PY4T01 Condensed Matter Theory: Lecture 4

Bond Energy

Consider again the eigenvalues equation for the heteronuclear molecule

$$\begin{pmatrix} \epsilon_A & \gamma \\ \gamma & \epsilon_B \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = E \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$$

The solutions are the bonding and antibonding states

$$\begin{pmatrix} \psi_A^{\rm bond} \\ \psi_B^{\rm bond} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \psi_A^{\rm anti} \\ \psi_B^{\rm anti} \end{pmatrix}$$

Consider for the moment only the bonding state

$$\begin{pmatrix} \epsilon_A & \gamma \\ \gamma & \epsilon_B \end{pmatrix} \begin{pmatrix} \psi_A^{\rm bond} \\ \psi_B^{\rm bond} \end{pmatrix} = E_{\rm bond} \begin{pmatrix} \psi_A^{\rm bond} \\ \psi_B^{\rm bond} \end{pmatrix}$$

and multiply to the left by $(\psi_A^{\rm bond},\ \psi_B^{\rm bond})$

$$\boxed{E_{\rm bond} = \epsilon_A(\psi_A^{\rm bond})^2 + \epsilon_B(\psi_B^{\rm bond})^2 + 2\gamma\psi_A^{\rm bond}\psi_B^{\rm bond}}$$

- $\underline{(\psi_A^{\rm bond})^2}$ is the probability to find an electron on the atom A in the bonding state.

  $\underline{\epsilon_A(\psi_A^{\rm bond})^2}$ is the energy contribution coming from the time spent by the electron on the atom A in the bonding state.

- $\underline{\Theta_{\rm AB}^{\rm bond} = \psi_A^{\rm bond}\psi_B^{\rm bond}}$ is the interference term. It is called **partial bond order** of the AB bond.

- $\underline{2\gamma\psi_A^{\rm bond}\psi_B^{\rm bond}}$ is **partial bond energy** of the AB bond.

The total bond order is the sum of the partial bond order over all the occupied states.

$$\Theta_{\rm AB}^{\rm total} = \sum_j^{\rm occupied} \Theta_{\rm AB}^j$$

The total bond energy is the sum of the partial bond energy over all the occupied states.

$$E^{\rm total} = \sum_j^{\rm occupied} 2\gamma\Theta_{\rm AB}^j$$

The total bond energy is a measure of the stability of a specific bond

Example:

Consider the H_2 molecule. Then:

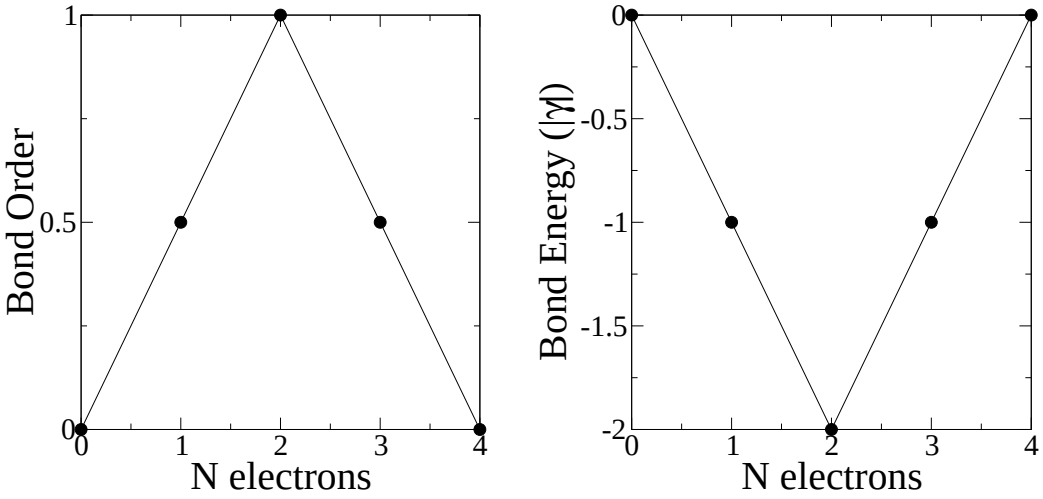
$$\Psi_{\rm bond} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad \Psi_{\rm anti} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Therefore:

$$E_{\rm bond} = 1/2\epsilon_0 + 1/2\epsilon_0 + \gamma \quad \longrightarrow \quad \Theta^{\rm bond} = 1/2$$

$$E_{\rm anti} = 1/2\epsilon_0 + 1/2\epsilon_0 - \gamma \quad \longrightarrow \quad \Theta^{\rm anti} = -1/2$$

Consider how the bond order and the bond energy change with electron number



The Density Matrix

Consider the AB dimer in its ground state. The charge density is:

$$\rho(\vec{r}) = 2\langle\vec{r}|\psi_{\rm bond}\rangle\langle\psi_{\rm bond}|\vec{r}\rangle$$

We define "charge density operator"

$$\hat{\rho} = \sum_{j}^{\rm occupied} |\psi_j\rangle\langle\psi_j|$$

For instance in the case we have only two electrons

$$\hat{\rho} = 2|\psi_{\rm bond}\rangle\langle\psi_{\rm bond}|$$

Now write the representation of $\hat{\rho}$ on our basis function $|A\rangle$, $|B\rangle$

$$\rho = \begin{pmatrix} \rho_{AA} & \rho_{AB} \\ \rho_{BA} & \rho_{BB} \end{pmatrix} = \begin{pmatrix} \psi_A^*\psi_A & \psi_A^*\psi_B \\ \psi_B^*\psi_A & \psi_B^*\psi_B \end{pmatrix}_{\rm bond}$$

where

$$\begin{aligned} \rho_{AA} &= \langle A|\hat{\rho}|A\rangle = 2\langle A|\psi_{\rm bond}\rangle\langle\psi_{\rm bond}|A\rangle = 2\psi_A^*\psi_A \\ \rho_{BB} &= \langle B|\hat{\rho}|B\rangle = 2\langle B|\psi_{\rm bond}\rangle\langle\psi_{\rm bond}|B\rangle = 2\psi_B^*\psi_B \\ \rho_{AB} &= \langle A|\hat{\rho}|B\rangle = 2\langle A|\psi_{\rm bond}\rangle\langle\psi_{\rm bond}|B\rangle = 2\psi_A^*\psi_B \\ &\ldots\ldots \end{aligned}$$

Note:

- $\hat{\rho}$ is hermitian, so all its representations are hermitian matrices
- Diagonal terms: probability to find an electron in the specific state A or B
- Off-Diagonal terms: Bond Order
- The expectation value L of a generic operator $\hat{L}$ can be calculated simple as:

$$L = \mathrm{Tr}[\hat{L}\hat{\rho}]$$

Demonstration of this last point:

$$L = \langle\psi|\hat{L}|\psi\rangle = \sum_{i,j}\langle\psi|i\rangle\langle i|\hat{L}|j\rangle\langle j|\psi\rangle =$$

$$\sum_{i,j}\langle i|\hat{L}|j\rangle\langle j|\psi\rangle\langle\psi|i\rangle = \sum_{i,j} L_{ij}\rho_{ji} = \mathrm{Tr}[L\rho]$$

The density matrix contains ALL the information about the ground state electronic structure of the system !!!