Linear-Response Relativistic Coupled Cluster: A Jacobian for General-Order Energy Calculations

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Motivation

Laboratoire de Chimie et Physique Quantiques

In general:

Rigorous and efficient relativistic correlation methods

Goal: Accurate electronic structure of small systems

Many-body method:

Relativistic Configuration Interaction approaches

Easy to implement, widely applicable

MR CI straightforward to obtain

Slow convergence with excitation level

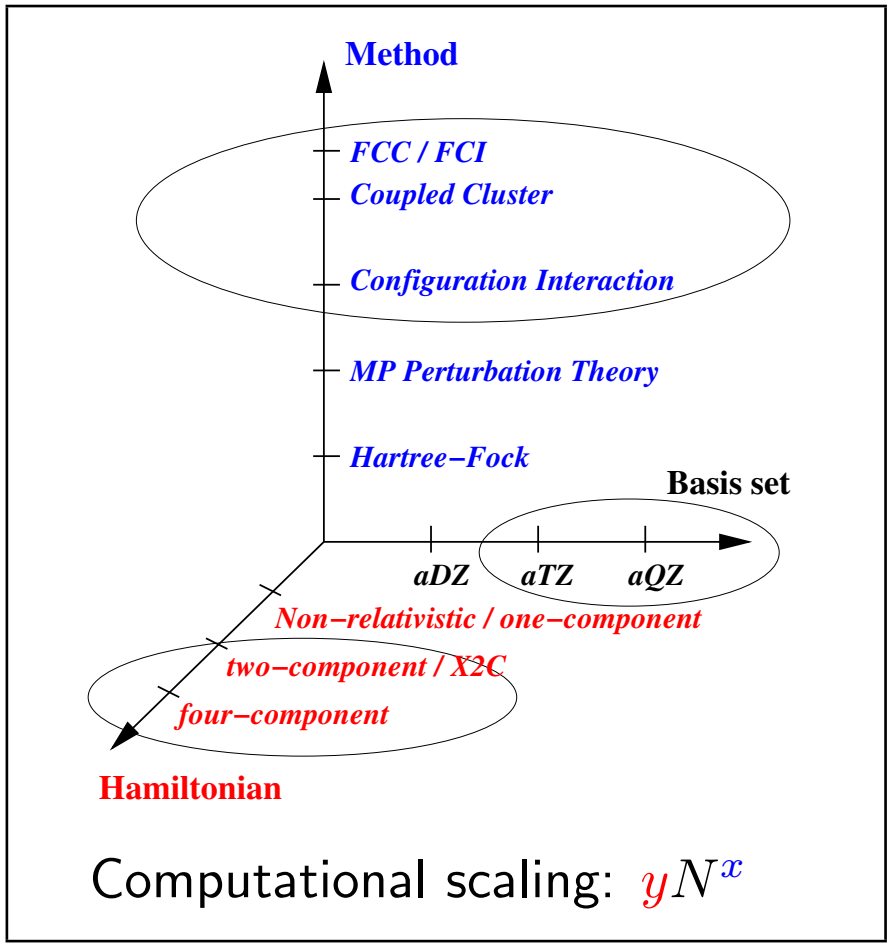
Relativistic Coupled Cluster approaches

Harder to devise, more difficult to apply

MR CC not straightforward to obtain

Faster convergence with excitation level

Rigorous Relativistic Many-Body Approaches[1]



Computational scaling: yN^x

Relativistic GAS-CI[2]

GAS Ansatz, 4- or 2-spinors

$$\left|\Psi^{\mathrm{GASCI}}\right\rangle = \hat{T}^{\mathrm{rel}}_{\mathrm{GAS}} \left|\Psi^{\mathrm{Ref}}\right\rangle$$

$\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$ General excitation level in Kramers-paired spinors

Relativistic GAS Coupled Cluster[3]

Generalized-Active-Space Ansatz

$$\begin{aligned}\left|\Psi^{\mathrm{GASCC}}\right\rangle &= e^{\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}} \left|\Psi^{\mathrm{Ref}}\right\rangle \\ &= exp(\sum_{\mu} t_\mu \hat{\tau}_{\mu_{\mathrm{GAS}}}) \left|\Psi^{\mathrm{Ref}}\right\rangle\end{aligned}$$

Hamiltonians based on Dirac theory

4- and 2-component operators, e.g.

$$\hat{H}^{\mathrm{rel}} = \hat{H}^{\mathrm{Dirac}} + \hat{H}^{\mathrm{Coulomb}}$$

[1] T. Fleig, **"Relativistic String-Based Electron Correlation Methods"** (2010) in "Challenges and Advances in Computational Chemistry and Physics, Vol. 10", *Eds. Barysz, Ishikawa*

[2] S. Knecht, H.J.Aa. Jensen, T. Fleig, *J Chem Phys* **132** (2010) *014108*

[3] L.K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*

Spinors and Strings

How do we parameterize $\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$?

General concept: Kramers-paired spinors

Time-reversal operator for a fermion:
$\hat{K} = e^{-\frac{\imath}{\hbar}\pi\left(\hat{\vec{s}}\cdot\vec{e}_y\right)}\,\hat{K}_0 = -\imath\Sigma_y\hat{K}_0$

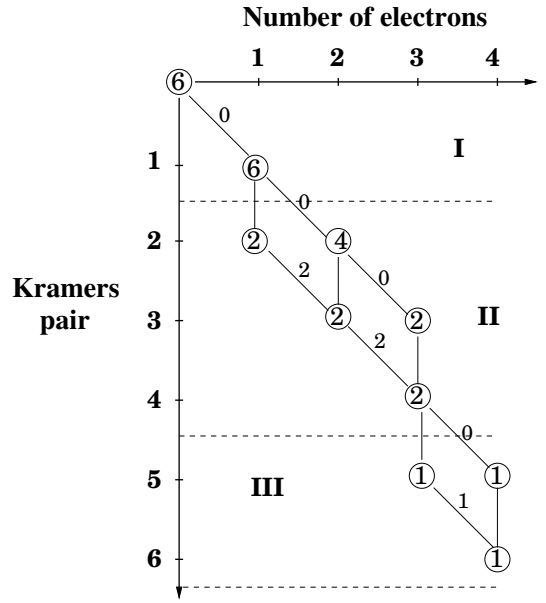
Spinorbitals	General spinors
$\hat{K}\varphi_i\,\alpha = \varphi_i^*\,\beta$	$\hat{K}\phi_i = \phi_{\bar{i}}$
$\hat{K}\varphi_i^*\,\beta = -\varphi_i\,\alpha$	$\hat{K}\phi_{\bar{i}} = -\phi_i$

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**

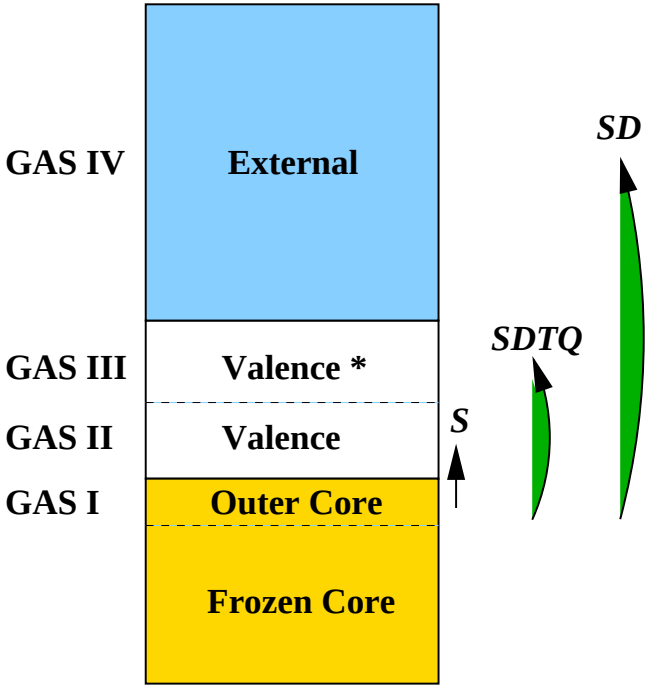


⊗ x: vertex weight
y: arc weight

Relativistic CI and CC

How do we parameterize $\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$?

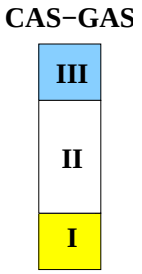
Space of orbitals / Kramers pairs



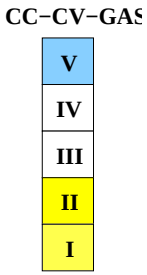
GAS concept

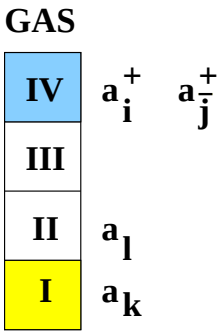
Full and restricted subspace expansions

Complete MR expansions
often impracticable



Flexible expansions
Adaptation to problem





Operator type
+
Occupation type

$\Longrightarrow$ Excitation class

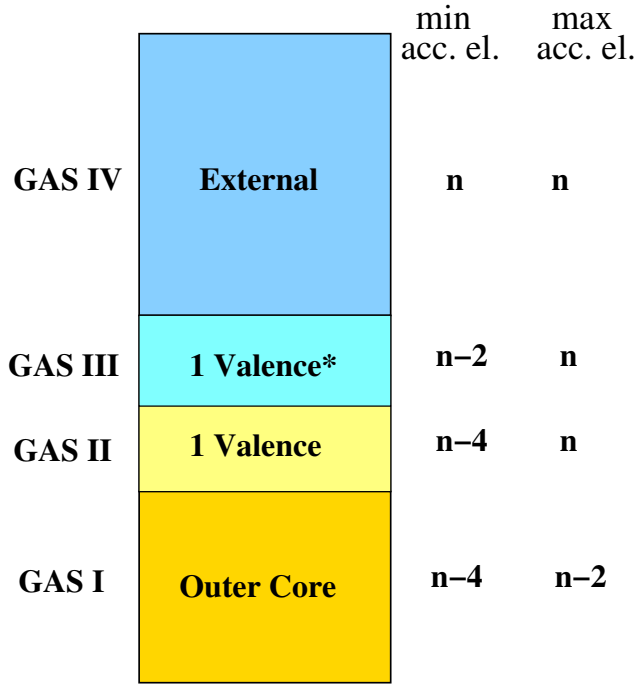
$\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$ defined

Relativistic Correlation Methods

Generalized Active Space Coupled Cluster

J. Olsen, *J Chem Phys* **113** (2000) *7140*
T. Fleig, L. K. Sørensen, J. Olsen, *Theo Chem Acc* **118,2** (2007) *347*
L. K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*

- "State-Selective" (SS) GAS-CC
  Simulation (SR-MRCC) of true multi-reference CC
- GAS-extended excitation manifold
  $\langle \mu_{\mathrm{GASCC}}| = \langle \Psi^{\mathrm{Ref}}| \, \hat{\tau}^{\dagger}_{\mu_{\mathrm{GAS}}}$
- $\hat{\tau}_{\mu_{\mathrm{GAS}}}$ contains "internal" 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:

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

Excited States in Coupled Cluster Theory

The CC Jacobian

- CI Theory : $\left|\psi^{\mathrm{CI}}\right\rangle = \hat{\mathrm{T}}\left|\psi^{\mathrm{Ref}}\right\rangle$

  CI Schrödinger equation for ground state :
  $\hat{\mathrm{H}}\left|\psi^{\mathrm{CI}}\right\rangle = \hat{\mathrm{H}}\hat{\mathrm{T}}\left|\psi^{\mathrm{Ref}}\right\rangle = E_0\hat{\mathrm{T}}\left|\psi^{\mathrm{Ref}}\right\rangle$
  $(\hat{\mathrm{H}} - E_0)\hat{\mathrm{T}}\left|\psi^{\mathrm{Ref}}\right\rangle = 0$

  CI coefficient equations : $\Omega_\mu^{\mathrm{CI}} = \langle\psi_\mu|\,(\hat{\mathrm{H}} - E_0)\hat{\mathrm{T}}\left|\psi^{\mathrm{Ref}}\right\rangle$

  CI Jacobian: $\frac{\partial}{\partial c_\nu}\Omega_\mu^{\mathrm{CI}} = \langle\psi_\mu|\,(\hat{\mathrm{H}} - E_0)\hat{\tau}_\nu\left|\psi^{\mathrm{Ref}}\right\rangle = \langle\psi_\mu|\,\hat{\mathrm{H}}\left|\psi_\nu\right\rangle - E_0\delta_{\mu\nu}$

  Diagonalisation yields CI excitation energies

- CC theory : $\left|\psi^{\mathrm{CC}}\right\rangle = e^{\hat{\mathrm{T}}}\left|\psi^{\mathrm{Ref}}\right\rangle$

  CC amplitude equations : $\Omega_\mu^{\mathrm{CC}} = \left\langle\psi_\mu|e^{-\hat{\mathrm{T}}}\hat{\mathrm{H}}e^{\hat{\mathrm{T}}}|\psi^{\mathrm{Ref}}\right\rangle$

  CC Jacobian: $\frac{\partial}{\partial t_\nu}\Omega_\mu^{\mathrm{CC}} = \left\langle\psi_\mu|e^{-\hat{\mathrm{T}}}\left[\hat{\mathrm{H}},\hat{\tau}_\nu\right]e^{\hat{\mathrm{T}}}|\psi^{\mathrm{Ref}}\right\rangle$

  Diagonalisation yields CC excitation energies

The CC Jacobian at General Excitation Level

A CI-Based Algorithm [4]

$$A_{\mu\nu} = \frac{\partial \Omega_\mu}{\partial t_\nu} = \left\langle \mu_{\mathrm{GAS}} | e^{-\hat{T}_{\mathrm{GAS}}} \left[\hat{H}, \hat{\tau}_{\nu_{\mathrm{GAS}}} \right] e^{\hat{T}_{\mathrm{GAS}}} | \psi^{\mathrm{Ref}} \right\rangle$$

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

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

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)

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

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

Relativistic GAS-CC

Two routes in comparison

CI-based CC vector function

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

1. $|a\rangle = e^{\hat{T}} |\mathrm{Ref}\rangle = \left(\sum_{n=0} \frac{1}{n!} \hat{T}^n \right) |\mathrm{Ref}\rangle$
2. $|b\rangle = \hat{H} |a\rangle$ (CI sigma vectors)
3. $|c\rangle = e^{-\hat{T}} |b\rangle = \left(\sum_{n=0} \frac{(-1)^n}{n!} \hat{T}^n \right) |b\rangle$
4. $\Omega_\mu = \langle \mu | c \rangle = \left\langle \mathrm{Ref} \left| \hat{\tau}_\mu^\dagger \right| c \right\rangle$ (CI density matrices)

T. Fleig, L. K. Sørensen, J. Olsen, *Theo Chem Acc* **118,2** (2007) *347*

Commutator-based CC vector function

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

- ↻ Loop over rel. excitation class of $\hat{H}$
  - ↻ Loop over commutator type, e.g. $\left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right]$
    - ↻ Loop over rel. excitation types $\hat{T}_i$ of $\hat{T}$ operators
      - ! Check for coupling with $\langle \mu |$
      - Yes? Contract with integrals
    - ↙ End loop
  - ↙ End loop
- ↙ End loop

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CI-based linear response (LR) function

$$A_{\mu\nu} = \left\langle \mu \left| e^{-\hat{T}} \left[\hat{H}, \hat{\tau}_\nu \right] e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$$

Commutator-based LR function

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

Properties of the implementation:

- Very general approach
- Increased "N-scaling": $O^{n+2}V^{n+2}$

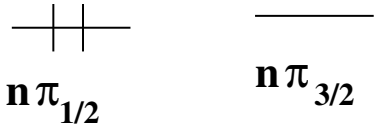
- General approach, currently some limitations
- Conventional "N-scaling": $O^n V^{n+2}$

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{N}, \mathrm{P}, \mathrm{As}, \mathrm{Sb}, \mathrm{Bi}\}$

Spin-orbit splitting of $^3\Sigma^-$ ground state into $\Omega = 0^+/1$

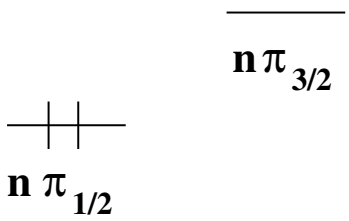
- Ground-state configuration $n\sigma^2\pi^2$
- ω-ω coupling picture for heavier elements
- $\Omega = 0 : \pi^1_{1/2}\pi^1_{-1/2}$ and $\pi^1_{3/2}\pi^1_{-3/2}$ (ground state)
- $\Omega = 1 : \pi^1_{3/2}\pi^1_{-1/2}$ (first excited state)

Situation in lighter elements



- Inappropriate Fermi vacuum
- Problem is ill–conditioned
- True multi–reference case
- Higher excitations into external space required

Situation in heavier elements



- Appropriate Fermi vacuum
- Problem is well–conditioned
- Quasi–single reference case
- Two particles in external space sufficient

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{N}, \mathrm{P}, \mathrm{As}, \mathrm{Sb}, \mathrm{Bi}\}$

Spin-orbit splitting of $^3\Sigma^-$ ground state into $\Omega = 0^+/1$

Technical notes

- CI-driven CC and LRCC
- Dyall TZ basis + valence correlating functions / cc-pVTZ Dunning for H
- Dirac-Coulomb Hamiltonian $\hat{H}^{\mathrm{DC}}$
- closed-shell and open-shell (os) DCHF spinors, 6 active electrons correlated

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Sb}\}$

Spin-orbit splitting of $(^3\Sigma^-)$ ground state into $\Omega = 0^+/1$

Method	Δ_{SO} [cm^{-1}]	# CC amplitudes
CCSD-2au	-1043.7	14.415
CCSD-4au	-1069.9	30.375
CCSD-100au	-1070.6	69.360
CCSD-6au(QZ)	-1072.8	82.140
CCSD-10au(QZ)	-1072.3	132.540
CC(4_2)-4au	476.0	103.855
osCC(4_2)-4au	555.0	103.855
CC(4_2)-6au(QZ)	434.4	284.496
CC(4_3)-4au	598.9	1.640.159
osCC(4_3)-4au	575.0	1.640.159
CCSDT-4au	484.7	1.205.175
CCSDTQ-4au	641.4	20.370.585
CCSDTQ5-4au	644.8	152.218.389
Exp.	654.97	

- **CCSD is qualitatively wrong**
- Ground state has large contribution of double excitation $\pi^1_{3/2}\pi^1_{-3/2}$
- Double excitation to too low order in CCSD $\longrightarrow$ failure

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Sb}\}$

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- **CC(4_2) corrects for the deficiency**
- Active space including $\pi_{1/2}$ and $\pi_{3/2}$
- Simulation of presence of second reference function $\longrightarrow$ qual. correct

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Sb}\}$

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- **CC(4_2) on open-shell DCHF gives large improvement**
- Yields more realistic reference orbitals
- Loses importance with higher external excitations

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Sb}\}$

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- **Systematic improvement towards exact value**
- Along series CC(4_2) - CCSDT - CC(4_3) - CCSDTQ - CCSDTQ5

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Bi}\}$

Spin-orbit splitting of $(^3\Sigma^-)$ ground state into $\Omega = 0^+/1$

Method	Δ_{SO} [cm^{-1}]	# CC amplitudes / CI coefficients
CCSD-2au	4177	14.415
CCSD-5au	4230	47.040
CCSD-20au	4241	96.000
CC(4_2)-5au	4756	161.880
CCSDT-5au	4682	2.203.575
GAS-CISD[5]	4514	1.832.846
GAS-CISDTQ[5]	4683	305.307.941
Exp.	4917[6]	

- **CCSD result qualitatively correct**
- quasi-single reference case
- transition to strongly relativistic 6th row evident

[5] S Knecht, HJAa Jensen, T Fleig, *J Chem Phys* (2010) *014108*

[6] Huber and Herzberg, NIST Chemistry Webbook

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Bi}\}$

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Exp.	4917[6]	

- **CC(4_2) gives large correction**
- Efficient handling of important higher excitations

[5] S Knecht, HJAa Jensen, T Fleig, *J Chem Phys* (2010) *014108*

[6] Huber and Herzberg, NIST Chemistry Webbook

A Test Case Study on $\mathrm{XH}, \mathrm{X} \in \{\mathrm{Bi}\}$

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Exp.	4917[6]	

- **CC outperforms CI**
- Remaining errors: Basis set, Bi $5d$ correlation, Gaunt interaction

[5] S Knecht, HJAa Jensen, T Fleig, *J Chem Phys* (2010) *014108*

[6] Huber and Herzberg, NIST Chemistry Webbook

Application of GAS-CC

BiH: Spectral constants of $0^+(^3\Sigma^-)$ ground state

L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* (2010) *to be submitted.*

- Setup:

  Unc. cc-pCVTZ (Bi) / cc-pVTZ (H)
  $[30s26p17d13f1g]$ / $[5s2p1d]$
  Cutoff virtual spinors: 5.6 a.u.

  Dirac-Coulomb Hamiltonian (no SOO)

  $\sigma_{1/2}$, $\pi_{1/2}$, $\pi_{3/2}$ occupied

CC model	R_e[Å]	ω_e[cm^{-1}]
CCSD 6	1.822	1694
GASCCSD (6in5)	1.826	1676
CCSD(T) 6	1.824	1685
CCSDT 6	1.824	1681
CCSDTQ 6	1.825	1681
CCSD 16	1.792	1726
CCSD(T) 16	1.793	1709
CCSDT 16	1.793	1709
Exp.[8]	1.809	1700

- R_e, ω_e:
  outer-core $(5d)$ correlation $>$ Higher excitations
- CCSDT 16 feasible for complete potential curves
- Alternative: GASCCSD (6in5) active-space model

[8] Diode laser / IR Spectroscopy, Bernath et al. (1991), Urban et al. (1989)

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P	rogram
•	for
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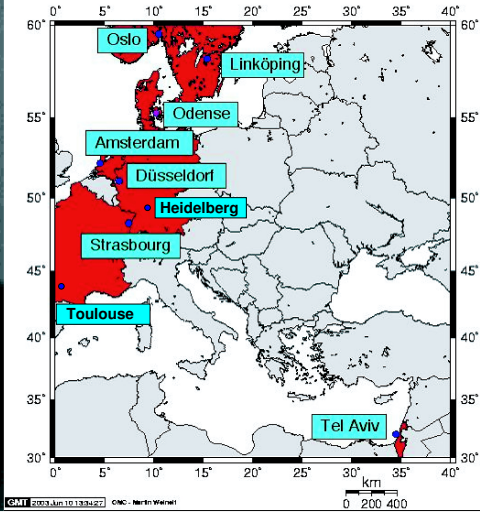
•	and
M	olecular
D	irect
I	terative
R	elativistic
A	ll-electron
C	alculations



- `KR-CI`.
  `Kramers-Restricted GAS Configuration Interaction Program`
  (released in DIRAC10)
  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, T Fleig

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