Homework #8 solutions

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1. **Long-range interaction between an excited atom and a ground-state atom**

(a) Distinguishable atoms

i. How does the energy of the state $|i_a g_b\rangle$ change as a function of the separation R for large distances? What about state $|g_a i_b\rangle$?

Solution: With the restriction that each atom is a two-level system we can solve this problem exactly. In keeping with convention we will denote the excited state of the two-level atom by $|e\rangle$ instead of the more general excited state notation $|i\rangle$ used in the previous problem set.
Choosing our basis set to be $|e_a g_b\rangle$ and $|g_a e_b\rangle$, the Hamiltonian is

$$H = \begin{bmatrix} E_e^a + E_g^b & V_1 \\ V_1^* & E_g^a + E_e^b \end{bmatrix}$$

where V_1 is the matrix element of H_{E1}.
We can change the zero of the energy scale by subtracting $E_g^a + E_g^b$ from the diagonal elements. We can do this without affecting the off-diagonal elements. The result is

$$H = \begin{bmatrix} \Delta E^a & V_1 \\ V_1^* & \Delta E^b \end{bmatrix}$$

It is now straightforward to solve for the eigenenergies of E in the presence of the perturbation V_1.

$$\begin{aligned} \det(H - E\mathbf{I}) &= \begin{vmatrix} \Delta E^a - E & V_1 \\ V_1^* & \Delta E^b - E \end{vmatrix} \\ &= E^2 - (\Delta E^a + \Delta E^b)E + (\Delta E^a \Delta E^b - V_1 V_1^*) \\ &= 0 \end{aligned}$$

Finding the roots of this equation gives

$$\begin{aligned} E^\pm &= \frac{1}{2}(\Delta E^a + \Delta E^b) \pm \frac{1}{2}\sqrt{(\Delta E^a + \Delta E^b)^2 - 4((\Delta E^a \Delta E^b) - V_1 V_1^*)} \\ &= \frac{1}{2}(\Delta E^a + \Delta E^b) \pm \frac{1}{2}\sqrt{(\Delta E^a - \Delta E^b)^2 + 4V_1 V_1^*} \\ E^\pm &= \overline{\Delta E} \pm \frac{1}{2}\sqrt{\delta E^2 + 4V_1 V_1^*} \end{aligned}$$

where $\overline{\Delta E} \equiv \frac{1}{2}(\Delta E^a + \Delta E^b)$ and $\delta E \equiv \Delta E^a - \Delta E^b$.

At large distances, $\delta E \gg V_1 V_1^*$ so we can approximate the square root.

$$E^\pm = \overline{\Delta E} \pm \delta E \pm (V_1 V_1^*)/\delta E$$

or

$$\boxed{\begin{aligned} E^+ &= \Delta E^a + V_1 V_1^*/\delta E \\ E^- &= \Delta E^b - V_1 V_1^*/\delta E \end{aligned}}$$

Under this approximation, the correction term $V_1 V_1^*/\delta E$ is similar to the 2nd order perturbation term for two ground state atoms, C_6/R^6, as found in the last problem. The difference is in the energy denominator, where for two ground state atoms the energy difference between the ground state of the system (both atoms in the ground state) and the first admixed excited state (both atoms in the excited state) is $(E_e^a + E_e^b) - (E_g^a + E_g^b) = \Delta E^a + \Delta E^b = 2\overline{\Delta E}$. In the subspace of two non-degenerate atoms with one excitation in the system, the energy difference between the ground state of the system (lower-transition-energy atom excited) and the admixed excited state (higher-transition-energy atom excited) is $\Delta E^a - \Delta E^b = \delta E$. So in this regime of large distances,

$$V_1 V_1^*/\delta E = \frac{C_6}{R^6} \frac{2\overline{\Delta E}}{\delta E}$$

Due to the sign of δE, the energies of the states will be pushed apart, so the lower energy state will lose energy and the higher energy state will gain energy.

ii. For what separation does perturbation theory become invalid?

Solution: Perturbation theory (or the above approximation) will become invalid when the atoms are close enough that the perturbation term H_{E1} is a significant part of the total Hamiltonian. Specifically, perturbation theory will break down when $V_1 V_1^*/\delta E \approx \delta E$. From this we can derive an approximate expression for the inter-nuclear separation at which perturbation theory will fail.

Using the results of HW5, we have

$$\frac{C_6}{R^6} = \frac{\frac{3}{2}\alpha_g^a \alpha_g^b E_{ig}^a E_{ig}^b}{(E_{ig}^a + E_{ig}^b)}$$

If the two atoms are nearly degenerate with transition energies E, then perturbation theory breaks down when

$$R^6 = C_6 \frac{2\overline{\Delta E}}{\delta E^2} \approx \frac{3}{2}\alpha_g^2 \frac{E^2}{\delta E^2}, \text{ or } R < \left(\frac{3}{2}\right)^{\frac{1}{6}} (\alpha_g)^{\frac{1}{3}} \left(\frac{E}{\delta E}\right)^{\frac{1}{3}}$$

Since $(\alpha_g)^{\frac{1}{3}}$ has units of length, this result is reasonable. Also we see that when $\delta E = 0$ ordinary non-degenerate perturbation theory is invalid at all distances, and we have to diagonalize the total Hamiltonian exactly.

(b) (20 Points) Indistinguishable atoms – Calculate the long-range interaction potential curves for the case of one excited atom and one ground state atom.

Solution: In this case the atoms are identical, i.e. $E_g^a = E_g^b$, $E_i^a = E_i^b \Rightarrow \Delta E^a = \Delta E^b = \overline{\Delta E} \equiv \Delta E$, and $\delta E = 0$. We must now diagonalize the matrix

$$H = \begin{bmatrix} 0 & V_1 \\ V_1^* & 0 \end{bmatrix}$$

We will get the standard result that the eigenvectors are not the original basis states $|e_a g_b\rangle$ and $|g_a e_b\rangle$ but symmetric and anti-symmetric combinations thereof

$$\Psi_S = \frac{1}{\sqrt{2}}\left(|e_a g_b\rangle + |g_a e_b\rangle\right)$$

$$\Psi_A = \frac{1}{\sqrt{2}}\left(|e_a g_b\rangle - |g_a e_b\rangle\right)$$

This result is sensible because we cannot distinguish between atoms a and b so labeling them as such is not physically meaningful.

The eigenvalues of our Hamiltonian are simply $E^{\substack{S \\ A}} = \langle \Psi_{\substack{S \\ A}} | H_{E1} | \Psi_{\substack{S \\ A}} \rangle$.

Evaluating $E^{\substack{S \\ A}} = \langle \Psi_{\substack{S \\ A}} | H_{E1} | \Psi_{\substack{S \\ A}} \rangle$,

$$
\begin{aligned}
E^{\substack{S \\ A}} &= \frac{1}{2}\left(\langle e_a g_b| \pm \langle g_a e_b|\right) H_{E1} \left(|e_a g_b\rangle \pm |g_a e_b\rangle\right) \\
&= \frac{1}{2}\left(\langle e_a g_b|H_{E1}|e_a g_b\rangle\right) \pm \left(\langle e_a g_b|H_{E1}|g_a e_b\rangle\right) \pm \left(\langle g_a e_b|H_{E1}|e_a g_b\rangle\right) + \left(\langle g_a e_b|H_{E1}|g_a e_b\rangle\right) \\
&= \frac{1}{2}\left(0 \pm \langle e_a g_b|H_{E1}|g_a e_b\rangle \pm \langle g_a e_b|H_{E1}|e_a g_b\rangle + 0\right) \\
&= \pm\frac{1}{2}\left(\langle e_a g_b|H_{E1}|g_a e_b\rangle + \langle g_a e_b|H_{E1}|e_a g_b\rangle\right)
\end{aligned}
$$

Since atoms a and b are indistinguishable, we get

$$
\begin{aligned}
E^{\substack{S \\ A}} &= \pm\frac{e^2}{2R^3}\left(\langle eg|x_a x_b + y_a y_b - 2z_a z_b|ge\rangle + \langle ge|x_a x_b + y_a y_b - 2z_a z_b|eg\rangle\right) \\
&= \pm\frac{e^2}{2R^3}\left(\langle e|x|g\rangle\langle g|x|e\rangle + \langle e|y|g\rangle\langle g|y|e\rangle - 2\langle e|z|g\rangle\langle g|z|e\rangle \right. \\
&\quad \left. + \langle g|x|e\rangle\langle e|x|g\rangle + \langle g|y|e\rangle\langle e|y|g\rangle - 2\langle g|z|e\rangle\langle e|z|g\rangle\right) \\
E^{\substack{S \\ A}} &= \pm\frac{e^2}{R^3}\left(|\langle e|x|g\rangle|^2 + |\langle e|y|g\rangle|^2 - 2|\langle e|z|g\rangle|^2\right)
\end{aligned}
$$

Next we must consider angular momentum. When two atoms come together to form a Van der Waals (or long-range) "molecule," we have two possibilities for the total "molecular" angular momentum. That is, we need to consider the projection of the excited level's angular momentum along the z-axis of the molecule. If this is ± 1, corresponding to a Π molecular state, then there will be contributions from the x and y terms. On the other hand, a Σ state will contain z terms with zero projection of angular momentum[1]. Note that in the following table the same shorthand used in HW5 is employed, with $\langle x\rangle$ taken to mean $\langle e|x|g\rangle$.

Σ states $(L=0)$	Π states $(L=1)$
$\begin{aligned}\lvert\langle x\rangle\rvert^2 &= 0 \\ \lvert\langle y\rangle\rvert^2 &= 0 \\ \lvert\langle z\rangle\rvert^2 &= \frac{\langle r\rangle^2}{3}\end{aligned}$	$\begin{aligned}\lvert\langle x\rangle\rvert^2 &= \frac{\langle r\rangle^2}{6} \\ \lvert\langle y\rangle\rvert^2 &= \frac{\langle r\rangle^2}{6} \\ \lvert\langle z\rangle\rvert^2 &= 0\end{aligned}$
$E_A^S = \frac{\mp 2e^2\langle r\rangle^2}{3R^3}$	$E_A^S = \frac{\pm e^2\langle r\rangle^2}{3R^3}$

Hence we have the results:

$$\boxed{E_A^S = \mp\frac{C_3^\Sigma}{R^3} \text{ for } \Sigma \text{ states}}$$

$$\boxed{E_A^S = \pm\frac{C_3^\Pi}{R^3} \text{ for } \Pi \text{ states}}$$

where $C_3^\Sigma = \frac{2e^2\langle r\rangle^2}{3}$ and $C_3^\Pi = \frac{1}{2}C_3^\Sigma$.

Note that in the regime where the separation of the two atoms is smaller than the optical wavelength associated with the atomic transition energy, $R \ll \lambda$, the two components of the symmetric state couple to the continuum of electromagnetic modes with the same phases and so the symmetric state decays twice as fast as a single atom. The two components of the antisymmetric state, however, couple to the continuum of modes with the opposite phases and so the antisymmetric state DOES NOT DECAY. This breaks down for separations of atoms larger than the optical wavelength, at which point both the symmetric and the antisymmetric states decay with the same rate as a single excited atom.

(c) (10 Points) For the case of indistinguishable atoms what is the relation between the spontaneous decay rate of the atom and its long-range interaction coefficient?

Solution: Using Fermi's golden rule we can derive the spontaneous decay rate for a single excited atom: $\Gamma = \frac{4e^2\omega^3}{3\hbar c^3}\lvert\langle e\rvert r\rvert g\rangle\rvert^2$.
Hence

$$\boxed{C_3^\Sigma = \frac{\hbar\Gamma}{2k^3}}$$

Again, only the symmetric states (of Σ and Π) can actually radiate via dipole processes in the limit $R \ll \lambda$.

2. Casimir model of the electron

The Casimir "vacuum pressure" pulling together plates infinite in extent and separated by a distance a is $\frac{\pi^2 \hbar c}{240 a^4}$. Therefore square plates of area $a \times a$ separated by a distance a experience an attractive force

$$F_{Cas} = \frac{\pi^2 \hbar c}{240 a^2} \tag{1}$$

We know that this is a crude estimate because it is correct only for plates of infinite size.

We can estimate the repulsive force between the plates using Gauss' law. The charge density on each plate is $\sigma = \frac{e}{2} \frac{1}{a^2}$. Applying Gauss' law and ignoring fringing fields[2]

$$\int E \cdot dS = E\left(2a^2\right) = 4\pi q_{in} = 4\pi \frac{e}{2} \tag{2}$$

Thus $E = \frac{\pi e}{a^2}$, and the electrostatic repulsion force is

$$F_{el} = \frac{e}{2} E = \frac{\pi e^2}{2a^2} \tag{3}$$

Equating forces

$$F_{Cas} = F_{el} \Rightarrow \frac{\pi^2 \hbar c}{240 a^2} = \frac{\pi e^2}{2a^2} \tag{4}$$

yields a value for the fine-structure constant

$$\alpha \equiv \frac{e^2}{\hbar c} = \frac{\pi}{120} \approx \frac{1}{38} \tag{5}$$

The actual value of α is approximately $\frac{1}{137}$ so the Casimir model is not very accurate. Nevertheless, it is surprising that such a crude model comes as close as it does.

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[1] Note that this treatment assumes that L and S are good quantum numbers individually, i.e. when spin-orbit coupling effects are small ($H_{E1} \gg H_{LS}$). If $H_{LS} > H_{E1}$, L and S are no longer good quantum numbers, and one must designate states by the quantum numbers J and M_J ($\mathbf{J} = \mathbf{L} + \mathbf{S}, M_J = J_z$).

[2] One can also argue that since the plates carry the same charge there is no electric field between the two plates. This introduces a factor of 2 which shows up in the end as $\alpha = \frac{\pi}{240}$. Either is acceptable.