neutrinos, which have spin $s = 1/2$) are fermions, as are the *baryons* (such as the proton and the neutron, which have spin $s = 1/2$, and the hyperons). A composite particle, such as an atom, is a boson if the sum of its protons, neutrons and electrons is an even number; it is a fermion if this sum is an odd number.

If a system is composed of different kinds of bosons (fermions), then its wave function must be separately totally symmetric (antisymmetric) with respect to permutations of each kind of identical particle. For example, the wave function of an alpha particle (that is, a ${}^4$He nucleus which contains two protons and two neutrons) must be antisymmetric under the interchange of the two protons and also antisymmetric under the interchange of the two neutrons. It should be noted, however, that in some physical situations one can ignore the possible composite structure of particles. For example, in studying the scattering of two alpha particles at low energies (where the effect of nuclear forces is negligible), the symmetrisation process must be accomplished only with respect to the permutation of the two alpha particles, each of them being considered as a spin zero boson [8]. Similarly, in studying the properties of atomic gases at low temperature, one can treat the atoms as 'elementary' bosons or fermions.

## 2.8 Approximation methods

As in the case of classical mechanics, there are relatively few physically interesting problems in quantum mechanics which can be solved exactly. Approximation methods are therefore of great importance in discussing the application of quantum theory to specific systems, such as the atomic and molecular ones considered in this book. In this section we shall review several approximation methods which will be used in further chapters.

### Time-independent perturbation theory

Perturbation theory deals with the changes induced in a system by a 'small' disturbance. Although we shall also apply perturbation methods to scattering problems at a later stage (see Chapters 12–14) we shall start here by discussing the *Rayleigh–Schrödinger perturbation theory*, which is concerned with the modifications in the *discrete* energy levels and corresponding eigenfunctions of a system when a perturbation is applied.

Let us assume that the time-independent Hamiltonian $H$ of a system may be separated into two parts,

$$H = H_0 + \lambda H' \tag{2.296}$$

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[8] On the other hand, if one wants to study the scattering of two alpha particles at high energies (where nuclear forces are important), the symmetrisation of the total wave function must be performed separately with respect to the constituent protons and neutrons.

where the 'unperturbed' Hamiltonian $H_0$ is sufficiently simple so that the corresponding Schrödinger eigenvalue equation

$$H_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)} \tag{2.297}$$

may be solved, and the term $\lambda H'$ is a small perturbation. The parameter $\lambda$ will be used below to distinguish between the various orders of the perturbation calculation; we shall take $\lambda = 1$ for the actual physical problem. We assume that the (known) eigenfunctions $\psi_k^{(0)}$ corresponding to the (known) eigenvalues $E_k^{(0)}$ of $H_0$ form a complete orthonormal set (which may be partly continuous). Thus, if $\psi_i^{(0)}$ and $\psi_j^{(0)}$ are two members of that set, we have

$$\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij} \quad \text{or} \quad \delta(i-j) \tag{2.298}$$

where the symbol $\delta(i-j)$ should be used when both $\psi_i^{(0)}$ and $\psi_j^{(0)}$ correspond to continuous states. In what follows we shall simplify the notation by extending the meaning of $\delta_{ij}$ to cover both possibilities in (2.298). The eigenvalue problem which we want to solve is

$$H \psi_k = E_k \psi_k \tag{2.299}$$

where we have used the notation $E_k$ and $\psi_k$ to denote the perturbed energy levels and eigenfunctions, respectively.

### Non-degenerate case

Let us focus our attention on a particular unperturbed, discrete energy level $E_k^{(0)}$, which we assume to be *non-degenerate*. We suppose that the effect of the perturbation $\lambda H'$ is small enough so that the perturbed energy level $E_k$ is much closer to $E_k^{(0)}$ than to any other unperturbed level. It is then reasonable to expand both $\psi_k$ and $E_k$ in powers of $\lambda$, namely

$$\psi_k = \sum_{n=0}^{\infty} \lambda^n \psi_k^{(n)} \tag{2.300}$$

and

$$E_k = \sum_{n=0}^{\infty} \lambda^n E_k^{(n)} \tag{2.301}$$

where the index $n$ refers to the order of the perturbation. Substituting the expansions (2.300) and (2.301) in (2.299), and using (2.296), we have

$$(H_0 + \lambda H')(\psi_k^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots)$$
$$= (E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots)(\psi_k^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots) \tag{2.302}$$

Let us now equate the coefficients of equal powers of $\lambda$. Beginning with $\lambda^0$, we see that

$$H_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)} \tag{2.303}$$

as expected. The coefficient of $\lambda$ then gives

$$H_0\psi_k^{(1)} + H'\psi_k^{(0)} = E_k^{(0)}\psi_k^{(1)} + E_k^{(1)}\psi_k^{(0)} \tag{2.304}$$

while that of $\lambda^2$ yields

$$H_0\psi_k^{(2)} + H'\psi_k^{(1)} = E_k^{(0)}\psi_k^{(2)} + E_k^{(1)}\psi_k^{(1)} + E_k^{(2)}\psi_k^{(0)} \tag{2.305}$$

and so on.

In order to obtain the first energy correction $E_k^{(1)}$, we premultiply (2.304) by $\psi_k^{(0)*}$ and integrate over all space. This gives

$$\langle\psi_k^{(0)}|H_0 - E_k^{(0)}|\psi_k^{(1)}\rangle + \langle\psi_k^{(0)}|H' - E_k^{(1)}|\psi_k^{(0)}\rangle = 0 \tag{2.306}$$

Now, using (2.297) and the fact that the operator $H_0$ is Hermitian, we have

$$\begin{aligned}\langle\psi_k^{(0)}|H_0|\psi_k^{(1)}\rangle &= \langle H_0\psi_k^{(0)}|\psi_k^{(1)}\rangle \\ &= E_k^{(0)}\langle\psi_k^{(0)}|\psi_k^{(1)}\rangle\end{aligned} \tag{2.307}$$

so that the first term on the left of (2.306) vanishes. Moreover, since $\langle\psi_k^{(0)}|\psi_k^{(0)}\rangle = 1$, we see that (2.306) reduces to

$$E_k^{(1)} = \langle\psi_k^{(0)}|H'|\psi_k^{(0)}\rangle \equiv H'_{kk} \tag{2.308}$$

This important result tells us that the first-order correction to the energy for a non-degenerate level is just the expectation value of the perturbation $H'$ with respect to the corresponding unperturbed state of the system.

Proceeding in a similar way with equation (2.305), we have

$$\langle\psi_k^{(0)}|H_0 - E_k^{(0)}|\psi_k^{(2)}\rangle + \langle\psi_k^{(0)}|H' - E_k^{(1)}|\psi_k^{(1)}\rangle - E_k^{(2)}\langle\psi_k^{(0)}|\psi_k^{(0)}\rangle = 0 \tag{2.309}$$

and therefore

$$E_k^{(2)} = \langle\psi_k^{(0)}|H' - E_k^{(1)}|\psi_k^{(1)}\rangle \tag{2.310}$$

An equivalent expression for $E_k^{(2)}$ may be obtained by starting from (2.304), and is given (Problem 2.19) by

$$E_k^{(2)} = -\langle\psi_k^{(1)}|H_0 - E_k^{(0)}|\psi_k^{(1)}\rangle \tag{2.311}$$

Expressions for higher order corrections $E_k^{(n)}$, $n \geqslant 3$, can be obtained in a similar way. For example, one has (Problem 2.19)

$$E_k^{(3)} = \langle\psi_k^{(1)}|H' - E_k^{(1)}|\psi_k^{(1)}\rangle - 2E_k^{(2)}\langle\psi_k^{(0)}|\psi_k^{(1)}\rangle \tag{2.312}$$

Let us now return to (2.304). The Rayleigh–Schrödinger method attempts to obtain the solution $\psi_k^{(1)}$ of that equation in the following way. First, the 'unperturbed' equation (2.297) is solved for all eigenvalues and eigenfunctions (including those belonging to the continuous part of the spectrum, if one exists). The unknown function $\psi_k^{(1)}$ is then expanded in the basis set of the unperturbed eigenfunctions. That is,

$$\psi_k^{(1)} = \sum_m a_m^{(1)}\psi_m^{(0)} \tag{2.313}$$

where the sum over $m$ means a summation over the discrete part of the set and an integration over its continuous part. Substituting (2.313) into (2.304), we obtain

$$(H_0 - E_k^{(0)}) \sum_m a_m^{(1)} \psi_m^{(0)} + (H' - E_k^{(1)}) \psi_k^{(0)} = 0 \tag{2.314}$$

Premultiplying by $\psi_l^{(0)*}$, integrating over all space and using the fact that $H_0 \psi_l^{(0)} = E_l^{(0)} \psi_l^{(0)}$ and $\langle \psi_l^{(0)} | \psi_k^{(0)} \rangle = \delta_{kl}$, we find that

$$a_l^{(1)}(E_l^{(0)} - E_k^{(0)}) + \langle \psi_l^{(0)} | H' | \psi_k^{(0)} \rangle - E_k^{(1)} \delta_{kl} = 0 \tag{2.315}$$

For $l = k$ this reduces to our basic result (2.308). On the other hand, for $l \neq k$ we have

$$a_l^{(1)} = \frac{H'_{lk}}{E_k^{(0)} - E_l^{(0)}}, \qquad l \neq k \tag{2.316}$$

where we have set $H'_{lk} \equiv \langle \psi_l^{(0)} | H' | \psi_k^{(0)} \rangle$. We note that the equation (2.304) does not determine the coefficient $a_k^{(1)}$, which is the 'component' of $\psi_k^{(1)}$ along $\psi_k^{(0)}$. We can thus require without loss of generality that

$$a_k^{(1)} = \langle \psi_k^{(0)} | \psi_k^{(1)} \rangle = 0 \tag{2.317}$$

and rewrite (2.313) as

$$\psi_k^{(1)} = \sum_{m \neq k} a_m^{(1)} \psi_m^{(0)}$$

$$= \sum_{m \neq k} \frac{H'_{mk}}{E_k^{(0)} - E_m^{(0)}} \psi_m^{(0)} \tag{2.318}$$

Substituting this result in (2.310) we obtain

$$E_k^{(2)} = \sum_{m \neq k} \frac{H'_{km} H'_{mk}}{E_k^{(0)} - E_m^{(0)}} = \sum_{m \neq k} \frac{|H'_{mk}|^2}{E_k^{(0)} - E_m^{(0)}} \tag{2.319}$$

The third-order correction $E_k^{(3)}$ may be obtained in a similar way from (2.312) and (2.318).

### Degenerate case

Thus far we have assumed that the perturbed eigenfunction $\psi_k$ differs slightly from a given function $\psi_k^{(0)}$, the solution of the 'unperturbed' equation (2.297). When the level $E_k^{(0)}$ is $\alpha$-fold degenerate, there are *several* 'unperturbed' wave functions $\psi_{kr}^{(0)}(r = 1, 2, \ldots, \alpha)$ corresponding to this level and we do not know *a priori* to which functions the perturbed eigenfunctions tend when $\lambda \to 0$. This means that the above treatment – and in particular the basic expansion (2.300) – must be modified to deal with the degenerate case.

The $\alpha$ unperturbed wave functions $\psi_{kr}^{(0)}$ corresponding to the level $E_k^{(0)}$ are orthogonal to the unperturbed wave functions $\psi_l^{(0)}$ corresponding to *other* energy levels $E_l^{(0)} \neq E_k^{(0)}$. Although they need not be orthogonal among themselves, it is always possible to construct from linear combinations of them a new set of $\alpha$ unperturbed wave functions which are mutually orthogonal and normalised to unity. We may therefore assume without loss of generality that this has already been done, so that

$$\langle \psi_{kr}^{(0)} | \psi_{ks}^{(0)} \rangle = \delta_{rs} \qquad (r, s = 1, 2, \ldots, \alpha) \tag{2.320}$$

Let us now introduce the correct zero-order functions $\chi_{kr}^{(0)}$ which yield the first term in the expansion of the exact wave function $\psi_{kr}$ in powers of $\lambda$. That is,

$$\psi_{kr} = \chi_{kr}^{(0)} + \lambda \psi_{kr}^{(1)} + \lambda^2 \psi_{kr}^{(2)} + \ldots \tag{2.321}$$

We shall also write the perturbed energy $E_{kr}$ as

$$E_{kr} = E_k^{(0)} + \lambda E_{kr}^{(1)} + \lambda^2 E_{kr}^{(2)} + \ldots \tag{2.322}$$

with $E_k^{(0)} \equiv E_{kr}^{(0)}$ $(r = 1, 2, \ldots, \alpha)$ since the level $E_k^{(0)}$ is $\alpha$-fold degenerate. Using the above expansions in (2.299) and equating the coefficients of $\lambda$ we find that

$$H_0 \psi_{kr}^{(1)} + H' \chi_{kr}^{(0)} = E_k^{(0)} \psi_{kr}^{(1)} + E_{kr}^{(1)} \chi_{kr}^{(0)} \tag{2.323}$$

Since the functions $\chi_{kr}^{(0)}$ are linear combinations of the unperturbed wave functions $\psi_{kr}^{(0)}$, we may write

$$\chi_{kr}^{(0)} = \sum_{s=1}^{\alpha} c_{rs} \psi_{ks}^{(0)} \qquad (r = 1, 2, \ldots, \alpha) \tag{2.324}$$

where the coefficients $c_{rs}$ are to be determined. Similarly, expanding $\psi_{kr}^{(1)}$ in the basis set of the unperturbed wave functions, we have

$$\psi_{kr}^{(1)} = \sum_m \sum_s a_{kr,ms}^{(1)} \psi_{ms}^{(0)} \tag{2.325}$$

where the indices $r$ and $s$ refer explicitly to the degeneracy. Substituting the above expressions of $\chi_{kr}^{(0)}$ and $\psi_{kr}^{(1)}$ in (2.323) and using the fact that $H_0 \psi_{ms}^{(0)} = E_m^{(0)} \psi_{ms}^{(0)}$, we find that

$$\sum_m \sum_s a_{kr,ms}^{(1)} (E_m^{(0)} - E_k^{(0)}) \psi_{ms}^{(0)} + \sum_s c_{rs} (H' - E_{kr}^{(1)}) \psi_{ks}^{(0)} = 0 \tag{2.326}$$

Premultiplying by $\psi_{ku}^{(0)*}$ and integrating over all space, we obtain

$$\sum_m \sum_s a_{kr,ms}^{(1)} (E_m^{(0)} - E_k^{(0)}) \langle \psi_{ku}^{(0)} | \psi_{ms}^{(0)} \rangle + \sum_s c_{rs} [\langle \psi_{ku}^{(0)} | H' | \psi_{ks}^{(0)} \rangle - E_{kr}^{(1)} \delta_{us}] = 0$$

$$(u = 1, 2, \ldots, \alpha) \tag{2.327}$$

where we have used (2.320). Since $\langle \psi_{ku}^{(0)} | \psi_{ms}^{(0)} \rangle = 0$ when $k \neq m$ and $E_k^{(0)} = E_m^{(0)}$ if $k = m$, we see that (2.327) reduces to

$$\sum_{s=1}^{\alpha} c_{rs}[\langle \psi_{ku}^{(0)}|H'|\psi_{ks}^{(0)}\rangle - E_{kr}^{(1)}\delta_{us}] = 0 \qquad (u = 1, 2, \ldots, \alpha) \tag{2.328}$$

This is a linear, homogeneous system of equations for the $\alpha$ unknown quantities $c_{r1}, c_{r2}, \ldots, c_{r\alpha}$. A non-trivial solution is obtained if the determinant of the quantity in square brackets vanishes,

$$\det |\langle \psi_{ku}^{(0)}|H'|\psi_{ks}^{(0)}\rangle - E_{kr}^{(1)}\delta_{us}| = 0 \qquad (s, u = 1, 2, \ldots, \alpha) \tag{2.329}$$

This equation yields $\alpha$ real roots $E_{k1}^{(1)}, E_{k2}^{(1)}, \ldots, E_{k\alpha}^{(1)}$. If all of these roots are *distinct* the degeneracy is *completely removed* to first order in the perturbation. On the other hand, if some or all roots of (2.329) are identical the degeneracy is only *partially* (or *not at all*) removed. The residual degeneracy may then either be removed in higher order of perturbation theory, or persist to all orders. The latter case occurs when the operators $H_0$ and $H$ share symmetry properties.

For a given value of $r$, the coefficients $c_{rs}$ ($s = 1, 2, \ldots, \alpha$) which determine the 'correct' unperturbed zero-order wave functions $\chi_{kr}^{(0)}$ via (2.324) may be obtained by substituting the value of $E_{kr}^{(1)}$ in the system (2.328) and solving for the coefficients $c_{r1}, c_{r2}, \ldots, c_{r\alpha}$ in terms of one of them. The last coefficient is then obtained (up to a phase factor) by requiring the function $\chi_{kr}^{(0)}$ to be normalised to unity. It is clear that this procedure does not lead to a unique result when two or more roots $E_{kr}^{(1)}$ of equation (2.329) coincide, since in this case the degeneracy is not fully removed.

### Time-dependent perturbation theory

We shall now discuss the perturbation theory for a system whose total Hamiltonian $H$ may be split as

$$H = H_0 + \lambda H'(t) \tag{2.330}$$

where the unperturbed Hamiltonian $H_0$ is time-independent and $\lambda H'(t)$ is a small *time-dependent* perturbation. The method which we outline below is known as *Dirac's method of variation of constants*.

Let us suppose that we know the eigenvalues $E_k^{(0)}$ of the unperturbed Hamiltonian $H_0$, together with the corresponding stationary eigenfunctions $\psi_k^{(0)}$, which we assume to be orthonormal and to form a complete set. Thus, since $H_0\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}$, the general solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi_0}{\partial t} = H_0\Psi_0 \tag{2.331}$$

is given by

$$\Psi_0 = \sum_k c_k^{(0)} \psi_k^{(0)} \exp(-iE_k^{(0)}t/\hbar) \tag{2.332}$$

where the coefficients $c_k^{(0)}$ are *constants* and the sum is over the entire set of eigenfunctions $\psi_k^{(0)}$. Because the functions $\psi_k^{(0)}$ form a complete set, the general solution $\Psi$ of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \tag{2.333}$$

can be expanded as

$$\Psi = \sum_k c_k(t)\psi_k^{(0)} \exp(-iE_k^{(0)}t/\hbar) \tag{2.334}$$

where the unknown coefficients $c_k(t)$ clearly *depend on the time*. Since the wave functions $\psi_k^{(0)}$ are orthonormal, and provided $\Psi$ is normalised to unity, we can interpret the quantity $|c_k(t)|^2$ as the probability of finding the system in the state labelled $k$ at the time $t$, and $c_k(t)$ as the corresponding probability amplitude. Upon comparison of (2.332) and (2.334) we see that if $H'(t) = 0$ the coefficients $c_k(t)$ reduce to the constants $c_k^{(0)}$ which are therefore the *initial values* of the $c_k$. Thus, as we expect from (2.332) the quantity $|c_k^{(0)}|^2$ gives the probability of finding the system in the stationary state $\psi_k^{(0)}$ before the perturbation is applied.

To find equations for the coefficients $c_k(t)$ the expansion (2.334) is inserted into the Schrödinger equation (2.333). From (2.330) and the fact that $H_0\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}$, we then have

$$i\hbar \sum_k \dot{c}_k(t)\psi_k^{(0)} \exp(-iE_k^{(0)}t/\hbar) = \sum_k c_k(t)\lambda H'(t)\psi_k^{(0)} \exp(-iE_k^{(0)}t/\hbar) \tag{2.335}$$

where the dot indicates a derivative with respect to the time. Taking the scalar product with a particular function $\psi_b^{(0)}$ belonging to the set $\{\psi_k^{(0)}\}$ and using the fact that $\langle \psi_b^{(0)} | \psi_k^{(0)} \rangle = \delta_{bk}$, we then find from (2.335) the set of coupled equations

$$\dot{c}_b(t) = (i\hbar)^{-1} \sum_k \lambda H'_{bk}(t) c_k(t) \exp(i\omega_{bk}t) \tag{2.336}$$

where

$$H'_{bk}(t) = \langle \psi_b^{(0)} | H'(t) | \psi_k^{(0)} \rangle \tag{2.337}$$

and where the *Bohr angular frequency* $\omega_{bk}$ is defined by

$$\omega_{bk} = \frac{E_b^{(0)} - E_k^{(0)}}{\hbar} \tag{2.338}$$

The system of coupled differential equations (2.336) is completely equivalent to the original time-dependent Schrödinger equation (2.333), and no approximation has been made thus far. However, if the perturbation $\lambda H'$ is weak, we can expand the coefficients $c_k$ in powers of the parameter $\lambda$ as

$$c_k = c_k^{(0)} + \lambda c_k^{(1)} + \lambda^2 c_k^{(2)} + \dots \tag{2.339}$$

Substituting this expansion into the system (2.336) and equating the coefficients of equal powers of $\lambda$, we find that

$$\dot{c}_b^{(0)} = 0 \tag{2.340a}$$

$$\dot{c}_b^{(1)} = (i\hbar)^{-1} \sum_k H_{bk}'(t) \exp(i\omega_{bk}t) c_k^{(0)} \tag{2.340b}$$

$$\vdots \quad \vdots \quad \vdots$$

$$\dot{c}_b^{(s+1)} = (i\hbar)^{-1} \sum_k H_{bk}'(t) \exp(i\omega_{bk}t) c_k^{(s)}, \qquad s = 0, 1, \dots \tag{2.340c}$$

Thus the original system (2.336) has been decoupled in such a way that the equations (2.340) can now in principle be integrated successively to any given order.

The first equation (2.340a) simply confirms that the coefficients $c_k^{(0)}$ are time-independent. As we have seen above, the constants $c_k^{(0)}$ define the initial conditions of the problem. In what follows, we shall assume for the sake of simplicity that the system is initially (that is, for $t \leqslant t_0$) in a well-defined stationary state $\psi_a^{(0)}$ of energy $E_a^{(0)}$. Thus

$$c_k^{(0)} = \begin{cases} \delta_{ka} & \text{for discrete states} \\ \delta(k-a) & \text{for continuous states.} \end{cases} \tag{2.341}$$

We note that this statement is not in contradiction with the uncertainty relation $\Delta E \, \Delta t \gtrsim \hbar$ since we have essentially an 'infinite' amount of time available to prepare our initial state. Upon substitution of (2.341) into (2.340b) we then have

$$\dot{c}_b^{(1)}(t) = (i\hbar)^{-1} H_{ba}'(t) \exp(i\omega_{ba}t) \tag{2.342}$$

where $\omega_{ba} = (E_b^{(0)} - E_a^{(0)})/\hbar$. The solution of these first-order equations is

$$c_a^{(1)}(t) = (i\hbar)^{-1} \int_{t_0}^{t} H_{aa}'(t') \, \mathrm{d}t' \tag{2.343a}$$

for $b = a$, while for $b \neq a$ one has

$$c_b^{(1)}(t) = (i\hbar)^{-1} \int_{t_0}^{t} H_{ba}'(t') \exp(i\omega_{ba}t') \, \mathrm{d}t', \qquad b \neq a \tag{2.343b}$$

where the integration constant has been chosen in such a way that $c_a^{(1)}(t)$ and $c_b^{(1)}(t)$ vanish at $t = t_0$, before the perturbation is applied. To first order in the perturbation, the *transition probability* corresponding to the transition $a \to b$ is therefore given by

$$P_{ba}^{(1)}(t) = |c_b^{(1)}(t)|^2 = \hbar^{-2} \left| \int_{t_0}^{t} H_{ba}'(t') \exp(i\omega_{ba}t') \, \mathrm{d}t' \right|^2, \qquad b \neq a \tag{2.344}$$

It is also worth noting that for $t > t_0$ the coefficient $c_a$ of the state $a$ is given to first order in the perturbation by

$$c_a(t) \simeq c_a^{(0)} + c_a^{(1)}(t)$$

$$\simeq 1 + (i\hbar)^{-1} \int_{t_0}^t H'_{aa}(t')dt'$$

$$\simeq \exp\left[-\frac{i}{\hbar} \int_{t_0}^t H'_{aa}(t')\,dt'\right] \tag{2.345}$$

so that $|c_a(t)|^2 \simeq 1$ and the main effect of the perturbation on the initial state is to change its phase.

### Time-independent perturbation

The results (2.343) take a particularly simple form if the perturbation $H'$ is independent of time, except for being switched on suddenly at a given time (say $t_0 = 0$). We then have

$$c_a^{(1)}(t) = (i\hbar)^{-1}H'_{aa}t \tag{2.346a}$$

and

$$c_b^{(1)}(t) = \frac{H'_{ba}}{\hbar\omega_{ba}}[1 - \exp(i\omega_{ba}t)], \qquad b \neq a \tag{2.346b}$$

Note that if the perturbation is switched off at time $t$, the above amplitudes are also those at any subsequent time $t_1 > t$. The first-order transition probability from state $a$ to state $b \neq a$ is given by

$$P_{ba}^{(1)}(t) = |c_b^{(1)}(t)|^2 = \frac{2}{\hbar^2}|H'_{ba}|^2 F(t, \omega_{ba}) \tag{2.347}$$

where

$$F(t, \omega) = \frac{1 - \cos\omega t}{\omega^2} = \frac{2\sin^2(\omega t/2)}{\omega^2} \tag{2.348}$$

The function $F(t, \omega)$ is shown in Fig. 2.9 for fixed $t$. We see that it exhibits a sharp peak about the value $\omega = 0$. The height of this peak is proportional to $t^2$, while its width is approximately $2\pi/t$. Setting $x = \omega t/2$, we also note that

$$\int_{-\infty}^{+\infty} F(t, \omega)\,d\omega = t \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2}\,dx = \pi t \tag{2.349}$$

where we have used a standard integral. Using (2.31c) we also deduce that in the limit $t \to \infty$

$$F(t, \omega) \underset{t \to \infty}{\sim} \pi t\, \delta(\omega) \tag{2.350}$$

Let us first analyse (2.347) for a fixed value of $t$. Since the function $F(t, \omega_{ba})$ has a sharp peak of width $2\pi/t$ about the value $\omega_{ba} = 0$, it is clear from (2.347) that
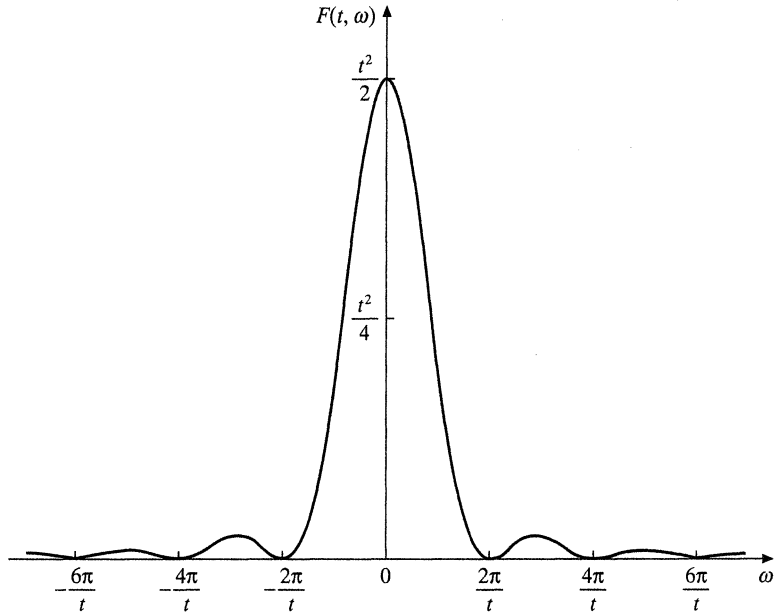
*Figure 2.9* The function $F(t, \omega)$ of equation (2.348), for fixed $t$.

transitions to those final states $b$ for which $\omega_{ba}$ does not deviate from zero by more than $\delta\omega_{ba} \simeq 2\pi/t$ will be strongly favoured. Therefore the transitions $a \to b$ will occur mainly towards those final states whose energy $E_b^{(0)}$ is located in a band of width

$$\delta E \simeq 2\pi\hbar/t \tag{2.351}$$

about the initial energy $E_a^{(0)}$, so that the unperturbed energy is conserved to within $2\pi\hbar/t$. This result may easily be related to the time–energy uncertainty relation $\Delta E \, \Delta t \gtrsim \hbar$. Indeed, since the perturbation gives a way of measuring the energy of the system by inducing transitions $a \to b$, and because this perturbation acts during a time $t$, the uncertainty related to this energy measurement should be approximately $\hbar/t$, in qualitative agreement with (2.351).

We now study the transition probability (2.347) as a function of $t$. For a transition to a *given state* $b$ we must distinguish two cases:

1.  If the transition is such that $\omega_{ba} = 0$ (so that $E_b^{(0)} = E_a^{(0)}$ and the states $a$ and $b$ are degenerate), then we see from (2.347) that

$$P_{ba}^{(1)}(t) = \frac{|H'_{ba}|^2}{\hbar^2} t^2 \tag{2.352}$$

so that the transition probability increases as $t^2$. Thus, after a sufficient length of time the quantity $P_{ba}^{(1)}(t)$ will no longer satisfy the inequality

$$P_{ba}^{(1)}(t) \ll 1 \tag{2.353}$$

required by a perturbative approach. Hence, the present perturbation method cannot be applied to degenerate systems which are perturbed over long periods of time.

2.　If on the contrary $\omega_{ba} \neq 0$ (so that the state $b$ is not degenerate with the initial state $a$), we have

$$P_{ba}^{(1)}(t) = \frac{4|H'_{ba}|^2}{\hbar^2 \omega_{ba}^2} \sin^2(\omega_{ba} t/2) \tag{2.354}$$

and we note that $P_{ba}^{(1)}(t)$ oscillates with a period $2\pi/|\omega_{ba}|$ about the average value $2|H'_{ba}|^2/(\hbar^2 \omega_{ba}^2)$. Since

$$P_{ba}^{(1)}(t) \leq \frac{4|H'_{ba}|^2}{\hbar^2 \omega_{ba}^2} \tag{2.355}$$

the condition (2.353) can always be satisfied if the perturbation $H'$ is sufficiently weak. It is also worth noting that for times $t$ small with respect to the period of oscillation $2\pi/|\omega_{ba}|$ one has $\sin(\omega_{ba} t/2) \simeq \omega_{ba} t/2$ so that $P_{ba}^{(1)}(t) \simeq |H'_{ba}|^2 t^2/\hbar^2$ increases quadratically with time.

Instead of considering transitions to a particular state $b$, it is often necessary to deal with transitions involving a *group of states* $n$ whose energy $E_n$ lies within a given interval $(E_b^{(0)} - \eta, E_b^{(0)} + \eta)$ centred about the value $E_b^{(0)}$. Let us denote by $\rho_n(E_n)$ the density of levels on the energy scale, so that $\rho_n(E_n)\,dE_n$ is the number of final states $n$ in an interval $dE_n$ containing the energy $E_n$. We shall continue to assume that the perturbation $H'$ is constant in time, except that it is switched on at $t = 0$. The first-order transition probability $P_{ba}^{(1)}(t)$ from the initial state $a$ to the group of final states $n$ is then given by

$$P_{ba}^{(1)}(t) = \frac{2}{\hbar^2} \int_{E_b^{(0)}-\eta}^{E_b^{(0)}+\eta} |H'_{na}|^2 F(t, \omega_{na}) \rho_n(E_n)\,dE_n \tag{2.356}$$

where $\omega_{na} = (E_n - E_a^{(0)})/\hbar$. Assuming that $\eta$ is small enough so that $H'_{na}$ and $\rho_n(E_n)$ are nearly constant within the integration range, we have

$$P_{ba}^{(1)}(t) = \frac{2}{\hbar^2} |H'_{ba}|^2 \rho_b(E_b^{(0)}) \int_{E_b^{(0)}-\eta}^{E_b^{(0)}+\eta} F(t, \omega_{na})\,dE_n \tag{2.357}$$

We shall also assume that $t$ is large enough so that the quantity $\eta$ satisfies the condition

$$\eta \gg 2\pi\hbar/t. \tag{2.358}$$

It is clear from the examination of the function $F(t, \omega)$ (see (2.348) and Fig. 2.9) that the overwhelming part of the integral on the right of (2.357) arises from

transitions which conserve the energy (within $\delta E = 2\pi\hbar/t$). Since $\eta \gg 2\pi\hbar/t$, we may write

$$\int_{E_b^{(0)}-\eta}^{E_b^{(0)}+\eta} F(t, \omega_{na}) \, dE_n \simeq \hbar \int_{-\infty}^{+\infty} F(t, \omega_{na}) \, d\omega_{na} = \pi\hbar t \qquad (2.359)$$

where we have used (2.349). Thus, (2.357) reduces to

$$P_{ba}^{(1)}(t) = \frac{2\pi}{\hbar} |H_{ba}'|^2 \rho_b(E) t \qquad (2.360)$$

with $E = E_a^{(0)} = E_b^{(0)}$. Thus the transition probability increases linearly with time for energy-conserving transitions to a group of states. It is worth stressing that the result (2.360) is soundly based only if the condition (2.353) required by a perturbative approach is obeyed.

Introducing the *transition probability per unit time* or *transition rate*

$$W_{ba} = \frac{dP_{ba}}{dt} \qquad (2.361)$$

we see from (2.360) that to first order in perturbation theory, we have

$$W_{ba} = \frac{2\pi}{\hbar} |H_{ba}'|^2 \rho_b(E) \qquad (2.362)$$

This formula, first obtained by P.A.M. Dirac, was later called by E. Fermi 'The Golden Rule' of perturbation theory. Although we have derived it here for a perturbation $H'$ which is constant in time (except for being switched on at $t = 0$), it can be generalised to other perturbations, as we shall now illustrate.

### Periodic perturbation

Let us now consider a perturbation $H'(t)$ which is a *periodic* function of time, except for being turned on at $t = 0$. This case is of particular importance for studying the interaction of atoms and molecules with electromagnetic fields, as we shall see in further chapters. We shall assume first that the perturbation is *harmonic* in time, with angular frequency $\omega$. That is,

$$H'(t) = A \exp(i\omega t) + A^\dagger \exp(-i\omega t) \qquad (2.363)$$

where $A$ is a time-independent operator and $A^\dagger$ is its adjoint so that the operator $H'$ is Hermitian. It is supposed that the system is initially (for $t \leqslant 0$) in the unperturbed bound state $\psi_a^{(0)}$, of energy $E_a^{(0)}$, so that the initial conditions are $c_a(t \leqslant 0) = 1$ and $c_b(t \leqslant 0) = 0$ for $b \neq a$.

According to (2.345), we have $|c_a(t)|^2 \simeq 1$ for $t > 0$. In order to find the coefficient $c_b^{(1)}(t)$ for $t > 0$ and $b \neq a$, we substitute (2.363) into (2.343b) and use the fact that $t_0 = 0$. This gives

$$c_b^{(1)}(t) = (i\hbar)^{-1}\left\{A_{ba}\int_0^t \exp[i(\omega_{ba} + \omega)t']\,dt' + A_{ba}^\dagger\int_0^t \exp[i(\omega_{ba} - \omega)t']\,dt'\right\} \quad (2.364)$$

where $A_{ba} = \langle\psi_b^{(0)}|A|\psi_a^{(0)}\rangle$ and $A_{ba}^\dagger = A_{ab}^*$. Performing the integrals, and remembering that $\hbar\omega_{ba} = E_b^{(0)} - E_a^{(0)}$, we find that the corresponding first-order transition probability is given by

$$P_{ba}^{(1)}(t) = \left| A_{ba}\frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} + \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} + \hbar\omega}\right.$$

$$\left. + A_{ba}^\dagger\frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} - \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} - \hbar\omega}\right|^2 \quad (2.365)$$

It is clear from this equation that if $t$ is large enough the probability of finding the system in the state $b$ will only be appreciable if the denominator of one or the other of the two terms on the right-hand side is close to zero. Moreover, assuming that $E_b^{(0)} \neq E_a^{(0)}$ (so that the levels $E_a^{(0)}$ and $E_b^{(0)}$ are not degenerate), both denominators cannot simultaneously be close to zero. A good approximation is therefore to neglect the interference between the two terms in calculating the transition probability. Thus, if the energy $E_b^{(0)}$ lies in a small band about the value

$$E = E_a^{(0)} + \hbar\omega \quad (2.366)$$

only the second term in (2.365) will have an appreciable magnitude, the corresponding transition probability being given by

$$P_{ba}^{(1)}(t) = \frac{2}{\hbar^2}|A_{ba}^\dagger|^2 F(t, \omega_{ba} - \omega) \quad (2.367)$$

The main difference with the expression (2.347), obtained for a time-independent perturbation, is that the angular frequency $\omega_{ba}$ has now been replaced by $\omega_{ba} - \omega$. From the properties of the function $F(t, \omega)$ it is apparent that the transition probability (2.367) will only be significant if $E_b^{(0)}$ is located in an interval of width $2\pi\hbar/t$ about the value $E_a^{(0)} + \hbar\omega$. Hence the first-order transition probability (2.367) will be appreciable if the system has *absorbed* an amount of energy given (to within $2\pi\hbar/t$) by $\hbar\omega = E_b^{(0)} - E_a^{(0)}$. This, of course, is nothing but the Bohr frequency rule (1.70). When it is exactly satisfied, so that $\omega = \omega_{ba}$, *resonance* is said to occur and we see from (2.367) and (2.348) that the first-order transition probability increases quadratically with time according to the formula

$$P_{ba}^{(1)}(t) = \frac{|A_{ba}^\dagger|^2}{\hbar^2}t^2 \quad (2.368)$$

In the same way, if the energy $E_b^{(0)}$ lies in a small interval in the neighbourhood of the value

$$E = E_a^{(0)} - \hbar\omega \quad (2.369)$$

only the first term on the right of (2.365) will be significant. The corresponding first-order transition probability will be given by

$$P^{(1)}_{ba}(t) = \frac{2}{\hbar^2}|A_{ba}|^2 F(t, \omega_{ba} + \omega) \tag{2.370}$$

and will only be significant if the system has *emitted* an amount of energy given (to within $2\pi\hbar/t$) by $\hbar\omega = E_a^{(0)} - E_b^{(0)}$. Again *resonance* occurs if this condition is exactly satisfied, in which case $\omega = -\omega_{ba}$ and the transition probability (2.370) increases quadratically with time. It should be noted that in practice $t$ is large enough ($t \gg 2\pi/\omega$) so that the two bands of width $2\pi\hbar/t$ about the values (2.366) and (2.369) do not overlap. Thus our neglect of the interference between the two terms on the right of (2.365) in calculating $P^{(1)}_{ba}$ is indeed justified.

As in the case of a time-independent perturbation, one can consider transitions to a *group* of final states $n$ whose energy $E_n$ lies within an interval $(E_b^{(0)} - \eta, E_b^{(0)} + \eta)$ about the value $E_b^{(0)} = E_a^{(0)} + \hbar\omega$ (for absorption) or $E_b^{(0)} = E_a^{(0)} - \hbar\omega$ (for emission) with $\eta \gg 2\pi\hbar/t$. Let $\rho_n(E_n)$ be the density of levels $E_n$ on the energy scale. Under conditions similar to those discussed above for a time-independent perturbation, a transition probability per unit time (transition rate) can be defined. For transitions in which the system *absorbs* an energy $\hbar\omega \simeq E_b^{(0)} - E_a^{(0)}$, this transition rate is given to first order by

$$W_{ba} = \frac{2\pi}{\hbar}|A^\dagger_{ba}|^2 \rho_b(E) \tag{2.371}$$

where $E = E_a^{(0)} + \hbar\omega$. The above expression is clearly the direct generalisation of the Golden Rule (2.362). Similarly, for transitions in which the system *emits* an energy $\hbar\omega \simeq E_a^{(0)} - E_b^{(0)}$ by making transitions to a group of final states, the corresponding transition rate is given (under the same conditions) by

$$W_{ba} = \frac{2\pi}{\hbar}|A_{ba}|^2 \rho_b(E) \tag{2.372}$$

with $E = E_a^{(0)} - \hbar\omega$.

Until now we have considered a perturbation $H'(t)$ which is a harmonic function of time. However, the generalisation of the above results to a perturbation $H'(t)$ which is a general periodic function of time is straightforward. Indeed, we can then develop $H'(t)$ in the Fourier series

$$H'(t) = \sum_{n=1}^{\infty} [A_n \exp(in\omega t) + A^\dagger_n \exp(-in\omega t)] \tag{2.373}$$

where the operators $A_n$ are time-independent. For large enough times ($t \gg 2\pi/\omega$), there is no interference between the contributions of the various terms of this development to the transition probability, because each term corresponds to a different energy transfer. A term of the type $A_n \exp(in\omega t)$ will therefore lead to the *emission* by the system of an energy given (to within $2\pi\hbar/t$) by $n\hbar\omega = E_a^{(0)} - E_b^{(0)}$

while a term of the type $A_n^\dagger \exp(-in\omega t)$ corresponds to the *absorption* by the system of the energy $n\hbar\omega = E_b^{(0)} - E_a^{(0)}$ (to within $2\pi\hbar/t$). The corresponding first-order transition probabilities are readily obtained, either for transitions to a given state $b$ or to a group of final states.

## Two-level system with harmonic perturbation

As a simple application of some of the concepts developed above, let us consider a two-level system, with unperturbed energies $E_a^{(0)} < E_b^{(0)}$ and corresponding eigenfunctions $\psi_a^{(0)}$ and $\psi_b^{(0)}$, respectively. The system being initially in the state $a$, a perturbation of the form (2.363) is switched on at time $t = 0$. Setting $\lambda = 1$ in (2.336), we obtain the two coupled equations

$$i\hbar\dot{c}_a(t) = \{A_{aa} \exp(i\omega t) + A_{aa}^\dagger \exp(-i\omega t)\}c_a$$
$$+ \{A_{ab} \exp[i(\Delta\omega)t] + A_{ab}^\dagger \exp[-i(\omega + \omega_{ba})t]\}c_b \qquad (2.374a)$$

and

$$i\hbar\dot{c}_b(t) = \{A_{ba} \exp[i(\omega_{ba} + \omega)t] + A_{ba}^\dagger \exp[-i(\Delta\omega)t]\}c_a$$
$$+ \{A_{bb} \exp(i\omega t) + A_{bb}^\dagger \exp(-i\omega t)\}c_b \qquad (2.374b)$$

where $\omega_{ba} = (E_b^{(0)} - E_a^{(0)})/\hbar$ and we have introduced the 'detuning' angular frequency

$$\Delta\omega = \omega - \omega_{ba} \qquad (2.375)$$

The system (2.374) must be solved subject to the initial conditions

$$c_a(t \leq 0) = 1, \qquad c_b(t \leq 0) = 0 \qquad (2.376)$$

The equations (2.374) cannot be solved exactly, but if it is assumed that $|\Delta\omega| \ll \omega$ (so that the angular frequency $\omega$ is always close to its resonant value $\omega = \omega_{ba}$) then the terms in $\exp[\pm i(\Delta\omega)t]$ will be much more important than those in $\exp[\pm i(\omega + \omega_{ba})t]$ and $\exp[\pm i\omega t]$. This is because the latter terms oscillate much more rapidly and on the average make little contribution to $\dot{c}_a$ or $\dot{c}_b$. It is therefore reasonable to neglect the higher frequency terms. This is known as the *rotating wave approximation* because the only terms which are kept are those in which the time dependence of the system and of the perturbation are in phase. In this approximation, the pair of equations (2.374) reduces to

$$i\hbar\dot{c}_a(t) = A_{ab} \exp[i(\Delta\omega)t]c_b \qquad (2.377\ a)$$

and

$$i\hbar\dot{c}_b(t) = A_{ba}^\dagger \exp[-i(\Delta\omega)t]c_a \qquad (2.377b)$$

This system, which is much simpler than (2.374), can be solved exactly. The solutions $c_a(t)$ and $c_b(t)$ satisfying the initial conditions (2.376) are

$$c_a(t) = \exp[i(\Delta\omega)t/2]\left[\cos(\omega_R t/2) - i\left(\frac{\Delta\omega}{\omega_R}\right)\sin(\omega_R t/2)\right] \qquad (2.378a)$$

and

$$c_b(t) = \frac{2A_{ba}^\dagger}{i\hbar\omega_R} \exp[-i(\Delta\omega)t/2] \sin(\omega_R t/2) \tag{2.378b}$$

where

$$\omega_R = \left[ (\Delta\omega)^2 + \frac{4|A_{ba}^\dagger|^2}{\hbar^2} \right]^{1/2} \tag{2.379}$$

is called the Rabi 'flopping frequency'.

The probability of finding the system at time $t > 0$ in the state $a$ is therefore given by

$$|c_a(t)|^2 = \cos^2(\omega_R t/2) + \frac{(\Delta\omega)^2}{\omega_R^2} \sin^2(\omega_R t/2) \tag{2.380}$$

while that of finding it in the state $b$ (that is, the probability that the transition $a \to b$ will take place) is

$$P_{ba}(t) = |c_b(t)|^2 = \frac{4|A_{ba}^\dagger|^2}{\hbar^2 \omega_R^2} \sin^2(\omega_R t/2) \tag{2.381}$$

As expected, the excitation is a typical *resonance* process, since the probability (2.381) rapidly decreases when the absolute value $|\Delta\omega|$ of the detuning angular frequency increases. It is also readily verified from (2.378)–(2.381) that $|c_a(t)|^2 + |c_b(t)|^2 = 1$, and that the system oscillates between the two levels with a period $T = 2\pi/\omega_R$.

Having obtained 'exact' results for this problem (within the framework of the rotating wave approximation), we can compare them with those arising from first-order perturbation theory. Using (2.380), we see that when $\omega_R t \ll 1$ we have $|c_a(t)|^2 \simeq 1$, which is in agreement with the perturbative result following from (2.345). From (2.367) and (2.348) we also note that the first-order transition probability is given by

$$P_{ba}^{(1)}(t) = \frac{2}{\hbar^2} |A_{ba}^\dagger|^2 F(t, \Delta\omega)$$

$$= \frac{4|A_{ba}^\dagger|^2}{\hbar^2 (\Delta\omega)^2} \sin^2[(\Delta\omega)t/2] \tag{2.382}$$

If $\Delta\omega \neq 0$ this result agrees with (2.381) provided that the perturbation is weak enough so that one can write $\omega_R \simeq \Delta\omega$ (see (2.379)). At resonance ($\Delta\omega = 0$), we see that $P_{ba}^{(1)}(t)$ increases quadratically with time according to (2.368). As expected, this result is only in agreement with the 'exact' expression (2.381) for small enough times and small enough perturbations.