CHM 673
Lecture 13: Coupled cluster method

Suggested reading:

Chapter 4.9, 4.10 from Jensen

http://vergil.chemistry.gatech.edu/notes/sahan-cc-2010.pdf

Recall CI method

Trial wave function – a linear combination of Slater determinants:

$$\Psi_{CI} = a_0 \Phi_{HF} + \sum_S a_S \Phi_S + \sum_D a_D \Phi_D + \sum_T a_T \Phi_T + ... = \sum_{i=0} a_i \Phi_i$$

Φ_S, Φ_D, Φ_T - singly, doubly, triply excited determinants

Can be rewritten using excitation operators C:

$$\Phi_S = \hat{C}_1 \Phi_0 = \Phi_i^a \qquad \text{single excitation operator}$$

$$\hat{C}_1 = \sum_i^{occ} \sum_a^{vir} c_i^a \hat{a}_a^+ \hat{a}_i$$

$$\Phi_D = \hat{C}_2 \Phi_0 = \Phi_{ij}^{ab} \qquad \text{double excitation operator}$$

$$\hat{C}_2 = \sum_{i<j}^{occ} \sum_{a<b}^{vir} c_{ij}^{ab} \hat{a}_a^+ \hat{a}_b^+ \hat{a}_i \hat{a}_j$$

$$\Phi_T = \hat{C}_3 \Phi_0 = \Phi_{ijk}^{abc}$$

$$\Psi_{CI} = \Phi_0 + \sum_{i\neq0} c_i \Phi_i = (1 + \hat{C}_1 + \hat{C}_2 + ... + \hat{C}_N)\Phi_0$$

CI methods provide a hierarchy of approximations: HF $\rightarrow$ CISD $\rightarrow$ CISDT $\rightarrow$ ... $\rightarrow$ FCI
However, truncated CI methods are not size-consistent: accuracy of truncated CI decreases with system size

Solution to size consistency problem

If $H_{AB} = H_A + H_B$ → $E_{AB} = E_A + E_B$, $\Psi_{AB} = \Psi_A \times \Psi_B$

But $\Psi_A^{CISD} \times \Psi_B^{CISD} \neq \Psi_{AB}^{CISD}$

Solution to size-consistency problem: Coupled Cluster (CC) ansatz: $\Psi = e^{\hat{T}}\Phi_0$

T – excitation operators, $T = T_1 + T_2 + \ldots$ similar to excitation operators C!

$$\hat{T}_1 = \sum_i^{occ}\sum_a^{vir} t_i^a \hat{a}_a^+ \hat{a}_i$$

$$\hat{T}_2 = \sum_{i<j}^{occ}\sum_{a<b}^{vir} t_{ij}^{ab} \hat{a}_a^+ \hat{a}_b^+ \hat{a}_i \hat{a}_j$$

Coupled cluster ansatz

$$\Psi = e^{\hat{T}}\Phi_{HF} = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + ...)\Phi_{HF}$$

This is an infinite Taylor series in powers of operator T!

Let's consider truncated operator T, e.g. T = T_1 + T_2 - this is CC**SD** model

$$\Psi = e^{\hat{T}_1+\hat{T}_2}\Phi_{HF} = \left(1 + (\hat{T}_1 + \hat{T}_2) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2)^2 + \frac{1}{6}(\hat{T}_1 + \hat{T}_2)^3 + ...\right)\Phi_{HF} =$$

$$\left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + ...\right)\Phi_{HF}$$

This term was missing in CISD!

Thus, CCSD

- has higher excitations present in the wavefunction
- is size-consistent: $\Psi_A \times \Psi_B = e^{\hat{T}_A}\Phi_{HF_A} \times e^{\hat{T}_B}\Phi_{HF_B} = e^{\hat{T}_A+\hat{T}_B}\Phi_{HF}$

Variational principle for Coupled Cluster ansatz

SE for CC wavefunction: $\qquad \hat{H}e^{\hat{T}}\Phi_0 = Ee^{\hat{T}}\Phi_0$

In order to use variational principle (like in CI), the energy functional is:

$$E_{CC}^{var} = \frac{\langle \Psi_{CC}|\hat{H}|\Psi_{CC}\rangle}{\langle \Psi_{CC}|\Psi_{CC}\rangle} = \frac{\langle e^{\hat{T}}\Phi_0|\hat{H}|e^{\hat{T}}\Phi_0\rangle}{\langle e^{\hat{T}}\Phi_0|e^{\hat{T}}\Phi_0\rangle}$$

Recall in CI: $\quad \langle \Psi_{CI}|\hat{H}|\Psi_{CI}\rangle = \Sigma_{ij}c_i^*c_j\langle \Phi_i|\hat{H}|\Phi_j\rangle = \Sigma_{ij}c_i^*c_j H_{ij}$

$$\langle \Psi_{CI}|\Psi_{CI}\rangle = \Sigma_{ij}c_i^*c_j\langle \Phi_i|\Phi_j\rangle = \Sigma_i|c_i|^2$$

These integrals have a finite number of terms if CI is truncated

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Non-vanishing terms up to Nelec excitations even for truncated CC!

For example, denominator in CCSD model : $\langle e^{\hat{T}_1+\hat{T}_2}\Phi_0|e^{\hat{T}_1+\hat{T}_2}\Phi_0\rangle =$

$$\langle(1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_2^2+...)\Phi_0|(1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_2^2+...)\Phi_0\rangle$$

Thus, truncating at some order of excitation operator T does not decrease dimensionality of the problem (size of the Hamiltonian matrix)
Variational principle is not practical!

Projection technique

An alternative to the variational principle: a projection technique

Multiply SE $\quad \hat{H}e^{\hat{T}}\Phi_0 = Ee^{\hat{T}}\Phi_0 \quad$ by $\quad \langle\Phi_0|, \langle\Phi_i^a|, \langle\Phi_{ij}^{ab}| \quad$ from left and integrate.

The resulting set of equations will allow to determine unknown *t* amplitudes (weights of each excited determinant in the CC wavefunction)

1. Multiplying by $\langle\Phi_0|$:

$$\langle\Phi_0|\hat{H}|e^{\hat{T}}\Phi_0\rangle = E_{CC}\langle\Phi_0|e^{\hat{T}}\Phi_0\rangle = E_{CC}\langle\Phi_0|(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + ...)\Phi_0\rangle$$

$$E_{CC} = \langle\Phi_0|\hat{H}|e^{\hat{T}}\Phi_0\rangle \qquad \leftarrow \text{coupled cluster energy}$$

these terms give 0!

Coupled cluster energy

$$E_{CC} = \langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle$$

Electronic Hamiltonian contains only one- and two-electron operators
Maximum of two-electron excitations give non-zero terms →

$$E_{CC} = \langle \Phi_0 | \hat{H} | (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \Phi_0 \rangle =$$

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} | \hat{T}_1 \Phi_0 \rangle + \langle \Phi_0 | \hat{H} | \hat{T}_2 \Phi_0 \rangle + \langle \Phi_0 | \hat{H} | \frac{1}{2}\hat{T}_1^2 \Phi_0 \rangle =$$

$$E_{HF} + \sum_{i}^{occ} \sum_{a}^{vir} t_i^a \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle + \sum_{i<j}^{occ} \sum_{a<b}^{vir} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle$$

In the coupled cluster energy expression, e^T terminates at T_2 level naturally, due to Hamiltonian nature.

Coupled cluster energy is completely determined by single and double amplitudes.

Coupled cluster amplitudes

First, multiply $\hat{H}e^{\hat{T}}\Phi_0 = Ee^{\hat{T}}\Phi_0$ by e^{-T} from left ($-T$ is deexcitation operator):

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CC}|\Phi_0\rangle \longrightarrow E_{CC} = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{\bar{H}} = e^{-\hat{T}}\hat{H}e^{\hat{T}} \quad \text{similarity transformed Hamiltonian}$$

Thus, E_{CC} is the expectation value of the similarity transformed Hamiltonian

2. Multiplying $\quad e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CC}|\Phi_0\rangle \quad$ by $\langle\Phi_i^a|, \langle\Phi_{ij}^{ab}| \quad$ to obtain amplitudes:

$$\langle\Phi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0 \quad\longrightarrow\quad \langle\Phi_i^a|(1-\hat{T}_1)\hat{H}(1+\hat{T}_1+(\hat{T}_2+\frac{1}{2}\hat{T}_1^2)+$$

$$\langle\Phi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

$$(\hat{T}_3+\hat{T}_1\hat{T}_2+\frac{1}{6}\hat{T}_1^3))|\Phi_0\rangle = 0$$

$$\langle\Phi_{ijk}^{abc}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

triple amplitudes

...

So far, everything is exact

Similarly to energy equation, equations for amplitudes are naturally truncated

Truncated coupled cluster models

Let's truncate the excitation operator T at the level of double excitations, i.e., T = T_1 + T_2
This defines the coupled cluster with single and double excitations method (CCSD)
Working equations are:

$$\langle \Phi_i^a | (1 - \hat{T}_1) \hat{H} (1 + \hat{T}_1 + (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) + (\cancel{\hat{T}_3} + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3)) | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | (1 - \hat{T}_1 - \hat{T}_2) \hat{H} (1 + \hat{T}_1 + (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) + (\cancel{\hat{T}_3} + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3) +$$

$$(\cancel{\hat{T}_4} + \hat{T}_1\cancel{\hat{T}_3} + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4)) | \Phi_0 \rangle = 0$$

T_3, T_4 disappear from the amplitude equations but terms like $\quad \hat{T}_1^3, \hat{T}_2^2 \quad$ stay and account for higher excitations (up to quartic)

These are coupled non-linear equations for single and double amplitudes $\quad t_i^a, t_{ij}^{ab}$
→ solved iteratively

When all $\quad t_i^a, t_{ij}^{ab} \quad$ are known, wave function and energy are calculated

Coupled cluster method: summary

CC methods are not variational → CC energy is not necessarily an upper bound to the exact energy
All truncated CC methods are size consistent

Hierarchy of approximations of truly increasing accuracy:

$$CCSD, CCSDT, CCSDTQ, ... CCSDTQ..N, \text{where } CCSDTQ..N = FCI$$

Computational scaling: N^6 N^8 N^{10} : same as in the truncated CI of the same order

In truncated CC methods, the excitations higher than the truncation level enter the amplitude equations and consequently the CC energy and wavefunction: the truncated CC methods are more correlated than the corresponding CI methods

CC methods are applicable for the ground state only → stay tuned for the EOM-CC extension for the excited states

Single excitations make only a small contribution to the correlation energy → single excitations can be made exactly zero through orbital relaxation (Brueckner theory, optimized-orbitals doubles methods, etc) → useful for cases of strong non-dynamical correlation

CI, CC and MP methods are related

$\hat{T}_2^2$ terms can be added to CISD to make it size consistent → e.g., QCISD method

Several hybrids of CC and MP methods exist, e.g., famous CCSD(T)
  coupled cluster with single, double and perturbative triple excitations →
  triple excitations by perturbation theory on top of a similarity transformed CCSD
    Hamiltonian

CCSD is similar in accuracy to MP4 that also includes single, double and quadrupole excitations