

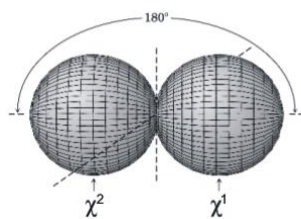
Ερωτήσεις και ασκήσεις Κεφ. 10 (για μόρια) ΠΑΡΑΔΟΣΗ 29/11/2016

- The coefficient  $A$  of the van der Waals interaction is:
  - $A \propto e^2 r_{a1}^3 r_{a2}^3 / (r_{a1} + r_{a2})$
  - $A \propto e^2 r_{a1}^2 r_{a2}^2 / (r_{a1} + r_{a2})$
  - $A \propto e^2 r_{a1}^3 r_{a2}^3 / (r_{a1}^2 + r_{a2}^2)$
  - $A \propto e^4 r_{a1}^3 r_{a2}^3 / (r_{a1} + r_{a2})$
- The bond length of  $\text{H}_2$  is about (in units of  $10^{-10}$  m)
  - 3.12
  - 2.06
  - 1.57
  - 0.74
- The bond length of  $\text{N}_2$  is about (in units of  $10^{-10}$  m)
  - 0.5
  - 1.1
  - 1.62
  - 2.13
- The bond length of  $\text{O}_2$  is about (in units of  $10^{-10}$  m)
  - 3.22
  - 2.45
  - 1.82
  - 1.21
- The bond length of  $\text{Na}_2$  is about (in units of  $10^{-10}$  m)
  - 1.02
  - 1.52
  - 3.08
  - 4.93
- The dissociation energy of  $\text{Na}_2$  is about (in units of eV)
  - 5.2
  - 3.4
  - 1.7
  - 0.8
- The dissociation energy of  $\text{N}_2$  is about (in units of eV)
  - 1
  - 21
  - 10
  - 2
- The van der Waals interaction between two neutral atoms at a distance  $d$  ( $1\text{\AA} \ll d \ll 20\text{\AA}$ ) is of the form
  - $-A/d^3$
  - $-A/d^4$
  - $-A/d^5$
  - $-A/d^6$
- The vibrational quantum energy of  $\text{N}_2$  in meV is about
  - 20
  - 300
  - 800
  - 1100
- The vibrational quantum of  $\text{Na}_2$  in meV is about
  - 20
  - 300
  - 800
  - 1100
- The rotational quantum  $\hbar^2/J$  of  $\text{Na}_2$  in meV is about
  - 2
  - 28
  - 0.04
  - 0.001
- The rotational quantum  $\hbar^2/J$  of  $\text{H}_2$  in meV is about
  - 1,5
  - 15
  - 150
  - 0,15
- The polarity index  $a_p$  is defined as follows ( $V_3 = |\varepsilon_1 - \varepsilon_2|/2$ ):
  - $a_p = V_3 / \sqrt{V_2^2 + V_3^2}$
  - $a_p = V_2 / \sqrt{V_2^2 + V_3^2}$
  - $a_p = \sqrt{|V_2^2 - V_3^2|} / \sqrt{V_2^2 + V_3^2}$
  - $\sqrt{|V_2^2 - V_3^2|} / V_3$
- We assume that in the formation of a diatomic molecule each atom is employing only one atomic orbital  $\psi_i$  of eigenenergy  $\varepsilon_i$ , ( $i=1, 2$ ). In terms of the quantities  $V_2 \equiv \langle \psi_1 | \hat{H} | \psi_2 \rangle$ ,  $\bar{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$ , and  $V_3 = |\varepsilon_1 - \varepsilon_2|/2$  the ground state energy of the molecule is given by the formula (omit  $U$ )
  - $\varepsilon_b = \bar{\varepsilon} - V_2$ ,
  - $\varepsilon_b = \bar{\varepsilon} - V_3$ ,
  - $\varepsilon_b = \bar{\varepsilon} - |V_2| - V_3$
  - $\varepsilon_b = \bar{\varepsilon} - \sqrt{V_2^2 + V_3^2}$

15. We assume that in the formation of a diatomic molecule each atom is employing only one atomic orbital  $\psi_i$  of eigenenergy  $\varepsilon_i$ , ( $i=1, 2$ ). In terms of the quantities  $a_p = V_3 / \sqrt{V_2^2 + V_3^2}$ ,  $V_2 \equiv \langle \psi_1 | \hat{H} | \psi_2 \rangle$ , and  $V_3 = \{(\varepsilon_1 - \varepsilon_2) / 2\} > 0$  the ground state of the molecule is given by the formula

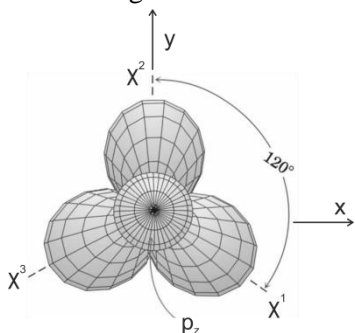
$$\begin{aligned} \text{(a)} \quad \phi_b &= \frac{1}{\sqrt{2}} (\sqrt{1-a_p} \psi_1 + \sqrt{1+a_p} \psi_2) & \text{(b)} \quad \phi_b &= \frac{1}{\sqrt{2}} (\sqrt{1+a_p} \psi_1 + \sqrt{1-a_p} \psi_2) \\ \text{(c)} \quad \phi_b &= \frac{1}{\sqrt{2}} (\psi_1 + \psi_2) & \text{(d)} \quad \phi_b &= \frac{1}{\sqrt{2}} (\psi_1 - \psi_2), \end{aligned}$$

16. In the figure below the two  $sp^1$  hybrids,  $\chi^1$  and  $\chi^2$ , are shown pointing along the  $\pm x$ -axis. Which one of the following formulae is the right one?



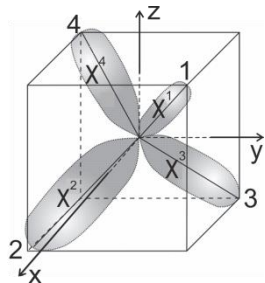
$$\begin{aligned} \text{(a)} \quad \chi^1 &= \frac{1}{\sqrt{2}} (\psi_s - \psi_{p_x}) \\ \text{(b)} \quad \chi^1 &= \frac{1}{\sqrt{2}} (\psi_s - \psi_{p_y}) \\ \text{(c)} \quad \chi^2 &= \frac{1}{\sqrt{2}} (\psi_s - \psi_{p_x}) \\ \text{(d)} \quad \chi^2 &= \frac{1}{\sqrt{2}} (\psi_s + \psi_{p_x}) \end{aligned}$$

17. In the figure below the three  $sp^2$  hybrids are shown. Which one of the following formulae is the right one?



$$\begin{aligned} \text{(a)} \quad \chi^1 &= \frac{1}{\sqrt{3}} (\psi_s + \sqrt{2} \psi_{p_x}), \\ \text{(b)} \quad \chi^2 &= \frac{1}{\sqrt{3}} (\psi_s - \frac{1}{\sqrt{2}} \psi_{p_x} + \frac{\sqrt{3}}{\sqrt{2}} \psi_{p_y}) \\ \text{(c)} \quad \chi^3 &= \frac{1}{\sqrt{3}} (\psi_s - \frac{1}{\sqrt{2}} \psi_{p_x} - \frac{\sqrt{3}}{\sqrt{2}} \psi_{p_y}), \\ \text{(d)} \quad \chi^2 &= \frac{1}{\sqrt{3}} (\psi_s + \sqrt{2} \psi_{p_y}) \end{aligned}$$

18. In the figure below the four  $sp^3$  hybrids are shown. Which one of the following formulae is the right one?



$$\begin{aligned} \text{(a)} \quad \chi^4 &= \frac{1}{2} (\psi_s + \psi_{p_z} - \psi_{p_x} - \psi_{p_y}), \\ \text{(b)} \quad \chi^3 &= \frac{1}{2} (\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\ \text{(c)} \quad \chi^2 &= \frac{1}{2} (\psi_s + \psi_{p_z} - \psi_{p_x} - \psi_{p_y}), \\ \text{(d)} \quad \chi^1 &= \frac{1}{2} (\psi_s + \psi_{p_z} - \psi_{p_x} - \psi_{p_y}) \end{aligned}$$

19. The matrix element  $V_{2h}$  of the Hamiltonian between two  $sp^1$  hybrids belonging to neighboring atoms, lying on the same line, and pointing in opposite directions is given by  $\frac{1}{2} \langle \psi_s^1 + \psi_{p_x}^1 | \hat{H} | \psi_s^2 - \psi_{p_x}^2 \rangle$ . Taking into account that  $\langle \psi_i^1 | \hat{H} | \psi_j^2 \rangle = \eta_{ij} (\hbar^2 / m_e d^2)$ ,  $\eta_{ij} = -1.32 \quad 1.42 \quad 2.22$  for  $ij = ss \quad sp_x \quad p_x p_x$  we find that

$$(a) V_{2h} = -1.77 \frac{\hbar^2}{m_e d^2} \qquad (b) V_{2h} = -1.42 \frac{\hbar^2}{m_e d^2}$$

$$(c) V_{2h} = -3.19 \frac{\hbar^2}{m_e d^2} \qquad (d) V_{2h} = 2.22 \frac{\hbar^2}{m_e d^2}$$

20. The matrix element  $V_{2h}$  of the Hamiltonian between two  $sp^2$  hybrids belonging to neighboring atoms, lying on the same line, and pointing in opposite directions is given by  $\frac{1}{3} \langle \psi_s^1 + \sqrt{2} \psi_{p_x}^1 | \hat{H} | \psi_s^2 - \sqrt{2} \psi_{p_x}^2 \rangle$ . Taking into account that  $\langle \psi_i^1 | \hat{H} | \psi_j^2 \rangle = \eta_{ij} (\hbar^2 / m_e d^2)$ ,  $\eta_{ij} = -1.32 \ 1.42 \ 2.22$  for  $ij = ss \ sp_x \ p_x p_x$  we find that

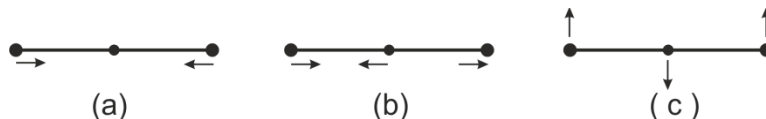
$$(a) V_{2h} = -3.26 \frac{\hbar^2}{m_e d^2} \qquad (b) V_{2h} = -1.92 \frac{\hbar^2}{m_e d^2}$$

$$(c) V_{2h} = -1.48 \frac{\hbar^2}{m_e d^2} \qquad (d) V_{2h} = 4.44 \frac{\hbar^2}{m_e d^2}$$

21. The bond of the diatomic molecule  $O_2$  is

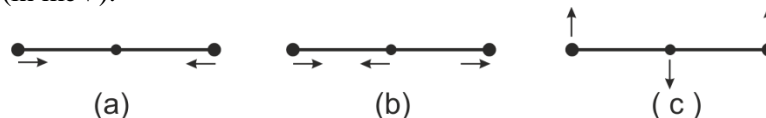
- (a) single between  $p_x, p_x$ ,  
 (b) double, a strong one between  $p_x, p_x$  and a weak one between  $((p_y, p_y) + (p_z, p_z)) / \sqrt{2}$   
 (c) double, a strong one between  $p_x, p_x$  and a weak one between  $(p_y, p_z)$   
 (d) triple, a strong one between  $p_x, p_x$  and two weak ones between  $p_y, p_y$  and  $p_z, p_z$

22. In the figure below the four normal vibrational modes of the  $CO_2$  molecule are shown (mode (c) is doubly degenerate). Which one(s) are capable of absorbing or emitting electromagnetic (EM) radiation?



- (a) a,b                      (b)b,c                      (c)a,c                      (d) all of them

23. In the figure below the four normal vibrational modes of the  $CO_2$  molecule are shown. (Mode (c) is doubly degenerate and is responsible for the greenhouse effect). The eigenfrequency of this vibration is approximately (in meV):



- (a) 300                      (b) 516                      (c) 160                      (d) 80

24. The energy of the system of two neutral hydrogen atoms as a function of the distance  $d'$  between their protons is given approximately by the relation,  $E = (0.343/d'^2) - (0.49/d')$  in atomic units and for  $d'$  around the bond length  $d$ . The bond length (in Angstroms) of the molecule  $H_2$  is according to this relation:

- (a) 0.74                      (b) 0.53                      (c) 1.06                      (d) 1.41

25. The energy of the system of two neutral hydrogen atoms as a function of the distance  $d'$  between their protons is given approximately by the relation,  $E = (0.343/d'^2) - (0.49/d')$  in atomic units and for  $d'$  around the bond length  $d$ . The vibrational frequency of the molecule  $\text{H}_2$  in meV is according to this relation:  
 (a) 516 meV                      (b) 258 meV                      (c) 380 meV                      (d) 760 meV

## 11.8 Solved problems

1. The energy of the system of two neutral hydrogen atoms as a function of the distance  $d'$  between their protons is given approximately by the relation,  $E = (0.343/d'^2) - (0.49/d')$  in atomic units and for  $d'$  around the bond length  $d$ . Obtain the dissociation energy of the molecule  $\text{H}_2$ .

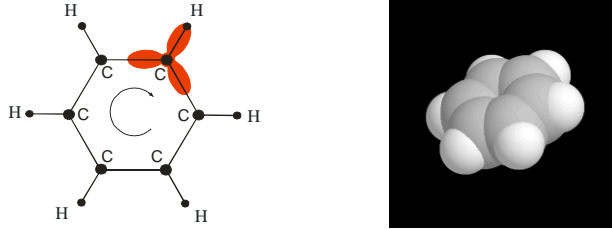
**Solution:** The dissociation energy  $D$  is equal to  $|E_0| - \frac{1}{2}\hbar\omega$ , where  $E_0$  is the minimum of  $E$ ,  $\omega = \sqrt{\kappa/m_r}$ ,  $\kappa = \partial^2 E / (\partial d')^2_{d'=d}$ , and  $m_r = m_p/2 = 918m_e$ . Thus the distance at minimum  $E$  is  $d = 2 \times 0.343/0.49 = 1.4$  and  $E_0 = -0.343/d^2 = -0.175$ ;  $\kappa = (1/d)(0.49/d^2) = 0.1786$ ;  $\omega = \sqrt{0.1786/918} = 0.0139$ . Thus, finally,  $D = 0.175 - \frac{1}{2} \times 0.0139 = 0.168 = 0.168 \times 27.2 = 4.57$  eV

2. Show that the matrix element between two  $sp^3$  hybrids belonging to two neighboring atoms, lying on the same line, and having opposite directions is given by the formula  $V_{2h} = -3.22(\hbar^2/m_e d^2)$

**Solution:** We shall choose the line connecting the two atoms as the x-axis. Then the  $sp^3$  hybrid lying along the x-axis and belonging to the atom on the left has the form  $\chi_l = \frac{1}{2}(s + \sqrt{3}p_x)$ , while the  $sp^3$  hybrid lying along the x-axis and belonging to the atom on the right has the form  $\chi_r = \frac{1}{2}(s - \sqrt{3}p_x)$ . Thus

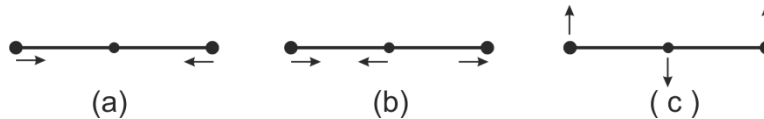
$$\begin{aligned} \langle \chi_l | H | \chi_r \rangle &= \frac{1}{4} \langle s + \sqrt{3}p_x | H | s - \sqrt{3}p_x \rangle = \frac{1}{4} (-1.32 - 1.42\sqrt{3} - 1.42\sqrt{3} - 2.22 \times 3) \times \\ &\times \frac{\hbar^2}{m_e d^2} = -3.22 \frac{\hbar^2}{m_e d^2} \end{aligned}$$

3. Consider the benzene molecule shown below and its six unhybridized  $p_z$  atomic orbitals. Show that the energy gain would be equal to  $6|V_{2zz}|$ , if three bonds were formed between three pairs of neighboring  $p_z$  orbitals, while the gain is  $8|V_{2zz}|$ , if delocalized molecular orbitals according to Eq. (11.16) are formed. (Coulomb repulsion effects have been omitted)



**Solution:** According to Eq. (11.10) by placing two electrons at the bonding level for each of the three bonds between neighboring  $p_z$  atomic orbitals the lowering of the energy is equal to  $2|V_{2zz}|$ , since in the present case  $V_3 \equiv 0$ . Thus the total lowering of the energy for the three bond case is indeed  $3 \times 2|V_{2zz}| = 6|V_{2zz}|$ . On the other hand for the actual case where the delocalized molecular orbitals are given by (11.16) we shall occupy by two electrons the lowest energy given by  $\varepsilon_z + 2V_{2zz} = \varepsilon_z - 2|V_{2zz}|$  so that the contribution to the lowering of the energy will be  $4|V_{2zz}|$ ; the next doubly degenerate level at  $\varepsilon_z + 2V_{2zz} \cos(\pm\pi/3) = \varepsilon_z - |V_{2zz}|$  will be occupied by the remaining four electrons contributing thus to the lowering of the energy by another  $4|V_{2zz}|$  to a total reduction by  $8|V_{2zz}|$ . We see that the delocalized configuration according to Eq. (11.16) produces lower total energy compared to the localized three bond configuration which is definitely not the ground state of the six  $p_z$  orbitals in benzene.

4. In the figure below the four normal vibrational modes of the  $\text{CO}_2$  molecule are shown (the mode (c) is doubly degenerate). Prove that the four vibrational eigenfrequencies of this molecule satisfy the following double inequality:  $\omega_c < \omega_a < \omega_b$  and estimate their values



**Solution:** We assume that the stretching/compression spring constant of the C/O bond is  $\kappa$ , while the bending one is  $\kappa'$ . Since bending is much easier than stretching/compressing we expect that  $\kappa' \ll \kappa$ . For the mode (a) the carbon atom remains unmoved so that  $\omega_a = \sqrt{\kappa/m_O} = \sqrt{\kappa/(16u)}$ . For the mode (b), as for every pure vibrational mode, the center of mass of the system is not moving so that  $2m_O x_O + m_C x_C = 0 \Rightarrow x_C = -(2m_O/m_C)x_O$ ; the equation of motion is  $-\omega_b^2 m_O x_O = k(x_C - x_O) \Rightarrow -\omega_b^2 m_O x_O = -k\{(2m_O/m_C)+1\}x_O$ . Thus we have

$\omega_b = \sqrt{\kappa(2m_c^{-1} + m_o^{-1})} = \sqrt{\kappa / (4.36u)}$ , hence  $\omega_a < \omega_b$ . For the mode (c) we have as a result of the immobile center of mass  $2m_o y_o + m_c y_c = 0 \Rightarrow y_c = -(2m_o / m_c) y_o$  and  $-\omega_c^2 m_o y_o = k'(y_c - y_o) \Rightarrow -\omega_c^2 m_o y_o = -k' \left\{ (2m_o / m_c) + 1 \right\} y_o$  from the equation of motion. Thus  $\omega_c = \sqrt{\kappa'(2m_c^{-1} + m_o^{-1})} = \sqrt{\kappa' / (4.36u)}$  and the ordering of the eigenfrequencies is  $\omega_c < \omega_a < \omega_b$ .

To estimate the values of these eigenfrequencies we shall start with  $\omega_a$  and we shall use Eq. (11.5b) with  $\bar{d}$  the experimental value of 2.19.

$$\hbar\omega_a = c'_v \frac{\hbar^2}{m_e d^2} \sqrt{\frac{m_e}{m_r}} \approx \frac{3026}{\bar{d}^2 \sqrt{A_{Wr}}} = \frac{3026}{2.19^2 \sqrt{16}} = 158 \text{ meV}$$

while the experimental value is 165 meV. From the above analysis we have that  $\omega_b / \omega_a = \sqrt{16 / 4.36} = 1.91$  so that  $\hbar\omega_b = 1.91 \times 158 = 302 \text{ meV}$  vs. 291 meV for the experimental value. Finally, to estimate  $\omega_c$  we shall use the information that mode c is responsible for the greenhouse effect; this implies that the eigenfrequency of this mode is close to the frequency  $\omega_m$  of maximum emission from the ground of Earth. Assuming an average temperature of the ground equal to 290K (see section 13.3, p. 196) and a black body emission we have  $\hbar\omega_m = 2.822 k_B T = 70.5 \text{ meV}$ . Actually the eigenfrequency  $\hbar\omega_c$  is equal to 82.7 meV which means that  $\kappa' = 0.08\kappa$ .

## 11.9 Unsolved problems

1. The interaction energy between two identical noble atoms as a function of the distance  $d$  between their nuclei is given by the formula

$$\mathcal{V}_{ij}(d) = 4\epsilon \left\{ \left( \frac{\sigma}{d} \right)^{12} - \left( \frac{\sigma}{d} \right)^6 \right\}, \quad d \geq (\sigma / 2)$$

For the Ar atoms  $\epsilon = 10 \text{ meV}$  and  $\sigma = 3.4 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ). Does the diatomic argon molecule exist at absolute zero temperature? If yes, what is the bond length? What is its vibration frequency? Will this molecule survive at room temperature?

2. Consider the CO molecule. Which atomic orbitals are involved in its bond? Is the latter single, double, or triple? Any similarity with the nitrogen molecule?

3. Find the energy gap (i.e. the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO)) of the molecule  $\text{C}_6\text{H}_6$ .