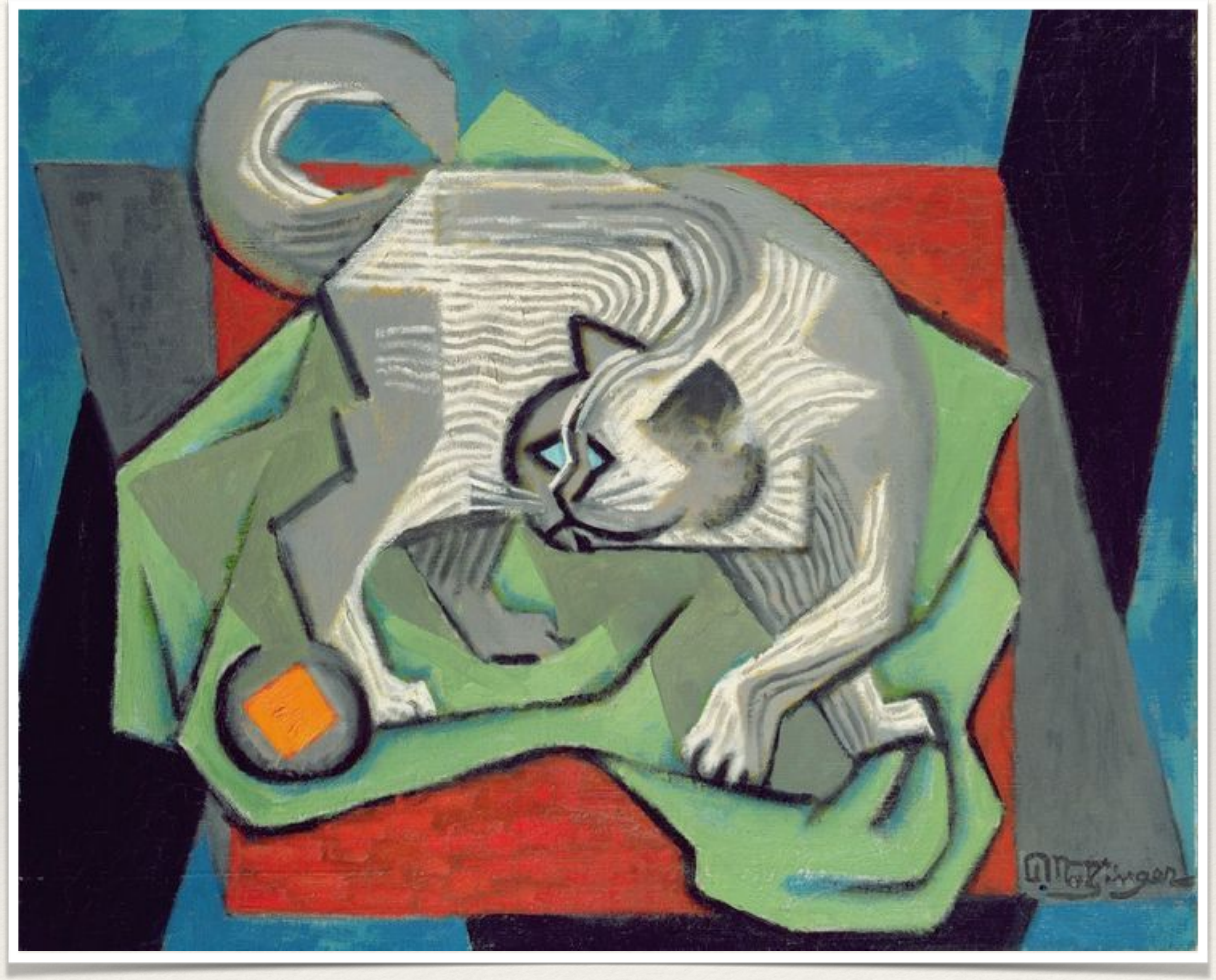
Prof. Steven Flammia

Quantum Mechanics

Lecture 16

Fermi's golden rule.



A quick recap

Time-dependent perturbation theory requires a new perturbative ansatz:

$$H(t) = H_0 + H_1(t) \qquad |\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

(Simplify notation:
$|E_n^{(0)}\rangle \to |n\rangle$
The full eigenstates
might not even exist.)

It is convenient to work in the "relative coordinates" of the interaction picture, where the evolution equations become:

$$\dot{O}_I = \frac{i}{\hbar}[H_0, O_I] \qquad H_I(t) = e^{iH_0 t/\hbar} H_1(t) \, e^{-iH_0 t/\hbar} \qquad i\hbar |\dot{\psi}_I(t)\rangle = H_I(t) |\psi_I(t)\rangle$$

The perturbative part c of the amplitude to transition from an initial eigenstate i of the bare Hamiltonian to a final eigenstate f is given by:

$$c_f(t) = \langle f | U_I(t) | i \rangle = \delta_{fi} - \frac{i}{\hbar} \int_0^t dt' \, e^{i(E_f - E_i)t'/\hbar} \langle f | H_1(t') | i \rangle + \ldots$$

Bohr frequency

From now on, we will work exclusively to **first order** and assume that $\boldsymbol{f \neq i}$. Looking carefully at the amplitude, it has the form of a Fourier transform:

Introduce the **Bohr frequency:**

$$\omega_{fi} := (E_f - E_i)/\hbar$$

$$c_f(t) = \frac{-i}{\hbar} \int_0^t \mathrm{d}t' \, \mathrm{e}^{i\omega_{fi}t'} \langle f \,|\, H_1(t') \,|\, i \rangle$$

Looks like the Fourier transform of $\langle f \,|\, H_1 \,|\, i \rangle$ at ω_{fi}.

Thus, we have the intuition that if $\langle f \,|\, H_1 \,|\, i \rangle$ has frequency components near the Bohr frequency then this amplitude should be large in magnitude.

Conversely, if $\langle f \,|\, H_1 \,|\, i \rangle$ has no frequency components near ω_{fi}, then we expect this amplitude to have a small magnitude.

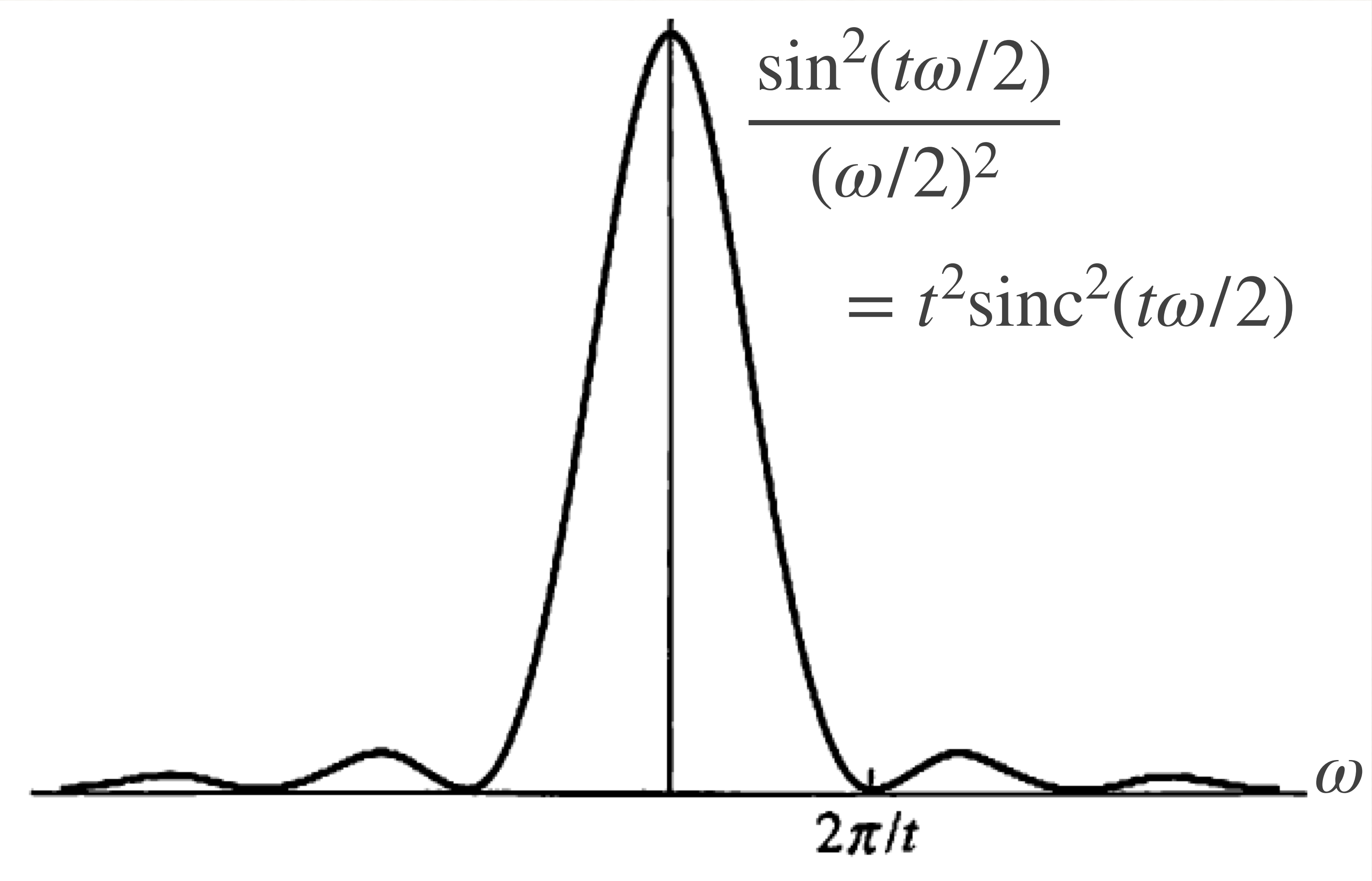
Constant perturbation

If H_1 is constant in time, then the integral is very easy:

$$c_f(t) = \frac{-i}{\hbar}\langle f | H_1 | i \rangle \int_0^t e^{i\omega_{fi}t'} dt' = \frac{-i}{\hbar}\langle f | H_1 | i \rangle \left(\frac{e^{i\omega_{fi}t/2}}{\omega_{fi}/2} \sin(\omega_{fi}t/2) \right)$$

The transition probability is therefore:

$$P_{i\to f} = |c_f(t)|^2 = \frac{1}{\hbar^2} \frac{\sin^2(\omega_{fi}t/2)}{(\omega_{fi}/2)^2} |\langle f | H_1 | i \rangle|^2$$



As t increases, this function limits to a Dirac delta function:

$$t \lim_{t\to\infty} \frac{1}{t} |c_f(t)|^2 = \frac{\pi t \delta(\omega_{fi}/2)}{\hbar^2} |\langle f | H_1 | i \rangle|^2$$

Characteristic spreading of probability to transition is called lifetime broadening.

What about energy conservation?

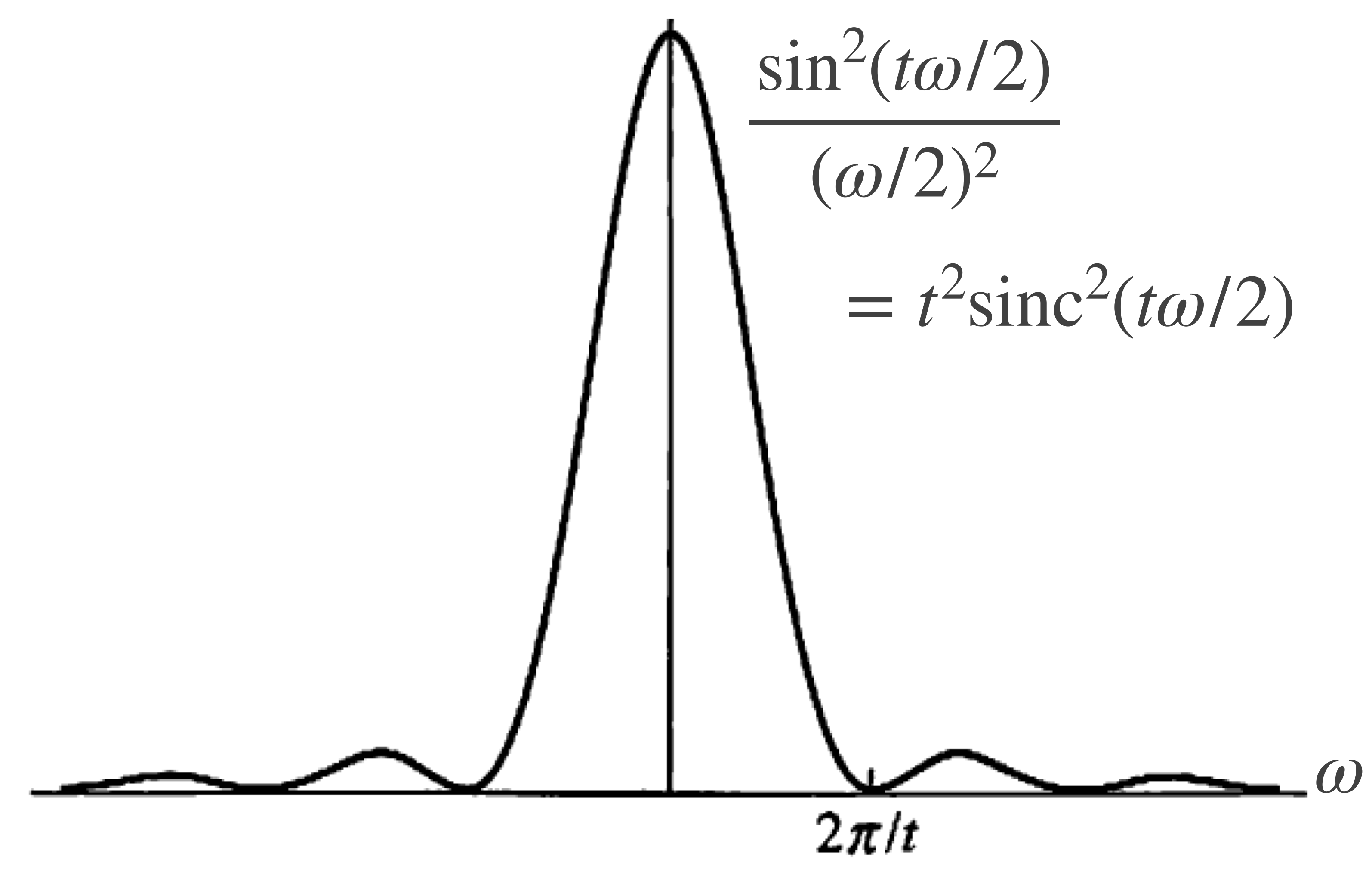
The approach to a delta function suggests that as time increases, only final states at the Bohr frequency have allowed transitions. What about smaller t?

For small t, the system can transition to a state with different energy!

Fortunately, we have the Time-Energy uncertainty principle:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Small times can have large energy jumps;
for large times, only small energy jumps occur.



Furthermore, we don't expect strict energy conservation if the Hamiltonian is explicitly time-dependent. The extra energy could come from driving the system's time dependence, in fact.

Harmonic perturbation

If H_1 is has a pure frequency ω, the integral is just as easy:

$$H_1(t) = 2V(\hat{\mathbf{r}})\cos(\omega t) = V(\hat{\mathbf{r}})\left(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t}\right)$$

$$c_f(t) = \frac{-i}{\hbar}\langle f\,|\,V(\hat{\mathbf{r}})\,|\,i\rangle \int_0^t (\mathrm{e}^{i\omega t'} + \mathrm{e}^{-i\omega t'})\mathrm{e}^{i\omega_{fi}t'}\mathrm{d}t'$$

$$= \frac{-i}{\hbar}\langle f\,|\,V(\hat{\mathbf{r}})\,|\,i\rangle \left(\mathrm{e}^{i\eta_+ t}\,\frac{\sin(\eta_+ t)}{\eta_+} + \mathrm{e}^{i\eta_- t}\,\frac{\sin(\eta_- t)}{\eta_-}\right)$$

Introduce:

$$\eta_\pm := \frac{\omega_{fi} \pm \omega}{2}$$

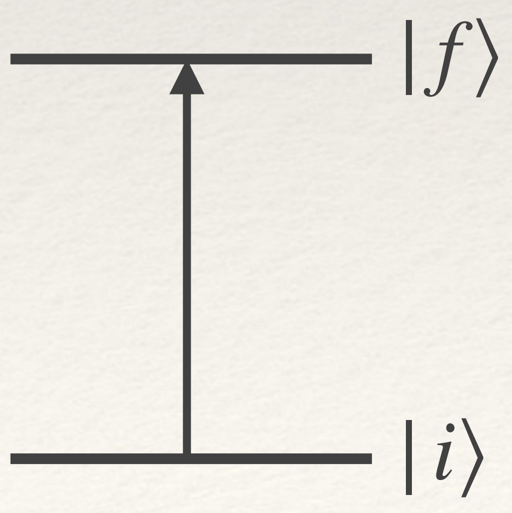
deviation of driving frequency from Bohr frequency

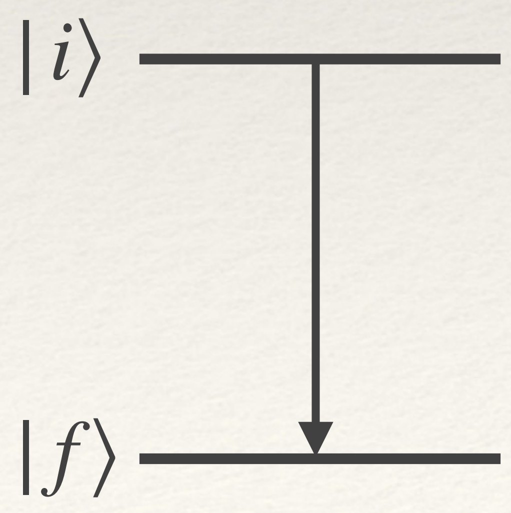
Each term is nearly a δ-function, so only one term will substantially contribute if the drive frequency ω is on resonance with the Bohr frequency. Broadly two paradigms:

η_- term dominates

$\omega_{fi} > 0$

absorption





$\omega_{fi} < 0$

stimulated emission

η_+ term dominates

Absorption in the long time limit

Consider the case of absorption (for stimulated emission, just change ω to -ω). The transition probability in the long time limit becomes a δ function:

$$P_{i\to f} = \frac{1}{\hbar^2} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 \left(\frac{\sin(\eta\_t)}{\eta_-} \right)^2 \xrightarrow{t \gg 1/\eta\_} \frac{2\pi t}{\hbar^2} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 \delta(\omega_{fi} - \omega)$$

As the probability increases linearly with time, it is convenient to define a **rate**:

$$\boxed{R_{i\to f} = \frac{\mathrm{d}}{\mathrm{d}t} P_{i\to f} = \frac{2\pi}{\hbar^2} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 \delta(\omega_{fi} - \omega)}$$

This is the δ-function version of **Fermi's golden rule** for a harmonic drive. Physically, the rate is the probability per unit time of transitioning from *i* to *f*.

Fermi's golden rule

The transition rate seems to require strict energy conservation. However, as we've seen, for finite times the system can still transition to states that nearly satisfy the resonance condition. We should integrate over these states!

Integrate with a density of states $g(E)$

$$R_{i\to f} = \int_{E_f-\epsilon}^{E_f+\epsilon} \frac{2\pi}{\hbar^2} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 \delta(\omega' - \omega_i - \omega)\, g(E')\, \mathrm{d}E'$$

$$= \frac{2\pi}{\hbar} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 \int_{E_f-\epsilon}^{E_f+\epsilon} \delta(E' - E_i - E)\, g(E')\, \mathrm{d}E'$$

$$= \frac{2\pi}{\hbar} |\langle f | V(\hat{\mathbf{r}}) | i \rangle|^2 g(E_f)\Big|_{E_f \simeq E_i + \hbar\omega}$$

This version of the golden rule is nice because the δ function is gone.