Rigorous Relativistic Many-Body Methods for Exploring Fundamental Physics in Atoms and Molecules

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A Question at Large Scale

What "Happened" to Antimatter ?

- *Matter* and *antimatter* particles are created (and annihilated) in pairs.
- Matter-antimatter symmetric universe is empirically excluded[1]
- A tiny portion of *matter*, about one particle per billion, managed to survive the Big Bang.

$\longrightarrow$ Baryon Asymmetry Problem of the Universe (BAU)

- Fundamental symmetry violation could be at the heart of this problem.

[1] A.G. Cohen, A. De Rújula, S.L. Glashow, *Astrophys. J.* **495** (1998) *539*

A Possible Explanation Via:

Sakharov's Conditions[2]

Condition 1: Distinguished direction of time (time arrow)
Departure from thermal equilibrium

Condition 2: $Baryon\ number\ (A)$ violation
Inflation suggests that universe started with $A = 0$

Condition 3: $(\mathcal{CP})$-violating physics present
Standard Model $(\mathcal{CP})$ violation is regarded as insufficient
(SM-Baryogenesis, SM-Leptogenesis?)

[2] M. Dine, A. Kusenko, "Origin of the matter-antimatter asymmetry", *Rev. Mod. Phys.* **76** (2004) *1*
A. Sakharov, *J. Exp. Theor. Phys. Lett.* **5** (1967) *24*

Fundamental Discrete Symmetries

A bit of safe ground ?

$\mathcal{CPT}$ theorem:[3]
Local QFTs invariant

One example: The free Dirac equation (Weyl notation)

$$\hat{\mathcal{K}}^\dagger\hat{\mathcal{P}}^\dagger\hat{\mathcal{C}}^\dagger\left(-\imath\hbar\gamma^\mu\partial_\mu + m_0c^2\mathbb{1}_4\right)\hat{\mathcal{C}}\hat{\mathcal{P}}\hat{\mathcal{K}}\,\hat{\mathcal{K}}^\dagger\hat{\mathcal{P}}^\dagger\hat{\mathcal{C}}^\dagger\,\underline{\Psi}(x) = \underline{0}$$

$$(\gamma^3)^\dagger(\gamma^1)^\dagger\hat{K}_0\,\gamma^0\,\imath(\gamma^2)^\dagger\hat{K}_0\,\left(-\imath\hbar\gamma^\mu\partial_\mu + m_0c^2\mathbb{1}_4\right)\imath\gamma^2\hat{K}_0\,\gamma^0\,\gamma^1\gamma^3\hat{K}_0$$
$$(\gamma^3)^\dagger(\gamma^1)^\dagger\hat{K}_0\,\gamma^0\,\imath(\gamma^2)^\dagger\hat{K}_0\,\underline{\Psi}(x) = \underline{0}$$
$$\left(-\imath\hbar\gamma^\mu\partial_\mu + m_0c^2\mathbb{1}_4\right)\underline{\Psi}(x) = \underline{0}$$

- $\mathcal{CPT}$ invariance is connected to Lorentz invariance
- We have good reasons to "believe" in $\mathcal{CPT}$ symmetry

[3] R. F. Streater, A. S. Wightman, *"PCT, Spin and Statistics, and All That"*

Fundamental Discrete Symmetries

Individual/combined symmetries may be violated

- The fall of $\mathcal{P}$ invariance[4]

$$\pi^+ \longrightarrow \mu^+ + \nu_\mu \qquad \xrightarrow{\hat{\mathcal{P}}} \qquad \pi^+ \longrightarrow \mu^+ + \nu_\mu$$

both left-handed helicity — both right-handed helicity (impossible)

$$\pi^+ \longrightarrow \mu^+ + \nu_\mu \qquad \xrightarrow{\hat{\mathcal{C}}\hat{\mathcal{P}}} \qquad \pi^- \longrightarrow \mu^- + \overline{\nu}_\mu$$

both left-handed helicity — both right-handed helicity (possible)

Perhaps it is $(\mathcal{CP})$ that is always conserved ?

- The fall of $(\mathcal{CP})$ invariance[5]

$$K_2 = \frac{1}{\sqrt{2}}\left(K_0 + \overline{K}_0\right) \longrightarrow \pi + \pi$$

is $(\mathcal{CP})$-odd, about 0.2% of events.

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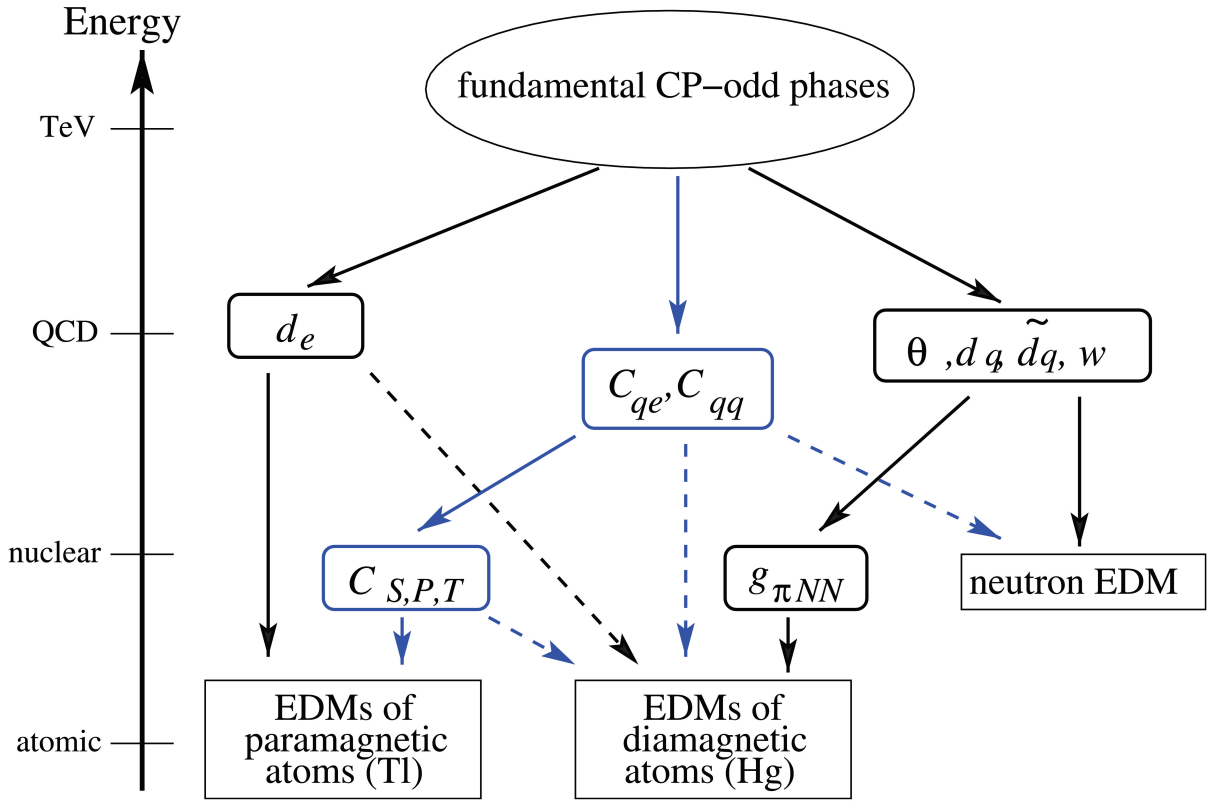
[4] C. S. Wu et al., *Phys Rev* **105** (1957) *254*

[5] J. H. Christenson et al., *Phys Rev Lett* **13** (1964) *138*

Electric Dipole Moment of Paramagnetic Atoms/Molecules

Possible sources[6]

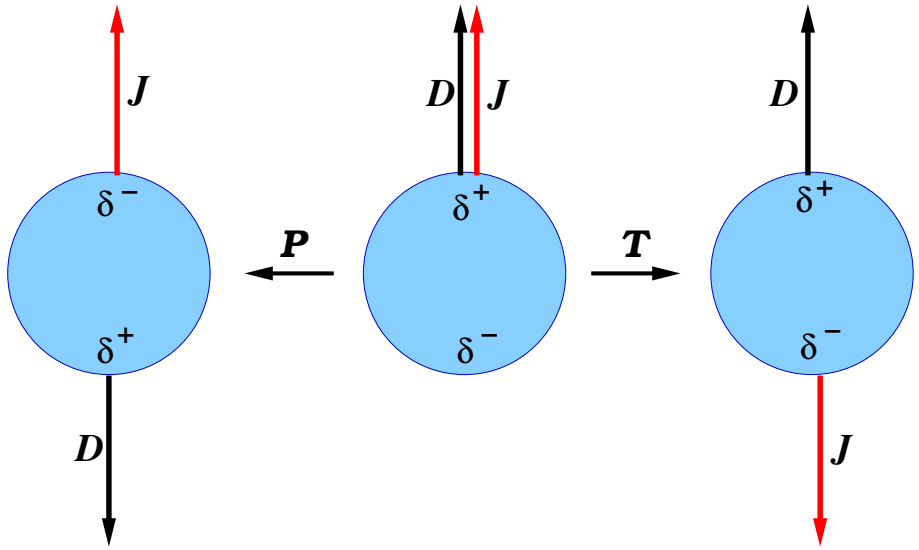


1. Intrinsic EDM of an electron
2. ($\mathcal{P}$ and $\mathcal{T}$) violating electron-nucleon interaction

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

Testing Time-Reversal Invariance:

The Electron Electric Dipole Moment (eEDM) $\vec{D}$



$\vec{D}$ and $\vec{J}$ (anti-)collinear, $\longleftarrow$ Pauli exclusion principle[7]

Implies violation of **Parity**($\mathcal{P}$) and **Motion-Reversal**($\mathcal{T}$) symmetries[8]

$\mathcal{CPT} \Rightarrow$ a kind of ($\mathcal{CP}$) violating interaction

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[7] Hunter, *Science* **252** (1991) *73*

[8] 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 particle EDM

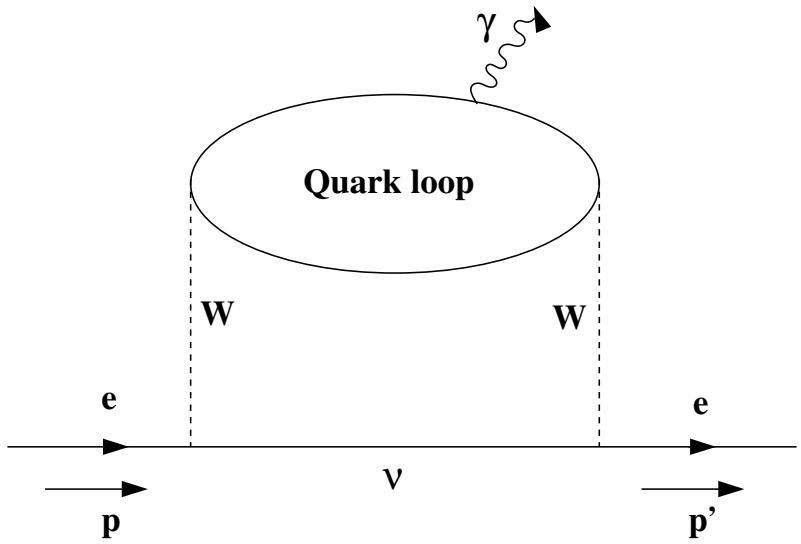
$$E_{\rm EDM} = -d_e \left\langle \Psi \left| \gamma^0 \mathbf{\Sigma}\cdot\mathbf{E} \right| \Psi \right\rangle$$

$\mathcal{P}$-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



- 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[9]

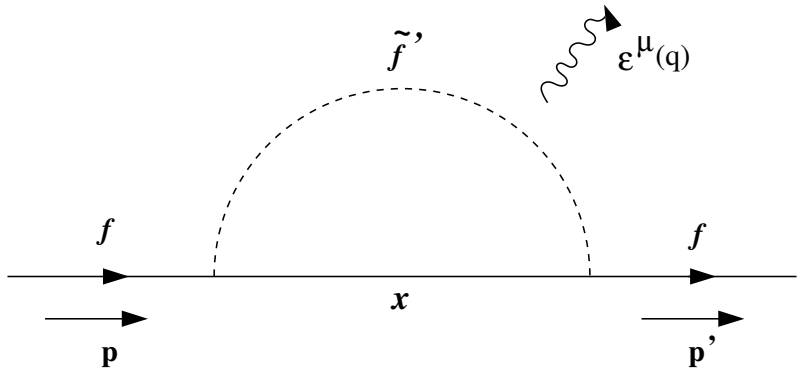
- Three-loop $\mathcal{CP}$-odd contributions zero in the absence of gluonic corrections[10]
- The standard-model prediction is immeasurably small: $d_e^{SM} \leq 10^{-38}\, e$ cm

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

[10] 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:[11]

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

MSSM ("naïve SUSY") prediction:

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

[11] 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) $\Delta\epsilon_t$ of atomic/molecular quantum states.
- Theory determination of an **enhancement**[12]

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

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

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

[12] 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[13])

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

- Relativistic view leads to a non-zero value, essentially due to length contraction in the obeserver frame[14]
- Scaling with nuclear charge Z, for alkali atoms[15]

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

- Heavy atoms required. Typical values in practice:

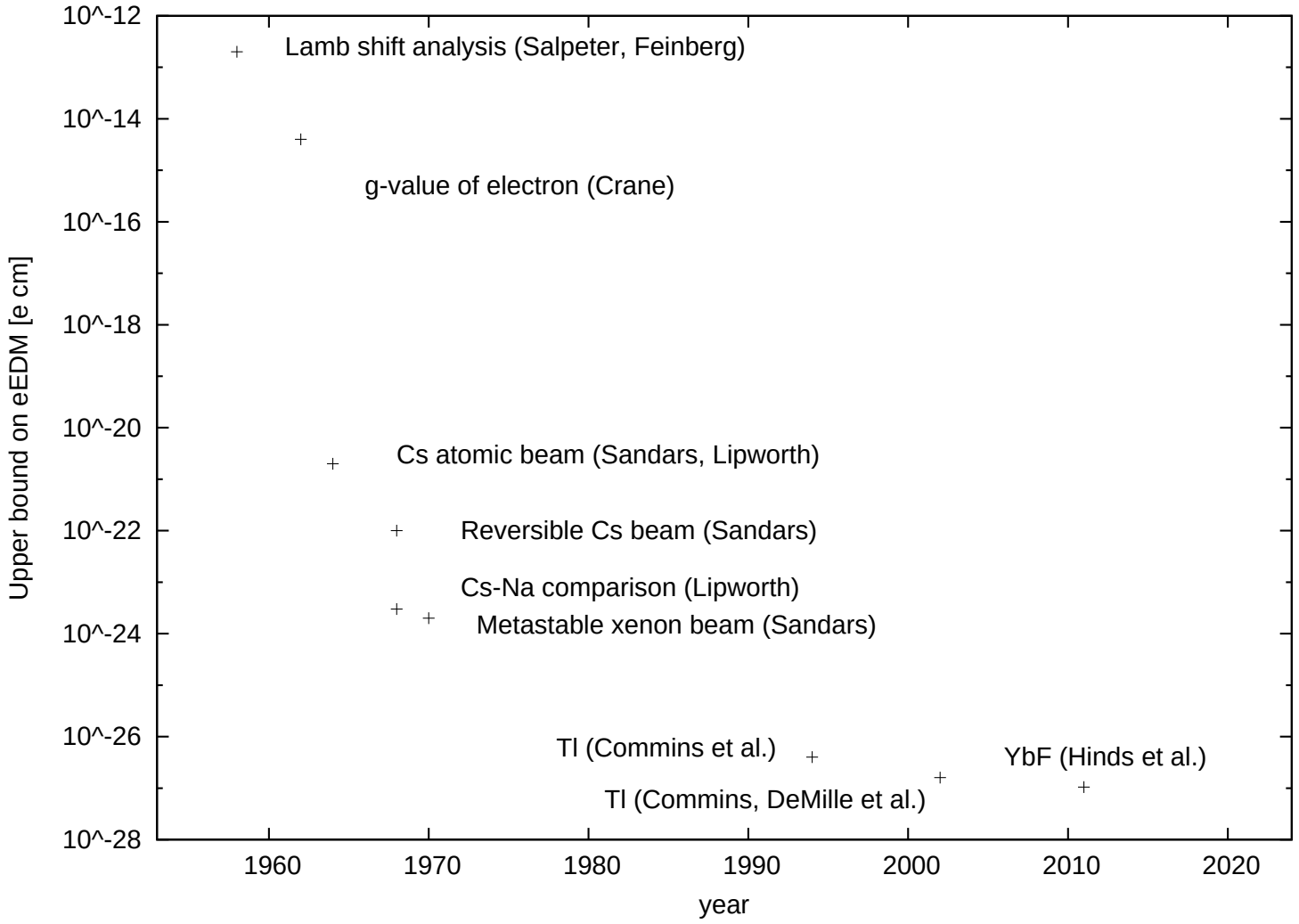
$$Z > 50$$

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

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

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

Historical Development of eEDM Upper Bound[16]



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

The eEDM in a molecular framework

Perturbative EDM operator

Single-particle $\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[17]:

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

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[18]

Electric field contributions

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

with an internal nuclear and electronic contribution

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

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

[18] 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[19]

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

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 ?

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

Relativistic Generalized-Active-Space Configuration Interaction[20]

- Basis of time-reversal paired four-spinors

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

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

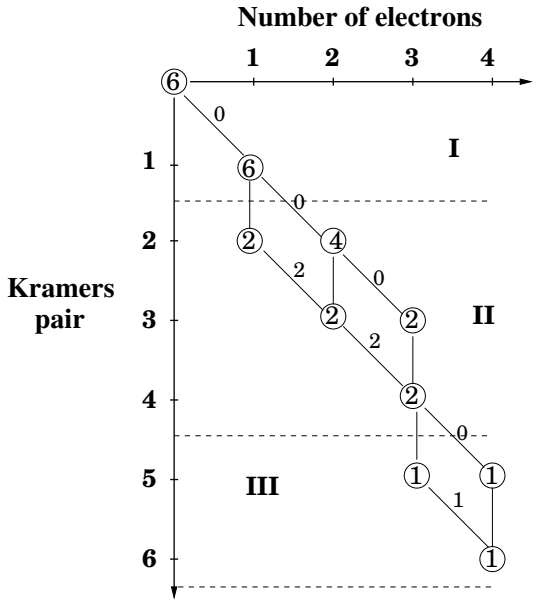
- Many-particle wavefunction defined as

  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**

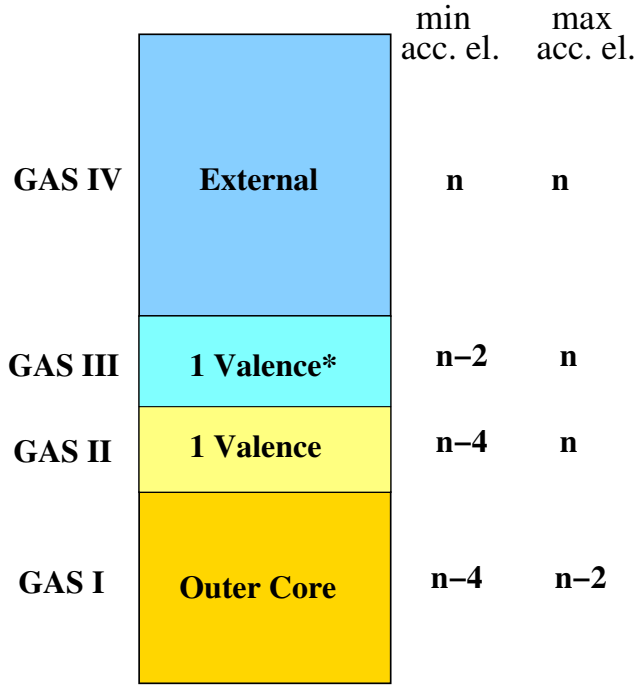


[20] S. Knecht, H.J.Aa. Jensen, TF, *J Chem Phys* **132** (2010) *014108*
TF, H.J.Aa. Jensen, J. Olsen, L. Visscher, *J Chem Phys* **124** (2006) *104106*

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 [22]

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.

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

[22] 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[23]

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

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

Algorithm for Jacobian matrix elements[24]

- 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.

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

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

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

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

Correlated Wavefunction Theory for E_{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[25] 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[26]

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

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

[26] 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[27] $E_{\rm eff} \approx 0.05\,\left[\frac{\rm GV}{\rm cm}\right]$

2. Molecular fields:
   YbF[28]: $E_{\rm eff} \approx 26\,\left[\frac{\rm GV}{\rm cm}\right]$, HgF[29]: $E_{\rm eff} \approx 100\,\left[\frac{\rm GV}{\rm cm}\right]$,

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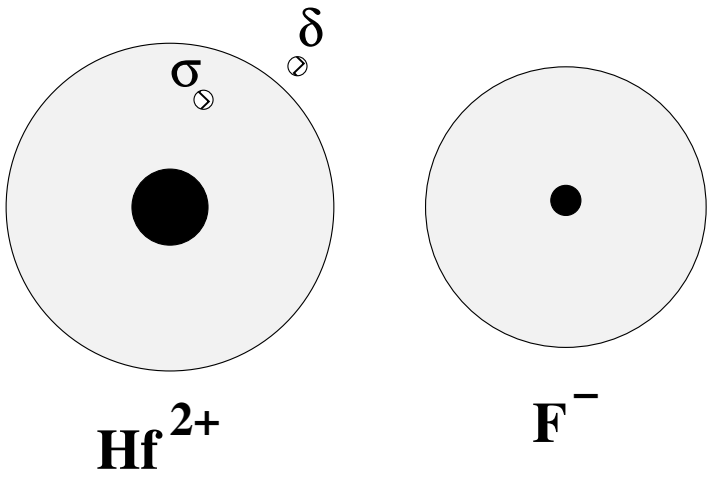
[27] V.V. Flambaum, *Sov J Nucl Phys* **24** (1976) *199*

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

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

The eEDM in a molecular framework

$^3\Delta$ molecules[30]



- 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 molecule (fluorides)
- Small Λ (Ω)-doublet splitting[31] (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

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

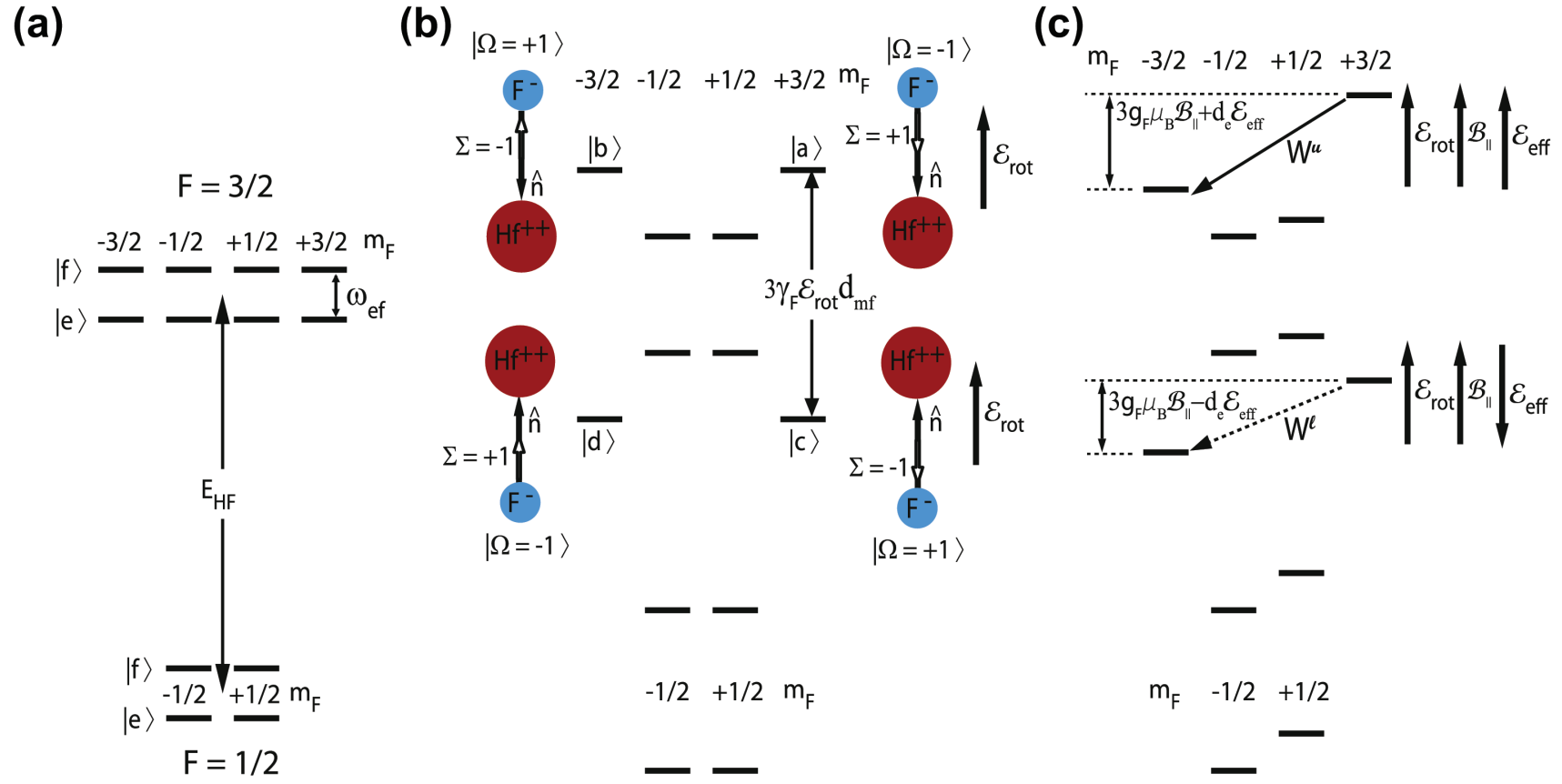
[31] TF, C.M. Marian, *J Mol Spectrosc* **178** (1996) *1*

HfF^+/ThF^+

JILA, Boulder, Colorado (Cornell group)

The eEDM in a molecular framework

A Proposed Measurement[32] on HfF^+



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

[32] 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*

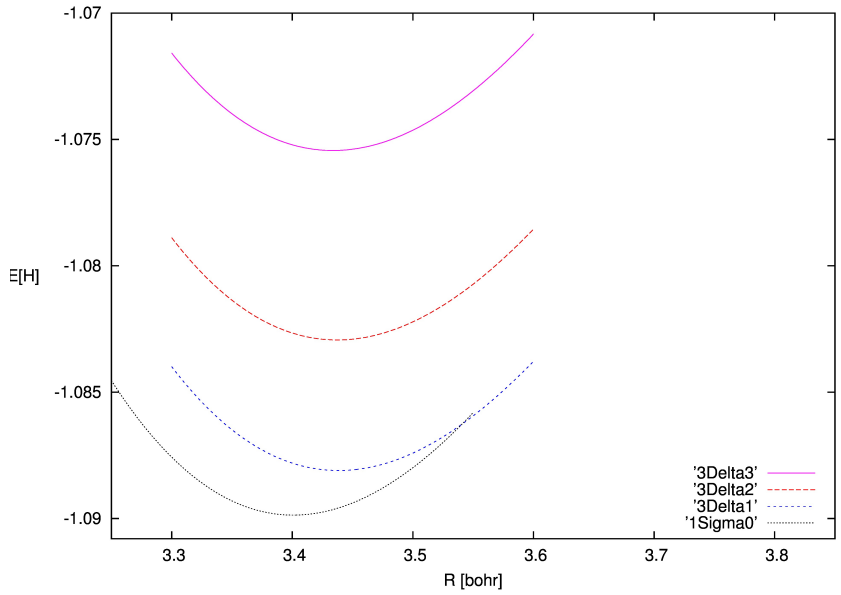
HfF^+ electronic states and spectroscopic constants

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

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

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

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



	R_e [a.u.]				ω_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[33]					790.76	760.9		
Experiment[34]	3.374	3.407			791.2	761.3	762.3	761.5

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

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

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)	22.9	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	36 e^- corr., Titov et al.	≈ 45

(HfF^+)

Similar results with various methods
System currently under exp. study

(ThF^+)

Different results with various methods
Meyer's model inaccurate
Titov's sr-CCSD(T) underestimates s-p mixing

35 TF and M.K. Nayak, *Phys Rev A* **88** (2013) *032514*
M. Denis, M.K. Nayak, TF, et al., *New J Phys* (2014) *in preparation*

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

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

ThO

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

Most Recent Measurement: ThO Molecule

ACME Collaboration, Harvard/Yale

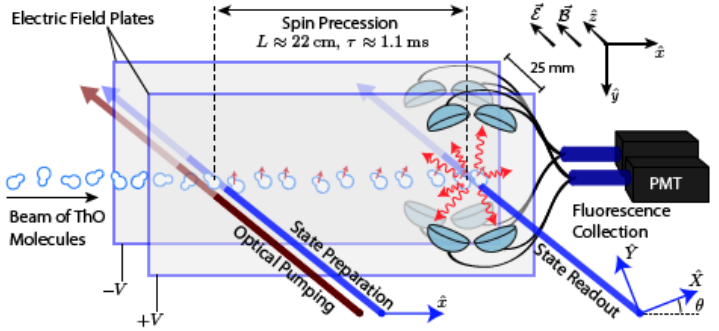
Order of Magnitude Smaller Limit on the Electric Dipole Moment of the Electron

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]

[1] *Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Paul Sabatier Toulouse III, 118 Route de Narbonne, F-31062 Toulouse, France*

[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 ($\Omega = 1$)

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 [cm^{-1}]	E_{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:

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

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

Number of Correlated Electrons

CI Model	T_v [cm^{-1}]	E_{eff} [$\frac{\mathrm{GV}}{\mathrm{cm}}$]	$A_{\|\|}$ [MHz]
MR-CISD(2)	5929	68.5	−1264
MR_3-CISD(18)	3832	81.0	−1292
MR_3-CISD(28)	3752	80.0	−1297
MR_3-CISD(36)[38]	3742	80.8	−1287

Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of $R = 3.477$ 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

[38] 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 [cm^{-1}]	E_{eff} [$\frac{\mathrm{GV}}{\mathrm{cm}}$]	$A_{\|\|}$ [MHz]
MR_3-CISD(18)	3832	81.0	−1292
MR_5-CISD(18)	4054	79.7	−1291
MR_7-CISD(18)	4321	80.1	−1318
MR_{10}-CISD(18)	5329	75.6	−1335
MR_{13}-CISD(18)	**5437**	**75.2**	**-1339**
Exp. (T_e)[39]	5317		

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

[39] J. Paulovič, T. Nakajima, K. Hirao, R. Lindh, and P.-Å. Malmqvist, *J. Chem. Phys.* **119** (2003) *798*
G. Edvinsson, A. Lagerqvist, *J. Mol. Spectrosc.* **113** (1985) *93*

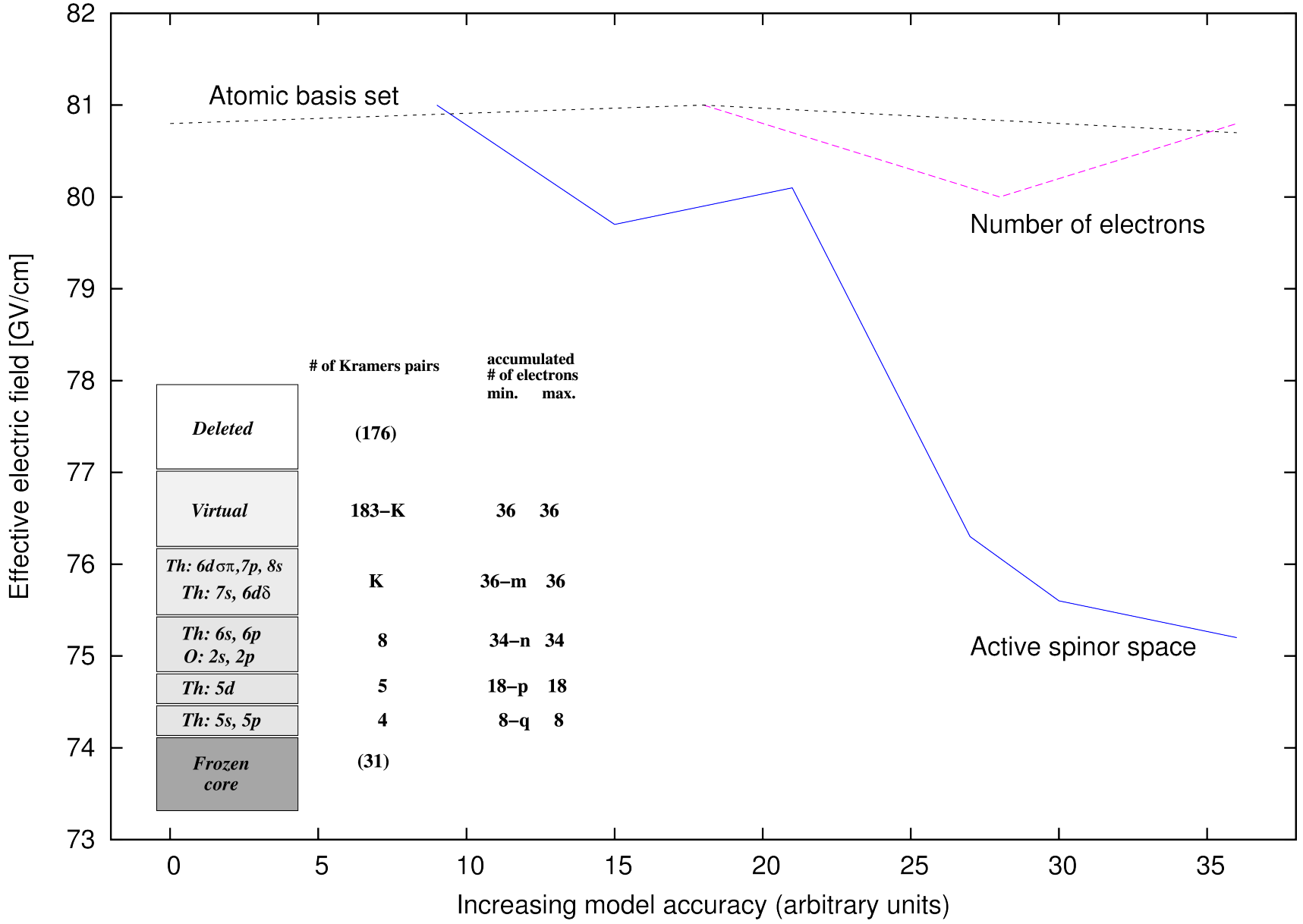
The eEDM in ThO ($\Omega = 1$)

Higher Excitations

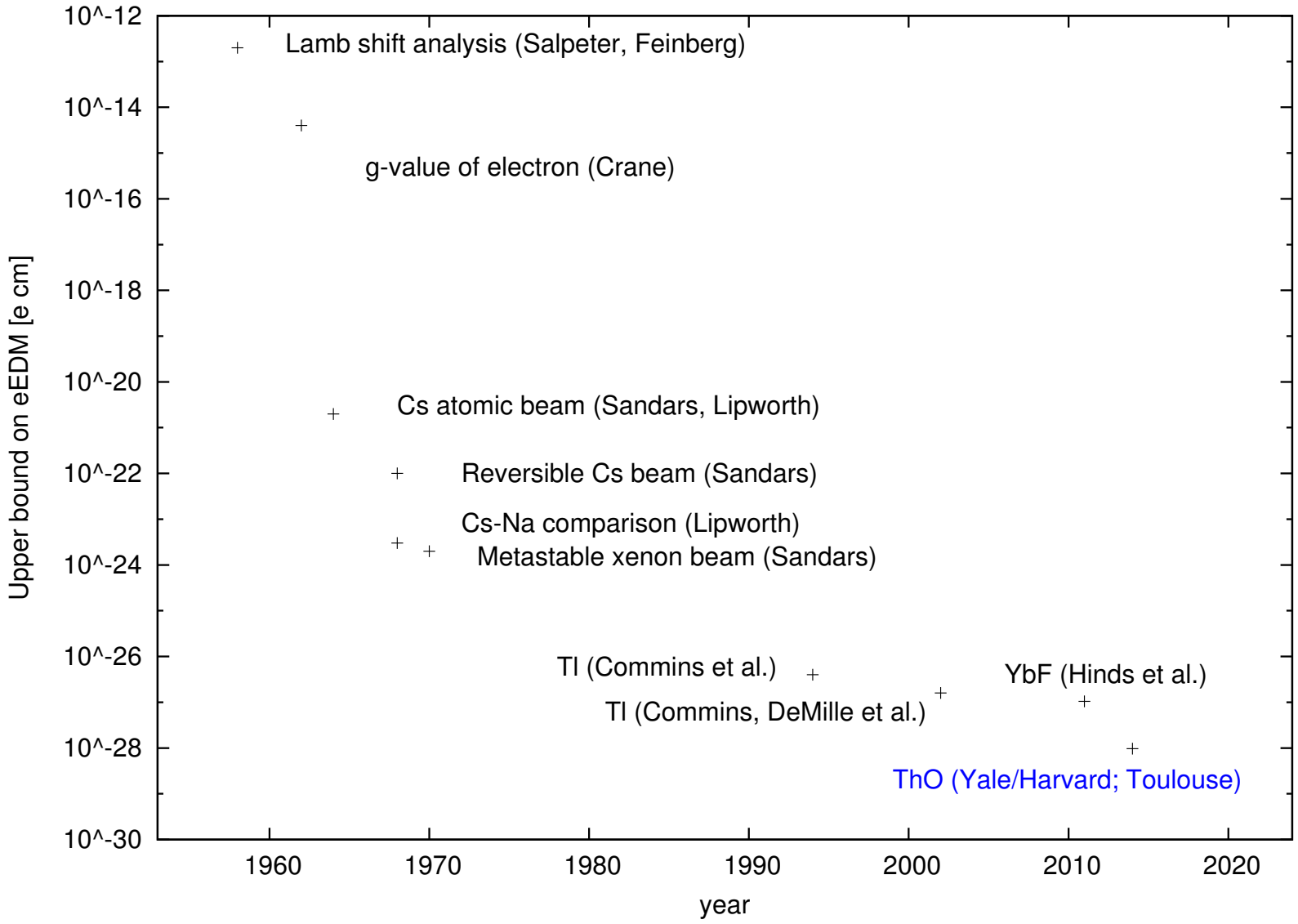
CI Model	T_v [cm^{-1}]	E_{eff} [$\frac{\mathrm{GV}}{\mathrm{cm}}$]	$A_{\|\|}$ [MHz]
MR_3-CISD(18)	4535	80.8	−1283
MR_9-CISD(18)	5703	73.8	−1321
MR_3-CISDT(18)	5166	74.5	−1340

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

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

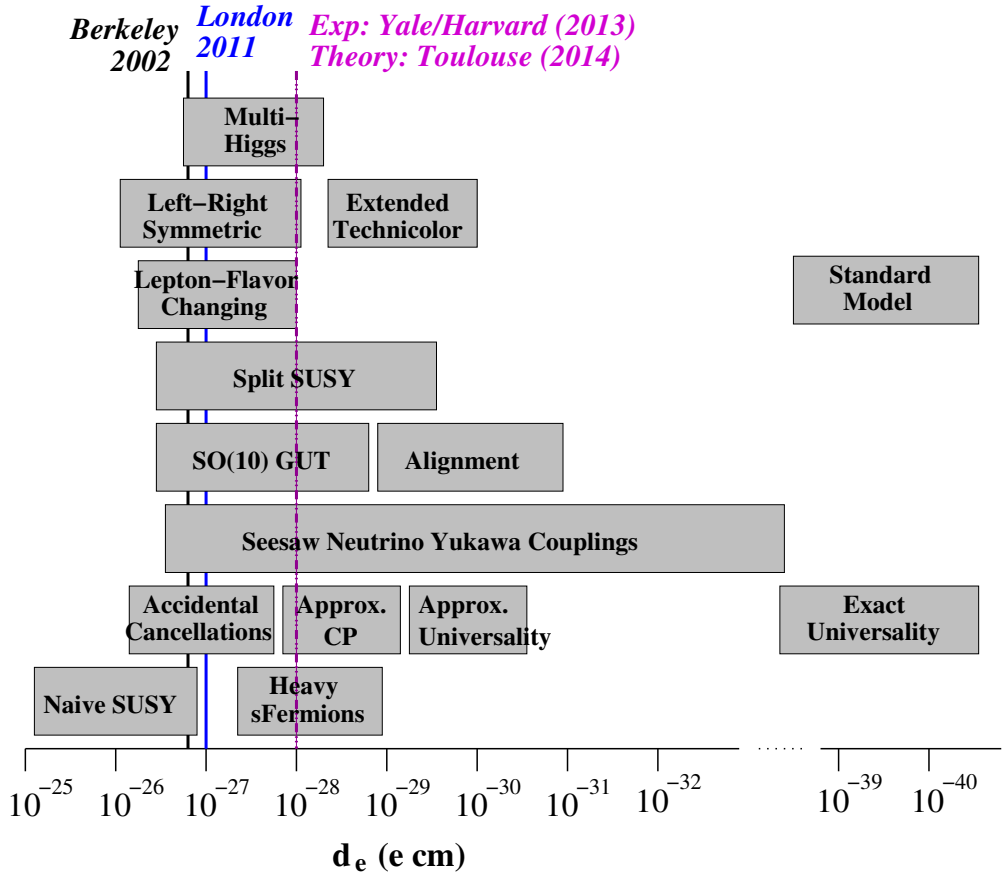


Historical Development of eEDM Upper Bound[40]



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

eEDM Constraint on Beyond-Standard-Model Theories[41]



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)[42]	$< 1.6 \cdot 10^{-27}$
Experimental limit (YbF)[43]	$< 10.5 \cdot 10^{-28}$
Experimental limit (ThO)[44]	$< 9.7 \cdot 10^{-29}$

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

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

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

[44] ACME Collaboration, *Science* **6168** (2014) *269*, TF and M. K. Nayak, *J. Mol. Spectrosc.* **300** (2014) *16*

Outlook

Project EDMeDM.

- Hyperfine interaction constants for an experimentally known diatomic molecule comparison with our calculations (WC[45])
- Scalar-pseudoscalar $\mathcal{P}$ and $\mathcal{T}$ odd electron-nucleon interaction constant C_S
- Development of approximately size-extensive approach to calculation of enhancement factors (Coupled Cluster theory)
- Study of other diatomic molecules (in particular ThF^+ (JILA, Boulder), WC (Leanhardt, Ann Arbor))
- Nuclear Schiff moment electronic-structure study (diamagnetic systems)

[45] 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*

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