

## Atomic physics

This chapter is devoted to an introduction to atomic physics which will be mainly concerned with one-electron atoms. After a brief discussion of the perturbation and variational methods in Section 14.1, in Section 14.2 we study the fine and hyperfine structure of the energy levels as well as the effect of a magnetic field on these levels. In Section 14.3 we examine the coupling of an atom to an electromagnetic field and important applications of this coupling such as the photoelectric effect and the rate of spontaneous emission. In Section 14.4 we give a brief introduction to a subject which has been expanding enormously in the last twenty years, the laser manipulation of atoms, and we discuss Doppler cooling and magneto-optical traps. Finally, Section 14.5 is devoted to a short discussion of two-electron atoms.

### 14.1 Approximation methods

#### 14.1.1 Generalities

In classical physics it is only in exceptional cases that it is possible to solve the Newton or Maxwell equations analytically given the initial conditions at time  $t = t_0$  and, in the first case, the forces, or, in the second, the sources of electromagnetic field. In general, it is necessary to resort to an approximation method such as numerical integration of the equations, the perturbation method, or something else. The situation is no different in quantum physics: only in exceptional cases do we know how to “solve the Schrödinger equation” exactly, that is, how to obtain the time evolution of the state vector  $|\varphi(t)\rangle$  as a function of its value  $|\varphi(t_0)\rangle$  at initial time  $t = t_0$ . In the case where the Hamiltonian is time-independent, which is what we shall consider in this section, knowledge of this time evolution implies that we know how to diagonalize the Hamiltonian, that is, find its eigenvalues and eigenvectors. Except in some special cases (the square well, the harmonic oscillator, the hydrogen atom, and so on), we do not know how to diagonalize the Hamiltonian exactly, and approximation methods such as numerical integration or the perturbation method must be used.

In this section we shall present the method of time-independent perturbation theory. It consists of starting from a Hamiltonian  $H_0$  which we know how to diagonalize exactly, and

then perturbing it by adding a term  $W$  which gives the “exact” Hamiltonian  $H = H_0 + W$  within some predefined domain of approximation (cf. Section 4.3). We write

$$H(\lambda) = H_0 + \lambda W, \quad (14.1)$$

where we have introduced a real parameter  $\lambda$  such that  $H = H_0$  if  $\lambda = 0$  and  $H = H_0 + W$  if  $\lambda = 1$ . If  $\lambda \rightarrow 0$ , we can hope that the perturbation  $\lambda W$  is in some sense “small” compared with  $H_0$ .<sup>1</sup> It may happen that it is possible to effectively vary  $\lambda$ . For example, if  $\lambda W$  corresponds to the interaction of an atomic system with an external electromagnetic field, the value of this external field and therefore also  $\lambda$  can be varied at will, and  $\lambda \rightarrow 0$  if the field is made to vanish. However, in general the perturbation is fixed by physical conditions that cannot be changed. In this case  $\lambda$  is a fictitious parameter that we vary artificially, and then at the end of the calculations we set it to its physical value  $\lambda = 1$ . We have already used this trick in the introduction to time-dependent perturbation theory in Section 9.6.3, where we wrote the perturbation as  $\lambda W(t)$  and then took  $\lambda = 1$  at the end of the calculation.

We therefore assume that the spectrum of  $H_0$  is known. Let  $E_0^{(n)}$  be its eigenvalues and  $|n, r\rangle$  its eigenvectors, where  $r$  is the degeneracy index as in Section 2.3.1:

$$H_0|n, r\rangle = E_0^{(n)}|n, r\rangle. \quad (14.2)$$

We seek the eigenvalues and eigenvectors of  $H(\lambda)$  in the form of series in powers of  $\lambda$ , called *perturbation series*. If  $H(\lambda)|\varphi(\lambda)\rangle = E(\lambda)|\varphi(\lambda)\rangle$ , we can write the series for the eigenvector  $|\varphi(\lambda)\rangle$  and the energy  $E(\lambda)$  as

$$|\varphi(\lambda)\rangle = |\varphi_0\rangle + \lambda|\varphi_1\rangle + \lambda^2|\varphi_2\rangle + \cdots, \quad (14.3)$$

$$E(\lambda) = E_0^{(n)} + \lambda E_1^{(n)} + \lambda^2 E_2^{(n)} + \cdots. \quad (14.4)$$

If  $\lambda = 0$ ,  $|\varphi(\lambda = 0)\rangle = |\varphi_0\rangle = |n, r\rangle$  and  $E = E_0^{(n)}$ . Our implicit hypothesis is that a series in  $\lambda$  with nonzero radius of convergence exists or, in other words, that the energy is an analytic function of  $\lambda$  at the point  $\lambda = 0$ . Two cases must be distinguished.

- The eigenvalue  $E_0^{(n)}$  of  $H_0$  is simple: then we have the case of *nondegenerate perturbation theory*.
- The eigenvalue  $E_0^{(n)}$  of  $H_0$  is degenerate with degeneracy  $N$ : then we have the case of *degenerate perturbation theory*.

We shall discuss these two cases one after the other, without entering into the details of the general method of calculating to all orders in  $\lambda$ . We limit ourselves to the lowest nontrivial order in  $\lambda$  and refer the reader to the classic texts for the general case.

<sup>1</sup> Rigorously proving that one operator is “small” compared with another is a most delicate mathematical problem.

### 14.1.2 Nondegenerate perturbation theory

We start from  $H_0|n\rangle = E_0^{(n)}|n\rangle$  and set  $|\varphi_0\rangle = |n\rangle$  with  $\langle\varphi_0|\varphi_0\rangle = 1$ , as well as  $E_0 = E_0^{(n)}$  in order to simplify the notation. In practice, we shall be interested in the perturbative expansion (14.4) of the energy, treating the perturbative expansion (14.3) of the vector  $|\varphi(\lambda)\rangle$  as auxiliary to the calculation permitting us to fix  $|\varphi(\lambda)\rangle$  by a convenient condition:  $\langle\varphi_0|\varphi(\lambda)\rangle = \langle\varphi_0|\varphi_0\rangle = 1$ . With this condition  $|\varphi(\lambda)\rangle$  is in general not a normalized vector, but it is always possible to make it one if we wish. Through order  $\lambda$  we have, on the one hand,

$$H(\lambda)|\varphi(\lambda)\rangle = H_0|\varphi_0\rangle + \lambda W|\varphi_0\rangle + \lambda H_0|\varphi_1\rangle,$$

while on the other

$$H(\lambda)|\varphi(\lambda)\rangle = (E_0 + \lambda E_1)|\varphi(\lambda)\rangle = E_0|\varphi_0\rangle + \lambda E_1|\varphi_0\rangle + \lambda E_0|\varphi_1\rangle,$$

from which, identifying the terms of order  $\lambda$ ,

$$W|\varphi_0\rangle + H_0|\varphi_1\rangle = E_1|\varphi_0\rangle + E_0|\varphi_1\rangle.$$

Multiplying the two terms of this equation on the left by the bra  $\langle\varphi_0|$  and using  $\langle\varphi_0|H_0 = E_0\langle\varphi_0|$ , we obtain<sup>2</sup>

$$E_1 = \langle\varphi_0|W|\varphi_0\rangle, \quad (14.5)$$

and so, denoting by  $\Delta E_1$  the energy difference between the cases  $\lambda \neq 0$  and  $\lambda = 0$  to first order in  $\lambda$ , we can write

$$\Delta E_1 = \lambda \langle\varphi_0|W|\varphi_0\rangle. \quad (14.6)$$

The order- $\lambda^2$  term is also found fairly easily (Exercise 14.6.1):

$$\Delta E_2^{(n)} = \lambda^2 \sum_{k \neq n} \frac{|\langle k|W|n\rangle|^2}{E_0^{(n)} - E_0^{(k)}}. \quad (14.7)$$

As an application, let us calculate the shift of the levels of the one-dimensional harmonic oscillator acted on by an anharmonic perturbation proportional to  $q^4$ :

$$\lambda W = \lambda \frac{m^2 \omega^3}{\hbar} Q^4. \quad (14.8)$$

From the result of Exercise 11.5.1 and (14.6) we obtain the shift of the  $n$ th level through order  $\lambda$ :

$$\Delta E_1^{(n)} = \frac{3}{4} \lambda \hbar \omega (2n^2 + 2n + 1). \quad (14.9)$$

Even if  $\lambda$  is small, the result diverges for large  $n$ , because the larger  $n$  is the more important the wave function is at large values of  $q$ , and therefore the more important

<sup>2</sup> This expression (14.5) can be obtained directly using the Feynman–Hellmann theorem; see Exercise 4.4.3, Eq. (4.35).

the perturbation  $\propto q^4$  is: the perturbation  $\lambda Q^4$  is never “small.” We have begun with the hypothesis that there exists a series in powers of  $\lambda$  with nonzero radius of convergence. In practice, this hypothesis of analyticity at  $\lambda = 0$  is not always satisfied, and the anharmonic oscillator we have just studied provides an example of this. Actually, it is easy to see in this case that  $E^{(n)}$  cannot be analytic at  $\lambda = 0$ , because the nature of the Hamiltonian changes abruptly at this point. For  $\lambda > 0$  it is bounded below and bound states are present, but for  $\lambda < 0$  it is no longer bounded below and the problem becomes meaningless, unless one adds, for example, a  $\lambda' q^6$ ,  $\lambda' > 0$  term to avoid the difficulty. The perturbative series is therefore no longer meaningful for  $\lambda < 0$ , and it gives an example of an asymptotic series, which gives good results for  $\lambda > 0$  if sufficiently few terms are kept, but which diverges if we try to keep too many. This type of series is well known in mathematics. A good example is the Stirling formula valid for  $n \gg 1$ :

$$\Gamma(n+1) = n! = \left(\frac{n}{e}\right)^n \sqrt{2\pi n} \left(1 + \frac{1}{12n} + \frac{1}{288n^2} + \cdots\right), \quad (14.10)$$

which is a nonconvergent asymptotic series in powers of  $1/n$ . Sophisticated methods have been developed for summing such asymptotic series.<sup>3</sup>

### 14.1.3 Degenerate perturbation theory

Let us now consider the case of a degenerate level, using  $\mathcal{H}^{(n)}$  to denote the subspace of dimension  $N$  of the eigenvalue  $E_0^{(n)}$ . The projector  $\mathcal{P}^{(n)}$  on  $\mathcal{H}^{(n)}$  is written as

$$\mathcal{P}^{(n)} = \sum_{r=1}^N |n, r\rangle \langle n, r|. \quad (14.11)$$

In the subspace  $\mathcal{H}^{(n)}$  the operator  $W$  is represented by an  $N \times N$  matrix with elements  $W_{sr}^{(n)} = \langle n, s | W | n, r \rangle$  which can be diagonalized. The eigenvectors  $|\varphi_0^{(n,q)}\rangle$  of  $W$  in  $\mathcal{H}^{(n)}$  are linear combinations of the  $|n, r\rangle$ :

$$|\varphi_0^{(n,q)}\rangle = \sum_{r=1}^N c_{qr} |n, r\rangle, \\ W |\varphi_0^{(n,q)}\rangle = E_1^{(n,q)} |\varphi_0^{(n,q)}\rangle.$$

The coefficients  $c_{qr}$  are of zeroth order in  $\lambda$  since  $W$  can be diagonalized without affecting  $H_0$ , which is a multiple of the identity in  $\mathcal{H}^{(n)}$ :

$$H_0 |\varphi_0^{(n,q)}\rangle = E_0^{(n)} |\varphi_0^{(n,q)}\rangle.$$

The diagonalization of  $W$  in  $\mathcal{H}^{(n)}$  gives the result for the energy through order  $\lambda$ . We recover the results of the nondegenerate case by taking the dimension of  $\mathcal{H}^{(n)}$  equal to

<sup>3</sup> See, for example, J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, Oxford: Oxford University Press (1989), Chapter 37.

unity. In summary, through order  $\lambda$  we can calculate the energy levels and eigenvectors as for a system with a finite number  $N$  of levels by diagonalizing the matrix representing  $H_0 + \lambda W$  in  $\mathcal{H}^{(n)}$ . In fact, an approximation by a system with a finite number of levels is often obtained by neglecting the interactions between the subspaces  $\mathcal{H}^{(n)}$ . A final remark is that the quasi-degenerate case should also be treated by this method.

#### 14.1.4 The variational method

We shall again limit ourselves to the study of a simple case, that of finding the ground-state energy, and leave the use of the variational method in other cases to the classic texts. Let  $E_0$  be the ground-state energy of a Hamiltonian  $H$  and  $|0\rangle$  be the corresponding eigenvector

$$H|0\rangle = E_0|0\rangle,$$

and let  $|\varphi\rangle$  be an arbitrary unit vector in the Hilbert space of states. We write the expectation value of  $H$  in the state  $|\varphi\rangle$  by decomposing  $|\varphi\rangle$  on the basis of eigenstates  $|n\rangle$  of  $H$ ,  $H|n\rangle = E_n|n\rangle$ :

$$\langle\varphi|H|\varphi\rangle = \sum_{n,m} c_m^* c_n \langle m|H|n\rangle = \sum_n E_n |c_n|^2.$$

We find that

$$\langle\varphi|H|\varphi\rangle - \langle 0|H|0\rangle = \sum_n (E_n - E_0) |c_n|^2 \geq 0, \quad (14.12)$$

where we have used  $\sum_n |c_n|^2 = 1$  and  $E_n \geq E_0$ . The variational method consists of specifying a trial vector  $|\varphi(\alpha)\rangle$  depending on a parameter  $\alpha$ , or several parameters  $\alpha_i$ , which we try to choose to be as close as possible to the assumed form of  $|0\rangle$ . The result (14.12) shows that

$$\langle H\rangle(\alpha) = \langle\varphi(\alpha)|H|\varphi(\alpha)\rangle \geq E_0.$$

Within the framework of the chosen parametrization, the best result for  $E_0$  will be obtained by seeking the minimum of  $\langle H\rangle(\alpha)$ :

$$\left. \frac{d}{d\alpha} \langle H\rangle(\alpha) \right|_{\alpha=\alpha_0} = 0, \quad (14.13)$$

and an upper bound on  $E_0$  is

$$E_0 \leq \langle\varphi(\alpha_0)|H|\varphi(\alpha_0)\rangle. \quad (14.14)$$

To compare two different choices  $|\varphi(\alpha)\rangle$  and  $|\tilde{\varphi}(\beta)\rangle$  we compare the two minima. The best choice will be the one that gives the smallest value of  $\langle H\rangle$ . The generalization to a vector depending on several parameters  $\alpha_1, \dots, \alpha_p$  is immediate: we seek the minimum of  $\langle H\rangle$  using

$$\left. \frac{\partial}{\partial \alpha_i} \langle H\rangle(\alpha_1, \dots, \alpha_p) \right|_{\alpha_j=\alpha_{j0}} = 0.$$

As an example, let us study the variational calculation of the ground state of the harmonic oscillator, choosing the trial wave function to be a normalizable function of unit norm:

$$\langle x | \varphi(\alpha) \rangle = \varphi_\alpha(x) = \sqrt{\frac{2}{\pi}} \alpha^{3/2} \frac{1}{x^2 + \alpha^2}. \quad (14.15)$$

The integrals needed in the following calculations can be derived from the expression

$$I(\alpha) = \int_{-\infty}^{\infty} \frac{dx}{x^2 + \alpha^2} = \frac{\pi}{\alpha} \quad (14.16)$$

by differentiating  $I(\alpha)$  with respect to  $\alpha^2$ . Starting from the form (11.9) of the Hamiltonian of the harmonic oscillator, we calculate  $\langle H \rangle(\alpha)$ :

$$\begin{aligned} \langle H \rangle(\alpha) &= \frac{1}{2} \hbar \omega \int_{-\infty}^{\infty} dx \left[ \left( \frac{d\varphi_\alpha}{dx} \right)^2 + x^2 \varphi_\alpha^2(x) \right] \\ &= \frac{1}{2} \hbar \omega \left[ \frac{1}{2\alpha^2} + \alpha^2 \right]. \end{aligned}$$

The first term in the square brackets is the kinetic energy and the second is the potential energy. The value of  $\langle H \rangle(\alpha)$  is a minimum for  $\alpha^2 = \alpha_0^2 = 1/\sqrt{2}$  and

$$\langle H \rangle(\alpha_0) = \frac{\hbar \omega}{\sqrt{2}} > E_0 = \frac{\hbar \omega}{2}.$$

For  $\alpha = \alpha_0$  the average kinetic energy and the average potential energy are equal:

$$\frac{1}{2m} \langle P^2 \rangle = \frac{1}{2} m \omega^2 \langle X^2 \rangle = \frac{\hbar \omega}{2\sqrt{2}}.$$

The choice (14.15) for the trial wave function is not very good (the error is  $\sim 40\%$ ), because this wave function decreases much too slowly at infinity. If we use a Gaussian trial wave function, we of course find the exact result  $\hbar \omega/2$ . The power of the variational method will be illustrated in Section 14.5.1.

## 14.2 One-electron atoms

### 14.2.1 Energy levels in the absence of spin

In Chapter 10 we studied the spectrum of the hydrogen atom, which has a single electron. An immediate generalization can be made to the ions  $\text{He}^+$ ,  $\text{Li}^{++}$ , etc. When there is more than one electron, it is no longer possible to analytically solve for the energy levels. It is necessary to resort to approximation methods, which are sometimes very accurate, as in the case of light atoms and, in particular, helium (Section 14.5). Alkaline atoms can also be treated using a simple approximation. Actually, to a first approximation an alkaline atom is an atom with a single outer electron subject to the effective potential produced by the nucleus and the other  $(Z - 1)$  electrons, called the inner-shell electrons. The spectrum is therefore similar to that of the hydrogen atom, with the difference that no degeneracy

is observed between levels of different orbital angular momentum, because the effective potential does not behave as  $1/r$ . In the case of sodium, for example, the ground state is a  $3s$  level, and the  $3p$  level lies between the  $3s$  and  $4s$  levels (Fig. 10.7).

The spectra of Figs. 10.6 and 10.7 were obtained neglecting the spin of the outer electron as well as the nuclear spin. We are going to study the modifications introduced when these spins are taken into account, namely the *fine structure* due to the interaction between the electron orbital angular momentum and spin (Section 14.2.2), the *Zeeman effect* in the presence of an external magnetic field (Section 14.2.3), and the *hyperfine structure* due to the interaction between the nuclear spin and the electron spin and orbital angular momentum (Section 14.2.4).

### 14.2.2 The fine structure

The fine structure is an effect of relativistic origin whose correct study is based on a relativistic quantum wave equation which is valid for spin-1/2 particles, namely, the Dirac equation.<sup>4</sup> Within the framework of a classical description we are going to make an intuitive argument, which is not entirely correct, to justify the expression for the fine-structure Hamiltonian. In the reference frame where the nucleus is at rest, or the nucleus frame, the electromagnetic field is the gradient of the electrostatic potential  $V(r)/q_e$  produced by the nucleus and the  $(Z - 1)$  inner-shell electrons, and the external electron moves with velocity  $\vec{v}$  in this reference frame. In its rest frame, the electron sees the nucleus moving with velocity  $-\vec{v}$  and an electromagnetic field which is the transform of the field in the nucleus frame. This transformed field consists of not only an electric field, but also a magnetic field given as a function of the electrostatic field  $\vec{E}$  in the nucleus frame as<sup>5</sup>

$$\vec{B} \simeq -\frac{1}{c^2} \vec{v} \times \vec{E} \simeq \frac{1}{q_e c^2} \left[ \frac{1}{r} \frac{dV(r)}{dr} \right] \left( \frac{\vec{p}}{m_e} \times \vec{r} \right). \quad (14.17)$$

This magnetic field interacts with the magnetic moment  $\vec{\mu} = \gamma \vec{s}$  of the outer electron, leading to an interaction energy

$$W_{\text{so}} = -\vec{\mu} \cdot \vec{B} \simeq -\frac{q_e}{m_e} \vec{s} \cdot \vec{B}, \quad (14.18)$$

because the gyromagnetic ratio  $\gamma \simeq q_e/m_e$ . Combining these two equations and introducing the orbital angular momentum  $\vec{l} = \vec{r} \times \vec{p}$ , we derive the spin-orbit potential:

$$W_{\text{so}} = \frac{1}{m_e^2 c^2} \left[ \frac{1}{r} \frac{dV(r)}{dr} \right] \vec{l} \cdot \vec{s}. \quad (14.19)$$

Our argument can be criticized because we have used the formulas for transformations between inertial reference frames, while the electron reference frame is accelerated with

<sup>4</sup> The Dirac equation is not the only relativistic quantum wave equation. Another important one is the Klein-Gordon equation, which describes particles of spin 0. However, neither of these equations is completely consistent, as the real unification of quantum mechanics and relativity requires quantized field theory.

<sup>5</sup> In (14.17) we have used the approximation  $v \ll c$ ; the exact expression contains factors of  $(1 - v^2/c^2)^{-1/2}$ .

respect to the nuclear frame because the electron rotates about the nucleus. This rotational motion leads to the phenomenon of spin precession, called Thomas precession,<sup>6</sup> which reduces the result (14.19) by a factor of two. In the end, the correct quantum expression for the spin-orbit potential is obtained by correcting (14.19) by a factor of 1/2 and replacing the classical quantities  $\vec{l}$  and  $\vec{s}$  by the operators  $\vec{L}$  and  $\vec{S}$ :

$$W_{\text{so}} = \frac{1}{2m_e^2 c^2} \left[ \frac{1}{r} \frac{dV(r)}{dr} \right] \vec{L} \cdot \vec{S}. \quad (14.20)$$

Let us evaluate the order of magnitude of the correction to the energy levels for the hydrogen atom. Since  $\vec{L}$  and  $\vec{S}$  are of order  $\hbar$  and  $V(r) = -e^2/r$ , in a state  $n$  we obtain

$$\langle W_{\text{so}} \rangle \sim \frac{\hbar^2 e^2}{2m_e^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \sim \frac{\hbar^2 e^2}{2m_e^2 c^2 n^3 a_0^3} = \left( \frac{e^2}{2a_0} \right) \left( \frac{e^2}{\hbar c} \right)^2 \frac{1}{n^3} = \frac{\alpha^2 R_\infty}{n^3},$$

where we have introduced the Bohr radius  $a_0$ , the fine-structure constant  $\alpha$ , and the Rydberg constant  $R_\infty$  (see (1.39)–(1.41)). The corrections to the energy levels are therefore of order  $\alpha^2$  in relative value, which is what we expect for relativistic corrections, because  $(v/c)^2 \sim \alpha^2$ .<sup>7</sup>

Let us examine the effect of the potential (14.20) on a level ( $nl$ ) with principal quantum number  $n$  and orbital angular momentum  $l$ . Since the effect on the levels is small,  $\sim \alpha^2$ , we can use perturbation theory. Neither the orbital angular momentum  $\vec{L}$  nor the spin  $\vec{S}$  commutes with  $W_{\text{so}}$ . However, the scalar operator  $\vec{L} \cdot \vec{S}$  commutes with the *total* angular momentum  $\vec{J} = \vec{L} + \vec{S}$  and moreover, since  $[\vec{L}^2, \vec{L}] = 0$  and  $[\vec{L}^2, f(r)] = 0$ , the potential (14.20) commutes with  $\vec{L}^2$ , which implies that levels with different  $l$  are not related. In summary, the spin-orbit potential is diagonal in the basis  $|l \ 1/2 \ j m_j\rangle$ . In the absence of the spin-orbit potential, the degeneracy of a level ( $nl$ ) is  $2(2l+1)$  and it is necessary in principle to use degenerate perturbation theory. However, in the present case the situation is very simple, because we already know the basis  $|l \ 1/2 \ j m_j\rangle$  in which  $W_{\text{so}}$  is diagonal. The spin-orbit potential will partially lift the degeneracy. In fact, two values  $j = l \pm 1/2$  of the total angular momentum are possible, and according to (10.138) and using  $\vec{J}^2 = (\vec{L} + \vec{S})^2$ ,

$$\vec{L} \cdot \vec{S} = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \quad (14.21)$$

or

$$\begin{aligned} \vec{L} \cdot \vec{S} &= -\frac{\hbar^2}{2} (l+1), & j &= l - \frac{1}{2}, \\ \vec{L} \cdot \vec{S} &= +\frac{\hbar^2}{2} l, & j &= l + \frac{1}{2}. \end{aligned} \quad (14.22)$$

<sup>6</sup> See, for example, E. Taylor and J. Wheeler, *Space-Time Physics*, New York: Freeman (1963), Section 103, or Jackson [1999], Section 11.8.

<sup>7</sup> For a nucleus of charge  $Z$  and a single electron,  $(v/c)^2 \sim (Z\alpha)^2$ .



The states of total angular momentum  $j = l - 1/2$  and  $j = l + 1/2$  therefore have different energies and the spin-orbit potential partially lifts the degeneracy. Naturally, each of the two corresponding energy levels still has a  $(2j + 1)$ -fold degeneracy. We note that the spin-orbit potential does not affect  $s$ -waves ( $l = 0$ ).

As a special case, let us consider the  $2p$  ( $l = 1$ ) level of hydrogen. The two possible values of  $j$  are  $j = 1/2$  and  $j = 3/2$ . The corresponding levels are denoted as  $2p_{1/2}$  and  $2p_{3/2}$ . The  $2p \rightarrow 1s$  transition is split, which is easily confirmed by spectroscopy. In the case of hydrogen, the  $2s_{1/2}$  and  $2p_{1/2}$  levels are degenerate in the approximation of the Dirac equation. They differ in energy from the  $2p_{3/2}$  level by about  $4.5 \times 10^{-5}$  eV, which corresponds to a frequency difference of about 10 GHz. The order-of-magnitude calculation we have just done gives an energy difference  $\sim \alpha^2 R_\infty / 8 \sim 10^{-4}$  eV, in qualitative agreement with experiment. Experiment shows that, in contrast to the prediction of the Dirac equation, the  $2s_{1/2}$  and  $2p_{1/2}$  levels are in fact nondegenerate: the  $2p_{1/2}$  level is lower by about  $5 \times 10^{-5}$  eV, which corresponds to about 1 GHz. This difference, known as the Lamb shift, is explained by effects of quantum electrodynamics, the theory of the quantized electromagnetic and electron-positron fields.

The above notation  $(nl)_j$  can be generalized to higher levels: for a  $d$ -wave ( $l = 2$ ) the possible values of  $j$  are  $3/2$  and  $5/2$  and the levels are denoted as  $nd_{3/2}$  and  $nd_{5/2}$ . For an  $f$ -wave ( $l = 3$ ) we will have the  $nf_{5/2}$  and  $nf_{7/2}$  levels, and so on. A classic example in spectroscopy is the splitting of the yellow line of sodium, which corresponds to a  $3p \rightarrow 3s$  transition; the two lines are called  $D_1$  at 589.6 nm and  $D_2$  at 589.0 nm. In general, the  $j = l + 1/2$  level is higher than the  $j = l - 1/2$  level because the expectation value  $\langle dV/dr \rangle > 0$ , but there are some exceptions. In the nuclear shell model, where the spin-orbit potential plays a crucial role, this order is systematically inverted.

### 14.2.3 The Zeeman effect

The  $(2j + 1)$ -fold degeneracy of the  $(nl)_j$  level is lifted by placing the atom in a constant magnetic field  $\vec{B}$ . This is the *Zeeman effect*. It arises from the interaction of the magnetic field with the orbital magnetic moment due to the motion of the electron in its orbit, and also to the magnetic moment associated with the spin of this electron. The magnetic moment associated with  $\vec{L}$  is given by the classical gyromagnetic ratio (3.30)  $\gamma = q_e/2m_e$ , and the gyromagnetic ratio due to the spin is roughly  $q_e/m_e$ . The interaction energy is derived from the coupling between the magnetic moment and the field:<sup>8</sup>

$$W = -\frac{q_e}{2m_e}(\vec{L} + 2\vec{S}) \cdot \vec{B} \quad (14.23)$$

<sup>8</sup> However, this argument gives only the dominant term in the interaction; see Exercise 14.6.5 for a detailed justification of (14.23).

It is usual to choose  $\vec{B}$  to be parallel to  $Oz$ :

$$W = -\frac{q_e B}{2m_e} (L_z + 2S_z). \quad (14.24)$$

When the Zeeman energy (14.23) is sufficiently small compared with the characteristic energy of the fine structure of the level under consideration, we can use degenerate perturbation theory for each level  $(nl)_j$ . If this is not the case, it is necessary to simultaneously diagonalize the Hamiltonian of the fine structure and that of the Zeeman effect; see Exercise 6.5.4. Let us consider the case of small Zeeman effect. The matrix elements of the perturbation (14.24) in the  $(nl)_j$  level are

$$W_{mm'}^{nlj} = -\frac{q_e B}{2m_e} \langle nljm | L_z + 2S_z | nljm' \rangle. \quad (14.25)$$

The operators  $\vec{L}$  and  $\vec{S}$  are vector operators, and according to the Wigner–Eckart theorem (10.150) for these operators the matrix elements for, for example,  $L_z$  are given by

$$\begin{aligned} \langle nljm | L_z | nljm' \rangle &= \frac{1}{\hbar^2 j(j+1)} \langle j || (\vec{J} \cdot \vec{L}) || j \rangle \langle nljm | J_z | nljm' \rangle \\ &= \frac{m}{\hbar j(j+1)} \langle (\vec{J} \cdot \vec{L}) \rangle \delta_{mm'}. \end{aligned}$$

Using

$$\vec{S}^2 = (\vec{J} - \vec{L})^2 \quad \text{and} \quad \vec{L}^2 = (\vec{J} - \vec{S})^2$$

to write out  $\vec{J} \cdot \vec{S}$  and  $\vec{J} \cdot \vec{L}$ , we find

$$\langle \vec{J} \cdot (\vec{L} + 2\vec{S}) \rangle = \frac{3}{2} \vec{J}^2 + \frac{1}{2} \vec{S}^2 - \frac{1}{2} \vec{L}^2$$

and then

$$\begin{aligned} \langle nljm | L_z + 2S_z | nljm' \rangle &= \frac{m\hbar}{2j(j+1)} \left[ 3j(j+1) + \frac{3}{4} - l(l+1) \right] \delta_{mm'} \\ &= m\hbar \left\{ 1 + \frac{1}{2j(j+1)} \left[ j(j+1) + \frac{3}{4} - l(l+1) \right] \right\} \delta_{mm'}. \end{aligned}$$

The final result can be written as

$$W_{mm'}^{nlj} = -g \frac{q_e B}{2m_e} m\hbar \delta_{mm'}. \quad (14.26)$$

Within our approximation the shifts of the Zeeman sublevels are linear in  $B$ . They are controlled by the *Landé g factor*:

$$g = 1 + \frac{1}{2j(j+1)} \left[ j(j+1) + \frac{3}{4} - l(l+1) \right]. \quad (14.27)$$

The quantity  $gq_e/2m_e$  can be interpreted physically as an effective gyromagnetic ratio. For a free electron in a magnetic field we have seen that the Landé  $g$  factor is 2. This is also the case for an  $s$ -wave, as can be verified by setting  $l = 0$  in (14.27).

#### 14.2.4 The hyperfine structure

An even smaller effect, of order  $10^{-6}$  in relative value, arises from the interaction between the nuclear magnetic moment and the orbital and spin magnetic moments of the outer electron. The interaction between a nuclear magnetic dipole moment  $\mu_n$  and an electron magnetic dipole is a priori weaker than that between two electric dipoles by a factor  $\sim 10^{-3}$ , as the nuclear Bohr magneton  $\mu_N = q_p \hbar / 2m_p$  is smaller than the Bohr magneton  $\mu_B = |q_e| \hbar / 2m_e$  by a factor of  $m_p / m_e \sim 2000$ . We recall the expressions for the electron and proton magnetic moment operators:

$$\vec{\mu}_e = \gamma_e \vec{S}_e \simeq -2\mu_B \frac{\vec{S}_e}{\hbar}, \quad \mu_p = \gamma_p \vec{S}_p \simeq 5.59\mu_N \frac{\vec{S}_p}{\hbar}. \quad (14.28)$$

In classical electrodynamics it can be shown<sup>9</sup> that the magnetic field  $\vec{B}(\vec{r})$  of a point dipole  $\vec{\mu}_n$  at the origin is

$$\vec{B}(\vec{r}) = -\frac{\mu_0}{4\pi r^3} [\vec{\mu}_n - 3(\vec{\mu}_n \cdot \hat{r})\hat{r}] + \frac{2\mu_0}{3} \vec{\mu}_n \delta(\vec{r}). \quad (14.29)$$

The energy of the orbital magnetic moment and the spin of the outer electron in this magnetic field can be written as in (14.23). We shall limit ourselves to the case of an  $s$ -wave electron, where only the spin magnetic moment needs to be taken into account, as in the  $s$ -wave there is no contribution from the orbital angular momentum to the atomic magnetic moment. Moreover, the term inside the square brackets in (14.29) gives a vanishing contribution. Actually, if we use perturbation theory to calculate the magnetic energy  $\langle W' \rangle = -\langle \vec{\mu}_e \cdot \vec{B} \rangle$  corresponding to the interaction of the electron magnetic moment with the term inside the square brackets in (14.29) for an  $s$ -wave, where the wave function  $\varphi(r)$  depends only on  $r$ , we find

$$\begin{aligned} \langle W' \rangle &= \frac{\mu_0}{4\pi} \int d^3r |\varphi(r)|^2 \frac{1}{r^3} [(\vec{\mu}_n \cdot \vec{\mu}_e) - 3(\vec{\mu}_n \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r})] \\ &= \frac{\mu_0}{4\pi} \left\langle \frac{1}{r^3} \right\rangle \left[ (\vec{\mu}_n \cdot \vec{\mu}_e) - 3 \sum_{i,j=1}^3 \mu_{ni} \mu_{ej} I_{ij} \right]. \end{aligned}$$

To obtain the second line of the above equation we separated the radial part of the integral of the second term in the square brackets from the angular part by writing

$$\int d^3r = 4\pi \int_0^\infty r^2 dr \int \frac{d\Omega}{4\pi}.$$

<sup>9</sup> See, for example, Jackson [1999], Section 5.6.

The radial integral gives

$$\int_0^\infty r^2 dr |\varphi(r)|^2 \frac{1}{r^3} = \left\langle \frac{1}{r^3} \right\rangle.$$

The angular integral  $I_{ij}$  is

$$I_{ij} = \int \frac{d\Omega}{4\pi} \hat{r}_i \hat{r}_j = \frac{1}{3} \delta_{ij}.$$

To prove this, we observe that the only rotationally invariant rank-2 tensor that can be constructed using the indices  $(i, j)$  is  $\delta_{ij}$ :

$$I_{ij} = c \delta_{ij} \quad \text{and} \quad \sum_{ij} \delta_{ij} I_{ij} = 1,$$

which shows that  $c = 1/3$ . Thus, the term between square brackets in (14.29) gives a vanishing contribution and we are left with just the contact term:

$$\begin{aligned} W_{\text{cont}} &= -\frac{2\mu_0}{3} \vec{\mu}_n \cdot \vec{\mu}_e \delta(\vec{r}) \\ &= -\frac{2\mu_0}{3} \gamma_n \gamma_e (\vec{S}_n \cdot \vec{S}_e) \delta(\vec{r}). \end{aligned} \quad (14.30)$$

As an example, let us take the hyperfine structure of the ground state of the hydrogen atom:  $\mu_n \rightarrow \mu_p$ ,  $n = 1$ ,  $l = 0$ . The state vector is the tensor product of a spatial wave function derived from (10.94)

$$\varphi(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right) \quad (14.31)$$

and a spin wave function, which itself is the tensor product of the state vectors in the electron and proton spin spaces. The spatial part and the spin part are completely decoupled. First we find the expectation value of the spatial part:

$$\begin{aligned} \langle W_{\text{cont}} \rangle_{\text{spat}} &= -\frac{2\mu_0}{3} \gamma_n \gamma_e |\varphi(0)|^2 (\vec{S}_p \cdot \vec{S}_e) \\ &= \frac{A}{\hbar^2} (\vec{S}_p \cdot \vec{S}_e). \end{aligned} \quad (14.32)$$

The constant  $A$  is

$$A = \frac{2\mu_0}{3} (2\mu_B) (5.59\mu_N) \frac{1}{\pi a_0^3} \simeq 5.87 \times 10^{-6} \text{ eV}.$$

Then the effective Hamiltonian is  $A(\vec{S}_p \cdot \vec{S}_e)/\hbar^2$ , which acts in the four-dimensional Hilbert space that is the tensor product of the two spin spaces. In the absence of the hyperfine perturbation, the  $1s_{1/2}$  ground state of the hydrogen atom is four-fold degenerate. It is necessary to diagonalize  $A(\vec{S}_p \cdot \vec{S}_e)/\hbar^2$  in this subspace, which is straightforward if we introduce the total spin  $\vec{S} = \vec{S}_p + \vec{S}_e$  and the identity

$$\vec{S}_p \cdot \vec{S}_e = \frac{1}{2} (\vec{S}^2 - \vec{S}_p^2 - \vec{S}_e^2) = \frac{\hbar^2}{2} \left[ s(s+1) - \frac{3}{2} \right]. \quad (14.33)$$

According to the results of Section 10.6.1, the two possible values of  $s$  are  $s = 1$  (the triplet state) and  $s = 0$  (the singlet state). The eigenvalues of the Hamiltonian are

$$\begin{aligned} s = 1, \quad \text{triplet state : } E_{\text{tr}} &= E_0 + \frac{1}{4}A, \\ s = 0, \quad \text{singlet state : } E_{\text{sing}} &= E_0 - \frac{3}{4}A, \end{aligned}$$

where  $E_0$  is the energy in the absence of the hyperfine effect, and the eigenvectors are given by (10.125) and (10.126). The two levels are separated by an amount  $A \simeq 5.87 \times 10^{-6}$  eV, which corresponds to the emission of a photon of wavelength 21 cm when the atom makes a transition from the triplet to the singlet level. Although the lifetime of the triplet level is very long,  $10^7$  years, and a priori seems difficult to observe, it is of great importance in astrophysics. It has given fundamental information about the interstellar clouds of atomic hydrogen making up 10% to 50% of the mass of the galaxy, permitting measurements of mass and velocity distributions, magnetic fields, and so on.<sup>10</sup>

## 14.3 Atomic interactions with an electromagnetic field

### 14.3.1 The semiclassical theory

In this section we shall study the interaction between an electromagnetic field and an atom, modeled as before by an outer electron in a spherically symmetric potential. We shall begin with the *semi-classical approximation*, already introduced in Section 5.3.2, where the electromagnetic field is described classically while the atom is described in a quantum manner. In Section 5.3 we postulated a phenomenological interaction between an electromagnetic wave and an electric dipole responsible for transitions from one level to another. In this section we shall complete these results by justifying the dipole approximation and giving an explicit expression for the transition amplitude. At this point it is useful to summarize the various possible approximations which can be used to study interactions between an atom (or molecule) and the electromagnetic field (see Table 14.1). In principle, the atom and the field should both be treated in a quantum manner, but it may prove convenient to use a classical approximation for one or the other when it is clear that such an approximation is valid.

In the approach of Section 11.3.3, the classical electromagnetic wave is described in the Coulomb gauge  $\vec{\nabla} \cdot \vec{A} = 0$  by a transverse vector potential  $\vec{A}(\vec{r}, t)$ . A plane wave of wave vector  $\vec{k}$  and frequency  $\omega$  can be written as

$$\vec{A}(\vec{r}, t) = \text{Re} \left[ \vec{A}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \right], \quad \vec{k} \cdot \vec{A}_0 = 0. \quad (14.34)$$

Let us recall the action of the divergence and curl operators in the Fourier space:

$$\vec{\nabla} \cdot \rightarrow i\vec{k} \cdot, \quad \vec{\nabla} \times \rightarrow i\vec{k} \times, \quad (14.35)$$

<sup>10</sup> More details can be found in, for example, Basdevant and Dalibard [2002], Chapter 13.

Table 14.1 *Various approximation schemes*

Electromagnetic field	Atom	Examples
classical	classical	classical radiation Section 1.5.3
classical	quantum	absorption and stimulated emission Section 5.3.2, Sections 14.3.1 to 14.3.3
quantum	classical	coupling to a classical source Exercise 11.5.4
quantum	quantum	spontaneous emission Section 14.3.4, Section 14.4

which leads to the following electric and magnetic fields:

$$\vec{E}(\vec{r}, t) = -\frac{\partial \vec{A}}{\partial t} = \text{Re} \left[ i\omega \vec{A}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \right], \quad (14.36)$$

$$\vec{B}(\vec{r}, t) = \vec{\nabla} \times \vec{A} = \text{Re} \left[ i(\vec{k} \times \vec{A}_0) e^{i(\vec{k} \cdot \vec{r} - \omega t)} \right]. \quad (14.37)$$

The energy flux is given by the Poynting vector

$$\vec{S} = \varepsilon_0 c^2 \vec{E} \times \vec{B}, \quad (14.38)$$

and averaging over time using  $\langle \cos^2(\omega t) \rangle = 1/2$  we find

$$\langle \vec{S} \rangle = \frac{1}{2} \varepsilon_0 c \omega^2 |\vec{A}_0|^2 \hat{k} = \mathcal{I}(\omega) \hat{k}. \quad (14.39)$$

The intensity  $\mathcal{I}(\omega)$  is related to the photon flux  $\mathcal{F}$  as

$$\mathcal{I}(\omega) = \hbar \omega \mathcal{F},$$

or, denoting the photon density by  $n$ ,

$$\mathcal{F} = nc = \frac{1}{2\hbar} \varepsilon_0 c \omega |\vec{A}_0|^2. \quad (14.40)$$

According to (11.115), the Hamiltonian describing the interaction between the electron and the field is

$$H = \frac{1}{2m_e} \left[ \vec{P} - q_e \vec{A}(\vec{R}, t) \right]^2 + V(\vec{R}), \quad (14.41)$$

where  $V(\vec{R})$  represents the effective interaction of the outer electron with the nucleus and the  $(Z - 1)$  inner-shell electrons. The Hamiltonian (14.41) can be split into the unperturbed part  $H_0$

$$H_0 = \frac{1}{2m_e} \vec{P}^2 + V(\vec{R}) \quad (14.42)$$

and a perturbation

$$W(\vec{R}, t) = -\frac{q_e}{2m_e} \left( \vec{P} \cdot \vec{A} + \vec{A} \cdot \vec{P} \right) + \frac{q_e^2}{2m_e} \vec{A}^2. \quad (14.43)$$

To first order in  $q_e \vec{A}$  we can neglect the second term of (14.43), or the diamagnetic term  $(q_e^2/2m_e)\vec{A}^2$  (Exercise 14.5.5). Moreover, the first term is simplified in the Coulomb gauge  $\vec{\nabla} \cdot \vec{A} = 0$  because

$$\begin{aligned}\vec{P} \cdot [\vec{A} f(\vec{r})] &= -i\hbar(\vec{\nabla} \cdot \vec{A})f(\vec{r}) - i\hbar\vec{A} \cdot \vec{\nabla} f(\vec{r}) \\ &= -i\hbar\vec{A} \cdot \vec{\nabla} f(\vec{r}) = (\vec{A} \cdot \vec{P})f(\vec{r}).\end{aligned}$$

The perturbation  $W(\vec{R}, t)$  is finally written as

$$W(\vec{R}, t) = -\frac{q_e}{m_e} [\vec{A}(\vec{R}, t) \cdot \vec{P}]. \quad (14.44)$$

We shall work in a representation in which  $\vec{R}$  is diagonal,  $\vec{R} \rightarrow \vec{r}$ . Using (14.34), we have

$$W(\vec{r}, t) = -\frac{q_e}{2m_e} \left[ e^{i(\vec{k} \cdot \vec{r} - \omega t)} \vec{A}_0 \cdot \vec{P} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \vec{A}_0^* \cdot \vec{P} \right]. \quad (14.45)$$

Now we can use the results of Section 9.6.3: the term involving  $\exp(-i\omega t)$  in (14.45) corresponds to energy absorption by the atom and the term involving  $\exp(i\omega t)$  corresponds to energy emission. If there exist two energy levels  $E_i$  and  $E_f$  with  $E_i < E_f$  corresponding to a resonance  $E_f - E_i = \hbar\omega_0 \simeq \hbar\omega$ , the atom will absorb energy  $\hbar\omega_0$  in a transition  $i \rightarrow f$ , and emit energy  $\hbar\omega_0$  in a transition  $f \rightarrow i$ . In a particle interpretation this would of course mean that the atom absorbs or emits a photon of energy  $\hbar\omega_0$ , but such an interpretation falls outside the framework of the semi-classical theory. According to (9.170), the probability per unit time of absorption  $i \rightarrow f$  is given by

$$\Gamma_{fi} = \frac{2\pi}{\hbar} \left( \frac{q_e}{2m_e} \right)^2 \left| \langle f | \exp(i\vec{k} \cdot \vec{r}) \vec{A}_0 \cdot \vec{P} | i \rangle \right|^2 \delta(E_f - (E_i + \hbar\omega)). \quad (14.46)$$

### 14.3.2 The dipole approximation

Let us introduce a polarization unit vector  $\vec{e}_s$ ,  $\vec{e}_s^* \cdot \vec{e}_s = 1$ , writing  $\vec{A}_0 = |\vec{A}_0| \vec{e}_s$ . The intensity  $\mathcal{J}(\omega)$  per unit frequency is given by (14.39):

$$\mathcal{J}(\omega) = \frac{1}{2} \varepsilon_0 c \omega^2 |\vec{A}_0(\omega)|^2.$$

We rewrite (14.46) by integrating over  $\omega$  and separating the squared modulus of the transition matrix element from the characteristics of the incident wave:

$$\begin{aligned}\Gamma_{fi} &= \frac{2\pi}{\hbar} \left( \frac{q_e}{2m_e} \right)^2 \int d\omega |\vec{A}_0(\omega)|^2 \left| \vec{e}_s \cdot \langle f | \exp(i\vec{k} \cdot \vec{r}) \vec{P} | i \rangle \right|^2 \delta(E_f - (E_i + \hbar\omega)) \\ &= \frac{4\pi^2 \alpha}{\hbar \omega_0^2 m_e^2} \mathcal{J}(\omega_0) \left| \vec{e}_s \cdot \langle f | \exp(i\vec{k} \cdot \vec{r}) \vec{P} | i \rangle \right|^2.\end{aligned} \quad (14.47)$$

The transition matrix element in (14.47) can be simplified by using the fact that the wavelength of the emitted or absorbed radiation,  $0.1 \mu\text{m} \lesssim \lambda \lesssim 1 \mu\text{m}$ , is very large

compared with the atomic dimensions  $a_0 \sim 0.1$  nm, which makes it possible to replace  $\exp(i\vec{k} \cdot \vec{r})$  by unity because  $\langle \vec{k} \cdot \vec{r} \rangle \sim ka_0 \sim a_0/\lambda \ll 1$ :

$$\begin{aligned}\langle f | e^{i\vec{k} \cdot \vec{r}} \vec{P} | i \rangle &= \int d^3r \varphi_f^*(\vec{r}) e^{i\vec{k} \cdot \vec{r}} (-i\hbar \vec{\nabla}) \varphi_i(\vec{r}) \\ &\simeq \int d^3r \varphi_f^*(\vec{r}) (-i\hbar \vec{\nabla}) \varphi_i(\vec{r}).\end{aligned}$$

Moreover,  $\vec{P}$  can be written as the commutator between  $\vec{R}$  and  $H_0$ :

$$[\vec{R}, H_0] = \frac{i\hbar}{m_e} \vec{P},$$

which gives

$$\begin{aligned}\langle f | \vec{P} | i \rangle &= \frac{m_e}{i\hbar} \langle f | \vec{R} H_0 - H_0 \vec{R} | i \rangle \\ &= \frac{m_e}{i\hbar} (E_i - E_f) \langle f | \vec{R} | i \rangle = im_e \omega_0 \langle f | \vec{R} | i \rangle.\end{aligned}\quad (14.48)$$

In classical physics  $\vec{r}$  is the vector joining the nucleus located at the origin to the outer electron and  $q_e \vec{r}$  is the electric dipole moment  $\vec{d}$  of the atom. The quantity  $\langle f | q_e \vec{R} | i \rangle$  is therefore the *matrix element*  $\vec{D}_{fi}$  of the *electric dipole moment operator*  $\vec{D} = q_e \vec{R}$  between the states  $|i\rangle$  and  $|f\rangle$ :

$$\vec{D}_{fi} = \langle f | \vec{D} | i \rangle = q_e \langle f | \vec{R} | i \rangle. \quad (14.49)$$

Substituting these results into (14.47), we obtain the transition probability per unit time for polarization  $\vec{e}_s$ :

$$\Gamma_{fi} = 4\pi^2 \left( \frac{|\vec{e}_s \cdot \vec{D}_{fi}|^2}{4\pi\epsilon_0 \hbar^2 c} \right) \mathcal{J}(\omega_0) \quad (14.50)$$

$$= \frac{4\pi^2 \alpha}{\hbar} |\vec{e}_s \cdot \vec{R}_{fi}|^2 \mathcal{J}(\omega_0), \quad (14.51)$$

in agreement with (5.66). The dipole moment  $d$  introduced phenomenologically in Section 5.3.2 takes the following explicit form for a one-electron atom:

$$d^2 \rightarrow |\vec{e}_s \cdot \vec{D}_{fi}|^2 = q_e^2 |\vec{e}_s \cdot \vec{R}_{fi}|^2.$$

The expression (14.50) is more general than (14.51), and is valid for any atomic or molecular system when the selection rules for electric dipole transitions are satisfied: the transition probability is governed by the transition matrix element of the electric dipole moment of the system, which involves all the charged particles. By an identical calculation we find the rate of stimulated emission  $\bar{\Gamma}_{if}$ , which is also given by (14.50):  $\bar{\Gamma}_{if} = \Gamma_{fi}$ . Actually, to go from absorption to emission it is sufficient to replace  $D_{fi}$  by  $D_{if} = D_{fi}^*$ . Following the argument based on the Einstein relations of Section 5.4, from



$\Gamma_{fi}$  we can deduce the probability for spontaneous emission of a photon by summing over the two possible polarization states  $s = 1, 2$  and taking the average  $\langle \bullet \rangle$  over angles and spins:

$$B' = \frac{4\omega_0^3}{c^2} \left\langle \frac{\frac{1}{2} \sum_{s=1}^2 \langle |\vec{e}_s \cdot \vec{D}_{fi}|^2 \rangle}{4\pi\epsilon_0\hbar c} \right\rangle = \frac{2\alpha\omega_0^3}{c^2} \left\langle \sum_{s=1}^2 |\vec{e}_s \cdot \vec{R}_{fi}|^2 \right\rangle. \quad (14.52)$$

The electric dipole moment operator  $\vec{D}$ , like the position operator  $\vec{R}$ , is a vector operator which is odd under a parity operation, that is, a polar vector. This property of  $\vec{D}$  implies certain *selection rules* for electric dipole transitions. The Wigner–Eckart theorem for vector operators gives the matrix elements of the spherical components (10.145)  $D_q$  of  $\vec{D}$ : if  $j_i$  and  $j_f$  are the angular momenta of the initial state  $i$  and the final state  $f$ , and  $m_i$  and  $m_f$  are the magnetic quantum numbers, then from (10.149) we obtain

$$\langle j_f m_f | D_q | j_i m_i \rangle = C_{q m_i; j_f m_f}^{1 j_i} \langle j_f || D || j_i \rangle. \quad (14.53)$$

The Clebsch–Gordan coefficient can be nonzero only if  $|j_i - 1| \leq j_f \leq j_i + 1$  and  $m_f = q + m_i$ . Moreover, the parities of the initial and final states must be opposite:  $\Pi_i \Pi_f = -1$ . Therefore, electric dipole transitions obey the following selection rules.

*Selection rules for electric dipole transitions*

$$|j_i - 1| \leq j_f \leq j_i + 1, \quad m_f = m_i + q, \quad q = -1, 0, +1, \quad \Pi_i \Pi_f = -1.$$

These rules generalize the results obtained in Section 10.5.2 in the special case  $j_i = 1$  and  $j_f = 0$ . The selection rules for the magnetic quantum number  $m$  are directly related to the conservation of the  $z$  component of the angular momentum, and some examples have already been given in Section 10.5.2 and Exercise 10.7.13.

### 14.3.3 The photoelectric effect

In the preceding subsection we studied a transition between two levels by generalizing the results of Section 5.3. Now let us consider a transition to the continuum. An electromagnetic wave of frequency  $\omega > R_\infty/\hbar$  and polarization  $\vec{e}_s$  arrives at a hydrogen atom in its ground state. In particle language the condition  $\omega > R_\infty/\hbar$  implies that the photon energy is sufficient for ionizing the atom by ejecting its electron, which provides a very simple example of the photoelectric effect and is a case which can be completely solved analytically. According to the Fermi Golden Rule and the definition (12.1) of the cross section, to first order in perturbation theory in  $W$  the cross section for photoelectron production is

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar\mathcal{F}} |\langle f | W | i \rangle|^2 \frac{\mathcal{V} m_e k_e}{(2\pi)^3 \hbar^2} \quad (14.54)$$

where  $\vec{k}_e$  is the wave vector of the final electron and the last factor is the electron density of states (9.151) in a volume  $\mathcal{V}$ . When  $\hbar\omega \gg R_\infty$  (but  $\hbar\omega \ll m_e c^2$  in order to preserve

the nonrelativistic kinematics and prevent electron–positron pair production<sup>11</sup>), we can neglect the interaction of the final electron with the proton and take a plane wave for the final state, thus obtaining the Born approximation:

$$\langle \vec{r} | f \rangle = \varphi_f(\vec{r}) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\vec{k}_e \cdot \vec{r}}.$$

We note that the dipole approximation is not valid under the kinematic conditions defined above. The initial state is described by the wave function (14.31) of the ground state of the hydrogen atom. The matrix element  $\langle f | W | i \rangle$  is given by (14.46):

$$\langle f | W | i \rangle = \left( -\frac{q_e}{2m_e} \right) |\vec{A}_0| \vec{e}_s \cdot \int d^3r \frac{1}{\sqrt{\mathcal{V}}} e^{i(\vec{k} - \vec{k}_e) \cdot \vec{r}} \left( -i\hbar \vec{\nabla} \varphi_i(\vec{r}) \right)$$

or, integrating by parts and using the fact that  $\vec{e}_s \cdot \vec{k} = 0$ ,

$$\begin{aligned} \langle f | W | i \rangle &= \left( -\frac{q_e}{2m_e} \right) |\vec{A}_0| \frac{\hbar(\vec{e}_s \cdot \vec{k}_e)}{\sqrt{\mathcal{V}\pi a_0^3}} \int d^3r e^{i(\vec{k} - \vec{k}_e) \cdot \vec{r}} e^{-r/a_0} \\ &= \left( -\frac{q_e}{2m_e} \right) |\vec{A}_0| \frac{\hbar(\vec{e}_s \cdot \vec{k}_e)}{\sqrt{\mathcal{V}\pi a_0^3}} \frac{8\pi/a_0}{(q^2 + 1/a_0^2)^2}, \end{aligned} \quad (14.55)$$

where we have defined  $\vec{q} = \vec{k} - \vec{k}_e$ , so that  $\hbar\vec{q}$  is the momentum transfer between the initial photon and the final electron. To calculate the integral in (14.55) we have used the formula

$$\begin{aligned} \int d^3r e^{i\vec{q} \cdot \vec{r}} e^{-\lambda r} &= 2\pi \int_0^\infty r^2 dr e^{-\lambda r} \int_{-1}^{+1} e^{iqr \cos \theta} d\cos \theta = \frac{2\pi}{q} \int_0^\infty r dr \sin qr e^{-\lambda r} \\ &= \frac{2\pi}{q} \text{Im} \int_0^\infty r dr e^{iqr} e^{-\lambda r} = \frac{4\pi}{q} \text{Im} \frac{1}{(\lambda - iq)^2} = \frac{8\pi\lambda}{(\lambda^2 + q^2)^2}. \end{aligned}$$

Assembling all the factors in (14.54), we obtain

$$\frac{d\sigma}{d\Omega} = \frac{32\alpha\hbar}{m_e \omega a_0^5} \frac{|\vec{e}_s \cdot \hat{k}_e|^2 k_e^3}{[(\vec{k} - \vec{k}_e)^2 + 1/a_0^2]^4}. \quad (14.56)$$

Let us make (14.56) explicit by choosing  $\vec{k}$  to be parallel to  $Oz$  and taking linear polarization  $\vec{e}_s$  parallel to  $Ox$ . Let  $(\Omega = \theta, \phi)$  be the polar angles defining  $\hat{k}_e$ :

$$(\vec{e}_x \cdot \hat{k}_e)^2 = \sin^2 \theta \cos^2 \phi.$$

This quantity is a maximum when  $\vec{e}_x$  and  $\vec{k}_e$  are parallel, or  $\theta = \pi/2$  and  $\phi = 0$  or  $\pi$ . The denominator in (14.56) varies slowly with  $\theta$ , because, with the kinematical conditions defined above, from energy conservation we have

$$\frac{k}{k_e} \simeq \frac{\hbar k_e}{2m_e c} = \frac{v_e}{2c} \ll 1,$$

<sup>11</sup> This approximation is valid in the case of X-rays, where the energy varies from 1 to 100 keV.

where  $v_e$  is the speed of the photoelectrons and

$$(\vec{k} - \vec{k}_e)^2 \simeq k_e^2 \left(1 - \frac{v_e}{c} \cos \theta\right).$$

Therefore, the electrons are preferentially ejected in a plane perpendicular to the incident wave vector and parallel to the electric field of the wave. If the incident wave is not polarized, the contributions of the polarizations in the  $x$  and  $y$  directions must be added incoherently and averaged over:

$$\frac{1}{2} \left[ (\vec{e}_x \cdot \hat{k}_e)^2 + (\vec{e}_y \cdot \hat{k}_e)^2 \right] = \frac{1}{2} \sin^2 \theta.$$

This still gives preferential emission in the plane perpendicular to  $\vec{k}$ :

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{unpol}} = \frac{16\alpha\hbar}{m_e \omega a_0^5} \frac{k_e^3 \sin^2 \theta}{[(\vec{k} - \vec{k}_e)^2 + 1/a_0^2]^4} \simeq \frac{16\alpha\hbar}{m_e \omega a_0^5 k_e^5} \frac{\sin^2 \theta}{\left[1 - \frac{v_e}{c} \cos \theta\right]^8}. \quad (14.57)$$

Under the chosen kinematical conditions we can neglect  $1/a_0^2$  compared to  $q^2$ , because

$$\frac{\hbar^2 k_e^2}{2m_e} \gg R_\infty = \frac{e^2}{2a_0} \Rightarrow (k_e a_0)^2 \gg \frac{m_e e^2}{\hbar^2} a_0 = 1.$$

It is important to note that we have managed to treat the photoelectric effect in a semiclassical approach without introducing the photon, contradicting the widespread belief that the photon concept is necessary to explain the threshold effect (Section 1.3.2). In the semiclassical approach the threshold effect arises from the resonance condition: the photoelectric effect is appreciable only if the light wave is in resonance with the ground state  $E_0$  and a level  $E_C$  of the continuum:  $E_C - E_0 = \hbar\omega$ . The photoelectric effect can be explained without the photon, but not without  $\hbar$ !

#### 14.3.4 The quantized electromagnetic field: spontaneous emission

We have often had recourse to the concept of the photon in order to interpret intuitively the results of the semiclassical theory, whereas strictly speaking this concept is foreign to this theory. Unless we use an indirect argument<sup>12</sup> like that of Section 5.4, it is not possible to calculate the probability of spontaneous emission by an atom in an excited state, because there is no pre-existing classical electromagnetic field and the interaction term  $\propto \vec{A} \cdot \vec{P}$  is zero. It is necessary to resort to the concept of quantized electromagnetic field developed in Section 11.3.3, because the annihilation and creation operators  $a_{\vec{k}s}$  and  $a_{\vec{k}s}^\dagger$  are capable of changing the number of photons. More precisely, if  $n_{\vec{k}s}$  is the number of photons in the mode of wave vector  $\vec{k}$  and polarization  $s$ , we are interested in transitions with the emission of a photon  $n_{\vec{k}s} \rightarrow n_{\vec{k}s} + 1$  or the absorption of a photon  $n_{\vec{k}s} \rightarrow n_{\vec{k}s} - 1$ ,

<sup>12</sup> The argument uses the Planck distribution, which implicitly involves the concept of photon: the occupation probability of a mode of the electromagnetic field is given by the quantum theory of the harmonic oscillator. It is therefore not surprising that it is possible to calculate spontaneous emission.

with spontaneous emission in the mode  $(\vec{k}, s)$  corresponding to  $n_{\vec{k}s} = 0$ . Let us recall the expansion of the quantized electromagnetic field (11.79) at  $t = 0$  in a volume  $L^3 = \mathcal{V}$ :

$$\vec{A}(\vec{r}) = \sqrt{\frac{\hbar}{2\varepsilon_0\mathcal{V}}} \sum_{\vec{k}} \sum_{s=1}^2 \frac{1}{\sqrt{\omega_k}} \left( a_{\vec{k}s} \vec{e}_s(\hat{k}) e^{i\vec{k}\cdot\vec{r}} + a_{\vec{k}s}^\dagger \vec{e}_s^*(\hat{k}) e^{-i\vec{k}\cdot\vec{r}} \right).$$

The coupling between the electromagnetic field<sup>13</sup> and the atom is, to first order in  $\vec{A}$ ,

$$W = -\frac{q_e}{m_e} \vec{A} \cdot \vec{P}. \quad (14.58)$$

This *time-independent* coupling  $\vec{A} \cdot \vec{P}$  brings in the terms

$$a_{\vec{k}s} e^{i\vec{k}\cdot\vec{r}} (\vec{e}_s(\hat{k}) \cdot \vec{P}), \quad (14.59)$$

and

$$a_{\vec{k}s}^\dagger e^{-i\vec{k}\cdot\vec{r}} (\vec{e}_s^*(\hat{k}) \cdot \vec{P}). \quad (14.60)$$

The term (14.59) destroys a photon and the term (14.60) creates a photon in the mode  $(\vec{k}, s)$ . Let  $|i, n_{\vec{k}s}\rangle$  be the initial state with  $i$  labeling the state of the atom and let  $|f, n_{\vec{k}s} \pm 1\rangle$  be the final state. The nonzero matrix elements of  $a_{\vec{k}s}$  and  $a_{\vec{k}s}^\dagger$  are given by (11.16) and (11.17):

$$\begin{aligned} \langle n_{\vec{k}s} + 1 | a_{\vec{k}s}^\dagger | n_{\vec{k}s} \rangle &= \sqrt{n_{\vec{k}s} + 1}, \\ \langle n_{\vec{k}s} - 1 | a_{\vec{k}s} | n_{\vec{k}s} \rangle &= \sqrt{n_{\vec{k}s}}. \end{aligned} \quad (14.61)$$

We shall examine spontaneous emission corresponding to the case  $n_{\vec{k}s} = 0$  and return briefly to absorption and stimulated emission at the end of this subsection. The interesting physical quantity is the probability per unit time for an atom to emit a photon of wave vector approximately equal to  $\vec{k}$  and polarization  $s$  at a solid angle  $d\Omega$ ,  $\Omega = (\theta, \phi)$ , about  $\vec{k}$ .<sup>14</sup> To obtain this probability we need the photon density of states:

$$\frac{\mathcal{V}}{(2\pi)^3} d^3k = \frac{\mathcal{V}}{(2\pi)^3 c^3} \omega^2 d\omega d\Omega \quad (14.62)$$

<sup>13</sup> It is necessary to take the electromagnetic field (11.79) at  $t = 0$ , that is, in the Schrödinger picture  $\vec{A}_S = \vec{A}_H(t = 0) = \vec{A}$ , because we are using the Schrödinger picture in the perturbative calculations and the operators  $\vec{A}$  and  $\vec{P}$  must also be in this picture. In Subsections 14.1.1 to 14.1.3 the time dependence of the classical field is fixed by an external source, that which produces the incident electromagnetic wave, whereas the quantized field is independent of any external source.

<sup>14</sup> To be rigorous, we should note that we are working in the reference frame where the initial atom is at rest. Energy conservation implies that

$$E_i - E_f = \hbar\omega + \frac{\hbar^2 k^2}{2M_{\text{at}}}$$

in this reference frame. The second term is the recoil energy, which will be discussed in (14.106). In general, this recoil energy is negligible; everything happens as though the atom were infinitely heavy,  $M_{\text{at}} \rightarrow \infty$ .

with  $\omega_k \rightarrow \omega$ . The transition probability per unit time is given by the Fermi Golden Rule (9.170) with a final photon  $(\vec{k}, s)$  of energy  $\hbar\omega$ :

$$d\Gamma_{fi}^s(\vec{k}, s) = \frac{2\pi}{\hbar} |\langle f, n_{\vec{k}s} = 1 | W | i, n_{\vec{k}s} = 0 \rangle|^2 \delta[\hbar\omega - (E_i - E_f)] \frac{\mathcal{V}}{(2\pi)^3 c^3} \omega^2 d\omega d\Omega, \quad (14.63)$$

with the matrix element  $\langle f, n_{\vec{k}s} = 1 | W | i, n_{\vec{k}s} = 0 \rangle$  given by (in contrast to Section 14.3.2, we now have  $E_i > E_f$  and  $\hbar\omega_0 = E_i - E_f$ )

$$\begin{aligned} \langle f, n_{\vec{k}s} = 1 | W | i, n_{\vec{k}s} = 0 \rangle &= -\frac{q}{m_e} \langle f, n_{\vec{k}s} = 1 | \vec{A} \cdot \vec{P} | i, n_{\vec{k}s} = 0 \rangle \\ &= -\frac{q}{m_e} \sqrt{\frac{\hbar}{2\varepsilon_0 \mathcal{V} \omega}} \langle f, n_{\vec{k}s} = 1 | a_{\vec{k}s}^\dagger e^{i\vec{k} \cdot \vec{r}} (\vec{\epsilon}_s^*(\hat{k}) \cdot \vec{P}) | i, n_{\vec{k}s} = 0 \rangle \\ &\simeq iq_e \omega_0 \sqrt{\frac{\hbar}{2\varepsilon_0 \omega \mathcal{V}}} \langle f | (\vec{\epsilon}_s^*(\hat{k}) \cdot \vec{R}) | i \rangle. \end{aligned} \quad (14.64)$$

We have used the dipole approximation  $\exp(i\vec{k} \cdot \vec{r}) \simeq 1$  and expressed the matrix element of  $\vec{P}$  using (14.48).

To obtain the probability for photon emission in a solid angle  $d\Omega$  we must integrate (14.63) over  $\omega$ . The  $\delta$  function fixes the photon energy to

$$\hbar\omega = E_i - E_f = \hbar\omega_0,$$

which, using (14.64) and defining  $\vec{R}_{fi} = \langle f | \vec{R} | i \rangle$ , gives

$$\frac{d\Gamma_{fi}^s}{d\Omega} = \frac{\alpha \omega_0^3}{2\pi c^2} |\vec{\epsilon}_s^*(\hat{k}) \cdot \vec{R}_{fi}|^2. \quad (14.65)$$

An equivalent expression involves the dipole moment  $\vec{D} = q_e \vec{R}$ :

$$\frac{d\Gamma_{fi}^s}{d\Omega} = \left( \frac{1}{4\pi\varepsilon_0} \right) \left( \frac{\omega_0^3}{2\pi\hbar c^3} \right) |\vec{\epsilon}_s^*(\hat{k}) \cdot \vec{D}_{fi}|^2. \quad (14.66)$$

To obtain the total transition probability  $\Gamma$ , which is the inverse of the lifetime  $\tau$  of the excited state  $\tau = 1/\Gamma$ , it is necessary to integrate over  $\Omega$  and sum over the two polarization states:

$$\Gamma = \frac{1}{\tau} = \sum_{s=1}^2 \int \frac{d\Gamma_{fi}^s}{d\Omega} d\Omega. \quad (14.67)$$

In order to calculate the matrix element in, for example, the form (14.65) we work in a representation where  $\vec{R}$  is diagonal:<sup>15</sup>

$$\vec{R}_{fi} = \int d^3r \varphi_f^*(\vec{r}) \vec{r} \varphi_i(\vec{r}), \quad (14.68)$$

<sup>15</sup> To simplify the formulas we neglect spin, which can easily be shown to play no role at all.

and we separate the  $r$ -dependent radial part and the  $\hat{r}$ -dependent angular part in the integral (14.68) by writing  $\vec{r} = r\hat{r}$ . To deal with a specific case, we take the example of the  $2p \rightarrow 1s$  transition of the hydrogen atom.<sup>16</sup> The initial wave function is written as the product of its radial part (10.96) and its angular part, which is the spherical harmonic  $Y_1^m(\hat{r})$ :

$$\varphi_i^m(\vec{r}) = \frac{1}{\sqrt{4!a_0^3}} r \exp\left(-\frac{r}{2a_0}\right) Y_1^m(\hat{r}), \quad (14.69)$$

and the final wave function is given by (14.31). It is convenient to introduce the spherical components (10.64) of the vectors  $\vec{e}_s(\hat{k})$  and  $\vec{r}$  noting that the scalar product  $\vec{e}_s^* \cdot \hat{r}$  is<sup>17</sup>

$$\vec{e}_s^* \cdot \hat{r} = (\vec{e}_s \cdot \hat{r})^* = \left( \sum_{q=\pm 1,0} e_{sq}^* \hat{r}_q \right)^* = \sum_{q=\pm 1,0} e_{sq} \hat{r}_q^*.$$

On the other hand, the projector (11.80) orthogonal to  $\vec{k}$  is written in spherical coordinates as

$$\sum_{s=1}^2 e_{sq}(\hat{k}) e_{sq'}^*(\hat{k}) = \delta_{qq'} - \hat{k}_q \hat{k}_{q'}^*,$$

which gives for the angular part

$$\left| \sum_s \vec{e}_s^*(\hat{k}) \cdot \langle f | \hat{r} | i \rangle \right|^2 = \sum_{qq'} (\delta_{qq'} - \hat{k}_q \hat{k}_{q'}^*) \langle f | \hat{r}_q^* | i \rangle \langle i | \hat{r}_{q'} | f \rangle.$$

The matrix element  $\langle f | \hat{r}_q^* | i \rangle$  is easily calculated by noting that according to (10.64)  $\hat{r}_q$  is proportional to the spherical harmonic  $Y_1^q(\hat{r})$ . If the magnetic quantum number of the initial state is  $m$ , then

$$\langle f | \hat{r}_q^* | i, m \rangle = \sqrt{\frac{4\pi}{3}} \int d^2\hat{r} [Y_1^q(\hat{r})]^* Y_1^m(\hat{r}) = \sqrt{\frac{4\pi}{3}} \delta_{qm},$$

where we have used the orthogonality relations (10.55) of the spherical harmonics. This then gives

$$\left| \sum_s \vec{e}_s^*(\hat{k}) \cdot \langle f | \hat{r} | i \rangle \right|^2 = \frac{4\pi}{3} (1 - |\hat{k}_m|^2).$$

The factor  $(1 - |\hat{k}_m|^2)$  becomes  $(1 - \frac{1}{2} \sin^2 \theta)$  for  $m = \pm 1$  and  $(1 - \cos^2 \theta)$  for  $m = 0$ , which gives the angular distribution of the emitted photon if the initial state has a

<sup>16</sup> In the general case of an initial state  $i$  of angular momentum  $(j_i, m_i)$  and a final state  $f$  of angular momentum  $(j_f, m_f)$ , we can use the Wigner–Eckart theorem to express the matrix element of the spherical components  $D_q$  of  $\vec{D}$  in the form (14.53).

<sup>17</sup> The scalar product of two vectors  $\vec{a}$  and  $\vec{b}$  is given as a function of their spherical coordinates by

$$\vec{a} \cdot \vec{b} = \sum_{q=\pm 1,0} a_q^* b_q = \sum_{q=\pm 1,0} (-1)^q a_{-q} b_q.$$

well-defined value of  $m$ . If the initial state is unpolarized, the angular distribution is of course isotropic because there is no preferred direction:

$$\frac{1}{3} \left[ 2 \left( 1 - \frac{1}{2} \sin^2 \theta \right) + (1 - \cos^2 \theta) \right] = \frac{2}{3}.$$

To obtain the total transition probability (14.67) we integrate over  $\Omega$ , the result being the same for the three cases  $m = \pm 1, 0$ :

$$\int d\Omega \left( 1 - \frac{1}{2} \sin^2 \theta \right) = \int d\Omega (1 - \cos^2 \theta) = \frac{8\pi}{3}.$$

The angular part gives an overall factor of  $32\pi^2/9$ . According to (14.31) and (14.69), the radial part of the matrix element is

$$\langle f|r|i \rangle = \frac{1}{a_0^4 \sqrt{4! \pi}} \int_0^\infty r^4 dr \exp\left(-\frac{3r}{2a_0}\right) = \sqrt{\frac{4!}{\pi}} \left(\frac{2}{3}\right)^5 a_0.$$

The combination of all these results gives the transition probability  $\Gamma(2p \rightarrow 1s)$ :

$$\Gamma(2p \rightarrow 1s) = \left[ \frac{\alpha \omega_0^3}{2\pi c^2} \right] \left[ \frac{4!}{\pi} \left(\frac{4}{9}\right)^5 a_0^2 \right] \left[ \frac{32\pi^2}{9} \right], \quad (14.70)$$

and using

$$\omega_0 = \frac{3}{4} \frac{R_\infty}{\hbar} = \frac{3}{8} \frac{\alpha^2 m_e c^2}{\hbar} \quad \text{and} \quad a_0 = \frac{\hbar^2}{m_e e^2} = \frac{\hbar}{\alpha m c},$$

we can write the result in the final form, recalling (cf. Section 1.5.3) that  $\hbar/m_e c^2 = 1.29 \times 10^{-21}$  s:

$$\Gamma(2p \rightarrow 1s) = \alpha^5 \left( \frac{m_e c^2}{\hbar} \right) \left( \frac{4}{9} \right)^4 \simeq 6.2 \times 10^8 \text{ s}^{-1}, \quad \tau = \frac{1}{\Gamma} \simeq 1.6 \times 10^{-9} \text{ s}. \quad (14.71)$$

Let us return to the qualitative aspects of these results. Starting from (14.52) or (14.65) with  $|\vec{e}_s^* \cdot \vec{R}_{fi}| \sim a$ , where  $a$  is the typical atomic scale ( $a \simeq 10^{-10}$  m), we obtain the estimate

$$\Gamma \sim \frac{\alpha \omega_0^3}{c^2} a^2 = \alpha \left( \frac{a \omega_0}{c} \right)^2 \omega_0 \sim \alpha^3 \omega_0 \sim \alpha^5 \left( \frac{m_e c^2}{\hbar} \right).$$

In fact, the speed  $v$  of the electron in its orbit is  $v \sim \alpha c$ .<sup>18</sup> The characteristic frequency  $\omega_0$  is given by  $\hbar \omega_0 \sim 1$  eV or  $\omega_0 \sim 1.5 \times 10^{15}$  rad s<sup>-1</sup>, and the lifetime  $\tau$  of the excited state is estimated to be

$$\tau = \frac{1}{\Gamma} \sim 2 \times 10^{-9} \text{ s}.$$

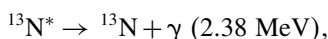
The lifetimes of excited states that de-excite by an electric dipole transition essentially lie between  $\sim 10^{-7}$  s and  $\sim 10^{-9}$  s. It is instructive also to study the case of an excited

<sup>18</sup> The factors that are assumed to be “near unity” in this type of estimate are not always so; the above estimate differs from the exact value (14.71) by a factor of  $(8/3)(4/9)^4 \simeq 1/10$ .

level of a nucleus which decays by emitting a photon  $\gamma$ . The typical energy of such a photon is  $\sim 1$  MeV, which corresponds to a wavelength  $\lambda \simeq 10^{-12}$  m. Since the nuclear dimensions are of the order of a fermi (or femtometer),  $R \simeq 10^{-15}$  m, the use of  $R/\lambda \ll 1$  and the electric dipole approximation is a priori justified. To estimate the lifetime, the result from atomic physics must be multiplied by a factor of  $10^{-18}$  to take into account the change of energy scale  $1 \text{ eV} \rightarrow 1 \text{ MeV}$ , and by a factor of  $10^{10}$  to take into account the change of dimension,  $a \rightarrow R$ , making a factor of  $10^{-8}$  altogether. The estimated lifetime of a nuclear excited state is then

$$\tau_{\text{nucl}} \sim 10^{-8} \tau_{\text{atom}} \sim 10^{-15} \text{ s.}$$

An example is the decay of an excited state of an isotope of nitrogen,  $^{13}\text{N}$ :



where the lifetime is  $10^{-15}$  s, in qualitative agreement with our estimate.

Let us conclude this discussion by returning briefly to emission and stimulated absorption. If we take into account the factors (14.61)–(14.62) for absorption and stimulated emission, the absorption probability (14.50) is not modified. On the other hand, if the atom is located in a cavity of volume  $\mathcal{V}$  containing  $\mathcal{N}_{\vec{k}s}$  photons in the mode  $(\vec{k}, s)$ , the semiclassical emission probability is proportional to the photon density  $n_{\vec{k}s} = \mathcal{N}_{\vec{k}s}/\mathcal{V}$ , while the use of the quantized field gives a factor of  $(\mathcal{N}_{\vec{k}s} + 1)/\mathcal{V}$ . The correction is in general negligible, except in the case of superconducting microwave cavities where the number of photons is small (Appendix B).

## 14.4 Laser cooling and trapping of atoms

### 14.4.1 The optical Bloch equations

It has long been known that light exerts forces on matter, the best-known example being radiation pressure. However, when the light comes from conventional sources these forces are very weak. It is only in the last twenty years that the use of lasers has made it possible to exert sizable forces on atoms, forces which can be up to  $10^5$  times their weight. A particularly interesting application is *laser cooling*, and we shall give an elementary example of it in Section 14.4.3. We shall use the model of the two-level atom: two atomic levels  $E_a$  and  $E_b$  ( $E_b > E_a$ ) are separated by  $E_b - E_a = \hbar\omega_0$ . We assume  $E_a$  is the ground state of the atom, or at least a metastable state of lifetime long enough not to be involved in the discussion. The atom is placed in an electromagnetic wave produced by a laser whose wave vector  $\vec{k}$  is parallel to  $Oz$  and whose frequency  $\omega$  is close to resonance:  $\omega \simeq \omega_0$ . As in Section 5.2.2, we call the difference  $\delta = \omega - \omega_0$  the *detuning*. The electric field at the position of the atom is of the form

$$\vec{E} = \vec{e}_s E_0 \cos \omega t. \quad (14.72)$$



For the time being we ignore the translational degrees of freedom of the atom, assuming it to be infinitely heavy.<sup>19</sup> Under these conditions, the Hamiltonian  $H$  is given by (5.52) written as

$$H = \begin{pmatrix} -\frac{\hbar}{2}\omega_0 & -dE_0 \cos \omega t \\ -dE_0 \cos \omega t & \frac{\hbar}{2}\omega_0 \end{pmatrix}. \quad (14.73)$$

The rows and columns are ordered as  $(a, b)$ , the zero of the energy in the absence of the field has been chosen to lie midway between  $E_a$  and  $E_b$ , and  $d$  is the matrix element  $(\vec{D} \cdot \vec{e}_s)_{ab}$  of the  $\vec{e}_s$  component of the electric dipole moment operator between the two levels. As in Section 5.3.2, we introduce the Rabi frequency  $\omega_1$ :

$$\omega_1 = -\frac{dE_0}{\hbar}. \quad (14.74)$$

The minus sign takes into account the negative charge of the electron, so that  $\omega_1 > 0$ . With this definition we can rewrite  $H$  as a function of the Pauli matrices  $\sigma_1$  and  $\sigma_3$ :

$$\frac{1}{\hbar}H = \begin{pmatrix} -\frac{1}{2}\omega_0 & \omega_1 \cos \omega t \\ \omega_1 \cos \omega t & \frac{1}{2}\omega_0 \end{pmatrix} = -\frac{1}{2}\omega_0\sigma_3 + (\omega_1 \cos \omega t)\sigma_1. \quad (14.75)$$

In general, the quantum state of the atom will be described by a state operator  $\rho$ . In fact, the atom is in continuous interaction with the quantized electromagnetic field, and even if the field + atom ensemble were in a pure state, the state of the atom would not be pure, because the atom is not a closed quantum system. As we have seen in Section 6.2.3, its state is described by taking the partial trace over the field variables, and the result is not a vector of the atom space of states, but a state operator, the reduced state operator of the atom represented by a  $2 \times 2$  matrix acting in the two-dimensional space of the two-level atom. We recall that the state matrix must be Hermitian  $\rho = \rho^\dagger$ , it must have unit trace  $\text{Tr} \rho = 1$ , and it must be positive. The results of Section 6.2.2 allow us to write the most general state matrix as a function of a real vector  $\vec{b}$ , the Bloch vector (6.24), such that  $\vec{b}^2 \leq 1$ :

$$\rho = \frac{1}{2} \left( I + \sum_{i=1}^3 \sigma_i b_i \right) = \frac{1}{2} (I + \vec{\sigma} \cdot \vec{b}). \quad (14.76)$$

Conforming to the usual notation, we use  $(u, v, -w)$  to denote the components of the Bloch vector:  $u = b_1$ ,  $v = b_2$ , and  $w = -b_3$ . We can also write  $\rho$  in the explicit matrix form

$$\rho = \begin{pmatrix} \frac{1}{2} - \frac{1}{2}(\rho_{bb} - \rho_{aa}) & \rho_{ab} \\ \rho_{ba} & \frac{1}{2} + \frac{1}{2}(\rho_{bb} - \rho_{aa}) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 - w & u - iv \\ u + iv & 1 + w \end{pmatrix}. \quad (14.77)$$

<sup>19</sup> More precisely, the translational degrees of freedom are treated classically, assuming that  $\hbar\Gamma \gg E_R$ , where  $\Gamma$  is the linewidth and  $E_R$  is the recoil energy (14.106). We also assume that the medium is dilute enough that collisions between atoms can be neglected.

In this expression for  $\rho$  we have taken into account the condition  $\rho_{aa} + \rho_{bb} = 1$ . The quantity  $w = \rho_{bb} - \rho_{aa}$  measures the population difference between the levels  $E_b$  and  $E_a$ : if we have a collection of  $N$  atoms, on average  $N\rho_{aa}$  will be in the state  $E_a$  and  $N\rho_{bb}$  in the state  $E_b$ . The off-diagonal matrix elements  $\rho_{ab} = \rho_{ba}^*$  are the coherences. The presence of nonzero coherences, that is, phase-dependent effects, is a sure signal of quantum effects.

If we first ignore the quantized electromagnetic field, the evolution equation for  $\rho$  is given by (6.37):

$$i\dot{\rho} = \left[ \frac{1}{\hbar} H, \rho \right]. \quad (14.78)$$

The commutator can be calculated directly by multiplying the matrices, but it is more elegant to use the Bloch form and the commutation relations (3.52) of the Pauli matrices. We find

$$\begin{aligned} \dot{u} &= \omega_0 v, \\ \dot{v} &= -\omega_0 u + 2\omega_1 w \cos \omega t, \\ \dot{w} &= -2\omega_1 v \cos \omega t. \end{aligned} \quad (14.79)$$

To complete these equations and justify an approximation which will be made below, it is convenient to rewrite them as a function of the coherence  $r = \rho_{ab} = (u - iv)/2$ :

$$\dot{w} = -2i\omega_1(r - r^*) \cos \omega t, \quad (14.80)$$

$$\dot{r} = i\omega_0 r - i\omega_1 w \cos \omega t. \quad (14.81)$$

These equations for the evolution of the state matrix are Hamiltonian, that is, they are governed by a law of the type (14.78) depending on a Hamiltonian. This evolution is unitary, because (14.78) is equivalent to

$$\rho(t) = U(t, 0)\rho(t=0)U^\dagger(t, 0),$$

where  $U(t)$  is the unitary evolution operator (4.14). Actually, though, these equations are incomplete. The interaction of the atom with its environment leads to equations that are not of the form (14.78), and so to an evolution which is non-Hamiltonian. It is the ensemble atom + environment that obeys a unitary evolution, and if we are interested only in the atomic degrees of freedom, the evolution is no longer Hamiltonian. This phenomenon is familiar in statistical mechanics, where we consider the interaction of a system with a heat bath, and nonunitary evolution is closely related to dissipation.<sup>20</sup> We are going to consider the case of an atomic environment limited to a quantized electromagnetic field, which is an excellent approximation for atoms trapped by lasers, which form a dilute medium. However, there could also be other sources of non-Hamiltonian evolution, such

<sup>20</sup> See, for example, Le Bellac *et al.* [2004], Chapter 2.

as collisions with other atoms in a dense medium.<sup>21</sup> The calculation based on (14.78) takes into account the interaction with the laser field and therefore absorption and stimulated emission, but it does not include the interaction with the quantized field and so spontaneous emission is neglected. Owing to spontaneous emission, an atom in the level  $E_b$  tends to return to the level  $E_a$  by emitting a photon with probability per unit time  $\Gamma$  (cf. (14.67)). The differential equation giving  $\dot{\rho}_{bb}$  must therefore include a term  $-\Gamma\rho_{bb}$  on the right-hand side, which in the absence of a laser field leads to exponentially decreasing population of the level  $E_b$ ,  $\exp(-\Gamma t)$ . One then deduces that the right-hand side of the differential equation for  $w$  contains a term  $-\Gamma(w+1)$ . The coherences must also decrease because, in the absence of a laser field, the atom returns to its ground state  $E_a$  for  $t \gg \tau = 1/\Gamma$ , and the only nonzero element of the density matrix is  $\rho_{aa} = 1$ . It will be shown in Section 15.2.4 that in our approximation of a diluted medium the decay rate for coherences is  $\Gamma/2$ . Therefore, equations (14.80) and (14.81) become

$$\dot{w} = -2i\omega_1(r - r^*) \cos \omega t - \Gamma(w+1), \quad (14.82)$$

$$\dot{r} = i\omega_0 r - i\omega_1 w \cos \omega t - \frac{\Gamma}{2} r. \quad (14.83)$$

Let us transform these equations using the rotating wave approximation of Section 5.3.2. We note that if  $\omega_1 \ll \omega_0$ , (14.83) implies that  $r \sim \exp(i\omega_0 t)$  whereas  $w$  varies slowly. Writing  $\cos \omega t$  as a sum of complex exponentials and neglecting the rapidly varying terms  $\propto \exp(\pm i(\omega + \omega_0)t)$  in the rotating wave approximation, Equations (14.82)–(14.83) become

$$\dot{w} = -i\omega_1(e^{-i\omega t} r - e^{i\omega t} r^*) - \Gamma(w+1), \quad (14.84)$$

$$\dot{r} = i\omega_0 r - \frac{i}{2} \omega_1 w (e^{i\omega t} + e^{-i\omega t}) - \frac{\Gamma}{2} r. \quad (14.85)$$

All the terms on the right-hand side of (14.84) vary slowly. To display the time evolution of the terms on the right-hand side of (14.85) we set

$$e^{-i\omega t} r = r', \quad e^{-i\omega t} \dot{r} = i\omega r' + \dot{r}',$$

which, multiplying (14.85) by  $\exp(-i\omega t)$ , gives

$$\dot{r}' = i(\omega_0 - \omega)r' - \frac{i}{2} \omega_1 w (1 + e^{-2i\omega t}) - \frac{\Gamma}{2} r'.$$

The rotating wave approximation consists of neglecting the rapidly varying term  $\propto \exp(-2i\omega t)$  in this expression. We then end up with the system of differential equations

$$\dot{w} = -i\omega_1(r' - r'^*) - \Gamma(w+1), \quad (14.86)$$

$$\dot{r}' = i(\omega_0 - \omega)r' - \frac{i}{2} \omega_1 w - \frac{\Gamma}{2} r'. \quad (14.87)$$

<sup>21</sup> An example is the active medium for a laser, which is described by optical Bloch equations analogous to (14.82)–(14.83), but with two unrelated relaxation rates for populations and coherences; see, for example, Mandel and Wolf [1995], Chapter 18.

### 14.4.2 Dissipative forces and reactive forces

When the atom interacts with the laser field during a time interval  $t \gg \tau$ , a stationary regime  $\dot{w} = \dot{r} = 0$  is reached where it is easy to write down the solution of the system of differential equations (14.86)–(14.87). Passing through the intermediate stage

$$r'_{\text{st}} = \frac{i\omega_1 w_{\text{st}}/2}{i(\omega_0 - \omega) - \Gamma/2},$$

we obtain for the stationary value  $w_{\text{st}}$  of  $w$

$$w_{\text{st}} = -\frac{(\omega - \omega_0)^2 + \Gamma^2/4}{(\omega - \omega_0)^2 + \Gamma^2/4 + \omega_1^2/2}. \quad (14.88)$$

We then find  $\rho_{bb} = (1 + w_{\text{st}})/2 < 1/2$ : there cannot be a population inversion, that is, a situation where the excited level is more populated than the ground state. The stationary result for  $r'$  is

$$r'_{\text{st}} = \frac{i\omega_1}{2} \frac{\Gamma/2 - i(\omega - \omega_0)}{(\omega - \omega_0)^2 + \Gamma^2/4 + \omega_1^2/2}. \quad (14.89)$$

It is convenient to introduce the *saturation parameter*  $s$  proportional to the intensity  $\mathcal{I}$  of the laser (we recall that the detuning  $\delta = \omega - \omega_0$ ):

$$s = \frac{\omega_1^2/2}{\delta^2 + \Gamma^2/4} \propto \mathcal{I}_{\text{laser}}, \quad (14.90)$$

so that we can write

$$\rho_{bb,\text{st}} = \frac{1}{2}(1 + w_{\text{st}}) = \frac{s}{2(1+s)}, \quad r'_{\text{st}} = \frac{i}{\omega_1} \left( \frac{s}{1+s} \right) \left( \frac{\Gamma}{2} - i\delta \right). \quad (14.91)$$

These results allow us to obtain the forces exerted by the laser light on an atom in the stationary regime. The equivalent of the radiation pressure on the atom can be found by a simple argument. Since in the stationary regime the probability of finding an atom in the excited state  $E_b$  is  $\rho_{bb,\text{st}}$ , the average number of photons spontaneously emitted per unit time is

$$\left\langle \frac{dN}{dt} \right\rangle = \Gamma \rho_{bb,\text{st}} = \frac{\Gamma}{2} \frac{s}{1+s}. \quad (14.92)$$

These photons are emitted isotropically and contribute to the disordered motion of the atom, which we shall study in the following subsection. However, once the atom has returned to its ground state it absorbs a photon of the laser field, and the momenta of these photons  $\hbar\vec{k}$  are all in the same direction. The number of photons absorbed is the same as the number of photons spontaneously emitted, and the atom is subject to a force due to photon absorption which is equal to the change of momentum per unit time:

$$\boxed{\vec{F}_{\text{diss}} = \hbar\vec{k} \left\langle \frac{dN}{dt} \right\rangle = \hbar\vec{k} \frac{\Gamma}{2} \left( \frac{s}{1+s} \right) = \hbar\vec{k} \frac{\Gamma}{2} \frac{\omega_1^2/2}{\delta^2 + \Gamma^2/4 + \omega_1^2/2}}. \quad (14.93)$$

When the saturation parameter  $s \gg 1$ , the acceleration  $\vec{a}$  approaches its maximum value

$$\vec{a}_{\max} = \frac{\hbar k}{M} \frac{\Gamma}{2}, \quad (14.94)$$

where  $M$  is the mass of the atom. In the case of the  $D_2$  line of sodium,  $\Gamma^{-1} = 1.6 \times 10^{-8}$  s and  $a_{\max} \sim 10^6 \text{ m s}^{-2}$ , which is about  $10^5$  times the gravitational acceleration.

Now let us rederive the result (14.93) for the dissipative force by examining the force exerted by the electromagnetic field (14.72) on an atomic dipole. The form of the dipole operator in the two-dimensional space of the two-level atom is  $D = d\sigma_1$ , and according to (6.21) its expectation value is

$$\begin{aligned} \langle D \rangle &= d \text{Tr}(\rho \sigma_1) = d(\rho_{ab} + \rho_{ab}^*) \\ &= d(r + r^*) = d(r' e^{i\omega t} + r'^* e^{-i\omega t}) \\ &= \frac{2ds}{\omega_1(1+s)} \left[ -\frac{\Gamma}{2} \sin \omega t + \delta \cos \omega t \right], \end{aligned} \quad (14.95)$$

where we have used the expression (14.91) for  $r'$  in the stationary regime. This expectation value of the dipole operator contains a term  $\propto \cos \omega t$  in phase with the field (14.72) and a term out of phase by  $\pi/2 \propto \sin \omega t$ . The work  $dW/dt$  done on the dipole per unit time by the field (14.72), that is, the power supplied to the atom,<sup>22</sup> is

$$\frac{dW}{dt} = E_0 \cos \omega t \frac{d\langle D \rangle}{dt}.$$

Using (14.95) immediately gives  $d\langle D \rangle/dt$  and we find

$$\frac{dW}{dt} = -\frac{2ds\omega E_0}{\omega_1(1+s)} \left[ \frac{\Gamma}{2} \cos^2 \omega t + \delta \sin \omega t \cos \omega t \right]. \quad (14.96)$$

Taking the time average, we obtain

$$\left\langle \frac{dW}{dt} \right\rangle = -\frac{2ds\omega E_0}{\omega_1(1+s)} \frac{\Gamma}{4} = \frac{\hbar\omega s}{1+s} \frac{\Gamma}{2}. \quad (14.97)$$

The number of photons absorbed per second is

$$\left\langle \frac{dN}{dt} \right\rangle = \frac{1}{\hbar\omega} \left\langle \frac{dW}{dt} \right\rangle = \frac{\Gamma}{2} \left( \frac{s}{1+s} \right),$$

in agreement with (14.92). Elementary study of the forced harmonic oscillator shows that it is the component involving the displacement out of phase by  $\pi/2$  with the external force which is responsible for the frictional dissipation, which gives rise to the expression “dissipative force” for the radiation pressure. The part in phase with the field is called

<sup>22</sup> It is useful to recall the elementary forced harmonic oscillator in one dimension:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = f \cos \omega t.$$

The power supplied to the oscillator is  $f \cos \omega t dx/dt$ . The correspondence with the present problem is given by  $f \rightarrow E_0$  and  $x \rightarrow \langle D \rangle$ .

the “reactive” part. The model we have studied does not contain any spatial dependence, and so the average value of the term of  $\langle D \rangle$  in phase with the field does not produce any work. In order to obtain a nonzero result, a spatial dependence must be introduced. It can then be shown (Exercise 14.6.7) that the reactive component of the force depends on the gradient of the Rabi frequency:

$$\vec{F}_{\text{react}} = -\frac{\hbar\delta}{2} \frac{\vec{\nabla}\omega_1^2(\vec{r})/2}{\delta^2 + \Gamma^2/4 + \omega_1^2/2}. \quad (14.98)$$

The reactive force is zero in a plane wave, where the Rabi frequency  $\omega_1$  is independent of  $\vec{r}$ . It does not transmit any energy to the atoms. If, for example, the spatial variation of the Rabi frequency is due to the use of several laser waves, the effect of the reactive force is to redistribute the energy among the various waves. In contrast to the dissipative force, the reactive force is not saturated when  $s \rightarrow \infty$ .

The reactive force is derived from a potential

$$\vec{F}_{\text{react}} = -\vec{\nabla}U(\vec{r}), \quad U(\vec{r}) = \frac{\hbar\delta}{2} \ln \left( 1 + \frac{\omega_1^2(\vec{r})/2}{\delta^2 + \Gamma^2/4} \right).$$

For  $\delta < 0$ , a region in which  $\omega_1^2(\vec{r})$  is a maximum appears as an attractive potential well for the atom. In a nonuniform laser field the atom is attracted toward the regions of stronger intensity. This has allowed the development of numerous practical applications where microscopic objects are manipulated. An example is the creation of “optical tweezers” for manipulating segments of DNA.

### 14.4.3 Doppler cooling

An important application of the dissipative force (14.93) is the *Doppler cooling* of atoms. The atoms are modeled as above by a system of two levels separated by  $\hbar\omega_0$ . They are localized in laser beams coming from opposite directions and having identical frequencies  $\omega$  close to the resonance frequency  $\omega_0$ , but with  $\omega < \omega_0$ , that is, with a detuning  $\delta = \omega - \omega_0 < 0$ . In order to simplify the discussion we limit ourselves to cooling along an axis which we shall choose to be the  $z$  axis, and use two laser beams with wave vectors  $\vec{k} \parallel \hat{z}$  and  $-\vec{k} \parallel -\hat{z}$  (Fig. 14.1). Cooling in three spatial dimensions requires the use of six lasers, two on each axis, with opposite wave vectors. We shall take the case of saturation parameter  $s \ll 1$ , which will permit us to neglect the term  $\omega_1^2$  in the denominator of (14.93).

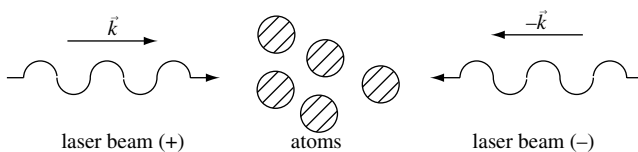


Fig. 14.1. The principle of Doppler cooling.

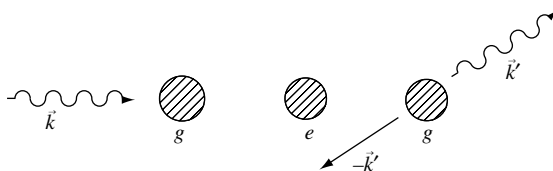


Fig. 14.2. The fluorescence cycle.

An atom in the field of the lasers undergoes *fluorescence cycles*. A fluorescence cycle consists of the absorption of a photon from one of the two lasers by an atom in its ground state so that it makes a transition to its excited state. This is followed by the spontaneous emission of a photon, returning the atom to its ground state (Fig. 14.2). Let  $n_+(v)$  be the number of fluorescence cycles per second that an atom of speed  $v$  (in the  $z$  direction since our discussion is limited to one dimension) undergoes with absorption of photons of wave vector  $+\vec{k}$ , and let  $n_-(v)$  be the number of fluorescence cycles with absorption of a photon of wave vector  $-\vec{k}$ . If an atom is moving toward the left ( $v < 0$ ), owing to the Doppler effect it will see photons of frequency  $\omega - kv$  coming from the  $+\vec{k}$  laser and photons of frequency  $\omega + kv$  coming from the  $-\vec{k}$  laser. Because of the negative detuning ( $\omega < \omega_0$ ), the photons of wave vector  $+\vec{k}$  are closer to resonance and are absorbed in greater numbers than the photons of wave vector  $-\vec{k}$  which are farther from resonance. This will give a force pointing toward the right for these atoms. Conversely, for atoms moving toward the right ( $v > 0$ ) the force will be toward the left. In summary, atoms moving toward the left will preferentially absorb photons of wave vector  $+\vec{k}$  and atoms moving toward the right will preferentially absorb photons of wave vector  $-\vec{k}$ . In both cases the atoms will be slowed down and a viscosity-like force will appear. This is the reason for the term “optical molasses.” The average force on an atom of speed  $v$  is

$$\langle \vec{F} \rangle = \hbar \vec{k} [n_+(v) - n_-(v)] \quad (14.99)$$

with

$$n_{\pm}(v) = \frac{\Gamma}{4} \frac{\omega_1^2}{(\delta \mp kv)^2 + \Gamma^2/4}. \quad (14.100)$$

Let us expand (14.100) in powers of the velocity through order  $v$ :

$$n_{\pm}(v) \simeq \frac{\Gamma \omega_1^2/4}{\delta^2 + \Gamma^2/4} \left( 1 \pm \frac{2\delta kv}{\delta^2 + \Gamma^2/4} \right). \quad (14.101)$$

This equation gives the average number of fluorescence cycles per second  $2n_0$ :

$$n_0 = \frac{1}{2} [n_+(v) + n_-(v)] = \frac{\Gamma \omega_1^2/4}{\delta^2 + \Gamma^2/4} = \frac{\Gamma}{2} s \quad (14.102)$$

and the force proportional to

$$n_+(v) - n_-(v) = n_0 \frac{4\delta kv}{\delta^2 + \Gamma^2/4},$$

which becomes

$$\langle \vec{F} \rangle = \hbar \vec{k} [n_+(v) - n_-(v)] = n_0 v \frac{4\hbar \delta k^2}{\delta^2 + \Gamma^2/4} \hat{k}. \quad (14.103)$$

The viscosity coefficient  $\gamma$  is defined as

$$\frac{dv}{dt} = -\gamma v \quad (14.104)$$

and its value is obtained from (14.103):

$$\gamma = -\frac{\langle F \rangle}{Mv} = -n_0 \frac{4\hbar k^2}{M} \frac{\delta}{\delta^2 + \Gamma^2/4}, \quad (14.105)$$

which is positive because  $\delta < 0$ . Taking  $n_0$  to be constant, the viscosity coefficient is a maximum for  $\delta = -\Gamma/2$ :

$$\gamma_{\max} = \frac{4\hbar k^2}{M\Gamma} n_0 = \frac{8n_0}{\hbar\Gamma} \frac{\hbar^2 k^2}{2M} = \frac{8n_0}{\hbar\Gamma} E_R. \quad (14.106)$$

The energy  $E_R = Mv_R^2/2$  is called the *recoil energy*: it is the recoil kinetic energy when the atom emits a photon of momentum  $\hbar k$ , and it is also the energy acquired by an atom at rest that absorbs a photon of momentum  $\hbar k$ . The speed  $v_R$  is the recoil velocity. Let us give some numerical values for the  $D_2$  line of rubidium. The transition wavelength is  $\lambda = 0.78 \mu\text{m}$ , the linewidth is  $\Gamma = 3.7 \times 10^7 \text{ s}^{-1}$ , and the atomic mass is  $M = 1.41 \times 10^{-25} \text{ kg}$ . These values correspond to energy  $\hbar\Gamma = 2.4 \times 10^{-8} \text{ eV}$ , recoil velocity  $v_R = \hbar k/m = 5.8 \times 10^{-3} \text{ m s}^{-1}$ , and recoil energy  $E_R = 1.5 \times 10^{-11} \text{ eV}$ , and therefore to *recoil temperature*  $T_R = E_R/k_B = 1.7 \times 10^{-7} \text{ K}$ .

Using these typical numerical values, we find

$$\gamma \simeq 5 \times 10^{-3} n_0 = 2.5 \times 10^{-3} \Gamma s.$$

We can take the saturation parameter  $s \ll 1$  such that

$$\Gamma^{-1} \ll n_0^{-1} \ll \gamma^{-1}.$$

Under these conditions, there are three distinct time scales in the problem (Fig. 14.3). The relation  $\Gamma^{-1} \ll n_0^{-1}$  shows that the fluorescence cycles do not overlap and are independent. Let us consider a time interval  $\delta t$ , with  $\Gamma^{-1} \ll \delta t \ll \gamma^{-1}$ . Let  $N_{\pm}$  be the number of fluorescence cycles  $\pm k$  in this interval  $\delta t$ . The condition  $\delta t \ll \gamma^{-1}$  implies that the speed  $v$  of the atom does not have the time to vary appreciably under the action of the viscosity force during the interval  $\delta t$  and so we can average over this interval, with  $\langle N_{\pm} \rangle = n_{\pm}(v)\delta t$ . Let  $p(N_+, N_-; \delta t)$  be the probability of observing  $N_+$  ( $+k$ ) cycles and  $N_-$  ( $-k$ ) cycles during the interval  $\delta t$ . Since the fluorescence cycles are independent, this probability obeys a Poisson law:

$$p(N_+, N_-; \delta t) = \frac{\langle N_+ \rangle^{N_+} \langle N_- \rangle^{N_-} \exp[-(\langle N_+ \rangle + \langle N_- \rangle)]}{N_+! N_-!}.$$



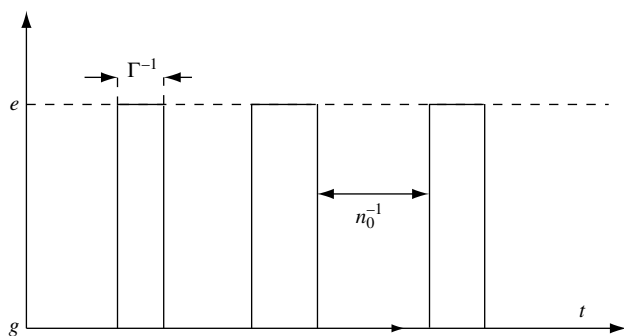


Fig. 14.3. A sequence of fluorescence cycles.

We use  $\hbar q_1, \dots, \hbar q_{(N_+ + N_-)}$  to designate the  $N_+ + N_-$  momenta of photons emitted spontaneously by the atom during the interval  $\delta t$  and  $\hbar Y$  to denote their sum:

$$\hbar Y = \hbar q_1 + \dots + \hbar q_{(N_+ + N_-)}.$$

The emitted photons are not correlated with each other and  $\langle Y \rangle = 0$ . The average variation of the momentum during the time  $\delta t$  is due only to the absorbed photons:

$$\langle p(\delta t) \rangle = (n_+(v) - n_-(v)) \hbar k \delta t. \quad (14.107)$$

Let us now evaluate the variance of  $p(\delta t)$ ,

$$\Delta p^2(\delta t) = \langle p^2(\delta t) - \langle p(\delta t) \rangle^2 \rangle.$$

Since the spontaneous photons are not correlated with the absorbed photons,  $\langle Yk \rangle = 0$  and the two contributions can be treated separately. The contribution to the variance from the absorbed photons is

$$\Delta p^2(\delta t)|_{\text{abs}} = \hbar^2 k^2 \left\langle (N_+ - N_-)^2 - (\langle N_+ \rangle - \langle N_- \rangle)^2 \right\rangle = 2\hbar^2 k^2 n_0 \delta t,$$

where we have used the classical property of the Poisson distribution  $\Delta N_{\pm}^2 = \langle N_{\pm} \rangle$  as well as the fact that the  $+$  and  $-$  cycles are independent:  $\langle N_+ N_- \rangle = \langle N_+ \rangle \langle N_- \rangle$ . The contribution from the emitted photons is

$$\Delta p^2(\delta t)|_{\text{em}} = \hbar^2 \langle Y^2 \rangle = \hbar^2 \sum_{i=1}^{N_+ + N_-} q_i^2 = \hbar^2 k^2 \langle N \rangle = 2n_0 \hbar^2 k^2 \delta t.$$

Since we have reduced the kinematics to one dimension, we have assumed that the emitted photons have momentum  $\pm \hbar k$  with probabilities of  $1/2$ .<sup>23</sup> Adding these two contributions,

<sup>23</sup> For three-dimensional kinematics and isotropic photon emission we would have  $\langle \hbar^2 Y^2 \rangle = \hbar^2 k^2 / 3$ .

we find<sup>24</sup>

$$\Delta p^2(\delta t) = 4n_0\hbar^2 k^2 \delta t. \quad (14.108)$$

As we shall soon show, this result corresponds to a random walk in one-dimensional momentum space. In a random walk on a line, the walker takes a step of length  $l$  to the right or to the left with probability  $1/2$ . After  $N$  steps the walker has moved an average distance  $\langle x \rangle = 0$ , but the average squared distance is nonzero:

$$\langle x^2 \rangle = \Delta x^2 = Nl^2,$$

and if each step takes a time  $\tau$ , after a time  $\delta t = N\tau$  we have

$$\Delta x^2 = \frac{l^2}{\tau} \delta t = 2D \delta t. \quad (14.109)$$

This equation defines the *diffusion coefficient*  $D$ . The proportionality of  $\Delta p^2$  to  $\delta t$  in (14.108) justifies the expression “random walk in momentum space” with diffusion coefficient  $D = 2n_0\hbar^2 k^2$ .

In this random walk the kinetic energy  $E$  of the atom increases by  $\Delta p^2(\delta t)/2M$ . The diffusion therefore tends to increase the kinetic energy. By analogy with statistical mechanics, we define a fictitious temperature  $T$  as

$$E = \frac{1}{2} k_B T, \quad (14.110)$$

where  $k_B$  is the Boltzmann constant. If  $E$  increases,  $T$  increases, and it can be said that the atoms are heated by the spontaneous emission, which creates a disordered motion analogous to thermal motion. However, the temperature is actually fictitious, because there is no thermodynamical equilibrium: the temperature (14.110) is perfectly well defined for an isolated atom. The viscosity tends to slow the atoms down, and thus to “cool” them. When the two effects are in equilibrium, we obtain an “equilibrium temperature” which is the fictitious temperature of the atoms in the stationary regime. This temperature in fact provides an intuitive way of measuring their average speed. According to (14.104), the viscosity gives the following contribution to the time variation of the energy:

$$\left. \frac{dE}{dt} \right|_{\text{visc}} = \frac{1}{2} M \frac{d}{dt} v^2 = -M\gamma v^2 = -\frac{\gamma p^2}{M}, \quad (14.111)$$

and adding the effect of spontaneous emission, we find

$$\frac{dE}{dt} = \frac{2n_0\hbar^2 k^2}{M} - \frac{\gamma p^2}{M}.$$

<sup>24</sup> In three-dimensional kinematics

$$\Delta p^2(\delta t) = \frac{8}{3} n_0 \hbar^2 k^2 \delta t.$$

The condition for the regime to be stationary  $dE/dt = 0$  gives the equilibrium value  $p_{\text{eq}}^2$  of  $p^2$ , and choosing  $\gamma = \gamma_{\text{max}}$  in (14.106), we have

$$p_{\text{eq}}^2 = \frac{2n_0 \hbar^2 k^2}{\gamma_{\text{max}}} = \frac{1}{2} \hbar \Gamma M,$$

which gives for the temperature  $T = T_D$

$$k_B T_D = \frac{p_{\text{eq}}^2}{M} = \frac{1}{2} \hbar \Gamma. \quad (14.112)$$

This temperature, which is of the order of  $100 \mu\text{K}$  for the  $D_2$  line of rubidium, is called the *Doppler temperature*. The equilibrium condition  $dE/dt = 0$  can also be written as a function of the momentum diffusion coefficient:

$$D = \gamma p_{\text{eq}}^2 = M \gamma k_B T. \quad (14.113)$$

This equation relating the diffusion coefficient  $D$  and the viscosity coefficient  $\gamma$  to temperature is very general<sup>25</sup> and is well known as the *Einstein relation*. In the case of Brownian motion, viscosity forces and diffusion have a common origin, namely, collisions of the Brownian particle with the fluid molecules, and it is not surprising that the diffusion and viscosity coefficients are not independent. Diffusion and viscosity are both dissipative processes. In our case the origin of the dissipative process is spontaneous emission, which we have seen corresponds to nonunitary evolution.

#### 14.4.4 A magneto-optical trap

Doppler cooling is the maximum cooling that can be obtained if we limit ourselves to the model of the two-level atom. To go farther, and in particular to consider cooling mechanisms which are even more effective, allowing temperatures of microkelvins and lower to be obtained, it is necessary to bring into play the level substructure, both fine and hyperfine. Let us consider an elementary example, taking a ground state  $j = 0$  and an excited state  $j = 1$  which we split into three sublevels using the Zeeman effect. This will permit us to trap atoms not only in velocity, as in Doppler cooling, but also in space. Since a magnetic field must be used to obtain the Zeeman effect, such a trap is called a *magneto-optical trap* (MOT). We use a nonuniform,  $z$ -dependent magnetic field pointing in the  $z$  direction,  $B(z) = -bz$ ,  $b > 0$ . According to (14.26), the Zeeman levels of the excited state ( $e$ ) with magnetic quantum number<sup>26</sup>  $m_e$  are given by

$$W_{m_e} = -\mu B m_e = -g \frac{q_e \hbar B}{2m} m_e \quad \text{with} \quad \mu = g \frac{q_e \hbar}{2m} < 0.$$

The Zeeman levels of the excited state then have energies  $-\mu b z$  ( $m_e = -1$ ),  $0$  ( $m_e = 0$ ), and  $+\mu b z$  ( $m_e = 1$ ), with  $Oz$  taken as the angular momentum quantization axis.

<sup>25</sup> See, for example, Le Bellac *et al.* [2004], Chapter 5.

<sup>26</sup>  $m_e$  should not be confused with the electron mass  $m_e$ .

We again take the configuration of laser beams used above for Doppler cooling, but now assuming that these beams are left-hand circularly polarized. Angular momentum conservation along  $Oz$  (cf. (10.106)–(10.107)) implies that  $m_e = -1$  if the atom absorbs a photon of wave vector  $+\vec{k}$  and  $m_e = +1$  if it absorbs one of wave vector  $-\vec{k}$ ; see Fig. 14.4. We assume that  $\delta < 0$ . For  $z > 0$  the sign of  $B$  implies that the level  $m_e = +1$  is lower than the level  $m_e = -1$  and therefore closer to resonance (Fig. 14.4). This implies that the atom will preferentially absorb photons of wave vector  $-\vec{k}$  and be pushed toward the left. The opposite occurs if the atom is in the region  $z < 0$  where the level  $m_e = -1$  is lower than the level  $m_e = +1$ : the atom preferentially absorbs photons of wave vector  $+\vec{k}$  and is pushed to the right. The action of the two beams is equivalent to the existence of two forces, a viscosity force  $-\gamma Mv$  and a restoring force  $-\kappa z$ :

$$F = -\gamma Mv - \kappa z, \quad (14.114)$$

to which we must add the diffusion in momentum space. The atoms are not only slowed down, but they are also confined by the recoil force in the region  $z \simeq 0$ ; this is the principle of the magneto-optical trap. In practice, we want to confine atoms in three-dimensional space, and so it is necessary to use six polarized laser beams (Fig. 14.5).

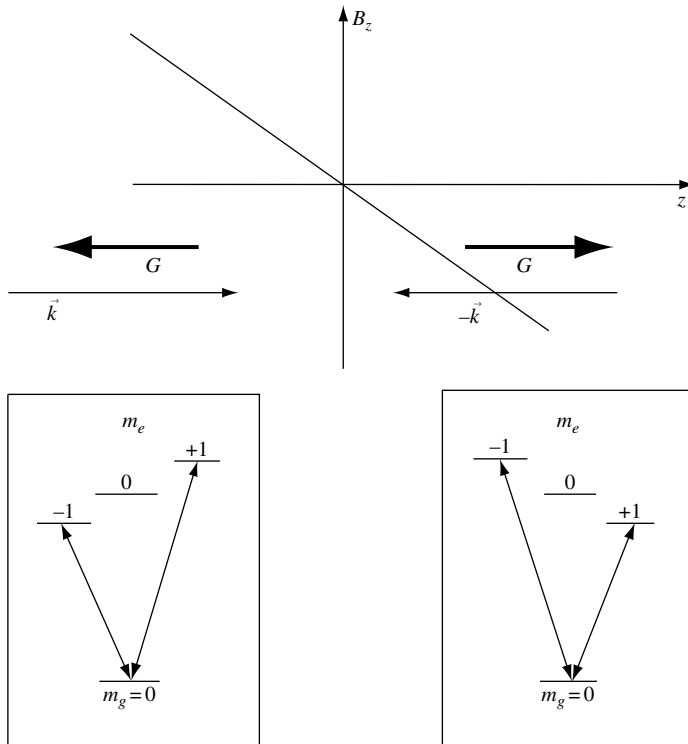


Fig. 14.4. Zeeman levels for  $z < 0$  and  $z > 0$ .

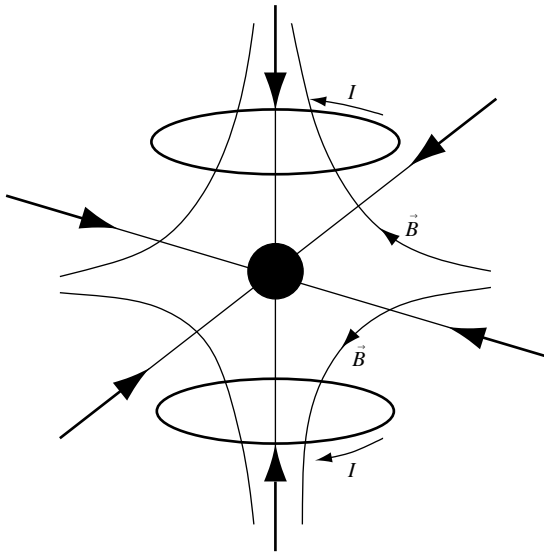


Fig. 14.5. Laser configuration for a magneto-optical trap.

## 14.5 The two-electron atom

### 14.5.1 The ground state of the helium atom

The helium atom is a two-electron atom with a nucleus of charge  $2q_e$ , which we write as  $Zq_e$ ,  $Z = 2$ , so that our theory also applies, for example, to the  $\text{Li}^+$  ion with  $Z = 3$ . Assuming the nucleus to be infinitely heavy (an approximation better than 0.1%), in a representation where the position operator is diagonal the Hamiltonian  $H$  reads as

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}. \quad (14.115)$$

The vectors  $\vec{r}_1$  and  $\vec{r}_2$  are the positions of electrons 1 and 2. We write  $H = H_0 + W$ , where  $H_0$  is the free Hamiltonian describing the electrons interacting with the nucleus,

$$H_0 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \quad (14.116)$$

and  $W$  is a perturbation, whose physical origin is the electrostatic repulsion between the two electrons:

$$W = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}. \quad (14.117)$$

Let us seek the lowest energy level by first neglecting  $W$ . This level is clearly a  $1s^2$  level, where the two electrons are in a  $1s$  state; the superscript counts the number of electrons in a given state. However, electrons are fermions, and the two electrons cannot be in the same state. Fortunately, spin saves the situation, since the electrons can be put in a singlet

spin state  $\chi_s$  (10.126), which is antisymmetric under the exchange of the two electrons. Our space + spin wave function then becomes

$$\begin{aligned}\Psi(\vec{r}_1, \vec{r}_2)\chi &= \varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\chi_s \\ &= \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Zr_1/a_0} e^{-Zr_2/a_0} \chi_s.\end{aligned}\quad (14.118)$$

The corresponding ground-state energy for helium is  $E_0^{(0)} = -8R_\infty \simeq -108.8$  eV, to be compared with the experimental result  $E^{\text{exp}} = -79.0$  eV. Thus  $E_0^{(0)}$  is too low by roughly 30%. However, we have neglected the repulsive interaction  $W$  in  $H$ , and we expect that this term will push our theoretical result upward. Let us be optimistic and blindly apply perturbation theory, although there is no obvious reason why  $W$  should be considered “small” compared with the other potential energy terms in  $H_0$ . From (14.6) we compute the first-order correction to  $E_0$ :

$$\Delta E = \langle \Psi | W | \Psi \rangle = \frac{Z^6 e^2}{\pi^2 a_0^6} \int \frac{e^{-2Zr_1/a_0} e^{-2Zr_2/a_0}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2. \quad (14.119)$$

To compute this six-dimensional integral, we use the following representation of  $1/r$ :<sup>27</sup>

$$\frac{1}{r} = \frac{4\pi}{(2\pi)^3} \int \frac{d^3 k}{k^2} e^{i\vec{k} \cdot \vec{r}},$$

and we find

$$\Delta E = \frac{Z^6 e^2}{2\pi^4 a_0^6} \int \frac{dk}{k^2} \left[ \int e^{-2Zr/a_0} e^{i\vec{k} \cdot \vec{r}} d^3 r \right]^2. \quad (14.120)$$

The integral in the square brackets has already been encountered in (14.55):

$$\int e^{-2Zr/a_0} e^{i\vec{k} \cdot \vec{r}} d^3 r = \frac{16\pi Z/a_0}{[k^2 + (2Z/a_0)^2]^2}, \quad (14.121)$$

and plugging this result into (14.120) gives

$$\Delta E = \frac{4Ze^2}{\pi a_0} \int_0^\infty \frac{dx}{(1+x^2)^4} = \frac{4Ze^2}{\pi a_0} \times \frac{5\pi}{32} = \frac{5}{4} Z R_\infty. \quad (14.122)$$

As expected,  $\Delta E$  is positive and

$$E_0^{(0)} + \Delta E \simeq -74.8 \text{ eV}, \quad (14.123)$$

which is much closer to the experimental value than we had a right to expect.

The variational method will give an even better result. As our trial function for one electron we take

$$\varphi(\vec{r}) = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0}, \quad (14.124)$$

<sup>27</sup> To check this formula, compute the Fourier transform of  $(k^2 + \alpha^2)^{-1}$  and take the limit  $\alpha \rightarrow 0$ .

where  $z$  is the variational parameter. In order to compute the expectation values, we write

$$\int d^3r \varphi^*(\vec{r}) \left( -\frac{1}{2m_e} \nabla^2 - \frac{ze^2}{r} \right) \varphi(\vec{r}) = -z^2 R_\infty, \quad (14.125)$$

since (14.124) is the ground-state solution of the Schrödinger equation for a one-electron atom in a Coulomb potential  $-ze^2/r$ . Since the potential energy is twice the total energy, we also have

$$\int d^3r \left( -\frac{ze^2}{r} \right) |\varphi(\vec{r})|^2 = -2ze^2 R_\infty. \quad (14.126)$$

Equations (14.125) and (14.126) allow us to compute the expectation value of  $H_0$ :

$$\langle H_0 \rangle = -2(2zZ - z^2) R_\infty.$$

The expectation value of  $W$  has just been computed in the perturbative approach:

$$\langle W \rangle = \frac{5}{4} z R_\infty.$$

Collecting all the contributions we find

$$E_0(z) = 2 \left( z^2 - 2Zz + \frac{5}{8} z \right) R_\infty. \quad (14.127)$$

The optimal value of  $z$  is obtained from  $dE(z)/dz = 0$ , so that  $z = Z - 5/16$  and

$$E_0^{\text{var}} = -2 \left( Z - \frac{5}{16} \right)^2 R_\infty. \quad (14.128)$$

In the case of helium, we find  $E_0^{\text{var}} \simeq -77.5$  eV, which is closer to the experimental result than the perturbative estimate. We can also check that  $E_0^{\text{var}} > E_0^{\text{exp}}$ , as must be the case. For the same volume of calculations, we see that the variational method with a good guess for the trial wave function gives much better results than the perturbative approach!

### 14.5.2 The excited states of the helium atom

As we have just seen, the ground state of the helium atom has zero orbital angular momentum and zero spin. Using the notation  $^{2S+1}L_J$ , where  $S$  is the total spin,  $L$  the total orbital angular momentum, and  $J$  the total angular momentum, the ground state of the helium atom is therefore a  $1^1S_0$  state. The next lowest energy levels are the  $1s^12s^1$  and  $1s^22p^2$  states. These levels are degenerate if  $H_0$  (14.116) is used as the Hamiltonian. However, it is a better strategy to try to take into account, at least approximately, the effect of the repulsion  $W$  by using not the Coulomb potential  $-Ze^2/r$ , but an *effective*

one-electron potential  $V_{\text{eff}}(r)$  which can be determined from self-consistency arguments. Therefore, instead of  $H_0$  we use a Hamiltonian  $H'_0$ :

$$H'_0 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + V_{\text{eff}}(r_1) + V_{\text{eff}}(r_2), \quad (14.129)$$

and instead of  $W$  a perturbation  $W'$ :

$$W' = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \left[ -\frac{Ze^2}{r_1} - V_{\text{eff}}(r_1) \right] + \left[ -\frac{Ze^2}{r_2} - V_{\text{eff}}(r_2) \right]. \quad (14.130)$$

With  $H'_0$  as the Hamiltonian, the  $2s$  and  $2p$  levels are no longer degenerate (see Fig. 10.7), and the  $2p$  level lies above the  $2s$  level. An important remark is that  $W'$  is invariant under spatial rotations, so that it commutes with the total orbital angular momentum  $\vec{L}$ :  $[\vec{L}, W'] = 0$ , although, for example,  $[\vec{L}_1, W'] \neq 0$ .  $W'$  therefore has vanishing matrix elements between the  $1s^1 2s^1$  and  $1s^1 2p^2$  states, which have total orbital angular momentum  $L = 0$  and  $L = 1$ , respectively. Thus, although these levels are not far from being degenerate, we can use nondegenerate perturbation theory within each of the levels.

Let us begin with the  $1s^1 2s^1$  state, which is the first excited level. We can build symmetric and antisymmetric wave functions:

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s}(\vec{r}_1) \varphi_{2s}(\vec{r}_2) \pm \varphi_{1s}(\vec{r}_2) \varphi_{2s}(\vec{r}_1)]. \quad (14.131)$$

The one-electron terms of  $W'$  are independent of the symmetry of  $\Psi$ , but the  $W$  contribution is symmetry-dependent:

$$\begin{aligned} \langle \Psi_{\pm} | W | \Psi_{\pm} \rangle &= e^2 \int d^3 r_1 d^3 r_2 \frac{|\varphi_{1s}(\vec{r}_1)|^2 |\varphi_{2s}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ &\quad \pm e^2 \int d^3 r_1 d^3 r_2 \varphi_{1s}(\vec{r}_1) \varphi_{2s}(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \varphi_{1s}(\vec{r}_2) \varphi_{2s}(\vec{r}_1) \\ &= K \pm J. \end{aligned} \quad (14.132)$$

The integral  $K$  is clearly positive, and it can be shown that  $J$ , called the *exchange integral*, is also positive, so that the energy of the antisymmetric wave function is lower than that of the symmetric one. This is easy to understand: since the antisymmetric wave function vanishes at  $\vec{r}_1 = \vec{r}_2$ , the expectation value of  $|\vec{r}_1 - \vec{r}_2|$ , which is a maximum (and in fact infinite) at  $\vec{r}_1 = \vec{r}_2$ , is lower in the antisymmetric case. These considerations are completely independent of the fermionic nature of the electrons, and would also hold if we had two kinds of electron in the helium atom, a red one and a green one. What the Pauli principle implies is that *the symmetry of the spatial wave function is related to that of the spin state*. Then the lowest energy state is a  $^3S_1$  state, and the highest is a  $^1S_0$  state (Fig. 14.6a). If the electrons were red and green, the total spin would not be related to the symmetry of the wave function.

In the  $1s^1 2p^1$  state the total angular momentum is  $L = 1$  and the possible states are  $^1P_1$  in the singlet spin state and  $^3P_0$ ,  $^3P_1$ , and  $^3P_2$  in the triplet spin state. The exchange



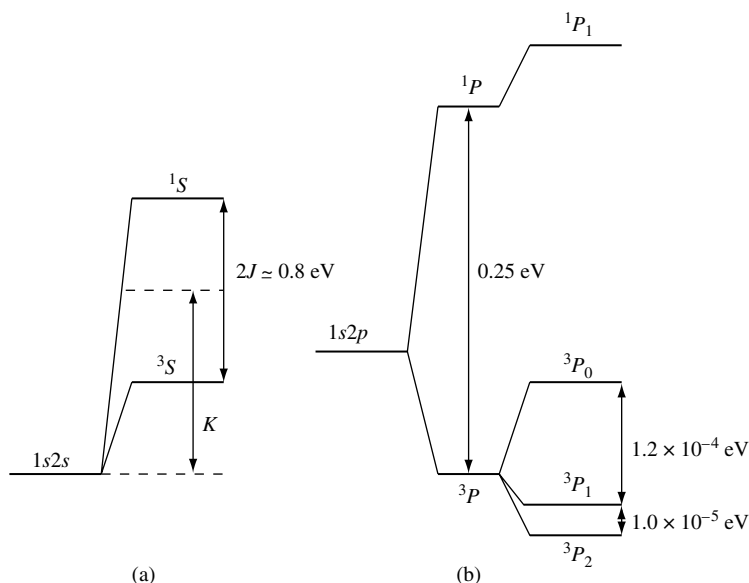


Fig. 14.6. The first two excited states of the helium atom. After Cohen-Tannoudji *et al.* [1977], Complement B<sub>XIV</sub>.

integral is again positive, so that the triplet states lie lower than the singlet state. The level scheme is sketched in Fig. 14.6b.

## 14.6 Exercises

### 14.6.1 Second-order perturbation theory and van der Waals forces

The van der Waals forces between two neutral atoms arise from the interactions between the induced dipole moments. We wish to evaluate them in the case of two hydrogen atoms in their ground states  $|\varphi_0\rangle$ . To do this we shall need to use second-order perturbation theory.

1. *Second-order perturbation theory.* First we determine  $|\varphi_1\rangle$  assuming that  $|\varphi_0\rangle$  is nondegenerate; the notation is the same as in Section 14.1.2. Show that

$$(E_0 - H_0)|\varphi_1\rangle = (W - E_1)|\varphi_0\rangle.$$

Keeping the term of second order in  $\lambda$  in the series (14.3) and (14.4), show that

$$E_2 = \langle \varphi_0 | W | \varphi_1 \rangle.$$

We recall that  $|\varphi_0\rangle \equiv |n\rangle$  and

$$H_0|n\rangle = E_0^{(n)}|n\rangle, \quad H_0|k\rangle = E_0^{(k)}|k\rangle.$$

Prove the identity

$$I = |n\rangle\langle n| + (E_0 - H_0)^{-1} \left( \sum_{k \neq n} |k\rangle\langle k| \right) (E_0 - H_0)$$

and derive (14.7):

$$E_2 = \sum_{k \neq n} \frac{|\langle n|W|k\rangle|^2}{E_0^{(n)} - E_0^{(k)}}.$$

2. The protons of the two hydrogen atoms are separated by a distance  $R \gg a_0$ , where  $a_0$  is the Bohr radius (1.34);  $\vec{R}$  is the vector joining proton 1 and proton 2 and the  $z$  axis points along  $\vec{R}$ . We use  $\vec{r}_1$  to denote the vector joining electron 1 to proton 1,  $\vec{r}_2$  the vector joining electron 2 to proton 2, and  $\vec{d}_i = q_e \vec{r}_i$  is the electric dipole moment of the atom  $i$ . Show that in classical physics the interaction energy of the two dipoles is  $[e^2 = q_e^2/(4\pi\epsilon_0)]$

$$\begin{aligned} W &= \frac{e^2}{R^3} [\vec{r}_1 \cdot \vec{r}_2 - 3(\vec{r}_1 \cdot \hat{R})(\vec{r}_2 \cdot \hat{R})] \\ &= \frac{e^2}{R^3} [x_1 x_2 + y_1 y_2 - 2z_1 z_2]. \end{aligned}$$

3. To obtain the quantum expression for  $W$ , we use the correspondence principle, replacing the numbers  $x_1, \dots, z_2$  by the operators  $X_1, \dots, Z_2$ :

$$W = \frac{e^2}{R^3} [X_1 X_2 + Y_1 Y_2 - 2Z_1 Z_2].$$

Show that the expectation value of  $W$  vanishes in first-order perturbation theory:

$$E_1 = \langle \varphi_{01} \varphi_{02} | W | \varphi_{01} \varphi_{02} \rangle = 0.$$

4. In second order, if  $|\varphi_\alpha\rangle$  designates an excited state or a continuum state of energy  $E_\alpha$ , then

$$E_2 = \sum_{\alpha_1, \alpha_2} \frac{|\langle \varphi_{\alpha_1} \varphi_{\alpha_2} | W | \varphi_{01} \varphi_{02} \rangle|^2}{-2R_\infty - E_{\alpha_1} - E_{\alpha_2}},$$

where  $R_\infty$  is the Rydberg constant (1.35). To obtain the order of magnitude of  $E_2$  we neglect  $E_{\alpha_1}$  and  $E_{\alpha_2}$  in the denominator. Show that

$$E_2 \sim -6 \frac{e^2}{R} \left( \frac{a_0}{R} \right)^5.$$

The interaction energy varies as  $R^{-5}$  and the force as  $R^{-6}$ . Show that the preceding estimate is no longer valid if  $R \gtrsim \hbar c/R_\infty$ . Show that the force law is  $R^{-7}$  for distances  $R \gg \hbar c/R_\infty$ .

### 14.6.2 Order- $\alpha^2$ corrections to the energy levels

Hint. In both this problem and the following one, it is recommended that for numerical work the energies be written in dimensionless form by using the factor  $R_\infty = 13.61$  eV.

In addition to the fine structure, there exist two other  $O(v/c)^2$  corrections to the energy levels of the hydrogen atom (or, more generally, one-electron atoms).

1. *The kinematical correction.* The relativistic form of the electron kinetic energy is

$$K = \sqrt{p^2 c^2 + m_e^2 c^4} = m_e c^2 + \frac{p^2}{2m_e} - \frac{1}{8} \frac{p^4}{m_e^3 c^2} + O\left(\frac{p^6}{m_e^5 c^4}\right).$$

Verify this series in powers of  $p/m_e c$  valid for  $p/m_e c \ll 1$ . The first term is the mass energy, a simple additive constant, and the second is the nonrelativistic form of the kinetic energy used in solving the Schrödinger equation. The objective is to evaluate the corrections due to the third term  $O(p^4)$ . Show that this term gives a correction  $\Delta E_K \propto \alpha^2 (v/c)^2 = O(\alpha^4)$  to the energy levels. In order to evaluate this correction precisely, we use perturbation theory. Show that in first order

$$\Delta E_K = -\frac{1}{8m_e^3 c^2} \int d^3 p p^4 |\tilde{\varphi}(\vec{p})|^2,$$

where  $\tilde{\varphi}(\vec{p})$  is the Fourier transform of the wave function  $\varphi(\vec{r})$ :

$$\tilde{\varphi}(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3 r e^{i\vec{p}\cdot\vec{r}/\hbar} \varphi(\vec{r}).$$

Calculate  $\Delta E_K$  for the  $1s$  level of the hydrogen atom. The necessary integrals can be derived from

$$I(x) = \int_0^\infty \frac{dq}{q^2 + x} = \frac{\pi}{2} x^{-1/2}$$

by differentiating with respect to  $x$  ( $x > 0$ ).

2. *The Darwin term.* The second correction arises from the fact that in the nonrelativistic approximation of the Dirac equation, the electron cannot be localized to better than within  $\hbar/m_e c$ , the electron Compton wavelength. To take this spatial extent into account, the potential energy is written as

$$E_{\text{pot}} = \int d^3 u f(|\vec{u}|) V(\vec{r} + \vec{u}),$$

where  $V$  is the usual potential energy and  $f(u)$ , which is spherically symmetric, has extent  $\sim \hbar/m_e c$  and is normalized by

$$\int d^3 u f(u) = 1.$$

Expanding  $V(\vec{r} + \vec{u})$  about  $u = 0$ , show that

$$E_{\text{pot}} = V(\vec{r}) + O\left[\left(\frac{\hbar}{m_e c}\right)^2\right] \nabla^2 V + O\left(\frac{\hbar}{m_e c}\right)^4.$$

The Dirac equation gives the exact coefficient:

$$E_{\text{pot}} = V(\vec{r}) + \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V + O\left(\frac{\hbar}{m_e c}\right)^4.$$

The second term in  $E_{\text{pot}}$  is called the *Darwin term*. Show that this term affects only  $s$ -waves and gives

$$\Delta E_D = \frac{\pi e^2 \hbar^2}{2m_e^2 c^2} |\varphi(\vec{r} = 0)|^2.$$

Evaluate  $\Delta E_D$  numerically for the  $1s$  level of hydrogen.

### 14.6.3 Muonic atoms

The muon ( $\mu$ ) is a lepton completely identical to the electron except that its mass is  $m_\mu \simeq 105.7 \text{ MeV } c^{-2} \simeq 206.8 m_e$  (cf. Section 1.1.3). An atom can capture a negative muon  $\mu^-$  into an orbit about the nucleus just like an electron, to form a “muonic atom.”

1. Calculate the Bohr radius  $a_\mu^Z$  of the muon, as a function of the atomic number  $Z$ , the ratio  $m_\mu/m_e$ , and  $a_0 = \hbar^2/m_e e^2$ , for an atom of atomic number  $Z$  by writing

$$a_\mu^Z = \frac{1}{Z\alpha(A)} a_0.$$

The reduced mass is used in the calculation of  $\alpha(A)$ . Compare  $a_\mu^Z$  to the nuclear radius  $R$  for aluminum ( $Z = 13$ ,  $A = 27$ ) and lead ( $Z = 82$ ,  $A = 208$ ). We recall that  $R$  is given by  $R \simeq 1.2 \times A^{1/3} \text{ fm}$ , where  $A$  is the number of nucleons.

2. Let  $\Delta E_e^{Z=1} = \Delta E_e = E_{2p} - E_{1s}$  be the energy difference between the  $2p$  and  $1s$  levels of the hydrogen atom. Calculate the corresponding quantity  $\Delta E_\mu^Z$  for an atom of atomic number  $Z$  as a function of  $\Delta E_e$  and  $m_\mu/m_e$ . Compare to the experimental values:

$$\text{Aluminum : } \Delta E_\mu^{13} = 0.3443 \text{ MeV}, \quad \text{Lead : } \Delta E_\mu^{82} = 5.96 \text{ MeV}.$$

What type of photon is emitted in these transitions?

3. Show that the screening of the inner-shell electrons is negligible. In contrast, an important correction comes from the finite size of the nucleus. Show that the potential seen by the muon is not  $-Ze^2/r$  but

$$V(r) = \frac{Ze^2}{2R} \left[ \left( \frac{r}{R} \right)^2 - 3 \right], \quad r < R,$$

$$V(r) = -\frac{Ze^2}{r}, \quad r > R.$$

We wish to calculate the level shift using first-order perturbation theory starting from the solution for the exact Coulomb potential. What perturbation  $W(r)$  should be used? Show qualitatively that the finite size of the nucleus is negligible except for  $s$  states, and that in this case for small  $Z$  and an orbit of principal quantum number  $n$  with radius large compared to  $R$  the shift will be

$$\Delta E_n = \frac{2\pi Ze^2}{5} R^2 |\varphi_n(\vec{r}=0)|^2,$$

where  $\varphi_n(\vec{r})$  is the unperturbed wave function. Show that for the  $1s$  state

$$\Delta E = \frac{4}{5} R_\infty \left( \frac{Z^2 m'_\mu}{m_e} \right) \left( \frac{R}{a_\mu^Z} \right)^2,$$

where  $m'_\mu$  is the reduced mass. Find the numerical value of this shift for aluminum.<sup>28</sup> Is the correction in the right direction? Is it reasonable to apply the method to the case of lead?

<sup>28</sup> Aside from the correction due to the finite size of the nucleus, the most important correction comes from the vacuum polarization due to virtual electron-positron pairs. The correction for the  $1s$  state of aluminum is  $-2.25 \text{ keV}$ . The sign of this correction is negative; in fact, at short distances  $\alpha$  is larger than  $1/137$  and the muon, which sees a larger charge, is more tightly bound than if  $\alpha$  were constant. This behavior of  $\alpha$  was mentioned in Footnote 36 of Chapter 1:  $\alpha$  grows with energy and, according to the Heisenberg inequality, short distance implies large momentum and therefore high energy.

4. Show that the ratio of the typical fine-structure energies to the typical level energies is the same for the electron and the muon. Show that this ratio, however, is larger by a factor  $m_\mu/m_e$  for the hyperfine structure.

### 14.6.4 Rydberg atoms

The results of Exercise 10.7.9 allow us to write down the radial wave functions  $u_{nl}(r)$  of the hydrogen atom in the form

$$u_{nl}(r) = \sum_{q=0}^{n-l-1} c_q \left(\frac{r}{a_0}\right)^{q+l+1} \exp\left(-\frac{r}{na_0}\right).$$

To write down the formula for the coefficients  $c_q$ , it is convenient to define  $k = n - l$ :

$$c_q = \left(-\frac{2}{n}\right)^q \frac{(k-1)!(2l+1)!}{q!(q+2l+1)!(k-q-1)!},$$

where  $c_0$  is fixed by the normalization condition of the wave function. We are interested in values  $n \gg 1$ , typically  $n \sim 50$ .

1. Show that if  $l$  takes its maximum value  $l = l_{\max} = n - 1$ , the radial wave function displays a narrow peak near the point  $r = a_0 n^2$ . What is the width  $\Delta r$  of this peak? Hint: study the function

$$f_n(x) = x^n e^{-x/n}$$

and show that for  $x \simeq x_0 = n^2$ ,

$$f_n(x) \simeq f_n(x_0) \exp\left[-\frac{1}{2n^3} (x - x_0)^2\right].$$

Show qualitatively that if  $l < n - 1$ , the dispersion  $\Delta r$  is larger than for  $l = n - 1$ .

2. We are now interested in the angular part. According to (10.53),

$$Y_l^m(\theta, \phi) = e^{im\phi} f_l^m(\theta).$$

Using  $L_+ Y_l^l = 0$  and the expression (10.48) for  $L_+$ , show that

$$Y_l^l(\theta, \phi) \propto e^{il\phi} \sin^l \theta.$$

Show that if  $l \gg 1$ ,  $|Y_l^l(\theta, \phi)|^2$  is nonzero only near the  $xOy$  plane (that is, for  $\theta = \pi/2$ ) and calculate the dispersion  $\Delta\theta$ . What happens if  $|m| \neq l$ ?

3. Using the first two questions, show that for  $n \gg 1$  the states  $l = n - 1$  and  $|m| = l$  are localized in a horizontal torus of radius  $n^2 a_0$  whose cross section is a circle of radius  $a_0 n^{3/2}$ . Compare with the orbits (1.33) obtained using the Bohr prescriptions of Section 1.5.2.

### 14.6.5 The diamagnetic term

When we derived the form of the Hamiltonian (14.23) of the Zeeman effect, we neglected a term  $\propto \vec{A}^2$  called the *diamagnetic term*. To justify this approximation, let us consider

the case of a uniform, constant magnetic field  $\vec{B}$ , a possible expression for  $\vec{A}$  being (cf. Section 11.4.2)

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}.$$

1. Show that the quantum Hamiltonian of an electron of charge  $q$  in this magnetic field can be written as

$$\begin{aligned} H &= \frac{1}{2m_e} (\vec{P} - q\vec{A})^2 \\ &= \frac{\vec{P}^2}{2m_e} - \frac{q}{2m_e} \vec{B} \cdot \vec{L} + \frac{q^2}{8m_e} [\vec{R}^2 \vec{B}^2 - (\vec{R} \cdot \vec{B})^2] \\ &= H_0 + H_Z + H_D, \end{aligned}$$

where  $\vec{L} = \vec{R} \times \vec{P}$  is the orbital angular momentum. Carefully justify the operator commutations.

2. Identify  $H_Z$  as the part of the Zeeman Hamiltonian (14.23) of orbital origin and give the order of magnitude of this term for a magnetic field of 1 T when the electron is bound in an atom. The diamagnetic term  $H_D$  can be written as

$$H_D = \frac{q^2 B^2}{8m_e} \bar{R}_\perp^2,$$

where  $\bar{R}_\perp$  is the component of  $\vec{R}$  perpendicular to  $\vec{B}$ . What can we take for the order of magnitude of  $\langle \bar{R}_\perp^2 \rangle$ ? Show that  $|\langle H_D \rangle| \ll |\langle H_Z \rangle|$  for an electron bound in an atom, and that the diamagnetic term can be neglected in calculating the Zeeman effect. However, this term cannot be neglected in calculating the Landau levels, because the radius of the electron orbits is macroscopic in that case.

#### 14.6.6 Vacuum Rabi oscillations

Let us assume that the eigenfrequency  $\omega$  of a cavity is close to the frequency  $\omega_0 = (E_e - E_g)/\hbar$  of a transition between two levels  $e$  and  $g$  of an atom, and use  $\delta = \omega - \omega_0$  to denote the detuning. If the atom interacts with the quantized electromagnetic field inside the cavity, we can to an excellent approximation limit the expansion (11.136) of the quantized field to a single frequency mode  $\omega$ , because this mode is the only one that interacts with the atom in a resonant fashion. We work in one dimension, keeping only the dependence on  $z$  and the polarization in the  $x$  direction, so that the field can be treated as a scalar.

1. Using (11.136), show that for the quantized field  $\mathbf{E}$  we can write

$$\mathbf{E}_H(z, t) = i \sqrt{\frac{\hbar \omega}{\varepsilon_0 \mathcal{V}}} (a e^{-i\omega t} - a^\dagger e^{i\omega t}) \sin kz.$$

We assume that the atom always moves along the line of constant phase  $\sin kz = 1$ .

2. The atom + field Hamiltonian is

$$H = H_{\text{atom}} + H_{\text{field}} + W,$$

where  $W$  represents the interaction between the atom and the field. We take  $|g\rangle$  to be the zero-energy state with no photons. Derive the form of  $H$

$$H = \hbar\omega_0|e\rangle\langle e| + \hbar\omega N + W,$$

where  $N$  is the number operator for photons in the mode of frequency  $\omega$ . Give the spectrum of  $H$  first neglecting  $W$  and assuming that  $|\delta| \ll \omega_0$ , but  $\delta \neq 0$ . Let  $\mathcal{H}^{(n)}$  be the subspace of the Hilbert space formed from the following basis states, where  $n$  is the number of photons in the cavity:

$$\varphi_n^e = |e \otimes (n-1)\rangle, \quad \varphi_n^g = |g \otimes n\rangle.$$

Show that these states are nearly degenerate if  $W$  is neglected.

3. We define the operators

$$b = |g\rangle\langle e|, \quad b^\dagger = |e\rangle\langle g|$$

and the dipole moment of the atom (cf. Section 5.2.2)

$$D = d(b + b^\dagger).$$

Write down the interaction term  $W$  explicitly in the dipole approximation. Show that if  $W$  is constrained to the subspaces  $\mathcal{H}^{(n)}$ , then

$$W = -i\frac{\hbar\Omega_R}{2}(ab^\dagger - a^\dagger b)$$

with

$$\hbar\Omega_R = 2d\sqrt{\frac{\hbar\omega}{\epsilon_0\mathcal{V}}}.$$

The frequency  $\Omega_R$  is called the *vacuum Rabi frequency*. What terms have been neglected in the approximate expression for  $W$  and how can this approximation be justified? The atom + field Hamiltonian involving the approximate expression for  $W$  is called the *Jaynes–Cummings Hamiltonian*.

4. What are the values of  $E_n$  and the corresponding eigenstates when  $W$  is taken into account? We shall take (cf. Section 2.3.2)

$$\tan 2\theta_n = \frac{\Omega_R\sqrt{n}}{\delta} = \frac{\Omega_n}{\delta}.$$

Qualitatively sketch the spectrum of the first few levels of  $H$  as a function of  $\delta$ .

5. The atom in the excited state  $|e\rangle$  is sent to the empty cavity along a trajectory such that  $\sin kz = 1$ . We take the resonant case  $\delta = 0$ . Show that the probability  $p_e(t)$  of finding the atom in the state  $|e\rangle$  after a time  $t$  spent in the cavity is a periodic function of  $t$ . We obtain Rabi oscillations, and since these oscillations arise from the interaction of the atom with the vacuum fluctuations, they

are called vacuum Rabi oscillations. The experimental observation of these oscillations provides direct proof of the quantization of the electromagnetic field. The numerical values are<sup>29</sup>

$$d = 1.1 \times 10^{-26} \text{ C m}, \quad \frac{\omega}{2\pi} = 5.0 \times 10^{10} \text{ Hz}, \quad \mathcal{V} = 1.87 \times 10^{-6} \text{ m}^3.$$

Compare to the experimental value  $\Omega_R/2\pi = 47 \text{ kHz}$ .

6. Calculate  $p_e(t)$  away from resonance, and show that the oscillation frequency is now (always in the case where there are no photons in the cavity)

$$\Omega = \sqrt{\delta^2 + \Omega_R^2}.$$

Show that for the detuning  $\Omega_R \ll |\delta| \ll \omega_0$  the atom nearly always remains in its excited state: spontaneous emission is inhibited by the presence of the cavity.

7. How should the results of the two preceding questions be modified if the cavity contains exactly  $n$  photons? If  $\delta = 0$ , what happens when the cavity contains a coherent state of the field?

### 14.6.7 Reactive forces

We take the Jaynes–Cummings Hamiltonian of the preceding Exercise 14.5.6 for an atom with two levels  $|g\rangle$  and  $|e\rangle$  immersed in the quantized electric field of a cavity:

$$H = i\mathcal{E}(a - a^\dagger) \sin kz, \quad \mathcal{E} = \sqrt{\frac{\hbar\omega}{\epsilon_0 \mathcal{V}}},$$

with the notation of the preceding exercise. The Hamiltonian is given by

$$H = \hbar\omega_0|e\rangle\langle e| + \hbar\omega N + W$$

with<sup>30</sup>

$$W = \frac{1}{2} \hbar\Omega_1(ab^\dagger + a^\dagger b),$$

where  $b = |g\rangle\langle e|$  and  $b^\dagger = |e\rangle\langle g|$ . The frequency  $\Omega_1$  defined as

$$\Omega_1(z) = 2 \frac{d\mathcal{E}}{\hbar} \sin kz$$

is a function of  $z$ .

1. In the two-dimensional subspace  $\mathcal{H}^{(n)}$  in which the states  $|g \otimes n\rangle$  and  $|e \otimes (n-1)\rangle$  form an orthonormal basis, show that up to an additive constant the Hamiltonian takes the form

$$H = \frac{1}{2} \hbar \begin{pmatrix} \delta & \Omega_1 \sqrt{n} \\ \Omega_1 \sqrt{n} & -\delta \end{pmatrix},$$

where  $\delta = \omega - \omega_0$  is the detuning. We set

$$\Omega_{1n}(z) = \sqrt{\delta^2 + n\Omega_1^2(z)} = \sqrt{\delta^2 + \Omega_n^2(z)}$$

<sup>29</sup> M. Brune, *et al.* Quantum Rabi oscillations: a direct test of field quantization in a cavity, *Phys. Rev. Lett.* **76**, 1800 (1996).

<sup>30</sup> A suitable choice of phase for the vectors  $|e\rangle$  and  $|g\rangle$  has allowed us to eliminate the factors of  $i$  of the preceding exercise.



and define the angle  $\theta_n(z)$  as

$$\cos 2\theta_n(z) = \frac{\delta}{\Omega_{1n}(z)}, \quad \sin 2\theta_n(z) = \frac{\Omega_n(z)}{\Omega_{1n}(z)}.$$

Show that the eigenvectors of  $H$  restricted to  $\mathcal{H}^{(n)}$  are

$$\begin{aligned} |\chi_{1n}(z)\rangle &= -\sin \theta_n(z)|g \otimes n\rangle + \cos \theta_n(z)|e \otimes (n-1)\rangle, \\ |\chi_{2n}(z)\rangle &= \cos \theta_n(z)|g \otimes n\rangle + \sin \theta_n(z)|e \otimes (n-1)\rangle. \end{aligned}$$

What are the eigenvalues of  $H$ ? Calculate the force on an atom at rest at  $z$  when this atom is in the state  $|\chi_{1n}\rangle$  or the state  $|\chi_{2n}\rangle$ .

2. In what follows we assume that the field inside the cavity is that of a laser in a coherent state with an average number of photons  $\langle n \rangle \gg 1$  such that  $\Delta n \ll \langle n \rangle$ . We can then write down a classical expression for this field:

$$E_L(t, z) = \mathcal{E}_0 \cos \omega t \sin kz.$$

Using (11.93), show that

$$\hbar \Omega_1(z) \sqrt{\langle n \rangle} = \hbar \omega_1(z), \quad \omega_1(z) = \frac{d\mathcal{E}_0}{\hbar} \sin kz,$$

where  $\omega_1(z)$  is the usual Rabi frequency (cf., for example, (14.74)). In the preceding discussion we have neglected spontaneous emission, which has the effect of depopulating the laser mode in favor of the vacuum mode. The rate of transitions between the states with  $n$  and  $n-1$  photons is given by

$$\Gamma_{ij}(z) = \Gamma |\langle \chi_{i,n-1}(z) | b + b^\dagger | \chi_{jn}(z) \rangle|^2$$

with  $(i, j) = 1, 2$ . Calculate  $\Gamma_{ij}(z)$  as a function of the angles  $\theta_n(z)$  and  $\theta_{n-1}(z)$ . In what follows we assume that the laser is intense,  $n \gg 1$  and  $\Omega_{1n} \simeq \Omega_{1\langle n \rangle}(z) = \sqrt{\delta^2 + \omega_1^2(z)}$ .

3. The populations  $p_i(z)$  are defined as

$$p_i(z) = \sum_n \langle \chi_{in}(z) | \rho | \chi_{in}(z) \rangle,$$

where  $\rho$  is the state operator of the atom dressed by the field. Show that if  $\Omega_{1\langle n \rangle} \gg \Gamma$  the populations obey the master equation

$$\begin{aligned} \dot{p}_1(z) &= -\Gamma_{21}(z)p_1(z) + \Gamma_{12}(z)p_2(z), \\ \dot{p}_2(z) &= \Gamma_{21}(z)p_1(z) - \Gamma_{12}(z)p_2(z). \end{aligned}$$

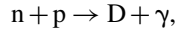
What are the stationary values of the populations  $p_i^{\text{st}}$  as a function of  $z$ ? Show that an atom at rest feels a force

$$F(z) = \frac{1}{4} \hbar \frac{\partial \omega_1^2(z)}{\partial z} \frac{1}{\sqrt{\delta^2 + \omega_1^2(z)}} (p_1^{\text{st}}(z) - p_2^{\text{st}}(z)).$$

Substitute the values of  $p_1^{\text{st}}$  and  $p_2^{\text{st}}$  into this result and compare with (14.98).

### 14.6.8 Radiative capture of neutrons by hydrogen

NB It is useful to reread Sections 12.2.3 and 12.2.4. In a boiling-water or pressurized-water nuclear reactor a fraction of the neutrons is absorbed by the hydrogen of the water in the reaction



where  $n$  is a neutron,  $p$  is a proton,  $D$  is a deuteron, and  $\gamma$  is a photon. This reaction, called radiative capture, has the drawback of decreasing the number of neutrons available for fission. The deuteron is a neutron–proton bound state of total angular momentum  $J = 1$  and binding energy  $B = 2.23$  MeV. It is a mixture of the  $^3S_1$  and  $^3D_1$  states, but to simplify the discussion we shall take into account only the  $^3S_1$  state. The goal is to calculate the radiative capture cross section. In the numerical calculations it will be convenient to use a system of units in which  $\hbar = c = 1$ . In this system the mass, momentum, and energy have the dimensions of inverse length, and the conversion factor is

$$1 \text{ (fm)}^{-1} \simeq 200 \text{ MeV}.$$

1. The reactor neutrons have very low energy ( $\ll 1$  MeV), and so the  $n$ - $p$  potential in the  $S$ -wave can to a good approximation be represented by a delta function  $\delta(\vec{r})$  (see (12.44)). The bound-state wave function is given by (12.45), with  $a \rightarrow a_t \simeq 5.40$  fm. Calculate the normalization constant  $C$  and  $\kappa^{-1}$  in fm. We note that  $\kappa^{-1}$  fixes the length scale of the problem.

The scattering states of interest to us will be the  $^1S_0$  states, where the scattering length is  $a_s$ ,  $a_s \simeq -23.7$  fm. It is convenient to fix the normalization by writing

$$\psi(r) = \frac{\sin[pr + \delta(p)]}{pr}.$$

Show that for  $p \rightarrow 0$

$$\psi(r) \simeq -\frac{a}{r} \left(1 - \frac{r}{a}\right), \quad a = a_t \quad \text{or} \quad a = a_s.$$

2. The neutron of the capture reaction is very slow, and, owing to the centrifugal barrier, the reaction occurs in the  $S$ -wave, which a priori presents two possibilities:

$$(n-p : ^3S_1) \rightarrow D(^3S_1) + \gamma, \quad (n-p : ^1S_0) \rightarrow D(^3S_1) + \gamma.$$

Electric dipole transitions are negligible because they would correspond to initial state in a  $P$ -wave (why?). The reaction comes from the coupling  $\vec{\mu} \cdot \vec{B}$  between the deuteron magnetic moment  $\vec{\mu}$  and the quantized magnetic field  $\vec{B}$ , with

$$\begin{aligned} \vec{\mu} &= \frac{1}{2} \mu_N (g_p \vec{\sigma}_p + g_n \vec{\sigma}_n) \\ &= \frac{1}{4} \mu_N [(g_p + g_n)(\vec{\sigma}_p + \vec{\sigma}_n) + (g_p - g_n)(\vec{\sigma}_p - \vec{\sigma}_n)], \end{aligned} \quad (14.133)$$

where  $\mu_N = q_p \hbar / 2M$ . The quantities  $g_p \simeq 5.59$  and  $g_n \simeq -3.83$  are related to the proton and neutron gyromagnetic ratios and  $\vec{\sigma}$  are the Pauli matrices. Show that the coupling to the quantized electromagnetic field responsible for the reaction is

$$W' = -\frac{i}{c} \sqrt{\frac{\hbar \omega}{2\varepsilon_0 \mathcal{V}}} \vec{\mu} \cdot [\hat{k} \times \vec{e}_\lambda^*(\vec{k})] a_{\vec{k}\lambda}^\dagger e^{-i\vec{k} \cdot \vec{r}},$$

where the photon has wave vector  $\vec{k}$  and frequency  $\omega = ck$ ,  $\hat{k} = \vec{k}/k$ ,  $\vec{e}_\lambda$  is a polarization unit vector which we can take to be real, and  $\mathcal{V}$  is the normalization volume. Neglecting the deuteron recoil and noting that the incident neutron energy  $\varepsilon \ll B$ , calculate  $k$  in  $\text{fm}^{-1}$  and show that it is possible to make the approximation  $\exp(-i\vec{k} \cdot \vec{r}) \simeq 1$ .

3. Justify the various factors in the following expression for the cross section, where  $\Omega$  is the emission direction of the photon with wave vector  $\vec{k}$  and  $\mathcal{F}$  is the incident neutron flux:

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar \mathcal{F}} |\langle f | W | i \rangle|^2 \delta(\hbar\omega - (E_i - E_f)) \frac{\mathcal{V} \omega^2 d\omega}{(2\pi)^3 c^3}$$

with

$$W = -\frac{i}{c} \sqrt{\frac{\hbar \omega}{2\varepsilon_0 \mathcal{V}}} \vec{\mu} \cdot \vec{e}'_\lambda(\vec{k}), \quad \vec{e}'_\lambda(\vec{k}) = \hat{k} \times \vec{e}_\lambda.$$

Here  $|i\rangle$  is the initial n-p state and  $|f\rangle$  is the deuteron state.

4. The matrix element  $\langle f | W | i \rangle$  breaks up into a spin part and a spatial part, because the total state vector  $\Psi_{i,f}$  is a product of the spin vector  $\chi_{i,f}$  and the spatial wave function  $\psi_{i,f}(\vec{r})$ :

$$\Psi_{i,f} = \psi_{i,f}(\vec{r}) \chi_{i,f}.$$

- (a) If  $\chi_t^m$ ,  $m = \pm 1, 0$ , and  $\chi_s$  denote the triplet and singlet spin states, the spin part of  $\langle f | W | i \rangle$  will be

$$W_{\text{spin}} = \frac{1}{4} \mu_N \langle \chi_f | (g_p + g_n)(\vec{\sigma}_p + \vec{\sigma}_n) \cdot \vec{e}'_\lambda + (g_p - g_n)(\vec{\sigma}_p - \vec{\sigma}_n) \cdot \vec{e}'_\lambda | \chi_i \rangle,$$

where  $\chi_f = \chi_t^m$  and  $\chi_i = \chi_t^m$  or  $\chi_s$ . Show that

$$(\vec{\sigma}_p + \vec{\sigma}_n) | \chi_s \rangle = 0, \quad \langle \chi_s | \vec{\sigma}_p | \chi_s \rangle = 0.$$

- (b) The spatial part will involve the integral

$$I_{fi} = \int d^3r \psi_f^*(\vec{r}) \psi_i(\vec{r}) = \int d^3r \psi_D^*(\vec{r}) \psi_i(\vec{r}).$$

Show without calculation that  $I_{fi} = 0$  if  $\psi_i$  and  $\psi_f$  are the  $L = 0$  wave functions of the triplet state. Calculate  $I_{fi}$  explicitly if  $\psi_i$  is a singlet wave function using the approximations of question 1.

5. The above results can be summarized as

$$\begin{aligned} W_{\text{spin}} &= \frac{1}{4} \mu_N (g_p - g_n) \langle \chi_t^m | (\vec{\sigma}_p - \vec{\sigma}_n) \cdot \vec{e}'_\lambda | \chi_s \rangle \\ &\rightarrow \frac{1}{2} \mu_N (g_p - g_n) \langle \chi_t^m | \vec{\sigma}_p \cdot \vec{e}'_\lambda | \chi_s \rangle = \frac{1}{2} \mu_N (g_p - g_n) W'_{\text{spin}}. \end{aligned}$$

It is necessary to square this, sum over the final photon polarizations ( $\sum_\lambda$ ), sum over the final deuteron spins ( $\sum_m$ ), and average over the initial spins (the factor of  $1/4$ ). Show that

$$\begin{aligned}\langle |W'_{\text{spin}}|^2 \rangle &= \frac{1}{4} \sum_m \sum_\lambda |\langle \chi_t^m | \vec{\sigma}_p \cdot \vec{e}_\lambda' | \chi_s \rangle|^2 \\ &= \frac{1}{4} \sum_{i,j} (\delta_{ij} - \hat{k}_i \hat{k}_j) \langle \chi_s | \sigma_{pi} \sigma_{pj} | \chi_s \rangle.\end{aligned}$$

Hint: show that  $\sum_m |\chi_t^m\rangle \langle \chi_t^m|$  can be replaced by the identity operator in spin space. Obtain the result  $\langle |W'_{\text{spin}}|^2 \rangle = 1/2$ .

6. Assemble all these factors to show that

$$\frac{1}{4} \sum_{\text{spins}} \sum_\lambda |\langle f | W | i \rangle|^2 = \frac{\hbar}{16\epsilon_0 \mathcal{V}} \frac{\omega}{c^2} \mu_N^2 (g_p - g_n)^2 I_{fi}^2.$$

Taking into account the normalization of the spatial wave functions, it can be shown that the flux factor is  $\mathcal{F} = \sqrt{2\epsilon/M}$ . Derive the total cross section for the capture reaction ( $\alpha = q_p^2/4\pi\epsilon_0\hbar c$ ):

$$\sigma_{\text{tot}} = \int d\Omega \frac{d\sigma}{d\Omega} = \frac{\alpha\pi\hbar^2}{2c^4} \frac{B^{3/2}}{\sqrt{2\epsilon}} \frac{1}{M^3} (g_p - g_n)^2 (1 - \kappa a_s)^2.$$

Compare to the experimental result for thermal neutrons at 300 K:

$$\sigma_{\text{tot}} = 0.329 \pm 0.006 \times 10^{-28} \text{ m}^2 = 32.9 \pm 0.6 \text{ fm}^2.$$

## 14.7 Further reading

Perturbation theory and the variational method are described in all the classic texts. A source for further details about the energy level structure is Cohen-Tannoudji *et al.* [1977]: fine structure, Chapter XII; Zeeman effect, Complement D<sub>VII</sub>; hyperfine structure, Chapter XII. See also B. Bransden and C. Joachain, *Physics of Atoms and Molecules*, Harlow: Longman Scientific and Technical (1983). Cohen-Tannoudji's course, 'Atomic motion in laser light', in *Optical Coherence and Quantum Optics*, Les Houches School, Amsterdam North-Holland (1992), contains a very complete discussion of the laser manipulation of atoms. See also D. Suter, *The Physics of Laser-Atom Interactions*, Cambridge: Cambridge University Press (1997). The helium atom is treated in great detail by Cohen-Tannoudji *et al.* [1977], Complement B<sub>XIV</sub>.