M01Q.2

Solution

Part (a)

The distance r between the atoms is large compared to the atomic size which means the electron wavefunction overlap is negligible. So the interaction between the two is the electrostatic interaction. But since the atoms are neutral, the main contribution to this interaction comes from higher order terms such as dipole-dipole, dipole-quadrupole etc. amongst which dipole-dipole term is the most dominant one.

The dipole-dipole interaction potential is

$$W_{dd} = \frac{e^2}{4\pi\epsilon_0 R^3}[\overrightarrow{r_A}.\overrightarrow{r_B} - 3(\overrightarrow{r_A}.\vec{n})(\overrightarrow{r_B}.\vec{n})] \tag{1}$$

Choosing the $\hat{n}$ along z axis, the interaction term can be written as:

$$W_{dd} = \frac{e^2}{4\pi\epsilon_0 R^3}[X_A X_B + Y_A Y_B - 2Z_A Z_B] \tag{2}$$

As the overlap of wavefunctions is almost zero, we can treat this interaction as perturbation potential. Ground state energy of the pair in the absence of perturbation would $-2E_0$ where $E_0 = 13.6eV$ where both the electrons are in $1s$ state.

The first order correction is

$$E_0^{(1)} = \langle 1s_A, 1s_B | W_{dd} | 1s_A, 1s_B \rangle \tag{3}$$

Since the expectation value of the position operators $X_A, X_B, Y_A, \ldots$ is zero the first order correction is also zero. By the triangle rule of Clebsch-Gordon, higher order terms are also zero as both the states are $l = 0$ states. So for gorund state, we will consider the second order effefct.

$$E_0^{(2)} = \sum_{nlm_A, n'l'm'_B} \frac{|\langle nlm_A, n'l'm'_B | W_{dd} | 1s_A, 1s_B \rangle|^2}{-2E_0 - E_n - E_{n'}} \tag{4}$$

Since W_{dd} is proportional to $1/R^3$, $E_0^{(2)}$ is proportional to $1/R^6$. Also it can be seen that the denominator is negative for all n, n'. Hence we can approximate this second order term as $-A_0/R^6$. There fore ground state energy of the pair is given by

$$E_0 = C_0 + A_0 r^{-\delta_0} \tag{5}$$

where $\delta_0 = 6$.

Part (b)

We have already mentioned why A_0 in general should be negative as all the terms in the denominator are negative. In fact second order pertubation term will always be negative when the zeroth order state is the ground state.

To get an order of mangnitude estimate, we can see the matrix element decreases with increasing n and the denominator increases so overall the terms decrease in magnitude as n becomes larger.

$$A_0 = \sum_{nlm_A, n'l'm'_B} \frac{|\langle nlm_A, n'l'm'_B | W_{dd} | 1s_A, 1s_B \rangle|^2}{2E_0 + E_n + E_{n'}} \tag{6}$$

Now using the closure approximation we can use following formula i.e. approximating the denominator as the same for all n by choosing $n \to \infty$ value $2E_o$, the numerator can be written as $1 - |0\rangle\langle 0|$. After some simple calculations we get,

$$A_0 \simeq \frac{e^4}{4\pi\epsilon_0 \times 2E_0} \langle 1s_A, 1s_B | \left(X_A X_B + Y_A Y_B - 2Z_A Z_B\right)^2 | 1s_A, 1s_B \rangle \tag{7}$$

This is simple to calculate as the cross terms like $X_A Y_A, X_B Z_B$ are zero because of the spherical symmetry of the $1s$ states. So only nonzero terms are expectations of $X_A^2 X_B^2$ and similar terms. This leads to

$$A_0 = \frac{e^4}{4\pi\epsilon_0 \times 2E_0} \times 6 |\langle 1s_A, 1s_B | \frac{R_A^2 R_B^2}{9} | 1s_A, 1s_B \rangle| \tag{8}$$

Using CGS units, $E_0 = e^2/2a_0$ and $\langle R^2 \rangle = 3a_0^2$, the above expression reduces to $A_0 = 6e^2 a_0^5$.

Part(c)

The first exccited level of the unperturbed Hamiltonian is a state in which one of the atoms is in the ground state $n = 1$ and the other one is in first excited state $n = 2$ which is four-fold. Thus the excited state has a degeneracy of 8. And in this degenerate space we will have matrix element of W_{dd} which will be nonzero for some of the tranistions.

We can see that the only non-zero matrix elements are those which connect a state $|(1,0,0)_A;(2,1,m)_B\rangle$ to a state $|(2,1,m)_B;(1,0,0)_A\rangle$. The operators X_A, Y_A, Z_A can be written in terms polar operators $A^1_m, m = -1, 0, 1$ which means they can couple $|(1,0,0)_A\rangle$ to $|(2,1,m)\rangle$. Similar argument follows for B operators.

Note that the W_{dd} interaction is symmetric about z axis. So it commutes with $L_z = L^A_z + L^B_z$ so sum of the ms on both the sides should be the same.
Thus 8×8 degenerate subspace can be broken down to 2×2 matrices. One of them is totally zero $1s - 2s$ transition. The remaining three look like :

$$\begin{pmatrix} 0 & \frac{k_m}{R^3} \\ \frac{k_m}{R^3} & 0 \end{pmatrix} \tag{9}$$

where

$$\langle (1,0,0)_A;(2,1,m)_B|W_{dd}\,|(2,1,m)_A;(1,0,0)_B\rangle = \frac{k_m}{R^3} \tag{10}$$

We can diagonalise the matrix and get eigenvalues which are k_m/R^3 and $-k_m/R^3$. Thus the first order correction is nonzero and it can be positive or negative. Also it goes as $1/R^3$. Hence the δ_1 in the question is 3.

Part(d)

It is clear that the discussiong in the previous parts must be altered at very large seperation distance when we cannot neglect the finite propogation time of electogmagnetic interaction. This transition takes place when the retardation time becomes comparable to atomic state evolution time which is $\sim \hbar/E_0$. The distance between the atoms would be $R \sim \hbar c/E_0 \sim 200A^0$. For distances comparable to or greater than this value, we must take retardation into account.