Physics 3220 – Quantum Mechanics 1 – Fall 2008
Problem Set #12

Due Wednesday, December 3 at 2pm

Problem 12.1: Analytic solution of radial equation for hydrogen. (20 points)

Stationary states for the hydrogen atom that are also eigenstates of L^2 and L_z were found to take the form

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_\ell^m(\theta,\varphi) \equiv \frac{u_{n\ell}(r)}{r} Y_\ell^m(\theta,\varphi)\,, \tag{1}$$

where the Y_ℓ^m are the spherical harmonics, and $u(r)$ solves the radial equation,

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left(-\frac{ke^2}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right) u = Eu\,, \tag{2}$$

where we have written m_e for the mass of the electron to avoid confusion with the azimuthal angular momentum quantum number m, and $k = 1/4\pi\epsilon_0$.

We will solve this equation using the method of Frobenius, the same method we explored for the analytic solution of the harmonic oscillator.

a) We begin by introducing a dimensionless variable to replace r, which we'll call ρ. Divide the radial equation (2) by E and define a variable $\rho \equiv r/\bar{r}$, where $\bar{r}$ is for you to determine, such that the first and last terms take the form

$$\frac{d^2u}{d\rho^2} + \ldots = u\,. \tag{3}$$

What is $\bar{r}$? Check that it has units of length. What is the sign of E appropriate to bound states, and given this, is $\bar{r}$ real and positive?

Next define a constant ρ_0 to absorb most of the remaining constants, so that the equation can be written

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u\,. \tag{4}$$

What is ρ_0? What are its units?

b) Next we will study the asymptotics of the solution. Unlike the harmonic oscillator case, where $x \to \infty$ and $x \to -\infty$ had the same behavior and could be examined at the same time, here we will separately consider $r \to \infty$ and $r \to 0$.

Explain why in the $r \to \infty$ limit (which implies $\rho \to \infty$), the radial equation reduces to

$$\frac{d^2u}{d\rho^2} \approx u\,. \tag{5}$$

Verify that the solution in this limit is

$$u(\rho) \approx Ae^{-\rho} + Be^{+\rho}\,. \tag{6}$$

Explain what constraint must we put on A or B to make sure the wavefunction can be normalized.

Now show that in the $r \to 0$ limit (implying $\rho \to 0$) the radial equation becomes

$$\frac{d^2u}{d\rho^2} \approx \frac{\ell(\ell+1)}{\rho^2}u\,. \tag{7}$$

This equation has a simple solution: consider $u(\rho) \approx C\rho^\alpha$ for some number α. What two values of α satisfy the equation? Which one must we throw out to prevent the wavefunction from blowing up?

c) We will now extract *both* asymptotic behaviors from $u(\rho)$ to define a new function to work with, $v(\rho)$, as:

$$u(\rho) \equiv \rho^{\ell+1}e^{-\rho}v(\rho)\,. \tag{8}$$

Verify that the radial equation becomes, in terms of $v(\rho)$,

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0\,. \tag{9}$$

d) To solve this differential equation, we will postulate a series solution for v:

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j\,, \tag{10}$$

where the c_j are constants. Show that the result of part c) implies the *recursion relation* for the constants:

$$c_{j+1} = \left[\frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}\right]c_j\,. \tag{11}$$

e) Let us explore what happens if the series goes on forever. Write down the large-j limit of the recursion formula, and demonstrate that if this approximate form were exact, it would imply

$$c_j = \frac{2^j}{j!}c_0\,. \tag{12}$$

This is only approximately true, but it correctly captures the large-ρ behavior. Using this formula, sum up $v(\rho)$ explicitly; the series should be familiar. Given this estimate for $v(\rho)$, how does $u(\rho) \equiv \rho^{\ell+1}e^{-\rho}v(\rho)$ behave at large ρ? Is this acceptable, and why or why not?

f) To ensure we can normalize our wavefunction, the series must stop at some point. Assume that there exists a value of j called j_{max} such that $c_{j_{max}} \neq 0$ but $c_{j_{max}+1} = 0$. Solve for the relation between ρ_0, j_{max} and ℓ that this situation requires.

Finally, defining $n \equiv j_{max} + \ell + 1$ for convenience and recalling the definition of ρ_0, find the allowed energies for the hydrogen atom, in terms of the original quantities $\hbar$, k and m_e as well as n. Put a big box around it, because it is the most important thing we have calculated this term, or perhaps ever.

For fixed ℓ, what is the smallest possible value of n, if any? For fixed ℓ what is the largest possible value of n, if any? Explain.

The functions $v(\rho)$ can be expressed in terms of special functions called Laguerre polynomials*; for more details, see the textbook.*

The constant $\bar{r}$ turns out to be proportional to n, and if this is extracted we are left with the Bohr radius *$a = \bar{r}/n$, which sets the length scale for atomic systems.*

Problem 12.2: Hydrogen atom wavefunction. (20 points)

Consider the hydrogen atom wavefunction

$$\psi(r,\theta,\varphi) = \frac{A}{a^{3/2}} \left(\frac{1}{\sqrt{\pi}} e^{-r/a} - \frac{1}{\sqrt{8\pi}} \frac{r}{a} e^{-r/2a} \cos\theta \right) . \tag{13}$$

a) Rewrite the wavefunction in terms of radial wavefunctions $R_{n\ell}(r)$ and spherical harmonics $Y_\ell^m(\theta,\phi)$, and determine the normalization constant A. Assuming the above wavefunction holds at $t = 0$, what is the wavefunction at all times?

b) Going back to the $t = 0$ wavefunction, consider making a measurement of energy, *or* a measurement of $\hat{L}^2$, *or* a measurement of $\hat{L}_z$. What are the possible results of each measurement, what are the probabilities of each possible result, and what does the wavefunction collapse to in each case? After which measurements does the resulting wavefunction have a probability density that changes with time? Explain your result.

c) Again at $t = 0$, what is the radial probability density $P(r)$ that the electron be found a distance r from the nucleus, regardless of the values of θ and φ? Check that your answer makes sense if you integrate over all r.

Problem 12.3: Emission lines and hydrogenic atoms. (10 points)

a) Calculate the wavelength in nanometers of the photons emitted by the following transitions between energy levels (n_f, n_i): i) "Lyman alpha" (Lyα): $(2,1)$, ii) "Balmer alpha" (Hα): $(3,2)$, iii) "Balmer beta" (Hβ): $(4,2)$. What colors are Hα and Hβ?

b) A hydrogenic atom consists of a single electron bound to a nucleus with Z protons (we won't worry about the number of neutrons); examples include ordinary hydrogen for $Z = 1$ and singly-ionized helium for $Z = 2$. Find the energies $E_n(Z)$, Bohr radius $a(Z)$, and Rydberg constant $R(Z)$ for the hydrogenic atoms. Hint: You don't have to calculate everything all over again, just try to track what changes when Z is introduced.

c) At what wavelength would Hα fall for $Z = 2$ and $Z = 3$? Where in the electromagnetic spectrum (X-rays, UV, IR, etc.) are these wavelengths?

Problem 12.4: Two-state system. (20 points)

Consider the simplest nontrivial quantum system: one with only two states. (A system with *one* state will sit in that state for all time and nothing will ever happen!)

a) Assume we have an orthonormal basis for the Hilbert space with states $|1\rangle$ and $|2\rangle$. (We could call them "spin up and spin down" or "happy and sad" or whatever we like without changing the way the quantum mechanics works. If you think "happy and sad" is silly, consider that particle physicists have a two-state quark system they call "strange and charm".) What does orthonormality imply about $\langle 1|1\rangle$, $\langle 1|2\rangle$, $\langle 2|1\rangle$ and $\langle 2|2\rangle$?

Since the Hilbert space is two-dimensional, we can now represent states $|1\rangle$ and $|2\rangle$ by the basis vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, respectively. The bra states $\langle 1|$ and $\langle 2|$ are represented by the row vectors $(1\ 0)$ and $(0\ 1)$. How is the inner product realized in this notation? If you calculate the inner products from the previous paragraph using this new notation, does it yield the same result?

b) A general state $|\psi\rangle$ has the form

$$|\psi\rangle = a|1\rangle + b|2\rangle\,, \tag{14}$$

where a and b are complex numbers. How are $|\psi\rangle$ and $\langle\psi|$ realized in the 2-component vector notation of the previous part? What is the norm of the state $|\psi\rangle$ in terms of a and b, and what condition does normalization put on these constants?

c) All linear operators act as 2×2 matrices in this Hilbert space:

$$\hat{Q} = \begin{pmatrix} c & d \\ e & f \end{pmatrix}\,, \tag{15}$$

where the constants c, d, e and f may be complex. Show that the Hermitian conjugate $\hat{Q}^\dagger$, defined by

$$\langle\psi_1|\hat{Q}\psi_2\rangle = \langle\hat{Q}^\dagger\psi_1|\psi_2\rangle\,, \tag{16}$$

corresponds to the matrix

$$\hat{Q}^\dagger \equiv (\hat{Q}^*)^T = \begin{pmatrix} c^* & e^* \\ d^* & f^* \end{pmatrix}, \tag{17}$$

where T indicates the transpose of the matrix. What is the most general form a Hermitian operator can take?

d) Consider the Hamiltonian

$$\hat{H} = \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix} E_0 \,. \tag{18}$$

Is this operator Hermitian?

How many eigenvalues and eigenvectors do you expect $\hat{H}$ to have? Find the eigenvalues of the Hamiltonian using the characteristic equation from linear algebra:

$$\det(\hat{H} - E\hat{I}) = 0\,, \tag{19}$$

where $\hat{I}$ is the identity operator and E is the eigenvalue to be solved for. Are there any degeneracies? Now solve for the eigenvectors of the Hamiltonian by explicitly solving the eigenvalue equation,

$$\hat{H}|E_n\rangle = E_n|E_n\rangle\,, \tag{20}$$

for *each* eigenvalue E_n; here we label the eigenvectors to be solved for in terms of the associated eigenvalues.

e) Consider a state that at $t = 0$ is simply $|\psi(t = 0)\rangle = |1\rangle$. Keeping the Hamiltonian from part d), what is $|\psi(t)\rangle$? You may give your answer either as a column vector or as linear combinations of $|1\rangle$ and $|2\rangle$. What would the Hamiltonian have to look like instead for $|1\rangle$ to be a stationary state?

Problem 12.5: Matrix mechanics for the SHO. (20 points)

Consider the simple harmonic oscillator in one dimension. We are always free to expand our wavefunction in the orthonormal basis of energy eigenstates $|u_n\rangle$, which for ease of notation we will simply call $|n\rangle$, with each multiplied by a complex coefficient c_n:

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle\,. \tag{21}$$

This basis is infinite-dimensional, but is labeled by the discrete number n rather than a continuous label like x or p. Accordingly, we can describe the state $|\psi\rangle$ just as well in terms of an *infinite-dimensional* column vector containing all the constants c_n:

$$|\psi\rangle \quad \leftrightarrow \quad \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{pmatrix}, \tag{22}$$

where it goes on forever in the downward direction.

a) What is the representation of the bra vector $\langle\psi|$? Verify that the inner product $\langle\psi|\psi\rangle$ gives the same result in either notation, eqn. (21) or eqn. (22). Would the agreement still hold if the basis $|n\rangle$ were not orthonormal?

b) An operator in this notation will be represented by an infinite-dimensional matrix. Use what we know about a_+ and a_-,

$$a_+|n\rangle = \sqrt{n+1}|n+1\rangle\,, \qquad a_-|n\rangle = \sqrt{n}|n-1\rangle\,, \tag{23}$$

to work out the matrix representation of both operators. Since it would take a while to write down a $\infty \times \infty$ matrix, write down the 4×4 block in the upper left of each, and describe how the pattern continues for the rest of each matrix.

c) Earlier in the semester we showed that the Hamiltonian in the SHO can be written

$$\hat{H} = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)\,. \tag{24}$$

Calculate the right-hand-side in the matrix basis, again writing the upper left 4×4 block and describing how the rest of the matrix continues. Does this result make sense for the Hamiltonian in the basis of stationary states? Explain.

d) How can we realize the operators $\hat{x}$ and $\hat{p}$ in the new matrix notation? Again write down the upper left 4×4 blocks. We expect these operators to satisfy

$$[\hat{x}, \hat{p}] = i\hbar\,. \tag{25}$$

Let us check whether this works. First, calculate $[\hat{x}, \hat{p}]$ using the 2×2 blocks at the upper left only. How close do you get to the right answer? Now repeat the calculation for the 3×3 blocks. How close are you now? What do you expect will happen as you consider larger and larger blocks, all the way to the full infinite matrices?

e) Which element of the $\hat{x}$ matrix corresponds to the expectation value $\langle 0|\hat{x}|0\rangle$? To $\langle 1|\hat{x}|1\rangle$? To $\langle n|\hat{x}|n\rangle$? What value do all these elements take? Is this what you expected? Explain.

Overall, just from looking at the matrix, which elements $\langle n|\hat{x}|m\rangle$ are nonzero? Does this seem reasonable?

Because of the relationship between inner products like $\langle n|\hat{x}|m\rangle$ and the matrix representation of $\hat{x}$, these inner products are frequently called *matrix elements.* Does the set of all elements $\langle n|\hat{x}|m\rangle$ contain less information, more information or the same information as the operator $\hat{x}$ itself? Explain your reasoning.