Electron Electric Dipole Moment in diatomic molecules

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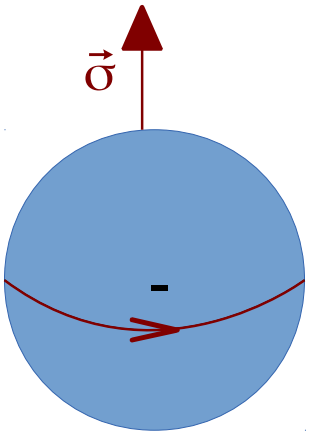
Is the electron a sphere ?



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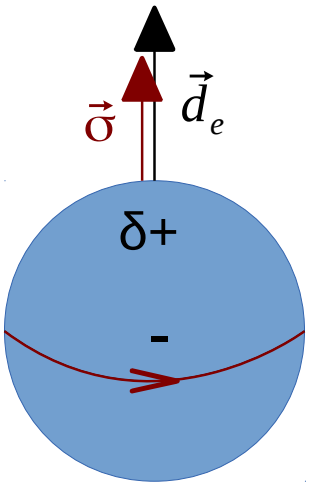

Distortion of charge distribution $\Rightarrow$ Electric Dipole Moment

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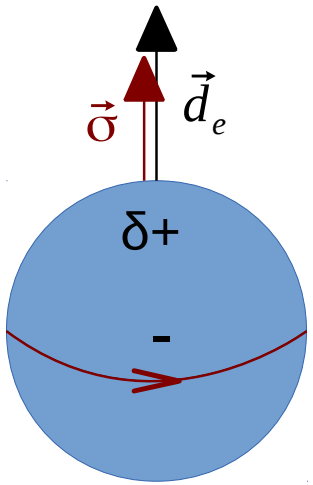
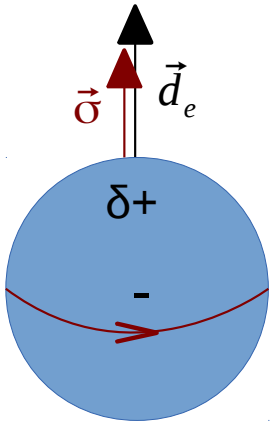


Distortion of charge distribution $\Rightarrow$ Electric Dipole Moment Permanent EDM of an electron colinear or anti-colinear to the spin (Projection theorem: $\langle \alpha', JM_J|\hat{V}_q|\alpha', JM_J\rangle = \frac{\langle \alpha', JM_J|\hat{\vec{J}}\cdot\hat{\vec{V}}|\alpha', JM_J\rangle}{\hbar^2 J^2(J+1)} \langle JM_J|\hat{J}_q|JM_J\rangle$.)

$\mathcal{P}$- and $\mathcal{T}$-symmetry violation.



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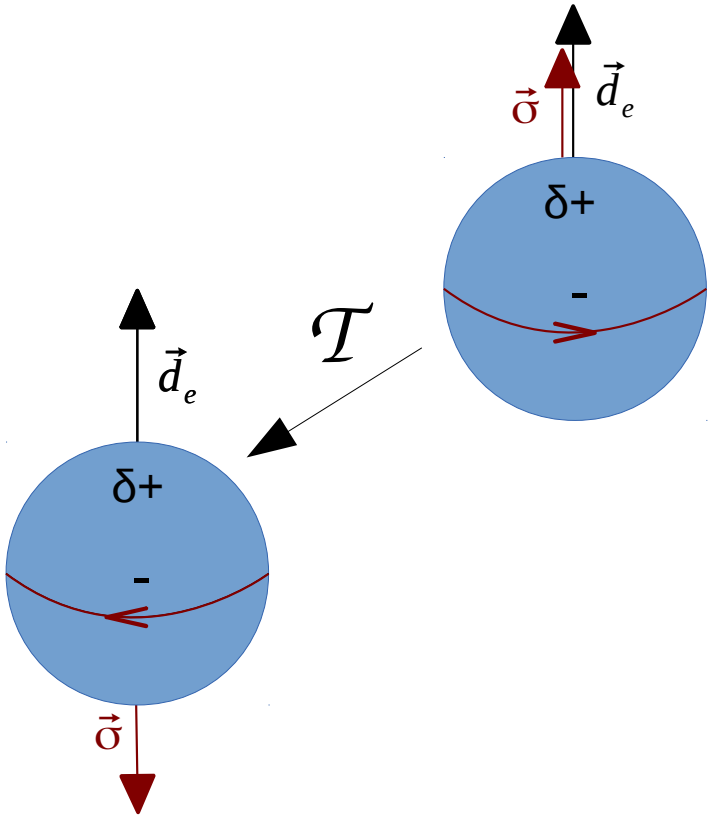

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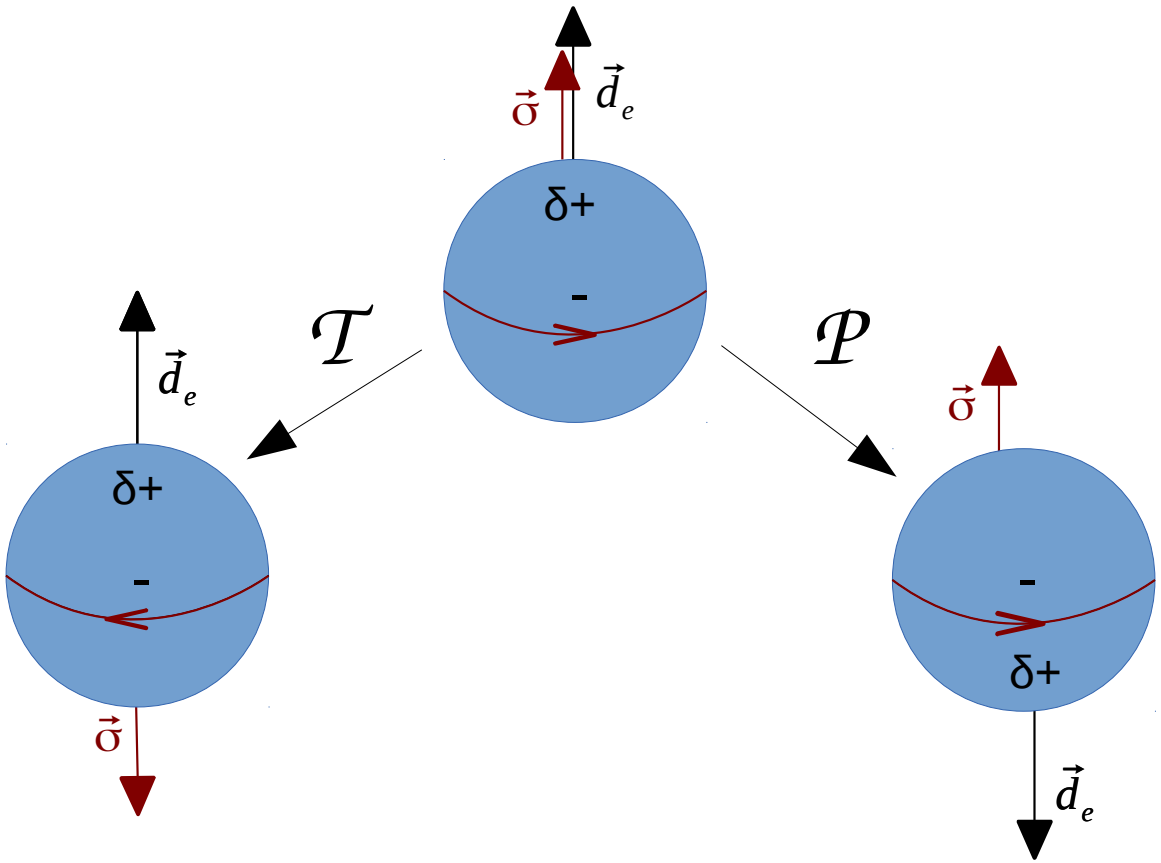

$\Rightarrow$ Violation of $\mathcal{P}$- and $\mathcal{T}$-symmetry

$\mathcal{CPT}$ theorem $\rightarrow$ $\mathcal{CP}$ violation

$\mathcal{CP}$ violation and BAU.

Sakharov[1]: $\mathcal{CP}$ violation as an explanation for the Baryon Asymmetry of the Universe (dominance of matter over antimatter).

- $\mathcal{CP}$ violating phenomena in the Standard Model
  Decay of neutral K mesons[2] :
  $K_2 = \frac{1}{\sqrt{2}}(K_0 + \overline{K_0}) \rightarrow \pi + \pi$.
- Insufficient level of $\mathcal{CP}$ violation to explain BAU
  $\Rightarrow$ new theories Beyond the Standard Model developped.

[1] A.D. Sakharov, *JETP Lett.* **5** (1967) *24-27*
[2] J. H. Christenson et al., *Phys Rev Lett* **13** (1964) *138*

Each BSM theory predicts a value for the electron EDM
$\Rightarrow$ eEDM as low-energy test for new physics.

Table : Predicted values of the electron EDM[3]

Model	$d_e[e.cm]$
Standard model	$< 10^{-38}$
Left-Right Symmetry	$10^{-28} - 10^{-26}$
Multi-Higgs	$10^{-28} - 10^{-27}$
Supersymmetry	$\leq 10^{-25}$
Experimental upper limit[4]	9.6×10^{-29}

[3] E.D. Commins, *Adv At Mol Opt Phys* **40** (1998) *1*
[4] ACME Collaboration, *Science* **6168** (2014) *269*

Measuring an EDM.

Choice of a system: why not on a bare electron?

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

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Sandars amplification[5]: $d_e E \rightarrow R d_e E$ $(R = \frac{d_a}{d_e} \propto Z^3)$

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R (enhancement factor): a few hundreds for an atom, until 10^6 for a polar diatomic molecule

$R = \frac{E_{eff}}{E_{lab}}$ (E_{eff} to be determined by theory)

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

$^3\Delta_1$ molecules.

- Ω-doublet structure:
  huge polarisability $\longrightarrow$ large internal electric field
  spectroscopy reversal: $\Omega \to -\Omega \Leftrightarrow \mathcal{E} \to -\mathcal{E}$

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  "s": science electron (relativistic EDM enhancement)
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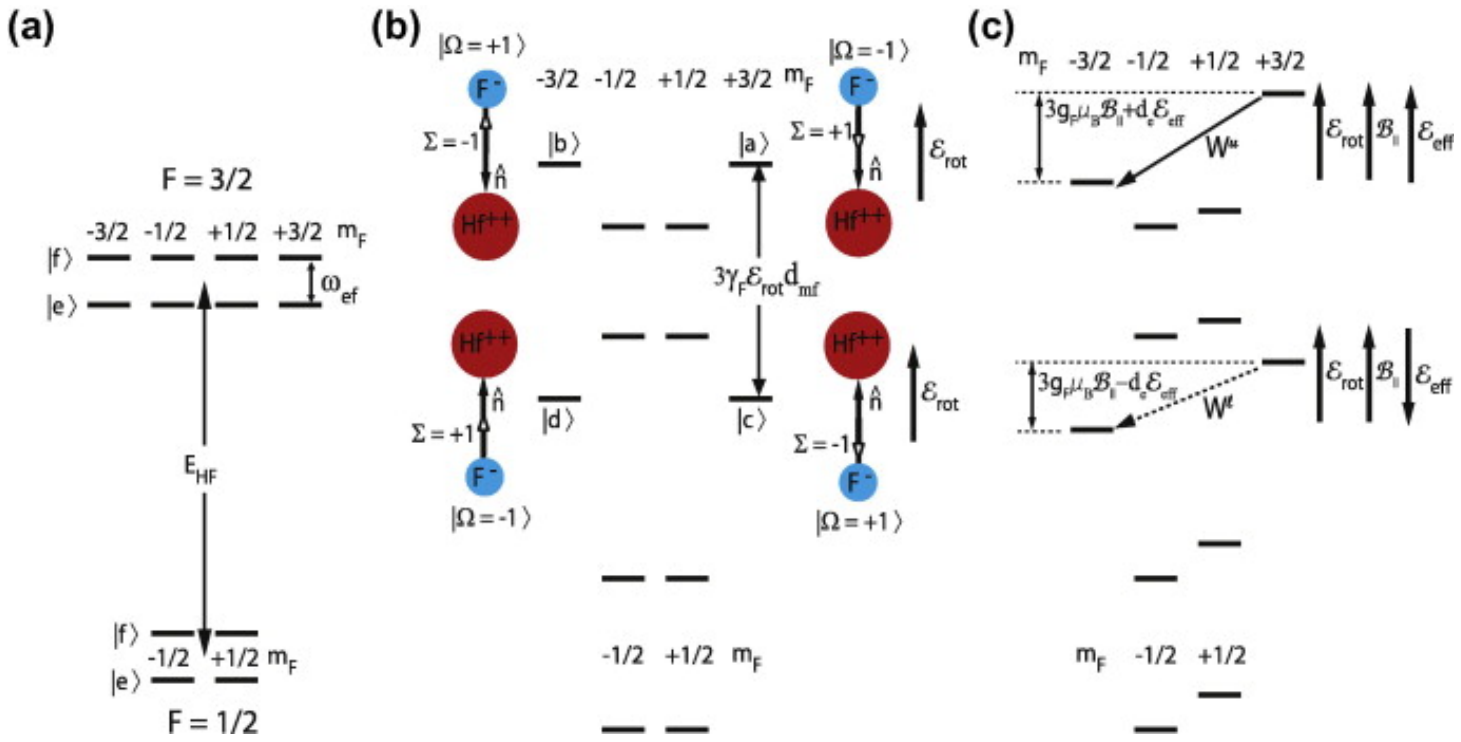
- $m_\Omega = -g_s \mu_B (\Sigma + \frac{\Lambda}{2}) \approx 0$ $(\Sigma = 1, \Lambda = -2)$

HfF^+ experiment in JILA



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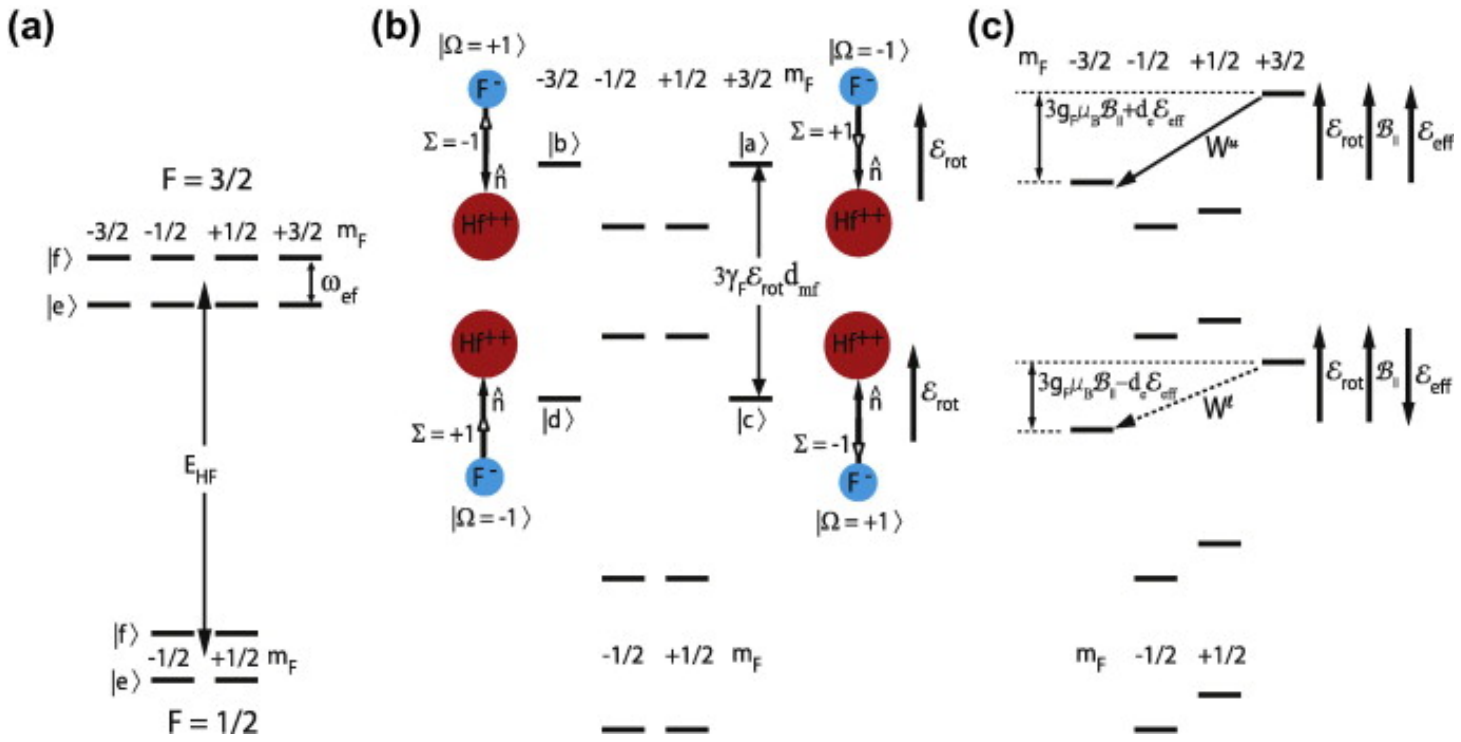

$$W^u(\mathcal{B}) - W^u(-\mathcal{B}) = W^u(\mathcal{B}) - W^l(\mathcal{B}) = 2d_e\mathcal{E}_{eff}$$

eEDM Hamiltonian

- Single-particle $\mathcal{P}, \mathcal{T}$-odd eEDM Hamiltonian[6]:

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

- Electromagnetic contributions:

$$H_{EDM} = -d_e\left[\gamma^0\mathbf{\Sigma}\cdot\mathbf{E} + \imath\gamma\cdot\mathbf{B}\right] \text{ with } \mathbf{E}(i) = \mathbf{E}_{int}(i) + \mathbf{E}_{ext}(i)$$

- Internal electric field contributions:

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

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

Symmetries

- Parity $\mathcal{P}$

$$\begin{aligned}\hat{\mathcal{P}}^\dagger \hat{H}_{EDM} \hat{\mathcal{P}} &= -d_e \hat{\mathcal{P}}^\dagger \gamma^0 \boldsymbol{\Sigma} \cdot \mathbf{E} \hat{\mathcal{P}} = -d_e \gamma^0 \hat{\mathcal{P}}^\dagger \boldsymbol{\Sigma} \hat{\mathcal{P}} \cdot \hat{\mathcal{P}}^\dagger \mathbf{E} \hat{\mathcal{P}} \\ &= -d_e \gamma^0 \boldsymbol{\Sigma} \cdot (-\mathbf{E}) = -\hat{H}_{EDM}.\end{aligned}$$

- Time-reversal $\mathcal{T}$

$$\begin{aligned}\hat{\mathcal{K}}^\dagger \hat{H}_{EDM} \hat{\mathcal{K}} &= -d_e \hat{\mathcal{K}}^\dagger \gamma^0 \boldsymbol{\Sigma} \cdot \mathbf{E} \hat{\mathcal{K}} = -d_e \gamma^0 \hat{\mathcal{K}}^\dagger \boldsymbol{\Sigma} \hat{\mathcal{K}} \cdot \hat{\mathcal{K}}^\dagger \mathbf{E} \hat{\mathcal{K}} \\ &= -\hat{H}_{EDM}.\end{aligned}$$

$\Rightarrow H_{EDM}$ is $\mathcal{P}, \mathcal{T}$-odd.

Expectation value

- Schiff's Theorem

$$\hat{H}_{EDM} = -d_e \mathbf{\Sigma} \cdot \mathbf{E} - d_e(\gamma^0 - 1)\mathbf{\Sigma} \cdot \mathbf{E}$$

Expectation value of the non-relativistic term vanishes but

$$E_{EDM} = \left\langle -d_e(\gamma^0 - 1)\mathbf{\Sigma} \cdot \mathbf{E} \right\rangle_{\psi_0} \neq 0$$

$\longrightarrow$ evasion of Schiff's theorem.

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- Lorentz contraction in lab frame

$$d_e^L = d_e - \frac{\gamma}{1+\gamma}\gamma^0 d_e \cdot \gamma^0$$

with $\gamma = (1-\beta^2)^{-\frac{1}{2}}$ and $\beta = \frac{v}{c}$.

Parity eigenstates

Expectation value of $\hat{H}_{EDM}$ over an atomic unperturbed state (parity $p = \pm 1$):

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

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Consequence of $\mathcal{P}$-odd characteristic of $\hat{H}_{EDM}$
$\longrightarrow$ vanishing expectation value over parity eigenstates
$\Rightarrow$ need to mix parity eigenstates either by:

1. perturbing laboratory E field (atomic experiments)
2. molecular internal fields (diatomic molecules experiments).

Theoretical input E_{eff}

- Input needed:

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

- Effective electric field E_{eff}

$$E_{eff} = -\left\langle \sum_{i=1}^{n} \gamma^0(i)\boldsymbol{\Sigma}(i)\cdot \mathbf{E}_{int}(i) \right\rangle_{\psi^{(0)}} \approx \frac{2\imath c}{e\hbar} \left\langle \sum_{i=1}^{n} \gamma^0(i)\gamma^5(i)\mathbf{p}^2(i) \right\rangle_{\psi^{(0)}}$$

Alternative form given by Lindroth stratagem II[7] used for the implementation.

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

$\mathcal{P}, \mathcal{T}$-odd interaction constants

- Electron EDM interaction

$$W_d := \frac{2\imath c}{\Omega e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5 \mathbf{p}^2 \right\rangle_{\psi_\Omega}$$

- Scalar-Pseudoscalar nucleon-electron interaction

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

- Hyperfine interaction constant as test of wavefunction quality

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

Correlated Wavefunction Theory

- Dirac-Coulomb Hamiltonian:

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

- Expansion of the wavefunctions over Slater determinants:

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

- Slater determinants made up from molecular time-reversal paired 4-spinors (Kramers pairs $\{\varphi_i, \varphi_{\bar{i}}\}$) related through $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

$\mathcal{P}, \mathcal{T}$-odd Property Calculations

- Expectation value over relativistic Configuration Interaction wavefunctions

$$\langle \hat{H}_{\mathcal{P},\mathcal{T}} \rangle_{\psi_k} = \sum_{I,J=1}^{dim\mathcal{F}^t(M,N)} c_{kI}^* c_{kJ} \langle (\mathcal{S}\overline{\mathcal{T}})_I | \sum_{i=1}^{N} \hat{H}_{\mathcal{P},\mathcal{T}}(i) | (\mathcal{S}\overline{\mathcal{T}})_J \rangle$$

- Property operator in basis of Kramers-paired molecular spinors

$$\hat{H}_{\mathcal{P},\mathcal{T}} = \sum_{p,q=1}^{P_u} h_{pq} a_p^\dagger a_q + \sum_{p=1}^{P_u} \sum_{q=P_u+1}^{P} h_{p\bar{q}} a_p^\dagger a_{\bar{q}} + \sum_{p=P_u+1}^{P} \sum_{q=1}^{P_u} h_{\bar{p}q} a_{\bar{p}}^\dagger a_q + \sum_{p,q=P_u+1}^{P} h_{\bar{p}\bar{q}} a_{\bar{p}}^\dagger a_{\bar{q}}$$

- First-term contribution to expectation value

$$W(\psi_k) = \sum_{I,J=1}^{dim\mathcal{F}^t(M,N)} c_{kI}^* c_{kJ} \sum_{m,n=1}^{P_u} h_{mn}$$
$$\langle | \prod_{p=1}^{N_p \in \mathcal{S}_I} \prod_{\bar{p}=N_p+1}^{N_p \in \mathcal{S}_I + N_{\bar{p}} \in \overline{\mathcal{T}}_I} a_{\bar{p}} a_p a_m^\dagger a_n \prod_{q=1}^{N_p \in \mathcal{S}_J} \prod_{\bar{q}=N_p+1}^{N_p \in \mathcal{S}_J + N_{\bar{p}} \in \overline{\mathcal{T}}_J} a_q^\dagger a_{\bar{q}}^\dagger | \rangle$$

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

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.

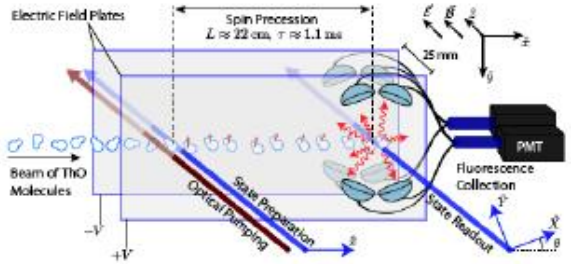

Figure : *Science* **6168** (2014) *269*

- Most constraining upper-bound on eEDM
- Need for an accurate theoretical input E_{eff} and minimized error bar

Theory	E_{eff} $\left[\frac{GV}{cm}\right]$	$W_S[kHz]$	$A_{\|\|}$ [MHz]
2c-CCSD(T)[8]	81.5	112	−1327
4c-MR-CISD[9]	75.2	107.8	−1339

[8] L. Skripnikov, A.V. Titov, *J Chem Phys* **142** (2015) *024301*
[9] TF, M.K. Nayak, *J Mol Spectrosc* **300** (2014) *16*

CI models

	# of Kramers pairs	Accumulated e^- #*min*	#*max*
Deleted			
Virtual	183-X	36	36
Th: 6d$\sigma\pi$, 7p, 8s Th: 7s, 6dδ	X	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)		

X : # of Kramers pairs in active space,
m, n, p, q: maximum ranks of excitations allowed.

In the following, we will use the nomenclature MR$_X$-SD18 where SD points out that single and double excitations are allowed between active spaces and towards the virtual space ($m = n = 2, p = q = 0$).

Base values

Previous base model: vTZ/MR_{12}-CISD(18)
New: vTZ/MR_{12}^{+T}-CISD(18)

- correlates subvalence and valence spinors (Th $6s, 6p$, O $2s, 2p$)
- allows for triple excitation from subvalence to occupied orbitals
- includes quintuple excitations

$$occ^{16} val^2 \longrightarrow occ^{13} val*^3 virt^2,$$
$$occ^{16} val^2 \longrightarrow occ^{13} val*^4 virt^1,$$
$$occ^{16} val^2 \longrightarrow occ^{13} val*^5 virt^0$$

- requires a 7-billion determinant CI calculation

occ: subvalence, *val*: minimal active space (Th $7s, 6d_\delta$), *val*$*$: active space (Th $7p, 8s, 8p_\pi$), *virt*: virtual space

DCHF spinor basis

Table : Calculated properties and molecular static electric dipole moment $D = \left\langle {}^{M}\Lambda_{\Omega}|\hat{D}_z|{}^{M}\Lambda_{\Omega}\right\rangle$ for $\Omega = 1$ at $R = 3.477$ a_0, using the wavefunction model MR_{12}-CISD(18), the vDZ basis set and a virtual cutoff value of 50 a.u.

Spinor basis	T_v $[cm^{-1}]$	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]	D [Debye]
DCHF_2in3 (vTZ)	5410	75.2	−1339	105.8	−4.165
DCHF_2in3	6069	75.1	−1333	105.3	−4.068
DCHF_1in1_1in2	6066	74.9	−1291	105.1	−4.089
DCHF_cs	7871	75.0	−1375	105.4	−4.125

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DCHF_cs	7871	75.0	−1375	105.4	−4.125

- $\mathcal{P},\mathcal{T}$-odd properties insensitivity to the choice of spinors $< 0.3\%$,
- $\mathcal{P},\mathcal{T}$-odd properties insensitivity to basis set enlargement.

Active spinor space

Table : Calculated properties for $\Omega = 1$ at $R = 3.477$ a_0, using different active spinor spaces (X) with the wavefunction model MR$_X$-CISD(18) and vDZ basis set with a virtual cutoff of 50 a.u.

Model	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]
MR$_3$-CISD(18)	80.8	−1283	113.7
vTZ/MR$_3$-CISD(18)	81.0	−1292	114.1
MR$_9$-CISD(18)	73.8	−1321	103.7
MR$_{12}$-CISD(18)	74.7	−1341	105.0
vTZ/MR$_{12}$-CISD(18)	75.2	−1339	106.0
MR$_{13}$-CISD(18)	74.7	−1343	104.9
vTZ/MR$_{13}$-CISD(18)	75.2	−1343	105.9
MR$_{17}$-CISD(18)	74.8	−1334	105.2
MR$_{31}$-CISD(18)	73.1	−1320	102.7

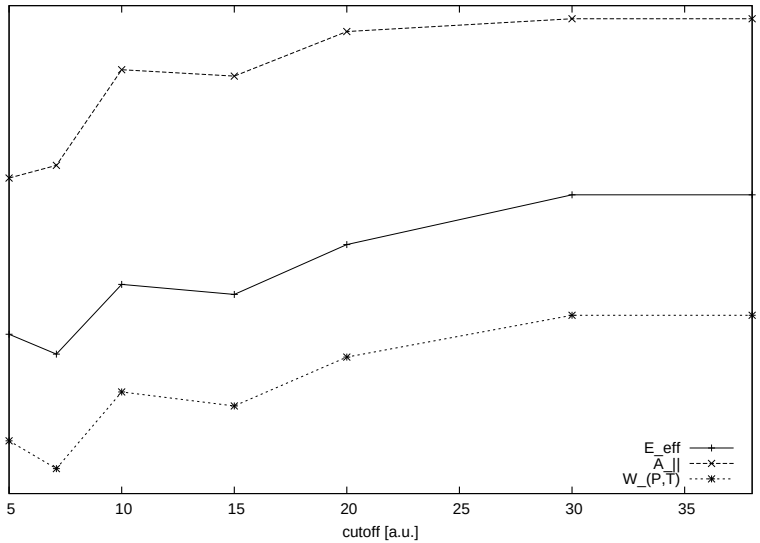
Active spinor space

Table : Calculated properties for $\Omega = 1$ at $R = 3.477$ a_0, using different active spinor spaces (X) with the wavefunction model MR$_X$-CISD(18) and vDZ basis set with a virtual cutoff of 50 a.u.

Model	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]
MR$_3$-CISD(18)	80.8	−1283	113.7
vTZ/MR$_3$-CISD(18)	81.0	−1292	114.1
MR$_9$-CISD(18)	73.8	−1321	103.7
MR$_{12}$-CISD(18)	74.7	−1341	105.0
vTZ/MR$_{12}$-CISD(18)	75.2	−1339	106.0
MR$_{13}$-CISD(18)	74.7	−1343	104.9
vTZ/MR$_{13}$-CISD(18)	75.2	−1343	105.9
MR$_{17}$-CISD(18)	74.8	−1334	105.2
MR$_{31}$-CISD(18)	73.1	−1320	102.7

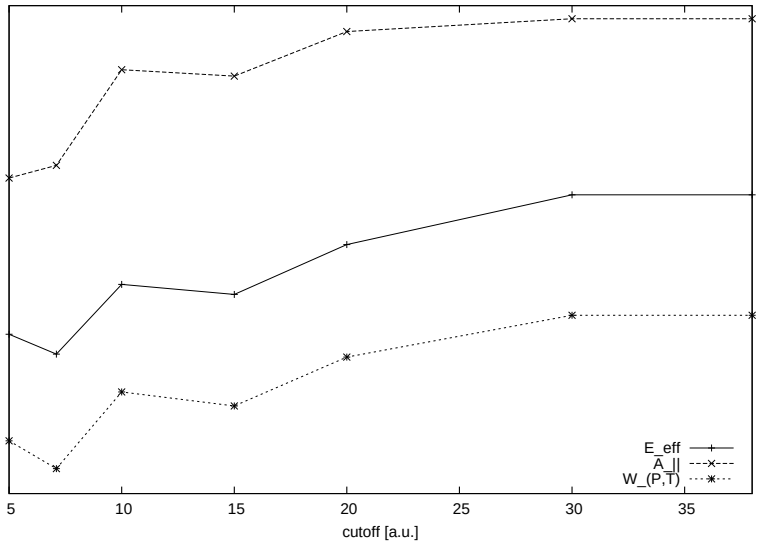
- E_{eff} drop independent of basis set
- Decrease of $\mathcal{P},\mathcal{T}$-odd properties when increasing active space $\rightarrow$ inclusion of quadruple excitation of the type $occ^{16}val^2 \longrightarrow occ^{14}val*^2virt^2$

Core correlations



Model vTZ/MR_3-CISD(36) $\rightarrow$ convergence reached at cutoff = 30 Hartree

Core correlations



Model vTZ/MR_3-CISD(36) $\rightarrow$ convergence reached at cutoff = 30 Hartree

Table : Calculated properties for $\Omega = 1$ at $R = 3.477$ a_0, correlating only core-valence and including core-core correlation using vTZ basis set with a virtual cutoff of 38 a.u.

Model (vTZ)	$E_{\text{eff}}\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]	D [Debye]
MR_3-CISD(36)	82.2	−1312	115.9	−4.050
MR_3-CISD(18)	81.0	−1292	114.1	−3.809

- Small 1.5% correction of the properties

Final values

$E_{\text{eff}}\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]	D [Debye]	
75.2[10]	−1339	106.0	−4.165	vTZ/MR$_{12}$-CISD(18)
77.1	−1309	108.5	−4.020	new base value from vTZ/MR$_{12}^{+T}$-CISD(18)
−0.2	+42	−0.2	−0.021	correction for Δ spinors
−1.6	+21	−2.3		correction for active space size
+1.2	−20	+1.8	−0.241	core correlations
−1.3				Gaunt correction
75.2	−1296	107.8		**Final values**[11]

[1] T. Fleig, M.K. Nayak, *J Mol Spectrosc* **300** (2014) *16*
[2] M. Denis, T. Fleig, arXiv:1605.03091v1 (2016)

Perspectives

- Calculation of the Nuclear Magnetic Quadrupole Moment interaction constant for ThO and ThF^+
- Accurate determination of $A_{||}(F)$ in ThF^+ for next JILA experiment.