

Solution of homework # 8

Exercise 1 – Butadiene

1. If we write the Hamiltonian:

$$H_{ij} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}, \quad (1)$$

and solve the secular problem $\det(H - \epsilon I)$ in terms of the variable $x = \frac{\alpha - \epsilon}{\beta}$:

$$\begin{vmatrix} \beta x & \beta & 0 & 0 \\ \beta & \beta x & \beta & 0 \\ 0 & \beta & \beta x & \beta \\ 0 & 0 & \beta & \beta x \end{vmatrix} = 0 \implies \beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \implies \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0, \quad (2)$$

where the $||$ symbol stands for determinant. We obtain the equation:

$$x^2(x^2 - 2) - (x^2 - 1) = 0, \quad (3)$$

that can be solved by changing variable $y = x^2$. The 4 solutions are:

$$x = \pm \left(\sqrt{\frac{3 \pm \sqrt{5}}{2}} \right), \quad (4)$$

so the energy eigenvalues are

$$\epsilon_i = \alpha \pm \beta \left(\sqrt{\frac{3 \pm \sqrt{5}}{2}} \right). \quad (5)$$

2. We know that $\beta < 0$ and that the ϵ_i are all different, which means that the molecular orbital are only spin degenerate and can accommodate at most 2 electrons.

So the energy of the HOMO is

$$\epsilon_{\text{HOMO}} = \alpha + \beta \left(\sqrt{\frac{3 - \sqrt{5}}{2}} \right). \quad (6)$$

3. The total degeneracy of the ground state is one, because the lowest two molecular orbitals are completely filled. Instead, the two molecular ions have both total degeneracy two: in both cases a molecular orbital is half filled and we have two possibilities for the spin part of the wavefunction (up or down).

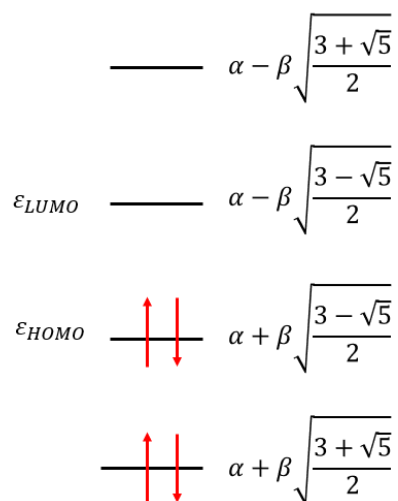


Figure 1: A simple scheme of the energy levels. Remember that $\beta < 0$.

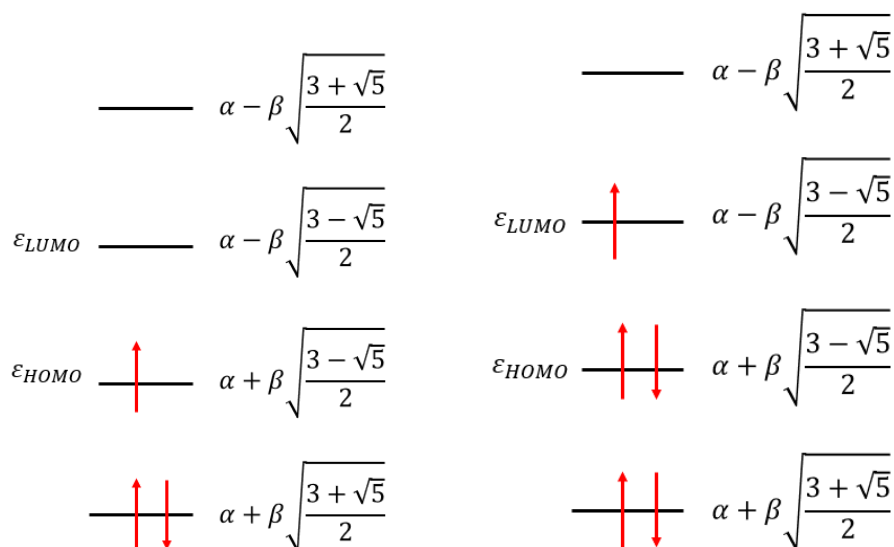
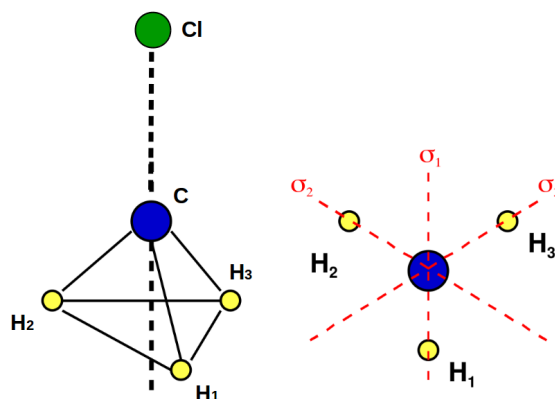


Figure 2: Molecular ions schematic energy levels for $(\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2)^+$ (left) and $(\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2)^-$. In both cases we have a double degeneracy because an electron can have spin $1/2$ or $-1/2$.

Exercise 2 – CH_3Cl

1. There are 6 symmetry operations which are:

- Identity (E);
- Rotations by $2\pi/3$ and $4\pi/3$ around the axis passing through C and Cl (C_3 , C_3^2 , see Fig. 3);
- Reflections through three vertical planes passing through C and Cl and each of the H atoms (σ_1 , σ_2 , σ_3 , see Fig. 3).

Figure 3: The CH_3Cl molecule. Left: side view, Right: bottom view.

2. These symmetry operations form a group. We can verify that the group is *closed* under multiplication by showing that the multiplication of each pair of symmetry operations belongs to the group (see Table 1).

Note that Table 1 is not symmetric: this is so because the symmetry operations do not in general commute: the order in which symmetry operations are applied matters.

\times	First operation					
	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_2	σ_3	σ_1
C_3^2	C_3^2	E	C_3	σ_3	σ_1	σ_2
σ_1	σ_1	σ_3	σ_2	E	C_3^2	C_3
σ_2	σ_2	σ_1	σ_3	C_3	E	C_3^2
σ_3	σ_3	σ_2	σ_1	C_3^2	C_3	E

Table 1: Table of symmetry operations

Exercise 3 – C_2H_4

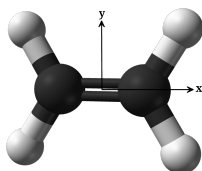


Figure 4: Ethylene molecule. We take the center of the molecule as the center of our coordinate system.

1. The matrices act on a generic point in space $\mathbf{r} = (x, y, z)$ and move it to another point $\mathbf{r}' = (x', y', z')$.

These symmetry operations are:

- Identity (E) which leaves all coordination unaffected;

- Inversion (i) which transforms positions (x, y, z) to $(-x, -y, -z)$.

$$\mathbf{r}' \equiv i\mathbf{r} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

- Symmetry operation $\mathcal{C}_n(i)$ with i being either x , y or z represents the rotation by $\frac{2\pi}{n}$ degree about the x , y or z axis respectively. For example, $\mathcal{C}_2(x)$ corresponds to the rotation π about the x axis and $\mathcal{C}_4(z)$ corresponds to the rotation $\frac{\pi}{2}$ about the z axis.
- Reflections through the three perpendicular planes xy , xz and yz . They are denoted by $\sigma(xy)$, $\sigma(xz)$ and $\sigma(yz)$. It can easily be understood that in reflection through a plane, the perpendicular axis coordinate changes sign. For example through reflection $\sigma(xy)$, the coordinate z changes sign.

$$\mathbf{r}'' \equiv \sigma(xy)\mathbf{r} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$$

Therefore, the matrix representation for the 11 types of symmetry operations are

$$\begin{aligned} E &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & i &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ \mathcal{C}_2(x) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \mathcal{C}_2(y) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \mathcal{C}_2(z) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \mathcal{C}_4(x) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} & \mathcal{C}_4(y) &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} & \mathcal{C}_4(z) &= \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned}$$

$$\sigma(xy) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \sigma(yz) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma(xz) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

We can easily conclude that C_2H_4 has E , i , $\mathcal{C}_2(x)$, $\mathcal{C}_2(y)$, $\mathcal{C}_2(z)$, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$ symmetries.

2. These symmetry operations form a group (called D_{2h}). We can verify this by showing that the four properties that define a group (*closure*, *associativity*, *identity*, *inverse*) are all satisfied:

- Associativity follows directly from the associativity of the matrix product;
- E is the identity element, indeed $E\mathcal{C}_2(x) = \mathcal{C}_2(x)$, $E\sigma(xy) = \sigma(xy)$ and so on;
- The inverse of every element is the element itself, indeed $\mathcal{C}_2(x)\mathcal{C}_2(x) = \sigma(xy)\sigma(xy) = ii = \dots = E$;
- We need to show that these eight operations are *closed* under multiplication, i.e. the multiplication of each pair of symmetry operations is still a symmetry operation:

\times	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
E	E							
$C_2(z)$	$C_2(z)$	E						
$C_2(y)$	$C_2(y)$	$C_2(x)$	E					
$C_2(x)$	$C_2(x)$	$C_2(y)$	$C_2(z)$	E				
i	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	E			
$\sigma(xy)$	$\sigma(xy)$	i	$\sigma(yz)$	$\sigma(xz)$	$C_2(z)$	E		
$\sigma(xz)$	$\sigma(xz)$	$\sigma(yz)$	i	$\sigma(xy)$	$C_2(y)$	$C_2(x)$	E	
$\sigma(yz)$	$\sigma(yz)$	$\sigma(xz)$	$\sigma(xy)$	i	$C_2(x)$	$C_2(y)$	$C_2(z)$	E

Table 2: Multiplication table of the D_{2h} symmetry group. The table is symmetric, thus only the bottom triangle under the diagonal is explicitly written.

3. The symmetries of vinyl chloride are of course lower than the ones of ethylene. Indeed only two of the eight symmetry operations of D_{2h} are still symmetry operations of the molecule: E and $\sigma(xy)$.

It is easy to show that also these two elements alone form a group (called C_s).