

QUANTUM CENTRAL FORCES

Abstract

The Schrödinger equation in a central potential is examined. The separation of variables procedure is used to turn this partial differential equation into a set of ordinary differential equations. The angular equations are solved, first for a particle confined to a ring and then for a particle confined to a sphere, thereby building up, one dimension at a time, toward the eigenstates of the hydrogen atom. Special attention is paid to linear combinations of states and time-dependent states.

The properties of the spherical harmonics are explored, including a brief introduction to angular-momentum raising and lowering operators. The relationship of spherical harmonics to spin 1 systems is discussed. The eigenstates on the surface of a sphere are shown to be the same as the rigid rotor problem and the properties of rotational spectra are discussed.

The radial equation is solved and the properties of the eigenstates of the (unperturbed) hydrogen atom are explored.

13 INTRODUCTION

We now begin our analysis of the central force problem in quantum mechanics. We will find that there are some similarities and some differences between the handling of this problem in classical mechanics and quantum mechanics. Concepts such as acceleration or Newton's third law have no counterpart in quantum physics. However, we shall find that reduction of the two-body problem to a fictitious one-body problem is also a characteristic of the quantum analysis. And we will again find that angular momentum is a critical aspect of our description of the motion of the system, related to spherical symmetry.

As we did in analyzing our classical central force problem, we again assume a two-particle system in which the only interaction is the mutual interaction of the two particles. We assume that this interaction depends only on the separation distance between the particles and not on any angle or orientation in space. In this case, as in the classical problem, we will find that the angular momentum is a constant of the motion, but in quantum mechanics angular momentum (like energy) is quantized.

As always in quantum mechanics, we begin with Schrödinger's equation

$$H_{\text{op}}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

14 Reduced Mass

It is helpful to consider briefly how the quantum two-body problem separates into an equation governing the center of mass and an equation describing the system around the center of mass, comparing this process to the classical problem. The quantum two-body problem in three dimensions is very messy, but all the essential features of the calculation show up in a simple one-dimensional model. So, for simplicity, let's consider a system of two particles, m_1 and m_2 , lying on a line at positions x_1 and x_2 , and let the interaction between the particles be represented by a potential energy U that depends only on $x = x_1 - x_2$, the separation distance between the particles. Don't worry about how the particles can get past each other on the line—this is a simple toy model; just imagine that they can pass right through each other.

Our first job, as always, is to identify the Hamiltonian H_{op} for the system. Because energies are additive, the kinetic part of the Hamiltonian is just the sum of the kinetic parts for two individual particles and the potential $U(x)$ describes the interaction between them. Therefore the Hamiltonian is

$$H_{\text{op}} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + U(x) \quad (63)$$

and the wave function Ψ is a function of the positions of both particles (and of course time) $\Psi = \Psi(x_1, x_2, t)$.

Inspired by our experience with classical two-body systems, we will try rewriting the Hamiltonian (63) in terms of the center-of-mass coordinate X , given by

$$X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \quad (64)$$

and the relative coordinate x . We will use the chain rule of calculus to transform the partial derivatives in equation (63) to derivatives with respect to x and X . (Please see Appendix A, especially the worked example on plane polar coordinates.) The transformations for first derivatives are:

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} = \frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} \quad (65)$$

$$\frac{\partial}{\partial x_2} = \frac{\partial x}{\partial x_2} \frac{\partial}{\partial x} + \frac{\partial X}{\partial x_2} \frac{\partial}{\partial X} = -\frac{\partial}{\partial x} + \frac{m_2}{m_1 + m_2} \frac{\partial}{\partial X} \quad (66)$$

It is important to note that we cannot simply write equations (65–66) for the second derivative, which is what we need for the Hamiltonian (63). To find the second derivative, we must apply the first derivative rules (65–66) twice:

$$\frac{\partial^2}{\partial x_1^2} \Psi = \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_1} \Psi \quad (67)$$

$$= \left(\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial X} \right) \left(\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial X} \right) \Psi \quad (68)$$

$$= \frac{\partial^2}{\partial x^2} \Psi + \frac{2m_1}{m_1 + m_2} \frac{\partial^2}{\partial x \partial X} \Psi + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial X^2} \Psi \quad (69)$$

$$\frac{\partial^2}{\partial x_2^2} \Psi = \frac{\partial}{\partial x_2} \frac{\partial}{\partial x_2} \Psi \quad (70)$$

$$= \left(\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial X} \right) \left(\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial X} \right) \Psi \quad (71)$$

$$= \frac{\partial^2}{\partial x^2} \Psi - \frac{2m_1}{m_1 + m_2} \frac{\partial^2}{\partial x \partial X} \Psi + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial X^2} \Psi \quad (72)$$

Substituting into the Hamiltonian (63), we obtain for Schrödinger's equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2(m_1 + m_2)} \frac{\partial^2}{\partial X^2} + U(x) \right\} \Psi(X, x, t) = i\hbar \frac{\partial}{\partial t} \Psi(X, x, t) \quad (73)$$

By transforming to these coordinates, the middle terms in equations (69) and (72) have canceled, enabling us to separate the dependence on x from the dependence on X . We can now write

$$\Psi(x, X, t) = \psi_M(X) \psi_\mu(x) T(t) \quad (74)$$

After a separation of variables procedure (see Appendix B) on equation (74), we find that the ordinary differential equation governing the variable X has a simple, recognizable form (see Problem 14.3b). The solution has the same form as the free-particle solution to the Schrödinger equation (also called the plane-wave solution to the equation)

$$\psi_M(X) = e^{iP_X X/\hbar} \quad (75)$$

where P_X represents the momentum associated with the motion of the center of mass. All observables in quantum mechanics involve the probability density, i.e. terms of the form $\Psi^*\Psi$, so if we are evaluating observables associated with the relative motion, the pure phase contribution from the center-of-mass has no effect. We can therefore ignore the center-of-mass motion and concentrate only on the relative motion.

We have arrived at a conclusion in the quantum analysis of the two-body problem that is similar to our analysis of the classical problem (but for different reasons). We have again replaced the more complicated two-body system with a fictitious one-body system, involving the relative coordinate and the reduced mass. Once we have solved the problem and found $\psi_\mu(x)$ and $T(t)$, we can then reverse the procedure in this section to find the wave function $\Psi(x_1, x_2, t)$ describing the original two-body system. The analysis in three dimensions is the same, except that we must do the calculation three times, once for each of the rectangular coordinates.

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1 Problems

1. Work through the steps of the chain rule to show that equation (73) follows from equation (63)
2. Where does the mass of a particle appear in Schrödinger's equation? In equation (73), what is the mass associated with the center-of-mass coordinate X ? what is the mass associated with the relative position coordinate x ? Does this make sense?
3. Use the separation of variables procedure in Appendix B to break equation (73) up into three ordinary differential equations.
 - (a) How many separation constants do you have? Is this the number you expect? Explain.
 - (b) Solve the equations for $\psi_M(X)$. What are the possible eigenvalues?
 - (c) Give an appropriate name to the eigenvalues of the (unsolved) equation for $\psi_\mu(x)$.
 - (d) Solve the equation for $T(t)$. Discuss how the energy E of the system depends on the separation constants.

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15 SCHRÖDINGER'S EQUATION IN SPHERICAL COORDINATES

Schrödinger's equation is

$$H_{\text{op}}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (76)$$

For one-dimensional waves, the Hamiltonian is

$$H_{\text{op}} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + U(x) \quad (77)$$

In a central potential the role of the second derivative with respect to x is played by the Laplacian operator ∇^2 and the potential energy is a function only on the separation variable $U = U(r)$, making the Hamiltonian:

$$H_{\text{op}} = -\frac{\hbar^2}{2\mu} \nabla^2 + U(r) \quad (78)$$

Because of the parameter r , this problem is clearly asking for the use of spherical coordinates, centered at the origin of the central force.

In rectangular coordinates, we know that the Laplacian ∇^2 is given by:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (79)$$

What is the Laplacian in spherical coordinates? Since $\nabla^2 \stackrel{\text{def}}{=}} \vec{\nabla} \cdot \vec{\nabla}$, we can combine the spherical coordinate definitions of gradient and divergence

$$\vec{\nabla} V = \frac{\partial V}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial V}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial V}{\partial \phi} \hat{\phi} \quad (80)$$

$$\vec{\nabla} \cdot \vec{v} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta v_\theta) + \frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} \quad (81)$$

to obtain:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (82)$$

For convenience, we will give the combination of angular derivatives which appears in (82) a new name:

$$L_{\text{op}}^2 \stackrel{\text{def}}{=} -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (83)$$

Notice the conventional factor of $-\hbar^2$. \hbar is a constant, 1.05459×10^{-27} erg-sec = 6.58217×10^{-16} eV-sec. Notice that the dimensions of \hbar are those of angular momentum. With this definition, (82) becomes:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} L_{\text{op}}^2 \quad (84)$$

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1 Practice Problems

1. Review the definition of spherical coordinates. Remember that in our conventions θ is always the angle measured from the z axis and ranges from 0 to π . ϕ is the angle in the x - y plane measured from the x axis towards the y axis and ranges from 0 to 2π .
2. Review the definition of gradient and divergence in spherical coordinates. See Griffiths E&M, Appendix A, for a nice derivation. What is the fastest place to look-up expressions for gradient, etc. in spherical and cylindrical coordinates?
3. Using the definition of gradient (80) and divergence (81) in spherical coordinates, derive equation (82).

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16 SEPARATION OF VARIABLES

We will use the “separation of variables” procedure (see Appendix B) on the Schrödinger equation in a central potential. Most of the calculation will involve using this procedure on the Laplacian operator. Since the Laplacian comes up in almost all physics problems with spherical symmetry, you will find yourself using the results of this section many times in your career.

Because there are several spatial dimensions, the procedure requires a number of rounds, each consisting of the same set of six steps. In the first round, we will separate out an ordinary differential equation in the time variable.

Step 1: Write the partial differential equation in appropriate coordinate system. For Schrödinger's equation in any potential we have:

$$H_{\text{op}}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \quad (85)$$

Step 2: Assume that the solution Ψ can be written as the product of functions, at least one of which depends on only one variable, in this case t . The other function(s) must not depend at all on this variable, i.e. assume

$$\Psi(r, \theta, \phi, t) = \psi(r, \theta, \phi)T(t) \quad (86)$$

Plug this assumed solution (203) into the partial differential equation (85). Because of the special form for Ψ , the partial derivatives each act on only one of the factors in Ψ .

$$(H_{\text{op}}\psi)T = i\hbar\psi\frac{dT}{dt} \quad (87)$$

Any partial derivatives that act only on a function of a single variable may be rewritten as total derivatives.

Step 3: Divide by Ψ in the form of (203).

$$\frac{1}{\psi}(H_{\text{op}}\psi) = i\hbar\frac{dT}{dt}\frac{1}{T} \quad (88)$$

Step 4: Isolate **all** of the dependence on one coordinate on one side of the equation. Do as much algebra as you need to do to achieve this. In our example, notice that in (205), all of the t dependence is on the right-hand side of the equation while all of the dependence on the spatial variable is on the other side. In this case, the t dependence is already isolated, without any algebra on our part.

Step 5: Now imagine changing the isolated variable t by a small amount. In principle, the right-hand side of (205) could change, but nothing on the left-hand side would. Therefore, if the equation is to be true for all values of t , the particular combination of t dependence on the right-hand side must be constant. By convention, we call this constant E .

$$\frac{1}{\psi}(H_{\text{op}}\psi) = i\hbar\frac{dT}{dt}\frac{1}{T} \stackrel{\text{def}}{=} E \quad (89)$$

In this way we have broken our original partial differential equation up into a pair of equations, one of which is an ordinary differential equation involving only t , the other is a partial differential equation involving only the three spatial variables.

$$\frac{1}{\psi} H_{\text{op}} \psi = E \quad (90)$$

$$i\hbar \frac{dT}{dt} \frac{1}{T} = E \quad (91)$$

The separation constant E appears in both equations.

Step 6: Write each equation in standard form by multiplying each equation by its unknown function to clear it from the denominator.

$$H_{\text{op}} \psi = E \psi \quad (92)$$

$$\frac{dT}{dt} = -\frac{i}{\hbar} E T \quad (93)$$

Notice that (209) is an eigenvalue equation for the operator H_{op} . You may never have thought of the derivation of this “time independent version of the Schrödinger equation” from the Schrödinger equation as just a simple example of the separation of variables procedure. At the moment, the eigenvalue E could be anything. Much of the rest of the Paradigm will be directed toward finding the possible values of E !

Now we must repeat the steps until each of the variables has been separated out into its own ordinary differential equation. In the next round, we will isolate the r dependence.

Step 1: Since we want to isolate the r dependence, we must rewrite H_{op} to show the r dependence explicitly using (84)

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} L_{\text{op}}^2 \right] \psi + U(r) \psi = E \psi \quad (94)$$

Step 2: Assume $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$.

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) Y - \frac{1}{\hbar^2 r^2} R(L_{\text{op}}^2 Y) \right] + U(r) R Y = E R Y \quad (95)$$

Step 3:

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{d}{dr} \frac{1}{R} \left(r^2 \frac{dR}{dr} \right) - \frac{1}{\hbar^2 r^2} \frac{1}{Y} (L_{\text{op}}^2 Y) \right] + U(r) = E \quad (96)$$

Step 4: To isolate the r dependence we must first clear the r dependence from the angular term (involving angular derivatives in L_{op} and angular functions in Y). To do this, we need to multiply (96) by r^2 to clear this factor out of the denominators of the angular pieces. Further rearranging (96) to get all of the r dependence on the right-hand side, we obtain:

$$-\frac{1}{\hbar^2} \frac{1}{Y} (L_{\text{op}}^2 Y) = -\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \frac{1}{R} - \frac{2\mu}{\hbar^2} (E - U(r)) r^2 \quad (97)$$

Step 5: In this case, I have called the separation constant A .

$$-\frac{1}{\hbar^2} \frac{1}{Y} (L_{\text{op}}^2 Y) = -\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \frac{1}{R} - \frac{2\mu}{\hbar^2} (E - U(r)) r^2 \stackrel{\text{def}}{=} A \quad (98)$$

In principle, A can be any complex number.

Step 6: Rearranging (98) slightly, we obtain the radial and angular equations in the more standard form:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - U(r)) r^2 R + AR = 0 \quad (99)$$

$$L_{\text{op}}^2 Y + \hbar^2 AY = 0 \quad (100)$$

Notice that the only place that the central potential enters the set of differential equations is in the radial equation (99). (99) is not yet in the form of an eigenvalue equation since it contains two unknown constants E and A . (100) is an eigenvalue equation for the operator L_{op}^2 with eigenvalue $\hbar^2 A$; it is independent of the form of the central potential.

In the last round, we must separate the θ dependence from the ϕ dependence. I will leave this as an important Practice Problem. The answer is:

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dP}{d\theta} \right) - A \sin^2 \theta P - BP = 0 \quad (101)$$

$$\frac{d^2 \Phi}{d\phi^2} + B\Phi = 0 \quad (102)$$

(102) is an eigenvalue equation for the operator $d^2/d\phi^2$ with eigenvalue B . (101) is not yet in the form of an eigenvalue equation since it contains two unknown constants A and B .

We started with a partial differential equation in four variables and we ended up with four ordinary differential equations (210), (99), (101), (102) by introducing **three** separation constants (E , A , and B). You should always get one fewer separation constant than the number of variables you started with; each separation constant should appear in two of the final set of equations.

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1 Practice Problems

1. Work carefully through all of the derivations in this section.
2. Use the separation of variables procedure on (100) to obtain (101) and (102).
3. Consider the problem of the motion of a quantum particle of mass μ confined to move on a ring of radius r_0 . Redo the separation of variables procedure in this section, assuming that $r = r_0$ is a constant and $\theta = \frac{\pi}{2}$ is a constant so that $\Psi = T(t)\Phi(\phi)$ only. How do the equations you get differ from the equations of this section? The solutions of these equations will be the subject of the next section.

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