Excited States

A. Excitation energies of H_2 molecule

In this exercise, you will calculate approximations to the excitation energies of the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states of the H_2 molecule using the Hartree-Fock method as well as the Kohn-Sham method with different density functionals, and compare the results to full configuration interaction calculations.

The Hartree-Fock and Kohn-Sham calculations of an excited state will be performed using the variational method, whereby the molecular orbitals are variationally optimized for the excited state. In practice, to calculate the energy of an excited state you will (1) perform a ground state calculation to obtain the ground state orbitals, (2) prepare the initial guess for the excited state calculation by promoting one or more electrons from ground state occupied orbitals to unoccupied orbitals, and (3) use this initial guess with an SCF method that can avoid variational collapse to the ground state in order to obtain an excited state solution. This procedure is illustrated below for the case of a calculation with Hartree-Fock.

Ground state calculation

Create the H_2 molecule with a bond length of 0.74 Å, and use the ORCA program to perform a ground state calculation using unrestricted Hartree-Fock (UHF) and the 6-311G** basis set. The calculation will generate a '.gbw' file with the same base name as the input file, containing the optimized orbitals of the ground state.

Preparing the initial guess and performing an excited state calculation

To perform a variational optimization of an excited state, you need to create a new ORCA input file:

```
!UHF 6-311G** MOREAD

%moinp "file_base_name.gbw"

%scf
  rotate
    {orb_i, orb_a, 90, spin_i, spin_a}
    ...
  end
CNVDIIS false
LShift 1.5
end
```

The first two lines at the beginning of the file read the orbitals from the ground state calculation:

```
!UHF 6-311G** MOREAD

%moinp "file_base_name.gbw"
```

where `file_base_name` is the base name of the input file of the ground state calculation.

The second part of the file uses the `rotate` feature (subblock of `%scf ... end`) to prepare the initial guess orbitals. The command:

Comp. Chem. 2022   **Lab 11**   **Gianluca Levi & Hannes Jónsson**

University of Iceland   **Excited States**   **André Wark & Yorick Schmerwitz**

```
rotate
  {orb_i, orb_a, 90, spin_i, spin_a}
  ...
end
```

swaps the molecular orbital with index `orb_i` in the spin channel `spin_i` with the molecular orbital with index `orb_a` in the spin channel `spin_a`, effectively promoting an electron from `orb_i` with `spin_i` to `orb_a` with `spin_a`. Keep in mind that ORCA starts counting molecular orbitals from index 0, and that the indices of spin channels α and β are 0 and 1, respectively. The dots '...' indicate that if the excitation involves multiple electrons, multiple {`orb_i, orb_a, 90, spin_i, spin_a`} lines should be included, one for each promoted electron. For example, for a double electron excitation, replace '...' with a second {`orb_i, orb_a, 90, spin_i, spin_a`} line for promotion of a second electron. *Don't forget to remove the '...' in the input script if the excitation involves only one electron!*

Excited state calculations are prone to variational collapse to the ground state. In order to avoid variational collapse during the SCF calculation, we use a technique called level shifting. You can read more about level shifting in the ORCA manual or in, e.g., Saunders & Hillier, *Int. J. of Quantum Chem.* **7** 699 (1973) and Carter-Fenk & Herbert *J. Chem. Theory Comput.* **16**, 5082 (2020). In order to use level shifting in ORCA, we set `LShift 1.5` within the `%scf ... end` block (see input script above). We further need to deactivate the DIIS procedure, which we do by setting `%CNVDIIS false`.

Calculating the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states with UHF

Now, you should be ready to calculate the excited states of the H_2 molecule with UHF. Follow the procedure outlined above to obtain approximations to the energies of the singlet $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states within Hartree-Fock with the 6-311G** basis set. The $\sigma_g \overline{\sigma}_u^*$ excited state can be viewed as resulting from promotion of one electron from the ground state HOMO σ_g orbital to the LUMO σ_u^* orbital in one spin channel, while the σ_u^{*2} excited state results from HOMO→LUMO excitation in both spin channels.

> **Q1:** *Sketch molecular orbital diagrams for the ground state (σ_g^2), and for the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states of H_2 using the values of the molecular orbital energies from the ORCA output files of the UHF calculations. Include only the two lowest energy orbitals for each spin channel and specify the occupation of the orbitals.*

> **Q2:** *Even if we use the unrestricted formalism, the calculation for the doubly excited σ_u^{*2} state of H_2 at a bond length of 0.74 Å provides a restricted, closed-shell solution (as can be confirmed by inspection of the spin density). What is the spin multiplicity of the Hartree-Fock solution of the σ_u^{*2} state? What is the spin multiplicity of the Hartree-Fock approximation of the $\sigma_g \overline{\sigma}_u^*$ state?*
>
> *Hint: Consider the (multideterminant) singlet and triplet wave functions of an open-shell system with two electrons:*
>
> $$|^1\Psi_1^2\rangle = \frac{1}{2}\left[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\right](\alpha(1)\beta(2) - \alpha(2)\beta(1))$$
>
> $$|^3\Psi_1^2\rangle = \frac{1}{2}\left[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\right](\alpha(1)\beta(2) + \alpha(2)\beta(1))$$
>
> *where ψ denotes a spatial orbital and α and β are the spin functions. Expand the two-electron Slater determinant $|\psi_1\overline{\psi_2}\rangle$ (see **Q4** of lab 3) and find the expression that relates the sum of $|^1\Psi_1^2\rangle$ and $|^3\Psi_1^2\rangle$ to $|\psi_1\overline{\psi_2}\rangle$, ignoring orbital relaxation effects. What can you deduce?*

Full configuration interaction calculations of the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states

Full configuration interaction (FCI) considers all possible electronic configurations that can be generated for a given basis set. Therefore, it is the best possible calculation that can be done for the chosen basis set and the results can be used to assess the quality of other methods.

We can use the CASSCF module available in ORCA to carry out an FCI calculation. This is because a CASSCF calculation for *all* electrons in the system and including *all* molecular orbitals available for the given basis set in the complete active space (the selection of orbitals involved in the formation of configurations in the linear expansion of the wave function) corresponds to full configuration interaction. To perform an FCI calculation using the CASSCF module in ORCA, include the following in an input script:

```
!CASSCF 6-311G**

%casscf
nel #electrons
norb #orbitals
nroots #roots
mult spin_multiplicity
end
```

`#electrons` and `#orbitals` should be the total number of electrons and spatial molecular orbitals. Check the output file of a previous UHF calculation with the 6-311G** basis set to know the total number of orbitals for an FCI calculation of H_2 with this basis set. Keep in mind that `norb` whould be the number of spatial orbitals and not spin orbitals. For example, if there 24 spin orbitals in the calculation, `norb` should be 12. `#roots` should be the number of roots (eigenvalues of the CI Hamiltonian matrix) to evaluate in the FCI calculation and it should be big enough to include the ground, $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} states of H_2. Finally, `spin_multiplicity` should be the spin multiplicity of the wanted states. The ORCA output for such calculation will report the energy and squared coefficient of the configurations that contribute the most in the expansion of the wave function for each of the states corresponding to the lowest `#roots` of the CI matrix. Here is an example, showing the information on the first root of an FCI calculation:

```
------------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 1 NROOTS= 5
------------------------------------------------


ROOT  0:  E=     -1.1683321290 Eh
      0.98207 [    0]: 200000000000
      0.00417 [   14]: 010100000000
      0.00358 [   12]: 020000000000
```

The example above shows that the configuration where the lowest orbital (orbital 0) is doubly occupied contributes by $\sim 98\%$ in the expansion of the wave function of the lowest state found in the FCI calculation, and that other configurations contribute by less than 0.5%.

Use the instructions above to perform an FCI calculation of the H_2 molecule with the 6-311G** basis set. Set up the calculation such to obtain the lowest 5 roots with singlet spin multiplicity. The first root (`ROOT  0`) corresponds to the ground state. By looking at the composition of the other four roots in the ORCA output file, identify which one corresponds to the $\sigma_g \overline{\sigma}_u^*$ excited state and which one corresponds to the σ_u^{*2} excited state.

Q3: *Calculate the vertical excitation energies for the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states of H_2 at a bond length of 0.74 Å using the total energies of the ground and excited states obtained from the UHF and FCI calculations. How do the excitation energies calculated with Hartree-Fock compare to those obtained with FCI?*

Q4: *First, focus on the results obtained for the $\sigma_g^2 \rightarrow \sigma_u^{*2}$ excitation. What does the difference between the total ground state energies obtained with FCI and with Hartree-Fock represent? And the difference between the total FCI and Hartree-Fock energies of the σ_u^{*2} excited state? Compare the errors in the Hartree-Fock energies of the ground and σ_u^{*2} states and comment on how they affect the vertical excitation energy.*

Q5: *Now, analyse the $\sigma_{\mathrm{g}}^2 \to \sigma_{\mathrm{g}}\overline{\sigma}_{\mathrm{u}}^*$ excitation. How does the error in the Hartree-Fock energy of the $\sigma_{\mathrm{g}}\overline{\sigma}_{\mathrm{u}}^*$ excited state compare to the error in the Hartree-Fock energy of the σ_{u}^{*2} state analysed in the previous question? Can you explain the observed difference?*

Hint: Refer to the conclusions of **Q2**.

Calculating the $\sigma_{\mathrm{g}}\overline{\sigma}_{\mathrm{u}}^*$ and σ_{u}^{*2} excited states with UKS

Repeat the variational calculations of the ground state and of the $\sigma_{\mathrm{g}}\overline{\sigma}_{\mathrm{u}}^*$ and σ_{u}^{*2} excited states of the H_2 molecule at a bond length of 0.74 Å using the unrestricted Kohn-Sham method with the BLYP and B3LYP exchange-correlation functionals (see lab 8 exercises) and the 6-311G** basis set.

Q6: *Collect in a table the vertical excitation energies for the $\sigma_{\mathrm{g}}\overline{\sigma}_{\mathrm{u}}^*$ and σ_{u}^{*2} states of H_2 calculated with FCI, Hartree-Fock and the Kohn-Sham method using BLYP and B3LYP. How do the Kohn-Sham excitation energies compare to the Hartree-Fock and FCI results?*

Q7: *Can you describe what type of error(s) affect the Kohn-Sham total energies of the ground and excited states (see lab 8)? Do such errors cancel in the calculation of the excitation energies? Is there a difference between the BLYP and B3LYP errors, and, if yes, can you provide an explanation?*

B. Configuration interaction of minimal basis H_2 molecule

Consider the minimal basis description of the H_2 molecule consisting of two 1s atomic orbitals, ϕ_1 and ϕ_2, each localized on one H atom. In this basis, there are only two restricted molecular orbitals, the σ_{g} and σ_{u}^* orbitals resulting from the symmetric and antisymmetric combination of ϕ_1 and ϕ_2. The (non-normalized) restricted molecular orbitals are:

$$\psi_1 \equiv \sigma_{\mathrm{g}} = \phi_1 + \phi_2 \tag{1}$$
$$\psi_2 \equiv \sigma_{\mathrm{u}}^* = \phi_1 - \phi_2 \tag{2}$$

The restricted Hartree-Fock solution for the ground state is the Slater determinant $|\psi_1\overline{\psi_1}\rangle$. In addition, one can form one doubly excited and four singly excited determinants.

As seen in the previous section, in the method of full configuration interaction (FCI), the wave function of a state is given by a linear combination of all possible configurations. On the other hand, the linear expansion can be simplified by including only configurations with the same spin and spatial symmetry (configurations with different symmetry do not contribute to the expansion). The Hartree-Fock ground state determinant $|\psi_1\overline{\psi_1}\rangle$ and the doubly excited determinant $|\psi_2\overline{\psi_2}\rangle$ have the same symmetry, but different symmetry compared to all other possible determinants. Therefore, we can write the FCI wave functions for the ground and doubly excited states of minimal basis H_2 as:

$$|\Phi_0\rangle = c_0^0 |\psi_1\overline{\psi_1}\rangle + c_1^0 |\psi_2\overline{\psi_2}\rangle \tag{3}$$
$$|\Phi_2\rangle = c_0^2 |\psi_1\overline{\psi_1}\rangle + c_1^2 |\psi_2\overline{\psi_2}\rangle \tag{4}$$

Using the linear variational method, the expansion coefficients and the energies of the two states, can be obtained as the eigenvectors and eigenvalues of the 2×2 FCI matrix:

$$\boldsymbol{H} = \begin{pmatrix} \langle\psi_1\overline{\psi_1}|\hat{H}|\psi_1\overline{\psi_1}\rangle & \langle\psi_1\overline{\psi_1}|\hat{H}|\psi_2\overline{\psi_2}\rangle \\ \langle\psi_2\overline{\psi_2}|\hat{H}|\psi_1\overline{\psi_1}\rangle & \langle\psi_2\overline{\psi_2}|\hat{H}|\psi_2\overline{\psi_2}\rangle \end{pmatrix} \tag{5}$$

The matrix elements can be obtained by using the rules for evaluating matrix elements between Slater determinants, which you have learnt in the lectures about Slater determinants and the Hartree-Fock theory in this course. $\langle\psi_1\overline{\psi_1}|\hat{H}|\psi_1\overline{\psi_1}\rangle$ is the Hartree-Fock energy of the ground state, which is given by $2h_{11} + J_{11}$.

Similarly, $\langle \psi_2 \overline{\psi_2} | \hat{H} | \psi_2 \overline{\psi_2} \rangle$ is given by $2h_{22} + J_{22}$. Both off-diagonal elements are equal to K_{12}. Therefore, we can rewrite the 2×2 FCI matrix for minimal basis H_2 in terms of one- and two-electron integrals as:

$$\boldsymbol{H} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix} \tag{6}$$

where h_{11} and h_{22} are the one-electron integrals giving the average kinetic and nuclear attraction energy of an electron, while J_{11}, J_{22} and K_{12} are the two-electron integrals giving the Coulomb repulsion and exchange interaction between electrons, respectively.

Q8: *Find the expression of the two eigenvalues of the FCI matrix of minimal basis H_2 (equation 6) in terms of one- and two-electron integrals.*

Hint: You can use that the eigenvalues ω_1 and ω_2 of a 2×2 matrix:

$$\boldsymbol{O} = \begin{pmatrix} O_{11} & O_{12} \\ O_{21} & O_{22} \end{pmatrix}$$

are:

$$\omega_1 = \frac{1}{2} \left[O_{11} + O_{22} - \sqrt{(O_{22} - O_{11})^2 + 4 O_{12} O_{21}} \right]$$
$$\omega_2 = \frac{1}{2} \left[O_{11} + O_{22} + \sqrt{(O_{22} - O_{11})^2 + 4 O_{12} O_{21}} \right]$$

Q9: *The eigenvalues of the 2×2 FCI matrix of equations 6 represent the exact energies of the ground and doubly excited states of the H_2 molecule in the minimal basis. Use the expression of the eigenvalues derived in question* **Q8** *to show analytically what is the limit of the energy for the ground and doubly excited states as H_2 dissociates, i.e. as $R \to \infty$, where R is the distance between the two H atoms. Can you provide a physical interpretation of the result?*

Hint: Use that when $R \to \infty$, the one-electron integrals tend to the energy of the isolated H atom, $h_{11} = h_{22} \to E(H)$, and ***all*** *two-electron integrals tend to the electron-electron Coulomb repulsion integral $\frac{1}{2}(\phi_1 \phi_1 | \phi_1 \phi_1)$.*

Q10: *Expand the FCI wave functions of the ground and doubly excited states of minimal basis H_2 (equations 3 and 4) in terms of the atomic orbitals ϕ_1 and ϕ_2, and show that at $R = \infty$ the coefficients in the expansions of the FCI wave functions are such that $c_1^0 = -c_0^0$ and $c_1^2 = c_0^2$.*

Hint: First expand the Slater determinants in terms of molecular orbitals, and then expand the molecular orbitals in terms of the atomic orbitals using equations 1 and 2). For simplicity, you can ignore the normalization constants and the spin functions. In the expansion in terms of atomic orbitals, identify covalent and ionic terms. Use the results of **Q9** *to deduce which terms should become zero as the bond is stretched for the ground state and for the doubly excited state.*

C. Excited state energy curves of H_2 molecule

In this exercise, you will calculate the energy of the $\sigma_g \overline{\sigma}_u^*$ and σ_u^{*2} excited states of H_2 as a function of the distance between the two H atoms using the Hartree-Fock method. You will analyse the shapes of the calculated curves and the behavior for long distances as compared to the ground state energy curve, and interpret the results based on the FCI treatment of the previous section.

Calculating the energy curve of an excited state with ORCA

The recommended procedure for obtaining an excited state energy curve with the Hartree-Fock method using ORCA is the following:

1. Perform a ground state calculation at the first geometry in the scan. For example, if the scan is from $R = 0.4$ Å to 4.0 Å, the ground state calculation should be carried out at $R = 0.4$ Å.

2. Perform an excited state calculation at the same geometry using the '.gbw' file generated in the ground state calculation as input. This step corresponds to a single-point excited state calculation and can be realized in the exact same way as done for the calculations of section A of this lab.

3. Using the '.gbw' file generated in the excited state calculation of the previous step as input, set up the calculation of the energy curve as illustrated below.

This is an example of ORCA input script to calculate the energy of the H_2 molecule in an excited state with UHF along a scan of the H_2 bond length:

```
!UHF 6-311G** MOREAD

%moinp "file_base_name.gbw"

%scf
CNVDIIS false
CNVSOSCF false
SOSCFStart 1.0
LShift 1.5
end

%paras
R = start_geometry,end_geometry,#steps
end

%method
SwitchToSOSCF true
end

*xyz 0 1
  H   0.0      0.0      0.0
  H   0.0      0.0      {R}
*
```

This input script instructs ORCA to scan the bond length of H_2, R, from the value specified by `start_geometry` to the value specified by `end_geometry` in a number of steps corresponding to `#steps` and calculate the energy with UHF and the 6-311G** basis set at each step. The first step will use the orbitals in the '`file_base_name.gbw`' file provided as input, while at each successive step, the calculation will use the orbitals optimized in the previous step as the initial guess. Since the optimized orbitals are already available from the '.gbw' at the first step, the first two commands in the `%scf` block disable the SCF procedure for the first step. The `%method` block specifies that successive steps use a method that directly finds the orbital rotations that optimize the orbitals, which is more robust than DIIS for excited state calculations at varying geometries (you can find more information about this algorithm here Neese *Chem. Phys. Lett* **325**, 93 (2000)).

UHF energy curve of the $\sigma_g \overline{\sigma}_u^*$ excited state

Use the procedure described above to calculate the energy curve of the $\sigma_g \overline{\sigma}_u^*$ excited state of H_2 from $R = 0.4$ Å to 4.0 Å in 40 steps using UHF and the 6-311G** basis set.

> **Q11:** *Is the minimum-energy bond length of the H_2 molecule in the $\sigma_g\bar{\sigma}_u^*$ excited state shorter, the same or longer compared to the equilibrium bond length of the ground state (0.735 Å for Hartree-Fock with the 6-311G** basis set)? Is this result expected based on the character of the electronic excitation?*

UHF energy curves of the σ_u^{2*} excited state

Use the procedure described above to calculate the energy curve of the σ_u^{2*} excited state of H_2 from $R = 0.4$ Å to 4.0 Å in 40 steps using UHF and the 6-311G** basis set.

> **Q12:** *Describe the behavior of the Hartree-Fock energy of the σ_u^{2*} excited state as H_2 is stretched. Does the Hartree-Fock energy curve that you calculated have a minimum? Do you expect the Hartree-Fock energy to underestimate, overestimate or be the same as the result from an FCI calculation at $R = \infty$?*
>
> *Hint: You can use that for minimal basis H_2 the energy of the doubly excited state is $2h_{22} + J_{22}$. What is the limit of this expression as $R \to \infty$ and how does it compare to the limit of the FCI energy found in **Q9**?*

As for the ground state (see lab 3 exercises), the Hartree-Fock calculations retain the symmetry of the initial guess. For this reason, the UHF calculations for the σ_u^{2*} excited state converge to a restricted solution with a wave function that is symmetric with respect to inversion around the center of the molecule. As done for the ground state in lab 3, we can also break the symmetry of the initial guess for an excited state calculation to drive the convergence towards a broken-symmetry solution.

In order to obtain a broken-symmetry solution for the σ_u^{2*} excited state of H_2, perform first a ground state calculation using the `Brokensym` functionality (see lab 3) at a bond length of 4.0 Å. *Be careful, it should be a bond length of **4.0 Å** and not 0.4 Å!* Why? If you don't know, have a look at the lab 3 exercises. Then, perform an excited state calculation using the '.gbw' file from the broken-symmetry ground state calculation specifying the following excitation:

```
%scf
  rotate
    {0, 1, 90.0, 0, 0}
  end
CNVDIIS false
CNVSOSCF true
SOSCFStart 1.0
LShift 1.5
end
```

NB: We have specified only one excitation in the `rotate ... end` subblock, and not two, as done so far for the σ_u^{2*} state. The reason for this will become apparent in a moment.

> **Q13:** *Visualize the spin α and spin β occupied orbitals of the excited state solution that you just calculated. How do the orbitals appear? Are they localized on a single H atom or delocalized among both atoms? Do the orbitals possess any symmetry with respect to inversion around the center of the molecule?*

Finally, scan the energy from 4.0 to 0.8 Å using the '.gbw' file generated in the previous calculation as input and the following SCF parameters, which will use an even more robust SCF method to ensure that the calculations converge to a broken-symmetry solution:

```
!UHF 6-311G** MOREAD NRSCF

%moinp "file_base_name.gbw"

%scf
CNVDIIS false
NRMaxIt 0
NRStart 1.0
```

end

Q14: *Plot in the same figure the energy curve that you just obtained for a broken-symmetry solution of the doubly excited state with the energy curve obtained previously for the same state without symmetry breaking. Does the energy curve of the broken-symmetry solution display a minimum? If yes, can you provide an explanation? Does the energy curve of the broken-symmetry solution have the correct limit for $R \to \infty$?*

Hint: For minimal basis H_2, at $R = \infty$, the molecular orbitals of the broken-symmetry solution become equal to the 1s atomic orbitals, ϕ_1 and ϕ_2, respectively. What is the energy of a Slater determinant formed by these two orbitals and how does how does it compare to the FCI energy of the doubly excited state obtained in the previous section?