Introduction to Quantum Mechanics for Engineers

151-0966-00L

Solutions to Problem Sets

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Solutions: Problem Set #1

① (i) $\int_{-\infty}^{\infty} A e^{-\lambda(x-a)^2} dx = 1$

let $u = x - a$ $\quad du = dx$ $\quad x = \pm\infty \rightarrow u = \pm\infty$

$\Rightarrow A \int_{-\infty}^{\infty} e^{-\lambda u^2} du = 1$ $\quad$ using integral tables

OR $A \sqrt{\pi/\lambda} = 1$

OR $\boxed{A = \sqrt{\frac{\lambda}{\pi}}}$

(ii) $\langle x \rangle = A \int_{-\infty}^{\infty} x e^{-\lambda(x-a)^2} dx = A \int_{-\infty}^{\infty} (u+a) e^{-\lambda u^2} du$

$$= A \left[\underbrace{\int_{-\infty}^{\infty} u e^{-\lambda u^2} du}_{0 \text{ (odd!)}} + a \int_{-\infty}^{\infty} e^{-\lambda u^2} du \right]$$

$$= A \left(0 + a \sqrt{\frac{\pi}{\lambda}} \right) = \boxed{a}$$

$$\langle x^2 \rangle = A \int_{-\infty}^{\infty} x^2 e^{-\lambda(x-a)^2} dx$$

$$= A \left[\underbrace{\int_{-\infty}^{\infty} u^2 e^{-\lambda u^2} du}_{\text{integral tables}} + 2a \underbrace{\int_{-\infty}^{\infty} u e^{-\lambda u^2} du}_{0 \text{ (odd!)}} + a^2 \underbrace{\int_{-\infty}^{\infty} e^{-\lambda u^2} du}_{\text{integral tables}} \right]$$

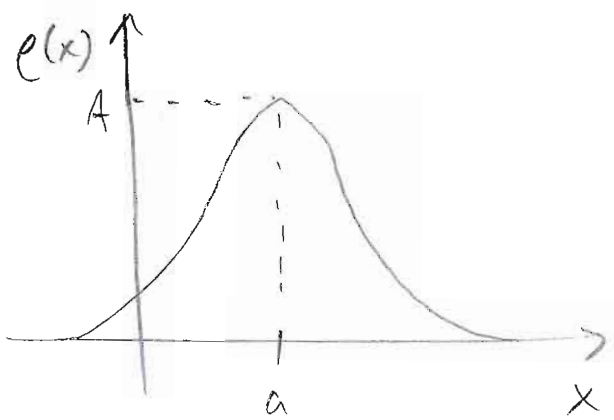
$$\langle x^2 \rangle = A \left[\frac{1}{2\lambda}\sqrt{\frac{\pi}{\lambda}} + 0 + a^2\sqrt{\frac{\pi}{\lambda}} \right]$$

$$= \boxed{\frac{1}{2\lambda} + a^2}$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{2\lambda} + a^2 - a^2$$

$$\sigma_x^2 = \frac{1}{2\lambda} \Rightarrow \boxed{\sigma_x = \frac{1}{\sqrt{2\lambda}}}$$

(iii)



(2.) $\Psi(x,t) = A e^{-\lambda|x|} e^{-i\omega t}$

(i) $$\int_{-\infty}^{\infty} |\Psi|^2 dx = A^2 \int_{-\infty}^{\infty} e^{-2\lambda|x|} dx$$

$$= 2A^2 \int_0^{\infty} e^{-2\lambda x} dx = 2A^2 \cdot \frac{1}{2\lambda}$$

$$= \frac{A^2}{\lambda} \Rightarrow \boxed{A = \sqrt{\lambda}}$$

(ii) $$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\Psi|^2\,dx = A^2 \int_{-\infty}^{\infty} x e^{-2\lambda|x|}\,dx \to 0 \text{ (odd!)}$$

$$\boxed{\langle x \rangle = 0}$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 |\Psi|^2\,dx = A^2 \int_{-\infty}^{\infty} x^2 e^{-2\lambda|x|}\,dx$$

$$= 2A^2 \int_0^{\infty} x^2 e^{-2\lambda x}\,dx = 2A^2 \cdot \frac{2}{(2\lambda)^3}$$

$$\Rightarrow \boxed{\langle x^2 \rangle = \frac{1}{2\lambda^2}}$$

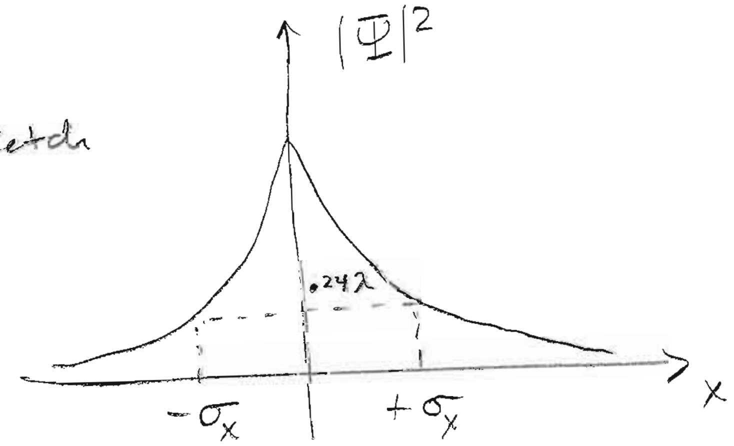
(iii) $$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{2\lambda^2}$$

$$\boxed{\sigma_x = \frac{1}{\sqrt{2}\,\lambda}}$$

$$|\Psi(\pm\sigma_x)|^2 = A^2 e^{-2\lambda\sigma_x} = \lambda e^{-2\lambda/\sqrt{2}\lambda} = \lambda e^{-\sqrt{2}}$$

$$= 0.243\,\lambda$$

Sketch



Probability of being outside $\pm \sigma_x$

$$= 2\int_{\sigma_x}^{\infty} |\Psi|^2 dx = 2A^2 \int_{\sigma_x}^{\infty} e^{-2\lambda x} dx$$

$$= 2\lambda \left(\frac{e^{-2\lambda x}}{-2\lambda} \right) \Bigg|_{\sigma_x}^{\infty}$$

$$= e^{-2\lambda \sigma_x}$$

plug in $\sigma_x = \frac{1}{\sqrt{2}\,\lambda}$

$$= e^{-\sqrt{2}}$$

$$= \boxed{0.243}$$

(3) We know that: $\langle p \rangle = m \frac{d\langle x \rangle}{dt}$
(e.g. Griffiths eqn 1.33)

$$= -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx$$

So $\frac{d\langle p \rangle}{dt} = -i\hbar \int \frac{\partial}{\partial t}\left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx$

Schrödinger Eqn says:

$$\begin{cases} \frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \\ \frac{\partial \Psi^*}{\partial t} = \frac{-i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^* \end{cases}$$

Then...

$$\frac{\partial}{\partial t}\left(\Psi^* \frac{\partial \Psi}{\partial x}\right) = \frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x} + \underbrace{\Psi^* \frac{\partial}{\partial x}\frac{\partial \Psi}{\partial t}}$$

since $\frac{\partial^2 \Psi}{\partial x \partial t} = \frac{\partial^2 \Psi}{\partial t \partial x}$

$$= \left[-\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*\right]\frac{\partial \Psi}{\partial x}$$

$$+ \Psi^* \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi\right]$$

$$= \frac{i\hbar}{2m}\left[\Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \frac{\partial^2 \Psi^*}{\partial x^2}\frac{\partial \Psi}{\partial x}\right]$$

$$+ \frac{i}{\hbar}\left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x}(V\Psi)\right]$$

check

First term, use integration by parts twice on 1st quantity in brackets:

$$\int_{-\infty}^{\infty} \Psi^* \frac{\partial^3 \Psi}{\partial x^3} = -\int \frac{\partial \Psi^*}{\partial x}\frac{\partial^2 \Psi}{\partial x^2} + \underbrace{\Psi^*}_{0} \frac{\partial^2 \Psi}{\partial x^2}\Big|_{-\infty}^{\infty}$$

integration by parts

Again, integration by parts

$$-\int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x}\frac{\partial^2 \Psi}{\partial x^2} = \int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2}\frac{\partial \Psi}{\partial x} + \underbrace{\frac{\partial \Psi^*}{\partial x}\frac{\partial \Psi}{\partial x}}_{0}\Big|_{-\infty}^{\infty}$$

Plugging all of this back in...

$$\frac{d\langle p\rangle}{dt} = -i\hbar \int_{-\infty}^{\infty} \frac{\partial}{\partial t}\left(\Psi^* \frac{\partial \Psi}{\partial x}\right) dx$$

$$\frac{d\langle p\rangle}{dt} = -i\hbar \left\{ \frac{i\hbar}{2m}\left[\int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2}\frac{\partial \Psi}{\partial x} - \frac{\partial^2 \Psi^*}{\partial x^2}\frac{\partial \Psi}{\partial x}\right]\right.$$

$$0$$

$$\left. + \frac{i}{\hbar}\int_{-\infty}^{\infty}\left[\cancel{V\Psi^*\frac{\partial \Psi}{\partial x}} - \cancel{\Psi^* V\frac{\partial \Psi}{\partial x}} - \Psi^*\frac{\partial V}{\partial x}\Psi\right]\right\}$$

$$\frac{d\langle p\rangle}{dt} = -i\hbar\left(\frac{i}{\hbar}\right)\int_{-\infty}^{\infty}\Psi^*\left(-\frac{\partial V}{\partial x}\right)\Psi$$

$$\frac{d\langle p\rangle}{dt} = \left\langle -\frac{\partial V}{\partial x}\right\rangle \qquad QED$$

Note: Newton's 2nd law $\quad F_x = m \cdot a$ ← acceleration (force ← F_x)

$$= \frac{dp}{dt}$$

$$dV = -F\,dx$$

and $\quad F_x = -\dfrac{dV}{dx}$

So the expectation values in quantum mechanical description follow classical description

(4.) $\lambda = \frac{h}{p}$ and $\frac{p^2}{2m} = \frac{3}{2} k_B T$

OR $p = \sqrt{3 m k_B T}$

So $\lambda = \frac{h}{\sqrt{3 m k_B T}}$

if $\lambda > d$ $\Rightarrow$ $\frac{h}{\sqrt{3 m k_B T}} > d$

then its quantum mechanical

OR $T < \frac{h^2}{3 m k_B d^2}$

(i) <u>Solid - electrons</u>

$$T < \frac{(6.6 \times 10^{-34}\ \text{J s})^2}{3\,(9.1 \times 10^{-31}\ \text{kg})(1.4 \times 10^{-23}\ \text{J/K})(3 \times 10^{-10}\ \text{m})^2}$$

$$\boxed{T_{elec} < 1.3 \times 10^5\ \text{K}}$$

mass of proton

<u>Solid - nuclei</u> Na $\Rightarrow$ $m = 23 m_p = 23 \cdot 1.7 \times 10^{-27}$ kg

$$T < \frac{(6.6 \times 10^{-34}\ \text{J} \cdot \text{s})^2}{3 \cdot (3.9 \times 10^{-26}\ \text{kg})(1.4 \times 10^{-23}\ \text{J/K})(3 \times 10^{-10}\ \text{m})^2}$$

$$\boxed{T_{nucl.} < 3.0\,K}$$

Therefore, electrons in solid are almost always "quantum mechanical". The nuclei are almost never "quantum mechanical."

(ii) Ideal Gas

$$PV = n \cdot R \cdot T$$ ideal gas law

pressure · volume = moles · Gas constant · T

Can be re-written $$PV = \frac{N}{N_A} \cdot k_B \cdot N_A \cdot T$$

number of molecules

Avogadro's number

$$PV = N k_B T$$

$$\frac{V}{N} = \text{average volume per gas molecules} = \frac{k_B T}{P}$$

$$d = \left(\frac{V}{N}\right)^{1/3} = \left(\frac{k_B T}{P}\right)^{1/3}$$

So $$T < \frac{h^2}{3 m k_B \left(\frac{k_B T}{P}\right)^{2/3}} \Rightarrow T^{5/3} < \frac{h^2 P^{2/3}}{3 m k_B{}^{5/3}}$$

OR $$T < \frac{1}{k_B}\left(\frac{h^2}{3m}\right)^{3/5} P^{2/5}$$

Q.E.D.

<u>Helium:</u> $m = 4 m_p = 6.8 \times 10^{-27}$ Kg

$P = 1\text{atm} = 1 \times 10^5 \text{ N/m}^2$

$$T < \frac{1}{(1.4 \times 10^{-23} \text{ J/K})} \left(\frac{(6.6 \times 10^{-34} \text{ J}\cdot\text{s})^2}{3(6.8 \times 10^{-27} \text{Kg})} \right)^{3/5} \left(1.0 \times 10^5 \frac{\text{N}}{\text{m}^2}\right)^{2/5}$$

$$\boxed{T_{He} < 2.8\text{K}}$$

<u>Hydrogen in outer space:</u> $d = 0.01$ m

$m = m_p = 1.7 \times 10^{-27}$ Kg

$$T < \frac{(6.6 \times 10^{-34} \text{ J}\cdot\text{s})^2}{3(1.7 \times 10^{-27} \text{ Kg})(1.4 \times 10^{-23} \text{ J/K})(10^{-2} \text{m})^2}$$

$$\boxed{T_H^{\text{outer space}} < 6.2 \times 10^{-14} \text{ K}}$$

At 3K H is definitely in the classical regime.

Quantum Mechanics : PS#2 Solutions

① To determine σ_x and σ_p, we need $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$

For square infinite well $\Rightarrow \psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$

$$\Rightarrow \langle x \rangle = \int x |\psi|^2 dx = \frac{2}{a}\int_0^a x \sin^2\left(\frac{n\pi}{a}x\right) dx$$

change of variables let $u \equiv \frac{n\pi}{a}x$ $\quad dx = \frac{a}{n\pi}du$

$x : 0 \rightarrow a$

$u : 0 \rightarrow n\pi$

So $$\langle x \rangle = \frac{2}{a}\left(\frac{a}{n\pi}\right)\left(\frac{a}{n\pi}\right)\int_0^{n\pi} u \sin^2 u \, du$$

$$= \frac{2a}{n^2\pi^2}\left[\frac{u^2}{4} - \frac{u \sin 2u}{4} - \frac{\cos 2u}{8}\right]\Bigg|_0^{n\pi}$$

$$= \frac{2a}{n^2\pi^2}\left[\frac{n^2\pi^2}{4} - \cancel{\frac{\cos 2n\pi}{8}} + \cancel{\frac{1}{8}}\right]$$

$$\boxed{\langle x \rangle = \frac{a}{2}}$$ does not depend on n

$$\langle x^2 \rangle = \frac{2}{a}\int_0^a x^2 \sin^2\left(\frac{n\pi}{a}x\right) dx$$ same substitution

$$= \frac{2}{a}\left(\frac{a}{n\pi}\right)^3 \int_0^{n\pi} u^2 \sin^2 u \, du$$

$$\langle x^2 \rangle = \frac{2a^2}{(n\pi)^3}\left[\frac{u^3}{6} - \left(\frac{u^2}{4} - \frac{1}{8}\right)\sin 2u - \frac{u\cos 2u}{4}\right]$$

$$= \frac{2a^2}{(n\pi)^3}\left[\frac{(n\pi)^3}{6} - \frac{n\pi\cos(2n\pi)}{4}\right]$$

$$\boxed{\langle x^2 \rangle = a^2\left[\frac{1}{3} - \frac{1}{2(n\pi)^2}\right]}$$

constant!

$\langle p \rangle \Rightarrow$ use $\boxed{\langle p \rangle = m\frac{d\langle x \rangle}{dt} = 0}$

$$\langle p^2 \rangle = \int \psi_n^* \left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 \psi_n \, dx = -\hbar^2 \int \psi_n^* \left(\frac{d^2\psi_n}{dx^2}\right) dx$$

From S.E. $\Rightarrow \frac{d^2\psi_n}{dx^2} = -\frac{2mE_n}{\hbar^2}\psi_n$

Thus $\langle p^2 \rangle = (-\hbar^2)\left(-\frac{2mE_n}{\hbar^2}\right)\underbrace{\int \psi_n^* \psi_n \, dx}_{1}$

$= 2mE_n$ where $E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$

$$\boxed{\langle p^2 \rangle = \left(\frac{n\pi\hbar}{a}\right)^2}$$

Putting all of this together...

PS #2 Solutions (cont.)

pg.

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = a^2\left(\frac{1}{3} - \frac{1}{2(n\pi)^2} - \frac{1}{4}\right)$$

$$= \frac{a^2}{4}\left[\frac{1}{3} - \frac{2}{(n\pi)^2}\right]$$

$$\Rightarrow \boxed{\sigma_x = \frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{(n\pi)^2}}}$$

$$\sigma_p^2 = \langle p^2\rangle - \langle p\rangle^2 = \left(\frac{n\pi\hbar}{a}\right)^2 \Rightarrow \boxed{\sigma_p = \frac{n\pi\hbar}{a}}$$

$$\therefore \quad \sigma_x\sigma_p = \frac{n\pi\hbar}{2}\sqrt{\frac{1}{3} - \frac{2}{(n\pi)^2}}$$

$$\boxed{\sigma_x\sigma_p = \frac{\hbar}{2}\sqrt{\frac{(n\pi)^2}{3} - 2}}$$

This is always larger than $\frac{\hbar}{2}$

since

$$\sqrt{\frac{(n\pi)^2}{3} - 2} > 1$$

The smallest value of uncertainty is obtained for $n=1$ when

$$\sqrt{\frac{n^2\pi^2}{3} - 2} = \sqrt{\frac{\pi^2}{3} - 2} = 1.136$$

2 (i) $\Psi(x,0) = A(\psi_1 + \psi_2)$

$$|\Psi|^2 = |A|^2 \left[(\psi_1^* + \psi_2^*)(\psi_1 + \psi_2) \right]$$

$$= |A|^2 \left[|\psi_1|^2 + \psi_1^* \psi_2 + \psi_1 \psi_2^* + |\psi_2|^2 \right]$$

$$1 = \int |\Psi|^2 dx = |A|^2 \int \Big(|\psi_1|^2 + \underbrace{\cancel{\psi_1^* \psi_2}}_{0} + \underbrace{\cancel{\psi_1 \psi_2^*}}_{0} + |\psi_2|^2 \Big) dx$$

orthogonal

$$= |A|^2 \cdot 2$$

$$\Rightarrow A = \frac{1}{\sqrt{2}} \Rightarrow \boxed{\Psi(x,0) = \frac{1}{\sqrt{2}} \left[\psi_1(x) + \psi_2(x) \right]}$$

(ii) $\Psi(x,t) = \frac{1}{\sqrt{2}} \left[\psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar} \right]$

we can define $\omega = \frac{\pi^2 \hbar}{2ma^2} \Rightarrow \frac{E_n}{\hbar} = n^2 \omega$

and we know that

$$\psi_1 = \sqrt{\frac{2}{a}} \sin \frac{\pi}{a} x \; ; \; \psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a} x \right)$$

$$\Rightarrow \Psi(x,t) = \frac{1}{\sqrt{2}} \sqrt{\frac{2}{a}} \left[\sin\left(\frac{\pi}{a} x\right) e^{-i\omega t} + \sin\left(\frac{2\pi}{a} x \right) e^{-i4\omega t} \right]$$

or $$\boxed{\Psi(x,t) = \frac{1}{\sqrt{a}}\, e^{-i\omega t}\left[\sin\left(\frac{\pi}{a}x\right) + \sin\left(\frac{2\pi}{a}x\right)e^{-3i\omega t}\right]}$$

$$|\Psi(x,t)|^2 = \frac{1}{a}\left[\sin^2\left(\frac{\pi}{a}x\right) + \sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)\left(e^{-3i\omega t} + e^{3i\omega t}\right) + \sin^2\left(\frac{2\pi}{a}x\right)\right]$$

using Euler's formula

$$\boxed{|\Psi(x,t)|^2 = \frac{1}{a}\left[\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + 2\sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)\cos(3\omega t)\right]}$$

(iii) $$\langle x\rangle = \int x\,|\Psi(x,t)|^2\,dx$$

$$= \frac{1}{a}\int_0^a x\left[\sin^2\frac{\pi x}{a} + \sin^2\frac{2\pi x}{a} + 2\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}\cos 3\omega t\right]dx$$

3 integrals (using tables)

#1 $$\int_0^a x\sin^2\left(\frac{\pi}{a}x\right)dx = \frac{a^2}{4}$$

#2 $$\int_0^a x\sin^2\left(\frac{2\pi}{a}x\right)dx = \frac{a^2}{4}$$

#3 $$\int_0^a 2x\sin\frac{\pi}{a}x\,\sin\frac{2\pi}{a}x\,dx = -\frac{16a^2}{9\pi^2}$$

$$\therefore \langle x \rangle = \frac{1}{a}\left[\frac{a^2}{4} + \frac{a^2}{4} - \frac{16a^2}{9\pi^2}\cdot\cos(3\omega t)\right]$$

$$\boxed{\langle x \rangle = \frac{a}{2}\left[1 - \frac{32}{9\pi^2}\cos(3\omega t)\right]}$$

Oscillates with an angular frequency

$$3\omega \Rightarrow \frac{3\pi^2\hbar}{2ma^2}$$

(iv) $\langle p \rangle = m\dfrac{d\langle x \rangle}{dt} = m\,\dfrac{a}{2}\left(\dfrac{-32}{9\pi^2}\right)(-3\omega)\sin(3\omega t)$

$$= \frac{\cancel{m}\,a\cdot 16}{3\cancel{\pi^2}}\,\frac{\cancel{\pi^2}\hbar}{2\cancel{m}a^2}\,\sin(3\omega t)$$

$$\boxed{\langle p \rangle = \frac{8\hbar}{3a}\sin(3\omega t)}$$

(v) If you measure the energy of this particle, you would obtain either E_1 or E_2

$$E_1 = \pi^2\hbar^2/2ma^2$$

$$E_2 = 4\pi^2\hbar^2/2ma^2$$

PS #2 Solutions continued

(vi) In general $|c_n|^2 \equiv$ probability that a measure will find the particle in stationary state n.

Pg

Since here $|c_1|^2 = |c_2|^2 = \frac{1}{2}$ $\Rightarrow$ equal probability of being in either ψ_1 or ψ_2

$P_{\psi_1} = P_{\psi_2} = 0.5$

(vii)

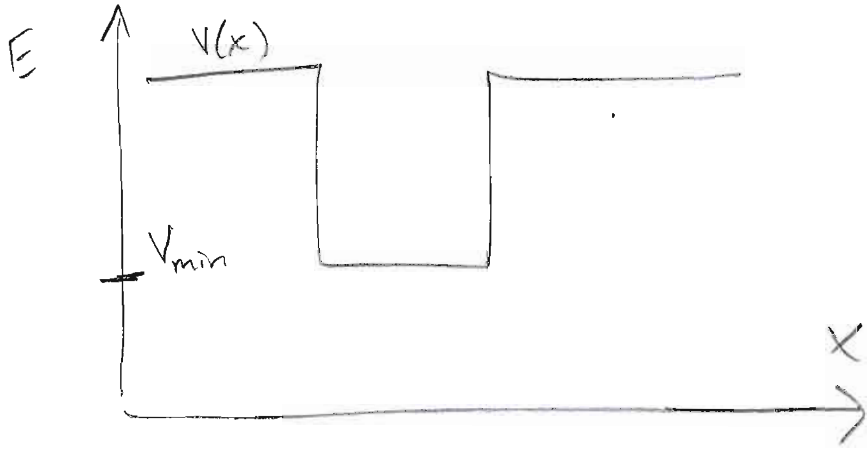
$$\langle H \rangle = \frac{1}{2}(E_1 + E_2) = \frac{1}{2}\left(\frac{\pi^2\hbar^2}{2ma^2} + \frac{4\pi^2\hbar^2}{2ma^2}\right)$$

$$\boxed{\langle H \rangle = \frac{5\pi^2\hbar^2}{4ma^2}}$$

Note: you would never actually measure this value. One measures either E_1 or E_2.

$$\left\{ \begin{aligned} E_1 &= \frac{\pi^2\hbar^2}{2ma^2} \\ E_2 &= \frac{4\pi^2\hbar^2}{2ma^2} \end{aligned} \right.$$

(3) Imagine a finite potential well.



This problem tries to address whether we can get a solution with

$$E < V_{min}$$

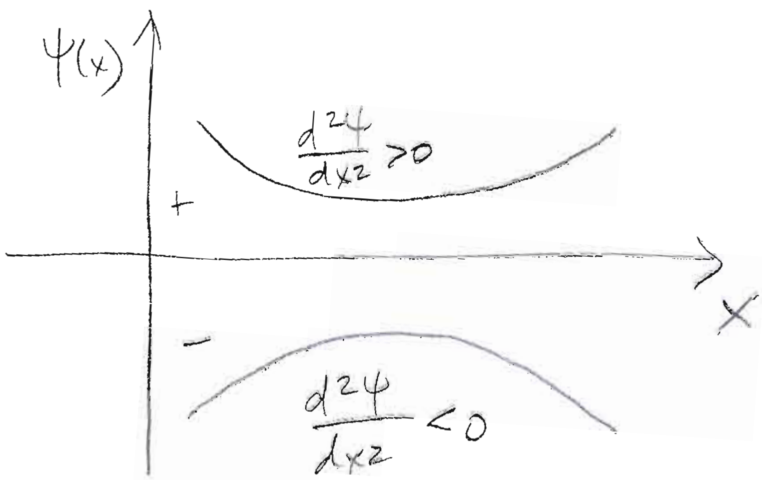
Taking the hint, we can re-write the time-independent Schrödinger equation as ...

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

If E is smaller than the minimum V(x)

then $\left[V(x) - E\right] > 0$

$$\Rightarrow \begin{cases} \dfrac{d^2\psi}{dx^2} > 0 & \text{if } \psi > 0 \\ \dfrac{d^2\psi}{dx^2} < 0 & \text{if } \psi < 0 \end{cases}$$



$\frac{d^2\psi}{dx^2}$ is the "curvature"

ψ can not "turn over" and go to zero as $x \to \pm\infty$

because curvature keeps pushing it away from x-axis

$$\boxed{\therefore\ \psi(x) \text{ cannot be normalized for } E < V_{min}}$$

Q.E.D

(4)

(i) In general, for a free particle we have:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k)\, e^{i(kx - \frac{\hbar k^2}{2m} t)}\, dk$$

with $g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0)\, e^{-ikx}\, dx$

So $g(k) = \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi}\right)^{1/4} \underbrace{\int_{-\infty}^{\infty} e^{-ax^2} e^{-ikx}\, dx}$

the integral $\int_{-\infty}^{\infty} e^{-(ax^2 + ikx)}\, dx$ can be solved by "completing the Square"

let $u \equiv \sqrt{a}\left[x + \frac{ik}{2a}\right]$ such that $dx = \frac{1}{\sqrt{a}}\, du$

OR $x = \frac{u}{\sqrt{a}} - \frac{ik}{2a}$

$x = -\infty \to \infty$
$u = -\infty \to \infty$

$$\Rightarrow ax^2 + ikx \Rightarrow a\left[\frac{u}{\sqrt{a}} - \frac{ik}{2a}\right]^2 + ik\left[\frac{u}{\sqrt{a}} - \frac{ik}{2a}\right]$$

$$= u^2 - \frac{k^2}{4a} - \cancel{2a \frac{u}{\sqrt{a}} \frac{ik}{2a}} + \cancel{\frac{iku}{\sqrt{a}}} + \frac{k^2}{2a}$$

$$= u^2 + \frac{k^2}{4a}$$

So the integral is:

$$\frac{1}{\sqrt{a}} \int_{-\infty}^{\infty} e^{(-u^2 - k^2/4a)}\, du \Rightarrow \frac{e^{-k^2/4a}}{\sqrt{a}} \int_{-\infty}^{\infty} e^{-u^2}\, du = \sqrt{\frac{\pi}{a}}\, e^{-k^2/4a}$$

$$g(k) = \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi}\right)^{1/4} \sqrt{\frac{\pi}{a}}\, e^{-k^2/4a} = \frac{1}{(2\pi a)^{1/4}} e^{-k^2/4a}$$

Thus,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \frac{1}{(2\pi a)^{1/4}} \int_{-\infty}^{\infty} e^{-k^2/4a} e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{(2\pi a)^{1/4}} \int_{-\infty}^{\infty} \exp\left[-\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right)k^2 + ixk\right] dk$$

Similar completing the square

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{(2\pi a)^{1/4}} \sqrt{\frac{\pi}{\frac{1}{4a} + i\hbar t/2m}}\, \exp\left[\frac{-x^2}{4\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right)}\right]$$

$$\boxed{\Psi(x,t) = \left(\frac{2a}{\pi}\right)^{1/4} \frac{\exp\left[-ax^2/(1+2i\hbar at/m)\right]}{\sqrt{1+2i\hbar at/m}}}$$

(ii) Let $\Gamma \equiv 2\hbar at/m$

$$\Rightarrow |\Psi|^2 = \frac{\sqrt{\frac{2a}{\pi}}\, \exp\left[\frac{-ax^2}{1+i\Gamma}\right] \exp\left[\frac{-ax^2}{1-i\Gamma}\right]}{\sqrt{(1+i\Gamma)(1-i\Gamma)}}$$

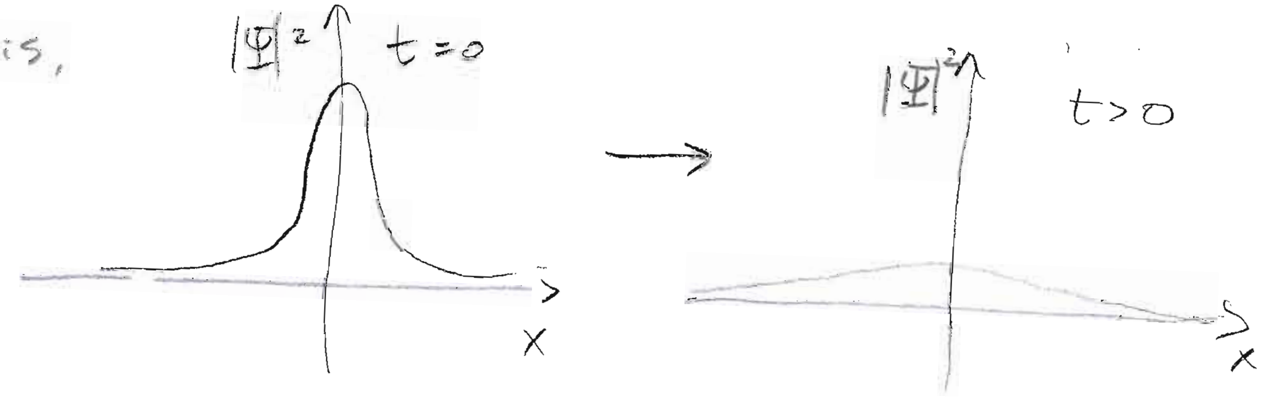
$$= \frac{\sqrt{\frac{2a}{\pi}}\, \exp\left[\frac{-2ax^2}{1+\Gamma^2}\right]}{\sqrt{1+\Gamma^2}}$$

setting $\omega \equiv \sqrt{\frac{a}{1+\Gamma^2}}$

$$\boxed{\left|\Psi(x,t)\right|^2 = \sqrt{\frac{2}{\pi}}\,\omega\, e^{-2\omega^2 x^2}}$$

(iii)
Qualitatively, as t increases Γ increases so ω decreases. The width of the Gaussian is proportional to $\frac{1}{\omega}$. Thus, as t increases the wave packet should broaden and decrease it's height.

That is,



(iv) $\langle x \rangle = \int_{-\infty}^{\infty} x\, |\Psi|^2\, dx = 0$ (odd function)

$\Rightarrow \langle p \rangle = m \frac{d\langle x \rangle}{dt} = 0$

$$\langle x^2 \rangle = \sqrt{\frac{2}{\pi}}\,\omega \int_{-\infty}^{\infty} x^2 e^{-2\omega^2 x^2} = \sqrt{\frac{2}{\pi}}\,\omega\, \frac{1}{4\omega^2}\sqrt{\frac{\pi}{2\omega^2}}$$

$$\langle x^2 \rangle = \frac{1}{4\omega^2}$$

$$\langle p^2 \rangle = -\hbar^2 \int_{-\infty}^{\infty} \Psi^* \frac{d^2}{dx^2} \Psi \, dx$$

Set $\Psi = B e^{-bx^2}$ where $B \equiv \left(\frac{2a}{\pi}\right)^{1/4} \frac{1}{\sqrt{1+i\Gamma}}$ and $b \equiv \frac{a}{1+i\Gamma}$

$$\Rightarrow \frac{d^2\Psi}{dx^2} = B \frac{d}{dx}\left(-2bx\, e^{-bx^2}\right) = -2bB(1-2bx^2)\, e^{-bx^2}$$

$$\Psi^* \frac{d^2\Psi}{dx^2} = -2b\,|B|^2 (1-2bx^2)\, e^{-(b+b^*)x^2}$$

But $$b+b^* = \frac{a}{1+i\Gamma} + \frac{a}{1-i\Gamma} = \frac{2a}{1+\Gamma^2} = 2\omega^2$$

$$|B|^2 = \sqrt{\frac{2a}{\pi}} \frac{1}{\sqrt{1+\Gamma^2}} = \sqrt{\frac{2}{\pi}}\, \omega$$

So $$\Psi^* \frac{d^2\Psi}{dx^2} = -2b\sqrt{\frac{2}{\pi}}\,\omega\,(1-2bx^2)\exp[-2\omega^2x^2]$$

$$\Rightarrow \langle p^2 \rangle = 2b\hbar^2\sqrt{\frac{2}{\pi}}\,\omega \int_{-\infty}^{\infty} (1-2bx^2)\exp[-2\omega^2x^2]\,dx$$

$$= 2b\hbar^2\sqrt{\frac{2}{\pi}}\,\omega\left[\sqrt{\frac{\pi}{2\omega^2}} - 2b\frac{1}{4\omega^2}\sqrt{\frac{\pi}{2\omega^2}}\right]$$

$$= 2b\hbar^2\left(1 - \frac{b}{2\omega^2}\right)$$

But $$\left(1-\frac{b}{2\omega^2}\right) = 1 - \left(\frac{a}{1+i\Gamma}\right)\left(\frac{1+\Gamma^2}{2a}\right) = \frac{1+i\Gamma}{2} = \frac{a}{2b}$$

$\therefore \langle p^2 \rangle = 2b\hbar^2 \cdot \frac{a}{2b} = \boxed{\hbar^2 a}$

$$\therefore \boxed{\sigma_x = \frac{1}{2w} \qquad \sigma_p = \hbar\sqrt{a}}$$

Whew!

(v) $\sigma_x \sigma_p = \frac{1}{2w} \cdot \hbar\sqrt{a} = \frac{\hbar}{2}\sqrt{1+\Gamma^2} = \frac{\hbar}{2}\sqrt{1+\left(\frac{2\hbar a t}{m}\right)^2}$

$\geq \frac{\hbar}{2}$ ✓

(vi) The system is closest to the uncertainty limit at $t=0$

In fact $\sigma_x \sigma_p = \frac{\hbar}{2}$ at $t=0$

so the particle is <u>at</u> the uncertainty limit at $t=0$

5 (i) $\Psi(x,t) = \psi(x)\, e^{-i(E_0 + i\Gamma)t/\hbar}$

$$= \psi(x)\, e^{\Gamma t/\hbar}\, e^{-iE_0 t/\hbar}$$

$$\Rightarrow |\Psi|^2 = |\psi|^2 e^{2\Gamma t/\hbar}$$

normalization condition: $\displaystyle\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = e^{2\Gamma t/\hbar} \underbrace{\int_{-\infty}^{\infty} |\psi|^2 dx}_{\text{independent of } t}$

For this to be equal to one for all t

$$\Rightarrow e^{2\Gamma t/\hbar} = \text{Constant}$$

Thus $\Gamma = 0 \Rightarrow E = E_0 + i\cancel{\Gamma}^{\,0}$

E is real Q.E.D.

(ii) If $\psi(x)$ satisfies time-independent S.E.

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

Take complex conjugate and note $V^* = V$ & $E^* = E$

$$\Rightarrow \frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^* = E\psi^*$$

Thus if ψ satisfies time-independent S.E. then so does ψ^*. Also, we know that if ψ_1 and ψ_2 satisfy time-independent SE so does any linear combination

$$\psi_3 = c_1 \psi_1 + c_2 \psi_2$$

(can easily show by plugging into Schrödinger Eqn)

$\Rightarrow$ $\left.\begin{array}{c} \psi + \psi^* \\ \text{and} \\ i(\psi - \psi^*) \end{array}\right\}$ Both are <u>real</u> and are also <u>solutions</u> to the time-independent Schrödinger Equation.

Hence, if we have a complex solution, we can always construct 2 real solutions. (If ψ is already real, the second solution will be zero.)

QED.

Quantum Mechanics: PS#3 Solutions

1. (i) $[\hat{a}_+, C] \Rightarrow [\hat{a}_+ C - C\hat{a}_+] f(x)$

$$\hat{a}_+ \equiv \frac{1}{\sqrt{2\hbar m\omega}}\left(-i\hat{p} + m\omega\hat{x}\right) = \frac{1}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right)$$

$$\hat{a}_+ C f(x) = \frac{1}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right) C\, f(x)$$

$$= \frac{C}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right) f(x)$$

$$C\,\hat{a}_+ f(x) = \frac{C}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right) f(x)$$

$$\therefore \boxed{[\hat{a}_+, C] = 0}$$

(ii) $[\hat{x}, \hat{p}] \Rightarrow [\hat{x}\hat{p} - \hat{p}\hat{x}] f(x) = \hat{x}\hat{p} f(x) - \hat{p}\hat{x} f(x)$

$$\hat{x}\hat{p} f(x) = x\frac{\hbar}{i}\frac{d}{dx} f(x)$$

$$\hat{p}\hat{x} f(x) = \frac{\hbar}{i}\frac{d}{dx}\left[x f(x)\right] = \frac{\hbar}{i}\left[f(x) + x\frac{df(x)}{dx}\right]$$

$$\hat{x}\hat{p} f(x) - \hat{p}\hat{x} f(x) = \cancel{\frac{\hbar}{i} x \frac{df(x)}{dx}} - \cancel{\frac{\hbar}{i} x \frac{df(x)}{dx}} - \frac{\hbar}{i} f(x)$$

$$\left[\hat{x}\hat{p} - \hat{p}\hat{x}\right] f(x) = -\frac{\hbar}{i} f(x) = i\hbar f(x)$$

$$\therefore \boxed{\left[\hat{x}, \hat{p}\right] = i\hbar}$$

(iii) $\left[\hat{a}_-, \hat{a}_+\right] \Longrightarrow \hat{a}_-\hat{a}_+ f(x) - \hat{a}_+\hat{a}_- f(x)$

$$\hat{a}_-\hat{a}_+ f(x) = \left(\frac{1}{2\hbar m\omega}\right)\left[i\hat{p} + m\omega\hat{x}\right]\left[-i\hat{p} + m\omega\hat{x}\right] f(x)$$

$$= \left\{\frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] - \frac{im\omega}{2\hbar m\omega}\left[\hat{x}\hat{p} - \hat{p}\hat{x}\right]\right\} f(x)$$

$$= \left\{\frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] - \frac{i}{2\hbar}\left[\hat{x}, \hat{p}\right]\right\} f(x)$$

$$= \left\{\frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] + \frac{1}{2}\right\} f(x)$$

Similarly

$$\hat{a}_+\hat{a}_- f(x) = \left\{\frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] - \frac{1}{2}\right\} f(x)$$

$$\hat{a}_-\hat{a}_+ f(x) - \hat{a}_+\hat{a}_- f(x) = 1 \cdot f(x)$$

$$\therefore \boxed{\left[\hat{a}_-, \hat{a}_+\right] = 1}$$

(iv) $\left[\frac{d^2}{dx^2}, \hat{x}\right] \Rightarrow \frac{d^2}{dx^2}\left[x f(x)\right] - x \frac{d^2 f(x)}{dx^2}$

$$= \frac{d}{dx}\left[f(x) + x\frac{df(x)}{dx}\right] - x\frac{d^2 f(x)}{dx^2}$$

$$= \frac{df(x)}{dx} + \frac{df(x)}{dx} + x\frac{d^2 f(x)}{dx} - x\frac{d^2 f(x)}{dx^2}$$

$$= 2\frac{d}{dx} f(x) \qquad \therefore \boxed{\left[\frac{d^2}{dx^2}, \hat{x}\right] = 2\frac{d}{dx}}$$

2 (i) Given $\hat{H}\psi = E\psi$, what is $\hat{H}(\hat{a}_+\psi)$?

From problem 1 (iii) we showed that

$$\hat{a}_+\hat{a}_- f(x) = \left\{\frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] - \frac{1}{2}\right\} f(x)$$

$$= \left\{\frac{\hat{H}}{\hbar\omega} - \frac{1}{2}\right\} f(x)$$

$$\Rightarrow \hat{H} f(x) = \hbar\omega\left\{\hat{a}_+\hat{a}_- + \frac{1}{2}\right\} f(x)$$

$$\Rightarrow \hat{H}(\hat{a}_+\psi) = \hbar\omega\left\{\hat{a}_+\hat{a}_- + \frac{1}{2}\right\}(\hat{a}_+\psi)$$

$$= \hbar\omega\left\{\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hat{a}_+\right\}\psi$$

$$= \hbar\omega\,\hat{a}_+\left\{\hat{a}_-\hat{a}_+ + \frac{1}{2}\right\}\psi$$

But since $[\hat{a}_-, \hat{a}_+] = 1 \Rightarrow \hat{a}_- \hat{a}_+ = \hat{a}_+ \hat{a}_- + 1$

So $\hat{H}(\hat{a}_+ \psi) = \hbar\omega\, \hat{a}_+ \left\{ \hat{a}_+ \hat{a}_- + \frac{1}{2} + 1 \right\} \psi$

$$\hat{H}(\hat{a}_+ \psi) = \hat{a}_+ \left\{ \hat{H} + \hbar\omega \right\} \psi$$

$$\hat{H}(\hat{a}_+ \psi) = \hat{a}_+ \left\{ E + \hbar\omega \right\} \psi$$

since $[\hat{a}_+, C] = 0$

$$H(\hat{a}_+ \psi) = \left\{ E + \hbar\omega \right\} (\hat{a}_+ \psi)$$

Thus $(\hat{a}_+ \psi)$ is also a solution with energy $E + \hbar\omega$

Q.E.D.

(ii) $a_- \psi_0 = 0\, \psi_0 = 0$

$$\frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0$$

OR $\hbar \frac{d}{dx} \psi_0 + m\omega x \psi_0 = 0$

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x \psi_0 \Rightarrow \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar} x\, dx$$

integrating $\int \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar} \int x\, dx$

$$\Rightarrow \ln \psi_0 = \frac{-m\omega}{2\hbar} x^2 + C$$

constant

$$\Rightarrow \psi_0 = C' \exp\left[-\frac{m\omega}{2\hbar} x^2\right]$$

normalizing $\quad |\psi_0|^2 = |C'|^2 \exp\left[-\frac{m\omega}{\hbar} x^2\right]$

$$\int_{-\infty}^{\infty} |\psi_0|^2 \, dx = 1 = |C'|^2 \int_{-\infty}^{\infty} \exp\left[-\frac{m\omega}{\hbar} x^2\right] dx$$

integral table

$$= |C'|^2 \sqrt{\frac{\pi\hbar}{m\omega}}$$

$$\Rightarrow |C'|^2 = \sqrt{\frac{m\omega}{\pi\hbar}} \Rightarrow C' = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

$$\therefore \boxed{\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} x^2\right]}$$

(3) Since $\psi_n = \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0$ and here $n = 1$

$$\Rightarrow \psi_1 = 1 \cdot \hat{a}_+ \psi_0 = \frac{1}{\sqrt{2\hbar m\omega}} \left(-\hbar \frac{d}{dx} + m\omega x\right) \psi_0$$

$$\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{(2\hbar m\omega)^{1/2}} \left[(-\cancel{\hbar})\left(-\frac{m\omega}{\cancel{2\hbar}}\right)\cancel{2}x + m\omega x\right] \exp\left[-\frac{m\omega}{2\hbar} x^2\right]$$

$$\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{(2\hbar m\omega)^{1/2}} \left[2 m\omega x \exp\left(-\frac{m\omega}{2\hbar} x^2\right)\right]$$

$$\boxed{\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(\frac{2m\omega}{\hbar}\right)^{1/2} x \exp\left[-\frac{m\omega}{2\hbar} x^2\right]}$$

(4) $\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[\frac{-m\omega}{2\hbar}x^2\right] = \alpha \exp\left(\frac{-\xi^2}{2}\right)$

$\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(\frac{2m\omega}{\hbar}\right)^{1/2} \cdot x \cdot \exp\left[\frac{-m\omega}{2\hbar}x^2\right] = \sqrt{2}\,\alpha\,\xi \cdot \exp\left(\frac{-\xi^2}{2}\right)$

Note: ψ_0 is even $\Rightarrow$ $\psi_0^* \cdot x \cdot \psi_0$ is odd

ψ_1 is odd $\Rightarrow$ $\psi_1^* \cdot x \cdot \psi_1$ is odd

Thus, for $\underline{n=0}$ $\langle x \rangle = \int_{-\infty}^{\infty} \psi_0^* x \psi_0 \, dx = 0$

$$\boxed{\langle x \rangle_0 = 0}$$

and $\langle p \rangle_0 = m \frac{d\langle x \rangle}{dt} = 0 \Rightarrow \boxed{\langle p \rangle_0 = 0}$

Similarly for $\underline{n=1}$ $\boxed{\begin{array}{l} \langle x \rangle_1 = 0 \\ \langle p \rangle_1 = 0 \end{array}}$

In fact, this holds for all ψ_n for harmonic oscillator!

For $\underline{n=0}$ $\langle x^2 \rangle_0 = \alpha^2 \int_{-\infty}^{\infty} x^2 \exp\left[-\xi^2\right] dx$

use $\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} x \Rightarrow x^2 = \frac{\hbar}{m\omega}\xi^2$ $dx = \left(\frac{\hbar}{m\omega}\right)^{1/2} d\xi$

$$\Rightarrow \langle x^2 \rangle_0 = \alpha^2 \left(\frac{\hbar}{m\omega}\right)^{3/2} \int_{-\infty}^{\infty} \xi^2 e^{-\xi^2} d\xi$$

From integral tables: $\langle x^2 \rangle_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \left(\frac{\hbar}{m\omega}\right)^{3/2} \frac{\sqrt{\pi}}{2}$

$$\therefore \boxed{\langle x^2 \rangle_0 = \frac{\hbar}{2m\omega}}$$

and $\langle p^2 \rangle_0 = -\hbar^2 \alpha^2 \int_{-\infty}^{\infty} \exp\left[-\frac{\xi^2}{2}\right] \frac{d^2}{dx^2} \exp\left[-\frac{\xi^2}{2}\right] dx$

since $dx = \left(\frac{\hbar}{m\omega}\right)^{1/2} d\xi$

$$\langle p^2 \rangle_0 = -\hbar^2 \alpha^2 \left(\frac{m\omega}{\hbar}\right)^{1/2} \int_{-\infty}^{\infty} \exp\left[-\frac{\xi^2}{2}\right] \frac{d^2}{d\xi^2} \exp\left[-\frac{\xi^2}{2}\right] d\xi$$

$$= \underbrace{-\hbar^2 \alpha^2 \left(\frac{m\omega}{\hbar}\right)^{1/2}}_{} \int_{-\infty}^{\infty} (\xi^2 - 1) \exp\left[-\xi^2\right] d\xi$$

$$= -\frac{m\hbar\omega}{\sqrt{\pi}} \left[\frac{\sqrt{\pi}}{2} - \sqrt{\pi}\right] = \frac{m\hbar\omega}{2}$$

$$\therefore \boxed{\langle p^2 \rangle_0 = \frac{m\hbar\omega}{2}}$$

For $n=1$ $\quad \langle x^2 \rangle_1 = 2\alpha^2 \int_{-\infty}^{\infty} x^2 \cdot \xi^2 \exp\left[-\xi^2\right] dx$

$$x^2 = \frac{\hbar}{m\omega} \xi^2 \qquad dx = \left(\frac{\hbar}{m\omega}\right)^{1/2} d\xi$$

$$\langle x^2 \rangle_1 = 2\alpha^2 \left(\frac{\hbar}{m\omega}\right)^{3/2} \underbrace{\int_{-\infty}^{\infty} \xi^4 \exp\left[-\xi^2\right] d\xi}$$

from integral tables $\Rightarrow \langle x^2 \rangle_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \left(\frac{\hbar}{m\omega}\right)^{3/2} \cdot 2 \cdot \frac{3}{4}\sqrt{\pi}$

$$\therefore \boxed{\langle x^2 \rangle_1 = \frac{3\hbar}{2m\omega}}$$

$$\langle p^2 \rangle_1 = -\hbar^2 \, 2\alpha^2 \left(\frac{m\omega}{\hbar}\right)^{1/2} \int_{-\infty}^{\infty} \xi \exp\left[-\frac{\xi^2}{2}\right] \frac{d^2}{d\xi^2}\left(\xi \exp\left[-\frac{\xi^2}{2}\right]\right) d\xi$$

$$= -\hbar^2 \, 2 \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \left(\frac{m\omega}{\hbar}\right)^{1/2} \int_{-\infty}^{\infty} \left(\xi^4 - 3\xi^2\right) \exp\left[-\xi^2\right] d\xi$$

$$= -\frac{2 m\hbar\omega}{\cancel{\sqrt{\pi}}} \left[\frac{3}{4}\cancel{\sqrt{\pi}} - \frac{3}{2}\cancel{\sqrt{\pi}}\right] = \frac{3}{2} m\hbar\omega$$

$$\therefore \boxed{\langle p^2 \rangle_1 = \frac{3}{2} m\hbar\omega}$$

(ii) For $\underline{n=0}$ $\quad \langle x^2 \rangle_0 - \langle x \rangle_0^2 = \sigma_x^2 = \frac{\hbar}{2m\omega}$

$$\Rightarrow \sigma_x = \sqrt{\frac{\hbar}{2m\omega}}$$

$$\langle p^2 \rangle_0 - \langle p \rangle_0^2 = \sigma_p^2 = \frac{m\hbar\omega}{2}$$

$$\Rightarrow \sigma_p = \sqrt{\frac{m\hbar\omega}{2}}$$

$$\boxed{\sigma_x \cdot \sigma_p = \frac{\hbar}{2}}_{n=0}$$

right at uncertainty limit!

Similarly, for $\underline{n=1}$ $\quad \sigma_x = \sqrt{\frac{3\hbar}{2m\omega}} \quad \sigma_p = \sqrt{\frac{3}{2} m\hbar\omega}$

$$\boxed{\sigma_x \sigma_p = \frac{3}{2}\hbar > \frac{\hbar}{2}} \checkmark$$

PS #3 Solutions cont.

(iii) For $\underline{n=0}$ $\langle T\rangle_0 = \frac{1}{2m}\langle p^2\rangle_0 = \frac{\hbar\omega}{4}$

$$\langle V\rangle_0 = \frac{1}{2}m\omega^2\langle x^2\rangle_0 = \frac{\hbar\omega}{4}$$

$$\boxed{\langle T\rangle_0 + \langle V\rangle_0 = \frac{\hbar\omega}{2}}$$ as $\underline{\text{expected}}$ for E_0

For $n=1$ $\langle T\rangle_1 = \frac{1}{2m}\langle p^2\rangle_1 = \frac{3}{4}\hbar\omega$

$$\langle V\rangle_1 = \frac{1}{2}m\omega^2\langle x^2\rangle_1 = \frac{3}{4}\hbar\omega$$

$$\boxed{\langle T\rangle_1 + \langle V\rangle_1 = \frac{3}{2}\hbar\omega}$$ as $\underline{\text{expected}}$ for E_1

Quantum Mechanics Problem Set #4 Solutions

(1.) (i) • Is ψ_1 of H.O. even or odd?

Let $\alpha \equiv \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \Rightarrow \psi_1 = \frac{\alpha}{\sqrt{2}}\, 2\xi \exp\left[-\frac{\xi^2}{2}\right]$

$$\underbrace{2\xi}_{\text{odd}} \cdot \underbrace{\exp\left[-\frac{\xi^2}{2}\right]}_{\text{even}} = \boxed{\text{odd}}$$

• Is ψ_3 of H.O. even or odd?

$$\psi_3 = \frac{\alpha}{\sqrt{8\cdot 6}}\left(8\xi^3 - 12\xi\right)\cdot \exp\left[-\frac{\xi^2}{2}\right]$$

$$\text{odd} \cdot \text{odd} \cdot \text{even} = \boxed{\text{odd}}$$

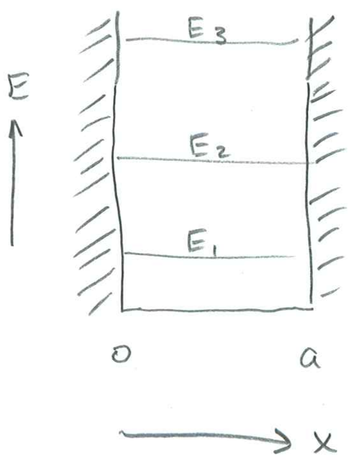
As we would expect. Remember for H.O., ψ_0 is the even ground state. Thus, we would expect:

$\psi_0, \psi_2, \psi_4 \cdots$ even

$\psi_1, \psi_3, \psi_5 \cdots$ odd

(ii) For infinite square well, $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$

So we must evaluate $\langle \psi_1 | \psi_3 \rangle = \int_0^a \psi_1^* \psi_3 \, dx$



note limits of integration are only over contents of square well!

$$\langle \psi_1 | \psi_3 \rangle = \int_0^a \left(\frac{2}{a}\right) \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{3\pi}{a} x\right) dx$$

Using the identity

$$\sin\theta\,\sin\varphi = \frac{1}{2}\Big(\cos(\theta-\varphi) - \cos(\theta+\varphi)\Big)$$

$$\Rightarrow \langle \psi_1 | \psi_3 \rangle = \frac{2}{a}\frac{1}{2}\int_0^a \left\{ \left[\cos\frac{2\pi}{a}x\right] - \left[\cos\frac{4\pi}{a}x\right] \right\} dx$$

$$= \frac{1}{a}\left[\frac{a}{2\pi}\sin\left(\frac{2\pi}{a}x\right)\Big|_0^a - \frac{a}{4\pi}\sin\left(\frac{4\pi}{a}x\right)\Big|_0^a \right]$$

$$= \frac{1}{a}\left[\frac{a}{2\pi}\left[\underbrace{\sin 2\pi}_{0} - \underbrace{\sin 0}_{0}\right] - \frac{a}{4\pi}\left[\underbrace{\sin 4\pi}_{0} - \underbrace{\sin 0}_{0}\right]\right]$$

$$= 0 \quad \checkmark$$

---

(2) To be Hermitian operator $\Rightarrow \langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$

(i) When $\hat{Q} = \hat{x}$ $\Rightarrow \langle f | \hat{x} g \rangle = \int f^* x\, g\, dx$

but $x^* = x$ and $[f^*(x), x] = 0$

So $\langle f | \hat{x} g \rangle = \int (xf)^* g\, dx = \langle \hat{x} f | g \rangle$ ✓

(ii) When $\hat{Q} = \hat{p} = \frac{\hbar}{i}\frac{d}{dx} \Rightarrow \langle f | \frac{\hbar}{i}\frac{dg}{dx} \rangle = \int_{-\infty}^{\infty} f^* \frac{\hbar}{i}\frac{dg}{dx}\, dx$

Use integration by parts: $\int_a^b f \frac{dg}{dx}\, dx = -\int_a^b g\frac{df}{dx}\, dx + fg\Big|_a^b$

$$\Rightarrow \langle f | \frac{\hbar}{i}\frac{dg}{dx} \rangle = -\int_{-\infty}^{\infty} g \cdot \frac{\hbar}{i}\frac{d}{dx} f^*\, dx + \underbrace{\frac{\hbar}{i} f^* g\Big|_{-\infty}^{\infty}}_{0}$$

(as usual, to be physical)

$$= \int_{-\infty}^{\infty} g \left[\frac{\hbar}{i}\frac{d}{dx}\right]^* f^*\, dx$$

or $$\langle f|\hat{p}g\rangle = \int_{-\infty}^{\infty}\left[\frac{\hbar}{i}\frac{d}{dx}f\right]^* \cdot g\,dx$$

$$\langle f|\hat{p}g\rangle = \left\langle\left(\frac{\hbar}{i}\frac{d}{dx}\right)f\middle|g\right\rangle = \langle\hat{p}f|g\rangle \quad \checkmark$$

(iii) When $\hat{O}_1$ and $\hat{O}_2$ are Hermitian

$$\langle f|(\hat{O}_1+\hat{O}_2)g\rangle = \langle f|\hat{O}_1 g\rangle + \langle f|\hat{O}_2 g\rangle$$
$$= \langle\hat{O}_1 f|g\rangle + \langle\hat{O}_2 f|g\rangle$$
$$= \langle(\hat{O}_1+\hat{O}_2)f|g\rangle \quad \checkmark$$

(iv) Given $\hat{O}_1$ and $\hat{O}_2$ as Hermitian operators:

$$\langle f|\hat{O}_1(\hat{O}_2 g)\rangle = \langle\hat{O}_1 f|\hat{O}_2 g\rangle = \langle\hat{O}_2\hat{O}_1 f|g\rangle$$

If $\hat{O}_2\hat{O}_1 = \hat{O}_1\hat{O}_2$ then $\langle\hat{O}_1\hat{O}_2 f|g\rangle$

and then the product $\hat{O}_1\hat{O}_2$ is Hermitian

Thus $\underline{\hat{O}_1\hat{O}_2 \text{ is Hermitian if and only if } [\hat{O}_1,\hat{O}_2]=0}$

---

(3) Given $\langle h|\hat{Q}h\rangle = \langle\hat{Q}h|h\rangle$ for all h

let $h = f+g \Rightarrow \underbrace{\langle f+g|\hat{Q}(f+g)\rangle}_{\text{LHS}} = \underbrace{\langle\hat{Q}(f+g)|f+g\rangle}_{\text{RHS}}$

$$\text{OR} \quad \overbrace{\cancel{\langle f|\hat{Q}f\rangle} + \langle f|\hat{Q}g\rangle + \langle g|\hat{Q}f\rangle + \cancel{\langle g|\hat{Q}g\rangle}}^{LHS}$$

$$= \underbrace{\cancel{\langle \hat{Q}f|f\rangle} + \langle \hat{Q}f|g\rangle + \langle \hat{Q}g|f\rangle + \cancel{\langle \hat{Q}g|g\rangle}}_{RHS}$$

Since $\langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle$ and $\langle g|\hat{Q}g\rangle = \langle \hat{Q}g|g\rangle$

$$\Rightarrow \quad \langle f|\hat{Q}g\rangle + \langle g|\hat{Q}f\rangle = \langle \hat{Q}f|g\rangle + \langle \hat{Q}g|f\rangle \qquad \text{(a)}$$

Now let $h = f + ig \Rightarrow \langle f+ig|\hat{Q}(f+ig)\rangle = \langle \hat{Q}(f+ig)|f+ig\rangle$

Same procedure as above yields:

$$i\langle f|\hat{Q}g\rangle - i\langle g|\hat{Q}f\rangle = i\langle \hat{Q}f|g\rangle - i\langle \hat{Q}g|f\rangle$$

$$\langle f|\hat{Q}g\rangle - \langle g|\hat{Q}f\rangle = \langle \hat{Q}f|g\rangle - \langle \hat{Q}g|f\rangle \qquad \text{(b)}$$

$$\text{(a)} + \text{(b)} \quad \Rightarrow \quad 2\langle f|\hat{Q}g\rangle = 2\langle \hat{Q}f|g\rangle$$

$$\text{OR} \quad \boxed{\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle} \quad \text{Q.E.D.}$$

---

(4) Remember $\displaystyle\int_{-\infty}^{\infty} f(x)\,\delta(x-a)\,dx \Rightarrow f(a)$

and from Plancherel's theorem $\longrightarrow$

lecture #3

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$$

where $F(k)$ is the Fourier transform of $f(x)$

$\Rightarrow$ F.T. of $\delta(x)$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \delta(x') e^{-ikx'} dx' = \frac{1}{\sqrt{2\pi}} e^{-ik\cdot 0} = \frac{1}{\sqrt{2\pi}}$$

and by Plancherel's theorem:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} dk = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk \quad \checkmark$$

Q.E.D.

---

5 Ground state of infinite square well $\Rightarrow \psi_1$

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right) \Rightarrow \hat{p}\psi_1 = \frac{\hbar}{i} \frac{d}{dx} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right)$$

$$= \frac{\hbar}{i} \sqrt{\frac{2}{a}} \cdot \frac{\pi}{a} \cos\left(\frac{\pi}{a} x\right)$$

Can be rewritten as:

$$\overbrace{\frac{\hbar}{i} \cdot \frac{\pi}{a}}^{C} \; \frac{\cos \frac{\pi}{a} x}{\sin \frac{\pi}{a} x} \cdot \overbrace{\sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right) x}^{\psi_1} = C \cdot \cot \frac{\pi}{a} x \cdot \psi_1$$

Since $\hat{p}\,\psi_1$ is not equal to a constant $\cdot\ \psi_1$

$\Rightarrow$ ψ_1 is <u>not</u> an eigenfunction of $\hat{p}$

Why not? Bcs eigensolutions (ψ_n) to infinite square well are standing waves that are mixtures of waves moving to the right and left

$\Rightarrow$ have both positive & negative momenta.

Intro to QM: Problem Set #5 Solutions

(1.) See the proof below from Griffiths p. 110-111.

3.5 THE UNCERTAINTY PRINCIPLE

I stated the uncertainty principle (in the form $\sigma_x \sigma_p \geq \hbar/2$), back in Section 1.6, and you have checked it several times, in the problems. But we have never actually *proved* it. In this section I will prove a more general version of the uncertainty principle, and explore some of its implications. The argument is beautiful, but rather abstract, so watch closely.

3.5.1 Proof of the Generalized Uncertainty Principle

For any observable A, we have (Equation 3.21):

$$\sigma_A^2 = \langle(\hat{A} - \langle A\rangle)\Psi|(\hat{A} - \langle A\rangle)\Psi\rangle = \langle f|f\rangle,$$

where $f \equiv (\hat{A} - \langle A\rangle)\Psi$. Likewise, for any *other* observable, B,

$$\sigma_B^2 = \langle g|g\rangle, \quad \text{where } g \equiv (\hat{B} - \langle B\rangle)\Psi.$$

Therefore (invoking the Schwarz inequality, Equation 3.7),

$$\sigma_A^2\sigma_B^2 = \langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2. \qquad [3.59]$$

Now, for any complex number z,

$$|z|^2 = [\text{Re}(z)]^2 + [\text{Im}(z)]^2 \geq [\text{Im}(z)]^2 = \left[\frac{1}{2i}(z - z^*)\right]^2. \qquad [3.60]$$

Therefore, letting $z = \langle f|g\rangle$,

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}[\langle f|g\rangle - \langle g|f\rangle]\right)^2. \qquad [3.61]$$

But

$$\begin{aligned}\langle f|g\rangle &= \langle(\hat{A} - \langle A\rangle)\Psi|(\hat{B} - \langle B\rangle)\Psi\rangle = \langle\Psi|(\hat{A} - \langle A\rangle)(\hat{B} - \langle B\rangle)\Psi\rangle \\ &= \langle\Psi|(\hat{A}\hat{B} - \hat{A}\langle B\rangle - \hat{B}\langle A\rangle + \langle A\rangle\langle B\rangle)\Psi\rangle \\ &= \langle\Psi|\hat{A}\hat{B}\Psi\rangle - \langle B\rangle\langle\Psi|\hat{A}\Psi\rangle - \langle A\rangle\langle\Psi|\hat{B}\Psi\rangle + \langle A\rangle\langle B\rangle\langle\Psi|\Psi\rangle \\ &= \langle\hat{A}\hat{B}\rangle - \langle B\rangle\langle A\rangle - \langle A\rangle\langle B\rangle + \langle A\rangle\langle B\rangle \\ &= \langle\hat{A}\hat{B}\rangle - \langle A\rangle\langle B\rangle.\end{aligned}$$

Similarly,

$$\langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle A\rangle\langle B\rangle,$$

PS #5 solutions, cont.

Pg. 2

so

$$\langle f|g\rangle - \langle g|f\rangle = \langle \hat{A}\hat{B}\rangle - \langle \hat{B}\hat{A}\rangle = \langle [\hat{A}, \hat{B}]\rangle,$$

where

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

is the commutator of the two operators (Equation 2.48). *Conclusion:*

$$\boxed{\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}\langle [\hat{A}, \hat{B}]\rangle\right)^2.} \qquad [3.62]$$

2 (i) $[\hat{A}\hat{B}, \hat{C}] = \hat{A}\hat{B}\hat{C} - \hat{C}\hat{A}\hat{B}$

$$= \hat{A}\hat{B}\hat{C} - \hat{A}\hat{C}\hat{B} + \hat{A}\hat{C}\hat{B} - \hat{C}\hat{A}\hat{B}$$

$$= \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} \quad \checkmark$$

(ii) Use test function, $f(x)$:

$$[\hat{x}^n, \hat{p}] f(x) = x^n \frac{\hbar}{i} \frac{df}{dx} - \frac{\hbar}{i} \frac{d}{dx}\left(x^n f(x)\right)$$

$$= x^n \frac{\hbar}{i} \frac{df}{dx} - \frac{\hbar}{i}\left[n x^{n-1} f + x^n \frac{df}{dx}\right]$$

$$= -\frac{\hbar}{i} n x^{n-1} f(x)$$

$$= i\hbar n x^{n-1} f(x)$$

OR $[\hat{x}^n, \hat{p}] = i\hbar n x^{n-1}$ ✓

(iii) Use test function $g(x)$:

$$[f(\hat{x}), \hat{p}] g(x) = f \frac{\hbar}{i} \frac{dg}{dx} - \frac{\hbar}{i} \frac{d}{dx}(fg)$$

$$= \frac{\hbar}{i}\left(f \frac{dg}{dx} - f \frac{dg}{dx} - g \frac{df}{dx}\right)$$

$$= i\hbar g \frac{df}{dx} = i\hbar \frac{df}{dx} \cdot g$$

since $\left[g, \frac{df}{dx}\right] = 0$.

eliminating test function, $g \Rightarrow [f(\hat{x}), p] = i\hbar \frac{df}{dx}$ ✓

(3) To use the generalized uncertainty principle for $\hat{A} = \hat{x}$ and $\hat{B} = \hat{H} \equiv \frac{\hat{p}^2}{2m} + \hat{V}$, we need

$$[\hat{x}, \hat{H}] = \frac{1}{2m}[\hat{x}, \hat{p}^2] + [\hat{x}, \hat{V}]$$

$$[\hat{x}, \hat{p}^2] = \hat{x}\hat{p}^2 - \hat{p}^2\hat{x} = \hat{x}\hat{p}\hat{p} - \hat{p}\hat{p}\hat{x}$$

$$= \hat{x}\hat{p}\hat{p} - \hat{p}\hat{x}\hat{p} + \hat{p}\hat{x}\hat{p} - \hat{p}\hat{p}\hat{x}$$

$$= [\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}]$$

$$= i\hbar\hat{p} + \hat{p}\, i\hbar = 2i\hbar\hat{p}$$

$$[\hat{x}, \hat{V}] = [x, V(x)] = 0$$

Thus, $[\hat{x}, \hat{H}] = \frac{1}{2m}(2i\hbar\hat{p}) + 0$

$$= \frac{i\hbar\hat{p}}{m}$$

Generalized Uncertainty principle thus gives ...

$$\sigma_{\hat{x}}^2 \sigma_{\hat{H}}^2 \geq \left(\frac{1}{2i}\left\langle\frac{i\hbar\hat{p}}{m}\right\rangle\right)^2 = \left(\frac{\hbar}{2m}\langle\hat{p}\rangle\right)^2$$

OR $$\sigma_{\hat{x}} \sigma_{\hat{H}} \geq \frac{\hbar}{2m}|\langle\hat{p}\rangle| \quad \checkmark$$

For a stationary state $\sigma_{\hat{H}} = 0$ and $\langle\hat{p}\rangle = 0$

So this relation does not tell us anything.

It says $0 \geq 0$

4. (i) We need $\sigma_{\hat{H}}^2 = \langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2$

$\hat{H}\Psi_n = E_n\Psi_n$ and $\hat{H}^2\Psi_n = E_n^2\Psi_n$

$$\Rightarrow \langle\hat{H}^2\rangle = \frac{1}{2}\left\langle\left(\Psi_1 e^{-iE_1t/\hbar} + \Psi_2 e^{-iE_2t/\hbar}\right)\Big|\left(E_1^2\Psi_1 e^{-iE_1t/\hbar} + E_2^2\Psi_2 e^{-iE_2t/\hbar}\right)\right\rangle$$

$$= \frac{1}{2}\Big\{\langle\Psi_1|\Psi_1\rangle\cdot E_1^2 + \cancelto{0}{\langle\Psi_1|\Psi_2\rangle}\cdot E_2^2 e^{-i(E_2-E_1)t/\hbar}$$

$$+ \cancelto{0}{\langle\Psi_2|\Psi_1\rangle}\cdot E_1^2 e^{-i(E_1-E_2)t/\hbar} + \langle\Psi_2|\Psi_2\rangle\cdot E_2^2\Big\}$$

$$= \frac{1}{2}\left\{E_1^2 + E_2^2\right\}$$

Similarly, $\langle\hat{H}\rangle = \frac{1}{2}\{E_1 + E_2\}$ See PS # 2 problem 2

$$\Rightarrow \sigma_{\hat{H}}^2 = \frac{1}{2}\left\{E_1^2 + E_2^2\right\} - \frac{1}{4}\left\{E_1 + E_2\right\}^2$$

OR $\sigma_{\hat{H}}^2 = \frac{1}{4}(E_2 - E_1)^2 \Rightarrow \sigma_{\hat{H}} = \frac{1}{2}(E_2 - E_1)$

(ii) $\sigma_{\hat{x}}^2 = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2$

$$\langle \hat{x}^2 \rangle = \frac{1}{2}\Big\{ \langle \psi_1 | x^2 \psi_1 \rangle + \langle \psi_2 | x^2 \psi_2 \rangle$$
$$+ \langle \psi_1 | x^2 \psi_2 \rangle \exp[i(E_1 - E_2)t/\hbar]$$
$$+ \langle \psi_2 | x^2 \psi_1 \rangle \exp[i(E_2 - E_1)t/\hbar] \Big\}$$

For infinite square well with $m \neq n$:

$$\langle \psi_n | x^2 \psi_m \rangle = \frac{2}{a}\int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right)\sin\left(\frac{m\pi}{a}x\right)$$

$$= \frac{2}{a}\cdot\frac{1}{2}\left\{ \int_0^a x^2 \cos\left[\frac{(n-m)\pi x}{a}\right]dx - \int_0^a x^2 \cos\left[\frac{(n+m)\pi x}{a}\right]dx \right\}$$

using integral tables:

$$= \frac{1}{a}\Bigg\{ \frac{2a^2 x}{(n-m)^2\pi^2}\cdot\cos\left[\frac{(n-m)\pi x}{a}\right] + \left(\frac{a}{(n-m)\pi}\right)x^2 \sin\left[\frac{(n-m)\pi x}{a}\right]$$
$$- \frac{2a^3}{(n-m)^3\pi^3}\sin\left[\frac{(n-m)\pi x}{a}\right] - \frac{2a^2 x}{(n+m)^2\pi^2}\cos\left[\frac{(n+m)\pi x}{a}\right]$$
$$- \left(\frac{a}{(n+m)\pi}\right)x^2 \sin\left[\frac{(n+m)\pi x}{a}\right] + \frac{2a^3}{(n+m)^3\pi^3}\sin\left[\frac{(n+m)\pi x}{a}\right]\Bigg\}\Bigg|_0^a$$

$$= \Bigg\{ \frac{2a^2}{(n-m)^2\pi^2} \cdot \cos\left[\cancelto{(-1)^{n-m}}{(n-m)\pi}\right] + \frac{a^2}{(n-m)\pi} \sin\left[\cancelto{0}{(n-m)\pi}\right] - \frac{2a^2}{(n-m)^3\pi^3} \sin\left[\cancelto{0}{(n-m)\pi}\right]$$

$$+ \frac{2a^2}{(n+m)^2\pi^2} \cos\left[\cancelto{(-1)^{n+m}}{(n+m)\pi}\right] - \frac{a^2}{(n+m)\pi} \sin\left[\cancelto{0}{(n+m)\pi}\right] + \frac{2a^2}{(n+m)^3\pi^3} \sin\left[\cancelto{0}{(n+m)\pi}\right]$$

$$+ \frac{2a^2}{(n-m)^3\pi^3} \sin\left[\cancelto{0}{0}\right] - \frac{2a^2}{(n+m)^3\pi^3} \sin\left[\cancelto{0}{0}\right] \Bigg\}$$

$$= \frac{2a^2}{\pi^2} \left[\frac{(-1)^{n-m}}{(n-m)^2} - \frac{(-1)^{n+m}}{(n+m)^2} \right]$$

$$\therefore \quad \left.\begin{matrix} \langle \psi_1 | x^2 \psi_2 \rangle \\ \langle \psi_2 | x^2 \psi_1 \rangle \end{matrix}\right\} = \frac{-16a^2}{9\pi^2}$$

PS #2 problem #1

Also $\langle \psi_n | x^2 \psi_n \rangle = a^2 \left[\frac{1}{3} - \frac{1}{2(n\pi)^2} \right]$

Thus, $$\langle x^2 \rangle = \frac{1}{2} \Bigg\{ a^2 \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) + a^2 \left(\frac{1}{3} - \frac{1}{8\pi^2} \right)$$

$$- \frac{16a^2}{9\pi^2} \Bigg[\underbrace{\exp\{ i(E_1 - E_2)t/\hbar \} + \exp\{ i(E_2 - E_1)t/\hbar \}}_{\cos x + i\sin x + \cos(-x) + i\sin(-x)} \Bigg] \Bigg\}$$

$$2\cos x + i\cancel{\sin x} - i\cancel{\sin x}$$

$$= 2\cos\left[(E_1 - E_2)t/\hbar\right] = 2\cos\left[(E_2 - E_1)\frac{t}{\hbar}\right]$$

$$\langle x^2 \rangle = \frac{a^2}{2} \left\{ \frac{2}{3} - \frac{5}{8\pi^2} - \frac{32}{9\pi^2} \cos\left[(E_2 - E_1)t/\hbar\right] \right\}$$

Using notation from PS#2, problem #2

$$\frac{E_2 - E_1}{\hbar} = 3\omega \quad \text{where} \quad \omega \equiv \frac{\pi^2 \hbar^2}{2ma^2}$$

So $$\langle x^2 \rangle = \frac{a^2}{2}\left[\frac{2}{3} - \frac{5}{8\pi^2} - \frac{32}{9\pi^2}\cos(3\omega t)\right]$$

$$\langle x \rangle = \frac{a}{2}\left[1 - \frac{32}{9\pi^2}\cos(3\omega t)\right] \Longleftarrow \text{PS \#2 problem \#2}$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{4}\left[\frac{4}{3} - \frac{5}{4\pi^2} - \frac{64}{9\pi^2}\cos(3\omega t) - 1 + \frac{64}{9\pi^2}\cos(3\omega t) - \left[\frac{32}{9\pi^2}\right]^2 \cos^2(3\omega t)\right]$$

$$\sigma_x^2 = \frac{a^2}{4}\left[\frac{1}{3} - \frac{5}{4\pi^2} - \left(\frac{32}{9\pi^2}\right)^2 \cos^2(3\omega t)\right]$$

(iii)

Finally $$\frac{d\langle x \rangle}{dt} = \frac{8\hbar}{3ma}\sin(3\omega t) \Longleftarrow \text{Ps \#2 problem \#2 (iv)}$$

(iv)

Time-Energy uncertainty relationship:

$$\sigma_{\hat{H}}^2 \sigma_{\hat{Q}}^2 \geq \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle Q \rangle}{dt}\right)^2$$

or here:

$$\sigma_{\hat{H}}^2 \sigma_{\hat{x}}^2 \geq \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle x \rangle}{dt}\right)^2$$

$$\sigma_{\hat{H}}^2 \sigma_{\hat{x}}^2 = \frac{1}{4}(3\hbar\omega)^2 \cdot \frac{a^2}{4}\left[\frac{1}{3} - \frac{5}{4\pi^2} - \left(\frac{32}{9\pi^2}\right)^2 \cos^2(3\omega t)\right]$$

$$= (\hbar\omega a)^2 \left(\frac{3}{4}\right)^2 \left[\frac{1}{3} - \frac{5}{4\pi^2} - \left(\frac{32}{9\pi^2}\right)^2 \cos^2(3\omega t)\right]$$

$$\frac{\hbar^2}{4}\left(\frac{d\langle x\rangle}{dt}\right)^2 = \frac{\hbar^2}{4} \frac{64\hbar^2}{9m^2a^2} \sin^2(3\omega t)$$

Since $\frac{\hbar}{ma} = \frac{2a\omega}{\pi}$

$$\frac{\hbar^2}{4}\left(\frac{d\langle x\rangle}{dt}\right)^2 = \left(\frac{8}{3\pi^2}\right)^2 (\hbar\omega a)^2 \sin^2(3\omega t)$$

For uncertainty relationship to hold:

$$\left(\frac{3}{4}\right)^2\left[\frac{1}{3} - \frac{5}{4\pi^2} - \left(\frac{32}{9\pi^2}\right)^2 \cos(3\omega t)\right] \geq \left(\frac{8}{3\pi^2}\right)^2 \sin^2(3\omega t)$$

OR

$$\left(\frac{1}{3} - \frac{5}{4\pi^2}\right) \geq \left(\frac{32}{9\pi^2}\right)^2 \cos^2(3\omega t) + \left(\frac{32}{9\pi^2}\right)^2 \sin^2(3\omega t)$$

$$\left(\frac{1}{3} - \frac{5}{4\pi^2}\right) \geq \left(\frac{32}{9\pi^2}\right)^2$$

$0.207 \geq 0.130$ ✓ it holds!

Quantum Mechanics: Problem Set #6 Solutions

(1.) (a) all the Cartesian coordinates, x, y, z commute with each other, i.e.

$[\hat{x},\hat{y}] = xy - yx = 0$

So $\boxed{[\hat{x},\hat{y}] = [\hat{x},\hat{z}] = [\hat{y},\hat{z}] = 0}$

We know from previous work that $[\hat{x},\hat{p}_x] = i\hbar$

Similarly, $\boxed{[\hat{y},\hat{p}_y] = [\hat{z},\hat{p}_z] = [\hat{x},\hat{p}_x] = i\hbar}$

Mixed terms like $[\hat{x},\hat{p}_y]f = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y}f - \frac{\partial}{\partial y}(xf)\right)$

$$= \frac{\hbar}{i}\left(x\frac{\partial f}{\partial y} - x\frac{\partial f}{\partial y}\right) = 0$$

So $\boxed{[\hat{x},\hat{p}_y] = [\hat{x},\hat{p}_z] = [\hat{y},\hat{p}_x] = [\hat{y},\hat{p}_z] = [\hat{z},\hat{p}_x] = [\hat{z},\hat{p}_y] = 0}$

Finally, terms like $[\hat{p}_x,\hat{p}_y]f = -\hbar^2\left[\frac{\partial}{\partial x}\frac{\partial}{\partial y}f - \frac{\partial}{\partial y}\frac{\partial}{\partial x}f\right]$

(bcs order of derivatives of different coordinates does not matter) $= 0$

$\therefore$ $\boxed{[\hat{p}_x,\hat{p}_y] = [\hat{p}_y,\hat{p}_z] = [\hat{p}_z,\hat{p}_x] = 0}$

(b)

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y,\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z]$$

$$= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) - (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)$$

$$= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - \underset{0}{[\hat{y}\hat{p}_z, \hat{x}\hat{p}_z]} - \underset{0}{\cancel{[\hat{z}\hat{p}_y, \hat{z}\hat{p}_x]}} + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z]$$

From commutation relations above, we can see

$$= \hat{y}\hat{p}_x \overset{-i\hbar}{[\hat{p}_z, \hat{z}]} + \hat{x}\hat{p}_y \overset{i\hbar}{[\hat{z}, \hat{p}_z]}$$

$$= i\hbar \left\{ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \right\} = i\hbar \hat{L}_z$$

The others can be similarly derived, or we can use permutation of the Cartesian coordinates:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

2. (a) Start with: $-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) = E\psi$

Separable solutions $\Rightarrow$ $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$

plug in $\Rightarrow$ $\frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{Y}\frac{d^2 Y}{dy^2} + \frac{1}{Z}\frac{d^2 Z}{dz^2} = -\frac{2m}{\hbar^2}E$

For this to be true $\Rightarrow$ each term on L.H.S. must be equal to constant

Let's call these constants k_x^2, k_y^2, and k_z^2, respectively.

So we have

$$\frac{d^2X}{dx^2} = -k_x^2 X \qquad \frac{d^2Y}{dy^2} = -k_y^2 Y \qquad \frac{d^2Z}{dz^2} = -k_z^2 Z$$

and $E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$

Following now the 1D solution for each coordinate:

$$\Rightarrow \quad \psi(x,y,z) = A_x A_y A_z \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right)$$

$$\boxed{E = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2}\left(n_x^2 + n_y^2 + n_z^2\right)} \qquad n_x, n_y, n_z = 1, 2, 3 \ldots$$

To normalize, it makes sense that $A_x = A_y = A_z$

So again following from 1D case: $A_x = A_y = A_z = \sqrt{\frac{2}{a}}$

and $$\boxed{\psi(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right)}$$

(b) To find the first six energies, we can simply consider $n_x^2 + n_y^2 + n_z^2$ and make a table

n_x	n_y	n_z	$n_x^2+n_y^2+n_z^2$		degeneracy
1	1	1	3	$E_1 = 3\frac{\pi^2\hbar^2}{2ma^2}$	$d=1$
1	1	2	6	$E_2 = 6\frac{\pi^2\hbar^2}{2ma^2}$	$d=3$
1	2	1	6		
2	1	1	6		
2	2	1	9	$E_3 = 9\frac{\pi^2\hbar^2}{2ma^2}$	$d=3$
2	1	2	9		
1	2	2	9		
3	1	1	11	$E_4 = 11\frac{\pi^2\hbar^2}{2ma^2}$	$d=3$
1	3	1	11		
1	1	3	11		
2	2	2	12	$E_5 = 12\frac{\pi^2\hbar^2}{2ma^2}$	$d=1$
1	2	3	14	$E_6 = 14\frac{\pi^2\hbar^2}{2ma^2}$	$d=6$
1	3	2	14		
3	2	1	14		
3	1	2	14		
2	3	1	14		
2	1	3	14		

(c) The next energy levels are permutations of the following quantum numbers:

$$E_7 = 17 \frac{\pi^2\hbar^2}{2ma^2} \quad 3\,2\,2$$

$$E_8 = 18 \frac{\pi^2\hbar^2}{2ma^2} \quad 4\,1\,1$$

$$E_9 = 19 \frac{\pi^2\hbar^2}{2ma^2} \quad 3\,3\,1$$

$$E_{10} = 21 \frac{\pi^2\hbar^2}{2ma^2} \quad 4\,2\,1$$

$$E_{11} = 22 \frac{\pi^2\hbar^2}{2ma^2} \quad 3\,3\,2$$

$$E_{12} = 24 \frac{\pi^2\hbar^2}{2ma^2} \quad 4\,2\,2$$

$$E_{13} = 26 \frac{\pi^2\hbar^2}{2ma^2} \quad 4\,3\,1$$

These degeneracies come about by simply changing the quantum numbers among n_x, n_y, n_z

e.g.

n_x	n_y	n_z
3	2	2
2	3	2
2	2	3

$$E_{14} = 27 \frac{\pi^2\hbar^2}{2ma^2} \quad \begin{cases} 3\,3\,3 \\ 5\,1\,1 \end{cases}$$

⇐ However, E_{14} is the first energy level where we get two different combinations of n_x, n_y, n_z that are degenerate.

⇒ Known as an "accidental degeneracy."

The degeneracy in this case is

$$\begin{array}{rl} 1 & (333) \\ +\ 3 & (511) \\ \hline 4 & \end{array}$$

(3) For Y_0^0 we need $P_0^0(\cos\theta)$

Using 4.27 $\Rightarrow$ $P_0^0(x) \equiv 1 \cdot P_0(x)$

Using 4.28 $\Rightarrow$ $P_0(x) = 1$ $\Rightarrow$ $P_0^0(\cos\theta) = 1$

Using 4.32 $\Rightarrow$ $Y_0^0 = \frac{1}{\sqrt{4\pi}} \cdot 1$ $\Rightarrow$ $\boxed{Y_0^0 = \frac{1}{\sqrt{4\pi}}}$

For Y_2^1 we need $P_2^1(\cos\theta)$

Using 4.27 $\Rightarrow$ $P_2^1(x) = \sqrt{1-x^2}\,\frac{d}{dx}P_2(x)$

4.28 $\Rightarrow$ $P_2(x) = \frac{1}{4\cdot 2}\left(\frac{d}{dx}\right)^2(x^2-1)^2 = \frac{1}{8}\cdot\frac{d}{dx}\left[2\cdot 2x\cdot(x^2-1)\right]$

$= \frac{1}{2}(3x^2-1)$

So $P_2^1(x) = \frac{\sqrt{1-x^2}}{2}\frac{d}{dx}(3x^2-1) = \frac{\sqrt{1-x^2}}{2}(6x) = 3x(1-x^2)^{1/2}$

$P_2^1(\cos\theta) = 3\cos\theta\cdot\sqrt{1-\cos^2\theta} = 3\cos\theta\cdot\sin\theta$

4.32 $\Rightarrow$ $Y_2^1 = -\sqrt{\frac{5}{4\pi}\cdot\frac{1}{6}}\;e^{i\phi}\cdot 3\cos\theta\cdot\sin\theta$

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

Normalization:

$$\iint |Y_0^0|^2 \sin\theta \, d\theta \, d\varphi = \frac{1}{4\pi}\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$\checkmark \qquad = \frac{1}{4\pi} \cdot 2 \cdot 2\pi = 1$$

$$\iint |Y_2^1|^2 \sin\theta \, d\theta \, d\varphi = \frac{15}{8\pi}\int_0^\pi \sin^2\theta \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{15}{4}\int_0^\pi (1-\cos^2\theta)\cos^2\theta \sin\theta \, d\theta$$

$$= \frac{15}{4}\left\{ \int_0^\pi \cos^2\theta \sin\theta \, d\theta - \int_0^\pi \cos^4\theta \sin\theta \, d\theta \right\}$$

using integral tables $\displaystyle\int \cos^m\theta \sin\theta \, d\theta = -\frac{\cos^{m+1}\theta}{(m+1)}$

$$\Rightarrow \quad = \frac{15}{4}\left\{ -\frac{\cos^3\theta}{3} + \frac{\cos^5\theta}{5} \right\}\Bigg|_0^\pi = \frac{15}{4}\left\{ \left(\frac{1}{3}+\frac{1}{3}\right) + \left(-\frac{1}{5}-\frac{1}{5}\right) \right\}$$

$$= \frac{15}{4}\left(\frac{2}{3} - \frac{2}{5}\right)$$

$$= \frac{15}{4}\left(\frac{10}{15} - \frac{6}{15}\right) = \frac{15}{4} \cdot \frac{4}{15}$$

$$= 1 \quad \checkmark$$

Orthogonalization:

$$\iint Y_0^{0*} Y_2^1 \sin\theta \, d\theta \, d\varphi = -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8\pi}}\int_0^\pi \sin^2\theta \cos\theta \, d\theta \cdot \int_0^{2\pi} e^{i\varphi} d\varphi$$

integral tables: $\displaystyle\int \sin^2\theta \cos\theta \, d\theta = \frac{\sin^3\theta}{3}$

PS #6 Solutions cont.

$$= -\sqrt{\frac{15}{32\pi^2}} \cdot \left[\cancel{\frac{\sin^3\theta}{3}}\right]\Bigg|_0^{\pi} \cdot \left[\cancel{\frac{e^{i\varphi}}{i}}\right]_0^{2\pi} = 0 \quad ✓$$

$\quad 0 \qquad 0$

(4.) (a) For $\psi_{200} \Rightarrow n=2,\ \ell=0,\ m_\ell=0$

and $\psi_{n\ell m_\ell} = R_{n\ell}\, Y_\ell^{m_\ell}$ So we need R_{20} and Y_0^0

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2}\left(1-\frac{1}{2}\frac{r}{a}\right)\exp\left[\frac{-r}{2a}\right] \qquad Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

(problem 3 above)

So
$$\boxed{\psi_{200} = \frac{1}{\sqrt{2\pi a}}\,\frac{1}{2a}\left(1-\frac{r}{2a}\right)\exp\left[\frac{-r}{2a}\right]}$$

(b) For
$$\begin{cases} \psi_{211} \Rightarrow n=2,\ \ell=1,\ m_\ell=1 \Rightarrow \psi_{211} = R_{21}\,Y_1^1 \\ \psi_{210} \Rightarrow n=2,\ \ell=1,\ m_\ell=0 \Rightarrow \psi_{210} = R_{21}\,Y_1^0 \\ \psi_{21-1} \Rightarrow n=2,\ \ell=1,\ m_\ell=-1 \Rightarrow \psi_{21-1} = R_{21}\,Y_1^{-1} \end{cases}$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2}\frac{r}{a}\exp\left[\frac{-r}{2a}\right] \qquad \text{from Table 4.7}$$

So
$$\psi_{21\pm1} = \frac{1}{\sqrt{24}} \cdot \mp\left(\frac{3}{8\pi}\right)^{1/2} a^{-3/2}\frac{r}{a}\exp\left[\frac{-r}{2a}\right]\sin\theta\, e^{\mp i\varphi} \qquad \text{Table 4.3}$$

$$\boxed{\psi_{21\pm1} = \mp\left(\frac{1}{\pi a}\right)^{1/2}\frac{1}{8a^2}\, r\exp\left[\frac{-r}{2a}\right]\sin\theta\,\exp[\mp i\varphi]}$$

$$\psi_{210} = \frac{1}{\sqrt{24}}\left(\frac{3}{4\pi}\right)^{1/2} a^{-3/2}\,\frac{r}{a}\exp\left[\frac{-r}{2a}\right]\cos\theta$$

$$\boxed{\psi_{210} = \frac{1}{\sqrt{2\pi a}}\;\frac{1}{4a^2}\; r\exp\left[\frac{-r}{2a}\right]\cos\theta}$$

5. (a) $\psi_{100} = \left(\frac{1}{4\pi}\right)^{1/2} \cdot 2\,a^{-3/2}\exp\left[\frac{-r}{a}\right] = \frac{1}{\sqrt{\pi a^3}}\exp\left[\frac{-r}{a}\right]$

$$\langle r\rangle = \frac{1}{\pi a^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} r\exp\left[\frac{-2r}{a}\right]\cdot r^2\sin\theta\,dr\,d\theta\,d\varphi$$

$$= \frac{4\cancel{\pi}}{\cancel{\pi}a^3}\underbrace{\int_0^\infty r^3\exp\left[\frac{-2r}{a}\right]dr}_{3!\left(\frac{a}{2}\right)^4\ \text{[from integral tables]}} = \frac{\cancel{4}}{a^3}\cdot 6\,\frac{a^4}{4\cancel{2}} = \boxed{\frac{3}{2}a}$$

$$\langle r^2\rangle = \frac{1}{\cancel{\pi}a^3}\cdot 4\cancel{\pi}\underbrace{\int_0^\infty r^4\exp\left[\frac{-2r}{a}\right]dr}_{4!\left(\frac{a}{2}\right)^5\ \text{[from integral tables]}} = \frac{4}{a^3}\cdot\frac{24\,a^5}{32} = \boxed{3a^2}$$

(b) $\langle x\rangle = 0$ by symmetry

$\langle x^2\rangle \Rightarrow$ since $r^2 = x^2+y^2+z^2$

$$\langle r^2\rangle = \iiint \psi^* r^2\psi\, r^2\sin\theta\,dr\,d\theta\,d\varphi$$

$$= \iiint \psi^*\left[x^2+y^2+z^2\right]r^2\sin\theta\,dr\,d\theta\,d\varphi$$

can be broken into 3 integrals

Ps #6 solutions cont.

So $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$

By symmetry, we expect $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$

Thus $\langle r^2 \rangle = 3 \langle x^2 \rangle$ or $\langle x^2 \rangle = \frac{1}{3} \langle r^2 \rangle$

$$\therefore \quad \boxed{\langle x^2 \rangle = a^2}$$

(c) $\psi_{211} = -\left(\frac{1}{\pi a}\right)^{1/2} \frac{1}{8a^2} \, r \exp\left[\frac{-r}{2a}\right] \sin\theta \exp\left[-i\varphi\right]$

(from above, problem 4b)

$$\langle x^2 \rangle = \frac{1}{\pi a} \frac{1}{64 a^4} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \exp\left[\frac{-r}{a}\right] \sin^2\theta \; r^2 \sin^2\theta \cos^2\phi \; r^2 \sin\theta \cdot dr \cdot d\theta \, d\varphi$$

$$= \frac{1}{64 \pi a^5} \underbrace{\int_0^\infty r^6 e^{-r/a} dr}_{6!\, a^7} \underbrace{\int_0^\pi \sin^5\theta \, d\theta}_{\frac{16}{15}} \underbrace{\int_0^{2\pi} \cos^2\varphi \, d\varphi}_{\pi}$$

using integral tables $\longrightarrow$

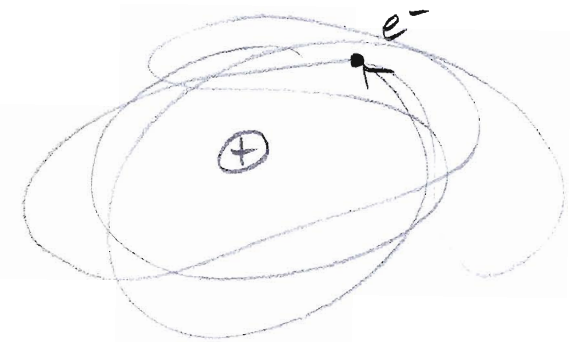
$$= \frac{1}{64 \pi a^5} \; 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \; a^7 \; \frac{16}{15} \cdot \pi$$

$$= \boxed{12 a^2}$$

Quantum Mechanics Problem Set #7 Solutions

(1) Hydrogen $\Rightarrow$ single electron orbiting single proton

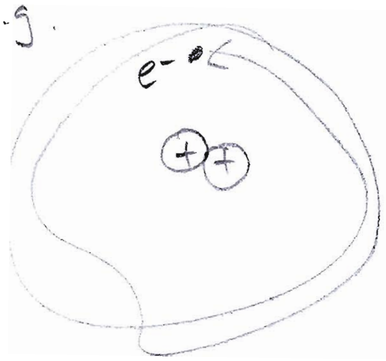
H

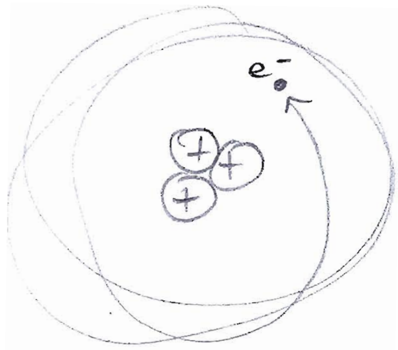


Hydrogenic atom $\Rightarrow$ single electron orbiting Z protons

e.g.

He^+





Li^{2+}

etc.

The only thing that changes is the potential

$$-\frac{e^2}{4\pi\varepsilon_0 r} \rightarrow \frac{(+Ze)(-e)}{4\pi\varepsilon_0 r} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

So replace e^2 by Ze^2 in final answers for hydrogen

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

$= \frac{E_1}{n^2}$

For Hydrogenic atoms this changes to

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

Similarly, for the binding energy and Bohr radius

$$\boxed{\begin{aligned} E_1(Z) &= Z^2 E_1 \\ a(Z) &= \frac{4\pi\varepsilon_0 \hbar^2}{m Z e^2} = \frac{a}{Z} \end{aligned}}$$

The binding energy will be much higher, as it is multiplied by Z^2. This makes sense since the single electron will be bound more tightly to multiple protons in nucleus of hydrogenic atom.

2

(a) $$[\hat{L}_z, \hat{x}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = \underbrace{[\hat{x}\hat{p}_y, \hat{x}]}_{0} - [\hat{y}\hat{p}_x, \hat{x}]$$

$$= -y[\hat{p}_x, \hat{x}] = \boxed{i\hbar y}$$

Similarly

$$[\hat{L}_z, \hat{y}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}] = [\hat{x}\hat{p}_y, \hat{y}] - \underbrace{[\hat{y}\hat{p}_x, \hat{y}]}_{0}$$

$$= \hat{x}[\hat{p}_y, \hat{y}]$$

$$= \boxed{-i\hbar x}$$

$$[\hat{L}_z, \hat{z}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{z}] = \underbrace{[\hat{x}\hat{p}_y, \hat{z}]}_{0} - \underbrace{[\hat{y}\hat{p}_x, \hat{z}]}_{0}$$

$$= \boxed{0}$$

$$[\hat{L}_z, \hat{p}_x] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{p}_x] = [\hat{x}\hat{p}_y, \hat{p}_x] = \boxed{i\hbar\hat{p}_y \text{ OR } = \hbar^2 \frac{\partial}{\partial y}}$$

Similarly

$$[\hat{L}_z, \hat{p}_y] = \boxed{-i\hbar\hat{p}_y \quad \text{OR} \quad -\hbar^2\frac{\partial}{\partial x}}$$

$$[\hat{L}_z, \hat{p}_z] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{p}_z] = \boxed{0}$$

(b) $$[\hat{L}_z, \hat{r}^2] = [\hat{L}_z, \hat{x}^2] + [\hat{L}_z, \hat{y}^2] + [\hat{L}_z, z^2]$$

$$= [\hat{L}_z, \hat{x}]\hat{x} + [\hat{L}_z, \hat{y}]\hat{y} + \cancelto{0}{[\hat{L}_z, \hat{z}]}\hat{z}$$
$$+ \hat{x}[\hat{L}_z, \hat{x}] + \hat{y}[\hat{L}_z, \hat{y}] + \hat{z}\cancelto{0}{[\hat{L}_z, \hat{z}]}$$

$$= i\hbar y x + (-i\hbar x y)$$
$$+ i\hbar x y + (-y i\hbar x y) = \boxed{0}$$

$$[\hat{L}_z, \hat{p}^2] = [\hat{L}_z, \hat{p}_x^2] + [\hat{L}_z, \hat{p}_y^2] + \cancelto{0}{[\hat{L}_z, \hat{p}_z^2]}$$

$$= [\hat{L}_z, \hat{p}_x]\hat{p}_x + \hat{p}_x[\hat{L}_z, \hat{p}_x]$$
$$+ [\hat{L}_z, \hat{p}_y]\hat{p}_y + \hat{p}_y[\hat{L}_z, \hat{p}_y]$$

$$= i\hbar \hat{p}_y \hat{p}_x + i\hbar \hat{p}_x \hat{p}_y$$
$$- i\hbar p_x p_y - i\hbar p_y p_x = \boxed{0}$$

(c) Since $[L_z, \hat{r}^2] = [L_z, \hat{p}^2] = 0$

$$\Rightarrow \begin{cases} [\hat{L}_x, \hat{r}^2] = [\hat{L}_x, \hat{p}^2] = 0 \\ [\hat{L}_y, \hat{r}^2] = [\hat{L}_y, \hat{p}^2] = 0 \end{cases}$$

For spherically symmetric potentials:

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

If we write r as $\sqrt{r^2}$ and consider

$$[\hat{L}_z, \sqrt{r^2}] = \hat{L}_z \sqrt{r^2} - \sqrt{r^2}\, L_z = \sqrt{\hat{L}_z^2 \hat{r}^2} - \sqrt{\hat{r}^2 \hat{L}_z^2}$$

$$= \sqrt{\hat{r}^2 \hat{L}_z^2} - \sqrt{r^2 \hat{L}_z^2} = 0$$

similarly $[\hat{L}_x, \sqrt{r^2}] = [\hat{L}_y \sqrt{r^2}] = 0$

So all three components of $\vec{L}$ commute

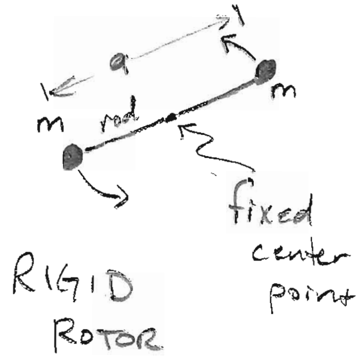
with $\hat{H} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\sqrt{r^2})$

So $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$ all commute

$\Rightarrow$ compatible observables $\Rightarrow$ which implies...

that the energy, angular momentum squared, and projection of the angular momentum along the z-axis can all be determined simultaneously.

(3) (a) Energy = Kinetic Energy



$$= 2 \times \frac{1}{2} m v^2$$

$$= m v^2$$

$$|L| = |\vec{r} \times \vec{p}| = 2 \cdot \frac{a}{2} \cdot mv$$

$$= amv$$

so $L^2 = a^2 m^2 v^2$

or $$\hat{H} = \frac{\hat{L}^2}{a^2 m}$$

But the eigenvalues of $\hat{L}^2 \longrightarrow \ell(\ell+1)\hbar^2$ $\ell = 0, 1, 2 \ldots$

or $n(n+1)\hbar^2$ $n = 0, 1, 2 \ldots$

(just renaming)

$\therefore$ $$\boxed{E_n = \frac{\hbar^2 n(n+1)}{ma^2} \quad \text{with } n = 0, 1, 2 \ldots}$$

(b) Since this problem is spherically symmetric with $V(r)=0$, we know the solutions are the spherical harmonics, which are already normalized:

$$\boxed{\psi_{nm_n} = Y_n^{m_n}(\theta,\varphi)}$$

for rigid rotor

As we know, the degeneracy for each value of n will be $2n+1$ due to m_n

(Recall for $Y_\ell^{m_\ell} \Rightarrow$ each value of ℓ has $m_\ell = -\ell, -\ell+1, \cdots, \ell-1, \ell$
i.e. $\Rightarrow 2\ell+1$)

4. Spin state $|\chi\rangle = A\begin{pmatrix} 3i \\ 4 \end{pmatrix}$

(a)

For normalization $\langle\chi|\chi\rangle = 1 = |A|^2 \begin{pmatrix} -3i & 4 \end{pmatrix}\begin{pmatrix} 3i \\ 4 \end{pmatrix}$

$$1 = |A|^2 (+9+16)$$

$$1 = |A|^2\, 25$$

$$\Rightarrow \boxed{A = \frac{1}{5}}$$

(b) $$\langle \hat{S}_x \rangle = \frac{1}{25}\frac{\hbar}{2}(-3i\ \ 4)\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}3i\\4\end{pmatrix} = \frac{\hbar}{50}(-3i\ \ 4)\begin{pmatrix}4\\3i\end{pmatrix}$$

$$= \frac{\hbar}{50}(-12i + 12i) = \boxed{0}$$

$$\langle \hat{S}_y \rangle = \frac{1}{25}\frac{\hbar}{2}(-3i\ \ 4)\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}3i\\4\end{pmatrix} = \frac{\hbar}{50}(-3i\ \ 4)\begin{pmatrix}-4i\\-3\end{pmatrix}$$

$$= \frac{\hbar}{50}\left[-12-12\right] = \boxed{\frac{-12}{25}\hbar}$$

$$\langle \hat{S}_z \rangle = \frac{1}{25}\frac{\hbar}{2}(-3i\ \ 4)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}3i\\4\end{pmatrix} = \frac{\hbar}{50}(-3i\ \ 4)\begin{pmatrix}3i\\-4\end{pmatrix}$$

$$= \frac{\hbar}{50}\left[9-16\right] = \boxed{\frac{-7}{50}\hbar}$$

(c) $$\hat{S}_x^2 = \left(\frac{\hbar}{2}\right)^2\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$\hat{S}_y^2 = \left(\frac{\hbar}{2}\right)^2\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$\hat{S}_z^2 = \left(\frac{\hbar}{2}\right)^2\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$\Rightarrow \langle \hat{S}_x^2 \rangle = \langle \hat{S}_y^2 \rangle = \langle \hat{S}_z^2 \rangle = \frac{\hbar^2}{4}$$

So $\sigma_{\hat{S}_x}^2 = \langle \hat{S}_x^2 \rangle - \langle \hat{S}_x \rangle^2 = \frac{\hbar^2}{4} - 0 = \frac{\hbar^2}{4}$

$\sigma_{\hat{S}_y}^2 = \langle \hat{S}_y^2 \rangle - \langle \hat{S}_y \rangle^2 = \frac{\hbar^2}{4} - \left(\frac{144}{625}\right)\hbar^2$

$= \frac{\hbar^2 (625 - 576)}{2500} = \frac{49}{2500}\hbar^2$

$\sigma_{\hat{S}_z}^2 = \langle \hat{S}_z^2 \rangle - \langle \hat{S}_z \rangle^2 = \frac{\hbar^2}{4} - \frac{49}{2500}\hbar^2 = \frac{\hbar^2}{2500}\left[625 - 49\right]$

$= \frac{576}{2500}\hbar^2 = \frac{144}{625}\hbar^2$

So $\boxed{\sigma_{\hat{S}_x} = \frac{\hbar}{2} \qquad \sigma_{\hat{S}_y} = \frac{7}{50}\hbar \qquad \sigma_{\hat{S}_z} = \frac{12}{25}\hbar}$

(d)

$\sigma_{\hat{A}}^2 \sigma_{\hat{B}}^2 \geq \left(\frac{1}{2i}\langle [\hat{A}, \hat{B}] \rangle\right)^2$

$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z \qquad [\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x \qquad [\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$

So $\sigma_{\hat{S}_x}^2 \sigma_{\hat{S}_y}^2 \overset{?}{\geq} \left(\frac{i\hbar}{2i}\langle \hat{S}_z \rangle\right)^2$

$\frac{\hbar^2}{4}\frac{49}{2500}\hbar^2 \overset{?}{\geq} \frac{\hbar^2}{4}\frac{7^2}{(50)^2}\hbar^2$

$$\frac{49}{10{,}000}\hbar^4 \overset{?}{\geq} \frac{49}{10{,}000}\hbar^4 \quad \checkmark$$

at the uncertainty limit

Similarly,

$$\sigma^2_{\hat{S}_y}\,\sigma^2_{\hat{S}_z} \overset{?}{\geq} \left(\frac{\hbar}{2}\langle \hat{S}_x\rangle\right)^2$$

$$\frac{49}{2500}\hbar^2\,\frac{144}{625}\hbar^2 \overset{?}{\geq} \frac{\hbar^2}{4}\,0$$

$$\frac{7056}{1.5625\times 10^6}\hbar^4 \geq 0 \quad \checkmark$$

and

$$\sigma^2_{\hat{S}_z}\,\sigma^2_{\hat{S}_x} \overset{?}{\geq} \left(\frac{\hbar}{2}\langle \hat{S}_y\rangle\right)^2$$

$$\frac{144}{625}\hbar^2\,\frac{\hbar^2}{4} \overset{?}{\geq} \left(\frac{\hbar}{2}\left(-\frac{12}{25}\hbar\right)\right)^2$$

$$\frac{144}{2500}\hbar^4 \geq \frac{144}{2500}\hbar^4 \quad \checkmark$$

right at uncertainty limit

5 (a) $\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ in our basis

So we need to solve the eigenvalue equation...

$$\hat{S}_y |?\rangle = \lambda |?\rangle \Rightarrow (\hat{S}_y - \lambda)|?\rangle = 0$$

we want eigenvectors... and eigenvalues in the basis given above

So we need to solve the characteristic equation

$$\begin{vmatrix} -\lambda & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 = \frac{\hbar^2}{4}$$

$$\boxed{\lambda = \pm\frac{\hbar}{2}}$$

eigenvalues

since $\hat{S}_y - \lambda = \begin{pmatrix} -\lambda & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & -\lambda \end{pmatrix}$

Makes sense!

If we measure the spin along y, it can only be "up" or "down"

To get eigenvectors, we plug back into eigenvalue eqn.

$$\frac{\hbar}{2}\underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\hat{S}_y}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm\frac{\hbar}{2}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} -i\beta \\ i\alpha \end{pmatrix} = \pm\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow -i\beta = \pm\alpha$$

we also know that

$$|\alpha|^2 + |\beta|^2 = 1$$

so this implies $|\alpha|^2 + |\alpha|^2 = 1$ or $\alpha = \frac{1}{\sqrt{2}}$

So eigenvectors for $\hat{S}_y \Rightarrow$ $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$ $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$

eigenvalues $+\frac{\hbar}{2}$ $-\frac{\hbar}{2}$

(b) If we measure $\hat{S}_y$ we will always get either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$. The probabilities depend on the projection of the general spin state into the two eigenvectors of $\hat{S}_y$ listed above. In other words, we need the coefficients:

$$C_{+\frac{\hbar}{2}} = \frac{1}{\sqrt{2}}(1 \; -i)\begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{\sqrt{2}}(a - ib)$$

So we get $+\frac{\hbar}{2}$ with probability $\frac{1}{2}|a-ib|^2$

$$C_{-\frac{\hbar}{2}} = \frac{1}{\sqrt{2}}(1 \; i)\begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{\sqrt{2}}(a + ib)$$

We get $-\frac{\hbar}{2}$ with probability $\frac{1}{2}|a+ib|^2$

Problem Set #7 solutions cont.

Check that probabilities add to one:

$$\frac{1}{2}(a-ib)(a^*+ib^*) + \frac{1}{2}(a+ib)(a^*-ib^*)$$

$$= \frac{1}{2}\left[|a|^2 - \cancel{ia^*b} + \cancel{iab^*} + |b|^2 + |a|^2 + \cancel{ia^*b} - \cancel{iab^*} + |b|^2\right]$$

$$= \frac{1}{2}\left[2|a|^2 + 2|b|^2\right] = |a|^2 + |b|^2 = 1 \checkmark$$

(c) $\boxed{\hat{S}_y^2 \text{ will always yield } \frac{\hbar^2}{4} \text{ with probability } 1}$

Why? Think about $\hat{S}_y^2$ as two successive measurements of $\hat{S}_y$, i.e. $\hat{S}_y \cdot \hat{S}_y$.

The first one will yield either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$.

However, now the general spin state is in an eigenvector of $\hat{S}_y$. The second measurement will thus yield the same eigenvalue.

If first $\hat{S}_y$ gives $+\frac{\hbar}{2}$, second one gives $+\frac{\hbar}{2}$

$$\Rightarrow \frac{\hbar^2}{4} \text{ total}$$

If first $\hat{S}_y$ gives $-\frac{\hbar}{2}$, second one gives $-\frac{\hbar}{2}$

$$\Rightarrow \frac{\hbar^2}{4} \text{ total}$$

Quantum Mechanics: Problem Set #8 Solutions

① (a) $\vec{r}_1 \stackrel{?}{=} \vec{R} + \frac{m_r}{m_1}\vec{r}$

$$\vec{r}_1 \stackrel{?}{=} \vec{R} + \frac{\cancel{m_1} m_2}{(m_1+m_2)\cancel{m_1}}\vec{r}$$

$$\vec{r}_1(m_1+m_2) \stackrel{?}{=} \vec{R}(m_1+m_2) + m_2\vec{r}$$

$$\vec{r}_1(m_1+m_2) - m_2\vec{r} \stackrel{?}{=} \frac{(m_1\vec{r}_1 + m_2\vec{r}_2)}{\cancel{(m_1+m_2)}}\cancel{(m_1+m_2)}$$

$$\vec{r}_1 m_1 + \vec{r}_1 m_2 - (\vec{r}_1 - \vec{r}_2)m_2 \stackrel{?}{=} m_1\vec{r}_1 + m_2\vec{r}_2$$

$$m_1\vec{r}_1 + m_2\vec{r}_2 \stackrel{?}{=} m_1\vec{r}_1 + m_2\vec{r}_2 \quad ✓$$

Similarly $\vec{r}_2 \stackrel{?}{=} \vec{R} - \frac{m_r}{m_2}\vec{r}$

$$\vec{r}_2 \stackrel{?}{=} \vec{R} - \frac{m_1\cancel{m_2}}{(m_1+m_2)\cancel{m_2}}\vec{r}$$

$$\vec{r}_2 m_1 + \vec{r}_2 m_2 \stackrel{?}{=} \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{\cancel{(m_1+m_2)}}\cancel{(m_1+m_2)} - m_1\vec{r}$$

$$m_1\vec{r}_2 + m_2\vec{r}_2 + m_1 r \stackrel{?}{=} m_1\vec{r}_1 + m_2\vec{r}_2$$

$$\cancel{m_1\vec{r}_2} + m_2\vec{r}_2 + m_1\vec{r}_1 - \cancel{m_1\vec{r}_2} \stackrel{?}{=} m_1\vec{r}_1 + m_2\vec{r}_2$$

$$m_1\vec{r}_1 + m_2\vec{r}_2 \stackrel{?}{=} m_1\vec{r}_1 + m_2\vec{r}_2 \quad ✓$$

Let $\vec{R} = (X, Y, Z)$ $\quad \vec{r} = (x, y, z)$

We can consider one component at a time

X-component: Since $(m_1+m_2)\vec{R} = m_1\vec{r}_1 + m_2\vec{r}_2$ by definition of $\vec{R}$

$$\Rightarrow (m_1+m_2)X = m_1 x_1 + m_2 x_2$$

OR $$X = \frac{m_1}{(m_1+m_2)}x_1 + \frac{m_2}{(m_1+m_2)}x_2$$

also Since $\vec{r} = \vec{r}_1 - \vec{r}_2$

then $x = x_1 - x_2$ $\qquad x_1(X, x)$

Using Chain Rule: $$(\vec{\nabla}_1)_x = \frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x}$$

x-component

$$= \frac{m_1}{(m_1+m_2)}\frac{\partial}{\partial X} + 1\cdot\frac{\partial}{\partial x}$$

OR $$(\vec{\nabla}_1)_x = \frac{m_r}{m_2}(\vec{\nabla}_R)_x + (\vec{\nabla}_r)_x$$

Can do the same for y- and z-components

$$\therefore \boxed{\vec{\nabla}_1 = \frac{m_r}{m_2}\vec{\nabla}_R + \vec{\nabla}_r = \vec{\nabla}_r + \frac{m_r}{m_2}\vec{\nabla}_R}$$ ✓

Similarly for $\vec{\nabla}_2$ except $\frac{\partial x}{\partial x_2} = -1$

$$\therefore \boxed{\vec{\nabla}_2 = \frac{m_r}{m_1}\vec{\nabla}_R - \vec{\nabla}_r = -\vec{\nabla}_r + \frac{m_r}{m_1}\vec{\nabla}_R}$$ ✓

(b) For T.I.S.E. we need ∇_1^2 and ∇_2^2

$$\nabla_1^2 \psi = \vec{\nabla}_1 \cdot \vec{\nabla}_1 \psi = \vec{\nabla}_1 \cdot \left[\frac{m_r}{m_2} \vec{\nabla}_R \psi + \vec{\nabla}_r \psi \right]$$

$$= \frac{m_r}{m_2} \vec{\nabla}_R \cdot \left[\frac{m_r}{m_2} \vec{\nabla}_R \psi + \vec{\nabla}_r \psi \right]$$

$$+ \vec{\nabla}_r \cdot \left[\frac{m_r}{m_2} \vec{\nabla}_R \psi + \vec{\nabla}_r \psi \right]$$

$$\Rightarrow \nabla_1^2 \psi = \left[\left(\frac{m_r}{m_2}\right)^2 \nabla_R^2 + 2 \frac{m_r}{m_2} \vec{\nabla}_R \cdot \vec{\nabla}_r + \nabla_r^2 \right] \psi$$

Similarly

$$\nabla_2^2 \psi = \left[\left(\frac{m_r}{m_1}\right)^2 \nabla_R^2 - 2 \frac{m_r}{m_1} \vec{\nabla}_R \cdot \vec{\nabla}_r + \nabla_r^2 \right] \psi$$

Thus $$\hat{H} \psi = \left[-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r_1, r_2) \right] \psi$$

the two $\nabla_R \cdot \nabla_r$ terms cancel

OR $$\hat{H} \psi = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_1} \frac{m_r^2}{m_2^2} + \frac{1}{m_2} \frac{m_r^2}{m_1^2} \right) \nabla_R^2 + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_r^2 \right] \psi$$

$$+ V(r) \psi$$

$$\Rightarrow \hat{H} \psi = -\frac{\hbar^2}{2} \left[\left(\frac{m_r^2}{m_1 m_2} \right) \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_R^2 + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_r^2 \right] \psi$$

$$+ V(r) \psi$$

But $\frac{1}{m_1} + \frac{1}{m_2} = \frac{1}{m_r}$

$$\Rightarrow H\Psi = -\frac{\hbar^2}{2}\left[\frac{m_r}{m_1 m_2}\nabla_R^2 + \frac{1}{m_r}\nabla_r^2\right]\Psi + V(r)\Psi = E\Psi$$

$$H\Psi = -\frac{\hbar^2}{2}\left[\frac{1}{(m_1+m_2)}\nabla_R^2 + \frac{1}{m_r}\nabla_r^2\right]\Psi + V(r)\Psi = E\Psi$$

$$\boxed{H\Psi = \left[\frac{-\hbar^2}{2(m_1+m_2)}\nabla_R^2 - \frac{\hbar^2}{2m_r}\nabla_r^2 + V(\vec{r})\right]\Psi = E\Psi}$$

(c) Put in $\Psi = \Psi_r(\vec{r})\Psi_R(\vec{R})$ and then divide by $\Psi_r\Psi_R$

$$\underbrace{\left[-\frac{\hbar^2}{2(m_1+m_2)}\frac{1}{\Psi_R}\nabla_R^2\Psi_R\right]}_{\text{depends only on } \vec{R}} + \underbrace{\left[-\frac{\hbar^2}{2m_r}\frac{1}{\Psi_r}\nabla_r^2\Psi_r + V(\vec{r})\right]}_{\text{depends only on } \vec{r}} = E$$

Each must be equal to constant

Call first E_R and second E_r

So $E_R + E_r = E$.

$$\boxed{-\frac{\hbar^2}{2(m_1+m_2)}\nabla^2\Psi_R = E_R\Psi_R} \qquad \boxed{\frac{-\hbar^2}{2m_r}\nabla^2\Psi_r + V(\vec{r})\Psi_r = E_r\Psi_r}$$

(d) For hydrogen atom $\quad E_1 \equiv$ energy of ground state (or binding energy)

$E_1 \propto$ mass $\qquad E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$

$$\Rightarrow \frac{\Delta E_1}{E_1} = \frac{\Delta m}{m_r} = \frac{m_r - m_e}{m_r} = 1 - \frac{m_e}{m_r}$$

$$= 1 - \frac{\cancel{m_e}}{\cancel{m_e} m_p}\cdot(m_e+m_p)$$

where $m_e \equiv$ mass of electron $\quad m_p \equiv$ mass of proton

Thus $$\frac{\Delta E_1}{E_1} = 1 - \frac{(m_e+m_p)}{m_p} = \frac{m_e}{m_p} = \frac{9.109\times10^{-31}\,kg}{1.673\times10^{-27}\,kg}$$

$$= 5.44\times10^{-4}$$

$$\boxed{\%\ \text{error} = 0.054\%}$$

very small!

#2 (a) We want $\int |\Psi_\pm|^2 \, d^3\vec{r}_1 \, d^3\vec{r}_2 = 1$

$$\Rightarrow |C|^2 \int [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]^* [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] \, d^3\vec{r}_1 \, d^3\vec{r}_2$$

$$= |C|^2 \Big[\int |\psi_a(\vec{r}_1)|^2 d^3\vec{r}_1 \int |\psi_b(\vec{r}_2)|^2 d^3\vec{r}_2$$

$$\pm \int \psi_a^*(\vec{r}_1)\psi_b(\vec{r}_1) \, d^3\vec{r}_1 \int \psi_b^*(\vec{r}_2)\psi_a(\vec{r}_2) \, d^3\vec{r}_2$$

$$\pm \int \psi_b^*(\vec{r}_1)\psi_a(\vec{r}_1) \, d^3\vec{r}_1 \int \psi_a^*(\vec{r}_2)\psi_b(\vec{r}_2) \, d^3\vec{r}_2$$

$$+ \int |\psi_b(\vec{r}_1)|^2 d^3\vec{r}_1 \int |\psi_a(\vec{r}_2)|^2 d^3\vec{r}_2 \Big]$$

$$= |C|^2 [1 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 1]$$

$$= |C|^2 \cdot 2 \quad \Rightarrow \quad 2|C|^2 = 1$$

OR $\boxed{C = \frac{1}{\sqrt{2}}}$

(b) If $\psi_a = \psi_b$ and it is normalized

$$\Psi_+ = C[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) + \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)]$$

$$\Psi_+ = 2C\,\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) \quad \text{and} \quad \Psi_- = 0$$

Ps #8

Then $$1 = |c|^2 \cdot 4 \cdot \int \left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\right]^* \left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\right] \cdot d^3\vec{r}_1\, d^3\vec{r}_2$$

$$1 = |c|^2 \cdot 4 \underbrace{\int |\psi_a(\vec{r}_1)|^2 d^3\vec{r}_1}_{1} \underbrace{\int |\psi_a(\vec{r}_2)|^2 d^3\vec{r}_2}_{1}$$

OR

$$\Rightarrow \quad |c|^2 = \frac{1}{4} \quad \text{or} \quad \boxed{c = \frac{1}{2}}$$

$\Rightarrow$ This case where $\psi_a = \psi_b$ is possible for either bosons or fermions. The overall wavefunction including spin should be symmetric for bosons and antisymmetric for fermions. Above we only have ψ_+ which is symmetric for spatial part of the wavefunction. It could be combined with a symmetric spin state (triplet) for bosons or an antisymmetric spin state (singlet) for fermions.

PS #8

(3.) For single-particle states, we can use solutions we saw from Chapter 2

$$\Rightarrow \quad \psi_n = \sqrt{\frac{2}{a}} \sin\left[\frac{n\pi}{a} x\right]$$

We want to calculate $\langle (x_1 - x_2)^2 \rangle$

But $\langle (x_1-x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

So for each case below we need to calculate the three expectation values for x_1^2, x_2^2, and $x_1 x_2$

(a) For two distinguishable particles (neglecting spin)

$$\psi = \psi_{n'}(x_1)\,\psi_{n''}(x_2) = \frac{2}{a} \sin\left[\frac{n'\pi}{a} x_1\right] \sin\left[\frac{n''\pi}{a} x_2\right]$$

So $$\langle x_1^2 \rangle = \int x_1^2 |\psi_{n'}(x_1)|^2 dx_1 \underbrace{\int |\psi_{n''}(x_2)|^2 dx_2}_{1}$$

$$= \langle x^2 \rangle_{n'}$$

$$\langle x_1^2 \rangle = a^2 \left[\frac{1}{3} - \frac{1}{2(n'\pi)^2}\right]$$ from PS #2, problem #1

Similarly

$$\langle x_2^2 \rangle = \langle x^2 \rangle_{n''} = a^2 \left[\frac{1}{3} - \frac{1}{2(n''\pi)^2}\right]$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_{n'}(x_1)|^2 dx_1 \int x_2 |\psi_{n''}(x_2)|^2 dx_2$$

$$= \langle x \rangle_{n'} \cdot \langle x \rangle_{n''} = \frac{a}{2} \cdot \frac{a}{2} = \frac{a^2}{4}$$

So $$\langle (x_1 - x_2)^2 \rangle = 2\frac{a^2}{3} - \frac{a^2}{2\pi^2}\left(\frac{1}{(n')^2} + \frac{1}{(n'')^2}\right) - \frac{a^2}{2}$$

$$\boxed{\langle (x_1 - x_2)^2 \rangle = a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{(n')^2} + \frac{1}{(n'')^2}\right)\right]}$$ Distinguishable particles

(b) Indistinguishable particles with symmetric wavefunction (neglecting spin):

$$\psi_+ = \frac{1}{\sqrt{2}}\left(\psi_{n'}(x_1)\psi_{n''}(x_2) + \psi_{n''}(x_1)\psi_{n'}(x_2)\right)$$

$$\langle x_1^2 \rangle = \frac{1}{2}\Big[\int x_1^2 |\psi_{n'}(x_1)|^2 dx_1 \underbrace{\int |\psi_{n''}(x_2)|^2 dx_2}_{1}$$

$$+ \int x_1^2 |\psi_{n''}(x_1)|^2 dx_1 \underbrace{\int |\psi_{n'}(x_2)|^2 dx_2}_{1}$$

$$+ \int x_1^2 \psi_{n'}^*(x_1)\psi_{n''}(x_1)dx_1 \underbrace{\int \psi_{n''}^*(x_2)\psi_{n'}(x_2)dx_2}_{0}$$

$$+ \int x_1^2 \psi_{n''}^*(x_1)\psi_{n'}(x_1)dx_1 \underbrace{\int \psi_{n'}^*(x_2)\psi_{n''}(x_2)dx_2}_{0}\Big]$$

Last two terms are zero due to orthogonality

$$\langle x_1^2 \rangle = \frac{1}{2}\left[\langle x^2 \rangle_{n'} + \langle x^2 \rangle_{n''} \right]$$

Similarly

$$\langle x_2^2 \rangle = \frac{1}{2}\left[\langle x^2 \rangle_{n'} + \langle x^2 \rangle_{n''} \right]$$

$$\begin{aligned}
\langle x_1 x_2 \rangle = \frac{1}{2}\Big[& \int x_1 |\psi_{n'}(x_1)|^2 dx_1 \int x_2 |\psi_{n''}(x_2)|^2 dx_2 \\
& + \int x_1 |\psi_{n''}(x_1)|^2 dx_1 \int x_2 |\psi_{n'}(x_2)|^2 dx_2 \\
& + \int x_1 \psi_{n'}^*(x_1) \psi_{n''}(x_1) dx_1 \int x_2 \psi_{n''}^*(x_2) \psi_{n'}(x_2) dx_2 \\
& + \int x_1 \psi_{n''}^*(x_1) \psi_{n'}(x_1) dx_1 \int x_2 \psi_{n'}^*(x_2) \psi_{n''}(x_2) dx_2 \Big]
\end{aligned}$$

$$\begin{aligned}
\langle x_1 x_2 \rangle = \frac{1}{2}\Big[& \langle x \rangle_{n'} \langle x \rangle_{n''} + \langle x \rangle_{n''} \langle x \rangle_{n'} + \langle x \rangle_{n'n''} \langle x \rangle_{n''n'} \\
& + \langle x \rangle_{n''n'} \langle x \rangle_{n'n''} \Big]
\end{aligned}$$

where $\langle x \rangle_{n'n''} \equiv \int x \, \psi_{n'}^* \psi_{n''} \, dx$

OR

$$\langle x_1 x_2 \rangle = \langle x \rangle_{n'} \langle x \rangle_{n''} + |\langle x \rangle_{n'n''}|^2$$

PS #8

$$\therefore \langle (x_1 - x_2)^2 \rangle_+ = \underbrace{\langle x^2 \rangle_{n'} + \langle x^2 \rangle_{n''} - 2\langle x \rangle_{n'} \langle x \rangle_{n''}}_{\text{Same as } \langle (x_1-x_2)^2 \rangle \text{ for distinguishable particles}} - 2\left| \langle x \rangle_{n'n''} \right|^2$$

$$= a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{(n')^2} + \frac{1}{(n'')^2} \right) \right] - 2\left| \langle x \rangle_{n'n''} \right|^2$$

And $\langle x \rangle_{n'n''} = \frac{2}{a}\int_0^a x \sin\left(\frac{n'\pi}{a}x\right) \sin\left(\frac{n''\pi}{a}x\right) dx$

$$= \frac{1}{a}\left[\int_0^a x \cos\left[\frac{(n'-n'')\pi}{a}x\right] dx - \int_0^a x \cos\left[\frac{(n'+n'')\pi}{a}x\right] dx \right]$$

$$= \frac{1}{a}\left[\left(\frac{a}{(n'-n'')\pi}\right)^2 \cos\left[\frac{(n'-n'')\pi}{a}x\right] + \frac{ax}{(n'-n'')\pi} \underbrace{\cancel{\sin\left[\frac{(n'-n'')\pi}{a}x\right]}}_{0} \right.$$
$$\left. - \left(\frac{a}{(n'+n'')\pi}\right)^2 \cos\left[\frac{(n'+n'')\pi}{a}x\right] - \frac{ax}{(n'+n'')\pi} \underbrace{\cancel{\sin\left[\frac{(n'+n'')\pi}{a}x\right]}}_{0} \right]\Bigg|_0^a$$

$$= \frac{1}{a}\left[\left(\frac{a}{(n'-n'')\pi}\right)^2 \left(\cos\{(n'-n'')\pi\} - 1\right) - \left(\frac{a}{(n'+n'')\pi}\right)^2 \left(\cos\{(n'+n'')\pi\} - 1\right) \right]$$

But $\cos\{(n' \pm n'')\pi\} = (-1)^{n'+n''}$

$$\Rightarrow \langle x \rangle_{n'n''} = \frac{a}{\pi^2}\left[(-1)^{n'+n''} - 1\right]\left(\frac{1}{(n'-n'')^2} - \frac{1}{(n'+n'')^2}\right)$$

$$= \begin{cases} 0 & \text{if } n' \text{ and } n'' \text{ have same parity} \\ \dfrac{-8\,a\,n'n''}{\pi^2\left((n')^2-(n'')^2\right)^2} & \text{if } n' \text{ and } n'' \text{ have opposite parity} \end{cases}$$

$$\therefore \boxed{\langle (x_1-x_2)^2 \rangle_+ = a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{(n')^2} + \frac{1}{(n'')^2}\right)\right] - \frac{128\,a^2 (n')^2 (n'')^2}{\pi^4\left[(n')^2-(n'')^2\right]^4}}$$

where the last term is only present when n' and n'' have opposite parity

(c) Same analysis for ψ_-

$$\psi_- = \frac{1}{\sqrt{2}}\left[\psi_{n'}(x_1)\,\psi_{n''}(x_2) - \psi_{n''}(x_1)\,\psi_{n'}(x_2)\right]$$

$$\langle (x_1-x_2)^2 \rangle_- = \langle x^2 \rangle_{n'} + \langle x^2 \rangle_{n''} - 2\langle x \rangle_{n'} \langle x \rangle_{n''} + 2\left|\langle x \rangle_{n'n''}\right|^2$$

$$\therefore \boxed{\langle (x_1 - x_2)^2 \rangle_- = a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{(n')^2} + \frac{1}{(n'')^2} \right) \right] + \frac{128\, a^2 (n')^2 (n'')^2}{\pi^4 \left[(n')^2 - (n'')^2 \right]^4}}$$

where again last term is only present when n' and n'' have opposite parity

<u>Overall lesson:</u> Symmetry requirements actually affect where the particles are in space.

Specifically in $\psi_+ \Rightarrow$ electrons are closer together

$\psi_- \Rightarrow$ " " farther apart

Quantum Mechanics Problem Set #9 Solutions

1. (a) • $n=3$, $l=2$, $m_l=1$, $m_s=0$ ✗ cannot exist

everything is ok except m_s. M_s must be $+\frac{1}{2}$ or $-\frac{1}{2}$

• $n=2$, $l=0$, $m_l=0$, $m_s=-\frac{1}{2}$ ✓ can exist

called "2s", spin down

• $n=7$, $l=2$, $m_l=-2$, $m_s=+\frac{1}{2}$ ✓ can exist

called 7d

• $n=3$, $l=-3$, $m_l=-2$, $m_s=-\frac{1}{2}$ ✗ cannot exist

l is positive

(b) electronic configurations - see periodic table

B $Z=5$ $1s^2\,2s^2\,2p^1$

$[He]\,2s^2\,2p^1$

F $Z=9$ $[He]\,2s^2\,2p^5$

Na $Z=11$ $[Ne]\,3s^1$

PS #9

P $Z = 15$ $[Ne]\, 3s^2\, 3p^3$

C $Z = 6$ $[He]\, 2s^2\, 2p^2$

Cr $Z = 24$ $[Ar]\, 4s\, 3d^5$ ← exception!

moves one to make half-filled d-orbital

↑ ↑ ↑ ↑ ↑

5 d-orbitals

Mn $Z = 25$ $[Ar]\, 4s^2\, 3d^5$

Fe $Z = 26$ $[Ar]\, 4s^2\, 3d^6$

Cu $Z = 29$ $[Ar]\, 4s\, 3d^{10}$ ← exception!

moves one electron to make full set of d-orbitals:

↑↓ ↑↓ ↑↓ ↑↓ ↑↓

Kr $Z = 36$ $[Ar]\, 4s^2\, 3d^{10}\, 4p^6$

(C) Note: For any filled subshell such as ns^2 or np^6 or nd^{10} etc.

$M_L = \sum_{\text{all electrons}} m_l = 0$ and $M_s = \sum_{\text{all electrons}} m_s = 0$

So $L=0$, $S=0$, and $J=L+S=0$

($L=0$ is the only combination that always yields $M_\ell=0$. Similarly $S=0$ is the only combination that always yields $M_S=0$)

This means that to determine the term symbols $^{2S+1}L_J$ all we need to do is consider the electrons in partially filled subshell.

So for boron $\rightarrow$ $1s^2 2s^2 2p$

we only need consider $2p$ electron

It has $S=\frac{1}{2}$ and $l=1$, therefore by rules of addition of angular momentum

$J = 1 + \frac{1}{2}$ and $J = 1 - \frac{1}{2}$

$J = \frac{3}{2}$ or $J = \frac{1}{2}$

Boron $1s^2 2s^2 2p \Rightarrow$ $\boxed{^2P_{3/2} \text{ or } ^2P_{1/2}}$ $\leftarrow$ Boron

---

For Carbon, now have 2 p electrons

$\ell_1 = 1$ $\ell_2 = 1$: can combine to give $L = 2, 1, 0$

$S_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$: can combine to give $S = 1$ or 0

For $J = L + S$ we then have 10 combinations:

$L = 2, S = 1 \Rightarrow J = 3, 2, 1$ — $^3D_3 \quad ^3D_2 \quad ^3D_1$

$L = 2, S = 0 \Rightarrow J = 2$ — $^1D_2$

$L = 1, S = 1 \Rightarrow J = 2, 1, 0$ — $^3P_2 \quad ^3P_1 \quad ^3P_0$

$L = 1, S = 0 \Rightarrow J = 1$ — $^1P_1$

$L = 0, S = 1 \Rightarrow J = 1$ — $^3S_1$

$L = 0, S = 0 \Rightarrow J = 0$ — $^1S_0$

CARBON

For nitrogen, now have 3 p electrons

$l_1 = 1, l_2 = 1, l_3 = 1$ can combine to give

$$L = 3, 2, 1, 0$$

$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, s_3 = \frac{1}{2}$ can combine to give

$$S = \frac{3}{2}, \frac{1}{2}$$

$\Rightarrow$ For $J = L + S$ we have 19 combinations:

P.S. #9 solns.

$L=3,\ S=\frac{3}{2} \Rightarrow J=\frac{9}{2},\frac{7}{2},\frac{5}{2},\frac{3}{2}$

$L=3,\ S=\frac{1}{2} \Rightarrow J=\frac{7}{2},\frac{5}{2}$

$L=2,\ S=\frac{3}{2} \Rightarrow J=\frac{7}{2},\frac{5}{2},\frac{3}{2},\frac{1}{2}$

$L=2,\ S=\frac{1}{2} \Rightarrow J=\frac{5}{2},\frac{3}{2}$

$L=1,\ S=\frac{3}{2} \Rightarrow J=\frac{5}{2},\frac{3}{2},\frac{1}{2}$

$L=1,\ S=\frac{1}{2} \Rightarrow J=\frac{3}{2},\frac{1}{2}$

$L=0,\ S=\frac{3}{2} \Rightarrow J=\frac{3}{2}$

$L=0,\ S=\frac{1}{2} \Rightarrow J=\frac{1}{2}$

$$\boxed{\begin{array}{c} {}^4F_{9/2}\ {}^4F_{7/2}\ {}^4F_{5/2}\ {}^4F_{3/2} \\ {}^2F_{7/2}\ {}^2F_{5/2} \\ {}^4D_{7/2}\ {}^4D_{5/2}\ {}^4D_{3/2}\ {}^4D_{1/2} \\ {}^2D_{5/2}\ {}^2D_{3/2} \\ {}^4P_{5/2}\ {}^4P_{3/2}\ {}^4P_{1/2} \\ {}^2P_{3/2}\ {}^2P_{1/2} \\ {}^4S_{3/2} \\ {}^2S_{1/2} \end{array}}$$

Nitrogen

PS #9

(2) (a) For nd^{10}

The ten electrons occupy each of the following single electron states

electrons	m_{l_i}	m_{s_i}
1	+2	+1/2
2	+2	-1/2
3	+1	+1/2
4	+1	-1/2
5	0	+1/2
6	0	-1/2
7	-1	+1/2
8	-1	-1/2
9	-2	+1/2
10	-2	-1/2
Sum	$M_L = 0$	$M_S = 0$

Because M_L and M_S are only zero

$\Rightarrow$ $L = 0$ and $S = 0$

$L + S = J$

$\Rightarrow$ $J = 0$

Term Symbol is $\boxed{^1S_0}$

(b) Looking at the table, we must determine L and S from M_L and M_S
The largest value of M_L is 2 and it occurs with $M_S = 0$

This implies $L = 2$ $S = 0$

and $J = 2$

This means table entries 1, 3, 5, 12, and 15

$\Rightarrow \boxed{{}^1D_2}$

The next largest value of M_L is 1

implying $L = 1$. This would lead to

$M_L = \pm 1, 0$. But each of these values

of M_L occurs with $M_S = \pm 1, 0$. This

indicates that $L = 1$ and $S = 1$, yielding

$J = 2, 1, 0$

$M_J = +2, +1, 0, -1, -2$ $M_J = +1, 0, -1$ $M_J = 0$

So this accounts for table entries

2, 4, 6, 7, 8, 9, 11, 13, and 14

$\Rightarrow \boxed{{}^3P_2, \ {}^3P_1, \ {}^3P_0}$

The last entry (#10) has $L = 0, S = 0, J = 0$

$\Rightarrow \boxed{{}^1S_0}$

2 (c) Ground state of Carbon:

5 possible term symbols

$^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1S_0$

Hund's rule #1 $\Rightarrow$ must be a triplet state ($S=1$)

$\Rightarrow$ $^3P_2$, $^3P_1$, $^3P_0$ are still possible

Hund's rule #2 $\Rightarrow$ Largest L

All of them have $L=1$

$\Rightarrow$ $^3P_2$, $^3P_1$, $^3P_0$ are still possible

Hund's rule #3 $\Rightarrow$ Smallest J (p subshell less than half full)

$\Rightarrow$ $\boxed{^3P_0 \text{ is ground state}}$

(3) We have 3 particles and 3 possible one-particle states: ψ_a, ψ_b, ψ_c

(a) 3 distinguishable particles $\Rightarrow$ any combination possible

Each particle can occupy any of the 3 states

$\Rightarrow$ $3 \times 3 = \boxed{27 \text{ possible states}}$

(b) 3 indistinguishable particles with symmetric $\psi_{spatial}$

possibilities: • All in the same state:

$\psi_a \psi_a \psi_a$, $\psi_b \psi_b \psi_b$, $\psi_c \psi_c \psi_c$ $\Rightarrow$ 3

notation: particle #1, particle #2, particle #3

• Then 2 particles in the same state:

$\psi_a \psi_a \psi_b$
$\psi_a \psi_a \psi_c$
$\psi_b \psi_b \psi_a$
$\psi_b \psi_b \psi_c$
$\psi_c \psi_c \psi_a$
$\psi_c \psi_c \psi_b$

all of these need to be "symmetrized" (see below)

$\Rightarrow$ 6

- All 3 in different States

$\psi_a \psi_b \psi_c$ "symmetrized" (1)

$$\boxed{\text{Total possibilities} = 3 + 6 + 1 = 10}$$

For this course, you do not need to know how to symmetrize 3 particle States, but if you are interested:

$$\psi_a \psi_b \psi_c \Rightarrow \frac{1}{\sqrt{6}} \Big[\psi_a \psi_b \psi_c + \psi_a \psi_c \psi_b + \psi_b \psi_a \psi_c + \psi_b \psi_c \psi_a + \psi_c \psi_a \psi_b + \psi_c \psi_b \psi_a \Big]$$

and $\psi_a \psi_a \psi_b \Rightarrow \frac{1}{\sqrt{3}} \Big[\psi_a \psi_a \psi_b + \psi_a \psi_b \psi_a + \psi_b \psi_a \psi_a \Big]$

etc.

(c) 3 indistinguishable particles with antisymmetric ψ_{spatial}

$$\boxed{\text{There is only one possible combination}}$$

$\psi_a \psi_b \psi_c$ that can be antisymmetric

Again, we would have to "antisymmetrize" this, which if you are interested:

$$\psi_a\psi_b\psi_c \Rightarrow \frac{1}{\sqrt{6}}\Big[\psi_a\psi_b\psi_c - \psi_a\psi_c\psi_b - \psi_b\psi_a\psi_c + \psi_b\psi_c\psi_a + \psi_c\psi_a\psi_b - \psi_c\psi_b\psi_a\Big] \quad -(1)$$

Note that if we exchange particles 1 and 2, we get:

$$\frac{1}{\sqrt{6}}\Big[\psi_b\psi_a\psi_c - \psi_c\psi_a\psi_b - \psi_a\psi_b\psi_c + \psi_c\psi_b\psi_a + \psi_a\psi_c\psi_b - \psi_b\psi_c\psi_a\Big] \quad -(2)$$

which is indeed the same as eqn (1) multiplied by -1 $\Rightarrow$ so it is antisymmetric

Quantum Mechanics: Problem Set #10 Solutions

① (a) $E_F = \frac{\hbar^2}{2m}\left(3\frac{N}{V} q\pi^2\right)^{2/3}$ with $q = 1$

$$\frac{N}{V} = \frac{\text{atoms}}{\text{volume}} = \frac{\text{atoms}}{\text{mole}}\ \frac{\text{moles}}{\text{gram}}\ \frac{\text{grams}}{\text{volume}} = \underbrace{N_A}_{\text{Avogadro's number}} \cdot \frac{1}{\underbrace{M_a}_{\text{Atomic weight}}} \cdot (\text{density})$$

$$\frac{N}{V} = \left(6.02 \times 10^{23}\right) \frac{1}{63.5} (8.96) \frac{1}{cm^3}$$

$$\frac{N}{V} = 8.49 \times 10^{22}\ cm^{-3} = 8.49 \times 10^{28}\ m^{-3}$$

$$\Rightarrow E_F = \frac{\left(1.055 \times 10^{-34}\ J\cdot s\right)^2}{2 \cdot 9.11 \times 10^{-31}\ Kg}\left[3 \cdot \pi^2 \cdot 8.49 \times 10^{28}\ m^{-3}\right]^{2/3}$$

$$E_F = 6.11 \times 10^{-39} \cdot 1.76 \times 10^{20} = 1.08 \times 10^{-18}\ J$$

$$E_F = 1.08 \times 10^{-18}\ J \quad 6.24 \times 10^{18}\ \frac{eV}{J}$$

$$\boxed{E_F = 6.24\ eV}$$

(b) $E_F = \frac{1}{2} m v^2 \Rightarrow v = \left(\frac{2E_F}{m}\right)^{1/2} = \left(\frac{2 \cdot 1.08 \times 10^{-18}\ J}{9.11 \times 10^{-31}\ Kg}\right)^{1/2}$

$v = 1.54 \times 10^6 \frac{m}{s}$

$\frac{v}{c} = 5.1 \times 10^{-3}$

$c = 3.00 \times 10^8 m/s$

much less than 1

Speed of light

$\Rightarrow$ so nonrelativistic!

(c) $E_F \equiv k_B T_F \Rightarrow T_F = \frac{E_F}{k_B} = \frac{1.08 \times 10^{-18} J}{1.38 \times 10^{-23} J/K}$

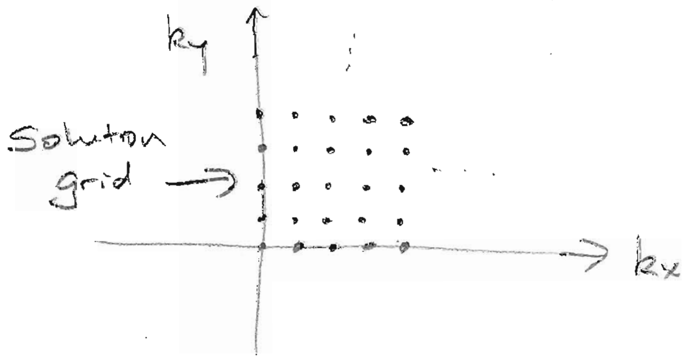
$\boxed{T_F = 78.3 \times 10^3 K}$

Yes, the T_F is ridiculously high
Copper is always "cold"

(2) For 2D infinite square well

$$E_{n_x,n_y} = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right] = \frac{\hbar^2 k^2}{2m} \quad \text{with} \quad \vec{k} = \frac{n_x \pi}{l_x}\hat{u}_x + \frac{n_y \pi}{l_y}\hat{u}_y$$

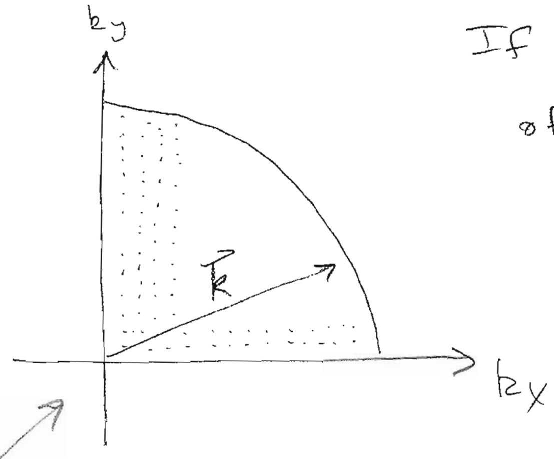
Now k-space is a plane and every solution can be represented by a point:



Each solution occupies an area of

$$\frac{\pi^2}{l_x l_y} = \frac{\pi^2}{A}$$

Where $A = l_x l_y$ is the area of the well



If we have a large number of particles, N, then

$|k| >>$ grid spacing

and we can determine the Fermi energy by

using the area of the quadrant drawn above

$$\frac{1}{4}\pi k_F^2 = \frac{Nq}{2} \cdot \frac{\pi^2}{A}$$

(Remember q = # of valence electrons each atom contributes)

Area in k-space up to E_F = $\frac{\text{Number of electrons}}{2 \text{ electrons/solution}}$ · area/solution

Area in k-space up to E_F = Number of solutions · $\frac{\text{area}}{\text{solution}}$ = area in k-space up to E_F

OR $$k_F = \left(\frac{2Nq\pi}{A}\right)^{1/2} = (2\pi\sigma)^{1/2}$$

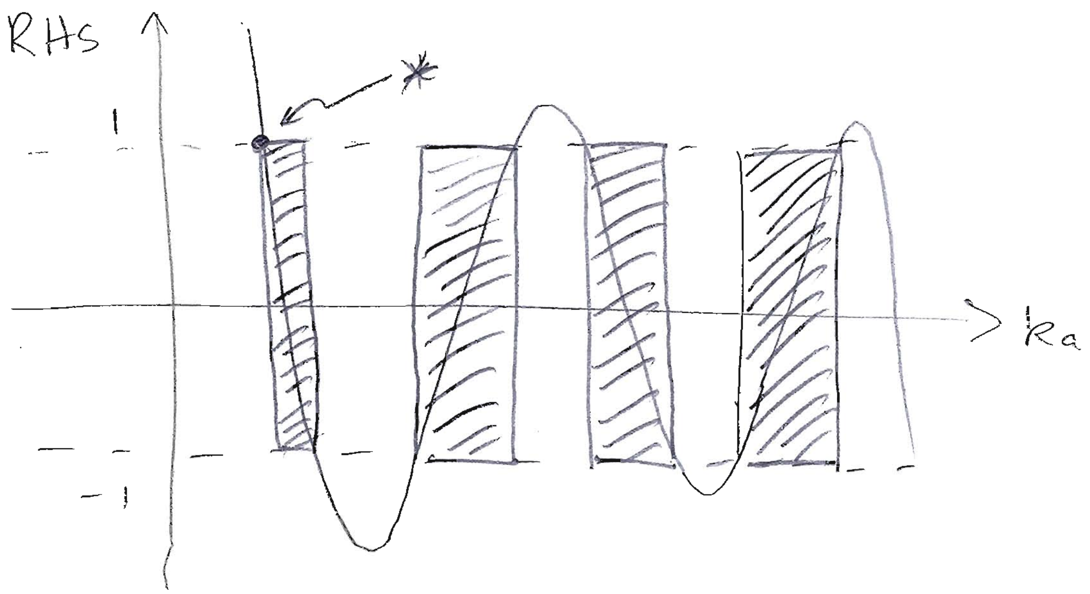
where $\sigma \equiv \frac{Nq}{A}$ ← the number of electrons per unit area of infinite square well

$$\therefore \quad E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} 2\pi\sigma = \boxed{\frac{\pi \hbar^2 \sigma}{m}}$$

3 The allowed energies satisfy the equation:

$$\underbrace{\cos(Ka)}_{\text{LHS}} = \underbrace{\cos ka + \beta \frac{\sin ka}{ka}}_{\text{RHS}}$$

If we plot the RHS versus ka, we saw that:



Since the LHS is a cosine, it has to be between ± 1. Also, the energy is proportional to k. Thus, the energy at the bottom of the lowest band will be at the point marked with the * in the plot above.

So we must solve

$$1 = \cos ka + \beta \frac{\sin ka}{ka} \quad \text{with } \beta = 10$$

$$1 = \cos ka + 10 \frac{\sin ka}{ka}$$

Using the "goal seek" function in Excel

$$\Rightarrow \quad ka = 2.628$$

The energy then is

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (2.628)^2}{2ma^2}$$

$$= \frac{(2.628)^2}{2\beta} \frac{\alpha}{a}$$

$$= \frac{(2.628)^2}{20} \cdot 1\,eV$$

$$\boxed{E = 0.345\ eV}$$

(4) In lecture we proved Bloch's Theorem as

$$\psi(x+a) = e^{iKa}\,\psi(x) \qquad \text{— (3)}$$

Assume $\psi(x) = e^{iKx}\,u(x)$ where $u(x)$ has the same periodicity as the lattice, i.e. $u(x+a) = u(x)$

Is this equivalent to Eq. 3 ?

$$\psi(x) = e^{iKx}\,u(x)$$

$$\Rightarrow \quad \psi(x+a) = e^{iK(x+a)}\,u(x+a)$$

$$\psi(x+a) = e^{iKa}\,e^{iKx}\,u(x+a)$$

$$\psi(x+a) = e^{iKa}\,\underbrace{e^{iKx}\,u(x)}_{\psi(x)}$$

$$\Rightarrow \quad \psi(x+a) = e^{iKa}\,\psi(x) \quad \checkmark$$

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(5) (a) electron concentration $n \doteq N_i\, e^{-E_g/k_BT}$

$$\Rightarrow \quad \ln \frac{n}{N_i} = -E_g/k_BT$$

OR $$T = \frac{E_g}{k_B \ln\left[N_i/n\right]}$$

Solutions, Problem Set #10

$$T = \frac{1.12\ eV}{8.62\times10^{-5}\ \frac{eV}{K} \cdot \ln\left[\frac{1.71\times10^{19}}{2\times10^{17}}\right]}$$

$k_B = 8.62\times10^{-5}\ eV/K$

$$T = \frac{1.12\ eV}{3.83\times10^{-4}\ eV/K}$$

$$\boxed{T = 2920\ K}\ !$$

Si melts at 1683 K

(b) For doped Silicon

$$n = N_D \exp\left[-E_D/k_BT\right]$$

$N_D \equiv$ donor concentration $= 10^{18}$ per cm^3

$$\ln\frac{n}{N_D} = \frac{-E_D}{k_BT} \Rightarrow T = \frac{E_D}{k_B \ln\left[N_D/n\right]}$$

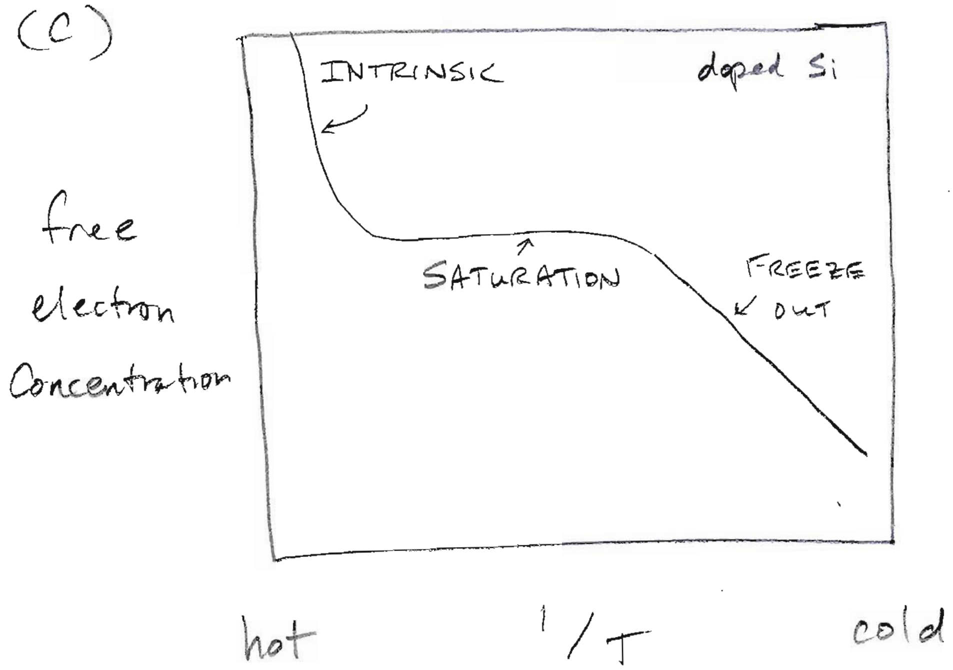
OR

$$T = \frac{0.045\ eV}{8.62\times10^{-5}\ eV/K\ \ln\left[10^{18}/2\times10^{17}\right]}$$

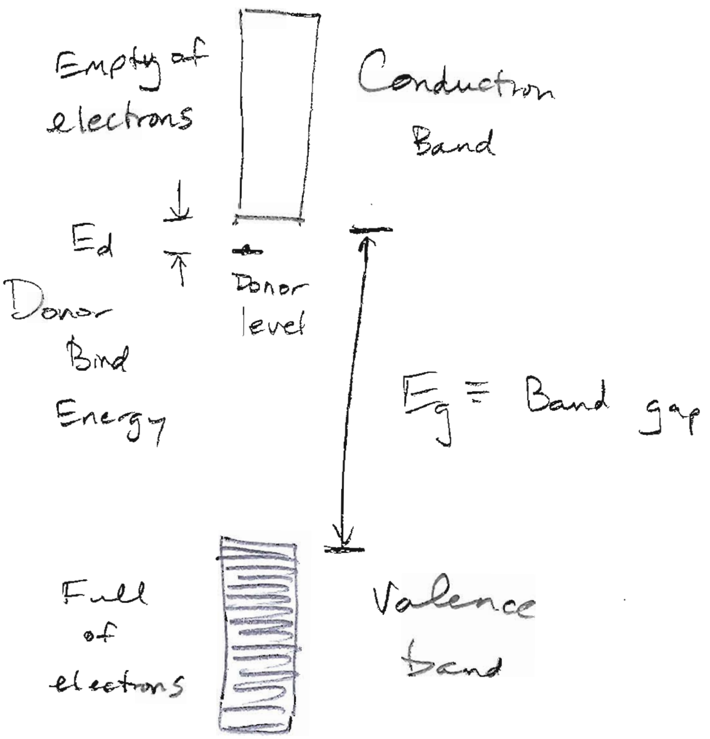
$$\boxed{T = 324\ K}$$

Solutions, Problem Set # 10

(c)



The plot shows free electron concentration vs. $1/T$. It has three regions. At cold temperature (the right of the plot) very few of the donors are ionized because $k_B T << E_d$, the binding energy. However, as we warm (move left) we ionize more and more of the donor electrons, which increases the free electron concentration. This low temperature regime is known as "freeze out". As the sample is warmed further, eventually all the donors are ionized when $k_B T \sim E_d$. Then further increases in the temperature do not introduce any additional free electrons. This regime is known as "saturation". However if we move far enough to the left, i.e. we heat the silicon hot enough, then $k_B T \sim E_g$ and we start to thermally excite electrons from the valence band to the conduction band directly. This third regime is known as the "intrinsic" regime. Thus, the plot can be understood in terms of the relative magnitudes of E_g, E_d, and $k_B T$.



Quantum Mechanics Problem Set #11 Solutions

① (a) $\psi_n^{(0)}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\right)x \qquad H' = \alpha\,\delta\left(x - \frac{a}{2}\right)$

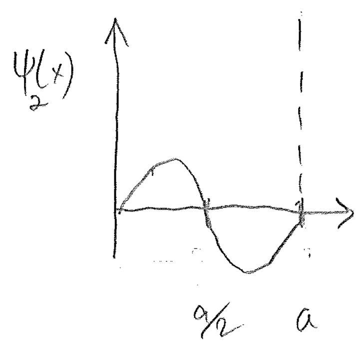
$$\Rightarrow E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = \frac{2}{a}\alpha \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) \delta\left(x - \frac{a}{2}\right) dx$$

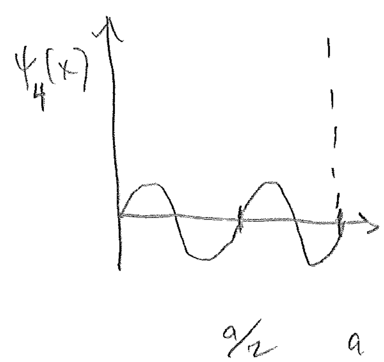
$$E_n^{(1)} = \frac{2\alpha}{a} \sin^2\left(\frac{n\pi}{a}\frac{a}{2}\right) = \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{2}\right) \qquad n = 1, 2, 3 \ldots$$

$$\boxed{E_n^{(1)} = \begin{cases} 0 & \text{if } n = \text{even} \\ \frac{2\alpha}{a} & \text{if } n = \text{odd} \end{cases}}$$

Why is $E_n^{(1)} = 0$ when $n =$ even?

$\Rightarrow$ for $n = 2$, $n = 4$, ... the wave function has a node at $x = \frac{a}{2}$ so the perturbation has no influence on the energy.





(b) Looking for $\psi_1^{(1)}(x)$ $\Rightarrow$ we need $\langle \psi_m^{(0)} | \hat{H}' \psi_1^{(0)} \rangle$ $m \neq 1$

$$\langle \psi_m^{(0)} | \hat{H}' \psi_1^{(0)} \rangle = \frac{2\alpha}{a} \int_0^a \sin\left(\frac{m\pi}{a} x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{\pi}{a} x\right) dx$$

$$= \frac{2\alpha}{a} \left[\sin\left(\frac{m\pi}{2}\right) \underbrace{\sin\left(\frac{\pi}{2}\right)}_{1} \right] = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right)$$

$\Rightarrow \langle \psi_m^{(0)} | \hat{H}' \psi_1^{(0)} \rangle = 0$ for even m and the first three non-zero terms will be: $m = 3, 5, 7$

Also $$E_1^{(0)} - E_m^{(0)} = \frac{\pi^2 \hbar^2}{2ma^2} (1 - m^2)$$

$$\therefore \psi_1^{(1)} = \sum_{m=3,5,7} \frac{(2\alpha/a) \sin(m\pi/2)}{E_1^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$= \frac{2\alpha}{a} \frac{2ma^2}{\pi^2 \hbar^2} \left[\frac{-1}{1-9} \psi_3^{(0)} + \frac{1}{1-25} \psi_5^{(0)} + \frac{-1}{1-49} \psi_7^{(0)} + \dots \right]$$

$$= \frac{4ma\alpha}{\pi^2 \hbar^2} \sqrt{\frac{2}{a}} \left[\frac{1}{8} \sin\left(\frac{3\pi}{a} x\right) - \frac{1}{24} \sin\left(\frac{5\pi}{a} x\right) + \frac{1}{48} \sin\left(\frac{7\pi}{a} x\right) + \dots \right]$$

$$\boxed{\psi_1^{(1)} = \frac{m\alpha}{\pi^2 \hbar^2} \sqrt{\frac{a}{2}} \left[\sin\left(\frac{3\pi}{a} x\right) - \frac{1}{3} \sin\left(\frac{5\pi}{a} x\right) + \frac{1}{6} \sin\left(\frac{7\pi}{a} x\right) + \dots \right]}$$

(c) Following part (b) $\langle \psi_m^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi}{2}\right)$

This equals zero unless m and n are odd

That is $\langle \psi_m^{(0)} | \hat{H}' \psi_n^{(0)} \rangle = \pm \frac{2\alpha}{a}$ if m and n are odd

$$\Rightarrow E_n^{(2)} = \sum_{m \neq n, \text{odd}} \left(\frac{2\alpha}{a}\right)^2 \frac{1}{E_n^{(0)} - E_m^{(0)}}$$

We know

$$E_n^{(0)} = \frac{\pi^2 \hbar^2}{2 \underset{\substack{\uparrow \\ \text{mass}}}{m} a^2} n^2$$

$$\boxed{E_n^{(2)} = \begin{cases} 0 & \text{if } n \text{ is even} \\ 2 \underset{\substack{\uparrow \\ \text{mass}}}{m} \left(\frac{2\alpha}{\pi\hbar}\right)^2 \displaystyle\sum_{m \neq n, \text{odd}} \frac{1}{(n^2 - m^2)} & \text{if } n \text{ is odd} \end{cases}}$$

To sum the series, note $\frac{1}{n^2 - m^2} = \frac{1}{2n}\left(\frac{1}{m+n} - \frac{1}{m-n}\right)$

__n=1__ $\displaystyle\sum_{m=3,5,7\ldots} \frac{1}{2}\left(\frac{1}{m+1} - \frac{1}{m-1}\right) = \frac{1}{2}\left(\frac{1}{4} + \frac{1}{6} + \frac{1}{8} + \cdots - \frac{1}{2} - \frac{1}{4} - \frac{1}{6} - \frac{1}{8} \cdots\right)$

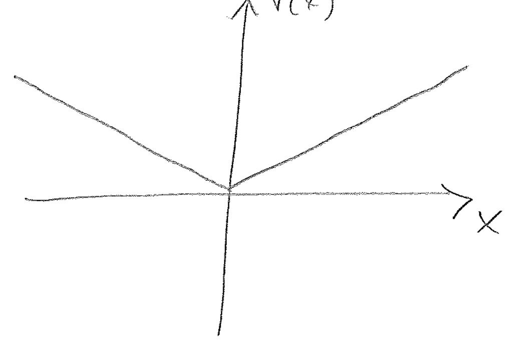
$$= \frac{1}{2}\left(-\frac{1}{2}\right) = -\frac{1}{4}$$

__n=3__ $\displaystyle\sum_{1,5,7\ldots} \frac{1}{6}\left(\frac{1}{4} + \frac{1}{8} + \frac{1}{10} + \cdots + \frac{1}{2} - \frac{1}{2} - \frac{1}{6} - \frac{1}{8} - \frac{1}{10} \cdots\right) = \frac{1}{6}\left(-\frac{1}{6}\right) = \frac{-1}{36}$

In general the summation gives $\frac{1}{2n}\left(-\frac{1}{2n}\right) = -\frac{1}{(2n)^2}$

$$\therefore \quad \boxed{E_n^{(2)} = \begin{cases} 0 & \text{if } n \text{ is even} \\ -2m\left(\dfrac{\alpha}{\pi\hbar n}\right)^2 & \text{if } n \text{ is odd} \end{cases}}$$

(2) $V(x) = C|x|$



$\langle \psi_{trial} | \hat{H} \psi_{trial} \rangle$

with $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + C|x|$

$$\langle \psi_{trial} | \hat{H} \psi_{trial} \rangle = \underbrace{2 \cdot \int_0^\infty \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left[-\frac{\alpha x^2}{2}\right]\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right]\left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left[-\frac{\alpha x^2}{2}\right] dx}_{\text{from lecture}}$$

$$+ \; 2\int_0^\infty \left(\frac{\alpha}{\pi}\right)^{1/2} \exp\left[-\frac{\alpha x^2}{2}\right][Cx]\exp\left[-\frac{\alpha x^2}{2}\right] dx$$

$$= \frac{\hbar^2 \alpha}{4m} + 2C\left(\frac{\alpha}{\pi}\right)^{1/2} \underbrace{\int_0^\infty x \exp\left[-\alpha x^2\right] dx}_{\frac{1}{2\alpha}}$$

$$= \frac{\hbar^2 \alpha}{4m} + \left(\frac{C^2}{\alpha \pi}\right)^{1/2}$$

Now we want to minimize this with respect to the parameter α. That is, $\frac{d}{d\alpha}\langle \Psi_{trial} | \hat{H} \Psi_{trial} \rangle$

$$\Rightarrow \quad \frac{\hbar^2}{4m} - \frac{1}{2}\left(\frac{C^2}{\alpha^3 \pi}\right)^{1/2} \Rightarrow \frac{\hbar^2}{2m} = \left(\frac{C^2}{\alpha^3 \pi}\right)^{1/2}$$

$$\Rightarrow \quad \alpha^3 = \frac{4m^2 C^2}{\pi \hbar^4} \Rightarrow \alpha = \left[\frac{4m^2C^2}{\pi\hbar^4}\right]^{1/3}$$

$$\therefore \quad \langle \Psi_{trial} | \hat{H} \Psi_{trial} \rangle \Big|_{min} = \frac{\hbar^2}{4m}\left[\frac{4m^2C^2}{\pi\hbar^4}\right]^{1/3} + \frac{C}{\sqrt{\pi}}\left[\frac{\pi\hbar^4}{4m^2C^2}\right]^{1/3 \cdot 1/2}$$

$$= \left[\frac{4\hbar^6 C^2 m^2}{4^3 m^3 \pi \hbar^4}\right]^{1/3} + \left[\frac{C^6 \pi \hbar^4}{\pi^3 \cdot 4 m^2 C^2}\right]^{1/6}$$

$$= \left(\frac{\hbar^2 C^2}{16 m \pi}\right)^{1/3} + \left[\frac{C^4 \hbar^4}{4\pi^2 m^2}\right]^{1/6}$$

$$= \left(\frac{\hbar^2 C^2}{16 m \pi}\right)^{1/3} + \left[\frac{\hbar^2 C^2}{2 m \pi}\right]^{1/3}$$

$$= \left(\frac{\hbar^2 C^2}{2 m \pi}\right)^{1/3}\left[\frac{1}{2} + 1\right] = \boxed{\frac{3}{2}\left(\frac{C^2\hbar^2}{2\pi m}\right)^{1/3}}$$

(3) (a) For the unperturbed Hamiltonian:

$$\hat{H} = V_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$; so it is already diagonal.

$\Rightarrow$ eigenvectors $|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ with eigenvalue V_0

$|2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ " " V_0

$|3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$ " " $2V_0$

(b) We need to solve eigenvalue equation

$\hat{H}\psi = E\psi$ $\Rightarrow$ solve "characteristic equation"

$\det(\hat{H} - \lambda) = 0$ where λ are the eigenvalues

$$\begin{vmatrix} [V_0(1-\epsilon)-\lambda] & 0 & 0 \\ 0 & [V_0-\lambda] & \epsilon V_0 \\ 0 & \epsilon V_0 & [2V_0-\lambda] \end{vmatrix} = 0$$

or $\left[V_0(1-\epsilon)-\lambda\right]\left[(V_0-\lambda)(2V_0-\lambda)-(\epsilon V_0)^2\right]=0$

$\Downarrow$ $\Downarrow$

If this equals zero:

$$\boxed{\lambda_1 = V_0(1-\epsilon)}$$

E_1

If this equals zero:

$$\lambda^2 - 3V_0\lambda + (2V_0^2 - \epsilon^2 V_0^2) = 0$$

$$\lambda = \frac{3V_0 \pm \sqrt{9V_0^2 - 4(2V_0^2 - \epsilon^2 V_0^2)}}{2}$$

$$= \frac{V_0}{2}\left[3 \pm \sqrt{1+4\epsilon^2}\right]$$

E_2 $\quad \lambda_2 = \frac{V_0}{2}\left(3-\sqrt{1+4\epsilon^2}\right)$

E_3 $\quad \lambda_3 = \frac{V_0}{2}\left(3+\sqrt{1+4\epsilon^2}\right)$

Taylor expansion

$$\Rightarrow \quad \lambda_2 \simeq \frac{V_0}{2}\left(3-\left[1+2\epsilon^2\right]\right) \simeq V_0(1-\epsilon^2)$$

$$\lambda_3 \simeq \frac{V_0}{2}\left(3+\left[1+2\epsilon^2\right]\right) \simeq V_0(2+\epsilon^2)$$

(c) The nondegenerate eigenvector of $\hat{H}$ when $\epsilon=0$ is [see part (a)] $|3\rangle$

$$H' = \epsilon V_0 \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \Rightarrow E_3^{(1)} = \langle 3 | H' 3 \rangle$$

$$\Rightarrow E_3^{(1)} = \epsilon V_0 \, (0\,0\,1) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \epsilon V_0 \, (0\,0\,1) \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0$$

$\Rightarrow$ $\boxed{\text{no first-order correction}}$

$$E_3^{(2)} = \sum_{m=1,2} \frac{|\langle m | H' 3 \rangle|^2}{E_3^{(0)} - E_m^{(0)}} \Rightarrow \langle 1 | H' 3 \rangle = (1\,0\,0) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$= 0$$

and $\langle 2 | H' 3 \rangle = \epsilon V_0 \, (0\,1\,0) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \epsilon V_0 \, (0\,1\,0) \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$

$$= \epsilon V_0$$

$$\therefore \; E_3^{(2)} = 0 + \frac{|\epsilon V_0|^2}{E_3^{(0)} - E_2^{(0)}} = \frac{(\epsilon V_0)^2}{2V_0 - V_0} = \epsilon^2 V_0$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = 2V_0 + 0 + \epsilon^2 V_0 = \boxed{V_0 (2 + \epsilon^2)}$$

$\Rightarrow$ exactly the same as in part (b) for λ_3

(d) Now λ_1 and λ_2 were degenerate, so we need to use degenerate perturbation theory. We can use:

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

$$W_{aa} = \langle 1|\hat{H}'1\rangle = \epsilon V_0 \,(1\,0\,0)\begin{pmatrix}-1 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} = -\epsilon V_0$$

$$W_{bb} = \langle 2|\hat{H}'2\rangle = \epsilon V_0 \,(0\,1\,0)\begin{pmatrix}-1 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}0\\1\\0\end{pmatrix} = 0$$

$$W_{ab} = \langle 1|\hat{H}'2\rangle = \epsilon V_0 \,(1\,0\,0)\begin{pmatrix}-1 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}0\\1\\0\end{pmatrix} = 0$$

$$\Rightarrow E_\pm^{(1)} = \frac{1}{2}\left[-\epsilon V_0 + 0 \pm \sqrt{\epsilon^2 V_0^2 + 0}\right]$$

$$E_\pm^{(1)} = \frac{1}{2}\left[-\epsilon V_0 \pm \epsilon V_0\right]$$

To first order then

$$\boxed{\begin{aligned} E_1 &= V_0 - \epsilon V_0 \\ E_2 &= V_0 \end{aligned}}$$

Note: These are consistent to first order with what we got in (b).

(4) This proof follows what we did in lecture to verify $E_{gs} \leq \langle \psi | \hat{H} \psi \rangle \equiv \langle \hat{H} \rangle$

That is: $\psi_{trial} = \sum_n c_n \psi_n$ but $\langle \psi_{trial} | \psi_1 \rangle = 0$ (given)

$\Rightarrow c_1 = 0$ And we know $E_n \geq E_{fe}$ for $n > 1$

Thus $$\langle \hat{H} \rangle = \sum_{n=2}^{\infty} E_n |c_n|^2 \geq E_{fe} \underbrace{\sum_{n=2}^{\infty} |c_n|^2}_{1}$$

$\therefore \langle \hat{H} \rangle \geq E_{fe}$ Q.E.D.

Problem Set #12 Solutions

1. Nodes in the eigen-wavefunctions

a) Equation (1) can be shown the following way:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V\psi_n &= E_n\psi_n \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\psi_m\frac{d^2\psi_n}{dx^2} + V\psi_n\psi_m = E_n\psi_n\psi_m \\
-\frac{\hbar^2}{2m}\frac{d^2\psi_m}{dx^2} + V\psi_m &= E_m\psi_m \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\psi_n\frac{d^2\psi_m}{dx^2} + V\psi_n\psi_m = E_m\psi_n\psi_m
\end{aligned}$$

The difference in the two equation is then

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left[\psi_m\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\psi_m}{dx^2}\right] &= (E_n - E_m)\psi_m\psi_n \\
\left[\psi_n\frac{d^2\psi_m}{dx^2} - \psi_m\frac{d^2\psi_n}{dx^2}\right] &= \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n
\end{aligned}$$

Since

$$\frac{d}{dx}\left[\psi_n\frac{d\psi_m}{dx} - \psi_m\frac{d\psi_n}{dx}\right] = \frac{d\psi_n}{dx}\frac{d\psi_m}{dx} + \psi_n\frac{d^2\psi_m}{dx^2} - \frac{d\psi_m}{dx}\frac{d\psi_n}{dx} - \psi_m\frac{d^2\psi_n}{dx^2} = \psi_n\frac{d^2\psi_m}{dx^2} - \psi_m\frac{d^2\psi_n}{dx^2}.$$

Therefore

$$\frac{d}{dx}\left[\psi_n\frac{d\psi_m}{dx} - \psi_m\frac{d\psi_n}{dx}\right] = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n$$

which is the form of equation (1).

b) In this step, we integrate equation (1)

$$\int_{x_1}^{x_2}\frac{d}{dx}\left[\psi_n\frac{d\psi_m}{dx} - \psi_m\frac{d\psi_n}{dx}\right]\mathrm{d}x = \int_{x_1}^{x_2}\frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n\mathrm{d}x$$

After integration, we get

$$\left[\psi_n\frac{d\psi_m}{dx} - \psi_m\frac{d\psi_n}{dx}\right]_{x_1}^{x_2} = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\mathrm{d}x$$

Plugging in the integration limits at the left side, we get

$$\psi_n(x_2)\psi_m'(x_2) - \psi_n(x_1)\psi_m'(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\mathrm{d}x$$

as all terms with $\psi_m(x_2) = 0 = \psi_m(x_1)$.

c)

$$\psi_n(x_2)\psi_m'(x_2) - \psi_n(x_1)\psi_m'(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\mathrm{d}x$$

We assume now that ψ_n and ψ_m are positive in the range between x_1 and x_2. Then the right side of the equation is larger than zero. For the left hand side, we can also determine the signs of the terms:

$$\underbrace{\psi_n(x_2)}_{+}\underbrace{\psi_m'(x_2)}_{-} - \underbrace{\psi_n(x_1)}_{+}\underbrace{\psi_m'(x_1)}_{+}$$

And so the LHS is smaller than zero. This leads to a contradiction unless $E_m > E_n$.

2. Matrix representation of operators

Solution

a) If we have the matrix A and want to get out the element A_{11} e. g. , we multiply with the row vector $\begin{pmatrix}1 & 0 & 0 & \dots\end{pmatrix}$ from the right, and the column vector $\begin{pmatrix}1\\0\\\dots\end{pmatrix}$ from the left:

$$\begin{pmatrix}1 & 0 & 0 & \dots & 0\end{pmatrix}\begin{pmatrix}A_{11} & A_{12} & A_{13} & \cdots & A_{1N}\\ A_{21} & A_{22} & A_{23} & \cdots & A_{2N}\\ \vdots & & \ddots & & \vdots\\ A_{N1} & A_{N2} & A_{N3} & \cdots & A_{NN}\end{pmatrix}\begin{pmatrix}1\\0\\\dots\\0\end{pmatrix} = A_{11}.$$

Similarly, if we want to get the matrix element A_{ij}, we need to multiply from the right with the row vector with 1 on place i and zeros everywhere else, and the column vector with 1 on place j. These vectors are the vector representations of $\langle i|$ and $|j\rangle$! So

$$A_{ij} = \langle i|A|j\rangle.$$

More formally, we can write

$$\hat{A} = \sum_{mn} |m\rangle \underbrace{\langle m|\hat{A}|n\rangle}_{\equiv A_{mn}} \langle n| = \sum_{mn} A_{mn}|m\rangle\langle n|.$$

Here, $|m\rangle\langle n|$ is the *outer product*. In matrix representation, it is the matrix multiplication of a column vector on a row vector, which creates an $N \times N$ matrix with zeros everywhere except at row m and column n:

$$|m\rangle\langle n| \doteq \begin{pmatrix}0 & \cdots & 0 & 0 & \cdots\\ \vdots & \ddots & 0 & 0 & \vdots\\ 0 & \cdots & 1 & 0 & \cdots\\ \vdots & \ddots & 0 & 0 & \vdots\\ 0 & \cdots & 0 & 0 & \cdots\end{pmatrix}.$$

Thus, we get

$$\hat{A} = \sum_{mn} A_{mn}|m\rangle\langle n| \doteq A_{11}\begin{pmatrix}1 & 0 & \cdots\\ 0 & 0 & \cdots\\ \vdots & \ddots & \vdots\end{pmatrix} + A_{12}\begin{pmatrix}0 & 1 & \cdots\\ 0 & 0 & \cdots\\ \vdots & \ddots & \vdots\end{pmatrix} + \cdots = \begin{pmatrix}A_{11} & A_{12} & \cdots\\ A_{21} & A_{22} & \cdots\\ \vdots & \ddots & \vdots\end{pmatrix}.$$

Thus, $A_{mn} \equiv \langle m|\hat{A}|n\rangle$ is the matrix element on row m and column n.

b) The energy eigenstates satisfy

$$\langle \psi_n'|\hat{H}|\psi_n\rangle = E_n\delta_{n,n'}$$

so

$$\hat{H} \doteq \begin{pmatrix}E_1 & 0 & \cdots & 0\\ 0 & E_2 & \cdots & 0\\ \vdots & & \ddots & \vdots\\ 0 & 0 & \cdots & E_N\end{pmatrix}$$

c) Let's represent our basis as the vectors with the shorthand $|l = 1, m_l = p\rangle \equiv |p\rangle$:

$$|1\rangle \doteq \begin{pmatrix}1\\0\\0\end{pmatrix}, \ |0\rangle \doteq \begin{pmatrix}0\\1\\0\end{pmatrix}, \ |-1\rangle \doteq \begin{pmatrix}0\\0\\1\end{pmatrix}$$

This set of vectors (the 3D unit vectors) form a complete set and can be used to represent any 3D vector in the space of real 3D vectors. The matrix elements of $\hat{L}_z$ in this basis are

$$\langle p|\hat{L}_z|q\rangle = p\hbar\delta_{p,q}, \qquad p,q = -1,0,1$$

so the matrix representation of $\hat{L}_z$ is

$$\hat{L}_z \doteq \begin{pmatrix} \langle 1|\hat{L}_z|1\rangle & \langle 1|\hat{L}_z|0\rangle & \langle 1|\hat{L}_z|-1\rangle \\ \langle 0|\hat{L}_z|1\rangle & \langle 0|\hat{L}_z|0\rangle & \langle 0|\hat{L}_z|-1\rangle \\ \langle -1|\hat{L}_z|1\rangle & \langle -1|\hat{L}_z|0\rangle & \langle -1|\hat{L}_z|-1\rangle \end{pmatrix} = \begin{pmatrix} +\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\hbar \end{pmatrix}$$

Similarly, for $\hat{L}_+$ we get

$$\hat{L}_+ \doteq \begin{pmatrix} \langle 1|\hat{L}_+|1\rangle & \langle 1|\hat{L}_+|0\rangle & \langle 1|\hat{L}_+|-1\rangle \\ \langle 0|\hat{L}_+|1\rangle & \langle 0|\hat{L}_+|0\rangle & \langle 0|\hat{L}_+|-1\rangle \\ \langle -1|\hat{L}_+|1\rangle & \langle -1|\hat{L}_+|0\rangle & \langle -1|\hat{L}_+|-1\rangle \end{pmatrix} = \sqrt{2}\hbar \begin{pmatrix} 0 & \langle 1|1\rangle & \langle 1|0\rangle \\ 0 & \langle 0|1\rangle & \langle 0|0\rangle \\ 0 & \langle -1|1\rangle & \langle -1|0\rangle \end{pmatrix} = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

and for $\hat{L}_-$:

$$\hat{L}_- \doteq \sqrt{2}\hbar \begin{pmatrix} \langle 1|0\rangle & \langle 1|-1\rangle & 0 \\ \langle 0|0\rangle & \langle 0|-1\rangle & 0 \\ \langle -1|0\rangle & \langle -1|-1\rangle & 0 \end{pmatrix} = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

Now we can use the above results to find L_x and L_y as

$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-) \doteq \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-) \doteq \frac{\hbar}{i\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

We can verify these results by, e. g., calculate the commutator

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &\doteq \frac{\hbar^2}{2i} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ &= \frac{\hbar^2}{2i} \begin{pmatrix} -2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} = i\hbar \times \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \doteq i\hbar\hat{L}_z \end{aligned}$$

d) Plugging in the matrix represenation of L_+ evaluated in (c), we get

$$L_+|-1\rangle = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \sqrt{2}\hbar \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \sqrt{2}\hbar|0\rangle$$

3. Feynman – Hellman theorem

Solution

a) Let the unperturbed Hamiltonian be $H(\lambda_0)$, for some fixed value λ_0. Now tweak λ to $\lambda_0 + d\lambda$. The perturbing Hamiltonian is $H' = H(\lambda_0 + \partial\lambda) - H(\lambda_0) = (\partial H/\partial\lambda)d\lambda$ (derivative evaluated at λ_0).

The change in energy is given by Eq. (1):

$$dE_n = E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle = \langle\psi_n^0|\frac{\partial H}{\partial\lambda}|\psi_n^0\rangle\, d\lambda \text{ (all evaluate at } \lambda_0) : \text{ so } \frac{\partial E_n}{\partial\lambda} = \langle\psi_n|\frac{\partial H}{\partial\lambda}|\psi_n\rangle\,.$$

Note: Even though we used perturbation theory, the result is exact, since all we needed (to calculate the derivative) was the *infinitesimal* change in E_n.

b)

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega;\; H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2.$$

(*i*)

$$\frac{\partial E_n}{\partial\omega} = \left(n+\frac{1}{2}\right)\hbar;\; \frac{\partial H}{\partial\omega} = m\omega x^2; \text{ so F-H-theorem } \Longrightarrow \left(n+\frac{1}{2}\right)\hbar = \langle n|m\omega x^2|n\rangle\,. \text{ But}$$

$$V = \frac{1}{2}m\omega^2x^2, \text{ so } \langle V\rangle = \langle n|m\omega^2x^2|n\rangle = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega.$$

(*ii*)

$$\frac{\partial E_n}{\partial\hbar} = \left(n+\frac{1}{2}\right)\omega;\; \frac{\partial H}{\partial\hbar} = -\frac{\hbar}{m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} = \frac{2}{\hbar}\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right) = \frac{2}{\hbar}T;$$

$$\text{so F} - \text{H} \Longrightarrow \left(n+\frac{1}{2}\right)\omega = \frac{2}{\hbar}\langle n|T|n\rangle\,, \text{ or } \langle T\rangle = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega.$$

(*iii*)

$$\frac{\partial E_n}{\partial m} = 0;\; \frac{\partial H}{\partial m}\frac{\hbar^2}{2m^2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}\omega^2x^2 = -\frac{1}{m}\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right) + \frac{1}{m}\left(\frac{1}{2}m\omega^2x^2\right) = -\frac{1}{m}T + \frac{1}{m}V.$$

So F-H $\Longrightarrow$ $0 = \frac{1}{m}(\langle V\rangle - \langle T\rangle)$, or $\langle T\rangle = \langle V\rangle$. These results are consistent with what we saw in the Virial theorem.

4. Two particles with spin in potential well

Solution

a) Since the spin part of the wavefunction for the two electrons is symmetric, the spatial part should be asymmetric. Since we are looking for the ground state, then the only possibility would be

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left(\Psi_1(r_1)\Psi_2(r_2) - \Psi_2(r_1)\Psi_1(r_2)\right)$$

Similar to lecture r_1 (r_2) denotes the position of particle 1 (2). The total wavefunction is then given by:

$$\Psi = \Psi(r_1, r_2)\chi_s = \frac{1}{\sqrt{2}} \left(\Psi_1(r_1)\Psi_2(r_2) - \Psi_2(r_1)\Psi_1(r_2)\right) \chi_+\chi_+$$

, where χ_s denotes the spin part of two-particle system.

b) In order to calculate the energy we have

$$\begin{aligned}\langle H \rangle &= \langle \Psi(r_1, r_2)|H_1 + H_2|\Psi(r_1, r_2)\rangle \\ &= \langle \frac{1}{\sqrt{2}} \left(\Psi_1(r_1)\Psi_2(r_2) - \Psi_2(r_1)\Psi_1(r_2)\right) |H_1 + H_2| \frac{1}{\sqrt{2}} \left(\Psi_1(r_1)\Psi_2(r_2) - \Psi_2(r_1)\Psi_1(r_2)\right)\rangle\end{aligned}$$

Here we should note that H_1 only acts on $\Psi_n(r_1)$, and H_2 only acts on $\Psi_n(r_2)$! For simplicity of writing we drop the $r_{1,2}$ form our notation, but we keep in mind that the first Ψ_n denotes the wavefunction of particle 1, and the second one the wavefunction of particle 2.

Therefore, we have

$$\begin{aligned}\langle H\rangle &= \frac{1}{2}\left[\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle - \langle\Psi_1\Psi_2|H|\Psi_2\Psi_1\rangle - \langle\Psi_2\Psi_1|H|\Psi_1\Psi_2\rangle + \langle\Psi_2\Psi_1|H|\Psi_2\Psi_1\rangle\right] \\ &= \frac{1}{2}\left[(E_1+E_2) - 0 - 0 + (E_1+E_2)\right] = E_1+E_2\end{aligned}$$

The detail of calculation the first term is:

$$\begin{aligned}\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle &= \langle\Psi_1\Psi_2|H_1+H_2|\Psi_1\Psi_2\rangle \\ &= \langle\Psi_1\Psi_2|H_1|\Psi_1\Psi_2\rangle + \langle\Psi_1\Psi_2|H_2|\Psi_1\Psi_2\rangle \\ &= \langle\Psi_1|H_1|\Psi_1\rangle\langle\Psi_2|\Psi_2\rangle + \langle\Psi_1|\Psi_1\rangle\langle\Psi_2|H_2|\Psi_2\rangle \\ &= E_1\times 1 + 1\times E_2 = E_1+E_2\end{aligned}$$

The detail of calculation the second term is:

$$\begin{aligned}\langle\Psi_1\Psi_2|H|\Psi_2\Psi_1\rangle &= \langle\Psi_1\Psi_2|H_1+H_2|\Psi_2\Psi_1\rangle \\ &= \langle\Psi_1\Psi_2|H_1|\Psi_2\Psi_1\rangle + \langle\Psi_1\Psi_2|H_2|\Psi_2\Psi_1\rangle \\ &= \langle\Psi_1|H_1|\Psi_2\rangle\langle\Psi_2|\Psi_1\rangle + \langle\Psi_1|\Psi_2\rangle\langle\Psi_2|H_2|\Psi_1\rangle \\ &= 0\end{aligned}$$

You can imagine the same thing for the third and forth term. You also notice how much our writing can be summarized thanks to Dirac notation! We do not need to do cumbersome calculation of integrals, if we know the eigenstates of the infinite square well are orthonormal.

c) If we can consider all the possibilities for the spin part of the wavefunction, minimum possible energy would be achieved when we choose the two particles in the state Ψ_1. Therefore, the spatial part of the wavefunction should be symmetric:

$$\Psi(r_1,r_2) = \Psi_1(r_1)\Psi_1(r_2)$$

Since the total wavefunction should be asymmetric, for the spin part of the wavefunction we have

$$\chi_s = \frac{1}{\sqrt{2}}(\chi_+\chi_- - \chi_-\chi_+)$$

The total wavefunction is

$$\Psi = \Psi_1(r_1)\Psi_1(r_2)\frac{1}{\sqrt{2}}(\chi_+\chi_- - \chi_-\chi_+)$$

The ground state energy in this case (you can do the calculation again) is:

$$\langle H\rangle = \langle\Psi_1\Psi_1|H|\Psi_1\Psi_1\rangle = 2E_1$$