

# Coupled Cluster theory

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## Introduction

Coupled Cluster theory is an important ab initio technique in computational chemistry. It is considered the most reliable and also computationally affordable method for solving the electronic Schrödinger equation.

### A non-practical way of solving the eigenvalue problem

In our FCI discussions, we rewrote the solution of the Schrödinger equation as a set of coupled equations in the unknown coefficients  $C$ . Let us repeat some of these arguments. To obtain the eigenstates and eigenvalues in terms of non-linear equations is not a very practical approach. However, it serves the scope of linking FCI theory with approximative solutions to the many-body problem like Coupled cluster (CC) theory

If we assume that we have a two-body operator at most, the Slater-Condon rule gives then an equation for the correlation energy in terms of  $C_i^a$  and  $C_{ij}^{ab}$  only. We get then

$$\langle \Phi_0 | \hat{H} - E | \Phi_0 \rangle + \sum_{ai} \langle \Phi_0 | \hat{H} - E | \Phi_i^a \rangle C_i^a + \sum_{abij} \langle \Phi_0 | \hat{H} - E | \Phi_{ij}^{ab} \rangle C_{ij}^{ab} = 0,$$

or

$$E - E_0 = \Delta E = \sum_{ai} \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle C_i^a + \sum_{abij} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle C_{ij}^{ab},$$

where the energy  $E_0$  is the reference energy and  $\Delta E$  defines the so-called correlation energy. The single-particle basis functions could be the results of a Hartree-Fock calculation or just the eigenstates of the non-interacting part of the Hamiltonian.

In our notes on Hartree-Fock calculations, we have already computed the matrix  $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle$  and  $\langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$ . If we are using a Hartree-Fock basis, then

the matrix elements  $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = 0$  and we are left with a *correlation energy* given by

$$E - E_0 = \Delta E^{HF} = \sum_{abij} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle C_{ij}^{ab}.$$

Inserting the various matrix elements we can rewrite the previous equation as

$$\Delta E = \sum_{ai} \langle i | \hat{f} | a \rangle C_i^a + \sum_{abij} \langle ij | \hat{v} | ab \rangle C_{ij}^{ab}.$$

This equation determines the correlation energy but not the coefficients  $C$ . We need more equations. Our next step is to set up

$$\langle \Phi_i^a | \hat{H} - E | \Phi_0 \rangle + \sum_{bj} \langle \Phi_i^a | \hat{H} - E | \Phi_j^b \rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a | \hat{H} - E | \Phi_{jk}^{bc} \rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a | \hat{H} - E | \Phi_{jkl}^{bcd} \rangle C_{jkl}^{bcd} = 0,$$

as this equation will allow us to find an expression for the coefficients  $C_i^a$  since we can rewrite this equation as

$$\langle i | \hat{f} | a \rangle + \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle C_i^a + \sum_{bj \neq ai} \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a | \hat{H} | \Phi_{jk}^{bc} \rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a | \hat{H} | \Phi_{jkl}^{bcd} \rangle C_{jkl}^{bcd} = EC_i^a.$$

We see that on the right-hand side we have the energy  $E$ . This leads to a non-linear equation in the unknown coefficients. These equations are normally solved iteratively ( that is we can start with a guess for the coefficients  $C_i^a$ ). A common choice is to use perturbation theory for the first guess, setting thereby

$$C_i^a = \frac{\langle i | \hat{f} | a \rangle}{\epsilon_i - \epsilon_a}.$$

The observant reader will however see that we need an equation for  $C_{jk}^{bc}$  and  $C_{jkl}^{bcd}$  as well. To find equations for these coefficients we need then to continue our multiplications from the left with the various  $\Phi_H^P$  terms.

For  $C_{jk}^{bc}$  we need then

$$\begin{aligned} & \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_0 \rangle + \sum_{kc} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_k^c \rangle C_k^c + \\ & \sum_{cdkl} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_{kl}^{cd} \rangle C_{kl}^{cd} + \sum_{cdeklm} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_{klm}^{cde} \rangle C_{klm}^{cde} + \sum_{cdefklmn} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_{klmn}^{cdef} \rangle C_{klmn}^{cdef} = 0, \end{aligned}$$

and we can isolate the coefficients  $C_{kl}^{cd}$  in a similar way as we did for the coefficients  $C_i^a$ . A standard choice for the first iteration is to set

$$C_{ij}^{ab} = \frac{\langle ij | \hat{v} | ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}.$$

At the end we can rewrite our solution of the Schroedinger equation in terms of  $n$  coupled equations for the coefficients  $C_H^P$ . This is a very cumbersome way of

solving the equation. However, by using this iterative scheme we can illustrate how we can compute the various terms in the wave operator or correlation operator  $\hat{C}$ . We will later identify the calculation of the various terms  $C_H^P$  as parts of different many-body approximations to full CI. In particular, we can relate this non-linear scheme with Coupled Cluster theory and many-body perturbation theory.

## Summarizing FCI and bringing in approximative methods

If we can diagonalize large matrices, FCI is the method of choice since:

- It gives all eigenvalues, ground state and excited states
- The eigenvectors are obtained directly from the coefficients  $C_H^P$  which result from the diagonalization
- We can compute easily expectation values of other operators, as well as transition probabilities
- Correlations are easy to understand in terms of contributions to a given operator beyond the Hartree-Fock contribution. This is the standard approach in many-body theory.

The correlation energy is defined as, with a two-body Hamiltonian,

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a \rangle C_i^a + \sum_{abij} \langle ij|\hat{v}|ab \rangle C_{ij}^{ab}.$$

The coefficients  $C$  result from the solution of the eigenvalue problem. The energy of say the ground state is then

$$E = E_{ref} + \Delta E,$$

where the so-called reference energy is the energy we obtain from a Hartree-Fock calculation, that is

$$E_{ref} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle.$$

However, as we have seen, even for a small case like the four first major shells and a nucleus like oxygen-16, the dimensionality becomes quickly intractable. If we wish to include single-particle states that reflect weakly bound systems, we need a much larger single-particle basis. We need thus approximative methods that sum specific correlations to infinite order.

Popular methods are

- Many-body perturbation theory (in essence a Taylor expansion)
- Coupled cluster theory (coupled non-linear equations)
- Green's function approaches (matrix inversion)

- Similarity group transformation methods (coupled ordinary differential equations)

All these methods start normally with a Hartree-Fock basis as the calculational basis.

**A quick tour of Coupled Cluster theory.** The ansatz for the wavefunction (ground state) is given by

$$|\Psi\rangle = |\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle = \left(\sum_{n=1}^A \frac{1}{n!} \hat{T}^n\right) |\Phi_0\rangle,$$

where  $A$  represents the maximum number of particle-hole excitations and  $\hat{T}$  is the cluster operator defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_A$$

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{\substack{i_1, i_2, \dots, i_n \\ a_1, a_2, \dots, a_n}} t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} a_{a_1}^\dagger a_{a_2}^\dagger \dots a_{a_n}^\dagger a_{i_n} \dots a_{i_2} a_{i_1}.$$

The energy is given by

$$E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle,$$

where  $\bar{H}$  is a similarity transformed Hamiltonian

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

$$\hat{H}_N = \hat{H} - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle.$$

The coupled cluster energy is a function of the unknown cluster amplitudes  $t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}$ , given by the solutions to the amplitude equations

$$0 = \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \bar{H} | \Phi_0 \rangle.$$

The similarity transformed Hamiltonian  $\bar{H}$  is expanded using the Baker-Campbell-Hausdorff expression,

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

$$\frac{1}{n!} [\dots [\hat{H}_N, \hat{T}], \dots \hat{T}] + \dots$$

and simplified using the connected cluster theorem

$$\bar{H} = \hat{H}_N + \left(\hat{H}_N \hat{T}\right)_c + \frac{1}{2} \left(\hat{H}_N \hat{T}^2\right)_c + \dots + \frac{1}{n!} \left(\hat{H}_N \hat{T}^n\right)_c + \dots$$

A much used approximation is to truncate the cluster operator  $\hat{T}$  at the  $n = 2$  level. This defines the so-called singles and doubles approximation to the Coupled Cluster wavefunction, normally shortened to CCSD..

The coupled cluster wavefunction is now given by

$$|\Psi_{CC}\rangle = e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle$$

where

$$\begin{aligned}\hat{T}_1 &= \sum_{ia} t_i^a a_a^\dagger a_i \\ \hat{T}_2 &= \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i.\end{aligned}$$

The amplitudes  $t$  play a role similar to the coefficients  $C$  in the shell-model calculations. They are obtained by solving a set of non-linear equations similar to those discussed above in connection with the FCI discussion.

If we truncate our equations at the CCSD level, it corresponds to performing a transformation of the Hamiltonian matrix of the following type for a six particle problem (with a two-body Hamiltonian):

	$0p-0h$	$1p-1h$	$2p-2h$	$3p-3h$	$4p-4h$	$5p-5h$	$6p-6h$
$0p-0h$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	0	0	0	0
$1p-1h$	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	0	0	0
$2p-2h$	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	0	0
$3p-3h$	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	0
$4p-4h$	0	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$
$5p-5h$	0	0	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$
$6p-6h$	0	0	0	0	$\tilde{x}$	$\tilde{x}$	$\tilde{x}$

In our FCI discussion the correlation energy is defined as, with a two-body Hamiltonian,

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a\rangle C_i^a + \sum_{abij} \langle ij|\hat{v}|ab\rangle C_{ij}^{ab}.$$

In Coupled cluster theory it becomes (irrespective of level of truncation of  $T$ )

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a\rangle t_i^a + \sum_{abij} \langle ij|\hat{v}|ab\rangle t_{ij}^{ab}.$$

Coupled cluster theory has several interesting computational features and is the method of choice in quantum chemistry. The method was originally proposed by Coester and Kummel, two nuclear physicists (way back in the fifties). It came back in full strength in nuclear physics during the last decade.

There are several interesting features:

- With a truncation like CCSD or CCSDT, we can include to infinite order correlations like  $2p-2h$ .
- We can include a large basis of single-particle states, not possible in standard FCI calculations

However, Coupled Cluster theory is

- non-variational
- if we want to find properties of excited states, additional calculations via for example equation of motion methods are needed
- if correlations are strong, a single-reference ansatz may not be the best starting point
- we cannot quantify properly the error we make when truncations are made in the cluster operator

## The CCD approximation

We will now approximate the cluster operator  $\hat{T}$  to include only  $2p - 2h$  correlations. This leads to the so-called CCD approximation, that is

$$\hat{T} \approx \hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i,$$

meaning that we have

$$|\Psi_0\rangle \approx |\Psi_{CCD}\rangle = \exp \hat{T}_2 |\Phi_0\rangle.$$

Inserting these equations in the expression for the computation of the energy we have, with a Hamiltonian defined with respect to a general vacuum (see the exercises in the second quantization part)

$$\hat{H} = \hat{H}_N + E_{\text{ref}},$$

with

$$\hat{H}_N = \sum_{pq} \langle p|\hat{f}|q\rangle a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r,$$

we obtain that the energy can be written as

$$\langle \Phi_0 | \exp -\hat{T}_2 \hat{H}_N \exp \hat{T}_2 | \Phi_0 \rangle = \langle \Phi_0 | \hat{H}_N (1 + \hat{T}_2) | \Phi_0 \rangle = E_{CCD}.$$

This quantity becomes

$$E_{CCD} = E_{\text{ref}} + \frac{1}{4} \sum_{abij} \langle ij|\hat{v}|ab\rangle t_{ij}^{ab},$$

where the latter is the correlation energy from this level of approximation of CC theory. Similarly, the expression for the amplitudes reads

$$\langle \Phi_{ij}^{ab} | \exp -\hat{T}_2 \hat{H}_N \exp \hat{T}_2 | \Phi_0 \rangle = 0.$$

These equations can be reduced to (after several rounds of contractions) to MORE material to come.