Approximation method

Time independent

- Assume that the Hamiltonian is a sum of two terms,

$$H = H_0 + \lambda H_1$$

- Let {|α>} be a complete set of eigenstates of the unperturbed Hamiltonian H_0 with energy eigenvalues E_α

$$H_0|\alpha\rangle = E_\alpha|\alpha\rangle$$

- The eigenstates {|*a*>} and eigenvalues {E_a} of the complete Hamiltonian *H*

$$H|a\rangle = E_a|a\rangle$$

Non-degenerate case

- unperturbed results

$$|a\rangle \simeq |\alpha\rangle \qquad\qquad E_a \simeq E_\alpha$$

- perturbed states

$$|a\rangle = c_\alpha |\alpha\rangle + \sum_{\beta \neq \alpha} d_\beta |\beta\rangle$$

$$|c_\alpha|^2 + \sum_{\beta \neq \alpha} |d_\beta|^2 = 1$$

- Perturbation theory evaluates the eigenvalues E_a, and the coefficients c_α and d_β , as power series in λ

- To find E_a $\quad \langle\alpha|(H - E_a)|a\rangle = 0$

$$
\begin{aligned}
\langle\alpha|(H - E_a)|a\rangle &= \langle\alpha|(H_0 + \lambda H_1 - E_a)|a\rangle \\
&= c_\alpha \langle\alpha|(H_0 - E_a + \lambda H_1)|\alpha\rangle + \sum_{\beta\neq\alpha} d_\beta \langle\alpha|(H_0 - E_a + \lambda H_1)|\beta\rangle \\
&= \lambda c_\alpha \langle\alpha|H_1|\alpha\rangle + c_\alpha (E_\alpha - E_a) + \sum_{\beta\neq\alpha} \lambda d_\beta \langle\alpha|H_1|\beta\rangle \\
&= 0
\end{aligned}
$$

- *d* is on the order of λ, and *c* is on the order of $1+O(\lambda^2)$

$$
\begin{aligned}
E_a &= E_\alpha + \lambda\langle\alpha|H_1|\alpha\rangle + \frac{\lambda}{c_\alpha}\sum_{\beta\neq\alpha} d_\beta \langle\alpha|H_1|\beta\rangle \\
&= E_\alpha + \lambda\langle\alpha|H_1|\alpha\rangle + O(\lambda^2)
\end{aligned}
$$

- To find *d*

$$\langle \gamma | (H - E_a) | a \rangle = 0 \qquad\qquad \gamma \neq \alpha$$

$$\begin{aligned}
\langle \gamma | (H - E_a) | a \rangle &= \langle \gamma | (H_0 + \lambda H_1 - E_a) | a \rangle \\
&= c_\alpha \langle \gamma | (H_0 - E_a + \lambda H_1) | \alpha \rangle + \sum_{\beta \neq \alpha} d_\beta \langle \gamma | (H_0 - E_a + \lambda H_1) | \beta \rangle \\
&= \lambda c_\alpha \langle \gamma | H_1 | \alpha \rangle + d_\gamma (E_\gamma - E_a) + \sum_{\beta \neq \alpha} \lambda d_\beta \langle \gamma | H_1 | \beta \rangle \\
&= 0
\end{aligned}$$

- *d* is on the order of λ, and *c* is on the order of $1+O(\lambda^2)$

$$d_\gamma = c_\alpha \lambda \frac{\langle \gamma | H_1 | \alpha \rangle}{E_a - E_\gamma} + O(\lambda^2) = \lambda \frac{\langle \gamma | H_1 | \alpha \rangle}{E_a - E_\gamma} + O(\lambda^2)$$

- To leading order E_a can be replaced by the unperturbed eigenvalue E_α. Hence

$$|a\rangle = |\alpha\rangle + \sum_{\beta \neq \alpha} |\beta\rangle \frac{\lambda \langle \beta | H_1 | \alpha \rangle}{E_\alpha - E_\beta} + O(\lambda^2)$$

- This formula requires that for all β

$$\left| \frac{\lambda \langle \beta | H_1 | \alpha \rangle}{E_\alpha - E_\beta} \right| \ll 1$$

- If the off-diagonal matrix elements of H_1 do not grow as the energy difference $|E_\alpha - E_\beta|$ increases, the more "distant" a state is from the state of interest the smaller its influence will be.

- Consider the second order correction in E_a

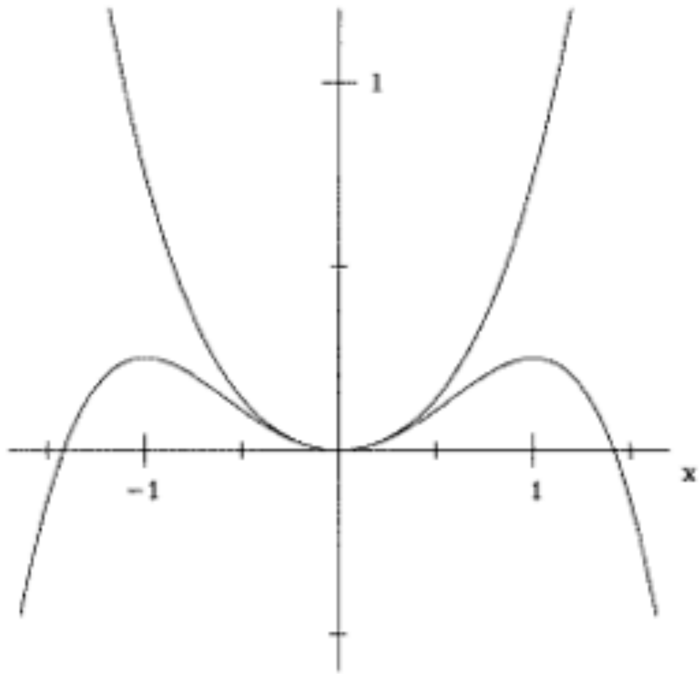
$$E_a = E_\alpha + \lambda\langle\alpha|H_1|\alpha\rangle + \frac{\lambda}{c_\alpha}\sum_{\beta\neq\alpha} d_\beta\langle\alpha|H_1|\beta\rangle$$

$$= E_\alpha + \lambda\langle\alpha|H_1|\alpha\rangle + \lambda^2\sum_{\beta\neq\alpha}\frac{\left|\langle\alpha|H_1|\beta\rangle\right|^2}{E_\alpha - E_\beta} + O\left(\lambda^3\right)$$

- The leading contribution to the energy shift is the expectation value of the perturbation in the unperturbed state. The second-order term involves the other unperturbed states, and in many situations this is the leading correction because the 1st order value vanishes by symmetry.

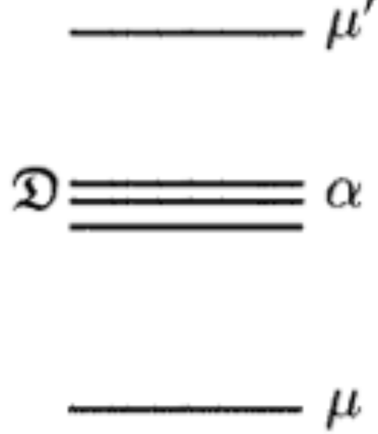
The validity of the perturbation expansion

- The anharmonic oscillator



Degenerate-State case

- the perturbation produces large effects on unperturbed states that have nearby neighbors
- Consider the spectrum of H_0, which contains a degenerate or nearly degenerate subspace *D*



- Within D, no constraint is put on the magnitude of matrix elements. The problem comes from

$$\left|\lambda\langle\beta|H_1|\alpha\rangle\right| \ll \left|E_\alpha - E_\beta\right|$$

- In view of these characteristics of the unperturbed spectrum, the unperturbed state is amended to

$$|a\rangle = \sum_\alpha c_\alpha|\alpha\rangle + \sum_\mu d_\mu|\mu\rangle$$

- Now *c* are on the order O(1) and *d* are on the order O(λ)

- Starting from the equation $\left(H - E_a\right)\left|a\right\rangle = 0$
- Project it to a state |β> in D $\left|\beta\right\rangle \neq \left|\alpha\right\rangle$

$$
\begin{aligned}
\left\langle\beta\right|\left(H - E_a\right)\left|a\right\rangle &= \left\langle\beta\right|\left(H_0 + \lambda H_1 - E_a\right)\left|a\right\rangle \\
&= \sum_\alpha c_\alpha \left\langle\beta\right|\left(H_0 - E_a + \lambda H_1\right)\left|\alpha\right\rangle + \sum_\mu d_\mu \left\langle\beta\right|\left(H_0 - E_a + \lambda H_1\right)\left|\mu\right\rangle \\
&= c_\beta\left(E_\beta - E_a\right) + \lambda\sum_\alpha c_\alpha \left\langle\beta\right|H_1\left|\alpha\right\rangle + \lambda\sum_\mu d_\mu \left\langle\beta\right|H_1\left|\mu\right\rangle \\
&= 0
\end{aligned}
$$

- Project it to a state |ν> outside D

$$
\begin{aligned}
\left\langle\nu\right|\left(H - E_a\right)\left|a\right\rangle &= \left\langle\nu\right|\left(H_0 + \lambda H_1 - E_a\right)\left|a\right\rangle \\
&= \sum_\alpha c_\alpha \left\langle\nu\right|\left(H_0 - E_a + \lambda H_1\right)\left|\alpha\right\rangle + \sum_\mu d_\mu \left\langle\nu\right|\left(H_0 - E_a + \lambda H_1\right)\left|\mu\right\rangle \\
&= \lambda\sum_\alpha c_\alpha \left\langle\nu\right|H_1\left|\alpha\right\rangle + d_\nu\left(E_\nu - E_a\right) + \lambda\sum_\mu d_\mu \left\langle\beta\right|H_1\left|\mu\right\rangle \\
&= 0
\end{aligned}
$$

- Consider equation for |ν> first

$$\lambda \sum_\alpha c_\alpha \langle \nu | H_1 | \alpha \rangle + d_\nu \left(E_\nu - E_a \right) + \lambda \sum_\mu d_\mu \langle \beta | H_1 | \mu \rangle = 0$$

- In D, energy are similar and can be chosen as an average energy E_D

$$d_\nu = \lambda \sum_\alpha c_\alpha \frac{\langle \nu | H_1 | \alpha \rangle}{E_a - E_\nu} + O\left(\lambda^2\right)$$

$$= \frac{\lambda}{E_D - E_\nu} \sum_\alpha c_\alpha \langle \nu | H_1 | \alpha \rangle + O\left(\lambda^2\right)$$

- Put into the equation for |β>

$$c_\beta \left(E_\beta - E_a \right) + \lambda \sum_\alpha c_\alpha \langle \beta | H_1 | \alpha \rangle + \lambda \sum_\mu d_\mu \langle \beta | H_1 | \mu \rangle = 0$$

$$c_\beta \left(E_\beta - E_a \right) + \sum_\alpha c_\alpha \left[\lambda \langle \beta | H_1 | \alpha \rangle + \lambda^2 \sum_\mu \frac{\langle \beta | H_1 | \mu \rangle \langle \mu | H_1 | \alpha \rangle}{E_D - E_\nu} \right] + O\left(\lambda^3\right) = 0$$

$$c_\beta\left(E_\beta - E_a\right) + \sum_\alpha c_\alpha \left[\lambda\langle\beta|H_1|\alpha\rangle + \lambda^2 \sum_\mu \frac{\langle\beta|H_1|\mu\rangle\langle\mu|H_1|\alpha\rangle}{E_D - E_\nu}\right] = 0$$

- This is an eigenvalue problem

$$-c_\beta \eta_\beta + \sum_\alpha c_\alpha \left(H_{\text{eff}}\right)_{\alpha\beta} = 0$$

$$\langle\beta|H_{\text{eff}}|\alpha\rangle = \lambda\langle\beta|H_1|\alpha\rangle + \lambda^2 \sum_\mu \frac{\langle\beta|H_1|\mu\rangle\langle\mu|H_1|\alpha\rangle}{E_D - E_\nu}$$

- Use the projection operator

$$P = \sum_\alpha |\alpha\rangle\langle\alpha|$$

$$H_{\text{eff}} = \lambda P H_1 P + \lambda^2 P H_1 \frac{1-P}{E - H_0} H_1 P$$

Example: 3-level system

$$H = \begin{pmatrix} 0 & 0 & \lambda M \\ 0 & 0 & \lambda M \\ \lambda M & \lambda M & \Delta \end{pmatrix} \qquad H_1 = M \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

$$P = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$H_{\text{eff}} = \lambda P H_1 P + \lambda^2 P H_1 \frac{1 - P}{E - H_0} H_1 P$$

$$P H_1 P = M \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = 0$$

$$PH_1 \frac{1-P}{E_D - H_0} H_1 P = M^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1/\Delta \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$= -\frac{M^2}{\Delta} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 1 & 0 \end{pmatrix}$$

$$= -\frac{M^2}{\Delta} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$H_{eff} = -\frac{M^2}{\Delta} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$E_A = 0 \qquad \left| E_A \right\rangle = \left(\left|1\right\rangle - \left|2\right\rangle \right) / \sqrt{2}$$

$$E_S = -2M^2/\Delta \qquad \left| E_S \right\rangle = \left(\left|1\right\rangle + \left|2\right\rangle \right) / \sqrt{2}$$

Time dependent

- The Hamiltonian of the system is

$$H = H_0 + V(t)$$

- where V(t), called the perturbation, may be time-dependent
- The state of interest, $|\Psi_i(t)\rangle$, is a solution of the complete Schrodinger equation

$$i\hbar \frac{\partial}{\partial t}\left|\Psi_i(t)\right\rangle = \left[H_0 + V(t)\right]\left|\Psi_i(t)\right\rangle$$

- This solution is to evolve out of a solution $|\Phi_i(t)\rangle$ of the unperturbed Schrodinger equation,

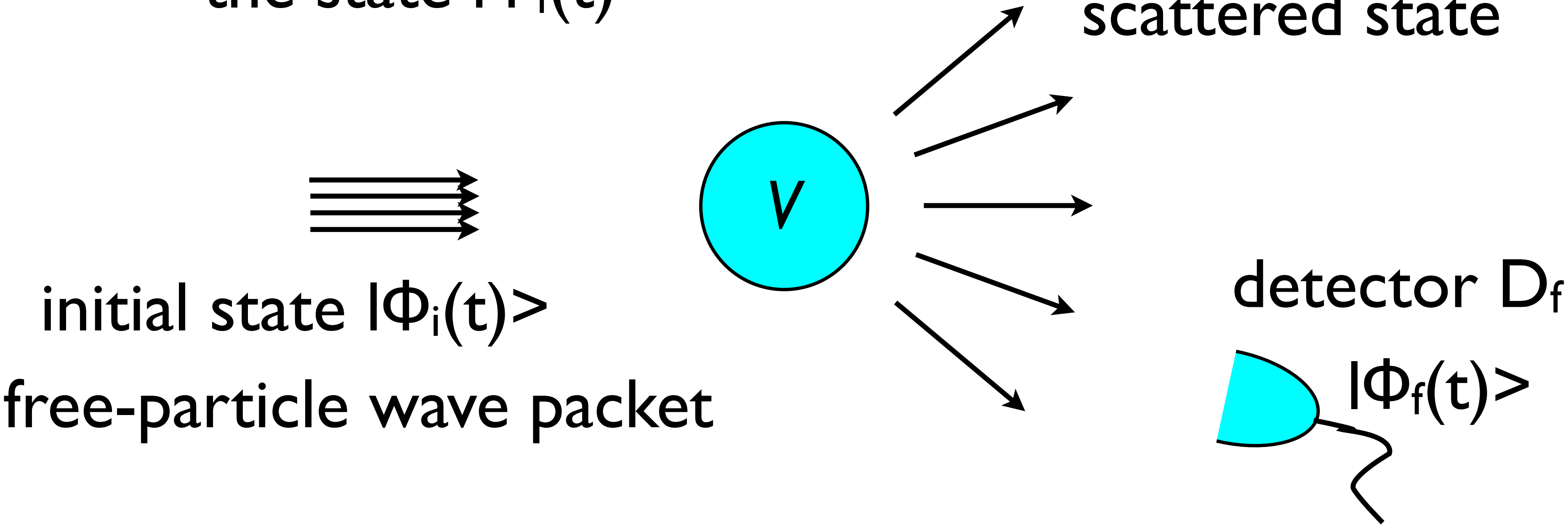
$$\left|\Psi_i(t)\right\rangle \to \left|\Phi_i(t)\right\rangle \quad \text{when} \quad t \to -\infty$$

- where $|\Phi_i(t)\rangle$ is a solution of

$$i\hbar \frac{\partial}{\partial t}\left|\Phi_i(t)\right\rangle = H_0\left|\Phi_i(t)\right\rangle$$

- The first type of problem is one where $V(t)$ is explicitly time-dependent. It is "turned on," at $t = 0$, and the initial state $|\Phi_i(t)>$ is a stationary state of H_0.
- For $t > 0$ we wish to know the probability for the system to be in some other stationary state $|\Phi_f(t)>$ of H_0.
- example : an atom in its ground state which is subjected to an applied electromagnetic field.

- The second example : the collision of a particle with a time-independent potential V of finite range.
- a distant detector D_f which, in effect, asks for the probability that the state has evolved into the state $|\Phi_f(t)>$



- This transition probability is

$$P_{i\to f}(t) = \left|\langle \Phi_f(t) | \Psi_i(t) \rangle\right|^2$$

- P_{if} is closely related to such observable quantities as scattering cross sections, but to make this connection important details remain to be settled.

- the term transition amplitude can be introduced

$$A_{i\to f}(t) = \langle \Phi_f(t) | \Psi_i(t) \rangle$$

- lowest-order time-dependent perturbation

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right)\left|\Psi_i(t)\right\rangle = V(t)\left|\Psi_i(t)\right\rangle \simeq V(t)\left|\Phi_i(t)\right\rangle$$

- To solve this equation, consider first a similar ordinary differential equation

$$\left(i\frac{d}{dt} - C\right)\psi(t) = s(t)$$

- The solution with initial condition

$\psi(t) = \phi(t) \quad \text{when} \quad t \to -\infty$

$s(t) \to 0 \quad \text{as} \quad t \to -\infty$ sufficiently rapidly.

$$\psi(t) = \phi(t) - i\int_{-\infty}^{t} e^{-iC(t-t')} s(t')dt'$$

- because H_0 commutes with itself

$$\left|\Psi_i(t)\right\rangle = \left|\Phi_i(t)\right\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} e^{-iH_0(t-t')/\hbar} V(t')\left|\Phi_i(t')\right\rangle dt'$$

- The transition amplitude

$$A_{i\to f}(t) = \left\langle \Phi_f(t) \middle| \Phi_i(t) \right\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} \left\langle \Phi_f(t) \right| e^{-iH_0(t-t')/\hbar} V(t') \left| \Phi_i(t') \right\rangle dt'$$

- Consider an atom exposed to a uniform time-dependent electric field $E(t)$, in which case the perturbation $V(t)$ is $-E(t)d$, where d is the operator that corresponds to the component of the atom's electric dipole moment parallel to E.
- this problem has the form $V(t)=f(\mathrm{t})Q$ where $f(t)$ is a numerical function and Q some observable of the system.

- the initial and final states are eigenstates of H_0,

$$\left|\Phi_{i,f}(t)\right\rangle = e^{-iE_{i,f}t/\hbar}\left|\Phi_{i,f}\right\rangle$$

- The transition probability

$$P_{i\to f}(t) = \left|\left\langle\Phi_f(t)\middle|\Psi_i(t)\right\rangle\right|^2 = \frac{1}{\hbar^2}\left|\int_{-\infty}^{t}\left\langle\Phi_f(t)\right|e^{-iH_0(t-t')/\hbar}V(t')\left|\Phi_i(t')\right\rangle dt'\right|^2$$

$$= \frac{1}{\hbar^2}\left|\int_{-\infty}^{t}dt' e^{iE_f t/\hbar}e^{-iE_i t'/\hbar}e^{-iE_f(t-t')/\hbar}f(t')\left\langle\Phi_f\right|Q\left|\Phi_i\right\rangle\right|^2$$

$$= \frac{1}{\hbar^2}\left|\left\langle\Phi_f\right|Q\left|\Phi_i\right\rangle\right|^2\left|\int_{-\infty}^{t}dt' e^{i(E_f-E_i)t'/\hbar}f(t')\right|^2$$

$$= \frac{1}{\hbar^2}\left|\left\langle\Phi_f\right|Q\left|\Phi_i\right\rangle\right|^2\left|F(\omega_{fi},t)\right|^2$$

- Consider a periodic perturbation $f(t) = \sin\nu t$ that turns on at $t = 0$,

$$F(\omega,t) = \int_0^t dt' e^{i\omega t'} \sin\nu t' = \frac{1}{2i}\int_0^t dt' \left[e^{i(\omega+\nu)t'} - e^{i(\omega-\nu)t'} \right]$$

$$= \frac{1}{2}\frac{e^{i(\omega-\nu)t}-1}{\omega-\nu} - \frac{1}{2}\frac{e^{i(\omega+\nu)t}-1}{\omega+\nu} = i\frac{e^{i(\omega-\nu)t/2}\sin\frac{\omega-\nu}{2}t}{\omega-\nu} - i\frac{e^{i(\omega+\nu)t/2}\sin\frac{\omega+\nu}{2}t}{\omega+\nu}$$

- the perturbation is resonant, i.e., has a frequency ν that is close to one of the excitation frequencies ω_{fi}.

$$\left|F(\omega,t)\right|^2 \simeq \left| i \frac{e^{i(\omega-\nu)t/2}\sin\frac{\omega-\nu}{2}t}{\omega-\nu} \right|^2 + 2\,\mathrm{Re}\left(e^{i(\omega-\nu)t/2}e^{-i(\omega+\nu)t/2}\right)\frac{\sin\frac{\omega-\nu}{2}t}{\omega-\nu}\frac{\sin\frac{\omega+\nu}{2}t}{\omega+\nu}$$

$$= \frac{\sin^2\frac{\omega-\nu}{2}t}{(\omega-\nu)^2} + 2\cos\omega t\sin\omega t\frac{\sin\frac{\omega-\nu}{2}t}{\omega(\omega-\nu)}$$

- At resonance,

$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\langle \Phi_f | Q | \Phi_i \rangle\right|^2 \frac{\sin^2 \frac{\omega - \nu}{2} t}{(\omega - \nu)^2}$$

- Assume the more realistic form of perturbation

$$V(t) = Q e^{-t/\tau} \sin \nu t$$

$$P_{i\to f}(t) = \frac{1}{4\hbar^2}\left|\langle \Phi_f | Q | \Phi_i \rangle\right|^2 \frac{1}{(\omega - \nu)^2 + 1/\tau^2} \qquad t \gg \tau$$

The Golden Rule

- Consider the second type of problem
- Unless the scattering is in the exact forward direction, only the second term in contributes,

$$A_{i\to f}(t) = -\frac{i}{\hbar}\langle\Phi_f|V|\Phi_i\rangle\int_{-\infty}^{t} e^{-i\omega_{fi}t'/\hbar}\,dt'$$

- first assume that for some very large but finite time - T in the past,

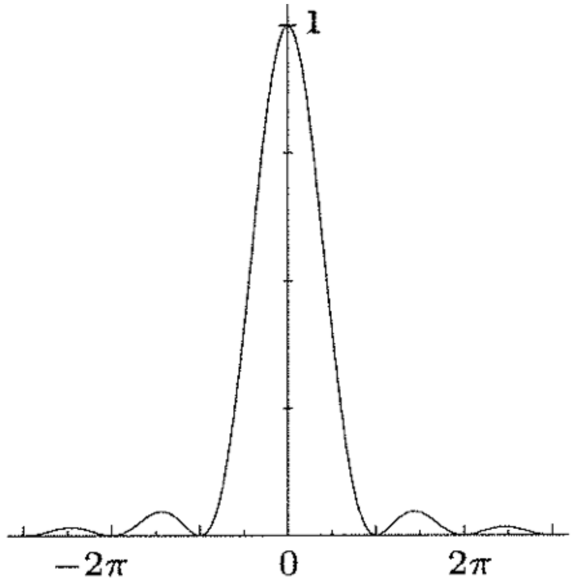
$$A_{i\to f}(T) = -\frac{i}{\hbar}\langle\Phi_f|V|\Phi_i\rangle\int_{-T}^{T} e^{-i\omega_{fi}t'/\hbar}\,dt'$$

- the transition probability

$$P_{i\to f}\left(T\right)=\frac{4}{\hbar^2}\left|\left\langle \Phi_f\left|V\right|\Phi_i\right\rangle\right|^2\frac{\sin^2\omega_{fi}T}{\omega_{fi}^2}$$

- As $\omega T\to\infty$ height ~T², width ~T⁻¹

$$\int\frac{\sin^2\omega T}{\omega^2}d\omega=\pi T$$



- When $T\to\infty$ $\omega\to 0$

$$\lim_{T\to\infty}\frac{\sin^2\omega T}{\omega^2}=\pi T\delta\left(\omega\right)$$

- The transition probability

$$P_{i\to f}\left(T\to\infty\right)=\frac{4\pi}{\hbar}\left|\left\langle\Phi_f\left|V\right|\Phi_i\right\rangle\right|^2 T\delta\left(E_f-E_i\right)$$

- the steady transition rate

$$\frac{dP_{i\to f}}{dt}=\frac{2\pi}{\hbar}\left|\left\langle\Phi_f\left|V\right|\Phi_i\right\rangle\right|^2 \delta\left(E_f-E_i\right)$$

- We call this formula Golden rule