Homework #7 solutions

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1. **Rayleigh and Thomson scattering using two different interaction Hamiltonians**.

(a) Transition matrix calculation (8 points)
The quantized fields at **R=0** are given by

$$\mathbf{A}(\mathbf{0}) = \int d^3k \sum_{\hat{\varepsilon}} \frac{\mathcal{E}_\omega}{\omega} \left[a_{\hat{\varepsilon}}(\mathbf{k}) + a^\dagger_{\hat{\varepsilon}}(\mathbf{k}) \right] \hat{\varepsilon}$$

$$\mathbf{E}_\perp(\mathbf{0}) = \int d^3k \sum_{\hat{\varepsilon}} \mathrm{i}\mathcal{E}_\omega \left[a_{\hat{\varepsilon}}(\mathbf{k}) - a^\dagger_{\hat{\varepsilon}}(\mathbf{k}) \right] \hat{\varepsilon}$$

where $\mathcal{E}_\omega = \sqrt{\frac{\hbar\omega}{2\varepsilon_0 L^3}}$
The Born expansion of the transition matrix $\mathcal{T}_{fi}$ is

$$\mathcal{T}_{fi} = \langle\psi_f|H_I|\psi_i\rangle + \lim_{\epsilon\to 0^\dagger} \sum_j \frac{\langle\psi_f|H_I|\psi_j\rangle\langle\psi_j|H_I|\psi_i\rangle}{E_i - E_j + \mathrm{i}\epsilon} + ... = \mathcal{T}_{fi}(1) + \mathcal{T}_{fi}(2) + ...$$

The Dipole Hamiltonian
The interaction Hamiltonian H_I' does not couple $|a;\mathbf{k}\hat{\boldsymbol{\varepsilon}}\rangle$ to$|a;\mathbf{k}'\hat{\boldsymbol{\varepsilon}}'\rangle$. Hence, the intermediate state of the scattering process is either $|b;0\rangle$ or $|b;\mathbf{k}\hat{\boldsymbol{\varepsilon}},\mathbf{k}'\hat{\boldsymbol{\varepsilon}}'\rangle$. The relevant matrix elements are the following:

$$\langle b;0|H_I'|a;\mathbf{k}\hat{\boldsymbol{\varepsilon}}\rangle = -\mathrm{i}\mathcal{E}_\omega\langle b|\mathbf{d}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle$$
$$\langle b;\mathbf{k}\hat{\boldsymbol{\varepsilon}},\mathbf{k}'\hat{\boldsymbol{\varepsilon}}'|H_I'|a;\mathbf{k}\hat{\boldsymbol{\varepsilon}}\rangle = \mathrm{i}\mathcal{E}_\omega\langle b|\mathbf{d}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle$$

The transition matrix element to lowest order comes in at second order, where we sum over the intermediate states b.

$$\mathcal{T}_{fi}'(1) = 0$$

$$\mathcal{T}_{fi}'(2) = \frac{q^2\hbar}{2\varepsilon_0 L^3}\frac{1}{\sqrt{\omega\omega'}}\sum_b(\omega\omega')\left[\frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle}{\hbar(\omega-\omega_{ba})} - \frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle}{\hbar(\omega'+\omega_{ba})}\right]$$

where $\omega_{ba} = (E_b - E_a)/\hbar$
The scattering is elastic, hence $\omega = \omega'$ and it follows that,

$$\mathcal{T}_{fi}' = \frac{q^2\hbar}{2\varepsilon_0 L^3}\omega\sum_b\left[\frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle}{\hbar(\omega-\omega_{ba})} - \frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle}{\hbar(\omega+\omega_{ba})}\right]$$

(i) **Rayleigh scattering**

For Rayleigh scattering $\hbar\omega << E_b - E_a$

$$\mathcal{T}'_{fi} = -\frac{q^2\hbar}{2\varepsilon_0 L^3}\omega \sum_b \left[\frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle + \langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle}{\hbar\omega_{ba}}\right]$$

(ii) **Thomson scattering**

For Thomson scattering $\hbar\omega >> E_b - E_a$, we must expand $\mathcal{T}'_{fi}$ to lowest non-vanishing order in $x \equiv (E_b - E_a)/\hbar\omega$

$$\begin{aligned} T'_{fi} &= \frac{q^2\hbar}{2\varepsilon_0 L^3}\sum_b \left[\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle(1+x)^{-1} - \langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle(1-x)^{-1}\right] \\ &= \frac{q^2}{2\varepsilon_0 L^3}\frac{1}{\hbar\omega}\sum_b \left[\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle + \langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle\right](E_b - E_a) \end{aligned}$$

Using the commutation relation, $[\mathbf{r}, H] = \frac{i\hbar}{m}\mathbf{p}$, we can write the following identity:

$$\frac{< b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a >}{(E_b - E_a)} = \mathrm{i}\frac{m}{\hbar} < b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a >$$

Plugging in this identity and using the closure relation of the states $|b\rangle$, we obtain,

$$\begin{aligned} T'_{fi} &= -\mathrm{i}\frac{1}{m}\frac{q^2}{2\varepsilon_0 L^3}\frac{1}{\omega}\sum_b \left[\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle - \langle a|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle\right] \\ &= -\mathrm{i}\frac{1}{m}\frac{q^2}{2\varepsilon_0 L^3}\frac{1}{\omega}\langle a|[\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}', \mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}']|a\rangle \\ &= \frac{q^2\hbar}{2\varepsilon_0 L^3}\frac{1}{\omega}\frac{1}{m}\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}' \end{aligned}$$

The Coulomb-gauge Hamiltonian

For the Coulomb-gauge Hamiltonian $H_I = -\frac{q}{m}\mathbf{p}\cdot\mathbf{A}(\mathbf{0}) + \frac{q^2}{2m}\mathbf{A}^2(\mathbf{0})$

Again we use the Born expansion, but this time the first order term is non-vanishing, because $\mathbf{A^2}(\mathbf{0})$ can couple $|i\rangle$ and $|f\rangle$ directly. There are two kind of terms, one corresponding to $\langle f|\boldsymbol{A}^2(0)|i\rangle$ and the other to $\langle f|\mathbf{p}\cdot\mathbf{A(0)}|i\rangle$. The relevant matrix elements are given by:

$$\langle b;0|H_I|a;\mathbf{k}\hat{\boldsymbol{\varepsilon}}\rangle = \frac{\mathcal{E}_\omega}{\omega}\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle$$
$$\langle b;\mathbf{k}\hat{\boldsymbol{\varepsilon}},\mathbf{k}'\hat{\boldsymbol{\varepsilon}}'|H_I|a;\mathbf{k}\hat{\boldsymbol{\varepsilon}}\rangle = \frac{\mathcal{E}_\omega}{\omega}\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle$$

The contribution due to the first and second terms are thus,

$$\mathcal{T}_{fi}(1) = \frac{q^2\hbar}{2\varepsilon_0 L^3}\frac{1}{\sqrt{\omega\omega'}}\frac{1}{m}\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}'$$

$$\mathcal{T}_{fi}(2) = \frac{q^2\hbar}{2\varepsilon_0 L^3}\frac{1}{\sqrt{\omega\omega'}}\frac{1}{m^2}\sum_b\left[\frac{\langle a|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle}{\hbar(\omega-\omega_{ba})} - \frac{\langle a|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle}{\hbar(\omega'+\omega_{ba})}\right]$$

(i) **Rayleigh scattering**

For Rayleigh scattering and assuming $\omega = \omega'$, we expand $\mathcal{T}_{fi}$ in powers of $x \equiv \frac{\hbar\omega}{E_b - E_a}$.

$$\mathcal{T}_{fi}(2) = -\frac{q^2}{m^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\sum_b\left(\frac{\langle a|\mathbf{p}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{p}\cdot\boldsymbol{\epsilon}|a\rangle}{E_b-E_a}(1-x)^{-1} + \frac{\langle a|\mathbf{p}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{p}\cdot\epsilon'|a\rangle}{E_b-E_a}(1+x)^{-1}\right)$$

Expanding $\mathcal{T}_{fi}$ up to second order, we obtain:

$$\mathcal{T}_{fi}(2) = -\frac{q^2}{m^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\frac{m}{i\hbar}\sum_b\left(\langle a|\mathbf{p}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{r}\cdot\boldsymbol{\epsilon}|a\rangle(1-x)^{-1} - \langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{p}\cdot\epsilon'|a\rangle(1+x)^{-1}\right)$$

$$= -\mathrm{i}\frac{q^2}{m\hbar}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\langle a|[\boldsymbol{p}\cdot\epsilon', \boldsymbol{r}\cdot\epsilon]|a\rangle - \mathrm{i}\frac{q^2}{m\hbar}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\cdot(\hbar\omega)\sum_b\left(\frac{\langle a|\mathbf{p}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{r}\cdot\boldsymbol{\epsilon}|a\rangle}{E_b-E_a} + \frac{\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{p}\cdot\epsilon'|a\rangle}{E_b-E_a}\right)$$

$$-\mathrm{i}\frac{q^2}{m\hbar}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}(\hbar\omega)^2\sum_b\left(\frac{\langle a|\mathbf{p}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{r}\cdot\boldsymbol{\epsilon}|a\rangle}{(E_b-E_a)^2} - \frac{\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{p}\cdot\epsilon'|a\rangle}{(E_b-E_a)^2}\right) + O(x^3)$$

Using the same identity on $\frac{<b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a>}{(E_b-E_a)}$ and using the canonical commutation relation, we get

$$\mathcal{T}_{fi}(2) = -\frac{q^2}{m}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\boldsymbol{\epsilon}\cdot\epsilon'$$

$$-\frac{q^2}{\hbar^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\cdot(\hbar\omega)\sum_b\left(\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{r}\cdot\boldsymbol{\epsilon}|a\rangle-\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{r}\cdot\epsilon'|a\rangle\right)$$

$$-\frac{q^2}{\hbar^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\cdot(\hbar\omega)^2\sum_b\left(\frac{\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}'|b\rangle\langle b|\mathbf{r}\cdot\boldsymbol{\epsilon}|a\rangle+\langle a|\mathbf{r}\cdot\boldsymbol{\epsilon}|b\rangle\langle b|\mathbf{r}\cdot\epsilon'|a\rangle}{E_b-E_a}\right)+O(x^3)$$

The first term cancels the contribution from $\mathcal{T}_{fi}(1)$, the middle term is zero; therefore, we are left with

$$\mathcal{T}_{fi}=\frac{q^2\hbar}{2\varepsilon_0 L^3}\omega\sum_b\left[\frac{\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle+\langle a|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle}{\hbar\omega_{ab}}\right]+O(x^3)$$

which is the same as the one we found with the dipole Hamiltonian.

(ii) **Thomson scattering**

For Thomson scattering $\hbar\omega >> E_b - E_a$, we can ignore $E_b - E_a$ compared to $\hbar\omega$. One can expand $\mathcal{T}_{fi}^2$ in powers of $x \equiv \frac{E_b-E_a}{\hbar\omega}$, as has been done before for the dipole interaction. We find that the zeroth order term vanishes:

$$\mathcal{T}_{fi}(2)\approx-\frac{q^2}{m^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\sum_b\left(\langle a|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}'|b\rangle\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|a\rangle+\langle a|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}|b\rangle\langle b|\mathbf{p}\cdot\hat{\boldsymbol{\varepsilon}}'|a\rangle\right)\frac{(E_b-E_a)}{(\hbar\omega)^2}$$

By replacing $(E_b - E_a)$ by E_I in the numerator and by then using the closure relation over b we obtain

$$\mathcal{T}_{fi}(2)\approx-\frac{q^2}{m^2}\frac{\hbar}{2\epsilon_0 L^3}\frac{1}{\omega}\frac{E_I}{\hbar\omega}\frac{\langle a|(p^2/m)|a\rangle}{\hbar\omega}$$

Now, twice the average kinetic energy is the same order of magnitude as E_I. Thus, we prove that

$$\mathcal{T}_{fi}(2)\sim\mathcal{T}_{fi}(1)\left(\frac{E_I}{\hbar\omega}\right)^2$$

$\mathcal{T}_{fi}(1)$ is thus larger than $\mathcal{T}_{fi}(2)$ and we obtain the same result as with the dipole Hamiltonian upon substitution of $< b|\mathbf{r}\cdot\hat{\boldsymbol{\varepsilon}}|a >$ and using the commutation relation, namely

$$\mathcal{T}_{fi}=\frac{q^2\hbar}{2\varepsilon_0 L^3}\frac{1}{\omega}\frac{1}{m}\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}'$$

One can also show from general arguments that the transition amplitudes calculated from both Hamiltonians are exactly the same (see Photon and Atoms by C.Cohen-Tannoudji)

(b) Thomson scattering cross section calculations (2 points)
The transition probability per unit time and per unit solid angle is

$$\begin{aligned}\frac{\delta w_{fi}}{\delta \mathbf{\Omega'}} &= \frac{2\pi}{\hbar}(\frac{q^2}{2m}\frac{\hbar}{\varepsilon_0 L^3\omega})^2(\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}')^2\frac{L^3}{8\pi^3}\frac{(\hbar ck)^2}{\hbar^3c^3} \\ &= \frac{e^4}{m^2c^3L^3}(\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}')^2\end{aligned}$$

where $e^2 = \frac{q^2}{4\pi\varepsilon_0}$. If we divide by the photon flux, which is equal to c/L^3, the differential cross section is

$$\frac{d\sigma}{d\mathbf{\Omega'}} = r_0^2(\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}')^2$$

To find the total cross section, sum $(\hat{\boldsymbol{\varepsilon}}\cdot\hat{\boldsymbol{\varepsilon}}')^2$ over the two polarizations orthogonal to $\mathbf{k}'$ and to make the angular average.
Thus the total cross section for Thomson scattering is $\frac{8\pi}{3}r_0^2$, where r_0 is the classical electron radius.

2. **Long-range (Van der Waals) interaction between ground-state atoms**

(a) (2 Points) What is the first non-vanishing term in the series for the perturbed ground state energy of the system?
Solution: Using standard perturbation theory, the series for the perturbed ground state energy of the system is

$$\Delta E_{gg} = V_{gg} + \sum_{i\neq g}\frac{|V_{ig}|^2}{E_g^0 - E_i^0} + \text{higher-order terms}$$

Take the z-axis to be along the internuclear separation vector $\vec{R}$. The perturbation Hamiltonian becomes

$$H_{E1} = e^2\frac{(x_a x_b + y_a y_b - 2z_a z_b)}{R^3}$$

and

$$\begin{aligned}\Delta E_g \;=\; & e^2\frac{\langle g_a g_b|x_a x_b + y_a y_b - 2z_a z_b|g_a g_b\rangle}{R^3} + e^4\sum_{i_a i_b}\frac{|\langle i_a i_b|\frac{x_a x_b + y_a y_b - 2z_a z_b}{R^3}|g_a g_b\rangle|^2}{(E_g^a + E_g^b) - (E_i^a + E_i^b)} \\ & + \text{higher-order terms}\end{aligned}$$

The first-order term in this perturbation series vanishes regardless of the parity of the ground state because H_{E1} is an odd-parity operator [1].
Thus, the first non-vanishing term in the perturbation series is the second-order term which varies like $\frac{1}{R^6}$.

(b) (5 Points) Express the result from (a) in terms of oscillator strengths.
Solution: We need to evaluate the second-order term:

$$\begin{aligned}\Delta E_{g_a g_b} &= \sum_{n_a,l_a,n_b,l_b} \sum_{m_a,m_b} e^4 \frac{|\langle i_a i_b| \frac{x_a x_b + y_a y_b - 2 z_a z_b}{R^3} |g_a g_b\rangle|^2}{(E_g^a + E_g^b) - (E_i^a + E_i^b)} \\ &= e^4 \sum_{n_a,l_a,n_b,l_b} \frac{\frac{1}{R^6}\left[\sum_{m_a m_b} |\langle i_a i_b| x_a x_b + y_a y_b - 2 z_a z_b |g_a g_b\rangle|^2\right]}{(E_g^a + E_g^b) - (E_i^a + E_i^b)}\end{aligned}$$

Notice that the sum over the upper states has been explicitly separated into sums over quantum numbers n and l and sums over the orientational quantum number m.
Next the sum over the upper state orientational quantum numbers m_a and m_b is calculated

$$\begin{aligned}\sum_{m_a m_b} |\langle i_a i_b| x_a x_b + y_a y_b - 2 z_a z_b |g_a g_b\rangle|^2 &= \sum_{m_a m_b} S_a^{11} S_b^{11} + S_a^{12} S_b^{12} - 2 S_a^{13} S_b^{13} + \\ S_a^{21} S_b^{21} + S_a^{22} S_b^{22} - 2 S_a^{23} S_b^{23} &- 2 S_a^{31} S_b^{31} - 2 S_a^{32} S_b^{32} + 4 S_a^{33} S_b^{33}\end{aligned}$$

To save space above, I have used some shorthand notation:

$$S_a^{ij} \equiv \langle n_a, l_a, m_a | x_a^i | g_a \rangle \langle g_a | x_a^j | n_a, l_a, m_a \rangle$$

$$S_b^{ij} \equiv \langle n_b, l_b, m_b | x_b^i | g_b \rangle \langle g_b | x_b^j | n_b, l_b, m_b \rangle$$

Where $(x^1, x^2, x^3) = (x, y, z)$. For simple cases (such as the hydrogen atom), we expect that the "off-diagonal" terms in the above sum will "average" to zero and that $S^{ij} = S^{ij}\delta_{ij}$. We can simplify the above sum to be

$$\begin{aligned}\sum_{m_a m_b} |\langle i_a i_b| x_a x_b + y_a y_b - 2 z_a z_b |g_a g_b\rangle|^2 = \sum_{m_a m_b} S_a^{11} S_b^{11} + 0 - 0 + 0 + \\ S_a^{22} S_b^{22} - 0 - 0 - 0 + 4 S_a^{33} S_b^{33}\end{aligned}$$

Let us calculate this explicitly for the case of upper states $|i\rangle$ which have $l = 1$ (i.e. $|P\rangle$ states) and lower states $|g\rangle$ which have $l = 0$ (i.e. $|S\rangle$ states). To do so we express the dipole operator and the angular dependences of the $|P\rangle$ and $|S\rangle$ states in terms of spherical harmonics

$$\begin{aligned} x &= r\sqrt{\frac{4\pi}{3}} \frac{1}{\sqrt{2}} \left(Y_1^{-1} - Y_1^1\right) \\ y &= r\sqrt{\frac{4\pi}{3}} \frac{i}{\sqrt{2}} \left(Y_1^{-1} + Y_1^1\right) \\ z &= r\sqrt{\frac{4\pi}{3}} Y_1^0 \end{aligned}$$

Two facts:

i. The angular dependence of a state $|l, m\rangle$ is given by Y_l^m.

ii. The orthogonality condition for spherical harmonics, $\int \left(Y_{l_1}^{m_1}\right)^* Y_{l_2}^{m_2} \ \mathrm{d}\Omega = \delta_{l_1 l_2}\delta_{m_1 m_2}$.

Using these facts we obtain the following results for our matrix elements (Of course, the calculation is made simpler by the fact that $|S\rangle$ states have no angular dependence because $Y_0^0 = \frac{1}{\sqrt{4\pi}}$. Another way: I chose the $|S\rangle$ states for a reason!)

$$\langle l=1,m=+1|x|l=0,m=0\rangle = \frac{-\langle r\rangle}{\sqrt{6}} \qquad \langle l=1,m=+1|y|l=0,m=0\rangle = \frac{i\langle r\rangle}{\sqrt{6}}$$
$$\langle l=1,m=0|x|l=0,m=0\rangle = 0 \qquad \langle l=1,m=0|y|l=0,m=0\rangle = 0$$
$$\langle l=1,m=-1|x|l=0,m=0\rangle = \frac{\langle r\rangle}{\sqrt{6}} \qquad \langle l=1,m=-1|y|l=0,m=0\rangle = \frac{i\langle r\rangle}{\sqrt{6}}$$
$$\langle l=1,m=+1|z|l=0,m=0\rangle = 0$$
$$\langle l=1,m=0|z|l=0,m=0\rangle = \frac{\langle r\rangle}{\sqrt{3}}$$
$$\langle l=1,m=-1|z|l=0,m=0\rangle = 0$$

Our sum over orientations becomes

$$\sum_{m_a m_b} |\langle i_a i_b|x_a x_b + y_a y_b - 2z_a z_b|g_a g_b\rangle|^2 = \left(\frac{\langle r_a\rangle^2}{3}\right)\left(\frac{\langle r_b\rangle^2}{3}\right) + \left(\frac{\langle r_a\rangle^2}{3}\right)\left(\frac{\langle r_b\rangle^2}{3}\right) + 4\left(\frac{\langle r_a\rangle^2}{3}\right)\left(\frac{\langle r_b\rangle^2}{3}\right) = 6\left(\frac{\langle r_a\rangle^2}{3}\right)\left(\frac{\langle r_b\rangle^2}{3}\right)$$

There are several other ways to verify this result: (1) by writing the Hamiltonian in terms of $Y_{1(a,b)}^m$, to find that only terms $Y_{1(a)}^m Y_{1(b)}^{m'}$ satisfying the conservation of angular momentum $m = -m'$ remain or (2) by choosing the orthogonal p_x, p_y, p_z basis for $l = 1$ where selection rules for x, y, z are simpler.

Thus we have the result

$$\boxed{\Delta E_{g_a g_b} = -\frac{e^4}{R^6} \sum_{n_a, l_a, n_b, l_b} \frac{6\left(\frac{\langle r_a\rangle^2}{3}\frac{\langle r_b\rangle^2}{3}\right)}{(E_i^a - E_g^a) + (E_i^b - E_g^b)}}$$

Now we introduce oscillator strengths: $f_{ig} \equiv \frac{2m_e\omega_{ig}}{\hbar}|\langle m_i|x|m_g\rangle|^2$. Note that the mass, m_e, is the electron mass. After all, it is the oscillator.

The choice of x,y, or z in our definition of oscillator strength represents an artificial choice of axis; we should obtain the same f_{ig} if we sum over upper m states and average over lower m states.

Using the dipole operator matrix elements derived above for $|P\rangle \to |S\rangle$ transitions, we obtain (In this case there is no need to average over lower m states because there is only one.)

$$\sum_{m_i} |\langle m_i|x|m_g\rangle|^2 = \sum_{m_i} |\langle m_i|y|m_g\rangle|^2 = \sum_{m_i} |\langle m_i|z|m_g\rangle|^2 = \frac{\langle r\rangle^2}{3}$$

Therefore,

$$f_{ig} \equiv \frac{2m_e\omega_{ig}}{\hbar}\frac{\langle r\rangle^2}{3} \Rightarrow \frac{\langle r\rangle^2}{3} = \frac{\hbar}{2m_e}\frac{f_{ig}}{\omega_{ig}}$$

Finally,

$$\begin{aligned}\Delta E_{g_a g_b} &= -\frac{3}{2}\frac{e^4}{R^6}\frac{\hbar^2}{m_e^2}\sum_{n_a,l_a,n_b,l_b}\frac{\frac{f^a_{ig}}{\omega^a_{ig}}\frac{f^b_{ig}}{\omega^b_{ig}}}{(E^a_i - E^a_g)+(E^b_i - E^b_g)} \\ &= -\frac{C_6}{R^6}\end{aligned}$$

where

$$\boxed{C_6 = \frac{3e^4\hbar}{2m_e^2}\sum_{n_a,l_a,n_b,l_b}\frac{f^a_{ig}f^b_{ig}}{\omega^a_{ig}\omega^b_{ig}(\omega^a_{ig}+\omega^b_{ig})}}$$

(c) (3 Points) Express your result for C_6 from (b) in terms of polarizabilities $\alpha_g^{(a)}$ and $\alpha_g^{(b)}$. We will make the dominant-level approximation: assume $f^a_{ig} \approx 1$, $f^b_{ig} \approx 1$ for only one transition and drop the sums over excited states.

$$\Delta E_{g_a g_b} = -\frac{3e^4\hbar}{2m_e^2}\frac{1}{R^6}\frac{1}{\omega^a_{ig}\omega^b_{ig}(\omega^a_{ig}+\omega^b_{ig})}$$

Recall that the static polarizability of the ground state is defined by

$$\alpha_g \equiv 2e^2\sum_i \frac{|\langle i|z|g\rangle|^2}{E_i - E_g} = \frac{e^2}{m_e}\sum_i \frac{f_{ig}}{\omega^2_{ig}}$$

Using the dominant level approximation $\Rightarrow \alpha_g \approx \frac{e^2}{m_e\omega^2_{ig}}$ or $\frac{1}{\omega_{ig}} \approx \frac{m_e w_{ig}\alpha_g}{e^2}$. As a result we obtain

$$\boxed{C_6 = \frac{3}{2}\frac{\alpha^a_g\alpha^b_g E^a_{ig}E^b_{ig}}{E^a_{ig}+E^b_{ig}} = \frac{3}{2}\hbar\frac{\alpha^a_g\alpha^b_g\omega^a_{ig}\omega^b_{ig}}{\omega^a_{ig}+\omega^b_{ig}}}$$

Note that this result has the correct units of [Energy] $\times$ [Length]^6 because polarizability has units of [Volume]= [Length]^3.

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[1] There is an exception: if both "atoms" possess space-fixed electric dipole or permanent electric quadrupole moments. This can occur if the atoms are in a strong external field, if the "atoms" are a special type of polyatomic molecule, or if the atoms are in $l \geq 1$ ground states.