

Lecture Notes: Configuration Interaction and Coupled Cluster Theory

1 Introduction

Up to now we considered the use of small expansions (Configuration Interaction, CI) to calculate approximate:

- Ionization potentials
- Electron affinities
- Excitation energies

These use the excitations of the Hartree–Fock (HF) ground-state determinant.

$$E(\Psi) = \langle \Psi | H | \Psi \rangle$$

Such expansions often give good *total energies* (about 99% of the correlation energy) but are **not size-consistent**. On a chemical scale, large errors appear. CI cannot be reliably used to calculate reaction energies or potential energy surfaces.

2 Beyond CI

We need to go beyond simple CI. The simplest approach is still the *variational principle*.

2.1 Single-Reference Approaches

1. Configuration Interaction (CISD, CEPA)

Problems:

- Not size-consistent ($E_{AB} \neq E_A + E_B$)
- Often insufficient for high accuracy

2. Fixing Size-Consistency: Coupled Cluster (CC)

CCSD(T) is excellent for good HF references, but:

- Limited for bond breaking
- Poor convergence outside a good one-particle basis set

2.2 Multi-Reference and Advanced Methods

- Solving the **multi-reference problem**:
 - MR-CI
 - MR-ACPF (size-consistent)
 - MR-CC
- **Excited States**:
 - Equation-of-Motion Coupled Cluster (EOM-CC, CCSDT)
 - Similarity-transformed Fock
- **Large Systems**:
 - Local correlation
 - Explicit correlation (F12 methods)

3 Configuration Interaction (CI)

We approximate the wavefunction as:

$$\Psi = \Phi_0 + \sum_i c_i \Phi_i + \sum_{ij} c_{ij} \Phi_{ij} + \dots$$

- CISD: singles + doubles excitations.
- Full CI: all possible N -fold excitations for N electrons.

3.1 Hartree–Fock Singles and Brillouin Condition

For a singly excited determinant:

$$\langle \Phi_i^a | H | \Phi_{\text{HF}} \rangle = F_{ai}$$

In HF orbitals, the **Brillouin condition** applies:

$$\langle \Phi_i^a | H | \Phi_{\text{HF}} \rangle = 0$$

Thus the HF energy cannot be lowered by adding only single excitations.

4 Limitations of CI

4.1 Size Consistency

CISD and higher single-reference CI are **not size-consistent**:

$$E_{AB} \neq E_A + E_B$$

This violates the extensivity principle and makes CI unreliable for separated subsystems.

5 Coupled Cluster (CC) Theory

The CC wavefunction is defined as:

$$\Psi = e^T \Phi_0$$

where

$$T = T_1 + T_2 + T_3 + \dots$$

Each T_n represents all n -tuple excitations. This exponential ansatz ensures **size-consistency** and good scaling.

5.1 CC Equations

Define the similarity-transformed Hamiltonian:

$$\bar{H} = e^{-T} H e^T$$

Project onto the reference and excited determinants to obtain the amplitude equations.
Note: \bar{H} is **non-Hermitian**.

5.2 Expansion of \bar{H}

$$\bar{H} = H + [H, T] + \frac{1}{2}[[H, T], T] + \dots$$

This nested commutator expansion *terminates* because T only contains excitations.

6 Practical CC Levels

- **CCSD**: singles and doubles
- **CCSDT**: singles, doubles, triples (very expensive)
- **CCSD(T)**: CCSD with perturbative triples — the **gold standard** of quantum chemistry

CC methods work well for:

- Geometries
- Vibrational frequencies
- Thermochemistry

But can fail for **multi-reference** cases (e.g., bond breaking).

7 Excited States

- **EOM-CC**: Equation-of-Motion CC for excited states, ionization potentials (IP-CC), electron affinities (EA-CC).
- Spin-flip and multi-reference CC exist for strongly correlated systems.

8 Accuracy

- CCSD(T) typically yields ~ 0.01 – 0.02 eV accuracy for valence states.
- Not reliable for Rydberg states.
- EOM-CC IP/EA works well for small molecules.

9 Summary

- CI is conceptually simple but suffers from size-consistency and scaling issues.
- Coupled Cluster (CC) uses an exponential ansatz ensuring size-consistency.
- CCSD(T) is the practical “gold standard” for many systems.
- EOM-CC extends CC to excited, ionized, and electron-attached states.
- Multi-reference situations (e.g., bond breaking) require more advanced MR-CC methods.