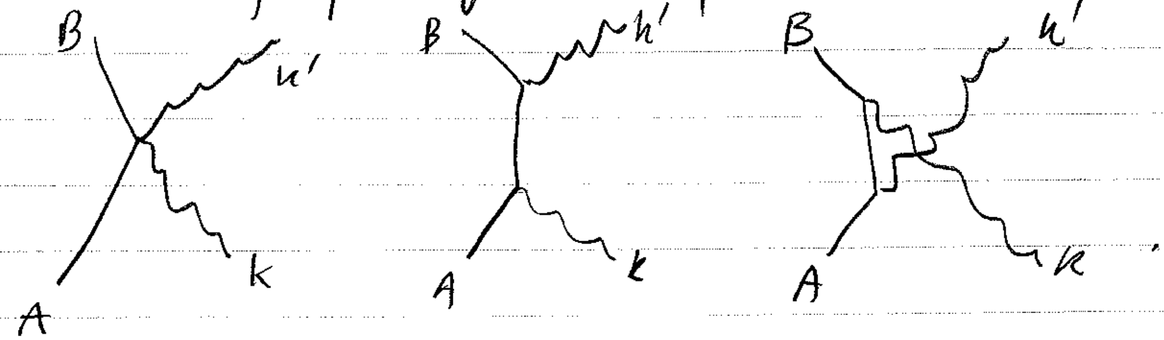
# Rayleigh Scattering

Three diagrams describe the scattering of a photon by an atom:




(1)

We analyzed the first diagram, called the seagull diagram, in our discussion of Thomson scattering. The other two occur when $S(t,0)$ is computed to second order in $q$:

$$\langle B k' | S(t,0) | A k \rangle = \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \; \langle B k' |$$

$$\sum_{i,j=1}^{Z} e^{i(H_{om}+H_{oF})t_1/\hbar} \left(-\frac{q}{m}\right) \vec{p}_i \cdot \vec{A}(x_i,0) e^{-i(H_{om}+H_{oF})t_1/\hbar} \sum_\phi |\phi\rangle\langle\phi|$$

$$e^{i(H_{om}+H_{oF})t_2/\hbar} \left(-\frac{q}{m}\right) \vec{p}_j \cdot \vec{A}(x_j,0) e^{-i(H_{om}+H_{oF})t_2/\hbar} |A, k\rangle \qquad (2)$$

in which the operators $p \cdot A$ are time-ordered and the sum over states $\phi$ is complete

$$I = \sum_\phi |\phi\rangle\langle\phi|. \qquad (3)$$

The exponentials $e^{\pm i H_{0F} t_i/\hbar}$ put $\vec{A}(\vec{x},0)$ in the interaction picture

$$e^{iH_{0F}t/\hbar}\vec{A}(\vec{x},0)\,e^{-iH_{0F}t/\hbar} = \vec{A}(x,t) \tag{4}$$

$$= \sum_{r,k}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}}\Big[\vec{\epsilon}_r(k)\,a_r(\vec{k})\,e^{i(k\cdot x-\omega_k t)} + \vec{\epsilon}_r^{\,*}(k)\,a_r^{\dagger}(k)\,e^{-i(k\cdot x-\omega t)}\Big].$$

So (2) becomes

$$\langle Bk'|S(t,0)|Ak\rangle = \left(\frac{-i}{\hbar}\right)^2\int_0^t dt_1\int_0^{t_1} dt_2\sum_{i,j=1}^{N}\langle Bk'|e^{i(E_B-E_C)t_1/\hbar}\,\frac{q}{m}\vec{p}\cdot A(x_i,t_1)$$

$$\times\left[\sum_C |C\rangle\langle C| + \sum_{C,k}|C,k,k'\rangle\langle C,k,k'|\right]$$

$$\times\ \frac{q}{m}\vec{p}_j\cdot A(x_j,t_2)\,|A,k\rangle\,e^{i(E_C-E_A)t_2/\hbar}. \tag{5}$$

The sum over $|c\rangle\langle c|$ gives the middle term in figure (1); that over $|C,k,k'\rangle\langle C,k,k'|$ gives the last term.

In the dipole approximation, we find

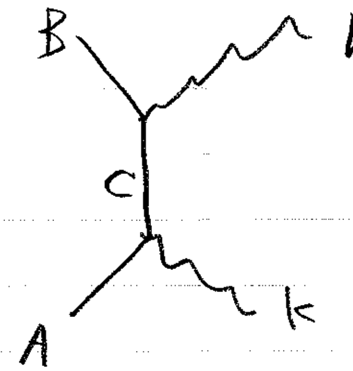
$$\langle Bk'|S(t,0)|Ak\rangle = \left(\frac{iq}{\hbar m}\right)^2\frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}}\int_0^t dt_1\int_0^{t_1}dt_2\, e^{i(E_B-E_C)t_1/\hbar}$$

$$\times\sum_{i,j=1}^{2}\langle Bk'|\,\vec{p}_i\cdot\left[\vec{\epsilon}_r(k)\,a_r(k)\,e^{-i\omega t_1} + \vec{\epsilon}_{r'}^{\,*}(k')\,a_{r'}^{\dagger}(k')\,e^{i\omega' t_1}\right]$$

$$\times\sum_c\Big(|c\rangle\langle c| + |ckk'\rangle\langle ckk'|\Big)\,p_j\cdot\left[\epsilon a\,e^{-i\omega t_2} + \epsilon'^{*}a'^{\dagger}e^{i\omega t_2}\right]$$

$$\times\ e^{i(E_C-E_A)t_2/\hbar}\,|Ak\rangle \tag{6}$$

The amplitude for the diagram




(7)

is

$$\langle B k' | S(t,0) | A k\rangle_{R1} = \left(\frac{iq}{\hbar m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \int_0^t dt_1 \int_0^{t_1} dt_2 \, e^{i(E_B+\hbar\omega'-E_C)t_1/\hbar}$$

$$\times \sum_{ij=1}^{Z} \langle B k' | \vec{p}_i \cdot \vec{\epsilon}^{\,*}_{r'}(k')\, a^{\dagger}_{r'}(k') \sum_C |C\rangle\langle C| p_j \cdot \epsilon_r(k)\, a_r(k) | A k\rangle$$

$$\times e^{i(E_C-E_A-\hbar\omega)t_2/\hbar} . \qquad (8)$$

We do the $t$ integrals:

$$\langle B k' | S(t,0) | A k\rangle_{R1} = \frac{i}{\hbar}\left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \int_0^t dt_1 \, e^{i(E_B+\hbar\omega'-E_C)t_1/\hbar}$$

$$\times \sum_{ij=1}^{Z} \langle B | \vec{p}_i \cdot \vec{\epsilon}^{\,*} \sum_C |C\rangle\langle C| p_j \cdot \epsilon | A\rangle \left(\frac{e^{i(E_C-E_A-\hbar\omega)t_1/\hbar}-1}{E_C-E_A-\hbar\omega}\right),$$

$$= \left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \left[\frac{e^{i(E_B+\hbar\omega'-E_A-\hbar\omega)t/\hbar}-1}{E_B+\hbar\omega'-E_A-\hbar\omega} - \frac{e^{i(E_B+\hbar\omega'-E_C)t/\hbar}-1}{E_B+\hbar\omega'-E_C}\right]$$

$$\times \sum_{ij=1}^{Z} \frac{\langle B | \vec{p}_i \cdot \vec{\epsilon}^{\,*}_r(k') \sum_C |C\rangle\langle C| \vec{p}_j \cdot \vec{\epsilon}_r(k) | A\rangle}{E_C-E_A-\hbar\omega} . \qquad (9)$$

We assume that $E_C \mp E_B + \hbar\omega'$ so that

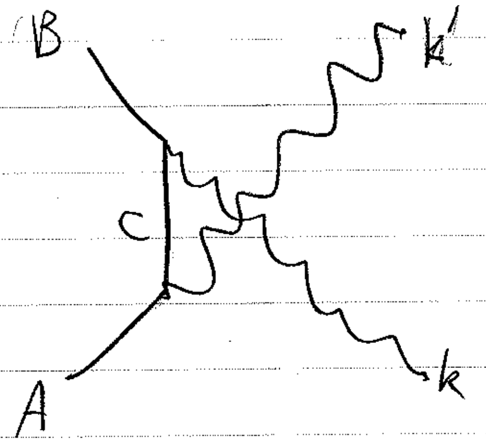
$$\frac{e^{i(E_B+\hbar\omega'-E_C)t/\hbar}-1}{E_B+\hbar\omega'-E_C}$$

is not resonant. This term does, however, contribute to resonance fluorescence, which is a different process. So here diagram (7) gives

$$\langle Bk'|S(t,0)|Ak\rangle_{RI} = \left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \sum_{ij=1}^{Z} \frac{\langle B|p_i\cdot\epsilon'^* \sum_C |C\rangle\langle C| p_j\cdot\epsilon|A\rangle}{E_C-E_A-\hbar\omega}$$

$$\times\ \frac{e^{i\Delta E t/\hbar}}{\Delta E}\ . \qquad (10)$$

The amplitude for the diagram




(11)

involves the intermediate states

$$\sum_C |Ckk'\rangle\langle Ckk'|\ . \qquad (12)$$

This amplitude is

$$\langle Bk'|S(t,0)|Ak\rangle_{R2} = \left(\frac{iq}{\hbar m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \int_0^t dt_1 \int_0^{t_1} dt_2\, e^{i(E_B - E_C - \hbar\omega)t_1/\hbar}$$

$$\times \sum_{ij=1}^{Z} \langle Bk'|\, p_i \cdot \epsilon\, a_r(k)|Ckk'\rangle\langle Ckk'|\, p_j \cdot \epsilon'^{*} a^{\dagger}_{r'}(k')\,|Ak\rangle$$

$$\times\, e^{i(E_C - E_A + \hbar\omega')t_2/\hbar} . \tag{13}$$

We do the $t$ integrals:

$$\langle Bk'|S(t,0)|Ak\rangle_{R2} = \frac{i}{\hbar}\left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \int_0^t dt_1\, e^{i(E_B - E_C - \hbar\omega)t_1/\hbar}$$

$$\times \sum_{ij=1}^{Z} \langle B|\, p_i \cdot \epsilon\, |C\rangle\langle C|\, p_j \cdot \epsilon'^{*}\,|A\rangle \left(\frac{e^{i(E_C - E_A + \hbar\omega')t_1/\hbar} - 1}{E_C - E_A + \hbar\omega'}\right)$$

$$= \left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}} \left[\frac{e^{i(E_B + \hbar\omega' - E_A - \hbar\omega)t/\hbar} - 1}{E_B + \hbar\omega' - E_A - \hbar\omega} - \frac{e^{i(E_B - E_C - \hbar\omega)t/\hbar} - 1}{E_C - E_A - \hbar\omega}\right]$$

$$\times \sum_{ij=1}^{Z} \frac{\langle B|\, p_i \cdot \epsilon\, |C\rangle\langle C|\, p_j \cdot \epsilon'^{*}\,|A\rangle}{E_C - E_A + \hbar\omega'} . \tag{14}$$

We assume that $E_C \neq E_A + \hbar\omega$ so that the second term in [ ] is not resonant. This term does, however, contribute to resonant fluorescence, which is a different process.

Dropping that non-resonant term, we have

$$\langle Bk'|S(t,0)|Ak\rangle_{RZ} = \left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}}\left(\frac{e^{i\Delta E t/\hbar}-1}{\Delta E}\right)$$

$$\times \sum_{ij=1}^{Z} \frac{\langle B|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^*|A\rangle}{E_C - E_A + \hbar\omega'} \quad (15)$$

where, as before, $\Delta E = E_B + \hbar\omega' - E_A - \hbar\omega$.

The full amplitude to order $q^2$ is the sum of all three amplitudes represented in Fig. (1) including the one due to the $\vec{A}^2$ term:

$$\langle Bk'|S(t,0)|Ak\rangle = \left(\frac{q}{m}\right)^2 \frac{\hbar}{2\epsilon_0 V\sqrt{\omega\omega'}}\left(\frac{e^{i\Delta E t/\hbar}-1}{\Delta E}\right)$$

$$\times \Big[ -mZ\delta_{AB}\,\vec{\epsilon}_r(k)\cdot\vec{\epsilon}^{\,*}_{r'}(k') + \sum_{ij=1}^{Z}\frac{\langle B|\vec{p}_i\cdot\vec{\epsilon}^{\,*}_{r'}(k')|C\rangle\langle C|\vec{p}_j\cdot\epsilon_r(k)|A\rangle}{E_C - E_A - \hbar\omega}$$

$$+ \sum_{ij=1}^{Z}\frac{\langle B|\vec{p}_i\cdot\vec{\epsilon}_r(k)\sum_C|C\rangle\langle C|\vec{p}_j\cdot\vec{\epsilon}^{\,*}_{r'}(k')|A\rangle}{E_C - E_A + \hbar\omega'}\Big]. \quad (16)$$

We form $|\langle Bk'|S(t,0)|Ak\rangle|^2$ and use

$$\lim_{t\to\infty}\left|\frac{e^{i\Delta E t/\hbar}-1}{\Delta E}\right|^2 = \lim_{t\to\infty}\frac{4\sin^2\Delta E t/(2\hbar)}{\Delta E^2} = \frac{2\pi t}{\hbar}\,\delta(\Delta E) \quad (17)$$

The rate $\hat{w}$ then is

$$\hat{w} = \frac{2\pi}{\hbar}\left(\frac{q^2 \hbar}{m\, 2\epsilon_0 V\sqrt{\omega\omega'}}\right)^2 \delta(\Delta E)\Bigg| - Z\delta_{AB}\,\epsilon\cdot\epsilon^{*\prime}$$

$$+ \frac{1}{m}\sum_{ij=1}^{Z}\sum_{C}\left(\frac{\langle B|p_i\cdot\epsilon'^{*}|C\rangle\langle C|p_j\cdot\epsilon|A\rangle}{E_C - E_A - \hbar\omega} \quad (18)$$

$$+ \frac{\langle B|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^{*}|A\rangle}{E_C - E_A + \hbar\omega'}\right)\Bigg|^2 .$$

The full rate including a sum over final states is

$$W = \frac{V}{(2\pi)^3}\int \hat{w}\, d^3k \quad (19)$$

$$= \frac{2\pi}{\hbar}\,\frac{q^4\hbar^2}{4m^2\epsilon_0^2 V^2\omega\omega'}\, V\int \Big|\quad\Big|^2 \delta(E_B + \hbar\omega' - E_A - \hbar\omega)\,\frac{k^2\, d\hbar\omega}{(2\pi)^3\,\hbar c}.$$

Dividing by the incident flux $F = c/V$, we find

$$\frac{d\sigma}{d\Omega} = \frac{q^4}{16\pi^2}\,\frac{k^2}{c^2 m^2\epsilon_0^2\omega\omega'}\Bigg| Z\,\delta_{AB}\,\epsilon\cdot\epsilon^{*\prime} \quad (20)$$

$$- \frac{1}{m}\sum_{ij=1}^{Z}\sum_{C}\left(\frac{\langle B|p_i\cdot\epsilon'^{*}|C\rangle\langle C|p_j\cdot\epsilon|A\rangle}{E_C - E_A - \hbar\omega}\right.$$

$$\left. + \frac{\langle B|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^{*}|A\rangle}{E_C + \hbar\omega' - E_A}\right)\Bigg|^2 .$$

Since $q^2 = 4\pi\epsilon_0 \alpha\hbar c$, the prefactor is

$$\frac{(4\pi\epsilon_0 \alpha \hbar c)^2 \; h^2}{16\pi^2 c^2 m^2 \epsilon_0^2 \omega\omega'} = \frac{\alpha^2\hbar^2}{m^2c^2}\frac{\omega}{\omega'} = r_0^2 \frac{\omega}{\omega'} \qquad (21)$$

where $r_0 = \dfrac{\alpha\hbar}{mc} \approx 2.82 \times 10^{-13}\,\text{cm}$ (22)

is the classical radius of the electron. So

$$\frac{d\sigma}{d\Omega} = r_0^2 \frac{\omega'}{\omega}\Bigg| Z\delta_{AB}\,\epsilon\cdot\epsilon'^* - \frac{1}{m}\sum_{i,j=1}^{Z}\sum_c \Bigg( \frac{\langle B|\vec{p}_i\cdot\epsilon'^*|C\rangle\langle C|p_j\cdot\epsilon|A\rangle}{E_C - E_A - \hbar\omega}$$

$$+ \frac{\langle B|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^*|A\rangle}{E_C + \hbar\omega' - E_A}\Bigg)\Bigg|^2 . \qquad (23)$$

We now do something that is very counterintuitive:

$$\delta_{ij}\,\epsilon\cdot\epsilon'^* = \frac{1}{i\hbar}\left[x_i\cdot\epsilon'^*, p_j\cdot\epsilon\right] \qquad (24)$$

$$Z\langle A|\epsilon\cdot\epsilon'^*|A\rangle = \frac{1}{i\hbar}\sum_{i,j=1}^{Z}\Big[\langle A|x_i\cdot\epsilon'^*|C\rangle\langle C|p_j\cdot\epsilon|A\rangle \qquad (25)$$

$$-\langle A|p_j\cdot\epsilon \sum_c |C\rangle\langle C|x_i\cdot\epsilon'^*|A\rangle\Big].$$

We now specialize to the case $B=A$ and use

$$[\vec{x}_i, H_{0m}] = i\hbar\frac{\vec{p}_i}{m} \qquad (26)$$

to write

$$\langle A|\vec{x}_i|C\rangle = \frac{\langle A|[\vec{x}_i, H_{om}]|C\rangle}{E_C - E_A}$$

$$= \frac{i\hbar}{m}\frac{\langle A|\vec{p}_i|C\rangle}{E_c - E_A} \qquad (27)$$

and

$$Z\,\epsilon\cdot\epsilon'^{*} = \sum_{ij=1}^{Z}\sum_{C}\frac{1}{m}\left[\frac{\langle A|\,p_i\cdot\epsilon'^{*}|C\rangle\langle C|\,p_j\cdot\epsilon\,|A\rangle}{E_c - E_A}\right. \qquad (28)$$

$$\left. + \frac{\langle A|\,p_j\cdot\epsilon\,|C\rangle\langle C|\,p_i\cdot\epsilon'^{*}|A\rangle}{E_c - E_A}\right]$$

$$= \frac{1}{m}\sum_{ij=1}^{Z}\sum_{C}\frac{1}{E_c - E_A}\left[\langle A|p_i\cdot\epsilon'^{*}|C\rangle\langle C|p_j\cdot\epsilon\,|A\rangle + \langle A|p_j\cdot\epsilon\,|C\rangle\langle C|p_i\cdot\epsilon'^{*}|A\rangle\right].$$

We may interchange $i$ & $j$ in the last term since they are dummy indices.

$$Z\,\epsilon\cdot\epsilon'^{*} = \frac{1}{m}\sum_{ij=1}^{Z}\sum_{C}\frac{\langle A|\,p_i\cdot\epsilon'^{*}|C\rangle\langle C|p_j\cdot\epsilon|A\rangle + \langle A|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^{*}|A\rangle}{E_c - E_A}. \qquad (29)$$

So now we have for $B = A$

$$\omega = \omega' \quad \text{and so} \qquad (30)$$

$$Z\,\epsilon\cdot\epsilon'^{*} - \frac{1}{m}\sum_{ij=1}^{Z}\sum_{c}\frac{\langle A|p_i\cdot\epsilon'^{*}|c\rangle\langle c|p_j\cdot\epsilon|A\rangle}{E_c-E_A-\hbar\omega}+\frac{\langle A|p_i\cdot\epsilon|c\rangle\langle c|p_j\cdot\epsilon'^{*}|A\rangle}{E_c+\hbar\omega-E_A}$$

$$=\frac{1}{m}\sum_{ij=1}^{Z}\sum_{c}\Big\{\langle A|p_i\cdot\epsilon'^{*}|c\rangle\langle c|p_j\cdot\epsilon|A\rangle\left(\frac{1}{E_c-E_A}-\frac{1}{E_c-E_A-\hbar\omega}\right)$$

$$+\langle A|p_i\cdot\epsilon|c\rangle\langle c|p_j\cdot\epsilon'^{*}|A\rangle\left(\frac{1}{E_c-E_A}-\frac{1}{E_c+\hbar\omega-E_A}\right)\Big\}. \quad (30)$$

We set $E_{cA}=E_c-E_A$ and find

$$\frac{1}{E_{cA}}-\frac{1}{E_{cA}-\hbar\omega}=\frac{-\hbar\omega}{E_{cA}(E_{cA}-\hbar\omega)} \quad (31)$$

and

$$\frac{1}{E_{cA}}-\frac{1}{E_{cA}+\hbar\omega}=\frac{+\hbar\omega}{E_{cA}(E_{cA}+\hbar\omega)} \quad (32)$$

so that (30) becomes

$$-\frac{\hbar\omega}{m}\sum_{ij=1}^{Z}\sum_{c}\frac{\langle A|p_i\cdot\epsilon'^{*}|c\rangle\langle c|p_j\cdot\epsilon|A\rangle}{E_{cA}(E_{cA}-\hbar\omega)}-\frac{\langle A|p_i\cdot\epsilon|c\rangle\langle c|p_j\cdot\epsilon'^{*}|A\rangle}{E_{cA}(E_{cA}+\hbar\omega)}. \quad (33)$$

So

$$\frac{d\sigma}{d\Omega}=\frac{r_0^2\hbar^2\omega^2}{m^2}\left|\sum_{ij=1}^{Z}\sum_{c}\frac{\langle A|p_i\cdot\epsilon'^{*}|c\rangle\langle c|p_j\cdot\epsilon|A\rangle}{E_{cA}(E_{cA}-\hbar\omega)}-\frac{\langle A|p_i\cdot\epsilon|c\rangle\langle c|p_j\cdot\epsilon'^{*}|A\rangle}{E_{cA}(E_{cA}+\hbar\omega)}\right|^2 \quad (34)$$

is the x-section for the elastic scattering of light by an atom.

This expression (34) simplifies in the limit

$$\omega << E_{CA} \tag{35}$$

for then

$$\frac{1}{E_{CA} \mp \hbar\omega} = \frac{1}{E_{CA}} \frac{1}{1 \mp \frac{\hbar\omega}{E_{CA}}} \approx \frac{1}{E_{CA}}\left(1 \pm \frac{\hbar\omega}{E_{CA}}\right). \tag{36}$$

In this limit, the dominant terms cancel since by (26&27)

$$\sum_{ij=1}^{Z}\sum_{C}\frac{1}{E_{CA}^2}\left(\langle A|p_i\cdot\epsilon'^*|C\rangle\langle C|p_j\cdot\epsilon|A\rangle - \langle A|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^*|A\rangle\right)$$

$$= \sum_{ij=1}^{Z}\sum_{C} m^2 \langle A|x_i\cdot\epsilon'^*|C\rangle\langle C|x_j\cdot\epsilon|A\rangle - \langle A|x_i\cdot\epsilon|C\rangle\langle C|x_j\cdot\epsilon'^*|A\rangle$$

$$= \sum_{ij=1}^{Z} m^2 \langle A|\,[x_i\cdot\epsilon'^*, x_j\cdot\epsilon]\,|A\rangle = 0 \tag{37}$$

in which we again switched $i$ & $j$. So for $\omega << E_{CA}$, the differential x-section is

$$\frac{d\sigma}{d\Omega} = \frac{r_0^2(\hbar\omega)^4}{m^2}\left|\sum_{ij=1}^{Z}\sum_{C}\frac{1}{E_{CA}^3}\left(\langle A|p_i\cdot\epsilon'^*|C\rangle\langle C|p_j\cdot\epsilon\rangle + \langle A|p_i\cdot\epsilon|C\rangle\langle C|p_j\cdot\epsilon'^*|A\rangle\right)\right|^2$$

$$= \left(\frac{r_0 m}{\hbar^2}\right)^2(\hbar\omega)^4\left|\sum_{ij=1}^{Z}\sum_{C}\frac{1}{E_{CA}}\left(\langle A|x_i\cdot\epsilon'^*|C\rangle\langle C|x_j\cdot\epsilon\rangle + \langle A|x_i\cdot\epsilon|C\rangle\langle C|x_j\cdot\epsilon'^*|A\rangle\right)\right|^2.$$

The x-section goes as $\omega^4$ or as $1/\lambda^4$. So blue light scatters much more that red light. Hence the sky is blue and dawns and sunsets are red.