Computational Chemistry Lab.

Name: Marta Dominika Stanik **Exercise completion date:** 11.09.2025

Molecular orbitals and energy curves for diatomic molecules

A. Molecular orbitals of N_2

Q1: *Display all the MOs of the N_2 molecule in your report and classify each one of them as bonding, antibonding or non-bonding, and say whether the symmetry of the orbital is σ or π. Sketch a molecular orbital diagram using the values of the energy of the MOs from the output file and compare your diagram with the one in your physical chemistry or first year chemistry textbook.*

A1:

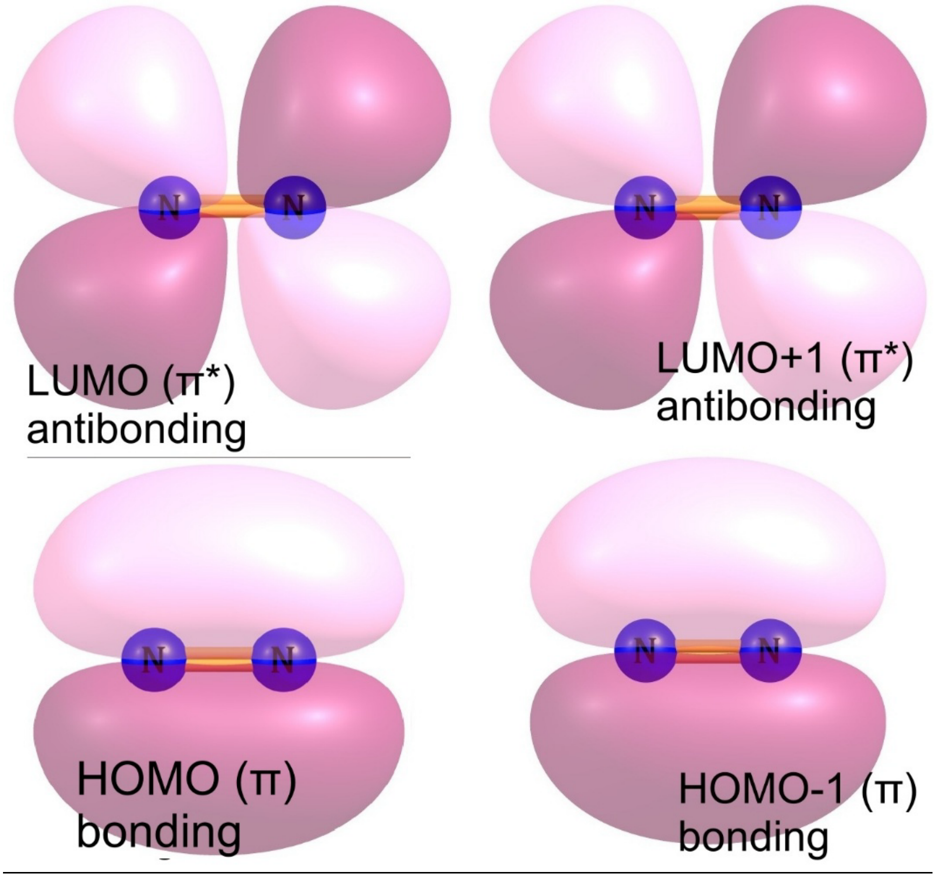


Figure 1. Orbitals LUMO, LUMO+1, HOMO and HOMO-1 for N_2 molecule

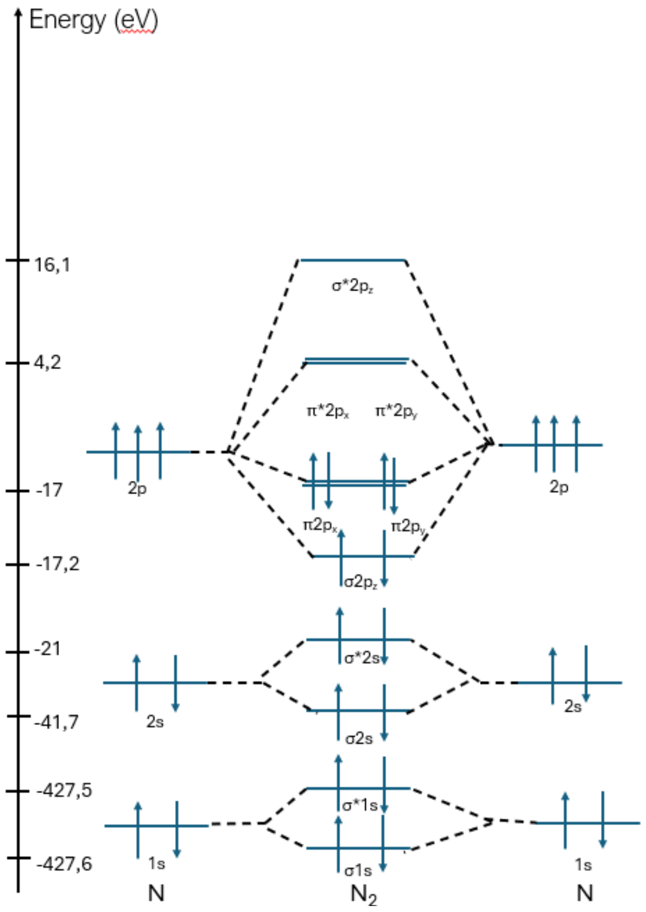
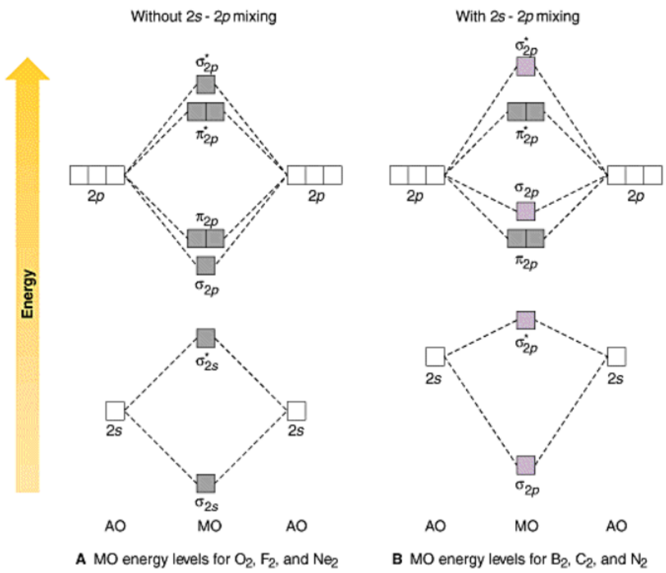


Figure 2. Sketch of N_2 molecular orbital diagram

It is important to mention that the drawing above is out of scale (the energy). It is, however, a sketch, with the purpose of displaying different energies of different molecular orbitals.



A MO energy levels for O_2, F_2, and Ne_2 **B** MO energy levels for B_2, C_2, and N_2

the relative order of sigma_2p and pi_2p is actually different

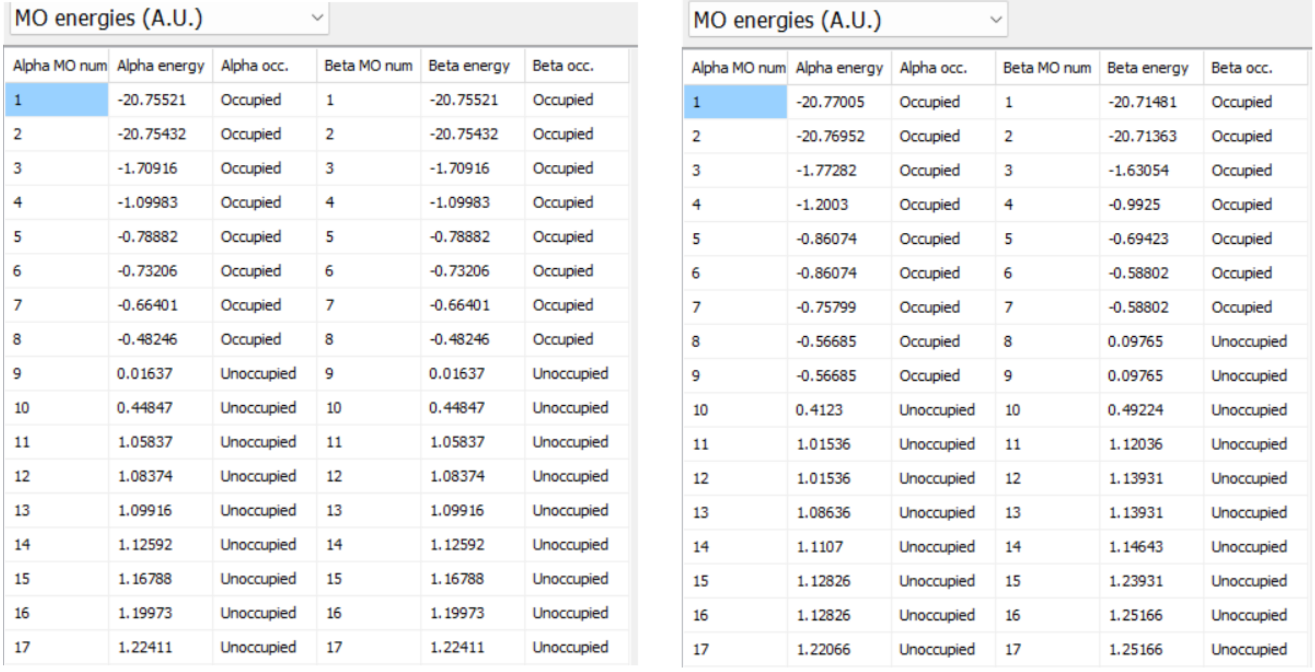
The diagram above shows similar pattern to the one drawn by hand. It does not, however, display the exact energy values (they may differ due to different calculation methods and basis sets). Nevertheless, the overall display remains similar to the textbook one.

B. Molecular orbitals of O2

<u>Q2:</u> *Which spin state is lower in energy for the O_2 molecule? Explain by referring to the energy of the MOs (recall Hund's rule). Note, that when you do calculations of the triplet state, there is a listing of both alpha and beta MOs.*

A2:

Single point energy for O_2 singlet state is -149.461724539527 au. For O_2 triplet state it is -149.545838024518 au. Therefore, triplet state is the lower in energy state for O_2 molecule.



Alpha MO num	Alpha energy	Alpha occ.	Beta MO num	Beta energy	Beta occ.
1	-20.75521	Occupied	1	-20.75521	Occupied
2	-20.75432	Occupied	2	-20.75432	Occupied
3	-1.70916	Occupied	3	-1.70916	Occupied
4	-1.09983	Occupied	4	-1.09983	Occupied
5	-0.78882	Occupied	5	-0.78882	Occupied
6	-0.73206	Occupied	6	-0.73206	Occupied
7	-0.66401	Occupied	7	-0.66401	Occupied
8	-0.48246	Occupied	8	-0.48246	Occupied
9	0.01637	Unoccupied	9	0.01637	Unoccupied
10	0.44847	Unoccupied	10	0.44847	Unoccupied
11	1.05837	Unoccupied	11	1.05837	Unoccupied
12	1.08374	Unoccupied	12	1.08374	Unoccupied
13	1.09916	Unoccupied	13	1.09916	Unoccupied
14	1.12592	Unoccupied	14	1.12592	Unoccupied
15	1.16788	Unoccupied	15	1.16788	Unoccupied
16	1.19973	Unoccupied	16	1.19973	Unoccupied
17	1.22411	Unoccupied	17	1.22411	Unoccupied

Alpha MO num	Alpha energy	Alpha occ.	Beta MO num	Beta energy	Beta occ.
1	-20.77005	Occupied	1	-20.71481	Occupied
2	-20.76952	Occupied	2	-20.71363	Occupied
3	-1.77282	Occupied	3	-1.63054	Occupied
4	-1.2003	Occupied	4	-0.9925	Occupied
5	-0.86074	Occupied	5	-0.69423	Occupied
6	-0.86074	Occupied	6	-0.58802	Occupied
7	-0.75799	Occupied	7	-0.58802	Occupied
8	-0.56685	Occupied	8	0.09765	Unoccupied
9	-0.56685	Occupied	9	0.09765	Unoccupied
10	0.4123	Unoccupied	10	0.49224	Unoccupied
11	1.01536	Unoccupied	11	1.12036	Unoccupied
12	1.01536	Unoccupied	12	1.13931	Unoccupied
13	1.08636	Unoccupied	13	1.13931	Unoccupied
14	1.1107	Unoccupied	14	1.14643	Unoccupied
15	1.12826	Unoccupied	15	1.23931	Unoccupied
16	1.12826	Unoccupied	16	1.25166	Unoccupied
17	1.22066	Unoccupied	17	1.25166	Unoccupied

Figure 3. Molecular orbitals energies for O_2 molecule's singlet (left) and triplet (right) state

The figure above shows MO energies for O_2 molecule in single and triple states. Alpha and Beta molecular orbitals number 8 and 9 show different electrons distribution – in single state orbital number 8 is occupied by 2 electrons (alpha and beta) whilst orbital number 9 remains unoccupied and in triple state both orbitals nr 8 and 9 are occupied by alpha electrons. This arrangement lowers the MO energies from -0,48246 to -0,56685 au, which is consistent with Hund's rule stating that electrons occupy degenerate orbitals singly with parallel spins before pairing. This minimizes electron–electron repulsion and lowers the total energy.

<u>Q3:</u> *Display the MOs for the ground state of the O_2 molecule in your report and classify each one as bonding, antibonding or non-bonding, and say whether the symmetry of the orbital is σ or π. Sketch a molecular orbital diagram using the values of the energy of the MOs from the output file. If you found the triplet state to be lower in energy, include both the spin-up and spin-down orbital energy in the diagram.*

A3:

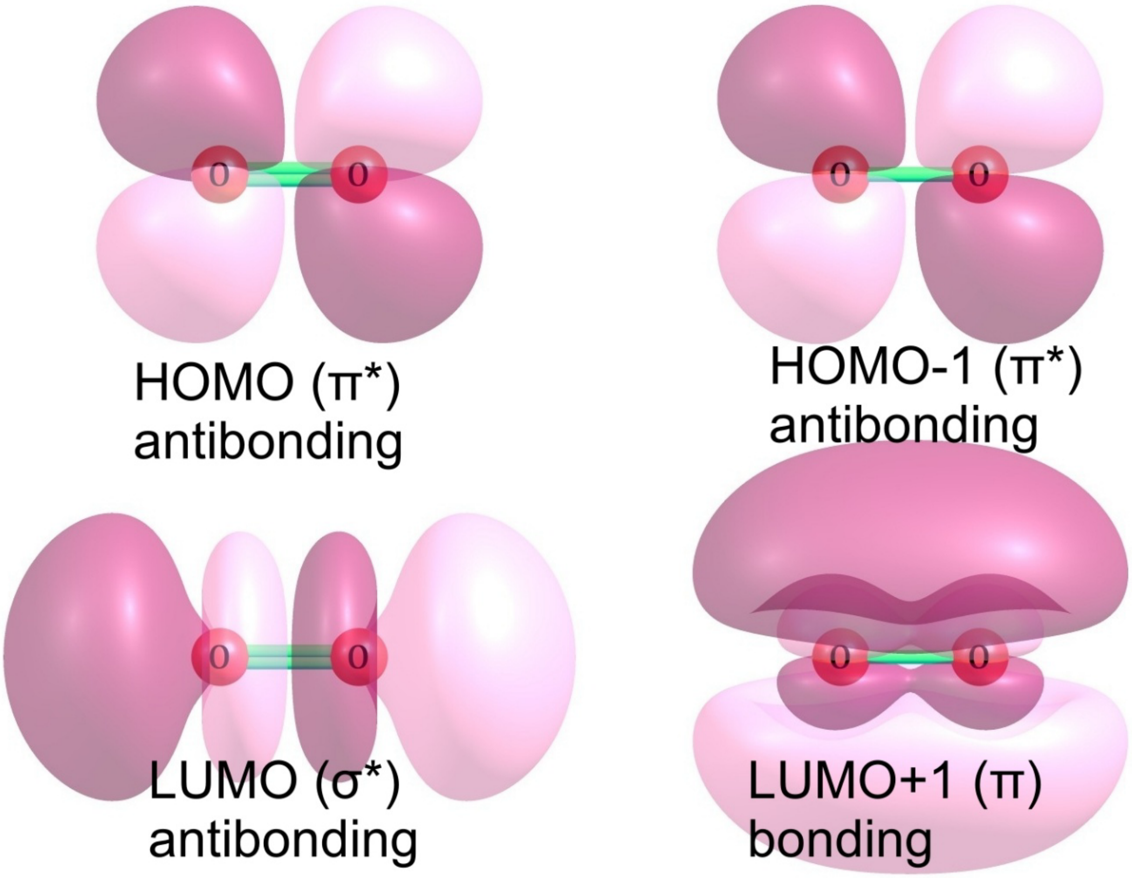


Figure 4. HOMO, HOMO-1, LUMO and LUMO+1 molecular orbitals for O_2 molecule in triplet state

should only show spin-up arrows on the left and spin-down on the right

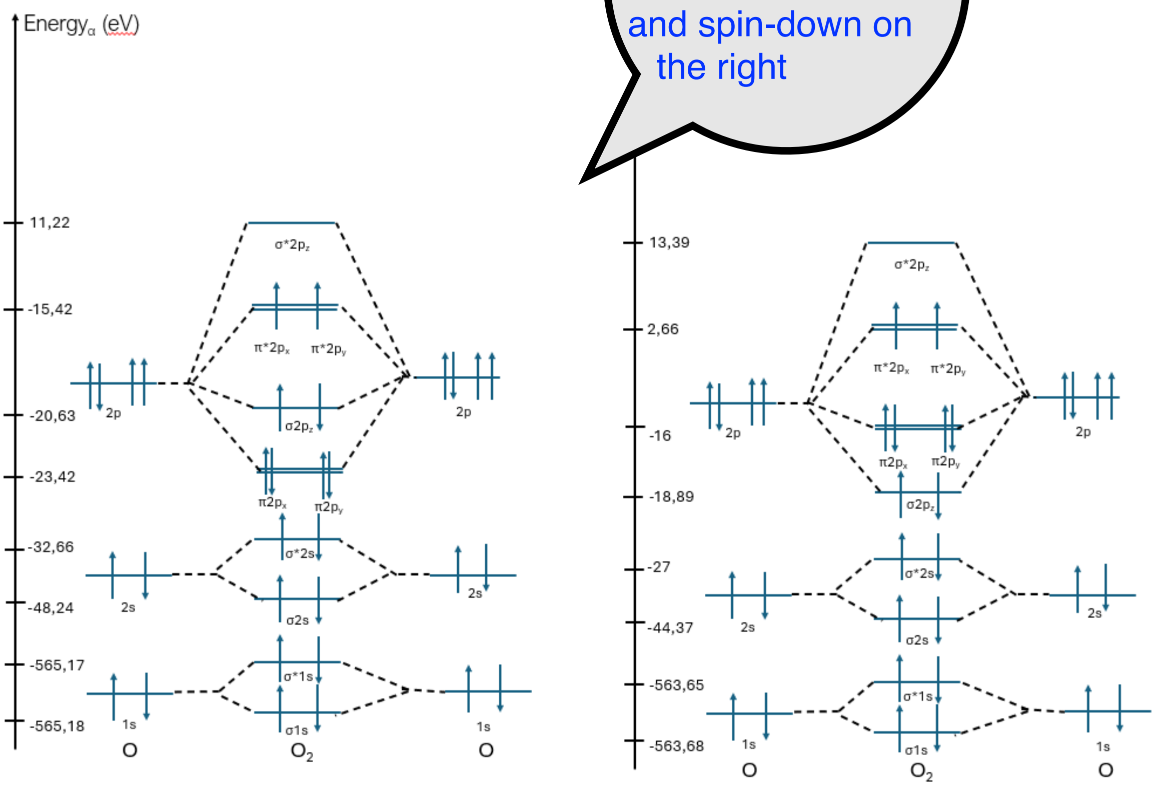


Figure 5. Out of scale sketch of molecular orbital energy diagram for O_2 molecule in triplet state for spin up (left) and spin down (right) orbital energies

Given energies (eV) in the sketch above vary for α and β orbitals, which is why two different diagrams were drawn. For spin-down electrons the energy is higher. That is because, in triplet state the spin-up electrons occupy the degenerate π* orbitals with parallel spins (which lowers their energy because of electron-electron repulsion) and, as an outcome, β electrons are destabilized.

C. H_2 energy profile #1

Q4: *Write the Slater determinant wavefunction for (a) He and (b) Li atom, expand the determinant and simplify.*

A4:

$$\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$

a) He

2ē: $\chi_1 = 1s\alpha$; $\chi_2 = 1s\beta$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix}$$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]$$

$$\Psi(x_1,x_2)=\frac{1}{\sqrt{2}}[\phi_1(\vec{r_1})\alpha(\omega_1)\phi_2(\vec{r_2})\beta(\omega_2)-\phi_2(\vec{r_1})\beta(\omega_1)\phi_1(\vec{r_2})\alpha(\omega_2)]$$

$$\Psi(x_1,x_2)=\frac{\phi_1(\vec{r_1})\phi_2(\vec{r_2})}{\sqrt{2}}[\alpha(\omega_1)\beta(\omega_2)-\beta(\omega_1)\alpha(\omega_2)]$$

b) Li

3ē: $\chi_1 = 1s\alpha$; $\chi_2 = 1s\beta$; $\chi_3 = 2s\alpha$

$$\Psi(x_1,x_2,x_3)=\frac{1}{\sqrt{3!}}\begin{vmatrix}\chi_1(1) & \chi_2(1) & \chi_3(1)\\ \chi_1(2) & \chi_2(2) & \chi_3(2)\\ \chi_1(3) & \chi_2(3) & \chi_3(3)\end{vmatrix}$$

$$\Psi(x_1,x_2,x_3)=\frac{1}{\sqrt{6}}\begin{bmatrix}\chi_1(1)\chi_2(2)\chi_3(3)+\chi_1(2)\chi_2(3)\chi_3(1)\\ +\chi_1(3)\chi_2(1)\chi_3(2)-\chi_1(3)\chi_2(2)\chi_3(1)\\ -\chi_1(2)\chi_2(1)\chi_3(3)-\chi_1(1)\chi_2(3)\chi_3(2)\end{bmatrix}$$

$$\begin{aligned}\Psi(x_1,x_2,x_3)=\frac{1}{\sqrt{6}}[&\phi_1(\vec{r_1})\alpha(\omega_1)\phi_2(\vec{r_2})\beta(\omega_2)\phi_3(\vec{r_3})\alpha(\omega_3)+\phi_1(\vec{r_2})\alpha(\omega_2)\phi_2(\vec{r_3})\beta(\omega_3)\phi_3(\vec{r_1})\alpha(\omega_1)\\ &+\phi_1(\vec{r_3})\alpha(\omega_3)\phi_2(\vec{r_1})\beta(\omega_1)\phi_3(\vec{r_2})\alpha(\omega_2)-\phi_1(\vec{r_3})\alpha(\omega_3)\phi_2(\vec{r_2})\beta(\omega_2)\phi_3(\vec{r_1})\alpha(\omega_1)\\ &-\phi_1(\vec{r_2})\alpha(\omega_2)\phi_2(\vec{r_1})\beta(\omega_1)\phi_3(\vec{r_3})\alpha(\omega_3)-\phi_1(\vec{r_1})\alpha(\omega_1)\phi_2(\vec{r_3})\beta(\omega_3)\phi_3(\vec{r_2})\alpha(\omega_2)]\end{aligned}$$

$$\begin{aligned}\Psi(x_1,x_2,x_3)=\frac{1}{\sqrt{6}}[&\alpha_1\beta_2\alpha_3\big(\phi_1(\vec{r_1})\phi_2(\vec{r_2})\phi_3(\vec{r_3})-\phi_1(\vec{r_3})\phi_2(\vec{r_2})\phi_3(\vec{r_1})\big)\\ &+\alpha_2\beta_3\alpha_1\big(\phi_1(\vec{r_2})\phi_2(\vec{r_3})\phi_3(\vec{r_1})-\phi_1(\vec{r_1})\phi_2(\vec{r_3})\phi_3(\vec{r_2})\big)\\ &+\alpha_3\beta_1\alpha_2\big(\phi_1(\vec{r_3})\phi_2(\vec{r_1})\phi_3(\vec{r_2})-\phi_1(\vec{r_2})\phi_2(\vec{r_1})\phi_3(\vec{r_3})\big)]\end{aligned}$$

where $\alpha_1=\alpha(\omega_1)$, $\beta_2=\beta(\omega_2)$ *etc.*

<u>Q5:</u> *Make a graph of the energy of the* H_2 *molecule versus the distance between the atoms (using, for example, the program gnuplot). Select the zero of energy to be the energy of two isolated H atoms.*

<u>A5:</u>

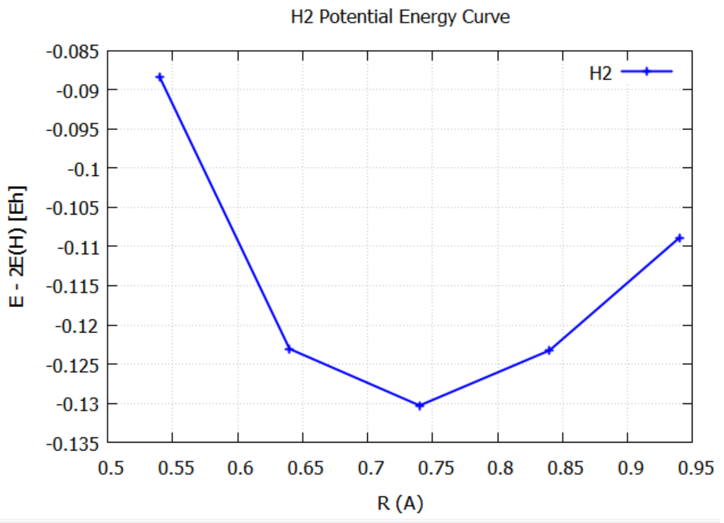


Figure 6. Energy graph for H_2 *molecule relative to two isolated H atoms*

Q6: *What value should the energy approach when the bond length is increased to infinity? Does the binding curve you calculated indicate this?*

A6:

The Calculated Surface using the SCF energy

0.40000000	-0.93300420
0.50000000	-1.05802482
0.60000000	-1.11003090
0.70000000	-1.12612316
0.80000000	-1.12371294
0.90000000	-1.11168637
1.00000000	-1.09480796
1.10000000	-1.07568569
1.20000000	-1.05575928
1.30000000	-1.03582611
1.40000000	-1.01632567
1.50000000	-0.99749729
1.60000000	-0.97946955
1.70000000	-0.96231013
1.80000000	-0.94605220
1.90000000	-0.93070722
2.00000000	-0.91627125

If the bond length were to increase to infinity, the system would be considered as two separate H atoms and the energy would reach ~~approximately~~ -0,5 a.u. for each H atom. However, the calculated data indicates as if the continuous increasement of the bond length is linear to that of the energy.

Q7: *Create one graph with three curves: (1) the singlet state calculated using restricted Hartree-Fock (RHF), (2) the singlet state calculated using unrestricted Hartree-Fock (UHF), and (3) the triplet state. Also, add a horizontal line corresponding to the energy of two isolated hydrogen atoms.*

A7:

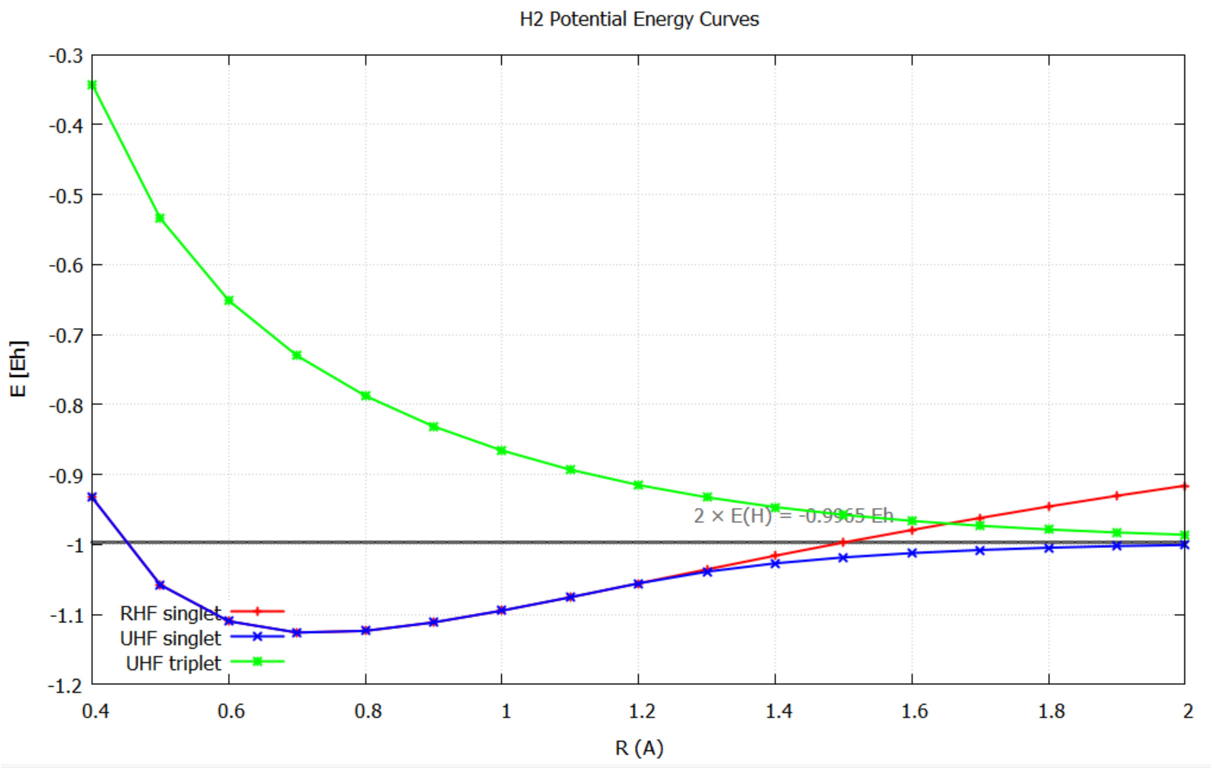


Figure 7. Energy graph for H_2 molecule using RHF, UHF in singlet state and UHF in triplet state

Q8: *Compare the RHF and the UHF curves for the singlet state. Describe the problem that occurs in the RHF calculation for large distances between the H atoms. What is the reason for this? Hint: This is a limitation of the single Slater determinant representation of the wave function. Write the Slater determinant for H_2 using bonding molecular orbitals (in terms of 1s atomic orbitals), then expand and simplify to identify the terms responsible for the large increase in energy as the distance between the atoms increases. (See the discussion in the document "OnMOsForH2andDissociation").*

A8:

The RHF curve is ~~linearly~~ increasing with the bond length (large R), which does not occur for the UHF singlet state curve. The RHF energy does not approach the correct dissociation limit for 2H, and therefore does not meet with the UHF curve.

RHF

For 2ē:

$$\chi_1(x) = \phi(i)\alpha(j)\,;\ \chi_2(x) = \phi(i)\beta(j)$$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2!}}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix}$$

$$\phi_1 = \phi_2 = \sigma_g$$

$$|A> \equiv 1s_A; |B> \equiv 1s_B$$

For small R:

$$S =< A|B > \neq 0$$

$$\sigma_g = N_\sigma(|A> + |B>);\ <\sigma_g|\sigma_g> = 1$$

$$1 =< \sigma_g|\sigma_g \geq N_g^2(<A|A> + <A|B> + <B|A> + <B|B>) = N_g^2(2+2S)$$

$$N_g = \frac{1}{\sqrt{2(1+S)}}$$

Again,

$$\phi_1 = \phi_2 = \sigma_g$$

and so, for RHF:

$$\Psi_{RHF} = \frac{1}{\sqrt{2}}\sigma_g(1)\alpha(1)\sigma_g(2)\beta(2) - \sigma_g(1)\beta(1)\sigma_g(2)\alpha(2) = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2)\big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\big)$$

$$\sigma_g(1)\sigma_g(2) = \frac{1}{2(1+S)}[\underset{ionic}{A(1)A(2)} + \underset{covalent}{A(1)B(2)} + \underset{covalent}{B(1)A(2)} + \underset{ionic}{B(1)B(2)}]$$

for $R \to \infty, S \to 0,$

and so

$$\frac{1}{2(1+S)} = \frac{1}{2}$$

which means that 50% of the terms are ionic and 50% covalent.

So, in case of R→∞, ionic terms are of issue. It means that even though the atoms are separated, there's 50% probability that atom A/B contains both electrons, which is inaccurate and causes energy increasement.

UHF

The problem regarding dissociation in RHF can be fixed by UHF:

$$\chi_1 = \phi_1\alpha \approx 1s_A\ ;\ \chi_2 = \phi_2\beta \approx 1s_B$$

and

$$\phi_1 \neq \phi_2$$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2!}}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\big(\phi_1(1)\alpha(1)\phi_2(2)\beta(2) - \phi_2(1)\beta(1)\phi_1(2)\alpha(2)\big)$$

$$\Psi_{UHF} = \frac{1}{\sqrt{2}}[1s_A(1)\alpha(1)1s_B(2)\beta(2) - 1s_B(1)\beta(1)1s_A(2)\alpha(2)]$$

In UHF we don't use σ_g built from atomic orbitals: in large R orbitals are no longer a combination of A and B. Therefore, α and β are localized on separate atoms, and so: S = <A|B> → 0

<u>Q9:</u> *Can two H-atoms form a bond in the triplet state? Explain*

<u>A9:</u>

one electron in bonding MO and the other in antibonding, so no net bond

Two H-atoms cannot form a bond covalently in a triplet state. Triplet state of H_2 molecule means that the spins are parallel to each other and therefore cannot both occupy the same bonding orbital (Pauli's exclusion) without increasing the energy of the system.

Q10: *How does the binding curve of this calculation differ from the previous UHF calculation? Explain.*

A10:

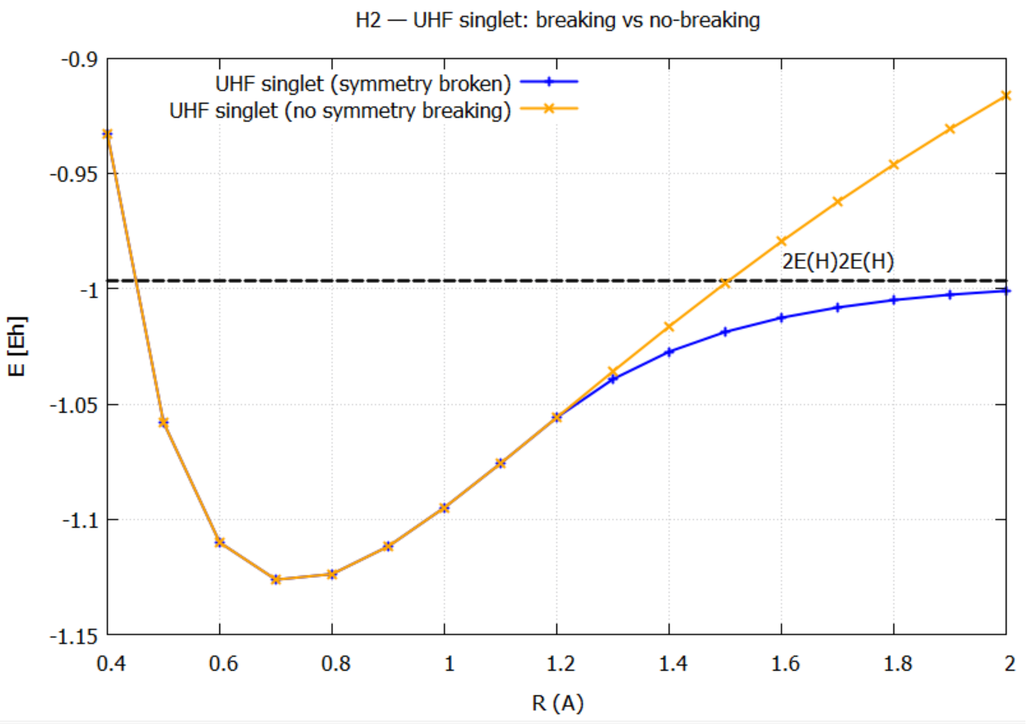


Figure 8. H_2 molecule in singlet state curve calculated using UHF with and without breaking the symmetry

Without breaking the symmetry, the UHF calculated curve for singlet state of H_2 looks identically to the one calculated previously by RHF. Even though Orca was instructed to do an UHF calculation, without breaking the symmetry in the initial guess for the wave function, the result appears to be same as the RHF one. That is because the initial guess converges to a solution in which α and β orbitals remain identical.