Chapter 4

Angular momentum and the central potential

4.1 3D motion

The Hilbert space of three-dimensional motional states of a point-like particle can be seen as a tensor product of Hilbert spaces associated with individual coordinates:

$$\mathbb{V}_{3D} = \mathbb{V}_x \otimes \mathbb{V}_y \otimes \mathbb{V}_z. \tag{4.1}$$

The position and momentum operators are vectors: $\hat{\vec{r}} = (\hat{x}, \hat{y}, \hat{z})$, $\hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$, and the commutation relation between them takes the form $[x_i, p_j] = i\hbar\delta_{ij}$. Eigenstates of vector operators are defined as

$$\hat{\vec{r}}\,|\vec{r}_0\rangle = \vec{r}_0\,|\vec{r}_0\rangle\,. \tag{4.2}$$

In other words, the state $|\vec{r}_0\rangle$ with $\vec{r}_0 = (\hat{x}_0, \hat{y}_0, \hat{z}_0)$ must simultaneously satisfy three equations:

$$\hat{x}\,|\vec{r}_0\rangle = x_0\,|\vec{r}_0\rangle\,; \tag{4.3}$$

$$\hat{y}\,|\vec{r}_0\rangle = y_0\,|\vec{r}_0\rangle\,; \tag{4.4}$$

$$\hat{z}\,|\vec{r}_0\rangle = z_0\,|\vec{r}_0\rangle\,. \tag{4.5}$$

Exercise 4.1 Show that the only state satisfying Eq. (4.2) is the state $|\vec{r}_0\rangle = |x_0\rangle \otimes |y_0\rangle \otimes |z_0\rangle$, with each of the states $|x_0\rangle$, $|y_0\rangle$, and $|z_0\rangle$ being eigenstates of the 1D position operator in spaces $\mathbb{V}_x$, $\mathbb{V}_y$, and $\mathbb{V}_z$, respectively.

Exercise 4.2 Write the three-dimensional de Broglie wave, i.e. the inner product $\langle\vec{x}|\,\vec{p}\rangle$
Solution. According to the result of the previous exercise and the definition of the inner product for tensor product spaces,

$$\langle\vec{x}|\,\vec{p}\rangle = \langle x|\,p_x\rangle\,\langle y|\,p_y\rangle\,\langle z|\,p_z\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}(xp_x + yp_y + zp_z)} = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{x}\cdot\vec{p}}. \tag{4.6}$$

Exercise 4.3 Show that the state $|\vec{p}\rangle$ is an eigenstate of the kinetic energy operator $T = |\hat{\vec{p}}|^2/2m = (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)/2m$ with the eigenvalue $(p_x^2 + p_y^2 + p_z^2)/2m$.

Exercise 4.4 a) Show that the action of the momentum operator in the position representation is $\langle\vec{x}|\,\hat{\vec{p}}|\psi\rangle = -i\hbar\nabla\,\langle\vec{x}|\,\psi\rangle = -i\hbar\nabla\psi(\vec{x})$ (in other words, in the position basis, $\vec{p} \leftrightarrow -i\hbar\vec{\nabla}$).

b) The time-independent Schrödinger equation in the position representation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}), \tag{4.7}$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the Laplacian.

Exercise 4.5 The three-dimensional generalization of the probability current density (see Ex. 3.34) is

$$\vec{j} = -i\frac{\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right). \tag{4.8}$$

a) Show that

$$\frac{\mathrm{pr}(\vec{r},t)}{dt} = -\vec{\nabla}\cdot\vec{j}. \tag{4.9}$$

This is the 3D form of the continuity equation.

b) Verify this equation for the 3D de Broglie wave.

Note 4.1 If the Hamiltonian can be written in the form $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$, where each of the operators $\hat{H}_x$, $\hat{H}_y$, $\hat{H}_z$ act on quantum states in their respective Hilbert subspace, the energy eigenstates can be written as tensor products of subspace states states: $|\psi_E\rangle = |\psi_{Ex}\rangle\otimes|\psi_{Ey}\rangle\otimes|\psi_{Ez}\rangle$, with $\hat{H}_i|\psi_{Ei}\rangle = E_i|\psi_{Ei}\rangle$ (where $i = x, y, z$) and $E = E_x + E_y + E_z$. Example: de Broglie wave. Otherwise, the energy eigenstates are "entangled" with respect to coordinate subspaces.

Exercise 4.6 Find the energy eigenstates and their degeneracy for a three-dimensional isotropic harmonic oscillator with $V(\vec{r}) = m\omega^2 r^2/2$.

4.2 Angular momentum

Eq. (4.7) is a three-dimensional differential equation and is generally difficult to solve. In this chapter, we will study the specific case of rotationally invariant fields, i.e. such that $V(\vec{r}) = V(r)$. In this potential, the solution is simplified by introducing the notion of angular momentum.

Definition 4.1 *Angular momentum* is the operator defined as

$$\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{p}}. \tag{4.10}$$

Exercise 4.7 Show that the angular momentum is a Hermitian operator.

Note 4.2 Generally, a product of two Hermitian operators is not necessarily Hermitian. Example: position and momentum associated with the same dimension.

Note 4.3 In studying the angular momentum algebra we shall frequently use the *antisymmetric unity tensor of rank 3*, ϵ_{jkl}, which is defined as follows:

- For any $i,\ j,\ k$, the value of ϵ_{jkl} changes sign whenever any two indices are exchanged. Consequently, whenever any two indices are equal, $\epsilon_{jkl} = 0$
- $\epsilon_{123} \equiv \epsilon_{xyz} = 1$

Explicitly:

$$\epsilon_{xyz} = 1,\ \epsilon_{xzy} = -1,\ \epsilon_{zxy} = 1,\ \epsilon_{zyx} = -1,\ \epsilon_{yzx} = 1,\ \epsilon_{yxz} = -1, \tag{4.11}$$

all other $\epsilon_{jkl} = 0$.

Note 4.4 In all tensor expressions in these notes, repeated indices imply summation, e.g. for two vectors $\vec{a}$ and $\vec{b}$: $a_i b_i = a_x b_x + a_y b_y + a_z b_z = \vec{a}\cdot\vec{b}$.

Exercise 4.8 Verify that $\epsilon_{jkl}\epsilon_{jkl} = 6$; $\epsilon_{jkl}\epsilon_{jkm} = 2\delta_{lm}$; $\epsilon_{jkl}\epsilon_{jmn} = \delta_{km}\delta_{ln} - \delta_{kn}\delta_{lm}$.

Exercise 4.9 Verify that Eq. (4.10) can be written as $L_j = \epsilon_{jkl}\hat{r}_k\hat{p}_l$.

Exercise 4.10 Verify the following commutation properties of the angular momentum operator:

a) $[\hat{L}_j, \hat{r}_k] = i\hbar\epsilon_{jkl}\hat{r}_l$;

b) $[\hat{L}_j, \hat{p}_k] = i\hbar\epsilon_{jkl}\hat{p}_l$;

c) $[\hat{L}_j, \hat{L}_k] = i\hbar\epsilon_{jkl}\hat{L}_l$;

d) $[\hat{L}_j, \hat{r}^2] = 0$;

e) $[\hat{L}_j, \hat{p}^2] = 0$;

f) $[\hat{L}_j, \hat{L}^2] = 0$;

Exercise 4.11 Show that the Hamiltonian $\hat{H} = \hat{\vec{p}}^2/2m + V(\hat{\vec{r}})$ can be rewritten as

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2m\hat{r}^2} + V(\hat{\vec{r}}), \tag{4.12}$$

where $\hat{p}_r = \hat{p}^2 - \hat{L}^2/\hat{r}^2$ is the projection of the momentum onto the radius-vector.

Exercise 4.12 Show that if the potential $V(\hat{\vec{r}})$ is rotationally invariant (i.e. depends only on $\hat{r} = |\hat{\vec{r}}|$), the operators $\hat{\vec{L}}_i$ and $\hat{\vec{L}}^2$ commute with the Hamiltonian (4.12)

Note 4.5 This corresponds to the classical law of angular momentum conservation in a central potential.

4.3 Angular momentum eigenstates

We see that all components of the angular momentum commute with the Hamiltonian. As we know (Chapter I), for two commuting operators one can find a common eigenbasis in which they both diagonalize. This fact simplifies our task to find the eigenstates and eigenvalues of the Hamiltonian. Our strategy is, *first*, to find all eigenstates of the angular momentum operator and, *second*, to select those among them that are eigenstates of the Hamiltonian.

The trouble is, the three components of $\hat{\vec{L}}$ do not commute with each other and thus have different sets of eigenstates. One option would be to look for eigenstates of just one component, e.g. $\hat{L}_z$; however, these turn out to ne highly degenerate. The value of L_z alone is insufficient to fully describe a quantum state. Therefore we will seek common eigenstates of two operators, $\hat{L}^2$ and $\hat{L}_z$. This will lift (at least partially) the undesired degeneracy. We will denote the sought eigenstates as $|\lambda m\rangle$, with λ being the eigenvalue of $\hat{L}^2/\hbar^2$ and m being the eigenvalue of $\hat{L}_z/\hbar$. Both l and m are dimensionless.

Note 4.6 Caution: we use the same letter m to denote the mass of the particle.

Note 4.7 The choice of the z-component of the angular momentum is due to historic reasons. We could as well have chosen $\hat{L}_x$ or $\hat{L}_y$.

Exercise 4.13 Show that m^2 cannot be greater than λ.

Definition 4.2 The *raising and lowering operators* are defined as $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$.

Exercise 4.14 Show that:

a) $\hat{L}_- = \hat{L}_+^\dagger$;

b) $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar L_\pm$, $[\hat{L}^2, \hat{L}_\pm] = 0$, $[\hat{L}_+, \hat{L}_-] = 2\hbar L_z$;

c) $\hat{L}^2 = \hat{L}_+\hat{L}_- + \hat{L}_z^2 - \hbar\hat{L}_z = \hat{L}_-\hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z$.

Exercise 4.15 Suppose some state $|\lambda m\rangle$ is a common eigenstate of $\hat{L}^2/\hbar^2$ and $\hat{L}_z/\hbar$. Then

a) the state $\hat{L}_+ |\lambda m\rangle$ is also a common eigenstate of these operators with eigenvalues λ, $m+1$;

b) the state $\hat{L}_- |\lambda m\rangle$ is also a common eigenstate of these operators with eigenvalues λ, $m-1$.

Hint: Use $[\hat{L}_z, \hat{L}_\pm]$.

Note 4.8 The above exercise shows that the states $\hat{L}_+ |\lambda m\rangle$ and $\hat{L}_- |\lambda m\rangle$ are proportional to the normalized states $|\lambda, m+1\rangle$ and $|\lambda, m-1\rangle$, respectively. In the following, we find the proportionality coefficient.

Exercise 4.16 Using Ex. 4.15, find $\langle \lambda m| \hat{L}_+ \hat{L}_- |\lambda m\rangle$ and $\langle \lambda m| \hat{L}_- \hat{L}_+ |\lambda m\rangle$. Show that

a) $\hat{L}_+ |\lambda m\rangle = \hbar\sqrt{\lambda - m(m+1)}\, |\lambda, m+1\rangle$;

b) $\hat{L}_- |\lambda m\rangle = \hbar\sqrt{\lambda - m(m-1)}\, |\lambda, m-1\rangle$.

Note 4.9 We found that, unless $\lambda = m(m+1)$ or $\lambda = m(m-1)$, if the state $|\lambda m\rangle$ exists (i.e. is an element of the Hilbert space), so do the states $|\lambda, m+1\rangle$ and $|\lambda, m-1\rangle$. Similarly, states $|\lambda, m+2\rangle$, $|\lambda, m-2\rangle$ etc. must also exist. On the other hand, we must have $m^2 \le \lambda$. The only way to resolve this contradiction is to assume that

$$\lambda = l(l+1), \tag{4.13}$$

where l is a nonnegative integer or a half-integer. Then the chain is broken at both $m = +l$ and $m = -l$.

Exercise 4.17 Find the degree of degeneracy of eigenstates of $\hat{L}^2$ with respect to the observable $\hat{L}_z$.
Answer: m can take values from $-l$ to $+l$, a total of $2l+1$ possibilities.

Definition 4.3 From now on we will use notation $|lm\rangle$ to denote the common eigenstates of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively.

Exercise 4.18 Show that the matrix element $\left\langle lm \middle| \hat{L}_z \middle| l'm' \right\rangle$ vanishes whenever $l \neq l'$. Show the same for $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_\pm$, and $\hat{L}^2$.
Hint: this result can be obtained without calculations from Ex. 4.10(f).

Note 4.10 Because, according to the previous problem, angular momentum operators do not couple states with different l, their matrices are usually written for a subspace associated with a particular value of l. In these matrices, the angular momentum basis eigenvectors are traditionally listed in the order of *decreasing* m.

Exercise 4.19 Find the general expression for the matrix elements of $\hat{L}_x$ and $\hat{L}_y$ in the $|lm\rangle$-basis. Write the matrices of $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, $\hat{L}_\pm$, and $\hat{L}^2$ explicitly for $l = 1/2$, $l = 1$.
Answer for $l = 1/2$:

$$\hat{L}_x \leftrightarrow \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \hat{L}_y \leftrightarrow \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \hat{L}_z \leftrightarrow \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \hat{L}^2 \leftrightarrow \frac{3\hbar}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4.14}$$

Definition 4.4 The matrices of operators $2\hat{L}_i/\hbar$ in the subspace $l = 1/2$ are called the *Pauli matrices* [cf. Eq. (1.34)].

Exercise 4.20 Verify explicitly for the $l = 1$ case that the angular momentum matrices obey $\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}^2$.

Exercise 4.21 Find the expectation values and uncertainties of operators $\hat{L}_x$ and $\hat{L}_y$ in a state $|lm\rangle$. Verify the uncertainty principle.

Note 4.11 In the states $m = l$ and $m = -l$, $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = \langle \hat{L}^2 - \hat{L}_z^2 \rangle = \hbar^2[l(l+1) - l^2] = \hbar^2 l$. Even though L_z takes its maximum possible value, there is still some room left for the fluctuations of L_x and L_y so the uncertainty principle can be upheld.

4.4 Wavefunctions of angular momentum eigenstates

Our next goal is to find the wavefunctions corresponding to the states derived in the previous section. Because of an axially symmetric $V(r)$, it is more convenient to work in spherical coordinates ($x = r\sin\theta\cos\phi,\ y = r\sin\theta\sin\phi,\ z = r\cos\theta$). We begin by reformulating the Schrödinger equation in these coordinates. The mathematics is straightforward but cumbersome, so in these notes I will only present the most important results.

Exercise 4.22 Show that the angular momentum operator is expressed in the position basis as follows: $\langle\vec{r}|\,\hat{\vec{L}}\,|\psi\rangle = -i\hbar(\vec{r}\times\vec{\nabla})\psi(\vec{r})$.

Exercise 4.23 Using partial derivatives, express the angular momentum components in spherical coordinates and show that, in the coordinate basis,

$$\hat{L}_z \leftrightarrow -i\hbar\frac{\partial}{\partial\phi}; \tag{4.15}$$

$$\hat{L}^2 \leftrightarrow (-\hbar^2)\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right]; \tag{4.16}$$

$$\hat{\nabla}^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right]; \tag{4.17}$$

Note 4.12 Comparing Eqs. (4.16) and (4.17) we see that the angular momentum component corresponds to the last two terms in $\vec{\nabla}$. The first term in $\vec{\nabla}$ corresponds to the radial momentum term in Eq. (4.12).

Exercise 4.24 Find the eigenwavefunction of the operators (4.15) and (4.16) corresponding to the eigenvalues $\hbar m$ and $\hbar^2 l(l+1)$, respectively.
Answer:

$$\psi_l^m(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi), \tag{4.18}$$

where $R(r)$ is an arbitrary function dependent only on the radius, and

$$Y_l^m(\theta,\phi) = (-1)^l\sqrt{\frac{(2l+1)!}{4\pi}}\frac{1}{2^l l!}\sqrt{\frac{(l+m)!}{(2l)!(l-m)!}}\sin^{-m}\theta\frac{d^{l-m}}{d(\cos\theta)^{l-m}}(\sin\theta)^{2l}e^{im\phi} \tag{4.19}$$

are the *spherical harmonics*.

Note 4.13 Spherical harmonics satisfy the orthonormality condition

$$\int Y_l^{m*}(\theta,\phi)Y_{l'}^{m'}(\theta,\phi)d\Omega = \delta_{ll'}\delta_{mm'}. \tag{4.20}$$

and form a complete set, i.e. any function of θ and ϕ can be written as a linear combination of Y_l^m's

Note 4.14 Spherical harmonics contain a factor $e^{im\phi}$. For a half-integer l, m is also half-integer and this factor results in $\psi(r,\theta,\phi) = -\psi(r,\theta,\phi+2\pi)$, which is impossible. Therefore, *a material pointlike particle in a radially symmetric field must have integer angular momentum.* On the other hand, some particles also have "intrinsic" rotation "about their own axes" — *spin.* Spins are allowed to be half-integer.

Note 4.15 The eigenstates of the angular momentum (4.18) are infinitely degenerate with respect to the function $R(r)$. Our next task is to select, out of all possible radial functions, those with which the solution (4.18) becomes an eigen wavefunction of the Hamiltonian.

Exercise 4.25 Write the differential equation that $R(r)$ must satisfy in order for $\psi_l^m(r,\theta,\phi)$ to be an eigenstate of the Hamiltonian with eigenvalue E.
Solution: writing the time-independent Schrödinger equation with the Hamiltonian (4.12) and, according to Eq. (4.17),

$$\hat{p}_r^2 \leftrightarrow -\hbar^2 \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right], \tag{4.21}$$

we find

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]R_{El}(r)=ER_{El}(r). \tag{4.22}$$

The subscript El means that $R(r)$ satisfying the above equation depends on E and l. Note that $R(r)$ is independent from m: the energy eigenvalues, just like the eigenstates of L_z, are $2l+1$ times degenerate with respect to this parameter.

Exercise 4.26 Solve Ex. 4.6 in spherical coordinates and verify consistency.

4.5 The hydrogen atom

A hydrogen atom is a physical example of the central field motion problem. There, a light electron orbits around a heavy nucleus in a potential

$$V(r) = -e^2/r, \tag{4.23}$$

where e is the electron charge (we use the Gaussian system of units).

Exercise 4.27 Redefine $R_{El}(r) = U_{El}(r)/r$ and rewrite Eq. (4.22) with respect to $U_{El}(r)$.
Answer:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 r}+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]U_{El}(r)=EU_{El}(r). \tag{4.24}$$

Note 4.16 We shall look for bound states of the electron with the energy $E<0$.

Exercise 4.28 Find the asymptotic behavior of $U_{El}(r)$ at $r\to\infty$.
Answer: The second and third terms in the brackets will vanish at infinity, so

$$U_{El}(r) \propto e^{-\kappa r}, \tag{4.25}$$

where $\kappa = \sqrt{-2mE}/\hbar$.

Exercise 4.29 Find the asymptotic behavior of $U_{El}(r)$ at $r\to 0$.
Solution: At $r\to 0$, the first and second terms in the Hamiltonian will dominate, so Eq. (4.24) becomes

$$\frac{\partial^2}{\partial^2 r}U_{El}(r) = \frac{l(l+1)}{r^2}U_{El}(r), \tag{4.26}$$

whose solutions are either $U_{El}(r)\propto r^{-l}$ or $U_{El}(r)\propto r^{l+1}$. The first option results in a discontinuous wavefunction at $r=0$ and must be rejected.

Note 4.17 The above findings indicate that the solution for $U_{El}(r)$ can be presented in the form of a series

$$U_{El}(r) = \sum_{j=l+1}^{\infty} A_j r^j e^{-\kappa r}. \tag{4.27}$$

We just need to determine the coefficients A_j.

Exercise 4.30 Establish a recursive relation for A_j.
Solution:

$$\frac{d^2}{dr^2}U_{El}(r) = e^{-\kappa r}\left[\kappa^2\sum_j A_j r^j - 2\kappa\sum_j jA_j r^{j-1} + \sum_j j(j-1)A_j r^{j-2}\right]. \tag{4.28}$$

Substituting into Eq. (4.24) and expressing $E = -\hbar^2\kappa^2/2m$ we obtain

$$\begin{aligned} &-\left[\kappa^2\sum_j A_j r^j - 2\kappa\sum_j jA_j r^{j-1} + \sum_j j(j-1)A_j r^{j-2}\right] \\ &+l(l+1)\sum_j A_j r^{j-2} - \frac{2me^2}{\hbar^2}\sum_j A_j r^{j-1} = -\kappa^2\sum_j A_j r^j. \end{aligned} \tag{4.29}$$

The first term in the brackets can be cancelled with the right-hand side. Collecting similar terms in front of r^{j-1}, we find the desired recursion

$$\left[2\kappa j - \frac{2me^2}{\hbar^2}\right]A_j + \left[l(l+1) - j(j+1)\right]A_{j+1} = 0. \tag{4.30}$$

Note 4.18 For large j, $A_{j+2}/A_{j+1} \to 2\kappa/j$, which indicates divergence of the series (4.27). To prevent this, we must demand that the series terminate at some $j = n$. This requirement is fulfilled if the factor in front of A_j in Eq. (4.30) vanishes for $j = n$, i.e.

$$2\kappa n = \frac{2me^2}{\hbar^2} \tag{4.31}$$

or

$$E_n = -\frac{e^4 m}{2\hbar^2 n^2}. \tag{4.32}$$

These are the eigenvalues of the energy operator.

Definition 4.5 In the context of atomic physics, the number n is called the *principal quantum number*, l is the *orbital quantum number*, and m is the *magnetic quantum number*. The motional state $|nlm\rangle$ of the electron is fully defined in terms of these quantum numbers.

Note 4.19 The energy eigenvalues of the H-atom do not depend on l; however, because the sum in the series runs from $j = l + 1$ to n, we require $n \geq l + 1$. Each energy level is degenerate with respect to l which can take any integer value from 0 to $n - 1$. An additional degeneracy comes from the electron spin whose z-projection can take values $\pm 1/2$ (see below). The total degeneracy associated with a particular principal quantum number is

$$2\sum_{l=0}^{n-1}(2l+1) = 2n^2. \tag{4.33}$$

Definition 4.6 The energy levels of the hydrogen atom can be expressed as $E_n = -\mathrm{Ry}/n^2$, where

$$\mathrm{Ry} = -\frac{e^4 m}{2\hbar^2} \approx -13.6 \text{ eV} \tag{4.34}$$

is the *Rydberg constant*[1]. The quantity

$$a_0 = \frac{1}{\kappa_1} = \frac{\hbar^2}{e^2 m} \approx 0.53 \text{ Å} \tag{4.35}$$

(where $\kappa_1 = \sqrt{-2mE_1}/\hbar$), determining the approximate size of the atom, is called the *Bohr radius*.

[1] In SI units, $\mathrm{Ry} = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2$.

Note 4.20 Calculation of the actual spectrum of the hydrogen atom needs to take a finite mass of the nucleus into account. This is done by replacing in Eq. (4.32) the electron mass m by a slightly lower *reduced mass* $m_r = Mm/(M+m)$, where M is the mass of the nucleus. By tradition, however, the Rydberg constant and the Bohr radius are defined in terms of the electron mass.

Exercise 4.31 Evaluate numerically the experimentally observable wavelengths of the transitions of the Lyman ($n = 2, 3, 4, ... \to n' = 1$), Balmer ($n = 3, 4, 5, ... \to n' = 2$), and Paschen ($n = 4, 5, 6, ... \to n' = 3$) series. Which one lies in the visible range?

Note 4.21 Only in the hydrogen atom are energy levels degenerate with respect to l. States with a large angular momentum are located, on average, further away from the nucleus. Therefore, in a multielectron atom, an electron in a state with large l is screened from the nucleus's field by other electrons and has therefore a higher energy than an electron with the same n, but lower l. The magnetic quantum number m does not affect the energy even in multielectron atoms.

Exercise 4.32 Calculate the coefficients A_n explicitly for $n = 1$, $l = 0$ and $n = 2$, $l = 0, 1$. Normalize the wavefunctions according to $\int |\psi(\vec{r})|^2 d^3\vec{r} = 1$.
Hint: use $d^3\vec{r} = r^2 dr d\Omega$ and Eq. (4.20). $\int_0^\infty x^n e^{-x} dx = n!$.

Exercise 4.33 Find the expectation value and the uncertainty of the observables $\hat{x}$, $\hat{y}$, $\hat{z}$ in the states (a) $|1,0,0\rangle$, (b) $|2,1,0\rangle$, (c) $|2,1,1\rangle$.

Exercise 4.34 Assuming the radius of the proton to be $\sim 10^{-15}$ m, estimate the probability to find the electron in the state $|1,0,0\rangle$ inside the nucleus.

Exercise 4.35 Which of the matrix elements of the observables $\hat{A} = \hat{x}, \hat{y}, \hat{z}$ in (a) $\langle 1,0,0| \hat{A} |2,0,0\rangle$, (b) $\langle 1,0,0| \hat{A} |2,1,0\rangle$, (c)$\langle 1,0,0| \hat{A} |2,1,1\rangle$ vanish?

Note 4.22 The atomic electric dipole operator has the form $\hat{\vec{d}} = e\hat{\vec{r}}$. Therefore, those transitions in the previous exercise whose matrix elements vanish cannot be detected by optical means if the laser field is polarized along the respective coordinate.

Exercise 4.36 Make order-of-magnitude estimates for the energies of elementary electronic[2], rotational, and vibrational excitations of the H_2 molecule using the following assumptions:

- atoms in a molecule are separated by a_0;
- to evaluate the "spring constant" of the molecule, assume that the molecule dissociates (the "spring" breaks) when the atoms are pulled apart by more than the Bohr radius. The molecular binding energy is on the order of the Rydberg constant.

Express your answers is terms of the electron and proton masses and the Bohr radius. Compare them with the experimental data: $E_{\text{rot}} = \hbar^2/2I = 7.56 \times 10^{-3} eV$, $E_{\text{vib}} = \hbar\omega = 0.52 eV$, $E_{\text{el}} = \text{Ry} = 13.6 eV$.
Answer: $E_{\text{rot}} \sim \hbar^2/Ma_0^2$, $E_{\text{vib}} \sim \hbar^2/\sqrt{Mm}a_0^2$, $E_{\text{el}} \sim \hbar^2/ma_0^2$.

4.6 Spin

Definition 4.7 *Spin* $\hat{S}$ is the internal angular momentum of an elementary particle. Any particle is always in an eigenstate of the internal observable $\hat{L}^2$ with the value of l being determined by the nature of the particle. For example, all electrons, protons, neutrons have spin $l = 1/2$. Photons have spin $l = 1$.

Note 4.23 The eigenvalue m_s of the projection of the spin observable onto a particular axis is *not* determined by the nature of the particle and can be controlled by external means.

[2] i.e. associated with orbital states of electrons in atoms

Exercise 4.37 Determine the matrices of $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ in the m_s-basis for a spin-3/2 particle.

Exercise 4.38 An electron is prepared in an eigenstate of its spin's projection $\hat{S}_{\vec{R}}$ onto an axis $\vec{R}$ characterized by polar angles (θ_0, ϕ_0). The eigenvalue is equal to $m_{\vec{R}} = 1/2$. Express the electron's state in the canonical m_s-basis.
Hint: $\hat{S}_{\vec{R}} = \sin\theta_0 \cos\phi_0 \hat{S}_x + \sin\theta_0 \sin\phi_0 \hat{S}_y + \cos\theta_0 \hat{S}_z$. Find the matrix of $\hat{S}_{\vec{R}}$ in the m_s-basis and its eigenstates.

Definition 4.8 Particles with a half-integer spin are called *fermions*. Particles with an integer spin are called *bosons*.

Pauli exclusion principle: Two identical fermions cannot be in the same quantum state.

Note 4.24 In an atom, due to the Pauli principle, every electron has a unique combination of four quantum numbers $|n, l, m, m_s\rangle$.

Exercise 4.39 Discuss how the Pauli principle results in a quasiperiodic dependence of the atomic species' chemical properties on the nuclear charge.

4.7 Magnetic moment and magnetic field

We begin with recalling some classical facts about magnetic moments.

Definition 4.9 The *magnetic moment* of a conductor loop of area A carrying a current I is

$$\vec{\mu} = I\vec{A}/c, \tag{4.36}$$

where the area of the loop is treated as a vector directed perpendicular to the loop.

Exercise 4.40 Show that the energy of a magnetic moment placed in a magnetic field $\vec{B}$ is $H_{\text{int}} = -\vec{\mu} \cdot \vec{B}$ (the symbol H_{int} stands for the "interaction Hamiltonian").

Exercise 4.41 Show that if a pointlike particle of mass m and charge e moves along some orbit with angular momentum $\vec{L}$, it has a magnetic moment

$$\vec{\mu} = \vec{L}\frac{e}{2mc}. \tag{4.37}$$

Definition 4.10 The quantity $\vec{\mu}/\vec{L}$ in the context of the previous problem is called the *gyromagnetic ratio*.

Note 4.25 In quantum mechanics, all previous relations remain valid, but the magnetic moment and the angular momentum become operators. We can apply the formalism for the angular momentum derived in the previous section.

Exercise 4.42 Show that for an orbiting particle in a state with a definite magnetic quantum number m_l, the projection of the magnetic moment onto the z axis is given by

$$\mu_z = \frac{e}{2mc}\hbar m_l. \tag{4.38}$$

Definition 4.11 The quantity

$$\mu_B = \frac{e}{2mc}\hbar \tag{4.39}$$

is called the *Bohr magneton* of a particle. For the electron, it is equal to 0.58×10^{-8} eV/Gauss $= 9.3 \times 10^{-24}$ J/T.

Gyromagnetic ratio for the electron spin. For the magnetic moment associated with the spin, Eq. (4.37) needs to be modified:

$$\vec{\mu}_s = g\vec{S}\frac{e}{2mc}, \tag{4.40}$$

where g is the *Landé factor* which is determined by the "internal" properties of the particle. For the electron it is very close to 2.

Note 4.26 The Landé factor for the electron spin can be derived theoretically using methods of relativistic quantum electrodynamics, but this derivation is beyond this course. A naïve way to visualize this factor is the picture of an electron which in not exactly pointlike but has a finite size, with different distributions of mass and charge over the volume: while the mass is more concentrated in the particle's center, the charge is spread over the periphery. As a result, the ratio between the magnetic moment and the mechanical angular momentum is higher than that expected from a particle with identical distributions of mass and charge.

Definition 4.12 The *Stern-Gerlach apparatus* serves to measure a particle's magnetic moment. It contains a permanent magnet with a field gradient. When a particle is propagating through such apparatus, it experiences a force proportional to the projection of its magnetic moment onto the field direction and deviates from its original path. In this manner, μ_z (where the z-axis is determined by the field direction) is determined. Because the magnetic moment is proportional to the angular momentum, effectively *the Stern-Gerlach measurement is the measurement of the component of the angular momentum along the direction of the field.*

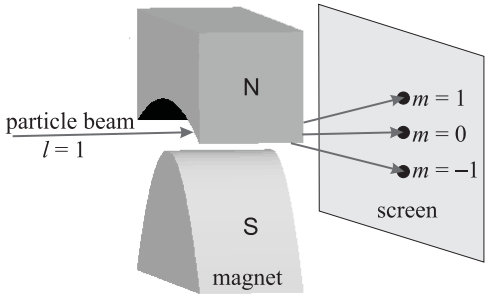


Figure 4.1: The Stern-Gerlach apparatus

Exercise 4.43 Free electrons are prepared with the spin projection onto the z-axis $m_s = +1/2$. At $t = 0$, a magnetic field B in the direction of y-axis is turned on. After time t_0 has elapsed, the field is turned off and the electrons are subjected to the Stern-Gerlach measurement with the magnetic field along the z axis. What fraction of the electrons will be measured with $m_s = 1/2$?

Exercise 4.44 Solve the previous problem with the magnetic field direction in the $x - z$ plane, at angle θ_0 to the z-axis (**Hint:** use Ex. 1.88).

Exercise 4.45 Find the evolution of the state of Ex. 4.38 in a magnetic field oriented along the z-axis. Show that it evolves into an eigenstate of the operator $\hat{S}_{\vec{R}'}$, where $\vec{R}'$ obtains from $\vec{R}$ through precession around the magnetic field direction.

Exercise 4.46 A beam of electrons prepared with $m_s = -1/2$ passes through a Stern-Gerlach apparatus with the field gradient vector oriented in the $x - z$ plane, at angle θ_0 to the z-axis. How will the beam split?

Exercise 4.47 Solve the previous problem for spin-1 particles.