Lecture notes 14

14 Time-dependent perturbation theory

(Sections 11.1–2 in Hemmer, 9.1–3 in B&J, 9.1 in Griffiths)

14.1 Introduction

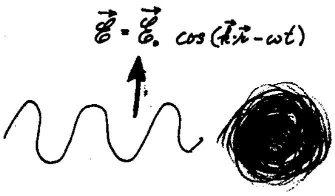
To illustrate what time-dependent perturbation theory is all about, let us as an example consider a hydrogen atom. If we neclect all interactions except the Coulomb interaction between the electron and the proton, the Hamiltonian is

$$\widehat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r},$$

with the well-known energy eigenfunctions and stationary states given respectively by

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi) \qquad \text{and} \qquad \Psi^{(0)}_{nlm}(\mathbf{r},t) = \psi_{nlm}(\mathbf{r})e^{-iE_nt/\hbar},$$

corresponding to bound states. The unbound states of the electron-proton system (for $E \geq 0$), corresponding to $\psi_{Elm}(\mathbf{r})$ and $\Psi^{(0)}_{Elm}(\mathbf{r},t) = \psi_{Elm}(\mathbf{r})\exp(-iEt/\hbar)$, are probably less well known.



Now suppose that this atom is influenced by an electromagnetic wave. The electron (and the proton) then experience oscillatory electromagnetic forces corresponding to a time-dependent potential-energy term $\widehat{V}(t)$ which together with $\widehat{H}_0$ add up to the Hamiltonian

$$\widehat{H} = \widehat{H}_0 + \widehat{V}(t).$$

For such a time-dependent Hamiltonian, stationary solutions do not exist and, what is even worse, it is no longer possible to find exact solutions of the Schrödinger equation. However, *approximate* solutions can be found, and this is where time-dependent perturbation theory enters the picture. In this theory, $\widehat{V}(t)$ is considered as a "perturbation", and the aim of the theory is to find out how this term affects the behaviour of the system.

With the simplified notation [1]

$$\Psi_k^{(0)}(\mathbf{r},t)=\psi_k(\mathbf{r})e^{-iE_kt/\hbar};\qquad i\hbar\frac{\partial\Psi_k^{(0)}(\mathbf{r},t)}{\partial t}=\widehat{H}_0\Psi_k^{(0)}(\mathbf{r},t)\tag{T14.1}$$

for the "unperturbed" stationary solutions, we note that these solutions do not satisfy the Schrödinger equation for the perturbed system,

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}=[\widehat{H}_0+\widehat{V}(t)]\Psi(\mathbf{r},t).\tag{T14.2}$$

However, in spite of this, they turn out to be very useful: Firstly, we are free to assume that the system is prepared in one of the unperturbed solutions at time $t=0$,

$$\Psi(\mathbf{r},0)=\Psi_i^{(0)}(\mathbf{r},0)=\psi_i(\mathbf{r}).\tag{T14.3}$$

Here, i stands for *initial*, and the initial state could for example be the unperturbed ground state, ψ_{100}. Secondly, the unperturbed states constitute a *complete* set of states, and it turns out to be useful to write the unknown solution of (T14.2) as an expansion in terms of the unperturbed stationary states:

$$\Psi(\mathbf{r},t)=\sum_k a_k(t)\Psi_k^{(0)}(\mathbf{r},t)=a_i(t)\Psi_i^{(0)}(\mathbf{r},t)+\sum_{k\neq i}a_k(t)\Psi_k^{(0)}(\mathbf{r},t).\tag{T14.4}$$

Here it is important to note that the expansion coefficients a_k are not time independent:

With the initial state $\Psi(\mathbf{r},0)=\psi_i(\mathbf{r})$, we start out with the coefficient $a_i(0)=1$, while all the other coefficients are equal to zero. However, because the unperturbed state $\Psi_i^{(0)}(\mathbf{r},t)$ is not a solution of the Schrödinger equation $i\hbar\partial\Psi(\mathbf{r},t)/\partial t=\widehat{H}\Psi(\mathbf{r},t)$ for the perturbed system, the system can not stay in the state $\Psi_i^{(0)}(\mathbf{r},t)$. This means that the coefficient $a_i(t)$ (which is the probability amplitude of finding the system in the initial state $\Psi_i^{(0)}(\mathbf{r},t)$) will decrease from 1, while some of the other coefficients (amplitudes) will start to deviate from zero. We remember that $|a_k(t)|^2$ is the probability of measuring the energy E_k and leaving the system in the corresponding state, or as we frequently put it, of "finding" the system in the eigenstate $\psi_k^{(0)}$ of $\widehat{H}_0$. Thus, for $k\neq i$ the squares $|a_k(t)|^2$ are **transition probabilities**; there is a finite probability that the atom which was at $t=0$ prepared in e.g. the ground state, will at time t be "found" in excited states. (Note that $\sum_k|a_k(t)|^2=1$.) Finding these transition probabilities is usually the the main task when quantum mechanics is applied to physical processes where something *happens*.[2]

---

[1] The superscript $^{(0)}$ indicates that these are solutions for the unperturbed Hamiltonian $\widehat{H}_0$. We drop this superscript for the energy eigenvalues E_k and the energy eigenfunctions $\psi_k(\mathbf{r})$.

[2] Strictly speaking, if we want to interpret the coefficient $a_k(t)$ as the probability amplitude of measuring the unperturbed energy E_k and leaving the system in the corresponding state $\Psi_k^{(0)}(\mathbf{r},t)$, we should turn *off* the perturbation just before the measurement at time t. Then, according to the measurement postulate, the energy E_k and the state $\Psi_k^{(0)}(\mathbf{r},t)$ would really be a possible outcome of the measurement. Similarly, the preparation of the initial unperturbed state ψ_i could be done immediately before turning *on* the perturbation at $t=0$. In such a setting, we can really talk about **transitions between stationary states**. Note also that transitions between states with different energies are possible because the time-dependent perturbation corresponds to a non-conservative system; the energy of a hydrogen atom is not constant when it is experiencing an external force.

14.2 Formulation of time-dependent perturbation theory

We wish to solve the Schrödinger equation (T14.2), or more generally the equation of motion

$$i\hbar\,\frac{d}{dt}\,|\,\Psi(t)\,\rangle = (\widehat{H}_0 + \widehat{V}(t)\ )\,|\,\Psi(t)\,\rangle, \tag{T14.5}$$

where we assume that $\widehat{H}_0$ is time independent, with a complete set of orthonormalized stationary eigenstates

$$|\,\Psi_n^{(0)}(t)\,\rangle = e^{-iE_nt/\hbar}\,|\,\psi_n\,\rangle \qquad \Big(\langle\,\mathbf{r}\,|\,\Psi_n^{(0)}(t)\,\rangle = \Psi_n^{(0)}(\mathbf{r},t)\Big)\,. \tag{T14.6}$$

We suppose that these are known. Following the discussion above, we expand the unknown solution of (T14.5) as

$$|\,\Psi(t)\,\rangle = \sum_n a_n(t)\,|\,\Psi_n^{(0)}(t)\,\rangle, \tag{T14.7}$$

which is the Hilbert-space version of (T14.4). Note that the expansion coefficient

$$a_n(t) = \langle\,\Psi_n^{(0)}(t)\,|\,\Psi(t)\,\rangle \tag{T14.8}$$

is the amplitude of finding the system in the unperturbed state $|\,\Psi_n^{(0)}\,\rangle$ at time t, while $|a_n(t)|^2$ is the corresponding probability. Given that $\widehat{V}(t)$ and hence $\widehat{H}$ are Hermitian, we know that $|\,\Psi(t)\,\rangle$ stays normalized for all times, so that

$$\sum_n |a_n(t)|^2 = 1, \tag{T14.9}$$

even if the individual probabilities $|a_n(t)|^2$ do change with time. This time dependence (which is our main aim) is of course determined by the "Schrödinger equation" (T14.5). Inserting the expansion (T14.7) we get

$$\sum_n \left(i\hbar\,\frac{da_n}{dt}\,|\,\Psi_n^{(0)}(t)\,\rangle + a_n\ \underbrace{i\hbar\,\frac{d}{dt}\,|\,\Psi_n^{(0)}(t)\,\rangle}_{E_n|\,\Psi_n^{(0)}(t)\,\rangle} \right) = \sum_n\ a_n\ \left(\underbrace{\widehat{H}_0\,|\,\Psi_n^{(0)}(t)\,\rangle}_{E_n|\,\Psi_n^{(0)}(t)\,\rangle} + \widehat{V}(t)|\,\Psi_n^{(0)}(t)\,\rangle \right).$$

Here we observe that the second term on the left cancels against the first term on the right, because

$$i\hbar\,\frac{d}{dt}\,|\,\Psi_n^{(0)}(t)\,\rangle = \widehat{H}_0\,|\,\Psi_n^{(0)}(t)\,\rangle = E_n\,|\,\Psi_n^{(0)}(t)\,\rangle.$$

Multiplication from the left by $\langle\,\Psi_k^{(0)}(t)\,|$ and use of the orthonormality relation

$$\langle\,\Psi_k^{(0)}(t)\,|\,\Psi_n^{(0)}(t)\,\rangle = \langle\,\psi_k\,|\,\psi_n\,\rangle = \delta_{kn} \tag{T14.10}$$

then gives a set of first-order differential equations for the amplitudes:

$$i\hbar\,\frac{da_k(t)}{dt} = \sum_n \langle\,\Psi_k^{(0)}(t)\,|\widehat{V}(t)|\,\Psi_n^{(0)}(t)\,\rangle\,a_n(t), \tag{T14.11}$$

or

$$\boxed{i\hbar\,\frac{d}{dt}\,a_k(t) = \sum_n e^{i\omega_{kn}t}\,V_{kn}(t)\,a_n(t).} \tag{T14.12}$$

Here we have introduced the abbreviations

$$\begin{aligned} V_{kn}(t) &\equiv \langle\psi_k|\widehat{V}(t)|\psi_n\rangle \equiv \int \psi_k^*(\mathbf{r})\,\widehat{V}(\mathbf{r},t)\,\psi_n(\mathbf{r})d^3r, \quad \text{and} \\ \omega_{kn} &\equiv (E_k - E_n)/\hbar, \end{aligned} \tag{T14.13}$$

which are called respectively a **matrix element** of the perturbation and a **Bohr frequency**.

Note that the coupled set of differential equations (T14.11) can be written on matrix form, if we wish:

$$i\hbar\,\frac{d}{dt}\begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \cdots \\ V_{21}e^{-i\omega_{12}t} & V_{22} & \\ \vdots & & \end{pmatrix}\begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \end{pmatrix}. \tag{T14.14}$$

This coupled set of equations, (T14.12) or (T14.14), is completely equivalent to the Schrödinger equation; we have made no approximations so far.

Note that if the perturbation term $\widehat{V}(t)$ is put equal to zero, then "nothing happens"; the coefficients $a_k(t)$ keep the values they had at $t = 0$. Thus, if in our example above we had $a_k(0) = \delta_{ki}$, then $a_k(t) = \delta_{ki}$, and the atom remains in the initial state $|\Psi_i^{(0)}(t)\rangle$.

Time-dependent perturbation theory

In time-dependent perturbation theory we assume that the perturbation $\widehat{V}(t)$ is *weak*, so that the coefficients $a_k(t)$ change only slowly from their initial values. We also suppose that the system was prepared in the unperturbed state $|\psi_i\rangle$ at $t = 0$, so that $a_k(0) = \delta_{ki}$. As a first approximation we may then set $a_n(t)$ on the right-hand side of (T14.12) equal to $a_n(0) = \delta_{ni}$. For sufficiently short times and/or sufficiently weak perturbations we thus have the following approximation:

$$i\hbar\,\frac{d\,a_k(t)}{dt} \approx \sum_n e^{i\omega_{kn}t}V_{ni}(t)\,\delta_{ni} = e^{i\omega_{ki}t}\,V_{ki}(t).$$

The amplitude of finding the perturbed system in the unperturbed state number f (f for final) at time t then is

$$\boxed{a_f(t) \approx \delta_{fi} + \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'}\,V_{fi}(t')\,dt'.} \tag{T14.15}$$

For $f \neq i$ this is a transition amplitude. We note that this amplitude is of first order in the perturbation $\widehat{V}$. (There is only one power of $\widehat{V}$ in the integral.) This means that the transition *probability* is of second order in $\widehat{V}$. Equation (T14.9) then implies that the probability of finding the system in the initial state is

$$|a_i(t)|^2 = 1 - \sum_{f\neq i}|a_{f\neq i}(t)|^2 = 1 - \mathcal{O}(\widehat{V}^2). \tag{T14.16}$$

that is, deviates from 1 only to second order in the perturbation.

Detailed balancing

Since the perturbation $\widehat{V}(t)$ is supposed to be Hermitian, the matrix element entering the first-order transition amplitude (T14.15) for the process $1 \to 2$ satisfies the relation

$$V_{21}(t) \equiv \langle \psi_2 | \widehat{V}(t) | \psi_1 \rangle = \langle \psi_1 | \widehat{V}(t) | \psi_2 \rangle^* \equiv V_{12}^*(t). \qquad \text{(T14.17)}$$

For the "reversed" process — transition from state number 2 at time $t = 0$ to state number 1 at time t — we then have from (T14.15) to first order (for $\psi_2 \neq \psi_1$)

$$\begin{aligned} a_{2\to 1}(t) &= \frac{1}{i\hbar}\int_0^t V_{12}(t')e^{i\omega_{12}t'}dt' = \frac{1}{i\hbar}\int_0^t V_{21}^*(t')e^{-i\omega_{f21}t'}dt' \\ &= -a_{1\to 2}^*(t). \end{aligned} \qquad \text{(T14.18)}$$

Thus, taking the absolute squares on both sides of this equation, we find that the first-order transition probability from the state $|\Psi_1(0)\rangle$ at time $t = 0$ to the state $|\Psi_2(t)\rangle$ at time t is the same as for the reverse process. This equality, valid to first order in the perturbation $\widehat{V}$, is an example of the so-called **principle of detailed balance**.

Perturbation expansion

The approximate result (T14.15) can easily be improved. Integrating (T14.12) we have

$$a_k(t) = \delta_{ki} + \frac{1}{i\hbar}\sum_n \int_0^t dt'\, e^{i\omega_{kn}t'} V_{kn}(t') a_n(t'). \qquad \text{(T14.19)}$$

Substituting $k \to n$ and $t \to t'$, we have

$$a_n(t') = \delta_{ni} + \frac{1}{i\hbar}\sum_m \int_0^{t'} dt''\, e^{i\omega_{nm}t''} V_{nm}(t'') a_m(t''), \qquad \text{(T14.20)}$$

which may be inserted into (T14.19), giving

$$\begin{aligned} a_k(t) &= \delta_{ki} + \frac{1}{i\hbar}\int_0^t dt'\, e^{i\omega_{ki}t'} V_{ki}(t') \\ &\quad + \frac{1}{i\hbar}\sum_n \int_0^t dt'\, e^{i\omega_{kn}t'}\, V_{kn}(t') \cdot \frac{1}{i\hbar}\sum_m \int_0^{t'} dt''\, e^{i\omega_{nm}t''} V_{nm}(t'') a_m(t''). \end{aligned}$$

This iteration procedure can be repeated. If we break it off by putting $a_m(t'') \approx a_m(t'' = 0) = \delta_{mi}$, we get

$$\begin{aligned} a_k(t) &= \delta_{ki} + \frac{1}{i\hbar}\int_0^t dt'\, e^{i\omega_{ki}t'} V_{ki}(t') \\ &\quad + \left(\frac{1}{i\hbar}\right)^2 \sum_n \int_0^t dt'\, e^{i\omega_{kn}t'} V_{kn}(t') \int_0^{t'} dt''\, e^{i\omega_{ni}t''} V_{ni}(t'') \qquad \text{(T14.21)} \\ &\quad + \mathcal{O}(\widehat{V}^3). \end{aligned}$$

I guess that you will have no problem writing down the next term simply from the systematics.

14.3 Qualitative discussion

Let us try to understand qualitatively what happens after the initial preparation of the system in the state $|\psi_i\rangle$ at $t = 0$. As we have seen above, probability will immediately start to "leak" from the initial state into the other states. In the beginning, for small t, this leakage is fairly modest; the integrals in (T14.15) (for $f \neq i$) are small, corresponding to transition probabilities $|a_{f\neq i}(t)|^2$ much smaller than 1, so that the amplitude $a_i(t)$ of being found in the initial state is almost equal to 1. The first-order result (T14.15) then is a good approximation.

In this course we shall only make use of the first-order result (T14.15), assuming that the perturbation is sufficiently weak, or that the time t is sufficiently small, to make this a good approximation.

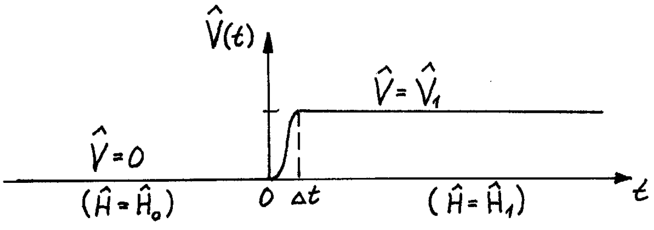
"Sudden" changes of the Hamiltonian

In what follows we shall try to gain a little more insight by considering two extreme cases in time-dependent perturbation theory, namely so-called **sudden** changes of the Hamiltonian $\widehat{H}(t)$, and the opposite case which is a very slow change, called an **adiabatic** change.

In the first case a change of $\widehat{H}(t)$, from $\widehat{H}_0$ to $\widehat{H}_1$, takes place very rapidly, during a time interval Δt which is much shorter than any of the natural periods for the system we are considering:

$$\Delta t << T_{fi} \equiv \frac{2\pi}{\omega_{fi}} = \frac{2\pi\hbar}{E_f - E_i}.$$

This is what we call a *sudden* change of $\widehat{H}$:



The phase factors $e^{i\omega_{fi}t'}$ in (T14.15) then stay approximately constant under the integration. Therefore the transition probabilities at the time $t_0 + \Delta t$ will be of the order of

$$|a_{i\to f}(t_0 + \Delta t)|^2 \sim \left|\frac{1}{\hbar}(V_1)_{fi}\Delta t\right|^2 << \left|\frac{2\pi(V_1)_{fi}}{E_f - E_i}\right|^2 \;; \qquad f \neq i. \qquad \text{(T14.22)}$$

If we suppose that the matrix elements $(V_1)_{fi}$ are not much larger than the energies of the system, these probabilities will be much smaller than 1. This means that the "leakage" to other states is insignificant, and that the probability of finding the system in the original state is practically unchanged:

$$|a_i(t_0 + \Delta t)| \approx a_i(t_0) = 1.$$

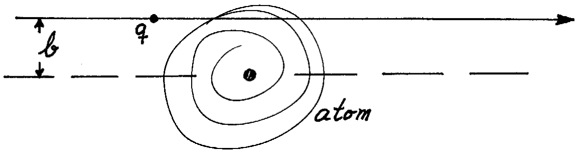
Thus the state vector $|\Psi(t)\rangle$ and the corresponding wave function Ψ are "unable to react immediately" to the sudden change of $\widehat{H}$.

This can also be understood directly. When the change in $\widehat{H}(t)$, from $\widehat{H}_0$ to $\widehat{H}_1$, takes place in the time interval Δt, we see from the Schrödinger equation that the state vector changes by the amount

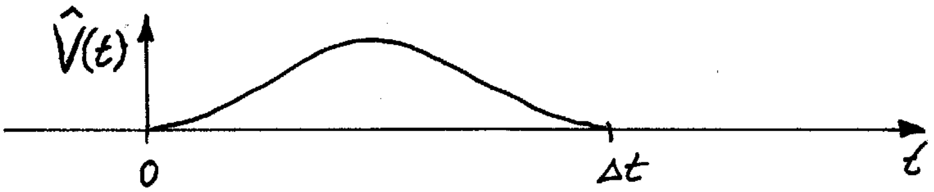
$$\Delta|\,\Psi(t)\rangle = \Delta t \cdot \frac{1}{i\hbar}\,\widehat{H}(t)\,|\,\Psi(t)\rangle$$

during this interval. Thus, when Δt is sufficiently small, $|\,\Psi(t)\rangle$ is essentially unchanged.[3]

In the discussion above we have considered a "permanent" change of $\widehat{H}$. As another example we might consider a case of a short **transient** perturbation, where $\widehat{V}(t)$ is a short pulse, so that $\widehat{H} = \widehat{H}_0$ both before $t = 0$ and after $t = \Delta t$. As an example of such a short pulse-like perturbation we may consider a heavy charged particle like a proton travelling through matter with a velocity close to c.



An atomic electron close to the track of the proton will then experience a "Coulomb pulse" of very short duration, $\Delta t \sim a_0/c \sim 10^{-19}$ s, which is much shorter than the "natural periods" of the outer electrons, $T_{fi} = 2\pi/\omega_{fi} \sim 10^{-16}$ s.



With matrix elements V_{fi} of the order of $e^2/(4\pi\epsilon_0 a_0)$ we then get transition probabilities of the order of

$$\begin{aligned}|a_{i\to f}|^2 &= \left|\frac{1}{i\hbar}\int_0^{\Delta t} V_{fi}(t')\,dt'\right|^2 \sim \left|\frac{\Delta t \cdot V_{fi}}{\hbar}\right|^2 \\ &= \left|\frac{a_0/c}{\hbar}\,\frac{e^2}{4\pi\epsilon_0 a_0}\right|^2 = \alpha^2,\end{aligned}$$

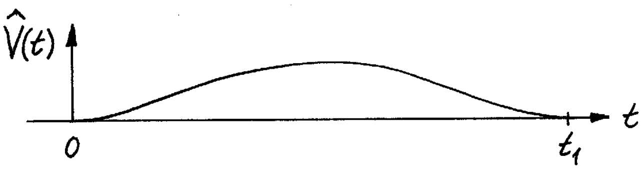
where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 127.036^{-1}$ is the fine-structure constant. Thus, for each of the atoms along the track the probablity of excitation or ionization is small when the proton is moving fast. This means that the average energy loss for the proton is small for each "collision" along the track.

Adiabatic changes of $\widehat{H}$

The opposite extreme (compared to the sudden change) is a case in which the Hamiltonian changes very *slowly* compared to the natural periods T_{fi} of the system. Suppose that the change is **transient**, as indicated in the figure.

---

[3] This is also how we prove that the state vector and the wave function are continuous in time.



Here, $\widehat{V}(t)$ is zero for $t < 0$ and for $t > t_1$, where $t_1 >> T_{fi} = 2\pi/\omega_{fi}$. According to (T14.15) the transition amplitudes for $t > t_1$ then are given by

$$a_{f\neq i}(t) = \frac{1}{i\hbar}\int_0^{t_1} e^{i\omega_{fi}t'}\, V_{fi}(t')\, dt', \qquad (t \geq t_1)$$

where $V_{fi}(t')$ is a very slowly varying function compared to the oscillations of the exponential

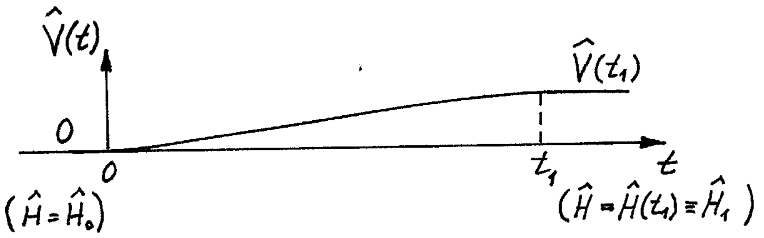
$$e^{i\omega_{fi}t'} = \cos(\omega_{fi}t') + i\sin(\omega_{fi}t')$$

(provided that $E_f \neq E_i$). Because of these rapid oscillations the contributions to the integral above cancel almost completely. Thus for a very slow (adiabatic) change of $\widehat{H}$ we arrive at

The adiabatic approximation:
The transition probabilities are negligible. (T14.23)

Note that the integral above essentially is the Fourier transform of the matrix element $V_{fi}(t)$, for the frequency ω_{fi}. The transition amplitude is essentially a "high-frequency" component of V_{fi}, and these components are very small. The *dominant* Fourier componets of V_{fi} are those for frequencies in the range $\omega \sim 2\pi/t_1$ ($<< \omega_{fi}$).

An adiabatic change of $\widehat{H}$ does not have to be transient (as in the discussion above), but can also lead to a permanent change of $\widehat{H}$, as indicated in the next figure.

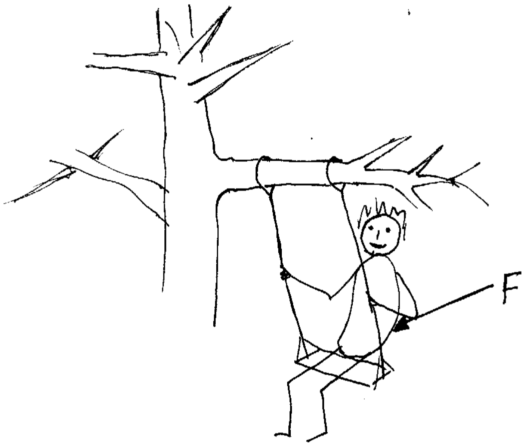


It can be shown that if the system is in a given eigenstate of $\widehat{H}_0$ at $t = 0$, then at $t = t_1$ it will be in the corresponding eigenstate of $\widehat{H}(t_1) = \widehat{H}_1$ (e.g. the ground state), with a probability close to 1. A classical analogy: A violin string vibrating in the first harmonic mode will remain in this mode during adiabatic (slow) changes of the string tension.

When the change in $\widehat{H}$ is neither sudden nor adiabatic,

transitions do occur. An example is a proton travelling with a velocity of the same order as that of the atomic electrons it encounters on its way. The electrons then experience a perturbation $\widehat{V}(t)$ with significant Fourier components in the same frequency range as ω_{fi}. This may result in sizable transition amplitudes into excited or ionized states, corresponding to a much higher rate of energy loss for the proton than in the case of a high proton velocity (discussed above). Semiclassically we may state that under such conditions the chances are fairly high that an atomic electron recieves a Coulomb "push" (or "pull") which takes it to a higher energy level.

The figure shows a classical setting which can be used to illustrate the different cases discussed above: Applying a (rather strong) force over a very short time interval only hurts, and does not add much to the excitement. A very slowly varying force, more or less constant over several periods, is also very boring. However, if we push with a force comparable with the other forces in the system over let us say half a period, there will be cheers.



14.4 Harmonic perturbations

Another way to reach the same goal is to apply a periodic force, $F = F_0\cos(\omega t)$. Here, we know from mechanics and from practical experience that if ω is close to the eigenfrequency of the swing, the energy can increase or decrease considerably, depending on whether the force acts *in phase* or *in counterphase* with the motion, even with a fairly weak force. On the other hand, if ω is not close to the eigenfrequency, the applied force does not help much.

A similar **resonance phenomenon** also occurs in quantum mechanics, where **harmonic perturbations** play an important role. We assume a perturbation term with the form

$$\widehat{V}(\mathbf{r},t) = \widehat{\mathcal{V}}(\mathbf{r})e^{-i\omega t} + \widehat{\mathcal{V}}^\dagger(\mathbf{r})e^{i\omega t}. \tag{T14.24}$$

(An example would be an electromagnetic wave $\boldsymbol{\mathcal{E}} = \hat{\mathbf{e}}_z\mathcal{E}_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$ incident on a hydrogen atom. This would roughly correspond to $\widehat{\mathcal{V}}(\mathbf{r}) = \frac{1}{2}e\mathcal{E}_0 z\exp(i\mathbf{k}\cdot\mathbf{r})$. [4]) With

$$\langle\psi_f|\widehat{\mathcal{V}}(\mathbf{r})|\psi_i\rangle \equiv \mathcal{V}_{fi} \quad \text{and} \tag{T14.25}$$

$$\langle\psi_f|\widehat{\mathcal{V}}^\dagger(\mathbf{r})|\psi_i\rangle = \langle\psi_i|\widehat{\mathcal{V}}(\mathbf{r})|\psi_f\rangle^* = \mathcal{V}_{if}^*, \tag{T14.26}$$

the matrix elements $V_{fi}(t)$ occurring in the transition amplitude (T14.15) then become

$$V_{fi}(t) = \langle\psi_f|\widehat{V}(\mathbf{r},t)|\psi_i\rangle = \mathcal{V}_{fi}\,e^{-i\omega t} + \mathcal{V}_{if}^*\,e^{i\omega t}. \tag{T14.27}$$

---

[4] There is also a magnetic force $-e\mathbf{v}\times\mathbf{B}$, but since the amplitude of the $\mathbf{B}$-field is a factor c smaller than that of the $\boldsymbol{\mathcal{E}}$-field, the ratio between the magnetic and electric forces goes as v/c, which is of the order of the fine-structure constant for the electron in the hydrogen atom.

Here, the quantities $\mathcal{V}_{fi}$ are time independent. The first-order transition amplitude (for $f \neq i$) then is given by two simple integrals over oscillating exponentials:

$$\begin{aligned} a_{i\to f}(t) &= \frac{1}{i\hbar}\mathcal{V}_{fi}\int_0^t e^{i(\omega_{fi}-\omega)t'}dt' + \frac{1}{i\hbar}\mathcal{V}_{if}^{*}\int_0^t e^{i(\omega_{fi}+\omega)t'}dt' && \text{(T14.28)} \\ &= \mathcal{V}_{fi}\,\frac{1-e^{i(\omega_{fi}-\omega)t}}{\hbar(\omega_{fi}-\omega)} + \mathcal{V}_{if}^{*}\,\frac{1-e^{i(\omega_{fi}+\omega)t}}{\hbar(\omega_{fi}+\omega)}. && \text{(T14.29)} \end{aligned}$$

Let us consider a transition from the hydrogen ground state (ψ_1) to a state (ψ_2) belonging to the first excited level. The excitation energy then is $E_f - E_i = E_2 - E_1 = 10.2$ eV, corresponding to a Bohr frequency $\omega_{fi} = (E_2 - E_1)/\hbar = 10.2\ \text{eV}/(6.58\cdot 10^{-16}\text{eVs}){=}1.55{\cdot}10^{16}\ \text{s}^{-1}$. It turns out that the size of $\mathcal{V}_{fi}$ is of the order that could be expected from the analogy with the swing, namely the force $e\mathcal{E}_0$ on the electron multiplied by the atomic radius: $\mathcal{V}_{fi} \sim e\mathcal{E}_0 a_0$. This energy amount is in practice much smaller than $\hbar\omega_{fi} = E_f - E_i$. As a consequence, the transition amplitude is very small, except for the case where the denominator in the first term, $\hbar(\omega_{fi} - \omega)$, is small. This happens when

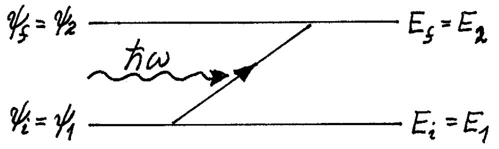
$$\omega \approx \omega_{fi}, \tag{T14.30}$$

which is the quantum-mechanical **resonance condition** in this case. In this example, the second term never is large, because the denominator $\omega_{fi} + \omega > \omega_{fi}$ never is small.

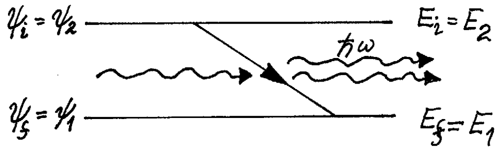
We could, however, turn the example around, and consider a transition from the first excited level to the ground state. Then the Bohr frequency $\omega_{fi} = (E_1 - E_2)/\hbar$ is negative, and it is only the second term in (T14.29) that can become large; the resonance condition in this case is

$$\omega \approx -\omega_{fi}. \tag{T14.31}$$

In our example the harmonic perturbation is due to an electromagnetic wave with angular frequency ω. When the resonance condition is satisfied, $\hbar\omega \approx E_2 - E_1$, we see that the transition from ψ_1 to ψ_2 corresponds to **absorption** of the energy $\hbar\omega$ from the wave:



In the reverse prosess we have **stimulated emission** of the same amount.



Experimentally, these processes correspond respectively to absorption and stimulated emission of a photon; cf Einstein's argument in 1917, which was discussed in Lecture notes 8 (section 8.3.d).[5]

---

[5] The theoretical description of photons requires quantization of the electromagnetic field, which will be done in a later course.

The transition probabilities of both processes depend critically on how closely the resonance condition is satisfied, i.e. on what we might call the "energy mismatch". In the absorption case this is

$$\hbar(\omega_{fi}-\omega)=E_f-E_i-\hbar\omega=E_2-E_1-\hbar\omega\equiv\epsilon .$$

In the emission case it is

$$\hbar(\omega_{fi}+\omega)=E_f-E_i+\hbar\omega=E_1+\hbar\omega-E_2 .$$

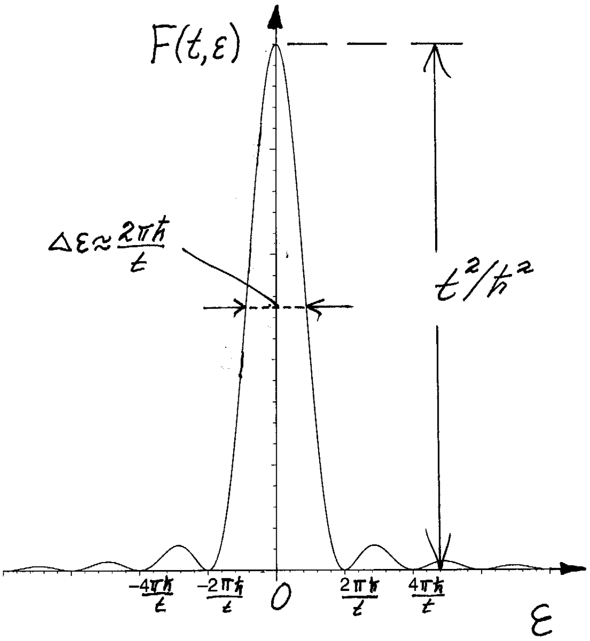
Thus in the absorption case we have

$$|a_{i\to f}(t)|^2=|\mathcal{V}_{fi}|^2F(t,E_f-E_i-\hbar\omega)=|\mathcal{V}_{fi}|^2F(t,\epsilon), \tag{T14.32}$$

where

$$\begin{aligned} F(t,\epsilon) &\equiv \left|\frac{1-e^{i\epsilon t/\hbar}}{\epsilon}\right|^2=\left|\frac{e^{i\epsilon t/2\hbar}}{\epsilon}(e^{-i\epsilon t/2\hbar}-e^{i\epsilon t/2\hbar})\right|^2 \\ &= \frac{t^2}{\hbar^2}\,\frac{\sin^2(\epsilon t/2\hbar)}{(\epsilon t/2\hbar)^2}. \end{aligned} \tag{T14.33}$$

Here, $\mathcal{V}_{fi}(E_f,E_i)$ is a slowly varying function of the energies, while $F(t,\epsilon)$ is very sharply peaked about $\epsilon=0$ (except for very short times t). The maximum is $F(t,0)=t^2/\hbar^2$, and the half-width $\Delta\epsilon$ is roughly half the distance between the two zeros at $\epsilon t/2\hbar=\pm\pi$, so that $\Delta\epsilon\cdot t/2\hbar\approx\pi$, that is, $\Delta\epsilon\approx 2\pi\hbar/t$.



Thus, for increasing t the maximum increases as $t^2/\hbar^2$, while the width decreases as $2\pi\hbar/t$. This means that the area under the curve is proportional to t. For increasing t the function $F(t,\epsilon)$ therefore approaches a delta function in ϵ, multiplied by t and some constant C, $F(t,\epsilon)\to C\,t\,\delta(\epsilon)$. This constant is easily determined by calculating the area under the curve:

$$\begin{aligned} C\,t &= \int_{-\infty}^{\infty} F(t,\epsilon)d\epsilon = \frac{t^2}{\hbar^2}\int_{-\infty}^{\infty}\frac{\sin^2(\epsilon t/2\hbar)}{(\epsilon t/2\hbar)^2}\,d\epsilon \\ &= \frac{t^2}{\hbar^2}\,\frac{2\hbar}{t}\underbrace{\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\,dx}_{\pi} \qquad \Longrightarrow \qquad C = \frac{2\pi}{\hbar}. \end{aligned}$$

Thus for large t

$$\begin{aligned} F(t,\epsilon) &\approx \frac{2\pi}{\hbar}\,t\,\delta(\epsilon) \\ &= \frac{2\pi}{\hbar}\,t\,\delta(E_f - E_i - \hbar\omega), \end{aligned} \tag{T14.34}$$

so that the transmission probability for absorption is given approximately by

$$\boxed{|a_{i\to f}(t)|^2 \approx \frac{2\pi}{\hbar}\,|\mathcal{V}_{fi}|^2\,t\,\delta(E_f - E_i - \hbar\omega)} \qquad (\text{ absorption }). \tag{T14.35}$$

For the reverse process of stimulated emission we get in the same manner (with $|\mathcal{V}_{if}^*| = |\mathcal{V}_{if}|$)

$$\boxed{|a_{i\to f}(t)|^2 \approx \frac{2\pi}{\hbar}\,|\mathcal{V}_{if}^*|^2\,t\,\delta(E_f - E_i + \hbar\omega)} \qquad \begin{pmatrix}\text{stimulated}\\ \text{emission}\end{pmatrix}. \tag{T14.36}$$

The proportionality with t in these equations is important for two reasons:

(i) Firstly, it is obvious that these formulae are not valid for arbitrarily large t. Otherwise the probabilities $|a_{i\to f}(t)|^2$ would sooner or later exceed 1, and that is certainly not allowed. In fact, the first-order formulae above are only valid as long as the probability $|a_i(t)|^2$ stays close to 1, requiring that the sum

$$\sum_{f\neq i}|a_{i\to f}(t)|^2$$

of all the transition probabilities is much smaller than 1 (cf equation (T14.9) and the discussion in section 14.2 above). The formulae (T14.35) and (T14.36) can therefore only be used in a limited time interval. The upper limit will depend on the system we are considering, the strength of the perturbation, etc. Thus the delta functions are only approximate; the width of the peak above is finite. There is also a limitation on t from below; we want t to be so large that the width $\Delta\epsilon = 2\pi\hbar/t$ is much smaller than the relevant energy scale (given by E_i and E_f).

(ii) Secondly, these limitations on t usually pose no problem, because what is really interesting about the formulae above is that the transition probabilities per unit time, i.e., the **transition <u>rates</u>** for respectively absorption and stimulated emission are time independent. Thus, for the case where absorption causes excitation from ψ_1 to ψ_2 the transition rate is

$$\boxed{w_{1\to 2} \equiv \frac{|a_{1\to 2}(t)|^2}{t} = \frac{2\pi}{\hbar}\,|\mathcal{V}_{21}|^2\,\delta(E_2 - E_1 - \hbar\omega).} \tag{T14.37}$$

For the reverse process, de-excitation via stimulated emission, the rate is (with $\mathcal{V}_{if} = \mathcal{V}_{21}$)

$$\boxed{w_{2\to 1} \equiv \frac{|a_{2\to 1}(t)|^2}{t} = \frac{2\pi}{\hbar}\, |\mathcal{V}_{21}|^2\, \delta(E_1 - E_2 + \hbar\omega).} \tag{T14.38}$$

Since the two δ-functions are equal, we arrive at the following conclusion:

With a harmonic perturbation (T14.24), we can state that for any pair of states (ψ_1 and ψ_2) the first-order transition rate for stimulated emission equals that for absorption: (T14.39)

$$w_{2\to 1} = w_{1\to 2}.$$

In the example mentioned above, we considered transitions between the discrete states ψ_1 and ψ_2, which are examples of what we might call **discrete** → **discrete** transitions. The resonance condition, $\omega \approx (E_2 - E_1)/t$, can then be met only if the atom is perturbed by a continuous spectrum of radiation. We shall return to this problem later.

14.5 Discrete → continuous transitions. Fermi's Golden Rule

As another example, we could use monochromatic radiation with a photon energy $\hbar\omega$ high enough to ionize the atom. If the initial state ψ_i is the hydrogen ground state ψ_1, this requires photons with an energy higher than 13.6 eV. Then the relevant final states ψ_f are continuum states for the emitted electron, with an energy $E_f \approx \hbar\omega - 13.6$ eV, and the process we are considering is photo-ionization or the photoelectric effect.

The total rate of transitions, W_i, from the initial state ψ_i then is given by

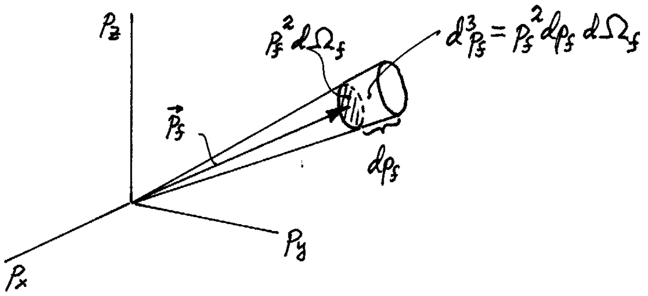
$$W_i = \sum_f w_{i\to f}, \tag{T14.40}$$

where the summation goes over all states ψ_f with energies close to or within the peak discussed above. Here we seem to be running into a problem, because the number of continuum states really is infinite. We can avoid this (apparent) problem by imagining our atom (and the whole experiment) being enclosed in a large box (cubical if you like) with a finite but large volume V_0. By taking this "reaction volume" $V_0 = L^3$ sufficiently large, we will then have what is called a quasi continuum of states. With periodic boundary conditions the normalized wave functions are (cf Lecture notes 8, section 8.1)

$$\psi_f(\mathbf{r}) = \frac{1}{\sqrt{V_0}}\, e^{i\mathbf{p}_f\cdot\mathbf{r}/\hbar}, \qquad \mathbf{p}_f = \frac{2\pi\hbar}{L}\{n_x, n_y, n_z\}, \quad n_x = 0, \pm 1, \cdots, \text{ etc.} \tag{T14.41}$$

This way the number of final states within our "peak" is very large, but finite.

The electrons can be emitted in any direction.



Let us consider electrons emitted into the solid-angle element $d\Omega_f$. We then remember from the discussion in section 8.1.d that the number of electron states in the phase-space element $V_0 d^3p_f = V_0 p_f^2 dp_f\, d\Omega_f$ is

$$dN = \frac{V_0\, d^3p_f}{h^3} = \frac{V_0}{h^3}\, p_f^2\, \frac{dp_f}{dE_f}\, dE_f\, d\Omega_f \equiv \rho(E_f)\, dE_f. \qquad \text{(T14.42)}$$

With $dp_f/dE_f = 1/v_f$ we then get the following **density of final states** (number of states per unit energy within $d\Omega_f$):

$$\begin{aligned} \rho(E_f) = \frac{dN}{dE_f} &= \frac{V_0}{h^3}\frac{p_f^2}{v_f}\, d\Omega_f \qquad \left(\begin{array}{c}\text{relativistic, for}\\ \text{particles and photons}\end{array}\right) \\ &= \frac{V_0}{h^3}\, m p_f\, d\Omega_f. \qquad \left(\begin{array}{c}\text{non-relativistic, for}\\ \text{particles with mass } m\end{array}\right) \end{aligned} \qquad \text{(T14.43)}$$

Since the number of final states within the peak around $E_f = E_i + \hbar\omega$ is very large, we may replace the summation over final states (within $d\Omega_f$) by an integral over E_f. Because the emission angles are fixed (within $d\Omega_f$), and because the energies E_f are restricted by the δ-like peak, we understand that the matrix element $\mathcal{V}_{fi}$ will be approximately constant during the integration. According to (T14.37) the transition rate (into $d\Omega_f$) therefore becomes

$$dW_{(i\to d\Omega_f)} = \sum_f w_{i\to f} = \frac{2\pi}{\hbar}\int |\mathcal{V}_{fi}|^2\, \delta(E_f - E_i - \hbar\omega)\, \rho(E_f)\, dE_f,$$

or

$$\boxed{dW_{(i\to d\Omega_f)} = \frac{2\pi}{\hbar}\left\{|\mathcal{V}_{fi}|^2\, \rho(E_f)\right\}_{E_f = E_i + \hbar\omega}} \qquad \left(\begin{array}{c}\text{Fermi's}\\ \text{Golden Rule}\end{array}\right). \qquad \text{(T14.44)}$$

This very important formula, first discovered by Dirac, is known as **Fermi's Golden Rule**. Because this equation is so intimately connected with (T14.37), also the latter is sometimes called Fermi's golden rule.

Note that the square of the matrix element includes a factor $1/V_0$ from (T14.41), which cancels against the factor V_0 in $\rho(E_f)$. Thus the transition rate is independent of the imagined volume V_0, as it should be.

To find the *total* rate of transitions (T14.40) from the state ψ_i, we would have to calculate the matrix element $\mathcal{V}_{fi}$ for the photoelectric effect, including the way it depends on the emission angles, and then integrate the above formula over all angles. (See section 12.6 in Hemmer.)

14.6 Scattering on static potential

In a scattering process the particles are unbound both before and after the scattering, so here we are talking about **continuous** $\to$ **continuous** transitions. Suppose that one particle collides with another, and that the interaction potential is $V(\mathbf{r}_1-\mathbf{r}_2)$. Introducing the **relative coordinate** $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ and the **reduced mass** $m=m_1m_2/(m_1+m_2)$, we can treat this scattering problem as a one-particle problem, where a (fictitious) particle with mass m is scattered on the static potential $V(\mathbf{r})$. (Cf section 5.8 in Hemmer, and 5.7 in B&J).

The Hamiltonian for this "reduced" particle may be written as $\widehat{H}=\widehat{H}_0+V(\mathbf{r})$, where $\widehat{H}_0=\widehat{\mathbf{p}}^2/2m$ is the free-particle Hamiltonian and the potential $V(\mathbf{r})$ is considered as a perturbation (time independent in this case). As our unperturbed basis we may then use the momentum eigenfunctions (T14.41), which are eigenfunctions of $\widehat{H}_0$.

Suppose that the particle is at $t=0$ preparered in the state

$$\psi_i(\mathbf{r})=\frac{1}{\sqrt{V_0}}\,e^{i\mathbf{p}_i\cdot\mathbf{r}/\hbar}.$$

Since this initial state is an eigenfunction of $\widehat{H}_0$, but not of the complete Hamiltonian $\widehat{H}$, the perturbation (i.e. the potential) will immediately begin to cause a "leakage of probability" into other momentum eigenstates

$$\psi_f(\mathbf{r})=\frac{1}{\sqrt{V_0}}\,e^{i\mathbf{p}_f\cdot\mathbf{r}/\hbar},$$

and we may ask to find the transition rate from ψ_i to ψ_f.

One way to solve this problem is to use time-dependent perturbation theory.[6] With the time-independent matrix element

$$\begin{aligned} V_{fi}(t)=V_{fi} &\equiv \int \psi_f^*(\mathbf{r})V(\mathbf{r})\psi_i(\mathbf{r})d^3r \\ &= \frac{1}{V_0}\int e^{i(\mathbf{p}_i-\mathbf{p}_f)\cdot\mathbf{r}/\hbar}V(\mathbf{r})d^3r, \end{aligned} \qquad \text{(T14.45)}$$

the integral in (T14.15) simplifies to $\int_0^t \exp(i\omega_{fi}t')dt'$. For $\mathbf{p}_f\neq\mathbf{p}_i$ we then find the transition probability

$$\begin{aligned} |a_{i\to f}(t)|^2 &= \left|\frac{V_{fi}}{i\hbar}\int_0^t e^{i\omega_{fi}t'}dt'\right|^2=|V_{fi}|^2\cdot\left|\frac{1-e^{i\omega_{fi}t}}{\hbar\omega_{fi}}\right|^2 \\ &\equiv |V_{fi}|^2\cdot F(t,E_f-E_i). \end{aligned}$$

Here, according to (T14.34),

$$F(t,E_f-E_i)\approx\frac{2\pi}{\hbar}\,t\,\delta(E_f-E_i).$$

Thus the transition *rate* to the state ψ_f is

$$w_{i\to f}\approx\frac{2\pi}{\hbar}\,|V_{fi}|^2\delta(E_f-E_i). \qquad \text{(T14.46)}$$

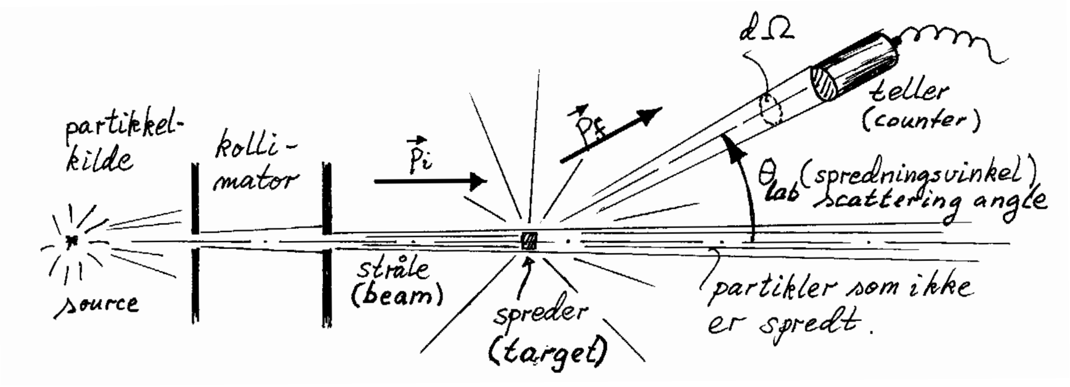
In this example of Fermi's golden rule, the delta function is only approximate, as in (T14.37). Thus transitions occur only to final states with energy $E_f=E_i+\mathcal{O}(2\pi\hbar/t)$.

---

[6] Another way is to use scattering theory, which is not a part of the present course, but will be taught in TFY4205 Quantum Mechanics.

Scattering cross section

In a scattering experiment the initial state ψ_i can be prepared by **collimating** a beam of particles with reasonably sharp energy, so that the collimated beam contains particles with a well-defined momentum $\mathbf{p}_i$ incident on the **target**. (The target usually contains many particles.)



In many experiments the projectile particle is scattered on one of several target particles which are at rest in the lab. Note that the scattering angle θ_{lab} in the lab system differs from the scattering angle θ in the center-of-mass system (cf Bransden & Joachain, page 591).

Suppose that the detector accepts particles scattered into the solid angle $d\Omega$. Then, according to (T14.43) and (T14.46), the probability rate for the particle to be counted is

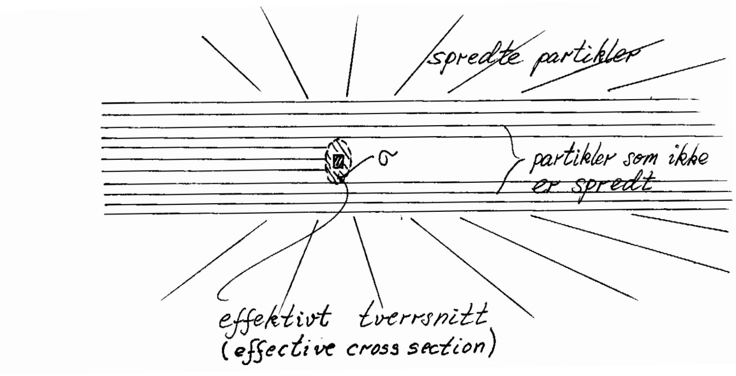
$$\begin{aligned} dW_{(i\to d\Omega)} &= \int w_{i\to f}\,\rho(E_f)dE_f = \frac{2\pi}{\hbar}\{|V_{fi}|^2\,\rho(E_f)\}_{(E_f=E_i)} \\ &= \frac{2\pi}{\hbar}\,|V_{fi}|^2\,\frac{V_0}{h^3}\,mp\,d\Omega; \qquad (p_f = p_i \equiv p). \qquad \text{(T14.47)} \end{aligned}$$

The integral over this quantity over all angles,

$$W_i = \int_\Omega dW_{(i\to d\Omega)},$$

is the probability per unit time that the incident particle is scattered, i.e. the total scattering rate.

> Before proceeding, let us make a (completely unrealistic) thought experiment: Suppose that we have an incoming flux j_i of 100 particles per cm^2 per second, and suppose that our target causes a scattering rate of $W = 300$ particles per second. This means that the target *effectively* removes a **cross section** of $\sigma = 3\,\text{cm}^2$ of the incoming flux:



$$\boxed{\sigma = \frac{W}{j_i} = \frac{\text{scattering rate}}{\text{incoming flux}}} \qquad \left(\begin{array}{c}\text{scattering}\\ \text{cross section}\end{array}\right) \qquad \text{(T14.48)}$$

$$= \frac{300\ \text{s}^{-1}}{100\ \text{cm}^{-2}\text{s}^{-1}} = 3\ \text{cm}^2.$$

The moral of this thought experiment is that the quantity $\sigma = W/j_i$ is a measure of the *scattering ability* of the target. This ability can even be differentiated with respect to angles: Suppose that the scattering rate into the solid angle $d\Omega$ is dW. Then the scattering into $d\Omega$ effectively removes a cross section

$$\boxed{d\,\sigma = \frac{dW}{j_i} = \frac{\text{scattering rate into } d\Omega}{\text{incoming flux}}} \qquad \left(\begin{array}{c}\text{differential scattering}\\ \text{cross section}\end{array}\right) \qquad \text{(T14.49)}$$

of the incident flux.

Let us now return to our scattering experiment, where we again imagine that the whole experiment is enclosed in a fictitious box with volume $V_0 = L^3$. In the initial state there is one particle in this volume. This corresponds to a density $\rho_i = |\psi_i|^2 = 1/V_0$ and a flux

$$j_i = \Re\mathrm{e}[\psi_i^* \frac{\hbar}{im}\psi_i'] = |\psi_i|^2 v_i = \frac{1}{V_0}\frac{p}{m}. \qquad \text{(T14.50)}$$

With a target consisting of only one particle we thus arrive at the following **differential scattering cross section** (per target particle):

$$\frac{d\sigma}{d\Omega} = \frac{dW}{j_i\,d\Omega} = \left|\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{Q}\cdot\mathbf{r}}V(\mathbf{r})d^3r\right|^2 \equiv |f^B(\mathbf{Q})|^2, \qquad \text{(T14.51)}$$

where

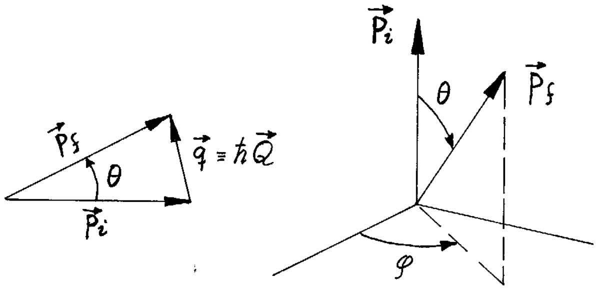
$$\mathbf{Q} \equiv (\mathbf{p}_f - \mathbf{p}_i)/\hbar \equiv \mathbf{q}/\hbar. \qquad \text{(T14.52)}$$

Comments:

(i) The result is independent of the "reaction volume" V_0, as it should be.

(ii) The quantity $f^B(\mathbf{Q})$ is called the **scattering amplitude in the first Born approximation.** The formula is only approximate because it has been derived by the use of first-order perturbation theory.

(iii) The vector $\mathbf{q} \equiv \mathbf{p}_f - \mathbf{p}_i \equiv \hbar\mathbf{Q}$ is the momentum transfer from the target particle to the projectile particle (see the figure below). Note that the dependence on angles of this differential cross section enters only through $\mathbf{Q}$ if the potential $V(\mathbf{r})$ is spherically symmetric.



(iv) Note also that the scattering amplitude $f^B(\mathbf{Q})$ essentially is the Fourier transform of the potential $V(\mathbf{r})$. If the Born approximation is reasonably accurate, we can map out $f^B(\mathbf{Q})$ as a function of $\mathbf{Q}$ experimentally, by measuring the differential cross section $d\sigma/d\Omega$ as a function of the scattering angles (θ and ϕ) for various energies $E_i = p^2/2m$. By Fourier inversion from $f^B(\mathbf{Q})$ to $V(\mathbf{r})$ we can then determine the interaction potential between the two particles.

(v) Scattering experiments are in general the most important method in the investigation of the structure of particles and of the interactions between them. Contrary to the example above, the scattering usually is **inelastic**, in the sense that the particle content (and the *number* of particles) in the final state differs from that in the initial state. This is particularly noteworthy in modern high-energy experiments, where the number of particles (multiplicity) in the final state increases more or less in proportion to the energy available. Happily, there are a few events where this not the case. This is when the collision results in the creation of one or more very heavy particles, maybe even new ones that have not been seen before. The detection of new heavy particles is one of the main goals of the experiments that are now being carried out at CERN.