when a stationary perturbation is switched on
when the perturbation is time varying.
eg electromagnetic radiation - transition probabilities
- transition rates
- spectral line intensities

Two-Level System
\[ \psi(t) = \psi^{(0)}(t) + \psi^{(1)}(t) \]
\[ \psi^{(0)}(t) \psi_1 = E_1 \psi_1; \quad \psi^{(0)}(t) \psi_2 = E_2 \psi_2; \quad \psi^{(1)}(t) = e^{\frac{iE_{12}}{\hbar} t} \psi_0 \]

In the presence of a perturbation, the state is
\[ \psi(t) = a_1(t) \psi_1 + a_2(t) \psi_2(t) \]

Note time-dependent coefficients, since the system evolves under the influence of the perturbation. We want to know how the coefficients evolve with time!

Subst. \[ \psi(t) \] into \[ \dot{\psi} = i\hbar \frac{\partial \psi}{\partial t} \] ⇒
\[ \dot{\psi} = a_1 \dot{\psi}^{(0)}_1 + a_1 \dot{\psi}^{(1)}(t) \psi_1 + a_2 \dot{\psi}^{(0)}_2 + a_2 \dot{\psi}^{(1)}(t) \psi_2 \]
\[ = i\hbar \frac{\partial}{\partial t} (a_1 \psi_1 + a_2 \psi_2) \]
\[ = i\hbar a_1 \frac{\partial \psi_1}{\partial t} + i\hbar a_2 \frac{\partial \psi_2}{\partial t} \]
\[ = a_1 \dot{\psi}^{(0)}_1 + i\hbar a_2 \dot{\psi}^{(0)}_2 \]

so \[ a_1 \dot{\psi}^{(1)}(t) \psi_1 + a_2 \dot{\psi}^{(0)}(t) \psi_2 = i\hbar a_1 \dot{\psi}_1 + i\hbar a_2 \dot{\psi}_2 \]

NEED: rates of change of the coefficients, \( a_1, a_2 \), from this!
Some math. + rearranging (see handout) \[ \dot{a}_1 = \frac{1}{i} a_2 \mu_{12}^{(n)}(t) e^{i\omega_0 t} ; \quad \dot{a}_2 = \frac{1}{i} a_1 \mu_{21}^{(n)}(t) e^{i\omega_0 t} \]

where \[ \mu_{ij}^{(n)}(t) = \int \psi_i^{*(n)}(t) \psi_j(t) \, dt ; \quad \omega_0 = \omega_2 - \omega_1 \]

**Zero Perturbation** \[ \mu_{ij}^{(n)} = 0 \]

Then \( \dot{a}_1 = \dot{a}_2 = 0 \) + the probability of finding the system in one state or the other remains constant.

**Constant Perturbation switched on at** \( t = 0 \)

\[ t < 0, \quad \dot{a}_1 = 0, \quad \dot{a}_2 = 0 \]

\[ t > 0, \quad \dot{a}_1 = \frac{1}{i} a_2 \mu_{12}^{(n)}(t) e^{-i\omega_0 t} ; \quad \dot{a}_2 = \frac{1}{i} a_1 \mu_{21}^{(n)}(t) e^{i\omega_0 t} \]

Solve coupled differential eqns. (see handout)

\[
\begin{align*}
\dot{a}_1 &= \left\{ \cos \Omega t + i \frac{\omega_0}{2\Omega} \sin \Omega t \right\} e^{-\frac{1}{2}i\omega_0 t} \\
\dot{a}_2 &= -i\nu \sin \Omega t e^{\frac{1}{2}i\omega_0 t} \\
\Omega &= \frac{1}{2} (\omega_0^2 + 4\nu^2)^{1/2}
\end{align*}
\]

- Let us calculate the coefficients at any time after the perturbation was switched on.

Probability of finding system in one state or the other, \( P_1 = |a_1|^2, \quad P_2 = |a_2|^2 \)

For the initially unoccupied state, we get the Rabi Formula:

\[
P_2 = 1 |a_2|^2 = \left( \frac{4\nu^2}{\omega_0^2 + 4\nu^2} \right) \sin^2 \frac{1}{2} (\omega_0^2 + 4\nu^2)^{1/2} t
\]
\[ P_2 = \left( \frac{4V^2}{\omega_0^2 + 4V^2} \right) \sin^2 \frac{1}{2} \left( \frac{(\omega_0^2 + 4V^2)^{1/2}}{2} \right) t \]

**Degenerate States**

- System oscillates at freq. \( 2V \)
- Strong perturbations drive system between states more quickly
- System can make transition completely however break the perturbation

**Non-Degenerate States**

- Energy separation of levels large compared to perturbation strength \( \omega_0^2 \gg 4V^2 \)
- \[ P_2 = \left( \frac{2V}{\omega_0} \right)^2 \sin^2 \frac{1}{2} \omega_0 t \]
- System oscillates but \( P_2(\text{max}) \) is only \( \frac{4V^2}{\omega_0^2} \ll 1 \)
- Frequency of oscillation is determined by energy separation
- As \( V \to 0 \), \( P_2 \to 0 \)

Can prepare mixed states by waiting until (for example) \( P_1 = P_2 = \frac{1}{2} \), then switching off the perturbation. The mixed state persists, since \( \hat{a}_1 = \hat{a}_2 = 0 \).
Dirac's Method of Variation of Constants (1)

As before:
\[ \psi = \psi^{(0)} + \psi^{(1)}(t); \quad \psi^{(0)} \psi_n = E_n \psi_n; \quad \psi^{(1)} \psi_n = \psi_n e^{-iE_n \tau}; \quad \psi^{(1)} \psi_n = i \tau \psi_n \]

Also, as before, express state of perturbed system as:
\[ \psi = \sum_n a_n \psi_n = \sum_n a_n \psi_n e^{-iE_n \tau}; \quad \frac{\partial}{\partial \tau} \psi = i \tau \psi \]

We want to find the \( a_n(t) \). Proceed as before.

\[
\frac{\partial}{\partial \tau} \psi = \sum_n a_n \psi^{(1)} \psi_n + i \sum_n \tau a_n \psi^{(1)} \psi_n
\]

\[
\Rightarrow \sum_n a_n \psi^{(1)} \psi_n e^{-iE_n \tau} = i \tau \sum_n a_n \psi_n e^{-iE_n \tau}
\]

\[ x \text{ by } \psi_n \text{ over all space } \Rightarrow \]
\[ \sum_n \langle k | \psi^{(1)} | n \rangle a_n \psi_n e^{-iE_n \tau} = i \tau \sum_n a_n \psi_n e^{-iE_n \tau} \]

or
\[ a_k = \frac{1}{i \tau} \sum_n \langle k | \psi^{(1)} \psi_n \rangle e^{-iE_n \tau}; \quad \langle k | \psi^{(1)} \psi_n \rangle = E_k - E_n \]

and
\[ a_k(t) - a_k(0) = \frac{1}{i \tau} \sum_n \int_0^t \psi_n e^{-iE_n \tau} d\tau \]

- gives coefficient \( a_k \) in terms of all other coeff. we approximate.

Assume:
- perturbation is weak
- system is initially in state \( i \), st. \( a_i(0) = 1 \)
- probability that system is in any state other than \( i \) is always so low that
- all terms in the sum on the right can be set to zero except the term with \( n = i \).
The coefficient to be in some final state \( f \neq i \) is
\[
a_f(t) - a_f(0) = \frac{1}{ik} \int_{0}^{t} a_i(t) \phi^{(n)}_f(t) e^{i\omega_f t} dt
\]
(note 1 term only on RHS)

As before, as barely changes from its initial value \( 1 \) :: we set \( a_i(t) = 1 \); also \( a_f(0) = 0 \) \( \Rightarrow \)
\[
a_f(t) = \frac{1}{ik} \int_{0}^{t} \phi^{(n)}_f(t) e^{i\omega_f t} dt
\]
an expression for the coefficient of an initially unoccupied state

Nature of the Approximations

System changes from \( i \) to \( f \) only by the direct route. This is first-order perturbation theory - the perturbation only acts once.

first-order

\[
\begin{array}{c}
\text{direct transitions - included}
\end{array}
\]

second-order

\[
\begin{array}{c}
\text{indirect transitions - not included}
\end{array}
\]