Problem Set 5 Solutions

Daily problem for 14 Oct

(a) Show that the speed of an electron in the nth Bohr orbit of hydrogen is $\alpha c/n$, where α is the fine structure constant, equal to $e^2/4\pi\epsilon_o\hbar c \approx 1/137$.

(b) What would be the speed in a hydrogen-like atom with a nuclear charge of Ze?

(c) Let's say our threshold for worrying about relativistic effects when it amounts to a 10% correction, where $\gamma = 1.10$ (implying $v/c \approx 0.42$). For the ground state of a hydrogen-like atom, for which element do we reach this threshold?

(d) Following the previous question, at what element is the correction 50% ($\gamma = 1.5$, $v/c \approx 0.745$).[i]

Solution: **(a)** Our main condition in deriving the Bohr model was the quantization of angular momentum (or, if you like, that the electron orbit is an integral number of wavelengths), $mvr = n\hbar$. We also figured out that the radius for the n^{th} state is $r_n = 4\pi\epsilon_o\hbar^2 n^2/me^2$. Putting this together,

$$v = \frac{n\hbar}{mr} = \frac{n\hbar}{m}\frac{me^2}{4\pi\epsilon_o\hbar^2 n^2} = \frac{1}{n}\frac{e^2}{4\pi\epsilon_o\hbar} = \frac{1}{n}\frac{e^2}{4\pi\epsilon_o\hbar}\frac{c}{c} = \frac{\alpha c}{n} \tag{1}$$

(b) For a nuclear charge Z in a hydrogen-like atom of atomic number Z, the Coulomb force between the nucleus and electron is Z times larger. If you follow back through the Bohr model derivation, this means that the radius is decreased by a factor Z, and the velocity increased by a factor Z.

$$v = \frac{\alpha c Z}{n} \tag{2}$$

(c) If we want relativistic effects to be less than 10%, $v/c \approx 0.42$. That means

$$\frac{v}{c} = \frac{\alpha Z}{n} = 0.42 \qquad \Longrightarrow \qquad Z = \frac{nv}{\alpha c} \approx 57 \tag{3}$$

This means, roughly speaking, that for elements of atomic number 57-58 (Lanthanum and Cerium) relativistic effects are becoming important (at least for the case where all but one electron is ionized away, but the rough conclusion holds). For understanding the details of properties like magnetism, however, we have to worry about relativity much earlier, even for light transition metals like Fe and Co. For understanding the more subtle and nuanced effects in, say, atomic spectra, even hydrogen has relativistic corrections to worry about, if your experiment is accurate enough.

[i] The inclusion of relativistic effects on electron orbitals has dramatic consequences for heavier elements like Hg: `http://www.rsc.org/chemistryworld/2013/06/why-mercury-liquid-relativity-evidence`

(d) The point at which relativity is a 75% correction, $v/c \approx 0.745$ - long past the point when classical physics will have failed us even *qualitatively* - comes at

$$Z = \frac{nv}{\alpha c} \approx 102 \tag{4}$$

This is Nobelium. By the time one gets into the actinides, relativity isn't just a correction, it is required for even a basic understanding of what's going on.

Daily problem for 16 Oct The wave function for a particle is given by

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad \{A, B\} \in \mathbb{R} \tag{5}$$

Identifying $|\psi(x)|^2$ as a 'probability density,' the quantum-mechanical analog of current density is[ii]

$$j(x) = \frac{\hbar}{2mi}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right) \tag{6}$$

(a) What current does the wave function above represent? *Be careful with signs and complex conjugates.*

(b) What is the physical interpretation of your result (hint: the wave function is the sum of right- and left-traveling waves).

(c) For a bound-state wave function (a wave that isn't traveling), ψ can be chosen to be purely real, and $\psi^* = \psi$. What does this indicate about the current density for bound states?

Solution: We will need the complex conjugate, and derivatives of it and ψ. Assuming A and B to be real is convenient, but also still perfectly general - if they were complex, the imaginary part could be absorbed into the complex exponential and would end up canceling out. Just to prove that it won't make a difference, though, we'll assume A and B could be complex (even though the problem tells us otherwise), since it doesn't make things much harder.

$$\psi^* = A^*e^{-ikx} + B^*e^{ikx} \tag{7}$$

$$\frac{\partial\psi}{\partial x} = ikAe^{ikx} - ikBe^{-ikx} \tag{8}$$

$$\frac{\partial\psi^*}{\partial x} = -ikA^*e^{-ikx} + B^*ike^{ikx} \tag{9}$$

Now we are at the plug & chug stage. Be careful, it is messy ... but the end result is fairly simple.

[ii] The current density may be regarded as a 'probability current' whose integral over a closed surface is equal to the rate of change of the probability that the particle will be found inside this surface. You may also note that $\frac{\hbar}{mi}\frac{\partial}{\partial x}$ is just the operator for the velocity of the particle (compare it to the momentum operator).

$$
\begin{aligned}
j &= \frac{\hbar}{2mi}\left[\left(A^*e^{-ikx}+B^*e^{ikx}\right)\left(ikAe^{ikx}-ikBe^{-ikx}\right)-\left(Ae^{ikx}+Be^{-ikx}\right)\left(-ikA^*e^{-ikx}+ikB^*e^{ikx}\right)\right] \\
&= \frac{\hbar}{2mi}\left[ik|A|^2-ikA^*Be^{-2ikx}+ikAB^*e^{2ikx}-ik|B|^2+ik|A|^2-ikAB^*e^{2ikx}+ikA^*Be^{-2ikx}-ik|B|^2\right] \\
&= \frac{\hbar}{2mi}\left[ik|A|^2-ik|B|^2+ik|A|^2-ik|B|^2\right]=\frac{\hbar k}{m}\left(|A|^2-|B|^2\right)
\end{aligned}
\tag{10}
$$

What is the physical interpretation? If we let $B=0$, our wave function is $\psi=Ae^{ikx}$, so we just have a plane wave traveling along $+x$. The flux associated with this plane wave is $j=\hbar k|A|^2/m$. On the other hand, if we let $A=0$ we have $\psi=Be^{-ikx}$, a plane wave traveling along $-x$, and the flux will be $j=-\hbar k|B|^2/m$. The overall form must then represent the sum of a flux to the right associated with the Ae^{ikx} term and a flux to the left associated with the Be^{-ikx}. The net flux would be zero if the two waves are of equal amplitude ($|A|=|B|$).

If ψ is perfectly real, as is the case for a bound state, then $\psi^*=\psi$ and $d\psi/dx=d\psi^*/dx$, so j must be zero since both terms would be the same. Bound states are just what they sound like – bound – and do not flow into our out of a region.

The remaining problems are due 18 Oct 2013

1. In electromagnetic theory, the conservation of charge is represented by the continuity equation (in one dimension)

$$
\frac{\partial j}{\partial x}=-\frac{\partial \rho}{\partial t}
\tag{11}
$$

Make use of the quantum-mechanical probability current density given in the preceding problem.

(a) Show that the continuity equation above is satisfied with the quantum definition of current density and probability density $\rho=|\psi|^2$. *Be careful with signs and complex conjugates, and note problem 5 part iii.*

(b) For a plane wave $\psi=Ae^{i(kx-\omega t)}$, show that probability current can be written $|A|^2v=\rho v$, where v is the particle's velocity.

(c) For the same plane wave, show that the probability density has no explicit time dependence. This illustrates that the particle may be moving (nonzero current) even though the probability density isn't changing in time.

Solution: **(a)** Nothing to do but grind through it and see if it works. Let's start with $\partial j/\partial x$, making liberal use of the chain rule.

$$\frac{\partial j}{\partial x} = \frac{\partial}{\partial x}\left[\frac{\hbar}{2mi}\left(\psi^*\frac{\partial \psi}{\partial x} - \psi\frac{\partial \psi^*}{\partial x}\right)\right] = \frac{\hbar}{2mi}\left[\frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} + \psi^*\frac{\partial^2 \psi}{\partial x^2} - \frac{\partial \psi}{\partial x}\frac{\partial \psi^*}{\partial x} - \psi\frac{\partial^2 \psi^*}{\partial x^2}\right] \tag{12}$$

The mixed first derivatives are all the same, and cancel out. We are left with:

$$\frac{\partial j}{\partial x} = \frac{\hbar}{2mi}\left[\psi^*\frac{\partial^2 \psi}{\partial x^2} - \psi\frac{\partial^2 \psi^*}{\partial x^2}\right] \tag{13}$$

Next, $\partial \rho/\partial t$.

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}\left(\psi^*\psi\right) = \frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} \tag{14}$$

This doesn't look like much help, but we can use the time-dependent Schrödinger equation to replace the time derivatives with spatial derivatives. We'll need both the equation and its complex conjugate. We will assume V is real for convenience.[iii]

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi \qquad \text{Schrödinger} \tag{15}$$

$$-i\hbar\frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \qquad \text{Schrödinger complex conjugate} \tag{16}$$

We should solve these for the time derivatives to make the substitution easier. Watch the signs.

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi}\frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}\psi \tag{17}$$

$$\frac{\partial \psi^*}{\partial t} = +\frac{\hbar}{2mi}\frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar}\psi^* \tag{18}$$

Substituting into our expression for $\partial \rho/\partial t$,

$$\frac{\partial \rho}{\partial t} = \left(\frac{\hbar}{2mi}\frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar}\psi^*\right)\psi + \psi^*\left(-\frac{\hbar}{2mi}\frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}\psi\right) \tag{19}$$

$$\frac{\partial \rho}{\partial t} = -\frac{\hbar}{2mi}\left(\psi^*\frac{\partial^2 \psi}{\partial x^2} - \psi\frac{\partial^2 \psi^*}{\partial x^2}\right) = -\frac{\partial j}{\partial x} \tag{20}$$

$$\tag{21}$$

This proves the desired result.

[iii]There is such a thing as an imaginary potential, you have to use this to model particles that might decay into something else. Nothing we're going to worry about.

(b) For a plane wave like Ae^{ikx}, we have already found the current from one of our daily problems:

$$j = \frac{\hbar k}{m}|A|^2 \tag{22}$$

Now we can recall that $\hbar k$ is the momentum, which we can also write as mv.[iv] That means $\hbar k/m = p/m = v$. The probability density is

$$\rho = |\psi|^2 = \psi^* \psi = A^* e^{-ikx} A e^{ikx} = |A|^2 \tag{23}$$

Substitutions now give the desired result

$$j = \frac{\hbar k}{m}|A|^2 = v|A|^2 = \rho v \tag{24}$$

Now this looks a lot more like a classical flux. For instance, for an electrical current density we would write $j = (nq)v_d$. Here n is the density of charges and q their charge, making nq the equivalent of ρ, and this is multiplied by the drift velocity v_d.

(c) We've already established $\rho = |A|^2$. Since A is a constant, the time derivative of probability density is plainly zero.

$$\frac{d\rho}{dt} = \frac{d|A|^2}{dt} = 0 \tag{25}$$

On the other hand, we know that $j = v|A|^2$, meaning we have a non-zero current even though the probability density isn't changing in time. For our plane wave, this just means we have a steady current to the right at all times, completely unchanging. The fact that $dj/dx = 0$ does preserve continuity, however.

2. An electron is in the $n = 5$ state of hydrogen. To what states can the electron make transitions, and what are the energies of the emitted photons?

Solution: From the $n = 5$ state, the electron can only transition to states of lower energy, which would be to the first through fourth energy levels.[v] The energy of the n^{th} level in the Bohr model is

$$E_n = \frac{-13.6\,\text{eV}}{n^2} \tag{26}$$

[iv] Since Schrödinger's equation is not relativistic, we can't really justify using relativistic momentum.

[v] Of course, if the electron went from, say, 5 to 3, it could then go from 3 to 2 and 2 to 1, or directly from 3 to 1. Eventually, the electron in the $n = 5$ state would find its way back to the lowest $n = 1$ energy level. If you wanted to find all the possible ways to get there, you'd need the number of ways 5 things can be combined in pairs in which the order doesn't matter - mathematically, a combination. Here we would want $\binom{5}{2} = 5!/2!(3-2)! = 10$, so there are 10 ways to get to the ground state from $n = 5$.

The energy of the emitted photons must be the same as the energy difference between the 5^{th} level and the final level (which we'll just call m). The energy difference is then

$$\Delta E_{5m} = E_5 - E_m = -13.6\,\text{eV}\left(\frac{1}{5^2} - \frac{1}{m^2}\right) \tag{27}$$

Below, we tabulate the results. One emission in the visible range results.

m	Δ (eV)	spectrum range
4	$-13.6\left(\frac{1}{25}-\frac{1}{16}\right)=0.306$	mid infrared
3	$-13.6\left(\frac{1}{25}-\frac{1}{9}\right)=0.967$	near infrared
2	$-13.6\left(\frac{1}{25}-\frac{1}{4}\right)=2.86$	blue/violet visible
1	$-13.6\left(\frac{1}{25}-\frac{1}{1}\right)=13.1$	extreme UV

3. Find the directions in space where the angular probability density for the $l=2$, $m_l=0$ electron in hydrogen has its maxima and minima.

Solution: The principle quantum number n was not specified. Since $l=2$, we know $n\geq 3$. Since you only have the $n\leq 3$ wavefunctions available in your text, we may as well pick $n=3$ for convenience.The $(3,2,0)$ wave function is[vi]

$$\Theta(\theta) = \sqrt{\frac{3}{8}}\left(3\cos^2\theta - 1\right) \tag{28}$$

The angular probability density is just the square of this

$$P(\theta) = |\Theta(\theta)|^2 = \frac{3}{8}\left(3\cos^2\theta - 1\right)^2 \tag{29}$$

The maxima and minima will be when $dP/d\theta=0$. We can ignore the overall constant $3/8$ (since we'll be setting everything to zero anyway), and then just take the derivative.

$$\frac{dP}{d\theta} = -12\sin\theta\cos\theta\left(3\cos^2\theta - 1\right) = 0 \tag{30}$$

We are basically done. The $\sin\cos$ pre-factor will be zero at $\{0, 90°, 180°\}$ and integer multiples thereof. The other roots are

$$0 = 3\cos^2\theta - 1 \qquad \Longrightarrow \qquad \theta = \cos^{-1}\left(\frac{\pm 1}{\sqrt{3}}\right) \approx \{55°, 155°\} \tag{31}$$

Which are maxima and which are minima? Either use the second derivative test, or make a quick

[vi]In lecture, I used $P(\theta)$ for the angular wave function depending on θ. I'll try to make the solutions consistent with the text.

plot.[vii] You can by inspection notice that the last set of roots would be zeroes of P, and since $P \geq 0$ they must be minima. You'd still need to verify what the first three roots are though.

Anyway: a plot quickly leads us to identify

$$\begin{aligned} \{0, 90°, 180°\} &\qquad \text{maxima} \\ \{55°, 125°\} &\qquad \text{minima} \end{aligned}$$

4. What is the probability of finding an $n = 2$, $l = 1$ electron between a_o and $2a_o$?

Solution: Now our first problem is that m wasn't specified, and we can have $m = \{0, \pm 1\}$. Does m make a difference in finding the probability? Should either φ or θ make any difference in a quantity which is only a function of the radius?

The answer is no, but one can't just guess that. There is really only one way to find out. As it turns out, we can do all three possibilities with almost no extra work. The relevant wave functions are, in full,

$$\psi_{210}(r, \theta, \varphi) = \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \sqrt{\frac{3}{2}} \cos\theta \frac{1}{\sqrt{2\pi}} \tag{32}$$

$$\psi_{21\pm1}(r, \theta, \varphi) = \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \left(\mp \frac{\sqrt{3}}{2} \sin\theta \right) \frac{1}{\sqrt{2\pi}} e^{\pm i\varphi} \tag{33}$$

We first notice that the $e^{\pm i\varphi}$ factor in the second equation will go away when we find $|\psi_{21\pm1}|$, so it is irrelevant for finding probability. Similarly, the $\mp$ sign on the sine term will go away. The only real difference between the two functions is sine in place of cosine, and a factor of $\sqrt{2}$ overall. As it turns out, the two differences will cancel each other out, and the probability is independent of m.

First, we need to find the probability density, $|\psi|^2\, dV$. The volume element in spherical coordinates is $r^2 \sin\theta\, dr\, d\theta\, d\varphi$, with $\theta \in \{0, \pi\}$ and $\varphi \in \{0, 2\pi\}$. Noting this, we can just square the wave functions above and set up the integrals. Since we're worried about radii from a_o to $2a_o$, that sets the limits for r. For φ and θ, we integrate over the full range of each variable.

[vii] In addition to Wolfram Alpha, try typing `plot of y=(3(cos(x))^2-1)^2` in google.

$$P_{210} = \int_0^{2\pi} \frac{1}{2\pi}\,d\varphi \int_0^{\pi} \frac{3}{2}\cos^2\theta \sin\theta\,d\theta \int_{a_o}^{2a_o} \frac{1}{24a_o^3}\frac{r^2}{a_o^2}e^{-r/a_o}r^2\,dr \tag{34}$$

$$P_{21\pm1} = \int_0^{2\pi} \frac{1}{2\pi}\,d\varphi \int_0^{\pi} \frac{3}{4}\sin^2\theta \sin\theta\,d\theta \int_{a_o}^{2a_o} \frac{1}{24a_o^3}\frac{r^2}{a_o^2}e^{-r/a_o}r^2\,dr \tag{35}$$

Now, the φ integral is just going to give us a factor 2π in each, no problem. What about the θ integrals? The integrands are different, but so are the pre-factors. Curious.

$$P_{210}: \quad \int_0^{\pi} \frac{3}{2}\cos^2\theta \sin\theta\,d\theta = \frac{3}{2}\cdot\frac{2}{3} = 1 \tag{36}$$

$$P_{21\pm1}: \quad \int_0^{\pi} \frac{3}{4}\sin^2\theta \sin\theta\,d\theta = \frac{4}{3}\cdot\frac{3}{4} = 1 \tag{37}$$

There is no θ or ϕ dependence, and this must be the case: since we asked a question that didn't depend on either angle, and then integrated over the whole range of both angles, it couldn't come out any differently. The angular functions are normalized, so it had to be the case that when we integrated over their whole range the result is unity.

So: with sufficiently clever (and documented) reasoning, you could have started at this point right here, recognizing that m doesn't matter at all and you can just work with the radial functions. Specifically, $P_{210}=P_{21\pm1}\equiv P_{21}$, so one can just use the radial function.

$$P_{21} = \int_{a_o}^{2a_o} \frac{1}{24a_o^3}\frac{r^2}{a_o^2}e^{-r/a_o}r^2\,dr = \frac{1}{24a_o^5}\int_1^2 a_o\cdot a_o^4u^4e^{-u}\,du \quad (\text{let } u=r/a_o,\ du=dr/a_o) \tag{38}$$

$$P_{21} = \frac{1}{24}\int_1^2 u^4e^{-u}\,du = \frac{1}{24}\left(\frac{65e-168}{e^2}\right) \approx 0.049 \tag{39}$$

The expectation value of the radius in the $n=2$, $l=1$ state is $5a_o$, so it is not crazy that the probability of finding the electron much closer to the nucleus than this is rather small. If you look at the plot on pg. 208 in your textbook, you can see that the answer is reasonable. You can also see that the answer does *definitely* depend on l, if not m, since the radial function is different for $l=0$ and $l=\pm1$.

5. *Links between quantum and classical physics.* In classical mechanics, from the definition of momentum, we can put $dx/dt=p_x/m$. In quantum mechanics, this is replaced by a corresponding relation between expectation values:

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p_x\rangle}{m} \tag{40}$$

Verify this result with the help of the following outline:

(i) Take the basic definition

$$\langle x\rangle = \int\limits_{\text{all } x} \psi^*(x,t)x\psi(x,t)\,dx \tag{41}$$

We do not need to specify the precise form of ψ.

(ii) Taking the time derivative, we find

$$\frac{d}{dt}\langle x\rangle = \int\limits_{\text{all } x} \frac{\partial\psi^*}{\partial t}x\psi\,dx + \int\limits_{\text{all } x} \psi^* x\frac{\partial\psi}{\partial t}\,dx \tag{42}$$

(On the right, x is just the variable of integration, and is not subject to the d/dt operation.)

(iii) Replace $\partial\psi/\partial t$ and $\partial\psi^*/\partial t$ by using the time-independent Schrödinger equation and its counterpart for ψ^*:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V(x)\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t} \tag{43}$$

(iv) Carry out the integrations over all x, taking advantage of the fact that ψ vanishes for $x\to\pm\infty$ (integration by parts is involved; what did you get for $\partial j/\partial x$ in problem 1?).[viii]

(v) Use the relationship $p_{\text{op}}\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x}$

Solution: Part (i) is given, and part (ii) nothing more than applying the chain rule. For part (iii), we again need Schrödinger's equation and its complex conjugate to replace the time derivatives with spatial derivatives

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \qquad \text{Schrödinger} \tag{44}$$

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^* \qquad \text{Schrödinger complex conjugate} \tag{45}$$

Again, we will solve for the time derivatives to make the substitution easier.

[viii] You might find `http://farside.ph.utexas.edu/teaching/qmech/lectures/node35.html` useful. Be careful, they are not doing exactly what I'm asking you to do.

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi}\frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}\psi \tag{46}$$

$$\frac{\partial \psi^*}{\partial t} = +\frac{\hbar}{2mi}\frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar}\psi^* \tag{47}$$

Using these substitutions in our expression for $d\langle x\rangle/dt$,

$$\frac{d}{dt}\langle x\rangle = \int\limits_{\text{all } x} \left(\frac{\hbar}{2mi}\frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar}\psi^*\right) x\psi \, dx + \int\limits_{\text{all } x} \psi^* x \left(-\frac{\hbar}{2mi}\frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}\psi\right) dx \tag{48}$$

$$= \frac{\hbar}{2mi}\int\limits_{\text{all } x} \psi \frac{\partial^2 \psi^*}{\partial x^2} - \psi^* \frac{\partial^2 \psi}{\partial x^2} \, dx \tag{49}$$

Note that the potential terms just cancel out, because we will assume as usual that V is purely real. This still looks ugly, but recall from problem 1

$$\frac{\partial j}{\partial x} = \frac{\hbar}{2mi}\left[\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2}\right] \tag{50}$$

Our integrand is just $-\partial j/\partial x$. Plug it in, and integrate by parts ($u{=}-x$, $dv{=}\partial j/\partial x$).

$$\frac{d}{dt}\langle x\rangle = \int\limits_{\text{all } x} -x\frac{\partial j}{\partial x}\, dx = -xj\Big|_{-\infty}^{\infty} + \int\limits_{\text{all } x} j \, dx \tag{51}$$

What to do with this? We know on general grounds that ψ has to vanish a $\pm\infty$, otherwise we would never be able to come up with a finite probability of finding a particle anywhere. If the wave function tends to zero as $x \to \pm\infty$, so does its complex conjugate, and so do their time derivatives. That means the current density must also be zero as $x \to \pm\infty$. Physically, this amounts to saying that we can't have current flowing off to infinity, it must eventually circle back to its source if we are to have conservation of matter and energy. If you are to have current density integrated over a closed surface equal to zero at infinity, then j must tend to zero faster than area ($\propto x^2$) tends to infinity, which means it also tends to zero faster than x diverges.

That leaves us with just one term. Plug in the definition for j and simplify a bit.

$$\frac{d}{dt}\langle x\rangle = \int\limits_{\text{all } x} j \, dx = \int\limits_{\text{all } x} \frac{\hbar}{2mi}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right) dx = \frac{1}{2m}\int\limits_{\text{all } x} \psi^* \frac{\hbar}{i}\frac{\partial \psi}{\partial x}\, dx - \frac{1}{2m}\int\limits_{\text{all } x} \psi \frac{\hbar}{i}\frac{\partial \psi^*}{\partial x}\, dx \tag{52}$$

Now what? We can show that the two integrals are the same. Take just the second term, and integrate by parts ($u{=}\psi$, $dv{=}\partial \psi^*/\partial x$).

$$\int_{-\infty}^{\infty} \psi \frac{\partial \psi^*}{\partial x}\, dx = \psi\psi^* \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x}\, dx \tag{53}$$

The first term is the probability density $|\psi|^2$ evaluated at $\pm\infty$. As noted above, the wave function must vanish at $\pm\infty$, and so must $|\psi|^2$. That amounts to saying there is a zero percent chance to find the particle an infinite distance away. That leaves us

$$\int_{-\infty}^{\infty} \psi \frac{\partial \psi^*}{\partial x}\, dx = -\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x}\, dx \tag{54}$$

Using that result,

$$\frac{d}{dt}\langle x \rangle = \frac{1}{2m} \int_{\text{all } x} \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x}\, dx - \frac{1}{2m} \int_{\text{all } x} \psi \frac{\hbar}{i} \frac{\partial \psi^*}{\partial x}\, dx = \frac{1}{m} \int_{\text{all } x} \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x}\, dx \tag{55}$$

The integral that is left is just the expectation value of momentum, since $\frac{\hbar}{i}\frac{\partial \psi}{\partial x} = p\psi$. Thus,

$$\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p \rangle \tag{56}$$

6. Referring to the preceding question, see if by means of a similar approach you can obtain the quantum-mechanical counterpart of Newton's second law:

$$\frac{d}{dt}\langle p_x \rangle = \langle F_x \rangle = \langle -\frac{\partial V}{\partial x} \rangle \tag{57}$$

Solution: This is in principle no less tedious than the previous one, but we will be able to reuse several key intermediate results. Both are specific consequences of *Ehrenfest's theorem*, which is frankly more than we want to go in to here. Anyway: start with the definition of $\langle p \rangle$. Presume all integrals to be over $[-\infty, \infty]$.

$$\langle p \rangle = \int \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x}\, dx \tag{58}$$

Now we can use the result of the previous problem (Eq. 52).

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = m \int j\, dx \tag{59}$$

From the definition of current density,

$$\langle p \rangle = m \int \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx \tag{60}$$

Again from the last problem we know

$$\int_{-\infty}^{\infty} \psi \frac{\partial \psi^*}{\partial x} \, dx = - \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} \, dx \tag{61}$$

Which gives

$$\langle p \rangle = \frac{\hbar}{i} \int \psi^* \frac{\partial \psi}{\partial x} \, dx = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, dx \tag{62}$$

The time derivative is now straightforward, just use the chain rule . . .

$$\frac{d\langle p \rangle}{dt} = -i\hbar \int \frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x} + \psi^* \frac{\partial^2 \psi}{\partial t \partial x} \, dx = \int \left(-i\hbar \frac{\partial \psi^*}{\partial t} \right) \frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x} \left(i\hbar \frac{\partial \psi}{\partial t} \right) dx \tag{63}$$

Now we can substitute Schrödinger's equation and its complex conjugate (see previous problems) for the terms in brackets

$$\frac{d\langle p \rangle}{dt} = \int \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V \psi^* \right) \frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \psi \right) dx \tag{64}$$

Now we have to notice a couple of things. First,

$$\frac{\partial}{\partial x} \left(\frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} \right) = \frac{\partial^2 \psi^*}{\partial x^2} \frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x} \frac{\partial^2 \psi}{\partial x^2} \tag{65}$$

This lets us combine the second derivative terms

$$\frac{d\langle p \rangle}{dt} = \int -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left(\frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} \right) + V \psi^* \frac{\partial \psi}{\partial x} + V \psi \frac{\partial \psi^*}{\partial x} \, dx \tag{66}$$

Finally, we notice that for a purely real V,

$$V \frac{\partial}{\partial x} |\psi|^2 = V \frac{\partial}{\partial x} (\psi^* \psi) = V \psi^* \frac{\partial \psi}{\partial x} + V \psi \frac{\partial \psi^*}{\partial x} \tag{67}$$

Now we have

$$\frac{d\langle p \rangle}{dt} = \int -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left(\frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} \right) + V \frac{\partial}{\partial x} |\psi|^2 \, dx \tag{68}$$

The first term is a perfect differential, and gives

$$-\frac{\hbar^2}{2m}\left(\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x}\right)\Bigg|_{-\infty}^{\infty} = 0 \tag{69}$$

The wavefunction and its derivative must vanish at $x \to \pm\infty$, so this term evaluates to zero. This leaves

$$\frac{d\langle p\rangle}{dt} = \int V\frac{\partial}{\partial x}|\psi|^2\,dx \tag{70}$$

We can integrate this by parts ($u\!=\!V$, $dv\!=\!\frac{\partial}{\partial x}|\psi|^2$), giving

$$\frac{d\langle p\rangle}{dt} = V|\psi|^2\Bigg|_{-\infty}^{\infty} - \int\limits_{-\infty}^{\infty}|\psi|^2\frac{\partial V}{\partial x}\,dx \tag{71}$$

Again, at $x \to \pm\infty$, ψ and therefore $|\psi|^2$ must vanish, and the remaining term is the definition of the expectation value of dV/dx. Thus,

$$\frac{d\langle p\rangle}{dt} = -\left\langle\frac{\partial V}{\partial x}\right\rangle \tag{72}$$

This is the quantum equivalent of Newton's law $F\!=\!\frac{dp}{dt}\!=\!-\frac{dU}{dx}$.

7. Find the most probable radius **and** the expected value of the radial position $\langle r\rangle$ of an electron in the $2p$ state.

$$\psi_{2p} = \frac{1}{\sqrt{3}\,(2a_o)^{3/2}}\frac{r}{a_o}e^{-r/2a_o} \tag{73}$$

where $a_0\!=\!\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\!=\!0.529\!\times\!10^{-10}\,\text{m}$ is the Bohr radius.

Solution: The most likely distance corresponds to the distance at which the probability of finding the electron is maximum. This is distinct from the expected value of the radius $\langle r\rangle$. For a 3D wavefunction in spherical coordinates (r,θ,φ), the probability of finding an electron at a distance r in the interval $[r, r+dr]$ is the squared magnitude of the wavefunction times the volume of a spherical shell of thickness dr and radius r, $4\pi r^2$. However, the wave function above is only the radial function ($R(r)$), the θ and φ dependence has been neglected. That means to be formally correct, the probability is

$$P(r)\,dr = |\psi|^2\cdot r^2\,dr \qquad \text{or} \qquad P(r) = |\psi|^2\cdot r^2 \tag{74}$$

That is, the factor 4π comes from integrating over θ and φ in the case when we have a wavefunction which is *independent* of the angular coordinates. The $2p$ state does have an angular dependence, so either we need to use the full wavefunction with the θ and φ dependence included, or we need to use the probability density as given above. We will do the latter .Given ψ_{2p} above, that gives us

$$P(r) = \left| \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \right|^2 \cdot r^2 = \frac{r^4}{24a_o^5} e^{-r/a_o} \tag{75}$$

The most probable radius is when $P(r)$ takes a maximum value, which must occur when $dP/dr = 0$ and $d^2P/dr^2 < 0$. Thus:

$$\frac{dP}{dr} = 0 = \left(\frac{1}{24a_o^5}\right) \frac{d}{dr}\left(r^4 e^{-r/a_o}\right) = \left(\frac{1}{24a_o^5}\right)\left(4r^3 e^{-r/a_o} - \frac{r^4}{a_o} e^{-r/a_o}\right) \tag{76}$$

$$0 = \left(\frac{r^3}{24a_o^5} e^{-r/a_o}\right)\left(4 - \frac{r}{a_o}\right) \tag{77}$$

$$\implies \quad r = \{0, 4a_o, \infty\} \tag{78}$$

One can either apply the second derivative test or make a quick plot of $P(r)$ to verify that $r = 4a_o$ is the sole maximum of the probability distribution, and hence the most probable radius, while $r = 0$ and $r = \infty$ are minima.

The expectation value is

$$\langle r \rangle = \int r P(r)\,dr = \int_0^\infty \frac{r^5}{24a_o^5} e^{-r/a_o}\,dr = \frac{a_o}{24} \int_0^\infty u^4 e^{-u}\,du = \frac{a_o}{24} \cdot 5! = 5a_o \tag{79}$$