Spontaneous Emission of Light

(for example: $2S \to 1S$ for H atom gives $(-3.4\,eV) - (-13.6\,eV) = 10.2\,eV$ photon

Treatment so far (and in Sakurai) can't handle this.

To do it, need to treat light quantum mechanically as well.

Results (without proof) in dipole approximation:

Absorption rate $\quad w_{(i+\text{photon})\to n} = \dfrac{4\alpha}{3c^2}\,\omega^3\, N_{\text{photons}}\, |\langle n|\vec{R}|i\rangle|^2$

Emission rate $\quad w_{i\to(n+\text{photon})} = \dfrac{4\alpha}{3c^2}\,\omega^3\, (\underset{\text{stimulated}}{N_{\text{photons}}} + \underset{\text{spontaneous}}{1})\, |\langle n|\vec{R}|i\rangle|^2$

N_{photons} = number of photons in initial state $|i; N_{\text{photons}}\rangle$

The terms with N_{photons} are what we've seen already.

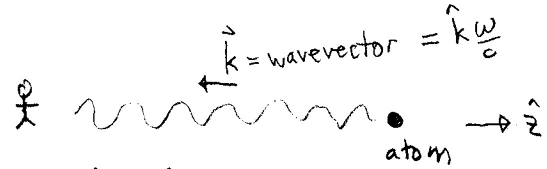
The $+1$ term is new, non-classical = spontaneous emission.

Define power radiated $= \underbrace{\hbar\omega}_{\frac{\text{energy}}{\text{transition}}}\ \underbrace{w_{i\to(n+\text{photon})}}_{\frac{\text{transitions}}{\text{time}}} = P_{i\to n}$

Then $$\frac{dP^{\text{spontaneous}}_{i\to n}}{d\Omega} = \frac{\hbar\alpha}{2\pi c^2}\,\omega^4\, |\langle n|\hat{n}\cdot\vec{R}|i\rangle|^2$$

$d\Omega = d(\cos\theta)\,d\phi$ for polarization vector $\hat{n}$ at angle θ, ϕ.

For a given observer, can sum over two $\hat{n}$'s $\perp$ to $\hat{k}$.



$\hat{n} = \hat{x}$ or $\hat{y}$

Photoelectric Effect (Sakurai 5.7 p. 339)

Light hits an atom, ejects an electron.

Suppose: initial state $|i\rangle$ of electron is an atomic bound state
final state $|\vec{k}_f\rangle$ is a momentum eigenstate (plane wave)
(valid if electron not too slow).

Use the $\sigma_{abs}(\omega)$ as before, but need appropriate $\rho(E_f)$.

Need $|\langle \vec{k}_f| e^{i(\frac{\omega}{c})\hat{k}\cdot\vec{r}}\, \hat{n}\cdot\vec{p}|i\rangle|^2$ to be nearly constant, so consider groups of states with nearly same $\vec{k}_f$ magnitude (energy) and direction.

To make sense of $\rho(E_f)$, put states in a large box of sides L.

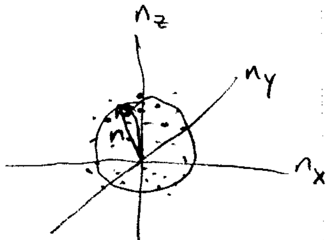
$$\langle \vec{r}|\vec{k}_f\rangle = \psi_f(\vec{r}) = \frac{e^{i\vec{k}_f\cdot\vec{r}}}{L^{3/2}}, \quad \text{with} \quad 0 < x, y, z < L$$

Periodic boundary conditions: $k_x = \frac{2\pi n_x}{L}$, $k_y = \frac{2\pi n_y}{L}$, $k_z = \frac{2\pi n_z}{L}$.

Define $n^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{L}{2\pi}\right)^2 k_f^2$.

Each integer 3-tuple (n_x, n_y, n_z) = 1 state.

As $L \to \infty$, treat as continuous variables.



Number of states between n and $n+dn$, and in a solid angle $d\Omega = d(\cos\theta)\,d\phi$, is

$dN = n^2\, dn\, d\Omega$ (volume element in spherical coordinates).

Also, $$E_f = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 n^2 \quad \Rightarrow \quad dE_f = \frac{\hbar^2}{m_e}\left(\frac{2\pi}{L}\right)^2 n\, dn$$

So $$dN = n^2 \frac{dn}{dE_f} dE_f\, d\Omega = \underbrace{n}_{=\frac{L}{2\pi}k_f}\left(\frac{m_e}{\hbar^2}\right)\left(\frac{L}{2\pi}\right)^2 dE_f\, d\Omega$$

So $$\boxed{dN = \left(\frac{L}{2\pi}\right)^3 \frac{m_e}{\hbar^2} k_f\, dE_f\, d\Omega} = \#\text{ of states between: } \begin{cases} (E,\ E+dE) \\ (\cos\theta,\ \cos\theta + d(\cos\theta)) \\ (\phi,\ \phi + d\phi) \end{cases}$$

So:

$$d\sigma = \frac{4\pi^2\hbar}{m_e^2\omega}\,\alpha\,\left|\langle \vec{k}_f | e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R})}\hat{n}\cdot\vec{P}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)\left(\frac{L}{2\pi}\right)^3 \frac{m_e}{\hbar^2} k_f \, dE_f \, d\Omega$$

Integrate with respect to E_f (but leave $d\Omega$ unintegrated)

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{4\pi^2\alpha\hbar}{m_e^2\omega}\underbrace{\left|\langle \vec{k}_f | e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R})}\hat{n}\cdot\vec{P}|i\rangle\right|^2}_{\text{matrix element } \sim \frac{1}{L^3}.} \frac{m_e k_f L^3}{\hbar^2(2\pi)^3}}$$

So far, we haven't been specific about initial state $|i\rangle$.

Now, suppose it is H ground state (or K-shell state of an atom)

$$\langle \vec{r}|i\rangle = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} = \psi_i(\vec{r})$$

So $$\langle \vec{k}_f|\ldots|i\rangle = \int d^3\vec{r}\left(\frac{e^{-i\vec{k}_f\cdot\vec{r}}}{L^{3/2}}\right) e^{i\vec{k}\cdot\vec{r}}\,\hat{n}\cdot(-i\hbar\vec{\nabla})\left[\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}\right]$$

Here, we've written $\vec{k} = \frac{\omega}{c}\hat{k}$.

Integrate by parts, use $\hat{n}\cdot\vec{k} = 0$ (EM wave is transverse).

$$\langle \vec{k}_f|\ldots|i\rangle = \frac{\hbar\,\hat{n}\cdot\vec{k}_f}{\sqrt{\pi}\,L^{3/2}}\left(\frac{Z}{a_0}\right)^{3/2}\underbrace{\int d^3\vec{r}\; e^{-i(\vec{k}_f - \vec{k})\cdot\vec{r}}\, e^{-Zr/a_0}}$$

Let $\vec{q} = \vec{k}_f - \vec{k}$. Integral only depends on q.
Call it $I(q)$

$$I(q) = \int d^3\vec{r}\; e^{-iqz} e^{-Zr/a_0}$$ (Take $\vec{q}$ along $\hat{z}$, since doesn't depend on direction.)

$$= \int_0^\infty r^2 dr \int_{-1}^{1} d(\cos\theta)\underbrace{\int_0^{2\pi} d\phi}_{2\pi}\; e^{-iqr\cos\theta} e^{-Zr/a_0}$$

Do the $d(\cos\theta)$ integral first:

$$\int_{-1}^{1} d(\cos\theta)\; e^{-iqr\cos\theta} = \frac{-i}{qr}\left(e^{iqr} - e^{-iqr}\right)$$

So $I(q) = -\frac{2\pi i}{q} \int_0^\infty r\, e^{-Zr/a_0} \left(e^{iqr} - e^{-iqr}\right)$

Now use $\int_0^\infty r\, e^{-Ar} = \frac{1}{A^2}$, with $A = \frac{Z}{a_0} - iq$ and $\frac{Z}{a_0} + iq$.

Then $I(q) = -\frac{2\pi i}{q}\left[\frac{1}{\left(\frac{Z}{a_0} - iq\right)^2} - \frac{1}{\left(\frac{Z}{a_0} + iq\right)^2}\right] = -\frac{2\pi i}{q}\left[\frac{4\frac{Z}{a_0} iq}{\left\{\left(\frac{Z}{a_0}\right)^2 + q^2\right\}^2}\right]$

$$= \frac{8\pi Z/a_0}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^2}$$

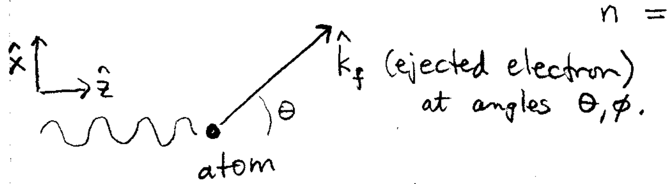
So $|\langle \vec{k}_f | \ldots | i\rangle|^2 = \frac{64\pi\hbar^2}{L^3} (\hat{n}\cdot\vec{k}_f)^2 \left(\frac{Z}{a_0}\right)^5 \frac{1}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^4}$

Plug this in:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{32\alpha\hbar}{m_e\omega} k_f (\hat{n}\cdot\vec{k}_f)^2 \left(\frac{Z}{a_0}\right)^5 \frac{1}{\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^4}}$$

Choose coordinates so that $\hat{k} = \hat{z}$ (direction of incident EM wave)

$\hat{n} = \hat{x}$ (polarization " " " ")



Then $(\hat{n}\cdot\vec{k}_f)^2 = k_f^2 \sin^2\theta \cos^2\phi$

$q^2 = (\vec{k}_f - \vec{k})^2 = k_f^2 - 2\vec{k}_f\cdot k + k^2 = k_f^2 - 2k_f \frac{\omega}{c}\cos\theta + \left(\frac{\omega}{c}\right)^2$

Note: * We did <u>not</u> use dipole approximation here.

* Denominator is small (large cross-section) when $\vec{q} = 0$, $(\vec{k}_f = \vec{k})$.
* Numerator is large when $\vec{k}_f$ is parallel to polarization $(\pm\hat{n})$.
* Now we can find the total cross-section...

$\int_0^{2\pi} \cos^2\phi\, d\phi = \pi$ $\quad\quad \int_{-1}^{1} \frac{\sin^2\theta}{(C_1 - C_2\cos\theta)} d(\cos\theta) = \frac{4/3}{(C_1^2 - C_2^2)^2}$

So total cross-section is:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \frac{128\pi\alpha\hbar k_f^3}{3m_e\omega}\left(\frac{Z}{a_0}\right)^5 \frac{1}{(c_1^2-c_2^2)^2} \approx \frac{128\pi}{3}\frac{\alpha\hbar}{m_e\omega}\left(\frac{Z}{k_f a_0}\right)^5$$

for large $k_f \gg k, \frac{Z}{a_0}$

where $C_2 = 2k_f\frac{\omega}{c} = 2k_f k$

$C_1 = \left(\frac{Z}{a_0}\right)^2 + k_f^2 + k^2$

Decay widths and energy shifts (5.8 of Sakurai)

Consider an e-state $|i\rangle$ of H_0.

In the presence of a perturbation $H = H_0 + V$, constant in time

$|i\rangle$ will: 1) get an energy shift $\Delta E_i = \langle i|V|i\rangle + \sum_{n\neq i}\frac{|V_{ni}|^2}{E_n-E_i} + \ldots$ from t-independent perturbation theory

2) Transition to other states at a rate we'll call Γ_i.

Claim: It is useful to write:

$$E_i = E_i^{(0)} + \underbrace{\langle i|V|i\rangle + \sum_{n\neq i}\frac{|V_{ni}|^2}{E_n-E_i} - \frac{i}{2}\Gamma_i}_{\text{complex energy shift for unstable states}}$$

Let's show this, and find Γ_i in the process.

Introduce a small number η ($\eta\to 0$ later), and write:

$V(t) = e^{\eta t}V$ (turns off for $t\to-\infty$).

Now use time-dependent perturbation theory.

First, for states $|n\rangle$ other than $|i\rangle$.

$c_n^{(0)}(t) = 0$

$$c_n^{(1)}(t) = -\frac{i}{\hbar}V_{ni}\lim_{t_0\to-\infty}\int_{t_0}^{t} e^{\eta t'}e^{i\omega_{ni}t'}\,dt'$$

$$= -\frac{i}{\hbar}V_{ni}\frac{e^{(i\omega_{ni}+\eta)t}}{i\omega_{ni}+\eta}$$

So $\mathcal{P}_{i\to n}(t) = |c_n(t)|^2 \simeq \dfrac{|V_{ni}|^2}{\hbar^2} \dfrac{e^{2\eta t}}{\omega_{ni}^2+\eta^2}$

So the rate of transition is:

$$\frac{d}{dt}|c_n(t)|^2 = \frac{2|V_{ni}|^2}{\hbar^2}\left(\frac{\eta e^{2\eta t}}{\eta^2+\omega_{ni}^2}\right)$$

Now take $\eta \to 0$:

$$\lim_{\eta\to 0} \frac{\eta}{\eta^2+\omega_{ni}^2} = \pi\,\delta(\omega_{ni}) = \pi\hbar\,\delta(E_n-E_i)$$

So $w_{i\to n} = \dfrac{d}{dt}|c_n(t)|^2 = \dfrac{2\pi}{\hbar}|V_{ni}|^2\,\delta(E_n-E_i)$ (Golden Rule again)

Now repeat for $c_i(t)$:

$$c_i^{(0)}(t) = 1$$

$$c_i^{(1)}(t) = \frac{-i}{\hbar} V_{ii} \lim_{t_0\to-\infty}\int_{t_0}^{t} e^{\eta t'} \underbrace{e^{i\omega_{ii}t'}}_{1,\text{ since } \omega_{ii}=0} dt' = \frac{-i}{\hbar\eta} V_{ii}\, e^{\eta t}$$

$$c_i^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \sum_n |V_{ni}|^2 \lim_{t_0\to-\infty}\int_{t_0}^{t} e^{\eta t'} e^{i\omega_{in}t'} \underbrace{\int_{t_0}^{t'} dt''\, e^{\eta t''} e^{i\omega_{ni}t''}}_{\frac{e^{i\omega_{ni}t'+\eta t'}}{i\omega_{ni}+\eta}}$$

$$= \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(\frac{-i}{\hbar}\right)\sum_{n\neq i}\frac{|V_{ni}|^2 e^{2\eta t}}{2\eta(E_i-E_n+i\hbar\eta)}$$

Therefore:

$$\frac{\dot{c}_i}{c_i} = -\frac{i}{\hbar}\left[V_{ii} + \sum_{n\neq i}\frac{|V_{ni}|^2}{E_i-E_n+i\hbar\eta}\right] + \mathcal{O}(V^3)$$

Now impose boundary condition $c_i(0) = 1$,
solve differential equation by trying a solution:

$$c_i(t) = e^{-i\Delta_i t/\hbar} \quad\Rightarrow\quad \Delta_i = \left(\frac{\hbar}{-i}\right)\frac{\dot{c}_i}{c_i} = V_{ii} + \sum_{n\neq i}\frac{|V_{ni}|^2}{E_i-E_n+i\hbar\eta}$$

Now we want to take $\eta \to 0$. Use:

$$\lim_{\eta\to 0} \frac{1}{x+i\eta} = P_r\left(\frac{1}{x}\right) - i\pi\,\delta(x) \equiv \begin{cases} 1/x & (\text{for } x \neq 0), \\ -i\pi\,\delta(x) & (\text{for } x = 0). \end{cases}$$

So
$$\boxed{\Delta_i = V_{ii} + \sum_{E_n \neq E_i} \frac{|V_{ni}|^2}{E_i - E_n} - i\pi \sum_{n\neq i} |V_{ni}|^2\,\delta(E_n - E_i)}$$

So the state formerly known as $|i\rangle$, in Interaction picture:

$$|\psi\rangle_I = e^{-i\Delta_i t/\hbar}\,|i\rangle.$$

In Schrodinger picture:
$$|\psi\rangle = e^{-i(E_i^{(0)}+\Delta_i)t/\hbar}\,|i\rangle$$

So $E_i^{(0)} \to E_i^{(0)} + \Delta_i$ Also, $\boxed{\Gamma_i = 2\pi \sum_{n\neq i} |V_{ni}|^2\,\delta(E_n - E_i)}$ (Note: positive definite.)

Γ_i is akin to 2nd-order shift in energy.

Complex $\Delta_i \Leftrightarrow$ state $|i\rangle$ is decaying

$$|c_i|^2 = e^{-\Gamma_i t/\hbar} \qquad (\to 0 \text{ as } t \to \infty)$$

A check $\quad 1 = |c_i|^2 + \sum_{n\neq i} |c_n|^2 = (1 - i\Gamma_i t/\hbar + \dots) + \sum_{n\neq i} w_{i\to n}\, t + \dots$

cancel ✓

Mean lifetime τ of $|i\rangle$:

$$|c_i|^2 = e^{-t/\tau} \quad \Rightarrow \quad \boxed{\tau = \hbar/\Gamma_i}$$

Why "decay width"?

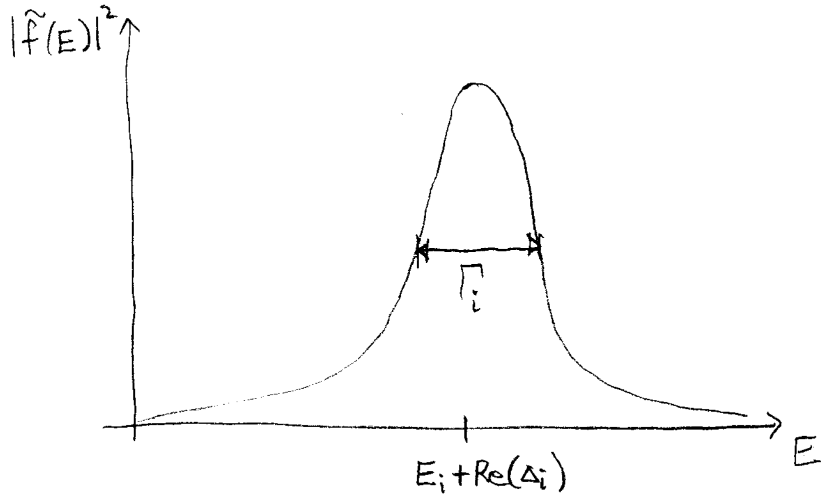
Look at the factor $f(t) = e^{-i(E_i+\Delta_i)t/\hbar}$ in front of $|i\rangle$ in Schrodinger picture.

Fourier transform with respect to t:

$$\int_{-\infty}^{\infty} \tilde{f}(E)\, e^{-iEt/\hbar}\, dE = f(t) = e^{-i(E_i + \mathrm{Re}(\Delta_i))t/\hbar}\, e^{-\Gamma_i t/2\hbar}$$

$$\tilde{f}(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{iEt/\hbar} f(t)\, \frac{dt}{\hbar}$$

Get: $|\tilde{f}(E)|^2 \propto \dfrac{1}{(E_i + \mathrm{Re}(\Delta_i) - E)^2 + \Gamma_i^2/4}$



So Γ_i = full width at half max of the energy distribution of the evolution of $|i\rangle$ in the Schrodinger picture

Claim (without proof):

If instead $V \to \tilde{V} e^{i\omega t} + \tilde{V}^\dagger e^{-i\omega t}$, then

$$\Gamma_i = 2\pi \sum_{n \neq i} |\tilde{V}_{ni}|^2 \left[\delta(E_n - E_i + \hbar\omega) + \delta(E_n - E_i - \hbar\omega) \right]$$

The energy of the state $|i\rangle$ is "smeared out" over a width Γ_i, even if it is a (naively discrete) bound state.