Chapter 14
Time-Dependent Perturbation Theory

14.1 Introduction

In many physical problems it is necessary to consider the collision of a particle with another particle or system of particles. The treatment based on Classical Mechanics is given in Sects. 3.5, 3.6 with reference to the motion's asymptotic conditions, without considering the form of the interaction, while Sect. 3.8 shows a detailed treatment of the Coulomb interaction. Here the approach based on Quantum Mechanics is shown, dealing with the following problem: a particle in a conservative motion enters at $t = 0$ an interaction with another particle or system of particles; such an interaction has a finite duration t_P, at the end of which the particle is in a conservative motion again. The perturbation produced by the interaction, which is described by a suitable Hamiltonian operator, may change the total energy of the particle; the analysis carried out here, called *time-dependent perturbation theory*, allows one to calculate such an energy change. The other particle or system, with which the particle under consideration interacts, is left unspecified. However, it is implied that the larger system, made of the particle under consideration and the entity with which it interacts, form an isolated system, so that the total energy is conserved: if the particle's energy increases due to the interaction, then such an energy is absorbed from the other entity, or vice versa. As in Classical Mechanics, other dynamical properties of an isolated system are conserved; an example of momentum conservation is given in Sect. 14.8.3.

The discussion is carried out first for the case where the eigenvalues prior and after the perturbation are discrete and non degenerate. Starting from the general solution of the perturbed problem, a first-order approximation is applied, which holds for small perturbations, and the probability per unit time of the transition from a given initial state to another state is found. The analysis is repeated for the degenerate case (still for discrete eigenvalues) and, finally, for the situation where both the initial and final state belong to a continuous set. The last section shows the calculation of the perturbation matrix for a screened Coulomb perturbation. The complements deal with the important problems of a perturbation constant in time and a harmonic perturbation; a short discussion about the Fermi golden rule and the transitions from discrete to continuous levels follows.

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14.2 Discrete Eigenvalues

Let $\mathcal{H}$ be the Hamiltonian operator that describes the dynamics of the particle when the perturbation is absent. Such an operator is assumed to be conservative, namely, $\mathcal{H} = -\hbar^2 \nabla^2/(2\,m) + V(\mathbf{r})$. When the perturbation is present, namely, for $0 \le t \le t_P$, the Hamiltonian operator is referred to as $\mathcal{H}'$. The two operators, respectively called *unperturbed Hamiltonian* and *perturbed Hamiltonian*, are Hermitean, so their difference $\delta\mathcal{H} = \mathcal{H}' - \mathcal{H}$, called *perturbation Hamiltonian*, is Hermitean as well. Also, it is assumed that $\mathcal{H}$ and $\mathcal{H}'$ are real, and that $\delta\mathcal{H}$ does not act on time; however, it is $\delta\mathcal{H} = \delta\mathcal{H}(t)$ because the perturbation is present only when $0 \le t \le t_P$.

For $t < 0$ and $t > t_P$ the wave function is unperturbed; remembering the concepts introduced in Sect. 9.2 and considering the case of discrete eigenvalues, it reads

$$\psi = \sum_n c_n\, w_n(\mathbf{r}) \exp(-\mathrm{i}\, E_n\, t/\hbar), \tag{14.1}$$

with w_n the solutions of $\mathcal{H} w_n = E_n\, w_n$. As usual, n stands for a single index or a set of indices. For the sake of simplicity, here it is assumed provisionally that the energy eigenvalues are not degenerate, so that a one-to-one correspondence exists between E_n and w_n; this assumption will be removed later (Sect. 14.5). The wave function is assumed to be square integrable and normalized to unity, whence $|c_n|^2$ is the probability that the particle under consideration is found in the nth state, and $\langle w_s | w_n \rangle = \delta_{sn}$. As noted above, expansion (14.1) holds for both $t < 0$ and $t > t_P$. However, prior to the perturbaton and as a consequence of a measurement, the additional information about the energy state is available; assuming that the outcome of the measurement was the rth state, it follows (Sect. 9.2) that for $t < 0$ it is $c_n = 0$ when $n \ne r$, and[1]

$$|c_r|^2 = 1, \qquad c_r = 1, \qquad \psi = w_r(\mathbf{r}) \exp(-\mathrm{i}\, E_r\, t/\hbar). \tag{14.2}$$

When $t \to 0$ the last relation in (14.2) yields $\psi(\mathbf{r}, t = 0) = w_r$ which, by continuity, provides the initial condition for the time-dependent Schrödinger equation to be solved in the interval $0 \le t \le t_P$; such an equation reads

$$(\mathcal{H} + \delta\mathcal{H})\ \psi = \mathrm{i}\,\hbar\, \frac{\partial \psi}{\partial t}. \tag{14.3}$$

Thanks to the completeness of the w_ns one expands the wave function as $\psi = \sum_n b_n(t)\, w_n(\mathbf{r})$, where functions b_n are unknown (compare with (9.10)). However, it is convenient to transfer the role of unknowns to a new set of functions $a_n(t) = b_n(t) \exp(\mathrm{i}\, E_n\, t/\hbar)$, so that the expansion reads

$$\psi = \sum_n a_n(t)\, w_n(\mathbf{r}) \exp(-\mathrm{i}\, E_n\, t/\hbar). \tag{14.4}$$

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[1] The phase of c_r is irrelevant and is set to zero.

By this token, the initial condition yields $a_n(0) = \delta_{nr}$. Replacing (14.4) in (14.3),

$$\sum_n a_n \exp(-\mathrm{i}\, E_n\, t/\hbar)\; (\mathcal{H} w_n + \delta\mathcal{H} w_n) =$$

$$= \mathrm{i}\,\hbar \sum_n w_n \exp(-\mathrm{i}\, E_n\, t/\hbar)\; (\mathrm{d}a_n/\mathrm{d}t - \mathrm{i}\, E_n\, a_n/\hbar)\,, \tag{14.5}$$

where the first and last terms cancel out due to $\mathcal{H} w_n = E_n\, w_n$. The next step is a scalar multiplication of the remaining terms by one of the eigenfunctions of the unperturbed problem, say, w_s. The sum $\mathrm{i}\,\hbar \sum_n w_n \exp(-\mathrm{i}\, E_n\, t/\hbar)\, \mathrm{d}a_n/\mathrm{d}t$ at the right hand side of (14.5) transforms, due to $\langle w_s | w_n \rangle = \delta_{sn}$, into the single term $\mathrm{i}\,\hbar \exp(-\mathrm{i}\, E_s\, t/\hbar)\, \mathrm{d}a_s/\mathrm{d}t$. In conclusion, the time-dependent Schrödinger equation (14.3) becomes a set of infinite, coupled linear equations in the unknowns a_s:

$$\frac{\mathrm{d}a_s}{\mathrm{d}t} = \frac{1}{\mathrm{i}\,\hbar} \sum_n a_n\, h_{ns} \exp(-\mathrm{i}\, \omega_{ns}\, t), \qquad a_s(0) = \delta_{sr}, \tag{14.6}$$

with

$$h_{ns}(t) = \int_\Omega w_s^*\, \delta\mathcal{H} w_n\, \mathrm{d}^3 r, \qquad \omega_{ns} = (E_n - E_s)/\hbar. \tag{14.7}$$

The coefficients of (14.6) embed the eigenvalues and eigenfunctions of the unperturbed problem. Due to its form, the set of elements $h_{ns}(t)$ is called *perturbation matrix*; remembering that $\delta\mathcal{H}$ is real, the definition (14.7) of the elements shows that $h_{sn} = h_{ns}^*$.

14.3 First-Order Perturbation

The differential equations (14.6) are readily transformed into a set of integral equations by integrating from $t = 0$ to $t \le t_P$ and using the initial condition:

$$a_s = \delta_{sr} + \frac{1}{\mathrm{i}\,\hbar} \int_0^t \sum_n a_n(t')\, h_{ns}(t') \exp(-\mathrm{i}\, \omega_{ns}\, t')\, \mathrm{d}t'. \tag{14.8}$$

As mentioned above, the solution of the Schrödinger equation for $t > t_P$ is (14.1), with $|c_n|^2$ the probability that a measurement carried out at $t = t_P$ yields the eigenvalue E_n. The coefficients c_n are found by observing that, after the solution of (14.6) or (14.8) is calculated, the time-continuity of ψ and the uniqueness of the expansion yield $c_n = a_n(t_P)$. It follows that the probability that at $t = t_P$ an energy measurement finds the eigenvalue E_s is $|a_s(t_P)|^2$. On the other hand, the energy state prior to the perturbation was assumed to be E_r, and the functions $a_n(t)$ inherit this assumption through the initial condition $a_n(0) = \delta_{nr}$; as a consequence, the quantity

$|a_s(t_P)|^2 = |b_s(t_P)|^2$ can be thought of as the probability that the perturbation brings the particle from the initial state E_r to the final state E_s: for this reason, $P_{rs} = |a_s(t_P)|^2$ is called *transition probability from state* r *to state* s. Thanks to the normalization condition it is $\sum_s P_{rs} = \int_\Omega |\psi(t_P)|^2 \, \mathrm{d}^3 r = 1$; the term of equal indices, P_{rr}, is the probability that the perturbation leaves the particle's state unchanged.

The two forms (14.6) and (14.8) are equivalent to each other; however, the second one is better suited for an iterative-solution procedure, that reads

$$a_s^{(k+1)} = \delta_{sr} + \frac{1}{\mathrm{i}\,\hbar} \int_0^t \sum_n a_n^{(k)} \, h_{ns} \, \exp\left(-\mathrm{i}\,\omega_{ns}\, t'\right) \mathrm{d}t', \tag{14.9}$$

where $a_n^{(k)}(t)$ is the kth iterate. The iterations are brought to an end when $||a_s^{(k+1)} - a_s^{(k)}|| < \varepsilon$, where the bars indicate a suitable norm and ε is a small positive constant. To start the procedure it is necessary to choose the iterate of order zero, $a_n^{(0)}(t)$, which is typically done by letting $a_n^{(0)}(t) = a_n^{(0)}(0) = \delta_{nr}$; in other terms, the initial iterate of a_n is selected as a constant equal to the initial condition of a_n. Replacing this value into the integral of (14.9) yields the first-order iterate

$$a_r^{(1)} = 1 + \frac{1}{\mathrm{i}\,\hbar} \int_0^t h_{rr} \, \mathrm{d}t', \qquad a_s^{(1)} = \frac{1}{\mathrm{i}\,\hbar} \int_0^t h_{rs} \, \exp\left(-\mathrm{i}\,\omega_{rs}\, t'\right) \mathrm{d}t', \tag{14.10}$$

$s \ne r$. If the perturbation is small enough, the first-order iterate is already close to the solution, so that $a_r \simeq a_r^{(1)}$, $a_s \simeq a_s^{(1)}$. This case happens when the norm of the integrals in (14.10) is much smaller than unity; it follows $P_{rr} \simeq 1$, $P_{rs} \ll 1$. The approximate solution thus found is called *first-order solution*, or *first-order perturbation*. Note that, as h_{rr} is real, the iterate $a_r^{(1)}$ is a complex number whose real part equals unity; as a consequence it is $|a_r^{(1)}|^2 > 1$. This non-physical result is due to the approximation.

14.4 Comments

Considering the case where the initial and final states are different, and observing that the entries of the perturbation matrix vanish for $t < 0$ and $t > t_P$, one can calculate $a_s(t_P)$ by replacing the integration limits 0 and t_P with $-\infty$ and $+\infty$, respectively. This shows that $a_s^{(1)}$ is proportional to the Fourier transform (C.16) of h_{rs} evaluated at $\omega_{rs} = (E_r - E_s)/\hbar$,

$$a_s^{(1)} = \frac{1}{\mathrm{i}\,\hbar} \int_{-\infty}^{+\infty} h_{rs} \, \exp(-\mathrm{i}\,\omega_{rs}\, t') \, \mathrm{d}t' = \frac{\sqrt{2\,\pi}}{\mathrm{i}\,\hbar} \, \mathcal{F} h_{rs}|_{\omega=\omega_{rs}} \,. \tag{14.11}$$

In conclusion, the first-order solution of the time-dependent Schrödinger equation (14.3) yields the following probability of a transition from state r to state s:

$$P_{rs} = \frac{2\,\pi}{\hbar^2} \, |\mathcal{F} h_{rs}|^2 \,. \tag{14.12}$$

The units of h_{ns} are those of an energy. It follows that the units of $\mathcal{F}h_{rs}$ are those of an action, and P_{rs} is dimensionless, as expected. Some important consequences derive from (14.12):

1. It may happen that for a given perturbation Hamiltonian $\delta\mathcal{H}$ the eigenfunctions w_r, w_s ($s \neq r$) are such that $h_{rs} = 0$. In this case $\delta\mathcal{H}$ is not able to induce the transition from state r to state s: the transition is *forbidden*. Basing on this observation one can determine the pairs of indices for which the transitions are permitted, thus providing the so-called *transition rules* or *selection rules*. For this analysis it is sufficient to consider the symmetry of the integrand in the definition (14.7) of h_{rs}, without the need of calculating the integral itself.
2. By exchanging r and s one finds $h_{sr} = h^*_{rs}$, while ω_{rs} becomes $-\omega_{rs}$. From (14.11) it follows that $\mathcal{F}h_{sr} = (\mathcal{F}h_{rs})^*$, whence $P_{sr} = P_{rs}$: for a given perturbation Hamiltonian $\delta\mathcal{H}$ the probability of the $r \to s$ and $s \to r$ transitions are the same.

The transition from an energy state to a different one entails a change in the total energy of the particle under consideration. Such a change is due to the interaction with another particle or system of particles whence $\delta\mathcal{H}$ originates. Examples are given in Sects. 14.8.1 and 14.8.2.

The replacement of the integration limits 0 and t_P with $-\infty$ and $+\infty$, carried out above, has the advantage of making the presence of the Fourier transform clearer; however, remembering that the duration t_P of the perturbation is finite, one observes that the probability P_{rs} is a function of t_P proper. From this, the *probability per unit time* of the transition is defined as

$$\dot{P}_{rs} = \frac{\mathrm{d}P_{rs}}{\mathrm{d}t_P}. \tag{14.13}$$

14.5 Degenerate Energy Levels

In Sect. 14.2 non-degenerate energy levels have been assumed for the sake of simplicity. The case of degenerate levels is considered here, still assuming that the indices are discrete. By way of example, let each energy value E_n correspond to a set $w_{n1}, \dots, w_{n\gamma}, \dots$ of linearly-independent, mutually-orthogonal eigenfunctions. An example of this is given by the eigenvalues (13.49) of the Schrödinger equation for a central force of the Coulomb type, whose degree of degeneracy in the spinless case is given by (13.50). Expression (14.1) of the unperturbed wave function, that holds for $t < 0$ and $t > t_P$, becomes in this case

$$\psi = \sum_{n\gamma} c_{n\gamma}\, w_{n\gamma}(\mathbf{r}) \exp(-\mathrm{i}\, E_n\, t/\hbar), \tag{14.14}$$

with $w_{n\gamma}$ the solutions of $\mathcal{H}w_{n\gamma} = E_n\, w_{n\gamma}$. As before, the wave function is assumed to be square integrable and normalized to unity, whence $|c_{n\gamma}|^2$ is the probability that the particle under consideration is found in the state labeled by n, γ, and $\langle w_{s\beta} | w_{n\gamma} \rangle = \delta_{sn}\, \delta_{\beta\gamma}$. Prior to the perturbaton and as a consequence of measurements, the additional information about the energy state is available, along with that of the observable associated to index γ, whose measurement is compatible with that of energy (compare with Sect. 10.4); assuming that the outcome of the measurements was the state labeled r, α, it follows that for $t < 0$ it is $c_{r\alpha} = 1$, $\psi = w_{r\alpha}(\mathbf{r}) \exp(-\mathrm{i}\, E_r\, t/\hbar)$, while all other coefficients vanish. As a consequence, the initial condition for the time-dependent Schrödinger equation to be solved in the interval $0 \le t \le t_P$ is $\psi(\mathbf{r}, t = 0) = w_{r\alpha}$. Following the same reasoning as in Sect. 14.2 shows that in such an interval the expansion $\psi = \sum_{n\gamma} a_{n\gamma}(t)\, w_{n\gamma}(\mathbf{r}) \exp(-\mathrm{i}\, E_n\, t/\hbar)$ holds, and the time-dependent Schrödinger equation transforms into the set of infinite, coupled linear equations

$$\frac{\mathrm{d}a_{s\beta}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} \sum_{n\gamma} a_{n\gamma}\, h_{ns}^{\gamma\beta} \exp(-\mathrm{i}\, \omega_{ns}\, t), \qquad a_{s\beta}(0) = \delta_{sr}\, \delta_{\beta\alpha}, \tag{14.15}$$

with

$$h_{ns}^{\gamma\beta}(t) = \int_\Omega w_{s\beta}^*\, \delta\mathcal{H} w_{n\gamma} \mathrm{d}^3 r, \qquad \omega_{ns} = (E_n - E_s)/\hbar. \tag{14.16}$$

The first-order perturbative solution of (14.15) is obtained following the same path as in Sect. 14.3. Within this approximation, and considering a final state s, β different from the initial one, the probability of a $r, \alpha \to s, \beta$ transition induced by the perturbation is

$$P_{rs}^{\alpha\beta} = \frac{1}{\hbar^2} \left| \int_0^{t_P} h_{rs}^{\alpha\beta}(t) \exp(-\mathrm{i}\, \omega_{ns}\, t)\, \mathrm{d}t \right|^2. \tag{14.17}$$

Thanks to the normalization condition it is $\sum_{s\beta} P_{rs}^{\alpha\beta} = \int_\Omega |\psi(t_P)|^2\, \mathrm{d}^3 r = 1$, which can be expressed as

$$\sum_s P_{rs}^{\alpha} = 1, \qquad P_{rs}^{\alpha} = \sum_\beta P_{rs}^{\alpha\beta}. \tag{14.18}$$

This shows that the inner sum P_{rs}^{α} is the probability that the perturbation induces a transition from the initial state r, α to any final state whose energy is $E_s \neq E_r$.

14.6 Continuous Energy Levels

When the spectrum is continuous, the wave packet describing a particle in a three-dimensional space and in a conservative case is given by (9.5), namely

$$\psi(\mathbf{r}, t) = \iiint_{-\infty}^{+\infty} c_{\mathbf{k}}\, w_{\mathbf{k}}(\mathbf{r}) \exp(-\mathrm{i}\, E_{\mathbf{k}}\, t/\hbar)\, \mathrm{d}^3 k, \tag{14.19}$$

with $E_{\mathbf{k}}$, $w_{\mathbf{k}}$ the eigenvalues and eigenfunctions of $\mathcal{H} w_{\mathbf{k}} = E_{\mathbf{k}}\, w_{\mathbf{k}}$, and $\mathbf{k}$ a three-dimensional vector whose components are continuous. If the wave function is square integrable and normalized to unity, (9.7) holds:

$$\int_\Omega |\psi|^2\, \mathrm{d}^3 r = \iiint_{-\infty}^{+\infty} |c_{\mathbf{k}}|^2\, \mathrm{d}^3 k = 1. \tag{14.20}$$

Remembering the discussion of Sects. 9.2, 9.6, and 10.2, the product $|\psi(\mathbf{r},t)|^2\, \mathrm{d}^3 r$ is the infinitesimal probability that at time t the particle is localized within $\mathrm{d}^3 r$ around $\mathbf{r}$, and the product $|c_{\mathbf{k}}|^2\, \mathrm{d}^3 k$ is the infinitesimal probability that the outcome of an energy measurement belongs to the range of $E(\mathbf{k})$ values whose domain is $\mathrm{d}^3 k$.

To proceed one assumes that the unperturbed Hamiltonian operator is that of a free particle, $\mathcal{H} = -(\hbar^2/2\,m)\,\nabla^2$; it follows that the wave function and energy corresponding to a wave vector $\mathbf{k}$ read (Sect. 9.6)

$$w_{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2\,\pi)^{3/2}}\, \exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}), \qquad E_{\mathbf{k}} = \frac{\hbar^2}{2\,m}\, \left(k_1^2 + k_2^2 + k_3^2\right) = \hbar\,\omega_{\mathbf{k}}. \tag{14.21}$$

Thanks to the completeness of the eigenfunctions (14.21), during the perturbation the wave function is given by

$$\psi(\mathbf{r},t) = \iiint_{-\infty}^{+\infty} a_{\mathbf{k}}(t)\, w_{\mathbf{k}}(\mathbf{r})\, \exp(-\mathrm{i}\, E_{\mathbf{k}}\, t/\hbar)\, \mathrm{d}^3 k. \tag{14.22}$$

Due to (14.20), the units of $|c_{\mathbf{k}}|^2$ and, consequently, of $|a_{\mathbf{k}}|^2$, are those of a volume. The same reasoning as in Sect. 14.2 yields in this case

$$\int \frac{\mathrm{d}a_{\mathbf{k}}}{\mathrm{d}t}\, w_{\mathbf{k}}(\mathbf{r})\, \exp(-\mathrm{i}\, E_{\mathbf{k}}\, t/\hbar)\; \mathrm{d}^3 k = \int \frac{a_{\mathbf{k}}}{\mathrm{i}\,\hbar}\, \delta\mathcal{H} w_{\mathbf{k}}(\mathbf{r})\, \exp(-\mathrm{i}\, E_{\mathbf{k}}\, t/\hbar)\; \mathrm{d}^3 k \tag{14.23}$$

(for the sake of simplicity, the symbol of triple integral over $\mathbf{k}$ or $\mathbf{r}$ is replaced with $\int$ in (14.23) and in the relations below). Considering a state $\mathbf{g}$, a scalar multiplication of (14.23) by the corresponding eigenfunction $w_{\mathbf{g}}$ is carried out; performing the integration over $\mathbf{r}$ first, yields at the right hand side the entry of the perturbation matrix of labels $\mathbf{k}$ and $\mathbf{g}$:

$$h_{\mathbf{kg}}(t) = \frac{1}{(2\,\pi)^3} \int \exp(-\mathrm{i}\,\mathbf{g}\cdot\mathbf{r})\, \delta\mathcal{H}\, \exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})\, \mathrm{d}^3 r, \tag{14.24}$$

where the units of $h_{\mathbf{kg}}(t)$ are those of an energy times a volume. At the left hand side of (14.23), still performing the integration over $\mathbf{r}$ first, and using (C.56), provides

$$\int \frac{\mathrm{d}a_{\mathbf{k}}}{\mathrm{d}t}\, \delta(\mathbf{k}-\mathbf{g})\, \exp(-\mathrm{i}\, E_{\mathbf{k}}\, t/\hbar)\; \mathrm{d}^3 k = \frac{\mathrm{d}a_{\mathbf{g}}}{\mathrm{d}t}\, \exp\left(-\mathrm{i}\, E_{\mathbf{g}}\, t/\hbar\right) \tag{14.25}$$

which, combined with (14.24) and (14.23), yields

$$\frac{\mathrm{d}a_{\mathbf{g}}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\,\hbar} \int a_{\mathbf{k}}\, h_{\mathbf{kg}}\, \exp\left[-\mathrm{i}\,(E_{\mathbf{k}} - E_{\mathbf{g}})\, t/\hbar\right]\, \mathrm{d}^3 k, \tag{14.26}$$

the analogue of (14.6) and (14.15). However, a difference with respect to the discrete case exists, because a_n in (14.6) and $a_{n\gamma}$ in (14.15) are dimensionless quantities, whereas $a_{\mathbf{k}}$ in (14.26) is not. As a consequence, when the first-order perturbation method is used, and $a_{\mathbf{k}}$ within the integral of (14.26) is replaced with the initial condition, its expression contains one or more parameters whose values enter the final result. Given these premises, choose for the initial condition, e.g., a Gaussian function centered on some vector $\mathbf{b} \neq \mathbf{g}$,

$$a_{\mathbf{k}}(0) = \pi^{-3/4}\, \lambda^{3/2}\, \exp\left(-\lambda^2\, |\mathbf{k} - \mathbf{b}|^2/2\right), \tag{14.27}$$

with $\lambda > 0$ a length. Inserting (14.27) into (14.22) yields the initial condition for the wave function (compare with (C.82)),

$$\psi(\mathbf{r}, 0) = \pi^{-3/4}\, \lambda^{-3/2}\, \exp\left[-r^2/(2\,\lambda^2) + \mathrm{i}\, \mathbf{b} \cdot \mathbf{r}\right]. \tag{14.28}$$

Both (14.27) and (14.28) are square integrable and normalized to unity for any positive λ; when the latter becomes large, $\psi(\mathbf{r}, 0)$ becomes more and more similar to a plane wave, while the peak of $a_{\mathbf{k}}(0)$ around $\mathbf{b}$ becomes narrower and higher. Assuming that the $\mathbf{k}$-dependence of $h_{\mathbf{kg}}$ is weaker than that of $a_{\mathbf{k}}(0)$, one replaces $\mathbf{k}$ with $\mathbf{b}$ in $h_{\mathbf{kg}}$ and $E_{\mathbf{k}}$, so that in (14.26) only the integral of $a_{\mathbf{k}}(0)$ is left, which yields $(2\sqrt{\pi}/\lambda)^{3/2}$. Completing the calculation as in Sects. 14.4 and 14.5, and remembering that $\mathbf{g} \neq \mathbf{b}$, provides

$$a_{\mathbf{g}}(t_P) \simeq \frac{(2\sqrt{\pi}/\lambda)^{3/2}}{\mathrm{i}\,\hbar} \int_0^{t_P} h_{\mathbf{bg}}(t)\, \exp\left(-\mathrm{i}\,\omega_{\mathbf{bg}}\, t\right)\, \mathrm{d}t, \qquad \omega_{\mathbf{bg}} = \frac{E_{\mathbf{b}} - E_{\mathbf{g}}}{\hbar}. \tag{14.29}$$

The product $\mathrm{d}P_{\mathbf{bg}} = |a_{\mathbf{g}}(t_P)|^2\, \mathrm{d}^3 g$ is the infinitesimal probability that at the end of the perturbation the outcome of an energy measurement belongs to the range of $E(\mathbf{g})$ values whose domain is $\mathrm{d}^3 g$.

Typical applications of (14.26) are encountered in the cases where the perturbation matrix is independent of time, $h_{\mathbf{bg}} = h_{\mathbf{bg}}^{(0)} = \text{const} \neq 0$. A calculation similar to that of Sect. 14.8.1 yields in this case

$$\mathrm{d}P_{\mathbf{bg}} = \frac{8\,\pi^{3/2}\, |h_{\mathbf{bg}}^{(0)}|^2}{\lambda^3\, \hbar^2}\, f(\omega_{\mathbf{bg}})\, \mathrm{d}^3 g, \qquad f(\omega_{\mathbf{bg}}) = \left[\frac{\sin\left(\omega_{\mathbf{bg}}\, t_P/2\right)}{\omega_{\mathbf{bg}}/2}\right]^2. \tag{14.30}$$

In place of the domain $\mathrm{d}^3 g$ one can consider the corresponding range of energy $\mathrm{d}E_{\mathbf{g}}$; for this, one profits by the concept of density of states introduced in Sect. B.5. Here the calculation is simple because the $E = E(\mathbf{g})$ relation is given by (14.21) so that, by the same calculation leading to (B.34), one obtains $\mathrm{d}^3 g = (1/2)\, \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi\, (2\,m/\hbar^2)^{3/2} \sqrt{E_{\mathbf{g}}}\, \mathrm{d}E_{\mathbf{g}}$. Considering that the initial state $\mathbf{b}$ and the duration t_P are prescribed, the factor $f(\omega_{\mathbf{bg}})$ in (14.30) depends only on $E_{\mathbf{g}}$, while $h_{\mathbf{bg}}^{(0)}$ may depend on the angles ϑ, φ (compare with Prob. 14.1). Integrating (14.30) over the angles and letting

$$H_{\mathbf{b}}^{(0)}(E_{\mathbf{g}}) = \int_0^{\pi} \int_0^{2\pi} |h_{\mathbf{bg}}^{(0)}|^2\, \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi, \tag{14.31}$$

yields the infinitesimal probability that a perturbation constant in time induces a transition from the initial condition (14.28) to a final state whose energy belongs to the range $\mathrm{d}E_{\mathbf{g}}$:

$$\mathrm{d}P_{\mathbf{b}} = \int_0^{\pi} \int_0^{2\pi} \mathrm{d}P_{\mathbf{bg}} \sin\vartheta \, \mathrm{d}\vartheta \, \mathrm{d}\varphi = \left(\frac{2\pi\, m}{\hbar^2}\right)^{3/2} \frac{4\, f(\omega_{\mathbf{bg}})\, H_{\mathbf{b}}^{(0)}}{\lambda^3\, \hbar^2} \sqrt{E_{\mathbf{g}}}\, \mathrm{d}E_{\mathbf{g}}. \tag{14.32}$$

14.7 Screened Coulomb Perturbation

An important case of perturbation is that of a charged particle deflected by another charged particle fixed in the origin. The perturbation Hamiltonian is independent of time and, *in vacuo*, takes the form (3.31) of the Coulomb potential energy.[2] Though, the perturbation matrix (14.24) calculated using (3.31) diverges. Such an outcome is explained by observing that, as the vanishing behavior of the Coulomb potential energy away from the origin is weak, the particle is actually subjected to it at large distances from the origin; as a consequence, using the free particle's eigenfunctions $\exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})/(2\pi)^{3/2}$ as solutions of the unperturbed Schrödinger equation is too strong an approximation. A more appropriate approach adopts for the perturbation Hamiltonian the *screened Coulomb potential energy*

$$\delta\mathcal{H} = \frac{A}{4\pi\, r} \exp(-q_c\, r), \qquad r > 0, \qquad A = \frac{\kappa\, Z\, e^2}{\varepsilon_0}, \tag{14.33}$$

with $e > 0$ the elementary electric charge, Z a positive integer, ε_0 the vacuum permittivity, $q_c > 0$ the *inverse screening length* and, finally, $\kappa = 1\,(-1)$ in the repulsive (attractive) case. The asymptotic vanishing of (14.33) is much stronger than that of the pure Coulomb case, and the resulting matrix elements are finite, as shown below. Although the choice of a screened potential energy is not realistic *in vacuo*, an expression like (14.33) is more appropriate than (3.31) when a solid material is considered (Sect. 20.5).

To calculate (14.24) one lets $\mathbf{q} = \mathbf{k} - \mathbf{g}$ and chooses a Cartesian reference such that $\mathbf{q}$ is aligned with the z axis: turning to spherical coordinates (B.1) transforms $\mathrm{d}^3 r$ into $r^2 \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi\, \mathrm{d}r$ and $\mathbf{q}\cdot\mathbf{r}$ into $q\, r\, \cos\vartheta$. Letting $\mu = \cos\vartheta$, and observing that the integration over φ yields a 2π factor, one gets

$$h_{\mathbf{kg}}^{(0)} = \frac{A/2}{(2\pi)^3} \int_0^{\infty} \left[\int_{-1}^{+1} \exp(-\mathrm{i}\, q\, r\, \mu)\, \mathrm{d}\mu\right] \exp(-q_c\, r)\, r\, \mathrm{d}r = \frac{A/(2\pi)^3}{q_c^2 + q^2}. \tag{14.34}$$

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[2] This case is the quantum analogue of that treated in classical terms in Sect. 3.8.

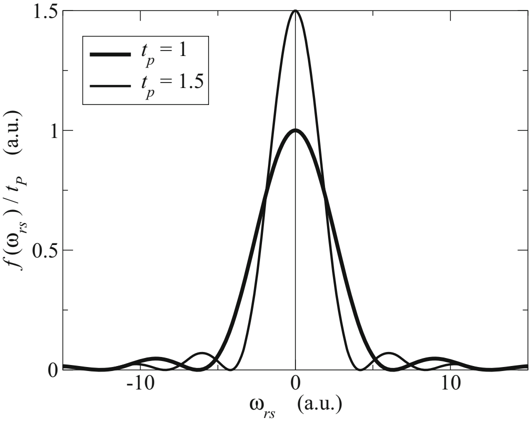

Fig. 14.1 Form of $f(\omega_{rs})/t_P$, with f given by the second expression in (14.36), for different values of t_P (in arbitrary units)

14.8 Complements

14.8.1 Perturbation Constant in Time

The simplest example of the time-dependent perturbation theory of Sect. 14.1 occurs when the matrix elements h_{rs} are constant in time during the perturbation. In this case one lets $h_{rs} = h_{rs}^{(0)} = \text{const} \neq 0$ for $0 \leq t \leq t_P$, and $h_{rs} = 0$ elsewhere. From (14.10) it follows

$$h_{rs}^{(0)} \int_0^{t_P} \exp(-\mathrm{i}\,\omega_{rs}\,t)\,\mathrm{d}t = h_{rs}^{(0)} \exp(-\mathrm{i}\,\omega_{rs}\,t_P/2)\,\frac{\sin(\omega_{rs}\,t_P/2)}{\omega_{rs}/2}, \qquad (14.35)$$

$$P_{rs} = \frac{|h_{rs}^{(0)}|^2}{\hbar^2}\,f(\omega_{rs}), \qquad f(\omega_{rs}) = \left[\frac{\sin(\omega_{rs}\,t_P/2)}{\omega_{rs}/2}\right]^2. \qquad (14.36)$$

The form of $f(\omega_{rs})/t_P$ is shown in Fig. 14.1 in arbitrary units. The zeros of f nearest to $\omega_{rs} = 0$ are $\omega^+ = 2\,\pi/t_P$ and $\omega^- = -2\,\pi/t_P$, which provides the width $\omega^+ - \omega^- = 4\,\pi/t_P$ of the peak; in turn, the height of the peak is $f(\omega_{rs} = 0) = t_P^2$, this indicating that the area of the peak is proportional to t_P. In fact, from (C.15) one obtains

$$\int_{-\infty}^{+\infty} f(\omega_{rs})\,\mathrm{d}\omega_{rs} = 2\,\pi\,t_P. \qquad (14.37)$$

The form of $f(\omega_{rs})/t_P$ suggests that, if t_P is sufficiently large, such a ratio may be approximated with a Dirac delta (Sect. C.4), namely, $f(\omega_{rs}) \approx 2\,\pi\,t_P\,\delta(\omega_{rs})$, where the coefficient $2\,\pi\,t_P$ is chosen for consistency with (14.37). To this purpose one also notes that, due to the smallness of $\hbar$, the modulus of $\omega_{rs} = (E_r - E_s)/\hbar$ is very large (whence $f(\omega_{rs})$ is very small) unless $E_s = E_r$. Using the approximate form within the probability's definition (14.36) yields

$$P_{rs} \approx 2\,\pi\,\frac{|h_{rs}^{(0)}|^2}{\hbar^2}\,t_P\,\delta(\omega_{rs}) = 2\,\pi\,\frac{|h_{rs}^{(0)}|^2}{\hbar}\,t_P\,\delta(E_r - E_s). \tag{14.38}$$

As expected, P_{rs} is invariant when r and s are interchanged (compare with (C.55) and comments therein). Differentiating (14.38) with respect to t_P yields the probability[3] per unit time of the transition from state r to state s:

$$\dot{P}_{rs} \approx 2\,\pi\,\frac{|h_{rs}^{(0)}|^2}{\hbar^2}\,\delta(\omega_{rs}) = 2\,\pi\,\frac{|h_{rs}^{(0)}|^2}{\hbar}\,\delta(E_r - E_s). \tag{14.39}$$

This shows that the particle's energy is approximately conserved when the perturbation lasts for a long time. The result is intuitive, because in the limit $t_P \to \infty$ a constant perturbation is equivalent to a shift in the potential energy, which makes the Hamiltonian operator conservative at all times. On the other hand, the conservation of energy does not imply the conservation of other dynamic quantities like, e.g., momentum (compare with the analysis of the two-particle collision carried out in classical terms in Sect. 3.6 and in quantum terms in Sect. 14.6).

14.8.2 Harmonic Perturbation

Another important example is that of the harmonic perturbation at an angular frequency $\omega_0 > 0$: in this case the matrix elements read $h_{rs} = h_{rs}^{(0)}\cos(\omega_0\,t)$ for $0 \le t \le t_P$, $h_{rs}^{(0)} = \text{const} \ne 0$, and $h_{rs} = 0$ elsewhere. From (14.10) it follows

$$\int_0^{t_P} h_{rs}\,\exp(-\,\mathrm{i}\,\omega_{rs}\,t)\,\mathrm{d}t = \frac{h_{rs}^{(0)}}{2}\left[\exp\left(\frac{S\,t_P}{2\,\mathrm{i}}\right)\sigma(S) + \exp\left(\frac{D\,t_P}{2\,\mathrm{i}}\right)\sigma(D)\right], \tag{14.40}$$

with $S = \omega_{rs} + \omega_0$, $D = \omega_{rs} - \omega_0$, $\sigma(\eta) = \sin(\eta\,t_P/2)/(\eta/2)$. Comparing the definition of σ with (14.36) shows that $f = \sigma^2$, whence

$$P_{rs} = \frac{|h_{rs}^{(0)}|^2}{4\,\hbar^2}\,F(\omega_{rs}), \qquad F = f(S) + f(D) + 2\,\sigma(S)\,\sigma(D)\,\cos(\omega_0\,t_P). \tag{14.41}$$

The form of $F(\omega_{rs})/t_P$ is shown in Fig. 14.2 in arbitrary units. The largest peaks correspond to $\omega_{rs} = \omega_0$ and $\omega_{rs} = -\omega_0$; if $t_P \gg 1/\omega_0$ holds, the two peaks are practically separate whence, using as in Sect. 14.8.1 the approximation $f \simeq 2\,\pi\,t_P\,\delta$, one finds

$$P_{rs} \simeq 2\,\pi\,\frac{|h_{rs}^{(0)}|^2}{4\,\hbar^2}\,[\delta(\omega_{rs} + \omega_0) + \delta(\omega_{rs} - \omega_0)]\,t_P. \tag{14.42}$$

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[3] The expressions in terms of energy in (14.38, 14.39) are obtained from $\delta(\omega)\,\mathrm{d}\omega = \delta(E)\,\mathrm{d}E = \delta(E)\,\mathrm{d}\hbar\omega$. Compare with the comments about the dimension of Dirac's δ made in Sect. C.5.

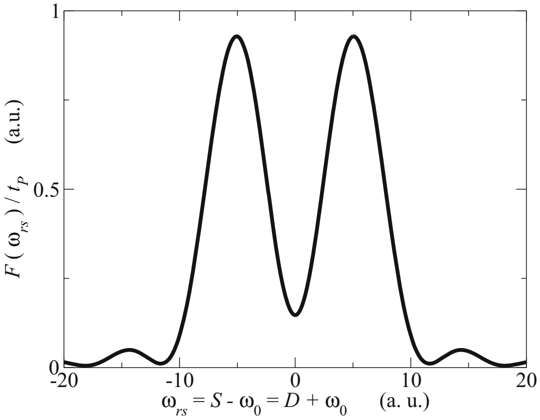

Fig. 14.2 Form of $F(\omega_{rs})/t_P$, with F given by the second expression in (14.41), with $t_P = 1$, $\omega_0 = 5$ (in arbitrary units)

Remembering that $\omega_{rs} = (E_r - E_s)/\hbar$, the transition probability per unit time due to the harmonic perturbation is finally found to be

$$\dot{P}_{rs} = 2\pi\,\frac{|h_{rs}^{(0)}|^2}{4\hbar}\,\left[\delta(E_r - E_s + \hbar\,\omega_0) + \delta(E_r - E_s - \hbar\,\omega_0)\right]. \tag{14.43}$$

When r and s are interchanged, the two summands between brackets replace each other. As $\omega_0 \neq 0$, the arguments of δ in (14.42) or (14.43) cannot vanish simultaneously. If the first vanishes it is $E_s = E_r + \hbar\,\omega_0 > E_r$, namely, the final energy E_s is larger than the initial one: the particle acquires the quantum of energy $\hbar\,\omega_0$ from the perturbing entity (*absorption*). If the second argument vanishes it is $E_s = E_r - \hbar\omega_0 < E_r$: the particle releases the energy quantum to the perturbing entity (*emission*). For example, the energy can be absorbed from, or emitted towards, an electromagnetic field; in this case the particle interacts with the mode at angular frequency ω_0 by absorbing or emitting a photon (Sect. 12.28). The total energy of the particle and field is conserved in both cases.[4] The same description applies to the interaction with a vibrational field; in this case the particle absorbs or emits a phonon (Sect. 12.5).

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[4] The spatial dependence of the field is embedded in $h_{rs}^{(0)}$.

14.8.3 Fermi's Golden Rule

Expression (14.32) gives the infinitesimal probability that a perturbation constant in time induces a transition from the initial state **b** to a final state whose energy belongs to the range $\mathrm{d}E_{\mathbf{g}}$; it is an example of a more general expression denoted with *Fermi's Golden Rule*. Remembering from Sect. 14.8.1 that, for a sufficiently large value of t_P, it is $f(\omega_{\mathbf{bg}}) \approx 2\pi\, t_P\, \delta(\omega_{\mathbf{bg}})$, one finds from (14.32)

$$\mathrm{d}P_{\mathbf{b}} \approx \left(\frac{2\pi\, m}{\hbar^2}\right)^{3/2} \frac{8\pi\, t_P\, \delta(E_{\mathbf{b}} - E_{\mathbf{g}})\, H_{\mathbf{b}}^{(0)}}{\lambda^3\, \hbar} \sqrt{E_{\mathbf{g}}}\, \mathrm{d}E_{\mathbf{g}}. \tag{14.44}$$

Dividing (14.44) by t_P provides the infinitesimal probability per unit time. Factor $\delta(E_{\mathbf{b}} - E_{\mathbf{g}})$ entails the conservation of energy; as the unperturbed Hamiltonian operator, upon which the derivation of (14.44) is based, is that of a free particle, the relation $E_{\mathbf{g}} = E_{\mathbf{b}}$ combined with the second relation in (14.21) implies $g^2 = b^2$, namely, the modulus of momentum is also conserved. The result is the same as in the case of the classical treatment of a particle's collision with another particle having a much larger mass (Sect. 3.6).

14.8.4 Transitions from Discrete to Continuous Levels

The transition probability is calculated following a reasoning similar to that of Sect. 14.5 also in the case where the initial state is labeled by a discrete index and the final state belongs to a continuous set. A physical situation where such a transition may occur is that of a particle initially trapped within a well: with reference to Sect. 11.5, the energy levels are discrete if $E < 0$, whereas they are continuous for $E > 0$, namely, the spectrum is mixed (Sect. 8.4). A particle whose initial state belongs to the discrete set may absorb from the perturbation an amount of energy sufficient for reaching the continuous set of states, thus leaving the well. As the final energy belongs to a continuous set, the outcome of the calculation is the expression of an infinitesimal probability like in Sect. 14.6.

Problems

14.1 Using (14.31) and (14.34), find $H_{\mathbf{b}}^{(0)}$ for the screened Coulomb perturbation. Assume for simplicity that the condition $g = b$ holds (Sect. 14.8.3).