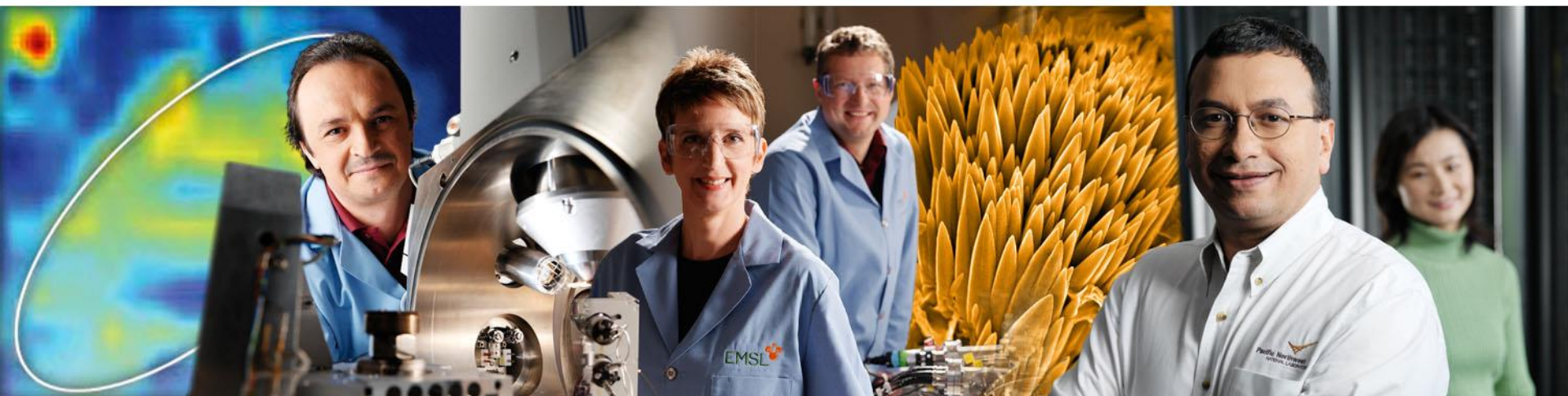


NWChem: Correlated Methods



- 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, 1 600 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 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
```

- 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_2H_4

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

- 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`

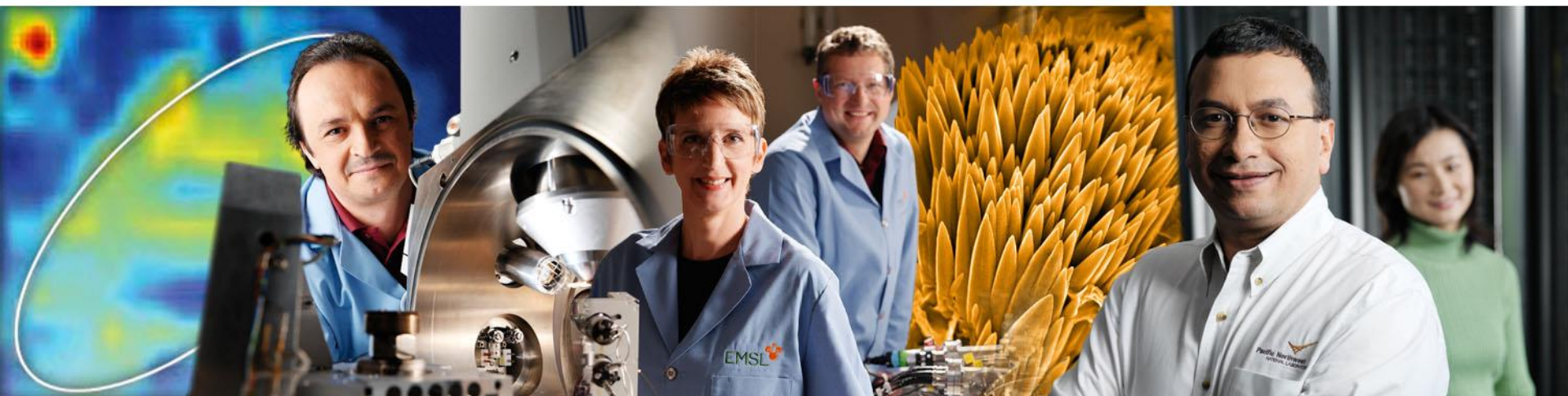
`ccsd; freeze core; end`

`task mp2 optimize`

`task ccsd(t) optimize`

`task ccsd(t) freq`

NWChem: Coupled Cluster Method (Tensor Contraction Engine)



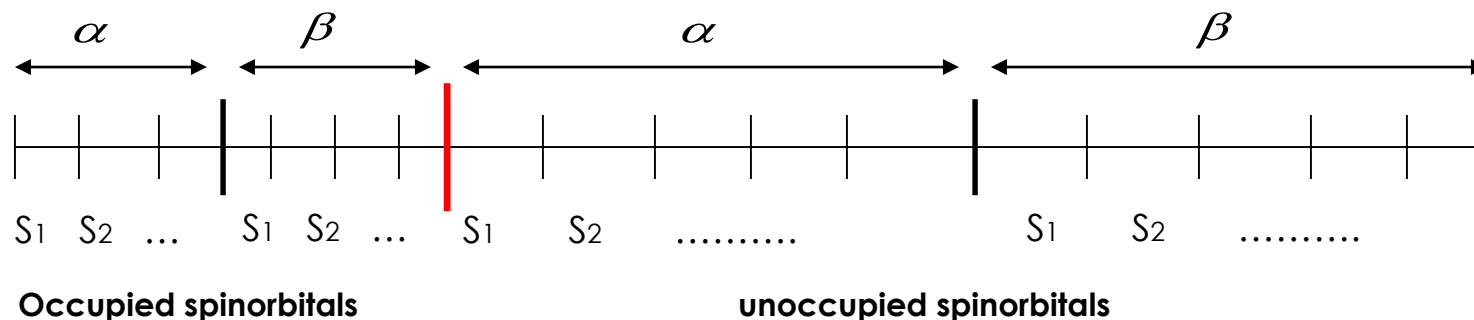
- Correlation effects are important!
- CC is size-extensive theory: can be used to describe dissociation processes.
- Higher-order effects can be approximated by products of lower rank cluster amplitudes.
- Strong ties with many body perturbation theory (MBPT). Effective perturbative methods (CCSD(T)) 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.

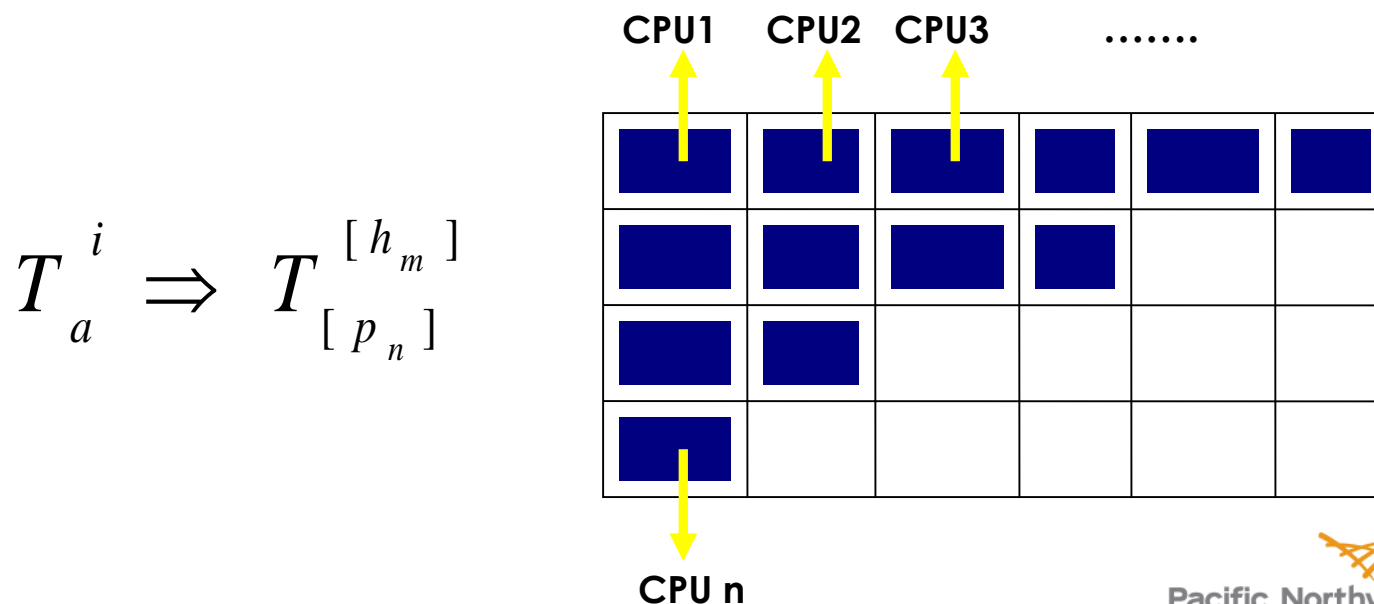
- Granularity of the parallel CC TCE codes is provided by the so-called tiles, which define the partitioning of the whole spinorbital domain.

What is Tensor Contraction Engine (TCE)

Tile structure:

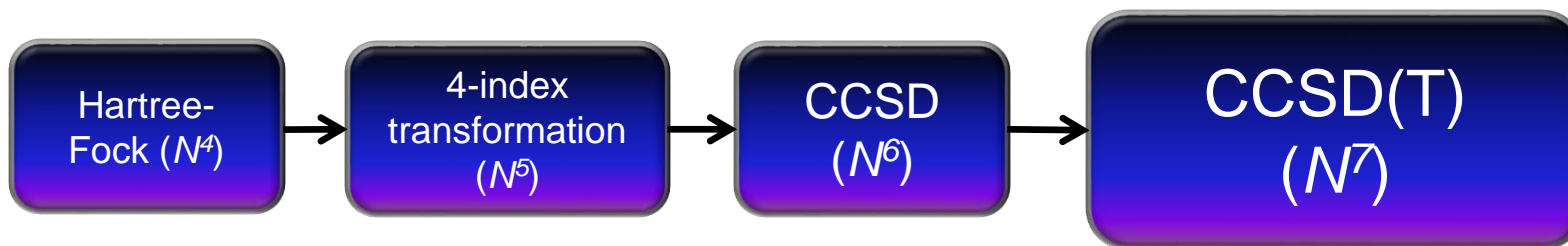


Tile-induced block structure of the CC tensors:



- 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[†], 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

tce ◆ Alternatives: orbital 4-index transformations

```
...
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)

$$\sim (\text{tilesize})^4$$

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

$$2 * (\text{tilesize})^6$$

choose tilesize wisely

- Iterative CCSD \dagger ,CCSDT,EOMCCSD \dagger ,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 → 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
rohlf
end
```

```
tce
freeze atomic
```

```
ccsd(t) →
```

CCSD(T) calculation will be performed

```
maxiter 100
```

```
tilesize 15
```

```
diis 5
```

```
lshift 0.2 →
```

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

```
thresh 1.0d-5
```

```
2eorb
```

```
2emet 13
```

```
attilesize 40
```

```
end
```

Task tce

Examples: CCSDT calculations

Example: h2o_dimer_ccsdt_cc_pvdz.nw

```
tce
freeze atomic
ccsdt
maxiter 100
tilesize 10
diis 3
thresh 1.0d-2
2eorb
2emet 13
attilesize 40
end

task tce energy
```

Annotations:

- ccsdt → CCSDT theory is invoked. To reduce memory requirements one can make diis cycle length smaller
- diis 3 ←
- thresh 1.0d-2 → 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 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

tce

freeze atomic

ccsd

tilesize 20

diis 5

thresh 1.0d-5

2eorb

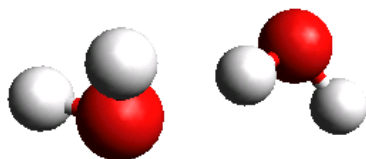
2emet 13

nroots 2

eomsol 1

end

task tce energy



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

...

number of roots

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

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_t_cc-pvdz.nw
```

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

```
tce
```

```
freeze core atomic
```

```
ccsd_t
```

```
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
```

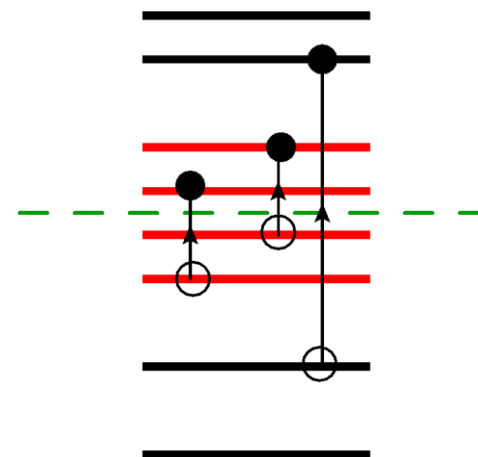
```
symmetry
```

```
targetsym a1
```

```
end
```

```
task tce energy
```

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

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
  ccscd
  io ga
  2eorb
end
```

```
set tce:lineresp T
set tce:respaxis T F T
set tce:afreq 0.000000000 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

Example: `tce_polar_ccsd_benzene.nw`

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

```
end
tce
  scf
  freeze core
  ccsd
  io ga
  2eorb
end
```

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	

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

```
task tce energy
```

static case

Questions?

