Quantum theory of Rayleigh scattering and Raman scattering: Kramers-Heisenberg formula

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Raman scattering or the Raman effect, which is the inelastic scattering of a photon was discovered by C. V. Raman and K. S. Krishnan in liquids, and by G. Landsberg and L. I. Mandelstam in crystals. The effect had been predicted theoretically by Adolf Smekal in 1923. When photons are scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering). A small fraction of the scattered photons are scattered by an excitation, with the scattered photons having a frequency different from that of the incident photons. Raman received Nobel Prize for his work on the scattering of light.

The Kramers-Heisenberg dispersion formula is an expression for the cross section for scattering of a photon by an atomic electron. It was derived before the advent of quantum mechanics by Hendrik Kramers and Werner Heisenberg in 1925, based on the correspondence principle applied to the classical dispersion formula for light. Heisenberg's breakthrough to matrix mechanics was directly stimulated by studies of interaction of quantized material systems with electromagnetic radiation.

The historical siginificance of the Kramers-Heisenberg formula is discussed in detail by M. Dresden (see the Appendix).

Classical electron radius

$$r_0 = \frac{e^2}{mc^2} = 2.81795 \text{ x } 10^{-13} \text{ cm}$$

Bohr radius

$$a_B = \frac{\hbar^2}{me^2} = 5.2917721067 \text{ x } 10^{-9} \text{ cm}$$

Fine structure constant:

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.035999139}$$

((Note))

$$\frac{r_0}{a_B} = \frac{e^4}{\hbar^2 c^2} = \frac{1}{\alpha^2}$$

1. Rayleigh scattering

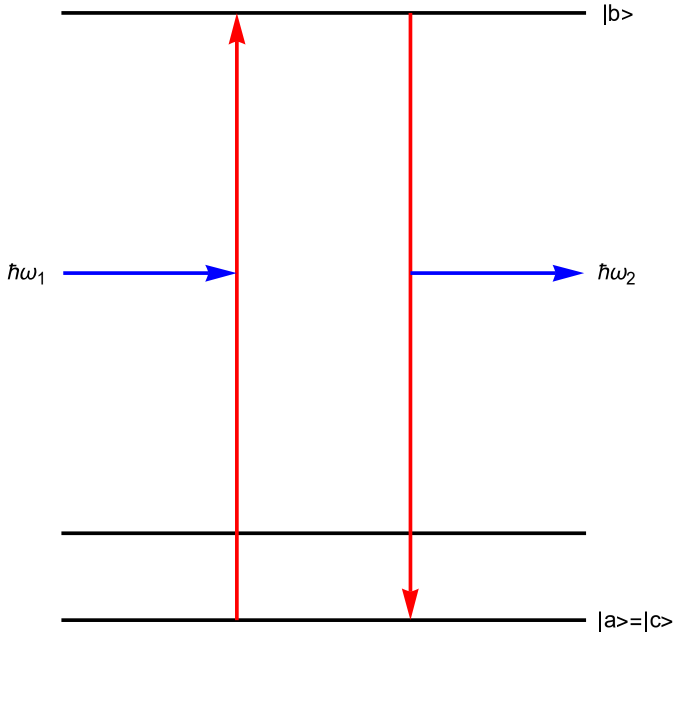

Fig. Rayleigh scattering. $\hbar\omega_1 = \hbar\omega_2$. The elastic scattering.

Why the sky is blue in daytime? That is because of the Rayleigh scattering. The wavelength of blue light is much shorter than that of red light. The Rayleigh scattering is an elastic scattering. The cross section of the Rayleigh scattering due to the small particles with diameter *d* is given by

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$

where *n* is the refractive index *n* of particles from a beam of unpolarized light of wavelength λ. Such a strong wavelength dependence of the scattering ($\sim\lambda^{-4}$) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths. This results in the indirect blue light coming from all regions of the sky. Rayleigh scattering is a good approximation of the manner in which light scattering occurs within various media for which scattering particles have a small size parameter.

Why is the sky red in sunset? The reddening of sunlight is intensified when the sun is near the horizon, because the density of air and particles near the earth's surface through which sunlight must pass is significantly greater than when the sun is high in the sky. The Rayleigh scattering effect is thus increased, removing virtually all blue light from the direct path to the observer. The remaining un-scattered light is mostly of a longer wavelength, and therefore appears to be orange.

2. Raman scattering

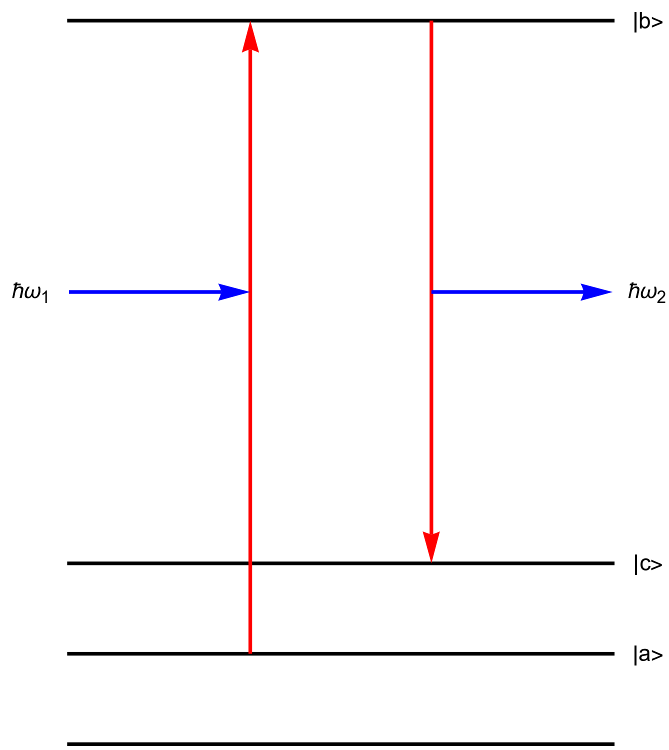

Fig. Raman scattering. Stokes' line. $E_i + \hbar\omega_1 = E_f + \hbar\omega_2$ (energy conservation). $\hbar\omega_2 = \hbar\omega_1 - (E_f - E_i) < \hbar\omega_1$ since $E_f > E_i$. A Stokes' line in atomic spectra is more reddish than that of the incident radiation. The inelastic scattering.

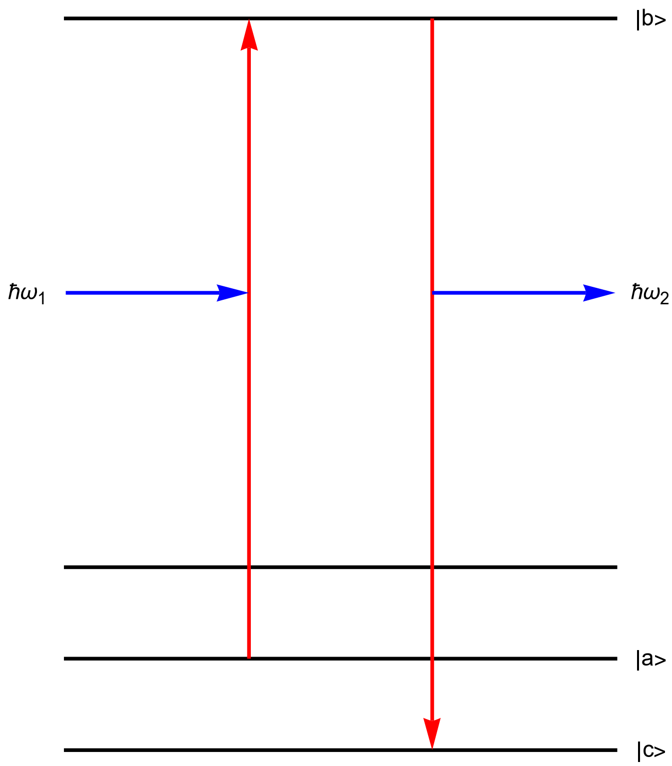

Fig. Raman scattering. Anti-Stokes' line. $E_i + \hbar\omega_1 = E_f + \hbar\omega_2$ (energy conservation). $\hbar\omega_2 = \hbar\omega_1 + (E_i - E_f) > \hbar\omega_1$ since $E_f > E_i$. A Stokes' line in atomic spectra is more more violet than that of the incident radiation. The inelastic scattering.

Here we consider the scattering of photon by atomic electrons. Before the scattering, the atom is the state $|i\rangle$, and the incident photon is denoted by $(\boldsymbol{k}, \boldsymbol{\varepsilon}_\nu)$. After the scattering, the atom is left in the state $|f\rangle$, and the outgoing photon is denoted by $(\boldsymbol{k}', \boldsymbol{\varepsilon}'_{\nu'})$

The initial state is

$$|i\rangle = |a\rangle \otimes |n_1, n_2\rangle$$

The final state is

$$|f\rangle = |b\rangle \otimes |n_1 - 1, n_2 + 1\rangle$$

Note that $\hat{H}_1$ and $\hat{H}_2$ are the Hamiltonian for the interaction between radiation field and atoms. $\hat{H}_1$ is a linear $(\boldsymbol{A}\cdot\boldsymbol{p})$ term (related to one photon), while $\hat{H}_2$ is a quadratic $(\boldsymbol{A}\cdot\boldsymbol{A})$ term (related to two photons). So $\hat{H}_2$ is higher order perturbation compared to $\hat{H}_1$.

$$\hat{H}_1 = -\sum_j \frac{e_j}{2m_j}\sum_{\boldsymbol{k},\nu}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}(\hat{a}_{\boldsymbol{k}\nu}+\hat{a}^+_{-\boldsymbol{k}\nu})\{\boldsymbol{p}_j\cdot\boldsymbol{\varepsilon}_\nu(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{r}_j}+e^{i\boldsymbol{k}\cdot\boldsymbol{r}_j}\boldsymbol{\varepsilon}_\nu(\boldsymbol{k})\cdot\boldsymbol{p}_j\}$$

$$\hat{H}_2 = \sum_j \frac{e_j^{\ 2}}{m_j}\sum_{\boldsymbol{k},\nu}\sum_{\boldsymbol{k}',\nu'}\frac{\pi\hbar}{\sqrt{\omega_{\boldsymbol{k}}\omega_{\boldsymbol{k}'}V^2}}\boldsymbol{\varepsilon}_\nu(\boldsymbol{k})\cdot\boldsymbol{\varepsilon}_{\nu'}(\boldsymbol{k}')(\hat{a}_{\boldsymbol{k}\nu}+\hat{a}^+_{-\boldsymbol{k}\nu})(\hat{a}_{\boldsymbol{k}'\nu'}+\hat{a}^+_{-\boldsymbol{k}'\nu'})e^{i(\boldsymbol{k}+\boldsymbol{k}')\cdot\boldsymbol{r}_j}$$

The above process is made of the absorption of photon with ω_1 and the emission of photon with ω_2. The transition rate in this case is given by

$$w_{i\to f} = \frac{2\pi}{\hbar}\left|\langle f|\hat{H}_2|i\rangle + \sum_m \frac{\langle f|\hat{H}_1|m\rangle\langle m|\hat{H}_1|i\rangle}{E_f - E_i}\right|^2 \delta(E_f - E_i)\,.$$

The first term is calculated as

$$\langle f|\hat{H}_2|i\rangle = \sum_j \frac{2\pi\hbar e_j^{\ 2}}{m_j}\sqrt{\frac{n_1(n_2+1)}{\omega_1\omega_2V^2}}\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\langle f|e^{i(\boldsymbol{k}_1-\boldsymbol{k}_2)\cdot\boldsymbol{r}_j}|i\rangle$$

where

$$\omega_{\boldsymbol{k}} = c|\boldsymbol{k}| = c\frac{2\pi}{\lambda}$$

$$\omega_1 = \omega_{\boldsymbol{k}_1}\,, \qquad \omega_2 = \omega_{\boldsymbol{k}_2}$$

Using the electric dipole approximation, we assume that

$$e^{i(\boldsymbol{k}_1-\boldsymbol{k}_2)\cdot\boldsymbol{r}_j} = 1$$

Then we have

$$\langle f|\hat{H}_2|i\rangle = \frac{2\pi\hbar e^2}{mV}\sqrt{\frac{n_1(n_2+1)}{\omega_1\omega_2}}\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{ca}$$

where $\boldsymbol{\varepsilon}_\nu(\boldsymbol{k})$ is the polarization vector for the photon with the wave vector $\boldsymbol{k}$.

$$\boldsymbol{\varepsilon}_\nu(\boldsymbol{k})\cdot\boldsymbol{k} = 0 \quad \text{with} \quad \nu = 1, 2$$

$$\boldsymbol{\varepsilon}_\nu(-\boldsymbol{k}) = \boldsymbol{\varepsilon}_\nu(\boldsymbol{k})$$

We next calculate the second term. There are two types of the intermediate state $|b\rangle$.

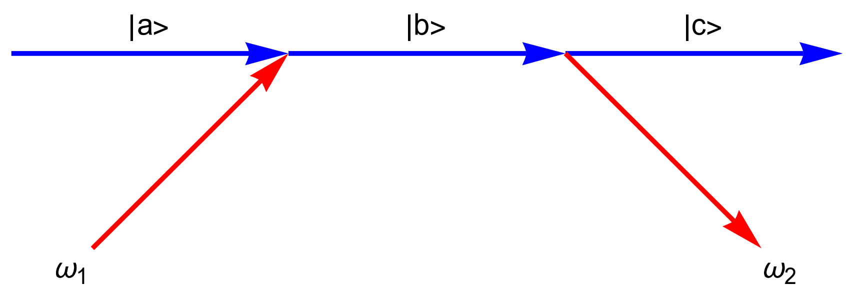

Fig. Light scattering due to the Hamiltonian $\hat{H}_1$ (type-1). The horizontal axis is time. The intermediate state is $|b\rangle\otimes|n_1-1,n_2\rangle$

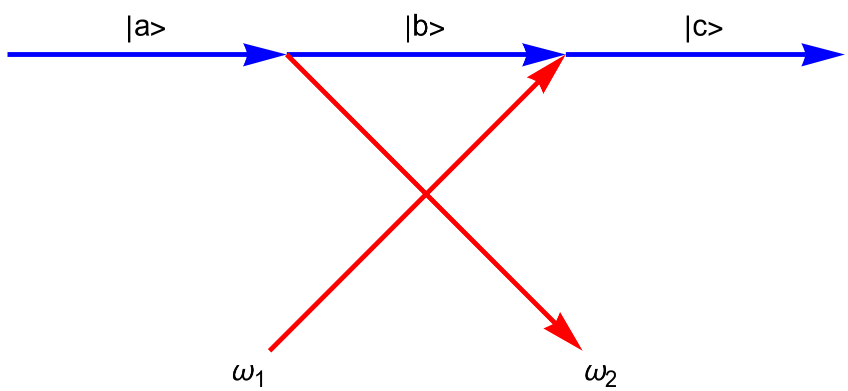

Fig. The light scattering due to the Hamiltonian $\hat{H}_1$ (type-2). The horizontal axis is time. The intermediate state is $|b\rangle\otimes|n_1,n_2+1\rangle$

The resultant transition rate for this process is given by

$$w_{i\to f} = 2\pi\hbar\left(\frac{2\pi e^2}{mV}\right)^2 \frac{n_1(n_2+1)}{\omega_1\omega_2}$$

$$\times\left|\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{ca}+\frac{1}{m}\sum_b\{\frac{\langle c|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|a\rangle}{E_c-E_b+\hbar\omega_2}+\frac{\langle c|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|a\rangle}{E_c-E_b-\hbar\omega_1}\}\right| \qquad (1)$$

$$\times\delta(E_a+\hbar\omega_1-E_c-\hbar\omega_2)$$

The first term is the Rayleigh component since $E_c = E_a$. We note that the Rayleigh component exists in the second term. The contribution with $E_c \neq E_a$ is called the Raman component. Equation (1) is called the Kramers-Heisenberg formula for steady state light scattering. We define $R_{21}{}^{ac}(\omega_1)$ as

$$R_{21}{}^{ac}(\omega_1)=\frac{1}{m}\sum_b\{\frac{\langle c|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|a\rangle}{E_b-E_c+\hbar\omega_1+i\hbar\gamma}+\frac{\langle c|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|a\rangle}{E_b-E_a-\hbar\omega_1+i\hbar\gamma}\}$$

which is called the Raman tensor.

$$\begin{aligned}R_{21}{}^{ac}(\omega_1)&=\frac{1}{m}\sum_b\{\frac{\langle c|\varepsilon_{1\mu}\hat{p}_\mu|b\rangle\langle b|\varepsilon_{2\nu}\hat{p}_\nu|a\rangle}{E_b-E_c+\hbar\omega_1+i\hbar\gamma}+\frac{\langle c|\varepsilon_{2\nu}\hat{p}_\nu|b\rangle\langle b|\varepsilon_{1\mu}\hat{p}_\mu|a\rangle}{E_b-E_a-\hbar\omega_1+i\hbar\gamma}\}\\&=\varepsilon_{1\mu}\frac{1}{m}\sum_b\{\frac{\langle c|\hat{p}_\mu|b\rangle\langle b|\hat{p}_\nu|a\rangle}{E_b-E_c+\hbar\omega_1+i\hbar\gamma}+\frac{\langle c|\hat{p}_\nu|b\rangle\langle b|\hat{p}_\mu|a\rangle}{E_b-E_a-\hbar\omega_1+i\hbar\gamma}\}\varepsilon_{2\nu}\end{aligned}$$

Note that E_b is replaced by

$$E_b \to E_b + i\hbar\gamma$$

because of the finite width ($2\hbar\gamma$) in the intermediate (excited) state [so-called natural width].
Then we have

$$w_{i\to f} = 2\pi\hbar\left(\frac{2\pi e^2}{mV}\right)^2 \frac{n_1(n_2+1)}{\omega_1\omega_2}\left|\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{ca}-R_{21}{}^{ac}(\omega_1)\}\right| \qquad (1)$$

$$\times\delta(E_a+\hbar\omega_1-E_c-\hbar\omega_2)$$

When $a \neq c$ we have

$$w_{i\to f} = 2\pi\hbar\left(\frac{2\pi e^2}{mV}\right)^2 \frac{n_1(n_2+1)}{\omega_1\omega_2}\left|R_{21}{}^{ac}(\omega_1)\right|^2 \delta(E_a + \hbar\omega_1 - E_c - \hbar\omega_2)$$

This expression can be rewritten using the electric dipole moment ($\mu = -er$), as

$$R_{21}{}^{ac}(\omega_1) = -\frac{m\omega_1\omega_2}{e^2} P_{21}{}^{ac}(\omega_1)$$

where

$$\begin{aligned} P_{21}{}^{ac}(\omega_1) &= \frac{e^2}{m}\sum_b \{\frac{\langle c|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{r}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{r}}|a\rangle}{E_b - E_c + \hbar\omega_1 + i\hbar\gamma} + \frac{\langle c|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{r}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{r}}|a\rangle}{E_b - E_a - \hbar\omega_1 + i\hbar\gamma}\} \\ &= \varepsilon_{1\mu}\frac{e^2}{m}\sum_b \{\frac{\langle c|\hat{r}_\mu|b\rangle\langle b|\hat{r}_\nu|a\rangle}{E_b - E_c + \hbar\omega_1 + i\hbar\gamma} + \frac{\langle c|\hat{r}_\nu|b\rangle\langle b|\hat{r}_\mu|a\rangle}{E_b - E_a - \hbar\omega_1 + i\hbar\gamma}\}\varepsilon_{2\nu} \end{aligned}$$

Then we have

$$w_{i\to f} = 2\pi\hbar\left(\frac{2\pi e^2}{mV}\right)^2 \omega_1\omega_2 n_1(n_2+1)\left|P_{21}{}^{ac}(\omega_1)\right|^2 \delta(E_a + \hbar\omega_1 - E_c - \hbar\omega_2)$$

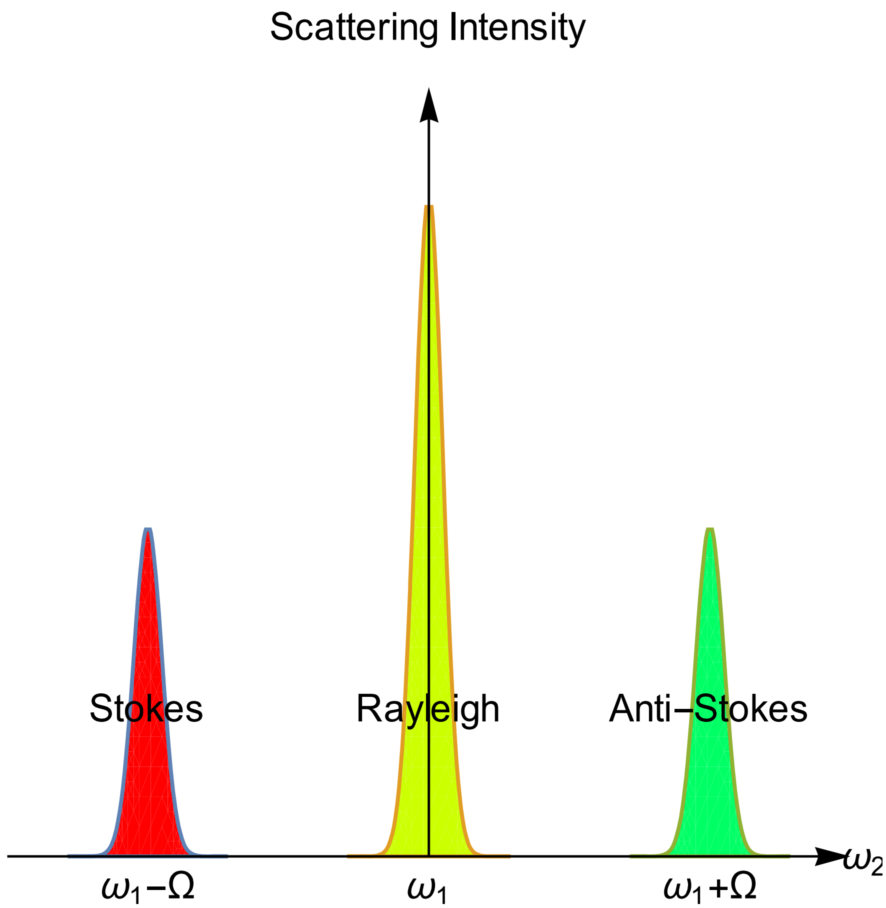

Fig. Schematic diagram for the Stokes' line, Rayleigh scattering, and anti-Stokes' line.

3. Brillouin scattering

The light scattering experimental technique is an exceedingly valuable tool for the study of fundamental excitations in solids, such as phonons. We now consider the Brillouin scattering when the incident light interacts with phonon.

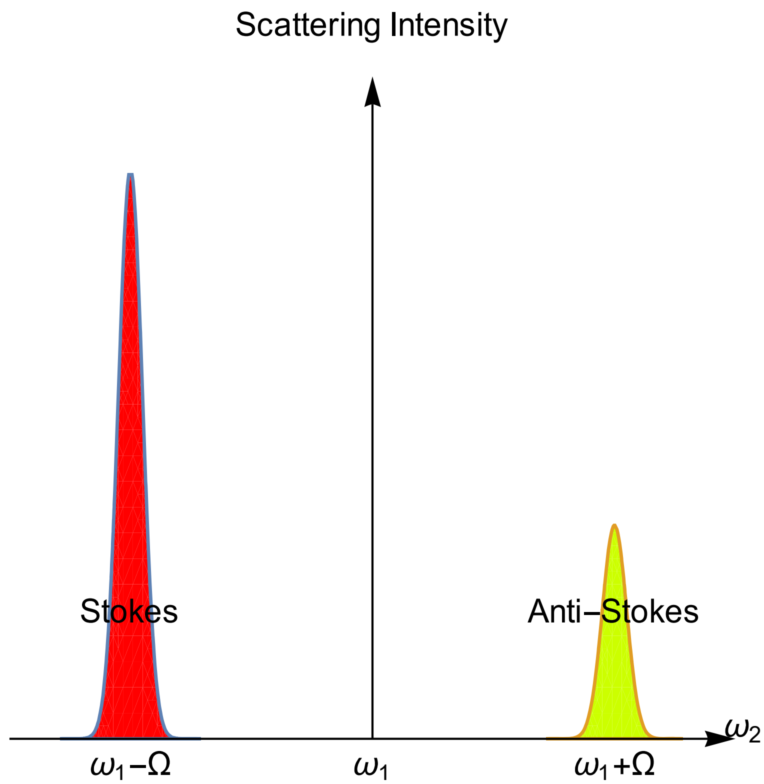

Fig. Stokes line at $\omega_2 = \omega_1 - \Omega$. Anti-Stokes line at $\omega_2 = \omega_1 + \Omega$

The Brillouin scatterings are schematically shown in the above figure. , in which ω_1 and ω_2 is the frequency of the incident and outgoing light.

$$\omega_2 = \omega_1 \pm \Omega(\boldsymbol{q}) . \qquad \text{(energy conservation)}$$

$$\boldsymbol{k}_1 - \boldsymbol{k}_2 = \pm \boldsymbol{q} \qquad \text{(momentum conservation)}$$

$\Omega(\boldsymbol{q})$ is the angular frequency of phonon at the wave vector $\boldsymbol{q}$. The photon at $\omega_2 = \omega_1 - \Omega$ is called the Stokes line and that at $\omega_2 = \omega_1 + \Omega$ is called the anti-Stokes line. The intensity of the Stokes line involve the matrix element for phonon creation,

$$I(\omega_2 = \omega_1 - \Omega) \propto \left| \langle n_q | \hat{u} | n_q + 1 \rangle \right|^2 \propto (n_q + 1)$$

where n_q is the initial population of phonon mode $\boldsymbol{q}$.

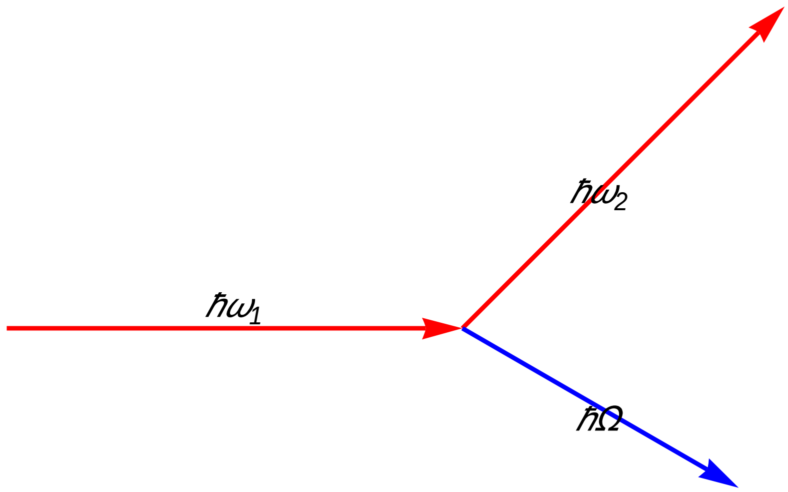

Fig. Brillouin scattering. Stokes line. Creation of phonon. Red (photon). Blue (phonon).

The intensity of the anti-Stokes line involve the matrix element for phonon annihilation,

$$I(\omega_2 = \omega_1 + \Omega) \propto \left| \langle n_q - 1 | \hat{u} | n_q \rangle \right|^2 \propto n_q$$

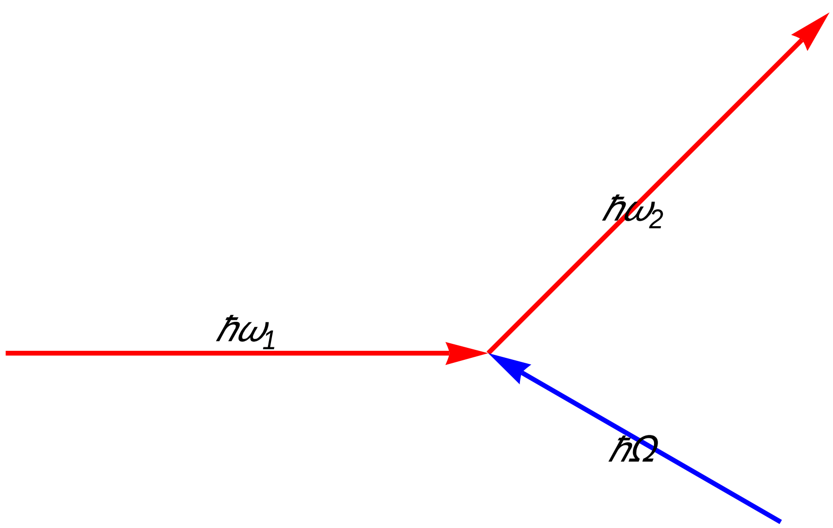

Fig. Brillouin scattering. Anti-Stokes line. Annihilation of phonon. Red (photon). Blue (phonon).

If the phonon population is initially in thermal equilibrium at temperature *T*, the intensity ratio of the two lines is

$$\frac{I(\omega_1+\Omega)}{I(\omega_1-\Omega)}=\frac{\langle n_q\rangle}{\langle n_q\rangle+1}=\frac{\frac{1}{e^{\beta\hbar\Omega}-1}}{1+\frac{1}{e^{\beta\hbar\Omega}-1}}=e^{-\beta\hbar\Omega}<1$$

where $\langle n_q\rangle$ is the Planck's distribution function

$$\langle n_q\rangle=\frac{1}{e^{\beta\hbar\Omega}-1}.$$

Note that the intensity of the Stokes line is stronger than that of the anti-Stokes line.

4. Rayleigh scattering (revisited)

We consider the case when

$$E_c=E_f\,,\qquad E_a=E_i\qquad \hbar\omega_1=\hbar\omega_2=\hbar\omega$$

This corresponds to the elastic scattering of light. It is also called Rayleigh scattering because this problem was treated classically by Lord Rayleigh.

$$\begin{aligned}w_{i\to f}&=2\pi\hbar\left(\frac{2\pi e^2}{mV}\right)^2\frac{n_1(n_2+1)}{\omega_1\omega_2}\\&\times\left|\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{fi}+\frac{1}{m}\sum_b\{\frac{\langle f|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|i\rangle}{E_f-E_b+\hbar\omega_2}+\frac{\langle f|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|i\rangle}{E_f-E_b-\hbar\omega_1}\}\right|\qquad(1)\\&\times\delta(E_i+\hbar\omega_1-E_f-\hbar\omega_2)\frac{\omega_2{}^2d\omega_2d\Omega_2}{(2\pi)^3c^3}\end{aligned}$$

In order to simplify Eq.(1), we rewrite the factor $\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{fi}$ as follows.

$$
\begin{aligned}
(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2) &= \sum_{i,j}(\hat{x}_i\varepsilon_{1i})(\hat{p}_j\varepsilon_{2j}) \\
&= \sum_{i,j}(\hat{x}_i\hat{p}_j)\varepsilon_{1i}\varepsilon_{2j} \\
&= \sum_{i,j}(\hat{p}_j\hat{x}_i + i\hbar\hat{1}\delta_{i,j})\varepsilon_{1i}\varepsilon_{2j} \\
&= \sum_{i,j}\hat{p}_j\varepsilon_{2j}\hat{x}_i\varepsilon_{1i} + i\hbar\hat{1}\delta_{i,j}\varepsilon_{1i}\varepsilon_{2j}) \\
&= (\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1) + i\hbar\hat{1}(\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2)
\end{aligned}
$$

Thus we get

$$
(\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2)\hat{1} = \frac{1}{i\hbar}(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2) - (\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)
$$

and

$$
(\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2)\langle f|i\rangle = \frac{1}{i\hbar}\sum_b[\langle f|(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle - \langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)|i\rangle] \tag{2}
$$

where $|i\rangle$ is the initial state, $|f\rangle$ is the final state, and $|b\rangle$ is the intermediate state. We note that

$$
[\hat{H},\hat{x}] = \frac{1}{2m}[\hat{p}^2,\hat{x}] = -\frac{1}{2m}[\hat{x},\hat{p}^2] = -\frac{i\hbar}{m}\hat{p}
$$

or

$$
\hat{\boldsymbol{p}} = \frac{im}{\hbar}[\hat{H},\hat{\boldsymbol{r}}]
$$

Thus we get

$$
\begin{aligned}
\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle &= \frac{im}{\hbar}\langle f|[\hat{H},\hat{\boldsymbol{r}}]\cdot\boldsymbol{\varepsilon}_1|b\rangle \\
&= \frac{im}{\hbar}\langle f|(\hat{H}\hat{\boldsymbol{r}} - \hat{\boldsymbol{r}}\hat{H})\cdot\boldsymbol{\varepsilon}_1|b\rangle \\
&= \frac{im}{\hbar}(E_f - E_b)\langle f|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1|b\rangle
\end{aligned}
$$

or

$$\begin{aligned}\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle &= \frac{im}{\hbar}\langle f|[\hat{H},\hat{\boldsymbol{r}}]\cdot\boldsymbol{\varepsilon}_1|b\rangle \\ &= \frac{im}{\hbar}\langle f|(\hat{H}\hat{\boldsymbol{r}}-\hat{\boldsymbol{r}}\hat{H})\cdot\boldsymbol{\varepsilon}_1|b\rangle \\ &= im\omega_{fb}\langle f|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\end{aligned}$$

or

$$\langle f|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1|b\rangle = \frac{1}{im\omega_{fb}}\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle$$

where $\hbar\omega_{fb} = E_f - E_b$. Using this relation, Eq.(2) can be rewritten as

$$\begin{aligned}(\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2)\langle f|i\rangle &= \frac{1}{i\hbar}\sum_b[\frac{1}{im\omega_{fb}}\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle - \frac{1}{im\omega_{bi}}\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle] \\ &= -\frac{1}{\hbar}\sum_b[-\frac{1}{m\omega_{bf}}\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle - \frac{1}{m\omega_{bi}}\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle] \\ &= \frac{1}{m\hbar}\sum_b\frac{1}{\omega_{bi}}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle + \langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\end{aligned}$$

where $\omega_{bi} = \omega_{bf} = -\omega_{fb}$. Thus we get

$$\begin{aligned}&\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{fi} - \frac{1}{m\hbar}\sum_b\{\frac{\langle f|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|i\rangle}{\omega_{bi}-\omega} + \frac{\langle f|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|i\rangle}{\omega_{bi}+\omega}\} \\ &= \frac{1}{m\hbar}\sum_b\frac{1}{\omega_{bi}}[\langle c|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|a\rangle + \langle c|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|a\rangle] \\ &- \frac{1}{m\hbar}\sum_b\{\frac{\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2|i\rangle}{\omega_{bi}+\omega} + \frac{\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle}{\omega_{bi}-\omega} + \} \\ &= \frac{1}{m\hbar}\sum_b\{(\frac{1}{\omega_{bi}} - \frac{1}{\omega_{bi}+\omega})[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle + (\frac{1}{\omega_{bi}} - \frac{1}{\omega_{bi}-\omega})\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\} \\ &= \frac{\omega}{m\hbar}\sum_b\{\frac{1}{\omega_{bi}(\omega_{bi}+\omega)}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle - \frac{1}{\omega_{bi}(\omega_{bi}-\omega)}\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\}\end{aligned}$$

For $\omega \ll \omega_{bi}$

$$\frac{1}{\omega_{bi}+\omega}=\frac{1}{\omega_{bi}}(1-\frac{\omega}{\omega_{bi}}), \qquad \frac{1}{\omega_{bi}-\omega}=\frac{1}{\omega_{bi}}(1+\frac{\omega}{\omega_{bi}})$$

$$\begin{aligned}
&\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\varepsilon}_2\,\delta_{fi}-\frac{1}{m\hbar}\sum_b\{\frac{\langle f|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|i\rangle}{\omega_{ba}-\omega}+\frac{\langle f|\boldsymbol{\varepsilon}_1\cdot\hat{\boldsymbol{p}}|b\rangle\langle b|\boldsymbol{\varepsilon}_2\cdot\hat{\boldsymbol{p}}|i\rangle}{\omega_{ba}+\omega}\}\\
&=\frac{\omega}{m\hbar}\sum_b\{\frac{1}{\omega_{bi}{}^2}(1-\frac{\omega}{\omega_{bi}})[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle-\frac{1}{\omega_{bi}{}^2}(1+\frac{\omega}{\omega_{bi}})\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\}\\
&=\frac{\omega}{m\hbar}\sum_b\{\frac{1}{\omega_{bi}{}^2}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle-\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\}\\
&-\frac{\omega^2}{m\hbar}\sum_b\{\frac{1}{\omega_{bi}{}^3}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle+\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\}
\end{aligned}$$

Here we note that the first term reduces to zero, since

$$\begin{aligned}
&\sum_b\{\frac{1}{\omega_{bi}{}^2}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|f\rangle-\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|f\rangle]\}\\
&=m^2\sum_b[\langle f|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2|i\rangle-\langle f|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2|b\rangle\langle b|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1|f\rangle]\\
&=m^2\langle f|(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)-(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)|i\rangle\\
&=0
\end{aligned}$$

The second term is

$$\begin{aligned}
&-\frac{\omega^2}{m\hbar}\sum_b\{\frac{1}{\omega_{bi}{}^3}[\langle f|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|b\rangle\langle b|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|i\rangle+\langle f|(\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_2)|b\rangle\langle b|\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}_1|i\rangle]\}\\
&=-\frac{m\omega^2}{\hbar}\sum_b\{\frac{1}{\omega_{bi}}[\langle f|(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)+(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)|i\rangle]
\end{aligned}$$

The factor $n_1\frac{c}{V}$ can be interpreted as the flux of incoming photons. Thus the scattering cross section is defined as

$$d\sigma=\frac{\text{rate of photons arriving in the solid angle element }\Omega_2}{\text{flux of incoming photons}}$$

Thus we get the differential cross section for the Rayleigh scattering is

$$d\sigma_R = \frac{1}{n_1 \frac{c}{V}} 2\pi\hbar \left(\frac{2\pi e^2}{mV}\right)^2 \frac{n_1(n_2+1)}{\omega_1\omega_2}$$

$$\times \left| -\frac{m\omega^2}{\hbar} \sum_b \{ \frac{1}{\omega_{bi}} [\langle f | (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2) + (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1) | i \rangle] \right|^2 \frac{\delta(\omega_1 - \omega_2)}{\hbar} \frac{V\omega_2^{\ 2}}{(2\pi)^3} \frac{d\Omega_2}{c^3}$$

$$\rightarrow \frac{\omega^4 e^4}{c^4 \hbar^2} (n_2+1) d\Omega_2 \left| \sum_b \{ \frac{1}{\omega_{bi}} [\langle f | (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2) + (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1) | i \rangle] \right|^2$$

$$= \frac{\omega^4 e^4}{c^4 \hbar^2} (n_2+1) d\Omega_2 \left| \sum_b \{ \frac{1}{\omega_{bi}} [\langle f | (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2) + (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1) | i \rangle \right|^2$$

Using the relation $m^2 r_0^{\ 2} = \frac{e^4}{c^4}$

$$\frac{d\sigma_R}{d\Omega_2} = \omega^4 \left(\frac{m r_0}{\hbar}\right)^2 (n_2+1) \left| \sum_b \{ \frac{1}{\omega_{bi}} [\langle f | (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2) + (\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_2)(\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}_1) | i \rangle] \right|^2$$

5. Polarization pattern in the sky

From a book

I.R. Kenyon, The Light Fantastic: A Modern Introduction to Classical and Quantum Optics (Oxford University, 2008).

The Rayleigh scattering is an elastic scattering and is proportional to ω^4. It explains the blue color of the sky. The blue color of the sky is caused by the Rayleigh scattering of sunlight off the molecules of the atmosphere. The Rayleigh scattering, is more effective at short wavelengths (the blue end of the visible spectrum). Therefore the light scattered down to the earth at a large angle with respect to the direction of the sun's light is predominantly in the blue end of the spectrum.

The scattering of sunlight from gas molecules in the upper atmosphere is responsible for the blue of the sky. In addition if the blue sky is viewed through a Polaroid, looking at right angles to the direction linking the observer to the Sun, the light is found to be strongly polarized. Scattering, as in this example, in which the particles doing the scattering are much smaller than the wavelength of the radiation is called Rayleigh scattering. The strong dependence on wavelength causes blue light to be scattered about ten times more effectively than red light, which accounts for the blue of a clear sky. It also explains why light from the setting Sun, which has a long path through the atmosphere, should look red.

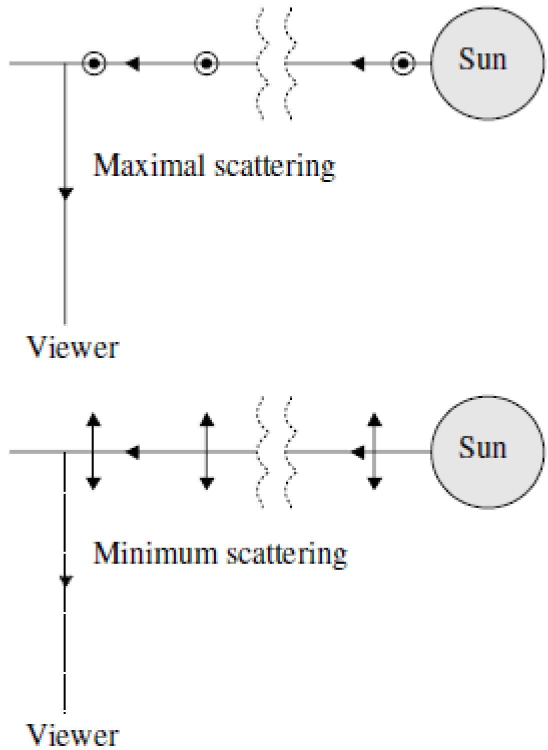

Fig.1 Rayleigh scattering at 90. In the upper panel light is polarized perpendicular to the scattering plane, and in the lower panel it is polarized in the scattering plane.

Figure 1 has a viewer looking at the blue sky in a direction at right angles to the line passing through the Sun. Any molecule scattering light first absorbs the light, becoming polarized in essentially the same direction as the light absorbed, and then re-emits light. When the molecule is excited by light polarized perpendicular to the plane of scattering, as seen in the upper panel of Fig.1, the observer is viewing in a direction for which the intensity is at a maximum. On the other hand, if the light is polarized in the plane of scattering, as illustrated in the lower panel of **Fig.1**, then the molecular dipole points towards the observer and no light would be seen. However there can be some misalignment of the molecular dipole axis with the electric field inducing it due to asymmetry of the structure of the molecule, and then a little light would be seen. In any case the light received is strongly polarized perpendicular to the plane of scattering. Away from this viewing direction the polarization falls off rapidly.

REFERENCES

J.J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, 1967).

M. Dresden, *H.A. Kramers Between Tradition and Revolution* (Springer, 1987).

F. Shibata, Solid State Physics vol.20 (1985); The theory of Light Scattering: Interaction between Matter and Electromagnetic Field (in Japanese).
R. Loudon, *The Quantum Theory of Light*, Third edition (Oxford, 2000).
D.A. Long, The Raman Effect (John Wiley & Sons, 2002).
F. Han, A Modern Course in the Quantum Theory of Solids (World Scientific, 2013).
K. Schulten, Notes on Quantum Mechanics (University of Illinois at Urbana-Champaign, 1991).

APPENDIX

Background for the development of Kramers and Heisenberg formula

M. Dresden, H.A. Kramers: Between Tradition and Revolution

The joint paper by Kramers and Heisenberg, "On the Dispersion of Radiation by Atoms", was completed in Copenhagen in December 1924. It was a remarkable paper on several counts. It was the last, and certainly as far as physics was concerned, the most important paper in which the BKS (Bohr-Kramers-Slater) philosophy was expressed explicitly. Although the detailed dependence of the Kramers-Heisenberg results on the BKS approach was rather slight, there are frequent allusions to the BKS papers, and at least in one important instance, specific use is made of the BKS ideas. Furthermore, the Kramers Heisenberg paper contains the first (and only) organized, systematic exposition of Kramers' ideas on dispersion theory. Up until that time ideas were hinted at in short notices and abbreviated comments; Kramers had long planned to write a detailed paper on this material but it took about a year (from December 1923 until December 1924) before such a paper was completed. Thus, the Kramers-Heisenberg paper includes-apart from a number of new results such as the Smekal-Raman effect - an overview of Kramers' thinking during that period. But perhaps most important is that the Kramers Heisenberg paper contained the main elements and basic method from which Heisenberg later developed his matrix mechanics. The notation, general approach, and some specific results of the Kramers-Heisenberg paper were all essential ingredients in Heisenberg's fundamental paper on matrix mechanics. None of this detracts in any way from Heisenberg's monumental contribution, but the recognition of these particular circumstances is necessary to put Kramers' contributions in their proper perspective. The influence of the Kramers-Heisenberg paper on the later Heisenberg paper was certainly considerable, and Kramers, without any doubt, was the senior and major author of the Kramers-Heisenberg paper. To appreciate Kramers' contribution, it is necessary to analyze the evolution of his thinking on dispersion theory during this period. Unfortunately, this is not made any easier by Kramers' erratic publishing schedule and his simultaneous preoccupation with the BKS theory. Nevertheless, published papers, available letters, and recent interviews allow the reconstruction of a coherent, plausible picture of this development. The innovations in the Kramers-Heisenberg paper can be understood most simply if its contents are presented against the background of Kramers' earlier work in dispersion theory. To make the discussion transparent and self-contained, it is best to summarize t some of these earlier results.