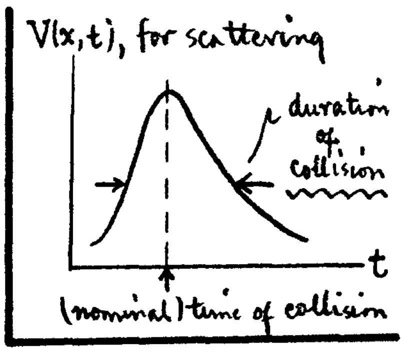
Need for a dynamical perturbation theory.

Time-Dependent Perturbation Theory ref. Davydov: ¶ 90, 92, 93; Sakurai: Secs. 5.5–5.6.

In stationary-state perturbation theory, both the unperturbed Hamiltonian $\mathcal{H}_0$ and the applied perturbation V are independent of time, so the total energy $\mathcal{H} = \mathcal{H}_0 + V$ is a constant of the motion, i.e. energy is conserved. This is an interesting problem in that we can use the methods developed to extend the applicability of known bound-state problems... e.g. we can use hydrogenlike atom wavefcns as a 0^{th} approximation to two-electron problems (He atom, H_2 molecule), with some guarantee of getting "reasonable" energies out of the calculation. But SS perturbation theory is restricted to describing static systems which do not evolve in time, and for which there is no (significant) energy transfer into or out of the system, nor any (interesting) changes -- i.e. "transitions" -- between given states. We just don't account for any of the possible dynamics.



But often the dynamics are of primary interest, as in a collision or scattering encounter -- where the coupling V constitutes an impulse of energy into the system which acts over a finite time ($V(x,t)$ vanishes as $t \to \pm\infty$). Such impulses -- characterized by time-dependent V's -- can cause transitions (or excitations) in each of the colliding QM systems... they will in general be in different states after the collision than they were before. What we need is a (perturbation) theory to decide how $V(x,t)$ drives these transitions. That is what we will do now, assuming $V(x,t)$ is "weak."

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1) We start with an unperturbed system (@ $t \to -\infty$):

$$\mathcal{H}_0 \psi^{(0)}(x,t) = i\hbar \frac{\partial}{\partial t} \psi^{(0)}(x,t); \qquad (1)$$

$\mathcal{H}_0$ is time-indpt $\Rightarrow$ solutions: $\psi_n^{(0)}(x,t) = \phi_n(x) e^{-i\omega_n t}$, w/ $\mathcal{H}_0 \phi_n = E_n^{(0)} \phi_n$, and: $\omega_n = E_n^{(0)}/\hbar$.

t-dependent problem in Interaction Representation

NOTE: In what follows, when a $V(x,t)$ is "turned on" for a finite time Δt, we will be interested in transitions $n(t\to-\infty)\to m(t\to+\infty)$ between eigenstates n & m of $\mathcal{H}_0$, rather than the transient corrections to ϕ_n & $E_n^{(0)}$ which are induced by V. We could follow $E_n^{(0)}$ & $\phi_n(x)$ as fcns of t,¶ but we are more interested in the before $(t\to-\infty)$ vs. after $(t\to+\infty)$ comparison.

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2) Now let $\mathcal{H}_0 \to \mathcal{H} = \mathcal{H}_0 + V$, w/ $V = V(x,t)$ time-dependent. New S. Eq. is:

$$\rightarrow \mathcal{H}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t), \text{ w/ } \mathcal{H} = \mathcal{H}_0 + V. \tag{2}$$

Expand the new wavefcn in terms of the complete set $\{\psi_n^{(0)}(x,t)\}$ as...

$$\rightarrow \psi(x,t) = \sum_n a_n(t)\,\psi_n^{(0)}(x,t) = \sum_n a_n(t)\,\phi_n(x)\,e^{-i\omega_n t}. \tag{3}$$

The expansion coefficients a_n are fcns of time t, and this particular choice of representing $\psi(x,t)$ is called the "interaction representation". The problem is now to solve for the set of $\{a_n(t)\}$. Before we do that, we note...

$$\rightarrow \langle\phi_m|\psi\rangle = \sum_n a_n(t)\langle\phi_m|\phi_n\rangle e^{-i\omega_n t} = a_m(t)\,e^{-i\omega_m t}$$

so// $$a_n(t) = \langle\phi_n(x)|\psi(x,t)\rangle\, e^{i\omega_n t}$$

and// $$\underline{|a_n(t)|^2 = |\langle\phi_n(x)|\psi(x,t)\rangle|^2} = \left\{\begin{array}{l}\text{probability of finding system } (\psi)\\ \text{in state } n \text{ (i.e. } \phi_n) \text{ at time } t.\end{array}\right. \tag{4}$$

Also note: $\langle\psi|\psi\rangle = \sum_n |a_n(t)|^2 = 1$, time-indpt cnst (assuming $\mathcal{H}$ Hermitian). Although the a_n may change in time individually, the sum $\sum_n |a_n|^2$ is still conserved. This represents conservation of particles.

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3) Now plug ψ of Eq. (3) into S. Eq., i.e. Eq. (2). Recall that $\mathcal{H}_0\phi_n = E_n^{(0)}\phi_n$. With all of the a's functions of t...

¶ See formulation in Davydov's Eq. (90.7), p. 389.

Fundamental Eqtn of tD Pert$^{\underline{b}}$n Theory

$\mathcal{H}\psi = i\hbar\, \partial\psi/\partial t \Rightarrow$

$$\rightarrow \sum_n a_n (E_n^{(0)} + V)\phi_n e^{-i\omega_n t} = \sum_n (i\hbar \dot{a}_n + \hbar\omega_n a_n)\phi_n e^{-i\omega_n t} \tag{5}$$

cancel

... operate through by $\langle \phi_k|\ \rangle$. With $\langle\phi_k|\phi_n\rangle = \delta_{kn}$, get...

$$\boxed{i\hbar \dot{a}_k = \sum_n V_{kn} a_n e^{i\omega_{kn} t}}$$

w/ $V_{kn} = \langle \phi_k(x)|V(x,t)|\phi_n(x)\rangle = V_{kn}(t)$, in general;†

& $\omega_{kn} = \frac{1}{\hbar}(E_k^{(0)} - E_n^{(0)}) \leftarrow$ Bohr transition frequency for $k \rightarrow n$. (6)

This is the Fundamental Equation of QM tD perturbation theory (plays same role as Eq. (5), p. SS 2 does for SS pert$^{\underline{b}}$n theory). Eq. (6) is equivalent to Davydov Eq. (90.5), and Sakurai Eq. (5.5.15). It is an ∞ set of coupled 1$^{\text{st}}$ order differential equations, which is equivalent to the Schrodinger eqtn $\mathcal{H}\psi = i\hbar\,\partial\psi/\partial t$, and which can be written in matrix form as:

$$\mathbb{a}(t) = \begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \end{pmatrix}, \quad \underset{\sim}{V}(t) = (V_{kn} e^{i\omega_{kn}t}) = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \cdots \\ V_{12}^* e^{-i\omega_{12}t} & V_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix},$$

$$\xrightarrow{\text{So}} i\hbar \frac{\partial}{\partial t}\mathbb{a}(t) = \underset{\sim}{V}(t)\,\mathbb{a}(t). \tag{7}$$

Such an eqtn is not solvable in general. So here we resort to pert$^{\underline{b}}$n methods.

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4) As before, we introduce a turn-on parameter λ, i.e....

$V \rightarrow \lambda V$, w/ $\lim_{\lambda\to 1}$ understood for full effect of pert$^{\underline{b}}$n V,

and $a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \ldots = \sum_{\mu=1}^{\infty} \lambda^\mu a_n^{(\mu)}(t)$. (8)

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† The integration is over space cds x, not time, i.e. $\langle\phi_k|V|\phi_n\rangle = \int dx\, \phi_k^* V \phi_n$.

Iteration for the amplitudes $a_k^{(\mu)}(t)$.

When the $a_n(t)$ series of Eq. (8) is plugged into Eq. (6) and like powers of λ are equated, there results...

$$\left[\begin{array}{l} i\hbar\,\dot{a}_k^{(0)} = 0, \Rightarrow \text{all the } a_k^{(0)} = \text{time-indpt constants}; \qquad (9a) \\ i\hbar\,\dot{a}_k^{(\mu+1)} = \sum_n V_{kn}\,a_n^{(\mu)}\,e^{i\omega_{kn}t}; \quad \mu = 0,1,2,\ldots,\infty. \qquad (9b) \end{array}\right.$$

REMARKS

1. Eq. (9a) $\Rightarrow$ all $a_k^{(0)}$ = cnst frees the set $\{a_k^{(0)}\}$ to specify the <u>initial</u> <u>conditions</u> of the problem, i.e. the state of the system <u>before</u> $V(x,t)$ becomes significant. A typical choice here is...

$$a_k^{(0)} = \begin{cases} 1, & \text{for } k=m \\ 0, & \text{for } k \neq m \end{cases} \Bigg\| \begin{array}{l} \text{System is "initially" in eigenstate} \\ \Psi_m(x,t) = \phi_m(x)\,e^{-i\omega_m t} \text{ of } \mathcal{H}_0. \end{array} \qquad (10)$$

"Initially" here means the state Ψ_m pertains for times $t < t_0$, where t_0 is a time at which $V(x,t)$ becomes "appreciable".

2. Eq. (9b) permits an <u>iteration</u> procedure whereby the $a_k^{(1)}$ can be determined from the chosen $a_k^{(0)}$, the $a_k^{(2)}$ from the $a_k^{(1)}$, etc. In general, the $a_k^{(\mu+1)}$ are obtained from the $a_k^{(\mu)}$ by a "simple" integration, viz...

$$\boxed{i\hbar\,a_k^{(\mu+1)}(t) = \sum_n \int_{t_0}^{t} V_{kn}(\tau)\,a_n^{(\mu)}(\tau)\,e^{i\omega_{kn}\tau}\,d\tau}. \qquad (11)$$

At the lower limit t_0, $V_{kn}(\tau)$ is supposedly negligible, and there we have chosen all the $a_k^{(\mu+1)}(t_0) = 0$ [except we retain the $a_k^{(0)}(t_0)$ = cnsts].