

# 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,

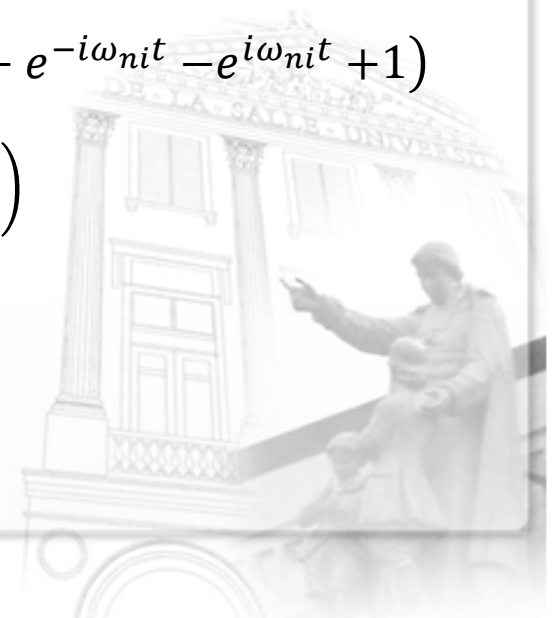
$$c_n^{(1)} = \left(-\frac{i}{\hbar}\right) \int_0^t V_{ni} e^{i\omega_{ni}t'} dt' = \left(-\frac{i}{\hbar}\right) \frac{V_{ni}}{i\omega_{ni}} (e^{i\omega_{ni}t} - 1)$$

To first order, the transition probability is then

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

or

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



# Transition Probability

Noting that

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

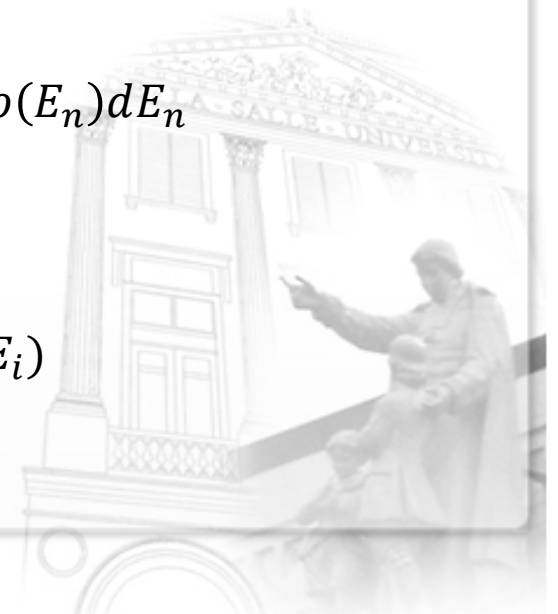
As  $t$  becomes large, the transition probability is thus appreciable only for the final states that satisfy energy conservation  $E_n = E_i$ .

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  $E_n \approx E_i$

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

As  $t \rightarrow \infty$ ,

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



# Fermi's Golden Rule

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

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

The transition rate is therefore

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

This relation is called the Fermi's Golden Rule.



# Second Order

The second-order perturbation term is

$$\begin{aligned} c_n^{(2)} &= \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \int_0^t dt' e^{i\omega_{nm}t'} \int_0^{t'} dt'' e^{i\omega_{mi}t''} \\ &= \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t dt' e^{i\omega_{nm}t'} (e^{i\omega_{mi}t'} - 1) = \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \left[ \frac{e^{i\omega_{ni}t} - 1}{E_n - E_i} - \frac{e^{i\omega_{nm}t} - 1}{E_n - E_m} \right] \end{aligned}$$

Thus to second order,

$$\begin{aligned} P(i \rightarrow [n]) &= |c_n^{(1)} + c_n^{(2)}|^2 \\ &= \left| \left[ V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \right] \frac{(e^{i\omega_{ni}t} - 1)}{E_n - E_i} + \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \frac{(e^{i\omega_{nm}t} - 1)}{E_n - E_m} \right|^2 \end{aligned}$$

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

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

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.

