Internally contracted multireference coupled-cluster theory

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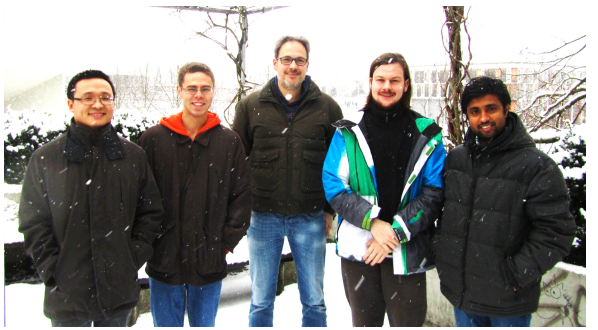

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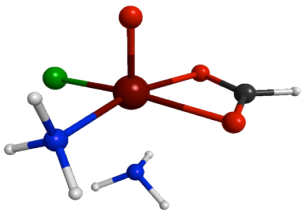
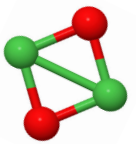
DFG Deutsche Forschungsgemeinschaft

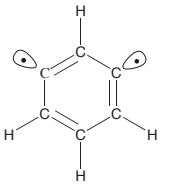
Target now: Molecules

Actually: Electrons in the field of (point-like) nuclei fixed in space

(Keywords: Born-Oppenheimer approximation, clamped nuclei approximation)







We solve for (mostly) stationary states of the electronic (non-relativistic) Hamiltonian

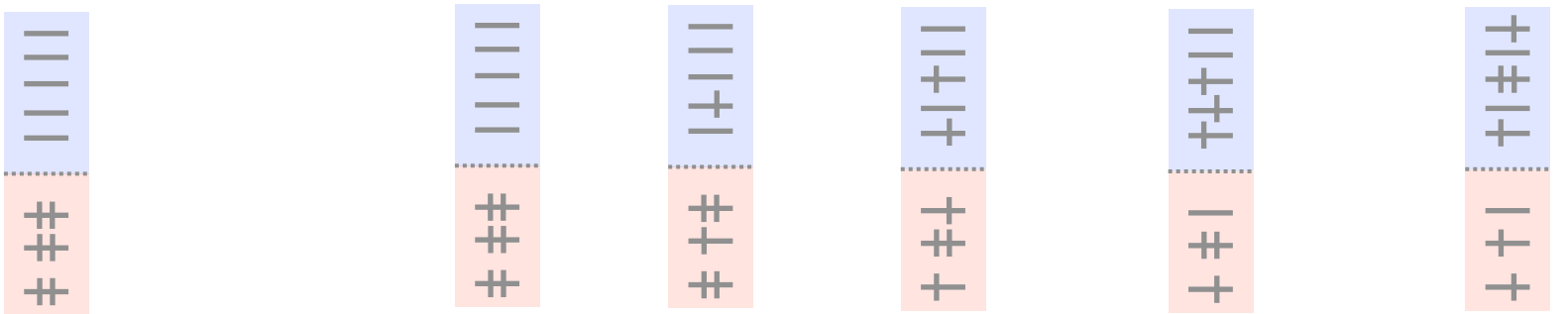
$$h_p^q = \langle p| \left(-\frac{1}{2}\Delta - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} \right) |q\rangle \qquad g_{pr}^{qs} = \langle pr| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |qs\rangle$$

$$\hat{H} = \sum_{pq} h_p^q a_p^\dagger a_q + \tfrac{1}{4} \sum_{pqrs} g_{pr}^{qs} a_p^\dagger a_r^\dagger a_s a_q \quad = h_p^q a_q^p + \tfrac{1}{4} g_{pr}^{qs} a_{qs}^{pr}$$

short-hand notation

creation/annihilation of spin-orbitals

Many-electron states in molecules



$$|\Phi_0\rangle \implies |\Psi\rangle = c_0|\Phi_0\rangle + c_a^i|\Phi_i^a\rangle + c_{ab}^{ij}|\Phi_{ij}^{ab}\rangle + c_{abc}^{ijk}|\Phi_{ijk}^{abc}\rangle + c_{abcd}^{ijkl}|\Phi_{ijkl}^{abcd}\rangle + \ldots$$

$$\propto \quad |\Phi_0\rangle \quad + \quad |\Psi_{\mathrm{korr}}\rangle$$

Coupled-Cluster (CC) ansatz:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle = |\Phi_0\rangle + \hat{T}|\Phi_0\rangle + \frac{1}{2}\hat{T}^2|\Phi_0\rangle + \ldots$$

Coester, Kümmel (1958)
Čížek, Paldus (1966)
Bartlett (1978)

Coupled-cluster expansion

Ansatz:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

single determinant

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$

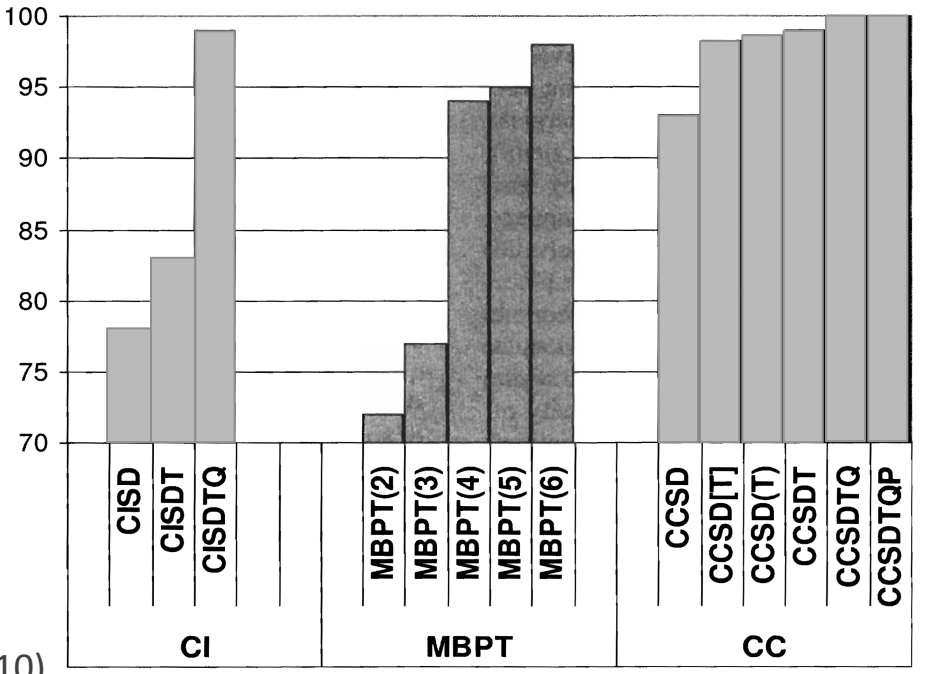
Features:

separability

$$\begin{aligned}|\Psi_{\mathrm{CC}}^{AB}\rangle &= e^{\hat{T}_A+\hat{T}_B}|\Phi_0^{AB}\rangle \\ &= \hat{\mathcal{A}}\left(e^{\hat{T}_1}|\Phi_0^A\rangle\right)\left(e^{\hat{T}_2}|\Phi_0^B\rangle\right) \\ &= \hat{\mathcal{A}}|\Psi_{\mathrm{CC}}^A\rangle|\Psi_{\mathrm{CC}}^B\rangle\end{aligned}$$

$$E^{AB} = E^A + E^B$$

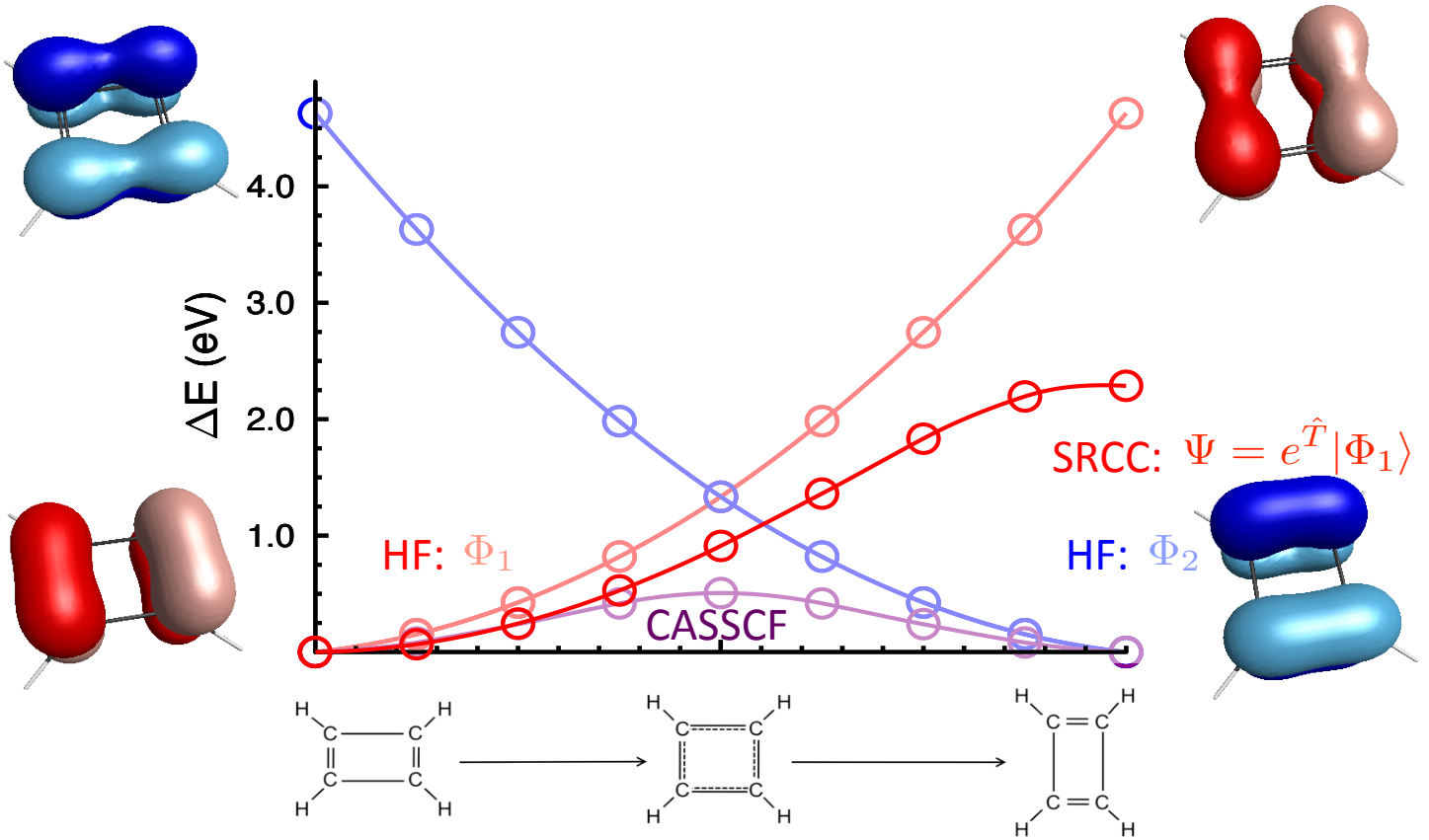
fast convergence with cluster rank

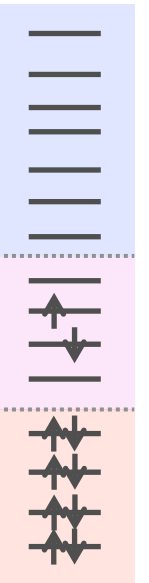


Percentage of E_{corr} recovered for set of small molecules
Bartlett, Mol Phys 108, 2905 (2010)

Multireference cases

Example: Automerization of cyclobutadiene





Complete Active Space

N active electrons
M active orbitals

CAS(M,N)

Overview: Different approaches

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

$$|\Psi_{\text{ext-SRCC}}\rangle = e^{\hat{T}_{\mathrm{ex}}} e^{\hat{T}_{\mathrm{int}}} |\Phi_0\rangle$$

Adamowicz (1992), Piecuch, Kallay, Olsen, Paldus, Bartlett, ...

$$|\Psi_{\mathrm{JM}}\rangle = \sum_{\mu} e^{\hat{T}(\mu)} |\Phi_\mu\rangle c_\mu$$

Jeziorski, Monkhorst (1981)

$$|\Psi_{\mathrm{ic}}\rangle = e^{\hat{T}} \sum_{\mu} |\Phi_\mu\rangle c_\mu$$

[Cicek, 1967], Mukherjee (1975)

State-universal

Piecuch, Jeziorski; Kucharski, Bartlett; Li, Paldus

State-specific

Mášik, Hubač (1998)
Pittner et al. (2006)
Mahapatra, .
Datta, Mukherjee (1998)
Evangelista, Allen, Gauss et al. (2007)
Das, Kallay, Mukherjee (2009)
Hanrath (2005)

Valence universal: Fock-Space MRCC

Haque, Mukherjee (1984)
Stolarczyk, Monkhorst (1985)
Kaldor (1986)
recent work by: Musiał, Bartlett

State-specific: ic-MRCC

Banerjee, Simons (1981)
Nooijen et al. (2001,2011)
Olsen (2005)
Evangelista, Gauss (2011)
Hanauer, AK (2011)

compare: CT theory
Chan, Yanai (2006)

Reviews about MRCC: For example …

Lyakh, Musiał, Lotrich, Bartlett, Chem. Rev. 112, 182 (2012)
Köhn, Hanauer, Mück, Jagau, Gauss, WIREs CMS 3, 176 (2013)

Design of a multireference CC theory

Single reference:

$$|\Phi_0\rangle \quad \Rightarrow \quad |\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle$$

State-universal ansatz: (Jeziorski, Monkhorst)

$$\{|\Phi_\mu\rangle\} \quad \Rightarrow \quad |\Psi_{\mathrm{JM}}\rangle = \sum_\mu e^{\hat{T}(\mu)}|\Phi_\mu\rangle c_\mu$$

Intruder state problems: State-specific versions

State-specific internally contracted ansatz

$$|\Psi_0\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu \quad \Rightarrow \quad |\Psi_{\mathrm{ic}}\rangle = e^{\hat{T}} \sum_\mu |\Phi_\mu\rangle c_\mu$$

+ Simpler, better control of intruders

– Questionable at state crossings (!)

Internally contracted MRCC: Why?

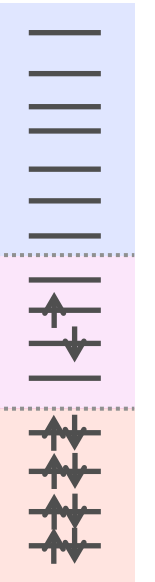
$$|\Psi_{\mathrm{ic}}\rangle = e^{\hat{T}} \sum_{\mu} |\Phi_{\mu}\rangle c_{\mu}$$

"internally contracted": originally used in CI context by Siegbahn, Mayer, Werner (1980s)

Promising features:

Genuine multireference scheme (no bias within model space)
Compact amplitude manifold (no scaling with model space size)
Spin adaption or spin-free formulation is easy
Orbital invariance

Evangelista, Gauss, JCP 134, 114102 (2011)
Hanauer, Köhn, JCP 134, 204111 (2011)



What is scary:

Non-commuting operator manifold
Linear dependencies

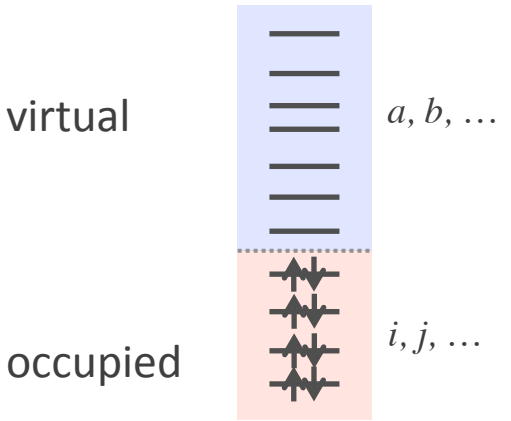
Simplified approaches, see e.g.

Banerjee, Simons, IJQC 19, 207 (1981)
Laidig, Saxe, Bartlett, JCP 86, 887 (1987)
Fink, Staemmler, TCA 87, 129 (1993)

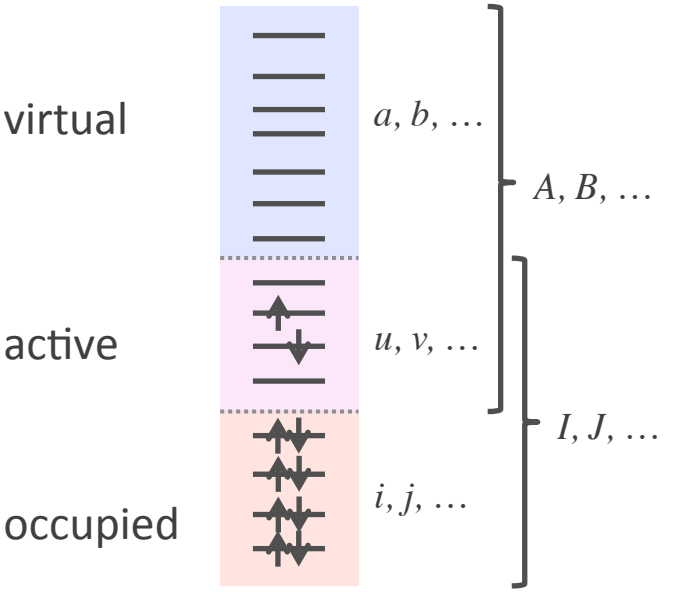
ic-MRCC vis-à-vis single-reference CC

Orbital space:

Hartree-Fock



CASSCF



Reference wave function:

$$|\Phi_0\rangle \qquad |\Psi_0\rangle = \sum_{\mu} |\Phi_\mu\rangle c_\mu$$

Correlated wave function:

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \qquad |\Psi_{\mathrm{ic}}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

Cluster operator:

$$\hat{T} = \sum_{ia} t_a^i a_i^a + \tfrac{1}{4}\sum_{ijab} t_{ab}^{ij} a_{ij}^{ab} + \ldots \qquad \hat{T} = \sum_{IA} t_A^I a_I^A + \tfrac{1}{4}\sum_{IJAB} t_{AB}^{IJ} a_{IJ}^{AB} + \ldots$$

ic-MRCC vis-à-vis single-reference CC

Correlated wave function:

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \qquad |\Psi_{\rm ic}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

Cluster operator:

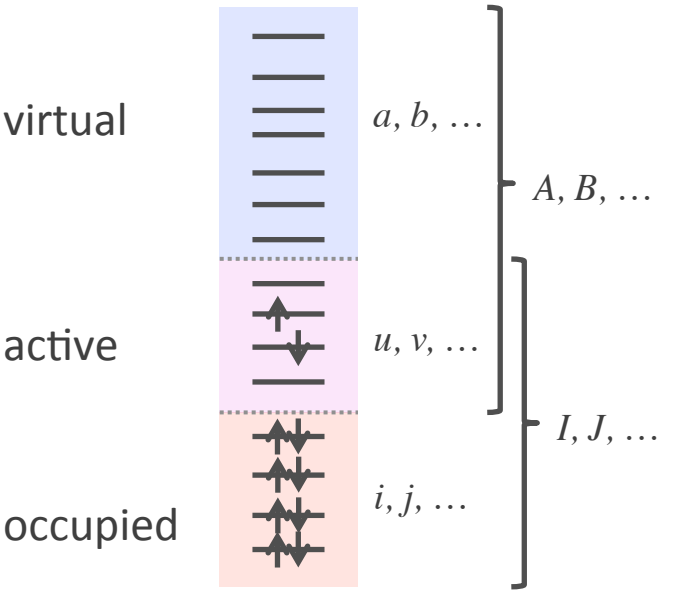
$$\hat{T} = \sum_{ia} t_a^i a_i^a + \tfrac{1}{4}\sum_{ijab} t_{ab}^{ij} a_{ij}^{ab} + \ldots = \sum_\rho t_\rho \hat{\tau}_\rho$$

$$\hat{T} = \sum_{IA} t_A^I a_I^A + \tfrac{1}{4}\sum_{IJAB} t_{AB}^{IJ} a_{IJ}^{AB} + \ldots = \sum_\rho t_\rho \hat{\tau}_\rho$$

Excitation types (singles&doubles):

$$\hat{\tau}_\rho = \left\{ \hat{a}_i^a \;\; \hat{a}_{ij}^{ab} \right.$$

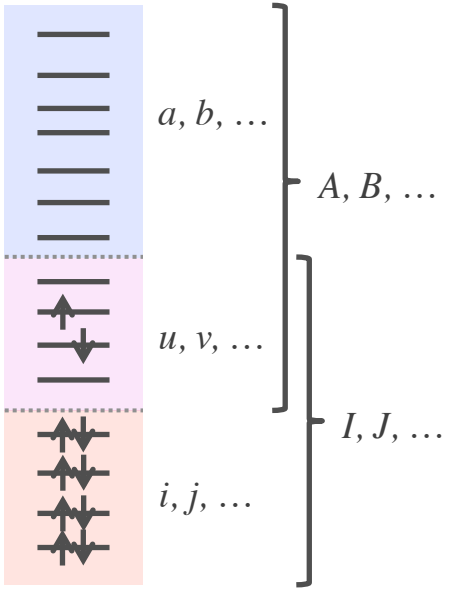
$$\hat{\tau}_\rho = \left\{ \hat{a}_i^a \;\; \hat{a}_{\color{magenta}u}^a \;\; \hat{a}_i^{\color{magenta}u} \;\; \hat{a}_{ij}^{ab} \;\; \hat{a}_{\color{magenta}uj}^{ab} \;\; \hat{a}_{\color{magenta}uv}^{ab} \;\; \hat{a}_{ij}^{\color{magenta}ub} \;\; \hat{a}_{\color{magenta}vj}^{\color{magenta}ub} \;\; \hat{a}_{\color{magenta}vx}^{\color{magenta}ub} \;\; \hat{a}_{ij}^{\color{magenta}uw} \;\; \hat{a}_{\color{magenta}vj}^{\color{magenta}uw} \right.$$



avoid active-active excitations, instead: optimize

$$|\Psi_0\rangle = \sum_\mu |\Phi^\mu\rangle c_\mu$$

ic-MRCC vis-à-vis single-reference CC



Correlated wave function:

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \qquad |\Psi_{\rm ic}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

Energy

$$E = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle \qquad E = \langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle$$

Equations for reference function

$$|\Psi_0\rangle = \sum_\mu |\Phi^\mu\rangle c_\mu$$

$$\sum_\nu \langle\Phi_\mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi^\nu\rangle c_\nu = E c_\mu \quad \equiv \quad \hat{\mathbf{H}}^{\rm eff}\mathbf{c} = E\mathbf{c}$$

Amplitude equations

$$0 = \langle\Phi_0|(\hat{\tau}_\rho)^\dagger\, e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle \qquad 0 = \langle\Psi_0|(\hat{\tau}_\rho)^\dagger\, e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle$$

Here it becomes more difficult!

Linear dependencies

$$0 = \langle\Psi_0|(\hat{\tau}_\rho)^\dagger e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Psi_0\rangle$$

non-orthogonal

$$S_{\rho\sigma} = \langle\Psi_0|(\hat{\tau}_\rho)^\dagger \hat{\tau}_\sigma|\Psi_0\rangle \neq \delta_{\rho\sigma}$$

linear dependencies, e.g.

$$\hat{a}^{ab}_{1\bar{1}}\left(c_1|1\bar{1}\rangle + c_2|2\bar{2}\rangle\right) = c_1|ab\rangle$$
$$\hat{a}^{ab}_{2\bar{2}}\left(c_1|1\bar{1}\rangle + c_2|2\bar{2}\rangle\right) = c_2|ab\rangle$$

$$\sum_u \hat{a}^{ua}_{ui}|\Psi_0\rangle = n_a \hat{a}^a_i|\Psi_0\rangle$$

Consequences:

covariant and contravariant quantities

$$\hat{A} = \sum_\rho A_\rho \hat{\tau}_\rho$$

$$\bar{A}_\rho = \langle\Psi_0|(\hat{\tau}_\rho)^\dagger \hat{A}|\Psi_0\rangle = \sum_\sigma S_{\rho\sigma} A_\sigma$$

projection $\langle\Psi_0|(\hat{\tau}_\rho)^\dagger$ has less degrees of freedom than operator basis $\sum_\rho t_\rho \hat{\tau}_\rho$

particle ranks are not orthogonal, e.g. $\langle\Psi_0|a^{ui}_{vw} a^w_i|\Psi_0\rangle \neq 0$

Linear dependencies

icMRCCSD: up to 3-particle density

project to orthogonalized, non-redundant basis:

technically identical to ic-MRCI, CASPT2 etc. $S_{\rho\sigma} = \langle\Psi_0|(\hat{\tau}_\rho)^\dagger\hat{\tau}_\sigma|\Psi_0\rangle = S^{\text{act.}}_{\rho_\text{a}\sigma_\text{a}} \otimes 1^{\text{inact.}}_{\rho_\text{i}\sigma_\text{i}}$

$\Longrightarrow \quad \hat{\tau}'_{\tilde{\rho}} = X^\sigma_{\tilde{\rho}}\tau_\sigma \qquad$ where $\hat{\boldsymbol{\tau}}' = \hat{\boldsymbol{\tau}}^{||} + \hat{\boldsymbol{\tau}}^{\perp} \qquad$ with $\hat{\tau}^\perp_{\tilde{\rho}}|\Psi_0\rangle = 0$

$\Longrightarrow \quad \hat{T} = \hat{T}^{||} + \hat{T}^{\perp}$

we have the *freedom* to set $\hat{T}^\perp = 0$ (will still converge to full CI)*

*Evangelista, Hanauer, Köhn, Gauss, JCP 136, 204108 (2012)

Modified amplitude equations

$$0 = \langle\Psi_0|(\hat{\tau}^{||}_{\tilde{\rho}})^\dagger\, e^{-\hat{T}^{||}}\hat{H}e^{\hat{T}^{||}}|\Psi_0\rangle$$

! A nasty problem: near-linear dependencies !

Technical note: $X^\sigma_{\tilde{\rho}} = (S_\eta^{-\frac{1}{2}})^\sigma_{\tilde{\rho}}$ + Schmidt-orthog. betw. particle ranks

$$\Omega^{||}_{\tilde{\rho}} = X^\sigma_{\tilde{\rho}}\langle\Psi_0|(\tau_\sigma)^\dagger\bar{H}|\Psi_0\rangle$$
$$\Delta t^{||}_\rho = (X^\dagger)^{\tilde{\sigma}}_\rho\left(\Omega^{||}_{\tilde{\sigma}}/\Delta\epsilon_{\tilde{\sigma}}\right)$$

$\Longrightarrow \quad \langle\Psi_0|\hat{T}_1^\dagger\hat{T}_2|\Psi_0\rangle \stackrel{!}{=} 0$

proper choice important for extensivity!

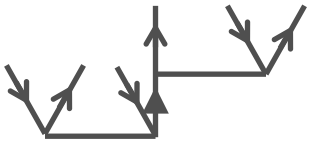
Hanauer, Köhn, JCP 134, 204111 (2011)
Hanauer, Köhn, JCP 137, 131103 (2012)

Numerical evaluation

$$\sum_\nu \langle \Phi_\mu | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi^\nu \rangle c_\nu = E c_\mu \qquad 0 = \langle \Psi_0 | (\hat{\tau}_{\tilde{\rho}}^{||})^\dagger \, e^{-\hat{T}^{||}} \hat{H} e^{\hat{T}^{||}} | \Psi_0 \rangle$$

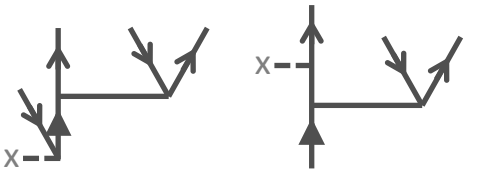
$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \tfrac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \ldots$$

$\hat{T}\hat{T}$



$[\hat{\tau}_\rho, \hat{\tau}_\sigma] \neq 0$

$$[\hat{H}, \hat{T}] = \hat{H}\hat{T} - \hat{T}\hat{H}$$



icMRCCSD Energy: up to 4-fold comm. Equations: up to 8-fold comm.

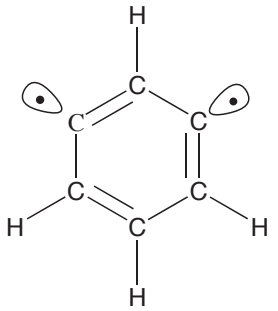
$e^{-\hat{T}} \hat{H} e^{\hat{T}}$	CCSD	ic-MRCCSD / CAS(6,6)
$= \hat{H}$	2	27
$+[\hat{H}, \hat{T}]$	13	690
$+\frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}]$	21	8 766
$+\frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}]$	8	70 997
$+\frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$	1	399 839
$+\ldots$	0	...

Commutator approximation

$$\langle \Psi_0 | (\tau'_\rho)^\dagger \, \hat{\overline{H}} | \Psi_0 \rangle = 0$$

$$\sum_\nu \langle \Phi_\mu | \hat{\overline{H}} | \Phi^\nu \rangle c_\nu = E c_\mu$$

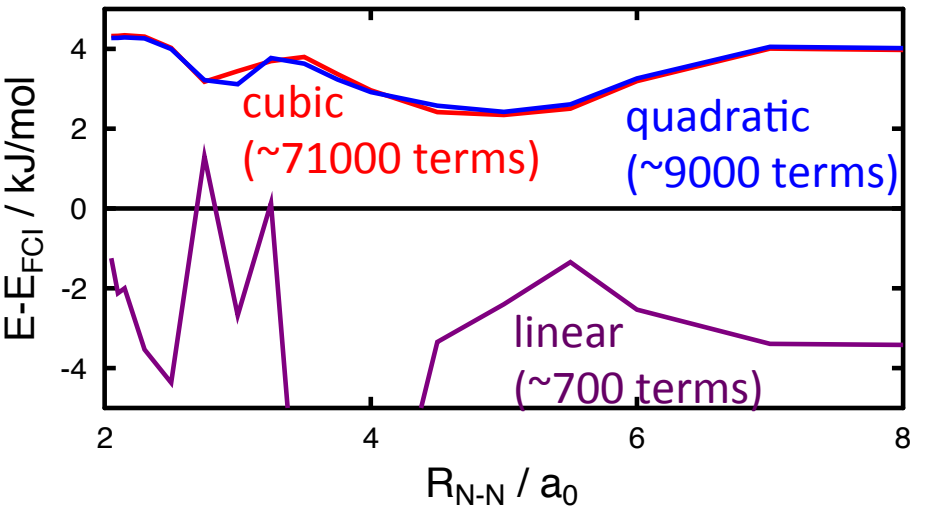
Singlet-Triplet separation of m-Benzyne:
icMRCCSD, cc-pVDZ basis, CAS(2,2)
frozen core



N_{com} (t)	N_{com}(E)	ΔE_{ST} / kcal mol^{-1}
4	4	17.289
3	3	17.289
2	2	17.415
2	4	17.415

N_2 stretching:

N_2, cc-pVDZ, CAS(6,6)
ic-MRCCSD vs. FCI



Numerical evaluation

Dealing with complex equations:

- Derivation by **automated techniques**

  using GeCCo program
  (Integrals, CASSCF: DALTON, GAMESS, Molpro)

- **Approximations:** Truncate after double commutator

  tested: Evangelista, Gauss, JCP 134, 114102(2011)
  Hanauer, Köhn, J. Chem. Phys. 134, 204111 (2011)

- Present implementation (GeCCo):

  Certainly not perfect ...
  ... BUT: correct N^6 scaling (for ic-MRCCSD and fixed active space)

GeCCo

Very new:

PYTHON powered
input language for F90 back-end

define operators

```
#####################################################################
# operators associated with T
#####################################################################
new_target('T-Operators')

PRINT({STRING:'=== Cluster Operators ==='})

DEF_OP_FROM_OCC({LABEL:'Tex',DESCR:'[PV],H|P,V|P[PV],[HV][HV]|VV,H[HV]
DEF_ME_LIST({LIST:'TLST',OPERATOR:'Tex',IRREP:1,'2MS':0,AB_SYM:+1})
PRINT_MEL_INFO({LIST:'TLST'})

CLONE_OPERATOR({LABEL:'Tp',TEMPLATE:'Tex'})
```

symbolic algebra with operators

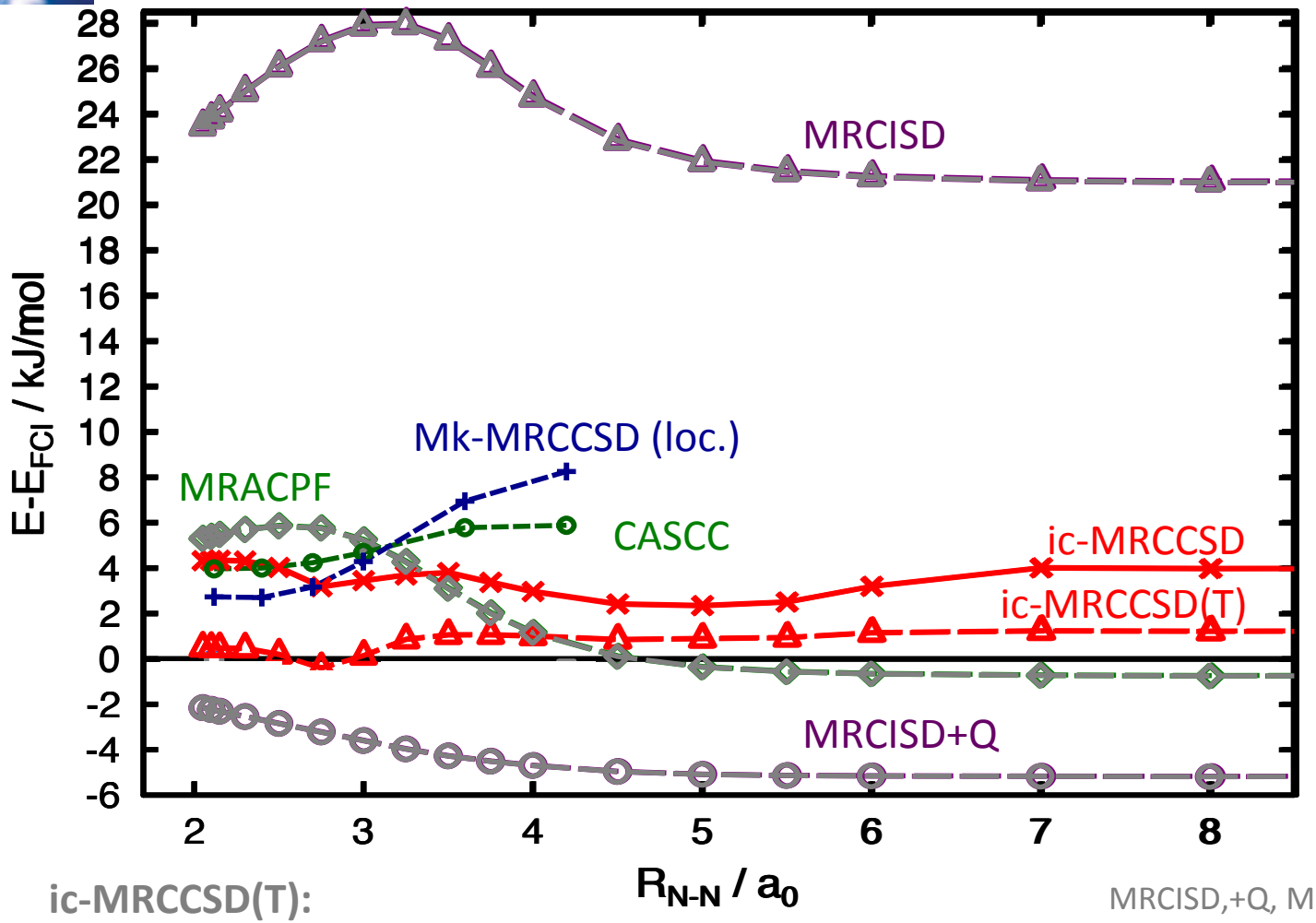
```
# Formula for overlap matrix
EXPAND_OP_PRODUCT({LABEL:'F_SMAT',NEW:True,OP_RES:'SSCAL',
  OPERATORS:['C0^+','Tv^+','Tv','C0'],
  IDX_SV:[1,2,3,4]})
FACTOR_OUT({LABEL_RES:'F_SMAT',LABEL_IN:'F_SMAT',INTERM:'F_GAM0'})
PRINT_FORMULA({LABEL:'F_SMAT'})
```

general order contraction kernel for numerical evaluation

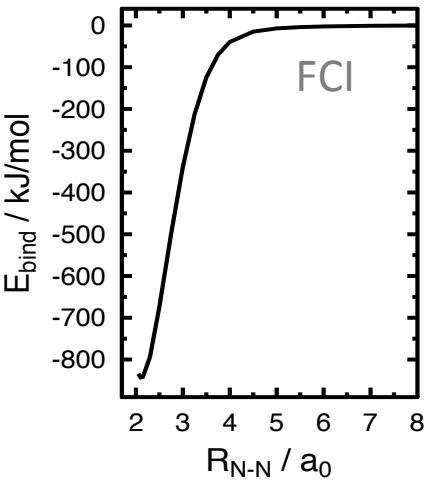
```
OPTIMIZE({LABEL_OPT:'FOPT_H_C0',LABELS_IN:'F_H_C0'})

PRINT({STRING:'Prepare diagonal ...'})
PRECONDITIONER({LIST_PRC:'D0LST',LIST_INP:'H0',MODE:'dia-H'})

PRINT({STRING:'Solving equations ...'})

SOLVE_EVP({LIST_OPT:'C0LST',LIST_PRC:'D0LST',OP_MVP:'H_C0',OP_SVP:'C0',
   FORM:'FOPT_H_C0',MODE:'DIA',N_ROOTS:1})
```

A few examples

N_2 dissociation



cc-pVDZ basis set



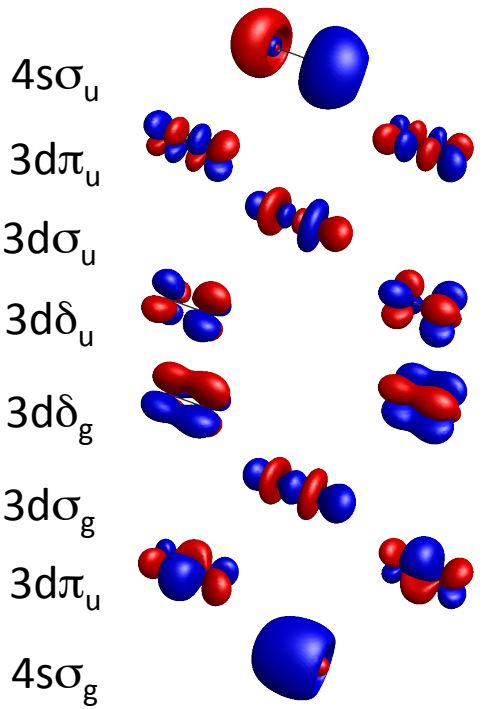
all MR methods use CAS(6,6)

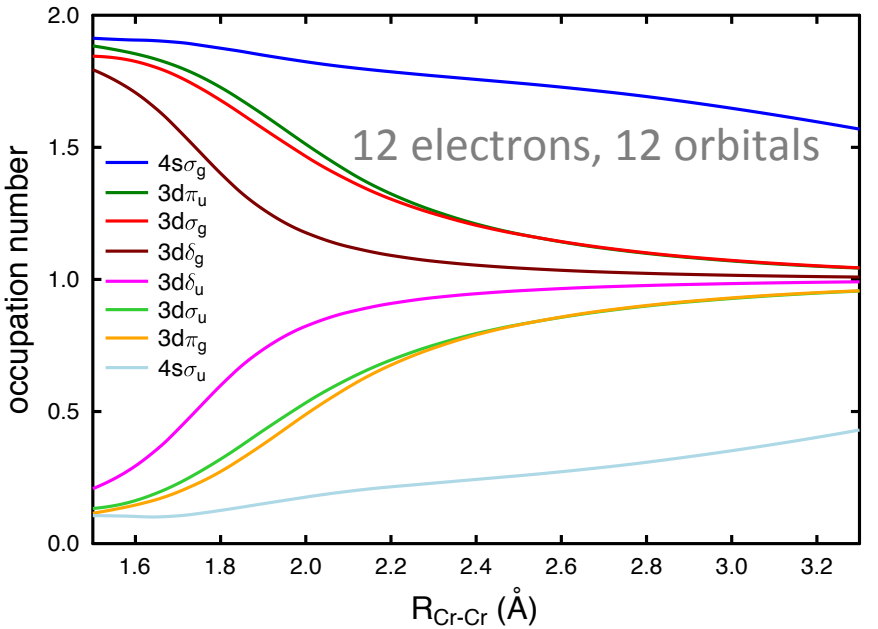
ic-MRCCSD(T):
Hanauer, Köhn, JCP 136, 204107 (2012)

MRCISD,+Q, MRACPF: Werner, private comm.
MRAQCC: Yanai, Chan, JCP 127, 104107
CASCC: Lyakh et al., Mol. Phys. 105, 1335 (2007)
Mk-MRCCSD: Das, Kallay, Mukherjee, CP 392, 83 (2012)

Chromium dimer

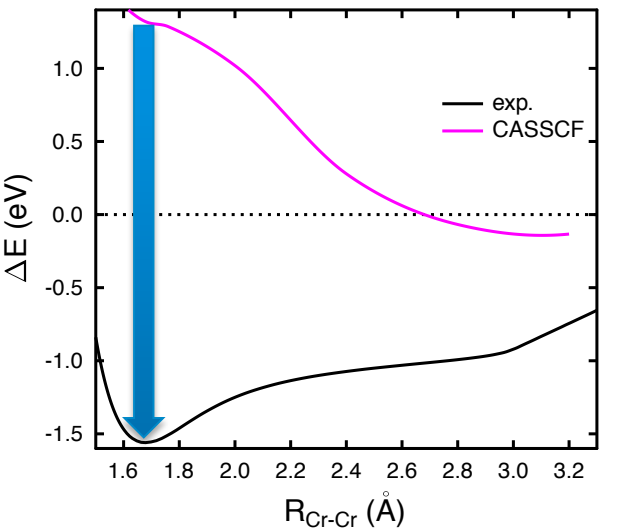
Strong multireference character



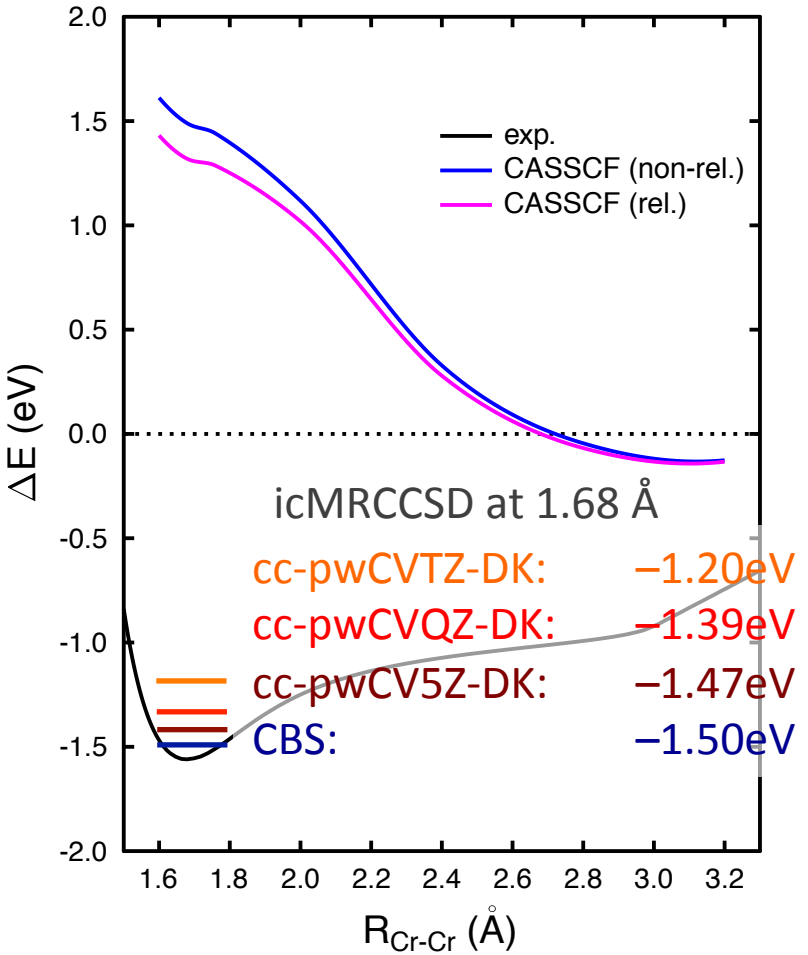


Huge contribution from dynamic correlation

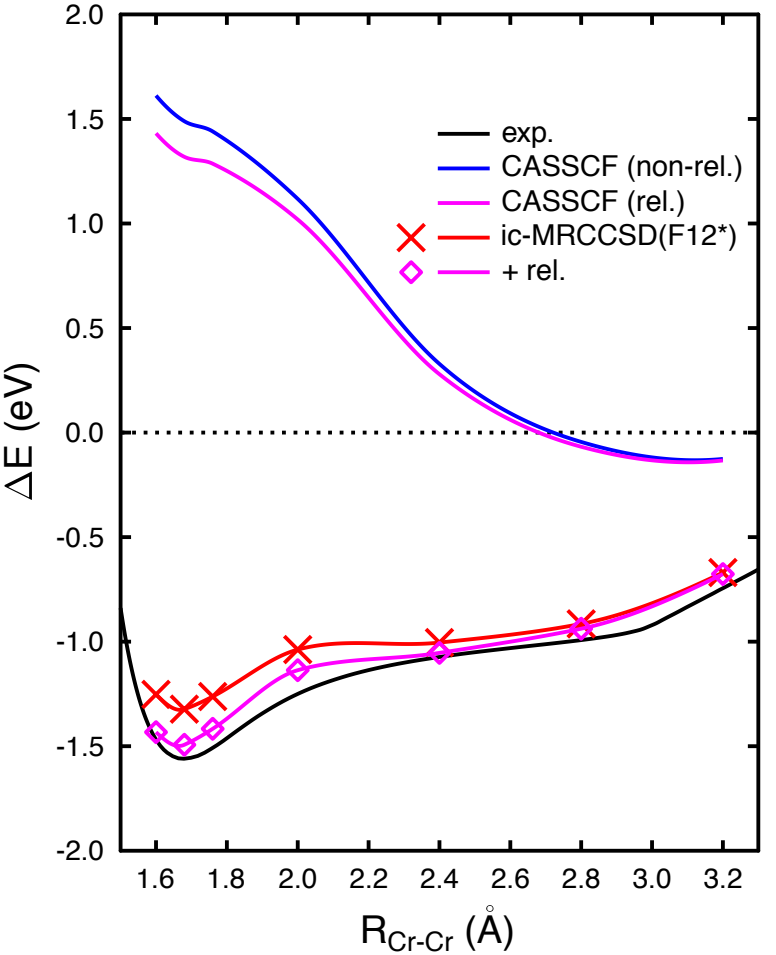
3s3p-correlation important!!



Some preliminary results



cc-pwCVTZ with geminal terms



2nd-order DKH transf. for scalar rel. effects

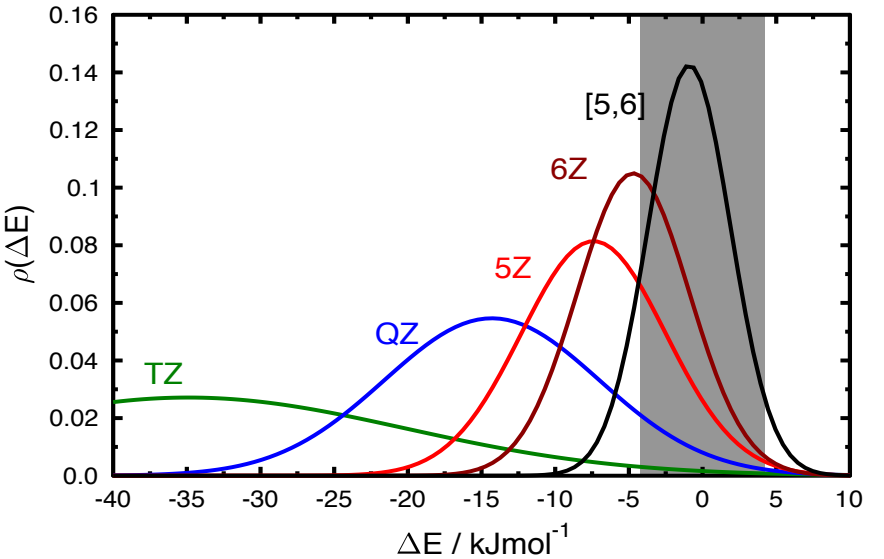
F12 methods

Molecular CC calculations need large basis sets!

Example:
CCSD(T) atomization energies
(20 small molecules)

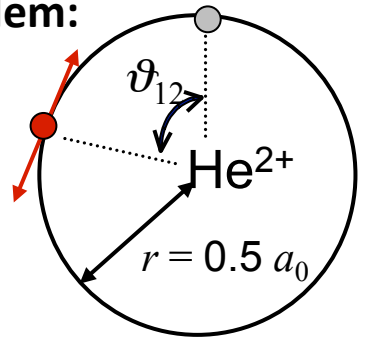
Error in electronic contribution
compared to reference values
(derived from experiment)

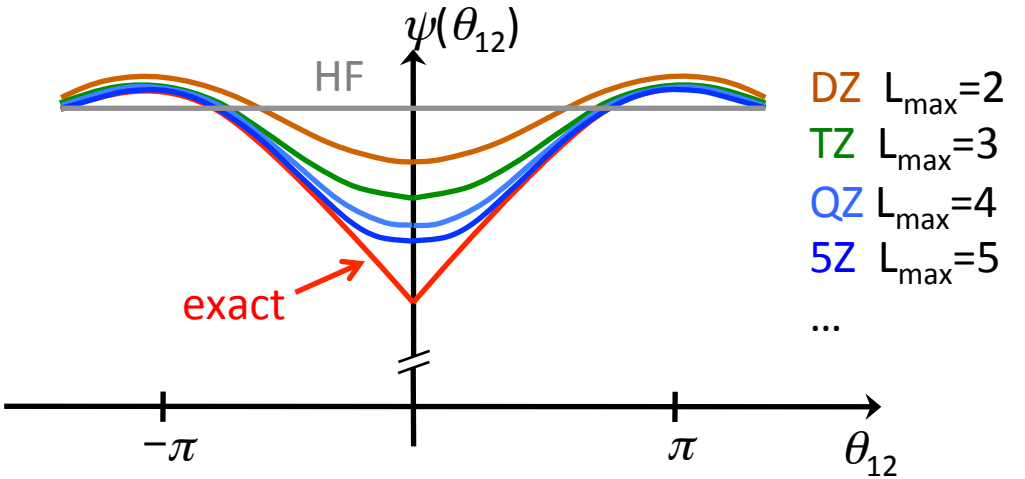
Values from: Helgaker, Jørgensen, Olsen,
"Electronic structure theory", Wiley (2000)



Root of the problem:
Behavior of ψ
for $\mathbf{r}_1 \longrightarrow \mathbf{r}_2$ due to

$$\hat{V}_{ee} \propto \frac{1}{r_{12}}$$





F12 theory: concepts

Ansatz for pair-function:

$$|u_{ij}\rangle = \sum_{a>b} t_{ab}^{ij}|ab\rangle + \sum_{k>l} c_{kl}^{ij}\hat{Q}_{12}f(r_{12})|kl\rangle$$

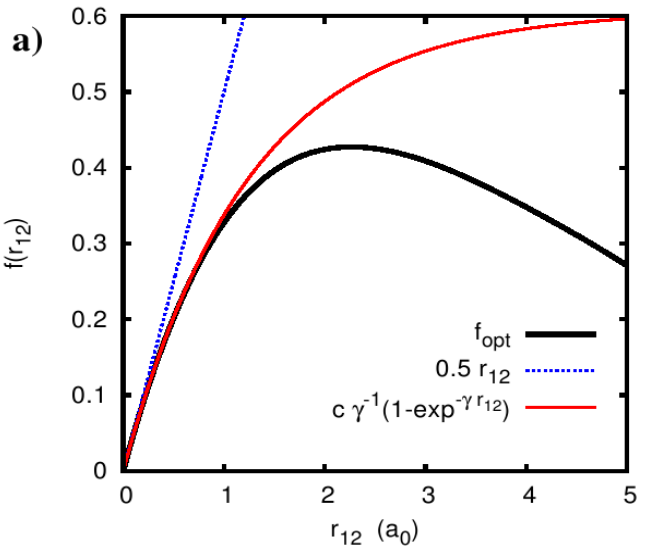
correlation factor

Correlation factor:

F12-theory (Ten-no):

$$f(r_{12}) = \frac{1}{\gamma}(1 - e^{-\gamma r_{12}})$$

$\gamma \approx 1\ a_0^{-1}$ is a fixed basis set parameter



From: Tew, Hättig, Klopper, Bachorz. In: "Recent Progress in Coupled Cluster Methods ...", Csarsky, Pittner, Paldus (Eds.), Springer

Combination with CC theory (Kutzelnigg, Klopper, Noga)

$$T_{2'} = \frac{1}{8}c_{kl}^{ij}\langle\alpha\beta|\hat{Q}_{12}f(r_{12})|kl\rangle a_{ij}^{\alpha\beta}$$

Efficient combination with CC theory possible:

CCSD-F12a/b (Werner, Adler, Knizia),
CCSD(F12*) (Hättig, Köhn, Tew)

Kutzelnigg (1985), Kutzelnigg, Klopper (1987, 1991), Ten-no (2004), May, Manby (2004), Tew, Klopper (2005)

Analogous development: icMRCCSD(F12*)

Liu, Hanauer, Köhn, Chem. Phys. Lett. 565, 122 (2013)

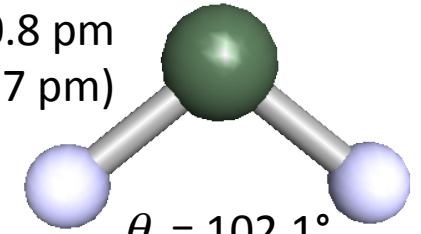
$$T_{2'} = \frac{1}{8}c_{KL}^{IJ}\langle\alpha\beta|\hat{Q}_{12}f(r_{12})|KL\rangle a_{IJ}^{\alpha\beta}$$

icMRCCSD(F12*) theory

CH_2

Singlet

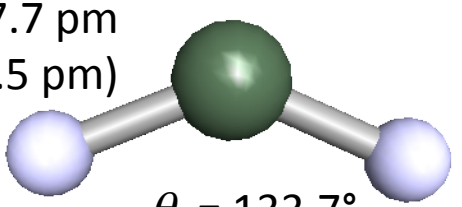
r_e = 110.8 pm
(Exp: 110.7 pm)



θ_e = 102.1°
(Exp: 102.4°)

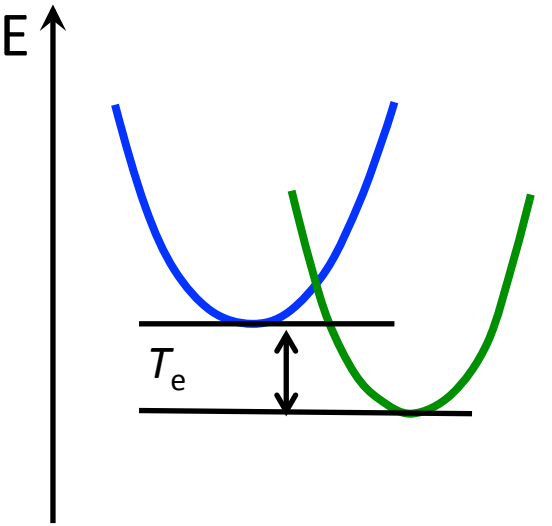
Triplet

r_e = 107.7 pm
(Exp: 107.5 pm)



θ_e = 133.7°
(Exp: 133.8°)

CAS(2,2)
ic-MRCCSD(F12*)+(T)/cc-pVQZ-F12
(frozen core, numerical gradients)



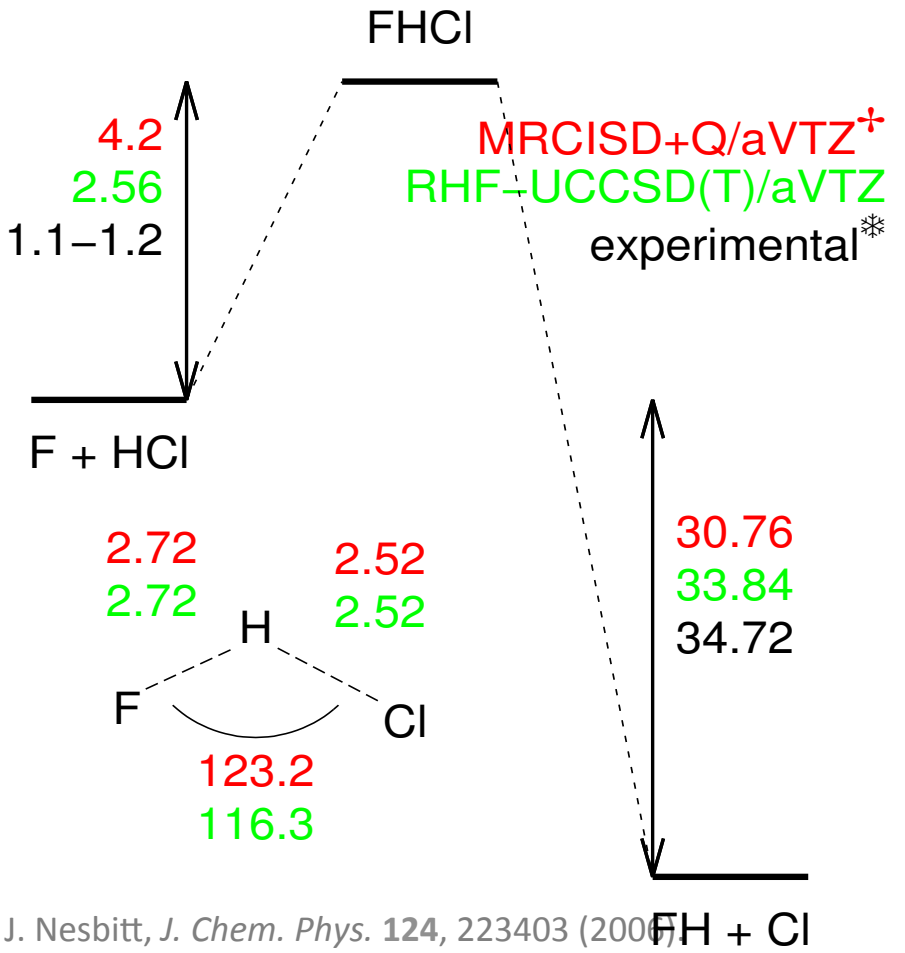
T_e = 37.2 kJ/mol
(Exp: 37.7 kJ/mol)

Exp. values: Petek et al, JCP 91, 6566 (1989)
Bunker, Sears, JCP 83, 4866 (1985)
Bunker, Jensen, JCP 79, 1224 (1983)

The F + HCl ⟶ Cl + HF reaction

Traditional theoretical calculations overestimate experimental barrier height! ✢★

Experimental ro-vibrational distribution not reproduced by quantum dynamics.★

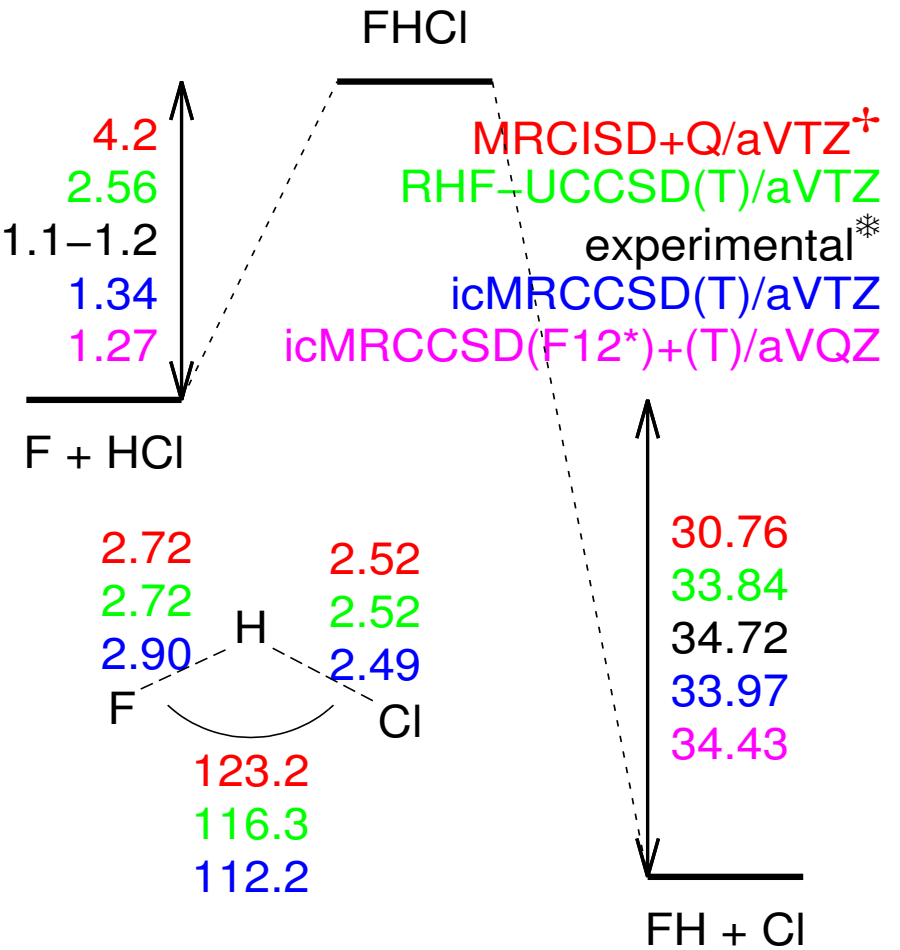


✢M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje and D. J. Nesbitt, *J. Chem. Phys.* **124**, 223403 (2006).
★A. Li, H. Guo, Z. Sun, J. Klos and M. H. Alexander, *Phys. Chem. Chem. Phys.* **15**, 15347 (2013).
❄N. Jonathan *et al.*, *Chem. Phys. Lett.* **7**, 257 (1970); A. M. G. *Ding et al.*, Faraday Discuss. Chem. Soc. **55**, 252 (1973).

The F + HCl ⟶ Cl + HF reaction

Barrier height and exothermicity obtained with icMRCCSD(T) theory are very close to the experimental values!

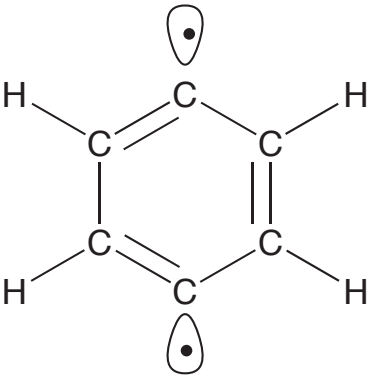
CAS(3,3) sufficient!
[MRCI uses CAS(15,9)]



✢M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje and D. J. Nesbitt, *J. Chem. Phys.* **124**, 223403 (2006).
❄N. Jonathan *et al.*, *Chem. Phys. Lett.* **7**, 257 (1970); A. M. G. *Ding et al.*, Faraday Discuss. Chem. Soc. **55**, 252 (1973).

Active-space size

Singlet-Triplet splitting of p-benzyne



ΔE_{S-T}/kcal mol^{-1}	icMRCCSD	icMRCCSD(T)
CAS(2,2)	3.7	4.8
CAS(8,8)	4.7	4.9

cc-pVDZ basis
Structures: RHF/UHF-CCSD(T)/cc-pVDZ
from: Evangelista et al., JCP 127, 024102 (2007)

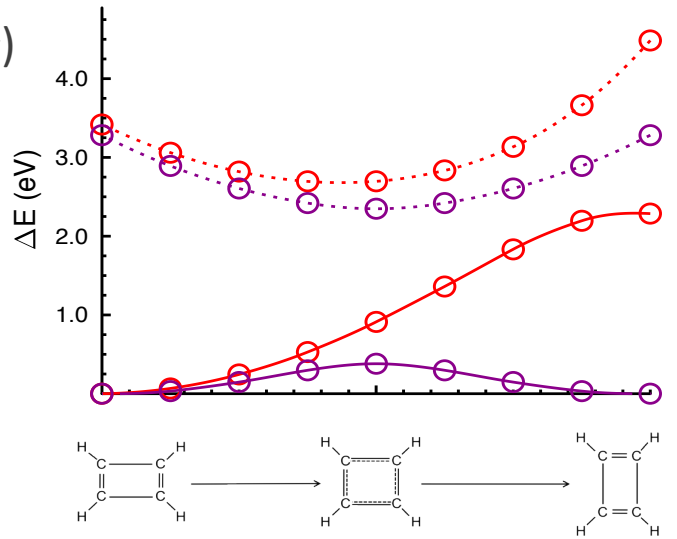
keep the active space as small as physically necessary

Hanauer, Köhn, JCP 136, 204107 (2012)
see also: Evangelista, Hanauer, Köhn, Gauss, JCP 136, 204108 (2012)

Additional aspects (now and future)

Full spin adaptation (eigenfunctions of S^2)

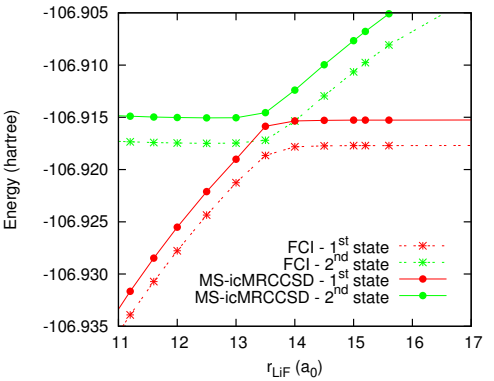
Excited states via linear-response and/or EOM frameworks



single-reference CCSD

ic-MRCCSD

Multi-state extension



Response properties

Lower-order approximations (perturbation theory, CEPA-like theories)

Success and criticism

Full analogy to single-reference CC

$$|\Psi_{\mathrm{ic}}\rangle = e^{\hat{T}} \sum_{\mu} |\Phi_{\mu}\rangle c_{\mu}$$

Proper formal scaling, compact excitation manifold

Fully extensive energy, orbital invariance

Very accurate results

Problems, criticism:

Threshold for near-linear dependencies

Commutator approximation

Some consistency problems remain (for dissociating singlets)

Efficiency