\frac{U\cdot V}{3}\delta_{ij}}_{\substack{\text{scalar}\\ 1}} + \underbrace{\frac{U_iV_j - U_jV_i}{2}}_{\substack{\text{anti-symmetric tensor}\\ 3}} + \underbrace{\left(\frac{U_iV_j + U_jV_i}{2} - \frac{U\cdot V}{3}\delta_{ij}\right)}_{\substack{\text{traceless symmetric tensor}\\ 5}}$$

⇒ The circled #'s represent the number of independent componets per term, which happen to match the multiplicity of states for $l = 0, 1, 2, \ldots$ respectively

↳ Replacing $\hat{n}$ by $\vec{v}$ in our definition of spherical tensors, we see:

$$T_q^{(k)} = Y_{l=k}^{m=q}(\vec{v})$$

ex. $Y_1^0 = \sqrt{\frac{3}{4}}\cos\theta = \sqrt{\frac{3}{4}}\, V_z$

$Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}}\, e^{\pm i\varphi}\cos\theta = \sqrt{\frac{3}{2\pi}}\, V_x \pm i V_y$

Tensor Operators (cont.)

* To derive the transformation properties, we return to our definition of the spherical harmonics

$$Y_\ell^m(\hat{n}) = \langle \hat{n} | \ell, m \rangle$$

⇒ Remembering $|n'\rangle = \mathcal{D}(R)|n\rangle \Leftrightarrow \langle n'| = \langle n| \mathcal{D}(R^{-1})$, we see our angular momentum kets transform as:

$$\mathcal{D}(R^{-1})|\ell, m\rangle = \sum_{m'} |\ell, m'\rangle\langle \ell, m'| \mathcal{D}(R^{-1})|\ell, m\rangle$$

$$= \sum_{m'} |\ell, m'\rangle \mathcal{D}_{mm'}^{(\ell)}(R^{-1})$$

* Applying $\langle n|$ to both sides of the equation

$$\langle n|\mathcal{D}(R^{-1})|\ell, m\rangle = \sum_{m'} \langle n|\ell, m'\rangle \mathcal{D}_{mm'}^{(\ell)}(R^{-1})$$

$$\langle n'|\ell, m\rangle = \sum_{m'} Y_\ell^{m'}(n) \mathcal{D}_{mm'}^{(\ell)}(R^{-1})$$

$$Y_\ell^m(n') = \sum_{m'} Y_\ell^{m'}(n) \mathcal{D}_{mm'}^{(\ell)}(R^{-1})$$

* Now switching to operator formulations:

$$\mathcal{D}^\dagger(R)\, Y_\ell^m(v)\, \mathcal{D}(R) = \sum_{m'} Y_\ell^{m'}(v) \left[\mathcal{D}_{mm'}^{(\ell)}(R)\right]^*$$

* Finally moving to tensor notation:

$$\mathcal{D}^\dagger(R)\, T_q^{(k)}\, \mathcal{D}(R) = \sum_{q'} T_{q'}^{(k)} \left[\mathcal{D}_{qq'}^{(k)}(R)\right]^*$$

* Applying this equation to an infinitesimal rotation:

$$[J\cdot n, T_q^{(k)}] = \sum_{q'} T_{q'}^{(k)} \langle k, q'| J\cdot n | k, q\rangle$$

⇒ Evaluating the above in the $z, \pm$ directions yields:

$$[J_z, T_q^{(k)}] = \hbar q T_q^{(k)}$$

$$[J_\pm, T_q^{(k)}] = \hbar \sqrt{(k \mp q)(k \pm q + 1)}\, T_{q\pm1}^{(k)}$$

* We have a theorem that defines spherical tensors in terms of Cartesian tensors:

$$T_q^{(k)} = \sum_{q_1} \sum_{q_2} \underbrace{\langle k_1, k_2; q_1, q_2 | k_1, k_2; k, q\rangle}_{\text{CG coefficient (from table)}} X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)} \quad \text{(irreducible spherical tensors)}$$

Tensor Operators (cont.)

↳ To show our above formula transforms as a spherical tensor:

$$\mathcal{D}^{+}(R)T_q^{(k)}\mathcal{D}(R) = \sum_{q_1 q_2} \langle k_1 k_2; q_1 q_2 | k_1 k_2; k, q\rangle \mathcal{D}^{+}(R) X_{q_1}^{(k_1)} \mathcal{D}(R)\mathcal{D}^{+}(R) Z_{q_2}^{(k_2)}\mathcal{D}(R)$$

$$= \sum_{q_1}\sum_{q_2}\sum_{q_1'}\sum_{q_2'} \langle k_1 k_2; q_1 q_2 | k_1 k_2; k q\rangle X_{q_1'}^{(k_1)}\left[\mathcal{D}_{q_1 q_1'}^{(k_1)}(R)\right]^* Z_{q_2'}^{(k_2)}\left[\mathcal{D}_{q_2 q_2'}^{(k_2)}(R)\right]^*$$

*using $\mathcal{D}_{m_1 m_1'}^{(j_1)}(R)\mathcal{D}_{m_2 m_2'}^{(j_2)}(R) = \sum_j \sum_m \sum_{m'} \langle j_1 j_2, m_1 m_2 | j_1 j_2; j, m\rangle \langle j_1 j_2, m_1' m_2' | j_1 j_2, j, m'\rangle \mathcal{D}_{m m'}^{(j)}$

$$= \sum_{k''}\sum_{q_1}\sum_{q_2}\sum_{q_1'}\sum_{q_2'}\sum_{q'}\sum_{q''} \langle k_1 k_2; q_1 q_2 | k_1 k_2; k q\rangle \langle k_1 k_2, q_1 q_2 | k_1 k_2; k'' q'\rangle \langle k_1 k_2; q_1 q_2 | k_1 k_2; k'' q''\rangle$$

$$\cdot \left[\mathcal{D}_{q' q''}(R)\right]^* X_{q_1'}^{(k_1)} Z_{q_2'}^{(k_2)}$$

$$= \sum_{q'} T_{q'}^{(k)}\left[\mathcal{D}_{q q'}^{(k)}(R)\right]^*$$

*We can determine the matrix elements of a spherical tensor via <u>Wigner-Eckart Theorem</u>

⇒ Starting from $[J_z, T_q^{(k)}] = \hbar q T_q^{(k)}$

$$\langle \alpha', j', m' | J_z T_q^{(k)} - T_q^{(k)} J_z - \hbar q T_q^{(k)} | \alpha, j, m\rangle = 0$$

$$\langle \alpha', j', m' | m' T_q^{(k)} - T_q^{(k)} m - q T_q^{(k)} | \alpha, j, m\rangle = 0$$

↳ $m' = m + q$ where q is the ang. momentum added by spherical tensor

⇒ We apply the Wigner-Eckart Thm by noting $\langle \alpha', j' m' | T_q^{(k)} | \alpha, j m\rangle$ can be written in terms of a CG coefficient and a reduced matrix element

$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m\rangle = \langle j k; m q | j k; j' m'\rangle \frac{1}{\sqrt{2j+1}} \langle \alpha' j' \| T_q^{(k)} \| \alpha j\rangle$$

↳ Our general approach is to calculate the reduced matrix element in a simple case then use that result in our case of interest

ex.

$$\langle 3, 0 | T_0^{(2)} | 1, 0\rangle = \langle 1, 2; 0, 0 | 1, 2; 1, 0\rangle \langle 3 \| T^{(2)} \| 1\rangle$$

$$\int Y_3^0(\theta,\varphi) Y_2^0(\theta,\varphi) Y_1^0(\theta,\varphi)\, d\Omega = \langle 1, 2; 0, 0 | 1, 2; 1, 0\rangle \langle 3 \| T^{(2)} \| 1\rangle$$

↳ $\langle 3 \| T^{(2)} \| 1\rangle = \sqrt{\frac{3}{4\pi}}$

Perturbation Theory

* Perturbation theory is an approximation technique that allows us to solve non-idealized problems in quantum mechanics and other fields

* In the case of time-independent, non-degenerate perturbations:

⇒ For a given Hamiltonian, we write it as:

$H = H_0 + V$, where the solutions to H_0 are known, but not for V

ex. Two State System

↳ $H = E_1^{(0)} |1^{(0)}\rangle\langle 1^{(0)}| + E_2^{(0)} |2^{(0)}\rangle\langle 2^{(0)}| + \lambda V_{12} |1^{(0)}\rangle\langle 2^{(0)}| + \lambda V_{21} |2^{(0)}\rangle\langle 1^{(0)}|$

$\doteq \begin{bmatrix} E_1 & \lambda V_{12} \\ \lambda V_{21} & E_2 \end{bmatrix}$; $V_{12} = V_{21}$, $V_{12}, V_{21} \in \mathbb{R}$ for Hermiticity

⇒ From normal matrix operations, we see:

$$E_1 = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) + \sqrt{\frac{1}{4}(E_1^{(0)} - E_2^{(0)}) + \lambda^2 V_{12}^2}$$

$$E_2 = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) - \sqrt{\frac{1}{4}(E_1^{(0)} - E_2^{(0)}) + \lambda^2 V_{12}^2}$$

⇒ However, if we are unable to find an exact solution, we proceed as follows:

↳ We know: $H_0 |n\rangle = E_n^{(0)} |n\rangle$

$$(H_0 + \lambda V)|n\rangle = E_n |n\rangle$$

⇒ If we define $\Delta_n = E_n - E_n^{(0)}$

↳ $E_n^{(0)} - H_0 |n\rangle = \lambda V - \Delta_n |n\rangle$

$$\langle n^{(0)}| E_n^{(0)} - H_0 |n\rangle = \langle n^{(0)} | \lambda V - \Delta_n |n\rangle$$

$$0 = \langle n^{(0)} | \lambda V - \Delta_n |n\rangle$$

* Now defining the projection operator: $\varphi_n = \mathbb{I} - |n^{(0)}\rangle\langle n^{(0)}|$

$$= \sum_{k \neq n}' |k^{(0)}\rangle\langle k^{(0)}|$$

↳ $|n\rangle = \frac{1}{E_n^{(0)} - H_0} \varphi_n (\lambda V - \Delta_n) |n\rangle$

* but as $\lambda \to 0$, we must approach $H^{(0)} |n^{(0)}\rangle = E_n^{(0)} |n\rangle$

Perturbation Theory (cont.)

$\Rightarrow$ We redefine $|n\rangle$ as:

$$|n\rangle = c_n(\lambda)|n^{(0)}\rangle + \frac{1}{E_n^{(0)} - H_0}\varphi_n(\lambda V - \Delta_n)|n\rangle, \quad c_n(\lambda) = \langle n^{(0)}|n\rangle$$

*Note: Since we choose $\langle n^{(0)}|n\rangle = 1$, we must always normalize $|n\rangle$ after we solve for it

$$\hookrightarrow \boxed{|n\rangle = |n^{(0)}\rangle + \frac{1}{E_n^{(0)} - H_0}\varphi_n(\lambda V - \Delta_n)|n\rangle}$$

*If we multiply both sides by $\langle n^{(0)}|$, we can extract Δ_n

$$\boxed{\Delta_n = \lambda\langle n^{(0)}|V|n\rangle}$$

*Now if we expand both $|n\rangle$ and Δ_n in power series:

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots$$

$$\Delta_n = \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \ldots$$

*Substituting these into our above equations + matching powers of λ:

$$\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$$

$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle = \sum_{k\neq n}' \frac{|V_{nk}|^2}{(E_n^{(0)} - E_k^{(0)})^2}$$

$$|n^{(1)}\rangle = \frac{1}{E_n^{(0)} - H_0}\varphi_n|n^{(0)}\rangle = \sum_{k\neq n}' \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle$$

*Proceeding to the time-independent, degenerate perturbation case:

$\Rightarrow$ Simply put we must diagonalize the degenerate submatrix however possible

$\hookrightarrow$ For our degenerate energies, our eigenkets become:

$$|l^{(0)}\rangle = \sum_{m\in D}' |m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle$$

$\hookrightarrow$ To solve the eigenvalue equation ($H = H_0 + V$):

$$(E - H_0 - V)|l\rangle = 0$$

$\hookrightarrow$ We isolate the degenerate/non-degenerate spaces with:

$$\tilde{P}_0 = \sum_{k\in D}' |k^{(0)}\rangle\langle k^{(0)}| \qquad \tilde{P}_1 = \sum_{k\notin D}' |k^{(0)}\rangle\langle k^{(0)}| = \hat{\mathbb{I}} - \tilde{P}_0$$

Perturbation Theory (cont.)

⇒ We can now rewrite the eigenvalue equation as:

$$(E-H_0-\lambda V)P_0|l\rangle + (E-H_0-\lambda V)P_1|l\rangle = 0$$

* Applying the projection operators to the above equation yields:

① $(E-H_0-\lambda V)\tilde{P}_0^2|l\rangle + (E-H_0-\lambda V)P_0P_1|l\rangle = 0$

* using $P_0P_0 = 1$, $P_0P_1 = 0$

$$(E-E_D^{(0)}-\lambda P_0 V)P_0|l\rangle - \lambda P_0 V P_1|l\rangle = 0$$

② $-\lambda P_1 V P_0|l\rangle + (E-H_0-\lambda P_1 V)P_1|l\rangle = 0$

* Solving the above system of equations yields:

$$|l\rangle = \lambda[E-H_0-\lambda P_1 V P_1]^{-1} P_1 V P_0 |l\rangle$$

↳ $P_1|l\rangle = \tilde{P}_1 \dfrac{\lambda}{E-H_0-\lambda P_1 V P_1} P_1 V P_0 |l\rangle$

* expanding $|l\rangle$ as a power series and $\dfrac{1}{E-H_0-\lambda P_1 V P_1} \approx \dfrac{1}{E-H_0} + \dfrac{\lambda P_1 V P_1}{(E-H_0)^2} + \dots$

$$\Rightarrow P_1|l^{(1)}\rangle = \sum_{k\notin D} \frac{V_{kl}}{E_D^{(0)}-E_k^{(0)}} |k^{(0)}\rangle$$

ex. Linear Stark Effect

* Our physical set-up is a hydrogen like atom in a uniform $\vec{E}$-field

↳ $V = -ezE_0$; $n = N+l+1$, where $n \in \mathbb{Z}^+$, $l \in [0, n-1]$, $N \in \{0, \mathbb{Z}^+\}$

⇒ $H|nlm\rangle = E_n|nlm\rangle$ $\quad$ $L_z|nlm\rangle = m\hbar|nlm\rangle$

$L^2|nlm\rangle = l(l+1)\hbar^2|nlm\rangle$ $\quad$ $\Pi|nlm\rangle = (-1)^l|nlm\rangle$ (Parity)

* Remember, in terms of spherical tensors: $z = T_0^{(1)}$

↳ $\langle n, l'm'|T_0^{(1)}|nlm\rangle$ → $m=m'$ b/c no addition of ang. momentum

$l' \in [l+1, |l-1|]$

* Notice that: $\Pi^\dagger z \Pi = -z$

↳ $\langle odd|z|even\rangle = \langle odd|\Pi^\dagger\Pi z \Pi^\dagger\Pi|even\rangle$

$= \langle odd|z|even\rangle$

$\langle odd|z|odd\rangle = -\langle odd|z|odd\rangle$

$\langle even|z|even\rangle = -\langle even|z|even\rangle$

> must equal 0

⇒ From this we see $l' = l\pm1$ and that we can now write out the interaction matrix

Perturbation Theory (cont.)

ex. Linear Stark Effect (cont.)

$$\Rightarrow V \doteq \begin{bmatrix} 0 & \langle 200|V|210\rangle \\ \langle 210|V|200\rangle & 0 \end{bmatrix} = \begin{bmatrix} 0 & 3ea_0E_0 \\ 3ea_0E_0 & 0 \end{bmatrix} \quad \text{for } n=2,\ \ell=0,1$$

↳ via diagonalization:

$$|+\rangle = \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle) \qquad \Delta_+^{(1)} = 3ea_0E_0$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle) \qquad \Delta_-^{(1)} = -3ea_0E_0$$

⇒ Further corrections to H-atom from perturbation theory include:

① "Relativistic Correction"

$$E = \sqrt{(pc)^2 + m^2c^4}$$

$$T = \sqrt{(pc)^2 + m^2c^4} - m_ec^2$$

$$= mc^2\left(1 + \frac{(pc)^2}{m^2c^4}\right)^{1/2} - m_ec^2$$

↳ $T \approx \frac{p^2}{2m} - \frac{p^4}{8m_e^3c^2}$ ⟵ becomes interaction term in perturbed Hamiltonian

$$\Rightarrow H = \frac{p^2}{2m} - \frac{e^2}{r} - \frac{p^4}{8m_e^3c^2}$$

* But since $[L, p^2] = 0$, we can proceed via non-degenerate P.T b/c perturbation doesn't break the degeneracy

↳ $\Delta_{n\ell}^{(1)} = \langle n\ell m| \frac{-p^4}{8m_e^3c^2}|n\ell m\rangle$

* but $\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = \frac{p^4}{8m_e^3c^2} = \frac{1}{2mc^2}\left(H_0 + \frac{e^2}{r}\right)^2$

$$= \left[\langle n\ell m|\frac{e^4}{r^2}|n\ell m\rangle + 2E_n^{(0)}\langle n\ell m|\frac{e^2}{r}|n\ell m\rangle + (E_n^{(0)})^2\right]\cdot\frac{1}{2mc^2}$$

$$= \frac{-1}{2}mc^2\alpha^4\left(\frac{-3}{4n^2} - \frac{1}{n^3(\ell+\frac{1}{2})}\right)$$

$$= \frac{-mc^2\alpha^2}{2n^2}\left(\alpha^2\left[\frac{-3}{4} + \frac{1}{n(\ell+\frac{1}{2})}\right]\right)$$

② Spin-Orbit Coupling

$\vec{B} = \frac{-\vec{v}}{c}\times\vec{E}$, $\vec{\mu} = \frac{e\vec{S}}{m_ec}$ ($\vec{S}$ = spin vector)

$$H_{LS} = -\vec{\mu}\cdot B$$

$$= \frac{eS}{m_ec}\left(\frac{v}{c}\times\frac{\vec{r}}{r}\frac{dV_c}{dr}\left(\frac{-1}{e}\right)\right) \qquad * V_c = \text{central potential}$$

$$= \frac{eS}{m_ec}\left[\frac{p}{m_ec}\times\frac{\vec{r}}{r}\frac{dV_c}{dr}\left(\frac{-1}{e}\right)\right] = \frac{1}{m_e^2c^2r}\frac{dV_c}{dr}\vec{L}\cdot\vec{S}$$

Perturbation Theory (cont.)

* Rewriting $L\cdot S$ as $J^2 = (L+S)^2$

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

* Introducing the spin-angular functions

$$\mathcal{Y}_{l}^{j=l+1/2} \equiv \frac{1}{\sqrt{2l+1}}\begin{bmatrix} \pm\sqrt{l\pm m+1/2}\; Y_l^{m-1/2}(\theta,\varphi) \\ \sqrt{l\mp m+1/2}\; Y_l^{m+1/2}(\theta,\varphi)\end{bmatrix}$$ * Note: $m = m_l + m_s$

$= (\;)Y_l^m \chi^+ + (\;)Y_l^m\chi^-$, where $\chi^\pm$ are spinor states

$\Rightarrow \Delta_{nl}^{(1)} = \frac{1}{2m_e^2c^2}\langle \frac{1}{r}\frac{dV_c}{dr}\rangle_{nl}\frac{\hbar}{2}\begin{Bmatrix} l \\ -l+1\end{Bmatrix}$ for $j = l+1/2$, $= l-1/2$ (choose a j)

where $\frac{1}{2}\int \mathcal{Y}^+(J^2-L^2-S^2)\mathcal{Y}\,d\Omega = \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)](\;)$ is used in the expectation value calculation

$\Rightarrow$ In H-atom: $V_c = \frac{e^2}{r} \rightarrow \langle\frac{1}{r}\frac{dV}{dr}\rangle = \langle\frac{e^2}{r^3}\rangle$

$$= \frac{-2m_e^2c^2\alpha^2}{nl(l+1)(l+1/2)\hbar^2}$$

* Now considering a time-dependent perturbation such that:

$H = H_0 + V(t)$ $\Rightarrow$ Note: Our normal time evolution operator $U(t,t_0) = \exp[\frac{-i}{\hbar}Ht]$ only works when H is time independent

$\Rightarrow$ We must develop the interaction picture

$|\alpha\rangle = \sum_n' c(0)|n\rangle$; $c(0) = \langle n|\alpha\rangle|_{t=0}$

$|\alpha, t_0=0, t\rangle = \sum_n' c_n(t)\exp[-iE_nt/\hbar]|n\rangle \rightarrow c_n(t)$ only associated w/ V

↳ $c_n \rightarrow 0$ yields normal evolution

$\Rightarrow |\alpha, t_0; t\rangle_I = e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S$ (time evolve only unperturbed Hamiltonian)

* Operators now transform as: $\hat{A}_I = e^{+iH_0t/\hbar}\hat{A}_S e^{-iH_0t/\hbar}$

↳ $i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = i\hbar\frac{\partial}{\partial t}(e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S)$

$= i\hbar\frac{H_0}{-i\hbar}e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S + i\hbar e^{iH_0t/\hbar}(\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_S)$

$= -H_0 e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S + e^{iH_0t/\hbar}(H_0 + V(t))|\alpha, t_0; t\rangle_S$

$= e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S$

$= V_I(t)|\alpha, t_0; t\rangle_I$

Perturbation Theory (cont.)

* we convert the above equation to a # by multiplying both sides by $\langle n|$

$$\Rightarrow i\hbar \frac{\partial}{\partial t}\langle n|\alpha, t_0; t\rangle_I = \langle n|V_I|\alpha, t_0; t\rangle_I$$

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_m{}' \langle n|V_I|m\rangle\langle m|\alpha, t_0; t\rangle_I$$

$$= \sum_m{}' V_{nm}\, c_m(t)\, e^{i\omega_{nm}t}$$

* If we now expand c_n in a power series to develop perturbation theory

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \ldots$$

<u>ex.</u> Exact Solution to a 2 state problem

$$H_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2|, \quad E_2 > E_1$$

$$V(t) = \gamma e^{i\omega t}|1\rangle\langle 2| + \gamma e^{-i\omega t}|2\rangle\langle 1|$$

$$> H \doteq \begin{bmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & E_2 \end{bmatrix}$$

* From the above system we get the following differential equations:

$$i\hbar \frac{\partial}{\partial t} c_1(t) = V_{12}(t)\, e^{-i(E_2-E_1)t/\hbar} c_2(t)$$

$$i\hbar \frac{\partial}{\partial t} c_2(t) = V_{21}(t)\, e^{+i(E_2-E_1)t/\hbar} c_1(t)$$

* Assume $c_1(0) = 1$, $c_2(0) = 0$

$\Rightarrow$ we solve this system by taking the derivative of one equation and substituting it into the other, yielding:

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2} \sin^2\left[\left(\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right)^{1/2} t\right]$$

$$|c_1(t)|^2 = 1 - |c_2(t)|^2$$

* But we really want an approximation technique for this problem

$$\Rightarrow i\hbar \frac{dc_n^{(j)}}{dt} = \sum_m{}' V_{nm}\, e^{i\omega_{nm}t}\, c_m^{(j-1)}(t)$$

* We now must develop a proper time evolution operator

$$\hookrightarrow |\alpha, t_0; t\rangle_I = U_I(t, t_0)|\alpha, t_0; t\rangle_I$$

* if we take the time derivative of the above equation:

$$i\hbar \frac{\partial}{\partial t}\left(U_I(t,t_0)|\alpha, t_0; t\rangle_I\right) = V_I\, U_I(t, t_0)|\alpha, t_0; t\rangle_I$$

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = V_I\, U_I(t, t_0)$$

$$\hookrightarrow U_I(t, t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\, U_I(t', t_0)\, dt'$$

* but since most problems aren't directly integerable, we approximate by

$$U_I(t, t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\,dt' + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, V_I(t')\, V_I(t') + \ldots$$

Quantom Qualifier Breakdown

January 2008
Q1: Infinite Square Well, Schrödingers Eqn, Spin 1/2 Particles
Q2: SHO, Expectation value, uncertainty relation
Q3: Variational Principle
Q4: Hermitian Operators, Probabilities,
Q5: Infinite Square Well, Perturbation Theory
Q6: Central Potential, Hydrogen Atom, Schrödingers Eqn

August 2008
Q1: 3-D Spherical Well, Schrödingers Eqn
Q2: Perturbation Theory, Degenerate Perturbation Theory
Q3: SHO; Schrödinger Eqn, Ladder Operators
Q4: Infinite Square Well, Probabilities, Perturbation Theory (Widening box)
Q5: Time Evolution, Schrödinger Eqn
Q6: Hydrogen Atom, Expectation value, Angular Momentum

January 2009
Q1: Spin 1/2 Particles, Spinors, Expectation Value, probabilities
Q2: Perturbation Theory
Q3: 2-D well, Schrödinger Eqn,
Q4: Angular Momentum, Clebsh-Gordon Coefficients, Spin Scattering?
Q5: Probabilities, Time Evolution
Q6: Hydrogen Atom, Angular Momentum

August 2009
Q1: Step Potential, Schrödingers Eqn, Probability
Q2: Variational Method, Expectation Value
Q3: Eigenvalue/Eigenvectors, Perturbation Theory
Q4: Central Potential, Angular Momentum
Q5: Infinite Square Well, Identical Particles
Q6: Spin 1/2 Particles, Time Evolution, Probabilities

January 2010

Q1: δ-Function Potential, Schrödinger Eqn, expectation value
Q2: Hydrogen Atom, Probability, Uncertainty principle
Q3: Time-Dependent Perturbation Theory,
Q4: Spin 1/2 Particles, Probability, Time Evolution
Q5: Two-level system, Coupling
Q6: Hyperfine Splitting, e^- & p^+ spin

August 2010

Q1: Step Potential, Zero-Potential, Probability
Q2: SHO, Ladder Operators, Uncertainty principle, multiple particles, degeneracy
Q3: Dirac Formalism, Matrix Mechanics
Q4: 3-D SHO, Perturbation Theory
Q5: Hydrogen Atom, Variational Method, Expectation value
Q6: Step Potential, Gamow Factor

August 2011

Q1: Completeness Relation, Probability, Time Evolution, Schrödinger Picture, Heisenberg Picture
Q2: SHO, Probability, Parity?
Q3: Angular Momentum, Probability
Q4: Spin System, Spin 1/2 Particles, Probability
Q5: Perturbation Theory, Infinite Square Well
Q6: Variational Method, SHO, Matrix Mechanics

January 2012

Q1: Stationary States, Time Evolution, Probability, Uncertainty principle
Q2: Dirac Notation, Hermitian Operators
Q3: SHO, Schrödinger Eqn, Expectation Value
Q4: Angular Momentum, Hydrogen Atom, Hyperfine splitting
Q5: Interaction Picture, Schrödinger Eqn
Q6: Perturbation Theory, SHO

August 2012

Q1: Matrix Manipulation, Time Evolution
Q2: Spin 1/2 Particles; Uncertainty Principle
Q3: Spin 1/2 Particles, Clebsh-Gordon Coefficients, Coupling
Q4: Hydrogen-like Atom, Perturbation Theory, Probability
Q5: SHO, Time-dependent Perturbation Theory
Q6: Time Evolution, Expectation Value

January 2013:

Q1: δ-Function Potential, Scattering, Schrödinger Eqn
Q2: Scattering, Born Approx,
Q3: Spin 1/2 Particles, Matrix Manipulation, Expectation value, Probability
Q4: SHO, Ladder operators
Q5: Infinite Square Well, Perturbation Theory,
Q6: 3-D Well, Schrödinger Eqn

August 2013:

Q1: Infinite Square Well, Schrödinger Eqn, Box Expansion
Q2: Angular Momentum, Ladder Operators,
Q3: Step Potential, Scattering, Schrödinger Eqn
Q4: Hydrogen Atom, Probabilities
Q5: Matrix Manipulation, Perturbation Theory
Q6: SHO, Perturbation Theory, Time Evolution, Time Dependent Perturbation Theory

January 2014:

Q1: Schrödinger Eqn, Angular Momentum, Perturbation Theory
Q2: Infinite Square Well, Schrödinger Eqn, Probability
Q3: Matrix Manipulation, Probability
Q4: Clebsh-Gordon Coefficients, Angular Momentum
Q5: Zeeman Splitting, Hydrogen Atom
Q6: SHO, Perturbation Theory

August 2014:

Q1: Schrödinger Eqn, Expectation Values, SHO, Uncertainty principle

Q2: Spin 1/2 Particles, Angular Momentum, Ladder Operators

Q3: SHO, Perturbation Theory, Probability

Q4: Identical Particles, Infinite Square Well, Spin 1/2 Particles

Q5: Angular Momentum, Expectation Value

Q6: Variational Method

January 2015:

Q1: SHO, Ladder operators

Q2: Hydrogen Atom, Angular Momentum, Time Evolution, Probability, Expectation Value

Q3: Step Potential, Schrödinger Eqn, Infinite Square Well

Q4: Matrix Manipulation, Time Evolution

Q5: Interaction Picture

Q6: 2-D Well, Perturbation Theory

August 2015:

Q1: Step Potential, Scattering, Probability Current

Q2: Confined Harmonic Oscillator, Angular Momentum

Q3: Matrix Manipulation

Q4: Infinite Square Well, Well Expansion, Probability

Q5: SHO, Perturbation Theory

Q6: Hydrogen Atom, Expectation Value, Probability

January 2016:

Q1: Clebsh-Gordon Coefficients, Spinor States, Probability

Q2: SHO, Perturbation Theory, Parity

Q3: Identical Particles, Infinite Square Well, Spin 1/2 Particles

Q4: Matrix Manipulation, Time Evolution

Q5: Spin 1/2 Particles, Spinor States, Time Evolution, Probability

Q6: Finite Square Well, Schrödinger Eqn, Scattering