

Rigorous Relativistic Methods for Addressing \mathcal{P} - and \mathcal{T} -Nonconservation in Heavy-Element Molecules

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Overview

- 1. Principles of relativistic molecular electronic-structure theory**
- 2. Implementation of \mathcal{P} - and \mathcal{T} -non-conserving operators**
- 3. Electron EDM interaction constant in HfF^+**
- 4. Outlook: Other systems, other effects, new methods**

1. Four-Component Electronic-Structure Theory

Some Essentials

- Atomic basis sets; in low-energy approximation

$$\psi^S(\vec{r}) \approx \frac{\sigma \cdot \mathbf{p}}{m_0 c} \psi^L(\vec{r})$$

Kinetic-balance condition

- Solution of the Dirac-Coulomb Hartree-Fock equations

$$\begin{pmatrix} (\hat{V}_{\text{nuc}} + \hat{v}_{\text{DCHF}}) \mathbb{1}_2 & c\sigma \cdot \mathbf{p} \\ c\sigma \cdot \mathbf{p} & (\hat{V}_{\text{nuc}} + \hat{v}_{\text{DCHF}} - 2m_0c^2) \mathbb{1}_2 \end{pmatrix} \begin{pmatrix} \psi_a^L(\vec{r}) \\ \psi_a^S(\vec{r}) \end{pmatrix} = \varepsilon \begin{pmatrix} \psi_a^L(\vec{r}) \\ \psi_a^S(\vec{r}) \end{pmatrix}, \quad \forall a$$
$$\varepsilon = E - m_0c^2$$

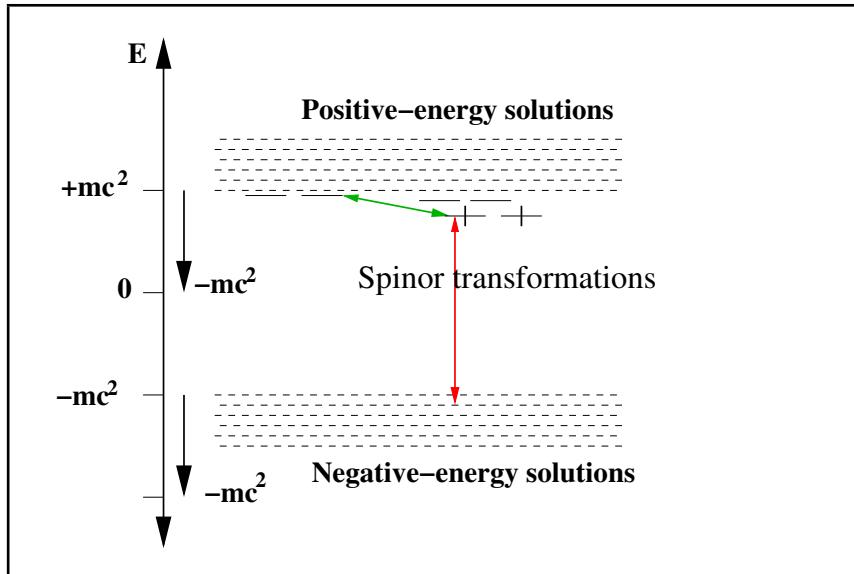
- Fock matrix for “frozen” atomic core

$$1) \text{ Core energy: } \varepsilon_{\text{core}} = \sum_{i,j>i}^{2N_{\text{core}}} \{2 \langle ij|ij \rangle - \langle ij|ji \rangle - \langle i\bar{j}|\bar{j}i \rangle\}$$

$$2) \text{ Inactive Fock matrix: } f_{pq}^{\text{DC}} = h_{pq}^{\text{D}} + \sum_j^{2N_{\text{core}}} \{2 \langle pj|qj \rangle - \langle pj|jq \rangle - \langle p\bar{j}|\bar{j}q \rangle\}$$

1. Four-Component Electronic-Structure Theory

The “empty-Dirac” picture



- Occupied positive-energy bound-state spinors
Fermi vacuum state $|0\rangle$
- Empty continuum of negative-energy states
- Expectation value of parameterized state vector
 $\langle Ref | \hat{H} | Ref \rangle = \langle 0 | e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} | 0 \rangle$

- Approximation of general expectation value to first order:

$$\langle 0 | e^{-\hat{\kappa}} \hat{H}^{DC} e^{\hat{\kappa}} | 0 \rangle \approx \langle 0 | [\hat{H}^{DC}, \hat{\kappa}] | 0 \rangle = \sum_{pq} \kappa_{pq} \left[\langle 0 | \hat{H}^{DC} a_p^\dagger a_q | 0 \rangle - \langle 0 | \hat{H}^{DC} a_q^\dagger a_p | 0 \rangle^* \right]$$

- Parameterized Dirac-spinor transformations:

$$\hat{\kappa} = \sum_{pq} \left[\kappa_{p+q+} a_p^\dagger a_{q+} + \kappa_{p+q-} a_p^\dagger a_{q-} + \kappa_{p-q+} a_p^\dagger a_{q+} + \kappa_{p-q-} a_p^\dagger a_{q-} \right]$$

- Green terms: minimization of energy w.r.t. rotations
- Red terms: maximization of energy w.r.t. rotations
⇒ **minimax** variation

Four-Component Correlation Methods

. . . and why they are not more expensive than two-component ones

Integrals over positive-energy 4-spinors:

$$\begin{aligned} h_{mn}^+ &= \left\langle \psi_m^+ | \hat{h} | \psi_n^+ \right\rangle = \left\langle \begin{pmatrix} \psi_m^L & \psi_m^S \end{pmatrix} | \begin{pmatrix} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{pmatrix} | \begin{pmatrix} \psi_n^L \\ \psi_n^S \end{pmatrix} \right\rangle \\ &= \left\langle \psi_m^L | \hat{h}_{11} | \psi_n^L \right\rangle + \left\langle \psi_m^L | \hat{h}_{12} | \psi_n^S \right\rangle + \left\langle \psi_m^S | \hat{h}_{21} | \psi_n^L \right\rangle + \left\langle \psi_m^S | \hat{h}_{22} | \psi_n^S \right\rangle \\ &= \sum_{J=1}^{N^L} \sum_{K=1}^{N^L} c_{mJ}^{L*} \left\langle \phi_J^L | \hat{h}_{11} | \phi_K^L \right\rangle c_{nK}^L + \sum_{J=1}^{N^L} \sum_{K=1}^{N^S} c_{mJ}^{L*} \left\langle \phi_J^L | \hat{h}_{12} | \phi_K^S \right\rangle c_{nK}^S \\ &\quad + \sum_{J=1}^{N^S} \sum_{K=1}^{N^L} c_{mJ}^{S*} \left\langle \phi_J^S | \hat{h}_{21} | \phi_K^L \right\rangle c_{nK}^L + \sum_{J=1}^{N^S} \sum_{K=1}^{N^S} c_{mJ}^{S*} \left\langle \phi_J^S | \hat{h}_{22} | \phi_K^S \right\rangle c_{nK}^S \end{aligned}$$

- Key: Four-component no-virtual-pair (NVP) approximation
- $\dim[\mathcal{F}^{4c}] = \dim[\mathcal{F}^{2c}]$
- Direct comparison of 4- and 2-component Hamiltonians possible

Special Relativity and Electron Correlation

Principal Approaches for Molecules

Spinor-based models

Hartree–Fock

2– or 4–component
Hamiltonian



Dynamic Correlation

2– or 4–component
Hamiltonian

Double-group MPPT/CI/CC

computational
cost

Spinorbital-based models

Hartree–Fock

scalar relativistic
Hamiltonian



Dynamic Correlation

2–component
Hamiltonian

Spin-orbit CI

Spin-orbit Coupled Cluster

rigor
of
theory

Additive models

Hartree–Fock

scalar relativistic
Hamiltonian



Dynamic Correlation

scalar relativistic
Hamiltonian



Magnetic Couplings

2–component
Hamiltonian

Spin-orbit QDPT

CASPT2–Spin-orbit RASSI

Spinors and Strings

General principles of rigorous relativistic correlation methods

General concept: Kramers-paired spinors

Time-reversal operator for a fermion:

$$\hat{K} = e^{-\frac{i}{\hbar}\pi(\hat{\vec{s}} \cdot \vec{e}_y)} \hat{K}_0 = -i\Sigma_y \hat{K}_0$$

Double group symmetry and quaternion algebra

Spinorbitals	General spinors
$\hat{K}\varphi_i \alpha = \varphi_i^* \beta$	$\hat{K}\phi_i = \phi_{\bar{i}}$
$\hat{K}\varphi_i^* \beta = -\varphi_i \alpha$	$\hat{K}\phi_{\bar{i}} = -\phi_i$

Spinor basis:

$$\phi_i = a_i^\dagger | \rangle \quad \phi_{\bar{i}} = a_{\bar{i}}^\dagger | \rangle$$

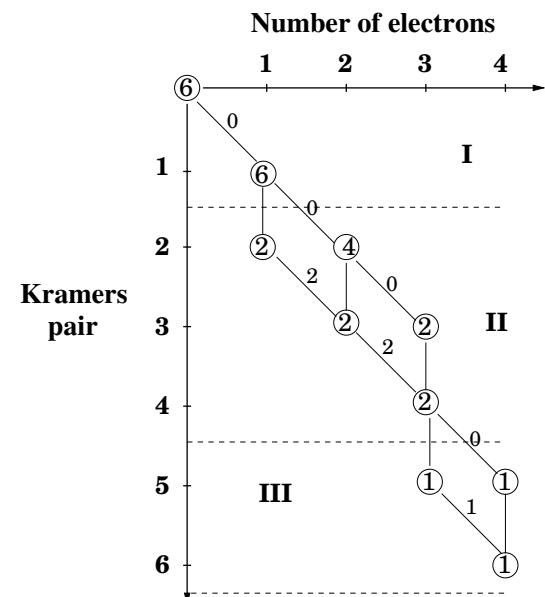
- Many-particle wavefunction defined as

1 unbarred (Kramers up) string $S = a_i^\dagger a_j^\dagger a_k^\dagger \dots$

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

- Configuration Interaction: **Slater determinants**

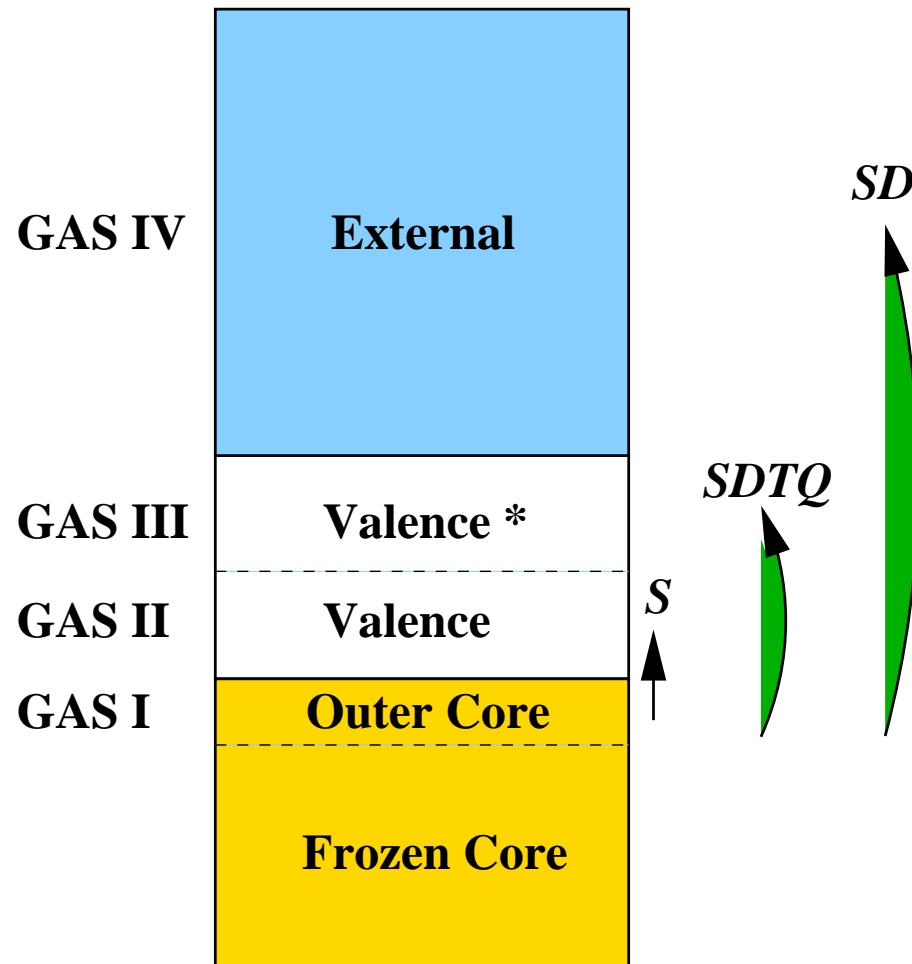
Coupled Cluster: **Individual strings**



⊗ x: vertex weight
y: arc weight

Parameterization of the Wavefunction

Generalized Active Spaces



Special Relativity and Electron Correlation

Methods in comparison

Chalcogen homonuclear and heteronuclear diatomics¹

Vertical excitation energies among $\pi^*{}^2$ state manifold
 ΛS States ${}^3\Sigma^-$, ${}^1\Delta$, ${}^1\Sigma^+$ \longrightarrow $0^+, 1, 2, 0^+$, (Ω)

Splitting of $0^+, 1$ is a second-order spin-orbit effect

Purely molecular spin-orbit splitting

Contenders:

“Additive”²: *SO-DDCI3, SO-CASPT2*

“Non-additive”³: *4c-IH-FSCC, 4c-GACI*

¹J.-B. Rota, S. Knecht, T. Fleig, D. Ganyushin, T. Saue, F. Neese, H. Bolvin *J Chem Phys* **135** (2011) 114106

²F. Neese, *J Chem Phys* **119** (2003) 9428

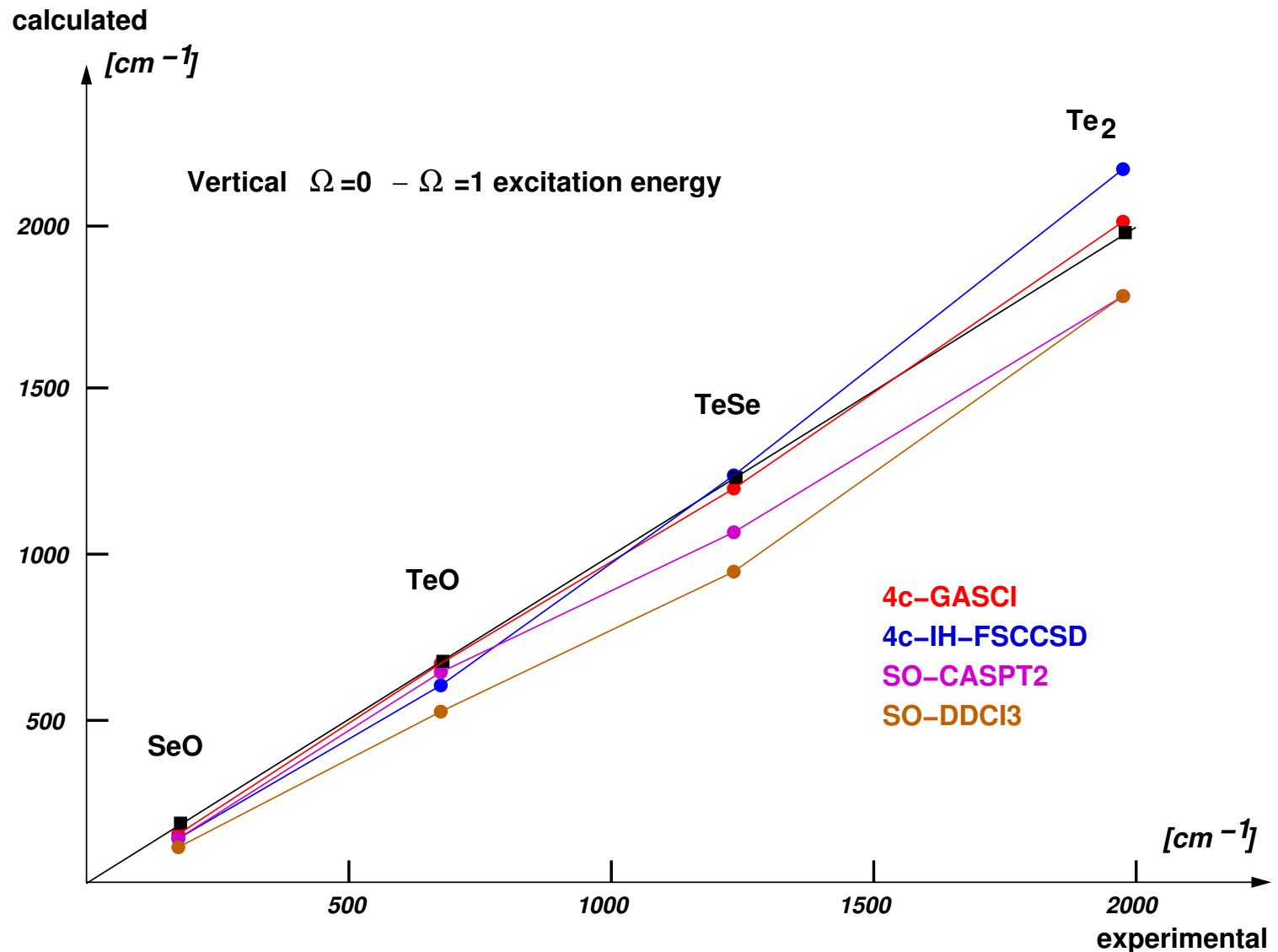
P.-Aa. Malmqvist, B.O. Roos, B. Schimmelpfennig, *Chem Phys Lett* **357** (2002) 357

³L. Visscher, E. Eliav, U. Kaldor, *J Chem Phys* **115** (2001) 9720

S. Knecht, H.J.Aa. Jensen, T. Fleig, *J Chem Phys* **132** (2010) 014108

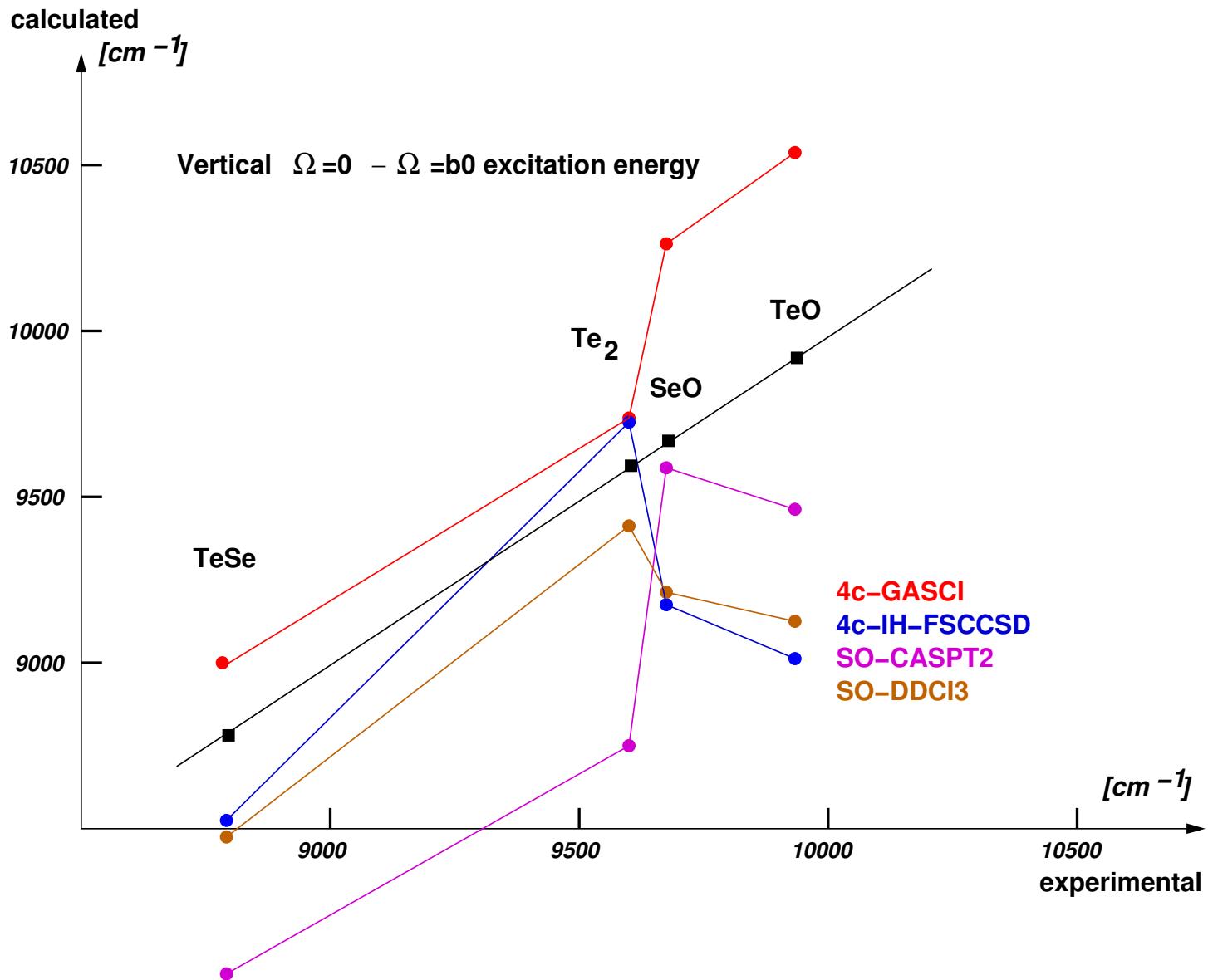
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Special Relativity and Electron Correlation

Methods in comparison

Conclusions in the light of evidence

Non-additive, spinor-based methods largely superior for excitation energies

4c-GASCI allows for balanced treatment of ground and excited states

CI not size extensive

CI inefficient in treating higher excitations

Goal: More efficient spinor-based size-extensive electron correlation methods

Relativistic Generalized-Active-Space CC

L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) 214102

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

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

- “State-Selective” (SS) GAS-CC

Generalized “Oliphant/Adamowicz” Ansatz⁴

- GAS-extended excitation manifold

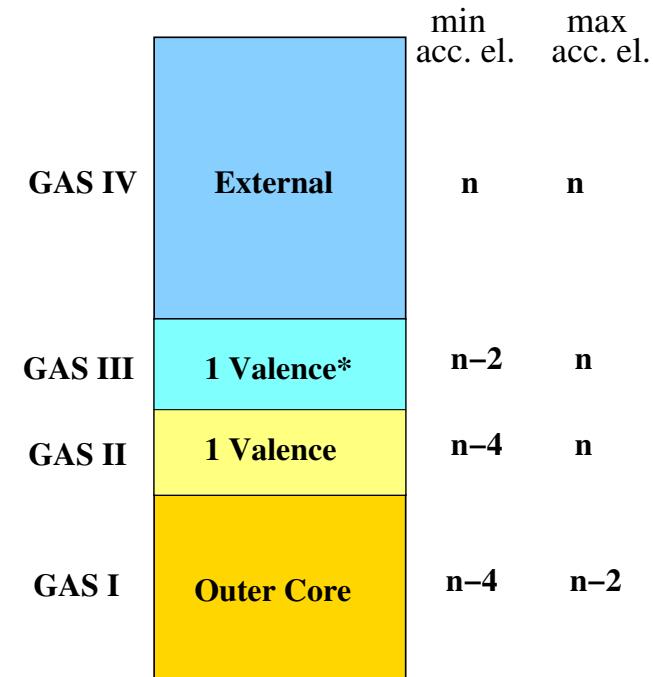
$$\langle \mu_{\text{GASCC}} | = \langle \psi^{\text{Ref}} | \hat{\tau}_{\mu_{\text{GAS}}}^\dagger$$

- $\hat{\tau}_{\mu_{\text{GAS}}}$ contains GAS-selected higher excitations

$$| \psi^{\text{GASCC}} \rangle = \exp(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu_{\text{GAS}}}) | \psi^{\text{Ref}} \rangle$$

- Relativistic generalization of cluster operators

$$\hat{T}_1 = \sum_{ia} \left\{ t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \right\}; \hat{T}_2 = \dots$$



Example for constructed higher excitations:

$$\begin{aligned} \langle \mu_{\text{GASCC}} | &= \left\langle \mu^{S(\text{III}^1)} \right| + \left\langle \mu^{S(\text{IV}^1)} \right| + \left\langle \mu^{D(\text{III}^2)} \right| + \left\langle \mu^{D(\text{IV}^2)} \right| + \left\langle \mu^{D(\text{III}^1+\text{IV}^1)} \right| \\ &\quad + \left\langle \mu^{T(\text{III}^1+\text{IV}^2)} \right| + \left\langle \mu^{T(\text{III}^2+\text{IV}^1)} \right| + \left\langle \mu^{Q(\text{III}^2+\text{IV}^2)} \right| \end{aligned}$$

⁴N. Oliphant, L. Adamowicz *J Chem Phys* **94** (1991) 1229

Relativistic Generalized-Active-Space CC

Electronic Ground States ⁵

CC vector function

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

- Loop over **relativistic** $N\Delta M_K$ classes of \hat{H}, \hat{T}
Determines min./max. commutator nesting
- Loop over commutator type, e.g. $[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}]$
- Loop over **relativistic** $N\Delta M_K$ classes of \hat{T} operators
Find all possible contractions
- Loop over contractions and perform, e.g.

$$[[\hat{H}_{2v,2v}, \hat{T}_{2v,2o}], \hat{T}_{2v,2o}] \\ = \frac{1}{4} \sum_{abcd, i'j'a'b', i''j''a''b''} (ad|bc) t_{i'j'}^{a'b'} t_{i''j''}^{a''b''} a_a^\dagger a_b^\dagger a_c^\dagger a_d^\dagger a_{a'}^\dagger a_{b'}^\dagger a_{i'}^\dagger a_{j'}^\dagger a_{a''}^\dagger a_{b''}^\dagger a_{i''}^\dagger a_{j''}^\dagger.$$

⁵L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) 214102

L. K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) 999

Relativistic Generalized-Active-Space CC⁶

Excitation Energies⁷

$$J_{\mu}^{CC} = \sum_{\nu} \left\langle \mu_{\text{GAS}} \left| e^{-\hat{T}_{\text{GAS}}} \left[\hat{H}, \hat{\tau}_{\nu_{\text{GAS}}} \right] e^{\hat{T}_{\text{GAS}}} \right| \psi^{\text{Ref}} \right\rangle x_{\nu}$$

1. $|a\rangle = e^{\hat{T}_{\text{GAS}}} |\psi^{\text{Ref}}\rangle = \left(\sum_{k=0}^{\infty} \frac{1}{k!} \hat{T}_{\text{GAS}}^k \right) |\psi^{\text{Ref}}\rangle$

$\hat{T}_{\text{GAS}} |\psi^{\text{Ref}}\rangle$ corresponds to calculating a sigma vector with amplitudes.

2. $|b\rangle = [\hat{H}, \hat{\tau}_{\nu_{\text{GAS}}}] |a\rangle = (\hat{H}\hat{\tau}_{\nu_{\text{GAS}}} - \hat{\tau}_{\nu_{\text{GAS}}}\hat{H}) |a\rangle \quad (\text{CI sigma vectors})$

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

4. $\Omega_{\mu_{\text{GAS}}} = \langle \mu_{\text{GAS}} | c \rangle = \langle \psi^{\text{Ref}} | \hat{\tau}_{\mu_{\text{GAS}}}^{\dagger} | c \rangle \quad (\text{CI transition density matrices})$

Computational scaling:

CI-based implementation $O^{n+2}V^{n+2}$

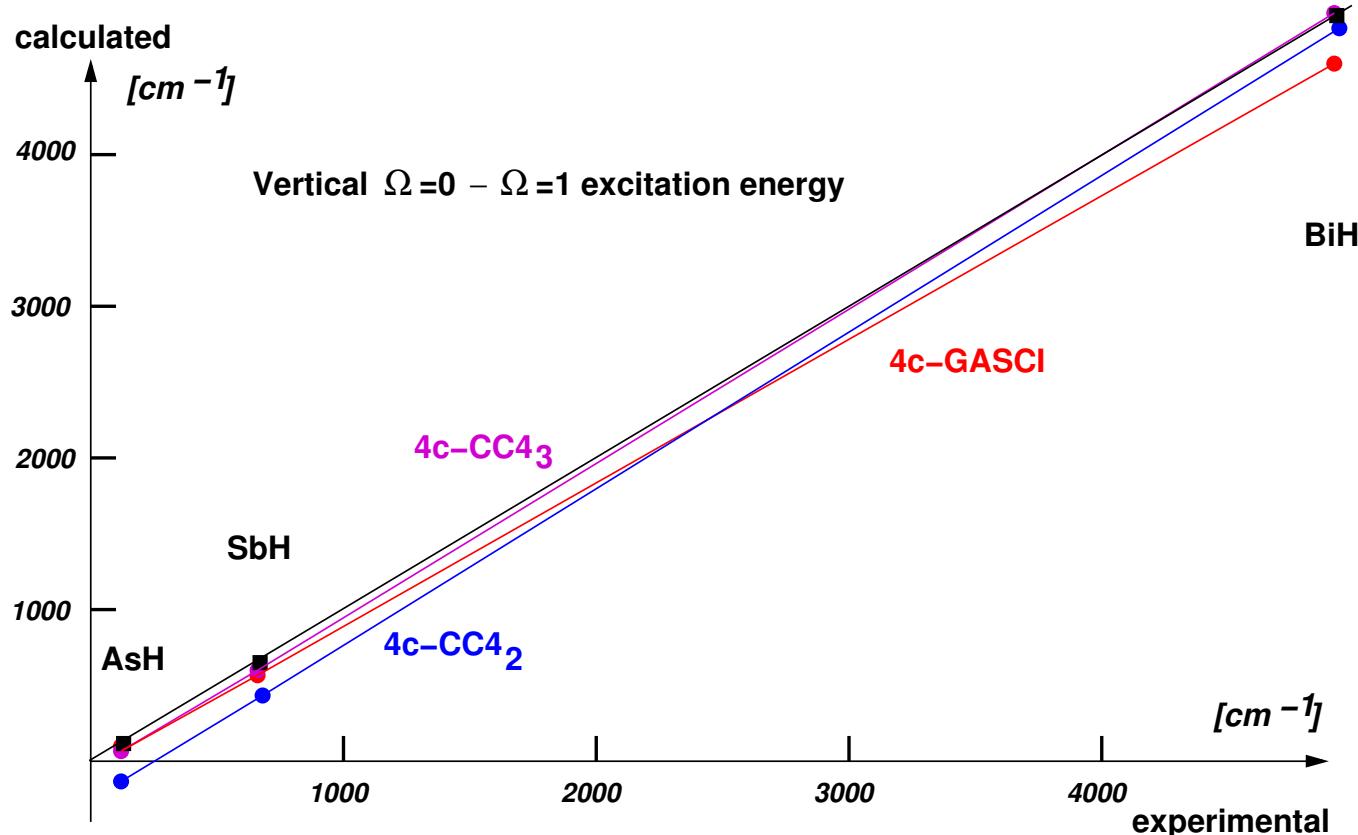
Conventional CC: $O^n V^{n+2}$

⁶M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **86** (2012) 012503

⁷K. Hald, P. Jørgensen, J. Olsen, and M. Jaszuński, *J Chem Phys* **115** (2001) 671

Series AsH, SbH, BiH

When is CC superior to GAS-Cl?



- CC₄₃ calculations consistently better than CAS-CISD⁸

⁸M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **86** (2012) 012503

2. Correlated Wavefunction Theory for \mathbf{E}_{eff}

The pseudo-scalar \mathcal{PT} -odd eEDM Hamiltonian:

- Salpeter's⁹ modified Dirac equation:

$$[\gamma^\mu \left(-i\hbar\partial_\mu - \frac{e}{c}A_\mu \right) + m_0 c \mathbb{1}_4] \psi(x) = \frac{d_e}{4} \gamma^0 \gamma^5 (\gamma^\mu \gamma^\nu - \gamma^\nu \gamma^\mu) F_{\mu\nu} \psi(x)$$

- from which the eEDM operator can be written as an expectation value:

$$\langle -d_e \gamma^0 \Sigma \cdot \mathbf{E} \rangle_{\psi_H} = \frac{2icd_e}{e\hbar} \langle \gamma^0 \gamma^5 \vec{p}^2 \rangle_{\psi_H}$$

- Requires kinetic-energy integrals of the type:

$$\langle \psi^L | \vec{p}^2 | \psi^S \rangle$$

- and therefore explicitly the Small-component wave functions.

- Implemented in the DIRAC11 program package¹⁰

⁹E. Salpeter, *Phys Rev* **112** (1958) 1642

¹⁰DIRAC, a relativistic ab initio electronic structure program, Release DIRAC11 (2011), written by R. Bast, H. J. Aa. Jensen, T. Saue, L. Visscher, et al.

2. Correlated Wavefunction Theory for E_{eff}

Configuration Interaction Expectation Value

- Dirac-Coulomb Hamiltonian operator

$$\hat{H}^{DC} = \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + \beta_i m_0 c^2 + V_{iA}] + \sum_{i,j > i} \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_{A,B > A} V_{AB}$$

- All-electron Dirac-Coulomb Hartree-Fock (DCHF) calculation
set of time-reversal paired 4-spinors $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

- Expansion and variation in N -electron sector of Fock space

$$|\psi_k\rangle = \sum_{I=1}^{\dim \mathcal{F}^t(M,N)} c_{kI} |(\mathcal{S}\bar{\mathcal{T}})_I\rangle$$

- Expectation value with eEDM interaction Hamiltonian¹¹

$$\langle \hat{H}_{\text{edm}} \rangle_{\psi_k} = \sum_{I,J=1}^{\dim \mathcal{F}^t(M,N)} c_{kI}^* c_{kJ} \langle (\mathcal{S}\bar{\mathcal{T}})_I | \sum_{i=1}^N \hat{H}_{\text{edm}}(i) | (\mathcal{S}\bar{\mathcal{T}})_J \rangle$$

¹¹T. Fleig and M. K. Nayak, submitted.

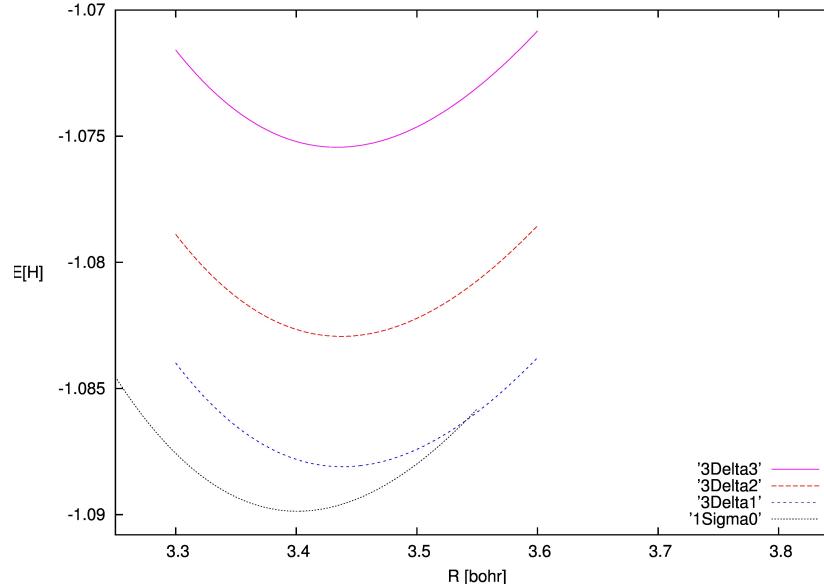
3. HfF⁺ Electronic Structure and EDM Interaction Constant

GAS-CI definitions

	# of Kramers pairs	accumulated # of electrons	
		min.	max.
<i>Virtual Kramers pairs</i>	118	34	34
<i>Hf: 6s, 5d</i>	6	34-p	34
<i>F: 2s, 2p</i>	4	32-(m+n)	32
<i>Hf: 5s, 5p</i> <i>F: 1s</i>	5	24-m	24
<i>Hf: 4f</i>	7	14-q	14
<i>Frozen core</i>	(23)		

HfF⁺ electronic states and spectroscopic constants

$\Omega = 3$ (Hf²⁺6s¹5d¹)
 $\Omega = 2$ (Hf²⁺6s¹5d¹)
 $\Omega = 1$ (Hf²⁺6s¹5d¹)
 $\Omega = 0$ (Hf²⁺6s²)



Model	R _e [a.u.]				ω _e [cm ⁻¹]			
	Ω = 0	Ω = 1	Ω = 2	Ω = 3	Ω = 0	Ω = 1	Ω = 2	Ω = 3
CAS-Cl(10)	3.400	3.436	3.434	3.431	796	774	775	778
MR-CISD(10)	3.506	3.558	3.557	3.552	656	643	643	644
MR-CISD+T(10)	3.510	3.560			654	643		
MR-CISD(20)	3.401	3.438	3.437	3.434	800	768	769	772
Experiment ¹²					790.76	760.9		
Experiment ¹³	3.374	3.407			791.2	761.3	762.3	761.5

¹K. Cossel et al., *Chem. Phys. Lett.* **546** (2012) 1

^mB.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) 201102

HfF⁺ spectroscopy; excitation energies

Model	T_e [cm ⁻¹]				$T_v^{3.4[\text{a.u.}]}$ [cm ⁻¹]	
	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$	$\Omega = 0$	$\Omega = 1$
CAS-CI(10)	1543	0	1058	2480	1488	0
MR-CISD(10)	65	0	1007	2487	0	358
MR-CISD+T(10)	0	25			0	442
MR-CISD(20)	0	387	1521	3166	0	451
MR-CISD+T(20)					0	679
Experiment ¹⁴	0	993	2166	3951		

- Active-space triples correction gives important contribution.
- Estimated MR-CISD+T(20) value for $T_e \approx 1180$ cm⁻¹ ($\Omega = 1$)
- Ongoing investigation of full PECs, transition dipole moments, and vibrational states

¹⁴B.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) 201102

HfF⁺: E_{eff} in the $\Omega = 1$ science state¹⁵

Model	E_{eff} [GV/cm]
CAS-CI(10)	24.1
MR-CISD(10)	22.4
MR-CISD(20)	23.3
MR-CISD+T(20)	23.7
MR-CISD(34)	22.9
MR-CISD(34)+T	23.3
Estimate, Meyer et al. ¹⁶	≈ 30
20 e ⁻ corr., Titov et al. ¹⁷	24.2

- | | |
|---|---|
| (+) All-electron calculation | (-) Basis-set incompleteness
→ vQZ corrections |
| (+) No configuration selection | (-) Higher excitations
→ CC expectation values |
| (+) Spinors as one-particle basis functions | |
| (+) Dirac-Coulomb Hamiltonian | |

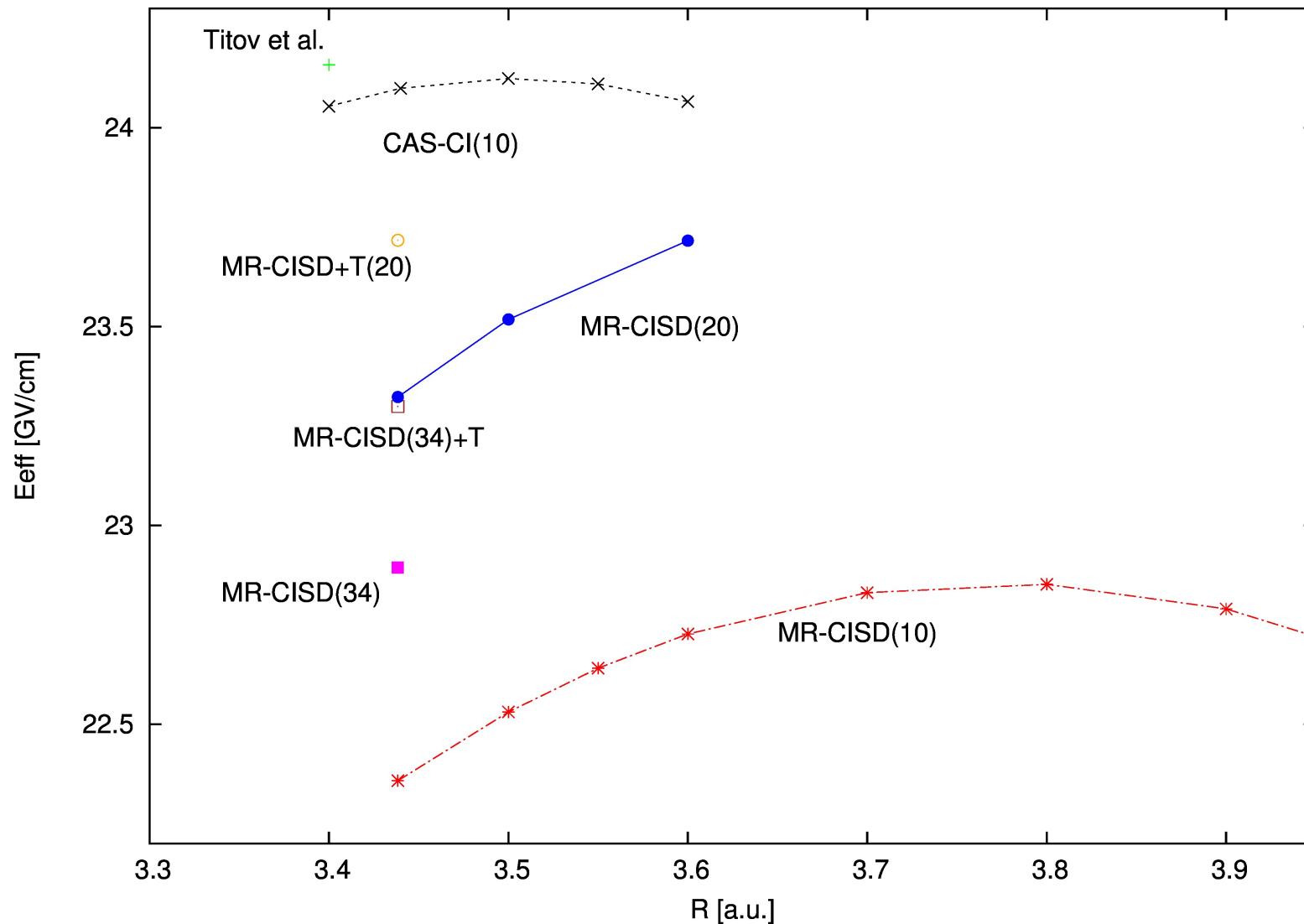
15 T. Fleig and M. K. Nayak, submitted.

¹⁶A.N. Petrov, N.S. Mosyagin, T.A. Isaev, A.V. Titov, *Phys Rev A* **76** (2007) 030501(R)

¹⁷E.R. Meyer, J.L. Bohn, *Phys Rev A* **78** (2008) 010502(R)

The eEDM in a molecular framework

$$\left\langle \hat{H}_{\text{edm}} \right\rangle_{\psi_{\Omega=1}} \text{as a function of } R$$



Ongoing Work

- Commutator-based GER CC Jacobian, **non-relativistic version**
(with Mickael Hubert and Jeppe Olsen)
- Commutator-based GER CC Jacobian, **relativistic version**
(with Mickael Hubert and Lasse Sørensen)
- 4-component **Gaunt / Breit operator** in correlated approaches
(with Jessica Loras)
- 4-Component commutator-based GER CC expectation values
(with Avijit Shee and Malika Denis)

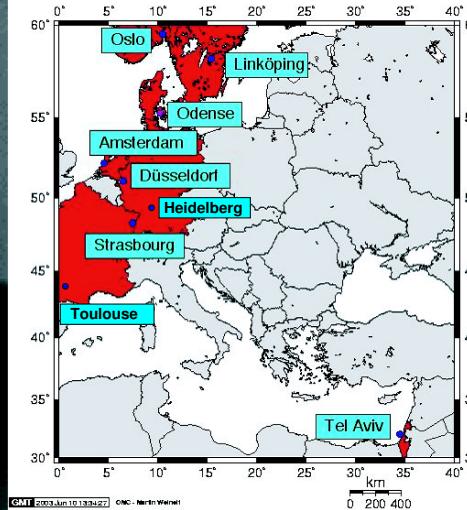
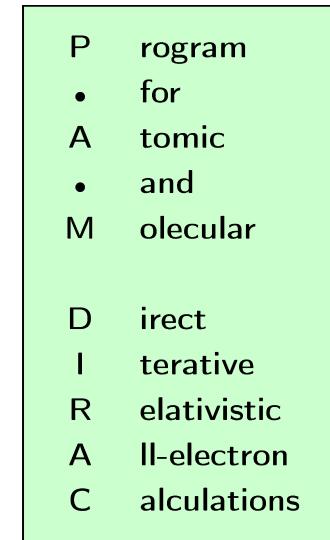
Future Work

Blanc proposal, submitted January 2013.

- **Malika Denis**
- **T. F.**, *Coordinator*
- **Mikhail G. Kozlov**, *St. Petersburg Nuclear Physics Institute*
- **Malaya K. Nayak**, *Bhabha Atomic Research Centre, Mumbai*
- **Jessica Loras**
- **Trond Saue**
- **Avijit Shee**

ThO, ThF⁺, WC
other \mathcal{P} - and \mathcal{P}, \mathcal{T} -nonconserving operators

DIRAC a metalaboratory for the development of relativistic 4- and 2-component electronic-structure methodology



- KR-CI.

Kramers-Restricted GAS Configuration Interaction Program
(released in DIRAC10/DIRAC11/DIRAC12)

Authors: S Knecht, T Fleig, J Olsen, HJAa Jensen

- KR-CC.

Kramers-Restricted GAS Coupled Cluster Program
(not yet released)

Authors: LK Sørensen, J Olsen, M Hubert, T Fleig