HW 7

G 4.1 (a) $[x, p_x] f(\vec{r}) = \frac{\hbar}{i}\left(x \frac{\partial}{\partial x} - \frac{\partial}{\partial x} x \right) f(\vec{r})$

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

$= i\hbar f(\vec{r}) \quad \therefore [x, p_x] = i\hbar$

similarly, $[y, p_y] = [z, p_z] = i\hbar$

Obviously, $[p_x, x] = -[x, p_x]$

So $[r_i, p_i] = -[p_i, r_i] = i\hbar$

Now $[x, p_y] f(\vec{r}) = \frac{\hbar}{i}\left(x \frac{\partial}{\partial y} - \frac{\partial}{\partial y} x \right) f(\vec{r})$

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

So $[x, p_y] = 0$, and similarly
$[r_i, p_j] = 0$ if $i \neq j$

Combining all ~~these~~, $\underline{[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}}$

Since $xy = yx$, $xz = zx$ and $yz = zy$
trivially $\underline{[r_i, r_j] = 0.}$

Also, since $\frac{\partial}{\partial x}\frac{\partial}{\partial y} = \frac{\partial}{\partial y}\frac{\partial}{\partial x}$, etc,

$\underline{[p_i, p_j] = 0}$

(b) Eq. 3.71 should be valid for any dimensions, because we did not rely on any particular dimension in the derivation.

Then $\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, x]\rangle$

$$[\hat{H}, x] = \left[\frac{P_x^2+P_y^2+P_z^2}{2m} + V(\vec{r}), x\right]$$

Since $[P_y^2, x] = [P_z^2, x] = 0$
and $[V(x,y,z), x] = 0$,

$$[\hat{H}, x] = \frac{1}{2m}[P_x^2, x] = \frac{1}{2m}\big(P_x[P_x, x] + [P_x, x]P_x\big) = \frac{1}{2m}(-2i\hbar P_x) = -i\hbar\frac{P_x}{m}$$

$$\therefore \frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\left(-i\hbar\frac{\langle P_x\rangle}{m}\right) = \frac{\langle P_x\rangle}{m}$$

Similarly $\frac{d\langle y\rangle}{dt} = \frac{\langle P_y\rangle}{m}$ and $\frac{d\langle z\rangle}{dt} = \frac{\langle P_z\rangle}{m}$

$$\therefore \underline{\frac{d\langle\vec{r}\rangle}{dt} = \frac{\langle\vec{P}\rangle}{m}}$$

Now $\frac{d\langle P_x\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, P_x]\rangle$

$$[\hat{H}, P_x] = \left[\frac{P_x^2+P_y^2+P_z^2}{2m} + V(\vec{r}), P_x\right]$$
$$= [V(\vec{r}), P_x] = i\hbar\frac{\partial}{\partial x}V(\vec{r})$$

Thus $\frac{d\langle p_x\rangle}{dt} = \left\langle -\frac{\partial V}{\partial x}\right\rangle$

Similarly $\frac{d\langle p_y\rangle}{dt} = \left\langle -\frac{\partial V}{\partial y}\right\rangle$ and $\frac{d\langle p_z\rangle}{dt} = \left\langle -\frac{\partial V}{\partial z}\right\rangle$

Thus $\frac{d\langle \vec{p}\rangle}{dt} = \langle -\nabla V\rangle$

(c) From Eq 3.62,

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

$$\sigma_x^2\sigma_{p_x}^2 \geq \left(\frac{1}{2i}\langle[x, p_x]\rangle\right)^2$$

$$= \left(\frac{\hbar}{2}\right)^2$$

$$\Rightarrow \sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}$$

Similarly $\sigma_y\sigma_{p_y} \geq \frac{\hbar}{2}$ and $\sigma_z\sigma_{p_z} \geq \frac{\hbar}{2}$

Since $[x, p_y] = 0$, etc,

there is no restriction on $\sigma_{r_i}\sigma_{p_j}$ if $i \neq j$.

Q 4.2 T.I.S.E. within the box is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)$$

$$= E\psi(x,y,z)$$

With $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$

$$\left(\frac{d^2}{dx^2}X\right)YZ + \left(\frac{d^2}{dy^2}Y\right)XZ + \left(\frac{d^2}{dz^2}Z\right)XY$$
$$= -\frac{2mE}{\hbar^2}XYZ$$

With $\sqrt{\frac{2mE}{\hbar^2}} \equiv k$ and dividing both sides by XYZ, we have

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -k^2$$

For this equation to be valid for any (x, y, z) each term should be a constant

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2$$
$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2, \text{ and } \frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2$$

Then $k_x^2 + k_y^2 + k_z^2 = k^2$.

Now the boundary condition requires

$$X(0) = X(a) = Y(0) = Y(a) = Z(0) = Z(a) = 0$$

The general solution for each single variable differential equation is

$$X(x) = A\sin(k_x x) + B\cos(k_x x)$$
$$\Rightarrow X(0) = X(a) = 0 \Rightarrow B = 0,\ k_x a = n_x \pi$$

$$\Rightarrow \quad X(x) = A \sin\left(\frac{n_x \pi}{a} x\right)$$

with $n_x = 1, 2, 3, \ldots$

$$\int_0^a |X(x)|^2 \, dx = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{a}}$$

Using similar methods for $Y(y)$ and $Z(z)$,

The full stationary states are

$$\psi_{(n_x, n_y, n_z)}(x, y, z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \cdot \sin\left(\frac{n_z \pi}{a} z\right)$$

with $n_x = 1, 2, \ldots$

$n_y = 1, 2, \ldots$, $n_z = 1, 2, \ldots$

The corresponding energies are

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\left(\frac{n_x \pi}{a}\right)^2 + \left(\frac{n_y \pi}{a}\right)^2 + \left(\frac{n_z \pi}{a}\right)^2\right)$$

$$= \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

(b) (n_x, n_y, n_z) combination in the order of increasing energies are

$(1, 1, 1)$: $d = 1$ $\quad E_1 = \frac{\hbar^2 \pi^2}{2ma^2} \cdot 3$

, here "d" stands for degeneracy.

$$\left.\begin{matrix}(2,1,1)\\(1,2,1)\\(1,1,2)\end{matrix}\right\} d=3, \quad E_2=\frac{\hbar^2\pi^2}{2ma^2}\cdot 6$$

$$\left.\begin{matrix}(2,2,1)\\(2,1,2)\\(1,2,2)\end{matrix}\right\} d=3, \quad E_3=\frac{\hbar^2\pi^2}{2ma^2}\cdot 9$$

$$\left.\begin{matrix}(3,1,1)\\(1,3,1)\\(1,1,3)\end{matrix}\right\} d=3, \quad E_4=\frac{\hbar^2\pi^2}{2ma^2}\cdot 11$$

$$(2,2,2),\ d=1, \quad E_5=\frac{\hbar^2\pi^2}{2ma^2}\cdot 12$$

$$\left.\begin{matrix}(3,2,1)\\(3,1,2)\\(2,3,1)\\(2,1,3)\\(1,3,2)\\(1,2,3)\end{matrix}\right\} d=6, \quad E_6=\frac{\hbar^2\pi^2}{2ma^2}\cdot 14$$

$E_7 \Rightarrow (3,2,2)\ (9+4+4=17)$

$E_8 \Rightarrow (4,1,1)\ (16+1+1=18)$

$E_9 \Rightarrow (3,3,1)\ (9+9+1=19)$

$E_{10} \Rightarrow (4,2,1)\ (16+4+1=21)$

$E_{11} \Rightarrow (3,3,2)\ (9+9+4=22)$

$E_{12} \Rightarrow (4,2,2)\ (16+4+4=24)$

$E_{13} \Rightarrow (4,3,1)\ (16+9+1=26)$

$$E_{14} \Rightarrow \begin{cases} (3,3,3)\ (9\times 3=27) \\ (5,1,1)\ (25+1+1=27) \end{cases}$$

Dedeneracy of $E_{14} = 1+3 = 4$

: unlike the other energy values, E_{14} is composed of two number combinations (3,3,3) and (5,1,1).

Prob. 4.13

(a) $\langle r \rangle_{\psi_{100}} = \langle R_{10} | r | R_{10} \rangle \underbrace{\langle Y_0^0 | Y_0^0 \rangle}_{=1}$

$\psi_{100} = R_{10} Y_0^0$

$= \int_{r=0}^{\infty} r^3 R_{10}^2 \, dr = 4 a^{-3} \int_0^{\infty} r^3 e^{-2r/a} \, dr$

$= 4 a^{-3} \, 3! \left(\frac{a}{2}\right)^4 = \frac{3}{2} a$

$\langle r^2 \rangle_{\psi_{100}} = \langle R_{10} | r^2 | R_{10} \rangle = \int_0^{\infty} r^4 R_{10}^2 \, dr$

$= 4 a^{-3} \int_0^{\infty} r^4 e^{-2r/a} \, dr = 4 a^{-3} \, 4! \left(\frac{a}{2}\right)^5$

$= \underline{3 a^2}$

(b) $\langle x \rangle_{\psi_{100}} = 0$, because ψ_{100} is spherically symmetric and "x" is "odd" w.r.t. $x \to -x$.

$\langle x^2 \rangle_{\psi_{100}} = \frac{1}{3} \langle r^2 \rangle_{\psi_{100}} = \underline{a^2}$

(c) $\langle x^2 \rangle_{\psi_{211}} = \langle r^2 \sin^2\theta \cos^2\phi \rangle_{\psi_{211}}$

$= \int_0^{\infty} r^4 |R_{21}|^2 \, dr \iint |Y_1^1|^2 \sin^3\theta \cos^2\phi \, d\theta d\phi$

Radial part $= \frac{a^{-3}}{24} \int_0^{\infty} r^4 \frac{r^2}{a^2} \exp(-r/a) \, dr$

$$= \frac{a^{-5}}{24} \int_0^\infty r^6 \exp(-\tfrac{r}{a})\, dr$$

$$= \frac{a^{-5}}{24}\, 6!\, a^7 = \underline{30a^2}$$

Angular part $= \frac{3}{8\pi} \int_0^\pi \sin^5\theta\, d\theta \int_0^{2\pi} \cos^2\varphi\, d\varphi$

$$= \cancel{\frac{3}{8\pi}} \cdot \left(\cancel{2} \cdot \frac{2 \cdot \cancel{4}}{1 \cdot \cancel{3} \cdot 5}\right) \left(\cancel{\tfrac{1}{2} \cdot 2\pi}\right)$$

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$$= \frac{2}{5}$$

$$\therefore \langle x^2 \rangle_{\psi_{211}} = \underline{12\, a^2}$$

4.14 $\psi(\vec{r}) = \psi_{100}(\vec{r}) = R_{10} Y_0^0$

$P(r)\, dr$ = probability of finding the electron between r and $r+dr$

$$= \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} |\psi_{100}(\vec{r}')|^2 d^3\vec{r}' = |R_{10}|^2 r^2 dr \cdot \langle Y_0^0 | Y_0^0 \rangle$$

$$= |R_{10}|^2 r^2 dr$$

$$\Rightarrow P(r) = |R_{10}|^2 r^2 = 4a^{-3} \exp(-\tfrac{2r}{a}) \cdot r^2$$

Maximum of $P(r)$ occurs when

$$\frac{dP(r)}{dr} = 0 \Rightarrow \underbrace{-\frac{2}{a} \exp(-\tfrac{2r}{a}) r^2 + 2\exp(-\tfrac{2r}{a}) r}_{=0}$$

$$\Rightarrow \quad r\left(-\frac{r}{a}+1\right)=0$$

$$\Rightarrow \quad r=0 \quad \text{or} \quad r=a$$

$$p(r=0) = 0 \;, \quad p(r=a) = 4a^{-3} e^{-2} a^2$$
$$= \frac{4}{ae^2}$$

$\Rightarrow$ $p(r=0)=0$ must be the minimum and $p(r=a) = \dfrac{4}{ae^2}$ must be the maximum

Thus the most probable value of r is $\underline{r=a}$

4.15

(a) $$\Psi(\vec{r},t) = \frac{1}{\sqrt{2}}\left(\psi_{211}\, e^{-i\frac{E_2}{\hbar}t} + \psi_{21-1}\, e^{-i\frac{E_2}{\hbar}t}\right)$$
$$= \frac{1}{\sqrt{2}}\left(\psi_{211}+\psi_{21-1}\right) e^{-i\frac{E_2}{\hbar}t}$$
$$= \frac{1}{\sqrt{2}} R_{21}\left(Y_1^{1} + Y_1^{-1}\right) e^{-i\frac{E_2}{\hbar}t},$$ where $E_2 = -\dfrac{13.6\,eV}{4}$

(b) $$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r}\right\rangle$$

$$\left\langle \frac{1}{r}\right\rangle = \left\langle \Psi(\vec{r},t)\right| \frac{1}{r} \left|\Psi(\vec{r},t)\right\rangle$$
$$= \frac{1}{2}\left\langle \psi_{211}+\psi_{21-1}\right| e^{i\frac{E_2}{\hbar}t}\cdot\frac{1}{r}\, e^{-i\frac{E_2}{\hbar}t}\left|\psi_{211}+\psi_{21-1}\right\rangle$$
$$= \frac{1}{2}\left\langle \psi_{211}+\psi_{21-1}\right| \frac{1}{r}\left|\psi_{211}+\psi_{21-1}\right\rangle$$

$$= \frac{1}{2} \langle R_{21} | \frac{1}{r} | R_{21} \rangle \langle Y_1^1 + Y_1^{-1} | Y_1^1 + Y_1^{-1} \rangle$$

$$= \frac{1}{2} \int_0^\infty \frac{1}{24} a^{-3} \frac{r^2}{a^2} e^{-r/a} \cdot \frac{1}{r} \cdot r^2 dr$$

$$\times \left[\underbrace{\langle Y_1^1 | Y_1^1 \rangle}_{=1} + \cancelto{0}{\langle Y_1^1 | Y_1^{-1} \rangle} + \cancelto{0}{\langle Y_1^{-1} | Y_1^1 \rangle} + \underbrace{\langle Y_1^{-1} | Y_1^{-1} \rangle}_{=1} \right]$$

$$= \frac{1}{24} \cdot a^{-5} \int_0^\infty r^3 e^{-r/a} dr$$

$$= \frac{1}{24} \cdot a^{-5} \cdot 3! \ a^4 = \frac{1}{4a}$$

Thus

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{4a} = \frac{1}{2} \left(-\frac{1}{2a} \frac{e^2}{4\pi\epsilon_0} \right)$$

$$= \frac{E_1}{2}$$ From Eq. 4.70 and Eq. 4.72

$= -6.8$ eV, independent of time.