

Project 2 Fyss4480, The CCD approximation

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Project 2 introduction

In this project we will study the Coupled Cluster method. In particular we will explore the Coupled Cluster Doubles (CCD) approximation. The first part of the project will be to derive the relevant energy and amplitude equations. The second part will be to write a CCD program and apply it to the Helium and Beryllium atom as in Project1 and compare the resulting energies with results from configuration interaction, Hartree-Fock and many-body perturbation theory.

In the Coupled Cluster method the ansatz for the ground state is given by

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}} |c\rangle, \quad (1)$$

where \hat{T} is the cluster operator

$$\begin{aligned} \hat{T} &= \hat{T}_1 + \hat{T}_2 + \dots \\ \hat{T}_n &= \left(\frac{1}{n!}\right)^2 \sum_{abc\dots} \sum_{ijk\dots} t_{ijk\dots}^{abc\dots} a_a^\dagger a_b^\dagger a_c^\dagger \dots a_k a_j a_i. \end{aligned}$$

The energy is given by

$$E_{\text{CC}} = \langle c | \bar{H} | c \rangle \quad (2)$$

where \bar{H} is the *similarity transformed* Hamiltonian

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}. \quad (3)$$

The amplitudes $t_{ijk\dots}^{abc\dots}$ are given by the solution of the non-linear amplitude equations

$$\langle \Phi_{ijk\dots}^{abc\dots} | \bar{H} | c \rangle = 0. \quad (4)$$

In order to setup the above equations, the similarity transformed Hamiltonian is expanded using the Baker-Campbell-Hausdorff (BCH) expansion,

$$\begin{aligned} \bar{H} &= \hat{H} + [\hat{H}, \hat{T}] \\ &+ \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}] \\ &+ \frac{1}{6} [[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] \\ &+ \frac{1}{24} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] \\ &+ \dots \end{aligned} \quad (5)$$

When \hat{H} is a two-body Hamiltonian this series truncates after the four nested commutators listed above.

In this project we will consider the so-called Coupled Cluster Doubles approximation where we have

$$\hat{T} = \hat{T}_2 = \frac{1}{4} \sum_{ab} \sum_{ij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \quad (6)$$

Part a) The CCD energy Let the Hamiltonian be given on normal ordered form as discussed in the lectures

$$\hat{H} = E_{\text{ref}} + \hat{F} + \hat{H}_I \quad (7)$$

$$= E_{\text{ref}} + \sum_{pq} \langle p | \hat{f} | q \rangle \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle_{\text{AS}} \{a_p^\dagger a_q^\dagger a_s a_r\}. \quad (8)$$

The subscript AS will be dropped in the remainder of the text, but the matrix elements are still antisymmetrized.

Using Wicks generalized theorem, show that

$$\langle c | \hat{H} | c \rangle = E_{\text{ref}} \quad (9)$$

$$\langle c | [\hat{H}, \hat{T}_2] | c \rangle = \frac{1}{4} \sum_{abij} \langle ij | \hat{v} | ab \rangle t_{ij}^{ab} \quad (10)$$

and argue that

$$\langle c | [[\hat{H}, \hat{T}_2], \hat{T}_2] | c \rangle = 0. \quad (11)$$

Thus, we have that the CCD energy is given by

$$E_{\text{CCD}} = E_{\text{ref}} + \frac{1}{4} \sum_{abij} \langle ij | \hat{v} | ab \rangle t_{ij}^{ab} \quad (12)$$

Part b) Deriving the CCD amplitude equation The next step is to obtain an algebraic expressions for the amplitude equation

$$\langle \Phi_{ij}^{ab} | \hat{H} | c \rangle = 0. \quad (13)$$

We will break this up into several steps. First, show that

$$\langle \Phi_{ij}^{ab} | \hat{F} | c \rangle = 0 \quad (14)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}_I | c \rangle = \langle ab | \hat{v} | ij \rangle \quad (15)$$

Secondly, show that

$$\langle \Phi_{ij}^{ab} | [\hat{F}, \hat{T}_2] | c \rangle = \hat{P}(ij) \sum_k f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_c f_c^a t_{ij}^{bc} \quad (16)$$

$$\begin{aligned} \langle \Phi_{ij}^{ab} | [\hat{H}_I, \hat{T}_2] | c \rangle &= \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | ij \rangle t_{kl}^{ab} + \hat{P}(ab) \hat{P}(ij) \sum_{kc} \langle ak | \hat{v} | ic \rangle t_{jk}^{bc} \\ &+ \frac{1}{2} \sum_{cd} \langle ab | \hat{v} | cd \rangle t_{ij}^{cd} \end{aligned} \quad (17)$$

Here we have defined

$$\hat{P}(ab) = (1 - \hat{P}_{ab}) \quad (18)$$

$$\hat{P}(ab)\hat{P}(ij) = (1 - \hat{P}_{ab}) (1 - \hat{P}_{ij}) \quad (19)$$

where \hat{P}_{ab} permutes the indices a and b (or i and j).

Thirdly, argue that

$$\langle \Phi_{ij}^{ab} | [[\hat{F}, \hat{T}_2], \hat{T}_2] | c \rangle = 0 \quad (20)$$

and show that

$$\begin{aligned} \frac{1}{2} \langle \Phi_{ij}^{ab} | [[\hat{H}_I, \hat{T}_2], \hat{T}_2] | c \rangle &= \frac{1}{4} \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{kl}^{ab} t_{ij}^{cd} - \frac{1}{2} \hat{P}(ij) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{il}^{ab} t_{kj}^{cd} \\ &\quad - \hat{P}(ab) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{ik}^{ac} t_{lj}^{bd} - \frac{1}{2} \hat{P}(ab) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{ij}^{ac} t_{kl}^{bd}. \end{aligned} \quad (21)$$

Finally, argue that

$$\langle \Phi_{ij}^{ab} | [[[\hat{H}, \hat{T}_2], \hat{T}_2], \hat{T}_2] | c \rangle = 0. \quad (22)$$

Collecting all terms we have that

$$\begin{aligned} \langle \Phi_{ij}^{ab} | \bar{H} | c \rangle &= \langle ab | \hat{v} | ij \rangle + \hat{P}(ij) \sum_k f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_c f_c^a t_{ij}^{bc} \\ &\quad + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | ij \rangle t_{kl}^{ab} + \hat{P}(ab) \hat{P}(ij) \sum_{kc} \langle ak | \hat{v} | ic \rangle t_{jk}^{bc} \\ &\quad + \frac{1}{2} \sum_{cd} \langle ab | \hat{v} | cd \rangle t_{ij}^{cd} + \frac{1}{4} \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{kl}^{ab} t_{ij}^{cd} - \frac{1}{2} \hat{P}(ij) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{il}^{ab} t_{kj}^{cd} \\ &\quad - \hat{P}(ab) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{ik}^{ac} t_{lj}^{bd} - \frac{1}{2} \hat{P}(ab) \sum_{klcd} \langle kl | \hat{v} | cd \rangle t_{ij}^{ac} t_{kl}^{bd}. \end{aligned} \quad (23)$$

Part c) Setting up an iterative scheme We want to solve Eq. 13 with the left-hand side given by Eq. 23 for the unknown amplitudes t_{ij}^{ab} .

Define $\epsilon_p = f_p^p$ and $D_{ab}^{ij} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$ and show that

$$t_{ij}^{ab} D_{ab}^{ij} = \langle ab | \hat{v} | ij \rangle + \hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc} + (\dots) \quad (24)$$

where (\dots) refers to the rest of Eq. 23. Furthermore, argue that

$$\hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc} = 0 \quad (25)$$

if the single-particle functions are given by the Hartree-Fock solution.

Equation 24 is a non-linear equation in the amplitudes and must be solved iteratively. The way we have rewritten the equation suggests that we define an iterative scheme as

$$(t_{ij}^{ab})^{(k+1)} = \frac{g((t_{ij}^{ab})^{(k)})}{D_{ab}^{ij}} \quad k = 0, 1, 2, \dots \quad (26)$$

for some initial guess $(t_{ij}^{ab})^{(0)}$. Here we have defined

$$\begin{aligned}
g\left((t_{ij}^{ab})^{(k)}\right) = & \langle ab|\hat{v}|ij\rangle + \hat{P}(ij) \sum_{k \neq i} f_i^k(t_{jk}^{ab})^{(k)} - \hat{P}(ab) \sum_{c \neq a} f_c^a(t_{ij}^{bc})^{(k)} \\
& + \frac{1}{2} \sum_{kl} \langle kl|\hat{v}|ij\rangle (t_{kl}^{ab})^{(k)} + \hat{P}(ab) \hat{P}(ij) \sum_{kc} \langle ak|\hat{v}|ic\rangle (t_{jk}^{bc})^{(k)} \\
& + \frac{1}{2} \sum_{cd} \langle ab|\hat{v}|cd\rangle (t_{ij}^{cd})^{(k)} + \frac{1}{4} \sum_{klcd} \langle kl|\hat{v}|cd\rangle (t_{kl}^{ab})^{(k)} (t_{ij}^{cd})^{(k)} \\
& - \frac{1}{2} \hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd\rangle (t_{il}^{ab})^{(k)} (t_{kj}^{cd})^{(k)} - \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle (t_{ik}^{ac})^{(k)} (t_{lj}^{bd})^{(k)} \\
& - \frac{1}{2} \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle (t_{ij}^{ac})^{(k)} (t_{kl}^{bd})^{(k)}. \tag{27}
\end{aligned}$$

Part d) The initial guess Iterative solvers need a guess for the amplitudes. A good starting point is to use the correlated wave operator from perturbation theory to first order in the interaction. This means that we define the zeroth approximation to the amplitudes as

$$(t_{ij}^{ab})^{(0)} = \frac{\langle ab|\hat{v}|ij\rangle}{D_{ab}^{ij}}. \tag{28}$$

Insert this expression into the CCD energy 12 and compare with the energy expression from second-order perturbation theory.

Part e) Writing a program that solves the amplitude equations The final part of the program is write a program to solve the amplitude equations. That is, write a program that computes the amplitudes according to the scheme 26 with the initial guess given by Eq. 28.

One particular nice way of writing the program in Python is to use numpy's einsum function np.einsum to evaluate the contributions to Eq. 27. This is by no means mandatory and you can equally well write the program as you want.

Compute the CCD energy for Helium and Beryllium using the same basis functions as in Project1 and compare the resulting energies with energies obtained with the Hartree-Fock and configuration interaction method. You can use the code template found at the github page code template as a starting point for your program.

Part f) Computing in Hartree-Fock basis Finally, using the program you wrote in Project1 you can do a basis transformation to the Hartree-Fock basis given by

$$\begin{aligned}
\langle p|\hat{f}|q\rangle &= \epsilon_p \delta_{pq} \\
\langle pq|\hat{v}|rs\rangle &= \sum_{\alpha\beta\gamma\delta} C_{\alpha p}^* C_{\beta q}^* C_{\gamma r} C_{\delta s} \langle \alpha\beta|\hat{v}|\gamma\delta\rangle.
\end{aligned}$$

Perform this transformation and repeat the calculations in part e) and compare the resulting energies with those you already have computed.