Exercise Session 5
IESM Fall 2025-2026

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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)

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

- 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

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

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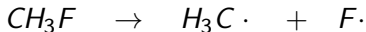
$$E^{BDE} = E^{H_3C\cdot} + E^{F\cdot} - E^{CH_3F}$$

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
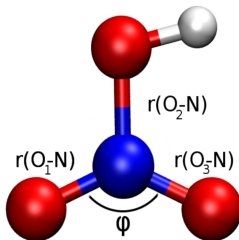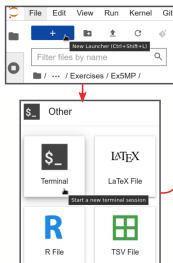

	hf	mp2	mp3	exp
r(O1-N) Å				1.198
r(O2-N) Å				1.410
r(O3-N) Å				1.213
φ(O-N-O) °				130.200

Note: also these calculations may take some time!

Exercise 5 - Tips

Tips!

- MPn theory was treated in detail during the lecture yesterday
- CC method used for B atom will be treated in future lectures - 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 file.log` command