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## Computational Nanoscience: Solution to Exercise Sheet No. 1

### Exercise 1.1: Molecular geometry of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O

- Successfully launch avogadro2.
- Test features - create simple molecules, import fragments, load preexisting files.
- Either use the measure tool or align the bond to axes and read the value from "Atomic Coordinate Editor" or exported coordinate file. Following values are examples after running the force field optimisation.

Molecule	Bond length [Å]
H <sub>2</sub>	0.64
O <sub>2</sub>	1.282
H <sub>2</sub> O	0.969

- Such methods are much more computationally expensive - as a preliminary calculation, force field calculation achieves sufficient precision.

### Exercise 1.2: Total energy in MO theory

(a)

$$\hat{H}\Psi^{\text{Prod}} = \sum_{n=1}^N \left( \prod_{k=1, k \neq n}^N \psi_k(\mathbf{r}_k) \right) \left( -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_n}^2 \psi_n(\mathbf{r}_n) - \sum_A \frac{Z_a e^2}{|\mathbf{r}_n - \mathbf{R}_A|} \psi_n(\mathbf{r}_n) \right) + V_{\text{NN}} \Psi^{\text{Prod}} = \quad (1)$$

$$= \sum_{n=1}^N \left( \prod_{k=1, k \neq n}^N \psi_k(\mathbf{r}_k) \right) (\hat{h} \psi_n(\mathbf{r}_n)) + V_{\text{NN}} \Psi^{\text{Prod}} = \left( \sum_{n=1}^N \epsilon_n + V_{\text{NN}} \right) \Psi^{\text{Prod}} \quad (2)$$

The factor of 2 accounts for the spin degeneracy - each molecular orbital is assumed to be occupied by 2 electrons.

- Wavefunction  $\Psi^{\text{Prod}}$  is not anti-symmetric under the particle exchange of electrons - swapping  $\mathbf{r}_n \leftrightarrow \mathbf{r}_m$  leaves  $\Psi^{\text{Prod}}$  unchanged, as multiplication is commutative.

### Exercise 1.3: Molecular orbital diagram of Li<sub>2</sub>

- Li<sub>2</sub> has 6 electrons in total. We can assume that 1s and 2s orbitals will predominantly participate in bonding.

- (b) Lets order the basis in following order :  $\psi_{1,1s}, \psi_{2,1s}, \psi_{1,2s}, \psi_{2,2s}$ , where  $\psi_{n,ms}$  stands for  $ms$  orbital on lithium atom  $n$ . Since the atomic orbitals with different principal quantum number should be orthogonal on the same atom, we are left with

$$H_{\text{MO}} = \begin{pmatrix} E_{1s} & h_{11} & 0 & h_{12} \\ h_{11} & E_{1s} & h_{12} & 0 \\ 0 & h_{12} & E_{2s} & h_{22} \\ h_{12} & 0 & h_{22} & E_{2s} \end{pmatrix} \quad (3)$$

As a further approximation, we will neglect the  $h_{12}$  terms, as is also done in the lecture notes in case of oxygen MO theory example. The Hamiltonian is then block diagonal.

- (c) Solving the eigenvalue equation leads to characteristic polynomial in MO energy  $E$

$$0 = \begin{vmatrix} E_{1s} - E & h_{11} & 0 & 0 \\ h_{11} & E_{1s} - E & 0 & 0 \\ 0 & 0 & E_{2s} - E & h_{22} \\ 0 & 0 & h_{22} & E_{2s} - E \end{vmatrix} = [(E_{1s} - E)^2 - h_{11}^2][(E_{2s} - E)^2 - h_{22}^2] = \quad (4)$$

$$= (E_{1s} - h_{11} - E)(E_{1s} + h_{11} - E)(E_{2s} - h_{22} - E)(E_{2s} + h_{22} - E) \quad (5)$$

Hence, we have four energies of the 4 MO orbitals  $E = E_{1s} \pm h_{11}$  and  $E = E_{2s} \pm h_{22}$

- (d) For the energy terms, we can deduce ordering  $|h_{11}| < |h_{22}| \ll |E_{1/2s}|$  and  $E_{1s} < E_{2s}$ . Then, the following MO diagram is valid

