



# NWChem: Coupled Cluster Method (Tensor Contraction Engine)



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# Why CC 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 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 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.



# CC TCE calculations



- Closed- & open-shell CC calculations with RHF/ROHF/UHF references
- Many-body perturbation theory
- CI methods: CISDT, CISDT, ...
- 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

# Coupled Cluster method

$$|\Psi_0\rangle = e^T |\Phi\rangle$$

cluster operator

reference function (HF determinant)

Coupled cluster equations

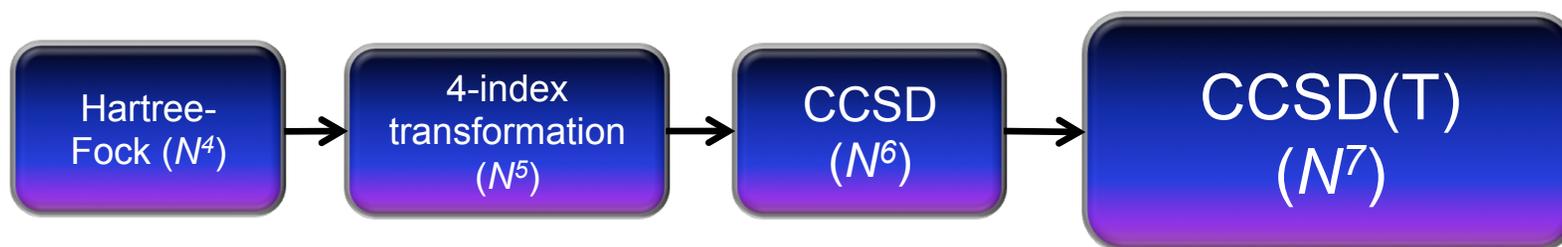
$$\langle \Phi_{ijk\dots}^{abc\dots} | (He^T)_c | \Phi \rangle = 0$$

- CC eqs. are energy independent
- Connected diagrams only:  
CC theory can properly describe dissociation processes - energy is a sum of energies in the non-interacting system limit

$$E = \langle \Phi | (He^T)_c | \Phi \rangle$$

# Coupled Cluster method

| Method   | Numerical complexity |
|--|----------------------|
| CCSD<br>(singles & doubles)                          | $N^6$                |
| CCSD(T)<br>(perturbative triples)                    | $N^7$                |
| CCSDT<br>(singles & doubles & triples)               | $N^8$                |
| CCSDTQ<br>(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: spinorbital 4-index transformation
  - ◆ Alternatives: orbital 4-index transformations

```
tce
...
tilesize 20
2eorb
2emet 4
split 2
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 spinorbital 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)

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

- 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

# Challenging situations – bond breaking processes: renormalized methods



Example: `tce_cr_ccsd_t_ozone_poll.nw`

**# in single-bond breaking/forming processes  
renormalized methods may provide better  
description of ground-state potential energy  
surfaces**

```
tce  
freeze atomic  
2eorb  
2emet 13  
cr-ccsd(t)  
tilesize 15  
thresh 1.0d-5  
end
```



completely renormalized CCSD(T)  
method is invoked

# 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
```

CCSDT theory is invoked. To reduce memory requirements one can make 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 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
```

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

```
task tce energy
```

# Excited-state EOMCC calculations



$$|\Psi_K\rangle = R_K e^T |\Phi\rangle$$

cluster operator

reference function (HF determinant)

“excitation” operator

$$\bar{H} R_K |\Phi\rangle = E_K R_K |\Phi\rangle$$

$$\bar{H} = e^{-T} H e^T$$

(Equation of Motion Coupled Cluster Equations )

# Excited-state EOMCC calculations



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

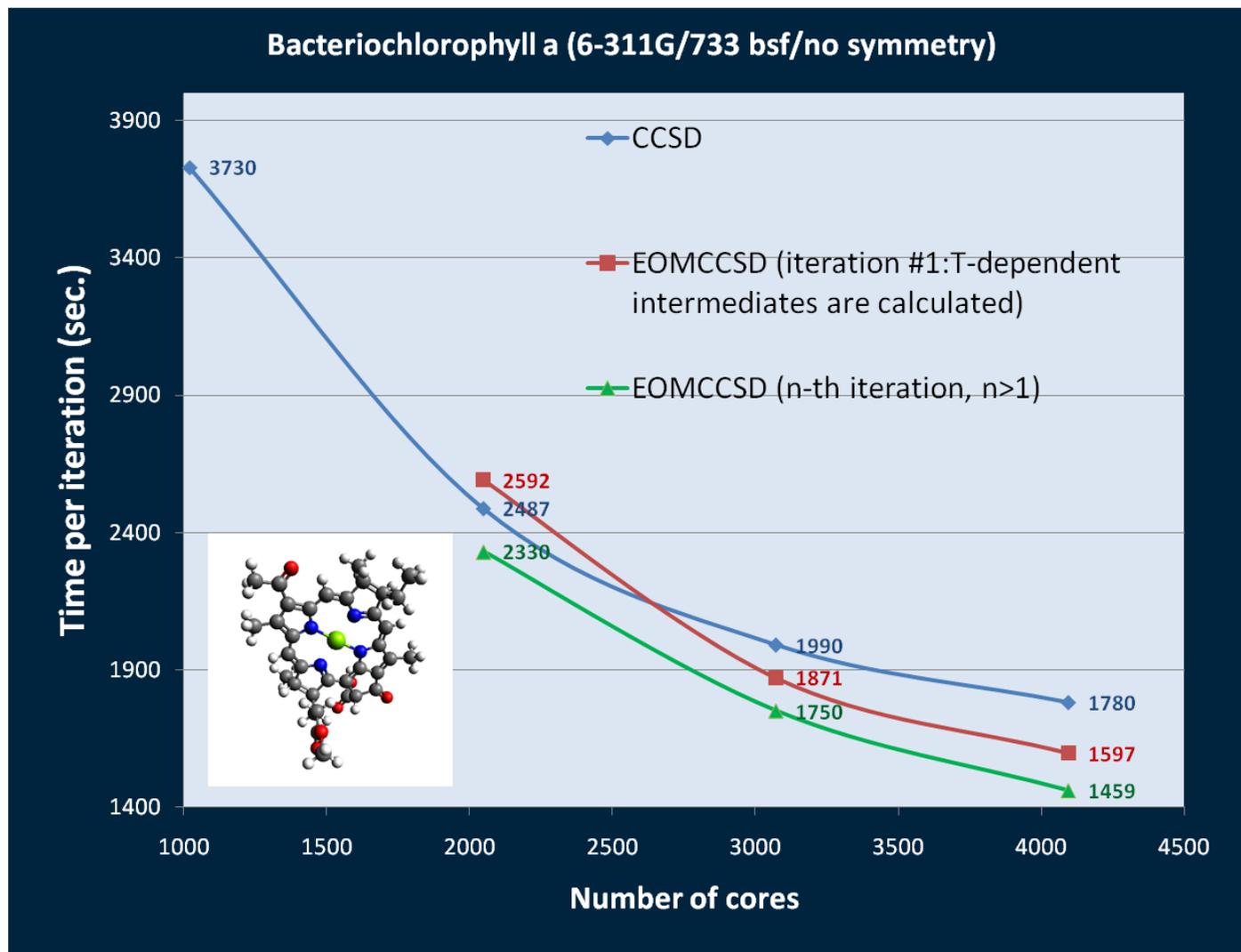
| Method  | Numerical complexity |   |
|---|----------------------|---|
| EOMCCSD<br>(singles & doubles)                          | $N^6$                | Excitation energies of singly Excited states                  |
| CR-EOMCCSD(T)<br>(perturbative triples)                 | $N^7$                | Excited-state potential energy surfaces, doubly excited state |
| EOMCCSDT<br>(singles & doubles & triples)               | $N^8$                |   |
| EOMCCSDTQ<br>(singles & doubles & triples & quadruples) | $N^{10}$             |   |



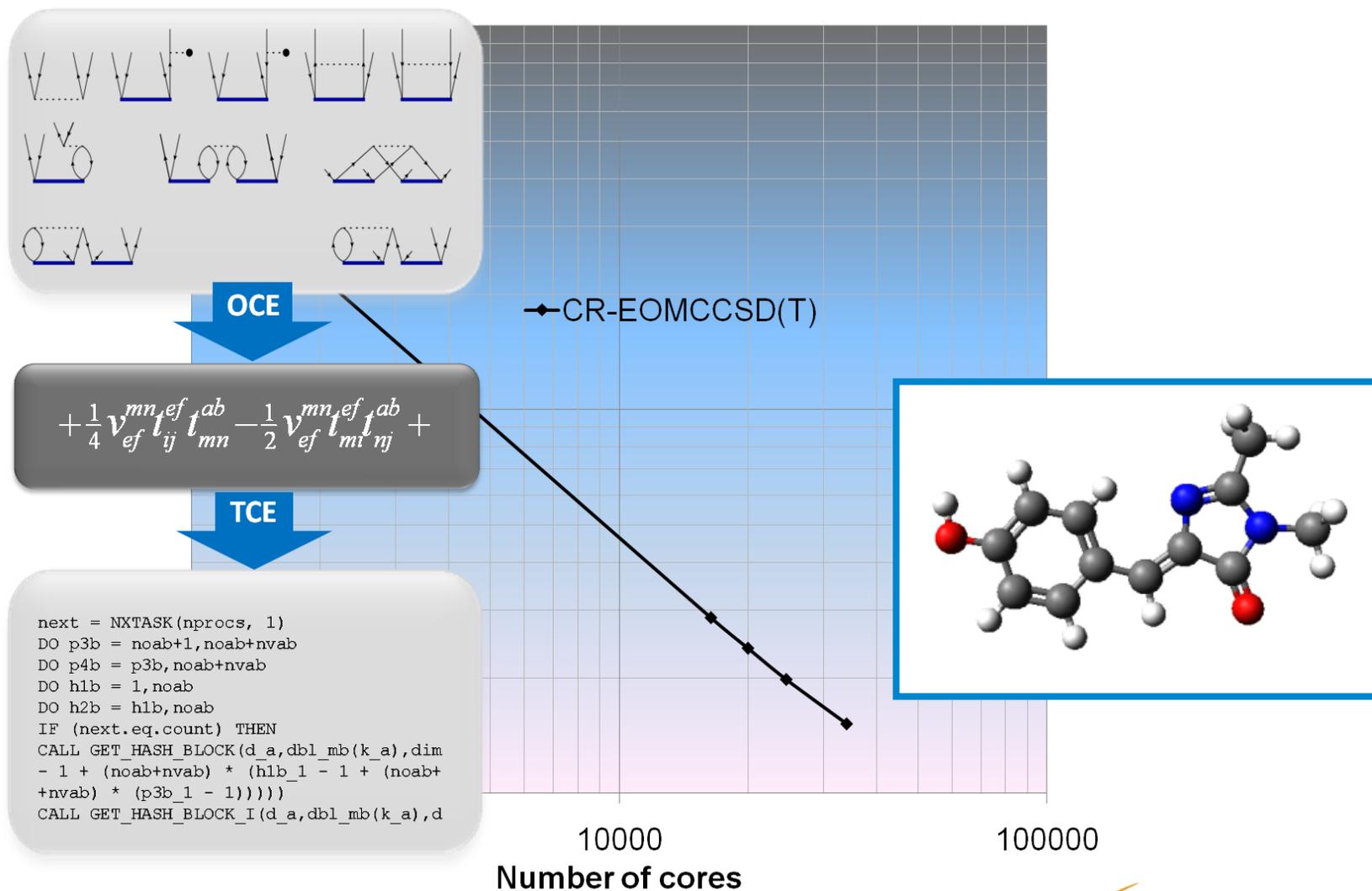
Excitation energies of singly Excited states

Excited-state potential energy surfaces, doubly excited state

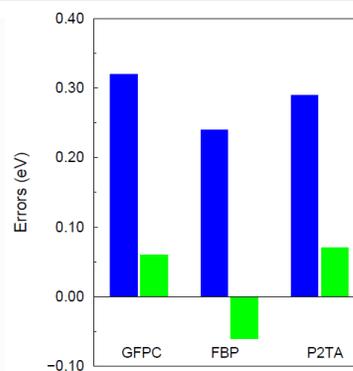
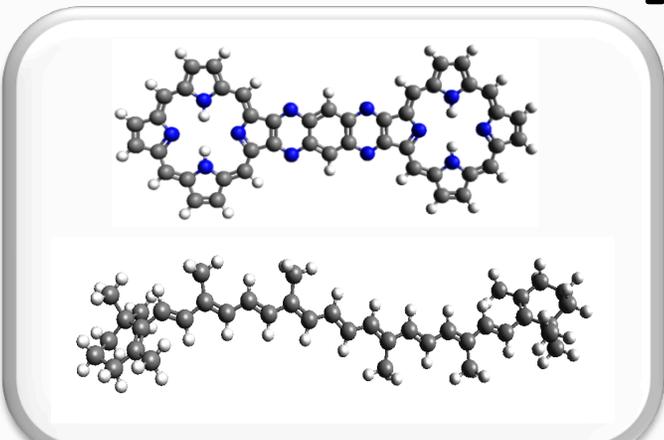
# Excited-state EOMCC calculations



# Excited-state EOMCC calculations



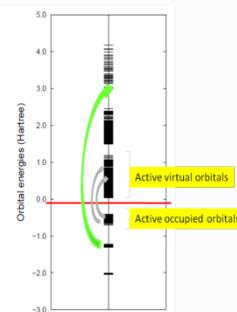
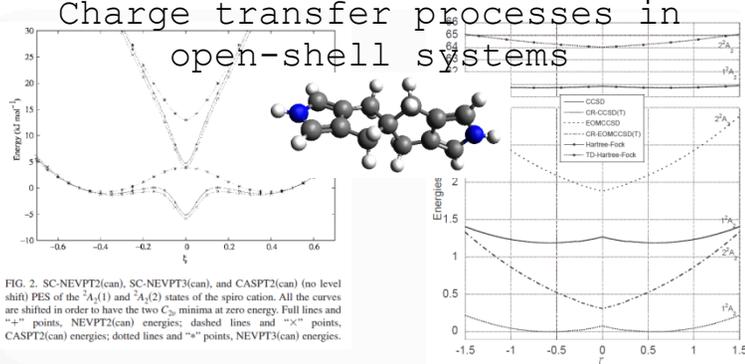
## Towards experimental accuracy



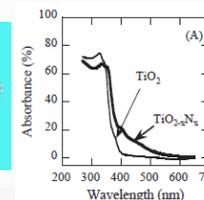
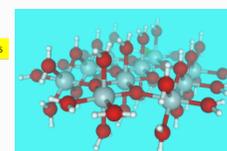
Errors of the EOMCCSD (blue) and CR-EOMCCSD(T) (green) vertical excitation energies with respect to the experimental data.

## Modeling complex excited state processes

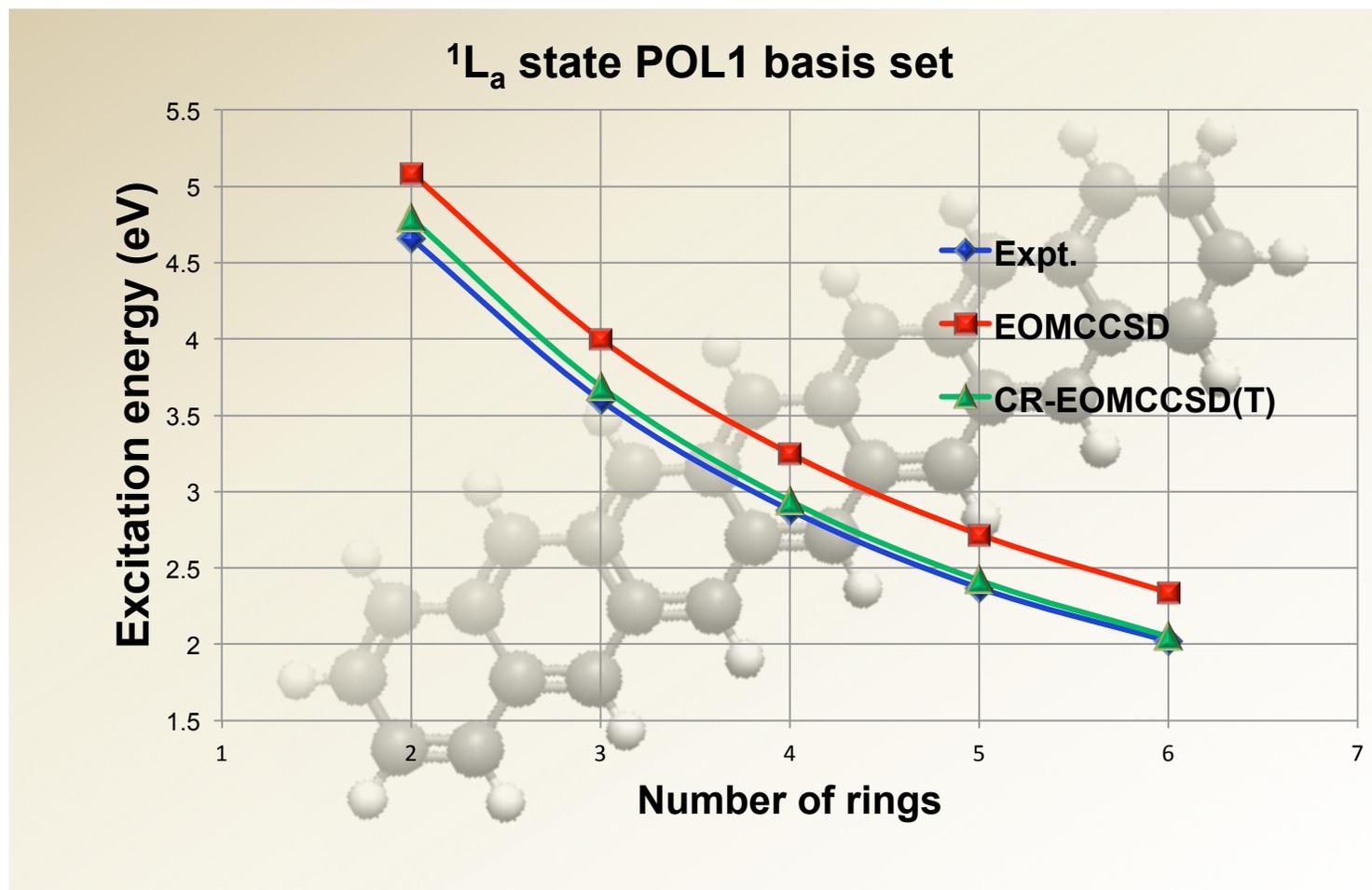
### Charge transfer processes in open-shell systems



TiO<sub>2</sub>  
EOMCCSD → 3.69 eV  
N-doped TiO<sub>2</sub>  
EOMCCSD → 2.51 eV



# Excited-state EOMCC calculations



# 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

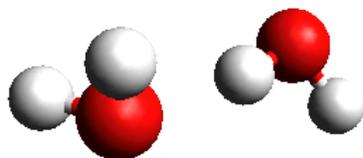
Singles contributions

|                  |             |               |
|------------------|-------------|---------------|
| 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
```

# 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  
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)



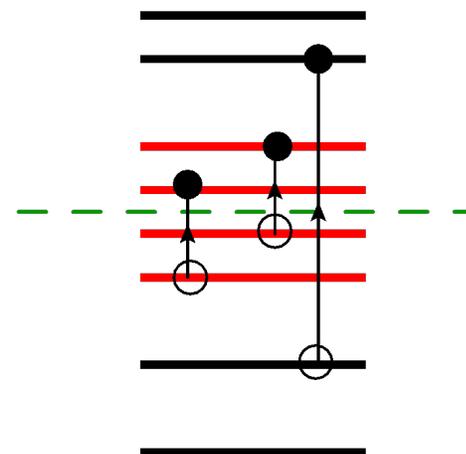
Example:

```
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 1  
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_pol1.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
```

# Linear response CC calculations



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

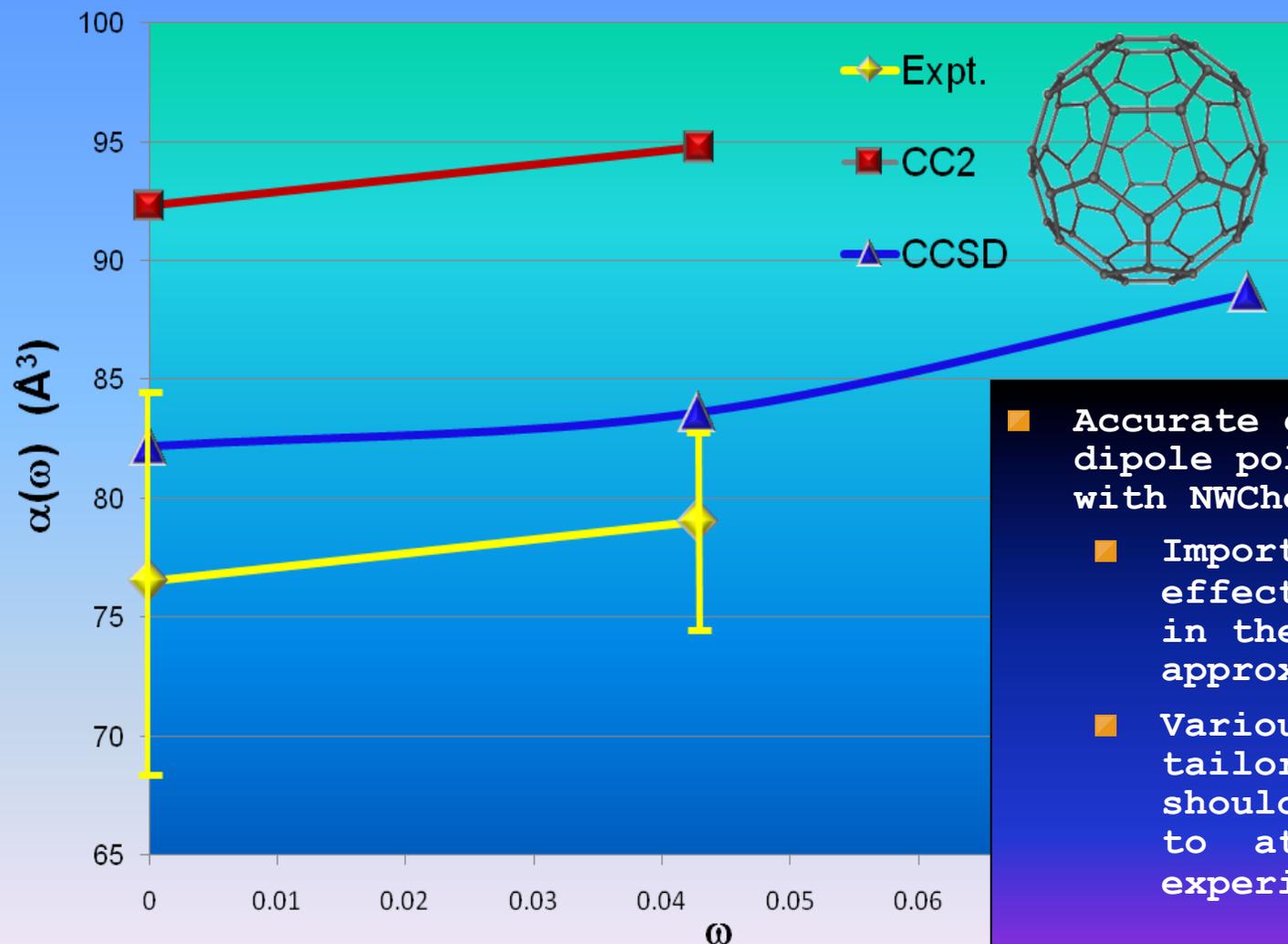
$$T(t) = T^{(0)} + T^{(1)}(t) + T^{(2)}(t) + \dots$$

- 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.

# Linear response CC calculations



- Accurate calculations for dipole polarizabilities with NWChem:
  - Important correlation effects can be included in the CCSD and CCSDT approximations
  - Various property-tailored basis sets should be used in order to attain the experimental accuracy

# 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?

