Recent Progress on the Development of Relativistic Four-Component Electron Correlation Methods and their Applications in Spectroscopy and Fundamental Physics

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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)

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[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)

The Methods

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1) **Spinor-string based GAS Coupled Cluster**

2) Spinor-string based GAS Configuration Interaction

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

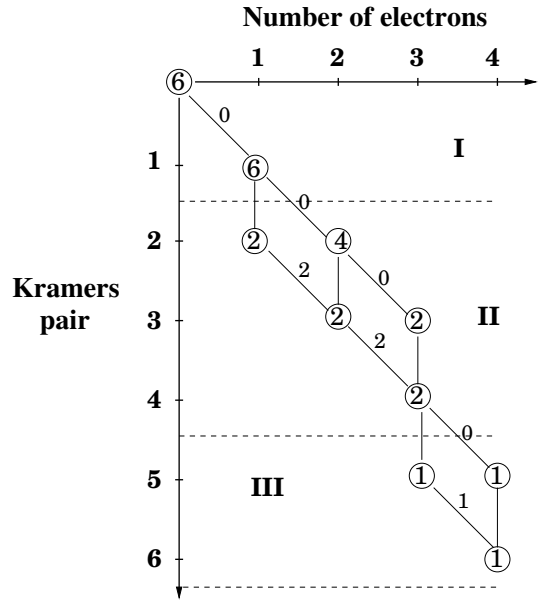
Spinor basis:

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

- Many-particle wavefunction defined as
  - 1 unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$
  - 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**

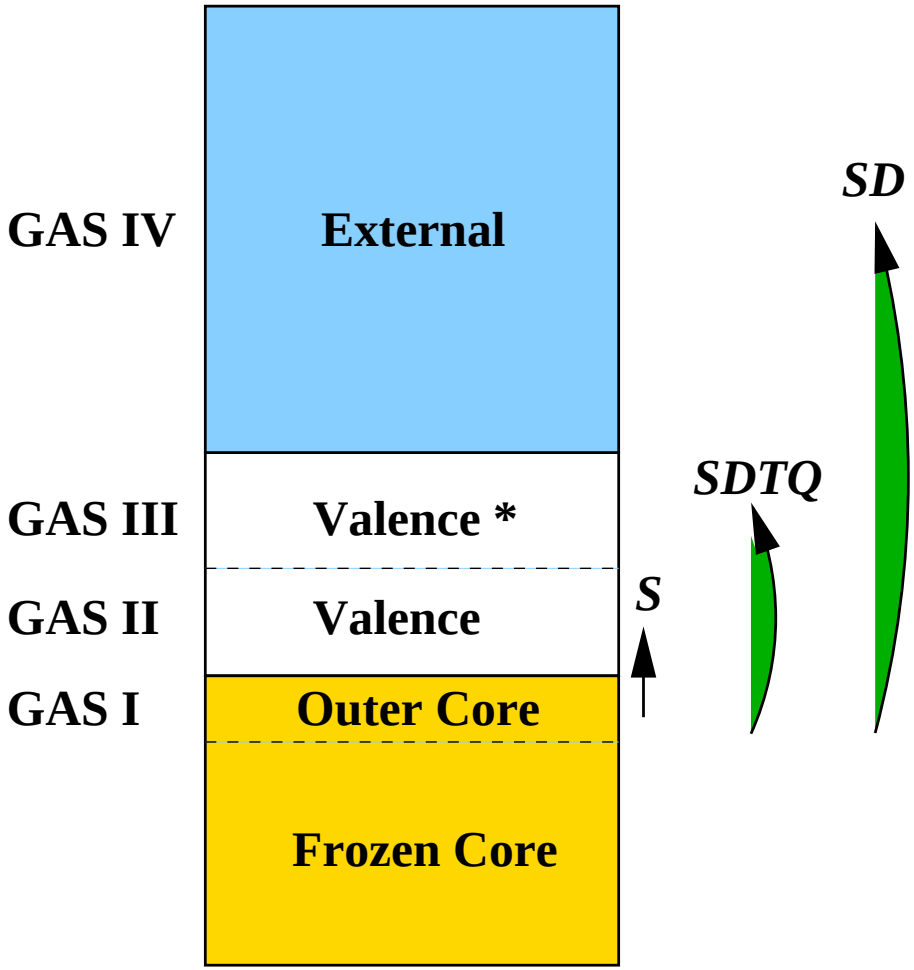
  Coupled Cluster: **Individual strings**



⊗ x: vertex weight
y: arc weight

Parameterization of the Wavefunction

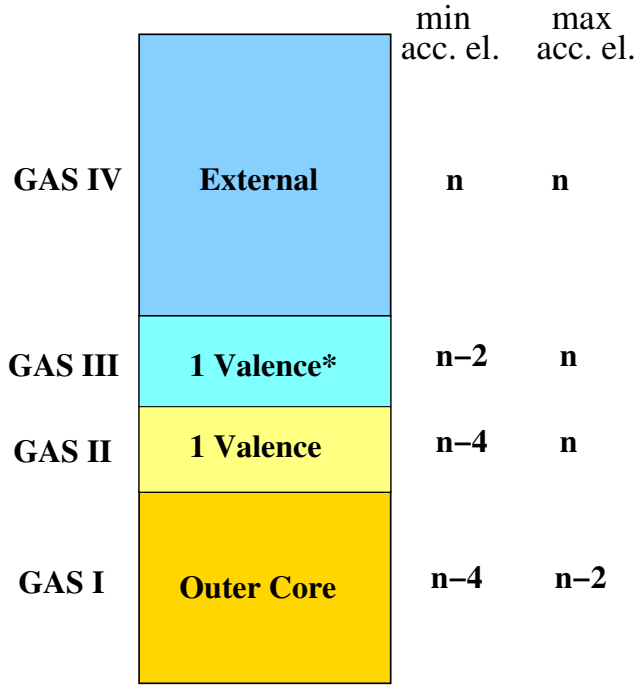
Generalized Active Spaces



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[5]
- 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:

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

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

Relativistic Generalized-Active-Space CC

Electronic Ground States [6]

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.

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

[6] 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[7]

Excitation Energies[8]

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

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

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

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

Computational scaling:

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

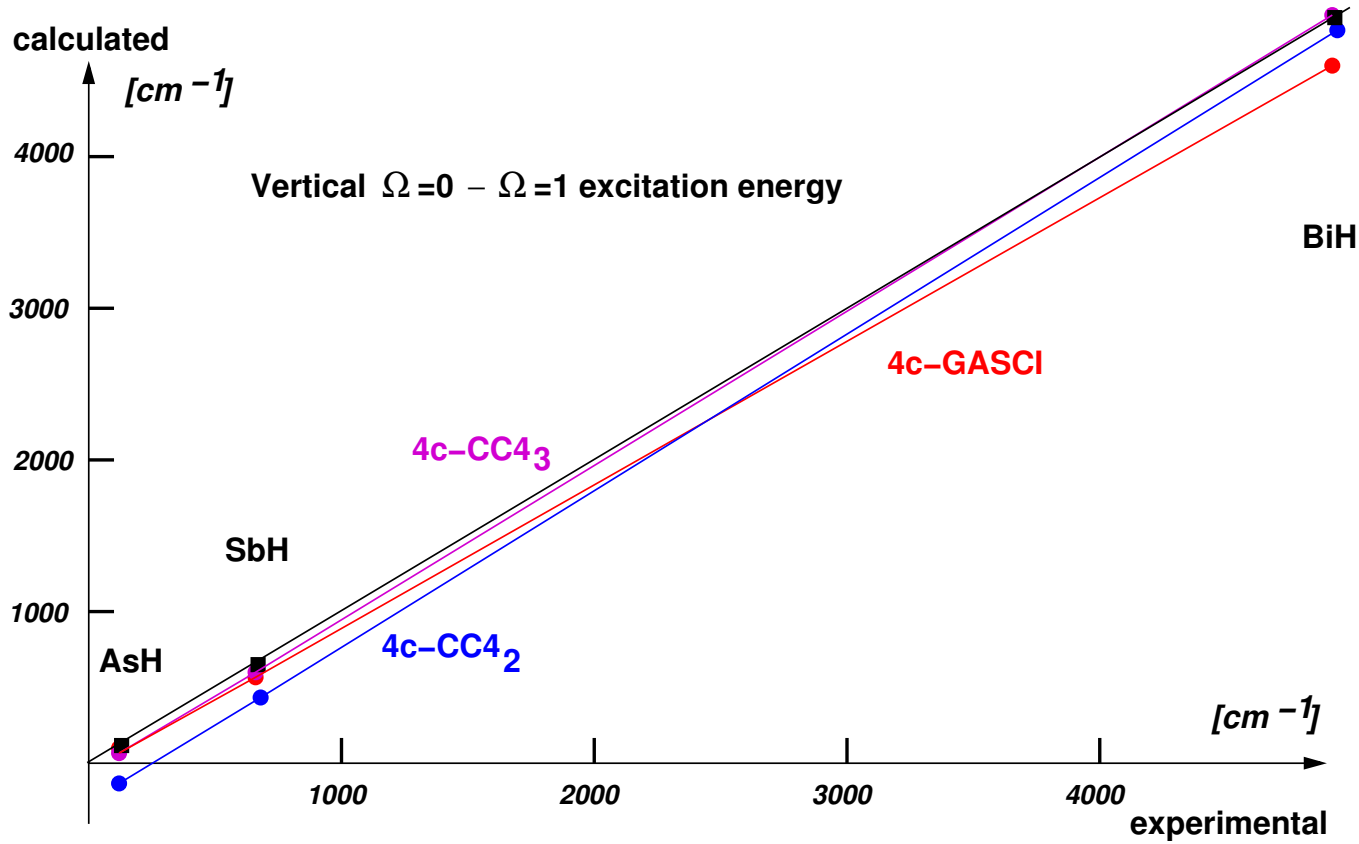
Conventional CC: $O^{n}V^{n+2}$

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

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

Series AsH, SbH, BiH

When is CC superior to GAS-CI?



- $CC4_3$ calculations consistently better than CAS-CISD[9]

[9] 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
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M olecular

D irect
I terative
R elativistic
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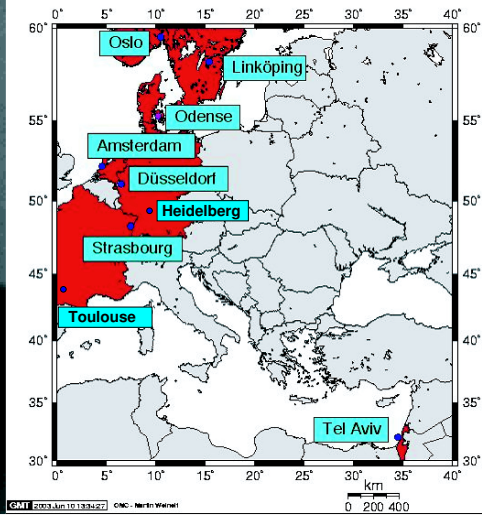
C alculations



- `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

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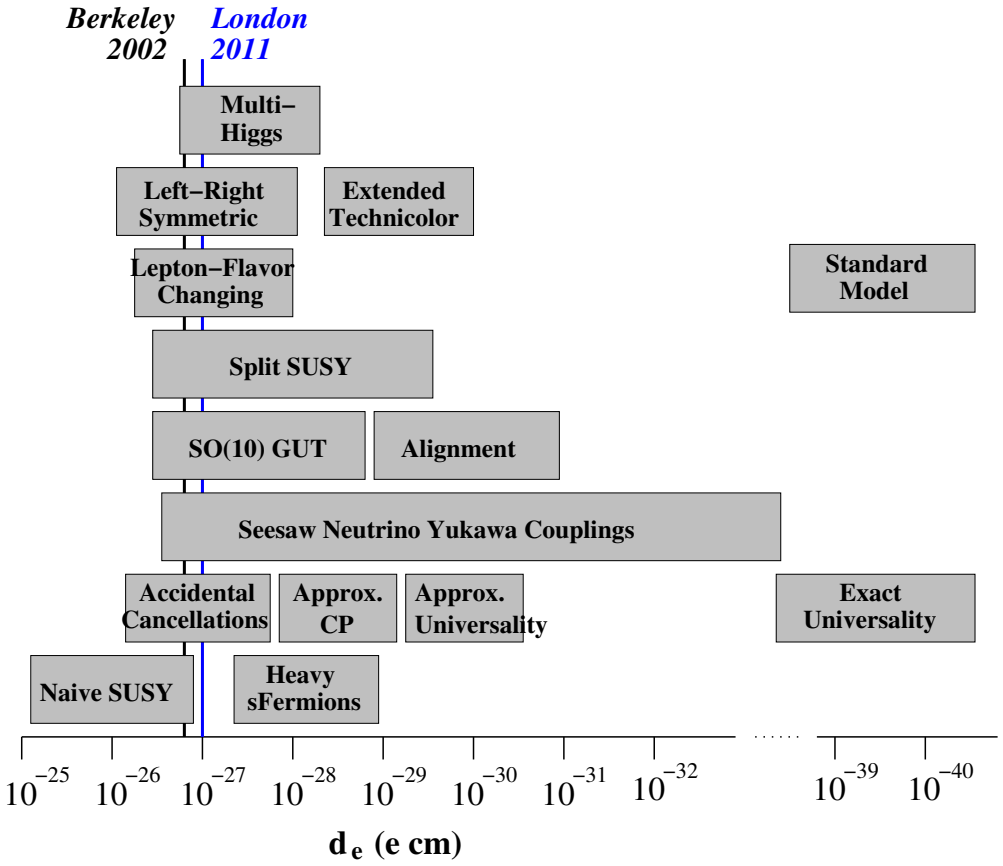
The Electron Electric Dipole Moment

Testing fundamental physics:

Current predictions for the eEDM[10]



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[11]	$< 1.6 \cdot 10^{-27}$
Experimental limit[12]	$< 10.5 \cdot 10^{-28}$

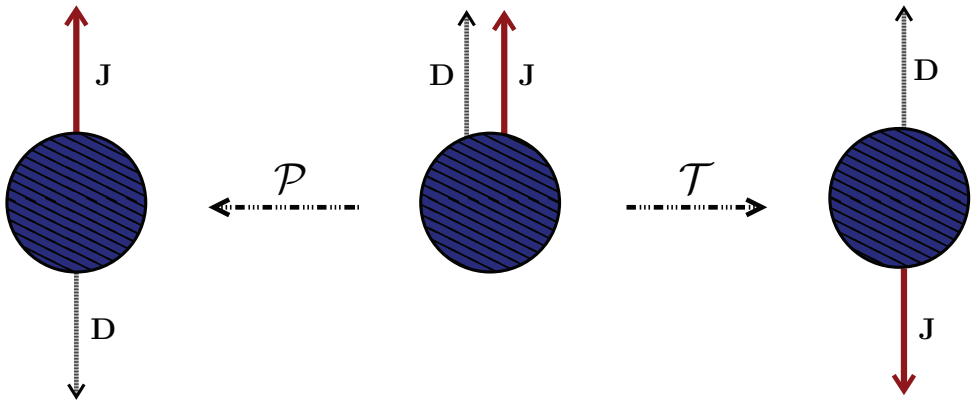
[10] A.V. Titov, N.S. Mosyagin, A.N. Petrov, T.A. Isaev, D.P. DeMille, *Recent Advances in the Theory of Chemical and Physical Systems* (2006) *253-283*; courtesy: Huliyar (2009), DeMille (2005)

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

[12] 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 combined violation of **Parity**($\mathcal{P}$) and **Time-Reversal**($\mathcal{T}$) symmetries[13]

The $\mathcal{CPT}$ theorem remains valid

[13] 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[14] modified Dirac equation:
$$\left[\left(p_\mu + \tfrac{e}{c}A_\mu\right)\gamma_\mu - \imath m_0 c\right]\psi(\vec{r}) = \zeta\left(\tfrac{\imath e\hbar}{4m_0c^2}\right)\gamma^5\gamma_\mu\gamma_\nu F^{\mu\nu}\psi(\vec{r})$$

- from which the eEDM operator can we written as an expectation value:
$$\left\langle -d_e\gamma^0\boldsymbol{\Sigma}\cdot\mathbf{E}\right\rangle_{\psi_H} = \tfrac{2\imath c d_e}{e\hbar}\left\langle\gamma^0\gamma^5\vec{p}^{\,2}\right\rangle_{\psi_H}$$

- 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[15].

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

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

The eEDM in a molecular framework

Some candidate molecules

- ThF^+, HfF^+ (Experiment[16], Cornell group)
- WC (Experiment, Leanhart group, Michigan)
- ThO (DeMille group; Theory[17] , Meyer et al.)
- IH^+ (Theory, Titov et al.[18])

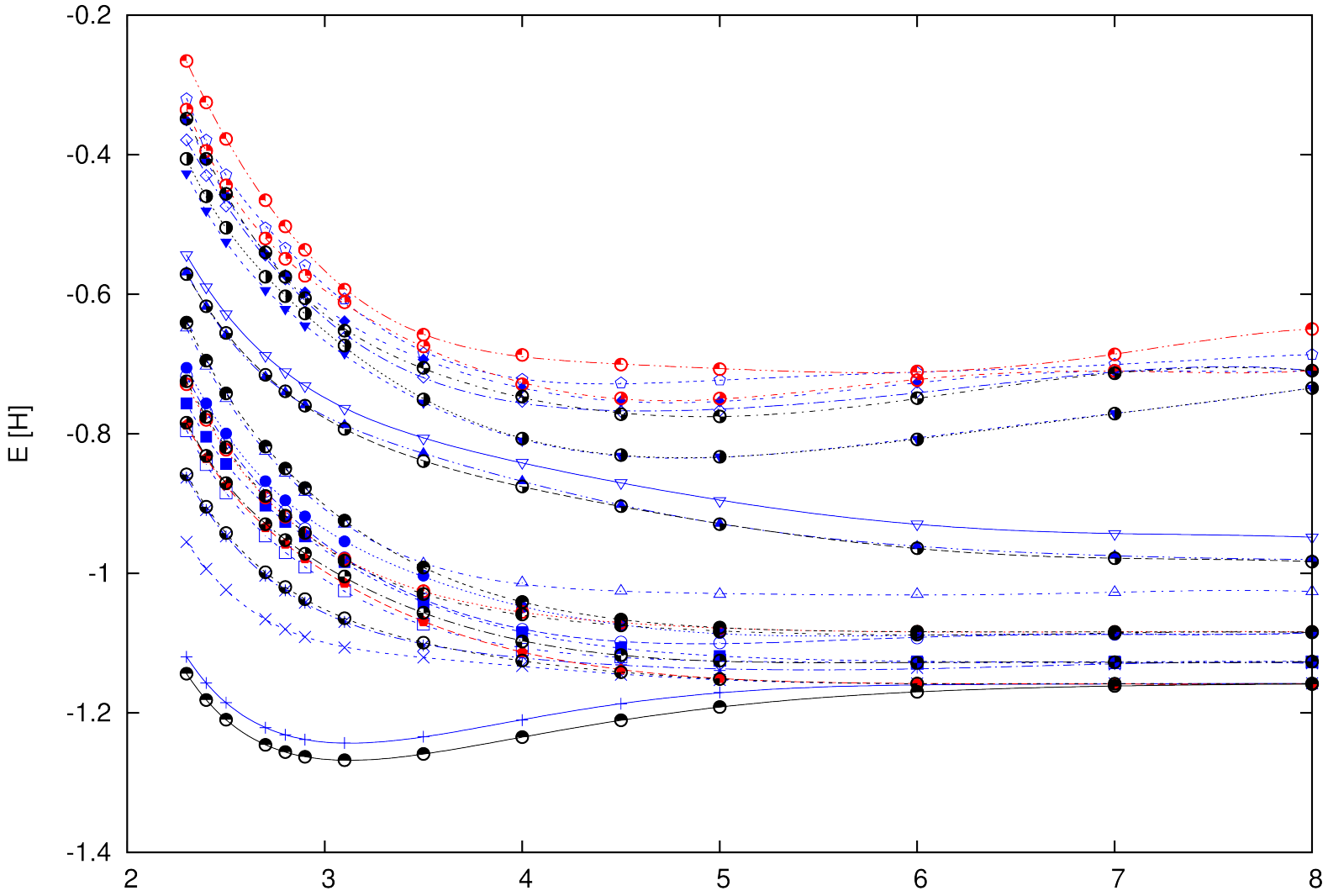
[16] A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

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

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

The eEDM in a molecular framework

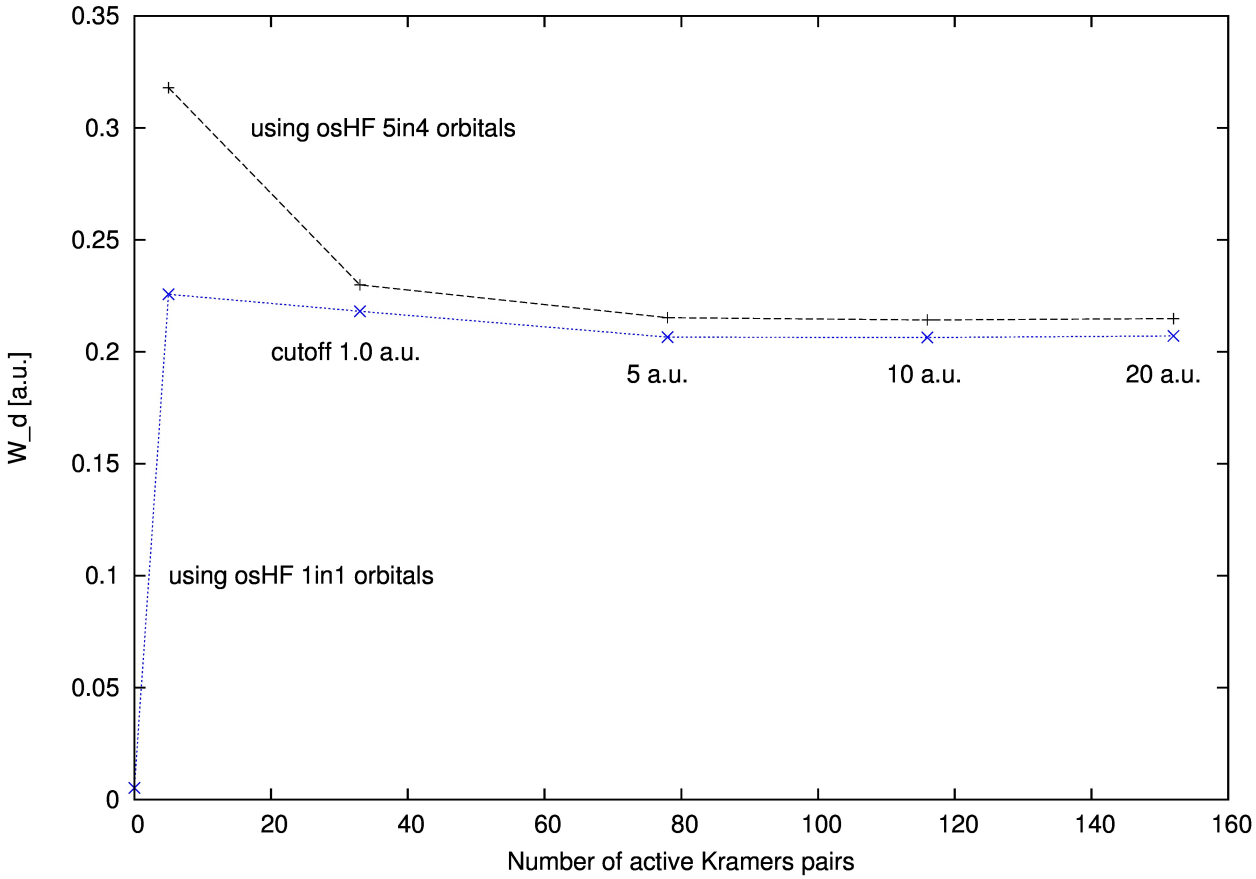
IH^+ as a candidate system



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

The eEDM in a molecular framework

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



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

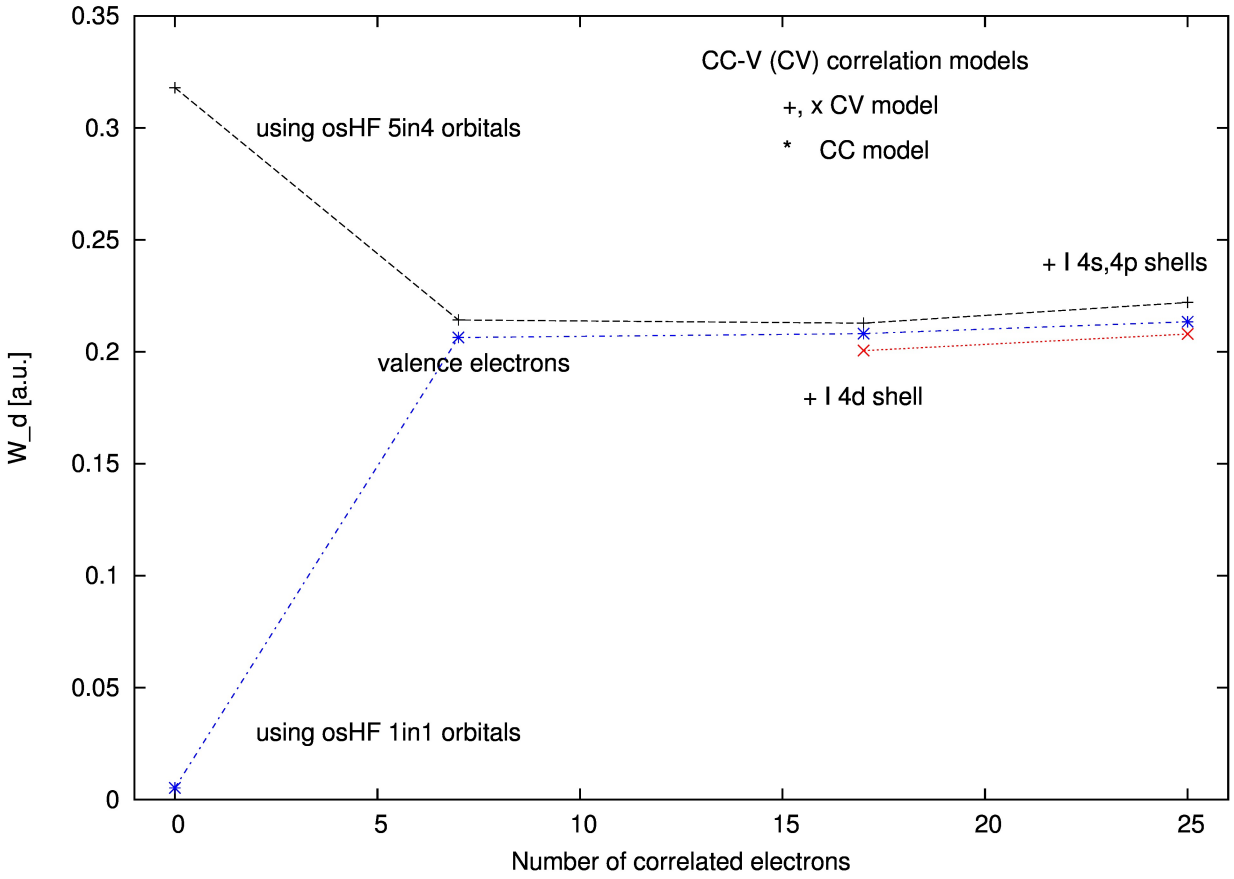
IH^+:

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

7 correlated electrons

The eEDM in a molecular framework

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



IH^+:

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

cutoff: 10 a.u.

The eEDM in a molecular framework

Results for W_d in comparison[19]

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

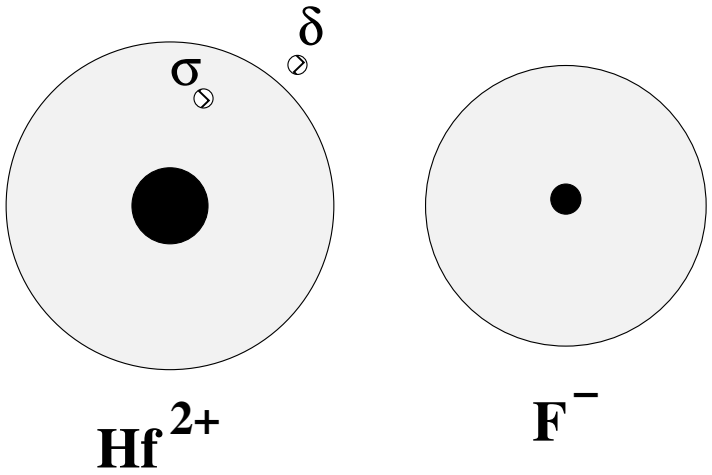
(+) More rigorous electronic-structure model

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

[19] 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

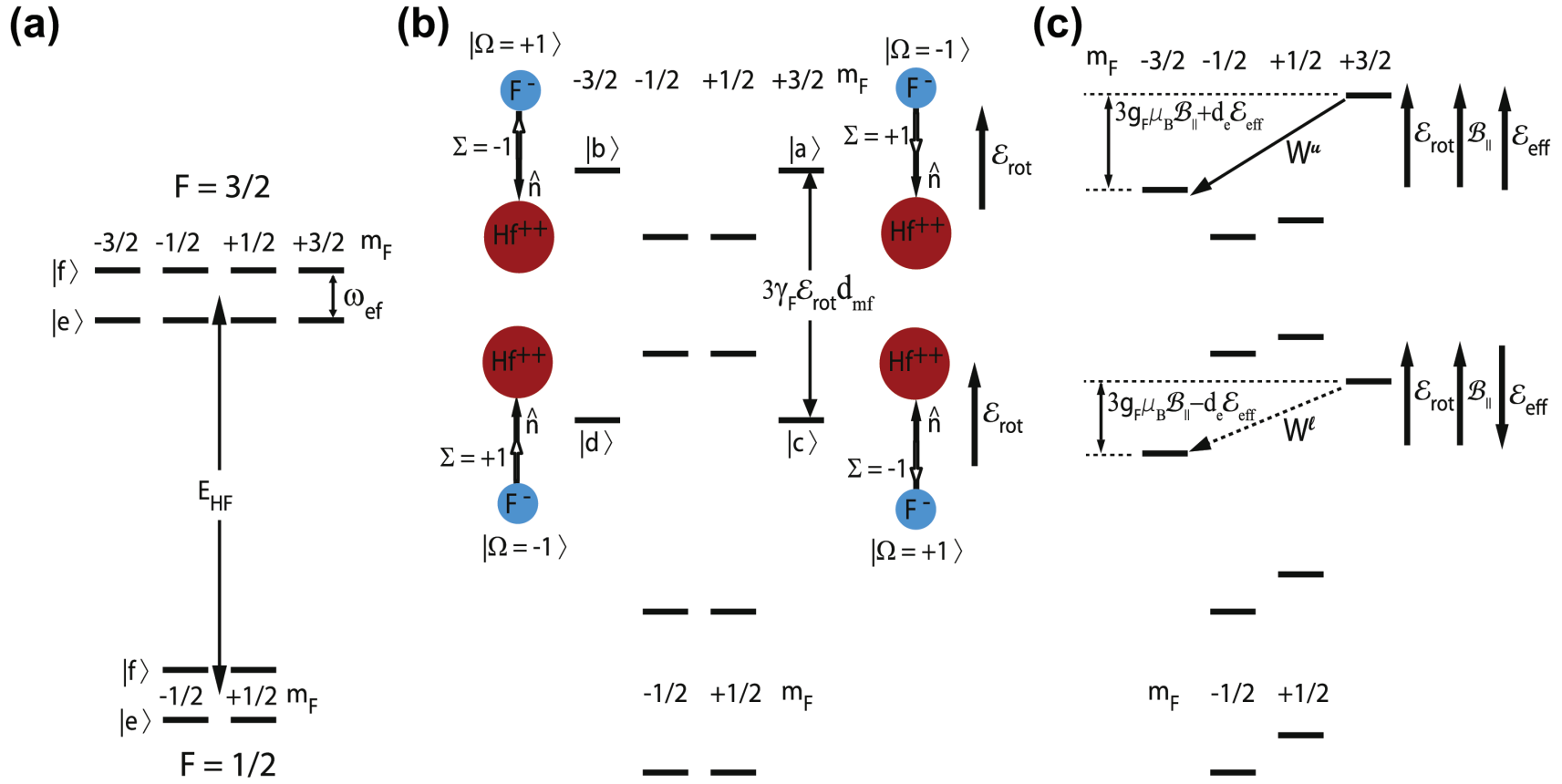


- Heavy nucleus (relativistic effect)
- One "science" electron (σ^1), one "spectroscopy" electron (δ^1)
- Large E_{eff} for σ^1 electron

- 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[20] on HfF^+

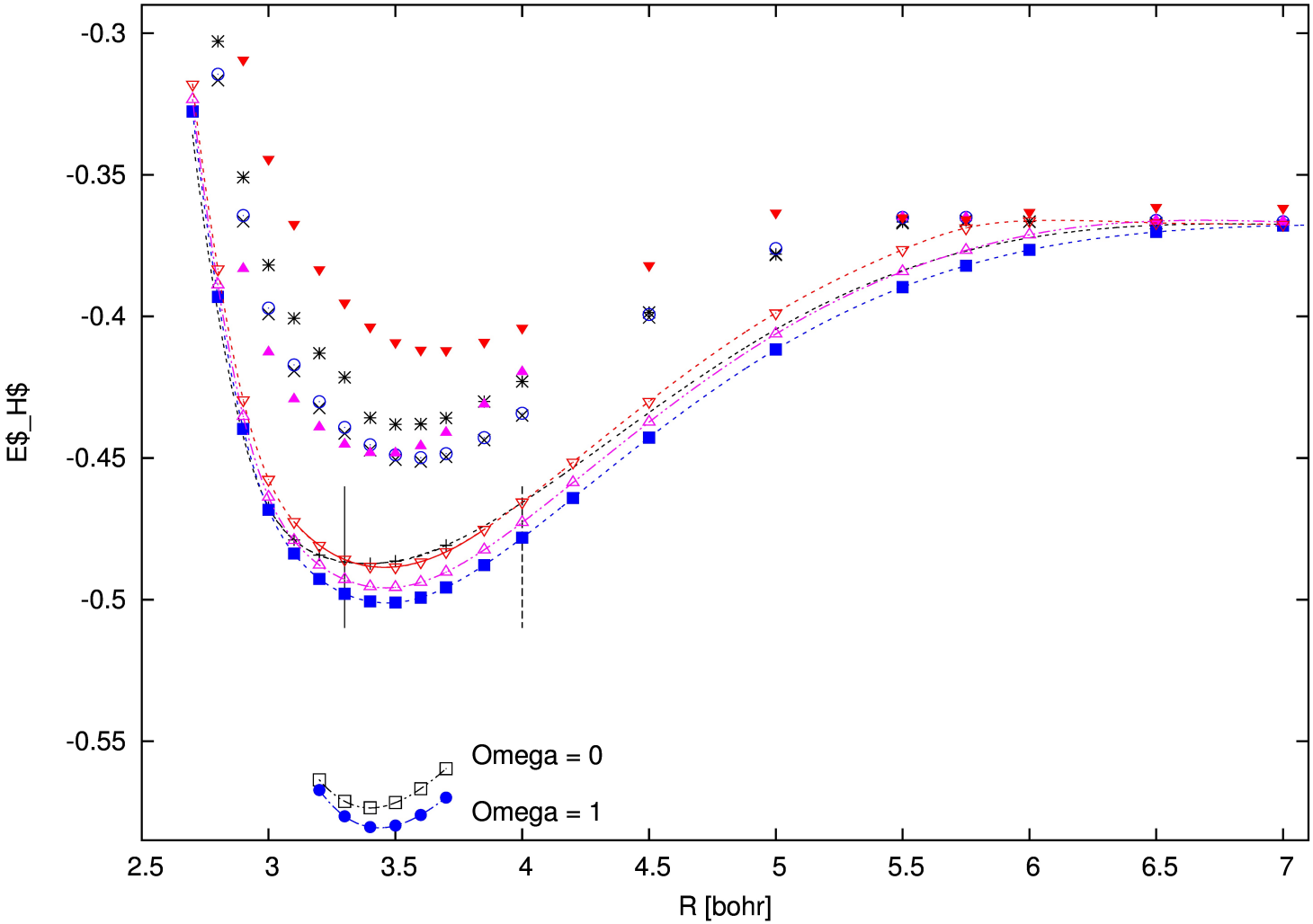


$$W^u(B) - W^u(-B) = 2d_e E_{\text{eff}}$$

[20] 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*

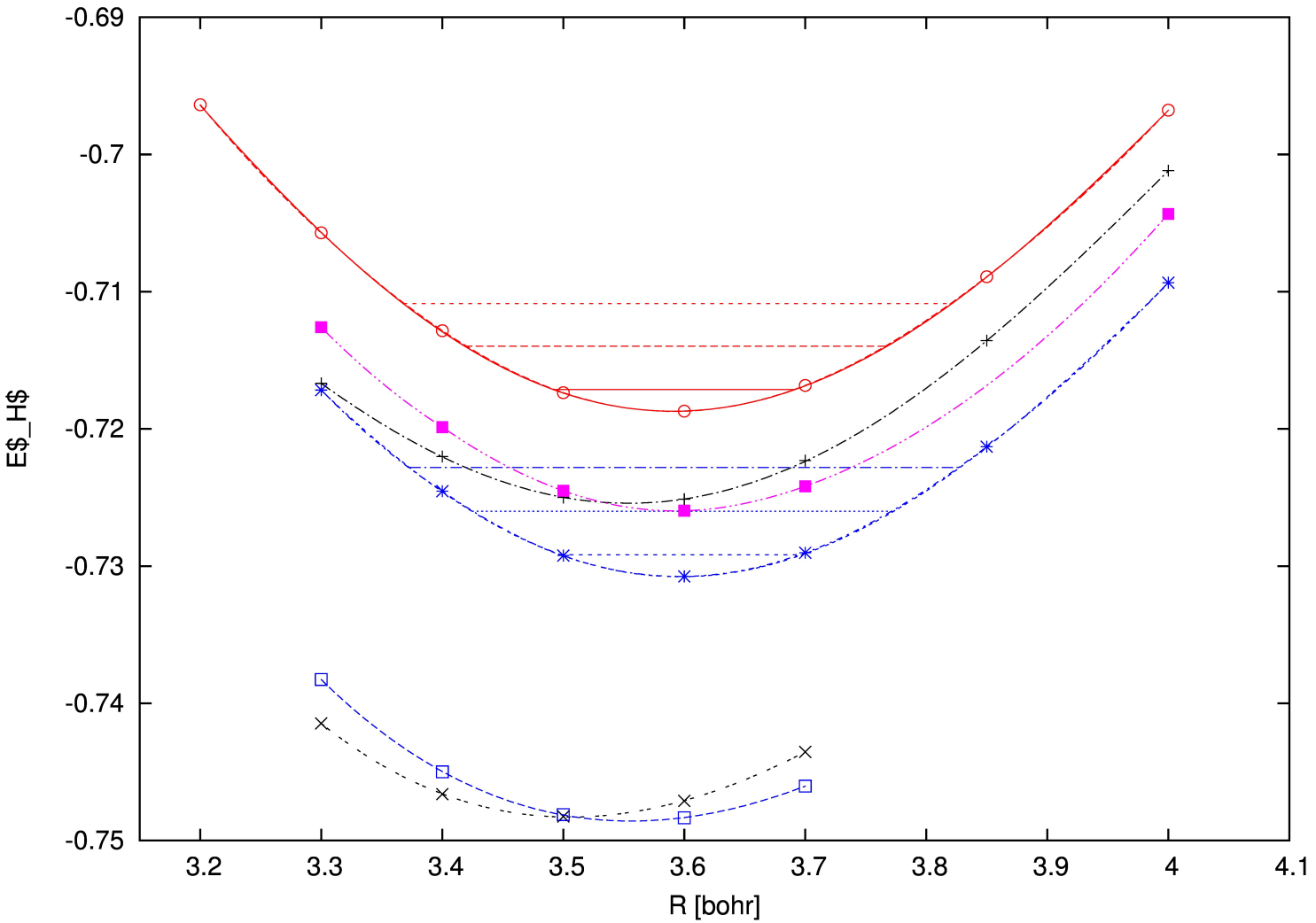
The eEDM in a molecular framework

HfF^+ potential curves in RASCI approximation



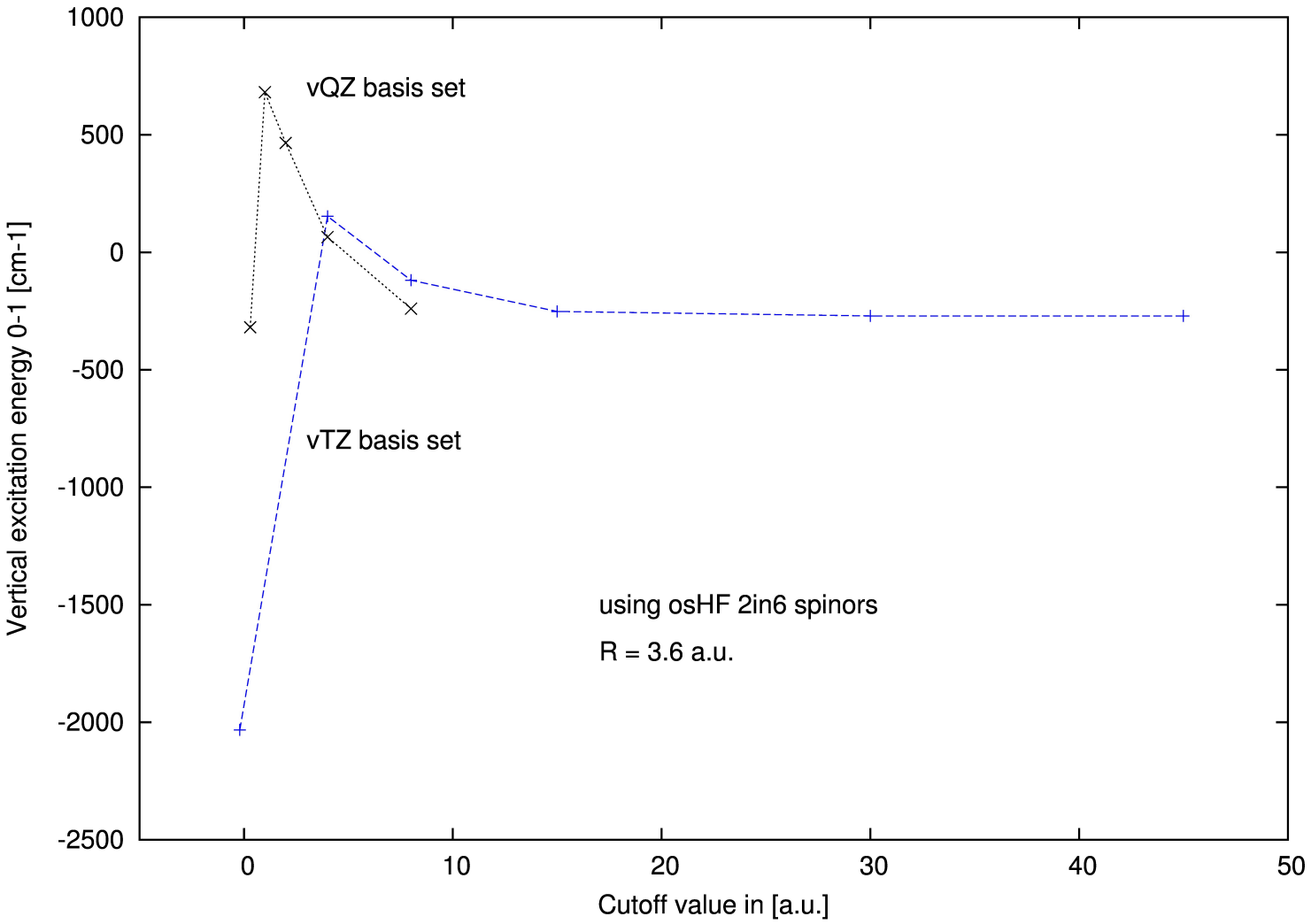
The eEDM in a molecular framework

HfF^+ potential curves in RASCISD approximation



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			
Titov: 20 e^- corr.[21]	3.366	3.413	1633
Experiment[22]			993

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

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

[22] 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^+: $E_{\rm eff}$ in the $\Omega = 1$ science state

Model	$E_{\rm eff}$ $\left[\frac{\rm GV}{\rm cm}\right]$
SD8_CAS2in6	24.77
SD8_CAS2in6_SD10	23.26
SDT8_CAS2in6_SD10	23.18
S18_CAS2in6_SD20	23.31
Titov: 20 e^- corr.[23]	36.28
Estimate, Meyer et al.[24]	≈ 30

Theory differences:

(+) No effective core potentials

(+) More rigorous electronic-structure model

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

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

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

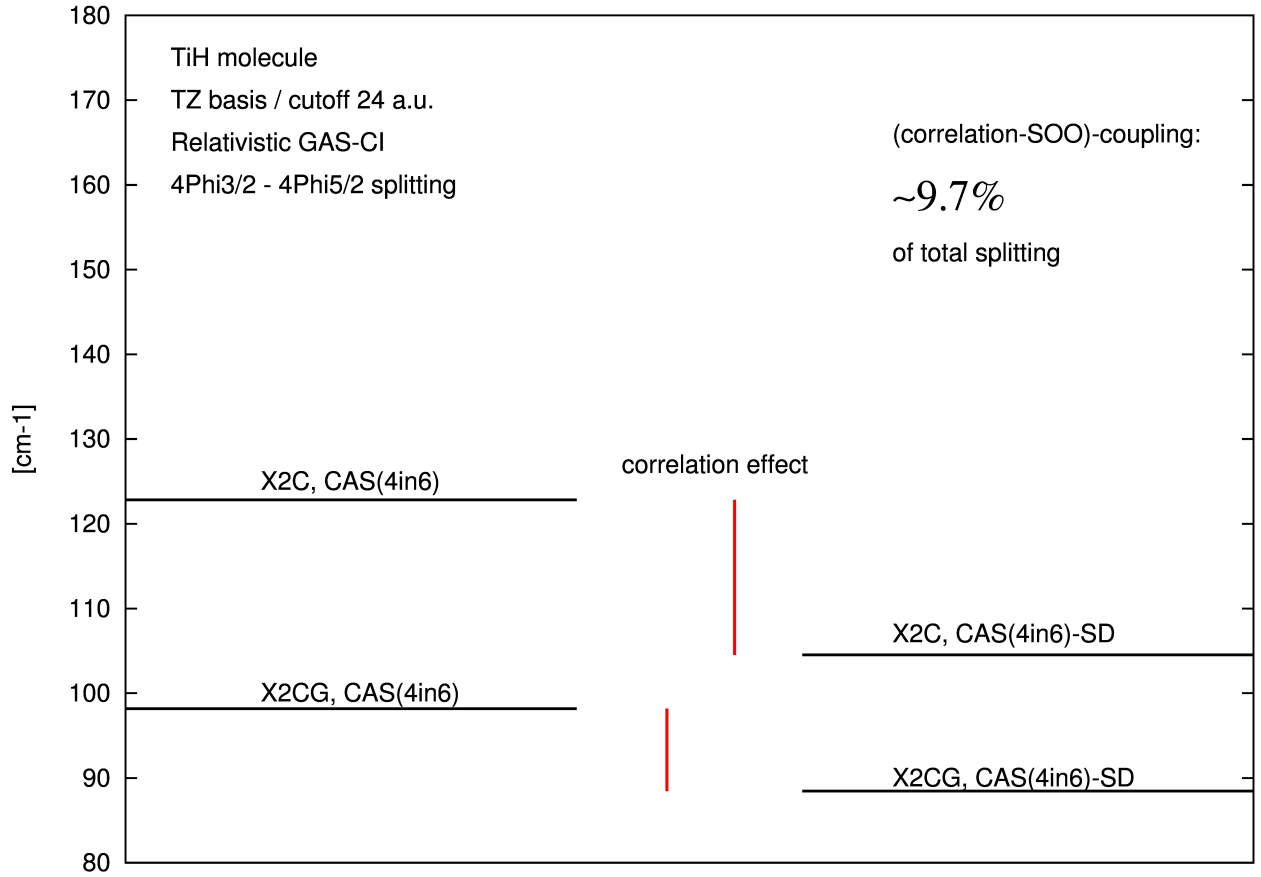
Ongoing Work

- Commutator-based GER CC Jacobian, non-relativistic version
  (with Mickael Hubert and Jeppe Olsen)
  Application to ScH $\rightarrow$ **Poster!**
- Commutator-based GER CC Jacobian, relativistic version
  (with Mickael Hubert and Lasse Sørensen)
- Electron EDM constants in other diatomic molecules
  (with Malaya K. Nayak)

Ongoing Work

- 4-component Gaunt / Breit operator in correlated approaches (with Jessica Loras → **Poster!**)

Decoupling correlation and 2-electron spin-orbit terms ?



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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: $O^m V^{m+2} o^{n-m} v^{n-m}$