5) As a first application of Eq. (11), we find the $\Theta(V)$ amplitudes. For $\mu = 0$:

$$\rightarrow i\hbar\, a_k^{(1)}(t) = \sum_n a_n^{(0)} \int_{t_0}^{t} V_{kn}(\tau)\, e^{i\omega_{kn}\tau}\, d\tau. \tag{12}$$

First order transition amplitude for $m \to k$.

Choose $a_n^{(0)} = \delta_{nm}$, i.e. system initially in eigenstate m (for $t < t_0$). Then...

$$\boxed{a_k^{(1)}(t) = -(i/\hbar) \int_{t_0}^{t} V_{km}(\tau)\, e^{i\omega_{km}\tau}\, d\tau}\text{, from initial state } m. \tag{13}$$

The system wavefcn is by now...

$$\psi(x,t) = \sum_n \left[a_n^{(0)} + a_n^{(1)}(t) + \ldots\right] \phi_n(x)\, e^{-i\omega_n t}$$

or/

$$\rightarrow \psi(x,t) \simeq \underbrace{\phi_m(x)\, e^{-i\omega_m t}}_{\text{initial state}} + \underbrace{\sum_k a_k^{(1)}(t)\, \phi_k(x)\, e^{-i\omega_k t}}_{\text{states mixed into } m \text{ by } V(x,t)}. \tag{14}$$

The overlap of ψ on state k, i.e. the amplitude for state k to appear here is:

$$\langle \phi_k | \psi \rangle \simeq \delta_{km}\, e^{-i\omega_m t} + a_k^{(1)}(t)\, e^{-i\omega_k t}. \tag{15}$$

Suppose $k \neq m$. Then the 1st term RHS here vanishes, and...

$$|\langle \phi_k | \psi \rangle|^2 \simeq |a_k^{(1)}(t)|^2 = (1/\hbar^2) \left| \int_{t_0}^{t} V_{km}(\tau)\, e^{i\omega_{km}\tau}\, d\tau \right|^2. \tag{16}$$

$\boxed{\text{INTERPRETATION}}$. This is the probability (to lowest order in V) of a <u>transition $m \to k$</u> induced by V (which supplies or absorbs the the excitation energy $(\omega_m - \omega_k)$). Hence $a_k^{(1)}$ is called the "<u>1st order transition amplitude</u>" for $m \to k$.

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6) With Eq. (16) in hand, we do an <u>example</u> of how a time-dependent coupling $V(x,t)$ actually drives transitions out of state m into states $k \neq m$.

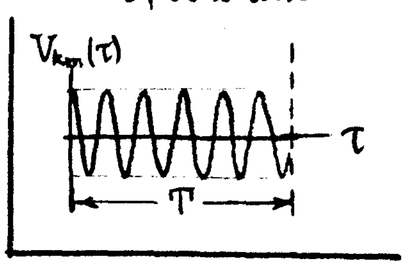
EX. PULSED HARMONIC PERTURBATION

$$V(x,t) = \hbar\Omega(x)\left[e^{+i\omega t} + e^{-i\omega t}\right] = 2\hbar\, \Omega(x) \cos\omega t \quad \begin{cases} \text{for } 0 \leq t \leq T, \text{ and} \\ 0, \text{ otherwise} \end{cases}$$

So

$$\rightarrow V_{km}(\tau) = \hbar\Omega_{km}\left[e^{i\omega\tau} + e^{-i\omega\tau}\right], \text{ over } 0 \leq \tau \leq T$$

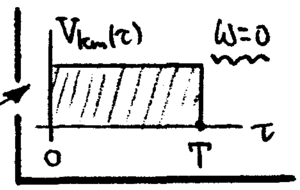
where: $\hbar\Omega_{km} = \langle \phi_k(x) | V(x) | \phi_m(x) \rangle$. (17)



Example of Pulsed Harmonic Perturbation

Such a coupling $V(x,t)$ could represent the effect of a laser pulse (monochromatic, at freq. ω) shining on an atom [initially in state m] for some finite time T.

Notice that when $\omega \to 0$, then $V_{km}(\tau) = 2\hbar\Omega_{km} = \text{cnst}$, $0 \leq \tau \leq T$, and zero, otherwise... so the "atom" is exposed to a cnst field pulse.



Put $V_{km}(\tau)$ of Eq. (17) into the first-order amplitude of Eq. (13)...

$$a_k^{(1)}(t \geq T) = -\frac{i}{\hbar}\,\hbar\Omega_{km}\int_0^T \left(e^{i\omega\tau} + e^{-i\omega\tau}\right) e^{i\omega_{km}\tau}\,d\tau,$$

$$\xrightarrow{\text{So}}\; a_k^{(1)}(t \geq T) = \Omega_{km}\Bigg[\underbrace{\frac{1-e^{i(\omega_{km}+\omega)T}}{\omega_{km}+\omega}}_{1} + \underbrace{\frac{1-e^{i(\omega_{km}-\omega)T}}{\omega_{km}-\omega}}_{2}\Bigg] \quad \left\{ \begin{array}{l} t \geq T \text{ means} \\ \text{pulse } V \text{ is} \\ \text{finished.} \end{array} \right. \tag{18}$$

REMARKS on Eq. (18).

1. V "small" here $\Rightarrow |\Omega_{km}| \ll |\omega_{km}|$. Then $a_k^{(1)}(t \geq T)$ is appreciable only at the "resonances": $\omega_{km} \simeq \mp\omega$, when: $a_k^{(1)}(t \geq T) \simeq -i\Omega_{km}T$. This can become large as $T \to$ large (and requires higher order pertⁿ theory to handle completely).

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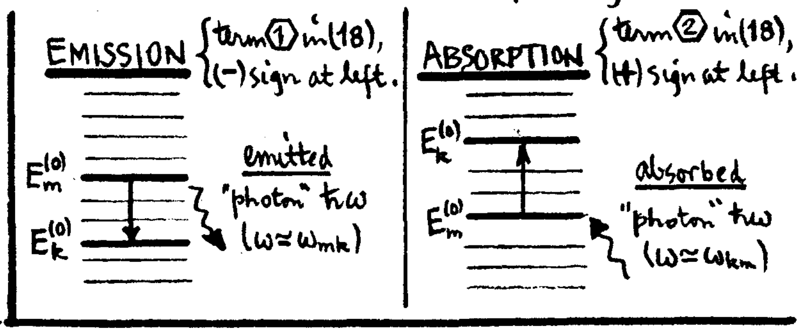
2. The resonant condition $\omega_{km} \simeq \mp\omega$ can be written in terms of energies as...

$$\boxed{E_k^{(0)}\left[\begin{smallmatrix}\text{final}\\ \text{state}\end{smallmatrix}\right] = E_m^{(0)}\left[\begin{smallmatrix}\text{initial}\\ \text{state}\end{smallmatrix}\right] \mp \hbar\omega} \tag{19}$$



Interpretation: the resonant behavior of $a_k^{(1)}(t \geq T)$ in Eq. (18) is associated with either the emission (term ①) or absorption (term ②) of a "photon" of energy $\hbar\omega$, $\omega \simeq |\omega_{km}|$, from V-field.

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3. If we are interested in absorptive processes only (which pump energy into the "atom"), then in Eq. (18) only term ② is important, and we can write...

for $E_m^{(0)} \to E_k^{(0)} > E_m^{(0)}$, absorption, the $m \to k$ transition probability is:

$$|a_k^{(1)}|^2 = 4|\Omega_{km}|^2 \sin^2 \tfrac{1}{2}(\omega_{km}-\omega)T \,/\, (\omega_{km}-\omega)^2 \quad \left\{ \begin{array}{l} \text{for irradiation by pulse} \\ \text{of length } T \text{ @ frequency } \omega. \end{array} \right. \tag{20}$$

This is the lowest order result. The emission probability is gotten via $\omega \to (-)\omega$ here.

Further general remarks on 1st order amplitude

7) Two other general remarks can be made about the first-order amplitude in Eq.(13):

4. Even though emissive or absorptive transitions $m \to k$ are induced by V, the population of the initial state m is barely depleted (in this order of pert$^{\text{b}}$n theory). The argument goes as follows. By time t after turn-on, V has induced the state

$$\rightarrow \psi(x,t) = \underbrace{\phi_m(x)e^{-i\omega_m t}}_{\text{initial state}} + \underbrace{\sum_n a_n^{(1)}(t)\,\phi_n(x)\,e^{-i\omega_n t}}_{\text{admixture due to } V}, \text{ to } O(V). \tag{21}$$

The amplitude of ϕ_m still present in ψ is...

$$\rightarrow \langle\phi_m|\psi\rangle = e^{-i\omega_m t}\left[1 + a_m^{(1)}(t)\right] = e^{-i\omega_m t}\underbrace{\left[1 - \frac{i}{\hbar}\int_{t_0}^{t} V_{mm}(\tau)\,d\tau\right]}_{= e^{-\frac{i}{\hbar}\int V_{mm}d\tau}, \text{ to } O(V);}$$

So $\langle\phi_m|\psi\rangle = e^{-i\omega_m t}\, e^{-\frac{i}{\hbar}\int_{t_0}^{t} V_{mm}(\tau)d\tau}$,

and population of initial state m at time t $\Big\}$ $$\underline{\underline{|\langle\phi_m|\psi\rangle|^2 = \left|e^{-\frac{i}{\hbar}\int^{t} V_{mm}d\tau}\right|^2 \to 1}}. \tag{22}$$

All that is needed here is to assume V is real (necessary to ensure $\mathcal{H}_0 + V$ is Hermitian). The depletion of state m by transitions $m \to k$ is at most an $O(V^2)$ effect.

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5. Consider $m \to k$ couplings via $V_{km}(\tau)$ which last a "long" time [e.g. could be $V_{mk}(\tau) \propto e^{-\alpha\tau^2}$, a Gaussian; all we really need is duration $\Delta\tau \gg 1/|\omega_{km}|$]. Formally, the $m \to k$ transitions are not finished till $t \to \infty$, so we need:

$$\rightarrow a_k^{(1)}(\infty) = -\frac{i}{\hbar}\int_{-\infty}^{\infty} V_{km}(\tau)\,e^{i\omega_{km}\tau}\,d\tau, \tag{23}$$

to find out the final $m \to k$ transfer. Except for the factor $(i\hbar)^{-1}$ out in front, the required amplitude is just the Fourier Transform of $V_{km}(\tau)$. So the way a quantum system reacts to an impressed time-dependent perturbation $V(\tau)$ is to Fourier analyse $V(\tau)$ w.r.t. its own natural freqs. ω_{km}.

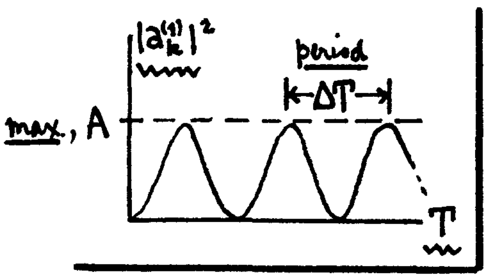
$m \to k$ transition dynamics (leading order)

8) We backtrack to the Pulsed Harmonic Perturbation of Eqs. (17)–(20) above, in order to learn more about the $m \to k$ transition dynamics.

Consider absorptive probability for $m \to k$ per Eq. (20), viz.

$$\boxed{|a_k^{(1)}|^2 = \frac{4|\Omega_{km}|^2}{(\omega_{km}-\omega)^2} \sin^2 \tfrac{1}{2}(\omega_{km}-\omega)T} \quad \text{for } m \to k \text{ via pulse of duration } T \text{ @ freq. } \omega. \tag{24}$$

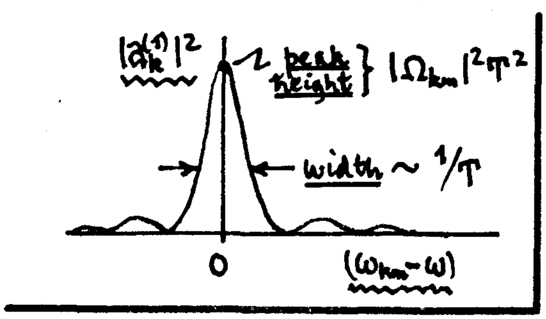
A. Plot $|a_k^{(1)}|^2$ vs. pulse duration T; all other parameters fixed.



max.: $A = 4|\Omega_{km}|^2/(\omega_{km}-\omega)^2$; period: $\Delta T = 2\pi/|\omega_{km}-\omega|$.

System exhibits a "quantum oscillation" $m \rightleftarrows k$ out of and back into initial state m @ freq. $|\omega_{km}-\omega|$.

B. Plot $|a_k^{(1)}|^2$ vs. off-resonance freq. $\omega_{km}-\omega$; all other parameters fixed

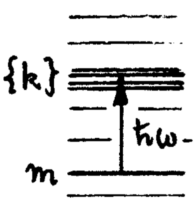


Area under curve $\sim$ peak height $\times$ width $\sim T$. As $T \to$ large, transition $m \to k$ with $E_k^{(0)} = E_m^{(0)} + \hbar\omega$ becomes more certain. Curve width $\sim 1/T$ is consistent with energy uncertainty $\Delta E \sim \hbar/T$ for $m \to k$.

NOTE: $(|a_k^{(1)}|^2/T)$ is a nascent delta-function.

C. Suppose the absorption is $m \to \{k\}$, a set of final states k. Then consider:

$$\left[\begin{matrix}\text{total transition}\\ \text{probability}: m \to \{k\}\end{matrix}\right\} \; P_m = \sum_k |a_k^{(1)}|^2, \quad \text{w/ } E_k^{(0)} \simeq E_m^{(0)} + \hbar\omega. \tag{25}$$



[Keep in mind we are working to lowest order (leading order) in V].

Now suppose the final states $\{k\}$ lie close together in energy, and define

$$\rightarrow \rho(k)\, dE_k = \text{number of final states } k \text{ with energy in range } E_k^{(0)} \text{ to } E_k^{(0)} + dE_k. \tag{26}$$

$\rho(k)$ is called the "density of states" function. Now in these terms, write P_m

Derivation of Fermi's Golden Rule

$$\rightarrow P_m = \sum_k |a_k^{(1)}|^2 \rightarrow \int_{\{k\}} |a_k^{(1)}|^2 \rho(k)\, dE_k = \int_{\{k\}} |\Omega_{km}|^2 \frac{\sin^2 \frac{1}{2}(\omega_{km}-\omega)T}{[\frac{1}{2}(\omega_{km}-\omega)]^2} \rho(k)\, \hbar\, d\omega_k$$

... let: $x = \frac{1}{2}(\omega_{km}-\omega)T$, so: $dx = \frac{1}{2}T\, d\omega_k$. Then...

$$\left[\!\left[P_m = 2\hbar T \int_{\{k\}} \rho(k) |\Omega_{km}|^2 \left(\frac{\sin^2 x}{x^2}\right) dx. \right.\right. \qquad (27)$$

The integrand in (27) has a strong peak @ $x=0$, which corresponds to strict energy conservation: $E_k^{(0)} = E_m^{(0)} + \hbar\omega$, for $m \to k$ via absorption of photon $\hbar\omega$. But the integrand also has a finite width $\Delta x \sim T\Delta\omega_k$, which is demanded by the final state energy uncertainty $\Delta E_k = \hbar\Delta\omega_k \sim \hbar/T$ for $m \to k$ in a finite time T. We integrate over all such "uncertain" transitions.

Assume $\rho(k)$ & Ω_{km} are "slowly varying" functions of k (or ω_k) near the $x=0$ peak in the integrand of (27). Take them out of the integral, so as to write...

Davydov Eq. (93.4)
Sakurai Eq. (5.6.34)

$$\rightarrow P_m \simeq 2\hbar T \left[\rho(k)|\Omega_{km}|^2\right]_{AVG.} \underbrace{\int_{-\infty}^{\infty} \left(\frac{\sin^2 x}{x^2}\right) dx}_{\pi} \qquad (28)$$

The "AVG." means an average (typical) value of $\rho(k)|\Omega_{km}|^2$ near $E_k^{(0)} = E_m^{(0)} + \hbar\omega$. The integral $= \pi$, and we put in $\Omega_{km} = \frac{1}{\hbar}\langle k|V|m\rangle$ [see Eq. (17)]. Then:

$$\boxed{W(m \to \{k\}) = P_m/T = \frac{2\pi}{\hbar}\left(|\langle k|V|m\rangle|^2 \rho(k)\right)_{AVG.}} \qquad \text{FERMI'S GOLDEN RULE} \qquad (29)$$

W is the transition probability per unit time for $m \to \{k\}$, induced by the coupling V. $\rho(k)$ is the density of final states k, and (on average) energy is conserved: $E_k^{(0)} = E_m^{(0)} + \hbar\omega$, with the "photon" $\hbar\omega$ supplied by the V-field.

NOTE that $W(m \to \{k\})$ is independent of the time T over which V acts... that is the surprising feature of this calculation. The result for W can be derived on very general grounds (S-matrix theory), and evidently is a controlling fact for all transition rate calculations. To leading order, anyway.