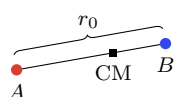


## Week 4

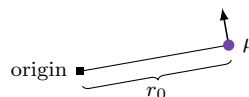
# The Hydrogen Atom and Angular Momentum

### 4.1 Rotational Motion

- 10/18: • Consider the diatomic molecule AB at a distance  $r_0$  apart rotating about its center of mass.



(a) Diatomic.



(b) An equivalent system.

Figure 4.1: Diatomic rotation.

- To simplify the problem, replace the two particles rotating about the center of mass with one particle of reduced mass  $\mu$  rotating about the center of mass with lever arm  $r_0$ .
- Classically, the kinetic energy of the translational motion is

$$T = \frac{L^2}{2I}$$

where  $I = \mu r_0^2$  and  $L = p \times r_0 = pr_0$  (for this kind of rotation; see Figure 4.1b).

- To further talk about this problem, we should introduce **spherical coordinates**.
- **Spherical coordinates:** The coordinate system  $(r, \theta, \phi)$  related to the Cartesian coordinates  $(x, y, z)$  by

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- Classically, we will have

$$H = \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

in Cartesian coordinates.

- In spherical coordinates, this becomes

$$H = \frac{1}{2\mu} \left( p_r^2 + \frac{L^2}{r^2} \right) + V(r)$$

- Thus, in quantum mechanics, we get

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(x, y, z) \\ &= \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r)\end{aligned}$$

- Thus, we have in spherical coordinates that

$$\hat{T}\psi = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \psi \right) + \frac{1}{r^2 \sin \theta} \left( \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \psi \right) \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi \right]$$

- 2D rigid rotor:

- Let the system from Figure 4.1b be confined to rotating in two dimensions.
- This simplifies the problem since both the  $\partial/\partial r$  and  $\partial/\partial \theta$  terms in the kinetic energy operator disappear (since, respectively, the particle is at a fixed distance from the center of mass and it cannot move out of the 2D plane).
- Thus, our Schrödinger equation for this system is

$$-\frac{\hbar^2}{2\mu r_0^2} \frac{\partial^2}{\partial \phi^2} \psi(\phi) = E\psi(\phi)$$

- Solution: Let  $\psi(\phi) = e^{im\phi}$ ; then

$$E_m = \frac{\hbar^2 m^2}{2\mu r_0^2}$$

- $m = 0, 1, 2, \dots$  is a new quantum number.
  - $m$  doesn't go to infinity because  $|m|$  is bounded by  $\ell$  (the total angular momentum).
- Remembering our original restriction, we have that this math describes the system from Figure 4.1a but confined to rotate in the  $xy$  plane with angular momentum in the  $z$  direction.
  - Thus, for example, the energies of the system from Figure 4.1a are dependent on  $m$  and  $I = \mu r_0^2$ .
- Such a system occurs in physical reality when we put the diatomic in an external field, or attach to it a big functional group.
- Zero point energy:  $m = 0$  does not violate the UR since we still have  $\Delta L \Delta \theta \geq \hbar/2$  (as everything is still rotating in the sense that we have equal probability of the particle being everywhere [as opposed to more localized/normal rotation with higher values of  $m$ ]).

- 3D rigid rotor:

- Assume that the potential energy is zero on the surface of the sphere (so we basically have a particle on a sphere).
- Then

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_0^2} = \frac{\hat{L}^2}{2I}$$

- Solving  $\hat{H}\psi = E\psi$  asserts that the eigenfunctions of the Hamiltonian are the spherical harmonics  $Y_{\ell m}(\theta, \phi)$ .
- Energy:

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell + 1)$$

where  $\ell = 0, 1, 2, \dots$

- Recall that  $m$  corresponds to the projection of angular momentum onto the  $z$ -axis, so that

$$m = -\ell, \dots, +\ell$$

## 4.2 Hydrogen Atom

10/20:

- Microwaves (for food) excite the rotational motion of water molecules.
- Spherical harmonics: The solution of  $\psi_{lm}(\theta, \phi) = Y_{lm}(\theta, \phi)$ , where  $l, m$  are quantum numbers.
- $E_l = \hbar^2/2I \cdot l(l+1)$  for  $l = 0, 1, 2, \dots$

- Form of the spherical harmonics:

$$Y(\theta, \phi) = P_{lm}(\cos \theta) e^{im\phi}$$

where  $P_{lm}(\cos \theta)$  is a polynomial.

- The polynomials  $P_{lm}(\cos \theta)$  are the associated Legendre polynomials.
- When  $m = 0$ , we have the Legendre polynomials.

- The differential equation describing these is

$$\frac{d}{dx} \left( (1-x^2) \frac{d}{dx} P_l(x) + l(l+1) P_l(x) \right) = 0$$

- The Legendre polynomials converge very quickly to functions on  $[-1, 1]$ .
- People map these polynomials onto other domains, too, to solve a variety of problems.
- Legendre polynomials have more of their roots at the boundaries — since the boundary conditions are the most important part of solving a differential equation, it makes sense that accurate representations would sample near the boundary more.
- Examples:

$$P_0(x) = 1$$

$$P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$$

$$P_1(x) = x$$

$$P_3(x) = \frac{5}{2}x^3 - \frac{3}{2}x$$

- Consider HCl.

- For it,

$$\frac{\hbar^2}{2I} = 1.3 \times 10^{-3} \text{ eV}$$

- Rotational spectral lines may arise from different values of the quantum number  $l$ .
- The molecule vibrates in harmonic oscillation with spacings  $\approx 0.1 \text{ eV}$  (it's not strictly rigid).
- Rovibrational spectra includes both forms of movement.
  - Very high precision.
  - Very big in the 90s.
- Electronic spectra: A few electron volts.

- The hydrogen atom.

- Two generalizations of the 3D rigid rotor combine to treat the hydrogen atom:
  1. An addition of the kinetic energy in the radial direction  $\hat{r}$ .
  2. An addition of the Coulomb potential.

- Schrödinger equation:

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r) \\ \hat{p}_r^2 &= -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \psi(r) \right) \\ V(r) &= -\frac{e(eZ)}{4\pi\epsilon_0 r}\end{aligned}$$

- Because the particle has spherical symmetry (that it, does not depend on  $\theta$  or  $\phi$ ), the wave function is separable, that is, it may be written as a product

$$\psi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$$

- Note that there is no analytic solution to the Schrödinger equation in Cartesian coordinates — we need spherical coordinates to take advantage of the spherical symmetry.
- Substitution into the Schrödinger equation yields

$$\left( \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r) \right) R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi)$$

where  $\mu$  is the reduced mass of the electron and the nucleus (which is approximately the mass of the electron).

- But since

$$\frac{1}{2\mu r^2} \hat{L}^2 Y_{lm}(\theta, \phi) = \frac{l(l+1)}{2\mu r^2} \hbar^2 Y_{lm}(\theta, \phi)$$

we have that

$$\frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2} + V(r) \right) R_n(r) = E_n R_n(r)$$

- We have reduced the three-dimensional case of the hydrogen atom to a one-dimensional differential equation.

### 4.3 Hydrogen Atom (cont.)

10/22:

- We want to solve the SE  $\hat{H}\psi_n = E\psi_n$  for the hydrogen atom.
- To exploit the spherical symmetry of the hydrogen atom, we use  $(r, \theta, \phi)$ .
- Thus, our Hamiltonian is equal to

$$\hat{H} = \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r)$$

- Since  $V$  is just a function of  $r$ , the wave function is separable:  $\psi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$ .
- “Whenever you have a separation of variables additively in the Hamiltonian, you have a separation of variables multiplicatively in the wave function.”

- Substitute the wave function into the Schrödinger equation:

$$\begin{aligned}\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)\right) R_n(r) Y_{lm}(\theta, \phi) &= E R_n(r) Y_{lm}(\theta, \phi) \\ \left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right) R_n(r) Y_{lm}(\theta, \phi) &= E R_n(r) Y_{lm}(\theta, \phi) \\ \left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right) R_n(r) &= E_{nl} R_n(r)\end{aligned}$$

- Noting that we only care about the behavior of the differential equation on  $[0, \infty)$ , specifically at really large distances, we perform an asymptotic analysis.

$$\lim_{r \rightarrow \infty} \left(\frac{1}{2\mu}\hat{p}_r^2\right) R(r) = E R(r)$$

- Plugging in the value of the momentum operator, we have that

$$\begin{aligned}-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} R(r) &= E R(r) \\ R(r) &= e^{-\alpha r}\end{aligned}$$

where  $\alpha = i\hbar/\sqrt{2\mu E}$ .

- But we want to multiply  $e^{-\alpha r}$  by some type of polynomial. Namely, **Laguerre polynomials**.

- These polynomials may be found by expanding a power series.
- Let

$$L\left(\frac{\alpha r}{n}\right) = \sum_{j=0}^{\infty} c_j \left(\frac{\alpha r}{n}\right)^j$$

- A recursion relation may be found.
- The quantization of energy in the hydrogen atom again arises from the truncation of the polynomials.
- Thus, the general solution of  $R_{nl}(r)$  is

$$R_{nl}(r) = \left(\frac{\alpha r}{n}\right)^l L_{n+1, 2l+1}\left(\frac{\alpha r}{n}\right) e^{-\alpha r/2n}$$

- Energy levels:

$$E_n = -\frac{\mu}{2\hbar^2} \left(\frac{(Ze)e}{4\pi\epsilon}\right)^2 \frac{1}{n^2}$$

- These are the discrete energies of Bohr!
- But now we also have the electron's probability distributions, i.e., the ground state wave function is

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

- Thus, we can now take a look at the probabilities. *picture*

- The probability is

$$\text{Pr} = |\psi(r, \theta, \phi)|^2 r^2 \sin \theta$$

- The radial probability is

$$\text{Pr}(r) = r^2 |R_{nl}(r)|^2$$

- The radial probability peaks at  $a_0$ , the **Bohr radius**.
  - Thus, the Bohr radius (the radius of the circular orbit of Bohr's hydrogen electron) is just the most probable distance from the nucleus!
- The average distance from the nucleus (the expectation value of  $r$ ) is

$$\begin{aligned}\langle r \rangle &= \int_0^\infty \text{Pr}(r) r \, dr \\ &= \int_0^\infty \psi^*(r) r \psi(r) \, dr\end{aligned}$$

- Note we also find that  $\langle \hat{H} \rangle = E$ , so there is no uncertainty in the energy.
- Note that in some ways, quantum mechanics is more certain than classical mechanics since, for instance, in quantum we know the energy exactly.

## 4.4 Chapter 5: The Harmonic Oscillator and the Rigid Rotator — Two Spectroscopic Models

*From McQuarrie and Simon (1997).*

- 10/19:
- **Rigid-rotator model:** Two point masses  $m_1$  and  $m_2$  at fixed distances  $r_1$  and  $r_2$  from their center of mass.
    - Since the vibrational amplitude of a rotating molecule is small compared to its amplitude, this is a good model.
  - Kinetic energy of the rigid rotator:

$$\begin{aligned}K &= \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \\ &= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 \\ &= \frac{1}{2} I \omega^2\end{aligned}$$

- Note that

$$\begin{aligned}I &= m_1 r_1^2 + m_2 r_2^2 \\ &= \mu r^2\end{aligned}$$

(see Problem 5-29).

- It follows that we the two-body problem of the rigid rotator is equivalent to the one-body problem of a single body of mass  $\mu$  rotating at a distance  $r$  from a fixed center.
- Since there are no external forces on the rigid rotator (we're not applying any electric or magnetic fields), the energy of the molecule is solely kinetic (i.e., there is no potential energy term in the Hamiltonian).
  - Thus, for a rigid rotator,

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu} \nabla^2$$

- Since this particle has a natural center of spherical symmetry, we opt for spherical coordinates. However, this necessitates expressing  $\nabla^2$  as the following.

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right)_{r, \theta}$$

– See Problem 5-32 for a derivation.

- With respect to the rigid rotator,  $r$  is constant. Thus,

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ \hat{H} &= -\frac{\hbar^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right) \right] \\ \hat{L}^2 &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right) \right]\end{aligned}$$

– Note that since both  $\theta$  and  $\phi$  are unitless, the units of angular momentum for quantum system are  $\hbar$ .

- Rigid-rotator wave functions are customarily denoted by  $Y(\theta, \phi)$ .
- In solving  $\hat{H}Y(\theta, \phi) = EY(\theta, \phi)$ , it will be useful to multiply the original Schrödinger equation by  $\sin^2 \theta$  and let  $\beta = 2IE/\hbar^2$  to obtain the partial differential equation

$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} + (\beta \sin^2 \theta)Y = 0$$

- The solutions to the above equation are intimately linked to those for the hydrogen atom.
- Solving the above equation yields the condition that  $\beta = J(J+1)$  for  $J = 0, 1, 2, \dots$ . Therefore,

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

for  $J = 0, 1, 2, \dots$

■ Each energy level has a degeneracy  $g_J = 2J + 1$  as well.

- Once again, electromagnetic radiation can cause a rigid rotator to undergo transitions from one state to another subject to the selection rules that only transitions between adjacent states are allowed and the molecule must possess a permanent dipole moment.
- As before, we can calculate

$$\Delta E = \frac{h^2}{4\pi^2 I} (J+1)$$

and the frequencies at which absorption transitions occur are

$$\nu = \frac{h}{4\pi^2 I} (J+1)$$

for  $J = 0, 1, 2, \dots$

- It follows from reduced mass, bond length, and moment of inertia data that the frequencies typically lie in the microwave region.
- **Microwave spectroscopy:** The direct study of rotational transitions.
- **Rotational constant** (of a molecule): The following quantity. *Given by*

$$B = \frac{h}{8\pi^2 I}$$

- We often write the absorption frequencies as  $\nu = 2B(J + 1)$ .
- The spacing of lines in a microwave spectrum is  $2B$ .
- Like IR spectroscopy can be used to determine the force constants of molecular attractions in diatomics, microwave spectroscopy can be used to determine the bond lengths of diatomics.

## Problems

**5-29.** Show that the moment of inertia for a rigid rotator can be written as  $I = \mu r^2$  where  $r = r_1 + r_2$  (the fixed separation of the two masses) and  $\mu$  is the reduced mass.

*Answer.* First, note that  $m_1 r_1 = m_2 r_2$  for such a rotation about the center of mass. Then

$$\begin{aligned}
 I &= \mu r^2 \\
 &= \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2 \\
 &= \frac{m_1 m_2 r_1}{m_1 r_1 + m_2 r_1} (r_1 + r_2)^2 \\
 &= \frac{m_1 m_2 r_1}{m_2 r_2 + m_2 r_1} (r_1 + r_2)^2 \\
 &= \frac{m_1 r_1}{r_2 + r_1} (r_1 + r_2)^2 \\
 &= m_1 r_1 (r_1 + r_2) \\
 &= m_1 r_1^2 + m_1 r_1 r_2 \\
 &= m_1 r_1^2 + m_2 r_2^2
 \end{aligned}$$

as desired. □

**5-30.** Consider the transformation from Cartesian coordinates to plane polar coordinates where

$$\begin{aligned}
 x &= r \cos \theta & r &= \sqrt{x^2 + y^2} \\
 y &= r \sin \theta & \theta &= \tan^{-1} \left( \frac{y}{x} \right)
 \end{aligned}$$

If a function  $f(r, \theta)$  depends upon the polar coordinates  $r$  and  $\theta$ , then the chain rule of partial differentiation says that<sup>[1]</sup>

$$\left( \frac{\partial f}{\partial x} \right)_y = \left( \frac{\partial f}{\partial r} \right)_\theta \left( \frac{\partial r}{\partial x} \right)_y + \left( \frac{\partial f}{\partial \theta} \right)_r \left( \frac{\partial \theta}{\partial x} \right)_y$$

and that

$$\left( \frac{\partial f}{\partial y} \right)_x = \left( \frac{\partial f}{\partial r} \right)_\theta \left( \frac{\partial r}{\partial y} \right)_x + \left( \frac{\partial f}{\partial \theta} \right)_r \left( \frac{\partial \theta}{\partial y} \right)_x$$

For simplicity, we will assume that  $r$  is constant so that we can ignore terms involving derivatives with respect to  $r$ . In other words, we will consider a particle that is constrained to move on the circumference of a circle. This system is sometimes called a **particle on a ring**. Using the above equations, show that

$$\left( \frac{\partial f}{\partial x} \right)_y = -\frac{\sin \theta}{r} \left( \frac{\partial f}{\partial \theta} \right)_r \qquad \left( \frac{\partial f}{\partial y} \right)_x = \frac{\cos \theta}{r} \left( \frac{\partial f}{\partial \theta} \right)_r$$

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<sup>[1]</sup>Note that the subscript means that the subscripted variable is held constant.



for  $r$  fixed. Now apply the above equations again to show that

$$\begin{aligned}\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= \left[\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x}\right)_y\right]_y \\ &= \left[\frac{\partial}{\partial \theta} \left(\frac{\partial f}{\partial x}\right)_y\right]_r \left(\frac{\partial \theta}{\partial x}\right)_y \\ &= \left\{\frac{\partial}{\partial \theta} \left[-\frac{\sin \theta}{r} \left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_r \left(-\frac{\sin \theta}{r}\right) \\ &= \frac{\sin \theta \cos \theta}{r^2} \left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\sin^2 \theta}{r^2} \left(\frac{\partial^2 f}{\partial \theta^2}\right)_r\end{aligned}$$

for  $r$  fixed. Similarly, show that

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -\frac{\sin \theta \cos \theta}{r^2} \left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos^2 \theta}{r^2} \left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

and that

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \longrightarrow \frac{1}{r^2} \left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

both for  $r$  fixed. Now show that the Schrödinger equation for a particle of mass  $m$  constrained to move on a circle of radius  $r$  (see Problem 3-28) is

$$-\frac{\hbar^2}{2I} \frac{\partial^2 \psi(\theta)}{\partial \theta^2} = E\psi(\theta)$$

where  $I = mr^2$  is the moment of inertia and  $0 \leq \theta \leq 2\pi$ .

*Answer.* We have that

$$\begin{aligned}\left(\frac{\partial \theta}{\partial x}\right)_y &= \frac{\partial}{\partial x} \left(\tan^{-1} \left(\frac{y}{x}\right)\right) & \left(\frac{\partial \theta}{\partial y}\right)_y &= \frac{\partial}{\partial y} \left(\tan^{-1} \left(\frac{y}{x}\right)\right) \\ &= \frac{1}{\left(\frac{y}{x}\right)^2 + 1} \cdot y \cdot -\frac{1}{x^2} & &= \frac{1}{\left(\frac{y}{x}\right)^2 + 1} \cdot \frac{1}{x} \\ &= -\frac{y}{x^2 + y^2} & &= \frac{x}{x^2 + y^2} \\ &= -\frac{r \sin \theta}{r^2} & &= \frac{r \cos \theta}{r^2} \\ &= -\frac{\sin \theta}{r} & &= \frac{\cos \theta}{r}\end{aligned}$$

This combined with the fact that  $r$  is constant yields

$$\begin{aligned}\left(\frac{\partial f}{\partial x}\right)_y &= \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y & \left(\frac{\partial f}{\partial y}\right)_x &= \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x \\ &= 0 \cdot \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \cdot -\frac{\sin \theta}{r} & &= 0 \cdot \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \frac{\cos \theta}{r} \\ &= -\frac{\sin \theta}{r} \left(\frac{\partial f}{\partial \theta}\right)_r & &= \frac{\cos \theta}{r} \left(\frac{\partial f}{\partial \theta}\right)_r\end{aligned}$$

as desired.

The rest of the differential equation derivations follow fairly easy with simple calculus rules.

As for the Schrödinger equation, we know that there is no potential field for this particle. Additionally, although we could choose to express  $\psi$  as a function of  $x, y$ , owing to the radial symmetry, we choose to express it as a function of  $r, \theta$ . In fact, we need only express  $\psi$  as a function of  $\theta$  since  $r$  is invariant throughout the chosen free space. Thus, expanding from the general form, we get

$$\begin{aligned}\hat{H}\psi(\theta) &= E\psi(\theta) \\ \left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi(\theta) &= E\psi(\theta) \\ -\frac{\hbar^2}{2m} \cdot \frac{1}{r^2} \left(\frac{\partial^2\psi(\theta)}{\partial\theta^2}\right)_r &= E\psi(\theta) \\ -\frac{\hbar^2}{2I} \frac{\partial^2\psi(\theta)}{\partial\theta^2} &= E\psi(\theta)\end{aligned}$$

as desired. □

- 5-31.** Generalize Problem 5-30 to the case of a particle moving in a plane under the influence of a central force; in other words, convert

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

to plane polar coordinates, this time without assuming that  $r$  is constant. Use the method of separation of variables to separate the equation for this problem. Solve the angular equation.

*Answer.* We have

$$\begin{aligned}\frac{\partial r}{\partial x} &= \frac{1}{2\sqrt{x^2+y^2}} \cdot 2x & \frac{\partial r}{\partial y} &= \frac{1}{2\sqrt{x^2+y^2}} \cdot 2y \\ &= \frac{x}{r} & &= \frac{y}{r} \\ &= \cos\theta & &= \sin\theta\end{aligned}$$

Thus

$$\frac{\partial f}{\partial x} = \cos\theta \frac{\partial f}{\partial r} - \frac{\sin\theta}{r} \frac{\partial f}{\partial\theta} \qquad \frac{\partial f}{\partial y} = \sin\theta \frac{\partial f}{\partial r} + \frac{\cos\theta}{r} \frac{\partial f}{\partial\theta}$$

Also note that

$$\begin{aligned}\frac{\partial^2 f}{\partial x^2} &= \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial x} \right) \\ &= \frac{\partial}{\partial\theta} \left( \frac{\partial f}{\partial x} \right) \frac{\partial\theta}{\partial x} + \frac{\partial}{\partial r} \left( \frac{\partial f}{\partial x} \right) \frac{\partial r}{\partial x}\end{aligned}$$

The rest of the expansions are routine, leading to

$$\nabla^2 f = \frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{1}{r^2} \frac{\partial^2 u}{\partial\theta^2}$$

□

- 5-32.** Using Problems 5-30 and 5-31 as a guide, convert  $\nabla^2$  from three-dimensional Cartesian coordinates to spherical coordinates.

## 4.5 Chapter 6: The Hydrogen Atom

From McQuarrie and Simon (1997).

- 10/29: • Idealize the hydrogen atom to a proton fixed at the origin and an electron of mass  $m_e$  interacting with the proton through a Coulombic potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

- Because of the spherical geometry of the model, we opt for spherical coordinates.
- The appropriate Hamiltonian is thus

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

- Expressing the Laplacian in spherical coordinates gives us

$$\left\{ -\frac{\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

as the Schrödinger equation for the hydrogen atom.

- Multiply through by  $2m_e r^2$  and move all terms over to the lefthand side of the equality to get the above equation into the following separable form.

$$\left\{ -\hbar^2 \left( \frac{\partial}{\partial r} r^2 \frac{\partial \psi}{\partial r} \right) - \hbar^2 \left[ \frac{1}{\sin \theta} \left( \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - 2m_e r^2 \left[ \frac{e^2}{4\pi\epsilon_0 r} + E \right] \right\} \psi(r, \theta, \phi) = 0$$

- Since all the  $\theta, \phi$  dependence occurs within the large square brackets, assume that

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

- Substituting into the differential equation and separating terms (dividing by  $R(r)Y(\theta, \phi)$ ) yields

$$-\frac{\hbar^2}{R(r)} \left[ \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m_e r^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right] - \frac{\hbar^2}{Y(\theta, \phi)} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = 0$$

- All terms containing  $r$  are in the first set of square brackets, and all terms containing  $\theta, \phi$  are in the second set of square brackets. Since the above equation must hold for all  $r, \theta, \phi$ , and  $r, \theta, \phi$  are independent variables, we must have that varying  $r$  while holding  $\theta, \phi$  constant does not change the  $r$  term of the above equation (as this would violate the equality). Similarly, changing  $\theta, \phi$  must not change the  $\theta, \phi$  term. Therefore, we may let

$$\begin{aligned} -\beta &= -\frac{1}{R(r)} \left[ \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m_e r^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right] \\ \beta &= -\frac{1}{Y(\theta, \phi)} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] \end{aligned}$$

where  $\beta$  is a **separation constant** into which we have incorporated  $\hbar^2$ .

- **Radial equation:** The first equation above.
- **Angular equation:** The second equation above after having been multiplied by  $\sin^2 \theta Y(\theta, \phi)$ . *Given by*

$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} + \frac{\partial^2 Y}{\partial \phi^2} + \beta \sin^2 \theta Y \right) = 0$$

- Note that this is identical to the partial differential equation derived in Chapter 5 for the rigid rotator.
- Thus, the angular parts of hydrogen atomic orbitals are also rigid-rotator wave functions.

- **Spherical harmonic:** A wave function of the rigid rotator.
- We now solve the angular equation.
- Invoking separation of variables again with  $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$  yields

$$\frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin \theta + \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = 0$$

- We now introduce a new separation constant (written in a form that predicts future algebraic manipulations) to get

$$\begin{aligned} \frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta &= m^2 \\ \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} &= -m^2 \end{aligned}$$

- Solving the bottom equation above gives solutions

$$\Phi(\phi) = A_m e^{im\phi} \qquad \Phi(\phi) = A_{-m} e^{-im\phi}$$

where the constants  $A_m, A_{-m}$  may depend on the value of  $m$ .

- From the domain of  $\phi$ , we have the boundary condition  $\Phi(\phi + 2\pi) = \Phi(\phi)$ .
- This yields

$$\begin{aligned} A_m e^{im(\phi+2\pi)} &= A_m e^{im\phi} & A_{-m} e^{-im(\phi+2\pi)} &= A_{-m} e^{-im\phi} \\ e^{i2\pi m} &= 1 & e^{-i2\pi m} &= 1 \end{aligned}$$

from which it follows that we must have

$$\begin{aligned} 1 + 0i &= 1 \\ &= e^{\pm i2\pi m} \\ &= \cos(2\pi m) \pm i \sin(2\pi m) \end{aligned}$$

- Therefore,  $m = 0, \pm 1, \pm 2, \dots$
- It follows that we can express the solutions to the bottom angular equation in the more compact form

$$\Phi_m(\phi) = A_m e^{im\phi}$$

where  $m = 0, \pm 1, \pm 2, \dots$

- Normalizing gives us the coefficient  $A_m$ :

$$\begin{aligned} 1 &= \int_0^{2\pi} \Phi_m^*(\phi) \Phi_m(\phi) d\phi \\ &= \int_0^{2\pi} (A_m e^{-im\phi})(A_m e^{im\phi}) d\phi \\ &= A_m^2 \int_0^{2\pi} 1 d\phi \\ A_m &= \frac{1}{\sqrt{2\pi}} \end{aligned}$$

- Thus, the normalized wave functions of  $\Phi(\phi)$  are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

for  $m = 0, \pm 1, \pm 2, \dots$

- We now direct our attention to solving the differential equation containing  $\Theta(\theta)$ .
- Let  $x = \cos \theta$  and  $P(x) = \Theta(\theta)$ . Substituting, we have (see Problem 6-2)

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[ \beta - \frac{m^2}{1-x^2} \right] P(x) = 0$$

where  $m = 0, \pm 1, \pm 2, \dots$

– Note that since  $x = \cos \theta$ ,  $0 \leq \theta \leq \pi$ , the range of  $x$  is  $-1 \leq x \leq 1$ .

- Solving the above equation gives **Legendre's equation**.
- **Legendre's equation:** The following equation. *Given by*

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[ l(l+1) - \frac{m^2}{1-x^2} \right] P(x) = 0$$

– The key difference between Legendre's equation and the previous one is that solving the previous one finds  $\beta$  equal to  $l(l+1)$  with  $l = 0, 1, 2, \dots$  and  $|m| \leq l$  if the solutions are to remain finite.

- **Legendre polynomials:** The solutions to Legendre's equation when  $m = 0$ . *Denoted by  $P_l(x)$ .*

---


$$\begin{aligned} P_0(x) &= 1 \\ P_1(x) &= x \\ P_2(x) &= \frac{1}{2}(3x^2 - 1) \\ P_3(x) &= \frac{1}{2}(5x^3 - 3x) \\ P_4(x) &= \frac{1}{8}(35x^4 - 30x^2 + 3) \end{aligned}$$


---

Table 4.1: The first few Legendre polynomials.

- Notice that  $P_l(x)$  is an even function if  $l$  is even and an odd function if  $l$  is odd.
- The factors in front of  $P_l(x)$  are chosen such that  $P_l(1) = 1$ .
- The Legendre polynomials are orthogonal: If  $l \neq n$ , then

$$\int_{-1}^1 P_l(x) P_n(x) dx = 0$$

- We have that

$$\int_{-1}^1 [P_l(x)]^2 dx = \frac{2}{2l+1}$$

for each  $l$ , so the normalization constant of  $P_l(x)$  is

$$\sqrt{\frac{2l+1}{2}}$$

- **Associated Legendre functions:** The solutions to Legendre's equation when  $m \neq 0$ . *Denoted by  $P_l^{(m)}(x)$ . Given by*

$$P_l^{(m)}(x) = (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x)$$

10/30:

Function	$x$ -coordinates	$\theta$ -coordinates
$P_0^0(x)$	1	1
$P_1^0(x)$	$x$	$\cos \theta$
$P_1^1(x)$	$\sqrt{1-x^2}$	$\sin \theta$
$P_2^0(x)$	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}(3\cos^2 \theta - 1)$
$P_2^1(x)$	$3x\sqrt{1-x^2}$	$3\cos \theta \sin \theta$
$P_2^2(x)$	$3(1-x^2)$	$3\sin^2 \theta$
$P_3^0(x)$	$\frac{1}{2}(5x^2-3x)$	$\frac{1}{2}(5\cos^2 \theta - 3\cos \theta)$
$P_3^1(x)$	$\frac{3}{2}(5x^2-1)\sqrt{1-x^2}$	$\frac{3}{2}(5\cos^2 \theta - 1)\sin \theta$
$P_3^2(x)$	$15x(1-x^2)$	$15\cos \theta \sin^2 \theta$
$P_3^3(x)$	$15\sqrt{1-x^2}$	$15\sin^2 \theta$

Table 4.2: The first few associated Legendre functions.

- Note that only the magnitude of  $m$  is present because  $m^2$  is the only form of  $m$  present in Legendre's equation.
- Relating the normalization and orthogonality conditions back to the variable of interest ( $\theta$ ), we have (for the Legendre polynomials) that

$$\int_0^\pi P_l(\cos \theta) P_n(\cos \theta) \sin \theta d\theta = \frac{2\delta_{ln}}{2l+1}$$

- Similarly, for the associated Legendre functions, we have that

$$\int_0^\pi P_l^{|m|}(\cos \theta) P_n^{|m|}(\cos \theta) \sin \theta d\theta = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ln}$$

- Thus, the normalization constant for the associated Legendre functions is

$$N_{lm} = \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}}$$

- Thus, the normalized wave functions of  $\Theta(\theta)$  are

$$\Theta(\theta) = N_{lm} P_l^{|m|}(\cos \theta)$$

for  $l = 0, 1, 2, \dots$  and  $m = 0, \pm 1, \dots, \pm l$ .

- **Spherical harmonics:** The orthonormal set of angular wave functions of the hydrogen atom. *Given by*

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

- Note that  $l = 0, 1, 2, \dots$  and  $m = 0, \pm 1, \dots, \pm l$ .
- The orthonormality condition:

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi)^* Y_n^k(\theta, \phi) = \delta_{ln} \delta_{mk}$$

---

$Y_0^0 = \frac{1}{\sqrt{4\pi}}$	$Y_2^1 = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$
$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$	$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi}$
$Y_1^1 = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$	$Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$
$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$	$Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi}$
$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$	

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Table 4.3: The first few spherical harmonics.

- 10/31: • Recalling the definition of  $\hat{L}^2$  from Chapter 5, we have that

$$\beta = -\frac{1}{Y_l^m(\theta, \phi)} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y_l^m(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y_l^m(\theta, \phi)}{\partial \phi^2} \right]$$

$$\hbar^2 l(l+1) Y_l^m(\theta, \phi) = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y_l^m(\theta, \phi)$$

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi)$$

- Implication: The spherical harmonics are eigenfunctions of  $\hat{L}^2$ .
- Additionally, the square of the angular momentum  $L^2$  can only have the values given by  $\hbar^2 l(l+1)$  for  $l = 0, 1, 2, \dots$
- We can also adapt the above to reflect energy with  $\hat{H} = \hat{L}^2/2I$ .

- 11/1: • We can apply partial differentiation to convert the expressions for  $\hat{L}_x, \hat{L}_y, \hat{L}_z$  in Table 3.1 to spherical coordinates.

- Doing so yields complex expressions for  $\hat{L}_x$  and  $\hat{L}_y$ , but a simple expression for  $\hat{L}_z$ :

$$\hat{L}_z = -i\hbar \frac{d}{d\phi}$$

- The spherical harmonics are eigenfunctions of  $\hat{L}_z$ :

$$\begin{aligned} \hat{L}_z Y_l^m(\theta, \phi) &= -i\hbar \frac{d}{d\phi} \left( N_{lm} P_l^{|m|}(\cos \theta) e^{im\phi} \right) \\ &= -i\hbar N_{lm} P_l^{|m|}(\cos \theta) \frac{d}{d\phi} (e^{im\phi}) \\ &= m\hbar N_{lm} P_l^{|m|}(\cos \theta) e^{im\phi} \\ &= m\hbar Y_l^m(\theta, \phi) \end{aligned}$$

- It follows that  $L_z$  is quantized by  $m\hbar$ .
- This implies that  $\hbar$  is a fundamental measure of the angular momentum of a quantum mechanical system.
- Note that the spherical harmonics are not eigenfunctions of  $\hat{L}_x$  or  $\hat{L}_y$ .
- The last two results imply that we can determine precise values of  $L^2$  and  $L_z$  simultaneously, and that  $\hat{L}^2, \hat{L}_z$  commute.

- Proving that  $|m| < l$ .

– We have that

$$\hat{L}_z Y_l^m(\theta, \phi) = m^2 \hbar^2 Y_l^m(\theta, \phi) \quad \hat{L}^2 Y_l^m(\theta, \phi) = l(l+1) \hbar^2 Y_l^m(\theta, \phi)$$

– Subtracting and substituting  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$  yields

$$(\hat{L}^2 - \hat{L}_z^2) Y_l^m(\theta, \phi) = [l(l+1) - m^2] \hbar^2 Y_l^m(\theta, \phi)$$

$$(\hat{L}_x^2 + \hat{L}_y^2) Y_l^m(\theta, \phi) = [l(l+1) - m^2] \hbar^2 Y_l^m(\theta, \phi)$$

– It follows since  $m, l \in \mathbb{Z}$  that

$$0 \leq L_x^2 + L_y^2 = [l(l+1) - m^2] \hbar^2$$

$$0 \leq l(l+1) - m^2$$

$$m^2 \leq l(l+1)$$

$$|m| \leq l$$

as desired.

- Consider the case  $l = 1$ .

– In this case,  $L^2 = 2\hbar^2$  and  $L_z = -\hbar, 0, \hbar$ .

– It follows from the first condition that  $|L| = \sqrt{L^2} = \sqrt{2}\hbar$ , i.e., the magnitude of the angular momentum vector is  $\sqrt{2}\hbar$ .

– Since  $L$  and  $L_z$  have differing magnitudes, their vectors cannot point in the same direction.

– Since  $\hat{L}^2$  commutes with each of  $\hat{L}_x, \hat{L}_y, \hat{L}_z$  individually but the three directional components don't commute among themselves, it is possible to measure the values of  $L^2$  and any directional component simultaneously to any precision, but this leads to complete uncertainty in the other two directional components.

– This combined with the fact that  $\langle L_x \rangle = \langle L_y \rangle = 0$  leads to this nice interpretation: Imagine  $\mathbf{L}$  precessing around a cone whose axis is the  $z$ -axis. We know that the height of  $\mathbf{L}$  (its  $z$ -coordinate) never changes, but the  $x, y$ -coordinates could be anywhere.

- Solving the radial equation.

– Energy is quantized by

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2 n^2} = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{e^2}{8\pi \epsilon_0 a_0 n^2}$$

for  $n = 1, 2, \dots$  where  $a_0$  is the Bohr radius.

- Note that these energies are identical to those predicted by the Bohr model, even though the electron here is not restricted to sharply defined circular orbits but rather is described by  $\psi(r, \theta, \phi)$ .

– We also have the condition

$$0 \leq l \leq n - 1$$

on the quantum number  $n$ .

– Thus, the radial wave functions depend on the quantum numbers  $n$  and  $l$  as follows.

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

- The  $L_{n+l}^{2l+1}(2r/na_0)$  are the **associated Laguerre polynomials**.



## Problems

10/29: **6-2.** In terms of the variable  $\theta$ , Legendre's equation is

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + (\beta \sin^2 \theta - m^2) \Theta(\theta) = 0$$

Let  $x = \cos \theta$  and  $P(x) = \Theta(\theta)$ . Show that

$$(1-x^2) \frac{d^2 P(x)}{dx^2} - 2x \frac{dP(x)}{dx} + \left[ \beta - \frac{m^2}{1-x^2} \right] P(x) = 0$$

*Answer.* If  $\cos \theta = \frac{x}{1}$ , then

$$\sin \theta = \sqrt{1-x^2}$$

Additionally,

$$\frac{d\Theta}{d\theta} = \frac{dP}{d\theta} = \frac{dP}{dx} \frac{dx}{d\theta} = -\sin \theta \frac{dP}{dx} = -\sqrt{1-x^2} \frac{dP}{dx}$$

Therefore, we have by substitution and simplification that

$$\begin{aligned} 0 &= \sqrt{1-x^2} \frac{d}{d\theta} \left( \sqrt{1-x^2} \cdot -\sqrt{1-x^2} \frac{dP}{dx} \right) + (\beta^2(1-x^2) - m^2)P(x) \\ &= \sqrt{1-x^2} \frac{d}{dx} \left( -(1-x^2) \frac{dP}{dx} \right) \frac{dx}{d\theta} + (\beta^2(1-x^2) - m^2)P(x) \\ &= (1-x^2) \frac{d}{dx} \left( (1-x^2) \frac{dP}{dx} \right) + (\beta^2(1-x^2) - m^2)P(x) \\ &= (1-x^2) \left[ (1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} \right] + (\beta^2(1-x^2) - m^2)P(x) \\ &= (1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[ \beta^2 - \frac{m^2}{1-x^2} \right] P(x) \end{aligned}$$

□