

## 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

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

Two paths

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

Using the Coulomb-gauge Hamiltonian

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

Two paths for  $H_{I1}$

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

Since

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

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}^* \\
 &\quad + \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 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}^* \\
 &\quad + \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{aligned}$$

Thomson Scattering

Using the Coulomb gauge 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  $E_b - E_a \ll \hbar \omega$

$$\begin{aligned}
 \mathcal{T}_{fi1} &\approx \sum_b \frac{q^2 \omega_0}{m^2 \varepsilon_0 \omega V} \left( \frac{\langle a | \vec{p} \cdot \vec{e} | b \rangle \langle b | \vec{p} \cdot \vec{e}^* | a \rangle}{\omega^2} \right) \\
 &\approx \sum_b \frac{q^2 \hbar \omega_0^2}{m^2 \varepsilon_0 \omega^3 V} \vec{e} \cdot \vec{e}^* \\
 &\ll \mathcal{T}_{fi2}
 \end{aligned}$$

Therefore

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

(b)

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

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

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

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

(b)

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

(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,

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