Couple Cluster

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Introduction

Truncating The Couple cluster ansatz and its working equations

Problem We Will be addressing

Truncating The Couple cluster ansatz and its working equations. Problem we will be addressing We are interested in Solving the molecular Schrodinger equations, N electrons.

$$\psi = \psi \left(r_1, \ldots, r_N \right)$$

wave function is the function of the coordinates of N-electrons.

$$H|\psi\rangle = E|\psi\rangle$$

This is a very difficult equation to solve we need to invent some kind of approximation to it.

Hartree Fork Theory

Representing the wave function by a single slated determinant.

$$|\psi\rangle \approx |\varphi_0\rangle$$

Configuration Interation. We expressed the wave function as all possible configuration iterations.

Configuration Interation

$$|\psi\rangle = |\varphi_0\rangle + \sum_{ia} c_i^a \left|\varphi_i^{ab}\right\rangle + \frac{1}{4}\sum_{ia} c_{ij}^{ab}\left|\varphi_{ij}^{ab}\right\rangle + ...$$

Note: $|\varphi_0\rangle$ means Hartree Fork Slater Determinant (Ground State wave function).
$|\varphi_i^a\rangle =$ is a slater determinant where we have removed an electron from orbital i and put it in orbital a (single excitation).
$\sum_{ia} c_i^a |\varphi_i^a\rangle$ all possible single substituted configurations.

Couple Cluster Method

$$|\psi\rangle = e^{T} |\varphi_0\rangle$$

Why Study Couple-Cluster

* The most successful approach to accurately Solve many-electron (molecular) systems.
* It's quite rich and comes in many different variants.
- Tailored CC ("multi-reference method")
- Extended CC (more elaborate, QCC).
- Unitary CC (Hermitian, Quantum Computing). etc

Excitations

How Do we mathematically formulate couple cluster

* One-particle basis, Orbitals: $\chi_k, k = 1, \ldots, K > N$
$K > N \Rightarrow$ This Means We have more orbitals than electron we want to excite into.
* Configuration interaction (CI) method: We generate determinant basis by just populating k-orbitals with N-electrons.
HF Slater determinant
$\Phi_0 = \det\left(\chi_j\right)_{j=1}^{N}$ (Reference slated determinant).
We label all these determinant with ϕ_μ

$$\begin{aligned} &\Phi_\mu = x_\mu \Phi_0 = \det x_{\mu_j} \in \text{Span}\left\{\Phi_\mu\right\} \\ &\mu_j \in \{1, 2, \ldots, K\}. \end{aligned}$$

Where μ is a multiple index that just tells you which of the orbitals was used in constructing this determinant.

$$\psi = \sum_{\mu\geq 0} C_\mu \left|\Phi_\mu\right\rangle = \sum_{\mu>0} C_\mu x_\mu \left|\phi_0\right\rangle + C_0 \left|\phi_0\right\rangle$$
$$\psi = \left(I + \sum_{\mu>0} C_\mu X_\mu\right) \left|\Phi_0\right\rangle$$

$$\psi = (1+B)\left|\Phi_0\right\rangle \text{; where} \quad B = \sum_{\mu\geqslant 0} C_\mu x_\mu$$

which is called the cluster operator.
And the energy equation becomes;

$$H(I+B)\left|\Phi_0\right\rangle = \varepsilon(I+B)\left|\Phi_0\right\rangle$$

parametrization

- CI: $\psi = \left(I + \sum_{\mu>0} C_\mu X_\mu\right) |\Phi_0\rangle$
- CC: $\psi = \underbrace{(I+B)\Phi_0}_{CI} = \underbrace{e^T\Phi_0}_{CC} = \left(1 + T + \frac{1}{2}T^2 + \cdots + \frac{T^N}{N!}\right)\Phi_0$

We partition C and T according to the number of electrons they excited.

$$\begin{cases} C = \sum_{k=1}^N C_k = C_1 + \cdots + C_N \\ T = \sum_{k=1}^N T_k = T_1 + \cdots + T_N \end{cases}$$

$$C_1 = T_1$$

$$C_2 = T_2 + \frac{1}{2}(T_1)^2$$

$$C_3 = T_3 + T_2 T_1 + \frac{1}{6}(T_1)^3$$

$$C_4 = \ldots.$$

The cluster operator expansion is given by

$$
\begin{aligned}
T &= T_1 + T_2 + T_3 + \cdots + T_N \\
e^T &= 1 + T + \frac{1}{2} T^2 + \frac{1}{6} T^3 + \cdots = \sum_{k=1}^{N} \frac{T^k}{k!} \\
&= 1 + (T_1 + T_2 + T_3 + \cdots) + \frac{1}{2}(T_1 + T_2 + \cdots)^2 + \frac{1}{6}(T_1 + \cdots)^3 +
\end{aligned}
$$

Here, T_1 is called a single excitation operator and T_2 is called a double excitation operator.

Rearranging the operators according to the number k of excitations

$$= 1 + T_1 + \left\{ T_2 + \frac{1}{2} T^2 \right\} + \left\{ T_1 + \frac{1}{6} T_1^3 + T_2 T_1 \right\} + \cdots$$

The Schrödinger equation is given by $H|\psi\rangle = E|\psi\rangle$.
Substituting the ansatz $He^T|\Phi_0\rangle = Ee^T|\Phi_0\rangle$ yields:

$$e^{-T}He^T|\Phi_0\rangle = E|\Phi_0\rangle$$

Projecting on the reference and on the orthogonal complement

$$\left\langle \phi_\mu \middle| e^{-T}He^T \middle| \Phi_0 \right\rangle = E$$

.

$$\left\langle \phi_\mu \middle| e^{-T}He^T \middle| \Phi_0 \right\rangle = 0$$

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