Recent Progress on Relativistic General Excitation Rank Electron Correlation Methods

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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 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) State-of-the-art applications with **established methods**

2) Some **recent developments**:
   Generalized Active Space Coupled Cluster

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

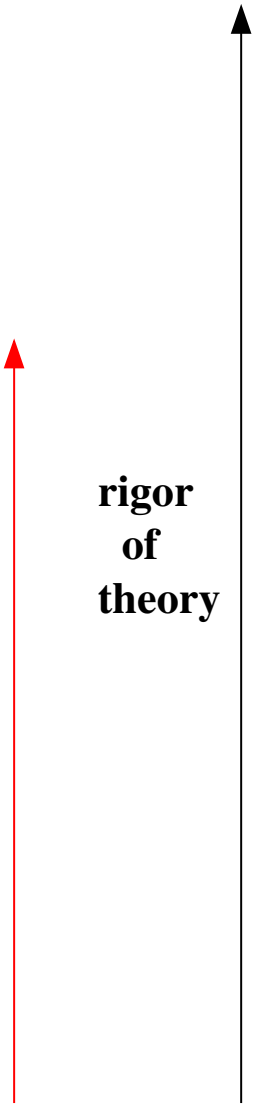
Hartree–Fock		*Dynamic Correlation*
scalar relativistic Hamiltonian	+	2–component Hamiltonian

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

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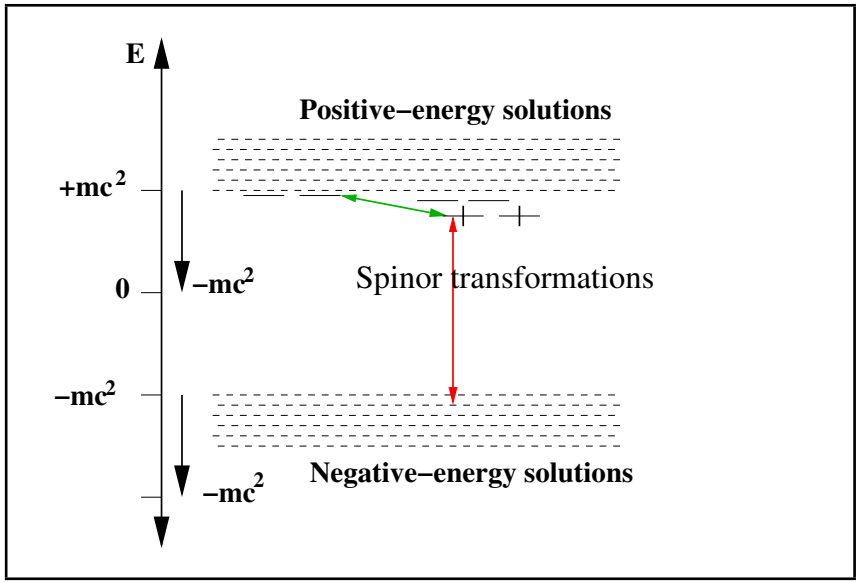
The "empty-Dirac" picture



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

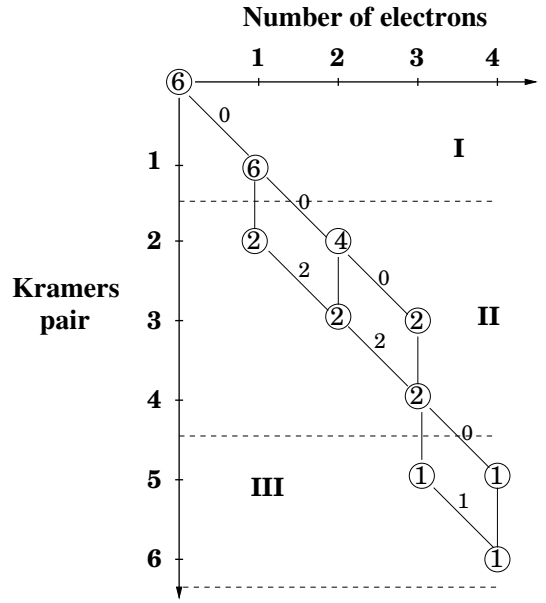
Spinor basis:

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

- 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**

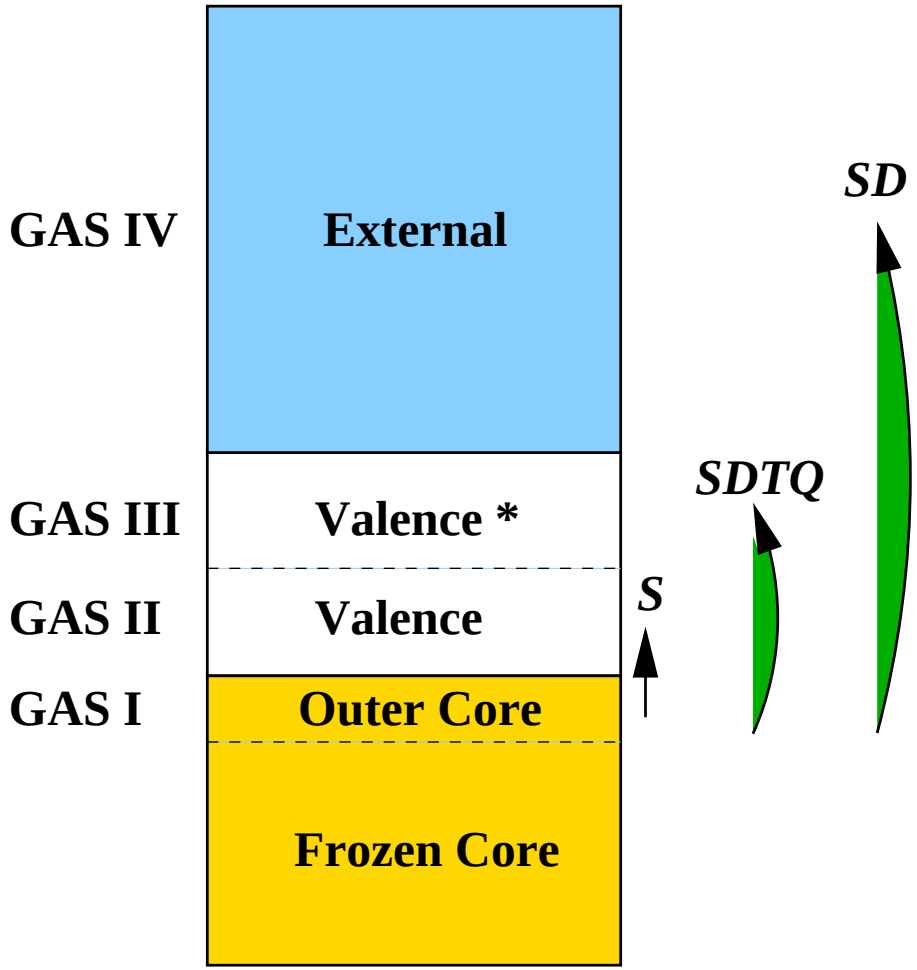
  Coupled Cluster: **Individual strings**



⊗ 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[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*

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[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*

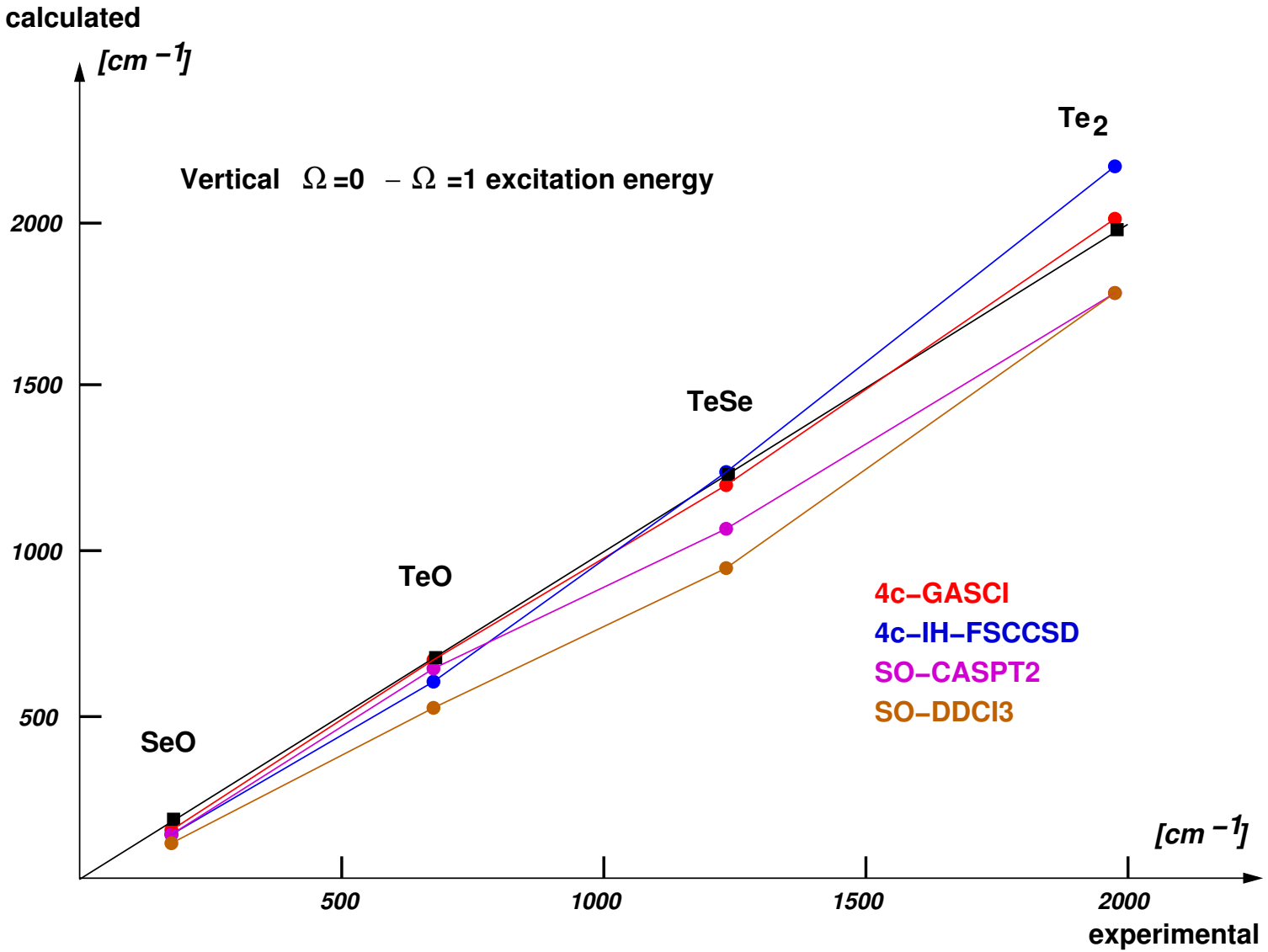
P.-Aa. Malmqvist, B.O. Roos, B. Schimmelpfennig, *Chem Phys Lett* **357** (2002) *357*

[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*

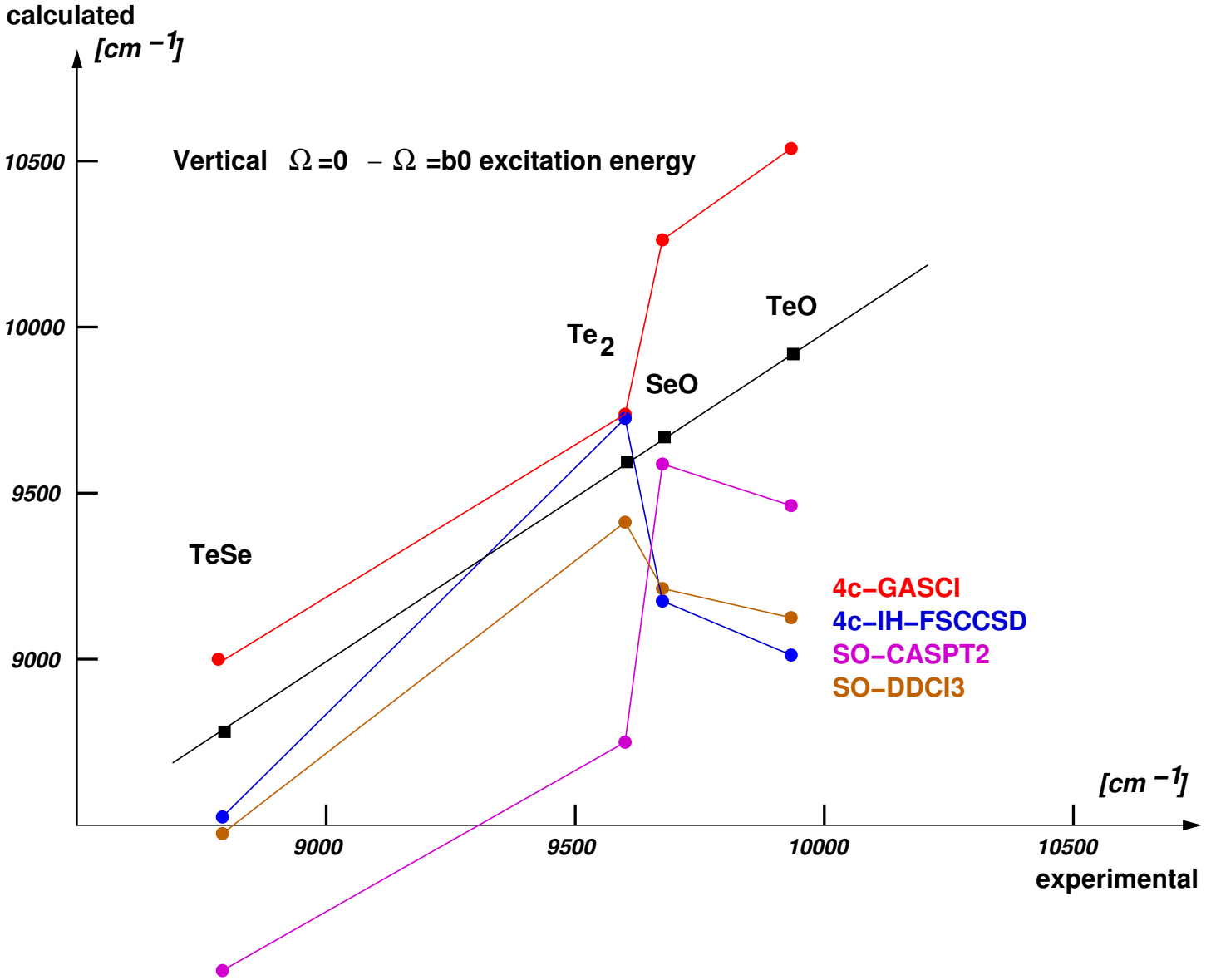
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



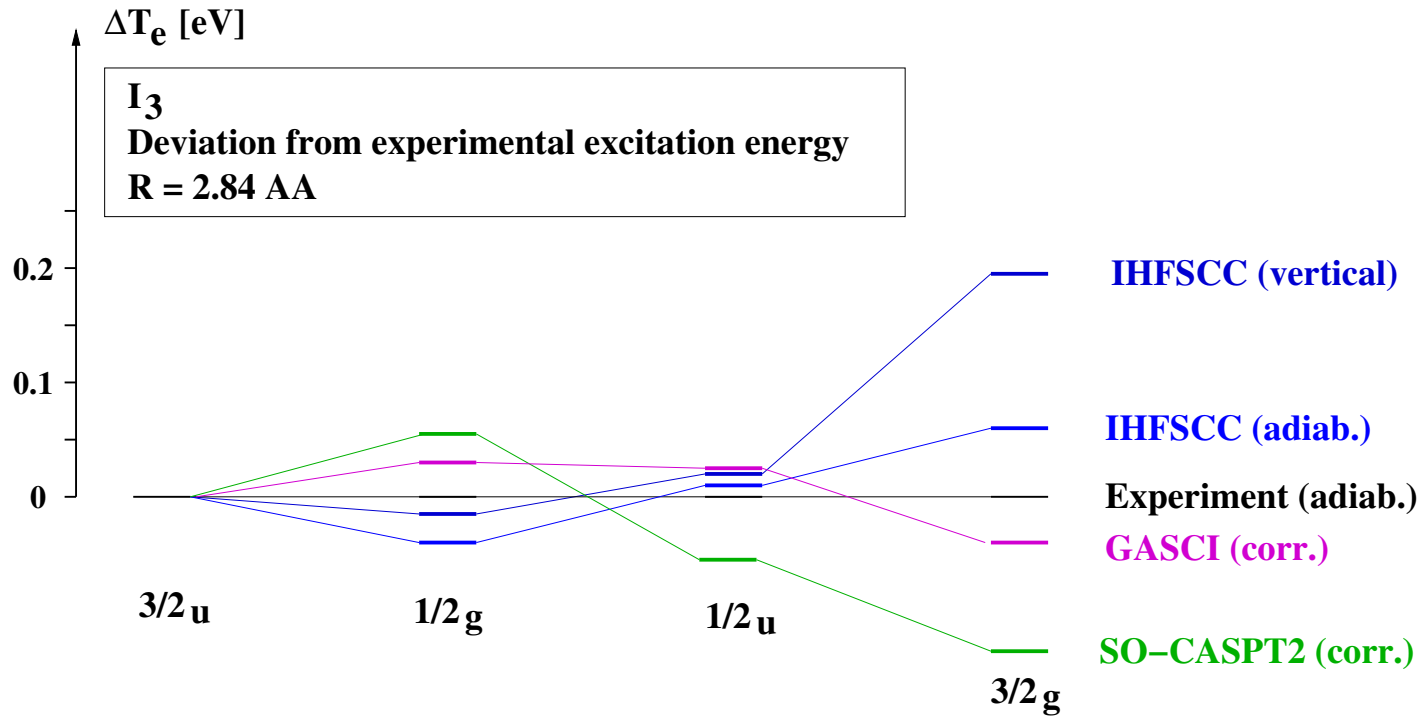
Special Relativity and Electron Correlation

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 shows smallest errors (also in closed-shell I_3^- system)
- 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

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

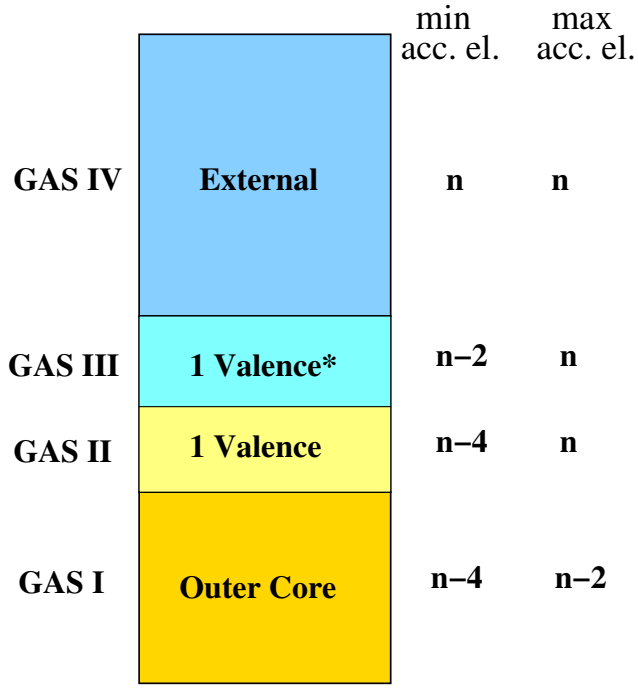
CI inefficient in treating higher excitations

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



Example for constructed higher excitations:

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

[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]

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

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

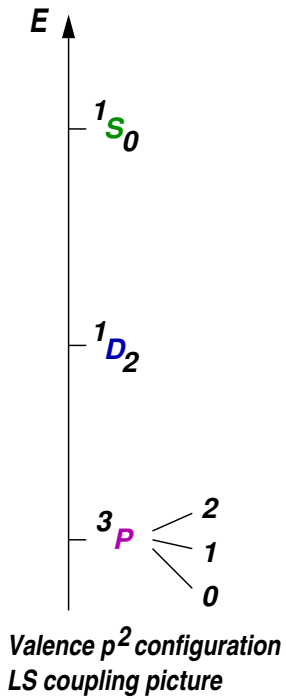
Conventional CC: $O^{n}V^{n+2}$

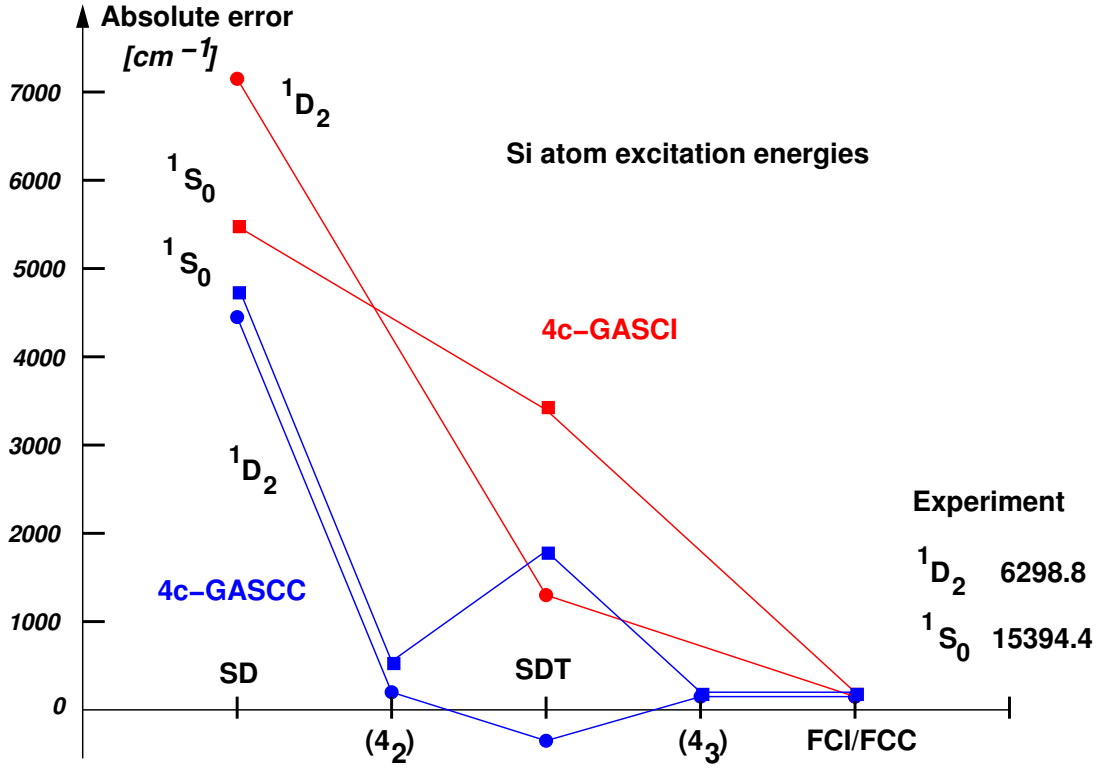
[11] M. Hubert, L. K. Sørensen, J. Olsen, T. Fleig, *Phys Rev A* **XXX** (2011) *to be submitted.*

[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:

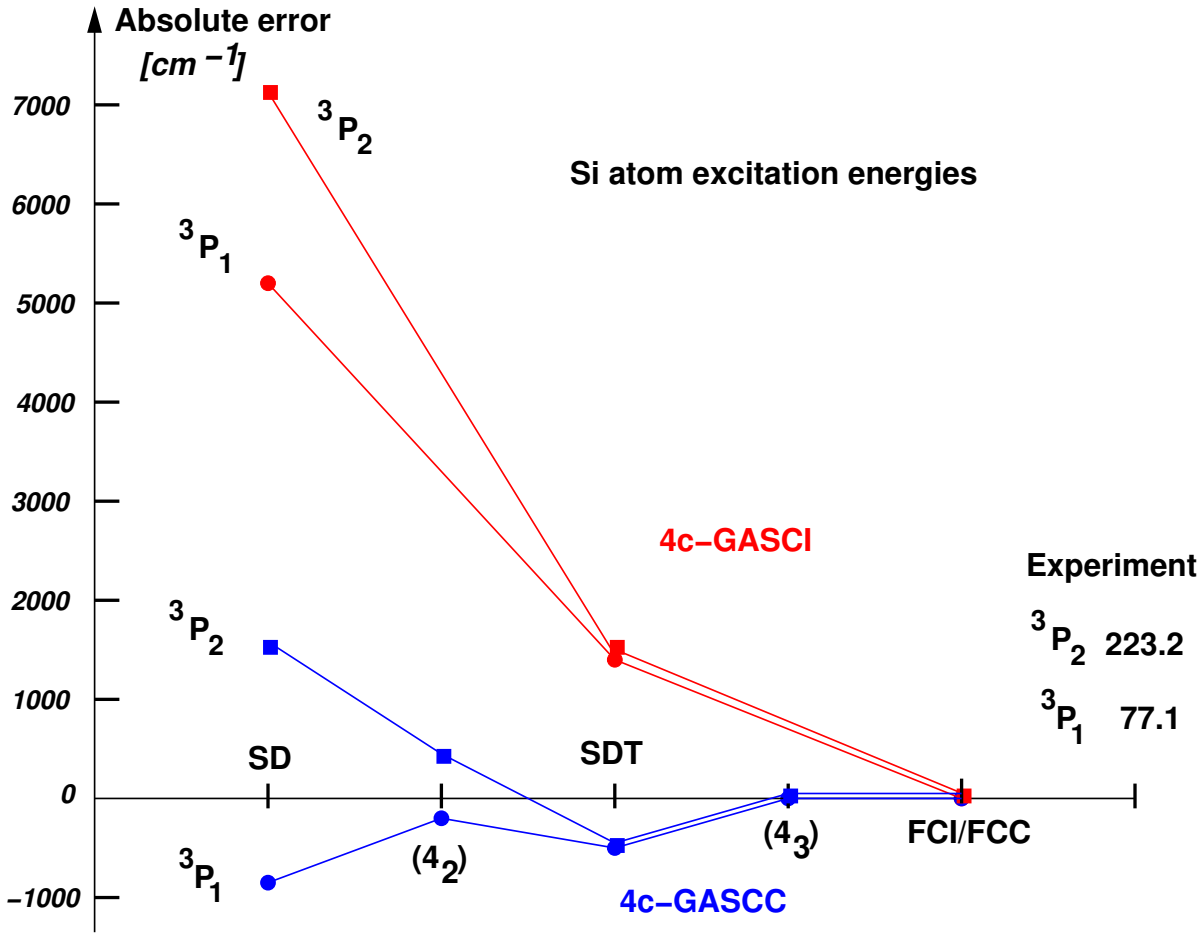
$$\left|\frac{3}{2},\frac{1}{2};\frac{1}{2},\frac{1}{2}\right| = -\frac{1}{2}\,{}^3P_1 - \frac{1}{2}\,{}^3P_2 + \frac{1}{\sqrt{2}}\,{}^1D_2$$

- 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

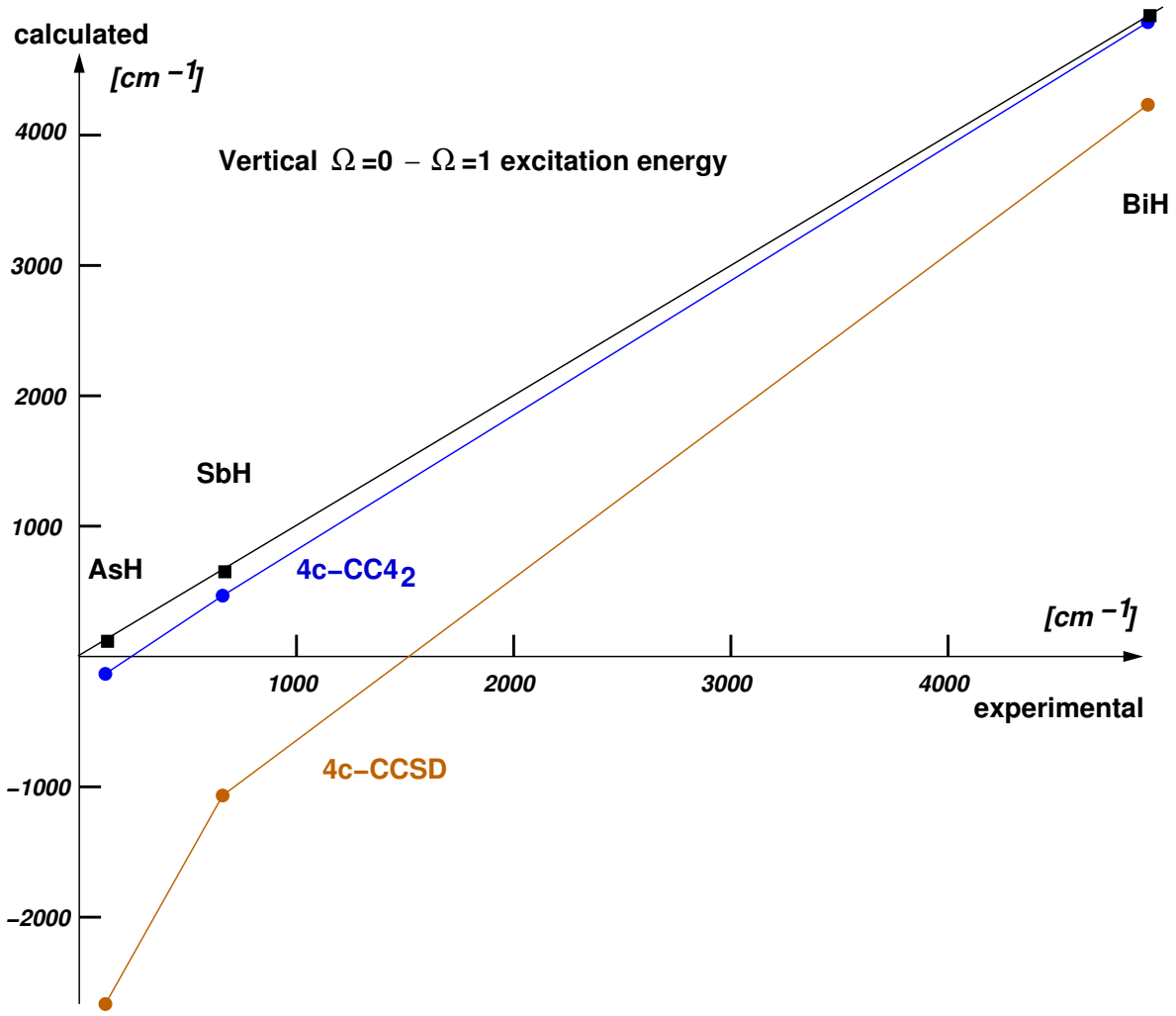
AsH, SbH, BiH

- 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** (2011) *to be submitted.*

Series AsH, SbH, BiH

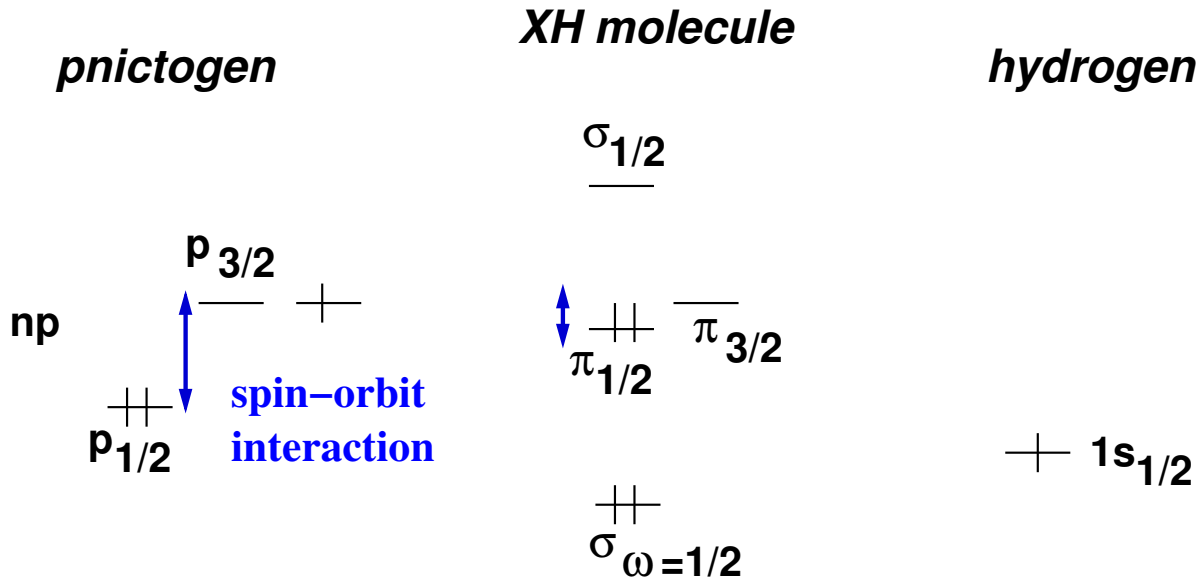
The strange behavior of CCSD



- Huge errors for As homologue

Series AsH, SbH, BiH

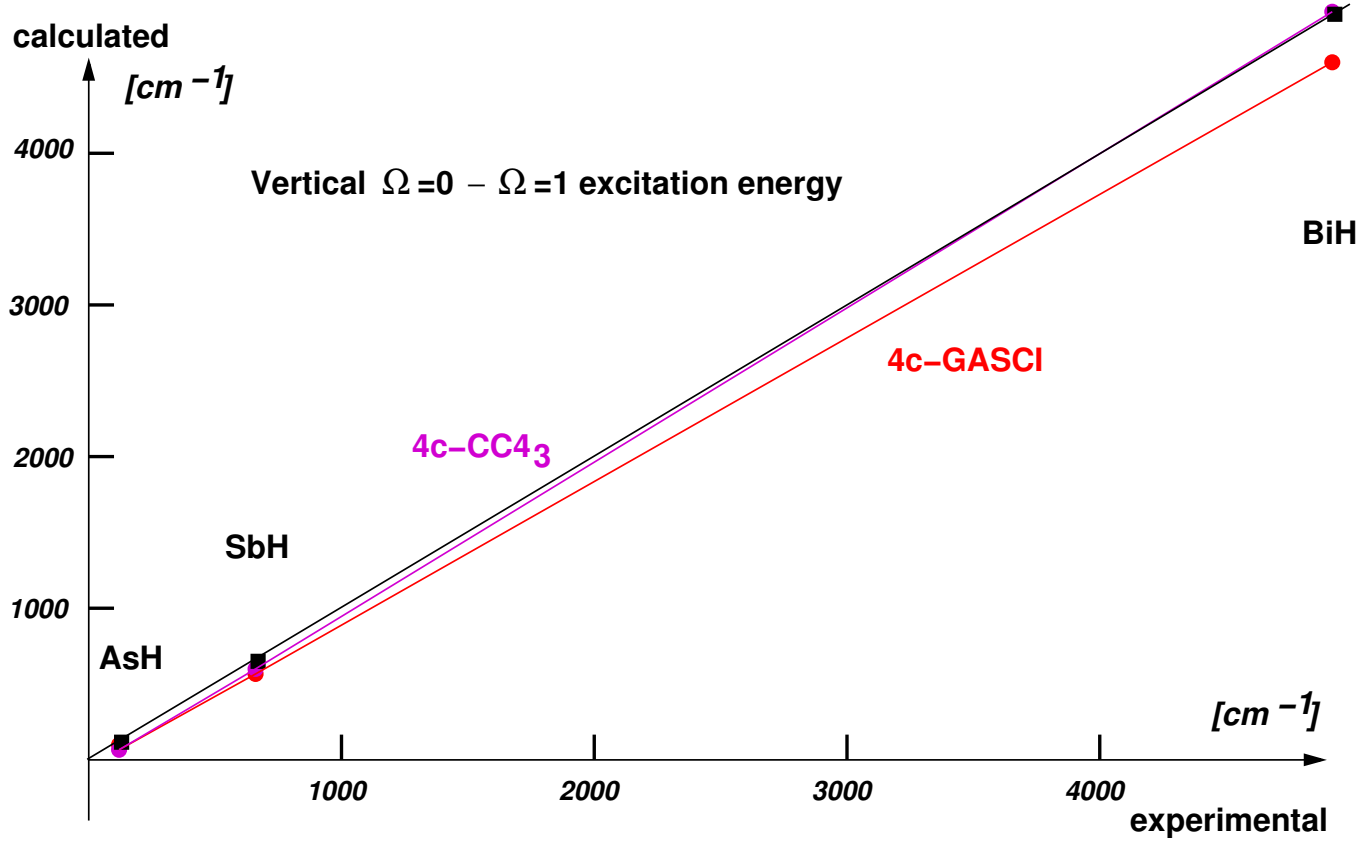
Spinors and the molecular field



- ω coupled spinors: $\pi_{1/2}$ has σ component artificially large for lighter systems
- 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

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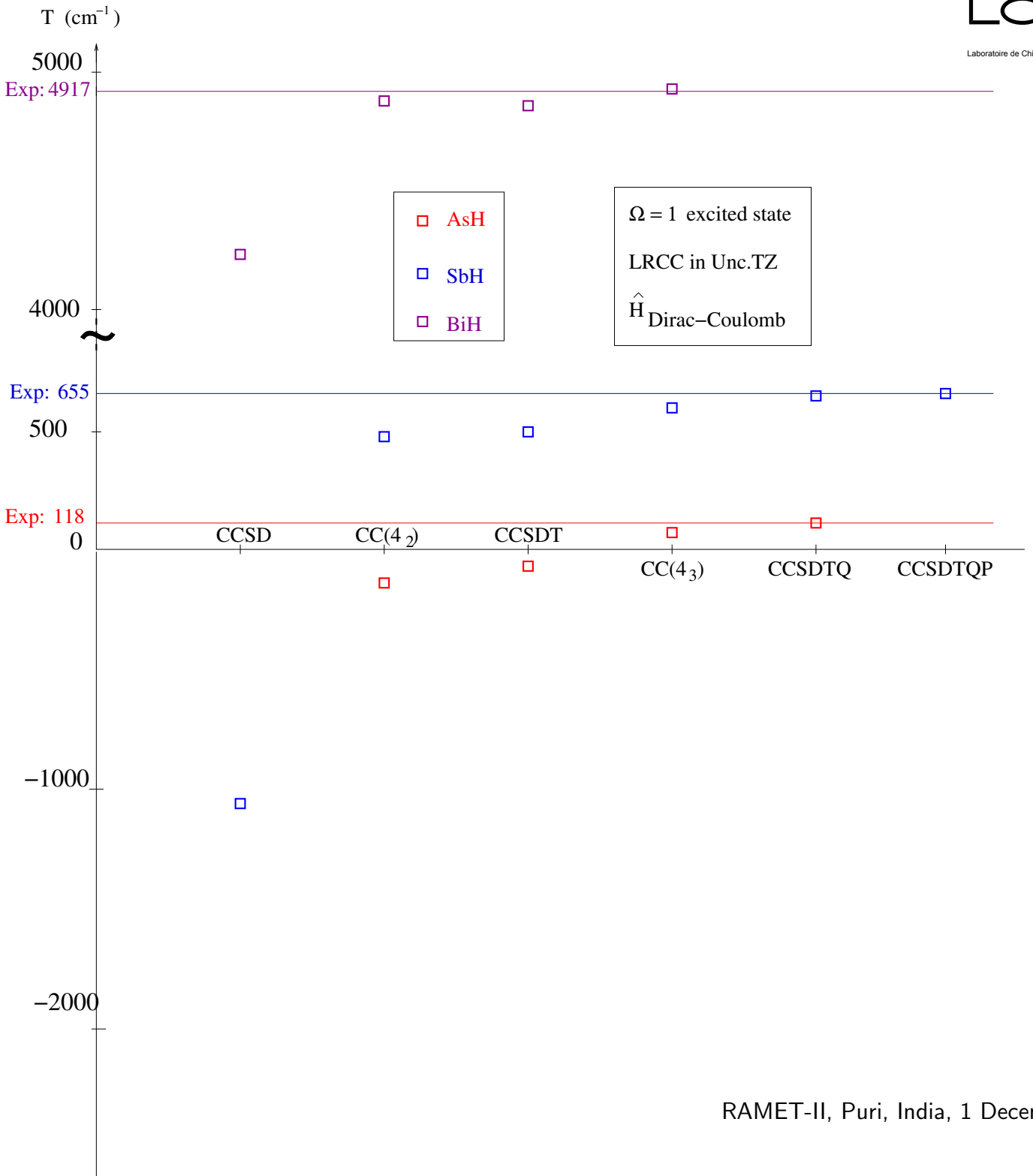
T (cm^{-1})
5000
Exp: 4917
4000
Exp: 655
500
Exp: 118
0
−1000
−2000
AsH
SbH
BiH
Ω = 1 excited state
LRCC in Unc.TZ
$\hat{H}$ Dirac−Coulomb
CCSD
CC(4 2)
CCSDT
CC(4 3)
CCSDTQ
CCSDTQP

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

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)

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Toulouse, France

Jeppe Olsen

Århus, Denmark

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

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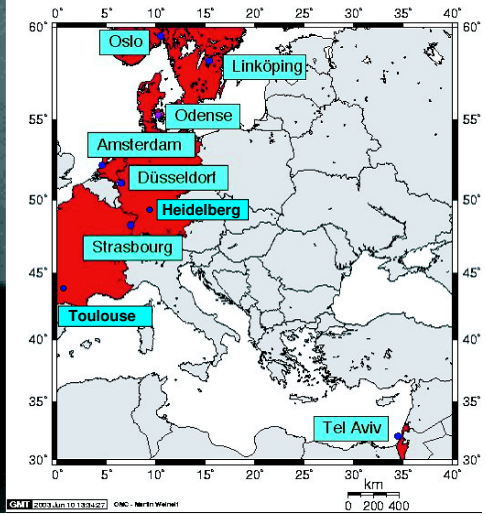

- `KR-CI`.
  `Kramers-Restricted GAS Configuration Interaction Program`
  (released in DIRAC10/DIRAC11)
  Authors: S Knecht, T Fleig, J Olsen, HJAa Jensen

- `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