Photon Scattering

In this section we will treat scattering of photons from atoms to second order in e^2. This encompasses a surprising number of processes which have been and continue to be important. Most of our formulae will apply to many electron atoms and molecules, but for definiteness, think of the atom as a hydrogen atom with an infinitely heavy nucleus at the origin.

Our method is again time dependent perturbation theory. The unperturbed Hamiltonian is $H_{at} + H_\gamma$, and the interaction Hamiltonian, denoted as V, is

$$V = \frac{e}{mc}\vec{A}\cdot\vec{p} + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A} + \frac{e\hbar}{mc}\vec{S}\cdot(\vec{\nabla}\times\vec{A})$$

The dominant term in scattering will be caused by the first term in V, treated in second order, and the second term in V, treated in first order. The last term will be ignored (it has an extra power of inverse wavelength and will be much smaller than the first two terms).

States Our states are eigenstates of $H_{at} + H_\gamma$, which means they are eigenstates of the atom, plus free photons. Since we are discussing scattering, we have one photon initially and one photon finally. The initial state of the atom will be denoted in Dirac notation as $|a>$, and the final state of the atom denoted as $|b>$. For ease of writing, we will most of the time suppress the polarization index on photon states, replacing $\vec{k}, \lambda$ by simply $\vec{k}$. We then have an initial photon $\vec{k}$, which scatters from the atom in the state $|a>$ to produce a final photon $\vec{k'}$ plus the atom in state $|b>$. The photon vacuum (no photons present) is denoted by $|0>$. Our space is really a product space, so a proper notation for the initial state of the system would be

$$|i>= a^\dagger_{\vec{k}}|0>\otimes|a>,$$

but we will simplify this to

$$|i>= a^\dagger_{\vec{k}}|a>, \text{ and } |f>= a^\dagger_{\vec{k'}}|b> .$$

When there is any confusion, refer back to the original notation.

$U(\infty,-\infty)$ Operator Recalling the definition of the evolution operator in the interaction picture, we have

$$U(\infty,-\infty) = I - \frac{i}{\hbar}\int_{-\infty}^{\infty} dt V_I(t) + (\frac{-i}{\hbar})^2\int_{-\infty}^{\infty} dt_1\int_{-\infty}^{t_1} dt_2 V_I(t_1)V_I(t_2) + \ldots$$

Second order in $(e/mc)\vec{A}\cdot\vec{p}$ Denoting intermediate states by $|g>$, the second order U operator is

$$< f|U^{(2)}(\infty,-\infty)|i >= (\frac{-i}{\hbar})^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_g < f|V_I(t_1|g >< g|V_I(t_2|i >$$

Carrying out the time integrations, we obtain for $(e/mc)\vec{A}\cdot\vec{p}$ in second order,

$$\frac{i}{\hbar^2}\left(\sum_g < f|(e/mc)\vec{A}\cdot\vec{p}|g > \frac{1}{\omega_{gi}} < g|(e/mc)\vec{A}\cdot\vec{p}|i >\right) 2\pi\delta(\omega_{fi}), \tag{1}$$

where

$$\omega_f = \frac{E_b}{\hbar} + \omega', \;\; \omega_i = \frac{E_a}{\hbar} + \omega, \;\; \omega_g = \frac{E_g}{\hbar},$$

and

$$\omega_{fi} = \omega_f - \omega_i, \;\; \omega_{gi} = \omega_g - \omega_i$$

In writing Eq.(1) we have made the electric dipole approximation.

There are two types of terms that give non-zero contributions to Eq.(1). The first type is when in the factor

$$< g|(e/mc)\vec{A}\cdot\vec{p}|i >,$$

the vector potential destroys the initial photon. In this case the intermediate state $|g>$ has no photons, only the atom is present in some arbitrary state $|n>$. The energy denominator in this case is

$$\omega_{gi} = \omega_n - \omega_a - \omega \equiv \omega_{na} - \omega.$$

In the other type of term, again looking at

$$< g|(e/mc)\vec{A}\cdot\vec{p}|i >,$$

the vector potential creates the final photon. In this case the intermediate state contains both initial and final photons. The energy denominator is

$$\omega_n + \omega + \omega' - \omega_a - \omega \equiv \omega_{na} + \omega'$$

Our second order matrix element is now

$$\frac{i}{\hbar^2}\sqrt{\frac{4\pi c^2\hbar}{2\omega V}}\sqrt{\frac{4\pi c^2\hbar}{2\omega' V}} 2\pi\delta(\omega_{fi})\frac{e^2}{(mc)^2} \tag{2}$$

$$\cdot\left(\sum_n < b|\vec{\epsilon}'\cdot\vec{p}|n > \frac{1}{\omega_{na}-\omega} < n|\vec{\epsilon}\cdot\vec{p}|a > + \sum_n < b|\vec{\epsilon}\cdot\vec{p}|n > \frac{1}{\omega_{na}+\omega'} < n|\vec{\epsilon}'\cdot\vec{p}|a >\right)$$

NOTE If circularly polarized or other complex polarization vectors are used, the final polarization vector should be complex conjugated.

First order in $e^2A^2/(2mc^2$ This matrix element is very simple. Calculating in first order we obtain

$$\frac{-i}{\hbar}\sqrt{\frac{4\pi c^2\hbar}{2\omega V}}\sqrt{\frac{4\pi c^2\hbar}{2\omega' V}}2\pi\delta(\omega_{fi})\frac{e^2}{mc^2}\vec{\epsilon}'\cdot\vec{\epsilon} \tag{3}$$

Thomson Scattering Thomson scattering takes place at large ω. This can happen in scattering from a hydrogen or other atom if the incident photon has energy n the range of 10's of electron volts. Provided ω is not too large, this still allows validity of the electric dipole approximation. We will consider elastic scattering in this situation, so $|a>=|b>$, and $\omega=\omega'$. As ω becomes large, the two terms in our second order matrix element Eq.(2) tend to cancel each other, leaving only the simple matrix element of Eq.(3).

Calculating the transition rate, keeping only the matrix element of Eq.(3), we have

$$\mathcal{R}=\frac{V}{(2\pi c)^3}\int d\Omega'(\omega')^2 d\omega'(\frac{e^2}{mc^2})^2\frac{(2\pi c^2\hbar)^2}{\omega\omega'}\frac{1}{(\hbar V)^2}|\vec{\epsilon}'\cdot\vec{\epsilon}|^2 2\pi\delta(\omega'-\omega).$$

Introducing the classical electron radius

$$r_0\equiv\frac{e^2}{mc^2}=2.82\times10^{-5}\ \mathring{A},$$

and cancelling factors, we have

$$\mathcal{R}=\frac{r_0^2 c}{V}\int d\Omega'|\vec{\epsilon}'\cdot\vec{\epsilon}|^2.$$

To get a crossection, we divide by the so-called "incident flux." This represents the number of particles/sec/cm^2 impinging on the target. In our case the flux is simply c/V.

We have for the crossection,

$$\sigma_{thom}=r_0^2\int d\Omega'|\vec{\epsilon}'\cdot\vec{\epsilon}|^2,$$

or the differential crossection,

$$\frac{d\sigma}{d\Omega'}=r_0^2|\vec{\epsilon}'\cdot\vec{\epsilon}|^2,$$

This simple formula does contain angular dependence. The incident photon can be taken to travel along the z axis, $\vec{k}=k\hat{z}$. As such, its polarization $\vec{\epsilon}$ is a vector (possibly complex) in the $x-y$ plane. The outgoing photon $\vec{k'}$ is in a general direction, defined by the scattering angles θ and ϕ. Its polarization $\vec{\epsilon}'$, lies in the plane perpendicular to $\vec{k'}$. The scalar product between these two polarization vectors gives the differential crossection its angular dependence.

Summing and Averaging on Polarizations In many problems, not just in Thomson scattering, the polarization of the emitted or scattered photon is not detected. Photons may be detected and their direction and wavelength found, but any polarization accepted. This often simplifies formulas for differential crossections. For Thomson scattering the sum on final polarizations would involve the sum

$$\sum_{\lambda} |\vec{\epsilon}^{*}_{\lambda}(\vec{k'}) \cdot \vec{\epsilon}|^2. \tag{4}$$

Here we have replaced our schematic notation $\vec{\epsilon}'$ for the final photon with the more explicit notation, $\vec{\epsilon}_{\lambda}(\vec{k'})$, where the subscript λ could refer either to circular or plane polarization. Rewriting the sum in Eq.(4), we have

$$\sum_{\lambda} |\vec{\epsilon}^{*}_{\lambda}(\vec{k'}) \cdot \vec{\epsilon}|^2 = \sum_{\lambda} (\vec{\epsilon}^{*} \cdot \vec{\epsilon}_{\lambda}(\vec{k'}))(\vec{\epsilon}^{*}_{\lambda}(\vec{k'}) \cdot \vec{\epsilon}). \tag{5}$$

The sum over λ inserts a sum over two independent unit vectors perpendicular to $\vec{k'}$ between $\vec{\epsilon}^{*}$ and $\vec{\epsilon}$. Writing this in terms of Cartesian indices l, m, we have

$$\sum_{\lambda} |\vec{\epsilon}^{*}_{\lambda}(\vec{k'}) \cdot \vec{\epsilon}|^2 = \sum_{l,m} \vec{\epsilon}^{*}_{l} P_{lm} \vec{\epsilon}_{m} \tag{6}$$

The projector P_{lm} acts like the identity on the subspace perpendicular to the direction of the emitted photon, but must give zero for any vector parallel to the emitted photon. Explicitly, we then have

$$P_{lm} = \delta_{lm} - \hat{k'}_{l} \hat{k'}_{m}.$$

Making use of this expression, if we sum over final polarizations, and the incident photon is polarized along the x axis, we obtain

$$\frac{d\sigma_x}{d\Omega'} = r_0^2 (1 - \sin^2(\theta) \cos^2(\phi))$$

Similarly, if the incident photon is polarized along the y axis, we obtain

$$\frac{d\sigma_y}{d\Omega'} = r_0^2 (1 - \sin^2(\theta) \sin^2(\phi)).$$

If no information is available about the incident polarization, we would take the average of these two, obtaining

$$\frac{d\sigma_{unpol}}{d\Omega'} = \frac{1}{2} (\frac{d\sigma_x}{d\Omega'} + \frac{d\sigma_y}{d\Omega'}) = \frac{r_0^2}{2} (1 + \cos^2(\theta)),$$

a well-known classical formula.

Energy Scales in Photon Scattering Before going to other regions we roughly map out the energy scales which are important in scattering of photons from atoms, using the hydrogen atom as our example. Define

$$\omega_n = \frac{E_n}{\hbar},$$

where here the n really does mean the nth Bohr level. Elastic scattering from a hydrogen atom in its ground state is then

$$\omega + \omega_1 \rightarrow \omega + \omega_1,$$

while inelastic scattering would be

$$\omega + \omega_1 \rightarrow \omega' + \omega_n,$$

for some n.

Starting from small energy or ω, as we increase the photon frequency, we will reach

$$\omega = \omega_2 - \omega_1 \equiv \omega_{21}.$$

As ω moves from less than to greater than this value, we pass through the first region of *resonant* scattering. Also for $\omega > \omega_{21}$, we can scatter *inelastically* i.e the system can be left in the excited $n = 2$ state. This process repeats itself an infinite number of times. The next threshold would be $\omega = \omega_{31}$. Passing through ω_{31}, we have another region of resonant scattering. A more complex form of inelastic scattering also occurs. Inelastic final states now include both $n = 3$ and $n = 2$ final states. After passing this infinite number of thresholds, ω finally reaches ω_1, the threshold for *ionizing* the atom. It is not surprising that there is much complex behavior in going from small values of ω to values beyond ω_1. As ω moves well beyond ω_1, the scattering crossection rapidly approaches the Thomson value. In the next two sections, we treat the behavior in the lower ω regions.

Rayleigh Scattering Here we are in the lowest frequency range, $\omega << \omega_{21}$.

$$\frac{i}{\hbar^2}\sqrt{\frac{4\pi c^2\hbar}{2\omega V}}\sqrt{\frac{4\pi c^2\hbar}{2\omega' V}}2\pi\delta(\omega_{fi})\frac{e^2}{(mc)^2} \tag{7}$$

$$\cdot\left\{\sum_n < b|\vec{\epsilon}'\cdot\vec{p}|n > \frac{1}{\omega_{na}-\omega} < n|\vec{\epsilon}\cdot\vec{p}|a > + \sum_n < b|\vec{\epsilon}\cdot\vec{p}|n > \frac{1}{\omega_{na}+\omega'} < n|\vec{\epsilon}'\cdot\vec{p}|a >\right.$$

$$\left. -m\hbar\vec{\epsilon}'\cdot\vec{\epsilon} < b|a >\right\}$$

This form is not particularly useful for going to low frequency. We transform it, by using the equation of motion,

$$\vec{p} = m\frac{d\vec{x}}{dt} = \frac{im}{\hbar}[H, \vec{x}].$$

We will apply this in stages, first using it on the terms in $\vec{\epsilon}\cdot\vec{p}$. We have

$$< n|\vec{\epsilon}\cdot\vec{p}|a >= \frac{im}{\hbar} < n|[H,\vec{\epsilon}\cdot\vec{x}]|a >= im\omega_{na} < n|\vec{\epsilon}\cdot\vec{x}|a >,$$

where $\omega_{na} = (E_n - E_a)/\hbar$. Likewise, we have

$$< b|\vec{\epsilon}\cdot\vec{p}|n >= im\omega_{bn} < b|\vec{\epsilon}\cdot\vec{x}|n > .$$

We will use these to remove the denominators in certain parts of our matrix elements. First,we note that

$$\omega_a + \omega = \omega_b + \omega',$$

so

$$\omega_n - \omega_b + \omega = \omega_n - \omega_a + \omega',$$

or

$$\omega_{na} + \omega' = \omega_{nb} + \omega.$$

We now rewrite the { } of Eq.(7) as follows:

$$\{\ \} = im\left(\sum_n < b|\vec{\epsilon}'\cdot\vec{p}|n >< n|\vec{\epsilon}\cdot\vec{x}|a > \frac{\omega_{na}-\omega+\omega}{\omega_{na}-\omega}\right)$$

$$-im\left(\sum_n < b|\vec{\epsilon}\cdot\vec{x}|n >< n|\vec{\epsilon}'\cdot\vec{p}|a > \frac{\omega_{nb}+\omega-\omega}{\omega_{nb}+\omega}\right) - m\hbar\vec{\epsilon}'\cdot\vec{\epsilon} < b|a >$$

Canceling the obvious denominators, we have

$$\{\ \} = im < b|\vec{\epsilon}'\cdot\vec{p}\,\vec{\epsilon}\cdot\vec{x} - \vec{\epsilon}\cdot\vec{x}\,\vec{\epsilon}'\cdot\vec{p}|a >$$

$$+\left(\sum_n < b|\vec{\epsilon}'\cdot\vec{p}|n >< n|\vec{\epsilon}\cdot\vec{x}|a > \frac{im\omega}{\omega_{na}-\omega}\right)$$

$$+\left(\sum_n < b|\vec{\epsilon}\cdot\vec{x}|n >< n|\vec{\epsilon}'\cdot\vec{p}|a > \frac{im\omega}{\omega_{nb}+\omega}\right) - m\hbar\vec{\epsilon}'\cdot\vec{\epsilon} < b|a > .$$

Now

$$im < b|\vec{\epsilon}'\cdot\vec{p}\,\vec{\epsilon}\cdot\vec{x} - \vec{\epsilon}\cdot\vec{x}\,\vec{\epsilon}'\cdot\vec{p}|a >= im\epsilon'_l\epsilon_n < b|p_l x_n - x_n p_l|a >= im\epsilon'_l\epsilon_n\delta_{ln} < b|a >$$

$$= m\hbar\vec{\epsilon}'\cdot\vec{\epsilon} < b|a >,$$

which cancels against the $-m\hbar\vec{\epsilon}'\cdot\vec{\epsilon} < b|a >$ term in { }.

A second use of the equation of motion for $\vec{p}$ transforms the expression further. The final form for { } is

$$\{\ \} = m^2\omega\omega'\left(\sum_n < b|\vec{\epsilon}'\cdot\vec{x}|n >< n|\vec{\epsilon}\cdot\vec{x}|a > \frac{1}{\omega_{na}-\omega}\right)$$

$$+m^2\omega\omega'\left(\sum_n < b|\vec{\epsilon}\cdot\vec{x}|n >< n|\vec{\epsilon}'\cdot\vec{x}|a > \frac{1}{\omega_{na}+\omega}\right)$$

This is a much more useful formula for investigating low frequencies. For elastic scattering, we set $|b>=|a>$, so $\omega=\omega'$. Dropping the frequency ω in the energy denominators, we define the *polarization tensor*

$$\alpha_{lm}=\sum_n(< a|ex_l|n >< n|ex_m|a > + < a|ex_m|n >< n|x_m >)\frac{1}{\omega_{na}}$$

The polarization tensor is an example of a *linear response function.* These in general measure the linear response of a quantity, in this case polarization, to an external force, here the electric field (of the photon). The electric dipole moment of a molecule $\vec{d}$, is related to the applied electric field $\vec{E}$, by

$$d_l=\alpha_{lm}E_m.$$

Summed over the molecules/volume in a gas of molecules, this formula could be generalized to relate the macroscopic polarization, $\vec{P}$, to the applied electric field. (See Jackson's *Classical Electrodynamics* for more.) The subject of linear response is a large one. Linear response functions like α_{lm} are generically called "Kubo functions," after the Japanese physicist Ryogo Kubo, who first defined them.

Returning to the photon scattering crossection, the steps to obtain the crossection from the matrix element are standard, and give for low frequency elastic (Rayleigh) scattering,

$$\frac{d\sigma}{d\Omega}=(\frac{\omega}{c})^4|\epsilon'_l\epsilon_m\alpha_{lm}|^2. \tag{8}$$

The factor of $(\omega/c)^2$ means that Rayleigh scattering goes like Λ^{-4}, where Λ is the wavelength of the light. This is the origin of Rayleigh's famous explanation of why the sky appears blue, familiar to every elementary physics student. Here we have derived the formula from quantum mechanics, which produces a precise definition of the coefficient of Λ^{-4}. **NOTE** If we retain the frequency ω in the denominators, we can extend the range of validity of the formula Eq.(8) out of the extreme low frequency region. However, the formula will break down when $\omega+\omega_a=\omega_n$, for any excited state $|n>$ of the system. This is *resonant scattering,* the subject of the next section.

Resonant Scattering As mentioned earlier, when

$$\omega+\omega_a=\omega_n,$$

the term in the matrix element with no photons in the intermediate state would appear to blow up. This is a defect of our use of perturbation theory, no physical matrix element will ever be infinite. Since it involves going outside of perturbation theory, the resolution of this difficulty involves some advanced methods, specific to field theory. However, writing down the corrected formula is easy to do.

Let us start by going back to the time integral which produces the energy denominator. The term of interest to us is

$$\int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 < b|V|n >< n|V|a > \exp(i(\omega' + \omega_{bn})t_1) \exp(i(\omega_{na} - \omega)t_2)$$

The integral over t_2 needs a damping factor to be well-defined. This is accomplished by replacing ω by $\omega + i\epsilon$, where ϵ is an infinitesimal positive quantity (polarization vector NOT.) The integral over t_2 then produces the denominator

$$\frac{1}{\omega_{na} - \omega - i\epsilon}.$$

This does not cure the problem, since ϵ is infinitesimal, but it does give a clue to the correct formula. The correct result is accomplished by replacing ϵ by one half the rate of decay of the state $|n>$. The resulting formula (correct for ω in the vicinity of ω_{na}) is

$$\frac{1}{\omega_{na} - \omega - i\frac{\mathcal{R}_n}{2}},$$

where $\mathcal{R}_n$ is the *total* rate of decay of the state $|n>$. Since $\mathcal{R}_n$ appears in the denominator, and is at least itself $O(e^4)$, it is clear that the derivation of this formula requires going outside of perturbation theory in e. The *width* of the resonance is often quoted as an energy, Γ_n, where

$$\Gamma_n = \hbar\mathcal{R}_n.$$

Near a resonance involving the state $|n>$, , the resonant term will dominate the crossection, and we have

$$\frac{d\sigma}{d\Omega} \approx (\frac{d\sigma}{d\Omega})_{res} \approx (\frac{\omega_{na}}{c})^4 \left| < a|\vec{\epsilon}' \cdot \vec{x}|n >< n|\vec{\epsilon} \cdot \vec{x}|a > \frac{1}{\omega_{na} - \omega - i\frac{\mathcal{R}_n}{2}} \right|^2,$$

where there is no $\sum_n$ involved, since the system can only be resonant at one state at a time. The frequency dependent part of this formula will plot as a Lorentzian in ω. In this plot, $\mathcal{R}_n$ will be the so-called "full width at half maximum."

While we cannot give a proper derivation of the formula for resonant scattering, it is possible to get some insight into why it is $\mathcal{R}_n/2$ that appears, rather than $\mathcal{R}_n$. The state n is unstable and once formed at $t = 0$ will decay according to the formula

$$Pr_n(t) = \exp(-\mathcal{R}t), \tag{9}$$

where $Pr_n(t)$ is the probability at time t. In quantum mechanics all probabilities are absolute squares of probability *amplitudes.* So

$$Pr_n(t) = |A_n(t)|^2,$$

where $A_n(t)$ is the amplitude for the evolution of the unstable state,which was formed at $t = 0$. We may write the following formula for $A_n(t)$.

$$A_n(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{1}{\omega - \omega_{na} + i\frac{\mathcal{R}_n}{2}} e^{-i\omega t}.$$

Doing the integral over ω, we have

$$A_n(t) = i \exp(-i\omega_{na} t - \frac{\mathcal{R}_n}{2} t),$$

which leads to Eq.(9).

Resonant scattering is very common, occuring in atomic, nuclear, and particle physics.

Raman Scattering Raman scattering in general is inelastic scattering of photons. It is of particular importance in scattering from molecules and larger systems. For a molecule, the spacing between energy levels is very small, usually a tiny fraction of an eV. If such a molecule is radiated with visible light from a laser, the photon energy is much larger than the typical molecular energy spacing. Since the wavelengths of visible light is several thousand angstroms, the electric dipole approximation is still very good for most cases of Raman scattering. The matrix element (as used in Rayleigh scattering, but not ignoring photon frequencies in denominators) is

$$i\sqrt{\frac{4\pi c^2\hbar}{2\omega V}}\sqrt{\frac{4\pi c^2\hbar}{2\omega' V}} 2\pi\delta(\omega_{fi}) \frac{e^2\omega\omega'}{(\hbar c)^2} \tag{10}$$

$$\cdot \left\{ \sum_n < b|\vec{\epsilon}' \cdot \vec{x}|n >< n|\vec{\epsilon} \cdot \vec{x}|a > \frac{1}{\omega_{na} - \omega} \right.$$

$$\left. + \sum_n < b|\vec{\epsilon} \cdot \vec{x}|n >< n|\vec{\epsilon}' \cdot \vec{x}|a > \frac{1}{\omega_{na} + \omega'} \right\}.$$

The conservation of energy in terms of frequency is still

$$\omega_a + \omega = \omega_b + \omega'.$$

In say a gas of molecules, the molecules will be in various states, dependent on the temperature of the gas. So it is possible that the initial state $|a >$, is an excited state of higher energy than the final state, $|b >$. In this case the frequency of the emitted photon, ω', will be greater than that of the incident photon, ω. The more typical case is when $\omega' < \omega$. This is called a "Stokes line." The case where $\omega' > \omega$ is then called an "anti-Stokes line."

It is important to realize that the important intermediate states $|n >$ in the matrix element of Eq.(10) are independent of the frequencies ω, and ω'. The fact that the incident and emitted frequencies are large does not mean that the important intermediate states have correspondingly large energy. This point is often stated incorrectly in elementary

treatments of Raman scattering, where it is stated that the high frequency incident photon puts the molecule in a high energy "virtual state," from which it decays and emits the final photon. There are two ways in which this is misleading. First, the intermediate states do not conserve energy. All possible intermediate states $|n>$ are allowed. That is what $\sum_n$ implies. Second, the important intermediate states may be only those nearby in energy to the states $|a>$ and $|b>$. The matrix elements of $\vec{x}$ will generally tend to become very small for states far in energy from $|a>$ and $|b>$.

There is a huge technology associated with Raman scattering, as applied to various molecules and condensed matter systems. Inelastic scattering can reveal important information about the structure and dynamics of the target system.