# Time-dependent perturbation

Suppose that a quantum mechanical system is described by a Hamiltonian $H_0$. Then we proceed to act on the system by a time-dependent external force described by a potential $V(t)$ added to $H_0$. The new Hamiltonian is

$$H = H_0 + V(t) \quad \text{- - - - - - (1)}$$

The problem with $V(t) = 0$ is assumed to be solved exactly. In other words, the energy eigenvalues $E_n$ and the eigenkets $|n\rangle$ defined by

$$H_0 |n\rangle = E_n |n\rangle \quad \text{- - - - - (2)}$$

are known exactly.

We are interested in situations where the system is initially in an eigenstate of $H_0$, say $|i\rangle$. The time-dependent potential $V(t)$ can cause transitions to states other than $|i\rangle$. The basic question we ask is: what is the probability, at some later time $t$, for the system to be found in the state $|n\rangle$ with $n \neq i$. As an example we might shine light on an atom and ask what are the chances that light ionises the atom.

To formulate the problem, we have to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = [H_0 + V(t)] |\psi(t)\rangle \qquad (3)$$

with the initial condition

$$|\psi(t_0)\rangle = |i\rangle, \qquad (4).$$

where $t_0$ is some earlier time. Then the probability that at some later time $t$ $(t > t_0)$ the system makes a transition to the state $|n\rangle$ is

$$P_{i \to n}(t) = \left| \langle n | \psi(t) \rangle \right|^2 . \quad - - - - \quad (5)$$

To solve the problem, it is convenient to work in the interaction picture defined by

$$|\psi_I(t)\rangle = e^{iH_0(t-t_0)/\hbar} \, |\psi(t)\rangle$$

$$\hat{A}_I(t) = e^{iH_0(t-t_0)/\hbar} \, A \, e^{-iH_0(t-t_0)/\hbar} . \quad (6)$$

In the interaction picture we have

$$i\hbar \frac{\partial}{\partial t} |\psi_I(t)\rangle = V_I(t) \, |\psi_I(t)\rangle , \quad - - - (7)$$

i.e., the time evolution of the state vector in the interaction picture is determined by the time-dependent potential $V_I(t)$ expressed in

the interaction picture:

$$V_I(t) = e^{iH_0(t-t_0)/\hbar} V(t) e^{-iH_0(t-t_0)/\hbar} \quad (8)$$

Note that the state vector in the interaction picture coincides with the state vector in the Schrödinger picture at the initial time $t_0$, i.e.,

$$|\Psi_I(t_0)\rangle = |\Psi(t_0)\rangle = |i\rangle \quad (9)$$

Now, from Eq. (5), the probability for transition from state $|i\rangle$ to state $|n\rangle$ can be written as

$$P_{i\to n}(t) = \left| \langle n | e^{-iH_0(t-t_0)/\hbar} |\Psi_I(t)\rangle \right|^2$$

$$= \left| \langle n | e^{-iE_n(t-t_0)/\hbar} |\Psi_I(t)\rangle \right|^2$$

$$= \left| \langle n | \Psi_I(t)\rangle \right|^2 \quad (10)$$

We can now solve Eq. (7) for $|\Psi_I(t)\rangle$ with the initial condition (9) and then find the transition probability using Eq. (10).

In the interaction picture we can continue using $\{|n\rangle\}$ as our base kets and expand

$$|\psi_I(t)\rangle = \sum_n a_n(t)\,|n\rangle, \qquad \text{----(11)}$$

where $a_n(t) = \langle n|\psi_I(t)\rangle$. The expansion coefficients $a_n(t)$ satisfy the initial conditions

$$a_n(t_0) = \begin{cases} 0 & \text{if } n \neq i \\ 1 & \text{if } n = i, \end{cases} \qquad (12)$$

In our subsequent discussions we will take $t_0 = 0$ without any loss of generality.

Now, taking the scalar product of Eq. (7) with $\langle n|$ we obtain

$$i\hbar \frac{\partial}{\partial t}\langle n|\psi_I(t)\rangle = \sum_m \langle n|V_I(t)|m\rangle\langle m|\psi_I(t)\rangle \qquad \text{---(13)}$$

where we have used the completeness relation

$$\sum_m |m\rangle\langle m| = 1$$

on the right hand side of Eq. (13).

Next, we express the matrix elements $\langle n|V_I(t)|m\rangle$ as:

$$\langle n|V_I(t)|m\rangle = \langle n| e^{iH_0(t-t_0)/\hbar} V(t) e^{-iH_0(t-t_0)/\hbar} |m\rangle$$

$$= e^{i(E_n - E_m)t/\hbar} \langle n|V(t)|m\rangle \quad (\text{with } t_0 = 0)$$

$$= e^{i\omega_{nm}t} V_{nm}(t) \quad ----(14)$$

where we have defined

$$\omega_{nm} = \frac{(E_n - E_m)}{\hbar} \quad -----(15)$$

and

$$V_{nm}(t) = \langle n|V(t)|m\rangle \quad ----(16)$$

Thus, Eq.(3) can be written as

$$i\hbar \frac{da_n(t)}{dt} = \sum_m{}' V_{nm}(t)\, e^{i\omega_{nm}t}\, a_m(t) \quad \cdots (17)$$

Explicitly this equation is

$$i\hbar \frac{\partial}{\partial t}\begin{bmatrix} a_1(t) \\ a_2(t) \\ \vdots \\ \vdots \\ \vdots \end{bmatrix} = \begin{bmatrix} V_{11}(t) & V_{12}(t)e^{i\omega_{12}t} & \cdot & \cdot \\ V_{21}(t)e^{i\omega_{21}t} & V_{22} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{bmatrix} \quad (18)$$

This is the basic coupled differential equation we must solve, with the boundary condition (12). So far no approximation has been made.

## • Perturbation Scheme for solving Eq. (17).

The exact solutions of the coupled differential equations (17) is very difficult. We can devise a perturbation scheme by writing

$$V_{nm}(t) = \lambda V_{nm}(t)$$

and then expanding $a_n(t)$ in a power series in $\lambda$:

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \cdots \quad (19)$$

The parameter $\lambda$ is introduced just to count the order of perturbation and $\lambda$ will be set equal to 1 at the end. Substituting (19) in (17) and equating the coefficients of equal powers of $\lambda$ we find

$$\dot{a}_n^{(0)}(t) = 0$$

$$\dot{a}_n^{(1)}(t) = \frac{1}{i\hbar} \sum_m V_{nm}(t)\, e^{i\omega_{nm}t}\, a_m^{(0)}$$

$$\dot{a}_n^{(2)}(t) = \frac{1}{i\hbar} \sum_m V_{nm}(t)\, e^{i\omega_{nm}t}\, a_m^{(1)}(t) \qquad (20)$$

$$\vdots \qquad\qquad \vdots$$

$$\dot{a}_n^{(s+1)}(t) = \frac{1}{i\hbar} \sum_m V_{nm}(t)\, e^{i\omega_{nm}t}\, a_m^{(s)}(t) .$$

These equations can now, in principle, be integrated successively to any given order in perturbation. The first of Eq. (20) simply confirms that $a_n^{(0)}$ is independent of time. We take

$$a_n^{(0)} = \begin{cases} 1 & \text{if } n = i \\ 0 & \text{if } n \neq i \end{cases} \qquad (21)$$

In order to satisfy the initial condition (11),

the higher order corrections $a_n^{(1)}(t), a_n^{(2)}(t), \ldots$ have to be evaluated by solving Eq. (20) with the initial conditions

$$a_n^{(1)}(t_0) = a_n^{(2)}(t_0) = \cdots = 0 \qquad (22)$$

Now, substituting Eq. (21) in the second of Eqs. (20), we obtain in first order

$$\dot{a}_n^{(1)}(t) = \frac{1}{i\hbar} V_{ni}(t) e^{i\omega_{ni} t} \quad \text{(for all } n\text{)}. \qquad (23)$$

Integrating this we get

$$\boxed{a_n^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} V_{ni}(t') e^{i\omega_{ni} t'} dt'.} \qquad (24)$$

The initial condition $a_n^{(1)}(t_0) = 0$ is automatically satisfied in the above equation.

Next, substituting Eq. (24) into the third of Eqs. (20), we obtain in second order

$$\dot{a}_n^{(2)}(t) = \frac{1}{i\hbar} \sum_m{}' V_{nm}(t)\, e^{i\omega_{nm}t}\, a_m^{(1)}(t),$$

Integrating we have

$$a_n^{(2)}(t) = \frac{1}{i\hbar} \sum_m{}' \int_{t_0}^{t} dt'\, V_{nm}(t')\, e^{i\omega_{nm}t'}\, a_m^{(1)}(t')$$

or,

$$a_n^{(2)}(t) = \frac{1}{i\hbar} \sum_m{}' \int dt' V_{nm}(t')\, e^{i\omega_{nm}t'} \cdot \frac{1}{i\hbar} \int_{t_0}^{t'} dt''\, V_{mi}(t'') e^{i\omega_{mi}t''}$$

i.e.,

$$a_n^{(2)}(t) = \frac{1}{(i\hbar)^2} \sum_m{}' \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t'}\, V_{nm}(t')\, e^{i\omega_{mi}t''}\, V_{mi}(t'')$$

. . . . (25)

Continuing in this fashion we can obtain the higher order corrections to $a_n(t)$.

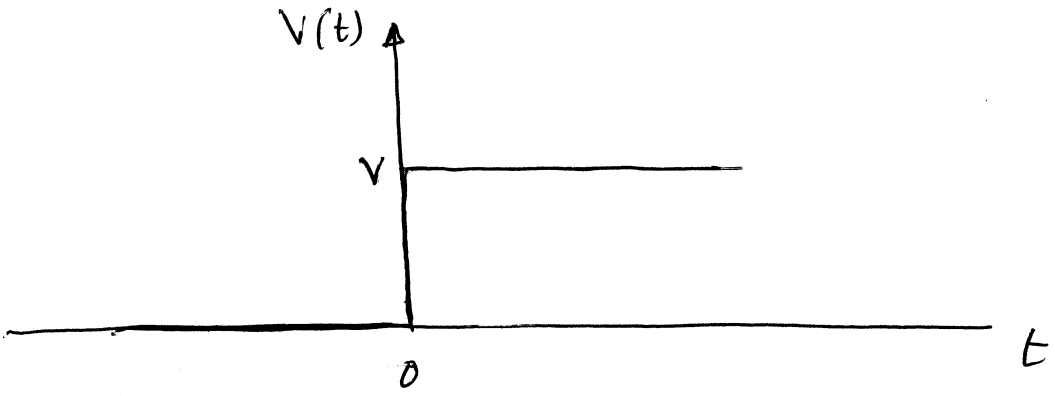
We have now completed the formalism for time-dependent perturbation theory. We will now apply the formalism to some specific problems.

# Examples

## (a) Constant perturbation switched on at $t=0$.

As an application of the time-dependent perturbation theory, let us consider a constant perturbation suddenly turned on at $t=0$.

$$V(t) = \begin{cases} 0 & \text{for } t<0 \\ V & \text{for } t \geq 0. \end{cases} \qquad (26)$$




We have

$$a_n^{(0)} = \delta_{ni}$$

and (with $t_0 = 0$)

$$a_n^{(1)}(t) = \frac{1}{i\hbar} V_{ni} \int_0^t e^{i\omega_{ni} t'} dt'$$

Integrating

$$a_n^{(1)}(t) = \frac{1}{i\hbar} V_{ni} \left. \frac{e^{i\omega_{ni} t'}}{i\omega_{ni}} \right|_0^t$$

$$= \frac{1}{i\hbar} V_{ni} \left( \frac{e^{i\omega_{ni} t} - 1}{i\omega_{ni}} \right)$$

$$= \frac{1}{i\hbar} V_{ni} \, e^{i\omega_{ni} t/2} \, \frac{\sin \omega_{ni} t/2}{\omega_{ni}/2} . \qquad (27)$$

Therefore, in first order, the probability of transition from an initial state $|i\rangle$ to a final state $|n\rangle$ $(n \neq i)$ is

$$P_{i \to n}(t) = \left| a_n^{(1)}(t) \right|^2$$

or

$$P_{i \to n}(t) = \frac{1}{\hbar^2} |V_{ni}|^2 \, \frac{\sin^2 \frac{\omega_{ni} t}{2}}{\left(\frac{\omega_{ni}}{2}\right)^2} . \qquad (28)$$

The probability of transition to the state $n$

depends not only on $|V_{ni}|^2$ but also on $\omega_{ni}$, i.e., on the energy difference $E_n - E_i$. Note that if $V_{ni} = 0$, there would be no transition to the state $|n\rangle$. In other words, to have a transition to the final state $|n\rangle$, the potential $V$ should have a spatial dependence such that $V_{ni} = \langle n|V|i\rangle \neq 0$.

The transition probability is shown as a function of $E_n$ in figure 1 below.

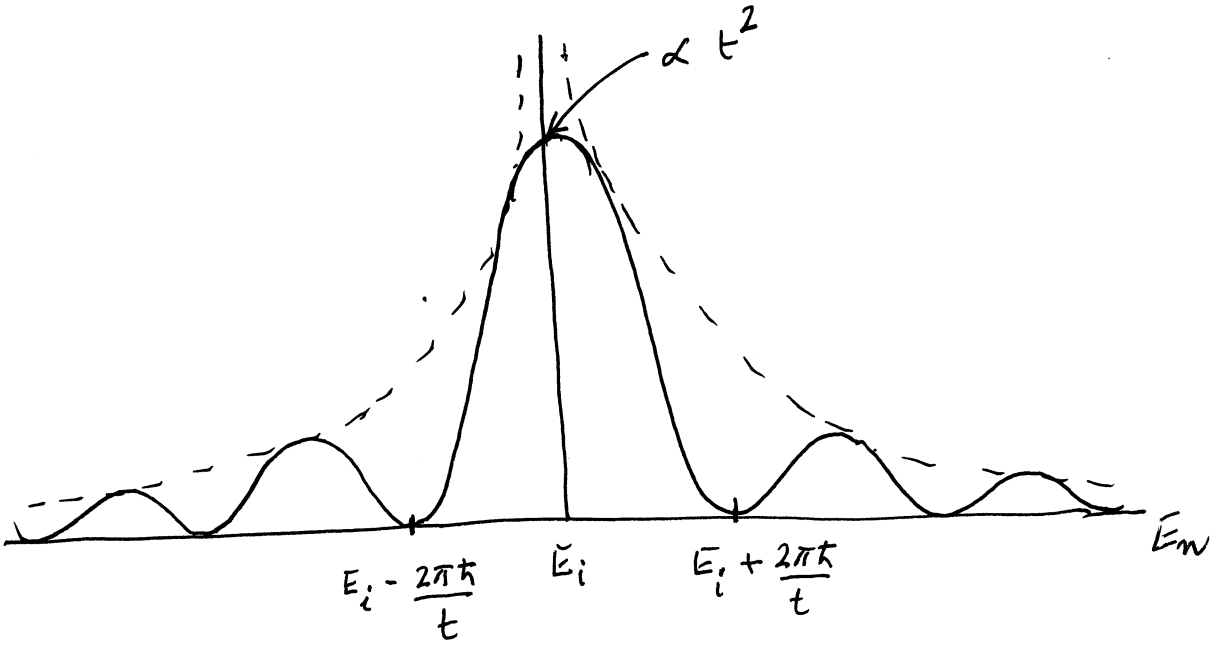



Figure 1: Transition probability $P_{i\to n}$ as a function of $E_n$.

We see that $P_{i\to n}(t)$ exhibits a sharp peak about $E_n = E_i$. The height of the peak is proportional to $t^2$ while its width is approximately $2\pi\hbar/t$. Thus the probability of transition to a state $n$ is large when its energy lies under the bump around $E_i$. The final energy will lie under the bump if

$$|(E_n - E_i)| < \frac{2\pi\hbar}{t}.$$

This means that transitions $i \to n$ will occur mainly towards those final states whose energy

is located in a band of width

$$\delta E \simeq \frac{2\pi\hbar}{t}$$

about the initial energy $E_i$, so that energy of the system is conserved within $2\pi\hbar/t$. This result can be readily related to the time-energy uncertainty relation

$$\Delta E \cdot \Delta t \sim \hbar$$

where $\Delta t\ (= t)$ is the length of time the perturbation has acted and $\Delta E \sim \delta E$. If $\Delta t$ is small we have a broader peak, and as a result we can tolerate a fair amount of energy non-conservation. On the other hand, if the perturbation has been on for a very long time, we have a narrow peak, and approximate energy conservation is required for a transition with appreciable probability.

In practice, we are interested to find the transition probability to a group of final states $[n]$ whose energy is roughly degenerate with the initial state energy and lies within the range

$$(E_n - \epsilon/2 \,,\; E_n + \epsilon/2)$$

centered about the value $E_n$. This is the case, for example, when one studies transitions to states belonging to the continuous spectra.

In such a case we are interested in the total probability, that is transition probabilities summed over final states with $E_n \simeq E_i$:

$$P_{i \to [n]} = \sum_{\substack{n \\ E_n \simeq E_i}} |a_n^{(1)}(t)|^2 \,, \qquad (29)$$

Let us now define by $\rho(E_n)$ the density of levels on the energy scale, so that $\rho(E_n)\,dE_n$ is the number of final states within the energy

interval $(\bar{E}_n, \bar{E}_n + d\bar{E}_n)$. Thus Eq. (29) can be written as

$$P_{i \to [n]}(t) = \int d\bar{E}_n \rho(E_n) \left| a_n^{(1)}(t) \right|^2 \quad \cdots (30)$$

where the spread in the final state energy is $\epsilon$. Using (28) in (30) we obtain

$$P_{i \to [n]}(t) = 4 \int \sin^2 \left[ \frac{(E_n - E_i)t}{2\hbar} \right] \frac{|V_{ni}|^2}{(E_n - E_i)^2} \rho(E_n) dE_n . \quad (31)$$

Now, as $t$ becomes large, we take advantage of the fact that

$$\lim_{t \to \infty} \frac{1}{(E_n - E_i)^2} \sin^2 \left[ \frac{(E_n - E_i)t}{2\hbar} \right] = \frac{\pi t}{2\hbar} \delta(E_n - E_i)$$

which follows from

$$\lim_{\alpha \to \infty} \frac{1}{\pi} \frac{\sin^2 \alpha x}{\alpha x^2} = \delta(x) .$$

Thus, for large times the contribution to the integral in Eq. (31) comes from a small band of energy

around $E_i$. It is now possible to take $|V_{ni}|^2$ outside the integral and perform the integration with the $\delta$-function. Thus

$$P_{i \to [n]}(t) = |V_{ni}|^2 \frac{4\pi t}{2\hbar} \int \delta(E_n - E_i) \rho(E_n) dE_n$$

or,

$$\boxed{P_{i \to [n]}(t) = \frac{2\pi t}{\hbar} |V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i}.} \quad (32)$$

Thus the total probability is proportional to t for large values of t. Notice that linearity in t is a consequence of the fact that the total transition probability is proportional to the area under the peak in figure 1 where the height varies as $t^2$ and the width as $1/t$.

It is conventional to consider the transition rate — that is the transition probability per unit time. The transition rate to a group of final states is

$$W_{i\to[n]} = \frac{d}{dt} P_{i\to[n]}(t)$$

$$\boxed{W_{i\to[n]} = \frac{2\pi}{\hbar} |V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i}} \qquad (33)$$

This formula, which is of great practical importance, is called Fermi's golden rule. We sometimes write (33) as

$$W_{i\to[n]} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i) \qquad (34)$$

where it must be understood that the expression is integrated with $\int dE_n \rho(E_n)$.

We should also understand what is meant by $|V_{ni}|^2$. There may be several different groups of final states $n_1, n_2 \cdots$ all of which have about the same energy $E_i$ but for which the perturbation matrix elements $|V_{ni}|^2$ and the density of states $\rho(E_n)$ although nearly constant within each group, differ from one group to another. In such cases we must treat each group separately even though they are degenerate in energy.

Example.

A system of hydrogen atoms in the ground state is contained between the plates of a parallel-plate capacitor. A voltage pulse is applied to the capacitor so as to produce a homogeneous electric field

$$\mathcal{E} = \begin{cases} 0 & \text{for } t < 0 \\ \mathcal{E}_0 e^{-t/\tau} & \text{for } t > 0. \end{cases}$$

(a) Show that after a long time, the fraction of atoms in the $2p\,(m=0)$ state ($|n\ell m\rangle = |210\rangle$) is, to first-order

$$\frac{2^{15}}{3^{10}} \frac{a_0^2 e^2 \mathcal{E}^2}{\hbar^2 \left(\omega^2 + \frac{1}{\tau^2}\right)}$$

where $a_0$ is the Bohr radius and $\hbar\omega$ is the energy difference between the $2p$ and the ground state.

(b) What is the fraction of atoms in the 2s state?

Given:

$$\psi_{\substack{100\\ n\ell m}}(\vec{r}) = R_{10}(r)\,Y_{00} = \frac{2}{\sqrt{4\pi}}\,\frac{1}{a_0^{3/2}}\,e^{-r/a_0}$$

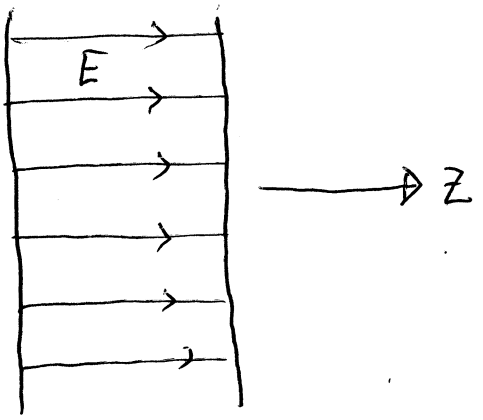
$$\psi_{210}(\vec{r}) = R_{21}(r)\,Y_{10}(\theta,\varphi)$$

$$= \frac{1}{\sqrt{4\pi}}\,\frac{1}{(2a_0)^{3/2}}\left(\frac{r}{r_0}\right)e^{-r/2a_0}\cos\theta.$$

and

$$\int_0^\infty r^n e^{-\beta r}\,dr = \frac{n!}{\beta^{n+1}}.\quad (\beta>0,\ n = \text{positive integers})$$

Ans:

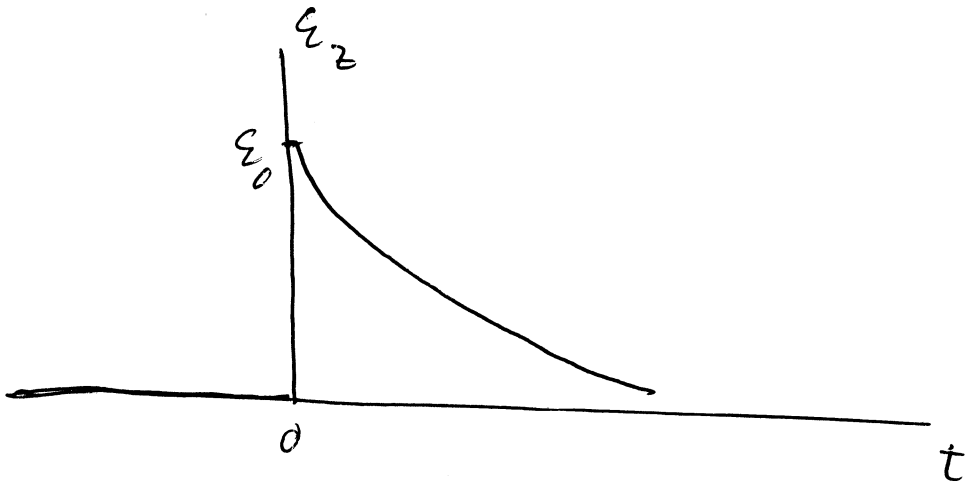


The electric field is homogeneous but time varying. Suppose $\vec{E}$ points along the z-axis. Therefore

$$\vec{\mathcal{E}} = (0, 0, \mathcal{E}_z)$$

with

$$\mathcal{E}_z = \mathcal{E}_0 e^{-t/\tau} \quad (\text{for } t > \tau),$$




The force on the electron has only z-component.

We have

$$F_z = q_e \mathcal{E}_z = -e \mathcal{E}_0 e^{-t/\tau}$$

$q_e = -e$ = charge of electron

Now

$$F_z = -\frac{\partial V}{\partial z}$$

Therefore

$$V = e\mathcal{E}_0 z e^{-t/\tau} \quad (t>0), \qquad \text{------(1)}$$

The hydrogen atom is in the ground state $|100\rangle$ at $t=0$. The perturbation is switched on at $t=0$. In the first-order perturbation theory, the probability of transition from state $i$ to state $n$ is

$$P_{i\to n}(t) = \left|a_n^{(1)}(t)\right|^2,$$

where

$$a_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \langle n|V(t')|i\rangle e^{i\omega_{ni}t'}\,dt'$$

where

$$\omega_{ni} = \frac{E_n - E_i}{\hbar}.$$

Writing $\omega \equiv \omega_{ni}$, we find in the present example

$$a_n^{(1)}(t) = \frac{1}{i\hbar} e\mathcal{E}_0 \langle n|z|i\rangle \int_0^t e^{(i\omega - 1/\tau)t'} dt'$$

For large $t$ ($t >> \tau$) we have

$$a_n^{(1)}(t) = \frac{e\mathcal{E}_0}{i\hbar} \langle n|z|i\rangle \left[ - \frac{1}{(i\omega - 1/\tau)} \right]$$

or
$$a_n^{(1)}(t) = \frac{e\mathcal{E}_0}{\hbar(\omega + i/\tau)} \langle n|z|i\rangle . \qquad (2)$$

Now, states of the hydrogen atoms (disregarding spin) are denoted by $|nlm\rangle$. The initial state is the ground state, i.e.,

$$|i\rangle = |100\rangle$$

while the final state $|n\rangle$ is $2p$ ($m=0$), i.e.,

$$|n\rangle = |210\rangle .$$

Also,

$$\langle \vec{r}|100\rangle = \psi_{100}(\vec{r}) = \frac{2}{\sqrt{4\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0}$$

$$\langle \vec{r}|210\rangle = \psi_{210}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \cdot \frac{1}{(2a_0)^{3/2}} e^{-r/2a_0} \cos\theta$$

Therefore

$\langle 210 | z | 100 \rangle$

$= \int \psi^*_{210}(\vec{r})\, r\cos\theta\, \psi_{100}(\vec{r})$

$= \frac{2}{4\pi} \cdot \frac{1}{2^{3/2} a_0^4} \int e^{-r/2a_0} \cos\theta\, r^2 \cos\theta\, e^{-r/a_0}\, r^2 dr\, d\Omega$

$(d\Omega = \sin\theta\, d\theta\, d\varphi)$

$= \frac{2}{4\pi} \cdot \frac{1}{2^{3/2} a_0^4} \int_0^\infty r^4 e^{-3r/2a_0} \underbrace{\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta}_{2/3} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi}$

$= \frac{2}{4\pi} \frac{1}{2^{3/2} a_0^4} \cdot 2\pi \cdot \frac{2}{3} \int_0^\infty r^4 e^{-3r/2a_0} dr$

$= \frac{2}{2^{3/2} 3 a_0^4} \cdot \frac{4!}{\left(\frac{3}{2a_0}\right)^5}$

$\left| \int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}} \right.$

$n = +ve$ integer

$= \frac{4!}{2^{3/2}} \left(\frac{2}{3}\right)^6 a_0 .$

Therefore, the probability of transition from the state $|100\rangle$ to the state $|210\rangle$ is

$$P_{i\to n}(t) = \left| a_n^{(1)}(t) \right|^2$$

$$= \frac{e^2 \mathcal{E}_0^{\,2}}{\hbar^2\left(\omega^2 + \frac{1}{\tau^2}\right)} \cdot \underbrace{\frac{(4!)^2\, 2^{12}}{2^3\, 3^{12}}}_{2^{15}/3^{10}} a_0^2$$

$$= \left(\frac{2^{15}}{3^{10}}\right) \frac{e^2 \mathcal{E}_0^{\,2} a_0^2}{\left(\omega^2 + \frac{1}{\tau^2}\right)} .$$

This is the fraction of atoms in the state $|210\rangle$ for large times ($t >> \tau$).

(c) Probability of transition to the 2s ($|200\rangle$) state.

The matrix element of $z$ between the initial and final states is

$$\langle 200 | z | 100 \rangle = 0$$

because the integrand is odd. So there is no transition to the $|200\rangle$ state from the ground state.

# Harmonic perturbation

We now consider a sinusoidally varying time-dependent potential, commonly referred to as harmonic perturbation:

$$\hat{V}(t) = \hat{V} e^{i\omega t} + \hat{V}^{\dagger} e^{-i\omega t} \qquad (1)$$

where $\hat{V}$ may still depend on $\hat{\vec{r}}$, $\hat{\vec{p}}$ and $\hat{\vec{s}}$.

We assume that only one of the eigenstates of $H_0$ is populated initially. The perturbation is turned on at $t = 0$. So, in first-order, the transition amplitude from state $i$ to state $n$ is

$$a_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \left( V_{ni} e^{i\omega t'} + V_{ni}^{\dagger} e^{-i\omega t'} \right) e^{i\omega_{ni} t'} dt'$$

or,

$$a_n^{(1)}(t) = \frac{1}{\hbar} \left[ \frac{1 - e^{i(\omega + \omega_{ni})t}}{(\omega + \omega_{ni})} V_{ni} + \frac{1 - e^{i(\omega_{ni} - \omega)t}}{(-\omega + \omega_{ni})} V_{ni}^{\dagger} \right] . \qquad \cdots (2)$$

It is clear from the above equation that if $t$ is large enough, the probability of finding the system will be appreciable if the denominator of the one or the other of the two terms on the right hand side of Eq. (2) is close to zero.

Moreover, assuming that $E_n \neq E_i$ (so that the levels $E_n$ and $E_i$ are not degenerate), both the denominators cannot simultaneously close to zero. A good approximation is therefore to neglect the interference between the two terms in calculating the transition probability.

Case 1

Suppose

$$\omega_{ni} + \omega \simeq 0$$

i.e.,

$$E_n \simeq E_i - \hbar\omega .$$

Then

$$P_{i\to n}(t) = \left| a_n^{(1)}(t) \right|^2$$

$$\simeq \frac{|V_{ni}|^2}{\hbar^2} \left| \frac{1 - e^{i(\omega+\omega_{ni})t}}{(\omega+\omega_{ni})} \right|^2$$

$$= \frac{|V_{ni}|^2}{\hbar^2} \frac{\sin^2 (\omega+\omega_{ni})t/2}{\left[ (\omega+\omega_{ni})/2 \right]^2} . \quad (3)$$

If $t$ is large, we obtain

$$P_{i\to n}(t) = \frac{|V_{ni}|^2}{\hbar^2} . 2\pi t\, \delta(\omega+\omega_{ni}) \quad (4)$$

where we have used

$$\lim_{\alpha\to\infty} \frac{1}{\pi} \frac{\sin^2 \alpha x}{\alpha x^2} = \delta(x) .$$

The transition rate is then

$$W_{i\to n} = \frac{d}{dt} P_{i\to n}(t)$$

$$= \frac{2\pi}{\hbar^2} |V_{ni}|^2 \delta(\omega + \omega_{ni})$$

$$= \frac{2\pi}{\hbar^2} |V_{ni}|^2 \delta\left(\omega + \frac{E_n - E_i}{\hbar}\right)$$

$$= \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i + \hbar\omega),$$

Note: $\delta(ax) = \frac{1}{|a|}\delta(x)$

Therefore the transition rate to a group of final states is

$$W_{i\to[n]} = \frac{2\pi}{\hbar} |V_{ni}|^2 \int \delta(E_n - E_i + \hbar\omega)\, \rho(E_n)\, dE_n$$

or,

$$\boxed{W_{i\to[n]} = \frac{2\pi}{\hbar} |V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i - \hbar\omega}} \quad (5)$$

Case 2

Next suppose that the denominator of the second term of Eq. (2) is close to zero. Therefore

$$-\omega + \omega_{ni} = 0$$

i.e.,

$$E_n = E_i + \hbar\omega.$$

Then proceeding exactly as in case 1, we have

$$W_{i\to[n]} = \frac{2\pi}{\hbar} \left| V^{\dagger}_{ni} \right|^2 \rho(E_n) \Big|_{E_n = E_i + \hbar\omega}. \qquad (6)$$

We see from Eqs. (5) and (6) that, in case of harmonic perturbation, we do not have energy conservation satisfied by the quantum-mechanical system alone. Rather, the apparent lack of energy conservation is compensated by the energy given out to or energy taken away from the external potential $V(t)$.

In case of Eq. (5) we have <u>stimulated emission</u>: the quantum mechanical system gives up energy $\hbar\omega$ to V (Fig. 2).

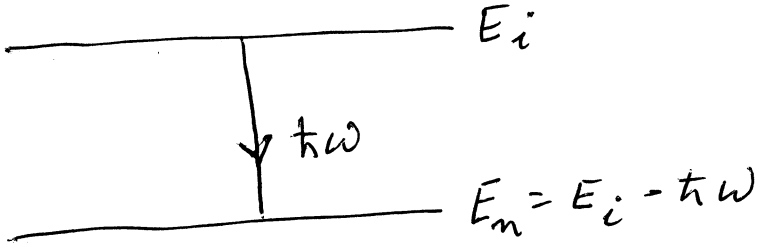



Fig. 2 Stimulated emission: the system gives up energy $\hbar\omega$ to V. This is possible if the initial state i is an excited state.

Clearly, stimulated emission is possible if the quantum-mechanical system is in an excited state.

Next, in case of Eq. (6) we have absorption. The quantum-mechanical system receives energy $\hbar\omega$ from V and ends up in an excited state (Fig. 3).

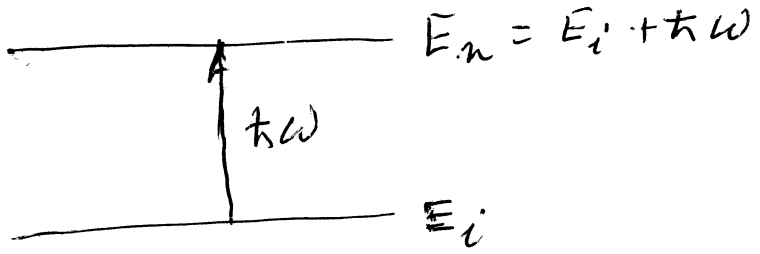



Fig 3. Stimulated absorption.

Thus a time-dependent perturbation can be regarded as an inexhaustible source or sink of energy.

Now, note that

$$V_{ni} = \langle n|V|i\rangle = \langle i|V^{\dagger}|n\rangle^{*} = V_{in}^{\dagger *}$$

Therefore

$$|V_{ni}|^2 = |V_{in}^{\dagger}|^2 . \quad \text{---------- (7)}$$

Combining (7) with (5) and (6) we have

$$\frac{\text{emission rate for } i \to [n]}{\text{density of final states for } [n]} = \frac{2\pi}{\hbar}|V_{ni}|^2$$

$$= \frac{2\pi}{\hbar}|V_{in}^{\dagger}|^2 = \frac{\text{Absorption rate for } n \to [i]}{\text{density of final states for } [i]}$$

--- (8)

where in the absorption case we let $i$ stand for the final state. Eq. (8) which expresses symmetry between absorption and emission is known as <u>detailed balancing</u>.

To summarize:

For constant perturbation, we obtain appreciable transition probability for $|i\rangle \to |n\rangle$ only if $E_n \simeq E_i$. In contrast, for harmonic perturbation, we have appreciable transition probability only if $E_n \simeq E_i - \hbar\omega$ (stimulated emission) or if $E_n \simeq E_i + \hbar\omega$ (stimulated absorption).