

Foundations 3A - QM, Worksheet 1

Problem 1

(a) Show that the $(l = 0, m = 0)$ and $(l = 1, m = 1)$ spherical harmonics are normalized to unity, i.e., that

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{0,0}^*(\theta, \phi) Y_{0,0}(\theta, \phi) = 1$$

and also that

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{1,1}^*(\theta, \phi) Y_{1,1}(\theta, \phi) = 1.$$

[Hints: The relevant spherical harmonics are given at the end of the question. For the latter integral, think about setting $u = \cos \theta$ and integrating over u rather than over θ .]

(b) Also, show that the $(l = 1, m = 1)$ spherical harmonic is orthogonal to the $(l = 1, m = -1)$ and $(l = 2, m = 1)$ spherical harmonics. I.e., show that

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{1,-1}^*(\theta, \phi) Y_{1,1}(\theta, \phi) = 0$$

and that

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{2,1}^*(\theta, \phi) Y_{1,1}(\theta, \phi) = 0.$$

(c) Write the function $\cos \theta \sin \theta \cos \phi$ as a linear superposition of spherical harmonics.

$$\begin{aligned} Y_{0,0}(\theta, \phi) &= \frac{1}{\sqrt{4\pi}} \\ Y_{1,\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi), \\ Y_{2,\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(\pm i\phi). \end{aligned}$$

Problem 2

The ground state of a hydrogen atom and the first excited state with $l = 0$ are often referred to as, respectively, the 1s state and the 2s state (1 and 2 because these are the values of the principal quantum number for these two states, and s because states with $l = 0$ are called “s-states”). If one adopts a system of units in which the unit of length is the Bohr radius, then the corresponding wave functions read

$$\begin{aligned} \psi_{100}(\mathbf{r}) &= 2 \exp(-r) Y_{0,0}(\theta, \phi) \\ \psi_{200}(\mathbf{r}) &= (1/\sqrt{2})(1 - r/2) \exp(-r/2) Y_{0,0}(\theta, \phi). \end{aligned}$$

(a) Show that $\psi_{100}(\mathbf{r})$ is normalized to unity. Show, also, that $\psi_{100}(\mathbf{r})$ is orthogonal to $\psi_{200}(\mathbf{r})$.

You may use the fact that the spherical harmonics are normalized for doing the angular integral and, for the radial integral, use the fact that

$$\int_0^\infty r^k \exp(-\alpha r) dr = k!/\alpha^{k+1}.$$

(b) By what function of time should you multiply $\psi_{100}(\mathbf{r})$ to obtain a solution of the time-dependent Schrödinger equation?

(c) Can a linear combination of the wave functions $\psi_{100}(\mathbf{r})$ and $\psi_{200}(\mathbf{r})$ ever represent a stationary state? (Justify your answer.)

(d) Suppose that an atom of hydrogen is prepared in a certain state of wave function $\Psi(\mathbf{r}, t)$ and that at $t = 0$ one tests (somehow) whether this atom is in the ground state. What is the probability of finding it in this state at that time if $\Psi(\mathbf{r}, t = 0) = (1/\sqrt{2}) \exp(-r/2) Y_{0,0}(\theta, \phi)$?

Problems for extra practice

Problem 3

Given a state of the hydrogen atom for which $l = 1$ and $m = 0$, calculate the probability that the bound electron is in a cone with vertex in the nucleus, axis along the positive z -axis and aperture of 120 degrees. [Hints: 120 degrees is the total aperture of the cone, counted from “side to side”, not from the z -axis to the border of the cone. Write the wave function as $R(r)Y_{1,0}(\theta, \phi)$ with $Y_{1,0}(\theta, \phi) = (3/4\pi)^{1/2} \cos \theta$. You do not need to know the radial wave function $R(r)$ to complete the calculation, but you may want to take into account the fact that there is a probability of 1 that the electron is somewhere, wherever this might be.]

Problem 4

Recall how the Cartesian coordinates x , y and z are related to the spherical polar coordinates r , θ and ϕ : $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$.

(a) Show that

$$\begin{aligned} -\frac{1}{\sqrt{2}} [Y_{1,1}(\theta, \phi) - Y_{1,-1}(\theta, \phi)] &= \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \\ \frac{i}{\sqrt{2}} [Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi)] &= \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \\ Y_{1,0}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \frac{z}{r}. \end{aligned}$$

(b) Further, show that these three functions are eigenfunctions of, respectively, the x -, y - and z -components of the orbital angular momentum operator. What are the corresponding eigenvalues? Note: In spherical polar coordinates,

$$\begin{aligned} L_x &= -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right), \\ L_y &= -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right), \\ L_z &= -i\hbar \frac{\partial}{\partial\phi}. \end{aligned}$$

(c) Someone says that it is perfectly fine to work with p-state wave functions whose angular dependence is given by x/r , y/r and z/r , someone else says that this is impossible unless one multiplies x/r , y/r and z/r by a normalization factor of $(3/4\pi)^{1/2}$, and a third person says that this is all rubbish anyway because only functions whose angular dependence is either $Y_{1,0}(\theta, \phi)$ or $Y_{1,1}(\theta, \phi)$ or $Y_{1,-1}(\theta, \phi)$ are valid p-state wave functions. Who is right, if anyone?

Problem 5

Throughout this problem, we use atomic units whereby the Bohr radius (a_0), the absolute charge of the electron (e), the mass of the electron, (m), the reduced Planck's constant ($\hbar$) and the constant $4\pi\epsilon_0$ are all unity.

Apart for small differences due to relativistic effects (which we shall neglect here), the 2s and 2p states of hydrogen all have the same energy, $-1/8$ atomic units. The corresponding normalized wave functions are given by the following equations:

$$\psi_{200}(\mathbf{r}) = (1/\sqrt{2})(1 - r/2) \exp(-r/2) Y_{0,0}(\theta, \phi) \quad (1)$$

$$\psi_{21m}(\mathbf{r}) = (1/\sqrt{24})r \exp(-r/2) Y_{1,m}(\theta, \phi), \quad (2)$$

with $m = 0, 1$ or -1 . Eq. (1) refers to the 2s state and Eq. (2) to the 2p _{m} states.

Suppose that the interaction of the electron with the nucleus is not a pure Coulomb potential ($-1/r$), but rather

$$V(r) = -\frac{1}{r} + H'(r)$$

with

$$H'(r) = -V_0 \frac{\exp(-3r)}{r},$$

where V_0 a constant.

(a) Using the orthonormality property of the spherical harmonics,

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y_{\ell',m'}^*(\theta, \phi) Y_{\ell,m}(\theta, \phi) = \delta_{\ell'\ell} \delta_{m'm},$$

show that

$$\int \psi_{211}^*(\mathbf{r}) H'(r) \psi_{200}(\mathbf{r}) d^3r = 0.$$

(b) Further, show that

$$\int \psi_{200}^*(\mathbf{r}) H'(r) \psi_{200}(\mathbf{r}) d^3r = -19 V_0/1024$$

and that

$$\int \psi_{21m}^*(\mathbf{r}) H'(r) \psi_{21m}(\mathbf{r}) d^3r = -V_0/1024$$

for $m = 0, 1$ and -1 . Hints: Use the facts that the spherical harmonics are normalized for doing the angular integral and that

$$\int_0^\infty r^k \exp(-\alpha r) dr = k!/\alpha^{k+1}.$$

(c) As shown by these last results, the effect of the perturbation $H'(r)$ is weaker on the 2p states than on the 2s state. Why could this be expected to be so, from a physical point of view? [Hint: consider how the charge distribution differs between these different states.]

(d) [Optional] Use time-independent degenerate perturbation theory to calculate how the unperturbed energy level ($-1/8$ atomic units) shifts and splits under the effect of $H'(r)$, to first order in $H'(r)$.

(e) [Optional] Does this perturbation mix states of different values of l or m ?

Note: This problem shows that the 2s state and the 2p states split in energy under the effect of this perturbation. In fact, the energy degeneracy of the 2s and 2p states is a specific feature of the Coulomb potential. S and p states of a same principal quantum numbers are not degenerate in more complex atoms.