CompLab Report 2: Molecules

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December 30, 2023

1 Electron eigenvalues of the oxygen molecule O_2

- *Calculate the electronic energy levels of the O_2 molecule as a function of the distance d between the two O ions. Discuss the trend of the eigenvalues and total energy of the system.*

Following the instructions listed in the guide I have configured the POSCAR file in order for the system to have a cubic cell of side 10. One of the oxygen atoms is at the origin, while the other at position d, iterated from the values of 0.75 to 4 Å in a script. From running this simulation, we will obtain the electronic energy levels and the total energy of the system as a function of the interatomic distance.

```
O2
1
10 0 0
0 10 0
0 0 10
O
2
Cartesian
0 0 0
4.0 0 0
```

Figure 1. One of the POSCAR files used for the electron eigenvalues calculations of the O_2 molecule. The file is modified at each iteration. The value `4.0` is replaced by the values of d at each iteration in the given range.

In order to enforce the spin-polarized calculations, the ISPIN variable has been set to 2. The parameters LWAVE and LCHARG are specifying not to override the previously calculated WAVECAR and CARCHG files. The following INCAR file has been used.

```
SYSTEM = O2
ISMEAR = 0
SIGMA = 0.01

NELMDL = 5
ISPIN = 2

LWAVE = .FALSE.
LCHARG = .FALSE.
```

Figure 2. INCAR file used for the electron eigenvalues calculations of the O_2 molecule.

Finally, the GGA functional in the POTCAR file has been adequately chosen from the list of given potentials. The KPOINTS file remains immodified from the first report.

The next images respectively display the spin-up and spin-down eigenvalues as a function of the interatomic distance d. More specifically, it's showing an interpolation of the points.
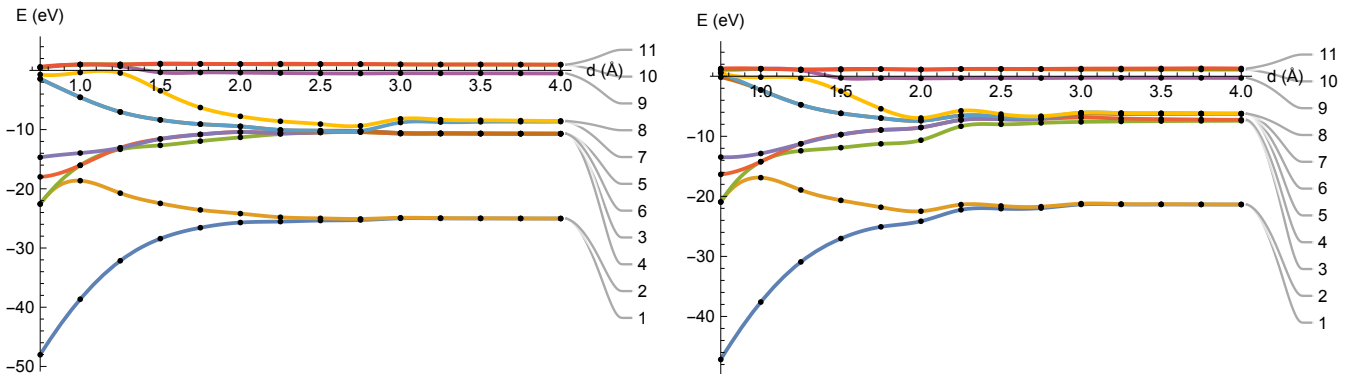

Figure 3. Spin-up and spin-down igenvalues of the O_2 molecule as a function of the distance between the two O ions.

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The trend of the eigenvalues is to converge in blocks to specific values. For example, the 1st and 2nd eigenvalues become very similar once the distance increases above a certain threshold of around 4 Å. The same happens to the eigenvalues from the 3rd to the 8th, The convergence of which various slightly from the spin-up to spin-down case.

The occupations...

Next is the plot of the variable total energy of the system as a function of the interatomic distance d. The data was obtained from the OUTCAR file by using grep and searching for the last TOTEN[1].
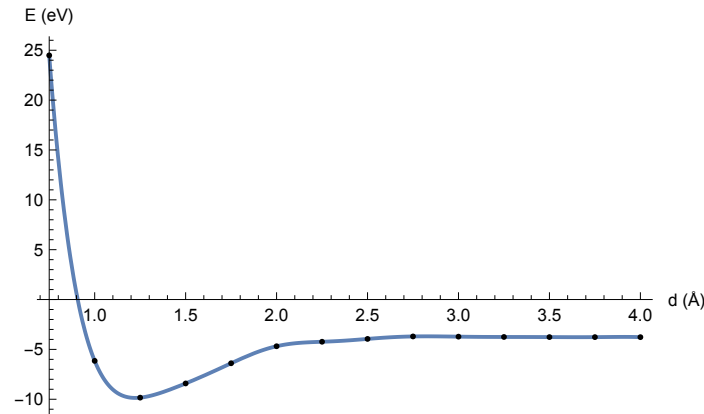

Figure 4. Total energy of the O_2 molecule as a function of the distance between the two O ions.

The total energy of the molecule paints a picture of stability only around the interatomic distance of 1.2 Å, but it doesn't seem like the system total energy converges to zero as the interatomic distance approaches greater values, or at least it doesn't seem to converge as quickly as one might hypothesize.

2 Ground state structure and binding energy of molecules

2.1 Manual relaxation

- *Calculate the ground state structures of O_2, CO and a third molecule of your choice (among H_2, N_2, and NO).*

By iterating in the same way as in the first part over the interatomic distance d, we estimated the theoretical bond lengths d^{DFT} of the O_2, CO and NO. The main idea is to calculate d^{DFT} based on a quadratic fit of the free energy TOTEN around the experimental minimum d^{exp}.

The POSCAR file is exactly the same as in the previous part. The same INCAR file has been used for all the molecules, and here is listed, the only change is the SYSTEM parameter.

```
SYSTEM = O2

ISMEAR = 0
SIGMA = 0.01
NELMDL = 5

LWAVE = .FALSE.
LCHARG = .FALSE.
```

Figure 5. INCAR file used for the molecules' calculations.

The NELMDL[2] flag gives the number off the non-self-consistent steps of the loop at the beginning.

By iterating around $\pm 10\%$ of d^{exp} and then fitting quadratically we've made the following free energy graphs. They show that d^{DFT} and d^{exp} in good agreement.

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1. Ironically, this doesn't seem to be documented on the VASP wiki. I barely found any information about the free energy TOTEN at https://www.vasp.at/wiki/index.php/O_atom.
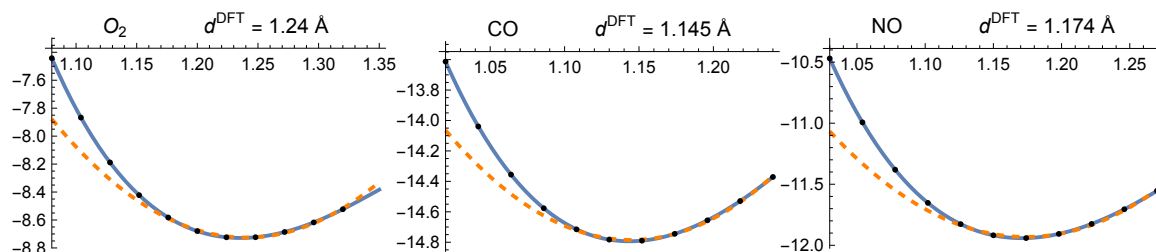
2. https://www.vasp.at/wiki/index.php/NELMDL

Figure 6.

- *Is the spin polarization (ISPIN = 2) required or not? Hint: count the number of electrons and distribute them on the available orbitals.*

  I don't know if it's necessary...

- *Compare the results for the DFT ground-state bond-length d^{DFT} with the experimental values d^{exp} in Table 1. Report the absolute values and the relative deviations in a table.*

  The experimental bound length d^{exp} is overestimated by around 1 to 3% in all the cases. This is reflected in the asymmetry of the d sampling around d^{exp} to estimate d^{DFT}.

	O_2	CO	NO
d^{DFT} (Å)	1.240	1.145	1.174
R.D.	+3.25%	+1.51%	+2.00%

Table 1. Values of the ground-state bond-length d^{DFT} for the three case-study molecules. The second row shows the relative difference with respect to the d^{exp} values tabulated in the exercise document.

- *Extract the binding energy of the O_2 molecule, by comparing the ground state energy and the energy calculated for the dissociated molecule (from Excercise 1). The total free energy can be found in the OUTCAR file ('free energy' or 'TOTEN')*

  Huh...?

3 Molecular vibrational frequency

- *Calculate the vibrational frequencies of O_2 and CO in the harmonic approximation. Compare your vibrational frequencies calculated from the quadratic fit of the energy values with the experimental values in Table 1, and report the deviations.*

  The theoretical ground-state vibrational frequencies ν^{DFT} of O_2, CO and NO are reported in the table below. They are understimated by around 5 to 15% with respect to the experimental values ν^{exp}. This could be due to an undersampled fit, but the inclusion of more data points leads to an overestimation for the O_2. The data we sampled had the same count of data points on the left and right of the d^{exp} value in order to yield a proper parabola which wasn't skewed by an unequal sampling.

	O_2	CO	NO
ν^{DFT} (THz)	44.8	57.5	52.3
R.D.	−5.57%	−13.22%	−13.38%

Table 2. Values of the ground-state fibrational frequencies ν^{DFT} for the three case-study molecules. The second row shows the relative difference with respect to the ν^{exp} values tabulated in the exercise document.

4 Bond-order model

- *Calculate the bond order b of the Li_2, Be_2, B_2 C_2, N_2, O_2, and F_2 molecules.*

  By performing the automatic relaxation for each molecule, we estimated their bond order.

The POSCAR file changes from molecule to molecule only in the ionic species. The initial bond length of 1.2 Å has been selected as a rough estimate that should rapidly converge to the proper one.

```
Li2
1
10 0 0
0 10 0
0 0 10
Li
2
Cartesian
0 0 0
1.2 0 0
```

Figure 7. POSCAR file for the bond-order model. This one is specific for Li_2, but the ionic species are changed at each iteration in order to match the correct configuration.

The INCAR file has the following configuration for each molecule, where the only parameter that changes from molecule to molecule is the SYSTEM, in order to match the one specified in the POSCAR.

```
SYSTEM = Li2
ISMEAR = 0
SIGMA = 0.01
NELMDL = 5
ISPIN = 2

IBRION = 2
NSW = 20
POTIM = 0.1
EDIFFG = 0.1

LCHARG = .TRUE.
LWAVE = .TRUE.
```

Figure 8. INCAR file for the bond-order model

The IBRION[3] is a flag which determines how the ions are updated and moved, specifically the value of 2 selects the conjugate gradient algorithm due to the relaxation problem at hand being quite difficult to evaluate for VASP. The NSW[4] flag selects the maximum number of ionic steps, and because the IBRION flag isn't 0, then it is set correctly. The POTIM[5] flag sets the time step in molecular dynamics or the step width in ionic relaxations, in this case it is on the conservative end, being lower than the suggested value for IBRION = 2 as configured previously. Finally, the EDIFFG[6] flag defines the break condition for the ionic relaxation loop. That means that the relaxation is stopped when the change of the total energy is smaller than EDIFF between two ionic steps.

The bond order of Li_2 is...

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3. https://www.vasp.at/wiki/index.php/IBRION

4. https://www.vasp.at/wiki/index.php/NSW

5. https://www.vasp.at/wiki/index.php/POTIM

6. https://www.vasp.at/wiki/index.php/EDIFFG