Main application: Absorption/Emission of radiation

from atom,

\[ \hat{H} = \hat{H}_0 + \hat{A} V(t) \]

\[ \text{not a "real" time dependence} \]

\[ \text{Heisenberg product} \quad e^{i\hat{A}t}\hat{H}_0 e^{-i\hat{A}t} \]

Assume we understand \( \hat{H}_0 \) part

\[ \hat{H}_0 \Phi_n = E_n \Phi_n \quad \text{and} \quad E_n = \hbar \Omega (n) \]

\[ \Phi_n(\vec{r}, t) = e^{-i\Omega n t} \Phi_n(\vec{r}) \]

We know how to solve \( \lambda = 0 \)

\[ \Psi(\vec{r}, t=0) = \sum c_n \Phi_n(\vec{r}) \quad c_n = \langle \Phi_n | \Psi(\vec{r}, t=0) \rangle \]

\[ \Psi(\vec{r}, t) = \sum c_n e^{-i\Omega n t} \Phi_n(\vec{r}) \]
For $\lambda \neq 0$ let's write

$$\Psi(r,t) = \sum_n c_n(t) \psi_n(r,t)$$

$$i\hbar \frac{d\Psi}{dt} = (\hat{H}_0 + \lambda \hat{V}) \Psi$$

$$i\hbar \sum_n c_n e^{i\omega_n t} \psi_n + \sum_n c_n e^{-i\omega_n t} \psi_n$$

$$= \sum_n c_n e^{-i\omega_n t} \psi_n + \sum_n c_n e^{-i\omega_n t} \lambda V \psi_n$$

Take inner product with $\phi_k$

$$\Rightarrow \quad i\hbar \frac{\partial}{\partial t} c_k = \lambda \sum_n \langle k | \hat{V} | n \rangle c_n$$

Expand $c_k = c_{k0} + \lambda c_{k1} + \lambda^2 c_{k2}$

$$i\hbar \frac{\partial}{\partial t} c_{k0} = 0 \quad \leftarrow \text{expected!}$$

$$i\hbar \frac{\partial}{\partial t} c_{k1} = \sum_n \langle k | \hat{V} | n \rangle c_{n0}$$

$\vdots$ \quad NB: $\phi_n = e^{-i\omega_n t} \phi_n$ has its time dep.

Let's suppose system starts in definite state $\phi_k$ at $t = -\infty$ so that $c_{n0}(-\infty) = \delta_{nk}$
\[ C_{kl}(t) = \langle k | V | l \rangle \]

\[ C_{kl}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} \langle k | \hat{V}(t') | l \rangle dt' \]

Often \( \hat{V} \) is "factorizable" i.e. \( \hat{V} \) looks like some operators \( (\hat{x}, \hat{p}, \hat{L}, ...) \) multiplied by some scalar \( f(t) \). E.g. time dependent electric field in \( z \) direction \( \hat{V} = -e\varepsilon z f(t) \)

\[ \hat{V} = i\hbar f(t) \]

\[ C_{kl}(t) = \langle k | \hat{V} | l \rangle \int_{-\infty}^{t} e^{-i\omega t'} e^{i\omega t'} e^{-i\omega f(t')} dt' \]

\[ \text{Peak} = |C_{kl}(t)|^2 = \frac{1}{\hbar^2} |\langle k | \hat{V} | l \rangle|^2 \int_{-\infty}^{t} e^{i(\omega_k - \omega_l)t'} e^{-i\omega t'} |f(t')|^2 dt' \]

Physically reasonable: Probability of transition \( \theta \)

must "connect" \( l \) to \( k \). \( f(t) \) must have Fourier component at correct energy difference

\[ \text{QM analogy of resonance} \]
left specialise to sinusoidal perturbation

which is turned on at \( t = 0 \):

\[
\hat{V}(t) = \hat{V}_0 \cos \omega t
\]

\[
\langle k | \hat{V}(t) | e \rangle = \frac{\langle k | \hat{V}_0 | e \rangle}{i \hbar} \int_0^t e^{-i \omega \kappa t'} dt'
\]

\[
= \frac{\langle k | \hat{V}_0 | e \rangle}{2i \hbar} \left[ e^{(\omega \kappa \kappa) t} - 1 + e^{(\omega \kappa \kappa) t} - 1 \right]
\]

Consider \( \omega \kappa \kappa \) close to \( \omega \kappa \kappa \) discard

\[
\langle k | \hat{V}(t) | e \rangle = \frac{\langle k | \hat{V}_0 | e \rangle}{2i \hbar} \frac{e^{(\omega \kappa \kappa) t/2} - e^{(-i \omega \kappa \kappa) t/2}}{\omega \kappa \kappa}
\]

\[
P_{\kappa \rightarrow \kappa} = \frac{\langle k | \hat{V}_0 | e \rangle^2}{\hbar^2} \frac{\sin^2(\omega \kappa \kappa) t/2}{(\omega \kappa \kappa - \omega \kappa \kappa)^2}
\]

\[
\frac{1}{4 \hbar^2}
\]

Most likely to excite \( \omega \kappa \kappa = \omega \)

Longer \( t \) more severe resonance

\[
\Delta \omega \sim \frac{t}{\hbar}
\]

Resonance again
In fact \( S(w) = \lim_{t \to 0} \frac{\sin^2(\omega t/2)}{\omega^2} \)

So that \( P \rightarrow k = \frac{2\pi}{\hbar} \frac{|\langle k| \hat{\Psi} | e \rangle|^2}{E_e - E_k} \delta(E_k - E_e) \)

where \( W_e \rightarrow k = \frac{P_e ightarrow k}{t} = \frac{2\pi}{\hbar} \frac{|\langle k| \hat{\Psi} | e \rangle|^2}{E_e - E_k} \delta(E_k - E_e) \)

Q: Does anyone know what this is called?

"Fermi's Golden Rule"

Also sometimes formulated in terms of "density of states"

\[ W_e \rightarrow k = \frac{2\pi}{\hbar} \frac{|\langle k| \hat{\Psi} | e \rangle|^2}{\text{# of states with energy } E_k} \]
We discussed keeping only the term
\[ \frac{e^{i(\omega_k + \omega)t} - 1}{\omega_k + \omega} \]
and discarding
\[ \frac{e^{i(\omega_k - \omega)t} - 1}{\omega_k - \omega} \]

The correct thing to say is that both terms are present.

The one we retained corresponds to \( E_k = E_0 + \hbar \omega \)

absorption of a photon
\[ \hbar \omega \uparrow \quad E_k \quad \downarrow E_0 \]

The other is emission of a photon
\[ \hbar \omega \downarrow \quad E_k = E_0 - \hbar \omega \quad \uparrow \quad E_2 \]

One refers to this as "stimulated emission."

A photon in the perturbing field of frequency \( \omega \)
encourages an atom in an excited state to emit
another photon at some \( \omega \).
Stimulated emission first predicted by Einstein.

Actually this is fundamental principle behind laser operation.

Need population inversion for this to occur.

Light amplification by stimulated emission of radiation.

Q: Does this all mean atom in excited state with no external field would never decay? 

A: No. Can have spontaneous emission.

Even vacuum has fluctuating E, B fields (like harmonic oscillator which has ground state energy)

Might think answer "yes" because eigenstate only evolves by trivial phase
Consider an atom exposed to \( \vec{E} = E_0 \cos \omega t \hat{z} \)

\[
\hat{V} = -q E_0 \cos \omega t \hat{z} \quad (q = -e)
\]

The relevant matrix element is \( \langle k | \hat{\tau} | l \rangle \)

or, in general \( \langle k | \hat{r} | l \rangle \)

Many of these are zero "Selection Rules"

More precisely, for atom \( \langle n' l' m' | \hat{r} | n l m \rangle \)

\[
\begin{align*}
[\hat{L}_z, \hat{x}] &= [\hat{x}, \hat{p}_y] - [\hat{y}, \hat{p}_x] = -[\hat{p}_x, \hat{x}] \\
&= -\gamma [\hat{p}_x, \hat{x}] - [\gamma \hat{\gamma}, \hat{x}] \hat{p}_x = i \hbar \gamma \\
[\hat{L}_z, \hat{\gamma}] &= -i \hbar \hat{x} \\
[\hat{L}_z, \hat{\gamma}] &= \phi
\end{align*}
\]

\[
\phi = \langle n' l' m' | [\hat{L}_z, \hat{x}] | n l m \rangle
\]

\[
= \hbar (m' - m) \langle n' l' m' | \hat{z} | n l m \rangle
\]

\( \Rightarrow m' = m \) or \( \langle n' l' m' | \hat{z} | n l m \rangle = 0 \).

\[
\langle n' l' m' | [\hat{L}_z, \hat{\gamma}] | n l m \rangle = (m' - m) \hbar \langle n' l' m' | \hat{y} | n l m \rangle
\]

\[
= i \hbar \langle n' l' m' | \hat{y} | n l m \rangle
\]

So NIE of \( \hat{\gamma} \) obtained from \( \hat{x} \),
\[ \langle n' \ell' m' | [\hat{L}^2, \hat{J}] | n e m \rangle = (m' - m) \langle n' \ell' m' | \hat{x} | n e m \rangle \]

\[ = -i \hbar \langle n' \ell' m' | \hat{x} | n e m \rangle \]

Combining,\n
\[ (m' - m)^2 \langle n' \ell' m' | \hat{x} | n e m \rangle = \langle n' \ell' m' | \hat{x} | n e m \rangle \]

So \[ \langle n' \ell' m' | \hat{x} | n e m \rangle = 0 \quad \text{or} \quad (m' - m)^2 = 1 \]

\[ \Rightarrow \quad \Delta m = 0, \pm 1 \]

Q: How else to understand this?

What is spin of photon?

A: Spin 1 \( m = 0, \pm 1 \)

Another comm reln \[ [\hat{L}^2, [\hat{L}^2, \hat{F}]] = 2\hbar^2 (\hat{F} \hat{L}^2 + \hat{L}^2 \hat{F}) \]

Insert this inside \[ \langle n' \ell' m' | \hat{x} | n e m \rangle \]

\[ \Rightarrow \quad \Delta \ell = \pm 1 \]

algebra
as tree is "stuck"
We talked about a spatially uniform, but time-dependent, electric field. If we are really interested in light incident on an atom

\[ \hat{H} = \frac{1}{2m} \left( \hat{\mathbf{p}} - \frac{e}{c} \hat{\mathbf{A}}(r,t) \right)^2 + V(r) \]

perturbation is

\[ -\frac{e}{2mc} \left( \hat{\mathbf{p}} \cdot \hat{\mathbf{A}} + \hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \right) \]

Need matrix elements of \( \hat{\mathbf{p}} \) in, e.g., hydrogenic states.

Q: Any ideas about this

\[ \hat{\mathbf{p}} = \frac{i\hbar}{\hbar} \left[ \hat{H}_0, \hat{\mathbf{r}} \right] \]

so

\[ \langle n' | \hat{\mathbf{p}} | n \rangle = -\frac{i\hbar}{\hbar} \left( E_{n'} - E_{n} \right) \langle n' | \hat{\mathbf{r}} | n \rangle \]

our selection rule discussion for \( \hat{\mathbf{p}} \) carried over to \( \hat{\mathbf{p}} \).
\[ \hat{A}(r,t) = \mathbf{x} A_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \]

Q: What is this related to?
A: Polarization \( A: \mathbf{x} \cdot \mathbf{k} = 0 \)

\[ \hat{A} = \frac{A_0}{2} \mathbf{x} \left[ e^{i (\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{-i (\mathbf{k} \cdot \mathbf{r} - \omega t)} \right] \]

P \cdot \hat{A} involves actually \( P \cdot e^{i (\mathbf{k} \cdot \mathbf{r})} \)

Electric dipole approximation \( e^{i (\mathbf{k} \cdot \mathbf{r})} = 1 \)

Q: Why true / plausible
A: For visible light \( \lambda \approx 600 \text{ nm} \)
Bohr radius \( a_0 \approx 0.5 \text{ nm} \)
\[ 0.5 \mathbf{A} = 0.5 \times 10^{-8} \text{ cm} = 5 \times 10^{-10} \text{ m} \]