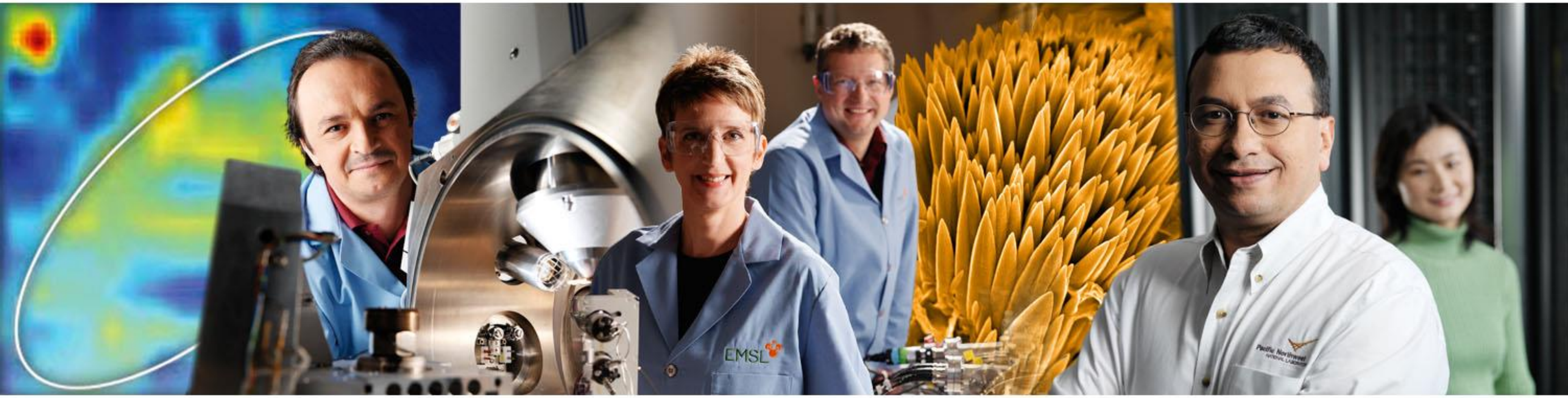
EMSL

NWChem: Coupled Cluster Method (Tensor Contraction Engine)



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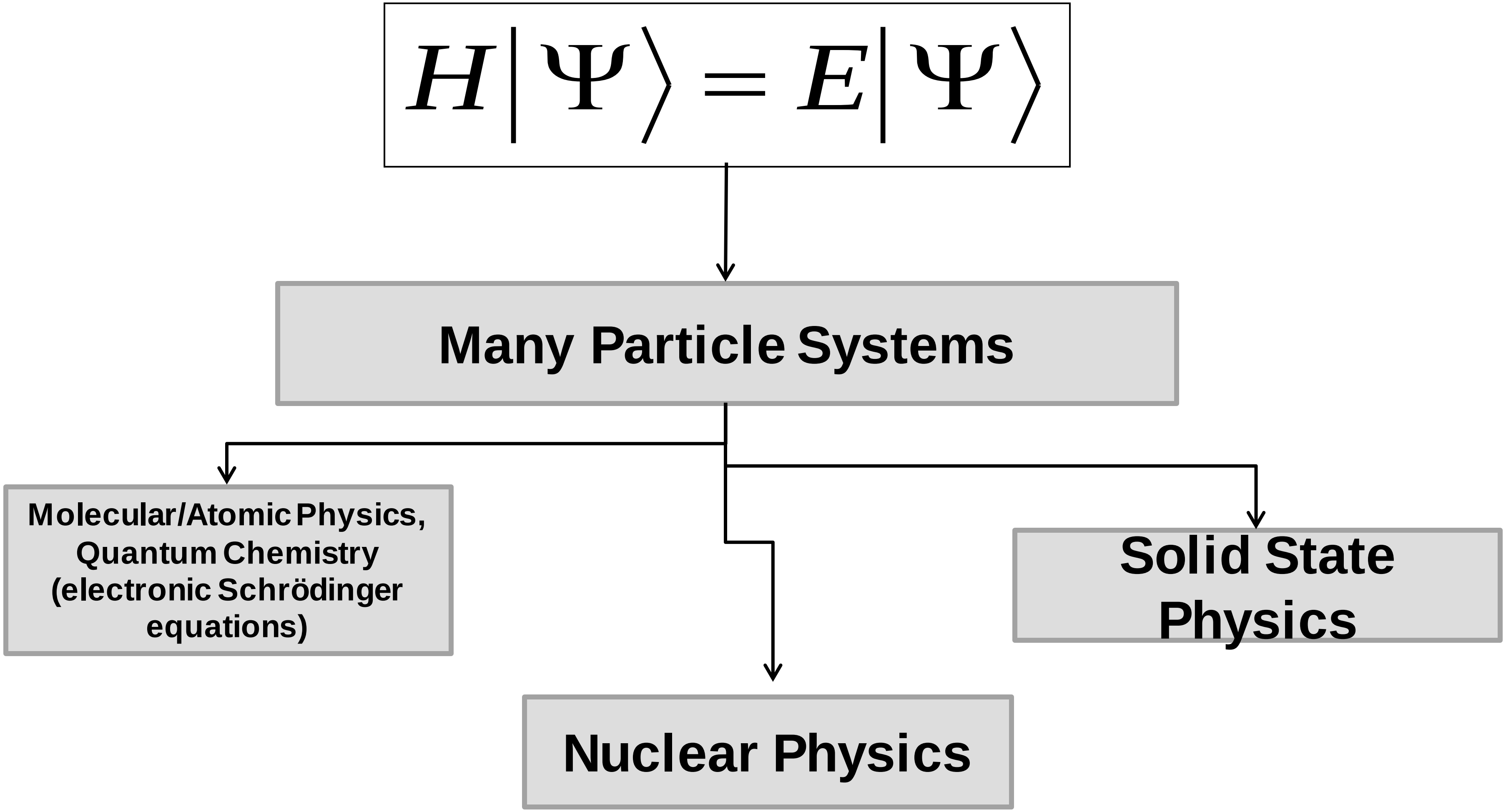
What we want to solve



$$H|\Psi\rangle = E|\Psi\rangle$$

Many Particle Systems

Molecular/Atomic Physics, Quantum Chemistry (electronic Schrödinger equations)

Solid State Physics

Nuclear Physics

Exact solution of Schrödinger equation

Weyl formula (dimensionality of full configuration interaction space) – exact solution of Schrödinger equation

$$f(n,N,S)=\frac{2S+1}{n+1}\binom{n+1}{N/2-S}\binom{n+1}{N/2+S+1}$$

n – total number of orbitals

N – total number of correlated electrons

S – spin of a given electronic state

C_2 molecule:

12 electrons, 100 orbitals:

$\#\mathrm{FCI}\ \ \mathrm{config.}\ \approx\ 10^{17}$!!!

Efficient approximations are needed

Approximate wavefunction (WF) methods

- Hartree-Fock method (single determinant)

  E_{HF} is used to define the correlation energy ΔE

  $$\Delta E = E - E_{HF}$$

  In molecules E_{HF} accounts for 99% of total energy

  but without ΔE making any reliable predictions is impossible
- Correlated methods (going beyond single determinant description)
  - Configuration interaction method (linear parametrizaton of WF)
  - Perturbative methods (MBPT-n)
  - Coupled Cluster methods
  - and many other approaches

Why CC is important?

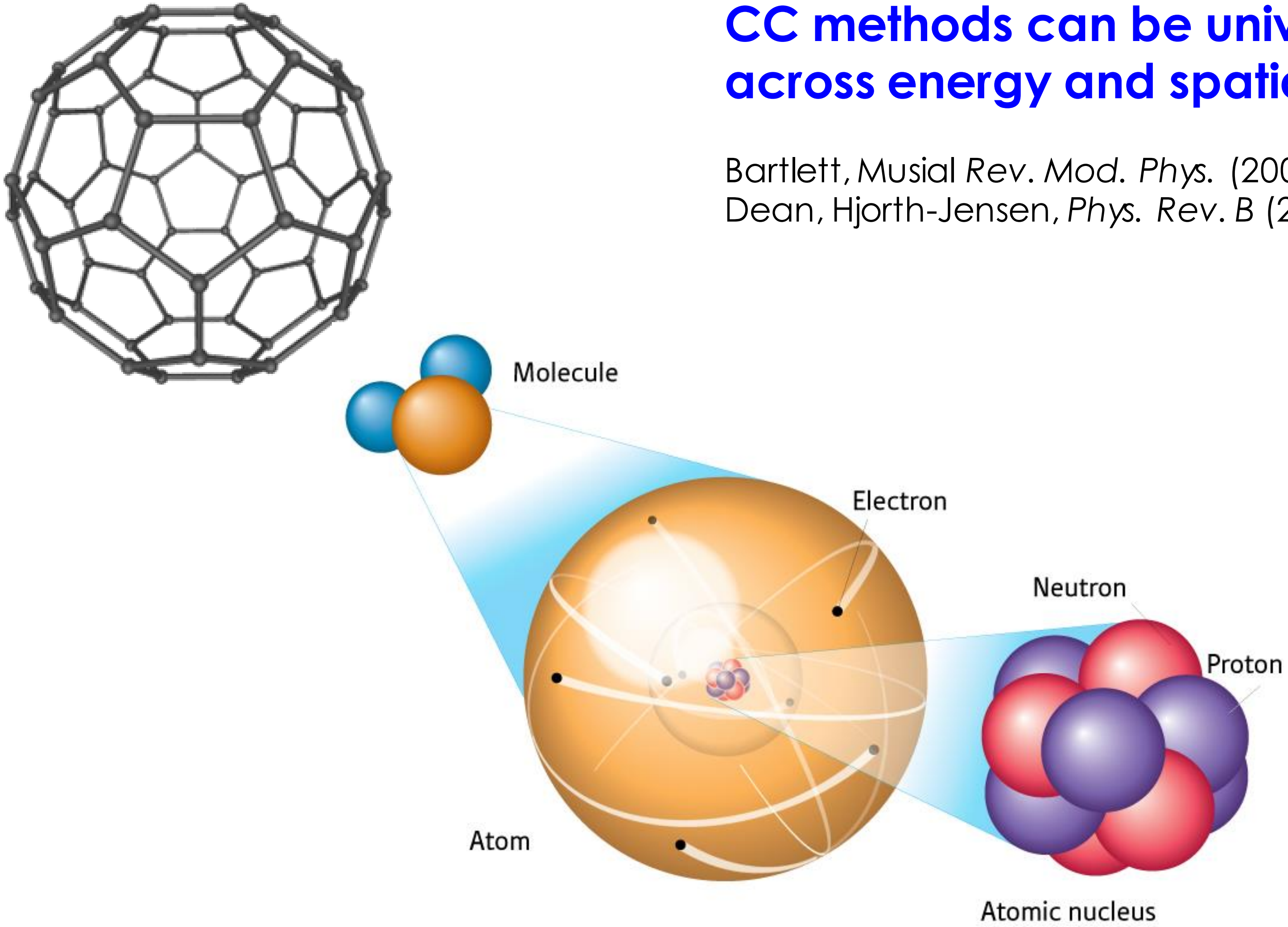
- Correlation effects are important!
- CC is size-extensive theory: can be used to describe dissociation processes.
- Higher-order effects can be approximated by products of lower rank cluster amplitudes.
- Strong ties with many body perturbation theory (MBPT). Effective perturbative methods (CCSD(T))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

CC methods: across the energy and spatial scales

CC methods can be universally applied across energy and spatial scales!

Bartlett, Musial *Rev. Mod. Phys.* (2007)
Dean, Hjorth-Jensen, *Phys. Rev. B* (2004)



CC method

- CC method

cluster operator

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

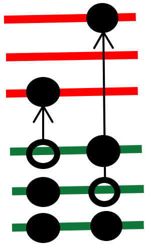
$$T = T_1 + T_2 + T_3 + \ldots + T_N$$

reference function (HF determinant)

$$T_n = \frac{1}{(n!)^2}\sum_{\substack{i_1\ldots i_n\\ a_1\ldots a_n}} t_{i_1\ldots i_n}^{a_1\ldots a_n}\, a_{a_1}^+ \ldots a_{a_n}^+\, a_{i_n}\ldots a_{i_1}$$

cluster amplitudes

$$T_2|\Phi\rangle = \sum_{\substack{i<j\\ a<b}} t_{ab}^{ij}$$



CI (configuration interaction) and CC methods

- Full CI and full CC expansions are equivalent (and this is the only case when CI=CC)

$$\boxed{(1+C)\left|\Phi\right\rangle = e^{T}\left|\Phi\right\rangle}$$

$$C_1 = T_1$$

$$C_2 = T_2 + \tfrac{1}{2}T_1^{\,2}$$

$$C_3 = T_3 + T_1T_2 + \tfrac{1}{6}T_1^{\,3}$$

$$C_4 = T_4 + T_1T_3 + \tfrac{1}{2}T_2^{\,2} + \tfrac{1}{2}T_1^{\,2}T_2 + \tfrac{1}{24}T_1^{\,4}$$

...

CI amplitudes are calculated from the variational principle while the cluster amplitudes are obtained from projective methods

CC formalism

- Working equations:

$$e^{-T}|$$

$$He^{T}|\Phi\rangle = Ee^{T}|\Phi\rangle$$

$$e^{-T}He^{T}|\Phi\rangle = E|\Phi\rangle$$

$$\langle\Phi_{ijk\ldots}^{abc\ldots}|(He^{T})_{C}|\Phi\rangle = 0$$

$$\langle\Phi|(He^{T})_{C}|\Phi\rangle = E$$

- 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

Approximations: CCD,CCSD,CCSDT …

- CC with doubles (CCD): $T \approx T_2$
- CC with singles and doubles (CCSD): $T \approx T_1 + T_2$
- CC with singles, doubles, and triples (CCSDT): $T \approx T_1 + T_2 + T_3$
- CC with singles, doubles, triples, quadruples (CCSDTQ): $T \approx T_1 + T_2 + T_3 + T_4$

…….

Performance of the CC method

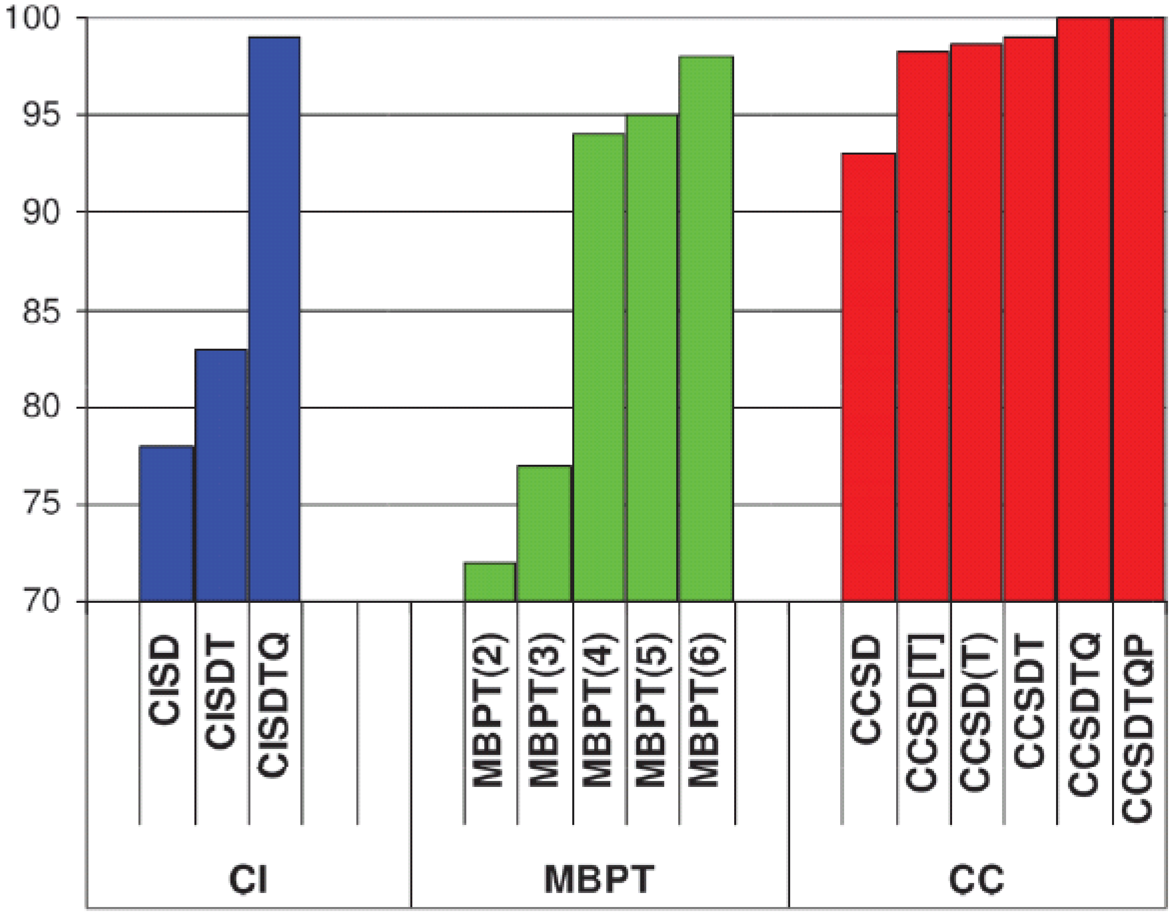
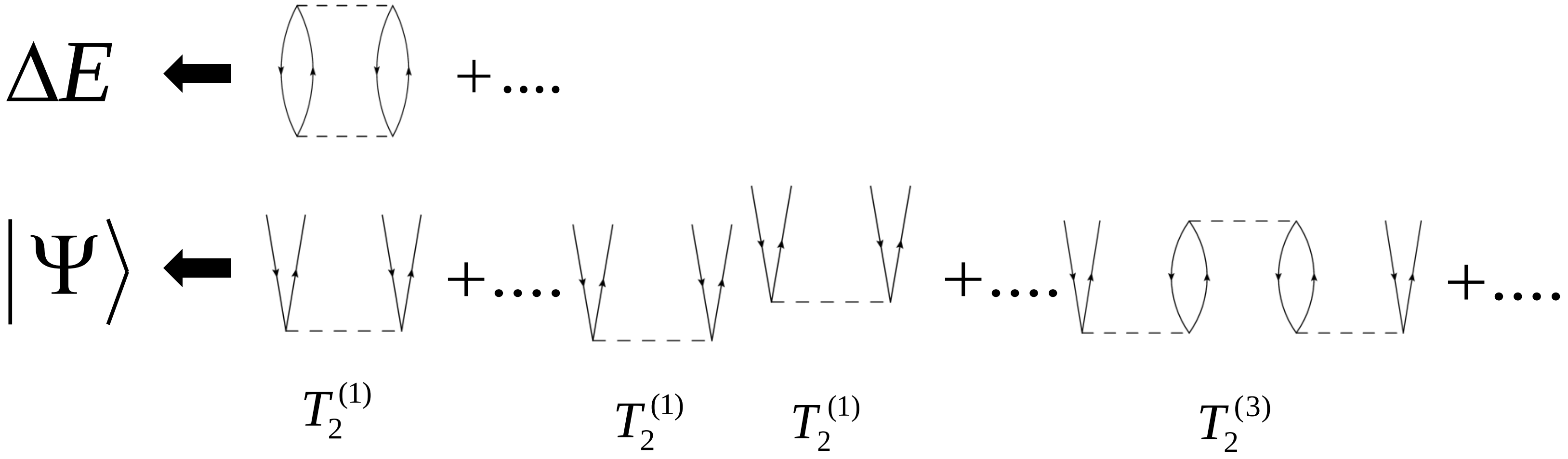


Figure 1. Comparison of CI, MBPT, and CC results with full CI. Results averaged over the series of small molecules: BH, HF, H_2O, SiH_2 and CH_2 in DZP basis set at R_e, $1.5R_e$, $2.0R_e$ and N_2 in cc-pVDZ basis set at R_e and C_2 in cc-pVDZ basis set augmented by diffuse functions at R_e.

R.J. Bartlett Mol. Phys. 108, 2905 (2010).

CC and Perturbation Theory (Linked Cluster Theorem)

- Linked Cluster Theorem states:
  - Perturbative expansion for the energy is expressed in terms of closed (having no external lines) connected diagrams only
  - Perturbative expansion for the wavefunction is expressed in terms of linked diagrams (having no disconnected closed part) only



Cluster operator *T* is represented by connected diagrams only

CC and Perturbation Theory

- Enable us to categorize the importance of particular cluster amplitudes

$$T_1 = T_1^{(2)} + \dots$$

$$T_2 = T_2^{(1)} + \dots$$

$$T_3 = T_3^{(2)} + \dots$$

$$T_4 = T_4^{(3)} + \dots$$

- Enable us to express higher-order contributions through lower-order contribution (CCSD(T))

$$T_3 \approx R_3^{(0)} V_N T_2$$

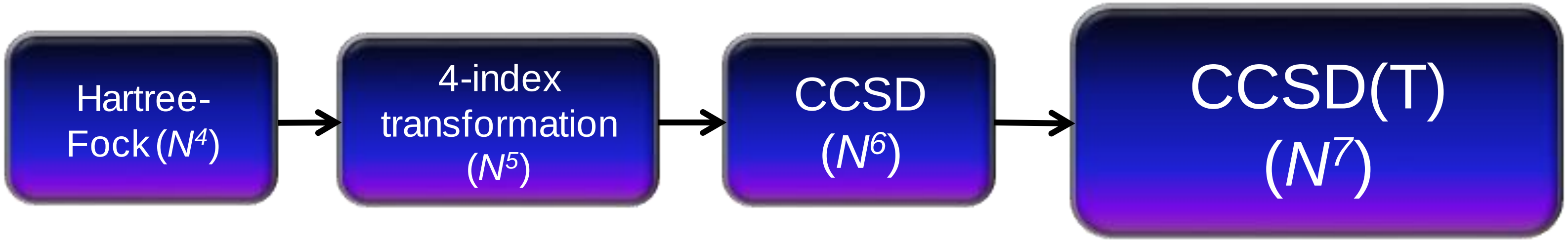
$$E^{CCSD(T)} = E^{CCSD} + E^{[4]} + E^{[5]}$$

CCSD(T) method

- Driving force of modern computational chemistry (ground-state problems)
- Belongs to the class of non-iterative methods
- Enable to reduce the cost of the inclusion of triple excitations to : required triply excited amplitudes can be generated on-the-fly.
- Storage requirements as in the CCSD approach

Coupled Cluster method

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}



Hartree-Fock (N^4) → 4-index transformation (N^5) → CCSD (N^6) → CCSD(T) (N^7)

Diagrammatica

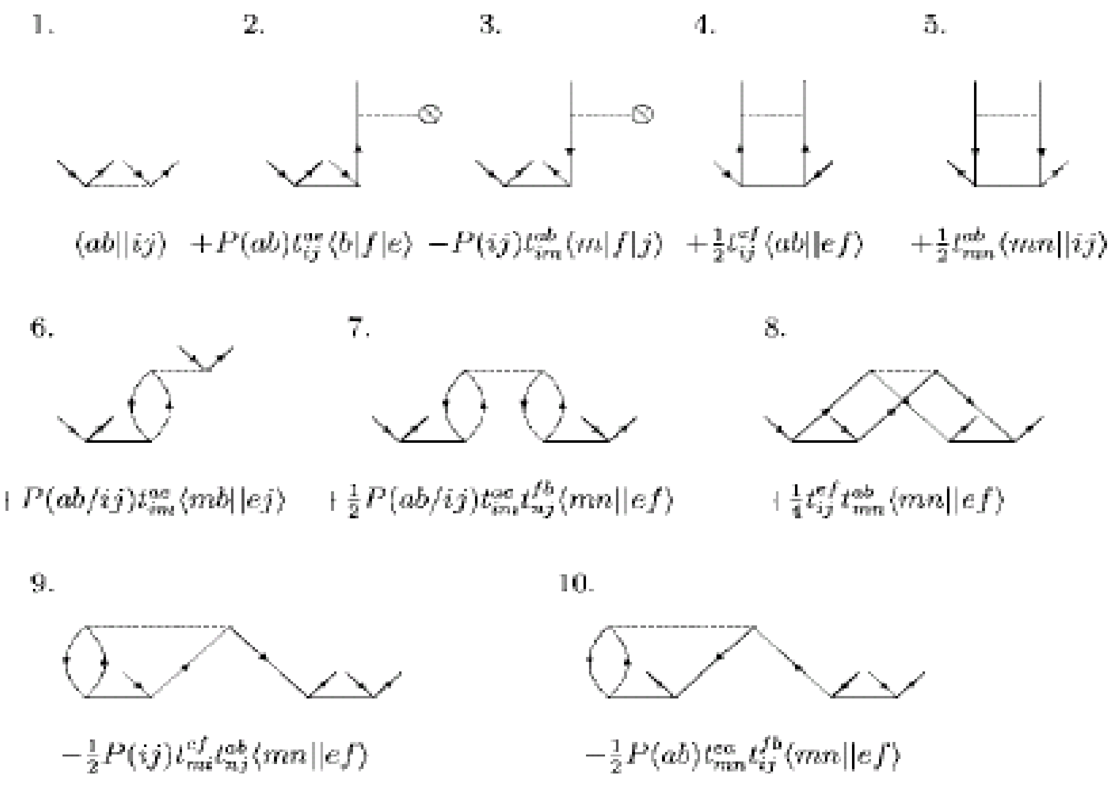
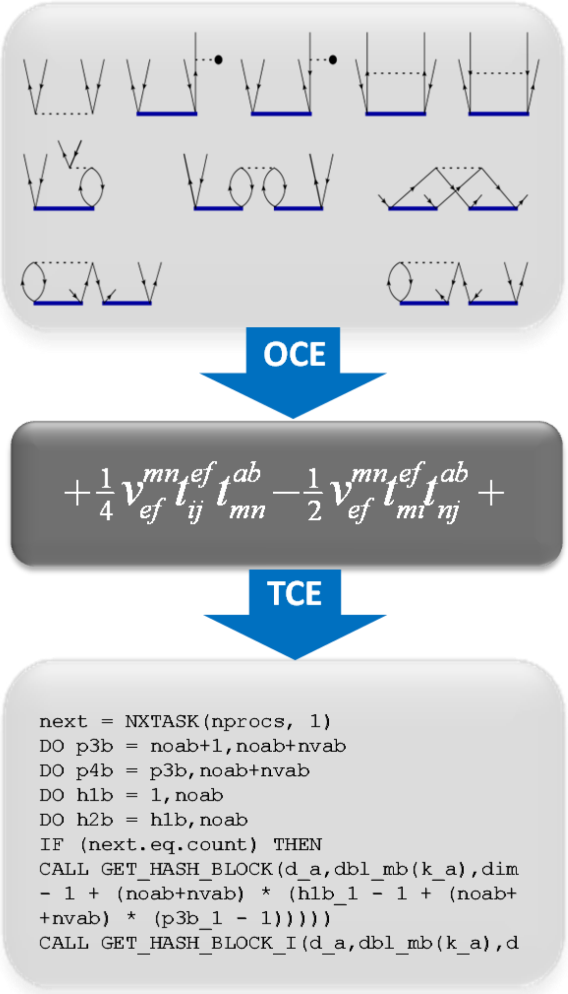


FIG. 10. Diagrammatic representation of the CCD method in the generic spin-orbital form together with the corresponding algebraic expression. Summation over repeated upper and lower indices is assumed. The antisymmetric permutation operator $P(pq/rs)$ is defined as $P(pq/rs)=P(pq)(rs)=1+(qp)(sr)-(qp)(rs)-(pq)(sr)$.

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.

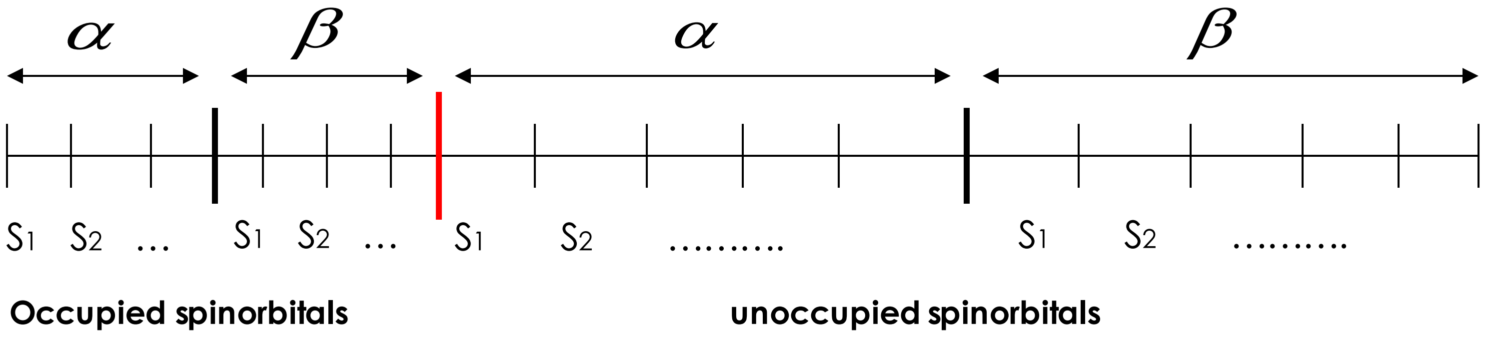


$$+\frac{1}{4}v^{mn}_{ef}t^{ef}_{ij}t^{ab}_{mn}-\frac{1}{2}v^{mn}_{ef}t^{ef}_{mi}t^{ab}_{nj}+$$

```
next = NXTASK(nprocs, 1)
DO p3b = noab+1,noab+nvab
DO p4b = p3b,noab+nvab
DO h1b = 1,noab
DO h2b = h1b,noab
IF (next.eq.count) THEN
CALL GET_HASH_BLOCK(d_a,dbl_mb(k_a),dim
- 1 + (noab+nvab) * (h1b_1 - 1 + (noab+
+nvab) * (p3b_1 - 1)))))
CALL GET_HASH_BLOCK_I(d_a,dbl_mb(k_a),d
```

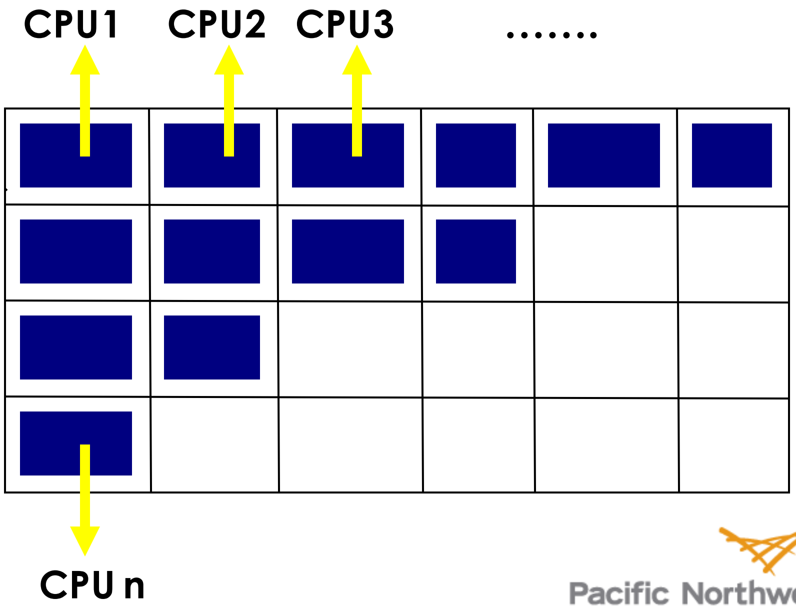
What is Tensor Contraction Engine (TCE)

Tile structure:



Tile-induced block structure of the CC tensors:

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



CC TCE 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

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
rohf
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 tarnsformation
  - 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 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)

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

- 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

task tce energy
```

maxiter 100 → max. number of iterations

diis 5 → length of the diis cycle

thresh 1.0d-5 → conv. threshold

attilesize 40 → default value 40

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) → CCSD(T) calculation will be performed

lshift 0.2 → Level shifting may be helpful in converging open-shell CCSD equations

Challenging situations – bond breaking processes: renormalized methods

Example: tce_cr_ccsd_t_ozone_pol1.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`

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

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Excited-state EOMCC formalism

cluster operator

$$\boxed{|\Psi_K\rangle = R_K e^{T} |\Phi\rangle}$$

reference function (HF determinant)

“excitation” operator

$$\boxed{\bar{H} R_K |\Phi\rangle = E_K R_K |\Phi\rangle} \qquad \boxed{\bar{H} = e^{-T} H e^{T}}$$

(Equation of Motion Coupled Cluster Equations)

EOMCC approximations

- EOMCCSD: singly-excited states

$$\left|\Psi_K^{EOMCCSD}\right\rangle = (R_{K,o} + R_{K,1} + R_{K,2})e^{T_1+T_2}\left|\Phi\right\rangle$$

- EOMCCSDT: singly and doubly excited states

$$\left|\Psi_K^{EOMCCSDT}\right\rangle = (R_{K,o} + R_{K,1} + R_{K,2} + R_{K,3})e^{T_1+T_2+T_3}\left|\Phi\right\rangle$$

- Perturbative methods: EOMCCSD(T) formulations

Excited-state EOMCC calculations

EOMCCSD < CR-EOMCCSD(T) < EOMCCSDT < 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}*

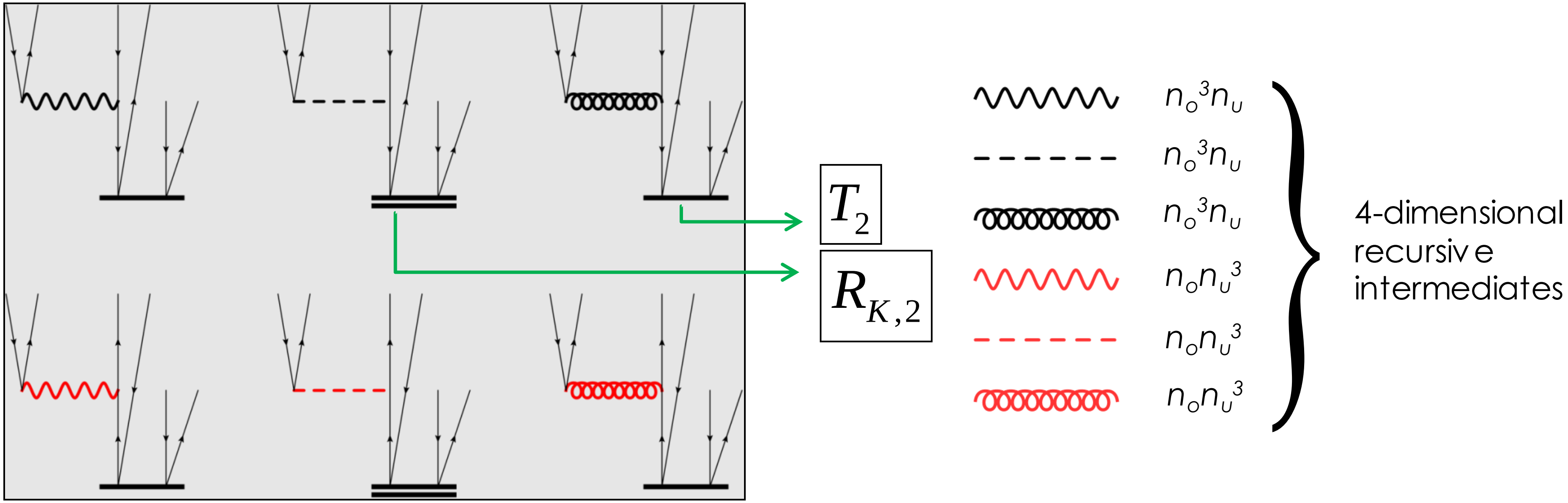
→ Excitation energies of singly Excited states

} Excited-state potential energy surfaces, doubly excited state

Non-iterative EOMCC methods: CR-EOMCCSD(T) approach

$$\boxed{\omega_K^{CR-EOMCCSD(T)} = \omega_K^{EOMCCSD} + \delta_K(T)} \Leftarrow \boxed{\delta_K(T) = \frac{\langle \Psi_K | Q_3 M_{K,3} | \Phi \rangle}{\langle \Psi_K | e^{T_1+T_2}(R_{K,0} + R_{K,1} + R_{K,2}) | \Phi \rangle}}$$

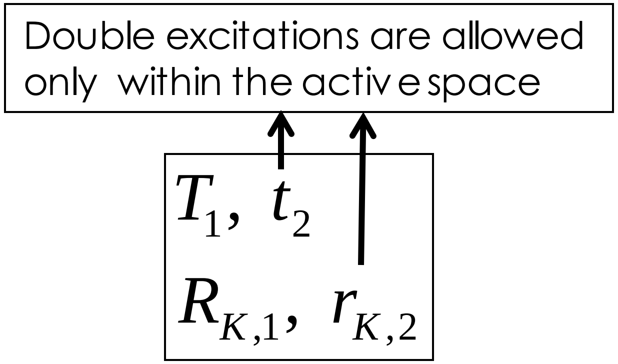
Kowalski and Piecuch "*A new class of non-iterative correction for the excited states: completely renormalized EOMCCSD(T) approach*" J. Chem. Phys. **120**, 1715 (2004)



4-dimensional recursive intermediates

Reduced cost CR-EOMCCSD(T) methods

- Active-space CR-EOMCCSD(T) approach
  - Active space can be defined by orbitals with orbital energies falling into a predefined energy interval $[\alpha, \beta]$
  - Significant reduction of the numerical cost associated with calculating (T) correction: $N^7 \Rightarrow N_{act}{}^5 N^2$: Applicable to large molecular systems



Double excitations are allowed only within the active space

$$T_1, \; t_2$$

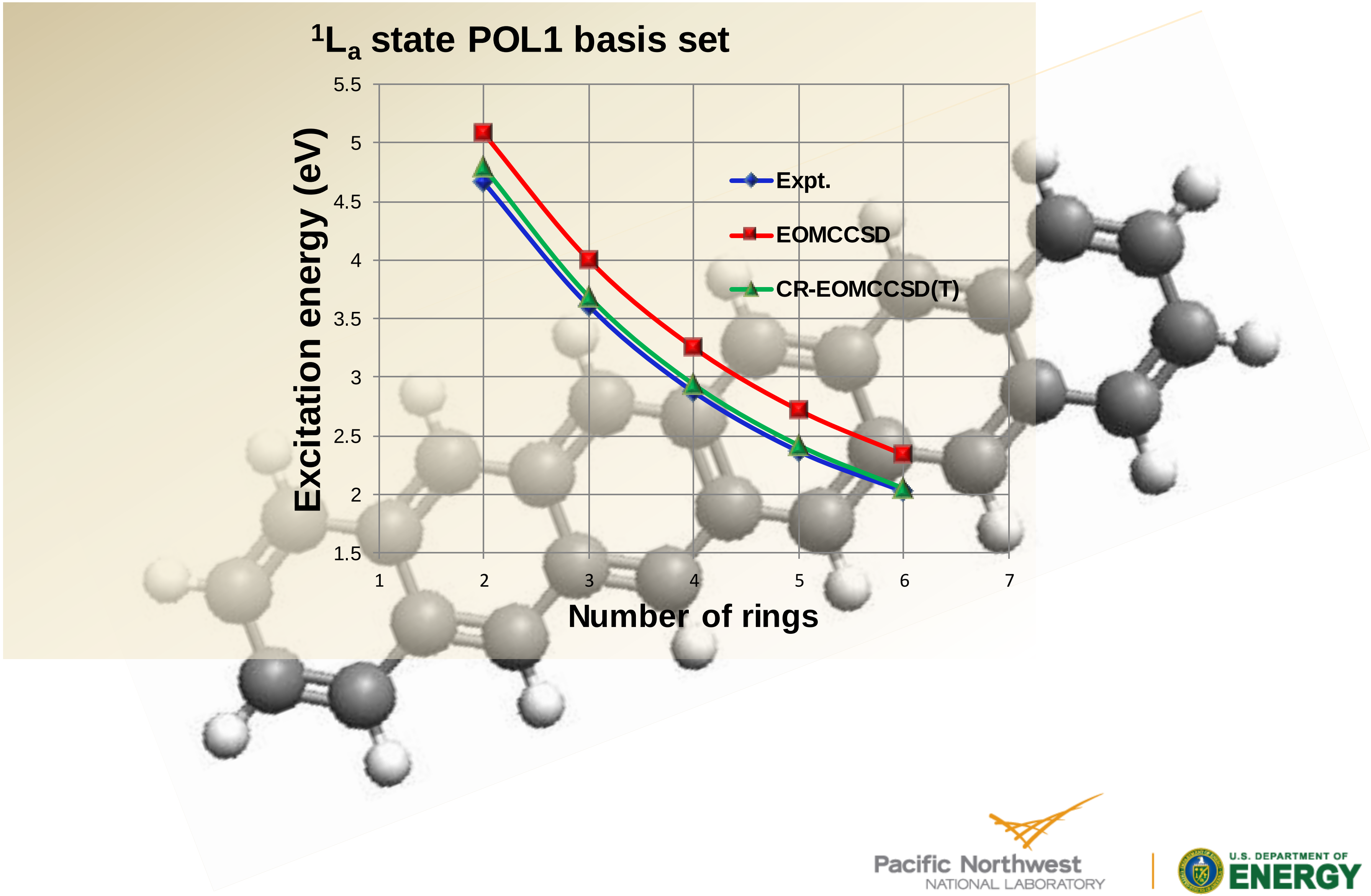
$$R_{K,1}, \; r_{K,2}$$

Active-space CR-EOMCCSD(T) correction

$$\delta_K(t) = \frac{\langle \Psi_K | q_3 M_{K,3} | \Phi \rangle}{\langle \Psi_K | e^{T_1+t_2}(R_{K,0} + R_{K,1} + r_{K,2}) | \Phi \rangle}$$

$$q_3 = \sum_{\substack{i<J<K \\ A<B<c}} | \Phi_{iJK}^{ABc} \rangle \langle \Phi_{iJK}^{ABc} |$$

Illustrative examples of large-scale excited-state calculations – components of light harvesting systems

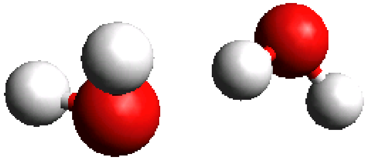


Excited-state calculations: EOMCCSD

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
eomsol 1
end

task tce energy
```



nroots 2 → number of roots

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

```
 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

task tce energy
```

eomsol 2 → new EOMCCSD solver with improved memory management – should be used for singly excited states only; initial starts taken from the CIS calculations

symmetry / targetsym a' } states of a’ symmetry will be calculated

Excited-state calculations: EOMCCSD

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

set tce:thresheom 1.0d-4
set tce:threshl 1.0d-3

task tce energy
```

Sometimes it is easier to converge n-root in the presence of the n+1 root. We can apply separate conv. criteria for n roots of interest (thresheom) and auxiliary (n+1-st) root (threshl).

Excited-state calculation: EOMCCSDT

```
Example:
tce_h2o_eomccsdt_cc-pvdz.nw
```

```
# CCSDT/EOMCCSDT methods are much more expensive than
# the CCSD/EOMCCSD formalisms
 tce
 freeze core atomic
 ccsdt
 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)

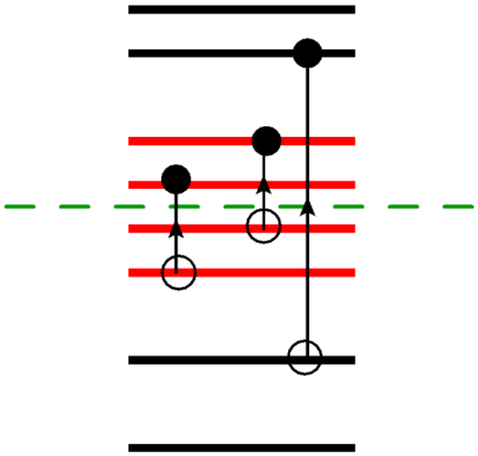
Example:

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
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
Aactive virtual beta spinorbitals



Only t_{iJK}^{ABc} amplitudes included

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

task tce energy
```

2eorb, 2emet 13: RHF reference is employed, orbital from of 2-electron integrals can be used

creomsd(t) → 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

Excited-state calculations: active-space CR-EOMCCSD(T) method

```
tce
freeze atomic
2eorb
2emet 13
creom(t)ac
oact 21     }
uact 99     }  →
tilesize 15
thresh 1.0d-4
nroots 1
symmetry
targetsym a'
end

task tce energy
```

Number of active occupied/unoccupied orbitals. Alternative the active orbitals can be defined by "energy window"

```
emin_act -0.5
emax_act 1.0
```

Linear response CC calculations

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

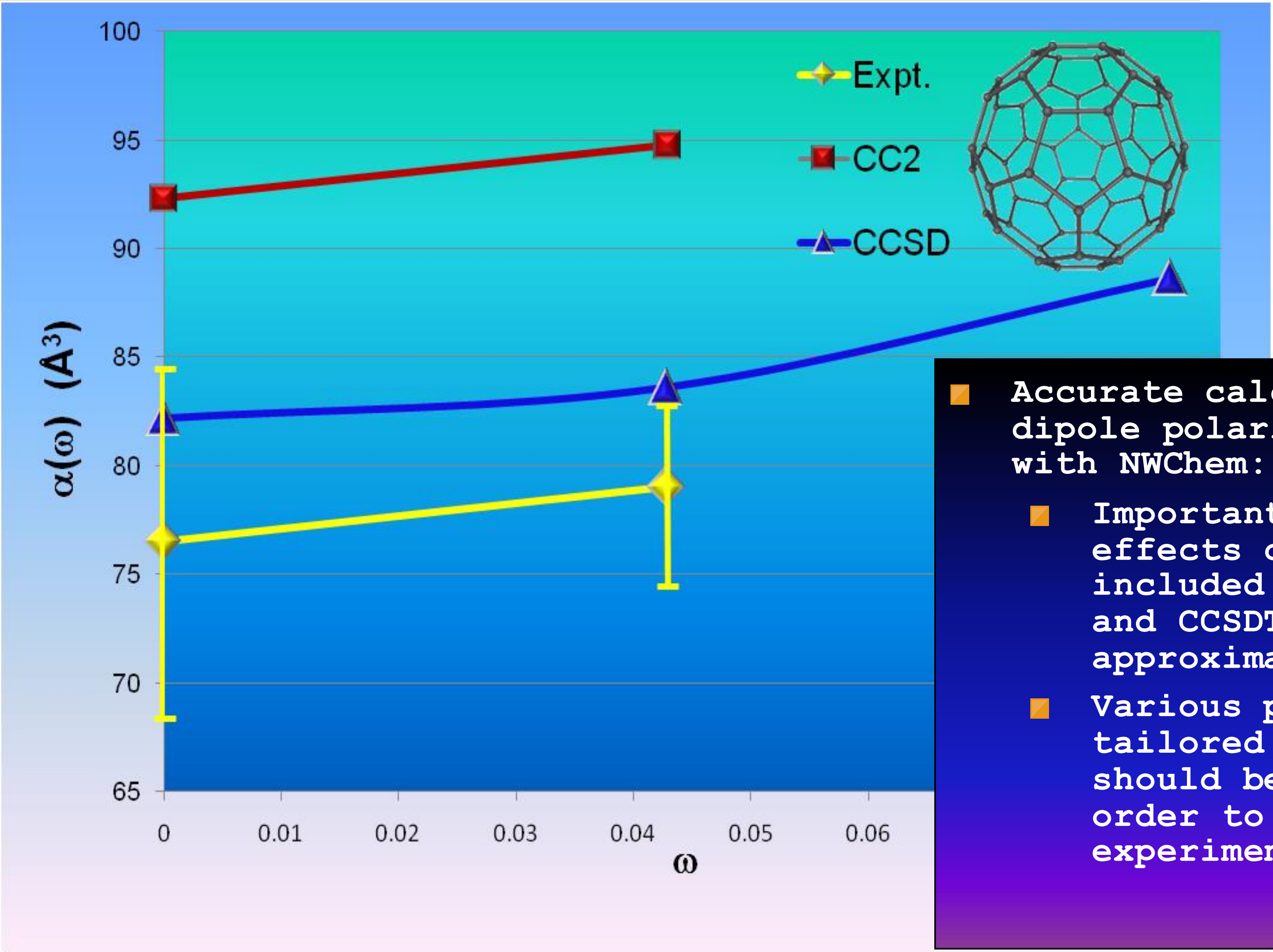
$$T(t) = T^{(0)} + T^{(1)}(t) + T^{(2)}(t) + \ldots$$

- Dipole polarizabilities can be calculated as a linear response function

$$\alpha_{ij}(\omega) = - << \mu_i ; \mu_j >>_\omega$$

CC eq. ➔ Λ-CC eq. ➔ 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. α(xx) α(zz) α(xz) will be available)

List of required ω values

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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

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

task tce energy
```

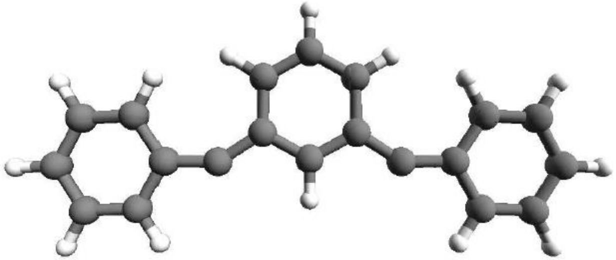
```
CCSD Linear Response polarizability / au
 Frequency  =      0.0000000  / au
 Wavelength =            Inf / nm
 ---------------------------------------------------|-----------------------------------------------
              atomic units (bohr^3)                 |              angstroms^3
                   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
 ---------------------------------------------------|-----------------------------------------------
```

static case

Multireference CC (MRCC) theory

Polycarbene (n=2). Structure of the model space representation of the lowest singlet state ($c_{\mu}{}^{2}$s). (4,4) model space and 6-31G basis set was used (208 functions).

Occupation/Method	12R-BWCCSD a p.	12R-MkCCSD
2200	0.000	0.000
$\alpha\alpha\beta\beta$	0.654	0.533
$\alpha\beta\alpha\beta + \alpha\beta\beta\alpha$	0.240	0.437
2020 + 0220 + 2002 + 0202	0.106	0.030
0022	0.000	0.000



12R-BW-MRCCSD-ap	12R-Mk-MRCCSD	
-766.792581		**Closed-shell singlet**
-766.884663	-766.883870	**Open-shell singlet**

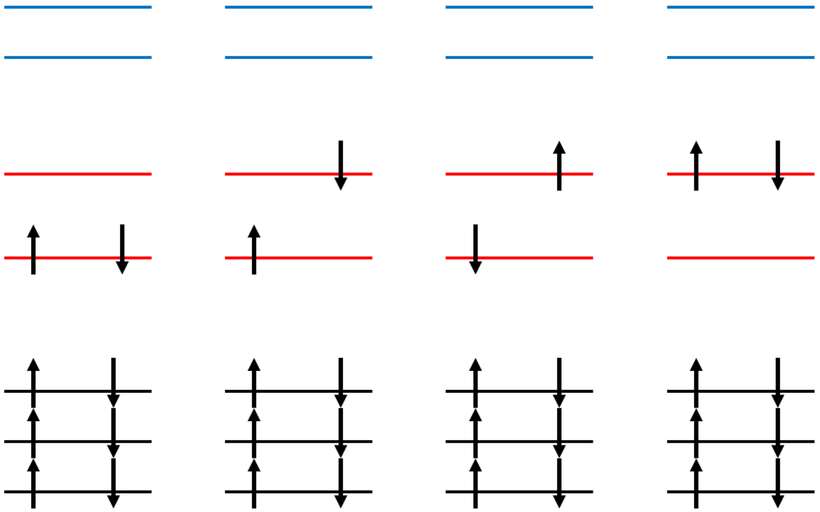
MRCC theory

$$\boxed{|\Psi\rangle = \sum_{\mu=1}^{M} c_{\mu} e^{T^{(\mu)}} |\Phi_{\mu}\rangle}$$

Jeziorski-Monkhorst Ansatz

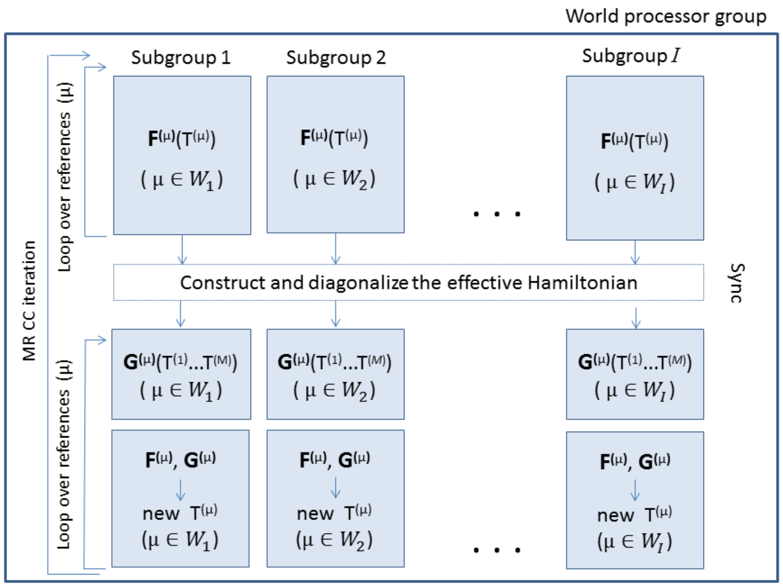
$$\boxed{M_0 = ls\left\{|\Phi_{\mu}\rangle\right\}_{\mu=1}^{M}}$$

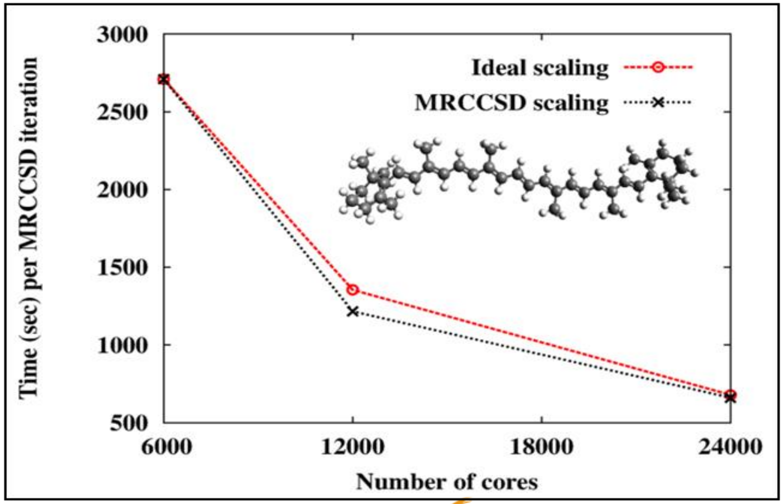
Model space



MRCC implementations in NWChem

- Multireference CC methods in NWChem (next release)
  - Strongly correlated excited states
  - Implemented MRCC approaches
    - Brillouin-Wigner MRCCSD
    - Mukherjee Mk-MRCCSD approach
    - State-Universal MRCCSD (under testing)
    - Perturbative triples corrections MRCCSD(T)
  - Novel paralellization strategies based on the processor groups
  - Demonstrated scalability of MRCCSD across 24,000 cores





Questions?