CHMY 564

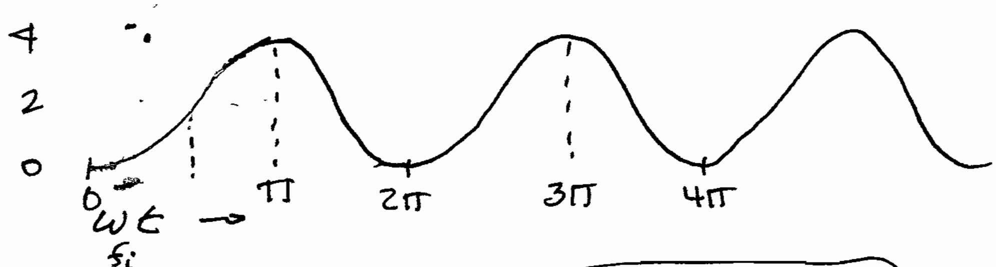
April 4, 2011

Lecture #20: Constant Perturbation (Continued)

$$P^{(1)}_{fi} = \frac{|W_{fi}|^2}{(\hbar\omega_{fi})^2}\left(2 - 2\cos\omega_{fi}t\right)$$

This probability depends on <u>3 factors</u>

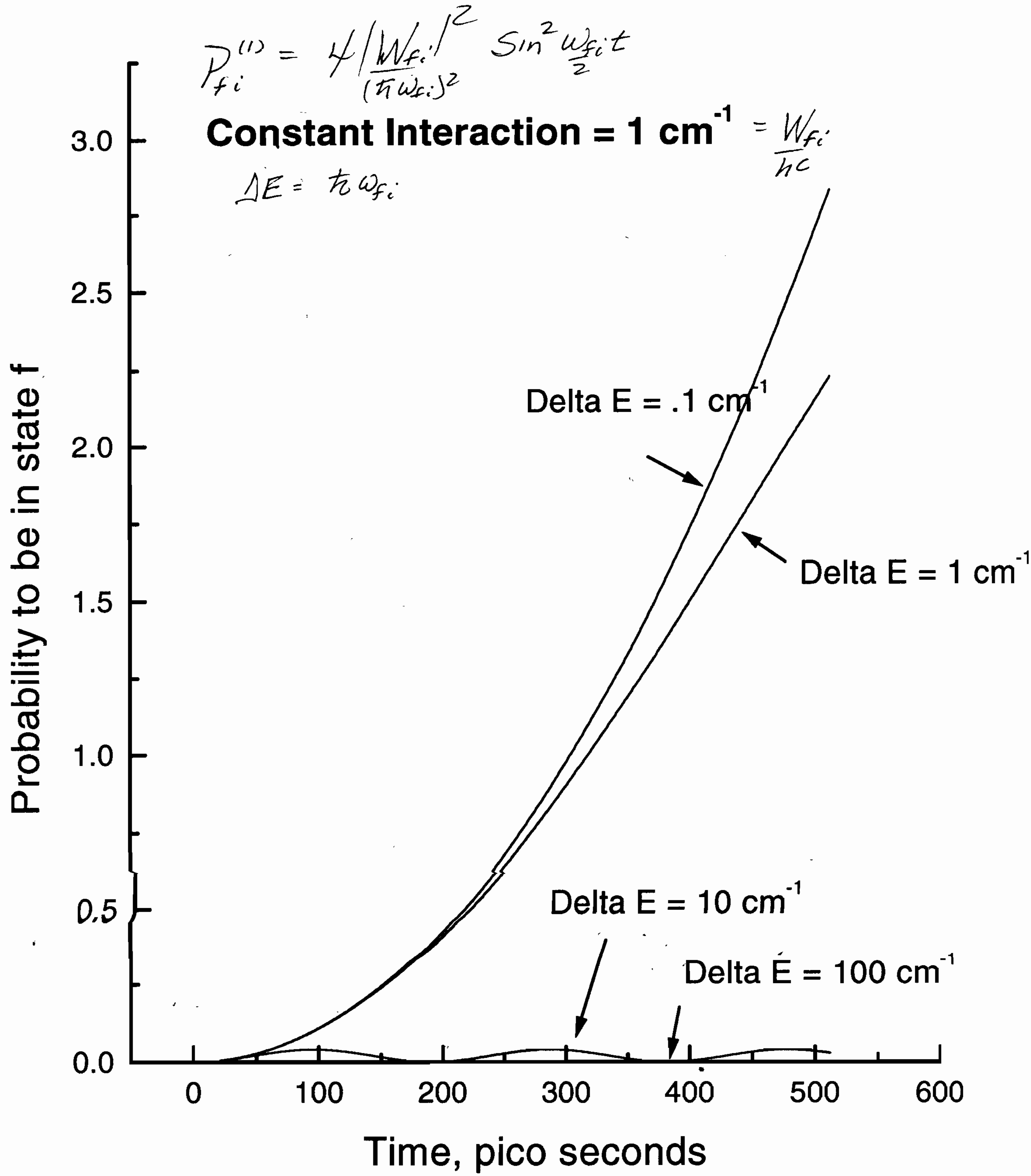
1) square of perturbation matrix element
2) inversely on square of energy difference between the coupled states
3). a term that oscillates at a frequency 1/2 the energy difference

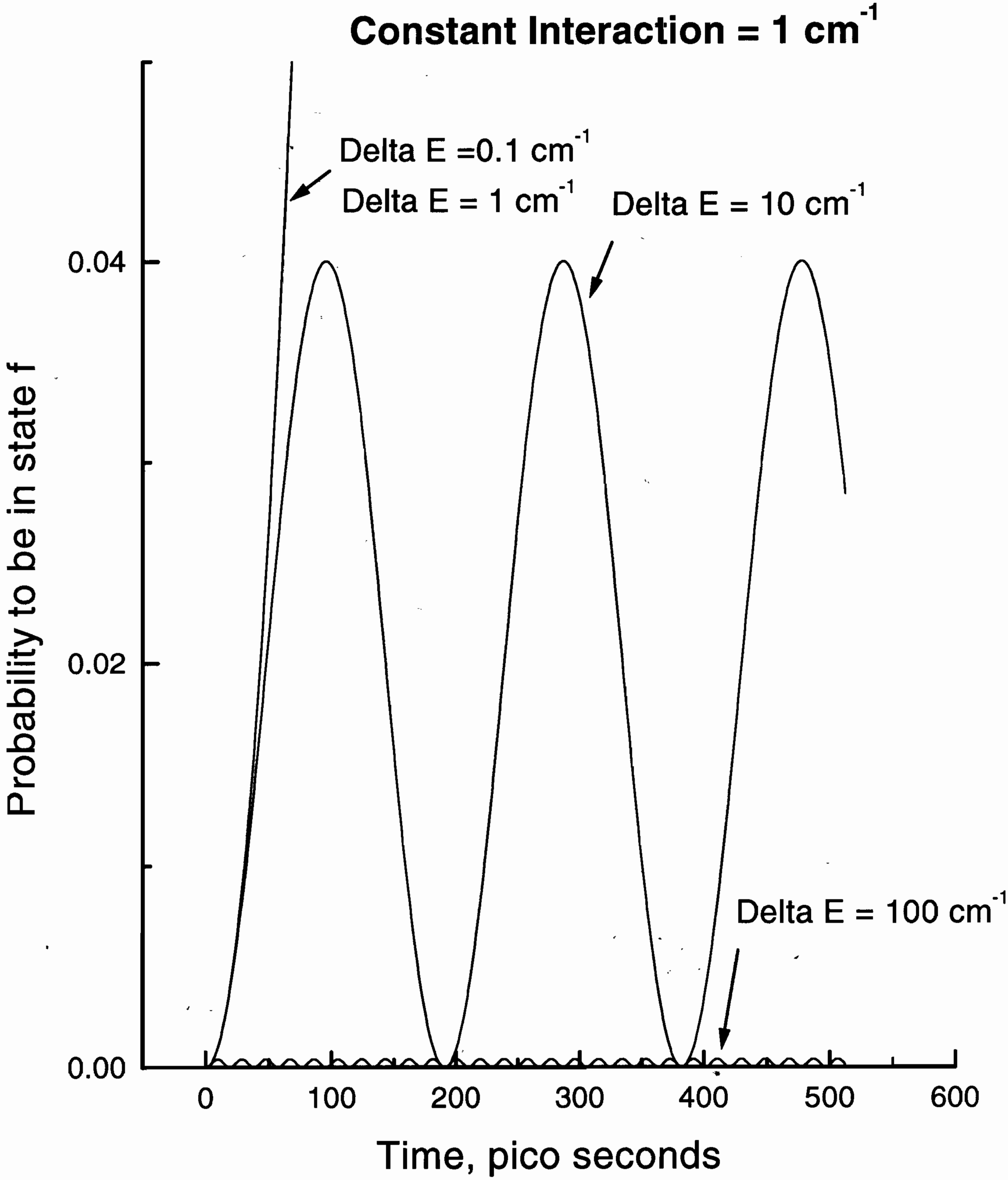


This can be seen to be $4\sin^2\frac{\omega_{fi}}{2}t$

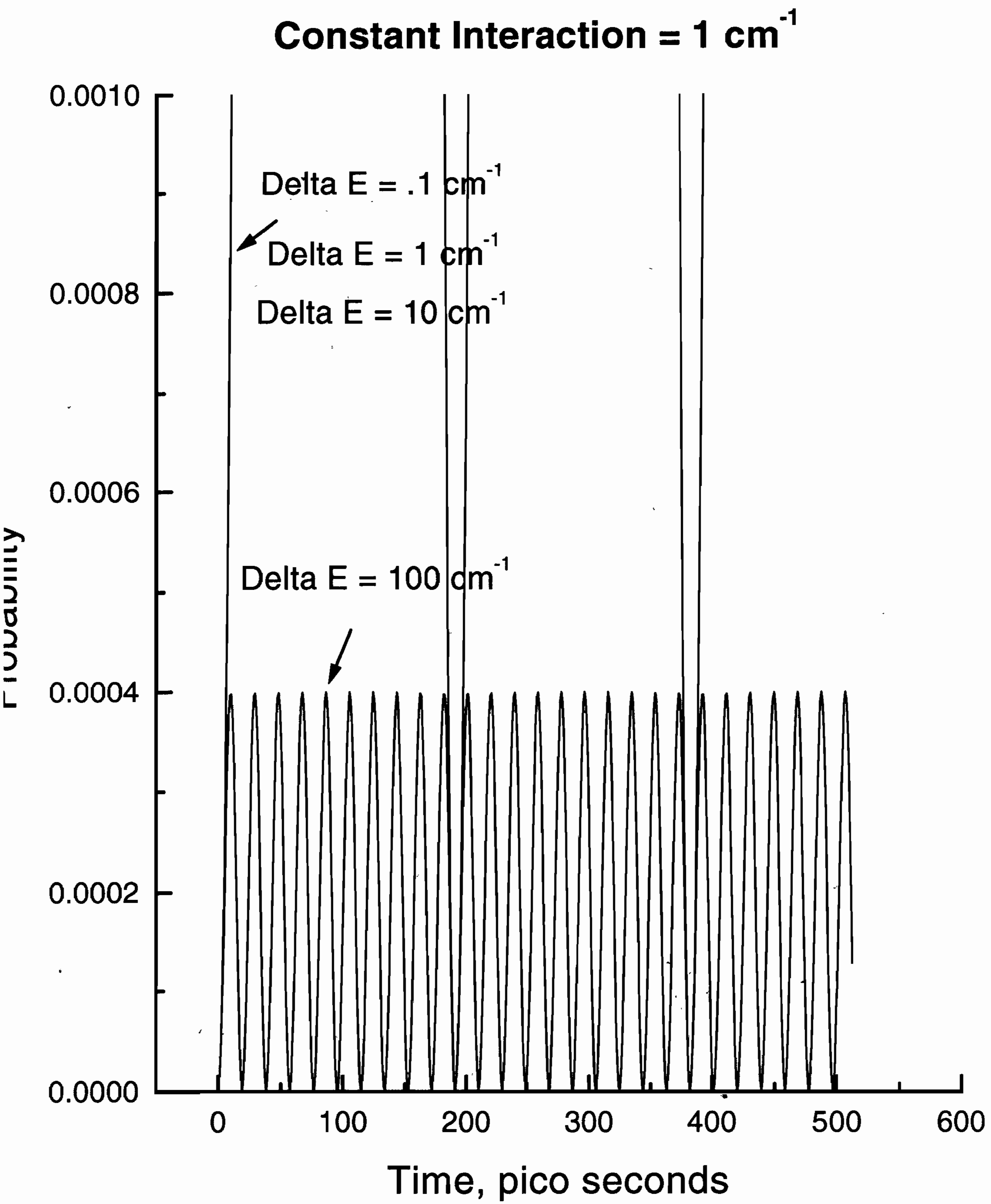
[Note that $\left(\frac{e^{ix/2} - e^{-ix/2}}{2i}\right)^2 = \frac{1}{2} - \frac{1}{2}\left(\frac{e^{ix} + e^{-ix}}{2}\right)$]

$$\boxed{P^{(1)}_{fi} = 4\frac{|W_{fi}|^2}{(\hbar\omega)^2}\sin^2\frac{\omega_{fi}}{2}t}$$


$P_{fi}^{(1)} = 4\frac{|W_{fi}|^2}{(\hbar\omega_{fi})^2}\sin^2\frac{\omega_{fi}t}{2}$
Constant Interaction = 1 cm^{-1} $= \frac{W_{fi}}{hc}$
$\Delta E = \hbar\omega_{fi}$
Delta E = .1 cm^{-1}
Delta E = 1 cm^{-1}
Delta E = 10 cm^{-1}
Delta E = 100 cm^{-1}
Probability to be in state f
Time, pico seconds
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
100
200
300
400
500
600


Constant Interaction = 1 cm-1
Delta E =0.1 cm-1
Delta E = 1 cm-1
Delta E = 10 cm-1
Delta E = 100 cm-1
0.04
0.02
0.00
0
100
200
300
400
500
600
Probability to be in state f
Time, pico seconds

/C



Constant Interaction = 1 cm^{-1}
Delta E = .1 cm^{-1}
Delta E = 1 cm^{-1}
Delta E = 10 cm^{-1}
Delta E = 100 cm^{-1}
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
Probability
0
100
200
300
400
500
600
Time, pico seconds

Limits of Validity for this first order result.

1. <u>Weak coupling</u> $\frac{W_{fi}}{E_f - E_i} \ll 1$

Corresponds to

E_f —— E_f'

E_i —— E_i'

$$\psi_i \cong |i\rangle - \left(\frac{W_{fi}}{E_f - E_i}\right)|f\rangle$$

$$\psi_f \cong |f\rangle + \left(\frac{W_{fi}}{E_f - E_i}\right)|i\rangle$$

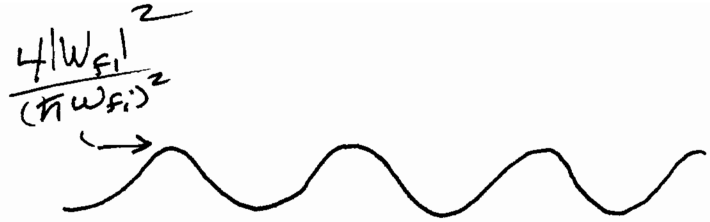
$$E_{\pm} = \frac{E_f + E_i}{2} \pm \sqrt{\left(\frac{E_f - E_i}{2}\right)^2 + W_{fi}^2}$$

The Stationary states are mostly $|i\rangle$ or $|f\rangle$ with small amounts of the other.

e.g. $|i\rangle \cong \psi_i + \left(\frac{W_{fi}}{E_f - E_i}\right)\psi_f$

So that $|i\rangle$ is a mixture of the energy eigenstates of $H_0 + W$ once the perturbation is turned on -- and so $|i\rangle\langle i|$ must oscillate at the frequency given by $\frac{E_+ - E_-}{h} \cong \frac{E_f - E_i}{h}$

In this limit P_{fi} =

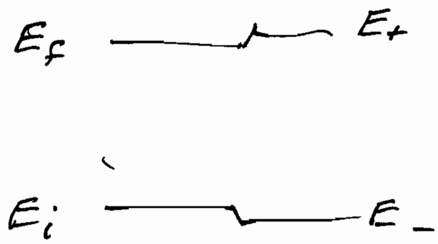


To be reasonably accurate, $P_{fi} \leq 0.01$ because of the assumption that $b_i = 1$ at all times, and $b_f^2 + b_i^2 = 1$

So $\dfrac{4\,|W_{fi}|^2}{(E_f - E_i)^2} \leq .01$

or $\dfrac{|W_{fi}|}{|E_f - E_i|} \leq 0.05$

By second order perturbation theory for the energy:



$E_+ - E_f \cong \dfrac{|W_{fi}|^2}{E_f - E_i}$

The fractional change in energy = $\left|\dfrac{W_{fi}}{E_f - E_i}\right|^2 = \underline{\underline{0.0025}}$

The "quantum beats" have frequency of

$$\boxed{\nu_{beat} \doteq \frac{E_f - E_i}{h}}$$

2. STRONG COUPLING (near resonance case)

$$\frac{|W_{fi}|}{|\Delta E_{fi}|} > 1 \qquad \text{where } \Delta E_{fi} = E_f - E_i$$

a. Deduce time dependence from exact energy eigenvalues of $H_0 + W$

Linear Variation for $E_i = E_f$ gives.

$$E_i = E_f \quad \begin{cases} E_+ = E_i + |W_{fi}| \\ \psi_+ = \left(|f\rangle + \dfrac{W_{fi}}{|W_{fi}|} |i\rangle \right) \dfrac{1}{\sqrt{2}} \\[2ex] E_- = E_i - |W_{fi}| \\ \psi_- = \left(|i\rangle - \dfrac{W_{fi}}{|W_{fi}|} |f\rangle \right) \dfrac{1}{\sqrt{2}} \end{cases}$$

So in terms of ψ_- & ψ_+

$$|i\rangle = \frac{1}{\sqrt{2}} \left(\psi_- + \frac{W_{fi}}{|W_{fi}|} \psi_+ \right)$$

But $\psi_\pm = |\psi_\pm\rangle \, e^{-i(E_i \pm |W|_{fi})t/\hbar}$

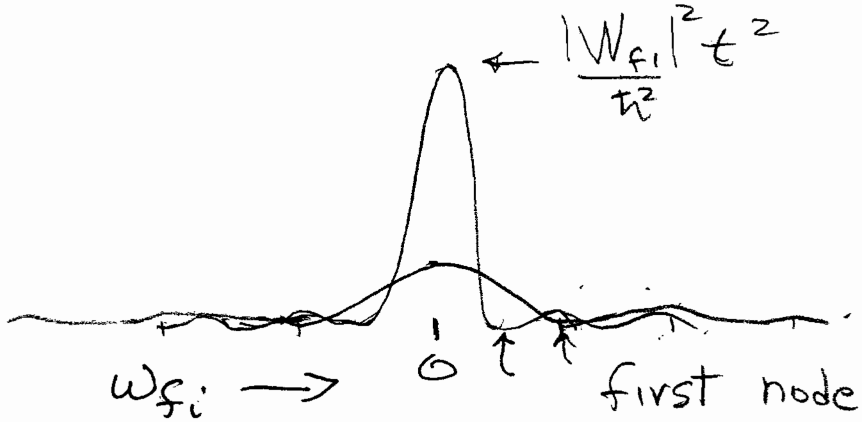
so the density $|i\rangle\langle i|$ will have an oscillating term $\propto e^{\pm \frac{2 W_{fi} t}{\hbar}}$ ← Rabi frequency.

Note that time dependence in this limit depends only on the interaction W_{fi} and no longer on $E_f - E_i$

b. USING THE EARLY TIME VALUES TO DERIVE <u>FERMI'S GOLDEN RULE</u>

As $\omega_{fi} \rightarrow 0$, $\dfrac{\sin^2 \frac{\omega_{fi} t}{2}}{(\omega_{fi}/2)^2} \rightarrow t^2$

Thus, a plot of $P_{fi} = \dfrac{4|W_{fi}|^2}{(\hbar \omega_{fi})^2} \sin^2 \dfrac{\omega_{fi} t}{2}$ against ω_{fi} at different times gives.



first node is when

$\dfrac{\omega_{fi} t}{2} = \pi$ or $\omega_{fi} t = 2\pi$

or $\nu_{fi} t = 1$

or $\bar{\nu}_{fi} t = 1/c$

where $\bar{\nu}_{fi}$ = wavenumber.

Thus, the probability to be in state f at time t increases as t^2 for states i & f truely in resonance, but it is apparent that exact resonance is not required. At very short times there is a large uncertainty in the energy of the final state, but this uncertainty narrows inversely with time. Using the ω_{fi} value such that $\frac{\omega_{fi} t}{2} = \pi$ (i.e. the first node) as a measure of uncertainty, the time - energy uncertainty relation is:

$$\omega_{fi} t = 2\pi \Rightarrow \Delta\omega \Delta t$$

$$\text{or. } \nu_{fi} t = 1 \Rightarrow \Delta\nu \Delta t$$

$$h\nu_{fi} t = h \Rightarrow \Delta E \Delta t$$

and in terms of wavenumbers

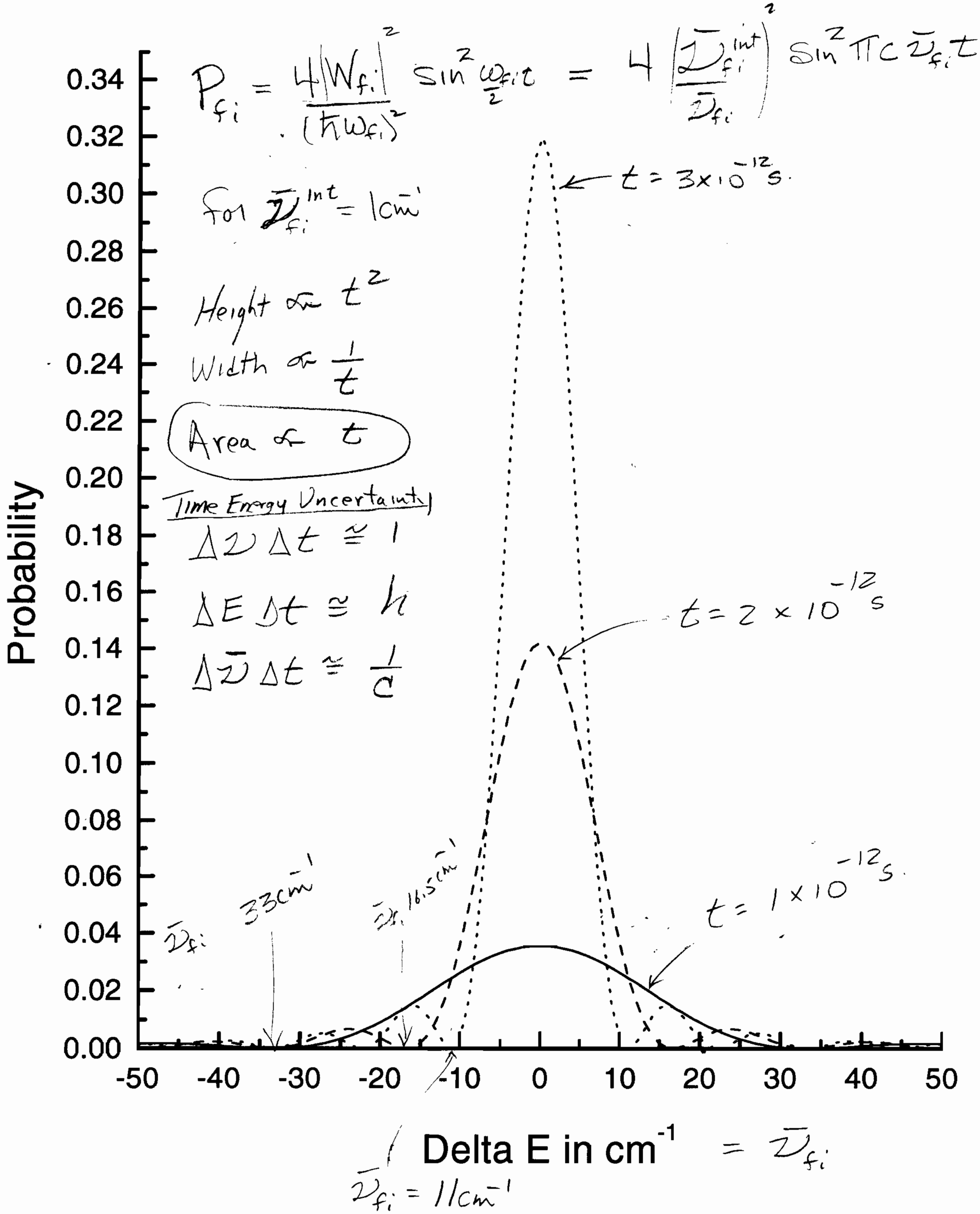
$$\nu_{fi} t = \frac{c}{\lambda_{fi}} t = 1$$

$$\frac{1}{\lambda_{fi}} t = \boxed{\bar{\nu}_{fi} t = \frac{1}{c}} \qquad c = \text{speed of light.}$$

Rewriting P_{fi} in terms of $\bar{\nu}$ so that

$$\frac{W_{fi}}{hc} = \nu_{fi}^{Int} \cdot \frac{\hbar\omega_{fi}}{hc} = \bar{\nu}_{fi} = \frac{\omega_{fi}}{2\pi c}$$

$$\boxed{P_{fi} = 4 \left| \frac{\bar{\nu}_{fi}^{Int}}{\bar{\nu}_{fi}} \right|^2 \sin^2(\pi c \bar{\nu}_{fi} t)}$$


$P_{fi} = \frac{4|W_{fi}|^2}{(\hbar\omega_{fi})^2} \sin^2 \frac{\omega_{fi} t}{2} = 4\left(\frac{\bar{\nu}_{fi}^{int}}{\bar{\nu}_{fi}}\right)^2 \sin^2 \pi c \bar{\nu}_{fi} t$
for $\bar{\nu}_{fi}^{int} = 1 cm^{-1}$
Height $\propto t^2$
Width $\propto \frac{1}{t}$
Area $\propto t$
Time Energy Uncertainty
$\Delta\nu \Delta t \cong 1$
$\Delta E \Delta t \cong h$
$\Delta\bar{\nu} \Delta t \cong \frac{1}{c}$
$t = 3 \times 10^{-12} s$
$t = 2 \times 10^{-12} s$
$t = 1 \times 10^{-12} s$
$\bar{\nu}_{fi}$ 33 cm^{-1}
$\bar{\nu}_{fi}$ 16.5 cm^{-1}
Probability
0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-50
-40
-30
-20
-10
0
10
20
30
40
50
Delta E in cm^{-1} $= \bar{\nu}_{fi}$
$\bar{\nu}_{fi} = 11 cm^{-1}$

The previous page shows plots for P_{fi} vs. $\bar{\nu}_{fi}$ in cm^{-1} when $W_{fi} \equiv \bar{\nu}_{fi}^{int} = 1 cm^{-1}$ for $t = 1, 2,$ and 3 pico seconds (10^{-12} seconds)

Note that $\Delta \bar{\nu}_{fi} \Delta t = \frac{1}{c}\ cm^{-1} s$

$$= \frac{1}{3 \times 10^{10}\ cm\, s^{-1}}$$

$$= \boxed{33\ cm^{-1}\ ps}$$

How do we get around the apparent inapplicability of this first order formula at times such that $P^{(1)}_{fi} > 0.01$?

It turns out that in Nature, exact resonance is a fleeting thing, and in addition, there is often a virtual continuum of final states f. For a macroscopic system, even an extremely weak interaction can create a measurable loss of state $|i\rangle$ because it is happening for so many systems (molecules).

The strategy is to calculate the initial sum of rates from $|i\rangle \to \{|f\rangle\}$, where the set of final states $\{|f\rangle\}$ differ by a small amount of energy and for which all have nearly the same W_{fi}

The "average" $P^{(1)}_{fi}$ to end up in one of states f is proportional to

$$\int_{-\infty}^{+\infty} d\omega_{fi}\, P^{(1)}_{fi}(\omega_{fi}, t) = \boxed{\frac{|W_{fi}|^2}{\hbar^2}\, 2\pi\, t}$$

$$= \int_{-\infty}^{+\infty} d\omega_{fi}\, \frac{|W_{fi}|^2}{\hbar^2}\, \frac{\sin^2 \frac{\omega_{fi} t}{2}}{\left(\frac{\omega_{fi}}{2}\right)^2} \cong \frac{|W_{fi}|^2}{\hbar^2}\frac{2}{t}\, t^2 \int_{-\infty}^{+\infty} d\left(\frac{\omega_{fi} t}{2}\right) \frac{\sin^2 \frac{\omega_{fi} t}{2}}{\left(\frac{\omega_{fi} t}{2}\right)^2}$$

and using from Handbook: $\displaystyle\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx = \pi$

The area under the curves on p. 7 increase linearly with t because their height $\propto t^2$ but width $\propto \frac{1}{t}$

Density of States: Note that the above integral has units of radians $\sec^{-1}$.

It must be multiplied by the number of states per unit ω_{fi} to be a physically meaningful quantity. This is called the density of states $\equiv \rho(\omega_{fi}) = \dfrac{dn_f}{d\omega_f}$

Thus the actual integral (sum) we do is.

$$\bar{P}_T = \int \frac{dn_f}{d\omega_f} d\omega_f \, P_{fi}^{(1)}(\omega_{fi}, t) = \int_{-\infty}^{+\infty} \rho(\omega_f)\, d\omega_f \, P_{fi}(\omega_{fi}, t)$$

It is assumed that $\rho(\omega_f) \cong$ Constant and $W_{fi} \cong$ constant over the range of States of interest. This is a narrow range because P_{fi} is sharply peaked except at the very early times. (Conservation of energy) Thus we get:

The transition Rate $= \dfrac{P_T}{t} = 2\pi \rho(\omega_f) \dfrac{|W_{fi}|^2}{\hbar^2}$

= Probability per unit time.

This is the famous Fermi Golden Rule.

Now Convert it to wavenumbers.

$$\rho(\omega) = \frac{dn}{d\omega} = \frac{dn}{d\, 2\pi \nu} = \frac{dn}{d\, 2\pi c \bar{\nu}} = \frac{1}{2\pi c} \frac{dn}{d\bar{\nu}}$$

$$= \frac{1}{2\pi c} \rho(\bar{\nu})$$

and $\left|\dfrac{W_{fi}}{\hbar}\right|^2 = |\omega_{fi}^{int}|^2 = (2\pi c)^2 |\bar{\nu}_{fi}^{int}|^2$

This gives

$$\text{rate} = \frac{P_T(i \to f)}{t} = \frac{2\pi}{(2\pi c)} \rho(\bar{\nu}_{fi}) (2\pi c)^2 \left| \bar{\nu}_{fi}^{\,int} \right|^2$$

$$= 4\pi^2 c \, \rho(\bar{\nu}_{fi}) \left| \bar{\nu}_{fi}^{\,int} \right|^2$$

For $\rho(\bar{\nu}) = 1$ state per cm^{-1}

$\bar{\nu}_{fi}^{\,int} = 1\ cm^{-1}$

$$\text{rate} = 4\pi^2 (3 \times 10^{10}\ cm\ s^{-1})\ 1(cm^{-1})^{-1}\ (1\ cm^{-1})^2$$

$$\frac{P_T(i \to f)}{t} = 1.184 \times 10^{12}\ s^{-1} \text{ per molecule.}$$