Relativistic Multi-Reference Electron Correlation Methods

Development and Application

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Acknowledgements

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Stefan Knecht

Hans Jørgen Aa. Jensen (Odense)

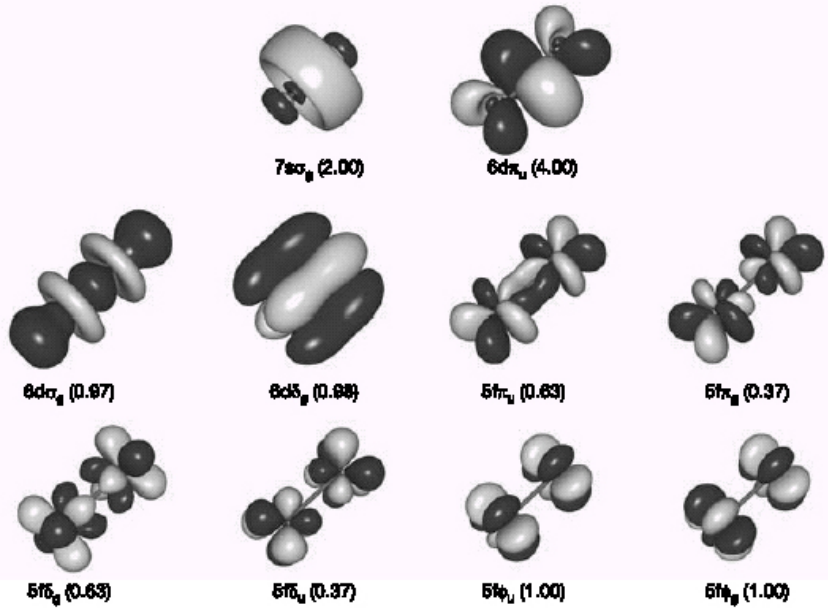
I. Motivation

Electronic structure studies

Systems:

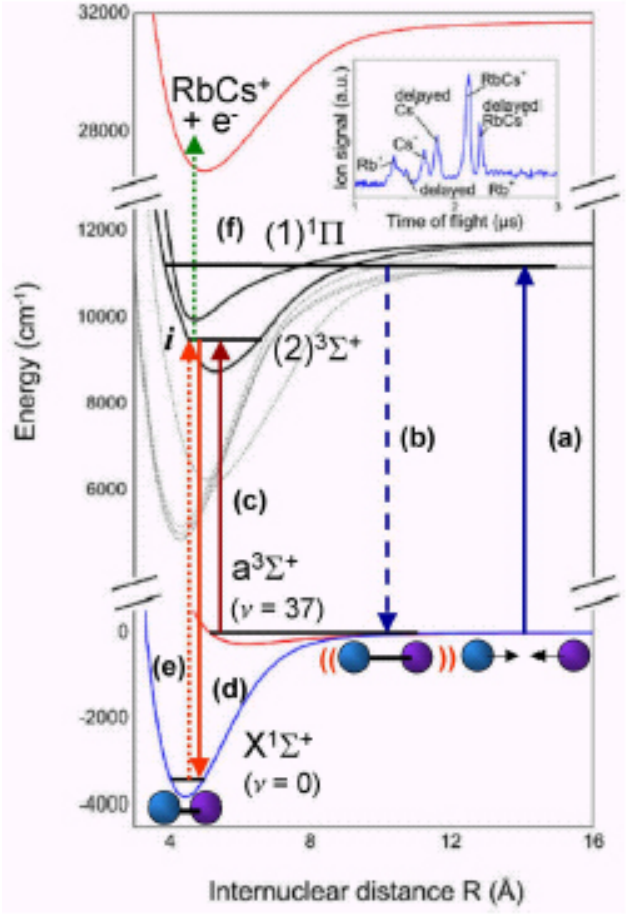
Small molecules with heavy atoms

Small actinide compounds



U_2 molecule; Roos et al., Nature (2005)

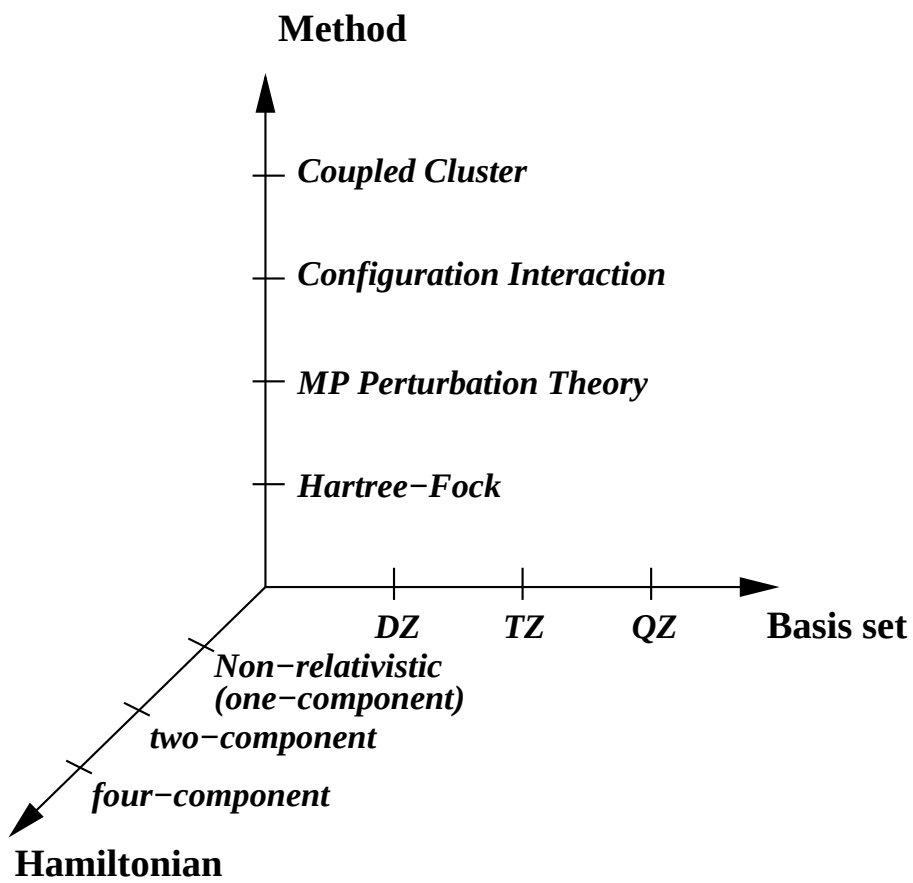
"Ultracold" molecules



$(Rb\text{-}Cs)^+$; J.M. Sage et al., Phys Rev Lett (2005)

I. Introduction

Wave-Function Methods: Controlled Accuracy



- **Electron Correlation:**
  Rigorous many-particle theories, here Coupled Cluster model
  General-order expansions
- **Hamiltonian:**
  4-Component Relativistic Hamiltonian
- **Basis set expansion:**
  Large one-particle basis sets: Typical angular momenta
  $s\,p\,d\,f\,g\,h\,(i)$

Kinetic balance condition[1] for kinetic energy $(c\boldsymbol{\sigma}\cdot\boldsymbol{p})^2$

$\longrightarrow$ Additional high-ℓ basis set for ψ^S

[1] R. E. Stanton and S. Havriliak, J Chem Phys **84** (1981) 1910

I. General Motivation

. . . for New Methodology

- Many open shells (d, f elements)

  $\longrightarrow$ Multi-reference methods (flexibility)

  $\longrightarrow$ Universal applicability !

- High density of states is typical

  $\longrightarrow$ Rigorous approaches (SOC $a\ priori$)

- High reliability / systematic improvements

  $\longrightarrow$ Series of approximations (CCSD,CCSDT,CCSDTQ,. . .)

- Many electrons to correlate

  $\longrightarrow$ Efficient large-scale techniques

Electron correlation problem is of major concern.

II. 4-/2-Component Relativistic Methodology

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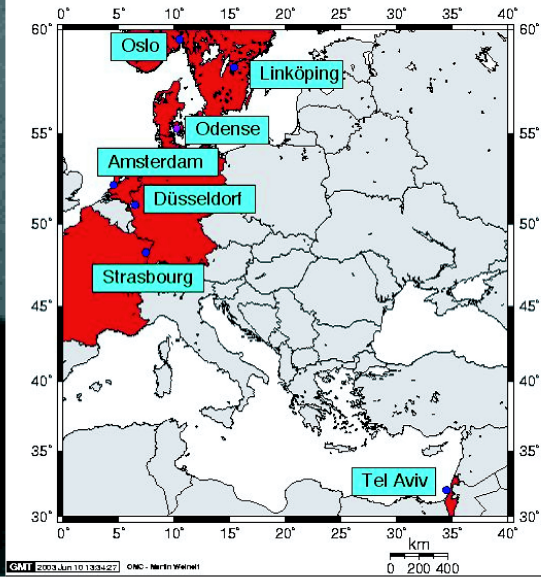
Quantum chemistry program package

P rogram
• for
A tomic
• and
M olecular

D irect
I terative
R elativistic
A ll-electron
C alculations



H J Aa Jensen, Odense

T Saue, Strasbourg

L Visscher, Amsterdam

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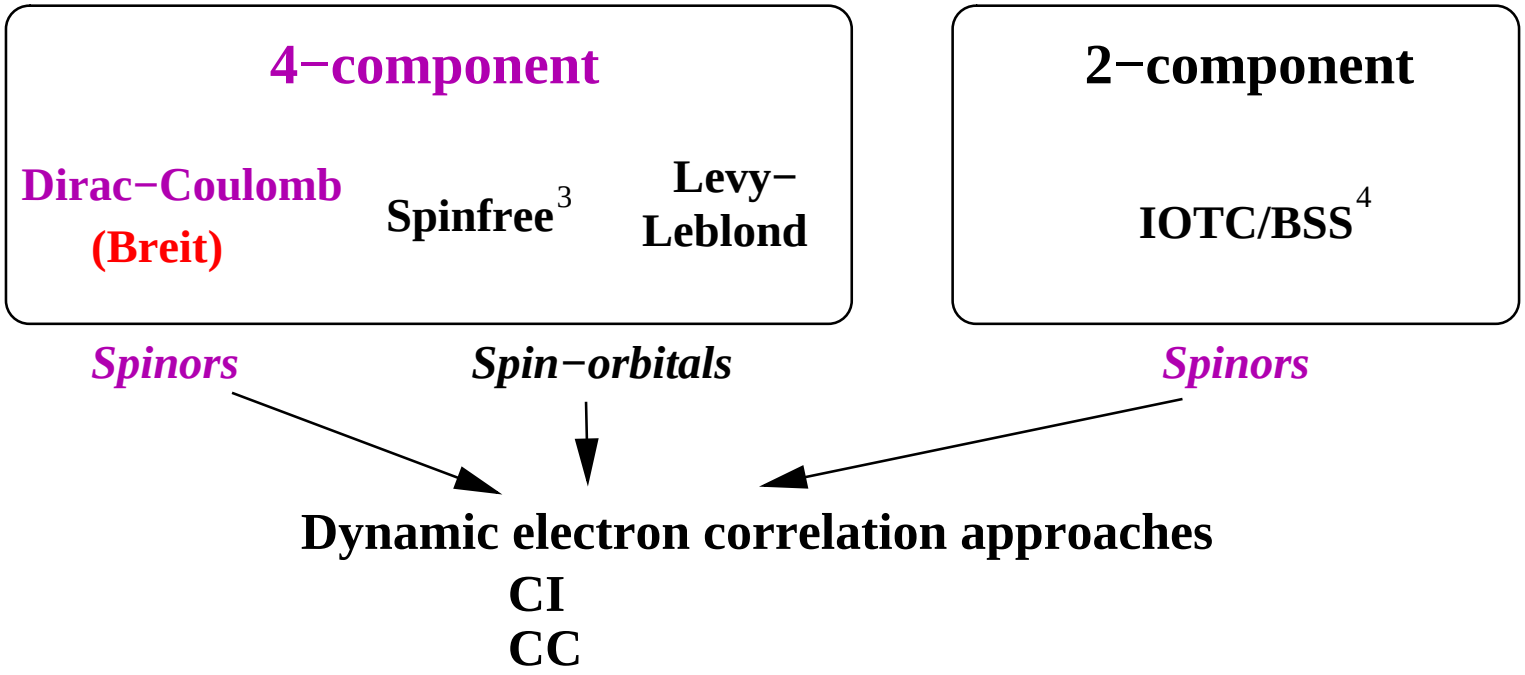
T Fleig, Düsseldorf

U Kaldor, E Eliav, Tel Aviv

P Norman, Linköping

II. 4-/2-Component Relativistic Methodology

Hamiltonians



Spinors:

- Rigorous treatment of spin-orbit interaction
- Shorter correlation expansions[2]

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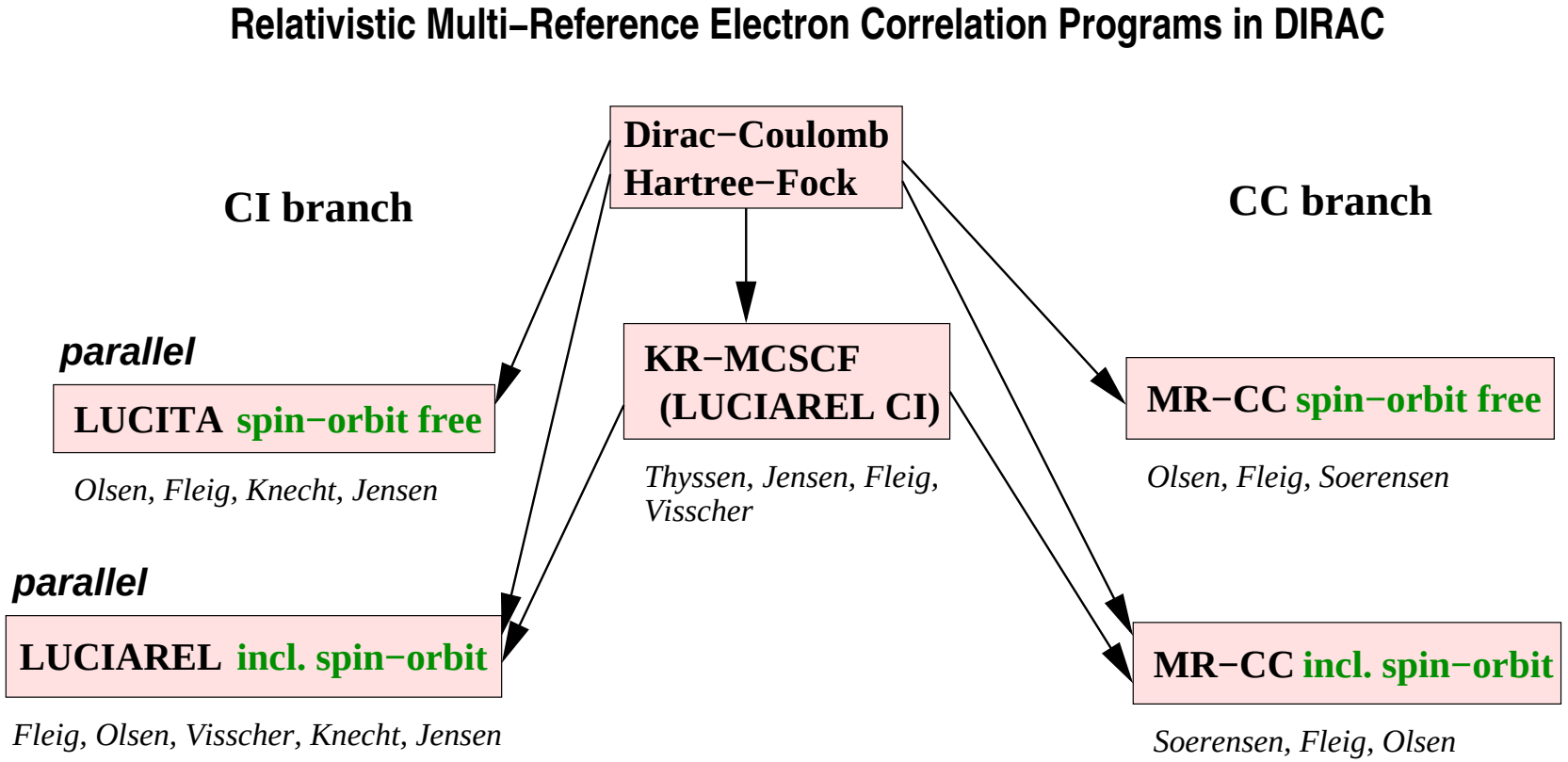
[2] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) 2963

[3] K.G. Dyall, J Chem Phys **100** (1994) 2118

[4] M. Ilias, T. Saue, J Chem Phys **126** (2007) 064102
H.J.Aa. Jensen, M. Ilias, unpublished.

II. 4-/2-Component Methodology[5 6 7 8 9 10]



[5] T. Fleig, L. Visscher, Chem Phys **311** (2005) *113*

[6] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) *2963*

[7] J Thyssen, H. J. Aa. Jensen, T. Fleig, J Chem Phys (2007) submitted.

[8] T. Fleig, H. J. Aa. Jensen, J. Olsen, L. Visscher, J Chem Phys **124,10** (2006) *104106*

[9] T. Fleig, L. K. Sørensen, J. Olsen, Theo Chem Acc **118,2** (2007) *347*

[10] S. Knecht, H. J. Aa. Jensen, T. Fleig, J Comput Phys (2007), submitted.

II. Relativistic Formalism

Time-Reversal Symmetry

General concept: Kramers-paired spinors

One-particle functions:

$$\begin{array}{ll} \hat{K}\,\phi_i = \phi_{\bar{i}} & \hat{K}\,\varphi_i\,\alpha = \varphi_i^*\,\beta \\ \hat{K}\,\phi_{\bar{i}} = -\phi_i & \hat{K}\,\varphi_i^*\,\beta = -\varphi_i\,\alpha \end{array}$$

$$\begin{aligned} \hat{K}\,|\Psi\rangle &= \left\{ \prod_{i=1}^{n} \hat{K}(i) \right\} a^\dagger_{1\,\beta}{}^{\alpha} a^\dagger_{2\,\beta}{}^{\alpha} \ldots a^\dagger_{i\,\beta}{}^{\alpha} \ldots a^\dagger_{n\,\beta}{}^{\alpha} \,|\,\rangle \\ &= \pm a^\dagger_{1\,\alpha}{}^{\beta} (\pm) a^\dagger_{2\,\alpha}{}^{\beta} \ldots (\pm) a^\dagger_{i\,\alpha}{}^{\beta} \ldots (\pm) a^\dagger_{n\,\alpha}{}^{\beta} \,|\,\rangle \end{aligned}$$

with $\hat{K}(i) a^\dagger_{i\,\beta}{}^{\alpha} = \pm a^\dagger_{i\,\alpha}{}^{\beta}$, as $\hat{K}^2 = (-\mathbf{1})^n$

- Determinant decomposed into

  1 unbarred (Kramers up) string $a_i^\dagger a_j^\dagger a_k^\dagger \ldots$

  1 barred (Kramers down) string $a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

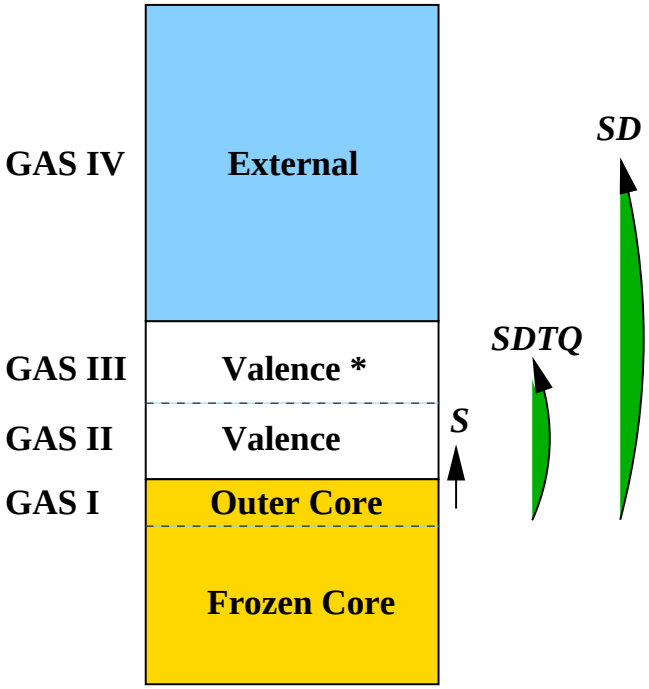
- Auxiliary quantum number M_K

Many-particle state	M_K
$a_i^\dagger \,\|\,\rangle$	$+\frac{1}{2}$
$a_{\bar{j}}^\dagger a_{\bar{k}}^\dagger \,\|\,\rangle$	-1
etc.	etc.

Labelling of operators, e.g.
$a_{\bar{i}}^\dagger a_{\bar{j}}^\dagger, a_k a_{\bar{l}}$, $\Delta M_K = -1$

II. Relativistic Formalism

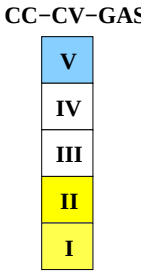
Generalized Active Spaces



GAS concept

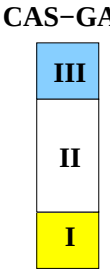
Full and restricted subspace expansions

Flexible expansions



Adaptation to problem

Efficient expansions



Concise MR spaces

- $\Rightarrow$ Mapping of excitation classes
- $\Rightarrow$ Couplings depend on occupation blocks

II. Relativistic Formalism

Excitation Classes

Dirac-Coulomb Hamiltonian:

$$
\begin{aligned}
\hat{H}_{DC} = & \sum_{ij}\left[h_{ij}\hat{X}^{+}_{ij} + \tfrac{1}{2}\left(h_{\bar{i}\bar{j}}\hat{X}^{+}_{\bar{i}\bar{j}} + h_{i\bar{j}}\hat{X}^{+}_{i\bar{j}}\right)\right] \\
& + \tfrac{1}{2}\sum_{ijkl}\left[(ij|kl)x^{++}_{ijkl} + (\bar{i}j|kl)x^{++}_{\bar{i}jkl}\right. \\
& \left. + (i\bar{j}|kl)x^{++}_{i\bar{j}kl}\right] \\
& + \tfrac{1}{4}\sum_{ijkl}(\bar{i}j|k\bar{l})x^{++}_{\bar{i}jk\bar{l}} \\
& + \tfrac{1}{8}\sum_{ijkl}\left[(\bar{i}j|\bar{k}l)x^{++}_{\bar{i}j\bar{k}l} + (i\bar{j}|k\bar{l})x^{++}_{i\bar{j}k\bar{l}}\right]
\end{aligned}
$$

operator	integral class	Kramers flip type
$a^{\dagger}_{i}a_{j}$	h_{ij}	$\Delta M_K = 0$
$a^{\dagger}_{\bar{i}}a_{\bar{j}}$	$h_{\bar{i}\bar{j}}$	$\Delta M_K = 0$
$a^{\dagger}_{i}a^{\dagger}_{k}a_{l}a_{j}$	$(ij\|kl)$	$\Delta M_K = 0$
$a^{\dagger}_{i}a^{\dagger}_{\bar{k}}a_{l}a_{\bar{j}}$	$(i\bar{j}\|\bar{k}l)$	$\Delta M_K = 0$
$\ldots$	$\ldots$	$\ldots$
$a^{\dagger}_{i}a_{\bar{j}}$	$h_{i\bar{j}}$	$\Delta M_K = +1$
$a^{\dagger}_{\bar{i}}a_{j}$	$h_{\bar{i}j}$	$\Delta M_K = -1$
$a^{\dagger}_{i}a^{\dagger}_{k}a_{l}a_{\bar{j}}$	$(i\bar{j}\|kl)$	$\Delta M_K = +1$
$a^{\dagger}_{i}a^{\dagger}_{k}a_{\bar{l}}a_{\bar{j}}$	$(i\bar{j}\|k\bar{l})$	$\Delta M_K = +2$
$\ldots$	$\ldots$	$\ldots$

GAS

IV	$\mathbf{a^{+}_{i}}$ $\mathbf{a^{+}_{\bar{j}}}$
III	
II	$\mathbf{a_{l}}$
I	$\mathbf{a_{k}}$

Operator type

$+$ Occupation type

$\Longrightarrow$ Excitation class

II. General Coupled-Cluster Theory

Notation

CC parameterization:

$$|CC\rangle = \left[\prod_{AI}\left(1+t_I^A\hat{\tau}_I^A\right)\right]\left[\prod_{\substack{A>B\\I>J}}\left(1+t_{IJ}^{AB}\hat{\tau}_{IJ}^{AB}\right)\right]\cdot\ldots|\mathrm{HF}\rangle$$

$$= e^{\left(\sum_{AI} t_I^A\hat{\tau}_I^A + \sum_{\substack{A>B\\I>J}} t_{IJ}^{AB}\hat{\tau}_{IJ}^{AB}+\ldots\right)}|\mathrm{HF}\rangle = e^{\hat{T}}|\mathrm{HF}\rangle$$

In practical terms: $\hat{T} = \sum_i^N \hat{T}_i$

Definition of a model theory, e.g. CCSDT:

$$\hat{T} = \sum_i^3 \hat{T}_i \quad \Rightarrow \quad e^{\hat{T}}|\mathrm{HF}\rangle = e^{\hat{T}_1+\hat{T}_2+\hat{T}_3}|\mathrm{HF}\rangle$$

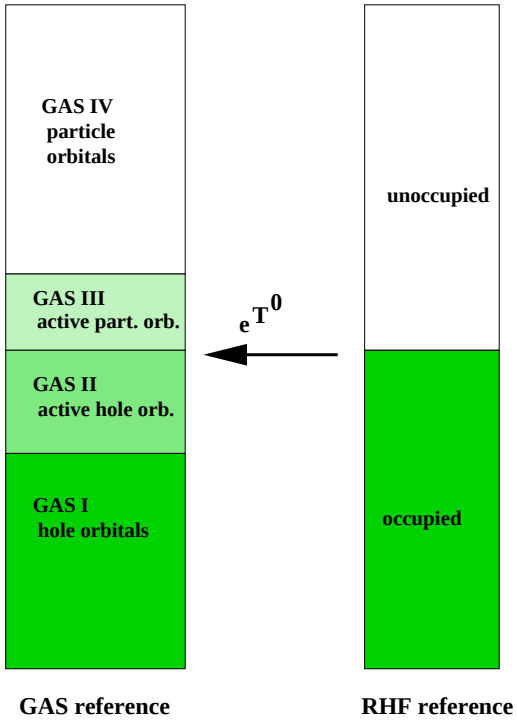
$$\langle\mu_{\mathrm{CCSDT}}| = \langle\mathrm{HF}|\left\{\hat{\tau}_{\mu_1}^\dagger,\hat{\tau}_{\mu_2}^\dagger,\hat{\tau}_{\mu_3}^\dagger\right\}$$

II. Relativistic Methodology

The Multi-Reference Coupled Cluster Approach

State-Selective (SS) GAS MRCC Method[11]

- Extended excitation manifold
  $\langle \mu_{\mathrm{MR}}| = \langle \mathrm{RHF}|\, \hat{\tau}_0^\dagger$
  $\langle \mu_{\mathrm{SSCC}}| = \langle \mu_{\mathrm{MR}}| \left\{ \hat{\tau}_{\mu_1}^\dagger, \hat{\tau}_{\mu_2}^\dagger, \ldots, \hat{\tau}_{\mu_N}^\dagger \right\}$
- Higher excitations included, e.g. in MRCCSD
  $\langle \mu_{\mathrm{SSCCSD}}| = \langle \mu_{\mathrm{MR}}| \left\{ \hat{\tau}_{\mu_1}^\dagger, \hat{\tau}_{\mu_2}^\dagger \right\}$
  contains some Q excitations
- GAS expansion (formally) replaces single-determinant reference
  $|\mathrm{SSCC}\rangle = e^{\sum_\mu t_\mu^i \hat{\tau}_\mu^i} |\mathrm{GAS}\rangle$



State-selective: "memory" of original reference state

[11] J. Olsen, J Chem Phys **113** (2000) 7140

II. Kramers-Unrestricted MRCC Implementation

Relativistic excitation operators

- Generalization of cluster operators:

$$\hat{T}_1 = \sum_{ia} \left\{ t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \right\}$$

$$\hat{T}_2 = \sum_{\substack{i<j \\ a<b}} \left\{ t_{ij}^{ab} \hat{\tau}_{ij}^{ab} + t_{\bar{i}\bar{j}}^{ab} \hat{\tau}_{\bar{i}\bar{j}}^{ab} \ldots + t_{\bar{i}j}^{\bar{a}b} \hat{\tau}_{\bar{i}j}^{\bar{a}b} \ldots \right\} \qquad \text{with } \hat{\tau}_{\bar{i}}^{a} := \hat{a}_a^\dagger \hat{a}_{\bar{i}}$$

$$\hat{T}_3 = \ldots$$

- Implications:
  - $\varphi_i, \varphi_a \ldots$ spinorbitals: $\equiv$ inclusion of spin-orbit interaction
  - General case: *Kramers-paired* spinors
  - *No* Kramers restriction at *many-particle* level

    $\longrightarrow$ Kramers contamination

II. Kramers-Unrestricted MRCC Implementation

CI-expansion based evaluation of the CC vector function

$$\Omega_\mu = \left\langle \mu \left| e^{-\hat{T}} \hat{H} e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$$

1. $|a\rangle = e^{\hat{T}} |\mathrm{Ref}\rangle = \left(\sum_{n=0} \frac{1}{n!} \hat{T}^n \right) |\mathrm{Ref}\rangle$

2. $|b\rangle = \hat{H} |a\rangle$ (CI sigma vectors)

3. $|c\rangle = e^{-\hat{T}} |b\rangle = \left(\sum_{n=0} \frac{(-1)^n}{n!} \hat{T}^n \right) |b\rangle$

4. $\Omega_\mu = \langle \mu | c \rangle = \left\langle \mathrm{Ref} \left| \hat{\tau}_\mu^\dagger \right| c \right\rangle$ (CI density matrices)

Implementation via 4-component CI code: **LUCIAREL CI** [12]

[12] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) 2963

II. Ingredients for Steps 2 and 4

Rel. CI Technology

with $A^{\mathcal{T}\overline{\mathcal{T}},\mathcal{S}\overline{\mathcal{S}}}_{i\bar{j}k\bar{l}} = \left\langle \mathcal{T}^\dagger, \overline{\mathcal{T}}^\dagger | a_i^\dagger a_k^\dagger a_{\bar{l}} a_{\bar{j}} | \mathcal{S}^\dagger, \overline{\mathcal{S}}^\dagger \right\rangle$

Calculation of σ vectors

Example:

$$\sigma^{+2}(\mathcal{T}^\dagger\overline{\mathcal{T}}^\dagger) = \sum_{ijkl} \sum_{\mathcal{S},\overline{\mathcal{S}}} (i\bar{j}|k\bar{l})\, A^{\mathcal{T}\overline{\mathcal{T}},\mathcal{S}\overline{\mathcal{S}}}_{i\bar{j}k\bar{l}}\, C_{\mathcal{S},\overline{\mathcal{S}}}$$

Contraction with integrals

Input: Integrals
Output: σ vector

(Transition) density matrices

Example:

$$\rho_2(i\bar{j}k\bar{l}) = \sum_{\mathcal{T},\overline{\mathcal{T}}} \sum_{\mathcal{S},\overline{\mathcal{S}}} C_{\mathcal{T},\overline{\mathcal{T}}}\, A^{\mathcal{T}\overline{\mathcal{T}},\mathcal{S}\overline{\mathcal{S}}}_{i\bar{j}k\bar{l}}\, C_{\mathcal{S},\overline{\mathcal{S}}}$$

Contraction with coefficients

Input: Left coefficient vector
Output: Density matrices

- Handling of general operators possible
- Concise code for various tasks (CI[13], MCSCF[14], CC)

[13] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) 2963
[14] T. Fleig, H.J.Aa. Jensen, J. Olsen, L. Visscher, J Chem Phys **124** (2006) 104106

II. Kramers-Unrestricted MRCC Implementation

Steps 1,2

1. **Expansion** $$|a\rangle = \left(\sum_{n=0} \frac{1}{n!}\hat{T}^n\right)|\mathrm{Ref}\rangle$$
$$= |\mathrm{Ref}\rangle + \hat{T}|\mathrm{Ref}\rangle + \frac{1}{2}\hat{T}\left\{\hat{T}|\mathrm{Ref}\rangle\right\} + \frac{1}{6}\ldots$$

   ("sigma vector" expansion) with current iteration's (k) amplitudes $t_\mu^{(k)}$ truncated at excitation level $N+2$ if $\langle\mu_N|$ is projection manifold.

2. **Sigma vector** $|b\rangle = \hat{H}|a\rangle$ linear transformation

   Sample partition (for $M_K = +2$, 2-particle):

$$\hat{H}^{(M_K=+2)}|a\rangle = \sigma^{+2}(\mathcal{T}^\dagger, \overline{\mathcal{T}^\dagger}) = \sum_{\substack{i\geq k\\ l\geq j}}\sum_{\mathcal{S}}\left\langle\mathcal{T}^\dagger|a_i^\dagger a_k^\dagger|\mathcal{S}^\dagger\right\rangle\sum_{\overline{\mathcal{S}}}\left\langle\overline{\mathcal{T}}^\dagger|a_{\bar{l}}a_{\bar{j}}|\overline{\mathcal{S}}^\dagger\right\rangle$$
$$\cdot\left[(i\bar{j}|k\bar{l}) - (k\bar{j}|i\bar{l})\right]C_{\mathcal{S},\overline{\mathcal{S}}}$$

II. Kramers-Unrestricted MRCC Implementation

Steps 3,4

3. **Expansion**

$$|c\rangle = \left(-\sum_{n=0} \frac{1}{n!}\hat{T}^n\right)|b\rangle$$
$$= |b\rangle - \hat{T}|b\rangle + \frac{1}{2}\hat{T}\left\{\hat{T}|b\rangle\right\} - \frac{1}{6}\ldots$$

with current iteration's (k) amplitudes $t_\mu^{(k)}$
truncation considering excitation manifold.

4. **Transition densities**

$\Omega_\mu = \langle\mu|c\rangle = \left\langle \mathrm{Ref}\left|\hat{\tau}_\mu^\dagger\right| c\right\rangle$

$C_{\mathcal{T},\overline{\mathcal{T}}}$ is a unit vector.

Transition density matrices

$$\rho_2(i\bar{j}k\bar{l}) = \sum_{\mathcal{T},\overline{\mathcal{T}}}\sum_{\mathcal{S},\overline{\mathcal{S}}} C_{\mathcal{T},\overline{\mathcal{T}}}\, A_{i\bar{j}k\bar{l}}^{\mathcal{T}\overline{\mathcal{T}},\mathcal{S}\overline{\mathcal{S}}}\, C_{\mathcal{S},\overline{\mathcal{S}}}$$

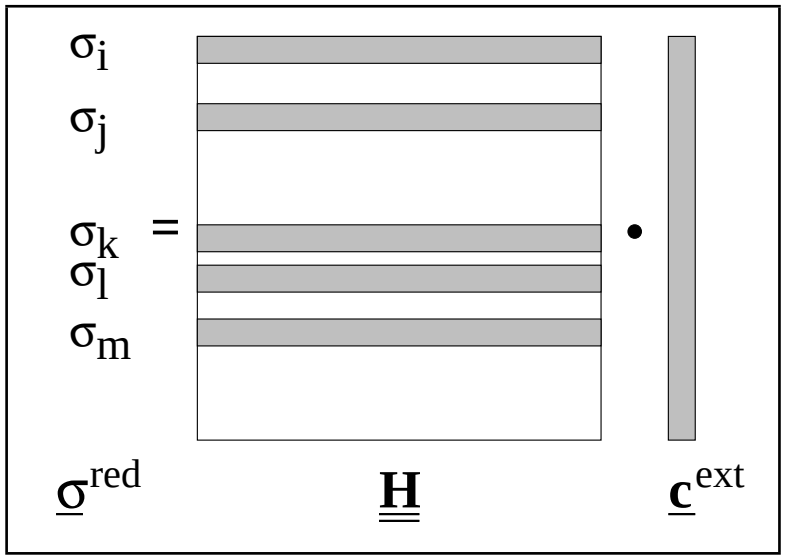
Contraction with coefficients

II. CI-Based MRCC Algorithm

Efficiency ?

$$\Omega_\mu = \left\langle \mu \left| e^{-\hat{T}} \hat{H} e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$$

- $e^{-\hat{T}}$ never decreases excitation rank (just as $e^{\hat{T}}$) !
- $\Rightarrow \hat{H} e^{\hat{T}} |\mathrm{Ref}\rangle$ required to be **inside** space of excitation manifold $\langle \mu |$
- $\hat{H}$ may have de-excitation rank of 2
- Therefore:
  $\hat{H} e^{\hat{T}} |\mathrm{Ref}\rangle$ CI problem with extended space!
- $\Rightarrow$ e.g. CCSD requires a CISDTQ linear transformation.
- Initial implementation $O^{n+2}V^{n+2}$
  Conventional CC: $O^{n}V^{n+2}$



III. CI-Based MRCC

Test case HBr

T. Fleig, L. K. Sørensen, J. Olsen, *Theo. Chem. Acc.* **118** (2007) *347*

Problem:

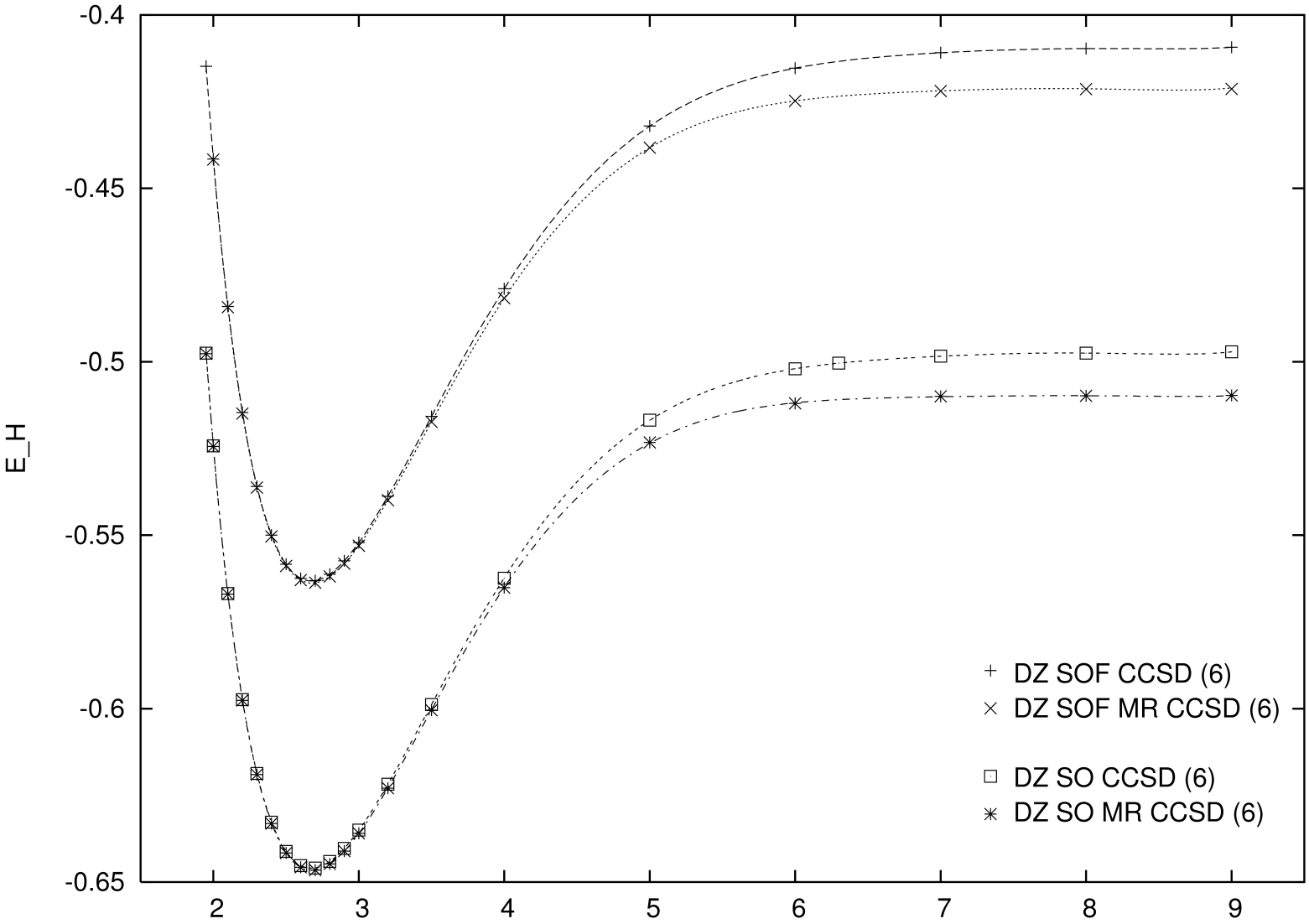
- Influence of SO interaction on ground-state spectral constants
- Molecular dissociation with/without multi-reference Ansatz
- Effect of higher excitations (than CC doubles)

Setup

- Uncontracted cc-pVDZ/cc-pVTZ basis sets, cutoff 10 a.u.
- Dirac-Coulomb/Spinfree Hamiltonian
- Correlated orbitals: $\sigma_{sp}, 2\pi, \sigma^*_{sp}$ (6 el.), + Br $4s$ (8 el.)
- CCSD (6/8), Single Reference (SR) and Multi Reference (MR) CI/CC
- MR space: CAS 6/8 in 4 orbitals/Kramers pairs

III. CI-Based MRCC

Application to HBr



III. CI-Based MRCC

Application to HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
DZ SO CCSDT (6)	1.4159	2690.8	3.74
DZ SO MRCISD (6)	1.4173	2678.7	3.72
DZ SO MRCCSD (6)	1.4173	2685.2	3.73
TZ SOF MRCISD (6)	1.4145	2675.1	4.04
TZ SOF MRCCSD (6)	1.4148	2675.1	4.05
TZ SO MRCISD (6)	1.4151	2668.4	3.90
TZ SO MRCCSD (6)	1.4154	2668.0	3.90
TZ SOF MRCISD (8)	1.4180	2641.4	3.90
TZ SOF MRCCSD (8)	1.4192	2637.1	3.90
TZ SOF CCSDT (8)	1.4178	2647.3	3.96
TZ SO MRCISD (8)	1.4187	2634.9	3.77
TZ SO MRCCSD (8)	1.4193	2630.6	3.76
TZ SOF CCSDT (18)	1.4142	2663.9	4.01
TZ SOF CCSDT (18) $+\Delta_{SO}$	1.4143	2657.4	3.87
Exp. (Huber, Herzberg 1979)	1.4144	2649.0	3.92

SR $\longrightarrow$ MR:

Bond length: $+0.002$ Å

Frequency: -13 cm^{-1}

D_e: -0.3 eV

III. CI-Based MRCC

Application to HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
DZ SO CCSDT (6)	1.4159	2690.8	3.74
DZ SO MRCISD (6)	1.4173	2678.7	3.72
DZ SO MRCCSD (6)	1.4173	2685.2	3.73
TZ SOF MRCISD (6)	1.4145	2675.1	4.04
TZ SOF MRCCSD (6)	1.4148	2675.1	4.05
TZ SO MRCISD (6)	1.4151	2668.4	3.90
TZ SO MRCCSD (6)	1.4154	2668.0	3.90
TZ SOF MRCISD (8)	1.4180	2641.4	3.90
TZ SOF MRCCSD (8)	1.4192	2637.1	3.90
TZ SOF CCSDT (8)	1.4178	2647.3	3.96
TZ SO MRCISD (8)	1.4187	2634.9	3.77
TZ SO MRCCSD (8)	1.4193	2630.6	3.76
TZ SOF CCSDT (18)	1.4142	2663.9	4.01
TZ SOF CCSDT (18) $+\Delta_{SO}$	1.4143	2657.4	3.87
Exp. (Huber, Herzberg 1979)	1.4144	2649.0	3.92

SOC:

Bond length: $+0.0005$ Å

Frequency: -7 cm^{-1}

D_e: -0.15 eV

III. CI-Based MRCC

Application to HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
DZ SO CCSDT (6)	1.4159	2690.8	3.74
DZ SO MRCISD (6)	1.4173	2678.7	3.72
DZ SO MRCCSD (6)	1.4173	2685.2	3.73
TZ SOF MRCISD (6)	1.4145	2675.1	4.04
TZ SOF MRCCSD (6)	1.4148	2675.1	4.05
TZ SO MRCISD (6)	1.4151	2668.4	3.90
TZ SO MRCCSD (6)	1.4154	2668.0	3.90
TZ SOF MRCISD (8)	1.4180	2641.4	3.90
TZ SOF MRCCSD (8)	1.4192	2637.1	3.90
TZ SOF CCSDT (8)	1.4178	2647.3	3.96
TZ SO MRCISD (8)	1.4187	2634.9	3.77
TZ SO MRCCSD (8)	1.4193	2630.6	3.76
TZ SOF CCSDT (18)	1.4142	2663.9	4.01
TZ SOF CCSDT (18) $+\Delta_{SO}$	1.4143	2657.4	3.87
Exp. (Huber, Herzberg 1979)	1.4144	2649.0	3.92

MRCI $\longrightarrow$ MRCC:

Very similar.

III. CI-Based MRCC

Application to HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
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TZ SOF CCSDT (18) $+\Delta_{SO}$	1.4143	2657.4	3.87
Exp. (Huber, Herzberg 1979)	1.4144	2649.0	3.92

CC correlation:

Bond length: -0.004 Å

Frequency: $+17$ cm^{-1}

D_e: $+0.05$ eV

III. CI-Based MRCC

Application to HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
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TZ SOF CCSDT (18) $+\Delta_{SO}$	1.4143	2657.4	3.87
Exp. (Huber, Herzberg 1979)	1.4144	2649.0	3.92

CC corr. + spin-orbit shift.

Deviation from exp.:

Bond length: -0.0001 Å

Frequency: $+8.4$ cm^{-1}

D_e: -0.05 eV

III. Spin-Orbit Free MRCC

Other Applications

T. Fleig, D. Edvardsson, S. T. Banks, J. H. D. Eland, *Chem. Phys.* **xxx** (2007) *xxx* in press.

Br_2 double photoionization; benchmarks

Method	Correlation	R_e [Å]	ω_e cm^{-1}
DZ SO MRCI	CV $4s$ CAS	2.353	282.7
TZ SOF MRCI	CV $4s$ CAS	2.315	308.0
TZ SO MRCI	CV $4s$ CAS	2.318	306.3
TZ SOF MRCI	CV $3d, 4s$ CAS	2.307	311.4
TZ SOF MRCC	CV $3d, 4s$ CAS	2.305	315.8
TZ SOF MRCC	CC $3d, 4s$ CAS	2.306	312.7
ANO-RCC SOF MRCC	CV $3d, 4s$ CAS	2.286	326.8
Exp.		2.281	325.3

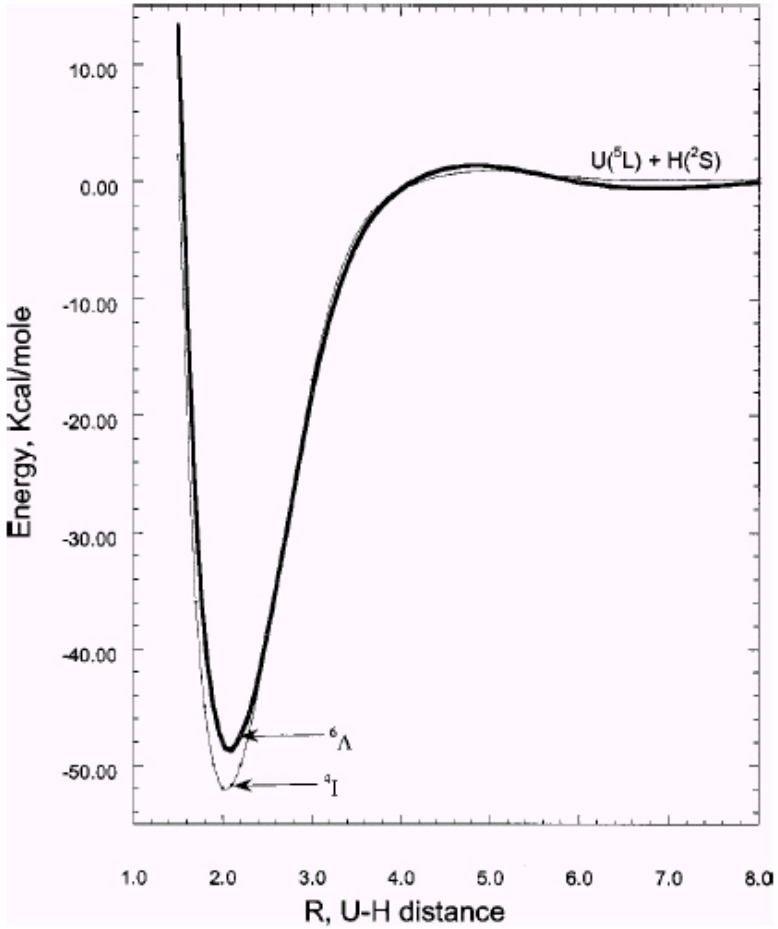
CsLi molecule; complete PECs including T

see Poster **Lasse K. Sørensen**

IV. Initial Application

Ground state of UH Molecule

K. Balasubramanian, W. J. Siekhaus, W. McLean II, *J. Chem. Phys.* **119,12** (2003) *5889*



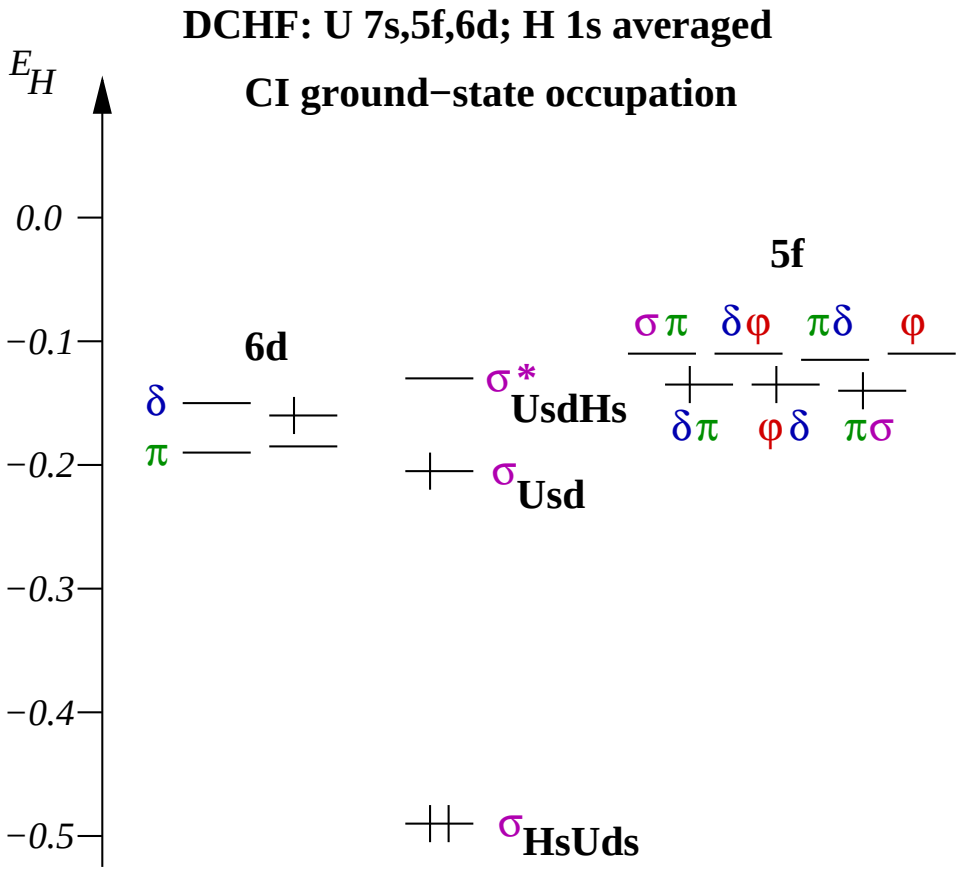
- Ground state ?
  ${}^4I_{\Omega=\frac{15}{2},\frac{13}{2},\frac{11}{2},\frac{9}{2}}$, ${}^6\Lambda_{\frac{21}{2},\frac{19}{2},\frac{17}{2},\frac{15}{2},\frac{13}{2},\frac{11}{2}}$
- Multi-reference character

State	T_e [eV] CASSCF/SOCI	CCSD(T)
${}^4I$	0.0	0.42
${}^6\Lambda$	0.14	0.0

- MRCC including spin-orbit interaction required !

IV. SO CI application to UH

Valence Kramers pairs



7s, 5f, 6d U shells
close in energy

Averaging in full valence space

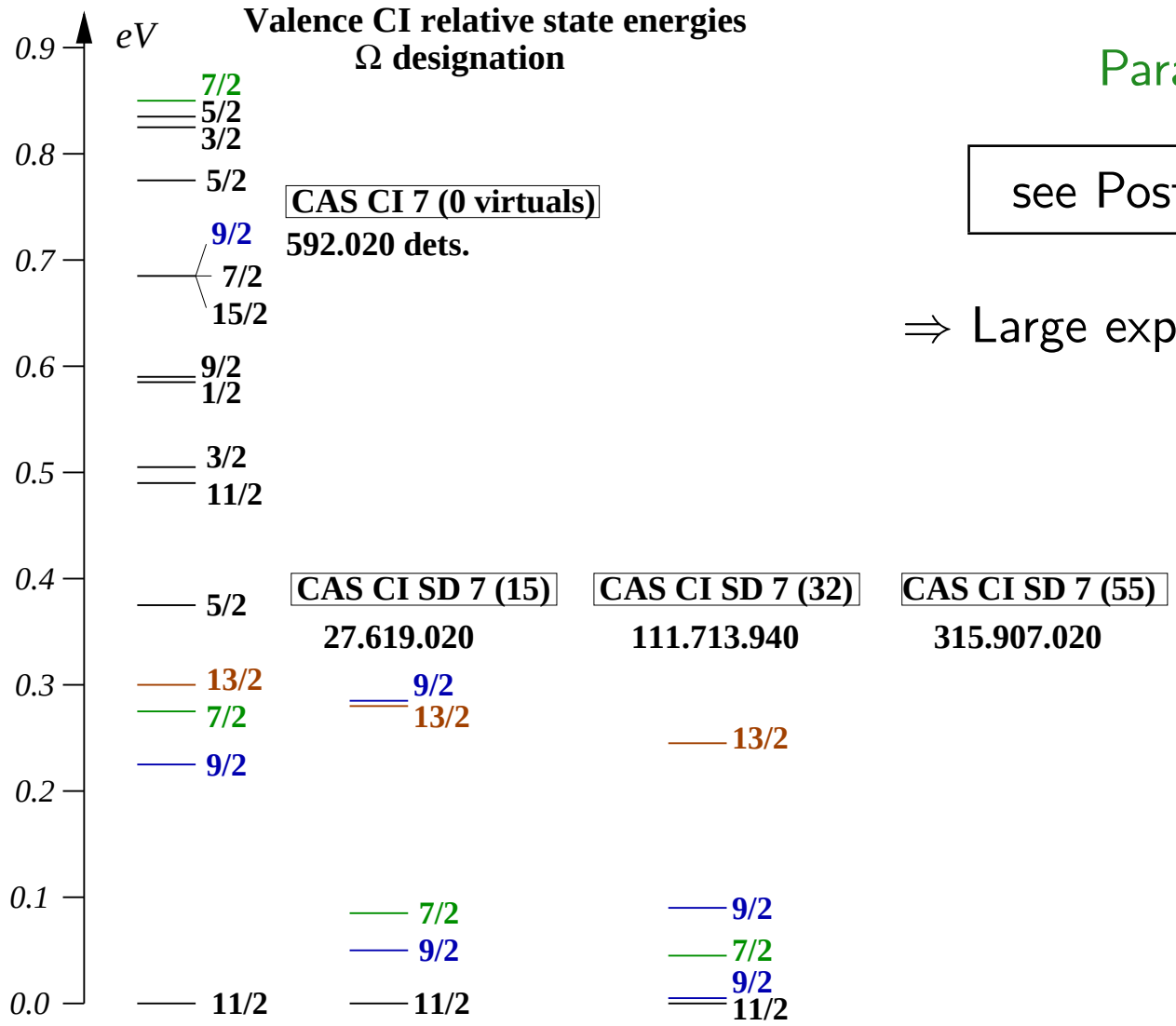
Many unpaired electrons (3,5 ?)

Lower state manifold:
7s^1**, 5f**^{3}**, 6d**^{1}

SOC lifts λs picture

IV. SO CI Application to UH

Vertical electronic spectrum



Parallel LUCIAREL

see Poster **Stefan Knecht**

⇒ Large expansion spaces

GAS CC study:

CI defines reference determinants/spaces

Determination of electronic ground state

V. Improvement

Commutator-Based CC Vector Function

J. Olsen, *unpublished.*

$$\Omega_\mu = \left\langle \mu \left| \left(\hat{H} + \left[\hat{H},\hat{T}\right] + \tfrac{1}{2}\left[\left[\hat{H},\hat{T}\right],\hat{T}\right] + \tfrac{1}{6}\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right] + \tfrac{1}{24}\left[\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right],\hat{T}\right] \right) \right| \mathrm{Ref} \right\rangle$$

- Loop over excitation class of $\hat{H}$
  - Loop over commutator type, e.g. $\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right]$
    - Loop over excitation types $\hat{T}_i$ of occurring $\hat{T}$ operators

      ! Check for coupling with $\langle\mu|$

      Yes? Contract with integrals

- Modular form: Replaces CI-driven vector function
- Relativistic generalization: Modify $\hat{H}$ excitation classes, $\hat{T}_i$ excitation types
- Introduce real/imaginary handling

V. Improvement

Kramers-Restricted Formulation

- General open-shell case: $\left[\hat{K}, \hat{T}\right] \neq 0$
- Condition on amplitudes from unlinked amplitude equation
  $\left\langle \mu \left| \hat{K} e^{\hat{T}} \right| \mathrm{HF} \right\rangle = \left\langle \mu \left| e^{\hat{T}} \right| \overline{\mathrm{HF}} \right\rangle \Rightarrow \left\langle \mu \left| \left[\hat{K}, e^{\hat{T}}\right] \right| \mathrm{HF} \right\rangle = 0$
- Evaluation delivers amplitude conditions

$$t_i^a = t_{\bar{i}}^{\bar{a}*} \qquad t_i^{\bar{a}} = -t_{\bar{i}}^{a*}$$
$$t_{ij}^{ab} = t_{\bar{i}\bar{j}}^{\overline{ab}*} \qquad t_{\bar{i}j}^{ab} = -t_{i\bar{j}}^{\overline{ab}*} \qquad \ldots$$
$$t_{ijk}^{abc} = t_{\bar{i}\bar{j}\bar{k}}^{\overline{abc}*} \qquad \ldots$$
$$\ldots$$

Even number of bars:
Kramers barring, $+$ sign

Odd number of bars:
Kramers barring, $-$ sign

- $\Rightarrow$ Removal of Kramers contamination (analogy: spin contamination)
- $\Rightarrow$ Reduction of free parameters (analogy: spin restriction[15])

[15] P G Szalay and J Gauss, J Chem Phys **107** (1997) 9028

V. Improvement

Kramers-Adapted Formulation

- Use of generalized $\hat{E}$ operators from non-relativistic theory

$$\hat{E}^{+}_{pq} := p^{\dagger}q + \overline{p}^{\dagger}\overline{q} \qquad \hat{E}^{-}_{pq} := i\left(p^{\dagger}q - \overline{p}^{\dagger}\overline{q}\right)$$
$$\hat{E}^{+}_{\overline{p}q} := \overline{p}^{\dagger}q - p^{\dagger}\overline{q} \qquad \hat{E}^{-}_{\overline{p}q} := i\left(\overline{p}^{\dagger}q + p^{\dagger}\overline{q}\right)$$
$$\hat{E}^{+}_{p\overline{q}} := p^{\dagger}\overline{q} - \overline{p}^{\dagger}q \qquad \hat{E}^{-}_{p\overline{q}} := i\left(p^{\dagger}\overline{q} + \overline{p}^{\dagger}q\right)$$

  which fulfill $\left[\hat{K}, \hat{E}^{\pm}\right] = 0$

- One-particle operator now splits into

$$\mathrm{Re}(\hat{W}) = \sum_{pq} \mathrm{Re}(W_{pq})\hat{E}^{+}_{pq} + \mathrm{Re}(W_{\overline{p}q})\hat{E}^{+}_{\overline{p}q}$$
$$\mathrm{Im}(\hat{W}) = -i\sum_{pq} \mathrm{Im}(W_{pq})\hat{E}^{-}_{pq} + \mathrm{Im}(W_{\overline{p}q})\hat{E}^{-}_{\overline{p}q}$$

- Express $\hat{T}, \hat{H}$ in terms of $\hat{E}^{\pm}$ operators:

$$\hat{T}_1 = \sum_{ia}\left\{\mathrm{Re}(t^{a}_{i})\hat{E}^{+}_{ai} + \mathrm{Re}(t^{\overline{a}}_{i})\hat{E}^{+}_{\overline{a}i} - \imath\mathrm{Im}(t^{a}_{i})\hat{E}^{-}_{ai} - \imath\mathrm{Im}(t^{\overline{a}}_{i})\hat{E}^{-}_{\overline{a}i}\right\}$$

V. Improvement

Kramers-Adapted Formulation

- $\hat{T}_2 = T_2\left(\hat{e}^{++}, \hat{e}^{+-}, \hat{e}^{--}\right)$ etc.
- $\hat{H} = \hat{H}\left(\hat{E}^{\pm}, \hat{e}^{++}, \hat{e}^{+-}, \hat{e}^{--}\right)$
- $\left[\hat{T}_\mu, \hat{T}_\nu\right]$ no longer commuting !
- $\Rightarrow \Omega_\mu = \left\langle \mu \left| e^{\hat{T}} \hat{H} e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$ truncates only after 8th-order commutator (CCSD)
  10th-order commutator (CCSDT)

Feasible implementation of Kramers symmetry

General contraction codes[16]

- Non-commuting model theories
- Truncation of higher-order commutators
- Internal contraction for reduction

[16] J. Olsen, unpublished.

Thanks for your attention!

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FL 356/3-1

IV. Rel. SIGMA/DENSITY Algorithm

- Loop over real/imaginary part of L vector
  - Loop over MK2 value of L vector
    - Loop over real/imaginary part of R vector
      - Loop over MK2 value of R vector
        - Loop over batches of R blocks
          - Loop over individual occupation (GAS) blocks of R
            - Loop over occupation blocks of L

$$\langle \text{L block with defined occupation and MK} \mid O^{+} \mid \text{R block with defined occupation and MK} \rangle$$

- Loop over operator classes (excitation formalism) coupling? If yes:
  - Loop over L unbarred symmetries determines L barred symmetry
    - Loop over R unbarred symmetries determines R barred symmetry
      - Loop over unbarred resolution block symmetries
        - Loop over barred resolution block symmetries
          - Loops over unbarred/barred batches of resolution strings
            - Loop over unbarred annihilation batches

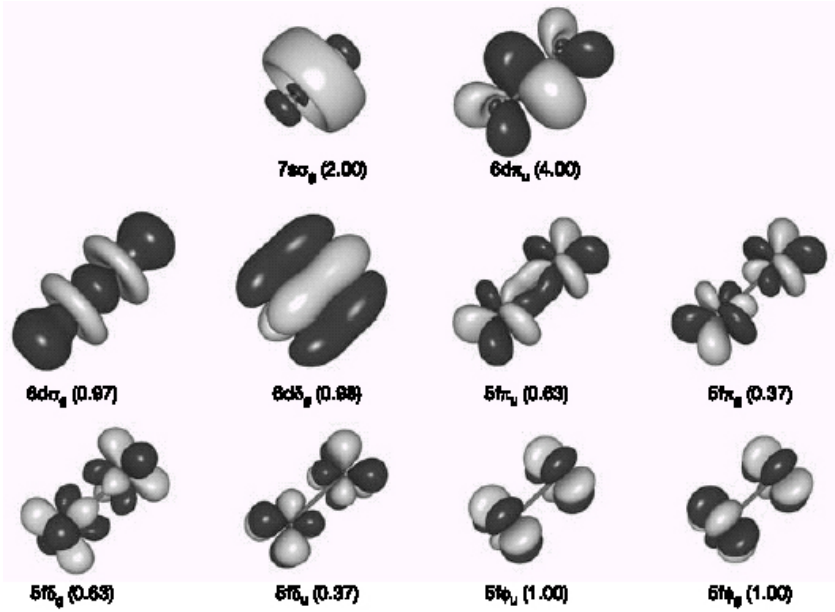
$\langle L \mid a \mid K \rangle$ coupling coefficient

- Loops over unb cre, bar ann, bar cre batches
  - evaluation of coupling coefficients
  - (|) contraction with symmetry block of integrals
  - (if sigma vector)
  - Determine sigma contribution and store

I. Specific Motivation

Multi-Reference Problem

Uranium dimer:[17]



- Electronic ground state:
  $$|\mathrm{MR}\rangle = \sum_{k=1}^{n} c_k \, |D_k\rangle \neq |\mathrm{HF}\rangle$$
- Bond-breaking (dissociation)

Several leading configurations

$$\begin{aligned}\Psi = & \, 0.782(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)^1(6d\delta_g)^1 \; (5f\delta_g)^1(5f\pi_u)^1 \; (5f\varphi_u)^1(5f\varphi_g)^1 \\ & +0.596(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)^1(6d\delta_g)^1 \; (5f\delta_u)^1(5f\pi_g)^1 \; (5f\varphi_u)^1(5f\varphi_g)^1 \\ & + \text{small terms}\end{aligned}$$

- Requirement: Multi-reference Coupled Cluster approaches

[17] L. Gagliardi, B. O. Roos, Nature **433** (2005) 848