Perturbation Calculations, MP2

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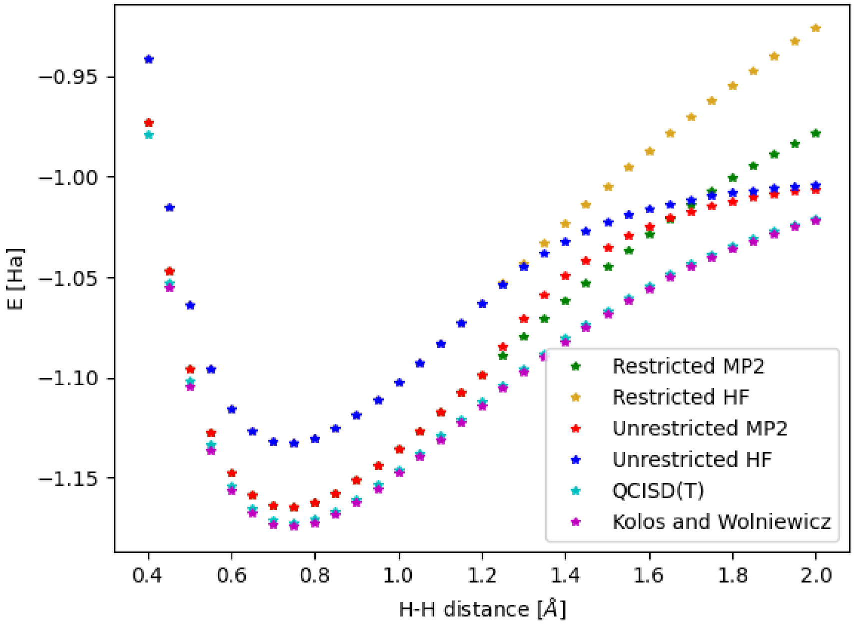
A. Dissociation curve of H_2

Q1: Make a graph showing the calculated binding curves for the restricted and unrestricted MP2 calculation, the corresponding HF values and the exact results by Kolos and Wolniewicz.



✓

Figure 1: *Potential energy curve of H_2 calculated using restricted and unrestricted MP2, HF, and UHF methods with the 6-311++G(3df,3pd) basis set. The magenta curve represents the near-exact results of Kolos and Wolniewicz, serving as a benchmark. The QCISD(T) calculation from the previous exercise (using the same basis set) is also included. The unrestricted MP2 and UHF methods correctly approach the dissociation limit, whereas the restricted methods deviate significantly at large internuclear separations.*

Q2: Describe and explain the difference between the restricted and unrestricted MP2 calculation. Identify the region of the unrestricted MP2 binding curve where the effect of spin contamination is significant. Is the effect of spin contamination still present at the dissociated limit?

Restricted MP2 (RMP2) and unrestricted MP2 (UMP2) differ in how they treat electron spins in the reference Hartree–Fock (HF) wavefunction. In RMP2, the α and β electrons are constrained to occupy the same spatial orbitals, maintaining a pure spin state. This works well near equilibrium but fails to describe bond dissociation correctly, as it cannot represent separated atoms with unpaired electrons. In contrast, UMP2 allows the α and β orbitals to differ, enabling an accurate description of the dissociation limit where each hydrogen atom contains one electron. However, this flexibility introduces spin contamination, which arises because the underlying UHF reference is not a pure total spin eigenfunction. As the H–H bond stretches, the UHF wavefunction mixes singlet and triplet components, leading to $\langle S^2 \rangle$ values greater than zero. This contamination carries over into the UMP2 correlation energy, causing deviations in the potential energy curve around 1.2–1.7 Å, but it vanishes at the dissociation limit where the electrons localize on separate atoms. ✓

Q3: How do the MP2 results compare with the QCISD(T) results obtained in the previous exercise?

The MP2 calculations deviate more from the results of Kolos and Wolniewicz than the QCISD(T) results obtained in the previous exercise, see Fig. 1. QCISD is more accurate in this case than MP2 because it iteratively optimizes the contributions of single and double excitations, allowing it to better handle near-degeneracy effects. As the H–H bond is stretched, the bonding and antibonding orbitals become nearly degenerate, making a single Hartree–Fock determinant inadequate. MP2 treats electron correlation only as a small, one-step perturbation based on a single Slater determinant, and therefore becomes less accurate in the dissociation limit. ✓

B. Bond angle and singlet-triplet splitting in CH_2

Q4: How does the geometry and singlet-triplet energy splitting obtained using MP2 compare with the Hartree–Fock and QCISD(T) results (from labs 5 and 6) and with the experimental values of 134 ° for the triplet, 102 ° for the singlet and a singlet/triplet energy splitting of 9.05 kcal/mol?

Table 1: *Calculated total energies (in kcal/mol), bond angles, singlet–triplet splittings, and percent deviations from experimental 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)	% Deviation (Angles)		% Deviation (ΔE)
	E [kcal/mol]	Angle [°]	E [kcal/mol]	Angle [°]	[kcal/mol]	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%
MP2	-24494.44	132.58	-24477.02	101.82	17.42	1.05%	0.18%	92.5%

The MP2 results give a triplet bond angle of 132.6 ° and a singlet angle of 101.8 °, both in good agreement with the experimental values of 134 ° and 102°, respectively. The singlet–triplet energy splitting, however, is significantly overestimated at 17.4 kcal/mol compared to the experimental 9.05 kcal/mol. QCISD(T) provides a more accurate splitting (12.1 kcal/mol), while Hartree–Fock overestimates it severely (28.7 kcal/mol). Overall, MP2 improves substantially over HF in both geometry and energy but remains less accurate than QCISD(T), except when it comes to the geometry of the singlet state, see table 1.

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C. Hydrogen bonded clusters

Q5: Why is the MP2 approximation often a good choice for calculations of the binding energy in a molecular cluster?

MP2 is often a good choice for calculations of the binding energy in a molecular cluster since it is size consistent.

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Q6: What is meant by 'size consistency'? Explain why MP2 is size consistent while QCISD is strictly not (only approximately).

"Size consistency" means that for two non-interacting systems, the total energy equals the sum of their individual energies:

$$E(A+B) = E(A) + E(B)$$

This ensures that energies scale correctly with system size and that dissociation and reaction energies are described properly. For example, describing two separated H_2 molecules requires excitations up to quadruples, beyond the doubles included in QCISD. Because QCISD is truncated at double excitations, it is not strictly size consistent, though the quadratic correction partially recovers this property.

MP2, on the other hand, is *strictly size consistent* because its perturbative correlation energy is additive for non-interacting fragments. The electron pair contributions are independent, so the total energy naturally separates into subsystem components: ✓

$$E_{\mathrm{MP2}}(A + B) = E_{\mathrm{MP2}}(A) + E_{\mathrm{MP2}}(B)$$

Q7: What is the binding energy of the methanol and methylamine dimers at the MP2/6-311G and HF/6 311G level of theory?

Table 2: *Total electronic energies (in Hartree) and binding energies (in kcal/mol) for methanol and methylamine dimers at HF and MP2 levels using the 6-311G basis set. Binding energies are computed as* $E_{dimer} - 2E_{monomer}$.

System	HF/6-311G		MP2/6-311G	
	E_{total} (Eh)	E_{bind} (kcal/mol)	E_{total} (Eh)	E_{bind} (kcal/mol)
Methanol monomer	-115.020508458092	—	-115.253335029555	—
Methanol dimer	-230.053597631439	-7.89	-230.522418749741	-9.88
Methylamine monomer	-95.193323688826	—	-95.411709623911	—
Methylamine dimer	-190.392041720920	-3.38	-190.831720452842	-5.21

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Q8: How does the binding energy of the dimers correlate with the boiling point of the two fluids (find values on the internet)?

The boiling point of methanol is 64.65 °C, while the boiling point of methylamine is -6.35 °C [1][2]. Thus the boiling point increases as a function of binding energy. That is, stronger binding (more negative value) leads to a higher boiling point, see table 2. ✓

References

[1] *Nist chemistry webbook — methyl alcohol (ch_3oh)*, `https://webbook.nist.gov/cgi/cbook.cgi?ID=C67561&Mask=4#Thermo-Phase`, Accessed: 2025-10-15, 2025.

[2] *Nist chemistry webbook — methylamine (ch_3nh_2)*, `https://webbook.nist.gov/cgi/cbook.cgi?ID=C74895&Mask=4#Thermo-Phase`, Accessed: 2025-10-15, 2025.