University of Regensburg
Institute of Theoretical Physics
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http://www.physik.uni-regensburg.de/forschung/evers/courses/2021/comp_nanoscience.phtml

Computational Nanoscience: Exercise Sheet No. 1

Exercise 1.1: Molecular geometry of H_2, O_2 and H_2O

(a) Install the program avogadro on your personal computer, see https://avogadro.cc/ We will need avogadro for all following exercises.

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

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

(c) Draw the molecules H_2, O_2, H_2O in avogadro. Relax[1] 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 indiviual xyz file. What are the bond lengths in each of the three molecules?

(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?

Exercise 1.2: Connection to the university computer

(a) Connect to one of the CIP pool computers. In case you have a Linux computer, open the terminal and enter

```
ssh wij11834@phy300.uni-regensburg.de
```

where you have to change `wij11834` to your RZ account. Please, also change 300 to any even number between 302 and 328 to ensure an equal distribution of students on different computers.

In case you have a Windows computer, you can install putty on your personal computer. The login works via entering `wij11834@phy300.uni-regensburg.de` into putty where the change of `wij11834` and 300 is identical to the Linux login. You can have a look at https://www.youtube.com/watch?v=9CZphjhQxIQ for a putty tutorial.

(b) In case you are new to the Linux terminal, please go through a tutorial, e.g. up to 46:05 in

https://www.youtube.com/watch?v=oxuRxtrO2Ag

[1] Relax = optimize the geometry to obtain the lowest-energy structure

(c) Create a directory `Sheet_1` on the university computer. Copy the files `H2.xyz`, `O2.xyz` and `H2O.xyz` that you have created with avogadro in Exercise 1.1 to this directory (e.g. opening `H2.xyz` on your computer with a text editor, selecting all lines, copying them and inserting them on the university computer, e.g. by opening `vim H2.xyz` with vim, then pressing `ESC` and `i` and then pasting the copied lines). Execute `cat H2.xyz`, `cat O2.xyz` and `cat H2O.xyz` on the Uni computer to check whether the files are there on the university computer.

Exercise 1.3: 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,

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

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

$$\Psi^\mathrm{Prod}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\, \psi_2(\mathbf{r}_2) \ldots \psi_N(\mathbf{r}_N) \,, \tag{2}$$

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

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

(a) Prove: Ψ^Prod from Eq. (2) satisfies

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

Why is a factor 2 appearing in the lecture notes?

(b) Which condition on many-body fermion wavefunctions Ψ is not fulfilled by product wavefunctions from Eq. (2)?

Exercise 1.4: Molecular orbital diagram of Li_2

The Li_2 molecule is a molecule known in the gas phase. We consider Li_2 because it is illustrative to treat in molecular orbital (MO) theory.

(a) How many electrons does Li_2 have and which atomic orbitals will be involved in the bonding?

(b) Follow MO theory and write the Hamiltonian in the atomic orbital basis of 1s / 2s functions of Li.

(c) Find the energy levels in MO theory. It is not necessary to explicitly compute the numerical values of the matrix elements.

(d) Draw the MO diagram using the eigenvalues from (c). Ensure that the splitting of the levels is qualitatively correct.