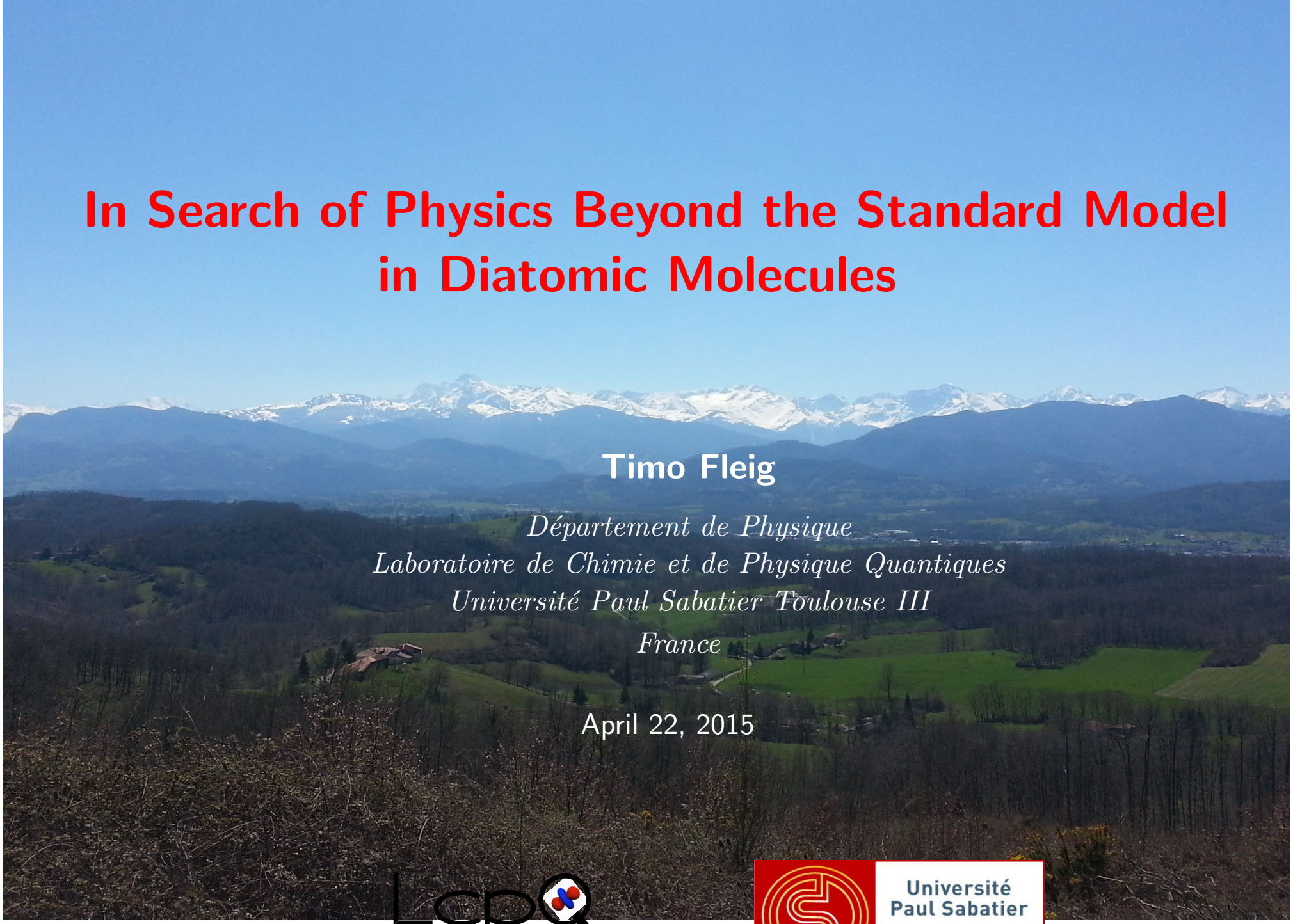
In Search of Physics Beyond the Standard Model in Diatomic Molecules



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April 22, 2015

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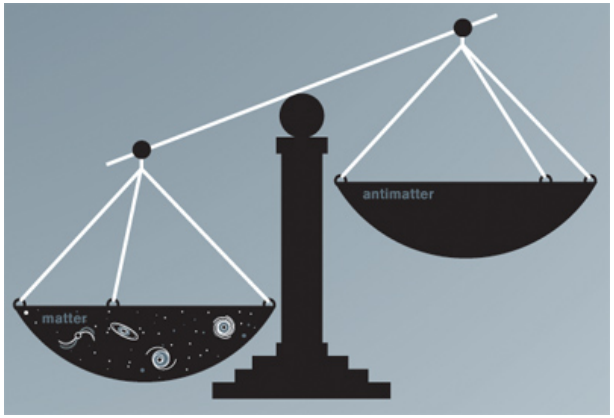
EDMe^-DM

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

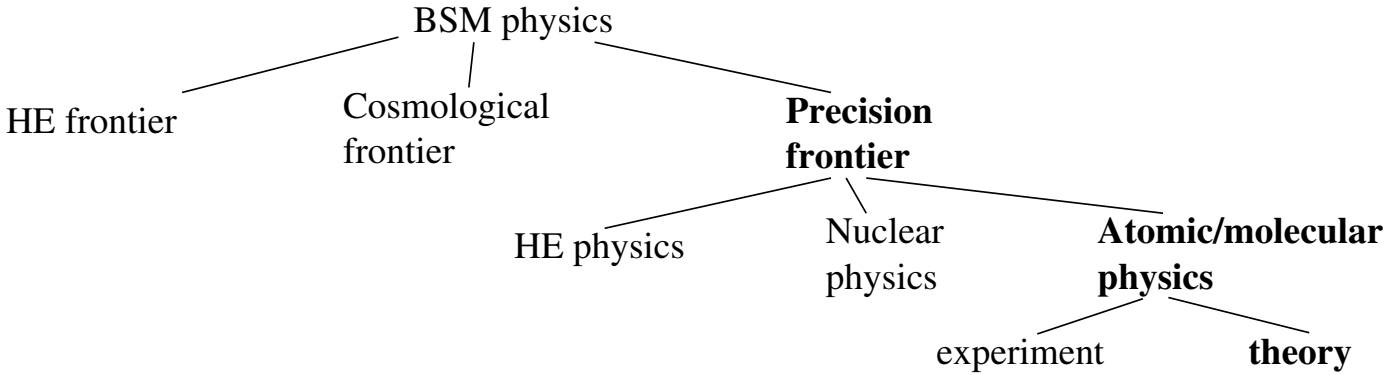
ANR

Open Questions at Large Scale and at Small Scale



- **Matter-antimatter asymmetry** of the universe[1]
- Nature of **cold dark matter**
- Degree of $\mathcal{CP}$ **violation** in nature[2]

- Detection/constraint of **EDMs** as a powerful probe of possible explanations/consequences[3]

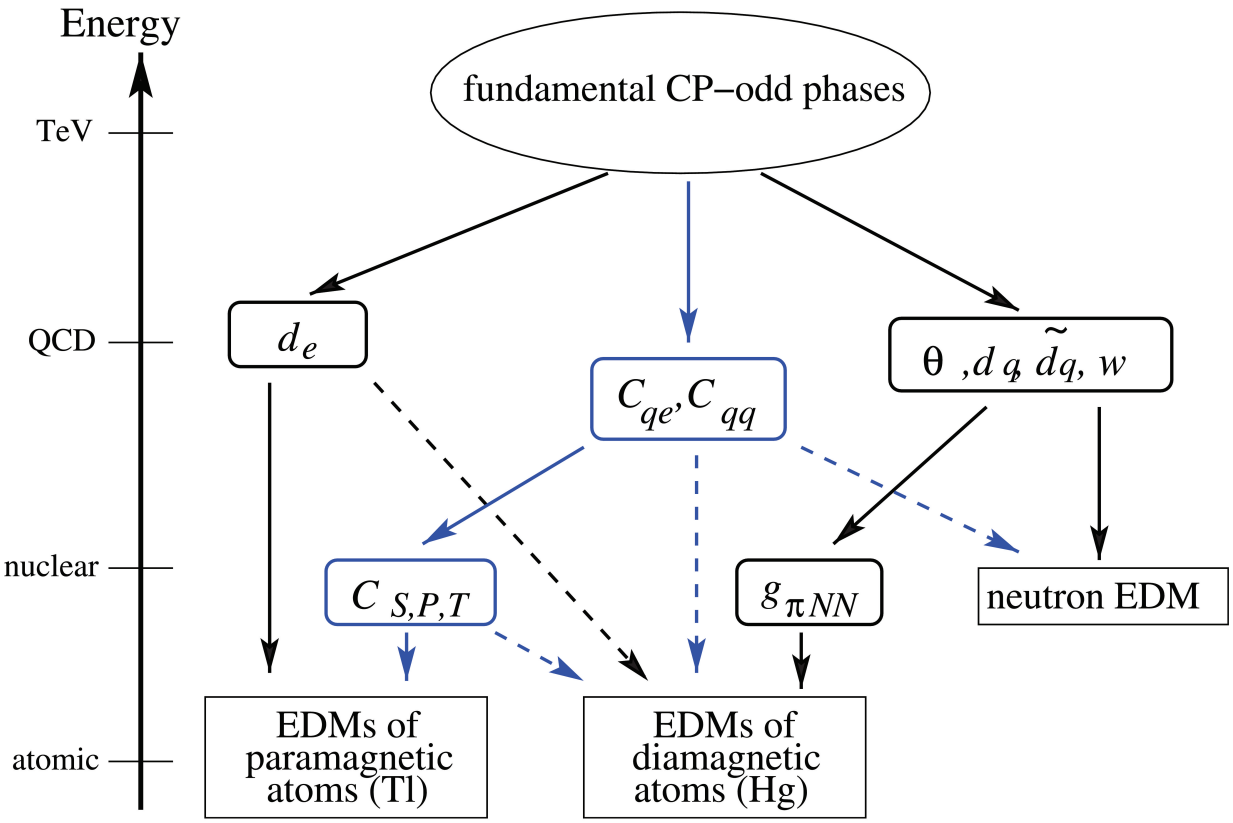


[1] M. Dine, A. Kusenko, *Rev. Mod. Phys.* **76** (2004) *1*

[2] G. C. Branco, R. G. Felipe, F. R. Joaquim, *Rev. Mod. Phys.* **84** (2012) *515*

[3] J. Engel, M. J. Ramsey-Musolf, U. van Kolck, *Prog. Part. Nuc. Phys.* **71** (2013) *21*

Electric Dipole Moments and Their Source Tree[4]



d_e: electron EDM

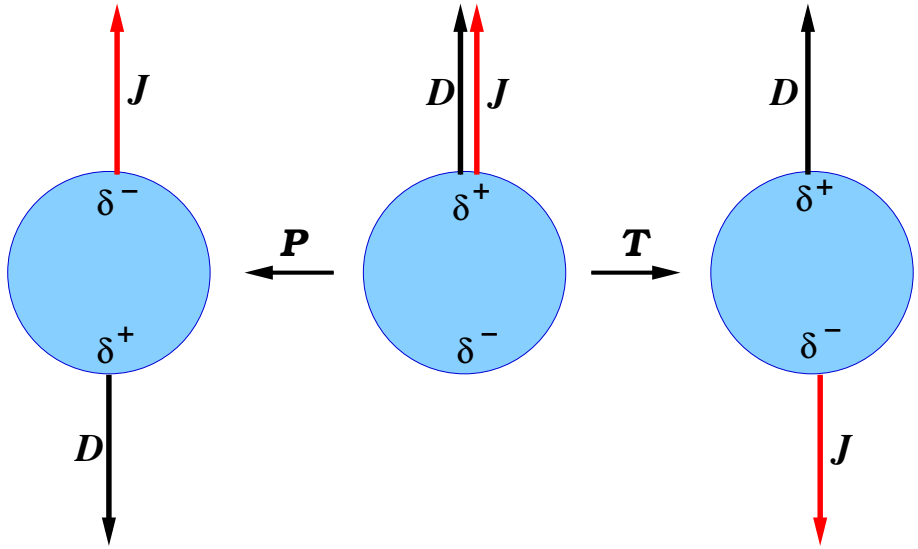
($\mathcal{P}$ and $\mathcal{T}$)-violating electron-nucleon interaction

($\mathcal{P}$ and $\mathcal{T}$)-violating NMQM interaction

- EDMs are low-energy physics probes of high-energy physics symmetry breaking

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

The Fermion Electric Dipole Moment (fEDM) $\vec{D}$



$\vec{D}$ and $\vec{J}$ (anti-)collinear, $\longleftarrow$ Pauli exclusion principle[5]

Implies violation of **Parity**($\mathcal{P}$) and **Motion-Reversal**($\mathcal{T}$) symmetries[6]

$\mathcal{CPT} \Rightarrow$ connects with ($\mathcal{CP}$) violation

---

[5] L.R. Hunter, *Science* **252** (1991) *73*

[6] T.D. Lee, C.N. Yang, *BNL* **443** (1957) *T91*

An Aside:

What is a fundamental EDM, what is not ?

Transformation properties for a quantum system

Non-relativistic electric dipole energy

$$E_{\rm dip} = -\left\langle \Psi \left| \mathbf{D}\cdot\mathbf{E}_{\rm ext} \right| \Psi \right\rangle$$

$\mathcal{P}$-even	$\mathcal{P}$-odd	$\mathcal{P}$-odd
$\mathcal{T}$-even	$\mathcal{T}$-even	$\mathcal{T}$-even

- EDM orthogonal to angular momentum and zero due to end-over-end rotation
- In $\mathbf{E}_{\rm ext}$ $\mathbf{D} \neq \mathbf{0}$, but mixed eigenstates

Potential energy due to a fermion EDM

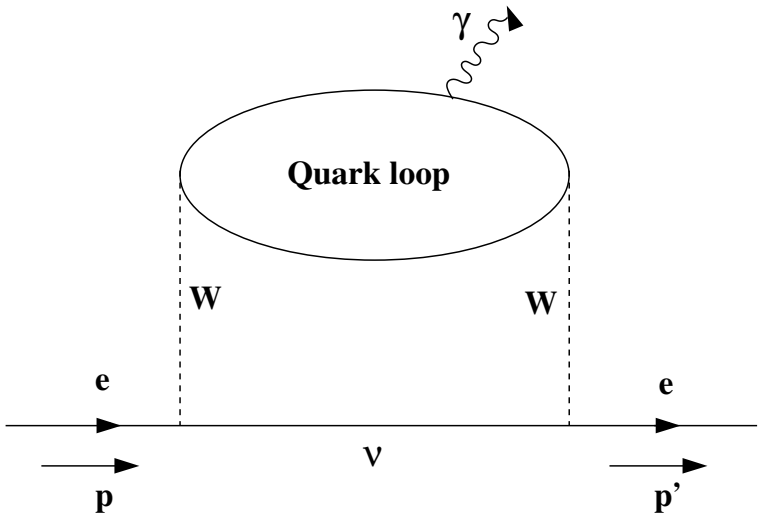
$$E_{\rm EDM} = -d_e \left\langle \Psi \left| \gamma^0 \mathbf{\Sigma}\cdot\mathbf{E} \right| \Psi \right\rangle$$

$\mathcal{P}$-odd	$\mathcal{P}$-even	$\mathcal{P}$-odd
$\mathcal{T}$-odd	$\mathcal{T}$-odd	$\mathcal{T}$-even

- EDM along angular momentum
- $d_e\gamma^0\mathbf{\Sigma} \neq \mathbf{0}$ in pure eigenstate

The induced fermion EDM

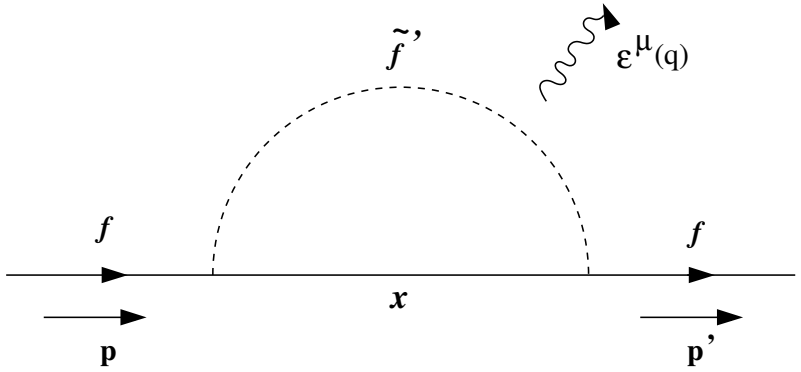
Standard Model Picture[7]



- Three-loop $\mathcal{CP}$-odd contributions zero in the absence of gluonic corrections[8]

  $d_e^{SM} \leq 10^{-38}\, e$ cm

BSM Picture



χ: chargino, neutralino

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

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

- MSSM ("naïve SUSY") prediction[9]:
  $d_e \leq 10^{-27}\, e$ cm

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

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

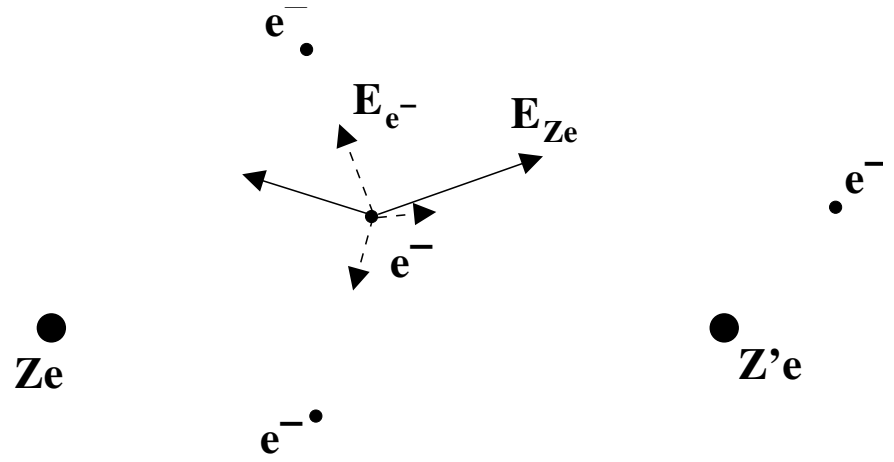
[9] J. Ellis, J.S. Lee, A. Pilaftsis, *J High Energy Phys* **10** (2008) *049*

Search for the Electron EDM

d_e from an atomic/molecular many-body problem

- Unpaired e^- in a stationary atomic/molecular state
- Measurement of an EDM dependent energy difference (transition energy/frequency shift) $\Delta\epsilon$ of atomic/molecular quantum states.
- Theory determination of an **EDM effective electric field**[10]

$$d_e = \frac{\Delta\epsilon}{E_{\text{eff}}} \begin{matrix}\text{(Experiment)}\\ \text{(Theory)}\end{matrix}$$



[10] P.G.H. Sandars, *J Phys B: At Mol Opt Phys* **1** (1968) *499*

Search for the Electron EDM

Atomic/molecular enhancement

- In the **non-relativistic limit** the EDM expectation value vanishes:

  (Schiff's Theorem[11])

$$\left\langle \hat{H}_{\mathrm{EDM}} \right\rangle = 0$$

- Relativistic view leads to a non-zero value, essentially due to length contraction in the obeserver frame[12]
- Scaling with nuclear charge Z, for alkali atoms[13]

$$R \propto Z^3 \, \alpha^2$$

- Heavy atoms required. Typical values in practice:

$$Z > 50$$

[11] L.I. Schiff, *Phys Rev* **132** (1963) *2194*

[12] E.D. Commins, J.D. Jackson, D.P. DeMille, *Am J Phys* **75** (2007) *532*

[13] P.G.H. Sandars, *Phys Lett* **14** (1965) *194*

The eEDM in a molecular framework

Perturbative EDM operator

Single-particle $\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[14]:

$$\hat{H}_{\mathrm{EDM}} = -\frac{d_e}{4}\gamma^0\gamma^5\left(\gamma^\mu\gamma^\nu - \gamma^\nu\gamma^\mu\right)F_{\mu\nu}$$

which comprises an electric and a "motional" part

$$\hat{H}_{\mathrm{EDM}} = -d_e\gamma^0\left[\boldsymbol{\Sigma}\cdot\mathbf{E} + \imath\boldsymbol{\alpha}\cdot\mathbf{B}\right]$$

Magnetic contribution does not enter to leading order[15]

Electric field contributions

$$\mathbf{E} = \mathbf{E}_{\mathsf{int}} + \mathbf{E}_{\mathsf{ext}}$$

with an internal nuclear and electronic contribution

$$\mathbf{E}_{\mathsf{int}}(i) = \sum_{A=1}^{N}\frac{Ze\left(\vec{r}_i - \vec{r}_A\right)}{||\vec{r}_i - \vec{r}_A||^3} - \sum_{j=1}^{n}\frac{e\left(\vec{r}_i - \vec{r}_j\right)}{||\vec{r}_i - \vec{r}_j||^3}$$

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

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

The eEDM in a molecular framework

Effective EDM many-body operator

Theoretical framework is relativistic quantum mechanics, no QED contributions

Exact reformulation of interaction constant for a single-particle expectation value[16]

$$\left\langle -d_e \gamma^0 \mathbf{\Sigma} \cdot \mathbf{E} \right\rangle_{\psi^{(0)}} = \frac{2\imath c d_e}{e\hbar} \left\langle \gamma^0 \gamma^5 \vec{p}^{\,2} \right\rangle_{\psi^{(0)}}$$

Approximate effective expectation value in many-body system

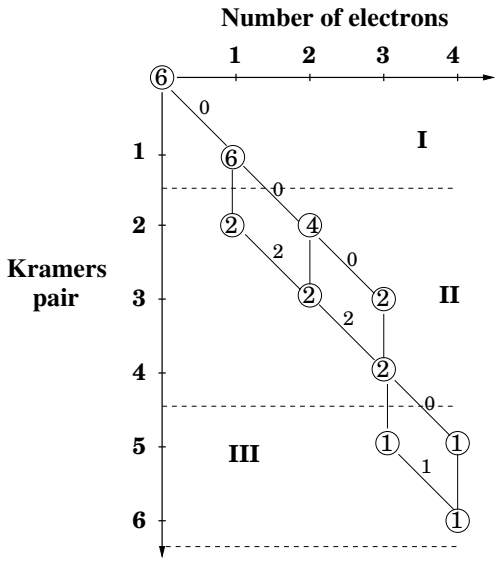
$$-d_e \left\langle \sum_{j=1}^{n} \gamma^0(j)\, \mathbf{\Sigma}(j) \cdot \mathbf{E}(j) \right\rangle_{\psi^{(0)}} \approx \frac{2\imath c d_e}{e\hbar} \left\langle \sum_{j=1}^{n} \gamma^0(j) \gamma^5(j)\, \vec{p}(j)^{\,2} \right\rangle_{\psi^{(0)}}$$

$\psi^{(0)}$ here is the atomic/molecular electronic wavefunction.

How do we optimize accurate electronic wavefunctions ?

[16] E. Commins, *Adv At Mol Opt Phys* **40** (1999) *1*

Relativistic Generalized-Active-Space Configuration Interaction[17]



- Basis of time-reversal paired four-spinors

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

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

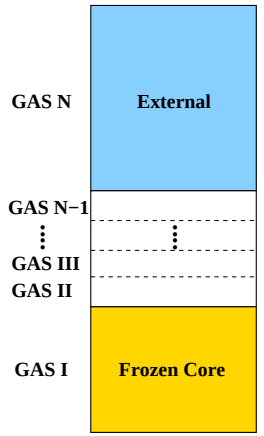
- Many-particle wavefunction defined as

  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**



[17] S. Knecht, H.J.Aa. Jensen, TF, *J Chem Phys* **132** (2010) *014108*
TF, H.J.Aa. Jensen, J. Olsen, L. Visscher, *J Chem Phys* **124** (2006) *104106*

Correlated Wavefunction Theory for $\mathbf{E}_{\mathrm{eff}}$

- Dirac-Coulomb Hamiltonian operator

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

- All-electron Dirac-Coulomb Hartree-Fock (DCHF) calculation

  set of time-reversal paired 4-spinors $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

- Expansion and variation[18] in n-electron sector of Fock space

$$|\psi_k\rangle = \sum_{I=1}^{\dim \mathcal{F}^{\mathrm{t}}(\mathrm{M,n})} c_{kI} \left| (\mathcal{S}\overline{\mathcal{T}})_I \right\rangle$$

  Expectation values over relativistic Configuration Interaction wavefunctions[19]

$$\left\langle \hat{H}_{\mathrm{EDM}} \right\rangle_{\psi_k^{(0)}} = \sum_{I,J=1}^{\dim \mathcal{F}^{\mathrm{t}}(\mathrm{M,n})} c_{kI}^* c_{kJ} \left\langle (\mathcal{S}\overline{\mathcal{T}})_I \right| \frac{2\imath c d_e}{e\hbar} \sum_{j=1}^{n} \gamma^0(j)\gamma^5(j)\, \vec{p}(j)^{\,2} \left| (\mathcal{S}\overline{\mathcal{T}})_J \right\rangle$$

[18] S Knecht, H J Aa Jensen, TF, *J Chem Phys* **132** (2010) *014108*

[19] TF and M K Nayak, *Phys Rev A* **88** (2013) *032514*

Search for the Electron EDM

Why molecules?

Be an atom in a parity eigenstate $\hat{\mathcal{P}}\,|\psi_p\rangle = \prod_{i=1}^{n} \hat{p}(i)\,\hat{\mathcal{A}}\,|\varphi_a(1)\ldots\varphi_m(n)\rangle$. Then

$$\begin{aligned}\left\langle\psi_p|\hat{H}_{\rm EDM}|\psi_p\right\rangle &= \left\langle\psi_p|\hat{\mathcal{P}}^\dagger\hat{\mathcal{P}}\hat{H}_{\rm EDM}\hat{\mathcal{P}}^\dagger\hat{\mathcal{P}}|\psi_p\right\rangle = -p^2\left\langle\psi_p|\hat{H}_{\rm EDM}|\psi_p\right\rangle \\ &= -\left\langle\psi_p|\hat{H}_{\rm EDM}|\psi_p\right\rangle = 0\end{aligned}$$

Parity eigenstates need to be mixed (polarization).

1. A perturbing laboratory $\mathbf{E}$ field is required to mix parity eigenstates.
   Tl experiment[20] $E_{\rm eff} \approx 0.05\,\left[\frac{\rm GV}{\rm cm}\right]$

2. Molecular fields:
   YbF[21]: $E_{\rm eff} \approx 26\,\left[\frac{\rm GV}{\rm cm}\right]$, HgF[22]: $E_{\rm eff} \approx 100\,\left[\frac{\rm GV}{\rm cm}\right]$,

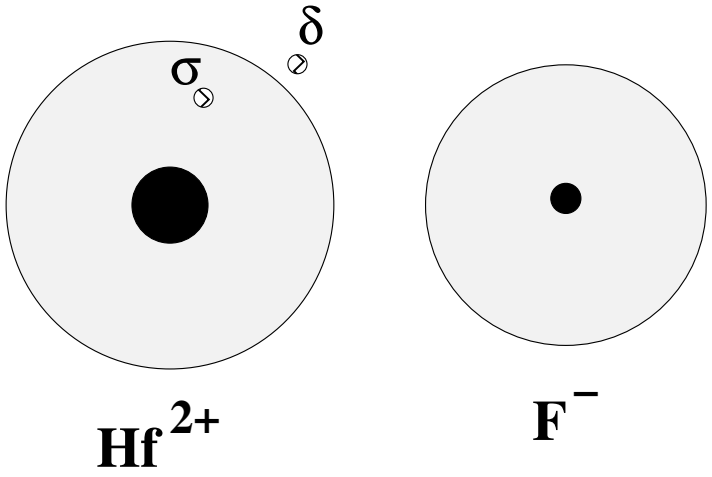
[20] V.V. Flambaum, *Sov J Nucl Phys* **24** (1976) *199*

[21] D.M. Kara, I.J. Smallman, J.J. Hudson, B.E. Sauer, M.R. Tarbutt, E.A. Hinds, *New J Phys* **14** (2012) *103051*

[22] Dmitriev et al., *Phys Lett* **167A** (1992) *280*

The eEDM in a molecular framework

$^3\Delta$ molecules[23]



- One heavy nucleus (relativistic effect)
- One "science" electron (σ^1)
  one "spectroscopy" electron (δ^1)
- Large $E_{\rm eff}$ for σ^1 electron

- Deeply bound and strongly polar molecules (fluorides, oxides, (nitrides))
- Small Λ (Ω)-doublet splitting[24] (optimal polarization)
- Large rotational constant (one heavy, one light atom)
- $\Omega = 1$ component preferred (small magnetic moment)

  $\Rightarrow$ Low-lying $^3\Delta_1$ as "science" state

[23] E. Meyer, J. Bohn, D.A. Deskevich, *Phys Rev A* **73** (2006) *062108*

[24] TF, C.M. Marian, *J Mol Spectrosc* **178** (1996) *1*

ThO

ACME Collaboration, Yale/Harvard, (DeMille/Doyle/Gabrielse groups)

Universe Colloquium, TUM München, April 22, 2015

Most Recent Measurement: ThO Molecule

ACME Collaboration, Harvard/Yale

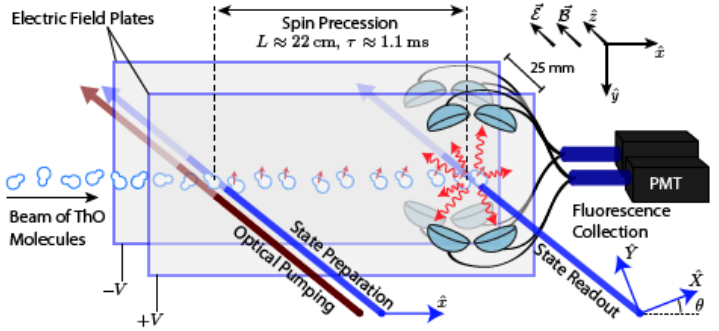
Order of Magnitude Smaller Limit on the Electric Dipole Moment of the Electron

The ACME Collaboration*: J. Baron[1], W. C. Campbell[2], D. DeMille[3], J. M. Doyle[1], G. Gabrielse[1], Y. V. Gurevich[1,**], P. W. Hess[1], N. R. Hutzler[1], E. Kirilov[3,#], I. Kozyryev[3,†], B. R. O'Leary[3], C. D. Panda[1], M. F. Parsons[1], E. S. Petrik[1], B. Spaun[1], A. C. Vutha[4], and A. D. West[3]

The Standard Model (SM) of particle physics fails to explain dark matter and why matter survived annihilation with antimatter following the Big Bang. Extensions to the SM, such as weak-scale Supersymmetry, may explain one or both of these phenomena by positing the existence of new particles and interactions that are asymmetric under time-reversal (T). These theories nearly always predict a small, yet potentially measurable (10^{-27}-10^{-30} e cm) electron electric dipole moment (EDM, d_e), which is an asymmetric charge distribution along the spin ($\vec{S}$). The EDM is also asymmetric under T. Using the polar molecule thorium monoxide (ThO), we measure $d_e = (-2.1 \pm 3.7_{\rm stat} \pm 2.5_{\rm syst}) \times 10^{-29}$ e cm. This corresponds to an upper limit of $|d_e| < 8.7 \times 10^{-29}$ e cm with 90 percent confidence, an order of magnitude improvement in sensitivity compared to the previous best limits. Our result constrains T-violating physics at the TeV energy scale.

The exceptionally high internal effective electric field ($\mathcal{E}_{\rm eff}$) of heavy neutral atoms and molecules can be used to precisely probe

is prepared using optical pumping and state preparation lasers. Parallel electric ($\vec{\mathcal{E}}$) and magnetic ($\vec{\mathcal{B}}$) fields exert torques on the electric and magnetic dipole moments, causing the spin vector to precess in the xy plane. The precession angle is measured with a readout laser and fluorescence detection. A change in this angle as $\vec{\mathcal{E}}_{\rm eff}$ is reversed is proportional to d_e.



Science **6168** (2014) *269*

Electron Electric Dipole Moment and Hyperfine Interaction Constants for ThO

Timo Fleig[1] and Malaya K. Nayak[2]

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[2] *Bhabha Atomic Research Centre, Trombay, Mumbai - 400085, India*

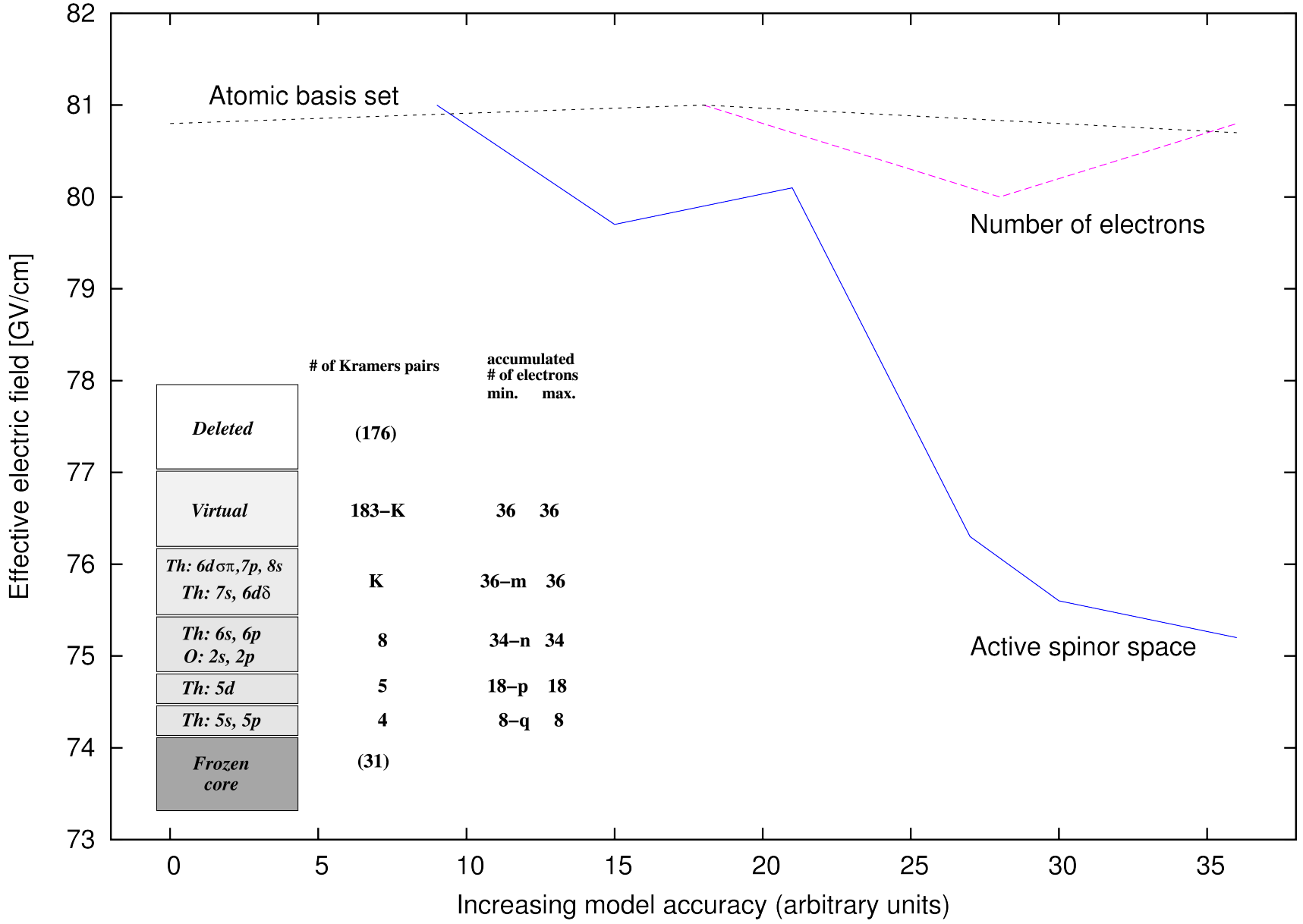
(Dated: June 10, 2014)

A recently implemented relativistic four-component configuration interaction approach to study $\mathcal{P}$- and $\mathcal{T}$-odd interaction constants in atoms and molecules is employed to determine the electron electric dipole moment effective electric field in the $\Omega = 1$ first excited state of the ThO molecule. We obtain a value of $E_{\rm eff} = 75.2\,\left[\frac{\rm GV}{\rm cm}\right]$ with an estimated error bar of 3% and 10% smaller than a previously reported result [*J. Chem. Phys.*, 139:221103, 2013]. Using the same wavefunction model we obtain an excitation energy of $T_v^{\Omega=1} = 5410\ [{\rm cm}^{-1}]$, in accord with the experimental value within 2%. In addition, we report the implementation of the magnetic hyperfine interaction constant $A_{||}$ as an expectation value, resulting in $A_{||} = -1339$ [MHz] for the $\Omega = 1$ state in ThO. The smaller effective electric field increases the previously determined upper bound [*Science*, 343:269, 2014] on the electron electric dipole moment to $|d_e| < 9.7 \times 10^{-29}\, e\,{\rm cm}$ and thus mildly mitigates constraints to possible extensions of the Standard Model of particle physics.

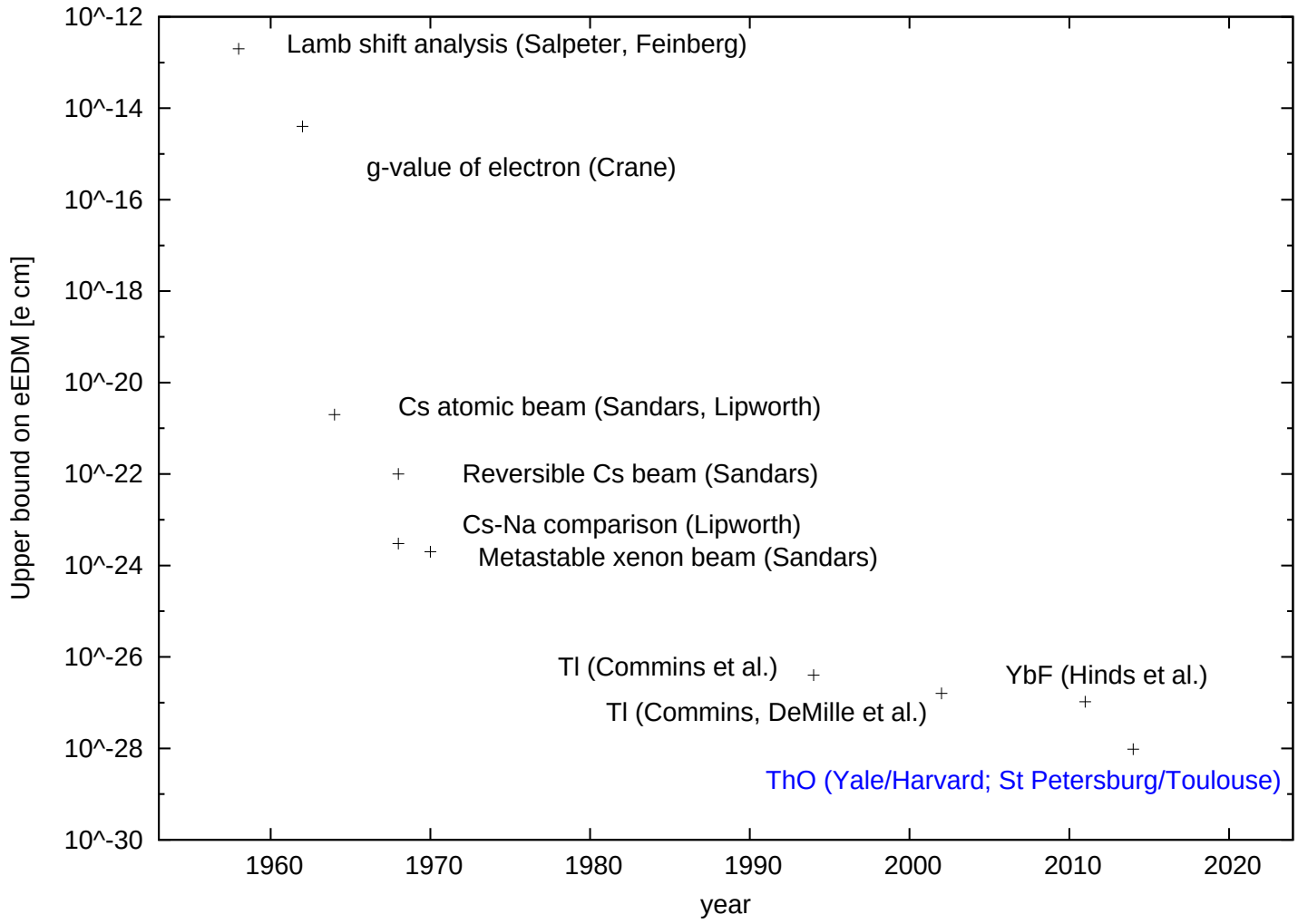
1401.2284v2

J Mol Spectrosc **300** (2014) *16*

The eEDM in ThO ($\Omega = 1$)

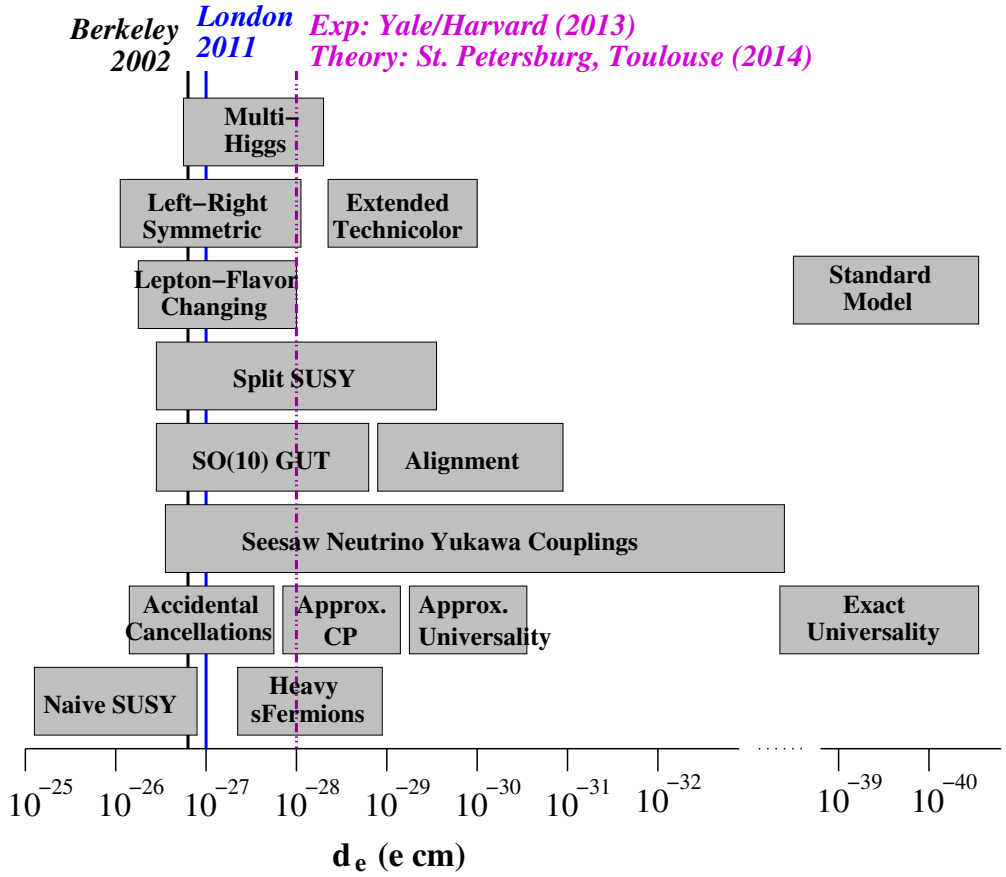


Historical Development of eEDM Upper Bound[25]



[25] Sandars (1975), Commins, DeMille (2008)

eEDM Constraint on Beyond-Standard-Model Theories[26]



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 (Tl)[27]	$< 1.6 \cdot 10^{-27}$
Experimental limit (YbF)[28]	$< 10.5 \cdot 10^{-28}$
Experimental limit (ThO)[29]	$< 9.6 \cdot 10^{-29}$

[26] Courtesy: DeMille (2005), Huliyar (2009)

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

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

[29] D. DeMille, ICAP 2014, Washington D.C., ACME Collaboration, *Science* **6168** (2014) *269*, TF and M. K. Nayak, *J. Mol. Spectrosc.* **300** (2014) *16*, L. V. Skripnikov, A. N. Petrov, A. V. Titov, *J. Chem. Phys.* **139** (2013) *221103*, L. V. Skripnikov, A. V. Titov, *J. Chem. Phys.* **142** (2015) *024301*

Molecular (cat)ions

HfF^+/ThF^+

JILA, Boulder, Colorado (Cornell group)

Universe Colloquium, TUM München, April 22, 2015

EDM Studies in Molecular Ions

as opposed to neutral molecules[30]

- Valence isoelectronic with neutral contenders (ThO, WC, $et\ al.$)
- Sufficiently large value of E_{eff}
  Hope for very large value[31] in ThF^+ due to $Z = 90$
- Use of ion traps and rotating electric fields
  $\Rightarrow$ Long interrogation times
- A related point:
  HfF^+ electronic ground state: $^1\Sigma_0^+$
  ThF^+ electronic ground state[32]: $^3\Delta_1$ **or** $^1\Sigma_0^+$

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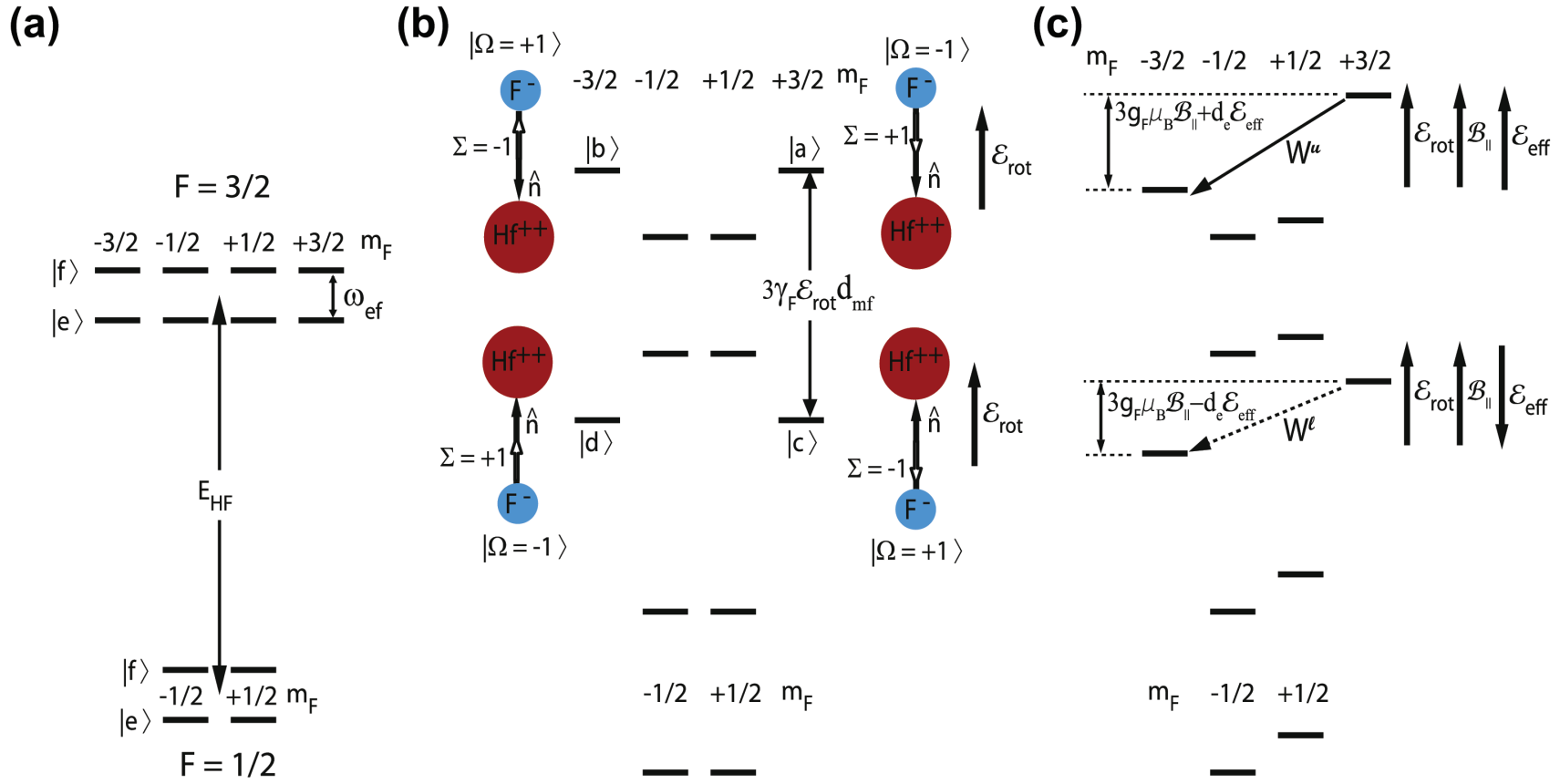
[30] H. Loh, K.C. Cossel, M.C. Grau, K.-K. Ni, E.R. Meyer, J.L. Bohn, J. Ye, E.A. Cornell, *Science* **342** (2013) *1220*
A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

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

[32] M. Denis, M.N. Pedersen, H.J.Aa. Jensen, A.S.P. Gomes, M.K. Nayak, S. Knecht, TF, *New J Phys* (2015) **7** (2015) 043005
B. Barker, I.O. Antonov, M.C. Heaven, K.A. Peterson, *J Chem Phys* **136** (2012) *104305*

The eEDM in a molecular framework

A Proposed Measurement[33] on HfF^+



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

[33] 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*

Molecular Wavefunctions from CC and CI

		Th spinor distribution on spaces				
	Model	4f5s5p	5d	6s6p	5f6d7s	7p7d8s8p6f
IHFSCC	$\mathcal{I}^{\mathcal{CC}}$	frozen	frozen	Q	P_m	P_i
	$\mathcal{II}^{\mathcal{CC}}$	frozen	Q	Q	P_m	P_i
	$\mathcal{III}^{\mathcal{CC}}$	Q	Q	Q	P_m	P_i
MRCI	$\mathcal{I}^{\mathcal{CI}}$	frozen	$Q-S$	$Q-S$	P_m	$Q-SD$
	$\mathcal{II}^{\mathcal{CI}}$	frozen	$Q-SD$	$Q-SD$	P_m	$Q-SD$

Model	Th $6s$,$6p$ F $2s$,$2p$	Th $7s$,$6d\delta$	Th $6d\pi$	Th $6d\sigma$,$7p\pi$	Th $7p\sigma$,$8s$	<10 a.u
$\mathcal{III}^{\mathcal{CI},3}$	$Q-SD$	P_m	$Q-SD$	$Q-SD$	$Q-SD$	$Q-SD$
$\mathcal{III}^{\mathcal{CI}+T,3}$	$Q-SD$	P_m	$Q-SDT$	$Q-SDT$	$Q-SDT$	$Q-SDT$
$\mathcal{III}^{\mathcal{CI},5}$	$Q-SD$	P_m	P_m	$Q-SD$	$Q-SD$	$Q-SD$
$\mathcal{III}^{\mathcal{CI},8}$	$Q-SD$	P_m	P_m	P_m	$Q-SD$	$Q-SD$
$\mathcal{III}^{\mathcal{CI},10}$	$Q-SD$	P_m	P_m	P_m	P_m	$Q-SD$
$\mathcal{IV}^{\mathcal{CI}}$	frozen	P_m	P_m	P_m	P_m	$Q-SD$

Low-Lying Electronic States[34] of ThF^+

Method	Model[a]	Hamiltonian	Electronic state energy				
			$^1\Sigma^+_{0+}$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$	$^3\Pi_{0-}$
IHFSCC	$\mathcal{IC}^{\mathcal{CC}}$	2c	285.29	0.00	1063.29	3096.14	5228.76
	$\mathcal{IIC}^{\mathcal{CC}}$	2c	27.89	0.00	1070.40	3166.36	4690.68
	$\mathcal{IIC}^{\mathcal{CC},\dagger}$	2c	42.16	0.00	1062.01	3146.00	4499.13
	$\mathcal{IIIC}^{\mathcal{CC},\dagger}$	2c	15.25	0.00	1062.22	3149.47	4510.50
	$\mathcal{IIIC}^{\mathcal{CC},\ddagger}$	2c	190.85	0.00	1048.27	3156.71	4123.14
	$\mathcal{IIIC}^{\mathcal{CC},\S}$	2c	0.00	108.26	1157.05	3235.93	4415.96
	$\boldsymbol{\mathcal{IIIC}^{\mathcal{CC},*}}$	**2c**	**318.99**	**0.00**	**1038.94**	**3161.99**	**3841.17**
MRCI	$\mathcal{IC}^{\mathcal{CI}}$	2c	854.32	0.00	1154.40	3188.81	3387.74
	$\mathcal{IIC}^{\mathcal{CI}}$	2c	630.04	0.00	1166.86	2986.27	-
CCSD(T)+SO[b]			500.7	0.0	889.5	2156.8	
CCSDT+SO[b]			143.3	0.0	889.7	2157.1	
CCSDT(Q)+SO[b]			0.0	65.5	955.3	2222.9	
Experiment[b]			0.00	315.0(5)	1052.5(5)	3150(15)	3395(15)

[34] [a] M. Denis, M.N. Pedersen, H.J.Aa. Jensen, A.S.P. Gomes, M.K. Nayak, S. Knecht, TF, *New J Phys* **7** (2015) *043005*
[b] B. Barker, I.O. Antonov, M.C. Heaven, K.A. Peterson, *J Chem Phys* **136** (2012) *104305*

$\mathcal{P},\mathcal{T}$-Odd Interactions in ThF^+ ($\Omega = 1$)

Basis Sets

Basis set	$T_v[\mathrm{cm}^{-1}]$	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	$A_{\|\|}$[MHz]	$W_{P,T}$[kHz]
DZ	378	37.8	1824	51.90
TZ'	787	36.9	1836	50.73
QZ'	877	36.9	1830	50.77

Vertical excitation energy for $\Omega = 0^+$, electron EDM effective electric field, magnetic hyperfine interaction constant, and scalar-pseudoscalar electron-nucleon interaction constant for $\Omega = 1$ at an internuclear distance of $R = 3.779\ a_0$ using basis sets with increasing cardinal number and the wavefunction model $\mathcal{III}^{\mathcal{CI},5}$.

Magnetic hyperfine interaction constant:

$$A_{||} = \frac{\mu_A}{I\Omega} \left\langle \sum_{i=1}^{n} \left(\frac{\vec{\alpha}_i \times \vec{r}_{iA}}{r_{iA}^3} \right)_z \right\rangle_\psi$$

Scalar-pseudoscalar electron-nucleon interaction constant:

$$W_{P,T} = \frac{\imath}{\Omega} \frac{G_F}{\sqrt{2}} Z \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5 \rho_N(\vec{r}_j) \right\rangle_\psi$$

The eEDM in ThF^+ ($\Omega = 1$)

Active 4-Spinor Spaces

CI model(TZ basis)	$T_v[\mathrm{cm}^{-1}]$	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	$A_{\|\|}$[MHz]	$W_{P,T}$[kHz]
$\mathcal{IV}^{\mathcal{CI}}$	274	35.4	1749	49.44
$\mathcal{III}^{\mathcal{CI},3}$	1029	47.5	1842	65.78
$\mathcal{III}^{\mathcal{CI},5}$	787	36.9	1836	50.73
$\mathcal{III}^{\mathcal{CI},6}$	709	36.2	1836	49.90
$\mathcal{III}^{\mathcal{CI},8}$	598	35.6	1834	49.04
$\boldsymbol{\mathcal{III}^{\mathcal{CI},10}}$	538	**35.2**	**1833**	**48.35**
$\mathcal{III}^{\mathcal{CI},12}$		35.1	1832	

Vertical excitation energy for $\Omega = 0^+$, electron EDM effective electric field, magnetic hyperfine interaction constant, and scalar-pseudoscalar electron-nucleon interaction constant for $\Omega = 1$ at an internuclear distance of $R = 3.779\ a_0$ using the TZ' basis set, varying number of correlated electrons and varying active spinor spaces.

- Large active space $\Rightarrow$ shifts electron density from Th(s) to Th(p) and Th(d), reducing E_{eff}.

The eEDM in ThF^+ ($\Omega = 1$)

Higher Excitations

CI model(DZ basis)	$T_v[\mathrm{cm}^{-1}]$	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	$A_{\|\|}$[MHz]	$W_{P,T}$[kHz]
$\mathcal{III}^{\mathcal{CI},3}$	654	47.0	1830	64.92
$\mathcal{III}^{\mathcal{CI},10}$	88	37.1	1832	51.06
$\mathcal{III}^{\mathcal{CI}+T,3}$	247	35.4	1834	48.64

Vertical excitation energy for $\Omega = 0^+$, electron EDM effective electric field, magnetic hyperfine interaction constant, and scalar-pseudoscalar electron-nucleon interaction constant for $\Omega = 1$ at an internuclear distance of $R = 3.779\ a_0$ using the DZ basis set and varying maximum excitation rank.

- Active space accounts for important higher excitations

ThF^+

Static Molecular Electric Dipole Moment

${}^M\Lambda_\Omega$ State	T_v [cm^{-1}]	$\left\langle {}^M\Lambda_\Omega \middle\vert \hat{D}_z \middle\vert {}^M\Lambda_\Omega \right\rangle$ [D]
${}^1\Sigma_0^+$	630	3.941
${}^3\Delta_1$	0	4.029
${}^3\Delta_2$	1167	3.970
${}^3\Delta_3$	2986	4.034

Molecular static electric dipole moments $\left\langle {}^M\Lambda_\Omega \middle\vert \hat{D}_z \middle\vert {}^M\Lambda_\Omega \right\rangle$, with $\hat{\vec{D}}$ the electric dipole moment operator, using the TZ basis set and the CI model $\mathcal{II}^{\mathcal{CI}}$. The origin is at the center of mass, and the internuclear distance is $R = 3.779$ $[a_0]$ (F nucleus at $z\vec{e}_z$ with $z < 0$).

- Very large center-of-mass dipole moment
  Effectively polarizable, suggest large value of E_{eff}

ThF^+

Electric Transition Dipole Moments

$^M\Lambda_\Omega$ State	Tv [cm^{-1}]	$^1\Sigma_0^+$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$	$^1\Sigma_0(^3\Pi_0)$	$^3\Pi_0$	$^{1,3}\Pi_1(^3\Sigma_1)$	$^3\Pi_0(^1\Sigma_0)$
$^1\Sigma_0^+$	274	−4.004							
$^3\Delta_1$	0	0.012	−4.075						
$^3\Delta_2$	724	0.000	0.070	−4.022					
$^3\Delta_3$	2198	0.000	0.000	0.052	−4.075				
$^1\Sigma_0(^3\Pi_0)$	6344	0.439	0.455	0.000	0.000	−3.752			
$^3\Pi_0$	6528	0.000	0.571	0.000	0.000	0.000	−2.116		
$^{1,3}\Pi_1(^3\Sigma_1)$	6639	0.868	0.142	0.218	0.000	0.197	0.000	−2.375	
$^3\Pi_0(^1\Sigma_0)$	6747	0.003	0.391	0.000	0.000	0.929	0.000	0.094	−2.717
$^{1,3}\Delta_2(^3\Pi_2)$	7008	0.000	0.473	0.334	0.298	0.000	0.000	0.529	0.000
$^3\Sigma_1$	7490	0.226	0.069	0.221	0.000	0.136	0.197	0.451	0.145
$^{1,3}\Pi_1$	7918	0.667	0.052	0.801	0.000	0.011	0.064	0.107	0.043
$^3\Phi_2(^3\Pi_2)$	8245	0.000	1.338	0.234	0.272	0.000	0.000	0.134	0.000

Electric transition dipole moments $\left|\left|\left\langle {}^M\Lambda'_\Omega|\hat{\vec{D}}|{}^M\Lambda_\Omega\right\rangle\right|\right|$, with $\hat{\vec{D}}$ the electric dipole moment operator, and vertical transition energies for low-lying electronic states in [D] units using the TZ' basis set and the CI model $\mathcal{IV}^{\mathcal{CI}}$. The origin is at the center of mass, and the internuclear distance is $R = 3.779$ $[a_0]$. $\left({}^M\Lambda_\Omega\right)$ denotes a term contributing at least 10% to the state. ^{1,3} denotes cases where Λ-S coupling breaks down significantly according to the analysis of our spinor-based ω-ω coupled wavefunctions.

HfF^+ and ThF^+: E_{eff} in the $\Omega = 1$ science state[35]

HfF^+		ThF^+	
Model	$E_{\mathrm{eff}}\ \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$	Model	$E_{\mathrm{eff}}\ \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$
CAS-CI(10)	24.1		
MR-CISD(10)	22.4		
MR-CISD(20)	23.3	MR_3-CISD(18)	47.5
MR-CISD+T(20)	23.7	MR_6-CISD(18)	36.2
MR-CISD(34)	23.3	MR_{10}-CISD(18)	35.2
MR-CISD(34)+T	23.3	MR_3-CISDT(18)	35.4
Estimate, Meyer et al.[36]	≈ 30	Meyer et al.	≈ 90
20 e^- corr., Titov et al.[37]	24.2	38 e^- corr., Titov et al.[38]	≈ 37.3

(HfF^+)

Similar results with various methods
System currently under exp. study

(ThF^+)

Meyer's model inaccurate
CC and CI approaches yield similar results

[35] TF and M.K. Nayak, *Phys Rev A* **88** (2013) *032514*
M. Denis, M. K. Nørby, H. J. Aa. Jensen, A. S. P. Gomes, M.K. Nayak, S. Knecht, TF, *New J Phys* **7** (2015) *043005*
[36] E.R. Meyer, J.L. Bohn, *Phys Rev A* **78** (2008) *010502(R)*
[37] A.N. Petrov, N.S. Mosyagin, T.A. Isaev, A.V. Titov, *Phys Rev A* **76** (2007) *030501(R)*
[38] L. V. Skripnikov, A.V. Titov, *arXiv:1503.01001v1* (2015)

Nuclear Magnetic Quadrupole Moment

TaN

Constraining $\mathcal{P}$,$\mathcal{T}$-violating hadron physics

- Nuclear MQM has two possible sources[39]:
  1. Intranuclear $\mathcal{P}$-,$\mathcal{T}$-odd interactions, described by QCD $(\mathcal{CP})$-violating parameter[40] $\tilde{\Theta}$,
  $$M_0^{p,n}(\tilde{\Theta}) \approx 2 \times 10^{-29}\, \tilde{\Theta}\, e\,\mathrm{cm}^2$$
  M: valence nucleon MQM
  2. Neutron/proton EDM (order of magnitude smaller)

- MQM is enhanced in non-spherical (deformed) nuclei[41]

- Enhancement[41] of ≈ 12 in ^{181}Ta, compared to $M_0^{p,n}$

- TaN is a "$^3\Delta$ molecule", experiments planned at ACME (Yale/Harvard)

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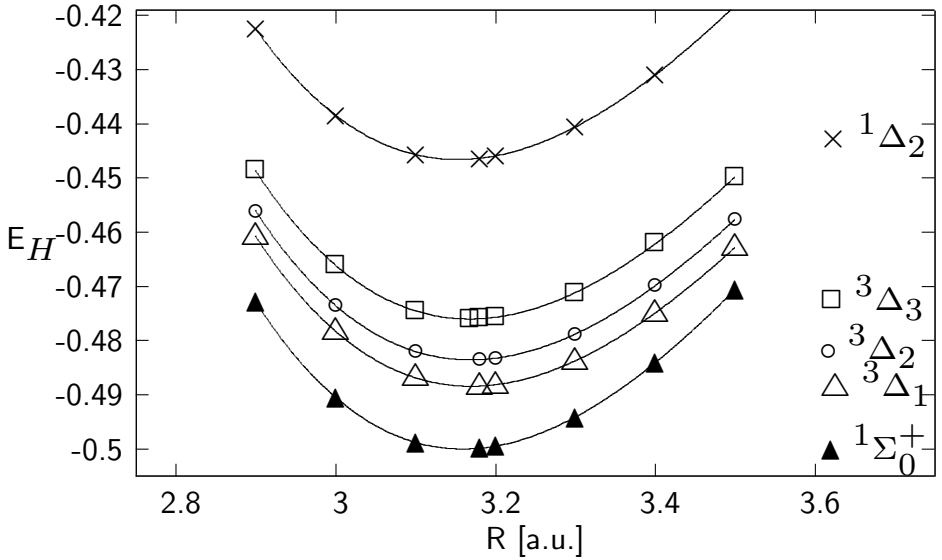
[39] V. V. Flambaum, D. DeMille, M. G. Kozlov, *Phys Rev Lett* **113** (2014) *103003*

[40] R. J. Crewther, P. Di Vecchia, G. Veneziano, E. Witten, *Phys Lett* **88B** (1979) *123*

[41] V. V. Flambaum, *Phys Lett B* **320** (1994) *211*

TaN, Spectroscopic properties

State	Model	R_e [a.u.]	ω_e [cm^{-1}]	B_e [cm^{-1}]	T_e [cm^{-1}]
	av. DCHF	3.115	1163	0.477	0
$^1\Sigma_0^+$	MR_{12}-CISD(10)	3.160	1161	0.464	0
	Exp.[42]	3.181	1070		0.0
$^3\Delta_1$	MR_{12}-CISD(10)	3.170	1116	0.461	2526
	Exp.[42]	3.196			2827.2917
$^3\Delta_2$	MR_{12}-CISD(10)	3.169	1117	0.461	3618
$^3\Delta_3$	MR_{12}-CISD(10)	3.168	1119	0.462	5276
$^1\Delta_2$	MR_{12}-CISD(10)	3.153	1123	0.466	11729



- Strongly bound molecule
- Low-lying "science state" $^3\Delta_1$ (long lifetime)
- Mol. dipole moment: ?

[42] M. Zhou, L. Andrews, *J Phys Chem A* **102** (1998) *9061*; R. S. Ram, J. Liévin, P. F. Bernath, *J Mol Spectrosc* **215** (2002) *275*

Molecular Nuclear Magnetic Quadrupole Moment

Theory

Effective molecular Hamiltonian

$$\hat{H} = -\frac{W_M\, M}{2I(2I-1)}\, \mathbf{J_e}\, \hat{\mathbf{T}}\, \mathbf{n}$$

with the components of the nuclear MQM

$$M_{i,k} = \frac{3M}{2I(2I-1)}\, T_{i,k} \qquad T_{i,k} = I_i I_k + I_k I_i - \frac{2}{3}\, \delta_{i,k}\, I(I+1),$$

with the nuclear MQM interaction constant

$$W_M := \frac{3}{2\Omega} \left\langle \Psi_\Omega \left| \sum_{j=1}^{n} \left(\frac{\boldsymbol{\alpha}_j \times \mathbf{r}_{jA}}{r_{jA}^5} \right)_k (r_{jA})_k \right| \Psi_\Omega \right\rangle$$

Implementation for a many-electron linear molecule:

$$W_M = \frac{3}{2\Omega} \sum_{I,J=1}^{\dim \mathcal{F}^{\mathrm{t}}(\mathrm{M,N})} c_{kI}^* c_{kJ} \left\langle (\mathcal{S}\overline{\mathcal{T}})_I \right| \sum_{j=1}^{n} \left(\frac{\boldsymbol{\alpha}_j \times \mathbf{r}_{jA}}{r_{jA}^5} \right)_z (r_{jA})_z \left| (\mathcal{S}\overline{\mathcal{T}})_J \right\rangle$$

Calculation via electric-field gradient with the help of

$$\left(\frac{\boldsymbol{\alpha}\times\mathbf{r}}{r^5}\right)_z r_z = \alpha_1 \frac{x_2 x_3}{r^5} - \alpha_2 \frac{x_1 x_3}{r^5}$$

Molecular Nuclear Magnetic Quadrupole Moment

Results for ^{181}TaN, $\Omega = 1$

Cutoff/CI Model	$E_{\text{eff}}\ [\frac{\text{GV}}{\text{cm}}]$	$A_{\|\|}$ [MHz]	$W_{P,T}$ [kHz]	$W_M\ [\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$
vTZ-30a.u./MR_{12}-CISD(10)	30.1	3104	27.4	1.898
vTZ-30a.u./MR_{12}^{+T}-CISD(10)	*31.5*	*3053*	*28.7*	*1.94*
Mosyagin *et al.*[43], Flambaum *et al.*[44]	25(YbF)			≈ 1

$\mu(^{181}\text{TaN}) = 2.35\mu_N \qquad I = \frac{7}{2}$

- EDM effective field (and $W_{P,T}$) sufficiently large
- NMQM interaction constant W_M significantly larger than earlier estimate

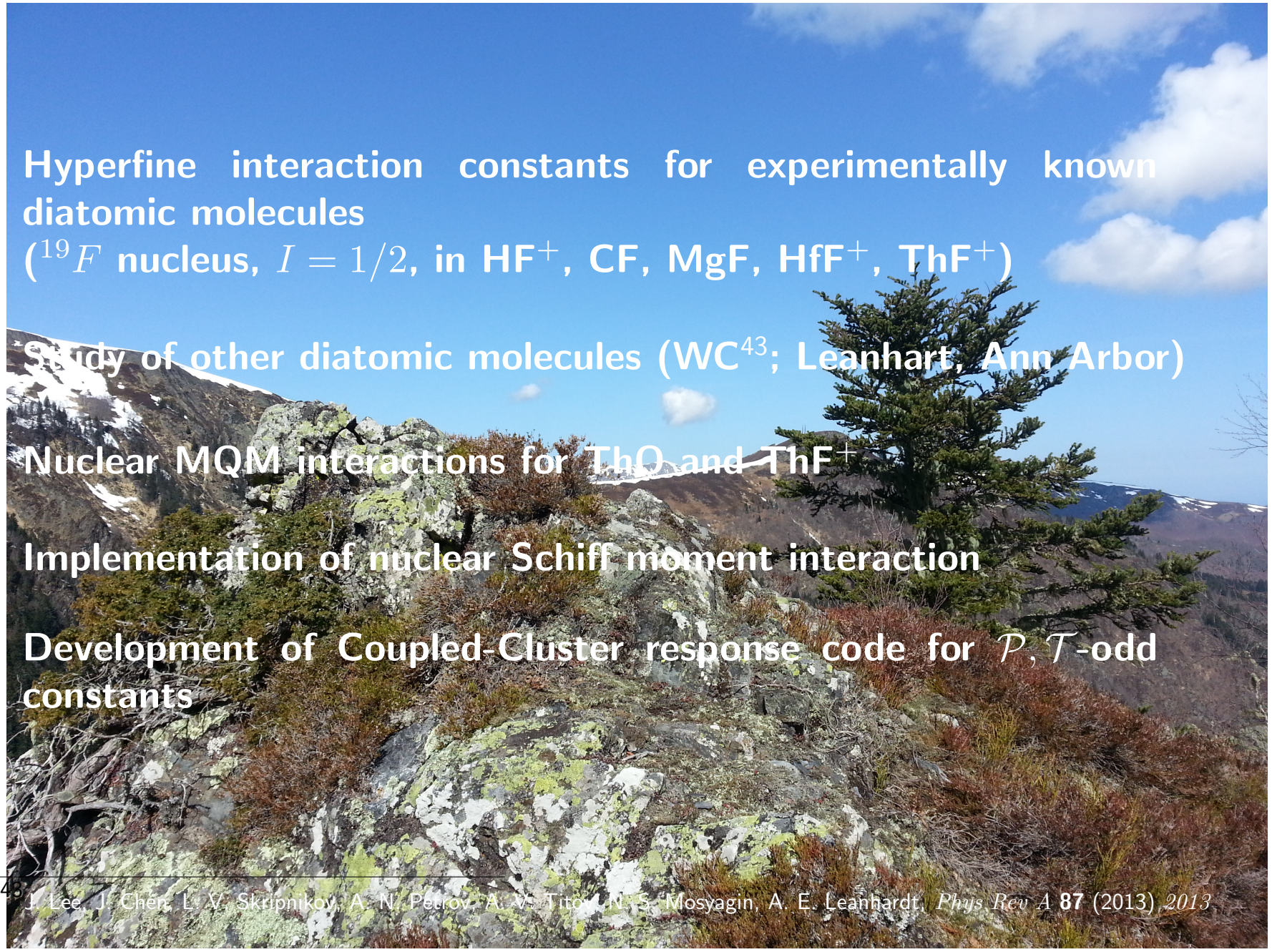
Reason:

- Estimate based on $W_M(\text{TaN}) \approx \frac{1}{2}W_M^{\sigma}(\text{YbF}) = 2.1[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$
- Spinor structures are very similar, and $Z(\text{Ta}) > Z(\text{Yb})$

[43] N. S. Mosyagin, M. G. Kozlov, A. V. Titov, *J Phys B* **31** (1998) *L763*

[44] V. V. Flambaum, D. DeMille, M. G. Kozlov, *Phys Rev Lett* **113** (2014) *103003*

Outlook



Hyperfine interaction constants for experimentally known diatomic molecules
(^{19}F nucleus, $I = 1/2$, in HF^+, CF, MgF, HfF^+, ThF^+)

Study of other diatomic molecules (WC^{43}; Leanhart, Ann Arbor)

Nuclear MQM interactions for ThO and ThF^+

Implementation of nuclear Schiff moment interaction

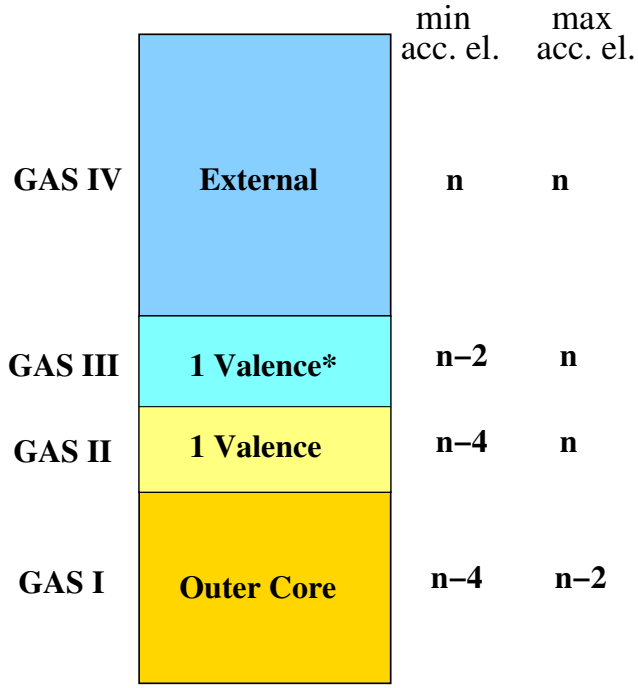
Development of Coupled-Cluster response code for $\mathcal{P},\mathcal{T}$-odd constants

J. Lee, J. Chen, L. V. Skripnikov, A. N. Petrov, A. V. Titov, N. S. Mosyagin, A. E. Leanhardt, *Phys Rev A* **87** (2013) *2013*

Relativistic Generalized-Active-Space Coupled Cluster

L. K. Sørensen, J. Olsen, TF, *J Chem Phys* **134** (2011) *214102*
TF, 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[21]
- GAS-extended excitation manifold
  $\langle \mu_{\mathrm{GASCC}}| = \langle \Phi_0 | \, \hat{\tau}^{\dagger}_{\mu_{\mathrm{GAS}}}$
- $\hat{\tau}_{\mu_{\mathrm{GAS}}}$ contains GAS-selected higher excitations
  $\left|\psi^{\mathrm{GASCC}}\right\rangle = exp(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu_{\mathrm{GAS}}}) \; |\Phi_0\rangle$
- 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:

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

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

Relativistic Generalized-Active-Space CC

Electronic Ground States [45]

CC vector function

$$\Omega_\mu = \left\langle \mu \left| \left(\hat{H} + \left[\hat{H},\hat{T}\right] + \tfrac{1}{2}\left[\left[\hat{H},\hat{T}\right],\hat{T}\right] \tfrac{1}{6}\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right] \ldots \right) \right| \Phi_0 \right\rangle$$

- 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.

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

[45] L. K. Sørensen, J. Olsen, TF, *J Chem Phys* **134** (2011) *214102*
L. K. Sørensen, TF, J. Olsen, *Z Phys Chem* **224** (2010) *999*

Relativistic Generalized-Active-Space CC

Excitation Energies[46]

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

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

Algorithm for Jacobian matrix elements[47]

- 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.

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

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

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

[47] L. K. Sørensen, J. Olsen, TF, *J Chem Phys* **134** (2011) *214102*
L. K. Sørensen, TF, J. Olsen, *Z Phys Chem* **224** (2010) *999*