Chapter 11

Time Dependent Perturbation Theory

Time dependent Schrödinger Equation

$$\underline{H}\left|\Psi\right\rangle = i\hbar\frac{\partial\left|\Psi\right\rangle}{\partial t}$$

Take

$$\underline{H} = \underset{\text{time independent}}{\underline{H}^0} + \underset{\substack{\text{time dependent}\\ \text{will treat as time dependent perturbation}}}{\underline{H}'}$$

time independent

time dependent
will treat as time dependent perturbation

$$\underline{H}^0\left|\Psi^0\right\rangle = i\hbar\frac{\partial\left|\Psi^0\right\rangle}{\partial t}$$

$\underline{H}^0$ time independent - solutions are

$$\left|\Psi_n^0(q,t)\right\rangle = \left|\psi_n^0(q)\right\rangle e^{-iE_n t/\hbar}$$

$\left|\psi_n^0(q)\right\rangle$ **complete set of time independent orthonormal eigenfunctions of $\underline{H}^0$.**

$e^{-iE_n t/\hbar}$ **time dependent phase factors**

To solve

$$\underline{H}\left|\Psi\right\rangle = i\hbar\frac{\partial\left|\Psi\right\rangle}{\partial t} \qquad \underline{H} = \underline{H}^{0} + \underline{H}^{\prime}$$

Expand

$$\left|\Psi(q,t)\right\rangle = \sum_{n} c_{n}(t)\left|\Psi_{n}^{0}(q,t)\right\rangle$$

$$\underline{H} = \underline{H}^{0} + \underline{H}^{\prime}$$

used derivative product rule

Substitute expansion

$$\sum_{n} c_{n}\underline{H}^{0}\left|\Psi_{n}^{0}\right\rangle + \sum_{n} c_{n}\underline{H}^{\prime}\left|\Psi_{n}^{0}\right\rangle = i\hbar\sum_{n}\dot{c}_{n}\left|\Psi_{n}^{0}\right\rangle + i\hbar\sum_{n} c_{n}\frac{\partial\left|\Psi_{n}^{0}\right\rangle}{\partial t}$$

These terms equal. Unperturbed problem.
They cancel.

Canceling gives

$$\sum_{n} c_{n}\underline{H}^{\prime}\left|\Psi_{n}^{0}\right\rangle = i\hbar\sum_{n}\dot{c}_{n}\left|\Psi_{n}^{0}\right\rangle$$

Have $\sum_n c_n \underline{H}' \left|\Psi_n^0\right\rangle = i\hbar \sum_n \dot{c}_n \left|\Psi_n^0\right\rangle$

Left multiply by

$$\left\langle\Psi_m^0\right|$$

$$\sum_n c_n \left\langle\Psi_m^0\right|\underline{H}'\left|\Psi_n^0\right\rangle = i\hbar\dot{c}_m$$

Eigenkets of time independent Hamiltonian are orthonormal.

Therefore,

$$\dot{c}_m = -\frac{i}{\hbar}\sum_n c_n \left\langle\Psi_m^0\right|\underline{H}'\left|\Psi_n^0\right\rangle$$

Exact to this point.

Set of coupled differential equations.

In Time Dependent Two State Problem (Chapter 8)

two coupled equations

$$\left\langle\Psi_m^0\right|\underline{H}'\left|\Psi_n^0\right\rangle = \gamma$$

Approximations

Usually start in a particular state $\left|\Psi_{\ell}^{0}\right\rangle$

Dealing with weak perturbation.
System is not greatly changed by perturbation.

Assume:

$c_{\ell}^{*} c_{\ell} \cong 1$ Time independent.

The probability of being in the initial state $\left|\Psi_{\ell}^{0}\right\rangle$ never changes significantly.

The probability of being in any other state never gets much bigger than zero.

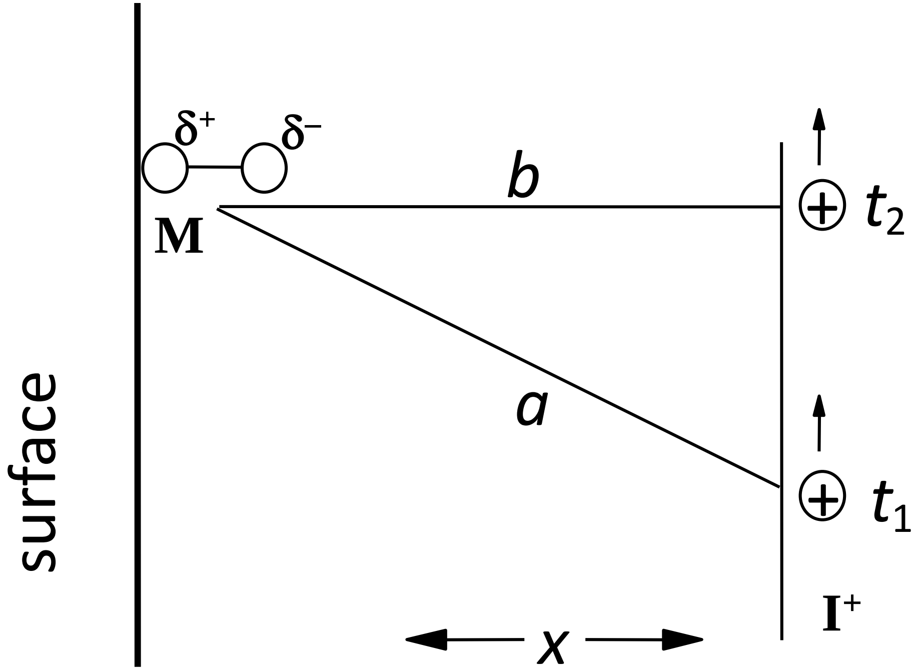
With these assumptions:

$$\dot{c}_m = -\frac{i}{\hbar}\left\langle \Psi_m^0(q,t) \middle| \underline{H}' \middle| \Psi_\ell^0(q,t) \right\rangle$$

No longer coupled equations

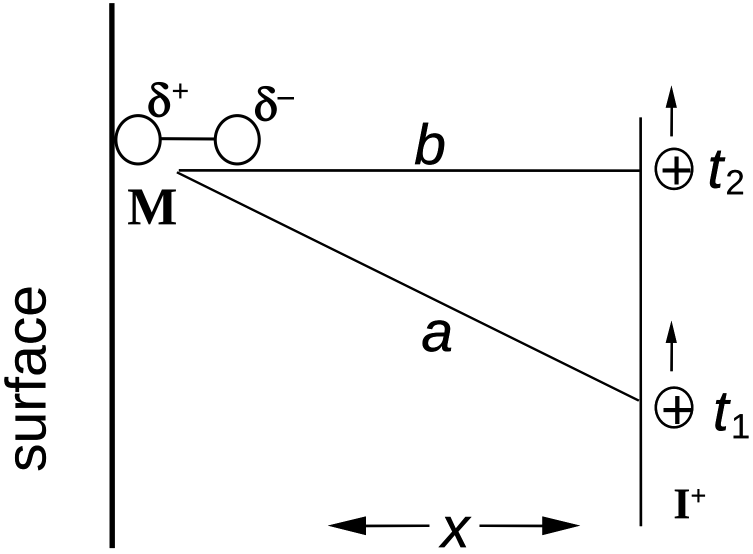
Excellent approximation in many common experiments.
UV/Vis spectrometer, FT-IR spectrometer, Fluorometer

Grazing Collision of an Ion and a Dipolar Molecule - Vibrational Excitation



M - molecule with dipole moment

1. **Molecule, M, weakly phys. absorbed on surface.**
   Not translating or rotating. **(Example, CO on Cu surface.)**
2. **Dipole moment points out of wall.**
   Interaction with wall very weak; can be ignored.
3. **When not interacting with ion – vibrations harmonic.**
4. **M has δ^- side to right.**



Positively charged ion, I^+, flies by M.

I^+ starts infinitely far away at $t = -\infty$

Passes by M at $t = 0$.

I^+ infinitely far away at $t = +\infty$

At any time, *t*,

I^+ to M distance = *a*.

$$a = \sqrt{b^2 + (Vt)^2}$$

b = distance of closest approach (called impact parameter).
V = Ion velocity.

Ion flies by molecule ⟶

Coulomb interaction perturbs vibrational states of M.

Model for Interaction

δ^{-} **end of M always closer to** I^{+} **than positive end of M.**

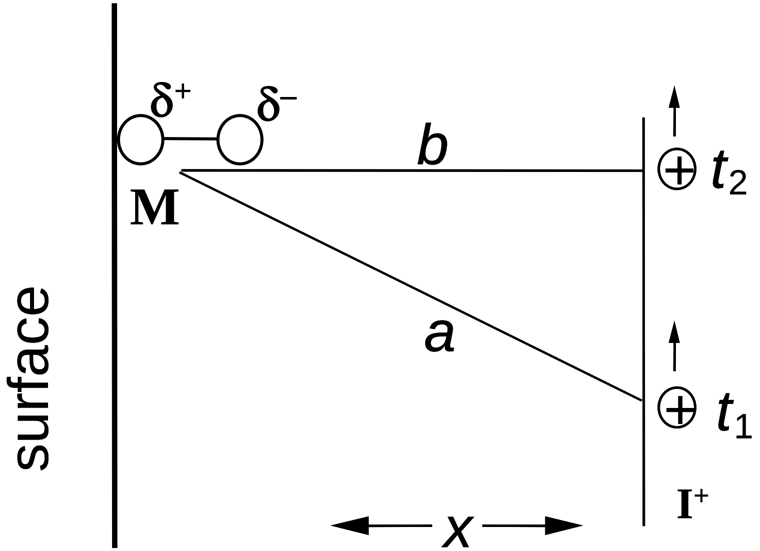
Bond stretch ⟶ **energy lowered**

δ^{-} **closer to** I^{+}**.**

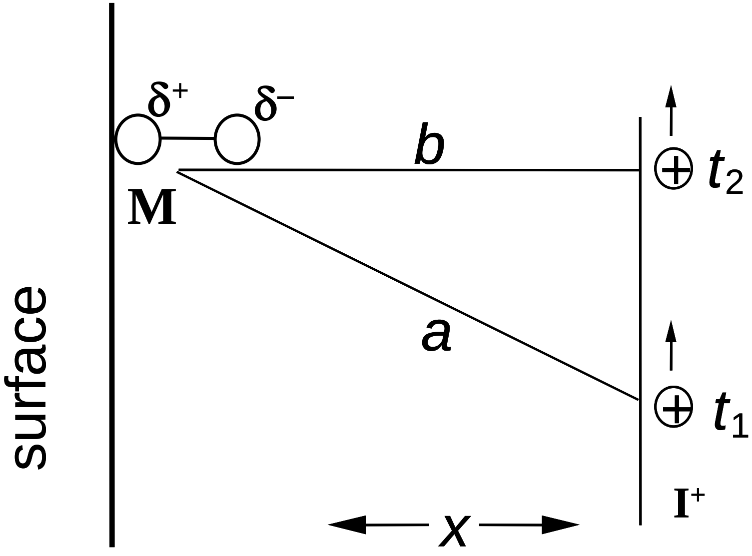
δ^{+} **further from** I^{+}**.**

Bond contracted ⟶ **opposite**

Energy raised.



Qualitatively Correct Model



Ion causes cubic perturbation of molecule.

→ Correct symmetry, odd.

Strength of Interaction →

Inversely proportional to square of separation.

Coulomb Interaction of charged particle and dipole.

Neglects orientational factor -

but most effect when ion close - angle small.

Strength of interaction time dependent

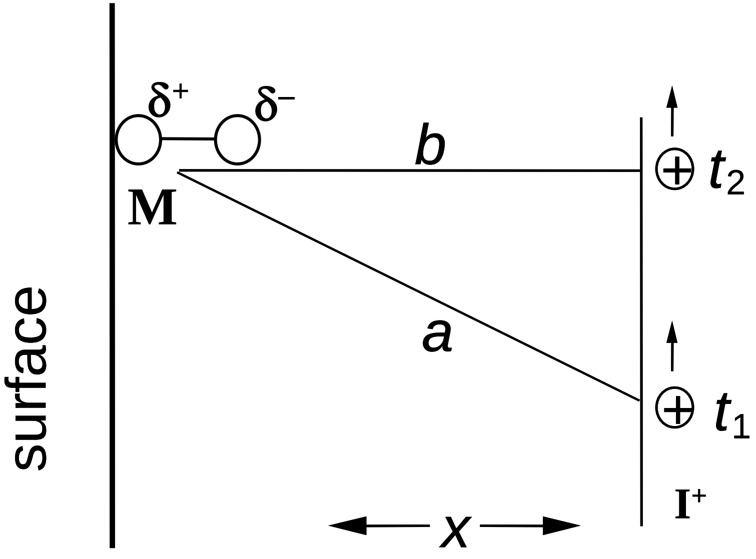
because distance is time dependent.

Time Dependent Perturbation

$$\underline{H}'(t) = A(t)\underline{x}^3$$

$$= \frac{q}{\left[b^2 + (Vt)^2\right]}\underline{x}^3$$

M - I$^+$ separation squared. Ion - dipole interaction.



q = a constant (size of dipole, etc.)

$\underline{x}$ = position operator for H.O.

M starts in H.O. state $|0\rangle$.

Want probabilities of finding it in states $|m\rangle$ after I$^+$ flies by.

→ Time Dependent Perturbation Theory

Take perturbation to be small.

Probability of system being in $\left|0\right\rangle \cong 1$.

Probability of system being in $\left|m\right\rangle \simeq 0$.

Therefore,

$$\dot{c}_m = -\frac{i}{\hbar}\left\langle \Psi_m^0 \middle| \underline{H}' \middle| \Psi_\ell^0 \right\rangle$$

Zeroth order time dependent kets.

For this problem

ket $\quad \left|\Psi_\ell^0\right\rangle = \left|0\right\rangle e^{-iE_0 t/\hbar}$

bra $\quad \left\langle\Psi_m^0\right| = \left\langle m\right| e^{iE_m t/\hbar}$

Substituting

ΔE_{m0}

$$\dot{c}_m = \frac{-i}{\hbar}\langle m|\frac{q}{(b^2+(Vt)^2)}\underline{x}^3|0\rangle e^{i(E_m-E_0)t/\hbar}$$

Doesn't depend on H.O. coordinate,
take out of bracket.

$$\dot{c}_m = \frac{-i}{\hbar}\frac{q}{(b^2+(Vt)^2)}\langle m|\underline{x}^3|0\rangle e^{i\Delta E_{m0}t/\hbar}$$

Multiply through by *dt* and integrate.

$$c_m = \frac{-i}{\hbar}q\langle m|\underline{x}^3|0\rangle\int_{-\infty}^{\infty}\frac{e^{i\Delta E_{m0}t/\hbar}}{\left[b^2+(Vt)^2\right]}dt$$

Need to evaluate time independent and time dependent parts.

Time independent part

$$\langle m|\underline{x}^3|0\rangle$$

$$\underline{x}=\left(\frac{\hbar\omega}{2k}\right)^{\frac{1}{2}}\left(\underline{a}+\underline{a}^{+}\right)$$

$$\underline{x}^3=\left(\frac{\hbar\omega}{2k}\right)^{3/2}(\underline{a}+\underline{a}^{+})^3$$

$$(\underline{a}+\underline{a}^{+})^3=\underline{a}^3+\underline{a}^{+}\underline{a}^2+\underline{a}^2\underline{a}^{+}+\underline{a}^{+}\underline{a}\,\underline{a}^{+}+\underline{a}\,\underline{a}^{+}\underline{a}+\underline{a}^{+2}\underline{a}+\underline{a}\,\underline{a}^{+2}+\underline{a}^{+3}$$

Because $\underline{x}^3$ operates on $|0\rangle \Rightarrow \underline{x}^3|0\rangle$.

must have more raising operators than lowering.

Can't lower past $|0\rangle$.

Can't have lowering operator on right. $\underline{a}^{+2}\underline{a}|0\rangle=0$

Only terms in red survive.

Then

$$\langle m|\underline{x}^3|0\rangle=\left(\frac{\hbar\omega}{2k}\right)^{3/2}\left[\langle m|\underline{a}^+\underline{a}\,\underline{a}^+|0\rangle+\langle m|\underline{a}\,\underline{a}^+\underline{a}^+|0\rangle+\langle m|\underline{a}^+\underline{a}^+\underline{a}^+|0\rangle\right]$$

$$=\left(\frac{\hbar\omega}{2k}\right)^{3/2}\left[1\langle m|1\rangle+2\langle m|1\rangle+\sqrt{6}\langle m|3\rangle\right]$$

Therefore,

m must be 1 or 3.

Perturbation will only cause scattering to m = 1 and m = 3 states. Only c_3 and c_1 are non-zero. **(Higher odd powers of $\underline{x}$ included in interaction – population in higher odd energy levels.)**

$$m=1\;\Rightarrow\qquad 3\left(\frac{\hbar\omega}{2k}\right)^{3/2}$$

$$m=3\;\Rightarrow\qquad \sqrt{6}\left(\frac{\hbar\omega}{2k}\right)^{\frac{3}{2}}$$

Time dependent part

$$\int_{-\infty}^{\infty} \frac{e^{i\Delta E_{m0}t/\hbar}}{\left[b^2+(Vt)^2\right]} dt =$$

$$\int_{-\infty}^{\infty} \frac{\cos \Delta E_{m0}t/\hbar}{\left[b^2+(Vt)^2\right]} dt + i \cancel{\int_{-\infty}^{\infty} \frac{\sin \Delta E_{m0}t/\hbar}{\left[b^2+(Vt)^2\right]} dt}$$

Integral of odd function.

Substituting

$$Vt = y \qquad dy = Vdt$$

$$\frac{\Delta E_{m0}t}{\hbar} = \frac{\Delta E_{m0}Vt}{V\hbar} = ay$$

$$\frac{2}{V}\int_{0}^{\infty} \frac{\cos(ay)}{\left[b^2+y^2\right]} dy = \frac{\pi}{Vb} e^{\frac{-\Delta E_{m0}b}{V\hbar}}$$

Putting the pieces together

$$c_1 = -i3\frac{q}{\hbar}\left(\frac{\hbar\omega}{2k}\right)^{\frac{3}{2}}\frac{\pi}{Vb}e^{-\Delta E_{10}b/V\hbar}$$

$$c_3 = -i\sqrt{6}\frac{q}{\hbar}\left(\frac{\hbar\omega}{2k}\right)^{\frac{3}{2}}\frac{\pi}{Vb}e^{-\Delta E_{30}b/V\hbar}$$

Probabilities $c_m^* c_m$

$$P_1 = c_1^* c_1 = 9q^2 \frac{\hbar\omega^3}{8k^3} \frac{\pi^2}{V^2 b^2} e^{-2\omega b/V}$$

using $\Delta E_{10} = \hbar\omega$

$$P_3 = c_3^* c_3 = 6q^2 \frac{\hbar\omega^3}{8k^3} \frac{\pi^2}{V^2 b^2} e^{-6\omega b/V}$$

using $\Delta E_{30} = 3\hbar\omega$

Probabilities are function of velocity.

Lim $V \to 0$ and $V \to \infty$

P_1 and $P_3 \longrightarrow$ go to 0.

Must be maximum in between.

Maximum value of $P_1 = c_1^* c_1$ as function of *V*.

$$\frac{dP_1}{dV} = 9q^2 \frac{\hbar\omega^3}{8k^3}\frac{\pi^2}{b^2}\left[\frac{1}{V^2}e^{-2\omega b/V}\left(2\omega b/V^2\right) + e^{-2\omega b/V}\left(-2/V^3\right)\right] = 0$$

$$\frac{2\omega b}{V^4} - \frac{2}{V^3} = 0$$

$$\frac{\omega b}{V} - 1 = 0$$

frequency of transition times
distance of closest approach (impact parameter)

$$V_1^{\max} = \omega b$$

$$P_1^{\max} = \frac{9\pi^2 q^2 \hbar\omega}{8k^3 b^4} e^{-2}$$

Note dependence on impact parameter.

Similarly

frequency of transition times
distance of closest approach

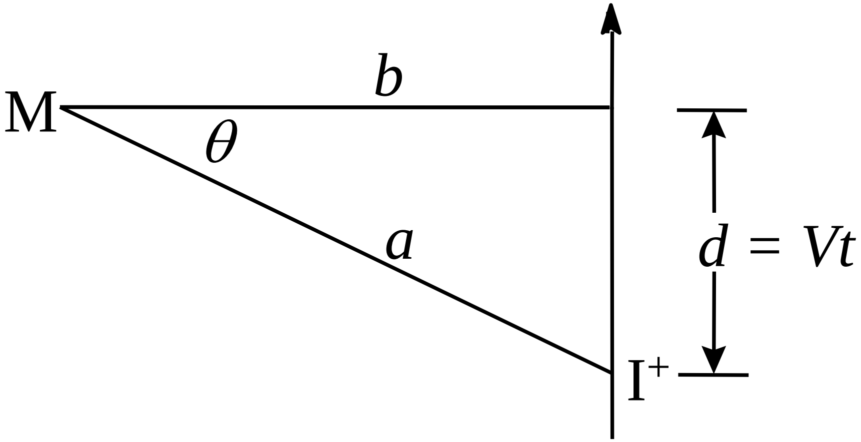
$$V_3^{\max} = 3\omega b$$

$$P_3^{\max} = \frac{2}{3}\frac{\pi^2 q^2 \hbar\omega}{8k^3 b^4} e^{-2}$$

$$P_1^{\max} = \frac{27}{2} P_3^{\max} \qquad V_3^{\max} = 3V_1^{\max}$$

Understanding maximum probabilities as function of *V*.

Calculate angular frequency when ion near molecule.



$$a = \sqrt{b^2 + (Vt)^2} \qquad \sin\theta = \frac{Vt}{\sqrt{b^2 + (Vt)^2}}$$

When ion very close to point of closest approach

$$\sin\theta \cong \theta$$

$$Vt \ll b$$

$$\therefore \quad \theta = \frac{Vt}{b}$$

$$\theta = \frac{Vt}{b}$$

For 0 → 1 transition, velocity for max. prob. is

$$V = \omega b.$$

Then

$$\theta = \frac{\omega bt}{b} = \omega t$$

Angular velocity – change in angle per unit time.

$$\frac{d\theta}{dt} = \omega$$

Angular velocity

$$\frac{d\theta}{dt} = \omega$$

Looks like charged particle moving by M with angular velocity ω.

Produces E-field changing at frequency ω.

On resonance → efficiently induces transition.

For $0 \rightarrow 3$ transition, velocity for max. prob. is

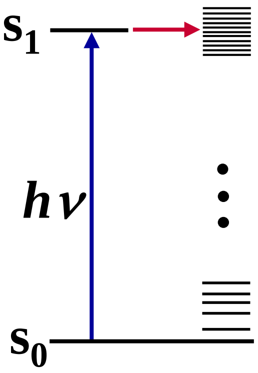
$$V = 3\omega b$$

$$\frac{d\theta}{dt} = 3\omega$$

Again on resonance.

Fermi's Golden Rule

an important result from time dependent perturbation theory

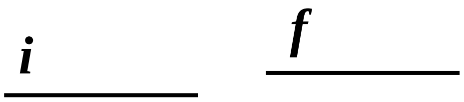


Dense manifold of vibrational states of ground state – S$_0$.
10^{12} to 10^{18} states/cm^{-1}

Radiationless relaxation competes with fluorescence.

Many problems in which an initially prepared state is coupled to a dense manifold of states.

First consider a pair of coupled state.



$\Delta E = E_f - E_i$ **, where *f* = final and *i* = initial.**

$\left|I^0(q,t)\right\rangle$ **and** $\left|F^0(q,t)\right\rangle$ **are eigenstates of the time independent Hamiltonian,** $\underline{H}^0$ **.**
These are eigenstates in the absence of coupling.

From time dependent perturbation theory

$$\dot{C}_F = -\frac{i}{\hbar}\left\langle F^0(q,t)\right|\underline{H}^{'}\left|I^0(q,t)\right\rangle$$

$\underline{H}'$ **is the time dependent piece of the Hamiltonian that couples the eigenstates.**

The time dependence of $\underline{H}'$ is given by

$$\left\langle F^0(q,t)\middle|\underline{H}'\middle|I^0(q,t)\right\rangle = 0 \qquad\qquad t < 0$$

$$\left\langle F^0(q,t)\middle|\underline{H}'\middle|I^0(q,t)\right\rangle = e^{iE_f t/\hbar}\left\langle f^0(q)\middle|\underline{H}'\middle|i^0(q)\right\rangle e^{-iE_i t/\hbar}$$

$$= e^{i(E_f - E_i)t/\hbar} H'_{fi} = e^{i(E_f - E_i)t/\hbar} z \qquad\qquad t \geq 0.$$

The time dependent perturbation is 0 for $t < 0$, and a constant for $t \geq 0$.

The probability of being in the final state is: $\dot{C}_F = -\frac{i}{\hbar}\left\langle F^0(q,t)\middle|\underline{H}'\middle|I^0(q,t)\right\rangle$

$$C_F = -\frac{i\,z}{\hbar}\int_0^t e^{i\Delta E t/\hbar}\,dt \qquad\qquad \Delta E = E_f - E_i$$

$$= -\frac{i\,z}{\hbar}\int_0^t \left[\cos\frac{\Delta E}{\hbar}t + i\sin\frac{\Delta E}{\hbar}t\right]dt$$

$$= -\frac{i\,z}{\hbar}\left[\frac{\hbar}{\Delta E}\sin\frac{\Delta E}{\hbar}t - i\frac{\hbar}{\Delta E}\cos\frac{\Delta E}{\hbar}t\right]\Bigg|_0^t$$

$$= -\frac{i\,z}{\Delta E}\left[\sin\frac{\Delta E}{\hbar}t - i\cos\frac{\Delta E}{\hbar}t + i\right]$$

The probability of finding the system in the final state

$$C_F C_F^* = \frac{|z|^2}{\Delta E^2}\left[\sin^2\left(\frac{\Delta E}{\hbar}t\right) + \cos^2\left(\frac{\Delta E}{\hbar}t\right) + 1 + i\sin\left(\frac{\Delta E}{\hbar}t\right)\cos\left(\frac{\Delta E}{\hbar}t\right)\right.$$
$$- i\sin\left(\frac{\Delta E}{\hbar}t\right)\cos\left(\frac{\Delta E}{\hbar}t\right) - \cos\left(\frac{\Delta E}{\hbar}t\right) - \cos\left(\frac{\Delta E}{\hbar}t\right)$$
$$\left. + i\sin\left(\frac{\Delta E}{\hbar}t\right) - i\sin\left(\frac{\Delta E}{\hbar}t\right)\right]$$

$$C_F C_F^* = \frac{2|z|^2}{\Delta E^2}\left[1 - \cos\frac{\Delta E}{\hbar}t\right]$$

Using

$$1 - \cos x = 2\sin^2(x/2)$$

$$C_F C_F^* = \frac{4|z|^2}{\Delta E^2}\sin^2\left(\frac{\Delta E}{2\hbar}t\right)$$

Probability of being in the final state as a function of t and ΔE. Only good when $C_F C_F^*$ small.

$$C_F C_F^* = \frac{4|z|^2}{\Delta E^2}\sin^2\left(\frac{\Delta E}{2\hbar}t\right)$$

Probability of being in the final state *F*.
Must be small – time dependent perturbation theory

Probability must be small to use time dependent perturbation theory.
Take very short time limit.

$$C_F C_F^* = \frac{|z|^2 t^2}{\hbar^2}$$

$$C_F C_F^* = \frac{2z^2}{\Delta E^2 + 4z^2}\left(1 - \cos\frac{\sqrt{\Delta E^2 + 4z^2}}{\hbar}t\right)$$

Exact solution from time dependent two state problem, Chapter 8

Expand exact solution for short time.

$$\cos x = 1 - \frac{x^2}{2!} + \cdots$$

$$C_F C_F^* = \frac{2z^2}{\Delta E^2 + 4z^2}\left(1 - 1 + \frac{\Delta E^2 + 4z^2}{2\hbar^2}t^2\right) = \frac{z^2 t^2}{\hbar^2}$$

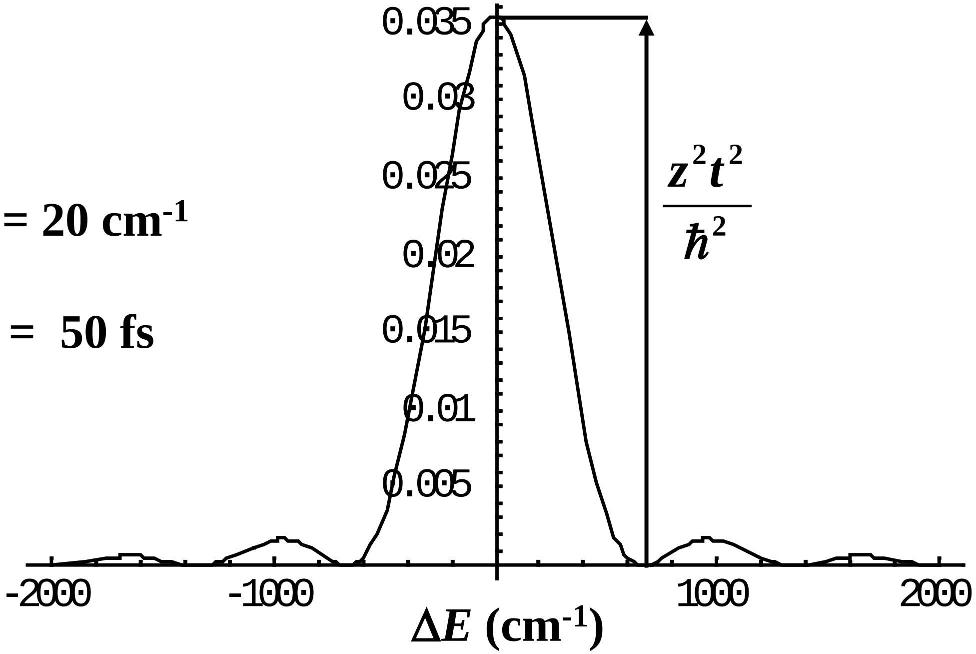
Same at short time.

$$C_F C_F^* = \frac{4|z|^2}{\Delta E^2}\sin^2\left(\frac{\Delta E}{2\hbar}t\right)$$

Square of zeroth order spherical Bessel function.

$z = 20$ cm^{-1}

t = 50 fs



This is a plot of the final probability at a single time with *z* and *t* picked to keep final max probability low as required to use time dependent perturbation theory.

To this point, initial state coupled to a single final state.

To obtain result for initial state coupled to dense manifold of final states, make following assumptions – very good for many physical situations.

1. Most of the transition probability is close to $\Delta E = 0$; ΔE^2 in denominator.
   Therefore, take the density of states, ρ, which is a function of energy, to be constant with the value at $\Delta E = 0$.

$$C_F C_F^* = \frac{4|z|^2}{\Delta E^2} \sin^2\left(\frac{\Delta E}{2\hbar} t\right)$$

2. The coupling bracket

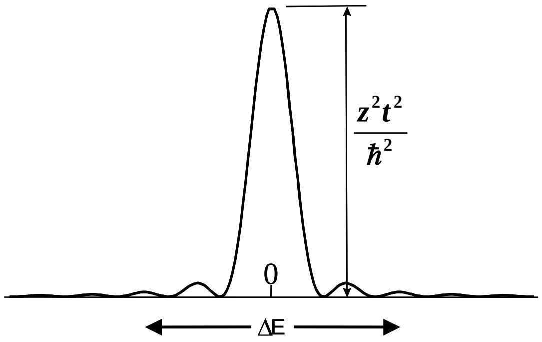
$$\left\langle f^0(q) \middle| \underline{H}' \middle| i^0(q) \right\rangle = H'_{fi} = z$$

can vary with f through the manifold of final states.
Take them all to be equal to z, which is now some average value for the final states couplings to the initial state.

$$P_{fman}(t) = 4|z|^2 \rho \int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{\Delta E\, t}{2\hbar}\right)}{\Delta E^2} d\Delta E$$

Probability of being in the manifold of final states. Area under Bessel function.

$$P_{fman}(t) = 4|z|^2 \rho \int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{\Delta E\, t}{2\hbar}\right)}{\Delta E^2} d\Delta E$$



Let

$$x = \frac{\Delta E\, t}{2\hbar} \text{ and } dx = \frac{t}{2\hbar} d\Delta E$$

Then

$$P_{fman}(t) = \frac{2|z|^2 \rho\, t}{\hbar} \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx$$

Using

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

$$P_{fman}(t) = \frac{2\pi |z|^2 \rho}{\hbar} t$$

$$P_{fman}(t) = \frac{2\pi |z|^2 \rho}{\hbar} t$$

$$P_{fman}(t) = \frac{2\pi\rho}{\hbar} \left| \left\langle f^{0}(q) \middle| \underline{H}^{'} \middle| i^{0}(q) \right\rangle \right|^2 t$$

The transition probability per unit time is

$$k = \frac{2\pi}{\hbar} \rho \left| \left\langle f^{0}(q) \middle| \underline{H}^{'} \middle| i^{0}(q) \right\rangle \right|^2$$

Fermi's Golden Rule

Rate constant for gain in probability in manifold of final states equals rate constant for loss of probability from initial state.

Initial state can decay to zero without violating time dependent perturbation theory approximation because so many states in final manifold that none gain much probability. Need not consider coupling among states in manifold.

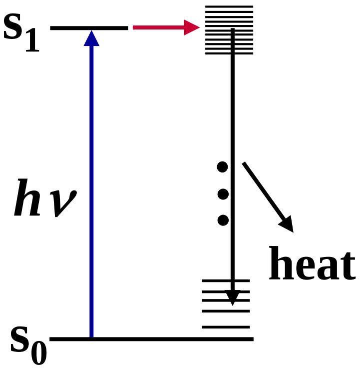
Loss of probability from initial state per unit time a constant, *k*, then

$$\frac{dP_i}{dt} = -kP_i$$

and

$$P_i = e^{-kt}.$$

Probability of being in the initial state (population) decays exponentially.



Nonradiative relaxation contribution to decay of excited state population, k_{nr}, from Fermi's Golden Rule.

Radiative contribution, fluorescence, spontaneous emission, k_r (Chapter 12, Einstein A coefficient).

Fluorescence decay $I(t) = I_0 e^{-(k_r + k_{nr})t} = I_0 e^{-t/\tau}$

$$1/\tau = k_r + k_{nr}$$

τ = fluorescence lifetime