Chapter 13
Time-dependent Perturbations in Quantum Mechanics

The development of time-dependent perturbation theory was initiated by Paul Dirac's early work on the semi-classical description of atoms interacting with electromagnetic fields[1]. Dirac, Wheeler, Heisenberg, Feynman and Dyson developed it into a powerful set of techniques for studying interactions and time evolution in quantum mechanical systems which cannot be solved exactly. It is used for the quantitative description of phenomena as diverse as proton-proton scattering, photo-ionization of materials, scattering of electrons off lattice defects in a conductor, scattering of neutrons off nuclei, electric susceptibilities of materials, neutron absorption cross sections in a nuclear reactor etc. The list is infinitely long. Time-dependent perturbation theory is an extremely important tool for calculating properties of any physical system.

So far all the Hamiltonians which we had studied were time-independent. This property was particularly important for the time-energy Fourier transformation from the time-dependent Schrödinger equation to a time-independent Schrödinger equation. Time-independence of H also ensures conservation of energy, as will be discussed in detail in Chapter 16. Time-dependent perturbation theory, on the other hand, is naturally also concerned with time-dependent Hamiltonians $H(t)$ (although it provides very useful results also for time-independent Hamiltonians, and we will see later that most of its applications in quantum field theory concern systems with time-independent Hamiltonians). We will therefore formulate all results in this chapter for time-dependent Hamiltonians, and only specify to time-independent cases where it is particularly useful for applications.

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[1] P.A.M. Dirac, Proc. Roy. Soc. London A 112, 661 (1926).

R. Dick, *Advanced Quantum Mechanics*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-25675-7_13

13.1 Pictures of quantum dynamics

As a preparation for the discussion of time-dependent perturbation theory (and of field quantization later on), we now enter the discussion of different *pictures* of quantum dynamics.

The picture which we have used so far is the *Schrödinger picture* of quantum dynamics: The time evolution of a system is encoded in its states $|\psi(t)\rangle$ which have to satisfy a Schrödinger equation $\mathrm{i}\hbar d|\psi_S(t)\rangle/dt = H(t)|\psi_S(t)\rangle$. However, every transformation on states and operators $|\psi\rangle \to U|\psi\rangle$, $A \to U \cdot A \cdot U^+$ with a unitary operator U leaves the matrix elements $\langle\phi|A|\psi\rangle$ and therefore the observables of a system invariant.

If U is in particular a time-dependent unitary operator, then this changes the time-evolution of the states and operators without changing the time-evolution of the observables. Application of a time-dependent $U(t)$ corresponds to a change of the picture of quantum dynamics, and two important cases besides the Schrödinger picture are the *Heisenberg picture* and the *interaction (or Dirac) picture*. In the Heisenberg picture all time dependence is cast from the states onto the operators, whereas in the Dirac picture the operators follow a “free” (or better: exactly solvable) time evolution, while the interaction (non-solvable) part of the Hamiltonian determines the time evolution of the states.

There are essentially two reasons for introducing the Heisenberg picture. The less important of these reasons is that the Hamilton-Poisson formulation of the classical limit of quantum systems is related to the Heisenberg picture. The really important reason is that quantum field theory in Chapter 17 appears first in the Heisenberg picture.

The rationale for introducing the Dirac picture is that time-dependent perturbation theory automatically leads to the calculation of matrix elements of the time evolution operator in the Dirac picture. As soon as we want to calculate transition probabilities in a quantum system under the influence of time-dependent perturbations, we automatically encounter the Dirac picture.

Before immersing ourselves into the discussion of the Heisenberg and Dirac pictures, we have to take a closer look at time evolution in the Schrödinger picture.

Time evolution in the Schrödinger picture

In the Schrödinger picture the basic operators Φ_S (like $\mathbf{x}$ or $\mathbf{p}$) are time-independent, $d\Phi_S/dt = 0$, and all the time evolution from the dynamics is carried by the states. The differential equation

$$\mathrm{i}\hbar\frac{d}{dt}|\psi_S(t)\rangle = H(t)|\psi_S(t)\rangle$$

yields an equivalent integral equation

$$|\psi_S(t)\rangle = |\psi_S(t_0)\rangle - \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)|\psi_S(\tau)\rangle,$$

and iteration of this equation yields

$$|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle$$

with the *time evolution operator*[2]

$$\begin{aligned}
U(t,t_0) &= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n\, H(\tau_1)H(\tau_2)\ldots H(\tau_n) \\
&= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t_0}^{t} d\tau_n \int_{\tau_n}^{t} d\tau_{n-1} \ldots \int_{\tau_2}^{t} d\tau_1\, H(\tau_1)H(\tau_2)\ldots H(\tau_n) \\
&= \mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right). \qquad (13.1)
\end{aligned}$$

Taking the adjoint switches t with t_0 in the argument of the time evolution operator,

$$\begin{aligned}
U^{+}(t,t_0) &= \sum_n \left(\frac{\mathrm{i}}{\hbar}\right)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \\
&= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t}^{t_0} d\tau_n \int_{t}^{\tau_n} d\tau_{n-1} \ldots \int_{t}^{\tau_2} d\tau_1\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \\
&= \mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{t}^{t_0} d\tau\, H(\tau)\right) = U(t_0,t). \qquad (13.2)
\end{aligned}$$

This and the composition law (13.7) below imply unitarity of the time evolution operator.

Please note that the *time ordering operator* T in equations (13.1) and (13.2) always ensures that the Hamiltonians are ordered from right to left such that their time arguments go from closer to the *lower integration boundary* (t_0 in equation (13.1), t in equation (13.2)) to the *upper integration boundary* (t in equation (13.1), t_0 in equation (13.2)), *irrespective of whether the upper integration boundary is larger or smaller than the lower integration boundary*, e.g. if $t > t_0$ in equation (13.1) then of course $t_0 < t$ in equation (13.2). Apparently, the identification of "lower" and "upper" integration boundary in the previous statement implies the convention that the integrand in the exponent is $-\mathrm{i}H(t)/\hbar$. Otherwise the statement would be ambiguous.

The re-ordering of integrations in the second lines of equations (13.1, 13.2) is trivial for the 0th and 1st order terms. For the higher order terms e.g. in equation (13.1) we can recursively use for any consecutive pair of integrations

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[2] F.J. Dyson, Phys. Rev. 75, 1736 (1949). Equation (13.1) gives three different representations of the time evolution operator. Equivalence of these representations is demonstrated in equations (13.3, 13.4) and in Problem 13.1.

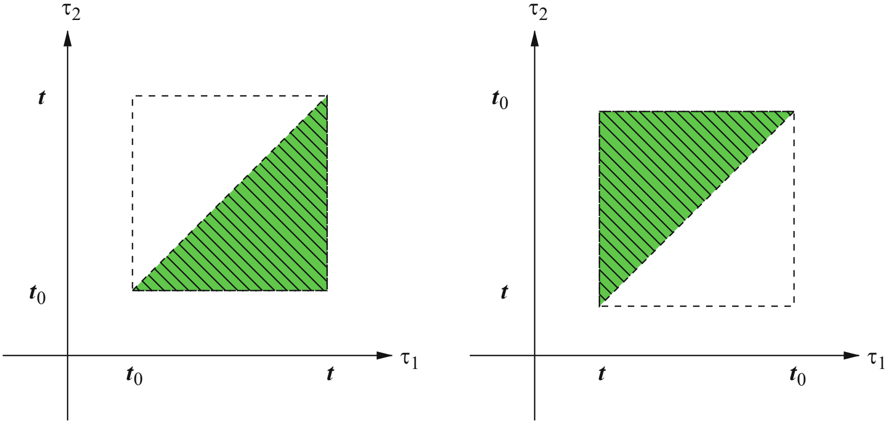

Fig. 13.1 The integration domain in equation (13.3) is shown in green. The left panel is for $t > t_0$ (forward evolution by $U(t, t_0)$), the right panel is for $t < t_0$ (backward evolution by $U(t, t_0)$). In either case re-arranging of the order of integration over the same domain yields equation (13.3)

$$\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2\, A(\tau_1, \tau_2) = \int_{t_0}^{t} d\tau_2 \int_{\tau_2}^{t} d\tau_1\, A(\tau_1, \tau_2), \tag{13.3}$$

which proves the re-ordering for $n = 2$, see also Figure 13.1. For higher n we can perform an induction step,

$$\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n+1}\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1})$$

$$= \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_{n+1} \int_{\tau_{n+1}}^{\tau_1} d\tau_n \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1})$$

$$= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_1 \int_{\tau_{n+1}}^{\tau_1} d\tau_n \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1})$$

$$= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \int_{\tau_n}^{t} d\tau_1 \int_{\tau_n}^{\tau_1} d\tau_{n-1} \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_{n+1})$$

$$= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \ldots \int_{\tau_3}^{t} d\tau_1 \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1})$$

$$= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \ldots \int_{\tau_3}^{t} d\tau_2 \int_{\tau_2}^{t} d\tau_1\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}), \tag{13.4}$$

which concludes the proof.

Time evolution operators satisfy several important properties which include Schrödinger type operator equations, unitarity, and a simple composition property. We begin with the Schrödinger type differential equations satisfied by $U(t,t')$.

The derivative with respect to the first time argument of the time evolution operator is most easily calculated using the representation in the first line of (13.1),

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U(t,t_0)=H(t)U(t,t_0), \tag{13.5}$$

while the derivative with respect to the second argument follows most easily from the second line in (13.1),

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U(t',t)=-\,U(t',t)H(t). \tag{13.6}$$

Taking the adjoint of (13.5) or using (13.2) yields

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U^{+}(t,t_0)=-\,U^{+}(t,t_0)H(t).$$

The time evolution operator is the unique solution of these differential equations with initial condition $U(t_0,t_0)=1$. The differential equations together with the initial condition also imply the integral equations

$$U(t,t')=1-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\,H(\tau)U(\tau,t')=1-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\,U(t,\tau)H(\tau).$$

Another important property of the time evolution operator is the composition law

$$U(t',t)U(t,t_0)=U(t',t_0). \tag{13.7}$$

Proving this through multiplication of the left hand side and sorting out the n-th order term is clumsy, due to the need to prove that the sum over $n+1$ n-fold integrals on the left hand side really produces the n-th order term on the right hand side. However, we can find a much more elegant proof by observing that $U(t',t)U(t,t_0)$ is actually independent of t due to equations (13.5, 13.6),

$$\frac{\partial}{\partial t}U(t',t)U(t,t_0)=0,$$

and therefore

$$U(t',t)U(t,t_0)=U(t',t')U(t',t_0)=U(t',t_0).$$

The composition law yields in particular

$$U(t_0,t)U(t,t_0)=U(t_0,t_0)=1,\quad U(t_0,t)=U^{-1}(t,t_0),$$

and combined with (13.2) this implies unitarity of the time evolution operator,

$$U^{+}(t,t_0)=U(t_0,t)=U^{-1}(t,t_0), \tag{13.8}$$

i.e. time evolution preserves the norm of states.

The time evolution operator for the harmonic oscillator

The time evolution operator for time-independent Hamiltonians H is invariant under time translations,

$$U(t-t_0)=\exp\!\left(-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right).$$

The matrix elements in x space can then be written in terms of the wave functions of energy eigenstates $H|E,\nu\rangle = E|E,\nu\rangle$, where ν is a set of degeneracy indices. There are no degeneracy indices in one dimension and the expansion takes the form

$$\langle x|U(t)|x'\rangle = \sum\!\!\!\!\!\!\int dE\,\exp\!\left(-\frac{\mathrm{i}}{\hbar}Et\right)\langle x|E\rangle\langle E|x'\rangle.$$

E.g. the time evolution operator of the harmonic oscillator

$$U(t)=\exp\!\left(-\mathrm{i}\omega a^{+}at\right)\exp(-\mathrm{i}\omega t/2)$$

has matrix elements

$$\begin{aligned}\langle x|\exp\!\left(-\mathrm{i}\omega a^{+}at\right)|x'\rangle &= \sum_{n=0}^{\infty}\langle x|n\rangle\langle n|x'\rangle\exp(-\mathrm{i}n\omega t)\\ &= \sqrt{\frac{m\omega}{\pi\hbar}}\sum_{n=0}^{\infty}\frac{\exp(-\mathrm{i}n\omega t)}{2^n n!}H_n\!\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\\ &\quad\times H_n\!\left(\sqrt{\frac{m\omega}{\hbar}}x'\right)\exp\!\left(-\frac{m\omega}{2\hbar}\left(x^2+x'^2\right)\right).\end{aligned}$$

Use of the Mehler formula (D.8) yields

$$\begin{aligned}\langle x|U(t)|x'\rangle &= \langle x|\exp\!\left(-\mathrm{i}\omega a^{+}at\right)|x'\rangle\exp(-\mathrm{i}\omega t/2)\\ &= \sqrt{\frac{m\omega}{2\pi\mathrm{i}\hbar\sin(\omega t)}}\exp\!\left(\mathrm{i}\frac{m\omega}{2\hbar}\frac{\left(x^2+x'^2\right)\cos(\omega t)-2xx'}{\sin(\omega t)}\right). \qquad (13.9)\end{aligned}$$

To use the Mehler formula we should take $\omega \to \omega - \mathrm{i}\epsilon$ for $t > 0$. This complies with the shifts $E' \to E' - \mathrm{i}\epsilon$,

$$\mathcal{G}(E)=\frac{1}{E-H+\mathrm{i}\epsilon}=\sum\!\!\!\!\!\!\int dE'\,\frac{|E'\rangle\langle E'|}{E-E'+\mathrm{i}\epsilon},$$

which define retarded Green's functions in the energy representation, see e.g. (11.8, 20.14). The time-dependent retarded Green's function for the oscillator is related to the propagator (13.9) in the standard way

$$\langle x|\mathcal{G}(t)|x'\rangle = \frac{\Theta(t)}{\mathrm{i}\hbar}\langle x|U(t)|x'\rangle.$$

The Heisenberg picture

In the Heisenberg picture we use the unitary time evolution operator $U(t, t_0)$ to cast the time dependence from the states onto the operators,

$$|\psi_H\rangle = |\psi_S(t_0)\rangle = U^+(t,t_0)|\psi_S(t)\rangle,$$
$$\Phi_H(t) = U^+(t,t_0)\Phi_S U(t,t_0).$$

For the time evolution of the operators in the Heisenberg picture we observe that

$$\begin{aligned}\Phi_H(t) &= U^+(t,t_0)\Phi_S U(t,t_0) = U^+(t,t_0)\Phi_S U^+(t_0,t)\\ &= U^+(t,t')U^+(t',t_0)\Phi_S U^+(t_0,t')U^+(t',t) = U^+(t,t')\Phi_H(t')U(t,t'),\end{aligned}$$

and the Heisenberg evolution equation

$$\begin{aligned}\mathrm{i}\hbar\frac{d}{dt}\Phi_H(t) &= -U^+(t,t_0)[H(t)\Phi_S - \Phi_S H(t)]U(t,t_0)\\ &= -U^+(t,t_0)H(t)U(t,t_0)U^+(t,t_0)\Phi_S U(t,t_0)\\ &\quad + U^+(t,t_0)\Phi_S U(t,t_0)U^+(t,t_0)H(t)U(t,t_0)\\ &= -[H_H(t),\Phi_H(t)]. \end{aligned}\tag{13.10}$$

In the last equation, $H_H(t)$ is the Hamiltonian written in terms of operators $\Phi_H(t)$ in the Heisenberg picture.

For time-dependent $\Phi_S(t)$ we have

$$\frac{d}{dt}\Phi_H(t) = U^+(t,t_0)\left(\frac{\mathrm{i}}{\hbar}[H(t),\Phi_S(t)] + \frac{d}{dt}\Phi_S(t)\right)U(t,t_0).$$

13.2 The Dirac picture

For the Dirac or interaction picture we split the Schrödinger picture Hamiltonian $H(t)$ into a "free" (or rather: solvable) part $H_0(t)$ and an "interaction" (or rather: perturbation) part $V(t)$,

$$H(t) = H_0(t) + V(t), \tag{13.11}$$

and define the "free" time evolution operator

$$U_0(t,t_0) = \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H_0(\tau)\right).$$

The common terminology of denoting $H_0(t)$ and $U_0(t,t_0)$ as "free" Hamiltonian and time evolution operator while $V(t)$ is the "interaction" part is motivated from scattering theory, which is one of the most common applications of time-dependent perturbation theory. However, we should always keep in mind that $H_0(t)$ does not really need to be a free particle Hamiltonian. E.g. for a hydrogen atom under the influence of an external electromagnetic field with wavelength $\lambda \gg a_0$, the "free" part H_0 would actually be the hydrogen Hamiltonian including the Coulomb interaction between the proton and the electron, while $V(t)$ would describe the effective coupling of the electromagnetic field to the quasiparticle which describes relative motion in the hydrogen atom. We will discuss this case in detail in Chapter 18, and in particular in Section 18.4.

The interaction picture splits off the solvable part of the time evolution from the states,

$$\begin{aligned}|\psi_D(t)\rangle &= U_0^+(t,t_0)|\psi_S(t)\rangle = U_0^+(t,t_0)U(t,t')|\psi_S(t')\rangle \\ &= U_0^+(t,t_0)U(t,t')U_0(t',t_0)|\psi_D(t')\rangle = U_D(t,t')|\psi_D(t')\rangle, \quad (13.12)\end{aligned}$$

where the last line identifies the time evolution operator $U_D(t,t')$ acting on the states in the interaction picture.

The solvable part of the time evolution is cast onto the operators

$$\Phi_D(t) = U_0^+(t,t_0)\Phi_S U_0(t,t_0) \quad (13.13)$$

to preserve the time evolution of matrix elements and expectation values in the interaction picture.

Substituting the composition law for time evolution operators confirms that $\Phi_D(t)$ evolves freely between different times,

$$\begin{aligned}\Phi_D(t) &= U_0^+(t,t_0)\Phi_S U_0^+(t_0,t) = U_0^+(t,t')U_0^+(t',t_0)\Phi_S U_0^+(t_0,t')U_0^+(t',t) \\ &= U_0^+(t,t')\Phi_D(t')U_0(t,t'), \quad (13.14)\end{aligned}$$

and substituting $\Phi_H(t)$ for Φ_S shows that $\Phi_D(t)$ is related to the operator in the Heisenberg picture through the particular variant $U_D(t,t_0)$ of the interaction picture evolution operator $U_D(t,t')$ (13.12),

$$\begin{aligned}\Phi_D(t) &= U_0^+(t,t_0)U(t,t_0)\Phi_H(t)U^+(t,t_0)U_0(t,t_0) \\ &= U_D(t,t_0)\Phi_H(t)U_D^+(t,t_0). \quad (13.15)\end{aligned}$$

The differential equation for time evolution of the operators is

$$\begin{aligned}
\mathrm{i}\hbar\frac{d}{dt}\Phi_D(t) &= -\,U_0^+(t,t_0)[H_0(t)\Phi_S - \Phi_S H_0(t)]U_0(t,t_0) \\
&= -\,U_0^+(t,t_0)H_0(t)U_0(t,t_0)U_0^+(t,t_0)\Phi_S U_0(t,t_0) \\
&\quad + U_0^+(t,t_0)\Phi_S U_0(t,t_0)U_0^+(t,t_0)H_0(t)U_0(t,t_0) \\
&= -\,[H_{0,D}(t),\Phi_D(t)],
\end{aligned}$$

where in the last equation (similar to the previous remark for the Heisenberg picture) $H_{0,D}(t)$ is written in terms of operators $\Phi_D(t)$ in the Dirac picture.

The interactions are encoded in the time evolution of the states,

$$\begin{aligned}
\mathrm{i}\hbar\frac{d}{dt}|\psi_D(t)\rangle &= U_0^+(t,t_0)[H(t)-H_0(t)]|\psi_S(t)\rangle \\
&= U_0^+(t,t_0)V(t)U_0(t,t_0)|\psi_D(t)\rangle = H_D(t)|\psi_D(t)\rangle, \qquad (13.16)
\end{aligned}$$

where again $U_0^+(t,t_0)V(t)U_0(t,t_0) = V_D(t) \equiv H_D(t)$ due to the operator transition $\Phi_S \to \Phi_D$ in the Hamiltonians.

Conversion of equation (13.16) into the equivalent integral equation gives us another equation for the time evolution operator $U_D(t,t')$ for the states in the Dirac picture,

$$U_D(t,t') = U_0^+(t,t_0)U(t,t')U_0(t',t_0) = \mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\, H_D(\tau)\right). \qquad (13.17)$$

This evolution operator apparently satisfies

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U_D(t,t') = H_D(t)U_D(t,t'), \quad \mathrm{i}\hbar\frac{\partial}{\partial t'}U_D(t,t') = -\,U_D(t,t')H_D(t').$$

We have split the time evolution asymmetrically between states and operators, and therefore there are two Hamiltonians and related time evolution operators in the interaction picture: the "free" Hamiltonian $H_0(t)$ for the evolution of the operators and the interaction Hamiltonian $H_D(t)$ for the evolution of the states (and then there is the third Hamiltonian $H(t)$ and its time evolution operator appearing in the derivation of the interaction picture).

If we substitute[3]

$$H_D(t) = U_0^+(t,t_0)V(t)U_0(t,t_0) = U_0(t_0,t)V(t)U_0(t,t_0)$$

into equation (13.17) and use the composition property for time evolution operators

$$U_0(\tau,t_0)U_0(t_0,\tau') = U_0(\tau,\tau'),$$

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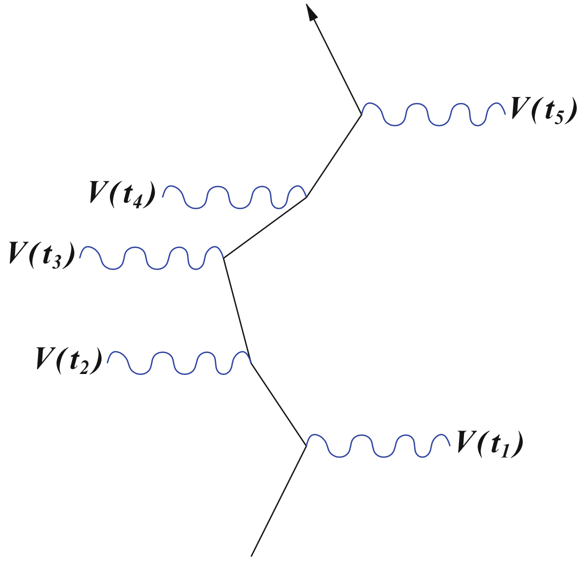
[3] The transformation law for operators from the Schrödinger picture into the interaction picture implies $H_D(t) \equiv V_D(t)$. The notation $V_D(t)$ is therefore also often used for $H_D(t)$.

Fig. 13.2 Scattering off a time-dependent perturbation



we find

$$
\begin{aligned}
U_D(t,t') &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right) \\
&= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t} d\tau_1\int_{t'}^{\tau_1} d\tau_2\ldots\int_{t'}^{\tau_{n-1}} d\tau_n\, H_D(\tau_1)H_D(\tau_2)\ldots H_D(\tau_n) \\
&= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t} d\tau_1\int_{t'}^{\tau_1} d\tau_2\ldots\int_{t'}^{\tau_{n-1}} d\tau_n\, U_0(t_0,\tau_1)V(\tau_1)U_0(\tau_1,\tau_2) \\
&\quad \times V(\tau_2)U_0(\tau_2,\tau_3)\ldots U_0(\tau_{n-1},\tau_n)V(\tau_n)U_0(\tau_n,t_0). \qquad (13.18)
\end{aligned}
$$

The n-th term in the sum can be interpreted as n scatterings at the perturbation $V(t)$, with "free" time evolution under the Hamiltonian $H_0(t)$ between any two scattering events, see Figure 13.2. In the end everything is evolved again to the fiducial time t_0. Equation (13.21) below will show that this as a consequence of the fact that we will express transition probability amplitudes in terms of states at some fixed time t_0.

Dirac picture for constant H_0

We have $H_0 = H_{0,D}$ if H_0 is a time-independent operator in the Schrödinger picture, because H_0 and $U_0(t,t_0) = \exp[-\mathrm{i}H_0(t-t_0)/\hbar]$ commute.

The Hamiltonian $H_D(t)$ acting on the states in the interaction picture is related to the Hamiltonian with the ordinary operators $\mathbf{p}$, $\mathbf{x}$,... of the Schrödinger picture via

$$H_D(t) = \exp\!\left(\frac{\mathrm{i}}{\hbar}H_0(t-t_0)\right) V(t) \exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(t-t_0)\right).$$

The time evolution operator for the states in the interaction picture is then

$$\begin{aligned}
U_D(t,t') &= \mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\, H_D(\tau)\right)\\
&= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ldots\int_{t'}^{\tau_{n-1}}d\tau_n\, \exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(t_0-\tau_1)\right)\\
&\quad\times V(\tau_1)\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_1-\tau_2)\right)V(\tau_2)\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_2-\tau_3)\right)\ldots\\
&\quad\times \exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_{n-1}-\tau_n)\right)V(\tau_n)\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_n-t_0)\right).
\end{aligned} \tag{13.19}$$

The case of time-independent unperturbed operators H_0 is the most common case in applications of time-dependent perturbation theory. Equation (13.19) therefore shows the most commonly employed form of $U_D(t,t')$ for the evaluation of the transition amplitudes or scattering matrix elements which will be introduced in Section 13.3.

13.3 Transitions between discrete states

We are now in a position to discuss transitions in a quantum system under the influence of time-dependent perturbations. We are still operating in the framework of "ordinary" quantum mechanics ("first quantized theory"), and at this stage time-dependent perturbations of a quantum system arise from time dependence of the parameters in the Schrödinger equation.

We will denote states as *discrete states* if they can be characterized by a set of discrete quantum numbers, e.g. the bound energy eigenstates $|n,\ell,m_\ell,m_s\rangle$ of hydrogen or the states $|n_1,n_2,n_3\rangle$ of a three-dimensional harmonic oscillator are discrete. States which require at least one continuous quantum number for their labeling are denoted as *continuous states*. Momentum eigenstates $|\boldsymbol{k}\rangle$ are examples of continuous states. Quantum mechanical transitions involving continuous states require special considerations. Therefore we will first discuss transitions between discrete states, e.g. transitions between atomic or molecular bound states.

We consider a system with an unperturbed Hamiltonian H_0 under the influence of a perturbation $V(t)$:

$$H(t) = H_0 + V(t).$$

The perturbation operator will in general be a function of the operators $\mathbf{p}$ and $\mathbf{x}$, $V(t) \equiv V(\mathbf{p}, \mathbf{x}, t)$. We will see later that in many applications $V(t)$ has the form

$$V(\mathbf{p}, \mathbf{x}, t) = V_1(\mathbf{x}, t) + \mathbf{p} \cdot \boldsymbol{V}_2(\mathbf{x}, t). \tag{13.20}$$

In this section we assume that all states under consideration can be normalized to 1.

For the calculation of transition probabilities in the system, recall that the expansion of a general state $|\phi\rangle$ in terms of an orthonormal complete set of states $|\psi_n\rangle$ is

$$|\phi\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\phi\rangle,$$

and therefore the probability $P_n(\phi)$ of finding the state $|\psi_n\rangle$ in a measurement performed on the state $|\phi\rangle$ is $P_n(\phi) = |\langle\psi_n|\phi\rangle|^2$. We can also understand this as the expectation value of the projection operator $|\psi_n\rangle\langle\psi_n|$ in the state $|\phi\rangle$.

Now assume that the state $|\phi\rangle$ is a state $|\psi_{in}(t)\rangle$, where the state at an earlier time $t' < t$ was an unperturbed state $|\psi_{in}^{(0)}(t')\rangle$, typically an eigenstate of H_0. Then we know that the state at time t is

$$|\psi_{in}(t)\rangle = U(t, t')|\psi_{in}^{(0)}(t')\rangle,$$

and since the state now evolved with the full Hamiltonian including the perturbation $V(t)$, it will not be an unperturbed state any more, but a superposition of unperturbed states. If at time t a measurement is performed on the state $|\psi_{in}(t)\rangle$, the probability to measure a certain unperturbed state $|\psi_{out}^{(0)}(t)\rangle$ will be $|\langle\psi_{out}^{(0)}(t)|\psi_{in}(t)\rangle|^2$.

Therefore the probability amplitude for transition from an unperturbed state $|\psi_{in}^{(0)}(t')\rangle$ to an unperturbed state $|\psi_{out}^{(0)}(t)\rangle$ between times t' and t is

$$\begin{aligned}\langle\psi_{out}^{(0)}(t)|\psi_{in}(t)\rangle &= \langle\psi_{out}^{(0)}(t)|U(t, t')|\psi_{in}^{(0)}(t')\rangle \\ &= \langle\psi_{out}^{(0)}(t_0)|U_0^+(t, t_0)U(t, t')U_0(t', t_0)|\psi_{in}^{(0)}(t_0)\rangle \\ &= \langle\psi_{out}^{(0)}(t_0)|U_D(t, t')|\psi_{in}^{(0)}(t_0)\rangle.\end{aligned} \tag{13.21}$$

The transition probability amplitudes between unperturbed states are matrix elements of the time evolution operator in the interaction picture, where the unperturbed states are taken at some arbitrary fixed time.

The Schrödinger equations for the unperturbed states $|\psi^{(0)}(t_0)\rangle$ and the free evolution operators $U_0(t',t_0)$ and $U_0^+(t,t_0)$ imply

$$\frac{\partial}{\partial t_0}\langle\psi_{out}^{(0)}(t_0)|U_0^+(t,t_0)U(t,t')U_0(t',t_0)|\psi_{in}^{(0)}(t_0)\rangle = 0, \tag{13.22}$$

i.e. the choice of the parameter t_0 is (of course) irrelevant for the transition matrix element. We set $t_0 = 0$ in the following.

If we substitute the expansion (13.18) for the time evolution operator in the interaction picture we get a series

$$\begin{aligned}\langle\psi_{out}^{(0)}(0)|U_D(t,t')|\psi_{in}^{(0)}(0)\rangle &= \langle\psi_{out}^{(0)}(0)|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau H_D(\tau)\right)|\psi_{in}^{(0)}(0)\rangle\\
= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ldots\int_{t'}^{\tau_{n-1}}d\tau_n\,&\langle\psi_{out}^{(0)}(0)|\exp\left(\frac{\mathrm{i}}{\hbar}H_0\tau_1\right)\\
\times V(\tau_1)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_1-\tau_2)\right)&V(\tau_2)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_2-\tau_3)\right)\\
\times\ldots\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_{n-1}-\tau_n)\right)&V(\tau_n)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0\tau_n\right)|\psi_{in}^{(0)}(0)\rangle.\end{aligned} \tag{13.23}$$

Now we assume that our unperturbed states are energy eigenstates

$$\begin{aligned}|\psi_{out}^{(0)}(0)\rangle &= |\psi_n(0)\rangle = |n\rangle,\ \ H_0|\psi_n(0)\rangle = E_n|\psi_n(0)\rangle,\\
|\psi_{in}^{(0)}(0)\rangle &= |\psi_m(0)\rangle = |m\rangle,\ H_0|\psi_m(0)\rangle = E_m|\psi_m(0)\rangle\end{aligned}$$

of the unperturbed Hamiltonian. Equation (13.23) then yields for the transition probability amplitude between eigenstates of H_0 (see also equation (13.19)),

$$\begin{aligned}\langle n|U_D(t,t')|m\rangle = \delta_{n,m} &- \frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\ \exp(\mathrm{i}\omega_{nm}\tau)\langle n|V(\tau)|m\rangle\\
&-\frac{1}{\hbar^2}\sum_l\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ \exp(\mathrm{i}\omega_{nl}\tau_1)\langle n|V(\tau_1)|l\rangle\\
&\times\exp(\mathrm{i}\omega_{lm}\tau_2)\langle l|V(\tau_2)|m\rangle + \ldots,\end{aligned} \tag{13.24}$$

with the transition frequencies $\omega_{nm} = (E_n - E_m)/\hbar$.

The transition probability from a discrete state $|m\rangle$ to a discrete state $|n\rangle$ is then

$$P_{m\to n}(t,t') = \left|\langle n|U_D(t,t')|m\rangle\right|^2. \tag{13.25}$$

Equation (13.24) assumes that we use eigenstates of H_0 for the initial and final states, but equation (13.25) holds for arbitrary discrete initial and final states, and we even do not have to require the same basis for the decomposition of the initial and the final state, i.e. equation (13.25) also holds if m and n are discrete quantum numbers referring to different bases of states.

$P_{m\to n}(t,t')$ is a dimensionless positive number if both the initial and final states are discrete states, i.e. dimensionless states (see the discussion of dimensions of states in Section 5.3), and due to the unitarity of $U_D(t,t')$ it is also properly normalized as a probability,

$$\sum_n P_{m\to n}(t,t') = \sum_n \langle m|U_D^+(t,t')|n\rangle\langle n|U_D(t,t')|m\rangle = \langle m|m\rangle = 1.$$

As a corollary, this observation also implies $0 \leq |\langle n|U_D(t,t')|m\rangle|^2 \leq 1$, as required for a probability.

We will denote the *transition probability amplitude* $\langle n|U_D(t,t')|m\rangle$ also as a *scattering matrix element* or *S matrix element*,

$$\begin{aligned}
S_{nm}(t,t') &= \langle n|U_D(t,t')|m\rangle = \langle n|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right)|m\rangle \\
&= \langle m|U_D^+(t,t')|n\rangle^* = \langle m|U_D(t',t)|n\rangle^* = \left(S_{mn}^{-1}(t,t')\right)^* \\
&= \left(S^{-1+}(t,t')\right)_{nm}.
\end{aligned} \tag{13.26}$$

In the literature this definition is more commonly employed with default values $t \to \infty$, $t' \to -\infty$ for the initial and final times, $S_{nm} \equiv S_{nm}(\infty,-\infty)$. It is also usually reserved for transitions with two particles in the initial state (to be discussed in Chapter 17 and following chapters), but here we are still dealing with a single particle perturbed by a potential $V(t)$, or an effective single particle description of relative motion of two particles. The connection with many particle scattering theory later on is easier if we introduce the scattering matrix already for single particle problems, and it is also useful to have this notion available for arbitrary initial and final times.

Møller operators

At this point it is also interesting to note a factorized representation of the time evolution operator in the interaction picture, which is applicable if both H and H_0 do not depend on time. In this case we have with $t_0 = 0$,

$$U_D(t,t') = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right) = \Omega^+(t)\Omega(t')$$

with the Møller operator

$$\Omega(t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right).$$

Let us repeat the basic equation (13.21) and substitute this definition,

$$\begin{aligned}\langle\psi_{out}^{(0)}(t)|\psi_{in}(t)\rangle &= \langle\psi_{out}^{(0)}(t)|U(t,t')|\psi_{in}^{(0)}(t')\rangle\\ &= \langle\psi_{out}^{(0)}|U_0^+(t)U(t,t')U_0(t')|\psi_{in}^{(0)}\rangle = \langle\psi_{out}^{(0)}|U_D(t,t')|\psi_{in}^{(0)}\rangle\\ &= \langle\psi_{out}^{(0)}|\Omega^+(t)\Omega(t')|\psi_{in}^{(0)}\rangle = \langle\Psi_{out}\{t\}|\Psi_{in}\{t'\}\rangle.\end{aligned}$$

Here we have introduced states

$$\begin{aligned}|\Psi\{t\}\rangle = \Omega(t)|\psi^{(0)}\rangle &= \exp\!\left(\frac{\mathrm{i}}{\hbar}Ht\right)\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0t\right)|\psi^{(0)}\rangle\\ &= \exp\!\left(\frac{\mathrm{i}}{\hbar}Ht\right)|\psi^{(0)}(t)\rangle.\end{aligned} \tag{13.27}$$

For the interpretation of these states we notice

$$\exp\!\left(-\frac{\mathrm{i}}{\hbar}Ht\right)|\Psi\{t\}\rangle = |\psi^{(0)}(t)\rangle,$$

i.e. $|\Psi\{t\}\rangle$ is the fictitious interacting state at time $t_0 = 0$ which yields the unperturbed state $|\psi^{(0)}(t)\rangle$ at time t under *full* time evolution from $t_0 = 0$ to t.

In the framework or quantum mechanics, the case that both H and H_0 are time-independent would often be dealt with in the framework of time-independent perturbation theory or potential scattering theory. However, we will see later that in the framework of quantum field theory, time-independent H and H_0 is very common in applications of time-dependent perturbation theory.

First order transition probability between discrete energy eigenstates

For $n \neq m$, the first order result for S_{nm} is the matrix element of the Fourier component $V(\omega_{nm})$,

$$\begin{aligned}S_{nm} &= -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}dt\,\exp(\mathrm{i}\omega_{nm}t)\langle n|V(t)|m\rangle\\ &= -\frac{\mathrm{i}}{\hbar}\sqrt{2\pi}\,\langle n|V(\omega_{nm})|m\rangle.\end{aligned} \tag{13.28}$$

If the time dependence of the perturbation $V(t)$ is such that the Fourier transform $V(\omega)$ exists in the sense of standard Fourier theory (i.e. if $V(\omega)$ is a sufficiently well behaved function, which is the case e.g. if $V(t)$ is absolutely integrable or square integrable with respect to t), then the first order scattering matrix (13.28) provides us with finite first order approximations for transition probabilities

$$P_{m\to n} = |S_{nm}|^2 = \frac{2\pi}{\hbar^2}\,|\langle n|V(\omega_{nm})|m\rangle|^2\,. \tag{13.29}$$

Note that the Fourier transform

$$V(\omega) = \frac{1}{\sqrt{2\pi}}\int dt\,\exp(\mathrm{i}\omega t)V(t)$$

of a potential $V(t)$ has the dimension energy×time. Therefore $P_{m\to n}$ is a dimensionless number, as it should be. Furthermore, the probability interpretation and the use of first order perturbation theory entail that we should have $|\langle n|V(\omega_{nm})|m\rangle| < \hbar/\sqrt{2\pi}$. Otherwise first order perturbation theory is not applicable and higher order terms must be included to estimate transition probabilities.

The first order transition probability between discrete states requires existence of a regular Fourier transform $V(\omega)$ of the perturbation $V(t)$. This condition is not satisfied in the important case of monochromatic perturbations like $V(t) = W\exp(-\mathrm{i}\omega t)$, which have a δ function as Fourier transform,

$$V(t) = W\exp(-\mathrm{i}\omega t), \quad V(\omega_{nm}) = \sqrt{2\pi}\,W\delta(\omega_{nm}-\omega).$$

Consistent treatment of this case requires that at least one of the states involved is part of a continuum of states, as discussed in Sections 13.4 and 13.5. If both the initial and final atomic or molecular state are discrete, then the perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ must be treated as arising from a quantized field which comes with its own continuum of states. Monochromatic perturbations $V(t) = W\exp(\pm\mathrm{i}\omega t)$ typically arise from photon absorption or emission, and the previous statement simply means that the consistent treatment of transitions between bound states due to monochromatic perturbations requires the full quantum theory of the photon, see Section 18.6. See also Problem 13.6 for an explanation why the Golden Rule of first order perturbation theory, which is discussed in the next section, cannot be used for transitions between discrete states.

13.4 Transitions from discrete states into continuous states: Ionization or decay rates

Ionization of atoms or molecules, transitions from discrete donor states into conduction bands in n-doped semiconductors, or disintegration of nuclei are processes where particles make a transition from discrete states into states in a continuum.

We assume that the unperturbed Hamiltonian H_0 contains an attractive radially symmetric potential which generates bound states $|n,\ell,m\rangle$, where ℓ and m are the usual angular momentum quantum numbers for the bound states and the quantum number n labels the energy levels. The free states for H_0 are usually given in terms of hypergeometric functions, e.g. the Coulomb waves $|k,\ell,m\rangle$ from Section 7.9.

Here we initially use plane wave states instead and ask for the probability for the system to go from a bound state $|n,\ell,m\rangle$ into a plane wave state $|\boldsymbol{k}\rangle$ under the influence of a perturbation $V(t)$. This is a simplification, but the prize that we pay is that the transition matrix elements from a bound state into plane waves do not necessarily tell us something about ionization or decay of a bound system, because those transition matrix elements will also not vanish for perturbations which primarily generate another bound state since the bound states can also be written as superpositions of plane waves, see e.g. Problem 13.7. Therefore the transition matrix elements into plane wave states generically correspond to a mixture of transitions into bound states and free states. However, the focus in this preliminary discussion is not the calculation of actual ionization or decay rates, but to explain how continuous final states affect the interpretation of transition matrix elements.

For continuous final states like $|\boldsymbol{k}\rangle$, the appropriate projection of $U_D(t,t')|\psi_{in}^{(0)}\rangle$ is onto the dimensionless combination $\sqrt{d^3\boldsymbol{k}}\langle\boldsymbol{k}|$ (recall from $\langle\boldsymbol{k}|\boldsymbol{k}'\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}')$ that the plane wave states $|\boldsymbol{k}\rangle$ in three dimensions have length dimension length$^{3/2}$, see Section 5.3). This means that in a transition from a discrete state $|n,\ell,m\rangle$ into a momentum eigenstate $\boldsymbol{k}$, the dimensionless quantity

$$\sqrt{d^3\boldsymbol{k}}\, S_{\boldsymbol{k};n,\ell,m}(t,t') = \sqrt{d^3\boldsymbol{k}}\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle$$

is a *differential transition probability amplitude*, in the sense that

$$dP_{n,\ell,m\to\boldsymbol{k}}(t,t') = d^3\boldsymbol{k}\,\left|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle\right|^2$$

is a *differential transition probability* for the transition from the discrete state into a volume element $d^3\boldsymbol{k}$ around the vector $\boldsymbol{k}$ in momentum space. The meaning of this statement is that

$$P_{n,\ell,m\to\mathcal{K}}(t,t') = \int_{\mathcal{K}} d^3\boldsymbol{k}\,\left|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle\right|^2 \tag{13.30}$$

is the *transition probability* from the discrete state $|n,\ell,m\rangle$ into a volume $\mathcal{K}$ in $\boldsymbol{k}$-space. Another way to say this is to denote the quantity with the dimension length^3

$$\mathcal{P}_{n,\ell,m\to\boldsymbol{k}}(t,t') = \frac{dP_{n,\ell,m\to\boldsymbol{k}}(t,t')}{d^3\boldsymbol{k}} = \left|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle\right|^2$$

as the *transition probability density* per $\boldsymbol{k}$-space volume. The S matrix element

$$S_{\boldsymbol{k};n,\ell,m}(t,t') = \langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle$$

is then a *transition probability density amplitude* (just like a wave function $\langle\boldsymbol{x}|\psi(t)\rangle$ is a *probability density amplitude* rather than a probability amplitude, but for obvious reasons neither of these designations are ever used).

With this interpretation, the transition amplitudes into continuous states yield correctly normalized probabilities, e.g. for plane waves,

$$\begin{aligned}\int d^3\boldsymbol{k}\,\mathcal{P}_{n,\ell,m\to\boldsymbol{k}}(t,t') &= \int d^3\boldsymbol{k}\,\left|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle\right|^2\\ &= \int d^3\boldsymbol{k}\,\langle n,\ell,m|U_D^+(t,t')|\boldsymbol{k}\rangle\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle\\ &= \langle n,\ell,m|U_D^+(t,t')U_D(t,t')|n,\ell,m\rangle\\ &= \langle n,\ell,m|n,\ell,m\rangle = 1.\end{aligned}$$

The important conclusion from this is that transition matrix elements of $U_D(t,t')$ from discrete states into continuous final states yield transition probability *densities*, which have to be integrated to yield transition probabilities. We will also rediscover this in the framework of the spherical Coulomb waves in the following subsection.

Ionization probabilities for hydrogen

Now that we have clarified the meaning of transition amplitudes from discrete states into continuous states with the familiar basis of plane wave states, let us come back to the ionization or decay problems, i.e. transitions from the discrete bound spectrum of an unperturbed Hamiltonian H_0 into the continuum of unbound states. We will use hydrogen states as an example, but the derivations go through in the same way for any Hamiltonian H_0 with discrete and continuous states.

The unperturbed Hamiltonian for hydrogen is

$$H_0 = \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}, \tag{13.31}$$

and the ionization problem concerns transitions from bound states $|n,\ell,m\rangle$ into Coulomb waves $|k,\ell,m\rangle$ under the influence of a time-dependent perturbation[4] $V(t)$. The contribution from Coulomb waves to the decomposition of unity in terms of hydrogen states came with a measure k^2dk (7.75),

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[4] If the perturbation $V(t)$ contains directional information (e.g. polarization of an incoming photon or the direction of an electric field), then we might also like to calculate probabilities for the direction of dissociation of the hydrogen atom. This direction would be given by the $\boldsymbol{k}$ vector of relative motion between the electron and the proton after separation. For the calculation of directional information we would have to combine the spherical Coulomb waves $|k,\ell,m\rangle$ into states which approximate plane wave states $|\boldsymbol{k}\rangle$ at infinity, similar to the construction of incoming approximate plane wave states in Section 13.5, see also the discussion of the photoeffect in [3].

$$
\begin{aligned}
1 &= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty}|n,\ell,m\rangle\langle n,\ell,m| + \int_0^{\infty}dk\,k^2|k,\ell,m\rangle\langle k,\ell,m|\right)\\
&= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty}|n,\ell,m\rangle\langle n,\ell,m| + \int_0^{\infty}dE\,|E,\ell,m\rangle\varrho(E)\langle E,\ell,m|\right),
\end{aligned}
$$

where we also introduced an energy representation for the spherical Coulomb waves, $|E,\ell,m\rangle = |k,\ell,m\rangle$,

$$E = \frac{\hbar^2k^2}{2\mu} = \frac{\hbar^2k^2}{2}\left(\frac{1}{m_e}+\frac{1}{m_p}\right),$$

and the corresponding density of spherical Coulomb waves in the energy scale,

$$\varrho(E) = \Theta(E)k^2\frac{dk}{dE} = \frac{\Theta(E)}{\hbar^3}\sqrt{2\mu^3E}. \tag{13.32}$$

This differs from (12.13) for $d = 3$ by missing a factor $g/2\pi^2 = g4\pi/8\pi^3$. The spin factor is $g = 1$, because spin flips can usually be neglected in ionization transitions. Inclusion of spin quantum numbers m_s and m_s' for the initial and final states would therefore result in a factor $\delta_{m_s,m_s'}$. There is no factor 4π because the angular directions in $\boldsymbol{k}$ space have been discretized in terms of angular momentum quantum numbers (ℓ,m), and there is no factor $(2\pi)^{-3}$ because the density $\varrho(E)$ in equation (13.32) is a number of states per unit of energy, but it is *not* a number of states per energy and *volume* (remember $V \to (2\pi)^3$ in the continuum limit). It comes in units $\mathrm{cm}^{-3}\mathrm{eV}^{-1}$ because the projector $|k,\ell,m\rangle\langle k,\ell,m|$ for spherical Coulomb waves has dimension length^3, and therefore scattering matrix elements $|\langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2$ from bound states into ionized states come in units of cm^3. Please also recall the remark after equation (12.8).

Suppose we start with an unperturbed bound state $|n,\ell,m\rangle$. We can calculate two kinds of scattering matrix elements, *viz.* for transitions into bound states,

$$S_{n',\ell',m';n,\ell,m} = \langle n',\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle,$$

and into ionized states

$$S_{E,\ell',m';n,\ell,m} = \langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle, \quad E > 0.$$

For the sums of the absolute squares of these scattering matrix elements, we observe from the completeness relation for hydrogen states, the unitarity of $U_D(\infty,-\infty)$, and $\langle n,\ell,m|n,\ell,m\rangle = 1$ that

$$\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\left(\sum_{n'=\ell'+1}^{\infty}|\langle n',\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2\right.$$
$$\left.+\int_0^\infty dE\,\varrho(E)\,|\langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2\right)=1.$$

This confirms $0 \leq |\langle n',\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2 \leq 1$, as is required for transition probabilities between bound states, but it also tells us that

$$\begin{aligned}P_{n,\ell,m\to E>0} &= 1-P_{n,\ell,m\to E<0}\\ &=\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\int_0^\infty dE\,\varrho(E)\,|\langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2\end{aligned} \qquad (13.33)$$

must be the ionization probability due to the perturbation $V(t)$, since the sum over all transition probabilities into bound states is

$$P_{n,\ell,m\to E<0}=\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\sum_{n'=\ell'+1}^{\infty}|\langle n',\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2.$$

This confirms again that absolute squares of scattering matrix elements into continuous final states must be integrated against final state densities to yield transition probabilities, where the appropriate density of final states follows from the completeness relation of the unperturbed system.

If we want to know the probability for the hydrogen atom to ionize into a state with energy $0 < E_1 \leq E \leq E_2$ for the relative motion between proton and electron, we have to calculate

$$P_{n,\ell,m\to[E_1,E_2]}=\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\int_{E_1}^{E_2} dE\,\varrho(E)\,|\langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2.$$

On the other hand, if we only know the energy level E_n of the initial bound state, we would calculate the ionization probability of the atom as a weighted average

$$P_{E_n\to E>0}=\frac{1}{n^2}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}P_{n,\ell,m\to E>0}. \qquad (13.34)$$

The first order results for the ionization probabilities follow from the first order scattering matrix elements

$$\begin{aligned}
S^{(1)}_{k,\ell',m';n,\ell,m} &= \langle k,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle^{(1)} \\
&= -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty} dt\,\exp\!\left(\frac{\mathrm{i}}{\hbar}\,(E_k-E_n)\,t\right)\langle k,\ell',m'|V(t)|n,\ell,m\rangle \\
&= -\mathrm{i}\frac{\sqrt{2\pi}}{\hbar}\langle k,\ell',m'|V(\omega_{kn})|n,\ell,m\rangle, \qquad (13.35)
\end{aligned}$$

with the transition frequency $\omega_{kn} = (E_k - E_n)/\hbar$. This assumes that the Fourier transformed operator $V(\omega_{kn})$ exists in the sense of standard Fourier theory. The case of a monochromatic perturbation, for which the Fourier transform is a δ function in frequency space, requires special treatment and is discussed in the following subsection.

Even for well behaved Fourier transform $V(\omega_{kn})$, use of the first order result (13.35) to estimate the ionization probability,

$$P^{(1)}_{n,\ell,m\to E>0} = \frac{2\pi}{\hbar^2}\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\int_0^{\infty} dk\,k^2\left|\langle k,\ell',m'|V(\omega_{kn})|n,\ell,m\rangle\right|^2,$$

can only make sense for $P^{(1)}_{n,\ell,m\to E>0} \leq 1$.

The Golden Rule for transitions from discrete states into a continuum of states

Now assume that we perturb a hydrogen atom in the initial bound state $|n,\ell,m\rangle$ with a monochromatic perturbation[5]

$$V(t) = W\exp(-\mathrm{i}\omega t) + W^{+}\exp(\mathrm{i}\omega t), \qquad (13.36)$$

$$V(\omega') = \sqrt{2\pi}W\delta(\omega'-\omega) + \sqrt{2\pi}W^{+}\delta(\omega'+\omega). \qquad (13.37)$$

The corresponding scattering matrix element for transition into the ionized state $|E,\ell',m'\rangle$ is in first order

$$\begin{aligned}
S_{E,\ell',m';n,\ell,m} = &-\frac{\mathrm{i}}{\hbar}2\pi\langle E,\ell',m'|W|n,\ell,m\rangle\delta\!\left(\frac{E-E_n}{\hbar}-\omega\right) \\
&-\frac{\mathrm{i}}{\hbar}2\pi\langle E,\ell',m'|W^{+}|n,\ell,m\rangle\delta\!\left(\frac{E-E_n}{\hbar}+\omega\right). \qquad (13.38)
\end{aligned}$$

---

[5] Recall that the notation tacitly implies dependence of the operators V and W on $\mathbf{x}$ and $\mathbf{p}$ (just like we usually write H instead of $H(\mathbf{x},\mathbf{p})$ for a Hamilton operator).

The cross multiplication terms in $|S_{E,\ell',m';n,\ell,m}|^2$ cancel for $\omega \neq 0$ due to the incompatibility of the δ functions, and therefore we can focus in the following discussion only on the first terms in equations (13.36–13.38), i.e. we continue with

$$S_{E,\ell',m';n,\ell,m} = -\frac{\mathrm{i}}{\hbar}2\pi\langle E,\ell',m'|W|n,\ell,m\rangle\delta\left(\frac{E-E_n}{\hbar}-\omega\right).$$

The square of this S matrix element yields a factor

$$\delta(0) = \lim_{\omega\to 0}\delta(\omega) = \lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2}dt\,\exp(\mathrm{i}\omega t) = \lim_{T\to\infty}\frac{T}{2\pi}$$

in $dP_{n,\ell,m\to E,\ell',m'}/dE = \varrho(E)|S_{E,\ell',m';n,\ell,m}|^2$. Dividing by the factor T provides us with a differential transition rate into a final state energy interval $[E, E+dE]$,

$$\begin{aligned} dw_{n,\ell,m\to E,\ell',m'} &= \frac{1}{T}dP_{n,\ell,m\to E,\ell',m'} = dE\,\varrho(E)\frac{1}{T}\left|S_{E,\ell',m';n,\ell,m}\right|^2 \\ &= dE\,\varrho(E)\frac{2\pi}{\hbar^2}\left|\langle E,\ell',m'|W|n,\ell,m\rangle\right|^2\delta\left(\frac{E-E_n}{\hbar}-\omega\right) \\ &= dE\,\varrho(E)\frac{2\pi}{\hbar}\left|\langle E,\ell',m'|W|n,\ell,m\rangle\right|^2\delta(E-E_n-\hbar\omega). \end{aligned}$$

Integration over the final state energy E then yields an expression for the transition rate,

$$w_{n,\ell,m\to E,\ell',m'} = \frac{2\pi}{\hbar}\left|\langle E,\ell',m'|W|n,\ell,m\rangle\right|^2\varrho(E)\Big|_{E=E_n+\hbar\omega}, \tag{13.39}$$

which is commonly referred to as the *Golden Rule*.

The total first order ionization rate of the state $|n,\ell,m\rangle$ under the perturbation (13.36) is then

$$w_{n,\ell,m} = \frac{2\pi}{\hbar}\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}\left|\langle E,\ell',m'|W|n,\ell,m\rangle\right|^2\varrho(E)\Bigg|_{E=E_n+\hbar\omega}. \tag{13.40}$$

The standard expression for the Golden Rule for the transition rate from a discrete state $|m\rangle$ into a continuous state $|n\rangle$ due to the perturbation $V = W\exp(-\mathrm{i}\omega t)$ is

$$w_{m\to n} = \int_{-\infty}^{\infty}dE\,\frac{dw_{m\to n}}{dE} = \frac{2\pi}{\hbar}\varrho(E_n)|\langle n|W|m\rangle|^2\Big|_{E_n=E_m+\hbar\omega}. \tag{13.41}$$

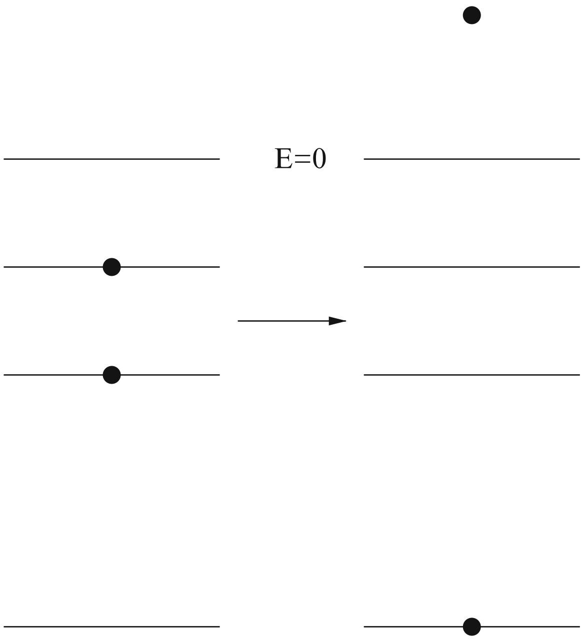

Fig. 13.3 Energy schematics for an Auger process. The initial bound state of the two electrons has the same energy as the final continuous state of an ion and a free electron

This is also particularly popular for time-independent V,

$$w_{m\to n}=\frac{2\pi}{\hbar}\varrho(E_n)|\langle n|V|m\rangle|^2\Big|_{E_n=E_m}. \tag{13.42}$$

Quantum systems can have degeneracy between states $|m\rangle$ which are labelled by discrete quantum numbers and states $|n\rangle$ with continuous quantum numbers. Metastable states, or excited bound states in many-electron atoms provide examples for this, and equation (13.42) would be the first order expression for the decay rate of these states. An example for this is the Auger effect, which is electron emission from atoms due to Coulomb repulsion. The perturbation operator[6] $V = e^2/4\pi|\mathbf{x}_1 - \mathbf{x}_2|$ is time-independent, and energy conservation is fulfilled because the discrete bound state of two electrons in an excited atom can exceed the sum of ground state energy and ionization energy, see Figure 13.3.

Time-dependent perturbation theory in second order and the Golden Rule #1

We will discuss a time-independent perturbation V,

$$H = H_0 + V,$$

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[6] G. Wentzel, Z. Phys. 43, 524 (1927).

and transition from a discrete state $|m\rangle$ into a continuous state $|n\rangle$. The completeness relation for the eigenstates of H_0 is

$$\sum_m |m\rangle\langle m| + \int dE_n \varrho(E_n)|n\rangle\langle n| = 1.$$

We will also write this symbolically as

$$\mathop{\sum\!\!\!\!\!\!\!\int}_l |l\rangle\langle l| = 1.$$

If $\langle n|V|m\rangle = 0$, the leading order term for the scattering matrix element $\langle n|U_D(\infty,-\infty)|m\rangle$ is the second order term

$$S^{(2)}_{nm} = -\frac{1}{\hbar^2}\mathop{\sum\!\!\!\!\!\!\!\int}_l \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp(\mathrm{i}\omega_{nl}\tau)\langle n|V|l\rangle \exp(\mathrm{i}\omega_{lm}\tau')\langle l|V|m\rangle.$$

To make the τ' integral convergent, we add a small negative imaginary part to $\omega_{lm} \to \omega_{lm} - \mathrm{i}\epsilon$, so that the time integrals yield

$$\begin{aligned}\int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp(\mathrm{i}\omega_{nl}\tau)\exp\big(\mathrm{i}\omega_{lm}\tau' + \epsilon\tau'\big) &= \frac{1}{\mathrm{i}\omega_{lm} + \epsilon}\int_{-\infty}^{\infty} d\tau \, \exp(\mathrm{i}\omega_{nm}\tau) \\ &= \frac{2\pi}{\mathrm{i}\omega_{lm} + \epsilon}\delta(\omega_{nm}). \qquad (13.43)\end{aligned}$$

This yields the second order scattering matrix element

$$\begin{aligned}S^{(2)}_{nm} &= \frac{2\pi \mathrm{i}}{\hbar^2}\delta(\omega_{nm})\mathop{\sum\!\!\!\!\!\!\!\int}_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{\omega_{lm} - \mathrm{i}\epsilon} \\ &= 2\pi \mathrm{i}\delta(E_n - E_m)\mathop{\sum\!\!\!\!\!\!\!\int}_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon},\end{aligned}$$

and the differential transition rate

$$\begin{aligned}dw_{m\to n} &= dE_n\varrho(E_n)\frac{1}{T}\,|S_{nm}|^2 \\ &= dE_n\varrho(E_n)\frac{2\pi}{\hbar}\delta(E_n - E_m)\left|\mathop{\sum\!\!\!\!\!\!\!\int}_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon}\right|^2. \qquad (13.44)\end{aligned}$$

Integration yields the second order expression for the transition rate,

$$w_{m\to n} = \frac{2\pi}{\hbar}\varrho(E_n)\left|\mathop{\sum\!\!\!\!\!\!\!\int}_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon}\right|^2\Bigg|_{E_n = E_m}. \qquad (13.45)$$

Equation (13.45) tells us how transitions through virtual intermediate states can generate the transition from $|m\rangle$ to $|n\rangle$ even if the direct transition is forbidden due to a selection rule $\langle n|V|m\rangle = 0$.

In his famous lectures on nuclear physics at the University of Chicago in 1949, Fermi coined the phrase "Golden Rule #2" for the first order transition rate (13.41, 13.42). He denoted the corresponding second order expression for transition rates as "Golden Rule #1", because it is important for nuclear reactions through intermediate compound nuclei [30].

13.5 Transitions from continuous states into discrete states: Capture cross sections

Transitions from continuous to discrete states arise e.g. in the capture of electrons by ions, in the absorption of an electron from a valence band into an acceptor state in a p-doped semiconductor, in neutron capture by nuclei etc. Consider e.g. the process $|k,\ell,m\rangle \to |n,\ell',m'\rangle$ of absorption of an electron by an H^+ ion, where we still assume that the hydrogen Hamiltonian (13.31) for relative motion is perturbed by addition of an operator $V(t)$. From our previous experience, we expect that the transition matrix element

$$S_{n,\ell',m';k,\ell,m} = \langle n,\ell',m'|U_D(\infty,-\infty)|k,\ell,m\rangle$$

yields a measure of probability for the absorption in the form of a transition probability density

$$\mathcal{P}_{k,\ell,m\to n,\ell',m'} = |S_{n,\ell',m';k,\ell,m}|^2 . \tag{13.46}$$

Indeed, the dimensionless number

$$\begin{aligned} P_{n,\ell',m'} &= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^\infty dk\,k^2\left|\langle n,\ell',m'|U_D(\infty,-\infty)|k,\ell,m\rangle\right|^2 \\ &= 1-\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n'=\ell+1}^{\infty}\left|\langle n,\ell',m'|U_D(\infty,-\infty)|n',\ell,m\rangle\right|^2 \end{aligned}$$

is the probability that the state $|n,\ell',m'\rangle$ emerged from some capture ($\mathrm{p}^+ + \mathrm{e}^- \to \mathrm{H}$) event rather than from an internal transition in the hydrogen atom. This assumes again that the perturbation $V(t)$ has a well behaved Fourier transform $V(\omega)$ such that the time integrals in the perturbation series can be defined as classical functions. However, a more common use of transition matrix elements from continuous initial states is the calculation of cross sections due to monochromatic perturbations. One possibility to calculate capture or absorption due to a Coulomb potential is to use parabolic coordinates because the incoming asymptotic plane wave can be described in parabolic coordinates, just like in Rutherford scattering [3]. However, radial coordinates are just as convenient for this problem.

Calculation of the capture cross section

We will outline how to calculate the first order cross section for the reaction $p^+ + e^- \to H$ due to a monochromatic perturbation[7] $V(t) = W\exp(\mathrm{i}\omega t)$. For a judicious choice of the operator $W \equiv W(\mathbf{p}, \mathbf{x})$ this describes electron-proton recombination due to emission of a photon with energy $\hbar\omega$. We will discuss these operators in Chapter 18, but here we do not specify the operator W further. Our present focus is rather to develop the formalism for calculating the capture or recombination cross section for a general perturbation $W(\mathbf{p}, \mathbf{x})\exp(\mathrm{i}\omega t)$. We should also mention that perturbations $V(t) = V(\mathbf{x}, t)$ due to interactions with additional nearby electrons or ions are much more efficient and therefore more important for electron capture than direct radiative recombination due to photon emission.

The wave function for the approach between a free electron and a proton in the effective single particle description for relative motion is given by the wave function $\langle \boldsymbol{x}|k\rangle_{MG}$ which was constructed by Mott and Gordon in 1928 (7.76). The normalization factor is irrelevant because it cancels in the cross section. For convenience, it was chosen in equation (7.76) such that the asymptotic incoming current density is

$$j_{in} = \frac{\hbar k}{\mu}, \tag{13.47}$$

where μ is the reduced mass of the two-particle system. This current density has units of $\mathrm{cm/s} = \mathrm{cm}^{-2}\mathrm{s}^{-1}/\mathrm{cm}^{-3}$ because it is actually a current density $dj_{in}/d^3\boldsymbol{k}$ per unit of volume in $\boldsymbol{k}$ space, which is a consequence of the use of an asymptotic plane wave state in its calculation. A current density per $\boldsymbol{k}$ space volume is the correct notion for the calculation of the electron-proton recombination cross section, because the S matrix element

$$S_{n,\ell,m;k} = \frac{2\pi}{\mathrm{i}\hbar}\langle n, \ell, m|W|k\rangle_{MG}\delta(\omega_{nk} + \omega)$$

yields a transition probability density per $\boldsymbol{k}$ space volume

$$\mathcal{P}_{k\to n,\ell,m} = |S_{n,\ell,m;k}|^2$$

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[7] See the discussion after equation (13.38) for an explanation why we can deal with monochromatic perturbations as abridged non-hermitian operators.

which comes in units of cm^3, again due to the use of an asymptotic plane wave state as incoming state.

$\mathcal{P}_{k\to n,\ell,m}$ contains the factor

$$\delta(0) = \lim_{\omega\to 0}\delta(\omega) = \lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2} dt\,\exp(\mathrm{i}\omega t) = \lim_{T\to\infty}\frac{T}{2\pi}.$$

We can use this to calculate a transition rate density per $\boldsymbol{k}$ space volume

$$\mathcal{W}_{k\to n,\ell,m} = \frac{1}{T}\left|S_{n,\ell,m;k}\right|^2 = \frac{2\pi}{\hbar^2}\left|\langle n,\ell,m|W|k\rangle_{MG}\right|^2\delta(\omega_{nk}+\omega)\,. \tag{13.48}$$

The transition rate is certainly proportional to the asymptotic current density j_{in}, and therefore we divide the transition rate density by this current density to get a measure for the probability of the absorption process $|k\rangle_{MG}\to|n,\ell,m\rangle$. This yields the absorption cross section

$$\sigma_{k\to n,\ell,m} = \frac{\mathcal{W}_{k\to n,\ell,m}}{j_{in}} = \frac{2\pi\mu}{\hbar^3 k}\left|\langle n,\ell,m|W|k\rangle_{MG}\right|^2\delta(\omega_{nk}+\omega) \tag{13.49}$$

with units of cm^2. The total absorption cross section due to the perturbation operator $W(\mathbf{p},\mathbf{x})\exp(\mathrm{i}\omega t)$ is then

$$\sigma_k = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n=\ell+1}^{\infty}\sigma_{k\to n,\ell,m}.$$

The capture cross section enters into the calculations of rate coefficients $(\sigma v)_{av}$, where the notation indicates averaging over the distribution of relative particle velocities in a plasma of ions and electrons. The rate coefficients go into the balance equations for electron and ion densities,

$$\frac{d\rho_e}{dt} = \frac{d\rho_p}{dt} = -\,(\sigma v)_{av}\,\rho_p\rho_e,$$

where in general additional terms due to collisional relaxation and ionization have to be included. Due to (13.47) the rate coefficients are directly related to the transition rates per $\boldsymbol{k}$ space volume calculated in the state (7.76),

$$v\sigma_k = j_{in}\sigma_k = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n=\ell+1}^{\infty}\mathcal{W}_{k\to n,\ell,m}.$$

Calculations of radiative capture cross sections for electron-proton recombination into arbitrary hydrogen shells were performed in parabolic coordinates by

Oppenheimer[8] and by Bethe and Salpeter [3]. Calculations in polar coordinates had been performed by Wessel, Stückelberg and Morse, and Stobbe[9]. All these authors had noticed that the electron capture cross sections for ions from radiative recombination were much too small to explain the experimental values, and it was eventually recognized that collisional relaxation due to interactions with spectator particles dominated the observed recombination rates. Therefore modern calculations of electron-ion recombination rates focus on collisional relaxation, which means that the relevant perturbation operators V are not determined by photon emission but by Coulomb interactions in a plasma, and the spectator particles also have to be taken into account in the initial and final states. Electron-ion recombination rates are particularly important for plasma physics and astrophysics.

13.6 Transitions between continuous states: Scattering

For transitions between continuous states, e.g. $|\boldsymbol{k}\rangle \to |\boldsymbol{k}'\rangle$, the S matrix element

$$S_{\boldsymbol{k}',\boldsymbol{k}} = \langle \boldsymbol{k}'|U_D(\infty,-\infty)|\boldsymbol{k}\rangle$$

is a quantity with the dimension length^3, because both external states have dimension length$^{3/2}$. We know from Section 13.4 how to make sense of transition matrix elements with continuous final states, *viz.* as transition probability densities $d^3\boldsymbol{k}'|S_{\boldsymbol{k}',\boldsymbol{k}}|^2$ in the final state space. We also know from the discussion in Section 13.5 that a continuous initial state in the scattering matrix will yield a transition probability density in the space of initial states if $V(\omega)$ is a classical function. In that case

$$P_{\mathcal{K}\to\mathcal{K}'} = \int_{\mathcal{K}'} d^3\boldsymbol{k}' \int_{\mathcal{K}} d^3\boldsymbol{k}\, |S_{\boldsymbol{k}',\boldsymbol{k}}|^2$$

will tell us the probability for transitions between states in $\boldsymbol{k}$ space volumes $\mathcal{K}$ and $\mathcal{K}'$ due to the perturbation $V(t)$.

However, just like in Section 13.5, the most important applications of scattering matrix elements with continuous initial states concern the calculation of cross sections due to monochromatic perturbations. We know from Sections 13.4 and 13.5 that monochromatic perturbations call for normalization of $|S_{\boldsymbol{k}',\boldsymbol{k}}|^2$ by the reaction time T, and we have learned in Section 13.5 that continuous initial states under the influence of a monochromatic perturbation require normalization of the transition rate with the current density j_{in} of incident particles to calculate a cross section

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[8] J.R. Oppenheimer, Z. Phys. 55, 725 (1929).

[9] W. Wessel, Annalen Phys. 397, 611 (1930); E.C.G. Stückelberg, P.M. Morse, Phys. Rev. 36, 16 (1930); M. Stobbe, Annalen Phys. 399, 661 (1930).

for the quantum mechanical reaction described by the S matrix element, see equation (13.49). Our previous experience with initial or final continuous states therefore motivates the definition of the *differential scattering cross section*

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\,\frac{|S_{\boldsymbol{k}',\boldsymbol{k}}|^2}{Tj_{in}}. \tag{13.50}$$

This has again the dimension length^2, because the incident current density j_{in} for plane waves has units of cm/s, see equation (13.47) and the following discussion.

The notion of a differential scattering cross section is sufficiently important to warrant rederivation of equation (13.50) in simple steps in the next paragraph.

Cross section for scattering off a periodic perturbation

We apply the transition probability between continuous states to calculate the scattering cross section for a monochromatic perturbation

$$V(t) = W\exp(-\mathrm{i}\omega t).$$

Our Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + W(\mathbf{x})\exp(-\mathrm{i}\omega t),$$

and our unperturbed states are plane waves $|\boldsymbol{k}\rangle$.

The first order result for the scattering matrix $S_{\boldsymbol{k}',\boldsymbol{k}} = \langle\boldsymbol{k}'|U_D(\infty,-\infty)|\boldsymbol{k}\rangle$ is

$$\begin{aligned} S_{\boldsymbol{k}',\boldsymbol{k}} &= -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}dt\,\exp\!\left[\mathrm{i}\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right)t\right]\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle \\ &= -\frac{2\pi\mathrm{i}}{\hbar}\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right) \\ &= -\mathrm{i}\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right). \end{aligned} \tag{13.51}$$

The factor $\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}$ in the scattering matrix element is also denoted as a *scattering amplitude*.

The transition probability density

$$\mathcal{P}_{\boldsymbol{k}\to\boldsymbol{k}'} = \left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2 = \left|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\right|^2\delta(0)\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right)$$

contains the factor

$$\delta(0) = \lim_{\omega\to 0}\delta(\omega) = \lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2}dt\,\exp(\mathrm{i}\omega t) = \lim_{T\to\infty}\frac{T}{2\pi},$$

and we can calculate a transition rate density

$$\begin{aligned}\mathcal{W}_{\boldsymbol{k}\to\boldsymbol{k}'} &= \frac{1}{T}\left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2 = \frac{\left|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\right|^2}{2\pi}\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right)\\ &= \frac{2\pi}{\hbar^2}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right).\end{aligned}$$

The corresponding differential transition rate into the final state volume $d^3\boldsymbol{k}'$ is

$$dw_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\,\mathcal{W}_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\,\frac{1}{T}\left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2.$$

However, this still comes in units of cm^3/s instead of s^{-1}, due to the initial plane wave state. For initial continuous states, we do not apply a volume measure (here $d^3\boldsymbol{k}$) in the space of initial states, but normalize by the current density of the incident particles. This yields a differential cross section for scattering of momentum eigenstates,

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = \frac{dw_{\boldsymbol{k}\to\boldsymbol{k}'}}{j_{in}} = d^3\boldsymbol{k}'\,\frac{2\pi}{\hbar^2 j_{in}}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right). \tag{13.52}$$

The motivation for dividing out the current density j_{in} of incoming particles from the scattering rate is the trivial dependence of the scattering rate on this parameter: if we double the number of incoming particles per second or per cm^2, we will trivially double the number of scattering events per second. Therefore all the interesting physics is in the proportionality factor $d\sigma$ between j_{in} and dw. This proportionality factor has the dimension of an area, and in classical mechanics, integration of $d\sigma$ over $d^3\boldsymbol{p}'$ for scattering of classical particles off a hard sphere of radius r yields the cross section area of the sphere $\sigma = \int d\sigma = \pi r^2$. Therefore the name *differential scattering cross section* for $d\sigma$.

The current density $\boldsymbol{j} = (\hbar/2\mathrm{i}m)(\psi^+\nabla\psi - \nabla\psi^+\cdot\psi)$ for a plane wave, $\boldsymbol{j} = \hbar\boldsymbol{k}/(2\pi)^3 m$, is actually a current density per unit of volume in $\boldsymbol{k}$-space. This is the correct current density to be used in (13.52), because $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ is a transition rate per unit of volume in $\boldsymbol{k}$-space, and the ratio yields a *bona fide* differential cross section[10]. Expressed in terms of continuum plane wave matrix elements, the differential scattering cross section is

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[10] Alternatively, we could have used box normalization for the incoming plane waves, $\langle\boldsymbol{x}|\boldsymbol{k}\rangle = \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/\sqrt{V}$ both in $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ and in $\boldsymbol{j}$ ($\Rightarrow \boldsymbol{j} = \hbar\boldsymbol{k}/(mV) = \boldsymbol{v}/V$), or we could have rescaled both $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ and $\boldsymbol{j}$ with the conversion factor $8\pi^3/V$ to make both quantities separately dimensionally correct, $[dw_{\boldsymbol{k}\to\boldsymbol{k}'}] = \mathrm{s}^{-1}$, $[j] = \mathrm{cm}^{-2}\mathrm{s}^{-1}$. All three methods yield the same result for the scattering cross section, of course.

$$\begin{aligned} d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} &= d^3\boldsymbol{k}'\,\frac{(2\pi)^4 m}{\hbar^3 k}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\!\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right) \\ &= d^3\boldsymbol{k}'\,(2\pi)^4\frac{2m^2}{\hbar^4 k}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\!\left(k'^2-k^2-\frac{2m}{\hbar}\omega\right). \end{aligned} \tag{13.53}$$

We can use the δ-function in (13.53) to integrate over k'. This leaves us with a differential cross section per unit of solid angle,

$$\frac{d\sigma}{d\Omega} = (2\pi)^4\frac{m^2}{\hbar^4}\sqrt{1+\frac{2m\omega}{\hbar k^2}}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\Bigg|_{k'=\sqrt{k^2+(2m\omega/\hbar)}}. \tag{13.54}$$

The corresponding result for $\omega = 0$ (scattering off a static potential) can also be derived within the framework of the time-independent Schrödinger equation, see Chapter 11. For the comparison note that we can write the differential scattering cross section (13.54) as

$$\frac{d\sigma}{d\Omega} = \sqrt{1+\frac{2m\omega}{\hbar k^2}}\,|f(\Delta\boldsymbol{k})|^2\Bigg|_{k'=\sqrt{k^2+(2m\omega/\hbar)}}, \tag{13.55}$$

with the scattering amplitude

$$f(\Delta\boldsymbol{k}) = -(2\pi)^2\frac{m}{\hbar^2}\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle = -2\pi\frac{m}{\hbar}\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}, \tag{13.56}$$

cf. (11.23), i.e. equation (13.55) reduces to (11.27) for scattering off a static potential if $\omega = 0$. The potential scattering formalism could be extended to time-dependent perturbations by using the asymptotic expansion of the time-dependent retarded Green's function (11.46). However, the equivalent scattering matrix formalism is more convenient.

Scattering theory in second order

We will discuss scattering off the time-independent potential V in second order. The Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + V.$$

If $\boldsymbol{k}' \neq \boldsymbol{k}$ and $\langle\boldsymbol{k}'|V|\boldsymbol{k}\rangle = 0$, the leading order term for the S-matrix is the second order term

$$S_{\boldsymbol{k}',\boldsymbol{k}} = -\frac{1}{\hbar^2}\int d^3\boldsymbol{q}\int_{-\infty}^{\infty}d\tau\int_{-\infty}^{\tau}d\tau'\,\exp\!\left(\frac{\mathrm{i}\hbar}{2m}\left(k'^2-q^2\right)\tau\right)$$
$$\times\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\exp\!\left(\frac{\mathrm{i}\hbar}{2m}\left(q^2-k^2\right)\tau'\right)\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle.$$

To make the τ' integral convergent, we add a term $\epsilon\tau'$ in the exponent, so that the time integrals yield

$$\int_{-\infty}^{\infty}d\tau\int_{-\infty}^{\tau}d\tau'\,\exp\!\left(\frac{\mathrm{i}\hbar}{2m}\left(k'^2-q^2\right)\tau\right)\exp\!\left(\frac{\mathrm{i}\hbar}{2m}\left(q^2-k^2\right)\tau'+\epsilon\tau'\right)$$
$$=\frac{1}{\frac{\mathrm{i}\hbar}{2m}\left(q^2-k^2\right)+\epsilon}\int_{-\infty}^{\infty}d\tau\,\exp\!\left(\frac{\mathrm{i}\hbar}{2m}\left(k'^2-k^2\right)\tau\right)$$
$$=\frac{2\pi}{\frac{\mathrm{i}\hbar}{2m}\left(q^2-k^2\right)+\epsilon}\delta\!\left(\frac{\hbar}{2m}\left(k'^2-k^2\right)\right)$$

and

$$S_{\boldsymbol{k}',\boldsymbol{k}} = \frac{2\pi\mathrm{i}}{\hbar^2}\delta\big(\omega(k')-\omega(k)\big)\int d^3\boldsymbol{q}\,\frac{\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle}{\omega(q)-\omega(k)-\mathrm{i}\epsilon}$$
$$=2\pi\mathrm{i}\delta\big(E(k')-E(k)\big)\int d^3\boldsymbol{q}\,\frac{\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q)-E(k)-\mathrm{i}\epsilon}.$$

The corresponding differential transition rate is

$$dw_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\frac{1}{T}\left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2.$$
$$=d^3\boldsymbol{k}'\frac{2\pi}{\hbar}\delta\big(E(k')-E(k)\big)\left|\int d^3\boldsymbol{q}\,\frac{\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q)-E(k)-\mathrm{i}\epsilon}\right|^2,$$

and the differential cross section for scattering of momentum eigenstates in second order is

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = \frac{dw_{\boldsymbol{k}\to\boldsymbol{k}'}}{j_{in}}$$
$$=d^3\boldsymbol{k}'\frac{(2\pi)^4 m}{\hbar^2 k}\delta\big(E(k')-E(k)\big)\left|\int d^3\boldsymbol{q}\,\frac{\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q)-E(k)-\mathrm{i}\epsilon}\right|^2$$
$$=d^3\boldsymbol{k}'\frac{(2\pi)^4 m^2}{\hbar^4 kk'}\delta\big(k'-k\big)\left|\int d^3\boldsymbol{q}\,\frac{\langle\boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle\boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q)-E(k)-\mathrm{i}\epsilon}\right|^2. \tag{13.57}$$

Integration over k' yields the differential scattering cross section per unit of solid angle in second order,

$$\frac{d\sigma}{d\Omega} = (2\pi)^4 \frac{m^2}{\hbar^4} \left| \int d^3\boldsymbol{q}\, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q)-E(k)-\mathrm{i}\epsilon} \right|^2 \Bigg|_{k'=k}. \tag{13.58}$$

Equations (13.54) and (13.58) could be denoted as Fermi's Golden Rules #2 and #1 for scattering theory.

13.7 Expansion of the scattering matrix to higher orders

For time-independent perturbation V we can write the expansion of the scattering matrix in the form

$$\begin{aligned}
S_{fi}(t,t') &= \langle f|U_D(t,t')|i\rangle = \langle f|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right)|i\rangle \\
&= \sum_{n=0}^{\infty} \frac{1}{(\mathrm{i}\hbar)^n} \int_{t'}^{t} d\tau_1 \int_{t'}^{\tau_1} d\tau_2 \ldots \int_{t'}^{\tau_{n-1}} d\tau_n\, \langle f|U_0(t_0,\tau_1)VU_0(\tau_1,\tau_2) \\
&\quad \times VU_0(\tau_2,\tau_3)\ldots U_0(\tau_{n-1},\tau_n)VU_0(\tau_n,t_0)|i\rangle \\
&= \sum_{n=0}^{\infty} \sum_{j_1,\ldots j_{n-1}} \frac{1}{(\mathrm{i}\hbar)^n} \int_{t'}^{t} d\tau_1 \int_{t'}^{\tau_1} d\tau_2 \ldots \int_{t'}^{\tau_{n-1}} d\tau_n\, \exp\left(-\frac{\mathrm{i}}{\hbar}E_f t_0\right) \\
&\quad \times \exp\left(\frac{\mathrm{i}}{\hbar}E_f\tau_1\right) V_{fj_1} \exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_1}\tau_1\right) \exp\left(\frac{\mathrm{i}}{\hbar}E_{j_1}\tau_2\right) V_{j_1j_2} \\
&\quad \times \exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_2}\tau_2\right) \exp\left(\frac{\mathrm{i}}{\hbar}E_{j_2}\tau_3\right) \ldots \exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{m-1}}\tau_m\right) V_{j_{m-1}j_m} \\
&\quad \times \exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_m}\tau_m\right) \ldots \exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{n-2}}\tau_{n-1}\right) V_{j_{n-2}j_{n-1}} \\
&\quad \times \exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_{n-1}}\tau_{n-1}\right) \exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{n-1}}\tau_n\right) V_{j_{n-1}i} \exp\left(-\frac{\mathrm{i}}{\hbar}E_i\tau_n\right) \\
&\quad \times \exp\left(\frac{\mathrm{i}}{\hbar}E_i t_0\right).
\end{aligned}$$

Taking the limits $t' \to -\infty$ and $t \to \infty$, we find the equation

$$\begin{aligned}
S_{fi} &= \delta_{fi} - 2\pi\mathrm{i}\delta(E_f-E_i)V_{fi} - 2\pi\mathrm{i}\delta(E_f-E_i) \\
&\quad \times \sum_{n=2}^{\infty} \sum_{j_1,\ldots j_{n-1}} V_{fj_1}V_{j_1j_2}\ldots V_{j_{n-2}j_{n-1}}V_{j_{n-1}i}\left[(E_i-E_{j_1}+\mathrm{i}\epsilon)\right. \\
&\quad \times \left.(E_i-E_{j_2}+\mathrm{i}\epsilon)\ldots(E_i-E_{j_{n-2}}+\mathrm{i}\epsilon)(E_i-E_{j_{n-1}}+\mathrm{i}\epsilon)\right]^{-1}.
\end{aligned} \tag{13.59}$$

However, we can also use

$$
\begin{aligned}
-2\pi\mathrm{i}\delta(E_f - E_i) &= -\frac{\mathrm{i}}{\hbar}\lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0}\int_{-\infty}^{t} d\tau\,\exp\!\left(\frac{\mathrm{i}(E_f - E_i) + \epsilon}{\hbar}\tau\right) \\
&= \lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0}\frac{1}{E_i - E_f + \mathrm{i}\epsilon}\exp\!\left(\frac{\mathrm{i}(E_f - E_i)t + \epsilon t}{\hbar}\right).
\end{aligned}
$$

This yields a form which resembles expressions for the shifts of wave functions in time-independent perturbation theory,

$$
\begin{aligned}
S_{fi} = \lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0}&\exp\!\left(\frac{\mathrm{i}(E_f - E_i)t + \epsilon t}{\hbar}\right)\Bigg(\delta_{fi} + \frac{V_{fi}}{E_i - E_f + \mathrm{i}\epsilon} \\
&+ \sum_{n=2}^{\infty}\sum\!\!\!\!\!\!\int_{j_1,\ldots j_{n-1}} V_{fj_1}V_{j_1j_2}\ldots V_{j_{n-2}j_{n-1}}V_{j_{n-1}i}\Big[(E_i - E_f + \mathrm{i}\epsilon) \\
&\times (E_i - E_{j_1} + \mathrm{i}\epsilon)\ldots(E_i - E_{j_{n-2}} + \mathrm{i}\epsilon)(E_i - E_{j_{n-1}} + \mathrm{i}\epsilon)\Big]^{-1}\Bigg). \qquad (13.60)
\end{aligned}
$$

If the initial state is continuous, $|S_{fi}|^2$ will enter into the calculation of cross sections. If only the final state is continuous, $|S_{fi}|^2$ will enter into the calculation of decay rates. If both external states are discrete, the perturbation V should be treated as arising from a quantum field, see the remarks at the end of Section 13.3.

We can write the result (13.60) also as

$$
S_{fi} = \lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0}\langle\psi_f|\exp\!\left(-\mathrm{i}\frac{E_i - H_0 + \mathrm{i}\epsilon}{\hbar}t\right)|\Psi_i^{(\epsilon)}\rangle \qquad (13.61)
$$

with the state

$$
|\Psi_i^{(\epsilon)}\rangle = \sum_{n=0}^{\infty}\left(\frac{1}{E_i - H_0 + \mathrm{i}\epsilon}V\right)^n|\psi_i\rangle. \qquad (13.62)
$$

This state satisfies the Lippmann-Schwinger equation (11.5)

$$
|\Psi_i^{(\epsilon)}\rangle = |\psi_i\rangle + \frac{1}{E_i - H_0 + \mathrm{i}\epsilon}V|\Psi_i^{(\epsilon)}\rangle \qquad (13.63)
$$

and therefore also

$$
\lim_{\epsilon\to 0}(E_i - H + \mathrm{i}\epsilon)|\Psi_i^{(\epsilon)}\rangle = 0.
$$

Indeed, one of the objectives of the original work of Lippmann and Schwinger was to relate states of the form (13.62) to the scattering matrix, and it was thought that they relate to the Møller states (13.27). However, we now see that they instead appear as stated in equation (13.61).

We can also write the result (13.61) in even neater form

$$S_{fi} = \lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0} \langle\psi_f|\Psi_i^{(\epsilon)}(t)\rangle \tag{13.64}$$

with the state

$$|\Psi_i^{(\epsilon)}(t)\rangle = \sum_{n=0}^{\infty}\left(\frac{1}{E_i - H_0 + \mathrm{i}\epsilon}H_D(t)\right)^n |\psi_i\rangle. \tag{13.65}$$

This state satisfies the equation

$$|\Psi_i^{(\epsilon)}(t)\rangle = |\psi_i\rangle + \frac{1}{E_i - H_0 + \mathrm{i}\epsilon}H_D(t)|\Psi_i^{(\epsilon)}(t)\rangle \tag{13.66}$$

and therefore also

$$\lim_{\epsilon\to 0}(E_i - H_0 + \mathrm{i}\epsilon)|\Psi_i^{(\epsilon)}(t)\rangle = \lim_{\epsilon\to 0} H_D(t)|\Psi_i^{(\epsilon)}(t)\rangle. \tag{13.67}$$

13.8 Energy-time uncertainty

We are now finally in a position to address the origin of energy-time uncertainty in a more formal way. Energy conservation in each term of the scattering matrix (13.59) came from the final time integral over τ_1, which in symmetric form for the initial and final time limits can be written as

$$\begin{aligned}\lim_{\Delta t\to\infty}\frac{1}{\hbar}\int_{-\Delta t/2}^{\Delta t/2} dt\,\exp(\mathrm{i}\Delta E_{fi}t/\hbar) &= 2\lim_{\Delta t\to\infty}\frac{\sin(\Delta E_{fi}\Delta t/2\hbar)}{\Delta E_{fi}} \\ &= 2\pi\delta(\Delta E_{fi}).\end{aligned} \tag{13.68}$$

However, this tells us that if we allocate only a finite time window Δt to observe the evolution of the system, or if the system is forced to make the transition within a time window Δt, then we will observe violations of energy conservation of order

$$|\Delta E_{fi}| \simeq \frac{4\hbar}{\Delta t}. \tag{13.69}$$

Here we used that the sinc function $\sin(x)/x$ is rather broad with half maximum near $x = \pm 2$.

How can that be? The theorem of energy conservation for time-independent Hamiltonian $H = H_0 + V$ in a static spacetime holds in quantum mechanics just as in any other physical field theory. We will see this in Section 16.2. However, by allocating a finite time window Δt for our measurement device to observe the system, or by constraining the system to make the transition within the fixed finite time window, we apparently introduce a time-dependent perturbation into the system that results in an energy uncertainty in excess of $\hbar/\Delta t$ in the final state.

13.9 Problems

13.1. The last lines in equations (13.1, 13.2) require the property

$$\mathrm{T}\frac{1}{n!}\left(\int_{t_0}^{t} d\tau\, H(\tau)\right)^n \equiv \frac{1}{n!}\mathrm{T}\int_{t_0}^{t} d\tau_1 \int_{t_0}^{t} d\tau_2 \ldots \int_{t_0}^{t} d\tau_n\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)$$
$$= \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n\, H(\tau_1)H(\tau_2)\ldots H(\tau_n). \tag{13.70}$$

Prove this property.

Hints: The equation for $n = 0$ and $n = 1$ is trivial, and for $n = 2$ it can easily be demonstrated from equation (13.3). This motivates a proof by induction with respect to n, which can easily be accomplished using the property

$$\mathrm{T}H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}) = \mathrm{T}[\mathrm{T}H(\tau_1)H(\tau_2)\ldots H(\tau_n)]H(\tau_{n+1}).$$

A more direct way to prove (13.70) is to express the ordering of operators through appropriate Θ functions under the assumption $t > t_0$ (forward evolution) or $t < t_0$ (backward evolution).

13.2. Use Fourier transformation to calculate the matrix elements $\langle x|U(t)|x'\rangle$ for the free time evolution operator in one dimension. Compare with the result (13.9) for the harmonic oscillator.

13.3. Calculate the annihilation and creation operators $a(t)$ and $a^+(t)$ of the harmonic oscillator in the Heisenberg picture.

Use the previous results to calculate the operators $\mathrm{x}(t)$ and $\mathrm{p}(t)$ for the harmonic oscillator in the Heisenberg picture.

13.4. Start from the definition

$$U_D(t,t') = U_0^+(t,t_0)U(t,t')U_0(t',t_0)$$

of the time evolution operator of states in the interaction picture to prove that

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U_D(t,t') = H_D(t)U_D(t,t'), \quad \mathrm{i}\hbar\frac{\partial}{\partial t'}U_D(t,t') = -U_D(t,t')H_D(t').$$

13.5. Calculate the first order transition probability for the transition 1s→2p for a hydrogen atom which is perturbed by a potential

$$V(t) = P\frac{\mathrm{z}}{2\tau}\exp(-|t|/\tau).$$

P and τ are constants. What is the meaning of P in the limit $\tau \to 0$?

13.6. The Golden Rule #2 for the first order transition rate (13.41) is often abused for the discussion of transitions between discrete states. In this problem you will be asked to figure out where the derivation of the Golden Rule #2 for transitions between discrete states breaks down.

13.6a. Calculate the first order transition probability for transitions between discrete energy eigenstates $|m\rangle \to |n\rangle$ under the influence of a monochromatic perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ which only acts between times t' and t. Which consistency requirements do you find from the condition that the first order result describes a transition probability $P_{m\to n}(t,t')$? Calculate also the transition rate $w_{m\to n}(t,t') = dP_{m\to n}(t,t')/dt$.

13.6b. Try to take the limit $t - t' \to \infty$ to derive the Golden Rule #2. Does this comply with the consistency requirements from 13.6a?

13.6c. Why do the inconsistencies of 13.6b not appear if the final state $|n\rangle$ is a continuous state?

Solution for Problem 13.6. For a periodic perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ the first order transition amplitude between times t' and t, and between different eigenstates of H_0 becomes

$$\begin{aligned}\langle n|U_D(t,t')|m\rangle &\approx -\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\ \exp[\mathrm{i}(\omega_{nm}-\omega)\tau]\langle n|W|m\rangle \\ &= \frac{\exp[\mathrm{i}(\omega_{nm}-\omega)t'] - \exp[\mathrm{i}(\omega_{nm}-\omega)t]}{\hbar(\omega_{nm}-\omega)}\langle n|W|m\rangle.\end{aligned}$$

The resulting transition probability is

$$\begin{aligned}P_{m\to n}(t-t') &= 2\frac{1-\cos[(\omega_{nm}-\omega)(t-t')]}{\hbar^2(\omega_{nm}-\omega)^2}|\langle n|W|m\rangle|^2 \\ &= \left(\frac{2\sin[(\omega_{nm}-\omega)(t-t')/2]}{\hbar(\omega_{nm}-\omega)}|\langle n|W|m\rangle|\right)^2, \qquad (13.71)\end{aligned}$$

and the rate of change of the transition probability follows as

$$w_{m\to n}(\Delta t) = \frac{d}{dt}P_{m\to n}(\Delta t) = \frac{2}{\hbar^2}\frac{\sin[(\omega_{nm}-\omega)\Delta t]}{\omega_{nm}-\omega}|\langle n|W|m\rangle|^2. \qquad (13.72)$$

Equations (13.71) and (13.72) yield perfectly well behaved, dimensionally correct expressions for the first order transition probability and transition rate between discrete states. Consistency with the probability interpretation for the extreme case $\omega_{nm} - \omega = 0$ requires

$$\Delta t = t - t' \leq \frac{\hbar}{|\langle n|W|m\rangle|}, \tag{13.73}$$

or alternatively, consistency of (13.71) with the probability interpretation for arbitrary Δt requires

$$|\omega_{nm} - \omega| \geq \frac{2}{\hbar}|\langle n|W|m\rangle|. \tag{13.74}$$

The problem arises with the limit $\Delta t \to \infty$, which would transform the transition rate from an ordinary function of frequencies into a δ function,

$$\begin{aligned} w_{m\to n} &= \lim_{\Delta t\to\infty} w_{m\to n}(\Delta t) = \frac{2\pi}{\hbar^2}|\langle n|W|m\rangle|^2\delta(\omega_{nm} - \omega) \\ &= \frac{2\pi}{\hbar}|\langle n|W|m\rangle|^2\delta(E_n - E_m - \hbar\omega). \end{aligned} \tag{13.75}$$

Here we used

$$\begin{aligned} \lim_{\Delta t\to\infty} \frac{\sin[(\omega_{nm} - \omega)\Delta t]}{\omega_{nm} - \omega} &= \lim_{\Delta t\to\infty} \frac{1}{2}\int_{-\Delta t}^{\Delta t} d\tau\, \exp[\mathrm{i}(\omega_{nm} - \omega)\tau] \\ &= \pi\delta(\omega_{nm} - \omega) = \pi\hbar\delta(E_n - E_m - \hbar\omega). \end{aligned}$$

Taking the limit $\Delta t \to \infty$ violates either the condition (13.73), or the condition (13.74) through its result $\omega_{nm} - \omega \to 0$ for a transition. From this point of view (and ignoring the fact that we should have at least one continuous external state when properly taking into account photons, see Section 18.6 and Problem 18.11), the resolution of the paradox of emergence of a δ function between discrete states in the limit $\Delta t \to \infty$ is that in the region of frequencies (13.74) where the first order result might be applicable, the first order result becomes subdominant for large Δt and (at the very least) higher order terms would have to be included to get estimates of transition probabilities and transition rates, or perturbation theory is just not suitable any more to get reliable estimates for those parameters.

These problems do not arise for continuous final states, because in these cases $P_{m\to n}(t,t') \to dP_{m\to n}(t,t') = dE_n\varrho(E_n)|S_{n,m}(t,t')|^2$ are not transition probabilities any more (which would be bounded by 1), but only transition probability densities for which only the integral over the energy scale with measure factor $\varrho(E_n)$ is bounded.

13.7. Calculate the representation of the ground state of hydrogen as a superposition of plane waves.

Solution. The $\boldsymbol{x}$ representation of the ground state of hydrogen is

$$\langle \boldsymbol{x}|1,0,0\rangle = \frac{1}{\sqrt{\pi a^3}}\exp(-r/a),$$

where a is the Bohr radius (7.62).

Fourier transformation to $\boldsymbol{k}$ space yields

$$\begin{aligned}
\langle \boldsymbol{k}|1,0,0\rangle &= \frac{1}{\pi\sqrt{2a^3}}\int_0^\infty dr\int_{-1}^{1} d\xi\, r^2\exp(-\mathrm{i}kr\xi)\exp(-r/a)\\
&= \frac{1}{\mathrm{i}k\pi\sqrt{2a^3}}\int_0^\infty dr\, r\exp(-r/a)[\exp(\mathrm{i}kr)-\exp(-\mathrm{i}kr)]\\
&= \frac{1}{\mathrm{i}k\pi\sqrt{2a^3}}\left[\left.\frac{1}{\kappa^2}\right|_{\kappa=(1/a)-\mathrm{i}k} - \left.\frac{1}{\kappa^2}\right|_{\kappa=(1/a)+\mathrm{i}k}\right]\\
&= \frac{\sqrt{2a}^3}{\pi}\frac{1}{[1+(ka)^2]^2}.
\end{aligned}$$

The representation in terms of plane waves is therefore

$$\langle \boldsymbol{x}|1,0,0\rangle = \sqrt{\frac{a}{\pi}}^3\int d^3\boldsymbol{k}\,\frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{\pi[1+(ka)^2]^2},$$

i.e. the ground state is an isotropic superposition of plane waves which is dominated by small wave numbers $k \lesssim 1/a$ or large wavelengths $\lambda \gtrsim 2\pi a$. This problem was included in this chapter to drive home the point that calculation of transition rates into plane wave states does not necessarily tell us something about scattering or ionization in a system with bound states, unless the energy of the final plane wave state is large compared to the binding energies of the bound states.

13.8. Calculate the first order ionization rate for particles which are trapped in a one-dimensional δ-function potential (Section 3.3), if the particles are perturbed by a potential $V(t) = F_0\mathrm{x}\exp(-\mathrm{i}\omega t)$. What is the meaning of the constant F_0?

13.9. Calculate the first order capture cross section for free particles with wave function (3.18) which can become trapped in a one-dimensional δ-function potential, if the particles are perturbed by a potential $V(t) = F_0\mathrm{x}\exp(\mathrm{i}\omega t)$. Recall that the normalization of initial states does not matter in the calculation of cross sections since it cancels in the ratio of capture rate to current density.

13.10. Calculate the cross section for recombination of an electron and a proton with energy $\hbar^2k^2/2\mu$ (in their relative motion) into the ground state of hydrogen. Perform the calculation both in parabolic and in polar coordinates.

13.11. Calculate the differential and total scattering cross sections for particles with initial momentum $\hbar\boldsymbol{k}$ which are scattered off the time-dependent potential

$$V(t) = \frac{A}{r}\Theta(R-r)\exp(-\mathrm{i}\omega t).$$

13.12. In 1984 Michael Berry published a paper studying (among other things) the following interesting question: Suppose $H(t)$ is a time-dependent Hamiltonian with the property that for each value of t there is a discrete spectrum $\mathcal{E}_n(t)$ such that

$$H(t)|\mathcal{E}_n(t)\rangle = \mathcal{E}_n(t)|\mathcal{E}_n(t)\rangle, \tag{13.76}$$

$$\langle\mathcal{E}_m(t)|\mathcal{E}_n(t)\rangle = \delta_{mn}, \quad \sum_n |\mathcal{E}_n(t)\rangle\langle\mathcal{E}_n(t)| = \underline{1}. \tag{13.77}$$

We can relate the eigenstates $|\mathcal{E}_n(t)\rangle$ of $H(t)$ to the states $|\psi_n(t)\rangle$ of the physical system described by $H(t)$ simply through the completeness relation (13.77),

$$|\psi_n(t)\rangle = \sum_m |\mathcal{E}_m(t)\rangle\langle\mathcal{E}_m(t)|\psi_n(t)\rangle. \tag{13.78}$$

However, assume that we start with an eigenstate $|\mathcal{E}_n(0)\rangle$ at time $t = 0$, i.e. we are seeking a solution of the initial value problem

$$\mathrm{i}\hbar\frac{d}{dt}|\psi_n(t)\rangle = H(t)|\psi_n(t)\rangle, \quad |\psi_n(0)\rangle = |\mathcal{E}_n(0)\rangle. \tag{13.79}$$

Can we directly relate $|\psi_n(t)\rangle$ to $|\mathcal{E}_n(t)\rangle$ without invoking a superposition (13.78) of all the eigenstates $|\mathcal{E}_m(t)\rangle$?

13.12a. Can you give an example of a time-dependent Hamiltonian satisfying the requirements (13.76, 13.77)?

13.12b. Since the states $|\psi_n(t)\rangle$ and $|\mathcal{E}_n(t)\rangle$ are both normalized they could only differ by a time-dependent phase if they are directly related,

$$|\psi_n(t)\rangle = \exp[-\mathrm{i}\Omega_n(t)]|\mathcal{E}_n(t)\rangle. \tag{13.80}$$

Which conditions would the phase $\Omega_n(t)$ have to fulfill for $|\psi_n(t)\rangle$ to satisfy the initial value problem (13.79)?

13.12c. What would be the solution for $\Omega_n(t)$ if a solution exists?
Which condition does $|\mathcal{E}_n(t)\rangle$ have to satisfy for existence of $\Omega_n(t)$?

Solution for 13.12b and 13.12c. Substitution of (13.80) into the time-dependent Schrödinger equation (13.79) and taking into account (13.76) yields

$$\begin{aligned} \mathrm{i}\hbar\frac{d}{dt}|\psi_n(t)\rangle - H(t)|\psi_n(t)\rangle &= \exp[-\mathrm{i}\Omega(t)] \\ &\times\left(\hbar\frac{d\Omega_n(t)}{dt}|\mathcal{E}_n(t)\rangle + \mathrm{i}\hbar\frac{d}{dt}|\mathcal{E}_n(t)\rangle - \mathcal{E}_n(t)|\mathcal{E}_n(t)\rangle\right), \end{aligned}$$

i.e. we would need to satisfy the conditions

$$\hbar\frac{d\Omega_n(t)}{dt}|\mathcal{E}_n(t)\rangle + \mathrm{i}\hbar\frac{d}{dt}|\mathcal{E}_n(t)\rangle - \mathcal{E}_n(t)|\mathcal{E}_n(t)\rangle = 0 \tag{13.81}$$

and $\Omega(0) = 0$ to ensure that the *Ansatz* (13.80) satisfies the initial value problem (13.79). *If* the condition (13.81) is consistent, it is equivalent to

$$\hbar\frac{d\Omega_n(t)}{dt} = \mathcal{E}_n(t) - \mathrm{i}\hbar\langle\mathcal{E}_n(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle \tag{13.82}$$

with solution

$$\Omega_n(t) = \int_0^t d\tau\left(\frac{\mathcal{E}_n(\tau)}{\hbar} - \mathrm{i}\langle\mathcal{E}_n(\tau)|\frac{d}{d\tau}|\mathcal{E}_n(\tau)\rangle\right). \tag{13.83}$$

However, the condition (13.81) will usually *not* be consistent and $\Omega_n(t)$ will not exist in many cases. The problem is that condition (13.81) requires that $d|\mathcal{E}_n(t)\rangle/dt \propto |\mathcal{E}_n(t)\rangle$,

$$\frac{d}{dt}|\mathcal{E}_n(t)\rangle = \mathrm{i}\left(\frac{d\Omega_n(t)}{dt} - \frac{\mathcal{E}_n(t)}{\hbar}\right)|\mathcal{E}_n(t)\rangle, \tag{13.84}$$

which would yield with (13.83)

$$\begin{aligned} |\mathcal{E}_n(t)\rangle &= \exp\!\left(\int_0^t d\tau\,\langle\mathcal{E}_n(\tau)|\frac{d}{d\tau}|\mathcal{E}_n(\tau)\rangle\right)|\mathcal{E}_n(0)\rangle \\ &= \exp[-\mathrm{i}\beta_n(t)]|\mathcal{E}_n(0)\rangle, \end{aligned} \tag{13.85}$$

with the *Berry phase*[11]

$$\beta_n(t) = \mathrm{i}\int_0^t d\tau\,\langle\mathcal{E}_n(\tau)|\frac{d}{d\tau}|\mathcal{E}_n(\tau)\rangle. \tag{13.86}$$

The constraints on the existence of physical states of the form (13.80) and on the usefulness of the Berry phase can most easily be seen from the fact that (13.85) is equivalent to

$$\frac{d}{dt}|\mathcal{E}_n(t)\rangle = |\mathcal{E}_n(t)\rangle\langle\mathcal{E}_n(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle, \tag{13.87}$$

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[11] M.V. Berry, Proc. Roy. Soc. London A 392, 45 (1984).

whereas generically time-dependence of the Hamiltonian mixes its eigenstates under time-evolution,

$$\frac{d}{dt}|\mathcal{E}_n(t)\rangle = \sum_m |\mathcal{E}_m(t)\rangle\langle\mathcal{E}_m(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle. \tag{13.88}$$

Stated differently, the condition for existence of $\Omega_n(t)$ is

$$\langle\mathcal{E}_m(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle = \delta_{m,n}\langle\mathcal{E}_n(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle, \tag{13.89}$$

or the condition for (13.80, 13.83) as an *approximate* solution of the time-dependent Schrödinger equation is that for every $m \neq n$

$$\left|\langle\mathcal{E}_m(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle\right| \ll \left|\langle\mathcal{E}_n(t)|\frac{d}{dt}|\mathcal{E}_n(t)\rangle\right|. \tag{13.90}$$

Note that if $\Omega_n(t)$ exists, the solution (13.80, 13.83) can also be written as

$$|\psi_n(t)\rangle = \exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_0^t d\tau\,\mathcal{E}_n(\tau)\right)|\mathcal{E}_n(0)\rangle. \tag{13.91}$$

Of course, the Berry phase always exists in the sense of the definition (13.86), and in the same manner one might simply adopt (13.83) as a definition of $\Omega_n(t)$. The problem is whether or not they are related to the evolution of the states $|\psi_n(t)\rangle$ of the system described by the Hamiltonian $H(t)$. We have found (13.90) as a condition for the usefulness of the Berry phase. Comparison of (13.91) with the exact evolution formula

$$|\psi_n(t)\rangle = \mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_0^t d\tau\,H(\tau)\right)|\mathcal{E}_n(0)\rangle \tag{13.92}$$

shows that the condition for usefulness of the Berry phase for the approximate description of the evolution of the system between times 0 and t can also be expressed in the form

$$H(\tau)|\mathcal{E}_n(0)\rangle \simeq \mathcal{E}_n(\tau)|\mathcal{E}_n(0)\rangle \tag{13.93}$$

for $0 \leq \tau \leq t$ or $t \leq \tau \leq 0$.