# Theoretical Contribution to a New Upper Bound on the Electron Electric Dipole Moment


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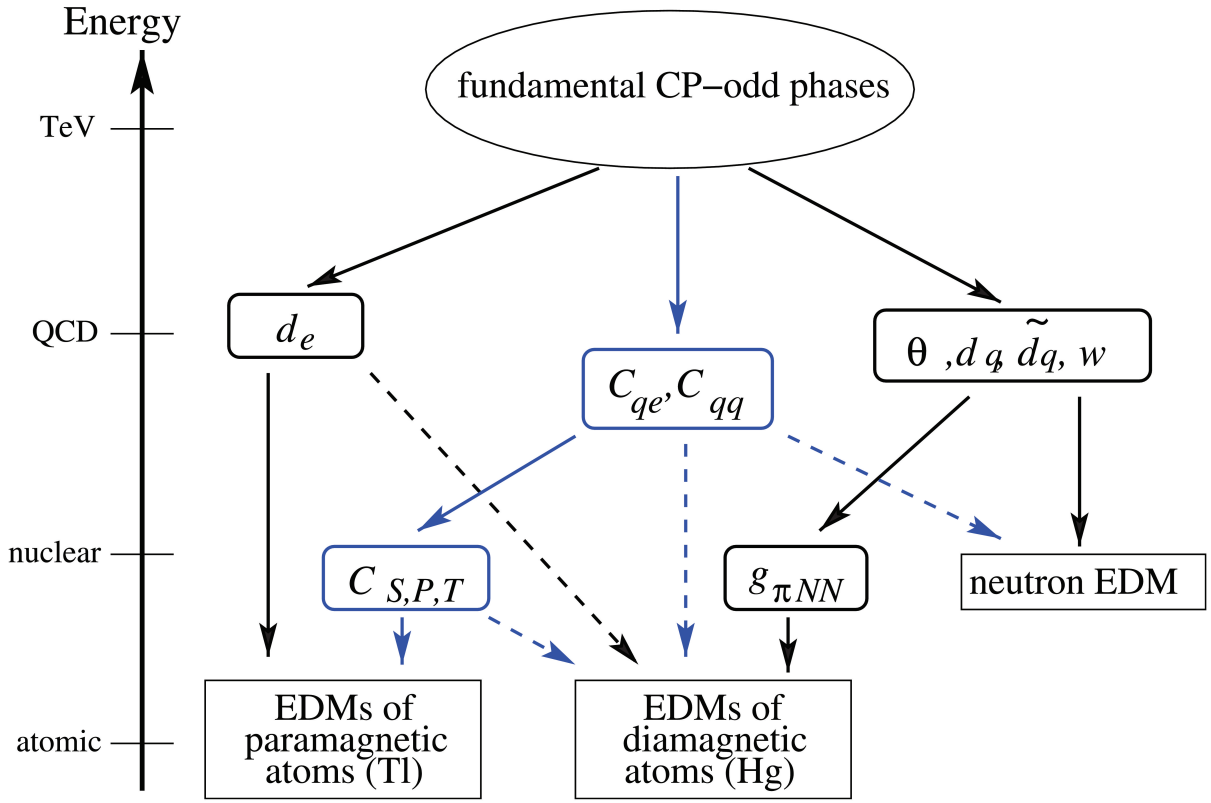
# Electric Dipole Moment of Paramagnetic Atoms/Molecules

## Possible sources[1]

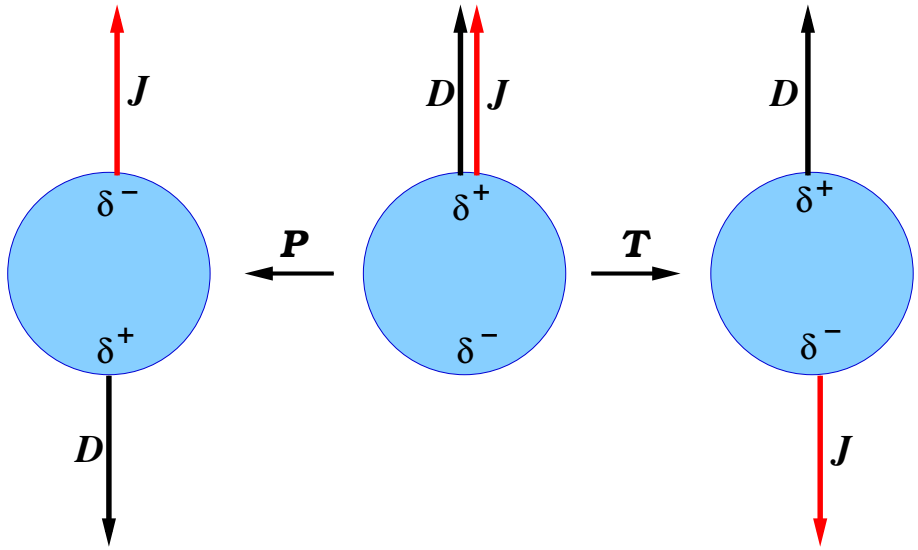



1. Intrinsic EDM of an electron
2. ($\mathcal{P}$ and $\mathcal{T}$) violating electron-nucleon interaction

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

# Testing Extensions to the Standard Model:

## The Electron Electric Dipole Moment ($e$EDM) $\vec{D}$




Implies violation of **Parity**($\mathcal{P}$) and **Motion-Reversal**($\mathcal{T}$) symmetries[2]

The $\mathcal{CPT}$ theorem assumed to be valid

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

# 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) $\Delta\epsilon_t$ of atomic/molecular quantum states.
- Theory determination of an **enhancement**[3]

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

- Enhancement factor $R$ "translates" between atomic and particle scales and is related to the **effective electric field** at the position of the electron,

$$R \propto E_{\rm eff}$$

[3] 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:

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

  (Schiff's Theorem[4])
- Relativistic view leads to a non-zero value, essentially due to length contraction in the obeserver frame[5]
- Scaling with nuclear charge $Z$, for alkali atoms[6]

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

- Heavy atoms required. Typical values in practice:

  $$Z > 50$$

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

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

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

# The eEDM in a molecular framework

## Perturbative EDM operator

$\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[7]:

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

which comprises an electric and a "motional" part

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

Magnetic contribution does not enter to leading order[8]

Electric field contributions

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

with an internal nuclear and electronic contribution

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

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

[8] 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 for a single-particle expectation value[9]

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

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.

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

# Correlated Wavefunction Theory for $E_{\rm eff}$

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

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

  Expectation values over relativistic Configuration Interaction wavefunctions[11]

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

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

[11] 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 $\hat{\mathcal{P}}\,|\psi_p\rangle = \prod_{i=1}^{n} \hat{p}(i)\,\hat{\mathcal{A}}\,|\varphi_a(1)\cdot\ldots\cdot\varphi_m(n)\rangle$.

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[12] $E_{\rm eff} \approx 0.05\,\left[\frac{\rm GV}{\rm cm}\right]$

2. Molecular fields:
   YbF[13]: $E_{\rm eff} \approx 26\,\left[\frac{\rm GV}{\rm cm}\right]$, HgF[14]: $E_{\rm eff} \approx 100\,\left[\frac{\rm GV}{\rm cm}\right]$,

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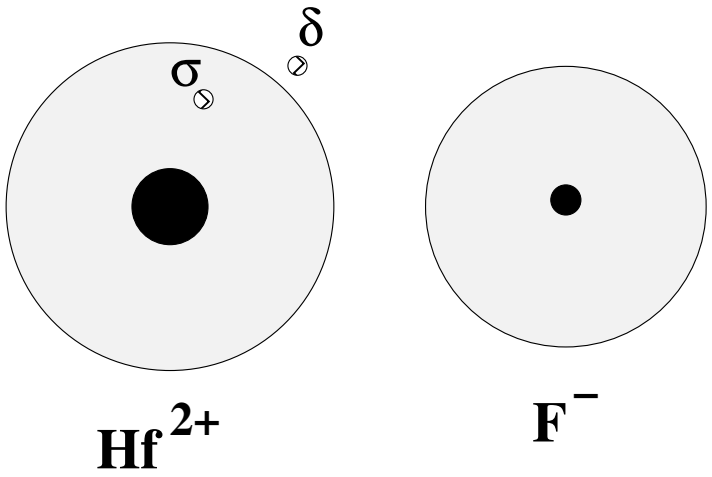
[12] V.V. Flambaum, *Sov J Nucl Phys* **24** (1976) *199*

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

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

# The eEDM in a molecular framework

## $^3\Delta$ molecules[15]




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

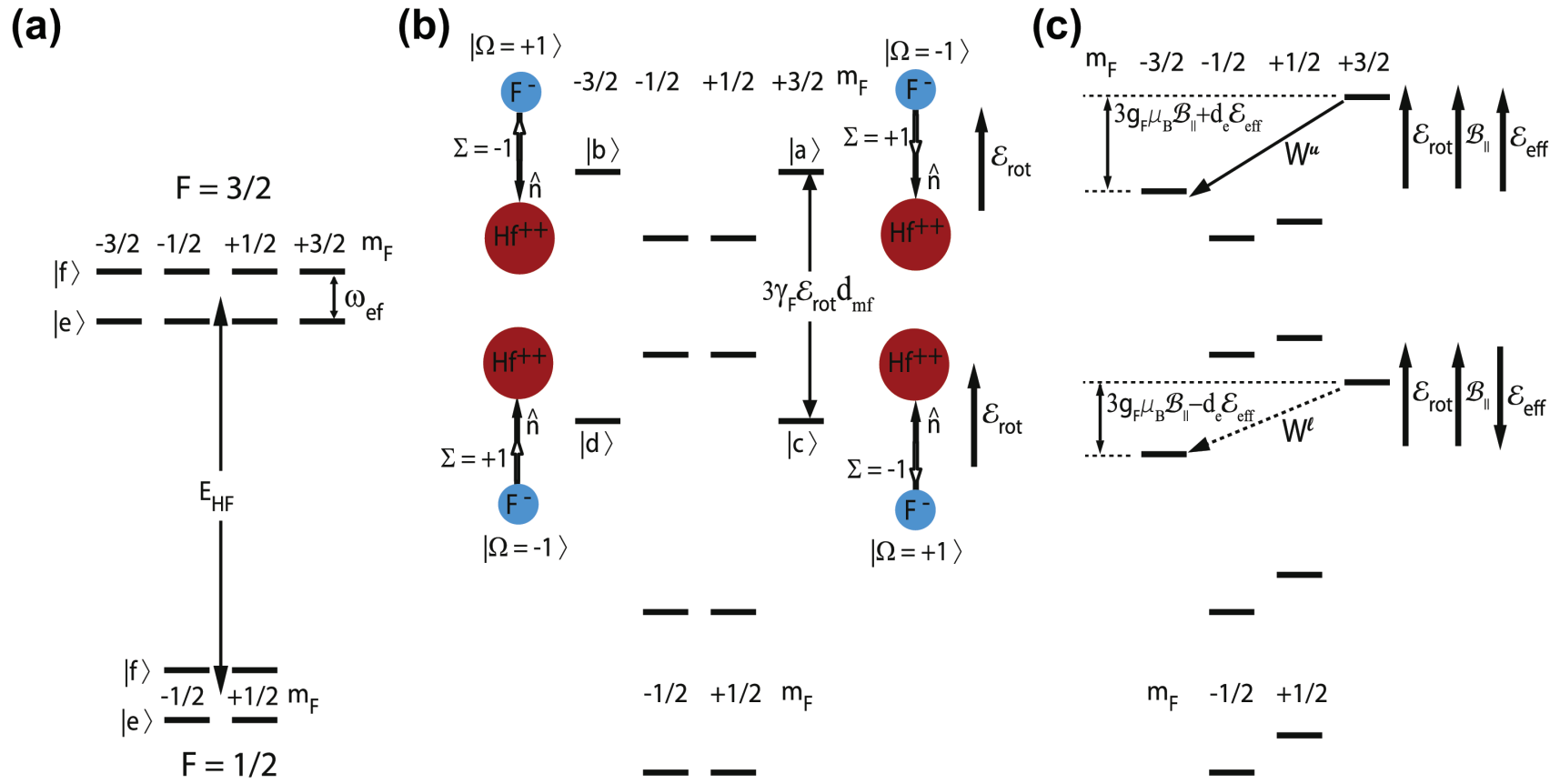
- Deeply bound molecule (fluorides)
- Small $\Lambda$ ($\Omega$)-doublet splitting (optimal polarization)
- Large rotational constant (one heavy, one light atom)
- $\Omega = 1$ component preferred (small magnetic moment)
- $\Rightarrow$ Low-lying $^3\Delta_1$ as "science" state

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


HfF+

# The eEDM in a molecular framework

## A Proposed Measurement[16] on $HfF^+$




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

[16] 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*

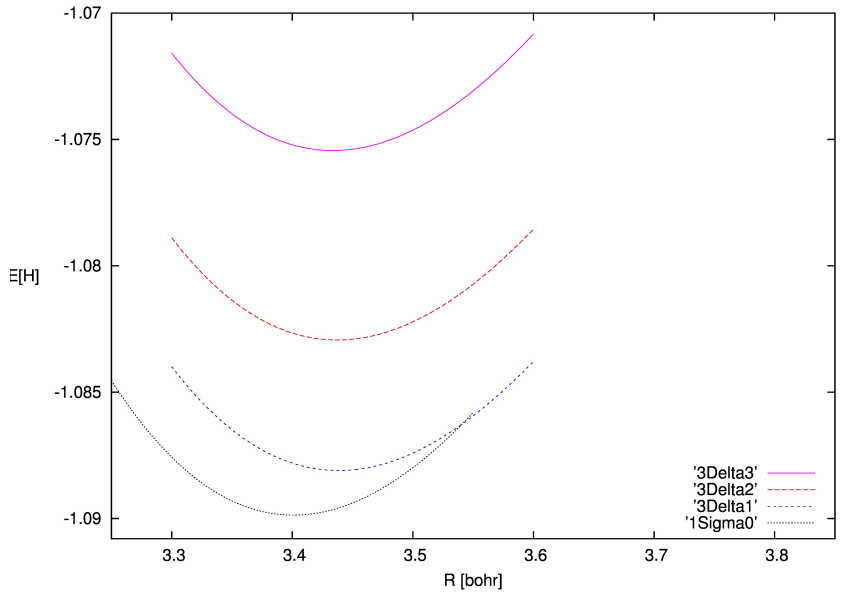
# $HfF^+$ electronic states and spectroscopic constants

$\Omega = 3$ $(Hf^{2+}6s^15d^1)$

$\Omega = 2$ $(Hf^{2+}6s^15d^1)$

$\Omega = 1$ $(Hf^{2+}6s^15d^1)$

$\Omega = 0$ $(Hf^{2+}6s^2)$




| | $R_e$ [a.u.] | | | | $\omega_e$ [$cm^{-1}$] | | | |
|---|---|---|---|---|---|---|---|---|
| Model | $\Omega = 0$ | $\Omega = 1$ | $\Omega = 2$ | $\Omega = 3$ | $\Omega = 0$ | $\Omega = 1$ | $\Omega = 2$ | $\Omega = 3$ |
| CAS-CI(10) | 3.400 | 3.436 | 3.434 | 3.431 | 796 | 774 | 775 | 778 |
| MR-CISD(10) | 3.506 | 3.558 | 3.557 | 3.552 | 656 | 643 | 643 | 644 |
| MR-CISD+T(10) | 3.510 | 3.560 | | | 654 | 643 | | |
| MR-CISD(20) | 3.401 | 3.438 | 3.437 | 3.434 | 800 | 768 | 769 | 772 |
| Experiment[17] | | | | | 790.76 | 760.9 | | |
| Experiment[18] | 3.374 | 3.407 | | | 791.2 | 761.3 | 762.3 | 761.5 |

[17] K. Cossel et al., *Chem. Phys. Lett.* **546** (2012) *1*

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

# $HfF^+$: $E_{\rm eff}$ in the $\Omega = 1$ science state[19]

| 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-CISD+T(20) | 23.7 |
| MR-CISD(34) | 22.9 |
| MR-CISD(34)+T | 23.3 |
| Estimate, Meyer et al.[20] | $\approx 30$ |
| 20 $e^-$ corr., Titov et al.[21] | 24.2 |

(+) All-electron calculation

(+) No configuration selection

(+) Spinors as one-particle basis functions

(+) Dirac-Coulomb Hamiltonian

(-) Basis-set incompleteness
→ vQZ corrections

(-) Higher excitations
→ CC expectation values

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

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

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

# ThO

# Most Recent Measurement: ThO Molecule

## ACME Collaboration, Harvard/Yale

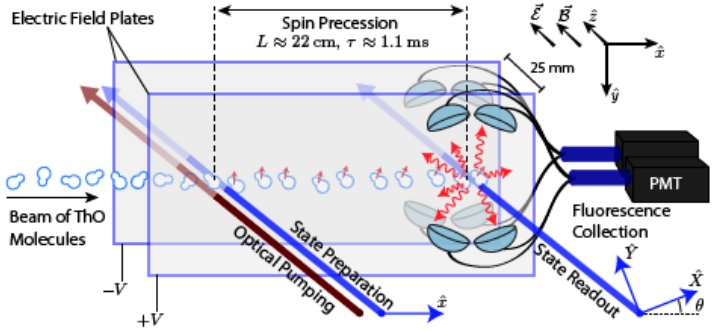
## Order of Magnitude Smaller Limit on the Electric Dipole Moment of the Electron

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

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

(Dated: January 22, 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 $E_{\rm eff} = 75.6\,\left[\frac{\rm GV}{\rm cm}\right]$ with an estimated error bar of 3% and 10% smaller than a previously reported result [arXiv:1308.0414 [physics.atom-ph]]. Using the same wavefunction model we obtain an excitation energy of $T_v^{\Omega=1} = 5329$ [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 $A_{||} = -1335$ [MHz] for the $\Omega = 1$ state in ThO. The smaller effective electric field increases the previously measured upper bound to the electron electric dipole moment interaction constant [arXiv:1310.7534v2 [physics.atom-ph]] and thus mildly mitigates constraints to possible extensions of the Standard Model of particle physics.

1401.2284v2

*J Mol Spectrosc* (2014) *submitted*

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

## Molecular Wavefunction for the "Science" State

| | # of Kramers pairs | accumulated # of electrons min. | max. |
|---|---|---|---|
| *Deleted* | (176) | | |
| *Virtual* | 183–K | 36 | 36 |
| *Th: 6dσπ,7p, 8s Th: 7s, 6dδ* | K | 36–m | 36 |
| *Th: 6s, 6p O: 2s, 2p* | 8 | 34–n | 34 |
| *Th: 5d* | 5 | 18–p | 18 |
| *Th: 5s, 5p* | 4 | 8–q | 8 |
| *Frozen core* | (31) | | |

$^3\Delta_1$ is the first molecular excited state

$7s^1 6d\delta^1$ configuration considerably mixed in this state

CI expansion space
$\leq 500.000.000$ terms

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

## Basis Sets

| Basis set/CI Model | $T_v$ [$\mathrm{cm}^{-1}$] | $E_{\mathrm{eff}}$ [$\frac{\mathrm{GV}}{\mathrm{cm}}$] | $A_{\|\|}$ [MHz] |
|---|---|---|---|
| vDZ/$MR_3$-CISD(18) | 4535 | 80.8 | −1283 |
| vTZ/$MR_3$-CISD(18) | 3832 | 81.0 | −1292 |
| vQZ/$MR_3$-CISD(18) | 3643 | 80.7 | −1298 |

Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of $R = 3.477$ $a_0$ for $\Omega = 1$ using basis sets with increasing cardinal number and the wavefunction model $MR_3$-CISD(18)

Magnetic hyperfine interaction constant:

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

1401.2284v2

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

## Number of Correlated Electrons

| CI Model | $T_v$ [$\mathrm{cm}^{-1}$] | $E_{\mathrm{eff}}$ [$\frac{\mathrm{GV}}{\mathrm{cm}}$] | $A_{\|\|}$ [MHz] |
|---|---|---|---|
| MR-CISD(2) | 5929 | 68.5 | −1264 |
| $\mathrm{MR}_3$-CISD(18) | 3832 | 81.0 | −1292 |
| $\mathrm{MR}_3$-CISD(28) | 3752 | 80.0 | −1297 |
| $\mathrm{MR}_3$-CISD(36)[22] | 3742 | 80.8 | −1287 |

Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of $R = 3.477$ $\mathrm{a}_0$ for $\Omega = 1$ correlating only the atomic valence shells down to including core-valence and core-core correlation and using the vTZ basis sets

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[22] Due to extreme computational demand the virtual cutoff is 5 a.u. here.

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

## Active 4-Spinor Spaces

| CI Model | $T_v$ [$\mathrm{cm}^{-1}$] | $E_{\mathrm{eff}}$ [$\frac{\mathrm{GV}}{\mathrm{cm}}$] | $A_{\|\|}$ [MHz] |
|---|---|---|---|
| $\mathrm{MR}_3$-CISD(18) | 3832 | 81.0 | −1292 |
| $\mathrm{MR}_5$-CISD(18) | 4054 | 79.7 | −1291 |
| $\mathrm{MR}_7$-CISD(18) | 4321 | 80.1 | −1318 |
| $\mathrm{MR}_{10}$-CISD(18) | **5329** | **75.6** | **-1335** |
| Exp. $(T_e)$[23] | 5317 | | |

Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of $R = 3.477$ $\mathrm{a}_0$ for $\Omega = 1$ using the vTZ basis set and varying active spinor spaces

1401.2284v2

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

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

## Higher Excitations

| CI Model | $T_v$ [$\mathrm{cm}^{-1}$] | $E_{\mathrm{eff}}$ [$\frac{\mathrm{GV}}{\mathrm{cm}}$] | $A_{\|\|}$ [MHz] |
|---|---|---|---|
| $MR_3$-CISD(18) | 4535 | 80.8 | −1283 |
| $MR_9$-CISD(18) | 5703 | 73.8 | −1321 |
| $MR_3$-CISDT(18) | 5166 | 74.5 | −1340 |

Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of $R = 3.477$ $a_0$ for $\Omega = 1$ using the vDZ basis set and varying maximum excitation rank

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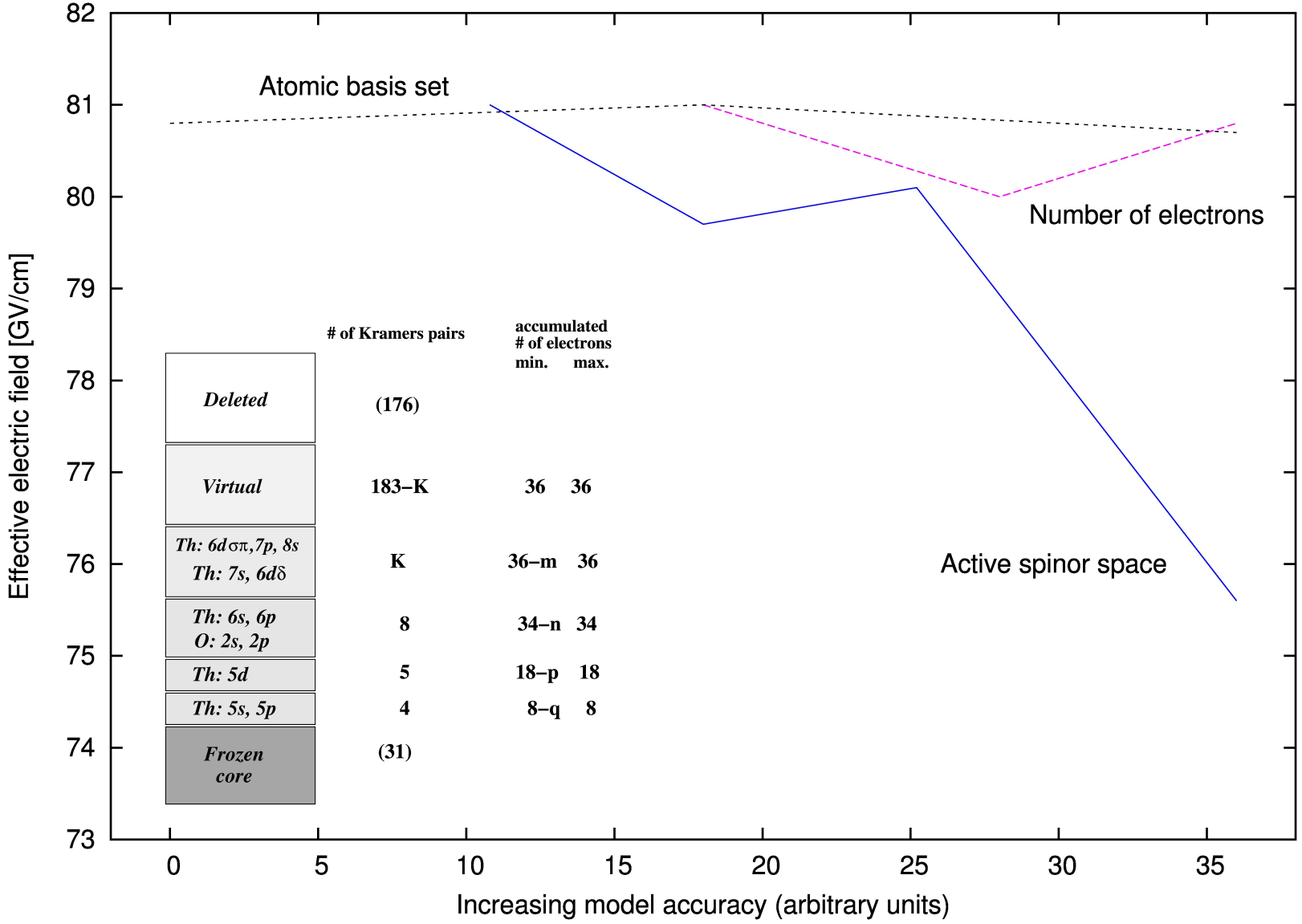
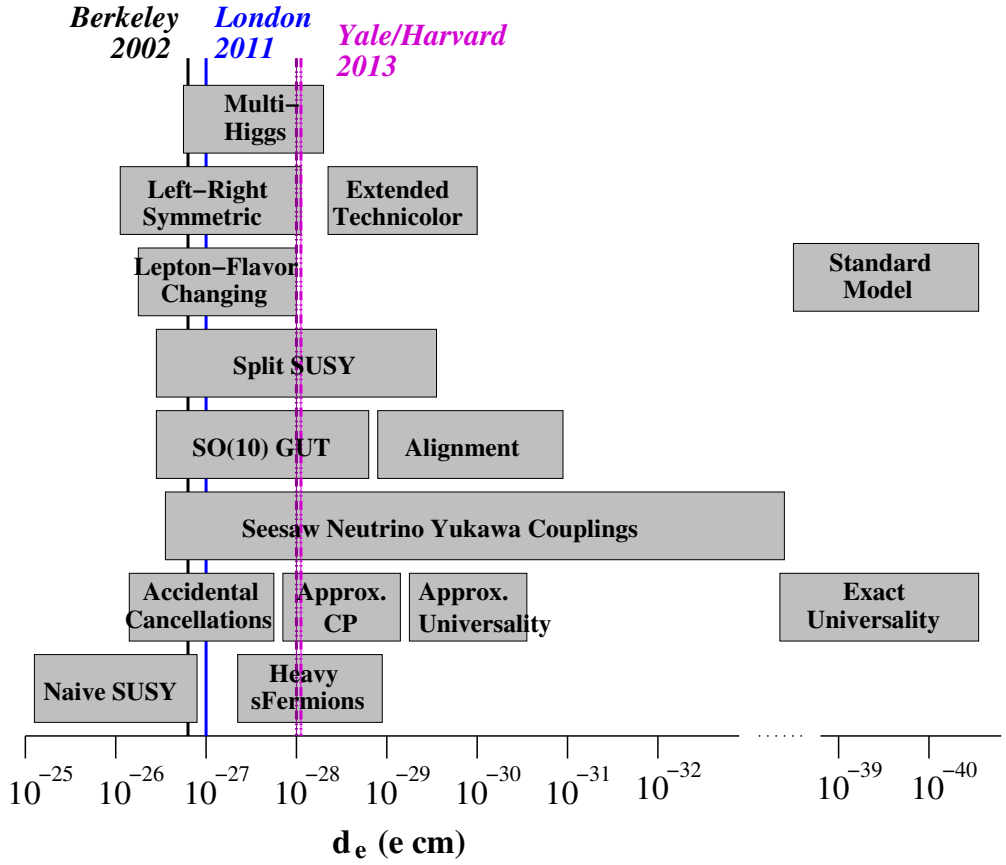
# The eEDM in ThO ($\Omega = 1$)



# Upper bounds on the eEDM[24]




| **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)[25] | $< 1.6 \cdot 10^{-27}$ |
| Experimental limit (YbF)[26] | $< 10.5 \cdot 10^{-28}$ |
| Experimental limit (ThO)[27] | $< 9.7 \cdot 10^{-29}$ |

[24] 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)

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

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

[27] ACME Collaboration, Science **6168** (2014) *269*, TF and MKN, 1401.2284v2

# Outlook


**Project EDMeDM.**

- Hyperfine interaction constants for an experimentally known diatomic molecule comparison with our calculations
- Implementation of the scalar-pseudoscalar $\mathcal{P}$ and $\mathcal{T}$ odd electron-nucleon interaction Hamiltonian
- Development of size-extensive approach to calculation of enhancement factors (Coupled Cluster theory)
- Study of other diatomic molecules (in particular $ThF^+$ (JILA, Boulder), WC)