12. Interaction of Radiation with Matter

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12.1 Scattering Theory

We want to describe the interaction of radiation with matter as a scattering process. Specifically, we are interested in calculating the rate of scattering (and then the cross section), which is nothing else than the transition rate from an initial state (initial state of the matter + incoming particle) and a final state (final state of the target + outgoing radiation)[39].
This is a problem that can be solved by TDPT. Instead of considering a constant perturbation as done to derive Fermi's Golden rule, we analyze the case of a scattering potential, in its most general form. We describe a scattering

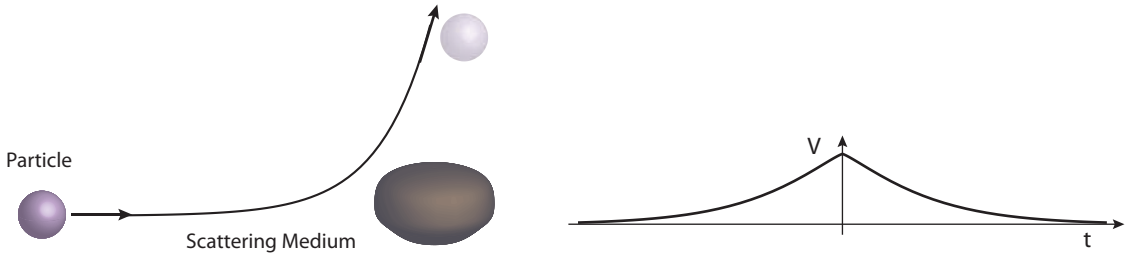


Fig. 20: Model for scattering: Left, particle trajectory, right time dependency of the potential.

event as a particle coming close to a target or a medium, interacting with it and then being deflected away. Thus, as a function of time, the interaction Hamiltonian V varies as in the figure 20.

[39] A very good resource for scattering theory is Chen, S.H.; Kotlarchyk, M., *Interactions of Photons and Neutrons with Matter,* (2007), which we follow closely in this chapter.

We want to calculate the probability of scattering from an initial state to a final state:

$$P_{scatt} = |\langle f| U_I(t) |i\rangle|^2 = |\langle f| (\mathbb{1} - i\int_{-\infty}^{\infty} V_I(t')dt' + \dots) |i\rangle|^2$$

Notice that we consider negative times as well. This corresponds to the so-called *adiabatic switching*, since the interaction is assumed to be turned on slowly from the beginning of time and to go down to zero again for long times.

A. Scattering and Transition matrices

In scattering problems, the propagator U_I is usually called the scattering matrix S. To simplify the calculation, we can assume again that V is actually time-independent. Then from the first order TDPT we obtain:

$$\langle f| S^{(1)} |i\rangle = -iV_{fi}\int_{-\infty}^{\infty} e^{i\omega_{fi}t}dt = -2\pi i\delta(\omega_f - \omega_i)\, V_{fi}$$

Now consider the second order contribution:

$$\langle f| S^{(2)} |i\rangle = -\langle f| \left(\sum_m V |m\rangle \langle m| V\right) |i\rangle \int_{-\infty}^{\infty} dt_1 e^{i\omega_{fm}t_1}\int_{-\infty}^{t_1} dt_2 e^{i\omega_{mi}t_2}$$

Notice that the last integral is not well defined for $t \to -\infty$. To solve it, we rewrite it as

$$\lim_{\epsilon\to 0^+}\int_{-\infty}^{t_1} dt_2 e^{i(\omega_{mi}-i\epsilon)t_2} = \lim_{\epsilon\to 0^+} -i\frac{e^{i\omega_{mi}t+\epsilon t}}{\omega_{mi}-i\epsilon}\Big|_{-\infty}^{t_1}$$

Now when taking the limit $t \to -\infty$ the exponential term $e^{\epsilon t} \to 0$ (thus getting rid of the oscillations). Then we are left with only

$$\int_{-\infty}^{t_1} dt_2 e^{i\omega_{mi}t_2} = \lim_{\epsilon\to 0^+} -i\frac{e^{i(\omega_{mi}-i\epsilon)t_1}}{\omega_{mi}-i\epsilon}$$

and we obtain (setting now $\epsilon = 0$)

$$\langle f| S^{(2)} |i\rangle = i\sum_m V_{fm}V_{mi}\int_{-\infty}^{\infty} dt_1 \frac{e^{i(\omega_{fi}-i\epsilon)t_1}}{\omega_{mi}-i\epsilon} = -2\pi i\delta(\omega_f-\omega_i)\sum_m \frac{\langle f| V |m\rangle \langle m| V |i\rangle}{\omega_i - \omega_m}$$

Looking at the first and second order of the scattering matrix, we start seeing a pattern emerge. We can thus rewrite :

$$\boxed{\langle f| S |i\rangle = -2\pi i\delta(\omega_f - \omega_i)\ \langle f| T |i\rangle}$$

where T is called the transition matrix. Its expansion is given by:

$$\langle f| T |i\rangle = \langle f| V |i\rangle + \sum_m \frac{\langle f| V |m\rangle \langle m| V |i\rangle}{\omega_i - \omega_m} + \sum_{m,n}\frac{V_{fm}V_{mn}V_{ni}}{(\omega_i-\omega_m)(\omega_i-\omega_n)} + \dots$$

B. Scattering Probability

We can now turn to calculate the scattering probability: $P_S = |\langle f| S |i\rangle|^2$. In order to obtain the total scattering probability, we will need to consider all possible final states. We found:

$$P_s = 4\pi^2 |\langle f| T |i\rangle|^2 \delta^2(\omega_f - \omega_i)$$

We calculate the square of the Dirac function from its definition based on the limit of the integral:

$$\delta^2(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t}\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\delta(\omega) = \lim_{t\to\infty}\frac{t}{\pi}\delta(\omega)$$

Then although the probability is not so well defined, since it contains a limit:

$$P_s = \lim_{t\to\infty} 4\pi t |\langle f|T|i\rangle|^2\delta(\omega_f - \omega_i)$$

the *rate* of scattering is well defined, since it is $W_S = P_S/(2t)$:

$$W_S = 2\pi |\langle f|T|i\rangle|^2\delta(\omega_f - \omega_i)$$

This is the rate for one isolated final state. If instead we have a continuum of final states, with density of states $\rho(\omega_f)$ we need to sum over all possible final states:

$$W_S = 2\pi\int 2\pi |\langle f|T|i\rangle|^2\delta(\omega_f - \omega_i)\rho(\omega_f)d\omega_f = 2\pi |\langle f|T|i\rangle|^2\rho(\omega_i)$$

Notice that to first order, this is equivalent to the Fermi Golden rule.

12.1.1 Cross Section

We now use the tools developed in TDPT to calculate the scattering cross section. This is defined as the rate of scattering divided by the incoming flux of "particles":

$$\boxed{\frac{d^2\sigma}{d\Omega dE} \propto \frac{W_S(\Omega, E)}{\Phi_{inc}}}$$

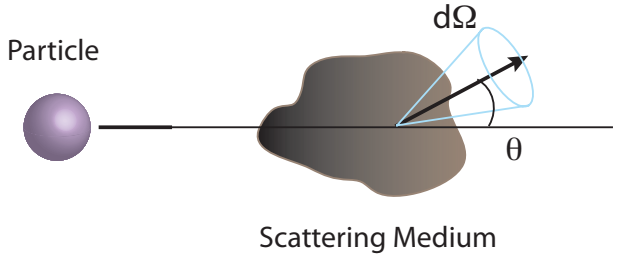
We consider a particle + medium system, where the particle is some radiation represented by a plane wave of momentum $\vec{k}$. In general, we will have to define also other degrees of freedom denoted by the index λ, e.g for photons we will have to define the polarization while for particles (e.g.e neutrons) the spin.
The unperturbed Hamiltonian is $\mathcal{H}_0 = \mathcal{H}_R + \mathcal{H}_M$ (radiation and medium). We assume that for $t \to \pm\infty$ the radiation and matter systems are independent, with (eigen)states:

$$|i\rangle = |k_i, m_i\rangle, \qquad |f\rangle = |k_f, m_f\rangle$$

with energies:

$$\mathcal{H}_R|k_i\rangle = \hbar\omega_i|k_i\rangle, \qquad \mathcal{H}_R|k_f\rangle = \hbar\omega_f|k_f\rangle, \qquad \mathcal{H}_M|m_i\rangle = \epsilon_i|k_i\rangle, \qquad \mathcal{H}_M|m_f\rangle = \epsilon_f|m_f\rangle$$

and total energies: $E_i = \hbar\omega_i + \epsilon_i$ and $E_f = \hbar\omega_f + \epsilon_f$.



Scattering Rate

The rate of scattering is given by the expression found earlier:

$$W_{fi} = \frac{2\pi}{\hbar} |\langle f| T |i\rangle|^2 \delta(E_f - E_i)$$

As usual, we want to replace, if possible, the delta-function with the final density of states. However, only the radiation will be left in a continuum of states, while the target will be left in one (of possibly many) definite state. To describe this distinction, we separate the final state into the two subsystems.
We first define the partial projection on radiation states only, $T_{k_f,k_i} = \langle k_f| T |k_i\rangle$. By writing the delta function as an integral we have:

$$W_{fi} = \frac{2\pi}{\hbar} \langle m_f| T_{k_f,k_i} |m_i\rangle \langle m_i| T^\dagger_{k_f,k_i} |m_f\rangle \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(\omega_f-\omega_i)t} e^{i(\epsilon_f-\epsilon_i)t/\hbar}$$

Now, since $e^{-i\mathcal{H}_R t/\hbar} |m_i\rangle = e^{-i\epsilon_i t/\hbar} |m_i\rangle$ (and similarly for $|m_f\rangle$ we can rewrite

$$\langle m_f| T_{k_f,k_i} |m_i\rangle e^{i(\epsilon_f-\epsilon_i)t/\hbar} = \langle m_f| e^{i\mathcal{H}_R t/\hbar} T_{k_f,k_i} e^{-i\mathcal{H}_R t/\hbar} |m_i\rangle = \langle m_f| T_{k_f,k_i}(t) |m_i\rangle$$

and obtain a new expression for the rate as a correlation of "transition" events:

$$W_{fi} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} e^{i(\omega_f-\omega_i)t} \langle m_i| T^\dagger_{k_f,k_i}(0) |m_f\rangle \langle m_f| T_{k_f,k_i}(t) |m_i\rangle$$

Final density of states

The final density of states describe the available states for the radiation. As we assumed that the radiation is represented by plane waves (and assuming for convenience they are contained in a cavity of edge L), the final density of states is

$$\rho(k_f) d^3k_f = \left(\frac{L}{2\pi}\right)^3 k_f^2 dk_f d\Omega$$

We can express this in terms of the energy, $\rho(k)d^3k = \rho(E)dEd\Omega$. For example, for photons, which have $k = E/\hbar c$ we have

$$\rho(E) = 2\left(\frac{L}{2\pi}\right)^3 \frac{E^2}{\hbar^3 c^3} = 2\left(\frac{L}{2\pi}\right)^3 \frac{\omega_k^2}{\hbar c^3}$$

where the factor 2 takes into account the possible polarizations. For neutrons (or other particles such that $E = \frac{\hbar^2 k^2}{2m}$):

$$\rho(E) = \left(\frac{L}{2\pi}\right)^3 \frac{k}{\hbar^2} = \left(\frac{L}{2\pi}\right)^3 \frac{\sqrt{2mE}}{\hbar^3}$$

If the material target can be left in more than one final state, we sum over these final states f. Then the average rate is given by $\overline{W}_S = \sum_f W_{fi}\rho(E)dEd\Omega$ (assuming that W_{fi} does not change very much in $d\Omega$ and dE).

Incoming Flux

The incoming flux is given by the number of scatterer per unit area and unit time, $\Phi = \frac{\#}{At}$. In the cavity considered, we can express the time as $t = L/v$, thus the flux is $\Phi = \frac{v}{L^3}$. For photons, this is simply $\Phi = c/L^3$, while for massive particles (neutrons) $v = \hbar k/m$, yielding $\Phi = \frac{\hbar k}{mL^3}$.

Average over initial states

If the scatterer is at a finite temperature T it will be in a mixed state, thus we need to sum over all possible initial states:

$$\rho_i = \frac{e^{-\beta \mathcal{H}_M}}{Z} \qquad \rightarrow \qquad P_i = \frac{e^{-\epsilon_i/k_b T}}{\sum_i e^{-\epsilon_i/k_b T}}$$

We can finally write the total scattering rate as:

$$W_S(i \rightarrow \Omega + d\Omega, E + dE) = \rho(E) \sum_i P_i \sum_f W_{fi}$$

$$= \rho(E) \sum_{f,i} \frac{P_i}{\hbar^2} \int_{-\infty}^{\infty} e^{i\omega_{fi}t} \langle m_i | T^\dagger_{k_f,k_i}(0) | m_f \rangle \langle m_f | T_{k_f,k_i}(t) | m_i \rangle \, dE d\Omega = \frac{\rho(E)}{\hbar^2} \int_{-\infty}^{\infty} e^{i\omega_{fi}t} \left\langle T^\dagger_{if}(0) T_{fi}(t) \right\rangle$$

where $\langle \cdot \rangle$ indicates an ensemble average at the given temperature.

12.1.2 Thermal Neutron Scattering

Using the scattering rate above and the incoming flux and density of state expression, we can find the cross section for thermal neutrons. From

$$\rho(E)/\Phi = \left[\left(\frac{L}{2\pi} \right)^3 \frac{m k_f}{\hbar^2} \right] / \left[\frac{\hbar k_i}{m L^3} \right] = \frac{(mL^3)^2}{(2\pi\hbar)^3} \frac{k_f}{k_i}$$

we obtain

$$\frac{d^2\sigma}{d\Omega d\omega} = \hbar \frac{W}{\Phi} = \hbar \frac{\rho(E)}{\Phi} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} e^{i\omega_{fi}t} \left\langle T^\dagger_{if}(0) T_{fi}(t) \right\rangle = \frac{1}{2\pi} \left(\frac{mL^3}{2\pi\hbar^2} \right)^2 \frac{k_f}{k_i} \int_{-\infty}^{\infty} e^{i\omega_{fi}t} \left\langle T^\dagger_{if}(0) T_{fi}(t) \right\rangle$$

Now the eigenstates $|k_{i,f}\rangle$ are plane waves, $\langle r|k\rangle = \psi_k(r) = e^{ik\cdot r}/L^{3/2}$. Then, defining $Q = k_i - k_f$ the transition matrix element is

$$T_{fi}(t) = \langle k_f | T(t) | k_i \rangle = \int_{L^3} d^3 r \psi_{k_f}(r)^* T(r,t) \psi_{k_i}(r) = \frac{1}{L^3} \int_{L^3} d^3 r e^{iQ\cdot r} T(r,t)$$

and

$$T_{fi}(0)^\dagger = \frac{1}{L^3} \int_{L^3} d^3 r e^{-iQ\cdot r} T(r,0)^\dagger$$

Fermi Potential

To first order, we can approximate T by V, the nuclear potential in the center of mass frame (of the neutron+nucleus). You might recall that the nuclear potential is a very strong ($V_0 \sim 30$MeV) and narrow ($r_0 \sim 2$fm) potential. These characteristics seem to preclude a perturbative approach, since the assumption of a weak interaction (compared to the unperturbed system energy) is not satisfied. Still, the fact that the potential is narrow means that the interaction only happens for a very short time. Thus, if we average over time, we expect a weak interaction. More precisely, the scattering interaction only depends on the so-called *scattering length* a, which is on the order $a \sim V_0 r_0$. If we keep a constant, different combinations of V, r will give the same scattering behavior. We can thus replace the strong nuclear potential with a weaker, pseudo-potential $\tilde{V}_0$, provided this has a much longer range $\tilde{r}_0$, such that $a \sim V_0 r_0 = \tilde{V}_0 \tilde{r}_0$. We can choose $\tilde{V}_0$, $\tilde{r}_0$ so that the potential is weak (eV) but the range is still short compared to the wavelength of the incoming neutron, $k\tilde{r}_0 \ll 1$. Then, it is possible to replace the potential with a simple delta-function at the origin.

$$V(r) = \frac{2\pi\hbar^2}{\mu} a \delta(r)$$

We can also define the bound scattering length, $b = \frac{\mu}{m_n} a \approx \frac{A+1}{A}$, were m_n is the neutron's mass and A the nucleus mass number. Then the potential is

$$V(r) = \frac{2\pi\hbar^2}{m_n} a\delta(r)$$

Note that b (interaction length or bound scattering length) is a function of the potential strength and range, which depend on the isotope from which the neutron is scattered off.
Then to first order the transition matrix is $T_{fi} = \frac{2\pi\hbar^2}{m_n} b$, or more generally, if there are many scatterers, each at a position $r_x(t)$, we have:

$$T_{fi}(t) = \frac{2\pi\hbar^2}{m_n} \sum_x b_x e^{iQ\cdot r_x(t)}$$

The scattering cross section becomes

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{2\pi}\frac{k_f}{k_i}\int_{-\infty}^{\infty} e^{i\omega_{fi}t}\left\langle \sum_{x,y} b_x b_y e^{-iQ\cdot r_x(0)} e^{iQ\cdot r_y(t)} \right\rangle$$

Notice that since the collisions are spin-dependent, we should average over isotopes and spin states and replace $b_x b_y$ with $\overline{b_x b_y}$.

Scattering Lengths

Notice that b does not depend explicitly on position, although the position determines which isotope/spin we should consider. What is $\overline{b_x b_y}$? We have two contributions. For $x = y$ this is $\overline{b^2}\delta_{x,y}$, while for $x \neq y$, it is $\overline{b}^2(1-\delta_{x,y})$. We then write $\overline{b_x b_y} = (\overline{b^2} - \overline{b}^2)\delta_{x,y} + \overline{b}^2 = b_i^2 + b_c^2$ which defines the coherent scattering length $b_c = \overline{b}$ and the incoherent scattering length $b_i^2 = \overline{b^2} - \overline{b}^2$. If there are N scatterers, we have $\sum b_x b_y = N(b_i^2 + b_c^2)$.

Structure Factors

Using these definition, we arrive at a simplified expression:

$$\frac{d^2\sigma}{d\Omega d\omega} = N\frac{k_f}{k_i}\left(b_i^2 S_S(Q,\omega) + b_c^2 S(Q,\omega)\right)$$

where we used the self-dynamic structure factor

$$S_S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega_{fi}t}\left\langle \frac{1}{N}\sum_x e^{-iQ\cdot r_x(0)} e^{iQ\cdot r_x(t)} \right\rangle$$

which simplifies to

$$S_S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega_{fi}t}\left\langle e^{-iQ\cdot r(0)} e^{iQ\cdot r(t)} \right\rangle$$

if all nuclei are equivalent (same isotope), and the full dynamic structure factor

$$S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega_{fi}t}\left\langle \frac{1}{N}\sum_{x,y} e^{-iQ\cdot r_x(0)} e^{iQ\cdot r_y(t)} \right\rangle$$

The structure factors depend only on the material properties. Thus they give information about the material when obtained from experiments.

Intermediate Scattering Function

From the expressions above for the structure factors, it is clear that they can be obtained as the Fourier Transform (with respect to time) of the quantities:

$$F_S(Q,t) = \frac{1}{N}\left\langle \sum_x e^{-iQ\cdot r(0)} e^{iQ\cdot r_x(t)} \right\rangle$$

and

$$F(Q,t) = \frac{1}{N}\left\langle \sum_{x,y} e^{-iQ\cdot r_x(0)} e^{iQ\cdot r_y(t)} \right\rangle$$

These are called the intermediate scattering functions. Going even further, we can write even these function as a Fourier Transform (with respect to position). For example, for equivalent targets (no distribution in isotope nor spin), we have

$$F_S(Q,t) = \left\langle e^{-iQ\cdot r(0)} e^{iQ\cdot r(t)} \right\rangle$$

By defining a the position of a test particle, $n(R,t) = \delta(R - r(t))$, we can calculate the fourier transform $n(Q,t)$:

$$n(Q,t) = \int d^3 r e^{iQ\cdot R} n(R,t) = e^{iQ\cdot r(t)}$$

Then we have $F_S(Q,t) = \langle n(Q,t) n(-Q,0)\rangle$. We can as well define the van-Hove space-time self correlation function,

$$G_s(r,t) = \int d^3 r' \, \langle n(r',0) n(r+r',t)\rangle$$

which represents a correlation of the test particle in space-time. The intermediate scattering function is obtained from G_s as

$$F_S(Q,t) = \int d^3 r e^{iQ\cdot r} G_s(r,t)$$

These final relationship makes it clear that F_S is the Fourier transform (with respect to space) of the time-dependent correlation of the test particle density, $n(R,t)$, which only depends on the target characteristics.

Example I: Resting, free nucleus

We consider the scattering from one resting free nucleus. We need only consider the self dynamics factor and we have $b_c = \overline{b} = b$:

$$\frac{d^2\sigma}{d\,\Omega d\omega} = \frac{k_f}{k_i} b^2 S(Q,\omega) = \frac{\sigma_b}{2\pi\hbar}\frac{k_f}{k_i} S(Q,\omega)$$

where we introduced the bound cross section $\sigma_b = 4\pi b^2$ (with units of an area). Since the nucleus is free, the intermediate function is very simple. From

$$F_S(Q,t) = \left\langle e^{-iQ\cdot r(0)} e^{iQ\cdot r(t)} \right\rangle$$

we can use the BCH formula to write

$$F_S(Q,t) = \left\langle e^{-iQ\cdot[r(0)-r(t)] + \frac{1}{2}[Q\cdot r(0), Q\cdot r(t)]} \right\rangle$$

Then we want to calculate $[r(0), r(t)]$ in order to simplify the product of the two exponential. For a free particle, $r(t) = r(0) + \frac{p}{m}t$ and $[r(0), p] = i\hbar$. Then we have

$$F_S(Q,t) = \left\langle e^{-iQ\cdot[r(0)-r(t)] + i\frac{\hbar}{2m}Q^2 t} \right\rangle = \left\langle e^{-iQ\cdot p/m} \right\rangle e^{+i\frac{\hbar}{2m}Q^2 t}$$

and for a nucleus at rest ($p = 0$) we have

$$F_S(Q,t) = e^{i\hbar t Q^2/(2m)}$$

This gives the structure factor

$$S_s(Q,\omega) = \delta\left(\omega - \frac{\hbar Q^2}{2m}\right)$$

and the cross-section

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\sigma_b}{2\pi\hbar}\frac{k_f}{k_i}\delta\left(\omega - \frac{\hbar Q^2}{2m}\right)$$

Since $Q = k_f - k_i$, we have $Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos\vartheta$. Also, $\omega = E_f - E_i$ and $k_a^2 = 2mE_a \approx 2AE_a$ where we substituted A for the mass of the nucleus.
We can then integrate the cross-section over the solid angle, to find $\frac{d\sigma}{dE}$:

$$\frac{d\sigma}{dE} = \int_0^\pi \frac{\sigma_b}{2\pi\hbar}\frac{k_f}{k_i}\delta\left(\omega - \frac{\hbar Q^2}{2m}\right)2\pi\sin\vartheta d\vartheta = \frac{A\sigma_b}{4E_i}\int_{(A-1)^2/(A+1)^2 E_i}^{E_i}\delta(x)dx$$

Defining the free-atom cross section σ_f

$$\sigma_f = \left(1 + \frac{1}{A}\right)^{-2}\sigma_b$$

we have

$$\frac{d\sigma}{dE} = \begin{cases} \sigma_f \frac{(A+1)^2}{4AE}, & \text{for } \left(\frac{A-1}{A+1}\right)^2 E < E_f < E \\ 0, & \text{otherwise} \end{cases}$$

This expression for the cross section can also be obtained more simply from an energy conservation argument.

Example II: Scattering from a crystal lattice

We consider now the scattering of neutrons from a crystal. For simplicity, we will consider a one-dimensional crystal lattice modeled as a 1D quantum harmonic oscillator. The position $r \to x$ (in 1D) of a nucleus in the lattice is then the position of an harmonic oscillator of mass M and frequency ω_0,

$$x = \sqrt{\frac{\hbar}{2M\omega_0}}(a + a^\dagger)$$

with evolution given by the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2M} + \frac{M\omega_0^2}{2}x^2 = \hbar\omega_0(a^\dagger a + \frac{1}{2})$$

If we consider no variation of isotope and spin for simplicity, we only need the self-intermediate structure function is

$$F_S(Q,t) = \quad e^{-iQ\cdot x(0)}e^{iQ\cdot x(t)} \quad = \quad e^{-iQ\cdot[x(0)-x(t)]}e^{+\frac{1}{2}[Q\cdot x(0), Q\cdot x(t)]}$$

First remember that

$$x(t) = x(0)\cos(\omega_0 t) + \frac{p(0)}{M\omega_0}\sin(\omega_0 t)$$

for an harmonic oscillator. Then $[x(0), x(t)] = [x(0), p(0)]\frac{1}{M\omega_0}\sin(\omega_0 t) = \frac{i\hbar}{M\omega_0}\sin(\omega_0 t)$. Also we have

$$\Delta x(t) = x(t) - x(0) = x(0)[1 - \cos(\omega_0 t)] + \frac{p(0)}{M\omega_0}\sin(\omega_0 t) = \sqrt{\frac{\hbar}{2M\omega_0}}(ae^{-i\omega_0 t} + a^\dagger e^{i\omega_0 t})$$

We want to evaluate $\left\langle e^{iQ\Delta x(t)}\right\rangle$. Using again the BCH formula, we have

$$e^{iQ\sqrt{\frac{\hbar}{2M\omega_0}}(ae^{-i\omega_0 t}+a^\dagger e^{i\omega_0 t})} = e^{\alpha a-\alpha^* a^\dagger} = e^{-\alpha^* a^\dagger}e^{\alpha a}e^{-|\alpha|^2[a,a^\dagger]/2}$$

with $\alpha = iQ\sqrt{\frac{\hbar}{2M\omega_0}}e^{-i\omega_0 t}$. Since $[a,a^\dagger]=1$, we only need to evaluate the expectation value $\left\langle e^{-\alpha^* a^\dagger}e^{\alpha a}\right\rangle$, by expanding in series the exponentials:

$$\left\langle e^{-\alpha^* a^\dagger}e^{\alpha a}\right\rangle = \sum_{n,m}\left\langle a^{\dagger m}a^n\right\rangle \frac{\alpha^n(-\alpha^*)^m}{n!m!}$$

Only the terms with $m=n$ survive (the other terms are not diagonal in the number basis)

$$\left\langle e^{-\alpha^* a^\dagger}e^{\alpha a}\right\rangle = \sum_{n}\left\langle (a^{\dagger n}a^n)\right\rangle \frac{(-|\alpha|^2)^n}{(n!)^2}$$

Now $\left\langle a^{\dagger n}a^n\right\rangle = n!\left\langle (a^\dagger a)^n\right\rangle$, thus we finally have

$$\left\langle e^{-\alpha^* a^\dagger}e^{\alpha a}\right\rangle = \sum_{n}\left\langle (a^\dagger a)^n\right\rangle \frac{(-|\alpha|^2)^n}{n!} = e^{-|\alpha|^2\langle a^\dagger a\rangle}$$

This result is a particular case of the Bloch identity, $\left\langle e^A\right\rangle = e^{\left\langle A^2\right\rangle/2}$ where $A=\alpha a+\beta a^\dagger$ is any combination of the creation and annihilation operators. Finally, we obtained for the intermediate function:

$$F_S(Q,t) = \quad e^{-iQ\cdot x(0)}e^{iQ\cdot x(t)} \quad = e^{-\frac{Q^2\hbar}{2M\omega_0}(\langle\hat{n}\rangle+\frac{1}{2})}e^{+\frac{1}{2}\frac{i\hbar Q^2}{M\omega_0}\sin(\omega_0 t)}$$

We can also rewrite this using the Bloch identity Using the Bloch identity, $\left\langle e^A\right\rangle = e^{\left\langle A^2\right\rangle/2}$ where $A=\alpha a+\beta a^\dagger$ is any combination of the creation and annihilation operators, we can rewrite this as

$$F_S(Q,t) = \left\langle e^{-iQ\cdot x(0)}e^{iQ\cdot x(t)}\right\rangle = \left\langle e^{iQ\Delta x}\right\rangle e^{+\frac{1}{2}[Q\cdot x(0),Q\cdot x(t)]} = e^{-Q^2\left\langle\Delta x^2\right\rangle/2}e^{+\frac{1}{2}[Q\cdot x(0),Q\cdot x(t)]}$$

Now,

$$\left\langle\Delta x^2\right\rangle = \left\langle x(0)^2\right\rangle + \left\langle x(t)^2\right\rangle + 2\left\langle x(0)x(t)\right\rangle - \left\langle[x(0),x(t)]\right\rangle = 2\left\langle x^2\right\rangle + 2\left\langle x(0)x(t)\right\rangle - \left\langle[x(0),x(t)]\right\rangle$$

from which we obtain

$$F_S(Q,t) = e^{-Q^2\left\langle x^2\right\rangle}e^{Q^2\langle x(0)x(t)\rangle}$$

If the oscillator is in a number state $|n\rangle$, we have

$$\left\langle x^2\right\rangle = \frac{\hbar}{2M\omega_0}(2n+1), \qquad \left\langle x(0)x(t)\right\rangle = \frac{\hbar}{2M\omega_0}[2n\cos(\omega_0 t)+e^{i\omega_0 t}]$$

If we consider an oscillator at thermal equilibrium, we need to replace n with $\langle n\rangle_{th}$. In the high temperature limit, $\langle n\rangle \gg 1$ and we can simplify:

$$F_S(Q,t) = e^{-\frac{\hbar Q^2}{M\omega_0}\langle n\rangle[1-\cos(\omega_0 t)]} = e^{-Q^2W_0/2}e^{Q^2W(t)/2}$$

with $W_0 = \frac{2\langle n\rangle\hbar}{M\omega_0}$ and $W(t) = W_0\cos(\omega_0 t)$. This form of the intermediate function is the same expression one would obtain from a classical treatment and the term $e^{-Q^2W_0/2}$ is called the Debye-Waller factor.
The intermediate structure function is thus a Gaussian function, with a time-dependent width, $W_0 - W(t)$. If $W_0 < 1$ we can make an expansion of the time-dependent term:

$$F_S(Q,t) = e^{-Q^2W_0/2}e^{Q^2W_0\cos(\omega_0 t)/2} \approx e^{-Q^2W_0/2}\left[1+W_0\cos(\omega_0 t)+\frac{1}{2}W_0^2\cos^2(\omega_0 t)+\dots\right]$$

Then the structure factor, which is the Fourier transform of F_S will be a sum of Dirac functions at frequencies $\omega = \pm n\omega_0$ corresponding to the n-phonon contribution to the scattering. Here the terms $\delta(\omega - n\omega_0)$ correspond to scattering events where the energy has been transfered from the neutron to the oscillator, while terms $\delta(\omega + n\omega_0)$ describe a transfer of energy from the lattice to the neutron. The constant term yields $\delta(\omega)$ which describes no energy exchange or elastic scattering (zero-phonon term). Note that the expansion coefficient, W_0 can be expressed in terms of the temperature, since in the high temperature limit, $\langle n \rangle \approx \frac{k_b T}{\hbar\omega_0}$, from which $W_0 = \frac{2k_b T}{M\omega_0^2}$.
In the low temperature limit, $\langle n \rangle \to 0$. Thus we have:

$$F_S(Q,t) = e^{-\frac{\hbar Q^2}{2M\omega_0}\{2\langle n\rangle[1-\cos(\omega_0 t)]+1-e^{i\omega_0 t}\}} \approx e^{-Q^2\frac{\hbar Q^2}{2M\omega_0}} e^{\frac{\hbar Q^2}{2M\omega_0}e^{i\omega_0 t}}$$

Expanding in series the second term, we have

$$F_S(Q,t) \approx e^{-Q^2\frac{\hbar Q^2}{2M\omega_0}} \left[1 + \frac{\hbar Q^2}{2M\omega_0}e^{i\omega_0 t} + \frac{1}{2}\left(\frac{\hbar Q^2}{2M\omega_0}\right)^2 e^{2i\omega_0 t} + \dots\right]$$

Even at low temperature, the structure factor (the Fourier transform of the expression above) is a sum of Dirac function, also called a phonon expansion. However in this case only terms $\delta(\omega - n\omega_0)$ appear, since energy can only be given from the neutron to the lattice (which is initially in its ground state).

12.2 Emission and Absorption

Atoms and molecules can absorb photons and make a transition from their ground state to an excited level. From the excited state, they can emit photons (either in the presence or absence of a preexisting e.m. filed) and transition to a lower level. Using TDPT and the quantization of the field we can calculate the transition rates.

12.2.1 Emission

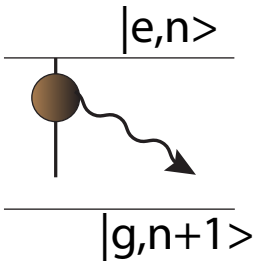


Fig. 21: Model for emission: the atom (molecule) makes a transition from the excited level ($|e\rangle$) to the ground state)$|g\rangle$) while the number of photons in the mode k, λ goes from n to $n+1$.

The rate of emission is given simply by

$$W = \frac{2\pi}{\hbar} |\langle f| V |i\rangle|^2 \rho(E_f).$$

We separate the field and the atom (or molecule) levels:

$$|i\rangle = |n_{k\lambda}\rangle |e\rangle, \qquad |f\rangle = |n_{k\lambda}+1\rangle |g\rangle$$

As we are looking at atomic/optical processes the dipolar approximation is adequate and the interaction is given by: $V = -\vec{d}\cdot\vec{E} = -e\vec{r}\cdot\vec{E}$. Remember the expression for the electric field:

$$\vec{E} = \sum_{k,\lambda} \sqrt{\frac{2\pi\hbar\omega_k}{L^3}} \left(a_{k\lambda} e^{ikr} + a^\dagger_{k\lambda} e^{-ikr}\right) \vec{\epsilon}_{k\lambda}$$

The position of the electron which makes the transition can be written as $\vec{r} = \vec{R} + \vec{\rho}$, where $\vec{R}$ is the nucleus position. Since the relative position of the electron with respect to the nucleus is $\rho \ll \lambda$, we can neglect it and substitute r with R in the exponential ($\vec{\rho}\cdot\vec{k} \ll 1$). This simplifies the calculation, since R is not an operator acting on the electron state. Then, from the rate:

$$W = \frac{2\pi}{\hbar} |\langle g| \vec{d} |e\rangle \cdot \langle n_{k\lambda}+1| \vec{E} |n_{k\lambda}\rangle|^2 \rho(E_f)$$

we obtain

$$W = \frac{(2\pi e)^2}{L^3} \sum_{k',\lambda'} \omega_{k',\lambda'} \left|\langle n_{k\lambda}+1| \left(a_{k'\lambda'} e^{ikR} + a^\dagger_{k'\lambda'} e^{-ikR}\right) |n_{k\lambda}\rangle \langle g| \vec{r}\cdot\epsilon_{k',\lambda'} |e\rangle\right|^2 \rho(E_f)$$

Since we are *creating* a photon, only terms $\propto a^\dagger$ survive and specifically the term with the correct wavevector and polarization: $\langle n_{k\lambda}+1| a^\dagger_{k\lambda} |n_{k\lambda}\rangle = \sqrt{n_{k\lambda}+1}$ (all other terms are zero). Then we have:

$$W = \frac{(2\pi e)^2}{L^3} \omega_{k,\lambda}(n_{k,\lambda}+1) |\langle g| \vec{r}\cdot\epsilon_{k,\lambda} |e\rangle|^2 \rho(E_f)$$

Since the atom is left in a specific final state, the density of states is defined by the e.m. field:

$$\rho(E_f) dE_f = \rho(\hbar\omega_k)\hbar d\omega_k$$

As $\omega_k = ck$ and $\rho(k)d^3k = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega = \left(\frac{L}{2\pi}\right)^3 \frac{\omega^2}{c^3} d\omega d\Omega$ we have:

$$\rho(E) = \left(\frac{L}{2\pi}\right)^3 \frac{\omega^2}{\hbar c^3} d\Omega$$

We define the dipole transition matrix element from the dipole operator $\vec{d} = e\vec{r}$, $d_{ge} = \langle g| d |e\rangle$. The rate of emission is then:

$$W = \frac{\omega_k^3}{2\pi\hbar c^3}(n_{k\lambda} + 1)|\vec{\epsilon}_{k\lambda} \cdot \vec{d}_{ge}|^2 d\Omega$$

From this expression it easy to see that there are two contributions to emission:
Spontaneous emission:

$$W = \frac{\omega_k^3}{2\pi\hbar c^3}|\vec{\epsilon}_{k\lambda} \cdot \vec{d}_{ge}|^2 d\Omega$$

which happens even in the vacuum e.m. and stimulated emission:

$$W = \frac{\omega_k^3}{2\pi\hbar c^3} n_{k\lambda}|\vec{\epsilon}_{k\lambda} \cdot \vec{d}_{ge}|^2 d\Omega$$

which happens only when there are already n photons of the correct mode.

Spontaneous Emission

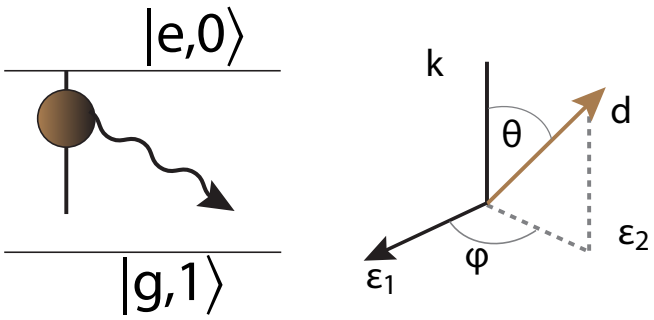


Fig. 22: Geometry of spontaneous emission

Since the photons emitted can have any polarization ϵ and any wavevector $\vec{k}$ direction, we have to sum over all possibilities. We assume that the dipole vector forms an angle ϑ with respect to the wavevector k. Then the two possible polarization vectors are perpendicular to k, as in Fig. 22. The rate is the sum of the rates for each polarization $W_{sp} = W_1 + W_2$, each proportional to $|d \cdot \epsilon_{k1,2}|^2$,

$$d \cdot \epsilon_{k,1} = d \sin\vartheta \cos\varphi, \qquad d \cdot \epsilon_{k,2} = d \sin\vartheta \sin\varphi$$

We thus obtain the typical $\sin^2\vartheta$ angular dependence of dipolar radiation (also seen for classical dipoles):

$$W_{sp} = \frac{\omega_k^3}{2\pi\hbar c^3}|d_{ge}|^2 \sin^2\vartheta d\Omega$$

The total emission coefficient, or Einstein's emission coefficient, is obtained by integrating over the solid angle:

$$A_e = \int_\Omega W d\Omega = \frac{\omega_k^3}{2\pi\hbar c^3}|d_{ge}|^2 2\pi \int_{-1}^{1}(1-\mu^2)d\mu = \frac{4}{3}\frac{\omega_k^3}{\hbar c^3} d_{ge}^2$$

Given the rate, we can also calculate the power emitted, as rate times energy

$$P = \hbar\omega_k A_e = \frac{4}{3}\frac{\omega_k^4}{c^3} d_{ge}^2$$

Notice that this is very similar to the power emitted by a *classical* oscillating dipole (as if the e.m. field was emitted by orbiting electrons).

Stimulated Emission

In the stimulated emission, $W_{st}^{k\lambda} = n_{k\lambda} W_{sp}^{k\lambda}$. Only photons with the same frequency ($\vec{k}$) and polarization of the ones already in the field can be emitted. Then, as more photons in a particular mode are emitted, it becomes even more probable to produce photons in the same mode: we produce a beam of coherent photons (i.e. all with the same characteristics and phase coherent with each other). If the atoms can be kept in the excited (emitting) levels, we obtain a LASER (light amplification by stimulated emission of radiation). Of course, usually it is more probable to have the photons absorbed than to have it cause a stimulated emission, since at equilibrium we usually have many more atoms in the ground state than in the excited state, $n_g \gg n_e$. A mechanism capable of inverting the population of the atomics states (such as optical pumping) is then needed to support a laser.

12.2.2 Absorption

The rate of absorption is obtained in a way very similar to emission. The result is

$$W = \frac{2\pi}{\hbar} |\langle e|\, \vec{d}\, |g\rangle \cdot \langle n_{k\lambda}|\, \vec{E}\, |n_{k\lambda}+1\rangle|^2 \rho(E_f) = \frac{\omega_k^3}{2\pi\hbar c^3} n_{k\lambda} |\vec{\epsilon}_{k\lambda} \cdot \vec{d}_{eg}|^2 d\Omega$$

(as $\langle n_{k\lambda}|\, a_{k\lambda}\, |n_{k\lambda}+1\rangle = \sqrt{n_{k\lambda}}$).

12.2.3 Blackbody Radiation

We consider a cavity with radiation in equilibrium with its wall. Then the polarization and $\vec{k}$-vector of the photons is random, and to obtain the total absorption rate we need to integrate over it, as done for the emission. We obtain

$$W_{ab} = \int_\Omega W_{ab}(\vartheta) d\Omega = n_k \frac{4}{3}\frac{\omega_k^3}{\hbar c^3} d_{ge}^2$$

for a given frequency (and wavevector length). Similarly, the total emission is obtained as the sum of spontaneous and stimulated emission:

$$W_e = W_{st} + W_{sp} = (n_k + 1)\frac{4}{3}\frac{\omega_k^3}{\hbar c^3} d_{ge}^2$$

In these expression n_k is the number of photons in the mode k. Since we assumed to be at equilibrium, n_k depends only on the energy density at the associated frequency ω_k. The energy density is given by the energy per volume, where the energy is given by the total number of photons times their energy, $E = n_k \rho(\omega_k)\hbar\omega_k$:

$$u(\omega_k) = \hbar\omega_k \rho(\omega_k) n_k / L^3$$

Then, from the density of states $\rho(\omega_k) = 2\left(\frac{L}{2\pi c}\right)^3 \omega^2 \int d\Omega = \frac{L^3}{c^3\pi^2}\omega^2$, we obtain

$$\boxed{n_k = \frac{\pi^2 c^3}{\hbar\omega_k^3} u(\omega_k)}$$

The rates can then be written in terms of the energy density and of Einstein's coefficients for absorption and emission:

$$B_{ab} = \frac{4}{3}\frac{\pi^2}{\hbar^2} d^2 \qquad \rightarrow \qquad W_{ab} = B_{ab} u(\omega_k)$$

$$B_{em} = B_{ab}, \quad A_e = \frac{4}{3}\frac{\omega_k^3}{\hbar c^3} d_{ge}^2 \qquad \rightarrow \qquad W_{em} = A_e + B_{em} u(\omega_k)$$

Detailed Balancing

At equilibrium, we need to have the same number of photons absorbed and emitted (to preserve their total number). Then $N_e W^k_{em} = N_g W^k_{ab}$. Using Einstein's coefficient, we have $N_e(A+uB) = N_g Bu$ which yields $N_e A = uB(N_g - N_e)$. This is the principle of detailed balancing.
We can solve for the energy density: $u = \frac{A/B}{N_g/N_e - 1}$. But from their explicit expressions we have $A/B = \frac{\hbar\omega^3}{\pi^2 c^3}$ and from the condition that atoms are in thermal equilibrium, their population ratio is given by $\frac{N_g}{N_e} = \frac{e^{-\beta E_g}}{e^{-\beta E_e}} = e^{-\beta(E_g - E_e)} = e^{\beta\hbar\omega_k}$ (since $\hbar\omega_k$ is the exact energy needed for the transition from ground to excited state). Finally, we obtain the energy density spectrum for the black-body:

$$u(\omega_k, T) = \frac{\hbar\omega^3/\pi^2 c^3}{e^{\beta\hbar\omega_k} - 1}$$

12.3 Wigner-Weisskopf Theory

12.3.1 Interaction of an atom with a single mode e.m. field

Recall what we studied in Section 10.5. We consider again a two-level system (an atom) interacting with a single mode of the e.m. field. The Hamiltonian simplifies to $\mathcal{H} = \mathcal{H}_0 + V$, with

$$\mathcal{H}_0 = \hbar\nu a^\dagger a + \hbar\frac{\omega}{2}\sigma_z, \qquad V = \hbar g(\sigma_+ a + \sigma_- a^\dagger)$$

where $g = \frac{1}{2}\sqrt{\frac{\nu}{\hbar L^3}} d \cdot \epsilon$ is the dipole operator.
We move to the interaction frame defined by the $\mathcal{H}_0$ Hamiltonian, $U = e^{i\mathcal{H}_0 t}$, then $\mathcal{H}_I = UVU^\dagger$ or

$$\mathcal{H}_I = \hbar g e^{i\nu t a^\dagger a} e^{i\omega\sigma_z t/2}(\sigma_+ a + \sigma_- a^\dagger) e^{-i\nu t a^\dagger a} e^{-i\omega\sigma_z t/2} = \hbar g\left[e^{i(\omega-\nu)t}\sigma_+ a + e^{-i(\omega-\nu)t}\sigma_- a^\dagger\right]$$

We will use the notation $\Delta = \omega - \nu$. We want now to study the evolution of a pure state in the interaction frame: $i\hbar\ \dot{\psi}\ = \mathcal{H}_I|\psi\rangle$. We can write a general state as $|\psi\rangle = \sum_n \alpha_n(t)\,|e,n\rangle + \beta_n(t)\,|g,n\rangle$. Notice that since we have a TLS, $\sigma_+\,|e\rangle = 0$ and $\sigma_-\,|g\rangle = 0$. The evolution is then given by:

$$i\hbar\sum_n \dot{\alpha}_n\,|e,n\rangle + \dot{\beta}_n\,|g,n\rangle = \hbar g\sum_n\left[\alpha_n\sigma_- a^\dagger e^{-i\Delta t}\,|e,n\rangle + \beta_n\sigma_+ a e^{i\Delta t}\,|g,n\rangle\right]$$

$$= \hbar g\sum_n\left[\alpha_n e^{-i\Delta t}\sqrt{n+1}\,|g,n+1\rangle + \beta_n e^{i\Delta t}\sqrt{n}\,|e,n-1\rangle\right]$$

We then project these equations on $\langle e,n|$ and $\langle g,n|$:

$$i\hbar\dot{\alpha}_n = \hbar g\beta_{n+1}(t)e^{i\Delta t}\sqrt{n+1}$$

$$i\hbar\dot{\beta}_n = \hbar g\alpha_{n-1}(t)e^{-i\Delta t}\sqrt{n}$$

to obtain a set of equations:

$$\begin{cases} \dot{\alpha}_n = -ig\beta_{n+1}e^{i\Delta t}\sqrt{n+1} \\ \dot{\beta}_{n+1} = -ig\alpha_n e^{-i\Delta t}\sqrt{n+1} \end{cases}$$

This is a closed system of differential equations and we can solve for α_n, β_{n+1}.
For example: we can assume that initially the atom is in the excited state $|e\rangle$ and it decays to the ground state $|g\rangle$ (that is, $\beta_n(0) = 0$, $\forall n$). Then we have:

$$\alpha_n(t) = \alpha_n(0)e^{i\Delta t/2}\left[\cos\left(\frac{\Omega_n t}{2}\right) - \frac{i\Delta}{\Omega_n}\sin\left(\frac{\Omega_n t}{2}\right)\right]$$

$$\beta_n(t) = -\alpha_n(0)e^{-i\Delta t/2}\left[\frac{2ig\sqrt{n+1}}{\Omega_n}\sin\left(\frac{\Omega_n t}{2}\right)\right]$$

with $\Omega_n^2 = \Delta^2 + 4g^2(n+1)$. If initially there is no field (i.e. the e.m. field is in the vacuum state) then $\alpha_0(0) = 1$, while $\alpha_n(0) = 0\ \forall n \neq 0$. Then there are only two components that are different than zero:

$$\alpha_0(t) = e^{i\Delta t/2}\left[\cos\left(\frac{\Omega_0 t}{2}\right) - \frac{i\Delta}{\sqrt{\Delta^2+4g^2}}\sin\left(\frac{\Omega_0 t}{2}\right)\right]$$

$$\beta_1(t) = -e^{-i\Delta t/2}\frac{2ig}{\sqrt{\Delta^2+4g^2}}\sin\left(\frac{\Omega_0 t}{2}\right)$$

Thus, even in the absence of field, it is possible to make the transition from the ground to the excited state! In the semiclassical case (where the field is treated as classical) we would have no transition at all. The oscillations obtained in the quantum case are called the vacuum Rabi oscillations.

12.3.2 Interaction with many modes of the e.m. field

In analyzing the interaction of an atom with a *single* mode of radiation we found that transitions can occur only if energy is conserved. In the real world however we are always confronted with a finite linewidth of any transition. In order to find the linewidth we need to look at a multi-mode field.
Consider the same Hamiltonian as used in the previous section, but now we treat a field with many modes. The interaction Hamiltonian in the interaction frame is given by

$$V_I = \hbar\sum_k g_k^* a_k \sigma_+ e^{i(\omega-\nu_k)t} + g_k a_k^\dagger \sigma_- e^{-i(\omega-\nu_k)t}$$

We consider a case similar to the one consider at the end of the previous section, where initially the e.m. field is in the vacuum state and the atomic transition creates one photon. Now, however, this photon can be in one of many modes. The state vector is then:

$$|\psi(t)\rangle = \alpha(t)\,|e,0\rangle + \sum_k \beta_k\,|g,1_k\rangle$$

(now the index k in β_k label the mode and not the photon number) and the initial conditions are $\alpha(0) = 1$, $\beta_k(0) = 0$, $\forall k$. The system of equations for the coefficients are

$$\begin{cases} \dot\alpha(t) = -i\sum_k g_k^* e^{i(\omega-\nu_k)t}\beta_k(t) \\ \dot\beta_k(t) = -ig_k e^{-i(\omega-\nu_k)t}\alpha(t) \end{cases}$$

If we consider this transition as a decay process from the excited to the ground state, $|\alpha(t)|^2$ gives the decay probability. To solve for $\alpha(t)$ we first integrate $\dot\beta$:

$$\dot\alpha = -i\sum_k g_k^* e^{i(\omega-\nu_k)t}\left(\int_0^t -ig_k e^{-i(\omega-\nu_k)t'}\alpha(t')dt'\right)$$

We can rewrite the expression as:

$$\dot\alpha = -\sum_k |g_k|^2 \int_0^t dt' e^{-i(\omega-\nu_k)(t'-t)}\alpha(t')$$

Assumption 1)
We assume that the modes of the e.m. form a continuum, so that we can replace the sum by an integral $\sum_k \to \int \rho(k)d^3k$, with the density of states set by $\nu_k = ck$ as usual: $\rho(k)d^3k = 2\left(\frac{L}{2\pi}\right)^3 k^2 dk\, d\varphi\, \sin\vartheta d\vartheta$.

We then remember the explicit form of the interaction coupling in terms of the dipole operator:

$$|g_k|^2 = \frac{\nu_k}{4\hbar L^3}|d_{eg}|^2 \sin^2\vartheta$$

and using again $\nu_k = ck$ we obtain

$$\dot{\alpha} = -\frac{4|d_{eg}|^2}{(2\pi)^2 6\hbar c^3}\int_0^\infty \nu_k^3 d\nu_k \int_0^t dt' e^{-i(\omega-\nu_k)(t'-t)}\alpha(t')$$

Assumption 2)
In order for the transition to happen, we still need $\nu_k \approx \omega$.
This allows two simplifications: i) we can replace ν_k^3 with ω^3 in the integral, and ii) we can extend the lower integral limit to $-\infty$ (since anyway we know that it will give contributions only for $\nu_k \approx \omega$). By furthermore inverting the order of the integrals we obtain

$$\int_0^\infty \nu_k^3 d\nu_k \int_0^t dt' \cdots \to \int_0^t dt'\alpha(t')\omega^3 \int_{-\infty}^\infty d\nu_k e^{-i(\omega-\nu_k)(t'-t)} = \int_0^t dt'\alpha(t')\omega^3 2\pi\delta(t-t') = 2\pi\alpha(t)\omega^3$$

Thus, the differential equation defining the evolution of $\alpha(t)$ simplifies to

$$\dot{\alpha}(t) = -\frac{1}{2\pi}\frac{d_{eg}^2\omega^3}{3\hbar c^3}\alpha(t) = -\frac{\Gamma}{2}\alpha(t)$$

Here we defined the rate of spontaneous emission

$$\Gamma = \frac{d_{eg}^2\omega^3}{3\pi\hbar c^3}$$

Notice that the decay rate is related to Einstein's emission rate, as $\Gamma = A_e/4\pi$ as we should expect, since it is related to the total emission (at any frequency) from the excited to the ground state.
Thus we have simply $\alpha(t) = e^{-\Gamma t/2}$ and the decay probability $P_d = e^{-\Gamma t}$.

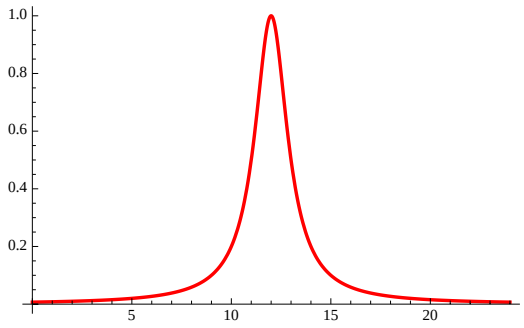


Fig. 23: Lorentzian lineshape, centered at $\omega = 12$ and with a linewidth $\Gamma = 2$

From the expression for $\alpha(t)$ we can go back and calculate an explicit form for $\beta_k(t)$:

$$\beta_k(t) = -i\int_0^t dt' g_k e^{-i(\omega-\nu_k)t'}e^{-\Gamma t'/2} = g_k\frac{1-e^{-i(\omega-\nu_k)t}e^{-\Gamma t/2}}{(\nu_k-\omega)+i\Gamma/2}$$

The frequency spectrum of the emitted radiation is given by $P(\nu_k) = \rho(\nu_k)\sum_{\lambda=1,2}\int_\Omega d\Omega\,|\beta_k(t)|^2$ in the limit where $t \to \infty$.

$$P(\nu_k) \propto \lim_{t\to\infty}\frac{1+e^{-\Gamma t}(1-2\cos[(\omega-\nu_k)t]}{\frac{\Gamma^2}{4}+(\omega-\nu_k)^2} \sim 1/\ \frac{\Gamma^2}{4}+(\omega-\nu_k)^2$$

Thus the spectrum is a Lorenztian centered around ω and with linewidth Γ.

12.4 Scattering of photons by atoms

In this section we want to study the scattering of photons by electrons (either free electrons or in an atom). We previously studied similar processes:

- Scattering theory (with an example for thermal neutrons)
- Emission and absorption of photons (in the dipole approximation)

Notice that these last processes only involved a single photon (either absorbed or emitted). Now we want to study the scattering of photons, meaning that there will be an incoming photon and an outgoing photon: this is a process that involves two photons.

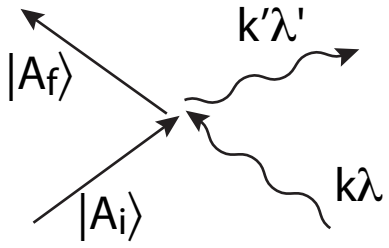


Fig. 24: Photon scattering cartoon

In order to study atom-photon interaction we need of course to start from the quantized e.m. field:

$$\mathcal{H} = \frac{\tilde{p}^2}{2m} + \hbar\omega(n+\frac{1}{2}) = \frac{1}{2m}\left(p - \frac{eA}{c}\right)^2 + \hbar\omega(n+\frac{1}{2})$$

We can separate the interaction Hamiltonian as:

$$\mathcal{H} = \mathcal{H}_0 + V = \underbrace{\frac{p^2}{2m} + \hbar\omega(n+\frac{1}{2})}_{\mathcal{H}_0} + \underbrace{-\frac{e}{2mc}(p\cdot A + A\cdot p) + \frac{e^2}{2mc^2}A^2}_{V}$$

More generally, if there are many electrons, the interaction Hamiltonian is given by

$$V = \sum_i -\frac{e}{2mc}\left[p_i \cdot A(r_i) + A(r_i)\cdot p_i\right] + \frac{e^2}{2mc^2}A(r_i)^2$$

We already used the first term (in the dipole approximation $\frac{e}{mc}p\cdot A \to d\cdot E$) to find emission and absorption processes. As stated, these processes only involve one photon. How do we obtain processes that involve two photons? Since from the term $p\cdot A$ and in the first order perturbation theory we do not get them, we will need

i) either terms $\propto A^2$, or

ii) second order perturbation for the term $\propto p\cdot A$.

Notice that both these choices yield transitions that are $\propto \alpha^2 = \left(\frac{e^2}{\hbar c}\right)^2$, that is, that are second order in the fine structure constant.
Thus we want to calculate scattering transition rates given by $W = \frac{2\pi}{\hbar}|K_1^{(2)} + K_2^{(1)}|^2\rho(E_f)$, where

- $K_1^{(2)}$ is the 2^{nd} order contribution from $V_1 = -\frac{e}{mc}\sum_i p_i\cdot A_i$ and
- $K_2^{(1)}$ is the 1^{st} order contribution from $V_2 = \frac{e^2}{2mc}\sum_i A_i^2$.

$K_1^{(1)}$ is instead zero, since it only connects state that differ by one photon (thus it's not a scattering process) and we neglect higher orders than the second.
The initial and final eigenstates and eigenvalues are as follow (where γ indicate the photon):

	Initial	Final	In. Energy	Fin. Energy
e^-:	$\|A_i\rangle$	$\|A_f\rangle$	ϵ_i	ϵ_f
γ:	$\|1_{k,\lambda}, 0_{k',\lambda'}\rangle$	$\|0_{k,\lambda}, 1_{k',\lambda'}\rangle$	$\hbar\omega_k$	$\hbar\omega'_k$
tot:	$\|i\rangle$	$\|f\rangle$	E_i	E_f

We first evaluate $K_2^{(1)}$ for a single electron. We recall the expression for the vector potential (see Section 10.3):

$$\vec{A} = \sum_{k,\lambda} \sqrt{\frac{2\pi\hbar c^2}{L^3\omega_k}} \left(a_{k\lambda} e^{ik\cdot r} + a^\dagger_{k\lambda} e^{-ik\cdot r} \right) \vec{\epsilon}_{k\lambda}.$$

$K_2^{(1)}$ is proportional to A^2, but we only retain terms that link the correct modes (k, k') and that are responsible for the annihilation of a photon in mode k and the creation of a photon of mode k'. These are terms $\propto a^\dagger_{k'} a_k$. We find:

$$\begin{aligned} K_2^{(1)} = \langle f| V_2 |i\rangle = \tfrac{e^2}{2mc^2} \tfrac{2\pi\hbar c^2}{L^3\sqrt{\omega_k\omega_{k'}}} \vec{\epsilon}_{k\lambda} \cdot \vec{\epsilon_{k'\lambda'}} \\ \times \langle f| a_{k\lambda} a^\dagger_{k'\lambda'} e^{i(k-k')\cdot r} + \cancel{a^\dagger_{k\lambda} a_{k'\lambda'} e^{-i(k-k')\cdot r}} + \cancel{a^\dagger_{k\lambda} a^\dagger_{k'\lambda'} e^{-i(k+k')\cdot r}} + \cancel{a_{k\lambda} a_{k'\lambda'} e^{i(k+k')\cdot r}} |i\rangle \end{aligned}$$

We now use the equality $\omega_k = c|k|$ and $\vec{k} - \vec{k}' = \vec{q} = \vec{p}/\hbar$ (the electron recoil momentum) to simplify the expression. Thus we obtain:

$$K_2^{(1)} = \frac{e^2}{2mc} \frac{2\pi\hbar c^2}{L^3\sqrt{kk'}} \vec{\epsilon}_{k\lambda} \cdot \vec{\epsilon_{k'\lambda'}} \langle A_f| e^{i\vec{q}\cdot\vec{r}} |A_i\rangle \langle 0_{k\lambda} 1_{k'\lambda'}| a_{k\lambda} a^\dagger_{k'\lambda'} |1_{k\lambda} 0_{k'\lambda'}\rangle ,$$

where the last inner product is just equal to 1. We can now extend $K_2^{(1)}$ to many electrons:

$$K_2^{(1)} = \langle f| V_2 |i\rangle = \frac{e^2}{2m} \frac{2\pi\hbar c}{L^3\sqrt{kk'}} \vec{\epsilon}_{k\lambda} \cdot \vec{\epsilon_{k'\lambda'}} \langle A_f| \sum_i e^{i\vec{q}\cdot\vec{r}_i} |A_i\rangle .$$

This is the first contribution to the scattering matrix element, first order in perturbation theory from the quadratic term in the field potential.

We now want to calculate $K_1^{(2)}$, the second order contribution from the linear part V_1 of the potential:

$$K_1^{(2)} = \sum_h \frac{\langle f| V_1 |h\rangle \langle h| V_1 |i\rangle}{E_i - E_h}$$

Note that this term describes virtual transitions to intermediate states since from first order transitions V_1 can only create or annihilate one photon at a time. So there are two possible processes that contribute to $K_1^{(2)}$,

- first absorption of one photon in the $k\lambda$ mode followed by creation of one photon in the $k'\lambda'$ mode: the intermediate state is zero photons in these two modes.
- first creation of one photon in the $k'\lambda'$ mode followed by annihilation of the photon in mode $k\lambda$: the intermediate state is one photon in each mode.

Explicitly we have:

$$\begin{aligned} K_1^{(2)} = \sum_h \frac{\langle A_f| \langle 0_{k\lambda} 1_{k'\lambda'}| V_1 |0_{k\lambda} 0_{k'\lambda'}\rangle |A_h\rangle \langle A_h| \langle 0_{k\lambda} 0_{k'\lambda'}| V_1 |1_{k\lambda} 0_{k'\lambda'}\rangle |A_i\rangle}{\epsilon_i - \epsilon_h + \hbar\omega_k} \\ + \sum_h \frac{\langle A_f| \langle 0_{k\lambda} 1_{k'\lambda'}| V_1 |1_{k\lambda} 1_{k'\lambda'}\rangle |A_h\rangle \langle A_h| \langle 1_{k\lambda} 1_{k'\lambda'}| V_1 |1_{k\lambda} 0_{k'\lambda'}\rangle |A_i\rangle}{\epsilon_i + \hbar\omega_k - (\epsilon_h + \hbar\omega_k + \hbar\omega_{k'})} \end{aligned}$$

Notice that $K_1^{(2)}$ has an extra factor $\propto \omega_k$ in the denominator with respect to $K_2^{(1)}$. Thus at higher energies of the incident photon (such as x-ray scattering) only $K_1^{(2)}$ survives, while at lower energies (optical regime) $K_2^{(1)}$ is more important.

A. Types of Scattering

Depending on the energy $\hbar\omega$ of the incident photon (with respect to the ionization energy E_I of the atom) and on the elastic or inelastic character of the scattering, the scattering process is designated with different names.

- Rayleigh scattering (Low energy, Elastic): $\hbar\omega \ll E_I, |E_h - E_I|$, $E_f = E_I$.
  The final state has the same energy as the initial one, $E_f = E_i$ since the scattering is elastic. The scattering thus involve intermediate virtual levels, with energies E_h. We will find a cross section $\sigma \propto \omega^4$.
- Raman scattering (Low energy, Inelastic): $\hbar\omega \ll E_I$, $E_f \neq E_I$.
  Usually the final state is a different rotovibrational state of the molecule, so the energy difference between initial and final state is small. If $E_f > E_I$ the scattering process is called *Stokes*, otherwise if $E_f < E_I$ the scattering process is called *anti-Stokes*.
- Thomson scattering (High energy, Elastic): $\hbar\omega \gg E_I$, $E_f = E_I$.
  This process is predominant for, e.g., soft x-ray scattering. This type of scattering can be interpreted in a semi-classical way, in the limit where the wavelength λ is larger than the atomic dimensions, $\lambda \ll a_0$. The cross section is then equivalent to what one would obtain for a free electron, $\sigma = \frac{8}{3}\pi r_0^2$ with r_0 the effective electron radius.
- Compton scattering (High energy, Inelastic): $\hbar\omega \gg E_I$, $\lambda \ll a_0$, $E_f = E_I$.
  For very high energy, the wavelength is small compared to the atom's size and the energy is much larger than the electron binding energy, so that the final state of the electron is an unbound state. Thus this scattering is very similar to Compton scattering (inelastic scattering) by a free electron.

Note that for x-ray scatterings the classification is slightly different than the one given above. There are two processes that competes with Coulomb scattering even at the x-ray energies:

- Electronic Raman scattering: an inelastic scattering process where the initial atomic state is the ground state and the final state an excited, discrete electronic state.
- Rayleigh scattering for x-rays: an elastic scattering process, where the final atomic state is the same as the initial state, since there is no atom excitation.

In addition to scattering processes, other processes involving the interaction of a photon with electrons are possible (besides absorption and emission of visible light that we already studied). In order of increasing photon energy, the interaction of matter with e.m. radiation can be classified as:

Rayleigh/Raman Scattering	Photoelectric Absorption	Thomson Scattering	Compton Scattering	Pair Production
$\hbar\omega < E_I$	$\hbar\omega \geq E_I$	$\hbar\omega \gg E_I$	$\hbar\omega \sim m_e c^2$	$\hbar\omega > 2m_e c^2$
$\sim$eV	$\sim$keV	$\sim$keV	$\sim$MeV	$\geq$MeV
Visible	X-rays	X-rays	γ-rays	hard γ-rays

B. Semi-classical description of scattering

A classical picture is enough to give some scaling for the scattering cross section. We consider the effects of the interaction of the e.m. wave with an oscillating dipole (as created by an atomic electron).
The electron can be seen as being attached to the atom by a "spring", and oscillating around its rest position with frequency ω_0. When the e.m. is incident on the electron, it exerts an additional force. The force acting on the electron is $F = -eE(t)$, with $E(t) = E_0 \sin(\omega t)$ the oscillating electric field. This oscillating driving force is in addition to the attraction of the electron to the atom $\sim -kx_e$, where k (given by the Coulomb interaction strength and related to the binding energy E_I) is linked to the electron's oscillating frequency by $\omega_0^2 = k/m_e$. The equation of motion for the electron is then

$$m_e \ddot{x}_e = -kx_e - eE(t) \qquad \rightarrow \qquad \ddot{x}_e + \omega_0^2 x_e = -\frac{e}{m_e} E(t)$$

We seek a solution of the form $x_e(t) = A\sin(\omega t)$, then we have the equation

$$(-\omega^2 + \omega_0^2)A = -\frac{e}{m_e} E_0 \qquad \rightarrow \qquad A = \frac{1}{\omega^2 - \omega_0^2} \frac{e}{m_e} E_0$$

An accelerated charge (or an oscillating dipole) radiates, with a power

$$P = \frac{2}{3}\frac{e^2}{c^3}a^2$$

where the accelaration a is here $a = -\omega^2 A\sin(\omega t)$, giving a mean square acceleration

$$\langle a^2\rangle = \left(\frac{\omega^2}{\omega_0^2-\omega^2}\frac{e}{m_e}E_0\right)^2\frac{1}{2}$$

The radiated power is then

$$P = \frac{1}{3}\left(\frac{e^2}{m_e c^2}\right)^2\frac{\omega^4}{(\omega_0^2-\omega^2)^2}cE_0^2$$

The radiation intensity is given by $I_0 = \frac{cE_0^2}{8\pi}$ (recall that the e.m. energy density is given by $u = \frac{1}{2}E^2$ and the intensity, or power per unit area, is then $I \sim cu$). Then we can express the radiated power as cross-section×radiation intensity:

$$P = \sigma I_0$$

This yields the cross section for the interaction of e.m. radiation with atoms :

$$\sigma = \frac{8\pi}{3}\left(\frac{e^2}{m_e c^2}\right)^2\left(\frac{\omega^2}{\omega_0^2-\omega^2}\right)^2$$

or in SI units:

$$\sigma = \frac{8\pi}{3}\left(\frac{e^2}{4\pi\epsilon_0 m_e c^2}\right)^2\left(\frac{\omega^2}{\omega_0^2-\omega^2}\right)^2 = 4\pi r_e^2\frac{2}{3}\left(\frac{\omega^2}{\omega_0^2-\omega^2}\right)^2$$

where we used the classical electron radius [40]:

$$r_e = \frac{e^2}{mc^2}$$

which is about 2.8 fm (2.8×10^{-15}m).

12.4.1 Thomson Scattering by Free Electrons

We consider first the Thomson scattering, which is well described by the scattering by free electrons. In this case we consider thus one single electron. Also in general, the photon should have energy high enough that the electron is seen as free even if in reality it is part of an atom (thus the photon energy must be larger than the atom's ionization energy, $\hbar\omega \gg E_I$ or in other terms $\lambda \gg$ than the atom's size). Note that in Thomson scattering the final electron is still a bound electron (elastic scattering) while in Compton scattering the electron is unbound (inelastic scattering). Still, since the binding energy is small compared to the other energy at play, the electron can be considered as a free electron, and many of the characteristics of Compton scattering still apply.

	Initial	Final
e^-:	$\|A_i\rangle$	$\|A_f\rangle$
φ:	$\|1_{k,\lambda}, 0_{k',\lambda'}\rangle$	$\|0_{k,\lambda}, 1_{k',\lambda'}\rangle$
tot:	$\|i\rangle$	$\|f\rangle$

	Initial		Final
En:	$mc^2+\hbar ck$	=	$\hbar ck' + \sqrt{p_e^2c^2+m^2c^4}$
p_x:	$\hbar k$	=	$\hbar k'\cos\vartheta + p\cos\varphi$
p_y:	0	=	$\hbar k'\sin\vartheta - p\sin\varphi$

[40] The Bohr radius is a different quantity: $r_B \sim \frac{\hbar^2}{me^2}$ with some constants (depending on the units chosen) to give about $r_B \sim 5\times10^{-11}$m

The initial and final states, as well as energies and momentum are written above. They result from the conservation of energy and momentum for a relativistic electron which is initially at rest.

? Question: What is the ratio k/k'? What is $\Delta\lambda = \lambda' - \lambda$? (This is the usual Compton scattering formula).
From conservation of energy and momentum and with the geometry of figure 25, we can calculate the energy of the scattered photon.

$$E_\gamma + E_e = E'_\gamma + E'_e \qquad \rightarrow \qquad \hbar\omega + m_e c^2 = \hbar\omega' + \sqrt{|p|^2c^2 + m^2c^4}$$

$$\hbar\vec{k} = \hbar\vec{k}' + \vec{p} \qquad \rightarrow \qquad \begin{cases} \hbar k = \hbar k' \cos\vartheta + p\cos\varphi \\ \hbar k' \sin\vartheta = p \sin\varphi \end{cases}$$

From these equations we find $p^2 = \frac{\hbar(\omega'-\omega)}{c^2}\left[\hbar(\omega'-\omega) - 2mc^2\right]$ and $\cos\varphi = \sqrt{1 - \hbar^2 k'^2 \sin^2\vartheta/p^2}$. Solving for the change in the wavelength $\lambda = \frac{2\pi}{k}$ we find (with $\omega = kc$):

$$\Delta\lambda = \frac{2\pi\hbar}{m_e c}(1 - \cos\vartheta)$$

or for the frequency:

$$\hbar\omega' = \hbar\omega\left[1 + \frac{\hbar\omega}{m_e c^2}(1 - \cos\vartheta)\right]^{-1}$$

□

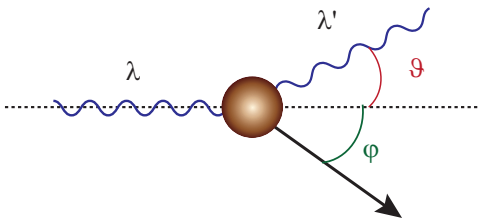


Fig. 25: Photon/Electron collision in Compton and Thomson scattering.

At these high energies, $K_1^{(2)} \ll K_2^{(1)}$ thus we can consider only the $K_2^{(1)}$ contribution, that we already calculated in the previous section.
To find the scattering rate and cross section we need the **density of states**:

$$\rho(E_f)dE_f = \left(\frac{L}{2\pi}\right)^3 k'^2 dk' d\Omega$$

where the final energy is $E_f = \hbar c k' + \sqrt{p_e^2c^2 + m^2c^4} \approx \hbar c k' + \frac{p_e^2}{2m}$ (non-relativistic approximation). Thus we need to calculate $\frac{d\,E_f}{d\,k'}$. Noting that

$$p^2/\hbar^2 = |k - k'|^2 = k^2 + k'^2 - 2kk'\cos\vartheta$$

we find

$$\frac{d\,E_f}{d\,k'} = \hbar c + \frac{\hbar^2}{2m}(2k' - 2k\cos\vartheta) = \hbar c\left[1 + \frac{\hbar k}{mc}\left(\frac{k'}{k} - \cos\vartheta\right)\right]$$

Solving the conservation of energy and momentum equations, we find

$$\frac{k'}{k} = \left[1 + \frac{\hbar k}{mc}(1 - \cos\vartheta)\right]^{-1}$$

Since $\hbar k \ll mc$, we can take only the first order term in $1 + \frac{\hbar k}{mc}\left(\frac{k'}{k} - \cos\vartheta\right)$. This is given by: $1 + \frac{\hbar k}{mc}(1 - \cos\vartheta)$. But this factor is just equal to k/k'. Thus we finally have:

$$\frac{d\,E_f}{d\,k'} = \hbar c \frac{k}{k'} \qquad \rightarrow \qquad \rho(E_f) = \left(\frac{L}{2\pi}\right)^3 \frac{k'^3}{k\hbar c} d\Omega$$

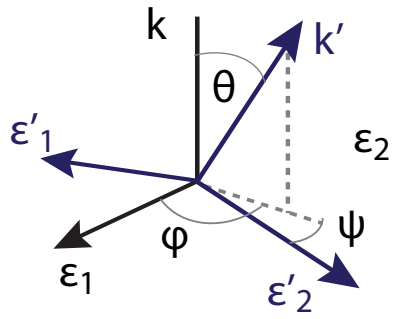


Fig. 26: Wave vectors and polarizations of scattering photons. $\cos\gamma = \sin\vartheta\cos\psi$

Finally, to calculate the cross section, we recall the expression for the incoming flux of photons $\Phi = c/L^3$.

$$\frac{d\,\sigma}{d\,\Omega} = \frac{W_{fi}/d\Omega}{c/L^3} = \frac{2\pi}{\hbar}|K_2^{(1)}|^2 \frac{\rho(E_f)}{d\Omega}\frac{L^3}{c} = \left(\frac{e^2}{mc^2}\right)^2 \left(\frac{k'}{k}\right)^2 |\epsilon_{k\lambda}\cdot\epsilon_{k'\lambda'}|^2$$

With the angles defined in Fig. 26 we find:

$$\frac{d\,\sigma}{d\,\Omega} = r_e^2 \left(\frac{\omega'_k}{\omega_k}\right)^2 \sin^2\gamma$$

where $(\sin\gamma)^2 = 1 - \sin^2\vartheta\cos^2(\varphi - \psi)$ and r_e is the classical electron radius. The average differential cross section (averaged over the polarization directions ψ) is then given by

$$\left\langle \frac{d\,\sigma}{d\,\Omega} \right\rangle = r_e^2 \left(\frac{\omega'_k}{\omega_k}\right)^2 (1 - \sin^2\vartheta/2) = \frac{1}{2} r_e^2 \left(\frac{\omega'_k}{\omega_k}\right)^2 (1 + \cos^2\vartheta)$$

12.4.2 Rayleigh Scattering of X-rays

Rayleigh scattering usually describes elastic scattering by low energy radiation. It describes for example visible light scattering from atoms: in that case, the predominant contribution comes from the term $K_1^{(2)}$. Rayleigh scattering also describes coherent, elastic scattering of x-rays from atoms (e.g. in a crystal) and is an important process in x-ray diffraction.
In the case of x-ray scattering, the photon energy is larger then the electronic excitation energy: $\hbar\omega \gg E_b$. Then we have, as stated above, $K_1^{(2)} \ll K_2^{(1)}$ and we can neglect the $K_1^{(2)}$ contribution. As we are considering now bound electrons, the recoil is zero, and $\frac{d\,E_f}{d\,k'} = \hbar c$. Then the density of states is simply $\rho(E_f) = \frac{L}{2\pi}^3 \frac{k'^2}{\hbar c} d\Omega$.
The cross section is given by

$$\frac{d\,\sigma}{d\,\Omega} = \frac{2\pi}{\hbar}\frac{|K_2^{(1)}|^2}{c/L^3}\frac{\rho(E_f)}{d\Omega} = \frac{2\pi}{\hbar}\frac{c^2 r_e^2}{c/L^3}\left(\frac{2\pi\hbar}{L^3}\right)^2 \frac{1}{kk'}\left(\frac{L}{2\pi}\right)^3 \frac{k'^2}{\hbar c}|\epsilon_{k\lambda}\cdot\epsilon_{k'\lambda'}|^2 |\langle A_f|\sum_i e^{i\vec{q}\cdot\vec{r}_i}|A_i\rangle|^2$$

$$= r_e^2\left(\frac{\omega'_k}{\omega}\right)|\epsilon_{k\lambda}\cdot\epsilon_{k'\lambda'}|^2 |\langle A_f|\sum_i e^{i\vec{q}\cdot\vec{r}_i}|A_i\rangle|^2$$

Consider an elastic scattering process (the inelastic scattering is called Raman scattering for x-rays). If the incoming x-ray is unpolarized, we have

$$\frac{d\,\sigma}{d\,\Omega} = \frac{r_e^2}{2}(1+\cos^2\vartheta)|\langle g|\sum_i e^{i\vec{q}\cdot\vec{r}_i}|g\rangle|^2$$

We define $f(p) = \langle g|\sum_i e^{i\vec{q}\cdot\vec{r}_i}|g\rangle$ the atomic form factor.

1) Notice that for $p \to 0$ $|\langle g|\sum_i 1|g\rangle|^2 = Z^2$ (the atomic number squared). Thus in general we expect Rayleigh scattering to be weaker for lighter elements.
2) In general we can rewrite the sum as an integral $\sum_i e^{i\vec{q}\cdot\vec{r}_i} \to \int e^{i\vec{q}\cdot\vec{r}}\tilde{\rho}(r)d^3r$ using the charge density $\tilde{\rho}(r) = \sum_i \delta(r-r_i)$. Then the atomic form factor takes the form:

$$f(p) = \langle g|\int e^{i\vec{q}\cdot\vec{r}}\tilde{\rho}(r)d^3r\,|g\rangle = \int e^{i\vec{q}\cdot\vec{r}}\overline{\rho}(r)d^3r$$

with $\overline{\rho}(r) = \langle g|\,\tilde{\rho}(r)\,|g\rangle$. Then the atomic form factor is the Fourier transform of the charge density.

Scattering from a crystal

In a crystal, we can rewrite the electron positions with the substitution $r_i \to R_l + r_{li}$, where R_l is the atom position (or the nucleus position or the atomic center of mass position). Then we need to sum over all atoms and all electrons in the atom. Then we have the structure factor:

$$G(q) = \langle g|\sum_{l,i} e^{i\vec{q}\cdot\vec{R}_l}e^{i\vec{q}\cdot\vec{r}_{il}}|g\rangle = \sum_l f_l(q)e^{i\vec{q}\cdot\vec{R}_l}$$

with $f_l = \langle g|\sum_i e^{i\vec{q}\cdot\vec{r}_{il}}|g\rangle$.
In a crystal we can rewrite the atom position as $R_{lj} = \underbrace{l_1a_1 + l_2a_2 + l_3a_3}_{\text{unit cell}} + \underbrace{r_j}_{\text{position in cell}}$. Then

$$G(q) = \sum_{lj}\underbrace{f_j(q)e^{i\vec{q}\cdot\vec{r}_j}}_{F(q)}e^{iq(l_1a_1+l_2a_2+l_3a_3)} = \sum_{l_1,l_2,l_3}F(q)e^{iq(l_1a_1+l_2a_2+l_3a_3)}$$

$F(q)$ is the form factor for the unit cell, which is tabulated for different crystals. The cross section can be written as:

$$\frac{d\,\sigma}{d\,\Omega} = \frac{r_e^2}{2}(1+\cos^2\vartheta)|F(q)|^2\frac{\sin^2(N_1qa_1/2)}{\sin^2(qa_1/2)}\frac{\sin^2(N_2qa_2/2)}{\sin^2(qa_2/2)}\frac{\sin^2(N_3qa_3/2)}{\sin^2(qa_3/2)}$$

Only when $qa_n = 2\pi h$ the interferences terms do not vanish: this is Bragg's diffraction law.

12.4.3 Visible Light Scattering

When considering visible light, the wavelength is large compared to the atomic size. Then, instead of using the full interaction $V_1 + V_2$ we can safely substitute it with the electric dipole Hamiltonian[41], $V = -\vec{d}\cdot\vec{E}$. This Hamiltonian does not produce any two-photon process to first order, so in this case we need to consider the term $K^{(2)}$. This term involves virtual transitions. Since the duration of these transitions is very small, we do not have to worry about conservation of energy. Recall:

$$K^{(2)} = \sum_h \frac{\langle f|\, V\,|h\rangle\,\langle h|\, V_1\,|i\rangle}{E_i - E_h},$$

where $V = -\vec{d}\cdot\vec{E}$. The intermediate states are either $|h\rangle = |A_h\rangle\,|0_{k\lambda}0_{k'\lambda'}\rangle$ or $|h\rangle = |A_h\rangle\,|1_{k\lambda}1_{k'\lambda'}\rangle$. It would be of course possible to derive the scattering cross section from the vector-potential/momentum Hamiltonian, and in that case both terms $K_2^{(1)}$ and $K_1^{(2)}$ should be included [42].
The electric field in the Lorentz gauge is

$$E = \sum_{\ell,\xi}\sqrt{\frac{2\pi\hbar\omega_\ell}{L^3}}\left(a_{\ell\xi}e^{i\ell\cdot R} + a^\dagger_{\ell\xi}e^{-i\ell\cdot R}\right)\epsilon_{\ell\xi},$$

and thus we obtain for $\langle h|\, V_1\,|i\rangle$ and $\langle f|\, V_1\,|h\rangle$:

- $\langle 0_{k\lambda}1_{k'\lambda'}|\left(a_{\ell\xi}e^{i\ell\cdot R} + a^\dagger_{\ell\xi}e^{-i\ell\cdot R}\right)|0_{k\lambda}0_{k'\lambda'}\rangle = e^{-ik'\cdot R}\delta_{\ell,k'}$
- $\langle 0_{k\lambda}0_{k'\lambda'}|\left(a_{\ell\xi}e^{i\ell\cdot R} + a^\dagger_{\ell\xi}e^{-i\ell\cdot R}\right)|1_{k\lambda}0_{k'\lambda'}\rangle = e^{ik\cdot R}\delta_{\ell,k}$
- $\langle 0_{k\lambda}1_{k'\lambda'}|\left(a_{\ell\xi}e^{i\ell\cdot R} + a^\dagger_{\ell\xi}e^{-i\ell\cdot R}\right)|1_{k\lambda}1_{k'\lambda'}\rangle = e^{ik\cdot R}\delta_{\ell,k}$
- $\langle 1_{k\lambda}1_{k'\lambda'}|\left(a_{\ell\xi}e^{i\ell\cdot R} + a^\dagger_{\ell\xi}e^{-i\ell\cdot R}\right)|1_{k\lambda}0_{k'\lambda'}\rangle = e^{-ik'\cdot R}\delta_{\ell,k'}$

thus we have

$$K_1^{(2)} = \frac{2\pi\hbar}{L^3}\sqrt{\omega_k\omega_{k'}}e^{i(k-k')R}\sum_h \frac{\langle A_f|\, d\cdot\epsilon_{k'}\,|A_h\rangle\,\langle A_h|\, d\cdot\epsilon_k\,|A_i\rangle}{\epsilon_i - \epsilon_h + \hbar\omega_k} + \sum_h \frac{\langle A_f|\, d\cdot\epsilon_k\,|A_h\rangle\,\langle A_h|\, d\cdot\epsilon_{k'}\,|A_i\rangle}{\epsilon_i + \hbar\omega_k - (\epsilon_h + \hbar\omega_k + \hbar\omega_{k'})}$$

The scattering cross section is given as usual by $\frac{d\,\sigma}{d\,\Omega} = \frac{W}{c/L^3}$. and the density of state (assuming no recoil) is

$$\rho(E_f) = \left(\frac{L}{2\pi}\right)^3 \frac{k'^2}{\hbar c}d\Omega.$$

Finally the cross section is given by:

$$\frac{d\,\sigma}{d\,\Omega} = \frac{2\pi}{\hbar}\left(\frac{2\pi\hbar}{L^3}\right)^2\omega_k\omega_{k'}\left(\frac{L}{2\pi}\right)^3\frac{k'^2}{\hbar c}\frac{L^3}{c}\left|\sum_h \frac{(d_{fh}\cdot\epsilon_{k'})(d_{hi}\cdot\epsilon_k)}{\epsilon_i - \epsilon_h + \hbar\omega_k} + \frac{(d_{fh}\cdot\epsilon_k)(d_{hi}\cdot\epsilon_{k'})}{\epsilon_i - \epsilon_h - \hbar\omega_{k'}}\right|^2$$

$$\frac{d\,\sigma}{d\,\Omega} = kk'^3\left|\sum_h \frac{(d_{fh}\cdot\epsilon_{k'})(d_{hi}\cdot\epsilon_k)}{\epsilon_i - \epsilon_h + \hbar\omega_k} + \frac{(d_{fh}\cdot\epsilon_k)(d_{hi}\cdot\epsilon_{k'})}{\epsilon_i - \epsilon_h - \hbar\omega_{k'}}\right|^2$$

[41] A unitary transformation changes the Coulomb-gauge Hamiltonian into an expansion in terms of multipoles of the electromagnetic fields. For atomic interactions, only the electric dipole is kept, while higher multipoles, such as magnetic dipole and electric quadrupole, can be neglected. This unitary transformation is describe, e.g., in Cohen-Tannoudji's book, Atom-Photons Interactions

[42] This derivation can be found in Chen, S.H.; Kotlarchyk, M., *Interactions of Photons and Neutrons with Matter,* (2007)

A. Rayleigh scattering

Rayleigh scattering describes elastic scattering, for which $\omega_k = \omega_{k'}$ since $|A_f\rangle = |A_i\rangle$. Then we can simplify the cross section:

$$\frac{d\,\sigma}{d\,\Omega} = k^4 \left| \sum_h \frac{(d_{ih}\cdot\epsilon_k)(d_{hi}\cdot\epsilon_k)}{\epsilon_i - \epsilon_h + \hbar\omega_k} + \frac{(d_{ih}\cdot\epsilon_k)(d_{hi}\cdot\epsilon_k)}{\epsilon_i - \epsilon_h - \hbar\omega_k} \right|^2$$

At long wavelengths $\hbar\omega_k \ll \epsilon_h - \epsilon_i$, thus we can neglect ω_k in the denominator. Then

$$\frac{d\,\sigma}{d\,\Omega} \propto \omega_k^4 \left| 2\sum_h \frac{(d_{ih}\cdot\epsilon_k)(d_{hi}\cdot\epsilon_k)}{\epsilon_i - \epsilon_h} \right|^2$$

and simplifying we obtain that

$$\frac{d\,\sigma}{d\,\Omega} \propto \omega_k^4$$

This expression could have been found from the classical cross section we presented earlier, in the same limit $\omega \ll \omega_0$. The Rayleigh scattering has a very strong dependence on the wavelength of the e.m. wave. This is what gives the blue color to the sky (and the red color to the sunsets): more scattering occurs from higher frequencies photons (with shorter wavelength, toward the blue color).
As light moves through the atmosphere, most of the longer wavelengths pass straight through. Little of the red, orange and yellow light is affected by the air. However, much of the shorter wavelength light is scattered in different directions all around the sky. Whichever direction one looks, some of this scattered blue light reaches you. Since the blue light is seen from everywhere overhead, the sky looks blue.Closer to the horizon, the sky appears much paler in color, since the scattered blue light must pass through more air. Some of it gets scattered away again in other directions and the color of the sky near the horizon appears paler or white. As the sun begins to set, the light must travel farther through the atmosphere. More of the light is reflected and scattered and the sun appears less bright. The color of the sun itself appears to change, first to orange and then to red. This is because even more of the short wavelength blues and greens are now scattered and only the longer wavelengths are left in the direct beam that reaches the eyes. Finally, clouds appear white, since the water droplets that make up the cloud are much larger than the molecules of the air and the scattering from them is almost independent of wavelength in the visible range.

B. Resonant Scattering

An interesting case arises when the incident photon energy matches the difference in energy between the atom's initial state and one of the intermediate levels. This phenomenon can occur both for elastic or inelastic scattering (Rayleigh or Raman). Assume that $\hbar\omega_k = \epsilon_h - \epsilon_i$ for a particular h in the sum over all possible intermediate levels. Then, only first term important in $K_1^{(2)}$ (describing first absorption and then emission) is important. In order to keep this term finite, we introduce a finite width of the level, Γ. The cross section then reduces to:

$$\frac{d\,\sigma}{d\,\Omega} = kk'^3 \left| \frac{(d_{fh}\cdot\epsilon_{k'})(d_{hi}\cdot\epsilon_k)}{\epsilon_h - \epsilon_i - \hbar\omega_k - i\hbar\Gamma/2} \right|^2_{\hbar\omega_k \approx \epsilon_h - \epsilon_i} = kk'^3 \left[\frac{|(d_{fh}\cdot\epsilon_{k'})(d_{hi}\cdot\epsilon_k)|^2}{(\epsilon_h - \epsilon_i - \hbar\omega_k)^2 + \hbar^2\Gamma^2/4} \right]_{\hbar\omega_k \approx \epsilon_h - \epsilon_i}$$

This cross section describes Raman resonance and, for $k = k'$ resonance fluorescence.

12.4.4 Photoelectric Effect

In this section we want to use scattering theory of a photon from electron(s) in an atom to explain the photoelectric effect. We consider the case of an hydrogen-like atom with atomic number Z and we calculate the differential cross section

$$\frac{d\sigma}{d\omega} = \frac{W_{fi}}{\Phi_{inc}}$$

where W_{fi} is the transition rate for the scattering event and Φ_{inc} is the incoming photon flux. The incoming photon flux can be calculated by assuming (for convenience) that the system is enclosed in a cavity of volume $V = L^3$ (so that there's only one photon in that volume). The incoming flux of photons in the cavity is given by the number of photons per unit area and time:

$$\Phi = \frac{\#photons}{time \cdot Area} = \frac{1}{L/cL^2} = \frac{c}{L^3}$$

where the area is L^2 and the time to cross the cavity is $t = L/c$. The transition rate W_{fi} is given by Fermi's Golden Rule, assuming an atom-photon interaction V and a density of final state $\rho(E_f)$:

$$W_{fi} = \frac{2\pi}{\hbar} |\langle f| V |i\rangle|^2 \rho(E_f)$$

Here the final density of states $\rho(E_f)$ is expressed in terms of the momentum p of the scattered electron and the solid angle $d\Omega$ where it is ejected. Indeed, as the photon is absorbed, the final density of states is only given by the free electron, again assumed to be enclosed in the volume V. The density of states for the electron is given by the density of momentum states in the cavity L^3 assuming the electron propagates as a plane wave:

$$\rho(E_f)dE_f = \rho(\vec{p})d^3\vec{p} = \left(\frac{L}{2\pi\hbar}\right)^3 p^2 dp d\Omega$$

with the (non-relativistic) energy for the electron given by $E_f = p^2/(2m)$ giving $dE_f = pdp/m$. Finally

$$\rho(E_f) = \left(\frac{L}{2\pi\hbar}\right)^3 mpd\Omega$$

We next want to calculate the transition matrix element $\langle f| V |i\rangle$, where $V = -\frac{e}{mc}\vec{A}\cdot\vec{p}$. The relevant states are the photon states $|1_{\vec{k}\lambda}\rangle$ and $|0_{\vec{k}\lambda}\rangle$ and the electron momentum eigenstates, which in the position representation are $\psi_i(\vec{r}) = \langle\vec{r}|i_e\rangle$ and $\psi_f(\vec{r}) = \langle\vec{r}|f_e\rangle$.
The matrix element between the relevant states is then:

$$V_{if} = -\frac{e}{mc}\langle f_e| \langle 0_{\vec{k}\lambda}| \sum_{\vec{h},\xi} \sqrt{\frac{2\pi\hbar c^2}{L^3\omega_h}} \left[a_{\vec{h}\xi} e^{i\vec{h}\cdot\vec{r}} + a^\dagger_{\vec{h}\xi} e^{-i\vec{h}\cdot\vec{r}}\right] \epsilon_{\vec{h},\xi}\cdot\vec{p}\ |1_{\vec{k}\lambda}\rangle |i_e\rangle$$

$$= -\sum_{\vec{h},\xi} \frac{e}{m}\sqrt{\frac{2\pi\hbar}{L^3\omega_h}} \langle f_e| \left(\langle 0_{\vec{k}\lambda}\ a_{\vec{h}\xi}\ 1_{\vec{k}\lambda}\rangle e^{i\vec{h}\cdot\vec{r}} + \langle 0_{\vec{k}\lambda}\ a^\dagger_{\vec{h}\xi}\ 1_{\vec{k}\lambda}\rangle e^{-i\vec{h}\cdot\vec{r}}\right) \epsilon_{\vec{h}\xi}\cdot\vec{p}|i_e\rangle$$

The only surviving term is

$$V_{if} = -\frac{e}{m}\sqrt{\frac{2\pi\hbar}{L^3\omega_k}} \langle f_e| e^{i\vec{k}\cdot\vec{r}} \epsilon_{\vec{k}\lambda}\cdot\vec{p}|i_e\rangle$$

Then turning to the position representation of $|i_e\rangle, |f_e\rangle$ and of the momentum operator, we can calculate an explicit expression. Using $\psi_i(\vec{r}) = \langle\vec{r}|i_e\rangle$, $\psi_f(\vec{r}) = \langle\vec{r}|f_e\rangle$ and $\epsilon_{\vec{k}\lambda}\cdot\vec{p} = \epsilon_{\vec{k}\lambda}\cdot(-i\hbar\nabla)$, we have:

$$\langle f_e| e^{i\vec{k}\cdot\vec{r}} \epsilon_{\vec{k}\lambda}\cdot\vec{p}|i_e\rangle = \int_V d^3\vec{r}\,\psi^*_f(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \epsilon_{\vec{k}\lambda}\cdot(-i\hbar\nabla\psi_i(\vec{r}))$$

Finally

$$\langle f| V |i\rangle = -\frac{e}{m}\sqrt{\frac{2\pi\hbar}{L^3\omega_k}} \int_V d^3\vec{r}\ \psi^*_f(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \epsilon_{\vec{k}\lambda}\cdot(-i\hbar\nabla\psi_i(\vec{r}))$$

The final wave function ψ_f is just a plane wave with momentum $\vec{q} = \vec{p}/\hbar$ (in the volume L^3). The initial wave function is instead a bound state. You should have seen that for an hydrogen-like atom the wave function is given by

$\psi_i(\vec{r}) = \frac{e^{-|\vec{r}|/a}}{\sqrt{\pi a^3}}$, where a is the Bohr radius scaled by the atomic number Z ($a = \hbar^2/(me^2Z)$). Replacing the explicit expressions for ψ_i and ψ_f in the previous result we obtain:

$$\langle f|\, V\, |i\rangle = -\frac{e}{m}\sqrt{\frac{2\pi\hbar}{L^3\omega_k}}\frac{1}{\sqrt{L^3}}\int_V d^3\vec{r}e^{i(\vec{k}-\vec{q})\cdot\vec{r}}\vec{\epsilon}_{\vec{k}\lambda}\cdot\left[-i\hbar\nabla\left(\frac{e^{-|\vec{r}|/a}}{\sqrt{\pi a^3}}\right)\right]$$

We now define $\Delta\vec{k} = \vec{k} - \vec{q}$ and evaluate the integral: $\int_V d^3\,\vec{r}e^{i\Delta\vec{k}\cdot\vec{r}}\vec{\epsilon}_{\vec{k}\lambda}\cdot\nabla\psi_i$ by parts:

$$\int_V d^3\,\vec{r}e^{i\Delta\vec{k}\cdot\vec{r}}\vec{\epsilon}_{\vec{k}\lambda}\cdot\nabla\psi_i = e^{i\Delta\vec{k}\cdot\vec{r}}\psi_i|_{L^3} - i\Delta\vec{k}\cdot\vec{\epsilon}_{\vec{k}\lambda}\int_V d^3\,\vec{r}e^{i\Delta\vec{k}\cdot\vec{r}}\psi_i(\vec{r})$$

Notice that the wavefunction vanishes at the boundaries, so the first term is zero. Also, by defining ϑ the angle between Δk and r we can rewrite the integral as:

$$-i2\pi\Delta\vec{k}\cdot\vec{\epsilon}_{\vec{k}\lambda}\int dr\, r^2\psi_i(r)\int_0^\pi e^{i\Delta kr\cos(\vartheta)}\sin(\vartheta)d\vartheta = -i\frac{\Delta\vec{k}\cdot\vec{\epsilon}_{\vec{k}\lambda}}{|\Delta\vec{k}|}\int dr\,\psi_i(r)r\,\sin(\Delta kr)$$

To evaluate this last integral, we can extend the interval of integration to infinity, under the assumption that $L \gg a$:

$$\langle f|\, V\, |i\rangle = -\frac{e}{mL^3}\sqrt{\frac{2\pi\hbar}{\omega_k}}(-i\hbar)(-i\frac{\Delta\vec{k}\cdot\vec{\epsilon}_{\vec{k}\lambda}}{|\Delta\vec{k}|})\sqrt{\pi a^3}\int_0^\infty e^{-r/a}r\sin(\Delta kr)dr$$

and use the equivalence $\int_0^\infty dre^{-r/a}r\sin(br) = \frac{2a^3b}{(1+a^2b^2)^2}$ to obtain:

$$-\frac{e2\pi\hbar}{mL^3}\sqrt{\frac{2\hbar\,a^3}{\omega_k}}\frac{\Delta\vec{k}\cdot\vec{\epsilon}a^3}{(1+a^2\Delta k^2)^2}$$

Notice that $\Delta\vec{k}\cdot\vec{\epsilon}_k = \vec{k}\cdot\vec{\epsilon}_k - \vec{q}\cdot\vec{\epsilon}_k = -\vec{q}\cdot\vec{\epsilon}_k$ since $\vec{k}$ and the polarization are always perpendicular.
Now considering the density of states and the incoming flux of photons $\Phi_{inc} = c/L^3$ we obtain the scattering cross section:

$$\frac{d\sigma}{d\Omega} = \frac{32e^2a^3q(\vec{q}\cdot\vec{\epsilon}_k)^2}{m\,c\,\omega_k(1+a^2\Delta k^2)^4}$$

When the energy of the incoming photon is much higher than the electron binding energy, we have $a\Delta k \gg 1$. In this limit, we can rewrite the scattering cross section as

$$\frac{d\sigma}{d\Omega} = \frac{32e^2a^3q(\vec{q}\cdot\vec{\epsilon}_k)^2}{m\,c\,\omega_k(a^2\Delta k^2)^4} \propto \frac{a^3}{a^8} \propto a^{-5}$$

Now the constant a is the Bohr radius scaled by the atomic number Z

$$a = \frac{\hbar^2}{me^2Z}$$

we thus find the well-known Z^5 dependence of the photoelectric effect cross-section.

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