

Physics 221A
Fall 2010
Notes 16
Central Force Motion

1. Introduction

In these Notes we provide an introduction to central force motion, including the example of the free particle. Later we will consider other examples, such as diatomic molecules and the hydrogen atom.

2. The Radial Schrödinger Equation

Initially we imagine a force center at the origin of a system of coordinates creating a force field described by a potential $V(r)$. The potential is a function only of the radius r and is invariant under rotations. A particle moves in this force field.

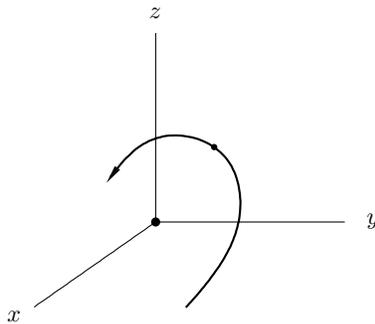


Fig. 1. If the object creating a central force field is very massive, we may treat the motion of a particle in the field as a one-body problem.

The force is presumably created by some particle or physical object that must be infinitely massive if the frame attached to it is to be an inertial frame. Sometimes this is not a bad approximation, for example, in atoms where the nucleus is much heavier than the electrons. If this is the case, then we obtain a one-body problem for the motion of the particle, which is described by the Hamiltonian

$$H = \frac{p^2}{2m} + V(r). \quad (1)$$

We assume the particle is spinless, or that spin effects can be neglected. Thus the Hilbert space for the particle is the space of wave functions $\psi(\mathbf{r})$. In Notes 15 we developed the theory of the

rotation operators $U(\mathbf{R})$ and angular momentum operators \mathbf{L} that act on this space. We also found the standard angular momentum basis, which consists of radial wave functions times $Y_{\ell m}$'s.

The Hamiltonian (1) possesses rotational symmetry, that is, it commutes with all rotation operators $U(\mathbf{R})$, whose action on wave functions is given by Eq. (15.13). Without going into details, this is obvious from the fact that the kinetic energy is proportional to $p^2 = \mathbf{p} \cdot \mathbf{p}$, the dot product of two vectors, while the potential energy is a function of $r = \sqrt{r^2}$, where $r^2 = \mathbf{r} \cdot \mathbf{r}$, another dot product of two vectors. Since the dot product of classical (c -number) vectors is invariant under classical rotations, we expect the same for vectors of quantum operators. We will explore this question in more detail later in the course, but for now the basic line of reasoning should be clear. If there is any doubt, one can explicitly verify the commutators

$$[\mathbf{L}, H] = 0, \quad (2)$$

which show that

$$[U(\mathbf{R}), H] = 0 \quad (3)$$

since $U(\mathbf{R})$ is a function of \mathbf{L} .

As a result, H commutes with the commuting operators L^2 and L_z , so the three operators (H, L^2, L_z) possess a simultaneous eigenbasis. From Notes 15 we already know the general form of a simultaneous eigenfunction of L^2 and L_z ; it is

$$\psi(r, \theta, \phi) = R(r)Y_{\ell m}(\theta, \phi), \quad (4)$$

where $R(r)$ is an arbitrary radial wave function. See Eq. (15.42). By demanding that this wave function also be an eigenfunction of H , we can determine the radial wave function $R(r)$.

To do this we substitute Eq. (4) into the Schrödinger equation for the Hamiltonian (1),

$$\left[\frac{p^2}{2m} + V(r) \right] \psi = E\psi. \quad (5)$$

Working on the kinetic energy first and using Eq. (15.30), we have

$$\frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{L^2}{2mr^2}\psi. \quad (6)$$

But if ψ has the form (4), then L^2 acting on the $Y_{\ell m}$ part brings out $\ell(\ell+1)\hbar^2$, and all terms have a common factor of $Y_{\ell m}$. This also applies to the potential energy and total energy terms in the Schrödinger equation, so the common factor of $Y_{\ell m}$ can be cancelled. We obtain an equation for the radial function $R(r)$ alone,

$$\boxed{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + U(r)R(r) = ER(r)}, \quad (7)$$

where $U(r)$ is the *effective potential*,

$$U(r) = \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r). \quad (8)$$

The effective potential is the sum of the *centrifugal potential* (the first term) and the true potential, $V(r)$. The centrifugal potential is physically a part of the kinetic energy but mathematically it looks like a potential and it is usually treated that way. Equation (7) is called the *radial Schrödinger equation*, or, as we shall call it, version one of the radial Schrödinger equation.

Version two of the radial Schrödinger equation is created by making the substitution

$$f(r) = rR(r), \quad (9)$$

which after a little algebra results in

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 f(r)}{dr^2} + U(r)f(r) = Ef(r).} \quad (10)$$

This version is easy to remember because it is almost the same as the one-dimensional Schrödinger equation (usually written in terms of some variable x with $-\infty < x < +\infty$). The only differences are the presence of the centrifugal potential in the radial Schrödinger equation and the fact that r lies in the range $0 \leq r < \infty$.

It is reasonable to define the normalization of the radial wave function $R(r)$ by the integral,

$$\int_0^\infty r^2 dr |R(r)|^2, \quad (11)$$

because that is the radial part of the three-dimensional normalization integral

$$\int d^3\mathbf{r} |\psi(\mathbf{r})|^2 = \int_0^\infty r^2 dr \int d\Omega |\psi(r, \theta, \phi)|^2 \quad (12)$$

when ψ has the form (4). Notice that this implies the normalization of the version two radial function $f(r)$,

$$\int_0^\infty dr |f(r)|^2, \quad (13)$$

which is the usual one for the one-dimensional Schrödinger equation apart from the range of integration.

3. Separation of Variables

The usual way of deriving the radial Schrödinger equation in introductory courses is to separate the three-dimensional Schrödinger equation in spherical coordinates. The results are the same as in Sec. 2. The method of separation of variables, when it works, is a powerful one for solving multidimensional partial differential equations that sometimes leads to exact solutions that would be difficult to find otherwise. Most wave equations are not separable in any coordinate system, however. Fortunately, many common model problems are separable in at least one coordinate system, while many others are close to a separable system and can be treated by perturbation theory. If this

is not so, then usually numerical techniques will be required to find solutions. Some systems are separable in more than one coordinate system, for example, the Schrödinger equation for all central force problems in three dimensions is separable in spherical coordinates, while the free particle is also separable in rectangular coordinates and the hydrogen atom is also separable in confocal parabolic coordinates.

In all cases, separability is related to the existence of constants of the motion, that is, operators that commute with the Hamiltonian that are related to some symmetry of the system. If the Schrödinger equation for some multidimensional system is not separable in any coordinate system, it probably means that the system does not possess any continuous symmetries at all. It may possess discrete symmetries, such as parity and time reversal, but these do not lead to separability of the wave equation in any coordinates. If the Schrödinger equation is separable in more than one coordinate system, it means that the system respects a larger symmetry group than that needed to ensure the solvability of the problem at all. For example, all central force problems in quantum mechanics are separable in spherical coordinates, which corresponds to the $SO(3)$ symmetry of the system under rotations. But the free particle is also invariant under translations, so the free particle Schrödinger equation is also separable in rectangular coordinates, while the hydrogen atom, which possesses an $SO(4)$ symmetry group, is separable also in confocal parabolic coordinates.

Thus, the success of the method of separation of variables is due to some symmetry of the system, although this is usually not obvious when we apply the method. In this course we are emphasizing the symmetries and their impact on our understanding of the quantum mechanics, so we have approached the solution of several problems by studying the symmetry operators first and then studying the Hamiltonian. For example, in solving the problem of the charged particle in a uniform magnetic field, we diagonalized the operators that commute with the Hamiltonian first, whereupon the Hamiltonian was easy to diagonalize. Also, in central force motion, we diagonalized the operators L^2 and L_z first, which led to the standard angular momentum basis, and then we turned our attention to the Hamiltonian (as in this set of notes). This approach leads to the solution of some problems or at least useful results even when the system is not separable. For example, in Sec. 14.6 we were able to understand some important general features of systems with rotational invariance, including very complicated ones, with no need to talk about separating the wave equation (indeed, in some cases we do not even know what the wave equation is, only the symmetries it possesses). We will accumulate several examples of this type before the course is over. In all cases, it turns out to be a good strategy to diagonalize the symmetry operators first, and then to turn our attention to the Hamiltonian.

4. Quantum Numbers and Degeneracies

The radial Schrödinger equation is parameterized by ℓ , with $\ell = 0, 1, 2, \dots$, because the centrifugal potential depends on ℓ . Thus we might say that there is a different radial Schrödinger equation for each value of ℓ . The energy eigenvalues for a given value of ℓ may be either discrete or continuous.

As for the discrete eigenvalues, let us label them $E_{n\ell}$, where n just sequences the levels for a given value of ℓ , using some scheme. Thus, the energy depends on two quantum numbers, n and ℓ , but not on m . Similarly, the radial wave functions $R(r)$ or $f(r)$ depend on the same two quantum numbers, so we shall write $R_{n\ell}(r)$ or $f_{n\ell}(r)$ to emphasize this. The total wave function is

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi). \quad (14)$$

The radial Schrödinger equation shares some features with the usual one-dimensional Schrödinger equation, for example, if the wave function vanishes anywhere on the interval $0 \leq r < \infty$, including at $r = \infty$, then the eigenfunctions are nondegenerate. This applies in particular to the case of bound states, which must vanish as $r \rightarrow \infty$. This nondegeneracy condition means that the discrete eigenvalues $E_{n\ell}$ are all distinct for a given value of ℓ . The nondegeneracy we are referring to here concerns the eigenvalues and eigenfunctions of the radial Schrödinger equation for a given value of ℓ , regarded as a one-dimensional wave equation.

When we consider the three-dimensional Schrödinger equation, however, and include the angular quantum numbers, then there are usually degeneracies. That is, the energies $E_{n\ell}$ are at least $(2\ell+1)$ -fold degenerate because they do not depend on m . This type of degeneracy in rotationally invariant systems was discussed from a general standpoint (including the case of very complex systems) in Sec. 14.6. Here we see a concrete example of those considerations in a rather simple (one-particle) system. It is possible that some $E_{n\ell}$ could be equal for different values of ℓ , in which case the degeneracy would be higher than $(2\ell+1)$. For a randomly chosen potential $V(r)$, however, this is not very likely, since the different radial wave equations for different values of ℓ will have spectra that are effectively independent of each other. Generically, the degeneracies are just $2\ell+1$ for each $E_{n\ell}$, no more than what is predicted by rotational invariance alone.

For some potentials, however, there are systematic degeneracies among different $E_{n\ell}$ for different values of n and ℓ . This applies to the Coulomb potential $V(r) = -k/r$ and the harmonic oscillator potential $V(r) = kr^2$. The harmonic oscillator we are referring to is the three-dimensional, isotropic harmonic oscillator. There are no other examples in three-dimensional central force motion. In both cases, the extra degeneracy is due to some extra symmetry that goes beyond ordinary $SO(3)$ (rotational) invariance. For the Coulomb potential, the symmetry group is $SO(4)$, while for the three-dimensional, isotropic harmonic oscillator, it is $SU(3)$. In the case of hydrogen, the extra degeneracy applies only in the electrostatic, spinless, nonrelativistic model. As we add extra physical effects, coming closer to a realistic description of hydrogen, we will see the extra degeneracy gradually disappear. When all physical effects are included, hydrogen, too, has only the $(2j+1)$ -fold degeneracy predicted on the basis of rotational invariance, as explained in Sec. 14.6.

5. Behavior of the Radial Eigenfunctions Near $r = 0$

The behavior of the radial wave function for small r is often important in applications. Let us assume the potential is either well behaved at the origin or that if it diverges it does so no faster

than $1/r$. This covers the important case of the Coulomb potential. Let us also assume that the wave function $R(r)$ goes as r^k for some power k near $r = 0$, something we will write as $R(r) \sim r^k$. This means that $R(r) = ar^k$ for some constant $a \neq 0$ plus other terms that go to zero more rapidly than r^k as $r \rightarrow 0$, or, equivalently,

$$\lim_{r \rightarrow 0} \frac{R(r)}{ar^k} = 1. \quad (15)$$

Then for small r we have

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) = -a \frac{\hbar^2}{2m} k(k+1) r^{k-2}, \quad (16)$$

and

$$\frac{\hbar^2 \ell(\ell+1)}{2mr^2} R(r) = a \frac{\hbar^2}{2m} \ell(\ell+1) r^{k-2}. \quad (17)$$

As for the term $V(r)R(r)$, it behaves at worst as r^{k-1} as $r \rightarrow 0$, so it is negligible compared to the terms (16) and (17) as $r \rightarrow 0$. The same is true for the term $ER(r)$, which behaves as r^k as $r \rightarrow 0$. The dominant terms in the radial Schrödinger equation at small r come from the kinetic energy alone (including the centrifugal potential). Since these terms have to cancel, we have

$$k(k+1) = \ell(\ell+1). \quad (18)$$

This has two solutions,

$$k = \ell \quad \text{and} \quad k = -\ell - 1. \quad (19)$$

The solution $k = -\ell - 1$ is not acceptable when $\ell \geq 1$, because then $|R(r)|^2$ would have a nonintegrable singularity at $r = 0$, that is, the wave function would not be normalizable and there would be an infinite amount of probability in a small neighborhood of $r = 0$. As for the case $\ell = 0$, this would result in $\psi(r) = a/r$ near $r = 0$, which would not satisfy the Schrödinger equation at $r = 0$ because

$$\nabla^2 \left(\frac{1}{r} \right) = -4\pi\delta(\mathbf{r}). \quad (20)$$

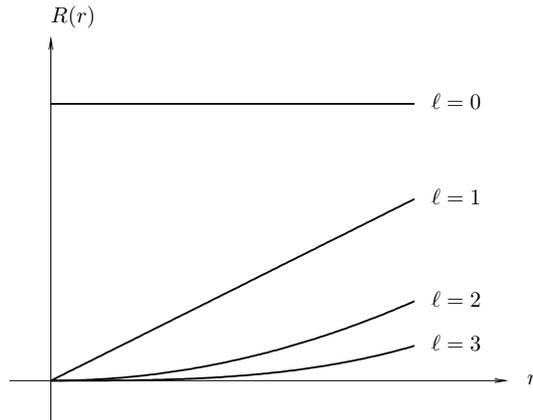


Fig. 2. The radial wave function $R(r)$ behaves as r^ℓ near $r = 0$. It lies down ever more flat against the r -axis as ℓ increases. This is only the leading behavior of $R(r)$ for small r ; as r increases, correction terms become important.

Thus, the only possible solution of Eq. (18) is $k = \ell$, and we see that the radial wave function has the behavior

$$R(r) \sim r^\ell \quad (21)$$

near $r = 0$. The leading behavior depends only on the angular momentum quantum number ℓ . This is a simple rule that is often important in practice. It means that the radial wave function $R(r)$ lies down more and more flat near $r = 0$ as ℓ increases (see Fig. 2), and that the probability of finding the particle in some small neighborhood of $r = 0$ goes to zero exponentially as ℓ increases. This applies, for example, to the probability of finding an atomic electron inside the nucleus.

6. Free Particle

Let us now take the case of the free particle, $V(r) = 0$. The free particle Hamiltonian is symmetric under both translations and rotations, so a complete set of commuting observables can be chosen in more than one way. If we choose (p_x, p_y, p_z) as the complete set, then the simultaneous eigenstate is

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (22)$$

a plane wave with $\mathbf{p} = \hbar\mathbf{k}$. The energy is given in terms of the momentum eigenvalues by

$$E = \frac{|\mathbf{p}|^2}{2m}. \quad (23)$$

The spectrum is continuous with $E \geq 0$.

If we choose (H, L^2, L_z) as the complete set, then we must solve the radial Schrödinger equation with $V = 0$. This is easier in version one, Eq. (7). Expressing the energy in terms of a wave number k by

$$E = \frac{\hbar^2 k^2}{2m}, \quad (24)$$

and writing $\rho = kr$ for a dimensionless radial variable, the radial Schrödinger equation becomes

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[1 - \frac{\ell(\ell+1)}{\rho^2} \right] R = 0, \quad (25)$$

which is the standard differential equation for the spherical Bessel functions. These come in two types, denoted $j_\ell(\rho)$ and $y_\ell(\rho)$ (see Abramowitz and Stegun, Chapter 10).

The functions $j_\ell(r)$ are regular at the origin and so are physically acceptable solutions for the free particle. Some examples are plotted in Fig. 3, which clearly shows the behavior $R(r) \sim r^\ell$ near $r = 0$. The functions $y_\ell(\rho)$ diverge at the origin and so are not acceptable free particle solutions if the particle is able to reach the origin. They are plotted in Fig. 4. On the other hand, the y -type spherical Bessel functions are useful in scattering theory where at large distances from the origin the particle becomes free, and it is desired to represent an arbitrary solution of the Schrödinger equation in that region. Since there is no attempt to extend those solutions all the way down to $r = 0$, the y -type solutions are acceptable (and necessary) in that case.

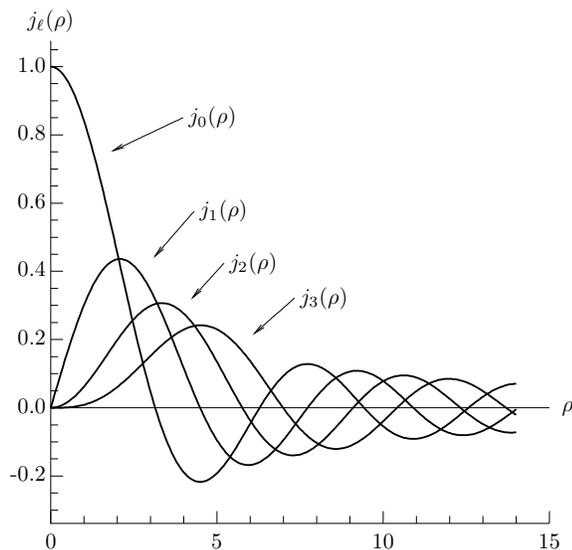


Fig. 3. Spherical Bessel functions $j_\ell(\rho)$ for different values of ℓ .

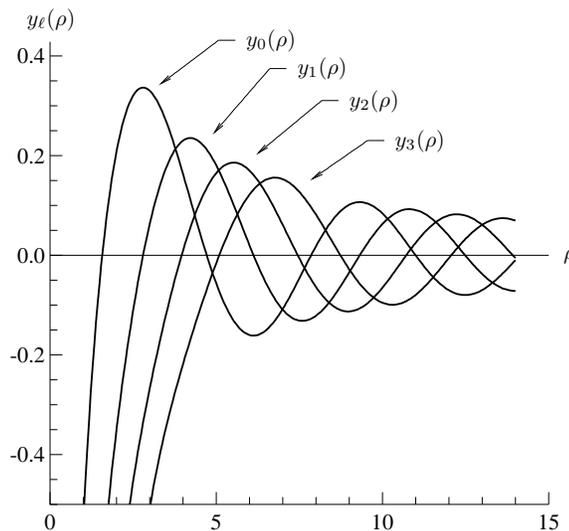


Fig. 4. Spherical Bessel functions $y_\ell(\rho)$ for different values of ℓ .

7. Limiting Forms of the Spherical Bessel Functions

Many problems involving special functions can be solved knowing only the limiting forms for large and small values of the arguments. In the case of the spherical Bessel functions, the limiting forms at small ρ are

$$j_\ell(\rho) \approx \frac{\rho^\ell}{1 \cdot 3 \cdot 5 \dots (2\ell + 1)}, \quad (26)$$

$$y_\ell(\rho) \approx -\frac{1 \cdot 3 \cdot 5 \dots (2\ell - 1)}{\rho^{\ell+1}}. \quad (27)$$

See Abramowitz and Stegun, Eqs. (10.1.2) and (10.1.3). As for $j_\ell(\rho)$, we see the small r rule (21), to within a constant (which we couldn't have guessed anyway because it is conventional). As for $y_\ell(\rho)$, we see the solution $k = -\ell - 1$ of Eq. (18) that we rejected earlier as nonphysical.

The limiting forms at large ρ are

$$j_\ell(\rho) \approx \frac{1}{\rho} \cos\left[\rho - (\ell + 1)\frac{\pi}{2}\right], \quad (28)$$

$$y_\ell(\rho) \approx \frac{1}{\rho} \sin\left[\rho - (\ell + 1)\frac{\pi}{2}\right]. \quad (29)$$

See Abramowitz and Stegun, Eqs. (10.1.1), (9.2.1) and (9.2.2). These are useful in scattering theory.

8. WKB Theory and Spherical Bessel Functions

The limiting forms at large ρ can be obtained by treating the radial Schrödinger equation (in version two) by one-dimensional WKB theory, apart from normalization. We discuss this briefly

without going into details because WKB theory provides an easy way to understand all the qualitative features of the functions $j_\ell(\rho)$ and $y_\ell(\rho)$, as seen in Figs. 3 and 4.

It turns out that the accuracy of the WKB approximation for radial wave equations is improved if the quantity $\ell(\ell + 1)$ is replaced by $(\ell + \frac{1}{2})^2$. This is called the *Langer modification*, and it has to do with the singularity in the centrifugal potential at $r = 0$. That is, for the purposes of WKB theory, we work with the effective radial potential,

$$U(r) = \frac{\hbar^2(\ell + \frac{1}{2})^2}{2mr^2} + V(r). \quad (30)$$

The centrifugal potential cannot be turned off and is present even for a free particle (except when $\ell = 0$). Thus the effective potential depends on ℓ , and we have different turning points etc depending on ℓ . In the case of the free particle ($V = 0$) the turning point r_0 is the solution of

$$E = \frac{\hbar^2 k^2}{2m} = U(r_0) = \frac{\hbar^2(\ell + \frac{1}{2})^2}{2mr_0^2}, \quad (31)$$

or,

$$kr_0 = \rho_0 = \ell + \frac{1}{2}. \quad (32)$$

The turning point moves out as ℓ increases, something that can also be seen from Fig. 5.

It might seem strange that a free particle should have a turning point at all. Of course, the only reason it does is because of the centrifugal potential, which, as mentioned, is really a part of the kinetic energy. Figure 6, which shows a classical orbit of a free particle of some energy $E = p^2/2m$ and angular momentum L , helps explain the situation. The orbit is a straight line which must pass at some minimum distance from the origin. In the figure, the orbit lies in the x - y plane. The minimum distance is $r_{\min} = L/p$. The family of all possible classical orbits of the given E and L is a set of straight lines tangent to the sphere $r = r_{\min}$. In quantum mechanics, the minimum radius becomes the radial turning point $r_0 = (\ell + \frac{1}{2})\hbar/p = (\ell + \frac{1}{2})/k$.

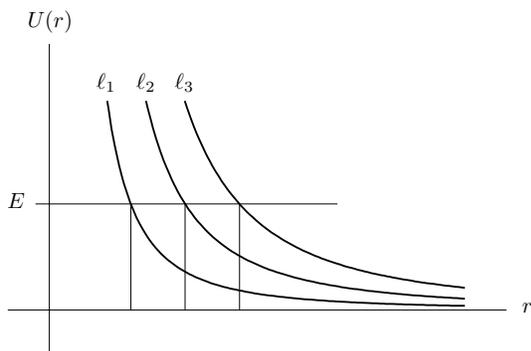


Fig. 5. The radial turning point for a free particle moves out as ℓ increases.

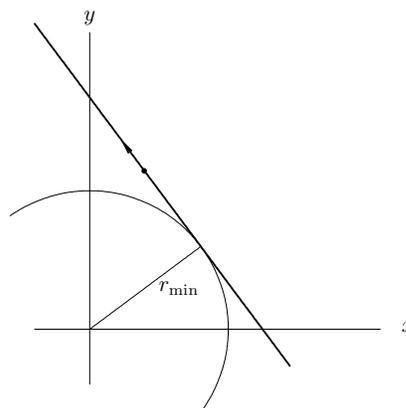


Fig. 6. The minimum distance of approach to the origin of a classical free particle of momentum p and angular momentum L is $r_{\min} = L/p$.

For $\ell > 0$ the exact spherical Bessel functions $j_\ell(\rho)$, which are 0 at $\rho = 0$, rise up to a first maximum somewhat after the point $\rho = \ell + \frac{1}{2}$, and then oscillate beyond that. From the standpoint of WKB theory, we clearly have a classically forbidden region to the left of the turning point $\rho = \ell + \frac{1}{2}$, an Airy-function type of behavior in the neighborhood of the turning point (see Fig. 7.8), and a classically allowed region to the right, exactly as we would expect on the basis of Fig. 5. The case $\ell = 0$ is an exception, since in that case the centrifugal potential vanishes and there is no turning point.

The functions $y_\ell(\rho)$ can also be understood from the standpoint of WKB theory; these are the functions that diverge exponentially as we move into the classically forbidden region (that is, as we move to the left of the turning point at $\rho = \ell + \frac{1}{2}$), and have the behavior of the Bi function in the neighborhood of the turning point (see Fig. 7.9).

It will be left as an exercise to work out the details of the WKB approximations to the spherical Bessel functions. The WKB solutions turn out to be more accurate than Eqs. (28) and (29) when ρ is not too much larger than $\ell + \frac{1}{2}$, but go over to them in the limit $\rho \gg \ell + \frac{1}{2}$.

9. Two-Body Central Force Motion

We return to the discussion of Sec. 2. If the source of the force field is not infinitely massive, then a coordinate system attached to it is not an inertial frame and we must take into account the dynamics of the force center itself. That is, we must deal with a two-body problem, which we describe in an arbitrary (“lab”) inertial frame. We let \mathbf{r}_1 and \mathbf{r}_2 be the coordinates of the two particles with respect to this frame, with masses m_1 and m_2 , respectively. We assume the force is described by a potential

$$V = V(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (33)$$

which depends only on the distance between the particles. The Hamiltonian is the sum of the kinetic and potential energies,

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (34)$$

where \mathbf{p}_1 and \mathbf{p}_2 are the momenta of the two particles.

We assume the particles are spinless or else we ignore spin. We write $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ for the configuration space wave function, upon which the operators \mathbf{p}_k act as differential operators,

$$\mathbf{p}_k = -i\hbar \frac{\partial}{\partial \mathbf{r}_k} = -i\hbar \nabla_k, \quad k = 1, 2. \quad (35)$$

Translation operators $T(\mathbf{a})$ act on the wave function according to

$$(T(\mathbf{a})\Psi)(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1 - \mathbf{a}, \mathbf{r}_2 - \mathbf{a}), \quad (36)$$

a two-particle, three dimensional generalization of Eq. (4.23). The generator of translations is the total momentum,

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2. \quad (37)$$

The Hamiltonian commutes with all translations because the distance between the particles is not changed when both particles are displaced by the same amount. Therefore H also commutes with the total momentum,

$$[H, \mathbf{P}] = 0. \quad (38)$$

The Hamiltonian is also invariant under rotations. Rotation operators act upon Ψ according to

$$(U(\mathbf{R})\Psi)(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}^{-1}\mathbf{r}_1, \mathbf{R}^{-1}\mathbf{r}_2), \quad (39)$$

as explained in Sec. 15.9. The angular momentum of the system (the generator of rotations) is

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2, \quad (40)$$

where

$$\mathbf{L}_k = \mathbf{r}_k \times \mathbf{p}_k, \quad k = 1, 2, \quad (41)$$

that is, it is the sum of the angular momenta of the two particles. The Hamiltonian (34) commutes with all rotations and hence with the total angular momentum \mathbf{L} ,

$$[H, \mathbf{L}] = 0. \quad (42)$$

To solve the Schrödinger equation $H\Psi = E\Psi$ for Hamiltonian (34) we introduce a change of coordinates,

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}, \quad (43)$$

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \quad (44)$$

where

$$M = m_1 + m_2 \quad (45)$$

is the total mass of the system, so that \mathbf{R} is the position of the center of mass and \mathbf{r} is the relative position vector between the particles. We write $\Psi(\mathbf{R}, \mathbf{r}) = \Psi(\mathbf{r}_1, \mathbf{r}_2)$ for the wave function transformed to the new coordinates. We also define momenta “conjugate” to \mathbf{R} and \mathbf{r} as the differential operators,

$$\mathbf{P} = -i\hbar \frac{\partial}{\partial \mathbf{R}}, \quad \mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}}, \quad (46)$$

when acting on wave functions $\Psi(\mathbf{R}, \mathbf{r})$. By the chain rule, we can express the momenta \mathbf{p}_1 and \mathbf{p}_2 of the particles in the lab frame in terms of \mathbf{P} and \mathbf{p} ,

$$\mathbf{p}_1 = -i\hbar \frac{\partial}{\partial \mathbf{r}_1} = -i\hbar \left(\frac{\partial \mathbf{R}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{R}} + \frac{\partial \mathbf{r}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{r}} \right) = -i\hbar \left(\frac{m_1}{M} \frac{\partial}{\partial \mathbf{R}} - \frac{\partial}{\partial \mathbf{r}} \right), \quad (47)$$

$$\mathbf{p}_2 = -i\hbar \frac{\partial}{\partial \mathbf{r}_2} = -i\hbar \left(\frac{\partial \mathbf{R}}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{R}} + \frac{\partial \mathbf{r}}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{r}} \right) = -i\hbar \left(\frac{m_2}{M} \frac{\partial}{\partial \mathbf{R}} + \frac{\partial}{\partial \mathbf{r}} \right), \quad (48)$$

or,

$$\mathbf{p}_1 = \frac{m_1}{M} \mathbf{P} - \mathbf{p}, \quad (49)$$

$$\mathbf{p}_2 = \frac{m_2}{M} \mathbf{P} + \mathbf{p}. \quad (50)$$

Solving these for \mathbf{P} and \mathbf{p} , we find

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2, \quad (51)$$

$$\mathbf{p} = \frac{m_1 \mathbf{p}_2 - m_2 \mathbf{p}_1}{M}, \quad (52)$$

and we see that \mathbf{P} defined by Eq. (46) is the total linear momentum of the system (the generator of translations), as in Eq. (37). The transformation $(\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2) \rightarrow (\mathbf{R}, \mathbf{P}; \mathbf{r}, \mathbf{p})$ specified by Eqs. (43), (44), (51) and (52) is an example of a “canonical transformation,” that is, one which preserves the canonical commutation relations. That is, we have

$$[R_i, P_j] = [r_i, p_j] = i\hbar \delta_{ij}, \quad [R_i, r_j] = [R_i, p_j] = [P_i, r_j] = [P_i, p_j] = 0. \quad (53)$$

We see that any function of (\mathbf{R}, \mathbf{P}) commutes with any function of (\mathbf{r}, \mathbf{p}) .

Transforming the Hamiltonian (34) to the new coordinates is straightforward. As for the potential, it becomes $V(|\mathbf{r}_1 - \mathbf{r}_2|) = V(|\mathbf{r}|) = V(r)$, where $r = |\mathbf{r}|$ is the distance between the two particles. Also transforming the kinetic energy, we find the Hamiltonian as a sum of a center-of-mass term and a relative term,

$$H = H_{\text{CM}} + H_{\text{rel}}, \quad (54)$$

where

$$H_{\text{CM}} = \frac{P^2}{2M}, \quad (55)$$

and

$$H_{\text{rel}} = \frac{p^2}{2\mu} + V(r). \quad (56)$$

Here μ is the *reduced mass*, defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}. \quad (57)$$

The Hamiltonian H_{CM} is a free particle Hamiltonian, containing physically the kinetic energy of the center of mass, while H_{rel} is physically the kinetic energy *about* the center of mass plus the potential energy. The two Hamiltonians H_{CM} and H_{rel} commute with each other,

$$[H_{\text{CM}}, H_{\text{rel}}] = 0, \quad (58)$$

because they are functions of different degrees of freedom, and they also commute with the total Hamiltonian H . Thus, H_{CM} and H_{rel} possess a simultaneous eigenbasis, which is also an eigenbasis of the total Hamiltonian H .

This simultaneous eigenbasis consists of functions of the form,

$$\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\psi(\mathbf{r}), \quad (59)$$

a product of a center-of-mass wave function Φ times a relative wave function ψ . Each of these are eigenfunctions of their respective Hamiltonians,

$$H_{\text{CM}}\Phi = E_{\text{CM}}\Phi, \quad (60)$$

$$H_{\text{rel}}\psi = E_{\text{rel}}\psi, \quad (61)$$

where the eigenvalue E of the total Hamiltonian H is given by

$$E = E_{\text{CM}} + E_{\text{rel}}. \quad (62)$$

The center-of-mass equation (60) is easy to solve since H_{CM} is just a free particle Hamiltonian. For example, if we choose the three components of \mathbf{P} as a complete set of commuting observables for the center-of-mass motion, we have eigenfunctions

$$\Phi(\mathbf{R}) = e^{i\mathbf{P}\cdot\mathbf{R}/\hbar}, \quad (63)$$

that is, plane wave with momentum \mathbf{P} (being somewhat sloppy about the distinction between the operator \mathbf{P} and its eigenvalues). Of course we may also solve this free particle equation in spherical coordinates.

The relative wave equation (61) has the form of a pseudo-one-body problem of the kind considered earlier in these Notes, but with a reinterpretation of the variables. Now \mathbf{r} is the relative position vector between the two particles, and \mathbf{p} is defined by Eq. (52). Also, the mass m used earlier in these Notes must be identified with the reduced mass μ . In the limit $m_1 \rightarrow \infty$ while holding m_2 fixed, we recover the earlier results in which we had an infinitely massive force center. It is worthwhile keeping in mind, however, that in real problems the position and momentum operators for relative motion in a two-body problem such as hydrogen are really functions of the positions and momenta of *both* particles.

As a final remark, we transform the total angular momentum of the system \mathbf{L} , expressed in terms of the coordinates of the two particles in Eqs. (40) and (41), over to the new coordinates. We find

$$\mathbf{L} = \mathbf{L}_{\text{CM}} + \mathbf{L}_{\text{rel}}, \quad (64)$$

where

$$\mathbf{L}_{\text{CM}} = \mathbf{R} \times \mathbf{P}, \quad \mathbf{L}_{\text{rel}} = \mathbf{r} \times \mathbf{p}. \quad (65)$$

The Hamiltonian H_{CM} commutes with \mathbf{L}_{CM} , and H_{rel} commutes with L_{rel} . In other language, the total Hamiltonian H commutes not only with overall rotations of the system, but with rotations of the center of mass and with rotations about the center of mass separately.

In subsequent notes we shall consider some more examples of central force motion.

Problems

1. In class we discussed the vibrational motion of the carbon monoxide molecule. Let the harmonic approximation to the bottom of the well of $V(r)$ be

$$V(r) \approx -V_0 + \frac{1}{2}M\omega_v^2(r - r_0)^2. \quad (66).$$

For CO , we have $r_0 = 1.1\text{\AA}$, and $V_0 = 11\text{eV}$. By assuming that $V(r) = 0$ (dissociation) when $r - r_0 = r_0$, solve numerically for ω_v (the vibrational frequency). Compare to the experimental value, which is $\nu = 2.5 \times 10^{13}\text{Hz}$. Note that $\omega = 2\pi\nu$.

What is the probability that the CO molecule is in the $n = 1$ vibrational state at 300 Kelvins? (You will see that CO is not a very good greenhouse gas.)

2. This problem involves some exercise with expectation values of powers of r in hydrogen-like atoms. These expectation values are useful in perturbation theory and other places. There are various ways to evaluate these expectation values; for example, one can use the generating function of the Laguerre polynomials. But I think the following method is somewhat easier, once you get it going.

(a) Write out the radial Schrödinger equation for a hydrogen-like atom. (“Hydrogen-like” means $V(r) = -Ze^2/r$.) Show that if $a = \hbar^2/\mu Ze^2$, then

$$\frac{d^2u}{dr^2} + \left[-\frac{\ell(\ell+1)}{r^2} + \frac{2}{ar} - \frac{1}{n^2a^2} \right] u = 0, \quad (67)$$

where u is the normalized radial wave function corresponding to quantum numbers n and ℓ . Now multiply this by $r^{k+1}(du/dr)$ and integrate from 0 to ∞ . Use integration by parts to show that

$$(k+1) \int_0^\infty r^k \left(\frac{du}{dr} \right)^2 dr = \frac{k+1}{n^2a^2} \langle r^k \rangle - \frac{2k}{a} \langle r^{k-1} \rangle + \ell(\ell+1)(k-1) \langle r^{k-2} \rangle. \quad (68)$$

In the integrations, you may assume that $k > -2\ell - 2$, which will cause the boundary terms to vanish.

(b) Now multiply Eq. (67) by $r^k u$ and do more integration by parts, and combine the result with Eq. (68) to show that

$$\frac{k+1}{n^2} \langle r^k \rangle - (2k+1)a \langle r^{k-1} \rangle + \frac{a^2k}{4} [(2\ell+1)^2 - k^2] \langle r^{k-2} \rangle = 0. \quad (69)$$

This is called the *Kramer's relation*.

(c) Use Eq. (69) to find $\langle r^k \rangle$ for $k = -1$, $k = 1$, and $k = 2$. Notice that you cannot evaluate $\langle 1/r^2 \rangle$ by this method. For that you need to face up to generating functions, or some other method. However, given that

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{a^2 n^3 (\ell + \frac{1}{2})}, \quad (70)$$

find $\langle 1/r^3 \rangle$. The latter is needed for the fine structure perturbations and the Zeeman effect.

3. Consider the helium atom in a lab frame. The positions of the nucleus, electron 1 and electron 2 are \mathbf{r}_n , \mathbf{r}_{e1} and \mathbf{r}_{e2} respectively. The mass of the nucleus is M and that of the electron is m . Thus the laboratory Hamiltonian is

$$H = \frac{|\mathbf{p}_n|^2}{2M} + \frac{|\mathbf{p}_{e1}|^2}{2m} + \frac{|\mathbf{p}_{e2}|^2}{2m} + V(\mathbf{r}_n, \mathbf{r}_{e1}, \mathbf{r}_{e2}). \quad (71)$$

We will only be interested in the kinetic energy in this problem.

Let \mathbf{R} be the center of mass position and let

$$\begin{aligned}\mathbf{r}_1 &= \mathbf{r}_{e1} - \mathbf{r}_n, \\ \mathbf{r}_2 &= \mathbf{r}_{e2} - \mathbf{r}_n,\end{aligned}\tag{72}$$

so that \mathbf{r}_1 and \mathbf{r}_2 are the positions of the two electrons relative to the nucleus. Also define new momentum operators,

$$\mathbf{P} = -i\hbar \frac{\partial}{\partial \mathbf{R}}, \quad \mathbf{p}_1 = -i\hbar \frac{\partial}{\partial \mathbf{r}_1}, \quad \mathbf{p}_2 = -i\hbar \frac{\partial}{\partial \mathbf{r}_2}.\tag{73}$$

Express the kinetic energy as a function of these new momentum operators. You will obtain a term proportional to $\mathbf{p}_1 \cdot \mathbf{p}_2$. This is called a “mass polarization” term.

The usual simple minded treatment of helium treats the nucleus as infinitely heavy. In this approach there are no mass polarization terms. Explain why its a good approximation to neglect those terms (thus, the usual approach is ok).