Recent Developments in Relativistic Many-Body Methods
Application to Problems in Fundamental Physics

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My Tenets for Today

1. **On relativistic Wavefunction Theory**

   4 components vs. 2 components

2. Precision spectroscopy

   Going for "Gold" without negative-energy states

3. Fundamental Physics

   No-go without 4-component wavefunctions

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[1]

- "Filled-sea Fock-space" approaches do not seem to be a satisfactory option[2]

  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

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

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

Four-Component Electronic-Structure Theory

Some Essentials

- Atomic basis sets; in low-energy approximation

  $\psi^S(\vec{r}) \approx \frac{\sigma \cdot \mathbf{p}}{m_0 c} \psi^L(\vec{r})$

  Kinetic-balance condition

- Solution of the Dirac-Coulomb Hartree-Fock equations

$$\begin{pmatrix} \left(\hat{V}_{\mathrm{nuc}} + \hat{v}_{\mathrm{DCHF}}\right) \mathbb{1}_2 & c\sigma \cdot \mathbf{p} \\ c\sigma \cdot \mathbf{p} & \left(\hat{V}_{\mathrm{nuc}} + \hat{v}_{\mathrm{DCHF}} - 2m_0c^2\right) \mathbb{1}_2 \end{pmatrix} \begin{pmatrix} \psi_a^L(\vec{r}) \\ \psi_a^S(\vec{r}) \end{pmatrix} = \varepsilon \begin{pmatrix} \psi_a^L(\vec{r}) \\ \psi_a^S(\vec{r}) \end{pmatrix}, \quad \forall a$$

$$\varepsilon = E - m_0 c^2$$

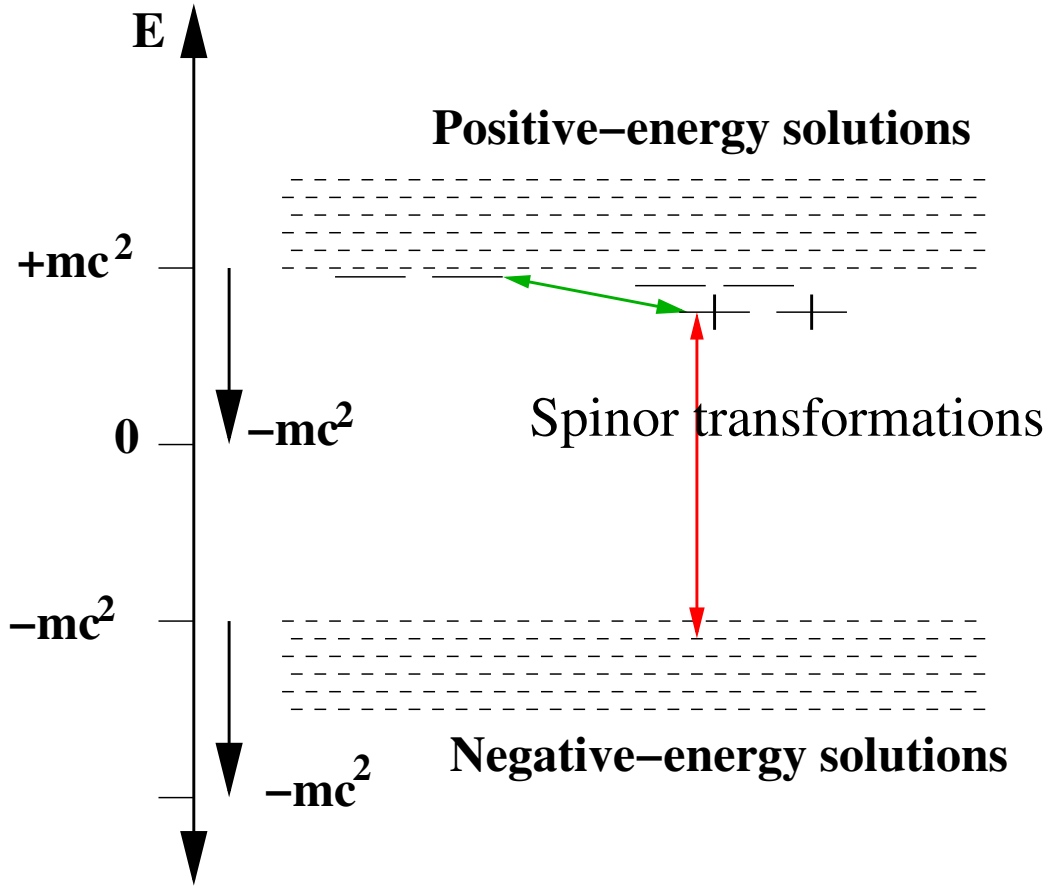
- Fock matrix for "frozen" atomic core

  1) Core energy: $\varepsilon_{\mathrm{core}} = \sum_{i,j>i}^{2N_{\mathrm{core}}} \left\{2 \langle ij|ij\rangle - \langle ij|ji\rangle - \langle i\bar{j}|\bar{j}i\rangle\right\}$

  2) Inactive Fock matrix: $f_{pq}^{\mathrm{DC}} = h_{pq}^{\mathrm{D}} + \sum_{j}^{2N_{\mathrm{core}}} \left\{2 \langle pj|qj\rangle - \langle pj|jq\rangle - \langle p\bar{j}|\bar{j}q\rangle\right\}$

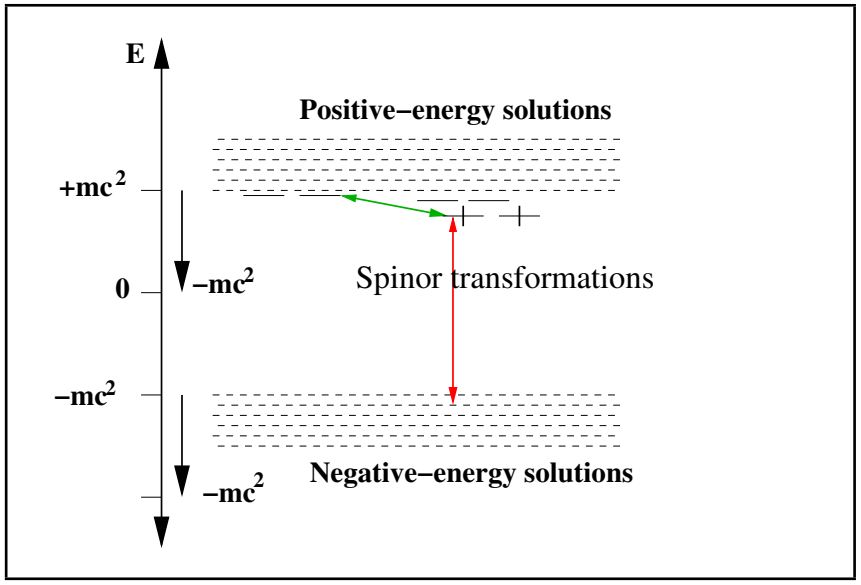
Four-Component Electronic-Structure Theory

Spectrum of the Dirac Hamiltonian



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

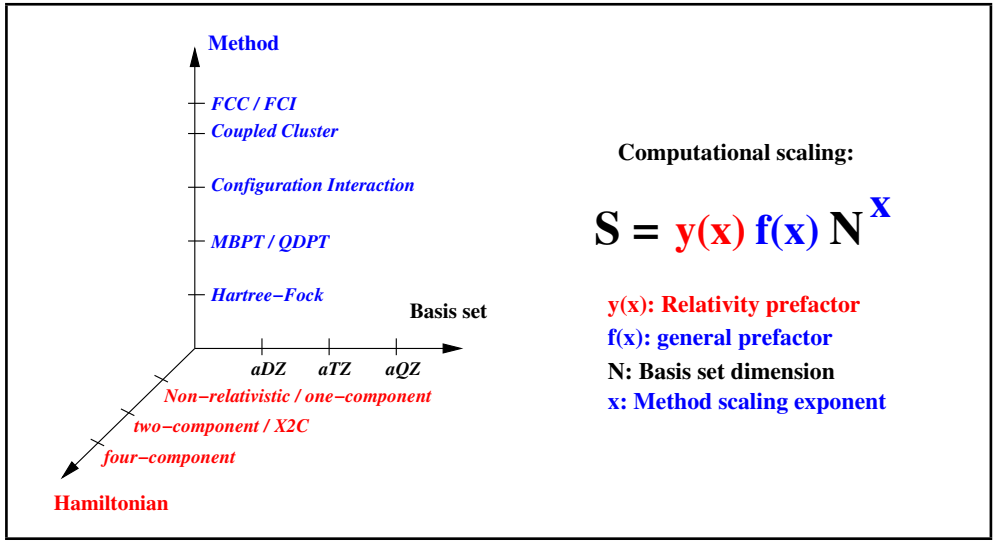
Integrals over positive-energy 4-spinors:

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

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

Special Relativity and Electron Correlation

Computational Scaling[3]



$$S^{\mathrm{rel.CC}} \approx 4\sqrt{\pi\left(\frac{x}{2}-1\right)}\,\frac{1}{4}\left[\frac{x^2}{4}-\frac{3}{2}x+2\right]\begin{pmatrix} x-2 \\ \frac{x}{2}-1 \end{pmatrix} O^{\frac{x}{2}-1}V^{\frac{x}{2}+1}$$

Method	Non-Rel.	2-comp.	4-comp.
Hartree-Fock	N^4	$8N^4$	$8\left(\frac{5}{2}N\right)^4$
4-Index transformation	$2N^5$	$32N^5$	$128N^5$
CCSD	$3N^6$	$10 \cdot 3N^6$	
CCSDT	$30N^8$	$12 \cdot 30N^8$	
CCSDTQ	$210N^{10}$	$14 \cdot 210N^{10}$	

$\Rightarrow$ The correlated stage is the computational bottleneck (no savings in 2c formalism).

[3] L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) *214102*

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

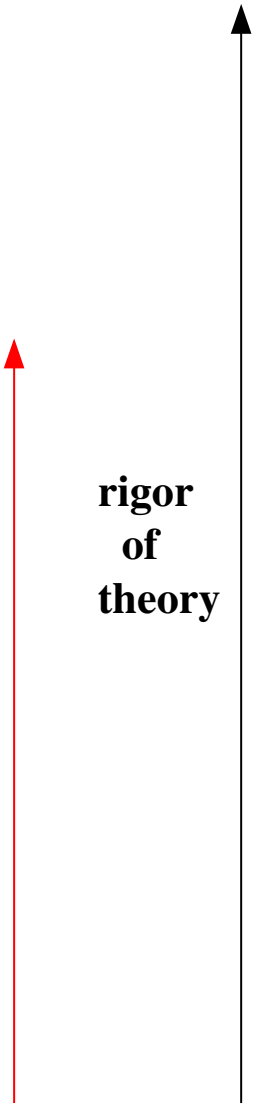
Hartree–Fock		*Dynamic Correlation*
scalar relativistic Hamiltonian	+	2–component Hamiltonian

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



Relativistic Electronic-Structure Theory

Electron-electron interaction

Approximated low-frequency limit QED Hamiltonian

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

$\frac{1}{r_{12}}\mathbf{1}_4$	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
$\{\dots\}$	Breit interaction
$\mathcal{O}\left(\alpha^3\right)$	Higher-order terms, radiative corrections

$\longrightarrow$ Currently truncation after Coulomb term

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

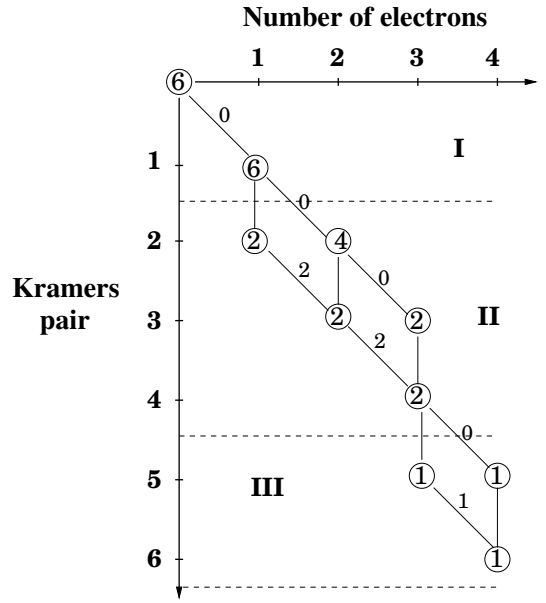
Spinor basis:

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

- 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**

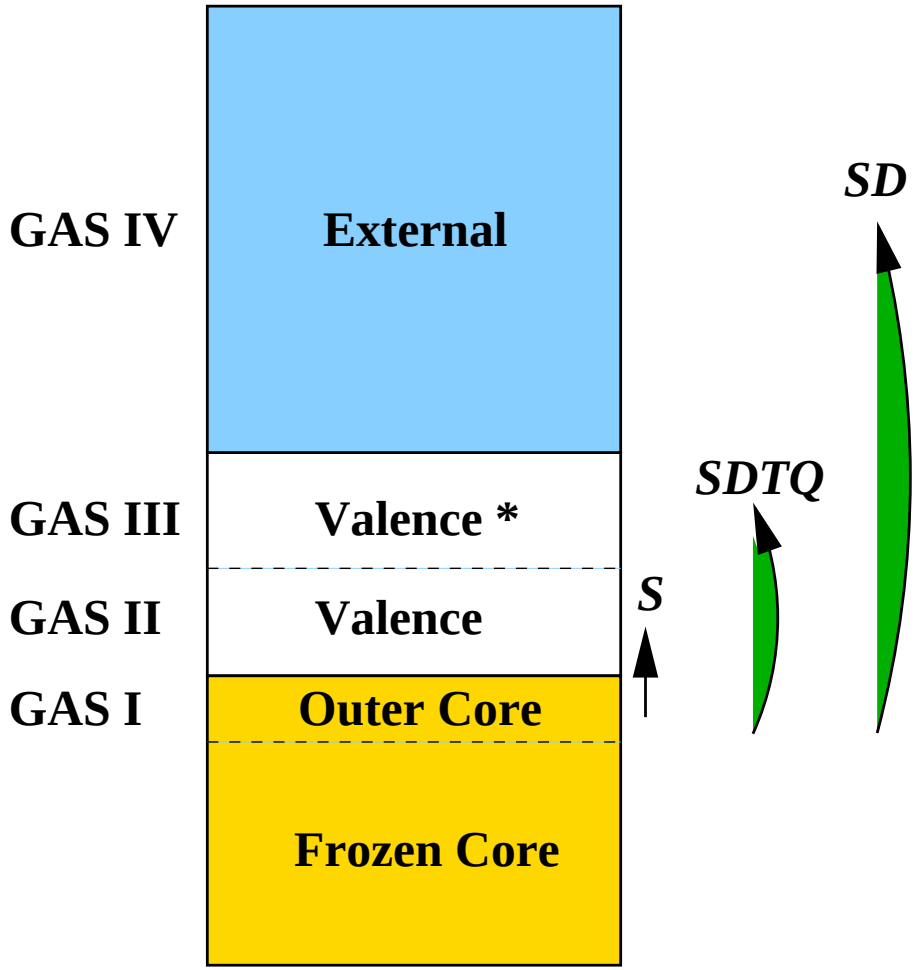
  Coupled Cluster: **Individual strings**



⊗ x: vertex weight
y: arc weight

Parameterization of the Wavefunction

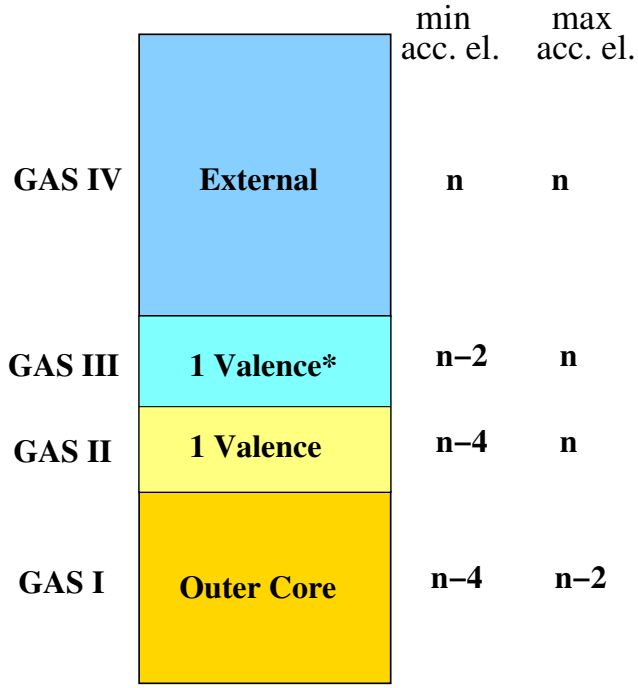
Generalized Active Spaces



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[4]
- 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
  $\hat{T}_1 = \sum_{ia} \left\{ t^a_i\hat{\tau}^a_i + t^{\bar{a}}_{\bar{i}}\hat{\tau}^{\bar{a}}_{\bar{i}} + t^{\bar{a}}_i\hat{\tau}^{\bar{a}}_i + t^a_{\bar{i}}\hat{\tau}^a_{\bar{i}} \right\}$; $\hat{T}_2 = \ldots$



Example for constructed higher excitations:

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

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

Relativistic Generalized-Active-Space CC

Electronic Ground States [5]

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.

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

[5] 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

Excitation Energies[6]

$$J^{CC}_{\mu} = \sum_{\nu} A_{\mu\nu} x_{\nu} = \sum_{\nu} \left\langle \mu_{\mathrm{GAS}} | e^{-\hat{T}_{\mathrm{GAS}}} \left[\hat{H}, \hat{\tau}_{\nu_{\mathrm{GAS}}} \right] e^{\hat{T}_{\mathrm{GAS}}} | \Phi_0 \right\rangle x_{\nu}$$

$$A_{\mu\nu} = \left\langle \mu \middle| \left(\left[\hat{H}, \hat{\tau}_{\nu_{\mathrm{GAS}}} \right] + \left[\left[\hat{H}, \hat{\tau}_{\nu_{\mathrm{GAS}}} \right], \hat{T} \right] + \tfrac{1}{2} \left[\left[\left[\hat{H}, \hat{\tau}_{\nu_{\mathrm{GAS}}} \right], \hat{T} \right], \hat{T} \right] \ldots \right) \middle| \Phi_0 \right\rangle$$

Algorithm for Jacobian matrix elements[7]

- Loop over relativistic $N\Delta M_K$ classes of $\hat{H}, \hat{T}$
  Determines min./max. commutator nesting
  - Loop over commutator type, e.g. $\left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right]$
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$$= \frac{1}{4} \sum_{abcd,i'j'a'b',i"j"a"b"} (ad|bc) t^{a'b'}_{i'j'} t^{a"b"}_{i"j"} a^{\dagger}_{a} a^{\dagger}_{b} \overbrace{a_c \overbrace{a_d a^{\dagger}_{a'} a^{\dagger}_{b'} a_{i'} a_{j'}}^{} a^{\dagger}_{a"}}^{} a^{\dagger}_{b"} a_{i"} a_{j"} .$$

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

[7] 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*

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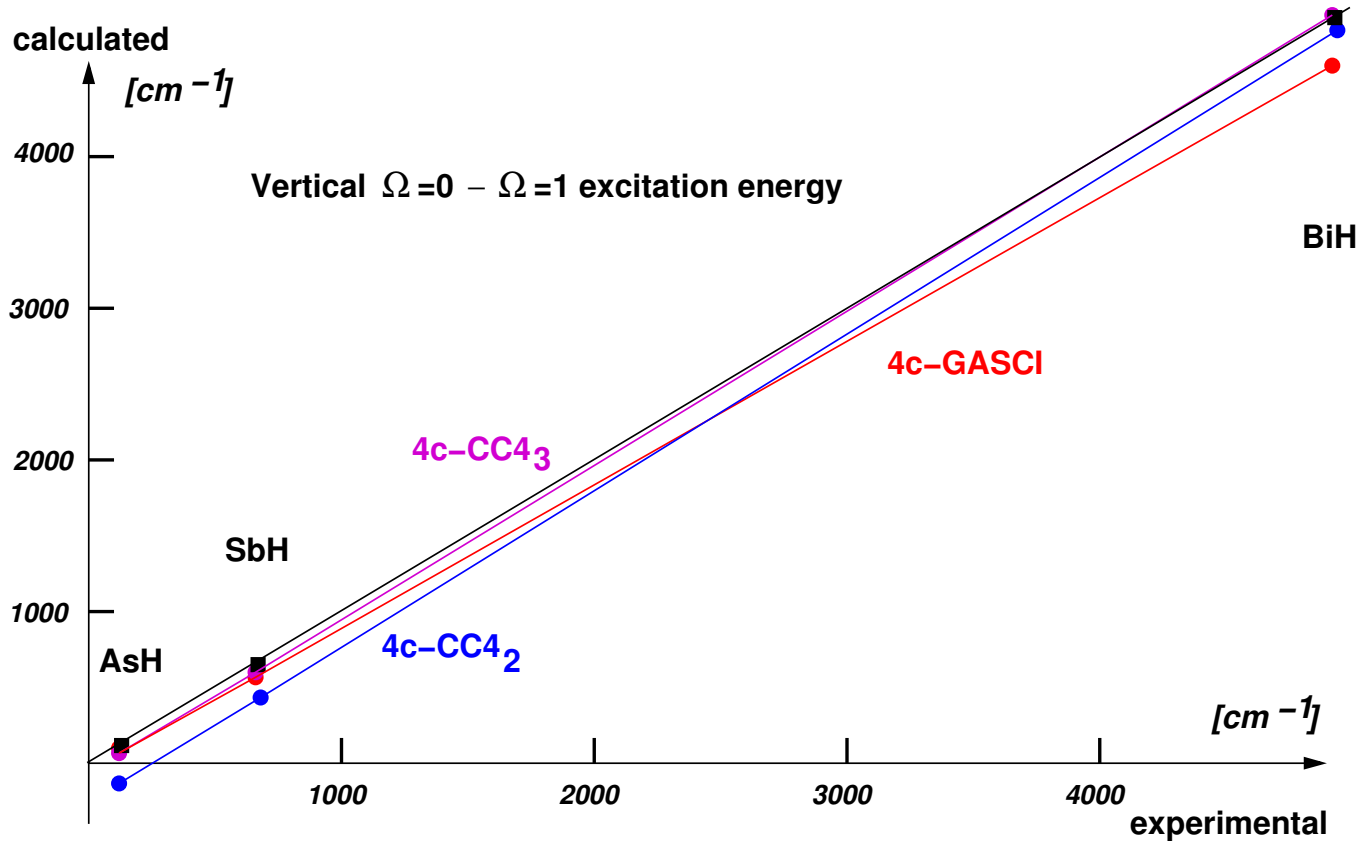
Series AsH, SbH, BiH

When is CC superior to GAS-CI?



- $CC4_3$ calculations consistently better than CAS-CISD[8]

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

Special Relativity and Electron Correlation

Methods in comparison

Chalcogen homonuclear and heteronuclear diatomics[9]

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

"Non-additive"[11]: *4c-IH-FSCC*, *4c-GASCI*

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

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

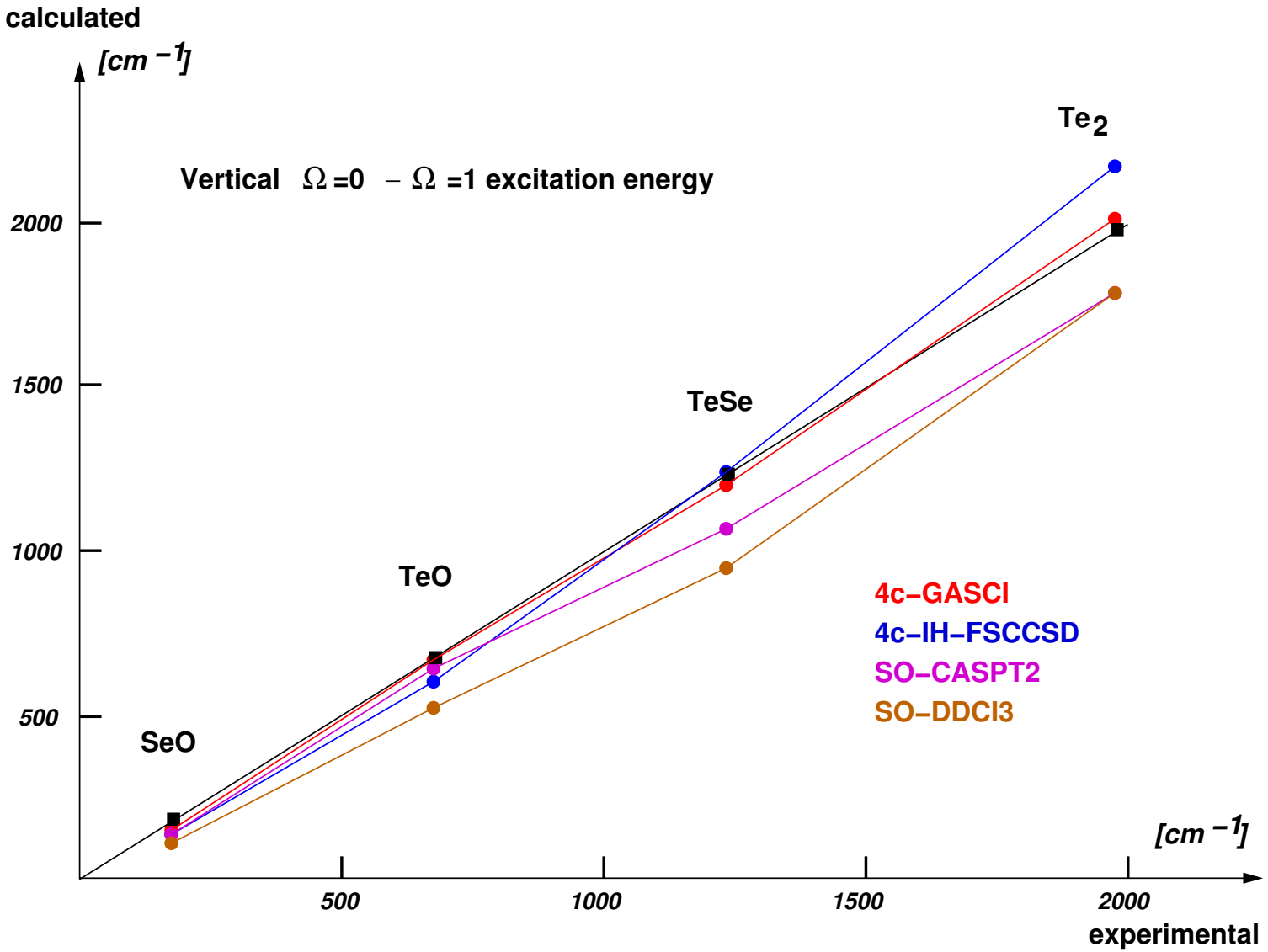
P.-Aa. Malmqvist, B.O. Roos, B. Schimmelpfennig, *Chem Phys Lett* **357** (2002) *357*

[11] 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*

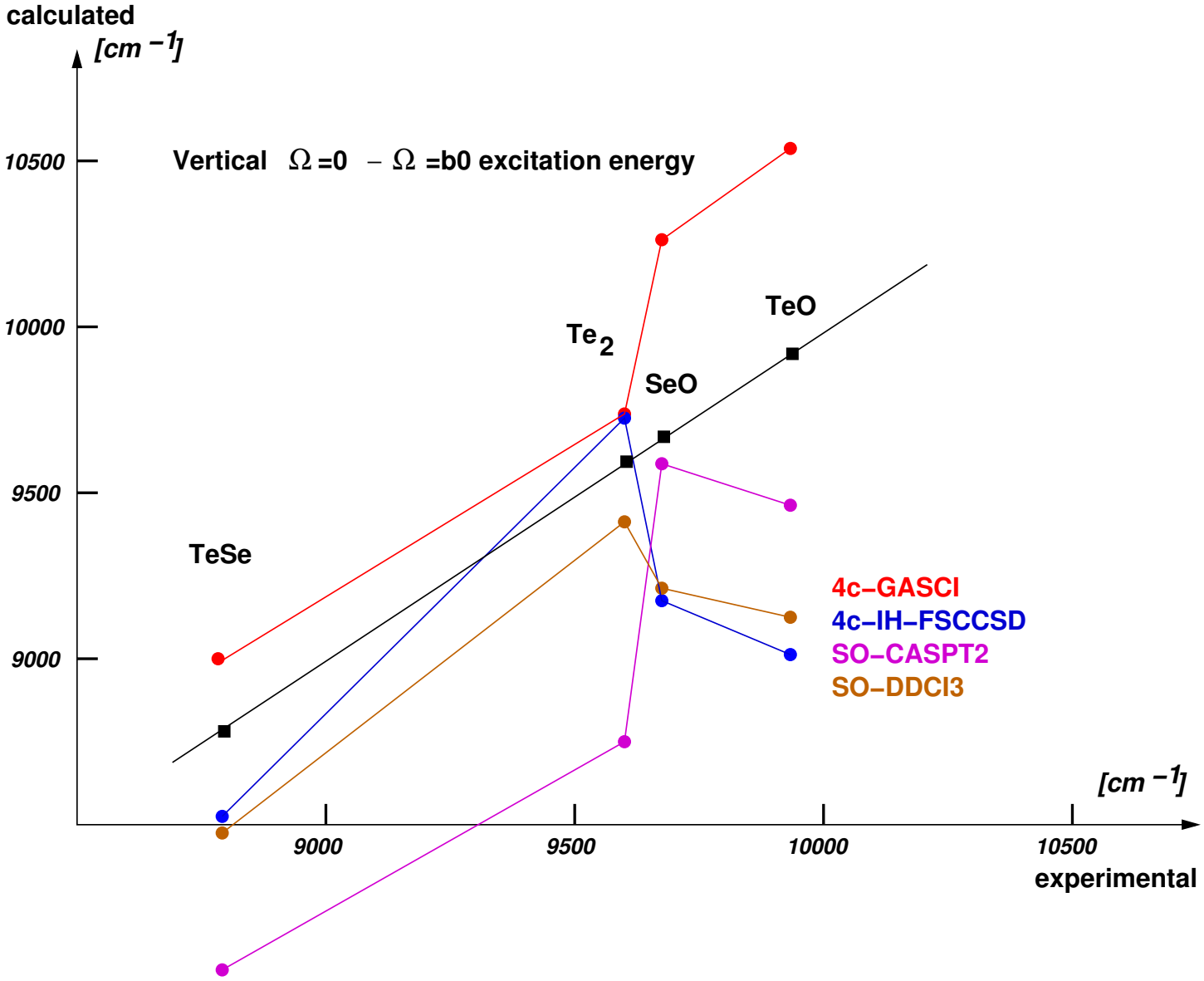
Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Special Relativity and Electron Correlation

Additive and non-additive methods in comparison



Special Relativity and Electron Correlation

Conclusions in the light of evidence

4c No-virtual-pair approximation is extremely accurate
4c-GASCC GER calculations

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 and inefficient in treating higher excitations

4c genuine MRCC is an important goal

$\Rightarrow$ The central problem in relativistic electronic-structure theory is non-relativistic.

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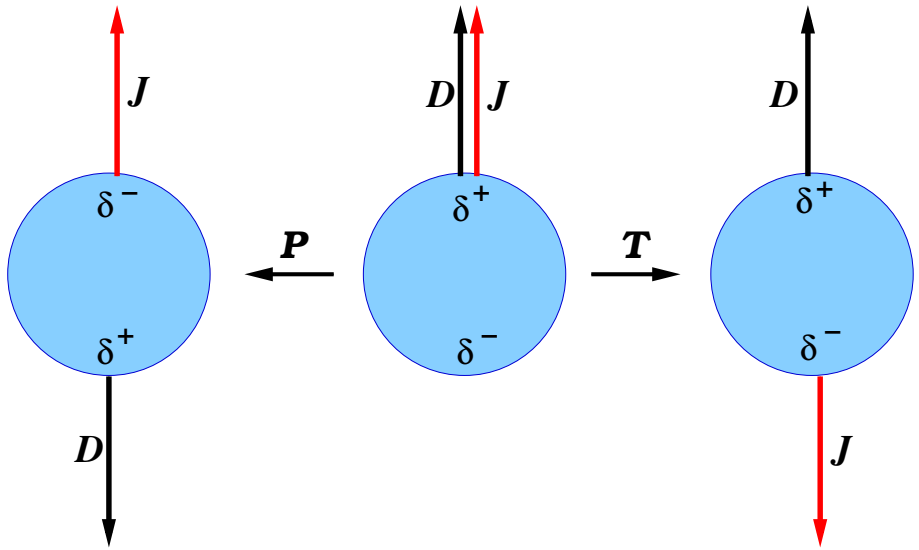
Testing fundamental physics:

Implications of an eEDM $\vec{D}$



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

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

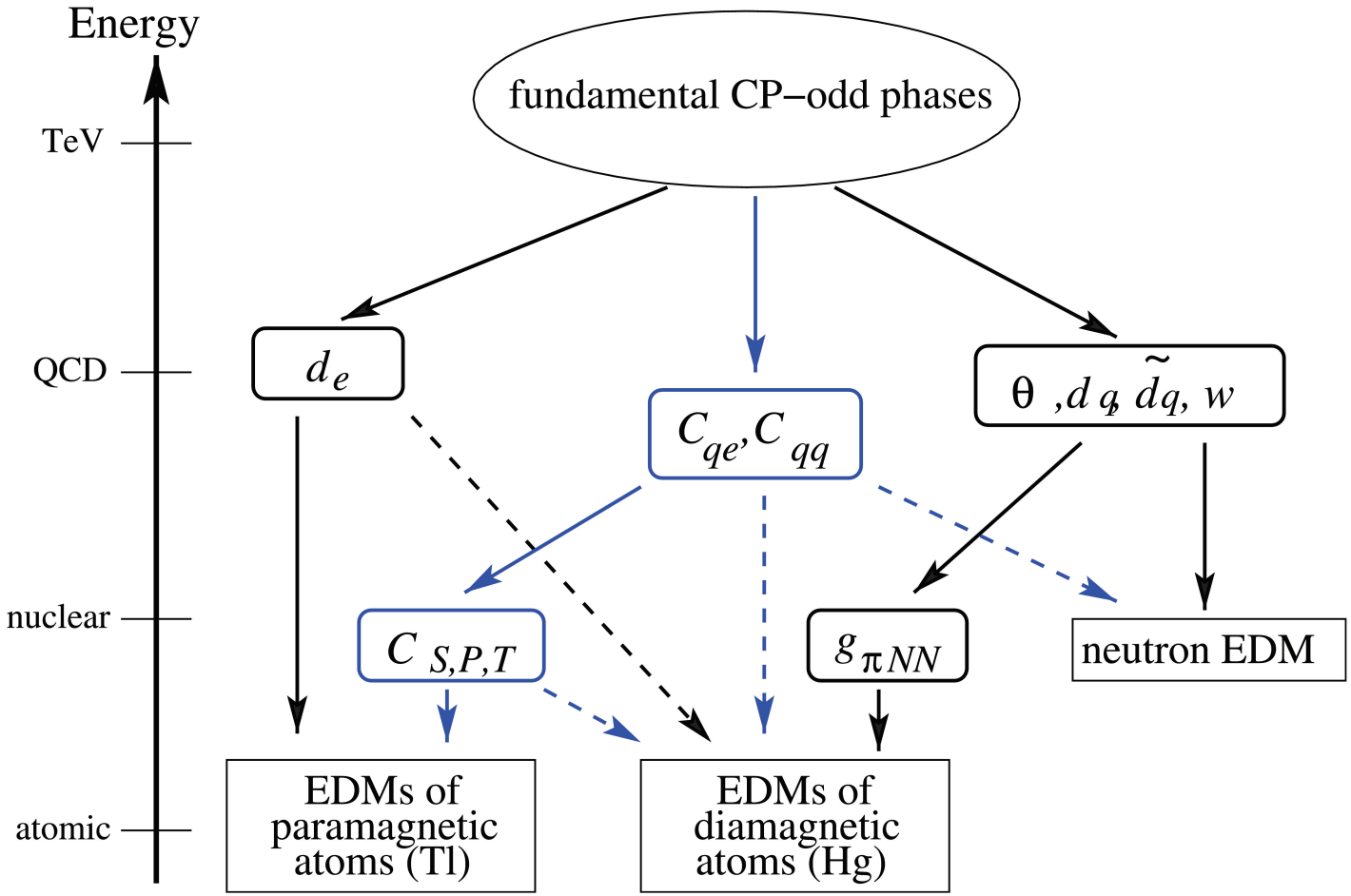
Implies violation of **Parity**($\mathcal{P}$) and **Time-Reversal**($\mathcal{T}$) symmetries[12]

The $\mathcal{CPT}$ theorem remains valid

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

CP-Violating Physics

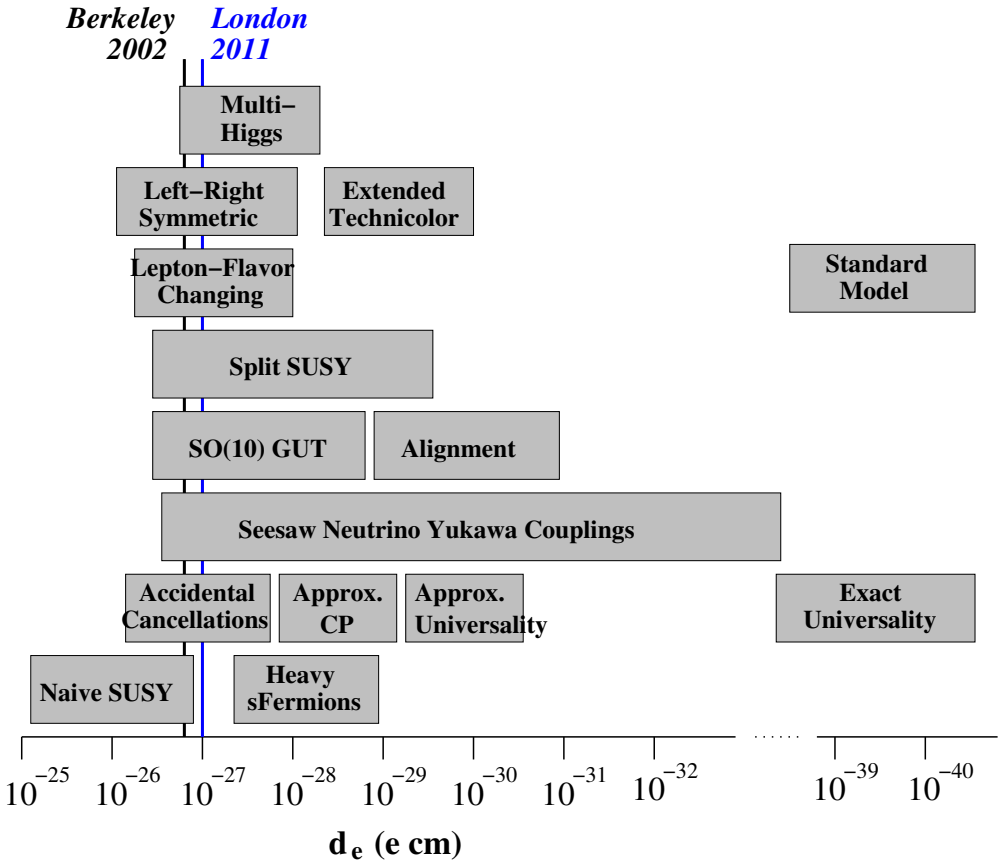
Characteristics and energy scales[13]



[13] M. Pospelov, A. Ritz, "Electric dipole moments as probes of new physics", *Ann. Phys.* **318** (2005) *119*

The search for physics beyond the standard model:

Current predictions for the eEDM[14]



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[15]	$< 1.6 \cdot 10^{-27}$
Experimental limit[16]	$< 10.5 \cdot 10^{-28}$

[14] 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)

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

[16] 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 formalism

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

- Point of departure: Salpeter's[17] modified Dirac equation:

$$\left[\gamma^\mu\left(-\imath\hbar\partial_\mu - \tfrac{e}{c}A_\mu\right) + m_0 c\mathbb{1}_4\right]\psi(x) = \tfrac{d_e}{4}\gamma^0\gamma^5\left(\gamma^\mu\gamma^\nu - \gamma^\nu\gamma^\mu\right)F_{\mu\nu}\,\psi(x)$$

- 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[18]

$$\left\langle\hat{H}_{\rm edm}\right\rangle_{\psi_k} = \sum_{I,J=1}^{\dim\mathcal{F}^{\rm t}({\rm M,N})} c^*_{kI}c_{kJ}\left\langle(\mathcal{S}\overline{\mathcal{T}})_I\right|\sum_{i=1}^{n}\hat{H}_{\rm edm}(i)\left|(\mathcal{S}\overline{\mathcal{T}})_J\right\rangle$$

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

[18] T Fleig and M K Nayak, *Phys Rev A* **88** (2013) *032514*

The eEDM in a molecular framework

Some candidate molecules

- ThF^+, HfF^+ (Experiment[19], Cornell group)
- WC (Experiment, Leanhart group, Michigan)
- ThO (DeMille group; Theory[20] , Meyer et al.)
- IH^+ (Theory, Titov et al.[21])
- PbO

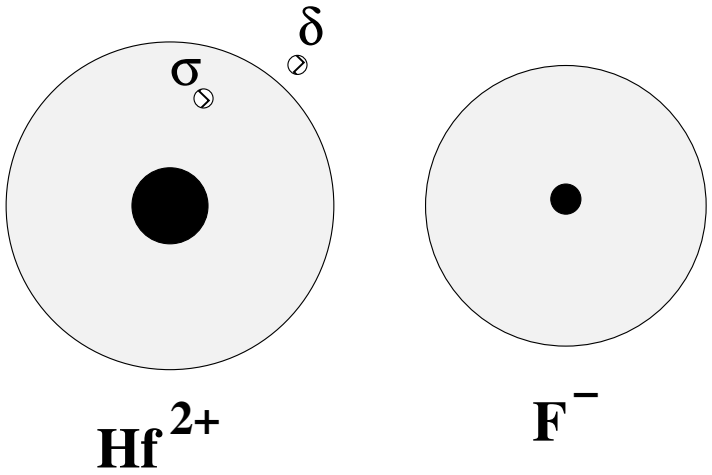
[19] A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

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

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

The eEDM in a molecular framework

$^3\Delta$ molecules

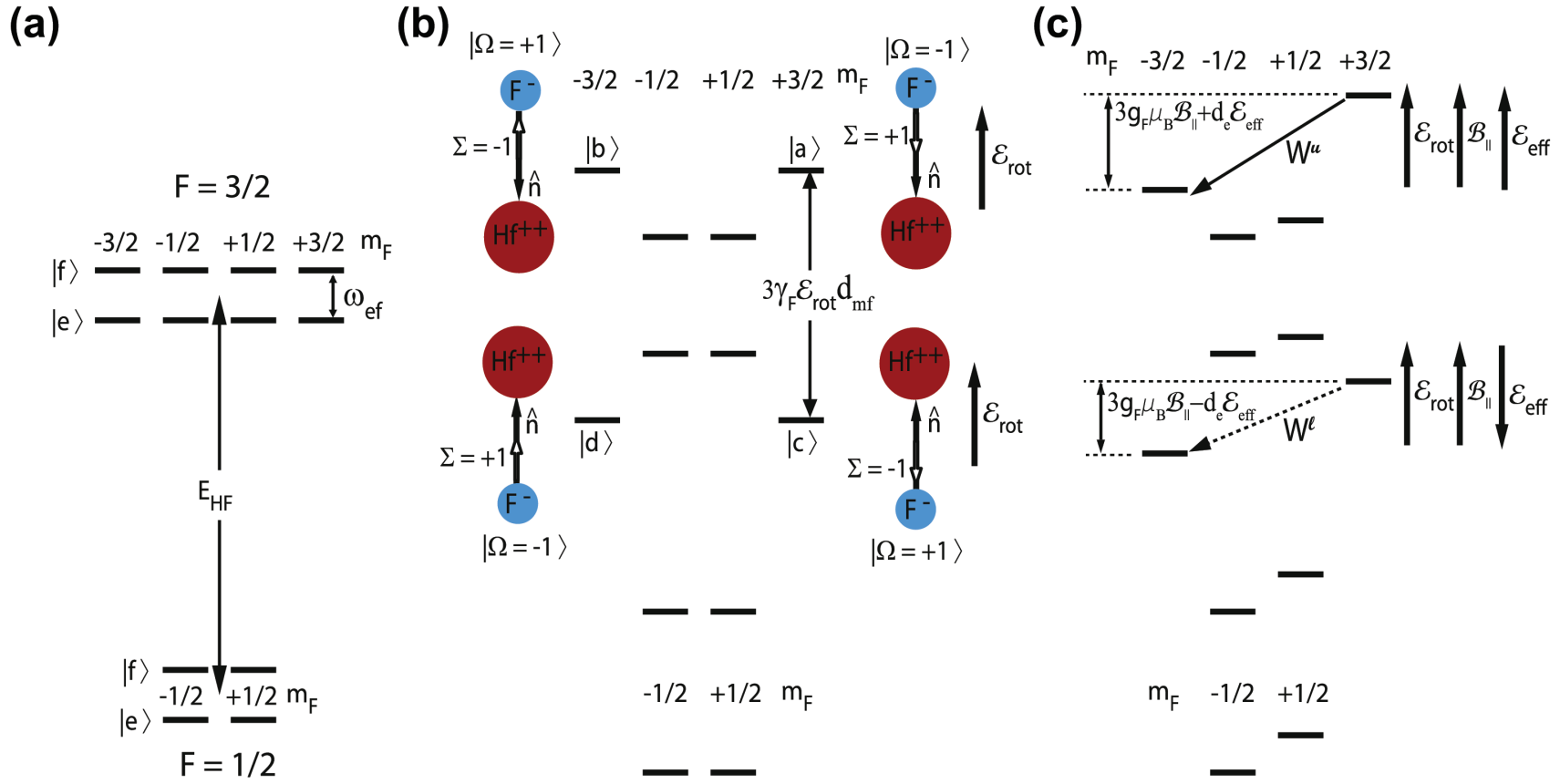


- Heavy nucleus (relativistic effect)
- One "science" electron (σ^1), one "spectroscopy" electron (δ^1)
- Large E_{eff} for σ^1 electron

- 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[22] on HfF^+



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

[22] 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

GASCI wavefunctions for HfF^+

Correct relative description of

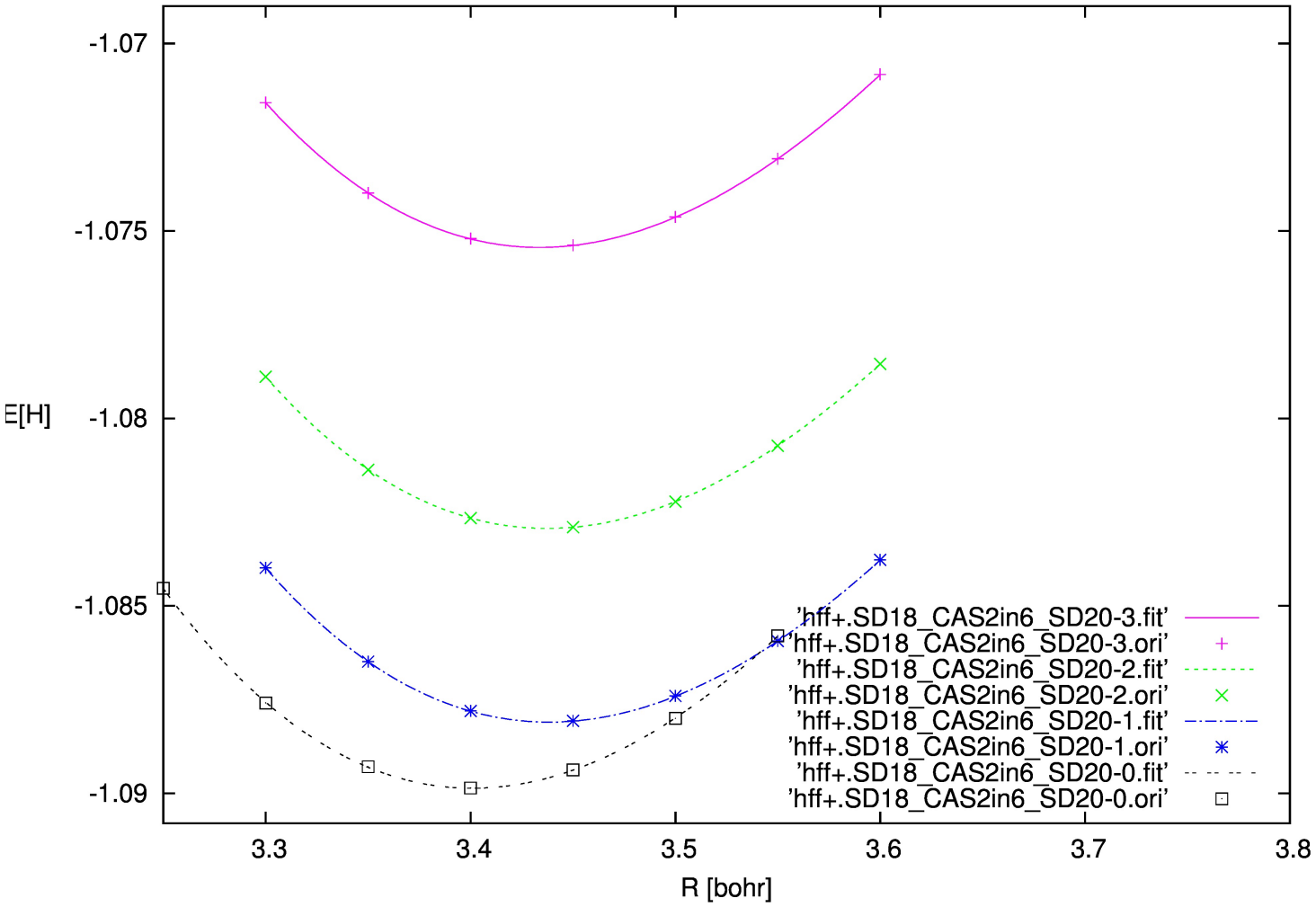
$\Omega = 0$ (Hf $6s^2$, $^1\Sigma_0^+$) and
$\Omega = 1$ (Hf $6s^1 5d^1$, $^3\Delta_1$) important for

1. Spectroscopic properties of involved states
2. Lifetime $\tau_{\Omega=1} = \left(\sum_k W^s_{k,\Omega=1}\right)^{-1}$ of "science" state

label	configurations
CAS-CI(10)	F$(2s2p)^8$ Hf$(6s5d)^2$, F$(2s2p)^7$ Hf$(6s5d)^3$, F$(2s2p)^6$ Hf$(6s5d)^4$
MR-CISD(10)	$+ v^1 + v^2$ configurations
MR-CISD(20)	+ up to 2 holes in Hf$(5s5p)$ and F$(1s)$ shells
MR-CISD+T(20)	+ active-space defined Triples replacements to MR-CISD(20)
MR-CISD(34)	MR-CISD(20) + up to 1 hole in Hf$(4f)$ shell
MR-CISD(34)+T	MR-CISD(34) + 20-electron Triples correction

The eEDM in a molecular framework

HfF^+ potential curves in RASCISD approximation



The eEDM in a molecular framework

HfF^+ spectroscopy; excitation energy and correlation model[23]

	R_e [a.u.]		ω_e [cm^{-1}]				T_e [cm^{-1}]			
Model	$\Omega=0$	$\Omega=1$	$\Omega=0$	$\Omega=1$	$\Omega=2$	$\Omega=3$	$\Omega=0$	$\Omega=1$	$\Omega=2$	$\Omega=3$
CAS-CI(10)	3.400	3.435	793	773	774	777	1543	0	1057	2480
MR-CISD(10)	3.506	3.558	651	639	639	640	68	0	1007	2489
MR-CISD+T(10)	3.510	3.560	649	640			0	26		
MR-CISD(20)	3.401	3.438	794	766	766	770	0	386	1519	3165
MR_{10}-CISD(20)	3.401	3.439	796	766	773	772	0	752	1890	3549
Experiment[24]			790.76	760.9			0	991.83		
Experiment[25]	3.374	3.407	791.2	761.3	762.3	761.5	0	993	2166	3951

- CAS-CI(10) reproduces relative energies of $\Omega=0$ and $\Omega=1$ incorrectly.
- MR-CISD(10) accounts for required differential electron correlations.
- MR-CISD(20) is an acceptable model.
- MR_{10}-CISD+T(20) will yield a very accurate description.

[23] T Fleig and M K Nayak, *Phys Rev A* **88** (2013) *032514*

[24] K.C. Cossel, D.N. Gresh, L.C. Sinclair, T. Coffrey, L.V. Skripnikov, A.N. Petrov, N.S. Mosyagin, A.V. Titov, R.W. Field, E.R. Meyer, E.A. Cornell, J. Ye, *Chem Phys Lett* **546** (2012) *1*

[25] 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_{eff} $\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$ vDZ	vTZ
CAS-CI(10)		24.1
MR-CISD(10)	21.6	22.4
MR-CISD(20)	22.9	23.3
MR_{10}-CISD(20)	23.0	
MR-CISD+T(20)		23.7
MR-CISD(34)		22.9
MR-CISD(34)+T		23.3
Estimate, Meyer et al.[26]	≈ 30	
Titov: 20 e^- corr.[27]	24.2	

Correction estimate:
($\pm 1\%$) Basis set
($\pm 2\%$) Number of correlated electrons
($\pm 2\%$) Higher excitations

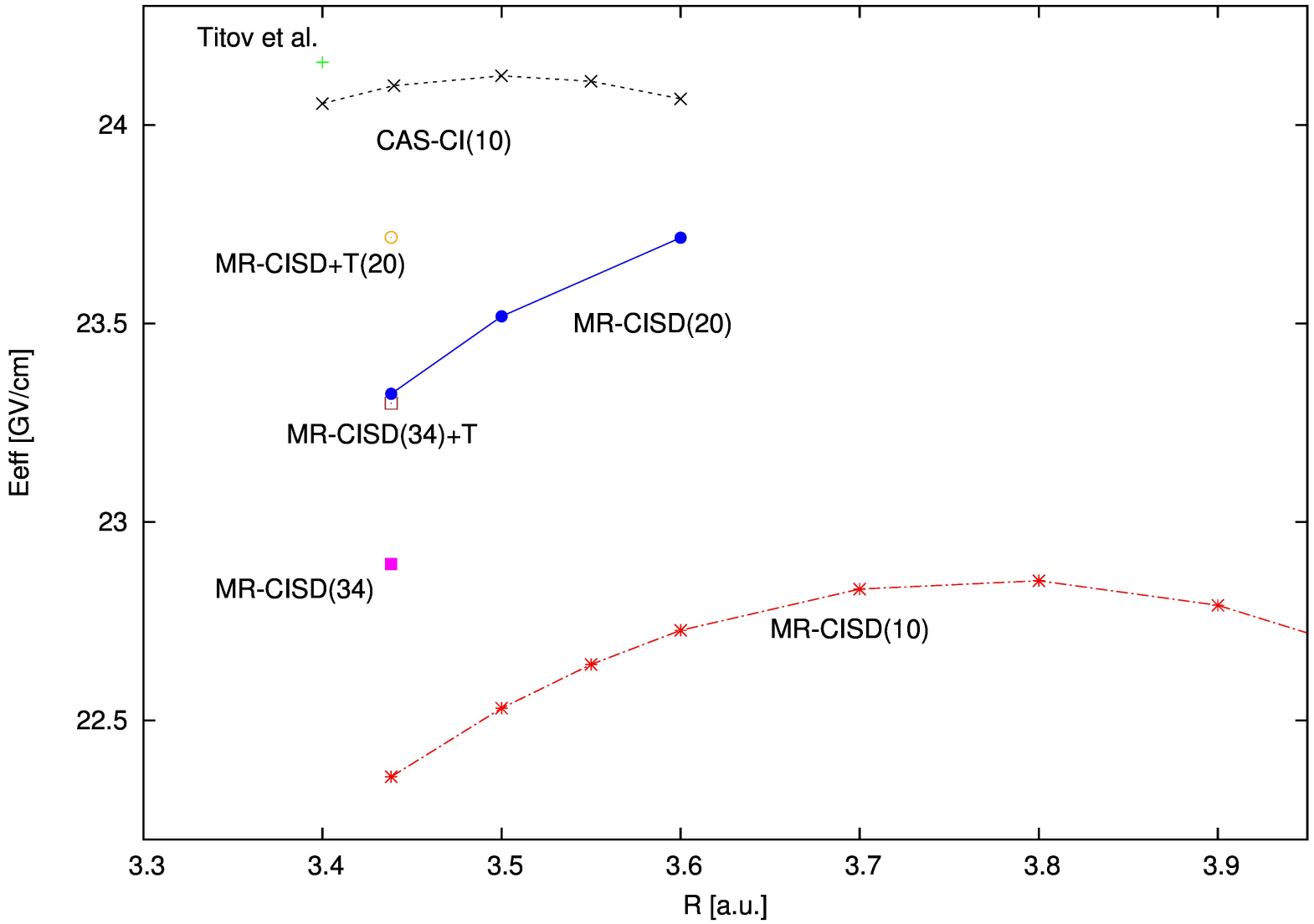
Modification of -3.7% to value of Titov et al.
(even larger taking internuclear distance into account)

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

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

The eEDM in a molecular framework

$\left\langle \hat{H}_{\rm edm} \right\rangle_{\psi_{\Omega=1}}$ as a function of R



eEDM in $^3\Delta$ Molecules

ThO

	# of Kramers pairs	accumulated # of electrons min.	max.
Virtual Kramers pairs	**X**	**18**	**18**
Th: 7s, 6d, 7p	**9**	**18–n**	**18**
Th: 6s, 6p O: 2s, 2p	**8**	**16–m**	**16**
(Th: 5s, 5p, 5d) Frozen core	**(41)**		

CAS2in9	$n = 0$	$m = 0$
CAS2in9_SD2	$n = 2$	$m = 0$
SD16_CAS2in9_SD18	$n = 2$	$m = 2$

Vertical excitation energies T_v $[\mathrm{cm}^{-1}]$

Correlation model	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$
CAS2in9	0	6706	7349	8333
CAS2in9_SD2	0	6598	7074	8090
SD16_CAS2in9_SD18	0	6420	7240	8527
Exp. [28] (T_e)	0	5317	6128	8600

$R = 3.477$ a.u., vDZ, Dirac-Coulomb

Effective electric field E_{eff} $\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$

CAS2in9	75.2
CAS2in9_SD2	71.7
SD16_CAS2in9_SD18	74.1
Meyer, Bohn	104

- Rather weak correlation effects
- $\longrightarrow$ Potential curves, deeper core correlation for E_{eff}, Th$(5s, 5p, 5d)$ shells, vTZ basis sets

[28] J. Paulovic, T. Nakajima, K. Hirao, R. Lindh, P.-Å. Malmqvist, *J Chem Phys* **119** (2003) *798*, and refs.

eEDM in $^3\Delta$ Molecules

ThF^+

	# of Kramers pairs	accumulated # of electrons min.	max.
Virtual Kramers pairs	X	18	18
Th: 7s, 6d	6	18–n	18
Th: 6s, 6p F: 2s, 2p	8	16–m	16
(Th: 5s, 5p, 5d) Frozen core	(41)		

CAS2in6	$n = 0$	$m = 0$
CAS2in6_SD2	$n = 2$	$m = 0$
SD16_CAS2in6_SD18	$n = 2$	$m = 2$

Vertical excitation energies T_v $[\mathrm{cm}^{-1}]$

Correlation model	$\Omega = 0$	$\Omega = 1$
CAS2in6	-1101	0
CAS2in6_SD2	-334	0
Exp. [29] (T_e)	0	315

$R = 3.8$ a.u., vDZ, Dirac-Coulomb

Effective electric field E_{eff} $\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$

CAS2in6	32.7
CAS2in6_SD2	45.2
Meyer, Bohn	90

- Strong correlation effects on spectroscopic constants and E_{eff}
- $\longrightarrow$ Valence and outer core shells to be considered, Th$(6s, 6p, 5s, 5p, 5d)$, O$(2s, 2p)$

[29] B. J. Barker, I. O. Antonov, M. C. Heaven, K. A. Peterson, *J Chem Phys* **136** (2012) *104305*

Future Work

Blanc program, Funding 2013 - 2017.

- **Malika Denis**
- **T. F.**, *Principal Investigator*
- **Mikhail G. Kozlov**, *St. Petersburg Nuclear Physics Institute*
- **Malaya K. Nayak**, *Bhabha Atomic Research Centre, Mumbai*
- **Jessica Loras**
- **Trond Saue**
- **Avijit Shee**

ThO, ThF^+, WC

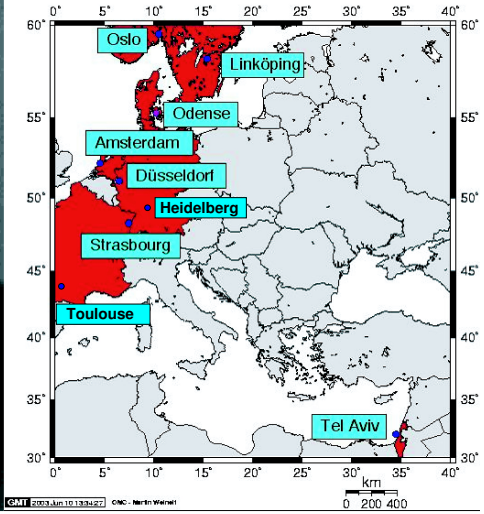
Hyperfine structure constants

Other $\mathcal{P}$- and $\mathcal{P},\mathcal{T}$-nonconserving operators

DIRAC a metalaboratory for the development of relativistic 4- and 2-component electronic-structure methodology

P rogram
• for
A tomic
• and
M olecular

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

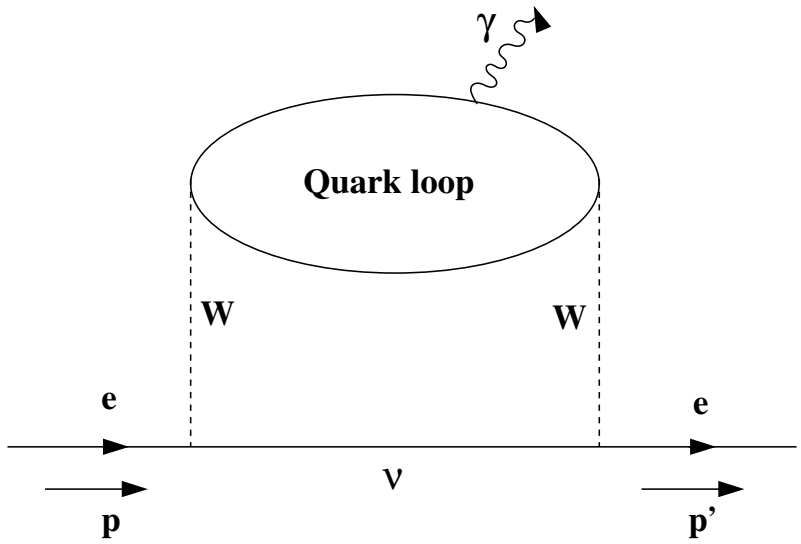


- `KR-CI`.
  `Kramers-Restricted GAS Configuration Interaction Program`
  (released in DIRAC10/DIRAC11/DIRAC12)
  Authors: S Knecht, T Fleig, J Olsen, HJAa Jensen

- `KR-CC`.
  `Kramers-Restricted GAS Coupled Cluster Program`
  (not yet released)
  Authors: LK Sørensen, J Olsen, M Hubert, T Fleig

The induced fermion EDM

Standard Model Picture



- Only $\mathcal{CP}$ violation in the quark-mixing matrix (CKM)
- Electron only interacts indirectly via weak interaction with virtual quarks
- Such two-loop diagrams give zero $\mathcal{CP}$-odd contribution[5]

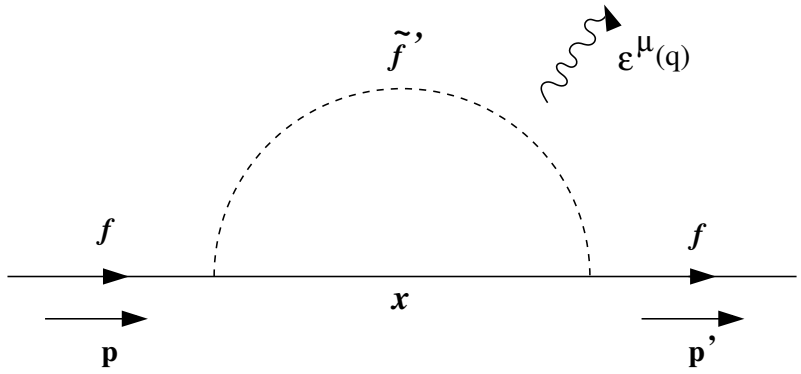
- Three-loop $\mathcal{CP}$-odd contributions zero in the absence of gluonic corrections[6]
- The standard-model prediction is immeasurably small: $d_e^{SM} \leq 10^{-38}\, e$ cm

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

[6] M. Pospelov, I.B. Khriplovich, *Sov J Nuc Phys* **53** (1991) *638*

The induced fermion EDM

Beyond the Standard Model



χ: chargino, neutralino

$\tilde{f}'_j$: supersymmetry (s)-fermion

$\epsilon^\mu(q)$: photon

Chargino ($\tilde{\chi}^{\pm}_{1,2}$), neutralino ($\tilde{\chi}^{0}_{1,2,3,4}$) or gluino ($\tilde{g}^a$) fermion/sfermion interaction Lagrangian:

$$\mathcal{L}_{\chi f \tilde{f}'} = g_{Lij}^{\chi f \tilde{f}'_j} \left(\overline{\chi}_i P_L f\right) \tilde{f}'^{*}_j + g_{Rij}^{\chi f \tilde{f}'_j} \left(\overline{\chi}_i P_R f\right) \tilde{f}'^{*}_j + h.c.$$

One-loop fermion EDM:[30]

$$\left(\frac{d_f^E}{e}\right)^{\chi} = \frac{m_{\chi_i}}{16\pi^2 m^2_{\tilde{f}'_j}} \mathcal{I}m\left[\left(g_{Rij}^{\chi f \tilde{f}'_j}\right)^{*} g_{Lij}^{\chi f \tilde{f}'_j}\right] \left[Q_\chi A\left(\frac{m_{\chi_i}}{m^2_{\tilde{f}'_j}}\right) + Q_{\tilde{f}'_j} B\left(\frac{m_{\chi_i}}{m^2_{\tilde{f}'_j}}\right)\right]$$

MSSM ("naïve SUSY") prediction:

$d_e \leq 10^{-27}\, e$ cm

[30] J. Ellis, J.S. Lee, A. Pilaftsis, *J High Energy Phys* **10** (2008) *049*

The eEDM in a molecular framework

HfF^+ spectroscopy; first vertical excitation energy

$$T_e(\text{exp.}) = 992\ [\text{cm}^{-1}]$$[31]

	$T_v^{3.4[\text{a.u.}]}\ [\text{cm}^{-1}]$			
	vDZ		vTZ	
Model	$\Omega = 0$	$\Omega = 1$	$\Omega = 0$	$\Omega = 1$
CAS-CI(10)	1487	0	1488	0
MR-CISD(10)	0	450	0	358
MR-CISD+T(10)			0	442
MR-CISD(20)	0	587	0	451
MR_{10}-CISD(20)	0	(1013)	0	816
MR-CISD+T(20)			0	679

- Error compensations among basis set, active-space size, higher excitations
- Final calculation: MR_{10}-CISD+T(20), ≈ 2.5 billion parameters

[31] K.C. Cossel, D.N. Gresh, L.C. Sinclair, T. Coffrey, L.V. Skripnikov, A.N. Petrov, N.S. Mosyagin, A.V. Titov, R.W. Field, E.R. Meyer, E.A. Cornell, J. Ye, *Chem Phys Lett* **546** (2012) *1*

A measure of accuracy:

Hyperfine interaction constants

$$A_{||} = \frac{\mu_{At}}{I} \sum_{i=1}^{n} \frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3}$$

- Measure of electron density in the vicinity of heavy nuclei
- Relevant atomic integrals implemented in local version of `DIRAC12` (by M. K. Nayak)
- Incorporate integrals into 4c-GASCI and 4c-GASCC expectation value modules

$\Rightarrow$ A possible calibrating criterion for electron EDM expectation values