

or,

$$\langle n | H_2 | i \rangle = \frac{2\pi}{\sqrt{\omega\omega'}} \hat{\epsilon} \cdot \hat{\epsilon}'^* \delta_{BA}$$

Evaluation of

$$\langle B\lambda' | \frac{1}{2c^2} \vec{A}(x)^2 | A\lambda \rangle$$

where  $\hat{\epsilon} = \hat{\epsilon}_\lambda$ ,  $\hat{\epsilon}' = \hat{\epsilon}_{\lambda'}$ ,  $\omega = \omega_\lambda$ ,  $\omega' = \omega_{\lambda'}$ .

Before proceeding to the  $H_i^2$ -term, we show how these terms are associated with Feynman diagrams. A Feynman diagram is basically a space-time diagram showing the interactions of various particles. The diagrams correspond to terms in the transition amplitude; thus, each diagram is a complex number.

The time sequence of events (particle interactions) in a diagram comes from the Dyson series in TDPT. Recall that the Dyson series is

$$\begin{aligned} |\psi_I(t)\rangle &= |i\rangle + \frac{1}{i\hbar} \int_0^t dt' H_{iI}(t') |i\rangle \\ &\quad + \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' H_{iI}(t') H_{iI}(t'') |i\rangle + \dots \end{aligned}$$

This is a power series in  $H_i$ , a solution of the t-dep. Sch. eqn in the interaction picture with init. condns  $|\psi_I(0)\rangle = |i\rangle$ .

$H_{iI}(t)$  is  $H_i$  in the interaction picture; it is t-dep. even when  $H_i$  (Sch. picture) is not, hence  $H_{iI}(t)$  at different

times do not commute. In the 2nd order term of the Dyson series we have an ordering of times:

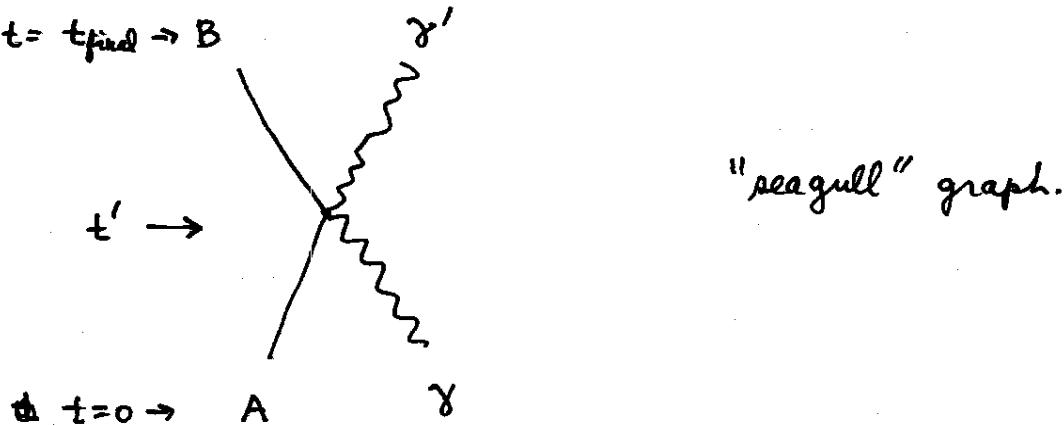
$$t \geq t' \geq t'' \geq 0$$

( $t =$  final time,  $0 =$  initial time,  $t', t'' =$  sequenced pair of intermediate times). As we say, in the second order term, the initial state  $|i\rangle$  is unchanged until  $t''$  when it is acted upon by  $H_{1I}(t'')$ , after which it is unchanged until  $t'$  when it is acted upon by  $H_{1I}(t')$ , after which it is unchanged until the final time  $t$ . The 2nd order contribution to the transition amplitude is the sum (integral) of all such contributions, for all possible (ordered) values of  $t'$  and  $t''$ .

Similarly, the 1st order term in the Dyson series involves interacting with ~~H<sub>1I</sub>~~  $H_{1I}$  at one intermediate time  $t'$ , and the 0th order term involves no interaction. Similarly for higher order terms.

To go back to our problem, the term  $\langle n | H_2 | i \rangle$  involves the 2nd order Hamiltonian, but comes from the 1st order term in the Dyson series. Thus there is one interaction with  $H_2$  at one intermediate time. This interaction kills the incident photon  $\lambda$  and creates the final photon  $\lambda'$ . Thus the Feynman diagram

is:  $t = t_{\text{final}} \rightarrow B$



Here time runs vertically. In the matrix element, time runs from right to left:

$$\langle n | H_2 | i \rangle$$

$\uparrow \quad \uparrow \quad \uparrow$   
 $t \quad t' \quad t=0$

Now we turn to the  $H_i^2$  term in the transition amplitude:

$$\sum_k \frac{\langle n | H_i | k \rangle \langle k | H_i | i \rangle}{E_k - E_i}. \quad (\text{general notation}).$$

Here  $k$  runs over a complete set of states of the matter + field system, in particular, it must include states of any number of photons ( $0, 1, 2, \dots$ ). But  $|i\rangle = |A\rangle$  and  $|n\rangle = |B\rangle$  contain only one photon, and  $H_i$  can create or destroy one photon, nothing else, so the only intermediate states  $|k\rangle$  that give nonvanishing matrix elements are those with either 0 or 2

photons. So there are 2 cases:

Case I: Intermediate state  $|Ik\rangle$  contains 0 photons. First  $H_i$  annihilates incident  $\gamma$ , second  $H_i$  creates final  $\gamma'$ .

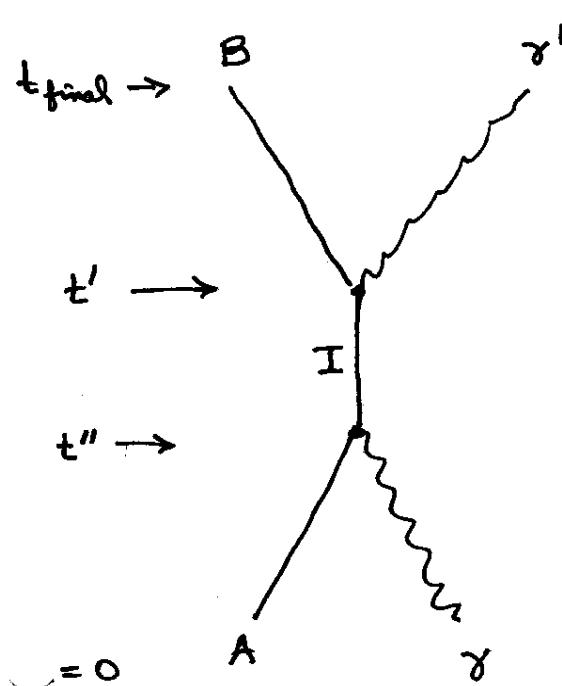
Case II: Int. state  $|Ik\rangle$  contains 2 photons. These must have modes  $\gamma, \gamma'$ . First  $H_i$  creates  $\gamma'$ , second destroys  $\gamma$ .

Thus:

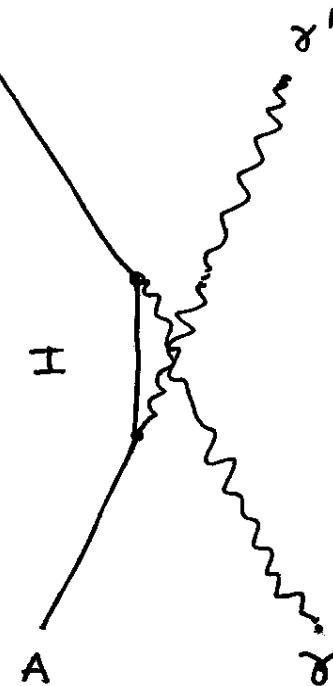
$$\text{Case I: } |Ik\rangle = |I\rangle |0\rangle = |I\rangle.$$

$$\text{Case II: } |Ik\rangle = |I\rangle a_x^+ a_x^- |0\rangle = |I\rangle \langle \gamma \gamma' |.$$

And corresponding Feynman diagrams:



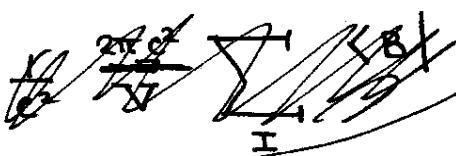
Case I



Case II

In Case I, the contribution to the scattering amplitude is

$$\sum_k \frac{\langle m | H_i | k \rangle \langle k | H_i | i \rangle}{E_i - E_k} \xrightarrow{\text{case I}} \sum_I \frac{\langle B\lambda' | H_i | I \rangle \langle I | H_i | A\lambda \rangle}{E_A + \omega - E_I}$$



$$= \frac{1}{c^2} \frac{2\pi c^2}{V} \frac{1}{\sqrt{\omega\omega'}} \sum_I \frac{\langle B | (\vec{p} \cdot \hat{\epsilon}'^*) | I \rangle \langle I | (\vec{p} \cdot \hat{\epsilon}) | A \rangle}{\omega - \omega_{IA}},$$

where field matrix elements have been taken and  $\omega_{IA} = E_I - E_A$

( $\hbar=1$  here). Similarly, for case II we have

$$\sum_I \frac{\langle B\lambda' | H_i | I\lambda\lambda' \rangle \langle I\lambda\lambda' | H_i | A\lambda \rangle}{(E_A + \omega) - (E_I + \omega + \omega')}$$

$$= \frac{1}{c^2} \frac{2\pi c^2}{V} \frac{1}{\sqrt{\omega\omega'}} \sum_I \frac{\langle B | (\vec{p} \cdot \hat{\epsilon}) | I \rangle \langle I | (\vec{p} \cdot \hat{\epsilon}'^*) | A \rangle}{-\omega_{IA} - \omega'}$$

Putting it all together, we get the total transition amplitude,

$$C_m^{\text{eff}}(t) = -2i e^{i\omega_{ni}t/2} \left( \frac{\sin \omega_{ni}t/2}{\omega_{ni}} \right) \cdot \frac{2\pi}{V} \frac{1}{\sqrt{\omega\omega'}} \left\{ \hat{\vec{\epsilon}} \cdot \hat{\vec{\epsilon}}'^* \delta_{BA} \right.$$

$$\left. + \sum_I \left[ \frac{\langle B | \vec{p} \cdot \hat{\vec{\epsilon}}'^* | I \rangle \langle I | \vec{p} \cdot \hat{\vec{\epsilon}} | A \rangle}{\omega - \omega_{IA}} - \frac{\langle B | \vec{p} \cdot \hat{\vec{\epsilon}} | I \rangle \langle I | \vec{p} \cdot \hat{\vec{\epsilon}}'^* | A \rangle}{\omega' + \omega_{IA}} \right] \right\}$$

(7)

Now compute the cross section for  $\gamma + A \rightarrow B + \gamma'$ . States  $\gamma, A, B$

are given, only  $\gamma'$  is variable (and then only its direction and polarization, not its energy), so we want  $d\sigma/d\Omega'$  ( $\Omega' = \text{solid angle for } \vec{k}' \text{ of photon } \gamma'$ ). The cross section is the transition rate divided by the incident flux. This is

$$J_{\text{inc}} = \frac{1}{V} c = \frac{c}{V}$$

since there is one incident photon ( $\gamma$ ) in the box, with velocity  $c$ . Thus,

$$\frac{d\sigma}{d\Omega'} = \frac{V}{c} \frac{1}{\Delta\Omega'} \frac{1}{t} \sum_{\substack{\vec{k}' \in \text{cone}}} |C_{B\lambda'}(t)|^2$$

where  $\lambda' = (\vec{k}' \mu')$  and  $n = B\lambda'$  (label of final state).  $C_{B\lambda'} = C_n$  given p. 6.

on ~~last page of notes~~. This gives

$$\frac{d\sigma}{d\Omega'} = \frac{V}{c} \frac{1}{\Delta\Omega'} \frac{1}{t} \sum_{\substack{\vec{k}' \in \text{cone}}} 4 \frac{\pi}{2} t \delta(\omega' + E_B - \omega - E_A) \frac{(2\pi)^2}{V^2} \frac{1}{\omega\omega'} |\{ \}|^2$$

where the cone is small cone centered about some final direction, and  $\{ \}$  is the main part of the transition amplitude,

$$\{ \} = \hat{\epsilon}^A \cdot \hat{\epsilon}'^* \delta_{BA} + \sum_I \left[ \frac{\langle B | \vec{p} \cdot \hat{\epsilon}'^* | I \rangle \langle I | \vec{p} \cdot \hat{\epsilon} | A \rangle}{\omega - \omega_{IA}} - \frac{\langle B | \vec{p} \cdot \hat{\epsilon} | I \rangle \langle I | \vec{p} \cdot \hat{\epsilon}'^* | A \rangle}{\omega' + \omega_{IA}} \right]$$

Now take  $V \rightarrow \infty$  and replace,

$$\sum_{\substack{\vec{k}' \in \text{cone}}} \rightarrow \frac{V}{(2\pi)^3} \Delta\Omega' \int_0^\infty k'^2 dk',$$

$$\text{also } \delta(\omega_{ni}) = \delta(\omega' + E_B - \omega - E_A) \\ = \delta(\omega' - \omega + \omega_{BA}) = \frac{1}{c} \delta(k' - k'_f),$$

where  $k'_f$  is the value of  $k'$  determined by energy conservation. Then clean it up, get

$$\frac{d\sigma}{d\Omega'} = \frac{1}{c^2} \frac{k'^2}{\omega\omega'} |\{f\}|^2 \Big|_{k'=k'_f} \\ = \frac{1}{c^4} \frac{\omega'}{\omega} |\{f\}|^2$$

where it is now understood that  $k' = k'_f$ . This is in atomic units. Treat  $\{f\}$  as dimensionless, use  $\frac{1}{c^4} = \alpha^4$ , and convert to ordinary units by multiplying by  $a_0^2$  (unit of area in a.u.,  $a_0 = \text{Bohr radius}$ ). Then

$$\boxed{\frac{d\sigma}{d\Omega'} = \alpha^4 a_0^2 \frac{\omega'}{\omega} |\{f\}|^2 = r_e^2 \frac{\omega'}{\omega} |\{f\}|^2}$$

where

$$r_e = \alpha^2 a_0 = \frac{e^2}{mc^2} = 2.8 \times 10^{-13} \text{ cm} = \text{"classical radius of electron".}$$

With  $\{f\}$  given on p.7, this is the Kramers-Heisenberg formula. It was first derived using the methods of the old quantum theory.

First note the order of magnitude. For optical photons in atoms, the transition amplitude  $\{f\}$  contains only quantities that

$\Omega(1)$  in a.u. Thus  $\{\}$  =  $\Omega(1)$ , unless one of the denominators (such as  $\omega - \omega_{IA}$ ) should be small. That occurs when the <sup>incident</sup> photo energy is near an atomic transition energy (an atomic resonance). We come back to that question later, and for now look just at the case where  $\omega$  is not too close to any  $\omega_{IA}$ . (If the state A is an excited state, so that  $\omega_{IA}$  can take on negative values, then there is a similar problem in the 3rd term of  $\{\}$ .) Thus,  $\{\} = \Omega(1)$  and  $\frac{d\sigma}{d\Omega'} = \Omega(\alpha^4) \sim 10^{-9}$  a.u. This is very small by atomic standards, e.g., electron-atom scattering at comparable ( $\omega$ ) energies has a cross section =  $\Omega(1)$  a.u. This is why ordinary gases are transparent to optical radiation unless in very thick depth.

Next consider the case of elastic scattering, that is,  $B=A$ . This means  $\omega=\omega'$  (by conservation of energy), so there is a little simplification:

$$\left(\frac{d\sigma}{d\Omega'}\right)_{\text{elastic}} = r_e^2 |\{\}|^2$$

where

$$\{\}_{\text{elastic}} = \hat{\epsilon} \cdot \hat{\epsilon}'^* + \sum_{I \neq A} \left[ \frac{\langle A | \hat{\epsilon}^* \cdot \hat{p} | I \rangle \langle I | \hat{\epsilon}' \cdot \hat{p} | A \rangle}{\omega - \omega_{IA}} - \frac{\langle A | \hat{\epsilon} \cdot \hat{p} | I \rangle \langle I | \hat{\epsilon}'^* \cdot \hat{p} | A \rangle}{\omega + \omega_{IA}} \right]$$

We exclude  $I=A$  term because it vanishes anyway (note  $\omega_{IA}=0$  when  $I=A$ ).

In this case it is possible to combine the first (seagull) term

with the other 2 terms. To begin, let's write the electric matrix element in terms of a certain tensor  $T_{ij}$ :

$$\{F\}_{\text{electric}} = \sum_{ij} \hat{\epsilon}_i^* T_{ij} \hat{\epsilon}_j = \hat{\epsilon}^* \cdot \vec{T} \cdot \hat{\epsilon}$$

↑ incident photon  
 ↓ scattered photon

where

$$T_{ij} = \delta_{ij} + \sum_{I \neq A} \left[ \frac{\langle A | p_i | I \rangle \langle I | p_j | A \rangle}{\omega - \omega_{IA}} - \frac{\langle A | p_j | I \rangle \langle I | p_i | A \rangle}{\omega + \omega_{IA}} \right]$$

Now let's do some "reverse engineering" on the term  $\delta_{ij}$ , which came from the seagull graph. That is, we "unimplify" it to make it look like the sum. Do this:

$$\begin{aligned}
 \delta_{ij} &= \langle A | \delta_{ij} | A \rangle && (\text{use } \delta_{ij} = -i [x_i, p_j]) \\
 &= -i \langle A | x_i p_j - p_j x_i | A \rangle && (\text{insert } \sum_I |I\rangle \langle I|) \\
 &= -i \sum_I \left[ \langle A | x_i | I \rangle \langle I | p_j | A \rangle - \langle A | p_j | I \rangle \langle I | x_i | A \rangle \right] \\
 &\quad \cancel{\text{swap } i,j} \quad \cancel{\text{use } \delta_{ij} = \delta_{ji}} \\
 &= +i \sum_{I \neq A} \left[ \langle A | p_i | I \rangle \langle I | x_j | A \rangle - \langle A | x_j | I \rangle \langle I | p_i | A \rangle \right]
 \end{aligned}$$

where we can exclude  $I=A$  term since it vanishes anyway.

Now for the major sum in  $T_{ij}$  above use the atomic physics trick for converting momentum matrix elements to position matrix elements,  $\vec{p} = -i [\vec{x}, H_0]$ , where  $H_0$  is the

atomic Hamiltonian of which  $|A\rangle, |I\rangle, |B\rangle$  etc. are eigenstates.

Thus,

$$\begin{aligned}\langle I | p_j | A \rangle &= -i \langle I | x_j H_0 - H_0 x_j | A \rangle = -i (\epsilon_A - \epsilon_I) \langle I | x_j | A \rangle \\ &= +i \omega_{IA} \langle I | x_j | A \rangle\end{aligned}$$

Similarly,

$$\langle A | p_j | I \rangle = -i \omega_{IA} \langle A | x_j | I \rangle \quad (\text{take h.c. of above}).$$

So,

$$T_{ij} = i \sum_{I \neq A} \left[ \langle A | p_i | I \rangle \langle I | x_j | A \rangle - \langle A | x_j | I \rangle \langle I | p_i | A \rangle \right]$$

$$+ i \sum_{I \neq A} \left[ \left( \frac{\omega_{IA}}{\omega - \omega_{IA}} \right) \langle A | p_i | I \rangle \langle I | x_j | A \rangle + \left( \frac{\omega_{IA}}{\omega + \omega_{IA}} \right) \langle A | x_j | I \rangle \langle I | p_i | A \rangle \right]$$

$$T_{ij} = -i \omega \sum_{I \neq A} \left[ \frac{\langle A | p_i | I \rangle \langle I | x_j | A \rangle}{\omega_{IA} - \omega} + \frac{\langle A | x_j | I \rangle \langle I | p_i | A \rangle}{\omega_{IA} + \omega} \right].$$

Use the atomic trick again,  $p_i = -i [x_i, H_0]$ , and we get

$$T_{ij} = \omega \sum_{I \neq A} \omega_{IA} \left[ \frac{\langle A | x_i | I \rangle \langle I | x_j | A \rangle}{\omega_{IA} - \omega} - \frac{\langle A | x_j | I \rangle \langle I | x_i | A \rangle}{\omega_{IA} + \omega} \right]$$

This is an exact result for the case of elastic scattering.

Now suppose A is the ground state of the atom. Then the sum on  $I \neq A$  is a sum over all excited states, and  $\omega_{IA}$  is  $> 0$  for all I. Suppose as a special case that  $\omega \ll \text{any } \omega_{IA}$  (that is,

$\omega \ll \omega_{IA}$  connecting the ground state with the first excited state.

$$\begin{array}{c} \hline \\ \hline \\ \hline \end{array} \begin{array}{c} I \\ \hline \\ \hline \\ \hline \end{array}$$

$$\begin{array}{c} \hline \\ \hline \\ \hline \end{array} A$$

This is the small (low) frequency limit. Then

$$\frac{\omega_{IA}}{\omega_{IA} + \omega} = 1 \pm \frac{\omega}{\omega_{IA}} \quad \text{to 1st order in } \omega.$$

$\uparrow \quad \uparrow$   
 const term       $\Theta(\omega)$  term.

The constant term is

$$\omega \sum_{I \neq A} \left[ \langle A | x_i | I \rangle \langle I | x_j | A \rangle - \langle A | x_j | I \rangle \langle I | x_i | A \rangle \right]$$

to which we can include the  $I=A$  term since it is 0 anyway, and we get resolutions of the identity  $\sum_I |I\rangle \langle I|$ , thus

$$\rightarrow = \omega \left[ \langle A | x_i x_j | A \rangle - \langle A | x_j x_i | A \rangle \right] = 0 \quad \text{since } [x_i, x_j] = 0.$$

So to  $\Theta(\omega)$  we get

↓ (elastic,  $\omega \ll \omega_{IA}$ )

$$T_{ij} = \omega^2 \sum_{I \neq A} \left[ \frac{\langle A | x_i | I \rangle \langle I | x_j | A \rangle}{\omega_{IA}} + \frac{\langle A | x_j | I \rangle \langle I | x_i | A \rangle}{\omega_{IA}} \right].$$

As a special, consider optical radiation passing through gases such as  $H_2, N_2, O_2$ . These have their first excited electronic state in the UV, so  $\omega < \omega_{IA}$ . The ratio  $\frac{\omega}{\omega_{IA}}$  might be  $\frac{1}{2}$

or  $1/3$  (it depends on  $\omega$ ) but it's not terribly small. Nevertheless as a rough estimate the small  $\omega$  formula is not bad. It shows that the scattering cross section is proportional to  $\omega^4$ . Thus the blue photons are 10-20 times more likely to be scattered than the red photons. This explains why the sky is blue, and also why sunsets are red. This small  $\omega$  result is called Rayleigh scattering.

The final form of the tensor  $T_{ij}$  is proportional to the polarizability tensor that we studied in connection with the Stark effect. This tensor gives the induced dipole moment of a system in terms of an applied electric field:

$$\vec{p} = \alpha \cdot \vec{E} \quad \text{or} \quad p_i = \sum_j \alpha_{ij} E_j$$

$\uparrow$        $\uparrow$  applied  $\vec{E}$   
dipole moment

In fact, the final form of  $T_{ij}$  is  $-\omega^2 \alpha_{ij}$ . This is the DC polarizability tensor, which appears when ~~colls~~  $\omega \ll \omega_{IA}$ . The physics is that the incident light wave induces an oscillating dipole moment in the atom, which radiates the scattered wave. For a detailed discussion of this problem at the classical level, see Jackson's book.

(14)

Another case of elastic scattering is  $\omega \gg \text{any } \omega_{IA}$ . Then the term  $\hat{\epsilon} \cdot \hat{\epsilon}'^*$  (the seagull graph) dominates, because the denominators  $\omega \pm \omega_{IA} \rightarrow \infty$  and kill the second term (p.6 or p.7). Then we have simply,

$$\frac{d\sigma}{d\Omega'} = r_e^2 |\hat{\epsilon} \cdot \hat{\epsilon}'^*|^2.$$

The physics is that if  $\omega \gg \text{any } \omega_{IA}$ , then  $\omega \gg \text{the binding energy of the } \text{~~at~~} \text{ electron}$ , and ...

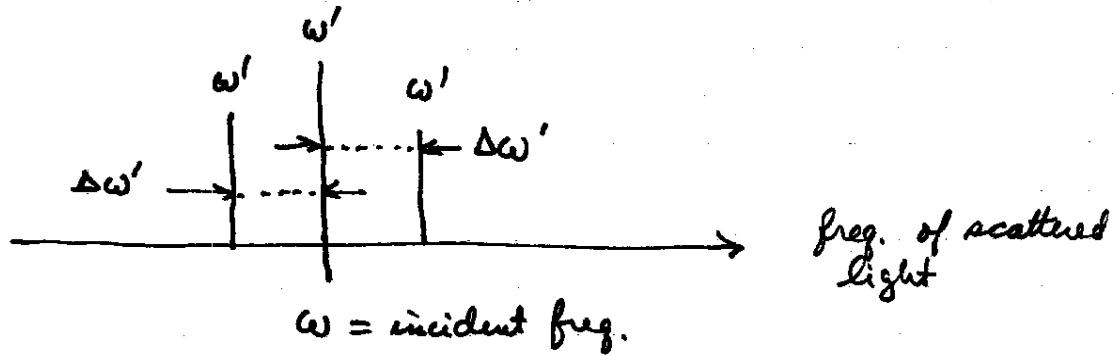
the photon interacts with the electron as if it were free. In fact, this cross section is that of scattering of a photon off a free electron, so-called Thompson scattering. The photon should have an energy  $\hbar\omega \ll mc^2$ , otherwise the process is called Compton scattering. The formula above is only valid for Thompson scattering (a more complicated formula applies when  $\hbar\omega \sim mc^2$  or  $> mc^2$ , the so-called Klein-Nishina cross section).

In Thompson scattering the outgoing photon is polarized even if the incident photon is not. Sakurai analyzes the polarization in Thompson scattering in some detail. Thinking of what could influence the angular dependence of the cross-section, we see that the electron polarization (the spin state) does not enter. This is because we made the dipole approximation (neglecting terms of order  $\vec{r} \cdot \vec{r} \sim O(\alpha)$ ), which means the electron only interacts with the light wave through the electric field (magnetic effects neglected). The relativistic version of the Thompson cross section, the Klein-Nishina formula, does depend on the spin.

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Another example of the Kramers-Heisenberg formula is the Raman scattering, which we describe in the most qualitative terms. Raman scattering is inelastic. Typically an example involves

the passage of optical radiation through a molecular gas ( $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , etc) and observing <sup>the</sup> scattered light. There is a line at  $\omega' = \omega$  (elastic scattering), but typically other lines shifted above and below by a frequency  $\Delta\omega'$  small compared to  $\omega$ .



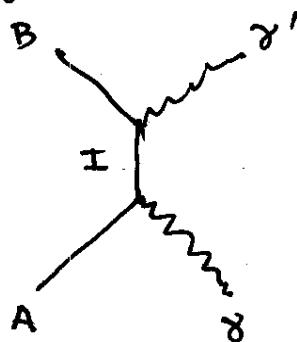
The  $\Delta\omega'$  corresponds to the absorption ( $\Delta\omega' < 0$ ) or emission ( $\Delta\omega' > 0$ ) of ~~energy released due to~~ vibrational energy by the molecule, so  $\omega'$  differs from  $\omega$  by  $\Delta E_{\text{vib}}/\hbar$ , where  $\Delta E_{\text{vib}}$  ~~=~~ is the difference between two vibrational states of the molecule.  $\Delta\omega' = \Delta E_{\text{vib}}/\hbar$  is typically in the infrared, so  $\Delta\omega' \ll \omega \approx \omega$ . In the harmonic oscillator approximation for molecular vibrations,  $\Delta\omega' = \omega_{\text{vib}}$ , the vibrational frequency. The lines with  $\Delta\omega' < 0$  are called Stokes lines, those with  $\Delta\omega' > 0$  are anti-Stokes lines. Anti-Stokes lines are usually weaker than Stokes lines, because the populations of excited vibrational states are suppressed by the Boltzmann factor.

Now we consider resonance fluorescence, which is what

happens when the incident frequency  $\omega$  is close to some  $\omega_{IA}$ .

For simplicity let's consider only elastic scattering ( $\omega = \omega'$ , see p.3 for the transition amplitude), and we assume  $A = \text{ground state}$ .

Then the sum  $\sum_{I \neq A}$  means summing over all excited states of the atom or molecule, and when  $\omega$  is close to some  $\omega_{IA}$ , then one term in the sum dominates the entire cross section. This term has the diagram,

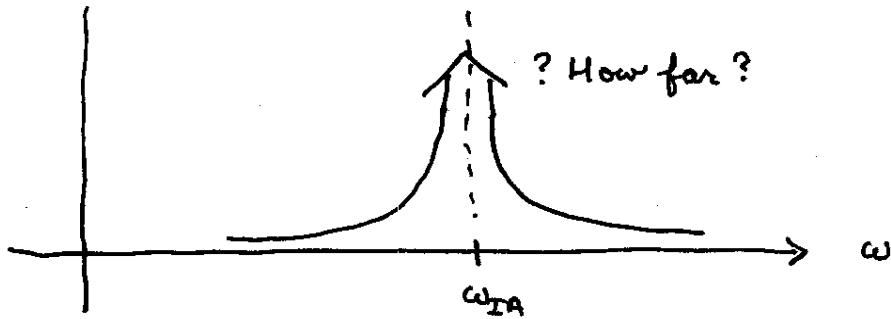


So it means that the incident energy  $E_A + \hbar\omega \approx E_I$  = energy of intermediate state. Obviously at such energy we would expect the incident photon to be absorbed, lifting the atom into the state I. This state could then decay,  $I \rightarrow A$ , emitting photon  $\gamma'$ .

The nominal prediction of the K-H formula is that  $d\sigma/d\Omega' \rightarrow \infty$  when  $\omega \rightarrow \text{some } \omega_{IA}$ . This is nonphysical, and in fact  $d\sigma/d\Omega'$  must saturate at some finite value when  $\omega = \omega_{IA}$ . Questions are: What is wrong with the K-H formula when  $\omega \approx \omega_{IA}$ ? How close can we come to  $\omega = \omega_{IA}$  before the K-H formula breaks down? And how high does

$d\sigma/d\omega'$  actually go when  $\omega = \omega_{IA}$ ?

$(d\sigma/d\omega')$



To answer these questions, we put the K-H formula on hold, and turn to the problem of the long-time behavior of quantum systems in time-dependent perturbation theory.