Q1: Present a table in your report, showing the calculated energy and angle of the triplet state CH2 using the various basis sets.

Basis set	**Energy (Hartree)**	**H–C–H angle°**	**C-H distances (Å)**
STO-3G	-38.43623	125.510	1.08200
3-21G	-38.70906	131.266	1.07076
6-31G	-38.91167	132.279	1.07049
6-311G	-38.9199	132.584	1.07068
6-311G*	-38.9297	131.093	1.07185
6-311G**	-38.9340	131.718	1.07222
6-311++G**	-38.9347	131.978	1.07218
6-311++G(2d,2p)	-38.9364	131.923	1.06933
6-311++G(2df,2pd)	-38.9370	131.935	1.06968
6-311++G(3df,3pd)	-38.93697	131.910	1.06961

✓

Q2: Explain the difference between the various basis sets and identify the simplest basis set that gives‘converged’ results.

The various basis sets differ in flexibility: minimal bases (STO-3G) use very few primitives, split-valence sets (3-21G, 6-31G, 6-311G) introduce multiple functions for valence orbitals, polarization functions (*) add higher-angular-momentum functions to allow angular distortion of the electronic density, and diffuse functions (+) extend the radial reach of the basis and are important for describing diffuse or open-shell density.

Numerical results (HF) show large changes when going from minimal to split-valence sets, while inclusion of polarization and diffuse functions produces progressively smaller changes. Using the 6-311++G(3df,3pd) result as reference, the energy differences reduce to = 0.00057 Hartree at the 6-311++G(2d,2p) level and to = −0.00003 Hartree at 6-311++G(2df,2pd). Thus, 6-311++G(2d,2p) = simplest basis set with accuracy.

✓

Q3: How well does the calculated bond angle agree with experiment (the experimental estimates can be found in the article of Schaeffer)? What could be the reason for the discrepancy between calculated and experimentally measured values?

Our best HF result (largest basis used) gives a H–C–H angle of 131.91° (6-311++G (3df,3pd)).

Experimental and high-level theoretical studies report a larger angle: experimental compilations list :135.5° and standard high-level post-HF calculations converge near =133–134°. The remaining 2–4° discrepancy between our HF geometry and experiment and theory is expected for missing electron correlation (method error) – Basis set incompleteness (Although our results show clear basis-set convergence trends, HF even at large basis sets cannot recover correlation energy, so increasing basis size ~~improves~~ gives the HF limit but does not remove the main HF deficiency) i.e. missing correlation ✓
– Zero point energy and vibrational averaging.

Q4: Consider starting with a linear geometry of the CH2 molecule and then carrying out geometry optimization. Would this lead to different results for the bond angle? Explain.

An unconstrained geometry optimization of CH_2 started from a linear geometry will normally relax to the same bent triplet minimum: the linear arrangement is a higher-energy stationary point (saddle) and is not the true ground state. Exceptions occur if molecular symmetry or coordinates are artificially constrained. ✓

It is possible that the geometry optimization does not bend the molecule since the atomic forces that would lead to bending are zero the saddle point due to symmetry.

Part B:

Q5: Present a table in your report showing the calculated energy and angle of the singlet state CH2 as well as the singlet-triplet splitting using the various basis sets.

Basis set	**Energy (Hartree)**	**H–C–H angle°**	**C-H distances (Å)**
STO-3G	-38.3723	100.452	1.12260
3-21G	-38.6518	104.648	1.10202
6-31G	-38.85338	105.675	1.10051
6-311G	-38.86439	105.745	1.10142
6-311G*	-38.8838	103.207	1.09714
6-311G**	-38.88751	103.208	1.09880
6-311++G**	-38.88903	103.579	1.09809
6-311++G(2d,2p)	-38.89172	103.666	1.09471
6-311++G(2df,2pd)	-38.89218	103.749	1.09494
6-311++G(3df,3pd)	-38.89241	103.769	1.09484

✓

Q6: How does the predicted singlet-triplet splitting using the Hartree-Fock approximation compare with the best estimate (see the article by Schaeffer)? What could be the reason for the discrepancy? (Recall the discussion of exchange-correlation and the Fermi hole).

Basis set	**ΔE =E(singlet) − E(triplet) (Hartree)**
STO-3G	+0.06393
3-21G	+0.05726
6-31G	+0.05829
6-311G	+0.05551
6-311G*	+0.04590
6-311G**	+0.04649
6-311++G**	+0.04567
6-311++G(2d,2p)	+0.04468
6-311++G(2df,2pd)	+0.04482
6-311++G(3df,3pd)	+0.04456

The HF(6-311++G(3df,3pd)) calculation yields a singlet–triplet splitting of ΔE = 0.04456 Hartree, considerably larger than the best experimental and high-level theoretical estimates of =0.01275–0.01594 Hartree. The primary reason for this discrepancy is methodological: Hartree–Fock includes exact exchange (the Fermi hole), which preferentially stabilizes same-spin (triplet) configurations, but it neglects dynamic electron correlation (the correlation hole) that stabilizes the singlet much more.

The singlet and triplet are therefore not presented at the same level of theory in HF calculations, the triplets having thus too large stabilization as compared to singlets. ✓

Q7: How does the predicted bond angle using the Hartree-Fock approximation compare with the best estimate?

Triplet state:
- HF (largest basis, 6-311++G(3df,3pd)) : Angle = 131.91°.
- Best estimate: Angle = 133.93° ✓
-HF underestimates the triplet angle by =2.02°.

Singlet state:
- HF (largest basis, 6-311++G(3df,3pd)) : Angle = 103.769°. ✓
- Best estimate: Angle = 102°.
-HF overestimates the singlet angle by =1.77°.

These discrepancies persist even with large basis sets because Hartree–Fock neglects dynamic electron correlation and, for the singlet state, the electronic structure has multireference character that HF cannot describe well. Correlation energy stabilizes the singlet relative to the triplet and slightly alters bond angles; therefore, correlated methods (MP2 or multireference approaches) and inclusion of zero-point energy and vibrational averaging are needed to reach quantitative agreement with experiment.

Q8: It is an important rule to add or subtract only numbers obtained at the same level of theory, in particular with the same basis set. Why is that? (make sure you follow that rule in the calculations of the singlet-triplet splitting).

because each level of theory and each basis set introduces different systematic errors and reference energy scales. When two results from different theoretical levels or basis sets are combined, these errors do not cancel out but rather accumulate.
For example, in the calculation of singlet–triplet splitting, using different basis sets for the two states would mix basis set incompleteness errors with the actual physical energy difference, making the comparison unreliable. Therefore, both the singlet and triplet energies must be computed consistently at the same theoretical level to ensure that only the true electronic energy difference is measured. ✓

C. Discussion

Q9: Why is the ground state of CH2 a triplet state? (recall the expression for the contribution of each pair of electrons to the total energy in restricted Hartree-Fock calculations and make use of that in your argument).

The triplet state of CH_2 is lower in energy because the two unpaired electrons have parallel spins and occupy different orbitals. This reduces electron–electron repulsion through the exchange interaction (Fermi hole effect). In contrast, in the singlet state both electrons occupy the same orbital, increasing Coulomb repulsion. Therefore, the exchange stabilization makes the triplet the ground state. ✓

Q10: Predict the hybridization of the carbon in the singlet state and in the triplet state of CH2. Use this to rationalise the bond angle in the singlet and triplet states of the molecule. How would the VSEPR rules predict qualitatively the bond angle in the singlet and triplet states?

In the singlet state, both nonbonding electrons are paired in one orbital, leading to an sp^2-like hybridization with one lone pair and two C–H σ bonds. The lone-pair–bonding repulsion compresses the H–C–H angle to about 102°.

In the triplet state, the two unpaired electrons occupy nearly pure ~~p~~ sp3 hybrid orbitals orbitals, so the bonding orbitals have more sp^3 character. The absence of strong lone-pair repulsion allows a wider H–C–H angle (~132°).

According to VSEPR theory, the singlet (one lone pair) should be more bent, while the triplet (two singly occupied orbitals) should be more open ,consistent with calculations and experiment. ✓