Relativistic Four-Component Electron Correlation Methods. Development and Applications in Spectroscopy and Fundamental Physics

Timo Fleig

Laboratoire de Chimie et de Physique Quantiques
Université Paul Sabatier Toulouse III
France

September 25, 2012

Motivation

Science with small heavy-element molecules

Ultracold molecular investigations[1]

Photoassociation via excited states

Astrophysics[2]

Collision processes in stellar atmospheres

Actinide/transition-metal theoretical spectroscopy[3]

Electronic structure in general

Fundamental physics[4]

Search for the electron Electric Dipole Moment (eEDM)

---

[1] J. Doyle, B. Friedrich, R.V. Krems, F. Masnou-Seeuws, *Eur Phys J D* **31** (2004) *149*

[2] M. Asplund, N. Grevesse, A.J. Sauval, and P. Scott, *Annu Rev Astron Astrophys* **47** (2009) *481*

[3] B.O. Roos, P.-Aa. Malmqvist, and L. Gagliardi, *J Am Chem Soc* **128** (2006) *17000*

[4] A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, and E.A. Cornell, *arXiv:1008.2997v2 [physics.atom-ph]* (2010)

Overview

1) **General Introduction: Relativity and Electron Correlation**

2) **Spinor-string based GAS Coupled Cluster and Configuration Interaction**

3) **Electron-EDM $\mathcal{P},\mathcal{T}$-odd Constants**

Relativistic Electronic-Structure Theory

Idealism and Pragmatism

- Quantum Electrodynamics (QED) is the most rigorous theoretical ground for atomic and molecular electronic structure

  Less adapted to situations where electron interactions dominate and/or electron correlation effects are strong[5]

- "Filled-sea Fock-space" approaches do not seem to be a satisfactory option[6]

  Problems related to Negative-energy State (NES) correlations

- A viable and widely used alternative is the "Empty-Dirac" picture

  Usually in conjunction with a No-Virtual-Pair (NVP) approximation

[5] W. Kutzelnigg, *Chem Phys* **395** (2012) *16*

[6] W. Liu, *Phys Chem Chem Phys* **14** (2012) *35*

Relativistic Electronic-Structure Theory

The Dirac Equation

Bi-spinor form with shifted energy

$$\begin{pmatrix} V\mathbf{1}_2 & c\boldsymbol{\sigma}\cdot\boldsymbol{p} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{p} & \left(V-2mc^2\right)\mathbf{1}_2 \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}^L \\ \boldsymbol{\psi}^S \end{pmatrix} = E \begin{pmatrix} \boldsymbol{\psi}^L \\ \boldsymbol{\psi}^S \end{pmatrix}$$

gives rise to 4-component solutions with

$\boldsymbol{\psi}^L$ Large component 2-spinor

$\boldsymbol{\psi}^S$ Small component 2-spinor

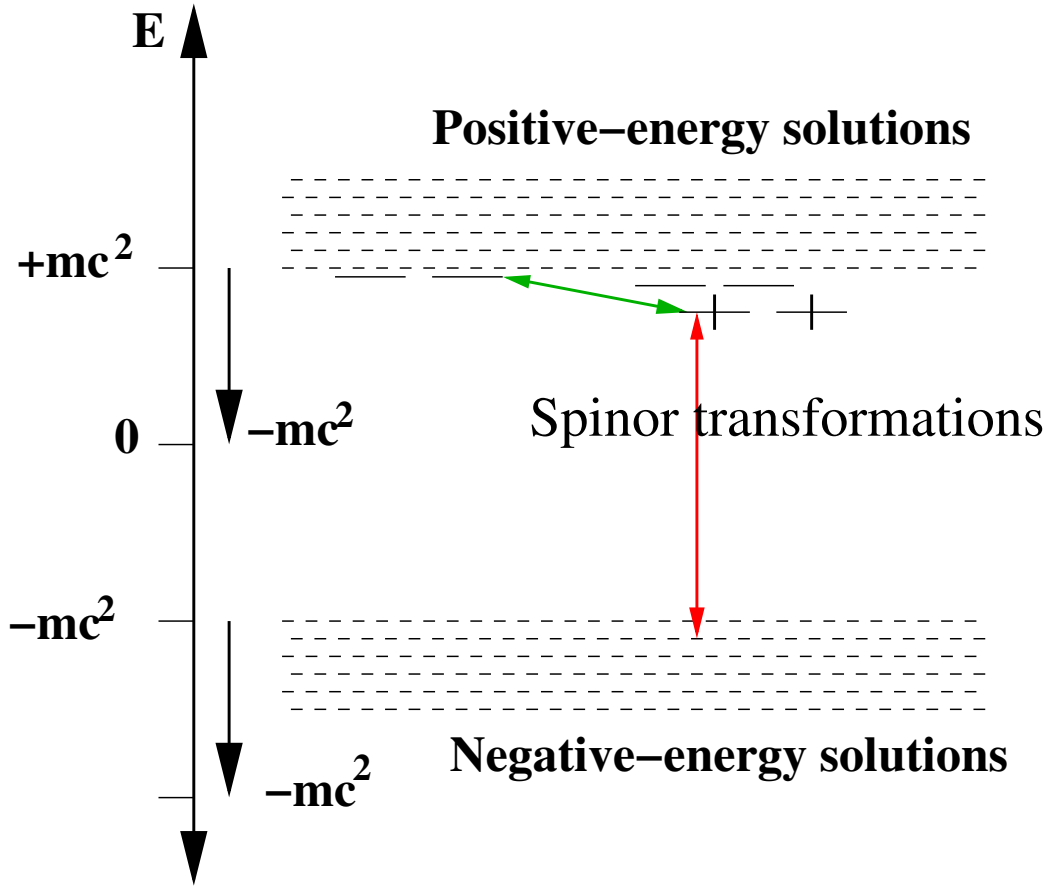
Kinetic balance condition[7] for kinetic energy $(c\boldsymbol{\sigma}\cdot\boldsymbol{p})^2$

$\longrightarrow$ Additional high-ℓ basis set for $\boldsymbol{\psi}^S$

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

Relativistic Electronic-Structure Theory

Spectrum of the Dirac Hamiltonian



Relativistic Electronic-Structure Theory

Laboratoire de Chimie et Physique Quantiques

Electron-electron interaction

Approximated low-frequency limit QED Hamiltonian

$$\hat{g}(1,2) = \frac{1}{r_{12}}\mathbf{1}_4 - \left\{ \frac{\boldsymbol{\alpha_1}\cdot\boldsymbol{\alpha_2}}{r_{12}} + \frac{(\boldsymbol{\alpha_1}\cdot\boldsymbol{\nabla_1})(\boldsymbol{\alpha_2}\cdot\boldsymbol{\nabla_2})r_{12}}{2} \right\} + \mathcal{O}\left(\alpha^3\right)$$

$\frac{1}{r_{12}}$ Coulomb term ($\rightarrow$ Spin-same-orbit interaction)

$-\frac{\boldsymbol{\alpha_1}\cdot\boldsymbol{\alpha_2}}{r_{12}}$ Gaunt term ($\rightarrow$ Spin-other-orbit interaction)

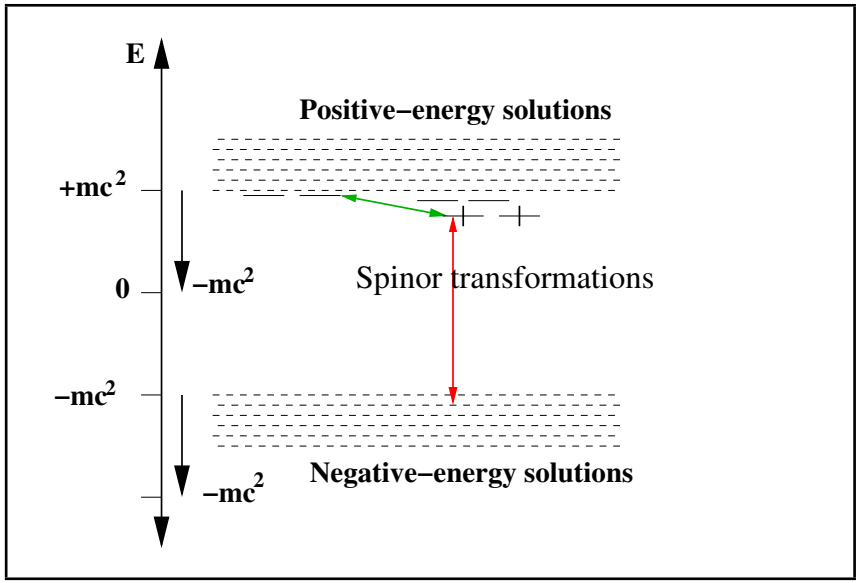
$-\frac{(\boldsymbol{\alpha_1}\cdot\boldsymbol{\nabla_1})(\boldsymbol{\alpha_2}\cdot\boldsymbol{\nabla_2})r_{12}}{2}$ Gauge term (Coulomb-, Feynman gauge)

$\{\dots\}$ Breit interaction

$\mathcal{O}\left(\alpha^3\right)$ Higher-order terms, QED corrections

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
  $\left\langle Ref|\hat{H}|Ref\right\rangle = \left\langle 0|e^{-\hat{\kappa}}\hat{H}e^{\hat{\kappa}}|0\right\rangle$

- Approximation of general expectation value to first order:
  $\left\langle 0|e^{-\hat{\kappa}}\hat{H}^{DC}e^{\hat{\kappa}}|0\right\rangle \approx \left\langle 0\right| \left[\hat{H}^{DC},\hat{\kappa}\right] \left|0\right\rangle = \sum_{pq} \kappa_{pq} \left[\left\langle 0|\hat{H}^{DC}a_p^\dagger a_q|0\right\rangle - \left\langle 0|\hat{H}^{DC}a_q^\dagger a_p|0\right\rangle^*\right]$
- Parameterized Dirac-spinor transformations:
  $\hat{\kappa} = \sum_{pq}\left[\kappa_{p+q+}a^\dagger_{p+}a_{q+} + \kappa_{p+q-}a^\dagger_{p+}a_{q-} + \kappa_{p-q+}a^\dagger_{p-}a_{q+} + \kappa_{p-q-}a^\dagger_{p-}a_{q-}\right]$
- Green terms: minimization of energy w.r.t. rotations
- Red terms: maximization of energy w.r.t. rotations
  $\Rightarrow$ **minimax** variation

Four-Component Correlation Methods

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

Integrals over positive-energy 4-spinors:

$$
\begin{aligned}
h^{+}_{mn} &= \left\langle \psi^{+}_{m} | \hat{h} | \psi^{+}_{n} \right\rangle = \left\langle \begin{pmatrix} \psi^{L}_{m} & \psi^{S}_{m} \end{pmatrix} \middle| \begin{pmatrix} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{pmatrix} \middle| \begin{pmatrix} \psi^{L}_{n} \\ \psi^{S}_{n} \end{pmatrix} \right\rangle \\
&= \left\langle \psi^{L}_{m} | \hat{h}_{11} | \psi^{L}_{n} \right\rangle + \left\langle \psi^{L}_{m} | \hat{h}_{12} | \psi^{S}_{n} \right\rangle + \left\langle \psi^{S}_{m} | \hat{h}_{21} | \psi^{L}_{n} \right\rangle + \left\langle \psi^{S}_{m} | \hat{h}_{22} | \psi^{S}_{n} \right\rangle \\
&= \sum_{J=1}^{N^L} \sum_{K=1}^{N^L} c^{L^*}_{mJ} \left\langle \phi^{L}_{J} | \hat{h}_{11} | \phi^{L}_{K} \right\rangle c^{L}_{nK} + \sum_{J=1}^{N^L} \sum_{K=1}^{N^S} c^{L^*}_{mJ} \left\langle \phi^{L}_{J} | \hat{h}_{12} | \phi^{S}_{K} \right\rangle c^{S}_{nK} \\
&+ \sum_{J=1}^{N^S} \sum_{K=1}^{N^L} c^{S^*}_{mJ} \left\langle \phi^{S}_{J} | \hat{h}_{21} | \phi^{L}_{K} \right\rangle c^{L}_{nK} + \sum_{J=1}^{N^S} \sum_{K=1}^{N^S} c^{S^*}_{mJ} \left\langle \phi^{S}_{J} | \hat{h}_{22} | \phi^{S}_{K} \right\rangle c^{S}_{nK}
\end{aligned}
$$

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

Special Relativity and Electron Correlation

Laboratoire de Chimie et Physique Quantiques

Principal Approaches for Molecules

Spinor–based models

Hartree–Fock		*Dynamic Correlation*
2– or 4–component Hamiltonian	+	2– or 4–component Hamiltonian

Double–group MPPT/CI/CC

Spinorbital–based models

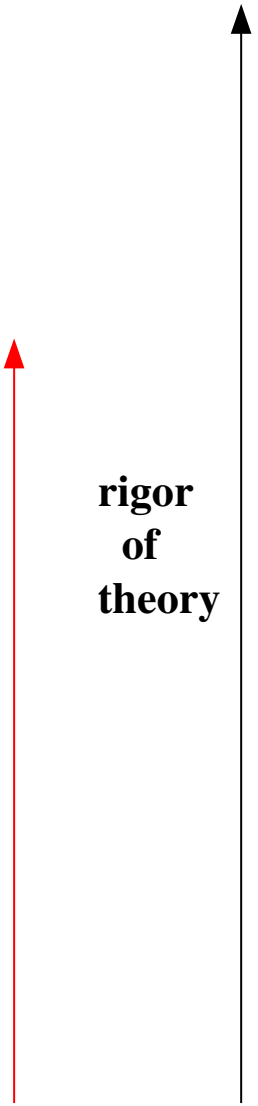
Hartree–Fock		*Dynamic Correlation*
scalar relativistic Hamiltonian	+	2–component Hamiltonian

Spin–orbit CI
Spin–orbit Coupled Cluster

Additive models

Hartree–Fock		*Dynamic Correlation*		*Magnetic Couplings*
scalar relativistic Hamiltonian	+	scalar relativistic Hamiltonian	+	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:

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

Double group symmetry and quaternion algebra

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

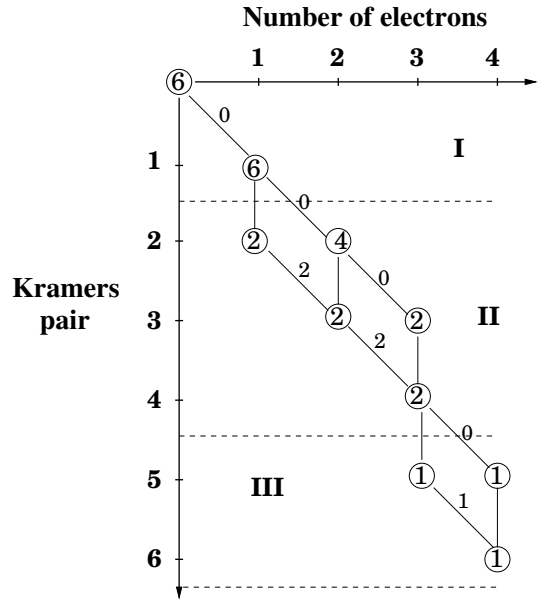
Spinor basis:

$\phi_i = a_i^\dagger \mid\rangle \qquad \phi_{\bar{i}} = a_{\bar{i}}^\dagger \mid\rangle$

- Many-particle wavefunction defined as
  - 1 unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$
  - 1 barred (Kramers down) string $\overline{\mathcal{S}} = a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

- Configuration Interaction: **Slater determinants**

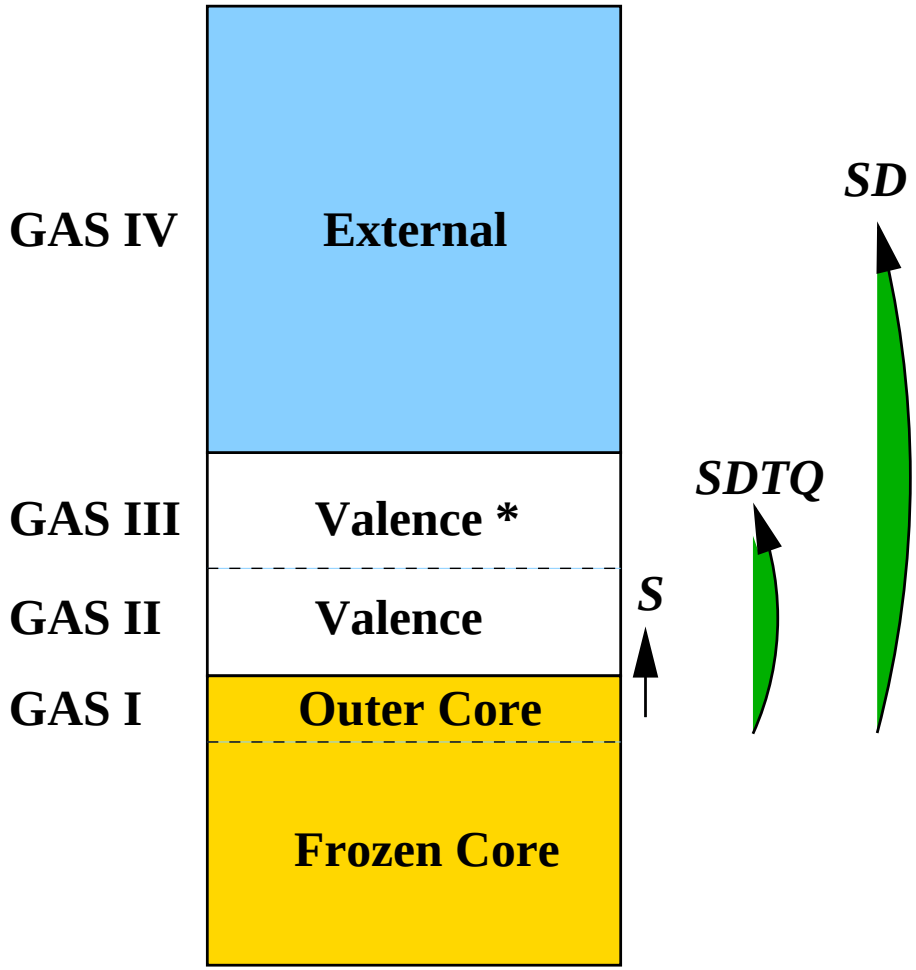
  Coupled Cluster: **Individual strings**



⊗ 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 diatomics[8]

Vertical excitation energies among π^{*2} state manifold

ΛS *States* ${}^3\Sigma^-, {}^1\Delta, {}^1\Sigma^+ \longrightarrow 0^+, 1, 2, 0^+, (\Omega)$

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

Purely molecular spin-orbit splitting

Contenders:

"Additive"[9]: *SO-DDCI3*, *SO-CASPT2*

"Non-additive"[10]: *4c-IH-FSCC*, *4c-GASCI*

---

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

[9] F. Neese, *J Chem Phys* **119** (2003) *9428*

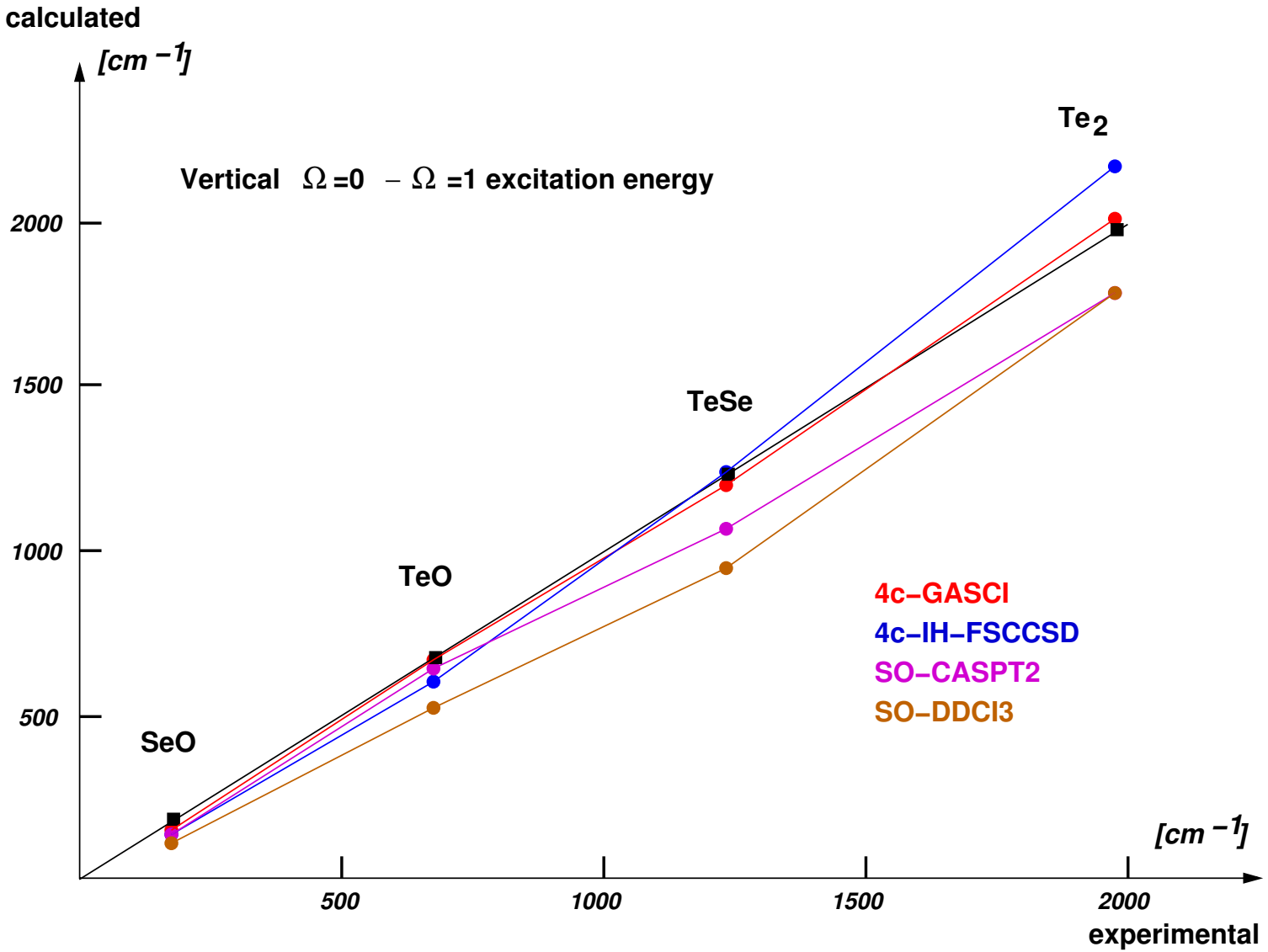
P.-Aa. Malmqvist, B.O. Roos, B. Schimmelpfennig, *Chem Phys Lett* **357** (2002) *357*

[10] L. 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*

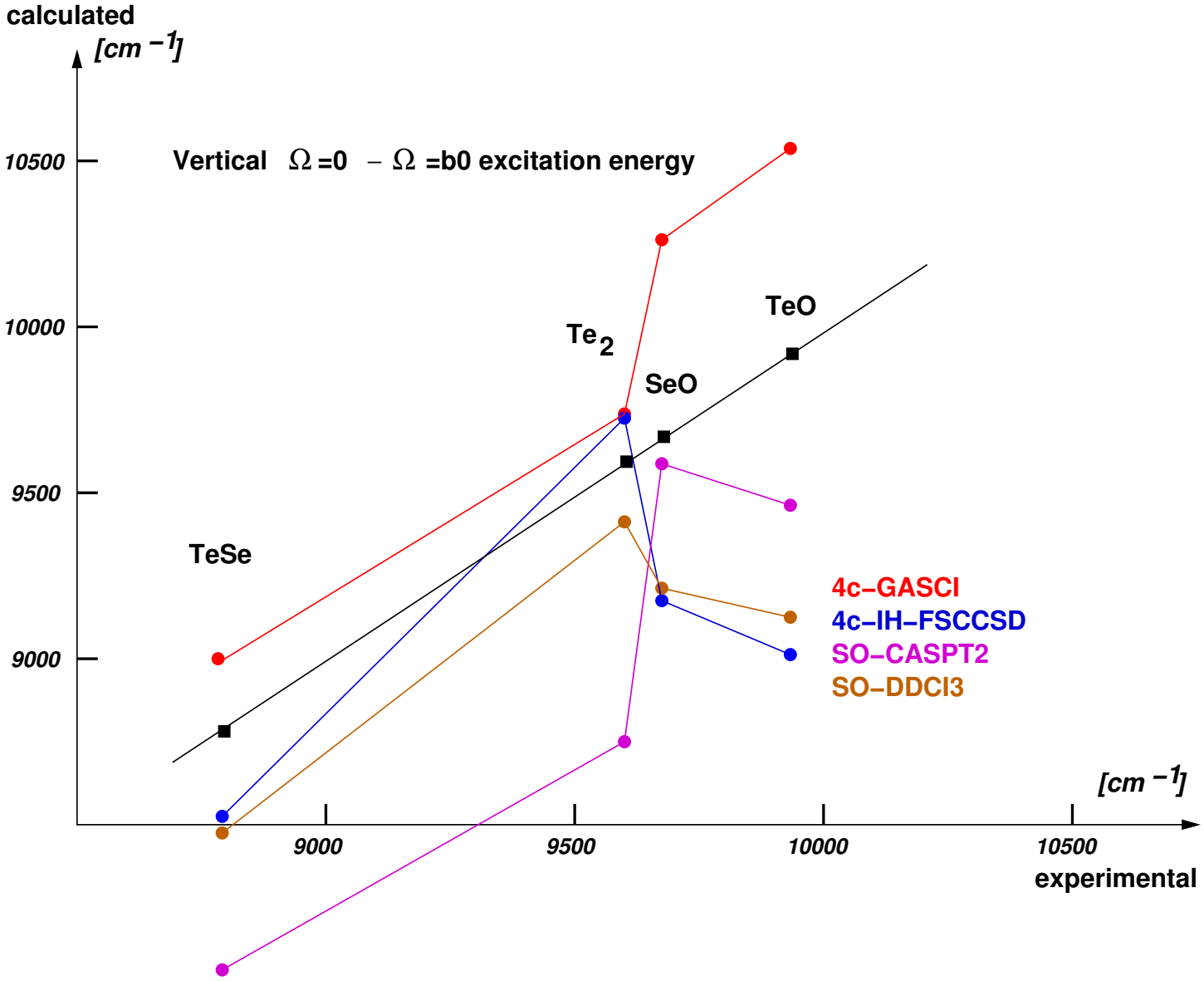
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



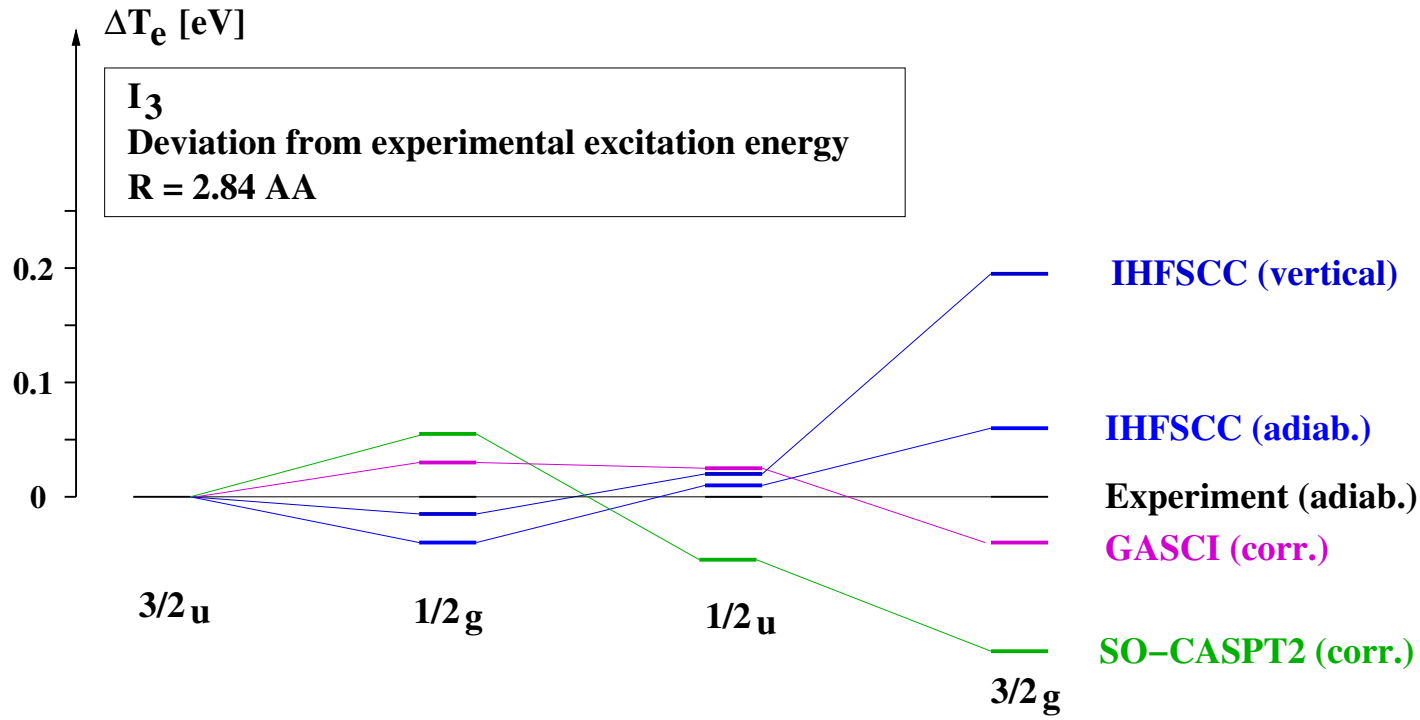
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Comparison of Methods

Electronic spectrum of I_3; Ω states[11]



- 2c-GASCI and SO-CASPT2 corrected for non-parallelity
- IH-FSCC shows smallest errors (also in closed-shell I_3^- system)
- Errors of 2c-GASCI < 0.05 eV

[11] A.S.P. Gomes, L. Visscher, H. Bolvin, T. Saue, S. Knecht, T. Fleig, E. Eliav, *J Chem Phys* **133** (2010) *064305*

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

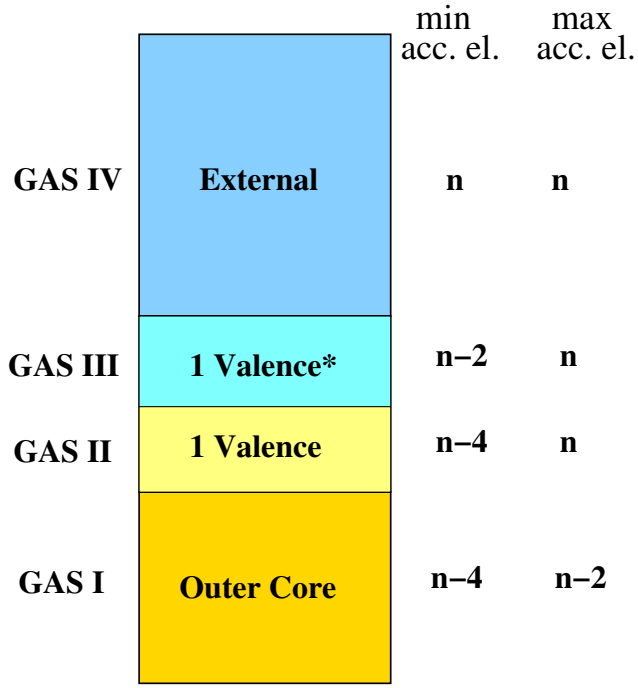
CI inefficient in treating higher excitations

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" Ansatz[12]
- GAS-extended excitation manifold
  $\langle \mu_{\mathrm{GASCC}}| = \langle \psi^{\mathrm{Ref}}| \, \hat{\tau}^{\dagger}_{\mu_{\mathrm{GAS}}}$
- $\hat{\tau}_{\mu_{\mathrm{GAS}}}$ contains GAS-selected higher excitations
  $|\psi^{\mathrm{GASCC}}\rangle = exp(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu_{\mathrm{GAS}}}) \; |\psi^{\mathrm{Ref}}\rangle$
- Relativistic generalization of cluster operators
  $\hat{T}_1 = \sum_{ia} \left\{ \; t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \; \right\}$; $\hat{T}_2 = \ldots$



Example for constructed higher excitations:

$$\langle \mu_{\mathrm{GASCC}}| \;\; = \;\; \left\langle \mu^{S(\mathrm{III}^1)} \right| + \left\langle \mu^{S(\mathrm{IV}^1)} \right| + \left\langle \mu^{D(\mathrm{III}^2)} \right| + \left\langle \mu^{D(\mathrm{IV}^2)} \right| + \left\langle \mu^{D(\mathrm{III}^1+\mathrm{IV}^1)} \right|$$
$$+ \left\langle \boldsymbol{\mu}^{\mathbf{T}(\mathbf{III}^1+\mathbf{IV}^2)} \right| + \left\langle \boldsymbol{\mu}^{\mathbf{T}(\mathbf{III}^2+\mathbf{IV}^1)} \right| + \left\langle \boldsymbol{\mu}^{\mathbf{Q}(\mathbf{III}^2+\mathbf{IV}^2)} \right|$$

[12] N. Oliphant, L. Adamowicz *J Chem Phys* **94** (1991) *1229*

Relativistic Generalized-Active-Space CC

Electronic Ground States [13]

CC vector function

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

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

$$[[\hat{H}_{2v,2v},\hat{T}_{2v,2o}],\hat{T}_{2v,2o}]$$
$$= \frac{1}{4} \sum_{abcd,i'j'a'b',i''j''a''b''} (ad|bc) t^{a'b'}_{i'j'} t^{a''b''}_{i''j''} a^\dagger_a a^\dagger_b \overbrace{a_c a_d a^\dagger_{a'} a^\dagger_{b'} a_{i'} a_{j'} a^\dagger_{a''} a^\dagger_{b''} a_{i''} a_{j''}}^{} .$$

[13] 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*

Relativistic Generalized-Active-Space CC[14]

Excitation Energies[15]

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

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

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

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

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

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

Computational scaling:

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

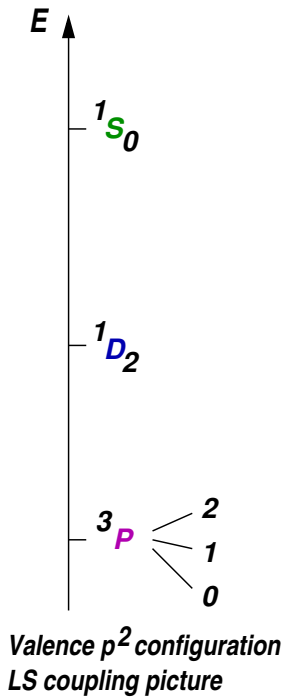
Conventional CC: $O^n V^{n+2}$

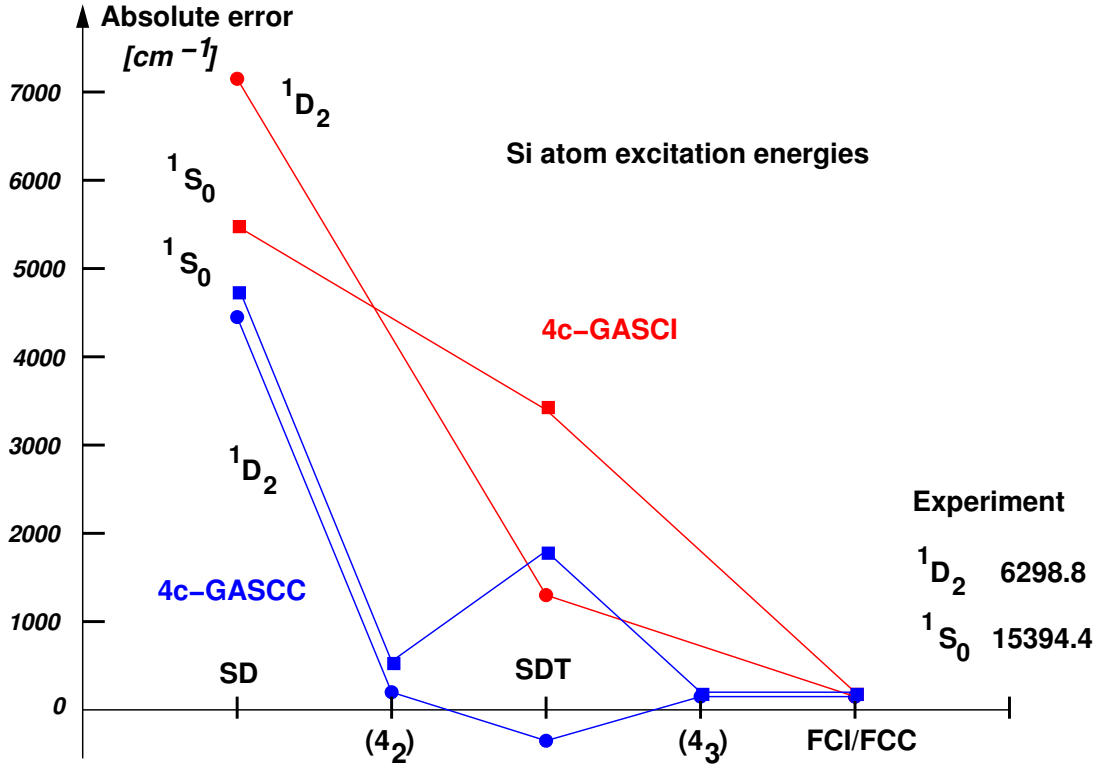
[14] M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **86** (2012) *012503*

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

A Simple (?) Test Case: Si Atom

- Closed-shell single-reference calculations





- CISD and CCSD exhibit huge (positive) errors
- Selected higher excitations give decisive correction

Test Case: Si Atom

Analysis of Fermi vacuum determinant

- Reference determinant built from $j-j$-coupled Pauli spinors:

$$|j(1),m_j(1);j(2),m_j(2)| = \left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right| = -\sqrt{\frac{2}{3}}\,{}^3P_0 - \frac{1}{\sqrt{3}}\,{}^1S_0$$

- Significant admixture from one excited state
- Reference determinant is biased and unbalanced
- Single excitations represent some excited states:

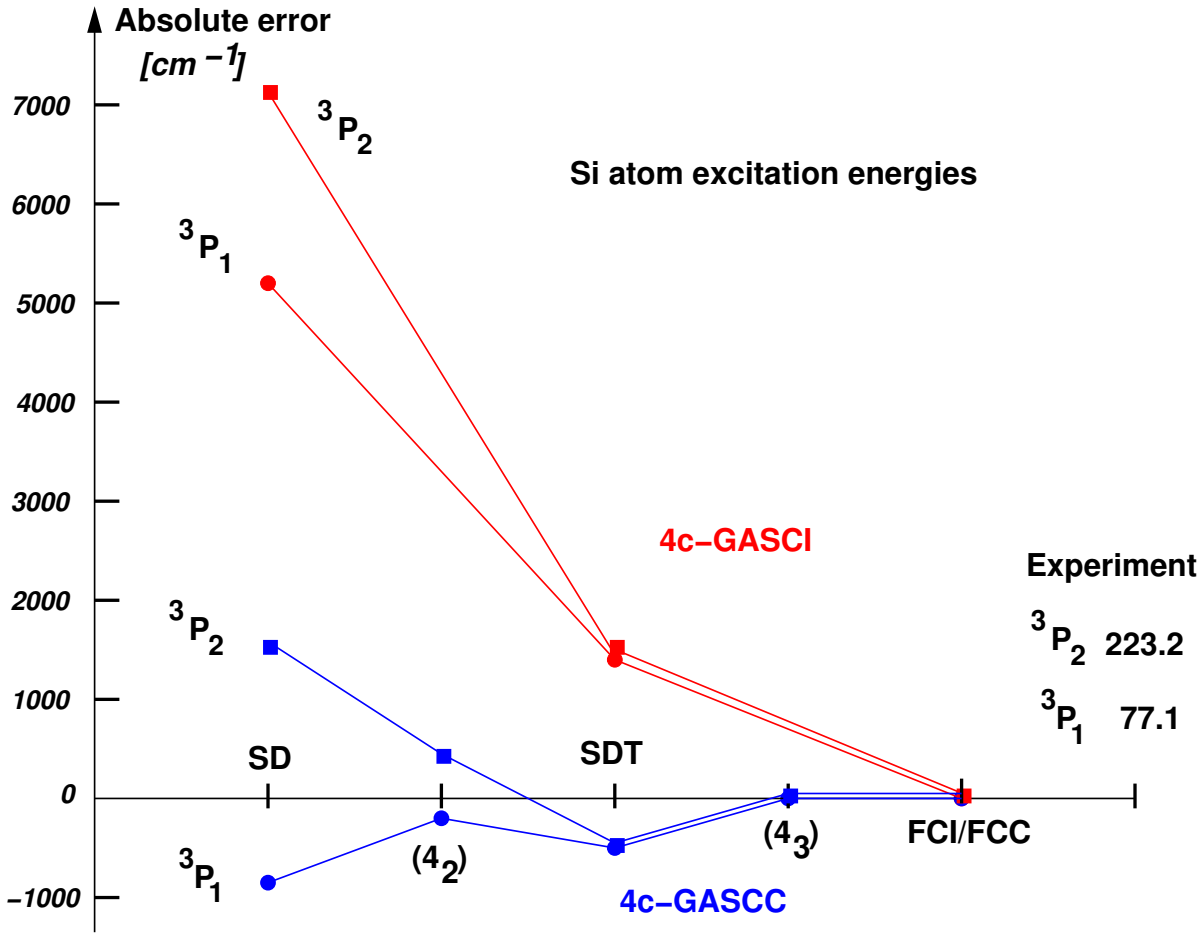
$$\left|\frac{3}{2},\frac{1}{2};\frac{1}{2},\frac{1}{2}\right| = -\frac{1}{2}\,{}^3P_1 - \frac{1}{2}\,{}^3P_2 + \frac{1}{\sqrt{2}}\,{}^1D_2$$

- Double excitations add ${}^1S_0$ character:

$$\left|\frac{3}{2},\frac{3}{2};\frac{3}{2},-\frac{3}{2}\right| = \frac{1}{\sqrt{3}}\,{}^3P_2 + \frac{1}{\sqrt{6}}\,{}^1D_2 - \frac{1}{\sqrt{6}}\,{}^3P_0 + \frac{1}{\sqrt{3}}\,{}^1S_0$$

Test Case: Si Atom

Understanding the first-order SO splitting



- Selected higher excitations give large correction, but
- CC(4_2) not sufficiently accurate

Study of a Molecular Series

The pnictogen monohydrides

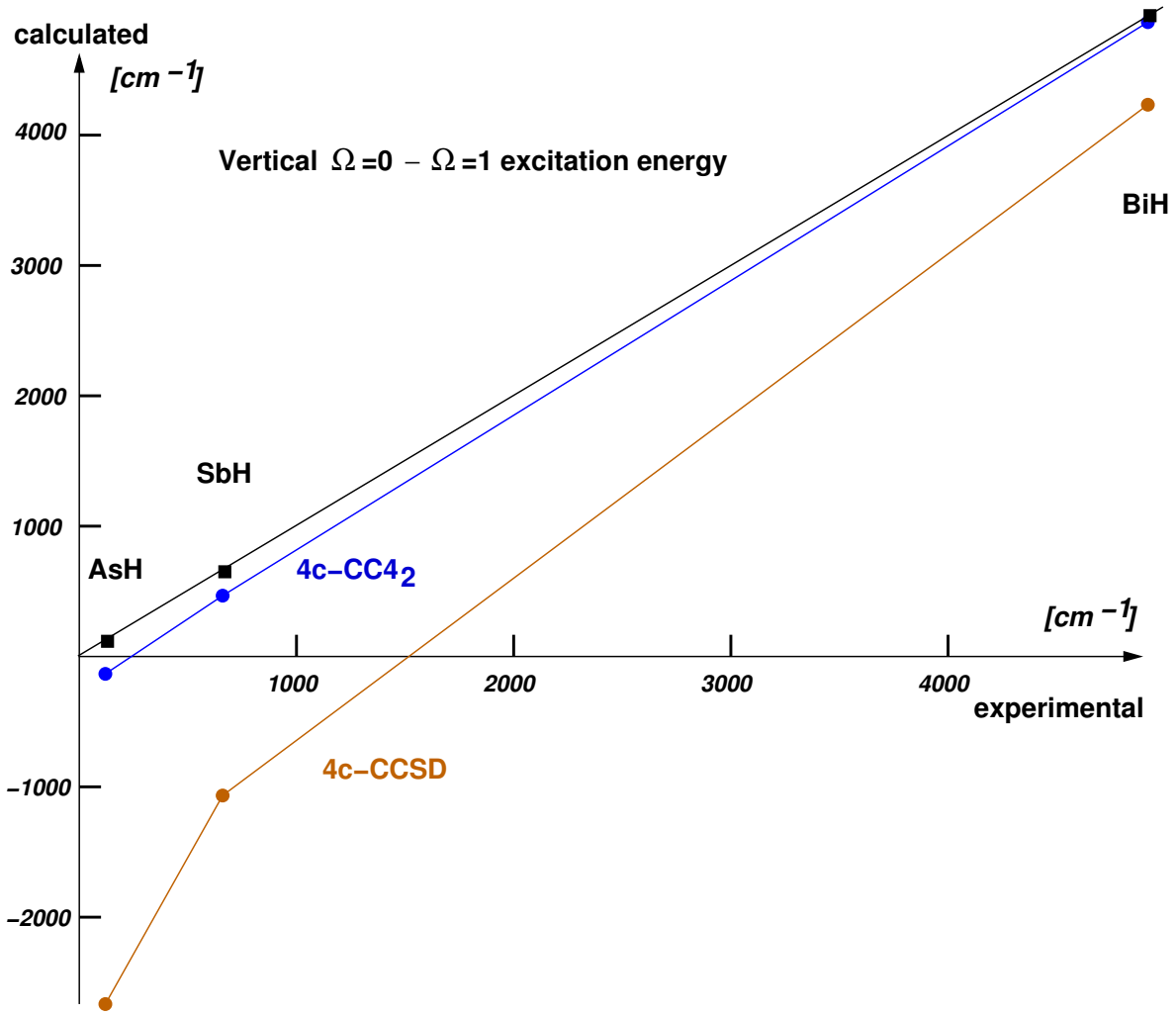
AsH, SbH, BiH

- Ground-state configuration $ns^2\sigma^2\pi^2$
- ω coupling picture for heavier elements
- $\Omega = 0 : \pi^1_{1/2}\pi^1_{-1/2}$ and $\pi^1_{3/2}\pi^1_{-3/2}$ (ground state)
- $\Omega = 1 : \pi^1_{3/2}\pi^1_{-1/2}$ (first excited state)
- Goal: Accurate description of the $\Omega = 0/\Omega = 1$ splitting [16]

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

Series AsH, SbH, BiH

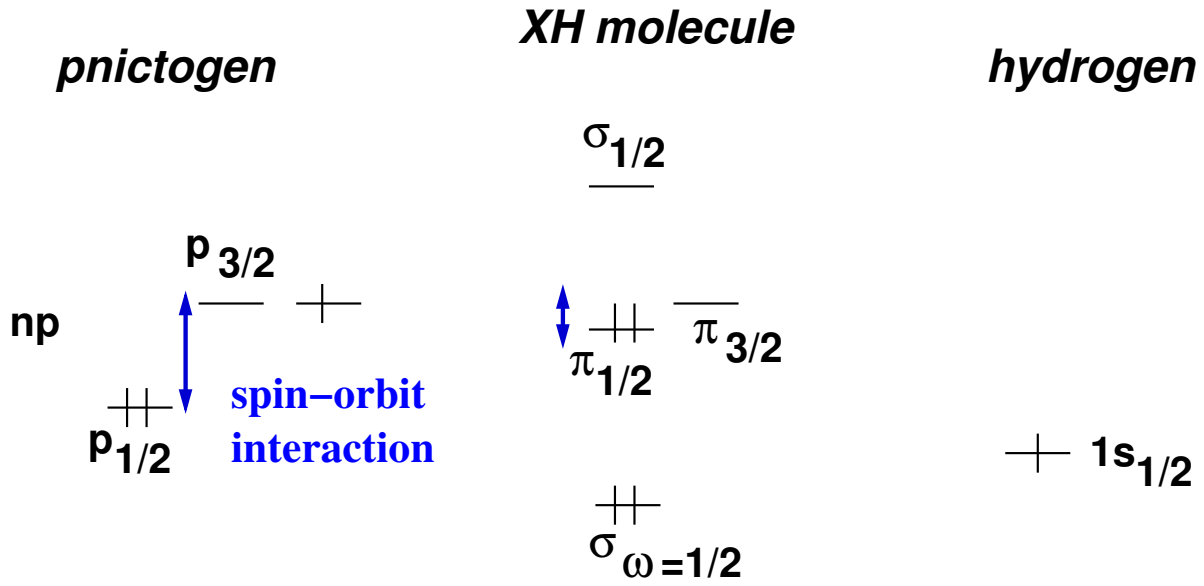
The strange behavior of CCSD



- Huge errors for As homologue

Series AsH, SbH, BiH

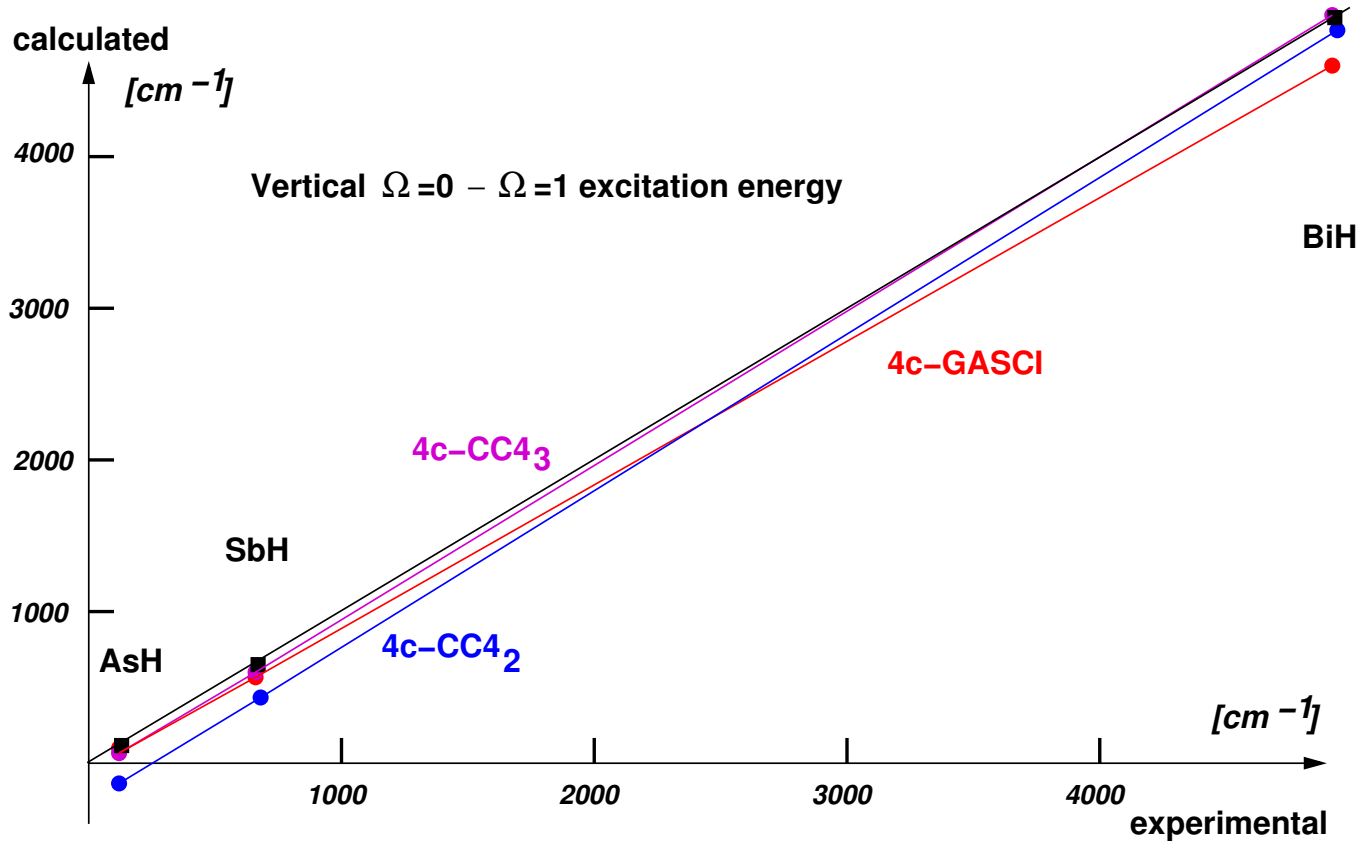
Spinors and the molecular field



- True ground state is a perturbed $^3\Sigma^-$ wavefunction (lighter homologues)
- Requires double excitation to compensate $\Rightarrow$ Bad description at CCSD level
- CC(4_2) corrects for this deficiency

Series AsH, SbH, BiH

When is CC superior to GAS-CI?



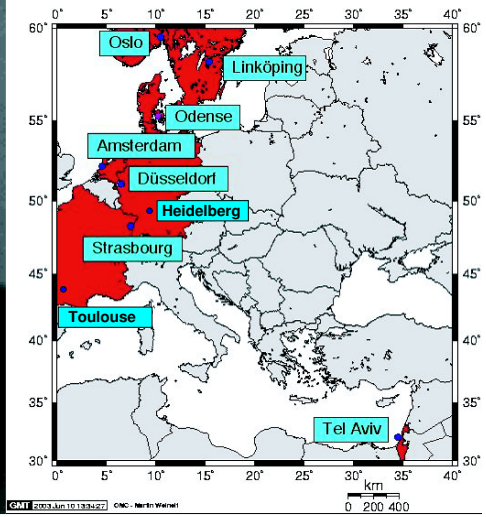
- $CC4_3$ calculations consistently better than CAS-CISD[17]

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

DIRAC a European metalaboratory for the development of relativistic 4- and 2-component quantum-physical and -chemical methodology

P rogram
• for
A tomic
• and
M olecular

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



- `KR-CI`.
  `Kramers-Restricted GAS Configuration Interaction Program`
  (released in DIRAC10/DIRAC11)
  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

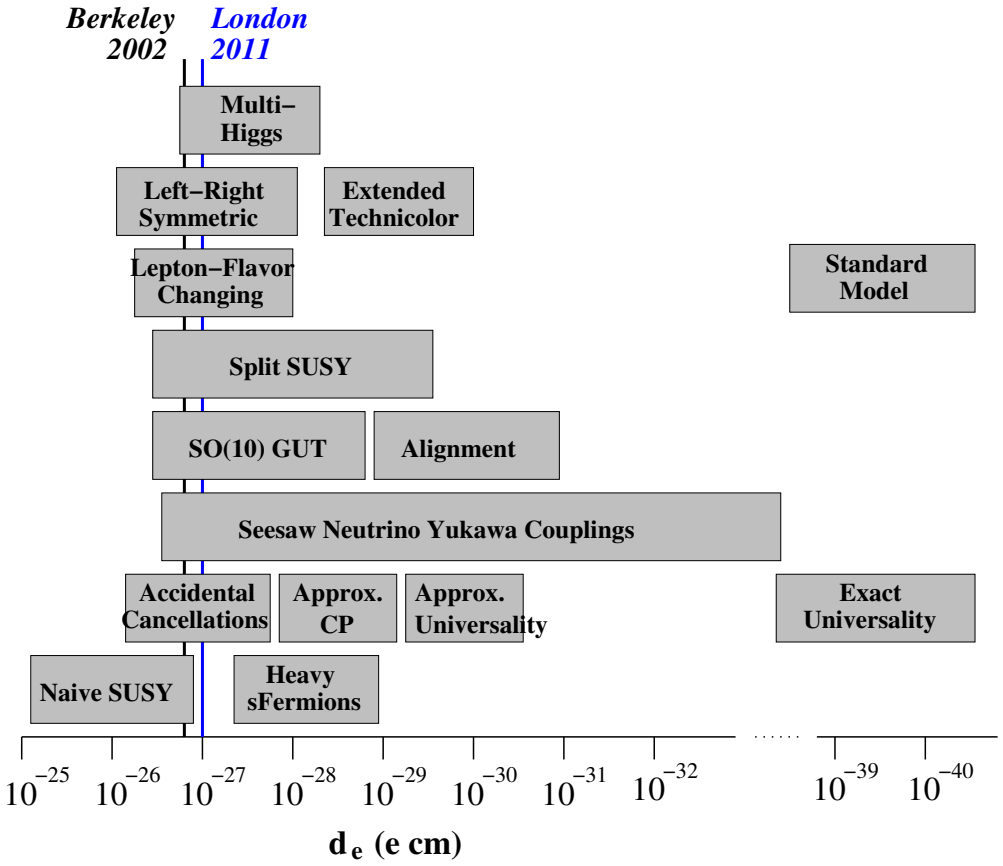
A Recent Development

Laboratoire de Chimie et Physique Quantiques

The Electron Electric Dipole Moment

Testing fundamental physics:

Current predictions for the eEDM[18]



Model	$\lvert d_e \rvert [e \cdot cm]$
Standard model	$< 10^{-38}$
Left-right symmetric	$10^{-28} \ldots 10^{-26}$
Lepton-flavor changing	$10^{-29} \ldots 10^{-26}$
Multi-Higgs	$10^{-28} \ldots 10^{-27}$
Supersymmetric	$\leq 10^{-25}$
Experimental limit[19]	$< 1.6 \cdot 10^{-27}$
Experimental limit[20]	$< 10.5 \cdot 10^{-28}$

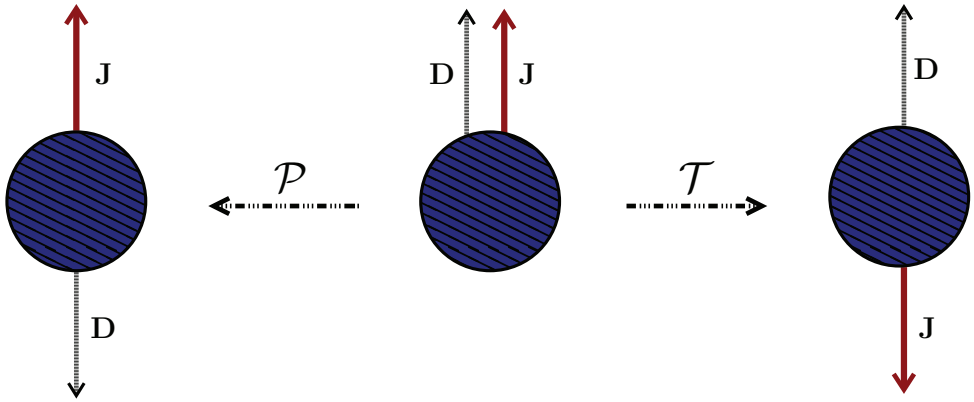
[18] A.V. Titov, N.S. Mosyagin, A.N. Petrov, T.A. Isaev, D.P. DeMille, *Recent Advances in the Theory of Chemical and Physical Systems* (2006) *253-283*; courtesy: Huliyar (2009), DeMille (2005)

[19] B.C. Regan, E.D. Commins, C.J. Schmidt, D.P. DeMille, *Phys Rev Lett* **88** (2002) *071805/1*

[20] J.J. Hudson, D.M. Kara, I.J. Smallman, B.E. Sauer, M.R. Tarbutt, E.A. Hinds, *Nature* **473** (2011) *493*

Testing fundamental physics:

Implications of an eEDM $\vec{D}$



$\vec{D}$ aligned with $\vec{J}$ due to projection theorem:

$$\left\langle \alpha', JM_J \left| \hat{V}_q \right| \alpha', JM_J \right\rangle = \frac{\left\langle \alpha', JM_J \left| \hat{\vec{J}} \cdot \hat{\vec{V}} \right| \alpha', JM_J \right\rangle}{\hbar^2 J^2 (J+1)} \left\langle JM_J \left| \hat{J}_q \right| JM_J \right\rangle$$

Implies violation of **Parity**($\mathcal{P}$) and **Time-Reversal**($\mathcal{T}$) symmetries[21]

The $\mathcal{CPT}$ theorem remains valid

[21] E.D. Commins, *Adv At Mol Opt Phys* **40** (1998) *1*

The eEDM in a molecular framework

Essentials of the formalism

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

- Point of departure: Salpeter's[22] modified Dirac equation:

$$\left[\left(p_\mu + \tfrac{e}{c}A_\mu\right)\gamma^\mu - \imath m_0 c\right]\psi(\vec{r}) = \zeta\left(\frac{\imath e\hbar}{4m_0c^2}\right)\gamma^5\gamma_\mu\gamma_\nu F^{\mu\nu}\psi(\vec{r})$$

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

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

- Requires kinetic-energy integrals of the type:

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

- and therefore explicitly the Small-component wave functions.

- Implementation as 4c-CI expectation values[23].

[22] E. Salpeter, *Phys Rev* **112** (1958) *1642*

[23] T Fleig and M K Nayak, in preparation.

The eEDM in a molecular framework

Some candidate molecules

- ThF^+, HfF^+ (Experiment[24], Cornell group)
- WC (Experiment, Leanhart group, Michigan)
- ThO (DeMille group; Theory[25] , Meyer et al.)
- IH^+ (Theory, Titov et al.[26])

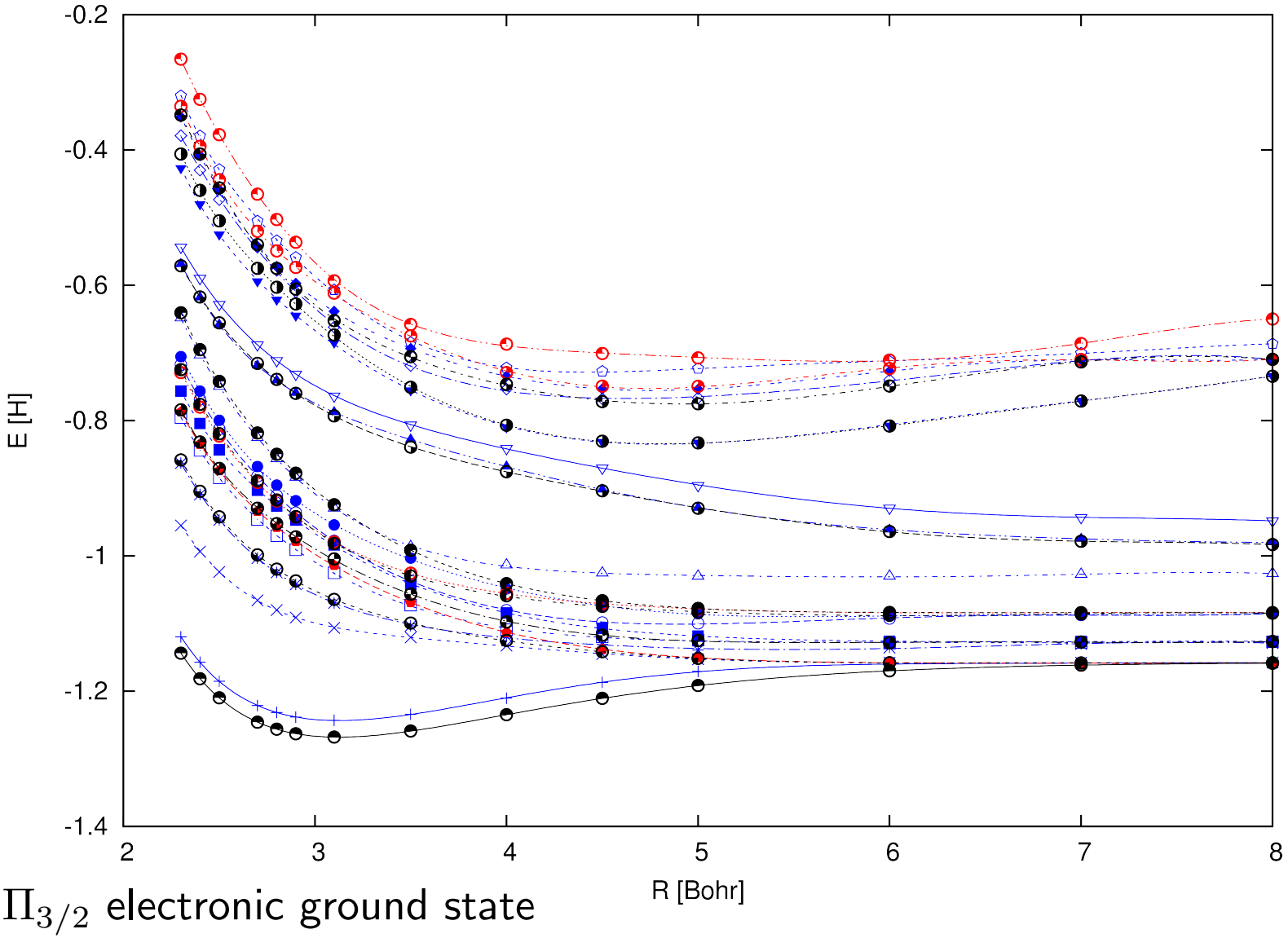
[24] A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

[25] J. Paulovič, T. Nakajima, K. Hirao, R. Lindh, P.-Å. Malmqvist, *J Chem Phys* **119** (2003) *798*

[26] T.A. Isaev, A.N. Petrov, N.S. Mosyagin, A.V. Titov, *Phys Rev Lett* **95** (2005) *163004*

The eEDM in a molecular framework

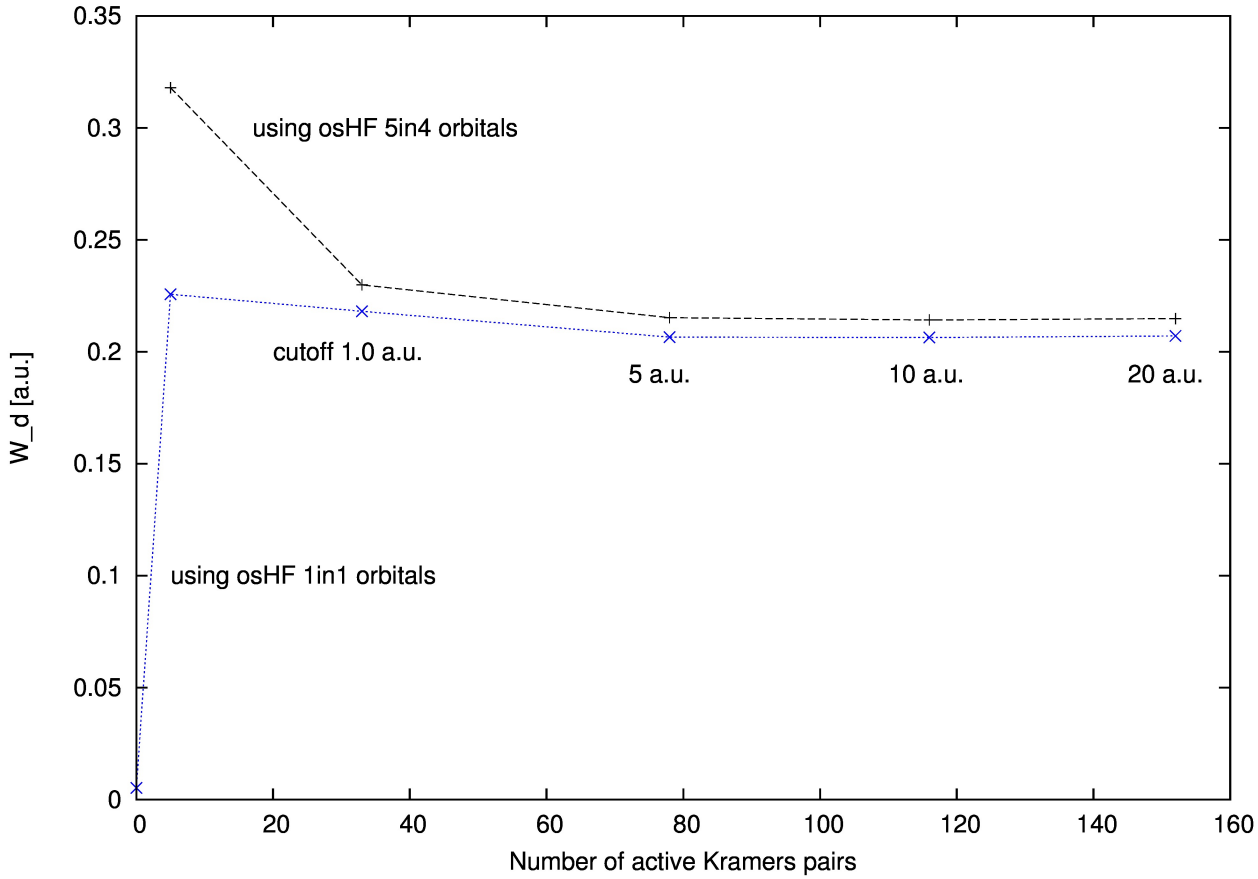
IH^+ as a candidate system



$^2\Pi_{3/2}$ electronic ground state

The eEDM in a molecular framework

Correlation dependence of $\mathcal{P}, \mathcal{T}$ -odd interaction constant W_d



$$W_d = \frac{2\imath c}{\Omega e\hbar} \left\langle \gamma^0\gamma^5 \vec{p}^2 \right\rangle_{\psi_H}$$

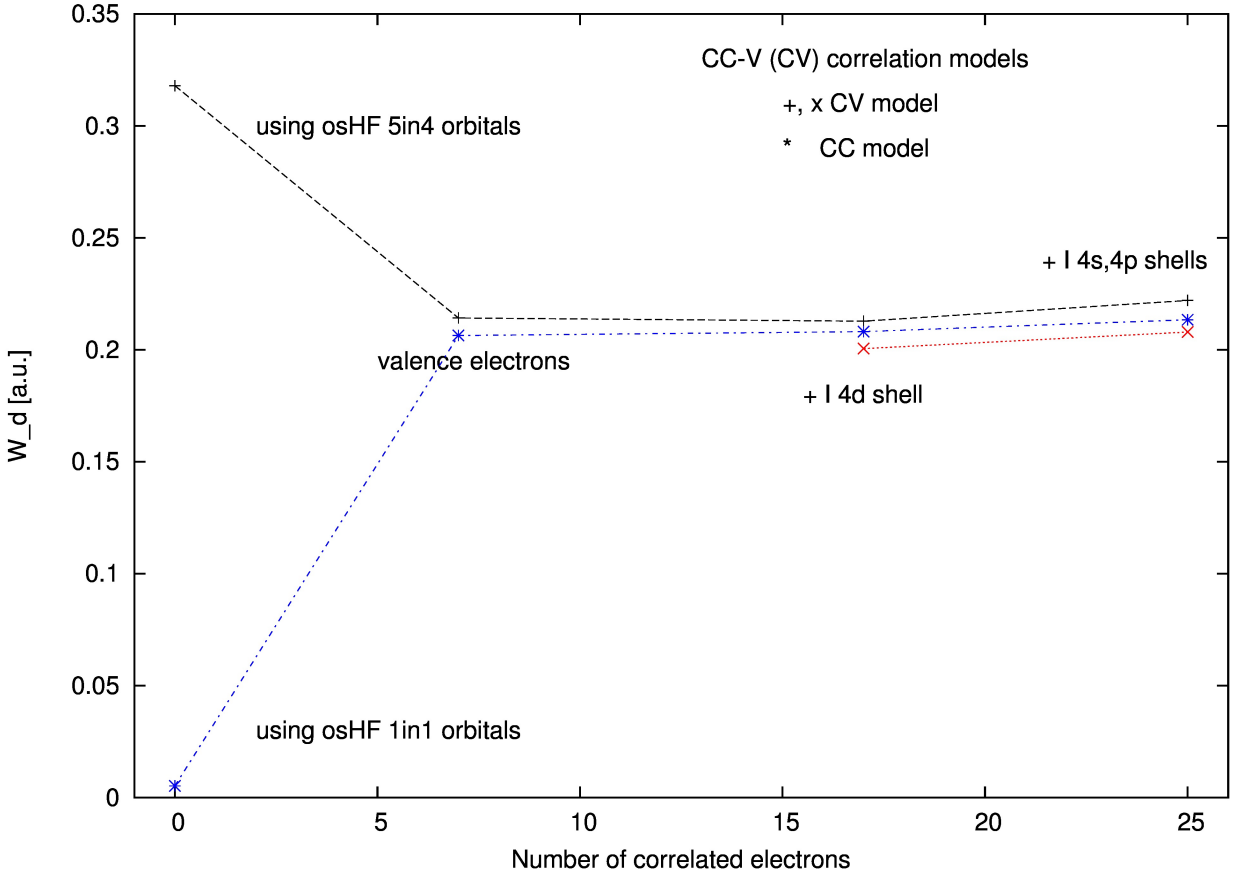
IH^+:

$^2\Pi_{3/2}$ ground state

7 correlated electrons

The eEDM in a molecular framework

Correlation dependence of $\mathcal{P},\mathcal{T}$ -odd interaction constant W_d



$$W_d = \frac{2\imath c}{\Omega e\hbar}\left\langle \gamma^0\gamma^5\vec{p}^{\,2}\right\rangle_{\psi_H}$$

IH^+:

$^2\Pi_{3/2}$ ground state

cutoff: 10 a.u.

The eEDM in a molecular framework

Results for W_d in comparison[27]

E_{eff}	W_d $[10^{24}\frac{\mathrm{Hz}}{\mathrm{e\cdot cm}}]$	
Correlation model	Present work	Titov et al.
0 e^- (HF)	0.007	0.010
7 e^-	0.257	0.336
7 e^- (+Triples)	0.251	
17 e^- (CV)	0.249	
17 e^- (CV,CC)	0.259	
25 e^- (CV)	0.259	
25 e^- (CV,CC)	0.265	0.336

- Valence electron correlation affects E_{eff} strongly.
- Outer-core correlations (CV or CC) have very small effect.
- Valence triple excitations lead to decrease of $\approx -2.3\%$.
- Present E_{eff} consistently smaller than reference values by Titov et al.

Theory differences:

(+) Larger basis set

(+) No effective core potentials

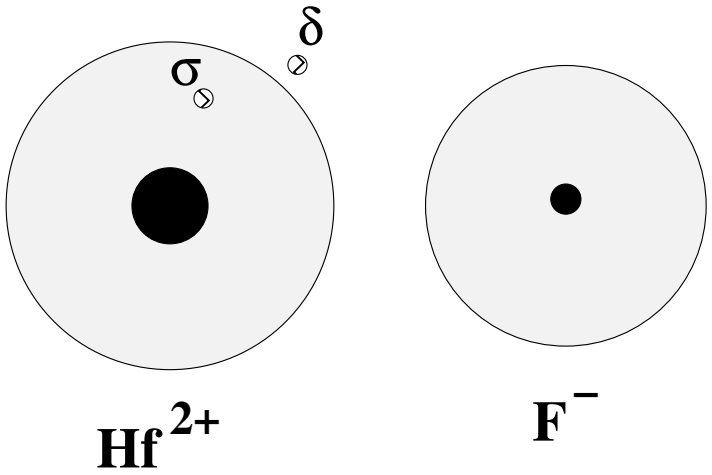
(+) More rigorous electronic-structure model

(-) No spin-other-orbit terms in Hamiltonian

[27] T.A. Isaev, A.N. Petrov, N.S. Mosyagin, and A.V. Titov, *Phys Rev Lett* **95** (2005) *163004*

The eEDM in a molecular framework

$^3\Delta$ molecules

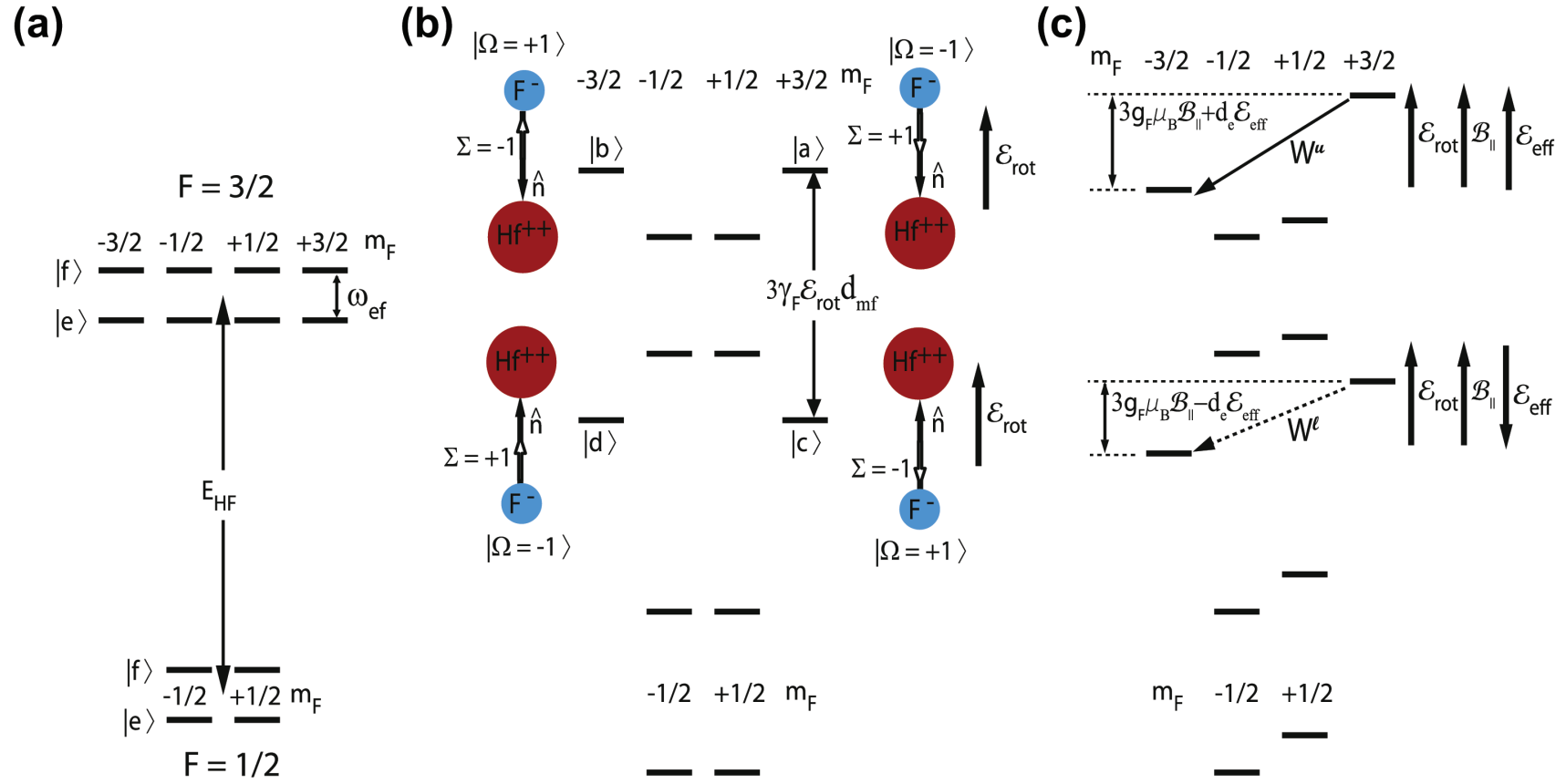


- Heavy nucleus (relativistic effect)
- One "science" electron (σ^1), one "spectroscopy" electron (δ^1)
- Large E_{eff} for σ^1 electron

- Deeply bound molecule (fluorides)
- Small Λ-doublet splitting (experimental, technical reasons)
- Large rotational constant (one heavy, one light atom)
- $\Omega = 1$ component preferred (small magnetic moment)
- $\Rightarrow$ Low-lying $^3\Delta_1$ as "science" state

The eEDM in a molecular framework

A Proposed Measurement[28] on HfF^+



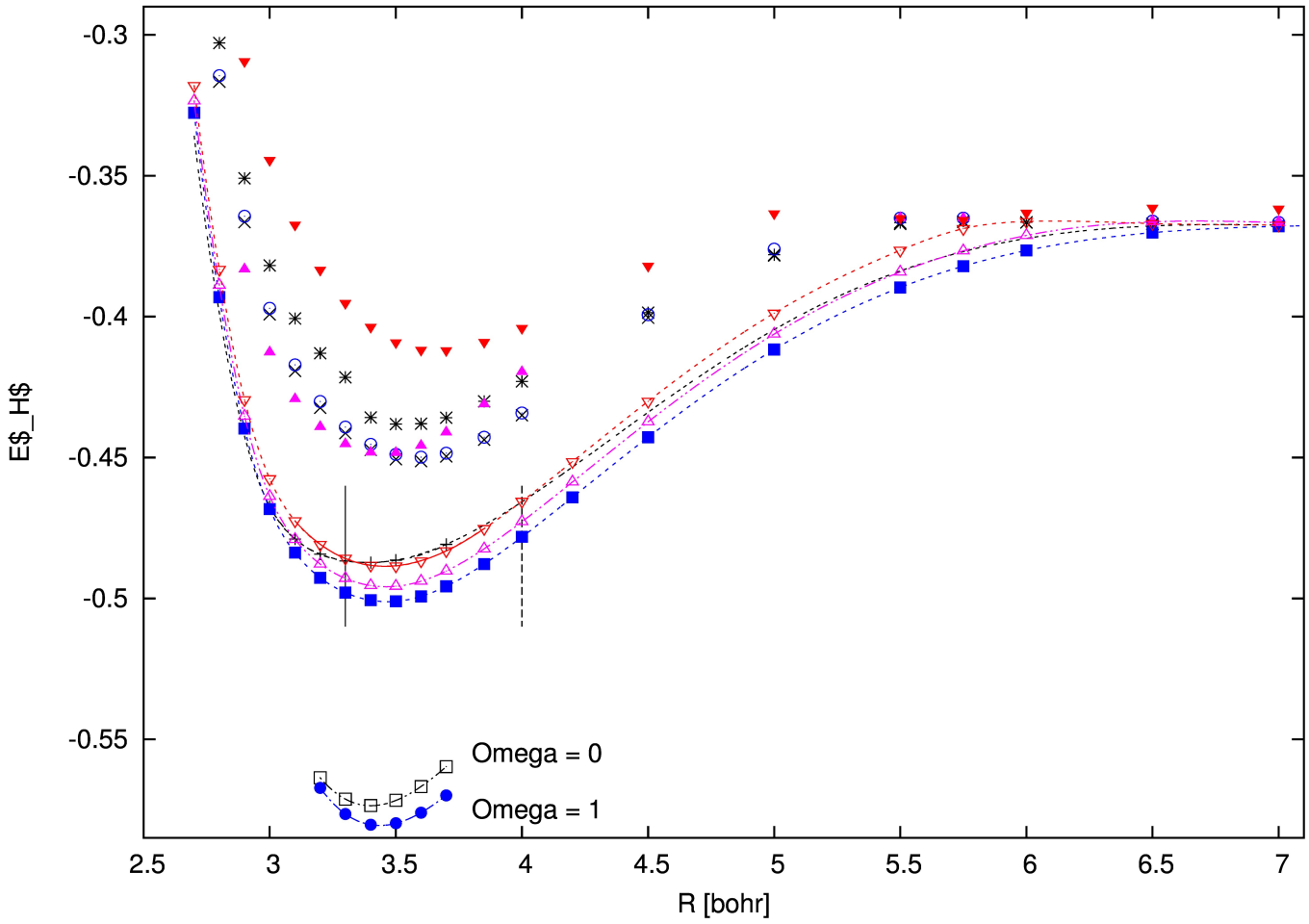
$$W^u(B) - W^u(-B) = 2d_e E_{\text{eff}}$$

[28] A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

The eEDM in a molecular framework

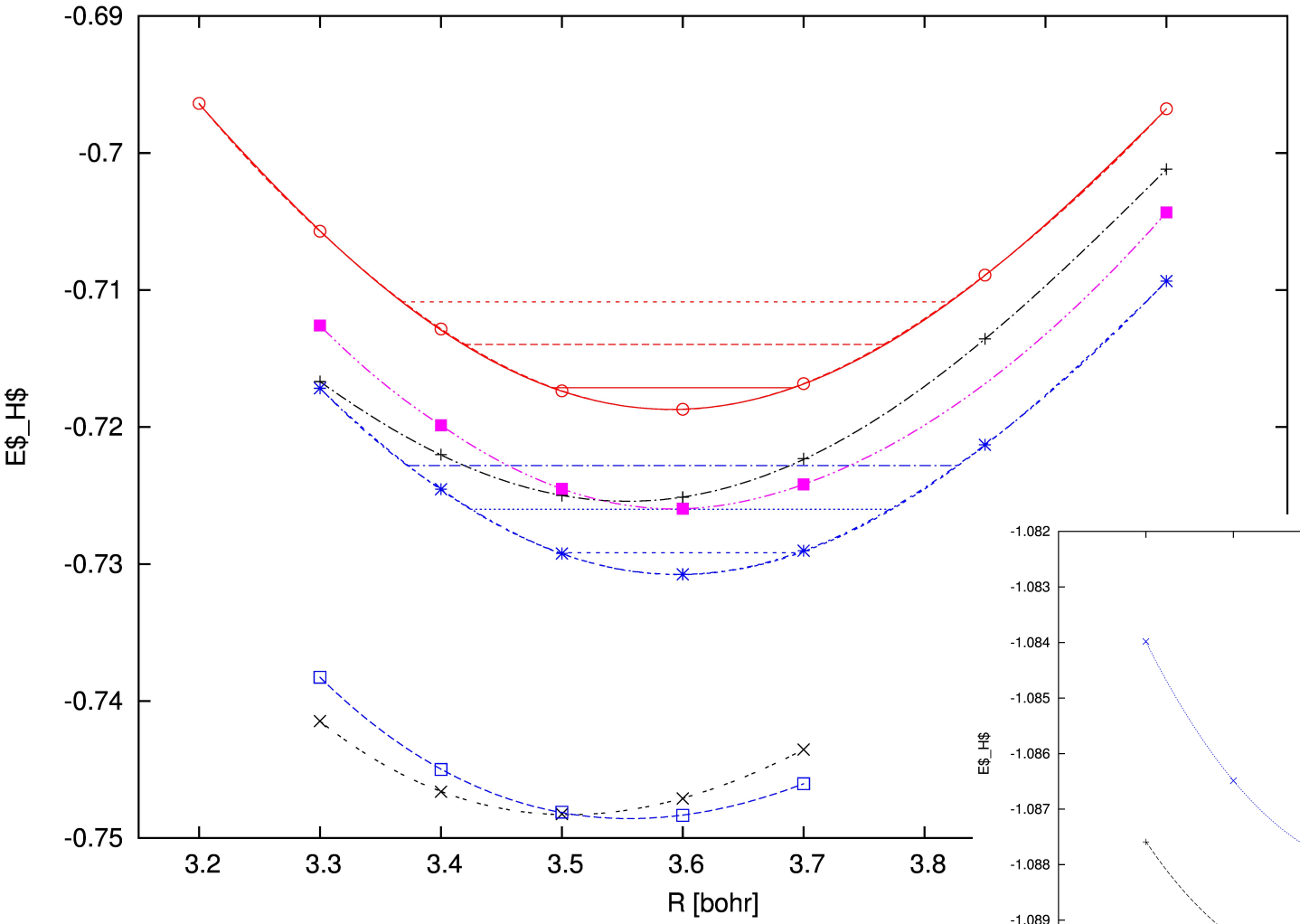
HfF^+ potential curves in RASCI approximation

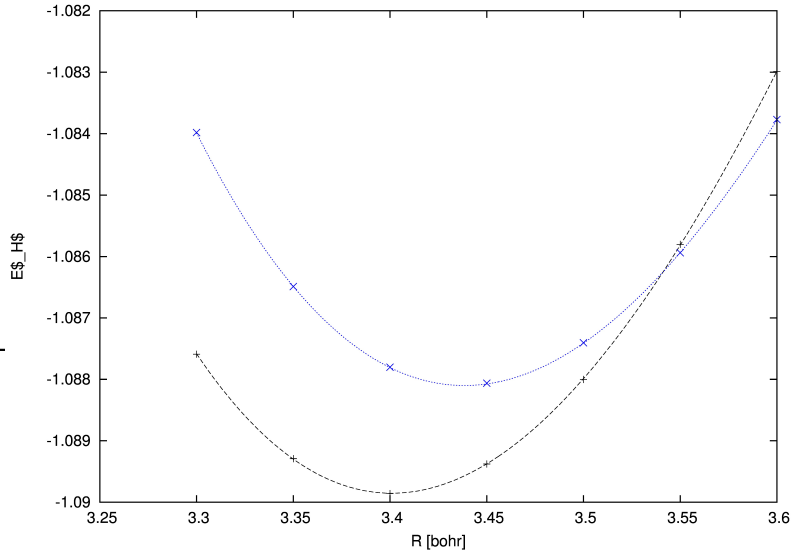
$\Omega = 0$ $(\mathrm{Hf}^{2+}6s^2)$, $\Omega = 1$ $(\mathrm{Hf}^{2+}6s^15d^1)$



The eEDM in a molecular framework

HfF^+ potential curves in RASCISD approximation



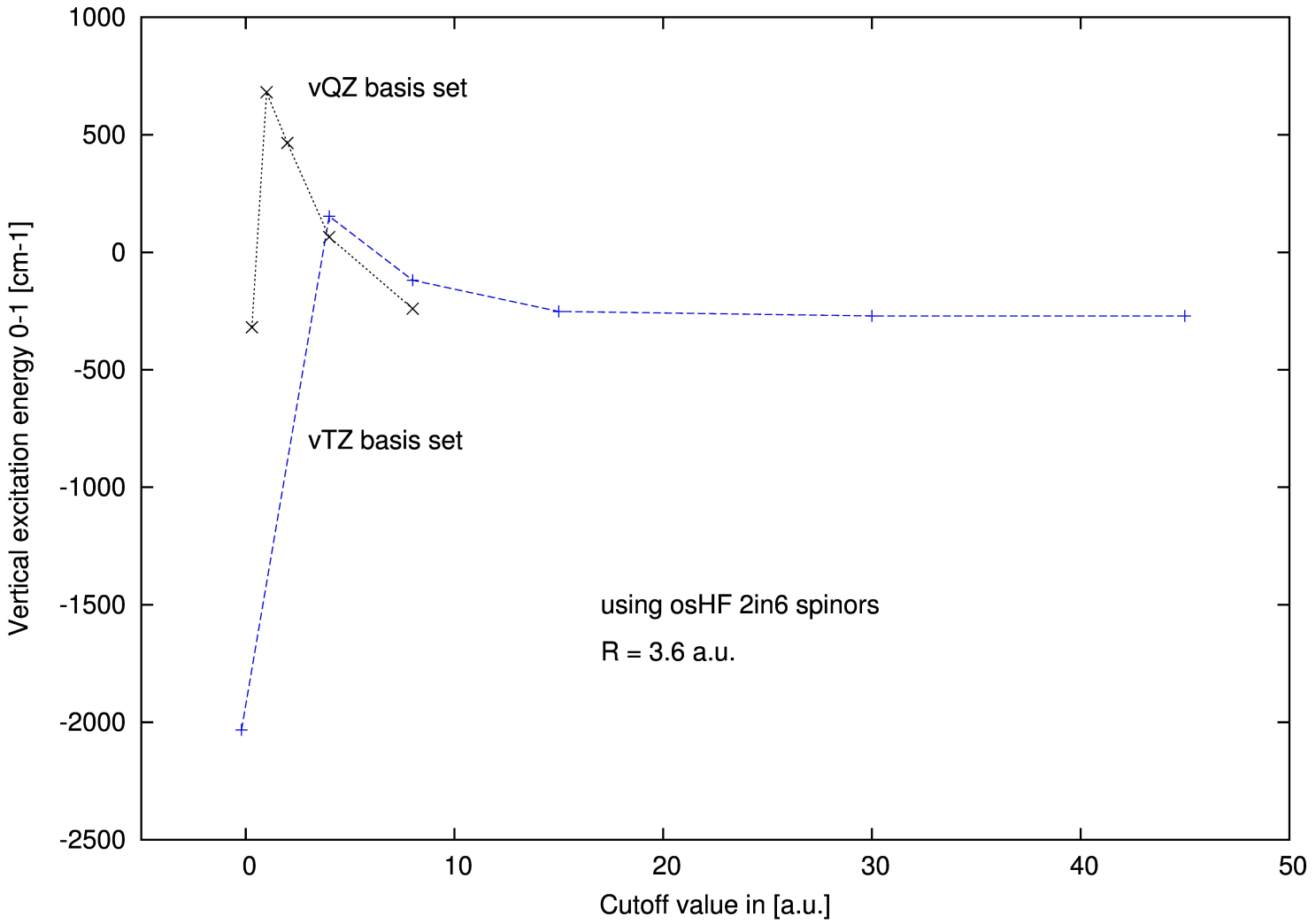


10 electrons

20 electrons:

The eEDM in a molecular framework

HfF^+ spectroscopy; excitation energy and basis set



The eEDM in a molecular framework

HfF^+ spectroscopy; excitation energy and correlation model

Model	R_e [a.u.] $\Omega = 0$	R_e [a.u.] $\Omega = 1$	$T_e{}^{0-1}$ [cm^{-1}]
SD4_CAS4in7	3.390	3.462	−3056
SD4_CAS4in7_SD8	3.554	3.597	−1176
SD8_CAS2in6	3.402	3.436	−1545
SD8_CAS2in6_SD10	3.505	3.556	−63
SD18_CAS2in6_SD20	3.401	3.438	385
SD10_SDT8_CAS2in6_SD20	?	?	$\approx +150$
Titov: 20 e^- corr.[29]	3.366	3.413	1633
Experiment[30]			993

Correlation of Hf $5s, 5p$ shells plays an important role.

[29] A.N. Petrov, N.S. Mosyagin, A.V. Titov, *Phys Rev A* **79** (2009) *012505*

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

The eEDM in a molecular framework

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

Model	$E_{\mathrm{eff}}\ \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$
SD8_CAS2in6	24.77
SD8_CAS2in6_SD10	23.26
SDT8_CAS2in6_SD10	23.18
S18_CAS2in6_SD20	23.31
Titov: 20 e^- corr.[31]	36.28
Estimate, Meyer et al.[32]	≈ 30

Theory differences:

(+) No effective core potentials

(+) More rigorous electronic-structure model

(-) No spin-other-orbit terms in Hamiltonian

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

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

Ongoing Work

- Commutator-based GER CC Jacobian, non-relativistic version
  (with Mickael Hubert and Jeppe Olsen)

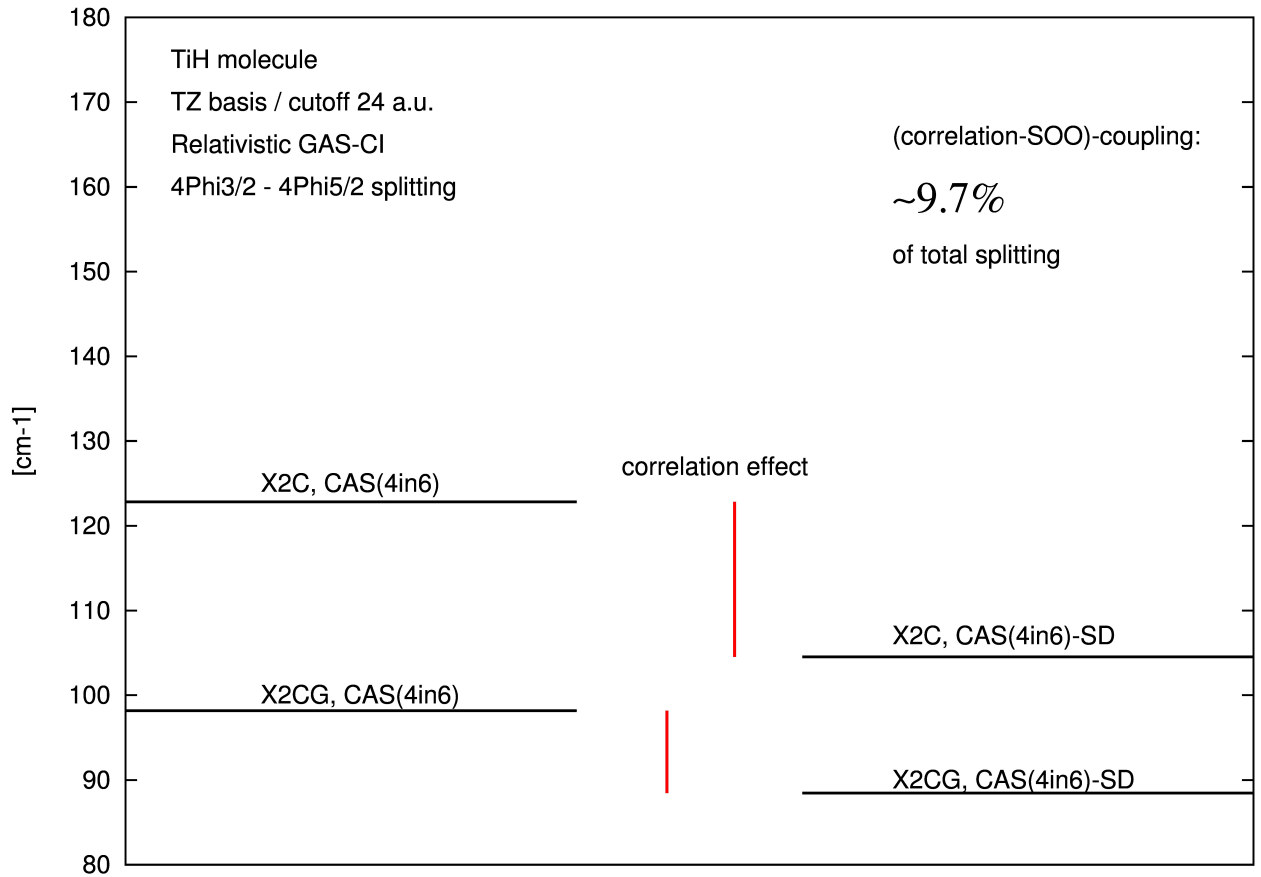
- Commutator-based GER CC Jacobian, relativistic version
  (with Mickael Hubert and Lasse Sørensen)

- Electron EDM constants in other diatomic molecules
  (with Malaya K. Nayak and Stefan Knecht)

Ongoing Work

- 4-component Gaunt / Breit operator in correlated approaches (with Jessica Loras

Decoupling correlation and 2-electron spin-orbit terms ?



Acknowledgement/Collaboration

Malaya K. Nayak

Bhabha Research Institute, India

Stefan Knecht

Odense, Denmark

Mickael Hubert

LCPQ, Toulouse, France

Jessica Loras

LCPQ, Toulouse, France

Lasse K. Sørensen

Århus, Denmark

Jeppe Olsen

Århus, Denmark

Hans Jørgen Aa. Jensen

Odense, Denmark

The CI-Based CC Jacobian

Scaling Properties

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

- $e^{-\hat{T}}$ increases 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.
- CI-based implementation $O^{n+2}V^{n+2}$
  Conventional CC: $O^n V^{n+2}$
- CI-based implementation, considering GAS: $O^{m+2}V^{m+2}o^{n-m}v^{n-m}$
  Conventional CC, considering GAS: $O^m V^{m+2} o^{n-m} v^{n-m}$