Lecture 12: Physics 212

Thursday, March 4, 1999
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1 Reading

1. Sections 4.3.2, 4.1 and 4.2 of Griffiths.
2. Sections 11-1, 11-2 and Chapter 12 of French and Taylor.

2 Thought Questions

1. Under the parity operation $P : (x, y, z) \to -(x, y, z)$, how does the corresponding spherical coordinate description ρ, θ, ϕ transform? Given this, how do the spherical harmonics (eigenvectors of angular momentum) transform under the parity operation?

2. Explain why the mass of a hydrogen atom m_H in its ground state is not the sum of the mass of an isolated proton m_p and of an isolated electron m_e, and determine the sign and relative magnitude of this mass difference, $(m_H - m_p - m_e)/m_H$. Do we have to worry about this fact when trying to solve the Schrodinger equation of the hydrogen atom?

   How about the mass of a proton in terms of the sum of the masses of its three constituent quarks?

3. In Physics 211, we saw that a necessary criterion for the wave function $\psi(t, x)$ of a single particle to be normalizable was:
$$\lim_{|x|\to\infty} |x|^{-1/2}\psi(x) \to 0, \tag{1}$$
   which is the condition for the integral $\int_{-\infty}^{\infty} |\psi|^2\, dx$ to converge. What is the generalization of this criterion for the wave function $\psi(t, x, y, z)$ of a three-dimensional particle in a bound state?

4. A particle of mass M is constrained to move on the surface of a sphere of radius R but is otherwise free. What are the energies and wavefunctions for this particle? Classically, the motion of such a particle would lie in a plane (why?!). Show that this classical behavior is recovered for large quantum numbers l and states of maximum z-component L_z.

5. As we will see, the energy levels of a hydrogen atom are degenerate. Explain qualitatively why applying a uniform external electric field $\mathbf{E}$ to a hydrogen atom will decrease the degeneracy of most hydrogen levels and also discuss qualitatively whether the degeneracy will be completely lifted (no degeneracy remains). Note: a constant homogeneous external electric field $\mathbf{E} = -eE\hat{\mathbf{z}} = -\nabla V$ corresponds to a potential $V(x) = eEz$.

6. The nucleus of a hydrogen atom is not a point particle but has a finite radius of order 10^{-13} cm. Would you expect the energy levels E_n of the hydrogen atom to become slightly larger or smaller if you replaced a point nucleus with a nucleus of small but finite radius?

7. A hydrogen atom is moving along at constant speed v along the x-axis. If the atom is brought to an abrupt halt by some collision, what is the probability that it will remain in the ground state?

   Note: I am more interested that you try to explore conceputally how to solve this problem, although it would be great if you could try to work out the details. As an important clue, explore how the Schrodinger equation for a hydrogen atom changes under a Galilean transformation, i.e., what does the Schrodinger equation look like in a frame of reference that is moving at constant velocity v in the

x-direction, compared to someone sitting still at the origin? From this, you can then try to work out the relation between the wave function in a moving frame of reference compared to a fixed frame of reference.

3 Concepts to Understand

1. You should know that the simultaneous eigenfunctions of the commuting variables L^2 and L_z where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is the *orbital* angular momentum are the normalized spherical harmonics

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos(\theta)), \tag{2}$$

where the coefficient ϵ is defined by

$$\epsilon = \begin{cases} (-1)^m & \text{for } m \geq 0 \\ 1 & \text{for } m < 0. \end{cases}, \tag{3}$$

and where the symbol $P_m^l(x)$ denotes the associated Legendre function of x and is defined by:

$$P_l^m(x) = \left(1 - x^2\right)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x), \tag{4}$$

where the Legendre polynomial $P_l(x)$ is itself defined by a recursion relation:

$$P_0 = 1, \qquad P_1 = x, \qquad P_{l+1} = \frac{2l+1}{l+1} x P_l - \frac{l}{l+1} P_{l-1}. \tag{5}$$

The P_l are polynomials of degree l and the associated Legendre functions are polynomials in the quantities x and $\sqrt{1-x^2}$.

With a bit of elbow grease, you should be able to show that the angular momentum operator L^2 in spherical coordinates becomes the following:

$$L^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \partial_\theta \left(\sin(\theta) \partial_\theta \cdot\right) + \frac{1}{\sin^2(\theta)} \partial_\phi^2\right], \tag{6}$$

and we already know that in spherical or cylindrical coordinates,

$$L_z = \frac{\hbar}{i} \partial_\phi. \tag{7}$$

The fact that the spherical harmonics are simultaneous eigenvectors of these operators then leads to the following results which you should memorize and know:

$$L^2 Y_l^m = l(l+1)\hbar^2 Y_l^m; \tag{8}$$

$$L_z Y_l^m = (m\hbar) Y_l^m; \tag{9}$$

$$\langle Y_l^m | Y_{m'}^{l'} \rangle = \int_0^{2\pi} \int_0^{\pi} Y_l^m(\theta, \phi)^* Y_{m'}^{l'}(\theta, \phi) \, \sin(\theta) \, d\theta \, d\phi \tag{10}$$

$$= \delta_{l,l'} \delta_{m,m'}. \tag{11}$$

This last result follows from our favorite theorem for Hermitian operators, that eigenvectors belonging to distinct eigenvalues are orthogonal. (Again you should remember how to prove this using ket notation!)

2. Eq. (6) is important for solving the three-dimensional Schrodinger equation for spherically symmetric potentials $V = V(r)$ since the kinetic energy term has a Laplacian operator ∇^2 which, in spherical coordinates, can be written:

$$
\begin{aligned}
\nabla^2 &= \partial_x^2 + \partial_y^2 + \partial_z^2 && (12)\\
&= \frac{1}{r^2}\partial_r\left(r^2\partial_r\cdot\right) + \frac{1}{r^2\sin(\theta)}\partial_\theta\left(\sin(\theta)\partial_\theta\cdot\right) + \frac{1}{r^2\sin^2(\theta)}\partial_\phi^2 \\
&= \frac{1}{r^2}\partial_r\left(r^2\partial_r\cdot\right) - \frac{1}{\hbar^2 r^2}L^2 \\
&= \frac{1}{r}\partial_r^2(r\cdot) - \frac{1}{\hbar^2 r^2}L^2. && (13)
\end{aligned}
$$

The angular dependence of the three-dimensional Laplacian in spherical coordinates is exactly the angular momentum operator squared!

3. Note: the spherical harmonics are quite important in many areas of applied science and mathematics. E.g., in meteorology and in oceanography, one often represents the three-dimensional time-dependent fields of velocity, pressure, temperature, etc., in terms of finite expansions of spherical harmonics (with radius-dependent coefficients) since this is a natural and economical way to approximate functions on the surface of a sphere. In particular, this approximation avoids the sometimes subtle issue of how to deal with coordinate singularities at $\theta = 0$ and $\theta = \pi$, i.e., at the north and south poles of a sphere.

   The argument goes something like this: since the Y_l^m are the eigenvectors of an observable L^2, they must form a complete set and so any function $f(\theta, \phi)$ must have an expansion in terms of them. If $w(\rho, \theta, \phi)$ denotes some field (e.g., the temperature), we can write:

$$w(\rho, \theta, \phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} w_{lm}(\rho) Y_l^m(\theta, \phi), \qquad (14)$$

   since, for any fixed radial distance ρ, we have a function of angles that can be expanded by the completeness of the Y_l^m.

4. Using Eq. (13), we can show the important result that the three-dimensional single-particle Schrodinger equation for a spherically symmetric potential $V = V(r)$ reduces to solving a one-dimensional single-particle Schrodinger equation for some radial function $u(r) = rR(r)$ in a potential

$$V_{1d}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}, \qquad (15)$$

   where the full stationary three-dimensional wave function is

$$\psi(\rho, \theta, \phi) = R(r) Y_l^m(\theta, \phi), \qquad (16)$$

   which is simultaneously an eigenfunction of the three operators H, L^2, and L_z.

   Since the spherical harmonics are already normalized, you should be able to see easily that the condition for the radial function $u = rR$ to be normalized is:

$$\int_0^\infty |u|^2\, dr = 1. \qquad (17)$$