

- 1 Introduction
- 2 Configuration Interaction Methods
- 3 Møller-Plesset Perturbation Theory
- 4 Coupled Cluster Methods

# Coupled Cluster wave function

- Idea behind CC

*“Perturbation methods add all types of corrections (S, D, T, Q, etc.) to the reference wave function to a given order (2, 3, 4, etc.). The idea in CC methods is to include all corrections of a given type to infinite order.*

- Excitation operator

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \mathbf{T}_4 + \dots$$

- Action on the HF wave function

$$\mathbf{T}_1 \Psi_0 = \sum_{ia} t_i^a \Psi_i^a \quad \mathbf{T}_2 \Psi_0 = \sum_{\substack{i < j \\ a < b}} t_{ij}^{ab} \Psi_{ij}^{ab}$$

- CI wave function

$$\Psi_{\text{CI}} = (\mathbf{1} + \mathbf{T}) \Psi_0$$

- CC wave function

$\Psi_{\text{CC}} = e^{\mathbf{T}} \Psi_0$

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T} + \frac{\mathbf{T}^2}{2} + \frac{\mathbf{T}^3}{6} + \dots = \sum_{k=0}^{\infty} \frac{\mathbf{T}^k}{k!}$$

# Coupled Cluster wave function

$$\begin{aligned}
 e^{\mathbf{T}} = & \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_3 + \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) \\
 & + \left( \mathbf{T}_4 + \mathbf{T}_3 \mathbf{T}_1 + \frac{\mathbf{T}_2^2}{2} + \frac{\mathbf{T}_2 \mathbf{T}_1^2}{2} + \frac{\mathbf{T}_1^4}{24} \right) + \dots
 \end{aligned}$$

- singles =  $\mathbf{T}_1$
- doubles = connected doubles  $\mathbf{T}_2$  + disconnected doubles  $\mathbf{T}_1^2$
- $\mathbf{T}_4$  = four electrons interacting simultaneously
- $\mathbf{T}_2^2$  = two non-interacting pairs of interacting electrons
- Compared to CI, CC contains additional terms arising from products of excitations at each excitation level  
 $\Rightarrow$  CC is size consistent!! but not variational!

# Coupled Cluster energy

- Schrödinger equation for CC wave function

$$\mathbf{H}|\Psi_{\text{CC}}\rangle = E_{\text{CC}}|\Psi_{\text{CC}}\rangle \Rightarrow \mathbf{H}|e^{\mathbf{T}}\Psi_0\rangle = E_{\text{CC}}|e^{\mathbf{T}}\Psi_0\rangle$$

- Projection onto  $\Psi_0$

$$\langle \Psi_0 | \mathbf{H} | e^{\mathbf{T}} \Psi_0 \rangle = E_{\text{CC}} \langle \Psi_0 | e^{\mathbf{T}} \Psi_0 \rangle$$

$$\begin{aligned} E_{\text{CC}} &= \langle \Psi_0 | \mathbf{H} | e^{\mathbf{T}} \Psi_0 \rangle \\ &= \langle \Psi_0 | \mathbf{H} | \Psi_0 \rangle + \langle \Psi_0 | \mathbf{H} | \mathbf{T}_1 \Psi_0 \rangle + \langle \Psi_0 | \mathbf{H} | \mathbf{T}_2 \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | \mathbf{H} | \mathbf{T}_1^2 \Psi_0 \rangle \\ &= E_0 + \sum_{ia} \textcolor{violet}{t}_i^a \langle \Psi_0 | \mathbf{H} | \Psi_i^a \rangle + \sum_{ijab} (\textcolor{red}{t}_{ij}^{ab} + \textcolor{violet}{t}_i^a t_j^b - \textcolor{violet}{t}_i^b t_j^a) \langle \Psi_0 | \mathbf{H} | \Psi_{ij}^{ab} \rangle \\ &= E_0 + \sum_{ijab} (\textcolor{red}{t}_{ij}^{ab} + \textcolor{violet}{t}_i^a t_j^b - \textcolor{violet}{t}_i^b t_j^a) \langle ij || ab \rangle \end{aligned}$$

# Coupled Cluster equations

- Projection onto singly, doubly, triply, etc., excited determinants

$$\langle \Psi_i^a | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Psi_0 \rangle = 0$$

$$\langle \Psi_{ij}^{ab} | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Psi_0 \rangle = 0$$

$$\langle \Psi_{ijk}^{abc} | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Psi_0 \rangle = 0$$

- $e^{-\mathbf{T}}$  is a deexcitation operator

$$\begin{aligned} e^{-\mathbf{T}} &= \mathbf{1} - \mathbf{T} + \frac{\mathbf{T}^2}{2} - \frac{\mathbf{T}^3}{6} + \frac{\mathbf{T}^4}{24} + \dots \\ &= \sum_{k=0}^{\infty} (-1)^k \frac{\mathbf{T}^k}{k!} \end{aligned}$$

# Truncated Coupled Cluster methods

- CCSD

$$e^{\mathbf{T}_1 + \mathbf{T}_2} = \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) + \left( \frac{\mathbf{T}_2^2}{2} + \frac{\mathbf{T}_2 \mathbf{T}_1^2}{2} + \frac{\mathbf{T}_1^4}{24} \right) + \dots$$

- How do determine the CCSD amplitudes?

$$\langle \Psi_i^a (\mathbf{1} - \mathbf{T}_1) | \mathbf{H} | \left[ \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) \right] \Psi_0 \rangle = 0$$

$$\langle \Psi_{ij}^{ab} \left[ \mathbf{1} - \mathbf{T}_1 - \left( \mathbf{T}_2 - \frac{\mathbf{T}_1^2}{2} \right) \right] | \mathbf{H} | \left[ \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) + \left( \frac{\mathbf{T}_2^2}{2} + \frac{\mathbf{T}_2 \mathbf{T}_1^2}{2} + \frac{\mathbf{T}_1^4}{24} \right) \right] | \Psi_0 \rangle = 0$$

- All the matrix elements can be evaluated in terms of MO integrals
- Coupled non-linear equations for the singles and doubles amplitudes
- Must be solved iteratively (quartic in the amplitudes)

# Connections between CI, CC and MP (Part 1)

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_3 + \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) + \left( \mathbf{T}_4 + \mathbf{T}_3 \mathbf{T}_1 + \frac{\mathbf{T}_2^2}{2} + \frac{\mathbf{T}_2 \mathbf{T}_1^2}{2} + \frac{\mathbf{T}_1^4}{24} \right) + \dots$$

- Each parenthesis generates all the excited determinants of the given type
- $\mathbf{T}_1$  is small  $\Rightarrow \mathbf{T}_1^2, \mathbf{T}_1^3, \mathbf{T}_1^4, \mathbf{T}_1 \mathbf{T}_2 \dots$  are small
- $\mathbf{T}_2$  is large, and  $\mathbf{T}_3 \gg \mathbf{T}_2 \mathbf{T}_1 \gg \mathbf{T}_1^3$
- $\mathbf{T}_2$  is large  $\Rightarrow \mathbf{T}_2^2 > \mathbf{T}_4$  and the rest is small because  $\mathbf{T}_1 \ll 0$
- $\mathbf{T}_m$  with  $m > 4$  expected to have small effects
- CISD lacks  $\mathbf{T}_2^2 \Rightarrow$  not size consistent
- $\mathbf{T}_2^2$  becomes large when number of electrons increases  $\Rightarrow$  Davidson correction

$$E_c(\text{CISD+Q}) = E_c(\text{CISD}) + (1 - c_0^2)E_c(\text{CISD})$$

# Connections between CI, CC and MP (Part 2)

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T}_1 + \left( \mathbf{T}_2 + \frac{\mathbf{T}_1^2}{2} \right) + \left( \mathbf{T}_3 + \mathbf{T}_2 \mathbf{T}_1 + \frac{\mathbf{T}_1^3}{6} \right) + \left( \mathbf{T}_4 + \mathbf{T}_3 \mathbf{T}_1 + \frac{\mathbf{T}_2^2}{2} + \frac{\mathbf{T}_2 \mathbf{T}_1^2}{2} + \frac{\mathbf{T}_1^4}{24} \right) + \dots$$

- MP2 and MP3 uses **only doubles**
- MP4 uses singles, doubles, triples ( $\mathbf{T}_3$ ) and quadruples ( $\mathbf{T}_2^2$ )
- CCD  $\approx$  MP4(DQ) and CCSD  $\approx$  MP4(SDQ)
- MP2, MP3 and MP4(SDQ) can be obtained in 1st CCSD iteration
- CCSD lacks connected triples  $\mathbf{T}_3$ 
  - ① CCSDT but very expensive!
  - ② CCSD(T) where **triples comes from MP4** (non-iterative)

# Illustration for the Be atom

## Correlation energy of Be

Level	$\Delta E_c$	%	Level	$\Delta E_c$	%	Level	$\Delta E_c$	%
MP2	0.053174	67.85						
MP3	0.067949	86.70	CISD	0.075277	96.05	CCSD	0.078176	99.75
MP4	0.074121	94.58				CCSD(T)	0.078361	99.99
MP5	0.076918	98.15	CISDT	0.075465	96.29	CCSDT	0.078364	99.99
MP6	0.078090	99.64						
MP7	0.078493	100.15	CISDTQ	0.078372	100	CCSDTQ	0.078372	100

# Cost of correlated methods

## Scaling of various correlated methods

Scaling	CI methods	MP methods	CC methods
$K^5$	CIS	MP2	CC2
$K^6$	CISD	MP3	CCSD
$K^7$		MP4	CC3,CCSD(T)
$K^8$	CISDT	MP5	CCSDT
$K^9$		MP6	
$K^{10}$	CISDTQ	MP7	CCSDTQ
$\exp(K)$	FCI		

As a rule of thumb:

HF  $\ll$  MP2  $<$  CISD  $<$  MP4(SDQ)  $\sim$  CCSD  $<$  MP4  $<$  CCSD(T)