The Time-Energy Uncertainty Principle and Fermi's Golden Rule

Suppose $|\psi,0\rangle = |i\rangle$ so that the coefficients $c_n(t)$ at $t=0$ are

$$c_n(0) = \langle n|\psi,0\rangle = \langle n|i\rangle = \delta_{ni}.$$

Then by (11) to first order

$$|\psi,t\rangle_I = \left(1 - \frac{i}{\hbar}\int_0^t dt'\, V_I(t')\right)|i\rangle$$

$$= \sum_n |n\rangle\langle n| \left(1 - \frac{i}{\hbar}\int_0^t dt'\, V_I(t')\right)|i\rangle$$

$$= |i\rangle - \frac{i}{\hbar}\sum_n |n\rangle \int_0^t dt' \langle n|V_I(t')|i\rangle.$$

Suppose V is time independent so that

$$\langle n|V_I(t')|i\rangle = \langle n| e^{iH_0t'/\hbar}\, V\, e^{-iH_0t'/\hbar}|i\rangle$$

$$= e^{i\omega_{ni}t'}\, V_{ni}$$

where $V_{ni} = \langle n|V|i\rangle$ and $\omega_{ni} = \dfrac{E_n - E_i}{\hbar}$.

Then

$$|\psi,t\rangle_I = |i\rangle - \frac{i}{\hbar}\sum_n |n\rangle V_{ni}\int_0^t dt'\, e^{i\omega_{ni}t'}$$

That is,

$$|\psi,t\rangle_I = |i\rangle - \frac{i}{\hbar}\sum_n |n\rangle V_{ni}\,\frac{e^{i\omega_{ni}t}-1}{i\omega_{ni}}$$

$$= |i\rangle + \sum_n |n\rangle V_{ni}\,\frac{1-e^{i\omega_{ni}t}}{E_n-E_i}$$

And for $n \neq i$

$$c_n(t) = \langle n|\psi,t\rangle_I = V_{ni}\,\frac{1-e^{i\omega_{ni}t}}{E_n-E_i},$$

So to first order in Dyson's expansion, the probability that the system is in the state $|n\rangle$ is

$$P_n(t) = |c_n(t)|^2 = \frac{|V_{ni}|^2}{(E_n-E_i)^2}\left(1-e^{i\omega_{ni}t}\right)\left(1-e^{-i\omega_{ni}t}\right)$$

$$= \frac{|V_{ni}|^2}{(E_n-E_i)^2}\left(2-2\cos\omega_{ni}t\right)$$

$$= \frac{4|V_{ni}|^2}{(E_n-E_i)^2}\sin^2\left(\frac{\omega_{ni}t}{2}\right) = \frac{1}{\hbar^2}|V_{ni}|^2\frac{\sin^2\frac{\omega_{ni}t}{2}}{(\omega_{ni}/2)^2}$$

or

$$P_n(t) = \frac{4|V_{ni}|^2}{(E_n - E_i)^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right].$$

When $\frac{\omega_{ni}t}{2} << 1$, $P_n(t)$ rises as $(\omega_{ni}t)^2$.

But at bigger t, states with

$$\frac{\omega_{ni}t}{2} \approx \frac{\pi}{2} \quad \text{or} \quad \omega_{ni}t = \pi$$

dominate. That is, states n with

$$(E_n - E_i)t = \pi\hbar.$$

dominate. (Sakurai's (5.6.24) is off by 2.)
This is an example of the time-energy uncertainty principle

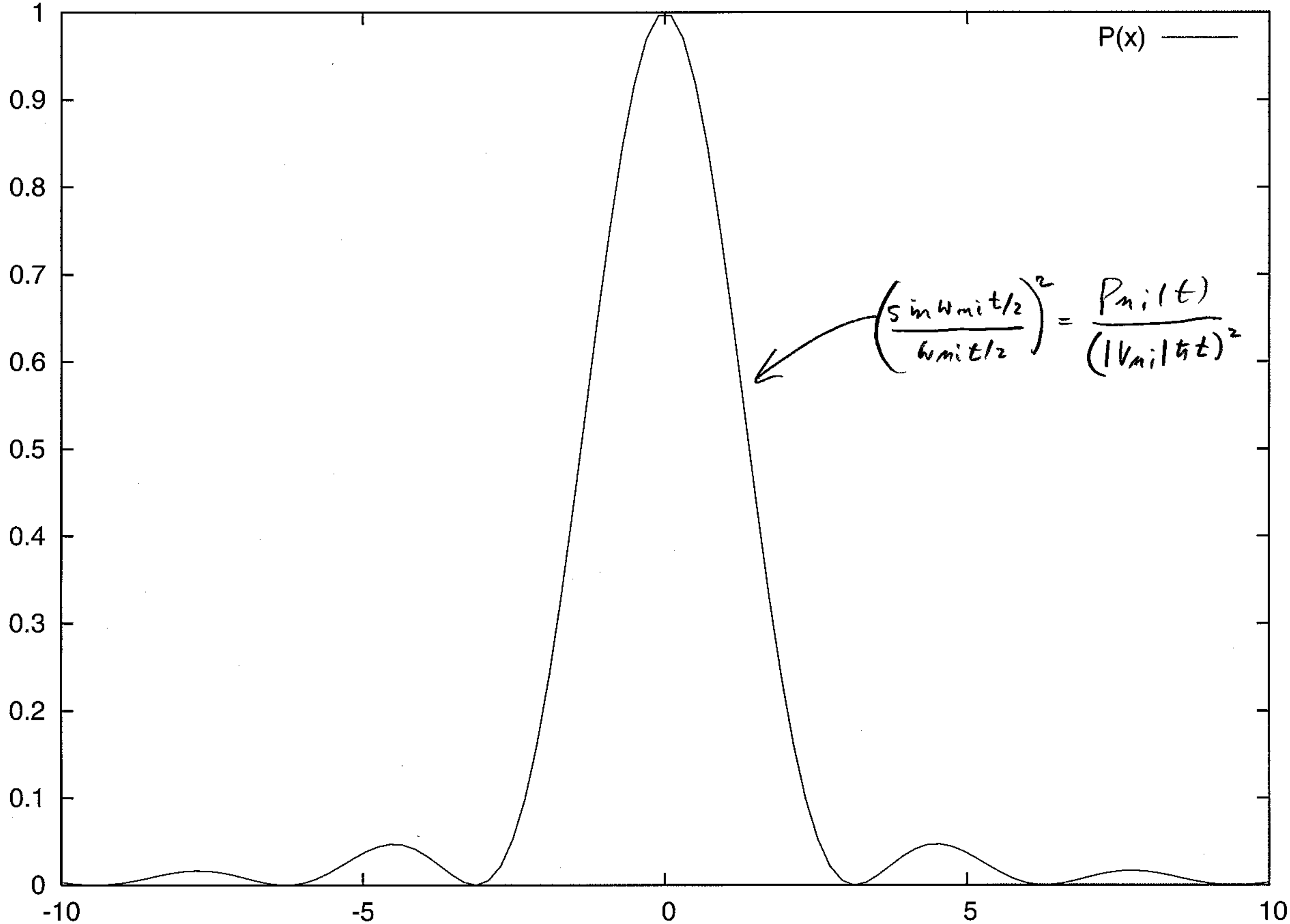
$$\Delta E \, \Delta t \gtrsim \pi\hbar.$$

If the perturbation is on very briefly, then transitions with big ΔE can occur.

The probability $P_n(t)$ is

$$P_n(t) = \left(|V_{ni}|^2 t/\hbar\right)^2 \left(\frac{\sin \omega_{ni}t/2}{\omega_{ni}t/2}\right)^2$$

and a graph of $(\sin x/x)^2 = P_n(t)/(\hbar|V_{ni}|t)^2$ with $x = \omega_{ni}t/2$ appears on next page


P(x)
$\left(\frac{\sin \omega_{mi} t/2}{\omega_{mi} t/2}\right)^2 = \frac{P_{mi}(t)}{(|V_{mi}| \hbar t)^2}$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-10
-5
0
5
10

In the limit $\Delta E = E_n - E_i \to 0$, the probability

$$|c_n(t)|^2 = \frac{4|V_{ni}|^2}{(E_n-E_i)^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right] \to \frac{|V_{ni}|^2 t^2}{\hbar^2}$$

but, of course, this first-order formula for $|c_n(t)|^2$ fails when

$$\frac{|V_{ni}|^2 t^2}{\hbar^2}$$

becomes of the order of 1.

In many cases, the states $|n\rangle$ form a continuum with $\rho(E)dE$ state in the energy interval dE. The probability then is

$$P(i\to n)dE_n = \int dE_n\, \rho(E_n)\, |c_n(t)|^2$$

$$= 4\int \sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]\frac{|V_{ni}|^2}{(E_n-E_i)^2}\rho(E_n)dE_n$$

Now since

$$\delta(x) = \lim_{\alpha\to\infty}\frac{\alpha}{\pi}\left(\frac{\sin\alpha x}{\alpha x}\right)^2 = \lim_{\alpha\to\infty}\frac{1}{\pi}\frac{\sin^2\alpha x}{\alpha x^2}$$

$$\lim_{t\to\infty}\frac{4\hbar^2}{t(E_n-E_i)^2\pi}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right] = \delta\left(\frac{E_n-E_i}{2\hbar}\right)$$

But

$$1 = \int d\alpha x \quad \delta(\alpha x) = \alpha \int dx\, \delta(\alpha x) = \int dx\, \delta(x)$$

So $\quad \delta(\alpha x) = \frac{1}{\alpha} \delta(x)$ whence

$$\lim_{t \to \infty} \frac{1}{(E_n - E_i)^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] = \frac{\pi t}{2\hbar} \delta(E_n - E_i).$$

So the probability is

$$P(i \to n)\, dE_n = 4 \int \frac{\pi t}{2\hbar} \delta(E_n - E_i) |V_{ni}|^2 \rho(E_n)\, dE_n$$

$$= \frac{2\pi t}{\hbar} |V_{ni}|^2 \rho(E_i) \Big|_{E_n = E_i}.$$

The transition rate $W_{i \to n}$ is

$$w_{i \to n} = \frac{d}{dt} P(i \to n) = \frac{2\pi}{\hbar} |V_{ni}|^2 \rho(E_i) \Big|_{E_n = E_i}.$$

which is Fermi's golden rule. Note that $|V_{ni}|^2$ is the squared modulus of the coefficient of $(e^{i\omega_{ni}t} - 1)/\Delta E$.

We often write

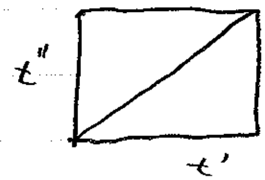
$$\hat{w}_{i \to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i)$$

as short for $\int \hat{W}_{i \to n} \rho(E_n)\, dE_n = W_{i \to n}$.

To second order

$$|\psi,t\rangle_I = \left(1 - \frac{i}{\hbar}\int_0^t dt'\, V_I(t') - \frac{1}{2\hbar^2}\int_0^t dt' \int_0^t dt''\, T\left(V_I(t')V_I(t'')\right)\right)|\psi,0\rangle_I$$

Now since



the region $t' > t''$ is half the whole square. Thus

$$|\psi,t\rangle_I = \left(1 - \frac{i}{\hbar}\int_0^t dt'\, V_I(t') - \frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt''\, V_I(t')\, V_I(t'')\right)|\psi,0\rangle_I .$$

So if $|\psi,0\rangle_I = |i\rangle$, then

$$c_n(t) = \langle n|\psi,t\rangle_I = \delta_{ni} - \frac{i}{\hbar}\int_0^t dt'\, \langle n|V_I(t')|i\rangle$$

$$- \frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' \sum_m \langle n|V_I(t')|m\rangle\langle m|V_I(t'')|i\rangle$$

So the second-order term is

$$c_n^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt''\, \langle n|V_I(t')|m\rangle\langle m|V_I(t'')|i\rangle$$

and for a time-independent V

$$V_I(t) = e^{iH_0 t/\hbar}\, V\, e^{-iH_0 t/\hbar}$$

and so $c^2_n(t)$ is

$$c_n^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' \sum_m e^{i(E_n-E_m)t'/\hbar} \langle n|V|m\rangle\langle m|V|i\rangle e^{i(E_m-E_i)t''/\hbar}$$

$$= -\frac{1}{\hbar^2}\sum_m V_{nm}V_{mi}\int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{nm}t' + i\omega_{mi}t''}$$

$$= -\frac{1}{\hbar^2}\sum_m \frac{V_{nm}V_{mi}}{i\omega_{mi}}\int_0^t dt' e^{i\omega_{nm}t'}\left(e^{i\omega_{mi}t'}-1\right)$$

$$= \frac{i}{\hbar}\sum_m \frac{V_{nm}V_{mi}}{E_m-E_i}\int_0^t dt'\left(e^{i\omega_{ni}t'} - e^{i\omega_{nm}t'}\right)$$

If there are no intermediate $|m\rangle$ states with

$$V_{nm}V_{mi} \neq 0 \quad \text{and} \quad E_n \cong E_m$$

then we may drop the second term and get

$$c_n^{(2)}(t) \simeq \frac{1}{\hbar}\sum_m \frac{V_{nm}V_{mi}}{(E_m-E_i)}\frac{1}{(E_n-E_i)}\left(e^{i\omega_{ni}t}-1\right)$$

which we may compare with

$$c_n^{(1)}(t) = \frac{V_{ni}\left(e^{i\omega_{ni}t}-1\right)}{E_i-E_n}$$

which shows that (apart from a minus sign) they have the same time dependence.

Thus the transition rate is

$$w_{i\to n} = \frac{2\pi}{\hbar}\left| V_{ni} + \sum_m \frac{V_{nm}V_{mi}}{E_i - E_m}\right|^2 \rho(E_n)\Big|_{E_n=E_i}.$$

If there are $|m\rangle$ states with $V_{nm}V_{mi} \neq 0$ and $E_m = E_n$, then one replaces

$$E_i - E_m \text{ by } E_i - E_m + i\epsilon$$

as shown in Sakurai's section (5.8).

Suppose V depends explicitly on t as

$$V(t) = Ve^{i\omega t} + V^{\dagger}e^{-i\omega t}.$$

Then

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\left(V_{ni}\, e^{i\omega t'} + V^{\dagger}_{ni} e^{-i\omega t'}\right) e^{i\omega_{ni}t'}$$

$$= \frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{ni})t}}{\omega+\omega_{ni}} V_{ni} + \frac{1-e^{i(\omega_{ni}-\omega)t}}{-\omega+\omega_{ni}} V^{\dagger}_{ni}\right]$$

where $V^{\dagger}_{ni} = \langle n|V^{\dagger}|i\rangle$. So this is just like the constant-V case, except that

$$\omega_{ni} = \frac{E_n - E_i}{\hbar} \longrightarrow \omega_{ni} \pm \omega.$$

So for long t $|C_n^{(1)}(t)|^2$ is significant only if

$$\omega_{ni} + \omega \simeq 0 \qquad E_n = E_i - \hbar\omega$$

which is stimulated emission

or $\quad \omega_{ni} - \omega \simeq 0 \qquad E_n = E_i + \hbar\omega$

which is absorption.

Only one of these can be true.

So as before

$$w_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \rho(E_n)\Big|_{E_n = E_i - \hbar\omega}$$

or

$$w_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}^{+}|^2 \rho(E_n)\Big|_{E_n = E_i + \hbar\omega}$$

or

$$w_{i\to n} = \frac{2\pi}{\hbar} \begin{Bmatrix} |V_{ni}|^2 \\ |V_{ni}^{+}|^2 \end{Bmatrix} \delta(E_n - E_i \pm \hbar\omega)$$

Note that

$$|V_{ni}|^2 = |\langle n|V|i\rangle|^2$$

$$= |V_{in}^{+}|^2 = |\langle i|V^{+}|n\rangle|^2$$

$$= |\langle n|V|i\rangle^{*}|^2.$$

It follows then that

$$\frac{w^{e}_{i\to n}}{\rho(E_n)} = \frac{2\pi}{\hbar}|V_{ni}|^2 = \frac{w^{a}_{n\to i}}{\rho(E_i)} = \frac{2\pi}{\hbar}|V^{+}_{in}|^2$$

which is called <u>detailed balancing</u>.