Atoms and Molecules as Laboratories for Probing Physics Beyond the Standard Model

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Overview

1. **General introduction:** Particle physics and Electric Dipole Moments

2. **Relativistic Electronic-Structure Methods:** A few words

   TF, *Chem Phys* **395** (2012) 2

3. **The search for Beyond-Standard-Model Physics:**
   The **ThO** and **ThF$^+$** systems
   Aspects of methodology and excited-state spectroscopy

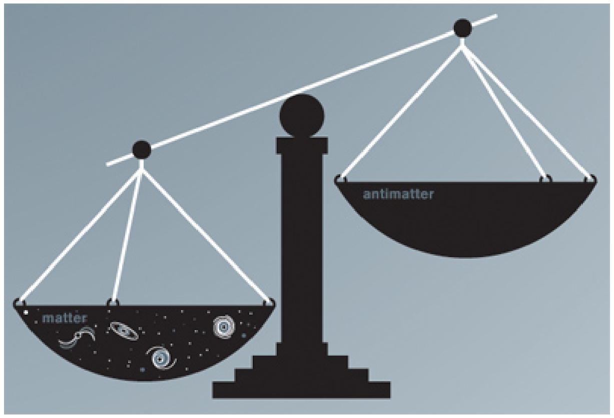
   M. Denis, M.N. Pedersen, H.J.Aa. Jensen, A.S.P. Gomes, M.K. Nayak, S. Knecht, TF, *New J Phys* **7** (2015) 043005

4. The **TaN** system; Link to nuclear theory

   TF, M.K. Nayak, M.G. Kozlov, *Phys Rev A*, **93** (2016) *012505*

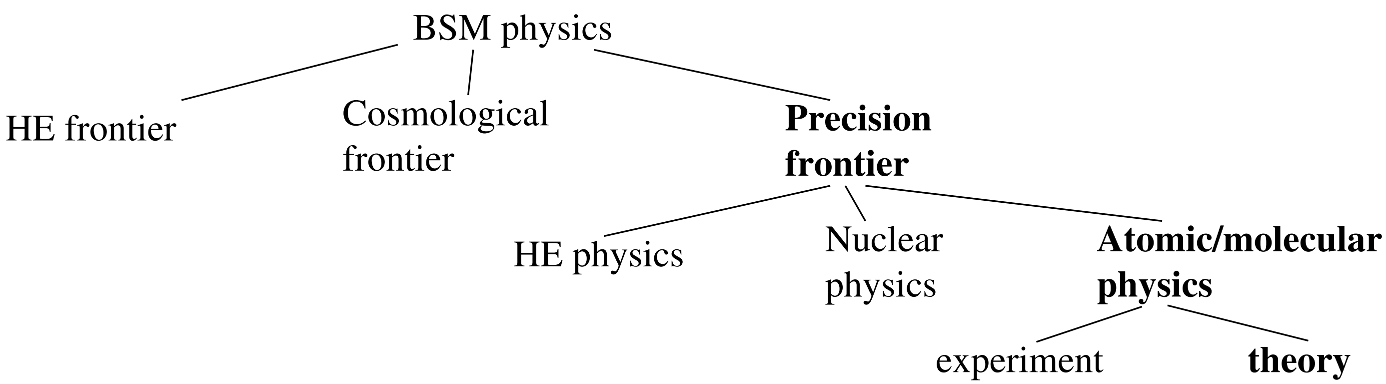
5. **Atomic EDMs**

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 **Electric Dipole Moments (EDM)s** as a powerful probe of possible explanations/consequences[3]



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

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

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

Fundamental Discrete Symmetries

A bit of safe ground ?

$\mathcal{CPT}$ theorem:[5]
Local QFTs invariant

One example: The free Dirac equation (Weyl representation)

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

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

- $\mathcal{CPT}$ invariance is connected to Lorentz invariance[4]
- We have good reasons to "believe" in $\mathcal{CPT}$ symmetry

[4] I. B. Khriplovich, S. K. Lamoreaux, *"(CP) Violation Without Strangeness"*
[5] R. F. Streater, A. S. Wightman, *"PCT, Spin and Statistics, and All That"*

Fundamental Discrete Symmetries

(CP) Violation

- The fall of $\mathcal{P}$ invariance[6]

$$\underset{\text{both left-handed helicity}}{\pi^+ \longrightarrow \mu^+ + \nu_\mu} \quad \overset{\hat{\mathcal{P}}}{\longrightarrow} \quad \underset{\text{both right-handed helicity (impossible)}}{\pi^+ \longrightarrow \mu^+ + \nu_\mu}$$

$$\underset{\text{both left-handed helicity}}{\pi^+ \longrightarrow \mu^+ + \nu_\mu} \quad \overset{\hat{\mathcal{C}}\hat{\mathcal{P}}}{\longrightarrow} \quad \underset{\text{both right-handed helicity (possible)}}{\pi^- \longrightarrow \mu^- + \overline{\nu}_\mu}$$

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

- The fall of $(\mathcal{C}\mathcal{P})$ invariance[7]

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

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

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

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

Fundamental Electromagnetic Moments

Particles that are endowed with ...

	Monopole	Dipole
Electric	$e^-, \mu^-, \pi^\pm, \ldots$	unknown
Magnetic	unknown[8]	$e^-, p^+, n, \ldots$

What is a fundamental **electric dipole moment** ?

Non-relativistic electric dipole energy

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

$\mathcal{P}$-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

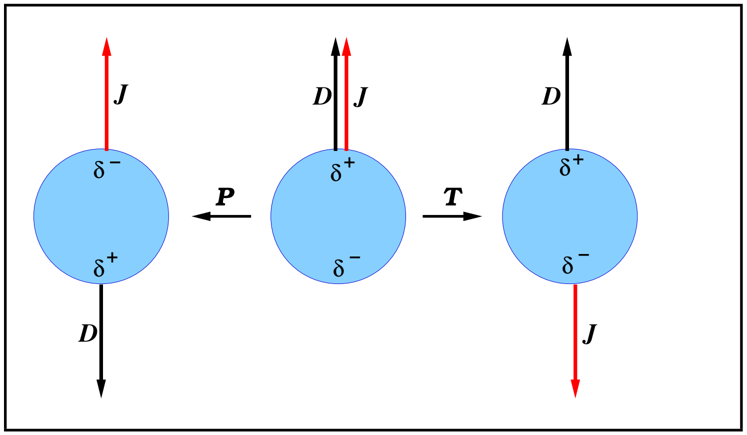
$$E_{\rm EDM} = -d_e \left\langle \Psi \left| \gamma^0 \mathbf{\Sigma} \cdot \mathbf{E} \right| \Psi \right\rangle$$

$\mathcal{P}$-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

[8] J. Preskill, "Magnetic Monopoles", *Ann. Rev. Nucl. Part. Sci.* **34** (1984) *461*,
A. Rajantie, "Magnetic Monopoles in Field Theory and Cosmology", *Phil. Trans. R. Soc. A* **370** (2012) *5705*

Electron Electric Dipole Moment (eEDM)



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

$$\lim_{c\to\infty} \left\langle \hat{H}_{\mathrm{EDM}} \right\rangle = 0$$ (Schiff's Theorem[9])

Lorentz length contraction in observer frame[10]

$$\mathbf{d_e^o} = \mathbf{d_e} - \frac{\gamma}{1+\gamma} \left(\frac{\mathbf{v}}{c} \cdot \mathbf{d_e}\right) \frac{\mathbf{v}}{c}$$

Atomic EDM enhancement[11], can be several orders of magnitude

$$R := \frac{\left\langle \sum_j \gamma_j^0 \, \mathbf{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_\Psi}{E_{\text{ext}}}$$

Scaling[11] with nuclear charge Z

$$R \propto Z^3$$

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

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

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

Cutting-Edge EDM Measurements

In the presence of a non-zero EDM d, the system's Hamiltonian is
$\hat{H} = -\left(\mu\mathbf{B} + d\mathbf{E}\right) \cdot \frac{\hat{\mathbf{J}}}{|J|}$

- **Paramagnetic systems**: Precession measurement on **ThO**
  ACME collaboration Yale/Harvard; DeMille, Doyle, Gabrielse[12]
  measured $\left|\omega^{\mathcal{N}\mathcal{E}}\right| \leq 2.6 \times 10^{-3}\,\frac{\text{rad}}{s} \Rightarrow |d_e| \leq 9.7 \times 10^{-29}\, e$ cm
- **Diamagnetic systems**: Precession measurement on **Hg**
  Seattle group; Heckel[13]
  measured $|d_{Hg}| \leq 5.0 \times 10^{-30}\, e$ cm
- **Neutron** (n) EDM experiment
  PSI, Switzerland[14]
  measured $|d_n| \leq 3.6 \times 10^{-26}\, e$ cm

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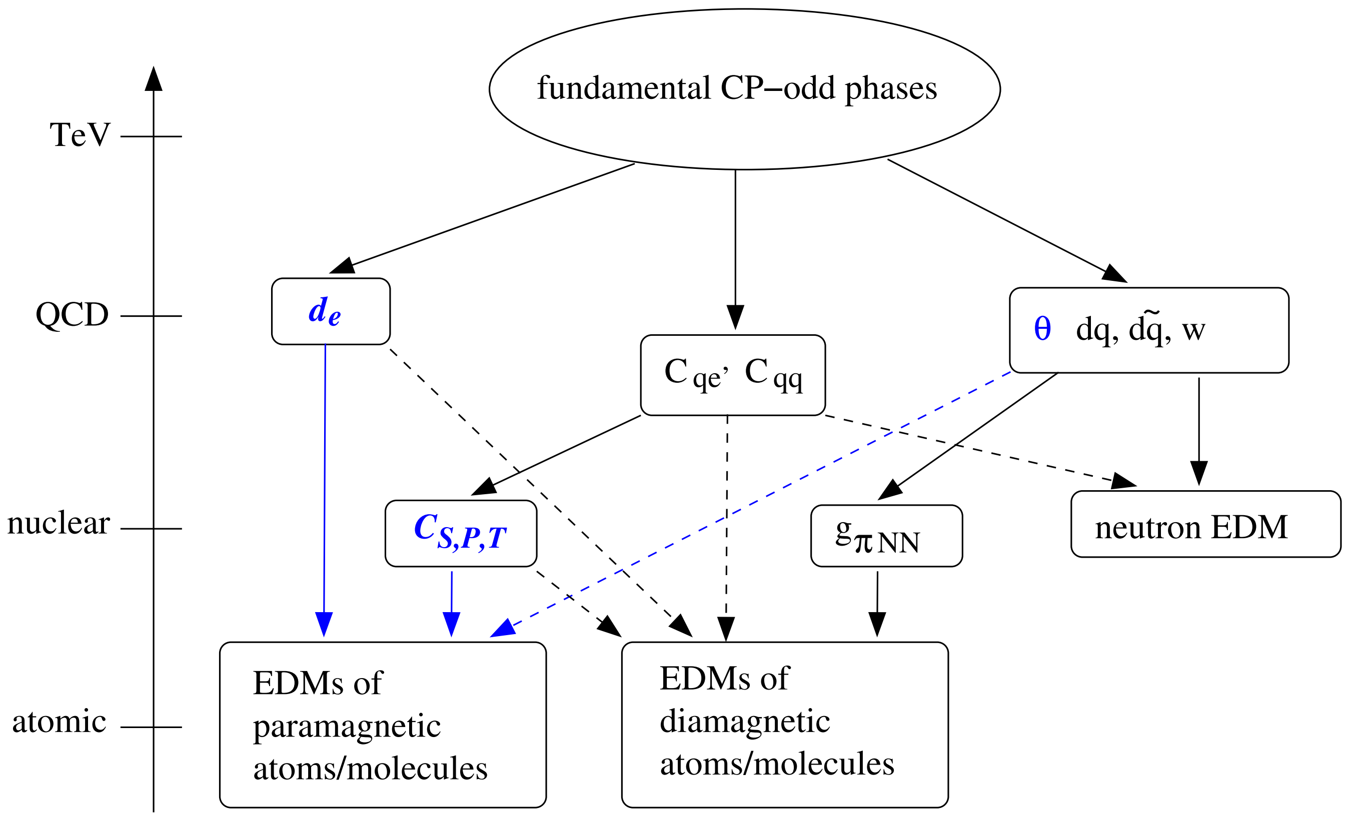
12 J. Baron *et al.*, Science **343** (2014) *269*

13 B. Graner *et al.*, arXiv:1601.04339v2 (2016)

14 J.M. Pendlebury *et al.*, Phys. Rev. D, **92** (2015) *092003*

Electric Dipole Moments and Their Source Tree[15]



d_e: electron EDM

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

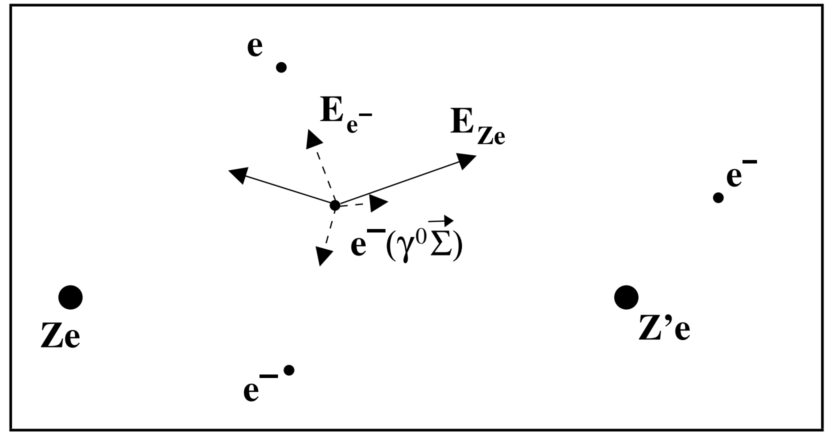
($\mathcal{P}$ and $\mathcal{T}$)-violating nMQM interaction

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

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

Electron EDM Interaction

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



Single-particle $\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[16]:

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

Internal electric field contributions

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

Expectation value in many-body system in accord with stratagem II[17]

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

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

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

$\mathcal{P}$,$\mathcal{T}$-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 nucleon-electron interaction constant

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

- Nuclear magnetic quadrupole - electronic magnetic field interaction

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

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

- Dirac-Coulomb Hamiltonian operator

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

- All-electron Dirac-Coulomb Hartree-Fock (DCHF) calculation
set of time-reversal paired 4-spinors $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

$$\hat{K}(n) := e^{-\frac{\imath}{2}\pi\left(\sum_{j=1}^{n} \boldsymbol{\sigma}\otimes\mathbb{1}_2(j)\right)\cdot\vec{e}_y} \prod_{j=1}^{n} \hat{K}_0(j)$$

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

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

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

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

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

Expectation values over relativistic Configuration Interaction wavefunctions[19]

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

Property operator in basis of Kramers-paired molecular spinors

$$\hat{H}' = \sum_{p,q=1}^{P_u} h'_{pq}\, a_p^\dagger a_q + \sum_{p=1}^{P_u} \sum_{q=P_u+1}^{P} h'_{p\overline{q}}\, a_p^\dagger a_{\overline{q}} + \sum_{p=P_u+1}^{P} \sum_{q=1}^{P_u} h'_{\overline{p}q}\, a_{\overline{p}}^\dagger a_q + \sum_{p,q=P_u+1}^{P} h'_{\overline{pq}}\, a_{\overline{p}}^\dagger a_{\overline{q}}$$

First-term contribution to expectation value

$$W'(\Psi_k)_1 = \sum_{I,J=1}^{\dim\mathcal{F}^{\rm t}(\rm P,N)} c_{kI}^* c_{kJ} \sum_{m,n=1}^{P_u} h_{mn}^M$$

$$\langle \,|\, \prod_{p=1}^{N_p \in \mathcal{S}_I} \prod_{\overline{p}=N_p+1}^{N_p\in\mathcal{S}_I + N_{\overline{p}}\in\overline{\mathcal{T}}_I} a_{\overline{p}} a_p\, a_m^\dagger a_n \prod_{q=1}^{N_p\in\mathcal{S}_J} \prod_{\overline{q}=N_p+1}^{N_p\in\mathcal{S}_J + N_{\overline{p}}\in\overline{\mathcal{T}}_J} a_q^\dagger a_{\overline{q}}^\dagger \,|\, \rangle$$

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

Search for the Electron EDM

Why paramagnetic 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[20] $E_{\mathrm{eff}} \approx 0.05\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$
2. Molecular fields:
   YbF[21]: $E_{\mathrm{eff}} \approx 26\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$, HgF[22]: $E_{\mathrm{eff}} \approx 100\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$,

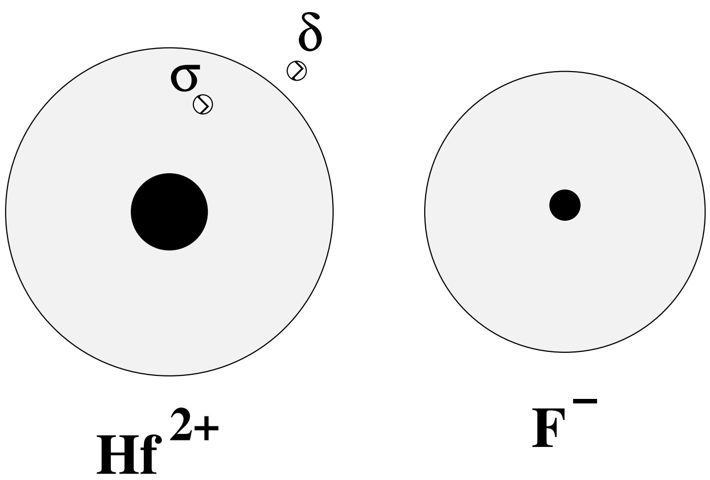
[20] V.V. Flambaum, *Sov J Nucl Phys* **24** (1976) *199*

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

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

The eEDM in a molecular framework

$^3\Delta$ molecules[23]



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

- Deeply bound and strongly polar molecules (fluorides, oxides, (nitrides))
- Small Λ (Ω)-doublet splitting[24] (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

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

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

ThO

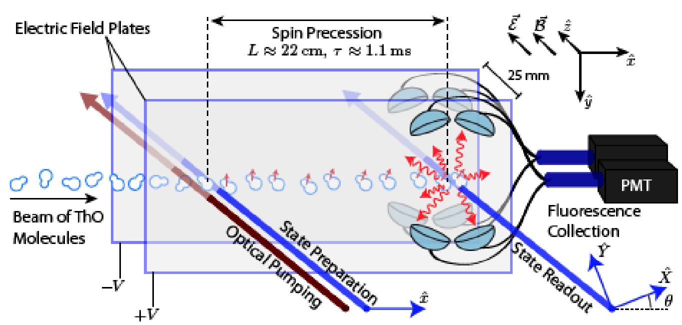
Experiment: ACME Collaboration, Yale/Harvard, (DeMille/Doyle/Gabrielse groups)

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



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

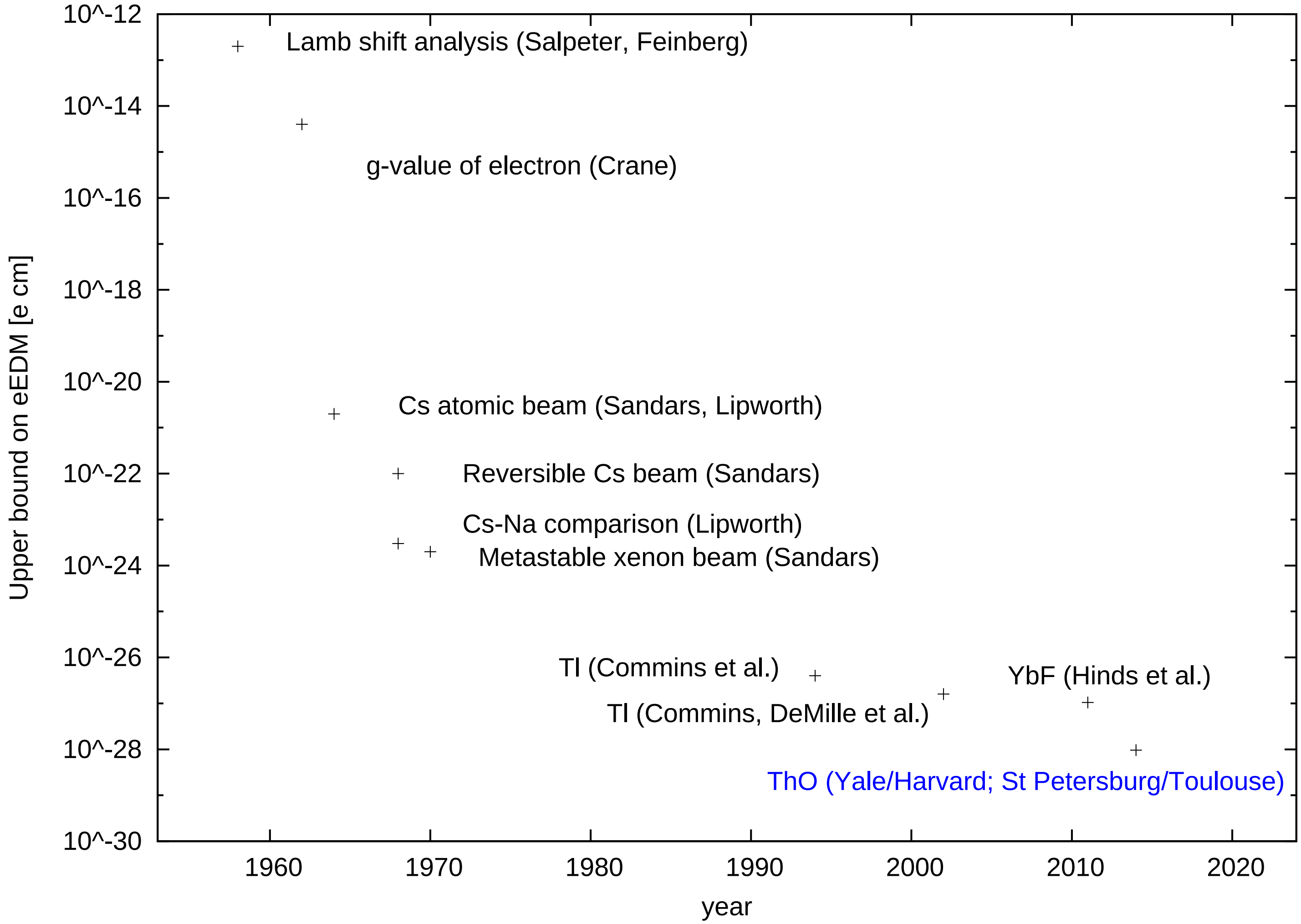
Theory	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	W_S [kHz]
2c-CCSD(T)[25]	81.5	112
4c-MR-CISD[26/27]	75.2/75.2	105/107.8

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

[26] TF, M.K. Nayak, *J Mol Spectrosc* **300** (2014) *16*

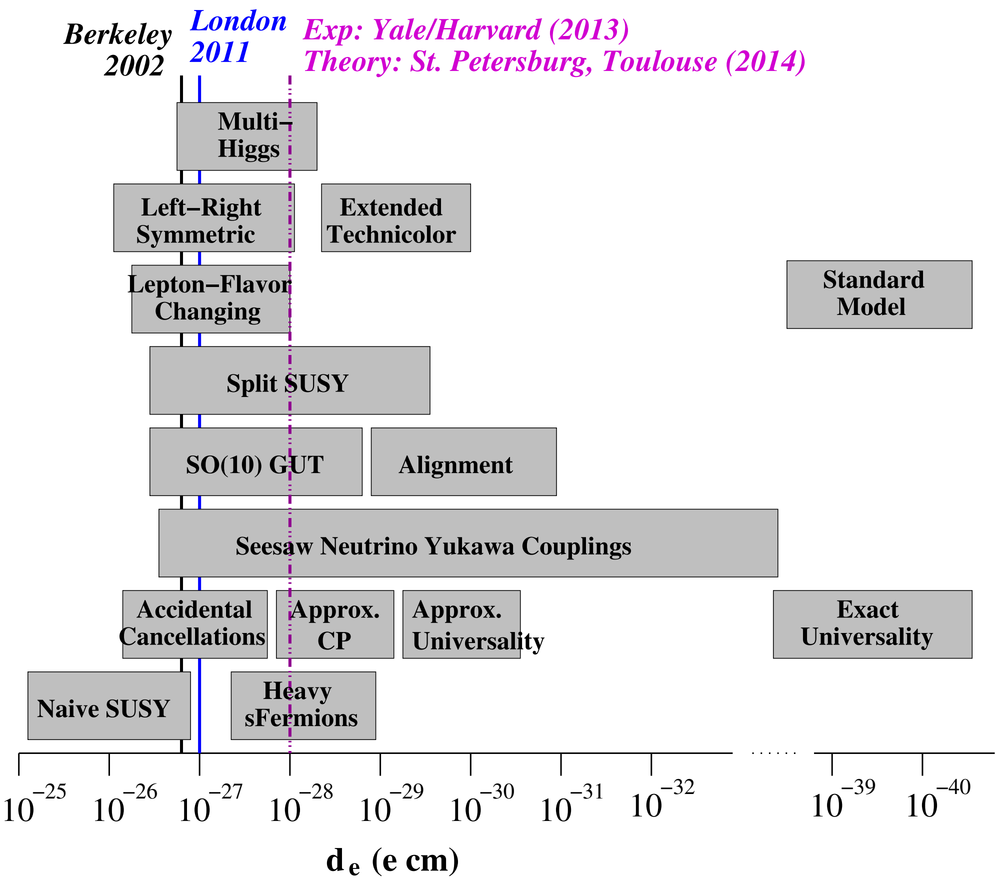
[27] M. Denis, TF, *J Chem Phys* (2016) *submitted*

Historical Development of eEDM Upper Bound[28]



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

eEDM Constraint on Beyond-Standard-Model Theories[29]



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)[30]	$< 1.6 \cdot 10^{-27}$
Experimental limit (YbF)[31]	$< 10.5 \cdot 10^{-28}$
Experimental limit (ThO)[32]	$< 9.6 \cdot 10^{-29}$

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

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

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

[32] 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*, M. Denis, TF, *J Chem Phys* (2016) *submitted*

Molecular (cat)ions

HfF^+/ThF^+

Experiment: JILA, Boulder, Colorado (Cornell group)

EDM Studies in Molecular Ions

as opposed to neutral molecules[33]

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

- Sufficiently large value of E_{eff}
  Hope for very large value[34] 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[35]: ${}^3\Delta_1$ **or** ${}^1\Sigma_0^+$

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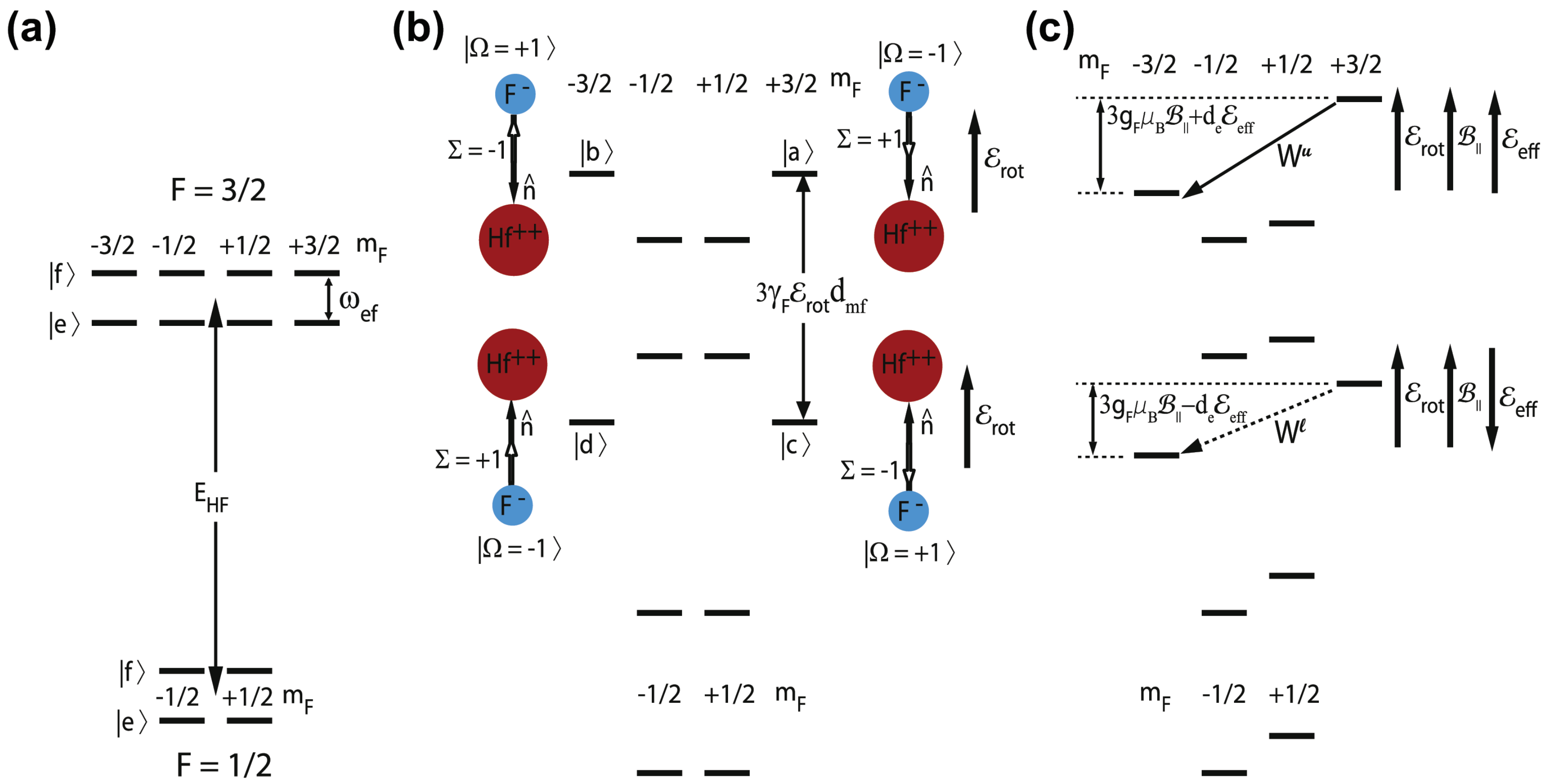
[33] H. Loh, K.C. Cossel, M.C. Grau, K.-K. Ni, E.R. Meyer, J.L. Bohn, J. Ye, E.A. Cornell, *Science* **342** (2013) *1220*
A.E. Leanhardt, J.L. Bohn, H. Loh, P. Maletinsky, E.R. Meyer, L.C. Sinclair, R.P. Stutz, E.A. Cornell, *J Mol Spectrosc* **270** (2011) *1*

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

[35] 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. 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[36] on HfF^+



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

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[36] 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

	Model	Th spinor distribution on spaces				
		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[37] of ThF^+

Method	Model[a]	Hamiltonian	Electronic state energy $^1\Sigma^+_{0+}$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$
IHFSCC	$\mathcal{II}^{\mathcal{CC}}$	2c	42	0.00	1062	3146
	$\mathcal{III}^{\mathcal{CC},\dagger}$	2c	15	0	1062	3149
	$\mathcal{III}^{\mathcal{CC},\ddagger}$	2c	191	0	1048	3157
	$\boldsymbol{\mathcal{III}^{\mathcal{CC},*}}$	**2c**	**319**	**0**	**1039**	**3162**
MRCI	$\mathcal{I}^{\mathcal{CI}}$	2c	854	0	1154	3189
	$\mathcal{II}^{\mathcal{CI}}$	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 (Heaven et al.)[b]			0	315.0(5)	1052.5(5)	3150(15)
Experiment (Cornell et al.)[c]			314.0(2)	0		

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

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

[37] [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*
[c] D.N. Gresh, K.C. Cossel, Y. Zhou, J. Ye, E.A. Cornell, (2015) *unpublished manuscript*

(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^+ ([38])	MR_{10}-CISD(20)	**8.9**	0.001 p_z(F)	3.75
	MR_{10}-CISD(18)	4.3		
HfF^+ ([39])	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

[38] 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

[39] 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	$T_v[\mathrm{cm}^{-1}]$	$E_{\mathrm{eff}}[\frac{\mathrm{GV}}{\mathrm{cm}}]$	$A_{\vert\vert}$[MHz]	W_S[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:

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

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

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

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

ThF^+

Electric Transition Dipole Moments

${}^{M}\Lambda_{\Omega}$ State	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_{eff} in the $\Omega = 1$ science state[40]

HfF$^+$ Model	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	ThF$^+$ Model	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$
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.[41]	≈ 30	Meyer et al.	≈ 90
20 e^- corr., Titov et al.[42]	24.2	38 e^- corr., Titov et al.[43]	≈ 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

[40] 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*

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

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

[43] L. V. Skripnikov, A.V. Titov, *arXiv:1503.01001v1* (2015)

TaN

Experiment: Yale/Harvard, (planned)

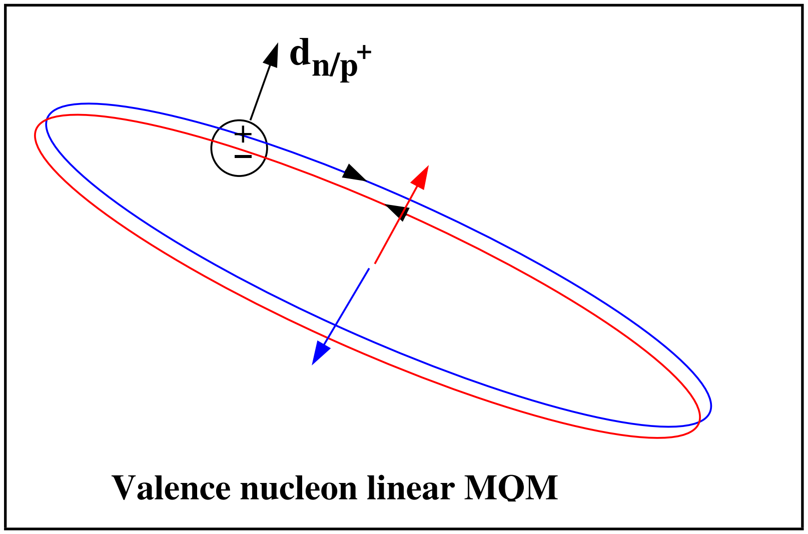
Constraining $\mathcal{P}$,$\mathcal{T}$-violating hadron physics

- Nuclear MQM has two possible sources[44]:
  1. Intranuclear $\mathcal{P}$-,$\mathcal{T}$-odd interactions, described by QCD $(\mathcal{CP})$-violating parameter[45] $\tilde{\Theta}$,
     $$M_0^{p,n}(\tilde{\Theta}) \approx 2 \times 10^{-29}\,\tilde{\Theta}\,e\,\text{cm}^2$$
     M: valence nucleon MQM
  2. Neutron/proton EDM (order of magnitude smaller)
- MQM is enhanced in non-spherical (deformed) nuclei[46]
- 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)

[44] V. V. Flambaum, D. DeMille, M. G. Kozlov, *Phys Rev Lett* **113** (2014) *103003*
[45] R. J. Crewther, P. Di Vecchia, G. Veneziano, E. Witten, *Phys Lett* **88B** (1979) *123*
[46] V. V. Flambaum, *Phys Lett B* **320** (1994) *211*

Nuclear Magnetic Quadrupole Moment Interaction[47]

Effective molecular Hamiltonian[48]
for linear molecule along **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

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

$$W_M \propto \left(\frac{\boldsymbol{\alpha}\times\mathbf{r}}{r^5}\right)_3 r_3$$

Implementation[49] via electric-field gradient with the help of

$$\left(\frac{\boldsymbol{\alpha}\times\mathbf{r}}{r^5}\right)_3 r_3 = \alpha_1\, \frac{r_2 r_3}{r^5} - \alpha_2\, \frac{r_1 r_3}{r^5} \qquad \iiint_{\mathcal{V}} \frac{r_i r_j}{r^5}\, d^3r = -\frac{1}{3} \iiint_{\mathcal{V}} \frac{\partial}{\partial r_i}\, \frac{r_j}{r^3}\, d^3r$$

[47] I.B. Khriplovich, *Sov. Phys. ZhETP* **44** (1976) *25*; O.P. Sushkov, V.V. Flambaum, I.B. Khriplovich, *Sov. Phys. ZhETP* **60** (1984) *873*

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

[49] TF, M.K. Nayak, M.G. Kozlov, *Phys Rev A*, **93** (2016) *012505*

Nuclear MQM - Electronic B-Field Interaction

- i-th component of the quadrupole term of the classical vector potential[50]
$$A_Q(\vec{r})_\imath = -\frac{1}{6}\sum_{k,l,n}\varepsilon_{\imath ln}\,M_{nk}\,\frac{\partial}{\partial r_l}\frac{\partial}{\partial r_k}\frac{1}{r} = \frac{1}{6}\sum_{k,l,n}\varepsilon_{\imath ln}\,M_{nk}\left(\frac{\delta_{kl}}{r^3}-\frac{3r_kr_l}{r^5}\right)$$

- M is a symmetric tensor, so
$$\vec{A}_Q(\vec{r}) = -\sum_{k,n} M_{nk}\,\frac{1}{2r^5}\sum_{\imath,l}\varepsilon_{\imath ln}\,r_lr_k\vec{e}_\imath$$

- Since $V_{Qe} = \frac{e}{c}\,\vec{v}\cdot\vec{A}_Q(\vec{r})$, we quantize as $\vec{v}\to c\vec{\alpha}$, and
$$\hat{H}_{Qe} = -\sum_{k,n} M_{nk}\,\frac{1}{2r^5}\sum_{\imath,j,l}\varepsilon_{\imath ln}\,r_lr_k\,\vec{e}_\imath\cdot\vec{e}_j\,\alpha_j = -\sum_{j,k,l,n}\frac{1}{2r^5}\,\varepsilon_{jln}\,\alpha_j\,r_lr_k\,M_{kn}$$

- Using a contracted tensor $(r\vec{M}) = \sum_\imath \vec{e}_\imath\,(rM)_i$, we get
$$\hat{H}_{Qe} = -\sum_{j,l,n}\frac{1}{2r^5}\,\varepsilon_{jln}\,\alpha_j\,r_l\,\vec{e}_n\cdot\left(r\vec{M}\right) = -\frac{\vec{\alpha}\times\vec{r}}{2r^5}\cdot\left(r\vec{M}\right)$$

- On the basis of which we define
$$W_M := \frac{3}{2\Omega}\left\langle\Psi_\Omega\left|\sum_{j=1}^{n}\left(\frac{\boldsymbol{\alpha}_j\times\mathbf{r}_{jA}}{r_{jA}^5}\right)_{k=3}(r_{jA})_{k=3}\right|\Psi_\Omega\right\rangle$$

[50] O.P. Sushkov, V.V. Flambaum, I.B. Khriplovich, *Sov. Phys. ZhETP* **60** (1984) *873*

About Ω Subspaces

- 2nd-order PT:
  $E^{(2)}_{\text{MQM}}(\Omega_j) = \sum_{k\neq j} \frac{\left|\langle\Omega_j|\hat{H}_{\text{MQM}}|\Omega_k\rangle\right|^2}{E^{(0)}_{\Omega_j} - E^{(0)}_{\Omega_k}}$ negligible

- In the two-dimensional subspace $\{\Omega_j, -\Omega_j\}$ with $\Omega_j > 0$,
  $$\left\langle \Omega_j \left| \hat{H}_{\text{MQM}} \right| -\Omega_j \right\rangle = \left\langle -\Omega_j \left| \hat{H}_{\text{MQM}} \right| \Omega_j \right\rangle = 0$$
  using axial rotation group
  $$\Gamma^{(-\Omega_j)^\dagger} \otimes \Gamma^{(\hat{H}_{\text{MQM}})} \otimes \Gamma^{(\Omega_j)} = \Gamma^{(\Omega_j+0+\Omega_j)} = \Gamma^{(2\Omega_j)} \notin \{\Gamma^0\}$$

- Furthermore,
  $$\left\langle -\Omega_j \left| \hat{H}_{\text{MQM}} \right| -\Omega_j \right\rangle = \left\langle \Omega_j \left| \hat{P}^\dagger \hat{H}_{\text{MQM}} \hat{P} \right| \Omega_j \right\rangle = -\left\langle \Omega_j \left| \hat{H}_{\text{MQM}} \right| \Omega_j \right\rangle$$
  and
  $$\left\langle -\Omega_j \left| \hat{H}_{\text{MQM}} \right| -\Omega_j \right\rangle = \left\langle \Omega_j \left| \hat{K}^\dagger \hat{H}_{\text{MQM}} \hat{K} \right| \Omega_j \right\rangle^* = -\left\langle \Omega_j \left| \hat{H}_{\text{MQM}} \right| \Omega_j \right\rangle^*$$

$\Rightarrow$ we need only determine $\left\langle \Omega_j \left| \hat{H}_{\text{MQM}} \right| \Omega_j \right\rangle$.

$\mathcal{P},\mathcal{T}$-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

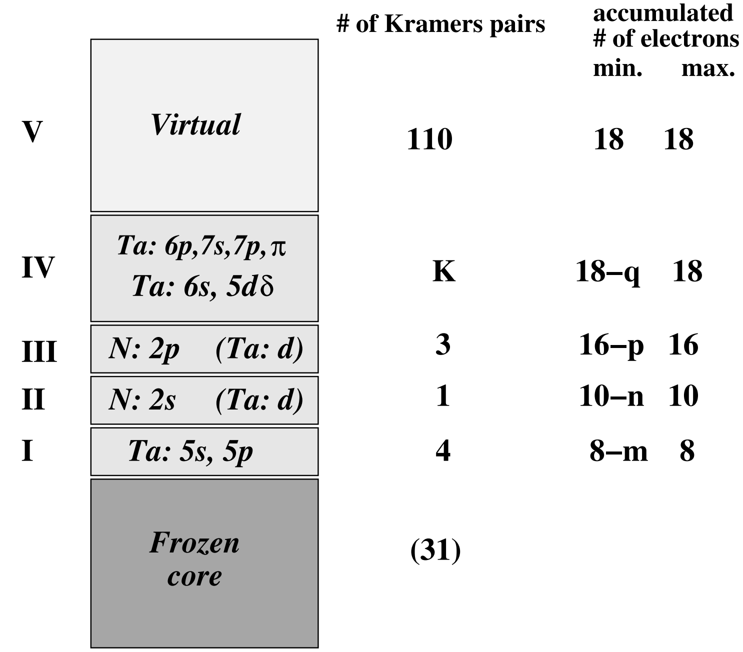
$$W_{\mathcal{P},\mathcal{T}} := \frac{\imath}{\Omega} \frac{G_F}{\sqrt{2}}\, Z \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \rho_N(\vec{r}_j) \right\rangle_{\psi_k^{(0)}} \qquad \left\langle \hat{H}_{\text{e-nSPS}} \right\rangle = k_s\, \Omega\, W_{\mathcal{P},\mathcal{T}}$$

- 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[51]

TaN sample system wavefunction parameterization



GAS-extended projection manifold

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

Selected sub-sets of higher excitations in projection manifold:

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

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

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

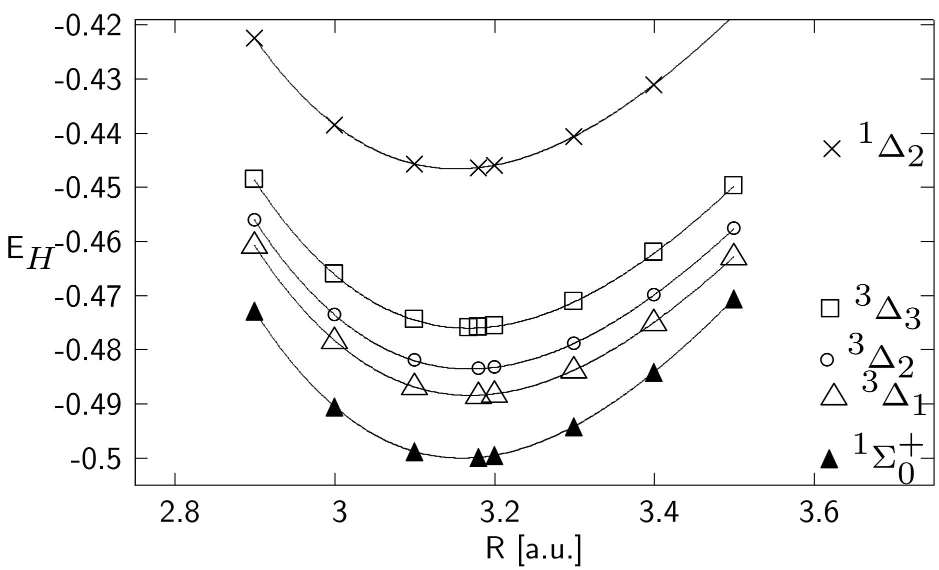
[51] TF, J. Olsen, L. Visscher, *J Chem Phys* **119** (2003) *2963* , S. Knecht, H.J.Aa. Jensen, TF, *J Chem Phys* **132** (2010) *014108* , J. Olsen, *J Chem Phys* **113** (2000) *7140*

TaN, Active-space spinors

No.	$\|m_j\|$	$\left\|\left\langle \hat{\ell}_z \right\rangle_{\varphi_i}\right\|$	$\varepsilon\varphi_i$ $[E_H]$	atomic population, Atom(ℓ_λ)
36	$1/2$	0.003	-0.879	81% N(s), 9% Ta(d_σ)
37	$1/2$	0.287	-0.362	46% N(p_σ), 17% N(p_π), 14% Ta(d_σ), 10% Ta(d_π)
38	$1/2$	0.713	-0.353	43% N(p_π), 24% Ta(d_π), 18% N(p_σ)
39	$3/2$	1.001	-0.353	61% N(p_π), 35% Ta(d_π)
40	$1/2$	0.002	-0.095	79% Ta(s), 10% Ta(d_σ), 8% Ta(p_σ)
41	$3/2$	1.996	-0.017	100% Ta(d_δ)
42	$5/2$	2.000	-0.007	100% Ta(d_δ)
43	$1/2$	0.990	0.022	88% Ta(p_π)
44	$3/2$	1.001	0.025	90% Ta(p_π)
45	$1/2$	0.008	0.041	60% Ta(p_σ), 14% Ta(s), 13% Ta(d_σ)
46	$1/2$	0.023	0.094	86% Ta(s), 13% Ta(d_σ)
47	$1/2$	0.636	0.103	51% Ta(p_π), 25% Ta(p_σ), 10% Ta(d_π)
48	$3/2$	1.001	0.113	77% Ta(p_π)
49	$1/2$	0.342	0.115	36% Ta(p_σ), 26% Ta(p_π), 16% Ta(d_σ)
50	$3/2$	1.030	0.240	47% Ta(d_π), 34% Ta(p_π), 13% N(p_π)
51	$1/2$	1.000	0.240	47% Ta(d_π), 34% Ta(p_π), 16% N(p_π)

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(18)+T	**3.181**	**1134**	0.458	0
	Exp.[52]	**3.181**	**1070**		0.0
$^3\Delta_1$	MR_{12}-CISD(18)+T	**3.196**	1095	0.454	**2967**
	Exp.[52]	**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



- Overall very good agreement with experiment
- Low-lying "science state" $^3\Delta_1$
  $\tau^{^3\Delta_1}$(TaN) >> $\tau^{^3\Delta_1}$(ThO)

[52] 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_S [kHz]	W_M $\left[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}\right]$
MR$_{12}$-CISD(10)	30.1	−3118	27.4	0.633
MR$_{12}$-CISDT(10)	29.7	−3092	27.1	0.626
MR$_{12}^{+T}$-CISD(10)	31.4	−3067	28.7	0.645
MR$'_{12}$-CISD(18)	33.3	−3147	30.3	0.714
MR$_{12}$-CISD(18)	33.6	−3059	30.5	0.718
MR$_{12}$-CISDT(18)	33.4	−3074	30.3	0.716
MR$_{12}^{\prime +T}$-CISD(18)	35.1	−3025	31.9	0.737
MR$_{12}^{+T}$-CISD(18)	35.2	−2917	32.0	0.739
MR$'_{12}$-CISD(26)	34.2	−3237	31.1	0.732
Skripnikov et al.[53]	34.9	−3132	31	1.08
Flambaum *et al.*[54]	25(YbF)			≈ 1

$\mu(^{181}\text{Ta}) = 2.361\mu_N \qquad I = \frac{7}{2}$

[53] L. V. Skripnikov, A. N. Petrov, N. S. Mosyagin, A. V. Titov, V. V. Flambaum *Phys Rev A* **92** (2015) *012521*

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

Final Corrected Results

D [Debye]	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]	W_M $\left[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}\right]$	
-4.97	35.2	-2917	32.0	0.739	base value MR$_{12}^{+T}$-CISD(18)
$+0.04$	-0.2	-15	-0.2	-0.002	external Triples correction
$+0.02$	$+0.1$	$+68$	$+0.2$	-0.013	correction for Δ spinors
$+0.0$	$+0.9$	-90	$+0.8$	$+0.018$	$4s, 4p$ core-valence correl.
-4.91	**36.0**	**-2954**	**32.8**	**0.742**	**Final value**
$\pm 0.74(15\%)$	$\pm 1.8(5\%)$	$\pm 177(6\%)$	$\pm 1.6(5\%)$	$\pm 0.037(5\%)$	estimated uncertainty
4.74	34.9	-3132	31	1.08	CCSD(T)[57]
				≈ 1	estimate[21]

- W_M(ThO) ≈ 1.1 $[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$[55], W_M(YbF) ≈ 2.1 $[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$[56]
  TaN is competitive candidate for probing $\mathcal{P}, \mathcal{T}$-violating hadron physics

- E_{eff} and W_S sufficiently large for further constraining $\mathcal{P}, \mathcal{T}$-violating lepton physics

[55] L. V. Skripnikov, A. N. Petrov, N. S. Mosyagin, A. V. Titov, V. V. Flambaum *Phys Rev A* **92** (2015) *012521*

[56] V. V. Flambaum, D. DeMille, M. G. Kozlov *Phys Rev Lett* **113** (2014) *103003*, M. G. Kozlov, V. F. Ezhov, *Phys Rev A* **49** (1994) *4502*

[57] L. V. Skripnikov, A. N. Petrov, A. V. Titov, V. V. Flambaum *Phys Rev Lett* **113** (2014) *263006*

Atomic EDMs

Leading contributions to **EDM** of a **paramagnetic atom**

$$d_a = R\, d_e + \alpha_{C_S}\, C_S \qquad\qquad \alpha_{C_S} = S\, A\, \frac{G_F}{\sqrt{2}}$$

Enhancement factor and S ratio:

$$R := \frac{\left\langle \sum_j \gamma_j^0\, \mathbf{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_\Psi}{E_{\text{ext}}} \qquad\qquad S := -\frac{\left\langle \imath \sum_j \gamma_j^0\, \gamma_j^5\, \rho_N(\mathbf{r}_j) \right\rangle_\Psi}{E_{\text{ext}}}$$

Model for **Tl atom**	R	S [a.u.]
vDZ/SD18_CAS_3in3_SDT21/10au	-473	-331
vDZ/SD18_CAS_3in3_SDT21/20au	-479	-335
vDZ/SD8_SDT10_CAS_3in3_SDT21/10au	-471	-331
vDZ/SD18_CAS_3in3_SDTQ21/10au	-469	-329
vTZ/SD18_CAS_3in3_SDT21/10au	-542	-383
vTZ/SD18_CAS_3in3_SDT21/20au	*-543*	*-383*
vQZ/SD18_CAS_3in3_SDT21/10au	-555	-391
Literature values		
Porsev *et al.*, *Phys. Rev. Lett.* **108** (2012) *173001*	-573	
Nataraj *et al.*, *Phys. Rev. Lett.* **106** (2011) *200403*	-470	
Dzuba *et al.*, *Phys. Rev. A* **80** (2009) *062509*	-582	
Liu *et al.*, *Phys. Rev. A* **45** (1992) *R4210*	-585	

Atomic EDMs

The first direct calculation of α_{C_S} for a **diamagnetic atom**

$$S := -\frac{\left\langle \imath \sum_j \gamma_j^0 \, \gamma_j^5 \, \rho_N(\mathbf{r}_j) \right\rangle_\Psi}{E_{\text{ext}}} \qquad \alpha_{C_S} = S\, A\, \frac{G_F}{\sqrt{2}}$$

$$\begin{aligned}
W_S &= \left\langle \psi_j^{(1)} \middle| \imath \sum_e \gamma_e^0 \, \gamma_e^5 \, \rho(\mathbf{r}_e) \middle| \psi_j^{(1)} \right\rangle \\
&= \left\langle \psi_j^{(0)} \middle| \imath \sum_e \gamma_e^0 \, \gamma_e^5 \, \rho(\mathbf{r}_e) \middle| \psi_j^{(0)} \right\rangle \\
&+ \sum_{k \neq j} \frac{\left\langle \psi_k^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_j^{(0)} \right\rangle}{\varepsilon_j^{(0)} - \varepsilon_k^{(0)}} \left\langle \psi_j^{(0)} \middle| \imath \sum_e \gamma_e^0 \, \gamma_e^5 \, \rho(\mathbf{r}_e) \middle| \psi_k^{(0)} \right\rangle \\
&+ \sum_{k \neq j} \frac{\left\langle \psi_j^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_k^{(0)} \right\rangle}{\varepsilon_j^{(0)} - \varepsilon_k^{(0)}} \left\langle \psi_k^{(0)} \middle| \imath \sum_e \gamma_e^0 \, \gamma_e^5 \, \rho(\mathbf{r}_e) \middle| \psi_j^{(0)} \right\rangle \\
&+ \sum_{k,l \neq j} \frac{\left\langle \psi_k^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_j^{(0)} \right\rangle \left\langle \psi_j^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_l^{(0)} \right\rangle}{\left(\varepsilon_j^{(0)} - \varepsilon_k^{(0)}\right)\left(\varepsilon_j^{(0)} - \varepsilon_l^{(0)}\right)} \left\langle \psi_l^{(0)} \middle| \imath \sum_e \gamma_e^0 \, \gamma_e^5 \, \rho(\mathbf{r}_e) \middle| \psi_k^{(0)} \right\rangle \qquad (1)
\end{aligned}$$

Hg atom, $^1S_0$ state: $\alpha_{C_S} \approx 10^{-23}\, e$ cm

Ongoing Projects

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

- **New systems in the search for EDMs: TaO$^+$**
  Experiment: D. DeMille and Yale-Harvard "offsprings"

- **Nuclear MQM interactions and electronic G tensors for ThO and ThF$^+$**
  with Malika Denis

- **Hyperfine-interaction-induced EDMs**
  The Hg and Xe atoms (with Martin Jung)

- **Nuclear Schiff moment interaction**
  Diamagnetic atoms

Collaborations and Funding

Malaya K. Nayak

BARC, Mumbai, India

Malika Denis

LCPQ, Toulouse, France

Mikhail Kozlov

LETI, St. Petersburg, Russia

Foundational Questions Institute (FQXi)

EDMe^-DM

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

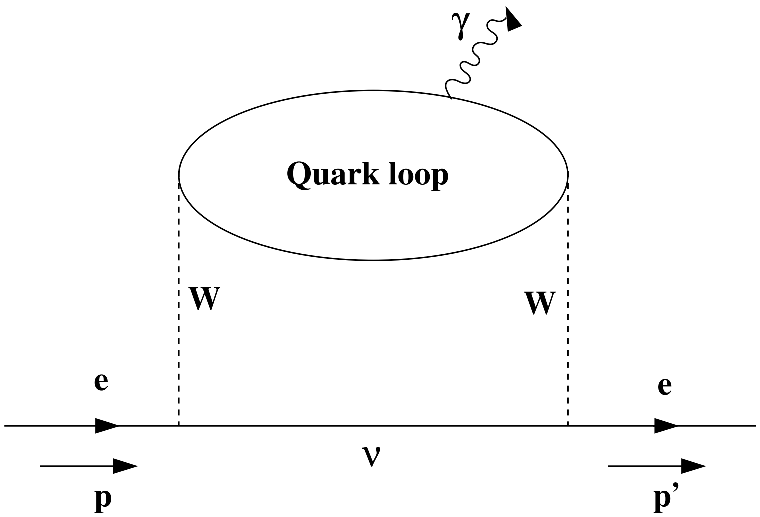
Martin Jung

Particle physics

"Excellence Cluster Universe", Munich

The induced fermion EDM

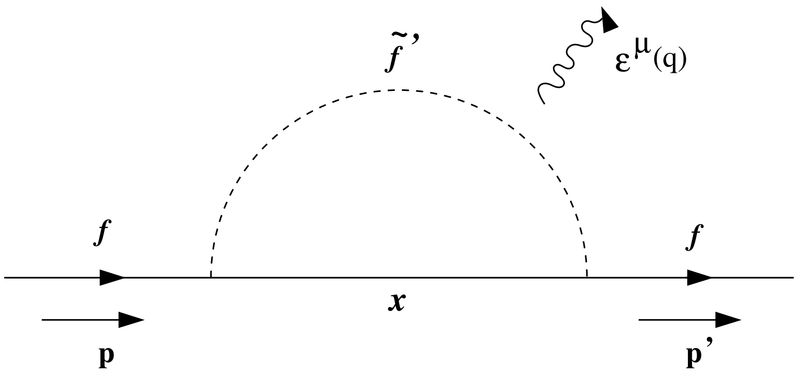
Standard Model Picture[58]



- Three-loop $\mathcal{CP}$-odd contributions zero in the absence of gluonic corrections[59]

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

BSM Picture



χ: chargino, neutralino
$\tilde{f}'_j$: supersymmetry (s)-fermion
$\epsilon^\mu(q)$: photon

- MSSM ("naïve SUSY") prediction[60]:
  $d_e \leq 10^{-27}\, e$ cm

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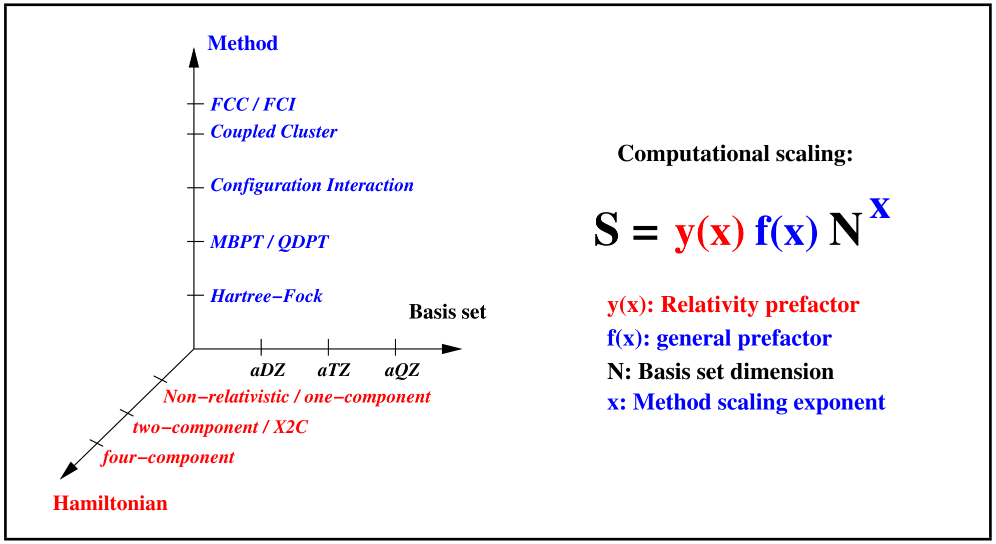
[58] E.D. Commins, *Adv At Mol Opt Phys* **40** (1998) *1*
[59] M. Pospelov, I.B. Khriplovich, *Sov J Nuc Phys* **53** (1991) *638*
[60] J. Ellis, J.S. Lee, A. Pilaftsis, *J High Energy Phys* **10** (2008) *049*

Special Relativity and Electron Correlation

Computational Scaling[60]



$$S^{\text{rel.CC}} \approx 4\sqrt{\pi\left(\frac{x}{2}-1\right)}$$

$$\frac{1}{4}\left[\frac{x^2}{4}-\frac{3}{2}x+2\right]\begin{pmatrix} x-2 \\ \frac{x}{2}-1 \end{pmatrix}$$

$$O^{\frac{x}{2}-1}V^{\frac{x}{2}+1}$$

Method	Non-Rel.	2-comp.	4-comp.
Hartree-Fock	N^4	$8N^4$	$8\left(\frac{5}{2}N\right)^4$
4-Index transformation	$2N^5$	$32N^5$	$128N^5$
CCSD	$3N^6$	$10 \cdot 3N^6$	
CCSDT	$30N^8$	$12 \cdot 30N^8$	
CCSDTQ	$210N^{10}$	$14 \cdot 210N^{10}$	

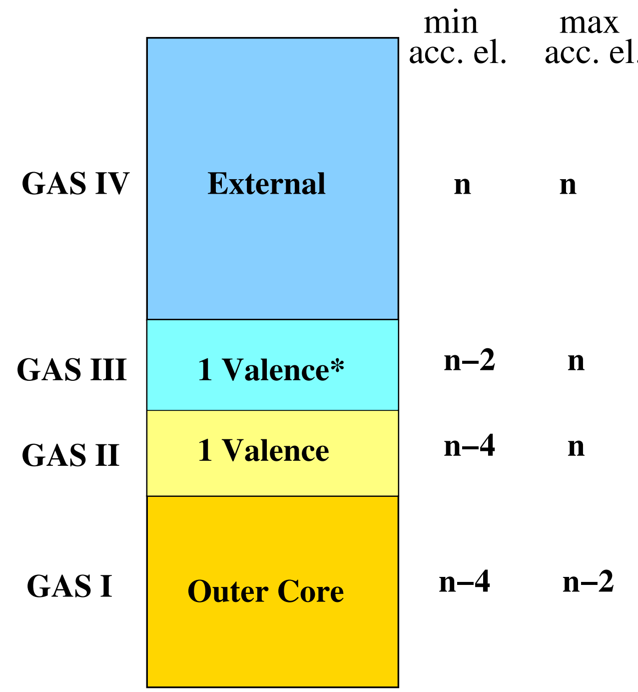
⇒ The correlated stage is the computational bottleneck (no savings in 2c formalism).

[60] L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) *214102*

Relativistic Generalized-Active-Space CC

L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) *214102*
T. Fleig, 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[61]
- GAS-extended excitation manifold
  $\langle \mu_{\rm GASCC}| = \langle \Phi_0 | \, \hat{\tau}^{\dagger}_{\mu_{\rm GAS}}$
- $\hat{\tau}_{\mu_{\rm GAS}}$ contains GAS-selected higher excitations
  $\left|\psi^{\rm GASCC}\right\rangle = exp(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu_{\rm GAS}}) \; |\Phi_0\rangle$
- 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:

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

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

Relativistic Generalized-Active-Space CC

Electronic Ground States [62]

CC vector function

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

- 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.

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

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

Relativistic Generalized-Active-Space CC

Excitation Energies[63]

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

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

Algorithm for Jacobian matrix elements[64]

- Loop over relativistic $N\Delta M_K$ classes of $\hat{H}, \hat{T}$
  Determines min./max. commutator nesting
  - Loop over commutator type, e.g. $\left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right]$
    - Loop over relativistic $N\Delta M_K$ classes of $\hat{T}$ operators
      Find all possible contractions
      - Loop over contractions and perform, e.g.

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

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

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

[64] L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* **134** (2011) *214102*

L. K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*