Wick theorem for coupled cluster and for equation of motion coupled cluster

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Schrödinger equation

- We work with the stationary Schrödinger equation in the Born-Openheimer approximation

$$\hat{\mathcal{H}}|\Psi\rangle = E|\Psi\rangle$$

- $|\Psi\rangle$ is the N-electron wave function
- $\hat{\mathcal{H}}$ is the Exact Hamiltonian that contains the the N-electron kinetic energy and the electron electron interaction term

$$\hat{\mathcal{H}} = \hat{\mathcal{T}} + \hat{\mathcal{W}}$$

Second Quantization:Exact wavefunction

$$|\Psi_{cc}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

Doing the cluster expansion of the exponential operator we obtain

$$|\Psi_{cc}\rangle = \left(1 + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + ...\right)|\Psi_0\rangle$$

Where the cluster operator is $\hat{T}$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...$$

$$\hat{T}_1 = \sum_{i,a} t_i^a\{\hat{a}^\dagger \hat{i}\} \qquad \hat{T}_2 = \frac{1}{4}\sum_{i,j,a,b} t_{ij}^{ab}\{\hat{a}^\dagger \hat{i}\hat{b}^\dagger \hat{j}\}$$

the indexes $\{i, j, k, \ldots\}$ take in to account the occupied orbitals and $\{a, b, c, \ldots\}$ virtual orbitals.

Second Quantization: Excitation operators

- We can define the Hamiltonian in normal order with respect the HF reference determinant

$$\hat{\mathcal{H}} = \sum_{pq} h_{pq} \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}$$

using the Wick Theorem:

$$\hat{\mathcal{H}} = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} + \langle 0|\hat{\mathcal{H}}|0\rangle$$

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_N + \langle 0|\hat{\mathcal{H}}|0\rangle \implies \hat{\mathcal{H}}_N = \hat{\mathcal{H}} - \langle 0|\hat{\mathcal{H}}|0\rangle$$

- The advantage of using the Hamiltonian in normal order is that we can compute a product of strings without moving the indices that belong to the reference

Foundations in Coupled Cluster

To solve the Schrödinger equation we use the Normal Order Hamiltonian in the following way

$$\hat{\mathcal{H}}_N e^{\hat{T}}|\Psi_0\rangle = \Delta E e^{\hat{T}}|\Psi_0\rangle \tag{1}$$

To calculate the energy we need the amplitudes, so we can project the Schrödinger equation in the reference and excited determinants

$$\langle\Psi_0|e^{-\hat{T}}\hat{\mathcal{H}}_N e^{\hat{T}}|\Psi_0\rangle = \Delta E$$

$$\langle\Psi_{ij\ldots}^{ab\ldots}|\left(\hat{\mathcal{H}}_N e^{\hat{T}}\right)_C|\Psi_0\rangle = 0$$

Similarity Transformed Hamiltonian in Coupled Cluster

- A more explicit form of the Similarity Transform Hamiltonian we can use the Backer-Campbell-Hausdorff Expansion.

$$\left(\hat{\mathcal{H}}_N e^{\hat{T}}\right)_C = \hat{\mathcal{H}}_N + \left[\hat{\mathcal{H}}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{\mathcal{H}}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{\mathcal{H}}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{\mathcal{H}}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] \tag{2}$$

$$\left(\hat{\mathcal{H}}_N e^{\hat{T}}\right)_C = e^{-\hat{T}}\hat{\mathcal{H}}_N e^{\hat{T}} = \hat{\mathcal{H}} + \hat{\mathcal{H}}\hat{T} + \frac{1}{2}\hat{\mathcal{H}}\hat{T}\hat{T} + \frac{1}{3!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T} + \frac{1}{4!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T}\hat{T} \tag{3}$$

- The terms that are not connected contain partial contractions Example:

$$\hat{\mathcal{H}}\hat{T}\hat{T}\color{red}{\hat{T}}$$

Similarity Transformed Hamiltonian in Coupled Cluster

Using the connected similarity Hamiltonian in the projected equations

$$\langle \Psi_{ij\dots}^{ab\dots} | \left(\hat{\mathcal{H}} + \hat{\mathcal{H}}\hat{T} + \frac{1}{2}\hat{\mathcal{H}}\hat{T}\hat{T} + \frac{1}{3!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T} + \frac{1}{4!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T}\hat{T} \right)_C | \Psi_0 \rangle = 0$$

Selecting one of the products of the expansion

$$\langle \Psi_{ij\dots}^{ab\dots} | \left(\hat{\mathcal{H}}\hat{T}\hat{T} \right)_C | \Psi_0 \rangle$$

An explicit example of the contraction is the following

$$\langle \Psi^{ab\ldots}_{ij\ldots} | \left(\hat{\mathcal{H}} \hat{T} \hat{T} \right)_C |\Psi_0\rangle$$

Selecting the simplest product of $\hat{T}\hat{T}$

$$\sum_{kl\ldots,cd\ldots} \sum_{pqrs} \langle pq||rs\rangle \langle\Psi_0|\{\hat{i}^\dagger \hat{j}^\dagger \ldots \hat{a}\hat{b}\ldots\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}$$

$$\{\hat{c}^\dagger\hat{d}^\dagger\ldots\hat{k}\hat{l}\ldots\}\{\hat{e}^\dagger\hat{f}^\dagger\ldots\hat{m}\hat{n}\ldots\}|\Psi_0\rangle t^{cd\ldots}_{kl\ldots} t^{ef\ldots}_{mn\ldots}$$

Expressing in a more simple notation

$$\{B^\dagger A\}\{H^\dagger H\}\{T1^\dagger T1\}\{T2^\dagger T2\}$$

Wick theorem for coupled cluster

Require:

$$\{B^\dagger A\}\{H^\dagger H\}\{T1^\dagger T1\}\{T2^\dagger T2\}$$

1. Obtain all the contractions between the different operators and separate them according the first operator
2. Obtain all the possibilities between different subsets without repeating operators. The simplest examples is $N[B^\dagger] = 1, N[A] = 1$, $N[T1] = N[T2] = N[T1^\dagger] = N[T2^\dagger] = 1$

$$\{B^\dagger H, AT2^\dagger, HT1^\dagger, H^\dagger T2, H^\dagger T1\}, \{B^\dagger T1, AH^\dagger, H^\dagger T2, HT2^\dagger, HT1^\dagger\}, \ldots$$

3. Obtain the sign

$$sgn = \prod_{i=\{B^\dagger, A, H^\dagger, H, T1^\dagger, T1, T2^\dagger, T2,\}} (-1)^{P_{in}[i] - P_{fin}[i]}$$

where $P_{in}[i] - P_{fin}[i]$ is the initial positions minus the final position

EE-EOMCCSD

We can diagonalize the similarity transformed Hamiltonian in a CISD basis to obtain the EE-EOMCCSD

$$\begin{pmatrix} \langle \Psi_i^a | \bar{\mathcal{H}} | \Psi_k^c \rangle & \langle \Psi_i^a | \bar{\mathcal{H}} | \Psi_{kl}^{cd} \rangle \\ \langle \Psi_{ij}^{ab} | \bar{\mathcal{H}} | \Psi_k^c \rangle & \langle \Psi_{ij}^{ab} | \bar{\mathcal{H}} | \Psi_{kl}^{cd} \rangle \end{pmatrix} \begin{pmatrix} s_k^c \\ s_{kl}^{cd} \end{pmatrix} = \omega_\lambda \begin{pmatrix} s_k^c \\ s_{kl}^{cd} \end{pmatrix}$$

We are interested in computing the elements like this:

$$\langle \Psi_{ij}^{ab} | \bar{\mathcal{H}} | \Psi_{kl}^{cd} \rangle$$

Expanding the similarity transformed Hamiltonian we obtain

$$\langle \Psi_{ij}^{ab} | \left(\hat{\mathcal{H}} + \hat{\mathcal{H}}\hat{T} + \frac{1}{2}\hat{\mathcal{H}}\hat{T}\hat{T} + \frac{1}{3!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T} + \frac{1}{4!}\hat{\mathcal{H}}\hat{T}\hat{T}\hat{T}\hat{T} \right)_C | \Psi_{kl}^{cd} \rangle = 0$$

Using the previous product of $\hat{T}\hat{T}$

$$\langle \Psi_{ij}^{ab} | \left(\frac{1}{2}\hat{\mathcal{H}}\hat{T}\hat{T} \right)_C | \Psi_{kl}^{cd} \rangle = 0$$

Using the simplified notation

$$\{B^\dagger A\}\{H^\dagger H\}\{T1^\dagger T1\}\{T2^\dagger T2\}\{C^\dagger D\}$$

Wick theorem for EE-EOMCCSD

Using the simplified notation

$$\{B^\dagger A\}\{H^\dagger H\}\{T1^\dagger T1\}\{T2^\dagger T2\}\{C^\dagger D\}$$

Now we have two different contractions:

- The external contractions: are made with respect the bra and the ket, and are all the possible CONECTED contractions considering $N[B^\dagger`] = N[A] = N[C^\dagger] = N[D] = 2$

$$\left[\left(B^\dagger D\right), \left(AC^\dagger\right)\right],$$
$$\left[\left(B^\dagger D, B^\dagger D\right), \left(AC^\dagger, AC^\dagger\right), \left(AC^\dagger, B^\dagger D\right), \ldots\right],$$
$$\left[\left(B^\dagger D, B^\dagger D, AC^\dagger\right), \left(AC^\dagger, AC^\dagger, B^\dagger D\right), \ldots\right]$$

- The internal contraction are made for each external. They are made by the rest of strings for a given external. The Wick theorem for coupled cluster is used for each internal

Categorize the integrals : Example

7. Categorize the integrals and amplitudes to obtain all the diagrams (programmable expressions)

$$\langle \Psi_{ij}^{ab} | \hat{\mathcal{W}}_N \hat{T}_1^2 | \Psi_0 \rangle$$

$$= \frac{1}{8} \sum_{kl,cd} \sum_{pqrs} \langle pq||rs \rangle \langle \Psi_0 | \{ \hat{i}^\dagger \hat{a} \hat{j}^\dagger \hat{b} \} \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} \{ \hat{c}^\dagger \hat{k} \} \{ \hat{d}^\dagger \hat{l} \} | \Psi_0 \rangle t_k^c t_l^d$$

Mathematica output after Wick theorem

$\{-\langle k, l| \; |i, j\rangle t_k^b t_l^a, \langle k, l| \; |i, j\rangle t_k^a t_l^b, -\langle l, b| \; |c, j\rangle t_l^a t_i^c, \langle l, a| \; |c, j\rangle t_l^b t_i^c,$
$\langle l, b| \; |c, i\rangle t_l^a t_j^c, -\langle l, a| \; |c, i\rangle t_l^b t_j^c, -\langle k, b| \; |d, j\rangle t_k^a t_i^d, -\langle k, a| \; |d, j\rangle t_k^b t_i^d,$
$-\langle a, b| \; |c, d\rangle t_i^d t_j^c, \langle k, b| \; |d, i\rangle t_k^a t_j^d, \langle k, a| \; |d, i\rangle t_k^b t_j^d, \langle a, b| \; |c, d\rangle t_i^c t_j^d\}$

Sorting the classes of terms with respect color an position

$\{-\langle k, l| \; |i, j\rangle t_k^b t_l^a, \langle k, l| \; |i, j\rangle t_k^a t_l^b, -\langle l, b| \; |c, j\rangle t_l^a t_i^c, \langle l, a| \; |c, j\rangle t_l^b t_i^c,$
$\langle l, b| \; |c, i\rangle t_l^a t_j^c, -\langle l, a| \; |c, i\rangle t_l^b t_j^c, -\langle k, b| \; |d, j\rangle t_k^a t_i^d, -\langle k, a| \; |d, j\rangle t_k^b t_i^d,$
$\langle k, b| \; |d, i\rangle t_k^a t_j^d, \langle k, a| \; |d, i\rangle t_k^b t_j^d, \langle a, b| \; |c, d\rangle t_i^c t_j^d, -\langle a, b| \; |c, d\rangle t_i^d t_j^c\}$

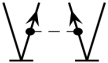
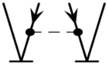
Play with the dummy indexes

$$\langle \Psi_{ij}^{ab} | \hat{\mathcal{W}}_N \hat{T}_1^2 | \Psi_0 \rangle = \sum_{kl} \langle kl||ij \rangle t_k^a t_l^b + P(i,j,a,b) \sum_{k,c} \langle ka||ci \rangle t_k^b t_j^c + \sum_{cd} \langle ab||cd \rangle t_i^c t_j^d$$

Categorize the integrals : Example

7. Categorize the integrals and amplitudes to obtain all the diagrams (programmable expressions)

$$\langle \Psi_{ij}^{ab} | \hat{\mathcal{W}}_N \hat{T}_1^2 | \Psi_0 \rangle = \sum_{kl} \langle kl || ij \rangle t_k^a t_l^b + P(i,j,a,b) \sum_{k,c} \langle ka || ci \rangle t_k^b t_j^c + \sum_{cd} \langle ab || cd \rangle t_i^c t_j^d$$

$\langle \Psi_{ij}^{ab} | \hat{\mathcal{W}}_N \hat{T}_1^2 | \Psi_0 \rangle$ =  +  + 

After classifying by the indexes that belong to the bra, playing with the dummy indexes and factorizing we can obtain the Goldstone diagrams, that represent the interaction between the Hamiltonian and excitation operators.

Conclusions

- A symbolic algebra program to obtain Coupled Cluster is described
- A procedure to contract an arbitrary number of second-quantization expressions and simplify them to map analytical result in to diagrams