Coupled Cluster Methods

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π Day Presentation

March 2011

Abstract

The Coupled Cluster Method (CCM) is widely recognised as providing one of the most powerful, universally applicable, and numerically accurate methods of microscopic quantum many-body theory. The number of successful applications of the method to a wide range of physical and chemical systems is impressively large. In almost all such cases the numerical results are either the best or among the best available.

This method acts exponentially on a sum of excitation operators to a reference state. This exponential approach produces a method which is both size consistent and size extensive. One disadvantage of the CCM is that it imposes pairwise constraint such as orthogonality. To remedy this shortcoming, we seek to remove the orthogonality constraint by applying it to non - orthogonal orbitals hoping that the computer cost of solving these problems will be reduced.

We consider the time - independent, non - relativistic, N - electron multiparticle Schrödinger equation $H\psi = \lambda\psi$. The wavefunction ψ is a function of N variables and is constrained to be antisymmetric under the exchange of any two spin variables, that is $\psi(\gamma_1, \gamma_2, \cdots) = -\psi(\gamma_2, \gamma_1, \cdots)$. The eigenvalues correspond to energies and H is the Hamiltonian.

We want to build an antisymmetric function to approximate the wavefunction ψ. We need to use antisymmetric functions to get an antisymmetric approximation. We approximate the wavefunction ψ by a linear combination of slater determinants which are antisymmetric. To accomplish this, we choose a set of orthonormal spin orbitals $\{\phi_i(r_i)\}_{i=1}^N$ where r_i denotes the position and spin of the singular electron. We then form a slater determinant (Φ_0) from first N. We make other slater determinant by replacing $\phi_1 \cdots \phi_N$ with $\phi_{N+1} \cdots$ using orbital excitation operators.

Example - Excitation Operator

The notation $E_i^a \Phi_0$ means that ϕ_i is replaced with ϕ_a in Φ_0. Let Φ_0 be given by

$$\Phi_0 = \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \cdots & \phi_N(r_N) \end{vmatrix}$$

Then $E_{12}^{ab}\Phi_0 = E_1^a E_2^b \Phi_0$ gives us the following:

$$E_1^a E_2^b \Phi_0 = E_1^a \begin{vmatrix} \phi_1(r_1) & \phi_b(r_1) & \cdots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_b(r_2) & \cdots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_b(r_N) & \cdots & \phi_N(r_N) \end{vmatrix} = \begin{vmatrix} \phi_a(r_1) & \phi_b(r_1) & \cdots & \phi_N(r_1) \\ \phi_a(r_2) & \phi_b(r_2) & \cdots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(r_N) & \phi_b(r_N) & \cdots & \phi_N(r_N) \end{vmatrix}$$

The excitation operators are constrained to act on orthogonal orbitals. We can express the excitation operator T in the form:

$$T = T_1 + T_2 + T_3 + T_4 + \cdots \tag{1}$$

with T_m defined as:

$$T_m = \sum_{i,j,\cdots,a,b\cdots} t_{ij\cdots}^{ab\cdots} E_{ij\cdots}^{ab\cdots} \tag{2}$$

where $E_{ij\cdots}^{ab\cdots}$ are the orbital excitation operators and the unknown coefficients $t_{ij\cdots}^{ab\cdots}$ are called cluster amplitudes. Finding the unknown coefficients $t_{ij\cdots}^{ab\cdots}$ is the same as approximating the solution of the wavefunction ψ. T_1 is the operator of all single excitations, T_2 is the operator of all double excitations and so forth. Each T_m is excited to some some level, for example, CCSD means a Couple Cluster Method with Single and Double excitations, i.e. $T = T_1 + T_2$.

In Coupled Cluster Method (CCM), the ψ function is represented as an exponential function of sums of excitation operators acting on a reference state i.e. $\psi = e^T |\phi\rangle$, where T is the excitation operator and $|\phi\rangle$ is the reference slater determinant. Since $\psi = e^T |\phi\rangle$, then the Schrödinger equation can be expressed as :

$$\begin{aligned} H\psi &= \lambda\psi \\ He^T |\phi\rangle &= \lambda e^T |\phi\rangle \end{aligned} \tag{3}$$

Premultiplying by e^{-T}, we get

$$\begin{aligned} e^{-T}He^T |\phi\rangle &= \lambda e^{-T}e^T |\phi\rangle \\ e^{-T}He^T |\phi\rangle &= \lambda |\phi\rangle \end{aligned} \tag{4}$$

Now, we can project the above equation to $\langle f |$ and we get

$$\langle f | e^{-T}He^T |\phi\rangle = \lambda \langle f | \phi\rangle \tag{5}$$

If we let $f = \phi$, $f = \phi_i^a$ (single excitation operator) and $f = \phi_{ij}^{ab}$ (double excitation operator) respectively, we get the following set of equations:

$$\begin{aligned} \left\langle \phi \left| e^{-T} H e^{T} \right. \phi \right\rangle &= \lambda \left\langle \phi \left| \phi \right. \right\rangle = \lambda \\ \left\langle \phi_i^a \left| e^{-T} H e^{T} \right. \phi \right\rangle &= \lambda \left\langle \phi_i^a \left| \phi \right. \right\rangle = 0 \\ \left\langle \phi_{ij}^{ab} \left| e^{-T} H e^{T} \right. \phi \right\rangle &= \lambda \left\langle \phi_{ij}^{ab} \left| \phi \right. \right\rangle = 0 \end{aligned} \tag{6}$$

Hence for a CCSD ($T = T_1 + T_2$),we get the following set of algebraic equations.

$$\begin{aligned} \left\langle \phi_i^a \left| e^{-T} H e^{T} \right| \phi \right\rangle &= 0 \\ \left\langle \phi_{ij}^{ab} \left| e^{-T} H e^{T} \right| \phi \right\rangle &= 0 \end{aligned} \tag{7}$$

Lets define $\overline{H} = e^{-T} H e^{T}$. The last equation above transforms to:

$$\left\langle \phi_{ij}^{ab} \left| \overline{H} \right. \phi \right\rangle = 0 \tag{8}$$

$$
\begin{aligned}
\overline{H} &= e^{-T} H e^{T} \\
&= \left(I - T + \frac{T^2}{2!} - \cdots \right) H \left(I + T + \frac{T^2}{2!} + \cdots \right) \\
&= \left(H - TH + \frac{T^2 H}{2!} - \cdots \right) \left(I + T + \frac{T^2}{2!} + \cdots \right) \\
&= H + TH - TH + \frac{1}{2!}(HT^2 + T^2 H) + \cdots \\
&= H + [H, T] + \frac{1}{2!}[[H, T], T] + \cdots \\
&= \sum_{n=0}^{4} \frac{1}{n!}[\cdots[[H, T], T], \cdots]
\end{aligned}
\tag{9}
$$

This series is infinite, but when you do $< \phi_{ij}^{ab} | \cdots | \phi >$ the terms above four contribute 0 and thus it terminates, hence the CCSD equations are algebraic.

Goals of the Project

One of our goals was to understand the Coupled Cluster Method which we accomplished. We were to find out if there is anyone else who is working with non - orthogonal orbitals. Recent literature shows that there is no one. We then asked ourselves if it is possible to work with non - orthogonal orbitals.

There seems to be more questions than answers and it doesn't look good. The operator E_i^a means that ϕ_i is replaced by ϕ_a from a set of orthonormal orbits. Now, mathematically, "What is this operator E_i^a?", "How do we excite ϕ_i into an arbitrary function f?", "How could we compute He^T and $\overline{H} = e^{-T}He^T$ for such T"?, and lastly, "What does $e^{-T}He^T$ mean"?

All these questions remain unanswered.

References

[1] R.J. Bartlet, M. Musial, V. Lotrich and T. Kus *The Yearn To be Hermitian*, Recent Progress in Coupled Cluster Methods, Springer Sciences and Business Media B.V. 2010.

[2] R.F. Bishop, *The Coupled Cluster Method*, University of Manchester Institute of Science and Technology.

[3] M.J. Mohlenkamp, *Capturing the Inter-electron Cusp using a Geminal Layer on an Unconstrained Sum of Slater Determinants*, to be published.

[4] π Diagram modified from M.J. Mohlenkamp code.