Interaction between EM radiation and hydrogen-like atoms: semiclassical theory

References

- B.H. Bransden & C.J. Joachain, “Physics of atoms and molecules”, 2nd edition, Pearson Education – Prentice Hall (2003)
  Chapter 4 (except 4.4), in parts

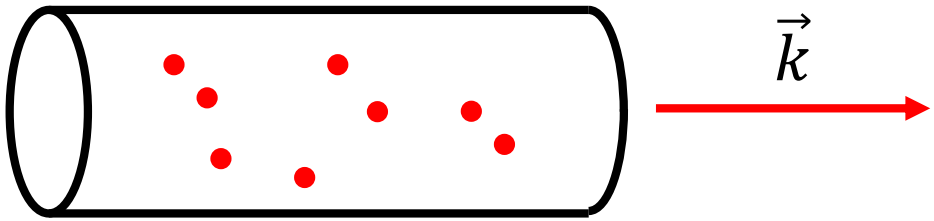
Introduction

- Semi-classical theory of the interaction between radiation and hydrogen – like atoms.
- Semi-classical since
  - Radiation is treated as wave
  - Atom is treated with quantum mechanics
- This approach is adequate since it can describe scattering and stimulated absorption and emission
  - It cannot describe spontaneous emission
- Full quantum treatment requires quantization of EM field: more formal
- All phenomena occurring in hydrogen – like atoms are present in many electron ones

A monochromatic photon beam

- Even within the semi-classical approach we will find that absorption and emission of energy between the beam and atoms occurs in quanta of magnitude $\hbar\omega$, that is photons
- Even scattering will be describe in terms of photons.
- Therefore: extend definitions of intensity and flux in particle – like terms.

Monochromatic radiation beam: definitions



$N =$

(Number of photons which cross a surface perpendicular to $\vec{k}$)/ (unit time)

I : Intensity = (Energy crossing the surface) / (unit time)

Φ : Photon flux =
(Number of photons crossing the surface) / (unit time × area)

F: Energy flux= (Energy crossing the surface) / (unit time × area)

$$I = N\hbar\omega \qquad F = \frac{N}{A}\hbar\omega \qquad F = \Phi\ \hbar\omega$$

Interaction between a wave and an atom

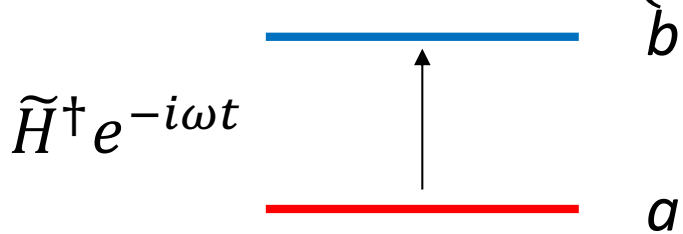
- The interaction is treated with time dependent pertubation theory
- The unperturbed atom's Hamiltonian is H_o
- The pertubation is an EM wave and the time dependent interaction Hamiltonian is $H'(t)$
- The EM wave has a harmonic dependence on time, thus it is expressed by an Hermitian operator of the type

$$H'(t) = \widetilde{H}e^{i\omega t} + \widetilde{H}^{\dagger}e^{-i\omega t}$$

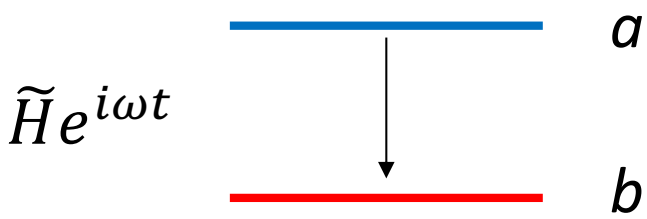
in which $\widetilde{H}$ is an operator which does not depend on time

Time dependent perturbation theory

- The unpertubed atom has eigenstates labelled «a» and «b» with energies ${E_a}^0$ and ${E_b}^0$
  - ➢ Often called the «initial» and «final» states
- It can be demonstrated that the transition probability is maximized for two «resonant» conditions deriving from different terms in $H'(t)$

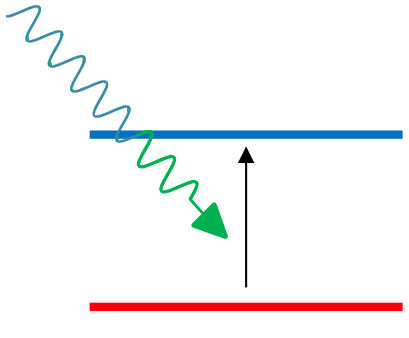


$$\hbar\omega = {E_b}^0 - {E_a}^0$$



$$\hbar\omega = {E_a}^0 - {E_b}^0$$

Time dependent perturbation theory

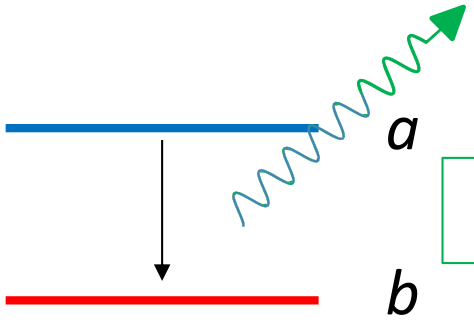


$\tilde{H}^{\dagger} e^{-i\omega t}$

$$\hbar\omega = E_b{}^0 - E_a{}^0$$

Stimulated absorption

- A photon of energy $\hbar\omega$ is absorbed by the atom
- The atom makes a transition from *a* to *b*



$\tilde{H} e^{i\omega t}$

$$\hbar\omega = E_a{}^0 - E_b{}^0$$

Stimulated emission

- A photon of energy $\hbar\omega$ is emitted from the atom
- The atom makes a transition from *a* to *b*

Fermi's golden rule: transition to discrete states

- For the case of absorption it can be demonstrated that, to first order in the pertubation, the transition probability per unit time for transitions between discrete levels *a* and *b* is

$$W_{ba} = \frac{2\pi}{\hbar}\left|\tilde{H}^{\dagger}{}_{ba}\right|^2 \delta\left(E_b{}^0 - E_a{}^0 - \hbar\omega\right)$$

- $\tilde{H}^{\dagger}{}_{ba} = \langle b|\tilde{H}^{\dagger}|a\rangle$ is the matrix element of the perturbation
- The Dirac δ function is an expression of the conservation of energy
  - Apparently unphysical: the probability is always 0 except at resonance in which case it diverges. This will be resolved by introducing the concept of lifetime of the eigenstates

Fermi's golden rule: transition to continuum states

- For absorption with final states b in the continuum it can be shown that

$$W_{ba} = \frac{2\pi}{\hbar}\left|\tilde{H}^{\dagger}{}_{ba}\right|^2 \rho\left({E_b}^0\right)$$

with the condition that ${E_b}^0 = {E_a}^0 + \hbar\omega$

- $\rho(E)$ is the density of states, such that the number of states between E and $E + dE$ is

$$dN = \rho(E)\, dE$$

The classical EM field

- The EM field is described in terms of the vector and scalar potentials $\vec{A}(\vec{r},t)$ and $\phi(\vec{r},t)$

;

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\varphi(\vec{r},t) - \frac{\partial \vec{A}(\vec{r},t)}{\partial t}$$ Electric field

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A}(\vec{r},t).$$ Magnetic induction field

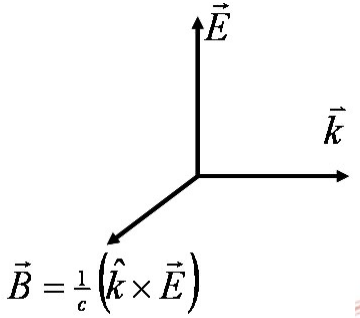
A plane monochromatic EM wave

$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^*(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

$$\vec{E}(\vec{r},t) = -\frac{\partial\vec{A}(\vec{r},t)}{\partial t} = i\omega\hat{\varepsilon}\left[-A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^*(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

$$\vec{B}(\vec{r},t) = \frac{1}{c}\left(\hat{k}\times\vec{E}\right) = i\left(\vec{k}\times\hat{\varepsilon}\right)\left[-A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^*(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

- The polarization is defined by $\hat{\varepsilon}$.
  It can be linear or circular
- $A(\omega)$ determines the amplitude and intensity of the wave
  - Actually it is real, but we keep the complex notation for consistency



Interaction Hamiltonian

- The unpertubed Hamiltonian for a H – like atom with nucleus of charge *Z* is

$$H_0 = \frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r}$$

- It can be proved that the total Hamiltonian, including the interaction term is

$$H = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r} - i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2$$

Interaction Hamiltonian

$$H = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r} - i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2$$

- Two pertubation terms: one linear and the other quadratic in $\vec{A}$
- Consider now the linear term

$$H' = -i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla}$$

- Since $\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$ it is precisely of the form

$$H'(t) = \widetilde{H}e^{i\omega t} + \widetilde{H}^{\dagger}e^{-i\omega t}$$

considered in time dependent pertubation theory

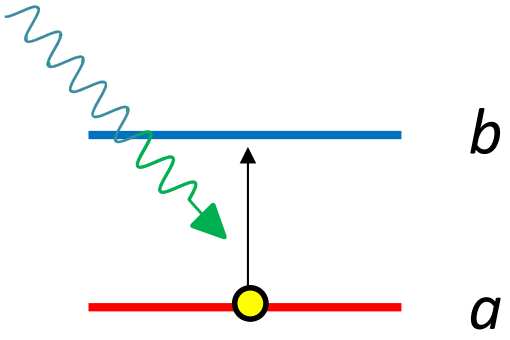
  - $\widetilde{H} = \hat{\varepsilon}A(\omega)e^{-i\vec{k}\cdot\vec{r}}$, $\widetilde{H}^{\dagger} = \hat{\varepsilon}A(\omega)e^{i\vec{k}\cdot\vec{r}}$

Interaction Hamiltonian

$$H' = -i\hbar \frac{e}{m} \vec{A} \cdot \vec{\nabla}$$

$$H'(t) = \tilde{H} e^{i\omega t} + \tilde{H}^{\dagger} e^{-i\omega t}$$

- This term describes stimulated absorption and emission processes. Let's concentrate on absorption, also aptly called photoelectric absorption since in the atom an electron makes a transition induced by the absorption of a photon.
- Absorption is due to $\tilde{H}^{\dagger} e^{-i\omega t}$, emission to $\tilde{H} e^{i\omega t}$



Cross section for photoelectric absorption

- Use Fermi's golden rule. Consider transitions between discrete bound states *a* and *b*.

$$W_{ba} = \frac{2\pi}{\hbar}\left|\widetilde{H}^{\dagger}{}_{ba}\right|^2 \delta\left({E_b}^0 - {E_a}^0 - \hbar\omega\right)$$

$$\widetilde{H}^{\dagger} = -i\left(\frac{\hbar e}{m}\right)\hat{\varepsilon}A(\omega)e^{i\vec{k}\cdot\vec{r}}\cdot\vec{\nabla}$$

$$W_{ba} = \frac{2\pi}{\hbar}\left(\frac{\hbar^2 e^2}{m^2}\right)A^2(\omega)\left|\langle\psi_b|e^{i\vec{k}\bullet\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\psi_a\rangle\right|^2 \delta\left(E_b^{(0)} - E_a^{(0)} - \hbar\omega\right)$$

Dipole approximation

- Consider the matrix element

$$M_{ba} = \langle \psi_b | e^{i\vec{k}\bullet\vec{r}} \hat{\varepsilon} \cdot \vec{\nabla} | \psi_a \rangle$$

- An important approximation can be performed in most spectral ranges. Re-write the matrix element as an integral in real space:

$$M_{ba} = \int_V d^3r \ \psi_b{}^*(\vec{r}) \, e^{i\vec{k}\cdot\vec{r}} \ \hat{\varepsilon} \cdot \vec{\nabla} \, \psi_a(\vec{r})$$

Dipole approximation

- $M_{ba} = \int_V \; d^3r \; \psi_b{}^*(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}\; \hat{\varepsilon}\cdot\vec{\nabla}\,\psi_a(\vec{r})$
- The spatial extent of the wavefunctions is at most of the order of the typical atomic size $d_a \sim 1$ Å: this determines the maximum effective value of r in the integral
- The modulus of the wavevector is $k = \frac{2\pi}{\lambda}$
- Therefore if the wavelength is such that

$$\frac{2\pi d_a}{\lambda} \ll 1$$

we can make the approximation that

$$e^{i\vec{k}\cdot\vec{r}} = 1$$

Dipole approximation

- For valence initial states the dipole approximation $e^{i\vec{k}\cdot\vec{r}} = 1$ is valid up to the UV.
- For core level initial states of not too light atoms the dipole approximation continues to be valid.

The cross section in the dipole approx.

$$\sigma = 4\pi^2 \ \hbar\omega \ \alpha \ |\langle\psi_b|\hat{\varepsilon}\cdot\vec{r}|\psi_a\rangle|^2 \delta\left(E_b^{(0)} - E_a^{(0)} - \hbar\omega\right)$$

- Clearly, dimensions = L^2
- The order of magnitude is determined by the dipole matrix element, an effective "area" roughly of the order of ${a_0}^2$, depending on the overlap of initial and final wavefunctions
- The Dirac δ function is an expression of the conservation of energy
- The apparent unphysical divergence will be solved introducing the concept of lifetime of states

Selection rules

- Using the properties of the spherical harmonics it can be shown that the selection rule on ℓ is

$$\Delta\ell = \pm 1$$

- The selection rule on m depends on the state of polarization of the radiation
  - For linealy polarized radiation $\Delta m = 0$
  - For circularly polarized radiation $\Delta m = \pm 1$

Selection rules

$$\Delta \ell = \pm 1$$

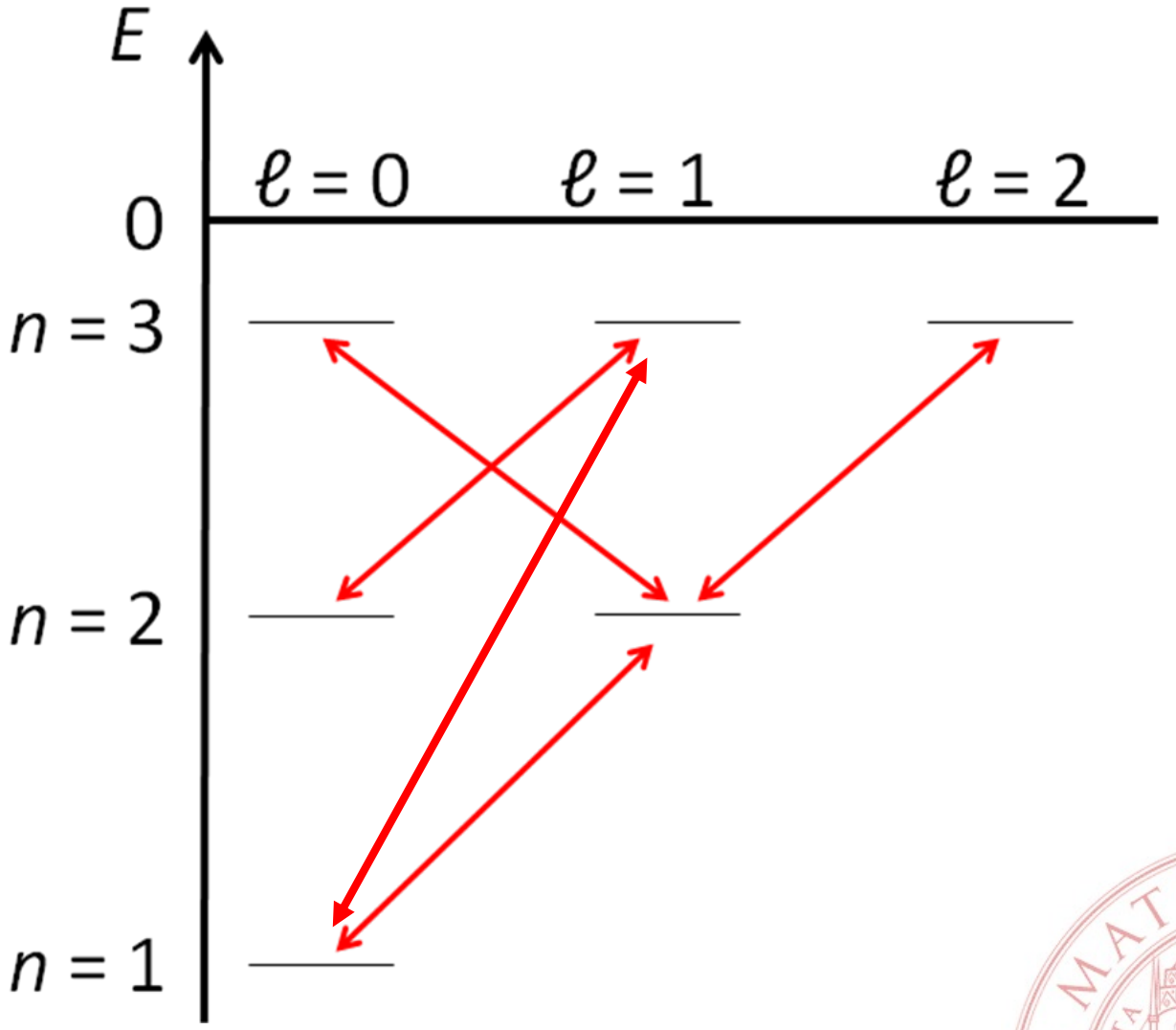
Conservation of angular momentum (modulus)

$$\Delta m = \pm 1$$

Conservation of angular momentum (quantization axis component)

Selection rules

$\Delta\ell = \pm 1$
$\Delta m_\ell = 0, \quad \text{lin}$
$\quad = \pm 1, \quad \text{circ}$



Lifetime and lineshape

- We have implicitly assumed that all atomic eigenstates have infinite lifetime. Apart from the fundamental state (1*s*) this is not true.
- All states have a finite lifetime due to
  - Spontaneous emission, also present for isolated atoms
  - Collisions between atoms, which induce electron transitions, present in gases at non negligible pressure
- If N_0 atoms are in a given state at $t = 0$, their number decays exponentially as

$$N(t) = N_0 e^{-\frac{t}{\tau}}$$

- For the H atom, the lifetimes τ of electronic states are

Level	2p	3s	3p	3d	4s	4p	4d	4f
Lifetime (ns)	1.6	160	5.4	15.6	230	12.4	36.5	73

Lifetime and lineshape

- A finite lifetime implies a spectral broadening
  - Transitions do not occur at a single photon energy

$$\hbar\omega_{ba} = E_b{}^0 - E_a{}^0$$

  - Transitions occur in a band centered around $\hbar\omega_{ba}$ with a broadening Γ which can be estimated from the Heisenberg uncertainty principle
- From the energy – time Heisenberg uncertainty principle, interpret τ as uncertainty in time, thus

$$\Gamma \geq \frac{\hbar}{\tau}$$

Lifetime and lineshape

- It can be proved that this spectral broadening results in a Lorentzian lineshape as a function of energy
- For a transition between states with lifetimes τ_a and τ_b the Lorentzian half width at half maximum (HWHM) is

$$\Gamma = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right)$$

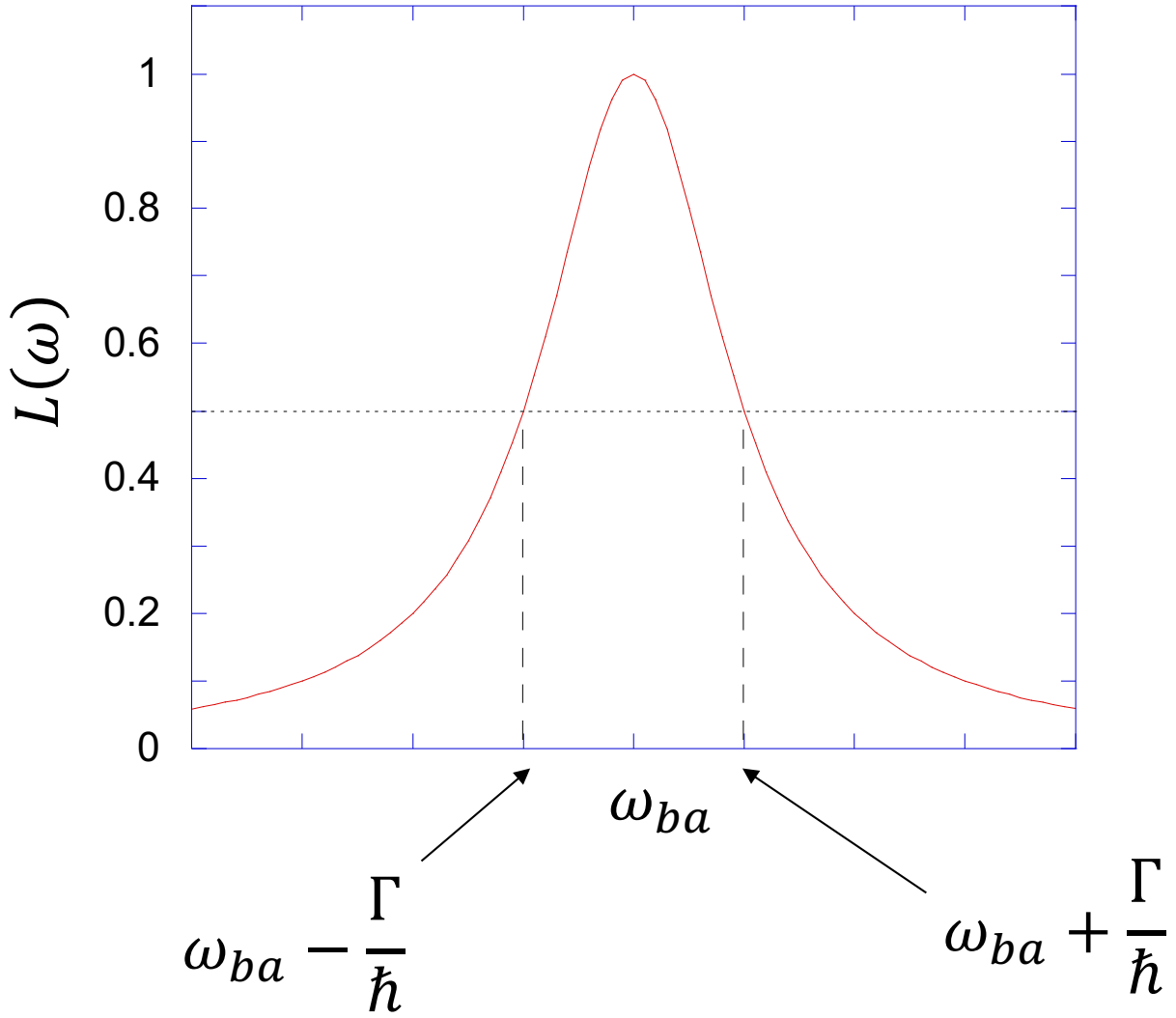
- The energy dependence of the cross section, the lineshape, is proportional to

$$L(\omega) = \frac{\Gamma^2}{\hbar^2(\omega_{ba} - \omega)^2 + \Gamma^2}$$

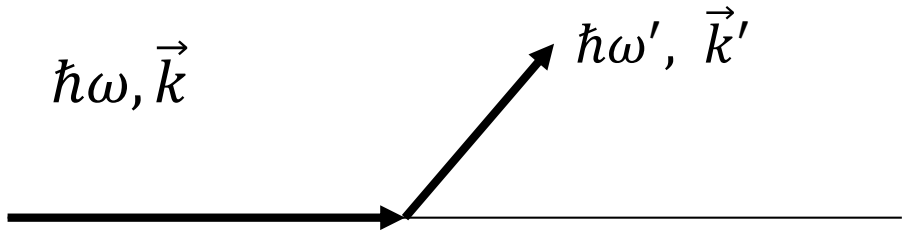
- This spectral broadening resolves the apparently unphysical result that the cross section is proportional to a δ function.

Lifetime and lineshape

$$L(\omega) = \frac{\Gamma^2}{\hbar^2(\omega_{ba} - \omega)^2 + \Gamma^2}$$



Scattering of radiation



- From the particle point of view scattering is a 2 photon process: a photon is absorbed (destroyed) and another is emitted (created).
- The scattered photon in general has a different energy and different wave vector (modulus and/or direction)

- $\omega' = \omega$: elastic scattering
  - In general: Raleigh
  - For a free electron: Thomson

- $\omega' \neq \omega$: inelastic scattering
  - In general: Raman
  - For a free electron: Compton ($\omega' < \omega$)

Scattering cross section

- Recall that the interaction Hamiltonian is

$$H' = \frac{e}{m}\vec{A}\cdot\vec{p} + \frac{e^2}{2m}\vec{A}^2$$

with

$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

- Absorption is due to $A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}$
- Emission is due to $A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})}$

Scattering cross section

- Scattering is a 2 photon process which is due to
  - The quadratic term $\frac{e^2}{2m}\vec{A}^2$, in first order pertubation theory (Fermi's golden rule)
  - The linear term $\frac{e}{m}\vec{A}\cdot\vec{p}$, treated as a second order pertubation
- Qualitatively, it can be justified by interpreting each $\vec{A}$ term as involving 1 photon (either absorbed or emitted).

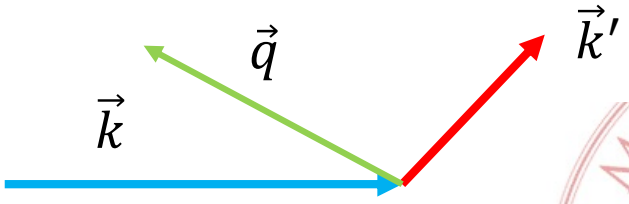
X-ray scattering cross section

- Term which describes scattering of X-rays (high energy limit) is $\frac{e^2}{2m}\vec{A}^2$ using 1st order pertubation theory.

- Define

$$\vec{q} = \vec{k}' - \vec{k}$$

the exchanged wavevector.



Fermi's GD for continuum final states

- Fermi's GD for final states in the continuum is

$$W_{ba} = \frac{2\pi}{\hbar}\left|\tilde{H}^{\dagger}{}_{ba}\right|^2 \rho\left(E_b{}^0\right)$$

$$E_b{}^0 = E_a{}^0 + \hbar\omega$$

- The density of states $\rho(E)$ is the number of states of energy between E and $E + dE$:

$$dN = \rho(E)\, dE$$

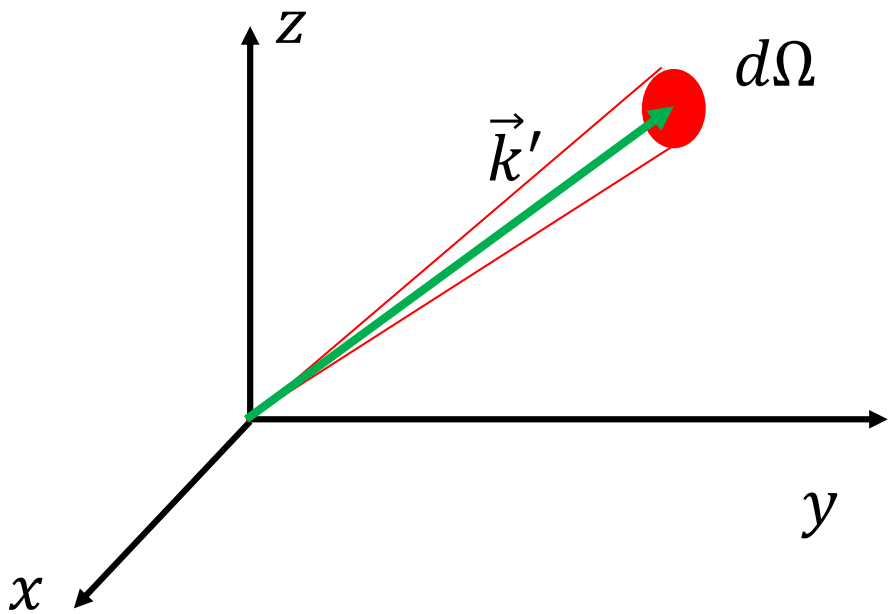
with the specification of the dispersion relation applicable for photons

$$\omega = ck$$

$$E = \hbar\omega = \hbar ck$$

Scattering geometry

- We will discuss the cross section for scattering in which the scattered photon has direction defined by the wave vector $\vec{k}'$ within an infinitesimal solid angle $d\Omega$



X-ray scattering cross section

- It can be proved that the differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{e^4}{16\pi^2\varepsilon_0^2 m^2 c^4}\left(\frac{\omega'}{\omega}\right)(\hat{\varepsilon}\cdot\hat{\varepsilon}')^2\left|\langle b|e^{-i\vec{q}\cdot\vec{r}}|a\rangle\right|^2$$

$$= r_0^2\left(\frac{\omega'}{\omega}\right)(\hat{\varepsilon}\cdot\hat{\varepsilon}')^2\left|\langle b|e^{-i\vec{q}\cdot\vec{r}}|a\rangle\right|^2$$

$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} \cong 2.82 \times 10^{-15}\ m$, the «classical electron radius» or «Thomson scattering length»

Scattering of radiation: general case

- In the general case (not only X-rays) one has to use both terms of the interaction Hamiltonian

$$H' = -i\hbar \frac{e}{m} \vec{A} \cdot \vec{\nabla} + \frac{e^2}{2m} \vec{A}^2$$
$$=$$
$$= \frac{e}{m} \vec{A} \cdot \vec{p} + \frac{e^2}{2m} \vec{A}^2.$$

Linear term: second order pertubation theory
Quadratic term: first order pertubation theory

Scattering of radiation: general case

- It can be demonstrated that in the dipole approximation the differential cross section is the Kramers – Heisenberg formula

$$\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 \left| m \sum_n \left[\frac{(\hat{\varepsilon}' \cdot \vec{r}_{bn})(\hat{\varepsilon} \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon} \cdot \vec{r}_{bn})(\hat{\varepsilon}' \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$$

with the condition that

$$E_a^0 + \hbar\omega = E_b^0 + \hbar\omega'$$

and the sum is over all atomic states n.

Scattering of radiation: general case

- $\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 \left| m \sum_n \left[\frac{(\hat{\varepsilon}' \cdot \vec{r}_{bn})(\hat{\varepsilon} \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon} \cdot \vec{r}_{bn})(\hat{\varepsilon}' \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$
- A «picture» of this equation
  - Scattering is due to the sum of «virtual» transitions to intermediate states.
  - Conservation of energy is valid only globally, not for transitions to intermediate «virtual» states