13) ADIABATIC APPROXIMATION (Davydov, ¶92).

1. Assume the eigenfcns ϕ_n and eigenenergies E_n of total system Hamiltonian $\mathcal{H}(x,p;t)$ are known at all t, i.e. $\mathcal{H}\phi_n(x;t) = E_n(t)\phi_n(x;t)$. The set $\{\phi_n\}$ are orthonormal; t is just a parameter which accommodates slow changes in the ϕ_n & E_n. The general system state is the superposition:

$$\rightarrow \psi(x,t) = \sum_n a_n(t)\,\phi_n(x;t)\,\exp\left\{-i\int_{t_0}^{t}\omega_n(\tau)\,d\tau\right\},\quad \omega_n = \frac{E_n}{\hbar}. \tag{40}$$

The problem is "solved" if we can find the expansion coefficients $a_n(t)$.

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2. The system dynamics is prescribed by $\mathcal{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$. For ψ of (40), get:

$$\rightarrow \sum_n \left[\dot{a}_n\phi_n + a_n\frac{\partial\phi_n}{\partial t}\right]\exp\left\{-i\int_{t_0}^{t}\omega_n\,d\tau\right\} = 0.$$

... operate through with $\langle\phi_k|\ \rangle$, assume $\langle\phi_k|\phi_n\rangle = \delta_{kn}$ ...

$$\text{Soll}\ \left[\!\left[\dot{a}_k = (-)\sum_n a_n\langle\phi_k|(\partial\phi_n/\partial t)\rangle\exp\left\{i\int_{t_0}^{t}(\omega_k-\omega_n)\,d\tau\right\}\right]\!\right]. \tag{41}$$

This is the **MASTER EQTN** for this method. The a's, ω's etc. depend on t.

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3. We can get a simpler expression for the $\langle\phi_k|(\partial\phi_n/\partial t)\rangle$ in (41). Note that:

$$\frac{\partial}{\partial t}\times\left(\mathcal{H}\phi_n = E_n\phi_n\right) \Rightarrow \left(\frac{\partial\mathcal{H}}{\partial t}\right)\phi_n + \mathcal{H}\left(\frac{\partial\phi_n}{\partial t}\right) = \left(\frac{\partial E_n}{\partial t}\right)\phi_n + E_n\left(\frac{\partial\phi_n}{\partial t}\right). \tag{42}$$

... operate through (42) by $\langle\phi_k|\ \rangle$, $k\neq n$, to get...

$$\langle\phi_k|(\partial\mathcal{H}/\partial t)|\phi_n\rangle + \langle\phi_k|\mathcal{H}|(\partial\phi_n/\partial t)\rangle = 0 + E_n\langle\phi_k|(\partial\phi_n/\partial t)\rangle$$

operate to left to generate E_k

$$\xrightarrow{\text{Soll}}\langle\phi_k|(\partial\phi_n/\partial t)\rangle = \frac{1}{E_n - E_k}\langle\phi_k|(\partial\mathcal{H}/\partial t)|\phi_n\rangle,\quad k\neq n. \tag{43}$$

We can use this in (41) for $k\neq n$.

Adiabatic Approximation: lowest order $m \to k$ amplitude.

4. The case of $k=n$ in (43) can be handled as follows...

$$\rightarrow \frac{\partial}{\partial t} \times \left(\langle \phi_n | \phi_n \rangle = 1 \right) \Rightarrow 2\,\mathrm{Re}\,\underbrace{\langle \phi_n | (\partial \phi_n / \partial t) \rangle} = 0. \qquad (44)$$

... pure imaginary, so set: $\langle \phi_n | \dot{\phi}_n \rangle = i\,\alpha_n(t)$ $\left\{ \begin{array}{l} \text{the dot} \\ \Rightarrow \partial/\partial t \end{array} \right.$ ...

$$\left[\!\!\left[\begin{array}{l} \text{Choose new eigenfcns: } \tilde{\phi}_n = \phi_n e^{i\beta_n},\ \beta_n = \beta_n(t) \text{ a phase.} \\ \text{so} /\!/ \ \langle \tilde{\phi}_n | \dot{\tilde{\phi}}_n \rangle = \langle \phi_n | \dot{\phi}_n \rangle + i\dot{\beta}_n = i(\alpha_n + \dot{\beta}_n) \\ \text{and} /\!/ \ \langle \tilde{\phi}_n | \dot{\tilde{\phi}}_n \rangle = 0, \text{ if } \dot{\beta}_n = -\alpha_n, \ \text{i.e.} /\!/ \ \beta_n = -\int_{t_0}^{t} \alpha_n(\tau)\, d\tau. \end{array} \right. \right\} (45)$$

But we could have made this phase choice to begin with. So we claim...

$$\rightarrow \langle \phi_k | (\partial \phi_n / \partial t) \rangle = 0, \text{ for } k=n, \text{ by choice of phase.} \qquad (46)$$

5. Use of (43) & (46) in the <u>MASTER EQTN</u> (41) gives...

$$\left[\!\!\left[\dot{a}_k = \sum_{n \neq k} a_n \left[\frac{\dot{\mathcal{H}}_{kn}}{\hbar \omega_{kn}(t)} \right] \exp\left\{ i \int_{t_0}^{t} \omega_{kn}(\tau)\, d\tau \right\} \right]\!\!\right] \int \begin{array}{l} \dot{\mathcal{H}}_{kn} = \langle \phi_k | \frac{\partial \mathcal{H}}{\partial t} | \phi_n \rangle, \\ \omega_{kn}(t) = \frac{1}{\hbar}\left[E_k(t) - E_n(t) \right]. \end{array} \qquad (47)$$

This eqtn is still <u>exact</u>; we have not yet made any approximations.

6. Now we <u>do</u> make an approxn. Let $a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \ldots$, where λ is connected with the power of $\dot{\mathcal{H}}$ occurring in (47). Then, as usual, choose $a_n^{(0)} = \delta_{nm} \Rightarrow$ system initially in state m, and iterate (47) to get:

$$\rightarrow \dot{a}_k^{(1)} = \left[\dot{\mathcal{H}}_{km} / \hbar \omega_{km} \right] e^{i \int_{t_0}^{t} \omega_{km}(\tau)\, d\tau}, \text{ to 1st order in } \dot{\mathcal{H}}. \qquad (48)$$

$a_k^{(1)}(t)$ will provide the 1st (lowest) order $m \to k$ transition amplitude as driven by $\dot{\mathcal{H}}$. Now in (48), both ω_{km} and $\dot{\mathcal{H}}_{km}$ are in general time-dependent (by assumption). The $\sim$ crude part of this approximation comes now:

[next page]

$m \to k$ Transition Probability via Adiabatic Approx$^{\underline{n}}$.

assume ω_{km} and $\dot{\mathcal{H}}_{km}$ vary "slowly" with t, to the extent that in (48):

$$\left[\!\!\left[\begin{array}{l}\omega_{km}\ \&\ \dot{\mathcal{H}}_{km} \text{ are both} \simeq \text{cnst in time, and may be evaluated as:} \\ \underline{\omega_{km} \simeq \omega_{km}^{(0)},\ \dot{\mathcal{H}}_{km} = \dot{\mathcal{H}}_{km}^{(0)}}, \text{ at some convenient reference time } t_0.\end{array}\right\} \quad (49)$$

We shall remark below on how restrictive this assumption is. In (48), it means

$$\dot{a}_k^{(1)} \simeq [\dot{\mathcal{H}}_{km}^{(0)}/\hbar\omega_{km}^{(0)}]\, e^{i\omega_{km}^{(0)}(t-t_0)}$$

so// $$a_k^{(1)}(t) - \cancel{a_k^{(1)}(t_0)} \simeq [\dot{\mathcal{H}}_{km}^{(0)}/\hbar\omega_{km}^{(0)}]\frac{1}{i\omega_{km}^{(0)}}\left[e^{i\omega_{km}^{(0)}(t-t_0)} - 1\right]$$

$\to$ set $\equiv 0$, since system assumed in state $m \neq k$ @ time t_0.

or// $$a_k^{(1)}(t) \simeq -\frac{i}{\hbar}\left[\dot{\mathcal{H}}_{km}^{(0)}/\omega_{km}^{(0)2}\right]\left[e^{i\omega_{km}^{(0)}(t-t_0)} - 1\right],\ k \neq m. \quad (50)$$

This is the lowest order $m\to k$ transition amplitude. The corresponding $m \to k$ transition probability is: $\mathcal{P}(m\to k) \simeq |a_k^{(1)}(t)|^2$, or (w/ $|e^{ix}-1|^2 = 4\sin^2(x/2)$):

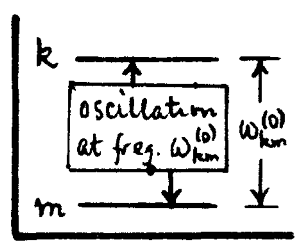
$$\boxed{\mathcal{P}(m\to k) \simeq 4\left|\frac{1}{\omega_{km}^{(0)}}\left\langle k\left|\frac{\partial\mathcal{H}}{\partial t}\right|m\right\rangle^{(0)}\Big/\hbar\omega_{km}^{(0)}\right|^2 \sin^2\tfrac{1}{2}\omega_{km}^{(0)}(t-t_0)}, \quad (51)$$

where: $\omega_{km}^{(0)}$ & $\dot{\mathcal{H}}_{km}^{(0)}$ are evaluated at $t = t_0$.

[equiv. to Davydov Eq. (92.5a), p. 395.]

Eq. (51) is the Adiabatic Approximation for the $m\to k$ transition probability.

REMARKS



(a) The "quantum oscillation" between the states m (initial) and k (final) is automatically built into the Adiabatic Approx$^{\underline{n}}$. Previously we saw this oscillation for the particular choice of the pulsed harmonic perturbation [see Eq. (24), p. tD 8]; now we have it for all slowly varying $\mathcal{H}$'s.

[next page]

Adiabatic Approx$^{\underline{n}}$: Remarks (cont'd)

(b) To assess the range of validity of the Adiabatic Approx^n, we claim that the transition probability $\mathcal{P}(m\to k)$ in Eq. (51) should be small (Fourier argument again). This means the coefficient $|\;\;|^2$ in (51) should be $\ll 1$. Write:

$$\left\langle k \left| \frac{\partial \mathcal{H}}{\partial t} \right| m \right\rangle^{(0)} \sim (\Delta\mathcal{H})^{(0)}_{km} / \Delta t \quad \int \begin{array}{l}\Delta\mathcal{H} \text{ is the amount by which} \\ \mathcal{H} \text{ changes during time } \Delta t\end{array} \tag{52}$$

So

$$\left| \text{in Eq. (51)} \right|^2 \ll 1 \Rightarrow \boxed{\left|\frac{(\Delta\mathcal{H})^{(0)}_{km}}{E^{(0)}_k - E^{(0)}_n}\right| \ll \left|\omega^{(0)}_{km}\Delta t\right| = 2\pi\frac{\Delta t}{\tau^{(0)}_{km}}}. \tag{53}$$

Here $\tau^{(0)}_{km} = 2\pi / |\omega^{(0)}_{km}|$ is the Bohr period for the transition $m\to k$. In words:

> The Adiabatic Approximation is valid so long as the energy transfer $\Delta\mathcal{H}$ (in to or out of the system) is fractionally small compared to the Bohr energy gaps during time intervals Δt of the order of one Bohr period. If the system changes at all, it changes "slowly".

For an atom, in semi-classical language, the fractional change in orbit energy, per orbit, must be "small".

(c) Eq. (53) also gives an indication of how crude the approx$^{\underline{n}}$ in Eq. (49) -- viz that ω_{km} & $\dot{\mathcal{H}}_{km}$ are $\simeq$ cnst during the process -- really is. Answer: __not__ very crude... any secular changes in $\omega^{(0)}_{km}$ & $\dot{\mathcal{H}}^{(0)}_{km}$ must be small during the change $\Delta\mathcal{H}$ in Δt in order to qualify for Eq. (53), so both ω_{km} & $\dot{\mathcal{H}}_{km}$ must be $\simeq$ cnst for the whole approximation to work.

(d) One could hope to use the Adiabatic Approx$^{\underline{n}}$, for example, in <u>low</u>-energy atom-atom collisions, at kinetic energies (~ 1 eV) $\ll$ binding (~ 10 eV).