1.

(a)

Rayleigh scattering.

$$|i\rangle = |a; \vec{k}\vec{e}\rangle$$

 $|f\rangle = |a; \vec{k}'\vec{e}'\rangle$

Using the electric-dipole Hamiltonian

$$H_I' = -i \sum_{\vec{e},\vec{k}} \sqrt{\frac{\hbar \omega}{2V \varepsilon_0}} \vec{d} \cdot \left(\vec{e} a_{ke} - \vec{e}^* a_{ke}^{\dagger} \right)$$

Two paths

$$\begin{split} \langle b; 0|H_I'|a; \vec{k}\vec{e}\rangle &= -\mathrm{i}\sqrt{\frac{\hbar\omega}{2V\varepsilon_0}}\langle b|\vec{d}\cdot\vec{e}|a\rangle \\ \langle b; \vec{k}\vec{e}, \vec{k}'\vec{e}'|H_I'|a; \vec{k}\vec{e}\rangle &= \mathrm{i}\sqrt{\frac{\hbar\omega}{2V\varepsilon_0}}\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle \\ \mathcal{T}_{fi} &= \frac{\hbar\omega}{2\varepsilon_0 V} \left(\frac{\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle}{E_a - E_b + \hbar\omega} + \frac{\langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle}{E_a - E_b - \hbar\omega}\right) \\ &\approx \frac{\omega}{2\omega_0\varepsilon_0 V} \left(\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle + \langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle\right) \end{split}$$

Using the Coulomb-gauge Hamiltonian

$$\begin{split} H_{I1} &= -\frac{q}{m} \sum_{\vec{e},\vec{k}} \sqrt{\frac{\hbar}{2\omega V \varepsilon_0}} \vec{p} \cdot \left(\vec{e} a_{ke} + \vec{e}^* a_{ke}^{\dagger} \right) \\ H_{I2} &= \frac{\hbar q^2}{4mV \varepsilon_0} \sum_{\vec{e},\vec{k},\vec{e}',\vec{k}'} \frac{1}{\sqrt{\omega' \omega}} \left(\vec{e} a_{ke} + \vec{e}^* a_{ke}^{\dagger} \right) \left(\vec{e}' a_{k'e'} + \vec{e}'^* a_{k'e'}^{\dagger} \right) \end{split}$$

Two paths for H_{I1}

$$\begin{split} \langle b; 0 | H_{I1} | a; \vec{k} \vec{e} \rangle &= -\frac{q}{m} \langle b; 0 | \sum_{\vec{e}, \vec{k}} \sqrt{\frac{\hbar}{2\omega V \varepsilon_0}} \vec{p} \cdot \left(\vec{e} a_{ke} + \vec{e}^* a_{ke}^{\dagger} \right) | a; \vec{k} \vec{e} \rangle \\ &= -\frac{q}{m} \sqrt{\frac{\hbar}{2\omega V \varepsilon_0}} \langle b | \vec{p} \cdot \vec{e} | a \rangle \\ \langle b; \vec{k} \vec{e}, \vec{k}' \vec{e}' | H_{I1} | a; \vec{k} \vec{e} \rangle &= -\frac{q}{m} \langle b; \vec{k} \vec{e}, \vec{k}' \vec{e}' | \sum_{\vec{e}, \vec{k}} \sqrt{\frac{\hbar}{2\omega V \varepsilon_0}} \vec{p} \cdot \left(\vec{e} a_{ke} + \vec{e}^* a_{ke}^{\dagger} \right) | a; \vec{k} \vec{e} \rangle \\ &= -\frac{q}{m} \sqrt{\frac{\hbar}{2\omega V \varepsilon_0}} \langle b | \vec{p} \cdot \vec{e}'^* | a \rangle \end{split}$$

Since

$$\begin{split} [\vec{x}, H_0] = & \frac{1}{2m} [\vec{x}, p^2] \\ = & \frac{\mathrm{i}\hbar}{m} \vec{p} \\ \langle b | \vec{p} \cdot \vec{e} | a \rangle = & \frac{m}{\mathrm{i}\hbar} \langle b | [\vec{x}, H_0] \cdot \vec{e} | a \rangle \\ = & \frac{m}{\mathrm{i}\hbar} \langle b | (E_a - E_b) \vec{x} \cdot \vec{e} | a \rangle \\ = & \mathrm{i}m \omega_0 \langle b | \vec{x} \cdot \vec{e} | a \rangle \end{split}$$

Matrix element

$$\begin{split} \mathcal{T}_{fi1} = & \frac{q^2 \hbar}{2m^2 \varepsilon_0 \omega V} \left(\frac{\langle a|\vec{p} \cdot \vec{e'}^*|b\rangle \langle b|\vec{p} \cdot \vec{e}|a\rangle}{E_a - E_b + \hbar \omega} + \frac{\langle a|\vec{p} \cdot \vec{e}|b\rangle \langle b|\vec{p} \cdot \vec{e'}^*|a\rangle}{E_a - E_b - \hbar \omega} \right) \\ \mathcal{T}_{fi2} = & \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e'}^* \\ \mathcal{T}_{fi} = & \frac{q^2 \hbar}{2m^2 \varepsilon_0 \omega V} \left(\frac{\langle a|\vec{p} \cdot \vec{e'}^*|b\rangle \langle b|\vec{p} \cdot \vec{e}|a\rangle}{E_a - E_b + \hbar \omega} + \frac{\langle a|\vec{p} \cdot \vec{e}|b\rangle \langle b|\vec{p} \cdot \vec{e'}^*|a\rangle}{E_a - E_b - \hbar \omega} \right) + \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e'}^* \\ \approx & \frac{q^2 \hbar}{2m^2 \varepsilon_0 \omega V} \left(\frac{\langle a|\vec{p} \cdot \vec{e'}^*|b\rangle \langle b|\vec{p} \cdot \vec{e}|a\rangle}{E_a - E_b} + \frac{\langle a|\vec{p} \cdot \vec{e}|b\rangle \langle b|\vec{p} \cdot \vec{e'}^*|a\rangle}{E_a - E_b} \right) + \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e'}^* \\ + & \frac{q^2 \hbar \omega}{2m^2 \varepsilon_0 \omega_0^2 V} \left(\frac{\langle a|\vec{p} \cdot \vec{e'}^*|b\rangle \langle b|\vec{p} \cdot \vec{e}|a\rangle}{E_a - E_b} + \frac{\langle a|\vec{p} \cdot \vec{e}|b\rangle \langle b|\vec{p} \cdot \vec{e'}^*|a\rangle}{E_a - E_b} \right) \\ \approx & \frac{q^2 \hbar}{2m^2 \varepsilon_0 \omega_0 V} \frac{\langle a|2p^2|a\rangle}{E_a - E_b} \vec{e} \cdot \vec{e'}^* + \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e'}^* \\ + & \frac{q^2 \omega}{2\varepsilon_0 \omega_0 V} \left(\langle a|\vec{d} \cdot \vec{e'}^*|b\rangle \langle b|\vec{d} \cdot \vec{e}|a\rangle + \langle a|\vec{d} \cdot \vec{e}|b\rangle \langle b|\vec{d} \cdot \vec{e'}^*|a\rangle \right) \\ \approx & \frac{q^2 \omega}{2\varepsilon_0 \omega_0 V} \left(\langle a|\vec{d} \cdot \vec{e'}^*|b\rangle \langle b|\vec{d} \cdot \vec{e}|a\rangle + \langle a|\vec{d} \cdot \vec{e}|b\rangle \langle b|\vec{d} \cdot \vec{e'}^*|a\rangle \right) \end{split}$$

Thomson Scattering

Using the Coulomb guage Hamiltonian

$$\mathcal{T}_{fi2} = \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e}'^*$$

$$\mathcal{T}_{fi1} = \sum_b \frac{q^2 \hbar}{2m^2 \varepsilon_0 \omega V} \left(\frac{\langle a|\vec{p} \cdot \vec{e}'^*|b\rangle \langle b|\vec{p} \cdot \vec{e}|a\rangle}{E_a - E_b + \hbar \omega} + \frac{\langle a|\vec{p} \cdot \vec{e}|b\rangle \langle b|\vec{p} \cdot \vec{e}'^*|a\rangle}{E_a - E_b - \hbar \omega} \right)$$

Since $E_b - E_a \ll \hbar \omega$

$$\mathcal{T}_{fi1} \approx \sum_{b} \frac{q^{2}\omega_{0}}{m^{2}\varepsilon_{0}\omega V} \left(\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e'}^{*}|a\rangle}{\omega^{2}} \right)$$

$$\approx \sum_{b} \frac{q^{2}\hbar\omega_{0}^{2}}{m^{2}\varepsilon_{0}\omega^{3}V} \vec{e}\cdot\vec{e'}^{*}$$

$$\ll \mathcal{T}_{fi2}$$

Therefore

$$\mathcal{T}_{fi} \approx \frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e}^{\prime *}$$

(b)

$$\begin{split} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \frac{V}{c} \frac{2\pi}{\hbar} \frac{V}{8\pi^3} \frac{h^2 \omega^2}{\hbar^3 c^3} \left(\frac{\hbar q^2}{2m\omega V \varepsilon_0} \vec{e} \cdot \vec{e}'^* \right)^2 \\ &= \frac{e^4}{16\pi^2 \varepsilon_0^2 m^2 c^4} (\vec{e} \cdot \vec{e}'^*)^2 \\ &= r_0^2 (\vec{e} \cdot \vec{e}'^*)^2 \\ \sigma &= \int \mathrm{d}\Omega r_0^2 (1 - \cos\theta)^2 \\ &= \frac{8\pi}{3} r_0^2 \end{split}$$

2.

(a)

For atoms in an isotropic environment

$$\langle g|\vec{d}|g\rangle = \langle i|\vec{d}|i\rangle$$

$$= 0$$

The first order correction to the energy is 0. Second order

$$\begin{split} \delta E = -\sum_{i_a,i_b} \frac{\left| \langle i_a i_b | H_{el} | gg \rangle \right|^2}{\hbar \omega_{ig}^a + \hbar \omega_{ig}^b} \\ \langle i_a i_b | H_{el} | gg \rangle = & \frac{e^2}{R^3} \left(\vec{r}_{ig}^a \cdot \vec{r}_{ig}^b - 3x_{ig}^a x_{ig}^b \right) \end{split}$$

Since the system is symmetric for rotation around \vec{R} , the "good" states to calculate the energy shift should also have the same symmetry. Therefore \vec{r}^a and \vec{r}^b should be along the \vec{R} (x) direction

$$\langle i_{a}i_{b}|H_{el}|gg\rangle = -\frac{2e^{2}x_{ig}^{a}x_{ig}^{b}}{R^{3}}$$

$$\delta E = -\sum_{i_{a},i_{b}} \frac{1}{\hbar\omega_{ig}^{a} + \hbar\omega_{ig}^{b}} \left| \frac{2e^{2}x_{ig}^{a}x_{ig}^{b}}{R^{3}} \right|^{2}$$

$$= -\frac{4e^{4}}{\hbar R^{6}} \sum_{i_{a},i_{b}} \frac{\left|x_{ig}^{a}\right|^{2} \left|x_{ig}^{b}\right|^{2}}{\omega_{ig}^{a} + \omega_{ig}^{b}}$$

(b)

$$\begin{split} |x_{ig}|^2 &= \frac{\hbar f_{ig}}{2m\omega_{ig}} \\ \delta E &= -\frac{4e^4}{\hbar R^6} \sum_{i_a,i_b} \frac{1}{\omega^a_{ig} + \omega^b_{ig}} \frac{\hbar f^a_{ig}}{2m\omega^a_{ig}} \frac{\hbar f^b_{ig}}{2m\omega^b_{ig}} \\ &= -\frac{\hbar e^4}{m^2 R^6} \sum_{i_a,i_b} \frac{f^a_{ig} f^b_{ig}}{(\omega^a_{ig} + \omega^b_{ig})\omega^a_{ig}\omega^b_{ig}} \end{split}$$

(c)

Since the oscillator strength for the ground state is always positive, if the first excited state has $f \approx 1$, the contribution from other transitions are small. With this approximation,

$$\begin{split} |x_{ig}|^2 &= \frac{\hbar \omega_{ig}}{2e^2} \alpha_g \\ \delta E &= -\frac{4e^4}{\hbar R^6} \frac{1}{\omega_{ig}^a + \omega_{ig}^b} \frac{\hbar \omega_{ig}^a}{2e^2} \alpha_g^a \frac{\hbar \omega_{ig}^b}{2e^2} \alpha_g^b \\ &= -\frac{\hbar}{R^6} \frac{\omega_{ig}^a \omega_{ig}^b}{\omega_{ig}^a + \omega_{ig}^b} \alpha_g^a \alpha_g^b \\ C_6 &= \hbar \frac{\omega_{ig}^a \omega_{ig}^b}{\omega_{ig}^a + \omega_{ig}^b} \alpha_g^a \alpha_g^b \end{split}$$