Rigorous Relativistic Methods for Addressing $\mathcal{P}$- and $\mathcal{T}$-Nonconservation in Heavy-Element Molecules

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Overview

1. **Relativistic Wavefunction Theory**

   4-component electron correlation methods

2. Application to "$^3\Delta$ molecules"

   Spectroscopy and eEDM data

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

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

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

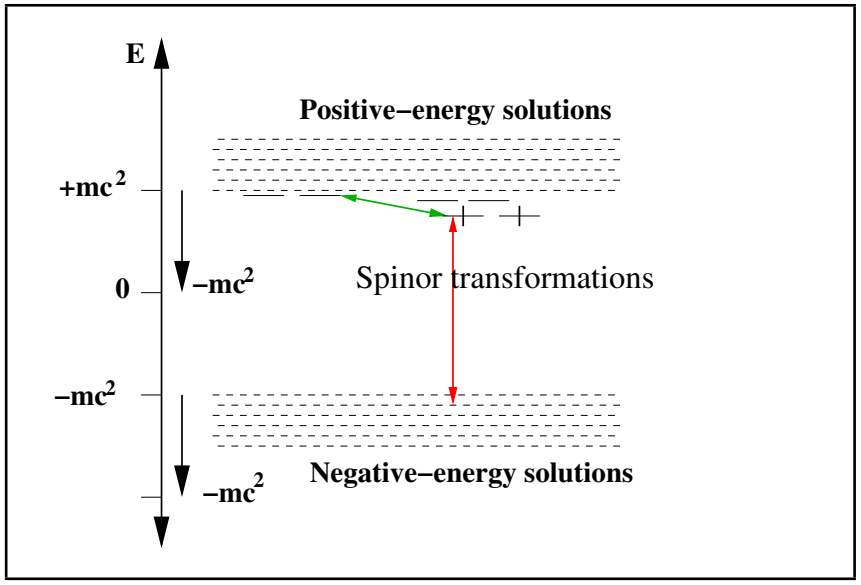
- Fock matrix for "frozen" atomic core

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

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

Four-Component Electronic-Structure Theory

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:
  $\left\langle 0|e^{-\hat{\kappa}}\hat{H}^{DC}e^{\hat{\kappa}}|0\right\rangle \approx \left\langle 0|\left[\hat{H}^{DC},\hat{\kappa}\right]|0\right\rangle = \sum_{pq}\kappa_{pq}\left[\left\langle 0|\hat{H}^{DC}a_p^\dagger a_q|0\right\rangle - \left\langle 0|\hat{H}^{DC}a_q^\dagger a_p|0\right\rangle^*\right]$
- Parameterized Dirac-spinor transformations:
  $\hat{\kappa} = \sum_{pq}\left[\kappa_{p+q+}a_{p+}^\dagger a_{q+} + \kappa_{p+q-}a_{p+}^\dagger a_{q-} + \kappa_{p-q+}a_{p-}^\dagger a_{q+} + \kappa_{p-q-}a_{p-}^\dagger a_{q-}\right]$
- 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
$\hat{K}\varphi_i\,\alpha = \varphi_i^*\,\beta$	$\hat{K}\phi_i = \phi_{\bar{i}}$
$\hat{K}\varphi_i^*\,\beta = -\varphi_i\,\alpha$	$\hat{K}\phi_{\bar{i}} = -\phi_i$

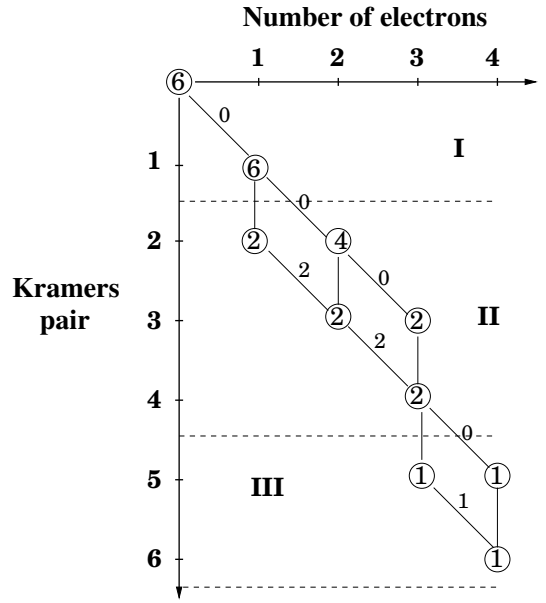
Spinor basis:

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

- 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**

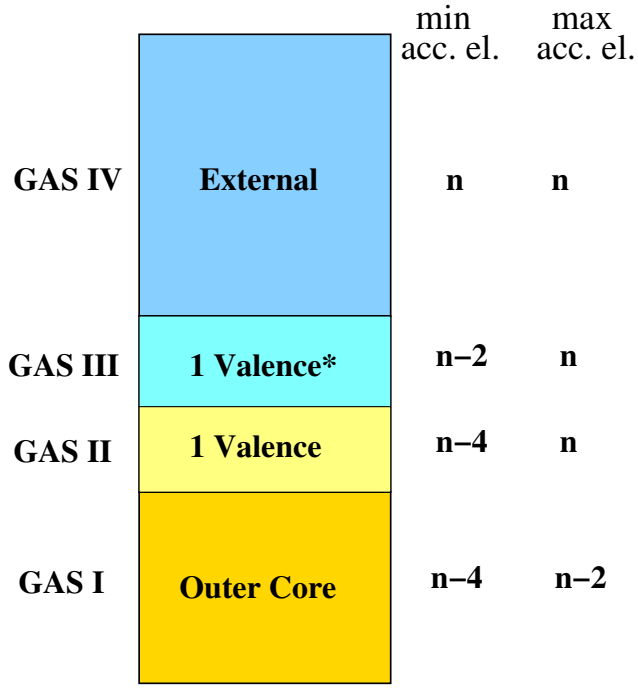


⊗ x: vertex weight
y: arc weight

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" (or SR-MR) GAS-CC
  Generalized "Oliphant/Adamowicz" Ansatz[1]
- 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
  $\hat{T}_1 = \sum_{ia} \left\{ \; t^a_i \hat{\tau}^a_i \; + t^{\bar{a}}_{\bar{i}} \hat{\tau}^{\bar{a}}_{\bar{i}} + t^{\bar{a}}_i \hat{\tau}^{\bar{a}}_i + t^{\bar{a}}_{\bar{i}} \hat{\tau}^{\bar{a}}_{\bar{i}} \; \right\}$; $\hat{T}_2 = \ldots$



Example for constructed higher excitations:

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

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

Relativistic Generalized-Active-Space CC

Excitation Energies[2]

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

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

Algorithm for Jacobian matrix elements[3]

- 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.

$$[[\hat{H}_{2v,2v}, \hat{T}_{2v,2o}], \hat{T}_{2v,2o}]$$

$$= \frac{1}{4} \sum_{abcd,i'j'a'b',i"j"a"b"} (ad|bc) t_{i'j'}^{a'b'} t_{i"j"}^{a"b"} a_a^\dagger a_b^\dagger \overbrace{a_c a_d a_{a'}^\dagger a_{b'}^\dagger a_{i'} a_{j'} a_{a"}^\dagger}^{} a_{b"}^\dagger a_{i"} a_{j"} .$$

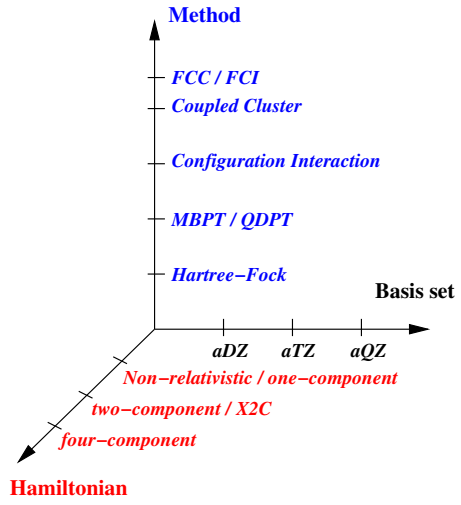
---

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

[3] 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*

Special Relativity and Electron Correlation

Computational Scaling



Computational scaling:

$$\mathbf{S = y(x)\ f(x)\ N^{x}}$$

y(x): Relativity prefactor
f(x): general prefactor
N: Basis set dimension
x: Method scaling exponent

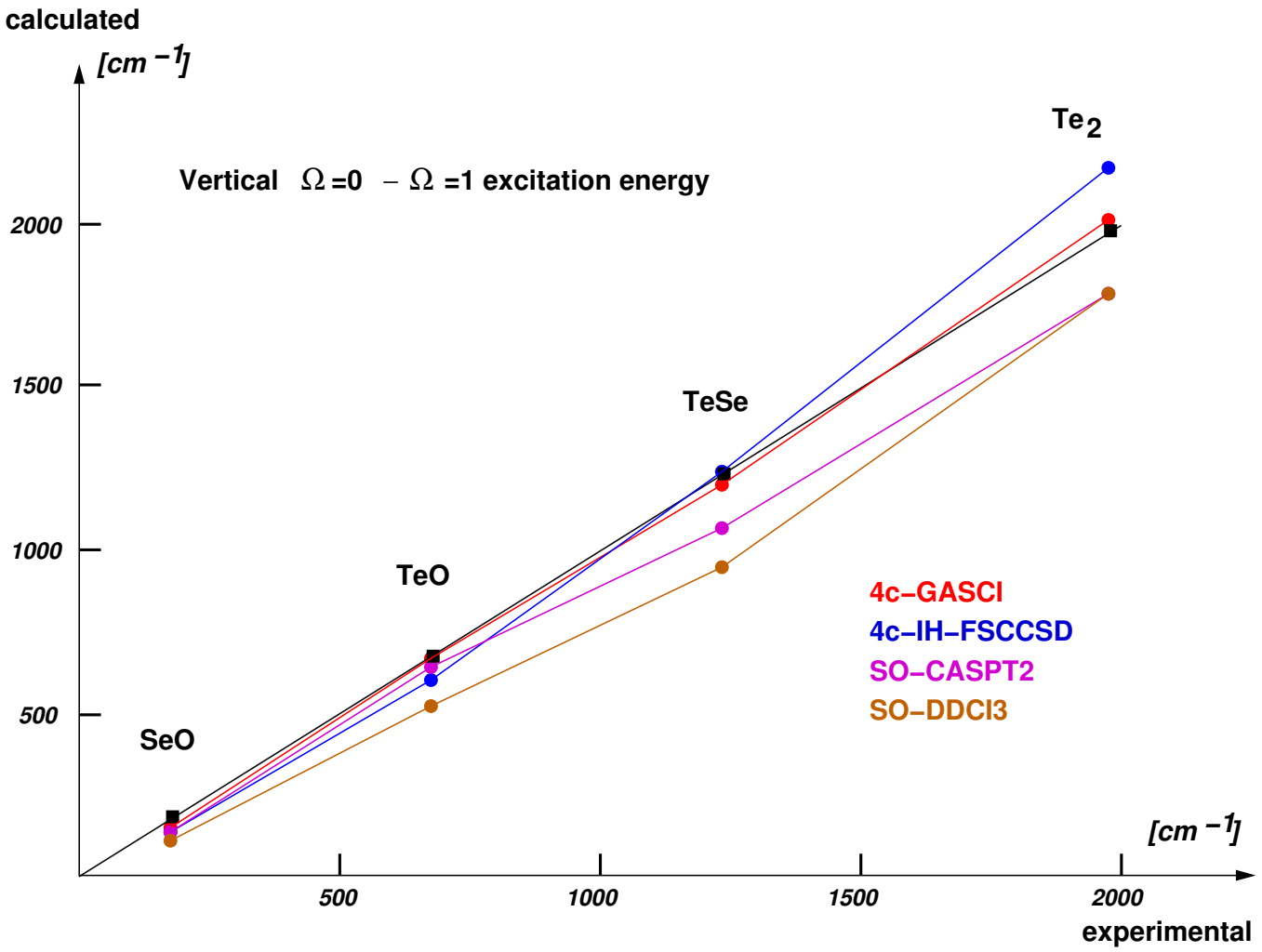
$$S^{\mathrm{rel.CC}} \approx 4\sqrt{\pi\left(\frac{x}{2}-1\right)}\ \frac{1}{4}\left[\frac{x^2}{4}-\frac{3}{2}x+2\right]\begin{pmatrix} x-2 \\ \frac{x}{2}-1 \end{pmatrix} O^{\frac{x}{2}-1}V^{\frac{x}{2}+1}$$

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).

Special Relativity and Electron Correlation

Additive and non-additive methods, CI and CC[4]



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

Overview

1. Relativistic Wavefunction Theory

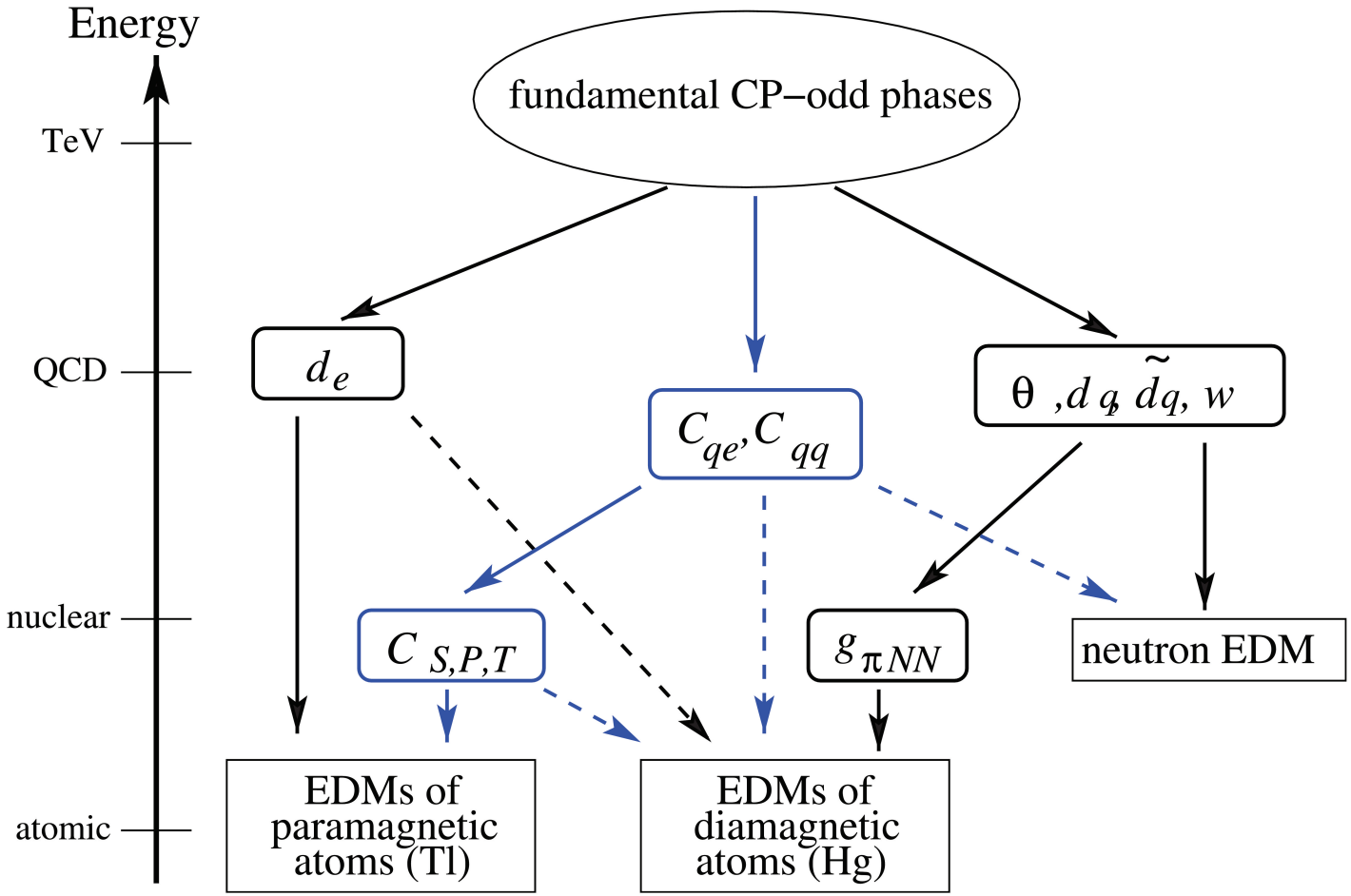
   4 components electron correlation methods

2. **Application to "$^3\Delta$ molecules"**

   Spectroscopy and eEDM data

CP-Violating Physics

Characteristics and energy scales[5]



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

The eEDM in a molecular framework

Wavefunction theory

- Molecular Dirac-Coulomb Hamiltonian:
$$\hat{H}^{DC} = \sum_A \sum_i \left[c(\vec{\alpha} \cdot \vec{p})_i + \beta_i m_0 c^2 + V_{iA} \right] + \sum_{i,j>i} \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_{A,B>A} V_{AB}$$

- Gaunt term absent; only small errors in heavy-element molecules

- Variationally optimized coefficients $\{c_{kI}\}$ of wavefunction expansion
$$|\psi_k\rangle = \sum_{I=1}^{\dim \mathcal{F}^{\mathrm{t}}(\mathrm{M,N})} c_{kI} \left| (\mathcal{S}\overline{\mathcal{T}})_I \right\rangle$$

- 4c-CI expectation values[6] over eEDM Hamiltonian
$$\left\langle \hat{H}_{\mathrm{edm}} \right\rangle_{\psi_k} = \sum_{I,J=1}^{\dim \mathcal{F}^{\mathrm{t}}(\mathrm{M,N})} c_{kI}^* c_{kJ} \left\langle (\mathcal{S}\overline{\mathcal{T}})_I \right| \sum_{i=1}^{n} \hat{H}_{\mathrm{edm}}(i) \left| (\mathcal{S}\overline{\mathcal{T}})_J \right\rangle .$$

[6] T. Fleig and M. K. Nayak, PRX, submitted, under revision.

The eEDM in a molecular framework

EDM Hamiltonian

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

- Point of departure: Salpeter's[7] modified Dirac equation:
$$\left[\gamma^\mu\left(-\imath\hbar\partial_\mu - \tfrac{e}{c}A_\mu\right) + m_0 c\mathbb{1}_4\right]\psi(x) = \tfrac{d_e}{4}\gamma^0\gamma^5\left(\gamma^\mu\gamma^\nu - \gamma^\nu\gamma^\mu\right)F_{\mu\nu}\,\psi(x)$$
- neglecting the less important[8] magnetic part $-d_e\imath\vec{\gamma}\cdot\mathbf{B}$
- from which the eEDM operator can we written as an expectation value:
$$\left\langle -d_e\gamma^0\boldsymbol{\Sigma}\cdot\mathbf{E}\right\rangle_{\psi_H} = \tfrac{2\imath c d_e}{e\hbar}\left\langle\gamma^0\gamma^5\vec{p}^{\,2}\right\rangle_{\psi_H}$$
- In a many-body system $\hat{H}_{\rm edm}$ appears as
$$\sum_{i=1}^{N}\hat{H}_{\rm edm}(i) = -d_e\sum_{i=1}^{N}\gamma^0(i)\boldsymbol{\Sigma}(i)\cdot\mathbf{E}(i).$$
- Required kinetic-energy integrals of the type $\left\langle\psi^L|\vec{p}_j^{\,2}|\psi^S\right\rangle$

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

[8] E. Lindroth, B. W. Lynn, P. G. H. Sandars, *J Phys B: At Mol Opt Phys* **22** (1989) *559*

The eEDM in a molecular framework

GASCI wavefunctions for HfF^+

Correct relative description of

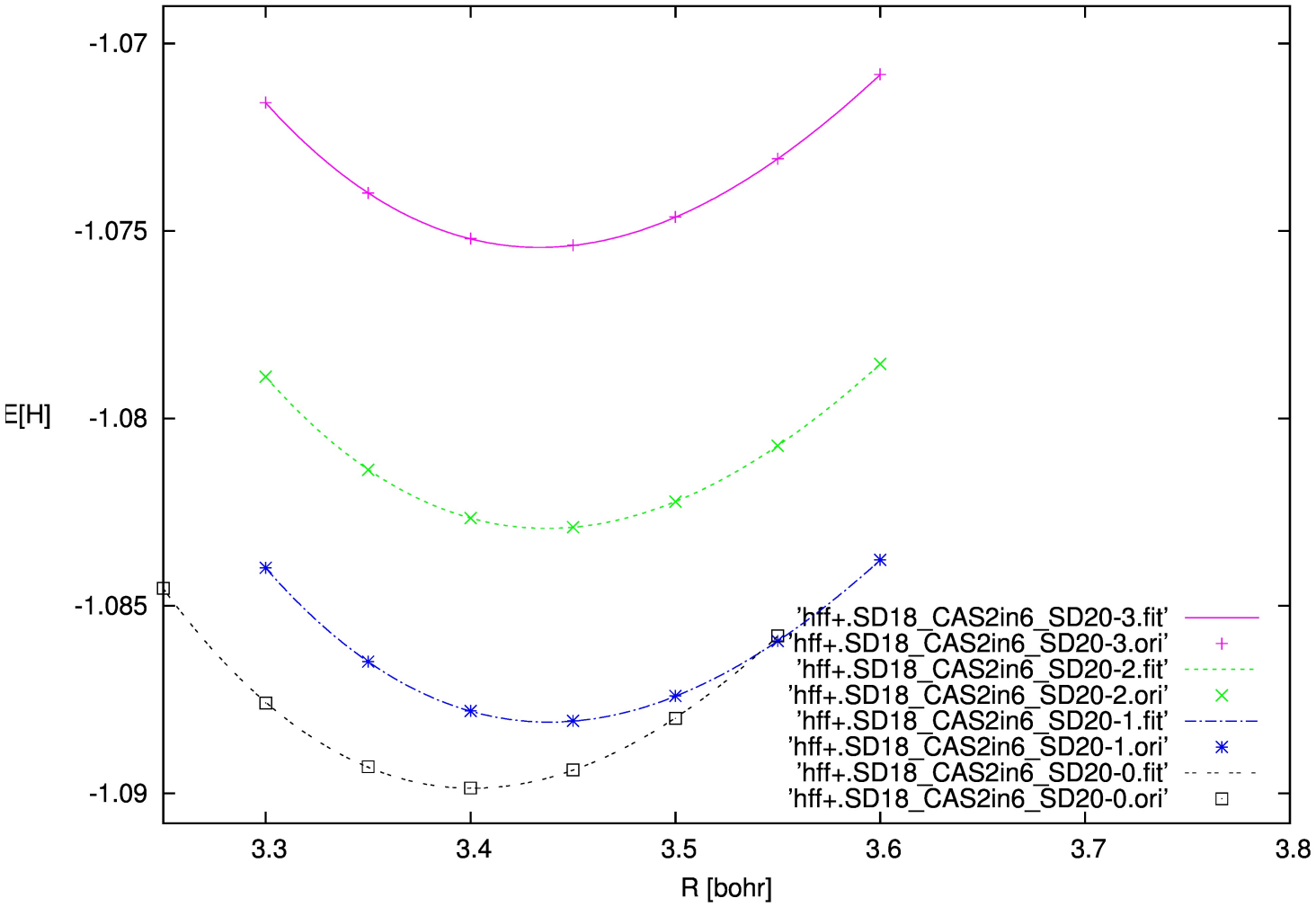
$\Omega = 0$ (Hf $6s^2$, $^1\Sigma_0^+$) and
$\Omega = 1$ (Hf $6s^1 5d^1$, $^3\Delta_1$) important for

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

	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	769	769	0	752	1881	3533
Experiment[9]			790.76	760.9			0	991.83		
Experiment[10]	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.

[9] 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*

[10] B.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) *201102*

The eEDM in a molecular framework

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

Model	$E_{\rm eff}$ $\left[\frac{\rm GV}{\rm cm}\right]$ 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
Meyer et al.[11]	≈ 30	
Titov: 20 e^- corr.[12]	24.2	

Correction estimate:

($\pm 1\%$) Basis set

($\pm 2\%$) Number of correlated electrons

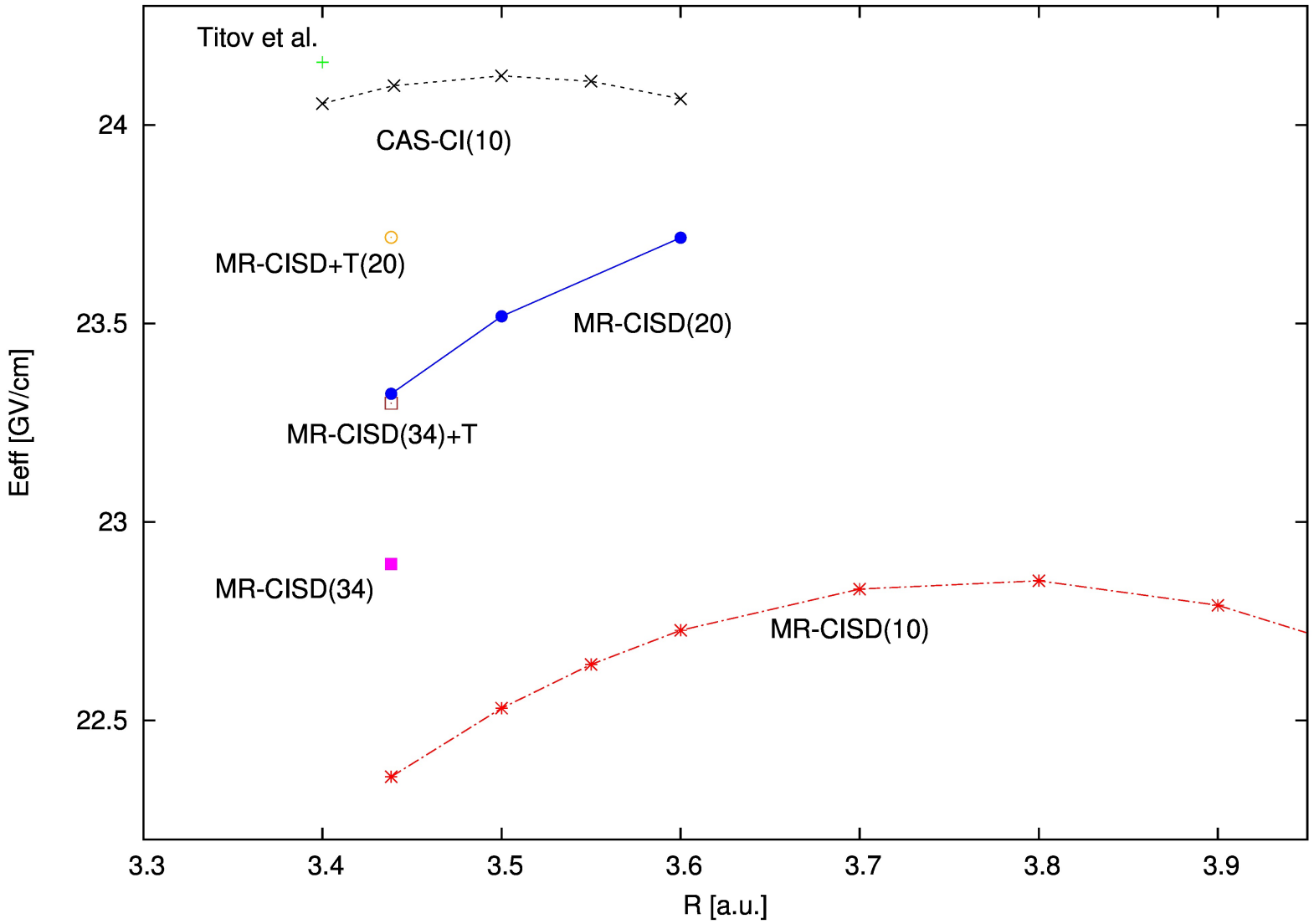
($\pm 2\%$) Higher excitations

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

[12] 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. [13] (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

[13] 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 $[cm^{-1}]$

Correlation model	$\Omega = 0$	$\Omega = 1$
CAS2in6	-1101	0
CAS2in6_SD2	-334	0
Exp. [14] (T_e)	0	315

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

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

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$(2s, 2p)$

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

Future Work

Blanc program.

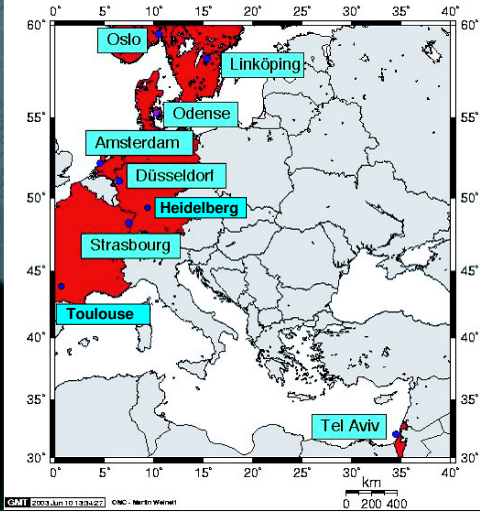
- **Malika Denis** (Toulouse)
- **T. F.**, *Coordinator*
- **Mikhail G. Kozlov**, *St. Petersburg Nuclear Physics Institute*
- **Malaya K. Nayak**, *Bhabha Atomic Research Centre, Mumbai*
- **Jessica Loras** (Toulouse)
- **Trond Saue** (Toulouse)
- **Avijit Shee** (Toulouse)

ThO, ThF^+, WC; (transition) dipole moments; hyperfine coupling 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

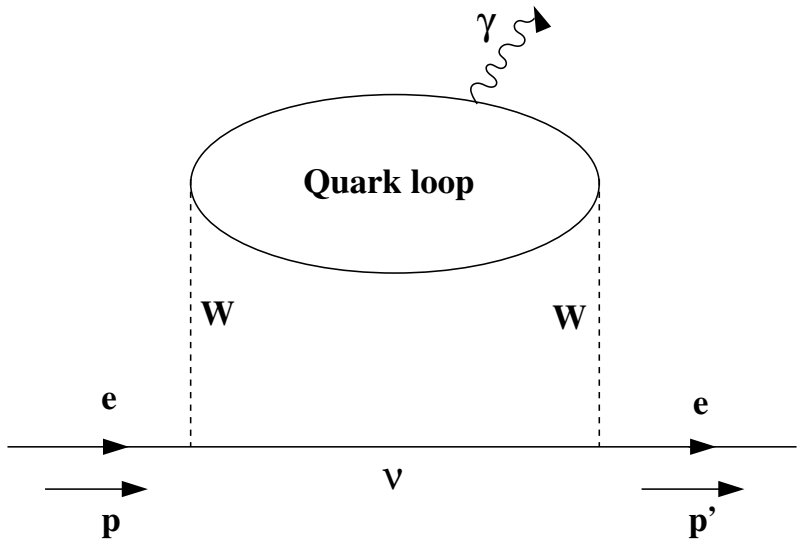


- `KR-CI`.
  `Kramers-Restricted GAS Configuration Interaction Program`
  (released in DIRAC10/DIRAC11/DIRAC12)
  Authors: S Knecht, T Fleig, J Olsen, HJAa Jensen

- `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]

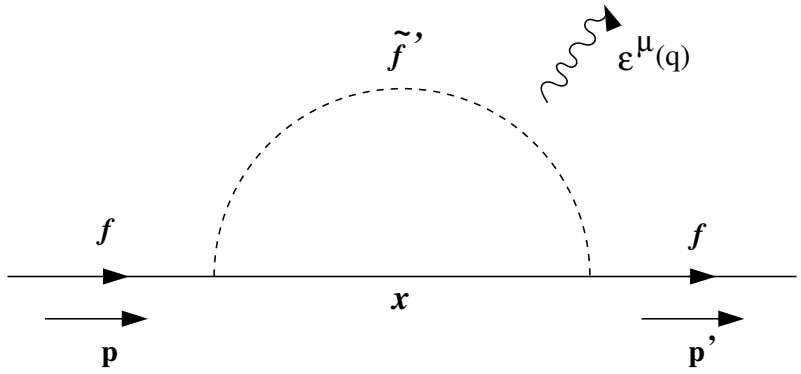
- Three-loop $\mathcal{CP}$-odd contributions zero in the absence of gluonic corrections[6]
- The standard-model prediction is immeasurably small: $d_e^{SM} \leq 10^{-38}\, e$ cm

[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:[15]

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

MSSM ("naïve SUSY") prediction:

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

[15] 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

$$T_e(\text{exp.}) = 992\ [\text{cm}^{-1}]$$[16]

	$T_v^{3.4[\text{a.u.}]}\ [\text{cm}^{-1}]$			
	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

[16] 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