

Physics 143a – Workshop 10

Radial Schrödinger Equation and Spherical Harmonics

Week Summary

- **Radial Schrödinger Equation and Wavefunction:** For a particle of mass m in a central force potential well $V(r)$, the Schrödinger equation and its wave function solution can be reduced to

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{n\ell}(r)}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u_{n,\ell}(r) = E_{n,\ell} u_{n,\ell}(r) \quad \text{and} \quad \psi_{n,\ell,m} = \frac{1}{r} u_{n,\ell}(r) Y_{\ell,m}(\theta, \phi), \quad (1)$$

where n , ℓ , and m are the principal, azimuthal, and magnetic quantum numbers, respectively, and $Y_{\ell,m}(\theta, \phi)$ is a spherical harmonic. We note in particular that although the energy eigenvalues of the system are, in general, written in terms of the quantum numbers n and ℓ , for the Hydrogen atom, the energy only depends on the n quantum number.

- **Orbital Angular Momentum:** The orbital angular momentum operator $\hat{\mathbf{L}}$ satisfies the standard properties of angular momentum operators:

$$\hat{\mathbf{L}}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle, \quad \hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle, \quad (2)$$

where m can take on the $2\ell+1$ values $-\ell, -\ell+1, \dots, \ell$. Additionally, unlike general angular momentum operators, the operators $\hat{\mathbf{L}}^2$ and \hat{L}_z have the coordinate representations

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \quad (3)$$

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (4)$$

- **Spherical Harmonics:** Spherical harmonics are the mutual eigenfunctions of \hat{L}_z and $\hat{\mathbf{L}}^2$ written in the θ, ϕ basis:

$$Y_{\ell,m}(\theta, \phi) \equiv \langle \theta, \phi | \ell, m \rangle. \quad (5)$$

The first few spherical harmonics are as follows:

$$Y_{0,0}(\theta, \phi) = \left(\frac{1}{4\pi} \right)^{1/2}, \quad (6)$$

$$Y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta, \quad Y_{1,\pm 1}(\theta, \phi) = \mp \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}, \quad (7)$$

$$Y_{2,0}(\theta, \phi) = \left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1), \quad Y_{2,\pm 1}(\theta, \phi) = \mp \left(\frac{15}{8\pi} \right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}, \quad (8)$$

$$Y_{2,\pm 2}(\theta, \phi) = \left(\frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}. \quad (9)$$

1 Problems

1. Practicing Harmonics

The wave function of a particle subjected to a spherically symmetric potential $V(r)$ is given by

$$\psi(\mathbf{x}) = \left(\frac{x^2}{r^2} + \frac{y^2}{r^2} + 3\frac{z}{r} \right) g(r). \quad (10)$$

- (a) Is $\psi(\mathbf{x})$ an eigenfunction of L^2 ? What is the average of L^2 ?
- (b) Suppose it is somehow known that $\psi(\mathbf{x})$ (which is different from the $\psi(\mathbf{x})$ given above) is an energy eigenfunction of the Hamiltonian with eigenvalue E and additional quantum numbers ℓ and m . Explain how we may find $V(r)$.

2. Constructing Hamiltonians, I

For the following physical systems

- (i) Write the quantum mechanical Hamiltonian, identifying and defining all needed operators and parameters
 - (ii) Calculate the frequency of a photon released in transitioning from the first excited state to the ground state
- (a) A pendulum of fixed mass and length undergoing small oscillations about its equilibrium position
 - (b) An electron which is confined to move linearly along a hydrocarbon chain of fixed length. The electron does not interact with any molecules in the chain, but it is restricted to stay within the length of the chain
 - (c) A rod which is constrained to rotate within a plane (*Hint*: Only a single angular momentum coordinate direction is relevant here.)

3. Studying Diatomic molecules

An experimentalist is attempting to understand the quantum transitions a diatomic molecule can undergo. He knows the diatomic molecule consists of two molecules of mass m interacting through a roughly quadratic potential, and the two-molecule configuration can rotate like a dumbbell of length R (where R is the intermolecular distance) in three dimensional space.

Knowing that you are studying quantum mechanics, he thinks you're the perfect person to answer the questions he has about this system. Specifically, he wants to know

- (a) the possible frequencies of photons released if the diatomic molecule system falls from an excited state to the next-nearest excited state
- (b) the most likely position and angular configuration of the ground state of the molecule

What are the questions you would need to answer in order to answer the experimentalist's questions? What is the answer to his first question?

2 Solutions

1. (a) Writing $\psi(\mathbf{x})$ in terms of angular coordinates we have

$$\psi(\mathbf{x}) = (\sin^2 \theta + 3 \cos \theta) g(r). \quad (11)$$

The fact that Eq.(11) has no ϕ variable in its expression indicates that it must be expanded in terms of spherical harmonics which are independent of ϕ . Considering the spherical harmonics available to us, we find it should be expanded in terms of the functions

$$Y_{2,0}(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1), \quad Y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta, \quad \text{and} \quad Y_{0,0}(\theta, \phi) = \left(\frac{1}{4\pi}\right)^{1/2}. \quad (12)$$

Noting that $3 \cos^2 \theta - 1 = 2 - 3 \sin^2 \theta$, we can then solve for $\sin^2 \theta$ and $\cos \theta$ in terms of the above listed spherical harmonics. We then find

$$\begin{aligned} \sin^2 \theta &= \frac{1}{3} \left[2 - \left(\frac{16\pi}{5}\right)^{1/2} Y_{2,0}(\theta, \phi) \right] \\ &= \frac{2}{3} (4\pi)^{1/2} Y_{0,0}(\theta, \phi) - \frac{1}{3} \left(\frac{16\pi}{5}\right)^{1/2} Y_{2,0}(\theta, \phi) \end{aligned} \quad (13)$$

$$\cos \theta = \left(\frac{4\pi}{3}\right)^{1/2} Y_{1,0}(\theta, \phi). \quad (14)$$

Thus we see that $\psi(\mathbf{x})$ can be written as

$$\begin{aligned} \psi(\mathbf{x}) &= g(r) \left[\frac{2}{3} (4\pi)^{1/2} Y_{0,0}(\theta, \phi) - \frac{1}{3} \left(\frac{16\pi}{5}\right)^{1/2} Y_{2,0}(\theta, \phi) + 3 \left(\frac{4\pi}{3}\right)^{1/2} Y_{1,0}(\theta, \phi) \right] \\ &= g(r) \frac{(4\pi)^{1/2}}{3} \left[2Y_{0,0}(\theta, \phi) - \frac{2}{\sqrt{5}} Y_{2,0}(\theta, \phi) + \frac{9}{\sqrt{3}} Y_{1,0}(\theta, \phi) \right]. \end{aligned} \quad (15)$$

And we can conclude that $\psi(\mathbf{x})$ is not an eigenfunction of \mathbf{L}^2 .

Now, in order to compute the average of \mathbf{L}^2 we need to compute the probability of obtaining each possible value of ℓ associated with the wavefunction. First we compute the normalization of the angular parts of the wavefunction. We only focus on the coefficients contained in the brackets of Eq.(15) because it is only the relative magnitude of the spherical harmonics which is important. We find the normalization (squared) of the quantity in the brackets is

$$(2)^2 + \left(-\frac{2}{\sqrt{5}}\right)^2 + \left(\frac{9}{\sqrt{3}}\right)^2 = 4 + \frac{4}{5} + 27 = \frac{159}{5}. \quad (16)$$

Thus, the probabilities of obtaining the various possible values of \mathbf{L}^2 are

$$\ell = 2: \quad \hbar^2 \ell(\ell + 1) = 6\hbar^2 \quad \text{with} \quad \text{probability} = \frac{4}{159/5} = \frac{20}{159} \quad (17)$$

$$\ell = 1: \quad \hbar^2 \ell(\ell + 1) = 2\hbar^2 \quad \text{with} \quad \text{probability} = \frac{4/5}{159/5} = \frac{4}{159} \quad (18)$$

$$\ell = 0: \quad \hbar^2 \ell(\ell + 1) = 0 \quad \text{with} \quad \text{probability} = \frac{27}{159/5} = \frac{135}{159}, \quad (19)$$

and the average of \mathbf{L}^2 is

$$\langle \mathbf{L}^2 \rangle = 6\hbar^2 \cdot \frac{20}{159} + 2\hbar^2 \cdot \frac{4}{159} + 0 \cdot \frac{135}{159} = \frac{128}{159} \hbar^2. \quad (20)$$

■

- (b) If we know $\psi(\mathbf{x})$ is an eigenfunction of the Hamiltonian with energy E and additional quantum numbers ℓ and m , then we should be able to write $\psi(\mathbf{x})$ as

$$\psi(\mathbf{x}) = \frac{u_{n,\ell}(r)}{r} Y_{\ell,m}(\theta, \phi), \quad (21)$$

which implies

$$u_{n,\ell}(r) = \frac{r\psi(\mathbf{x})}{Y_{\ell,m}(\theta, \phi)}. \quad (22)$$

Given that $\psi(\mathbf{x})$ is an eigenfunction of the Hamiltonian, the function $u_{n,\ell}(r)$ must satisfy the radial Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{n,\ell}(r)}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u_{n,\ell}(r) = E u_{n,\ell}(r), \quad (23)$$

Solving for the term proportional to $V(r)$, we find

$$V(r)u_{n,\ell}(r) = \left[E + \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{2mr^2} \right] u_{n,\ell}(r). \quad (24)$$

Thus, to find the potential $V(r)$ for this system we would need to determine $u_{n,\ell}(r)$ from Eq.(22), compute the RHS of Eq.(24), and then isolate the function which ultimately multiplies $u_{n,\ell}(r)$.

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2. (a) (i) We determine the quantum mechanical Hamiltonian by first determining the classical energy. Say we have a physical pendulum of total mass M and moment of inertia I placed in a constant gravitational field of downward acceleration g . Taking θ to be the angle the pendulum makes with the vertical, the energy of the pendulum would be

$$E = \frac{1}{2} I \dot{\theta}^2 + Mgl_{\text{CM}}(1 - \cos \theta), \quad (25)$$

where l_{CM} is the distance from the pivot point to the center of mass of the pendulum. To write this energy in Hamiltonian form, we must express the angular derivative $\dot{\theta}$ in terms of the angular momentum L_z through $L_z = I\dot{\theta}$. The classical Hamiltonian then becomes

$$H = \frac{L_z^2}{2I} + Mgl_{\text{CM}}(1 - \cos \theta) = \frac{L_z^2}{2I} + \frac{1}{2} Mgl_{\text{CM}} \theta^2 + \mathcal{O}(\theta^4), \quad (26)$$

where in the final equality we took the approximated $\cos \theta$ in the limit $|\theta| \ll 1$. Promoting the angular momentum and the angular coordinate to Hermitian operators, we finally have the quantum mechanical Hamiltonian:

$$\hat{H} = \frac{\hat{L}_z^2}{2I} + \frac{1}{2} Mgl_{\text{CM}} \hat{\theta}^2 + \mathcal{O}(\hat{\theta}^4). \quad (27)$$

■

- (ii) To compute the energy of a photon released in transitioning from the first excited state to

the ground state, we need to compute the energy eigenvalues of our system. Neglecting the higher-order corrections, the Hamiltonian Eq.(27) is reminiscent of the harmonic oscillator Hamiltonian

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{1}{2}M\omega^2\hat{X}^2. \quad (28)$$

In fact, within this approximation, the two are mathematically identical, and we can find the energy eigenvalue spectrum of Eq.(27) by computing the angular frequency ω for the physical pendulum. We can make this more rigorous by defining a dictionary between Eq.(27) and Eq.(28). If we make the transformations

$$\hat{X} \rightarrow \hat{\theta}, \quad \hat{P} \rightarrow \hat{L}_z, \quad M \rightarrow I, \quad \text{and} \quad \omega \rightarrow \sqrt{\frac{Mg\ell_{\text{CM}}}{I}}, \quad (29)$$

then Eq.(28) becomes Eq.(27). More simply, we can note that the angular frequency (squared) in Eq.(28) is the numerator of the coordinate term divided by the denominator of the momentum term: For Eq.(27), the analogous quantity is $Mg\ell_{\text{CM}}/I$. Given the angular frequency of the pendulum, we find the energy eigenvalues of Eq.(27) are

$$E_n \simeq \hbar\omega \left(n + \frac{1}{2} \right) = \hbar\sqrt{\frac{Mg\ell_{\text{CM}}}{I}} \left(n + \frac{1}{2} \right). \quad (30)$$

The frequency of a photon released in the $1 \rightarrow 0$ transition is then

$$f = \frac{E_1 - E_0}{2\pi\hbar} = \frac{1}{2\pi} \sqrt{\frac{Mg\ell_{\text{CM}}}{I}}. \quad (31)$$

Given that pendulums are fundamentally classical systems, this problem may not seem terribly physical. However, there are some atom-electromagnetic field systems whose dynamics are well modeled by the full pendulum Hamiltonian Eq.(26). ■

- (b) (i) If we have an electron of mass m_e which is free to move within a hydrocarbon chain of length L , then the electron essentially exists in an infinite potential well. Therefore, the Hamiltonian for the system is

$$\hat{H} = \begin{cases} \frac{\hat{P}^2}{2m_e} & \text{for } 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}. \quad (32)$$

- (ii) Given that this "electron-in-hydrocarbon" system is modeled by Eq.(32), we can infer that the eigenvalue spectrum is

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad (33)$$

where n can be any nonzero integer. Therefore, the frequency of a photon released in making the transition from the first excited state to a ground state¹ is

$$f = \frac{E_2 - E_1}{2\pi\hbar} = \frac{3\hbar\pi}{4m_e L^2}. \quad (34)$$

- (c) (i) A rod of mass M and length ℓ which is constrained to rotate within a plane has the energy

$$E = \frac{1}{2}I\dot{\theta}^2, \quad (35)$$

¹For the infinite potential well, the ground state is defined by $n = 1$.

where $I = \frac{1}{12}M\ell^2$ is the moment of inertia about the center of mass of the rod. By analogy with (a), we can postulate the quantum mechanical Hamiltonian of the system to be

$$\hat{H} = \frac{\hat{L}_z^2}{2I}, \quad (36)$$

where \hat{L}_z is the z angular momentum operator. ■

- (ii) To determine the energy eigenvalues of Eq.(36), we can solve the Schrödinger equation. In angular coordinates the relevant Schrödinger equation becomes

$$-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \psi(\phi) = E\psi(\phi), \quad (37)$$

valid for $0 \leq \phi \leq 2\pi$. Eq.(37) is reminiscent of the Schrödinger equation for the infinite square well except our wave function $\psi(\phi)$ has the periodic boundary conditions $\psi(\phi) = \psi(\phi + 2\pi)$. Imposing this boundary condition on solutions to Eq.(37), we find the energy eigenvalues

$$E_m = \frac{\hbar^2 m^2}{2I}, \quad (38)$$

where m is any nonzero integer. Thus, the frequency of a photon released in a transition from the first excited state to the ground state is

$$f = \frac{E_2 - E_1}{2\pi\hbar} = \frac{3\hbar}{4\pi I}. \quad (39)$$

3. In order to determine the frequency of a photon released in the state transitions and the most likely configurations of the diatomic molecules, we would need to determine three main quantities in this system

- (1) the Hamiltonian
- (2) the energy eigenvalues
- (3) the wave functions

- (a) Because we have a closed system of interacting particles we will ignore the center of mass dynamics of the system. Consequently, we can take the system to be a vibrating and rotating diatomic molecule fixed in space. To determine the Hamiltonian of this system we will at first consider each type of motion separately.

For a diatomic molecule consisting of two masses m and interacting through a quadratic potential, we can approximate the interaction energy as

$$V(R) = \frac{1}{2}k(R - R_0)^2, \quad (40)$$

where k is the spring constant of the interaction and R_0 is the equilibrium distance. The vibrational part of the Hamiltonian for this system is then

$$\hat{H}_{\text{vib}} = \frac{\hat{P}_R^2}{2\mu} + \frac{1}{2}k(\hat{R} - R_0)^2, \quad (41)$$

where \hat{P}_R is the one-dimensional momentum of the vibrations and $\mu = m^2/(m + m) = m/2$ is the reduced mass of the system.

For a diatomic molecule consisting of two masses m separated by a distance R , we have a Hamiltonian defined by the angular momentum squared operator:

$$\hat{H}_{\text{rot}} = \frac{\hat{\mathbf{L}}^2}{2I(R)}, \quad (42)$$

where

$$I(R) \equiv m(R/2)^2 + m(R/2)^2 = mR^2/2 \quad (43)$$

is the moment of inertia of the system.

Adding Eq.(41) and Eq.(42), we find that the full Hamiltonian of the system is

$$\hat{H} = \frac{\hat{P}_R^2}{2\mu} + \frac{1}{2}k(\hat{R} - R_0)^2 + \frac{\hat{\mathbf{L}}^2}{2I(R)}. \quad (44)$$

Now, although we have two seeming independent systems represented in Eq.(44), the two are actually coupled through the variable R : The vibrational system which consists of oscillations of R also determines the moment of inertia $I(R)$ of the rotational system. To solve for the eigenvalue spectrum of Eq.(44), we will approximately decouple the two systems by taking $R \gg |R - R_0|$. This is a sensible approximation presuming our masses remain near their equilibrium configuration. With this approximation Eq.(44) becomes

$$\hat{H} = \frac{\hat{P}_R^2}{2\mu} + \frac{1}{2}k(\hat{R} - R_0)^2 + \frac{\hat{\mathbf{L}}^2}{2I(R_0)} + \mathcal{O}((\hat{R} - R_0)^2). \quad (45)$$

The first two terms in Eq.(45) represent a harmonic oscillator Hamiltonian which is independent of the "rigid rotor" Hamiltonian represented by the third term. Given the standard eigenvalue spectrum solutions to the harmonic oscillator and the rigid rotor, we have

$$\hat{H}_{\text{vib}}|n\rangle = \hbar\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right)|n\rangle, \quad \text{and} \quad \hat{H}_{\text{rot}}|\ell, m\rangle = \frac{\hbar^2\ell(\ell+1)}{2I(R_0)}|\ell, m\rangle, \quad (46)$$

where n is the quantum number defining the energy level of the vibrational system, ℓ is the azimuthal quantum number, and m is the magnetic quantum number. Thus, the energy spectrum of the entire diatomic molecule system is

$$E_{n,\ell} = \hbar\sqrt{\frac{2k}{m}}\left(n + \frac{1}{2}\right) + \frac{\hbar^2\ell(\ell+1)}{mR_0^2}, \quad (47)$$

where we used $\mu = m/2$ and $I(R_0) = mR_0^2/2$.

If we are interested in "excited state \rightarrow next-nearest lower excited state" transitions, Eq.(47) implies we are interested in the transitions $n, \ell \rightarrow n-1, \ell$ or $n, \ell \rightarrow n, \ell-1$. By Eq.(47), the frequencies of photons released from these transitions are

$$f_{n,\ell \rightarrow n-1,\ell} = \frac{1}{2\pi\hbar}(E_{n,\ell} - E_{n-1,\ell}) = \frac{1}{2\pi}\sqrt{\frac{2k}{m}}, \quad (48)$$

and

$$f_{n,\ell \rightarrow n,\ell-1} = \frac{1}{2\pi\hbar}(E_{n,\ell} - E_{n,\ell-1}) = \frac{\hbar\ell}{\pi m R_0^2}. \quad (49)$$

■

- (b) To find the most probable configurations of the ground state of the diatomic molecule, we would need to determine the energy eigenfunctions of this system. Given that we have separable harmonic oscillator and rotational parts, we can conclude that the wave function is

$$\psi_{n,\ell,m}(R, \theta, \phi) = \psi_n(R - R_0)Y_{\ell,m}(\theta, \phi), \quad (50)$$

where $\psi_n(x)$ is the energy eigenfunction of the harmonic oscillator centered at $x = 0$, and $Y_{\ell,m}(\theta, \phi)$ is a spherical harmonic, the energy eigenfunction of $\hat{\mathbf{L}}^2$. The ground state wave function of this system is given by

$$\begin{aligned} \psi_{0,0,0}(R, \theta, \phi) &= \psi_0(R - R_0)Y_{0,0}(\theta, \phi) \\ &= \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} e^{-\mu\omega(R-R_0)^2/2} \left(\frac{1}{4\pi}\right)^{1/2}, \end{aligned} \quad (51)$$

which, unsurprisingly, suggests that, in the ground state, the most probable radial configuration is the one where the diatomic molecules are separated $R = R_0$ and all angular configurations are equally likely. ■