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## Computational Nanoscience: Exercise Sheet No. 1

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

- (a) We will need Avogadro2 program for all following exercises. This program is already pre-installed on the university computers.

For installation on your personal computer, see <https://avogadro.cc/>. Find and launch the program. [1]

- (b) Familiarize yourself with the basic features of avogadro, e.g. by going through the tutorial

<https://www.youtube.com/watch?v=fDk3T9aD4bU>

or by exploring on your own. Practice by drawing an approximate structure of vinylchloride (chloroethene). [2]

- (c) Draw the molecules H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O in avogadro. Relax<sup>1</sup> each of them with the build-in force field of avogadro. Take care of the bond order (single bond, double bond, ...). Save each of the three molecules as individual xyz file. What are the bond lengths in each of the three molecules? [2]

- (d) A force field is used in avogadro to obtain the geometry with the lowest energy. Details on force fields can be found in the literature, e.g. by consulting the book Jensen: Computational Chemistry. What might be the reason why more accurate methods based on quantum mechanics, as DFT or Hartree-Fock, are not used in avogadro? [2]

### Exercise 1.2: Total energy in MO theory

In MO theory, we assume the electrons to be non-interacting, e.g. there is no electrostatic electron-electron interaction in the Hamiltonian,

$$\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \underbrace{\hat{V}_{ee}}_{=0} + V_{NN} = \sum_{n=1}^N \left[ -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_n}^2 - \sum_A \frac{Z_A e^2}{|\mathbf{r}_n - \mathbf{R}_A|} \right] + V_{NN}. \quad (1)$$

In case of the non-interacting Hamiltonian from Eq. (1) and the neglect of the fermionic character of electrons, the many-body wavefunction  $\Psi$  can be found as a product of one-particle states,

$$\Psi^{\text{Prod}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N), \quad (2)$$

where  $\psi_n(\mathbf{r})$ ,  $n \in \{1, 2, \dots, N\}$  are normalized and solve a one-particle Schrödinger equation with a one-particle Hamiltonian  $\hat{h}$ :

$$\hat{h}\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r}), \quad \hat{h} = -\frac{\hbar^2}{2m} \nabla^2 - \sum_A \frac{Z_A e^2}{|\mathbf{r} - \mathbf{R}_A|}.$$

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<sup>1</sup>Relax = optimize the geometry to obtain the lowest-energy structure

- (a) Prove:  $\Psi^{\text{Prod}}$  from Eq. (2) satisfies

$$\hat{H} \Psi^{\text{Prod}}(\mathbf{r}) = E \Psi^{\text{Prod}}(\mathbf{r}) \quad \text{with} \quad E = \sum_{n=1}^N \varepsilon_n + V_{\text{NN}}.$$

Why is a factor 2 appearing in the lecture notes? [4]

- (b) Which condition on many-body fermion wavefunctions  $\Psi$  is not fulfilled by product wavefunctions from Eq. (2)? [4]

### Exercise 1.3: Molecular orbital diagram of $\text{Li}_2$

The  $\text{Li}_2$  molecule is a molecule known in the gas phase. We consider  $\text{Li}_2$  because it is illustrative to treat in molecular orbital (MO) theory.

- (a) How many electrons does  $\text{Li}_2$  have and which atomic orbitals will be involved in the bonding? [1]
- (b) Follow MO theory and write the Hamiltonian in the atomic orbital basis of 1s / 2s functions of Li. [2]
- (c) Find the energy levels in MO theory. It is not necessary to explicitly compute the numerical values of the matrix elements. [3]
- (d) Draw the MO diagram using the eigenvalues from (c). Ensure that the splitting of the levels is qualitatively correct. [2]