Configuration Interaction

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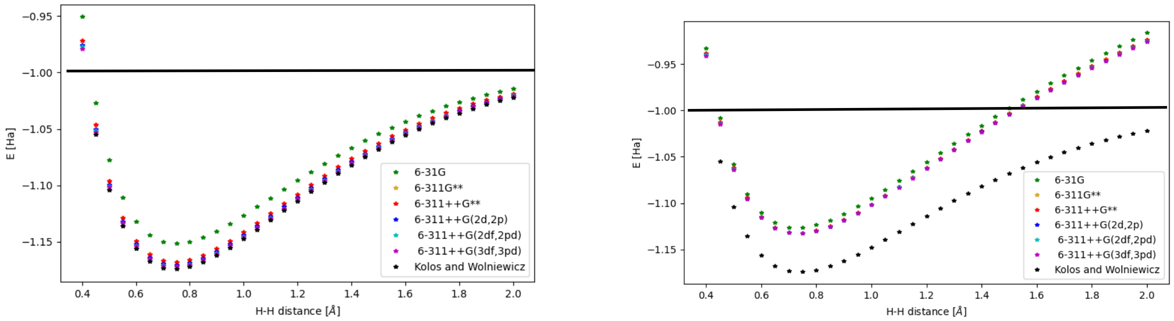
A. Dissociation curve of H_2

Q1: Make a graph showing the binding curve for the H2 molecule calculated using QCISD(T) and the various basis sets together with the results of Kolos and Wolniewicz. Do the same for the Hartree-Fock results. Discuss the comparison.



(a) *Calculations with QCISD(T).*

(b) *Calculations with Hartree–Fock.*

Figure 1: *Binding curve of the H_2 molecule calculated with various basis sets compared to the results of Kolos and Wolniewicz (black curve).*

✓

The binding curve of H_2 calculated with QCISD(T) follows Kolos' and Wolniewicz's curve for all basis sets, except 6-31G which has too low binding energy but reaches the correct limit at infinite distance between the hydrogen atoms, see Fig. 1a. However, in the restricted Hartree-Fock case, the binding energy is underestimated for all basis sets, and the limit at infinite bond length is incorrect, see Fig. 1b. due to the ionic terms.

Q2: How do the QCISD and QCISD(T) values compare? What would you expect a full CI calculation to give? Explain.

The QCISD and QCISD(T) calculations give identical results for H_2 because triple excitations are impossible for a two-electron system. A full CI calculation would also give the same result as QCISD, since doubles already span all possible excitations. ✓

B. Bond angle and singlet-triplet splitting in CH_2

Q3: How does the geometry and singlet-triplet splitting obtained using QCISD(T) compare with the Hartree–Fock results (from the previous assignment) and with the experimental values of the bond angle (134° for triplet and 102° for singlet) and a singlet-triplet energy splitting of 9.05 kcal/mol? Make a table listing the values obtained in the two types of calculations as well as the percentage difference with respect to the experimental values.

Table 1: *Calculated total energies (in kcal/mol), bond angles, singlet–triplet splittings, and percent deviations from theoretical values (134° for triplet, 102° for singlet, and* $\Delta E = 9.05$ *kcal/mol) for* CH_2.

Method	Triplet (ground)		Singlet (excited)		ΔE (Singlet-Triplet) [kcal/mol]	% Deviation (Angles)		% Deviation (ΔE)
	E [kcal/mol]	Angle [°]	E [kcal/mol]	Angle [°]		Triplet	Singlet	
QCISD(T)	-24508.05	133.07	-24495.95	101.40	12.11	0.69%	0.59%	33.78%
HF	-24431.93	131.98	-24403.25	103.58	28.68	1.51%	1.55%	216.9%

✓

Q4: Does the QCISD energy differ from the QCISD(T) energy? Why is that?

The QCISD(T) energy is slightly lower than the QCISD energy. While QCISD includes single and double excitations and approximately accounts for connected quadruple excitations through a quadratic (Davidson) correction, QCISD(T) further incorporates a perturbative treatment of triple excitations. These triple excitations capture additional electron correlation effects, leading to a more accurate and typically lower total energy estimate. ✓

Q5: Is the single Slater determinant (approximate 'Hartree-Fock') energy from these calculations, E(0), different from the one you calculated in Lab 5? If so, is it higher or lower? Explain your observation.

The single Slater determinant energy from the QCISD(T) calculations is slightly higher than the energy obtained from the Hartree–Fock calculations. This occurs because, in QCISD(T), the ~~total energy~~ geometry is minimized with respect to the inclusion of double and triple excitations, ~~while the reference Hartree–Fock determinant itself is not further optimized at this stage.~~ As a result, full minimization is not achieved at the Hartree–Fock level, leading to a slightly higher E(0) value. ✓

C. The C-C bond length in hydrocarbons

Q6: Compare the calculated C-C, C=C and C≡C bond lengths with the experimental values (1.531 Å, 1.339 Å, and 1.203 Å, respectively). What is the error in each case and what is the trend?

Table 2: *Calculated C–C bond lengths for ethane, ethylene, and acetylene, with percent deviations from experimental values (1.531 Å, 1.339 Å, and 1.203 Å, respectively).*

Method	r_{c-c} [Å]	Dev. [%]	$r_{c=c}$ [Å]	Dev. [%]	$r_{c\equiv c}$ [Å]	Dev. [%]
HF	1.5424	0.746	1.3150	1.796	1.1875	1.287
QCISD	1.5574	1.726	1.3441	0.383	1.2177	1.224

✓

The calculated bond lengths decrease from ethane to acetylene, reflecting the increasing bond order. In the HF results, the percent deviation increases for multiple bonds (C=C and C≡C) compared to the single bond, indicating HF underestimates bond length in double and triple bonds. For QCISD, the trend is reversed: the percent deviation is largest for the single bond (CC) and smaller for double and triple bonds, showing that correlation effects improve the description of multiple bonds. Overall, QCISD gives more accurate bond lengths for multiple bonds than HF.

Q7: Is the HOMO classified as bonding, non-bonding or anti-bonding for the carbon-carbon bond? How about the LUMO? Would you expect the carbon-carbon bond in the first excited state of ethylene to be longer, shorter or unchanged from that in the ground state? Elaborate.

The HOMO of ethylene is a bonding π orbital, whereas the LUMO is an antibonding π^* orbital (Fig. 2). In the first excited state, an electron is promoted from the bonding π orbital to the antibonding π^* orbital, which reduces the overall bond order. Consequently, the C–C bond in the excited state is expected to be longer than in the ground state.

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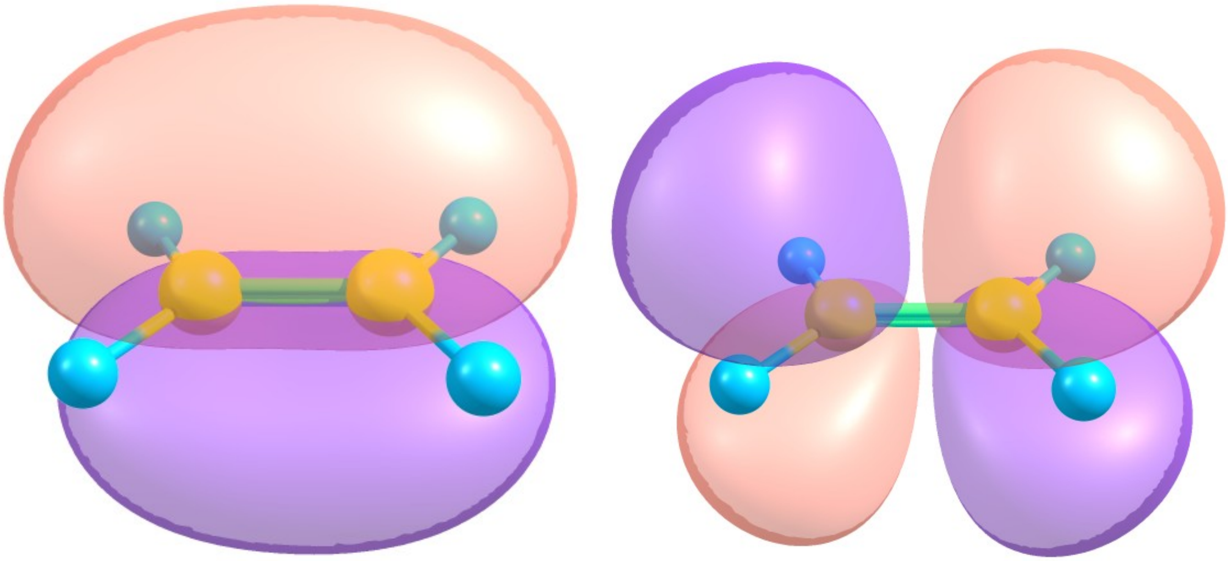
(a) (b)

Figure 2: *Molecular orbitals of the ethylene molecule; (a) HOMO and (b) LUMO. Hartree-Fock calculations were done using the 3-21G basis set.*

Q8: How does the addition of excited state determinants change the calculated carbon-carbon bond length in ethylene (explain the effect)?

The inclusion of excited-state determinants accounts for electron excitations from bonding to antibonding molecular orbitals. In ethylene, excitation from the bonding π orbital (HOMO) to the antibonding π^* orbital (LUMO) decreases the bond order from two to approximately one. This redistribution of electron density weakens the C–C π bond, resulting in a longer equilibrium bond length in the excited state compared to the ground state. In correlated methods, these excited determinants provide a more accurate description of the electronic structure by capturing the partial occupation of antibonding orbitals and the corresponding bond weakening effect. ✓