

Notes of the course “Mécanique Quantique II”
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The textbooks of the course are

- R. Shankar, *Principles of Quantum Mechanics*, 2nd edition, Plenum 1994
- D. J. Griffiths, *Introduction to Quantum Mechanics*, Prentice-Hall 1995.

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1 A remainder of the mathematical formalism of QM.

In this chapter we simply list important definitions and theorems that you should already know from Mécanique Quantique I. For details and explanations see Shankar, Sects. 1.1–1.3.2, 1.5–1.8, 1.10.

Linear vector spaces of finite dimension. Definition of linear spaces over the complex numbers, $V^n(C)$; linear independence, dimension of the space, basis.

Inner product; orthonormal basis:

$$|V\rangle = \sum_i v_i |i\rangle, \quad |W\rangle = \sum_j w_j |j\rangle \quad \Rightarrow \quad \langle V|W\rangle = \sum_i v_i^* w_i. \quad (1.1)$$

Dual spaces and Dirac notations (bra and kets); adjoint operation, $\langle aV| = \langle V|a^*$.

Linear operators. Definitions; commutators, matrix elements, projection operators, identity operator,

$$I = \sum_{i=1}^n |i\rangle\langle i|. \quad (1.2)$$

Definitions of adjoint operator. Hermitean, anti-hermitian, and unitary operators. We will often use the notation $\Omega|\psi\rangle = |\Omega\psi\rangle$ and $\langle\psi|\Omega^\dagger = \langle\Omega\psi|$.

Active and passive transformations: transforming all vectors in the linear space as $|V\rangle \rightarrow U|V\rangle$ is equivalent to keeping the vectors fixed and transforming the operators Ω as $\Omega \rightarrow U^\dagger \Omega U$.

Eigenvectors and eigenvalues (in vector space of finite dimension).

Theorem: every operator in $V^n(C)$ has n eigenvalues.

Theorem: the eigenvalues of a Hermitian operators are real. Eigenfunctions belonging to different eigenvalues are orthogonal.

Theorem: the eigenvectors of hermitian operators (in finite dimension!) form a complete set.

Theorem: Every hermitian operator can be diagonalized by a unitary change of basis.

Theorem: if Ω and Λ are hermitian and $[\Omega, \Lambda] = 0$, there exists (at least) one basis of common eigenvectors that diagonalizes both.

Functions of operators, Definition by Taylor expansion. Example: e^Ω . Derivative of operators with respect to parameters; e.g.

$$\frac{d}{dt}e^{t\Omega} = \Omega e^{t\Omega} = e^{t\Omega}\Omega. \quad (1.3)$$

Here it works as for c -numbers. However, e.g.

$$e^A e^B \neq e^{A+B}, \quad (1.4)$$

unless $[A, B] = 0$. A useful formula: if $[A, B]$ is a c -number,

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]}. \quad (1.5)$$

Vector spaces of infinite dimension (Hilbert spaces).

Example. The space of functions $f(x)$ over an interval $[a, b]$. Scalar product:

$$\langle f|g \rangle = \int_a^b dx f^*(x)g(x). \quad (1.6)$$

The basis vector $|x\rangle$. Completeness and orthogonality,

$$\int_a^b dx |x\rangle\langle x| = I, \quad (1.7)$$

$$\langle x|x' \rangle = \delta(x - x'). \quad (1.8)$$

Definition of the Dirac delta and of its derivative.

Operators in infinite dimension. Example: the derivative operator,

$$D|f \rangle \equiv |df/dx \rangle. \quad (1.9)$$

Matrix elements: multiplying by $\langle x|$ and inserting a complete set using (1.7),

$$\int dx' \langle x|D|x' \rangle \langle x'|f \rangle = \frac{df}{dx}, \quad (1.10)$$

so

$$\langle x|D|x' \rangle = \delta(x - x') \frac{d}{dx'} = \delta'(x - x'). \quad (1.11)$$

Hermiticity. It now depends also on the boundary conditions. Example: when is $K \equiv -id/dx$ hermitian, i.e. when

$$\langle g|K|f \rangle = \langle f|K|g \rangle^* \quad ? \quad (1.12)$$

Write

$$\begin{aligned}\langle g|K|f\rangle &= \int_a^b dx \int_a^b dx' \langle g|x\rangle \langle x|K|x'\rangle \langle x'|f\rangle \\ &= \int_a^b dx g^*(x) (-i) \frac{df}{dx}.\end{aligned}\tag{1.13}$$

Integrating by parts (without forgetting the boundary terms!) we get that K is hermitian only in the space of functions that satisfy the condition

$$g^*(b)f(b) = g^*(a)f(a).\tag{1.14}$$

This is satisfied by functions that vanish at $x = a$ and $x = b$, or by periodic functions, $f(a) = f(b)$.

Eigenvectors of hermitian operators. In a vector space of infinite dimension it can happen that the eigenvectors are no longer normalizable. E.g. if $K = -id/dx$,

$$K|k\rangle = k|k\rangle \Rightarrow \psi_k(x) \equiv \langle k|x\rangle = A e^{ikx},\tag{1.15}$$

and

$$\langle k|k'\rangle \propto \delta(k - k').\tag{1.16}$$

(Choosing $A = 1/(2\pi)^{1/2}$ the proportionality constant is one.) These are called *improper vectors*. In general, in a vector space of infinite dimension the eigenvectors fall into two categories:

- *discrete spectrum.* The eigenvalues are separated from each other. These states are normalizable (proper vectors).
- *continuous spectrum.* These are improper vectors, and can only be normalized to a Dirac delta. They are not physical; e.g. $|\psi_k(x)|^2$ is a constant all over an infinite space for $\psi_k(x) = e^{ikx}$ and $-\infty < x < \infty$, so the probability of finding this state within any finite volume is zero! Physical states in this case are given by wave-packets. However, improper states are useful mathematical idealizations.

In infinite dimension the theorem that states that the eigenvectors of a hermitian operator form a complete set no longer holds. However this property is essential to the internal consistency of QM, so we define as *observables* the hermitian operators whose eigenvectors do form a complete set.

2 The postulates of QM

(Here again most of the material should be familiar from *Mécanique Quantique I*. However, we will take a somewhat more abstract point of view, especially when discussing representation theory)

- I. The state of a particle is represented by a vector $|\psi(t)\rangle$ in Hilbert space.
- II. The variables x and p of classical mechanics are replaced by hermitian operators X and P satisfying¹

$$[X, P] = i\hbar. \quad (2.1)$$

The operator corresponding to a classical quantity $\omega(x, p)$ is the hermitian operator $\Omega(X, P) = \omega(x \rightarrow X, p \rightarrow P)$.²

- III. If the particle is in a state $|\psi\rangle$, normalized so that $\langle\psi|\psi\rangle = 1$, a measurement of the variable corresponding to an operator Ω will yield one of its eigenvalues ω , with a probability

$$P(\omega) = |\langle\omega|\psi\rangle|^2. \quad (2.2)$$

The state of the system changes from $|\psi\rangle$ to $|\omega\rangle$ as a result of the measurement.

- IV. The state vector $|\psi(t)\rangle$ obeys the Schrödinger equation,

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle, \quad (2.3)$$

where $H(X, P) = \mathcal{H}(x \rightarrow X, p \rightarrow P)$ is the quantum Hamiltonian operator and \mathcal{H} the Hamiltonian for the corresponding classical problem.

If the operator Ω has degenerate eigenvalues, postulate III must be generalized. Consider for instance the case where two eigenvalues are degenerate, $\omega_1 = \omega_2 \equiv \omega$. In this degenerate subspace, choose an orthonormal basis $|\omega, 1\rangle$, $|\omega, 2\rangle$. Then postulate III is generalized by

$$P(\omega) = |\langle\omega, 1|\psi\rangle|^2 + |\langle\omega, 2|\psi\rangle|^2. \quad (2.4)$$

¹We consider here a one-dimensional system. The (trivial) generalization to many dimensions will come below.

²When in the classical variable appears the product of powers of x and p there is an ordering ambiguity in this prescription. For a simple term such as xp the rule is to use the symmetric sum $(XP + PX)/2$, which is hermitian.

It is useful to introduce the projection operator for the eigenspace,

$$\mathbb{P}_\omega = |\omega, 1\rangle\langle\omega, 1| + |\omega, 2\rangle\langle\omega, 2|. \quad (2.5)$$

so that

$$P(\omega) = \langle\psi|\mathbb{P}_\omega|\psi\rangle. \quad (2.6)$$

The average value of the operator Ω in a (normalized) state $|\psi\rangle$ is defined as

$$\langle\Omega\rangle \equiv \sum_\omega \omega P(\omega), \quad (2.7)$$

i.e. is the sum over the possible outcomes, each one weighted with its probability. Using eq. (2.2), together with $\Omega|\omega\rangle = \omega|\omega\rangle$ and $\sum_\omega |\omega\rangle\langle\omega| = I$,

$$\begin{aligned} \langle\Omega\rangle &= \sum_\omega \omega \langle\psi|\omega\rangle\langle\omega|\psi\rangle \\ &= \sum_\omega \langle\psi|\Omega|\omega\rangle\langle\omega|\psi\rangle \\ &= \langle\psi|\Omega|\psi\rangle. \end{aligned} \quad (2.8)$$

Therefore the average value is equal to the expectation value of the operator over the state $|\psi\rangle$.

See Shankar, Sect. 4.1, for a clear discussion of these postulates.

Collapse of the wave function. According to postulate III, the effect of the measurement which gives the eigenvalue ω changes the state of the system as follows:

$$|\psi\rangle \rightarrow \frac{|\mathbb{P}_\omega\psi\rangle}{\langle\mathbb{P}_\omega\psi|\mathbb{P}_\omega\psi\rangle^{1/2}}. \quad (2.9)$$

In this form, it holds even if ω is a degenerate eigenvalue.

Remark. If the measurement gives a non-degenerate eigenvalue ω , we know that the system after the measurement is in the state $|\omega\rangle$, even if we did not know the initial state $|\psi\rangle$. If ω is degenerate the situation is different: if we did not know the initial state $|\psi\rangle$, we only know that the final state is somewhere in the space spanned by $|\omega, 1\rangle$ and $|\omega, 2\rangle$. If instead we knew $|\psi\rangle$, then the final state is fixed by eq. (2.9).

Representation theory. Consider the commutator (2.1). For the moment we can think to X and P as abstract mathematical objects, defined by the fact that they satisfy eq. (2.1), which is called the *Heisenberg algebra*. We

now wish to attach to these abstract objects some concrete meaning, interpreting them as operators acting on some space, and whose action is such that they satisfy eq. (2.1). In the mathematical language, such a concrete expression for X and P is called a *representation* of the Heisenberg algebra. Such explicit expression of X and P will also depend on the space on which the operators act. In the mathematical language, this space is called the *basis* for the representation.

As an example, let us choose as basis the space of (differentiable) functions of a variable x . In this space, we define the action of X and P as

$$Xf(x) = xf(x), \quad Pf(x) = -i\hbar \frac{df}{dx}. \quad (2.10)$$

Therefore

$$(XP - PX)f = x \left(-i\hbar \frac{df}{dx} \right) - \left(-i\hbar \frac{d}{dx} \right) (xf) = i\hbar f. \quad (2.11)$$

Since this holds for any function f , we can write it in operator form as $XP - PX = i\hbar$, so the assignement

$$X \rightarrow x, \quad P \rightarrow -i\hbar \frac{d}{dx} \quad (2.12)$$

indeed provides a representation of the Heisenberg algebra. This is called the coordinate representation, since the basis is given by functions of the coordinate x . In terms of the Hilbert space vector

$$|f\rangle = \int dx f(x)|x\rangle, \quad (2.13)$$

eq. (2.10) reads

$$X|f\rangle = x|f\rangle, \quad P|f\rangle = -i\hbar|df/dx\rangle. \quad (2.14)$$

Using eqs. (1.8) and (1.11) we find the matrix elements of X and P in the coordinate representation,

$$\langle x|X|x'\rangle = x\delta(x - x'), \quad (2.15)$$

$$\langle x|P|x'\rangle = -i\hbar\delta(x - x')\frac{d}{dx'}. \quad (2.16)$$

The coordinate representation is by no means the only possible representation of the Heisenberg algebra. For instance we can consider the *momentum*

representation, that is, we consider as basis the space of functions of momentum, $\tilde{f}(p)$, and we make the assignments

$$P\tilde{f}(p) = p\tilde{f}(p), \quad X\tilde{f}(p) = +i\hbar\frac{d\tilde{f}}{dp}, \quad (2.17)$$

which again satisfies the Heisenberg algebra. So, in the coordinate representation X just multiplies f by x while P is a differential operator. Conversely, in the momentum representation P just multiplies by p while X is a differential operator.

Below we will recall the harmonic oscillator and we will see that in its study it is useful to introduce a third representation, based on creation and annihilation operators a, a^\dagger , where neither X nor P are diagonal.

Remark. Consider, in the coordinate representation, the assignment

$$X \rightarrow x, \quad P \rightarrow -i\hbar\frac{d}{dx} + \alpha(x), \quad (2.18)$$

where $\alpha(x)$ is an arbitrary real function. This assignment satisfies the Heisenberg algebra and, if $\alpha(x)$ is real, it does not spoil the hermiticity of P , so eq. (2.18), even if unconventional, gives a fully acceptable expressions for P in the coordinate basis. Consider the state

$$|\tilde{x}\rangle = e^{-i\beta(x)/\hbar}|x\rangle. \quad (2.19)$$

With the assignment (2.18) we have

$$P|\tilde{x}\rangle = e^{-i\beta(x)/\hbar} \left(-i\hbar\frac{d}{dx} + \alpha - \beta' \right) |x\rangle. \quad (2.20)$$

Choosing β so that $\beta' = \alpha$ we get

$$P|\tilde{x}\rangle = e^{-i\beta(x)/\hbar} \left(-i\hbar\frac{d}{dx} \right) |x\rangle. \quad (2.21)$$

Thus, using the unconventional definition (2.18) is equivalent to using the conventional one, $P \rightarrow -i\hbar d/dx$, and then multiplying all vectors of the Hilbert space by the common phase factor, $\exp\{-(i/\hbar) \int^x dx \alpha(x)\}$. Such an overall phase factor cancels in all matrix elements, and is therefore unobservables. In other words, the representations (2.12) and (2.18) are physically equivalent. (See Shankar, Ex. 7.4.9)

3 The Schrödinger equation

In the Schrödinger picture the operators X and P are time-independent quantities, while the states $|\psi(t)\rangle$ evolve according to the Schrödinger equation (2.3). We consider a Hamiltonian of the form

$$H = \frac{P^2}{2m} + V(X). \quad (3.1)$$

Equation (2.3) gives the Schrödinger equation in an abstract vector form. To obtain its explicit form in the coordinate representation we multiply both sides by $\langle x|$, so

$$i\hbar \frac{\partial}{\partial t} \langle x|\psi(t)\rangle = \langle x|H|\psi(t)\rangle. \quad (3.2)$$

We write

$$\langle x|\psi(t)\rangle \equiv \psi(x, t), \quad (3.3)$$

while, using $V(X)|x\rangle = V(x)|x\rangle$ and $V(X) = V^\dagger(X)$,

$$\langle x|V(X)|\psi(t)\rangle = V(x)\langle x|\psi(t)\rangle = V(x)\psi(x, t). \quad (3.4)$$

To compute $\langle x|P^2|\psi(t)\rangle$ we insert twice a complete set as in eq. (1.7)

$$\langle x|P^2|\psi(t)\rangle = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx'' \langle x|P|x'\rangle \langle x'|P|x''\rangle \langle x''|\psi(t)\rangle. \quad (3.5)$$

Using eq. (2.16),

$$\langle x|P^2|\psi(t)\rangle = (-i\hbar)^2 \frac{d^2\psi}{dx^2}. \quad (3.6)$$

So eq. (2.3) becomes

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(\mathbf{x}, t). \quad (3.7)$$

This is the Schrödinger equation in the coordinate representation. In other words, to pass from the Schrödinger equation written in abstract vector form, to the Schrödinger equation in the coordinate representation, we replace $|\psi(t)\rangle \rightarrow \psi(x, t)$, $X \rightarrow x$ and $P \rightarrow -i\hbar d/dx$. We now restrict to a time-independent Hamiltonian. Writing

$$\psi(\mathbf{x}, t) = e^{-iEt/\hbar} \psi_E(x), \quad (3.8)$$

we get the time-independent Schrödinger equation in the coordinate representation,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \psi_E(x) = E\psi_E(x), \quad (3.9)$$

Remark. Rather than using the coordinate representation, we might equally well choose to work in the momentum representation, in which case, according to eq. (2.17), we would replace $|\psi(t)\rangle \rightarrow \psi(p, t)$, $P \rightarrow p$ and $X \rightarrow +i\hbar d/dp$. The fact that the coordinate representation of the Schrödinger equation is the most commonly used stems from the fact that the kinetic energy $T(P)$ has a very simple quadratic dependence on P , $T(P) = P^2/2m$ while, usually, the potential $V(X)$ is a more complicated function of X . So, it is convenient to choose a representation where x is diagonal, in order to simplify as much as possible the potential term. Consider for instance the case $V(X) = 1/\cosh^2 X$. In coordinate space the time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{\cosh^2 x}\right) \psi_E(x) = E\psi_E(x) \quad (3.10)$$

which is a second-order differential equation. In the momentum representation, we would have

$$\left(-\frac{p^2}{2m} + \frac{1}{\cosh^2(i\hbar d/dp)}\right) \psi_E(p) = E\psi_E(p), \quad (3.11)$$

which is a horrible equation containing derivatives of arbitrarily high order, obtained from the Taylor expansion of $1/\cosh^2(i\hbar d/dp)$.

However, there can be exception to this rule. If the potential is linear in X , $V(X) = -fX$ (corresponding to an external classical force f acting on the system), in the momentum representation we get a first-order differential equations,

$$\left(-\frac{p^2}{2m} - i\hbar f \frac{d}{dp}\right) \psi_E(p) = E\psi_E(p), \quad (3.12)$$

while in the coordinate representation we have a second-order equation,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - fx\right) \psi_E(x) = E\psi_E(x). \quad (3.13)$$

Another exception is the harmonic oscillator, since the potential term is quadratic in X , and is as simple as the kinetic term; in this case the solution

can be obtained very elegantly in a basis where neither X nor P are diagonal, as we will see below. (References: Shankar, Sect. 4.3, page 149.)

We discuss now the general approach to the solution. We consider again a time-independent Hamiltonian, and we denote by $|E\rangle$ its eigenvectors, $H|E\rangle = E|E\rangle$. The formal solution of eq. (2.3) is obtained by writing

$$|\psi(t)\rangle = \sum_E |E\rangle \langle E|\psi(t)\rangle \equiv \sum_E a_E(t) |E\rangle. \quad (3.14)$$

The Schrödinger equation becomes

$$i\hbar \dot{a}_E = E a_E, \quad (3.15)$$

(we used the fact that the states $|E\rangle$ are linearly independent) so

$$a_E(t) = a_E(0) e^{-iEt/\hbar}, \quad (3.16)$$

and therefore

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \quad (3.17)$$

where

$$U(t) = \sum_E e^{-iEt/\hbar} |E\rangle \langle E|. \quad (3.18)$$

Using $I = \sum_E |E\rangle \langle E|$ and $H|E\rangle = E|E\rangle$ we can observe that

$$\begin{aligned} e^{-iHt/\hbar} &= e^{-iHt/\hbar} \sum_E |E\rangle \langle E| = \sum_E e^{-iHt/\hbar} |E\rangle \langle E| \\ &= \sum_E e^{-iEt/\hbar} |E\rangle \langle E|, \end{aligned} \quad (3.19)$$

and therefore

$$U(t) = e^{-iHt/\hbar}. \quad (3.20)$$

The operator $U(t)$ is called the *propagator*. If H is hermitian, $U(t)$ is unitary, and the norm $\langle \psi(t)|\psi(t)\rangle$ is invariant under time evolution, as is necessary for the probabilistic interpretation of QM.

(References: Shankar, Sect. 4.3)

Evolution in the Heisenberg picture.

Consider a generic matrix element $\langle \psi_1(t)|\Omega|\psi_2(t)\rangle$. In the formalism that we have discussed above the kets evolve as

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle, \quad (3.21)$$

so the bra evolve as

$$\langle \psi(t) | = \langle \psi(0) | e^{+iHt/\hbar}, \quad (3.22)$$

while the operators X and P are time-independent. This way of describing the time evolution is called the *Schrödinger picture*. There is an equivalent way of describing the time evolution based on the observation that the physics is contained in the matrix elements, and

$$\langle \psi_1(t) | \Omega | \psi_2(t) \rangle = \langle \psi_1(0) | e^{+iHt/\hbar} \Omega e^{-iHt/\hbar} | \psi_2(0) \rangle. \quad (3.23)$$

Therefore, an equivalent description of the time-evolution is obtained by saying that the states do not evolve in time, while operators Ω such as X , P and their combinations that do not involve an explicit time dependence, evolve as

$$\Omega(t) = e^{+iHt/\hbar} \Omega(0) e^{-iHt/\hbar}. \quad (3.24)$$

This description of the time evolution is called the *Heisenberg picture*. From eq. (3.24) it follows that, in the Heisenberg picture,

$$\frac{d\Omega}{dt} = -\frac{i}{\hbar} [\Omega, H]. \quad (3.25)$$

Sometimes one encounters operators that have an explicit time-dependence. For instance, the Hamiltonian describing the interaction with a classical time-dependent force $f(t)$ is $H = P^2/(2m) - f(t)X$. In this case, in the Schrödinger picture H depends on time only through $f(t)$, while in the Heisenberg picture it depends on time through $f(t)$ and through $X(t), P(t)$. For a generic operator Ω with an explicit time dependence, eq. (3.25) generalizes to

$$\frac{d\Omega}{dt} = -\frac{i}{\hbar} [\Omega, H] + \frac{\partial \Omega}{\partial t}. \quad (3.26)$$

If we denote by Ω_S an operator in the Schrödinger picture and by Ω_H the corresponding operator in the Heisenberg picture, we have

$$\Omega_H(t) = e^{+iHt/\hbar} \Omega_S e^{-iHt/\hbar} \quad (3.27)$$

(observe that the Hamiltonian is the same, $H_S = H_H \equiv H$, since H commutes with $e^{-iHt/\hbar}$), while the states are related by

$$|\psi\rangle_H = e^{+iHt/\hbar} |\psi\rangle_S. \quad (3.28)$$

In particular $P_H(t) = e^{+iHt/\hbar} P_S e^{-iHt/\hbar}$ and $X_H(t) = e^{+iHt/\hbar} X_S e^{-iHt/\hbar}$. From $[X_S, P_S] = i\hbar$ it follows that

$$[X_H(t), P_H(t)] = i\hbar. \quad (3.29)$$

Observe that the canonical commutation relation, in the Heisenberg picture, holds only at equal time. In general $[X_H(t), P_H(t')]$ with $t' \neq t$ is not simply equal to $i\hbar$.

We will normally work in the Schrödinger picture. However, the Heisenberg picture is interesting for making contact with classical mechanics. Note in fact the similarity between eq. (3.25) and the classical equation

$$\frac{d\omega}{dt} = \{\omega, \mathcal{H}\}, \quad (3.30)$$

where ω is the classical variable corresponding to the quantum operator Ω , \mathcal{H} is the classical Hamiltonian, and $\{ , \}$ is the Poisson bracket.³ (References: Shankar, page 490-491)

Ehrenfest's theorem.

Consider an operator Ω , with no explicit time dependence, in the Schrödinger picture. Then

$$\frac{d}{dt} \langle \psi(t) | \Omega | \psi(t) \rangle = \langle \dot{\psi}(t) | \Omega | \psi(t) \rangle + \langle \psi(t) | \Omega | \dot{\psi}(t) \rangle, \quad (3.31)$$

where

$$|\dot{\psi}(t)\rangle \equiv \frac{d}{dt} |\psi(t)\rangle = -\frac{i}{\hbar} H |\psi(t)\rangle, \quad (3.32)$$

and therefore $\langle \dot{\psi}(t) | = +(i/\hbar) \langle \psi(t) | H$. Then we get

$$\frac{d}{dt} \langle \psi(t) | \Omega | \psi(t) \rangle = -\frac{i}{\hbar} \langle \psi(t) | [\Omega, H] | \psi(t) \rangle, \quad (3.33)$$

or, using the notation $\langle \psi(t) | \Omega | \psi(t) \rangle \equiv \langle O \rangle$,

$$\frac{d}{dt} \langle O \rangle = -\frac{i}{\hbar} \langle [\Omega, H] \rangle, \quad (3.34)$$

³Furthermore, the Heisenberg picture is the natural one in relativistic quantum field theory. This follows from the fact that in quantum field theory the operators are fields, i.e. they depend on the space variable \mathbf{x} (think for instance to the electromagnetic field). In the Heisenberg picture therefore they depend both on space and time, i.e. they are of the form $\phi_H(\mathbf{x}, t)$, while in the Schrödinger picture they are only function of space, $\phi_S(\mathbf{x})$. The Heisenberg picture is therefore more natural from the point of view of Lorentz covariance, since it treats \mathbf{x} and t on the same footing. Quantum field theory will be the subject of the course “Champs et Particules”, in the 4th year.

which is Ehrenfest's theorem. Let us now consider a Hamiltonian of the form $H = P^2/(2m) + V(X)$. Setting $\Omega = X$ in eq. (3.34), we get

$$\frac{d}{dt}\langle X \rangle = \frac{1}{m}\langle P \rangle, \quad (3.35)$$

while setting $\Omega = P$ we get

$$\frac{d}{dt}\langle P \rangle = -\frac{dV}{dX}. \quad (3.36)$$

We can rewrite these equations as

$$\frac{d}{dt}\langle X \rangle = \left\langle \frac{\partial H}{\partial P} \right\rangle, \quad (3.37)$$

$$\frac{d}{dt}\langle P \rangle = \left\langle -\frac{\partial H}{\partial X} \right\rangle. \quad (3.38)$$

This is the analogous of the Hamilton equations in classical mechanics. When quantum fluctuations are small, we can replace

$$\langle H(X, P) \rangle \rightarrow H(\langle X \rangle, \langle P \rangle), \quad (3.39)$$

and we get the Hamilton equations for the expectation values of X and P . (References: Shankar, page 179-184)

4 The harmonic oscillator

(We conclude our reminder of *Mécanique Quantique I* with the harmonic oscillator, paying special attention to the formulation in terms of lowering and raising operators)

The Hamiltonian is

$$\frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2. \quad (4.1)$$

Coordinate basis. In the coordinate representation, the time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) \psi_E(x) = E\psi_E(x). \quad (4.2)$$

This equation can be solved by series. Imposing the boundary condition $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$, the solution exists only when E takes one of the values E_n given by

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2. \quad (4.3)$$

Defining

$$y = (m\omega/\hbar)^{1/2}x, \quad (4.4)$$

the corresponding wave-functions are

$$\psi_n(y) = c_n H_n(y) e^{-y^2/2}, \quad (4.5)$$

where

$$c_n = \frac{1}{\pi^{1/4} 2^{n/2} (n!)^{1/2}} \quad (4.6)$$

is a normalization constant⁴ and $H_n(y)$ are polynomials of degree n , known as Hermite polynomials. They can be written as

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}. \quad (4.7)$$

(Rodrigues formula). For instance,

$$H_0(y) = 1, \quad (4.8)$$

$$H_1(y) = 2y, \quad (4.9)$$

$$H_2(y) = 4y^2 - 2. \quad (4.10)$$

⁴Equations (4.5) and (4.6) give the wavefunction normalized so that $|\psi_n(y)|^2 dy$ is the probability that the particle is between y and $y + dy$. Since $dy = (m\omega/\hbar)^{1/2} dx$, the wavefunction $\psi_n(x)$ that gives the probability that the particle is between x and $x + dx$ has a further factor $(m\omega/\hbar)^{1/4}$.

They satisfy the useful recursion relations

$$H'_n(y) = 2nH_{n-1}, \quad (4.11)$$

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y). \quad (4.12)$$

Observe that for n even the wavefunctions are invariant under $y \rightarrow -y$ while for n odd they change sign (and therefore vanish in $y = 0$). We refer to such wavefunctions as even and odd, respectively, under parity.

Some observations on the probability distribution $|\psi_n(y)|^2$ are useful to illustrate some general features of quantum mechanics.

1) Classically, an oscillator with energy E_n has turning points at $y \equiv \pm y_{\max}$, where $y_{\max} = (2n+1)^{1/2}$. The quantum probability distribution extend well beyond these classical points, for small n . In the large n limit, however, the excursion outside the turning points becomes smaller and smaller. See Figs. 1, 2 and 3.

2) In the classical case, the position of the oscillator is of course known exactly, in principle. Suppose however that we have a collection of a very large number of particles, moving in the same harmonic oscillator potential (and non interacting among themselves). In this case, we could resort to the methods of classical statistical mechanics and ask what is the probability of finding a particle between y and $y + dy$. The answer is that this probability density is proportional to the time that the particle spends between y and $y + dy$, and therefore is inversely proportional to the velocity in y ,

$$P_{\text{class}}(y) \propto \frac{1}{v(y)} \propto \frac{1}{[y_{\max}^2 - y^2]^{1/2}}, \quad (4.13)$$

where $y = \pm y_{\max}$ are the classical turning points. Normalizing the classical distribution so that

$$\int_{-y_{\max}}^{y_{\max}} dy P_{\text{class}}(y) = 1 \quad (4.14)$$

we get

$$P_{\text{class}}(y) = \frac{1}{\pi[y_{\max}^2 - y^2]^{1/2}}. \quad (4.15)$$

This distribution is peaked at the turning points, where $v = 0$, and is lowest at $y = 0$, where the velocity is maximum. This behavior is just the inverse of the probability distribution for the quantum harmonic oscillator in the ground state, compare with Fig. 1! However, for large values of the quantum number n the situation is different. We see from Fig. 4 that for large n the quantum probability distribution oscillates very quickly. If we have only a

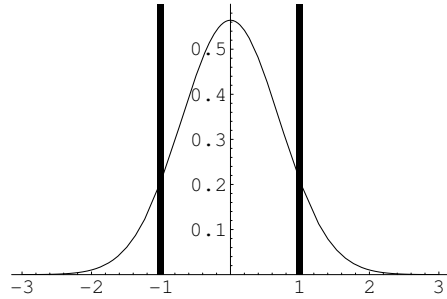


Figure 1: The probability distribution for the harmonic oscillator with $n = 0$, compared to the classical turning points (black lines).

coarse-grained spatial resolution, what we actually measure is an average over adjacent wiggles, and this coincides indeed, in the large n limit, with the classical probability distribution. This is an example of the *correspondence principle*.

(References: Shankar, Sect. 7.3, and Griffiths, Sect. 2.3.2)

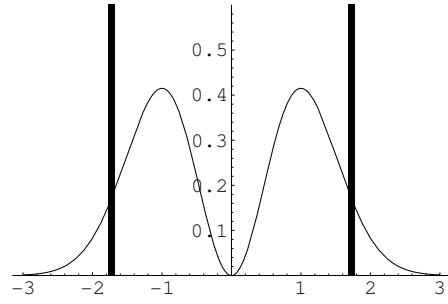


Figure 2: The probability distribution for the harmonic oscillator with $n = 1$, compared to the classical turning points (black lines).

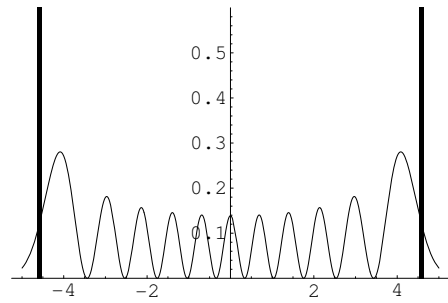


Figure 3: The probability distribution for the harmonic oscillator with $n = 10$, compared to the classical turning points (black lines).

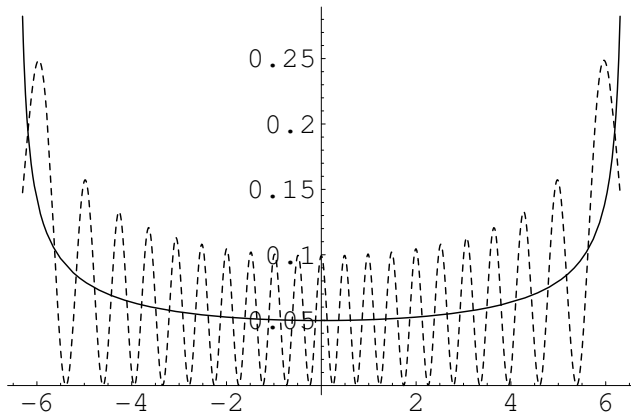


Figure 4: The probability distribution for the quantum harmonic oscillator with $n = 20$ (dashed line), compared to the classical probability distribution (solid line).

Raising and lowering operators. We define the operator

$$a = \left(\frac{m\omega}{2\hbar}\right)^{1/2} X + \frac{i}{(2m\omega\hbar)^{1/2}} P, \quad (4.16)$$

and its adjoint

$$a^\dagger = \left(\frac{m\omega}{2\hbar}\right)^{1/2} X - \frac{i}{(2m\omega\hbar)^{1/2}} P. \quad (4.17)$$

They satisfy

$$[a, a^\dagger] = 1. \quad (4.18)$$

In terms of a, a^\dagger the Hamiltonian of the harmonic oscillator can be written as

$$H = \hbar\omega \left(a^\dagger a + \frac{1}{2}\right) \equiv \hbar\omega \left(N + \frac{1}{2}\right). \quad (4.19)$$

For reasons that will become clear below, N is called the *number operator*. It satisfies

$$[N, a^\dagger] = +a^\dagger, \quad [N, a] = -a. \quad (4.20)$$

Suppose that $|s\rangle$ is an eigenvector of N with eigenvalue s . Then, using eq. (4.20), we find that

$$N(a^\dagger|s\rangle) = ([N, a^\dagger] + a^\dagger N)|s\rangle = (s+1)a^\dagger|s\rangle, \quad (4.21)$$

and similarly $N(a|s\rangle) = (s-1)a|s\rangle$. Therefore, if $|E\rangle$ is an eigenvector of the Hamiltonian (4.19) with eigenvalue E , then $a|E\rangle$ is also an eigenvector, with eigenvalue $E - \hbar\omega$, $aa|E\rangle$ is an eigenvector with eigenvalue $E - 2\hbar\omega$, etc. while $a^\dagger|E\rangle$ has eigenvalue $E + \hbar\omega$, etc. For this reason a and a^\dagger are called lowering and rising operators, respectively.

It now looks as if the Hamiltonian were unbounded from below, since repeated applications of a lower indefinitely the eigenvalue. This cannot be true, since X and P are Hermitian, so on any state $|\psi\rangle$

$$\langle\psi|X^2|\psi\rangle = \langle X\psi|X\psi\rangle \geq 0, \quad (4.22)$$

and similarly for $\langle\psi|P^2|\psi\rangle$, so $\langle\psi|H|\psi\rangle \geq 0$. The loophole in the above reasoning is that $a|E\rangle$ is an eigenvector of the Hamiltonian with eigenvalue $E - \hbar\omega$, unless it vanishes. So, there must exist a state, that we denote by $|0\rangle$, such that

$$a|0\rangle = 0, \quad (4.23)$$

and the process of lowering the eigenvalue terminates.⁵ It then follows that

$$N(a^\dagger|0\rangle) = (a^\dagger|0\rangle) \quad (4.24)$$

$$N(a^\dagger a^\dagger|0\rangle) = 2(a^\dagger a^\dagger|0\rangle), \quad (4.25)$$

and, in general, the state obtained applying n times the raising operator a^\dagger to the vacuum is an eigenvector of N with *integer* eigenvalue n .

We normalize $|0\rangle$ so that $\langle 0|0\rangle = 1$, and we denote by $|n\rangle$ the eigenvector of N with eigenvalue n , again normalized so that $\langle n|n\rangle = 1$. With this normalization, $a|n\rangle$, with $n > 0$, will be proportional to $|n-1\rangle$, times some proportionality constant C_n ,

$$a|n\rangle = C_n|n-1\rangle. \quad (4.26)$$

Combining this with the adjoint equation

$$\langle n|a^\dagger = \langle n-1|C_n^*, \quad (4.27)$$

we get

$$\langle n|a^\dagger a|n\rangle = |C_n|^2 \langle n-1|n-1\rangle. \quad (4.28)$$

Using $a^\dagger a|n\rangle = n|n\rangle$ and $\langle n-1|n-1\rangle = 1$ we get $C_n = n^{1/2}$ (a part from a phase that we fix to zero), so

$$a|n\rangle = n^{1/2}|n-1\rangle. \quad (4.29)$$

Similarly we find

$$a^\dagger|n\rangle = (n+1)^{1/2}|n+1\rangle. \quad (4.30)$$

The states $|n\rangle$ satisfy

$$H|n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle, \quad n = 0, 1, 2, \dots \quad (4.31)$$

The introduction of a, a^\dagger allowed us to find directly a basis which diagonalize the Hamiltonian, without going first to the coordinate representation, that diagonalizes X . The states $|n\rangle$ define the *energy representation*. In the energy representation, X and P are not diagonal. In fact, inverting eqs. (4.16)

⁵Do not make confusion between the state that we denote as $|0\rangle$, which is just a state in the sense of quantum mechanics, i.e. it belongs to a Hilbert space of vectors, and the number zero on the right-hand side of eq. (4.23)!

and (4.17),

$$X = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (a^\dagger + a), \quad (4.32)$$

$$P = i \left(\frac{m\omega\hbar}{2} \right)^{1/2} (a^\dagger - a). \quad (4.33)$$

From eqs. (4.29) and (4.30) (recalling that eigenvectors of hermitian operators with different eigenvalues are orthogonal, so $\langle n'|n\rangle = 0$ if $n \neq n'$)

$$\langle n'|a|n\rangle = n^{1/2}\delta_{n',n-1}, \quad (4.34)$$

$$\langle n'|a^\dagger|n\rangle = (n+1)^{1/2}\delta_{n',n+1}. \quad (4.35)$$

Then

$$\langle n'|X|n\rangle = \left(\frac{\hbar}{2m\omega} \right)^{1/2} \left[n^{1/2}\delta_{n',n-1} + (n+1)^{1/2}\delta_{n',n+1} \right], \quad (4.36)$$

and similarly for P .

Remark. (see Shankar, page 209). It is interesting to compare the computation of matrix elements in the energy representation and in the coordinate representation. Consider for instance the matrix element of X^3 between the state $|n\rangle$ with $n = 2$ and $\langle n'|$ with $n' = 3$, $\langle 3|X^3|2\rangle$. In the coordinate representation we must compute the integral

$$\int_{-\infty}^{+\infty} dx \psi_{n'=3}^*(x) x^3 \psi_{n=2}(x) \propto \int_{-\infty}^{+\infty} dy H_3(y) H_2(y) y^3 e^{-y^2}, \quad (4.37)$$

see eq. (4.5). The integral is elementary, since the $H_n(y)$ are polynomials. However, if one compute it by writing explicitly the Hermite polynomials, there are many terms (even more if we consider larger values of n and n'), and the explicit computation would be quite tedious. In the energy representation, we rather have to compute

$$\langle 3|(a + a^\dagger)^3|2\rangle. \quad (4.38)$$

This can be done using eqs. (4.29) and (4.30). In this way we see that only terms with two raising and one lowering operators, such as $a^\dagger a^\dagger a$, contribute to this matrix element, so the computation is straightforward. Observe that, in the formulation in terms of a, a^\dagger , it is trivial to see that, e.g. $\langle 7|X^3|2\rangle = 0$. Simply, there are at most 3 operators a^\dagger in X^3 , so the state $|2\rangle$ can be raised

at most up to $|5\rangle$, but not up to $|7\rangle$. In the coordinate representation, the vanishing of

$$\int_{-\infty}^{+\infty} dy H_7(y) H_2(y) y^3 e^{-y^2}, \quad (4.39)$$

comes instead from the cancellation among the various terms present in the polynomials $H_n(y)$, and is far less obvious.

The wave-functions $\psi_n(x)$, that we obtained by solving the Schrödinger equation in the coordinate basis, can also be derived very simply from the solution in the energy basis. We start from eq. (4.23), which implies that $\langle x|a|0\rangle = 0$, and we insert a complete set,

$$\int_{-\infty}^{\infty} dx' \langle x|a|x'\rangle \langle x'|0\rangle = 0. \quad (4.40)$$

Using eq. (4.16), together with eqs. (2.15) and (2.16), we get

$$\left[\left(\frac{m\omega}{2\hbar} \right)^{1/2} x + \left(\frac{\hbar}{2m\omega} \right)^{1/2} \frac{d}{dx} \right] \psi_0(x) = 0, \quad (4.41)$$

where $\psi_0(x) = \langle x|0\rangle$. In other words, we have projected the equation $a|0\rangle = 0$ onto the coordinate basis, which in practice amounts to replacing

$$|0\rangle \rightarrow \psi_0(x), \quad (4.42)$$

and

$$a \rightarrow \left(\frac{m\omega}{2\hbar} \right)^{1/2} x + \left(\frac{\hbar}{2m\omega} \right)^{1/2} \frac{d}{dx}. \quad (4.43)$$

Using the dimensionless variable y as in eq. (4.4), the above relation reads simply

$$a \rightarrow \frac{1}{\sqrt{2}} \left(y + \frac{d}{dy} \right), \quad (4.44)$$

and eq. (4.41) becomes

$$\left(y + \frac{d}{dy} \right) \psi_0(y) = 0, \quad (4.45)$$

whose solution is

$$\psi_0 = A e^{-y^2/2}, \quad (4.46)$$

with A a normalization constant. We have therefore recovered the ground state wave-function already found in eqs. (4.5) and (4.8). The wave-functions of the excited states can be obtained using

$$a^\dagger \rightarrow \frac{1}{\sqrt{2}} \left(y - \frac{d}{dy} \right), \quad (4.47)$$

and applying it repeatedly to $\psi_0(y)$. (Reference: Shankar, Sect. 7.5).

Remark. The fact that the energy levels of the harmonic oscillator are uniformly spaced allows for the following interpretation. We can pretend that, associated to a quantum oscillator with frequency ω , there exist fictitious particles with energy $\hbar\omega$. The term $n\hbar\omega$ in eq. (4.3) can then be interpreted as the energy due to n of these quanta (non-interacting among them) while the term $(1/2)\hbar\omega$ is the energy of a state with no quanta: a “vacuum energy”. In this picture, the state $|0\rangle$ is called the “vacuum”. Acting with a^\dagger on any state creates a quantum, while a destroys a quantum (unless it acts on $|0\rangle$, where there are no more quanta to destroy; then $a|0\rangle = 0$). In this context a and a^\dagger are called the destruction and creation operator, respectively.

In non-relativistic quantum mechanics, the use of these words is just a matter of semantics. However, if you will study quantum field theory (next year) you will see that free fields, such as for instance the electromagnetic field, can be quantized in a way that formally reduces them to a collection of harmonic oscillators,⁶ so the description in terms of quanta becomes really meaningful. For the electromagnetic field these quanta will be the photons, for the excitation in a solid they could be phonons, excitons, polaritons, etc. All particles in relativistic quantum field theory are described in this way. Observe that $N = a^\dagger a$ is the number of these quanta, and is therefore called the number operator.

⁶More precisely, we will have a collection of operators $a_{\mathbf{k}}, a_{\mathbf{k}}^\dagger$ that destroy and create particles with momentum \mathbf{k} . If the particle has spin, we will have operators $a_{\mathbf{k},s}, a_{\mathbf{k},s}^\dagger$ where the label s takes spin into account.

5 Symmetries in quantum mechanics

In classical mechanics, symmetries correspond to conservation laws. E.g. invariance under space translations implies momentum conservation, invariance under time translation implies conservation of energy, and invariance under rotation gives the conservation of angular momentum.

The implementation of symmetries into the formalism of quantum mechanics gives rise to a richer mathematical structure. The underlying mathematics is that of group theory. While this mathematical formalism in itself might seem quite abstract at a first encounter, it is really useful in order to get a deep understanding of the concept of spin, that does not have a classical counterpart, or to understand issues such as the composition of angular momenta.

We will not develop the mathematical formalism of group theory in abstract form, but we will rather get acquainted to it through examples and applications. We will begin with the simpler cases of invariance under spatial or temporal translations, and we will then move on to the more complicated case of invariance under rotations.

5.1 Spatial translations

In classical mechanics, an infinitesimal spatial translation is defined as the transformation of the coordinate and momentum x, p , given by

$$x \rightarrow x + \epsilon, \quad p \rightarrow p. \quad (5.1)$$

In quantum mechanics, we define it in terms of expectation values,

$$\langle \psi | X | \psi \rangle \rightarrow \langle \psi | X | \psi \rangle + \epsilon, \quad \langle \psi | P | \psi \rangle \rightarrow \langle \psi | P | \psi \rangle. \quad (5.2)$$

We still have the freedom to say that the state transform, while the operators do not, or viceversa (active or passive transformations, see page 1). In active form,

$$|\psi\rangle \rightarrow |\psi_\epsilon\rangle \equiv T(\epsilon)|\psi\rangle \quad (5.3)$$

while $X \rightarrow X$ and $P \rightarrow P$. The operator $T(\epsilon)$ is defined requiring that

$$\langle \psi_\epsilon | X | \psi_\epsilon \rangle = \langle \psi | X | \psi \rangle + \epsilon, \quad (5.4)$$

$$\langle \psi_\epsilon | P | \psi_\epsilon \rangle = \langle \psi | P | \psi \rangle. \quad (5.5)$$

In the passive point of view, we rather transform the operators as

$$X \rightarrow T^\dagger(\epsilon) X T(\epsilon), \quad P \rightarrow T^\dagger(\epsilon) P T(\epsilon), \quad (5.6)$$

and we require that

$$T^\dagger(\epsilon)XT(\epsilon) = X + \epsilon I, \quad T^\dagger(\epsilon)PT(\epsilon) = P. \quad (5.7)$$

We consider first the active point of view. To determine $T(\epsilon)$ we ask how it should act on a ket of definite position $|x\rangle$. A sensible ansatz is

$$T(\epsilon)|x\rangle = |x + \epsilon\rangle. \quad (5.8)$$

Then

$$\begin{aligned} T(\epsilon)|\psi\rangle &= T(\epsilon) \int_{-\infty}^{\infty} dx |x\rangle \langle x|\psi\rangle \\ &= \int_{-\infty}^{\infty} dx |x + \epsilon\rangle \langle x|\psi\rangle \\ &= \int_{-\infty}^{\infty} dx' |x'\rangle \langle x' - \epsilon|\psi\rangle \end{aligned} \quad (5.9)$$

where $x' = x + \epsilon$. So

$$\psi_\epsilon(x) \equiv \langle x|T(\epsilon)|\psi\rangle = \psi(x - \epsilon). \quad (5.10)$$

Then

$$\begin{aligned} \langle \psi_\epsilon|X|\psi_\epsilon\rangle &= \int_{-\infty}^{\infty} dx \psi_\epsilon^*(x) x \psi_\epsilon(x) = \int_{-\infty}^{\infty} dx \psi^*(x - \epsilon) x \psi(x - \epsilon) \\ &= \int_{-\infty}^{\infty} dx \psi^*(x) (x + \epsilon) \psi(x) = \langle \psi|X|\psi\rangle + \epsilon. \end{aligned} \quad (5.11)$$

Similarly you can verify that

$$\int_{-\infty}^{\infty} dx \psi_\epsilon^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi_\epsilon(x) = \int_{-\infty}^{\infty} dx \psi^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi(x), \quad (5.12)$$

so also eq. (5.5) holds.⁷ Then, the operator $T(\epsilon)$, defined by eq. (5.8) indeed does the job. Since ϵ is infinitesimal, we can write

$$T(\epsilon) = I - \frac{i\epsilon}{\hbar} G. \quad (5.13)$$

⁷One might try the more general ansatz $T(\epsilon)|x\rangle = e^{i\alpha(x)}|x + \epsilon\rangle$, with $\alpha(x)$ an arbitrary function. It is easy to check that eq. (5.10) is still obeyed, independently of $\alpha(x)$. However, eq. (5.12) only holds if $\alpha(x)$ is a constant and, if $\alpha(x)$ is independent of x , we can set it to be zero without loss of generality.

The operator G is called the *generator* of translations. The factor i in front has been inserted in the definition so that, if T is unitary, then G is Hermitian (verify it!). From

$$\langle x|T(\epsilon)|\psi\rangle = \psi(x - \epsilon) = \psi(x) - \epsilon \frac{d}{dx}\psi(x) \quad (5.14)$$

it follows that G is the operator that, in the coordinate representation, is given

$$G = -i\hbar \frac{d}{dx}. \quad (5.15)$$

Therefore the generator of translations is nothing but the momentum P .

Having defined translation, we can now define translation invariance, by requiring that the expectation value of Hamiltonian H on any state $|\psi\rangle$ satisfies

$$\langle \psi|H|\psi\rangle = \langle \psi_\epsilon|H|\psi_\epsilon\rangle. \quad (5.16)$$

This means that

$$\begin{aligned} \langle \psi|H|\psi\rangle &= \langle \psi|T^\dagger(\epsilon)HT(\epsilon)|\psi\rangle \\ &= \langle \psi|H|\psi\rangle + \frac{i\epsilon}{\hbar} \langle \psi|[P, H]|\psi\rangle. \end{aligned} \quad (5.17)$$

Thus, invariance under translations is equivalent to saying that P commutes with the Hamiltonian,

$$[P, H] = 0. \quad (5.18)$$

This is the quantum mechanics equivalent of the fact that, for a classical system invariant under translation, momentum is conserved.

In the passive point of view, we rather start from eq. (5.7) and we expand again T as in eq. (5.13). This gives

$$[X, G] = i\hbar, \quad [P, G] = 0, \quad (5.19)$$

whose solution is again $G = P$. Translation invariance is defined, as before, by requiring that $\langle \psi|H|\psi\rangle$ is invariant, which in the passive picture gives

$$T^\dagger(\epsilon)HT(\epsilon) = H, \quad (5.20)$$

and hence again $[H, G] = 0$.

Finite translations. We can now find the operator corresponding to a finite translation $T(a)$. We split the finite interval a into N parts of size $\epsilon = a/N$. Then

$$T(a) = \lim_{N \rightarrow \infty} [T(a/N)]^N = e^{-iaP/\hbar}. \quad (5.21)$$

In the x -representation, we therefore have

$$T(a)\psi(x) = e^{-a\frac{d}{dx}}\psi(x), \quad (5.22)$$

which in fact is the full Taylor expansion of $\psi(x - a)$. Verify that

$$T(a)T(b) = T(a + b), \quad (5.23)$$

as indeed we expect from the combination of two translations.

(Reference: Shankar, Sect. 11.2).

5.2 Time translations

If at time t_1 we prepare a system in a state $|\psi_0\rangle$ and we evolve it for a time $\Delta t = \epsilon$, for a generic time-dependent Hamiltonian we end up with the state

$$|\psi(t_1 + \epsilon)\rangle = \left[I - \frac{i\epsilon}{\hbar} H(t_1) \right] |\psi_0\rangle. \quad (5.24)$$

If we rather prepare the system in the same state $|\psi_0\rangle$, but at a different time t_2 , and we evolve it for a time ϵ , we get

$$|\psi(t_2 + \epsilon)\rangle = \left[I - \frac{i\epsilon}{\hbar} H(t_2) \right] |\psi_0\rangle. \quad (5.25)$$

Invariance under time translations means that $|\psi(t_1 + \epsilon)\rangle = |\psi(t_2 + \epsilon)\rangle$ for all $|\psi_0\rangle$, and therefore $H(t_1) = H(t_2)$. That is, invariance under time translations means that the Hamiltonian is time-independent.

According to eqs. (3.17) and (3.18), for a time-independent Hamiltonian

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle. \quad (5.26)$$

Comparing with eq. (5.21) we see that H is the generator of time translation, just as P is the generator of spatial translations.

5.3 Parity

This is a different kind of symmetry, since it is a discrete, rather than a continuous transformation. Classically, in one dimension it is defined by $x \rightarrow -x$ and $p \rightarrow -p$ and, in three dimensions, by $\mathbf{x} \rightarrow -\mathbf{x}$ and $\mathbf{p} \rightarrow -\mathbf{p}$.⁸ In QM, in the active viewpoint (and using the notation appropriate to three dimensions), we define it on the kets by

$$\Pi|\mathbf{x}\rangle = |-\mathbf{x}\rangle, \quad \Pi|\mathbf{p}\rangle = |-\mathbf{p}\rangle. \quad (5.27)$$

In the $|\mathbf{x}\rangle$ basis, we therefore have

$$\langle \mathbf{x}' | \Pi | \mathbf{x} \rangle = \delta^{(3)}(\mathbf{x} + \mathbf{x}'), \quad (5.28)$$

where $\delta^{(3)}(\mathbf{x})$ is the three-dimensional Dirac delta, that satisfies

$$\int d^3x \delta^{(3)}(\mathbf{x}) = 1. \quad (5.29)$$

Observe, from eq. (5.28) that $\langle \mathbf{x}' | \Pi | \mathbf{x} \rangle = \langle \mathbf{x} | \Pi | \mathbf{x}' \rangle^*$, so Π is a hermitian operator, $\Pi^\dagger = \Pi$. From this it follows that

$$\begin{aligned} \langle \mathbf{x} | \Pi &= \langle \mathbf{x} | \Pi^\dagger = (\Pi | \mathbf{x} \rangle)^\dagger = |-\mathbf{x}\rangle^\dagger \\ &= \langle -\mathbf{x} |. \end{aligned} \quad (5.30)$$

Therefore, if we denote as usual $\langle \mathbf{x} | \psi \rangle = \psi(\mathbf{x})$, we have

$$\langle \mathbf{x} | \Pi | \psi \rangle = \psi(-\mathbf{x}). \quad (5.31)$$

Observe that $\Pi^2 = I$ and therefore its eigenvalues are ± 1 . In the coordinate representation, where under Π we have $\psi(\mathbf{x}) \rightarrow \psi(-\mathbf{x})$, the eigenfunctions with eigenvalues $+1$ are the even functions, $\psi(-\mathbf{x}) = +\psi(\mathbf{x})$, while those with eigenvalue -1 are the odd functions, $\psi(-\mathbf{x}) = -\psi(\mathbf{x})$.

If $[\Pi, H] = 0$, we can diagonalize Π and H simultaneously, which means that the eigenfunctions of the energy can be classified into even and odd functions. (Compare with the harmonic oscillator, where we found that the states with n even are also even under parity, and those with n odd are odd under parity.)

⁸Note that in two dimensions the transformation $(x, y) \rightarrow (-x, -y)$ is rather a rotation by 180° in the (x, y) plane. We always define parity so that, on the coordinates, is represented by a matrix with determinant -1 . So, in two dimensions, one can rather consider the transformations $(x, y) \rightarrow (-x, y)$ or $(x, y) \rightarrow (x, -y)$.

In the passive viewpoint, we do not transform the states, and we rather define parity through its action on the operators,

$$\Pi^\dagger X \Pi = -X, \quad \Pi^\dagger P \Pi = -P. \quad (5.32)$$

Observe that $\Pi = \Pi^{-1}$ (since $\Pi^2 = I$) and $\Pi = \Pi^\dagger$, as we saw above, so $\Pi = \Pi^\dagger = \Pi^{-1}$.

Consider now the nuclear β -decay



The nucleus of ${}^{60}\text{Co}$ has spin \mathbf{S} . We denote by \mathbf{P}_e the momentum of the electron. Consider the observable $\mathbf{S} \cdot \mathbf{P}_e$. Under parity \mathbf{S} is a pseudovector (just as orbital angular momentum) so it does not change sign, while $\mathbf{P}_e \rightarrow -\mathbf{P}_e$, as any momentum. Then

$$\Pi^\dagger \mathbf{S} \cdot \mathbf{P}_e \Pi = -\mathbf{S} \cdot \mathbf{P}_e. \quad (5.34)$$

If parity were a symmetry of nature, on any state $|\psi\rangle$ we should have

$$\langle \psi | \mathbf{S} \cdot \mathbf{P}_e | \psi \rangle = \langle \psi | \Pi^\dagger \mathbf{S} \cdot \mathbf{P}_e \Pi | \psi \rangle, \quad (5.35)$$

and therefore

$$\langle \psi | \mathbf{S} \cdot \mathbf{P}_e | \psi \rangle = -\langle \psi | \mathbf{S} \cdot \mathbf{P}_e | \psi \rangle = 0. \quad (5.36)$$

The experiment shows instead that the expectation value of $\mathbf{S} \cdot \mathbf{P}_e$, in the final state of the decay (5.33), is non-zero. The electron comes out preferentially in the direction opposite to the spin of the ${}^{60}\text{Co}$ nucleus. Thus, parity is violated in this process. More generally, parity is conserved in processes involving only the electromagnetic or the strong interaction, but it can be violated in processes involving weak interactions, such as β -decay.

(Reference: Shankar, Sect. 11.4)

5.4 Rotations in two dimensions

We now consider rotations, starting from the simpler case of rotations in the (x, y) plane, i.e. rotations around the z -axis. Classically, if we perform a rotation by an angle ϕ around the z axis, the coordinates (x, y) of a particle transform as

$$\begin{aligned} x &\rightarrow x \cos \phi - y \sin \phi, \\ y &\rightarrow x \sin \phi + y \cos \phi. \end{aligned} \quad (5.37)$$

In quantum mechanics, following the same procedure discussed above for translations, we define the transformation in terms of the expectation values of the operators X and Y on the state $|\psi\rangle$ of the particle,

$$\begin{aligned}\langle\psi|X|\psi\rangle &\rightarrow \langle\psi|X|\psi\rangle\cos\phi - \langle\psi|Y|\psi\rangle\sin\phi, \\ \langle\psi|Y|\psi\rangle &\rightarrow \langle\psi|X|\psi\rangle\sin\phi + \langle\psi|Y|\psi\rangle\cos\phi.\end{aligned}\quad (5.38)$$

In the active viewpoint, the operators do not transform, while the state $|\psi\rangle$ transform as

$$|\psi\rangle \rightarrow |\psi_R\rangle = U(R)|\psi\rangle. \quad (5.39)$$

Similarly to eq. (5.13), we define the action of $U(R)$ on the position eigenkets by⁹

$$U(R)|x, y\rangle = |x\cos\phi - y\sin\phi, x\sin\phi + y\cos\phi\rangle. \quad (5.40)$$

Consider now an infinitesimal rotation, by an angle $\phi \equiv \epsilon$. To first order in ϵ , eq. (5.40) becomes

$$U(R)|x, y\rangle = |x - \epsilon y, y + \epsilon x\rangle. \quad (5.41)$$

Projecting onto the coordinate basis, and proceeding as we did in eq. (5.9), we get

$$\begin{aligned}\langle x, y|U(R)|\psi\rangle &= \int dx' dy' \langle x, y|U(R)|x' y'\rangle \langle x' y'|\psi\rangle \\ &= \int dx' dy' \langle x, y|x' - \epsilon y', y' + \epsilon x'\rangle \langle x' y'|\psi\rangle \\ &= \int dx' dy' \delta[x' - (x + \epsilon y)] \delta[y' - (y - \epsilon x)] \psi(x', y') \\ &= \psi(x + \epsilon y, y - \epsilon x) \\ &= \psi(x, y) + \epsilon (y\partial_x - x\partial_y) \psi(x, y).\end{aligned}\quad (5.42)$$

where we used the notation

$$\partial_x \equiv \frac{\partial}{\partial x}, \quad \partial_y \equiv \frac{\partial}{\partial y} \quad (5.43)$$

and the fact that, to first order in ϵ , $x = x' - \epsilon y'$ is equivalent to $x' = x + \epsilon y$. Since ϵ is infinitesimal, we can write

$$U(\epsilon) = I - \frac{i\epsilon}{\hbar} L_z. \quad (5.44)$$

⁹In principle, we could add an arbitrary phase factor. Just as with translation, setting this phase to zero gives the correct transformation properties for the momentum, which in this case must transform just as the coordinates, or any other vector, i.e. $p_x \rightarrow p_x \cos\phi - p_y \sin\phi$ and $p_y \rightarrow p_x \sin\phi + p_y \cos\phi$.

The operator L_z is called the generator of rotations around the z axis [just as in eq. (5.13)]. Comparing with eq. (5.42) we see that, in the coordinate representation,

$$L_z \rightarrow -i\hbar(x\partial_y - y\partial_x). \quad (5.45)$$

Since, in the coordinate representation, $P_x \rightarrow -i\hbar\partial_x$ and $P_y \rightarrow -i\hbar\partial_y$, eq. (5.45) is just the projection, onto the coordinate representation, of the operator relation

$$L_z = XP_y - YP_x, \quad (5.46)$$

and we discover that L_z is nothing but the z component of the angular momentum: *angular momentum is the generator of rotations*.

If we use polar coordinates (ρ, ϕ) instead of cartesian coordinates (x, y) , eq. (5.45) becomes

$$L_z = -i\hbar\frac{\partial}{\partial\phi} \equiv -i\hbar\partial_\phi, \quad (5.47)$$

as you can check performing the change of variables in the derivative,

$$\frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\partial_x + \frac{\partial y}{\partial\phi}\partial_y. \quad (5.48)$$

For a finite rotation, the same argument used for translations show that

$$U(\phi) = \exp\{-i\phi L_z/\hbar\}. \quad (5.49)$$

In the passive viewpoint, we rather transform the operators by requiring that, for ϵ infinitesimal,

$$U^\dagger(R)XU(R) = X - \epsilon Y, \quad (5.50)$$

$$U^\dagger(R)YU(R) = Y + \epsilon X, \quad (5.51)$$

$$U^\dagger(R)P_xU(R) = P_x - \epsilon P_y, \quad (5.52)$$

$$U^\dagger(R)P_yU(R) = P_y + \epsilon P_x. \quad (5.53)$$

Writing $U(R)$ as in eq. (5.44), and expanding the left-hand sides to first order in ϵ , we get

$$[X, L_z] = -i\hbar Y, \quad (5.54)$$

$$[Y, L_z] = +i\hbar X, \quad (5.55)$$

$$[P_x, L_z] = -i\hbar P_y, \quad (5.56)$$

$$[P_y, L_z] = +i\hbar P_x. \quad (5.57)$$

You can check that $L_z = XP_y - YP_x$ satisfy these commutations relations (you can also show that it is in fact the unique solution).

Similarly to what we have done for translations, we define invariance under rotations by requiring that $\langle \psi | H | \psi \rangle$ is invariant. Similarly to eq. (5.16), in the active picture this means that

$$\langle \psi | H | \psi \rangle = \langle \psi_R | H | \psi_R \rangle \quad (5.58)$$

while in the passive picture it means that

$$H = U^\dagger(R) H U(R). \quad (5.59)$$

In both cases, expanding to first order in ϵ , we get

$$[L_z, H] = 0, \quad (5.60)$$

which expresses the conservation of angular momentum in quantum mechanics.

The eigenvalue problem for L_z Consider the eigenvalue equation

$$L_z |l_z\rangle = l_z |l_z\rangle. \quad (5.61)$$

Projecting it on the space of functions of polar coordinates (ρ, ϕ) , defining

$$\psi_{l_z}(\rho, \phi) = \langle \rho, \phi | l_z \rangle, \quad (5.62)$$

and using eq. (5.47), we get

$$-i\hbar \partial_\phi \psi_{l_z}(\rho, \phi) = l_z \psi_{l_z}(\rho, \phi), \quad (5.63)$$

whose solution is

$$\psi_{l_z}(\rho, \phi) = R(\rho) e^{il_z \phi / \hbar}, \quad (5.64)$$

where the radial function $R(\rho)$ is arbitrary. Proceeding as in eqs. (1.12)–(1.14), we find that L_z is hermitian only if $\psi_{l_z}(\rho, \phi)$ is periodic,

$$\psi_{l_z}(\rho, \phi) = \psi_{l_z}(\rho, \phi + 2\pi). \quad (5.65)$$

Then eq. (5.64) gives

$$l_z = m\hbar, \quad (5.66)$$

where $m = 0, \pm 1, \pm 2, \dots$ is an integer. We will refer to L_z as an *orbital* angular momentum, to distinguish it from spin, an intrinsic angular momentum to be introduced below. We have therefore found that *the orbital angular momentum L_z is quantized*, and is given by an integer number m , times \hbar .

5.5 Angular momentum in three dimensions

We found above that the generator of rotations around the z axis is $L_z = XP_y - YP_x$. Repeating the same reasoning, the generator of rotations around the x axis is $L_x = YP_z - ZP_y$ and the generator of rotations around the y axis is $L_y = ZP_x - XP_z$. In compact form,

$$L_i = \epsilon_{ijk} X_j P_k, \quad (5.67)$$

where the sum over repeated indices is understood. From $[X_i, P_j] = i\hbar\delta_{ij}$ it follows that

$$[L_i, L_j] = i\hbar\epsilon_{ijk} L_k. \quad (5.68)$$

This is called *the algebra of angular momenta*. Observe that rotations around different axes do not commute; e.g.

$$e^{i\theta_x L_x/\hbar} e^{i\theta_y L_y/\hbar} \neq e^{i\theta_y L_y/\hbar} e^{i\theta_x L_x/\hbar} \quad (5.69)$$

since $[L_x, L_y] \neq 0$. However, rotations form a *group*. The composition of two rotations is still a rotation (and there is the identity element, the inverse of any rotation, and the composition is associative).

Since there is nothing special about the choice of the z axis in eq. (5.49), the operator that describes a finite rotations, by an angle θ , around a generic axis identified by the unit vector $\hat{\mathbf{n}}$ is

$$U(R) = \exp\{-i\boldsymbol{\theta}\cdot\mathbf{L}/\hbar\}. \quad (5.70)$$

where $\boldsymbol{\theta} = \theta\hat{\mathbf{n}}$. We can check this result observing that, when a vector \mathbf{r} is rotated by an infinitesimal angle $\delta\boldsymbol{\theta}$, it changes to $\mathbf{r} + \delta\boldsymbol{\theta}\times\mathbf{r}$. Therefore we demand that the wavefunction transforms as

$$\begin{aligned} \psi(\mathbf{r}) &\rightarrow \psi(\mathbf{r} - \delta\boldsymbol{\theta}\times\mathbf{r}) \\ &= \psi(\mathbf{r}) - (\delta\boldsymbol{\theta}\times\mathbf{r})\cdot\nabla\psi \\ &= \psi(\mathbf{r}) - \epsilon_{ijk}\delta\theta_i x_j \partial_k \psi. \end{aligned} \quad (5.71)$$

where $\partial_k = \partial/\partial x^k$. On the other hand, $\boldsymbol{\theta}\cdot\mathbf{L} = \theta_i L_i = \theta_i \epsilon_{ijk} X_j P_k$. Acting on function of coordinates, $X_j \rightarrow x_j$ and $P_k \rightarrow -i\hbar\partial_k$, so

$$-\frac{i}{\hbar}\boldsymbol{\theta}\cdot\mathbf{L}\psi(\mathbf{r}) = -\epsilon_{ijk}\theta_i x_j \partial_k \psi. \quad (5.72)$$

Therefore, for $\delta\boldsymbol{\theta}$ infinitesimal,

$$\exp\{-i\delta\boldsymbol{\theta}\cdot\mathbf{L}/\hbar\}\psi(\mathbf{r}) = \psi(\mathbf{r}) - \epsilon_{ijk}\delta\theta_i x_j \partial_k \psi, \quad (5.73)$$

showing that $\boldsymbol{\theta} \cdot \mathbf{L}$ is indeed the generator of rotations around the $\hat{\boldsymbol{\theta}}$ axis.

The total angular momentum operator squared is

$$L^2 = L_x^2 + L_y^2 + L_z^2. \quad (5.74)$$

Observe that

$$[L^2, L_i] = 0, \quad (5.75)$$

for $i = x, y, z$. Similarly to what we have seen for translations and for rotations in a plane, a Hamiltonian is invariant under rotations if

$$U^\dagger(R) H U(R) = H, \quad (5.76)$$

which implies

$$[H, L_i] = 0, \quad (5.77)$$

and therefore $[H, L^2] = 0$. If a problem is invariant under rotations, we can therefore diagonalize simultaneously H , L^2 , and one of the components L_i , conventionally chosen as L_z . Observe that we cannot diagonalize simultaneously different components of L_i .

5.5.1 The eigenvalue problem for L^2, L_z

The determination of the possible eigenvalues of L^2, L_z is conceptually similar to the determination of the eigenvalues of the Hamiltonian of the harmonic oscillator using the raising and lowering operators a, a^\dagger , that we discussed in Section 4. We assume that we have found a state $|\alpha\beta\rangle$ such that

$$L^2|\alpha\beta\rangle = \alpha|\alpha\beta\rangle, \quad (5.78)$$

$$L_z|\alpha\beta\rangle = \beta|\alpha\beta\rangle. \quad (5.79)$$

We define the *raising and lowering operators*

$$L_\pm = L_x \pm iL_y. \quad (5.80)$$

They satisfy

$$[L_z, L_\pm] = \pm\hbar L_\pm, \quad (5.81)$$

and

$$[L^2, L_\pm] = 0. \quad (5.82)$$

Then, L_+ raises the eigenvalue of L_z by \hbar , while leaving the eigenvalue of L^2 invariant

$$L_z(L_+|\alpha\beta\rangle) = (\beta + \hbar)(L_+|\alpha\beta\rangle), \quad (5.83)$$

$$L^2(L_+|\alpha\beta\rangle) = \alpha(L_+|\alpha\beta\rangle). \quad (5.84)$$

(verify this!) and similarly L_- lowers the eigenvalue of L_z by \hbar , while leaving the eigenvalue of L^2 invariant.

The fact that we can apparently raise or lower indefinitely β gives rise to a problem similar to the fact that in the harmonic oscillator it seems that we could lower indefinitely the eigenvalue of the Hamiltonian. In fact, from the hermiticity of L_x and L_y , it follows that, on any state $|\alpha\beta\rangle$,

$$\langle\alpha\beta|L_x^2 + L_y^2|\alpha\beta\rangle \geq 0. \quad (5.85)$$

On the other hand $L_x^2 + L_y^2 = L^2 - L_z^2$, so

$$\langle\alpha\beta|L_x^2 + L_y^2|\alpha\beta\rangle = \alpha - \beta^2, \quad (5.86)$$

and therefore

$$\beta^2 \leq \alpha. \quad (5.87)$$

This means that it is impossible to raise, or to lower, β indefinitely, at fixed α . There must exist a maximum value β_{\max} such that

$$L_+|\alpha\beta_{\max}\rangle = 0. \quad (5.88)$$

Acting with L_- and using $L_-L_+ = L^2 - L_z^2 - \hbar L_z$, we get

$$(L^2 - L_z^2 - \hbar L_z)|\alpha\beta_{\max}\rangle = 0, \quad (5.89)$$

and therefore

$$\alpha = \beta_{\max}(\beta_{\max} + \hbar). \quad (5.90)$$

Similarly, from $L_-|\alpha\beta_{\min}\rangle = 0$, acting with L_+ , we get $\alpha = \beta_{\min}(\beta_{\min} - \hbar)$ and therefore $\beta_{\min} = -\beta_{\max}$. Since we go from β_{\min} to β_{\max} applying an integer number of time, say k , the raising operator, raising each time β by \hbar , we have $\beta_{\max} - \beta_{\min} = 2\beta_{\max} = \hbar k$, so

$$\beta_{\max} = \frac{\hbar k}{2}, \quad (5.91)$$

where k can take the values $0, 1, 2, \dots$. We write $\beta_{\max} = l\hbar$, so that $l = 0, 1/2, 1, \dots$. From eq. (5.90),

$$\alpha = \hbar^2 l(l+1). \quad (5.92)$$

We have therefore found that the common eigenvectors of L^2 and L_z have the form $|lm\rangle$, where l is an integer or an half-integer, while m takes the value between $-l$ and l , in integer steps, and

$$L^2|lm\rangle = \hbar^2 l(l+1)|lm\rangle, \quad (5.93)$$

$$L_z|lm\rangle = \hbar m|lm\rangle. \quad (5.94)$$

If we compare with our discussion of rotations in a plane, the quantization of angular momentum that we have found is quite unexpected. In fact, beside the integer values of m , that we found already in eq. (5.66), we also find half-integer values. The reason is that what we have done in this section is purely algebraic, and follows simply from the angular momentum algebra. Nowhere we used the explicit expression of the angular momentum L_i in terms of X and P .

Let us then enlarge our setting, and define in general *angular momentum* any vector whose components satisfy the angular momentum algebra. In this more general setting we denote angular momentum by J_i . Thus, the components J_i are defined by the fact that they satisfy

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k. \quad (5.95)$$

One particular solution of this algebraic equation is given by $L_i = \epsilon_{ijk}X_jP_k$, that we now call the *orbital* angular momentum.

So we have found that, if we only require that the algebra (5.95) is satisfied, the possible eigenvectors and eigenvalues satisfy

$$J^2|jm\rangle = \hbar^2 j(j+1)|jm\rangle, \quad (5.96)$$

$$J_z|jm\rangle = \hbar m|jm\rangle, \quad (5.97)$$

where j can be either an integer or a half integer, $j = 0, 1/2, 1, 3/2, \dots$ and, for each j , m goes from $-j$ to $+j$ in integer steps. So, for instance, we can have

$$j = 0, \quad m = 0, \quad (5.98)$$

$$j = \frac{1}{2}, \quad m = -\frac{1}{2}, +\frac{1}{2}, \quad (5.99)$$

$$j = 1, \quad m = -1, 0, 1, \quad (5.100)$$

$$j = \frac{3}{2}, \quad m = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, \frac{3}{2}, \quad (5.101)$$

and so on.

For orbital angular momentum, however, the situation is different. Once we use the explicit expression in terms of X and P , we have found in eq. (5.47) that $L_z = -i\hbar\partial_\phi$, where ϕ is the angle in the (x, y) plane. Its eigenfunctions are therefore proportional to $e^{im\phi}$, as we saw in eq. (5.64), and requiring the hermiticity of L_z restricts the space of wavefunction to functions periodic under $\phi \rightarrow \phi + 2\pi$, and therefore to integer m . The half-integer solutions are not allowed, for *orbital* angular momentum. We will see below, however, that half-integer solutions reappear in a more general context, and are indeed physically very important.

5.5.2 The matrix elements of J_i

We want to determine the matrix elements $\langle j'm'|J_i|jm\rangle$. (We use the more general notation J_i rather than L_i , since we will not use the explicit form of the orbital angular momentum, but only the angular momentum algebra). We proceed just as we did for the harmonic oscillator to get $\langle n'|X|n\rangle$, in eqs. (4.26) to (4.36). Since J_\pm , applied to $|jm\rangle$, raise or lower m while leaving j unchanged, we must have

$$J_+|jm\rangle = C_+(j, m)|j, m+1\rangle, \quad (5.102)$$

$$J_-|jm\rangle = C_-(j, m)|j, m-1\rangle. \quad (5.103)$$

To determine $C_\pm(j, m)$ we take the adjoint of eq. (5.102), and we use the fact that $J_+^\dagger = J_-$, see eq. (5.80), so

$$\langle jm|J_- = \langle j, m+1|C_+^*(j, m). \quad (5.104)$$

Multiplying this by eq. (5.102) and using

$$J_- J_+ = J^2 - J_z^2 - \hbar J_z \quad (5.105)$$

we get

$$C_+(j, m) = \hbar[j(j+1) - m(m+1)]^{1/2} = \hbar[(j-m)(j+m+1)]^{1/2}. \quad (5.106)$$

Similarly,

$$C_-(j, m) = \hbar[j(j+1) - m(m-1)]^{1/2} = \hbar[(j+m)(j-m+1)]^{1/2}. \quad (5.107)$$

Observe that $C_+(j, m)$ vanishes when $m = j$ and $C_-(j, m)$ vanishes when $m = -j$, as they should. Writing $J_x = (J_+ + J_-)/2$ we find

$$\langle j'm'|J_x|jm\rangle = \frac{1}{2} \delta_{jj'} [\delta_{m',m+1} C_+(j, m) + \delta_{m',m-1} C_-(j, m)], \quad (5.108)$$

and similarly, from $J_y = (J_+ - J_-)/(2i)$,

$$\langle j'm'|J_y|jm\rangle = \frac{1}{2i} \delta_{jj'} [\delta_{m',m+1} C_+(j, m) - \delta_{m',m-1} C_-(j, m)], \quad (5.109)$$

while, of course,

$$\langle j'm'|J_z|jm\rangle = \hbar m \delta_{jj'} \delta_{mm'}. \quad (5.110)$$

5.5.3 The eigenfunctions of L_i

We now restrict to *orbital* angular momentum L_i . In this case, we have its explicit form in the coordinate representation,

$$L_i = \epsilon_{ijk} X_j P_k \rightarrow -i\hbar \epsilon_{ijk} x_j \partial_k. \quad (5.111)$$

It is convenient to use polar coordinates (r, θ, ϕ) rather than cartesian coordinates (x, y, z) . Then, performing the change of variables, we find

$$L_x \rightarrow i\hbar (\sin \phi \partial_\theta + \cos \phi \cot \theta \partial_\phi), \quad (5.112)$$

$$L_y \rightarrow i\hbar (-\cos \phi \partial_\theta + \sin \phi \cot \theta \partial_\phi), \quad (5.113)$$

$$L_z \rightarrow -i\hbar \partial_\phi, \quad (5.114)$$

where we used the shorthand notation

$$\partial_\theta = \frac{\partial}{\partial \theta}, \quad \partial_\phi = \frac{\partial}{\partial \phi}. \quad (5.115)$$

From this it also follows that

$$L_{\pm} \rightarrow \pm \hbar e^{\pm i\phi} (\partial_{\theta} \pm i \cot \theta \partial_{\phi}), \quad (5.116)$$

and

$$L^2 \rightarrow -\hbar^2 \left[\frac{1}{\sin \theta} \partial_{\theta} (\sin \theta \partial_{\theta}) + \frac{1}{\sin^2 \theta} \partial_{\phi}^2 \right]. \quad (5.117)$$

Consider now the vector equations

$$L^2 |lm\rangle = \hbar^2 l(l+1) |lm\rangle, \quad (5.118)$$

$$L_z |lm\rangle = \hbar m |lm\rangle. \quad (5.119)$$

Just as in the case of rotations in two dimensions (see page 36), the condition that L_z be hermitian requires that m , and therefore l , be integer, and excludes the half-integer values. Therefore, while the angular momentum algebra admits representations with both integer or half-integer values of l , if one uses the explicit form (5.111) of the orbital angular momentum operator, only integer values of l are allowed.

Projecting eqs. (5.118) and (5.119) onto the (polar) coordinate representation, defining

$$Y_{lm}(\theta, \phi) = \langle \theta\phi | lm \rangle, \quad (5.120)$$

and using eqs. (5.117) and (5.114) we get

$$\left[\frac{1}{\sin \theta} \partial_{\theta} (\sin \theta \partial_{\theta}) + \frac{1}{\sin^2 \theta} \partial_{\phi}^2 \right] Y_{lm} = -l(l+1) Y_{lm}, \quad (5.121)$$

$$-i \partial_{\phi} Y_{lm} = m Y_{lm}. \quad (5.122)$$

The functions Y_{lm} that satisfy eqs. (5.121) and (5.122) are called *spherical harmonics*. They have the form

$$Y_{lm}(\theta, \phi) = c_{lm} e^{im\phi} P_{lm}(\cos \theta), \quad (5.123)$$

where c_{lm} is a normalization constant, and $P_{lm}(\cos \theta)$ is a polynomial in $\cos \theta$ and $\sin \theta$, called the associated Legendre polynomial. For explicit form of the spherical harmonics with $l = 0, 1, 2$ see Shankar, eq. (12.5.39) or Griffiths, page 139.

Spherical harmonics with different values of l, m are orthogonal, in the sense that

$$\int d\Omega Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}. \quad (5.124)$$

Observe that the Laplacian, in polar coordinates, can be written as

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \partial_r (r^2 \partial_r) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right], \\ &= \frac{1}{r^2} \partial_r (r^2 \partial_r) - \frac{L^2}{\hbar^2 r^2},\end{aligned}\quad (5.125)$$

and therefore, since $Y_{lm}(\theta, \phi)$ are independent of r , eq. (5.121) can be written as

$$\nabla^2 Y_{lm}(\theta, \phi) = -\frac{l(l+1)}{r^2} Y_{lm}(\theta, \phi). \quad (5.126)$$

Another useful relation satisfied by the spherical harmonics can be obtained projecting the equation

$$L_\pm |lm\rangle = C_\pm(l, m) |l, m \pm 1\rangle, \quad (5.127)$$

onto the polar coordinate representation, and using (5.116):

$$e^{\pm i\phi} (\partial_\theta \pm i \cot \theta \partial_\phi) Y_{lm}(\theta, \phi) = [l(l+1) - m(m \pm 1)]^{1/2} Y_{l, m \pm 1}(\theta, \phi). \quad (5.128)$$

The fact that the spherical harmonics indeed satisfy this relation can also be checked from their explicit expression.

(Reference: Shankar, Section 12.5)

5.5.4 Solution of rotationally invariant problems

Consider the time-independent Schrödinger equation in three dimension, with a spherically symmetric potential $V(r)$,

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_E(r, \theta, \phi) = E \psi_E(r, \theta, \phi). \quad (5.129)$$

Equation (5.126) allows us to perform the separation of variables. Writing

$$\psi_E(r, \theta, \phi) = R_{Elm}(r) Y_{lm}(\theta, \phi), \quad (5.130)$$

we get an equation involving only the radial wave function $R_{Elm}(r)$,

$$\left\{ \frac{-\hbar^2}{2m} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] + V(r) \right\} R_{Elm}(r) = E R_{Elm}(r). \quad (5.131)$$

Observe that the equation depends on l but not on the quantum number m , so we can drop the index m in $R_{Elm}(r)$ and write it simply as $R_{El}(r)$. It is useful to introduce a new radial function $U_{El}(r)$ defined by

$$R_{El}(r) = \frac{1}{r} U_{El}(r). \quad (5.132)$$

Then eq. (5.131) becomes simpler,

$$\left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2mr^2} \right] \right\} U_{El}(r) = 0. \quad (5.133)$$

Formally, this is the same as a Schrödinger equation in one dimension, on the half-line $0 \leq r < \infty$, with an effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (5.134)$$

Observe that angular momentum generates a repulsive potential. This corresponds just to the centrifugal potential in classical mechanics.

The boundary conditions to be imposed on $U(r)$ at $r = 0$ and as $r \rightarrow \infty$ are as follows. Using eq. (5.124),

$$\begin{aligned} \int d^3x |\psi_{Elm}|^2 &= \int_0^\infty dr r^2 |R_{El}|^2 \\ &= \int_0^\infty dr |U_{El}|^2. \end{aligned} \quad (5.135)$$

Thus, in order to have a state normalizable to unity (i.e. a bound state), it is necessary that $U_{El}(r) \rightarrow 0$ as $r \rightarrow \infty$, sufficiently fast so that the integral converges. If, instead,

$$U_{El}(r) \rightarrow e^{ikr}, \quad (5.136)$$

we have a state normalizable to a Dirac delta, i.e. an unbound state.

At $r = 0$, requiring that the Schrödinger equation is satisfied, one finds that we must have $U_{El}(r) \rightarrow 0$, unless the potential has a Dirac delta singularity in the origin (see Shankar, pages 340–343).

6 Spin

We have seen above that angular momentum, in QM, is defined as the vector \mathbf{J} whose components J_i satisfy

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k. \quad (6.1)$$

Using only this algebraic relation, we have proved that the eigenvectors have the form $|jm\rangle$, where $j = 0, 1/2, 1$, etc. and m takes the values between $-j$ and $+j$, in integer steps. We have also found, again using only the algebra (6.1), the matrix elements $\langle j'm'|J_i|jm\rangle$, see eqs. (5.108)–(5.110).

We have then seen that a particular solution of eq. (6.1) is given by $J_i = L_i$, where L_i is called the *orbital* angular momentum, $L_i = \epsilon_{ijk}X_jP_k$. We have found however that in this case hermiticity restricts the quantum number j (which, when we consider orbital angular momentum, is rather denoted as l) to integer values, while half-integers are not allowed. We can check explicitly that this expression for the operators L_i gives the matrix elements of eqs. (5.108)–(5.110), writing the matrix elements in the (polar) coordinate representation: by making use of eqs. (5.112)–(5.114), we get

$$\begin{aligned} \langle l'm'|L_x|lm\rangle &= i\hbar \int d\Omega Y_{l'm'}^*(\theta, \phi) (\sin\phi \partial_\theta + \cos\phi \cot\theta \partial_\phi) Y_{lm}(\theta, \phi), \quad (6.2) \\ \langle l'm'|L_y|lm\rangle &= i\hbar \int d\Omega Y_{l'm'}^*(\theta, \phi) (-\cos\phi \partial_\theta + \sin\phi \cot\theta \partial_\phi) Y_{lm}(\theta, \phi), \quad (6.3) \end{aligned}$$

$$\langle l'm'|L_z|lm\rangle = -i\hbar \int d\Omega Y_{l'm'}^*(\theta, \phi) \partial_\phi Y_{lm}(\theta, \phi). \quad (6.4)$$

Using the explicit expression of the spherical harmonics, we can verify that eqs. (5.108)–(5.110) are indeed obeyed.¹⁰

In the language of group theory, the explicit expression L_i given by the right-hand side of eqs. (5.112)–(5.114) is just a particular *representation* of the angular momentum algebra (6.1). That is, the abstract mathematical objects J_i , defined by the fact that they satisfy eq. (6.1), have been given an explicit form, in terms of operators acting on some space. This is completely analogous to the fact that, when confronted with the Heisenberg algebra $[X, P] = i\hbar$, we have found an explicit representation given by $X \rightarrow x$ and $P \rightarrow -i\hbar\partial_x$. In both cases the space on which the operators act (called the

¹⁰ Actually, eqs. (6.2)–(6.4) follow automatically from the property (5.128) of the spherical harmonics, which is just the transcription of eq. (5.127) in the polar coordinate representation.

basis of the representation, in the mathematical language) is the space of functions of coordinates, and the operators J_i are represented by differential operators L_i acting on these functions, given by $L_i = -i\hbar\epsilon_{ijk}x_j\partial_k$ or, in polar coordinates, by the right-hand side of eqs. (5.112)–(5.114).

We now want to look for more general representations of the angular momentum algebra, and in particular we want to understand the appearance of half-integer values of j in the algebraic solution. To begin, rather than considering representations of the algebra (6.1) in terms of operators acting on a space of functions (i.e. representations whose base space is infinite-dimensional) we start from something more elementary, namely representations in terms of matrices of finite dimensions.

Consider a state $|jm\rangle$. Under rotations, it transforms as

$$|jm\rangle \rightarrow U(R)|jm\rangle = \exp\{-i\theta_i J_i/\hbar\}|jm\rangle. \quad (6.5)$$

The fact that the states $|jm\rangle$ form a basis for a representation of angular momentum means that, when acting on it, the ‘abstract’ operators J_i , defined by the fact that they satisfy the algebra (6.1), take a concrete form as operators, which depends on the representation chosen. The action of the operators J_i on the representation $|jm\rangle$ is given by eqs. (5.102), (5.103) and (5.97). From this we see that, acting with any of the J_i over the state $|jm\rangle$, we do not change the value of j , while J_x and J_y change the value of m . Therefore, under a generic rotation, the state $|jm\rangle$ is sent into a combination of states with, in general, different values of m , but with the same value of j . In the language of representation theory, this means that the states $|jm\rangle$, with j fixed (to an integer or half-integer value) and m ranging from $-j$ to j in integer steps, form a representation of the rotation group. The corresponding dimension of the representation is $2j + 1$, which is the number of possible values of m for given j . In other words, the kets $|jm\rangle$ with j fixed and m taking the $(2j + 1)$ values from $-j$ to j in integer steps, transform among them under rotations.

This allows us to construct all possible finite-dimensional representation of the angular momentum algebra. The most obvious one corresponds to $j = 0$ (and therefore $m = 0$). This is a single object, $|00\rangle$, on which the generators take the value $J_i = 0$, which is the trivial solution of the algebra (6.1). Such an object is invariant under rotation, i.e. $U(R) = I$ on it.

We next consider the two-dimensional representation corresponding to $j = 1/2$.

6.1 Spin 1/2

Consider now $j = 1/2$. In this case the base space $|jm\rangle$ is two-dimensional, and a basis is given by

$$|\frac{1}{2}, +\frac{1}{2}\rangle, \quad |\frac{1}{2}, -\frac{1}{2}\rangle. \quad (6.6)$$

A generic ket in this space has the form

$$|\xi\rangle = \alpha |\frac{1}{2}, +\frac{1}{2}\rangle + \beta |\frac{1}{2}, -\frac{1}{2}\rangle, \quad (6.7)$$

with α and β complex numbers. Let us denote such a ket as a column,

$$\xi = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}; \quad (6.8)$$

ξ is called a *spinor*.¹¹ It is an element of the vector space spanned by $|\frac{1}{2}, +\frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$. In this notation, $|\frac{1}{2}, +\frac{1}{2}\rangle$ is written as the spinor

$$\xi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (6.9)$$

while $|\frac{1}{2}, -\frac{1}{2}\rangle$ is written as

$$\xi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (6.10)$$

and a generic spinor ξ is written as

$$\xi = \alpha \xi_+ + \beta \xi_-. \quad (6.11)$$

We have already found the matrix elements of J_i for j, m arbitrary, see eqs. (5.108)–(5.110). For $j = 1/2$, these matrix elements can be arranged into a 2×2 matrix. Using the shorthand notation

$$|\frac{1}{2}, +\frac{1}{2}\rangle = |+\rangle, \quad |\frac{1}{2}, -\frac{1}{2}\rangle = |-\rangle \quad (6.12)$$

we write

$$(J_i)_{\alpha\beta} = \begin{pmatrix} \langle +|J_i|+\rangle & \langle +|J_i|-\rangle \\ \langle -|J_i|+\rangle & \langle -|J_i|-\rangle \end{pmatrix}_{\alpha\beta}, \quad (6.13)$$

¹¹More precisely, we will see below that a spinor is defined as a two-component object with a well-defined transformation law under rotations.

where the indices α and β run over the values 1, 2. Using the explicit expressions (5.108)–(5.110) we find that, for $j = 1/2$,

$$J_i = \frac{\hbar}{2} \sigma_i, \quad (6.14)$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (6.15)$$

The matrices σ_i are called the *Pauli matrices*. Observe that they satisfy the relations

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I, \quad (6.16)$$

where I is the 2×2 identity matrix, and

$$\sigma_x \sigma_y = i \sigma_z, \quad (6.17)$$

plus its cyclic permutations. These relations can be summarized compactly as

$$\sigma_i \sigma_j = \delta_{ij} I + i \epsilon_{ijk} \sigma_k. \quad (6.18)$$

The explicit expression of J_i given in (6.14) must satisfy the angular momentum algebra by construction, since the matrix elements (5.108)–(5.110) have been determined requiring that the J_i satisfy it. We can easily check it explicitly: using eq. (6.18) and the antisymmetry of ϵ_{ijk} , we have

$$\sigma_i \sigma_j - \sigma_j \sigma_i = 2i \epsilon_{ijk} \sigma_k, \quad (6.19)$$

and therefore $J_i = \sigma_i/2$ satisfies the angular momentum algebra.

What we have done, in mathematical terms, is to find a new representation of the angular momentum algebra. This representation has nothing to do with the representation of orbital angular momentum discussed above. Even the base space is completely different. Above, the basis was the space of functions of the variables θ, ϕ . As any functional space, this is a vector space of infinite dimension, recall our discussion on page 6. Here, in contrast, the basis is a vector space of *finite* dimension, actually two-dimensional, see eqs. (6.7) or (6.11).

Observe that, on the spinors ξ_{\pm} given in eqs. (6.9) and (6.10), we have

$$J_z \xi_{\pm} = \frac{\hbar}{2} \sigma_z \xi_{\pm} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \xi_{\pm} = \pm \xi_{\pm}. \quad (6.20)$$

Therefore ξ_+ can be visualized as a state carrying an arrow pointing upward, corresponding to $J_z = +\hbar/2$, and ξ_- as a state carrying an arrow pointing downward, corresponding to $J_z = -\hbar/2$. Such an angular momentum is called *spin* angular momentum, or simply spin, to distinguish it from orbital angular momentum, and we use the symbol S_i to denote it.

Since in ξ_+ and ξ_- there is no reference to the spatial coordinates, we can think to them as describing a state carrying an intrinsic arrow, and located at some fixed point in space. We can add a spatial dependence considering a spinor of the form

$$\xi(\mathbf{x}) = \begin{pmatrix} \xi^1(\mathbf{x}) \\ \xi^2(\mathbf{x}) \end{pmatrix}. \quad (6.21)$$

This quantity is now a basis for the representation of both orbital angular momentum L_i and of spin S_i . Orbital angular momentum acts on the coordinates, so for instance L_z , acting on $\xi(\mathbf{x})$, produces the spinor

$$L_z \xi(\mathbf{x}) = \begin{pmatrix} L_z \xi^1(\mathbf{x}) \\ L_z \xi^2(\mathbf{x}) \end{pmatrix} = -i\hbar \begin{pmatrix} (x\partial_y - y\partial_x)\xi^1(\mathbf{x}) \\ (x\partial_y - y\partial_x)\xi^2(\mathbf{x}) \end{pmatrix}, \quad (6.22)$$

compare with eq. (5.45). If we prefer to use polar coordinates (r, θ, ϕ) ,

$$L_z \xi(r, \theta, \phi) = -i\hbar \begin{pmatrix} \partial_\phi \xi^1(r, \theta, \phi) \\ \partial_\phi \xi^2(r, \theta, \phi) \end{pmatrix}, \quad (6.23)$$

see eq. (5.47). In contrast, S_z acts on $\xi(\mathbf{x})$ as

$$S_z \xi(\mathbf{x}) = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \xi^1(\mathbf{x}) \\ \xi^2(\mathbf{x}) \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \xi^1(\mathbf{x}) \\ -\xi^2(\mathbf{x}) \end{pmatrix}, \quad (6.24)$$

while, e.g.

$$S_x \xi(\mathbf{x}) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \xi^1(\mathbf{x}) \\ \xi^2(\mathbf{x}) \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \xi^2(\mathbf{x}) \\ \xi^1(\mathbf{x}) \end{pmatrix}. \quad (6.25)$$

In other words, denoting generically the two components $\xi^1(\mathbf{x})$ and $\xi^2(\mathbf{x})$ of the spinor as $\xi^\alpha(\mathbf{x})$, the spin S_i is represented as a matrix $(S_i)_{\alpha\beta}$ acting on the index $\alpha = 1, 2$, while it leaves the \mathbf{x} dependence unaffected.

One might be tempted to interpret physically spin as the angular momentum due to the rotation of the particle around one of its axes. So, the fact that an electron in the hydrogen atom is characterized both by orbital angular momentum and by spin could be seen as analogous to the fact that a macroscopic body, such as the Earth in orbit around the Sun, performs both a motion of revolution around the Sun (orbital angular momentum) and a

motion of rotation around its axis (spin). However, such a classical analogy has its limitations and, if carried too far, leads to erroneous predictions (for instance for the magnetic moment of particles), as we will see below.¹² Spin is actually a genuinely quantum property of matter.

6.1.1 Transformation of spinors under rotations

In eq. (6.8) we have defined spinors as objects with two complex components. However, if you think for instance to the definition of a vector $\mathbf{v} = (v_x, v_y, v_z)$, you realize immediately that it is not enough to say that it is a set of three objects. We must also require that these three objects transform in an appropriate way under rotations. Similarly, the definition of spinor is completed by stating what is its transformation under a generic rotation. Consider first a spinor ξ with no spatial dependence. Its transformation under a rotation by an angle $\boldsymbol{\theta}$ is defined by

$$\xi \rightarrow \exp\{-i\boldsymbol{\theta}\cdot\mathbf{S}/\hbar\} \xi \quad (6.26)$$

where

$$S_i = \frac{\hbar}{2} \sigma_i, \quad (6.27)$$

and σ_i are the Pauli matrices. Observe that $\exp\{-i\boldsymbol{\theta}\cdot\mathbf{S}/\hbar\} = \exp\{-i\boldsymbol{\theta}\cdot\boldsymbol{\sigma}/2\}$ is a 2×2 matrix, acting on the two-component spinor

$$\xi = \begin{pmatrix} \xi^1 \\ \xi^2 \end{pmatrix}. \quad (6.28)$$

In other words, as we already stressed below eq. (6.5), as long as J_i are defined abstractly as operators that satisfy the angular momentum algebra, the generic, abstract, form of the rotation operator is

$$U(R) = \exp\{-i\boldsymbol{\theta}\cdot\mathbf{J}/\hbar\}. \quad (6.29)$$

Any given, explicit solution of the angular momentum algebra provides a *representation* of the algebra. In particular, the \mathbf{x} -independent spinors ξ provide a basis for a representation of the angular momentum algebra, where the abstract operators \mathbf{J} takes the explicit form (6.14). Since J_i are represented as 2×2 matrices, this is called a two-dimensional representation of

¹²Furthermore, in modern quantum field theory particles such as the electron (or more generally all leptons and quarks) are structureless, at least down to the shortest distances probed by accelerators (which are of order 10^{-17} cm), so it is not clear in what sense such pointlike objects could rotate around their axis.

the angular momentum algebra. On the spinor representation, the abstract operator $U(R)$ given in eq. (6.29) takes the explicit form

$$\exp\{-i\boldsymbol{\theta}\cdot\boldsymbol{\sigma}/2\}. \quad (6.30)$$

To understand how a \mathbf{x} -dependent spinor should transform, recall first how a scalar function transform. The transformation of a *scalar* function $\psi(\mathbf{x})$ under rotation is given by (see eq. (5.70))

$$\psi(\mathbf{x}) \rightarrow \exp\{-i\boldsymbol{\theta}\cdot\mathbf{L}/\hbar\}\psi(\mathbf{x}), \quad (6.31)$$

where \mathbf{L} is the orbital angular momentum operator. In the mathematical language of representation theory, the space of functions is a basis for the representation of the angular momentum algebra, where the abstract operator J_i are represented as orbital angular momentum L_i , i.e. as differential operators acting on the coordinates, and on this representation the abstract rotation operator $U(R)$ given in eq. (6.29) takes the explicit form

$$\exp\{-i\boldsymbol{\theta}\cdot\mathbf{L}/\hbar\}, \quad (6.32)$$

where L_i are the differential operator $-i\hbar\epsilon_{ijk}x_j\partial_k$. Observe that this representation is infinite-dimensional, since the space of functions has infinite dimension.

If we consider for instance a rotation by an angle α around the z -axis, using eq. (5.114) and working in polar coordinates,

$$\begin{aligned} \psi(r, \theta, \phi) &\rightarrow \exp\{-i\alpha L_z/\hbar\}\psi(r, \theta, \phi) \\ &= \exp\{-\alpha\partial_\phi\}\psi(r, \theta, \phi) \\ &= \psi(r, \theta, \phi - \alpha). \end{aligned} \quad (6.33)$$

So, the role of $\exp\{-i\boldsymbol{\theta}\cdot\mathbf{L}/\hbar\}$ is to transform the argument \mathbf{x} of ψ .¹³ Consider now an \mathbf{x} -dependent spinor $\xi(\mathbf{x})$. When we perform a rotation, first of all the argument \mathbf{x} changes. This change simply reflects the fact that a point that was labeled \mathbf{x} in a frame is now labeled \mathbf{x}' in the rotated frame, and therefore this change is the same as for a scalar function. This effects is taken into account by applying the angular momentum operator separately to the two components $\xi^1(\mathbf{x})$ and $\xi^2(\mathbf{x})$. Furthermore, the two components

¹³We can take for instance the passive point of view for rotations, that is we rotate the reference frame counterclockwise by an angle α around the z axis. Then a point that had polar coordinate (r, θ, ϕ) in the old frame has coordinates $(r, \theta, \phi - \alpha)$ in the new frame.

of the spinor will mix among themselves, and this is taken into account by the spin angular momentum, as in eq. (6.26). Thus,

$$\begin{aligned}\xi(\mathbf{x}) &= \begin{pmatrix} \xi^1(\mathbf{x}) \\ \xi^2(\mathbf{x}) \end{pmatrix} \rightarrow e^{-i\theta_i S_i/\hbar} \begin{pmatrix} e^{-i\theta_i L_i/\hbar} \xi^1(\mathbf{x}) \\ e^{-i\theta_i L_i/\hbar} \xi^2(\mathbf{x}) \end{pmatrix} \\ &= e^{-i\theta_i S_i/\hbar} \begin{pmatrix} e^{-i\theta_i L_i/\hbar} & 0 \\ 0 & e^{-i\theta_i L_i/\hbar} \end{pmatrix} \xi(\mathbf{x}).\end{aligned}\quad (6.34)$$

We use the notation

$$\begin{pmatrix} e^{-i\theta_i L_i/\hbar} & 0 \\ 0 & e^{-i\theta_i L_i/\hbar} \end{pmatrix} \xi(\mathbf{x}) = e^{-i\theta_i L_i/\hbar} \xi(\mathbf{x}),\quad (6.35)$$

Observe that L_i acts on the variables \mathbf{x} , but not on the spinor indices. Conversely, S_i is a matrix in the space of spinor indices but does not act on the coordinates. Therefore

$$[S_i, L_j] = 0,\quad (6.36)$$

since they act on different space, and we can rewrite eq. (6.34) as

$$\xi(\mathbf{x}) \rightarrow e^{-i\theta_i(L_i+S_i)/\hbar} \xi(\mathbf{x}),\quad (6.37)$$

showing that the generator of rotations, on a spinor function, is a sum of orbital angular momentum and spin,

$$J_i = L_i + S_i.\quad (6.38)$$

Having determined how a spinor function transforms, let us see what happens under a rotation by an angle α around the z axis. The effect of orbital angular momentum is computed as in eq. (6.33), so

$$\begin{aligned}\begin{pmatrix} \xi^1(r, \theta, \phi) \\ \xi^2(r, \theta, \phi) \end{pmatrix} &\rightarrow e^{-i\alpha\sigma_3/2} \begin{pmatrix} \xi^1(r, \theta, \phi - \alpha) \\ \xi^2(r, \theta, \phi - \alpha) \end{pmatrix} \\ &= \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{+i\alpha/2} \end{pmatrix} \begin{pmatrix} \xi^1(r, \theta, \phi - \alpha) \\ \xi^2(r, \theta, \phi - \alpha) \end{pmatrix}.\end{aligned}\quad (6.39)$$

Consider now $\alpha = 2\pi$. Taking ξ^1 and ξ^2 single-valued, we get

$$\xi(\mathbf{x}) \rightarrow -\xi(\mathbf{x}).\quad (6.40)$$

At first sight this is quite surprising, since a rotation by 2π should be the same as the identity transformation, so we should rather expect that ξ stays

unchanged. However, this behavior is fully acceptable, both physically and mathematically.

Physically, we should not forget that the spinor is a wavefunction. Thus, $\xi^1(\mathbf{x})$ gives the probability *amplitude* of finding a particle at \mathbf{x} and with $S_z = +\hbar/2$, while $\xi^2(\mathbf{x})$ gives the probability amplitude of finding a particle at \mathbf{x} and with $S_z = -\hbar/2$. Probabilities themselves are obtained taking the squared modulus of the wavefunction, so the probability remains invariant under a rotation by 2π . Mathematically, the issue is more subtle, and has to do with the difference between the groups $SO(3)$ and $SU(2)$, that we briefly discuss below.

6.2 The rotation groups $SO(3)$ and $SU(2)$ and their representations

The group $O(3)$ is defined as the group of linear transformations of a vector $\mathbf{x} = (x_1, x_2, x_3)$, i.e. transformations of the form

$$x_i \rightarrow x'_i = R_{ij}x_j, \quad (6.41)$$

that leave invariant the quadratic form $\mathbf{x}^2 = x_1^2 + x_2^2 + x_3^2$. Therefore we require that

$$R_{ij}R_{ik}x_jx_k = \delta_{jk}x_jx_k \quad (6.42)$$

for all \mathbf{x} . This means that $R_{ij}R_{ik} = \delta_{jk}$ or, in matrix notation

$${}^T R R = I, \quad (6.43)$$

where T denotes the transpose matrix. Therefore, the group $O(3)$ is the group of orthogonal matrices. Since $\det({}^T R) = \det R$ and $\det(AB) = \det(A)\det(B)$, from eq. (6.43) it follows that $(\det R)^2 = 1$, i.e. $\det(R) = \pm 1$. The set of matrices with $\det R = +1$ form a subgroup, called $SO(3)$. This is the group of rotations of 3-dimensional space that we normally consider in classical physics.¹⁴

The groups $SO(3)$ is parametrized by 3 parameters, that for instance can be chosen as the Euler angles. More generally, groups that are parametrized in a continuous (and differentiable) way by N parameters θ^a , $a = 1, \dots, N$, are called Lie groups.

It can be shown that the elements $g(\theta)$ of a Lie group can always be written in the form

$$g(\theta) = e^{i\theta^a T^a}, \quad (6.44)$$

¹⁴Restricting from $O(3)$ to $SO(3)$ eliminates discrete symmetries such as parity, that still leave invariant $x_1^2 + x_2^2 + x_3^2$.

where θ denotes collectively the parameters θ^a .¹⁵ The quantities T^a are called the *generators* of the Lie group. For an infinitesimal transformation,

$$g(\theta) = I + i\theta^a T^a + O(\theta^2). \quad (6.45)$$

It can also be shown¹⁶ that the generators satisfy an algebraic relation of the form

$$[T^a, T^b] = i f^{abc} T^c, \quad (6.46)$$

called the *Lie algebra* of the group. The constants f^{abc} are called the *structure constants* of the group. Each Lie group is characterized by its structure constants.

For the group $SO(3)$, we have seen that there are 3 parameters, hence 3 generators. These 3 generators are nothing but the components L_i of angular momentum, as we saw in eqs. (5.70)–(5.73), and therefore the Lie algebra of $SO(3)$ is just the angular momentum algebra that we have studied above.

Consider now the group $SU(2)$, defined as the group of unitary 2×2 matrices, with unit determinant. A generic complex 2×2 matrix U has 4 complex matrix elements, i.e. 8 real parameters. Requiring $UU^\dagger = I$ gives 4 real equations, which reduce the independent real parameters to 4, and the condition $\det U = +1$ reduces it further to 3. Therefore $SU(2)$ has 3 parameters and 3 generators, just as $SO(3)$. Writing $U = \exp\{iH\}$, U unitary means that H is a hermitian matrix, and $\det U = 1$ is equivalent to $\text{Tr} H = 0$, since $\det \exp\{A\} = \exp\{\text{Tr} A\}$. Since the 3 Pauli matrices are hermitian, traceless, and linearly independent, the most general 2×2 traceless hermitian matrix can be written as a combination of them,

$$H = \frac{1}{2} \theta^a \sigma^a, \quad (6.47)$$

(the factor $1/2$ is a convenient choice of normalization for the parameters θ^a) so the most general element of $SU(2)$ can be written as

$$U = \exp \left\{ i\theta^a \frac{\sigma^a}{2} \right\}. \quad (6.48)$$

¹⁵More precisely, this is true for connected groups; otherwise, it holds only for the part connected with the identity.

¹⁶For the proof, see e.g. M. Maggiore, *A Modern Introduction to Quantum Field Theory*, pages 13–15.

This shows that (apart from a normalization factor, which is always arbitrary) we can identify the generators T^a of $SU(2)$ with $\sigma^a/2$. Using eq. (6.19), we see that the Lie algebra of $SU(2)$ is

$$[T^a, T^b] = \left[\frac{\sigma^a}{2}, \frac{\sigma^b}{2} \right] = i\epsilon^{abc} \frac{\sigma^c}{2} = i\epsilon^{abc} T^c, \quad (6.49)$$

which is again the angular momentum algebra. This shows that the groups $SO(3)$ and $SU(2)$ have the same Lie algebra. This does not mean that, as groups, they are the same, since the Lie algebra only reflects the group properties close to the identity element. In particular, in $SO(3)$ a rotation by angle 2π around any axis is the same as the identity element, while in $SU(2)$ we see from eq. (6.48) that this is not the case. Rather, in $SU(2)$ a rotation by 4π corresponds to the identity.¹⁷ This fact has important consequences for the representation of the two groups. Let us first define more precisely what a representation is.

6.2.1 Representations

A (linear) *representation* R of a group is an operation that assigns to a generic, abstract element g of a group a linear operator $D_R(g)$ defined on a linear space,

$$g \mapsto D_R(g) \quad (6.50)$$

with the properties that

(i): $D_R(e) = I$, where e is the identity element of the group and I is the identity operator, and

(ii): $D_R(g_1)D_R(g_2) = D_R(g_1g_2)$, so that the mapping preserves the group structure.

The space on which the operators D_R act is called the *basis* for the representation R . A typical example of a representation is a *matrix representation*. In this case the basis is a vector space of finite dimension n , and an abstract group element g is represented by a $n \times n$ matrix $(D_R(g))^i_j$, with $i, j = 1, \dots, n$. The *dimension* of the representation is defined as the dimension n of the base space. Writing a generic element of the base space as (ϕ^1, \dots, ϕ^n) , a group element g induces a transformation of the vector space

$$\phi^i \rightarrow (D_R(g))^i_j \phi^j. \quad (6.51)$$

¹⁷Mathematically, $SU(2)$ is called the *double covering* of $SO(3)$: to each element of $SO(3)$ correspond 2 elements of $SU(2)$ (and this correspondence is respected by group multiplication).

Equation (6.51) allows us to attach a physical meaning to a group element: before introducing the concept of representation, a group element g is just an abstract mathematical object, defined by its composition rules with the other group members. Choosing a specific representation instead allows us to interpret g as a transformation on a certain space; for instance, taking as group $SO(3)$ and as base space the spatial vectors \mathbf{v} , an element $g \in SO(3)$ can be interpreted physically as a rotation in three-dimensional space.

A representation R is called reducible if it has an invariant subspace, i.e. if the action of any $D_R(g)$ on the vectors in the subspace gives another vector of the subspace. Conversely, a representation with no invariant subspace is called irreducible. A representation is *completely reducible* if, for all elements g , the matrices $D_R(g)$ can be written, with a suitable choice of basis, in block diagonal form. In other words, in a completely reducible representation the basis vectors ϕ^i can be chosen so that they split into subsets that do not mix with each other under eq. (6.51). This means that a completely reducible representation can be written, with a suitable choice of basis, as the direct sum of irreducible representations.

Two representations R, R' are called *equivalent* if there is a matrix S , independent of g , such that for all g we have $D_R(g) = S^{-1}D_{R'}(g)S$. Comparing with eq. (6.51), we see that equivalent representations correspond to a change of basis in the vector space spanned by the ϕ^i .

Rather than consider representations of a Lie group, we can consider the representation of its Lie algebra. In abstract form, the Lie algebra is given in eq. (6.46). Any specific solution of this algebraic equations gives a concrete expression for the generators, i.e. a representation of the Lie algebra. If we denote by T_R^a the explicit form of the generators in a representation R , we might think that this generates automatically a representation R of the abstract group elements g , using eq. (6.44),

$$D_R(g(\theta)) = e^{i\theta^a T_R^a}. \quad (6.52)$$

However, we must recall the property (i) above: when g is the identity element of the group, $D_R(g)$ must be the identity operator.

For $SO(3)$, the representations on the basis $|lm\rangle$ with l half-integer do not satisfy this requirement. A rotation by an angle 2π is the same as the identity element, and must be represented as $+I$, not as $-I$. Therefore, half-integer representations are not acceptable for $SO(3)$, as indeed we found, with a different argument based on hermiticity, in eq. (5.66).

In contrast, for $SU(2)$ a transformation with $\theta = 2\pi$ is not the same as the identity, so need not be represented as the identity operation. Rather,

a transformation with $\theta = 4\pi$ must be represented by the identity operator, but this is true also for the half-integer representations. Therefore, for $SU(2)$ the representations $|jm\rangle$ are perfectly acceptable even when j is an half-integer.

Physically, we have seen that these representations are acceptable, because even if the wavefunction changes sign under a rotation by 2π , the physical quantities are the probabilities, which are the squared modulus of the wavefunctions, and are therefore unchanged. It is therefore an experimental issue whether Nature makes uses of these representations or not. Experimentally, particles with spin $1/2$ do exist, which means that the symmetry group of Nature under rotation is $SU(2)$ rather than $SO(3)$.

6.3 Spin 1

We can study similarly the representation with spin 1. This representation is 3-dimensional, and a basis is given by the kets $|jm\rangle$ with $j = 1$ and $m = -1, 0, 1$,

$$|1, -1\rangle, |10\rangle, |1, 1\rangle. \quad (6.53)$$

It is convenient to introduce a new basis $|1\rangle, |2\rangle, |3\rangle$,

$$|1\rangle \equiv \frac{1}{\sqrt{2}}(|1, 1\rangle - i|1, -1\rangle), \quad (6.54)$$

$$|2\rangle \equiv \frac{1}{\sqrt{2}}(|1, 1\rangle + i|1, -1\rangle), \quad (6.55)$$

$$|3\rangle \equiv |10\rangle. \quad (6.56)$$

A generic ket in this space therefore has the form

$$|v\rangle = v_1|1\rangle + v_2|2\rangle + v_3|3\rangle, \quad (6.57)$$

for some coefficients v_i . We write them as a column vector,

$$\mathbf{v} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}, \quad (6.58)$$

compare with eq. (6.8). By definition, this spin-1 state transforms under rotations as

$$\mathbf{v} \rightarrow \exp\{-i\boldsymbol{\theta}\cdot\mathbf{S}/\hbar\} \mathbf{v}, \quad (6.59)$$

where \mathbf{S} is the explicit representation of the angular momentum algebra in terms of 3×3 matrices (compare with eq. (6.26) for the spin $1/2$ case). The

matrix elements $\langle 1m'|S_i|1m\rangle$ can be read from the general result found in eqs. (5.108)–(5.110). Rewriting it in terms of the basis $|k\rangle$ with $k = 1, 2, 3$ we find

$$(S_i)_{kl} \equiv \langle k|S_i|l\rangle = \hbar i \epsilon_{ikl}. \quad (6.60)$$

Under an infinitesimal rotation therefore v_k transforms as

$$\begin{aligned} v_k &\rightarrow [1 - i\theta_i S_i/\hbar]_{kl} v_l \\ &= v_k + \theta_i \epsilon_{ikl} v_l \\ &= v_k - \epsilon_{kil} \theta_i v_l, \end{aligned} \quad (6.61)$$

or

$$\mathbf{v} \rightarrow \mathbf{v} - \boldsymbol{\theta} \times \mathbf{v}. \quad (6.62)$$

However, this is just the transformation law of a spatial vector (as was already implicitly suggested by the notation \mathbf{v}). We therefore see that the 3 components of a spin-1 state are equivalent to the 3 components of a vector.

For the moment \mathbf{v} has no spatial dependence, so it represents an “arrow” at a fixed location in space. Just as we did for spinors, we can add a spatial dependence considering

$$\mathbf{v}(\mathbf{x}) = \begin{pmatrix} v_1(\mathbf{x}) \\ v_2(\mathbf{x}) \\ v_3(\mathbf{x}) \end{pmatrix}. \quad (6.63)$$

With the same argument used for spinors, we find that under rotations it transforms as

$$\mathbf{v}(\mathbf{x}) \rightarrow \exp\{-i\boldsymbol{\theta} \cdot (\mathbf{L} + \mathbf{S})/\hbar\} \mathbf{v}(\mathbf{x}), \quad (6.64)$$

where the orbital angular momentum \mathbf{L} acts on the coordinates while the spin \mathbf{S} mixes the different component according to eq. (6.61). In other words, when we perform a rotation of the reference frame, a vector $\mathbf{v}(\mathbf{x})$ changes both because the point that was labeled \mathbf{x} in a frame is now labelled \mathbf{x}' in the rotated frame, and because the projections of the components along the axis of the new frame are a combination of the components in the initial frame. The former change is implemented by $\exp\{-i\boldsymbol{\theta} \cdot \mathbf{L}/\hbar\}$ and the latter by $\exp\{-i\boldsymbol{\theta} \cdot \mathbf{S}/\hbar\}$.

In conclusion, a spin-0 particle is described by a scalar wavefunction $\psi(\mathbf{x})$. A spin-1/2 particle by a spinor wavefunction $\xi(\mathbf{x})$, which has two components that mix among them under rotation, and describe the two states with $S_z = \pm \hbar/2$. A spin-1 particle is described by a vector wavefunction $\mathbf{v}(\mathbf{x})$, whose

three components $v_1(\mathbf{x})$, $v_2(\mathbf{x})$ and $v_3(\mathbf{x})$ mix among them under rotation, and are in correspondence with the three states with $S_z = -\hbar, 0, +\hbar$: $v_3(\mathbf{x})$ describes the states with $S_z = 0$ while the states with $S_z = \pm\hbar$ are described by the combinations $v_1(\mathbf{x}) \pm iv_2(\mathbf{x})$.

This can be generalized to higher spins. A generic spin- j representation has dimension $2j + 1$ (since m takes the $2j + 1$ values $-j, -j + 1, \dots, +j$). Representations with integer j are both representations of $SU(2)$ and of $SO(3)$ and therefore can be put in correspondence with tensor representations of $SO(3)$. For instance, a spin-2 state has 5 degrees of freedom ($j = 2, m = -2, -1, 0, +1, +2$), that can be written in terms of the five independent components of a traceless symmetric tensor h_{ij} .¹⁸ Representations with half-integer j instead are only allowed in $SU(2)$.

6.4 Spin dynamics

In classical electromagnetism, a particle with charge q moving with velocity v in a circular orbit of radius r generates a current

$$I = \frac{qv}{2\pi r}, \quad (6.65)$$

and has a magnetic moment $\boldsymbol{\mu}$ whose modulus is

$$\mu = \frac{qv}{2\pi r} \frac{\pi r^2}{c} = \left(\frac{q}{2mc}\right) mvr. \quad (6.66)$$

Observe that $mvr = |\mathbf{L}| \equiv L$, where \mathbf{L} is the orbital angular momentum. The magnetic moment vector is

$$\boldsymbol{\mu} = \left(\frac{q}{2mc}\right) \mathbf{L}. \quad (6.67)$$

In an external magnetic field \mathbf{B} , classically a magnetic moment has an interaction energy $E = -\boldsymbol{\mu} \cdot \mathbf{B}$. Therefore, in quantum mechanics, for a particle with orbital angular momentum \mathbf{L} in a magnetic field \mathbf{B} , the Hamiltonian operator contains an interaction term¹⁹

$$H_{\text{int}} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\left(\frac{q}{2mc}\right) \mathbf{L} \cdot \mathbf{B}. \quad (6.68)$$

¹⁸The irreducible tensor representations of $SO(3)$ are given by tensor that are symmetric and traceless in all their pairs of indices. So we have scalars ψ , vectors v_i , tensors h_{ij} with $h_{ij} = h_{ji}$ and $h_{ii} = 0$, tensors with 3 indices T_{ijk} symmetric and traceless with respect to any pair of indices, etc.

¹⁹In a later section, when we study in general the coupling to electromagnetic fields, we will see how this term derives from the prescription of minimal coupling.

If one uses the intuitive picture of spin as due to the angular momentum of a particle spinning around its axis, it would be natural to associate to a charged particle a similar interaction term. So, for the electron (charge $q = -e$, where $e > 0$, and mass m_e) we would be lead to

$$H_{\text{int}} \stackrel{?}{=} \frac{e}{2m_e c} \mathbf{S} \cdot \mathbf{B} = \frac{e\hbar}{4m_e c} \boldsymbol{\sigma} \cdot \mathbf{B}. \quad (6.69)$$

However, as we mentioned already, the semiclassical view of spin as due to the intrinsic rotation of a particle is not correct, and as a consequence eq. (6.69) is not correct either. The fact that the coupling of spin to electromagnetic field is proportional to $\mathbf{S} \cdot \mathbf{B}$ is however still true. In fact, we can simply demand that the spin \mathbf{S} be coupled to electromagnetic field so to preserve invariance under rotation and parity (since electromagnetic interaction preserve parity). The spin \mathbf{S} is a pseudovector, just as any angular momentum. This follows simply from the fact that, in the angular momentum algebra, appears the tensor ϵ_{ijk} , that is a pseudotensor under parity. Thus, the only possibility is a scalar product between \mathbf{S} , and another pseudovector, and for the electromagnetic field the only available one is \mathbf{B} . However, the constant in front is not fixed by symmetry principles, so we write generically the coupling of the electron spin to the electromagnetic field as

$$H_{\text{int}} = g \left(\frac{e\hbar}{4m_e c} \right) \boldsymbol{\sigma} \cdot \mathbf{B}. \quad (6.70)$$

where g is a dimensionless constant. In other words, $H_{\text{int}} = -\boldsymbol{\mu} \cdot \mathbf{B}$, where the intrinsic magnetic moment of the electron is

$$\boldsymbol{\mu} = -\frac{ge}{2mc} \mathbf{S} \equiv \gamma \mathbf{S}, \quad (6.71)$$

where γ is known as the *gyromagnetic ratio*. For the electron, g is very close to 2. The experimentally measured value is

$$\frac{g-2}{2} \Big|_{\text{exp}} = 0.001\,165\,9208(6). \quad (6.72)$$

This result is nowadays understood using quantum field theory, in particular quantum electrodynamics (QED), that gives a theoretical prediction

$$\frac{g-2}{2} \Big|_{\text{th}} = 0.001\,165\,9181(7). \quad (6.73)$$

The agreement between theory and experiment is among the most accurate in physics, and is a great triumph for QED. However, you will to wait for a

quantum field theory course to understand how such a results comes out.²⁰ For objects such as protons and neutrons, the value of g is different. For the proton,

$$\boldsymbol{\mu}_p = +\frac{ge}{2m_p c} \mathbf{S}. \quad (6.74)$$

where m_p is the proton mass. and $g \simeq 5.6$. Observe that also the neutron, even if it is zero total charge, has a non-vanishing magnetic dipole moment,

$$\boldsymbol{\mu}_n = +\frac{ge}{2m_n c} \mathbf{S}, \quad (6.75)$$

with $g \simeq -3.8$.²¹ We can now study the evolution of the spin in a magnetic field. We consider a spin 1/2 particle at rest in a magnetic field, and we consider only the evolution of the spin degree of freedom. In a magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$ we have

$$H_{\text{int}} = -\gamma B S_z = -\frac{\gamma B \hbar}{2} \sigma_z. \quad (6.76)$$

The eigenstates of H_{int} are the same as those of S_z , and are the spinors ξ_{\pm} given in eqs. (6.9) and (6.10),

$$H_{\text{int}} \xi_+ = -\frac{\gamma B \hbar}{2} \xi_+ \equiv E_+ \xi_+ \quad (6.77)$$

$$H_{\text{int}} \xi_- = +\frac{\gamma B \hbar}{2} \xi_- \equiv E_- \xi_-. \quad (6.78)$$

²⁰A more advanced note: the prediction $g = 2$ is often presented as one of the successes of the Dirac equation, that will be studied in the course Champs et Particules. Actually, even if historically this success was very important for understanding how to build a relativistic generalization of quantum mechanics, nowadays the correct context for discussing these results is quantum field theory. The Dirac equation, when used simply as a relativistic generalization of the Schrödinger equation, leads to pathologies (such as unbounded negative energies, and the lack of a probabilistic interpretation) that only find their resolution in the broader context of quantum field theory. Furthermore, even the very fact that the Dirac equation really “predicts” $g = 2$ is quite questionable. This only happens if one couples the electromagnetic field to the electron using the so-called minimal coupling (that, for the Schrödinger equation, we will study in due course). Other types of coupling are in principle possible, which would modify the prediction into $g = 2 + a$ with a an arbitrary constant. The fact that this arbitrary constant is suppressed can be understood only in the context of quantum field theory, and is related to the fact that it is associated to a non-renormalizable interaction term, see Weinberg, *The Quantum Theory of Fields*, Vol. I, page 14.

²¹The fact the the values of g for the proton and for the neutron are not close to 2 is due to the fact that, at a fundamental level, they are made by three spin-1/2 particles (quarks), and their total magnetic moment results from the composition of the magnetic moments of the quarks.

The Schrödinger equation is

$$i\hbar \frac{\partial \xi}{\partial t} = H_{\text{int}} \xi. \quad (6.79)$$

The states ξ_{\pm} evolve as

$$\xi_+(t) = e^{-iE_+t/\hbar} \xi_+(0), \quad (6.80)$$

$$\xi_-(t) = e^{-iE_-t/\hbar} \xi_-(0). \quad (6.81)$$

Consider a generic spinor ξ that at time $t = 0$ has the form $\alpha \xi_+ + \beta \xi_-$, with $|\alpha|^2 + |\beta|^2 = 1$. It evolves as

$$\xi(t) = \alpha \xi_+(t) + \beta \xi_-(t) = \begin{pmatrix} \alpha e^{-iE_+t} \\ \beta e^{-iE_-t} \end{pmatrix}. \quad (6.82)$$

We compute now the expectation value of S_x , S_y and S_z on this state. In the bra and ket notation, we have a state

$$|\xi\rangle = \alpha e^{-iE_+t} \left| \frac{1}{2}, +\frac{1}{2} \right\rangle + \beta e^{-iE_-t} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle, \quad (6.83)$$

and we want to compute $\langle \xi | S_i | \xi \rangle$. In the spinor notation, where $|\xi\rangle$ is rather written as a column vector ξ , this is equivalent to computing $\xi^\dagger(t) S_i \xi(t)$. It is convenient to write $\alpha = \cos(\theta/2)$, $\beta = \sin(\theta/2)$ and define $\omega = \gamma B$. So, consider for instance

$$\begin{aligned} \langle S_x \rangle &= \xi^\dagger(t) S_x \xi(t) \\ &= (\cos(\theta/2)e^{-i\omega t/2}, \sin(\theta/2)e^{i\omega t/2}) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\theta/2)e^{i\omega t/2} \\ \sin(\theta/2)e^{-i\omega t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \sin \theta \cos \omega t. \end{aligned} \quad (6.84)$$

Similarly

$$\langle S_y \rangle = -\frac{\hbar}{2} \sin \theta \sin \omega t, \quad (6.85)$$

and

$$\langle S_z \rangle = \frac{\hbar}{2} \cos \theta. \quad (6.86)$$

So, $\langle \mathbf{S} \rangle$ makes an angle θ with the z axis, and rotates in the (x, y) plane with the *Larmor frequency*

$$\omega = \gamma B. \quad (6.87)$$

This is the Larmor precession.

(Reference: Griffiths, Sect. 4.4.2).

7 Addition of angular momenta

7.1 Example: composition of two spin 1/2

(Ref: Shankar, Section 15.1, pages 403–408).

We consider the tensor product

$$|s_1 m_1, s_2 m_2\rangle \equiv |s_1 m_1\rangle \otimes |s_2 m_2\rangle. \quad (7.1)$$

Define $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$ as

$$\begin{aligned} |++\rangle &= |s_1 = 1/2, m_1 = +1/2, s_2 = 1/2, m_2 = +1/2\rangle, \\ |+-\rangle &= |s_1 = 1/2, m_1 = +1/2, s_2 = 1/2, m_2 = -1/2\rangle, \\ |-+\rangle &= |s_1 = 1/2, m_1 = -1/2, s_2 = 1/2, m_2 = +1/2\rangle, \\ |--\rangle &= |s_1 = 1/2, m_1 = -1/2, s_2 = 1/2, m_2 = -1/2\rangle. \end{aligned} \quad (7.2)$$

The total spin is

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \quad (7.3)$$

since it generates the rotation of the ket (7.1). Observe that it still satisfies the angular momentum algebra. In the basis $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$, S_z is diagonal

$$S_z = \hbar \begin{pmatrix} ++ & +- & -+ & -- \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (7.4)$$

To compute the matrix elements of \mathbf{S}^2 , we write

$$\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (7.5)$$

Since we are composing two spin-1/2 particles, we have

$$\mathbf{S}_1^2 = \mathbf{S}_2^2 = \hbar^2 s(s+1) \quad (7.6)$$

with $s = 1/2$, so $\mathbf{S}_1^2 = \mathbf{S}_2^2 = (3/4)\hbar^2$. Then, for instance, the matrix element $\langle ++|\mathbf{S}^2|++\rangle$ is given by

$$\begin{aligned} \langle ++|\mathbf{S}^2|++\rangle &= \frac{3}{2}\hbar^2 + 2\langle ++|\mathbf{S}_1 \cdot \mathbf{S}_2|++\rangle \\ &= \frac{3}{2}\hbar^2 + 2\langle +|(\mathbf{S}_1)_i|+\rangle\langle +|(\mathbf{S}_2)_i|+\rangle. \end{aligned} \quad (7.7)$$

The matrix elements in the spin-1/2 representation have been computed in eqs. (6.12) and (6.13), and are given by the Pauli matrices,

$$\langle +|\mathbf{S}_i|+\rangle = \frac{\hbar}{2} (\sigma_i)_{11} = \frac{\hbar}{2} \delta_{i3}, . \quad (7.8)$$

Then, we get

$$\langle ++|\mathbf{S}^2|++\rangle = 2\hbar^2. \quad (7.9)$$

Computing similarly the other matrix elements we get

$$\mathbf{S}^2 = \hbar^2 \begin{pmatrix} ++ & +- & -+ & -- \\ 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \quad (7.10)$$

This matrix can be diagonalized by changing basis. The eigenvectors of the total spin are

$$|s = 1, m = +1\rangle = |++\rangle \quad (7.11)$$

$$|s = 1, m = 0\rangle = \frac{1}{\sqrt{2}} (|+-\rangle + |-+\rangle) \quad (7.12)$$

$$|s = 1, m = -1\rangle = |--\rangle \quad (7.13)$$

$$|s = 0, m = 0\rangle = \frac{1}{\sqrt{2}} (|+-\rangle - |-+\rangle). \quad (7.14)$$

The resulting diagonal matrix is

$$\mathbf{S}^2 = \hbar^2 \begin{pmatrix} 11 & 10 & 1-1 & 00 \\ 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (7.15)$$

Since $s(s+1) = 2$ when $s = 1$, we see that the first 3×3 block spanned by $|s = 1, m = +1\rangle$, $|s = 1, m = 0\rangle$ and $|s = 1, m = -1\rangle$ corresponds to total spin equal to 1, while the state $|s = 0, m = 0\rangle$ has spin 0. In the language of representation theory introduced in the previous section, we have decomposed the tensor product of two spin 1/2 representation into irreducible representations. Symbolically,

$$\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1. \quad (7.16)$$

Observe that the total- s states have also definite symmetry under the exchange of the two particles. The triplets are symmetric and the singlet is antisymmetric.

7.2 The general problem

We study now the composition of angular momenta \mathbf{J}_1 and \mathbf{J}_2 generic. As before, we start from the tensor product basis

$$|j_1 m_1, j_2 m_2\rangle \equiv |j_1 m_1\rangle \otimes |j_2 m_2\rangle. \quad (7.17)$$

where j_1 and j_2 are fixed. Since m_1 takes $2j_1 + 1$ values and m_2 takes $2j_2 + 1$ values, this space has dimension $(2j_1 + 1)(2j_2 + 1)$. The total J_z is already diagonal

$$J_z |j_1 m_1, j_2 m_2\rangle = \hbar(m_1 + m_2) |j_1 m_1, j_2 m_2\rangle, \quad (7.18)$$

while J^2 is not. The problem is therefore to find the change of basis that diagonalizes J^2 , i.e. a basis $|jm\rangle$, with $m = -j, \dots, +j$, and j ranging over some set of values, such that

$$J^2 |jm\rangle = \hbar^2 j(j+1) |jm\rangle, \quad (7.19)$$

$$J_z |jm\rangle = \hbar m |jm\rangle. \quad (7.20)$$

For $j_1 = j_2 = 1/2$, this basis was found in eqs. (7.11)–(7.14), and we saw that the allowed value of j were $j = 0, 1$.

If j_1 and j_2 have been specified, the problem just amounts to diagonalizing the matrix J^2 (although, in practice, there is a more clever algebraic method to solve the problem for j_1 and j_2 generic, see Shankar pages 409–412, based on the use of raising and lowering operators J_{\pm}). The result is that J^2 is diagonalized in a basis $|jm\rangle$ where, for each allowed j , m takes all values between $-j$ and $+j$ in integer steps, and j takes all the values between $|j_1 - j_2|$ and $j_1 + j_2$, in integer steps,

$$j = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2. \quad (7.21)$$

This generalizes the result that we found above, when we took $j_1 = j_2 = 1/2$ and we found that the possible values of j were $j = 0, 1$. From eq. (7.18), we see that $m = m_1 + m_2$.

As a check of this result, we can verify that the kets $|jm\rangle$ with $m = -j, -j + 1, \dots, j$ and j as in eq. (7.21) span a vector space of dimension

$(2j_1 + 1)(2j_2 + 1)$, just as the kets $|j_1 m_1, j_2 m_2\rangle$ given in eq. (7.17). Indeed, at each level j we have $2j + 1$ states, and

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = \sum_{j=0}^{j_1+j_2} (2j+1) - \sum_{j=0}^{j=|j_1-j_2|-1} (2j+1). \quad (7.22)$$

Using

$$\sum_{n=0}^N n = \frac{N(N+1)}{2} \quad (7.23)$$

this gives indeed $(2j_1 + 1)(2j_2 + 1)$. In the language of representation theory, this can be expressed as

$$j_1 \otimes j_2 = |j_1 - j_2| \oplus (|j_1 - j_2| + 1) \oplus \dots \oplus (j_1 + j_2), \quad (7.24)$$

which is the generalization of eq. (7.16) to j_1 and j_2 arbitrary. For instance,

$$1 \otimes 1 = 0 \oplus 1 \oplus 2. \quad (7.25)$$

We also want to know the explicit form of the kets $|jm\rangle$ in terms of the kets $|j_1 m_1, j_2 m_2\rangle$. For j_1 and j_2 , fixed, the kets $|j_1 m_1, j_2 m_2\rangle$ with $m_1 = -j_1, \dots, j_1$ and $m_2 = -j_2, \dots, j_2$ span the whole Hilbert space, so we have the completeness relation

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2| = 1. \quad (7.26)$$

We write as $|jm, j_1 j_2\rangle$ the eigenstates of J^2 and J_z , obtained composing the angular momenta j_1 and j_2 . Then

$$|jm, j_1 j_2\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | jm, j_1 j_2\rangle. \quad (7.27)$$

We can rewrite this as

$$|jm, j_1 j_2\rangle = \sum_{m_1, m_2} C_{m_1 m_2 m}^{j_1 j_2 j} |j_1 m_1, j_2 m_2\rangle, \quad (7.28)$$

where

$$C_{m_1 m_2 m}^{j_1 j_2 j} = \langle j_1 m_1, j_2 m_2 | jm, j_1 j_2\rangle \quad (7.29)$$

are called the Clebsch-Gordan coefficients. From the results found above, it follows that they are non-vanishing only if $|j_1 - j_2| \leq j \leq j_1 + j_2$, and if $m = m_1 + m_2$. It can be shown that they can be chosen to be real, and, if we change simultaneously the sign of m , m_1 and m_2 , they acquire a sign $(-1)^{j_1+j_2-j}$,

$$\langle j_1, -m_1; j_2, -m_2 | j, -m; j_1 j_2 \rangle = (-1)^{j_1+j_2-j} \langle j_1, m_1; j_2, m_2 | j m, j_1 j_2 \rangle. \quad (7.30)$$

Equation (7.28) generalizes eqs. (7.11)–(7.14) to j_1, j_2 arbitrary. If we assemble the Clebsch-Gordan coefficients into a matrix relating the $(2j_1 + 1)(2j_2 + 1)$ states $|jm\rangle$ to the $(2j_1 + 1)(2j_2 + 1)$ states $|m_1 m_2\rangle$, we find that this matrix is orthogonal, since it gives the transformation between two orthonormal basis.

For each fixed choice of j_1, j_2 , the Clebsch-Gordan coefficients can be computed performing explicitly the diagonalization of J^2 . Tables of Clebsch-Gordan coefficients are given in many books of quantum mechanics.

7.3 Addition of \mathbf{L} generic and spin $1/2$

When we study the hydrogen atom, we will be confronted with the addition of orbital angular momentum \mathbf{L} , whose eigenvector we denote as $|l, m_l\rangle$, and the spin \mathbf{S} of the electron, which has $s = 1/2$, and eigenvectors $|1/2, m_s\rangle$. We compute the Clebsch-Gordan coefficients for this case, with arbitrary l , using an algebraic method, rather than performing explicitly the diagonalization of J^2 .

We denote by $|jm\rangle$ the eigenstates of total angular momentum and by $|l, m_l; 1/2, m_s\rangle$ the tensor product of the eigenstate of orbital angular momentum and of spin. The allowed values of j are $l \pm 1/2$ if $l \neq 0$, and $j = 1/2$ if $l = 0$. Therefore, considering only the non-trivial case $l \neq 0$, we have in general

$$|j = l + \frac{1}{2}, m\rangle = \alpha |l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta |l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle, \quad (7.31)$$

$$|j = l - \frac{1}{2}, m\rangle = \alpha' |l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta' |l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle. \quad (7.32)$$

Orthonormality requires

$$\alpha^2 + \beta^2 = 1, \quad \alpha'^2 + \beta'^2 = 1, \quad \alpha\alpha' + \beta\beta' = 0. \quad (7.33)$$

A fourth equation is obtained observing that

$$\begin{aligned} J^2|j = l + \frac{1}{2}, m\rangle &= \hbar^2(l + \frac{1}{2})(l + \frac{3}{2})|j = l + \frac{1}{2}, m\rangle \\ &= \hbar^2(l + \frac{1}{2})(l + \frac{3}{2}) \left(\alpha|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta|l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \right). \end{aligned} \quad (7.34)$$

On the other hand, $J^2 = L^2 + S^2 + 2L_zS_z + L_-S_+ + L_+S_-$, so

$$\begin{aligned} J^2|j = l + \frac{1}{2}, m\rangle &= (L^2 + S^2 + 2L_zS_z + L_-S_+ + L_+S_-) \\ &\quad \left(\alpha|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta|l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \right). \end{aligned} \quad (7.35)$$

We now use

$$L^2|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = \hbar^2l(l+1)|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \quad (7.36)$$

$$S^2|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = \hbar^2\frac{1}{2}(\frac{1}{2}+1)|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \quad (7.37)$$

$$L_zS_z|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = \hbar^2(m - \frac{1}{2})\frac{1}{2}|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \quad (7.38)$$

$$L_-S_+|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = 0, \quad (7.39)$$

$$L_+S_-|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = C_+(l, m - \frac{1}{2})C_-(\frac{1}{2}, \frac{1}{2})|l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \quad (7.40)$$

(and similarly for the action on $|l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle$) where $C_{\pm}(j, m)$ were given in eqs. (5.106) and (5.107). Comparing the result with eq. (7.34) we get one more equation that can be solved for β/α . Putting it together with eq. (7.33) we can solve for $\alpha, \beta, \alpha', \beta'$. The result is

$$\begin{aligned} |j = l \pm \frac{1}{2}, m\rangle &= \frac{1}{(2l+1)^{1/2}} \left[\pm(l + \frac{1}{2} \pm m)^{1/2}|l, m - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle \right. \\ &\quad \left. + (l + \frac{1}{2} \mp m)^{1/2}|l, m + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \right] \end{aligned} \quad (7.41)$$

8 The hydrogen atom

(This is a subject that you already studied in *Mécanique Quantique I*. However, it is one of the most important applications of quantum mechanics, and it is useful to see it again, with the better understanding of the formalism that you should now have, especially for what concerns angular momentum and spin.)

8.1 Explicit solution of the Schrödinger equation

We follow Shankar, Chapter 13, and Griffiths, Sect. 4.2. Here we just summarize the results. The potential is $V(r) = -e^2/r$. We perform the separation of variables as in eqs. (5.130) and (5.132), and eq. (5.133) becomes

$$\left\{ \frac{d^2}{dr^2} + \frac{2m_e}{\hbar^2} \left[E + \frac{e^2}{r} - \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] \right\} U_{El}(r) = 0. \quad (8.1)$$

We look for solutions with $E < 0$. As $r \rightarrow \infty$ the terms $\sim 1/r$ and $\sim 1/r^2$ can be dropped and the solutions of eq. (8.1) are

$$U_{El}(r) \sim e^{\pm \kappa r}, \quad (r \rightarrow \infty). \quad (8.2)$$

where $\kappa = (-2m_e E/\hbar^2)^{1/2}$. Only the one with the minus sign is physically acceptable. As $r \rightarrow 0$, if $l \neq 0$ the dominant term in the square bracket in eq. (8.1) is the centrifugal potential $\sim l(l+1)/r^2$, and we see that the solution is

$$U_{El}(r) \sim r^{l+1}, \quad (r \rightarrow 0). \quad (8.3)$$

Equation (8.2) suggests the introduction of the dimensionless variable

$$\rho = \kappa r = (-2m_e E/\hbar^2)^{1/2} r, \quad (8.4)$$

and the asymptotic behaviors found above suggests the ansatz

$$U_{El}(\rho) = e^{-\rho} v_{El}(\rho), \quad (8.5)$$

with

$$v_{El}(\rho) = \rho^{l+1} \sum_{k=0}^{\infty} C_k \rho^k. \quad (8.6)$$

8.1.1 The energy levels

Just as with the harmonic oscillator, plugging this ansatz into eq. (8.1) one finds a recursion relation giving C_{k+1}/C_k as a function of the index k and of E, l . Looking at the asymptotics for $k \rightarrow \infty$ we find that, if the series does not terminate, it goes as $e^{+2\rho}$, transforming the asymptotic behavior of $U(\rho)$ into $e^{+\rho}$. This is clearly the other possible asymptotic solution of eq. (8.1), but it is unacceptable physically, so we require that the series terminates for some value of k , that we call k_{\max} . This result in the quantization condition

$$E_n = -\frac{m_e e^4}{2\hbar^2 n^2}, \quad (8.7)$$

where

$$n = k_{\max} + l + 1, \quad (8.8)$$

Since the possible values of k_{\max} are $0, 1, 2, \dots$, n takes the values $1, 2, 3, \dots$. The integer n is called the *principal quantum number* of the hydrogen atom. Observe that l no longer appear explicitly in eq. (8.7). Thus, states with the same n and different l are degenerate. From eq. (8.8), for fixed n , the allowed values of l are

$$l = 0, 1, \dots, n - 1. \quad (8.9)$$

The quantity

$$\text{Ry} \equiv \frac{m_e e^4}{2\hbar^2} \simeq 13.6 \text{ eV} \quad (8.10)$$

is called the Rydberg, so $E_n = -\text{Ry}/n^2$. The Rydberg is the binding energy of hydrogen in its ground state, $n = 1$. In terms of the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}, \quad (8.11)$$

we can rewrite

$$\text{Ry} = \frac{1}{2} m_e c^2 \alpha^2, \quad (8.12)$$

showing that this is smaller than the electron's rest energy $m_e c^2$ by a factor $O(\alpha^2)$. It is common to refer to the states with $l = 0, 1, 2, 3, 4, \dots$ as s, p, d, f, g, h, \dots . Then the lowest lying level are

$$1s \quad (n = 1, l = 0), \quad E = -\text{Ry}, \quad (8.13)$$

$$2s, 2p \quad (n = 2, l = 0, 1), \quad E = -\text{Ry}/4, \quad (8.14)$$

$$3s, 3p, 3d \quad (n = 3, l = 0, 1, 2), \quad E = -\text{Ry}/9, \quad (8.15)$$

and so on.

8.1.2 The wavefunctions

Once we require that the recurrence equation terminates, the function $v_{El}(\rho)$ becomes equal to ρ^{l+1} times a polynomial of degree $k = n - l - 1$, and the recurrence relation allows us to compute them, in terms of the first coefficient, which is then chosen so that the wave-function is normalized to one. In terms of the original wavefunction

$$\psi_{nlm}(r, \theta, \phi) = \frac{1}{r} U_{nl}(r) Y_{lm}(\theta, \phi) \quad (8.16)$$

the (normalized) wavefunction of the lowest-lying states are

$$\psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}, \quad (8.17)$$

$$\psi_{200} = \frac{1}{(32\pi a_0^3)^{1/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}, \quad (8.18)$$

$$\psi_{210} = \frac{1}{(32\pi a_0^3)^{1/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta, \quad (8.19)$$

$$\psi_{21,\pm 1} = \mp \frac{1}{(64\pi a_0^3)^{1/2}} \frac{r}{a_0} e^{-r/2a_0} e^{\pm i\phi} \sin \theta, \quad (8.20)$$

where

$$a_0 = \frac{\hbar^2}{me^2} \simeq 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ \AA} \quad (8.21)$$

is called the *Bohr radius*, and gives the typical size of the hydrogen atom. The general solution can be written in terms of associated Laguerre polynomials, see Griffiths, pages 152–153. See also the plots of $|\psi_{nlm}|^2$ for various n, l, m , in Griffiths, pages 156–157.

Computing the expectation value of r , and using the properties of the Laguerre polynomial, one finds

$$\langle r \rangle_{nlm} = \frac{a_0}{2} [3n^2 - l(l+1)]. \quad (8.22)$$

So a_0 is indeed the typical size of the hydrogen atom in a low-lying state. Observe that this size grows with n as n^2 . A hydrogen atom in the $3s$ state has a typical radius 9 times larger than in the fundamental state.

8.1.3 Transitions among stationary states

Stationary states are, indeed, stationary, only in the absence of external perturbations. However, such perturbations are always present. For instance,

atoms can collide among them, or can interact with external electromagnetic fields. We will learn how to compute these effects in due course, when we study perturbation theory. For the moment, we just observe that only the ground state, i.e. the $1s$ state, is really stable. All the other excited states decay to lower-lying states, and finally to the ground state. The simplest process is the decay with emission of a single photon of frequency ν . As you saw in Mécanique Quantique I, such a photon carries an energy

$$E_\gamma = h\nu = \hbar\omega, \quad (8.23)$$

where $\omega = 2\pi\nu$. In a transition from an initial level with principal quantum number n_i to a level with principal quantum number $n_f < n_i$, conservation of energy gives $E_{n_i} = E_{n_f} + E_\gamma$, so

$$h\nu = \text{Ry} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad (8.24)$$

or, in terms of the wavelength $\lambda = 1/\nu$,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad (8.25)$$

where $R_H \simeq 1.097 \times 10^5 \text{ cm}^{-1}$.

Transitions of the hydrogen atom to the ground state ($n_f = 1$) form the Lyman series. The transition $n_i = 2 \rightarrow n_f = 1$ is called Lyman- α , or L_α , and has a wavelength $\lambda \simeq 1216 \text{ \AA}$, in the ultraviolet. The transition $n_i = 3 \rightarrow n_f = 1$ is called L_β , etc. All transitions of the Lyman series are in the UV.

Transitions to $n_f = 2$ for the Balmer series, and are in the visible part of the spectrum. The transition $n_i = 3 \rightarrow n_f = 2$ is called Balmer- α , or H_α , and has $\lambda \simeq 6563 \text{ \AA}$ (it is red); $n_i = 4 \rightarrow n_f = 2$ is called H_β , and has $\lambda \simeq 4861 \text{ \AA}$ (it is turquoise), while H_γ ($n_i = 5 \rightarrow n_f = 2$, $\lambda \simeq 4340 \text{ \AA}$) is blue. The Balmer series is the characteristic spectrum of hydrogen seen in the spectra of most stars. Transitions to $n_f = 3$ form the Paschen series, P_α, P_β, \dots , in the infrared.

A free electron, with a kinetic energy $E_e > 0$ and a continuous spectrum, can also be captured by a proton forming a hydrogen atom in a state with quantum number n , emitting a photon whose energy satisfies

$$E_e = E_\gamma - \frac{\text{Ry}}{n^2}, \quad (8.26)$$

or

$$h\nu = \frac{\text{Ry}}{n^2} + E_e. \quad (8.27)$$

Since $E_e \geq 0$ is continuous, this gives a continuous spectrum. Capture to $n = 1$ gives rise to the Lyman continuum, that starts at $h\nu = \text{Ry}$, i.e. has a continuous spectrum on all wavelengths shorter than 912 Å.

8.1.4 Modified spectroscopic notation

For the moment, the spin of the electron played no role. We will see later that the spin of the electron actually couples to the spin of the proton, giving rise to the hyperfine splitting of the energy levels. For the moment, spin does not appear in the Hamiltonian, so it is just a “spectator” degree of freedom. However, the existence of the electron spin changes the total angular momentum state of the atom. The combination of spin 1/2 with orbital angular momentum l give rise to states with total angular momentum j . According to our discussion of the composition of angular momenta, if $l = 0$, the only possibility is $j = 1/2$, while for each $l \neq 0$ we have two possible values of the total angular momentum, $j = l \pm 1/2$.

To take this into account, the states of the hydrogen atom, and more generally of multi-electron atoms, are then labeled as $^{2S+1}L_J$, where the meaning of the symbols is as follows.

- The capital letter $L = S, P, D, \dots$ denotes orbital angular momentum, with S corresponding to $l = 0$, P to $l = 1$, etc. For the hydrogen atom this will be the angular momentum of the only electron present. For a more general atom, it will be result from the composition of the orbital angular momentum of all the electrons.
- The subscript J to the right indicates the total angular momentum
- The superscript $2S + 1$ to the left of L denotes the total spin. For a single electron $S = 1/2$, so $2S + 1$ is always equal to 2. For an atom with two electrons such as Helium, the total spin S can be 0 or 1, so $2S + 1$ can be equal to 1 (the singlet state) or 3 (the triplet state).

For instance, the symbol $^2P_{3/2}$ denotes a state with $l = 1$, $s = 1/2$, and $j = 3/2$, while $^2P_{1/2}$ denotes a state with $l = 1$, $s = 1/2$, and $j = 1/2$.

8.2 Understanding the physics of the hydrogen atom with order-of-magnitude estimates. Units $\hbar = c = 1$

Most of the physics of the hydrogen atom can be understood without actually solving explicitly the Schrödinger equation, simply by using some elementary physical input, and dimensional analysis.²² Such estimates are much simplified by the use of units $\hbar = c = 1$. To understand the meaning of these units, observe first of all that \hbar and c are universal constants, i.e. they have the same numerical value for all observers. The speed of light has the value $c = 299\,792\,458$ m/s, with no error because, after having defined the unit of time from a particular atomic transition (a hyperfine transition of cesium-133) this value of c is taken as the *definition* of the meter. However, instead of using the meter, we can decide to use a new unit of length (or a new unit of time) defined by the statement that in these units $c = 1$. Then, the velocity v of a particle is measured in units of the speed of light, which is very natural since in particle physics we typically deal with relativistic objects. In these units $0 \leq v < 1$ for massive particles, and $v = 1$ for massless particles.

The Planck constant \hbar is another universal constant, and it has dimensions [energy] \times [time] or [length] \times [momentum] as we see for instance from the uncertainty principle. We can therefore choose units of energy such that $\hbar = 1$. Then all multiplicative factors of \hbar and c disappear from our equations and formally, from the point of view of dimensional analysis,

$$[\text{velocity}] = \text{pure number}, \quad (8.28)$$

$$[\text{energy}] = [\text{momentum}] = [\text{mass}], \quad (8.29)$$

$$[\text{length}] = [\text{mass}]^{-1}. \quad (8.30)$$

The first two equations follow immediately from $c = 1$ while the third follows from the fact that $\hbar/(mc)$ is a length. Thus all physical quantities have dimensions that can be expressed as powers of mass or, equivalently, as powers of length. For instance an energy density, [energy]/[length]³, becomes a [mass]⁴. Units $\hbar = c = 1$ are called *natural units*.

The fine structure constant $\alpha = e^2/(\hbar c) \simeq 1/137$ is a pure number, and therefore in natural units the electric charge e becomes a pure number.²³

²²The following part is taken from Maggiore, *A Modern Introduction to Quantum Field Theory*, pages 4-6.

²³There are different possible convention for the unit of electric charge. We are following here the convention of Shankar, where $\alpha = e^2/(\hbar c)$. Another common system of units rather gives $\alpha = e^2/(4\pi\hbar c)$, where α always has the same numerical value $\simeq 1/137$.

To make numerical estimates, it is useful to observe that $\hbar c$, in ordinary units, has dimensions $[\text{energy} \times \text{time}] \times [\text{velocity}] = [\text{energy}] \times [\text{length}]$. In particle physics a useful unit of energy is the MeV ($= 10^6$ eV) and a typical length-scale is the fermi: $1 \text{ fm} = 10^{-13}$ cm; one fm is the typical size of a proton. Expressing $\hbar c$ in MeV \times fm, one gets

$$\hbar c \simeq 200 \text{ MeV fm} \quad (8.31)$$

(The precise value is 197.326 968 (17) MeV fm.) Then, in natural units, $1 \text{ fm} \simeq 1/(200 \text{ MeV})$. Note that in units $c = 1$ masses are expressed simply in MeV, as energies. Let us make some example of the use of these units.

The Compton radius. The simplest length-scale associated to a particle of mass m in its rest frame is its Compton radius, $r_C = 1/m$. In particular, for the electron

$$r_C = \frac{1}{m_e} \simeq \frac{200 \text{ MeV fm}}{0.5 \text{ MeV}} = 4 \times 10^{-11} \text{ cm} . \quad (8.32)$$

Since r_C does not depend on α , it is the relevant length-scale in situations in which there is no dependence on the strength of the interaction. Historically, r_C made its first appearance in the Compton scattering of X-rays off electrons. Classically, the wavelength of the scattered X-rays should be the same as the incoming waves, since the process is described in terms of forced oscillations. Quantum mechanically, treating the X-rays as photons, we understand that part of the momentum $h\nu$ of the incoming photon is used to produce the recoil of the electron, so the momentum of the outgoing photon is smaller, and its wavelength is larger. The wavelength of the outgoing photon is fixed by energy–momentum conservation, and therefore is independent of α , so the relevant length-scale must be r_C . Indeed, a simple computation gives

$$\lambda' - \lambda = r_C(1 - \cos \theta) , \quad (8.33)$$

where λ, λ' are the initial and final X-ray wavelengths and θ is the scattering angle.

The hydrogen atom. If we want to make dimensional estimates in the hydrogen atom the two parameters that enter are the fine structure constant $\alpha \simeq 1/137$ and the reduced mass of the electron–proton system; since $m_p \simeq 938 \text{ MeV}$ is much bigger than m_e we can identify the reduced mass with m_e , within a precision of 0.05 per cent.

Let us first estimate the Bohr radius r_B . The only mass that enters the problem is m_e , Dimensionally, again $r_B \sim 1/m_e$, but now α enters. Clearly, the radius of the bound state is smaller if the interaction responsible for the binding is stronger, while it must go to infinity in the limit $\alpha \rightarrow 0$, so α must be in the denominator and it is very natural to guess that $r_B \sim 1/(m_e\alpha)$. This is indeed the case, as can be seen with the following argument: by the uncertainty principle, an electron confined in a radius r has a momentum $p \sim 1/r$. If the electron in the hydrogen atom is non-relativistic (we will verify the consistency of this hypothesis a posteriori) its kinetic energy is $p^2/(2m_e) \sim 1/(2m_e r^2)$. This kinetic energy must be balanced by the Coulomb potential, so at the equilibrium radius $1/(2m_e r^2) \sim \alpha/r$, which indeed gives $r_B \sim 1/(m_e\alpha)$. In principle factors of 2 are beyond the power of dimensional estimates, but here it is quite tempting to observe that the virial theorem of classical mechanics states that, for a potential proportional to $1/r$, at equilibrium the kinetic energy is one half of the absolute value of the potential energy, so we would guess, more precisely, that $1/(2m_e r_B^2) = \alpha/(2r_B)$, i.e.

$$r_B = \frac{1}{m_e\alpha} \simeq 0.5 \times 10^{-8} \text{ cm}, \quad (8.34)$$

which is indeed the definition of the Bohr radius as found in the quantum mechanical treatment. The typical potential energy of the hydrogen atom is then

$$\langle V \rangle \sim V(r_B) = -\frac{\alpha}{r_B} = -m_e\alpha^2, \quad (8.35)$$

and, again using the virial theorem, the kinetic energy is

$$E = -\frac{1}{2}V \sim \frac{1}{2}m_e\alpha^2. \quad (8.36)$$

This is the kinetic energy of a non-relativistic electron with typical velocity

$$v \sim \alpha. \quad (8.37)$$

Since $\alpha \ll 1$, our approximation of a non-relativistic electron is indeed consistent. This of course was expected, since we know that, in a first approximation, the non-relativistic Schrödinger equation gives a good description of the hydrogen atom.

The sum of the kinetic and potential energy is $-(1/2)m_e\alpha^2$ so the binding energy of the hydrogen atom is

$$\text{binding energy} = \frac{1}{2}m_e\alpha^2 \quad (8.38)$$

and we have indeed found back the Rydberg, see eq. (8.12). In units $\hbar = c = 1$ the energy levels of the hydrogen atom predicted by the Schrödinger equations are

$$E_n = -\frac{m_e \alpha^2}{2n^2}. \quad (8.39)$$

9 Identical particles

9.1 Permutation symmetry in quantum mechanics

(Reference: Shankar, Section 10.3)

In classical mechanics we can distinguish among identical particles by following their trajectories. In quantum mechanics this is not possible (without disturbing the system). Therefore, two configurations related by the exchange of identical particles must be described by the same state vector. Let us see what are the consequences of this.

Consider first two *distinguishable* particles, that is, two particles which differ in some property such as the mass, the charge or other quantities. For example, consider an electron and a proton. We can measure the position of the first particle (say the electron) and we find it at $x = a$, and of the second (the proton), and we find it at $x = b$. The state just after the measurement is written as

$$|\psi\rangle = |x_1 = a, x_2 = b\rangle \equiv |ab\rangle, \quad (9.1)$$

while

$$|\psi\rangle = |x_1 = b, x_2 = a\rangle \equiv |ba\rangle, \quad (9.2)$$

represents the state where the electron is in b while the proton is in a . Clearly, for distinguishable particles $|ab\rangle \neq |ba\rangle$, if $a \neq b$.

Suppose now that the two particles are identical, e.g. two electrons. We find one electron in $x = a$ and one in $x = b$. Is the state vector after measurement $|ab\rangle$ or $|ba\rangle$? In fact, it is neither. Rather, if we demand that the exchange of the particle gives the same physical state, the state vector $|\psi(a, b)\rangle$ must satisfy

$$|\psi(a, b)\rangle = \alpha|\psi(b, a)\rangle \quad (9.3)$$

with α a phase. Neither $|ab\rangle$ nor $|ba\rangle$ satisfy this requirement. However, consider a general superposition of these states,

$$|\psi\rangle = c_1|ab\rangle + c_2|ba\rangle. \quad (9.4)$$

requiring (9.3) we get

$$c_1|ab\rangle + c_2|ba\rangle = \alpha(c_1|ba\rangle + c_2|ab\rangle), \quad (9.5)$$

so

$$c_1 = \alpha c_2, \quad c_2 = \alpha c_1, \quad (9.6)$$

which implies $\alpha^2 = 1$, i.e.

$$\alpha = \pm 1, \quad (9.7)$$

and the allowed states are the symmetric and the antisymmetric combinations,

$$|ab, S\rangle \equiv |ab\rangle + |ba\rangle, \quad (9.8)$$

$$|ab, A\rangle \equiv |ab\rangle - |ba\rangle. \quad (9.9)$$

One can now prove that *a given species of particle choose once and for all between S and A states*, simply because otherwise the superposition of generic symmetric and antisymmetric states gives back states with no symmetry under the exchange. Particles that choose the symmetric state are called *bosons*. Those in antisymmetric state are called *fermions*. In general, a particle will be labeled by a set of commuting quantum numbers $\{a_1, a_2, \dots, a_n\}$ (e.g. the three components of the position, and its spin component s_z). The states S, A are then the states symmetric and antisymmetric under the simultaneous exchange of all quantum numbers. Observe that, if we take $a = b$, $|aa, A\rangle = 0$: two fermions cannot be in the same state. This is the *Pauli exclusion principle*, and forbids the states in which all quantum numbers are simultaneously equal.

In the context of quantum field theory one can prove a theorem (the spin-statistic theorem), that states that particles whose spin is an integer (in units of \hbar) are bosons, while particles with half-integer spin are fermions. For example the electron, the muon, the proton, the neutron, are all spin $1/2$ particles and therefore fermions, while the pions (π^0, π^\pm) are spin-0 particles, so they are bosons.

The symmetry of the state vector (A or S) has observable consequences. Consider a two-particle system in which one particle is found in the state $|a\rangle$, with $\langle x|a\rangle = \psi_a(x)$, and the other in the state $|b\rangle$, with $\langle x|b\rangle = \psi_b(x)$ and $a \neq b$. The labels a and b denote here generically the quantum numbers of the particles, and do not refer necessarily to position. They could label, for instance, the energy level in a potential well, or the momentum of a free particle, etc. We neglect (only for the moment!) the spin degree of freedom. Then the S and A states have wavefunction

$$\psi_{S/A}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)] \quad (9.10)$$

and the probability of finding one particle in x_1 and the other in x_2 is

proportional to²⁴

$$\begin{aligned}
P_{S/A}(x_1, x_2) &= |\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)|^2 \\
&= |\psi_a(x_1)\psi_b(x_2)|^2 + |\psi_b(x_1)\psi_a(x_2)|^2 \\
&\quad \pm 2 \operatorname{Re} [\psi_a(x_1)\psi_b(x_2)\psi_b^*(x_1)\psi_a^*(x_2)]. \quad (9.11)
\end{aligned}$$

The sum of the first two terms gives the probability of finding two distinguishable particles (i.e. particles carrying a label, but otherwise identical), one in the state a and the other in the state b , regardless of which one is where,

$$P_D(x_1, x_2) \equiv |\psi_a(x_1)\psi_b(x_2)|^2 + |\psi_b(x_1)\psi_a(x_2)|^2. \quad (9.12)$$

(The subscript D denotes distinguishable particles). The last term is called the interference term, and is a purely quantum phenomenon. We see that the sign is observable, since it affects the probabilities. In the extreme case $x_1 = x_2$, we have $P_A(x, x) = 0$, (Pauli principle), while

$$P_S(x, x) = 4|\psi_a(x)\psi_b(x)|^2 = 2P_D(x, x), \quad (9.13)$$

so $P_S(x, x)$ is twice as large as the probability for distinguishable particles. This result can be described by saying that in the antisymmetric state two identical particles have a tendency to repel each other, while in the symmetric state they attract each other. This is a purely quantum phenomenon, which is sometimes ascribed to “exchange forces”. However, it is important to realize that it is not really a force, and there is no potential in the Hamiltonian describing this effect. It is a purely mathematical consequence of the symmetrization/antisymmetrization procedure.

The fact that we must symmetrize or antisymmetrize the wavefunction among all possible identical particles leads to a puzzle. Imagine that we have one particle in the lab and a second identical particle in a far galaxy. Should we really symmetrize or antisymmetrize among these two particles? Physical intuition tells us that in such cases it should be possible to forget about symmetrization or antisymmetrization. In fact, this happens because the interference term is negligible in this case. See the discussion in Shankar, pages 274–277.

²⁴One should be careful about factors of 2 in the proportionality factor, due to the fact that this probability gives one when integrated over *distinct* configuration, so $(1/2) \int_{-\infty}^{\infty} P_{S/A} dx_1 dx_2 = 1$, where the 1/2 is due to the fact that we should actually integrate only over the region $x_1 < x_2$. See Shankar, eq. (10.3.15) and (10.3.16).

For three or more identical particles the situation is similar. Consider three particles in the states a, b, c . If they are bosons, the state must be symmetric under the exchange of any pair of particles, so it is

$$|\psi_S\rangle = \frac{1}{\sqrt{3!}}(|abc\rangle + |acb\rangle + |bca\rangle + |bac\rangle + |cba\rangle + |cab\rangle), \quad (9.14)$$

or, in coordinate space,

$$\begin{aligned} \psi_S(x_1, x_2, x_3) = & \frac{1}{\sqrt{3!}}[\psi_a(x_1)\psi_b(x_2)\psi_c(x_3) + \psi_a(x_1)\psi_c(x_2)\psi_b(x_3) \\ & + \psi_b(x_1)\psi_c(x_2)\psi_a(x_3) + \psi_b(x_1)\psi_a(x_2)\psi_c(x_3) \\ & + \psi_c(x_1)\psi_b(x_2)\psi_a(x_3) + \psi_c(x_1)\psi_a(x_2)\psi_b(x_3)]. \end{aligned} \quad (9.15)$$

For three fermions, the state must be antisymmetric under the exchange of any pair of particles. This is given by

$$\begin{aligned} \psi_A(x_1, x_2, x_3) = & \frac{1}{\sqrt{3!}}[\psi_a(x_1)\psi_b(x_2)\psi_c(x_3) - \psi_a(x_1)\psi_c(x_2)\psi_b(x_3) \\ & + \psi_b(x_1)\psi_c(x_2)\psi_a(x_3) - \psi_b(x_1)\psi_a(x_2)\psi_c(x_3) \\ & - \psi_c(x_1)\psi_b(x_2)\psi_a(x_3) + \psi_c(x_1)\psi_a(x_2)\psi_b(x_3)]. \end{aligned} \quad (9.16)$$

Equation (9.16) can be rewritten more elegantly as a determinant,

$$\psi_A(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(x_1) & \psi_b(x_1) & \psi_c(x_1) \\ \psi_a(x_2) & \psi_b(x_2) & \psi_c(x_2) \\ \psi_a(x_3) & \psi_b(x_3) & \psi_c(x_3) \end{vmatrix}. \quad (9.17)$$

In this form, it readily generalizes to n identical fermions (with a normalization factor $1/\sqrt{n!}$). This is called the Slater determinant.

9.2 Inclusion of spin

In equations such as (9.10) we have neglected the spin of the particle, and therefore the spin wavefunction. We now include its effect, considering for definiteness a spin-1/2 particle, such as the electron. We denote by $|\psi\rangle$ the ket describing the orbital state of the system, i.e. $\psi(\mathbf{x}) \equiv \langle \mathbf{x} | \psi \rangle$ gives the probability amplitude for the coordinates \mathbf{x} . For instance, $|\psi\rangle$ could be the state $|nlm\rangle$ of an electron in the hydrogen atom, in which case $\psi_{nlm}(\mathbf{x}) = \langle \mathbf{x} | nlm \rangle$ would be the wavefunction of the hydrogen atom in the state with quantum numbers n, l, m , see eqs. (8.17)–(8.20). The Hilbert space of a spin-1/2 particle is a tensor product

$$|\psi\rangle \otimes |\xi\rangle \quad (9.18)$$

with $|\xi\rangle$ is an element of the Hilbert space spanned by the two vectors $|1/2, +1/2\rangle$ and $|1/2, -1/2\rangle$, that as usual we denote simply as $|+\rangle$ and $|-\rangle$,

$$|\xi\rangle = \alpha|+\rangle + \beta|-\rangle. \quad (9.19)$$

For two spin-1/2 particles, the Hilbert space is again the tensor product of the orbital and spin degrees of freedom, as in eq. (9.18). However, now $|\psi\rangle$ describes the joint probability amplitude in space of the two particles,

$$\langle \mathbf{x}_1, \mathbf{x}_2 | \psi \rangle = \psi(\mathbf{x}_1, \mathbf{x}_2), \quad (9.20)$$

while ξ is an element of the Hilbert space spanned by the four vectors

$$|s_1, m_1\rangle \otimes |s_2, m_2\rangle \equiv |s_1, m_1; s_2, m_2\rangle, \quad (9.21)$$

with $s_1 = s_2 = 1/2$, $m_1 = \pm 1/2$ and $m_2 = \pm 1/2$. As in eqs. (7.1)–(7.2) we use the simpler notation $|++\rangle$, $|+-\rangle$, $|--\rangle$, $|--\rangle$. It is convenient to use the basis (7.11)–(7.14) since these spin states have definite symmetry under the exchange of the two particles: the triplet is symmetric and the singlet is antisymmetric.

Now, the *total* state of two fermions must be antisymmetric. Therefore, if the spin wavefunction is symmetric, the coordinate wavefunction must be antisymmetric, and viceversa, if the spin wavefunction is antisymmetric, the coordinate wavefunction must be symmetric.

Thus, if the two electrons are found in state with orbital wavefunctions ψ_a and ψ_b , the possible states of the system are

$$[\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2)] \otimes |++\rangle, \quad (9.22)$$

$$[\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2)] \otimes \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}, \quad (9.23)$$

$$[\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2)] \otimes |--\rangle, \quad (9.24)$$

$$[\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) + \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2)] \otimes \frac{|+-\rangle - |-+\rangle}{\sqrt{2}}. \quad (9.25)$$

The first three states describe a two-electron system with total spin $s = 1$ and $s_z = +1, 0, -1$ respectively (i.e. the spin triplet). The spin wavefunction is symmetric, so the coordinate wavefunction must be antisymmetric. The fourth state has $s = 0$ and is the spin singlet; its spin wavefunction is antisymmetric, so the coordinate wavefunction must be symmetric.

Application: covalent bond. See Griffiths, pages 209–210.

10 Multi-electron atoms. Periodic table

10.1 Helium

(We follow Griffiths, pages 212–213).²⁵ For Helium $Z = 2$, and the Hamiltonian of the two electrons in the electric field of the nucleus with charge $+2e$ is

$$H = \left[-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{r_1} \right] + \left[-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{r_2} \right] + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (10.1)$$

If we simply ignore the last term (the repulsion between the two electron), the Schrödinger equation factorizes and the coordinate wave-function of the two electrons, before symmetrization or antisymmetrization, is the product of two hydrogen-like wave-functions,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2), \quad (10.2)$$

while the energy levels are obtained from eq. (8.39) by replacing $\alpha \rightarrow Z\alpha = 2\alpha$,

$$E_{nn'} = -4 \left(\frac{\text{Ry}}{n^2} + \frac{\text{Ry}}{n'^2} \right). \quad (10.3)$$

The total wavefunction is the product of the coordinate and spin wavefunctions. We saw that the composition of two spin $1/2$ can give a total spin $s = 0$ (singlet, antisymmetric) or $s = 1$ (triplet, symmetric). The singlet states are called *parahelium*, and the triplet *orthohelium*. For parahelium, the coordinate wave-function must be symmetric, since the spin wavefunction is antisymmetric. Conversely, for orthohelium the coordinate wave-function must be antisymmetric. In turn this means that for orthohelium the states where simultaneously $n = n'$, $l = l'$ and $m = m'$ are forbidden by the Pauli principle.

The lowest energy in eq. (10.3) is obtained setting $n = n' = 1$. This implies $l = m = 0$ and $l' = m' = 0$, so it is not allowed for orthohelium. So, the ground state of helium (at least in the approximation of neglecting the electron repulsion term, that we are using) is a spin singlet, and the orbital wavefunction is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}, \quad (10.4)$$

²⁵For the electric charge, we are using units that, in the notation of Griffiths, correspond to $\epsilon_0 = 1/(4\pi)$.

where we used eq. (8.17) with the replacement $e^2 \rightarrow 2e^2$ and therefore $a_0 \rightarrow a_0/2$. Its energy should be

$$E_{00} = -8 \text{ Ry} \simeq -109 \text{ eV}. \quad (10.5)$$

Of course, this result cannot be numerically accurate, since the repulsion between the two electrons is not a small effect compared to the proton-electron attraction. We will learn in due course how to include this effect, when we study perturbation theory and variational methods. Experimentally, it turns out that the ground state of He is indeed a spin singlet, as suggested by our crude approximation, and its binding energy is $E \simeq -78.975 \text{ eV}$. So, it is less bound compared to our estimate (10.5), as it should be, since we neglected a repulsive interaction.

The energy levels are summarized in Fig. 5.2 of Griffiths, for para- and ortho-helium. Observe that in that figure the energies are relative to the ground state of ionized Helium, He^+ . For states with energies larger than the energy of the ground state of He^+ it is energetically favorable to decay emitting a free electron, $\text{He} \rightarrow \text{He}^+e^-$. In particular, only the states where one electron is in an excited state but the other is in the ground state, can have an energy lower than the ground state of He^+ , which is $E = -4 \text{ Ry} \simeq -54.4 \text{ eV}$, so we need to consider only the states of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \quad (10.6)$$

since the others decay immediately into ionized He and a free electron.

10.2 Multielectron atoms

Here again we must resort to approximation methods, or to numerical solutions of the Schrödinger equation. The simplest approximation generalizes what we have done for He: we neglect altogether the repulsion among the electrons, and we say that the individual electrons occupy one-particle hydrogenic states (n, l, m) , called *orbitals*, in the Coulomb field of a nucleus with charge $+Ze$.

To obtain the ground state configuration, we then fill up the orbitals respecting the Pauli principle, which means that at each level (n, l, m) we can put two electrons (setting them in the spin singlet configuration). For each n , the number of allowed values of (l, m) is

$$\sum_{l=0}^{n-1} \sum_{m=-l}^l = \sum_{l=0}^{n-1} (2l+1) = n^2. \quad (10.7)$$

In our (very rough!) approximation these n^2 states are degenerate. These n^2 orbitals are said to form a *shell*.

A better approximation, due to Hartree, is as follows. Each electron moves in a potential determined by the nucleus and by all other electrons. If the b -th electron has coordinate wavefunction $\psi_b(\mathbf{x}')$, its charge density is $-e|\psi_b(\mathbf{x}')|^2$, and its contribution to the potential at the point \mathbf{x} is

$$-e \int d^3x' \frac{|\psi_b(\mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|}. \quad (10.8)$$

Thus the total potential experienced by the a -th electron is

$$V_a(\mathbf{x}) = -\frac{Ze^2}{r} + e^2 \sum_{b \neq a} \int d^3x' \frac{|\psi_b(\mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|}. \quad (10.9)$$

In a first approximation, we expect that this potential is approximately spherically symmetric, because the term Ze^2/r is spherically symmetric and is larger by a factor of Z than each of the separate term in the sum, while the $Z-1$ terms in the sum average among them, producing something closer to symmetric even when the separate terms are not. Furthermore, in each term there is an integral over the distribution probability of the b -th electron which, especially for low values of l , also has the effect of suppressing non-central contributions. This suggests that, in a first approximation, we can replace $V_a(\mathbf{x})$ by its angular average over the solid angle,

$$V_a(\mathbf{x}) \rightarrow V_a(r) = \int \frac{d\Omega}{4\pi} V_a(\mathbf{x}). \quad (10.10)$$

We then consider the Schrödinger equation for ψ_a in this potential $V_a(r)$,

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_a(r) \right] \psi_a(\mathbf{x}) = E_a \psi_a(\mathbf{x}), \quad (10.11)$$

or, explicitly,

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{r} + e^2 \sum_{b \neq a} \frac{d\Omega}{4\pi} \int d^3x' \frac{|\psi_b(\mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|} \right] \psi_a(\mathbf{x}) = E_a \psi_a(\mathbf{x}), \quad (10.12)$$

where $r = |\mathbf{x}|$ and $d\Omega$ is the unit solid angle relative to the variable \mathbf{x} , i.e. $d^3x = r^2 dr d\Omega$. Of course, dealing with a spherically symmetric potential greatly simplifies the problem, since it allows us to separate the

wavefunction into a radial part times the spherical harmonics. However, this potential depends of the wavefunction of all the other electrons, that must be determined similarly. One then proceed recursively. We begin with a zeroth-order ansatz for $V_a(r)$, e.g. we neglect all the interactions among the electrons (this was the approximation used previously). We determine the wavefunctions under this approximation, and we use them to compute a new, improved potential $V_a(r)$. We then solve the Schrödinger equation in this new potential, using the Pauli principle to fill up the levels, and we use the wave-function that we find to improve again the potential, and we proceed iteratively until a good convergence is obtained.

The states found in this way are still labeled by a set (n, l, m) of hydrogen-like quantum number for each electron, since we have a potential with spherical symmetry. The total wavefunction is taken to be the product of the single-electron wavefunctions, determined in this way,

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_Z) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots \psi_Z(\mathbf{x}_Z). \quad (10.13)$$

Therefore, in this approximation the correlation between the positions of the electrons are lost. The orbital wavefunction is then antisymmetrized among all electrons by means of the Slater determinant.

The most important qualitative difference compared to the hydrogenic levels is that the energies of the electrons are no longer degenerate in l . Mathematically, this is because the degeneracy in l of the hydrogen atom is a peculiar characteristic of a $1/r$ potential. It is actually due to the existence of a constant of motion specific to the $1/r$ potential, the Runge-Lenz vector

$$\mathbf{N} = \frac{\mathbf{p} \times \mathbf{L}}{m} - \frac{e^2}{r} \mathbf{r}. \quad (10.14)$$

In classical mechanics, the conservation of this vector is responsible for the fact that the bound-state orbits are closed (angular momentum conservation only implies that they are in a plane). In quantum mechanics, it is responsible for the degeneracy in l (see Shankar, page 360).

Physically, the fact that the degeneracy in l is lifted is because states with low l experience a lower centrifugal barrier and therefore have a larger amplitude of being near the origin, where they see the full “unshielded” charge of the nucleus, and therefore they are more strongly bound. As a result,

at each n , the energy grows with $l = 0, \dots, n - 1$.

10.3 The Periodic Table

We now have all the elements to understand, at least qualitatively, the structure of the Periodic Table. The ground state of an atom with generic Z is obtained by piling up the electrons in the various levels, according to the Pauli exclusion principle. Of course it is convenient to put the electrons in the lowest possible energy state. This means that each level (n, l, m) can be filled with two electrons, which must be in a spin singlet state (antisymmetric spinor wavefunction), so that their orbital quantum numbers (n, l, m) can be equal.

If we have only one electron, we put it in a $n = 1, l = 0$ state. It necessarily has $m = 0$, while s_z can be $+1/2$ or $-1/2$. This is the ground state of the hydrogen atom. In the spectroscopic notations discussed above, it is denoted as $(1s)$ or, in the $^{2S+1}L_J$ notation, it is $^2S_{1/2}$.

Helium (He) has two electrons in the $n = 1, l = 0$ state, which is written as $(1s)^2$. The two electrons are in the spin singlet state, to satisfy the Pauli principle. Therefore, this state is more precisely written as 1S_0 .

Recall that an “atomic shell” is defined as the set of levels with $l = 0, \dots, n - 1$, for given n . A filled shell is obtained when all the levels with $l = 0, \dots, n - 1$ are completely filled. According to eq. (10.7), the n -th shell is filled by $2n^2$ electrons, where the factor 2 is the spin multiplicity. Thus the $n = 1$ shell contains two electron, the $n = 2$ shell has 8 more electrons, and so on. In a closed shell the total electronic charge is spherically symmetric, since

$$|R_{nl}(r)|^2 \sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 \quad (10.15)$$

is independent of θ, ϕ . So this configuration shields the charge of the nucleus very effectively, and has no tendency to attract one more electron. A filled shell also has little tendency to have electrons in the excited state, since the next excited state is in a new shell with higher n , and there is a large energy gap to cross. Therefore these atoms are chemically inert, and form the *noble gases*. Thus He is inert because it has just filled the $n = 1$ shell.

The next entry is Lithium, with 3 protons in the nucleus and 3 electrons. Two of them fill the $n = 1$ shell as in He, and the remaining electron goes in a $n = 2, l = 0$ state. The electron in the $2s$ state is farther away from the nucleus, see eq. (8.22), and basically sees a spherical charge distribution with total charge $-2e$ due to the $n = 1$ electronic shell, which partially screens the charge $+3e$ of the nucleus, so its chemical properties are similar to that of hydrogen, and in the periodic it goes in the column below it.

Since it is farther away, and it sees a shielded charge, this electron has a relatively small binding energy, so Li has a strong tendency to donate it. The chemical properties of the elements are determined by their outermost electrons. The electrons that do not belong to filled shells, and that can be donated in chemical reactions, are called “valence” electrons. Elements which like to donate electrons are called *metals*, so Li is a metal.

The ground state configuration of Li is denoted as $(1s)^2(2s)$ or, more simply, as $(\text{He})(2s)$. Since the $n = 1$ filled shell has zero total angular momentum (the electrons are in spin singlet, and each one has $l = 0$), the total J is given by the spin of the electron in the $2s$ state, so $J = 1/2$, which means that the ground state of Li, in the generalized spectroscopic notation, is ${}^2S_{1/2}$.

The next element is Be, which fills the two $n = 2, l = 0$ levels, with the two electrons at level $n = 2, l = 0$ in spin singlet state. Even if it has two outer electrons, its properties are not the same as He, because it does not fill completely the $n = 2$ shell, so in the Periodic Table we put it into a new column. To fill the $n = 2$ shell we still must fill the levels $n = 2, l = 1, m = -1, 0, 1$, each one with two electrons in spin singlet. This gives 6 chemical elements, Boron to Neon, and Neon is inert because it has the $n = 2$ shell filled.

By definition, a *subshell* is formed by the states with $m = -l, \dots, l$, at fixed (n, l) . Some (but not all) elements with filled subshells are also inert, again because of a spherical charge distribution (which is assured by the sum over m in eq. (10.15)) and sometimes they can also have a large excitation gap. For instance, Be has filled the subshell $n = 2, l = 0$ and Mg has filled the subshell $n = 3, l = 0$; however, the gap to the levels $n = 2, l = 1$ (or, respectively, $n = 3, l = 1$) is not large, so they are not inert. Rather, they can be easily excited and can donate their valence electrons, so they are metals. In contrast, Ar has filled the subshell $n = 3, l = 1$ and is inert, because the subshell $n = 3, l = 2$ has a large energy with respect to subshell $n = 3, l = 1$, up to the point that, before filling it, it is filled the $n = 4, l = 0$ subshell (K, Ca). This is due to the fact that sometimes the raise in energy with l , discussed on page 87, can overcome the raise in energy with n .

Below we show the periodic table, and a more detailed discussion of it, taken from F. H. Shu, “The physical Universe. An Introduction to Astronomy, (1982)”,²⁶ and a table taken from Griffiths.

²⁶Incidentally, this is a beautiful book. Despite the fact that, from the point of view of astrophysics, it is by now outdated, it still provides an excellent elementary introduction to the “physics of astrophysics”.

speed of light, c , only two of these spin states can manifest themselves: $m_s = -1$ or $+1$ (antiparallel or parallel to the direction of propagation). The two independent spin states of the photon correspond to the classical fact that light has two independent senses of polarizations. (In Figure 2.4 we took these to be the two states of *linear* polarization, but we could as well take them to be two states of *circular* polarization in which the radiation field would carry [spin] angular momentum.)

Quantum Statistics

Particles with half-integer spins are called **fermions** (after Enrico Fermi); particles with integer spins are called **bosons** (after Satyendra Bose). Fermions include the electron, the proton, and the neutron, which constitute the vast bulk of the observable material universe. There is a fundamental difference between fermions and bosons because of the quantum-mechanical rule known as **Pauli's exclusion principle**. The origin of this rule—like that of many others in quantum mechanics—is highly mathematical, having to do with the symmetry and antisymmetry of allowable wavefunctions. This mathematical nature of modern quantum mechanics makes it very difficult to get an intuitive grasp of the subject. What is important for us is the result for fermions:

No two identical fermions can occupy the exact same quantum state.

The “quantum state” for the bound electron of an atom means the set of numbers n , l , m_l , and m_s . We may characterize this result colloquially by the statement that electrons behave antisocially: *they don't like to be any place where there's already another electron.*

Photons, being bosons, do not have to obey the Pauli exclusion principle. As a consequence, as many photons as one likes can occupy, in principle, the same quantum state. Thus, the wavelike aspect of each photon—see equation (3.6)—has a chance to reinforce the wavelike aspects of other similar photons and to produce a *macroscopic* effect. Indeed, it is only where very many photons are superimposed coherently that we have Maxwell's classical description of electromagnetic radiation (see Figure 2.4). Conversely, Pauli's exclusion principle *does* forbid a similar superposition of electrons or, more generally, of any of the fermions that make up ordinary matter. This is why the wavelike aspects of such particles—see equation (3.5)—were so late to be discovered. The intrinsic wave properties of ordinary matter cannot be manifested macroscopically. They can enter via the particles, so to speak, only one at a time. Nevertheless, because the physical world is built up with these particles, one at a time, the subtle but overwhelmingly important implications of the quantum basis of matter

touches every aspect of our daily existence. Let us begin with a discussion of the chemical properties of matter.

The Periodic Table of the Elements

With the information supplied above, we are in a position to elucidate the electronic shell structure of multi-electron atoms. The basic principles are spelled out in Box 3.3.

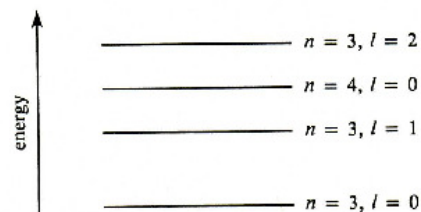
As an important application of the ideas in Box 3.3, let us now consider the periodic table of the chemical elements (Figure 3.24, also Appendix D).

Hydrogen (H), containing one proton in its nucleus and one orbital electron is the simplest atom; it is also the first entry in Mendeleev's periodic table. In its ground state, the electron occupies $n = 1$, $l = 0$, $m_l = 0$, and either $m_s = +1/2$ or $m_s = -1/2$.

BOX 3.3

Spherical approximation of electronic shell structure of multi-electron atoms

- In the lowest order of approximation, consider each electron in a multi-electron atom to be stationed in a spherically symmetric electric field provided by the attraction of the nucleus and the average repulsion of the rest of the electrons. Inner electrons “shield” outer electrons from feeling the full positive charge of the nucleus; thus the binding force does not generally vary as $1/r^2$. In this approximation, the orbital angular momentum of each electron is conserved, but its energy will depend on the quantum number l in addition to the principal quantum number n .
- Low values of the quantum number l associated with the orbital angular momentum allow the electron to sample regions which are closer to the nucleus for a given value of n . Thus, low values of l tend to correspond to lower energies than high values of l for the same n . Occasionally, the l consideration can overcome the n consideration. For example, the $n = 4$, $l = 0$ orbitals are lower in energy than the $n = 3$, $l = 2$ orbitals.



as in helium. The next two go into $n = 2$, $l = 0$, $m_l = 0$ (with opposite spins). Thus, beryllium contains two outer electrons just like helium; however, the $n = 2$ shell is not filled yet. It can take 6 more electrons (two each in $l = 1$ with $m_l = -1, 0, \text{ or } +1$). Thus, beryllium is not in the same family as helium, but forms a family of its own. Beryllium likes to donate two electrons; hence, beryllium is also a metal.

Six elements from beryllium is the next element in the helium family of "noble gases," neon (Ne). Neon has a complete $n = 2$ shell. The element just before neon is fluorine (F). Fluorine misses just one electron to have a filled $n = 2$ shell. Thus, chemically, fluorine would like to add an electron. The element before fluorine, oxygen (O), likes to add two electrons, for example, by combining with two hydrogen atoms to form a water molecule (H_2O). Roughly speaking, therefore, the elements on the left side of the periodic table are electron donors; the ones on the right (except for the noble gases) are electron acceptors. Carbon (C), with four valence electrons, is in the middle of this range, and it is a particularly versatile element in forming a rich variety of compounds. It is, of course, the basis of life on Earth.

Now, it might be thought that the next row down from neon, which starts filling the $n = 3$ shell, would have eighteen entries (refer back to Problem 3.8). Instead, this row only has eight entries: sodium (Na) to argon (Ar). When argon is reached, the $l = 0$ and $l = 1$ orbitals of the $n = 3$ shell are filled. According to Box 3.3, the $n = 3$, $l = 2$ orbitals are higher in energy than the $n = 4$, $l = 0$ orbitals. Thus, before the $l = 2$ orbitals of $n = 3$ are filled, a new row of chemical elements starts, with potassium (K) and calcium (Ca) adding the two electrons corresponding to the $n = 4$, $l = 0$ orbitals. Then, the ten electrons which can go into $n = 3$ and $l = 2$ are added—scandium (Sc) through zinc (Zn)—before we pick up yet the six electrons of $n = 4$ and $l = 1$, gallium (Ga) through krypton (Kr). With the outermost $n = 4$ and $l = 1$ subshell filled, krypton behaves as argon does with its outermost $n = 3$ and $l = 1$ subshell filled, namely, like a noble gas. With this and similar complications, the entire periodic table can be explained on the basis of known quantum-mechanical principles.

An important issue can be raised before we leave the topic of the chemical elements. If an atomic nucleus existed containing a million protons, the rules we outlined above would be perfectly content to organize its million orbital electrons into shells, subshells, etc. *But no such element exists.* Why is that? In Chapter 6, we shall see that the fault lies not in the outer electronic structure of the atom, but in the nucleus.

Atomic Spectroscopy

In the previous section, we have used the approximation that an electron in a multi-electron atom feels only

the radial attraction of the nucleus and the *spherically symmetric* part of the repulsion due to the other electrons. This approximation suffices for describing the ground state of an atom and for interpreting the *main features* of the periodic table of the elements, but the transitions to and from the excited states of an atom require an understanding of some additional complications.

These complications are associated with the angular momentum of the electrons. For a neutral atom, only the *valence electrons* generally need be considered, because the electrons in the inner *filled* subshells are usually in the lowest energy states consistent with Pauli's exclusion principle and have, in net, a spherically symmetric distribution. For the valence electrons, the important effects turn out to be those outlined in Box 3.4.

BOX 3.4

Atomic Spectroscopy and LS Coupling

- Electrons in the inner filled subshells have, in net, a spherically symmetric distribution. The valence electrons do not; consequently, their vector angular momenta, l and s , are not individually conserved. In LS coupling, the vector sums, L and S , of the orbital and spin angular momenta of all the valence electrons are assumed to be separately conserved.
- Quantum states with aligned spin angular momenta (large values of S) tend to have electrons which avoid each other (like Pauli's exclusion principle). This reduces the positive potential energy associated with the mutual repulsion of electrons. Thus, states with large values of S tend to have lower energies than states with small values of S .
- Quantum states with aligned orbital angular momenta (large values of L) correspond classically to electrons which revolve in the same sense about the nucleus. This again reduces the interaction between the electrons. Thus, states with large values of L tend to have lower energies than states with small values of L .
- The orientation of the spins of the electrons relative to their orbital angular momenta (characterized by the magnitude J of the total angular momentum $J = L + S$) leads to "fine structure." A spinning electron acts like a bar magnet, and can interact with the magnetic field associated with the motion of the orbiting electrons. The result is that spin-orbit states which are aligned (large values of J) tend to have higher energies than misaligned spin-orbit states (small values of J). A similar phenomenon involving the interaction of the spin of the electron with the spin of the nucleus is responsible for the "hyperfine structure" that gives rise to the 21-cm line of atomic hydrogen (Chapter 11).

*fine structure
due to spin-orbit
interaction
as in the
hydrogen*

TABLE 5.1: Ground state electron configurations for the first four rows of the Periodic Table.

| Z | Element | Configuration | |
|----|------------------|------------------------------------------------------------|-------------|
| 1 | H | (1s) | $^2S_{1/2}$ |
| 2 | He | (1s) ² | 1S_0 |
| 3 | Li | (He)(2s) | $^2S_{1/2}$ |
| 4 | Be | (He)(2s) ² | 1S_0 |
| 5 | B | (He)(2s) ² (2p) | $^2P_{1/2}$ |
| 6 | C | (He)(2s) ² (2p) ² | 3P_0 |
| 7 | N | (He)(2s) ² (2p) ³ | $^4S_{3/2}$ |
| 8 | O | (He)(2s) ² (2p) ⁴ | 3P_2 |
| 9 | F | (He)(2s) ² (2p) ⁵ | $^2P_{3/2}$ |
| 10 | Ne | (He)(2s) ² (2p) ⁶ | 1S_0 |
| 11 | Na | (Ne)(3s) | $^2S_{1/2}$ |
| 12 | Mg | (Ne)(3s) ² | 1S_0 |
| 13 | Al | (Ne)(3s) ² (3p) | $^2P_{1/2}$ |
| 14 | Si | (Ne)(3s) ² (3p) ² | 3P_0 |
| 15 | P | (Ne)(3s) ² (3p) ³ | $^4S_{3/2}$ |
| 16 | S | (Ne)(3s) ² (3p) ⁴ | 3P_2 |
| 17 | Cl | (Ne)(3s) ² (3p) ⁵ | $^2P_{3/2}$ |
| 18 | Ar | (Ne)(3s) ² (3p) ⁶ | 1S_0 |
| 19 | K | (Ar)(4s) | $^2S_{1/2}$ |
| 20 | Ca | (Ar)(4s) ² | 1S_0 |
| 21 | Sc | (Ar)(4s) ² (3d) | $^2D_{3/2}$ |
| 22 | Ti | (Ar)(4s) ² (3d) ² | 3F_2 |
| 23 | V | (Ar)(4s) ² (3d) ³ | $^4F_{3/2}$ |
| 24 | Cr | (Ar)(4s)(3d) ⁵ | 7S_3 |
| 25 | Mn | (Ar)(4s) ² (3d) ⁵ | $^6S_{5/2}$ |
| 26 | Fe | (Ar)(4s) ² (3d) ⁶ | 5D_4 |
| 27 | Co | (Ar)(4s) ² (3d) ⁷ | $^4F_{9/2}$ |
| 28 | Ni | (Ar)(4s) ² (3d) ⁸ | 3F_4 |
| 29 | Cu | (Ar)(4s)(3d) ¹⁰ | $^2S_{1/2}$ |
| 30 | Zn | (Ar)(4s) ² (3d) ¹⁰ | 1S_0 |
| 31 | Ga | (Ar)(4s) ² (3d) ¹⁰ (4p) | $^2P_{1/2}$ |
| 32 | Ge | (Ar)(4s) ² (3d) ¹⁰ (4p) ² | 3P_0 |
| 33 | As | (Ar)(4s) ² (3d) ¹⁰ (4p) ³ | $^4S_{3/2}$ |
| 34 | Se ⁹³ | (Ar)(4s) ² (3d) ¹⁰ (4p) ⁴ | 3P_2 |
| 35 | Br | (Ar)(4s) ² (3d) ¹⁰ (4p) ⁵ | $^2P_{3/2}$ |
| 36 | Kr | (Ar)(4s) ² (3d) ¹⁰ (4p) ⁶ | 1S_0 |

(From Griffiths)

11 Applications of the Pauli principle to many-electron systems

11.1 The free electron gas

(Reference: Griffiths, Sect. 5.3).

Consider a system of electrons in an infinite potential well, so $V(x, y, z) = 0$ if, simultaneously, $0 < x < l_x$, $0 < y < l_y$ and $0 < z < l_z$, while $V(x, y, z) = \infty$ otherwise. The Schrodinger equation factorizes, and the solution is (apart from a normalization factor)

$$\psi(x, y, z) = \sin(k_x x) \sin(k_y y) \sin(k_z z), \quad (11.1)$$

where

$$k_x = \frac{n_x \pi}{l_x}, \quad k_y = \frac{n_y \pi}{l_y}, \quad k_z = \frac{n_z \pi}{l_z}, \quad (11.2)$$

and n_i are *positive* integers,

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots \quad (11.3)$$

In k -space, we have one state in a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}, \quad (11.4)$$

and each state can be occupied by 2 electrons. Therefore, if we have N total electrons, with N large, in k space we fill an octant of a sphere with a radius k_F given by

$$N \frac{\pi^3}{V} = 2 \times \frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right), \quad (11.5)$$

so

$$k_F = (3\pi^2 n_e)^{1/3}, \quad (11.6)$$

where $n_e = N/V$ is the *number density* (number of electrons per unit volume) of the electron gas. The boundary between filled and empty states is called the *Fermi surface*, and

$$E_F \equiv \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2 n_e)^{2/3} \quad (11.7)$$

is called the *Fermi energy*. The *total* energy of the gas is obtained observing that a shell between k and $k + dk$ contains a volume

$$\frac{1}{8} 4\pi k^2 dk = \frac{1}{2} \pi k^2 dk. \quad (11.8)$$

Since each state occupies a volume π^3/V and we can put 2 electrons in each state, the total number of electron in this shell is

$$2 \frac{(1/2)\pi k^2 dk}{(\pi^3/V)} = \frac{V}{\pi^2} k^2 dk. \quad (11.9)$$

Each electron has energy $\hbar^2 k^2/(2m)$, so

$$\begin{aligned} E_{\text{tot}} &= \int_0^{k_F} \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk, \\ &= \frac{\hbar^2 k_F^5 V}{10\pi^2 m_e} \\ &= \frac{\hbar^2 (3\pi^2 N)^{5/3}}{10\pi^2 m_e} V^{-2/3}. \end{aligned} \quad (11.10)$$

This corresponds to a pressure

$$\begin{aligned} P_{\text{deg}} &= - \left(\frac{\partial E_{\text{tot}}}{\partial V} \right)_N = \frac{2}{3} \frac{E_{\text{tot}}}{V} \\ &= (3\pi^2)^{2/3} \frac{\hbar^2}{5m_e} n_e^{5/3}. \end{aligned} \quad (11.11)$$

This is called the *degeneracy pressure*. It represents the resistance to compression of the (non-relativistic) free electron gas, due to the Pauli principle. Observe that this pressure is independent of the temperature and is present even if the temperature of the gas vanishes.

11.1.1 The stability of white dwarfs

During their lifetime, the equilibrium of stars is determined by the balance between the gravitational attraction, that tends to provoke the collapse of the star under its own weight, and the pressure of the photons liberated by the thermonuclear reactions in the core, that try to make their way toward the surface of the star. When the nuclear fuel terminates, a complex dynamics takes place, in which the external layers are ejected explosively, and a remaining core, with no more support from the thermonuclear reactions, begins to collapse under its own weight. At some point, however, the electron degeneracy pressure becomes important. White dwarfs are remnant of stars, whose collapse has been halted by the degeneracy pressure of the electron.

To estimate the radius at which this can happen, we proceed as follows. The pressure P_c in the center of a star of mass M and radius R , due to the weight of the star itself, can be estimated as

$$P_c \sim \frac{1}{4\pi R^2} \frac{GM^2}{R^2} = \frac{GM^2}{4\pi R^4} \quad (11.12)$$

since GM^2/R^2 is the typical magnitude of the gravitational self-force and $4\pi R^2$ is the available scale for an area. Alternatively, we can estimate the typical gravitational self-energy of a sphere of mass M and radius R as

$$E_{\text{grav}} \sim -\frac{GM^2}{R}, \quad (11.13)$$

and the pressure required to support this weight (equal to minus the pressure $-\partial E_{\text{grav}}/\partial V$ exerted by the gas) is

$$\begin{aligned} P_c &\sim \frac{\partial E_{\text{grav}}}{\partial V} = \frac{1}{dV/dR} \frac{\partial E_{\text{grav}}}{\partial R} \\ &= \frac{1}{4\pi R^2} \frac{GM^2}{R^2}. \end{aligned} \quad (11.14)$$

A more precise value can be obtained by integrating the equation of the hydrostatic equilibrium inside the star, and gives

$$P_c \simeq 0.770 \frac{GM^2}{R^4}. \quad (11.15)$$

[(An aside that can be skipped). The hydrostatic equilibrium inside the star is governed by the equation

$$\nabla P = -\rho \nabla \Phi, \quad (11.16)$$

where Φ is the gravitational potential. In spherical symmetry, this becomes

$$\frac{dP}{dr} = -\frac{G\rho m(r)}{r^2}, \quad (11.17)$$

where

$$m(r) = 4\pi \int_0^r dr' r'^2 \rho(r'). \quad (11.18)$$

We can combine these equations into

$$\frac{d}{dr} \left(\frac{r^2}{\rho} \frac{dP}{dr} \right) = -4\pi G r^2 \rho(r). \quad (11.19)$$

Using an equation of state of the form $P = K\rho^\Gamma$, with $\Gamma > 1$, this becomes a differential equations for ρ , that gives the profile $\rho(r)$ in terms of the initial conditions $\rho(0)$, and $d\rho/dr(0)$. We require that the derivative $d\rho/dr(0)$ vanishes, because $m(r) \sim r^3$ near the center of the star. Then, eq. (11.17) shows that $dP/dr = 0$ at the center, and therefore, since we are assuming $P = K\rho^\Gamma$, also $d\rho/dr$ vanishes at the center. Then, we get the solution as a function of the central density $\rho(0)$, which is then fixed requiring that the integral of $\rho(r)$ over the volume gives the total mass M . For a gas with equation of state $P \propto \rho^{5/3}$, as in eq. (11.11), this gives eq. (11.15).]

This gravitational pressure is balanced by the degeneracy pressure (11.11). We can express it in terms of the mass density ρ observing that, if the star were made by electrons and protons, because of charge neutrality $n_e = n_p$, and the mass is dominated by the protons, so $\rho = m_p n_p$, and $n_e = \rho/m_p$. More precisely, if the positive charge is provided mostly by nuclei with atomic weight A , charge Z and number density n_+ , we have $n_e = Zn_+$ and $\rho = Am_p n_+$, so

$$n_e = \frac{Z}{A} \frac{\rho}{m_p}. \quad (11.20)$$

The central density ρ is related to M and R by

$$\rho \sim \frac{M}{R^3}. \quad (11.21)$$

Again, the precise numbers can be found integrating the hydrostatic equation, and one finds $\rho \simeq 1.43M/R^3$. So (apart from numerical factors of order one) the degeneracy pressure of the electrons can be written as

$$\begin{aligned} P_{\text{deg}} &\simeq (3\pi^2)^{2/3} \frac{\hbar^2}{5m_e m_p^{5/3}} \left(\frac{Z}{A}\right)^{5/3} \rho^{5/3} \\ &\sim (3\pi^2)^{2/3} \frac{\hbar^2}{5m_e m_p^{5/3}} \left(\frac{Z}{A}\right)^{5/3} \frac{M^{5/3}}{R^5}. \end{aligned} \quad (11.22)$$

Observe that the degeneracy pressure of the positively charge ions is much smaller, since the factor $1/m_e$ in P_{deg} replaced by $1/(Am_p)$. Requiring that this balances the gravitational pressure (11.12) we get

$$(3\pi^2)^{2/3} \frac{\hbar^2}{5m_e m_p^{5/3}} \left(\frac{Z}{A}\right)^{5/3} \frac{M^{5/3}}{R^5} \simeq \frac{GM^2}{R^4}, \quad (11.23)$$

This gives (inserting the correct numerical values)

$$R \simeq 0.114 \frac{(2\pi\hbar)^2}{Gm_em_p^{5/3}} \left(\frac{Z}{A}\right)^{5/3} M^{-1/3}, \quad (11.24)$$

which is the mass-radius relation of white dwarfs. Observe that, the larger the mass, the smaller is the radius of the white dwarf. For $M = 1M_\odot$ and $Z/A = 0.5$, this gives R of the order of the Earth radius.

[Note: The above equations assumed that the electron gas can be treated as non-relativistic. If we increase the mass, the radius R in eq. (11.24) becomes smaller, and therefore also the interdistance between the electrons gets smaller and smaller. In this situation the electrons finally become relativistic, and for a relativistic electron gas the degeneracy pressure grows with ρ only as $P \sim \rho^{4/3}$, and this leads to a maximum value of the mass for which the degeneracy pressure can balance the gravitational pressure. Therefore there is a maximum allowed value for the mass of the white dwarf, known as the Chandrasekhar mass, which is about $1.4M_\odot$.]

11.2 Band structure in solids

(Reference: Griffiths, Sect. 5.3.2). Consider a periodic potential with period a ,

$$V(x+a) = V(x). \quad (11.25)$$

Then *Bloch's theorem* states the solutions of the Schrödinger equation can be taken to satisfy

$$\psi(x+a) = e^{iKa}\psi(x). \quad (11.26)$$

The proof is obtained introducing the displacement operator D_a , defined by

$$D_a f(x) = f(x+a). \quad (11.27)$$

If the potential in the Hamiltonian is periodic with period a , we have $[D_a, H] = 0$, and therefore D_a and H can be diagonalized simultaneously. This means that the eigenfunctions ψ of the Hamiltonian can be chosen so that $D_a\psi = \lambda\psi$, i.e.

$$\psi(x+a) = \lambda\psi(x). \quad (11.28)$$

Clearly, $\lambda \neq 0$, since otherwise we get $\psi = 0$. Then, we can always write $\lambda = e^{iKa}$, for some (possibly complex) constant K . We will see in a moment that K is actually real.

Of course a solid has edges, which spoil the exact periodicity. However, as long as we are far from the edges, their effect should be negligible. We

therefore make a negligible error if we artificially modify the problem so to have exact periodicity. For a (one-dimensional) solid with N lattice spacing [with N huge, e.g. $O(10^{23})$], we can obtain this by wrapping the x -axis in a circle, i.e. by imposing

$$\psi(x + Na) = \psi(x). \quad (11.29)$$

With this modification Bloch theorem now holds, so in particular eq. (11.26) gives

$$\psi(x + Na) = e^{iKNa}\psi(x) \quad (11.30)$$

for some K . Combining eqs. (11.29) and (11.30) we find that K must be of the form

$$K = \frac{2\pi n}{Na}, \quad n = 0, \pm 1, \pm 2, \dots \quad (11.31)$$

In particular, this means that K is real, as we anticipated, so e^{iKa} is a phase. Equation (11.26) then implies

$$|\psi(x + a)|^2 = |\psi(x)|^2, \quad (11.32)$$

so the probability is periodic, as one would expect. Now, consider the “Dirac comb” potential

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja), \quad (11.33)$$

which can be taken as a rough schematization of the interaction of an electron with the nuclei of a one-dimensional lattice. Actually, the detailed form of the potential will not be important for what follows, and the main results are really a consequence of the periodic structure of the potential.

The solution of the Schrödinger equation in the cell $0 < x < a$ is

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad (0 < x < a). \quad (11.34)$$

Using Bloch’s theorem, in the cell immediately to the left we have

$$\psi(x) = e^{-iKa}[A \sin k(x + a) + B \cos k(x + a)] \quad (-a < x < 0). \quad (11.35)$$

We can now match these solutions in $x = 0$. We recall (see Griffiths, Sect. 2.5.2) that in a Dirac delta potential $V(x) = \alpha\delta(x)$, the wavefunction $\psi(x)$ is continuous in $x = 0$,

$$\lim_{x \rightarrow 0^+} \psi(x) = \lim_{x \rightarrow 0^-} \psi(x), \quad (11.36)$$

while the derivative has a jump,

$$\left(\lim_{x \rightarrow 0^+} - \lim_{x \rightarrow 0^-} \right) \frac{d\psi(x)}{dx} = \frac{2m\alpha}{\hbar^2} \psi(0). \quad (11.37)$$

Imposing the two conditions (11.36) and (11.37) on the solution (11.34), (11.35) we find the ratio A/B ,²⁷

$$A \sin(ka) = [e^{iKa} - \cos(ka)]B \quad (11.38)$$

and an equation for k ,

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka). \quad (11.39)$$

Introducing $z = ka$ and $\beta = m\alpha a/\hbar^2$, and using eq. (11.31), this equation can be rewritten as

$$\cos\left(\frac{2\pi n}{N}\right) = f(z) \quad (11.40)$$

where

$$f(z) \equiv \cos z + \beta \frac{\sin z}{z}. \quad (11.41)$$

The function $f(z)$ is not limited to the range $-1 < f(z) < 1$. For z such that $|f(z)| > 1$ the equation $\cos(Ka) = f(z)$ clearly has no solution. These values of k correspond to forbidden energy. These forms *gaps* between allowed regions. In contrast, if $f(z)$ goes from -1 to $+1$ in the interval $z_1 < z < z_2$, eq. (11.40) has N solutions in this interval, corresponding to the N possible values of n from $n = 0$ to $n = N - 1$ (the solution with $n = N$ is the same as that with $n = 0$). Since N is huge, say $O(10^{23})$, this looks like a continuum of allowed energies, and forms a *band*. Thus, the energy spectrum consists of allowed bands separated by gaps.

This band structure determines the property of the material. If each atom of the lattice has q valence electrons, there are Nq free electrons. Because of the Pauli principle, only two electrons can go in the same state. So, if $q = 1$, the first band will be half-filled, if $q = 2$ we completely fill the first band, etc. If a band is entirely filled, it is very difficult to excite an electron, since it has to jump to the next band, and it must overcome a large energy gap. These materials are therefore electric insulators. If, however, a band is only half-filled, very little energy is needed to excite an electron. We then have a conductor. If we dope an insulator adding a few

²⁷Of course an overall common numerical factor in A and B is determined by the normalization of the wavefunction.

atoms with larger q we have extra electrons in the next higher band, which are easily excited. Similarly, adding atoms with lower q creates “holes” in the lower band. In both cases, weak electric currents can flow, and we have a semiconductor.

12 Time-independent perturbation theory

12.1 The general formalism

(See Shankar, Section 17.1). Consider a Hamiltonian of the form

$$H = H^0 + H^1, \quad (12.1)$$

where H^1 contains a small expansion parameter.

Let $|n^0\rangle$ be the eigenkets of H^0 ,

$$H^0|n^0\rangle = E_n^0|n^0\rangle. \quad (12.2)$$

We write the eigenkets of the full Hamiltonian as

$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + \dots \quad (12.3)$$

and their eigenvalues as

$$E_n = E_n^0 + E_n^{(1)} + E_n^{(2)} + \dots \quad (12.4)$$

Solving order by order the equation $H|n\rangle = E_n|n\rangle$ we get, to first order,

$$H^0|n^1\rangle + H^1|n^0\rangle = E_n^0|n^1\rangle + E_n^{(1)}|n^0\rangle. \quad (12.5)$$

Multiplying both sides by $\langle n^0|$ and using $\langle n^0|H^0 = E_n^0\langle n^0|$ we get

$$E_n^0\langle n^0|n^1\rangle + \langle n^0|H^1|n^0\rangle = E_n^0\langle n^0|n^1\rangle + E_n^{(1)} \quad (12.6)$$

and therefore

$$E_n^{(1)} = \langle n^0|H^1|n^0\rangle. \quad (12.7)$$

This gives the shift in the energy levels, to first order in perturbation theory.

We also want to find the change in the eigenstate due to the perturbation, which, to first order, is $|n^1\rangle$. To this purpose we multiply eq. (12.5) by $\langle m^0|$, with $m^0 \neq n^0$. Using $\langle m^0|H^0|n^1\rangle = E_m^0\langle m^0|n^1\rangle$ on the left-hand side, and $E_n^{(1)}\langle m^0|n^0\rangle = 0$ on the right-hand side, we get

$$(E_n^0 - E_m^0)\langle m^0|n^1\rangle = \langle m^0|H^1|n^0\rangle. \quad (12.8)$$

We now write $|n^1\rangle = |n_{\parallel}^1\rangle + |n_{\perp}^1\rangle$, where $|n_{\parallel}^1\rangle$ is the projection of $|n^1\rangle$ in the direction of $|n^0\rangle$, and $|n_{\perp}^1\rangle$ is the component of $|n^1\rangle$ orthogonal to $|n^0\rangle$. The space of vectors orthogonal to $|n^0\rangle$ is spanned by the kets $|m^0\rangle$ with $m^0 \neq n^0$. Therefore

$$|n^1\rangle = |n_{\parallel}^1\rangle + \sum_{m \neq n} c_m |m^0\rangle. \quad (12.9)$$

Inserting this decomposition into eq. (12.8) we see that $|n_{\parallel}^1\rangle$ drops and therefore cannot be determined from this equation. Instead, for the coefficients c_m , using

$$\langle m^0 | \sum_{m' \neq n} c_{m'} |m'^0\rangle = c_m \quad (12.10)$$

we get

$$(E_n^0 - E_m^0)c_m = \langle m^0 | H^1 |n^0\rangle. \quad (12.11)$$

If $E_n^0 \neq E_m^0$, i.e. if there is no degeneracy in the spectrum, we therefore find

$$|n\rangle = |n^0\rangle + |n_{\parallel}^1\rangle + \sum_{m \neq n} \frac{|m^0\rangle \langle m^0 | H^1 |n^0\rangle}{E_n^0 - E_m^0}. \quad (12.12)$$

(The degenerate case will be examined later). The component $|n_{\parallel}^1\rangle$ can instead be obtained imposing the normalization condition $\langle n | n \rangle = 1$. To first-order in perturbation theory, this simply gives $|n_{\parallel}^1\rangle = 0$ [see Shankar eqs. (17.1.9)–(17.1.14) for the explicit computation]. Therefore

$$|n\rangle = |n^0\rangle + \sum_{m \neq n} \frac{|m^0\rangle \langle m^0 | H^1 |n^0\rangle}{E_n^0 - E_m^0}. \quad (12.13)$$

The result is consistent only if the first-order term are indeed perturbation of the zero-th order results, which means that $E_n - E_m$ cannot be small with respect to $\langle m^0 | H^1 |n^0\rangle$. In particular, this excludes the case of degenerate eigenvalues, that will be treated separately below.

We can continue the procedure to higher orders. To second order, $H|n\rangle = E_n|n\rangle$ gives

$$H^0|n^2\rangle + H^1|n^1\rangle = E_n^0|n^2\rangle + E_n^{(1)}|n^1\rangle + E_n^{(2)}|n^0\rangle. \quad (12.14)$$

We take the scalar product with $\langle n^0 |$, and we use the fact that, on the left-hand side, $\langle n^0 | H^0 |n^2\rangle = E_n^0 \langle n^0 | n^2\rangle$, which cancels the term coming from the first term on the right-hand side. Furthermore, we found above that $|n^1\rangle$ is orthogonal to $|n^0\rangle$. Then we get

$$\begin{aligned} E_n^{(2)} &= \langle n^0 | H^1 |n^1\rangle \\ &= \sum_{m \neq n} \frac{\langle n^0 | H^1 |m^0\rangle \langle m^0 | H^1 |n^0\rangle}{E_n^0 - E_m^0} \end{aligned} \quad (12.15)$$

$$= \sum_{m \neq n} \frac{|\langle m^0 | H^1 |n^0\rangle|^2}{E_n^0 - E_m^0}. \quad (12.16)$$

So, in general to compute the shift in the energy levels to second order, we must compute an infinite number of matrix elements $\langle m^0 | H^1 | n^0 \rangle$, for all $m^0 \neq n^0$.

Fortunately, often only a finite number of matrix elements actually contribute, due to the existence of selection rules, as we discuss below. When all matrix element contribute, we can often still use eq. (12.16) to get a rigorous upper bound on $E_n^{(2)}$. Consider for instance the hydrogen atom, with unperturbed states $|nlm\rangle$, so the ground state is $|100\rangle$. To first order the shift in the ground state energy due to some perturbation H^1 is

$$E_{100}^{(1)} = \langle 100 | H^1 | 100 \rangle. \quad (12.17)$$

The second order term is

$$E_{100}^{(2)} = \sum'_{nlm} \frac{|\langle nlm | H^1 | 100 \rangle|^2}{E_{100}^0 - E_{nlm}^0}, \quad (12.18)$$

where the prime means that, in the sum over n, l, m , we must omit the state $n = 1, l = m = 0$. Since the unperturbed energy levels are

$$E_{nlm}^0 = -\frac{\text{Ry}}{n^2}, \quad (12.19)$$

we see that $E_{100}^{(2)} < 0$, and for its absolute value, we have the bound

$$|E_{100}^{(2)}| < \frac{1}{|E_{n=1}^0 - E_{n=2}^0|} \sum'_{nlm} \langle 100 | H^1 | nlm \rangle \langle nlm | H^1 | 100 \rangle \quad (12.20)$$

Since

$$\sum'_{nlm} |nlm\rangle \langle nlm| = I - |100\rangle \langle 100|, \quad (12.21)$$

we get

$$|E_{100}^{(2)}| < \frac{1}{|E_{n=1}^0 - E_{n=2}^0|} [\langle 100 | (H^1)^2 | 100 \rangle - |\langle 100 | H^1 | 100 \rangle|^2]. \quad (12.22)$$

12.2 Selection rules

(Shankar, page 458). Perturbation theory can be greatly simplified by the fact that many matrix elements of H^1 vanish. For instance, suppose that an operator Ω commutes with the perturbation H^1 ,

$$[\Omega, H^1] = 0. \quad (12.23)$$

We denote the states of the systems as $|\alpha\omega\rangle$, where ω is the eigenvalue of Ω and α denotes collectively all the other quantum numbers, Then

$$\langle\alpha_2\omega_2|H^1|\alpha_1\omega_1\rangle \propto \delta_{\omega_1\omega_2}. \quad (12.24)$$

Proof:

$$0 = \langle\alpha_2\omega_2|\Omega H^1 - H^1\Omega|\alpha_1\omega_1\rangle = (\omega_2 - \omega_1)\langle\alpha_2\omega_2|H^1|\alpha_1\omega_1\rangle. \quad (12.25)$$

Example: if $H^1 = \lambda z$, then $[L_z, H^1] = 0$ and

$$\langle n'l'm'|H^1|nlm\rangle \propto \delta_{mm'}. \quad (12.26)$$

An equivalent way of deriving this result is to observe that, if $[\Omega, H^1] = 0$ and

$$\Omega|\omega_1\rangle = \omega_1|\omega_1\rangle, \quad (12.27)$$

then

$$\Omega(H^1|\omega_1\rangle) = H^1(\Omega|\omega_1\rangle) = \omega_1(H^1|\omega_1\rangle), \quad (12.28)$$

so the application of H^1 to $|\omega_1\rangle$ does not change its eigenvalue with respect to Ω . Then, eq. (12.24) expresses the orthogonality of eigenvectors (of hermitian operators) with different eigenvalues.

This result can be generalized to operators that change the eigenvalue ω in a definite way. Consider in particular the angular momentum states $|lm\rangle$, and consider the matrix elements $\langle l_2m_2|x_i|l_1m_1\rangle$. Performing the explicit calculation in coordinate space, you will see in the exercise session that

$$\langle l_2m_2|z|l_1m_1\rangle = 0 \quad \text{unless} \quad l_2 = l_1 \pm 1 \quad \text{and} \quad m_2 = m_1. \quad (12.29)$$

Similarly

$$\langle l_2m_2|x|l_1m_1\rangle = 0 \quad \text{unless} \quad l_2 = l_1 \pm 1 \quad \text{and} \quad m_2 = m_1 \pm 1. \quad (12.30)$$

and the same for $\langle l_2m_2|y|l_1m_1\rangle$. This is called the *dipole selection rule*. The reason for this name is that the interaction of the electric dipole moment, for instance of the hydrogen atom, with an external electric field \mathbf{E} is given by the Hamiltonian $H^1 = \mathbf{d} \cdot \mathbf{E}$, where $\mathbf{d} = e\mathbf{x}$ is the electric dipole moment, and \mathbf{x} is the relative distance of the electron and the proton. Therefore, taking the matrix elements between the unperturbed states of the hydrogen atom,

$$\langle n'l'm'|H^1|nlm\rangle = e\mathbf{E} \cdot \langle n'l'm'|\mathbf{x}|nlm\rangle, \quad (12.31)$$

and the selection rule discussed above applies.

These selection rule can be understood in a more formal language, observing that the components of a vector operator \mathbf{V} transform, under rotations, as the three components of a spin-1 state $|1m\rangle$, with $m = -1, 0, 1$. More precisely, comparing the transformation law of a vector under rotations with the transformation of the states $|1m\rangle$ under rotations (that we know because we know how the generator of rotations, J_i , are represented as explicit 3×3 matrices on the spin-1 representation, see Sections 5.5.2 and 6.3), one finds that the components V_m with $m = 0, \pm 1$ defined by

$$V_{\pm 1} = \mp \frac{1}{\sqrt{2}} (V_x \pm iV_y), \quad V_0 = V_z. \quad (12.32)$$

transform in the same way as $|1m\rangle$. Thus, under rotations, $V_m|l_1m_1\rangle$ transforms as the tensor product

$$|1m\rangle \otimes |l_1m_1\rangle. \quad (12.33)$$

However, we already know that this tensor product can be decomposed into irreducible representation of the rotation group, and that the resulting ket is a superposition of angular momenta $l = l_1 - 1, l_1$ and $l_1 + 1$, while it has $l_z = m + m'$. Therefore the matrix element

$$\langle l_2m_2|V_m|l_1m_1\rangle \quad (12.34)$$

can be different from zero only for $l_2 = l_1 \pm 1$ or $l_2 = l_1$, and $m_2 = m + m_1$.²⁸

Thus, the properties of the operator \mathbf{x} under rotations require that the matrix elements $\langle l_2m_2|\mathbf{x}|l_1m_1\rangle$ are non-vanishing only for $l_2 = l_1 \pm 1$ or for $l_2 = l_1$. The latter possibility is however forbidden by parity. In fact, in terms of the polar angles (θ, ϕ) (with $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$), a parity transformation $\mathbf{x} \rightarrow -\mathbf{x}$ becomes $\theta \rightarrow \pi - \theta$ and $\phi \rightarrow \phi + \pi$. Under this transformation, the spherical harmonics transform as

$$Y_{lm}(\theta, \phi) \rightarrow Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \quad (12.35)$$

Writing the matrix element $\langle l_2m_2|\mathbf{x}|l_1m_1\rangle$ in the (polar) coordinate representation, we have

$$\langle l_2m_2|x_i|l_1m_1\rangle = \int d\Omega Y_{l_2m_2}^*(\theta, \phi) x_i Y_{l_1m_1}(\theta, \phi). \quad (12.36)$$

In the integration over the solid angle $d\Omega$, for each direction $\hat{\mathbf{n}}$ there is a corresponding direction $-\hat{\mathbf{n}}$, so the integral is non-vanishing only if the

²⁸This construction can be generalized to tensor operators, leading to the *Wigner-Eckart* theorem. The interested reader can find it in Shankar, Section 15.3.

integrand is even under parity. Now, under parity $Y_{l_1 m_1}$ picks a factor $(-1)^{l_1}$, $Y_{l_2 m_2}^*$ picks a factor $(-1)^{l_2}$, and x_i picks a factor (-1) . In total, the integrand picks a factor $(-1)^{l_1+l_2+1}$. Therefore, among the three possibilities $l_2 = l_1 \pm 1$ and $l_2 = l_1$ selected above, only $l_2 = l_1 \pm 1$ are allowed by parity, while the matrix element for $l_2 = l_1$ vanishes.

12.3 Degenerate perturbation theory

(Reference: Shankar, Sect. 17.3). The perturbative scheme described above works if, for all $m^0 \neq n^0$,

$$\left| \frac{\langle m^0 | H^1 | n^0 \rangle}{E_n^0 - E_m^0} \right| \ll 1, \quad (12.37)$$

compare with eq. (12.13). Therefore, it fails in the case of degenerate eigenvalues. This failure can be understood as follows. Suppose that H^0 has two degenerate eigenvalues, while $H^0 + H^1$ is non-degenerate. Consider $H = H^0 + \lambda H^1$ and vary continuously λ from $\lambda = 1$ down to $\lambda = 0$. Each eigenvalue $|n\rangle$ of $H^0 + \lambda H^1$ changes continuously, and becomes a corresponding eigenvalue $|n^0\rangle$ of H^0 . However, for $\lambda = 0$, two eigenkets $|n_a\rangle$ and $|n_b\rangle$, which for $\lambda \neq 0$ have different eigenvalues, reduce to kets $|n_a^0\rangle$ and $|n_b^0\rangle$ with the same eigenvalue. The procedure is of course reversible. If we start from $|n_a^0\rangle$ and $|n_b^0\rangle$ and we switch on the interaction, these states smoothly go into $|n_a\rangle$ and $|n_b\rangle$.

However, in the degenerate space spanned by $|n_a^0\rangle$ and $|n_b^0\rangle$, we could start from different linear combinations of $|n_a^0\rangle$ and $|n_b^0\rangle$, and these jump discontinuously when we switch on the interaction. This is the source of non-analyticity signaled by the vanishing of the denominator in eq. (12.37)

So, we must start from the “right” basis when we have a degenerate subspace. This is the basis that diagonalizes H^1 within the degenerate subspace. Consider in fact eq. (12.8),

$$(E_n^0 - E_m^0) \langle m^0 | n^1 \rangle = \langle m^0 | H^1 | n^0 \rangle. \quad (12.38)$$

In the non-degenerate case we used it to determine $\langle m^0 | n^1 \rangle$. If instead $E_n^0 - E_m^0 = 0$ while $\langle m^0 | H^1 | n^0 \rangle \neq 0$, it gives a divergent result for $\langle m^0 | n^1 \rangle$, signaling the breaking of the approach. However, if also $\langle m^0 | H^1 | n^0 \rangle = 0$ when $m^0 \neq n^0$, then this equation is simply a harmless identity $0 = 0$, and no divergence appears. So, in this basis we can apply the “naive” non-degenerate perturbation theory and, since in this subspace we have already diagonalized H^1 , the shift in the energy levels can be obtained immediately.

Consider for instance the hydrogen atom in the $n = 2$ state, and the Hamiltonian

$$H^1 = eEz. \quad (12.39)$$

This is the interaction due to the electric dipole of the electron with an electric field along the z axis, and gives rise to the so-called *Stark effect*. If we naively applied eq. (12.7), we would conclude that the energy shift in the state $|2lm\rangle$ is

$$E_n^1 \stackrel{?}{=} eE\langle 2lm|z|2lm\rangle. \quad (12.40)$$

Because of parity, this is zero (recall the dipole selection rule studied above). However, eq. (12.40) is not correct, since $|n^1\rangle$ given in eq. (12.13) diverges, and the whole perturbative approach, in this form, is meaningless. Rather, we must start from the states that diagonalize H^1 . The explicit computation shows that, in the basis $|200\rangle, |210\rangle, |211\rangle, |21-1\rangle$,

$$H^1 \rightarrow \Delta \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (12.41)$$

where $\Delta = -3eEa_0$. Observe that the fact that the only non-vanishing matrix element is

$$\langle 210|z|200\rangle \quad (12.42)$$

together with $\langle 200|z|210\rangle = \langle 210|z|200\rangle^*$, is a consequence of the dipole selection rule. Even if the diagonal elements in eq. (12.41) are zero, there are non-vanishing elements off-diagonal. H^1 is diagonalized using

$$|\pm\rangle \equiv \frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle) \quad (12.43)$$

and, in the basis $|+\rangle, |-\rangle, |211\rangle, |21-1\rangle$, we have

$$H^1 \rightarrow \Delta \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (12.44)$$

Then the eigenstates of the Hamiltonian $H^0 + H^1$ are $|+\rangle, |-\rangle, |211\rangle, |21-1\rangle$. The first two have eigenvalues

$$E_{\pm} = -\frac{Ry}{4} \pm \Delta \quad (12.45)$$

where $-Ry/4$ is the unperturbed energy of the hydrogen atom in the state $n = 2$, while $|211\rangle$ and $|21-1\rangle$ have the same energy $-Ry/4$ as in the absence of the perturbation.

Observe that the eigenvalues $|+\rangle$ and $|-\rangle$ are mixtures of states with $l = 0$ and with $l = 1$. Thus they have indefinite parity and can have a non-vanishing dipole moment.

13 Applications of perturbation theory

13.1 The fine structure of the hydrogen atom

(Reference: M. Maggiore, “A modern introduction to quantum field theory”, pages 74–79. In this subsection we use units $\hbar = c = 1$.)

The Schrödinger equation receives relativistic corrections, that can be computed from the Dirac equation, or more generally in the framework of relativistic quantum field theory, as you will study next year. The result is that, in the non-relativistic limit, the Dirac equation reduces to a Schrödinger equations, of the form

$$\left[\frac{p^2}{2m} + V - \frac{p^4}{8m^3} - \frac{e}{4m^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) - \frac{e}{8m^2} (\nabla \cdot \mathbf{E}) \right] \psi = \varepsilon \psi, \quad (13.1)$$

where $V(\mathbf{x})$ is the interaction potential. For the hydrogen atom $V = V(r)$ and therefore

$$e\mathbf{E} = -\nabla V = -\mathbf{r} \left(\frac{1}{r} \frac{dV}{dr} \right), \quad (13.2)$$

so that

$$-\frac{e}{4m^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) = \frac{1}{2m^2} \frac{1}{r} \frac{dV}{dr} \mathbf{S} \cdot (\mathbf{r} \times \mathbf{p}) = \frac{1}{2m^2} \frac{1}{r} \frac{dV}{dr} \mathbf{S} \cdot \mathbf{L} \quad (13.3)$$

where $\mathbf{S} = \boldsymbol{\sigma}/2$ is the spin of the electron and \mathbf{L} is the orbital angular momentum. Therefore, in a radial potential $V(r)$, the first relativistic correction to the Schrödinger equation is given by

$$\left[\frac{p^2}{2m} + V - \frac{p^4}{8m^3} + \frac{1}{2m^2} \frac{1}{r} \frac{dV}{dr} \mathbf{S} \cdot \mathbf{L} - \frac{e}{8m^2} (\nabla \cdot \mathbf{E}) \right] \psi = \varepsilon \psi. \quad (13.4)$$

The correction term $-p^4/(8m^3)$ is easily understood, since it comes from the expansion of the relativistic expression $\varepsilon = (p^2 + m^2)^{1/2}$. The term $\sim \mathbf{S} \cdot \mathbf{L}$ is called the spin-orbit coupling and the term $\sim \nabla \cdot \mathbf{E}$ is known as the Darwin term.

Restricting now to the Coulomb potential

$$V(r) = -\frac{Z\alpha}{r} \quad (13.5)$$

we have

$$\frac{1}{r} \frac{dV}{dr} = \frac{Z\alpha}{r^3}. \quad (13.6)$$

Using

$$\nabla^2 \frac{1}{r} = -4\pi \delta^{(3)}(\mathbf{x}) \quad (13.7)$$

(see, e.g. Jackson (1975), Section 1.7 for the proof) we find

$$-e\nabla \cdot \mathbf{E} = +\nabla^2 V = -Z\alpha \nabla^2 \frac{1}{r} = 4\pi Z\alpha \delta^{(3)}(\mathbf{x}). \quad (13.8)$$

We can therefore write

$$(H_0 + H_{\text{pert}})\psi = \varepsilon\psi \quad (13.9)$$

where $H_0 = p^2/(2m) + V$ is the unperturbed Hamiltonian of the hydrogen atom and

$$H_{\text{pert}} = -\frac{p^4}{8m^3} + \frac{Z\alpha}{2m^2 r^3} \mathbf{S} \cdot \mathbf{L} + \frac{\pi Z\alpha}{2m^2} \delta^{(3)}(\mathbf{x}). \quad (13.10)$$

The spin-orbit term can be understood physically as follows. From eq. (6.70) we know that an electron with spin $\mathbf{S}_e = \boldsymbol{\sigma}/2$ in a magnetic field \mathbf{B} has an interaction energy

$$H_B = \frac{e}{m} \mathbf{S}_e \cdot \mathbf{B}, \quad (13.11)$$

where we used $g_e \simeq 2$ (recall also that in this section we set $\hbar = c = 1$). Examine the situation in the electron rest frame. In this frame, the nucleus rotates around the electron and generates a current $I = Ze/T$, where T is the orbital period. The period can be written in terms of the modulus L of the orbital angular momentum of the electron in the rest frame of the proton, using the fact that, for a circular orbit $L = mrv = 2\pi mr^2/T$. Using the Biot-Savart law,

$$B = \frac{2\pi I}{r} = \frac{2\pi Ze}{rT} = \frac{Ze}{mr^3} L. \quad (13.12)$$

and, since the magnetic field and the angular momentum point in the same direction,

$$\mathbf{B} = \frac{Ze}{mr^3} \mathbf{L}. \quad (13.13)$$

Therefore we would expect to have in the Hamiltonian a term

$$\frac{Z\alpha}{m^2 r^3} \mathbf{S} \cdot \mathbf{L}. \quad (13.14)$$

This agrees with eq. (13.10), except for a factor of 2. This is due to the fact that the electron rest frame is non-inertial, since the electron accelerates as it goes around the nucleus. The correct kinematic transformation gives the

missing factor $1/2$, and this effect goes under the name of Thomas precession. Dirac equation has the correct kinematic factor automatically built in, since it is the correct relativistic equation. Comparing with eq. (13.10), we see that the spin-orbit interaction is equivalent to the interaction of the spin with an internal magnetic field

$$\mathbf{B}_{\text{int}} = \frac{Ze}{2mr^3} \mathbf{L}. \quad (13.15)$$

The unperturbed levels of the hydrogen atom are highly degenerate, since they depend only on n . So, if we want to use non-degenerate perturbation theory, according to the discussion in Section 12.3 we must choose the “good” basis in each degenerate subspace, i.e. for each n .

For n given, there are two natural bases for an electron with angular momentum l and spin $s = 1/2$. One is given by the tensor products

$$|l_z\rangle \otimes |s s_z\rangle, \quad (13.16)$$

and the other by the kets

$$|j j_z; l s\rangle \quad (13.17)$$

which represent a state with total angular momentum j , made by the composition of orbital angular momentum l and spin s . The two bases are related by the Clebsch-Gordan coefficients. We saw that the “good” basis is the one which diagonalizes the perturbation Hamiltonian. Because of the spin-orbit term, l_z and s_z are not good quantum numbers, since

$$[L_z, \mathbf{S} \cdot \mathbf{L}] \neq 0, \quad [S_z, \mathbf{S} \cdot \mathbf{L}] \neq 0. \quad (13.18)$$

In contrast, l and s are good quantum numbers, since

$$[\mathbf{L}^2, \mathbf{S} \cdot \mathbf{L}] = [\mathbf{S}^2, \mathbf{S} \cdot \mathbf{L}] = 0. \quad (13.19)$$

Furthermore, all the components J_i of the total angular momentum commute with the Hamiltonian, so in particular J_z and \mathbf{J}^2 commute. This follows automatically from the fact that the Hamiltonian is invariant under rotation, but we can also easily check it explicitly: writing $\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{S} \cdot \mathbf{L}$ and using eq. (13.19), we see immediately that $[\mathbf{J}^2, \mathbf{S} \cdot \mathbf{L}] = 0$. Furthermore,

$$\begin{aligned} [J_z, 2\mathbf{S} \cdot \mathbf{L}] &= [J_z, \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2] \\ &= [J_z, \mathbf{J}^2] - [L_z + S_z, \mathbf{L}^2] - [L_z + S_z, \mathbf{S}^2] = 0. \end{aligned} \quad (13.20)$$

So, the “good” basis, that allows to use non-degenerate perturbation theory, is $|n j j_z; l s\rangle$. We will omit the label s , which for the electron has the fixed

value $s = 1/2$. Furthermore, it is clear from rotational invariance that the perturbed energy levels will not depend on j_z . Formally, this follows from the fact that $[J_{\pm}, H] = 0$, and J_{\pm} raise and lower the eigenvalue of J_z by one unit. So, we can also omit j_z , and to first order in perturbation theory the correction to the energy levels is given by

$$(\Delta E)_{njl} = \langle njl | H_{\text{pert}} | njl \rangle. \quad (13.21)$$

We must therefore compute the following expectation values:

(1) $\langle njl | p^4 | njl \rangle$: if ψ_{njl} is a solution of the unperturbed Schrödinger equation, then by definition $(p^2/(2m) + V)\psi_{njl} = \epsilon_n \psi_{njl}$, or

$$\frac{p^2}{2m} \psi_{njl} = \left(\epsilon_n + \frac{Z\alpha}{r} \right) \psi_{njl} \quad (13.22)$$

where

$$\epsilon_n = -\frac{mZ^2\alpha^2}{2n^2} \quad (13.23)$$

are the unperturbed energy levels. Therefore

$$\int d^3x \psi_{njl}^* p^4 \psi_{njl} = 4m^2 \langle njl | \left(\epsilon_n + \frac{Z\alpha}{r} \right)^2 | njl \rangle. \quad (13.24)$$

For a Coulomb potential $V = -Z\alpha/r$ one has

$$\langle njl | \frac{1}{r} | njl \rangle = \frac{m\alpha Z}{n^2}, \quad \langle njl | \frac{1}{r^2} | njl \rangle = \frac{(m\alpha Z)^2}{n^3(l + \frac{1}{2})} \quad (13.25)$$

and therefore

$$\langle njl | p^4 | njl \rangle = 4(mZ\alpha)^4 \left(-\frac{3}{4n^4} + \frac{1}{n^3(l + \frac{1}{2})} \right). \quad (13.26)$$

(2) $\langle njl | \mathbf{S} \cdot \mathbf{L} / r^3 | njl \rangle$: from $\mathbf{J} = \mathbf{L} + \mathbf{S}$ it follows that, when acting on $|njl\rangle$,

$$j(j+1) = l(l+1) + s(s+1) + 2\mathbf{S} \cdot \mathbf{L} \quad (13.27)$$

with $s = 1/2$, and using the wave function of the hydrogen atoms one has

$$\langle njl | \frac{1}{r^3} | njl \rangle = \frac{(m\alpha Z)^3}{n^3 l(l + \frac{1}{2})(l + 1)}, \quad \text{if } l \neq 0, \quad (13.28)$$

while, when $l = 0$, we have $j = s$ so, according to eq. (13.27), $\langle njl | \mathbf{S} \cdot \mathbf{L} | njl \rangle = 0$ if $l = 0$. Therefore

$$\langle njl | \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L} | njl \rangle = (1 - \delta_{l,0}) \frac{(m\alpha Z)^3}{2n^3 l(l + \frac{1}{2})(l + 1)} [j(j+1) - l(l+1) - \frac{3}{4}]. \quad (13.29)$$

(3) $\langle njl | \delta^3(\mathbf{x}) | njl \rangle$: this is easily computed:

$$\langle njl | \delta^3(\mathbf{x}) | njl \rangle = \int d^3x |\psi_{njl}(\mathbf{x})|^2 \delta^3(\mathbf{x}) = |\psi_{njl}(0)|^2 = \frac{(m\alpha Z)^3}{\pi n^3} \delta_{l,0}. \quad (13.30)$$

Putting all contributions together and considering the two cases $j = l \pm 1/2$ when $l \neq 0$, and $j = 1/2$ when $l = 0$, we find that the result can always be expressed only in terms of n, j , and there is no separate dependence on l . The final result is

$$(\Delta E)_{njl} = -\frac{m(Z\alpha)^4}{2n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right]. \quad (13.31)$$

Therefore the fine structure removes the degeneracy between states with the same principal quantum number n but different values of j . However, states with the same n, j and different l , as the states $2S_{1/2}$ and $2P_{1/2}$, are still degenerate at the level of the Dirac equation, i.e. at the level of the first relativistic correction. In principle one might look for higher-order corrections coming from the Dirac equation, using perturbation theory with respect to H_{pert} at higher orders (indeed, it is even possible to find a closed form for the energy levels predicted by the Dirac equation to all orders in α), but physically this is not meaningful since, starting from the next order, the corrections due to the quantum nature of the electromagnetic field come into play, and the correct framework for computing these corrections is quantum electrodynamics, rather than the Dirac equation where A_μ is treated as an external, given, classical field.

The structure of the energy levels of the hydrogen atom, including the fine structure correction (13.31) is shown in Fig. 5.

For instance, the separation between the states $2P_{3/2}$ and $2P_{1/2}$ of the hydrogen is, from eq. (13.31)

$$E_{2P_{3/2}} - E_{2P_{1/2}} = -\frac{m\alpha^4}{16} \frac{1}{8} + \frac{m\alpha^4}{16} \frac{5}{8} = \frac{m\alpha^4}{32} \simeq 4.53 \times 10^{-5} \text{ eV}, \quad (13.32)$$

corresponding to a frequency $f = \omega/(2\pi) \simeq 10.9$ GHz, in the domain of microwaves. Actually, the levels $2S_{1/2}$ and $2P_{1/2}$ are not exactly degenerate,

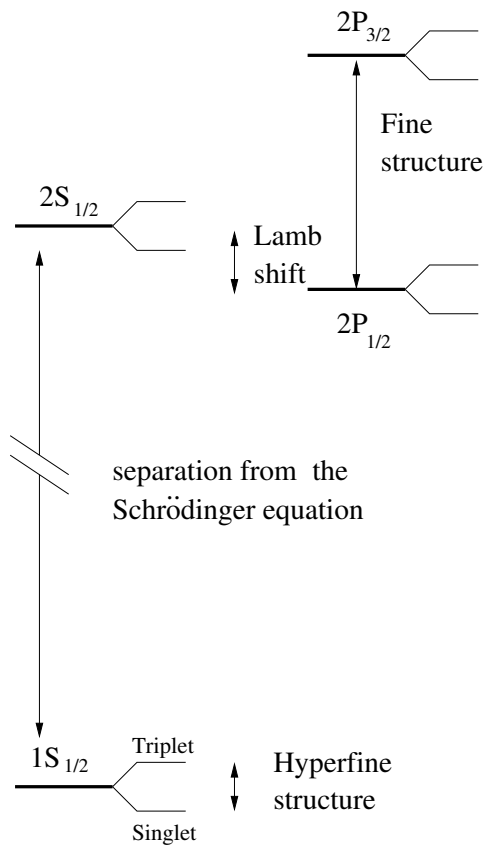


Figure 5: The lowest lying energy levels of the hydrogen atom. Note that the figure is *not* to scale. In reality, the fine structure splittings are smaller by a factor $\sim 10^{-5}$ compared to the separation between the levels $2S_{1/2}$ and $1S_{1/2}$, and the Lamb shift and the hyperfine structure are smaller by a factor ~ 10 compared to the fine structure.

as predicted by eq. (13.31), but rather have a splitting

$$E_{2S_{1/2}} - E_{2P_{1/2}} \simeq 1057 \text{ MHz} \quad (13.33)$$

known as the Lamb shift. The explanation for this splitting was, historically, one of the first successes of QED. At a comparable level, we find the hyperfine structure, due to the interaction between the spin of the nucleus and the spin of the electron, that we compute next.

13.2 Hyperfine structure

(Reference: Griffiths, Sect. 6.5). According to eqs. (6.71) and (6.74), the magnetic moments of the proton and of the electron are

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p c} \mathbf{S}_p, \quad \boldsymbol{\mu}_e = -\frac{g_e e}{2m_e c} \mathbf{S}_e, \quad (13.34)$$

where $g_e \simeq 2.0$ and $g_p \simeq 5.6$. A magnetic dipole $\boldsymbol{\mu}$ generates a magnetic field

$$\mathbf{B} = \frac{1}{r^3} [3(\boldsymbol{\mu} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}] + \frac{8\pi}{3} \boldsymbol{\mu} \delta^{(3)}(\mathbf{r}). \quad (13.35)$$

Then the Hamiltonian of the electron in the magnetic field of the proton is

$$\begin{aligned} H^1 &= -\boldsymbol{\mu}_e \cdot \mathbf{B} \\ &= \frac{g_p e}{2m_p c} \frac{g_e e}{2m_e c} \frac{1}{r^3} [3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e] \\ &\quad + \frac{8\pi}{3} \frac{g_p e}{2m_p c} \frac{g_e e}{2m_e c} \mathbf{S}_p \cdot \mathbf{S}_e \delta^{(3)}(\mathbf{r}). \end{aligned} \quad (13.36)$$

To first-order in perturbation theory the corresponding shift of the unperturbed energy levels of the hydrogen atom is therefore

$$E^1 = \langle njl | H^1 | njl \rangle. \quad (13.37)$$

We compute it for $l = 0$ (which also fixes $l_z = 0$). In this case $\psi_{n00}(\mathbf{x})$ depends only on r , so

$$\begin{aligned} &\int d^3x \psi_{n00}^*(\mathbf{x}) \frac{1}{r^3} [3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e] \psi_{n00}(\mathbf{x}) \\ &= \int_0^\infty dr r^2 |\psi_{n00}(r)|^2 \frac{1}{r^3} \int d\Omega [3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e]. \end{aligned} \quad (13.38)$$

For any two fixed vectors \mathbf{a} and \mathbf{b} , we have

$$\int d\Omega [3(\mathbf{a} \cdot \hat{\mathbf{r}})(\mathbf{b} \cdot \hat{\mathbf{r}}) - \mathbf{a} \cdot \mathbf{b}] = 0. \quad (13.39)$$

(Verify it!). Thus, the first term in H^1 does not contribute to the energy shift of the states $l = 0$.²⁹ The second term gives

$$E^1 = \frac{2\pi}{3} \frac{g_e g_p e^2}{m_p m_e c^2} |\psi_{n00}(0)|^2 \mathbf{S}_p \cdot \mathbf{S}_e. \quad (13.40)$$

So, there is an effective spin-spin coupling between the proton and the electron.³⁰ In the presence of this coupling, the spin of the electron and of the proton are not separately conserved, but the total spin $\mathbf{S} = \mathbf{S}_p + \mathbf{S}_e$ is conserved. In fact, observing that $[S_e^i, S_p^j] = 0$,

$$[S_e^i, \mathbf{S}_p \cdot \mathbf{S}_e] = [S_e^i, S_e^j S_p^j] = i\epsilon^{ijk} S_e^k S_p^j \quad (13.41)$$

is non-zero, but

$$[S_p^i, S_p^j S_e^j] = i\epsilon^{ijk} S_p^k S_e^j = -i\epsilon^{ijk} S_e^k S_p^j, \quad (13.42)$$

so

$$[S_e^i + S_p^i, S_e^j S_p^j] = 0. \quad (13.43)$$

Therefore, S^2 and S_z are good quantum numbers. We use the operator identity

$$\mathbf{S}^2 = \mathbf{S}_p^2 + \mathbf{S}_e^2 + 2\mathbf{S}_p \cdot \mathbf{S}_e \quad (13.44)$$

together with

$$\mathbf{S}_p^2 = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) = \frac{3}{4} \hbar^2, \quad (13.45)$$

and similarly $\mathbf{S}_e^2 = (3/4)\hbar^2$. On the other hand, the composition of two spin 1/2 gives a total spin $S = 0$ (singlet) or $S = 1$ (triplet), and

$$\mathbf{S}^2 = \hbar^2 S(S + 1). \quad (13.46)$$

²⁹Actually, the radial integral diverges at $r = 0$ since, on the states $l = 0$, $\psi_{nlm}(r)$ goes to a constant as $r \rightarrow 0$. However, this expression for the hydrogen wavefunction is certainly not valid down to $r = 0$, i.e. inside the nucleus. So we can simply cutoff the radial integral at a value r_{\min} . The radial integral then becomes finite and, when we multiply by the angular integral, which vanishes exactly, we get zero.

³⁰More precisely, the wavefunctions of the initial and final states are a tensor product of the orbital and spin wavefunctions, as in eq. (9.18). We are actually separating the problem of computing the matrix element into two steps. First, we have computed the matrix element with respect to the orbital wavefunction, remaining with an operator in the spin variables, and then we compute the matrix elements of this operator with respect to the spin states.

Thus

$$\begin{aligned}\mathbf{S}_p \cdot \mathbf{S}_e &= \frac{\hbar^2}{2} \left[S(S+1) - \frac{3}{2} \right] \\ &= \hbar^2 \begin{cases} -3/4 & (S=0) \\ +1/4 & (S=1) \end{cases}\end{aligned}\quad (13.47)$$

Thus, each level splits into a triplet and a singlet. For instance, for the ground state $n=1$, using eq. (8.17) we have

$$|\psi_{100}(0)|^2 = \frac{1}{\pi a_0^3}, \quad (13.48)$$

so finally

$$\begin{aligned}E_{1S_{1/2},\text{triplet}} - E_{1S_{1/2},\text{singlet}} &= \frac{2}{3} \frac{g_e g_p e^2 \hbar^2}{m_p m_e c^2 a_0^3} \\ &\simeq 5.88 \times 10^{-6} \text{ eV},\end{aligned}\quad (13.49)$$

or

$$\nu = \frac{E_{1S_{1/2},\text{triplet}} - E_{1S_{1/2},\text{singlet}}}{2\pi\hbar} \simeq 1420.4 \text{ MHz}. \quad (13.50)$$

The corresponding wavelength is $\lambda = c/\nu \simeq 21.105$ cm, in the radio waves. This line is of great importance in astrophysics for investigating the presence of neutral hydrogen in our and in other galaxies because radio waves, compared to most other wavelengths, are much less affected by absorption in the interstellar medium, and propagate to a very large distance. Furthermore, the temperature T such that $k_B T \simeq 5.88 \times 10^{-6}$ eV is $T \simeq 0.07$ K. Therefore, even in interstellar gas at very low temperatures, collisions easily excite the hydrogen atom into the triplet $1S_{1/2}$ state, from where it then decays into the (singlet) ground state, emitting radiation at $\lambda \simeq 21$ cm.

13.3 Zeeman effect

(Reference: Griffiths, Sect. 6.4). In the presence of an external magnetic field \mathbf{B}_{ext} , the electron in the hydrogen atom acquires an interaction energy

$$H_Z = -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S) \cdot \mathbf{B}_{\text{ext}}, \quad (13.51)$$

where

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e c} \mathbf{L}, \quad (13.52)$$

is the magnetic moment associated to the orbital motion, and

$$\boldsymbol{\mu}_S = -\frac{g_e e}{2m_e c} \mathbf{S} \simeq -\frac{e}{m_e c} \mathbf{S}, \quad (13.53)$$

is the spin magnetic moment. Therefore

$$H_Z \simeq \frac{e}{2m_e c} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}. \quad (13.54)$$

The effect of this perturbation (which is called the Zeeman effect) depends critically on whether the field \mathbf{B}_{ext} is smaller or larger than the typical magnetic field felt by the electron. The latter has been computed in eq. (13.15) and, taking $L \sim \hbar$, is of order 6 Tesla.

13.3.1 Weak-field Zeeman effect

If $B_{\text{ext}} \ll B_{\text{int}}$, the effect of the external magnetic field is much smaller than the fine structure perturbation. In this case we consider H_Z as a perturbation of the Hamiltonian $H_0 + H_{\text{pert}}$ given in eqs. (13.9) and (13.10), i.e. the Zeeman effect is a small perturbation of the fine-structure perturbation.

Therefore, when $B_{\text{ext}} \ll B_{\text{int}}$, we take as unperturbed Hamiltonian the Hamiltonian H_0 of the hydrogen atom plus the relativistic correction H_{pert} given in eq. (13.10), and we classify the unperturbed states as $|njj_zl\rangle$, as we already did in eq. (13.21), except that there we omitted j_z , since $H_0 + H_{\text{pert}}$ is rotationally invariant, so the levels cannot depend on j_z . Here the Zeeman perturbation will remove this degeneracy, so we keep j_z explicit. The perturbation Hamiltonian is H_Z , and the shift of the levels, to first order, is³¹

$$\Delta E_{njj_zl} = \langle njj_zl | H_Z | njj_zl \rangle = \frac{eB}{2m_e c} \langle njj_zl | L_z + 2S_z | njj_zl \rangle, \quad (13.55)$$

where we have chosen the z axis along the direction of B_{ext} , so $B_{\text{ext}} = B\hat{z}$. Writing $L_z + 2S_z = J_z + S_z$ we have

$$\langle jj_zl | L_z + 2S_z | jj_zl \rangle = \hbar j_z + \langle jj_zl | S_z | jj_zl \rangle. \quad (13.56)$$

³¹In principle, since the unperturbed states are degenerate with respect to j_z and l , here we should in principle consider the full matrix $\langle njj_zl | H_Z | njj'_z l' \rangle$, with j_z, j'_z, l and l' generic, and diagonalize it. However, the operator $L_z + 2S_z$ is clearly invariant under rotations around the z axis, so it commutes with J_z , and the matrix elements are automatically diagonal in j_z . Similarly, $L_z + 2S_z$ commutes with \mathbf{L}^2 .

where we suppressed the quantum number n , since this matrix of S_z does not depend on it. The action of S_z is known in the basis $|ll_z; ss_z\rangle$, where of course we have

$$S_z|ll_z; ss_z\rangle = \hbar s_z|ll_z; ss_z\rangle. \quad (13.57)$$

Thus, we must write the basis $|jj_z; ls\rangle$ in terms of the basis $|ll_z; ss_z\rangle$. The corresponding Clebsch-Gordan coefficients have already been computed explicitly in eq. (7.41). Recall that, for $l \neq 0$ we have two possibilities, $j = l + 1/2$ and $j = l - 1/2$. For $j = l + 1/2$, eq. (7.41) can be rewritten as

$$\begin{aligned} |j = l + \frac{1}{2}, j_z l\rangle &= \frac{1}{(2j)^{1/2}} \left[(j + j_z)^{1/2} |l, l_z = j_z - \frac{1}{2}; s = \frac{1}{2}, s_z = \frac{1}{2}\rangle \right. \\ &\quad \left. + (j - j_z)^{1/2} |l, l_z = j_z + \frac{1}{2}; s = \frac{1}{2}, s_z = -\frac{1}{2}\rangle \right] \end{aligned} \quad (13.58)$$

Therefore

$$\begin{aligned} \langle j = l + \frac{1}{2}, j_z l | S_z | j = l + \frac{1}{2}, j_z l \rangle &= \frac{\hbar}{2} \frac{1}{2j} [(j + j_z) - (j - j_z)] \\ &= \frac{\hbar j_z}{2j}. \end{aligned} \quad (13.59)$$

Similarly, when $j = l - 1/2$,

$$\begin{aligned} |j = l - \frac{1}{2}, j_z l\rangle &= \frac{1}{(2j + 2)^{1/2}} \left[-(j + 1 - j_z)^{1/2} |l, l_z = j_z - \frac{1}{2}; s = \frac{1}{2}, s_z = \frac{1}{2}\rangle \right. \\ &\quad \left. + (j + 1 + j_z)^{1/2} |l, l_z = j_z + \frac{1}{2}; s = \frac{1}{2}, s_z = -\frac{1}{2}\rangle \right], \end{aligned} \quad (13.60)$$

and

$$\langle j = l - \frac{1}{2}, j_z l | S_z | j = l - \frac{1}{2}, j_z l \rangle = -\frac{\hbar}{2} \frac{j_z}{j + 1}. \quad (13.61)$$

Equations (13.59) and (13.61) can be rewritten as a single equation valid for both cases,

$$\langle jj_z l | S_z | jj_z l \rangle = \frac{\hbar}{2} \frac{j(j + 1) - l(l + 1) + (3/4)}{j(j + 1)} j_z, \quad (13.62)$$

as one can check immediately substituting $j = l - 1/2$ or $j = l + 1/2$, respectively.

This result can be understood physically as follows. We observe that, since \mathbf{J} is constant, while \mathbf{S} is not, in a classical picture \mathbf{S} precesses rapidly

around \mathbf{J} , so classically, the time average of \mathbf{S} is equal to the projection of \mathbf{S} in the direction of \mathbf{J} ,

$$\mathbf{S}_{\text{ave}} = \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \mathbf{J}. \quad (13.63)$$

It is natural to expect that only \mathbf{S}_{ave} contributes to the matrix element.³² Then we expect that

$$\langle jj_z l | S_z | jj_z l \rangle = \langle jj_z l | \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} J_z | jj_z l \rangle. \quad (13.64)$$

Using $\mathbf{L} = \mathbf{J} - \mathbf{S}$ we have $L^2 = J^2 + S^2 - 2\mathbf{S} \cdot \mathbf{J}$, so

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2), \quad (13.65)$$

and

$$\langle jj_z l | S_z | jj_z l \rangle = \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \hbar j_z, \quad (13.66)$$

which indeed agrees with eq. (13.62). So we have found that

$$\begin{aligned} \langle jj_z l | L_z + 2S_z | jj_z l \rangle &= \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \hbar j_z \\ &\equiv g_J \hbar j_z, \end{aligned} \quad (13.67)$$

The factor g_J is called the Landé g -factor. In conclusion,

$$\Delta E_{njj_z l} = \mu_B B_{\text{ext}} g_J j_z, \quad (13.68)$$

where

$$\mu_B = \frac{e\hbar}{2m_e c} \simeq 5.788 \times 10^{-5} \text{ eV/T} \quad (13.69)$$

is called the Bohr magneton.

13.3.2 Strong-field Zeeman effect

We now consider the opposite limit, $B_{\text{ext}} \gg B_{\text{int}}$. In this regime, setting \mathbf{B}_{ext} along the z axis, the “good” quantum numbers are n, l, l_z, s_z , since \mathbf{L}^2 , L_z and S_z commute with the Zeeman Hamiltonian (13.54),

$$H_Z = \frac{e}{2m_e c} (L_z + 2S_z) B_{\text{ext}}. \quad (13.70)$$

³²This argument is somewhat heuristic since it uses the classical intuition for a quantity, such as spin, that does not have a classical counterpart. However, it will correctly reproduce the result (13.62) that we have obtained from first principles.

We consider first $H = H_0 + H_Z$, where as usual H_0 is the unperturbed Hamiltonian of the hydrogen atom. Clearly, the states $|nll_zs_z\rangle$ diagonalize it,

$$(H_0 + H_Z)|nll_zs_z\rangle = -\frac{Ry}{n^2} + \frac{e\hbar}{2m_e c}(l_z + 2s_z)B_{\text{ext}}. \quad (13.71)$$

The fine structure Hamiltonian H_{pert} given in eq. (13.10) is then treated as a perturbation of $H_0 + H_Z$, so to first order it induces a shift

$$\Delta E = \langle nll_zs_z | H_{\text{pert}} | nll_zs_z \rangle. \quad (13.72)$$

The contribution to ΔE of the terms $\sim p^4$ and $\sim \delta^{(3)}(\mathbf{x})$ in H_{pert} is computed exactly as before, since it only involves orbital degrees of freedom and therefore depends only on n, l . So, it is the same whether we use the basis $|nll_zs_z\rangle$, as we are doing here, or the basis $|njl\rangle$ that we used in Section 13.1. In contrast, for the spin-orbit term we use

$$\langle nll_zs_z | \mathbf{S} \cdot \mathbf{L} | nll_zs_z \rangle = \hbar^2 l_z s_z, \quad (13.73)$$

since the expectation values of S_x, S_y, L_x and L_y are zero on eigenstates of L_z and S_z .

If neither H_{pert} nor H_Z dominate, it is not obvious a priori what are the “good” state, in terms of which we can use the formulas of non-degenerate perturbation theory. Therefore, we must now resort to the full formalism of degenerate perturbation theory. Using for instance the basis $|nljj_z\rangle$, for each n we have a degenerate subspace. For instance, for $n = 2$ we have $l = 0$ or $l = 1$. If $l = 0$, necessarily $j = 1/2$, and $j_z = \pm 1/2$. So we have the two states

$$|n = 2, l = 0, j = 1/2, j_z = \pm 1/2\rangle. \quad (13.74)$$

For $l = 1$ we can have $j = 1/2$ or $j = 3/2$, so we have the six states

$$\begin{aligned} &|n = 2, l = 1, j = 1/2, j_z = \pm 1/2\rangle, \\ &|n = 2, l = 1, j = 3/2, j_z = \pm 1/2\rangle, \\ &|n = 2, l = 1, j = 3/2, j_z = \pm 3/2\rangle. \end{aligned} \quad (13.75)$$

So, in total we have eight states. In this space the perturbation Hamiltonian $H_{\text{pert}} + H_Z$ is an 8×8 matrix, which must be diagonalized to find the eigenkets and eigenvalues.

14 Variational principle

14.1 The method

(References: Shankar, Section 16.1, Griffiths, Chapter 7). Basic idea: if E_0 is the ground-state energy of an Hamiltonian H , and $|\psi\rangle$ is an arbitrary state, normalized so that $\langle\psi|\psi\rangle = 1$, we have

$$\langle\psi|H|\psi\rangle \geq E_0. \quad (14.1)$$

Proof. We denote by $|n\rangle$ be the normalized eigenkets of H , with eigenvalues E_n . Since they form a complete set, we can write

$$|\psi\rangle = \sum_n c_n |n\rangle. \quad (14.2)$$

The condition $\langle\psi|\psi\rangle = 1$ means that

$$\sum_n |c_n|^2 = 1. \quad (14.3)$$

Then

$$H|\psi\rangle = \sum_n c_n E_n |n\rangle, \quad (14.4)$$

and

$$\begin{aligned} \langle\psi|H|\psi\rangle &= \sum_m c_m^* \langle m|H \sum_n c_n |n\rangle \\ &= \sum_n |c_n|^2 E_n \\ &\geq E_0 \sum_n |c_n|^2 = E_0. \end{aligned} \quad (14.5)$$

To compute E_0 , the idea is therefore to try a class of trial wavefunctions, and minimize $\langle\psi|H|\psi\rangle$.

A nice feature of the method is that even a poor approximation to the wavefunction can yield a good approximation to the ground state energy. Suppose for instance that we try as eigenket a state $|\psi\rangle$ which is the superposition of the true ground state $|E_0\rangle$, with a small admixture of another energy eigenstate $|E_1\rangle$,

$$|\psi\rangle = (1 + \epsilon^2)^{-1/2} (|E_0\rangle + \epsilon|E_1\rangle). \quad (14.6)$$

where the factor $(1 + \epsilon^2)^{-1/2}$ ensures $\langle \psi | \psi \rangle = 1$. Recall that eigenkets with different eigenvalues are orthogonal, so $\langle E_0 | E_1 \rangle = 0$. Then

$$\begin{aligned} \langle \psi | H | \psi \rangle &= (1 + \epsilon^2)^{-1} (\langle E_0 | + \epsilon \langle E_1 |) H (|E_0\rangle + \epsilon |E_1\rangle) \\ &= (1 + \epsilon^2)^{-1} (\langle E_0 | + \epsilon \langle E_1 |) (E_0 | E_0\rangle + \epsilon E_1 | E_1\rangle) \\ &= (1 + \epsilon^2)^{-1} (E_0 + \epsilon^2 E_1) \end{aligned} \quad (14.7)$$

$$\begin{aligned} &= (1 - \epsilon^2) E_0 + \epsilon^2 E_1 + O(\epsilon^4) \\ &= E_0 + \epsilon^2 (E_1 - E_0) + O(\epsilon^4). \end{aligned} \quad (14.8)$$

Therefore, even if the error on $|\psi\rangle$ is $O(\epsilon)$, the error on the energy is only $O(\epsilon^2)$.

We next discuss some examples of the method.

Harmonic oscillator. Here of course we know the exact answer. However, let us pretend that we don't, and try a gaussian wavefunction, as would be suggested by the facts that: (1) the wavefunction must vanish at infinity. (2) it must be peaked around $x = 0$. (3) For the ground state, there must be no node (more nodes \rightarrow more wiggles \rightarrow more kinetic energy). So we try

$$\psi(x) = A e^{-bx^2}. \quad (14.9)$$

The normalization fixes $A = (2b/\pi)^{1/4}$, while b is treated as a free parameter, with respect to which we minimize $\langle \psi | H | \psi \rangle$. Using this wavefunction we can compute explicitly

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \int_{-\infty}^{\infty} dx \psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right] \psi(x) \\ &= \frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b}. \end{aligned} \quad (14.10)$$

Now we choose b so to minimize $\langle \psi | H | \psi \rangle$. Observe that the kinetic term favors b small (i.e. a very smooth wavefunction) and the potential term favors b large (i.e. a wavefunction peaked as much as possible around $x = 0$). The competition between these two effects gives

$$b_0 = \frac{m\omega}{2\hbar}, \quad (14.11)$$

$$E(b_0) = \langle \psi | H | \psi \rangle = \frac{1}{2} \hbar \omega. \quad (14.12)$$

In this case we even got the *exact* answer! However, this is a rather exceptional case, and in general with the variational principle we can only get close to the exact result.

Anharmonic oscillator. Consider the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \lambda x^4. \quad (14.13)$$

Using again the trial wavefunction (14.9) we get

$$\langle \psi | H | \psi \rangle = \frac{\hbar^2 b}{2m} + \frac{3\lambda}{16b^2}. \quad (14.14)$$

Minimizing,

$$b_0 = \left(\frac{3m\lambda}{4\hbar^2} \right)^{1/3}, \quad (14.15)$$

and

$$E(b_0) \equiv \langle \psi | H | \psi \rangle |_{b=b_0} = \frac{3}{8} \left(\frac{6\hbar^4 \lambda}{m^2} \right)^{1/3}. \quad (14.16)$$

Since H is positive definite, we conclude that the true ground state energy E_0 is in the range

$$0 < E_0 \leq E(b_0). \quad (14.17)$$

14.2 The ground state of Helium

In Section 10.1 we studied the He atom. The Hamiltonian is

$$H = \left[-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{r_1} \right] + \left[-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{r_2} \right] + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (14.18)$$

and we found that, neglecting the repulsion among the electrons,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2). \quad (14.19)$$

For the ground state, $nlm = n'l'm' = 100$ (and the spin state is the singlet). For an hydrogenoid atom with charge Ze ,

$$\psi_{100}(\mathbf{x}) = \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} e^{-Zr/a_0}, \quad (14.20)$$

so for the ground state, in this approximation,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0} \quad (14.21)$$

where, for He, $Z = 2$. The ground-state energy in this approximation is (see eq. (10.5))

$$E_{00} = -8 \text{ Ry} \simeq -109 \text{ eV}. \quad (14.22)$$

This is quite far from the observed value -78.6 eV, not surprisingly, since we neglected the repulsion among the two electron. The basic step in the variational principle is always to find a clever class of wavefunctions, not too complicated, but which still catches much of the physics, and here physical intuition plays an important role. In this problem, we can think that each electron actually does not see a charge $Z = +2$, but rather a screened charge, because of the effect of the other electron. This suggests to use the family of wavefunctions (14.21), treating Z as a variational parameter, rather than fixing it at $Z = 2$. This gives

$$E(Z) = \langle \psi | H | \psi \rangle = -2 \left(4Z - Z^2 - \frac{5}{8}Z \right) \text{Ry}, \quad (14.23)$$

which is minimized by

$$Z = Z_0 = 2 - \frac{5}{16}, \quad (14.24)$$

and

$$E(Z_0) = -2Z_0^2 \text{Ry} \simeq -77.5 \text{ eV}, \quad (14.25)$$

quite close to the exact result, and *above* it, as demanded by the inequality (14.1).

The method can be extended to compute the energies and wavefunction of higher excited states. Once we have determined our best approximation to the ground state $|E_0\rangle$, we can find the next excited state $|E_1\rangle$ searching for the minimum of $\langle \psi | H | \psi \rangle$ in the subspace orthogonal to $|E_0\rangle$. If we knew $|E_0\rangle$ exactly, we would get in this way a rigorous upper bound on the energy E_1 . However, the variational principle only gives us an approximation to the real ground state $|E_0\rangle$, so the corresponding upper bounds are not rigorous. However, if our approximation to $|E_0\rangle$ was good enough, the energy E_1 estimated for the first excited state will be close to the actual value.

In some cases we know exactly in which space to search for the next excited state. For instance, consider again the one-dimensional anharmonic oscillator $V(x) = \lambda x^4$. Since H is invariant under parity, the states have definite parity, i.e. the wavefunctions are classified as even or odd under $x \rightarrow -x$. Since more zeros requires more oscillations and therefore more kinetic energy, the energy of the eigenfunctions increases with the number of zeros: the ground state is a function with no zero, and in fact as a trial wavefunction we used a gaussian. The wavefunction of the next excited state will have a single zero at $x = 0$, and so on (compare with the wavefunctions of the harmonic oscillator shown in Figs. 1–4 on pages 20–22). Therefore,

we search the wavefunction for the first excited state in the space of odd wavefunctions. This space is exactly orthogonal to the space of state with even parity. In fact, if $\psi_{\text{even}}(x)$ is an even function, $\psi_{\text{even}}(-x) = \psi_{\text{even}}(x)$, and $\psi_{\text{odd}}(x)$ is an odd function, $\psi_{\text{odd}}(-x) = -\psi_{\text{odd}}(x)$, we obviously have

$$\int_{-\infty}^{\infty} dx \psi_{\text{even}}^*(x) \psi_{\text{odd}}(x) = 0. \quad (14.26)$$

In this case the resulting upper bound on E_1 is rigorous.

The same happens in three dimensions in a radial potential, where the wavefunction separates as $\psi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_{lm}(\theta, \phi)$. Since spherical harmonics with different values of l are orthogonal, we can apply the variational principle independently for each l .

14.3 The molecule H_2^+ . Covalent bond

(See Griffiths, Section 7.3, pages 304–308.) We consider now the hydrogen molecule ion H_2^+ , i.e. a single electron in the field of two separate protons. We want to show first of all that this molecule exists, i.e. that it is possible to put the two protons and the electron in a state that has lower energy, compared to a hydrogen atom plus a proton at infinity. Then, we will estimate the binding energy and the equilibrium distance between the protons.

The Hamiltonian of the system is

$$H = -\frac{\hbar^2}{2m_e} \nabla_x^2 - \frac{e^2}{|\mathbf{x} - \mathbf{x}_1|} - \frac{e^2}{|\mathbf{x} - \mathbf{x}_2|}, \quad (14.27)$$

where \mathbf{x} is the coordinate of the electron and ∇_x^2 is the Laplacian with respect to \mathbf{x} . The coordinates of the two protons are denoted by \mathbf{x}_1 and \mathbf{x}_2 , respectively. We put the first proton at the origin of the coordinates system, and the second in the position $\mathbf{x}_2 = (0, 0, R)$, and we treat R as our variational parameter. As trial wavefunction we take

$$\psi(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) = A [\psi_0(|\mathbf{x} - \mathbf{x}_1|) + \psi_0(|\mathbf{x} - \mathbf{x}_2|)], \quad (14.28)$$

where

$$\psi_0(r) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \quad (14.29)$$

is the usual wavefunction of the ground state of the hydrogen atom, and a_0 is the Bohr radius. This ansatz for the wavefunction is known as the LCAO techniques (Linear Combination of Atomic Orbitals). The constant A is determined by the normalization,

$$\begin{aligned} 1 &= \int d^3x |\psi(\mathbf{x})|^2 \\ &= |A|^2 \int d^3x \left[|\psi_0(|\mathbf{x} - \mathbf{x}_1|)|^2 + |\psi_0(|\mathbf{x} - \mathbf{x}_2|)|^2 \right. \\ &\quad \left. + 2\psi_0(|\mathbf{x} - \mathbf{x}_1|)\psi_0(|\mathbf{x} - \mathbf{x}_2|) \right]. \end{aligned} \quad (14.30)$$

Since d^3x is obviously invariant under translations $\mathbf{x} \rightarrow \mathbf{x} - \mathbf{x}_1$, we have

$$\int d^3x |\psi_0(|\mathbf{x} - \mathbf{x}_1|)|^2 = \int d^3x |\psi_0(|\mathbf{x}|)|^2 = 1, \quad (14.31)$$

and similarly for the second integral. To compute the third integral we introduce the notation

$$r_1 = |\mathbf{x} - \mathbf{x}_1|, \quad r_2 = |\mathbf{x} - \mathbf{x}_2|. \quad (14.32)$$

and we observe that, since $\mathbf{x}_1 = 0$ and $\mathbf{x}_2 = (0, 0, R)$, we have $r_1 = r$, while, denoting by θ the angle between the direction of \mathbf{x} and the z axis,

$$r_2^2 = (r \sin \theta)^2 + (r \cos \theta - R)^2, \quad (14.33)$$

i.e.

$$r_2 = \sqrt{r^2 + R^2 - 2rR \cos \theta}. \quad (14.34)$$

Thus

$$\begin{aligned} I &\equiv \int d^3x \psi_0(|\mathbf{x} - \mathbf{x}_1|) \psi_0(|\mathbf{x} - \mathbf{x}_2|) \\ &= \frac{2\pi}{\pi a_0^3} \int r^2 dr d \cos \theta \exp \left\{ -\frac{1}{a} \left[r + \sqrt{r^2 + R^2 - 2rR \cos \theta} \right] \right\}. \end{aligned} \quad (14.35)$$

We first perform the integral over $d \cos \theta$ at fixed r , introducing

$$y = \sqrt{r^2 + R^2 - 2rR \cos \theta}, \quad (14.36)$$

so that

$$d(y^2) = -2rR d \cos \theta, \quad (14.37)$$

i.e.

$$d \cos \theta = -\frac{y dy}{rR}. \quad (14.38)$$

The remaining integral over r is elementary, and gives

$$I = e^{-x} \left(1 + x + \frac{1}{3}x^2 \right), \quad (14.39)$$

where

$$x = \frac{R}{a_0}. \quad (14.40)$$

In terms of I , the normalization constant is

$$|A|^2 = \frac{1}{2(1+I)}. \quad (14.41)$$

The next step is to compute the expectation value of H on the trial wavefunction. We use the fact that the Laplacian with respect to \mathbf{x} is the same

as the Laplacian with respect to $\mathbf{x} - \mathbf{x}_1$, or $\mathbf{x} - \mathbf{x}_2$, so (setting for simplicity $\hbar = c = 1$, and therefore $e^2 = \alpha$)

$$\left[-\frac{1}{2m_e} \nabla_x^2 - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_1|} \right] \psi_0(|\mathbf{x} - \mathbf{x}_1|) = E_0 \psi_0(|\mathbf{x} - \mathbf{x}_1|), \quad (14.42)$$

where

$$E_0 = -\frac{1}{2} m_e \alpha^2 \simeq -13.6 \text{ eV} \quad (14.43)$$

is the ground state energy of the hydrogen atom. Similarly,

$$\left[-\frac{1}{2m_e} \nabla_x^2 - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_2|} \right] \psi_0(|\mathbf{x} - \mathbf{x}_2|) = E_0 \psi_0(|\mathbf{x} - \mathbf{x}_2|). \quad (14.44)$$

Therefore

$$\begin{aligned} H\psi(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) &= A \left[-\frac{1}{2m_e} \nabla_x^2 - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_1|} - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_2|} \right] \psi_0(|\mathbf{x} - \mathbf{x}_1|) \\ &\quad + A \left[-\frac{1}{2m_e} \nabla_x^2 - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_1|} - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_2|} \right] \psi_0(|\mathbf{x} - \mathbf{x}_2|) \\ &= A \left[E_0 \psi_0(|\mathbf{x} - \mathbf{x}_1|) - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_2|} \psi_0(|\mathbf{x} - \mathbf{x}_1|) \right] \\ &\quad + A \left[E_0 \psi_0(|\mathbf{x} - \mathbf{x}_2|) - \frac{\alpha}{|\mathbf{x} - \mathbf{x}_1|} \psi_0(|\mathbf{x} - \mathbf{x}_2|) \right] \\ &= E_0 \psi(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) \\ &\quad - A\alpha \left[\frac{1}{|\mathbf{x} - \mathbf{x}_2|} \psi_0(|\mathbf{x} - \mathbf{x}_1|) + \frac{1}{|\mathbf{x} - \mathbf{x}_1|} \psi_0(|\mathbf{x} - \mathbf{x}_2|) \right], \end{aligned} \quad (14.45)$$

and

$$\begin{aligned} \langle \psi | H | \psi \rangle &= E_0 - |A|^2 \alpha \int d^3x [\psi_0(|\mathbf{x} - \mathbf{x}_1|) + \psi_0(|\mathbf{x} - \mathbf{x}_2|)] \\ &\quad \times \left[\frac{1}{|\mathbf{x} - \mathbf{x}_2|} \psi_0(|\mathbf{x} - \mathbf{x}_1|) + \frac{1}{|\mathbf{x} - \mathbf{x}_1|} \psi_0(|\mathbf{x} - \mathbf{x}_2|) \right] \\ &= E_0 - |A|^2 \alpha \int d^3x \left[\frac{\psi_0^2(|\mathbf{x} - \mathbf{x}_1|)}{|\mathbf{x} - \mathbf{x}_2|} + \frac{\psi_0^2(|\mathbf{x} - \mathbf{x}_2|)}{|\mathbf{x} - \mathbf{x}_1|} \right] \\ &\quad - |A|^2 \alpha \int d^3x \left[\frac{\psi_0(|\mathbf{x} - \mathbf{x}_1|) \psi_0(|\mathbf{x} - \mathbf{x}_2|)}{|\mathbf{x} - \mathbf{x}_1|} + \frac{\psi_0(|\mathbf{x} - \mathbf{x}_2|) \psi_0(|\mathbf{x} - \mathbf{x}_1|)}{|\mathbf{x} - \mathbf{x}_2|} \right]. \end{aligned} \quad (14.46)$$

Observe that d^3x is invariant under the shift of integration variable $\mathbf{x} \rightarrow -\mathbf{x} + \mathbf{x}_1 + \mathbf{x}_2$. Under this transformation

$$|\mathbf{x} - \mathbf{x}_2| \rightarrow |-\mathbf{x} + \mathbf{x}_1| = |\mathbf{x} - \mathbf{x}_1|, \quad (14.47)$$

so the two terms in the first integral give the same result, and similarly for the two terms in the second integral. Then

$$\begin{aligned}
\langle \psi | H | \psi \rangle &= E_0 - 2|A|^2 \alpha \int d^3x \frac{\psi_0^2(|\mathbf{x} - \mathbf{x}_1|)}{|\mathbf{x} - \mathbf{x}_2|} \\
&\quad - 2|A|^2 \alpha \int d^3x \frac{\psi_0(|\mathbf{x} - \mathbf{x}_1|)\psi_0(|\mathbf{x} - \mathbf{x}_2|)}{|\mathbf{x} - \mathbf{x}_1|} \\
&\equiv E_0 - 2|A|^2 \alpha \frac{1}{a_0} [D + X] \\
&= E_0 - \frac{\alpha}{a_0} \frac{D + X}{1 + I}. \tag{14.48}
\end{aligned}$$

D is called the *direct integral*, and X the *exchange integral*. Computing them explicitly one finds

$$D = \frac{1}{x} - \left(1 + \frac{1}{x}\right) e^{-2x}, \tag{14.49}$$

and

$$X = (1 + x) e^{-x}, \tag{14.50}$$

where again $x = R/a_0$. Recall that we are using units $\hbar = c = 1$, so $a_0 = 1/(m_e \alpha)$, and

$$\frac{\alpha}{a_0} = m_e \alpha^2 = -2E_0. \tag{14.51}$$

Thus

$$\langle \psi | H | \psi \rangle = E_0 \left[1 + 2 \frac{D + X}{1 + I} \right]. \tag{14.52}$$

To this term we must subtract the repulsion energy between the two protons,

$$V_{pp} = +\frac{\alpha}{R} = \frac{a_0}{R} \frac{\alpha}{a_0} = -2 \frac{a_0}{R} E_0. \tag{14.53}$$

In conclusion, the total energy of the system is

$$\begin{aligned}
E(R) &= E_0 \left[1 + 2 \frac{D + X}{1 + I} \right] - 2 \frac{a_0}{R} E_0 \\
&\equiv (-E_0) F(x), \tag{14.54}
\end{aligned}$$

where

$$F(x) = -1 + \frac{2}{x} \frac{[1 - (2/3)x^2]e^{-x} + (1 + x)e^{-2x}}{1 + [1 + x + (1/3)x^2]e^{-x}}. \tag{14.55}$$

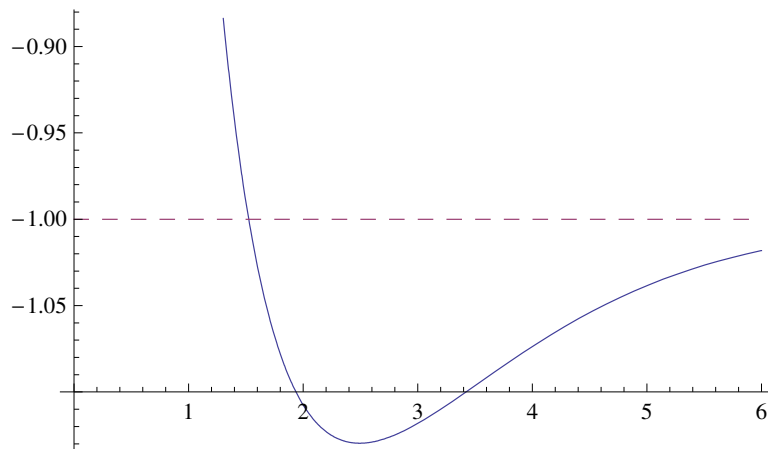


Figure 6: The function $F(x)$ (solid line), compared to the value -1 (dashed line).

The function $F(x)$ is plotted in Fig. 6. We see the following features. First of all, for $R \rightarrow \infty$, $F(x) \rightarrow -1$, as it should. The energy of the system becomes the same as the energy of the hydrogen atom when the second proton is at infinity. However, decreasing R , $F(x)$ goes *below* -1 . Recall that each value of R represent a trial wavefunction. Since the true energy of the system is lower or equal than the value that we find with the variational technique, this means that bonding *does* occur, since for some values of R the energy of this system is lower than the energy of a hydrogen atom.

Our best approximation to the true wavefunction and to the true value of the binding energy is obtained from the value of R that gives the lowest possible value of $F(x)$. The minimum of $F(x)$ is located at $x \simeq 2.493$, corresponding to

$$R \simeq 2.49a_0 \simeq 1.32 \text{ \AA}, \quad (14.56)$$

and, since at the minimum $F(x) \simeq -1.13$, we get a a binding energy

$$E_{\text{binding}} \simeq 0.13 \times 13.6 \text{ eV} \simeq 1.77 \text{ eV}. \quad (14.57)$$

This fits quite well with the experimental data: the true equilibrium radius is at $R \simeq 1.06 \text{ \AA}$, and the binding energy is 2.8 eV , higher than the binding energy obtained with the variational principle, as it should.

Physically what happens is that the the single electron of the H_2^+ molecule attracts both the first proton and the second with a strength that, except for

R below a critical value, overcomes the repulsion between the two protons. This is an example of *covalent bond*, in which the electron is shared among the two protons.

It is intuitively clear that, in order to do the job, the electron must be preferentially located between the two protons, i.e. in the middle of the H_2^+ molecule rather than on one side of it, otherwise the repulsion between the protons would be dominant. Indeed, with the test wavefunction (14.28) that we used, the wavefunction is large when $\mathbf{x} = (\mathbf{x}_1 + \mathbf{x}_2)/2$, since in this case the two terms in eq. (14.28) are equal, and sum up.

Consider in contrast the trial wavefunction

$$\psi(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) = A [\psi_0(|\mathbf{x} - \mathbf{x}_1|) - \psi_0(|\mathbf{x} - \mathbf{x}_2|)], \quad (14.58)$$

This wavefunction vanishes when $\mathbf{x} = (\mathbf{x}_1 + \mathbf{x}_2)/2$, and more generally it is suppressed when the electron is in the central region between the two protons. Thus, we expect that it does not lead to bonding. We can check it without performing any new calculation, simply by tracking the effect of this change of sign in the previous computation. We now find

$$|A|^2 = \frac{1}{2(1 - I)}, \quad (14.59)$$

and the contribution of the exchange integral gets a minus sign, so eq. (14.48) is replaced by

$$\begin{aligned} \langle \psi | H | \psi \rangle &= E_0 - \frac{\alpha}{a_0} \frac{D - X}{1 - I} \\ &\equiv (-E_0)G(x), \end{aligned} \quad (14.60)$$

where

$$G(x) = -1 + \frac{2}{x} \frac{-[1 - (2/3)x^2]e^{-x} + (1 + x)e^{-2x}}{1 - [1 + x + (1/3)x^2]e^{-x}}. \quad (14.61)$$

This function is plotted in Fig. 7, and we see that it is always above -1 .

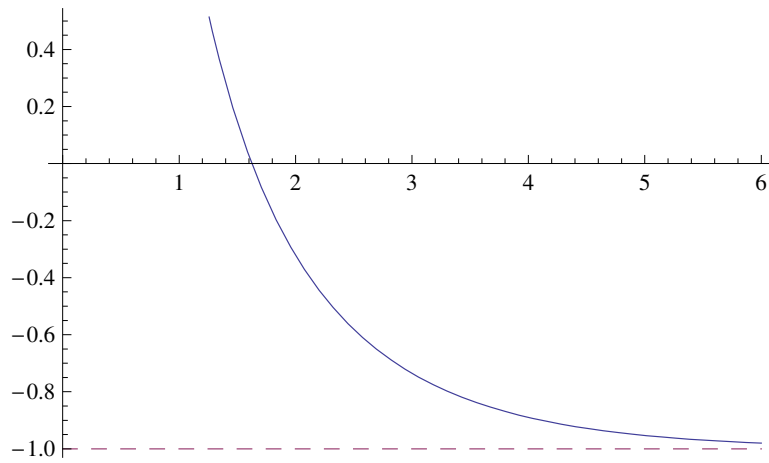


Figure 7: The function $G(x)$ (solid line), compared to the value -1 (dashed line).

15 WKB approximation

15.1 The method

In this section we discuss the WKB (Wentzel-Kramers-Brillouin) method, which, as we will see, corresponds to a semiclassical approximation. We start from the one-dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi. \quad (15.1)$$

Introducing

$$p(x) \equiv \sqrt{2m[E - V(x)]}, \quad (15.2)$$

the Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} = -\frac{p^2(x)}{\hbar^2}\psi. \quad (15.3)$$

We now define

$$\lambda(x) \equiv \frac{2\pi\hbar}{p(x)}. \quad (15.4)$$

Let l be the typical length-scale over which $V(x)$ changes appreciably. We wish to study the situation $\lambda(x) \ll l$, that is, over a distance several wavelengths $\lambda(x)$ the potential does not change much. If $V(x)$ were exactly constant, the solution would be a plane wave

$$\psi(x) = Ae^{\pm ikx}, \quad (15.5)$$

where

$$k = \sqrt{2m[E - V]}/\hbar. \quad (15.6)$$

If the typical length l over which $V(x)$ changes appreciably is much larger than $\lambda(x)$, over a region containing many wavelengths the potential $V(x)$ is approximately constant. So, if $E > V(x)$, we expect that the solution will remain practically sinusoidal, except for the fact that the wavelength and the amplitude change slowly with x .

In contrast, for $E < V$, if V is exactly constant we have the solutions

$$\psi(x) = Ae^{\pm\kappa x} \quad (15.7)$$

where

$$\kappa = \sqrt{2m[V - E]}/\hbar, \quad (15.8)$$

and again we expect that this will still be the approximate form of the solution when $V(x)$ depends slowly on x .

To formalize this intuition, we first of all write the complex function $\psi(x)$ in terms of two real functions $A(x)$ and $\phi(x)$,

$$\psi(x) = A(x)e^{i\phi(x)}, \quad (15.9)$$

Substituting this form of ψ into the Schrödinger equation and setting to zero the real and the imaginary parts of the equation, we get the two real equations

$$A'' = A \left[(\phi')^2 - \frac{p^2(x)}{\hbar^2} \right], \quad (15.10)$$

and

$$2A'\phi' + A\phi'' = 0, \quad (15.11)$$

where the prime denotes the derivative with respect to x . The second equation can be rewritten as

$$\partial_x (A^2 \partial_x \phi) = 0, \quad (15.12)$$

which gives

$$A(x) = \frac{\text{const.}}{\sqrt{\phi'}}. \quad (15.13)$$

Until now everything was exact, since eq. (15.9) is a completely general way of writing a complex function ψ in terms of two real functions A and ϕ . The approximation comes now, assuming that

$$\left| \frac{A''}{A} \right| \ll (\phi')^2, \quad (15.14)$$

and

$$\left| \frac{A''}{A} \right| \ll \frac{p^2(x)}{\hbar^2}. \quad (15.15)$$

This is motivated by the fact that, for an exactly constant potential, in the solution (15.18) the amplitude A is exactly constant, so $A''/A = 0$, while $\phi(x) = kx$, so $\phi' = k$; thus, in the more general case of $V(x)$ slowly varying, we expect that the amplitude will change over the scale of the potential, $A''/A = O(1/l^2)$, and we are assuming that $1/l \ll 1/\lambda$. Then eq. (15.10) gives

$$\phi' \simeq \pm \frac{p(x)}{\hbar}, \quad (15.16)$$

and therefore

$$\phi(x) \simeq \pm \frac{1}{\hbar} \int_{x_0}^x dx' p(x'). \quad (15.17)$$

Thus,

$$\psi(x) \simeq \frac{C}{\sqrt{p(x)}} \exp \left\{ \pm \frac{i}{\hbar} \int^x p(x') dx' \right\}. \quad (15.18)$$

Notice that

$$|\psi(x)|^2 = \frac{C^2}{p(x)}, \quad (15.19)$$

so it is inversely proportional to the speed $v(x)$ of the particle. This is exactly the behavior expected in the semiclassical limit, recall our discussion on eqs. (4.13)–(4.15). The reason is that, if we formally let $\hbar \rightarrow 0$, $\lambda(x)$ in eq. (15.4) goes to zero, and therefore it is necessarily much smaller than the scale on which the potential changes appreciably.³³ So, the approximation expressed by eqs. (15.14) and (15.15) is in fact a semiclassical approximation.

Before exploring in more detail the physical consequences of this result, it is useful to give an alternative derivation. We write

$$\psi(x) = e^{if(x)/\hbar}, \quad (15.20)$$

where now $f(x)$ is a generic *complex* function. The Schrödinger equation becomes

$$i\hbar f'' - (f')^2 + p^2(x) = 0. \quad (15.21)$$

We now expand

$$f(x) = f_0(x) + \hbar f_1(x) + \hbar^2 f_2(x) + \dots \quad (15.22)$$

and equate terms of the same order in \hbar (keeping only the first two orders). To zeroth order in \hbar we get

$$(f'_0)^2 = p^2(x). \quad (15.23)$$

so

$$f_0(x) = \pm \int_{x_0}^x dx' p(x'). \quad (15.24)$$

To order \hbar we get

$$if''_0 = 2f'_0 f'_1, \quad (15.25)$$

so

$$-2if'_1 = \frac{f''_0}{f'_0} = \partial_x \ln |f'_0|. \quad (15.26)$$

³³This statement will need some qualification when x is close to the classical turning points of the potential. We will come back to this point below.

Therefore

$$f_1 = i \ln |\partial_x f_0|^{1/2} + c, \quad (15.27)$$

and

$$\begin{aligned} \psi(x) &\simeq e^{i[f_0(x)+\hbar f_1(x)]/\hbar} \\ &= e^{-\ln |\partial_x f_0|^{1/2}} \exp \left\{ \pm \frac{i}{\hbar} \int_{x_0}^x dx' p(x') + ic \right\} \\ &= \frac{A}{\sqrt{|p(x)|}} \exp \left\{ \pm \frac{i}{\hbar} \int_{x_0}^x dx' p(x') \right\}, \end{aligned} \quad (15.28)$$

where the (complex) integration constant c has been reabsorbed in the overall constant A .

This derivation makes it even more clear that we are performing a systematic expansion for \hbar small (more precisely, small with respect to quantities with the same dimensions appearing in the wavefunction), so this is a semiclassical expansion.

Observe that the assumption that $\lambda(x)$ is small with respect to the scale on which $V(x)$ changes, becomes necessarily wrong near the turning points, because there $p(x)$ goes to zero, so $\lambda(x)$ diverges.

15.2 Potential with two infinite walls. Bohr-Sommerfeld conditions

As a first application consider a potential $V(x)$ that consists of two infinite walls at $x = 0$ and $x = a$, and changes gently for $0 < x < a$. The most general WKB solution for $0 < x < a$ is the superposition of the two solutions with the \pm signs at the exponential,

$$\psi(x) \simeq \frac{1}{\sqrt{p(x)}} \left[C_+ e^{i\phi(x)} + C_- e^{-i\phi(x)} \right] \quad (15.29)$$

where

$$\phi(x) = \frac{1}{\hbar} \int_0^x dx' p(x'). \quad (15.30)$$

We have chosen $x = 0$ as the lower limit of the integral. Observe that the choice of the lower integration limit x_0 in eq. (15.28) is arbitrary, since we can always reabsorb it in a redefinition of the constant A , so we have chosen $x_0 = 0$ without loss of generality. It is convenient to rewrite the solution as

$$\psi(x) \simeq \frac{1}{\sqrt{p(x)}} \left[C_1 \sin \phi(x) + C_2 \cos \phi(x) \right] \quad (15.31)$$

The condition that $\psi(x) = 0$ at $x = 0$ gives $C_2 = 0$ and the condition $\psi(a) = 0$ gives

$$\int_0^a p(x) dx \simeq n\pi\hbar, \quad (n = 1, 2, 3, \dots). \quad (15.32)$$

This is the Bohr-Sommerfeld quantization condition. For high values of n , this gives higher and higher values of $p(x)$, and therefore smaller $\lambda(x)$, therefore the semiclassical approximation becomes better and better: *the semiclassical approximation works well for large values of the quantum number n* . This is the modern form of the Bohr correspondence principle, which was a guiding principle in the early days of quantum mechanics. The corresponding energy quantization is obtained using eq. (15.2),

$$\int_0^a \sqrt{2m[E_n - V(x)]} dx = n\pi\hbar. \quad (15.33)$$

If the potential for $0 < x < a$ is exactly flat, we expect to recover the exact result. In fact, in this case eq. (15.32) gives

$$p_n = \frac{n\pi\hbar}{a}, \quad (15.34)$$

and $E_n = p_n^2/(2m) = n^2\pi^2\hbar^2/(2ma^2)$, which are indeed the exact results for a free particle confined between two infinite walls.

For a general, non-flat potential, the Bohr-Sommerfeld quantization condition determines approximately the allowed energy levels. The WKB approximation is better and better in the semiclassical limit $n \rightarrow \infty$.

15.3 Tunneling

(We follow Griffiths, Section 8.2). In the classically forbidden region $E < V(x)$ we have $p(x)$ imaginary, and

$$\psi(x) \simeq \frac{C}{\sqrt{|p(x)|}} \exp \left\{ \pm \frac{1}{\hbar} \int^x dx' |p(x')| \right\}. \quad (15.35)$$

If the classically forbidden region extends from, say, $x = 0$, up to $x = \infty$, the coefficient of the exponentially growing term must be zero, and

$$\psi(x) \simeq \frac{C}{\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int^x dx' |p(x')| \right\}. \quad (15.36)$$

If the forbidden region extend over a finite range $0 < x < a$ in principle we have both term, but the coefficient of the growing exponential is typically very small and can be neglected (see Griffiths, Problem 8.10).

Consider for instance the scattering from a rectangular barrier with a bumpy top. If the barrier is at $0 < x < a$, and the boundary condition is that there is an incident flux coming from the left, for $x < 0$ we have

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (15.37)$$

where A is the incident amplitude, B is the amplitude for reflection, and $k = \sqrt{2mE}/\hbar$. To the right of the barrier, for $x > a$, we only have the transmitted part,

$$\psi(x) = Fe^{ikx}. \quad (15.38)$$

The transmission probability is

$$T = \frac{|F|^2}{|A|^2}. \quad (15.39)$$

Suppose that the energy E is smaller than the height of the barrier. Then, in the intermediate region, the solution is

$$\psi(x) \simeq \frac{C}{\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_0^x dx' |p(x')| \right\}. \quad (15.40)$$

Actually, there will be also a small admixture of the exponentially growing solution, so we should write

$$\begin{aligned} \psi(x) \simeq & \frac{C}{\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_0^x dx' |p(x')| \right\} \\ & + \frac{D}{\sqrt{|p(x)|}} \exp \left\{ +\frac{1}{\hbar} \int_0^x dx' |p(x')| \right\}. \end{aligned} \quad (15.41)$$

However you can check, performing explicitly the matchings in $x = 0$ and $x = a$, that for a very high or very wide barrier D is very small and the contribution of the second term can be neglected. Then, the total decrease in amplitude for $x = 0$ to $x = a$ is

$$\frac{|F|}{|A|} \sim \exp \left\{ -\frac{1}{\hbar} \int_0^a dx |p(x)| \right\}. \quad (15.42)$$

Therefore, apart from prefactors, the transmission probability is

$$T \sim e^{-2\gamma}, \quad (15.43)$$

with

$$\gamma = \frac{1}{\hbar} \int_0^a dx |p(x)|. \quad (15.44)$$

15.3.1 Application: Gamow's theory of α -decay

(See Griffiths, pages 322-324.)

Radioactive nuclei can decay by spontaneous emission of an alpha particle (two protons and two neutrons bound together, i.e. the nucleus of ${}^4\text{He}$). In general, the formalism of quantum mechanics that we have developed cannot account for processes in which the number and type of particle changes, such as the process in which an initial nucleus decays into a final nucleus plus an alpha particle. This will rather be the subject of the course of Quantum Field Theory. However, for this process we can develop an instructive, although heuristic, picture, modeling it in terms of an interaction potential between a (hypothetical) pre-existing alpha particle and the final nucleus.

The α particle has charge $+2$, so there is a Coulomb repulsion with the remaining nucleus, but at short distances this is dominated by the attraction due to strong interactions. The overall potential felt by the α -particle can then be approximated by

$$V(x) = -V_0, \quad r < r_1, \quad (15.45)$$

where $r_1 \simeq 1$ fm is the typical radius of the nuclear potential, and

$$V(x) = \frac{2Ze^2}{r}, \quad r > r_1 \quad (15.46)$$

is the Coulomb potential between the α -particle (charge $+2e$) and the rest of the nucleus, with charge Ze . [We use units for the electric charge such that the Coulomb potential is q_1q_2/r . In these units the fine structure constant is $\alpha = e^2/(\hbar c)$]. The potential is shown in Fig. 8.

Denote by E the energy of the α particle. In order for the initial nucleus to exist at all, it is necessary that

$$E < \frac{2Ze^2}{r_1}, \quad (15.47)$$

so classically the α -particle is bound in the potential. In a potential well we can have bound states with energy E either positive or negative. In radioactive nuclei $E > 0$, so the α particle can escape via tunneling.

Let r_2 the classical turning point of a particle with energy E , given by

$$\frac{(Ze)(2e)}{r_2} = E. \quad (15.48)$$

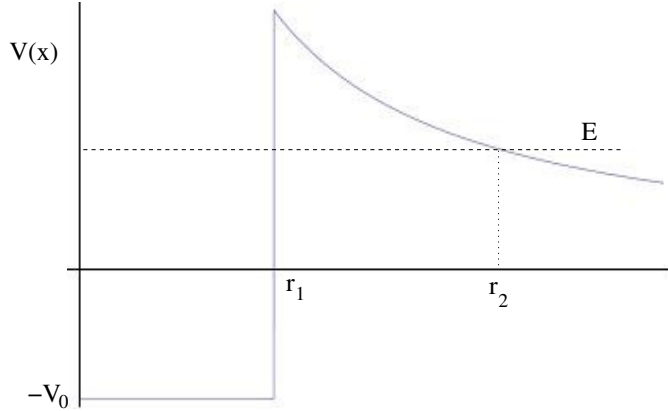


Figure 8: The potential $V(x)$

Then the tunneling probability is given by eq. (15.43) with

$$\gamma = \frac{1}{\hbar} (2m)^{1/2} \int_{r_1}^{r_2} dr \sqrt{\frac{2Ze^2}{r} - E}, \quad (15.49)$$

where m here is the mass of the α -particle. This integral can be performed exactly. However, one typically has $r_1 \ll r_2$, and in this limit one finds

$$\gamma \simeq \frac{K_1 Z}{E^{1/2}} - K_2 (Zr_1)^{1/2}, \quad (15.50)$$

with

$$K_1 = \frac{e^2 \pi \sqrt{2m}}{\hbar} = \frac{e^2}{\hbar c} \pi \sqrt{2mc^2} \simeq 1.980 \text{ MeV}^{1/2}, \quad (15.51)$$

and

$$K_2 = \frac{4e\sqrt{m}}{\hbar} \simeq 1.485 \text{ fm}^{-1/2}. \quad (15.52)$$

If the α -particle inside the nucleus has an average velocity v , $2r_1/v$ is the average time between collisions with the walls, so $v/(2r_1)$ is the number of collisions per unit time, and the probability of escape at each collision is $e^{-2\gamma}$. If we denote by P the probability that the α -particle is inside the nucleus, we have

$$\frac{dP}{dt} = -\frac{1}{\tau} P, \quad (15.53)$$

where

$$\frac{1}{\tau} = \frac{v}{2r_1} e^{-2\gamma} \quad (15.54)$$

so the lifetime of the radioactive nucleus is

$$\tau = \frac{2r_1}{v} e^{2\gamma}. \quad (15.55)$$

For a nucleus with nucleon number (number of protons plus number of neutrons) equal to A , one uses the relation

$$r_1 \simeq 1.07 \text{ fm } A^{1/3}, \quad (15.56)$$

which is well verified experimentally (the dependence on A expresses the fact that the volume of the nucleus is proportional to A). Since the α -particle is non-relativistic, its total energy $E_{tot} = \sqrt{m_\alpha c^2 + p^2}$ can be written approximately as $m_\alpha c^2 + E$ where $E = p^2/(2m_\alpha)$ is its kinetic energy. The kinetic energy E is then computed from

$$E \simeq m_P c^2 - m_D c^2 - m_\alpha c^2, \quad (15.57)$$

where P and D refer to the “parent” and “daughter” nuclei, i.e. the nuclei before and after the radioactive decay. Using these values, one can reproduce remarkably well the lifetime of nuclei that disintegrate via α -decay, over a huge range of scales for the lifetime, from approximately 10^{11} yr for U^{238} and Th^{232} down to approximately 10^{-5} yr for U^{226} and Th^{228} , see Fig. 8.6 of Griffiths. This huge range of possible lifetimes is due to the fact that the energy of the emitted α particle can change significantly, and it appears at the exponent.

15.3.2 Application: thermonuclear reactions in stars

The interaction between two nuclei is described, in a first approximation, by the potential given in eqs. (15.45) and (15.46) and shown in Fig. 8. More precisely, we can analyze the encounter of two nuclei with charges Z_1 and Z_2 and masses m_1 and m_2 , in terms of a single particle with reduced mass $m = m_1 m_2 / (m_1 + m_2)$, moving in the potential

$$V(x) = -V_0, \quad r < r_1, \quad (15.58)$$

where $r_1 \simeq 1 \text{ fm}$ is the typical radius of the nuclear potential, and

$$V(x) = \frac{Z_1 Z_2 e^2}{r}, \quad r > r_1. \quad (15.59)$$

Let v be the relative velocity, so

$$E = \frac{1}{2}mv^2, \quad (15.60)$$

it the kinetic energy in the center of mass. At large distances, the nuclei experience their mutually repulsive Coulomb interaction. If they approached with a sufficiently large speed, they could overcome the potential barrier classically, and fuse together. However, even in the most favorable case of two hydrogen nuclei, $Z_1 = Z_2 = 1$, with $r_1 = 1$ fm the height of the barrier is (using units $\hbar = c = 1$ and recalling eq. (8.31),

$$V(r_1) = \frac{\alpha}{1 \text{ fm}} \simeq \frac{200 \text{ MeV}}{137} \simeq 1.5 \text{ MeV}. \quad (15.61)$$

Using the value of the Boltzmann constant $k_B \simeq 8.6 \times 10^{-5} \text{ eV K}^{-1}$, this corresponds to a temperature

$$T \simeq \frac{1.5 \text{ MeV}}{k_B} \simeq 1.7 \times 10^{10} \text{ K}. \quad (15.62)$$

The temperature at the center of the Sun is about 1.5×10^7 K, so it is much lower than that required for the nuclei to overcome the barrier classically. They can however overcome it quantum-mechanically, tunneling under the barrier from the classical turning point (r_2 in Fig. 8) down to r_1 . Thus nuclear fusion in stars, which is their source of energy, can only take place because of quantum tunneling.

We want to compute the rate of nuclear reactions in the core of stars, as a function of their temperature. The penetration probability for a particle of kinetic energy E , from $r = r_2$ to $r = r_1$, is of course the same as the escape probability from $r = r_1$ to $r = r_2$ that we computed in the Gamow theory of α -decay, since it is given by the same WKB integral. Thus, we can simply use eqs. (15.43) and (15.50), replacing $2Z$ with Z_1Z_2 . Furthermore, we have seen that the energy E is very small with respect to the height of the barrier, so we can keep just the first term in eq. (15.50), and we get

$$\gamma \simeq \frac{e^2\pi\sqrt{2m}}{2\hbar} \frac{Z_1Z_2}{E^{1/2}}. \quad (15.63)$$

Writing $q_1 = Z_1e$, $q_2 = Z_2e$ and $E = (1/2)mv^2$, we can rewrite this as

$$\gamma = \frac{\pi q_1 q_2}{\hbar v}, \quad (15.64)$$

and the penetration probability is

$$T \sim \frac{1}{v} e^{-2\gamma} \simeq \frac{1}{v} \exp \left\{ -\frac{2\pi q_1 q_2}{\hbar v} \right\}, \quad (15.65)$$

where we also included the prefactor $1/v$ that comes from the $1/\sqrt{|p(x)|}$ dependence of the WKB wavefunction. The result is very sensitive to the relative speed v . In the star core, the nuclei are thermally distributed according to the Boltzmann distribution, so the probability of finding a nucleus with velocity between v and $v + dv$ is proportional to

$$d^3v e^{-E/k_B T} = 4\pi v^2 dv e^{-mv^2/(2k_B T)}. \quad (15.66)$$

The rate of the nuclear reactions is therefore proportional to

$$\int_0^\infty dv v \exp \left\{ -\frac{2\pi q_1 q_2}{\hbar v} - \frac{mv^2}{k_B T} \right\}. \quad (15.67)$$

This integral can be computed with the saddle point method, simply finding the value $v = v_*$ that maximizes the exponential (observe that prefactors play no role to leading order, so we could have neglected them from the beginning). This gives

$$v_* = \left(\frac{2\pi q_1 q_2 k_B T}{\hbar m} \right)^{1/3}. \quad (15.68)$$

Recall that eq. (15.50) was found assuming that $r_2 \gg r_1$. We can check the consistency of our approach verifying that the turning point $r_2 = r_*$, which corresponds to the velocity v_* , is indeed much larger than $r_1 \simeq 1$ fm. The turning point is determined by $E = V(r_2)$, so

$$\frac{1}{2} m v_*^2 = \frac{q_1 q_2}{r_*}, \quad (15.69)$$

or

$$r_* = \frac{2q_1 q_2}{m v_*^2}. \quad (15.70)$$

For the proton-proton reaction (recalling that the reduced mass is $m = m_p/2$) and $T = 1.5 \times 10^7$ K, this gives

$$r_* = \hbar c \left(\frac{4\alpha}{\pi^2} \right)^{1/3} \frac{1}{[m_p c^2 (k_B T)^2]^{1/3}} \simeq 250 \text{ fm}, \quad (15.71)$$

so $r_* \gg R_1 \simeq 1$ fm, and our approximations are indeed valid.

Coming back to reactions with Z_1 and Z_2 generic, the rate of the nuclear reaction is therefore proportional to the factor

$$P \equiv \exp \left\{ -\frac{2\pi q_1 q_2}{\hbar v_*} - \frac{mv_*^2}{k_B T} \right\} = \exp \{ -(T_0/T)^{1/3} \}, \quad (15.72)$$

where

$$T_0 = \left(\frac{3}{2} \right)^3 \left(\frac{2\pi q_1 q_2}{\hbar} \right)^2 \frac{m}{k_B}. \quad (15.73)$$

For the proton-proton reaction, we get

$$T_0 \simeq 3.9 \times 10^8 \text{ K}, \quad (15.74)$$

so at the center of the Sun, where $T = 1.5 \times 10^7 \text{ K}$, $P \simeq 0.05$. When moving outside the inner core of the star the temperature drops. For instance, when $T = 10^5 \text{ K}$, P drops to $O(10^{-7})$. We see that nuclear reactions in star depends very sensitively on the temperature, and for this reason they are called *thermonuclear* reactions.

15.4 Potential with smooth classical turning points

(Reference: Griffiths, Section 8.3).

We have seen above how the Bohr-Sommerfeld quantization emerges when we have infinite walls. If however the potential is smooth near the turning point, the matching of WKB solutions is more complicated. Close to the turning point $\lambda(x)$ diverges, and the WKB approximation is not valid. The strategy that we will adopt is then the following.

Near a turning point $x = x_0$ we approximate

$$V(x) \simeq V(x_0) + V'(x_0)(x - x_0) = E + V'(x_0)(x - x_0). \quad (15.75)$$

In a region sufficiently close to the turning point, so that eq. (15.75) is applicable, the Schrödinger equation can be solved exactly, as we will see in a moment. This exact solution can then be matched, both to its left and to its right, to the WKB solution. In this way we match the two WKB solutions, to the left and to the right of the turning point, not directly, since they cannot be extrapolated up to x_0 , but rather bridging them using the exact solution that holds close to the turning point.

We first compute the exact solution near the turning point. We assume for definiteness that $V'(x_0) > 0$. Inserting eq. (15.75) the Schrödinger equation becomes a Airy equation,

$$\frac{d^2\psi}{dz^2} = z\psi, \quad (15.76)$$

where $z = \alpha(x - x_0)$ and

$$\alpha = \left[\frac{2m}{\hbar^2} V'(x_0) \right]^{1/3}. \quad (15.77)$$

The general solution is eq. (15.76),

$$\psi(x) = a \text{Ai}(\alpha x) + b \text{Bi}(\alpha x), \quad (15.78)$$

where $\text{Ai}(z)$ and $\text{Bi}(z)$ are special functions known as Airy functions. They can be defined in terms of their integral representation

$$\text{Ai}(z) = \frac{1}{\pi} \int_0^\infty ds \cos\left(\frac{s^3}{3} + sz\right), \quad (15.79)$$

$$\text{Bi}(z) = \frac{1}{\pi} \int_0^\infty ds \left[\exp\left(-\frac{s^3}{3} + sz\right) + \sin\left(\frac{s^3}{3} + sz\right) \right]. \quad (15.80)$$

Any symbolic manipulation program, such as Mathematica or Maple, knows the Airy functions and treats them as easily as, say, the trigonometric functions, so you can easily compute their numerical value, plot them, differentiate them, etc. We will need below their asymptotic expansion. For $z \gg 1$,

$$\text{Ai}(z) \simeq \frac{1}{2\pi^{1/2} z^{1/4}} \exp\left\{-\frac{2}{3}z^{3/2}\right\}, \quad (15.81)$$

$$\text{Bi}(z) \simeq \frac{1}{\pi^{1/2} z^{1/4}} \exp\left\{+\frac{2}{3}z^{3/2}\right\}. \quad (15.82)$$

For z negative and large, instead,

$$\text{Ai}(z) \simeq \frac{1}{\pi^{1/2} (-z)^{1/4}} \sin\left[\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}\right], \quad (15.83)$$

$$\text{Bi}(z) \simeq \frac{1}{\pi^{1/2} (-z)^{1/4}} \cos\left[\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}\right]. \quad (15.84)$$

We next compute the WKB solution, to the left and to the right of the turning point x_0 . We set for simplicity $x_0 = 0$ (recall also that we assumed $V'(x_0) > 0$). To the left of the turning point, and sufficiently far from it so that the WKB approximation holds, the solution is

$$\psi(x) = \frac{1}{\sqrt{p(x)}} \left[B \exp\left\{\frac{i}{\hbar} \int_x^0 dx' p(x')\right\} + C \exp\left\{-\frac{i}{\hbar} \int_x^0 dx' p(x')\right\} \right] \quad (15.85)$$

where

$$\begin{aligned}
p(x) &= \sqrt{2m(E - V(x))} \\
&\simeq \sqrt{2m[E - (E + V'(0)x)]} \\
&= \sqrt{2mV'(0)} \sqrt{-x} \\
&= \hbar\alpha^{3/2} \sqrt{-x}.
\end{aligned} \tag{15.86}$$

Observe that $p(x)$ is real, since $x < 0$. Then

$$\begin{aligned}
\frac{1}{\hbar} \int_x^0 dx' p(x') &= \alpha^{3/2} \int_x^0 dx' (-x')^{1/2} \\
&= \frac{2}{3} (-\alpha x)^{3/2}.
\end{aligned} \tag{15.87}$$

So, to the left of the turning point and sufficiently far from it, so that the WKB approximation is valid, but still sufficiently close to it so that the expansion (15.75) holds, the WKB solution is

$$\psi(x) = \frac{1}{\hbar^{1/2} \alpha^{3/4} (-x)^{1/4}} \left[B \exp \left\{ i \frac{2}{3} (-\alpha x)^{3/2} \right\} + C \exp \left\{ -i \frac{2}{3} (-\alpha x)^{3/2} \right\} \right]. \tag{15.88}$$

To the right of the turning point, when the WKB approximation is again valid, we get

$$\begin{aligned}
\psi(x) &= \frac{D}{\sqrt{|p(x)|}} \exp \left\{ -\frac{1}{\hbar} \int_0^x dx' |p(x')| \right\} \\
&\simeq \frac{D}{\hbar^{1/2} \alpha^{3/4} x^{1/4}} \exp \left\{ -\frac{2}{3} (\alpha x)^{3/2} \right\}.
\end{aligned} \tag{15.89}$$

We now perform the matching of these solutions. We first compare the asymptotic form of (15.78) to the WKB solution valid to its right, given by eq. (15.89). Using the asymptotic expansion (15.81) we see that

$$a = \left(\frac{4\pi}{\alpha\hbar} \right)^{1/2} D, \quad b = 0. \tag{15.90}$$

We next perform the matching of eq. (15.78) with the WKB solution to its left. Using the expansion of $\text{Ai}(z)$ for $z \ll -1$, eq. (15.78) (and setting $b = 0$) becomes

$$\psi(x) \simeq \frac{a}{\pi^{1/2} (-\alpha x)^{1/4}} \sin \left[\frac{2}{3} (-\alpha x)^{3/2} + \frac{\pi}{4} \right]. \tag{15.91}$$

Comparing this with the WKB solution (15.88) we get B and C in terms of a and therefore, using eq. (15.90), in terms of D ,

$$B = -i e^{+i\pi/4} D, \quad C = +i e^{-i\pi/4} D. \quad (15.92)$$

Therefore, the solution (15.85) for $x < 0$ becomes

$$\psi(x) = \frac{2D}{\sqrt{p(x)}} \sin \left[\frac{1}{\hbar} \int_x^0 dx' p(x') + \frac{\pi}{4} \right]. \quad (15.93)$$

Consider now the situation in which there are two smooth turning points, one at x_1 (with $V'(x_1) < 0$) and one at $x_2 > x_1$ (with $V'(x_2) > 0$).

Performing the matching in x_2 , we find that the wavefunction in the region $x_1 < x < x_2$ is given by eq. (15.93), with $x_0 = 0$ replaced by $x_0 = x_2$,

$$\psi(x) = \frac{2D}{\sqrt{p(x)}} \sin \left[\frac{1}{\hbar} \int_x^{x_2} dx' p(x') + \frac{\pi}{4} \right]. \quad (15.94)$$

We can repeat a similar calculations at the leftmost turning point x_1 . The computation is basically the same, except that now $V'(x_1) > 0$. This second computation gives, for the wavefunction at $x_1 < x < x_2$

$$\psi(x) \simeq -\frac{2D'}{\sqrt{p(x)}} \sin \left[-\frac{1}{\hbar} \int_{x_1}^x dx' p(x') - \frac{\pi}{4} \right]. \quad (15.95)$$

Equations (15.94) and (15.95) are two expression for the same wavefunction in the region $x_1 < x < x_2$, so they must be equal. Therefore the arguments of the sines must be the same modulo π (an overall minus sign can be reabsorbed into the normalization constants D and D'), so we must have

$$\left[\frac{1}{\hbar} \int_x^{x_2} dx' p(x') + \frac{\pi}{4} \right] = \left[-\frac{1}{\hbar} \int_{x_1}^x dx' p(x') - \frac{\pi}{4} \right] + n\pi, \quad (15.96)$$

and therefore

$$\int_{x_1}^{x_2} dx' p(x') = \left(n - \frac{1}{2} \right) \pi \hbar, \quad n = 1, 2, \dots \quad (15.97)$$

Observe that, since $p(x) \geq 0$, the integral is positive and therefore the allowed values for the integer n are $n \geq 1$.

Equation (15.97) is the Bohr-Sommerfeld quantization condition, when both turning points are smooths, rather than given by infinite walls. Recall

that it holds when the WKB approximation is justified, i.e. in the semi-classical limit. Its power reside in the fact that we can use it to compute (approximately) the allowed energy level, without ever solving a Schrödinger equation, simply by computing an integral.

We can repeat the same computation when at $x = x_1$ there is an infinite wall while at $x_2 > x_1$ we have a smooth turning point. The result is

$$\int_{x_1}^{x_2} dx' p(x') = \left(n - \frac{1}{4} \right) \pi \hbar, \quad n = 1, 2, \dots \quad (15.98)$$

16 Time-dependent perturbation theory

(Reference: Shankar, Chapter 18). We consider the Hamiltonian

$$H = H_0 + H_1(t), \quad (16.1)$$

where H_0 is a time-independent Hamiltonian whose eigenvalue problem has already been solved, and $H_1(t)$ is a *time-dependent* perturbation. The eigenkets of H_0 are no longer stationary states because of the perturbation, i.e. it is no longer true that under time evolution they simply acquire a phase. Rather, in general they will mix among them (except in the case of adiabatic perturbations, that we will study below). The typical question in which we are interested in this case is the following: suppose that at an initial time (say, $t = 0$, or $t = -\infty$) the system is in an eigenstate $|i\rangle$ of H_0 .³⁴ What is the amplitude for it to be in an eigenstate $|f\rangle$ at a later time (e.g. at $t = +\infty$)?

To answer this question, we expand a generic time-dependent ket $|\psi(t)\rangle$ in the eigenstates $|n\rangle$ of H_0 , defined by

$$H_0|n\rangle = E_n|n\rangle. \quad (16.2)$$

These form a complete set, so we can write

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle. \quad (16.3)$$

If $H_1 = 0$, we know that

$$c_n(t) = c_n(0)e^{-iE_n t/\hbar}. \quad (16.4)$$

It is then useful to write $c_n(t) = d_n(t) \exp\{-iE_n t/\hbar\}$, so any time-dependence in $d_n(t)$ is due to the fact that there is a non-vanishing time-dependent perturbation H_1 . So, we write

$$|\psi(t)\rangle = \sum_n d_n(t)e^{-iE_n t/\hbar}|n\rangle. \quad (16.5)$$

The Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = [H_0 + H_1(t)]|\psi(t)\rangle \quad (16.6)$$

³⁴Shankar denotes the eigenstates of H_0 as $|i^0\rangle$, $|f^0\rangle$, etc. to stress that they are eigenstates of the *unperturbed* Hamiltonian. Since we will never consider the eigenstates of the full Hamiltonian H , we denote the eigenstates of H_0 simply as $|i\rangle$, $|f\rangle$, etc.

becomes

$$\sum_n e^{-iE_n t/\hbar} [i\hbar \dot{d}_n(t) + d_n(t)E_n] |n\rangle = \sum_n d_n(t) e^{-iE_n t/\hbar} [E_n + H_1(t)] |n\rangle, \quad (16.7)$$

or

$$\sum_n i\hbar \dot{d}_n(t) e^{-iE_n t/\hbar} |n\rangle = \sum_n d_n(t) e^{-iE_n t/\hbar} H_1(t) |n\rangle. \quad (16.8)$$

Taking the scalar product with $\langle f|$,

$$i\hbar \dot{d}_f(t) e^{-iE_f t/\hbar} = \sum_n d_n(t) e^{-iE_n t/\hbar} \langle f|H_1(t)|n\rangle. \quad (16.9)$$

Writing

$$\omega_{fn} = \frac{E_f - E_n}{\hbar}, \quad (16.10)$$

we get

$$\dot{d}_f(t) = -\frac{i}{\hbar} \sum_n \langle f|H_1(t)|n\rangle e^{i\omega_{fn} t} d_n(t). \quad (16.11)$$

This is the fundamental result. Until now we have made no approximation. Let us now assume that $H_1(t)$ is small, and solve perturbatively in H_1 . To zeroth order, i.e. if we neglect H_1 altogether, we have of course

$$d_n(t) = \delta_{ni}, \quad (16.12)$$

i.e. $d_n(t)$ is one if $|n\rangle$ is equal to the initial state $|i\rangle$, and zero otherwise. To first order, we plug this result into the right-hand side of eq. (16.11) and we get

$$\dot{d}_f(t) = -\frac{i}{\hbar} \langle f|H_1(t)|i\rangle e^{i\omega_{fi} t} \quad (16.13)$$

whose solution, with the initial condition $d_n(t_0) = \delta_{ni}$, is

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_{t_0}^t dt' \langle f|H_1(t')|i\rangle e^{i\omega_{fi} t'}. \quad (16.14)$$

This gives the transition amplitude to first order. One can compute the result to second order plugging this expression into the right-hand side of eq. (16.11), and so on. In principle, we can iterate the procedure to arbitrarily high orders. We will however limit ourselves to first-order perturbation theory.

For $i \neq f$, eq. (16.14) gives the probability amplitude

$$d_f(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' \langle f | H_1(t') | i \rangle e^{i\omega_{fi}t'}. \quad (16.15)$$

The probability of the transition $i \rightarrow f$ is

$$P_{i \rightarrow f} = |d_f(t)|^2. \quad (16.16)$$

We next analyze some examples of perturbations.

16.1 Sudden perturbations

Suppose that, at some time $t = 0$, the Hamiltonian changes suddenly from H to H' , so

$$\begin{aligned} H(t) &= H & (t < 0), \\ H(t) &= H' & (t > 0). \end{aligned} \quad (16.17)$$

This is an idealization of the situation in which the Hamiltonian changes on a time scale much shorter than the characteristic timescale of the system. Integrating the Schrödinger equation from $t = -\epsilon$ to $t = +\epsilon$ we get

$$|\psi(t = \epsilon)\rangle - |\psi(t = -\epsilon)\rangle = -\frac{i}{\hbar} \int_{-\epsilon}^{\epsilon} dt H(t) |\psi(t)\rangle. \quad (16.18)$$

If $H(t)$ is finite (i.e. it is not proportional to a Dirac delta), the right-hand side goes to zero for $\epsilon \rightarrow 0$, and therefore

$$\lim_{t \rightarrow 0^+} |\psi(t)\rangle - \lim_{t \rightarrow 0^-} |\psi(t)\rangle = 0. \quad (16.19)$$

In other words, the state of the system is unchanged under a sudden perturbation. Physically, the system had no time to adjust to the change of the Hamiltonian. However, if $|\psi\rangle$ was an eigenstate of H_0 , in general it will no longer be an eigenstate of $H_0 + H_1$. We can expand it in the basis $|n'\rangle$ of the new eigenstate, and compute the probability amplitude $\langle n' | \psi \rangle$.

Example 1. (Shankar, Exercise 18.2.3). Consider a particle in a box of length L , with $0 < x < L$. The wavefunctions of the stationary states are

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \quad (16.20)$$

for $0 < x < L$ and $\psi_n(x) = 0$ otherwise. Suppose that the width of the box changes suddenly to $2L$, and that the particle was in the ground state of the initial box. The amplitude that the particle is in the ground state of the new box is given by

$$\mathcal{M} = \int_0^{2L} dx \psi_{\text{before}}^*(x) \psi_{\text{after}}(x) \quad (16.21)$$

where

$$\psi_{\text{before}}(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \quad (16.22)$$

if $0 < x < L$ and vanishes for $L < x < 2L$, while

$$\psi_{\text{after}}(x) = \left(\frac{1}{L}\right)^{1/2} \sin\left(\frac{\pi x}{2L}\right). \quad (16.23)$$

for $0 < x < 2L$, and zero otherwise. This gives

$$\mathcal{M} = \frac{\sqrt{2}}{L} \int_0^L dx \sin\frac{\pi x}{L} \sin\frac{\pi x}{2L} = \frac{4\sqrt{2}}{3\pi}, \quad (16.24)$$

so the probability of remaining in the ground state is $32/(3\pi)^2 \simeq 0.36$.

Example 2. (Shankar, page 477). A more realistic example is an electron in the 1s state of a nucleus of charge Z . Suppose that the nucleus undergoes inverse β decay, $n \rightarrow pe^- \bar{\nu}_e$, i.e. it emits a relativistic electron (and an antineutrino), and becomes a nucleus of charge $Z + 1$. The time for a relativistic electron to get out of the 1s shell is

$$\tau \sim \frac{a_0}{Zc}, \quad (16.25)$$

since a_0/Z is the radius of the 1s shell. The characteristic timescale T of the electron in the 1s state can be estimated using again the fact that the size of the orbit is a_0/Z . On the other hand, the kinetic energy of the electron in the 1s state of a nucleus of charge Z can be estimated from eq. (8.38) with $\alpha \rightarrow Z\alpha$, so (reinstating c) $E_{\text{kin}} = (1/2)m_e c^2 (Z\alpha)^2$, which shows that the average velocity of the 1s electron is $v \sim Z\alpha c$. Thus

$$T \sim \frac{a_0/Z}{Z\alpha c} = \frac{a_0}{Z^2\alpha c}. \quad (16.26)$$

Therefore $\tau/T = Z\alpha$. If $Z \ll 137$ this is much smaller than one, and the sudden approximation holds. Thus, after the decay of the nucleus, the 1s

electron remains in the same state as before, i.e. in the 1s state of a nucleus with charge Z . The wavefunction is given by eq. (8.17) with $a_0 \rightarrow a_0/Z$,

$$\psi_{1s}^{(Z)} = \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} e^{-Zr/a_0}. \quad (16.27)$$

However, this is not the same as the wavefunction of the 1s state of the final nucleus, which has charge $Z + 1$, and therefore has

$$\psi_{1s}^{(Z+1)} = \left(\frac{(Z+1)^3}{\pi a_0^3} \right)^{1/2} e^{-(Z+1)r/a_0}. \quad (16.28)$$

The amplitude for the electron to remain in the 1s state of the new nucleus is therefore

$$\begin{aligned} A &= \int d^3x \left(\psi_{1s}^{(Z+1)} \right)^* \psi_{1s}^{(Z)} \\ &= 4\pi \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} \left(\frac{(Z+1)^3}{\pi a_0^3} \right)^{1/2} \int_0^\infty dr r^2 e^{-(2Z+1)r/a_0} \\ &= \frac{[Z(Z+1)]^{3/2}}{(Z+1/2)^3}. \end{aligned} \quad (16.29)$$

16.2 Adiabatic perturbations

The opposite limit is the one in which the Hamiltonian changes very slowly, compared to the typical timescale of the system. Suppose that at $t < 0$ $H = H_0$ and, at $t = 0$, we switch slowly a perturbation $H_1(t)$, so the total Hamiltonian becomes $H(t) = H_0 + H_1(t)$.

In this case one can prove a theorem (valid to all orders in perturbation theory) known as the *adiabatic theorem*, which states that, if at $t = 0$ the system is an eigenket $|n^0\rangle$ of the initial Hamiltonian H_0 , the state of the system will evolve smoothly into the corresponding eigenket $|n(t)\rangle$ of the Hamiltonian $H(t)$. (For the proof of the theorem, see Griffiths, sect. 10.1.2).

Taking again the case of a particle in a box that expands from length L to $2L$, if the particle is initially in the ground state of the box of size L , and we slowly expand the box to size $2L$, the particle will finally be in the ground state of the new box. Observe that here the overall change in the Hamiltonian is not small at all! However, the adiabatic theorem just require that the rate of change is slow.

The subtle issue here is when the perturbation can be considered slow enough. The result is that the typical frequency of the perturbation must

be much smaller than the typical frequency *differences* $\omega_n - \omega_m$ between the unperturbed energy levels (see again Griffiths, sect. 10.1.2). Therefore, in the presence of degeneracy, we are never in the condition where the adiabatic theorem can be applied.

16.3 Periodic perturbations. Fermi's golden rule

This is the most important case, since it represents for instance the interaction with an external electromagnetic wave. Consider

$$H_1(t) = 2V(\mathbf{x}) \cos \omega t = V(\mathbf{x})(e^{i\omega t} + e^{-i\omega t}). \quad (16.30)$$

We suppose that at an initial time $t_0 = 0$ the system is in an initial state $|i\rangle$, and we compute the transition amplitude to a state $|f\rangle \neq |i\rangle$. To first order in perturbation theory eq. (16.15) gives

$$\begin{aligned} d_f(t) &= -\frac{2i}{\hbar} \langle f|V(\mathbf{x})|i\rangle \int_0^t dt' e^{i\omega_{fi}t'} \cos \omega t' \\ &= -\frac{V_{fi}}{\hbar} \left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \right]. \end{aligned} \quad (16.31)$$

where $V_{fi} = \langle f|V(\mathbf{x})|i\rangle$. If the driving frequency ω is close to ω_{fi} the second term dominates, and

$$\begin{aligned} d_f(t) &\simeq -\frac{V_{fi}}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \\ &= -\frac{2i}{\hbar} V_{fi} e^{i(\omega_{fi}-\omega)t/2} \frac{\sin[(\omega_{fi} - \omega)t/2]}{\omega_{fi} - \omega}. \end{aligned} \quad (16.32)$$

The transition probability is therefore

$$P_{i \rightarrow f}(t) = |d_f(t)|^2 = \frac{4|V_{fi}|^2}{\hbar^2} \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2}. \quad (16.33)$$

The function $\sin^2 x/x^2$ is peaked at $x = 0$ with a width $\Delta x \simeq \pi$. Therefore are favored transitions toward states such that

$$|(\omega_{fi} - \omega)t/2| \leq \pi, \quad (16.34)$$

i.e.

$$\begin{aligned} E_f - E_i &= \hbar\omega \pm \frac{2\pi\hbar}{t} \\ &= \hbar\omega \left(1 \pm \frac{2\pi}{\omega t} \right). \end{aligned} \quad (16.35)$$

For small t there is no particular preference for the levels E_f such that $E_f - E_i \simeq \hbar\omega$. This preference shows up only when $\omega t \gg 2\pi$. The reason is that only after a number of cycles the system can realize that the perturbation is periodic, with frequency ω .

Consider now a perturbation that lasts for an infinite time. We set the system in the state $|i\rangle$ at time $t = -T/2$, and we look for the transition amplitude for being in a state $|f\rangle \neq |i\rangle$ at time $t = +T/2$. We will finally send $T \rightarrow \infty$. Now d_f is given by

$$\begin{aligned} d_f &= -\frac{2i}{\hbar} V_{fi} \int_{-T/2}^{T/2} dt e^{i\omega_{fi}t} \cos \omega t \\ &= -\frac{i}{\hbar} V_{fi} 2\pi \delta_T(\omega - \omega_{fi}), \end{aligned} \quad (16.36)$$

where

$$\delta_T(\omega) \equiv \frac{1}{2\pi} \int_{-T/2}^{T/2} dt e^{i\omega t}. \quad (16.37)$$

In the limit $T \rightarrow \infty$, $\delta_T(\omega) \rightarrow \delta(\omega)$.³⁵ When computing the modulus square we are confronted with the square of $\delta_T(\omega)$. For large T

$$\begin{aligned} \delta_T^2(\omega) &= \delta_T(\omega) \frac{1}{2\pi} \int_{-T/2}^{T/2} dt e^{i\omega t} \\ &\rightarrow \delta(\omega) \frac{1}{2\pi} \int_{-T/2}^{T/2} dt e^{i\omega t} \\ &= \delta(\omega) \frac{1}{2\pi} \int_{-T/2}^{T/2} dt \\ &= \delta(\omega) \frac{T}{2\pi}, \end{aligned} \quad (16.38)$$

where, going from the second to the third line, we use the fact that the first Dirac delta forces $\omega = 0$ into the remaining integral. Therefore the transition probability is

$$P_{i \rightarrow f} = \frac{2\pi |V_{fi}|^2}{\hbar^2} \delta(\omega - \omega_{fi}) T. \quad (16.39)$$

Since the external force is present for a very long time T , and the transition can happen at any time, the total transition probability is proportional to

³⁵On the right-hand side of eq. (16.36) we have neglected a term proportional to $\delta_T(\omega + \omega_{fi})$. Since we are taking both ω and $\omega_{fi} > 0$, this vanishes in the limit $T \rightarrow \infty$.

T . The transition rate, i.e. the transition probability *per unit time* is then

$$\begin{aligned}
 R_{i \rightarrow f} &\equiv \frac{P_{i \rightarrow f}}{T} \\
 &= \frac{2\pi}{\hbar^2} |V_{fi}|^2 \delta(\omega_{fi} - \omega) \\
 &= \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i - \hbar\omega). \tag{16.40}
 \end{aligned}$$

This is called *Fermi's golden rule*. The Dirac delta reflect the conservation of energy, but since it is infinite when $E_f - E_i - \hbar\omega = 0$, its presence might look puzzling. No transition rate can be infinite, of course. Physically, there is always some mechanism that smooths the Dirac delta and produces a finite result. For instance, if we consider the absorption of light from an incoming laser beam, we must take into account that no electromagnetic wave is exactly monochromatic. In general, it will have a spectrum of frequencies, described by a function $\rho(\omega)$, such that the intensity in the range ω to $\omega + d\omega$ is given by $\rho(\omega)d\omega$. Then, the actual transition rate induced by a laser beam with energy profile $\rho(\omega)$ is

$$\begin{aligned}
 R_{i \rightarrow f} &= \int d\omega \rho(\omega) \frac{2\pi}{\hbar^2} |V_{fi}|^2 \delta(\omega_{fi} - \omega) \\
 &= \rho(\omega_{fi}) \frac{2\pi}{\hbar^2} |V_{fi}|^2. \tag{16.41}
 \end{aligned}$$

In other words, in the limit $T \rightarrow \infty$, the only contribution to the transition comes from the Fourier mode of the laser beam which is exactly resonant with the transition.

If we rather consider the decay of an excited state into a lower energy state, we must also take into account that excited states have a finite lifetime τ , and therefore we cannot really take the limit $T \rightarrow \infty$ in the above computations. The maximum time for which the excited state can interact with the perturbation is $T \sim \tau$, and therefore the Dirac delta must really be replaced with a function such as δ_T with $T \sim \tau$. This gives a finite width to the transition lines, of the order $\Delta\omega \sim 1/\tau$. This linewidth can be understood more generally as a reflection of a time-energy uncertainty principle, as we now discuss.

16.4 The time-energy uncertainty principle

In quantum mechanics there is an uncertainty principle involving energy and time,

$$\Delta E \Delta t \geq \frac{\hbar}{2}, \tag{16.42}$$

whose meaning is quite different from the position-momentum uncertainty principle

$$\Delta p \Delta x \geq \frac{\hbar}{2}. \quad (16.43)$$

Recall, from the course of *Mécanique Quantique I*, (or see e.g. Shankar, chapter 9) that, for any two Hermitean operators A and B , and an arbitrary state $|\psi\rangle$, we have the mathematical identity

$$(\Delta A)^2 (\Delta B)^2 \geq \frac{1}{4} |\langle \psi | [A, B] | \psi \rangle|^2, \quad (16.44)$$

where

$$(\Delta A)^2 \equiv \langle \psi | (A - \langle A \rangle)^2 | \psi \rangle, \quad (16.45)$$

with

$$\langle A \rangle = \langle \psi | A | \psi \rangle, \quad (16.46)$$

and similarly for $(\Delta B)^2$. If we set $A = X$ and $B = P$, we recover eq. (16.43).

However, eq. (16.42) cannot be obtained in this way, since time is not represented by an operator in quantum mechanics. The meaning of eq. (16.42) is rather the following. As we have seen several times, an eigenstate of energy, with eigenvalue E , has a wavefunction with a time-dependence

$$e^{-iEt/\hbar}, \quad (16.47)$$

so it has a well defined frequency $\omega = E/\hbar$. However, such a state has a probability that is constant in time, since the modulus squared of $e^{-iEt/\hbar}$ is one. Thus, it cannot represent a system that has been in existence only for a finite time, e.g. an atom that was prepared in a given state in the laboratory on a given day, and that will eventually decay to another state.

A basic theorem of Fourier analysis tells us that, in order to have a function localized in time within a range Δt , its Fourier transform cannot be monochromatic, but rather it must be a superposition of frequencies with a spread $\Delta\omega$, such that

$$\Delta\omega \Delta t \geq \frac{1}{2}. \quad (16.48)$$

Equation (16.42) is therefore simply the translation of eq. (16.48) into the language of quantum mechanics, with the identification $E = \hbar\omega$.

To illustrate the meaning of the time-energy uncertainty, consider an atom, say hydrogen, in an excited state. When we first studied the hydrogen atom we found a set of stationary states with energies E_n , whose wavefunction are therefore proportional to $\exp\{-iE_n t/\hbar\}$. However, at this

level of description we have neglected the perturbations that make the atom decay, when it is not in the ground state. These could be external actions such as collisions with other atoms, or an incoming electromagnetic waves. Even in the absence of such perturbations, however, there is spontaneous decay. This is a phenomenon whose deeper origin resides in quantum field theory, and is due to the interaction of the atom with the quantum fluctuations of a quantized electromagnetic field, which are present even in the vacuum. Independently of the mechanism that induces the decay, the fact itself that an excited atomic state has a finite lifetime τ means that its true wavefunction is not exactly proportional to $\exp\{-i\omega_n t\}$, where $\omega_n = E_n/\hbar$. Rather, it must be a superposition of frequencies, with a spread $\Delta\omega$ such that

$$\Delta\omega \geq \frac{1}{2\tau}. \quad (16.49)$$

Therefore, the linewidth corresponding to the transition from this excited state to, say, the ground state, must have a minimum width ΔE given by

$$\Delta E \geq \frac{\hbar}{2\tau}. \quad (16.50)$$

The same happens if we rather switch on a perturbation with frequency ω_0 for a finite time T . As long as $\omega_0 T \ll 2\pi$, we have seen in eq. (16.35) that there is no preference for transitions with $E_f - E_i = \hbar\omega_0$, even if ω_0 was the nominal frequency of the perturbation. A more formal way to see it is that something that is switched on at $t = 0$ and off at $t = T$, and is proportional to $e^{-i\omega_0 t}$ in between, can be written as

$$\theta(t)\theta(T-t)e^{-i\omega_0 t}, \quad (16.51)$$

and its Fourier transform is not at all proportional to a Dirac delta $\delta(\omega - \omega_0)$, because of the theta functions. This is exactly the meaning of the result that we have found for the rate of periodic perturbations. The function $\delta_T(\omega)$ in eq. (16.37) provide the linewidth due to the fact that the perturbation only lasts for a finite time T .

17 Interaction of atoms with the electromagnetic field

Recall from classical electromagnetism that the electromagnetic field is described by a scalar potential ϕ and a vector potential \mathbf{A} . The electric and magnetic field are derived from the potentials using

$$\mathbf{E} = -\frac{1}{c}\partial_t\mathbf{A} - \nabla\phi, \quad (17.1)$$

$$\mathbf{B} = \nabla\times\mathbf{A}. \quad (17.2)$$

Classical electrodynamics is invariant under gauge transformations,

$$\mathbf{A} \rightarrow \mathbf{A} - \nabla\Lambda, \quad (17.3)$$

$$\phi \rightarrow \phi + \frac{1}{c}\partial_t\Lambda, \quad (17.4)$$

where Λ is an arbitrary function of \mathbf{x} and t . The electric and magnetic fields are invariant under gauge transformation.

In the case of a free electromagnetic field ($\rho = \mathbf{j} = 0$) gauge invariance can be used to choose \mathbf{A} and ϕ so that

$$\nabla\cdot\mathbf{A} = 0, \quad \phi = 0. \quad (17.5)$$

This is called the radiation gauge (or Coulomb gauge). In this gauge the Maxwell equations in vacuum become a simple wave equation for \mathbf{A} ,

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\partial_t^2\mathbf{A} = 0, \quad (17.6)$$

whose solutions are plane waves

$$\mathbf{A} = \mathbf{A}_0 \cos(\mathbf{k}\cdot\mathbf{x} - \omega t), \quad (17.7)$$

with $\omega = |\mathbf{k}|c$. The condition $\nabla\cdot\mathbf{A} = 0$ on the plane wave solution becomes

$$\mathbf{k}\cdot\mathbf{A}_0 = 0. \quad (17.8)$$

This states that \mathbf{A}_0 is orthogonal to the propagation direction \mathbf{k} (and therefore also \mathbf{E} and \mathbf{B} are orthogonal to \mathbf{k}).

Classically, the Hamiltonian of a non-relativistic particle of mass m and charge q in an electromagnetic field is

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{q}{c}\mathbf{A} \right)^2 - e\phi. \quad (17.9)$$

We would like to promote this to a quantum Hamiltonian, and study processes in which an atom emits or absorbs a photon. The formalism that we have developed until now strictly speaking does not allow us to study such processes. First of all, the notion itself of photon really belongs to relativistic quantum field theory, and emerges after one quantizes the electromagnetic field. Second, our formalism only allow us to study the quantum mechanics of a particle in a given external potential. We cannot study processes in which the number or the type of particle changes. Again, this is the subject of quantum field theory, and you can study it next year.

Within the scope of this course, we can however take a “mixed” approach in which the atom is treated quantum-mechanically, and the electromagnetic field is treated classically. This is called the “semiclassical theory of radiation”. While its deeper conceptual justification lies in quantum field theory, still it allows us to perform a number of important and instructive computations.³⁶

In this approximation the quantum Hamiltonian describing the interaction of a particle with an electromagnetic wave is given by eq. (17.9), with \mathbf{p} replaced by the quantum operator $-i\hbar\nabla$, while \mathbf{A} and ϕ are classical fields. It is convenient to use the radiation gauge, so $\phi = 0$ and

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{q^2}{2mc^2}\mathbf{A}^2. \quad (17.10)$$

We will neglect the term \mathbf{A}^2 , since we will only work to first order in perturbation theory in the external field, and the term \mathbf{A}^2 is second order. In the radiation gauge we have, for a generic function $f(\mathbf{x})$,

$$\begin{aligned} \mathbf{p}\cdot\mathbf{A}f &= -i\hbar\nabla\cdot(\mathbf{A}f) \\ &= -i\hbar\mathbf{A}\cdot\nabla f \\ &= \mathbf{A}\cdot\mathbf{p}f, \end{aligned} \quad (17.11)$$

where in the second line we used $\nabla\cdot\mathbf{A} = 0$. Therefore, in the radiation gauge,

$$[\mathbf{p}, \mathbf{A}] = 0, \quad (17.12)$$

and eq. (17.10) can be rewritten (neglecting the term \mathbf{A}^2) as

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{mc}\mathbf{A}\cdot\mathbf{p}. \quad (17.13)$$

³⁶One should however keep in mind that this mixed approach has intrinsic limitations that can only be overcome by developing a full quantum field theory formalism. For example, we can study the absorption of electromagnetic waves by atoms and the emission of a photon by an excited atom induced by an incoming electromagnetic wave (“stimulated emission”), but not the spontaneous emission of a photon by an excited atom.

Using eq. (17.7), we see that the interaction with the electromagnetic wave produces a time-dependent periodic perturbation, with

$$H_1(t) = -\frac{q}{2mc} [e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)} + e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)}] \mathbf{A}_0 \cdot \mathbf{p}. \quad (17.14)$$

We consider an electron bound in an atom, under the influence of this perturbation. This electron will perform transitions from its initial state $|i\rangle$ to some other final state $|f\rangle$. If $\omega_{fi} = \omega_f - \omega_i > 0$ then, repeating the same steps as in eqs. (16.31) and (16.32), we see that only the term proportional to $e^{-i\omega t}$ in $H_1(t)$ contributes (recall that we defined ω as $+|\mathbf{k}|c$, so $\omega > 0$). Viceversa, if we study a transition with $\omega_{fi} < 0$, only the term proportional to $e^{+i\omega t}$ in $H_1(t)$ contributes. Consider for definiteness $\omega_{fi} > 0$. Then the transition rate is given by Fermi golden rule, eq. (16.40), with

$$V(\mathbf{x}) = \frac{e}{2mc} e^{i\mathbf{k}\cdot\mathbf{x}} \mathbf{A}_0 \cdot \mathbf{p} \quad (17.15)$$

(recall that for the electron $q = -e$), so

$$V_{fi} = \frac{e}{2mc} \mathbf{A}_0 \cdot \int d^3x e^{i\mathbf{k}\cdot\mathbf{x}} \psi_f^*(\mathbf{x}) \mathbf{p} \psi_i(\mathbf{x}). \quad (17.16)$$

17.1 Dipole transitions

Given the initial and final wavefunctions, the matrix element can in principle be computed using $\mathbf{p} = -i\hbar\nabla$. The computation can however be simplified by observing that, if the photon has ω close to ω_{fi} , the factor $\mathbf{k}\cdot\mathbf{x}$ is small. To show this, consider for definiteness the hydrogen atom. Then

$$\begin{aligned} \hbar\omega &\simeq E_f - E_i \\ &= \frac{1}{2} m\alpha^2 c^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &\leq \frac{1}{2} m\alpha^2 c^2. \end{aligned} \quad (17.17)$$

Therefore

$$k = \frac{\omega}{c} \leq \frac{1}{2\hbar} m\alpha^2 c = \frac{\alpha}{2a_0}, \quad (17.18)$$

where $a_0 = \hbar/(m\alpha c)$ is the Bohr radius. This means that $ka_0 \leq O(\alpha/2)$. In eq. (17.16) \mathbf{x} is an integration variable, and the integrand is localized at $|\mathbf{x}|$ of order of at most a few Bohr radii, because the wavefunctions ψ_i and ψ_f vanish exponentially at $|\mathbf{x}|/a_0 \gg O(1)$. Therefore, when $\psi_f^*(\mathbf{x}) \mathbf{p} \psi_i(\mathbf{x})$

is non-negligible, the factor $\exp\{i\mathbf{k}\cdot\mathbf{x}\}$ is at most of order $\exp\{ika_0\}$ and $ka_0 \ll 1$. We can therefore expand the exponential,

$$e^{i\mathbf{k}\cdot\mathbf{x}} = 1 + i\mathbf{k}\cdot\mathbf{x} + \dots \quad (17.19)$$

To lowest order $\exp\{i\mathbf{k}\cdot\mathbf{x}\}$ is replaced simply by one and we get

$$V_{fi} \simeq \frac{e}{2mc} \mathbf{A}_0 \cdot \int d^3x \psi_f^*(\mathbf{x}) \mathbf{p} \psi_i(\mathbf{x}). \quad (17.20)$$

The physical meaning of this expression can be better understood as follows. If the unperturbed Hamiltonian has the general form

$$H_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}), \quad (17.21)$$

it follows that

$$[\mathbf{x}, H_0] = \frac{i\hbar}{m} \mathbf{p}. \quad (17.22)$$

Therefore

$$\begin{aligned} \int d^3x \psi_f^*(\mathbf{x}) \mathbf{p} \psi_i(\mathbf{x}) &= \langle f | \mathbf{p} | i \rangle \\ &= \frac{m}{i\hbar} \langle f | \mathbf{x} H_0 - H_0 \mathbf{x} | i \rangle \\ &= \frac{m}{i\hbar} (E_i - E_f) \langle f | \mathbf{x} | i \rangle \\ &= im\omega_{fi} \langle f | \mathbf{x} | i \rangle. \end{aligned} \quad (17.23)$$

Therefore

$$V_{fi} \simeq i \frac{\omega}{2c} \mathbf{A}_0 \cdot \int d^3x \psi_f^*(\mathbf{x}) e \mathbf{x} \psi_i(\mathbf{x}). \quad (17.24)$$

Observe that, since in the transition rate, $|V_{fi}|^2$ is multiplied by $\delta(\omega - \omega_{fi})$, in eq. (17.24) we have replaced ω_{fi} with ω . We see that V_{fi} is determined by the matrix element of the electric dipole operator $\mathbf{d} = q\mathbf{x} = -e\mathbf{x}$.

In fact, this result could have been obtained more simply postulating that $H_1(t)$ is given by the interaction between the electric field of the incoming wave and the dipole moment of the atom,

$$H_1(t) = -\mathbf{d} \cdot \mathbf{E}. \quad (17.25)$$

Using eqs. (17.1) and (17.7), in the radiation gauge

$$\mathbf{E} = -\frac{\omega}{c} \mathbf{A}_0 \sin(\mathbf{k}\cdot\mathbf{x} - \omega t). \quad (17.26)$$

Setting again $\mathbf{k} \cdot \mathbf{x} = 0$

$$\mathbf{E} = \mathbf{A}_0 \frac{\omega}{c} \sin \omega t = -\mathbf{A}_0 \frac{i\omega}{2c} (e^{i\omega t} - e^{-i\omega t}). \quad (17.27)$$

As usual, for an absorption process only the term $e^{-i\omega t}$ contributes, so we can write

$$\mathbf{E} = \mathbf{A}_0 \frac{i\omega}{2c} e^{-i\omega t} \quad (17.28)$$

and

$$H_1(t) = -\frac{i\omega}{2c} \mathbf{d} \cdot \mathbf{A}_0 e^{-i\omega t}. \quad (17.29)$$

This periodic perturbation produces the same matrix element that we have computed in eq. (17.24). Therefore, the approximation in which $\exp\{i\mathbf{k} \cdot \mathbf{x}\}$ is replaced by one is called the dipole approximation. To next order, the exponential produces a term $k_j x_j$ which combined with the x_i present in eq. (17.24) to give a matrix element of the form

$$\int d^3x \psi_f^*(\mathbf{x}) x_i x_j \psi_i(\mathbf{x}). \quad (17.30)$$

This can be rewritten using

$$x_i x_j = \left(x_i x_j - \frac{1}{3} \delta_{ij} r^2 \right) + \frac{1}{3} \delta_{ij} r^2. \quad (17.31)$$

The term in parentheses is a rank-2 traceless symmetric tensor (i.e. an irreducible representation of the rotation group, recall the discussion in Section 6.2), and is called the quadrupole moment.

The expansion of the exponential in powers of $\mathbf{k} \cdot \mathbf{x}$ defines the *multipole expansion*. So, to lowest order we have dipole transitions (that obey the dipole selection rule discussed in Section 12.2). To next order we have quadrupole transitions. Using the same arguments as in Section 12.2, one can verify that they obey the selection rule $\Delta l = \pm 0, 2$, since the quadrupole moment has $l = 2$ (and $\Delta l = 1$ is forbidden by parity). Similarly r^2 carries no angular momentum and mediates transitions with $\Delta l = 0$.

With respect to dipole transitions, the amplitude for a quadrupole transition has one more factor $\mathbf{k} \cdot \mathbf{x}$, i.e. a factor $O(ka) = O(\omega a/c) = O(\alpha)$, and the transition rate is smaller by a factor $O(\alpha^2)$.

17.2 Transitions in the continuum: ionization of an atom by an electromagnetic wave

As an application, we compute the ionization rate of the hydrogen atom in its ground state, due to an incoming photon, which, in this semiclassical theory of radiation, is just represented by a classic electromagnetic wave. We consider an electromagnetic wave propagating along the x axis, polarized so that the electric field points in the $\hat{\mathbf{z}}$ direction, impinging on a hydrogen atom at the origin. According to eq. (17.26), \mathbf{A}_0 then points along the $-\hat{\mathbf{z}}$ direction, and its modulus is equal to $c\mathcal{E}/\omega$, where $\mathcal{E} \equiv |\mathbf{E}|$, i.e. $\mathbf{A}_0 = -(c\mathcal{E}/\omega)\hat{\mathbf{z}}$. Equation (17.24) then gives

$$V_{fi} \simeq -i\frac{e\mathcal{E}}{2} \int d^3x \psi_f^*(\mathbf{x}) z \psi_i(\mathbf{x}). \quad (17.32)$$

As initial wave function we take the ground state of the hydrogen atom,

$$\psi_i(r) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}, \quad (17.33)$$

[see eq. (8.17)]. For the final state, we take a plane wave.³⁷ We idealize the incoming electromagnetic wave as exactly monochromatic. In the rate $R_{i \rightarrow f}$ given by eq. (16.40), the energy of the final state is then fixed by the Dirac delta. However, the final states of the electron, in a infinite volume, form a continuum. To understand precisely the interplay between the Dirac delta and this continuum of states, it is convenient to work in a finite volume V , with periodic boundary conditions. For the final state we then take

$$\psi_f(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{x}/\hbar}, \quad (17.34)$$

where \mathbf{p} is the final momentum of the electron. This normalization corresponds to one particle in a volume $V = L^3$. In a finite volume with periodic boundary conditions the momenta are quantized,

$$\mathbf{p}_\mathbf{n} = \frac{2\pi\hbar}{L} \mathbf{n}, \quad (17.35)$$

where $\mathbf{n} = (n_x, n_y, n_z)$ and n_x, n_y and n_z take the values $0, 1, 2, \dots$. Since the allowed final states are anyhow selected by the Dirac delta, in eq. (16.40)

³⁷Actually, this assumes that the energy of the final electron is much larger than the typical binding energy of the hydrogen atom, so that the final state can be taken to be a free particle. A more accurate wavefunction would be given by a particle moving in the Coulomb field of the proton.

we can sum over all possible final states, writing

$$R = \sum_{\mathbf{n}} \frac{2\pi}{\hbar} |V_{\mathbf{n},i}|^2 \delta(E_{\mathbf{n}} - E_i - \hbar\omega). \quad (17.36)$$

In the limit $V \rightarrow \infty$ we can pass from the discrete sum to an integration over momenta observing that, from eq. (17.35),

$$\int d^3p \leftrightarrow \left(\frac{2\pi\hbar}{L}\right)^3 \sum_{\mathbf{n}}, \quad (17.37)$$

so in the continuum limit

$$\sum_{\mathbf{n}} \rightarrow \frac{V}{(2\pi\hbar)^3} \int d^3p. \quad (17.38)$$

Observe now that, when computing the rate, the factor V in this expression cancels against the factor $|1/\sqrt{V}|^2$ coming from the normalization of the final wave function. Then, the rate in the infinite volume limit is well defined, and is given by

$$R = \frac{1}{(2\pi\hbar)^3} \frac{2\pi}{\hbar} \frac{e^2 \mathcal{E}^2}{4} \int d^3p |U(\mathbf{p})|^2 \delta\left(\frac{p^2}{2m_e} - \frac{p_f^2}{2m_e}\right), \quad (17.39)$$

where we have defined

$$U(\mathbf{p}) \equiv \int d^3x e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} z\psi_i(\mathbf{x}), \quad (17.40)$$

and

$$p_f \equiv [2m_e(E_i + \hbar\omega)]^{1/2} \quad (17.41)$$

is the modulus of the momentum of the final electron, fixed by the conservation of energy. We now use the property of the Dirac delta

$$\delta[f(x)] = \frac{1}{|f'(x_0)|} \delta(x - x_0), \quad (17.42)$$

valid if $f(x)$ has just one zero in $x = x_0$, with $f'(x_0) \neq 0$ (for functions with more zero, we must sum over all zeros) to write

$$\delta\left(\frac{p^2}{2m_e} - \frac{p_f^2}{2m_e}\right) = \frac{m_e}{p_f} \delta(p - p_f). \quad (17.43)$$

Then eq. (17.39) becomes

$$\begin{aligned} R &= \frac{1}{(2\pi)^2} \frac{e^2 \mathcal{E}^2}{4\hbar^4} \int p^2 dp d\Omega \frac{m_e}{p_f} \delta(p - p_f) |U(\mathbf{p})|^2 \\ &= \frac{1}{(2\pi)^2} \frac{e^2 \mathcal{E}^2}{4\hbar^4} m_e p_f \int d\Omega |U(\mathbf{p}_f)|^2. \end{aligned} \quad (17.44)$$

The differential rate per unit solid angle is therefore

$$\frac{dR}{d\Omega} = \frac{1}{(2\pi)^2} \frac{e^2 \mathcal{E}^2}{4\hbar^4} m_e p |U(\mathbf{p})|^2, \quad (17.45)$$

where we have now denote the final electron momentum \mathbf{p}_f simply by \mathbf{p} . We can compute explicitly the integral in $U(\mathbf{p})$ introducing $\mathbf{k} \equiv \mathbf{p}/\hbar$ and writing

$$U(\mathbf{p}) = \frac{i}{(\pi a_0^3)^{1/2}} \frac{\partial}{\partial k_z} \int d^3x e^{-i\mathbf{k}\cdot\mathbf{x}} e^{-r/a_0}. \quad (17.46)$$

Next observe that, for any function $f(r)$,

$$\begin{aligned} \int d^3x e^{-i\mathbf{k}\cdot\mathbf{x}} f(r) &= 2\pi \int_{-1}^1 d\cos\theta \int_0^\infty r^2 dr e^{-ikr\cos\theta} f(r) \\ &= 2\pi \int_0^\infty dr r^2 f(r) \frac{2\sin(kr)}{kr}, \end{aligned} \quad (17.47)$$

where we have used polar coordinates, choosing the polar axis in the direction of \mathbf{k} . Then (defining $u_0 = a_0 k = a_0 p/\hbar$),

$$\begin{aligned} U(\mathbf{p}) &= \frac{4\pi i}{(\pi a_0^3)^{1/2}} \frac{\partial}{\partial k_z} \frac{1}{k^3} \int_0^\infty du u e^{-u/u_0} \sin u \\ &= \frac{4\pi i}{(\pi a_0^3)^{1/2}} \frac{\partial}{\partial k_z} \frac{1}{k^3} \frac{2u_0^3}{(1+u_0^2)^2} \end{aligned} \quad (17.48)$$

$$= \frac{8\pi i a_0^3}{(\pi a_0^3)^{1/2}} \frac{\partial}{\partial k_z} \frac{1}{(1+u_0^2)^2} \quad (17.49)$$

Finally, using $\partial k/\partial k_z = k_z/k$, we have

$$\frac{\partial}{\partial k_z} = \frac{\partial k}{\partial k_z} \frac{\partial}{\partial k} = \frac{a_0 k_z}{k} \frac{\partial}{\partial u_0}, \quad (17.50)$$

and therefore, writing $k_z = k \cos\theta$, we finally get

$$U(\mathbf{p}) = -32i\pi^{1/2} a_0^{5/2} \frac{a_0 k \cos\theta}{(1+a_0^2 k^2)^3}, \quad (17.51)$$

which can be plug into eq. (17.45) to get the differential rate,

$$\frac{dR}{d\Omega} = \frac{64}{\pi\hbar^3} e^2 \mathcal{E}^2 m_e d_0^4 \frac{(a_0 k)^3 \cos^2 \theta}{(1 + a_0^2 k^2)^6}. \quad (17.52)$$

Observe that $dR/d\Omega \propto \cos^2 \theta$. This angular dependence is typical of the dipole interaction.

18 Scattering in three dimensions

At the beginning of this course we have studied scattering in one dimension. We considered a right-moving plane wave coming from $x = -\infty$ impinging on a potential barrier. As a result, part of the wave is reflected and part is transmitted. So at $x = -\infty$ we have a superposition of the initial wave e^{ikx} and of the reflected wave, proportional to e^{-ikx} , while at $x = +\infty$ we only have the transmitted wave, proportional to e^{ikx} . Observe that all these waves have the time-dependence $e^{-i\omega t}$. For a wave $e^{ikx-i\omega t}$ the surfaces of constant phase are given by $kx - \omega t = \text{const}$, or $x = +(\omega/k)t + \text{const}$., so this wave is right-moving. Similarly, a wave proportional to $e^{-ikx-i\omega t}$ is left-moving.

We now want to study the same problem in three dimensions. We consider a wave coming along the z axis from $z = -\infty$, therefore proportional to e^{ikz} . This wave impinges on a potential $V(\mathbf{x})$ and will therefore be scattered in all directions. Our first task is to understand what is the form of the scattered wave at $r \rightarrow \infty$. In the one-dimensional case, the fact that the scattered wave was proportional to e^{ikx} at $x = +\infty$ and to e^{-ikx} at $x = -\infty$ was a trivial consequence of the fact that we considered a potential $V(x)$ which goes to zero sufficiently fast at $x = \pm\infty$ (actually, we even considered potentials $V(x)$ with compact support), so the Schrödinger equations at $x = \pm\infty$ reduces to a free wave equation, whose solutions are $e^{\pm ikx}$. The fact that at $x = +\infty$ we only have e^{+ikx} was a consequence of our boundary conditions, i.e. we from the fact that we imposed that the incoming wave comes from $x = -\infty$.

We can now repeat the same reasoning in three dimensions. Assume first that the potential depends only on r . Recall from eqs. (5.130)–(5.133) that, when $V = V(r)$, the Schrödinger equation can be separated searching for solutions of the form $R_l(r)Y_{lm}(\theta, \phi)$ (we suppress for notational simplicity the label E), so the most general solution is

$$\psi(r, \theta, \phi) = \sum_{lm} c_{lm} R_l(r) Y_{lm}(\theta, \phi), \quad (18.1)$$

for some coefficients c_{lm} . Introducing the function $U_l(r)$ from

$$R_l(r) = \frac{1}{r} U_l(r), \quad (18.2)$$

the Schrödinger equation becomes

$$\left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2mr^2} \right] \right\} U_l(r) = 0. \quad (18.3)$$

At $r \rightarrow \infty$, if the potential goes to zero sufficiently fast³⁸ the equation becomes

$$\frac{d^2}{dr^2}U_l \simeq -k^2U_l \quad (18.4)$$

with $k^2 = 2mE/\hbar^2$. The solutions are therefore of the form $U_l(r) \simeq e^{\pm ikr}$. Recalling that the time dependence is $e^{-i\omega t}$, we see that a wave proportional to $\exp\{ikr - i\omega t\}$ is an outgoing radial wave, i.e. is a wave moving radially outward, while $\exp\{-ikr - i\omega t\}$ is an incoming radial wave. We impose the boundary conditions that there is no incoming radial wave. The only incoming wave is the one arriving from the z axis, proportional to $\exp\{ikz\}$, and therefore for the scattered wave we only retain the solution proportional to $\exp\{+ikr\}$ (just as, in the one-dimensional case, at $x = +\infty$ we only retained the term $\exp\{+ikx\}$).

In terms of the original radial factor $R_l(r)$, the asymptotic solution of the Schrödinger equation, representing an outgoing radial wave, is therefore

$$R_l(r) \simeq \frac{e^{ikr}}{r}, \quad (18.5)$$

apart from a constant that can be reabsorbed in the factors c_{lm} in eq. (18.1). For $r \rightarrow \infty$ the scattered wave is then

$$\begin{aligned} \psi_{\text{scat}} &= \sum_{lm} c_{lm} R_l(r) Y_{lm}(\theta, \phi) \\ &\simeq \frac{e^{ikr}}{r} \sum_{lm} c_{lm} Y_{lm}(\theta, \phi), \quad (r \rightarrow \infty) \\ &\equiv \frac{e^{ikr}}{r} f(\theta, \phi). \end{aligned} \quad (18.6)$$

The total wave function at large distances is the superposition of the incoming wave and of the scattered wave, so

$$\psi \simeq A \left[e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right], \quad (r \rightarrow \infty), \quad (18.7)$$

³⁸We will not enter into a precise mathematical discussion of what it means “sufficiently fast”. It turns out that our reasoning below is correct for potentials going to zero at least as $1/r^2$. The Coulomb potential decreases only as $1/r$ and it is sort of a “borderline” case, and gives rise to logarithmic corrections in the phase of the wavefunction. In all physically interesting cases, however, a Coulomb potential is always screened at large distances. A similar problem also appears classically, in the computation of the cross-section for Rutherford scattering, i.e. scattering from a $1/r$ potential, and is again solved by this screening effect.

where A is an overall normalization constant that we will set to one. In the case of a potential $V(r)$ that we have considered here, the problem is invariant under rotations around the z axis, because the incoming wavefunction e^{ikz} is left invariant by a rotation in the (x, y) plane, and the potential has spherical symmetry. This means that the function $f(\theta, \phi)$ must actually be independent of ϕ . By definition

$$f(\theta, \phi) = \sum_{lm} c_{lm} Y_{lm}(\theta, \phi), \quad (18.8)$$

see eq. (18.6). Since only the spherical harmonics with $m = 0$ are independent of ϕ , this means that in the scattering from a central potential the coefficients c_{lm} can be non-vanishing only if $m = 0$. Using the relation

$$Y_{l,m=0} = \left(\frac{2l+1}{4\pi} \right)^{1/2} P_l(\cos \theta), \quad (18.9)$$

where $P_l(\cos \theta)$ are the Legendre polynomial, we see that for the scattering by a central potential, at $r \rightarrow \infty$, we have

$$\psi = e^{ikz} + f(\theta) \frac{e^{ikr}}{r}, \quad (r \rightarrow \infty), \quad (18.10)$$

where $f(\theta)$ can be written as a superposition of Legendre polynomials,

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) a_l P_l(\cos \theta). \quad (18.11)$$

The factor $(2l+1)$ is a useful normalization of the coefficients a_l .

The above reasonings can be repeated for non-central potentials. Assuming that the non-central part goes to zero sufficiently rapidly, at large r we can still separate the Schrödinger equation as in eq. (18.3) and we get again eq. (18.7). However, now there is no longer symmetry under rotations around the z axis. When the incoming wave arrives in the region close to the origin, it feels a potential which depends on both θ and ϕ , and it is therefore scattered in different directions with different amplitudes. As a consequence, the function $f(\theta, \phi)$, which gives the scattered wave at large r , now depends both on θ and ϕ , and we must keep the general form (18.8), rather than the simpler form (18.11).

The basic problem of scattering theory is the computation of the cross-section $\sigma(\theta, \phi)$, or more precisely of the differential cross section $d\sigma/d\Omega$. This is defined, just as in classical mechanics, as follows. We consider a beam

of particles arriving on a target, and we measure the number of particles scattered into a cone centered on the direction (θ, ϕ) , with an (infinitesimal) aperture $d\Omega$. Then

$$\frac{d\sigma(\theta, \phi)}{d\Omega} d\Omega = \frac{\text{particles scattered into } d\Omega \text{ per unit time}}{\text{incident particles per unit time, and unit area in the transverse plane}} \quad (18.12)$$

In quantum mechanics, we can consider a single incident particle and compute the probability flowing into $d\Omega$ per unit time. Recall from Mécanique Quantique I that the Schrödinger equation implies a continuity equation for the probability density,

$$\frac{\partial}{\partial t} |\psi|^2 = -\nabla \cdot \mathbf{j}, \quad (18.13)$$

where the *probability current density* \mathbf{j} is

$$\mathbf{j} = \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*). \quad (18.14)$$

(See Shankar, Section 5.3). The probability current density associated to the incoming wave $\psi_{\text{in}} = e^{ikz}$ can be obtained by looking at the wavefunction at $x = y = 0$ and $z \rightarrow -\infty$. In this case $r = -z$ and the term $(1/r)e^{ikr}$ does not contribute, since it is suppressed by $O(1/r)$ with respect to e^{ikz} . So

$$\begin{aligned} \mathbf{j}_{\text{in}} &= \frac{\hbar}{2im} (e^{-ikz} \nabla e^{ikz} - e^{ikz} \nabla e^{-ikz}) \\ &= \frac{\hbar k}{m} \hat{\mathbf{z}}, \end{aligned} \quad (18.15)$$

and its modulus is

$$j_{\text{in}} = \frac{\hbar k}{m}. \quad (18.16)$$

Consider now the scattered wave. To distinguish the scattered wave $(1/r)e^{ikr}$ from the portion of the wavefront e^{ikz} that simply travels undisturbed to $z = +\infty$, it is convenient to take the limit $r \rightarrow \infty$ along a direction $\theta \neq 0$. For any $\theta \neq 0$, if r is sufficiently large the transverse distance $r \sin \theta$ is arbitrarily large. Observe that, physically, the plane wave e^{ikz} is an idealization, since it has infinite transverse extent. Any realistic incoming wave will rather be of the form $f(\rho)e^{ikz}$ where $\rho = (x^2 + y^2)^{1/2}$. The function $f(\rho)$ gives the transverse profile of the incoming wave, and in any physically realistic situation it must be a function that goes to zero quite fast (e.g. exponentially, or even with compact support) for ρ larger than some critical

value ρ_c . Therefore, taking r sufficiently large, we have $r \sin \theta > \rho_c$ (in more physical terms, we look at the wavefunction outside the incoming beam), and e^{ikr}/r dominates over $f(\rho)e^{ikz}$. The probability current associated to the scattered wave is therefore

$$\mathbf{j}_{\text{scat}} = \frac{\hbar}{2im}(\psi_{\text{scat}}^* \nabla \psi_{\text{scat}} - \psi_{\text{scat}} \nabla \psi_{\text{scat}}^*), \quad (18.17)$$

where

$$\psi_{\text{scat}} = f(\theta, \phi) \frac{e^{ikr}}{r}. \quad (18.18)$$

In polar coordinates,

$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}. \quad (18.19)$$

The last two terms are subleading as $r \rightarrow \infty$, so

$$\begin{aligned} \nabla \psi_{\text{scat}} &= \mathbf{e}_r \frac{\partial}{\partial r} \left[f(\theta, \phi) \frac{e^{ikr}}{r} \right] + O\left(\frac{1}{r^2}\right) \\ &= \mathbf{e}_r f(\theta, \phi) ik \frac{e^{ikr}}{r} + O\left(\frac{1}{r^2}\right), \end{aligned} \quad (18.20)$$

and

$$\mathbf{j}_{\text{scat}} = \mathbf{e}_r |f(\theta, \phi)|^2 \frac{\hbar k}{mr^2}. \quad (18.21)$$

Thus, probability flows into $d\Omega$ at a rate

$$\begin{aligned} R(d\Omega) &= \mathbf{j}_{\text{scat}} \cdot \mathbf{e}_r r^2 d\Omega \\ &= |f(\theta, \phi)|^2 \frac{\hbar k}{m} d\Omega. \end{aligned} \quad (18.22)$$

Then

$$\frac{d\sigma}{d\Omega} = \frac{R(d\Omega)}{j_{\text{in}}} = |f(\theta, \phi)|^2 d\Omega. \quad (18.23)$$

and we finally get

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2. \quad (18.24)$$

In conclusion, the computation of the differential scattering cross-section $d\sigma/d\Omega$ amounts to the computation of the function $f(\theta, \phi)$. In the next section we will discuss how $f(\theta, \phi)$ can be computed, given the potential $V(\mathbf{x})$.

18.1 Born approximation

(Reference: Griffiths, Section 11.4). The time-independent Schrödinger equation can be rewritten as

$$(\nabla^2 + k^2)\psi = Q, \quad (18.25)$$

where

$$k = +\frac{\sqrt{2mE}}{\hbar}, \quad Q = \frac{2mV}{\hbar^2}\psi, \quad (18.26)$$

and we are considering the case $E > 0$, as appropriate for a scattering problem. Observe that Q depends on ψ . Equation (18.25) is an inhomogeneous Helmholtz equation, and can be solved by the method of Green's functions. Let $G(\mathbf{x})$ be a Green's function of the operator $\nabla^2 + k^2$, i.e. a function that satisfies the differential equation

$$(\nabla^2 + k^2)G(\mathbf{x}) = \delta^3(\mathbf{x}). \quad (18.27)$$

Then a particular solution of eq. (18.25) is

$$\psi(\mathbf{x}) = \int d^3x' G(\mathbf{x} - \mathbf{x}')Q(\mathbf{x}'), \quad (18.28)$$

as can be verified directly applying $\nabla^2 + k^2$. The most general solution is then

$$\psi(\mathbf{x}) = \psi_{\text{hom}}(\mathbf{x}) + \int d^3x' G(\mathbf{x} - \mathbf{x}')Q(\mathbf{x}'), \quad (18.29)$$

where ψ_{hom} is the most general solution of the homogeneous equation. To find the Greens function we first observed that, since eq. (18.27) is invariant under rotations around the origin, we can look for a solution $G(r)$ which depends only on $r = |\mathbf{x}|$. Writing

$$G(r) = -\frac{1}{4\pi r} f(r) \quad (18.30)$$

and using

$$\nabla^2 \left(-\frac{1}{4\pi r} \right) = \delta^3(\mathbf{x}) \quad (18.31)$$

and the fact that, on a function of r only, for $r \neq 0$,

$$\nabla^2 \rightarrow \frac{1}{r^2} \partial_r (r^2 \partial_r), \quad (18.32)$$

[see eq. (5.125)], we get

$$(\nabla^2 + k^2)G(\mathbf{x}) = \delta^{(3)}(\mathbf{x})f(0) - \frac{1}{4\pi r}(f'' + k^2 f), \quad (18.33)$$

and therefore $f(0) = 1$ and $f'' + k^2 f = 0$. The most general solution of the latter equation is

$$f(r) = ae^{ikr} + be^{-ikr}, \quad (18.34)$$

and $f(0) = 1$ fixes $a + b = 1$. Imposing the boundary condition that there is no incoming spherical waves, we get $b = 0$, so $f(r) = e^{ikr}$ and

$$G(\mathbf{x}) = -\frac{e^{ikr}}{4\pi r}. \quad (18.35)$$

The most general solution of eq. (18.25) can therefore be written as

$$\psi(\mathbf{x}) = \psi_{\text{hom}}(\mathbf{x}) - \frac{m}{2\pi\hbar^2} \int d^3x' \frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} V(\mathbf{x}')\psi(\mathbf{x}'), \quad (18.36)$$

where ψ_{hom} satisfies

$$(\nabla^2 + k^2)\psi_{\text{hom}} = 0. \quad (18.37)$$

This is completely equivalent to the Schrödinger equation, and is called the *integral form of the Schrödinger equation*. Observe that this is not yet a solution of the Schrödinger equation: the wavefunction ψ in fact appears also on the right-hand side, under the integral sign. So, we have simply transformed a differential equation into an integral equation. However, we will see that the form (18.36) is a useful starting point if we wish to compute perturbatively in the potential V .

Consider in particular the scattering problem. If V is equal to zero, the incoming wave e^{ikz} simply travels undisturbed, so the solution of the homogeneous equation appropriate to our problem is just

$$\psi_{\text{hom}} = Ae^{ikz}. \quad (18.38)$$

As in the previous section, we choose the normalization $A = 1$. We are interested in the solution $\psi(\mathbf{x})$ at large r , and in particular we are only interested in the term $O(1/r)$, since this is what we need to determine $f(\theta, \phi)$. Consider a potential localized inside a region of radius a . Then, the integral in eq. (18.36) runs only over values of \mathbf{x}' such that $|\mathbf{x}'| < a$. In the limit of large r , where $r = |\mathbf{x}|$, we have

$$|\mathbf{x} - \mathbf{x}'| \simeq r - \mathbf{x}' \cdot \hat{\mathbf{r}} + O\left(\frac{a^2}{r}\right). \quad (18.39)$$

If we are only interested in the term $O(1/r)$, inside the integral sign in eq. (18.36) we can write

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \frac{1}{r[1 + O(a/r)]} = \frac{1}{r} + O\left(\frac{1}{r^2}\right). \quad (18.40)$$

In the exponential, we must rather keep the first two terms. In fact

$$\exp\{ik|\mathbf{x} - \mathbf{x}'|\} = \exp\{ikr - i(k\hat{\mathbf{r}})\cdot\mathbf{x}' + O(ika^2/r)\}. \quad (18.41)$$

In the limit $r \rightarrow \infty$ the first two terms survive, while the remainder vanishes. Thus, in the wave zone we get

$$\psi(\mathbf{x}) = e^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int d^3x' e^{-i\mathbf{k}\cdot\mathbf{x}'} V(\mathbf{x}')\psi(\mathbf{x}') + O\left(\frac{1}{r^2}\right), \quad (18.42)$$

where

$$\mathbf{k} \equiv k\hat{\mathbf{r}}. \quad (18.43)$$

So far, everything is *exact*, as long as we are interested only in the term $O(1/r)$. Now comes the *Born approximation*. We assume that the potential is, in some sense, small, and we work perturbatively in V . We use the same iterative strategy that we already employed when we studied time-dependent perturbation theory: to zeroth order in V , there is no potential and the solution is therefore

$$\psi_0(\mathbf{x}) = e^{ikz}. \quad (18.44)$$

It is convenient to introduce

$$\mathbf{k}' \equiv k\hat{\mathbf{z}}, \quad (18.45)$$

and rewrite it as

$$\psi_0(\mathbf{x}) = e^{i\mathbf{k}'\cdot\mathbf{x}}. \quad (18.46)$$

Next we plug this zeroth order solution into the right-hand side of eq. (18.42), obtaining the first-order solution

$$\psi_1(\mathbf{x}) = e^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int d^3x' e^{i(\mathbf{k}' - \mathbf{k})\cdot\mathbf{x}'} V(\mathbf{x}') + O\left(\frac{1}{r^2}\right). \quad (18.47)$$

This is called the *Born approximation*. We could continue, plugging this expression for ψ_1 in the right-hand side of eq. (18.42), and so on.

Comparing with eq. (18.7) we see that, in the Born approximation,

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2} \int d^3x' e^{i\mathbf{q}\cdot\mathbf{x}'} V(\mathbf{x}'), \quad (18.48)$$

where

$$\mathbf{q} = \mathbf{k}' - \mathbf{k} \quad (18.49)$$

is the transferred momentum. In other words, in the Born approximation the scattering amplitude $f(\theta, \phi)$ is obtained simply performing the Fourier transform of the potential.

If the potential is spherically symmetric, eq. (18.48) can be further simplified. We choose polar coordinates, with the direction of \mathbf{q} as polar axis. Then

$$\mathbf{q} \cdot \mathbf{x}' = qr' \cos \theta', \quad (18.50)$$

and (dropping the primes for notational simplicity)

$$\int d^3x' e^{i\mathbf{q} \cdot \mathbf{x}'} V(\mathbf{x}') = 2\pi \int_{-1}^1 d \cos \theta \int_0^\infty r^2 dr V(r) e^{iqr \cos \theta}. \quad (18.51)$$

Using

$$\int_{-1}^1 d\alpha e^{iqr\alpha} = \frac{2 \sin(qr)}{qr}, \quad (18.52)$$

we finally get

$$f(\theta) = -\frac{2m}{\hbar^2 q} \int_0^\infty dr r V(r) \sin(qr). \quad (18.53)$$

Observe that, for a potential with spherical symmetry, $f(\theta, \phi)$ actually depends only on θ , as we already knew.

Example: the Rutherford cross section. The Fourier transform of the $1/r$ Coulomb potential is not very well defined, since the convergence at $r \rightarrow \infty$ of the integral in eq. (18.53) is not evident. It is convenient to start first with a Yukawa potential,

$$V(r) = \beta \frac{e^{-\mu r}}{r}. \quad (18.54)$$

The Coulomb potential is recovered in the limit $\mu \rightarrow 0$ (setting $\beta = q_1 q_2$, in the case of two particles with charges q_1 and q_2 , respectively). The Fourier transform is now well defined. The integral is elementary and we get

$$f(\theta) = -\frac{2m\beta}{\hbar^2} \frac{1}{q^2 + \mu^2}. \quad (18.55)$$

Recall that $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. Since energy is conserved in the scattering by a (time-indepenent) potential, we have $|\mathbf{k}| = |\mathbf{k}'| \equiv k$. If θ is the scattering angle, i.e. the angle between \mathbf{k} and \mathbf{k}' , we have

$$q^2 = |\mathbf{k} - \mathbf{k}'|^2 = k^2 + k^2 - 2k^2 \cos \theta, \quad (18.56)$$

i.e.

$$q^2 = 2k^2(1 - \cos \theta) = 4k^2 \sin^2 \frac{\theta}{2}. \quad (18.57)$$

Then, in the limit $\mu \rightarrow 0$,

$$f(\theta) = -\frac{2m\beta}{\hbar^2} \frac{1}{4k^2 \sin^2(\theta/2)}. \quad (18.58)$$

Writing $p = \hbar k$ and $E = p^2/(2m)$,

$$f(\theta) = -\beta \frac{1}{4E \sin^2(\theta/2)}, \quad (18.59)$$

and (writing $\beta = q_1 q_2$)

$$\frac{d\sigma}{d\Omega} = \frac{(q_1 q_2)^2}{16E^2 \sin^4(\theta/2)}. \quad (18.60)$$

This is the *Rutherford cross section*. The quantum-mechanical computation, in the Born approximation, gives the same result as the classical computation. (See however the footnote on page 180.)

18.2 Validity of the Born approximation

(Reference: Shankar, pages 543-544). In the Born approximation, in the right-hand side of the integral form of the Schrödinger equation, we replaced the total wavefunction $\psi = e^{ikz} + \psi_{\text{scat}}$ simply by e^{ikz} . The approximation is therefore valid if, for all values of \mathbf{x} , $\psi_{\text{scat}}(\mathbf{x})$ is a small perturbation of e^{ikz} . Since $\psi_{\text{scat}}(\mathbf{x})$ is larger close to the origin (and then decays as $1/r$ for large r), we require that $\psi_{\text{scat}}(0)$ be a small perturbation of e^{ikz} , i.e.

$$|\psi_{\text{scat}}(0)| \ll |e^{ikz}| = 1. \quad (18.61)$$

Recall that, in the Born approximation,

$$\psi_{\text{scat}}(\mathbf{x}) = -\frac{m}{2\pi\hbar^2} \int d^3x' \frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} V(\mathbf{x}') e^{ikz'}, \quad (18.62)$$

so

$$\psi_{\text{scat}}(0) = -\frac{m}{2\pi\hbar^2} \int d^3x' \frac{e^{ikr'}}{r'} V(\mathbf{x}') e^{ikz'}, \quad (18.63)$$

For a central potential,

$$\begin{aligned}\psi_{\text{scat}}(0) &= -\frac{m}{2\pi\hbar^2} 2\pi \int_0^\infty dr' r'^2 \frac{e^{ikr'}}{r'} V(r') \int_{-1}^1 d\cos\theta e^{ikr' \cos\theta} \\ &= -\frac{2m}{\hbar^2 k} \int_0^\infty dr \sin(kr) e^{ikr} V(r).\end{aligned}\quad (18.64)$$

Then the condition for the validity of the Born approximation is

$$\frac{2m}{\hbar^2 k} \left| \int_0^\infty dr \sin(kr) e^{ikr} V(r) \right| \ll 1. \quad (18.65)$$

For a potential with a finite range r_0 this relation is satisfied if k is sufficiently large, both because of the factor $1/k$ in front of the integral, and because for large k the exponential and the sinus of kr oscillate fast and damps the integral. For example, if we take the Yukawa potential

$$V(r) = \beta \frac{e^{-\mu r}}{r}, \quad (18.66)$$

computing the integral in the limit $k \gg \mu$ one finds

$$\frac{2m|\beta|}{\hbar^2 k} \ln\left(\frac{k}{\mu}\right) \ll 1, \quad (18.67)$$

which is satisfied for sufficiently large k .³⁹

So, generally speaking, the Born approximation is a high-energy approximation. Depending on the potential, it can however hold also at low k . Taking the limit $k \rightarrow 0$ the condition (18.65) becomes

$$\frac{2m}{\hbar^2} \left| \int_0^\infty dr' r' V(r') \right| \ll 1. \quad (18.68)$$

For a potential with typical value V_0 and size r_0 , in order of magnitude this means that

$$\frac{2m}{\hbar^2} r_0^2 |V_0| \ll 1. \quad (18.69)$$

³⁹Observe that this is only true for $\mu \neq 0$. For $\mu = 0$ eq. (18.65) is never satisfied, so the derivation given above of the Rutherford cross section is not really correct! On the other hand, we mentioned that the treatment of scattering that we have discussed only holds for potentials that goes to zero at least as $1/r^2$ for $r \rightarrow \infty$, which is not the case for the Coulomb potential, otherwise the solutions at infinity are not simple spherical waves. It is possible to treat correctly the Coulomb potential using “distorted spherical waves” rather than simple spherical waves. One finds that eq. (18.58) is modified just by a phase factor (proportional to $\ln \sin^2(\theta/2)$), and therefore the cross-section is unaffected. See Shankar, page 532.

Observe that, if we take a potential well with $V = V_0 < 0$ if $r < r_0$, and $V = 0$ otherwise, one can prove that the first bound state appears if

$$\frac{2m}{\hbar^2} r_0^2 |V_0| \gtrsim 2.7. \quad (18.70)$$

In other words, for a negative potential, at low energies the Born approximation works if the potential is so shallow that it does not allow for bound states.