Chapter 9
Time Dependence in Quantum Mechanics

Up to now we have only considered static situations (except for the reduction of the state vector when a measurement takes place). We now discuss the time dependence of the state vector, which requires a new principle. The resultant time-dependent Schrödinger equation is solved exactly for simple (spin) cases and in perturbation theory. The notion of transition probability yields physical meaning to non-diagonal matrix elements and allows us to present the energy–time uncertainty relation, together with the concept of mean lifetime (Sect. 9.5).

In Chap. 1 we stressed the fact that the main reason for the development of quantum mechanics was the instability of the hydrogen atom under classical mechanics and electromagnetism. Thus, an exposition of quantum mechanics cannot be deemed complete without showing that this original crisis has been solved. This task requires an introduction to quantum electrodynamics (QED). The concepts of induced and spontaneous emission, laser optics and selection rules appear along the exposition.

9.1 The Time Principle

In the first place we stress the fact that in quantum mechanics, time is taken to be a parameter, not an observable. Although there is an evolution operator, there is no such thing as a time operator.[1]

[1] As Jun John Sakurai points out: "Ironically, in the historical development of wave mechanics both L. de Broglie and E. Schrödinger were guided by a kind of covariant analogy between energy and time on the one hand and momentum and position (spatial coordinate) on the other. Yet when we now look at quantum mechanics in its finished form, there is no trace of a symmetrical treatment between time and space. The relativistic quantum theory of fields does treat the time and space coordinates on the same footing, but it does so at the expense of demoting position from the status of being an observable to that of being just a parameter." [63], Chap. 2. Nevertheless, and

D. Bes, *Quantum Mechanics*, Graduate Texts in Physics,
DOI 10.1007/978-3-642-20556-9_9,

Assume that the system is represented at time t by the time-dependent state vector $\Psi(t)$. At time $t' > t$, the system will evolve in accordance with

$$\Psi(t') = \mathcal{U}(t', t)\Psi(t), \tag{9.1}$$

where $\mathcal{U}(t', t)$ is called the evolution operator. This operator satisfies the conditions of being unitary and

$$\lim_{t' \to t} \mathcal{U}(t', t) = 1. \tag{9.2}$$

Therefore, if $t' = t + \Delta t$,

$$\begin{aligned} \Psi(t + \Delta t) &= \mathcal{U}(t + \Delta t, t)\Psi(t) \\ &= \left[1 + \frac{\partial}{\partial t'} \mathcal{U}(t', t) \bigg|_{t'=t} \Delta t + \cdots \right] \Psi(t), \end{aligned}$$

$$\frac{\partial}{\partial t} \Psi(t) = \frac{\partial}{\partial t'} \mathcal{U}(t', t)|_{t'=t} \Psi(t). \tag{9.3}$$

A new quantum principle must be added to those stated in Chaps. 2 and 7.

Principle 5. *The operator yielding the change of the state vector over time is proportional to the Hamiltonian*

$$\frac{\partial}{\partial t'} \mathcal{U}(t', t)|_{t'=t} = -\frac{\mathrm{i}}{\hbar} \hat{H}(t). \tag{9.4}$$

Note the following consequences:

- The time evolution of the system is determined by the first-order linear equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H} \Psi(t). \tag{9.5}$$

  This is called the time-dependent Schrödinger equation. It is valid for a general state vector, and it is independent of any particular realization of quantum mechanics.
- The evolution is deterministic, since the state vector is completely defined once the initial state is fixed (quantum indeterminacy pertains to measurement processes).
- The evolution is unitary (i.e. the norm of the states is preserved).

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although the commutation relation $[\hat{x}, \hat{p}]$ has been postulated in the present text, it has also been derived in the non-relativistic limit of Lorentz transformations [18], thus suggesting a deeper link between relativity and quantum mechanics.

- The evolution of the system is reversible.
- The evolution satisfies the composition property

$$\mathcal{U}(t'-t) = \mathcal{U}(t'-t'')\,\mathcal{U}(t''-t) \qquad (t' > t'' > t). \tag{9.6}$$

- If $[\hat{H}(\tau_1), \hat{H}(\tau_2)] = 0$, the evolution operator is

$$\mathcal{U}(t', t) = \exp\left[-\frac{\mathrm{i}}{\hbar}\int_t^{t'} \hat{H}(\tau)\,\mathrm{d}\tau\right]. \tag{9.7}$$

In the case of a time–independent Hamiltonian satisfying the eigenvalue equation $\hat{H}\varphi_i = E_i\varphi_i$, the solution to the differential equation (9.5) may be found using the method for separation of variables. Hence,

$$\varphi_i(t) = f(t)\varphi_i, \qquad \mathrm{i}\hbar\frac{\mathrm{d}f}{\mathrm{d}t} = E_i f \rightarrow f = \exp(-\mathrm{i}E_i t/\hbar) \tag{9.8}$$

and thus,

$$\varphi_i(t) = \varphi_i \exp\left(-\frac{\mathrm{i}}{\hbar}E_i t\right). \tag{9.9}$$

We expect the solutions of a time-independent Hamiltonian to be independent of time. However, as usual, this requirement can only be enforced up to a phase. This is consistent with the result (9.9).

The constant of proportionality $-\mathrm{i}/\hbar$ chosen in (9.4) ensures that the time-dependent wave function for a free particle with energy $E = \hbar\omega$ is a plane wave, as expected [see (4.32)]:

$$\varphi_{\pm k}(x, t) = A\exp\left[\mathrm{i}(\pm kx - \omega t)\right]. \tag{9.10}$$

If the Hamiltonian is time independent and the state is represented at time $t = 0$ by the linear combination (2.6) of its eigenstates,

$$\Psi(t = 0) = \sum_i c_i\varphi_i, \tag{9.11}$$

(9.9) implies that at time t the state has evolved into[2]

$$\Psi(t) = \sum_i c_i\varphi_i \exp\left[-\frac{\mathrm{i}}{\hbar}E_i\,t\right]. \tag{9.12}$$

[2]The evolution is valid only for the Hamiltonian basis. Therefore, the expression $\Psi(t) = \sum_i c_i\varphi_i\exp(-\mathrm{i}q_i t/\hbar)$ makes no sense if φ_i, q_i are not eigenstates and eigenvalues of the Hamiltonian.

The relation $[\hat{Q}, \hat{H}] = 0$ implies a conservation law. If the system is initially in an eigenstate of the operator $\hat{Q}$ it remains so during its time evolution.

9.2 Time Dependence of Spin States

9.2.1 Larmor Precession

To begin with we give a simple but non-trivial example of a solution to (9.5). We use as Hamiltonian the interaction (5.15), with the magnetic field directed along the z-axis. The evolution operator (9.7) is given by

$$\mathcal{U}_z(t,0) = \exp[-\mathrm{i}\hat{H}_z t/\hbar] = \begin{pmatrix} \exp[\mathrm{i}\omega_\mathrm{L} t/2] & 0 \\ 0 & \exp[-\mathrm{i}\omega_\mathrm{L} t/2] \end{pmatrix}$$
$$\hat{H}_z = -\omega_\mathrm{L}\, \hat{S}_z, \tag{9.13}$$

where $\omega_\mathrm{L} \equiv \mu_v\, g_s\, B/\hbar$ is called the Larmor frequency [see (5.22)]. We have used (5.21) in the expansion of the exponential in (9.13).

The time evolution is given by

$$\Psi(t) = \begin{pmatrix} c_\uparrow(t) \\ c_\downarrow(t) \end{pmatrix} = \mathcal{U}_z(t,0) \begin{pmatrix} c_\uparrow(0) \\ c_\downarrow(0) \end{pmatrix}. \tag{9.14}$$

If the state of the system is an eigenstate of the operator $\hat{S}_z$ at $t = 0$, it remains so forever and (9.14) is just a particular case of (9.9). However, if at $t = 0$ the spin points in the positive x-direction [initial values: $c_\uparrow = c_\downarrow = 1/\sqrt{2}$, see (3.21)], then

$$\Psi(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \cos\frac{\omega_\mathrm{L} t}{2} + \mathrm{i}\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \sin\frac{\omega_\mathrm{L} t}{2}. \tag{9.15}$$

The probability of finding the system with spin aligned with the x-axis (or in the opposite direction) is $\cos^2(\omega_\mathrm{L} t/2)$ [or $\sin^2(\omega_\mathrm{L} t/2)$].

The expectation values of the spin components are

$$\langle\Psi|S_x|\Psi\rangle = \frac{\hbar}{2}\cos(\omega_\mathrm{L} t), \qquad \langle\Psi|S_y|\Psi\rangle = -\frac{\hbar}{2}\sin(\omega_\mathrm{L} t), \qquad \langle\Psi|S_z|\Psi\rangle = 0. \tag{9.16}$$

The spin precesses around the z-axis (the magnetic field axis), with the Larmor frequency ω_L in the clockwise direction ($x \to -y$). It never aligns itself with the z-axis. Unlike the case in which a definite projection of the angular momentum along the z-axis is well defined (see the discussion of Fig. 5.1 in Sect. 5.1.1), we are describing a true precession here, which is obtained at the expense of the determination of S_z.

If $t \ll 1/\omega_{\mathrm{L}}$, we speak of a transition from the initial state $\varphi_{S_x=\hbar/2}$ to the final state $\varphi_{S_x=-\hbar/2}$ with the probability $\omega_{\mathrm{L}}^2 t^2/4$. In this case, the probability per unit time is linear in time.

If the z-direction is substituted by the x-direction in the Hamiltonian (9.13), we obtain the transformation

$$\mathcal{U}_x(t,0) = \begin{pmatrix} \cos\omega_{\mathrm{L}} t/2 & \mathrm{i}\sin\omega_{\mathrm{L}} t/2 \\ \mathrm{i}\sin\omega_{\mathrm{L}} t/2 & \cos\omega_{\mathrm{L}} t/2 \end{pmatrix}. \tag{9.17}$$

9.2.2 Magnetic Resonance

We now add a periodic field along the x- and y-directions, of magnitude B' and frequency ω, to the constant magnetic field of magnitude B pointing along the z-axis. The Hamiltonian reads

$$\begin{aligned} \hat{H} &= -\mu_s B \hat{S}_z - \mu_s B' \left(\cos\omega t \hat{S}_x - \sin\omega t \hat{S}_y\right) \\ &= -\frac{1}{2}\mu_s \hbar \begin{pmatrix} B & B'\exp(\mathrm{i}\omega t) \\ B'\exp(-\mathrm{i}\omega t) & -B \end{pmatrix}. \end{aligned} \tag{9.18}$$

Since this Hamiltonian does not commute with itself at different times, we cannot use the evolution operator (9.7). We must solve instead the differential equation (9.5) for the amplitudes $c_i(t)$. Although the solution may be worked out analytically for any value of ω, it turns out that the maximum effect is obtained if this frequency equals the Larmor frequency ω_{L}. We make this assumption in the derivation below. We also set $\omega' \equiv \mu_s B'$.

We try a solution of the form (9.14), but with time-dependent amplitudes:

$$\begin{pmatrix} b_\uparrow(t) \\ b_\downarrow(t) \end{pmatrix} = \begin{pmatrix} \exp[i\omega t/2]\, c_\uparrow(t) \\ \exp[-i\omega t/2]\, c_\downarrow(t) \end{pmatrix}, \quad \begin{pmatrix} \dot{b}_\uparrow \\ \dot{b}_\downarrow \end{pmatrix} = \frac{\mathrm{i}}{2}\omega' \begin{pmatrix} b_\downarrow \\ b_\uparrow \end{pmatrix}. \tag{9.19}$$

The solution to the last equation is

$$\begin{pmatrix} b_\uparrow \\ b_\downarrow \end{pmatrix} = \begin{pmatrix} \cos\dfrac{\omega' t}{2} & \sin\dfrac{\omega' t}{2} \\ \mathrm{i}\sin\dfrac{\omega' t}{2} & -\mathrm{i}\cos\dfrac{\omega' t}{2} \end{pmatrix} \begin{pmatrix} b_\uparrow(0) \\ b_\downarrow(0) \end{pmatrix}. \tag{9.20}$$

This result ensures the occurrence of the spin flip: a spin pointing up (down) will eventually point down (up), i.e. it will be flipped. The probabilities that the initial spin is maintained or flipped are (Fig. 9.1)

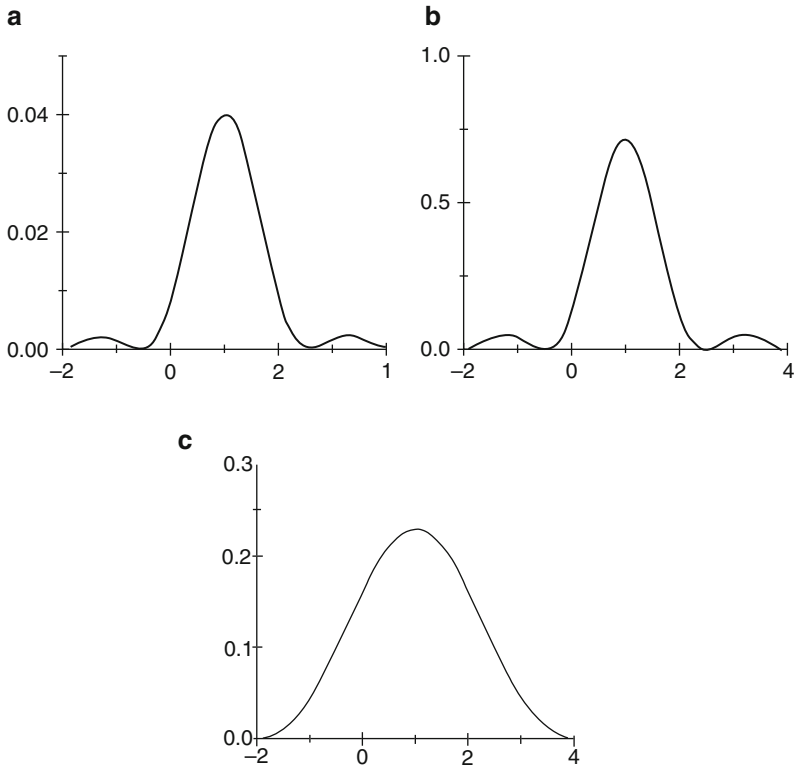

Fig. 9.1 Probability of a spin flip according to (9.22). Values of $\omega/\omega_{\mathrm{L}}$ are represented on the horizontal axis, while probabilities are indicated on the vertical axis. The resonant behavior for $\omega = \omega_{\mathrm{L}}$ is apparent. The parameters are $t\omega_{\mathrm{L}} = 4,\ \omega'/\omega_{\mathrm{L}} = 1/10$ (**a**); $t\omega_{\mathrm{L}} = 4,\ \omega'/\omega_{\mathrm{L}} = 1/2$ (**b**) and $t\omega_{\mathrm{L}} = 2,\ \omega'/\omega_{\mathrm{L}} = 1/2$ (**c**). The comparison between the last two graphs anticipates the complementary relation between time and energy [see (9.35) and Sect. 9.5]

$$P_{\uparrow\to\uparrow} = P_{\downarrow\to\downarrow} = \cos^2\left(\frac{1}{2}\omega' t\right),$$
$$P_{\uparrow\to\downarrow} = P_{\downarrow\to\uparrow} = \sin^2\left(\frac{1}{2}\omega' t\right). \tag{9.21}$$

For an arbitrary relation between ω and ω_{L}, the probability of a spin flip is given by

$$P_{\uparrow\to\downarrow}(t) = \frac{(\omega')^2}{(\omega-\omega_{\mathrm{L}})^2 + (\omega')^2} \sin^2\left[\frac{1}{2} t \sqrt{(\omega-\omega_{\mathrm{L}})^2 + (\omega')^2}\right]. \tag{9.22}$$

This equation expresses a typical resonance phenomenon (hence the name magnetic resonance): if $\omega \approx \omega_{\mathrm{L}}$, a very weak field B' produces large effects (Fig. 9.1). One cannot treat the interaction with the sinusoidal field as a small perturbation.

This would require $|\omega'| \ll |\omega - \omega_{\mathrm{L}}|$, a condition violated in the neighborhood of resonance.

Nuclear magnetic resonance (NMR) is an essential part of processes involving the alignment of spins. It has applications in many branches of physics, such as measuring magnetic moments of particles, including elementary particles, and determining properties of condensed matter. It is also an important tool in quantum computing.

In medicine, NMR is called magnetic resonance imaging (MRI). It is the result of three contributing quantum technologies:

- The patient is placed in a large magnetic field that is produced without heating, by means of superconducting coils (Sect. 10.1).
- The evolution of spins of the hydrogen atoms in our body is affected by both static and modulated fields, as described above.
- The signals picked by detection coils are transformed into images by computers employing hardwares based on transistor technologies (Sect. 7.4.3†).

An enormous amount of information is obtained from the medium. For instance, the brain activity can be directly observed through changes in the magnetic environment produced by the flux of blood.

9.3 Sudden Change in the Hamiltonian

We consider a time-dependent Hamiltonian $\hat{H}$ such that $\hat{H} = \hat{H}_0$ for $t < 0$ and $\hat{H} = \hat{K}_0$ for $t > 0$, where $\hat{H}_0$ and $\hat{K}_0$ are time-independent Hamiltonians. We know how to solve the problem for these two Hamiltonians:

$$\hat{H}_0 \varphi_i = E_i \varphi_i, \qquad \hat{K}_0 \phi_i = \epsilon_i \phi_i. \tag{9.23}$$

The system is initially in the state $\varphi_i \exp(-\mathrm{i}E_i t/\hbar)$. For $t > 0$, the solution is given by the superposition

$$\Psi = \sum_k c_k \phi_k \exp(-\mathrm{i}\epsilon_k t/\hbar), \tag{9.24}$$

where the amplitudes c_k are time independent, as is $\hat{K}_0$.

The solution must be continuous in time to satisfy a differential equation. Therefore, at $t = 0$,

$$\varphi_i = \sum_k c_k \phi_k \longrightarrow c_k = \langle \phi_k | \varphi_i \rangle. \tag{9.25}$$

The transition probability is given by

$$P_{\varphi_i \to \phi_k} = |c_k|^2. \tag{9.26}$$

9.4 Time-Dependent Perturbation Theory

If the Hamiltonian includes both a time-independent term $\hat{H}_0$ and a time-dependent contribution $\hat{V}(t)$, one may still use the expansion (9.12), but with time-dependent amplitudes $[c_i = c_i(t)]$. In that case, the Schrödinger equation for the Hamiltonian $\hat{H}_0 + \hat{V}$ is equivalent to the set of coupled equations

$$\mathrm{i}\hbar \sum_i \dot{c}_i \varphi_i \exp(-\mathrm{i}E_i t/\hbar) = \hat{V} \sum_i c_i \varphi_i \exp(-\mathrm{i}E_i t/\hbar). \tag{9.27}$$

The scalar product with φ_k yields

$$\mathrm{i}\hbar \dot{c}_k = \sum_i c_i \langle k|V|i\rangle \exp(\mathrm{i}\omega_{ki} t), \qquad \omega_{ki} = \frac{E_k - E_i}{\hbar}, \tag{9.28}$$

where ω_{ki} is the Bohr frequency. This set of coupled equations must be solved together with boundary conditions, such as the value of the amplitudes c_i at $t = 0$. The formulation of the time-dependent problem in terms of the coupled amplitudes $c_i(t)$ is attributed to Dirac.

The set of coupled equations (9.28) is not easier to solve than (9.5). Therefore, one must resort to a perturbation treatment. As in Sect. 8.1, we multiply the perturbation $\hat{V}(t)$ by the unphysical parameter λ $(0 \leq \lambda \leq 1)$ and expand the amplitudes

$$c_k(t) = c_k^{(0)} + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \cdots. \tag{9.29}$$

We impose the initial condition that the system be in the state $\varphi_i^{(0)}(t)$ at $t = 0$. This condition is enforced through the assignment $c_k^{(0)} = \delta_{ki}$, which accounts for terms independent of λ in (9.28).

The perturbation is applied at $t = 0$. Our aim is to calculate the probability of finding the system in another unperturbed eigenstate $\varphi_k^{(0)}$ at time t. The terms linear in λ yield

$$\dot{c}_k^{(1)} = -\frac{\mathrm{i}}{\hbar} \langle k|V|i\rangle \exp(\mathrm{i}\omega_{ki} t). \tag{9.30}$$

Therefore, the transition amplitudes are given by

$$c_k^{(1)}(t) = -\frac{\mathrm{i}}{\hbar} \int_0^t \langle k|V|i\rangle \exp(\mathrm{i}\omega_{ki}\tau)\mathrm{d}\tau. \tag{9.31}$$

The transition probability between the initial state i and the final state k, induced by the Hamiltonian $\hat{V}(t)$, is given in first-order of perturbation theory as

$$P_{i\to k}^{(1)}(t) = \left|c_k^{(1)}\right|^2. \tag{9.32}$$

9.5 Energy–Time Uncertainty Relation

Consider matrix elements of the perturbation $\langle k|V|i\rangle$ which do not depend on time in the interval $(0, t)$, and otherwise vanish. The first-order amplitude and transition probabilities (9.31) and (9.32) are given by

$$c_k^{(1)} = -\frac{\langle k|V|i\rangle}{\hbar\omega_{ki}}\left[\exp(\mathrm{i}\omega_{ki}t) - 1\right], \tag{9.33}$$

$$P_{i\to k}^{(1)} = \left|\frac{\langle k|V|i\rangle}{\hbar\omega_{ki}}\right|^2 4\sin^2(\omega_{ki}t/2). \tag{9.34}$$

The result (9.34) is common to many first-order transition processes. Therefore, we discuss it in some detail:

- If the final states φ_k belong to a continuous set, the transition probability is proportional to the function $f(\omega) = (4/\omega^2)\sin^2(\omega t/2)$ plotted in Fig. 9.2. The largest peak at $\omega = 0$ has a height proportional to t^2, while the next highest, at $\omega \approx 3\pi/t$, is smaller by a factor of $4/9\pi^2 \approx 1/20$. Therefore, practically all transitions take place for frequencies lying within the central peak, which is characteristic of the phenomena of resonance. The secondary peaks are associated with diffraction processes.
- The total probability is obtained by integrating over the frequencies. Assuming that the matrix element is not changed within the frequency interval of the main peak, and approximating the surface of the latter by the area of an isosceles triangle of height t^2 and half-base $2\pi/t$, we conclude that the total probability

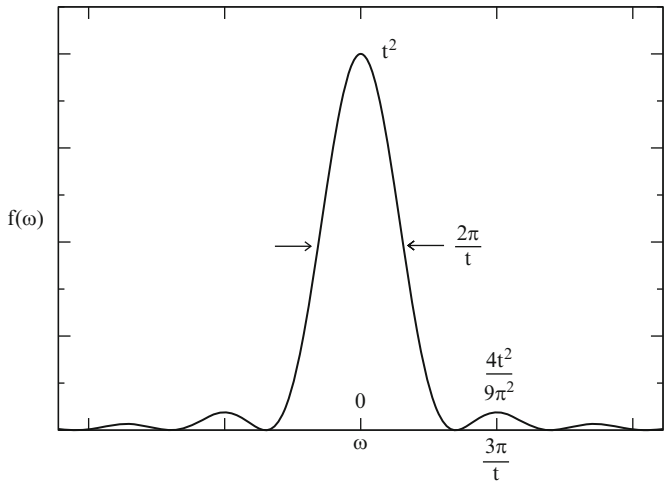

Fig. 9.2 The function $f(\omega)$ as a function of the frequency ω

increases linearly with time and that the probability per unit interval of time is constant.

- The energy of an initially excited atomic state may be obtained from the frequency of the photon resulting from de-excitation of this state (Sect. 9.8.4†). Therefore, the spread shown in Fig. 9.2 changes the notion of the eigenvalue in the case of an unstable state. Instead of a sharp energy, the existence of the spread is associated with an indeterminacy in the energy on the order of

$$\Delta E \geq \hbar \frac{2\pi}{t}. \tag{9.35}$$

This inequality is a manifestation of the uncertainty as applied to energy and time. There is a similar uncertainty if the energy of the excited states is obtained via a process of absorption of electromagnetic radiation.

This time–energy relation was anticipated in the caption of Fig. 9.1.

- It would be wrong to conclude from (9.35) that energy is not conserved at the microscopic quantum scale, since such conservation principle does not hold for a time-dependent Hamiltonian. What enters in (9.35) is the difference between eigenvalues of the unperturbed Hamiltonian.
- Non-diagonal matrix elements $\langle k|V|i\rangle$ acquire physical meaning, since they can be measured through transition rates.
- If there is a continuum of final states, we are interested in summing up the probabilities over the set K of these final states ($k \in K$):

$$P^{(1)}_{i\to K} = \int_{E_i-\Delta E/2}^{E_i+\Delta E/2} P^{(1)}_{i\to k}\rho(E_k)\mathrm{d}E_k, \tag{9.36}$$

where $\rho(E_k)$ is the density of the final states.[3] Assuming that both $|\langle k|V|i\rangle|^2$ and $\rho(E_k)$ remain constant during the interval ΔE, and that most of the transitions take place within this interval, then

$$P^{(1)}_{i\to K} \approx \frac{4}{\hbar^2}|\langle k|V|i\rangle|^2\rho(E_k)\int_{-\infty}^{\infty}\mathrm{d}E_k\frac{\sin^2\omega_{ki}t/2}{\omega_{ki}^2} = \frac{2\pi t}{\hbar}\,|\langle k|V|i\rangle|^2\,\rho(E_k). \tag{9.37}$$

The expression for the transition per unit time is called the Fermi golden rule:

$$\frac{\mathrm{d}P^{(1)}_{i\to K}}{\mathrm{d}t} = \frac{2\pi}{\hbar}\,|\langle k|V|i\rangle|^2\,\rho(E_k). \tag{9.38}$$

So far, the transition probability $\mathrm{d}P/\mathrm{d}t$ per unit time has been calculated for a single system. If there are $\mathcal{N}$ similar systems present (for instance, $\mathcal{N}$ atoms), one cannot ascertain when a particular system will decay. If $\mathrm{d}P/\mathrm{d}t$ is time-independent

[3] The density of states is given in (7.21) for the free particle case. A similar procedure is carried out for photons in (9.60).

(as in (9.38)), the total rate of change is given by

$$\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}t} = -\mathcal{N}\frac{\mathrm{d}P}{\mathrm{d}t}. \tag{9.39}$$

Therefore,

$$\mathcal{N} = \mathcal{N}_0 \exp\left(-\frac{\mathrm{d}P}{\mathrm{d}t}t\right) = \mathcal{N}_0 \exp(-t/\tau), \qquad \tau = \left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)^{-1}. \tag{9.40}$$

The constant τ is called the mean lifetime. It is the time required for the reduction of the size of the population by a factor of $1/e$ and thus it is a measure of the the time Δt at which the decay takes place. The energy–time uncertainty relation is written in analogy[4] with (2.37)

$$\Delta t\, \Delta E \geq \hbar. \tag{9.41}$$

A short mean lifetime implies a broad peak, and vice versa.

9.6† The Heisenberg Picture

So far, the expectation value of an operator $\hat{Q}$ not depending explicitly on time only depends on the time evolution of the state vector (Sect. 9.1). There is an alternative description – the Heisenberg picture – in which the state vector is frozen at, for instance, $t = 0$, and the operator evolves as

$$\hat{Q}^{(H)}(t) = \hat{\mathcal{U}}^{+}(t)\, \hat{Q}^{(S)}\, \hat{\mathcal{U}}(t), \tag{9.42}$$

where the superscripts (H) and (S) stand for Heisenberg and Schrödinger, respectively. We can easily verify that both pictures yield the same expectation value of the operator

$$\langle\Psi(t)|Q^{(S)}|\Psi(t)\rangle = \langle\Psi(0)|\mathcal{U}^{+}(t)Q^{(S)}\mathcal{U}(t)|\Psi(0)\rangle = \langle\Psi(0)|Q^{(H)}|\Psi(0)\rangle. \tag{9.43}$$

The time derivative of the Heisenberg version of the operator yields

$$\begin{aligned}\frac{\mathrm{d}\,\hat{Q}^{(H)}}{\mathrm{d}\,t} &= \frac{\mathrm{d}\hat{\mathcal{U}}^{+}(t)}{\mathrm{d}\,t}\, \hat{Q}^{(S)}\hat{\mathcal{U}}(t) \;+\; \hat{\mathcal{U}}^{+}\, \hat{Q}^{(S)}\, \frac{\mathrm{d}\hat{\mathcal{U}}(t)}{\mathrm{d}\,t} \\ &= \frac{\mathrm{i}}{\hbar}\hat{\mathcal{U}}^{+}(t)\, \hat{H}\, \hat{Q}^{(S)}\hat{\mathcal{U}}(t) \;-\; \frac{\mathrm{i}}{\hbar}\hat{\mathcal{U}}^{+}\hat{Q}^{(S)}\hat{H}\hat{\mathcal{U}}(t) \\ &= -\frac{\mathrm{i}}{\hbar}\,[\hat{Q}^{(H)}, \hat{H}],\end{aligned} \tag{9.44}$$

where (9.7) has been used. This is the Heisenberg equation of motion.

[4] However, it has a different origin (see footnote 1).

9.7† Time-Reversal Symmetry

The quantum mechanical version of the time-reversal operation is characterized, in the case of one particle, by the transformation $\hat{\Theta}$ of the position, momentum and spin operators

$$\begin{aligned}\hat{x}_i' &= \hat{\Theta}\,\hat{x}_i\,\hat{\Theta}^{-1} = \hat{x}_i\,,\\ \hat{p}_i' &= \hat{\Theta}\,\hat{p}_i\,\hat{\Theta}^{-1} = -\hat{p}_i\,,\\ \hat{S}_i' &= \hat{\Theta}\,\hat{S}_i\,\hat{\Theta}^{-1} = -\hat{S}_i\,.\end{aligned} \tag{9.45}$$

Thus, the time-reversal operation should more appropriately be called motion-reversal. A Hamiltonian such as $\hat{P}^2/2M + V(x)$ is invariant under this transformation.

Since a unitary transformation preserves relations between operators, the time-reversal transformation cannot be unitary. For instance,

$$[\hat{x}_i\,,\,\hat{p}_i] = -[\hat{x}_i'\,,\,\hat{p}_i']. \tag{9.46}$$

It is possible, however, to write $\hat{\Theta}$ as a product of a unitary transformation $\hat{\mathcal{U}}_\tau$ times an operation $\hat{K}$ defined as the complex conjugation of all c-numbers. This is called an *antiunitary* transformation. Therefore,

$$\hat{\Theta}\,\varphi_i = \hat{\mathcal{U}}_\tau\,\hat{K}\,\varphi_i = \sum_{i'}\langle i'|i\rangle^*\,\hat{\mathcal{U}}_\tau\,\varphi_{i'}. \tag{9.47}$$

If $[\hat{\Theta}, \hat{H}] = 0$, the Hamiltonian eigenstates φ_i and $\hat{\Theta}\,\varphi_i$ correspond to the same eigenvalue E_i, no mater how complicated the potential may be. For instance, if the central potential is not spherically symmetric, the $2J + 1$ degeneracy disappears, but the levels still display the twofold *Kramers degeneracy* $(m, -m)$, due to the time-reversal symmetry.

The universal validity of the time-reversal invariance is still not a closed subject.

9.8† Quantum Electrodynamics for Newcomers

In Chap. 1, we stated that the most relevant manifestation of the crisis in physics that took place at the beginning of the twentieth century was the (classical) instability of the motion of an electron circling around the nucleus. To show that quantum mechanics does indeed solve this problem, we must use that beautiful extension of quantum mechanics called quantum electrodynamics. In the following we present a very brief introduction to QED.

We first consider the electromagnetic field in the absence of charges (light waves). A quadratic expression for the energy is obtained in terms of canonical variables. Subsequently, the theory is quantized by replacing such variables with operators satisfying the relation (2.15) (or an equivalent). In the next step, we consider the interaction between particles and the electromagnetic field. Finally, we solve the ensuing time-dependent problem applying perturbation theory.

9.8.1† *Classical Description of the Radiation Field*

In the absence of charges, the classical electromagnetic vector potential $\boldsymbol{A}(\boldsymbol{r},t)$ satisfies the equation

$$\nabla^2\boldsymbol{A} = \frac{1}{c^2}\frac{\partial^2\boldsymbol{A}}{\partial t^2}. \tag{9.48}$$

The vector $\boldsymbol{A}$ may be written as the sum of a transverse and a longitudinal component. The latter can be included within the particle Hamiltonian, since it is responsible for the Coulomb interaction and does not cause the radiation field. The transverse component $\boldsymbol{A}_t(\boldsymbol{r},t)$ satisfies the equation

$$\mathrm{div}\boldsymbol{A}_t = 0. \tag{9.49}$$

It may be expanded in terms of a complete, orthonormal set $\boldsymbol{A}_\lambda(\boldsymbol{r})$ of functions of the coordinates:

$$\boldsymbol{A}_t = \sum_\lambda c_\lambda(t)\boldsymbol{A}_\lambda, \tag{9.50}$$

$$\int_{L^3} \boldsymbol{A}_\lambda^*\boldsymbol{A}_{\lambda'}\mathrm{d}V = \delta_{\lambda,\lambda'}, \tag{9.51}$$

where we assume a large volume L^3 enclosing the field. Insertion of (9.50) in (9.48) and separation of variables yield the two equations

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}c_\lambda + \omega_\lambda^2 c_\lambda = 0, \tag{9.52}$$

$$\nabla^2\boldsymbol{A}_\lambda + \frac{\omega_\lambda^2}{c^2}\boldsymbol{A}_\lambda = 0, \tag{9.53}$$

where ω_λ is introduced as a separation constant. The solution to the oscillator equation (9.52) is

$$c_\lambda = \eta_\lambda \exp(-\mathrm{i}\omega_\lambda t), \tag{9.54}$$

with η_λ independent of time. A solution to (9.53) is given by the three-dimensional generalization (7.17) of (4.43). Periodic boundary conditions are assumed, so that

$$\boldsymbol{A}_\lambda = \frac{1}{L^{3/2}} \boldsymbol{v}_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}), \qquad k_{\lambda i} = 2\pi n_{\lambda i}/L. \tag{9.55}$$

There are two independent directions of polarization $\boldsymbol{v}_\lambda$, since (9.49) implies $\boldsymbol{v}_\lambda \cdot k_\lambda = 0$.

We construct the electric field

$$\boldsymbol{E} = -\frac{\partial}{\partial t}\boldsymbol{A}_t = \mathrm{i}\sum_\lambda \omega_\lambda c_\lambda \boldsymbol{A}_\lambda. \tag{9.56}$$

The total field energy is expressed as

$$\begin{aligned} U &= \frac{1}{2}\int_{L^3} \left(\epsilon_0 |\boldsymbol{E}|^2 + \mu_0 |\boldsymbol{B}|^2\right) \mathrm{d}V = \int_{L^3} \epsilon_0 |\boldsymbol{E}|^2 \mathrm{d}V \\ &= \epsilon_0 \sum_\lambda \omega_\lambda^2 c_\lambda^* c_\lambda \\ &= \sum_\lambda \hbar\omega_\lambda a_\lambda^* a_\lambda, \end{aligned} \tag{9.57}$$

where the substitution

$$c_\lambda = c\sqrt{\frac{\hbar}{\epsilon_0 \omega_\lambda}} a_\lambda$$

has been made. Note that since the vector field has dimension $\mathrm{k\,m\,s^{-1}\,C^{-1}}$, the amplitudes c_λ have dimension $\mathrm{k\,m^{5/2}\,s^{-1}\,C^{-1}}$ and the amplitudes a_λ are dimensionless.

9.8.2† Quantization of the Radiation Field

We have obtained an expression for the energy of the radiation field that is quadratic in the amplitudes a_λ^*, a_λ. Quantization is achieved by replacing these amplitudes by the creation and annihilation operators a_λ^+, a_λ, satisfying the commutation relations (3.31) and (7.58). We thus obtain the Hamiltonian[5]

$$\hat{H} = \sum_\lambda \hbar\omega_\lambda \, a_\lambda^+ a_\lambda \, . \tag{9.58}$$

[5] We ignore the ground state energy of the radiation field.

This Hamiltonian implies that:

- The radiation field is made up of an infinite number of oscillators. The state of the radiation field is described by all the occupation numbers n_λ.
- The oscillators are of the simple, boson, harmonic type introduced in (3.29) and used in Sects. 7.4.4† and 7.8†, if the quantum radiation field is in a stationary state without residual interactions.
- In agreement with Einstein's 1905 hypothesis, each oscillator has an energy which is a multiple of $\hbar\omega_\lambda$. The energy of the field is the sum of the energies of each oscillator.
- Since the radiation field is a function defined at all points of space and time, the number of canonical variables needed for its description is necessarily infinite. However, by enclosing the field within the volume L^3, we have succeeded in transforming this infinity into a denumerable infinity.
- In the absence of any interaction between particles and radiation field, vector states may be written as products of the two Hilbert subspaces, and the energy $E_{b,n_1,n_2,\ldots}$ is the sum of particle and radiation terms [see (7.1)]

$$\begin{aligned}\Psi_{b,n_1,n_2,\ldots} &= \varphi_b(\text{particles}) \times \Pi_\lambda \frac{1}{\sqrt{n_\lambda!}}(a_\lambda^+)^{n_\lambda}\varphi_0,\\ E_{b,n_1,n_2,\ldots} &= E_b + \sum_\lambda \hbar\omega_\lambda n_\lambda.\end{aligned} \tag{9.59}$$

- The number of states up to a certain energy $n(E_\lambda)$ and per unit interval of energy $\rho(E_\lambda)$ for each independent direction of polarization is[6]

$$n(E_\lambda) = \frac{L^3k_\lambda^3}{6\pi^2} = \frac{L^3E_\lambda^3}{6\pi^2\hbar^3c^3}, \qquad \rho(E_\lambda) = \frac{\partial n}{\partial E_\lambda} = \frac{L^3\omega_\lambda^2}{2\pi^2\hbar c^3}. \tag{9.60}$$

- The Hermitian, quantized, vector potential reads

$$\hat{\boldsymbol{A}}_t = \frac{1}{2}\sum_\lambda \sqrt{\frac{\hbar}{\epsilon_0 L^3\omega_\lambda}}\Big[a_\lambda \boldsymbol{v}_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda\cdot\boldsymbol{r}) + a_\lambda^+ \boldsymbol{v}_\lambda \exp(-\mathrm{i}\boldsymbol{k}_\lambda\cdot\boldsymbol{r})\Big]. \tag{9.61}$$

- We may be only interested in the polarization states of the photon, ignoring wavelength and direction of motion. A complete description of this system requires only two basis states, as in the case of spin. The analogous to the Stern–Gerlach device is a calcite crystal: a beam of monochromatic light passing through this crystal will produce two parallel emergent beams with the same

[6] These expressions have been derived using a similar procedure to the one used to obtain (7.21). A factor of 2, which was included in (7.21) due to spin, is not needed in (9.60). It reappears in (9.66), where the two directions of polarization are taken into account.

frequency and polarization axis perpendicular to each other. Most of the thought quantum experiments have become real laboratory experiments through the use of polarized photons.

9.8.3† *Interaction of Light with Particles*

In the presence of an electromagnetic field, the momentum $\hat{\boldsymbol{p}}$ of the particles[7] is replaced in the Hamiltonian by the effective momentum [53]

$$\hat{\boldsymbol{p}} \longrightarrow \hat{\boldsymbol{p}} - e\hat{\boldsymbol{A}}_t, \tag{9.62}$$

$$\frac{1}{2M}\hat{\boldsymbol{p}}^2 \longrightarrow \frac{1}{2M}\hat{\boldsymbol{p}}^2 + \hat{V} + \cdots, \qquad \hat{V} = \sqrt{\frac{\alpha 4\pi\epsilon_0\hbar c}{M^2}}\hat{\boldsymbol{A}}_t\cdot\hat{\boldsymbol{p}}. \tag{9.63}$$

The various ensuing processes may be classified according to the associated power of the fine structure constant α. The smallness of α (Table A.1) ensures the convergence of perturbation theory. The linear, lowest order processes require only the perturbation term $\hat{V}$. This causes transitions in the unperturbed system, particle + radiation, by changing the state of the particle and simultaneously increasing or decreasing the number of field quanta by one unit (emission or absorption processes, respectively).

We apply the perturbation theory developed in Sects. 9.4 and 9.5. Since the radiation field has a continuous spectrum, a transition probability per unit time (9.38) is obtained.

According to (9.61) and (9.63), the matrix elements of the perturbation read

$$\begin{aligned}\langle b(n_\lambda+1)|V|an_\lambda\rangle &= K_\lambda\sqrt{n_\lambda+1},\\ \langle b(n_\lambda-1)|V|an_\lambda\rangle &= K_\lambda\sqrt{n_\lambda},\end{aligned} \tag{9.64}$$

where K_λ is given by

$$\begin{aligned}K_\lambda &= \frac{\hbar}{M}\sqrt{\frac{\alpha\pi c}{L^3\omega_\lambda}}\langle b\,|(\boldsymbol{v}_\lambda\cdot p)\exp(\pm\mathrm{i}\boldsymbol{k}_\lambda\cdot r)|\,a\rangle\\ &\approx \frac{\hbar}{M}\sqrt{\frac{\alpha\pi c}{L^3\omega_\lambda}}\langle b|\boldsymbol{v}_\lambda\cdot p|a\rangle\\ &= \mathrm{i}\hbar\omega_\lambda\sqrt{\frac{\alpha\pi c}{L^3\omega_\lambda}}\langle b|\boldsymbol{v}_\lambda\cdot\boldsymbol{r}\,|a\rangle.\end{aligned} \tag{9.65}$$

[7] $[\hat{\mathbf{p}}, \hat{\mathbf{A}}_t] = 0$ because of (9.49).

We have neglected the exponential within the matrix element, on the basis of the estimate $\langle k_\lambda r\rangle \approx \omega_\lambda a_0/c = O(10^{-4})$, for $\hbar\omega_\lambda \approx 1\,\mathrm{eV}$. The third line is derived using the relation $\hat{p} = (\mathrm{i}M/\hbar)[\hat{H}, \hat{x}]$ (Problem 9 of Chap. 2).

We next work out the product appearing in the golden rule (9.38):

$$\begin{aligned}\frac{2\pi}{\hbar}|K_\lambda|^2\,\rho(E_\lambda) &= \frac{\alpha|\omega_\lambda|^3}{c^2}\,|\langle b|\boldsymbol{v}_\lambda\cdot\boldsymbol{r}|a\rangle|^2 \\ &\longrightarrow \frac{2\alpha|\omega_\lambda|^3}{3c^2}\,|\langle b|\boldsymbol{r}|a\rangle|^2\,, \end{aligned} \tag{9.66}$$

where we have summed over the two final polarization directions and averaged over them.

9.8.4† *Emission and Absorption of Radiation*

The transition probabilities per unit time are given by

$$\frac{\mathrm{d}P^{(1)}_{an_\lambda\to b(n_\lambda-1)}}{\mathrm{d}t} = \frac{2\alpha|\omega_\lambda|^3}{3c^2}\,|\langle b|\boldsymbol{r}|a\rangle|^2\,\bar{n}_\lambda, \tag{9.67}$$

$$\frac{\mathrm{d}P^{(1)}_{an_\lambda\to b(n_\lambda+1)}}{\mathrm{d}t} = \frac{2\alpha|\omega_\lambda|^3}{3c^2}\,|\langle b|\boldsymbol{r}|a\rangle|^2\,(\bar{n}_\lambda+1), \tag{9.68}$$

for absorption and emission processes, respectively. Here $\bar{n}_\lambda$ is the average number of photons of a given frequency (Fig. 9.3).

Fundamental consequences can be extracted from (9.67) and (9.68):

- The probability of absorbing a photon is proportional to the intensity of the radiation field present before the transition. This intensity is represented by $\bar{n}_\lambda$. This is to be expected. However, the probability of emission consists of two terms: the first one also depends on the intensity of the radiation field (induced emission); the second term, independent of the field intensity, allows the atom to decay from an excited state in vacuo (spontaneous emission).

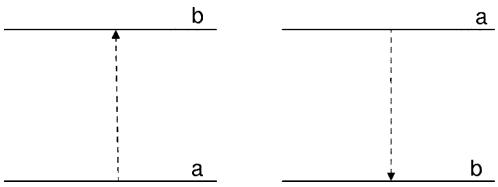

Fig. 9.3 The absorption process (9.67) (*left*) and the emission process (9.68) (*right*) of electromagnetic radiation. Labels **a**,**b** denote particle states

- The mean lifetime of the excited state φ_{210} in the hydrogen atom ($\hbar\omega = 10.2\,\text{eV}$) may be obtained[8] from (9.68) and (9.40). The result yields $\tau = 0.34 \times 10^{-9}$ s. Does this represent a short or a long time? In fact it is a long time, since this mean lifetime has to be compared with the period of the emitted radiation $\mathcal{T} = 2\pi/\omega = 0.41 \times 10^{-15}$ s. The mean lifetime is associated with a spread in energy of $1.23 \times 10^{-5}\,\text{eV}$, which is much smaller than the excitation energy. We can see now how effectively the great crisis of early twentieth century physics was resolved.
- The ratio $(\bar{n}_\lambda + 1)/\bar{n}_\lambda$ is needed to preserve the correct thermal equilibrium of the radiation with a gas: in a gas at temperature T, the number of atoms in the states a, b is given by $\exp(-E_a/k_\text{B}T)$ and $\exp(-E_b/k_\text{B}T)$, respectively. The condition for equilibrium is

$$P_\text{emission} \exp(-E_a/k_\text{B}T) = P_\text{absorption} \exp(-E_b/k_\text{B}T), \tag{9.69}$$

which yields

$$\bar{n}_\lambda = 1/\left[\exp(\hbar\omega_{ab}/k_\text{B}T) - 1\right]. \tag{9.70}$$

From this deduction of Planck's law, Einstein showed the need for spontaneous and induced emission in quantum theory [64].

9.8.5† *Selection Rules*

We now focus our attention on the particle matrix elements. The transition probabilities are also proportional to the squared modulus of the matrix elements $|\langle b|\boldsymbol{r}|a\rangle|^2$. Therefore, transition rates give information about the value of non-diagonal matrix elements. (Since Chap. 2, we know that diagonal matrix elements represent averages obtained in measurements of the eigenvalues of physical observables.)

Let l_b, π_b (l_a, π_a) be the orbital angular momentum and parity quantum numbers of the final (initial) state. Conservation of angular momentum requires the orbital angular momentum of the final state to equal the vector sum of the initial angular momentum and that of the radiation (see Sect. 5.3.1). The latter manifests itself through the operator $\hat{\boldsymbol{r}}$ in (9.68), which can be expressed as a sum of terms proportional to the spherical harmonics Y_{1m_l}. Therefore, the matrix elements must satisfy the selection rule $l_a + 1 \geq l_b \geq |l_a - 1|$ (5.33), or $\Delta l = 0, \pm 1$.

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[8] An order of magnitude of τ may be obtained by equating the rate of radiation of an oscillating classical dipole with the ratio between the emitted energy $\hbar\omega$ and the mean lifetime

$$\frac{\omega^4 D_0}{3c^2} = \frac{\hbar\omega}{\tau} \longrightarrow \tau = \frac{3\hbar c^2}{\omega^3 D_0}.$$

The amplitude of the dipole oscillation is approximated by $D_0 \approx -ea_0$. If the transition energy is assumed to be 10 eV, we obtain an estimated value $\tau = O(10^{-10}\ \text{s})$.

Since the operator $\boldsymbol{r}$ is odd under the parity operation (5.12), the non-vanishing of this matrix element also requires the initial and final states to carry a different parity, $\pi_a \pi_b = -1$. The combination of the conservation rules associated with orbital angular momentum and parity is condensed in the selection rule

$$\Delta l = \pm 1, \tag{9.71}$$

which defines allowed transitions (see, for instance, Fig. 8.4).

Forbidden (i.e. non-allowed) transitions may also occur, but are much weaker than the allowed ones. Their relative intensity may be estimated on the basis of the expectation value of the neglected terms in (9.65).

Let us now consider the final (initial) angular momentum j_b (j_a) with projection m_b (m_a)

$$\begin{aligned}\frac{3}{4\pi}|\langle j_b m_b|\mathbf{r}|j_a m_a\rangle|^2 &= \sum_\mu |\langle j_b m_b|r\, Y_{1\mu}|j_a m_a\rangle|^2 \\ &= \frac{1}{2j_b+1}|\langle j_b||r\, Y_1||j_a\rangle|^2 \sum_\mu c\big(j_a m_a; 1\mu; j_b m_b\big)^2 \\ &= \frac{1}{2j_a+1}|\langle j_b||r\, Y_1||j_a\rangle|^2 \sum_\mu c\big(j_b(-m_b); 1\mu; j_a(-m_a)\big)^2,\end{aligned} \tag{9.72}$$

where we have successively applied (5.65), the definition (5.49) of the reduced matrix element and the last one of equations (5.34). In general we must sum over all possible final projections m_b. If this is the case, the first of equations (5.36) yields

$$\sum_{m_b} |\langle j_b m_b|\mathbf{r}|j_a m_a\rangle|^2 = \frac{4\pi}{3}\frac{|\langle j_b||r\, Y_1||j_a\rangle|^2}{2j_a+1}, \tag{9.73}$$

which is independent of the initial projection m_a and of other geometrical terms (such as Wigner coefficients).

9.8.6† Lasers and Masers

The first material used to produce laser light[9] was ruby [65]. The ions undergoing laser transitions are Cr^{3+}, an impurity in the Al_2O_3 crystal.

[9]Laser, light amplification by stimulated emission of radiation; maser, microwave amplification by stimulated emission of radiation. These two devices differ in the range of electromagnetic frequency in which they operate.

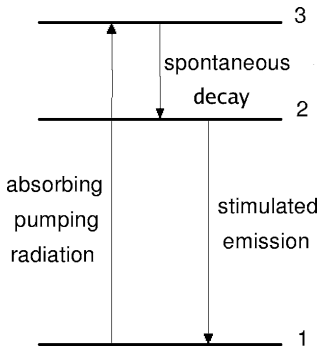

Fig. 9.4 Schematic representation of the levels of a ruby laser

Figure 9.4 schematizes the three relevant levels of Cr. At room temperature the population of state 2 is much smaller than that of state 1, since $E_2 - E_1 \gg kT$ (see Sect. 7.7†). A population inversion is achieved by means of auxiliary radiation (pumping radiation) exciting many atoms into higher energy states 3 (actually into two excited bands), from which they spontaneously decay into the state 2 (or back to 1) within 10^{-7} s. Since the spontaneous lifetime of state 2 is rather large (10^{-3} s), a considerable fraction of the population of state 1 is transferred to state 2 ($\geq 1/2$).

Some of the photons spontaneously emitted in the decay of state 2 are reflected back and forth between a completely reflecting and a partially reflecting surface of the crystal. Thus a standing electromagnetic wave is built. Its intensity increases very rapidly through induced emission of further photons, simultaneously with the depopulation of state 2. A pulse of laser light crosses over the partially reflecting surface. The main characteristics of this emitted light are:

- Extreme monochromaticity.
- Large power per unit area of cross section (more than 10^9 times the one obtained from conventional light sources).
- Extreme coherence. The phase of the light emitted from one atom is related to that from each other atom. As a consequence, the phase difference between the laser light beam will stay constant at two different points (the points may be separated as much as 100 km). On the contrary, light spontaneously emitted is incoherent.

Laser light is playing an ever increasing role in many scientific and technological applications: precise determinations of length and time, CD players and readers, non-linear optics, hot fusion, etc. In communications, laser light allows to transport 10^{12} information units per second through a single optical fiber across the oceans.

Problems

Problem 1. At $t = 0$, a state is given by the linear combination of the two lowest states of a linear, infinite square well potential of width a :

$$\Psi(t=0) = \frac{1}{\sqrt{3}}\varphi_1 - \mathrm{i}\sqrt{\frac{2}{3}}\varphi_2.$$

1. Write the wave function at time t.
2. Calculate the probability of finding the particle in the second half of the well.

Problem 2. Use the time-dependent Schrödinger equation to show that Newton's second law is obeyed on average in quantum mechanics (Ehrenfest theorem). Hint: calculate

$$\frac{\mathrm{d}\langle\Psi(t)|p|\Psi(t)\rangle}{\mathrm{d}t},$$

as in (4.15).

Problem 3. In the state (9.15), calculate the amplitude of the eigenstate of the operator $\hat{S}_y$, with spin pointing in the positive direction.

Problem 4. Write the evolution operator for a Hamiltonian $-\boldsymbol{\mu}\cdot\boldsymbol{B}$ if the magnetic field points to the same direction as vector $\mathbf{n}$ ($|\mathbf{n}| = 1$).

Problem 5. A particle is in the ground state of an infinite linear square well potential. What is the probability of finding it in the $n = 1, 2, 3$ states when the wall separation is suddenly doubled by displacing the right wall?

Problem 6. Calculate the probability of a spin flip in the first order of perturbation theory. Assume the Hamiltonian (9.18) and $|\omega'/(\omega - \omega_{\mathrm{L}})| \ll 1$. Compare with the exact result (9.22).

Problem 7. A particle in the ground state of a linear harmonic oscillator interacts with a projectile through an interaction of the form $V_0\delta(u - vt/x_{\mathrm{c}})$.

1. Express the amplitude for the transition to the first excited state as an integral over the time interval $t_1 \le t \le t_2$.
2. Calculate the probability of this transition for $t_1 = -\infty$, $t_2 = \infty$.

Problem 8. The Hamiltonian

$$\hat{V}(t) = \frac{V_0}{\hbar^2}\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2\cos(\omega t)$$

acts on a two-spin system. Find the time-dependent solution if:

1. The system has $m_s = 0$.
   Hint: try $\Psi(t) = \cos\theta\exp(\mathrm{i}\phi)\chi_0^1 + \sin\theta\exp(-\mathrm{i}3\phi)\chi_0^0$.
2. The system is in the Bell state $\Psi_{B_0} = \frac{1}{\sqrt{2}}\left[\varphi_\uparrow(1)\varphi_\uparrow(2) + \varphi_\downarrow(1)\varphi_\downarrow(2)\right]$.

Problem 9. What is the probability of exciting a linear harmonic oscillator from the ground state to the first excited state, assuming that a perturbation $V = Kx$, acting for an interval t, is added to the oscillator Hamiltonian?

Problem 10. 1. Obtain the expression for the second-order amplitudes $c_k^{(2)}(t)$ if the perturbation is constant in time.
2. Calculate the probability of a transition to the second excited state for the same case as in Problem 9.

Problem 11. 1. Interpret the ratio $2\Delta E\, \Delta l/\hbar c$, where Δl is the length of the system.
2. Calculate this ratio for the "giant resonance" ($\Delta E \approx 4\,\text{MeV}$) and for a slow neutron resonance ($\Delta E \approx 0.1\,\text{eV}$) in the case of a nucleus with $A \approx 100$. (See Problem 7, Chap. 6).
3. Do the same for a meson with a spread of 200 MeV (proton size $\approx 10^{-17}$ m).

Problem 12. Calculate the ratio between the populations of the states φ_{210} and φ_{310} if hydrogen atoms in their ground state are illuminated with white light.

Problem 13. 1. Calculate the ratio between the intensities of photons de-exciting the state φ_{310} of the hydrogen atom.
2. Calculate the mean lifetime of this state.
3. Calculate the width of this state.

Problem 14. Consider the transition $\varphi_{n,l=n-1} \to \varphi_{n-1,n-2}$ via the dipole operator $Q_{1\mu} = \sqrt{\frac{4\pi}{3}}\, rY_{1\mu}$ in a Rydberg atom. In the limit of large n, obtain

1. The reduced matrix element for the transition.
2. The mean lifetime τ for the $(n, n-1 \to n-1, n-2)$ transition.
3. The ratio between this lifetime and $\tau(2, 1 \to 1, 0)$.