Week 2 – Homework Assignment 1

Molecules

Problem 1. Two identical atoms make a bond along the z direction as shown in the picture below. Consider the molecular orbitals that can be formed as symmetric and anti-symmetric linear combinations of px (top) and pz (bottom) orbitals. The + and - signs on the orbitals denote the sign of the wave functions.

Question 1.1: Which of the two possible combinations (symmetric, both WF’s with the same sign, or anti-symmetric, WF’s with opposite sign) corresponds to the bonding state for the two px orbitals?

a) Symmetric

b) Anti-symmetric

Question 1.2: Which of the two possible combinations corresponds to the bonding for the two pz orbitals?

a) Symmetric

b) Anti-symmetric
Problem 2. You will use the knowledge about hybridization from the lectures to discuss bonding in molecules and crystals. Consider the tables below:

Table 1: Bonding properties of hydrocarbons

<table>
<thead>
<tr>
<th>Material</th>
<th>(C-C) Bond length (Å)</th>
<th>CC Bond Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.203*</td>
<td>9.93**</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.339*</td>
<td>7.42**</td>
</tr>
</tbody>
</table>

Table 2: Bonding properties of allomorphs of carbon

<table>
<thead>
<tr>
<th>Material</th>
<th>(C-C) Bond length (Å)</th>
<th>Bond Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>1.42*</td>
<td>?</td>
</tr>
<tr>
<td>Diamond</td>
<td>1.54*</td>
<td>3.60***</td>
</tr>
</tbody>
</table>


Nicolas: it would be great to get more authoritative references for these numbers.

Question 2.1: What is the hybridization (sp1, sp2, sp3) of the C atoms in acetylene, ethylene, graphene, and diamond.

a) All sp1
b) sp1, sp2, sp2, sp3
c) sp3, sp2, sp2, sp1

Question 2.2: What is the number of \(\pi\) bonds in ethylene per C-C?

a) 0
b) 1
c) 2

Question 2.3: Would you expect the C-C bonds in graphene to be stronger or weaker than those in diamond?

a) Stronger
b) Weaker
Problem 3. The heteropolar bond and partially ionic bonds. Within the LCAO approximation a hetero-polar bond is described by the following secular equation:
\[
\begin{bmatrix}
 h_0^R & -V_2 \\
 -V_2 & h_0^L
\end{bmatrix}
\begin{bmatrix}
 a_R \\
 a_L
\end{bmatrix}
= E
\begin{bmatrix}
 a_R \\
 a_L
\end{bmatrix},
\]
where the superscripts \(L\) and \(R\) indicate the two atoms.

Defining the polar energy as:
\[
V_3 = \frac{h_0^R - h_0^L}{2}
\]
and the average atomic energy of the cation and anion as:
\[
\bar{h} = \frac{h_0^R + h_0^L}{2},
\]
solve the secular equation and find the energies (eigenvalues) and coefficients for the wavefunction (eigenvectors).

**Question 3.1:** The energy of the bonding state (lowest energy eigenvalue) is:

a) \( h_0 - V_2 \)
b) \( h_0 - V_3 - V_2 \)
c) \( h_0 - \sqrt{V_2^2 + V_3^2} \)

**Question 3.2:** Consider \( h_0^R < h_0^L \), that is, the energy of the electron on atom \( R \) is lower than in atom \( L \). How do the linear coefficients \( a_L \) and \( a_R \) compare to each other? Which one is larger?

a) The electron spends more time on atom \( L \): \(|a_L| > |a_R|\)
b) The electron spends more time around atom \( R \): \(|a_L| < |a_R|\)

In the submit version, the letters \( L \) and \( R \) need to be swapped in the text.