



NWChem: Correlated Methods

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Correlated Methods

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

MP2

- Semi-direct MP2 - **task mp2**
 - RHF, UHF, > 4000 functions, energy and gradient
 - Multi-passing controlled by disk space
 - In-core algorithm avoids disk use

MP2: Freezing Orbitals

- 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 C₂H₄

`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`

MP2: Improving Precision

- 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 C₂H₄

```
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
```

Coupled Cluster

- 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 ccscd**
- CCSD(T) - **task ccscd(t)**
- CCSD+T(CCSD) - **task ccscd+t(ccscd)**
- Frozen core
 - same syntax as MP2 (but in ccscd block)

Coupled Cluster: Example

- N₂ 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)



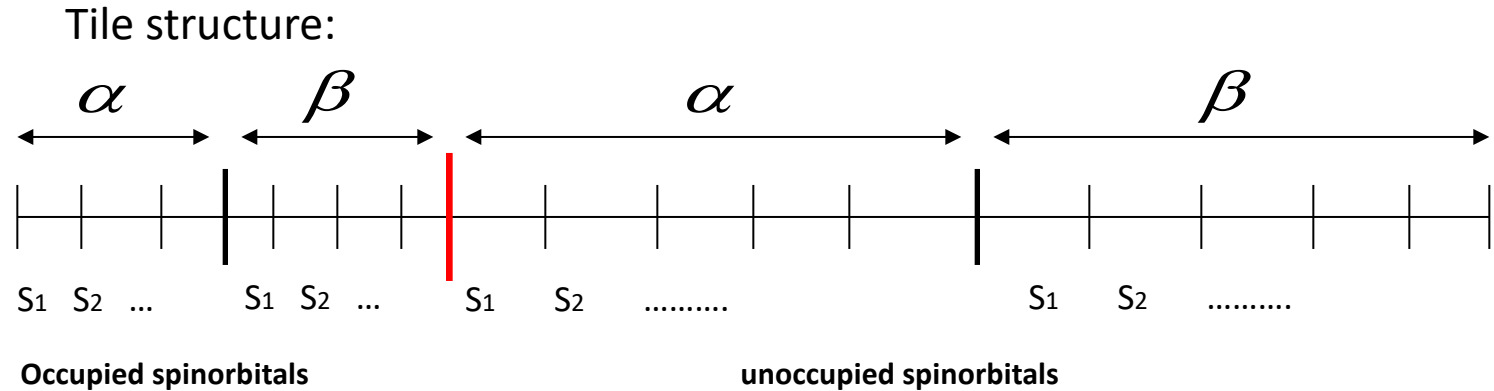
Why Coupled Cluster is important?

- 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

What is the Tensor Contraction Engine (TCE)?

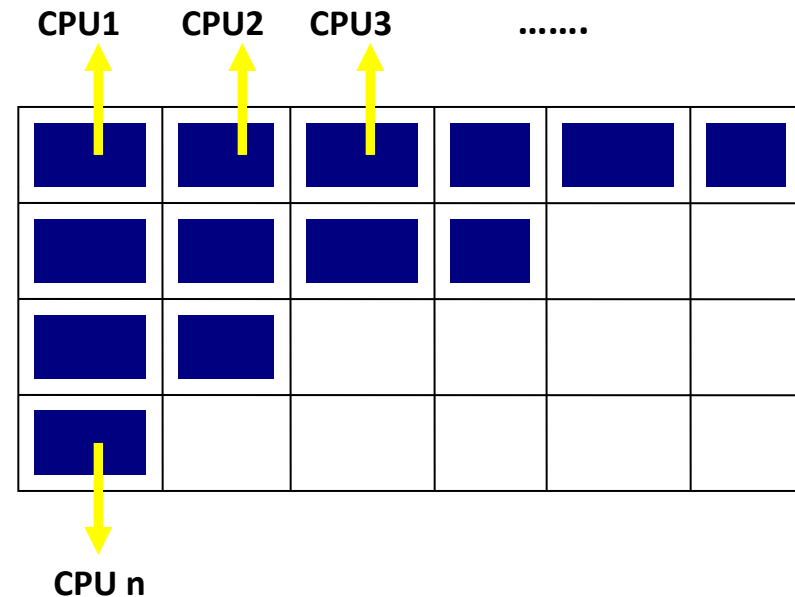
- Symbolic manipulation & program generator
 - Automates the derivation of complex working equations based on a well-defined second quantized many-electron theories
 - Synthesizing efficient parallel computer programs based on these equations.
- Granularity of the parallel CC TCE codes is provided by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

What is the Tensor Contraction Engine (TCE)?



Tile-induced block structure of the CC tensors:

$$T_a^i \Rightarrow T_{[p_n]}^{[h_m]}$$

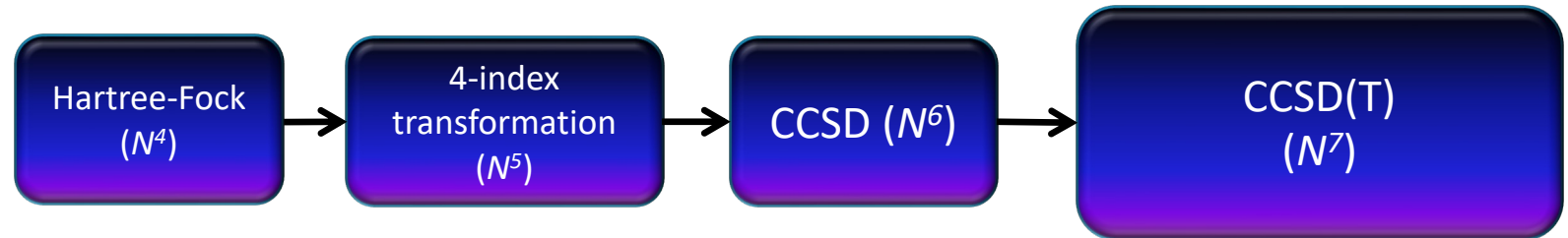


CC TCE c calculations

- 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), EOMCCSDt, EOMCCSDT
- Linear response CC methods for calculating molecular properties: static & dynamic CCSD polarizabilities, static CCSDT polarizabilities, static CCSD hyperpolarizabilities

Coupled Cluster methods

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}



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

How to define a reference?

```
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 the 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
```

Always: `tilesize <= attilesize;`

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

Local memory management in CC TCE module

- Approaches based on the single and double excitations (CCSD,EOMCCSD,LR-CCSD)
 - $\sim (\text{tilesize})^4$
- Perturbative CCSD(T) & CR-EOMCCSD(T) methods
 - $2 * (\text{tilesize})^6$ **# choose tilesize wisely**
- Iterative CCSDt,CCSDT,EOMCCSDt,EOMCCSDT methods
 - $4 * (\text{tilesize})^6$ **# choose tilesize 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
  tilesize 15
  diis 5
  thresh 1.0d-5
  2eorb
  2emet 13
  attilesize 40
end
```

max. number of iterations

length of the diis cycle

conv. threshold

default value 40

```
task tce energy
```

Examples: open-shell CCSD(T) calculation

Example: `cnh2o_ccsd_t_cc_pvdz.nw`

```
scf
  doublet
  rohff
end
```

```
tce
  freeze atomic
  ccscd(t)
  maxiter 100
  tilesize 15
  diis 5
  lshift 0.2
  thresh 1.0d-5
  2eorb
  2emet 13
  attilesiz 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
  ccscdt
  maxiter 100
  tilesize 10
  diis 3
  thresh 1.0d-2
  2eorb
  2emet 13
  attilesize 40
end

task tce energy
```


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

very relaxed conv. threshold

Examples: MBPT calculations

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 the initial guesses for cluster amplitudes are set equal to zero.

Examples:
MBPT
calculations –
towards higher
orders

Example: mbpt4sdq_h2o.nw

$\text{MBPT}(2) < \text{MBPT}(3) < \text{MBPT}(4, \text{SDQ}) < \text{MBPT}(4)$

```
tce  
  mbpt4 (sdq) —————>  
end
```

```
task tce energy
```

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

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

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
EOMCC
calculations

Excited-state calculations: EOMCCSD

Example:

h2o_dimer_eomccsd_aug_cc_pvdz.nw

tce

freeze atomic

ccsd

tilesize 20

diis 5

thresh 1.0d-5

2eorb

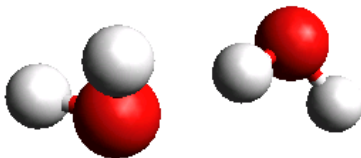
2emet 13

nroots 2 → number of roots

eomsol 1 → "old" eigensolvers (default option) - requires more memory but works for doubly excited states

end

task tce energy



EOM-CCSD right-hand side iterations

	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

...

Excited-state calculations: EOMCCSD

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
```


Excited-state calculation: EOMCCSDT

Example:

```
tce_h2o_eomccsd_t_cc-pvdz.nw
```

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

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

```
task tce energy
```

calculates excited-state
dipole moments and transition
moments

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

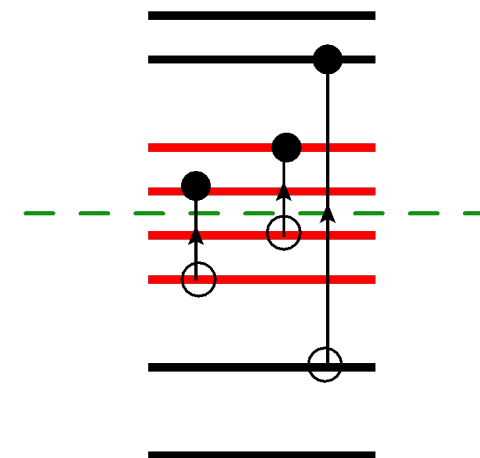
Example:

```
tce_active_ccsdt_be3.nw
```

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

```
tce
freeze atomic
ccsdt
tsize 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) →
tilesize 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 Λ -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 ω values

Property calculations: CCSD dipole polarizabilities – benzene

```
scf
  rhf
end
tce
  scf
  freeze core
  ccscd
  io ga
  2eorb
end
set tce:lineresp T
set tce:respaxis T T T
set tce:afreq 0.0
```

Example: tce_polar_ccsd_benzene.nw

static case

task tce energy

CCSD Linear Response polarizability / au

Frequency = 0.0000000 / au

Wavelength = Inf / nm

	atomic units (bohr ³)				angstroms ³		
	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		

Questions?

Thank you