1.

(a)

Rayleigh scattering.

$$\begin{aligned}|i\rangle =&|a;\vec{k}\vec{e}\rangle\\ |f\rangle =&|a;\vec{k}'\vec{e}'\rangle\end{aligned}$$

Using the electric-dipole Hamiltonian

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

Two paths

$$\begin{aligned}\langle b;0|H_I'|a;\vec{k}\vec{e}\rangle =& -\mathrm{i}\sqrt{\frac{\hbar\omega}{2V\varepsilon_0}}\langle b|\vec{d}\cdot\vec{e}|a\rangle\\ \langle b;\vec{k}\vec{e},\vec{k}'\vec{e}'|H_I'|a;\vec{k}\vec{e}\rangle =&\mathrm{i}\sqrt{\frac{\hbar\omega}{2V\varepsilon_0}}\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle\\ \mathcal{T}_{fi} =&\frac{\hbar\omega}{2\varepsilon_0V}\left(\frac{\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle}{E_a - E_b + \hbar\omega} + \frac{\langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle}{E_a - E_b - \hbar\omega}\right)\\ \approx&\frac{\omega}{2\omega_0\varepsilon_0V}\left(\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle + \langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle\right)\end{aligned}$$

Using the Coulomb-gauge Hamiltonian

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

Two paths for H_{I1}

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

Since

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

Matrix element

$$
\begin{aligned}
\mathcal{T}_{fi1}=&\frac{q^2\hbar}{2m^2\varepsilon_0\omega V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}'^*|b\rangle\langle b|\vec{p}\cdot\vec{e}|a\rangle}{E_a-E_b+\hbar\omega}+\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{E_a-E_b-\hbar\omega}\right)\\
\mathcal{T}_{fi2}=&\frac{\hbar q^2}{2m\omega V\varepsilon_0}\vec{e}\cdot\vec{e}'^*\\
\mathcal{T}_{fi}=&\frac{q^2\hbar}{2m^2\varepsilon_0\omega V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}'^*|b\rangle\langle b|\vec{p}\cdot\vec{e}|a\rangle}{E_a-E_b+\hbar\omega}+\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{E_a-E_b-\hbar\omega}\right)+\frac{\hbar q^2}{2m\omega V\varepsilon_0}\vec{e}\cdot\vec{e}'^*\\
\approx&\frac{q^2\hbar}{2m^2\varepsilon_0\omega V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}'^*|b\rangle\langle b|\vec{p}\cdot\vec{e}|a\rangle}{E_a-E_b}+\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{E_a-E_b}\right)+\frac{\hbar q^2}{2m\omega V\varepsilon_0}\vec{e}\cdot\vec{e}'^*\\
&+\frac{q^2\hbar\omega}{2m^2\varepsilon_0\omega_0^2V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}'^*|b\rangle\langle b|\vec{p}\cdot\vec{e}|a\rangle}{E_a-E_b}+\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{E_a-E_b}\right)\\
\approx&\frac{q^2\hbar}{2m^2\varepsilon_0\omega V}\frac{\langle a|2p^2|a\rangle}{E_a-E_b}\vec{e}\cdot\vec{e}'^*+\frac{\hbar q^2}{2m\omega V\varepsilon_0}\vec{e}\cdot\vec{e}'^*\\
&+\frac{q^2\omega}{2\varepsilon_0\omega_0V}\left(\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle+\langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle\right)\\
\approx&\frac{q^2\omega}{2\varepsilon_0\omega_0V}\left(\langle a|\vec{d}\cdot\vec{e}'^*|b\rangle\langle b|\vec{d}\cdot\vec{e}|a\rangle+\langle a|\vec{d}\cdot\vec{e}|b\rangle\langle b|\vec{d}\cdot\vec{e}'^*|a\rangle\right)
\end{aligned}
$$

Thomson Scattering
Using the Coulomb guage Hamiltonian

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

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

$$
\begin{aligned}
\mathcal{T}_{fi1}\approx&\sum_b\frac{q^2\omega_0}{m^2\varepsilon_0\omega V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{\omega^2}\right)\\
\approx&\sum_b\frac{q^2\hbar\omega_0^2}{m^2\varepsilon_0\omega^3V}\vec{e}\cdot\vec{e}'^*\\
\ll&\mathcal{T}_{fi2}
\end{aligned}
$$

Therefore

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

Using the dipole Hamiltonian

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

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

$$\begin{aligned}\mathcal{T}_{fi} \approx& \sum_b \frac{q^2\omega\omega_0}{\varepsilon_0 V}\left(\frac{\langle a|\vec{r}\cdot\vec{e}|b\rangle\langle b|\vec{r}\cdot\vec{e}'^*|a\rangle}{\omega^2}\right)\\ =& \sum_b \frac{q^2\omega}{m^2\varepsilon_0\omega_0 V}\left(\frac{\langle a|\vec{p}\cdot\vec{e}|b\rangle\langle b|\vec{p}\cdot\vec{e}'^*|a\rangle}{\omega^2}\right)\\ =& \frac{q^2}{m^2\varepsilon_0\omega\omega_0 V}\langle a|p^2|a\rangle\vec{e}\cdot\vec{e}'^*\\ \approx& \frac{\hbar q^2}{2m\varepsilon_0\omega V}\vec{e}\cdot\vec{e}'^*\end{aligned}$$

(b)

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

2.

(a)

For atoms in an isotropic environment

$$\begin{aligned}\langle g|\vec{d}|g\rangle =& \langle i|\vec{d}|i\rangle\\ =& 0\end{aligned}$$

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

$$\delta E = -\sum_{i_a, i_b}\frac{|\langle i_a i_b|H_{el}|gg\rangle|^2}{\hbar\omega_{ig}^a + \hbar\omega_{ig}^b}$$

$$\langle i_a i_b|H_{el}|gg\rangle = \frac{e^2}{R^3}\left(\vec{r}_{ig}^a\cdot\vec{r}_{ig}^b - 3x_{ig}^a x_{ig}^b\right)$$

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

$$\begin{aligned}
\langle i_a i_b | H_{el} | gg \rangle =& -\frac{2e^2 x_{ig}^a x_{ig}^b}{R^3} \\
\delta E =& -\sum_{i_a, i_b} \frac{1}{\hbar\omega_{ig}^a + \hbar\omega_{ig}^b} \left| \frac{2e^2 x_{ig}^a x_{ig}^b}{R^3} \right|^2 \\
=& -\frac{4e^4}{\hbar R^6} \sum_{i_a, i_b} \frac{\left|x_{ig}^a\right|^2 \left|x_{ig}^b\right|^2}{\omega_{ig}^a + \omega_{ig}^b}
\end{aligned}$$

(b)

$$\begin{aligned}
\left|x_{ig}\right|^2 =& \frac{\hbar f_{ig}}{2m\omega_{ig}} \\
\delta E =& -\frac{4e^4}{\hbar R^6} \sum_{i_a, i_b} \frac{1}{\omega_{ig}^a + \omega_{ig}^b} \frac{\hbar f_{ig}^a}{2m\omega_{ig}^a} \frac{\hbar f_{ig}^b}{2m\omega_{ig}^b} \\
=& -\frac{\hbar e^4}{m^2 R^6} \sum_{i_a, i_b} \frac{f_{ig}^a f_{ig}^b}{(\omega_{ig}^a + \omega_{ig}^b)\omega_{ig}^a \omega_{ig}^b}
\end{aligned}$$

(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,

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