TIME - DEPENDENT PERTURBATION THEORY

In non-relativistic (Schrodinger) Q.M. let us consider the effect of a small time and and spacially dependent perturbation to the static potential

$$V'(x,t) = \underbrace{V(x)}_{\text{static}} + \underbrace{U(x,t)}_{\text{perturbation.}}$$

The solution for the non-perturbed wave function of the schroedinger equation

$$\frac{-\hbar^2}{2M}\frac{\partial^2}{\partial x^2}\Psi_n + V\Psi_n = -i\hbar\frac{\partial}{\partial t}\Psi_n = E_n\Psi_n.$$

are characterised by the energy quantum number E_n

$$\Psi_n(x,t) = e^{-iE_n t/\hbar}\,\Psi_n(x)$$

These are a complete and orthonormal set of functions so we can always expand the solution of the wave function to the perturbed wave functions in terms of these non-perturbed wave functions.

$$\therefore \quad \Psi'(x,t) = \sum_n a_n(t) \, \Psi_n(x,t)$$

clearly the coefficients a_n of this expansion can also be time dependent

<u>Lets find $a_n(t)$:</u>

Lets substitute the equation above into the perturbed wave equation.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi'}{\partial x^2} + \left(V(x) + U(x,t)\right)\Psi' - i\hbar\frac{\partial \Psi'}{\partial t} = 0 .$$

$$\Rightarrow \sum_n a_n(t) \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi_n}{\partial x^2} + V\Psi_n - i\hbar\frac{\partial \Psi_n}{\partial t} \right]}_{=0}$$

$$+ \sum_n a_n(t) U(x,t) \Psi_n - i\hbar \sum_n \frac{d a_n(t)}{dt} \Psi_n = 0$$

$$\boxed{\sum_n a_n(t) V(x,t) \Psi_n = i\hbar \sum_n \dot{a}_n(t) \Psi_n}$$

We can use the orthonormal properties of the Ψ_n to project out a specific value (m) of $a_m(t)$ from the l.h.s.

$$\int_{-\infty}^{\infty} \psi_m^* \sum_n a_n(t)\, v(x,t)\, \psi_n \, dx$$

$$= i\hbar \int_{-\infty}^{\infty} \psi_m^* \sum_n \dot{a}(t)\, \Psi_n \, dx$$

remembering $\Psi_n(x,t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$

separating the time and space parts

$$\sum_n a_n(t)\, e^{-i\frac{(E_n - E_m)t}{\hbar}} \int_{-\infty}^{\infty} \psi_m\, U(x,t)\, \psi \, dx$$

$$= i\hbar \sum \dot{a}_n(t)\, e^{-i(E_n - E_m)t/\hbar} \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx$$

$$\frac{d\, a_m(t)}{dt} = \frac{-i}{\hbar} \sum_n a_n(t)\, e^{-i(E_n - E_m)t/\hbar} \int_{-\infty}^{\infty} \psi_m^* U(x,t) \psi_n \, dx$$

$$\boxed{V_{mn} \equiv \int_{-\infty}^{\infty} \psi_m^* \, v(x,t)\, \psi_n \, dx}$$

is called the MATRIX ELEMENT

$$\boxed{\dot{a}_m(t) = \frac{-i}{\hbar} \sum a_n(t)\, v_{mn}\, e^{\frac{-i(E_n - E_m)t}{\hbar}}}$$

If for all $t < 0$

$u(x, t) = 0$ ψ will be in an eigenstate of the unperturbed potential say ψ_k.

Thus at $t = 0$.

$$a_n(t) = 1 \qquad n = k$$
$$= 0 \qquad n \neq k.$$

At small times for small values of $u(x, t)$

$$a_n(t) \ll 1 \qquad n \neq k.$$
$$\simeq 1 \qquad n = k.$$

Thus the series can be approximated by just the k^{th} term.

$$\frac{d a_m(t)}{dt} \simeq \frac{-i}{\hbar}\, a_k(t)\, e^{-i(E_k - E_m)t/\hbar}\, v_{mk}$$

for the solution of $a_m(t)$ $m = k$.

$$\frac{d\,a_k(t)}{dt} \simeq \frac{-i}{\hbar}\, a_k(t)\, V_{kk}.$$

$$\therefore \quad \frac{d\,a_k(t)}{a_k(t)} \simeq \frac{-i}{\hbar} V_{kk}\, dt.$$

$$\boxed{a_k(t) \simeq e^{-i V_{kk} t/\hbar}}$$

but remember V_{kk} is just the energy expectation value $V_{kk} = \Delta E$ due to the perturbation.

Thus that term in the original expansion

$$\psi'(x,t) = \sum_n a_n(t)\, \Psi_n(x,t)$$

becomes.

$$e^{-i\,\Delta E t/\hbar}\, \psi_k(x)\, e^{-i E_k t/\hbar}.$$

$$= \psi_k(x)\, e^{-i(E_k + \Delta E)t/\hbar}.$$

Thus in this approximation the original term stays the same but the energy changes from $E_k \to E_k + \Delta E$.

$m \neq k$

$$\frac{d\,a_m(t)}{dt} \simeq \frac{-i}{\hbar}\, e^{-i(E_k - E_m)t/\hbar}\, V_{km}$$

$$\Big[a_m(t)\Big]_0^{t'} \simeq \left[\frac{V_{mk}}{E_k - E_m}\, e^{-i(E_k - E_m)t\,\cancel{/\hbar}}\right]_0^{t'}$$

since $a_m(0) = 0 \quad (t = 0)$

$$\boxed{a_m(t) \simeq \frac{V_{mk}}{E_k - E_m}\left[e^{i(E_k - E_m)t/\hbar} - 1\right]}$$

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Thus writing out the full wave equation

$$\psi(x,t) \simeq e^{-i(E_k + V_{kk})t/\hbar}\,\psi_k(x)$$

$$+ \sum_{\substack{m \\ m \neq k}} \underbrace{\frac{V_{mk}}{E_k - E_m}\left[e^{-i(E_k - E_m)t/\hbar} - 1\right]}_{a_m(t)} \psi_m(x)\, e^{-iE_m t/\hbar}$$

Note: $\left(e^{i\alpha} - 1\right)^* \left(e^{i\alpha} - 1\right) = \left(e^{-i\alpha} - 1\right)\left(e^{i\alpha} - 1\right)$

$$= \left(1 - e^{i\alpha} + e^{-i\alpha} + 1\right) = 2\left(1 - \cos\alpha\right)$$

$$= 4\sin^2(\alpha/2)$$

(N.B. $1 - \cos\alpha = \cos^2\alpha/2 + \sin^2\alpha/2 - \cos 2(\alpha/2)$

$(\cos\alpha+\beta = \cos\alpha\cos\beta - \sin\alpha\sin\beta)$

$= \cos^2\alpha/2 + \sin^2\alpha/2 - \cos^2\alpha/2 + \sin^2\alpha/2)$.

$= 2\sin^2\alpha/2$).

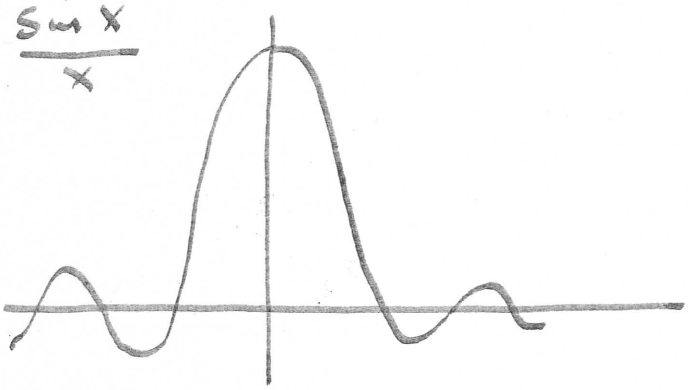
Thus

$$\boxed{\alpha_m^*(t)\, a_m(t) \simeq \frac{V_{mk}^* V_{mk}}{\hbar^2} \frac{\sin^2 (E_m - E_k)t/2\hbar}{\left(\frac{E_m - E_k}{2\hbar}\right)^2}}$$

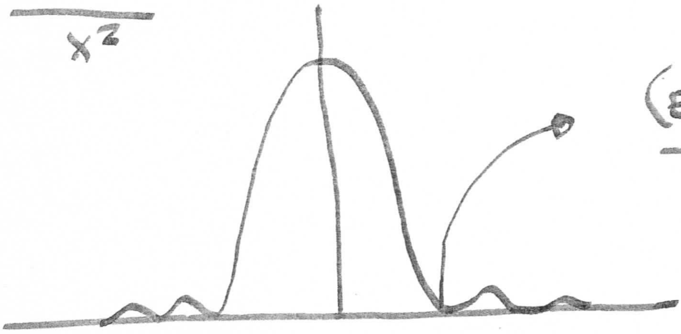
For fixed t the second term on the right hand side is proportional to $\sin^2 xt/x^2$

where
$$x = (E_m - E_k)/2\hbar$$

$\dfrac{\sin x}{x}$

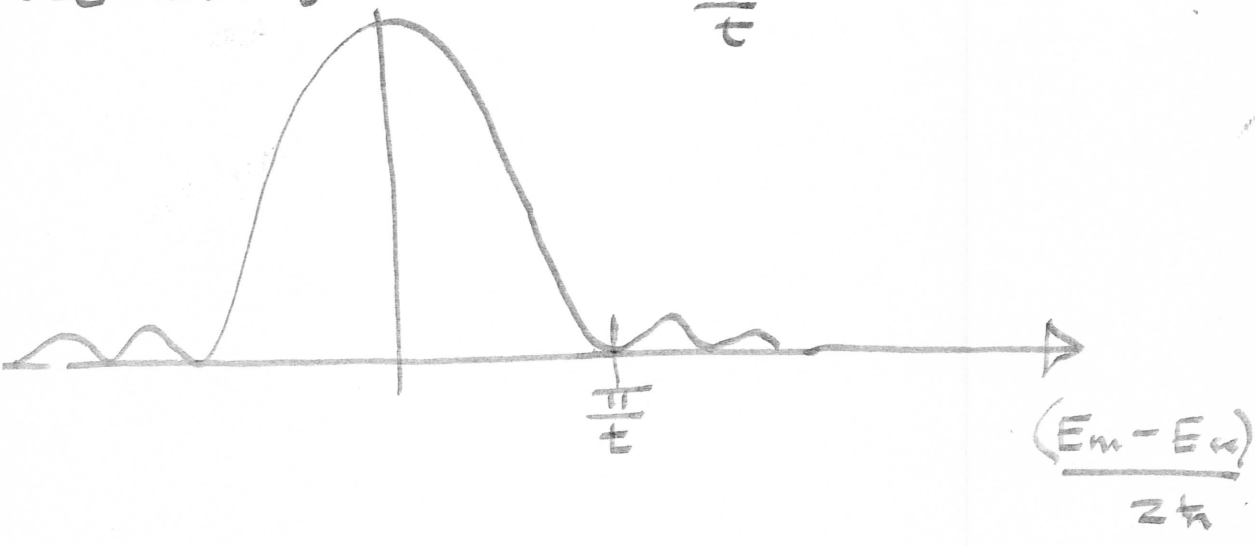


$\dfrac{\sin^2 x}{x^2}$



$$\frac{(E_m - E_k)t}{2\hbar} = \pi$$

If we now plot it as a function of $\dfrac{(E_m - E_k)}{2\hbar}$ the first zero is at $\dfrac{\pi}{t}$



Thus roughly since $\frac{E_m - E_k}{2\hbar} = \frac{\Delta E}{2\hbar}$

$$\frac{\Delta E}{2\hbar} \sim \pi/t$$

$$\Delta E \sim 2\hbar\pi/t.$$

but $t = \Delta t$ from 0.

$$\boxed{\Delta E \Delta t \sim 2\pi\hbar.}$$

Heisenberg's Uncertainty Principle.

The <u>Transition Probability</u> P_K (due to the perturbation) is simply the probability that the final state is not ψ_K (the original state).

Thus.

$$P_K \equiv \sum_{n \neq K} a_n^*(t)\, a_n(t)$$

since $\psi' = a_K \psi_K + \sum_n a_n \psi_n$

$$\int_{-\infty}^{\infty} \psi_m'^* \psi_m \, dx = a_K^* \int \psi_K^2 \, dx + \sum_{mn} a_m^* a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx$$

$$= |a_K|^2 + \sum_{mn} a_m^*(t)\, a_n(t)\, \delta_{mn}$$

$$= |a_K|^2 + \sum_m a_m^*(t)\, a_m(t).$$

Convert this into a summation over states then Energy.

$$P_K \simeq \int_{-\infty}^{\infty} a_n^*(t)\, a_n(t)\, dN_n.$$

$$\simeq \int_{-\infty}^{\infty} a_n^*(t)\, a_n(t) \left(\frac{dN_n}{dE_n}\right) dE_n.$$

$\left(\frac{dN_n}{dE_n}\right) = \rho_n$ "The density of states".

but

$$a_n^*(t)\, a_n(t) \simeq \frac{V_{mk}^* V_{mk}}{\hbar} \frac{\sin^2 \frac{(E_m - E_k)t}{2\hbar}}{\left(\frac{E_m - E_k}{2\hbar}\right)^2}$$

$$\therefore \quad P_k \simeq \hbar^{-2} \int_{-\infty}^{\infty} \frac{V_{mk}^* V_{nk}}{\hbar} \rho_n \frac{\sin^2 \frac{(E_m - E_n)t}{2\hbar}}{\left(\frac{E_m - E_k}{2\hbar}\right)^2} \, dE_n .$$

Thus if ρ_n is assumed to be only very slowly varying over the energy range which is contributing significantly to the states to which the perturbation can move its original state Ψ_k.

$$P_k \simeq \frac{V_{mk}^* V_{mk}}{\hbar^2} \rho_n \int_{-\infty}^{\infty} \frac{\sin^2 \frac{(E_m - E_k)t}{2\hbar}}{\left(\frac{E_m - E_k}{2\hbar}\right)^{2t}} \, dE_n .$$

change the variable to $z = (E_m - E_k)t / 2\hbar$.

$$\therefore \quad \frac{dz}{dE_m} = t/2\hbar .$$

$$P_k = \frac{V_{mk}^* V_{nk}}{\hbar^2} \rho t \int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} \, dz$$

Using a Contour Integral we can show

$$\int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2}\, dz = 2\pi .$$

$$\therefore \quad P_K \simeq \frac{2\pi}{\hbar} V_{mK}^{*} V_{mK} \rho_n t .$$

$\therefore$ Rate of transition

$$R_K = \frac{P_K}{t}$$

$$\boxed{R_K = \frac{2\pi}{\hbar} V_{mK}^{*} V_{mK} \rho_n}$$

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Thus we can see the central importance of the matrix element in the calculation of rates of transition in perturbation theory.

Cauchys Theorem.

$$\oint_c f(z)\,dz = 0.$$

Theorem of residues

$$\oint_c \frac{f(z)}{z - z_0}\,dz = 2\pi i\, f(z_0)$$

$$f^{(n)}(z_0) = \frac{n!}{2\pi i} \oint \frac{f(z)}{(z-z_0)^{n+1}}\,dz.$$