Post-Hartree-Fock Methods

Methods use a Hartree-Fock calculation as starting point and try to improve the HF results by taking account of electron correlation:

- **Configuration Interaction (CI)**
- **Many-Body Perturbation Theory (Moller-Plesset (MPn)**
- **Coupled Cluster (CC) Theory**

(Chapter 7 of the script)

Size Extensivity/Size Consistency

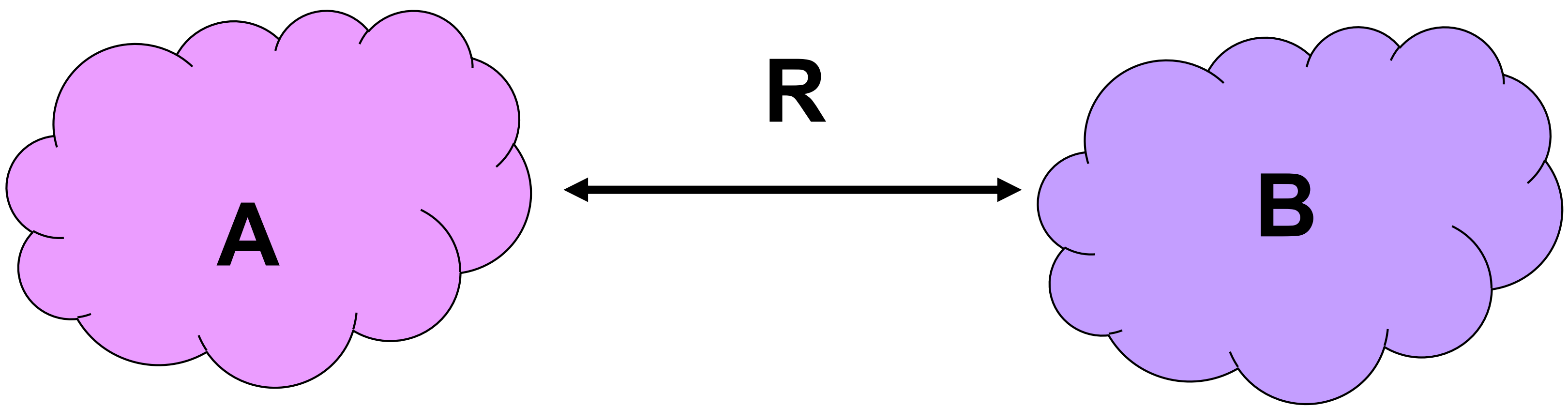
Extensive and intensive properties:

- *intensive* properties do not dependent on system size (but only on the type of system) e.g. density, melting point etc..
- *extensive* properties depend on size (amount of matter) e.g. mass, volume etc..

Size Extensivity:

- correct linear scaling with number of electrons n (⇔ error constant as a function of n)

Size Consistency:



E(A+B) -> E(A)+E(B) for R -> ∞ (when interaction is nullified)
(*strict separability*)

Quiz XV: Size-Consistency

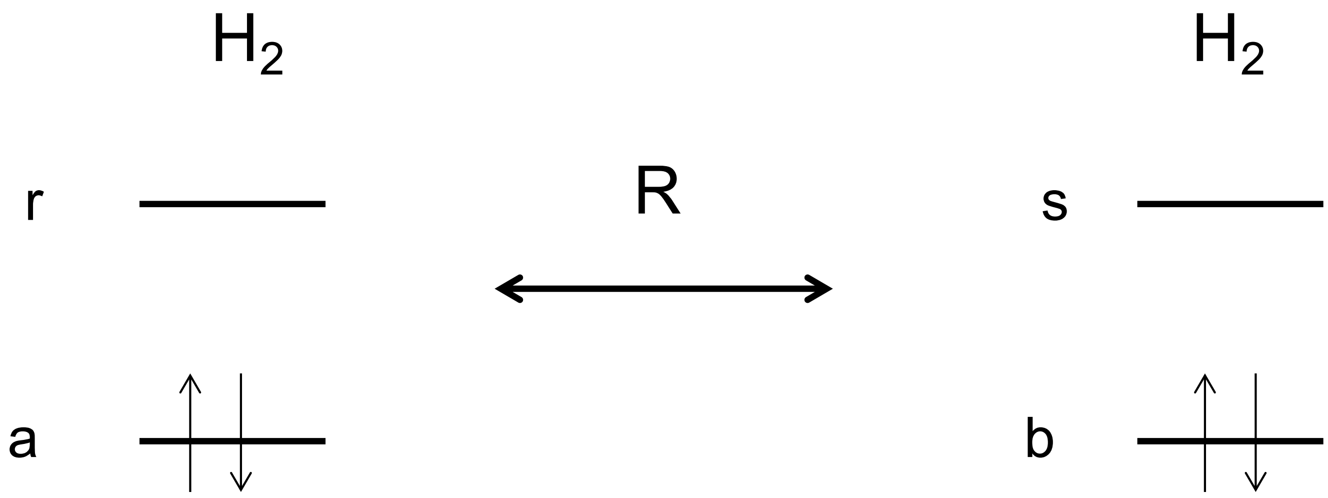
1) Is Hartree-Fock size-consistent (RHF, UHF)?

2) Is full CI size-consistent? Truncated CI?

3) Is MPn size-consistent?

Why is truncated CI not size-consistent?

Example: CISD of $(H_2)_2$ with minimal basis set



Determinants for full system:
gs: (aa'bb')
Singles: (arbb'),(aa'bs), (asbb'),(aa'br)
Doubles: (rr'bb'), (aa'ss'), (aa'rr'), (ss'bb'),(arbs)

For R -> ∞: **6 dets**
(aa'bb'),(arbb'),(aa'bs),(rr'bb'),
(aa'ss'),(arbs)

Single systems: 3 determinants each
gs: (aa')
Singles: (ar)
Doubles: (rr')

Total wavefunction product 3x3 =**9**
Slater determinants (includes triply and quadruply excited configurations!)
(arss'),(rr'bs),(rr'ss')

Truncated CI is not size-consistent!

Coupled Cluster (CC)

Yet another Ansatz for the Many-Body Wavefunction:

$$\boxed{\left|\Psi^{CC}\right\rangle = e^{\hat{T}}\left|\Phi_0\right\rangle}$$

where $\left|\Phi_0\right\rangle$ is a reference wavefunction. e.g. the Hartree-Fock determinant and $\hat{T}$ is the cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots$$

$\hat{T}_1$ is the one-particle excitation operator which generates singly excited configurations.

$\hat{T}_2$ Is the two-particle excitation operator which generates doubly excited Slater determinants.

Etc..

In analogy to the terminology used in case of CI calculations, coupled cluster methods are labelled according to the order of excitations that is included e.g. CCSD, CCSDT, CCSDTQ etc..In addition, acronyms of the type CCSD(T) refer to a coupled cluster calculation including singles and doubles and a perturbative treatment to include the effects of triple excitations.

Calculations of the coupled cluster type are nowadays one of the most popular approaches for very high accuracy calculations.

CCSD(T) is sometimes called the ‘gold standard of quantum chemistry’.

Another Notation: Second Quantization

Creation operator $\hat{a}_i^\dagger$ creates an electron in orbital i
Annihilation operator $\hat{a}_i$ removes an electron from orbital i

$$\hat{a}_i^\dagger \left|0\right\rangle = \left|\phi_i\right\rangle$$

$$\hat{a}_i \left|\phi_j\right\rangle = \partial_{ij} \left|0\right\rangle$$

Action is not commutative $\hat{a}_i^\dagger \hat{a}_i \neq \hat{a}_i \hat{a}_i^\dagger$ $\left[\hat{a}_i^\dagger, \hat{a}_i\right] = \hat{a}_i^\dagger \hat{a}_i - \hat{a}_i \hat{a}_i^\dagger \neq 0$

For fermions: anticommutation $\left\{\hat{a}_i^\dagger, \hat{a}_i\right\} = \hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger$

Canonical (normal) order: all creation operators left of annihilation operators

Cluster operators $\hat{T}_n$ in second quantization:

$$\boxed{\hat{T}_1 = \sum_a \sum_r t_a^r \hat{a}_r^\dagger \hat{a}_a}$$

$$\boxed{\hat{T}_2 = \sum_a \sum_{b \neq a} \sum_r \sum_{s \neq r} t_{ab}^{rs} \hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_b \hat{a}_a}$$

Coefficients = cluster amplitudes

The Advantage of an Exponential Form

$$\boxed{\left|\Psi^{CC}\right\rangle = e^{\hat{T}}\left|\Phi_0\right\rangle}$$

Taylor expansion of $e^{\hat{T}}$:

$$\boxed{e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \ldots}$$

Example: CCSD $\hat{T} = \hat{T}_1 + \hat{T}_2$

$$e^{\left(\hat{T}_1+\hat{T}_2\right)} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\left(\hat{T}_1^2 + 2\hat{T}_1\hat{T}_2 + \hat{T}_2^2\right) + \ldots$$

Includes given excitation level up to infinite order!

CC is size-consistent independent of reference wavefunction!

Quiz XVI: Exponential Form

1) Is CISD or CCSD more accurate?

Quiz XVI: Exponential Form

1) CCSD

$$e^{\left(\hat{T}_1+\hat{T}_2\right)} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \ldots$$

triples quadruples ….n tuples

CISD contains only singles and doubles
CCSD contains also higher order excitations up to infinite order!

Given level of excitations can be realized in different ways: e.g. doubles

$$\hat{T}_1^2 = \sum_a \sum_r \sum_b \sum_s \boxed{t_a^r t_b^s} \hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_b \hat{a}_a$$

disconnected cluster amplitudes

$$\hat{T}_2 = \sum_a \sum_{b \neq a} \sum_r \sum_{s \neq r} \boxed{t_{ab}^{rs}} \hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_b \hat{a}_a$$

Connected cluster amplitudes

Inclusion of disconnected clusters leads to size-consistency!

Coupled Cluster Energy

$$\boxed{\left|\Psi^{CC}\right\rangle = e^{\hat{T}}\left|\Phi_0\right\rangle}$$

Insert into
Schrodinger Eqs

$$\hat{H}e^{\hat{T}}\left|\Phi_0\right\rangle = E^{CC}e^{\hat{T}}\left|\Phi_0\right\rangle$$

Mutiply from left with
$\left\langle\Phi_0\right|$

$$\left\langle\Phi_0\left|\hat{H}e^{\hat{T}}\right|\Phi_0\right\rangle = E^{CC}\left\langle\Phi_0\left|e^{\hat{T}}\right|\Phi_0\right\rangle$$

$$\left\langle\Phi_0\left|\hat{H}e^{\hat{T}}\right|\Phi_0\right\rangle = E^{CC}\left\langle\Phi_0\left|\left(1+\hat{T}_1+\hat{T}_2+\ldots\right)\right|\Phi_0\right\rangle$$

$$\boxed{\left\langle\Phi_0\left|\hat{H}e^{\hat{T}}\right|\Phi_0\right\rangle = E^{CC}}$$

Coupled Cluster Energy: CCSD

e.g. for CCSD

$$E^{CCSD} = \left\langle \Phi_0 \middle| \hat{H} \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \ldots \right) \middle| \Phi_0 \right\rangle$$

$$E^{CCSD} = E_0 + \sum_a^{occ}\sum_r^{virt} t_a^r \left\langle \Phi_0 \middle| \hat{H} \middle| \Phi_a^r \right\rangle + \sum_{a,b>a}^{occ}\sum_{r,s>r}^{virt} \left(t_{ab}^{rs} + t_a^r t_b^s - t_a^s t_b^r \right) \left\langle \Phi_0 \middle| \hat{H} \middle| \Phi_{ab}^{rs} \right\rangle$$

$$E^{CCSD} = E_0 + \sum_{a,b>a}^{occ}\sum_{r,s>r}^{virt} \left(t_{ab}^{rs} + t_a^r t_b^s - t_a^s t_b^r \right) \left\langle \phi_a \phi_b \middle\| \phi_r \phi_s \right\rangle$$

Still have to determine cluster amplitudes!

Coupled Cluster Amplitudes tμ

Variational approach: direct variation of the energy with respect to cluster amplitudes => intractable set of nonlinear equations

$\Rightarrow$ Projected coupled-cluster equations by left projecting each determinant μ

$\Rightarrow$ $\binom{M}{N}$ equations for energy and amplitudes

$$\boxed{\begin{aligned} &\left\langle \Phi_0 \middle| \hat{H} e^{\hat{T}} \middle| \Phi_0 \right\rangle = E \\ &\left\langle \mu \middle| \hat{H} e^{\hat{T}} \middle| \Phi_0 \right\rangle = E \left\langle \mu \middle| e^{\hat{T}} \middle| \Phi_0 \right\rangle \end{aligned}}$$

Have to be solved self-consistently!

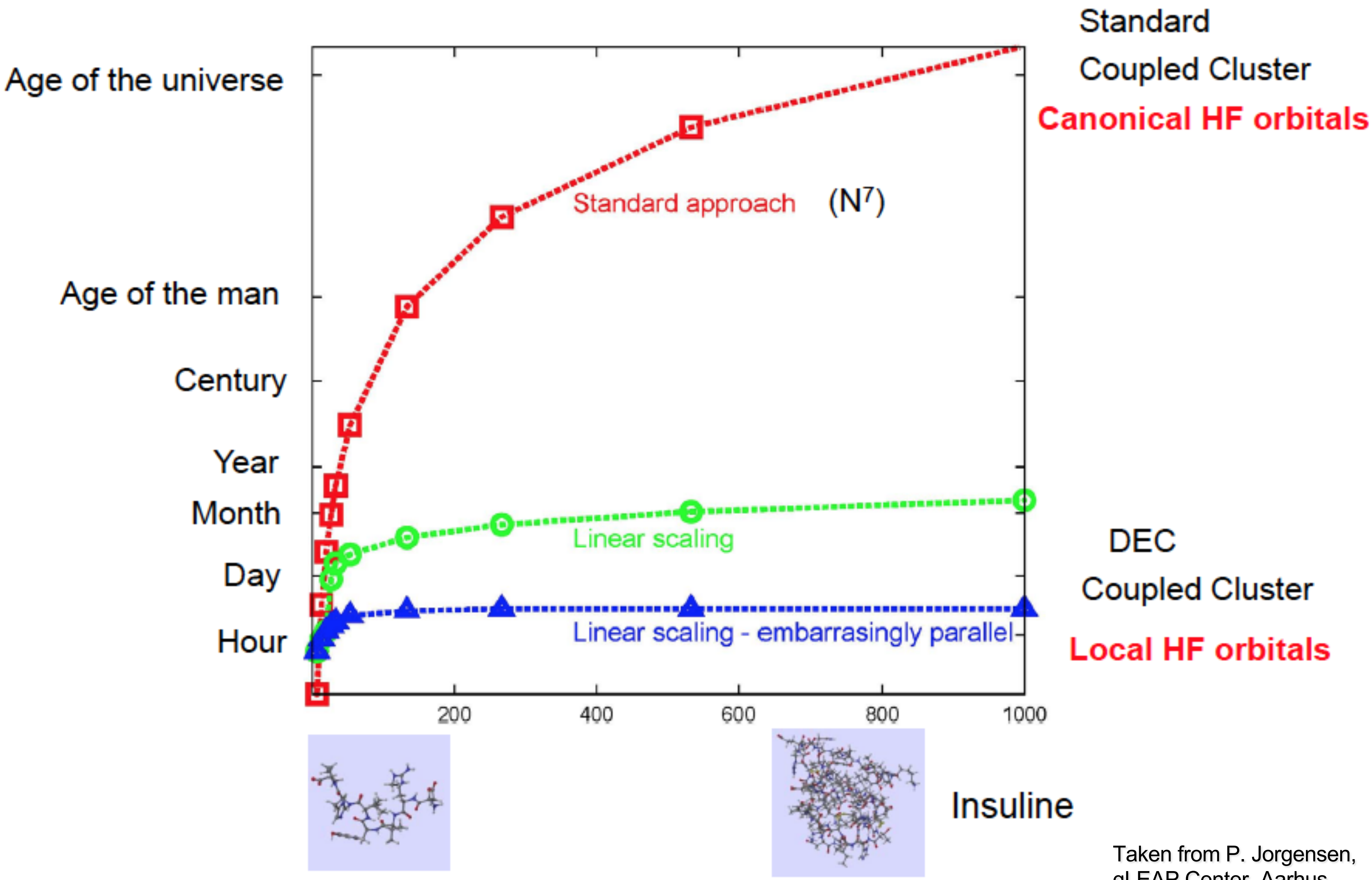
Convergence and Scaling

method	$R = R_{\text{ref}}$	$R = 2R_{\text{ref}}$
RHF	0.217822	0.363954
CCSD	0.003744	0.022032
CCSDT	0.000493	-0.001405
CCSDTQ	0.000019	-0.000446
CCSDTQ5	0.000003	

CCSD	N^6
CCSDT	N^8
CCSDTQ	N^{10}
CCSD(T)	N^7

Inclusion of triples via perturbation theory

Scaling in Coupled Cluster theory CCSD(T)



Taken from P. Jorgensen,
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