Chapter 1

Spherical Symmetry

Chapter summary: In the first book of *Visual Quantum Mechanics*, we considered mainly one- and two-dimensional systems. Now we turn to the investigation of three-dimensional systems. This chapter is devoted to the very important special case of systems with spherical symmetry.

In the presence of spherical symmetry, the Schrödinger equation has solutions that can be separated into a product of a radial part and an angular part. In this chapter, all possible solutions of the equation for the angular part will be determined once and for all.

We start by discussing symmetry transformations in general. In quantum mechanics, all symmetry transformations may be realized by unitary or antiunitary operators. We define the unitary transformations corresponding to rotations of a particle in $\mathbb{R}^3$. Their self-adjoint generators are the components of the orbital angular momentum $\mathbf{L}$. We describe the angular-momentum commutation relations and discuss their geometrical meaning.

A quantum system is called invariant under a given symmetry transformation if the Hamiltonian commutes with the corresponding unitary operator. A particle moving under the influence of a potential $V(\mathbf{x})$ is a spherically symmetric system (invariant under rotations) if the potential function depends only on the distance r from the origin. Spherical symmetry implies the conservation of the angular momentum and determines the structure of the eigenvalue spectrum of the Hamiltonian (degeneracy). The square L^2 and any component L_k of the angular momentum can be diagonalized simultaneously with the Hamiltonian of a spherically symmetric system. The structure of the common system of eigenvectors can essentially be derived from the angular-momentum commutation relations. In general, the possible eigenvalues of the angular-momentum operators are characterized by integer and half-integer quantum numbers. It turns out, however, that only integer quantum numbers occur in case of the orbital angular momentum.

The eigenvalues and eigenfunctions (spherical harmonics) of the orbital angular momentum are then determined explicitly. The spherical harmonics are the energy eigenfunctions of a particle whose configuration space is a sphere (rigid rotator). The rigid rotator can serve as a simple model for a diatomic molecule in its vibrational ground state.

The restriction of the eigenvalue problem to an angular-momentum eigenspace reduces the Schrödinger equation to an ordinary differential equation. We conclude the chapter with a brief discussion of this so-called radial Schrödinger equation.

1.1. A Note on Symmetry Transformations

1.1.1. Rotations as symmetry transformations

Consider a physical system S in three-dimensions, for example, a few particles moving under the influence of mutual and external forces. The state of S is described with respect to a given coordinate system I in terms of suitably chosen coordinates $\mathbf{x} \in \mathbb{R}^3$. We remind the reader of the following basic assumption.

Homogeneity and isotropy of space:

No point and no direction in $\mathbb{R}^3$ is in any way physically distinguished. Therefore, the behavior of physical systems should not depend on the location of the experimenter's lab or its orientation in space (*principle of relativity*).

In order to test the isotropy of space, we can perform an experiment with the physical system S in the coordinate system I and then repeat the experiment in a rotated coordinate system I'. This can be done in several different ways (see Fig. 1.1).

(1) **Rotate the system and the observer**. This procedure consists in rotating the whole experimental setup: the system S (the particles, the external forces, the devices for preparing the initial state) and the observer (the measurement devices). The isotropy of space means that with respect to the rotated frame of reference I', the system behaves exactly as it did in I. The mathematical description is exactly the same as before. The only difference is that the coordinates now refer to the new coordinate frame I'.

(2) **Rotate the system but not the observer** (*active transformation*). Now the rotated physical system has to be described by an observer in the old coordinate frame I. The motion of the system S will look different, and the observer has to change the mathematical description (in particular, the numerical values of the coordinates). From the point of view of the observer, the rotation changes the state of the system. Hence, the rotation corresponds to a transformation T in the state space of S. We say that the transformation T is a *representation* of the rotation in the state space of the system.

(3) **Rotate the observer but not the system** (*passive transformation*). This procedure is equivalent to procedure (2), but in the mathematical description, T has to be replaced by the inverse transformation. This can be seen as follows: With respect to the new coordinates in I' (that is, from the point of view of a rotated observer), the states of the physical system

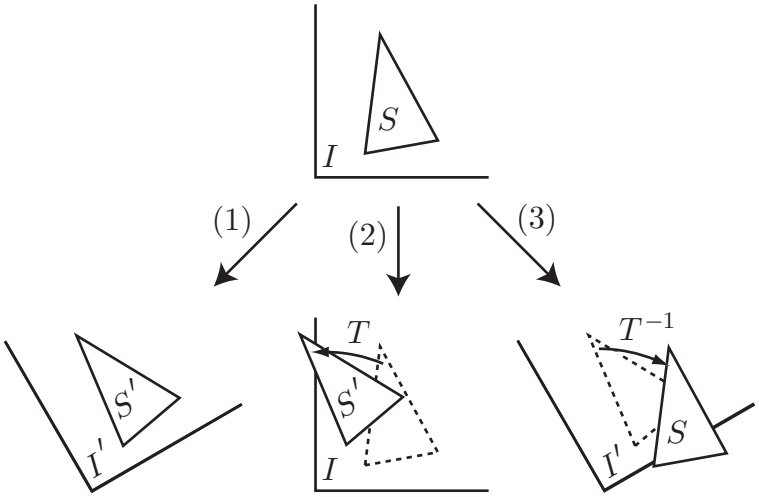


FIGURE 1.1. Symmetry transformations of a physical system. (1) Both the physical system S and the frame of reference I are transformed. The behavior of the system and the mathematical description remain unchanged (principle of relativity). (2) The system is transformed with respect to a fixed coordinate frame I. The states of the system undergo a transformation T. (3) The frame I is transformed, the system is left unchanged. T^{-1} maps the states in I to the states in I'.

appear to be transformed by a mapping T'. Now we can perform an active transformation by T, as described in (2), and we end up with situation (1): Both the physical system and the observer are rotated to I', and by the principle of relativity the behavior in I' is the same as it was in I. Hence, the transformation T' followed by the transformation T gives the identity. A similar argument applies to T followed by T'. We conclude that $T' = T^{-1}$.

In the following, we prefer the "active" point of view expressed in (2). We choose a fixed coordinate system and perform rotations with the objects. Let us assume that an experiment changes the system's initial state A to a certain final state B (with respect to the coordinate frame I). The rotated system has the initial state $A' = T(A)$ (again with respect to I). Repeating the experiment with the rotated system changes its state into B'. What is the relation between the final states B' and B? The principle of relativity states that the rotation does not change the physical laws that govern the system, that is, the mechanism relating the initial and the final state. Hence,

the same relation that holds for the initial states must also hold for the final states: $B' = T(B)$.

If the properties of the system depend on its orientation, then some additional influence would alter the transition to the final state, and B' would in general be different from $T(B)$. The same is true if not everything that is relevant to the behavior of the system is transformed in the same way. For example, one rotates the particles but not the external fields. In this case, the system is subject to a changed external influence, and the final state B' of the rotated system will differ from the rotated final state $T(B)$ of the original system.

The discussion above applies not only to rotations but also to other transformations of the system. In general, a symmetry transformation need not be related to geometry (an example is the exchange of two identical particles, see Section 5.9). Let us try to give a general (but somewhat vague) definition of a symmetry transformation.

A *symmetry transformation* of a physical system is an invertible transformation T that can be applied to all possible states of the system such that all physical relations among the states remain unchanged.

The mathematical description of a symmetry transformation T depends on how the states are described in a physical theory. The next section shows how symmetry transformations are implemented in quantum mechanics.

1.1.2. Symmetry transformations in quantum mechanics

Quantum states are usually described in terms of vectors in a Hilbert space $\mathfrak{H}$. But the correspondence between vectors and states is not one-to-one. For a given vector ψ, all vectors in the one-dimensional subspace (*ray*)

$$[\psi] = \{\lambda\psi \mid \lambda \in \mathbb{C}\} \tag{1.1}$$

represent the same state. Hence, the mathematical objects corresponding to the physical states are rays rather than vectors.

The set of states:

A quantum state of a physical system is a one-dimensional subspace $[\psi]$ of the Hilbert space $\mathfrak{H}$ of the system. The set of all possible quantum states will be denoted by $\hat{\mathfrak{H}}$,

$$\hat{\mathfrak{H}} = \{[\psi] \mid \psi \in \mathfrak{H}\} \tag{1.2}$$

In linear algebra, the set of one-dimensional subspaces of a linear space is called a *projective space*.

EXERCISE 1.1. *If ψ and $\lambda\psi$ both represent the same state, and if ϕ and $\mu\phi$ both represent some other state, why do $\psi+\phi$ and $\lambda\psi+\mu\phi$ in general represent different states?*

In quantum mechanics, all experimentally verifiable predictions can be formulated in terms of transition probabilities. The *transition probability* from a state $[\phi]$ to a state $[\psi]$ is defined by

$$P([\phi]\to[\psi]) = |\langle\psi,\phi\rangle|^2 = P([\psi]\to[\phi]), \tag{1.3}$$

where ϕ and ψ are arbitrary unit vectors in $[\phi]$ and $[\psi]$, respectively. Transition probabilities may be regarded as the basic physically observable relations among quantum states.

Hence, the basic requirement for a symmetry transformation is that the transition probability between any two states should be the same as between the corresponding transformed states.

Definition:

A *symmetry transformation* in quantum mechanics is a transformation of rays that preserves transition probabilities. More precisely, a map $T:\hat{\mathfrak{H}}\to\hat{\mathfrak{H}}$ is a symmetry transformation if it is one-to-one and onto and satisfies

$$P(T[\phi]\to T[\psi]) = P([\phi]\to[\psi]) \quad \text{for all states } [\phi] \text{ and } [\psi]. \tag{1.4}$$

1.1.3. Realizations of symmetry transformations

Instead of working with rays, it is more convenient to describe symmetry transformations in terms of the vectors in the underlying Hilbert space. Consider, for example, a unitary or antiunitary[1] operator U in the Hilbert space $\mathfrak{H}$. The operator U induces a ray transformation in a very natural way. To this purpose, choose a vector ψ representing the state $[\psi]$ and define the ray transformation $\hat{U}$ associated with the operator U by

$$\hat{U}[\psi] = [U\psi]. \tag{1.5}$$

$\hat{U}$ transforms the ray $[\psi]$ into the one-dimensional subspace spanned by the vector $U\psi$.

[1] An *antiunitary operator* A is a one-to-one map from $\mathfrak{H}$ onto $\mathfrak{H}$ which is antilinear, that is, $A(\alpha\psi+\beta\phi)=\overline{\alpha}\,A(\psi)+\overline{\beta}\,A(\phi)$, and satisfies $\langle A\psi, A\phi\rangle = \langle\phi,\psi\rangle$, whereas a unitary transformation U is linear and satisfies $\langle U\psi, U\phi\rangle = \langle\psi,\phi\rangle$.

EXERCISE 1.2. *Show that it follows from the linearity or antilinearity of U that the definition* (1.5) *does not depend on the chosen representative ψ.*

A unitary operator U leaves the scalar product invariant, and hence the corresponding ray transformation $\hat{U}$ must be a symmetry transformation. The same is true for an antiunitary operator, which does not change the absolute value of the scalar product.

The following famous theorem due to Eugene P. Wigner states that unitary and antiunitary operators are in fact the only ways to realize symmetry transformations.

Theorem of Wigner:

Every symmetry transformation T in $\hat{\mathfrak{H}}$ is of the form

$$T = \hat{U}, \quad \text{where } U \text{ is either unitary or antiunitary in } \mathfrak{H}. \tag{1.6}$$

Two operators U_1 and U_2 representing the same symmetry transformation differ at most by a phase factor,

$$U_1 = e^{\mathrm{i}\theta} U_2, \quad \text{for some } \theta \in [0, 2\pi). \tag{1.7}$$

In particular, U_1 and U_2 are either both unitary or both antiunitary.

The investigation and classification of the possible symmetry transformations has played an important role in mathematical physics. For example, according to the special theory of relativity, a relativistic system must admit the Lorentz transformations as symmetry transformations. It must be possible to implement all (proper orthochronous) Lorentz transformations as unitary operators in the corresponding Hilbert space. This imposes some restrictions on the possible choices of Hilbert spaces and scalar products for relativistic systems. In fact, the theory of group representations allows one to classify all possible relativistic wave equations and their associated Hilbert spaces (scalar products).

1.1.4. Invariance of a physical system

A symmetry transformation of the states also induces a similarity transformation of the linear operators in the Hilbert space of a physical system. Let U be a unitary or antiunitary operator representing a given symmetry transformation. Assume that two vectors ϕ and ψ are related by the equation $\phi = A\psi$, where A is a linear operator. After the symmetry transformation, the transformed states are related by

$$U\phi = UA\psi = UAU^{-1}U\psi. \tag{1.8}$$

Here, we have inserted the operator $U^{-1}U = 1$ (unitarity condition). Hence, the corresponding relation between the transformed vectors $U\phi$ and $U\psi$ is given by the linear operator UAU^{-1}. We see that after applying the symmetry transformation, an operator A has to be replaced by the operator UAU^{-1}.

EXERCISE 1.3. *Prove that UAU^{-1} is self-adjoint, whenever A is self-adjoint and U is unitary or antiunitary.*

EXERCISE 1.4. *Explain in what sense the expectation value of an observable is invariant under symmetry transformations.*

Sometimes an observable might be unchanged by a given symmetry transformation. In such a case the operator is said to be invariant. This is often very useful information about the system. A physical system for which the Hamiltonian operator itself is invariant is said to possess a symmetry or invariance.

Definition:

A physical system is *invariant* under a symmetry transformation U (or *symmetric* with respect to U) if the Hamiltonian H of the system has the property

$$H = UHU^{-1}. \tag{1.9}$$

The symmetry transformation U is called an *invariance transformation* of the system represented by H. Invariance transformations are usually very helpful for the solution of the Schrödinger equation. In this chapter, we want to investigate systems that are invariant under rotations (spherically symmetric). But first we have to describe the unitary operators corresponding to rotations, and their self-adjoint generators, the angular-momentum operators.

1.2. Rotations in Quantum Mechanics

1.2.1. Rotation of vectors in $\mathbb{R}^3$

Rotations in the three-dimensional space $\mathbb{R}^3$ are described by orthogonal 3×3 matrices with determinant $+1$. You are perhaps familiar with the following matrix that rotates any vector through an angle α about the x_3-axis of a fixed coordinate system

$$\mathbf{R}(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha \in \mathbb{R}. \tag{1.10}$$

There are similar matrices for rotations about the other coordinate axes. An arbitrary rotation can be most intuitively characterized by a rotation vector $\boldsymbol{\alpha} = \alpha\mathbf{n}$, where α specifies the angle of the rotation, and the unit vector $\mathbf{n}$ gives the axis (here the sense of the rotation is determined by the right-hand rule). We consider only rotation angles α with $-\pi < \alpha \leq \pi$ because the angles $\alpha + 2\pi k$ (with k an integer) may be identified with α. Moreover, a rotation through a negative angle about the axis $\mathbf{n}$ is the same as a rotation through a positive angle about the axis defined by $-\mathbf{n}$. Hence, it is sufficient to consider rotation angles α in the interval $[0, \pi]$.

The elements of the 3×3 rotation matrix $\mathbf{R}(\boldsymbol{\alpha})$ are given by

$$\mathbf{R}(\boldsymbol{\alpha})_{ik} = \delta_{ik}\,\cos\alpha + n_i\,n_k\,(1 - \cos\alpha) - \sum_{m=1}^{3} \epsilon_{ikm}\,n_m\,\sin\alpha. \tag{1.11}$$

Here, we have used the Kronecker delta symbol δ_{ik} and the totally antisymmetric tensor ϵ_{ikm}, which are defined by

$$\delta_{ik} = \begin{cases} 1, & \text{if } i = k, \\ 0, & \text{if } i \neq k. \end{cases} \tag{1.12}$$

$$\epsilon_{ikm} = \begin{cases} 1, & \text{if } (i,k,m) \text{ is a cyclic permutation of } (1,2,3), \\ -1, & \text{for other permutations,} \\ 0, & \text{else.} \end{cases} \tag{1.13}$$

Any rotation matrix has determinant 1 and is orthogonal, that is, the transposed matrix is equal to the inverse:

$$\mathbf{R}(\boldsymbol{\alpha})^{\top} = \mathbf{R}(\boldsymbol{\alpha})^{-1}. \tag{1.14}$$

EXERCISE 1.5. *Show that* (1.35) *can be written as*

$$[L_j, L_k] = \mathrm{i}\hbar \sum_{m=1}^{3} \epsilon_{jkm}\,L_m. \tag{1.15}$$

EXERCISE 1.6. *Show that an orthogonal transformation leaves the Euclidean scalar product invariant.*

EXERCISE 1.7. *What sort of transformation is described by an orthogonal matrix with determinant* -1*?*

EXERCISE 1.8. *Verify that the matrices* $\mathbf{R}(\alpha)$ *given by* (1.10) *form a commutative group under matrix multiplication. In particular:*

$$\mathbf{R}(0) = \mathbf{1}_3, \qquad \mathbf{R}(\alpha)\,\mathbf{R}(\beta) = \mathbf{R}(\alpha + \beta), \quad \alpha, \beta \in \mathbb{R}. \tag{1.16}$$

EXERCISE 1.9. *Prove that rotations around different axis in general do not commute.*

EXERCISE 1.10. *Verify that* (1.11) *reduces to* (1.10) *for* $\mathbf{n} = (0, 0, 1)$.

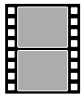
EXERCISE 1.11. *Prove the following formulas for the Kronecker delta and the totally antisymmetric tensor:*

$$\sum_m \epsilon_{klm}\, \epsilon_{ijm} = \delta_{ki}\, \delta_{lj} - \delta_{kj}\, \delta_{li}, \tag{1.17}$$

$$\sum_{l,m} \epsilon_{klm}\, \epsilon_{ilm} = 2\delta_{ki}, \tag{1.18}$$

$$\sum_{k,l,m} \epsilon_{klm}\, \epsilon_{klm} = 6. \tag{1.19}$$

Ψ The set of all rotation matrices $\mathbf{R}(\boldsymbol{\alpha})$ forms a (non-commutative) group. In particular, the composition of any two rotations is again a rotation. Mathematically, the composition of rotations is described by the product of the corresponding rotation matrices. The elements of the rotation group can be characterized by their coordinates $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$. The set of all possible coordinates $\boldsymbol{\alpha}$ forms a sphere with radius π in $\mathbb{R}^3$. Note that the matrix elements depend smoothly (analytically) on the parameters $\boldsymbol{\alpha}$. Such a group is called a Lie group. It is a group and a differentiable manifold at the same time. The rotation group is denoted by $SO(3)$, which means "special orthogonal group in three dimensions" ("special" refers to the fact that the determinant is $+1$). The sphere with radius π in $\mathbb{R}^3$ is a useful coordinate space for the rotation group. Every element of the rotation group is uniquely labeled by a rotation vector inside or on that sphere. The sphere is an image of the group manifold. It has unusual topological properties because two points on the surface of the sphere that are connected by a diameter correspond to the same group element (why?) and have to be identified.



CD 1.1 explores the rotation group. The group manifold is visually represented by the coordinate sphere. Any rotation is visualized by the rotation vector $\boldsymbol{\alpha}$ and by the orientation of a rectangular box to which the rotation is applied. The movies show how the orientation of the box changes as the rotation vector moves through the group manifold on straight lines or on closed circles. As a topological space, the group manifold is not simply connected: there are closed orbits that cannot be continuously deformed into a point.

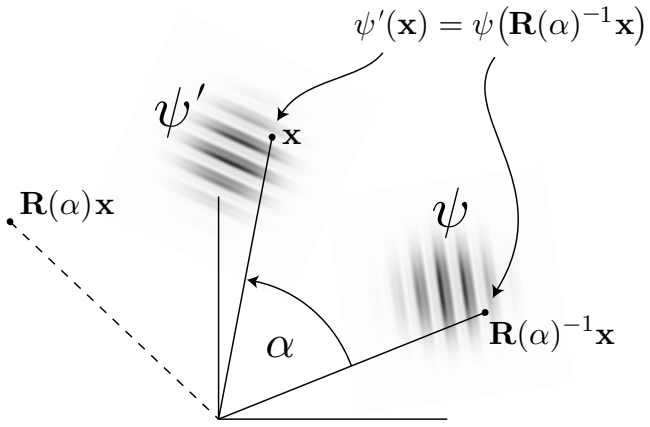


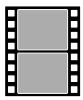
FIGURE 1.2. A rotation $\mathbf{x} \to \mathbf{R}(\alpha)\mathbf{x}$ maps a wave function ψ to $\psi' = U(\alpha)\psi$. The value of the rotated function ψ' at a point $\mathbf{x}$ is given by the value of ψ at the point $\mathbf{R}(\alpha)^{-1}\mathbf{x}$.

1.2.2. Rotation of wave functions

The wave functions considered here are complex-valued functions of the space variable $\mathbf{x}$. Such a function can be rotated by applying a linear operator $U(\boldsymbol{\alpha})$ defined by:

$$\big(U(\boldsymbol{\alpha})\,\psi\big)(\mathbf{x}) = \psi\big(\mathbf{R}(\boldsymbol{\alpha})^{-1}\mathbf{x}\big). \tag{1.20}$$

Here, $\mathbf{R}(\boldsymbol{\alpha})$ is the rotation matrix defined in (1.11). Figure 1.2 explains why we use the inverse rotation matrix in the argument of the function we want to rotate. The operator $U(\boldsymbol{\alpha})$ acts on wave function by a rotation in the literal sense. That is, the "cloud" of complex values that represents the wave function simply gets rotated according to the rotation vector $\boldsymbol{\alpha}$.



The rotations of a box in CD 1.1 can also be interpreted as the rotation of a wave function. Just take the box as an isosurface of some square-integrable wave function ψ, or as the outline of the characteristic function of the box-shaped region. The action of $U(\boldsymbol{\alpha})$ on the wave function ψ just appears as the action of the ordinary rotation $\mathbf{R}(\boldsymbol{\alpha})$ on the box.

For any rotation $\boldsymbol{\alpha}$, the operators $U(\boldsymbol{\alpha})$ are unitary in the Hilbert space $L^2(\mathbb{R}^3)$. The rotations around a fixed axis form a so-called *one-parameter strongly continuous unitary group*. Consider, for example, the rotations about the x_3-axis (see Exercise 1.8). The rotation vector is of the form $\boldsymbol{\alpha} = (0, 0, \alpha)$ with $-\pi \le \alpha \le \pi$. We write $U(\boldsymbol{\alpha}) = U(\alpha)$ and extend the

definition of U to arbitrary real arguments by $U(\alpha \pm 2\pi) = U(\alpha)$. Then we find for all real numbers α and β,

$$U(\alpha)^\dagger = U(\alpha)^{-1} = U(-\alpha), \quad U(0) = \mathbf{1}, \quad U(\alpha)\,U(\beta) = U(\alpha+\beta). \quad (1.21)$$

We refer to Appendix A.6 and to Book One for more details about unitary groups and their self-adjoint generators.

EXERCISE 1.12. *Let $U(\alpha)$, $\alpha \in \mathbb{R}$, describe the rotations around the x_3-axis in space. Using Exercise 1.8, prove that these operators form a unitary group.*

EXERCISE 1.13. *For differentiable functions ψ, and for operators $U(\alpha)$ as in the previous exercise, show that*

$$\frac{\partial}{\partial\alpha}\big(U(\alpha)\,\psi\big)(\mathbf{x})\bigg|_{\alpha=0} = \Big(x_2\,\frac{\partial}{\partial x_1} - x_1\,\frac{\partial}{\partial x_2}\Big)\,\psi(\mathbf{x}) = -\mathrm{i}\,L_3\,\psi(\mathbf{x}). \quad (1.22)$$

Exercise 1.13 above shows that the operator

$$L_3 = \mathrm{i}\hbar\Big(x_2\,\frac{\partial}{\partial x_1} - x_1\,\frac{\partial}{\partial x_2}\Big) \quad (1.23)$$

is the generator of rotations around the x_3-axis. The operator L_3 is the third component of the angular-momentum operator $\mathbf{L}$ defined in Book One (see also (1.30) below).

If ψ is a differentiable wave function (in the domain of L_3), then its dependence on the angle of rotation can be described by the differential equation

$$\mathrm{i}\hbar\,\frac{\partial}{\partial\alpha}\,\psi(\mathbf{x},\alpha) = L_3\,\psi(\mathbf{x},\alpha). \quad (1.24)$$

This equation is completely analogous to the Schrödinger equation for the time evolution. We can write

$$U(\alpha) = \exp\big(-\frac{\mathrm{i}}{\hbar}L_3\,\alpha\big). \quad (1.25)$$

Similar results hold for the rotations about the x_1- and x_2-axes and the components L_1 and L_2 of the angular momentum.

The components L_1, L_2, and L_3 of the angular-momentum operator $\mathbf{L}$ are the infinitesimal generators of the rotations about the x_1, x_2, and x_3-axis.

1.3. Angular Momentum

1.3.1. Angular momentum in classical mechanics

An observable that is intimately connected with rotations—both in classical and in quantum mechanics—is angular momentum. A classical particle that is at the point $\mathbf{x}$ with momentum $\mathbf{p}$ has angular momentum

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} = \begin{pmatrix} x_2 p_3 - x_3 p_2 \\ x_3 p_1 - x_1 p_3 \\ x_1 p_2 - x_2 p_1 \end{pmatrix}. \tag{1.26}$$

The angular-momentum vector is always perpendicular to the plane spanned by the position vector $\mathbf{x}$ and the momentum vector $\mathbf{p}$. In the classical Hamiltonian formalism, the angular momentum generates the canonical transformations describing the rotations of the system. The angular momentum is a constant of motion whenever the equation of motion is invariant under rotations. (This is a special case of *Noether's theorem*.)

CD 1.2 shows the classical angular momentum in various situations with spherical symmetry: circular motion (see also Figure 1.3), motion along a straight line, and the Coulomb motion. The angular momentum vector is perpendicular to the plane of motion and is conserved whenever the coordinate origin coincides with the center of spherical symmetry.

Exercise 1.14. *A classical particle moves with constant velocity on a straight line. Show that its angular momentum is constant in time.*

Exercise 1.15. *A classical particle with mass* m *performs a circular motion around the coordinate origin, as in Figure 1.3. Show that its angular momentum has the value*

$$L = I\omega, \tag{1.27}$$

where $I = \mathrm{m}r^2$ *is the moment of inertia,* r *is the radius of the circle, and* ω *is the angular velocity.*

Exercise 1.16. *Show that the kinetic energy of the particle in the previous exercise can be written as*

$$E = \frac{1}{2\mathrm{m}} \frac{L^2}{r^2} = \frac{L^2}{2I}. \tag{1.28}$$

1.3.2. Angular momentum in quantum mechanics

One can define the angular momentum in quantum mechanics as the operator corresponding to the classical expression (1.26) via the usual substitution rule. According to this heuristic rule, the transition to quantum mechanics

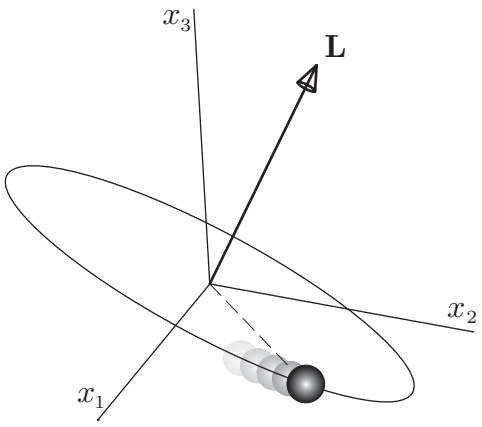


FIGURE 1.3. The angular-momentum vector for a particle moving with constant angular speed on a circle with center at the origin is a conserved quantity. Its magnitude is the product of the radius and the linear momentum, its direction is perpendicular to the plane of motion and determined by the right-hand rule: You are looking in the direction of L, when the motion is clockwise. (CD 1.5.4 is an animated version of this figure.)

is made by substituting linear operators acting on wave functions for the classical quantities $\mathbf{p}$ and $\mathbf{x}$. The classical momentum $\mathbf{p}$ is replaced by the differential operator $\mathbf{p} = -\mathrm{i}\hbar\nabla$, and the position $\mathbf{x}$ is replaced by the operator of multiplication with $\mathbf{x}$,

$$x_i \longrightarrow \text{multiplication by } x_i, \qquad p_i \longrightarrow -\mathrm{i}\hbar\,\frac{\partial}{\partial x_i}. \tag{1.29}$$

An application of this rule leads to the *angular-momentum operator*[2]

$$\mathbf{L} = -\mathrm{i}\hbar\,\mathbf{x}\times\nabla = \mathbf{x}\times\mathbf{p}, \tag{1.30}$$

which is perhaps familiar from Book One. This observable is also called the *orbital angular momentum* in order to distinguish it from other types of angular momentum (to be described later). The components of the "vector operator" $\mathbf{L}$ contain products of position and momentum operators, for example, $L_1 = x_2p_3 - x_3p_2$. The order of the position and momentum operators does not matter here, because x_i and p_j commute for $i \neq j$, and therefore the substitution rule is unambiguous (as explained in Book One).

[2]Usually, we denote the quantum mechanical operators by the same letter as the corresponding classical quantities.

As a generalization of the results in Section 1.2.2, we obtain the following connection between the angular momentum $\mathbf{L}$ and the unitary operators $U(\boldsymbol{\alpha})$ describing rotations in quantum mechanics:

Rotations about a fixed axis:

With a given unit vector $\mathbf{n}$, define for an arbitrary wave function ψ the rotated wave function

$$\psi(\mathbf{x},\alpha) = U(\alpha\mathbf{n})\,\psi(\mathbf{x}) = \psi\big(\mathbf{R}(\alpha\mathbf{n})^{-1}\mathbf{x}\big) \tag{1.31}$$

(rotation through the angle α about the axis defined by the unit vector $\mathbf{n}$). If ψ is differentiable, then it satisfies the equation

$$\mathrm{i}\hbar\,\frac{\partial}{\partial\alpha}\,\psi(\mathbf{x},\alpha) = \mathbf{n}\cdot\mathbf{L}\;\psi(\mathbf{x},\alpha). \tag{1.32}$$

The self-adjoint operator $\mathbf{n}\cdot\mathbf{L}$ is thus the generator of the rotations about a fixed axis, and the unitary group can be written as

$$U(\alpha\mathbf{n}) = \exp\big(-\frac{\mathrm{i}}{\hbar}\,\alpha\,\mathbf{n}\cdot\mathbf{L}\big). \tag{1.33}$$

1.3.3. Commutation relations of the angular-momentum operators

The individual components of the angular momentum $\mathbf{L}$ do not commute. Instead, we find, by an explicit calculation, the following result.

Angular-momentum commutation relations:

The three components of the angular-momentum operator

$$\mathbf{L} = -\mathrm{i}\hbar\,\mathbf{x}\times\nabla \tag{1.34}$$

satisfy the *angular-momentum commutation relations*

$$[L_1, L_2] = \mathrm{i}\hbar L_3, \quad [L_2, L_3] = \mathrm{i}\hbar L_1, \quad [L_3, L_1] = \mathrm{i}\hbar L_2. \tag{1.35}$$

As a consequence of the angular-momentum commutation relations, it is impossible to prepare a state where the values of all three components can be predicted with arbitrary accuracy. The product of the uncertainties of two components is related to the expectation value of the third component, as you can see from Eq. (A.12) in Appendix A. Hence, you have to be very cautious when you try to depict the angular momentum as an arrow as in

classical mechanics. Closely related to the angular momentum in a state ψ is the vector

$$\mathbf{L}_{\rm av} = (\langle L_1\rangle_\psi, \langle L_2\rangle_\psi, \langle L_3\rangle_\psi), \tag{1.36}$$

whose components are the *expectation values* of the three angular-momentum operators. This vector describes a statistical property of an ensemble of quantum systems. For an individual system, the components of $\mathbf{L}$ simply do not have sharp values simultaneously.

EXERCISE 1.17. *Determine the commutation relations between the components of the angular-momentum operator and the components of the position and momentum operators,*

$$[L_3, x_1] = \mathrm{i}\hbar\, x_2, \quad \textit{etc.} \tag{1.37}$$

EXERCISE 1.18. *Compute the angular-momentum commutation relations from the result of the previous exercise, using the algebraic rules for commutators, in particular,* $[A, BC] = B[A, C] + [A, B]C$.

EXERCISE 1.19. *Prove the operator identities*

$$\mathbf{p}\cdot\mathbf{L} = 0, \quad \mathbf{x}\cdot\mathbf{L} = 0, \tag{1.38}$$

$$\mathbf{L}\times\mathbf{L} = \mathrm{i}\hbar\,\mathbf{L}, \tag{1.39}$$

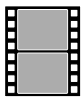
$$[\mathbf{n}\cdot\mathbf{L}, \mathbf{v}] = \mathrm{i}\hbar\,\mathbf{v}\times\mathbf{n}, \tag{1.40}$$

where $\mathbf{n}$ *is a unit vector and* $\mathbf{v}$ *is any of the operators* $\mathbf{x}$, $\mathbf{p}$, *or* $\mathbf{L}$.

The angular-momentum commutation relations are deeply connected with the properties of the rotation group. This is the topic of the next section.

1.3.4. The meaning of the angular-momentum commutation relations

The reason that the components of the angular momentum do not commute lies in the local structure of the group of rotations. It is an elementary observation, that two rotations about different axes do not commute.



CD 1.3.1 shows that the final orientation of a body depends on the order of the rotations applied to it.

Let us now consider the noncommutativity of small rotations. We denote by $\mathbf{R}_x(\alpha)$, $\mathbf{R}_y(\alpha)$, and $\mathbf{R}_z(\alpha)$ the matrices describing rotations about the x-, y-, and z-axis, respectively. The noncommutativity of the rotations about different axis means, for example, that

$$\mathbf{R}_x(\alpha)\mathbf{R}_y(\alpha) \neq \mathbf{R}_y(\alpha)\mathbf{R}_x(\alpha). \tag{1.41}$$

Now, consider the following matrix

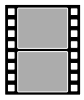
$$\mathbf{M}(\alpha) = \mathbf{R}_x(\alpha)\,\mathbf{R}_y(\alpha) - \mathbf{R}_z(\alpha^2)\,\mathbf{R}_y(\alpha)\,\mathbf{R}_x(\alpha). \tag{1.42}$$

The matrix $\mathbf{M}(\alpha)$ describes the difference between two operations. Each operation is a composition of rotations. We insert the explicit expressions for the rotation matrices and compute the matrix product. Thus, we obtain the explicit form of the matrix $\mathbf{M}(\alpha)$ by a little calculation (made easy with the help of a computer algebra system). Expanding the matrix elements of $\mathbf{M}(\alpha)$ in power series with respect to α (around $\alpha = 0$), we obtain

$$\mathbf{M}(\alpha) = \frac{\alpha^3}{2!} \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & -1 \\ 1 & 1 & 0 \end{pmatrix} + \mathrm{O}(\alpha^4). \tag{1.43}$$

What does this result mean? It means that whenever α is small, then $\mathbf{M}(\alpha)$ is very small. For small angles, the operations in (1.42) are thus comparable:

$$\mathbf{R}_x(\alpha)\,\mathbf{R}_y(\alpha) \approx \mathbf{R}_z(\alpha^2)\,\mathbf{R}_y(\alpha)\,\mathbf{R}_x(\alpha), \tag{1.44}$$
up to terms of order α^3.



CD 1.3.2 shows the difference between the final orientations of a body to which rotations about the x- and y-axes are applied in different order. If the angle α is small enough, then the final orientations differ only by a rotation about the z-axis through an angle α^2.

This property of the rotation group now must also be true for the rotations performed on wave functions. Hence, there has to be a relation analogous to (1.44) between the unitary groups generated by the angular-momentum operators L_1, L_2, and L_3. For small α we expect, by analogy with (1.44), something like

$$\mathrm{e}^{-\mathrm{i}L_1\alpha}\,\mathrm{e}^{-\mathrm{i}L_2\alpha} = \mathrm{e}^{-\mathrm{i}L_3\alpha^2}\,\mathrm{e}^{-\mathrm{i}L_2\alpha}\,\mathrm{e}^{-\mathrm{i}L_1\alpha} + \text{“a small correction”}. \tag{1.45}$$

(We choose units with $\hbar = 1$ in order to simplify the notation.) Formally, we can approximate the exponential functions by the lowest-order terms of the power series

$$\mathrm{e}^{-\mathrm{i}L_1\alpha} = \mathbf{1} - \mathrm{i}L_1\alpha - \frac{1}{2}\,L_1^2\,\alpha^2 + \ldots, \tag{1.46}$$

and similarly for L_2 and L_3. We insert these expansions into (1.45) and multiply everything out. Assuming that α is small, we keep only the terms

up to the order α^2. After cancellation of the terms that are linear in α, the right and left sides of (1.45) become

$$-L_1 L_2\, \alpha^2 = -(\mathrm{i}L_3 + L_2 L_1)\, \alpha^2 \alpha^2 + \mathrm{O}(\alpha^3). \tag{1.47}$$

We conclude that (1.45) is accurate for small α up to terms of order α^3 if and only if the generators L_1, L_2, and L_3 satisfy the commutation relation

$$[L_1, L_2] = \mathrm{i}L_3. \tag{1.48}$$

The angular-momentum commutation relations are an unavoidable consequence of the noncommutativity of rotations.

Ψ The power series expansion of the exponential function converges in the operator norm if the generator is a bounded operator. In the Hilbert space $L^2(\mathbb{R}^3)$, the angular-momentum operators are unbounded, and the expansion (1.46) makes sense only on a dense set of so-called analytic vectors. We omitted these details here for the sake of a short heuristic argument. But the above derivation of the commutation relations is rigorous for unitary representations in finite dimensional Hilbert spaces. See, for example, Section 4.4.2.

1.4. Spherical Symmetry of a Quantum System

1.4.1. Conservation of angular momentum

A physical system with Hamiltonian H is called *invariant under rotations* or *spherically symmetric* whenever H commutes with the unitary rotation operators $U(\boldsymbol{\alpha}) = \exp(-\mathrm{i}\boldsymbol{\alpha}\cdot\mathbf{L}/\hbar)$ defined in (1.20), that is, whenever

$$U(\boldsymbol{\alpha})\, H\, U(\boldsymbol{\alpha})^{-1} = H, \quad \text{for all angles } \boldsymbol{\alpha} = \alpha\mathbf{n}. \tag{1.49}$$

For the quantum systems considered in this book, H commutes with rotations whenever H commutes with the generators of rotations, the angular-momentum operators:

$$[H, L_k] = 0, \quad \text{for } k = 1, 2, 3, \text{ or simply } \quad [H, \mathbf{L}] = 0. \tag{1.50}$$

In the same way that H does not change under rotations, the components of $\mathbf{L}$ do not change under the time evolution,

$$e^{-\mathrm{i}Ht/\hbar}\, \mathbf{L}\, e^{\mathrm{i}Ht/\hbar} = \mathbf{L}, \tag{1.51}$$

that is, the angular momentum is a conserved quantity, a constant of motion.

In classical mechanics, the close connection between symmetries and conservation laws is known as Noether's theorem. Classically, as well as quantum mechanically, the physical quantity that is conserved during the time evolution of a spherically symmetric system is the angular momentum.

Ψ As usual, it is understood that a commutation relation like (1.50) holds on a suitable dense domain that is left invariant by the operators H and L_k. One may take, for example, the set $\mathcal{S}(\mathbb{R}^3)$ of rapidly decreasing smooth functions introduced in Book One, Section 7.7.1. We also note that the commutativity of unbounded self-adjoint operators is actually defined by the commutativity of the unitary groups (see also Book One, Section 6.11). The relation $[H, L_k] = 0$ on a dense domain implies the commutativity only if additional conditions are met, which are usually satisfied for the systems considered here.

1.4.2. Spherically symmetric potentials

If the Hamiltonian is of the particular form $H = H_0 + V(\mathbf{x})$, where H_0 is the free-particle Hamiltonian and $V(\mathbf{x})$ is a potential, then the physical system is spherically symmetric whenever the potential V is spherically symmetric. A potential $V(\mathbf{x})$ is spherically symmetric if it does not depend on the direction of $\mathbf{x}$, but only on the distance of the point $\mathbf{x}$ from the origin. We write

$$V(\mathbf{x}) = V(r), \quad \text{where} \quad r = \sqrt{x_1^2 + x_2^2 + x_3^2} = |\mathbf{x}|. \tag{1.52}$$

Thus, a potential is spherically symmetric if its isosurfaces (the surfaces over which V is constant) are concentric spheres around the origin. The line of action of the corresponding force field

$$\mathbf{F}(\mathbf{x}) = -\nabla V(r) = -\Big(\frac{d}{dr} V(r)\Big)\,\frac{\mathbf{x}}{r} \tag{1.53}$$

always passes through the coordinate origin (see Fig. 1.4), and the strength of the force does not depend on the direction of $\mathbf{x}$.

Ψ To a mathematician, Eq. (1.52) constitutes a slight abuse of notation, which is, however, very common in physics. Two different functions are denoted by the same letter V (one function depends on the three variables $\mathbf{x} = (x_1, x_2, x_3)$, the other is a function of the single variable r). In physics, the notation often emphasizes the physical quantity and not the explicit function describing its dependence on other quantities.

The most important example of a spherically symmetric potential is the Coulomb potential. It describes the electrostatic energy of an electron in the field of an atomic nucleus. The Schrödinger equation for this system will be solved in Chapter 2.

In the presence of spherical symmetry, the Schrödinger equation can be simplified by the separation of variables technique. This technique seeks a solution in the form of a product of three functions, one depending on the radial variable r and the others on angular variables ϑ and φ. In that way,

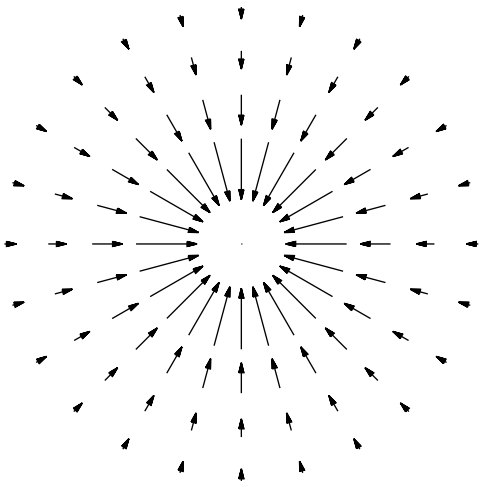
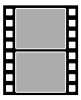


FIGURE 1.4. Example of a spherically symmetric force field. The line of action always passes through the coordinate origin.

the eigenvalue equation (a partial differential equation) splits into three ordinary differential equations, one for each variable. The spherically symmetric potential $V(r)$ enters only the equation for the radial part of the wave function, whereas the equations involving the angular variables ϑ and φ are the same for all systems with spherical symmetry. In this chapter, we are going to determine the possible solutions of the angular equations once and for all.



CD 1.4 presents three-dimensional views of an attractive harmonic oscillator force and a repulsive Coulomb force.

EXERCISE 1.20. *Show that the Hamiltonian for a particle in a spherically symmetric potential commutes with all components of the angular-momentum operator.*

1.4.3. Symmetry and degeneracy

A major step in the solution of the Schrödinger equation is to determine whether the Hamiltonian operator admits eigenstates. An eigenstate or eigenvector of H is a nonzero square-integrable function ψ for which there exists a number E (called an eigenvalue) such that

$$H\,\psi(\mathbf{x}) = E\,\psi(\mathbf{x}). \tag{1.54}$$

An eigenvector of the energy operator leads immediately to a stationary solution of the Schrödinger equation

$$\psi(\mathbf{x}, t) = e^{-\mathrm{i}Et/\hbar}\psi(\mathbf{x}), \tag{1.55}$$

for which the time-dependence is only a phase factor (with absolute value = 1), so that predictions of physical properties do not depend on time.

It is important to note that the invariance under a symmetry transformation may be related to a degeneracy of eigenvalues. An eigenvalue E is called *degenerate* if there are several linearly independent eigenvectors belonging to that eigenvalue. The subspace spanned by all these eigenvectors is called the *eigenspace* belonging to that eigenvalue. The dimension of the eigenspace is called the *degree of degeneracy* by physicists and the *multiplicity* by mathematicians.

Even if a Hamiltonian operator H is invariant under a symmetry transformation U, an eigenvector ψ need not be invariant. However, if ψ is an eigenvector of H, belonging to the eigenvalue E, then the transformed vector $U\psi$ is again an eigenvector of H belonging to the same eigenvalue. This can be seen as follows:

$$HU\psi = (UHU^{-1})U\psi = UH\psi = UE\psi = EU\psi. \tag{1.56}$$

Hence, the eigenspace of E is invariant under the transformation U, that is, $U\psi$ is in that eigenspace whenever ψ is.

Next, we consider the eigenvector ψ belonging to a non-degenerate eigenvalue of H. An eigenvalue is non-degenerate if the corresponding eigenspace is one-dimensional. A symmetry transformation U that leaves the eigenspaces of H invariant must turn ψ into a vector $U\psi$ in the same (one-dimensional) eigenspace. Hence, $U\psi$ is simply a multiple of ψ, and we may write $U\psi = \lambda\psi$ with some complex number λ. But $|\lambda| = 1$ because U is unitary. An eigenstate belonging to a non-degenerate eigenvalue is invariant (up to a phase factor). In the case of spherical symmetry this means that for non-degenerate energies the corresponding eigenfunctions are spherically symmetric.

Likewise, the eigenspaces of the angular-momentum operators (the *angular-momentum subspaces*) are invariant under the time evolution generated by a spherically symmetric Hamiltonian H. The operator H leaves the eigenspace of each of the angular-momentum operators invariant. It can be a major simplification to solve the eigenvalue problem for H in an eigenspace of the angular-momentum operators. Thus, our next task is the investigation of the possible angular-momentum eigenvalues and the associated eigenspaces. This is done in the next section.

1.5. The Possible Eigenvalues of Angular-Momentum Operators

In this section, we present a purely algebraic approach to the solution of the eigenvalue problem for the angular-momentum operators. For simplicity, we work with units where $\hbar$ has the numerical value 1. We consider a set of three symmetric operators J_1, J_2, and J_3 that satisfy the commutation relations

$$[J_1, J_2] = \mathrm{i}J_3, \quad [J_2, J_3] = \mathrm{i}J_1, \quad [J_3, J_1] = \mathrm{i}J_2. \tag{1.57}$$

A lot can be learned by studying these relations. Because of these relations, we cannot hope to find simultaneous eigenvectors belonging to nonzero eigenvalues.

Indeed, assume that ψ is a simultaneous eigenvector of, say, J_1 and J_2. Let $J_1\psi = m_1\psi$ and $J_2\psi = m_2\psi$. Then we find immediately that

$$\mathrm{i}J_3\psi = [J_1, J_2]\psi = (m_1m_2 - m_2m_1)\psi = 0.$$

Hence,

$$J_3(J_1 + \mathrm{i}J_2)\psi = [J_3, J_1]\psi + \mathrm{i}[J_3, J_2]\psi = (\mathrm{i}J_2 - J_1)\psi = (\mathrm{i}m_2 - m_1)\psi,$$

and

$$J_3(J_1 + \mathrm{i}J_2)\psi = J_3(m_1 + \mathrm{i}m_2)\psi = (m_1 + \mathrm{i}m_2)J_3\psi = 0.$$

Hence, $\mathrm{i}m_2 - m_1 = 0$, and because the eigenvalues of symmetric operators are always real, this implies that $m_1 = m_2 = 0$. We conclude that there are no nontrivial simultaneous eigenvectors belonging to nonzero eigenvalues.

The square of the angular-momentum vector $\mathbf{J} = (J_1, J_2, J_3)$, that is, the operator

$$J^2 = J_1^2 + J_2^2 + J_3^2 \tag{1.58}$$

commutes with all components J_k,

$$[J^2, J_k] = 0, \quad \text{for } k = 1, 2, 3. \tag{1.59}$$

Hence, we could try to find simultaneous eigenvectors for the operator J^2 and any one of the components, say J_3. We are going to prove the following theorem.

THEOREM 1.1. *Assume that there is a simultaneous eigenvector of the commuting operators J^2 and J_3. Then the eigenvalue of J^2 is $j(j+1)$ where j is one of the numbers $0, \frac{1}{2}, 1, \frac{3}{2}, 2 \ldots$. Moreover, there are $2j+1$ eigenvectors $\psi_{j,m}$ of J_3, such that*

$$J^2\,\psi_{j,m} = j(j+1)\,\psi_{j,m}, \qquad J_3\,\psi_{j,m} = m\,\psi_{j,m}, \tag{1.60}$$

for $m = -j, -j+1, \ldots, j-1, j$.

PROOF. We first define the operators

$$J_\pm = J_1 \pm \mathrm{i} J_2 \tag{1.61}$$

and note the following commutation properties

$$[J_3, J_\pm] = \pm J_\pm, \qquad [J^2, J_\pm] = 0. \tag{1.62}$$

The operators $J_\pm$ are not self-adjoint, but formally adjoint to each other,

$$J_+^\dagger = J_-, \qquad J_-^\dagger = J_+. \tag{1.63}$$

Their products can be expressed in terms of J^2 and J_3,

$$J_+ J_- = J^2 - J_3^2 + J_3, \qquad J_- J_+ = J^2 - J_3^2 - J_3. \tag{1.64}$$

Now, let us assume that there exists a simultaneous eigenvector ψ_m^λ belonging to eigenvalues λ for J^2 and m for J_3:

$$J^2\, \psi_m^\lambda = \lambda\, \psi_m^\lambda, \qquad J_3\, \psi_m^\lambda = m\, \psi_m^\lambda. \tag{1.65}$$

We can always multiply the eigenvector with a suitable complex constant, and therefore we may assume that ψ_m^λ is normalized,

$$\|\psi_m^\lambda\|^2 = \langle \psi_m^\lambda, \psi_m^\lambda \rangle = 1. \tag{1.66}$$

Next, consider the state $\psi_+ = J_+ \psi_m^\lambda$. Whenever ψ_+ is not the zero vector, it is an eigenstate of J_3 belonging to the eigenvalue $m+1$. This follows from the commutation property (1.62):

$$\begin{aligned} J_3\, \psi_+ &= J_3 J_+\, \psi_m^\lambda = (J_+ J_3 + [J_3, J_+])\, \psi_m^\lambda = (J_+ J_3 + J_+)\, \psi_m^\lambda \\ &= (J_+ m + J_+)\, \psi_m^\lambda = (m+1)\, J_+\, \psi_m^\lambda \\ &= (m+1)\, \psi_+. \end{aligned} \tag{1.67}$$

The vector ψ_+ is still an eigenvector of J^2 belonging to the same eigenvalue λ, because J_+ commutes with J^2:

$$J^2\, \psi_+ = J^2 J_+\, \psi_m^\lambda = J_+ J^2\, \psi_m^\lambda = J_+\, \lambda\, \psi_m^\lambda = \lambda\, J_+\, \psi_m^\lambda = \lambda\, \psi_+. \tag{1.68}$$

An analogous observation holds for the state $J_- \psi_m^\lambda$. Either this vector is the zero vector, or it is a simultaneous eigenstate with eigenvalues $m-1$ for J_3 and λ for J^2. In order to determine the norm of the vectors $J_\pm \psi_m^\lambda$, we perform the following calculation

$$\begin{aligned} \|J_\pm \psi_m^\lambda\|^2 &= \langle J_\pm\, \psi_m^\lambda\,,\, J_\pm\, \psi_m^\lambda \rangle \\ &= \langle \psi_m^\lambda\,,\, J_\mp\, J_\pm\, \psi_m^\lambda \rangle && \text{by (1.63)} \\ &= \langle \psi_m^\lambda\,,\, (J^2 - J_3^2 \mp J_3)\, \psi_m^\lambda \rangle && \text{by (1.64)} \\ &= \lambda - m^2 \mp m. \end{aligned} \tag{1.69}$$

From $\|J_\pm \psi_m^\lambda\|^2 \geq 0$ it follows immediately that

$$\lambda \geq m^2 \pm m = m(m \pm 1). \tag{1.70}$$

Moreover, we find that $J_+ \psi_{j,m} = 0$ if and only if $\lambda - m^2 - m = 0$, that is,

$$J_+ \psi_m^\lambda = 0 \quad \text{if and only if} \quad \lambda = m(m+1), \tag{1.71}$$

and similarly,

$$J_- \psi_m^\lambda = 0 \quad \text{if and only if} \quad \lambda = m(m-1). \tag{1.72}$$

Now it is easy to determine the possible values for λ and m. Whenever we have a simultaneous eigenvector of J^2 and J_3 with eigenvalues λ and m, we can also find eigenvectors belonging to eigenvalues $m+1$, $m+2$, and so forth, of J_3. These eigenvectors are obtained by successive application of the *ladder operator* J_+. All new eigenvectors belong to the same eigenvalue λ of J^2. This process of creating new eigenvectors will stop as soon as we reach a maximal value of m, say $m_{\max}$ for which $J_+ \psi_{m_{\max}}^\lambda = 0$, or equivalently, for which

$$\lambda = m_{\max}(m_{\max}+1). \tag{1.73}$$

It is crucial to observe that such a maximal value $m_{\max}$ must exist: Otherwise, we could raise the eigenvalue of J_3 indefinitely until the inequality (1.70) would be violated, thus giving a contradiction.

Similarly, using the ladder operator J_-, we can lower the eigenvalue m until we reach a minimum value $m_{\min}$ for which we must have

$$\lambda = m_{\min}(m_{\min}-1). \tag{1.74}$$

Combining Eqs. (1.73) and (1.74) we find

$$(m_{\max} - m_{\min} + 1)(m_{\max} + m_{\min}) = 0. \tag{1.75}$$

Here, because of $m_{\max} \geq m_{\min}$, only the second factor can be zero, that is, $m_{\min} = -m_{\max}$. Because we can get from $m_{\min}$ to $m_{\max}$ in integer steps (by applying the operator J_+ to the corresponding eigenvectors), we find that $m_{\max} - m_{\min} = 2m_{\max}$ must be a non-negative integer. Writing $m_{\max} = j$ we find that the only allowed values of j are $0, \frac{1}{2}, 1, \frac{3}{2}, 2$, and so forth. From (1.73) we see that $\lambda = j(j+1)$.

Finally, write $\psi_{j,m}$ instead of ψ_m^λ. □

Figure 1.5 visualizes the spectrum of possible simultaneous eigenvalues of J^2 and J_3 according to Theorem 1.1.

THEOREM 1.2. *For a fixed j, all the $2j+1$ eigenvalues of J_3 have the same multiplicity k (which might be infinite). The eigenspace of J^2 belonging to the eigenvalue $j(j+1)$ is therefore $k(2j+1)$-dimensional. This space is invariant under the action of the operators J_1, J_2, and J_3.*

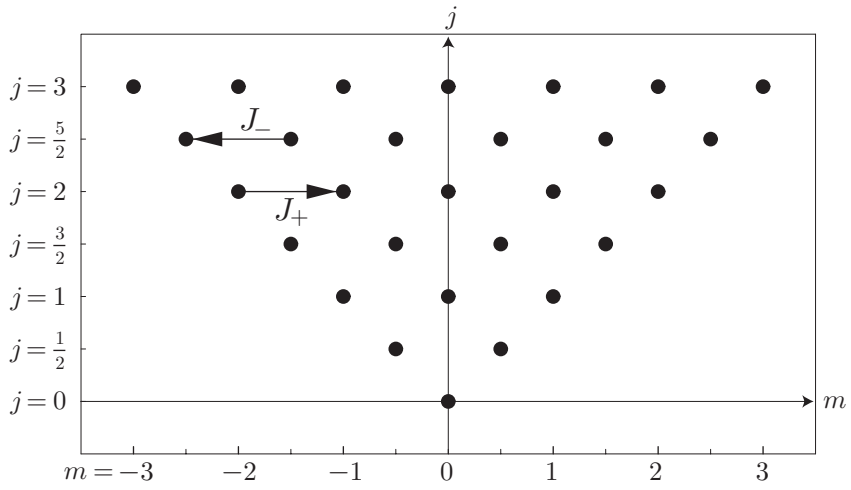


FIGURE 1.5. The possible values (j, m) for the operators J^2 and J_3 (with $j \leq 3$). Each point represents a simultaneous eigenvector of J^2 and J_3. The ladder operators $J_\pm$ let you jump from one point to the next in the horizontal direction, that is, within an eigenspace of J^2.

PROOF. Assume that there are two orthogonal vectors $\psi^{(1)}_{j,m}$ and $\psi^{(2)}_{j,m}$ both of which belong to the eigenvalues $j(j+1)$ of J^2 and m of J_3. Assume $m < j$. Then $J_+ \psi^{(1)}_{j,m}$ and $J_+ \psi^{(2)}_{j,m}$ are both nonzero vectors, and

$$\begin{aligned}\langle J_+ \psi^{(1)}_{j,m}\,,\, J_+ \psi^{(2)}_{j,m}\rangle &= \langle \psi^{(1)}_{j,m}\,,\, J_- J_+ \psi^{(2)}_{j,m}\rangle \\ &= \langle \psi^{(1)}_{j,m}\,,\, (J^2 - J_3^2 - J_3)\, \psi^{(2)}_{j,m}\rangle \\ &= \big(j(j+1) - m^2 - m\big)\langle \psi^{(1)}_{j,m}\,,\, \psi^{(2)}_{j,m}\rangle = 0. \end{aligned} \tag{1.76}$$

And, similarly, for $m > -j$ we find

$$\langle J_- \psi^{(1)}_{j,m}\,,\, J_- \psi^{(2)}_{j,m}\rangle = 0. \tag{1.77}$$

You can see that the orthogonality is preserved by the ladder operators J_+ and J_-. Hence, if there are precisely k orthogonal states for some eigenvalue m, then there are precisely k orthogonal states for all $m = -j, -j+1, \ldots, j-1, j$. For a given j there are $2j+1$ different values of m. Because the eigenvectors belonging to different eigenvalues of a symmetric operator are orthogonal, eigenvectors with different eigenvalues m are orthogonal. Therefore, the subspace spanned by all the eigenvectors belonging to the eigenvalue $j(j+1)$ of the operator J^2 is $k(2j+1)$-dimensional. This

eigenspace is clearly left invariant by the operators J^2, J_3, and $J_\pm$ (an operator leaves a subspace invariant if the operator maps any vector of this subspace to a vector in the same subspace). Hence, the eigenspace of J^2 is also left invariant by the operators J_1 and J_2, which can be written as linear combinations of J_+ and J_-. □

Our considerations in this section have shown that the possible eigenvalues of the angular momentum are characterized by *angular-momentum quantum numbers* j and m that can have integer and half-integer values. In the next section, we will find that for the *orbital* angular momentum $\mathbf{L} = \mathbf{x} \times \mathbf{p}$ only integer values can occur. Angular-momentum operators with half-integer quantum numbers are nevertheless important for describing the spin of elementary particles (see Chapter 3).

EXERCISE 1.21. *Verify the commutation relations*

$$[J^2, J_k] = 0, \quad \textit{for } k = 1, 2, 3. \tag{1.78}$$

EXERCISE 1.22. *Define the three* 2×2*-matrices*

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.79}$$

These matrices are called the Pauli matrices. They are symmetric and hence define self-adjoint operators in the Hilbert space $\mathbb{C}^2$*. Verify that the operators* $S_j = (1/2)\sigma_j$*,* $j = 1, 2, 3$*, satisfy the angular-momentum commutation relations* (1.57)*. Show that the only eigenvalue of* $S^2 = S_1^2 + S_2^2 + S_3^2$ *is* $s(s+1)$ *with* $s = 1/2$*.*

EXERCISE 1.23. *Show that if the operators* J_1*,* J_2*,* J_3 *satisfy the commutation relations* $[J_1, J_2] = \mathrm{i}\hbar J_3$*, and so forth, then the possible eigenvalues of* J^2 *are* $\hbar^2 j(j+1)$ *with* $j = 0, \frac{1}{2}, 1, \ldots$*, and for each* j *the possible eigenvalues of* J_3 *are* $\hbar m$ *with* $m = -j, -j+1, \ldots, j$*.*

EXERCISE 1.24. *Let* $\phi_{j,j}$ *be a simultaneous eigenvector of* J^2 *and* J_3*, with the maximal* $m = j$*. Assume that* $\phi_{j,j}$ *is normalized,* $\|\phi_{j,j}\| = 1$*. Define*

$$\phi_{j,m-1} = \frac{1}{\sqrt{j(j+1) - m(m-1)}}\, J_-\, \phi_{j,m}, \quad m = j, j-1, \ldots, -j+1. \tag{1.80}$$

Show that the vectors $\phi_{j,m}$*,* $m = -j, -j+1, \ldots, j$ *are normalized simultaneous eigenvectors of* J^2 *and* J_3*.*

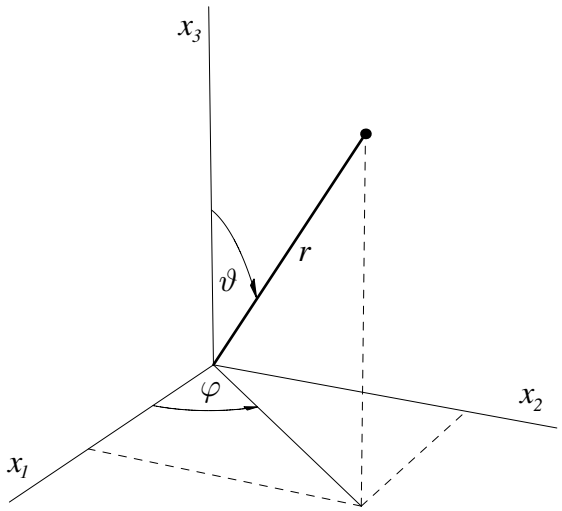


FIGURE 1.6. Spherical coordinates on $\mathbb{R}^3$. Instead of giving the Cartesian coordinates (x_1, x_2, x_3), we can also specify the position of a point in $\mathbb{R}^3$ by spherical coordinates (r, ϑ, φ). See also CD 1.5.

1.6. Spherical Harmonics

1.6.1. Spherical coordinates

In order to determine the eigenvalues and eigenfunctions of the orbital angular-momentum operators L^2 and L_3, it is convenient to express them as differential operators in spherical coordinates. On $\mathbb{R}^3 \setminus \{0\}$ (three-dimensional space without the origin) we can introduce spherical coordinates (r, ϑ, φ) as in Figure 1.6.

In a spherical coordinate system, the position of a point is specified by its distance r from the origin, its *polar angle* ϑ and its *azimuthal angle* φ. The Cartesian coordinates can be expressed in terms of the spherical coordinates as follows

$$\begin{aligned} x_1(r, \vartheta, \varphi) &= r \, \sin\vartheta \, \cos\varphi, \\ x_2(r, \vartheta, \varphi) &= r \, \sin\vartheta \, \sin\varphi, \\ x_3(r, \vartheta, \varphi) &= r \, \cos\vartheta. \end{aligned} \tag{1.81}$$

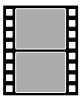
It is often necessary to invert this formula, that is, to express the spherical coordinates of a point in terms of its Cartesian coordinates

$$\begin{aligned} r(x_1, x_2, x_3) &= |\mathbf{x}| \in (0, \infty), \\ \vartheta(x_1, x_2, x_3) &= \arccos(x_3/|\mathbf{x}|) \in [0, \pi], \\ \varphi(x_1, x_2, x_3) &= \arctan(x_1, x_2) \in (-\pi, \pi]. \end{aligned} \tag{1.82}$$

Here, the function arctan of two variables is defined as

$$\arctan(x_1, x_2) \equiv \pi\, \theta(-x_1)\, \mathrm{sgn}(x_2) + \arctan(x_2/x_1). \tag{1.83}$$

(This definition has to be extended by continuity for $x_1 \to 0$ and $x_2 \neq 0$.) Here, $\mathrm{sgn}(x)$ is the sign of x, and θ is the step function ($\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x \leq 0$).



CD 1.5.1 is an animated view of a point in a Cartesian coordinate system similar to Figure 1.6. CD 1.5.2–4 deal with the uniform motion of a free particle and the circular motion of the rigid rotator and discuss the description of these systems in terms of spherical coordinates.

At each point in $\mathbb{R}^3 \setminus \{0\}$, we can define the unit vectors in the directions of the spherical coordinate lines (these are the curves on which two of the three spherical coordinates are held fixed)

$$\begin{aligned} \mathbf{e}_r &= (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta) = \frac{\mathbf{x}}{r}, \\ \mathbf{e}_\vartheta &= (\cos\vartheta\cos\varphi, \cos\vartheta\sin\varphi, -\sin\vartheta) = \frac{\partial \mathbf{e}_r}{\partial\vartheta}, \\ \mathbf{e}_\varphi &= (-\sin\varphi, \cos\varphi, 0) = \frac{1}{\sin\vartheta}\frac{\partial \mathbf{e}_r}{\partial\varphi}. \end{aligned} \tag{1.84}$$

Exercise 1.25. *Using* (1.84)*, verify the following formulas:*

$$\begin{aligned} &\mathbf{e}_r \cdot \mathbf{e}_\vartheta = 0, \quad && \mathbf{e}_r \cdot \mathbf{e}_r = 1, \quad && \mathbf{e}_r \times \mathbf{e}_\vartheta = \mathbf{e}_\varphi, \\ &\mathbf{e}_\vartheta \cdot \mathbf{e}_\varphi = 0, \quad && \mathbf{e}_\vartheta \cdot \mathbf{e}_\vartheta = 1, \quad && \mathbf{e}_\vartheta \times \mathbf{e}_\varphi = \mathbf{e}_r, \\ &\mathbf{e}_\varphi \cdot \mathbf{e}_r = 0, \quad && \mathbf{e}_\varphi \cdot \mathbf{e}_\varphi = 1, \quad && \mathbf{e}_\varphi \times \mathbf{e}_r = \mathbf{e}_\vartheta. \end{aligned} \tag{1.85}$$

At each point, the three unit vectors thus form a right-handed, orthonormal system.

Now, if $\psi(x_1, x_2, x_3)$ is a wave function in Cartesian coordinates, then the same function in spherical coordinates is obtained just by inserting the expressions (1.81) into the arguments of ψ

$$\phi(r, \vartheta, \varphi) = \psi\big(x_1(r, \vartheta, \varphi), x_2(r, \vartheta, \varphi), x_3(r, \vartheta, \varphi)\big) \tag{1.86}$$

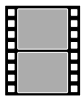
The collection of formulas is completed by giving the expression for the gradient operator ∇ in spherical coordinates

$$\hat{\nabla} = \mathbf{e}_r \frac{\partial}{\partial r} + \frac{1}{r}\left(\mathbf{e}_\vartheta \frac{\partial}{\partial \vartheta} + \mathbf{e}_\varphi \frac{1}{\sin\vartheta}\frac{\partial}{\partial \varphi}\right). \tag{1.87}$$

This formula has to be understood as follows. The gradient of a function can either be evaluated in Cartesian coordinates or in spherical coordinates. At some point (x_1, x_2, x_3) corresponding to (r, ϑ, φ) we have

$$\nabla\psi(x_1, x_2, x_3) = \hat{\nabla}\phi(r, \vartheta, \varphi), \tag{1.88}$$

with ϕ and ψ being related as in (1.86).



The spherical coordinate space is a three-dimensional space where the coordinate axes describe the r-, ϑ-, and φ-coordinates of a point in $\mathbb{R}^3$. CD 1.6 visualizes the familiar examples of linear and circular motion, which look rather unfamiliar in the spherical coordinate space.

$\boxed{\Psi}$ The transition to spherical coordinates, that is, the mapping $U : \psi \to \phi$ defined in (1.86) is a unitary transformation from the Hilbert space $L^2(\mathbb{R}^3)$ to the Hilbert space $L^2([0,\infty) \times S^2, dV)$. Here, S^2 denotes the two-dimensional surface of the unit sphere, and $dV = r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$ is the volume element in spherical coordinates. The points in $[0,\infty) \times S^2$ have the coordinates (r, ϑ, φ), and integration has to be done with respect to the volume element in spherical coordinates. It follows from the usual rules of variable substitution in an integral that

$$\int_{\mathbb{R}^3} |\psi(x_1, x_2, x_3)|^2\, d^3x = \int_0^\infty \int_{S^2} |\phi(r, \vartheta, \varphi)|^2\, r^2\, \sin\vartheta\, dr\, d\vartheta\, d\varphi. \tag{1.89}$$

This means that the norm of ψ in $L^2(\mathbb{R}^3)$ is equal to the norm of ϕ in $L^2([0,\infty) \times S^2, dV)$ (this is the unitarity of U). As a consequence, the operators ∇ and $\hat{\nabla}$ are unitarily equivalent, that is, $\hat{\nabla} = U\nabla U^{-1}$. In the following, we always put a hat on an operator in spherical coordinates in order to indicate that it acts on functions $\phi(r, \vartheta, \varphi)$.

1.6.2. Angular momentum in spherical coordinates

With the results of the previous section, it is easy to derive the expressions of the angular-momentum operators in spherical coordinates. Using the formulas from Exercise 1.25, we obtain

$$\hat{\mathbf{L}} = r\mathbf{e}_r \times (-\mathrm{i}\,\hbar\hat{\nabla}) = \mathrm{i}\hbar\left(\mathbf{e}_\vartheta \frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi} - \mathbf{e}_\varphi \frac{\partial}{\partial\vartheta}\right), \tag{1.90}$$

$$\hat{L}^2 = -\frac{\hbar^2}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) - \frac{\hbar^2}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}. \tag{1.91}$$

Again, the hat ($\hat{}$) simply indicates that the operator acts on wave functions in spherical coordinates. We have

$$\mathbf{L}\psi(x_1, x_2, x_3) = \hat{\mathbf{L}}\phi(r, \vartheta, \varphi), \tag{1.92}$$

where ϕ is the function ψ expressed in spherical coordinates as in (1.86). In particular, the operators L^2 and $\hat{L}^2$ have the same eigenvalues (as well as L_3 and $\hat{L}_3$). The angular-momentum operators fulfill the angular-momentum commutation relations. Hence, Theorem 1.1 in Section 1.5 shows that the possible eigenvalues of $\hat{L}^2$ are among the numbers $\hbar^2\ell(\ell+1)$, where ℓ is a non-negative integer or half-integer. For each eigenvalue of $\hat{L}^2$, the third component has the eigenvalues $\hbar m$ with $m = -\ell, -\ell+1, \ldots, \ell$.

The expression for L_3 in spherical coordinates is particularly simple. Just insert the third Cartesian component of $\mathbf{e}_\vartheta$ and $\mathbf{e}_\varphi$ (see Eq. (1.84)) into (1.90):

$$\hat{L}_3 = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}. \tag{1.93}$$

This expression is already familiar from the two-dimensional situation described in Book One, Section 8.8.

Now we can see that $\hat{L}_3$ cannot have half-integer eigenvalues m. The domain of the differential operator $\hat{L}_3$ consists of continuous functions. As a function of the azimuthal angle φ, any eigenfunction of $\hat{L}_3$ must therefore be a periodic function:

$$\phi(r, \vartheta, \varphi + 2\pi) = \phi(r, \vartheta, \varphi). \tag{1.94}$$

Denoting the eigenvalue of $\hat{L}_3$ by m, the eigenvalue equation reads

$$\hat{L}_3\phi = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}\,\phi = \hbar m\,\phi \tag{1.95}$$

so that the φ-dependence of ϕ must be described by $\exp(\mathrm{i}m\varphi)$, which is periodic with period 2π if and only if m is an integer.

The considerations in Section 1.5 thus also exclude the possibility that L^2 has half-integer eigenvalues. Only the numbers $\hbar^2\ell(\ell+1)$ with integer ℓ can occur as eigenvalues of L^2. Below, we are going to show that simultaneous eigenfunctions of L^2 and L_3 indeed exist for all non-negative integers ℓ. Hence, we obtain the following result:

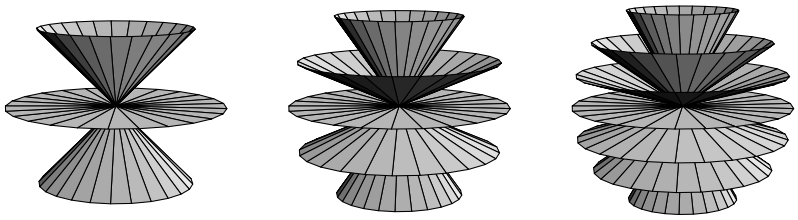


FIGURE 1.7. The absolute value $|\mathbf{L}| = \sqrt{L^2}$ of the angular momentum can only take the values $\hbar\sqrt{\ell(\ell+1)}$, with ℓ being a non-negative integer. For a given ℓ, the component of the angular momentum in an arbitrary direction (here taken as the vertical direction) is also quantized and can only have the values $-\hbar\ell, -\hbar(\ell+1), \ldots + \hbar\ell$. In a classical picture, the angular momentum vector (if measured with respect to a certain direction) thus lies on certain cones.

Eigenvalues of the orbital angular momentum:

The eigenvalues of the operator L^2 are precisely the numbers $\hbar^2\ell(\ell+1)$, where ℓ is a non-negative integer. For each ℓ, the operator L_3 has the eigenvalues $\hbar m$, where $m = -\ell, -\ell+1, \ldots, \ell$.

A classical vector $\mathbf{L}$ for which the values of L^2 and L_3 are restricted to the eigenvalues above would have to lie on certain cones which are described in Figure 1.7. In quantum mechanics, this picture should not be taken seriously because the same result would be obtained for the possible values of L_1 and L_2 (or the component of $\mathbf{L}$ in an arbitrary direction).

In spherical coordinates, the operators $\hat{L}_3$ and $\hat{L}^2$ only act on the angular variables. Hence, we may try a separation of the variables by writing

$$\phi(r, \vartheta, \varphi) = \frac{1}{r} f(r)\, \chi(\vartheta, \varphi). \tag{1.96}$$

The factor $1/r$ has been introduced for "cosmetic reasons." Later, it will simplify some formulas involving the radial part of the wave function.

It has to be noted that most wave functions $\phi(r, \vartheta, \varphi)$ cannot be written in the form of a product of an r-dependent part and a part depending only on the angular variables. But it turns out that the set of wave functions of the type (1.96) is large enough to contain an orthonormal basis of the

Hilbert space $L^2(\mathbb{R}^3)$. Therefore, any wave function has an expansion

$$\phi(r,\vartheta,\varphi) = \sum_{k=0}^{\infty} \frac{1}{r}\, f_k(r)\, \chi_k(\vartheta,\varphi), \tag{1.97}$$

the sum being convergent in the Hilbert space norm.

The wave function (1.96) consists of a radial part $f(r)/r$ and an angular part $\chi(\vartheta,\varphi)$. The norm is given by (see also (1.89))

$$\begin{aligned} \|\phi\|^2 &= \int |\phi(r,\vartheta,\varphi)|^2\, r^2 dr\, \sin\vartheta\, d\vartheta\, d\varphi \\ &= \int_0^\infty |f(r)|^2\, dr \int_{S^2} |\chi(\Omega)|^2\, d\Omega. \end{aligned} \tag{1.98}$$

Here, Ω is shorthand for the angular coordinates (ϑ,φ). The set of these coordinates forms the sphere S^2 (the two-dimensional surface of the unit sphere in three dimensions), and $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$ denotes the area element on this sphere.

Hence, the part $f(r)$ of the wave function in spherical coordinates is square-integrable on $[0,\infty)$, and the angular part is a square integrable function on the sphere S^2 (it belongs to the Hilbert space $L^2(S^2)$).

The application of the operators $\hat{L}^2$ and $\hat{L}_3$ only affects the angular part χ. It is thus sufficient to look for angular eigenfunctions

$$\hat{L}^2\, \chi_\ell^m(\vartheta,\varphi) = \hbar^2 \ell(\ell+1)\, \chi_\ell^m(\vartheta,\varphi), \quad \hat{L}_3\, \chi_\ell^m(\vartheta,\varphi) = \hbar m\, \chi_\ell^m(\vartheta,\varphi). \tag{1.99}$$

Because we know already that m must be an integer, we only have to look for solutions with integer ℓ. These can be determined, in principle, as follows. According to the proof of Theorem 1.1, we first look for a solution of

$$(\hat{L}_1 + \mathrm{i}\hat{L}_2)\chi(\vartheta,\varphi) = 0, \tag{1.100}$$

which can be written as

$$\mathrm{i}\, \cos\vartheta\, \frac{\partial\chi}{\partial\varphi} + \sin\vartheta\, \frac{\partial\chi}{\partial\vartheta} = 0. \tag{1.101}$$

It is easily checked that for each $\ell = 0, 1, 2, 3, \ldots$

$$\chi(\vartheta,\varphi) = N_\ell\, e^{\mathrm{i}\ell\varphi} \left(\sin\vartheta\right)^\ell \tag{1.102}$$

is a solution for this equation (where N_ℓ is a normalization constant). For each ℓ we can now obtain $2\ell+1$ eigenfunctions of $\hat{L}^2$ simply by differentiating, that is, by applying the differential operator $\hat{L}_1 - \mathrm{i}\hat{L}_2$ to the solution above. This procedure (which was described in Theorem 1.1) yields, one after another, the eigenfunctions of L_3 for $m = \ell, \ell-1, \ldots, -\ell$. It is convenient

to normalize these eigenfunctions by requiring

$$\int_{S^2} |\chi(\vartheta,\varphi)|^2 \, d\Omega = 1. \tag{1.103}$$

In that way, one obtains the *spherical harmonics* $Y_\ell^m(\vartheta,\varphi)$, which are described in more detail in the next section.

Eigenfunctions of the orbital angular momentum:

In spherical coordinates, the normalized simultaneous eigenfunctions of the angular-momentum operators $\hat{L}^2$ and $\hat{L}_3$ are the spherical harmonics $Y_\ell^m(\vartheta,\varphi)$,

$$\hat{L}^2 \, Y_\ell^m(\vartheta,\varphi) = \hbar^2 \, \ell(\ell+1) \, Y_\ell^m(\vartheta,\varphi), \qquad \ell = 0,1,2,3,\ldots, \tag{1.104}$$

$$\hat{L}_3 \, Y_\ell^m(\vartheta,\varphi) = \hbar m \, Y_\ell^m(\vartheta,\varphi), \qquad -\ell \le m \le \ell. \tag{1.105}$$

As an example, Figure 1.8 visualizes the spherical harmonic Y_4^1.

CD 1.7 visualizes the spherical harmonics Y_ℓ^m for $\ell \le 6$ by various methods. The spherical harmonics are complex-valued functions depending on two angles, hence the most natural visualization uses a color density plot on the surface of the sphere (either shown as a globe in three dimensions, or represented by a two-dimensional map).

1.6.3. Special topic: Properties of the spherical harmonics

The spherical harmonics are usually[3] defined by

$$Y_\ell^m(\vartheta,\varphi) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} \, e^{\mathrm{i}m\varphi} \, P_\ell^m(\cos\vartheta) \qquad \text{for } 0 \le m \le \ell, \tag{1.106}$$

$$Y_\ell^m(\vartheta,\varphi) = (-1)^m \, \overline{Y_\ell^{-m}(\vartheta,\varphi)} \qquad \text{for } -\ell \le m \le 0. \tag{1.107}$$

Here, the functions $P_\ell^m(z)$ are the *associated Legendre functions*,

$$P_\ell^m(z) = \frac{(-1)^m}{2^\ell \, \ell!} \, (1-z^2)^{m/2} \, \frac{d^{\ell+m}}{dz^{\ell+m}} (z^2-1)^\ell, \tag{1.108}$$

defined for $-1 \le z \le 1$ and integers $0 \le m \le \ell$. The function $P_\ell^0(z) = P_\ell(z)$ is called the *Legendre polynomial* of degree ℓ.

[3] In various books, these definitions can differ by phase factors. We follow the conventions made in *Mathematica*, $Y_\ell^m(\vartheta,\varphi) \equiv$ `SphericalHarmonicY`$[\ell, m, \vartheta, \varphi]$, and $P_\ell^m(z) \equiv$ `LegendreP`$[\ell, m, z]$.

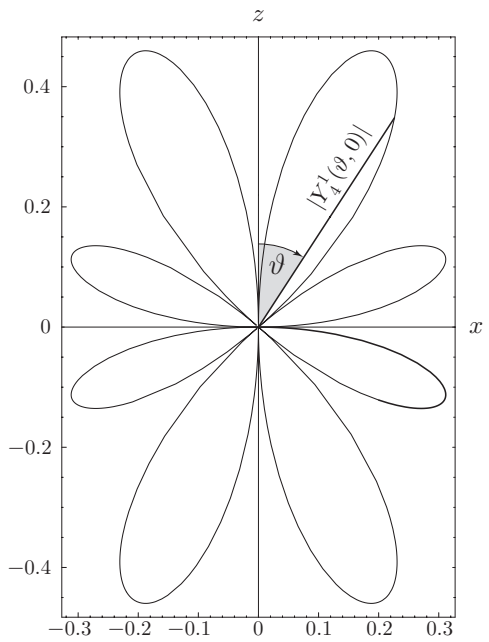


FIGURE 1.8. The absolute value of the spherical harmonics $Y_\ell^m(\vartheta,\varphi)$ depends only on ϑ. Therefore, we can visualize them by plotting a curve in the x_1x_3-plane where at each angle ϑ, the distance from the origin is $|Y_\ell^m(\vartheta,0)|$. This is shown here for $\ell = 4$ and $m = 1$. More examples and three-dimensional visualizations can be found on the CD-ROM; see CD 1.7.

Spherical harmonics with different indices are orthogonal, because they are eigenfunctions belonging to different eigenvalues of a self-adjoint operator, and because of their normalization we simply have

$$\int_{S^2} \overline{Y_\ell^m(\vartheta,\varphi)}\, Y_{\ell'}^{m'}(\vartheta,\varphi)\, d\Omega = \delta_{\ell\ell'}\, \delta_{mm'}. \tag{1.109}$$

The spherical harmonics are either symmetric or antisymmetric under a reflection through the origin,

$$Y_\ell^m(\pi-\vartheta,\varphi+\pi) = (-1)^\ell\, Y_\ell^m(\vartheta,\varphi). \tag{1.110}$$

Finally, we note the addition theorem:

$$\frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} \overline{Y_\ell^m(\vartheta,\varphi)}\, Y_\ell^m(\vartheta',\varphi') = P_\ell(\cos\alpha). \tag{1.111}$$

Here, α is the angle between the directions (ϑ, φ) and (ϑ', φ'). Denoting the corresponding unit vectors by $\boldsymbol{\omega}$ and $\boldsymbol{\omega}'$, we have $\cos\alpha = \boldsymbol{\omega} \cdot \boldsymbol{\omega}'$.

In Cartesian coordinates (x, y, z), with $r = (x^2+y^2+z^2)^{1/2}$, the spherical harmonics are (for $m \geq 0$)

$$Y_\ell^m(x,y,z) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\Big(\frac{x+\mathrm{i}y}{\sqrt{x^2+y^2}}\Big)^m P_\ell^m\Big(\frac{z}{r}\Big). \tag{1.112}$$

For example,

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}, \quad Y_1^0 = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}, \quad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\,\frac{x \pm \mathrm{i}y}{r}. \tag{1.113}$$

1.7. Particle on a Sphere

1.7.1. Classical particle on a sphere

Here, we consider a quantum mechanical system that is only able to perform a rotational motion. Imagine a particle with mass[4] m whose motion is restricted to the surface of a sphere. There are no other forces. This particle has two degrees of freedom, its position on the sphere is given by two angular coordinates, the longitude and the latitude, described by the angles ϑ and φ. A classical particle subject to these constraints will move along the geodesics of the sphere (great circles) with constant (angular) velocity. Its kinetic energy is given by

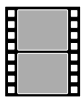
$$E = \frac{1}{2}\mathrm{m}v^2 = \frac{1}{2}\mathrm{m}(r\omega)^2 = \frac{1}{2}I\omega^2, \tag{1.114}$$

where we have introduced the angular speed $\omega = v/r$ and the moment of inertia

$$I = \mathrm{m}r^2. \tag{1.115}$$

The angular momentum of a particle moving with velocity v on a sphere of radius r is $L = \mathrm{m}vr$, or $v = L/\mathrm{m}r$. Insert this into the expression for the energy to obtain

$$E = \frac{L^2}{2\mathrm{m}r^2} = \frac{L^2}{2I}. \tag{1.116}$$



CD 1.2.1, CD 1.5.4, and CD 1.6.3 are all visualizations of the classical motion at a fixed distance from the coordinate origin.

[4]It is general custom to denote the mass of the particle and the eigenvalue of L_3 by the same letter. Usually there is little danger of confusion. To be on the safe side, we denote the mass by the roman letter m and use the italic letter m for the eigenvalue of L_3.

1.7.2. The rigid rotator

The particle on a sphere is a mathematical model for the rigid rotator. Consider two point-like particles of mass m_1 and m_2 that are connected by a weightless, rigid rod of length r. Denote by $\mathbf{x} = \mathbf{x}_2 - \mathbf{x}_1$ the vector pointing from m_1 to m_2. The position of the center of mass is given by

$$\mathbf{X} = \frac{\mathrm{m}_1\mathbf{x}_1 + \mathrm{m}_2\mathbf{x}_2}{\mathrm{m}_1 + \mathrm{m}_2} \tag{1.117}$$

The distances of the particles from the center of mass are therefore

$$r_1 = |\mathbf{x}_1 - \mathbf{X}| = \frac{\mathrm{m}_2\, r}{\mathrm{m}_1 + \mathrm{m}_2}, \quad r_2 = |\mathbf{x}_2 - \mathbf{X}| = \frac{\mathrm{m}_1\, r}{\mathrm{m}_1 + \mathrm{m}_2}. \tag{1.118}$$

If we are only interested in the internal motion of the two-particle system, we can choose a coordinate system that has its origin at the center of mass. In this coordinate system, the moment of inertia of the rotator is thus

$$I = \mathrm{m}_1 r_1^2 + \mathrm{m}_2 r_2^2 = \frac{\mathrm{m}_1\mathrm{m}_2}{\mathrm{m}_1 + \mathrm{m}_2}\, r^2. \tag{1.119}$$

This is precisely the moment of inertia of a particle with mass

$$\mu = \frac{\mathrm{m}_1\mathrm{m}_2}{\mathrm{m}_1 + \mathrm{m}_2} \tag{1.120}$$

at a distance r from the origin. Thus, we can replace the two-particle system with an effective one-particle system. This particle has the so-called *reduced mass* μ and the fixed distance r from the origin, that is, it is a particle on a sphere with radius r.

This is a good model for a diatomic molecule. It consists of two atoms that can oscillate along the line connecting their centers and rotate around the center of mass. The vibrational motion is much faster than the rotational motion. So, the vibrations belong to much higher energies. Quantum mechanically, oscillation states have a quantized energy. As long as the diatomic molecule is in its vibrational ground state, it is a rigid rotator.

1.7.3. Transition to quantum mechanics

In order to define the quantum mechanical Hamiltonian for a particle that is constrained to the surface of a sphere, we start with the classical expression (1.116) for the energy. From this, the Hamiltonian operator of the rigid rotator is obtained by replacing L^2 with the quantum mechanical angular-momentum operator. Note that r, the radius of the sphere, is treated as a fixed parameter. Using the expression (1.91) for the angular momentum in spherical coordinates, we arrive at

$$\hat{H} = \frac{1}{2\mathrm{m}\, r^2}\, \hat{L}^2 = \frac{1}{2I}\, \hat{L}^2. \tag{1.121}$$

The operator $\hat{L}^2$ has a discrete spectrum of eigenvalues, therefore the same is true for the energy of the rotator.

Eigenvalues of the rigid rotator:

A particle with mass m on a sphere with radius r can only have the energies

$$E_\ell = \frac{\hbar^2}{2\mathrm{m}r^2}\,\ell(\ell+1), \quad \ell = 0, 1, 2, 3, \ldots. \tag{1.122}$$

Each eigenvalue E_ℓ has the multiplicity $2\ell+1$, that is, there are $2\ell+1$ orthogonal wave functions all belonging to the eigenvalue E_ℓ:

$$\psi_{\ell,m}(\vartheta,\varphi) = \frac{1}{r}\,Y_\ell^m(\vartheta,\varphi), \quad m = -\ell, -\ell+1, \ldots, \ell. \tag{1.123}$$

It follows from (1.109) that

$$\int_{S_r^2} \left|\psi_{\ell,m}(\vartheta,\varphi)\right|^2 r^2\,\sin\vartheta\,d\vartheta\,d\varphi = 1. \tag{1.124}$$

The factor $1/r$ in (1.123) thus guarantees that the eigenfunctions are normalized on the sphere with radius r. We conclude that the eigenfunctions form an orthonormal basis in the Hilbert space $L^2(S_r^2)$ of square integrable functions on the sphere of radius r.

We want to stress that $\hat{L}^2$ is part of any single-particle Hamiltonian, because it appears in the angular part of the kinetic energy in spherical coordinates (see (1.150) below). For a particle constrained to the surface of a sphere, the operator $\hat{L}^2$ plays the same role as the operator $-\hbar^2\Delta$ for a particle in $\mathbb{R}^3$: It is proportional to the kinetic energy and it generates the free time evolution. (In fact, $\hat{L}^2/\hbar^2$ is the so-called Laplace-Beltrami operator of the sphere.) The action of the free time evolution $\exp(-\mathrm{i}\hat{L}^2 t/2I)$ on a sphere will be discussed next.

1.7.4. Dynamics of the rigid rotator

The time evolution of an eigenfunction of the rigid rotator Hamiltonian is rather trivial. If $\psi_{\ell,m}(\vartheta,\varphi)$ is an eigenfunction belonging to the eigenvalue E_ℓ, then the function

$$\psi_{\ell,m}(t,\vartheta,\varphi) = \exp(-\mathrm{i}E_\ell\,t)\,\psi_{\ell,m}(\vartheta,\varphi) \tag{1.125}$$

is a solution of the time-dependent Schrödinger equation. The ground state of the rigid rotator has energy $E_0 = 0$, and hence the corresponding wave function does not depend on time at all.

The fact that the Schrödinger equation is linear means that we can consider linear combinations of eigenfunctions. For example, for the initial function $\psi_0(\vartheta,\varphi) = \sum_{\ell,m} c_{\ell,m}\,\psi_{\ell,m}(\vartheta,\varphi)$, the time evolution is

$$\psi(t,\vartheta,\varphi) = \sum_{\ell,m} c_{\ell,m}\,\exp(-\mathrm{i}E_\ell\,t)\,\psi_{\ell,m}(\vartheta,\varphi) \tag{1.126}$$

and this clearly gives us the solution for any initial function that is square integrable on the sphere, because the set of functions $\psi_{\ell,m}$ forms an orthonormal basis in $L^2(S_r^2)$.

Given any initial function ψ_0, the expansion coefficient $c_{\ell,m}$ can be found by an integration,

$$c_{\ell,m} = \int_{S_r^2} \overline{\psi_{\ell,m}(\vartheta,\varphi)}\,\psi_0(\vartheta,\varphi)\,r^2\,d\Omega \tag{1.127}$$

(with $d\Omega = \sin\vartheta\,d\vartheta\,d\varphi$). It is remarkable that all nonzero energies $E_\ell = \ell(\ell+1)/2I$ are integer multiples of $E_1 = 1/I$, hence all time-dependent factors $\exp(-\mathrm{i}E_\ell\,t)$ have the same basic time period. Hence, any state of the rigid rotator is periodic in time.

For the unit sphere ($r = 1$), we summarize our results in the following box.

Time evolution of the rigid rotator:

For a particle with mass m = 1 on the unit sphere S^2 the time evolution of any square-integrable initial function $\psi_0(\vartheta,\varphi)$ is given by the formula

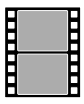
$$\psi(t,\vartheta,\varphi) = \sum_{\ell,m} c_{\ell,m}\,\exp(-\mathrm{i}E_\ell\,t)\,Y_\ell^m(\vartheta,\varphi) \tag{1.128}$$

with

$$c_{\ell,m} = \int_{S^2} \overline{Y_\ell^m(\vartheta,\varphi)}\,\psi_0(\vartheta,\varphi)\,d\Omega. \tag{1.129}$$

The time evolution of the wave function is periodic in time,

$$\psi(t+T,\vartheta,\varphi) = \psi(t,\vartheta,\varphi) \quad \text{with period} \quad T = 2\pi. \tag{1.130}$$



CD 1.9–CD 1.12 is a collection of several movies showing various time-dependent states of the rigid rotator. CD 1.13 visualizes the time evolution of initially well-localized (Gaussian) states. In CD 1.14, the initial state has roughly the shape of the letter Ψ. This illustrates that we can indeed compute the time evolution of any square-integrable initial function on the sphere.

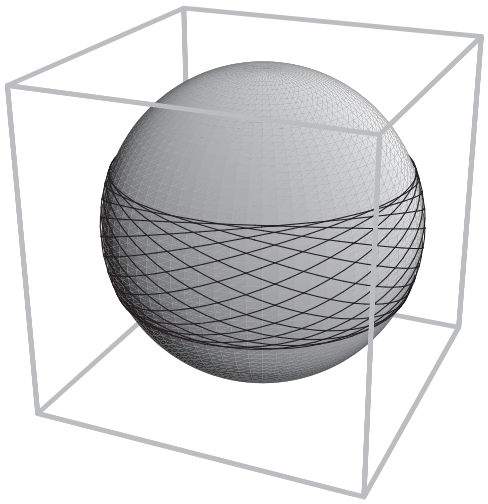


FIGURE 1.9. Possible trajectories of classical particles on a sphere. For all trajectories, the angular-momentum vector has $|\mathbf{L}| = \sqrt{\ell(\ell+1)}$, with $\ell = 6$ and $L_3 = 6$.

1.8. Quantization on a Sphere

1.8.1. Comparison of classical and quantum probability densities

Figure 1.9 shows a set of classical trajectories of particles for which the angular momenta have a fixed absolute value $|\mathbf{L}| = L$ and a fixed value of the third component L_3. The admissible positions of classical particles with these angular momenta form the classically allowed region on the sphere. This region is determined by the polar angle of the classical angular-momentum vector. We denote the polar angle of $\mathbf{L}$ by θ in order to distinguish it from the polar angle ϑ of the particle's position vector, see Figure 1.10.

Assuming $L_3 = m$, we find that the polar angle of $\mathbf{L}$ is

$$\theta = \arccos\Big(\frac{m}{L}\Big) \tag{1.131}$$

and hence the classically allowed region for the position of the particle is between the polar angles

$$\vartheta_{\min} = \pi/2 - \theta, \qquad \vartheta_{\max} = \pi/2 + \theta. \tag{1.132}$$

All the classical trajectories are grand circles of the sphere. The particles move on these circles with a constant angular velocity. When a particle circles around the sphere, the polar angle ϑ performs a periodic motion

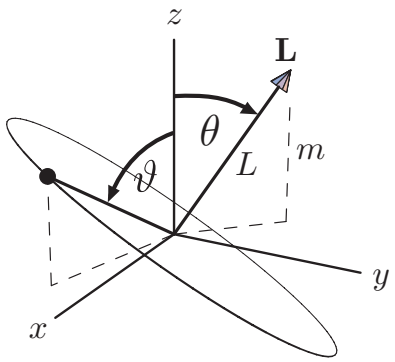


FIGURE 1.10. The polar angle $\theta = \arccos(m/L)$ of the angular momentum and the time-dependent polar angle ϑ of the position vector for a classical particle on a sphere.

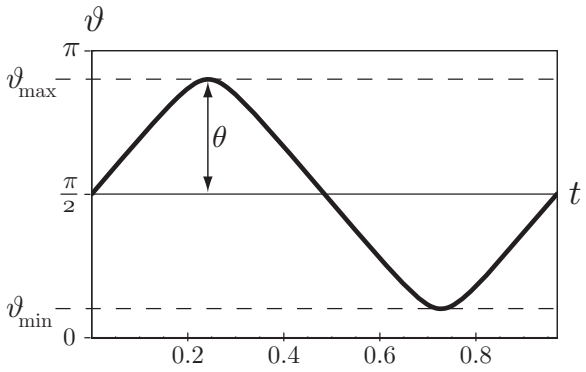


FIGURE 1.11. Polar angle ϑ as a function of time according to (1.133) for $L^2 = 42$ and $m = 2$.

between $\vartheta_{\min}$ and $\vartheta_{\max}$. It is given by

$$\vartheta(t) = \arccos\Big(-\frac{1}{L}\sqrt{L^2 - m^2}\,\sin(L\,t)\Big). \tag{1.133}$$

An example is shown in Figure 1.11.

The angular-momentum vector is normal to the plane of the circle, hence the angle θ defined in (1.131) describes the inclination of that plane. If m is small compared to L, the inclination is large. For $m = 0$, the classical motion is on a circle through the poles of the sphere. For $m = L$ (which is impossible quantum mechanically), the circle of the classical motion is the equator of the sphere.

We want to determine the classical probability density as a function of the coordinate ϑ. This can be done in complete analogy to the calculation for the harmonic oscillator in Book One, Section 7.2.3. The probability density that a particle will be found in an interval $d\vartheta$ around an angle ϑ is equal to the fraction of a period that is spent in the interval. We first calculate the time $dt(\vartheta)$ spent in an infinitesimal interval $d\vartheta$ at the point ϑ. During one period, the trajectory goes twice through ϑ, hence we multiply the time by 2 to obtain the total time spent in $d\vartheta$ during one period. The time needed to complete a period is $T = 2\pi/L$. Hence, the probability of finding the particle in $d\vartheta$ is

$$p(\vartheta)\,d\vartheta = \frac{L}{2\pi}\,2\,dt(\vartheta) = \frac{L}{\pi}\,\frac{dt(\vartheta)}{d\vartheta}\,d\vartheta. \tag{1.134}$$

Hence, one needs to invert the function $\vartheta(t)$ and differentiate with respect to ϑ. It is sufficient to invert the function $\vartheta(t)$ on a part of the time interval during which the trajectory goes through the point ϑ under consideration. Thus, we write

$$t(\vartheta) = -\frac{1}{L}\,\arcsin\Big(\frac{L}{\sqrt{L^2-m^2}}\,\cos\vartheta\Big). \tag{1.135}$$

The function $t(\vartheta)$ is inverse to $\vartheta(t)$ on the interval $(T/4, 3T/4)$. Inserting (1.135) into (1.134), we finally obtain for the classical position probability density

$$p(\vartheta) = \frac{L\,\sin\vartheta}{\pi\,\sqrt{L^2\,(\sin\vartheta)^2 - m^2}}. \tag{1.136}$$

This function is shown as a black line in Figure 1.12 for $m = 8$ and $L = \sqrt{\ell(\ell+1)}$ with $\ell = 24$.

We want to compare the classical position probability density $p(\vartheta)$ with the corresponding quantum mechanical density. With the eigenfunction $\psi_{\ell,m}$ defined in (1.123), we obtain

$$\int_{B\subset S_r^2} \big|\psi_{\ell,m}(\vartheta,\varphi)\big|^2\,r^2\,\sin\vartheta\,d\vartheta\,d\varphi \tag{1.137}$$

as the probability that a particle is found in a region B on S_r^2 (the surface of the sphere with radius r). Let us do the integration over the angle φ because we are interested in the ϑ-position irrespective of the φ-position. This gives only a factor 2π because the absolute value of $\psi_{\ell,m} = (1/r)\,Y_\ell^m$ does not depend on φ. Hence, $2\pi\,|\psi_{\ell,m}(\vartheta,\varphi)|^2\,r^2\,\sin\vartheta\,d\vartheta$ is the probability that a particle on the sphere is in an infinitesimal circular strip of width $d\vartheta$ around the polar angle ϑ. Inserting the definition (1.123) gives for the position probability density as a function of ϑ the expression

$$p_{\mathrm{qm}}(\vartheta) = 2\pi\,\sin\vartheta\,|Y_\ell^m(\vartheta,0)|^2. \tag{1.138}$$

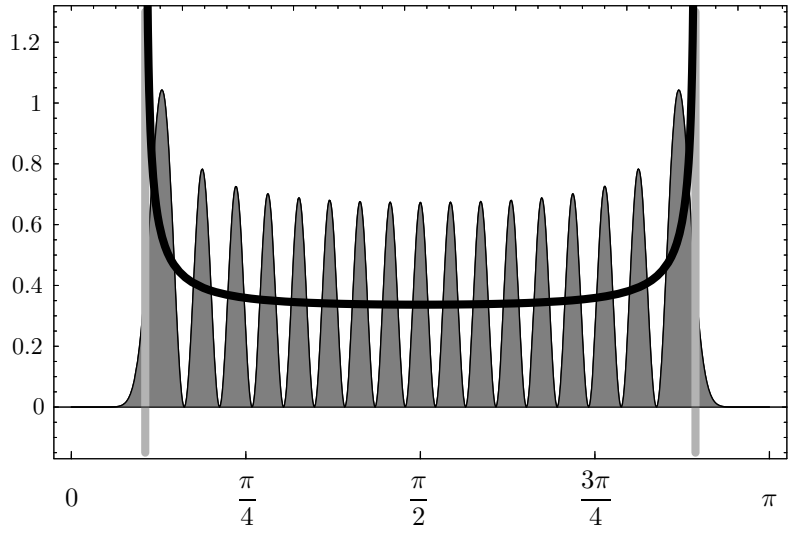
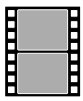


FIGURE 1.12. Classical versus quantum position probability densities as functions of the polar angle ϑ for the rigid rotator. The quantum probability (filled curve) oscillates around the classical probability (black line). The quantum wave function decreases rapidly outside the classically allowed region whose borders are indicated by the vertical gray lines.

Figure 1.12 compares the quantum and classical probability densities as functions of ϑ.



Similar to Figures 1.9, 1.11, and 1.12, but for various values of L_3, the images in CD 1.8 depict the relations between the classically allowed region of the rigid rotator, the classical ϑ-oscillation, and the quantum probability density as a function of ϑ.

1.8.2. Special topic: Curvilinear coordinates

It is worthwhile to consider the transition from classical to quantum mechanics for the rigid rotator in more detail. The classical kinetic energy of a particle with mass $\mathrm{m} = 1$ is given by

$$T(t) = \frac{1}{2}\sum_{i=1}^{3} \dot{x}_i(t)^2. \tag{1.139}$$

Assuming that the motion of the particle takes place on the surface of the unit sphere, we insert (1.81), that is, $x_1(t) = \sin\big(\vartheta(t)\big)\,\cos\big(\varphi(t)\big)$ and so forth,

and obtain an expression for the kinetic energy in spherical coordinates, namely

$$T(t) = \frac{1}{2}\Big(\dot\vartheta(t)^2 + \big(\sin\vartheta(t)\big)^2\,\dot\varphi(t)^2\Big). \tag{1.140}$$

If there are no external forces, the kinetic energy is a constant of motion. Another conserved quantity is the angular momentum. In fact, one finds that the above expression for the kinetic energy is just $T = L^2/2$. In spherical coordinates, we obtain a particularly simple expression for the third component of the angular momentum,

$$L_3(t) = x_1(t)\,\dot x_2(t) - \dot x_1(t)\,x_2(t) = \big(\sin\vartheta(t)\big)^2\,\dot\varphi(t). \tag{1.141}$$

Denoting the constant value of L_3 by m, we may eliminate the angular velocity $\dot\varphi$ and express the kinetic energy solely in terms of ϑ

$$T = \frac{1}{2}\Big(\dot\vartheta(t)^2 + \frac{m^2}{\sin^2\vartheta(t)}\Big). \tag{1.142}$$

This looks like the total energy of a particle with mass 1 in one dimension (coordinate ϑ), with $\dot\vartheta^2/2$ being the kinetic energy and $V(\vartheta) = \frac{1}{2}m^2/\sin^2\vartheta$ being the potential. This potential confines the motion to the interval $(0,\pi)$. Indeed, the equation of motion for the ϑ coordinate is obtained as

$$\ddot\vartheta = \frac{m^2}{\sin^2\vartheta}\,\cot\vartheta \tag{1.143}$$

and the solutions of this equation are given by (1.133) for arbitrary values of L and m.

It is tempting to try a transition to quantum mechanics by applying the standard substitution rule $p_\vartheta = \dot\vartheta \to -\mathrm{i}\partial/\partial\vartheta$ to the classical expression (1.142). This would lead, however, to the wrong equation. The correct equation for the ϑ-coordinate was obtained earlier, when we derived the expression for the Laplacian operator in spherical coordinates. It reads

$$\mathrm{i}\,\frac{\partial}{\partial t}\,\psi(\vartheta,t) = \frac{1}{2}\Big(-\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\,\sin\vartheta\,\frac{\partial}{\partial\vartheta} + \frac{m^2}{\sin^2\vartheta}\Big)\,\psi(\vartheta,t). \tag{1.144}$$

Obviously, the standard substitution rule does not work in spherical coordinates. The reason is that unlike the situation in Cartesian coordinates, the components $\dot\vartheta$ and $\dot\varphi$ of the velocity in curvilinear coordinates do not independently contribute to the total kinetic energy.

Let us just state how to obtain the operator for kinetic energy in general curvilinear coordinates. We denote the coordinates of a system with n degrees of freedom by $q^1, q^2, \ldots, q^n$. The classical kinetic energy in these

coordinates is an expression of the form

$$T = \frac{1}{2} \sum_{i,j=1}^{n} g_{ij}(q^1, \dots, q^n)\, \dot{q}^i\, \dot{q}^j \tag{1.145}$$

with a positive definite symmetric matrix g_{ij} that is defined at every point $(q^1, \dots, q^n)$ of the configuration space. The matrix $g = (g_{ij})$ (the *metric tensor*) defines a *Riemannian metric* on the configuration space, which thus becomes a *Riemannian manifold*. Let us denote the components of the inverse matrix g^{-1} by g^{ij}. Then, the operator for kinetic energy in the coordinates q^j is given by

$$H_0 = -\frac{1}{2}\,\Delta = -\frac{1}{2}\,\frac{1}{\sqrt{\det g}} \sum_{i,j} \frac{\partial}{\partial q^i} \Big(g^{ij}\, \sqrt{\det g}\, \frac{\partial}{\partial q^j} \Big). \tag{1.146}$$

This operator is called the *Laplace-Beltrami operator* on the Riemannian manifold with metric g.

The volume element in curvilinear coordinates is $\sqrt{\det g}\, dq^1\, dq^2 \cdots dq^n$, hence the Hilbert space consists of functions that are square-integrable in the sense that

$$\int |\psi(q^1, \dots q^n)|^2\, \sqrt{\det g}\; dq^1 \cdots dq^n < \infty. \tag{1.147}$$

As an example, we consider the unit sphere with $q^1 = \vartheta$, and $q^2 = \varphi$. From (1.140) we find

$$g = \begin{pmatrix} 1 & 0 \\ 0 & (\sin\vartheta)^2 \end{pmatrix}. \tag{1.148}$$

For the inverse matrix we have $g^{11} = 1$, $g^{22} = 1/(\sin\vartheta)^2$, $g^{12} = g^{21} = 0$. Because of the relation $\sqrt{\det g} = \sin\vartheta$, (1.146) reduces to the well-known expression (see (1.91))

$$H_0 = -\frac{1}{2}\, \left(\frac{1}{\sin\vartheta}\, \frac{\partial}{\partial\vartheta} \Big(\sin\vartheta \frac{\partial}{\partial\vartheta} \Big) + \frac{1}{\sin^2\vartheta}\, \frac{\partial^2}{\partial\varphi^2} \right) \tag{1.149}$$

in the Hilbert space of square-integrable function with respect to the volume element $\sin\vartheta\, d\vartheta\, d\varphi$.

A transition to a non-Cartesian coordinate system is also necessary to describe the influence of a gravitational field according to the general theory of relativity.

1.9. Free Schrödinger Equation in Spherical Coordinates

1.9.1. Solutions of the radial equation

For the free-particle Hamiltonian H_0, it is easy to obtain an expression in spherical coordinates by using $\hat{\Delta} = \hat{\nabla}^2$ and the expression (1.87) for the gradient:

$$\hat{H}_0 = -\frac{\hbar^2}{2\mathrm{m}}\hat{\Delta} = \frac{\hbar^2}{2\mathrm{m}}\Big(-\frac{d^2}{dr^2} - \frac{2}{r}\,\frac{d}{dr}\Big) + \frac{1}{2\mathrm{m}}\,\frac{1}{r^2}\hat{L}^2. \tag{1.150}$$

The first part, which involves only derivatives with respect to r, describes the kinetic energy of the radial motion. The second part, which contains the operator $\hat{L}^2$ given by (1.91), is the kinetic energy of the angular motion. $\hat{L}^2$ is a partial differential operator that involves only derivatives with respect to ϑ and φ. Hence, $\hat{L}^2$ commutes with the radial kinetic energy and hence with $\hat{H}_0$. The kinetic energy operator $\hat{H}_0$ also commutes with $\hat{L}_3$, because $\hat{L}_3 = -\mathrm{i}d/d\varphi$ commutes with $\hat{L}^2$ and with expressions depending on r. This proves that the operator of kinetic energy is invariant under rotations:

$$[\hat{H}_0, \hat{L}^2] = 0. \tag{1.151}$$

The same commutation relation holds for the operators in Cartesian coordinates, which are related to the operators in spherical coordinates by a unitary transformation. Hence, $[H_0, L^2] = 0$. Any eigenspace of L^2 is left invariant by H_0. If ψ_ℓ is an eigenvector of L^2, then $H_0\psi_\ell$ is an eigenvector of L^2 belonging to the same eigenvalue. We can thus restrict the operator H_0 to an arbitrary eigenspace of L^2. Using spherical coordinates, we see immediately that this restriction reduces the partial differential operator $\hat{H}_0$ to the ordinary differential operator

$$\mathbf{h}_{0\ell} = \frac{\hbar^2}{2\mathrm{m}}\Big(-\frac{d^2}{dr^2} - \frac{2}{r}\,\frac{d}{dr} + \frac{\ell(\ell+1)}{r^2}\Big), \tag{1.152}$$

which is called the *free radial Schrödinger operator*. Here, the angular kinetic energy appears in the form of a potential energy $\ell(\ell+1)/r^2$. This term is called the *centrifugal potential energy* or *centrifugal barrier*, because it has the effect of a repulsive force in the radial direction.

In order to solve the Schrödinger equation in spherical coordinates we could use the trial function

$$\phi(r, \vartheta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{r}\, f_{\ell m}(r)\, Y_\ell^m(\vartheta, \varphi) \tag{1.153}$$

and find immediately that $\hat{H}_0\phi = E\phi$ holds if $f_{\ell m}$ is a solution of the *radial Schrödinger equation*

$$\frac{\hbar^2}{2\mathrm{m}}\Big(-\frac{d^2}{dr^2}+\frac{\ell(\ell+1)}{r^2}\Big)\,f(r) = E\,f(r). \tag{1.154}$$

Note that the factor $1/r$ in (1.153) makes the first-order term $(2/r)\,d/dr$ disappear. The condition for square-integrability of the wave function ψ (see (1.98)) would mean that each $f_{\ell m}$ has to be square integrable in the radial Hilbert space $L^2([0,\infty)$, that is,

$$\int_0^\infty |f_{\ell m}(r)|^2\,dr < \infty. \tag{1.155}$$

But we know that the free-particle Schrödinger equation has no square-integrable solutions with sharp energy. Instead, the solutions of the stationary Schrödinger equation are plane waves with arbitrary momentum $\mathbf{k}$. We expect a similar behavior for the solutions of the radial Schrödinger equation. Hence, we expect that there exist bounded solutions for $E > 0$. The differential equation (1.154) is a Bessel equation. As a differential equation of second order it has two linearly independent solutions. These solutions are called *Riccati-Bessel functions*. With $k = \sqrt{2mE/\hbar^2}$ (positive square root, $E > 0$), the solutions are

$$\hat{\jmath}_\ell(kr) = \sqrt{\frac{\pi}{2}\,kr}\,J_{\ell+1/2}(kr), \qquad \hat{n}_\ell(kr) = \sqrt{\frac{\pi}{2}\,kr}\,N_{\ell+1/2}(kr) \tag{1.156}$$

where J_ν and N_ν are the Bessel function and Neumann functions of order ν. The function $\hat{\jmath}_\ell$ is regular for $r \to 0$ whereas $\hat{n}_\ell$ is singular for $\ell > 0$.

An interactive plot of the Riccati-Bessel function $\hat{\jmath}_\ell(r)$ in CD 1.15 allows investigation of the dependence on ℓ.

1.9.2. Special Topic: Properties of the Riccati-Bessel functions

The real-valued functions $\hat{\jmath}_\ell(z)$ and $\hat{n}_\ell(z)$ are for $z > 0$ solutions of the equation

$$-\frac{d^2y(z)}{dz^2}+\frac{\ell(\ell+1)}{z^2}y(z) - y(z) = 0. \tag{1.157}$$

We have

$$\hat{\jmath}_0(z) = \sin z, \quad \hat{n}_0(z) = \cos z, \tag{1.158}$$

and the Riccati-Bessel functions of higher order can be computed from

$$\hat{j}_\ell(z) = -(-z)^{\ell+1} \Big(\frac{1}{z}\,\frac{d}{dz}\Big)^\ell \Big(\frac{1}{z}\,\hat{j}_0(z)\Big), \tag{1.159}$$

$$\hat{n}_\ell(z) = -(-z)^{\ell+1} \Big(\frac{1}{z}\,\frac{d}{dz}\Big)^\ell \Big(\frac{1}{z}\,\hat{n}_0(z)\Big). \tag{1.160}$$

Their limiting behavior for small z is given by

$$\hat{j}_\ell(z) = \frac{2^\ell \ell!}{(2\ell+1)!}\, z^{\ell+1} \big(1 + \mathrm{O}(z^2)\big), \quad \text{as } z \to 0, \tag{1.161}$$

$$\hat{n}_\ell(z) = \frac{(2\ell)!}{2^\ell \ell!}\, z^{-\ell} \big(1 + \mathrm{O}(z^2)\big), \quad \text{as } z \to 0. \tag{1.162}$$

In scattering theory, one often defines the Riccati-Hankel functions

$$\hat{h}^\pm_\ell(z) = \hat{n}_\ell(z) \pm \mathrm{i}\hat{j}_\ell(z) = \mathrm{e}^{\pm \mathrm{i}(z-\ell\pi/2)} \big(1 + \mathrm{O}(1/z)\big), \quad \text{as } z \to \infty. \tag{1.163}$$

Further details about the Riccati-Bessel functions can be found in the book [**1**], where the notation $\hat{j}(z) = zj(z)$, and $\hat{n}(z) = zy(z)$ is used.

1.9.3. Special Topic: Expanding the plane wave

The plane waves $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{x})$ are important solutions of the free-particle Schrödinger equation, despite the fact that they are not square-integrable. Here, we show that plane waves have an expansion like (1.153). The radial part of a plane wave in the subspace with angular-momentum quantum number ℓ is just the Riccati-Bessel function $\hat{j}_\ell(kr)$. This result is important for the applications to stationary scattering theory with spherically symmetric potentials.

Representation of plane waves:

The stationary plane wave $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{x})$ has the following expansion in terms of spherical harmonics:

$$\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} = \frac{1}{r} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell,m}(\mathbf{k})\, \hat{j}_\ell(kr)\, Y_\ell^m(\vartheta,\varphi), \tag{1.164}$$

where (r,ϑ,φ) are the spherical coordinates of $\mathbf{x} \in \mathbb{R}^3$. The coefficients in this expansion are given by

$$c_{\ell,m}(\mathbf{k}) = \frac{4\pi \mathrm{i}^\ell}{k}\, \overline{Y_\ell^m(\vartheta',\varphi')}\,. \tag{1.165}$$

Here, (k,ϑ',φ') are the spherical coordinates of $\mathbf{k} \in \mathbb{R}^3$.

The proof of the expansion formula uses properties of the Legendre polynomials $P_\ell(x)$ and the addition theorem for spherical harmonics (1.111). The

Legendre polynomials form an orthogonal set in the Hilbert space of square-integrable functions on the interval $-1 \le x \le 1$. According to Abramowitz-Stegun [**1**], the Legendre polynomials satisfy

$$\int_{-1}^{1} P_\ell(x)\, P_{\ell'}(x)\, dx = \frac{2}{2\ell+1}\, \delta_{\ell\ell'}. \tag{1.166}$$

From this, we conclude that the functions

$$f_\ell(x) = \sqrt{\frac{2\ell+1}{2}}\, P_\ell(x) \tag{1.167}$$

form an orthonormal basis in the Hilbert space $L^2([-1,1])$.

For any wave number $\mathbf{k}$, the plane wave can be rewritten as

$$\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} = \mathrm{e}^{\mathrm{i}kr\cos\alpha} = \mathrm{e}^{\mathrm{i}krx}, \quad \text{with } x = \cos\alpha \in [-1,1]. \tag{1.168}$$

α is the angle between the vectors $\mathbf{k}$ and $\mathbf{x}$. As a function of x (for fixed k and r), the function $\exp(\mathrm{i}krx)$ belongs to the Hilbert space $L^2([-1,1])$. Hence, it can be expanded in the Legendre polynomials in the usual way,

$$\mathrm{e}^{\mathrm{i}krx} = \sum_\ell c_\ell(kr)\, f_\ell(x), \qquad c_\ell(kr) = \int_{-1}^{1} f_\ell(x)\, \mathrm{e}^{\mathrm{i}krx}\, dx. \tag{1.169}$$

The integral involving a Legendre polynomial and an exponential function can be evaluated analytically. It is best to consult a good book (see, for example, [**1**], Section 10.1.14), where we find

$$\int_{-1}^{1} P_\ell(x)\, \mathrm{e}^{\mathrm{i}qx}\, dx = \frac{2\mathrm{i}^\ell}{q}\, \hat{\jmath}_\ell(q), \quad \ell = 0, 1, 2, \ldots. \tag{1.170}$$

With the help of this formula, we find

$$c_\ell(kr) = \sqrt{2(2\ell+1)}\, \frac{\mathrm{i}^\ell}{kr}\, \hat{\jmath}_\ell(kr) \tag{1.171}$$

and hence

$$\mathrm{e}^{\mathrm{i}krx} = \frac{1}{kr} \sum_{\ell=0}^{\infty} (2\ell+1)\, \mathrm{i}^\ell\, \hat{\jmath}_\ell(kr)\, P_\ell(x) \quad \text{or} \tag{1.172}$$

$$\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} = \frac{1}{kr} \sum_{\ell=0}^{\infty} (2\ell+1)\, \mathrm{i}^\ell\, \hat{\jmath}_\ell(kr)\, P_\ell(\cos\alpha). \tag{1.173}$$

The expansion formula (1.173) is visualized in CD 1.16. The missing square integrability of a plane wave manifests itself in the fact that the series (1.173) does not converge in the usual sense. With increasing ℓ, the individual summands do not get smaller (with respect to the norm in $L^2(\mathbb{R}^3)$), but they contribute only in regions increasingly far away from the origin.

We may insert the summation rule (1.111) for spherical harmonics into (1.173). We choose the angles (ϑ', φ') in the direction of $\mathbf{k}$, which has an angle α with the direction of (ϑ, φ) (= the direction of $\mathbf{x}$). This leads to the result

$$\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} = \frac{4\pi}{kr} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \mathrm{i}^{\ell}\, \hat{\jmath}_{\ell}(kr)\, \overline{Y_{\ell}^{m}(\vartheta', \varphi')}\, Y_{\ell}^{m}(\vartheta, \varphi), \tag{1.174}$$

which is identical with (1.164).

1.9.4. Special topic: Spherical harmonics and the Fourier transformation

Consider a function $\psi(\mathbf{x})$ that can be separated into a radial part and an angular part,

$$\psi(\mathbf{x}) = \frac{1}{r}\, f(r)\, Y_{\ell}^{m}(\vartheta, \varphi), \tag{1.175}$$

where (r, ϑ, φ) are the spherical coordinates of the point $\mathbf{x} \in \mathbb{R}^3$. Obviously, ψ is an eigenfunction of the angular-momentum operators L^2 and L_3. We want to find the Fourier transform $\hat{\psi}(\mathbf{k})$. To that end, we insert (1.175) into the formula for the Fourier transform

$$\hat{\psi}(\mathbf{k}) = \Big(\frac{1}{2\pi}\Big)^{3/2} \int_{\mathbb{R}^3} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\, \psi(\mathbf{x})\, d^3x \tag{1.176}$$

$$= \Big(\frac{1}{2\pi}\Big)^{3/2} \int_0^{\infty} \int_{S^2} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\, \frac{1}{r}\, f(r)\, Y_{\ell}^{m}(\vartheta, \varphi)\, r^2 dr\, d\Omega \tag{1.177}$$

For the plane wave $\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}}$, we substitute the expansion in terms of spherical harmonics (the complex conjugate of (1.174)),

$$\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}} = \frac{4\pi}{kr} \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} (-\mathrm{i})^{\ell'}\, \hat{\jmath}_{\ell'}(kr)\, Y_{\ell'}^{m'}(\vartheta', \varphi')\, \overline{Y_{\ell'}^{m'}(\vartheta, \varphi)}. \tag{1.178}$$

Using the orthonormality of the spherical harmonics, Eq. (1.109), we can perform the integration over the angles ϑ and φ. This removes the sum over ℓ' and m', because only the term with $\ell' = \ell$ and $m' = m$ gives a contribution. The short calculation gives

$$\hat{\psi}(\mathbf{k}) = \Big(\frac{1}{2\pi}\Big)^{3/2} \int_0^{\infty} \frac{4\pi}{kr}\, (-\mathrm{i})^{\ell}\, \hat{\jmath}_{\ell}(kr)\, Y_{\ell}^{m}(\vartheta', \varphi')\, \frac{1}{r}\, f(r)\, r^2 dr \tag{1.179}$$

$$= \frac{1}{k}\, (-\mathrm{i})^{\ell} \Big(\frac{2}{\pi}\Big)^{1/2} \int_0^{\infty} f(r)\, \hat{\jmath}_{\ell}(kr)\, dr\, Y_{\ell}^{m}(\vartheta', \varphi') \tag{1.180}$$

$$= \frac{1}{k}\, h(k)\, Y_{\ell}^{m}(\vartheta', \varphi'), \tag{1.181}$$

where $(k, \vartheta', \varphi')$ are the spherical coordinates of $\mathbf{k} \in \mathbb{R}^3$. We have found that the Fourier transform $\hat{\psi}(k)$ is again an eigenfunction of L^2 and L_3 with the same quantum numbers ℓ and m. The Fourier transform maps an angular momentum eigenspace into itself.

The function h is connected to f via an integral transformation that is known as the *Hankel transformation*,

$$h(k) = (-\mathrm{i})^\ell \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty f(r)\, \hat{\jmath}_\ell(kr)\, dr. \tag{1.182}$$

The Hankel transformation is the "radial Fourier transformation" in the angular-momentum subspace belonging to the quantum number ℓ. The inverse Hankel transformation can be derived from the formula for the inverse Fourier transformation. It is given by

$$f(r) = \mathrm{i}^\ell \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty h(k)\, \hat{\jmath}_\ell(kr)\, dk. \tag{1.183}$$

Like the Fourier transformation on $L^2(\mathbb{R}^3)$, the Hankel transformation extends to a unitary transformation on $L^2([0,\infty))$,

$$\int_0^\infty |f(r)|^2\, dr = \int_0^\infty |h(k)|^2\, dk. \tag{1.184}$$

The quantum mechanical interpretation of f and h is straightforward. The function f is the radial position probability amplitude and h gives the radial momentum distribution:

$$\int_a^b |f(r)|^2\, dr \quad \text{is the probability of finding the particle in a distance between } a \text{ and } b \text{ from the origin.}$$

$$\int_a^b |h(k)|^2\, dk \quad \text{is the probability that the absolute value of the momentum is between } a \text{ and } b.$$

One should keep in mind that the relation between the radial momentum distribution and the radial position distribution depends on the angular-momentum quantum number ℓ. Let us finally put the main result into a box.

Radial-angular separation and the Fourier transform:
The Fourier transform of $\frac{1}{r}\, f(r)\, Y_\ell^m(\vartheta, \varphi)$ is given by $\frac{1}{k}\, h(k)\, Y_\ell^m(\vartheta', \varphi')$, where h is the Hankel transform of f. The Fourier transform thus leaves each angular-momentum subspace invariant.

An arbitrary function in $L^2(\mathbb{R}^3)$ has an expansion of the form

$$\psi(\mathbf{x}) = \frac{1}{r} \sum_{\ell,m} f_{\ell,m}(r)\, Y_\ell^m(\vartheta, \varphi), \tag{1.185}$$

and the result above can be applied, because the Fourier transformation is linear.

1.10. Spherically Symmetric Potentials

1.10.1. The structure of the eigenvalue spectrum

A spherically symmetric potential $V(\mathbf{x}) = V(r)$ is the operator of multiplication with a function that depends only on the distance $r = |\mathbf{x}|$ from the origin. Because the angular-momentum operators involve derivatives only with respect to the angular coordinates ϑ and φ, and because V does not depend on the angles, we have the commutation relation

$$[V(r), \mathbf{L}] = 0. \tag{1.186}$$

The angular momentum also commutes with the kinetic energy, and hence the quantum mechanical system described by the Hamiltonian $H = H_0 + V$ is rotationally invariant:

$$[H, \mathbf{L}] = 0. \tag{1.187}$$

The stationary Schrödinger equation in the angular-momentum subspace with quantum numbers ℓ, m is

$$\frac{\hbar^2}{2\mathrm{m}}\Big(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\Big)\, f(r) + V(r)\, f(r) = E\, f(r). \tag{1.188}$$

This is the radial Schrödinger equation with a potential. Clearly, this equation does not depend on the eigenvalue m of L_3, because a spherically symmetric Hamiltonian H does not contain L_3.

The eigenvalues of the three-dimensional Schrödinger equation

$$H\psi = \Big(-\frac{\hbar^2}{2\mathrm{m}}\,\Delta + V(|\mathbf{x}|)\Big)\psi = E\,\psi \tag{1.189}$$

are those numbers $E_{\ell;n_r}$ for which (1.188) has a nonzero square-integrable solution in the Hilbert space $L^2([0,\infty))$. Like the radial equation, the eigenvalues $E_{\ell;n_r}$ are independent of the quantum number m. The number n_r is called the *radial quantum number*. It just serves as a label for the different eigenvalues of the radial equation. We denote the radial eigenfunction belonging to the eigenvalue $E_{\ell;n_r}$ by $f_{\ell;n_r}(r)$.

Using the radial eigenfunctions, we define eigenfunctions of H belonging to the eigenvalues $E_{\ell;n_r}$ by

$$\psi_{\ell,m;n_r}(\mathbf{x}) = \frac{1}{r}\, f_{\ell;n_r}(r)\, Y_\ell^m(\vartheta,\varphi), \tag{1.190}$$

where (r,ϑ,φ) are the spherical coordinates of $\mathbf{x}$, and m is any of the eigenvalues of L_3. The functions $\psi_{\ell,m;n_r}$ are simultaneous eigenstates of H, L^2, and L_3, belonging to the eigenvalues $E_{\ell;n_r}$, $\ell(\ell+1)$, and m, respectively. For every possible energy $E_{\ell;n_r}$ and every possible ℓ we have $2\ell+1$ linearly independent eigenfunctions $\psi_{\ell,m;n_r}$, with $m = -\ell, -\ell+1, \ldots, +\ell$. Hence, the degree of degeneracy of the eigenvalue $E_{\ell;n_r}$ is at least $2\ell+1$. Experimentally, the states belonging to different eigenvalues of L_3 can only be distinguished in the presence of magnetic fields. Hence, m is often called the *magnetic quantum number*.

Eigenvalue problem with spherical symmetry:

The simultaneous eigenfunctions of L^2, L_3, and the spherically symmetric Schrödinger operator $H = p^2/2m + V(r)$ are given by

$$\psi_{\ell,m;n_r}(\mathbf{x}) = \frac{1}{r}\, f_{\ell;n_r}(r)\, Y_\ell^m(\vartheta,\varphi), \tag{1.191}$$

where $f_{\ell;n_r}$ is the n_r-th eigenfunction of the *radial Schrödinger operator*

$$\mathbf{h}_\ell = \frac{\hbar^2}{2\mathrm{m}}\Big(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\Big) + V(r). \tag{1.192}$$

The corresponding eigenvalues $E_{\ell;n_r}$ do not depend on the quantum number m. Hence, the multiplicity of each eigenvalue of H is at least $2\ell+1$.

The radial Schrödinger operator $\mathbf{h}_\ell$ is a self-adjoint differential operator in $L^2([0,\infty))$. We can order its eigenvalues according to their size,

$$E_{\ell;n_r} < E_{\ell,n_r+1}, \quad n = 0,1,2,\ldots. \tag{1.193}$$

The quantum number n_r counts the number of zeros of the radial eigenfunction $f_{\ell;n_r}(r)$ in the interval $(0,\infty)$. The ground state with angular momentum ℓ has no zero at all (except at $r=0$), the first excited state has precisely one zero, and so forth. To every eigenvalue $E_{\ell;n_r}$ belongs a unique eigenfunction $f_{\ell;n_r}$. Hence, the eigenvalues of $\mathbf{h}_\ell$ are non-degenerate (but not the eigenvalues of H).

Any linear combination of the eigenvectors $\psi_{\ell,m;n_r}$ belonging to some eigenvalue E of H is again an eigenvector belonging to the same eigenvalue E,

$$\psi_{\ell;n_r}(\mathbf{x}) = \sum_{m=-\ell}^{\ell} c_m \, \psi_{\ell,m;n_r}(\mathbf{x}), \quad \text{where } c_m \in \mathbb{C}. \tag{1.194}$$

In particular, the eigenfunctions

$$\psi^+_{\ell,|m|;n_r}(\mathbf{x}) = \frac{1}{\sqrt{2}} \big(\psi_{\ell,m;n_r}(\mathbf{x}) + (-1)^m \, \psi_{\ell,-m;n_r}(\mathbf{x})\big), \tag{1.195}$$

$$\psi^-_{\ell,|m|;n_r}(\mathbf{x}) = \frac{\mathrm{i}}{\sqrt{2}} \big(\psi_{\ell,m;n_r}(\mathbf{x}) - (-1)^m \, \psi_{\ell,-m;n_r}(\mathbf{x})\big) \tag{1.196}$$

are real-valued. (Note that the radial part $f_{\ell;n_r}$ can be chosen to be real because it is a solution of a real differential equation vanishing for $r \to 0$ and $r \to \infty$). These eigenfunctions are called *real orbitals*. A real orbital is an eigenfunction of the energy and of L^2, but not of L_3.

The states with angular momenta $\ell = 0, 1, 2$, and 3 are sometimes also denoted by the letters s, p, d, and f. This is the spectroscopic notation. The letters have the following historical meaning: s = simple, p = principal, d = diffuse, f = fundamental. Higher quantum numbers are then denoted alphabetically by g, h, and so forth.

Ψ As a differential equation of second order, (1.188) has two linearly independent solutions for every energy E, say $u(E, r)$ and $v(E, r)$. Typically, these solutions behave as $u(E, r) \sim r^{\ell+1}$ and $v(E, r) \sim r^{-\ell}$ for small r, see also (1.161) and (1.162). A physically correct solution is one for which the corresponding function (1.190) is in the domain of the self-adjoint operator H. The mathematical theory tells us that these functions have to be bounded and continuous on $\mathbb{R}^3$, at least for physically meaningful (that is, not too singular) potential functions V. Therefore, $(1/r)\, f_{\ell;n_r}(r)$ has to remain bounded, as $r \to 0$. Only the solution u has this property.[5] This solution is called the regular solution of (1.188). It is distinguished by the boundary condition $u(r) \to 0$, as $r \to 0$. The solution $u(E, r)$ turns out to be square-integrable only for exceptional values of the parameter E, that is, for the eigenvalues $E = E_{\ell;n_r}$. In these cases, the solution $f_{\ell;n_r}(r) = u(E_{\ell;n_r}, r)$ also vanishes at infinity.

[5]For $\ell = 0$, the second solution v is also bounded and hence square-integrable in a neighborhood of $r = 0$. Hence, the condition of square-integrability alone is not sufficient to select the physically correct solution.

1.10.2. The vibrating rotator: A model of a diatomic molecule

In Section 1.7.2, we stated that the rigid rotator is an approximate model for a diatomic molecule in a vibrational ground state. Here, we are going to refine the model and take into account the vibrational degree of freedom. We assume that the two atoms are bound together as a result of some complicated interaction between the two nuclei and all their electrons. The configuration with the minimal potential energy will have the two nuclei at some distance r_0 from each other. The effective force between the nuclei would be repulsive at closer distances $r < r_0$ and attractive at larger distances $r > r_0$. It is evident that the details of the effective interaction can be very complicated because many particles are involved. We are going to discuss a very simple model that nevertheless shows many essential features of diatomic molecules. This potential is called *Kratzer's molecular potential* (see Fig. 1.13). It is given by

$$V(r) = V_0 \left(\frac{r_0^2}{r^2} - 2\,\frac{r_0}{r} \right), \quad V_0 > 0, \quad r_0 > 0, \tag{1.197}$$

where r is the internuclear distance. This function is spherically symmetric, and it has a minimum for $r = r_0$, with $V(r_0) = V_0$. It is clear that this model is very unphysical both at very small distances and at very large distances. At small distances, the model potential describes a very strong repulsive potential with a $1/r^2$-singularity (too strong for the Coulomb repulsion of the positively charged nuclei which is proportional to $1/r$). For large r, the dominating term in $V(r)$ is an attractive Coulomb potential $-2V_0 r_0/r$. But at large distances, the two atoms are separated completely. As they are neutral, the effective force between them will be much weaker than the attractive Coulomb force described by the model. But nevertheless, the model is not bad within a certain range of energies. It describes a two-particle system that is able to perform rotations and simultaneous oscillations around an equilibrium distance. Moreover, Kratzer's model is convenient because the Schrödinger equation with this potential can be solved exactly.

We use the center-of-mass coordinates described in Section 1.7.2 and insert for m the reduced mass μ of the two atoms. The radial Schrödinger equation (1.188) with the potential (1.197) reads

$$\frac{\hbar^2}{2\mu}\Big(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1) + a}{r^2} \Big)\, f(r) - \frac{2\,V_0\,r_0}{r}\, f(r) = E\, f(r), \tag{1.198}$$

where we used the abbreviation

$$a = \frac{2\mu\, r_0^2}{\hbar^2}\, V_0. \tag{1.199}$$

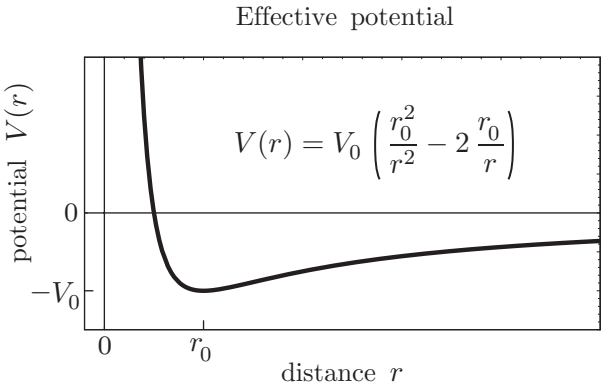


FIGURE 1.13. A simple model for the effective potential between the two nuclei in a diatomic molecule.

By the variable substitution

$$f(r) = g(x), \quad x = \frac{a}{r_0}\, r, \tag{1.200}$$

the radial Schrödinger equation is transformed into

$$\frac{1}{2}\Big(-\frac{d^2}{dx^2} + \frac{\ell(\ell+1)+a}{x^2}\Big)\, g(x) - \frac{1}{x}\, g(x) = \frac{1}{2aV_0}\, E\, g(x). \tag{1.201}$$

Writing

$$\epsilon = \frac{E}{2aV_0} \quad \text{and} \quad \lambda = -\frac{1}{2} + \left(\Big(\ell + \frac{1}{2}\Big)^2 + a \right)^{1/2} \tag{1.202}$$

such that $\lambda(\lambda+1) = \ell(\ell+1) + a$, we arrive at

$$\frac{1}{2}\Big(-\frac{d^2}{dx^2} + \frac{\lambda(\lambda+1)}{x^2}\Big)\, g(x) - \frac{1}{x}\, g(x) = \epsilon\, g(x). \tag{1.203}$$

This equation is formally identical to the radial Schrödinger equation for the Coulomb problem (except that the parameter λ need not be an integer). We are going to solve this equation in the next chapter (see Section 2.5.2, Eq. (2.99)). Here, we just quote the result (2.62) that (1.203) has the eigenvalues

$$\epsilon_{\lambda;n_r} = -\frac{1}{2(n_r + \lambda + 1)^2}, \quad n = 0, 1, 2, 3, \ldots. \tag{1.204}$$

Inserting the definitions of λ and ϵ, we obtain the energy-eigenvalues for this problem as

$$E_{\ell;n_r} = -\frac{2\mu r_0^2}{\hbar^2}\, V_0^2 \left(n_r + \frac{1}{2} + \left(\Big(\ell + \frac{1}{2}\Big)^2 + \frac{2\mu r_0^2}{\hbar^2}\, V_0 \right)^{1/2} \right)^{-2}. \tag{1.205}$$

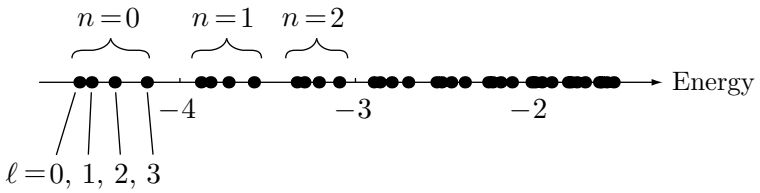


FIGURE 1.14. Energy eigenvalues arising from Kratzer's molecular potential with $V_0 = 5$ and $r_0 = 5$. The graph shows the eigenvalues with quantum numbers $n = n_r \leq 8$ and $\ell \leq 3$.

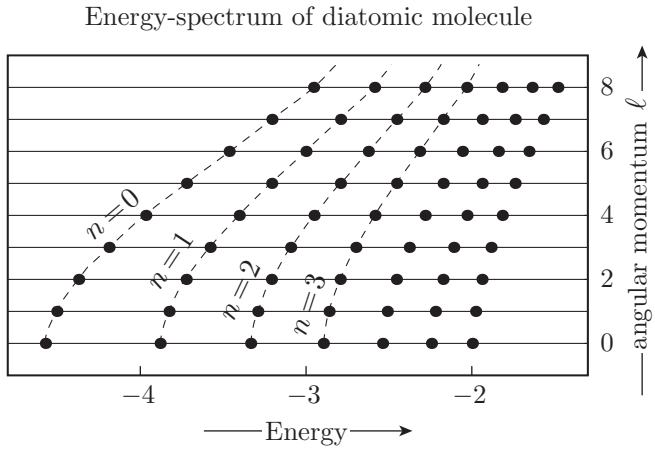


FIGURE 1.15. Two-dimensional diagram of the eigenvalue spectrum according to Kratzer's model of a diatomic molecule ($V_0 = 5$ and $r_0 = 5$), showing the quantum numbers $n = n_r \leq 8$ and $\ell \leq 8$.

The quantum number n_r enumerates the eigenvalues of the radial Schrödinger operator. It thus describes the vibration around the classical equilibrium at r_0. The quantum number ℓ describes the rotational state as usual. We expect that the formula (1.205) is a good approximation for a diatomic molecule if the radial oscillations are not too large. This is the case for small values of the quantum number n_r, where the corresponding eigenstates are localized sufficiently close to the classical equilibrium at $r = r_0$. Similar restrictions will apply to the quantum number ℓ.

Figures 1.14 and Figure 1.15 show the energies $E_{\ell;n_r}$ for small values of n_r and ℓ, assuming that $a \gg 1$ (as it is the case for most molecules). Obviously,

Figure 1.14 would become too cluttered if more than a few eigenvalues are shown. In Figure 1.15, we use a two-dimensional plot where the vertical position of an eigenvalue indicates the quantum number ℓ. For our choice of parameter values, the energy-difference between two vibrational levels $E_{\ell,n_r+1} - E_{\ell;n_r} \approx \mathrm{O}(1/a)$ is much larger than the spacing $E_{\ell+1;n_r} - E_{\ell;n_r}$ of the rotational levels, which is of order $1/a^2$. Hence, it needs much more energy to bring the system from $n_r = 0$ to $n_r = 1$ than to change the angular-momentum quantum number. If the energies involved are not too high, the quantum number n_r remains unchanged, and the system behaves like a rigid rotator.

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