

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

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June 18, 2013



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# Overview

## 1. Relativistic Wavefunction Theory

4-component electron correlation methods

## 2. Application to “ $^3\Delta$ molecules”

Spectroscopy and eEDM data

# Four-Component Electronic-Structure Theory

## Some Essentials

- Atomic basis sets; in low-energy approximation

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

Kinetic-balance condition

- Solution of the Dirac-Coulomb Hartree-Fock equations

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

$\varepsilon = E - m_0c^2$

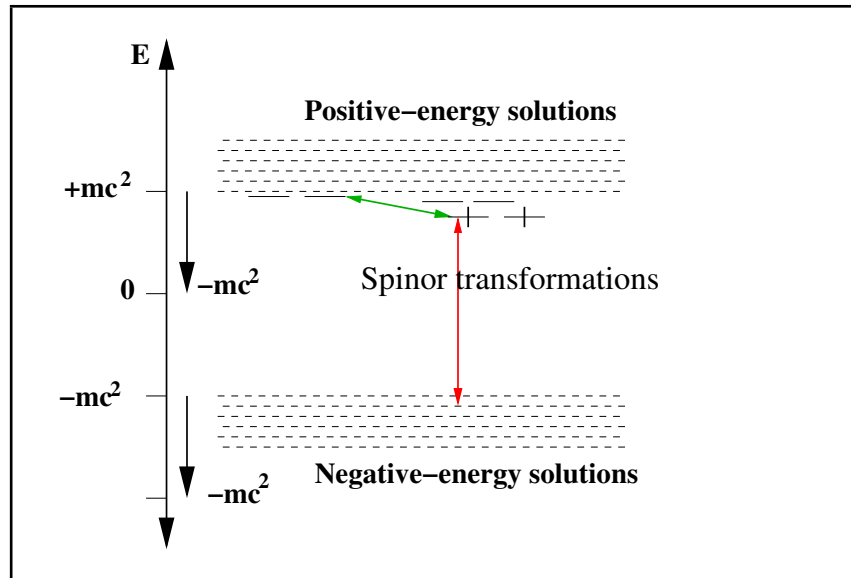
- Fock matrix for “frozen” atomic core

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

# 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  
 $\Rightarrow$  **minimax** variation

# Spinors and Strings

## General principles of rigorous relativistic correlation methods

General concept: Kramers-paired spinors

Time-reversal operator for a fermion:

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

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:

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

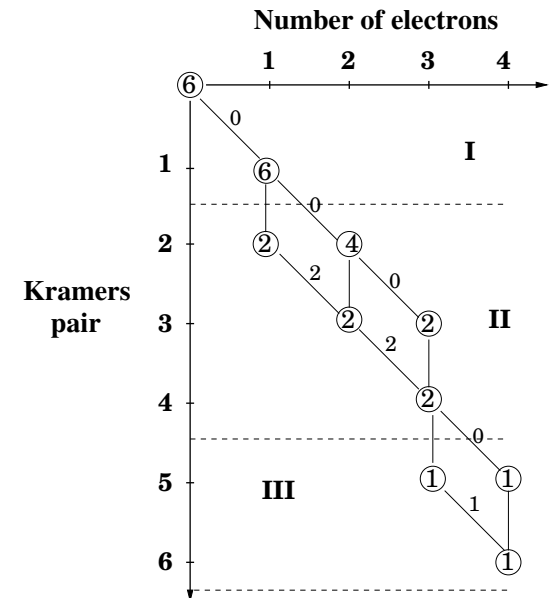
- Many-particle wavefunction defined as

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

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

- Configuration Interaction: Slater determinants

Coupled Cluster: Individual strings



# 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” (or SR-MR) GAS-CC  
Generalized “Oliphant/Adamowicz” Ansatz<sup>1</sup>

- 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

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

- Relativistic generalization of cluster operators

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

Example for constructed higher excitations:

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

		min acc. el.	max acc. el.
GAS IV	External	n	n
GAS III	1 Valence*	n-2	n
GAS II	1 Valence	n-4	n
GAS I	Outer Core	n-4	n-2

<sup>1</sup>N. Oliphant, L. Adamowicz *J Chem Phys* **94** (1991) 1229

# Relativistic Generalized-Active-Space CC

## Excitation Energies<sup>2</sup>

$$J_{\mu}^{CC} = \sum_{\nu} A_{\mu\nu} x_{\nu} = \sum_{\nu} \left\langle \mu_{\text{GAS}} | e^{-\hat{T}_{\text{GAS}}} \left[ \hat{H}, \hat{\tau}_{\nu\text{GAS}} \right] e^{\hat{T}_{\text{GAS}}} | \Phi_0 \right\rangle x_{\nu}$$

$$A_{\mu\nu} = \left\langle \mu | \left( \left[ \hat{H}, \hat{\tau}_{\nu\text{GAS}} \right] + \left[ \left[ \hat{H}, \hat{\tau}_{\nu\text{GAS}} \right], \hat{T} \right] + \frac{1}{2} \left[ \left[ \left[ \hat{H}, \hat{\tau}_{\nu\text{GAS}} \right], \hat{T} \right], \hat{T} \right] \dots \right) | \Phi_0 \right\rangle$$

## Algorithm for Jacobian matrix elements<sup>3</sup>

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

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

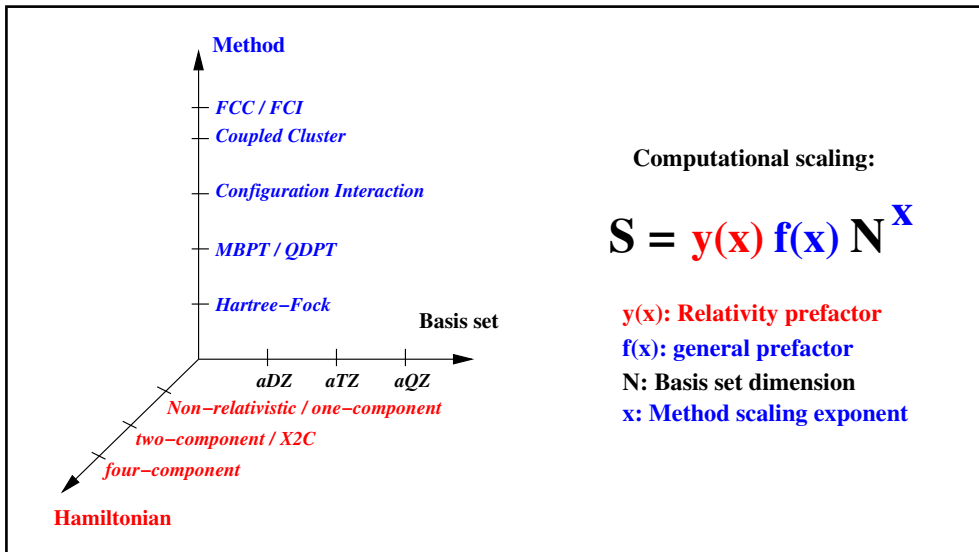
<sup>2</sup>M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **86** (2012) 012503

<sup>3</sup>L. 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

# Special Relativity and Electron Correlation

## Computational Scaling



$$S^{\text{rel. CC}} \approx 4 \sqrt{\pi \left(\frac{x}{2} - 1\right)} \frac{1}{4} \left[ \frac{x^2}{4} - \frac{3}{2}x + 2 \right] \begin{pmatrix} x - 2 \\ \frac{x}{2} - 1 \end{pmatrix} O^{\frac{x}{2}-1} V^{\frac{x}{2}+1}$$

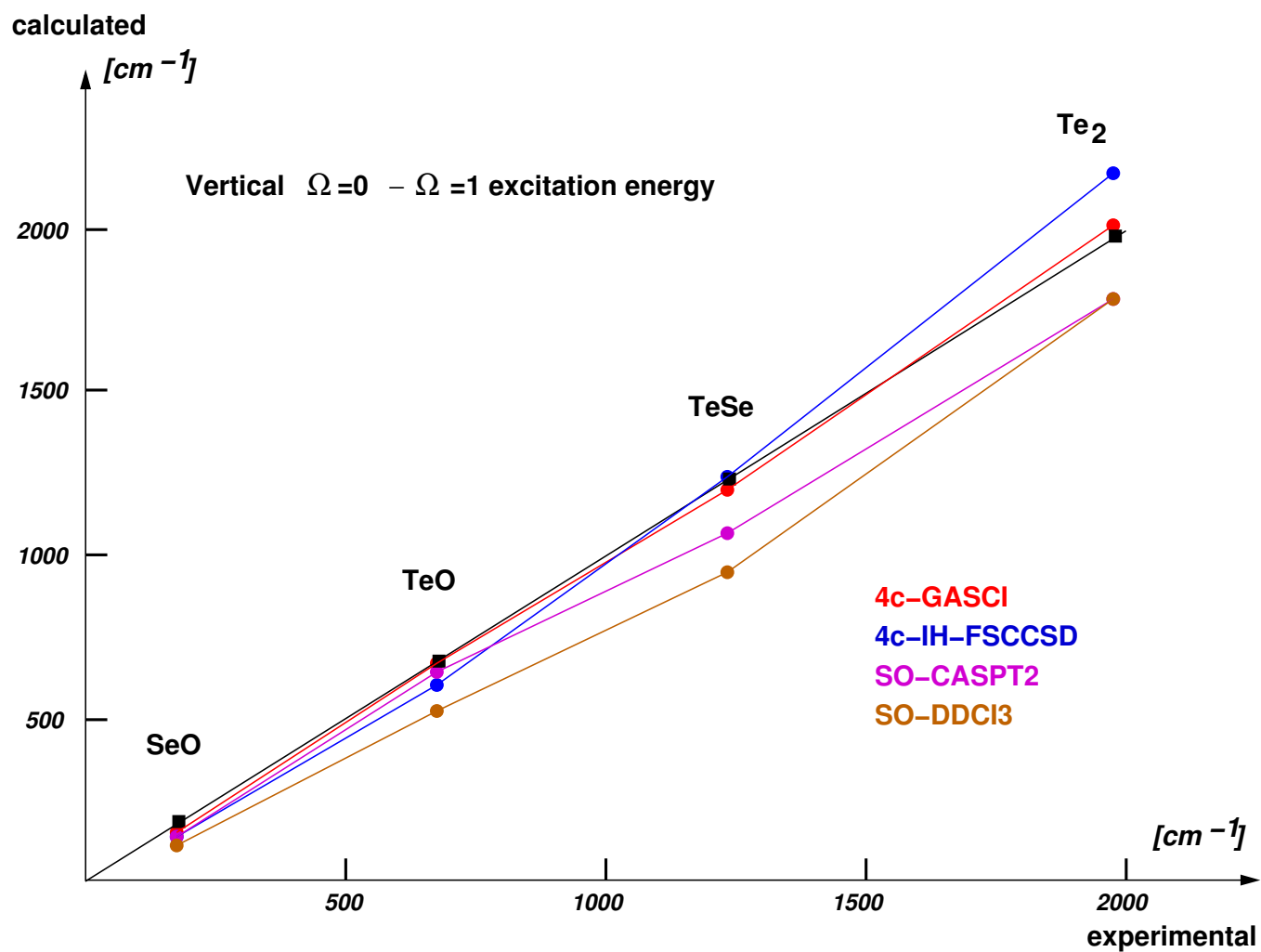
Method	Non-Rel.	2-comp.	4-comp.
Hartree-Fock	$N^4$	$8N^4$	$8 \left(\frac{5}{2}N\right)^4$
4-Index transformation	$2N^5$	$32N^5$	$128N^5$
CCSD	$3N^6$	$10 \cdot 3N^6$	
CCSDT	$30N^8$	$12 \cdot 30N^8$	
CCSDTQ	$210N^{10}$	$14 \cdot 210N^{10}$	

⇒ The correlated stage is the computational bottleneck (no savings in 2c formalism).



# Special Relativity and Electron Correlation

Additive and non-additive methods, CI and CC<sup>4</sup>



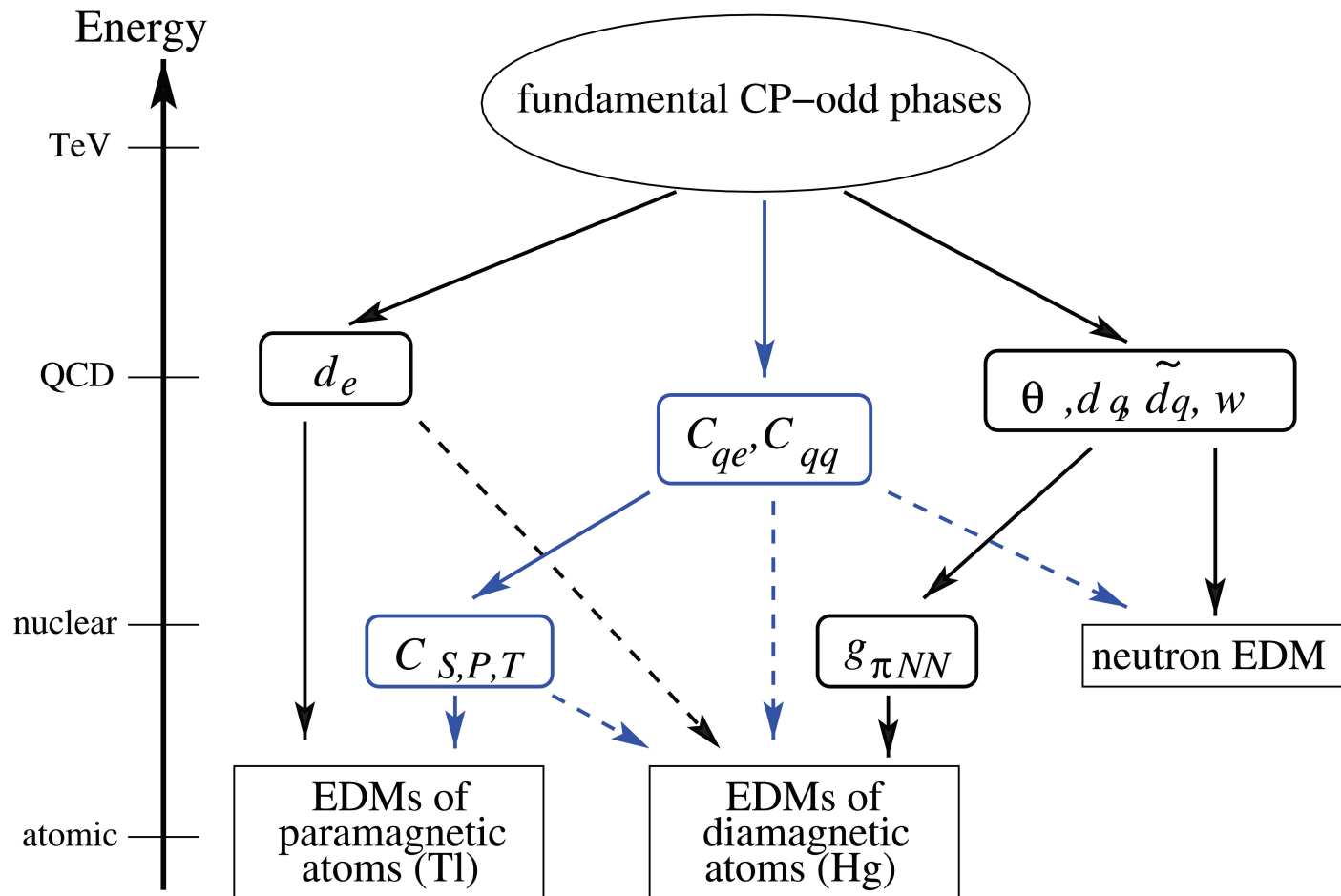
<sup>4</sup>J.-B. Rota, S. Knecht, T. Fleig, D. Ganyushin, T. Saue, F. Neese, H. Bolvin, *J Chem Phys* **135** (2011) 114106

# Overview

1. Relativistic Wavefunction Theory  
4 components electron correlation methods
- 2. Application to “ $^3\Delta$  molecules”  
Spectroscopy and eEDM data**

# CP-Violating Physics

## Characteristics and energy scales<sup>5</sup>



<sup>5</sup>M. Pospelov, A. Ritz, "Electric dipole moments as probes of new physics", *Ann. Phys.* **318** (2005) 119

# The eEDM in a molecular framework

## Wavefunction theory

- Molecular Dirac-Coulomb Hamiltonian:

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

- Gaunt term absent; only small errors in heavy-element molecules
- Variationally optimized coefficients  $\{c_{kI}\}$  of wavefunction expansion

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

- 4c-CI expectation values<sup>6</sup> over eEDM Hamiltonian

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

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<sup>6</sup>T. Fleig and M. K. Nayak, PRX, submitted, under revision.

# The eEDM in a molecular framework

## EDM Hamiltonian

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

- Point of departure: Salpeter's<sup>7</sup> modified Dirac equation:

$$\left[ \gamma^\mu \left( -i\hbar\partial_\mu - \frac{e}{c}A_\mu \right) + m_0c\mathbb{1}_4 \right] \psi(x) = \frac{d_e}{4} \gamma^0 \gamma^5 (\gamma^\mu \gamma^\nu - \gamma^\nu \gamma^\mu) F_{\mu\nu} \psi(x)$$

- neglecting the less important<sup>8</sup> magnetic part  $-d_e v \vec{\gamma} \cdot \mathbf{B}$
- from which the eEDM operator can be written as an expectation value:

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

- In a many-body system  $\hat{H}_{\text{edm}}$  appears as

$$\sum_{i=1}^N \hat{H}_{\text{edm}}(i) = -d_e \sum_{i=1}^N \gamma^0(i) \boldsymbol{\Sigma}(i) \cdot \mathbf{E}(i).$$

- Required kinetic-energy integrals of the type  $\langle \psi^L | \vec{p}_j^2 | \psi^S \rangle$

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<sup>7</sup>E. Salpeter, *Phys Rev* **112** (1958) 1642

<sup>8</sup>E. Lindroth, B. W. Lynn, P. G. H. Sandars, *J Phys B: At Mol Opt Phys* **22** (1989) 559

# The eEDM in a molecular framework

## GASCI wavefunctions for HfF<sup>+</sup>

Correct relative description of

$\Omega = 0$  (Hf  $6s^2$ ,  $^1\Sigma_0^+$ ) and

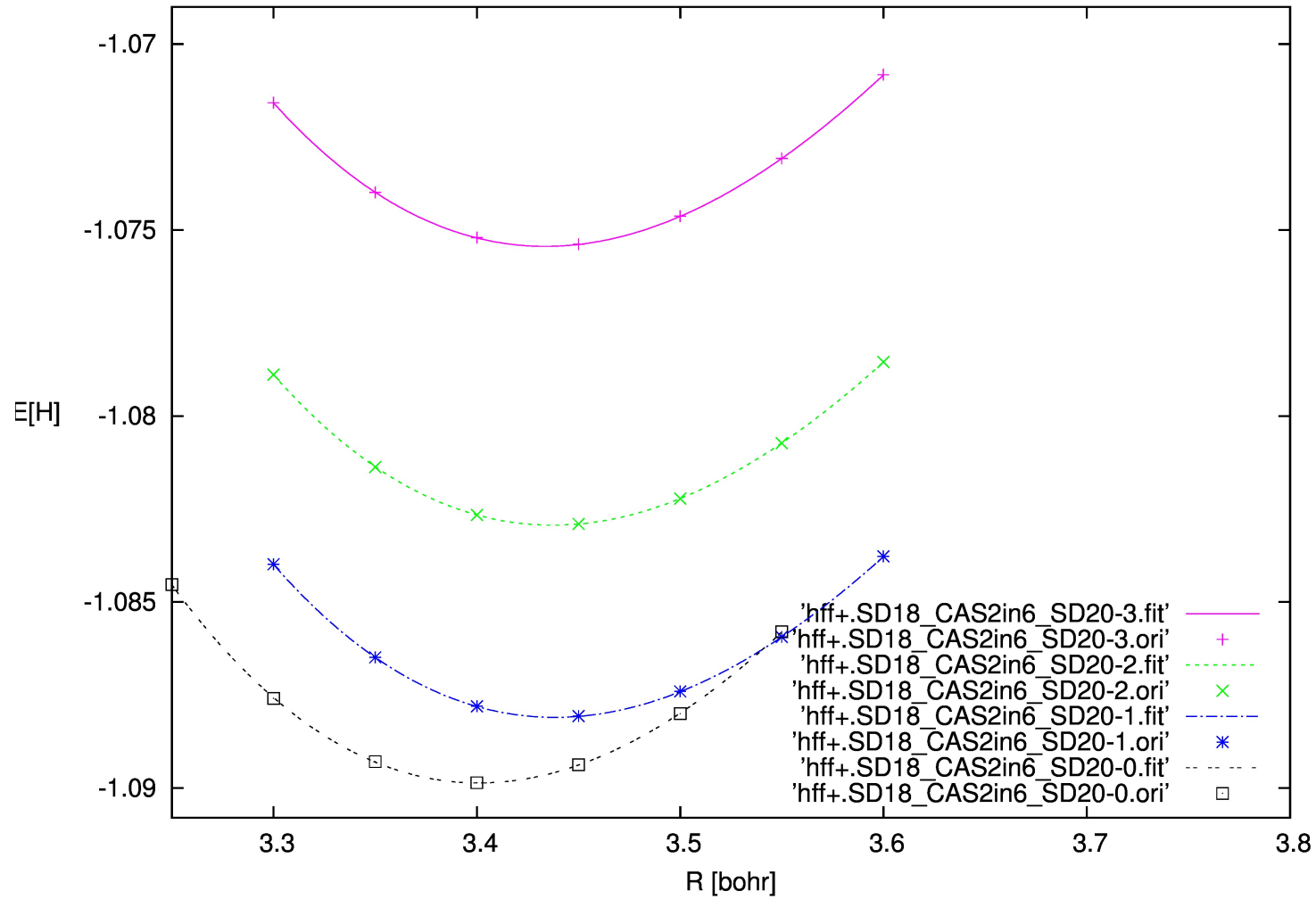
$\Omega = 1$  (Hf  $6s^1 5d^1$ ,  $^3\Delta_1$ ) important for

1. Spectroscopic properties of involved states
2. Lifetime  $\tau_{\Omega=1} = \left( \sum_k W_{k,\Omega=1}^s \right)^{-1}$  of “science” state

label	configurations
CAS-CI(10)	$F(2s2p)^8 \text{ Hf}(6s5d)^2, F(2s2p)^7 \text{ Hf}(6s5d)^3, F(2s2p)^6 \text{ Hf}(6s5d)^4$
MR-CISD(10)	+ $v^1 + v^2$ configurations
MR-CISD(20)	+ up to 2 holes in Hf(5s5p) and F(1s) shells
MR-CISD+T(20)	+ active-space defined Triples replacements to MR-CISD(20)
MR-CISD(34)	MR-CISD(20) + up to 1 hole in Hf(4f) shell
MR-CISD(34)+T	MR-CISD(34) + 20-electron Triples correction

# The eEDM in a molecular framework

$\text{Hff}^+$  potential curves in RASCISD approximation



# The eEDM in a molecular framework

## HfF<sup>+</sup> spectroscopy; excitation energy and correlation model

Model	R <sub>e</sub> [a.u.]		ω <sub>e</sub> [cm <sup>-1</sup> ]				T <sub>e</sub> [cm <sup>-1</sup> ]			
	Ω = 0	Ω = 1	Ω = 0	Ω = 1	Ω = 2	Ω = 3	Ω = 0	Ω = 1	Ω = 2	Ω = 3
CAS-CI(10)	3.400	3.435	793	773	774	777	1543	0	1057	2480
MR-CISD(10)	3.506	3.558	651	639	639	640	68	0	1007	2489
MR-CISD+T(10)	3.510	3.560	649	640			0	26		
MR-CISD(20)	3.401	3.438	794	766	766	770	0	386	1519	3165
MR <sub>10</sub> -CISD(20)	3.401	3.439	796	766	769	769	0	752	1881	3533
Experiment <sup>9</sup>			790.76	760.9			0	991.83		
Experiment <sup>10</sup>	3.374	3.407	791.2	761.3	762.3	761.5	0	993	2166	3951

- CAS-CI(10) reproduces relative energies of Ω = 0 and Ω = 1 incorrectly.
- MR-CISD(10) accounts for required differential electron correlations.
- MR-CISD(20) is an acceptable model.
- MR<sub>10</sub>-CISD+T(20) will yield a very accurate description.

<sup>9</sup>K.C. Cossel, D.N. Gresh, L.C. Sinclair, T. Coffrey, L.V. Skripnikov, A.N. Petrov, N.S. Mosyagin, A.V. Titov, R.W. Field, E.R. Meyer, E.A. Cornell, J. Ye, *Chem Phys Lett* **546** (2012) 1

<sup>10</sup>B.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) 201102



# The eEDM in a molecular framework

$\text{HfF}^+$ :  $E_{\text{eff}}$  in the  $\Omega = 1$  science state

Model	$E_{\text{eff}} \left[ \frac{\text{GV}}{\text{cm}} \right]$	
	vDZ	vTZ
CAS-CI(10)		24.1
MR-CISD(10)	21.6	22.4
MR-CISD(20)	22.9	23.3
MR <sub>10</sub> -CISD(20)	23.0	
MR-CISD+T(20)		23.7
MR-CISD(34)		22.9
MR-CISD(34)+T		23.3
Meyer et al. <sup>11</sup>	$\approx 30$	
Titov: 20 e <sup>-</sup> corr. <sup>12</sup>	24.2	

Correction estimate:

(±1%) Basis set

(±2%) Number of correlated electrons

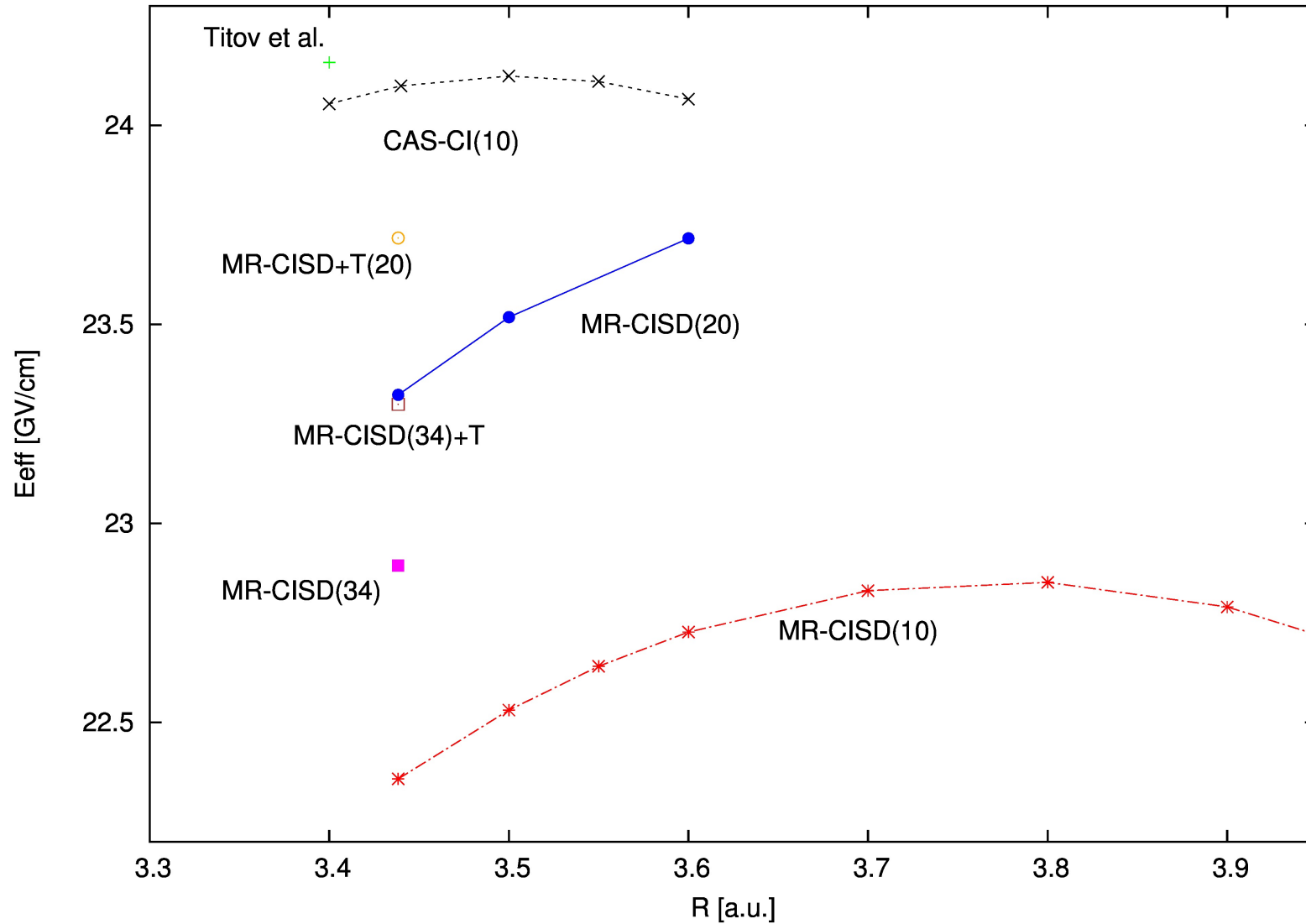
(±2%) Higher excitations

<sup>11</sup>E.R. Meyer, J.L. Bohn, *Phys Rev A* **78** (2008) 010502(R)

<sup>12</sup>A.N. Petrov, N.S. Mosyagin, T.A. Isaev, A.V. Titov, *Phys Rev A* **76** (2007) 030501(R)

# The eEDM in a molecular framework

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



# eEDM in $^3\Delta$ Molecules

## ThO

	# of Kramers pairs	accumulated # of electrons	
		min.	max.
<b>Virtual Kramers pairs</b>	<b>X</b>	<b>18</b>	<b>18</b>
<b>Th: 7s, 6d, 7p</b>	<b>9</b>	<b>18-n</b>	<b>18</b>
<b>Th: 6s, 6p O: 2s, 2p</b>	<b>8</b>	<b>16-m</b>	<b>16</b>
<b>(Th: 5s, 5p, 5d) Frozen core</b>	<b>(41)</b>		
CAS2in9		$n = 0$	$m = 0$
CAS2in9_SD2		$n = 2$	$m = 0$
SD16_CAS2in9_SD18		$n = 2$	$m = 2$

Vertical excitation energies  $T_v$  [ $\text{cm}^{-1}$ ]

Correlation model	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$
CAS2in9	0	6706	7349	8333
CAS2in9_SD2	0	6598	7074	8090
SD16_CAS2in9_SD18	0	6420	7240	8527
Exp. $^{13}$ ( $T_e$ )	0	5317	6128	8600

$R = 3.477$  a.u., vDZ, Dirac-Coulomb

Effective electric field $E_{\text{eff}}$ [ $\frac{\text{GV}}{\text{cm}}$ ]	
CAS2in9	75.2
CAS2in9_SD2	71.7
SD16_CAS2in9_SD18	74.1
Meyer, Bohn	104

- Rather weak correlation effects
- $\longrightarrow$  Potential curves, deeper core correlation for  $E_{\text{eff}}$ , Th(5s, 5p, 5d) shells, vTZ basis sets

<sup>13</sup>J. Paulovic, T. Nakajima, K. Hirao, R. Lindh, P.-Å. Malmqvist, *J Chem Phys* **119** (2003) 798, and refs.

# eEDM in ${}^3\Delta$ Molecules



	# of Kramers pairs	accumulated # of electrons	
		min.	max.
<i>Virtual Kramers pairs</i>	<b>X</b>	<b>18</b>	<b>18</b>
<i>Th: 7s, 6d</i>	<b>6</b>	<b>18-n</b>	<b>18</b>
<i>Th: 6s, 6p F: 2s, 2p</i>	<b>8</b>	<b>16-m</b>	<b>16</b>
<i>(Th: 5s, 5p, 5d) Frozen core</i>	<b>(41)</b>		
CAS2in6		$n = 0$	$m = 0$
CAS2in6_SD2		$n = 2$	$m = 0$
SD16_CAS2in6_SD18		$n = 2$	$m = 2$

Vertical excitation energies  $T_v$  [ $\text{cm}^{-1}$ ]

Correlation model	$\Omega = 0$	$\Omega = 1$
CAS2in6	-1101	0
CAS2in6_SD2	-334	0
Exp. <sup>14</sup> ( $T_e$ )	0	315

$R = 3.8$  a.u., vDZ, Dirac-Coulomb

Effective electric field  $E_{\text{eff}}$  [ $\frac{\text{GV}}{\text{cm}}$ ]

CAS2in6	32.7
CAS2in6_SD2	45.2
Meyer, Bohn	90

- Strong correlation effects on spectroscopic constants and  $E_{\text{eff}}$
- $\longrightarrow$  Valence and outer core shells to be considered,  $\text{Th}(6s, 6p, 5s, 5p, 5d)$ ,  $\text{O}(2s, 2p)$

<sup>14</sup>B. J. Barker, I. O. Antonov, M. C. Heaven, K. A. Peterson, *J Chem Phys* **136** (2012) 104305

# Future Work

AGENCE NATIONALE DE LA RECHERCHE  
ANR Blanc program.

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

ThO, ThF<sup>+</sup>, WC; (transition) dipole moments; hyperfine coupling constants  
other  $\mathcal{P}$ - and  $\mathcal{P}, \mathcal{T}$ -nonconserving operators