Excited Electronic States

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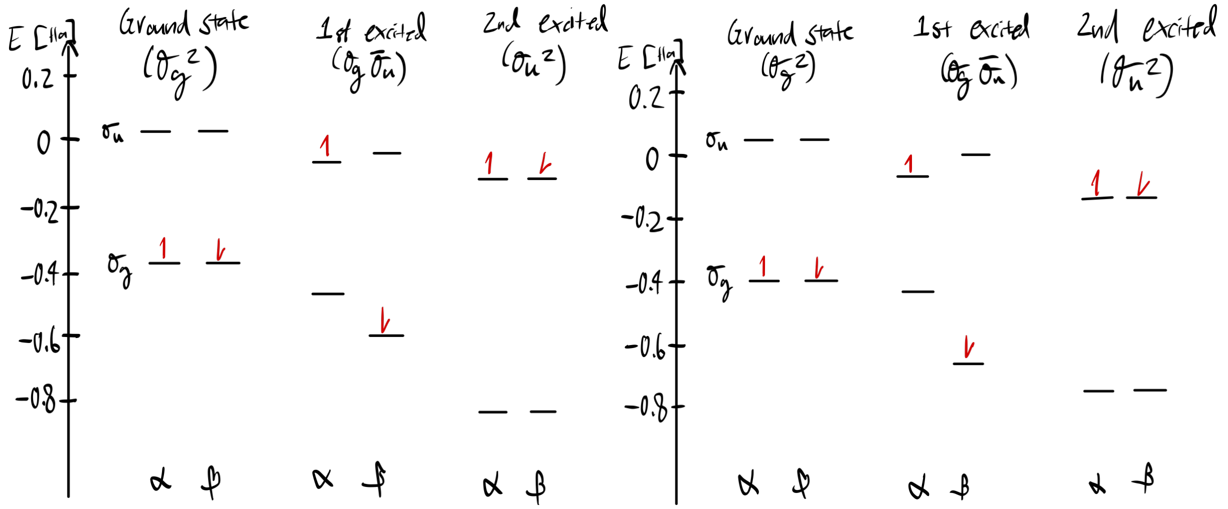
A. Energy of excited states of the H_2 molecule

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 UKS calculations. Include only the two lowest energy orbitals for each spin channel and specify the occupation of the orbitals.



(a) (b)

✓

Figure 1: *Calculated energies for the molecular orbitals of the hydrogen molecule using UKS and the 6-311G** basis set. Energies are shown for the ground state (σ_g^2) and the $\sigma_g\overline{\sigma}_u$ and σ_u^2 excited states. The calculations were performed using two different exchange and correlation functionals: (a) BLYP, and (b) B3LYP.*

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 $\sigma_g\bar{\sigma}_u$ state? Hint: Consider the (multideterminant) singlet and triplet wave functions of an open-shell system with two electrons:

$$\begin{aligned}
|{}^1\Psi_1^2\rangle &= \frac{1}{2}\Big[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\Big]\Big(\alpha(1)\beta(2) - \alpha(2)\beta(1)\Big), \\
|{}^3\Psi_1^2\rangle &= \frac{1}{2}\Big[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\Big]\Big(\alpha(1)\beta(2) + \alpha(2)\beta(1)\Big),
\end{aligned}$$

where ψ denotes a spatial orbital and α and β are the spin functions. Expand the two-electron Slater determinant $|\psi_1\bar{\psi}_2\rangle$ (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 $|\psi_1\bar{\psi}_2\rangle$, ignoring orbital relaxation effects. What can you deduce?

The spin multiplicity of the Hartree-Fock solution of the σ_u^2 state is a singlet since both electrons occupy the same spatial orbital. However, the spin multiplicity for the of the Hartree-Fock approximation of the $\sigma_g\bar{\sigma}_u$ state is not as obvious.

The two-electron Slater determinant $|\psi_1\bar{\psi}_2\rangle$ can be expanded in the following way

$$\begin{aligned}
|\psi_1\bar{\psi}_2\rangle &= \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1) & \overline{\psi}_2(1) \\ \psi_1(2) & \overline{\psi}_2(2)\end{vmatrix} \\
&= \frac{1}{\sqrt{2}}\Big[\psi_1(1)\overline{\psi}_2(2) - \psi_1(2)\overline{\psi}_2(1)\Big] \qquad (1) \\
&= \frac{1}{\sqrt{2}}\Big[\psi_1(1)\alpha(1)\,\psi_2(2)\beta(2) - \psi_1(2)\alpha(2)\,\psi_2(1)\beta(1)\Big].
\end{aligned}$$

The sum of $|{}^1\Psi_1^2\rangle$ and $|{}^3\Psi_1^2\rangle$ is given by

$$\begin{aligned}
|{}^1\Psi_1^2\rangle + |{}^3\Psi_1^2\rangle &= \frac{1}{2}\Big[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\Big]\Big(\alpha(1)\beta(2) - \alpha(2)\beta(1)\Big) \\
&\quad + \frac{1}{2}\Big[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\Big]\Big(\alpha(1)\beta(2) + \alpha(2)\beta(1)\Big) \\
&= \frac{1}{2}\Big[\psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_1(1)\psi_2(2)\alpha(2)\beta(1) + \psi_1(2)\psi_2(1)\alpha(1)\beta(2) \qquad (2) \\
&\quad - \psi_1(2)\psi_2(1)\alpha(2)\beta(1) + \psi_1(1)\psi_2(2)\alpha(1)\beta(2) + \psi_1(1)\psi_2(2)\alpha(2)\beta(1) \\
&\quad - \psi_1(2)\psi_2(1)\alpha(1)\beta(2) - \psi_1(2)\psi_2(1)\alpha(2)\beta(1)\Big] \\
&= \psi_1(1)\alpha(1)\,\psi_2(2)\beta(2) - \psi_1(2)\alpha(2)\,\psi_2(1)\beta(1).
\end{aligned}$$

Thus,

$$|{}^1\Psi_1^2\rangle + |{}^3\Psi_1^2\rangle = \sqrt{2}\,|\psi_1\bar{\psi}_2\rangle\,. \tag{3}$$

Therefore, the spin multiplicity of the Hartree-Fock approximation of the $\sigma_g\bar{\sigma}_u$ state is an equal mixture of the singlet and triplet configuration-state functions, and is no longer an eigenfunction of $\hat{S}^2$. ✓

Q3: Collect in a table the values of the vertical excitation energy for the $\sigma_g\bar{\sigma}_u$ and σ_u^2 states of H_2 calculated with the BLYP and B3LYP functionals. How do the values of the excitation energy obtained with the two functionals compare?

As shown in Table 1, both excited states have larger vertical excitation energies when computed with the B3LYP functional compared to BLYP.

Table 1: *Vertical excitation energy for the $\sigma_g\bar{\sigma}_u$ and σ_u^2 states of H_2 calculated with the BLYP and B3LYP functionals.*

State	σ_g^2	$\sigma_g\bar{\sigma}_u$		σ_u^2	
Functional	$E_{\sigma_g^2}$ [Ha]	E [Ha]	ΔE [Ha]	E [Ha]	ΔE [Ha]
BLYP	-1.16928	-0.75440	0.41487	-0.17104	0.99823
B3LYP	-1.17293	-0.75035	0.42258	-0.15837	1.01456

✓

Q4: Describe what type of error(s) can be expected in the estimated energy when a Kohn-Sham functional is used (see lab 8)? What type of error will likely not cancel out when the excitation energy is calculated? What is the difference between the BLYP and B3LYP functionals?

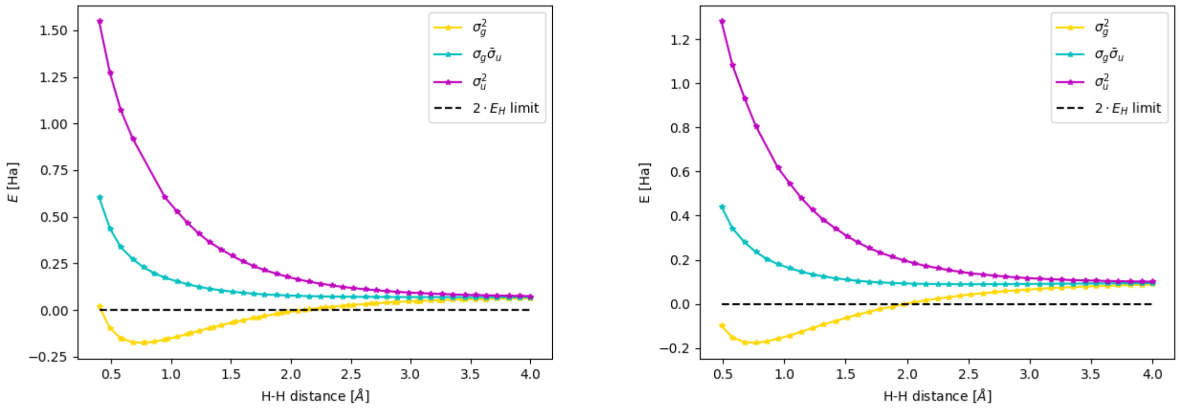
Kohn-Sham calculations tend to over-delocalize and thus overestimate binding energies. Self-interaction error (SIE) is also inherent in KS calculations.

However, SIE and density over-delocalization partly cancel when energy differences are taken between similar electronic states, such as in many ground-state reaction energies. However, this cancellation is much weaker for excitation energies and stretched-bond configurations, because the electron distributions differ significantly between the states being compared.

The BLYP functional is a pure GGA functional containing no Hartree–Fock (HF) exchange, whereas B3LYP is a hybrid GGA functional that incorporates a fixed fraction of exact HF exchange. This partial inclusion of HF exchange reduces over-delocalization and self-interaction error. ✓

B. Energy curves for the excited H_2 molecule

Q5: Describe the shape of the energy curves for the $\sigma_g\bar{\sigma}_u$ and σ_u^{2*} excited state as the H_2 molecule is stretched. Do the energy curves have a minimum?



(a) **(b)**

Figure 2: *Potential energy curves of H_2 calculated using unrestricted Kohn–Sham (UKS) with the 6-311G** basis set. Results are shown for two exchange–correlation functionals: (a) BLYP and (b) B3LYP. Each plot displays the PES for the ground state (σ_g^2) and the two excited states, $\sigma_g\bar{\sigma}_u$ and σ_u^2.*

Neither the $\sigma_g\bar{\sigma}_u$ nor the σ_u^2 excited state exhibits an energy minimum as the H_2 molecule is stretched when they are computed from a UKS ground state reference without symmetry breaking. At short internuclear distances, the σ_u^2 state lies significantly higher in energy than the $\sigma_g\bar{\sigma}_u$ state. As the H-H distance increases, both excited-state energies decrease monotonically and approach the same dissociation limit as the UKS ground state curve, which remains contaminated by ionic configurations when symmetry is not broken initially, see Figure 3.

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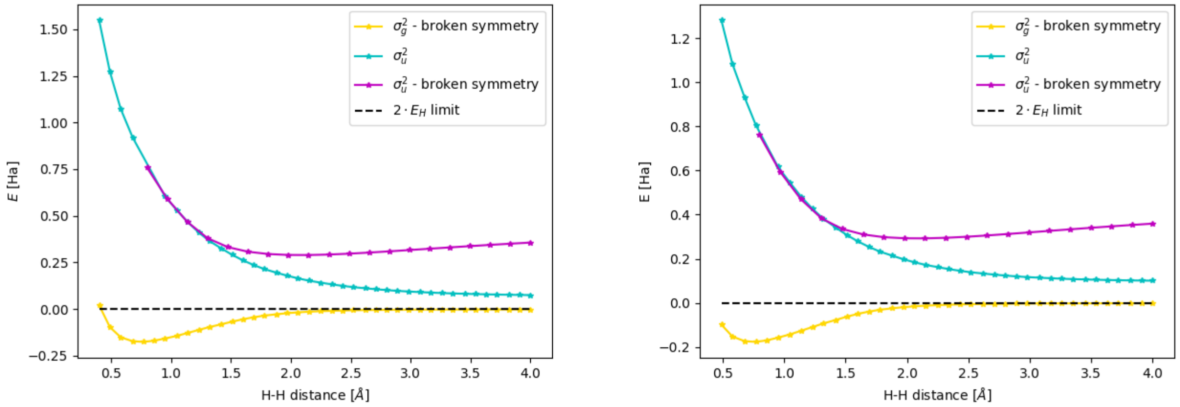
Q6: Plot the energy curve that you just obtained for a broken-symmetry solution of the doubly excited state on the same graph as the energy curve obtained previously for the same state without symmetry breaking. Does the energy curve of the broken-symmetry solution display a minimum? If yes, can you 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.



(a) **(b)**

Figure 3: *Potential energy curves of H_2 calculated using unrestricted Kohn–Sham (UKS) with the 6-311G** basis set. Results are shown for two exchange–correlation functionals: (a) BLYP and (b) B3LYP. Each plot displays the PES for the symmetry-broken ground state (σ_g^2) and the σ_u^2 excited state. The curves are shown once referenced to the symmetry-preserving ground-state energy and once referenced to the symmetry-broken ground-state energy.*

The energy curve of the broken-symmetry solution has an energy minimum. By breaking the symmetry, both electrons are allowed to localize on one atom. Thus, the partially positively charged atom weakly attracts the partially negative atom until they experience repulsion and the energy rises again.

The two-electron Slater determinant $|\psi_2\bar{\psi}_2\rangle$ can be expanded in the following way

$$\begin{aligned} |\psi_2\bar{\psi}_2\rangle &= \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_2(1) & \overline{\psi}_2(1) \\ \psi_2(2) & \overline{\psi}_2(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}\Big[\psi_2(1)\overline{\psi}_2(2) - \psi_2(2)\overline{\psi}_2(1)\Big] \\ &= \frac{1}{\sqrt{2}}\Big[\psi_2(1)\alpha(1)\,\psi_2(2)\beta(2) - \psi_2(2)\alpha(2)\,\psi_2(1)\beta(1)\Big] \\ &= \psi_2(1)\psi_2(2)\,\frac{1}{\sqrt{2}}\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big] \\ &= \psi_2(1)\psi_2(2)\,\chi_s(1,2), \end{aligned} \tag{4}$$

where

$$\chi_s(1,2) = \tfrac{1}{\sqrt{2}}\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big]$$

is the two-electron singlet spin function.

Thus, for the 1s atomic orbitals, ϕ_1 and ϕ_2 the configuration of the antibonding molecular orbital becomes

$$\begin{aligned}|\psi_2\bar{\psi}_2\rangle &= [\phi_1(1)-\phi_2(1)][\phi_1(2)-\phi_2(2)]\chi_s(1,2)\\ &= \Big[\underbrace{\phi_1(1)\phi_1(2)+\phi_2(1)\phi_2(2)}_{\text{ionic terms}}-\underbrace{\phi_1(1)\phi_2(2)-\phi_2(1)\phi_1(2)}_{\text{covalent terms}}\Big]\chi_s(1,2).\end{aligned}$$

Therefore, if symmetry is not broken the doubly excited state converges toward the RKS limit, which is contaminated by covalent terms that lower the energy. If symmetry is broken, however, the broken-symmetry solution converges toward a purely ionic solution. ✓