E6170: Van Der Waals Equation

Submitted by: Nimrod Nissim, Jonathan Gelva

The problem:
For a coloumb interaction between two hydrogen atoms which consists of proton a and electron 1, proton b and electron 2

$$\mathcal{H}_{int} = \frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}}$$

(a) Assuming that the distance between the nuclei is constant: Develop the perturbation hamiltonian up to the second order in terms of r_{a1} and r_{b2}. Show that it results in a dipole interaction between the atoms.
(b) In the given approximation, using the normal basis of each of the hydrogen atoms: Write a general expression for the adjustment to the ground level up to the second order in the given perturbation. Show that this adjustment can be written as $-\frac{A}{r_{ab}^6}$, and identify the coefficient A using the elements of the hydrogen atoms matrix.
(c) Using the approximation $E_1 - E_0 \approx E_1$ in the denominator of the receivced expression: Show that adjustment to the energy in this case is $-\frac{a_0}{e^2}\langle 1s|\mathcal{H}_{int}^2|1s\rangle$. Use this approximation to show that $A \approx 6a_0^5e^2$.

The solution:
(a) The Hamiltonian of the systhem is:

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \tag{1}$$

We neglect $\left(-\frac{e^2}{r_{ab}}\right)$ since r_{ab} is constant.
$\mathcal{H}$ is combined of two hydrogen atoms and a perturbation.

$$\mathcal{H}_0 = \frac{p_1^2}{2m} - \frac{e^2}{r_{a1}} + \frac{p_2^2}{2m} - \frac{e^2}{r_{b2}} \tag{2}$$

$$V = -e^2\left(-\frac{1}{r_{12}} + \frac{1}{r_{b1}} + \frac{1}{r_{a2}}\right) \tag{3}$$

We use the following relations:

$$\vec{r}_{12} = -\vec{r}_{a1} + \vec{r}_{ab} + \vec{r}_{b2} \tag{4}$$

$$\vec{r}_{b1} = -\vec{r}_{ab} + \vec{r}_{a1} \tag{5}$$

$$\vec{r}_{a2} = \vec{r}_{ab} + \vec{r}_{b2} \tag{6}$$

therefore:

$$V = -e^2 \left(-\frac{1}{|-\vec{r}_{a1} + \vec{r}_{ab} + \vec{r}_{b2}|} + \frac{1}{|-\vec{r}_{ab} + \vec{r}_{a1}|} + \frac{1}{|\vec{r}_{ab} + \vec{r}_{b2}|} \right) \tag{7}$$

The distance between the two atoms is much greater than the nucli to his electron, so we use a taylor approximation.

$$\frac{1}{|-\vec{r}_{ab} + \vec{r}_{a1}|} \approx \frac{1}{r_{ab}} \left(1 + \frac{\vec{r}_{a1} \cdot \vec{r}_{ab}}{r_{ab}^2} - \frac{1}{2}\frac{r_{a1}^2}{r_{ab}^2} + \frac{3}{2}\frac{\left(\vec{r}_{a1} \cdot \vec{r}_{ab}\right)^2}{r_{ab}^4} \right) \tag{8}$$

$$\frac{1}{|\vec{r}_{ab} + \vec{r}_{b2}|} \approx \frac{1}{r_{ab}} \left(1 - \frac{\vec{r}_{b2} \cdot \vec{r}_{ab}}{r_{ab}^2} - \frac{1}{2}\frac{r_{b2}^2}{r_{ab}^2} + \frac{3}{2}\frac{\left(\vec{r}_{b2} \cdot \vec{r}_{ab}\right)^2}{r_{ab}^4} \right) \tag{9}$$

$$\frac{1}{|\vec{r}_{ab} + (\vec{r}_{b2} - \vec{r}_{a1})|} \approx \frac{1}{r_{ab}} \left(1 - \frac{\left(\vec{r}_{b2} - \vec{r}_{a1}\right)^2}{2r_{ab}^2} - \frac{\vec{r}_{ab}\left(\vec{r}_{b2} - \vec{r}_{a1}\right)}{r_{ab}^2} + \frac{3}{8}\left(\frac{4\left(\vec{r}_{ab}\left(\vec{r}_{b2} - \vec{r}_{a1}\right)\right)^2}{r_{ab}^4} \right) \right) \tag{10}$$

done to the 2^{nd} order with respect to r_{a1}, r_{b2}.
We combine the contributions from (8), (9) and (10) to get

$$V = \underbrace{-\frac{e^2}{r_{ab}}}_{\text{Constant monopole}} + \underbrace{\frac{e^2}{r_{ab}^3}\left(\left(\vec{r}_{b2} \cdot \vec{r}_{a1}\right) - 3\left(\hat{r}_{ab} \cdot \vec{r}_{b2}\right)\left(\hat{r}_{ab} \cdot \vec{r}_{a1}\right)\right)}_{\text{Dipole-Dipole ineraction}} \tag{11}$$

(b) The hydrogen wave function for a single atom is:

$$\Psi_{nlm} = R_{nl}\left(r\right) Y_{lm}\left(\theta, \phi\right) \tag{12}$$

Assuming two different Hilbert spaces, the total graund state of the systhem is:

$$\Psi_G = \Psi_{1,0,0}^{(1)} \otimes \Psi_{1,0,0}^{(1)} \tag{13}$$

We difine the $\hat{z}$ as $\hat{r}_{ab}$. The dipole perturbation will be:

$$V = \frac{e^2}{r_{ab}^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right) \tag{14}$$

Using spherical coordinates and orthonormal basis of the Hilbert space Y_{lm} one gets:

$$V = \frac{e^2}{r_{ab}^3}\left(\frac{2\pi}{3}\right)\begin{pmatrix} r^{(1)}\left(Y_{1,-1}^{(1)} - Y_{1,1}^{(1)}\right) \otimes r^{(2)}\left(Y_{1,-1}^{(2)} - Y_{1,1}^{(2)}\right) \\ -\left(r^{(1)}\left(Y_{1,-1}^{(1)} + Y_{1,1}^{(1)}\right) \otimes r^{(2)}\left(Y_{1,-1}^{(2)} + Y_{1,1}^{(2)}\right)\right) \\ -4\left(\left(r^{(1)}Y_{1,0}^{(1)}\right) \otimes r^{(2)}Y_{1,0}^{(2)}\right) \end{pmatrix} \tag{15}$$

The "0" order energy for the ground state:

$$E^{(0)} = -\frac{Ry}{1} - \frac{Ry}{1} = -2Ry \tag{16}$$

The 1^{st} order energy adjustment for the ground state:

$$\langle \Psi_G | V | \Psi_G \rangle = E^{(1)} \tag{17}$$

where $\int Y_{lm}^* Y_{l'm'} d\Omega = \delta_{ll'}\delta_{mm'}$.
The first order correction is zero, since the perturbation includes only$l = 1$ terms.
The 2^{nd} order energy correction for the ground state:

$$E^{(2)} = \sum_{nlm,n'l'm' \neq 100} \frac{\langle nlm, n'l'm'|V|100,100\rangle^2}{2E_0 - E_n - E'_n} = \sum_{nlm,n'l'm' \neq 100} \frac{\langle nlm|V_1|100\rangle \langle n'l'm'|V_2|100\rangle}{2E_0 - E_n - E'_n} \tag{18}$$

First, we will calculate the perturbation for a single atom.
$Y_{00} = \frac{1}{\sqrt{4\pi}} = \text{const}$ and therefore only Y_{lm} which exist in the perturbation will survive. Hence only states with $l = l' = 1$ will survive.
Using (15) and taking the root of the coefficient for both particles one gets:

$$\langle Y_{1m}|V(\theta,\phi)|Y_{00}\rangle = -\frac{2\sqrt{\pi}e}{3r_{ab}^{\frac{3}{2}}}\left(\delta_{m,1} + 2\delta_{m0}\right) \tag{19}$$

$$\langle Y_{lm}|V(\theta,\phi)|Y_{00}\rangle^2 = \frac{4\pi e^2}{9r_{ab}^3}\left(\delta_{m,1} + 4\delta_{m,0}\right) \tag{20}$$

The $Y_{lm}s$ obey $l = 1$ so only $n = 2$ survive:

$$\langle R_{21}|r|R_{10}\rangle = \frac{2}{a_0^{\frac{3}{2}}}\int r^3 e^{-\frac{r}{a}} R_{21} dr = \frac{1}{\sqrt{6}a^4}\int r^4 e^{-\frac{3r}{2a}} dr \simeq 1.29a_0 \tag{21}$$

$$\langle R_{21}|r|R_{10}\rangle^2 = 1.66a_0^2 \tag{22}$$

For the two states $\langle 210|$,$\langle 211|$, The possible combinations are $\Psi_{210}\Psi_{210}$, $\Psi_{210}\Psi_{211}$, $\Psi_{211}\Psi_{210}$, $\Psi_{211}\Psi_{211}$.
$E_n = E'_n = -\frac{Ry}{4}$ since $n = n' = 2$.

Substitusion into (18) gives:

$$E^{(2)} = \frac{2 \cdot 2.7556 \cdot a_0^4}{-3Ry} \cdot \frac{16\pi^2 e^4}{81 r_{ab}^6}(16+4+4+1) = 9.07 \frac{a_0^4 \pi^2 e^4}{Ry r_{ab}^6} \Rightarrow A = 9.07 \frac{a_0^4 \pi^2 e^4}{Ry} \tag{23}$$

Now we can write the perturbation matrix for the ground state:

$$V \to \frac{4\pi e^2}{9 r_{ab}^3} 1.29^2 a_0^2 \begin{pmatrix} \Psi_{100}\Psi_{100}, & \Psi_{211}\Psi_{210}, & \Psi_{211}\Psi_{211}, & \Psi_{210}\Psi_{210} & ,\Psi_{210}\Psi_{211} \\ 0 & 2 & 1 & 4 & 2 \\ 2 & 0 & & & \\ 1 & & 0 & & \\ 4 & & & 0 & \\ 2 & & & & 0 \end{pmatrix} \tag{24}$$

One can identify A using the element of matrix:

$$-\frac{a_0}{e^2}\left\langle 1s|V^2|1s\right\rangle = -\frac{a_0}{e^2}\frac{16\pi^2 e^4 2.755 a_0^4}{81 r_{ab}^6}\left(2^2+1^2+4^2+2^2\right) = \frac{13.6 e^2 a_0^5 \pi^2}{r_{ab}^6} \tag{25}$$

(c) Using the approximation $E_1 - E_0 \approx E_1$, we get:

$$E^{(2)} = \sum_{nlm,n'l'm' \neq 100} \frac{\left(\langle nlm|V_1|100\rangle^{(1)} \langle n'l'm'|V_2|100\rangle^{(2)}\right)^2}{2E_0 - 2E_1} \approx \tag{26}$$

$$\sum_{nlm,n'l'm' \neq 100} \frac{\langle 100,100|V|nlm,n'l'm'\rangle \langle nlm,n'l'm'|V_2|100,100\rangle}{-2E_1}$$

The completness of the base:

$$\sum_{nlm} |nlm\rangle\langle nlm| = \mathbf{1} \tag{27}$$

$$Ry \approx -\frac{e^2}{2a_0} \Rightarrow -2E_1 = -2Ry \approx \frac{e^2}{a_0} \tag{28}$$

$$-\frac{a_0}{e^2}\left\langle 1s|V^2|1s\right\rangle = \frac{\left\langle 100|V^2|100\right\rangle}{-2E_1} \tag{29}$$

From (25) we get:

$$A = 13.6 e^2 a_0^5 \pi^2 \Rightarrow A \approx -9.07 a_0^4 \pi^2 e^4 \left(\frac{1}{Ry}\right) \tag{30}$$

From (28) we get:

$$13.6 e^2 a_0^5 \pi^2 \approx 18.14 e^2 \pi^2 a_0^5 \tag{31}$$

And this is such a fine approximation!