

# NWChem: Correlated Methods



- Second-order perturbation theory (MP2)
  - ◆ RHF/UHF energy and gradients
- Coupled-cluster methods
  - ◆ RHF, CCSD, CCSD(T), energies

- Semi-direct MP2 - **task mp2**
  - ◆ RHF, UHF, 1600 functions, energy and gradient
  - ◆ Multi-passing controlled by disk space
  - ◆ In-core algorithm avoids disk use

- Freezing orbitals - all methods can freeze core
  - ◆ Direct and RI can also freeze virtual orbitals

```
freeze [core] (atomic||<ncore>)
```

- E.g., MP2 geometry optimization of C<sub>2</sub>H<sub>4</sub>

```
geometry ; symmetry d2h
```

```
  C 0 0 0.659;  H 0 0.916  1.224
```

```
end
```

```
basis
```

```
  C library 6-31g*;H library 6-31g*
```

```
end
```

```
mp2; freeze atomic; end
```

```
task mp2 optimize
```

- Higher precision - **tight** directive
  - ◆ default adequate for most geometry optimizations
  - ◆ higher accuracy for floppy molecules, very tight geometry convergence, finite difference Hessians.
- E.g., frequencies for C<sub>2</sub>H<sub>4</sub>

```
geometry ; symmetry d2h; C 0 0 0.659; H 0 0.916 1.224; end
basis; C library 6-31g*;H library 6-31g*; end
driver; cvgopt 0.00001; end
mp2; freeze atomic; tight; print low; end
task mp2 optimize
mp2; print none; end
task mp2 freq
```

- Current CCSD(T) based on algorithm by Rendall, Lee, Kobayashi
  - ◆ No symmetry, RHF (closed-shell), 500 functions, energy
  - ◆ Triples are quite fast and scale well
  - ◆ Numerical derivatives do use symmetry
- CCSD - **task ccsd**
- CCSD(T) - **task ccsd(t)**
- CCSD+T(CCSD) - **task ccsd+t(ccsd)**
- Frozen core
  - ◆ same syntax as MP2 (but in ccsd block)

- N<sub>2</sub> CCSD(T) frequencies
  - ◆ Optimize with MP2, then CCSD(T)

```
geometry
```

```
symmetry d2h
```

```
n 0 0 0.542
```

```
end
```

```
basis; n library cc-pvdz; end
```

```
mp2; freeze core; end
```

```
ccsd; freeze core; end
```

```
task mp2 optimize
```

```
task ccsd(t) optimize
```

```
task ccsd(t) freq
```



# NWChem: Coupled Cluster Method (Tensor Contraction Engine)





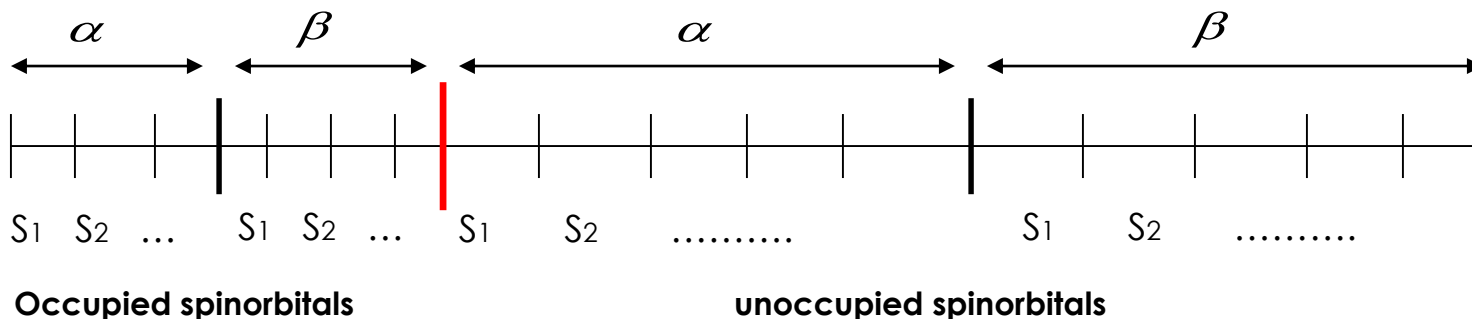
- Correlation effects are important!
- CC is size-extensive theory: can be used to describe dissociation processes.
- Higher-order effects can be approximated by products of lower rank cluster amplitudes.
- Strong ties with many body perturbation theory (MBPT). Effective perturbative methods (CCSD(T)) can be constructed in order to encapsulate higher-order correlation effects.
- Exact energy limit exists – full coupled cluster approach.
- Can be applied across energy and spatial scales: from nuclear structure theory to molecular nano-systems

- Symbolic manipulation & program generator
  - ◆ Automates the derivation of complex working equations based on a well-defined second quantized many-electron theories
  - ◆ Synthesizing efficient parallel computer programs on the basis of these equations.
  
- Granularity of the parallel CC TCE codes is provided by the so-called tiles, which define the partitioning of the whole spinorbital domain.

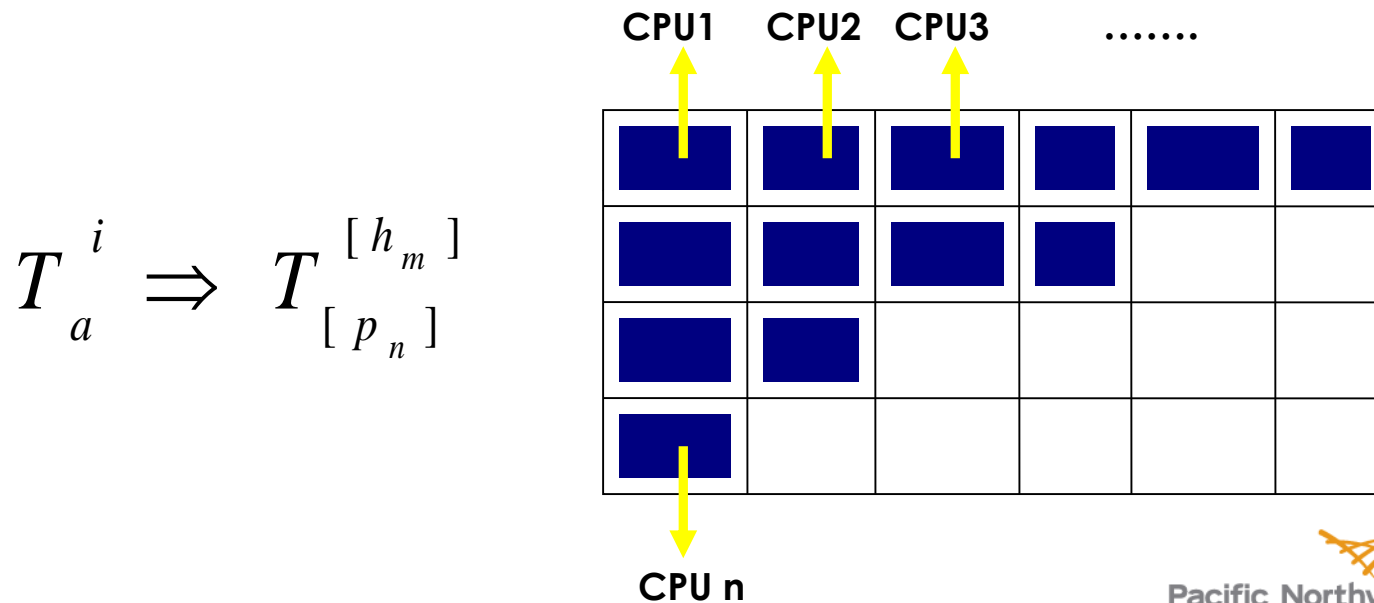
# What is Tensor Contraction Engine (TCE)



Tile structure:

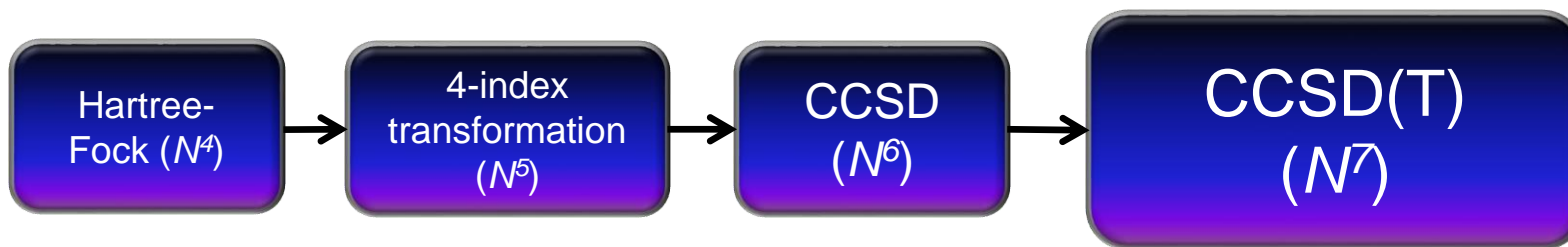


Tile-induced block structure of the CC tensors:



- Closed- & open-shell CC calculations with RHF/ROHF/UHF references
- Many-body perturbation theory
- CI methods: CISDT, CISDTQ, ...
- Ground-state methodologies: CCSD, CCSD(T), CCSDT, ...
- Excited-state methods: EOMCCSD, CC2, CR-EOMCCSD(T), EOMCCSD<sup>†</sup>, EOMCCSDT
- Linear response CC methods for calculating molecular properties: static & dynamic CCSD polarizabilities, static CCSDT polarizabilities, static CCSD hyperpolarizabilities

Method	Numerical complexity
CCSD (singles & doubles)	$N^6$
CCSD(T) (perturbative triples)	$N^7$
CCSDT (singles & doubles & triples)	$N^8$
CCSDTQ (singles & doubles & triples & quadruples)	$N^{10}$



# How to define reference?

- Three types of references can be used in single-reference TCE CC calculations: RHF, ROHF, UHF

```
scf
thresh 1.0e-10
tol2e 1.0e-10
singlet
maxiter 100
rhf
end
```

```
scf
thresh 1.0e-10
tol2e 1.0e-10
doublet
maxiter 100
rohff
end
```

```
scf
thresh 1.0e-10
tol2e 1.0e-10
singlet
maxiter 100
uhf
end
```

# How to choose 4-index transformation?

- RHF/ROHF references

- ◆ Default: spin-orbital 4-index transformation

- ◆ Alternatives: orbital 4-index transformations

```
tce
...
tilesize 20
2eorb
2emet 13
attilesize 40
...
end
```

```
tce
...
tilesize 20
2eorb
2emet 14
split 2
attilesize 40
...
end
```

4-index trans. Is performed using two batches of atomic 2-electron integrals. This is more memory efficient version, attilesize defines the so-called atomic tilesize for 4-index trans.

**# Always: tilesize <= attilesize; available in the GA version only**

- UHF reference: default spin-orbital 4-index transformation will be executed.



- Approaches based on the single and double excitations (CCSD,EOMCCSD,LR-CCSD)

$$\sim (\text{tile size})^4$$

- Perturbative CCSD(T) & CR-EOMCCSD(T) methods

$$2 * (\text{tile size})^6$$

**# choose tile size wisely**

- Iterative CCSDt,CCSDT,EOMCCSDt,EOMCCSDT methods

$$4 * (\text{tile size})^6$$

**# choose tile size wisely**

# Example: CCSD calculation

Example: h2o\_dimer\_ccsd\_aug\_cc\_pvdz.nw

```
scf
thresh 1.0e-10
tol2e 1.0e-10
singlet
rhf
end
```

```
tce
freeze atomic
```

```
ccsd
```

```
maxiter 100 → max. number of iterations
```

```
tilesize 15
```

```
diis 5 → length of the diis cycle
```

```
thresh 1.0d-5 → conv. threshold
```

```
2eorb
```

```
2emet 13
```

```
attilesize 40 → default value 40
```

```
end
```

```
task tce energy
```

# Examples: open-shell CCSD(T) calculation

Example: `cnh2o_ccsd_t_cc_pvdz.nw`

```
scf
thresh 1.0e-10
tol2e 1.0e-10
doublet
rohf
end
```

```
tce
freeze atomic
ccsd(t)
maxiter 100
tilesize 15
diis 5
lshift 0.2
thresh 1.0d-5
2eorb
2emet 13
attilesize 40
end
```

CCSD(T) calculation will be performed

Level shifting may be helpful in converging open-shell CCSD equations

Task tce

# Examples: CCSDT calculations

Example: h2o\_dimer\_ccsd\_t\_cc\_pvdz.nw

```
tce
freeze atomic
ccsd_t      →
maxiter 100
tilesize 10
diis 3 ←
thresh 1.0d-2 → very relaxed conv. threshold
2eorb
2emet 13
attilesize 40
end

task tce energy
```

CCSDT theory is invoked. To reduce memory requirements one can make diis cycle length smaller

Example: `mbpt2_h2o.nw`

```
scf
thresh 1.0e-10
tol2e 1.0e-10
singlet
rhf
end

tce
mbpt2 →
end

task tce energy
```

MBPT(n) approaches are by-products of various order CC implementations. For example, second order MBPT correction can be restored in the first iteration of the CCD method when initial guesses for cluster amplitudes are set equal to zero.

# Examples: MBPT calculations – towards higher orders

Example: `mbpt4sdq_h2o.nw`

`MBPT (2) < MBPT (3) < MBPT (4, SDQ) < MBPT (4)`

```
tce
mbpt4 (sdq) →
end
```

MBPT (3) + selected MBPT (4) contributions; an approximate method to include the effect of quadruply excited configurations

```
task tce energy
```

$$\text{EOMCCSD} < \text{CR-EOMCCSD(T)} < \text{EOMCCSDT} < \text{EOMCCSDTQ}$$

Method	Numerical complexity
EOMCCSD (singles & doubles)	$N^6$
CR-EOMCCSD(T) (perturbative triples)	$N^7$
EOMCCSDT (singles & doubles & triples)	$N^8$
EOMCCSDTQ (singles & doubles & triples & quadruples)	$N^{10}$



Excitation energies of singly Excited states



Excited-state potential energy surfaces, doubly excited state



# Excited-state calculations: EOMCCSD

EOM-CCSD right-hand side iterations

Example:

h2o\_dimer\_eomccsd\_aug\_cc\_pvdz.nw

	Residuum	Omega / hartree	Omega / eV	Cpu	Wall
...					
Iteration 29 using		48 trial vectors			
	0.0000082390224	0.2870037548132	7.80977		
	0.0000084487979	0.3499939129169	9.52382	2.0	2.3

Iterations converged

largest EOMCCSD amplitudes: R1 and R2

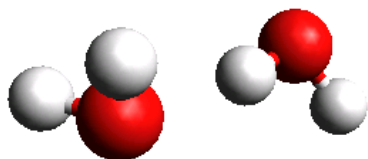
Singles contributions

11a' (alpha) ---	8a' (alpha)	0.2671088259
11a' (alpha) ---	9a' (alpha)	0.7493546713
13a' (alpha) ---	9a' (alpha)	0.1324980230
14a' (alpha) ---	9a' (alpha)	-0.1154368698
15a' (alpha) ---	9a' (alpha)	-0.1692193327
16a' (alpha) ---	8a' (alpha)	-0.1331210023
16a' (alpha) ---	9a' (alpha)	-0.3310076628
18a' (alpha) ---	9a' (alpha)	0.1419715795

Doubles contributions

...

```
tce
freeze atomic
ccsd
tilesize 20
diis 5
thresh 1.0d-5
2eorb
2emet 13
nroots 2
eomsol 1
end
```



number of roots

"old" eigensolvers (default option) - requires more memory but works for doubly excited states

```
task tce energy
```

Example:

```
h2o_dimer_eomccsd_aug_cc_pvdz_eomsol2.nw
```

```
tce
freeze atomic
ccsd
tilesize 20
diis 10
thresh 1.0d-5
2eorb
2emet 13
nroots 1
eomsol 2
symmetry
targetsym a' }
end
```

new EOMCCSD solver with improved memory management – should be used for singly excited states only; initial starts taken from the CIS calculations

states of a' symmetry will be calculated

```
task tce energy
```

Example:

```
tce_h2o_eomccsd_tcc-pvdz.nw
```

# CCSDT/EOMCCSDT methods are much more expensive than  
# the CCSD/EOMCCSD formalisms

```
tce  
freeze core atomic  
ccsd  
dipole →  
thresh 1.0d-6  
nroots 1  
end
```

calculates excited-state  
dipole moments and transition  
moments

```
task tce energy
```

# Excited-state calculations: active-space EOMCCSDT methods (EOMCCSDt)

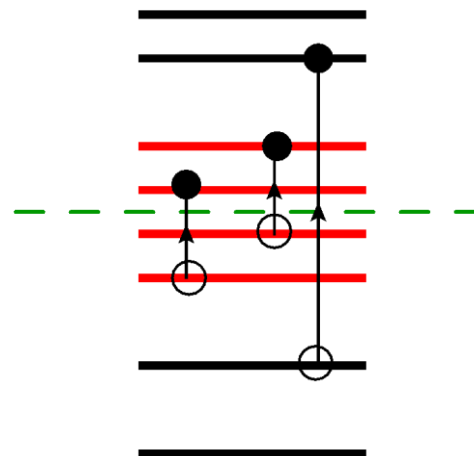
Example:

```
tce_active_ccsd_t_be3.nw
```

```
# EOMCCSDt uses selected set of triply excited amplitudes  
# - it makes it less expensive than the full EOMCCSDT approach !
```

```
tce  
freeze atomic  
ccsdta  
tilesize 12  
thresh 1.0d-4  
active_oa 3  
active_ob 3  
active_va 9  
active_vb 9  
t3a_lvl 2  
nroots 1  
symmetry  
targetsym a1  
end
```

Definition of the active space:  
active occupied alpha spinorbitals  
active occupied beta spinorbitals  
active virtual alpha spinorbitals  
Active virtual beta spinorbitals



Only  $t_{iJK}^{ABc}$  amplitudes included

```
task tce energy
```

# Excited-state calculations: CR-EOMCCSD(T)

Example:

```
tce_cr_eom_t_ozone_poll.nw
```

```
# Excitation energies accuracy:
```

```
# EOMCCSD < CR-EOMCCSD(T) < EOMCCSDT
```

```
tce
freeze atomic
2eorb
2emet 13
creomsd(t)
tilesiz 15
thresh 1.0d-4
nroots 1
symmetry
targetsym b2
end
```

RHF reference is employed, orbital from of 2-electron integrals can be used

CR-EOMCCSD(T) calculation is composed of several steps:

- (1) CCSD calculation
- (2) EOMCCSD calculation
- (3) calculation of the CR-EOMCCSD(T) non-iterative correction

```
task tce energy
```

- Property calculations with the CC method: The cluster operator  $T(t)$  is expanded in order of time-dependent perturbation

$$T(t) = T^{(0)} + T^{(1)}(t) + T^{(2)}(t) + \dots$$

- Dipole polarizabilities can be calculated as a linear response function

$$\alpha_{ij}(\omega) = - \langle\langle \mu_i ; \mu_j \rangle\rangle_{\omega}$$

CC eq.  $\rightarrow$   $\Lambda$ -CC eq.  $\rightarrow$  first-order LR-CC eq.

# Property calculations: CCSD dipole polarizabilities

Example: tce\_polar\_ccsd\_n2\_aug\_cc\_pvdz.nw

```
tce
  scf
  ccsd
  io ga
  2eorb
end

set tce:lineresp T
set tce:respaxis T F T
set tce:afreq 0.00000000 0.08855851 0.104551063

task tce energy
```

linear response CCSD calculations will be performed

only x and z components of the first-order response cluster amplitudes will be calculated (i.e.  $\alpha(xx)$   $\alpha(zz)$   $\alpha(xz)$  will be available)

List of required  $\omega$  values



# Property calculations: CCSD dipole polarizabilities – benzene

Example: `tce_polar_ccsd_benzene.nw`

```
scf
  singlet
  rhf
  thresh 1.0e-10
end
tce
  scf
  freeze core
  ccscd
  io ga
  2eorb
end
```

CCSD Linear Response polarizability / au  
Frequency = 0.0000000 / au  
Wavelength = Inf / nm

	atomic units (bohr <sup>3</sup> )				angstroms <sup>3</sup>		
	X	Y	Z		X	Y	Z
X	68.4305909	0.0000000	0.0000000		10.1403696	0.0000000	0.0000000
Y	0.0000000	68.4364388	0.0000000		0.0000000	10.1412361	0.0000000
Z	0.0000000	0.0000000	20.1980487		0.0000000	0.0000000	2.9930427
Eigs =	68.4305909	68.4364388	20.1980487		10.1403696	10.1412361	2.9930427
Isotropic =		52.3550261				7.7582161	
Anisotropic =		48.2354664				7.1477602	

```
set tce:lineresp T
set tce:respaxis T T T
set tce:afreq 0.0
```

```
task tce energy
```

static case

# Questions?

