# Relativistic Quantum Chemistry to the Limits: Accuracy for the Small and Heavy.

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# Motivation and Scientific Goals

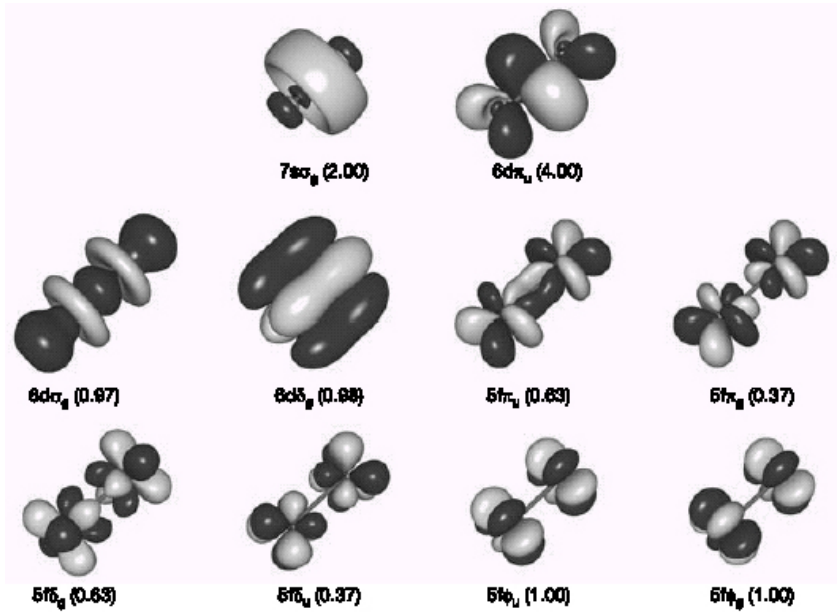
Electronic structure studies

(and derived properties)

**Systems:**

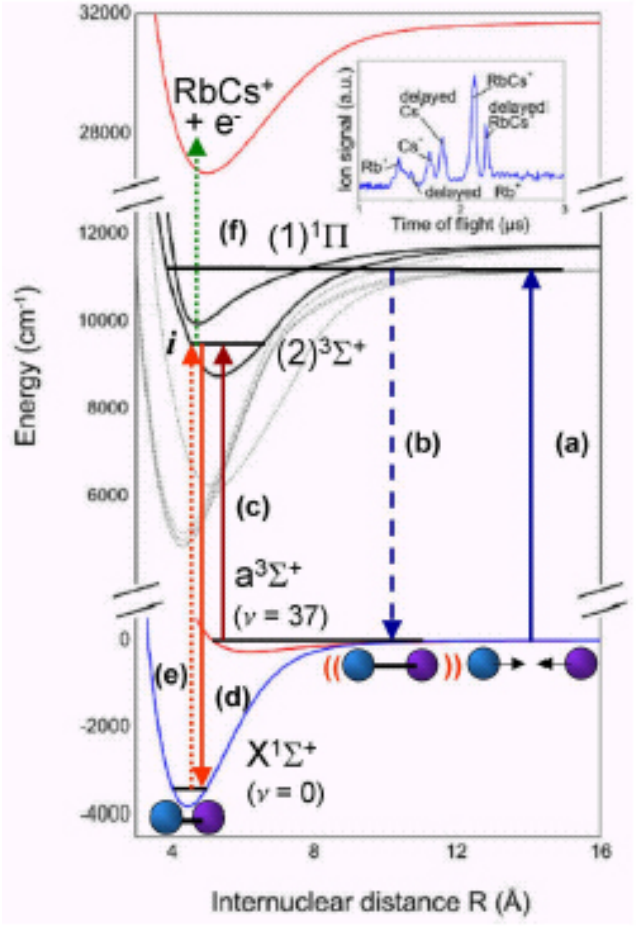
Small heavy-element molecules

## Small actinide compounds




$U_2$ Molecule; B. O. Roos et al., Nature **433** (2005) *848*

## "Ultracold" molecules




(Rb-Cs); D. DeMille et al., Phys Rev Lett **94** (2005) *203001*

# General Principles

## of rigorous methodology

**High density of states**

Electron correlation and special relativity
simultaneously

Spin-orbit interaction *a priori*

**In general many open shells (d, f elements)**

Flexible multi-reference approaches

Universal applicability !

PECs of $Th_2$ (CASPT2)

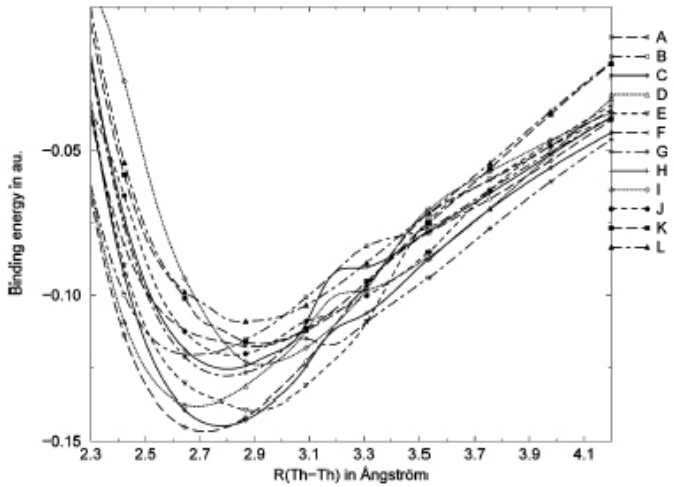



*Figure 3.* CASPT2 potentials for the lowest electronic states of $Th_2$. Labels: A = $^3\Delta_g$, B = $^3\Sigma_g^-$, C = $^1\Sigma_g^+$, D = $^1\Delta_g$, E = $^3\Sigma_u^+$, F = $^3\Delta_u$, G = $^3\Phi_u$, H = $^3\Pi_u$, I = $^1\Phi_g$, J = $^3\Pi_g$, K = $^3\Phi_g$.

B.O. Roos et al., J Am Chem Soc **128** (2006) *17000*

**Dynamic electron correlation for systems with many electrons**

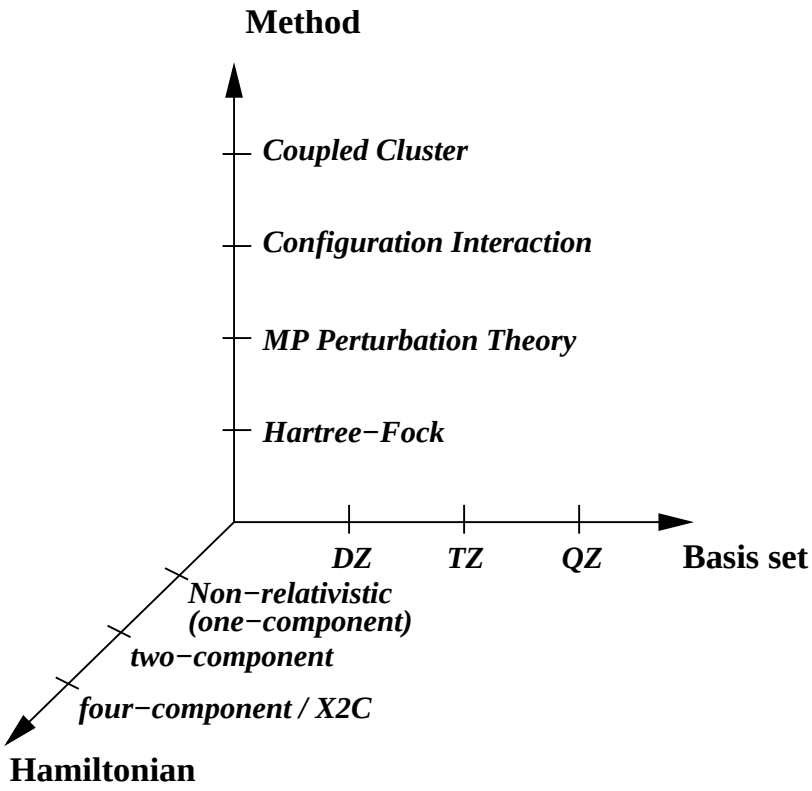
$\longrightarrow$ Efficient methodology; large expansion spaces

**Systematic control of accuracy**

$\longrightarrow$ Series of approximations (MR-CISD, CCSD, CC($4_2$), CCSDT, ...)

# Wave-Function-Based Methodology

## Accurate treatment of heavy-element systems




- **Hamiltonian:**

  *4-/2-component* relativistic
  Dirac-Coulomb or IOTC
  or *scalar/non-relativistic*

- **Electron correlation:**

  Rigorous n-particle theories,
  up to Coupled Cluster models
  *General-order* expansions

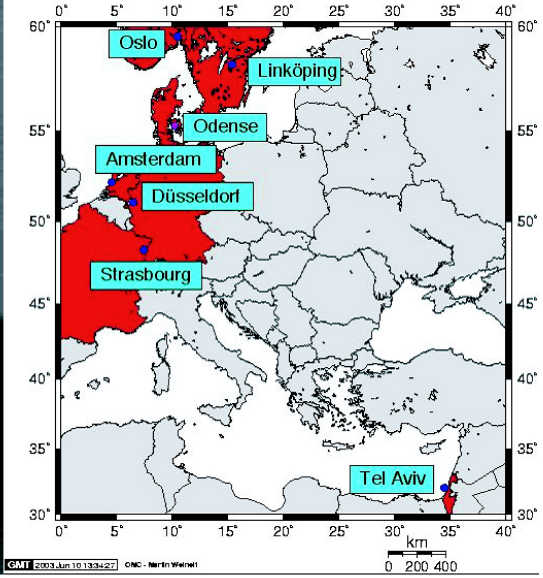
- **Atomic basis set expansions:**

  Typically:
  Necessity to include high angular momenta
  $s\ p\ d\ f\ g\ h\ (i)$

# DIRAC – a European metalaboratory for the development of 4-/2-component quantum chemical methodology

P rogram
• for
A tomic
• and
M olecular

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

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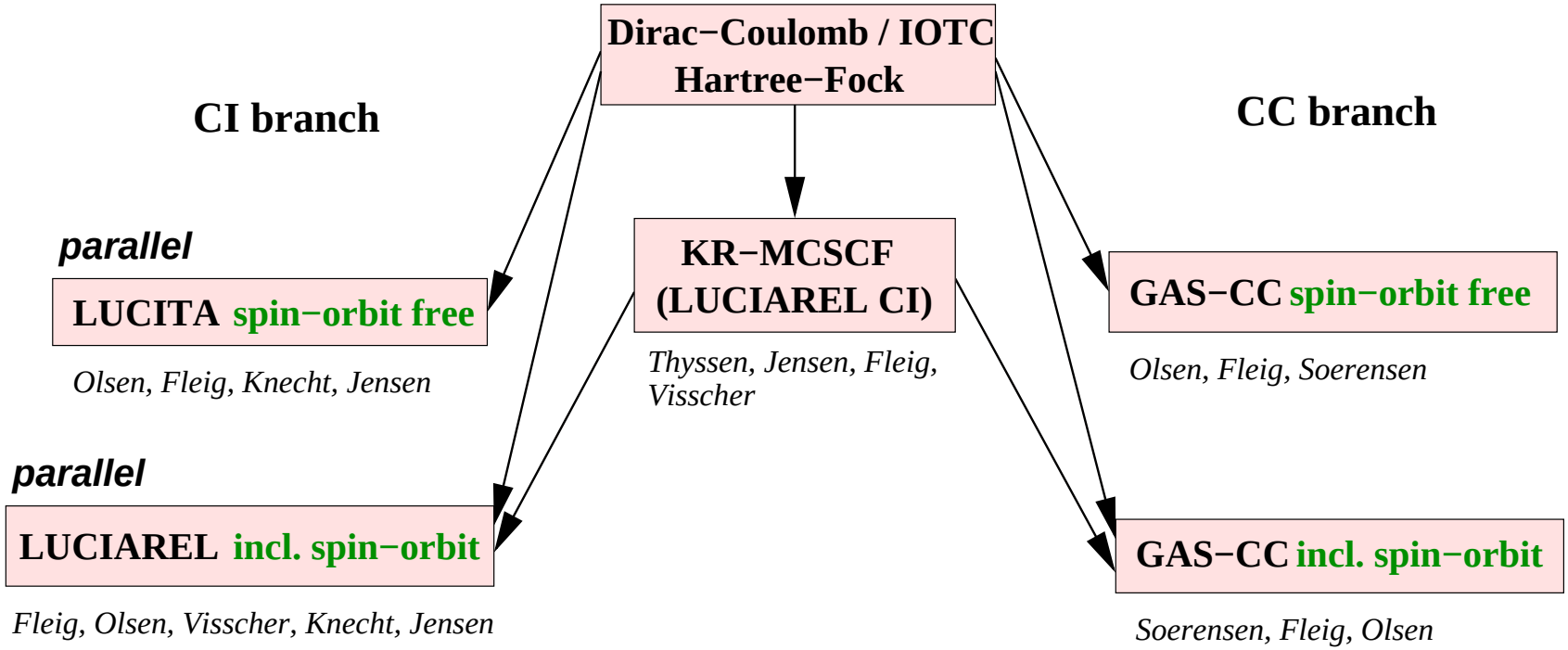
# String-Based Relativistic Methodology[1] [2] [3] [4] [5] [6]

HEINRICH HEINE UNIVERSITÄT DÜSSELDORF




[1] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) *2963*
[2] T. Fleig, L. Visscher, Chem Phys **311** (2005) *113*
[3] T. Fleig, H. J. Aa. Jensen, J. Olsen, L. Visscher, J Chem Phys **124,10** (2006) *104106*
[4] T. Fleig, L. K. Sørensen, J. Olsen, Theo Chem Acc **118,2** (2007) *347*
[5] S. Knecht, H. J. Aa. Jensen, T. Fleig, J Chem Phys **128,1** (2007) *014108*
[6] J Thyssen, H. J. Aa. Jensen, T. Fleig, J Chem Phys **129** (2008) *034109*

# Relativistic Correlation Methods

## Configuration Interaction

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

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

- One-step procedure **based on spinors**

  Simultaneous treatement of spin-orbit and electron correlation

- **QM Microreversibility principle**

  Kramers-paired spinor basis

  $\hat{K}\phi_i = \phi_{\bar{i}}$, $\hat{K}\phi_{\bar{i}} = -\phi_i$

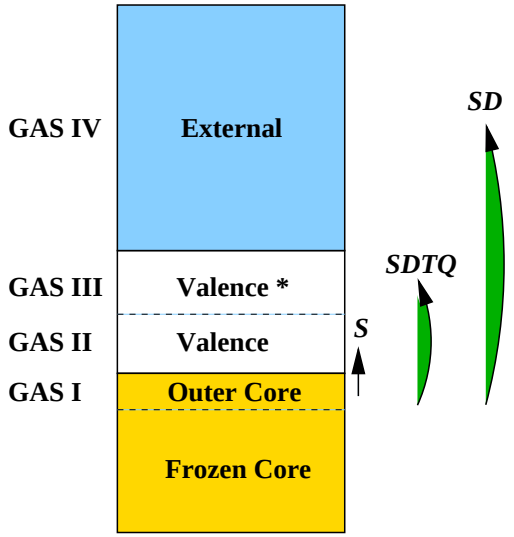
- **String-based algorithm**

  Determinant decomposes into

  $a_i^\dagger a_j^\dagger a_k^\dagger \ldots$ "Kramers up" string

  $a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$ "Kramers down" string

  Efficient treatment of higher excitations (than Doubles)




Flexible wave function definition:

– Valence-restricted expansions

– Core-valence expansions

– Core-core expansions

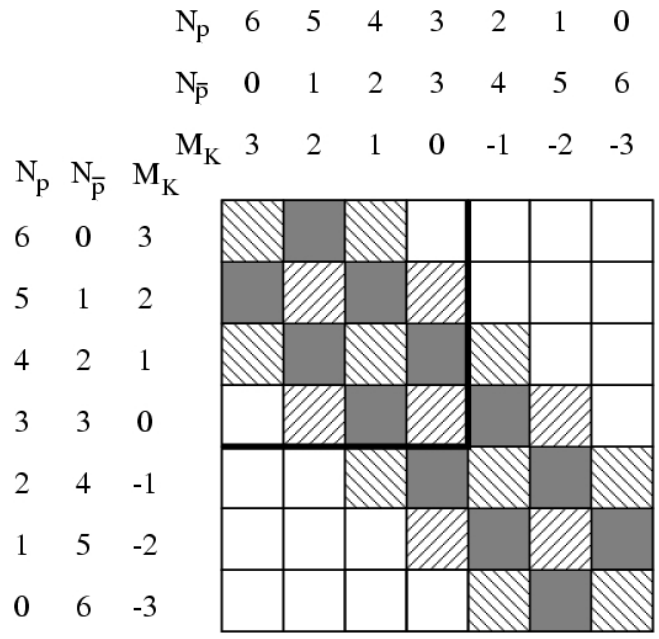
- Symmetry: **Double groups**
- **Quaternion** algebra

# Relativistic Correlation Methods

## Configuration Interaction (and general features)

- Double point-group symmetry fully exploited
  Currently $D_{2h}^*$ and subgroups

- Quaternion algebra at the integral level[7]
  $\Rightarrow$ For matrix groups $D_{2h}^*, D_2^*, C_{2v}^*$ entirely *real* algebra




- Only shaded blocks are non-vanishing
- Various shadings display block structure in quaternion/complex/real matrix groups
- Square indicates many-particle Kramers symmetry

[7] H.J.Aa. Jensen, K.G. Dyall, T. Saue, K. Fægri, J Chem Phys **104** (1996) *4083*

# Relativistic Correlation Methods

## General features: 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 |
|---|---|---|
| $a_i^\dagger a_j$ | $h_{ij}$ | $\Delta M_K = 0$ |
| $a_{\bar{i}}^\dagger a_{\bar{j}}$ | $h_{\bar{i}\bar{j}}$ | $\Delta M_K = 0$ |
| $a_i^\dagger a_k^\dagger a_l a_j$ | $(ij\|kl)$ | $\Delta M_K = 0$ |
| $a_i^\dagger a_{\bar{k}}^\dagger a_l a_{\bar{j}}$ | $(i\bar{j}\|\bar{k}l)$ | $\Delta M_K = 0$ |
| ... | ... | ... |
| $a_i^\dagger a_{\bar{j}}$ | $h_{i\bar{j}}$ | $\Delta M_K = +1$ |
| $a_{\bar{i}}^\dagger a_j$ | $h_{\bar{i}j}$ | $\Delta M_K = -1$ |
| $a_i^\dagger a_k^\dagger a_l a_{\bar{j}}$ | $(i\bar{j}\|kl)$ | $\Delta M_K = +1$ |
| $a_i^\dagger a_k^\dagger a_{\bar{l}} a_{\bar{j}}$ | $(i\bar{j}\|k\bar{l})$ | $\Delta M_K = +2$ |
| ... | ... | ... |

**GAS**

| | |
|---|---|
| **IV** | $\mathbf{a_i^+}$ $\mathbf{a_{\bar{j}}^+}$ |
| **III** | |
| **II** | $\mathbf{a_l}$ |
| **I** | $\mathbf{a_k}$ |

Operator type

\+ Occupation type

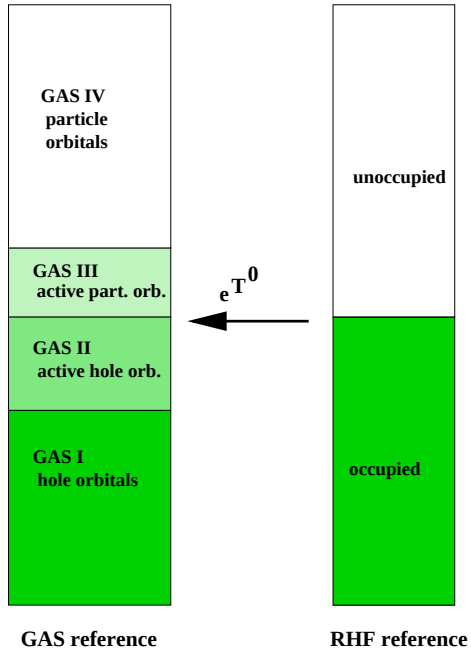
$\Longrightarrow$ Excitation class

# Relativistic Correlation Methods

## "Multi-Reference" Coupled Cluster[8]

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

- "State-Selective" (SS) GAS-CC
  Simulation of true MR-CC
- GAS-defined extended excitation manifold
  $\langle \mu_{\mathrm{MR}}| = \langle \mathrm{RHF}|\, \hat{\tau}_0^\dagger$
  $\langle \mu_{\mathrm{GAS-CC}}| = \langle \mu_{\mathrm{MR}}| \left\{ \hat{\tau}_{\mu_1}^\dagger, \hat{\tau}_{\mu_2}^\dagger, \ldots, \hat{\tau}_{\mu_N}^\dagger \right\}$
- $\hat{\tau}_{\mu_n}$ contains higher (internal) excitations
  $|\mathrm{GAS-CC}\rangle = e^{\sum_{\mu n} t_{\mu_n} \hat{\tau}_{\mu_n}} |\mathrm{RHF}\rangle$
- Generalisation of cluster operators
  $\hat{T}_1 = \sum_{ia} \left\{ t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \right\}$ ; $\hat{T}_2 = \ldots$
  including spin-orbit "terms"; Kramers contamination




"State-selective": "Memory" of original reference state

Concept for a fully "Kramers-adapted" CC theory:

T. Fleig, *Phys Rev A* **77** (2008) *062503*

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

# Relativistic Correlation Methods

## Rel. Kramers-Unrestricted GAS-CC

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

### CI-based 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)

### Commutator-based CC vector function

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

- ↻ Loop over rel. 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 rel. excitation types $\hat{T}_i$ of $\hat{T}$ operators
      - ! Check for coupling with $\langle \mu |$
      - Yes? Contract with integrals
    - ↙ End loop
  - ↙ End loop
- ↙ End loop

## Properties of the implementation:

- Very general approach
- Increased "N-scaling": $O^{n+2}V^{n+2}$

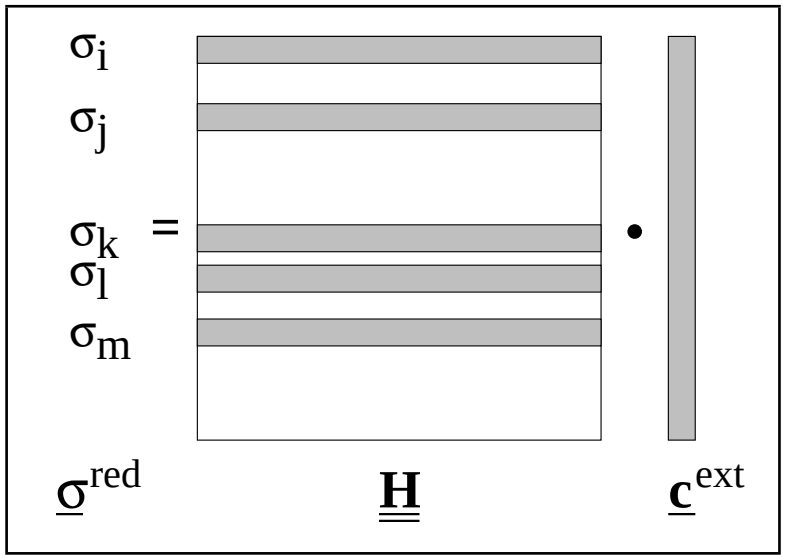
- General approach, currently some limitations
- Conventional "N-scaling": $O^n V^{n+2}$

# Relativistic Correlation Methods

## CI-Based GAS-CC: 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: $O^{n}V^{n+2}$



# Relativistic Correlation Methods

## Relativistic Commutator/String-Based GAS-CC

L. K. Sørensen, T. Fleig, J. Olsen, *J Chem Phys* (2008) *in preparation.*

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

- Rel. excitation class of $\hat{H}$ depends on number of GAS

  additional "Kramers flip" excitation classes

| Be atom | NRel | Rel |
|---|---|---|
| 2 GAS | 42 | 68 |
| 4 GAS | 488 | 720 |

- Loop over commutator nesting ranks, e.g. $\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right]$
  - . . . exc. types of $\hat{T}$ (commuting $\hat{T}$!)

    Non-vanishing connections with $|\mu\rangle$ (sample $\alpha^\dagger\alpha^\dagger\alpha\alpha$)

| Be atom | NRel | Rel |
|---|---|---|
| $\left[\hat{H},\hat{T}\right]$ | 1 | 1 |
| $\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right]$ | 72 | 493 |

    symmetries and batches of $\hat{T}(i)$

    Obtain strings of $\hat{H}$ and integrals

    Perform contractions: 1) $\left[\hat{H},\hat{T}(i)\right]$, 2) $\left[\left[\hat{H},\hat{T}(i)\right],\hat{T}(j)\right]$ etc.

- . . . End the loops

# Application of Relativistic GAS-CC

## PEC's of HBr; aTZ basis set

| Method | $R_e$ [Å] | $\omega_e$ [$cm^{-1}$] | $D_e$ [eV] |
|---|---|---|---|
| SO MRCISD (6) | 1.4151 | 2668 | 3.90 |
| SO MRCCSD (6) | 1.4154 | 2668 | 3.90 |
| SOF MRCISD (8) | 1.4180 | 2641 | 3.90 |
| SOF MRCCSD (8) | 1.4192 | 2637 | 3.90 |
| SOF CCSDT (8) | 1.4178 | 2647 | 3.96 |
| SO CISD (8) | 1.4121 | 2700 | |
| SO CCSD (8) | 1.4155 | 2666 | |
| SO CCSDT (8) | 1.4176 | 2647 | |
| SO MRCISD (8) | 1.4187 | 2635 | 3.77 |
| SO MRCCSD (8) | 1.4193 | 2631 | 3.76 |
| SOF CCSDT (18) | 1.4137 | 2665 | 4.01 |
| SO CISD (18) | 1.4064 | 2736 | |
| SO CCSD (18) | 1.4119 | 2683 | |
| SO CCSD(T) (18) | 1.4139 | 2664 | |
| SOF CCSDT (18) $+\Delta_{SO}$ | 1.4138 | 2659 | 3.87 |
| SO CCSDT (18) | 1.4140 | 2663 | 3.87 |
| Exp. (Huber, Herzberg 1979) | 1.4144 | 2649.0 | 3.92 |

**SR $\longrightarrow$ "MR" (GAS)**:

Bond length: $+0.004$ Å

Frequency: $-35$ $cm^{-1}$

$D_e$: GAS or T for satisfactory results

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**Spin-orbit coupling**:

Bond length: $+0.0005$ Å

Frequency: $-6/-2$ $cm^{-1}$

$D_e$: $-0.14$ eV

# Application of Relativistic GAS-CC

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**CI** $\longrightarrow$ **CC**:

Very similar at MR level.

# Application of Relativistic GAS-CC

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**CC correlation**:

Bond length: $-0.004$ Å

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

$D_e$: $+0.05$ eV

# Application of Relativistic GAS-CC

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**Standard models vs. full T**:

Improvement (T) $\rightarrow$ T:

Bond length: $+0.0001$ Å

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

# Application of Relativistic GAS-CC

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|---|---|---|---|
| SO MRCISD (6) | 1.4151 | 2668 | 3.90 |
| SO MRCCSD (6) | 1.4154 | 2668 | 3.90 |
| SOF MRCISD (8) | 1.4180 | 2641 | 3.90 |
| SOF MRCCSD (8) | 1.4192 | 2637 | 3.90 |
| SOF CCSDT (8) | 1.4178 | 2647 | 3.96 |
| SO CISD (8) | 1.4121 | 2700 | |
| SO CCSD (8) | 1.4155 | 2666 | |
| SO CCSDT (8) | 1.4176 | 2647 | |
| SO MRCISD (8) | 1.4187 | 2635 | 3.77 |
| SO MRCCSD (8) | 1.4193 | 2631 | 3.76 |
| SOF CCSDT (18) | 1.4137 | 2665 | 4.01 |
| SO CISD (18) | 1.4064 | 2736 | |
| SO CCSD (18) | 1.4119 | 2683 | |
| SO CCSD(T) (18) | 1.4139 | 2664 | |
| SOF CCSDT (18) $+\Delta_{SO}$ | 1.4138 | 2659 | 3.87 |
| SO CCSDT (18) | 1.4140 | 2663 | 3.87 |
| Exp. (Huber, Herzberg 1979) | 1.4144 | 2649.0 | 3.92 |

**CC corr. + spin-orbit shift vs. full calc.**:

Deviation from exp.:

Bond length: $-0.0004$ Å

Frequency: $+14$ $cm^{-1}$

$D_e$: $-0.05$ eV

# Application of GAS-CC / Parallel MRCI

## BiH: Spin-Orbit Splitting of $0^+(^3\Sigma^-) - 1(^3\Sigma^-)$

S. Knecht, H. J. Aa. Jensen, T. Fleig, J Chem Phys (2008) *in preparation.*

Uncontracted Dyall basis sets (Bi) / (ANO-RCC: H)

aTZ $[30s26p17d11f1g]$

aQZ $[34s31p21d17f3g1h]$

Cutoff virtual spinors: 5 a.u.

4c-/2c-Hamiltonians

| | | |
|---|---|---|
| $T_v$ [eV] | MR(2in2)CISD16 (aTZ) | 4526 |
| | MR(2in2)CISD16 (aQZ) | 4730 |
| | MR(2in2)CISDTQ16 (aTZ) | 4697 |
| $T_e$ [eV] | Alekseyev et al.[9] | 4303 |
| | Stoll et al.[10] | 4662 |
| | MR(2in2)CISD6 (aQZ) | 4661 |
| | MR(2in2)CISD16 (aQZ) | 4678 |
| Exp.[11] | | 4917 |

- Nearly all corrections increase SO splt.
- $T_v$, $T_e$:
  Basis set > higher excitations > core-el. correlation
- $R_e$, $\omega_e$:
  core-el. correlation > Basis set > higher excit.

| aTZ | $R_e$[Å] | $\omega_e$[cm$^{-1}$] |
|---|---|---|
| CCSD 6 | 1.824 | 1698 |
| CCSD(T) 6 | 1.825 | 1690 |
| CCSDT 6 | 1.826 | 1687 |
| CCSD 16 | 1.769 | 1800 |
| CCSD(T) 16 | 1.768 | 1791 |
| CCSDT 16 | *i.pr.* | *i.pr.* |

[9] RECP, orbital-based SOCI; A.B. Alekseyev, R.J. Buenker et al., J. Chem. Phys., **100** (1994) 2989

[10] 2c-MRCIS + 1c-CCSD(T) shift; H. Stoll, B. Metz, M. Dolg, J. Comp. Chem., **23** (2002) 767

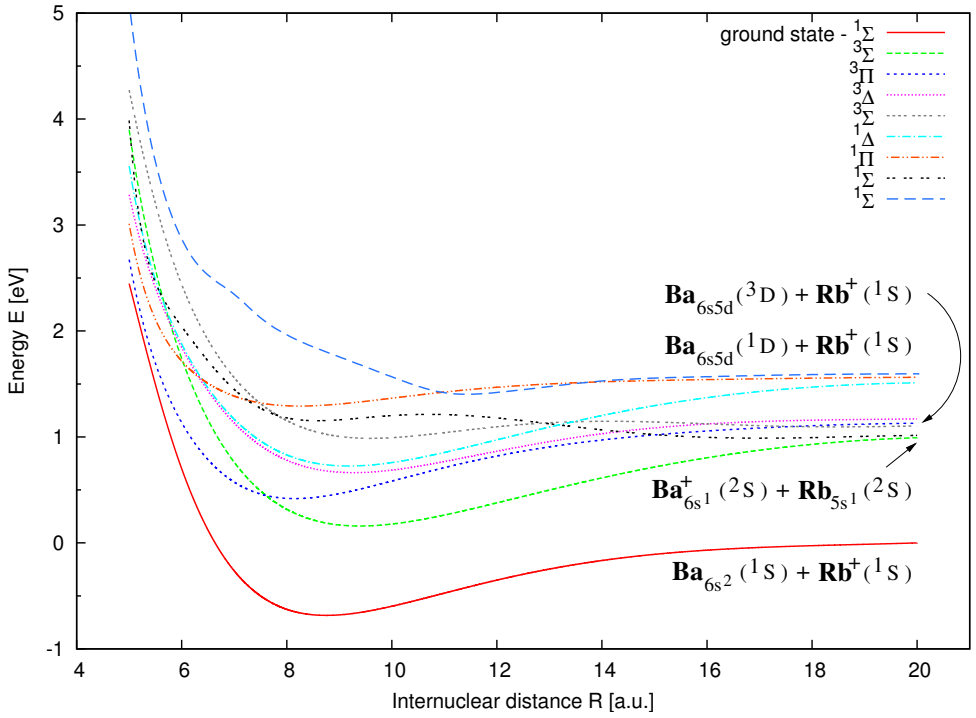
[11] Heimer, Z. Phys., **95** (1935) 328

# Application of Parallel MRCI

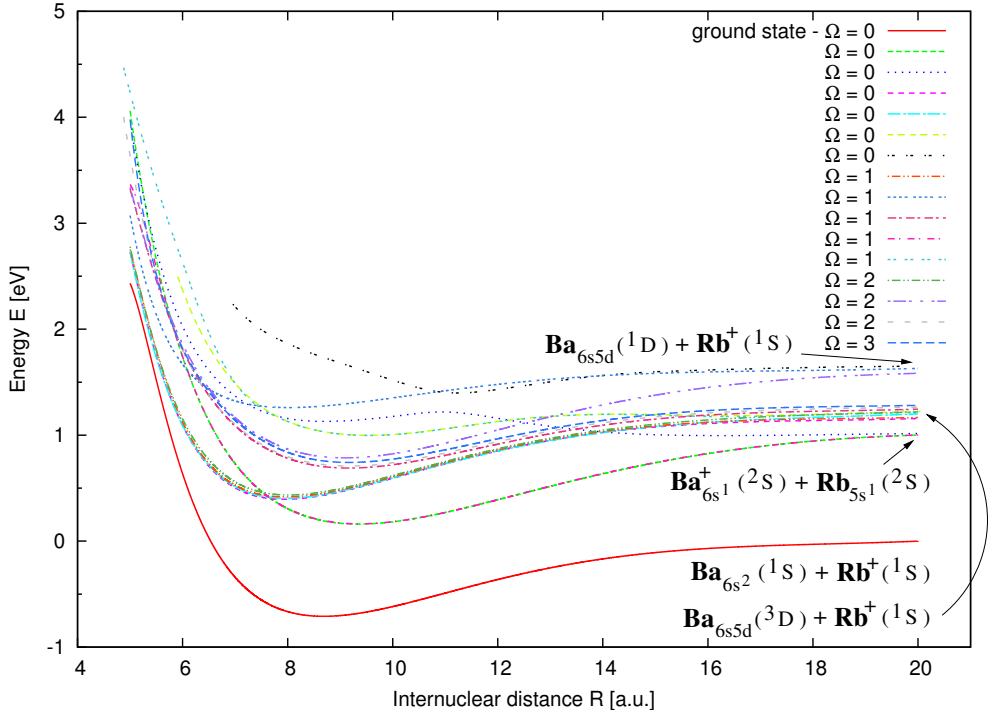
## Potential-Energy Curves of Rb-Ba$^+$

S. Knecht, H. J. Aa. Jensen, T. Fleig, *J Chem Phys* **128,1** (2008) *014108*

### Spin-orbit free (LUCITA)




### Fully relativistic (LUCIAREL)

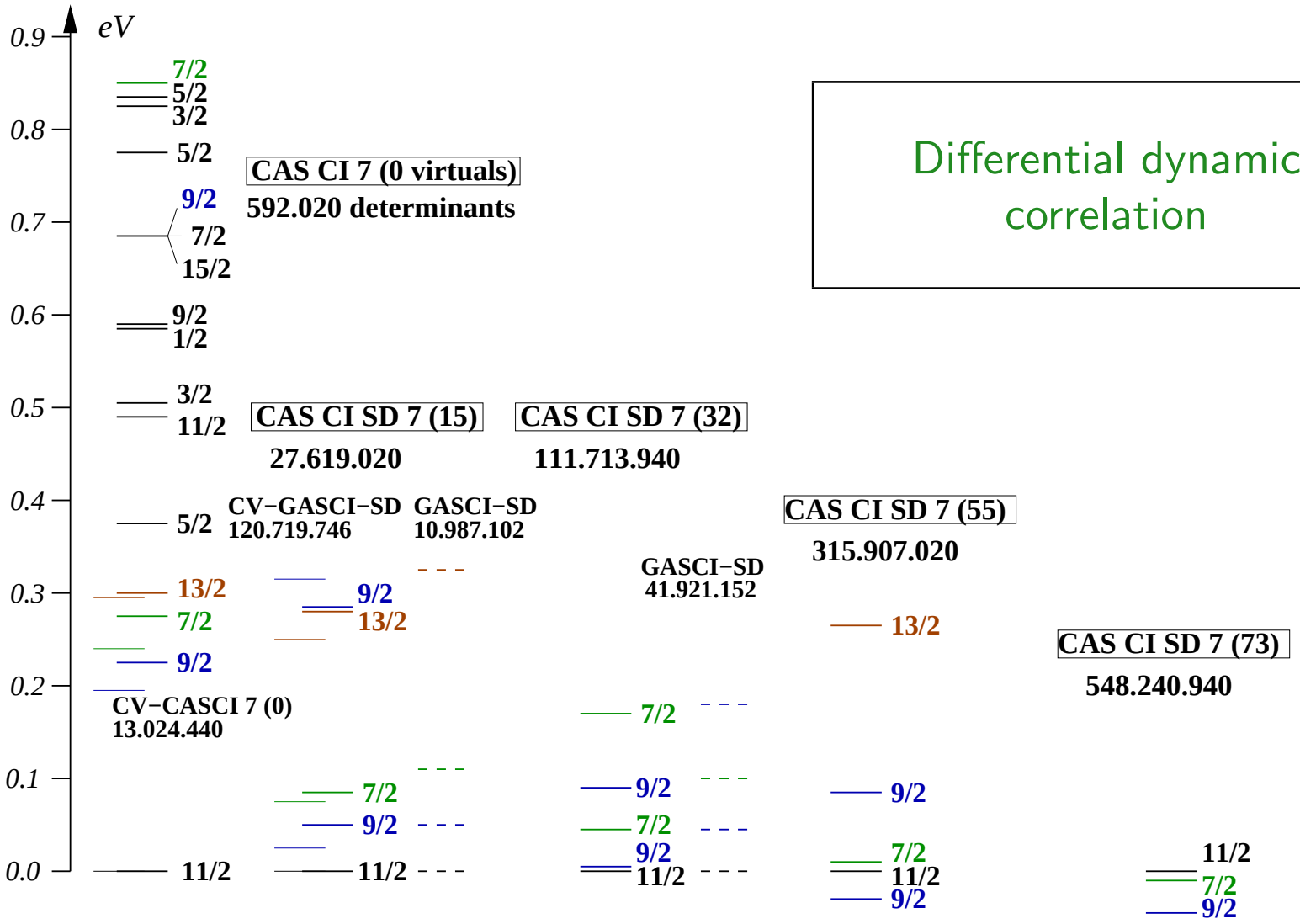



**Increased state density** including spin-orbit interaction

Predictions on "unknown" molecules **guiding experimental studies**

# Application of Parallel MRCI

## Vertical electronic spectrum of UH; 2.0 Å, Ω states




Differential dynamic correlation

# Theoretical Improvements

## Kramers-Restricted GAS-CC

T. Fleig, *Phys. Rev. A* (2008) *062503*

- 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

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

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[12])

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

# Theoretical Improvements

## Kramers-Restricted GAS-CC

- 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:

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

# Theoretical Improvements

## Kramers-Restricted GAS-CC

$N$-particle RITE operators

$$\hat{E}^{s_1,s_2}_{pq,rs} = \imath^{f(s_1)+f(s_2)} \left(\hat{1} + s_1 \hat{K}_{pq}\right) \left(\hat{1} + s_2 \hat{K}_{rs}\right) a^\dagger_p a^\dagger_r a_s a_q$$

$$\hat{E}^{s_1,s_2,s_3}_{pq,rs,tu} = \imath^{\sum_{j=1}^{3} f(s_j)} \left(\hat{1} + s_1 \hat{K}_{pq}\right) \left(\hat{1} + s_2 \hat{K}_{rs}\right) \left(\hat{1} + s_3 \hat{K}_{tu}\right) a^\dagger_p a^\dagger_r a^\dagger_t a_u a_s a_q$$

$$\hat{E}^{s_1,s_2,s_3,s_4}_{pq,rs,tu,vw} = \imath^{\sum_{j=1}^{4} f(s_j)} \left(\hat{1} + s_1 \hat{K}_{pq}\right) \left(\hat{1} + s_2 \hat{K}_{rs}\right) \left(\hat{1} + s_3 \hat{K}_{tu}\right) \left(\hat{1} + s_4 \hat{K}_{vw}\right) a^\dagger_p a^\dagger_r a^\dagger_t a^\dagger_v a_w a_u a_s a_q$$

$$\ldots$$

General commutators

$$\left[\hat{E}^{s}_{pq}, \hat{E}^{s'}_{rs}\right] = \imath^{f(s)+f(s')+f(s\cdot s')} \left\{\delta_{qr} \hat{E}^{s\cdot s'}_{ps} - \delta_{ps} \hat{E}^{s\cdot s'}_{rq}\right\}$$

$$\left[\hat{E}^{s}_{\overline{p}q}, \hat{E}^{s'}_{rs}\right] = \imath^{f(s)+f(s')+f(s\cdot s')} \left\{\delta_{qr} \hat{E}^{s\cdot s'}_{\overline{p}s} - s' \delta_{ps} \hat{E}^{s\cdot s'}_{\overline{r}q}\right\}$$

$$\left[\hat{E}^{s}_{\overline{p}q}, \hat{E}^{s'}_{\overline{r}s}\right] = \imath^{f(s)+f(s')+f(s\cdot s')} \left\{-s \delta_{qr} \hat{E}^{s\cdot s'}_{ps} + s' \delta_{ps} \hat{E}^{s\cdot s'}_{rq}\right\}$$

# Theoretical Improvements

## Kramers-Restricted GAS-CC

- $\hat{T}_2 = T_2\left(\hat{E}^{++}, \hat{E}^{+-}, \hat{E}^{--}\right)$ 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

**Commutator-based CC vector function**

- Modification of general implementation
- Non-commuting model theories
- Truncation of higher-order commutators

# Conclusion

## . . . and some plans

**Set of universally applicable relativistic correlation methods**

**Improvement of methodology**

GAS-CC: linear response theory (implemented)

MRCI: Distributed data model for integrals (implemented)
I/O models for $(VV|VV)$ integrals

**LARGER heavy-element compounds**

Series of rigorous size-consistent relativistic correlation models:

(4c)-(GAS)CCn and (4c)-GASPTn

On basis of approximations to commutator-based MRCC

Specifically advocated models:

Small HE molecules: (4c)-GASCC4$_2$ (+ linear response)

Larger HE molecules: (4c)-GASPT2

# Collaboration

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# Support


## DFG

FL 356/1 FL 356/2-1 FL 356/2-2 FL 356/2-3 (SPP 1145)

FL 356/3-1

FL 356/4-1 (Heisenberg), FL 356/5-1 (Heisenberg)

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NIC

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