- Time-dependent perturbation theory -

As in the case of time-independent perturbation theory, let \( \hat{H}_0 \) be the Hamiltonian of the "unperturbed system" (US) whose eigenvalues and eigenvectors are supposed to be known:

\[
\hat{H}_0 \phi_n = E_n \phi_n
\]  

1.1

The time-evolution of the US is, as usual, ruled by:

\[
i \hbar \frac{\partial \psi(t)}{\partial t} = \hat{H}_0 \psi(t)
\]  

2.1

Suppose that at \( t=0 \) the system was prepared in the state \( \psi_0 \):

\[
\psi(t=0) = \psi_0
\]

We can always write:

\[
\psi(t) = \sum_n \phi_n \chi_n(t)
\]

3.1

Where

\[
C_n(t) = \langle \phi_n | \psi(t) \rangle
\]

At \( t=0 \):

\[
C_n(0) = \langle \phi_n | \psi(0) \rangle = \langle \phi_n | \psi_0 \rangle
\]

Substituting 3.1) in 2.1) and using 1.1) we obtain:
\[ i \hbar \sum_n \dot{c}_n(t) |\phi_n\rangle = \hat{H}_0 \sum_n c_n(t) |\phi_n\rangle \]
\[ = \sum_n E_n^0 c_n(t) |\phi_n\rangle \]
\[ \Rightarrow \sum_n \left[ i \hbar \frac{d}{dt} c_n(t) - E_n^0 c_n(t) \right] |\phi_n\rangle = 0 \]

This equality is satisfied iff:
\[ \frac{d}{dt} c_n(t) = -i \frac{E_n^0}{\hbar} c_n(t) \]

whose solution is:
\[ c_n(t) = c_n(0) \exp \left( -i \frac{E_n^0}{\hbar} t \right) \]  \hspace{1cm} (1.2)

Suppose now that the system is perturbed by an external potential (possibly time-dependent)
\[ \hat{V}(t) \].

The new Hamiltonian of the perturbed system is:
\[ \hat{H}_{\text{perturbation}} \rightarrow \hat{H} = \hat{H}_0 + \lambda \hat{V}(t) \]

with \[ \hat{V}(t) = \hat{V}^+(t) \]

Our aim now is to solve the time-dependent Schrödinger equation:
\[ i \hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \]
\[ = (\hat{H}_0 + \lambda \hat{V}(t)) |\psi(t)\rangle \]  \hspace{1cm} (2.2)
with the initial condition:

\[ |4(t=0)\rangle = |4_0\rangle \]

As before, we look for a solution of the form:

\[ |4(t)\rangle = \sum_n \phi_n \times |4(t)\rangle = \sum_n c_n(t) |\phi_n\rangle \]

It is convenient to isolate from \( c_n(t) \) the time evolution of the non-perturbed (or free) system:

\[
    c_n(t) = \left[ c_n(t) e^{i E_n \frac{t}{\hbar}} \right] e^{-i E_n \frac{t}{\hbar}}
    = f_n(t) e^{-i E_n \frac{t}{\hbar}}
\]

Therefore:

\[ |4(t)\rangle = \sum_n f_n(t) e^{-i E_n \frac{t}{\hbar}} |\phi_n\rangle \quad 1.3 \]

This implies that when \( \lambda \to 0 \), \( c_n(t) \) tends to a constant.

Substituting 1.3) into 2.2) we obtain:

\[
    \sum_n \left[ i \hbar \frac{df_n(t)}{dt} + E_n f_n(t) \right] e^{-i E_n \frac{t}{\hbar}} |\phi_n\rangle =
    \hat{A} |4(t)\rangle
    = \sum_n \left[ E_n + \lambda \hat{V}(t) \right] f_n(t) e^{-i E_n \frac{t}{\hbar}} |\phi_n\rangle
\]
That is:

\[ \sum_n \left[ i \hbar \frac{d\phi_n(t)}{dt} - \hat{V}(t) \phi_n(t) \right] e^{-i E_n t / \hbar} |\phi_n\rangle = 0 \]

Now we multiply from left this expression by

\[ \langle \phi_n | e^{i E_n t / \hbar} \]

to obtain:

\[ i \hbar \frac{d\phi_n(t)}{dt} = \lambda \sum_n \phi_n(t) e^{i(E_n - E_0) t / \hbar} \langle \phi_m | \hat{V}(t) | \phi_n \rangle \]

(1.4)

where we have used \( \langle \phi_n | \phi_m \rangle = \delta_{nm} \)

Let us try to solve this equation to first order in \( \lambda \) choosing as initial condition:

\[ |\Psi(t=0)\rangle = |\phi_k\rangle \]

(2.4)

This means that at \( t=0 \) the system is in a given eigenvector of the energy. For example, imagine an atom in the lower (fundamental) energy state which is perturbed, from \( t=0 \), by an electromagnetic wave.

Using (2.4) in 1.3) we obtain:

\[ 1\Psi(t=0) = \sum_n f_n(t) |\phi_n\rangle = |\phi_k\rangle \Rightarrow f_n(0) = \delta_{nk} \]
If $\lambda = 0$, (1.4) gives:

$$\frac{df_m(t)}{dt} \big|_{\lambda=0} = 0 \Rightarrow f_m(t) \big|_{\lambda=0} = f_m(0) = \delta_{km}$$

If $\lambda \neq 0$, we look for a power series solution

$$f_m(t) = f^0_m(t) + \lambda f^1_m(t) + \lambda^2 f^2_m(t) + \cdots$$

with

$$f^0_m(t) = f_m(t) \big|_{\lambda=0} = \delta_{km} \Rightarrow f^0_m(0) = 0 \quad (2.1)$$

$$\Rightarrow f_m(t) = \delta_{km} + \lambda f^1_m(t) + \lambda^2 f^2_m(t) + \cdots \quad (1.5)$$

Substituting (1.5) into (1.6) gives

$$i\hbar \frac{d}{dt} \left( \delta_{km} + \lambda f^1_m(t) + \cdots \right) =$$

$$= \lambda \sum_n \left( \delta_{kn} + \lambda f^1_n(t) + \cdots \right) e^{iW_{mn}t} V_{mn}(t) \quad (2.5)$$

where we have defined the transition frequency

$$W_{mn} = \frac{E^m - E^n}{\hbar}$$

and

$$V_{mn}(t) = \langle \hat{f}_m(t) \hat{V} \rangle$$

The first-order solution of (2.5) is:
\[ i\hbar \frac{d f_m(t)}{dt} = e^{i\omega_m t} V_{mk}(t) \]

Whose solution is:

\[ f_m(t) = \frac{1}{i\hbar} \int_0^t dt' e^{-i\omega_m t'} \langle \phi_m | \hat{V}(t') | \phi_k \rangle \]

with \( f_m(0) = 0 \)

The probability that at a later time \( t \) the system, initially prepared in the state \( | \phi_k \rangle \), could be found in the state \( | \phi_n \rangle \) with \( n \neq k \), is:

\[ P_n(t) = \left| \langle \phi_n | \psi(t) \rangle \right|^2 = \left| \langle \phi_n | \left\{ \sum_m f_m(t) e^{-iE_m t/\hbar} | \phi_m \rangle \right\} \right|^2 = \left| f_n(t) e^{-iE_n t/\hbar} \right|^2 = \left| f_n(t) \right|^2 \]

\[ = (S_{kn} + \lambda f_n(t) + \lambda^2 f_n(t)') \left( S_{kn} + \lambda f_n(t) + \lambda^2 f_n(t) + \cdots \right) \]

\[ = S_{kn} + 2\lambda S_{kn} \text{Re} \left[ f_n'(t) \right] + \lambda^2 \left[ \left| f_n'(t) \right|^2 + 2 S_{kn} \text{Re} \left[ f_n'(t) \right] \right] + \cdots \]

\[ = \lambda^2 \left| f_n'(t) \right| + O(\lambda^3) \]
*Example*

A particle of electric charge $q$ in a one-dimensional harmonic oscillator is placed in an electric field of strength $\mathcal{E}$. The potential energy is:

$$\hat{V}(t) = q\mathcal{E} x e^{-t^2/\sigma^2} \quad \sigma > 0$$

If the particle is in the ground state at $t = -\infty$, what is the probability that at $t \gg \sigma$ is in the first (second) excited state?

In this case:

$$\hat{H}_0 = \hbar \omega (\hat{a}^+ \hat{a} + \frac{1}{2})$$

with

$$\hat{H}_0 |n\rangle = \hbar \omega (n+\frac{1}{2}) |n\rangle, \quad n = 0, 1, 2, \ldots$$

Note that at $t = \pm \infty$ we have

$$\hat{V}(t) = 0$$

Therefore the perturbation acts only for a finite time around $t = 0$. 

![Diagram](image_url)
According to 1.6 written for \( t = -\infty \), instead of \( t = 0 \), we have:

\[
f_n^t(t) = \frac{q^2}{i\hbar} \int_{-\infty}^{t} dt' e^{-i\omega_{0}t'} <\mathbf{n}\times\mathbf{10}> e^{-(t'/\tau)^2}
\]

where \( \omega_{0} = \frac{E_n - E_0}{\hbar} = \left[ \hbar \omega (n + \frac{1}{2}) - \hbar \omega (0 + \frac{1}{2}) \right] \left( \frac{1}{\hbar} \right)
\]

\[
= \omega_n
\]

For \( t \gg \tau \), because of the Gaussian form, we can replace the upper integration limit with \( t = +\infty \)
and write:

\[
f_n^t(\infty) = \frac{q^2}{i\hbar} <\mathbf{n}\times\mathbf{10}> \int_{-\infty}^{\infty} e^{i\omega_{n}t} e^{-t^2/\tau^2} dt
\]

\[
= \int_{-\infty}^{\infty} e^{-ax^2 + \beta x} dx = e^{\beta^2/(4a)} \left( \frac{\pi}{a} \right)^{1/2}
\]

with \( a = \frac{1}{\tau^2} \), \( \beta = i\omega_n \)

\[
= e^{\frac{(i\omega_n)^2}{4/\tau^2}} \sqrt{\frac{\pi}{2\tau^2}} = e^{-\frac{\hbar^2\omega_n^2\tau^2}{4}} \sqrt{\pi/2}
\]

\[
\Rightarrow f_n^t(\infty) = \frac{q^2}{i\hbar} <\mathbf{n}\times\mathbf{10}> \sqrt{\pi/2} \exp\left(-\frac{\hbar^2\omega_n^2\tau^2}{4}\right)
\]
It remains to calculate:

\[ \langle n\hat{x}10 \rangle \quad \text{where} \quad \hat{x} = \frac{\hbar}{\sqrt{2m\omega}} (\hat{a} + \hat{a}^*) \]

and \( \hat{a}10 = 0 \), \( \hat{a}^*10 = 11 \) \( \Rightarrow \)

\[ \Rightarrow \langle n\hat{x}10 \rangle = \frac{\hbar}{\sqrt{2m\omega}} \langle n1 \hat{a} + \hat{a}^*10 \rangle \]

\[ = \sqrt{\frac{\hbar}{2m\omega}} \langle n1 \rangle = S_{n1} \sqrt{\frac{\hbar}{2m\omega}} \]

Therefore, the probability of transition from the ground state to the first excited state is:

\[ P_n(\infty) = S_{n1} \frac{q^2\varepsilon^2}{2m\hbar \omega} e^{-\omega^2\varepsilon^2/2} \Rightarrow P_2(\infty) = P_3(\infty) = \ldots = 0 \]

- Note that for \( \omega^2 \gg 1 \) (which means that the electric field turns on very slowly), then \( P_1(\infty) \to 0 \), so the system manages to remain in the ground state.

- Note also that \( P_n(\infty) = 0 \) for \( n \geq 2 \) because of the linear dependence \( \hat{x} \) of the perturbation. If it was \( \hat{\chi} \propto \hat{x}^2 \), then \( P_2(\infty) \neq 0 \). This is called a \textbf{SELECTION RULE}.\]
Harmonic variation of the perturbation

In many cases of practical interest, like in the interaction of an atom with an electromagnetic wave, the potential has a harmonic time-dependence:

\[ \hat{V}(t) = \hat{M} e^{i\omega t} \quad \omega > 0 \]

where \( \hat{M} \) is some time-independent operator.

In this case (1.6) gives:

\[
\frac{\phi_m^*}{\phi_n}(t) = \frac{1}{i\hbar} \langle \phi_m | \hat{M} | \phi_n \rangle \int_0^t e^{i(W_{mn} + \omega)t} dt = \frac{e^{i(W_{mn} + \omega)t} - 1}{i(W_{mn} + \omega)} = e^{i(W_{mn} + \omega)t/2} \sin\left(\frac{\epsilon \Delta}{2}\right) \Delta/2.
\]

where \( \Delta = E_m^0 - E_n^0 \pm \omega \hbar \)

Therefore:

\[
|\frac{\phi_m^*}{\phi_n}(t)|^2 = \frac{1}{\hbar^2} |\langle \phi_m | \hat{M} | \phi_n \rangle|^2 \left[ \frac{\sin(\epsilon \Delta/2)}{\Delta/2} \right]^2.
\]
The function
\[ F(t) = \left[ \frac{\sin(t\Delta/2)}{\Delta/2} \right]^2 \]
has a Dirac-delta behaviour:

In fact, if \( f(x) \) is a smooth test function
\[
\int f(\Delta) \frac{4}{\Delta^2} \sin^2 \left( \frac{t \Delta}{2} \right) d\Delta \sim f(0) \int d\Delta \frac{4}{\Delta^2} \sin^2 \frac{t \Delta}{2} \quad \text{as} \quad \Delta \to 1
\]

So, for large \( t \):
\[
\frac{4}{\Delta^2} \sin^2 \left( \frac{t \Delta}{2} \right) \to 2\pi t \delta(\Delta) = 2\pi t \delta \left( E_m^0 - H^0 \right)
\]

And
\[
|f_m'(x)|^2 \to \frac{2\pi}{\hbar} \langle \phi_m | \hat{\mathbf{H}} | \phi_x \rangle^2 t \delta \left( E_m^0 - E_k^0 + \hbar \omega \right)
\]
This equation shows that the transition probability after a long time grows linearly with $t$ (won't exceed 1??).

However, the transition probability per unit of time is finite and time-independent:

$$\Gamma_{k\rightarrow m} \equiv \frac{\hbar}{i} \left| f_m(t) \right|^2 = \frac{2\pi}{\hbar} \left| \langle \phi_m | \hat{A}^\dagger | \phi_k \rangle \right|^2 S(E_m - E_k + \hbar \omega)$$

The delta function shows that transitions are induced only if:

$$\hbar \omega = |E_m - E_k|$$

If $E_k < E_m$, then the system is excited from the lower level $E_k$ to the upper level $E_m$:

If $E_k > E_m$, the system decays to the lower level.
The delta function is not physical, it is actually integrated over, if we take into account that the photon energy $\hbar \omega$ does not specify uniquely the photon state. The photon will in general be detected in some momentum interval $(k, k + \Delta k)$ in the vicinity of $|k| = \omega/c$, and the transition rate that is measured is really

$$R_{k \rightarrow m} = \sum_{\Delta k} \left( \frac{d}{d k} \right)$$

The sum is over all states in the range $\Delta k$. It is possible to show (but we do not do it here) that for a particle emitted within a volume $V$:

$$R_{k \rightarrow m} = \frac{2 \pi V}{\hbar} \frac{d}{d k} \left( \frac{3}{(2\pi)^3} \left| \langle \phi_m | \hat{H} \phi_k \rangle \right|^2 S (E_m - E_k + \hbar \omega) \right)$$