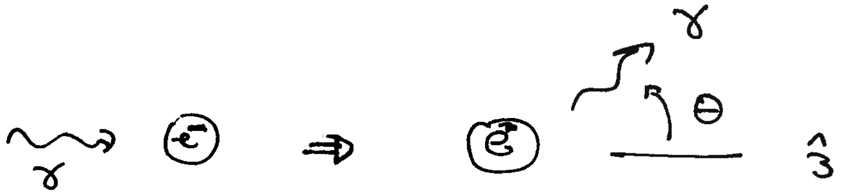
May 22

Thomson Cross Section

Before leaving the theory of electric dipole transitions, I would like to discuss two additional processes that appear at the second order in time-dependent perturbation theory. These are Thomson scattering, the elastic scattering of a photon from an electron, and Raman scattering, the inelastic scattering of a photon from an atom.

Consider first Thomson scattering. In this process



one photon is absorbed by the electron, and another photon is emitted. An accurate calculation requires a full accounting of terms a the second order of perturbation theory. I would like to quickly review, and improve, our previous treatment.

In the calculation of the transition rate from $|I\rangle$ to $|F\rangle$ in second order time-dependent perturbation theory, we encounter the expression

$$(-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \quad \langle F|\, \Delta H_I(t_1)\, \Delta H_I(t_2)\, |I\rangle$$

This is evaluated by inserting a complete set of intermediate states

$$= (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_k \langle F|\, \Delta H_I(t_1)\, |K\rangle\langle K|\, \Delta H_I(t_2)\, |I\rangle$$

$$= (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_k e^{iE_F t_1} e^{-iE_k t_1} e^{iE_k t_2} e^{-iE_I t_2} \langle F|\Delta H|K\rangle\langle k|\Delta H|I\rangle$$

$$= (-i)^2 \int_0^t dt_1 \quad e^{i(E_F - E_k)t_1} \frac{1}{i(E_k - E_I)} \left[e^{i(E_k - E_I)t_1} - 1\right] \langle F|\Delta H|K\rangle\langle K|\Delta H|I\rangle$$

When we evaluate the outer integral, we are looking for a term that increases linearly in time. For this, we must keep only the term that is resonant between E_I and E_F. This gives

$$\sum_{K} (-i) \frac{e^{i(E_F - E_I)t} - 1}{i(E_F - E_I)} \frac{\langle F|\Delta H|K\rangle\langle K|\Delta H|I\rangle}{(E_I - E_K)}$$

Squaring this result and taking the limit $t \to \infty$ as in our earlier derivation, we find the rate of transitions in the form

$$\frac{\text{transitions}}{\text{sec}} = 2\pi\,\delta(E_F - E_I)\,|a|^2$$

Recall that, in our earlier derivation, we found this result in first-order perturbation theory with the identification

$$a = -i \langle F|\Delta H|I\rangle$$

We now find the result in second-order perturbation theory with

$$a = -i \sum_{k} \frac{\langle F|\Delta H|K\rangle\langle K|\Delta H|I\rangle}{E_I - E_K}$$

You can see the generalization. In the nth order of perturbation theory, we will find an expression with n matrix elements bridging between $|I\rangle$ and $|F\rangle$, $(n-1)$ denominators,

$$\frac{1}{E_I - E_i}$$

and $(n-1)$ sums over a complete set of intermediate states.

To compute photon-electron scattering, we apply this theory to the Hamiltonian

$$\mathcal{H} = \frac{(\vec{p} - q\vec{A})^2}{2m} = \frac{p^2}{2m} - \frac{q}{2m}\{\vec{p}\,;\vec{A}\} + \frac{q^2}{2m} A^2$$

From here on, I will take $q = -e$ for an electron. Actually, there are two types of contributions to the perturbation theory, from the order q terms, taken in second order, and from the order q^2 term, taken in first order. There second order contributions are themselves of two types. First, the intermediate state might be an electron and zero photons, with

$$\langle e^-\gamma|\Delta H|e^-\rangle\langle e^-|\Delta H|e^-\gamma\rangle$$

Second, the intermediate state might be an electron and two photons, with

$$\langle e^-\gamma|\Delta H|e^-\gamma\gamma\rangle\langle e^-\gamma\gamma|\Delta H|e^-\gamma\rangle$$

In the first case, the ΔH on the right absorbs the initial photon and the ΔH on the left emits the final photon. In the second case, these roles are reversed. In the sum over all intermediate states, we add these contributions coherently in the amplitude. To put it another way, we do not observe the intermediate state, so we must add the two type of contribution coherently.

I will compute electron-photon scattering for photon energies of the order of eV or smaller. The change in momentum of the photon in the scattering process must be balanced by a change in the momentum of the electron. However, this corresponds to a kinetic energy for the electron of the order of

$$\frac{p_\gamma^2}{2m} \sim \frac{E_\gamma^2}{c^2}\frac{1}{2m} \sim E_\gamma \cdot \frac{E_\gamma}{2mc^2} \sim E_\gamma \frac{v_e^2}{c^2}$$

which is negligible in the energy balance. This equivalent to assuming that the electron is very heavy and does not recoil appreciably when the photon scatters.

We will now compute the scattering amplitude for the process

$$e^-(p)\,\gamma(q) \longrightarrow e^-(p')\,\gamma(q') \qquad p' = p+q-q'$$

The first contribution to the scattering amplitude is

$$(-i)\,\frac{\langle e^-\gamma|\,\Delta H\,|e^-\rangle\langle e^-|\,\Delta H\,|e^-\gamma\rangle}{E_e(p)+E_\gamma(q)-E_e(p+q)}$$

$$= (-i)\left(\frac{e}{2m}\right)^2 \frac{\langle e^-\gamma|\{\vec{p}\cdot\vec{A}\}|e^-(p+q)\rangle\langle e^-(p+q)|\{\vec{p}\cdot\vec{A}\}|e\gamma\rangle}{p^2/2m + qc - (p+q)^2/2m}$$

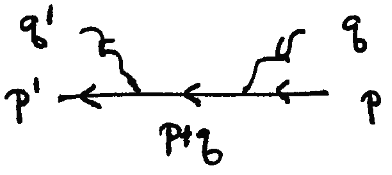
To evaluate the matrix elements with $\vec{A}$, we use the method of the previous lectures: Evaluate $\vec{A}$ with a classical electromagnetic wave, divide the wave into photons, and identify the component associated with one photon. This boils down to the correspondence

$$\vec{A} \rightarrow \left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\vec{\epsilon} \qquad (\text{or } \vec{\epsilon}^{\,*})$$

Then the above expression is equal to

$$= -i\,\frac{e^2}{4m^2}\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\frac{(\overrightarrow{p'+p+q})\cdot\vec{\epsilon}^{\,\prime *}\;(\overrightarrow{p+q+p})\cdot\vec{\epsilon}}{p^2/2m + qc - (p+q)^2/2m}$$

We can visualize this contribution to the amplitude by drawing a diagram, called a *Feynman diagram*,



The second contribution from second order pertubation theory is

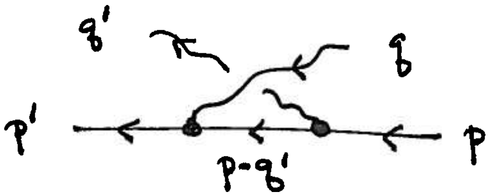
$$(-i)\ \frac{\langle e^-\gamma|\Delta H|e^-\gamma\gamma\rangle\langle e^-\gamma\gamma|\Delta H|e^-\gamma\rangle}{E_e(p)+E_\gamma(q)-\left(E_e(p'-q')+E_\gamma(q')+E_\gamma(q)\right)}$$

$$=(-i)\left(\frac{e}{2m}\right)^2\ \frac{\langle e^-\gamma|\{\vec{p},\vec{A}\}|e^-(p-q')\gamma\gamma\rangle\langle\gamma\gamma e^-(p-q')|\{\vec{p},\vec{A}\}|e^-\gamma\rangle}{p^2/2m-(p'-q)^2/2m-q'c}$$

which, using the correspondence above, is equal to

$$=(-i)\,\frac{e^2}{4m^2}\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\ \frac{(\overrightarrow{p'+p-q'})\cdot\vec{\varepsilon}\quad(p+p-q')\cdot\vec{\varepsilon}'^{\,*}}{p^2/2m-(p-q)^2/2m-qc}$$

The Feynman diagram for this process is



Using

$$qc,\ q'c\gg\frac{\vec{p}\cdot\vec{q}}{m}\sim q\cdot V_e$$

the sum of the two second order expressions simplifies to $\omega=qc\quad\omega'=q'c$

$$(-i)\,\frac{e^2}{4m^2}\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\left[\frac{1}{\omega}\,(p+p'+q)\cdot\vec{\varepsilon}'^{\,*}(p+p'+q')\cdot\vec{\varepsilon}+\frac{1}{-\omega'}\,(p+p'-q')\cdot\vec{\varepsilon}\,(p+p'-q)\cdot\vec{\varepsilon}'^{\,*}\right]$$

The approximation of ignoring recoil further implies that $\omega'\approx\omega$. Then the expression simplifies further to

$$(-i)\frac{e^2}{4m^2}\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\frac{1}{\omega}\left[2\vec{q}\cdot\vec{\varepsilon}\,'^{*}\,(\vec{p}+\vec{p}\,')\cdot\vec{\varepsilon} + 2\vec{q}\,'\cdot\vec{\varepsilon}\,(\vec{p}+\vec{p}\,')\cdot\vec{\varepsilon}\,'^{*}\right]$$

Finally, we add evaluate the contribution that results from taking the last term in the Hamiltonian to first order in perturbation theory.

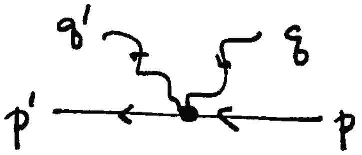
$$(-i)\frac{e^2}{2m}\langle e^-\gamma|\,\vec{A}\cdot\vec{A}\,|e^-\gamma\rangle \; .$$

To evaluate this, replace $\vec{A}$ by a classical field

$$\vec{A} = (\text{plane wave with } \vec{q},\omega) + (\text{plane wave with } \vec{q}\,'\omega')$$

Dividing each field into photons and taking one photon from each plane wave, we find

$$(-i)\frac{e^2}{2m}\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\cdot 2\cdot \vec{\varepsilon}\,'\cdot\vec{\varepsilon}$$



The factor of 2 comes from the cross term in the square of the expression for $\vec{A}$.

Notice that the first order term is larger than the two second order terms by a factor

$$\frac{q\cdot P}{m\omega} \sim \frac{P^2}{m}\frac{1}{\omega} \sim \frac{V_e}{c}$$

The cross section is then well approximated by using the first order terms only. This gives

$$\sigma = \frac{1}{c}\int d\Pi\,|a|^2$$

$$= \frac{1}{c}\left(\frac{\omega'^2}{\pi c^3}\right)\left(\frac{e^2}{m}\right)^2\left(\frac{1}{2\epsilon_0\omega'}\right)\left(\frac{1}{2\epsilon_0\omega}\right)\int\frac{d\Omega}{4\pi}\,|\vec{\epsilon}'^{*}\cdot\vec{\epsilon}\,|^2$$

$$= 4\pi\left[\frac{e^2}{4\pi\epsilon_0}\frac{1}{mc^2}\right]^2\int\frac{d\Omega}{4\pi}\,|\vec{\epsilon}'^{*}\cdot\vec{\epsilon}\,|^2$$

The quantity in brackets in the last line is the *classical electron radius*

$$r_0 = \frac{e^2}{4\pi\epsilon_0}\frac{1}{mc^2} = \alpha^2 a_0 = 2.8\times10^{-13}\,\mathrm{cm}$$

Summing and averaging over polarizations

$$\frac{1}{2}\sum_{\epsilon\epsilon'}|\vec{\epsilon}'^{*}\cdot\vec{\epsilon}\,|^2 = \frac{1}{2}(\delta^{ij}-\hat{q}'^i\hat{q}'^j)(\delta^{ji}-\hat{q}^j\hat{q}^i)$$

$$= \frac{1}{2}[2-|\hat{q}|^2-|\hat{q}'|^2+|\hat{q}'\cdot\hat{q}|^2)$$

$$= \frac{1}{2}(1+\cos^2\theta)$$

Then, finally, we find the unpolarized differential cross section

$$\left.\frac{d\sigma}{d\cos\theta}\right|_{\text{unpol.}} = 2\pi r_0^2\,(1+\cos^2\theta)$$

and the total cross section

$$\sigma = \frac{8\pi}{3}r_0^2 = \frac{8\pi}{3}\alpha^2\left(\frac{\hbar}{mc}\right)^2$$

This is the *Thomson cross section.* J. J. Thomson originally derived this result for the scattering of a classical electromagnetic wave from an electron. You might have seen that derivation in your electrodynamics course. The quantum mechanical answer agrees with the classical result in the value of the cross section, the angular distribution, and the dependence on polarization. However, classical mechanics cannot deal with the same situation for higher-energy photons, when the photon energy quantum becomes of the order of mc^2 and the recoil of the electron cannot be neglected. The quantum-mechanical derivation we have given, with the use of the relativistic Dirac equation for the electron, gives a suitable generalization of the results, called the *Klein-Nishina formula*, that is in good agreement with experimental data.

A related process in the environment of an atom is *Raman scattering*, the inelastic photon scattering process

$$a + \gamma(q) \longrightarrow b + \gamma(q')$$

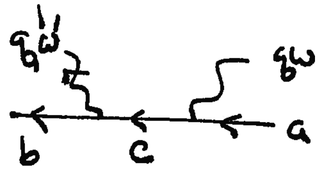
where b is an excited state of the atom and $\omega' \neq \omega$. Typically, $\omega' < \omega$. This situation is called *Stokes scattering.* It is also called *fluorescence*, especially in the context where a UV photon is down-converted to a photon of visible light. In laser fields, a can be an excited state of the atom and then we can have $\omega' > \omega$. This is called *anti-Stokes scattering.*

In an atom, we evaluate the first order photon matrix elements using the electric dipole approximation

$$\frac{e}{2m}\langle 1|\{\vec{p}\cdot\vec{A}\}|2\rangle \cong \left(\frac{1}{2\epsilon_0\omega}\right)^{1/2} ie(E_1-E_2)\langle 1|\vec{r}\cdot\vec{\epsilon}\,|2\rangle$$

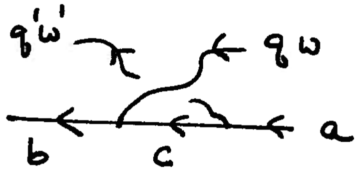
I would now like to evaluate the second order photon matrix elements needed for Raman scattering by applying this identity only for the incoming photon. The process in which photon absorption comes first in time order gives

$$-i\sum_c \frac{e}{2m}\, ie(E_c-E_a)\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2} \cdot \frac{\langle b|2\vec{\epsilon}'^{*}\cdot\vec{p}\,|c\rangle\langle c|\vec{\epsilon}\cdot\vec{r}\,|a\rangle}{E_a+\omega-E_c}$$



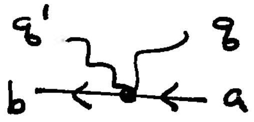
The process in which photon emission comes first in time order gives

$$-i\sum_c \frac{e}{2m}\, ie(E_b-E_c)\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon\omega}\right)^{1/2} \cdot \frac{\langle b|\vec{\varepsilon}\cdot\vec{r}\,|c\rangle\langle c|2\vec{\epsilon}'\cdot\vec{p}\,|a\rangle}{E_a-E_c-\omega'}$$



There is also a contribution of first order from the e^2A^2 term in the Hamiltonian

$$(-i)\,\frac{e^2}{2m}\langle b|\vec{\varepsilon}'^{*}\cdot\vec{\varepsilon}\,|a\rangle\left(\frac{1}{2\epsilon_0\omega'}\right)^{1/2}\left(\frac{1}{2\epsilon_0\omega}\right)^{1/2}\cdot 2$$



In the first two terms, put

$$E_c-E_a = (E_c-E_a-\omega)+\omega$$

$$E_b-E_c = (E_a+\omega-\omega'-E_c) = (E_a-E_c-\omega')+\omega$$

Then these become

$$(-i)\,\frac{e}{2m}(-ie)\left[\frac{1}{2\epsilon_0\omega'}\,\frac{1}{2\epsilon_0\omega}\right]^{1/2}\cdot 2\cdot\langle b|\,\vec{\varepsilon}^{*}\cdot p\,\vec{\varepsilon}\cdot r-\vec{\varepsilon}\cdot\vec{r}\,\varepsilon^{*}\cdot\vec{p}\,|a\rangle$$

$$+(-i)\,\frac{e}{2m}\sum_c ie\omega\left[\frac{1}{2\epsilon_0\omega'}\,\frac{1}{2\epsilon_0\omega}\right]^{1/2}\cdot 2\cdot\left[\frac{\langle b|\vec{\varepsilon}^{*}p|c\rangle\langle c|\vec{\varepsilon}\cdot\vec{r}\,|a\rangle}{E_a+\omega-E_c}+\frac{\langle b|\vec{\varepsilon}\cdot\vec{r}\,|c\rangle\langle c|\vec{\varepsilon}^{*}\cdot\vec{p}\,|a\rangle}{E_a-E_c-\omega'}\right.$$

The first line of this expression is

$$(-i)^2\,\frac{e^2}{m}\left[\frac{1}{2\epsilon_0\omega'\,2\epsilon_0\omega}\right]^{1/2}\langle b|[\varepsilon^{*}\cdot\vec{p},\vec{\varepsilon}\cdot\vec{r}\,]|a\rangle = +i\,\frac{e^2}{m}\left[\frac{1}{2\epsilon_0\omega'\,2\epsilon_0\omega}\right]^{1/2}\langle b|\vec{\varepsilon}\,\vec{\varepsilon}^{*}|a\rangle$$

and this exactly cancels the term from the A^2 operator. In the part that remains, we can convert the remaining operators $\vec{p}$ to electric dipole operators

$$e\omega\left[\frac{1}{2\epsilon_0\omega'}\frac{1}{2\epsilon_0\omega}\right]^{\frac{1}{2}} \sum_c \left\{ ie\,(E_b-E_c)\,\frac{\langle b|\vec{\varepsilon}'^{*}\cdot\vec{r}\,|c\rangle\langle c|\vec{\varepsilon}\cdot\vec{r}\,|a\rangle}{E_a+\omega-E_c}\right.$$

$$\left. +\,ie\,(E_c-E_a)\,\frac{\langle b|\vec{\varepsilon}\cdot\vec{r}\,|c\rangle\langle c|\vec{\varepsilon}'^{*}\cdot\vec{r}\,|a\rangle}{E_a-E_c-\omega'}\right.$$

Substituting

$$E_b-E_c = E_a+\omega-\omega'-E_c = (E_a+\omega-E_c)-\omega'$$

$$E_c-E_a = -(E_a-E_c-\omega')-\omega'$$

most of the expression cancels and we find

$$-ie^2\omega\omega'\left[\frac{1}{2\epsilon_0\omega\;2\epsilon_0\omega}\right]^{\frac{1}{2}} \sum_c \left\{ \frac{\langle b|\vec{\varepsilon}'^{*}\cdot\vec{r}\,|c\rangle\langle c|\vec{\varepsilon}\cdot\vec{r}\,|a\rangle}{E_a-E_c+\omega}\right.$$

$$\left. +\;\frac{\langle b|\vec{\varepsilon}\cdot\vec{r}\,|c\rangle\langle c|\varepsilon'^{*}\cdot\vec{r}\,|a\rangle}{E_a-E_c-\omega'}\right\}$$

In all, we find for the Raman scattering cross section

$$\sigma(\gamma(\omega)+a\longrightarrow b+\gamma(\omega')) = \frac{1}{c}\int d\Pi\,|a|^2$$

$$= 4\pi\alpha^2\,\frac{\omega'^3\omega}{c^4}\int\frac{d\Omega}{4\pi}\left|\sum_c \frac{\langle b|\varepsilon^{*}\cdot r|c\rangle\langle c|\varepsilon\cdot r|a\rangle}{E_a-E_c+\omega}+\frac{\langle b|\vec{\varepsilon}\cdot\vec{r}|c\rangle\langle c|\vec{\varepsilon}^{*}\cdot\vec{r}|a\rangle}{E_a-E_c-\omega'}\right|^2$$

The denominators in this expression are

$$E_a - E_c + \omega \qquad \underline{\text{and}} \qquad E_a - E_c - \omega'$$

or, equivalently,

$$-(E_c - E_a - \omega) \qquad \text{and} \qquad +(E_b - E_c - \omega)$$

Notice that if

$$E_c - E_a = E_b - E_c$$

that is, if the state *c* is halfway between *a* and *b*, the contribution of that state to Raman scattering cancels between the two terms. Also, if

$$\omega \gg (E_a - E_c),\ (E_b - E_c)$$

the two terms cancel. Thus, Raman scattering vanishes when the photon energy becomes much larger than the relevant atomic energies.