Special Relativity and Electron Correlation: Still a Major Challenge

Timo Fleig

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

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Motivation

Laboratoire de Chimie et Physique Quantiques

Science with small heavy-element molecules

Ultracold molecular investigations[1]

Photoassociation via excited states

Astrophysics[2]

Collision processes in stellar atmospheres

Actinide theoretical spectroscopy[3]

Electronic structure in general

Fundamental physics[4]

Search for the electron electric dipole moment

The electronic-structure problem for a general diatomic molecule remains unsolved.

[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) Performance of **established methods** in comparison

2) Some **rigorous developments**: Rel. GAS-CC for excited states

3) A recent development: **Electron EDM** interaction constants

Special Relativity and Electron Correlation

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

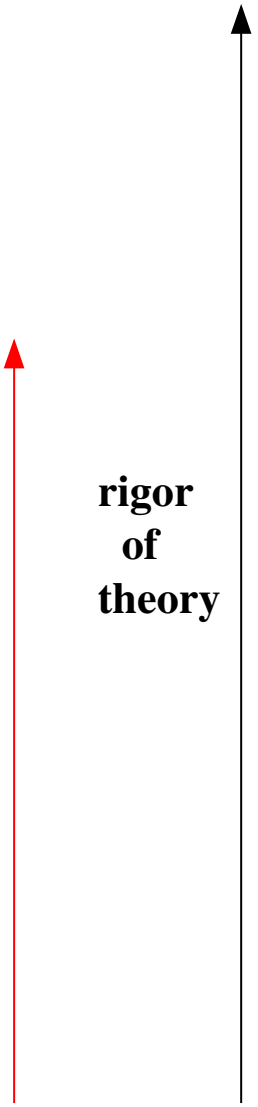
Hartree–Fock		*Dynamic Correlation*
scalar relativistic Hamiltonian	+	2–component Hamiltonian

Spin–orbit CI
Spin–orbit Coupled Cluster

Additive models

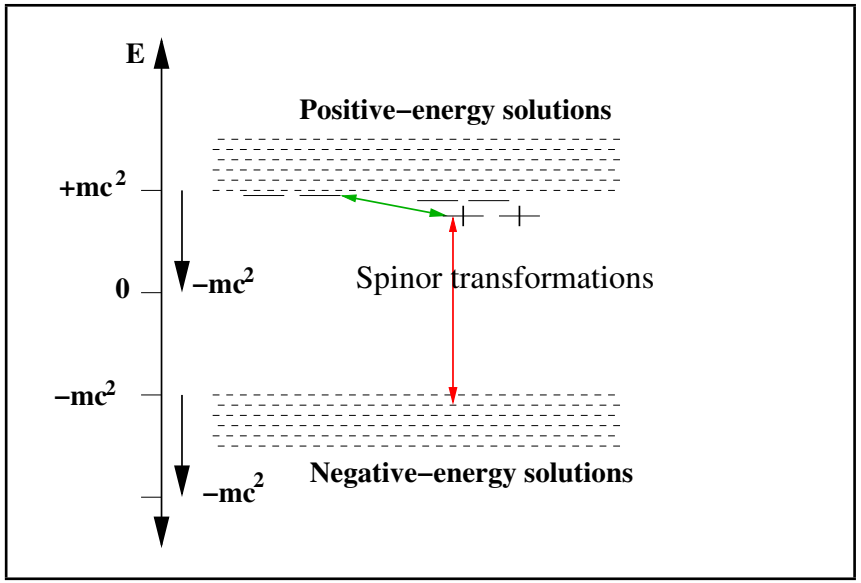
Hartree–Fock		*Dynamic Correlation*		*Magnetic Couplings*
scalar relativistic Hamiltonian	+	scalar relativistic Hamiltonian	+	2–component Hamiltonian

Spin–orbit QDPT
CASPT2–Spin–orbit RASSI



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

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

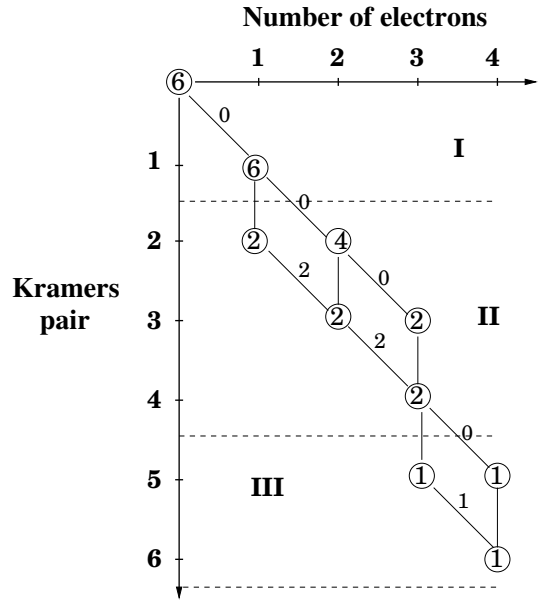
Spinor basis:

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

- 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**

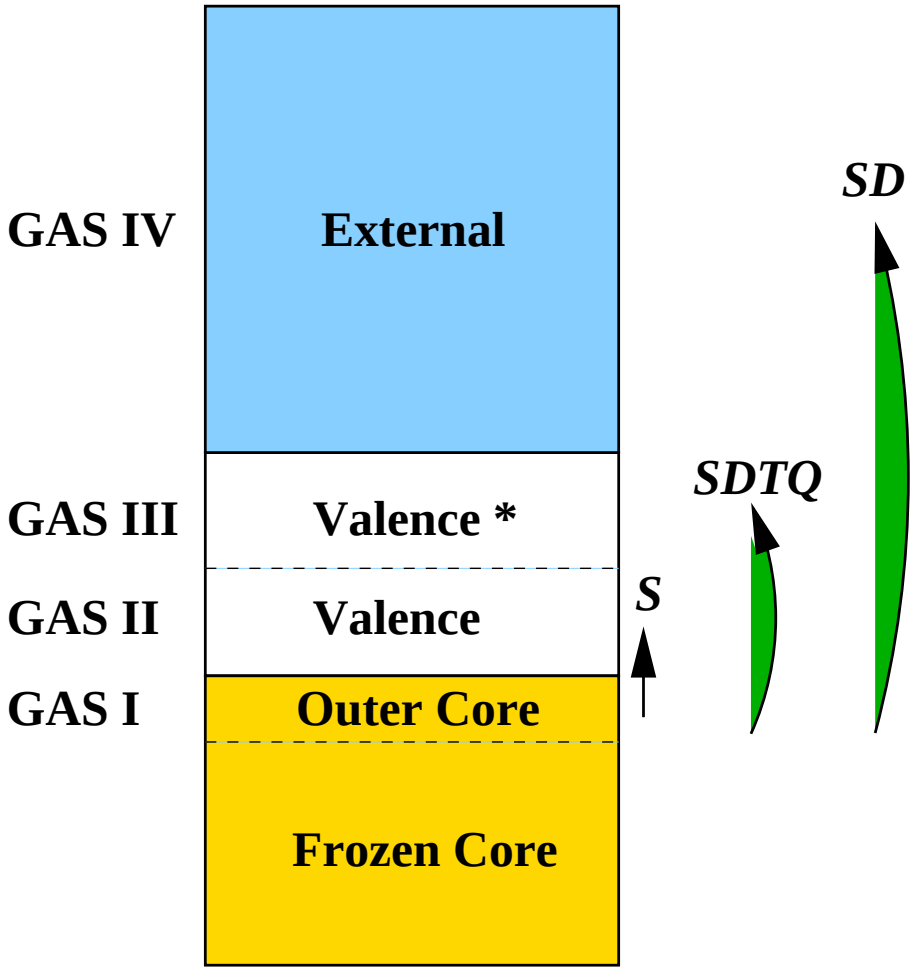
  Coupled Cluster: **Individual strings**



⊗ x: vertex weight
y: arc weight

Parameterization of the Wavefunction

Generalized Active Spaces



Special Relativity and Electron Correlation

Methods in comparison

Chalcogen homonuclear and heteronuclear diatomics[5]

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"[6]: *SO-DDCI3*, *SO-CASPT2*

"Non-additive"[7]: *4c-IH-FSCC*, *4c-GASCI*

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

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

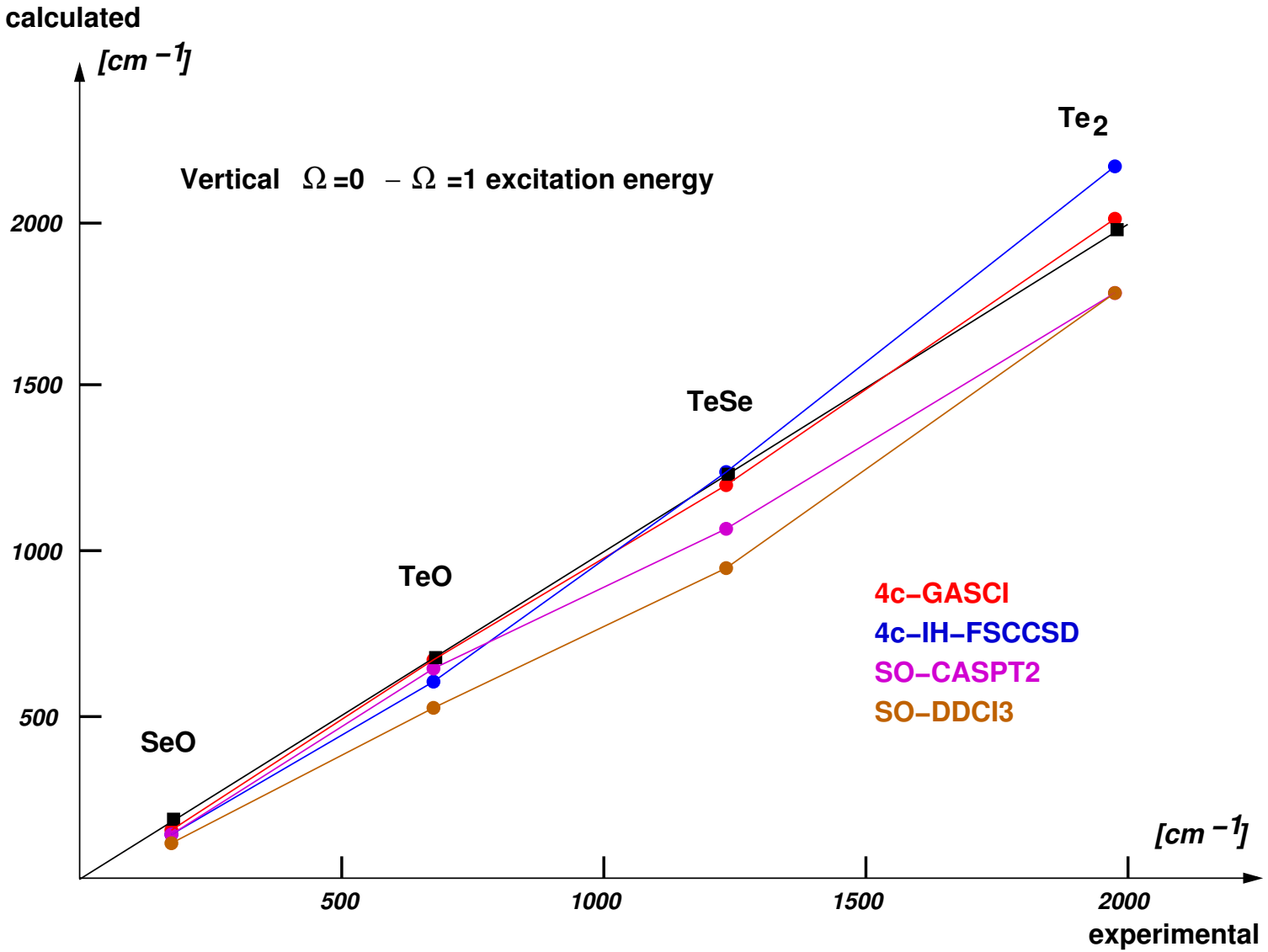
P.-Aa. Malmqvist, B.O. Roos, B. Schimmelpfennig, *Chem Phys Lett* **357** (2002) *357*

[7] 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*

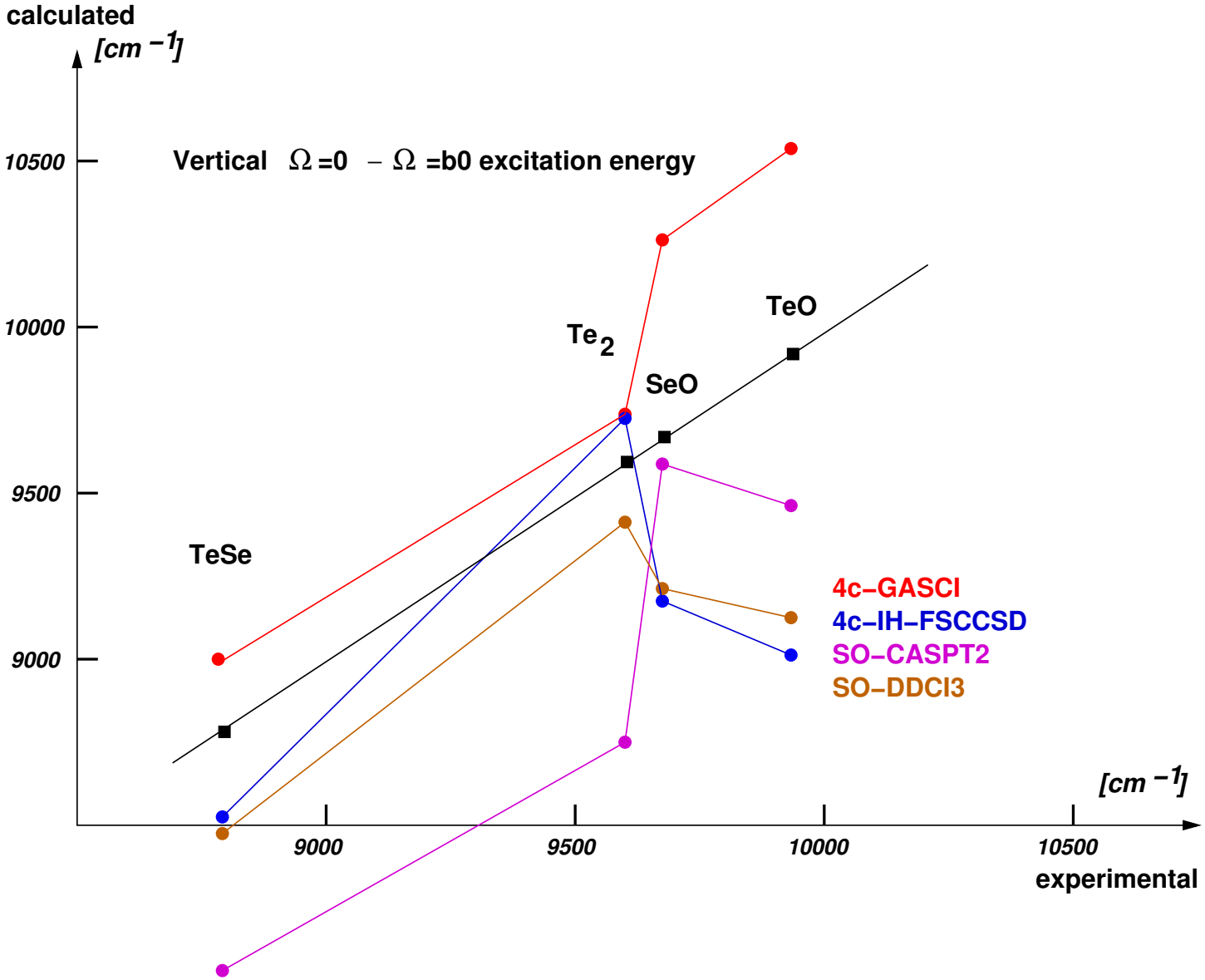
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



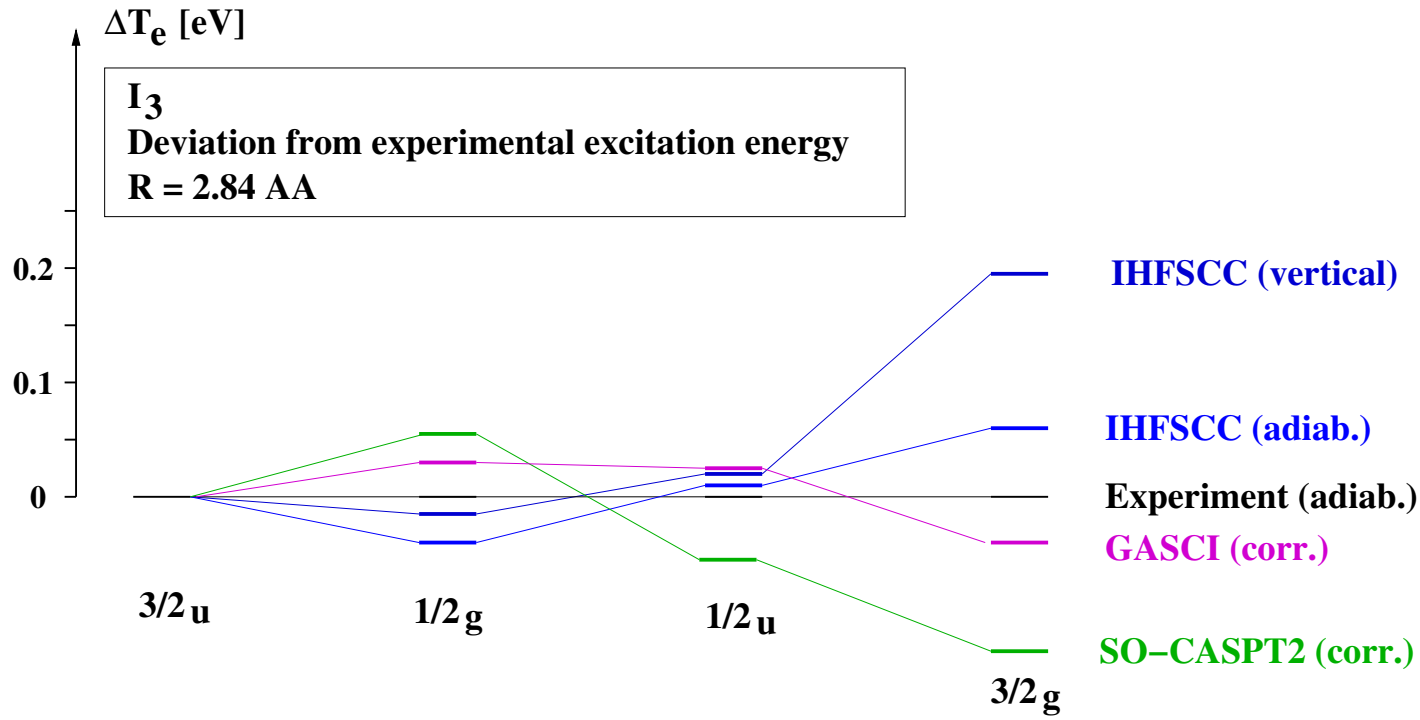
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Comparison of Methods

Vertical electronic spectrum of I_3; Ω states[8]



- 2c-GASCI and SO-CASPT2 corrected for non-parallelity
- IH-FSCC and 2c-GASCI roughly equivalent in quality
- Errors of 2c-GASCI < 0.05 eV

[8] 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

Decoupling correlation and 2-electron spin-orbit terms ?

- Origin of spin-other-orbit interactions in the Gaunt-like term in

$$\hat{H}^{DCB} = \sum_A \sum_i \left[c(\vec{\alpha} \cdot \vec{p})_i + \beta_i m_0 c^2 + V_{iA} \right] + \sum_{i,j>i} \left[\frac{1}{r_{ij}} \mathbf{1}_4 - \frac{1}{2} \left(\frac{\vec{\alpha}_i \vec{\alpha}_j}{r_{ij}} + \frac{(\vec{r}_{ij} \cdot \vec{\alpha}_i)(\vec{r}_{ij} \cdot \vec{\alpha}_j)}{r_{ij}^3} \right) \right] + \sum_{A,B>A} V_{AB}$$

- and extracted in Breit-Pauli two-component approximation

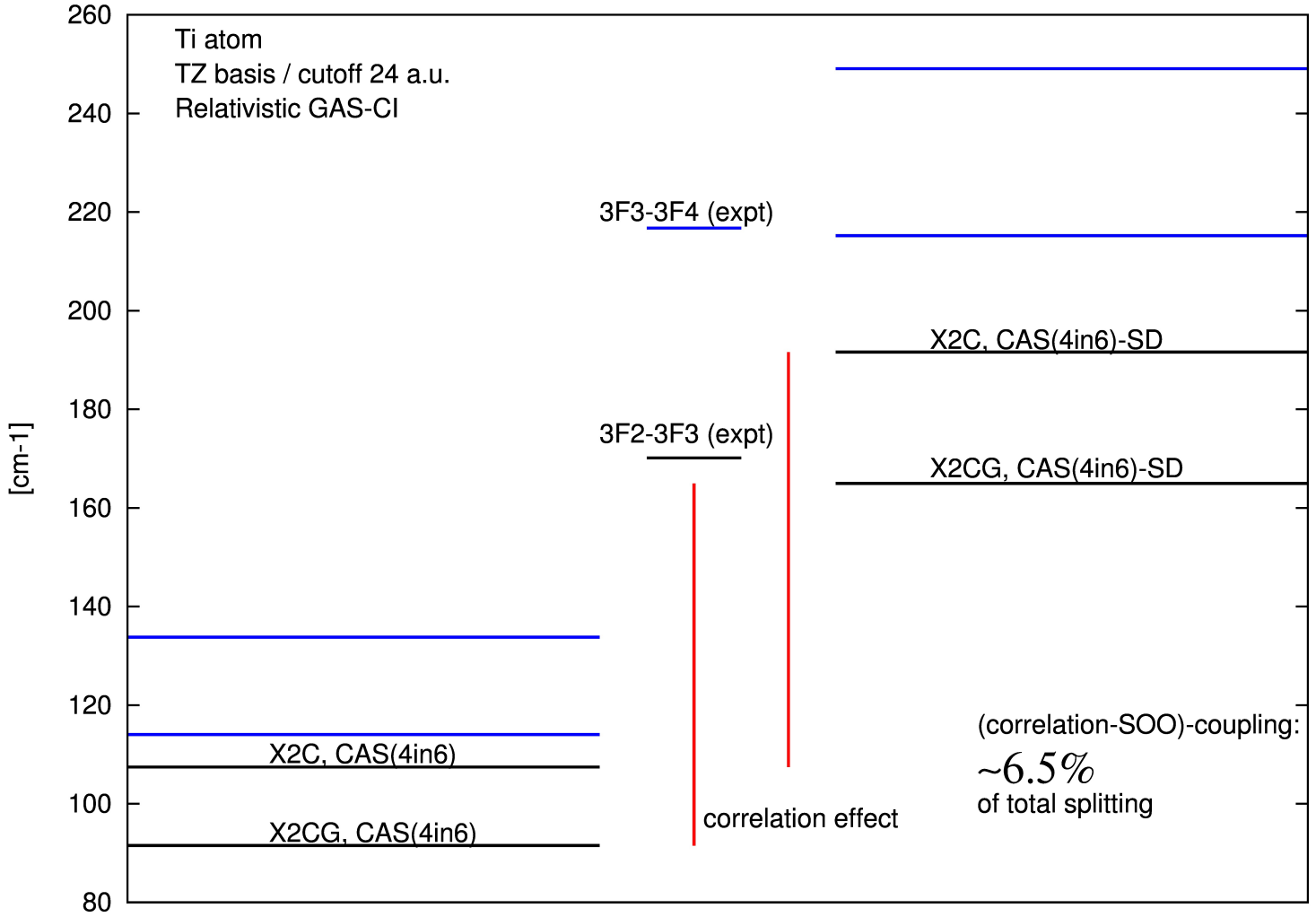
$$\hat{H}^{SOO} = -\frac{e^2}{m_0^2 c^2} \sum_{i,j>i} \frac{1}{r_{ij}^3} \left[(\vec{r}_j - \vec{r}_i) \times \vec{p}_j \cdot \vec{s}_i + (\vec{r}_i - \vec{r}_j) \times \vec{p}_i \cdot \vec{s}_j \right]$$

- Orbit-orbit and spin-spin couplings are neglected here.

- Test in selected atoms and molecules

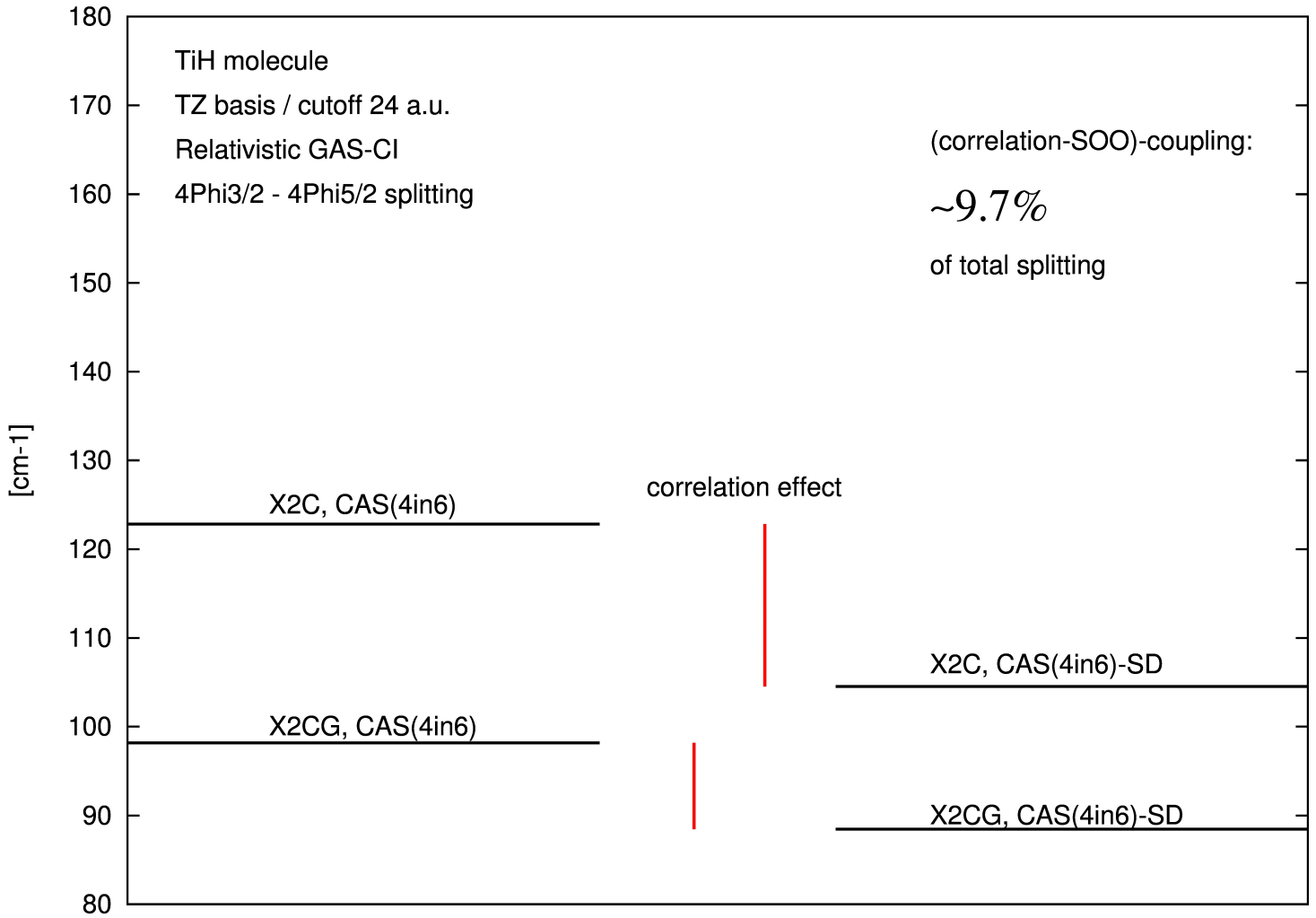
Special Relativity and Electron Correlation

Decoupling correlation and 2-electron spin-orbit terms ?



Special Relativity and Electron Correlation

Decoupling correlation and 2-electron spin-orbit terms ?



Special Relativity and Electron Correlation

Methods in comparison

Conclusions in the light of evidence

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

2c/4c-GASCI allows for balanced treatment of ground and excited states

CI not size extensive

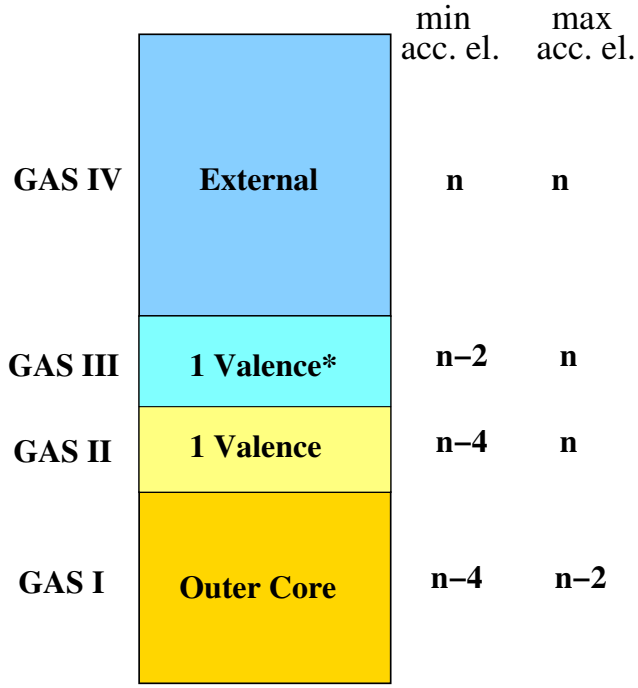
CI inefficient in treating higher excitations

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[9]
- 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
  $\hat{T}_1 = \sum_{ia} \left\{ \; t^a_i \hat{\tau}^a_i + t^a_{\bar{i}} \hat{\tau}^a_{\bar{i}} + t^{\bar{a}}_i \hat{\tau}^{\bar{a}}_i + t^{\bar{a}}_{\bar{i}} \hat{\tau}^{\bar{a}}_{\bar{i}} \; \right\}$; $\hat{T}_2 = \ldots$



Example for constructed higher excitations:

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

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

Relativistic Generalized-Active-Space CC

Electronic Ground States [10]

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.

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

[10] 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[11]

Excitation Energies[12]

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

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 $O^{n+2}V^{n+2}$

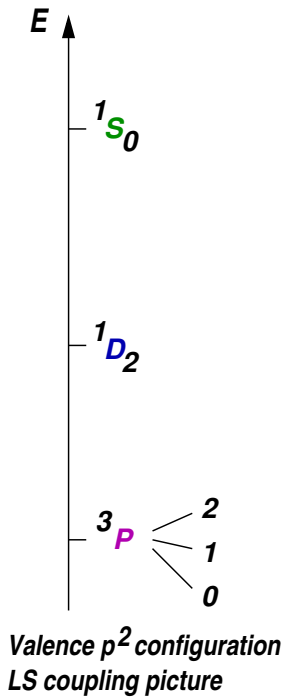
Conventional CC: $O^n V^{n+2}$

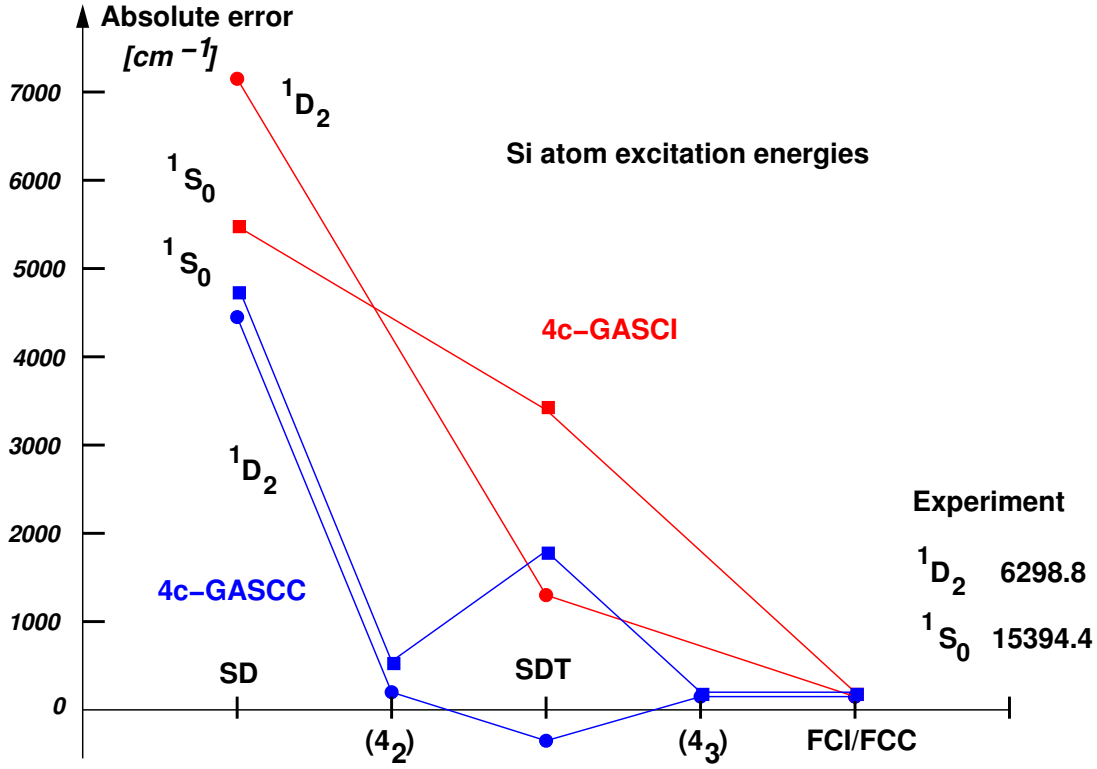
[11] M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **XXX** (2012) *in press.*

[12] 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:

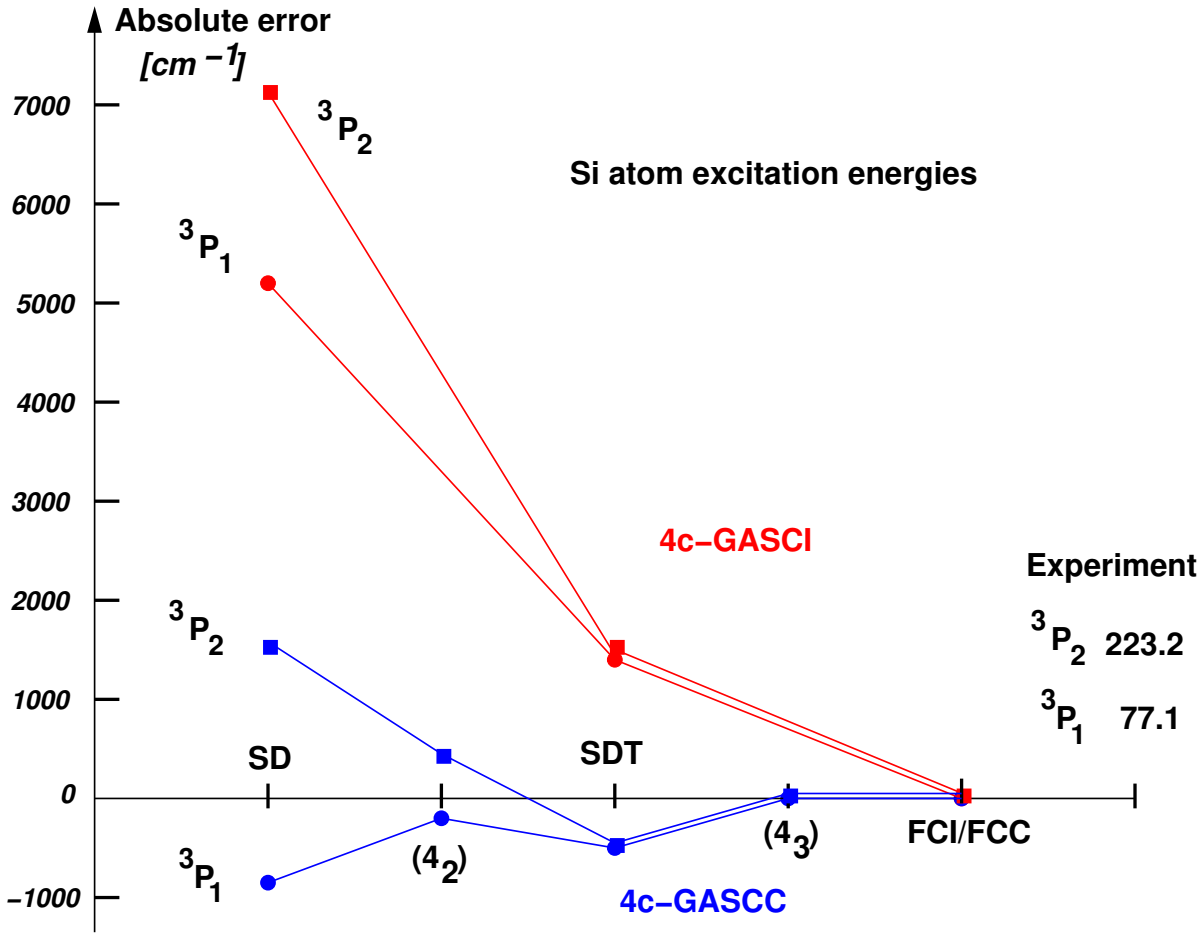
$$\left|\frac{3}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right| = -\frac{1}{2}\,{}^3P_1 - \frac{1}{2}\,{}^3P_2 + \frac{1}{\sqrt{2}}\,{}^1D_2$$

- 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

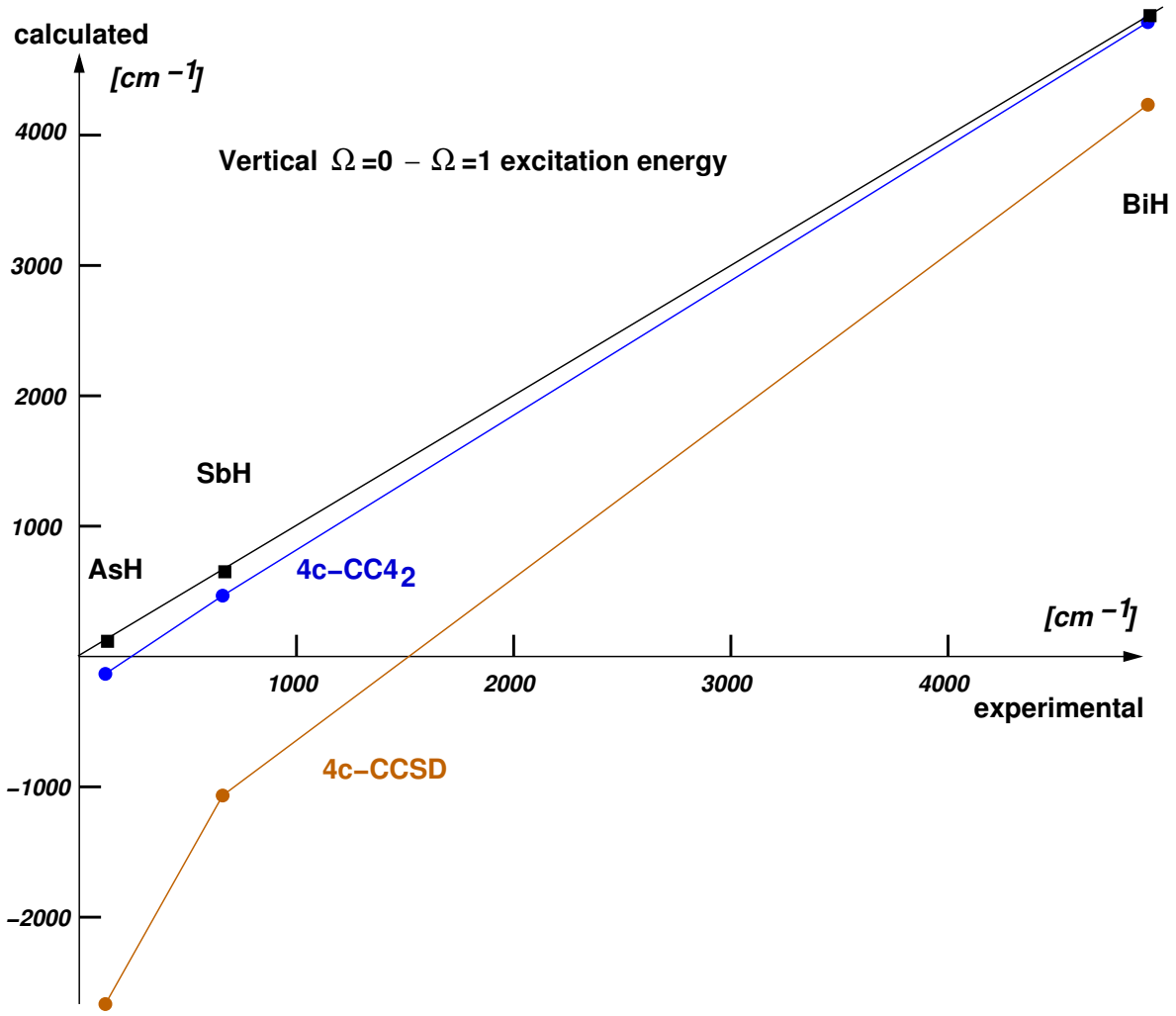
AsH, SbH, BiH

- 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 [13]

[13] M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **XXX** (2012) *in press.*

Series AsH, SbH, BiH

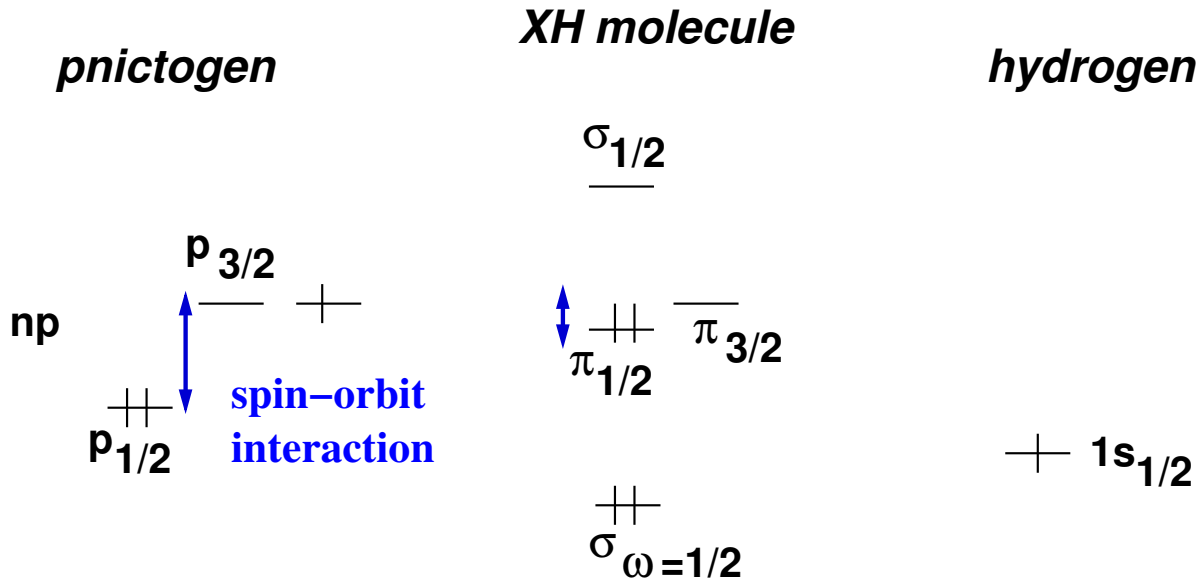
The strange behavior of CCSD



- Huge errors for As homologue

Series AsH, SbH, BiH

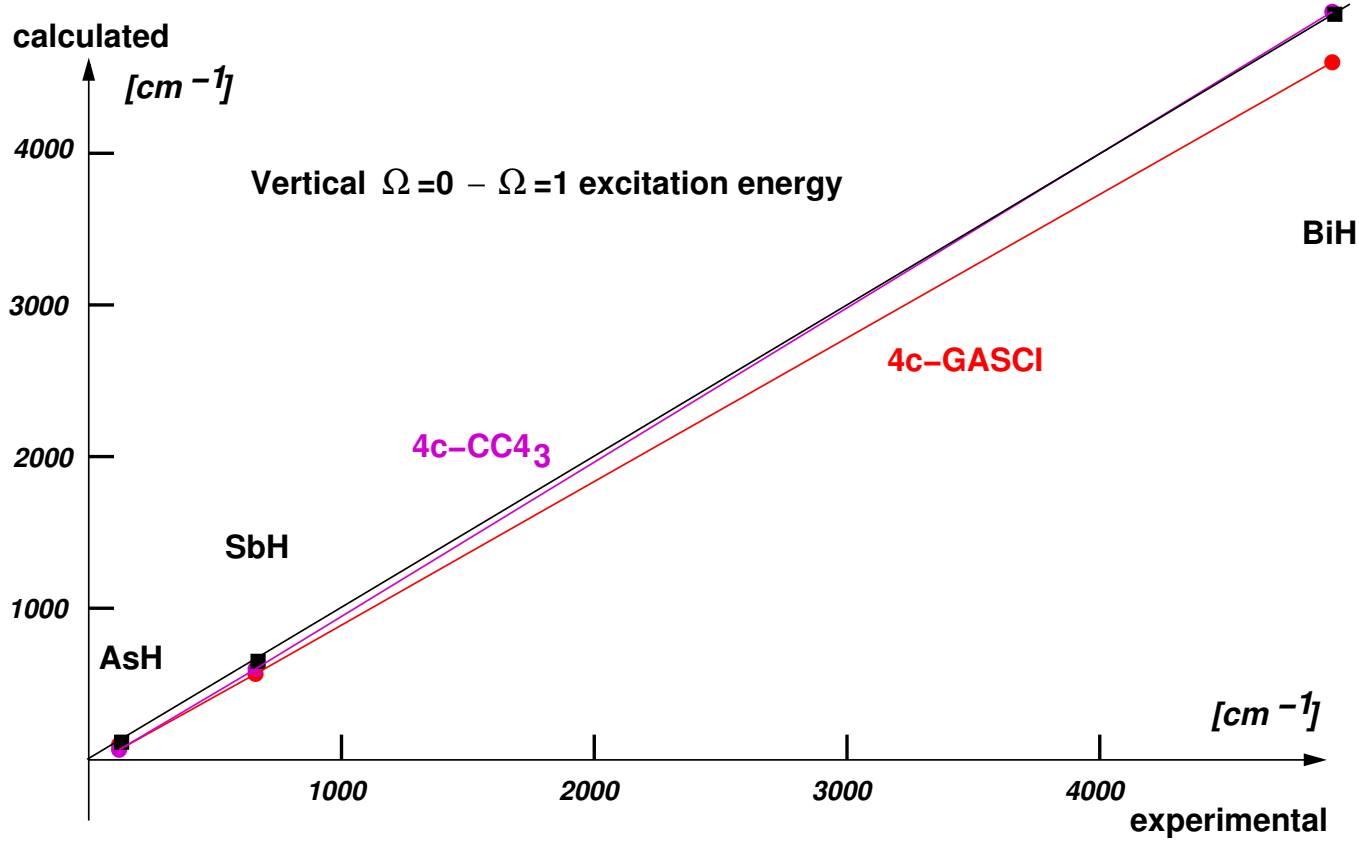
Spinors and the molecular field



- ω coupled spinors: $\pi^2_{1/2}$ Fermi vacuum
- 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

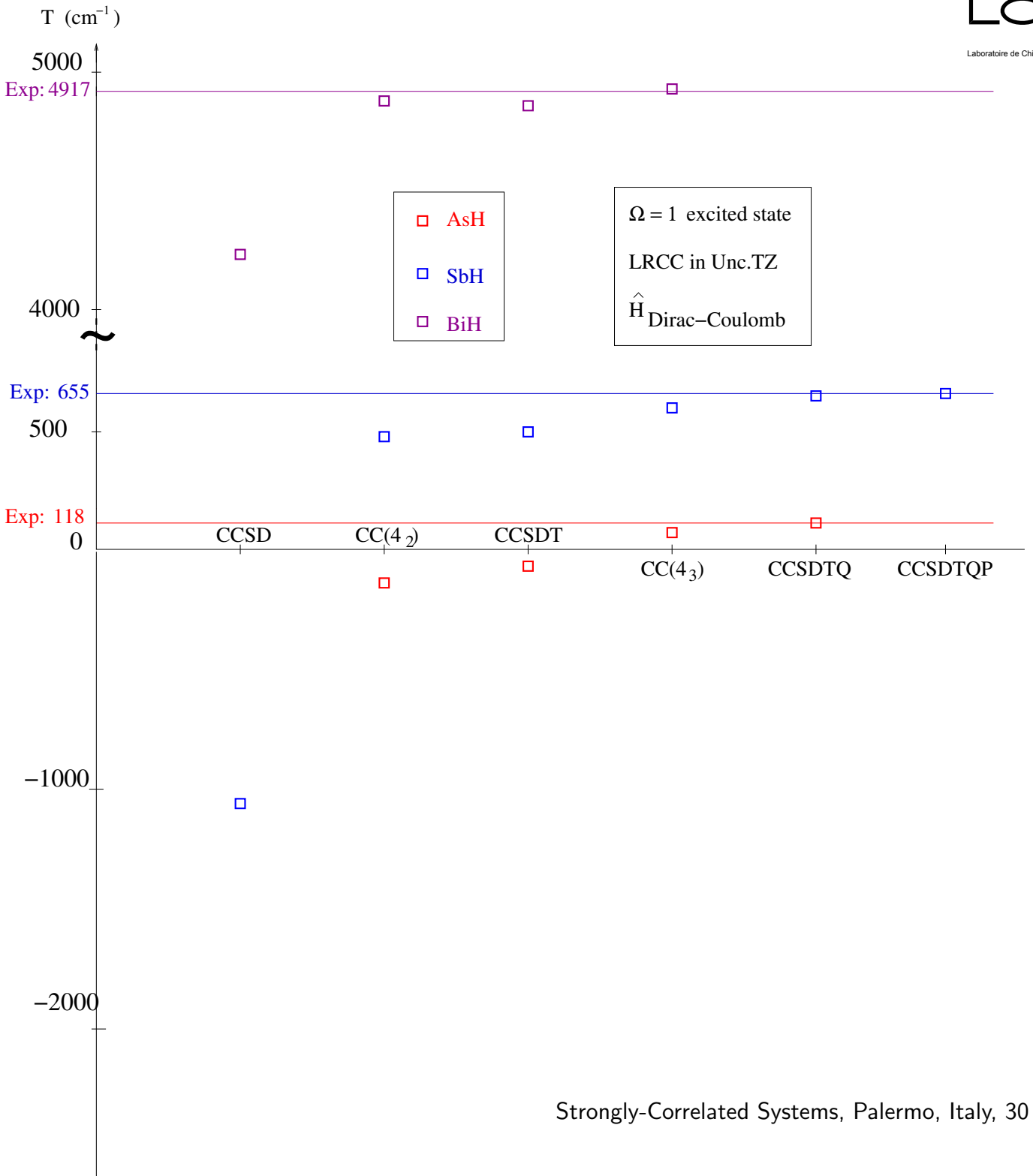
When is CC superior to GAS-CI?



- $CC4_3$ calculations consistently better than CAS-CISD

Convergence of GAS-CC models

AsH, SbH, BiH

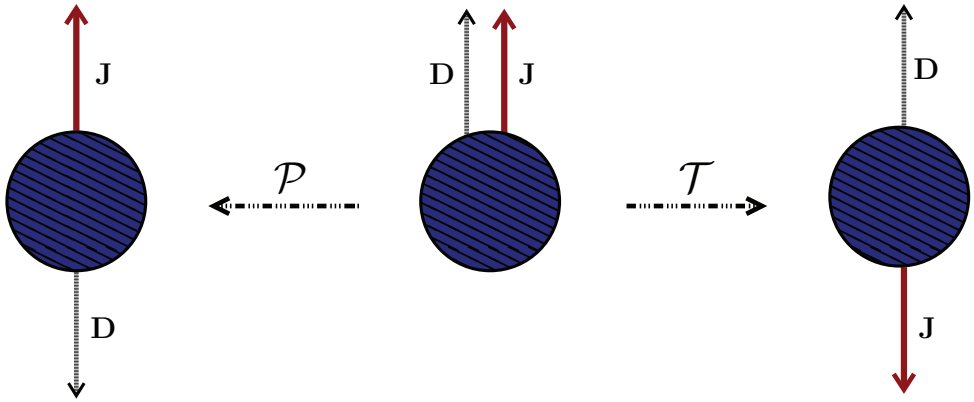

T (cm^{-1})
5000
Exp: 4917
4000
Exp: 655
500
Exp: 118
0
−1000
−2000
AsH
SbH
BiH
Ω = 1 excited state
LRCC in Unc.TZ
$\hat{H}$ Dirac−Coulomb
CCSD
CC(4 2)
CCSDT
CC(4 3)
CCSDTQ
CCSDTQP

Conclusion

- 4c-GASCI reliable method for excited-state calculations
- 4c-GASCI only practical as MR-SD model for demanding cases
- Higher accuracy through 4c-GASCC as (n_2) models in some cases
- CC(n_3) is too expensive in general
- Simple closed-shell reference state not desirable in general
- Fermi-vacuum dependance is major obstacle in excited-state calculations

Testing fundamental physics:

Could the e have a permanent electric dipole moment $\vec{D}$?



$\vec{D}$ 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** and **Time-Reversal** symmetries[14]

No violation of the $\mathcal{CPT}$ theorem

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

Testing fundamental physics:

Current predictions for the eEDM[15]

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	$10^{-28} \ldots 10^{-27}$
(naive) Supersymmetric	$\leq 10^{-25}$
Experimental limit[16]	$< 1.6 \cdot 10^{-27}$
Experimental limit[17]	$< 10.5 \cdot 10^{-28}$

[15] 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*

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

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

The eEDM in a molecular framework

Essentials of the physics

- Point of departure: Salpeter's[18] modified Dirac equation:

$$\left[\left(p_\mu + \tfrac{e}{c}A_\mu\right)\gamma_\mu - \imath m_0 c\right]\psi(\vec{r}) = -\zeta\left(\frac{e\hbar}{4m_0c^2}\right)\gamma_5\gamma_\mu\gamma_\nu F_{\mu\nu}\psi(\vec{r})$$

- 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[19].

[18] E. Salpeter, *Phys* XXX **XX** (1957) XXX

[19] M. K. Nayak and T. Fleig, unpublished.

The eEDM in a molecular framework

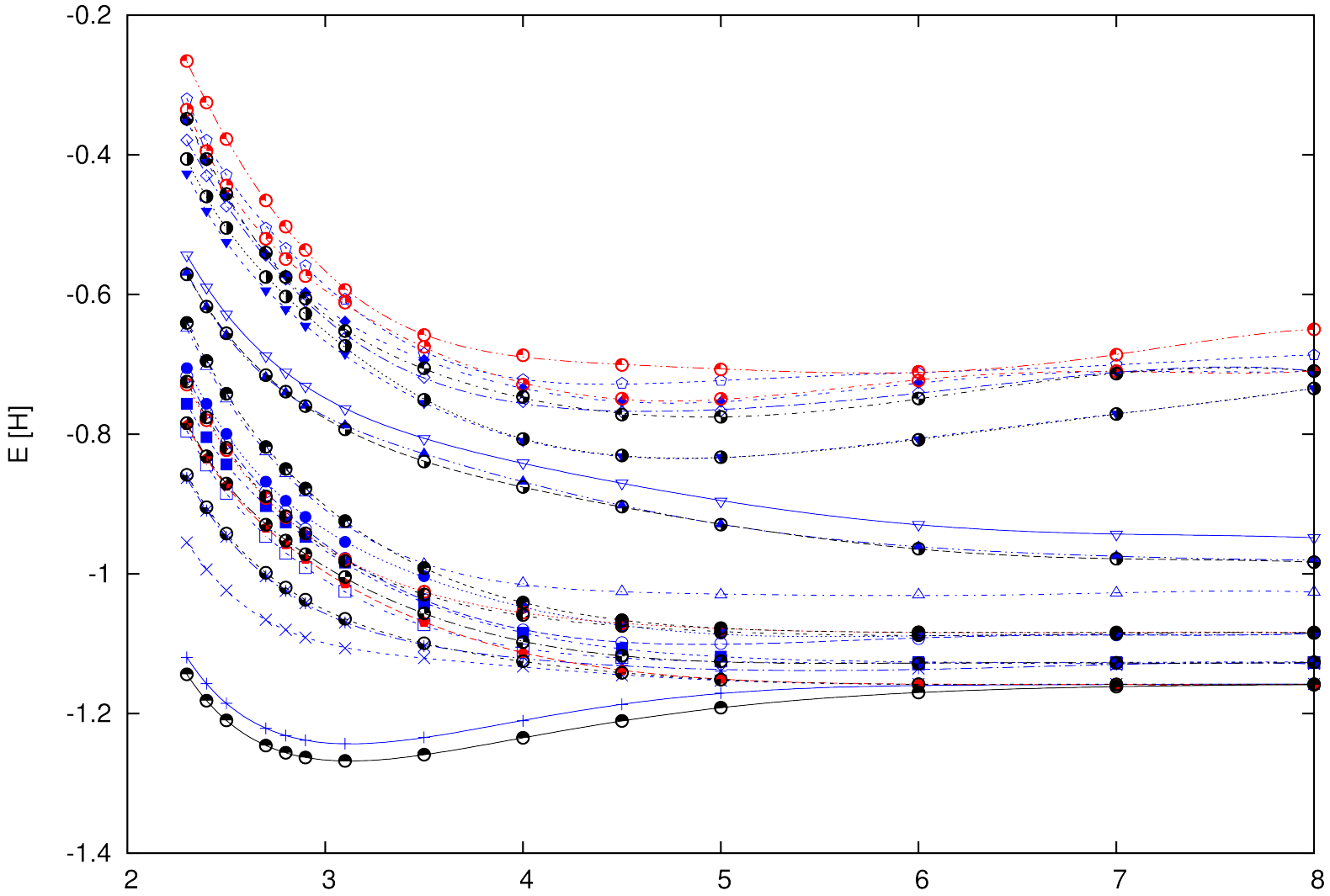
Some candidate molecules

- ThF^+, HfF^+ (Experiment, Cornell group)
- WC (Experiment, Leanhart group, Michigan)
- ThO[20] (Theory, Meyer et al.)
- IH^+ (Theory, Titov et al.)

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

The eEDM in a molecular framework

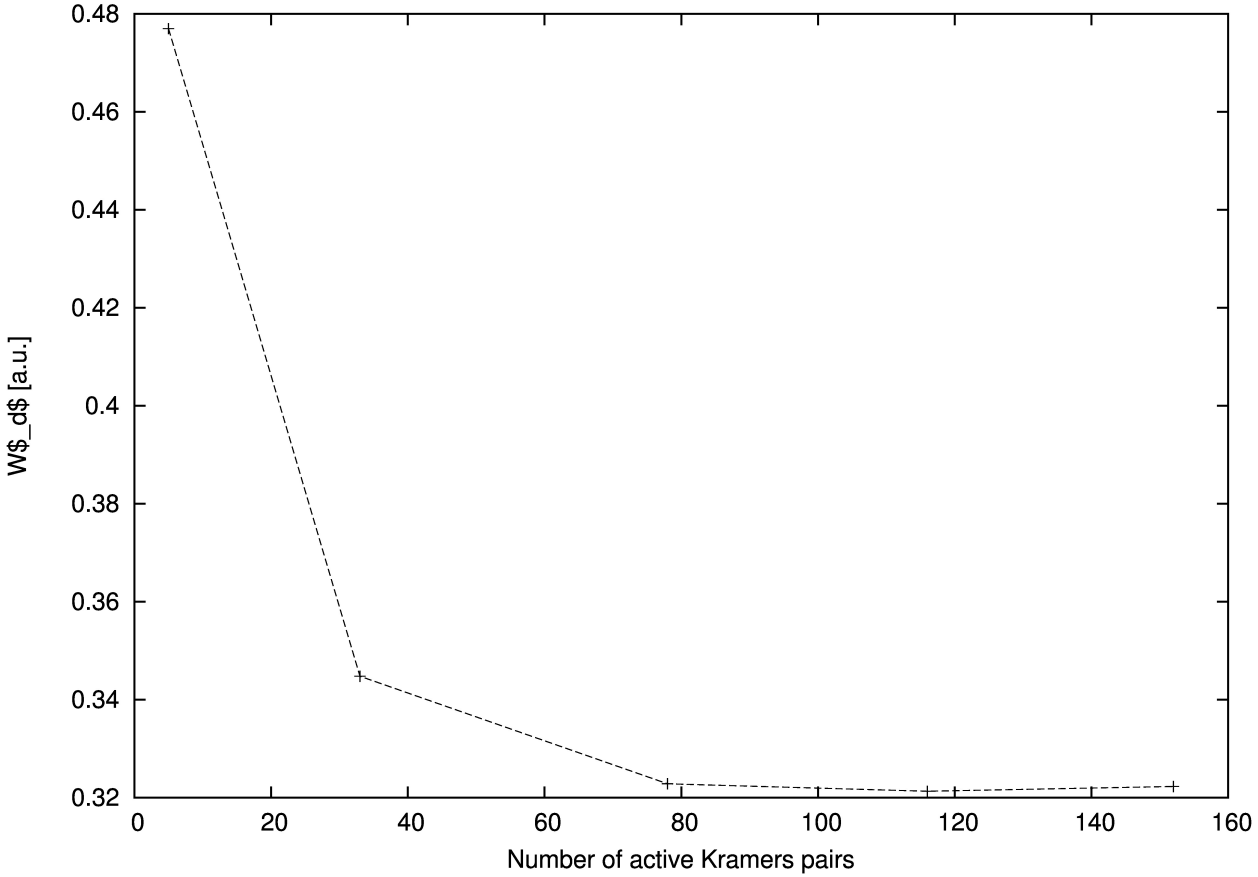
IH^+ as a candidate system



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

The eEDM in a molecular framework

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



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

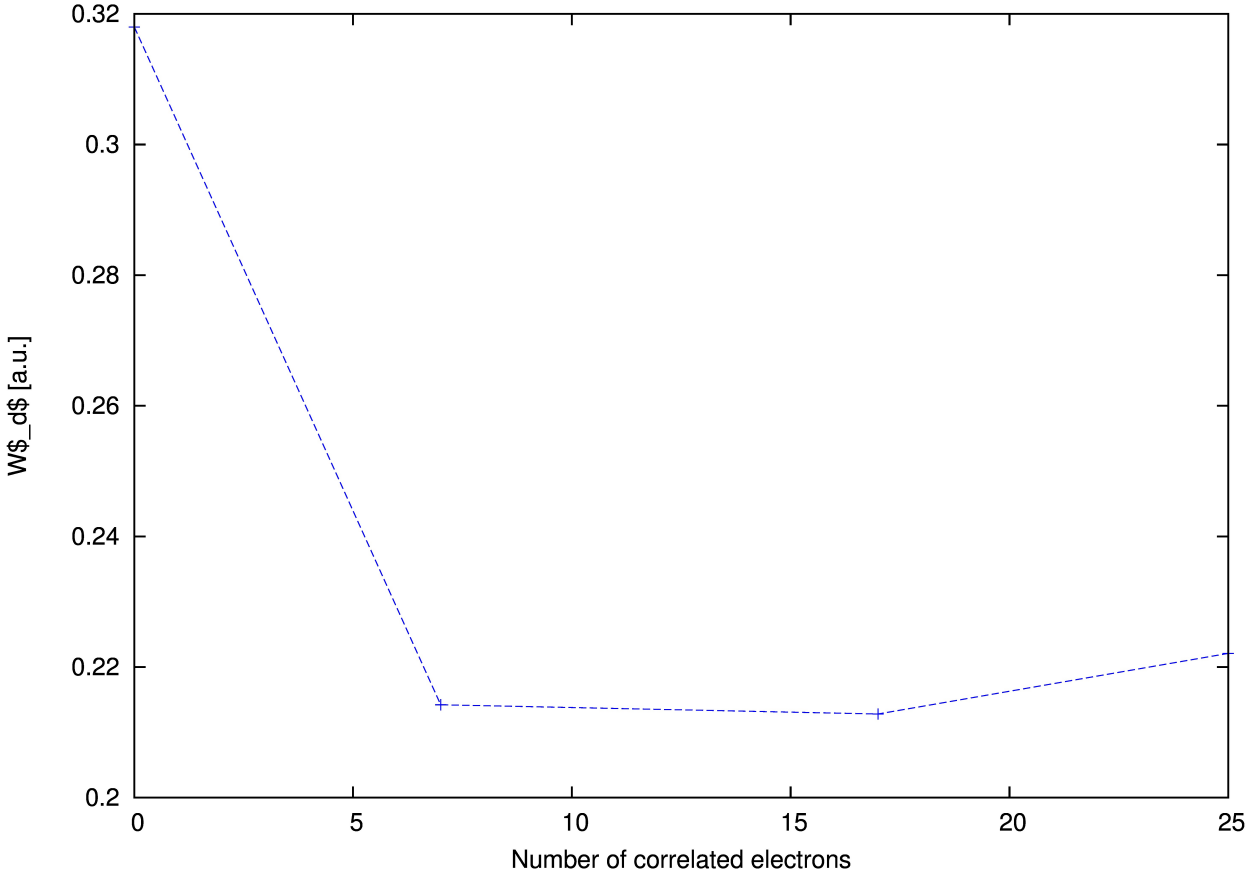
IH^+:

$^2\Pi_{3/2}$ 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.

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

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Mickael Hubert

Toulouse, France

Jessica Loras

Toulouse, France

Stefan Knecht

Odense, Denmark

Lasse K. Sørensen

Århus, Denmark

Jeppe Olsen

Århus, Denmark

Malaya K. Nayak

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Hélène Bolvin

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Trond Saue

Toulouse, France

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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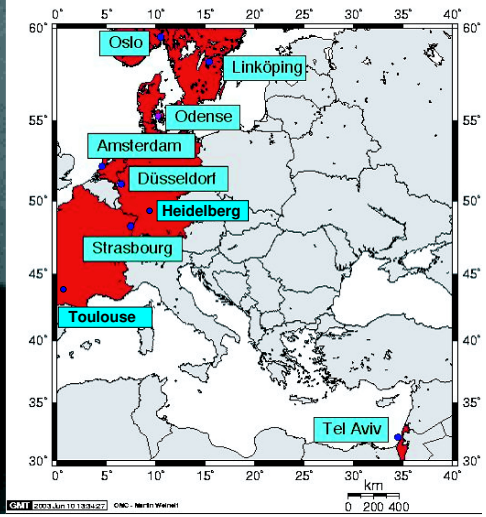
M olecular

D irect
I terative
R elativistic
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

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

I_3^- Molecular Ion

Different Methods in Comparison