Quantum Mechanics

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Switching on a Constant Perturbation

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Constant Perturbation

Let us consider a constant perturbation switched on at time $t = 0$

$$V(t) = \begin{cases} 0, & t < 0 \\ V, & t \geq 0 \end{cases}$$

and suppose the system is initially in an eigenstate $|i\rangle$ of H_0. In this case,

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

To first order, the transition probability is then

$$\left|c_n^{(1)}\right|^2 = \frac{|V_{ni}|^2}{|E_n - E_i|^2}\left(e^{-i\omega_{ni}t} - 1\right)\left(e^{i\omega_{ni}t} - 1\right) = \frac{|V_{ni}|^2}{|E_n - E_i|^2}\left(1 - e^{-i\omega_{ni}t} - e^{i\omega_{ni}t} + 1\right)$$

$$= \frac{|V_{ni}|^2}{|E_n - E_i|^2}(2 - 2\cos\omega_{ni}t) = \frac{2|V_{ni}|^2}{|E_n - E_i|^2}\left(1 - 1 + 2\sin^2\frac{\omega_{ni}t}{2}\right)$$

or

$$\left|c_n^{(1)}\right|^2 = \frac{4|V_{ni}|^2}{|E_n - E_i|^2}\sin^2\frac{(E_n - E_i)t}{2\hbar}$$

Transition Probability

Noting that

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

As t becomes large, the transition probability is thus appreciable only for the final states that satisfy energy conservation $E_n = E_i$.

In practice, we will be interested in situations where there are many states with $E \sim E_n$ so that we can talk about a continuum of final states with nearly the same energy. In such cases, the transition probability is summed over all the final states $E_n \approx E_i$

$$\int dE_n\, \rho(E_n) \left|c_n^{(1)}\right|^2 = \int \frac{4|V_{ni}|^2}{|E_n - E_i|^2} \sin^2 \frac{(E_n - E_i)t}{2\hbar} \rho(E_n) dE_n$$

As $t \to \infty$,

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

Fermi's Golden Rule

Thus, the transition probability from state $|i\rangle$ to a set of states $|[n]\rangle$

$$P(i \to [n]) = \frac{2\pi t}{\hbar} \langle |V_{ni}|^2 \rangle \, \rho(E_n) \Big|_{E_n \approx E_i}$$

The transition rate is therefore

$$w_{i\to[n]} = \frac{dP(i \to [n])}{dt} = \frac{2\pi}{\hbar} \langle |V_{ni}|^2 \rangle \, \rho(E_n) \Big|_{E_n \approx E_i}$$

This relation is called the Fermi's Golden Rule.

Second Order

The second-order perturbation term is

$$c_n^{(2)} = \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \int_0^t dt'\, e^{i\omega_{nm}t'} \int_0^{t'} dt''\, e^{i\omega_{mi}t''}$$

$$= \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t dt'\, e^{i\omega_{nm}t'} \left(e^{i\omega_{mi}t'} - 1\right) = \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \left[\frac{e^{i\omega_{ni}t'} - 1}{E_n - E_i} - \frac{e^{i\omega_{nm}t'} - 1}{E_n - E_m}\right]$$

Thus to second order,

$$P(i \to [n]) = \left|c_n^{(1)} + c_n^{(2)}\right|^2$$

$$= \left\|\left[V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i}\right] \frac{\left(e^{i\omega_{ni}t'} - 1\right)}{E_n - E_i} + \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \frac{\left(e^{i\omega_{nm}t'} - 1\right)}{E_n - E_m}\right|^2$$

The only important contributions arise from $E_n = E_i$. When E_m differs from both E_n and E_i, the last term gives rise to a rapid oscillation that does not contribute to a transition probability that grows with time.

Second Order Transition Rate

The second-order transition rate is then

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\left\langle\left|V_{ni} + \sum_m \frac{V_{nm}V_{mi}}{E_m - E_i}\right|^2\right\rangle \rho(E_n)\Big|_{E_n\approx E_i}$$

The transition due to the second term takes place in two steps. The initial state $|i\rangle$ first makes an energy non-conserving transition to state $|m\rangle$, which then makes another energy non-conserving transition to $|n\rangle$, but the two energy non-conserving transitions combine to make an overall energy conserving transition. Such energy non-conserving transitions are called virtual transitions, in contrast to energy-conserving real transitions.