Physics 472 Lecture 20

Time-dependent Perturbations

Suppose $H(t) = H_0 + \lambda H_1(t)$.

Such problems generally cannot be solved exactly, because one cannot separate variables and obtain a time-indep. Sch. eq. The time-dep. perturbation $H_1(t)$ will induce transitions — quantum jumps — between the various eigenstates of H_0.

The eigenstates of H_0 still form a complete basis, so

we can write

$$|\psi(t)\rangle = \sum_n C_n(t)\,|n\rangle,$$

where $H_0|n\rangle = E_n|n\rangle$. The eigenstates of H_0 evolve in time according to

$$|n(t)\rangle = e^{-\frac{iE_n t}{\hbar}}\,|n(0)\rangle,$$

so let us include that known behavior in our expansion for $|\psi(t)\rangle$,

$$|\psi(t)\rangle = \sum_n C_n(t)\, e^{-\frac{iE_n t}{\hbar}}\,|n\rangle.$$

$$|n(0)\rangle$$

Schrödinger's equation is

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \left(H_0 + \lambda H_1(t)\right) |\psi(t)\rangle .$$

$$\sum_n \left[i\hbar \frac{dC_n(t)}{dt} + \cancel{E_n C_n(t)} \right] e^{-\frac{iE_n t}{\hbar}} |n\rangle$$

$$= \sum_n \left[\cancel{E_n} + \lambda H_1(t) \right] C_n(t) e^{-\frac{iE_n t}{\hbar}} |n\rangle$$

Taking the inner product with $\langle m|$ gives

$$i\hbar \frac{dC_m(t)}{dt} e^{-\frac{iE_m t}{\hbar}} = \lambda \sum_n C_n(t) e^{-\frac{iE_n t}{\hbar}} \times \langle m | H_1(t) | n \rangle$$

$$i\hbar \frac{dC_m(t)}{dt} = \lambda \sum_n C_n(t) e^{\frac{i E_m - E_n}{\hbar} t} \langle m | H_1(t) | n \rangle$$

So far, this is just an exact rewriting of the Sch. eq. Now let's expand in powers of λ:

$$C_n(t) = C_n^{(0)} + \lambda C_n^{(1)}(t) + \lambda^2 C_n^{(2)}(t) + \cdots$$

Suppose initially the system is in a particular eigenstate $|i\rangle$ of H_0, i.e.,

$$C_n(0) = C_n^{(0)} = \delta_{ni}.$$

Then

$$i\hbar \frac{dC_m^{(1)}}{dt} = e^{i\frac{E_m - E_i}{\hbar}t} \langle m | H_1(t) | i \rangle$$

$$\rightarrow C_m^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt' \, e^{i\left(\frac{E_m - E_i}{\hbar}\right)t'} \langle m | H_1(t) | i \rangle$$

The probability that the perturbation induces a transition $i \to m$ after a time t is, to lowest order in perturbation theory (and taking $\lambda = 1$),

$$P_{i\to m}(t) = \left| C_m^{(1)}(t) \right|^2 .$$

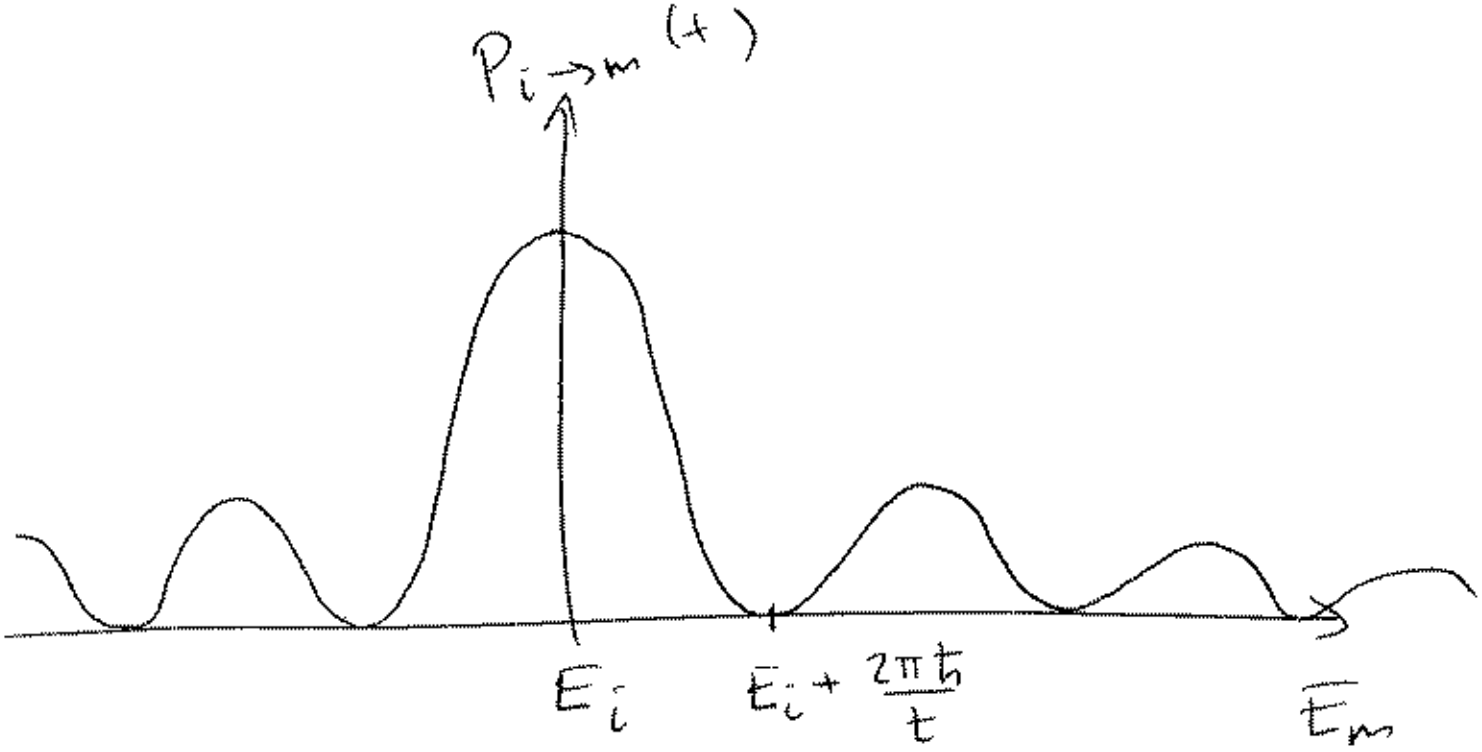
Case 1: Time-independent perturbation

Even if H_1 does not depend on time, it will induce transitions between the eigenstates of H_0.

$$C_m^{(1)}(t) = -\frac{i}{\hbar} \langle m|H_1|i\rangle \int_0^t dt' \, e^{i\left(\frac{E_m - E_i}{\hbar}\right)t'}$$

$$= \langle m|H_1|i\rangle \, \frac{1 - e^{i\left(\frac{E_m - E_i}{\hbar}\right)t}}{E_m - E_i}$$

$$P_{i\to m}(t) = |\langle m|H_1|i\rangle|^2 \frac{\sin^2\left(\frac{E_m - E_i}{2\hbar}\right)t}{\left[(E_m - E_i)/2\right]^2}$$



The height of the central peak grows as t^2, while its width decreases as $1/t$. If the states E_m form a continuum in the vicinity of E_i, then the

probability of a transition to one of these states grows linearly with time. The total probability of a transition out of the initial state is

$$\sum_m P_{i\to m}(t) = \sum_{m\neq i} |\langle m|H_1|i\rangle|^2 \left[\frac{\sin\left(\frac{E_m - E_i}{2\hbar}\right)t}{(E_m - E_i)/2}\right]^2$$

If the matrix elements $|\langle m|H_1|i\rangle|$ are similar for the group of states with large probabilities, we can take it outside the sum, and replace the sum by an integral over energy.

$$\sum_m P_{i\to m}(t) \approx \overline{|\langle m|H_1|i\rangle|^2} \times \int dE\, \rho(E) \left[\frac{\sin\left(\frac{E-E_i}{2\hbar}\right)t}{(E-E_i)/2}\right]^2$$

As t increases, the term in brackets becomes more and more sharply peaked about $E = E_i$. Then we can pull out $\rho(E) \approx \rho(E_i)$ from the integral too. The remaining integral

$$\int_{-\infty}^{\infty} dE \left[\frac{\sin\left(\frac{E-E_i}{2\hbar}\right)t}{(E-E_i)/2}\right]^2 = \frac{2\pi}{\hbar} t$$

Thus we can define the rate Γ of transitions as

$$\sum_m P_{i\to m}(t) = \Gamma t$$

$$\Gamma = \frac{2\pi}{\hbar} \overline{|\langle m|H_1|i\rangle|^2}\, \rho(E_m = E_i)$$

This result is known as Fermi's golden rule.

This result is so useful, and so widely used, that practicing physicists often forget that it is only an approximation!

Conditions for validity of Fermi's golden rule

First of all, since this is only the lowest-order result of perturbation theory, it can only be trusted if $|C_n(t)| \ll 1$.

Secondly, we have assumed that the final states form a continuum, so the level spacing must satisfy

$$\Delta E \ll \frac{2\pi\hbar}{t}$$

i.e.,

$$\boxed{t \ll \frac{h}{\Delta E}.}$$

Finally, we have assumed that the density of states $\rho(E_m)$ is constant over the interval $\frac{2\pi\hbar}{t}$ about E_i.

In general,

$$\rho(E_m) = \rho(E_i) + \rho'(E_i)(E_m - E_i) + \cdots$$

so we require

$$|\rho'(E_i)| \frac{2\pi\hbar}{t} \ll \rho(E_i) \quad \text{or}$$

$$\boxed{t \gg \hbar \frac{|\rho'(E_i)|}{\rho(E_i)}}.$$

Despite these restrictions, Fermi's golden rule is extremely useful in practice.

Case 2°. Harmonic perturbation

Another important case is that of a perturbation harmonic in time, such as that due to an electromagnetic wave incident on an atom or molecule.

Then $H_1(t) = 2H_1 \cos \omega t$

$$= H_1 \left(e^{i\omega t} + e^{-i\omega t} \right)$$

$$\rightarrow C_m^{(1)}(t) = -\frac{i}{\hbar} \langle m|H_1|i\rangle \int_0^t dt' \, e^{i\left(\frac{E_m - E_i}{\hbar}\right)t'} \times \left(e^{i\omega t} + e^{-i\omega t} \right)$$

$$C_m^{(1)}(t) = \langle m|H_1|i\rangle \left[\frac{1 - e^{i\frac{E_m - E_i + \hbar\omega}{\hbar}t}}{E_m - E_i + \hbar\omega} + (\omega \rightarrow -\omega) \right.$$

Since the matrix element $\langle m|H_1|i\rangle$ is assumed to be small, the transition probability will be large only if one of the energy denominators is small, i.e., if a resonance condition is satisfied:

$$E_m - E_i \pm \hbar\omega = 0.$$

The argument goes through as before, yielding the rates

$$\Gamma_{i\to m} = \frac{2\pi}{\hbar} |\langle m|H_1|i\rangle|^2 \, \delta(E_m - E_i \pm \hbar\omega)$$

Here the negative sign corresponds to absorption, and the positive sign to stimulated emission.