Advanced Quantum Mechanics

Homework 5: 4.1, 4.2, 4.16, 4.17

Kenny Roffo

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4.1 a) Work out all of the canonical commutation relations for components of the operators **r** and **p**:

$$[x, y] = [y, x] = xy - yx = xy - xy = 0$$
$$[x, z] = [z, x] = xz - zx = xz - xz = 0$$
$$[y, z] = [z, y] = yz - zy = yz - yz = 0$$

Since $r_x = x$, $r_y = y$ and $r_z = z$ this implies $[r_i, r_j] = 0$ where i and j are x, y or z. ($[r_i, r_i] = 0$ is trivial since the commutator of anything with itself is always 0).

Recall that $p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$. Letting f be a test function we have:

$$\begin{aligned}[p_x, p_y] &= \left[\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right) - \left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\right] f \\ &= -\hbar^2\left(\frac{\partial}{\partial x}\frac{\partial}{\partial y} f - \frac{\partial}{\partial y}\frac{\partial}{\partial x} f\right)\end{aligned}$$

But we know from calculus that for any function g, $\frac{\partial}{\partial x}\frac{\partial}{\partial y} g = \frac{\partial}{\partial y}\frac{\partial}{\partial x} g$, so this implies $[p_x, p_y] = 0$. Generalizing this tells us that $[p_i, p_j] = 0$ when i and j are x, y or z.

Now consider $[x, p_y]$. Applying a test function f we have:

$$\begin{aligned}[x, p_y] = -[p_y, x] = [x, \frac{\hbar}{i}\frac{\partial}{\partial y}] &= \left[x\frac{\hbar}{i}\frac{\partial}{\partial y} - \frac{\hbar}{i}\frac{\partial}{\partial y}x\right] f \\ &= x\frac{\hbar}{i}\frac{\partial f}{\partial y} - \frac{\hbar}{i}\frac{\partial x \cdot f}{\partial y} \\ &= x\frac{\hbar}{i}\frac{\partial f}{\partial y} - \left(x\frac{\hbar}{i}\frac{\partial f}{\partial y} + f\frac{\hbar}{i}\frac{\partial x}{\partial y}\right) \\ &= -f\frac{\hbar}{i}\frac{\partial x}{\partial y} \qquad\qquad \text{but } \frac{\partial x}{\partial y} = 0 \text{ so...} \\ &= 0\end{aligned}$$

So $[r_i, p_j] = 0$ when i and j are distinct and x, y or z. But what about when $i = j$?

$$\begin{aligned}
[x, p_x] = -[p_x, x] &= [x, \frac{\hbar}{i}\frac{\partial}{\partial x}] \\
&= \left[x\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x}x\right] f \\
&= x\frac{\hbar}{i}\frac{\partial f}{\partial x} - \frac{\hbar}{i}\frac{\partial x \cdot f}{\partial x} \\
&= x\frac{\hbar}{i}\frac{\partial f}{\partial x} - \left(x\frac{\hbar}{i}\frac{\partial f}{\partial x} + f\frac{\hbar}{i}\frac{\partial x}{\partial x}\right) \\
&= -f\frac{\hbar}{i}
\end{aligned}$$

Now removing the test function, we see $[r_i, p_i] = -\frac{\hbar}{i}$.
Synthesizing these results we see that the function is 0 except when i and j are 0. We can thus represent this by one function using the *kronecker delta function*:

$$[r_i, p_j] = -[p_i, r_j] = -\frac{\hbar}{i}\delta_{ij} = i\hbar\delta_{ij}$$

4.1 b) We must show that $\frac{\mathrm{d}}{\mathrm{d}t}\langle r\rangle = \frac{1}{m}\langle p\rangle$. We must first check for the x-component. From Equation 3.71 we know:

$$\frac{\partial\langle Q\rangle}{\partial t} = \frac{i}{\hbar}\left\langle[\hat{H}, \hat{Q}]\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle$$

Now

$$\begin{aligned}
[\hat{H}, \hat{x}] &= [\frac{p^2}{2m} + V, x] \\
&= \frac{1}{2m}[p_x^2 + p_y^2 + p_z^2, x] + [V, x] \\
&= \frac{1}{2m}\left([p_x^2, x] + [p_y^2, x] + [p_z^2, x]\right) + 0 \\
&= \frac{1}{2m}[p_x^2, x]\text{by } \mathbf{4.1\ a} \\
&= \frac{1}{2m}\left(p_x[p_x, x] + [p_x, x]p_x\right) \\
&= \frac{1}{2m}\left(p_x(-i\hbar\delta_{xx}) + p_x(-i\hbar\delta_{xx})\right)\text{ by } \mathbf{4.1\ a} \\
&= \frac{1}{2m}\left(-2p_x i\hbar\right) \\
&= \frac{-p_x i\hbar}{m} \\
&= \frac{p_x\hbar}{im}
\end{aligned}$$

By Equation 3.71 we have

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\left\langle [\hat{H},\hat{x}]\right\rangle + \left\langle \frac{\partial \hat{x}}{\partial t}\right\rangle$$

And now that we have $[\hat{H},\hat{x}]$ we see:

$$\begin{aligned}\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} &= \frac{i}{\hbar}\left\langle \frac{p_x\hbar}{im}\right\rangle + 0 && \text{since } \frac{\partial x}{\partial t} = 0\\ &= \frac{i}{\hbar}\frac{\hbar}{im}\langle p_x\rangle\\ &= \frac{1}{m}\langle p_x\rangle\end{aligned}$$

Thus $\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{1}{m}\langle p_x\rangle$. Applying the same steps to y and x we see:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle y\rangle = \frac{1}{m}\langle p_y\rangle \qquad\qquad \frac{\mathrm{d}}{\mathrm{d}t}\langle z\rangle = \frac{1}{m}\langle p_z\rangle$$

Therefore, synthesizing these results we have:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{r}\rangle = \frac{1}{m}\langle \mathbf{p}\rangle$$

Now we must show that $\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{p}\rangle = \langle \boldsymbol{\nabla} V\rangle$. Again we will start with the x-component:

$$\begin{aligned}[\hat{H},\hat{p}] &= [\frac{p^2}{2m} + V, p_x]\\ &= \frac{1}{2m}[p_x^2 + p_y^2 + p_z^2, p_x] + [V, p_x]\\ &= \frac{1}{2m}\Big([p_x^2, p_x] + [p_y^2, p_x] + [p_z^2, p_x]\Big) + [V, p_x]\\ &= [V, p_x] && \text{by } \mathbf{4.1\ a}\\ &= [V, -i\hbar\frac{\partial}{\partial x}]\end{aligned}$$

We will use a test function f to calculate this commutator:

$$\begin{aligned}[V, p_x] = [V, -i\hbar\frac{\partial}{\partial x}]f &= -Vi\hbar\frac{\partial f}{\partial x} + i\hbar\frac{\partial V\cdot f}{\partial x}\\ &= -Vi\hbar\frac{\partial f}{\partial x} + Vi\hbar\frac{\partial f}{\partial x} + fi\hbar\frac{\partial V}{\partial x}\\ &= fi\hbar\frac{\partial V}{\partial x}\end{aligned}$$

Now removing the test function we see $[\hat{H}, \hat{p_x}] = i\hbar \dfrac{\partial V}{\partial x}$. Now we can calculate $\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x \rangle$:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x \rangle &= \frac{i}{\hbar}\left\langle [\hat{H}, \hat{p_x}] \right\rangle + \left\langle \frac{\partial \hat{p_x}}{\partial t} \right\rangle \\
&= \frac{i}{\hbar}\left\langle i\hbar \frac{\partial V}{\partial x} \right\rangle + 0 && \text{since } \frac{\partial \hat{p_x}}{\partial t} = 0 \\
&= i^2 \left\langle \frac{\partial V}{\partial x} \right\rangle \\
&= \left\langle -\frac{\partial V}{\partial x} \right\rangle
\end{aligned}$$

Applying the same steps to y and z reveal that:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_y \rangle = \left\langle -\frac{\partial V}{\partial y} \right\rangle \qquad \frac{\mathrm{d}}{\mathrm{d}t}\langle p_z \rangle = \left\langle -\frac{\partial V}{\partial z} \right\rangle$$

Synthesizing these results we see:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{p} \rangle = \left\langle -\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) V \right\rangle$$

Thus we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{p} \rangle = \langle -\boldsymbol{\nabla} V \rangle$$

4.1 c) Formulate Heisenberg's uncertainty principle in three dimensions. From **section 3.5** we know the uncertainty principle for two operators $\hat{A}$ and $\hat{B}$ is:

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

by **4.1 a** we know the commutators of the different combinations among x, y, z, p_x, p_y and p_z. Thus to find the uncertainty principle for these combinations we must simply plug those commutators into this equation and calculate.

$$\begin{aligned}
\sigma_x \sigma_{p_x} &\geq \frac{1}{2i} i\hbar \delta_{xx} \\
&= \frac{i\hbar}{2i} \\
&= \frac{\hbar}{2}
\end{aligned}$$

And generalizing this implies that $\sigma_i, \sigma_{p_i} \geq \frac{\hbar}{2}$ when i is one of x, y or z.
Also, for all other combinations the commutator is 0, so the uncertainty principle for all other combinations is

$$\sigma_A \sigma_B \geq 0$$

when A and B are distinct and each one of x, y, z, p_x, p_y and p_z. This means there is no restriction on the uncertainty of these combinations (thought they cannot be negative).

4.2 Use seperation of variables in *cartesian* coordinates to solve the infinite *cubical* well:

$$V(x, y, z) = \begin{cases} 0 & \text{if } x,\ y,\ z \text{ are all between 0 and } a \\ \infty & \text{otherwise} \end{cases}$$

a) Find the stationary states, and the corresponding energies. The time-independent schrodinger equation for three dimensions is

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

Plugging in V, when the particle is in the box, we have

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

Assuming the wave function is seperable, it can be written as

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

Pluggin in we have

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + XZ\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + XY\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}\right) = E\psi$$

Dividing by ψ we have

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + \frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = -\frac{2m}{\hbar^2}E$$

This implies that each of the terms on the left side must be constant. Letting

$$C_x + C_y + C_z = -\frac{2m}{\hbar^2}E$$

we have that

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = -C_x \qquad \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = -C_y \qquad \frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = -C_z$$

But this implies

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + C_x = 0 \qquad \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + C_y = 0 \qquad \frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} + C_z = 0$$

These equations have general solutions:

$$\begin{aligned} X(x) &= A_x\sin(C_x x) + B_x\cos(C_x x) \\ Y(y) &= A_y\sin\big(C_y y\big) + B_y\cos\big(C_y y\big) \\ Z(z) &= A_z\sin(C_z z) + B_z\cos(C_z z) \end{aligned}$$

The boundary conditions state these functions must be 0 at $x, y, z = 0$. Thus the B coefficients must all be equal to 0, and so

$$\begin{aligned} X(x) &= A_x \sin(C_x x) \\ Y(y) &= A_y \sin(C_y y) \\ Z(z) &= A_z \sin(C_z z) \end{aligned}$$

Also, at $x, y, z = a$ these functions must be 0, so $\sin(C_x a) = 0$. $\sin(\theta) = 0$ when $\theta = n\pi$ so we have

$$\begin{aligned} C_x &= \frac{n_x \pi}{a} \\ C_y &= \frac{n_y \pi}{a} \\ C_z &= \frac{n_z \pi}{a} \end{aligned}$$

for integers n_x, n_y, n_z.

We now have

$$\psi(x, y, z) = X(x)Y(y)Z(z) = A_x \sin(C_x x) A_y \sin(C_y y) A_z \sin(C_z z)$$

Normalization of the function is shown for A_x:

$$\begin{aligned} 1 &= \int_0^a \left[A_x \sin(C_x x)\right]^* \left[A_x \sin(C_x x)\right] \mathrm{d}x \\ &= \int_0^a A_x^2 \sin^2(C_x x) \, \mathrm{d}x \\ &= \frac{a}{2} A_x^2 \\ \implies A_x &= \sqrt{\frac{2}{a}} \end{aligned}$$

By the same process we see $A_y = A_z = \sqrt{\frac{2}{a}}$ Therefore we now have the normalized equation for the energies of stationary states of a particle in a three-dimensional box.

$$\begin{aligned} -\frac{2m}{\hbar^2} E &= \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right) \\ \implies E &= -\sqrt{\frac{2\hbar^4}{a^3 m^2}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right) \end{aligned}$$

The Energy eigenvalues are now given by

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

b) Call the distinct energies $E_1, E_2, E_3, ...$ in order of increasing energy. Find $E_1, E_2, ..., E_6$ and determine their degeneracies:

For E_n the sum of $n_x + n_y + n_z - 2$ must equal n. Thus for E_1 there is only one such state, the ground state. However, for E_2 there are three possible ways to choose $\{n_x, n_y, n_z\}$: $\{2,1,1\}, \{1,2,1\}, \{1,1,2\}$ so E_2 has a degeneracy of 3. Via the same process we see the degeneracies are:

$$\begin{aligned}
E_1 &= \frac{3\pi^2\hbar^2}{2ma^2} : d = 1 \ \{1,1,1\} \\
E_2 &= \frac{6\pi^2\hbar^2}{2ma^2} : d = 3 \ \{2,1,1\}, \{1,2,1\}, \{1,1,2\} \\
E_3 &= \frac{9\pi^2\hbar^2}{2ma^2} : d = 9 \ \{1,2,2\}, \{2,1,2\}, \{2,2,1\} \\
E_4 &= \frac{11\pi^2\hbar^2}{2ma^2} : d = 3 \ \{3,1,1\}, \{1,3,1\}, \{1,1,3\} \\
E_5 &= \frac{12\pi^2\hbar^2}{2ma^2} : d = 1 \ \{2,2,2\} \\
E_6 &= \frac{14\pi^2\hbar^2}{2ma^2} : d = 6 \ \{3,2,1\}, \{3,1,2\}, \{2,3,1\}, \{1,3,2\}, \{1,2,3\}, \{2,1,3\}
\end{aligned}$$

c) What is the degeneracy of E_{14}, and why is this case interesting?

$$E_{14} = \frac{27\pi^2\hbar^2}{2ma^2} : d = 4 \ \{3,3,3\}, \{5,1,1\}, \{1,5,1\}, \{1,1,5\}$$

This case is very interesting as in all states before hand there was really only one way to choose n_x, n_y, n_z (then they could be shuffled around). However, at E_{14} there are *two* different ways to choose this. Either, all of them are 3, or one is 5 and the others are 1.

4.16)A hydrogenic atom consists of a single electron orbiting a nucleus with Z protons. Determine the Bohr energies, $E_n(Z)$, the binding energy $E_1(Z)$, and the Bohr radius $a(Z)$, and the Rydberg constant $R(Z)$ for a hydrogenic atom.

The allowed energies for an electron in a Hydrogen atom are

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

For a Hydrogenic atom, we know $e^2 \to Ze^2$, so the allowed energies for an electron in a Hydrogenic atom are

$$E_n(Z) = -\left[\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = Z^2\frac{E_1}{n^2}$$

So then the binding energy of a hydrogenic atom is

$$E_1(Z) = Z^2E_1 = -13.6Z^2$$

The Bohr Radius of Hydrogen is

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

Applying the conversion for a Hydrogenic atom we have

$$a(Z) = \frac{4\pi\epsilon_0\hbar^2}{Zme^2} = \frac{a_0}{Z}$$

The Rydberg constant for Hydrogen is

$$R_H \equiv \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2$$

Once again we convert this to find the Rydberg Constant for any Hydrogenic atom:

$$R(Z) = \frac{m}{4\pi c\hbar^3}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 = Z^2R_H$$

The wavelengths for the Lyman series of Hydrogen are in the Ultraviolet range. $R_{He^+} = 4.388\times10^{-7}$ and $R_{Li^{++}} = 9.873\times10^{-7}$This is not that significant of a change from R_H, and it comes as no surprise that the Lyman series for these two ions still lies in the UV range.

4.17) Consider the earth-sun system as a gravitational analog to the hydrogen atom.
a) What is the potential energy function? By comparison the potential energy function would be

$$V(r) = -\frac{GmM}{r}$$

where G is the Universal Gravitational Constant.

b) What is the "Bohr Radius", a_g, for this system?

$$a_g = \frac{\hbar^2}{Gm^2M} = \frac{(1.05457 \times 10^{-34})^2}{(6.67 \times 10^{-11})(6 \times 10^{24})^2(2 \times 10^{30})} \approx 2.316 \times 10^{-138}$$

c) Write down the gravitational "Bohr Formula", and, by equating E_n to the classical energy of a planet in a circular orbit of radius r_0, show that $n = \sqrt{r_0/a_g}$. From this, estimate the quantum number n of the Earth.

$$E_n = -\left[\frac{m}{2\hbar^2}\left(GmM\right)^2\right]\frac{1}{n^2} = -2\frac{GmM}{r_0}$$

Solving this equation for n we have:

$$\begin{aligned} n^2 &= \left[\frac{m}{2\hbar^2}\left(GmM\right)\right]2r_0 \\ n^2 &= \frac{Gm^2M}{\hbar^2}r_0 \\ n^2 &= \frac{r_0}{a_g} \\ n &= \sqrt{\frac{r_0}{a_g}} \end{aligned}$$

The principle quantum number of the Earth is then

$$n = \sqrt{\frac{1.5 \times 10^{11}}{2.31575 \times 10^{-138}}} = 2.54 \times 10^{74}$$

d) Suppose the earth made a transition to the lower level $(n-1)$. How much energy would be released? What would the wavelength of the emitted photon be?

$$\begin{aligned} E_\gamma &= \left[\frac{m}{2\hbar^2}\left(GmM\right)^2\right]\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ &= 2.1 \times 10^{-41} \text{ joules} \end{aligned}$$

Now we calculate the wavelength using $\lambda = \frac{hc}{E_\gamma}$

$$\begin{aligned} \lambda &\approx 9.496 \times 10^{15}\ \mathrm{m} \\ &\approx 1 \mathrm{lightyear} \end{aligned}$$

This is absolutely astonishing!