

7.1: Angular Momentum Operators

In classical mechanics, the vector angular momentum, \mathbf{L} , of a particle of position vector \mathbf{r} and linear momentum \mathbf{p} is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \quad (7.1.1)$$

It follows that

$$\begin{aligned} L_x &= y p_z - z p_y, \\ L_y &= z p_x - x p_z, \\ L_z &= x p_y - y p_x. \end{aligned}$$

Let us, first of all, consider whether it is possible to use the previous expressions as the definitions of the operators corresponding to the components of angular momentum in quantum mechanics, assuming that the x_i and p_i (where $x_1 \equiv x$, $p_1 \equiv p_x$, $x_2 \equiv y$, etc.) correspond to the appropriate quantum mechanical position and momentum operators. The first point to note is that expressions ([e8.1])–([e8.3]) are unambiguous with respect to the order of the terms in multiplicative factors, because the various position and momentum operators appearing in them all commute with one another. [See Equations ([commxp]).] Moreover, given that the x_i and the p_i are Hermitian operators, it is easily seen that the L_i are also Hermitian. This is important, because only Hermitian operators can represent physical variables in quantum mechanics. (See Section [s4.6].) We, thus, conclude that Equations ([e8.1])–([e8.3]) are plausible definitions for the quantum mechanical operators that represent the components of angular momentum.

Let us now derive the commutation relations for the L_i . For instance,

$$\begin{aligned} &= [y p_z - z p_y, z p_x - x p_z] = y p_x [p_z, z] + x p_y [z, p_z] \\ &= i \hbar (x p_y - y p_x) = i \hbar L_z, \end{aligned}$$

where use has been made of the definitions of the L_i [see Equations ([e8.1])–([e8.3])], and commutation relations ([commxx])–([commxp]) for the x_i and p_i . There are two similar commutation relations: one for L_y and L_z , and one for L_z and L_x . Collecting all of these commutation relations together, we obtain

$$\begin{aligned} [L_x, L_y] &= i \hbar L_z, \\ [L_y, L_z] &= i \hbar L_x, \\ [L_z, L_x] &= i \hbar L_y. \end{aligned}$$

By analogy with classical mechanics, the operator L^2 , that represents the magnitude squared of the angular momentum vector, is defined

$$L^2 = L_x^2 + L_y^2 + L_z^2. \quad (7.1.2)$$

Now, it is easily demonstrated that if A and B are two general operators then

$$[A^2, B] = A[A, B] + [A, B]A. \quad (7.1.3)$$

Hence,

$$\begin{aligned} &= [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= i \hbar (-L_y L_z - L_z L_y + L_z L_y + L_y L_z) = 0, \end{aligned}$$

where use has been made of Equations ([e8.6])–([e8.8]). In other words, L^2 commutes with L_x . Likewise, it is easily demonstrated that L^2 also commutes with L_y , and with L_z . Thus,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0. \quad (7.1.4)$$

Recall, from Section [smeas], that in order for two physical quantities to be (exactly) measured simultaneously, the operators that represent them in quantum mechanics must commute with one another. Hence, the commutation relations ([e8.6])–([e8.8]) and ([e8.12]) imply that we can only simultaneously measure the magnitude squared of the angular momentum vector, L^2 , together with, at most, one of its Cartesian components. By convention, we shall always choose to measure the z -component, L_z .

Finally, it is helpful to define the operators

$$L_{\pm} = L_x \pm i L_y. \quad (7.1.5)$$

Note that L_+ and L_- are not Hermitian operators, but are the Hermitian conjugates of one another (see Section [s4.6]): that is,

$$(L_{\pm})^{\dagger} = L_{\mp}, \quad (7.1.6)$$

Moreover, it is easily seen that

$$\begin{aligned} L_+ L_- &= (L_x + i L_y)(L_x - i L_y) = L_x^2 + L_y^2 - i[L_x, L_y] = L_x^2 + L_y^2 + \hbar L_z \\ &= L^2 - L_z^2 + \hbar L_z. \end{aligned}$$

Likewise,

$$L_- L_+ = L^2 - L_z^2 - \hbar L_z, \quad (7.1.7)$$

giving

$$[L_+, L_-] = 2 \hbar L_z. \quad (7.1.8)$$

We also have

$$[L_+, L_z] = [L_x, L_z] + i[L_y, L_z] = -i \hbar L_y - \hbar L_x = -\hbar L_+, \quad (7.1.9)$$

and, similarly,

$$[L_-, L_z] = \hbar L_-. \quad (7.1.10)$$

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7.2: Representation of Angular Momentum

Now, we saw earlier, in Section [s7.2], that the operators, p_i , which represent the Cartesian components of linear momentum in quantum mechanics, can be represented as the spatial differential operators $-i\hbar\partial/\partial x_i$. Let us now investigate whether angular momentum operators can similarly be represented as spatial differential operators.

It is most convenient to perform our investigation using conventional spherical polar coordinates: that is, r , θ , and ϕ . These are defined with respect to our usual Cartesian coordinates as follows:

$$\begin{aligned}x &= r \sin \theta \cos \phi, \\y &= r \sin \theta \sin \phi, \\z &= r \cos \theta.\end{aligned}$$

We deduce, after some tedious analysis, that

$$\begin{aligned}\frac{\partial}{\partial x} &= \sin \theta \cos \phi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \phi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \phi}{r \sin \theta} \frac{\partial}{\partial \phi}, \\ \frac{\partial}{\partial y} &= \sin \theta \sin \phi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \phi}{r \sin \theta} \frac{\partial}{\partial \phi}, \\ \frac{\partial}{\partial z} &= \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta}.\end{aligned}$$

Making use of the definitions ([e8.1])–([e8.3]), ([e8.9]), and ([e8.13]), the fundamental representation ([e6.12])–([e6.14]) of the p_i operators as spatial differential operators, Equations ([e8.21])–([e8zz]), and a great deal of tedious analysis, we finally obtain

$$\begin{aligned}L_x &= -i\hbar \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right), \\ L_y &= -i\hbar \left(\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right), \\ L_z &= -i\hbar \frac{\partial}{\partial \phi},\end{aligned}$$

as well as

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right], \quad (7.2.1)$$

and

$$L_{\pm} = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right). \quad (7.2.2)$$

We, thus, conclude that all of our angular momentum operators can be represented as differential operators involving the angular spherical coordinates, θ and ϕ , but not involving the radial coordinate, r .

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7.3: Eigenstates of Angular Momentum

Let us find the simultaneous eigenstates of the angular momentum operators L_z and L^2 . Because both of these operators can be represented as purely angular differential operators, it stands to reason that their eigenstates only depend on the angular coordinates θ and ϕ . Thus, we can write

$$\begin{aligned} L_z Y_{l,m}(\theta, \phi) &= m \hbar Y_{l,m}(\theta, \phi), \\ L^2 Y_{l,m}(\theta, \phi) &= l(l+1) \hbar^2 Y_{l,m}(\theta, \phi). \end{aligned}$$

Here, the $Y_{l,m}(\theta, \phi)$ are the eigenstates in question, whereas the dimensionless quantities m and l parameterize the eigenvalues of L_z and L^2 , which are $m \hbar$ and $l(l+1) \hbar^2$, respectively. Of course, we expect the $Y_{l,m}$ to be both mutually orthogonal and properly normalized (see Section [seig]), so that

$$\oint Y_{l',m'}^*(\theta, \phi) Y_{l,m}(\theta, \phi) d\Omega = \delta_{l'l} \delta_{m'm}, \quad (7.3.1)$$

where $d\Omega = \sin\theta d\theta d\phi$ is an element of solid angle, and the integral is over all solid angle.

Now,

$$\begin{aligned} L_z (L_+ Y_{l,m}) &= (L_+ L_z + [L_z, L_+]) Y_{l,m} = (L_+ L_z + \hbar L_+) Y_{l,m} \\ &= (m+1) \hbar (L_+ Y_{l,m}), \end{aligned}$$

where use has been made of Equation ([e8.19]). We, thus, conclude that when the operator L_+ operates on an eigenstate of L_z corresponding to the eigenvalue $m \hbar$ it converts it to an eigenstate corresponding to the eigenvalue $(m+1) \hbar$. Hence, L_+ is known as the *raising operator* (for L_z). It is also easily demonstrated that

$$L_z (L_- Y_{l,m}) = (m-1) \hbar (L_- Y_{l,m}). \quad (7.3.2)$$

In other words, when L_- operates on an eigenstate of L_z corresponding to the eigenvalue $m \hbar$ it converts it to an eigenstate corresponding to the eigenvalue $(m-1) \hbar$. Hence, L_- is known as the *lowering operator* (for L_z).

Writing

$$\begin{aligned} L_+ Y_{l,m} &= c_{l,m}^+ Y_{l,m+1}, \\ L_- Y_{l,m} &= c_{l,m}^- Y_{l,m-1}, \end{aligned}$$

we obtain

$$L_- L_+ Y_{l,m} = c_{l,m}^+ c_{l,m+1}^- Y_{l,m} = [l(l+1) - m(m+1)] \hbar^2 Y_{l,m}, \quad (7.3.3)$$

where use has been made of Equation ([e8.17]). Likewise,

$$L_+ L_- Y_{l,m} = c_{l,m-1}^+ c_{l,m}^- Y_{l,m} = [l(l+1) - m(m-1)] \hbar^2 Y_{l,m}, \quad (7.3.4)$$

where use has been made of Equation ([e8.15]). It follows that

$$\begin{aligned} c_{l,m}^+ c_{l,m+1}^- &= [l(l+1) - m(m+1)] \hbar^2, \\ c_{l,m-1}^+ c_{l,m}^- &= [l(l+1) - m(m-1)] \hbar^2. \end{aligned}$$

These equations are satisfied when

$$c_{l,m}^\pm = [l(l+1) - m(m \pm 1)]^{1/2} \hbar. \quad (7.3.5)$$

Hence, we can write

$$\begin{aligned} L_+ Y_{l,m} &= [l(l+1) - m(m+1)]^{1/2} \hbar Y_{l,m+1}, \\ L_- Y_{l,m} &= [l(l+1) - m(m-1)]^{1/2} \hbar Y_{l,m-1}. \end{aligned}$$

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7.4: Eigenvalues of L_z

It seems reasonable to attempt to write the eigenstate $Y_{l,m}(\theta, \phi)$ in the separable form

$$Y_{l,m}(\theta, \phi) = \Theta_{l,m}(\theta) \Phi_m(\phi). \quad (7.4.1)$$

We can satisfy the orthonormality constraint ([e8.31]) provided that

$$\int_0^\pi \Theta_{l',m'}^*(\theta) \Theta_{l,m}(\theta) \sin \theta d\theta = \delta_{l'l'},$$

$$\int_0^{2\pi} \Phi_{m'}^*(\phi) \Phi_m(\phi) d\phi = \delta_{mm'}.$$

Note, from Equation ([e8.26]), that the differential operator which represents L_z only depends on the azimuthal angle ϕ , and is independent of the polar angle θ . It therefore follows from Equations ([e8.26]), ([e8.29]), and ([e8.34]) that

$$-i \hbar \frac{d\Phi_m}{d\phi} = m \hbar \Phi_m. \quad (7.4.2)$$

The solution of this equation is

$$\Phi_m(\phi) \sim e^{i m \phi}. \quad (7.4.3)$$

Here, the symbol \sim just means that we are neglecting multiplicative constants.

Our basic interpretation of a wavefunction as a quantity whose modulus squared represents the probability density of finding a particle at a particular point in space suggests that a physical wavefunction must be single-valued in space. Otherwise, the probability density at a given point would not, in general, have a unique value, which does not make physical sense. Hence, we demand that the wavefunction ([e8.38]) be single-valued: that is, $\Phi_m(\phi + 2\pi) = \Phi_m(\phi)$ for all ϕ . This immediately implies that the quantity m is quantized. In fact, m can only take integer values. Thus, we conclude that the eigenvalues of L_z are also quantized, and take the values $m \hbar$, where m is an integer. [A more rigorous argument is that $\Phi_m(\phi)$ must be continuous in order to ensure that L_z is an Hermitian operator, because the proof of hermiticity involves an integration by parts in ϕ that has canceling contributions from $\phi = 0$ and $\phi = 2\pi$.]

Finally, we can easily normalize the eigenstate ([e8.38]) by making use of the orthonormality constraint ([e8.36]). We obtain

$$\Phi_m(\phi) = \frac{e^{i m \phi}}{\sqrt{2\pi}}. \quad (7.4.4)$$

This is the properly normalized eigenstate of L_z corresponding to the eigenvalue $m \hbar$.

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7.5: Eigenvalues of L^2

Consider the angular wavefunction $\psi(\theta, \phi) = L_+ Y_{l,m}(\theta, \phi)$. We know that

$$\oint \psi^*(\theta, \phi) \psi(\theta, \phi) d\Omega \geq 0, \quad (7.5.1)$$

because $\psi^* \psi \equiv |\psi|^2$ is a positive-definite real quantity. Hence, making use of Equations ([e5.48]) and ([e8.14]), we find that

$$\oint (L_+ Y_{l,m})^* (L_+ Y_{l,m}) d\Omega = \oint Y_{l,m}^* (L_+)^{\dagger} (L_+ Y_{l,m}) d\Omega = \oint Y_{l,m}^* L_- L_+ Y_{l,m} d\Omega \geq 0.$$

It follows from Equations ([e8.17]), and ([e8.29])–([e8.31]) that

$$\begin{aligned} \oint Y_{l,m}^* (L^2 - L_z^2 - \hbar L_z) Y_{l,m} d\Omega &= \oint Y_{l,m}^* \hbar^2 [l(l+1) - m(m+1)] Y_{l,m} d\Omega \\ &= \hbar^2 [l(l+1) - m(m+1)] \oint Y_{l,m}^* Y_{l,m} d\Omega \\ &= \hbar^2 [l(l+1) - m(m+1)] \geq 0. \end{aligned}$$

We, thus, obtain the constraint

$$l(l+1) \geq m(m+1). \quad (7.5.2)$$

Likewise, the inequality

$$\oint (L_- Y_{l,m})^* (L_- Y_{l,m}) d\Omega = \oint Y_{l,m}^* L_+ L_- Y_{l,m} d\Omega \geq 0 \quad (7.5.3)$$

leads to a second constraint:

$$l(l+1) \geq m(m-1). \quad (7.5.4)$$

Without loss of generality, we can assume that $l \geq 0$. This is reasonable, from a physical standpoint, because $l(l+1)\hbar^2$ is supposed to represent the magnitude squared of something, and should, therefore, only take non-negative values. If l is non-negative then the constraints ([e8.42]) and ([e8.44]) are equivalent to the following constraint:

$$-l \leq m \leq l. \quad (7.5.5)$$

We, thus, conclude that the quantum number m can only take a restricted range of integer values.

Now, if m can only take a restricted range of integer values then there must exist a lowest possible value that it can take. Let us call this special value m_- , and let Y_{l,m_-} be the corresponding eigenstate. Suppose we act on this eigenstate with the lowering operator L_- . According to Equation ([e8.32]), this will have the effect of converting the eigenstate into that of a state with a lower value of m . However, no such state exists. A non-existent state is represented in quantum mechanics by the null wavefunction, $\psi = 0$. Thus, we must have

$$L_- Y_{l,m_-} = 0. \quad (7.5.6)$$

From Equation ([e8.15]),

$$L^2 = L_+ L_- + L_z^2 - \hbar L_z \quad (7.5.7)$$

Hence,

$$L^2 Y_{l,m_-} = (L_+ L_- + L_z^2 - \hbar L_z) Y_{l,m_-}, \quad (7.5.8)$$

or

$$l(l+1) Y_{l,m_-} = m_- (m_- - 1) Y_{l,m_-}, \quad (7.5.9)$$

where use has been made of ([e8.29]), ([e8.30]), and ([e8.46]). It follows that

$$l(l+1) = m_- (m_- - 1). \quad (7.5.10)$$

Assuming that m_- is negative, the solution to the previous equation is

$$m_- = -l. \quad (7.5.11)$$

We can similarly show that the largest possible value of m is

$$m_+ = +l. \quad (7.5.12)$$

The previous two results imply that l is an integer, because m_- and m_+ are both constrained to be integers.

We can now formulate the rules that determine the allowed values of the quantum numbers l and m . The quantum number l takes the non-negative integer values $0, 1, 2, 3, \dots$. Once l is given, the quantum number m can take any integer value in the range

$$-l, -l+1, \dots, 0, \dots, l-1, l. \quad (7.5.13)$$

Thus, if $l = 0$ then m can only take the value 0 , if $l = 1$ then m can take the values $-1, 0, +1$, if $l = 2$ then m can take the values $-2, -1, 0, +1, +2$, and so on.

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7.6: Spherical Harmonics

The simultaneous eigenstates, $Y_{l,m}(\theta, \phi)$, of L^2 and L_z are known as the *spherical harmonics*. Let us investigate their functional form.

We know that

$$L_+ Y_{l,l}(\theta, \phi) = 0, \quad (7.6.1)$$

because there is no state for which m has a larger value than $+l$. Writing

$$Y_{l,l}(\theta, \phi) = \Theta_{l,l}(\theta) e^{il\phi} \quad (7.6.2)$$

[see Equations ([e8.34]) and ([e8.38])], and making use of Equation ([e8.28]), we obtain

$$\hbar e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \Theta_{l,l}(\theta) e^{il\phi} = 0. \quad (7.6.3)$$

This equation yields

$$\frac{d\Theta_{l,l}}{d\theta} - l \cot \theta \Theta_{l,l} = 0. \quad (7.6.4)$$

which can easily be solved to give

$$\Theta_{l,l} \sim (\sin \theta)^l. \quad (7.6.5)$$

Hence, we conclude that

$$Y_{l,l}(\theta, \phi) \sim (\sin \theta)^l e^{il\phi}. \quad (7.6.6)$$

Likewise, it is easy to demonstrate that

$$Y_{l,-l}(\theta, \phi) \sim (\sin \theta)^l e^{-il\phi}. \quad (7.6.7)$$

Once we know $Y_{l,l}$, we can obtain $Y_{l,l-1}$ by operating on $Y_{l,l}$ with the lowering operator L_- . Thus,

$$Y_{l,l-1} \sim L_- Y_{l,l} \sim e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) (\sin \theta)^l e^{il\phi}, \quad (7.6.8)$$

where use has been made of Equation ([e8.28]). The previous equation yields

$$Y_{l,l-1} \sim e^{i(l-1)\phi} \left(\frac{d}{d\theta} + l \cot \theta \right) (\sin \theta)^l. \quad (7.6.9)$$

Now,

$$\left(\frac{d}{d\theta} + l \cot \theta \right) f(\theta) \equiv \frac{1}{(\sin \theta)^l} \frac{d}{d\theta} [(\sin \theta)^l f(\theta)], \quad (7.6.10)$$

where $f(\theta)$ is a general function. Hence, we can write

$$Y_{l,l-1}(\theta, \phi) \sim \frac{e^{i(l-1)\phi}}{(\sin \theta)^{l-1}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right) (\sin \theta)^{2l}. \quad (7.6.11)$$

ikewise, we can show that

$$Y_{l,-l+1}(\theta, \phi) \sim L_+ Y_{l,-l} \sim \frac{e^{-i(l-1)\phi}}{(\sin \theta)^{l-1}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right) (\sin \theta)^{2l}. \quad (7.6.12)$$

We can now obtain $Y_{l,l-2}$ by operating on $Y_{l,l-1}$ with the lowering operator. We get

$$Y_{l,l-2} \sim L_- Y_{l,l-1} \sim e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \frac{e^{i(l-1)\phi}}{(\sin \theta)^{l-1}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right) (\sin \theta)^{2l}, \quad (7.6.13)$$

which reduces to

$$Y_{l,l-2} \sim e^{-i(l-2)\phi} \left[\frac{d}{d\theta} + (l-1) \cot \theta \right] \frac{1}{(\sin \theta)^{l-1}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right) (\sin \theta)^{2l}. \quad (7.6.14)$$

Finally, making use of Equation ([e8.64]), we obtain

$$Y_{l,l-2}(\theta, \phi) \sim \frac{e^{i(l-2)\phi}}{(\sin \theta)^{l-2}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right)^2 (\sin \theta)^{2l}. \quad (7.6.15)$$

Likewise, we can show that

$$Y_{l,-l+2}(\theta, \phi) \sim L_+ Y_{l,-l+1} \sim \frac{e^{-i(l-2)\phi}}{(\sin \theta)^{l-2}} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right)^2 (\sin \theta)^{2l}. \quad (7.6.16)$$

A comparison of Equations ([e8.59]), ([e8.64a]), and ([e8.68]) reveals the general functional form of the spherical harmonics:

$$Y_{l,m}(\theta, \phi) \sim \frac{e^{im\phi}}{(\sin \theta)^m} \left(\frac{1}{\sin \theta} \frac{d}{d\theta} \right)^{l-m} (\sin \theta)^{2l}. \quad (7.6.17)$$

Here, m is assumed to be non-negative. Making the substitution $u = \cos \theta$, we can also write

$$Y_{l,m}(u, \phi) \sim e^{im\phi} (1-u^2)^{-m/2} \left(\frac{d}{du} \right)^{l-m} (1-u^2)^l. \quad (7.6.18)$$

Finally, it is clear from Equations ([e8.60]), ([e8.65]), and ([e8.69]) that

$$Y_{l,-m} \sim Y_{l,m}^*. \quad (7.6.19)$$

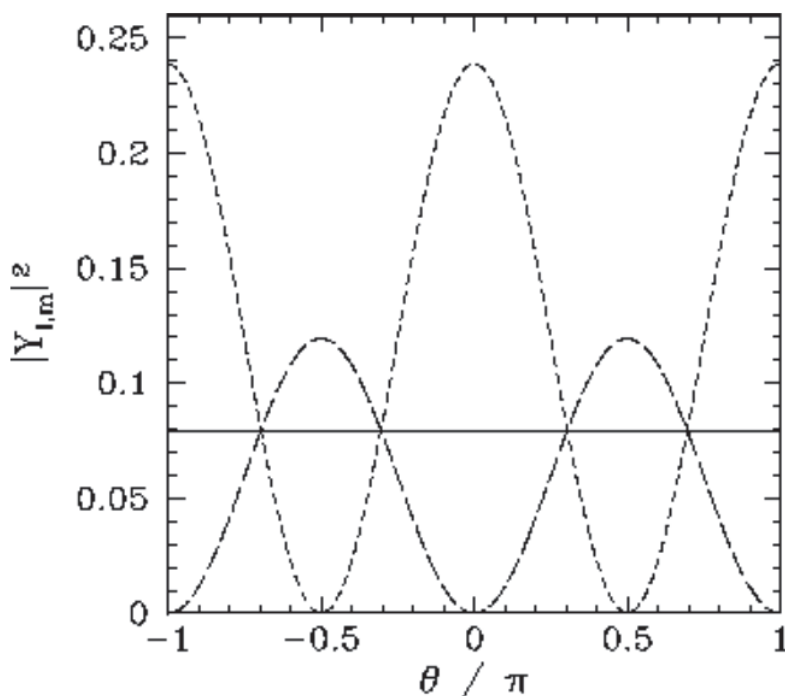


Figure 18: The $|Y_{l,m}(\theta, \phi)|^2$ plotted as a functions of θ . The solid, short-dashed, and long-dashed curves correspond to $l, m = 0, 0$, and $1, 0$, and $1, \pm 1$, respectively.

We now need to normalize our spherical harmonic functions so as to ensure that

$$\oint |Y_{l,m}(\theta, \phi)|^2 d\Omega = 1. \quad (7.6.20)$$

After a great deal of tedious analysis, the normalized spherical harmonic functions are found to take the form

$$Y_{l,m}(\theta, \phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_{l,m}(\cos \theta) e^{im\phi} \quad (7.6.21)$$

for $m \geq 0$, where the $P_{l,m}$ are known as *associated Legendre polynomials*, and are written

$$P_{l,m}(u) = (-1)^{l+m} \frac{(l+m)!}{(l-m)!} \frac{(1-u^2)^{-m/2}}{2^l l!} \left(\frac{d}{du} \right)^{l-m} (1-u^2)^l \quad (7.6.22)$$

for $m \geq 0$. Alternatively,

$$P_{l,m}(u) = (-1)^l \frac{(1-u^2)^{m/2}}{2^l l!} \left(\frac{d}{du} \right)^{l+m} (1-u^2)^l, \quad (7.6.23)$$

for $m \geq 0$. The spherical harmonics characterized by $m < 0$ can be calculated from those characterized by $m > 0$ via the identity

$$Y_{l,-m} = (-1)^m Y_{l,m}^*. \quad (7.6.24)$$

The spherical harmonics are orthonormal: that is,

$$\oint Y_{l',m'}^* Y_{l,m} d\Omega = \delta_{l'l} \delta_{m'm}, \quad (7.6.25)$$

and also form a complete set. In other words, any well-behaved function of θ and ϕ can be represented as a superposition of spherical harmonics. Finally, and most importantly, the spherical harmonics are the simultaneous eigenstates of L_z and L^2 corresponding to the eigenvalues $m \hbar$ and $l(l+1) \hbar^2$, respectively.

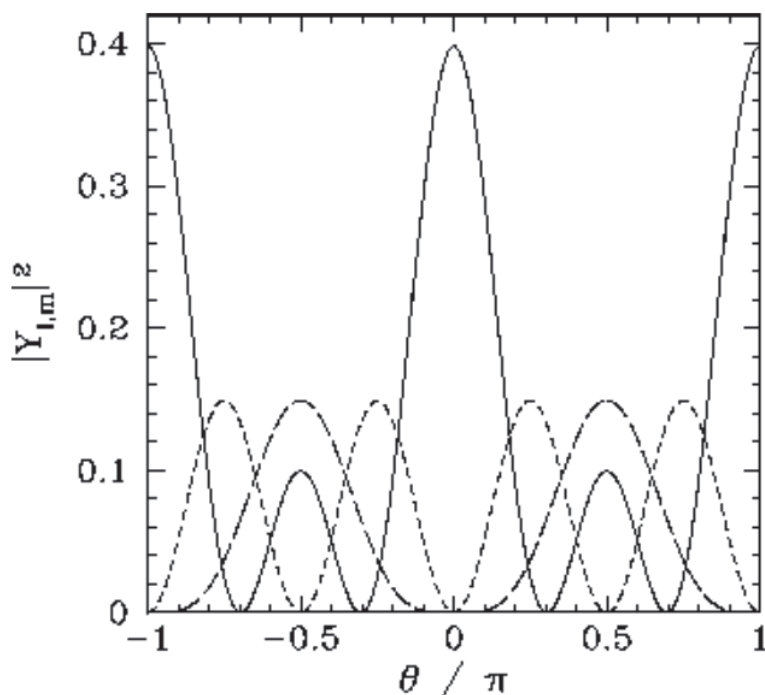


Figure 19: The $|Y_{l,m}(\theta, \phi)|^2$ plotted as a functions of θ . The solid, short-dashed, and long-dashed curves correspond to $l, m = 2, 0$, and $2, \pm 1$, and $2, \pm 2$ respectively.

All of the $l = 0$, $l = 1$, and $l = 2$ spherical harmonics are listed below:

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}},$$
$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta,$$
$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i \phi},$$
$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1),$$
$$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i \phi},$$
$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2 i \phi}.$$

The θ variation of these functions is illustrated in Figures [\[ylm1\]](#) and [\[ylm2\]](#).

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7.E: Orbital Angular Momentum (Exercises)

1. A system is in the state $\psi = Y_{l,m}(\theta, \phi)$. Calculate $\langle L_x \rangle$ and $\langle L_x^2 \rangle$.
2. Find the eigenvalues and eigenfunctions (in terms of the angles θ and ϕ) of L_x .
3. Consider a beam of particles with $l = 1$. A measurement of L_x yields the result \hbar . What values will be obtained by a subsequent measurement of L_z , and with what probabilities? Repeat the calculation for the cases in which the measurement of L_x yields the results 0 and $-\hbar$.
4. The Hamiltonian for an axially symmetric rotator is given by

$$H = \frac{L_x^2 + L_y^2}{2 I_1} + \frac{L_z^2}{2 I_2}. \quad (7.E.1)$$

What are the eigenvalues of H ?

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CHAPTER OVERVIEW

8: Central Potentials

In this chapter, we shall investigate the interaction of a non-relativistic particle of mass m and energy E with various so-called *central potentials*, $V(r)$, where $r = (x^2 + y^2 + z^2)^{1/2}$ is the radial distance from the origin. It is, of course, most convenient to work in spherical coordinates— r , θ , ϕ —during such an investigation. (See Section [\[s8.3\]](#).) Thus, we shall be searching for stationary wavefunctions, $\psi(r, \theta, \phi)$, that satisfy the time-independent Schrödinger equation (see Section [\[sstat\]](#))

$$H \psi = E \psi, \quad (8.1)$$

where the Hamiltonian takes the standard non-relativistic form

$$H = \frac{p^2}{2m} + V(r). \quad (8.2)$$

[8.1: Derivation of Radial Equation](#)

[8.2: Infinite Spherical Potential Well](#)

[8.3: Hydrogen Atom](#)

[8.4: Rydberg Formula](#)

[8.E: Central Potentials \(Exercises\)](#)

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8.1: Derivation of Radial Equation

Now, we have seen that the Cartesian components of the momentum, \mathbf{p} , can be represented as (see Section [s7.2])

$$p_i = -i\hbar \frac{\partial}{\partial x_i} \quad (8.1.1)$$

for $i = 1, 2, 3$, where $x_1 \equiv x$, $x_2 \equiv y$, $x_3 \equiv z$, and $\mathbf{r} \equiv (x_1, x_2, x_3)$. Likewise, it is easily demonstrated, from the previous expressions, and the basic definitions of the spherical coordinates [see Equations ([e8.21])–([e8zz])], that the radial component of the momentum can be represented as

$$p_r \equiv \frac{\mathbf{p} \cdot \mathbf{r}}{r} = -i\hbar \frac{\partial}{\partial r} \quad (8.1.2)$$

Recall that the angular momentum vector, \mathbf{L} , is defined

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (8.1.3)$$

[See Equation ([e8.0]).] This expression can also be written in the following form:

$$L_i = \epsilon_{ijk} x_j p_k. \quad (8.1.4)$$

Here, the ϵ_{ijk} (where i, j, k all run from 1 to 3) are elements of the so-called *totally anti-symmetric tensor*. The values of the various elements of this tensor are determined via a simple rule:

$$\epsilon_{ijk} = \begin{cases} 0 & \text{if } i, j, k \text{ not all different} \\ 1 & \text{if } i, j, k \text{ are cyclic permutation of } 1, 2, 3 \\ -1 & \text{if } i, j, k \text{ are anti-cyclic permutation of } 1, 2, 3 \end{cases} \quad (8.1.5)$$

Thus, $\epsilon_{123} = \epsilon_{231} = 1$, $\epsilon_{321} = \epsilon_{132} = -1$, and $\epsilon_{112} = \epsilon_{131} = 0$, et cetera. Equation ([e9.6]) also makes use of the *Einstein summation convention*, according to which repeated indices are summed (from 1 to 3). For instance, $a_i b_i \equiv a_1 b_1 + a_2 b_2 + a_3 b_3$. Making use of this convention, as well as Equation ([e9.7]), it is easily seen that Equations ([e9.5]) and ([e9.6]) are indeed equivalent.

Let us calculate the value of L^2 using Equation ([e9.6]). According to our new notation, L^2 is the same as $L_i L_i$. Thus, we obtain

$$L^2 = \epsilon_{ijk} x_j p_k \epsilon_{ilm} x_l p_m = \epsilon_{ijk} \epsilon_{ilm} x_j p_k x_l p_m. \quad (8.1.6)$$

Note that we are able to shift the position of ϵ_{ilm} because its elements are just numbers, and, therefore, commute with all of the x_i and the p_i . Now, it is easily demonstrated that

$$\epsilon_{ijk} \epsilon_{ilm} \equiv \delta_{jl} \delta_{km} - \delta_{jm} \delta_{kl}. \quad (8.1.7)$$

Here δ_{ij} is the usual *Kronecker delta*, whose elements are determined according to the rule

$$\delta_{ij} = \begin{cases} 1 & \text{if } i \text{ and } j \text{ the same} \\ 0 & \text{if } i \text{ and } j \text{ different} \end{cases} \quad (8.1.8)$$

It follows from Equations ([e9.8]) and ([e9.9]) that

$$L^2 = x_i p_j x_i p_j - x_i p_j x_j p_i. \quad (8.1.9)$$

Here, we have made use of the fairly self-evident result that $\delta_{ij} a_i b_j \equiv a_i b_i$. We have also been careful to preserve the order of the various terms on the right-hand side of the previous expression, because the x_i and the p_i do not necessarily commute with one another.

We now need to rearrange the order of the terms on the right-hand side of Equation ([e9.11]). We can achieve this goal by making use of the fundamental commutation relation for the x_i and the p_i :

$$[x_i, p_j] = i\hbar \delta_{ij}. \quad (8.1.10)$$

[See Equation ([commxp]).] Thus,

$$\begin{aligned}
 L^2 &= x_i (x_i p_j - [x_i, p_j]) p_j - x_i p_j (p_i x_j + [x_j, p_i]) \\
 &= x_i x_i p_j p_j - i \hbar \delta_{ij} x_i p_j - x_i p_j p_i x_j - i \hbar \delta_{ij} x_i p_j \\
 &= x_i x_i p_j p_j - x_i p_i p_j x_j - 2 i \hbar x_i p_i.
 \end{aligned}$$

Here, we have made use of the fact that $p_j p_i = p_i p_j$, because the p_i commute with one another. [See Equation ([\[commpp\]](#)).] Next,

$$L^2 = x_i x_i p_j p_j - x_i p_i (x_j p_j - [x_j, p_j]) - 2 i \hbar x_i p_i. \quad (8.1.11)$$

Now, according to Equation ([\[e9.12\]](#)),

$$[x_j, p_j] \equiv [x_1, p_1] + [x_2, p_2] + [x_3, p_3] = 3 i \hbar. \quad (8.1.12)$$

Hence, we obtain

$$L^2 = x_i x_i p_j p_j - x_i p_i x_j p_j + i \hbar x_i p_i. \quad (8.1.13)$$

When expressed in more conventional vector notation, the previous expression becomes

$$L^2 = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2 + i \hbar \mathbf{r} \cdot \mathbf{p}. \quad (8.1.14)$$

Note that if we had attempted to derive the previous expression directly from Equation ([\[e9.5\]](#)), using standard vector identities, then we would have missed the final term on the right-hand side. This term originates from the lack of commutation between the x_i and p_i operators in quantum mechanics. Of course, standard vector analysis assumes that all terms commute with one another.

Equation ([\[e9.17\]](#)) can be rearranged to give

$$p^2 = r^{-2} [(\mathbf{r} \cdot \mathbf{p})^2 - i \hbar \mathbf{r} \cdot \mathbf{p} + L^2]. \quad (8.1.15)$$

Now,

$$\mathbf{r} \cdot \mathbf{p} = r p_r = -i \hbar r \frac{\partial}{\partial r}, \quad (8.1.16)$$

where use has been made of Equation ([\[e9.4\]](#)). Hence, we obtain

$$p^2 = -\hbar^2 \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \right]. \quad (8.1.17)$$

Finally, the previous equation can be combined with Equation ([\[e9.2\]](#)) to give the following expression for the Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \right) + V(r). \quad (8.1.18)$$

Let us now consider whether the previous Hamiltonian commutes with the angular momentum operators L_z and L^2 . Recall, from Section [\[s8.3\]](#), that L_z and L^2 are represented as differential operators that depend solely on the angular spherical coordinates, θ and ϕ , and do not contain the radial coordinate, r . Thus, any function of r , or any differential operator involving r (but not θ and ϕ), will automatically commute with L^2 and L_z . Moreover, L^2 commutes both with itself, and with L_z . (See Section [\[s8.2\]](#).) It is, therefore, clear that the previous Hamiltonian commutes with both L_z and L^2 .

According to Section [\[smeas\]](#), if two operators commute with one another then they possess simultaneous eigenstates. We thus conclude that for a particle moving in a central potential the eigenstates of the Hamiltonian are simultaneous eigenstates of L_z and L^2 . Now, we have already found the simultaneous eigenstates of L_z and L^2 —they are the spherical harmonics, $Y_{l,m}(\theta, \phi)$, discussed in Section [\[sharm\]](#). It follows that the spherical harmonics are also eigenstates of the Hamiltonian. This observation leads us to try the following separable form for the stationary wavefunction:

$$\psi(r, \theta, \phi) = R(r) Y_{l,m}(\theta, \phi). \quad (8.1.19)$$

It immediately follows, from Equation ([\[e8.29\]](#)) and ([\[e8.30\]](#)), and the fact that L_z and L^2 both obviously commute with $R(r)$, that

$$\begin{aligned}
 L_z \psi &= m \hbar \psi, \\
 L^2 \psi &= l(l+1) \hbar^2 \psi.
 \end{aligned}$$

Recall that the quantum numbers m and l are restricted to take certain integer values, as explained in Section [\[slsq\]](#).

Finally, making use of Equations ([e9.1]), ([e9.21]), and ([e9.24]), we obtain the following differential equation which determines the radial variation of the stationary wavefunction:

$$-\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R_{n,l} + V R_{n,l} = E R_{n,l}. \quad (8.1.20)$$

Here, we have labeled the function $R(r)$ by two quantum numbers, n and l . The second quantum number, l , is, of course, related to the eigenvalue of L^2 . [Note that the azimuthal quantum number, m , does not appear in the previous equation, and, therefore, does not influence either the function $R(r)$ or the energy, E .] As we shall see, the first quantum number, n , is determined by the constraint that the radial wavefunction be square-integrable.

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8.2: Infinite Spherical Potential Well

Consider a particle of mass m and energy $E > 0$ moving in the following simple central potential:

$$V(r) = \begin{cases} 0 & \text{for } 0 \leq r \leq a \\ \infty & \text{otherwise} \end{cases}. \quad (8.2.1)$$

Clearly, the wavefunction ψ is only non-zero in the region $0 \leq r \leq a$. Within this region, it is subject to the physical boundary conditions that it be well behaved (i.e., square-integrable) at $r = 0$, and that it be zero at $r = a$. (See Section [s5.2].) Writing the wavefunction in the standard form

$$\psi(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi), \quad (8.2.2)$$

we deduce (see the previous section) that the radial function $R_{n,l}(r)$ satisfies

$$\frac{d^2 R_{n,l}}{dr^2} + \frac{2}{r} \frac{dR_{n,l}}{dr} + \left[k^2 - \frac{l(l+1)}{r^2} \right] R_{n,l} = 0 \quad (8.2.3)$$

in the region $0 \leq r \leq a$, where

$$k^2 = \frac{2mE}{\hbar^2}. \quad (8.2.4)$$

Defining the scaled radial variable $z = kr$, the previous differential equation can

be transformed into the standard form

$$\left[\frac{d^2}{dz^2} R_{n,l} + \left(1 - \frac{l(l+1)}{z^2} \right) R_{n,l} \right] = 0.$$

The two independent solutions to this well-known second-order differential equation are called *spherical Bessel functions*, and can be written

$$j_l(z) = z^l \left(-\frac{1}{z} \frac{d}{dz} \right)^l \left(\frac{\sin z}{z} \right),$$

$$y_l(z) = -z^l \left(-\frac{1}{z} \frac{d}{dz} \right)^l \left(\frac{\cos z}{z} \right).$$

Thus, the first few spherical Bessel functions take the form

$$j_0(z) = \frac{\sin z}{z},$$

$$j_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z},$$

$$y_0(z) = -\frac{\cos z}{z},$$

$$y_1(z) = -\frac{\cos z}{z^2} - \frac{\sin z}{z}.$$

These functions are also plotted in Figure [sph]. It can be seen that the spherical Bessel functions are oscillatory in nature, passing through zero many times. However, the $y_l(z)$ functions are badly behaved (i.e., they are not square integrable) at $z = 0$, whereas the $j_l(z)$ functions are well behaved everywhere. It follows from our boundary condition at $r = 0$ that the $y_l(z)$ are unphysical, and that the radial wavefunction $R_{n,l}(r)$ is thus proportional to $j_l(kr)$ only. In order to satisfy the boundary condition at $r = a$ [i.e., $R_{n,l}(a) = 0$], the value of k must be chosen such that $z = ka$ corresponds to one of the zeros of $j_l(z)$. Let us denote the n th zero of $j_l(z)$ as $z_{n,l}$. It follows that

$$ka = z_{n,l}, \quad (8.2.5)$$

for $n = 1, 2, 3, \dots$. Hence, from Equation ([e9.29]), the allowed energy levels are

$$E_{n,l} = z_{n,l}^2 \frac{\hbar^2}{2 m a^2}. \quad (8.2.6)$$

The first few values of $z_{n,l}$ are listed in Table [tsph]. It can be seen that $z_{n,l}$ is an increasing function of both n and l .

The first few zeros of the spherical Bessel function $j_l(z)$.

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$l = 0$	3.142	6.283	9.425	12.566
[0.5ex] $l = 1$	4.493	7.725	10.904	14.066
[0.5ex] $l = 2$	5.763	9.095	12.323	15.515
[0.5ex] $l = 3$	6.988	10.417	13.698	16.924
[0.5ex] $l = 4$	8.183	11.705	15.040	18.301

We are now in a position to interpret the three quantum numbers— n , l , and m —which determine the form of the wavefunction specified in Equation ([e9.27]). As is clear from Chapter [sorb], the azimuthal quantum number m determines the number of nodes in the wavefunction as the azimuthal angle ϕ varies between 0 and 2π . Thus, $m = 0$ corresponds to no nodes, $m = 1$ to a single node, $m = 2$ to two nodes, et cetera. Likewise, the polar quantum number l determines the number of nodes in the wavefunction as the polar angle θ varies between 0 and π . Again, $l = 0$ corresponds to no nodes, $l = 1$ to a single node, et cetera. Finally, the radial quantum number n determines the number of nodes in the wavefunction as the radial variable r varies between 0 and a (not counting any nodes at $r = 0$ or $r = a$). Thus, $n = 1$ corresponds to no nodes, $n = 2$ to a single node, $n = 3$ to two nodes, et cetera. Note that, for the case of an infinite potential well, the only restrictions on the values that the various quantum numbers can take are that n must be a positive integer, l must be a non-negative integer, and m must be an integer lying between $-l$ and l . Note, further, that the allowed energy levels ([e9.39]) only depend on the values of the quantum numbers n and l . Finally, it is easily demonstrated that the spherical Bessel functions are mutually orthogonal: that is,

$$\int_0^a j_l(z_{n,l} r/a) j_l(z_{n',l} r/a) r^2 dr = 0 \quad (8.2.7)$$

when $n \neq n'$. Given that the $Y_{l,m}(\theta, \phi)$ are mutually orthogonal (see Chapter [sorb]), this ensures that wavefunctions ([e9.27]) corresponding to distinct sets of values of the quantum numbers n , l , and m are mutually orthogonal.

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8.3: Hydrogen Atom

A hydrogen atom consists of an electron, of charge $-e$ and mass m_e , and a proton, of charge $+e$ and mass m_p , moving in the Coulomb potential

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}, \quad (8.3.1)$$

where \mathbf{r} is the position vector of the electron with respect to the proton. Now, according to the analysis in Section [stwo], this two-body problem can be converted into an equivalent one-body problem. In the latter problem, a particle of mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad (8.3.2)$$

moves in the central potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (8.3.3)$$

Note, however, that because $m_e/m_p \simeq 1/1836$ the difference between m_e and μ is very small. Hence, in the following, we shall write neglect this difference entirely.

Writing the wavefunction in the usual form,

$$\psi(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi), \quad (8.3.4)$$

it follows from Section 1.2 that the radial function $R_{n,l}(r)$ satisfies

$$-\frac{\hbar^2}{2m_e} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R_{n,l} - \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R_{n,l} = 0. \quad (8.3.5)$$

Let $r = az$, with

$$a = \sqrt{\frac{\hbar^2}{2m_e(-E)}} = \sqrt{\frac{E_0}{E}} a_0, \quad (8.3.6)$$

where E_0 and a_0 are defined in Equations ([e9.56]) and ([e9.57]), respectively. Here, it is assumed that $E < 0$, because we are only interested in bound-states of the hydrogen atom. The previous differential equation transforms to

$$\left[\frac{d^2}{dz^2} + \frac{2}{z} \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{\zeta}{z} - 1 \right] R_{n,l} = 0, \quad (8.3.7)$$

where

$$\zeta = \frac{2m_e a e^2}{4\pi\epsilon_0 \hbar^2} = 2\sqrt{\frac{E_0}{E}}. \quad (8.3.8)$$

Suppose that $R_{n,l}(r) = Z(r/a) \exp(-r/a)/(r/a)$. It follows that

$$\left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{\zeta}{z} \right] Z = 0. \quad (8.3.9)$$

We now need to solve the previous differential equation in the domain $z = 0$ to $z = \infty$, subject to the constraint that $R_{n,l}(r)$ be square-integrable.

Let us look for a power-law solution of the form

$$Z(z) = \sum_k c_k z^k. \quad (8.3.10)$$

Substituting this solution into Equation ([e9.48]), we obtain

$$\sum_k c_k \{ k(k-1)z^{k-2} - 2kz^{k-1} - l(l+1)z^{k-2} + \zeta z^{k-1} \} = 0. \quad (8.3.11)$$

Equating the coefficients of z^{k-2} gives the recursion relation

$$c_k [k(k-1) - l(l+1)] = c_{k-1} [2(k-1) - \zeta]. \quad (8.3.12)$$

Now, the power series ([e9.49]) must terminate at small k , at some positive value of k , otherwise $Z(z)$ behaves unphysically as $z \rightarrow 0$ [i.e., it yields an $R_{n,l}(r)$ that is not square integrable as $r \rightarrow 0$]. From the previous recursion relation, this is only possible if $[k_{\min}(k_{\min}-1) - l(l+1)] = 0$, where the first term in the series is $c_{k_{\min}} z^{k_{\min}}$. There are two possibilities: $k_{\min} = -l$ or $k_{\min} = l+1$. However, the former possibility predicts unphysical behavior of $Z(z)$ at $z=0$. Thus, we conclude that $k_{\min} = l+1$. Note that, because $R_{n,l}(r) \simeq Z(r/a)/(r/a) \simeq (r/a)^l$ at small r , there is a finite probability of finding the electron at the nucleus for an $l=0$ state, whereas there is zero probability of finding the electron at the nucleus for an $l>0$ state [i.e., $|\psi|^2 = 0$ at $r=0$, except when $l=0$].

For large values of z , the ratio of successive coefficients in the power series ([e9.49]) is

$$\frac{c_k}{c_{k-1}} = \frac{2}{k}, \quad (8.3.13)$$

according to Equation ([e9.51]). This is the same as the ratio of successive coefficients in the power series

$$\sum_k \frac{(2z)^k}{k!}, \quad (8.3.14)$$

which converges to $\exp(2z)$. We conclude that $Z(z) \rightarrow \exp(2z)$ as $z \rightarrow \infty$. It thus follows that $R_{n,l}(r) \sim Z(r/a) \exp(-r/a)/(r/a) \rightarrow \exp(r/a)/(r/a)$ as $r \rightarrow \infty$. This does not correspond to physically acceptable behavior of the wavefunction, because $\int |\psi|^2 dV$ must be finite. The only way in which we can avoid this unphysical behavior is if the power series ([e9.49]) terminates at some maximum value of k . According to the recursion relation ([e9.51]), this is only possible if

$$\frac{\zeta}{2} = n, \quad (8.3.15)$$

where n is an integer, and the last term in the series is $c_n z^n$. Because the first term in the series is $c_{l+1} z^{l+1}$, it follows that n must be greater than l , otherwise there are no terms in the series at all. Finally, it is clear from Equations ([e9.45]), ([e9.47]), and ([e9.54]) that

$$E = \frac{E_0}{n^2} \quad (8.3.16)$$

and

$$a = n a_0, \quad (8.3.17)$$

where

$$E_0 = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} = -13.6 \text{ eV}, \quad (8.3.18)$$

and

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 5.3 \times 10^{-11} \text{ m}. \quad (8.3.19)$$

Here, E_0 is the energy of so-called *ground-state* (or lowest energy state) of the hydrogen atom, and the length a_0 is known as the *Bohr radius*. Note that $|E_0| \sim \alpha^2 m_e c^2$, where $\alpha = e^2/(4\pi\epsilon_0 \hbar c) \simeq 1/137$ is the dimensionless *fine-structure constant*. The fact that $|E_0| \ll m_e c^2$ is the ultimate justification for our non-relativistic treatment of the hydrogen atom.

We conclude that the wavefunction of a hydrogen atom takes the form

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi). \quad (8.3.20)$$

Here, the $Y_{l,m}(\theta, \phi)$ are the spherical harmonics (see Section [sharm]), and $R_{n,l}(z = r/a)$ is the solution of

$$\left[\frac{1}{z^2} \frac{d}{dz} z^2 \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{2n}{z} - 1 \right] R_{n,l} = 0 \quad (8.3.21)$$

which varies as z^l at small z . Furthermore, the quantum numbers n , l , and m can only take values that satisfy the inequality

$$|m| \leq l < n, \quad (8.3.22)$$

where n is a positive integer, l a non-negative integer, and m an integer.

We expect the stationary states of the hydrogen atom to be orthonormal: that is,

$$\int \psi_{n',l',m'}^* \psi_{n,l,m} dV = \delta_{nn'} \delta_{ll'} \delta_{mm'}, \quad (8.3.23)$$

where dV is a volume element, and the integral is over all space. Of course, $dV = r^2 dr d\Omega$, where $d\Omega$ is an element of solid angle. Moreover, we already know that the spherical harmonics are orthonormal [see Equation ([\[spho\]](#))]: that is,

$$\oint Y_{l',m'}^* Y_{l,m} d\Omega = \delta_{ll'} \delta_{mm'}. \quad (8.3.24)$$

It, thus, follows that the radial wavefunction satisfies the orthonormality constraint

$$\int_0^\infty R_{n',l}^* R_{n,l} r^2 dr = \delta_{nn'}. \quad (8.3.25)$$

The first few radial wavefunctions for the hydrogen atom are listed below:

$$\begin{aligned} R_{1,0}(r) &= \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right), \\ R_{2,0}(r) &= \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right), \\ R_{2,1}(r) &= \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right), \\ R_{3,0}(r) &= \frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \exp\left(-\frac{r}{3a_0}\right), \\ R_{3,1}(r) &= \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \exp\left(-\frac{r}{3a_0}\right), \\ R_{3,2}(r) &= \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right). \end{aligned}$$

These functions are illustrated in Figures [\[coul1\]](#) and [\[coul2\]](#).

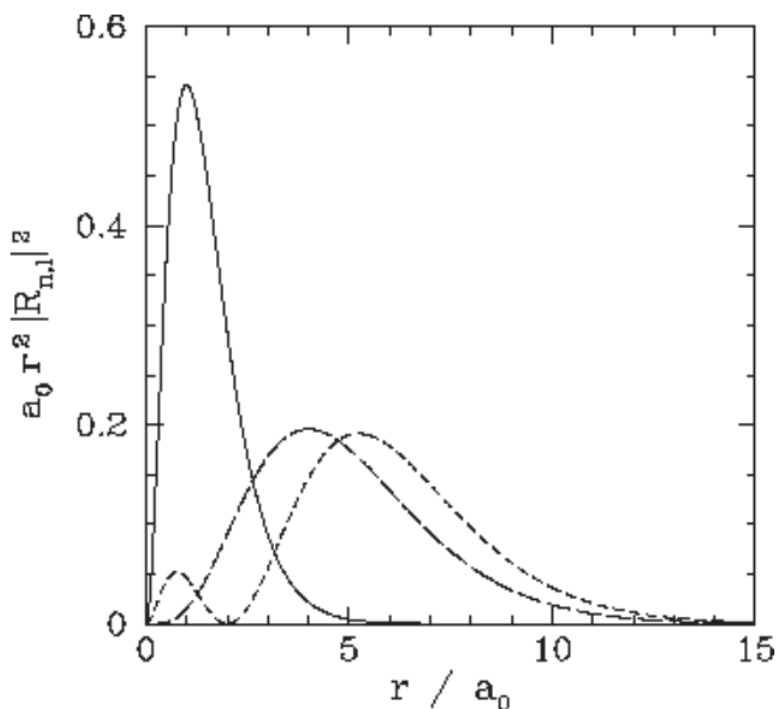


Figure 21: The $a_0 r^2 |R_{n,l}(r)|^2$ plotted as a functions of r/a_0 . The solid, short-dashed, and long-dashed curves correspond to $n, l = 1, 0$, and $2, 0$, and $2, 1$, respectively.

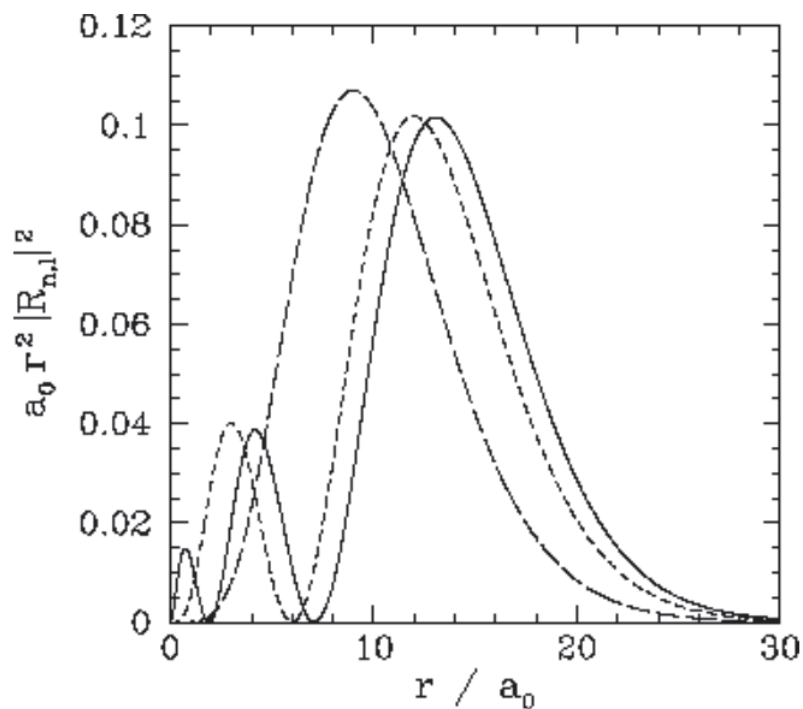


Figure 22: The $a_0 r^2 |R_{n,l}(r)|^2$ plotted as a functions of r/a_0 . The solid, short-dashed, and long-dashed curves correspond to $n, l = 3, 0$, and $3, 1$, and $3, 2$, respectively.

Given the (properly normalized) hydrogen wavefunction ([\[e9.59\]](#)), plus our interpretation of $|\psi|^2$ as a probability density, we can calculate

$$\langle r^k \rangle = \int_0^\infty r^{2+k} |R_{n,l}(r)|^2 dr, \quad (8.3.26)$$

where the angle-brackets denote an expectation value. For instance, it can be demonstrated (after much tedious algebra) that

$$\begin{aligned} \langle r^2 \rangle &= \frac{a_0^2 n^2}{2} [5n^2 + 1 - 3l(l+1)], \\ \langle r \rangle &= \frac{a_0}{2} [3n^2 - l(l+1)], \\ \left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a_0}, \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{(l+1/2)n^3 a_0^2}, \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{l(l+1/2)(l+1)n^3 a_0^3}. \end{aligned}$$

According to Equation ([e9.55]), the energy levels of the bound-states of a hydrogen atom only depend on the radial quantum number n . It turns out that this is a special property of a $1/r$ potential. For a general central potential, $V(r)$, the quantized energy levels of a bound-state depend on both n and l . (See Section 1.3.)

The fact that the energy levels of a hydrogen atom only depend on n , and not on l and m , implies that the energy spectrum of a hydrogen atom is highly degenerate: that is, there are many different states which possess the same energy. According to the inequality ([e9.61]) (and the fact that n , l , and m are integers), for a given value of l , there are $2l+1$ different allowed values of m (i.e., $-l, -l+1, \dots, l-1, l$). Likewise, for a given value of n , there are n different allowed values of l (i.e., $0, 1, \dots, n-1$). Now, all states possessing the same value of n have the same energy (i.e., they are degenerate). Hence, the total number of degenerate states corresponding to a given value of n is

$$1 + 3 + 5 + \dots + 2(n-1) + 1 = n^2. \quad (8.3.27)$$

Thus, the ground-state ($n=1$) is not degenerate, the first excited state ($n=2$) is four-fold degenerate, the second excited state ($n=3$) is nine-fold degenerate, et cetera (Actually, when we take into account the two spin states of an electron, the degeneracy of the n th energy level becomes $2n^2$.)

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8.4: Rydberg Formula

An electron in a given stationary state of a hydrogen atom, characterized by the quantum numbers n , l , and m , should, in principle, remain in that state indefinitely. In practice, if the state is slightly perturbed—for instance, via interaction with a photon—then the electron can make a transition to another stationary state with different quantum numbers. (See Chapter [s13].)

Suppose that an electron in a hydrogen atom makes a transition from an initial state whose radial quantum number is n_i to a final state whose radial quantum number is n_f . According to Equation ([e9.55]), the energy of the electron will change by

$$\Delta E = E_0 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \quad (8.4.1)$$

If ΔE is negative then we would expect the electron to emit a photon of frequency $\nu = -\Delta E/h$. [See Equation ([ee3.15]).] Likewise, if ΔE is positive then the electron must absorb a photon of energy $\nu = \Delta E/h$. Given that $\lambda^{-1} = \nu/c$, the possible wavelengths of the photons emitted by a hydrogen atom as its electron makes transitions between different energy levels are

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad (8.4.2)$$

where

$$R = \frac{-E_0}{hc} = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^3 c} = 1.097 \times 10^7 \text{ m}^{-1}. \quad (8.4.3)$$

Here, it is assumed that $n_f < n_i$. Note that the emission spectrum of hydrogen is quantized: that is, a hydrogen atom can only emit photons with certain fixed set of wavelengths. Likewise, a hydrogen atom can only absorb photons that have the same fixed set of wavelengths. This set of wavelengths constitutes the characteristic emission/absorption spectrum of the hydrogen atom, and can be observed as “spectral lines” using a spectroscope.

Equation ([e9.77]) is known as the *Rydberg formula*. Likewise, R is called the *Rydberg constant*. The Rydberg formula was actually discovered empirically in the nineteenth century by spectroscopists, and was first explained theoretically by Bohr in 1913 using a primitive version of quantum mechanics. Transitions to the ground-state ($n_f = 1$) give rise to spectral lines in the ultraviolet band—this set of lines is called the *Lyman series*. Transitions to the first excited state ($n_f = 2$) give rise to spectral lines in the visible band—this set of lines is called the *Balmer series*. Transitions to the second excited state ($n_f = 3$) give rise to spectral lines in the infrared band—this set of lines is called the *Paschen series*, and so on.

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8.E: Central Potentials (Exercises)

1. A particle of mass m is placed in a finite spherical well:

$$V(r) = \begin{cases} -V_0 & \text{for } r \leq a \\ 0 & \text{for } r > a \end{cases} \quad (8.E.1)$$

with $V_0 > 0$ and $a > 0$. Find the ground-state by solving the radial equation with $l = 0$. Show that there is no ground-state if $V_0 a^2 < \pi^2 \hbar^2 / (8m)$.

2. Consider a particle of mass m in the three-dimensional harmonic oscillator potential $V(r) = (1/2) m \omega^2 r^2$. Solve the problem by separation of variables in spherical coordinates, and, hence, determine the energy eigenvalues of the system.
3. The normalized wavefunction for the ground-state of a hydrogen-like atom (neutral hydrogen, He^+ , Li^{++} , et cetera.) with nuclear charge $Z e$ has the form

$$\psi = A \exp(-\beta r), \quad (8.E.2)$$

where A and β are constants, and r is the distance between the nucleus and the electron. Show the following:

1. $A^2 = \beta^3 / \pi$.
 2. $\beta = Z/a_0$, where $a_0 = (\hbar^2 / m_e) (4\pi \epsilon_0 / e^2)$.
 3. The energy is $E = -Z^2 E_0$ where $E_0 = (m_e / 2 \hbar^2) (e^2 / 4\pi \epsilon_0)^2$.
 4. The expectation values of the potential and kinetic energies are $2E$ and $-E$, respectively.
 5. The expectation value of r is $(3/2) (a_0 / Z)$.
 6. The most probable value of r is a_0 / Z .
4. An atom of tritium is in its ground-state. Suddenly the nucleus decays into a helium nucleus, via the emission of a fast electron that leaves the atom without perturbing the extranuclear electron, Find the probability that the resulting He^+ ion will be left in an $n = 1, l = 0$ state. Find the probability that it will be left in a $n = 2, l = 0$ state. What is the probability that the ion will be left in an $l > 0$ state?
 5. Calculate the wavelengths of the photons emitted from the $n = 2, l = 1$ to $n = 1, l = 0$ transition in hydrogen, deuterium, and positronium.
 6. To conserve linear momentum, an atom emitting a photon must recoil, which means that not all of the energy made available in the downward jump goes to the photon. Find a hydrogen atom's recoil energy when it emits a photon in an $n = 2$ to $n = 1$ transition. What fraction of the transition energy is the recoil energy?

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CHAPTER OVERVIEW

9: Spin Angular Momentum

Broadly speaking, a classical extended object (e.g., the Earth) can possess two different types of angular momentum. The first type is due to the rotation of the object's center of mass about some fixed external point (e.g., the Sun)—this is generally known as *orbital angular momentum*. The second type is due to the object's internal motion—this is generally known as *spin angular momentum* (because, for a rigid object, the internal motion consists of spinning about an axis passing through the center of mass). By analogy, quantum particles can possess both orbital angular momentum due to their motion through space (see Chapter [\[sorb\]](#)), and spin angular momentum due to their internal motion. Actually, the analogy with classical extended objects is not entirely accurate, because electrons, for instance, are structureless point particles. In fact, in quantum mechanics, it is best to think of spin angular momentum as a kind of intrinsic angular momentum possessed by particles. It turns out that each type of elementary particle has a characteristic spin angular momentum, just as each type has a characteristic charge and mass.

[9.1: Spin Operators](#)

[9.2: Spin Space](#)

[9.3: Eigenstates of \$S_z\$ and \$S^2\$](#)

[9.4: Pauli Representation](#)

[9.5: Spin Precession](#)

[9.E: Spin Angular Momentum \(Exercises\)](#)

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9.1: Spin Operators

Because spin is a type of angular momentum, it is reasonable to suppose that it possesses similar properties to orbital angular momentum. Thus, by analogy with Section [s8.2], we would expect to be able to define three operators— S_x , S_y , and S_z —that represent the three Cartesian components of spin angular momentum. Moreover, it is plausible that these operators possess analogous commutation relations to the three corresponding orbital angular momentum operators, L_x , L_y , and L_z . [See Equations ([e8.6])–([e8.8]).] In other words,

$$\begin{aligned} [S_x, S_y] &= i\hbar S_z, \\ [S_y, S_z] &= i\hbar S_x, \\ [S_z, S_x] &= i\hbar S_y. \end{aligned}$$

We can represent the magnitude squared of the spin angular momentum vector by the operator

$$S^2 = S_x^2 + S_y^2 + S_z^2. \quad (9.1.1)$$

By analogy with the analysis in Section [s8.2], it is easily demonstrated that

$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0. \quad (9.1.2)$$

We thus conclude (see Section [smeas]) that we can simultaneously measure the magnitude squared of the spin angular momentum vector, together with, at most, one Cartesian component. By convention, we shall always choose to measure the z -component, S_z .

By analogy with Equation ([e8.13]), we can define raising and lowering operators for spin angular momentum:

$$S_{\pm} = S_x \pm i S_y. \quad (9.1.3)$$

If S_x , S_y , and S_z are Hermitian operators, as must be the case if they are to represent physical quantities, then S_{\pm} are the Hermitian conjugates of one another: that is,

$$(S_{\pm})^{\dagger} = S_{\mp}. \quad (9.1.4)$$

Finally, by analogy with Section [s8.2], it is easily demonstrated that

$$\begin{aligned} S_+ S_- &= S^2 - S_z^2 + \hbar S_z, \\ S_- S_+ &= S^2 - S_z^2 - \hbar S_z, \\ [S_+, S_z] &= -\hbar S_+, \\ [S_-, S_z] &= +\hbar S_-. \end{aligned}$$

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9.2: Spin Space

We now have to discuss the wavefunctions upon which the previously introduced spin operators act. Unlike regular wavefunctions, spin wavefunctions do not exist in real space. Likewise, the spin angular momentum operators cannot be represented as differential operators in real space. Instead, we need to think of spin wavefunctions as existing in an abstract (complex) vector space. The different members of this space correspond to the different internal configurations of the particle under investigation. Note that only the directions of our vectors have any physical significance (just as only the shape of a regular wavefunction has any physical significance). Thus, if the vector χ corresponds to a particular internal state then $c\chi$ corresponds to the same state, where c is a complex number. Now, we expect the internal states of our particle to be superposable, because the superposibility of states is one of the fundamental assumptions of quantum mechanics. It follows that the vectors making up our vector space must also be superposable. Thus, if χ_1 and χ_2 are two vectors corresponding to two different internal states then $c_1\chi_1 + c_2\chi_2$ is another vector corresponding to the state obtained by superposing c_1 times state 1 with c_2 times state 2 (where c_1 and c_2 are complex numbers). Finally, the dimensionality of our vector space is simply the number of linearly independent vectors required to span it (i.e., the number of linearly independent internal states of the particle under investigation).

We now need to define the length of our vectors. We can do this by introducing a second, or *dual*, vector space whose elements are in one to one correspondence with the elements of our first space. Let the element of the second space that corresponds to the element χ of the first space be called χ^\dagger . Moreover, the element of the second space that corresponds to $c\chi$ is $c^*\chi^\dagger$. We shall assume that it is possible to combine χ and χ^\dagger in a multiplicative fashion to generate a real positive-definite number that we shall interpret as the length, or *norm*, of χ . Let us denote this number $\chi^\dagger\chi$. Thus, we have

$$\chi^\dagger\chi \geq 0 \quad (9.2.1)$$

for all χ . We shall also assume that it is possible to combine unlike states in an analogous multiplicative fashion to produce complex numbers. The product of two unlike states χ and χ' is denoted $\chi^\dagger\chi'$. Two states χ and χ' are said to be mutually orthogonal, or independent, if $\chi^\dagger\chi' = 0$.

Now, when a general spin operator, A , operates on a general spin-state, χ , it converts it into a different spin-state that we shall denote $A\chi$. The dual of this state is $(A\chi)^\dagger \equiv \chi^\dagger A^\dagger$, where A^\dagger is the Hermitian conjugate of A (this is the definition of an Hermitian conjugate in spin space). An eigenstate of A corresponding to the eigenvalue a satisfies

$$A\chi_a = a\chi_a. \quad (9.2.2)$$

As before, if A corresponds to a physical variable then a measurement of A will result in one of its eigenvalues. (See Section [smeas].) In order to ensure that these eigenvalues are all real, A must be Hermitian: that is, $A^\dagger = A$. (See Section [seig].) We expect the χ_a to be mutually orthogonal. We can also normalize them such that they all have unit length. In other words,

$$\chi_a^\dagger\chi_{a'} = \delta_{aa'}. \quad (9.2.3)$$

Finally, a general spin state can be written as a superposition of the normalized eigenstates of A : that is,

$$\chi = \sum_a c_a \chi_a. \quad (9.2.4)$$

A measurement of χ will then yield the result a with probability $|c_a|^2$.

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9.3: Eigenstates of S_z and S^2

Because the operators S_z and S^2 commute, they must possess simultaneous eigenstates. (See Section [smeas].) Let these eigenstates take the form [see Equations ([e8.29]) and ([e8.30])]:

$$\begin{aligned} S_z \chi_{s,m_s} &= m_s \hbar \chi_{s,m_s}, \\ S^2 \chi_{s,m_s} &= s(s+1) \hbar^2 \chi_{s,m_s}. \end{aligned}$$

Now, it is easily demonstrated, from the commutation relations ([e10.9]) and ([e10.10]), that

$$S_z (S_+ \chi_{s,m_s}) = (m_s + 1) \hbar (S_+ \chi_{s,m_s}), \quad (9.3.1)$$

and

$$S_z (S_- \chi_{s,m_s}) = (m_s - 1) \hbar (S_- \chi_{s,m_s}). \quad (9.3.2)$$

Thus, S_+ and S_- are indeed the raising and lowering operators, respectively, for spin angular momentum. (See Section [seian].) The eigenstates of S_z and S^2 are assumed to be orthonormal: that is,

$$\chi_{s,m_s}^\dagger \chi_{s',m'_s} = \delta_{ss'} \delta_{m_s m'_s}. \quad (9.3.3)$$

Consider the wavefunction $\chi = S_+ \chi_{s,m_s}$. Because we know, from Equation ([e10.11]), that $\chi^\dagger \chi \geq 0$, it follows that

$$(S_+ \chi_{s,m_s})^\dagger (S_+ \chi_{s,m_s}) = \chi_{s,m_s}^\dagger S_+^\dagger S_+ \chi_{s,m_s} = \chi_{s,m_s}^\dagger S_- S_+ \chi_{s,m_s} \geq 0, \quad (9.3.4)$$

where use has been made of Equation ([e10.7]). Equations ([e10.8]), ([e10.16]), ([e10.17]), and ([e10.20]) yield

$$s(s+1) \geq m_s(m_s+1). \quad (9.3.5)$$

Likewise, if $\chi = S_- \chi_{s,m_s}$ then we obtain

$$s(s+1) \geq m_s(m_s-1). \quad (9.3.6)$$

Assuming that $s \geq 0$, the previous two inequalities imply that

$$-s \leq m_s \leq s. \quad (9.3.7)$$

Hence, at fixed s , there is both a maximum and a minimum possible value that m_s can take.

Let $m_{s \min}$ be the minimum possible value of m_s . It follows that (see Section [slsq])

$$S_- \chi_{s,m_{s \min}} = 0. \quad (9.3.8)$$

Now, from Equation ([e10.7a]),

$$S^2 = S_+ S_- + S_z^2 - \hbar S_z. \quad (9.3.9)$$

Hence,

$$S^2 \chi_{s,m_{s \min}} = (S_+ S_- + S_z^2 - \hbar S_z) \chi_{s,m_{s \min}}, \quad (9.3.10)$$

giving

$$s(s+1) = m_{s \min}(m_{s \min} - 1). \quad (9.3.11)$$

Assuming that $m_{s \min} < 0$, this equation yields

$$m_{s \min} = -s. \quad (9.3.12)$$

Likewise, it is easily demonstrated that

$$m_{s \max} = +s. \quad (9.3.13)$$

Moreover,

$$S_- \chi_{s,-s} = S_+ \chi_{s,s} = 0. \quad (9.3.14)$$

Now, the raising operator S_+ , acting upon $\chi_{s,-s}$, converts it into some multiple of $\chi_{s,-s+1}$. Employing the raising operator a second time, we obtain a multiple of $\chi_{s,-s+2}$. However, this process cannot continue indefinitely, because there is a maximum possible value of m_s . Indeed, after acting upon $\chi_{s,-s}$ a sufficient number of times with the raising operator S_+ , we must obtain a multiple of $\chi_{s,s}$, so that employing the raising operator one more time leads to the null state. [See Equation ([e10.31]).] If this is not the case then we will inevitably obtain eigenstates of S_z corresponding to $m_s > s$, which we have already demonstrated is impossible.

It follows, from the previous argument, that

$$m_{s \max} - m_{s \min} = 2s = k, \quad (9.3.15)$$

where k is a positive integer. Hence, the quantum number s can either take positive integer or positive half-integer values. Up to now, our analysis has been very similar to that which we used earlier to investigate orbital angular momentum. (See Section [orb].) Recall, that for orbital angular momentum the quantum number m , which is analogous to m_s , is restricted to take integer values. (See Section [slz].) This implies that the quantum number l , which is analogous to s , is also restricted to take integer values. However, the origin of these restrictions is the representation of the orbital angular momentum operators as differential operators in real space. (See Section [s8.3].) There is no equivalent representation of the corresponding spin angular momentum operators. Hence, we conclude that there is no reason why the quantum number s cannot take half-integer, as well as integer, values.

In 1940, Wolfgang Pauli proved the so-called *spin-statistics theorem* using relativistic quantum mechanics. According to this theorem, all fermions possess half-integer spin (i.e., a half-integer value of s), whereas all bosons possess integer spin (i.e., an integer value of s). In fact, all presently known fermions, including electrons and protons, possess *spin one-half*. In other words, electrons and protons are characterized by $s = 1/2$ and $m_s = \pm 1/2$.

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