THE UNIVERSITY OF QUEENSLAND
SCHOOL OF MATHEMATICS AND PHYSICS
PHYS2041 – Quantum Physics

Tutorial 9 Solutions

Problem 9.1 (a) First, consider the case where the position and momentum operators are along the same axis, e.g. x and $\hat{p}_x$. Introducing a "test function" $f(x)$ will help us make sure we treat the derivatives properly,

$$
\begin{aligned}
[x, \hat{p}_x]\, f &= -i\hbar \left(x\frac{\partial}{\partial x} - \frac{\partial}{\partial x}x \right) f && (1)\\
&= -i\hbar \left(x\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}(xf) \right) && (2)\\
&= -i\hbar \left(\cancel{x\frac{\partial f}{\partial x}} - f - \cancel{x\frac{\partial f}{\partial x}} \right) \quad \text{(product rule)} && (3)\\
&= i\hbar f && (4)
\end{aligned}
$$

Dropping the test function we can conclude $[x, \hat{p}_x] = i\hbar$, and similarly for y and z. What about the situation where the position and momentum operators are along perpendicular axes, for instance x and $\hat{p}_y$? Again we'll introduce a test function $f(x, y)$,

$$
\begin{aligned}
[x, \hat{p}_y]\, f &= -i\hbar \left(x\frac{\partial}{\partial y} - \frac{\partial}{\partial y}x \right) f && (5)\\
&= -i\hbar \left(x\frac{\partial f}{\partial y} - x\frac{\partial f}{\partial y} \right) && (6)\\
&= 0 && (7)
\end{aligned}
$$

A similar proof for all other combinations leads us to the conclusion that position and momentum commute when they are along perpendicular axes.

What about the opposite commutator, $[\hat{p}_x, x]$? Well it's easy to show for any two operators,

$$
\begin{aligned}
[\hat{A}, \hat{B}] &= \hat{A}\hat{B} - \hat{B}\hat{A} && (8)\\
&= -\left(\hat{B}\hat{A} - \hat{A}\hat{B} \right) && (9)\\
&= -[\hat{B}, \hat{A}] && (10)
\end{aligned}
$$

which implies that $[\hat{p}_x, x] = -i\hbar$, etc. Putting this all together, we have that $[r_i, \hat{p}_j] = -[\hat{p}_i, r_j] = i\hbar\delta_{jk}$.

It's obvious that $[x, y] = xy - yx = 0$ - the position of a particle commutes with all other directions. We also know that partial derivatives of independent variables commute (Clairaut's theorem), so the same is true of momentum. In other words, $[r_i, r_j] = [\hat{p}_i, \hat{p}_j] = 0$.

(b) The generalised uncertainty principle is

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2 , \tag{11}$$

so all we need to do is plug in the commutation relations from the previous question. Notice that commuting observables do not have an uncertainty trade-off, which is why they're sometimes called *compatible observables.*

We have already seen that the only three combinations of position and momentum that are *incompatible* (i.e. non-commuting) are

$$\sigma_x^2 \sigma_{p_x}^2 \geq \frac{\hbar^2}{4}, \; \sigma_y^2 \sigma_{p_y}^2 \geq \frac{\hbar^2}{4}, \; \sigma_z^2 \sigma_{p_z}^2 \geq \frac{\hbar^2}{4}, \tag{12}$$

with all other combinations zero (e.g. $\sigma_x \sigma_y \geq 0$, and so on).

Problem 9.2 **[FOR ASSIGNMENT 5; max 10 points]**

(a) We use separation variables and write the wavefunction in the form of

$$\psi(x, y, z) = f(x) \; g(y) \; h(z) \tag{13}$$

and insert it in 3D time independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = E\psi, \tag{14}$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) f(x) \; g(y) \; h(z) = Ef(x) \; g(y) \; h(z), \tag{15}$$

$$\tag{16}$$

which after rearrangement can be written as

$$\frac{1}{f(x)} \frac{d^2 f(x)}{dx^2} + \frac{1}{g(y)} \frac{d^2 g(y)}{dy^2} + \frac{1}{h(z)} \frac{d^2 h(z)}{dz^2} = -\frac{2m}{\hbar^2} E. \tag{17}$$

Each term on the LHS depends only on one variable, and so it *must* equal to a constant, because the equation must be true for *all* values of x, y and z.; we will denote these three constants as $-\frac{2m}{\hbar^2} E_x$, $-\frac{2m}{\hbar^2} E_y$, and $-\frac{2m}{\hbar^2} E_z$, respectively. Therefore we can write the 3D TDSE (which is a partial differential equation) as three ordinary differential equations,

$$\frac{1}{f(x)} \frac{d^2 f(x)}{dx^2} = -\frac{2m}{\hbar^2} E_x, \tag{18a}$$

$$\frac{1}{g(y)} \frac{d^2 g(y)}{dy^2} = -\frac{2m}{\hbar^2} E_y, \tag{18b}$$

$$\frac{1}{h(z)} \frac{d^2 h(z)}{dz^2} = -\frac{2m}{\hbar^2} E_z, \tag{18c}$$

where the constant energies in each dimension E_x, E_y and E_z must add up to the total energy E,

$$E_x + E_y + E_z = E. \tag{19}$$

Equations (18 a-c) are simply the TISE for one dimensional infinite square well. Hence the 3D box potential is equivalent to three 1D square wells. We can use the solution for 1D

$$f_{n_x}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right), \qquad E_{n_x} = \frac{\hbar^2 \pi^2 n_x^2}{2ma^2}, \qquad n_x = 1, 2, 3, ..., \tag{20a}$$

$$g_{n_y}(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right), \qquad E_{n_y} = \frac{\hbar^2 \pi^2 n_y^2}{2mb^2}, \qquad n_y = 1, 2, 3, ..., \tag{20b}$$

$$h_{n_y}(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right), \qquad E_{n_z} = \frac{\hbar^2 \pi^2 n_z^2}{2mc^2}, \qquad n_z = 1, 2, 3, ..., \tag{20c}$$

Thus the solution to the Schrodinger equation for the particle in a 3D box is by a energy

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right), \tag{21}$$

and a wavefunction

$$\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right). \tag{22}$$

We can check the normalization by taking the integral

$$\begin{aligned}
&\sqrt{\frac{8}{abc}} \int_0^a \sin\left(\frac{n_x \pi x}{a}\right) dx \int_0^b \sin\left(\frac{n_y \pi y}{b}\right) dy \int_0^c \sin\left(\frac{n_z \pi z}{c}\right) dz \\
=&\sqrt{\frac{8}{abc}} \qquad \sqrt{\frac{a}{2}} \qquad \sqrt{\frac{b}{2}} \qquad \sqrt{\frac{c}{2}} \\
=&1.
\end{aligned} \tag{23}$$

(b) If $a = b = c = L$ solutions read as

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right), \tag{24}$$

with allowed energies

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2\right), \tag{25}$$

Now we calculate $E_{1,2,3}$

$$E_{1,2,3} = \frac{\hbar^2 \pi^2}{2mL^2} (1 + 4 + 9) = \frac{14\hbar^2 \pi^2}{2mL^2}, \tag{26}$$

which is equal to energy of the following

$$E_{1,2,3} = E_{1,3,2} = E_{2,1,3} = E_{2,3,1} = E_{3,1,2} = E_{3,2,1}, \tag{27}$$

so there are 6 degenerate states with energy $\frac{14\hbar^2\pi^2}{2mL^2}$.

<u>Problem 9.3</u> [FOR ASSIGNMENT 5; max 10 points]

(a) The ground-state wavefunction of the Hydrogen Hamiltonian is, in spherical coordinates:

$$\psi_{1,0,0}(r,\theta,\phi) = \frac{1}{\sqrt{a^3\pi}} e^{-\frac{r}{a}} \tag{28}$$

where $a > 0$ is the Bohr radius. Notice that this does not actually depend on θ or ϕ - only r. Such functions are called spherically symmetric.

Notice also that in cartesian coordinates, where $r = \sqrt{x^2 + y^2 + z^2}$, this wavefunction would look like

$$\psi_{1,0,0}(x,y,z) = \frac{1}{\sqrt{a^3\pi}} e^{-\frac{\sqrt{x^2+y^2+z^2}}{a}}. \tag{29}$$

This is, however, is a difficult function to deal with and to integrate, hence the advantage of using the spherical coordinates for integrations (in fact, I know of no other way of integrating this function except by going to spherical coordinates).

For any spherically symmetric function $f(r)$, the normalisation integral in spherical coordinates simplifies to a single integral over r (take care to include the Jacobian!), because the integrals over the angles are trivial and give a constant factor of 4π:

$$\begin{aligned}
&\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} f(r) r^2 \sin\theta dr d\phi d\theta && (30)\\
&= \int_0^{\infty} f(r) r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi && (31)\\
&= [\phi]_0^{2\pi} [-\cos\theta]_0^{\pi} \int_0^{\infty} f(r) r^2 dr && (32)\\
&= 4\pi \int_0^{\infty} f(r) r^2 dr && (33)
\end{aligned}$$

The expectation value of r or the average radius is

$$\langle r\rangle = \langle\psi_{1,0,0}|r|\psi_{1,0,0}\rangle = 4\pi\int_0^\infty r\,|\psi_{1,0,0}(r)|^2\,r^2dr \tag{34}$$
$$= 4\pi\int_0^\infty r^3|\psi_{1,0,0}(r)|^2dr \tag{35}$$
$$= \frac{4}{a^3}\int_0^\infty r^3e^{-\frac{2r}{a}}dr \tag{36}$$
$$= \frac{4}{a^3}\left(\cancel{\left[\frac{a}{2}r^3e^{-\frac{2r}{a}}\right]_0^\infty} + \frac{3a}{2}\int_0^\infty r^2e^{-\frac{2r}{a}}dr\right)\ \text{(integration by parts)} \tag{37}$$
$$= \frac{3a}{2}\langle\psi_{1,0,0}|\psi_{1,0,0}\rangle \tag{38}$$
$$= \frac{3a}{2} \tag{39}$$

where in the final line we made use of the normalisation of $\psi_{1,0,0}(r)$ (remember $\psi_{1,0,0}$ is spherically symmetric, its normalisation integral is in r only, Eq. (33)).

The mean-square radius is

$$\langle r^2\rangle = \langle\psi_{1,0,0}|r^2|\psi_{1,0,0}\rangle = 4\pi\int_0^\infty r^2\,|\psi_{1,0,0}(r)|^2\,r^2\,dr \tag{40}$$
$$= 4\pi\int_0^\infty r^4|\psi_{1,0,0}(r)|^2dr \tag{41}$$
$$= \frac{4}{a^3}\int_0^\infty r^4e^{-\frac{2r}{a}}dr \tag{42}$$
$$= \frac{4}{a^3}\left(\cancel{\left[\frac{a}{2}r^4e^{-\frac{2r}{a}}\right]_0^\infty} + \frac{4a}{2}\int_0^\infty r^3e^{-\frac{2r}{a}}dr\right)\ \text{(integration by parts)} \tag{43}$$
$$= \frac{4a}{2}\langle r\rangle\ \text{[Eq. (19)]} \tag{44}$$
$$= 3a^2 \tag{45}$$

(b) The ground state of hydrogen is spherically symmetric (it does not depend on θ or ϕ), which means that the particle is equally likely to be found either side of the x axis and thus $\langle x\rangle = 0$. This result could be obtained quantitatively by evaluating (remember $x = r\cos\phi\sin\theta$)

$$\langle x\rangle = \int_0^\pi\int_0^{2\pi}\int_0^\infty |\psi_{1,0,0}(r)|^2r^3\cos\phi\sin^2\theta drd\phi d\theta, \tag{46}$$

which we can see is zero because $\int_0^{2\pi}\cos\phi d\phi = 0$.

Because $r^2 = x^2+y^2+z^2$, it is also true that $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle$. Due to the spherical symmetry of $\psi_{1,0,0}$ we also know that $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$. Without having to even do any integrals, we can deduce $\langle r^2\rangle = 3\langle x^2\rangle$, or

$$\langle x^2\rangle = \frac{1}{3}\langle r^2\rangle = a^2. \tag{47}$$

The uncertainty $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ is therefore $\sigma_x = a$.

(c) As we will see here, the most likely value is *not* generally the same as the mean value.

We need to find the value of r that maximises the radial probability density. Remember that the probability of finding the particle inside a volume element $dV = dxdydz = r^2 \sin\theta dr d\theta d\phi$ is $dP = |\Psi(x,y,z,t)|^2 dV$, so even though we're not integrating $\psi_{1,0,0}$ we still need to include the Jacobian. Let's define the radial probability density (you can verify for yourself that $\int_0^\infty P(r)dr = 1$),

$$P(r) = 4\pi r^2 |\psi_{1,0,0}(r)|^2 = \frac{4}{a^3} r^2 e^{-\frac{2r}{a}}, \tag{48}$$

which unlike $|\psi_{1,0,0}(r)|^2$ goes to zero as $r \to 0$. If you think about it, the probability of finding the particle at $r = 0$ should always be zero, since this is the probability of finding the particle inside a sphere of zero volume! The value of r that maximises $P(r)$ can be found by examining the stationary points $dP/dr = 0$,

$$\frac{dP}{dr} = \frac{4}{a^3}\left(2r - \frac{2}{a}r^2\right) e^{-\frac{2r}{a}} = 0 \tag{49}$$

Exponentials are never zero, so this equation implies $2r - \frac{2}{a}r^2 = r(2 - \frac{2}{a}r) = 0$, which is solved for either $r = 0$ or $r = a$.

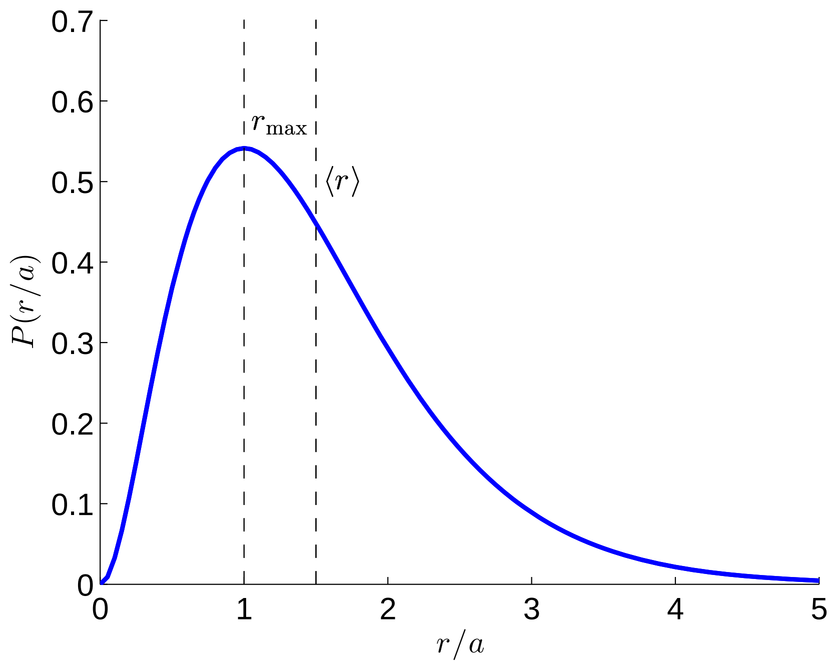

Figure 1: Radial probability distribution for the ground-state of Hydrogen. The most likely position $r_{\max}$ and mean position $\langle r \rangle$ are indicated by black dashed lines.

Clearly the $r = 0$ solution is a minimum, as $P(0) = 0$ [see also Figure 1], so the electron is most likely to be found at the Bohr radius,

$$r_{\max} = a. \tag{50}$$

This is an important result, as it helps reconcile the naive Bohr model with the Schrödinger's wave mechanics. Figure 1 shows $P(r)$, with both the most likely value and mean values of r indicated.

Problem 9.4

(a) $\Psi(\mathbf{r},t) = \frac{1}{\sqrt{2}}\left(\psi_{211}e^{-iE_2t/\hbar} + \psi_{21-1}e^{-iE_2t/\hbar}\right) = \frac{1}{\sqrt{2}}\left(\psi_{211} + \psi_{21-1}\right)e^{-iE_2t/\hbar};\quad E_2 = \frac{E_1}{4} = -\frac{\hbar^2}{8ma^2}.$

$$\psi_{211} + \psi_{21-1} = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-r/2a}\sin\theta\left(e^{i\phi} - e^{-i\phi}\right) = -\frac{i}{\sqrt{\pi a}\,4a^2}re^{-r/2a}\sin\theta\,\sin\phi.$$

$$\boxed{\Psi(\mathbf{r},t) = -\frac{i}{\sqrt{2\pi a}\,4a^2}re^{-r/2a}\sin\theta\,\sin\phi\,e^{-iE_2t/\hbar}.}$$

(b)

$$\begin{aligned}
\langle V\rangle &= \int|\Psi|^2\left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)d^3\mathbf{r} = \frac{1}{(2\pi a)(16a^4)}\left(-\frac{e^2}{4\pi\epsilon_0}\right)\int\left(r^2e^{-r/a}\sin^2\theta\,\sin^2\phi\right)\frac{1}{r}r^2\sin\theta\,dr\,d\theta\,d\phi \\
&= \frac{1}{32\pi a^5}\left(-\frac{\hbar^2}{ma}\right)\int_0^\infty r^3e^{-r/a}\,dr\int_0^\pi\sin^3\theta\,d\theta\int_0^{2\pi}\sin^2\phi\,d\phi = -\frac{\hbar^2}{32\pi ma^6}\left(3!a^4\right)\left(\frac{4}{3}\right)(\pi) \\
&= \boxed{-\frac{\hbar^2}{4ma^2} = \frac{1}{2}E_1 = \frac{1}{2}(-13.6\text{eV}) = -6.8\text{eV}}\quad\text{(independent of } t\text{).}
\end{aligned}$$