Problem Set 5 Hints

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: Since this one was already due, I'll just give the 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: You will need the complex conjugate, and derivatives of it and ψ. After that, it is just plug and chug - it is very messy, and there are plenty of opportunities to mix up signs, etc. If your result isn't purely real, you have a problem. There should be no exponential terms left.

What is the physical interpretation? If we let $B = 0$, the wave function is $\psi = Ae^{ikx}$, so we just have a plane wave traveling along $+x$. Think about what the flux means in that case, and in the corresponding case when $A = 0$.

If ψ is perfectly real, as is the case for a bound state, is there any point to taking complex conjugates?

The remaining problems are due 18 Oct 2013

1. In electromagnetic theory, the conservation of charge is represented by the continuity equation

[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).

(in one dimension)

$$\frac{\partial j}{\partial x} = -\frac{\partial \rho}{\partial t} \tag{7}$$

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 $|A|^2 v = \rho v$, 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: Look at HW6 from F10, and `http://en.wikipedia.org/wiki/Probability_current`.
(a) Nothing to do but grind through it and see if it works. Start with $\partial j/\partial x$, making liberal use of the chain rule. Next, find $\partial \rho/\partial t$.

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}\left(\psi^*\psi\right) = \frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} \tag{8}$$

At this point, you can use the time-dependent Schrödinger equation to replace the time derivatives with spatial derivatives. You'll need both the equation and its complex conjugate. You can assume V is real for convenience. Recall the time-dependent Schrödinger equation

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi \qquad \text{Schrödinger} \tag{9}$$

This substitutes in for $\partial\psi/\partial t$, take the complex conjugate of the whole thing to substitute for $\partial\psi^*/\partial t$. If you do everything right and plug it all in, it should work.

(b) For a plane wave like Ae^{ikx}, you should have found the flux for a plane wave from one of the daily problems already (try setting $B=0$ in the problem above).

$$j = \frac{\hbar k}{m}|A|^2 \tag{10}$$

Now you can recall that $\hbar k$ is the momentum, which you can also write as mv.[iii] That means $\hbar k/m = p/m = v$. It should be straightforward from here.

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

(c) Just calculate $\rho = |\psi|^2$ and try to take its time derivative.

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 electrons?

Solution: This is one of your textbook's problems, from chapter 6 (and an odd one, so you can see the answer; show your work). From $n = 5$, the electron can make transitions to all states of lower n. The energy of a state n is the same as what we found with the Bohr model.

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: Also an odd-numbered textbook problem from chapter 6. You can find the relevant wave function in your textbook. Have a look at example 7.7 to see how to go about it.

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

Solution: And, one more from chapter 6 of your text (but an even-numbered one). Look up the wave function, and integrate the probability density from a_o to $2a_o$.

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:

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m} \tag{11}$$

Verify this result with the help of the following outline:

(i) Take the basic definition

$$\langle x \rangle = \int_{\text{all } x} \psi^*(x,t) x \psi(x,t)\, dx \tag{12}$$

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

(ii) Taking the time derivative, we find

$$\frac{d}{dt}\langle x \rangle = \int_{\text{all } x} \frac{\partial \psi^*}{\partial t} x \psi\, dx + \int_{\text{all } x} \psi^* x \frac{\partial \psi}{\partial t}\, dx \tag{13}$$

(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^*:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V(x)\psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} \tag{14}$$

(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?).[iv]

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

Solution: This, and the next one, are really tough. Probably harder than I should have assigned, to be honest. Given that, I'm including almost the full solution below, but I've intentionally redacted key bits. Fill in the missing steps, using the hints provided, and you have your 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

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

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

Solve for the time derivatives to make the substitution easier.

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

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

Use these substitutions your expression for $d\langle x\rangle/dt$, figuring out what the "?" bits must be.

$$\frac{d}{dt}\langle x\rangle = \frac{\hbar}{2mi}\int\limits_{\text{all } x} \psi^{?}\frac{\partial^{?}?}{\partial x^{?}} - \psi^{?}\frac{\partial^{?}\psi}{\partial x^{?}}\,dx \tag{19}$$

Note that the potential terms just cancel out, and come up with a reason why. From problem 1, you should have found $\frac{\partial j}{\partial x}$, and you can plug this into the what you've got. Do that, and integrate by parts ($u = -x$, $dv = \partial j/\partial x$).

$$\frac{d}{dt}\langle x\rangle = \int\limits_{\text{all } x} -x\frac{\partial j}{\partial x}\,dx = -xj\Big|_{-\infty}^{\infty} + \int\limits_{\text{all } x} j\,dx \tag{20}$$

What to do with this? You know on general grounds that ψ has to vanish a $\pm\infty$, otherwise you 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

[iv] 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.

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.

That leaves you with just one term. Plug in the definition for j and simplify a bit. Integrate by parts again ($u = \psi$, $dv = \partial\psi^*/\partial x$) to show

$$\int_{-\infty}^{\infty} \psi \frac{\partial \psi^*}{\partial x}\, dx = \psi\psi^* \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x}\, dx \tag{21}$$

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. What is left will be proportional to the expectation value of momentum, and the result will follow. You will have them proved the quantum equivalent of $p = mv = m\frac{dx}{dt}$.

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:

$$\frac{d}{dt}\langle p_x \rangle = \langle F_x \rangle = \langle -\frac{\partial V}{\partial x} \rangle \tag{22}$$

Solution: This is in principle no less tedious than the previous one, but you 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 $[-\infty, \infty]$.

$$\langle p \rangle = \int \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x}\, dx \tag{23}$$

Now we can use a result you should have from the previous problem

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = m \int j\, dx \tag{24}$$

Plug in the definition of current density. Again from the last problem you know

$$\int_{-\infty}^{\infty} \psi \frac{\partial \psi^*}{\partial x}\, dx = -\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x}\, dx \tag{25}$$

From this point on, you might find the discussion at `http://farside.ph.utexas.edu/teaching/qmech/lectures/node35.html` useful. That discussion skips some key steps, you should not (or at least you should more explicitly justify what you're doing). What you'll have proved 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.

$$\psi_{2p} = \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \tag{26}$$

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

Solution: The most probable radius is obtained by finding the probability density $P = 4\pi r^2 |\psi|^2$ and finding its maximum. The expectation value is found as above, $\langle x \rangle = \int x |\psi|^2 4\pi r^2 \, dr$.