

# **Coupled-Cluster Theory: a Tool for High-Accuracy Quantum-Chemical Calculations**

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**I.**

# **Motivation**

# Motivation

- **high-accuracy treatment of electronic structure**

- **electron correlation**
- **non-perturbative approach**
- **cost effective**

not necessarily cheap, **optimal accuracy-cost ratio**

- **correct physical properties of many-body systems**

- **size consistency/extensivity**

=> **(one) answer: coupled-cluster theory**

## **II.**

# **Exponential Ansatz for Wavefunction**

# Hamilton Operator for Many-Electron Systems

**non-relativistic Hamiltonian for atoms and molecules**

$$\hat{H} = \sum_{\alpha} \hat{h}(\alpha) + \sum_{\alpha < \beta} \frac{1}{r_{\alpha\beta}}$$

**one-electron terms**

**two-electron terms**

**prohibits exact solution  
→ electron correlation**

# Exact Solution of Electron-Correlation Problem

**define effective (zeroth-order) Hamiltonian**

$$\hat{H}_0 = \sum_{\alpha} \hat{F}(\alpha)$$

**solve one-electron problem  
(e.g., HF equations)**

$$\hat{F} \varphi_p = \epsilon_p \varphi_p$$

**Slater determinants  
(take care of antisymmetry)**

$$\Phi_I = \frac{1}{\sqrt{N!}} |\varphi_{I1} \varphi_{I2} \dots \varphi_{IN}|$$

↓

$$\{\Phi_I, I = 1, \dots\}$$

**„complete“ one-electron basis  
(spin orbitals)**

$$\{\varphi_p, p = 1, \dots\}$$

**complete many-electron basis**

**within given AO basis**

# Exact Solution of Electron-Correlation Problem

expansion in a complete set of Slater determinants

$$\Psi = \sum_I c_I \Phi_I = c_0 \Phi_{HF} + \sum_{I \neq 0} c_I \Phi_I$$

excited determinants

together with variational principle

$$\sum_J H_{IJ} c_J = E c_I \qquad H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$$

**$\Rightarrow$  Full Configuration Interaction (FCI)**

# Excitation Level of Slater Determinants

virtual				
occupied				
	<b>HF</b>	<b>singly excited</b>	<b>doubly excited</b>	<b>triply excited</b>
number	1	$n_{\text{occ}} N_{\text{virt}}$	$n_{\text{occ}}^2 N_{\text{virt}}^2$	$n_{\text{occ}}^3 N_{\text{virt}}^3$



# Full and Truncated CI Methods

- Full CI:**
- factorial growth of cost
  - not practical, only for benchmarking

small molecules and basis (e.g., H<sub>2</sub>O, DZP)

benzene, DZP:  $\approx 10^{42}$  determinants

=> truncate determinantal basis (approximation)

=> truncated CI methods such as CISD

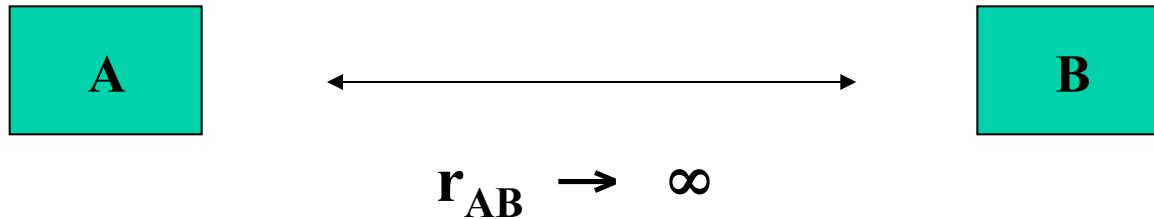
$$\Psi_{CISD} = c_0 \Phi_0 + \sum_{I \in S, D} c_I \Phi_I$$

polynomial growth of cost

excited determinants restricted to single + double excitations

# Size Consistency

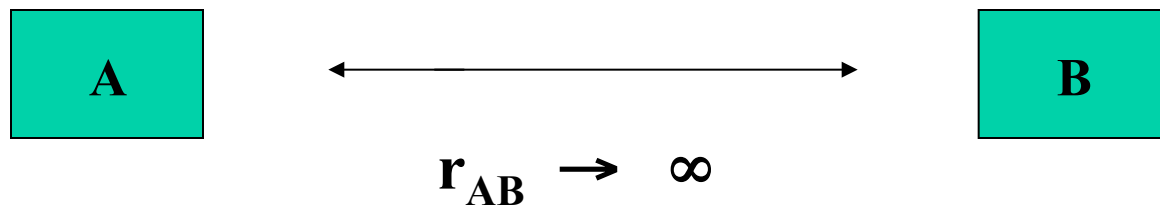
**non-interacting systems A and B:**



$$\mathbf{E}_{AB} = \mathbf{E}_A + \mathbf{E}_B$$

- additivity of energy
- multiplicability of wavefunction

# Size Consistency



A method is termed **size consistent** if the sum of energies computed for two non-interacting subsystems A and B is **equal** to the energy obtained for the supersystem consisting of both A and B

a) individual quantum-chemical calculations for A and B  $\rightarrow E_A + E_B$

b) one quantum-chemical calculations for A+B  $\rightarrow E_{AB}$

size consistency: 
$$E_{AB} = E_A + E_B$$

# Size-Consistency Problem of Truncated CI

**CISD approximation:**

**HF ... HF**

	$2 \times E_{\text{HF}}$	$E_{\text{HF} \dots \text{HF}}$	$\Delta$
<b>HF-SCF</b>	-200.558	-200.558	0.000
<b>CISD</b>	-200.576	-200.559	-0.017 $\approx 11 \text{ kcal/mol}$

calculations with tzp basis set

**truncated CI methods are not size consistent**

# Multiplicative Property of the Wavefunction

**non-interacting systems A and B**

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

**=> separation ansatz**

$$E_{AB} = E_A + E_B$$

**additive**

$$\Psi_{AB} = \hat{\mathcal{A}} \Psi_A \Psi_B$$

**multiplicative**

antisymmetrizer  


# Multiplicative Property of the Wavefunction

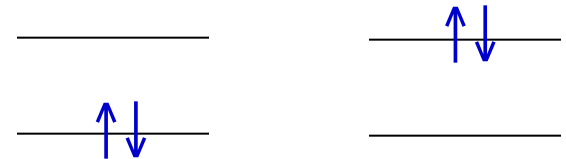
**H<sub>2</sub> molecule, minimal basis**

$$\Psi_{CID} = \Phi_{HF} + c \Phi_D$$

(not normalized)

$$= (1 + \hat{\tau}_D) \Phi_{HF}$$

operator, generates a by  $c$   
weighted double excitations



$\Phi_{HF}$

$\Phi_D$

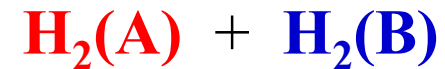
**HF  
determinant**

**double  
excitation**

**H<sub>2</sub>: CID = FCI = exact solution**

# Multiplicative Property of the Wavefunction

two H<sub>2</sub> molecule, minimal basis



CID wavefunction

$$\Psi_{CID} = (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B}) \Phi_{HF}$$

but

$$\begin{aligned} \hat{A} \Psi_{CID,A} \Psi_{CID,B} &= \hat{A} \{ (1 + \hat{\tau}_{D,A}) \Phi_{HF,A} \} \{ (1 + \hat{\tau}_{D,B}) \Phi_{HF,B} \} \\ &= \hat{A} (1 + \hat{\tau}_{D,A}) (1 + \hat{\tau}_{D,B}) \Phi_{HF,A} \Phi_{HF,B} \\ &= (1 + \hat{\tau}_{D,A}) (1 + \hat{\tau}_{D,B}) \Phi_{HF} \\ &= (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B} + \hat{\tau}_{D,A} \hat{\tau}_{D,B}) \Phi_{HF} \end{aligned}$$

quadruple excitation, missing in CID => problem

# Multiplicative Property of the Wavefunction

**problem of CI:**

**excitations are additive**

$$\sum_{i=A,B,\dots} \hat{\tau}_{D,i}$$

**contradiction !?!**

**required is a multiplicative property**

$$\prod_{i=A,B,\dots} \dots$$



# Multiplicative Property of the Wavefunction

one, two, three, ... H<sub>2</sub> molecules

$$\Psi_1 = (1 + \hat{\tau}_{D,A}) \Phi_{HF}$$

$$\Psi_2 = (1 + \hat{\tau}_{D,A}) (1 + \hat{\tau}_{D,B}) \Phi_{HF}$$

$$\Psi_3 = (1 + \hat{\tau}_{D,A}) (1 + \hat{\tau}_{D,B}) (1 + \hat{\tau}_{D,C}) \Phi_{HF}$$

...

$$\Psi = \prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i}) \Phi_{HF}$$

# Exponential Form for the Wavefunction

**proper form of wavefunction**

$$\Psi = \prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i}) \Phi_{HF}$$

**rewrite in exponential form**

$$\prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i}) \Phi_{HF} \equiv \exp\left(\sum_{i=A,B,\dots} \hat{\tau}_{D,i}\right) \Phi_{HF}$$

**multiplicative property via additivity in exponent**

# Exponential of Operators

**definition via a power series**

$$\exp(\hat{A}) = 1 + \hat{A} + \frac{1}{2!}\hat{A}^2 + \frac{1}{3!}\hat{A}^3 + \dots \frac{1}{n!}\hat{A}^n + \dots$$

**exponential of a number** → **non-terminating** power series

**exponential of an operator** → power series **can terminate**  
**dependent on operator**

# Exponential Form for the Wavefunction

$$\prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i}) \Phi_{HF} \equiv \exp\left(\sum_{i=A,B,\dots} \hat{\tau}_{D,i}\right) \Phi_{HF}$$

**proper counting**

$$\begin{aligned} \frac{1}{2} \left( \sum_i \hat{\tau}_{D,i} \right)^2 &\Rightarrow \frac{1}{2} \hat{\tau}_{D,A} \hat{\tau}_{D,B} + \frac{1}{2} \hat{\tau}_{D,B} \hat{\tau}_{D,A} + \dots \\ &\Rightarrow \hat{\tau}_{D,A} \hat{\tau}_{D,B} + \dots \end{aligned}$$

**same excitation cannot  
be applied twice**

$$\hat{\tau}_{D,A} \hat{\tau}_{D,A} = 0$$

# Exponential Form for the Wavefunction

**exponential ansatz**

$$\Psi = \exp(\hat{T}) \Phi_0$$

**excitations  
represented via an operator**

**reference determinant**

**proper multiplicative behaviour  $\Rightarrow$  size consistency**

# Connected and Disconnected Excitations

$$\Psi = \prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i}) \Phi_{HF}$$

$$\Psi = \Phi_{HF} + \hat{\tau}_{D,A} \Phi_{HF} + \dots + \hat{\tau}_{D,A} \hat{\tau}_{D,B} \Phi_{HF} + \dots$$

**connected excitations**

**disconnected excitations**

**(products of connected excitations)**

CI does not differ between **connected** and **disconnected** excitations

### **III. Coupled-Cluster Theory**

# Coupled-Cluster Theory

**ansatz for wavefunction**

$$|\Psi\rangle = \exp(T) |0\rangle$$

reference  
determinant

**cluster operator**

$$T = \sum_I t_I \tau_I$$

**excitation operators  
(in second quantization)**

sum over  
(all) excitations

**weighting factors  
(amplitudes)**

unknown parameters  
to be determined



# Coupled-Cluster Theory

**classification of excitation**

$$T = T_1 + T_2 + T_3 + \dots$$

$$T_1 = \sum_a \sum_i t_i^a a^\dagger i$$

**single excitations**

$$T_2 = \frac{1}{4} \sum_{a,b} \sum_{i,j} t_{ij}^{ab} a^\dagger i b^\dagger j$$

**double excitations**

$\dots$

**all possible excitations**

$$T = T_1 + T_2 + T_3 + \dots + T_N$$

**truncated schemes, e.g.**

$$T = T_1 + T_2$$

# Equivalence of CC and FCI

## CC wavefunction

$$|\Psi\rangle = \exp(T) |0\rangle$$

$$T_1 |0\rangle$$

singly excited

$$(T_2 + \frac{1}{2}T_1^2) |0\rangle$$

doubly excited

$$(T_3 + T_2T_1 + \frac{1}{3!}T_1^3) |0\rangle$$

triply excited

$$(T_4 + T_3T_1 + \frac{1}{2!}T_2^2$$

quadruply excited

$$+ \frac{1}{2}T_1^2T_2 + \frac{1}{4!}T_1^4) |0\rangle \dots$$

## CI wavefunction

$$\Psi = C |0\rangle$$

$$C_1 |0\rangle$$

$$C_2 |0\rangle$$

$$C_3 |0\rangle$$

$$C_4 |0\rangle$$

matching number of parameters

=> **CC ansatz parametrizes the exact wavefunction**

# Coupled-Cluster Theory

## truncated CC wavefunctions

$$T = T_2 \quad \text{truncation in the cluster operator}$$

**CCD = CC doubles**

$$|\Psi_{CCD}\rangle = |0\rangle + T_2 |0\rangle + \frac{1}{2!} T_2^2 |0\rangle + \frac{1}{3!} T_2^3 |0\rangle + \dots$$

**connected double excitations**

**disconnected quadruple, sextuple, ... excitations**

# Variational CC Approaches

**determination of amplitudes via variation principle**

**minimization of**

$$\tilde{E} = \frac{\langle 0 | \exp(T^\dagger) H \exp(T) | 0 \rangle}{\langle 0 | \exp(T^\dagger) \exp(T) | 0 \rangle}$$

**CC wavefunction  
not normalized**

**adjoint of CC wavefunction**

**non-truncating operator**

$$\exp(T^\dagger) H \exp(T) = H + T^\dagger H + HT + \frac{1}{2!} T^{\dagger 2} H + T^\dagger HT + \frac{1}{2!} HT^2 + \dots$$

**cost independent of choice of  $T$  always similar to FCI**

**=> not feasible for practical schemes**

# Standard CC Approach

**use of projection techniques**

**transform an operator equation into a set of algebraic equations**

$$\begin{array}{ccc} H|\Psi\rangle & = & E|\Psi\rangle \\ \downarrow & & \swarrow \text{equivalent} \\ \{\Phi_I, I = 1, \dots\} & & \\ \text{complete basis} & & \\ \langle\Phi_I|H|\Psi\rangle = E\langle\Phi_I|\Psi\rangle & I = 1, \dots & \searrow \end{array}$$

**matching number of equations and wavefunction parameters (amplitudes)**

# Standard CC Approach

matching number of equations and wavefunction parameters (amplitudes)

projection on all excited determinants

same number of excitations as in many-electron basis

**truncated CC approaches**

projection on all excited determinants  $\rightarrow$  unsolvable problem

project only on those determinants for which excitations are in  $T$

$T = T_2 \rightarrow$  project onto  $\Phi_D$

$T = T_1 + T_2 \rightarrow$  project onto  $\Phi_S + \Phi_D$

**Schrödinger equation cannot be solved and is no longer solved**

# Coupled-Cluster Theory

- insertion into Schrödinger equation

$$H \exp(T) |0\rangle = E \exp(T) |0\rangle$$

- multiplication from the left with  $\exp(-T)$

$$\exp(-T) H \exp(T) |0\rangle = E |0\rangle$$

- projection onto reference determinant

→ **CC energy**  $E = \langle 0 | \exp(-T) H \exp(T) |0\rangle$

- projection onto excited determinants

→ **CC equations**  $0 = \langle \Phi_P | \exp(-T) H \exp(T) |0\rangle$

**non-linear equations for amplitudes**

# Coupled-Cluster Equations

$$E = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle$$

$$0 = \langle \Phi_P | \exp(-T) H \exp(T) | 0 \rangle \quad P = 1, \dots$$

$$\textbf{with} \quad \langle \Phi_P | = \langle 0 | i a^\dagger \dots$$

→ **expectation value**

**evaluation using second-quantization techniques**



## **IV. Computational Realization**

# Detailed Expressions for the CC Equations

- **algebraic analysis via Wick's theorem**

**tedious, not recommended  
suitable for computer algebra**

- **analysis by means of diagrammatic techniques**

**simple access via graphical representations  
automatic elimination of non-contributing terms  
(better) suitable for computer algebra**

# Algebraic CCD Expressions

**CC energy:**

$$\Delta E = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij || ab \rangle t_{ij}^{ab}$$

**CC equations:**

$$\begin{aligned} 0 = & \langle ab || ij \rangle + P_{-}(ab) \sum_e f_{ae} t_{ij}^{eb} - P_{-}(ij) \sum_m f_{mi} t_{mj}^{ab} \\ & + \frac{1}{2} \sum_{mn} \langle mn || ij \rangle t_{mn}^{ab} + \frac{1}{2} \sum_{ef} \langle ab || ef \rangle t_{ij}^{ef} \\ & + P_{-}(ij) P_{-}(ab) \sum_m \sum_e \langle mb || ej \rangle t_{im}^{ae} \\ & - \frac{1}{2} P_{-}(ab) \sum_{mn} \sum_{ef} \langle mn || ef \rangle t_{mn}^{af} t_{ij}^{eb} - \frac{1}{2} P_{-}(ij) \sum_{mn} \sum_{ef} \langle mn || ef \rangle t_{in}^{ef} t_{mj}^{ab} \\ & + \frac{1}{4} \sum_{mn} \sum_{ef} \langle mn || ef \rangle t_{mn}^{ab} t_{ij}^{ef} + \frac{1}{2} P_{-}(ij) P_{-}(ab) \sum_{mn} \sum_{ef} \langle mn || ef \rangle t_{im}^{ae} t_{jn}^{bf} \end{aligned}$$

# Factorization of Terms

$$\sum_{m < n} \sum_{e < f} \langle mn || ef \rangle t_{mn}^{ab} t_{ij}^{ef} \implies Z_{ij}^{ab}$$

**one-step evaluation  $\Rightarrow$   $N^8$  computational cost**

$$\text{a) } \sum_{e < f} \langle mn || ef \rangle t_{ij}^{ef} \implies Y_{ij}^{mn}$$

$$\text{b) } \sum_{m < n} Y_{ij}^{mn} t_{mn}^{ab} \implies Z_{ij}^{ab}$$

**factorization**

**two-step evaluation  $\Rightarrow$   $2 N^6$  computational cost**

# Definition of Intermediates

- straightforward implementation (term by term)

$$\left. \begin{array}{l} \sum_{m < n} \langle mn || ij \rangle t_{mn}^{ab} \quad \text{N}^6 \text{ cost} \\ + \sum_{m < n} \sum_{e < f} \langle mn || ef \rangle t_{ij}^{ef} t_{mn}^{ab} \quad 2 \text{ N}^6 \text{ cost} \end{array} \right\} 3 \text{ N}^6 \text{ cost}$$

- via intermediates

$$\left. \begin{array}{l} \text{intermediate} \quad \tilde{\mathcal{W}}_{mnij} = \langle mn || ij \rangle + \sum_{e < f} \langle mn || ef \rangle t_{ij}^{ef} \quad \text{N}^6 \text{ cost} \\ \\ \text{contraction} \quad \sum_{m < n} \tilde{\mathcal{W}}_{mnij} t_{mn}^{ab} \quad \text{N}^6 \text{ cost} \end{array} \right\} 2 \text{ N}^6 \text{ cost}$$

# CCD Formulated via Intermediates

**CC energy:**

$$\Delta E = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij || ab \rangle t_{ij}^{ab}$$

**CC equations:**

$$\begin{aligned} 0 = & \langle ab || ij \rangle + P_{-}(ab) \sum_e \tilde{\mathcal{F}}_{ae} t_{ij}^{eb} - P_{-}(ij) \sum_m \tilde{\mathcal{F}}_{mi} t_{mj}^{ab} \\ & + \frac{1}{2} \sum_{mn} \tilde{\mathcal{W}}_{mni j} t_{mn}^{ab} + \frac{1}{2} \sum_{ef} \langle ab || ef \rangle t_{ij}^{ef} \\ & + P_{-}(ij) P_{-}(ab) \sum_m \sum_e \tilde{\mathcal{W}}_{mbej} t_{im}^{ae} \end{aligned}$$

**intermediates:**

$$\tilde{\mathcal{F}}_{mi} = f_{mi} + \frac{1}{2} \sum_n \sum_{ef} \langle mn || ef \rangle t_{in}^{ef} \quad \tilde{\mathcal{F}}_{ae} = f_{ae} - \frac{1}{2} \sum_{mn} \sum_f \langle mn || ef \rangle t_{mn}^{af}$$

$$\tilde{\mathcal{W}}_{mni j} = \langle mn || ij \rangle + \frac{1}{2} \sum_{ef} \langle mn || ef \rangle t_{ij}^{ef} \quad \tilde{\mathcal{W}}_{mbej} = \langle mb || ej \rangle + \frac{1}{2} \sum_n \sum_f \langle mn || ef \rangle t_{jn}^{fb}$$

# Computational Cost

$$\sum_{m < n} \langle mn || ij \rangle t_{mn}^{ab} \implies Z_{ij}^{ab}$$

target indices i,j,a,b  
do it for all i<j and a<b

summation over m < n  $\rightarrow \frac{1}{2} n_{\text{occ}}^2$

$\rightarrow \frac{1}{2} n_{\text{occ}}^2 * \frac{1}{2} N_{\text{virt}}^2$

$\implies$  total cost are  $\frac{1}{8} n_{\text{occ}}^4 * N_{\text{virt}}^2$

**CCD + CCSD:**

**total:**  $\frac{1}{4} n_{\text{occ}}^4 * N_{\text{virt}}^2 + \frac{1}{8} n_{\text{occ}}^2 * N_{\text{virt}}^4 + 2 n_{\text{occ}}^3 * N_{\text{virt}}^3$

$\implies N^6$  computational cost

# Computational Cost

$$\sum_{m < n} \langle mn || ij \rangle t_{mn}^{ab} \implies Z_{ij}^{ab}$$

target indices i,j,a,b  
 do it for all i<j and a<b  
 →  $\frac{1}{2} n_{\text{occ}}^2 * \frac{1}{2} N_{\text{virt}}^2$

summation over m < n →  $\frac{1}{2} n_{\text{occ}}^2$

$$\implies \text{total cost are } \frac{1}{8} n_{\text{occ}}^4 * N_{\text{virt}}^2$$

**CCD + CCSD:**

$$\text{total: } \frac{1}{4} n_{\text{occ}}^4 * N_{\text{virt}}^2 + \frac{1}{8} n_{\text{occ}}^2 * N_{\text{virt}}^4 + 2 n_{\text{occ}}^3 * N_{\text{virt}}^3$$

**less than 2 times as expensive as CID and CISD (linear terms only !)**



# Iterative Solution of CC Equations

- no direct solution of (non-linear) CC equations possible

**=> iterative schemes**

- rewrite CC equations

**CCD:**  $0 = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t_{ij}^{ab} + Z_{ij}^{ab}(t_{ij}^{ab})$

**zeroth-order term** **higher-order terms**

- iterative sequence

$$t_{ij}^{ab(n+1)} = \frac{Z_{ij}^{ab}(t_{ij}^{ab(n)})}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

**new amplitudes** **computed with old amplitudes**

**initial guess via MP2, convergence acceleration using DIIS**

## **V. Approximate CC Methods**

# Approximate CC Methods I

truncation of the cluster operator  $T$ :

cluster operator	approximation	cost
$T=T_1+T_2$	<b>CCSD</b>	$N^6$
$T=T_1+T_2+T_3$	<b>CCSDT</b>	$N^8$
$T=T_1+T_2+T_3+T_4$	<b>CCSDTQ</b>	$N^{10}$
$T=T_1+T_2+T_3+T_4+T_5$	<b>CCSDTQP</b>	$N^{12}$
...	...	...
$T=T_1+T_2+ \dots +T_N$	<b>FCI</b>	

# Approximate CC Methods II

**additional approximations in the amplitude equations**

- **no storage of amplitudes for highest excitation**
- **reduced scaling in computational cost**

→ **CCSDT-n (n=1-3)**

→ **CC3 (within CCn hierarchy)**

# Iterative Approximations to CCSDT

**triples equations:**

$$\begin{aligned}
 0 = \langle \mathcal{T} | & \left( \underbrace{f_N T_3}_{\text{blue}} + \underbrace{f_N T_3 T_1}_{\text{red}} + \frac{1}{2!} \underbrace{f_N T_2^2}_{\text{green}} + \underbrace{W_N T_2}_{\text{blue}} + \underbrace{W_N T_3}_{\text{red}} + \underbrace{W_N T_1 T_2}_{\text{black}} \right. \\
 & + \frac{1}{2!} \underbrace{W_N T_2^2}_{\text{green}} + \underbrace{W_N T_3 T_1}_{\text{red}} + \frac{1}{2!} \underbrace{W_N T_2 T_1^2}_{\text{black}} \\
 & \left. + \underbrace{W_N T_3 T_2}_{\text{red}} + \frac{1}{2!} \underbrace{W_N T_2^2 T_1}_{\text{black}} + \frac{1}{2!} \underbrace{W_N T_3 T_1^2}_{\text{red}} + \frac{1}{3!} \underbrace{W_N T_2 T_1^3}_{\text{black}} \right) c | 0 \rangle
 \end{aligned}$$

**N<sup>8</sup> terms:** — **to be skipped in all cases**

<b>CCSDT-1:</b>	<span style="color: blue;">—</span>	<b>CCSDT-3:</b>	<span style="color: blue;">—</span>	+	<span style="color: green;">—</span>	+	<span style="color: black;">—</span>
<b>CCSDT-2:</b>	<span style="color: blue;">—</span>	+	<span style="color: green;">—</span>	<b>CC3:</b>	<span style="color: blue;">—</span>	+	<span style="color: gray;">—</span>

# Approximate CC Methods III

**non-iterative treatment of higher excitations**

**two-step procedure:**

- **perform CCSD calculation**

$$T = T_1 + T_2$$

- **add perturbative corrections due to  $T_3$**

$$E = E(\text{CCSD}) + \Delta E(T)$$

**use of converged  $T_1$  and  $T_2$  amplitudes**

**→ CCSD+T(CCSD), CCSD(T), ....**

# CCSD(T)

## perturbative corrections on top of CCSD

- fourth-order contribution

$$\Delta E_T(4) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{|w_{ijk}^{abc}|^2}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c}$$

$$w_{ijk}^{abc} = P(ij/k)P(ab/c) \left\{ \sum_e \langle bc || ek \rangle t_{ij}^{ae} - \sum_m \langle mc || jk \rangle t_{im}^{ab} \right\}$$

- fifth-order contribution

computed with  
CCSD amplitudes

$$\Delta E_T(5) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{w_{ijk}^{abc} \tilde{w}_{ijk}^{abc}}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c}$$

$$\tilde{w}_{ijk}^{abc} = P(ij/k)P(ab/c) \langle bc || jk \rangle t_i^a$$

permutation operator:  $P(pq/r)Z(pqr) = Z(pqr) + Z(qrp) + Z(rpq)$

# Current Standard in CC Theory

importance of triple excitations for accurate predictions

	CCSD	CCSD(T)
energies	10 - 40 kJ/mol	5 – 10 kJ/mol
bond distances	~ 0.01 Å	~ 0.002 Å
<sup>13</sup> C NMR shieldings	~ 5 ppm	~ 1 ppm

**CCSD(T): currently standard approach in CC theory**



# Need for Quadruples, Quintuples, ...

- heats of formation, atomization energies ( $\rightarrow 1 \text{ kJ/mol}$ )
  - $\rightarrow$  thermochemistry, atmospheric chemistry
- geometrical parameters ( $\rightarrow 0.0001 \text{ \AA}$ )
  - $\rightarrow$  rotational spectroscopy (e.g., astrochemistry)
  - $\rightarrow$  benchmark calculations
- formulation of MR-CC based on „single-reference CC“
  - $\rightarrow$  MR-CC methods
  - $\rightarrow$  calculation of potential energy surfaces

# General Coupled-Cluster Methods

Problems:

	# terms	comp. cost
CCSD	45	$N^6$
CCSDT	99	$N^8$
CCSDTQ	180	$N^{10}$
CCSDTQP	286	$N^{12}$
CCSDTQPH	397	$N^{14}$
...	...	...

**Efficient Implementation?**

# Strategies for Implementing General CC Methods

**no simple hand-coded implementation**

**→ computer-aided implementation**

**three aspects:**

- formula generation**
- factorization/definition of intermediates**
- code generation**

# Implementation of General CC Models

## string-based many-body approaches (M. Kállay, Budapest)

- automatized generation of diagrams (CC,  $\Lambda$  equations, density matrices)
- optimization of factorization/definition of intermediates

e.g.:

$$\frac{1}{4} \sum_{m,n} \sum_{e,f} \langle mn || ef \rangle t_{mn}^{ab} t_{ij}^{ef} \begin{array}{l} \xrightarrow{(a)} \tilde{\mathcal{W}}_{mnij} \leftarrow \sum_{e,f} \langle mn || ef \rangle t_{ij}^{ef} \\ \xrightarrow{(b)} \tilde{\mathcal{W}}_{abef} \leftarrow \sum_{m,n} \langle mn || ef \rangle t_{mn}^{ab} \end{array}$$

- automatized evaluation of contractions

**$\Rightarrow$  CCSDTQ, CCSDTQP, ..., FCI energies, gradients, ...**

# Accuracy of CC versus CI Methods

**Deviation from FCI (in mH) for CO**

	CI	CC
SD	30.804	12.120
SDT	21.718	1.011
SDTQ	1.775	0.061
SDTQP	0.559	0.008
SDTQPH	0.035	0.002

**calculations with cc-pVDZ basis, frozen core**

## **V. Analytic Gradients in CC Theory**

# CC Gradients via Straightforward Differentiation

**energy**

$$E = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle$$

**gradient**

$$\frac{\partial E}{\partial x} = \langle 0 | \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle + \langle 0 | [\exp(-T) H \exp(T), \frac{\partial T}{\partial x}] | 0 \rangle$$

**$\Rightarrow$  integral derivatives**

**$\Rightarrow$  perturbed amplitudes**

**perturbed amplitudes via**

$$0 = \langle \Phi_I | \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle + \langle \Phi_I | [\exp(-T) H \exp(T), \frac{\partial T}{\partial x}] | 0 \rangle$$

**to be solved for all x; cost similar to CC equations**

**Efficiency?**

# CC Gradients using Lagrange Multipliers

**energy functional**

**Lagrange multipliers**

$$\tilde{E} = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle + \sum_I \lambda_I \langle \Phi_I | \exp(-T) H \exp(T) | 0 \rangle$$

**energy**

**CC equations as constraints**

**compact notation**

$$\tilde{E} = \langle 0 | (1 + \Lambda) \exp(-T) H \exp(T) | 0 \rangle$$

**$\Lambda$  deexcitation operator:**

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots$$

$$\Lambda_1 = \sum_i \sum_a \lambda_a^i \{i^+ a\}$$

$$\Lambda_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} \lambda_{ab}^{ij} \{i^+ a j^+ b\}$$

Arponen (1983), Adamowicz, Laidig, Bartlett (1984), Helgaker, Jørgensen (1988)



# CC Gradients using Lagrange Multipliers

**stationarity conditions**

$$\frac{\partial \tilde{E}}{\partial \lambda_I} = 0 \quad \Rightarrow \quad 0 = \langle \Phi_I | \exp(-T) H \exp(T) | 0 \rangle$$

**CC equations**

$$\frac{\partial \tilde{E}}{\partial t_I} = 0 \quad \Rightarrow \quad 0 = \langle 0 | (1 + \Lambda) (\exp(-T) H \exp(T) - E) | \Phi_I \rangle$$

**$\Lambda$  equations**

**gradient**

$$\frac{\partial E}{\partial x} = \langle 0 | (1 + \Lambda) \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle$$

**no perturbed wavefunction parameters required!**

# CC Gradients: Density-Matrix Formulation

## introduction of density matrices

$$\frac{\partial E}{\partial x} = \langle 0 | (1 + \Lambda) \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle$$

$$= \sum_{p,q} D_{pq} \frac{\partial f_{pq}}{\partial x} + \sum_{p,q,r,s} \Gamma_{pqrs} \frac{\partial \langle pq || rs \rangle}{\partial x}$$

**reduced one-particle  
density matrix**

**reduced two-particle  
density matrix**

$$\langle 0 | (1 + \Lambda) \exp(-T) \{p^+ q\} \exp(T) | 0 \rangle \quad \langle 0 | (1 + \Lambda) \exp(-T) \{p^+ q^+ sr\} \exp(T) | 0 \rangle$$

**gradients in terms of integral derivatives and density matrices**

# Accuracy of CC Geometrical Parameters

calculated  $r(\text{OH})$  and  $\angle(\text{HOH})$  for  $\text{H}_2\text{O}$

	$r(\text{OH})$	$\angle(\text{HOH})$
CCSD	0.96435	102.210
CCSD(T)	0.96575	101.941
CCSDT	0.96583	101.937
CCSDTQ	0.96614	101.912
CCSDTQP	0.96616	101.910
CCSDTQPH	0.96616	101.910
FCI	0.96616	101.910

calculations with cc-pVDZ basis

Kállay, Gauss, Szalay, *J. Chem. Phys.* **119**, 2991 (2003)