Exercise Session 5
IESM Fall 2024-2025

Yuri, Qihao, Junwu, Salomé, Andrea, Sophia

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🎯 Learning goals

Understanding what is correlation energy

Getting familiar with some Post-HF method and their advantages/disadvantages

📖 Chapter in script

Chapter 5 - An introduction to configuration interaction theory

Chapter 6 - Many-body perturbation theory

🗄 Resources

An Introduction to Configuration Interaction Theory - David Sherrill

Jensen, F. (2017). Introduction to computational chemistry. John wiley & sons.

- Chapter 4.8.1 - Møller–Plesset perturbation theory

Exercise 5 - Post-Hartree Fock Methods: Theory

- HF method neglects correlation between electrons (consequence of using a single Slater determinant)
- We defined **correlation energy** the difference between the total and the HF energy (in the complete basis set limit)

$$E^{total} = E^{HF}_{CBS} + E^{corr}$$

- Inclusion of correlation can be based on e.g. **Post-Hartree-Fock methods**, such as:
  - *Configuration Interaction* (**CI**)
  - *Møller Plesset Perturbation Theory* of *n* order (**MPn**)
  - *Coupled cluster* (**CC**)
- In this set of exercises, you will compare the performance of HF, CI and MPn (and CC) in describing bond dissociation energy and structural parameters

CI basics

- **idea**: instead of using a single Slater determinant (HF like), a linear combination of M N-electron basis functions can be used

$$|\Psi_j(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\rangle = \sum_{i=1}^{M} c_{ij} |\Phi_j(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\rangle$$

- The expansion can be expressed in terms of "excitations" from the HF "reference" determinant

$$|\Psi_j\rangle = c_0 |\Phi_0\rangle + \sum_{ra} c_a^r |\Phi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \ldots$$

- CI method is nothing more than the matrix solution of the time-independent non-relativistic Schrödinger equation, using the (truncated) expression for $|\Psi_j\rangle$ (CIS, CISD, CISDT, ..., FullCI).

- **in practice**:
  - Number of determinats grows extremely fast
  - Full CI performed for very small molecules for benchmarks studies
  - CIS sometimes used for approximate excited state calculations
  - In general, CI method not often used because it is too expensive and other methods give results of comparable quality at lower cost

MPn basics

- MPn is a **perturbation method**, i.e. the problem under investigation is assumed to only differ slightly from a problem which has already been solved, exactly or approximately
- In QM, the perturbation of a system with Hamiltonian $\hat{H}_0$ is described by the perturbed Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

  For a sufficiently weak perturbation, the eigenstates and eigenvalues may then be expanded in a power series
- In MPn theory, $\hat{V}$ is the difference between the true ground state Hamiltonian and the Hartree-Fock Hamiltonian; hence, the perturbation may be written in terms of excited Slater determinants

MPn basics

Energy correction terms can be computed, due to different excitations

$$E_0^{total} = E_0^{HF} + \sum_{n=1} E_0^{(n)}$$

- **in practice**:
  - The corrections are truncated to a certain n, setting the order of the MP calculation (hence the MPn notation)
  - The computational cost will increase with MPn order, usually calculations are not performed with order higher than MP4
  - MPn approach is often less expensive than CI (for sure FCI) and accurate enough
  - MPn is **not variational**, i.e. the resulting MPn energy may be lower than the true ground-state energy. The series is not necessarily converging.

Exercise 5 - Boron atom

ⓘ Exercise 1

- Calculate the HF energy for Boron using the 6-311+G** basis set, then determine the value of the correlation energy for boron assuming an "experimental" energy of -24.608 Hartrees (Schaefer III, Henry F., and Frank E. Harris. "Electronic Structure of Atomic Boron." Physical Review 167.1 (1968): 67).
- Using the same basis set, perform an energy calculation with CISD and full CI.
- Using the same basis set, perform an energy calculation with MP2, MP3 and MP4.
- Using the same basis set, perform an energy calculation with CCSD and CCSD(T).

Determine the percentage of the correlation energy recovered for HF, MP2, MP4, CCSD, CCSD(T).

Compare the performances of the different methods. In particular, you will see that some of the methods seem to overestimate the correlation recovered. How is it possible? (*Hint:* Think both about the theoretical aspects of the methods and *how* we are computing the recovered correlation energy).

- You'll need to perform many different calculations (not taking that long for a single atom)
- Keywords for each method can be found in Psi4 manual
- Options should be already set correctly with `psi4.set_options`

Exercise 5 - C-F bond cleavage

- influence of correlation on the BDE in a radical process by comparing HF to MPn results

$$CH_3F \quad \rightarrow \quad H_3C\cdot \quad + \quad F\cdot$$
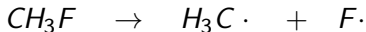
$$E^{BDE} = E^{H_3C\cdot} + E^{F\cdot} - E^{CH_3F}$$

> **ℹ Exercise 2**
>
> Perform the calculations below and complete the following table.
>
> | Method: | HF | MP2 | MP3 | Exp. |
> |---|---|---|---|---|
> | $E^{F\cdot}$ | | | | n/a |
> | $E^{H_3C\cdot}$ | | | | n/a |
> | E^{CH_3F} | | | | n/a |
> | E^{BDE} | | | | 109.2 kcal mol^{-1} |

Note: these calculations may take some time!

Exercise 5 - HNO3 geometry

- influence of correlation on electron correlation on structural parameters, such as bond lengths and angles
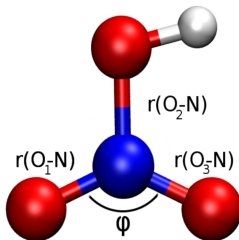
	hf	mp2	mp3	exp
r(O1-N) Å				1.198
r(O2-N) Å				1.410
r(O3-N) Å				1.213
φ(O-N-O) °				130.200

Note: also these calculations may take some time!

Exercise 5 - Tips

Tips!

- MPn theory will be treated in detail during lectures
- Same for CC method used for B atom - take it as just *another* post-HF method for now
- This is probably the first exercise where calculations are completed in minutes and not second - it is always a good idea to monitor their status, this can be done using the terminal `tail -f` command