In Search of Signatures of Beyond-Standard-Model Physics in Diatomic Molecules

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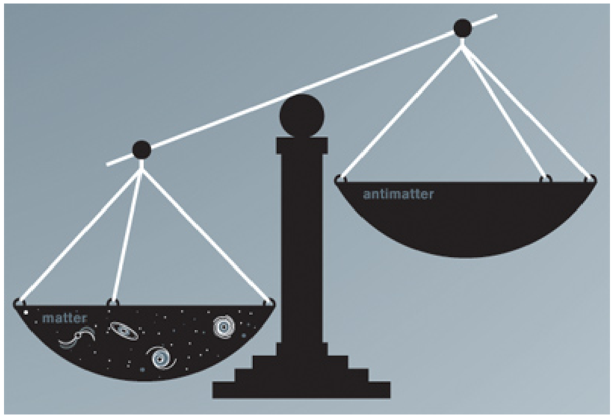
EDMe^-DM

Open Questions at Large Scale and at Small Scale



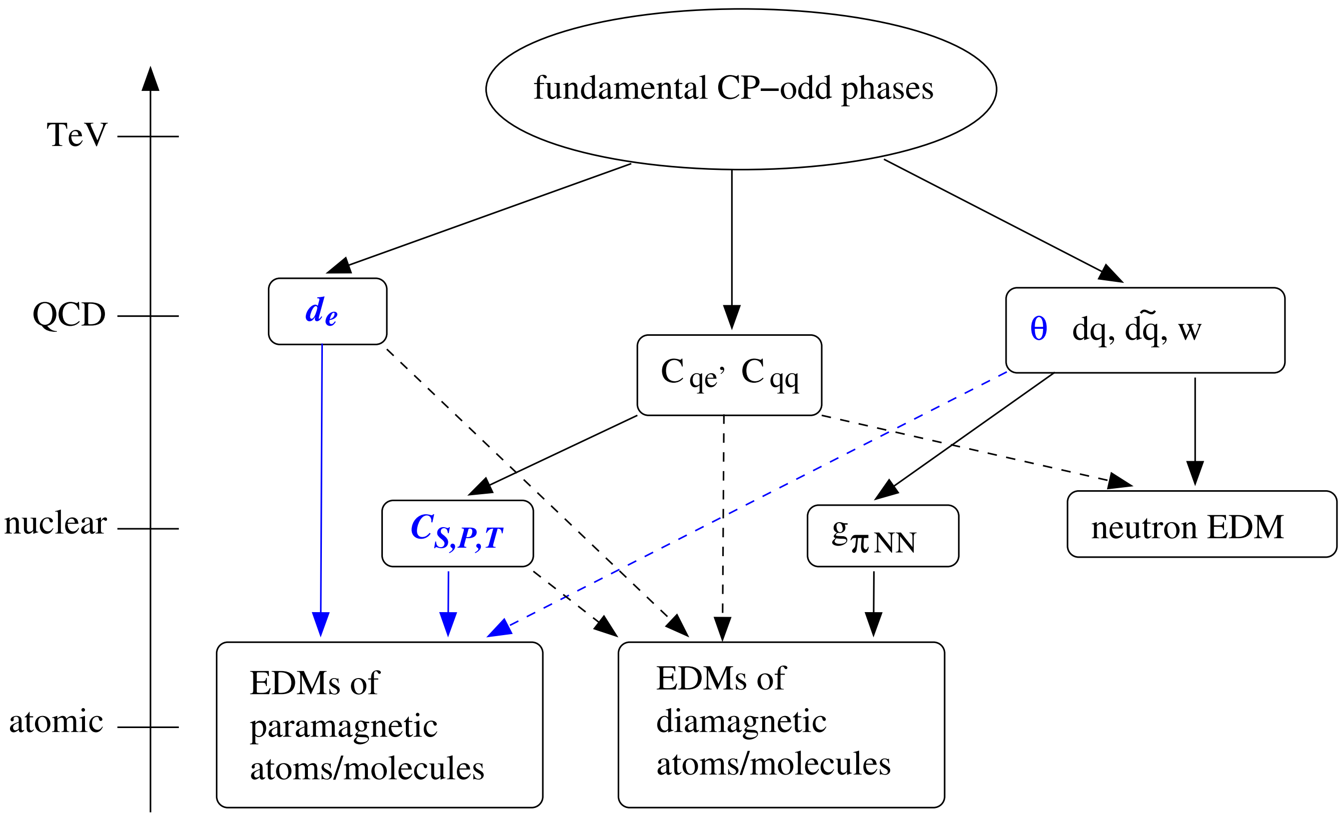
- **Matter-antimatter asymmetry** of the universe[1]
- Nature of **cold dark matter**
- Degree of $\mathcal{CP}$ **violation** in nature[2]

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

BSM physics
- HE frontier
- Cosmological frontier
- **Precision frontier**
  - HE physics
  - Nuclear physics
  - **Atomic/molecular physics**
    - experiment
    - **theory**

[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

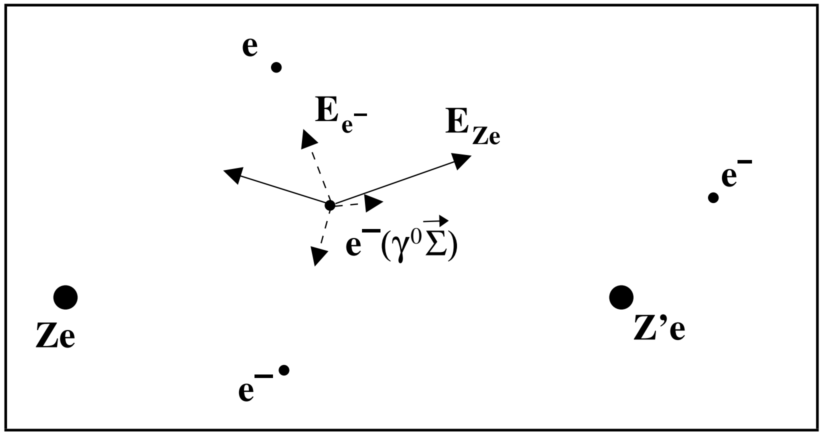
($\mathcal{P}$ and $\mathcal{T}$)-violating NMQM interaction

- 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*

Electron EDM Interaction

$$d_e = \frac{\Delta\epsilon}{E_{\rm eff}} \quad \begin{array}{c}\text{(Experiment)}\\ \text{(Theory)}\end{array}$$



Single-particle $\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[5]:

$$\hat{H}_{\rm EDM} = -\frac{d_e}{4}\gamma^0\gamma^5\left(\gamma^\mu\gamma^\nu - \gamma^\nu\gamma^\mu\right)F_{\mu\nu} = -d_e\gamma^0\left[\mathbf{\Sigma}\cdot\mathbf{E} + \imath\boldsymbol{\alpha}\cdot\mathbf{B}\right]$$

Internal electric field contributions

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

Expectation value in many-body system in accord with stratagem II[6]

$$-\left\langle \sum_{j=1}^{n}\gamma_j^0\,\mathbf{\Sigma}_j\cdot\mathbf{E}_j\right\rangle_{\psi^{(0)}} \approx \frac{2\imath c}{e\hbar}\left\langle\sum_{j=1}^{n}\gamma_j^0\gamma_j^5\,\vec{p}_j^{\;2}\right\rangle_{\psi^{(0)}} := E_{\rm eff}$$

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

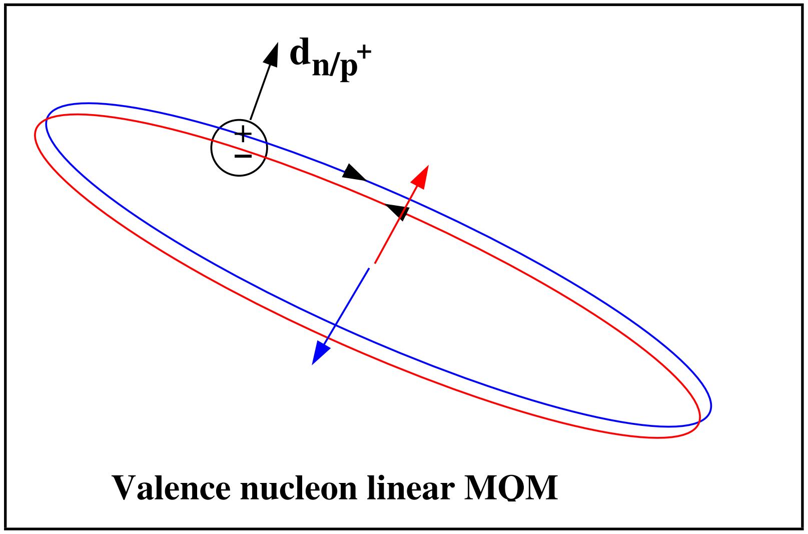
[6] E. Lindroth, E. Lynn, P.G.H. Sandars, *J Phys B: At Mol Opt Phys* **22** (1989) *559*

Nuclear Magnetic Quadrupole Moment Interaction[7]

Effective molecular Hamiltonian[8]
for linear molecule along $\mathbf{n}$:

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

W_M: MQM-electron-magnetic-field interaction constant



with the components of the nuclear MQM

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

$$W_M \propto \left(\frac{\boldsymbol{\alpha}\times\mathbf{r}}{r^5}\right)_3 x_3$$

Calculation[9] via electric-field gradient with the help of

$$\left(\frac{\boldsymbol{\alpha}\times\mathbf{r}}{r^5}\right)_3 x_3 = \alpha_1\, \frac{x_2 x_3}{r^5} - \alpha_2\, \frac{x_1 x_3}{r^5} \qquad \iiint_{\mathcal{V}} \frac{x_i x_j}{r^5}\, d^3x = \frac{1}{3} \iiint_{\mathcal{V}} \frac{\partial}{\partial x_i}\, \frac{x_j}{r^3}\, d^3x$$

[7] I.B. Khriplovich, *Sov. Phys. JETP* **44** (1976) *25*; O.P. Sushkov, V.V. Flambaum, I.B. Khriplovich, *Sov. Phys. JETP* **60** (1984) *873*
[8] V.V. Flambaum, D. DeMille, M.G. Kozlov, *Phys Rev Lett*, **113** (2014) *103003*
[9] TF, M.K. Nayak, M.G. Kozlov, *Phys Rev*, to be submitted

Correlated Wavefunction Theory for $\mathcal{P},\mathcal{T}$-odd Properties

- Dirac-Coulomb Hamiltonian operator

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

- 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[10] in n-electron sector of Fock space

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

unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$

barred (Kramers down) string $\overline{\mathcal{S}} = a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

  Expectation values over relativistic Configuration Interaction wavefunctions[11]

$$\left\langle \hat{H}' \right\rangle_{\psi_k^{(0)}} = \sum_{I,J=1}^{\dim \mathcal{F}^t(\mathrm{M,n})} c_{kI}^* c_{kJ} \, \langle\ | (\mathcal{S}\overline{\mathcal{T}})_I^\dagger \left| \hat{H}' \right| (\mathcal{S}\overline{\mathcal{T}})_J \,|\ \rangle$$

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

[11] S. Knecht, Dissertation, HHU Düsseldorf 2009

$\mathcal{P},\mathcal{T}$-odd Properties as Expectation Values

Interaction constants for n-electron system

- Electron eEDM interaction constant

$$W_d := \frac{2\imath c}{\Omega\, e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \vec{p}_j^{\;2} \right\rangle_{\psi_k^{(0)}} \qquad \left\langle \hat{H}_{\text{eEDM}} \right\rangle = d_e\, \Omega\, W_d$$

- S-PS electron-nucleon interaction constant

$$W_{\mathcal{P},\mathcal{T}} := \frac{\imath}{\Omega} \frac{G_F}{\sqrt{2}}\, Z \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \rho_N(\vec{r}_j) \right\rangle_{\psi_k^{(0)}} \qquad \left\langle \hat{H}_{\text{e-nSPS}} \right\rangle = k_s\, \Omega\, W_{\mathcal{P},\mathcal{T}}$$

- Nuclear magnetic quadrupole - electronic magnetic field interaction

$$W_M = \frac{3}{2\Omega} \left\langle \sum_{j=1}^{n} \left(\frac{\boldsymbol{\alpha}_j \times \mathbf{r}_{jA}}{r_{jA}^5} \right)_z (r_{jA})_z \right\rangle_{\psi_k^{(0)}}$$

Four-Spinor Based Generalized-Active-Space CI[12]

TaN sample system wavefunction parameterization

		# of Kramers pairs	accumulated # of electrons min.	max.
V	*Virtual*	110	18	18
IV	*Ta: 6p,7s,7p,π* *Ta: 6s, 5dδ*	K	18–q	18
III	*N: 2p (Ta: d)*	3	16–p	16
II	*N: 2s (Ta: d)*	1	10–n	10
I	*Ta: 5s, 5p*	4	8–m	8
	Frozen core	(31)		

GAS-extended projection manifold

$\left\langle \mu^{N}_{\mathrm{GASCI}} \right| = \left\langle \mu^{\text{particle space}}_{\text{hole space}} \right|$

Selected sub-sets of higher excitations in projection manifold:

$$\left\langle \mu^{T} \right| \in \left\{ \left\langle \mu^{IV^1,V^2}_{III^3} \right|, \ldots, \left\langle \mu^{IV^1,V^2}_{II^2,III^1} \right| \right\}$$

$$\left\langle \mu^{Q} \right| \in \left\{ \left\langle \mu^{IV^4}_{III^3,IV^1} \right|, \ldots, \left\langle \mu^{IV^2,V^2}_{III^3,IV^1} \right|, \ldots, \left\langle \mu^{IV^2,V^2}_{II^2,III^1,IV^1} \right| \right\}$$

$$\left\langle \mu^{5} \right| \in \left\{ \left\langle \mu^{IV^5}_{III^3,IV^2} \right|, \ldots, \left\langle \mu^{IV^3,V^2}_{III^3,IV^2} \right|, \ldots, \left\langle \mu^{IV^3,V^2}_{II^2,III^1,IV^2} \right|, \ldots, \left\langle \mu^{IV^3,V^2}_{I^1,II^1,III^1,IV^2} \right| \right\}$$

12 TF, J. Olsen, L. Visscher, *J Chem Phys* **119** (2003) *2963* , S. Knecht, H.J.Aa. Jensen, TF, *J Chem Phys* **132** (2010) *014108* , J. Olsen, *J Chem Phys* **113** (2000) *7140*

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

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

Parity eigenstates need to be mixed (polarization).

1. A perturbing laboratory $\mathbf{E}$ field is required to mix parity eigenstates.
   Tl experiment[13] $E_{\mathrm{eff}} \approx 0.05 \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$
2. Molecular fields:
   YbF[14]: $E_{\mathrm{eff}} \approx 26 \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$, HgF[15]: $E_{\mathrm{eff}} \approx 100 \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$,

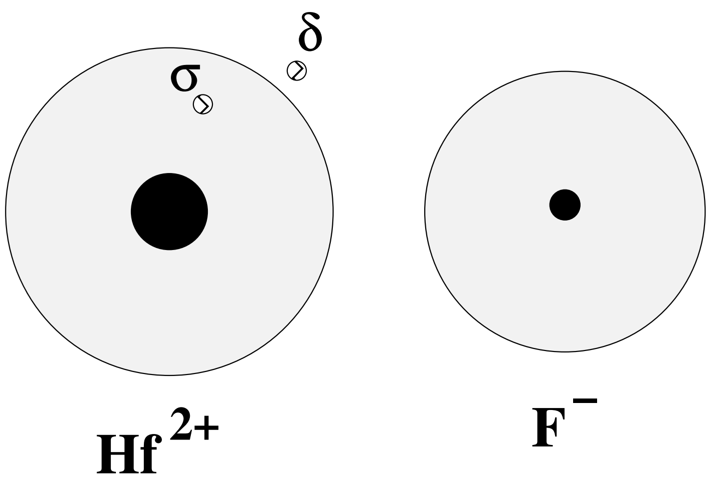
[13] V.V. Flambaum, *Sov J Nucl Phys* **24** (1976) *199*

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

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

The eEDM in a molecular framework

$^3\Delta$ molecules[16]



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

- Deeply bound and strongly polar molecules (fluorides, oxides, (nitrides))
- Small Λ (Ω)-doublet splitting[17] (optimal polarization)
- Small reduced mass (one heavy, one light atom)
- $\Omega = 1$ component preferred (small magnetic moment)

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

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

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

ThO

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

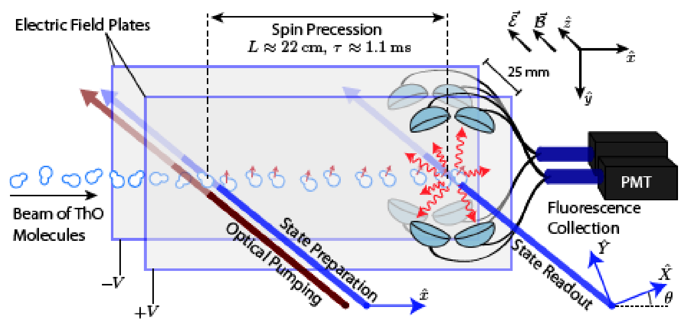
Order of Magnitude Smaller Limit on the Electric Dipole Moment of the Electron

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 $d_e = (-2.1 \pm 3.7_{\mathrm{stat}} \pm 2.5_{\mathrm{syst}}) \times 10^{-29}$ 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 ($\mathcal{E}_{\mathrm{eff}}$) of

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 $\vec{\mathcal{E}}_{\mathrm{eff}}$ is reversed is proportional to d_e.



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

Theory	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	$W_{P,T}$[kHz]
2c-CCSD(T)[18]	81.5	112
4c-MR-CISD[19]	75.2	105

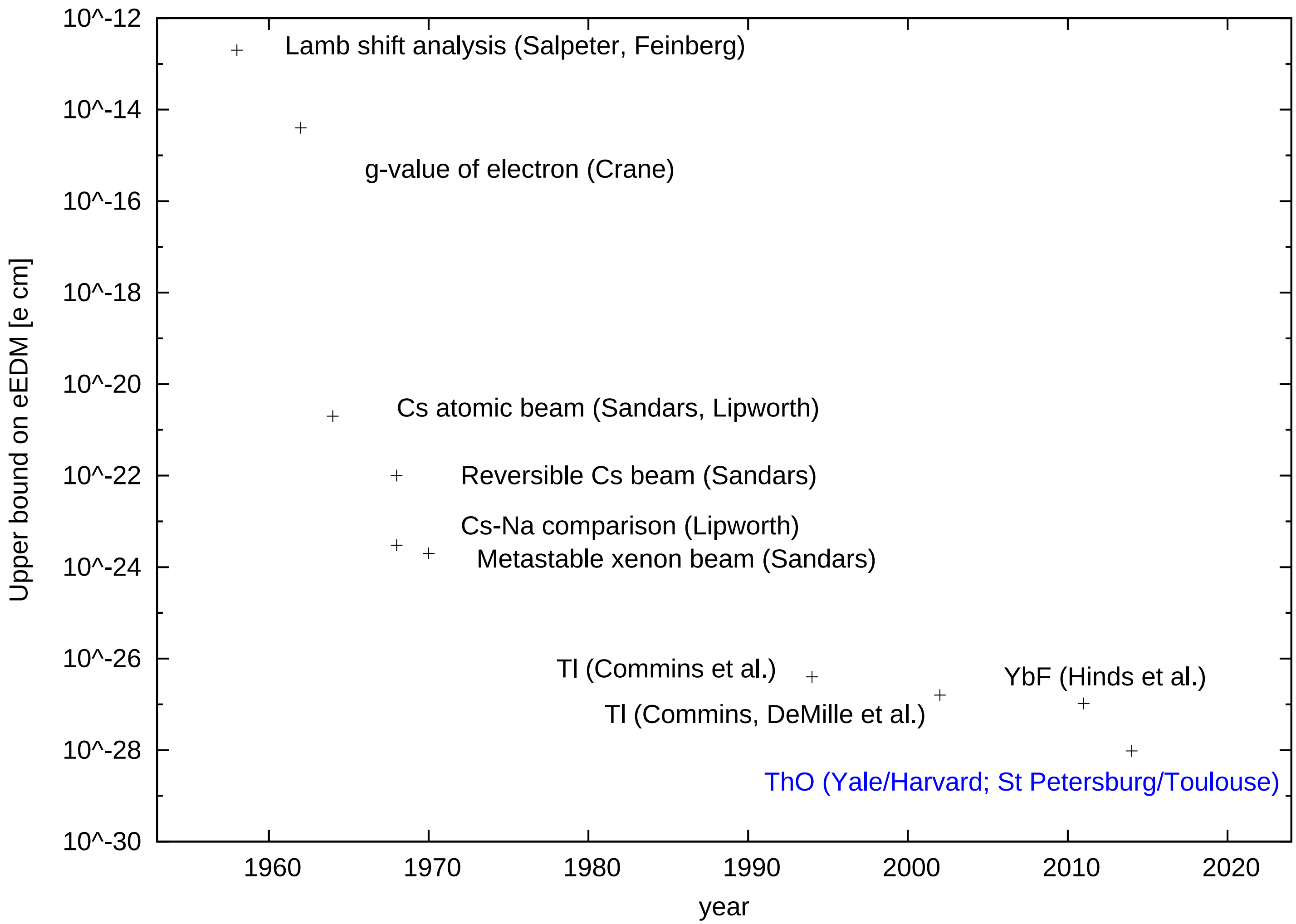
Variation due to spinor choice **0.2%**

Augmentation of virtual space: **further slight decrease**

[18] L. Skripnikov, A.V. Titov, *J Chem Phys* **142** (2015) *024301*

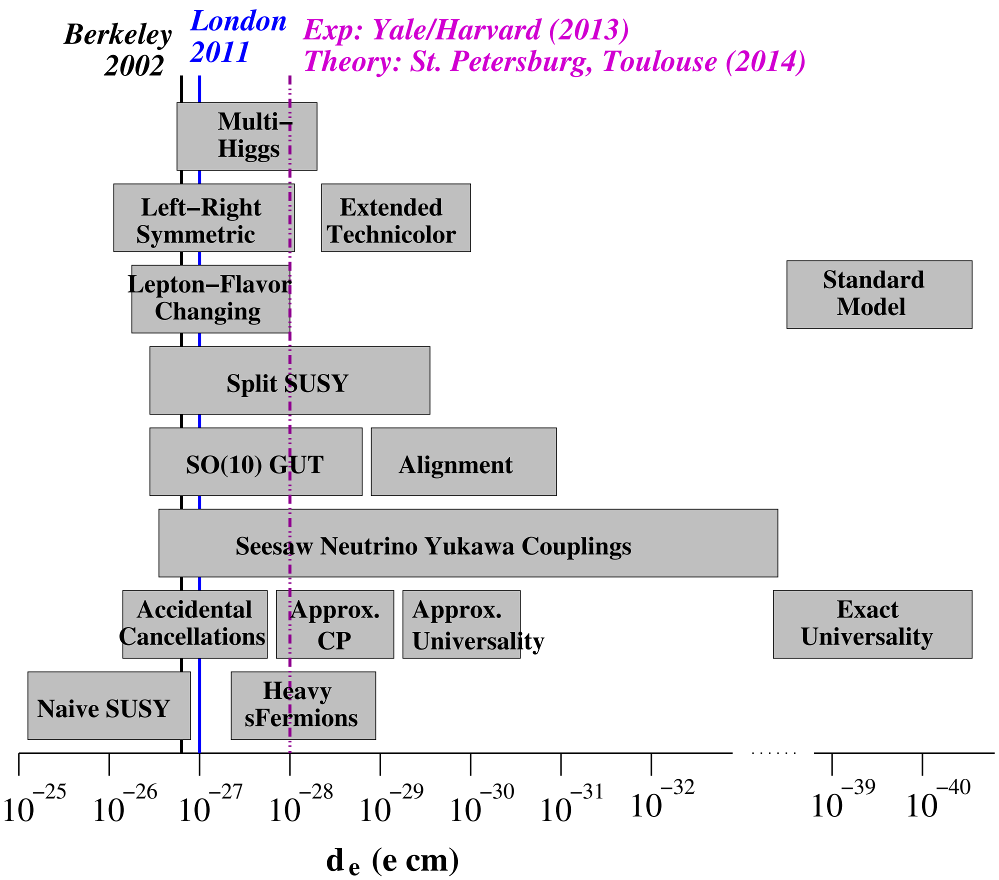
[19] TF, M.K. Nayak, *J Mol Spectrosc* **300** (2014) *16*; M. Denis, TF (2015)

Historical Development of eEDM Upper Bound[20]



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

eEDM Constraint on Beyond-Standard-Model Theories[21]



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)[22]	$< 1.6 \cdot 10^{-27}$
Experimental limit (YbF)[23]	$< 10.5 \cdot 10^{-28}$
Experimental limit (ThO)[24]	$< 9.6 \cdot 10^{-29}$

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

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

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

[24] 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^{+}

Experiment: JILA, Boulder, Colorado (Cornell group)

EDM Studies in Molecular Ions

as opposed to neutral molecules[25]

- Valence isoelectronic with neutral contenders (ThO, WC, *et al.*)

- Sufficiently large value of E_{eff}
  Hope for very large value[26] 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[27]: ${}^3\Delta_1$ **or** ${}^1\Sigma_0^+$

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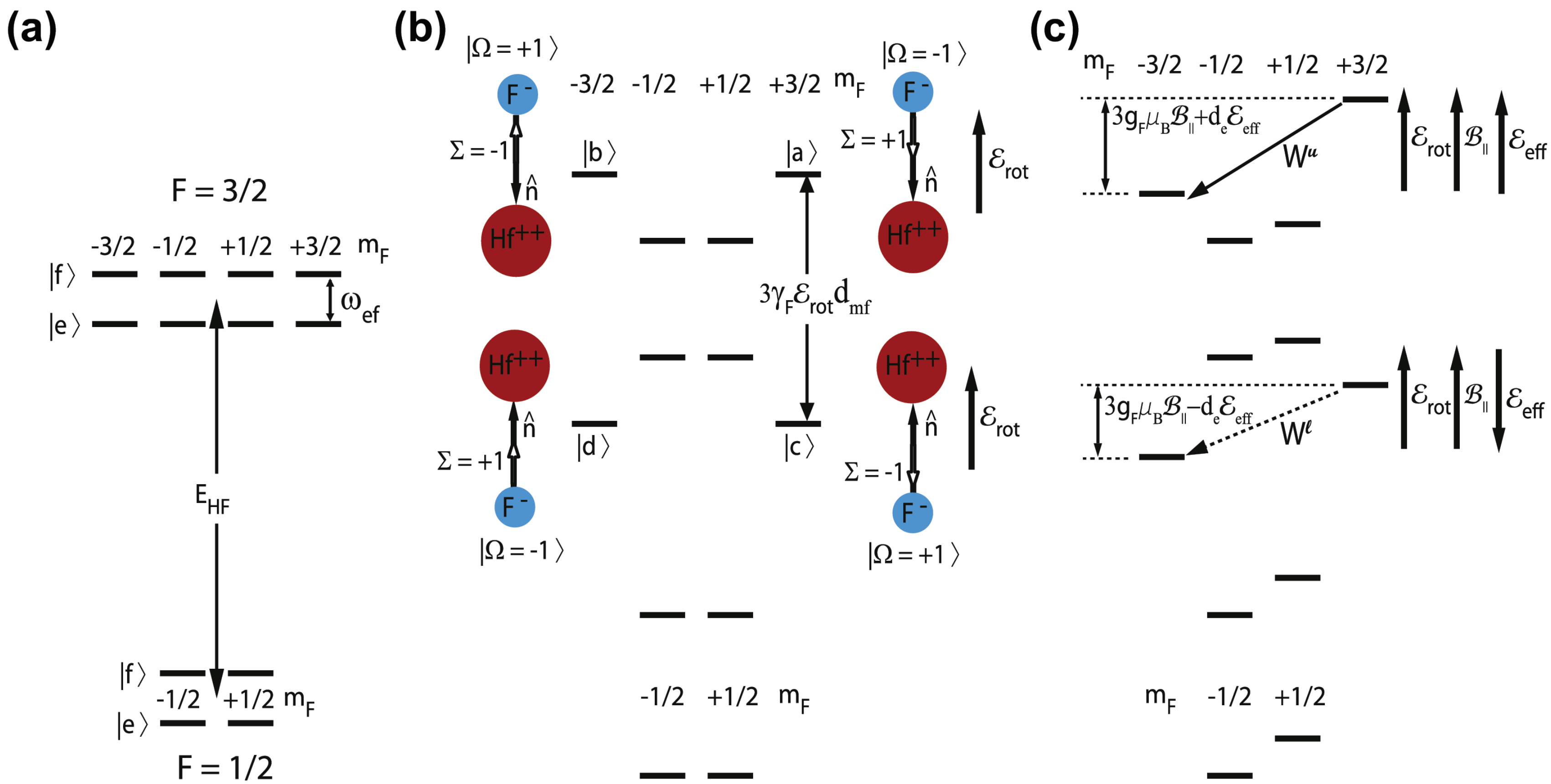
[25] H. Loh, K.C. Cossel, M.C. Grau, K.-K. Ni, E.R. Meyer, J.L. Bohn, J. Ye, E.A. Cornell, *Science* **342** (2013) *1220*
A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

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

[27] 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[28] on HfF$^+$



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

[28] 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[29] 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	$\mathcal{II}^{\mathcal{CC}}$	2c	42	0.00	1062	3146	4499
	$\mathcal{III}^{\mathcal{CC},\dagger}$	2c	15	0	1062	3149	4511
	$\mathcal{III}^{\mathcal{CC},\ddagger}$	2c	191	0	1048	3157	4123
	$\boldsymbol{\mathcal{III}^{\mathcal{CC},*}}$	**2c**	**319**	**0**	**1039**	**3162**	**3841**
MRCI	$\mathcal{I}^{\mathcal{CI}}$	2c	854	0	1154	3189	3388
	$\mathcal{II}^{\mathcal{CI}}$	2c	630	0	1167	2986	-
	$\boldsymbol{\mathcal{III}^{\mathcal{CI},10}}$	**4c**	**538**	**0**	**1155**	**3012**	-
CCSD(T)+SO[b]			501	0	890	2157	
CCSDT+SO[b]			143	0	890	2157	
CCSDT(Q)+SO[b]			0	66	955	2223	
Experiment[b]			0	315.0(5)	1052.5(5)	3150(15)	3395(15)

Spinor-based correlation methods yield **similar results**

Orbital-based perturbative correlation methods underestimate $^3\Delta$ **splittings dramatically**

[29][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*

(Four-)Spinors vs. Orbitals

The electronic ground state of of ThF^+

Hypothesis: Orbital-based correlation methods underestimate the splitting $\Delta\varepsilon_{\delta_{5/2}-\delta_{3/2}} = 2166\ \mathrm{cm}^{-1}$.

Configurational composition of ${}^3\Delta$ multiplet states (from MR_{10}-CISD(18) model)

${}^3\Delta_1$	$89\%\ \sigma^1_{-1/2}\,\delta^1_{3/2}$
${}^3\Delta_2$	$61\%\ \sigma^1_{1/2}\,\delta^1_{3/2}$, $28\%\ \sigma^1_{-1/2}\,\delta^1_{5/2}$
${}^3\Delta_3$	$89\%\ \sigma^1_{1/2}\,\delta^1_{5/2}$

Orbital-based methods underestimate term splittings

Error is large for ${}^3\Delta_2$-${}^3\Delta_3$ splitting
Error is smaller for ${}^3\Delta_1$-${}^3\Delta_2$ splitting

Suggested explanation for differing ground-state predictions

^{19}F Magnetic Hyperfine Interaction in ThF^+ and HfF^+ $(\Omega = 1)$

Magnetic hyperfine interaction constant:

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

System	Model	$A_{\|\|}$[MHz]	spinor character	R_e [a.u.]
ThF^+	MR_{10}-CISD(20)	**8.9**	0.001 p_z(F)	3.75
([30])	MR_{10}-CISD(18)	4.3		
HfF^+ ([31])	MR_6-CISD(20)	**45.3**	0.001 p_z(F)	3.41

- Unpaired electrons localized on heavy atom
- Correlation of $1s$ (F) electrons of crucial importance
- $A_{||}$ for ThF^+ very small due to long internuclear distance

[30] 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

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

$\mathcal{P},\mathcal{T}$-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 $\mathcal{III}^{\mathcal{CI},5}$.

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}]	$\left\langle {}^M\Lambda_\Omega \middle| \hat{D}_z \middle| {}^M\Lambda_\Omega \right\rangle$ [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 $\left\langle {}^M\Lambda_\Omega \middle| \hat{D}_z \middle| {}^M\Lambda_\Omega \right\rangle$, 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	T_v [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$^+$: $E_{\rm eff}$ in the $\Omega = 1$ science state[32]

HfF$^+$		ThF$^+$	
Model	$E_{\rm eff}$ $\left[\frac{\rm GV}{\rm cm}\right]$	Model	$E_{\rm eff}$ $\left[\frac{\rm GV}{\rm cm}\right]$
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)	22.9	MR_{10}-CISD(18)	35.2
MR-CISD(34)+T	23.3	MR_3-CISDT(18)	35.4
Estimate, Meyer et al.[33]	≈ 30	Meyer et al.	≈ 90
20 e^- corr., Titov et al.[34]	24.2	38 e^- corr., Titov et al.[35]	≈ 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

[32] 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*

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

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

[35] 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[36]:

  1. Intranuclear $\mathcal{P}$-,$\mathcal{T}$-odd interactions, described by QCD $(\mathcal{CP})$-violating parameter[37] $\tilde{\Theta}$,

  $$M_0^{p,n}(\tilde{\Theta}) \approx 2 \times 10^{-29}\,\tilde{\Theta}\,e\,\text{cm}^2$$

     M: valence nucleon MQM

  2. Neutron/proton EDM (order of magnitude smaller)

- MQM is enhanced in non-spherical (deformed) nuclei[38]

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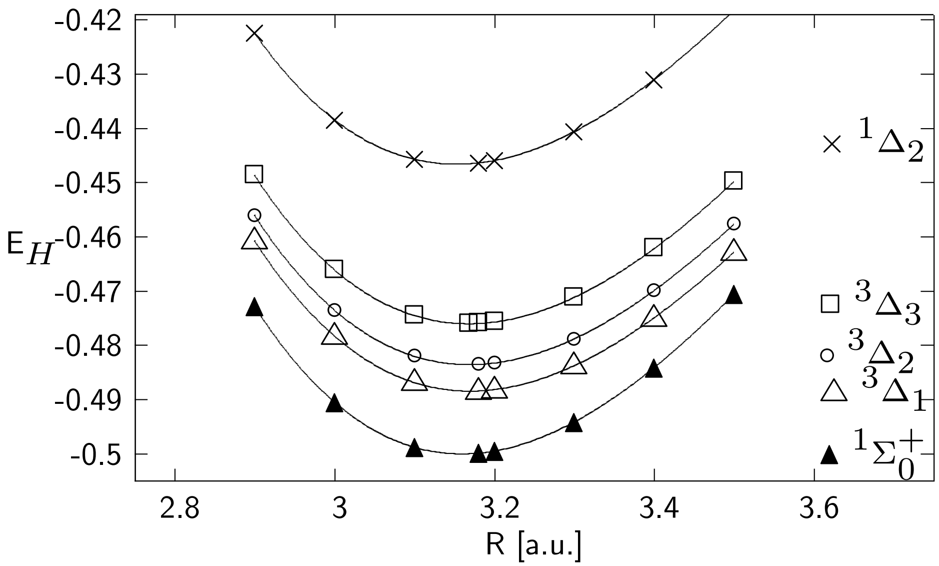
[36] V. V. Flambaum, D. DeMille, M. G. Kozlov, *Phys Rev Lett* **113** (2014) *103003*

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

[38] 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.[39]	3.181	1070		0.0
$^3\Delta_1$	MR$_{12}$-CISD(10)	3.170	1116	0.461	2526
	Exp.[39]	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)
- Large mol. dipole moment

[39]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*

TaN, Spectroscopic properties

${}^M\Lambda_\Omega$ State	${}^1\Sigma_0^+$	${}^3\Delta_1$	${}^3\Delta_2$	${}^3\Delta_3$	${}^1\Delta_2$
${}^1\Sigma_0^+$	-3.515				
${}^3\Delta_1$	0.028	-4.809			
${}^3\Delta_2$	0.000	0.085	-4.775		
${}^3\Delta_3$	0.000	0.000	0.087	-4.776	
${}^1\Delta_2$	0.000	0.139	0.114	0.164	-4.000

Molecular static electric dipole moments $\left\langle {}^M\Lambda_\Omega|\hat{D}_z|{}^M\Lambda_\Omega\right\rangle$, transition dipole moments $\left\|\left\langle {}^M\Lambda'_\Omega|\hat{\vec{D}}|{}^M\Lambda_\Omega\right\rangle\right\|$, with $\hat{\vec{D}}$ the electric dipole moment operator (both in [D] units) at $R = 3.1806$ a$_0$, using the model MR$_{12}^{+T}$-CISD(10)

- Large molecular electric dipole moment in ${}^3\Delta_1$ science state

- $\approx 3\%$ non-Δ character of science state
Transition to ${}^1\Sigma_0^+$ borrows intensity via ${}^3\Delta_1 - {}^1\Pi_1$ and other second-order spin-orbit couplings

Molecular Nuclear Magnetic Quadrupole Moment

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

Cutoff/CI Model	$E_{\text{eff}}\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	$W_{P,T}$ [kHz]	W_M $\left[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}\right]$
vTZ-30a.u./MR$_{12}$-CISD(10)	30.1	3104	27.4	0.633
vTZ-30a.u./MR$_{12}$-CISDT(10)	29.7	3092	27.1	0.626
vTZ-30a.u./MR$_{12}$-CISD(18)	*33.9*	*3063*	*30.8*	*0.72*
vTZ-30a.u./MR$_{12}^{+T}$-CISD(10)	31.4	3067	28.7	0.645
vTZ-30a.u./MR$_{12}^{+T}$-CISD(18)	*36*	*3029*	*32.5*	*0.75*
Skripnikov et al.[40]	34.9	-3132	31	1.08
Flambaum *et al.*[41]	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 smaller than reference values

[40] N. S. Mosyagin, M. G. Kozlov, A. V. Titov, *J Phys B* **31** (1998) *L763*
[41] V. V. Flambaum, D. DeMille, M. G. Kozlov, *Phys Rev Lett* **113** (2014) *103003*

Outlook

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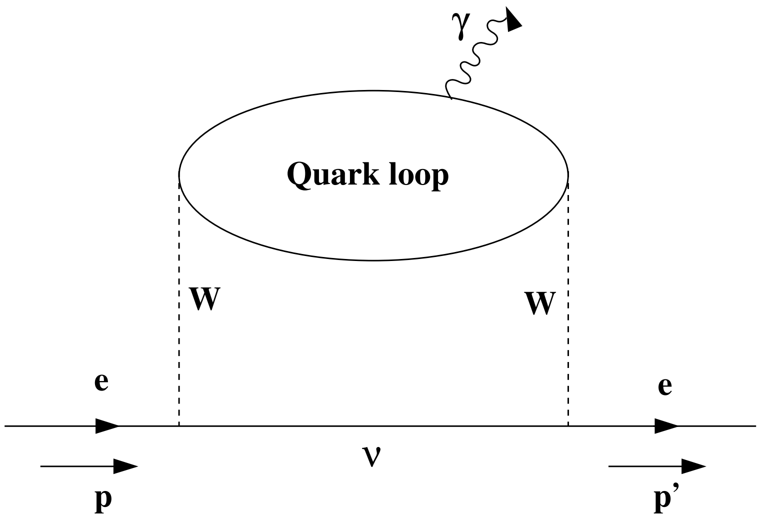
The induced fermion EDM

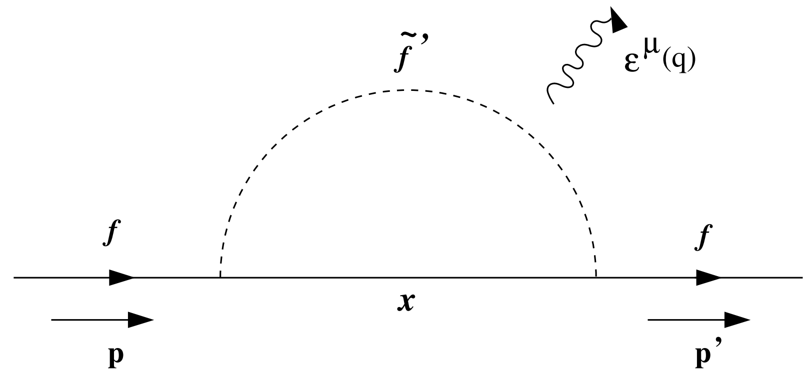
Standard Model Picture[7]



- 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

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[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*