Physics 2610H: Assignment IV

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Problem 1. Use the tables of $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$ to describe the mathematical dependence on the r, θ, and ϕ variables of the $n = 3$, $\ell = 2$, $m_\ell = 2$ energy eigenstate of the hydrogen atom. Use computer software of your choice (Excel, Matlab, *etc.*) to plot the shape of the radial probability density, $P(r)$, of this state against r. Include units! Denote on your plot the most probable radius for an electron in this state.

Solution 1. For the $n = 3$, $\ell = 2$, $m_\ell = 2$ state of the hydrogen atom the wavefunctions are

$$R(r) = \frac{1}{(3a_0)^{3/2}} \frac{2\sqrt{2}r^2}{27\sqrt{5}a_0^2} e^{-r/3a_0}$$

$$\Theta(\theta) = \sqrt{\frac{15}{32\pi}} \sin^2\theta$$

$$\Phi(\phi) = e^{2i\phi}$$

The radial wavefunction decays exponentially as we would expect it should. The Θ component of the angular wavefunction ramps up smoothly to 1 as the θ value approaches $\pi/2$. The Φ component of the angular wavefunction provides an oscillation that is seen more strongly in higher quantum numbers and only has one real oscillation before it is killed off by the real valued exponential in the radial component.
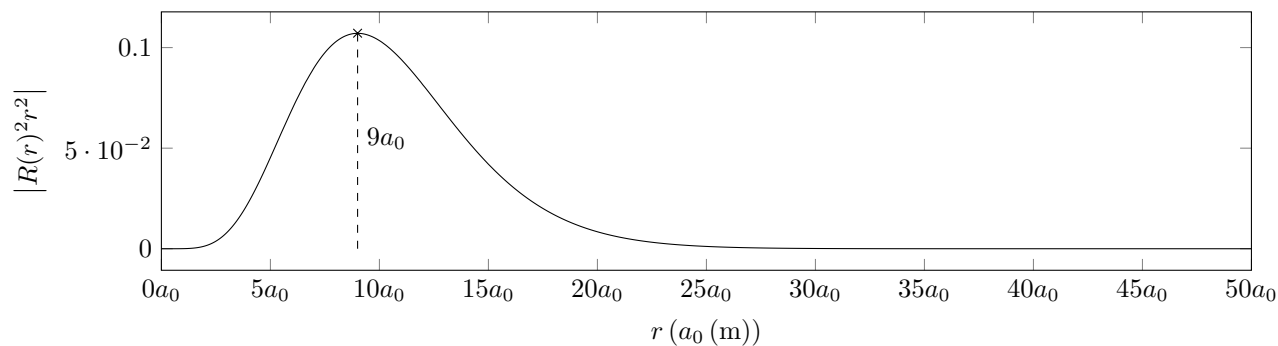
Problem 2. Show that the degeneracy of the n-th state of the hydrogen atom *if* the electron had no spin (so course material only up to Chapter 7) would be n^2. That is, prove the following equality and in a sentence or two state why this equation answers this question:

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$$

Solution 2. Note the sum is

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = 1 + (2 + 1) + \cdots + (2(n-1) + 1)$$

which is the sum of odd integers up to $n - 1$. The sum we are interested in can be split into two parts,

$$\sum_{\ell=0}^{n-1} (2\ell) + \sum_{\ell=0}^{n-1} 1$$

The second part of this sum, $\sum_{\ell=0}^{n-1} 1$, is the sum of 1 $n - 1 + 1$ times, the $+1$ arising due to the beginning index being at 0 (Fencepost problem! That took me a minute). This reduces to n. $\sum_{\ell=0}^{n-1}(2\ell)$ is simply twice the sum of the integers up to $n - 1$ which is equal to

$$(n-1)(n)$$

so the entire sum is

$$(n-1)(n) + (n) = n^2.$$

This equation gives the degeneracy of the n-th state of the hydrogen atom as ℓ runs from 0 to $n-1$ and m_ℓ runs from $-\ell$ to $+\ell$ which means m_ℓ could be any value from 0 to $\pm(n-1)$. Because degeneracy (without spin) is effectively a measure of the number of possible values of m_ℓ the degeneracy can be expressed as the sum given in the problem statement.

Problem 3. For a hydrogen atom in the $1s$ state

(a) What is the most probable value of r from a measurement of r?

(b) What is the average value of r?

(c) Where in 3-dimensional space is the electron most likely to be within a small volume of <u>fixed</u> size dV?

Solution 3.

(a) Here we are looking for the maximum of the probability,

$$R^2(r)r^2 = \left(\frac{2e^{-r/a_0}}{a_0^{3/2}}\right)^2 r^2 = \frac{4r^2 e^{-2r/a_0}}{a_0^3} = P(r)$$

This can be found by solving

$$\frac{dP}{dr} = \frac{8r(r-a_0)e^{-2r/a_0}}{a_0^4} = 0$$

Which gives solutions of $r = 0, a_0, \infty$. 0 and ∞ are non-physical so the most probable value is $r = a_0$.

(b)

$$\int_0^\infty R^2(r)r^3\,dr = \int_0^\infty \left(\frac{2e^{-r/a_0}}{a_0^{3/2}}\right)^2 r^3\,dr = \frac{4}{a_0^3}\int_0^\infty r^3 e^{-2r/a_0}\,dr$$

Which, using the integral table given on the formula sheet, is

$$\frac{4}{a_0^3}\frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{3a_0}{2}$$

(c) The probability density is maximum at the origin. Though this is nonphysical and does not align with the answer in (a) it makes sense when looking at a probability density plot of the $1s$ state. The inconsistency between this and part (a) can be resolved by noting that the radial probability considers a sphere of thickness dr centered about the origin with greatest probability density being where this sphere "intersects" the greatest "amount of probability" whereas the probability of a fixed volume is measured with a region of infinitesimal volume dV. Noting this the apparent inconsistency disappears as they are fundamentally different measurements.

Problem 4. Evaluate, in electron volts, the energies of the three lowest energy levels of the hydrogen atom. Then calculate the frequencies in Hz, and the wavelengths in Å of all the photons that can be emitted by the atom in transitions between these levels. In what range of the electromagnetic spectrum are these photons?

Solution 4. The energy levels of the hydrogen atom can be expressed as a function of the principle quantum number, n, only. These energies are given by the equation

$$E(n) = -\frac{mZ^2e^4}{(4\pi\epsilon_0)\,2\hbar^2 n^2} \approx -\frac{13.6\,\text{eV}}{n^2}$$

which gives energy levels of $-13.6\,\text{eV}$, $-3.4\,\text{eV}$, and $-1.51\,\text{eV}$ for $n = 1, 2, 3$. For frequencies associated with these transitions we only have to care about downward movement so we have

$$3 \to 2 : \lambda = \frac{hc}{\Delta E} \approx \frac{hc}{-3.4\,\text{eV} - -13.6\,\text{eV}} \approx 1.22\,\text{kÅ} \implies f \approx 2.47 \times 10^{15}\,\text{Hz}$$
$$3 \to 1 : \approx 1.02\,\text{kÅ} \implies f \approx 2.92 \times 10^{15}\,\text{Hz}$$
$$2 \to 1 : \approx 6.56\,\text{kÅ} \implies f \approx 4.57 \times 10^{14}\,\text{Hz}$$

The the first two transitions emit photons in the ultraviolet range and the last emits a photon in the near infrared range.

Problem 5. Consider the probability of finding the electron in the hydrogen atom somewhere inside a cone of $\theta = 23.5°$ ("arctic polar region").

(a) If the electron were equally likely to be found anywhere in space, what would be the probability of finding the electron in the arctic polar region?

(b) Suppose the electron is in the state $n = 2$, $\ell = 1$, $m_\ell = 0$ (i.e. a $2p_z$ orbital); recalculate the probability of finding the electron in the arctic polar region.

Solution 5.

(a) Because the probability distribution here is uniform we are looking for how much volume the arctic polar region occupies out of the total sphere. This is somewhat difficult to determine as both are technically infinite but by evaluating the improper integral we get using a limit the final answer is finite.

$$= \lim_{R\to\infty} \frac{1}{\frac{4}{3}\pi r^3} \int_0^{47\pi/360} \int_0^{2\pi} \int_0^R r^2 \sin\theta \, dr d\phi d\theta$$

$$= -\lim_{R\to\infty} \frac{1}{\frac{4}{3}\pi r^3} \left. \frac{2\pi r^3 \cos\theta}{3} \right|_{r=0,\theta=0}^{r=R,\theta=47\pi/360}$$

$$= -\left. \frac{\cos\theta}{2} \right|_{\theta=0}^{\theta=47\pi/360} \approx 4.15\%$$

(b)

$$= \iiint \left(\frac{1}{(2a_0)^{3/2}} \frac{r}{\sqrt{3a_0}} e^{-r/2a_0} \sqrt{\frac{3}{4\pi}} \cos\theta \right)^2 r^2 \sin\theta \, dV$$

$$= \frac{1}{16a_0^5} \iint r^4 e^{-r/a_0} \cos^2\theta \sin\theta \, dr d\theta$$

$$= \frac{3}{2} \int \cos^2\theta \sin\theta \, d\theta$$

$$= -\left. \frac{\cos^3(\theta)}{2} \right|_0^{47\pi/360} \approx 11.4\%$$

Problem 6. An electron (with spin) in a hydrogen atom is in the $4f_{5/2}$ state. Find the values of the quantum numbers n, ℓ and j. What is the magnitude of the electron's total angular momentum? What are the possible values for the z-component of the electron's total angular momentum?

Solution 6. $n = 4$, $\ell = 3$, $j = |\ell - s| = \left|3 - \frac{1}{2}\right| = 5/2$. $\|\vec{J}\| = \|\vec{L} + \vec{S}\| = \left(\sqrt{\ell(\ell+1)} + \sqrt{s(s+1)}\right)\hbar = \frac{5\sqrt{3}}{2}\hbar$. $J_z = m_j\hbar = \{-j, -j+1, \dots, j-1, j\}\hbar = \{-5/2, -3/2, -1/2, 1/2, 3/2, 5/2\}\hbar$.

Problem 7. Neglecting any effects of spin (i.e. if both particles are spinless), how many quantum states are possible for a two-particle system with orbital angular momentum quantum numbers $\ell_1 = 2$ and $\ell_2 = 1$? Write down all these states in what is called the *uncoupled* form: $(\ell_1 m_{\ell_1} \ell_2 m_{\ell_2})$. Then find all possible values of the total orbital angular momentum quantum number ℓ_T and the total orbital magnetic quantum number m_{ℓ_T}. Write down all these states in the *coupled* form: $(\ell_1 \ell_2 \ell_T m_{\ell_T})$.

Solution 7. For such a system there are 15 possible states. This arises because there are five values of m_{ℓ_1} $(-2, -1, 0, 1, 2)$ and three of m_{ℓ_2} $(-1, 0, 1)$ and $5 \cdot 3 = 15$. Each possible combination in both forms is tabulated below,

Uncoupled	Coupled
$(2(-2)1(-1))$	$(211(-1))$
$(2(-2)10)$	$(211(0))$
$(2(-2)11)$	$(211(1))$
$(2(-1)1(-1))$	$(212(-2))$
$(2(-1)10)$	$(212(-1))$
$(2(-1)11)$	(2120)
$(201(-1))$	(2121)
(2010)	(2122)
(2011)	$(213(-3))$
$(211(-1))$	$(213(-2))$
(2110)	$(213(-1))$
(2111)	(2130)
$(221(-1))$	(2131)
(2210)	(2132)
(2211)	(2133)

Problem 8. Two spinless particles, assumed initially to be distinguishable from each other, occupy two different states ($n = 2$ and $n' = 3$) in a 1-D infinite well of length L. The *product wave function* for the case with particle 1 in state $n = 2$ and particle 2 in state $n' = 3$ is

$$\psi(x_1, x_2) = A \sin\left(\frac{2\pi x_1}{L}\right) \sin\left(\frac{3\pi x_2}{L}\right), \qquad A = \frac{2}{L}$$

(a) Show that with this normalization constant this product wave function is correctly normalized.

(b) If the two particles are instead *identical* how should this product wave function be adapted to form two realistic wave functions? Given that the normalization constant for each of these wave functions is $L = \sqrt{2}/L$ in each case what is the probability of both particles being found in the left half of the well (i.e. between 0 and $L/2$).

Solution 8.

(a)

$$= \int_0^L \int_0^L A^2 \sin^2\left(\frac{2\pi x_1}{L}\right) \sin^2\left(\frac{3\pi x_2}{L}\right) dx_1 dx_2$$

$$= \frac{A^2}{4} \int_0^L \int_0^L \left(1 - \cos\left(\frac{4\pi}{L}x_1\right)\right)\left(1 - \cos\left(\frac{6\pi}{L}x_2\right)\right) dx_1 dx_2$$

$$= \frac{A^2}{4} \int_0^L \int_0^L 1 - \cos\left(\frac{4\pi}{L}x_1\right) - \cos\left(\frac{6\pi}{L}x_2\right) + \cos\left(\frac{4\pi}{L}x_1\right)\cos\left(\frac{6\pi}{L}x_2\right) dx_1 dx_2$$

$$= \frac{A^2}{4} \int_0^L \left[x_1 x_2 - \frac{L x_2}{4\pi}\sin\left(\frac{4\pi}{L}x_1\right) - \frac{L x_1}{6\pi}\sin\left(\frac{6\pi}{L}x_2\right) + \frac{L^2}{24\pi^2}\sin\left(\frac{4\pi}{L}x_1\right)\sin\left(\frac{6\pi}{L}x_2\right)\right]_0^L$$

$$= \frac{A^2}{4} \int_0^L \left[x_1 x_2 - \frac{L x_2}{4\pi}\sin\left(\frac{4\pi}{L}x_1\right) - \frac{L x_1}{6\pi}\sin\left(\frac{6\pi}{L}x_2\right) + \frac{L^2}{24\pi^2}\sin\left(\frac{4\pi}{L}x_1\right)\sin\left(\frac{6\pi}{L}x_2\right)\right]_0^L$$

$$= \frac{A^2}{4} \cdot L^2 = \frac{4}{4L^2} \cdot L^2 = 1$$

(b) Dependent on whether the particles are fermions or bosons the wavefunction must be made antisymmetric or symmetric, e.g. $\psi(x_1, x_2) = -\psi(x_2, x_1)$ for fermions (antisymmetric) and $\psi(x_1, x_2) = \psi(x_2, x_1)$ for bosons (symmetric). This can be accomplished by either adding or subtracting a copy of the given wavefunction with flipped particle identifiers,

$$A \sin\left(\frac{2\pi x_1}{L}\right) \sin\left(\frac{3\pi x_2}{L}\right) - A \sin\left(\frac{2\pi x_2}{L}\right) \sin\left(\frac{3\pi x_1}{L}\right) \qquad \text{Antisymmetric}$$

$$A \sin\left(\frac{2\pi x_1}{L}\right) \sin\left(\frac{3\pi x_2}{L}\right) + A \sin\left(\frac{2\pi x_2}{L}\right) \sin\left(\frac{3\pi x_1}{L}\right) \qquad \text{Symmetric}$$