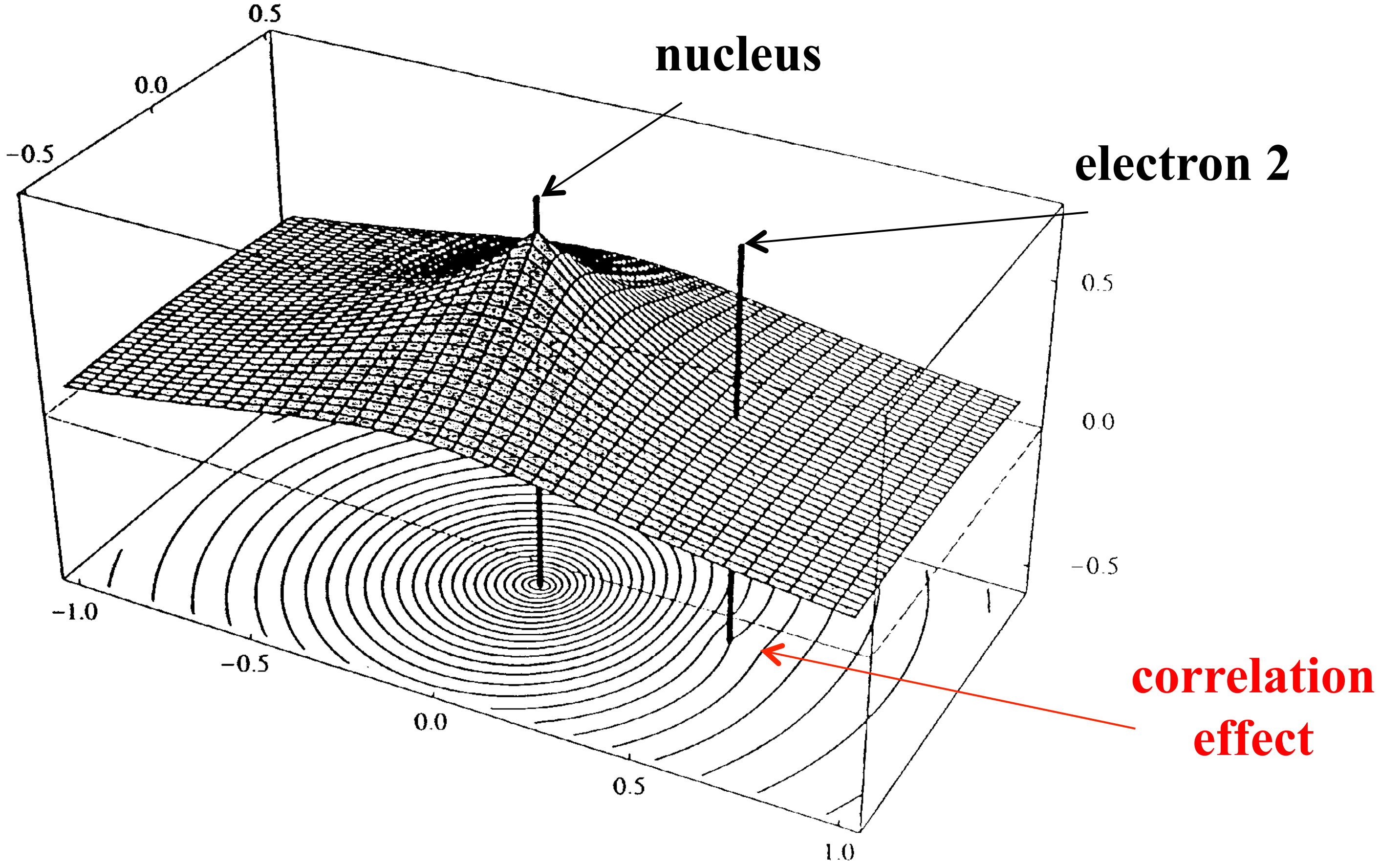
Coupled-Cluster Theory

Jürgen Gauss

JOHANNES GUTENBERG
UNIVERSITÄT MAINZ

Electron Correlation, Size Consistency, and Exponential Ansatz

Electron Correlation: the Helium Atom



nucleus

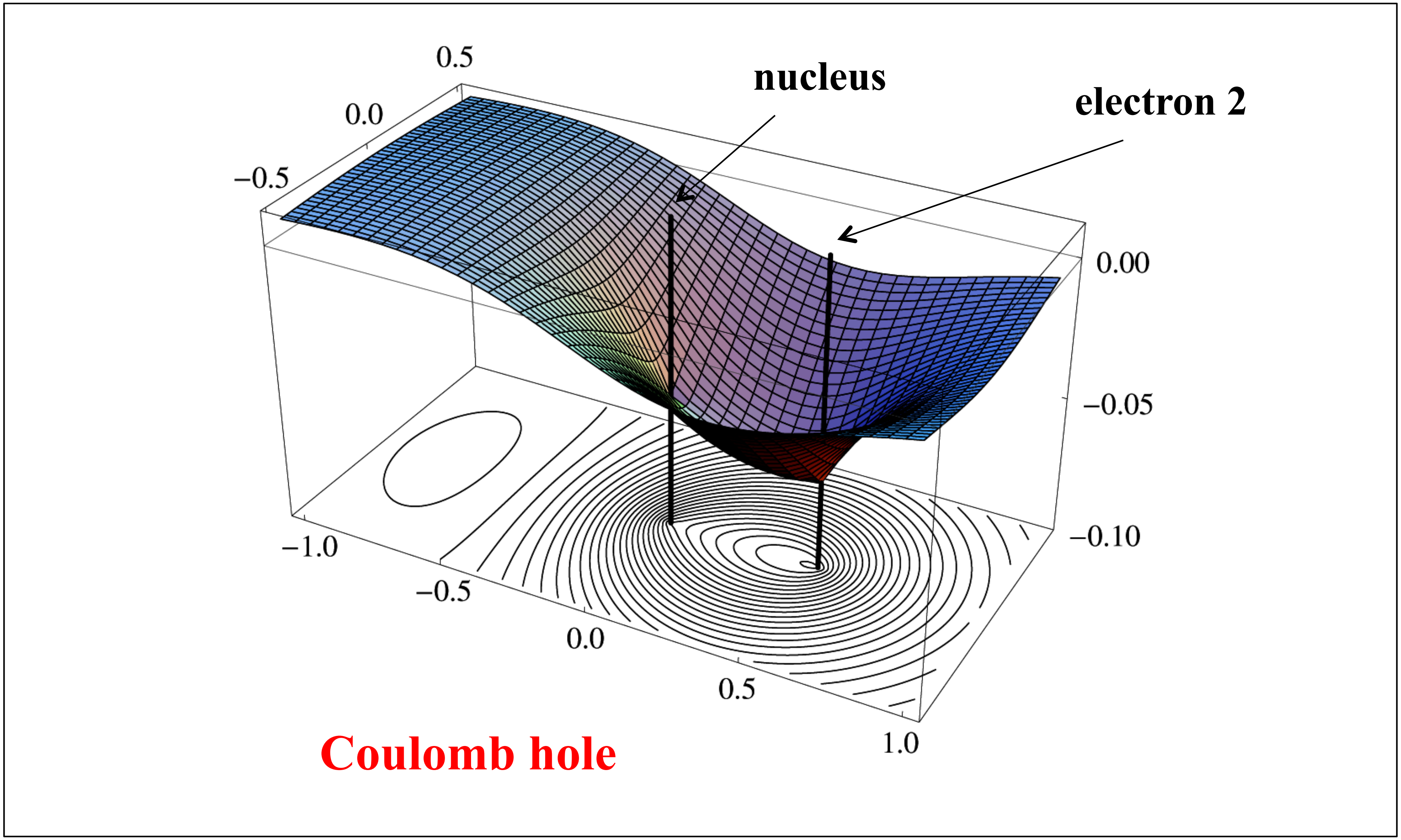
electron 2

correlation effect

wave function $\Psi_{exact}(r_1,r_2)$ as function of r_1

figure from T. Helgaker, P. Jørgensen, J. Olsen „Molecular Electronic-Structure Theory“

Electron Correlation: the Helium Atom



Coulomb hole

figure from T. Helgaker, P. Jørgensen, J. Olsen „Molecular Electronic-Structure Theory“

Magnitude of Correlation Energies

	H_2O	HCN
E_{HF}	-76.068	-92.916
ΔE_{corr}	-0.372	-0.518
ΔE_{rel}	-0.052	-0.044

correlation energies typically < 1% of the total energies

Chemical Relevance of Electron Correlation

0.001 Hartree $\widehat{=}$ 2.6255 kJ/mol

correlation energies strongly dependent on valence electrons

correlation effects always important when bonds are broken

Chemical Relevance of Electron Correlation

example: $CO \rightarrow C(^3P) + O(^3P)$

dissocation energy (D_e) of CO

	C	O	CO	D_e in a.u.
E(HF)	-37.693774	-74.819232	-112.790997	.277991
E(corr)	-.151537	-.248978	-.536591	.136076
E(total)	-37.845307	-75.068210	-113.327588	.414071

Chemical Relevance of Electron Correlation

example: $CO \rightarrow C(^3P) + O(^3P)$

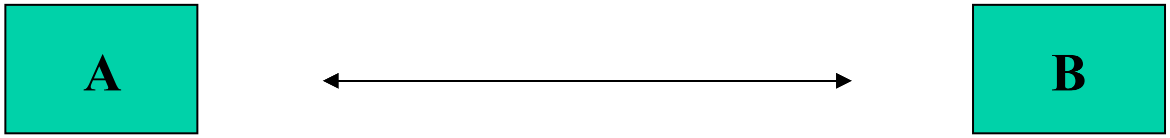
dissocation energy (D_e) of CO

	C	O	CO	D_e in kJ/mol
E(HF)	-37.693774	-74.819232	-112.790997	729.9
E(corr)	-.151537	-.248978	-.536591	357.3
E(total)	-37.845307	-75.068210	-113.327588	1087.2

electron-correlation effects are significant

Size Consistency

non-interacting systems A and B:

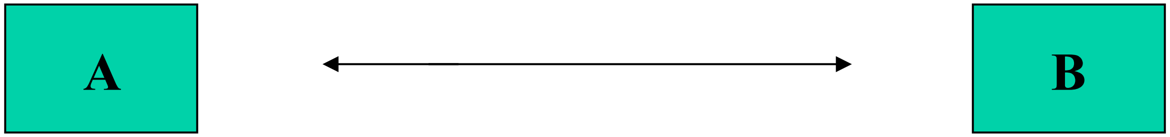


$r_{AB} \rightarrow \infty$

$$\boxed{E_{AB} = E_A + E_B}$$

- additivity of energy
- multiplicability of wavefunction

Size Consistency



$r_{AB} \rightarrow \infty$

A method is termed size consistent if the sum of energies computed for two non-interacting subsystems A and B is equal to the energy obtained for the supersystem consisting of both A and B

a) individual quantum-chemical calculations for A and B → $E_A + E_B$

b) one quantum-chemical calculations for A+B → E_{AB}

size consistency: $E_{AB} = E_A + E_B$

Multiplicative Property of the Wavefunction

non-interacting systems A and B

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

=> separation ansatz

$$E_{AB} = E_A + E_B$$

additive

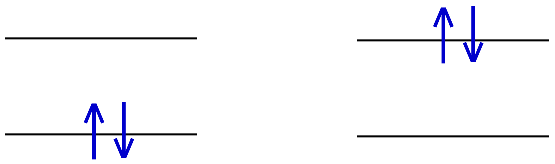
$$\Psi_{AB} = \hat{\mathcal{A}}\, \Psi_A\, \Psi_B$$

multiplicative

antisymmetrizer

Multiplicative Property of the Wavefunction

H_2 molecule, minimal basis



Φ_{HF} Φ_D

HF determinant **double excitation**

$$\Psi_{CID} = \Phi_{HF} + c\,\Phi_D$$

(not normalized)

$$= (1 + \hat{\tau}_D)\,\Phi_{HF}$$

operator, generates a by *c* weighted double excitations

H_2: CID = FCI = exact solution

Multiplicative Property of the Wavefunction

two H_2 molecule, minimal basis

H_2(A) + H_2(B)

CID wavefunction

$$\Psi_{CID} = (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B})\, \Phi_{HF}$$

but

$$\begin{aligned}
\hat{\mathcal{A}}\, \Psi_{CID,A}\, \Psi_{CID,B} &= \hat{\mathcal{A}} \{(1 + \hat{\tau}_{D,A})\, \Phi_{HF,A}\} \{(1 + \hat{\tau}_{D,B})\, \Phi_{HF,B}\} \\
&= \hat{\mathcal{A}}\, (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, \Phi_{HF,A}\, \Phi_{HF,B} \\
&= (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, \Phi_{HF} \\
&= (1 + \hat{\tau}_{D,A} + \hat{\tau}_{D,B} + \hat{\tau}_{D,A}\, \hat{\tau}_{D,B})\, \Phi_{HF}
\end{aligned}$$

quadruple excitation, missing in CID => problem

Multiplicative Property of the Wavefunction

problem of CI:

excitations are additive

$$\sum_{i=A,B,\ldots} \hat{\tau}_{D,i}$$

contradiction !?!

required is a multiplicative property

$$\prod_{i=A,B,\ldots} \cdots$$

Multiplicative Property of the Wavefunction

one, two, three, ... H_2 molecules

$$\begin{aligned}
\Psi_1 &= (1 + \hat{\tau}_{D,A})\, \Phi_{HF} \\
\Psi_2 &= (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, \Phi_{HF} \\
\Psi_3 &= (1 + \hat{\tau}_{D,A})\, (1 + \hat{\tau}_{D,B})\, (1 + \hat{\tau}_{D,C})\, \Phi_{HF} \\
&\dots \\
\Psi &= \prod_{i=A,B,\dots} (1 + \hat{\tau}_{D,i})\, \Phi_{HF}
\end{aligned}$$

Exponential Form for the Wavefunction

proper form of wavefunction

$$\Psi \;=\; \prod_{i=A,B,\ldots} (1 \,+\, \hat{\tau}_{D,i})\; \Phi_{HF}$$

rewrite in exponential form

$$\prod_{i=A,B,..} (1 \,+\, \hat{\tau}_{D,i})\; \Phi_{HF} \;\equiv\; \exp(\sum_{i=A,B,..} \hat{\tau}_{D,i})\; \Phi_{HF}$$

multiplicative property via additivity in exponent

Exponential Form for the Wavefunction

exponential ansatz

$$\Psi \quad = \quad \exp(\hat{T})\ \Phi_0$$

excitations represented via an operator

reference determinant

proper multiplicative behaviour => size consistency

Connected and Disconnected Excitations

$$\Psi = \prod_{i=A,B,\ldots} (1 + \hat{\tau}_{D,i})\, \Phi_{HF}$$

$$\Psi = \Phi_{HF} + \hat{\tau}_{D,A}\Phi_{HF} + \ldots + \hat{\tau}_{D,A}\hat{\tau}_{D,B}\Phi_{HF} + \ldots$$

connected excitations

disconnected excitations

(products of connected excitations)

CI does not differ between connected and disconnected excitations

Standard Coupled-Cluster Theory

Coupled-Cluster Theory

exponential ansatz for wavefunction

$$|\Psi_{CC}\rangle = \exp(T)|0\rangle$$

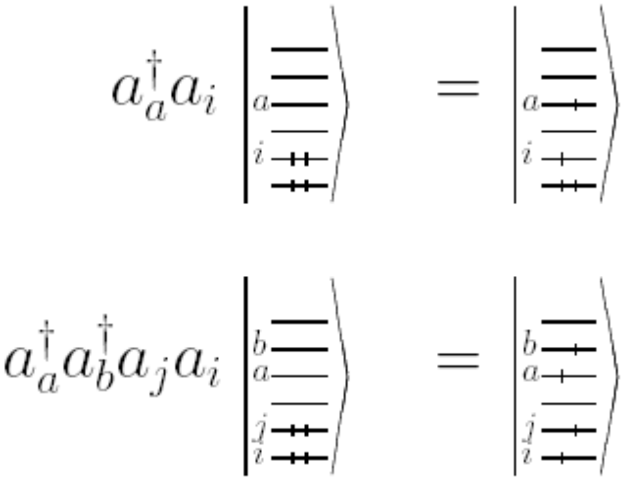
reference determinant

with excitation operator

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

$$T_1 = \sum_i \sum_a t_i^a a_a^\dagger a_i$$

$$T_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$



second quantization

unknown parameters:

amplitudes $t_i^a, t_{ij}^{ab}, \ldots$

equivalent to FCI, different parameterization of wavefunction

CC Energy and Equations

- **insertion into Schrödinger-Equation**

$$H\exp(T)|0\rangle \;=\; E\exp(T)|0\rangle$$

- **multiplication from left with exp(-T)**

$$\exp(-T)H\exp(T)|0\rangle \;=\; E|0\rangle$$

- **projection onto reference determinant**

→ CC energy

$$E \;=\langle 0|\exp(-T)H\exp(T)|0\rangle$$

- **projection onto excited determinants**

→ CC equations

$$0 \;=\langle \Phi_p|\exp(-T)H\exp(T)|0\rangle$$

non-linear equations for amplitudes

Algebraic Expressions for CC Equations

$$E \;= \langle 0|\exp(-T)H\exp(T)|0\rangle \qquad\qquad 0 \;= \langle\Phi_p|\exp(-T)H\exp(T)|0\rangle$$

Baker-Campbell-Hausdorff expansion

$$\exp(-T)\;H\;\exp(T) \;= H \;+\; [H,T] \;+\; \frac{1}{2!}\,[[H,T]\,,T] \;+\; \ldots$$

Commutator expressions:

$$E = \langle 0|H + [H,T] + \frac{1}{2}[[H,T],T]|0\rangle$$

$$0 = \langle\Phi_p|H + [H,T] + \frac{1}{2}[[H,T],T] + \ldots|0\rangle$$

evaluation via Slater-Condon rules, Wick‘s theorem,
diagrammatic rules, computer algebra, ...

Approximate CC Methods

truncation of the cluster operator T:

cluster operator	approximation	cost
$T=T_1+T_2$	CCSD	N^6
$T=T_1+T_2+T_3$	CCSDT	N^8
$T=T_1+T_2+T_3+T_4$	CCSDTQ	N^{10}
$T=T_1+T_2+T_3+T_4+T_5$	CCSDTQP	N^{12}
…	…	…
$T=T_1+T_2+\dots+T_N$	FCI	

CCD Approximation

truncated CC wavefunctions

$$T = T_2$$

truncation in the cluster operator

CCD = CC doubles

$$|\Psi_{CCD}\rangle = |0\rangle + T_2 |0\rangle + \frac{1}{2!}T_2^2 |0\rangle + \frac{1}{3!}T_2^3 |0\rangle + \ldots$$

connected
double excitations

disconnected
quadruple, sextuple, ... excitations

CCD Approximation

cluster operator

$$T = T_2$$

normal-ordered Hamiltonian

$$H_N = \underbrace{\sum_{p,q} f_{pq}\{a_p^\dagger a_q\}}_{f_N} + \underbrace{\frac{1}{4}\sum_{p,q,r,s} \langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}}_{W_N}$$

$$f_N \quad + \quad W_N$$

1el terms **2el terms**

CC energy:

$$\Delta E = \langle 0|W_N T_2|0\rangle$$

CC equations:

$$0 = \langle \mathcal{D}|W_N + [f_N, T_2] + [W_N, T_2] + \frac{1}{2}[[W_N, T_2], T_2]|0\rangle$$

Algebraic CCD Equations

CC energy:

$$\Delta E = \frac{1}{4}\sum_{ij}\sum_{ab}\langle ij||ab\rangle t_{ij}^{ab}$$

CC equations:

$$\begin{aligned}
0 \quad = \quad & \langle ab||ij\rangle + P_{-}(ab)\sum_{e} f_{ae}t_{ij}^{eb} - P_{-}(ij)\sum_{m} f_{mi}t_{mj}^{ab} \\
& +\frac{1}{2}\sum_{mn}\langle mn||ij\rangle t_{mn}^{ab} + \frac{1}{2}\sum_{ef}\langle ab||ef\rangle t_{ij}^{ef} \\
& +P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e}\langle mb||ej\rangle t_{im}^{ae} \\
& -\frac{1}{2}P_{-}(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{mn}^{af}t_{ij}^{eb} - \frac{1}{2}P_{-}(ij)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{in}^{ef}t_{mj}^{ab} \\
& +\frac{1}{4}\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{mn}^{ab}t_{ij}^{ef} + \frac{1}{2}P_{-}(ij)P_{-}(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{im}^{ae}t_{jn}^{bf}
\end{aligned}$$

Accuracy of CC versus CI Methods

deviation from FCI (in mH) for CO

	CI	CC
SD	30.804	12.120
SDT	21.718	1.009
SDTQ	1.775	0.061
SDTQP	0.559	0.008
SDTQPH	0.035	0.002

calculations with cc-pVDZ basis, frozen core

E(FCI) = -113.055853 H, ΔE_{korr} = 306.571 mH

Approximate Treatment of Higher Excitations

Need for Higher Excitations

High-Accuracy Calculations:

1 kJ/mol or better in thermochemical applications

0.1 pm accuracy in computed bond distances

...

require considerations of excitations beyond singles and doubles

=> triples, quadruples, ...

Additional Approximations for Triples

additional approximations in the amplitude equations

- **no storage of amplitudes for triple excitations**
- **reduced scaling in computational cost**

→ CCSDT-1, CCSDT-2, CCSDT-3, CC3, ...

Iterative Approximations to CCSDT

triples equations

$$\begin{aligned}
0 \quad = \quad \langle \Phi_T | \quad & ({\color{blue}\underline{\color{black}W_N T_2}})_c + ({\color{blue}\underline{\color{black}f_N T_3}})_c + (W_N T_3)_c \\
& + ({\color{gray}\underline{\color{black}\underline{W_N T_1 T_2}}})_c + (f_N T_3 T_1)_c + \frac{1}{2!}({\color{gray}\underline{{\color{green}\underline{\color{black}f_N T_2^2}}}})_c \\
& + \frac{1}{2!}({\color{green}\underline{\color{black}W_N T_2^2}})_c + (W_N T_3 T_1)_c + \frac{1}{2!}({\color{gray}\underline{\color{black}\underline{W_N T_2 T_1^2}}})_c \\
& + (W_N T_3 T_2)_c + \frac{1}{2!}(\underline{W_N T_2^2 T_1})_c + \frac{1}{2!}(W_N T_3 T_1^2)_c \\
& + \frac{1}{3!}({\color{gray}\underline{\color{black}\underline{W_N T_2 T_1^3}}})_c \quad |0\rangle
\end{aligned}$$

CCSDT-1: ${\color{blue}\rule{2em}{0.3em}}$

CCSDT-3: ${\color{blue}\rule{2em}{0.3em}}$ + ${\color{green}\rule{2em}{0.3em}}$ + $\rule{2em}{0.3em}$

CCSDT-2: ${\color{blue}\rule{2em}{0.3em}}$ + ${\color{green}\rule{2em}{0.3em}}$

CC3: ${\color{blue}\rule{2em}{0.3em}}$ + ${\color{gray}\rule{2em}{0.3em}}$

Non-Iterative Approximations to CCSDT

two-step procedure:

- **perform CCSD calculation**

$$T = T_1 + T_2$$

- **add perturbative corrections due to T_3**

$$\mathrm{E} = \mathrm{E(CCSD)} + \Delta\mathrm{E(T)}$$

use of converged T_1 and T_2 amplitudes

→ CCSD+T(CCSD), CCSD(T), ...

The CCSD(T) Approximation

perturbative corrections on top of CCSD

- **fourth-order contribution**

$$\Delta E_T(4) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{|w_{ijk}^{abc}|^2}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c}$$

$$w_{ijk}^{abc} = P(ij/k)P(ab/c)\{\sum_e \langle bc||ek\rangle\ t_{ij}^{ae} - \sum_m \langle mc||jk\rangle\ t_{im}^{ab}\}$$

- **fifth-order contribution**

computed with CCSD amplitudes

$$\Delta E_T(5) = \frac{1}{36} \sum_{i,j,k} \sum_{a,b,c} \frac{w_{ijk}^{abc} \tilde{w}_{ijk}^{abc}}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c}$$

$$\tilde{w}_{ijk}^{abc} = P(ij/k)P(ab/c)\ \langle bc||jk\rangle\ t_i^a$$

permutation operator: $P(pq/r)Z(pqr) = Z(pqr) + Z(qrp) + Z(rpq)$

The CCSD(T) Approximation

computational cost

$$w_{ijk}^{abc} \;=\; P(ij/k)P(ab/c)\{\sum_e \langle bc||ek\rangle\; t_{ij}^{ae} \;-\; \sum_m \langle mc||jk\rangle\; t_{im}^{ab}\}$$

one summaton index (e or m)

six target index (i,j,k,a,b,c) **=>** **cost scale with $n_{occ}^{3}N_{virt}^{4}$**

CCSD(T): cost N^6 per iteration, N^7 for non-iterative step

no need to store T_3 amplitudes

„gold standard“ of quantum chemistry

Accuracy of Approximate Treatment of Triples

deviation from FCI and CCSDT (in mH) for CO

	Δ(FCI)	Δ(CCSDT)
CCSD	12.12	11.11
CCSDT-1	0.13	-0.88
CCSDT-2	1.52	0.51
CCSDT-3	1.47	0.46
CC3	0.12	-0.89
CCSD(T)	1.47	0.46
CCSD+T	-0.05	-1.06

calculations with cc-pVDZ basis, frozen core

High-Accuracy Quantum Chemistry: Computational Thermochemistry

Computational Thermochemistry

definition:

(quantum-chemical) calculation of thermochemical energies via energy differences

most often computed:

atomization energies

heats of formation

calculation involves:

electronic part

non-electronic part

Chemical Accuracy

accuracy required for realistic chemical predictions

1 kcal/mol	$\hat{=}$	**4.184 kJ/mol**
		$4.33 \cdot 10^{-2}$ eV
		350 cm^{-1}
		1.59 mHartree

sub-chemical accuracy: **1 kJ/mol and better**

DFT usually not accurate enough

Thermochemistry with Sub-Chemical Accuracy

HEAT = High-accuracy Extrapolated Ab initio Thermochemistry

$$\boxed{\begin{aligned} E \quad = \quad & E_{\mathrm{HF}}^{\infty} + \Delta E_{\mathrm{CCSD(T)}}^{\infty} + \Delta E_{\mathrm{CCSDT}}^{\mathrm{cc-pVTZ}} + \Delta E_{\mathrm{CCSDT(Q)}}^{\mathrm{cc-pVDZ}} \\ & + \Delta E_{\mathrm{rel}} + \Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{DBOC}} \end{aligned}}$$

A. Tajti et al., *JCP* **121**, 11599 (2004)

Y.J. Bomble et al., *JCP* **125**, 064108 (2006)

M.E. Harding et al., *JCP* **128**, 113111 (2008)

Statistical Evaluation

High-accuracy Extrapolated Ab-initio Thermochemistry

atomization energies of

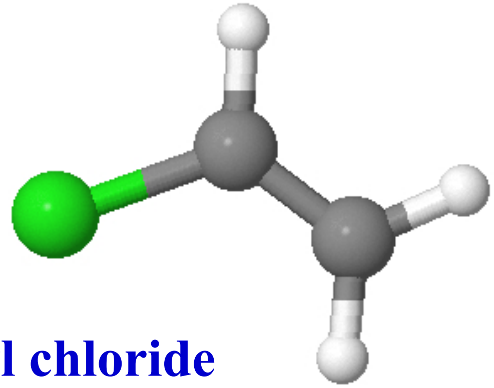
N_2, H_2, F_2, CO, O_2, C_2H_2, CCH, CH_2, CH, CH_3,
CO_2, H_2O_2, H_2O, HCO, HF, HO_2, NO, OH

mean error	max. error	RMS error
-0.24	0.87	0.42

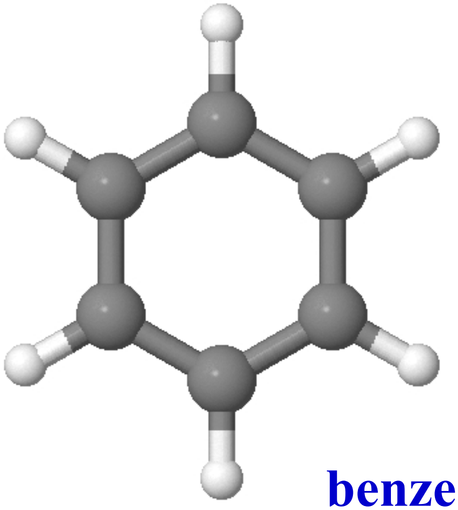
Harding et al., *J. Chem. Phys*. **128**, 114111 (2008)

Thermochemistry with Sub-Chemical Accuracy

atomization energies of



vinyl chloride



benzene

chemical accuracy ≈ 1 kcal/mol

1 kcal/mol ≈ 1.6 mH

1 kJ/mol ≈ 0.4 mH

Thermochemistry with Sub-Chemical Accuracy

	C_2H_3Cl	C_6H_6
E_{HF}^{∞}	**1669.49**	4295.3
$\Delta E_{\mathrm{CCSD(T)}}^{\infty}$	**609.73**	1439.8
$\Delta E_{\mathrm{CCSDT}}^{\mathrm{cc-pVTZ}}$	**-3.68**	-8.9
$\Delta E_{\mathrm{CCSDT(Q)}}^{\mathrm{cc-pVDZ}}$	**2.35**	6.8
ΔE_{rel}	**-2.42**	-4.0
ΔE_{SO}	**-4.23**	2.1
ΔE_{ZPE}	**-110.64**	-261.6
ΔE_{DBOC}	**0.47**	0.7
total	**2161.08**	
exp.	**2159.5±2.5**	5466.6±0.5

values in kJ/mol

M.E. Harding et al., *J. Phys. Chem. A* **111**, 13623 (2007)

Thermochemistry with Sub-Chemical Accuracy

	C_2H_3Cl	C_6H_6
E_{HF}^{∞}	1669.49	**4295.3**
$\Delta E_{\mathrm{CCSD(T)}}^{\infty}$	609.73	**1439.8**
$\Delta E_{\mathrm{CCSDT}}^{\mathrm{cc-pVTZ}}$	-3.68	**-8.9**
$\Delta E_{\mathrm{CCSDT(Q)}}^{\mathrm{cc-pVDZ}}$	2.35	**6.8**
ΔE_{rel}	-2.42	**-4.0**
ΔE_{SO}	-4.23	**2.1**
ΔE_{ZPE}	-110.64	**-261.6**
ΔE_{DBOC}	0.47	**0.7**
total		**5466.3**
exp.	2159.5±2.5	**5466.6±0.5**

values in kJ/mol

Harding et al., *JCP*, **135**, 044513 (2011)

Computational Requirements

CCSD(T)/cc-pCV5Z calculation **1200 basis functions**	**~ 41 hours** **(16 node single-core 3.4 GHz Xeon)**
CCSDT/cc-pVTZ calculation **264 basis functions**	**~ 77 hours** **(dual-core 3.0 GHz Xeon)**
CCSDT(Q)/cc-pVDZ calculation **114 basis functions**	**~ 32 hours** **(12 node AMD64)**

Bottleneck: large basis calculation at lower CC levels

Harding, Metzroth, Auer, Gauss, JCTC **4**, 64 (2008)

Analytic Derivatives in Coupled-Cluster Theory

Importance of Energy Derivatives for Molecular Properties

$\frac{\partial E}{\partial x}$	**forces on nuclei → geometries, transition states**
$\frac{\partial^2 E}{\partial x \partial y}$	**force constants → harmonic vibrational frequencies**
$\frac{\partial^3 E}{\partial x \partial y \partial z}$	**anharmonicities → fundamental frequencies, …**
$\frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j}$	**polarizabilities**
$\frac{\partial^2 E}{\partial m_i^N \partial B_j}$	**nuclear magnetic shieldings → NMR chemical shifts**
$\frac{\partial^2 E}{\partial I_i^N \partial I_j^N}$	**indirect spin-spin coupling constants**

etc.

Numerical vs Analytic Differentiation

- **numerical differentation**

e.g. $$\frac{\partial E}{\partial x} \approx \frac{E(\Delta x) - E(-\Delta x)}{2\Delta x}$$

- **analytic differentiation**

i.e., direct evaluation using analytic expressions

	numerical	analytic
implementation	easy	difficult
efficiency	low	high
precision	limited	high
imaginay perturbations	complex Ψ	yes
frequency dependence	no	yes

analytic differentiation preferable

Gradients via Straightforward Differentiation

energy

$$E = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle$$

gradient

$$\frac{\partial E}{\partial x} = \langle 0 | \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle + \langle 0 | [\exp(-T) H \exp(T), \frac{\partial T}{\partial x}] | 0 \rangle$$

⇒ integral derivatives **⇒ perturbed amplitudes**

perturbed amplitudes via

$$0 = \langle \Phi_p | \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle + \langle \Phi_p | [\exp(-T) H \exp(T), \frac{\partial T}{\partial x}] | 0 \rangle$$

to be solved for all *x*; cost similar to CC equations

efficiency?

Gradients Using Lagrange Multipliers

energy functional

Lagrange multipliers

$$\tilde{E} = \langle 0| \exp(-T) H \exp(T) |0\rangle \;+\; \sum_p \lambda_p \langle \Phi_p | \exp(-T) H \exp(T) |0\rangle$$

energy

CC equations as constraints

compact notation

$$\tilde{E} = \langle 0|(1+\Lambda) \exp(-T) H \exp(T) |0\rangle$$

Λ deexcitation operator:

$$\Lambda = \Lambda_1 + \Lambda_2 + \ldots$$

$$\Lambda_1 = \sum_i \sum_a \lambda_a^i \; a_i^\dagger a_a \qquad \Lambda_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} \lambda_{ab}^{ij} \; a_i^\dagger a_a a_j^\dagger a_b$$

Gradients Using Lagrange Multipliers

stationarity conditions

$$\frac{\partial \tilde{E}}{\partial \lambda_p} = 0 \qquad \Longrightarrow \qquad 0 \;=\; \langle \Phi_p | \exp(-T) H \exp(T) | 0 \rangle$$

CC equations

$$\frac{\partial \tilde{E}}{\partial t_p} = 0 \qquad \Longrightarrow \qquad 0 \;=\; \langle 0 | (1 + \Lambda) \; (\exp(-T) H \exp(T) - E) | \Phi_p \rangle$$

Λ equations

gradient

$$\frac{\partial \tilde{E}}{\partial x} \;=\; \langle 0 | (1 + \Lambda) \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle$$

no perturbed wavefunction parameters required

Algebraic Form of Λ Equations in the CCD Model

$$
\begin{aligned}
0 \;=\; & \langle ij||ab\rangle \;+\; P_{-}(ab)\sum_{e} \lambda^{ij}_{eb}\,\Big\{f_{ea} \;-\; \frac{1}{2}\sum_{m,n}\sum_{f} \langle mn||af\rangle\, t^{ef}_{mn}\Big\} \\
& - P_{-}(ij)\sum_{m} \lambda^{mj}_{ab}\,\Big\{f_{im} \;+\; \frac{1}{2}\sum_{n}\sum_{e,f} t^{ef}_{mn}\,\langle in||ef\rangle\Big\} \\
& + \frac{1}{2}\sum_{mn} \lambda^{mn}_{ab}\,\Big\{\langle ij||mn\rangle \;+\; \frac{1}{2}\sum_{ef} \langle ij||ef\rangle\, t^{ef}_{mn}\Big\} \\
& + \frac{1}{2}\sum_{ef} \lambda^{ij}_{ef}\,\Big\{\langle ef||ab\rangle \;+\; \frac{1}{2}\sum_{mn} \langle mn||ab\rangle\, t^{ef}_{mn}\Big\} \\
& + P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e} \lambda^{im}_{ae}\,\Big\{\langle ej||mb\rangle \;+\; \sum_{n}\sum_{f} \langle nj||fb\rangle\, t^{ef}_{mn}\Big\} \\
& - \frac{1}{2}P_{-}(ab)\sum_{mn}\sum_{ef} \langle ij||eb\rangle\, t^{ef}_{mn}\, \lambda^{mn}_{af} \;-\; \frac{1}{2}P_{-}(ij)\sum_{mn}\sum_{ef} \langle mj||ab\rangle\, t^{ef}_{mn}\, \lambda^{in}_{ef}
\end{aligned}
$$

(perturbation independent) linear equations for λ amplitudes

Density-Matrix Formulation of CC Gradients

introduction of density matrices

$$\frac{\partial E}{\partial x} = \langle 0| \; (1+\Lambda) \; \exp(-T) \; \frac{\partial H}{\partial x} \; \exp(T) \; |0\rangle$$

$$= \sum_{p,q} D_{pq} \frac{\partial f_{pq}}{\partial x} + \sum_{p,q,r,s} \Gamma_{pqrs} \frac{\partial \langle pq||rs\rangle}{\partial x}$$

reduced one-particle density matrix

$$\langle 0|(1+\Lambda)\exp(-T)\{a_p^\dagger a_q\}\exp(T)|0\rangle$$

reduced two-particle density matrix

$$\langle 0|(1+\Lambda)\exp(-T)\{a_p^\dagger a_q^\dagger a_s a_r\}\exp(T)|0\rangle$$

gradients in terms of integral derivatives and density matrices

Algebraic Expressions for CCD Density Matrices

- **one-particle density matrix**

$$D_{ij} = -\frac{1}{2}\sum_{m}\sum_{e,f}\lambda^{jm}_{ef}t^{ef}_{im} \qquad D_{ab} = \frac{1}{2}\sum_{m}\sum_{e,f}\lambda^{mn}_{ae}t^{be}_{mn}$$

- **two-particle density matrix**

$$\Gamma_{ijkl} = \frac{1}{8}\sum_{e,f}\lambda^{kl}_{ef}t^{ef}_{ij} \qquad \Gamma_{abcd} = \frac{1}{8}\sum_{m,n}\lambda^{mn}_{ab}t^{cd}_{mn}$$

$$\Gamma_{ajib} = \frac{1}{4}\sum_{m}\sum_{e}\lambda^{im}_{ae}t^{be}_{jm} \qquad \Gamma_{abij} = \frac{1}{4}\lambda^{ij}_{ab}$$

$$\begin{aligned}\Gamma_{ijab} = {} & \frac{1}{4}t^{ab}_{ij} + \frac{1}{16}\sum_{mn,}\sum_{e,f}\lambda^{mn}_{ef}t^{ef}_{ij}t^{ab}_{mn} + \frac{1}{2}\sum_{m,n,}\sum_{e,f}\lambda^{mn}_{ef}t^{ae}_{im}t^{bf}_{jm} \\ & -\frac{1}{4}\sum_{m,n}\sum_{e,f}\lambda^{mn}_{ef}t^{eb}_{mn}t^{af}_{ij} - \frac{1}{4}\sum_{m,n}\sum_{e,f}\lambda^{mn}_{ef}t^{ef}_{mj}t^{ab}_{in}\end{aligned}$$

CC Gradients with Orbital Relaxation

extended energy functional ≡ CC energy + constraints

$$\tilde{E} \; = \; \langle 0| \; (1+\Lambda) \;\; \exp(-T) H \exp(T) \; |0\rangle$$

Lagrange multipliers

CC energy and CC equations

$$+ \; 2 \sum_a \sum_i \; D_{ai} \; f_{ai} \; + \; \sum_{p,q} I_{pq} \left(\sum_{\mu,\nu} c^*_{\mu p} S_{\mu\nu} c_{\nu q} - \delta_{qp} \right)$$

Brillouin condition

orthonormality of MOs

stationarity conditions ⇒ elimination of MO derivatives

CC Gradients with Orbital Relaxation

parameterization of orbital changes

$$c'_{\mu p} = \sum_q c_{\mu q} T_{qp}$$

matrix *T*

$$\left(\begin{array}{c|c} \text{occ-occ} & \text{occ-vrt} \\ \hline \text{vrt-occ} & \text{vrt-vrt} \end{array}\right)$$

general (non-unitary) transformation

stationarity requirements

(1) $$\frac{\partial \tilde{E}}{\partial T_{ab}} = 0 \Longrightarrow \underline{I_{ab}}$$

(2) $$\frac{\partial \tilde{E}}{\partial T_{ia}} = 0 \Longrightarrow \underline{I_{ai} + I_{ia}}$$

(3) $$\frac{\partial \tilde{E}}{\partial T_{ai}} = 0 \Longrightarrow \underline{\text{Z vector equations for } D_{ai}}$$

(4) $$\frac{\partial \tilde{E}}{\partial T_{ij}} = 0 \Longrightarrow \underline{I_{ij}}$$

Z-Vector Equations for CC Gradients

Z-vector equations

$$\sum_{e}\sum_{e} D_{em}[\langle ae||im\rangle + \langle am||ie\rangle + \delta_{ae}\delta_{im}(\varepsilon_a - \varepsilon_i)] = -X_{ai}$$

with

$$\begin{aligned} X_{ai} \quad = \quad & \sum_{p,q,r}(\Gamma_{ipqr}\langle ap||qr\rangle + \Gamma_{qrip}\langle qr||ap\rangle) \\ & -\sum_{p,q,r}(\Gamma_{apqr}\langle ip||qr\rangle + \Gamma_{qrap}\langle qr||ip\rangle) \\ & +\frac{1}{2}\sum_{p,q} D_{pq}(\langle pa||qi\rangle + \langle pi||qa\rangle) \end{aligned}$$

linear equations for orbital relaxation contribution to D_{ai}

CC Gradients with Orbital Relaxation

differentiation of „extended“ energy functional

$$\frac{\partial \tilde{E}}{\partial x} = \langle 0| \, (1 + \Lambda) \, \exp(-T) \, H^x \, \exp(T) \, |0\rangle$$

$$+ \, 2 \sum_i \sum_a D_{ai} \sum_{\mu,\nu} c^*_{\mu a} \, \{ \frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma,\rho} D^{SCF}_{\sigma\rho} \frac{\partial \langle \mu\sigma || \nu\rho \rangle}{\partial x} \} \, c_{\nu i}$$

$$+ \sum_{p,q} I_{pq} \sum_{\mu,\nu} c^*_{\mu p} \frac{\partial S_{\mu\nu}}{\partial x} c_{\nu q}$$

contains no derivative of wavefunction parameters

H^x: Hamiltonian with AO derivative integrals

AO Formulation of CC Gradients

differentiation of „extended“ energy functional

$$\frac{\partial E}{\partial x} = \sum_{p,q} D_{pq}\, f_{pq}^{(x)} + \sum_{p,q,r,s} \Gamma_{pqrs}\, \langle pq||rs\rangle^{x} + \sum_{p,q} I_{pq}\, S_{pq}^{x}$$

integral derivatives contain no MO derivative contributions

reformulation in AO representation

$$\frac{\partial E}{\partial x} = \sum_{\mu\nu} D_{\mu\nu}\, (\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} D^{HF}_{\sigma\rho}\, \frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial x}) + \sum_{\mu\nu\sigma\rho} \Gamma_{\mu\nu\sigma\rho}\, \frac{\partial\langle\mu\sigma||\nu\rho\rangle}{\partial x} + \sum_{\mu\nu} I_{\mu\nu}\, \frac{\partial S_{\mu\nu}}{\partial x}$$

$$D_{\mu\nu} = \sum_{pq} c^{*}_{\mu p} D_{pq} c_{\nu q} \qquad \Gamma_{\mu\nu\sigma\rho} = \sum_{pqrs} c^{*}_{\mu p} c^{*}_{\nu q} \Gamma_{pqrs} c_{\sigma r} c_{\rho s} \qquad I_{\mu\nu} = \sum_{pq} c^{*}_{\mu p} I_{pq} c_{\nu q}$$

Implementation of CC Gradients

required steps for gradients

CC and Λ equations (~ $N^6, N^8, \ldots$)

↓

CC density matrices (~ $N^6, N^8, \ldots$)

↓

MO → AO transformation of density matrices (~ N^5)

↓

contraction with integral derivatives (no storage, ~ N^4)

computational cost do not scale with N_{pert}

available for all CC models (CCSD, CCSD(T), CCSDT, CCSDTQ, …, FCI)

Accuracy of CI and CC Geometrical Parameters

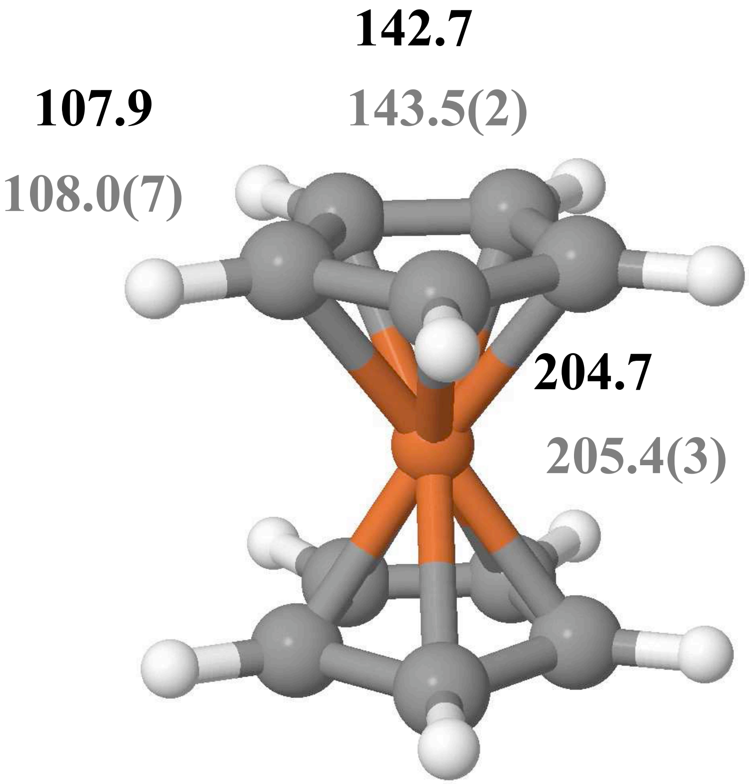
calculated r(OH) for H_2O (in Å)

	CI	**CC**
SD	**0.96131**	**0.96435**
SD(T)		**0.96575**
SDT	**0.96251**	**0.96583**
SDTQ	**0.96593**	**0.96614**
SDTQP	**0.96606**	**0.96616**
SDTQPH	**0.96616**	**0.96616**
FCI	**0.96616**	

calculations with cc-pVDZ basis

Kállay et al., *J. Chem. Phys*. **119**, 2991 (2003)

Equilibrium Structure of Ferrocene



r(FeC5): 164.8 pm, <(C5H): 0.52^{o}

r(FeC5): 166.1 pm, <(C5H): 3.7^{o}

CCSD(T)/cc-pwCVTZ

672 basis functions

96 correlated electrons

gas-phase
electron diffraction

Accuracy of CC Equilibrium Geometries

12 closed-shell molecules

CH_2, CH_4, NH_3, H_2O, HF, N_2, C≡O, HC≡N,

HN≡C, HC≡CH, O=C=O, F_2

wave function models

CCSD(T), CCSDT, CCSDTQ

basis sets

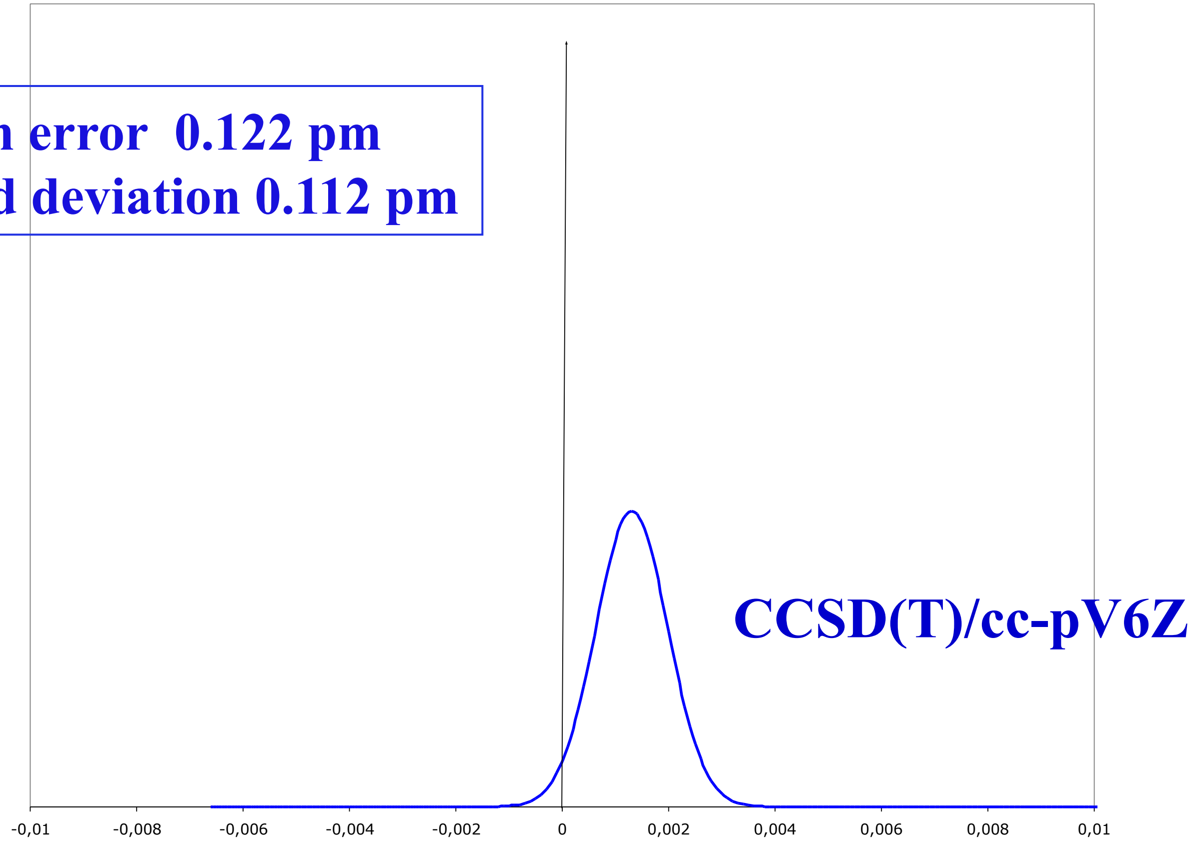
cc-p(C)VXZ, X = T,Q,5,6 + additivity assumptions

empirical equilibrium geometries

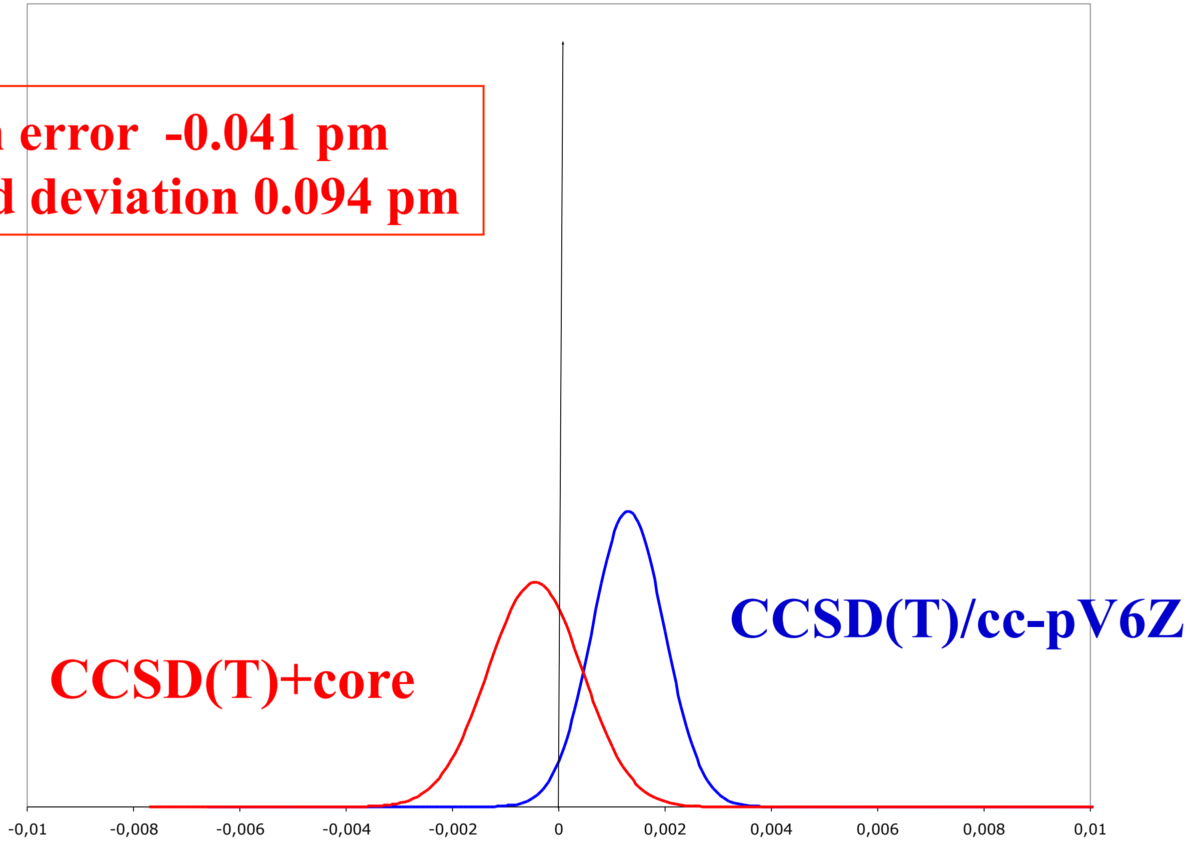
Heckert et al., *Mol. Phys.* **103**, 2109 (2005)

Statistical Evaluation

mean error 0.122 pm
standard deviation 0.112 pm



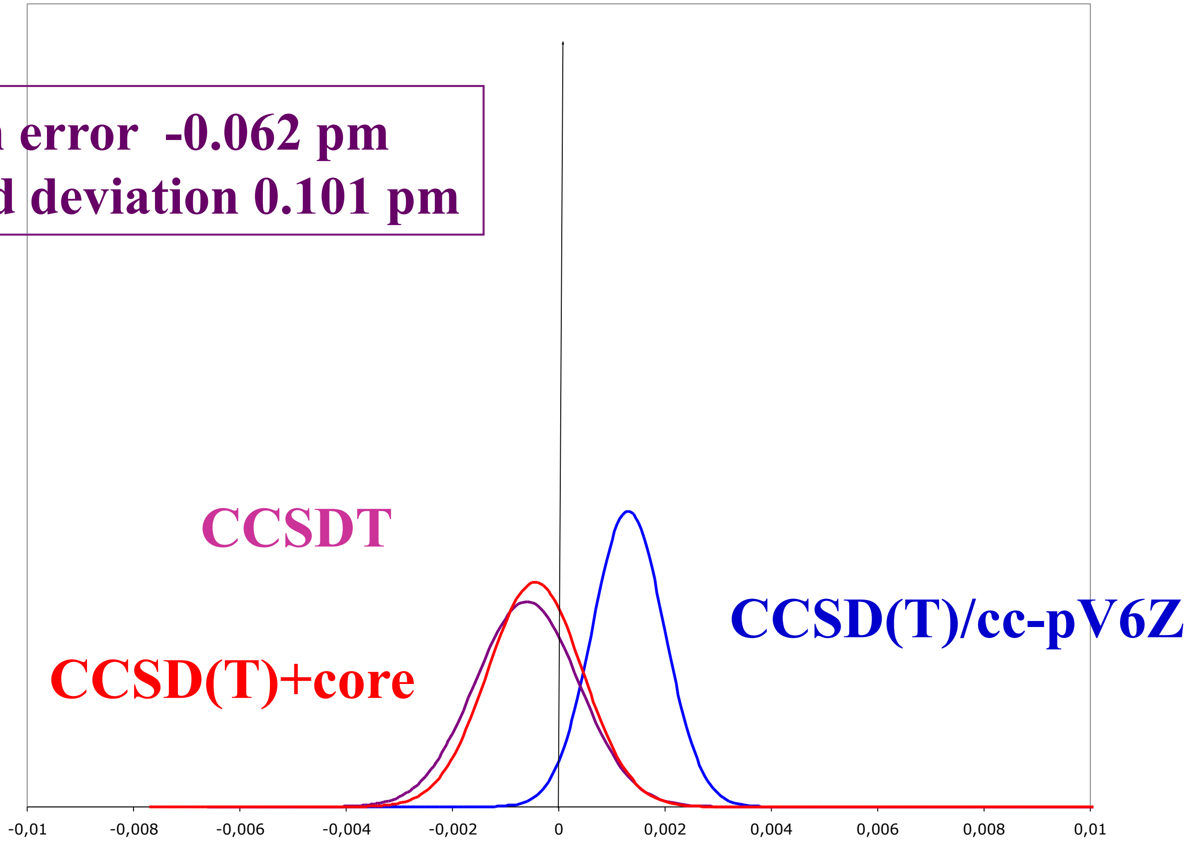
Statistical Evaluation



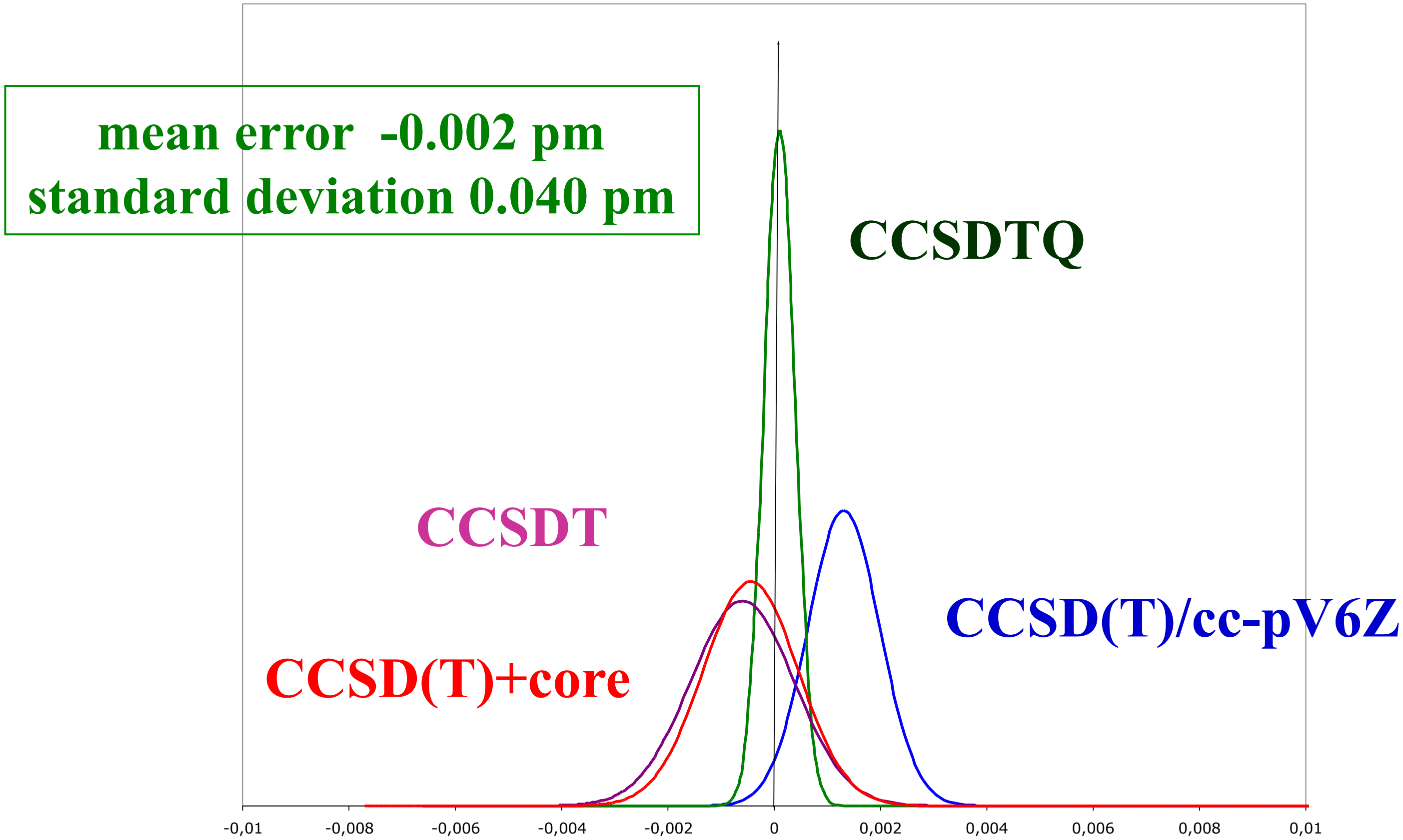
mean error -0.041 pm
standard deviation 0.094 pm

Statistical Evaluation

mean error -0.062 pm
standard deviation 0.101 pm

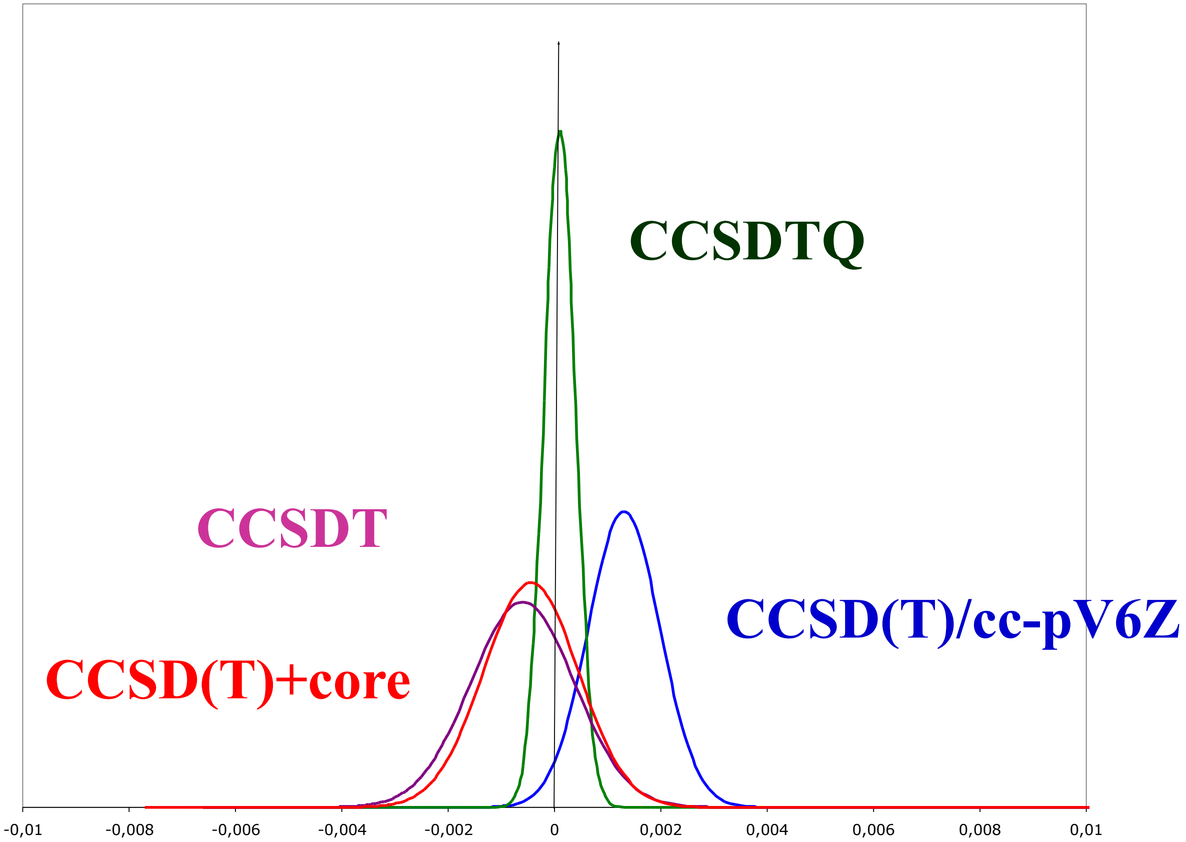


Statistical Evaluation



mean error -0.002 pm
standard deviation 0.040 pm

Statistical Evaluation

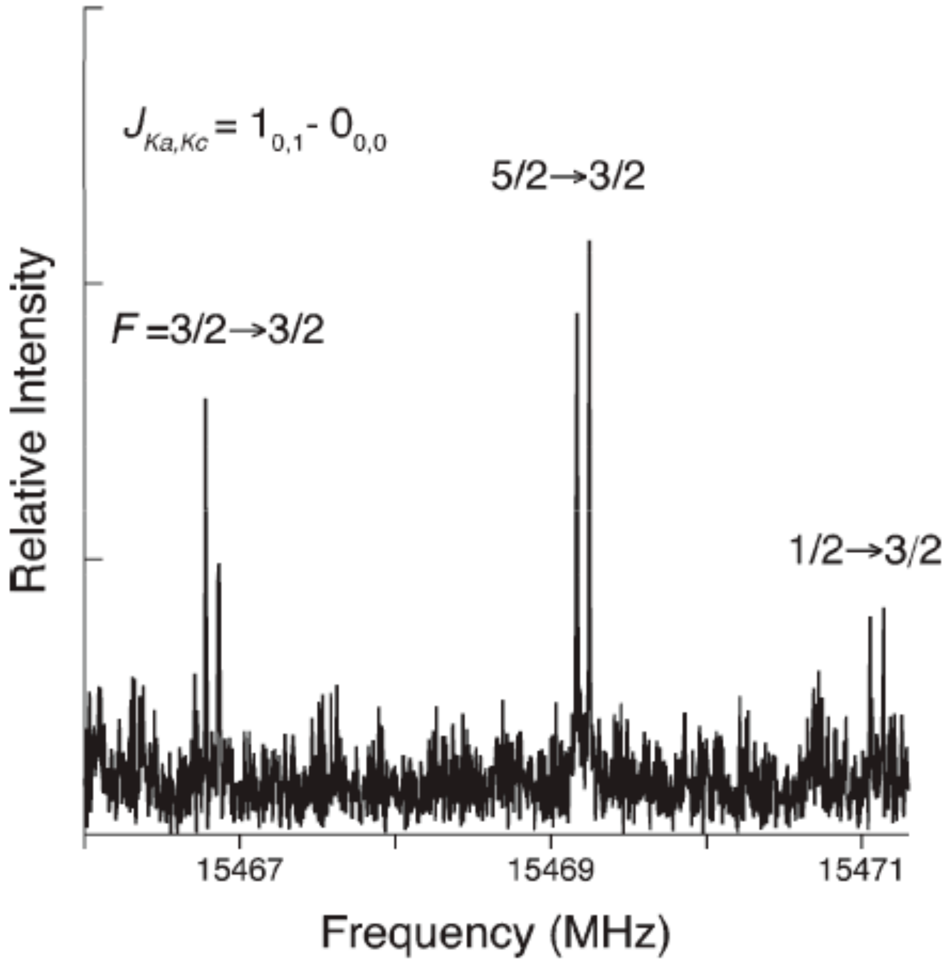


full CCSDT no improvement over CCSD(T)

CCSDTQ significantly more accurate than CCSD(T)

High-Accuracy Quantum Chemistry Rotational Spectroscopy and Equilibrium Geometries

Rotational Spectrum of $H_2Si=S$



investigation of ten isotopologues

McCarthy et al. (Harvard University)

Spectroscopic Parameters of $H_2Si{=}S$

	calc.	exp.
A_0	170336.5	170342.9(14)
B_0	8025.7	8030.9549(6)
C_0	7653.7	7658.0056(6)

all values in MHz

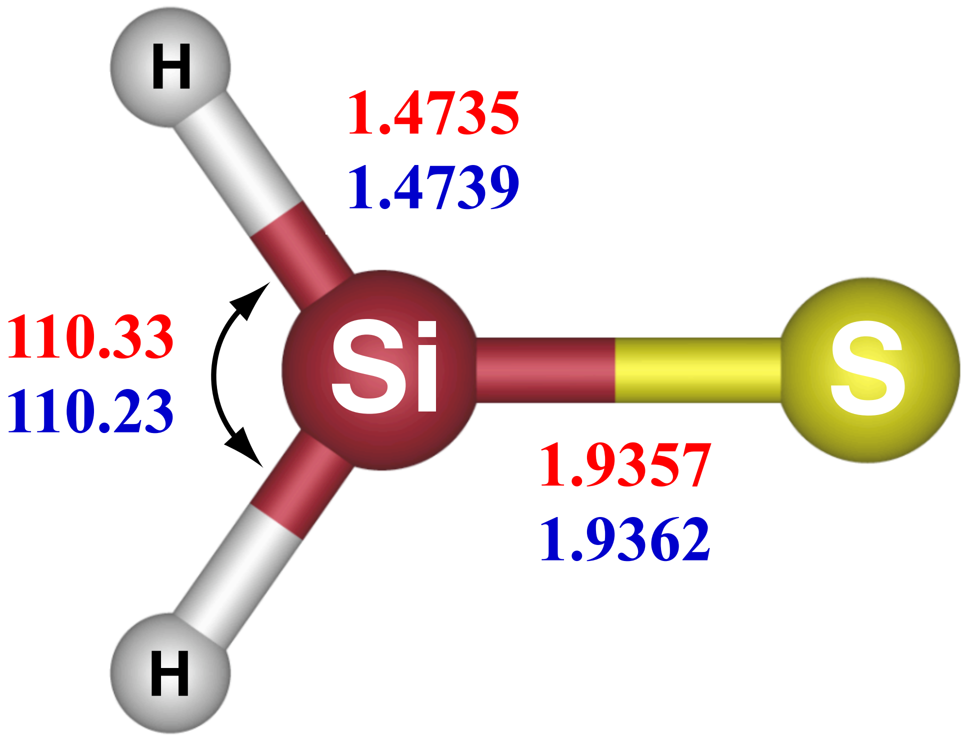
fc-CCSD(T)/cc-pV∞Z + ΔT/cc-pVTZ+ΔQ/cc-pVDZ+Δcore/cc-pCV5Z

plus CCSD(T)/cc-pV(Q+d)Z vibrational corrections

plus CCSD(T)/aug-cc-pVQZ electronic contributions

Thorwirth et al., *Chem. Comm*. 5292 (2008)

Equilibrium Structure of $H_2Si{=}S$



experimental structure using CCSD(T)/cc-pV(Q+d)Z vibrational corrections

fc-CCSD(T)/cc-pV∞Z + ΔT/cc-pVTZ+ΔQ/cc-pVDZ+Δcore/cc-pCV5Z

Thorwirth et al., *Chem. Comm*. 5292 (2008)

Multireference Coupled-Cluster Theory:
Recent Developments and Challenges

Coupled-Cluster Theory

exponential ansatz for wavefunction

$$|\Psi\rangle \;=\; \exp(T)\;|0\rangle$$

- **exact parameterization of Ψ**
- **truncation of T required for applicable schemes**
- **standard approach for high-accuracy calculations**

Multiconfigurational Theories

linear combination of determinants

$$|\Psi\rangle = \sum_{\mu} |\Phi_{\mu}\rangle \, c_{\mu}$$

- **non-dynamical/static correlation**
- **large coefficients for several determinants**
- **MCSCF, MRCI, ...**
- **needed for bond breaking, potential energy surfaces, ...**

Multireference Coupled-Cluster Theory

coupled-cluster ansatz

multiconfigurational ansatz

$$|\Psi\rangle \;=\; \exp(T)\;|0\rangle$$

$$|\Psi\rangle \;=\; \sum_{\mu}\;|\Phi_\mu\rangle\;c_\mu$$

what is the marriage?

Wish List for MRCC

- size extensivity
- orbital invariance
- low computational cost
- good accuracy

- efficient implementation
- multiplet problem
- spin adaptation

- molecular properties
- excitation energies

Multireference Coupled-Cluster Theory

coupled-cluster ansatz

$$|\Psi\rangle = \exp(T)\ |0\rangle$$

multiconfigurational ansatz

$$|\Psi\rangle = \sum_{\mu} |\Phi_{\mu}\rangle\ c_{\mu}$$

possible solution:

$$|\Psi\rangle = \exp(T) \sum_{\mu} |\Phi_{\mu}\rangle\ c_{\mu}$$

internally contracted MRCC

Internally Contracted MRCC

ansatz

$$|\Psi\rangle = \exp(T) \sum_{\mu} |\Phi_{\mu}\rangle \, c_{\mu}$$

multideterminantal reference $|\Phi\rangle$

cluster operator

$$T = \sum_{q} t_q \tau_q = \sum_{k}^{n} T_k$$

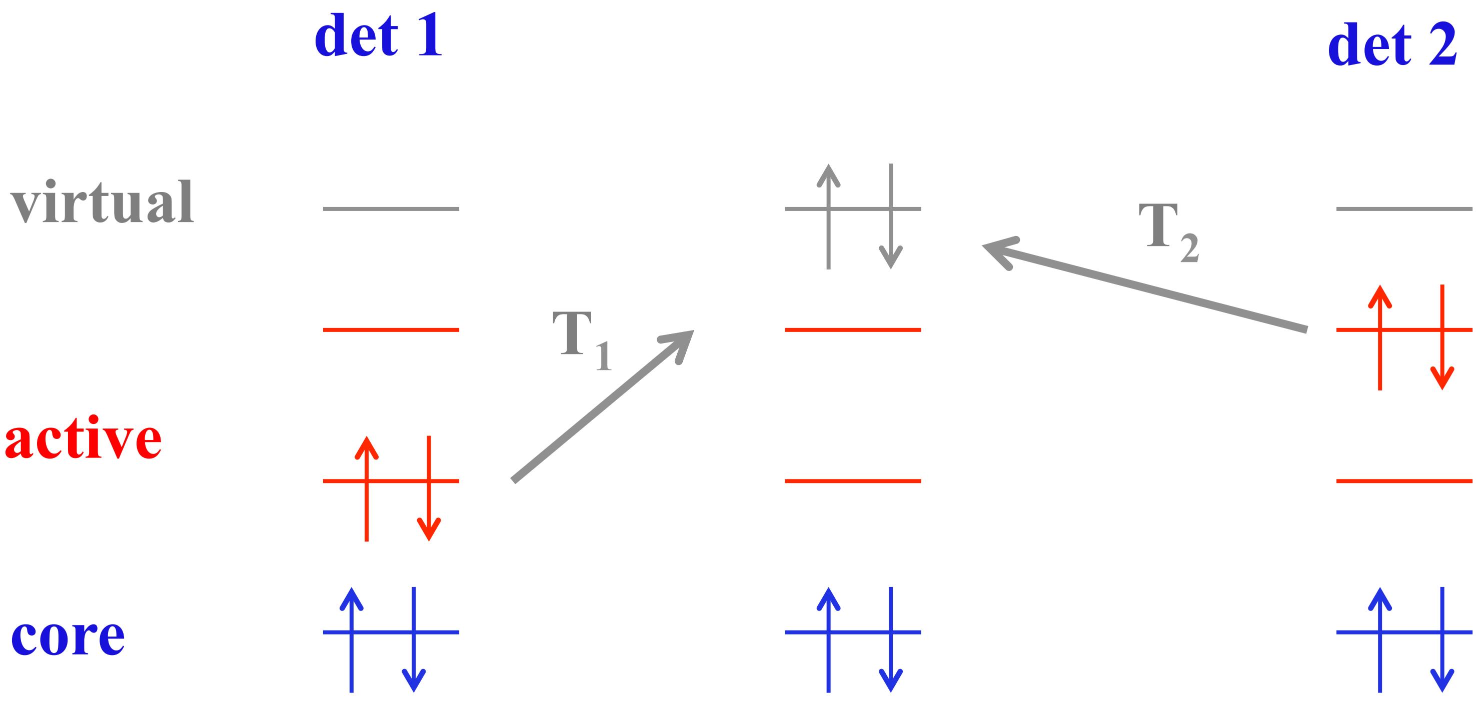
core + active

active + virtual

$$T_k = \frac{1}{(k!)^2} \sum_{ij...}^{C+A} \sum_{ab...}^{A+V} t_{ij...}^{ab...} \, a_a^{\dagger} a_b^{\dagger} \ldots a_j a_i$$

→ **non-commuting operators**

Internally Contracted MRCC



→ redundancies in T

linear dependencies to be eliminated

Internally Contracted MRCC

$$H \ \exp(T) \ |\Phi\rangle \ = \ \exp(T) \ |\Phi\rangle$$

amplitude equations via projection

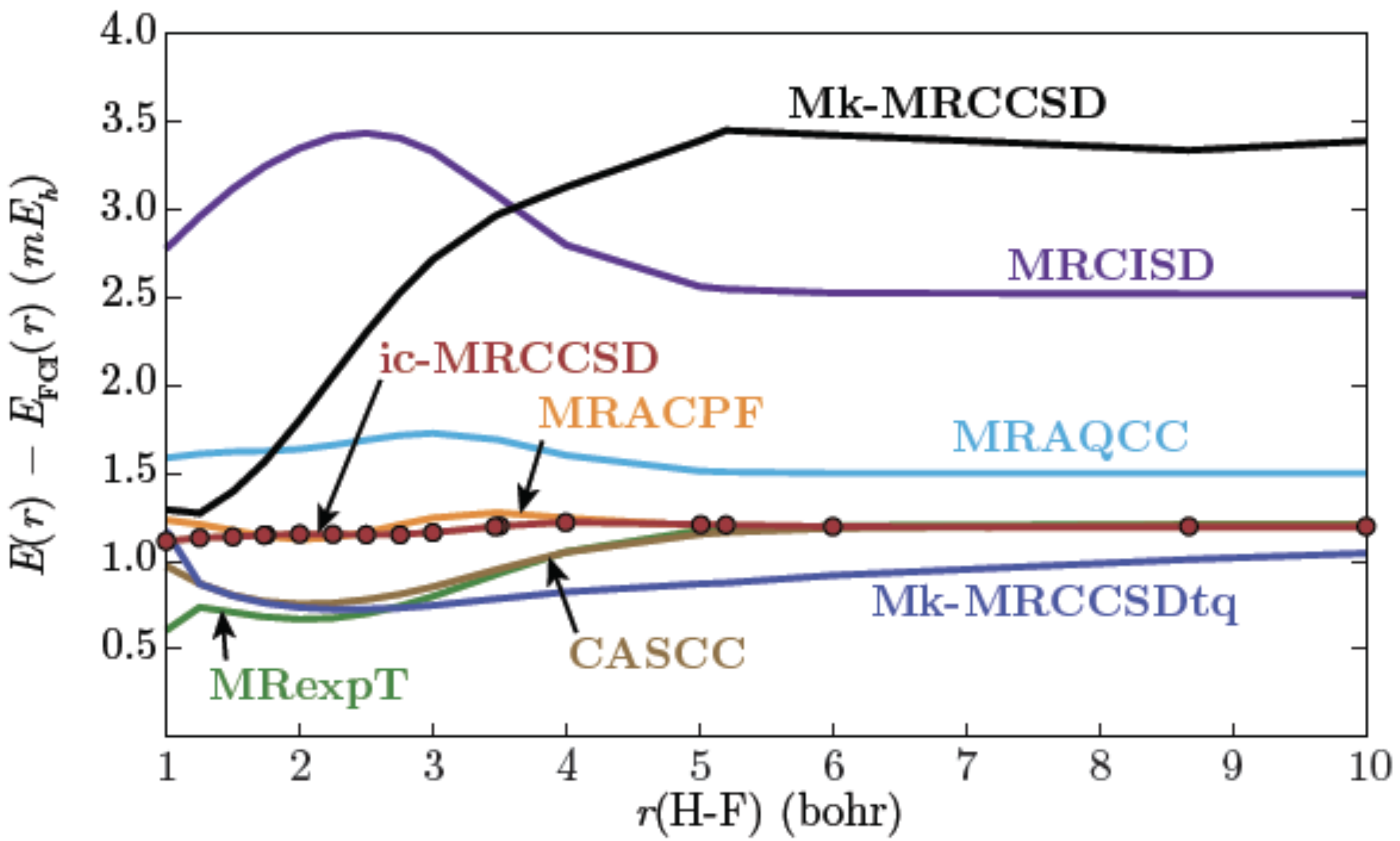
$$0 \ = \ \langle\Phi| \ \kappa_P^\dagger \ \exp(-T) \ H \ \exp(T) \ |\Phi\rangle$$

energy eigenvalue problem

$$\mathbf{H}^{eff} \ \mathbf{c} \ = \ E \ \mathbf{c} \qquad H_{\mu\nu}^{eff} \ = \ \langle\Phi_\mu| \ \exp(-T) \ H \ \exp(T) \ |\Phi_\nu\rangle$$

elimination of redundancies via singular-value decomposition

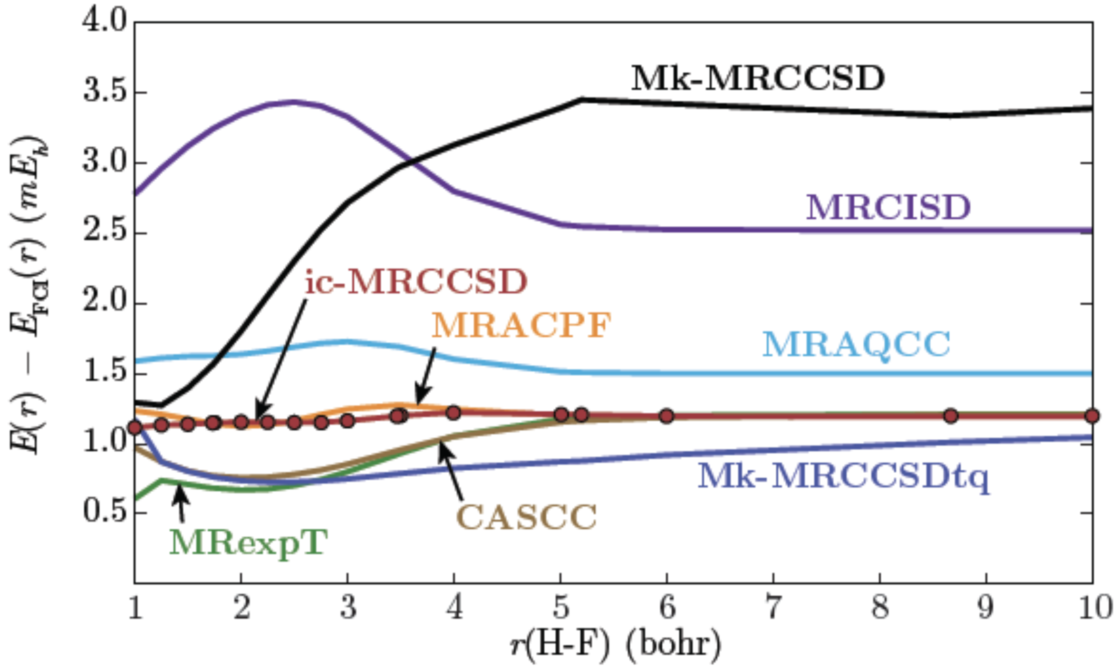
Accuracy of Internally Contracted MRCC



HF dissociation curve, deviation from FCI, CAS(2,2), DVZ

F.A. Evangelista, J. Gauss, *J. Chem. Phys.* **134**, 114102 (2011)

Internally Contracted MRCC



HF dissociation curve, deviation from FCI, CAS(2,2), DVZ

Early work by:

Mukherjee et al. (1975), Banerjee & Simons (1981), Kong (2009)

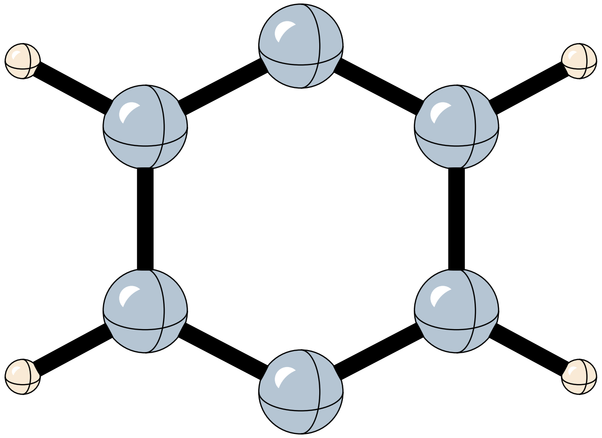
Recent progress by:

Evangelista & Gauss (2011, FCI based implementation)

Hanauer & Köhn (2011, automatized implementation)

Large-Scale Application of icMRCC

singlet-triplet splittings (in kcal/mol) in p-benzyne



Basis set	icMRCCSD
cc-pVDZ	3.72
cc-pVTZ	3.73
cc-pVQZ	3.74
extrapol.	3.75
ZPVE	+0.3
Experiment	3.8± 0.3

icMRCCSD/cc-pVQZ calculation (two commutators)

F. A. Evangelista, M. Hanauer, A. Köhn, J. Gauss, *J. Chem. Phys.* **136**, 204108 (2012)

Checklist for icMRCC

size extensivity	(yes)
orbital invariance	yes
scaling with N_{ref}	no
good accuracy	yes
efficient implementation	???
spin adaptation	in progress
molecular properties	numerically
excitation energies	in progress

main developers: M. Hanauer, A. Köhn (Mainz)

Multireference Coupled-Cluster Theory

coupled-cluster ansatz

$$|\Psi\rangle \;=\; \exp(T)\;|0\rangle$$

multiconfigurational ansatz

$$|\Psi\rangle \;=\; \sum_{\mu} |\Phi_{\mu}\rangle\; c_{\mu}$$

possible solution:

$$|\Psi\rangle \;=\; \sum_{\mu} \exp(T_{\mu})\;|\Phi_{\mu}\rangle\; c_{\mu}$$

Jeziorski-Monkhorst ansatz

Jeziorski-Monkhorst Ansatz

Jeziorski-Monkhorst ansatz for wavefunction

$$|\Psi_\alpha\rangle \;=\; \sum_{\mu=1}^{d} \;\exp(\hat{T}_\mu)\; |\Phi_\mu\rangle \; c_\mu^\alpha$$

sum over references

reference-specific cluster operator

weight of each reference

insertion into Schrödinger eq. and projection onto references

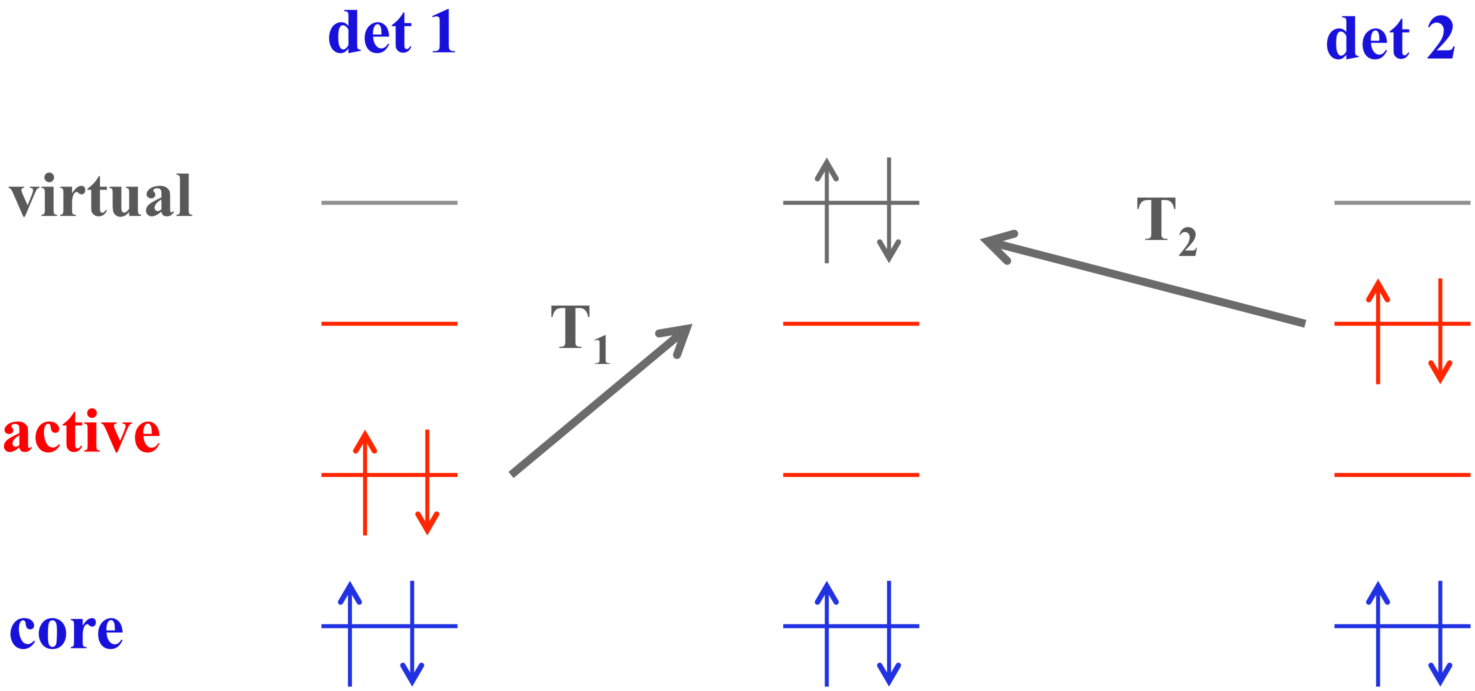
$$\sum_\nu \; H^{\text{eff}}_{\mu\nu}\; c_\nu^\alpha \;=\; E^\alpha \; c_\mu^\alpha$$

$$H^{\text{eff}}_{\mu\nu} \;=\; \langle \Phi_\mu | H \exp(T_\nu) | \Phi_\nu \rangle$$

$$\overset{\text{CMS}}{=} \; \langle \Phi_\mu | \exp(-T_\nu) H \exp(T_\nu) | \Phi_\nu \rangle$$

non-Hermitian eigenvalue problem

Redundancy Problem



- commuting operators for each reference
- redundancies in JM ansatz

Mk-MRCC Theory

$$\sum_{\mu} \left\{ H \, \exp(T_\mu) \, |\Phi_\mu\rangle \, c_\mu^\alpha \; - \; E^\alpha \, \exp(\hat{T}_\mu) \, |\Phi_\mu\rangle \, c_\mu^\alpha \right\} = 0$$

insert

$$1 = \exp(T_\mu) \, (P + Q) \, \exp(-T_\mu)$$

projector on reference space

projector on excitation manifold

Mahapatra, Datta, Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999)

Mk-MRCC Theory

$$\Rightarrow \quad \sum_{\mu} \exp(T_\mu)\; Q\; \exp(-T_\mu)\; H\; \exp(T_\mu)\; |\Phi_\mu\rangle\; c^\alpha_\mu$$

$$+ \sum_{\nu}\sum_{\mu} \exp(T_\nu)\; |\Phi_\mu\rangle\; H^{eff}_{\mu\nu}\; c^\alpha_\nu \;=\; E_\alpha \sum_{\mu} \exp(T_\mu)\; |\Phi_\mu\;\rangle\; c^\alpha_\mu$$

interchange μ and ν in second term

$$\exp(T_\mu)\; Q\; \exp(-T_\mu)\; H\; \exp(T_\mu)\; |\Phi_\mu\rangle\; c^\alpha_\mu$$

$$+ \sum_{\nu} \exp(T_\nu)\; |\Phi_\mu\rangle\; H^{eff}_{\mu\nu}\; c^\alpha_\nu \;=\; E_\alpha\; \exp(T_\mu)\; |\Phi_\mu\;\rangle\; c^\alpha_\mu$$

lift sum over μ => **sufficiency conditions**

Mahapatra, Datta, Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999)

Mk-MRCC Theory

$$\exp(T_\mu)\ Q\ \exp(-T_\mu)\ H\ \exp(T_\mu)\ |\Phi_\mu\rangle\ c_\mu^\alpha$$

$$+ \sum_\nu \exp(T_\nu)\ |\Phi_\mu\rangle\ H_{\mu\nu}^{eff}\ c_\nu^\alpha\ =\ E_\alpha\ \exp(T_\mu)\ |\Phi_\mu\ \rangle\ c_\mu^\alpha$$

multiplication with exp(-T_μ) and projection on $\Phi_q(\mu)$

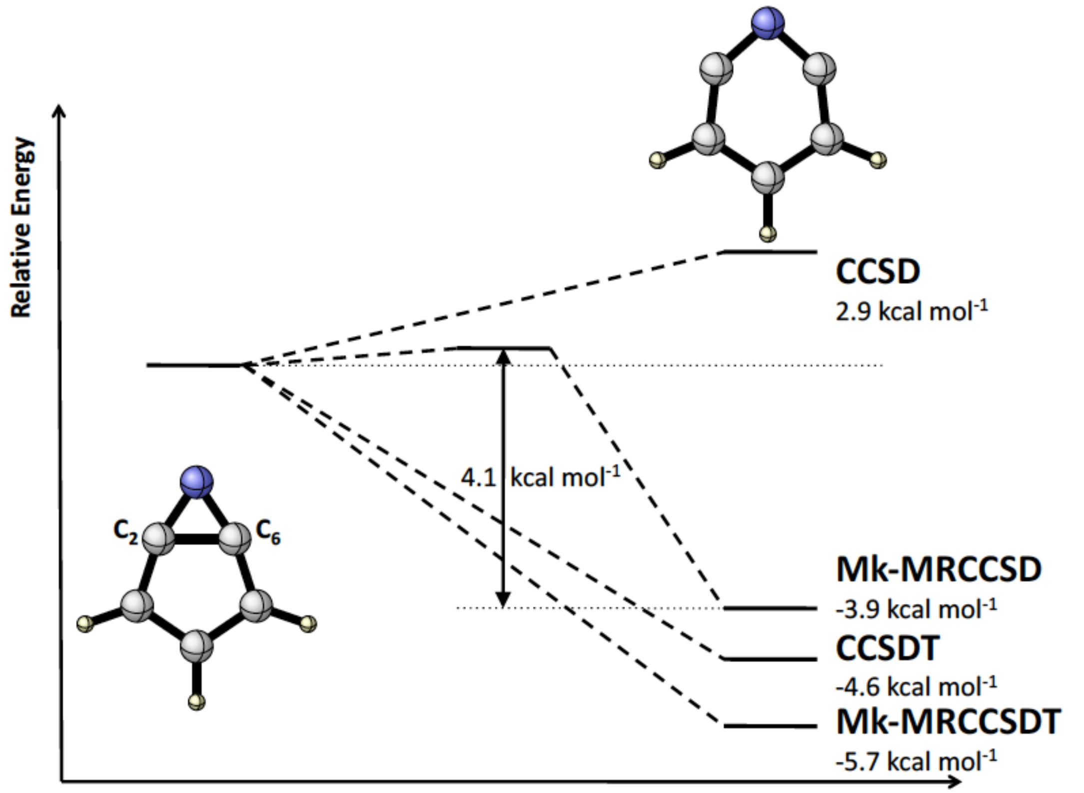
$$\langle\Phi_q(\mu)|\ \exp(-T_\mu)\ H\ \exp(T_\mu)\ |\Phi_\mu\rangle\ c_\mu^\alpha$$

$$+ \sum_{\nu(\neq\mu)} \langle\Phi_q(\mu)|\ \exp(-T_\mu)\ \exp(T_\nu)\ |\Phi_\mu\rangle\ H_{\mu\nu}^{\text{eff}}\ c_\nu^\alpha\ =\ 0$$

Mk-MRCC amplitude equations

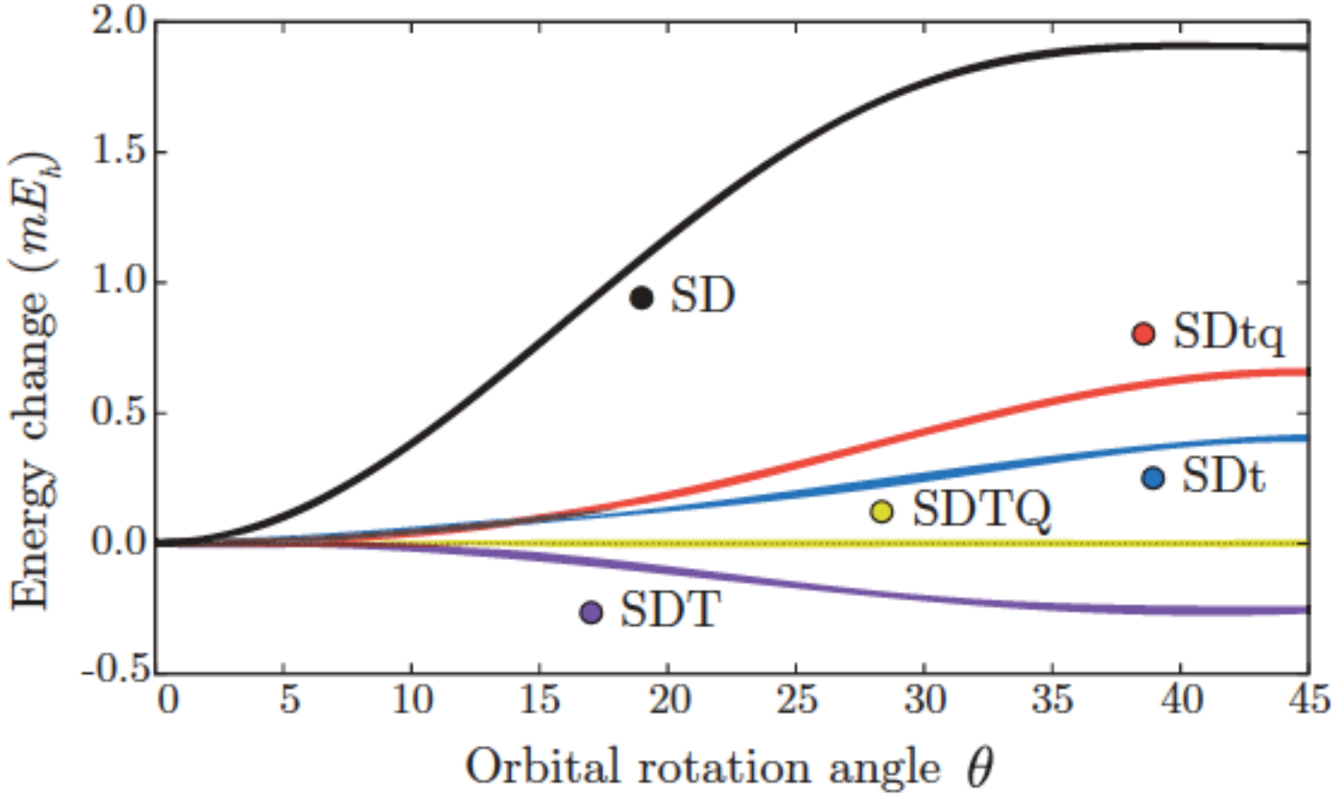
Mahapatra, Datta, Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999)

Mk-MRCCSD and Mk-MRCCSDT



Mk-MRCCSD and Mk-MRCCSDT in various program packages

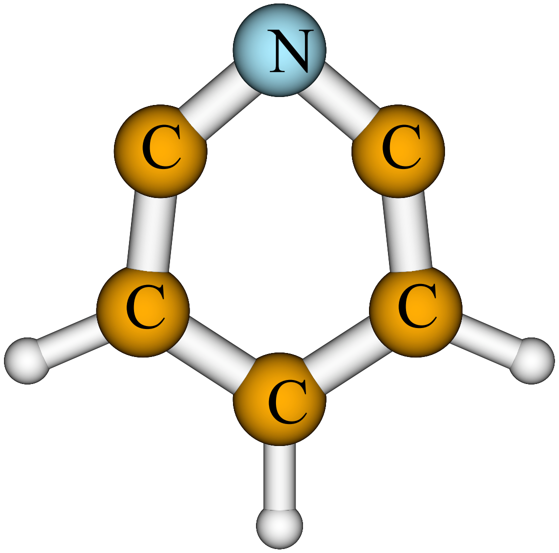
Orbital Invariance of Mk-MRCC



BeH$_2$ model system, CAS(2,2), DVZ basis

F. A. Evangelista, J. Gauss, J. Chem. Phys. 134, 044101 (2010)

Tools for Calculating Properties in MRCC



2,6-pyridyne

two reference determinants

- **equilibrium geometry**
- **vibrational frequencies**
- **excitation energies**

...

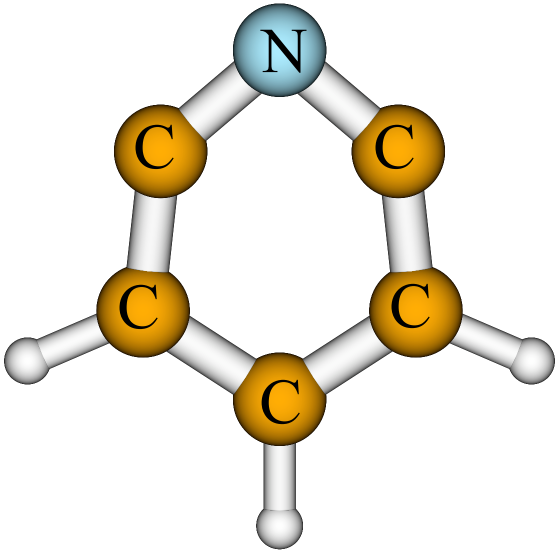
$\Downarrow$

analytic Mk-MRCC gradients

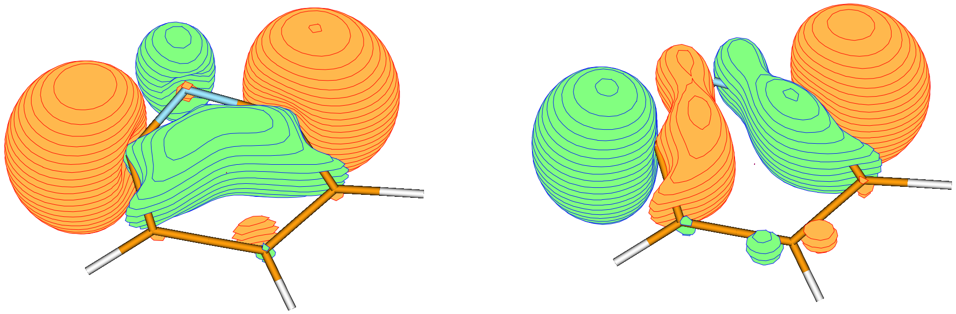
Mk-MRCC response theory

Mk-MRCC Gradients: Example

2,6-pyridyne



active orbitals



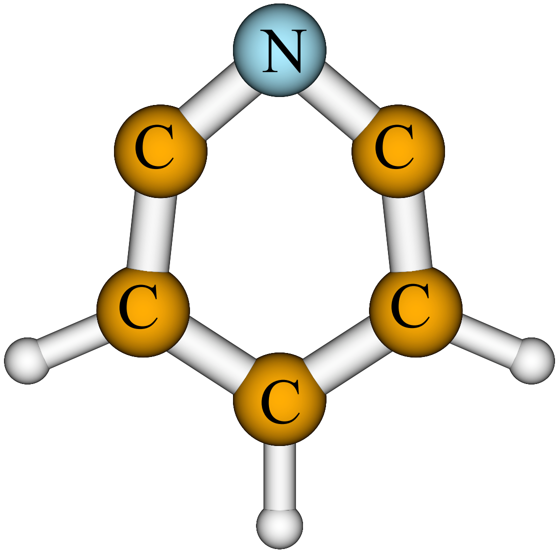
distance of radical centers

method	orbitals	distance (Å)
SR-CCSD	RHF	1.818
Mk-MRCCSD	RHF	2.017
Mk-MRCCSD	TCSCF	2.030

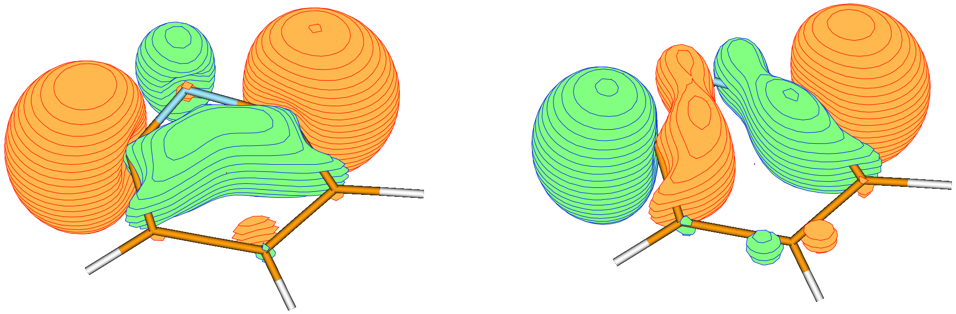
Jagau, Prochnow, Evangelista, Gauss, *J. Chem. Phys.* **132**, 144110 (2010)

Mk-MRCC Gradients: Example

2,6-pyridyne



active orbitals

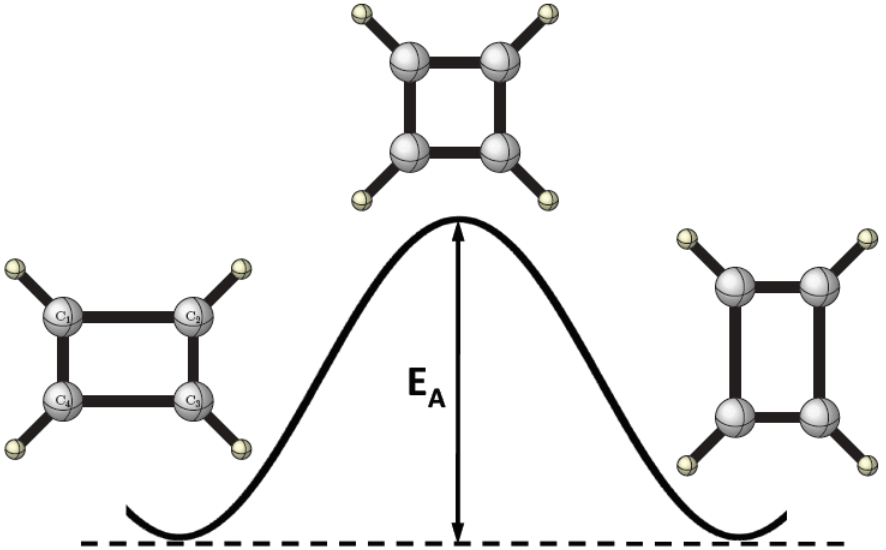


coefficients of reference determinants

method	c_1	c_2
TCSCF	0.833	-0.553
Mk-MRCCSD	0.914	-0.405

Jagau, Prochnow, Evangelista, Gauss, *J. Chem. Phys.* **132**, 144110 (2010)

Mk-MRCCSDT Gradients



method	ΔE_A
CCSD	21.13
CCSDT	7.62
MK-MRCCSD	7.79
Mk-MRCCSDT	7.87

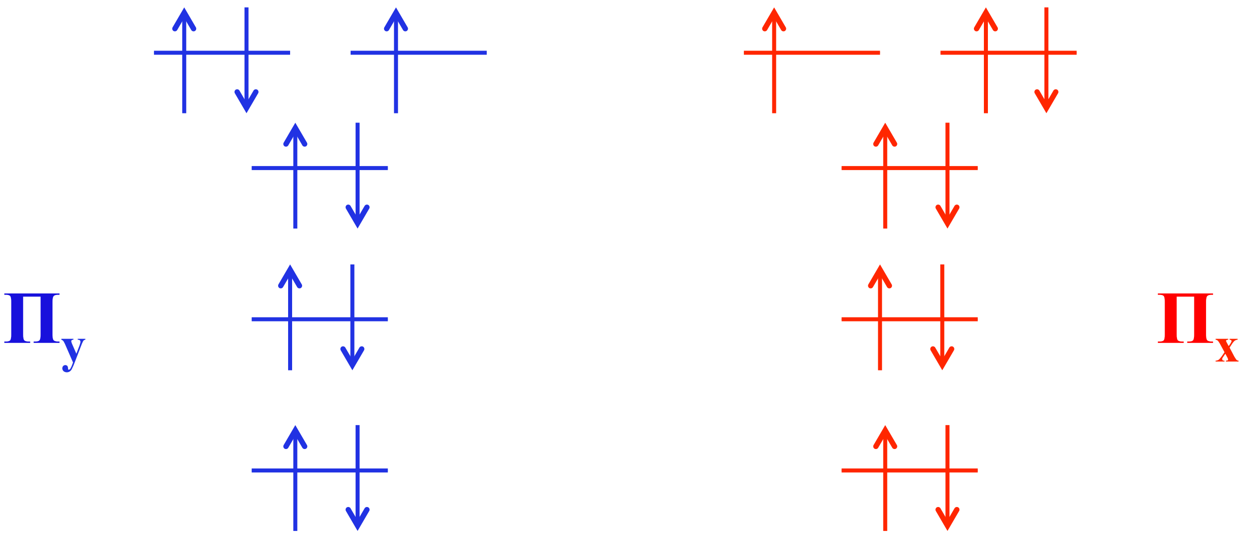
TCSCF orbitals, cc-pVDZ

automerization barrier ΔE_A of cyclobutadiene

E. Prochnow, J. Gauss, to be published

Spin-Orbit Splittings via Mk-MRCC

OH radical



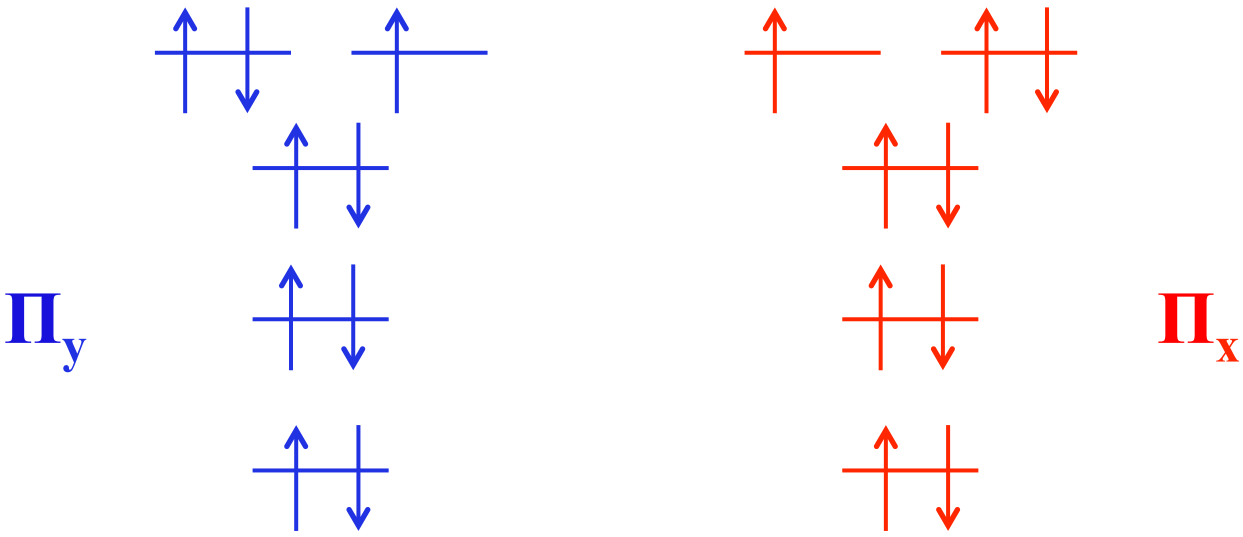
nonrelativistic treatment

Π_x and Π_y degenerate

single-reference case

Spin-Orbit Splittings via Mk-MRCC

OH radical



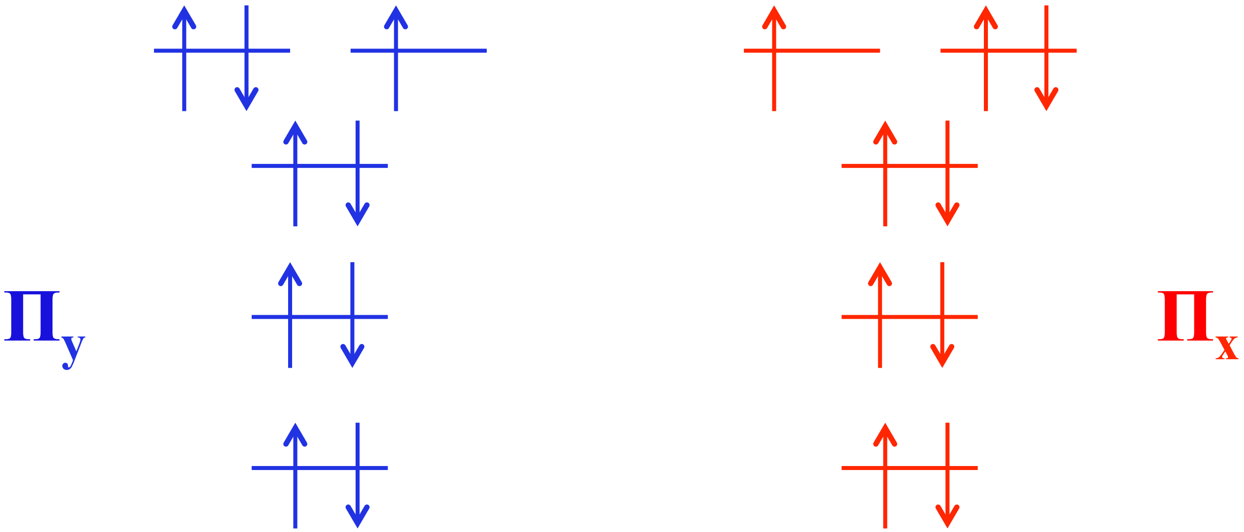
relativistic treatment

$$\Pi_{1/2}, \Pi_{3/2} = \frac{1}{\sqrt{2}} (\Pi_x \pm i\, \Pi_y)$$

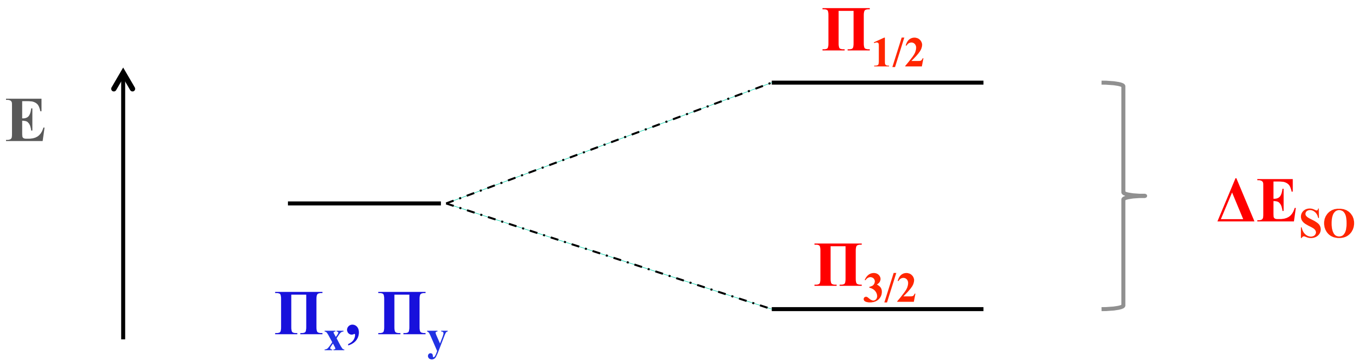
multideterminantal case

Spin-Orbit Splittings via Mk-MRCC

OH radical



relativistic treatment



Spin-Orbit Splittings via Mk-MRCC

- treat SO effects using degenerate perturbation theory
- zeroth-order wavefunctions $\Pi_{1/2}$ and $\Pi_{3/2}$ (Mk-MRCC)
- SO splittings

$$\Delta E_{SO} = 2 \, | \, \langle \Pi_{1/2} \, | \, \hat{H}_{SO} \, | \, \Pi_{1/2} \rangle \, |$$

$$= 2 \, \frac{d \; E(\Pi_{1/2})}{d \; \lambda_{SO}}$$

Mk-MRCC gradients

- spatially averaged π orbitals & mean-field SO treatment

L.A. Mück and J. Gauss, *J. Chem. Phys.* **136**, 111103 (2012)

Spin-Orbit Splittings via Mk-MRCC

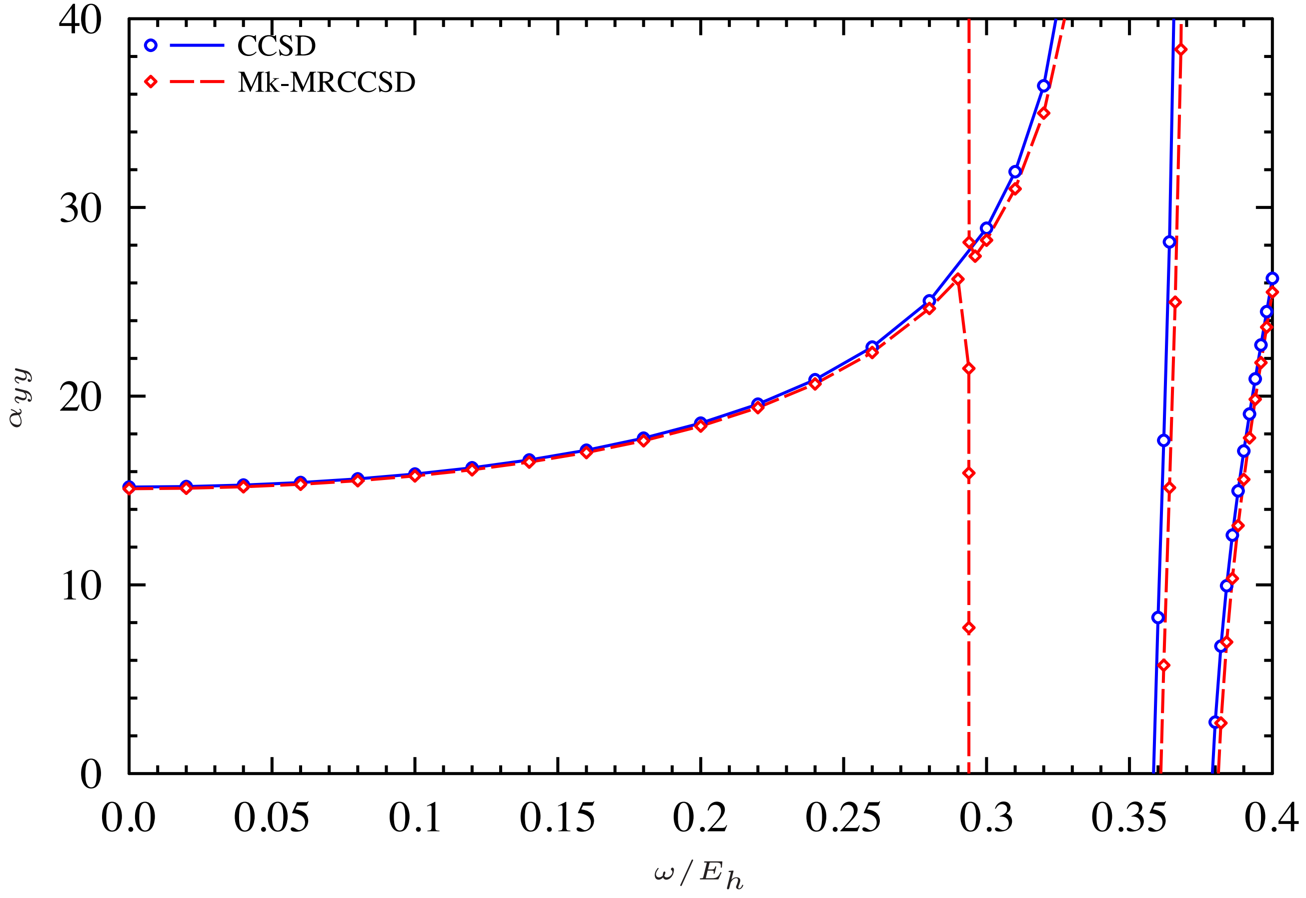
SO splittings (in cm^{-1}):

Species	Mk-MRCC	Exp.
OH	135.1	139.2
SH	375.2	377.0
SeH	1707.9	1764.4
ClO	312.3	320.3
BrO	918.6	975.4

Mk-MRCCSD/cc-pCVQZ(-g) calculations

L.A. Mück and J. Gauss, *J. Chem. Phys.* **136**, 111103 (2012)

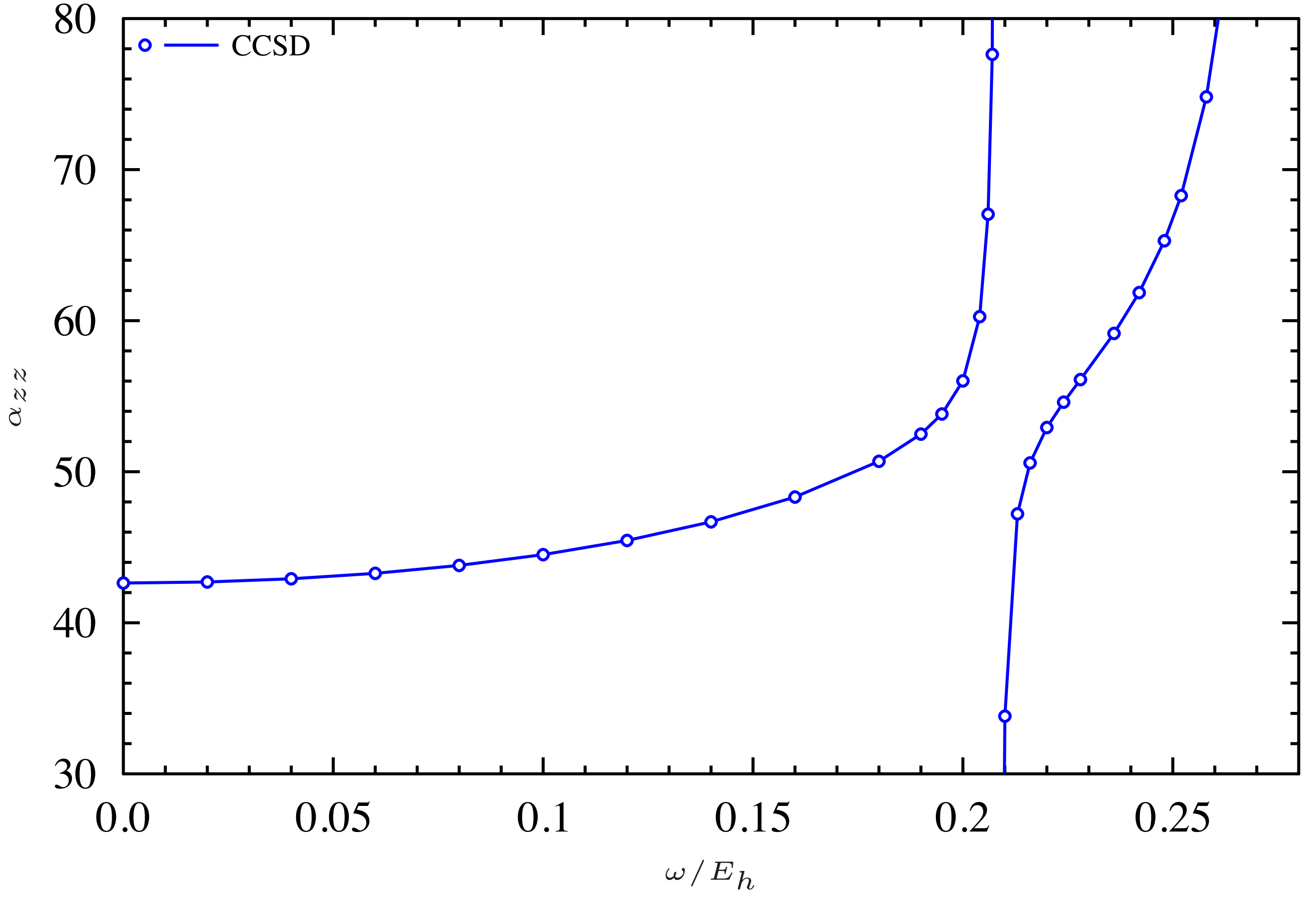
Dynamical Polarizability of CH_2



Mk-MRCC has wrong pole structure

T.-C. Jagau, J. Gauss, *J. Chem. Phys.* **137**, 044115 (2012)

Dynamical Polarizability of p-Benzyne

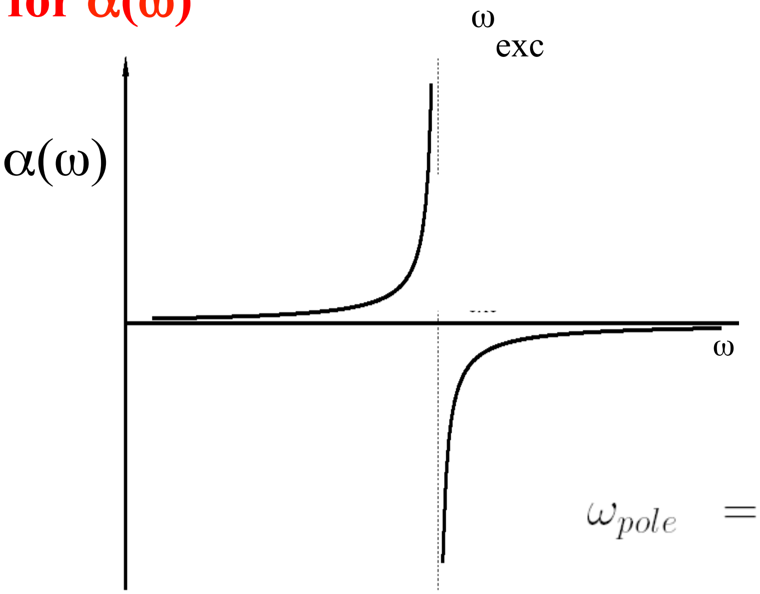


aug-cc-pCVDZ basis set at Mk-MRCCSD/cc-pCVTZ geometry

T.-C. Jagau, J. Gauss, *J. Chem. Phys.* **137**, 044115 (2012)

Response Theory for Excited States

- **dispersion for α(ω)**



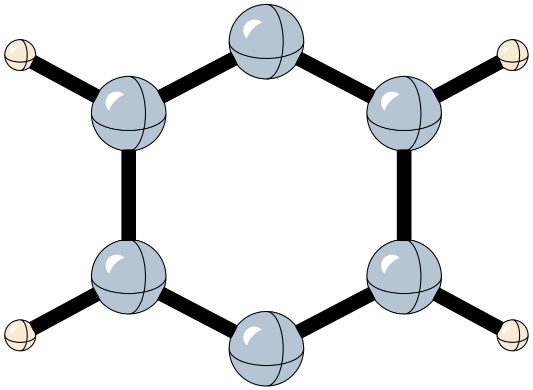
$$\omega_{pole} = (E_{exc} - E_0)/\hbar$$

- **exact theory**

$$\alpha(\omega) = \sum_i \frac{|\langle\Psi_0|\hat{\mu}|\Psi_i\rangle|^2}{\omega_{oi} - \omega} + \sum_i \frac{|\langle\Psi_0|\hat{\mu}|\Psi_i\rangle|^2}{\omega_{oi} + \omega}$$

⇒ **pole position at excitation frequency**

Mk-MRCCSD Excitation Energies



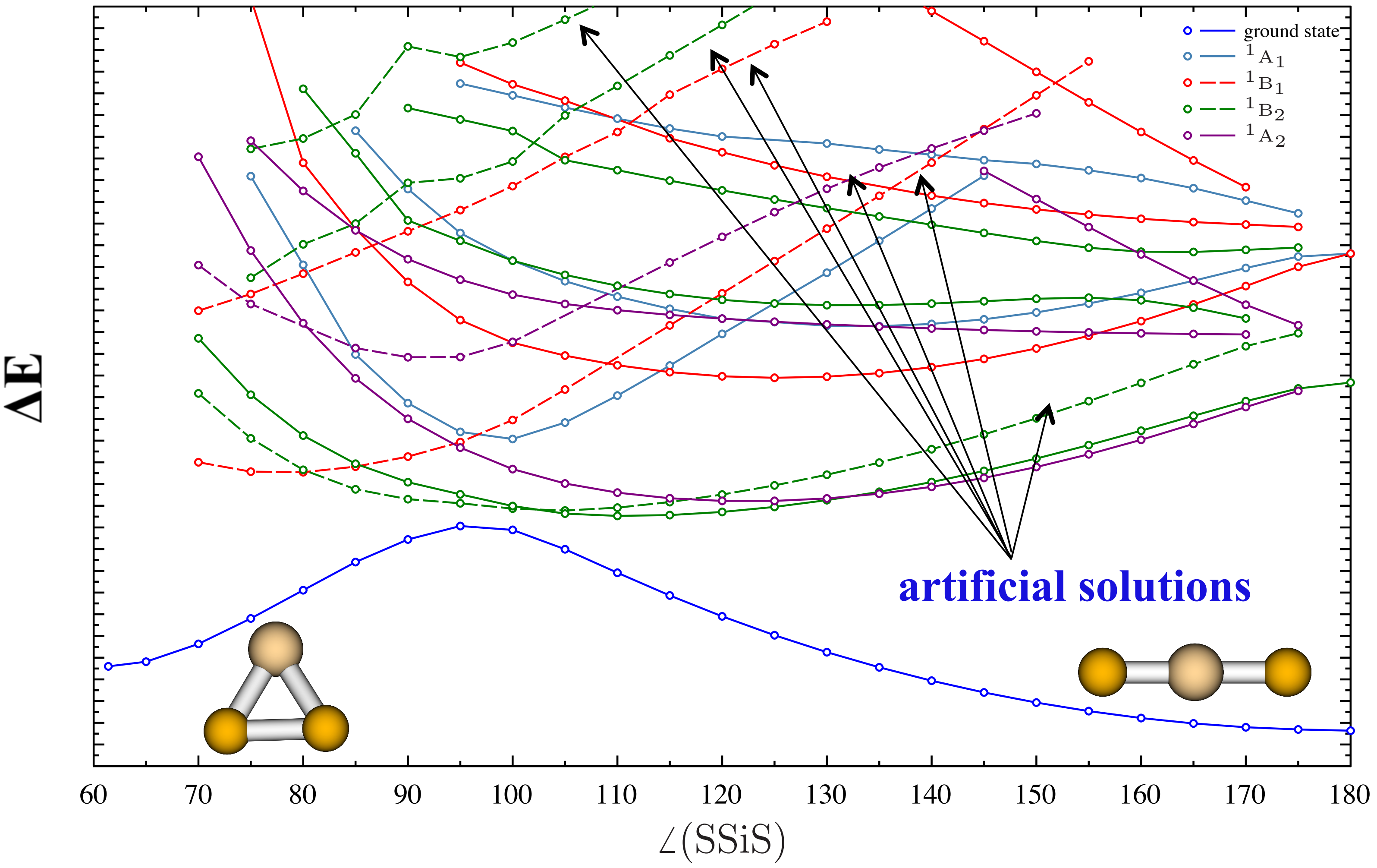
cc-pCVDZ basis,
Mk-MRCCSD/cc-pCVDZ
geometry

vertical excitation energies in eV

	CCSD	MkMRCCSD
1 $^3B_{3u}$	-0.48	0.39
1 $^1B_{3u}$	4.29	3.92
2 ^1A_g	5.79	5.46
1 $^3B_{2u}$	4.80	4.90
1 $^1B_{2u}$	5.28	5.34

T.-C. Jagau, J. Gauss, *J. Chem. Phys.* **137**, 044116 (2012)

Mk-MRCCSD Excitation Energies: SiS_2



Checklist for Mk-MRCC

size extensivity	yes
orbital invariance	no
scaling with N_{ref}	yes
good accuracy	???
efficient implementation	yes
spin adaptation	(yes)
molecular properties	gradients
excitation energies	wrong pole structure

Conclusions and Outlook

- **CC theory: main tool for high-accuracy calculations**

  → **computational thermochemistry, gas-phase spectroscopy**

current challenges:

- **large molecules → local correlation, pair natural orbitals, ...**
- **basis-set convergence → explicitly correlated CC**
- **heavy-elements → relativistic four- and two-component CC**
- **strong correlation → multi-reference CC**