Probing Fundamental Physics with Molecules

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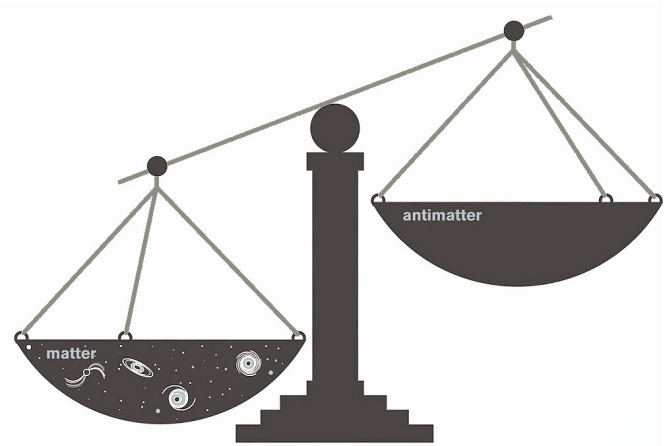
Philipps-Universitiät Marburg, Germany

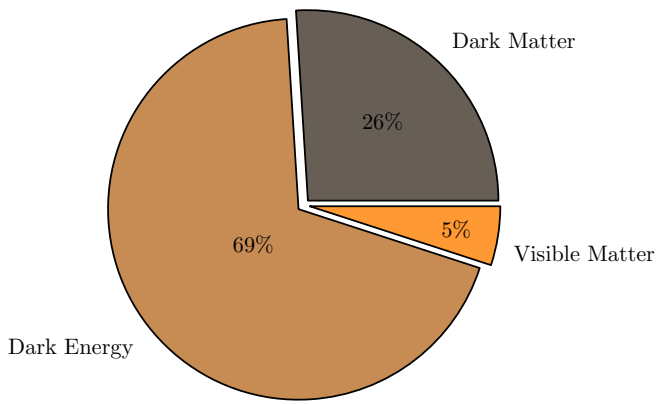
@New Opportunities for Fundamental Physics Research with Radioactive Molecules

July 01, 2021

Discrete Symmetry Violation — Towards New Physics

- Standard Model leaves important phenomena unexplained:





- Baryon asymmetry
- Dark matter and dark energy

$\Rightarrow$ Connected to symmetry violation

Discrete Symmetry Violation:

- Charge conjugation $\mathcal{C}$: $\psi \rightarrow \bar{\psi}$
- Parity $\mathcal{P}$: $x, y, z \rightarrow -x, -y, -z$
- Time-Reversal $\mathcal{T}$: $t \rightarrow -t$

$\mathcal{CPT}$-theorem $\Rightarrow$ ~~$\mathcal{T}$~~ $\leftrightarrow$ ~~$\mathcal{CP}$~~

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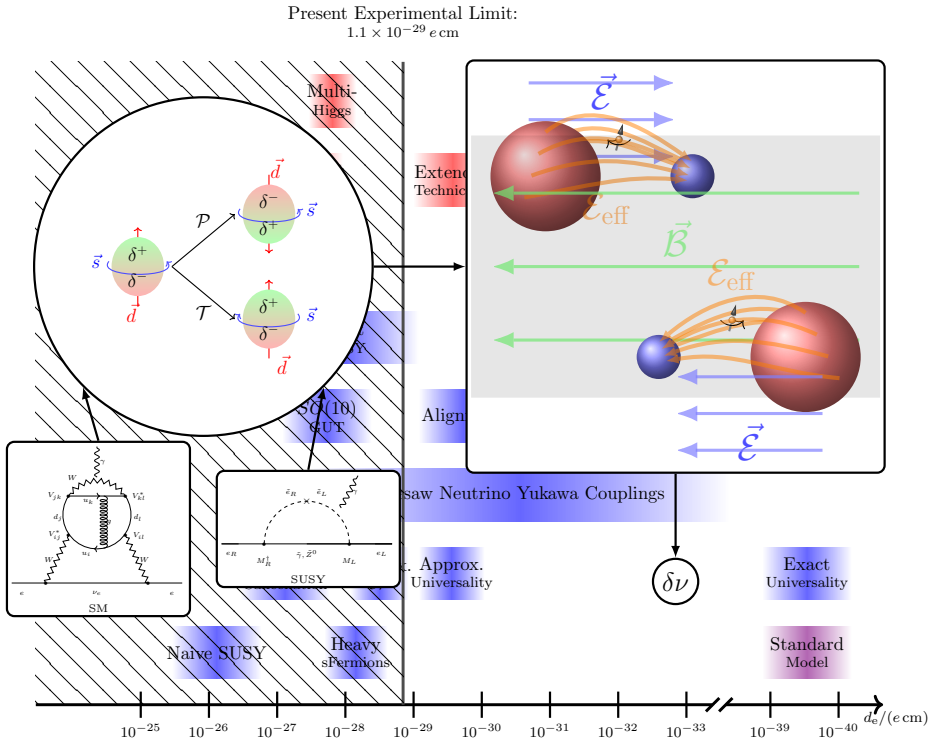
https://www.symmetrymagazine.org/article/october-2005/explain-it-in-60-seconds

A. D. Sakharov, *JETP Lett.* **1967**, *5*, 24.

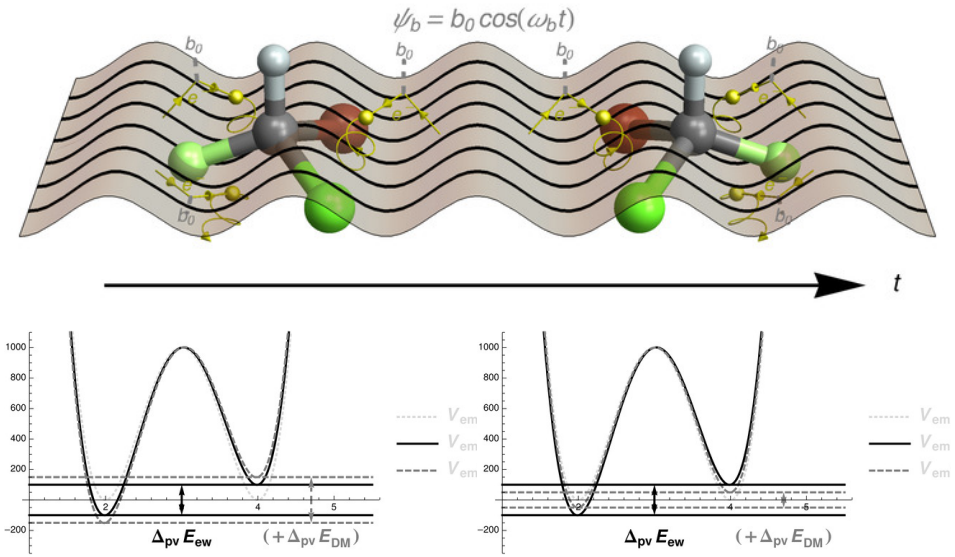
Discrete Symmetry Violation — Towards New Physics

Molecules as versatile probes of New Physics

$\mathcal{P}, \mathcal{T}$-Violation in molecules



Sensing dark matter with chiral molecules



K. Gaul et al., *Phys. Rev. Lett.* **2020**, *125*, 123004, K. Gaul et al., *Phys. Rev. A* **2020**, *102*, 032816.

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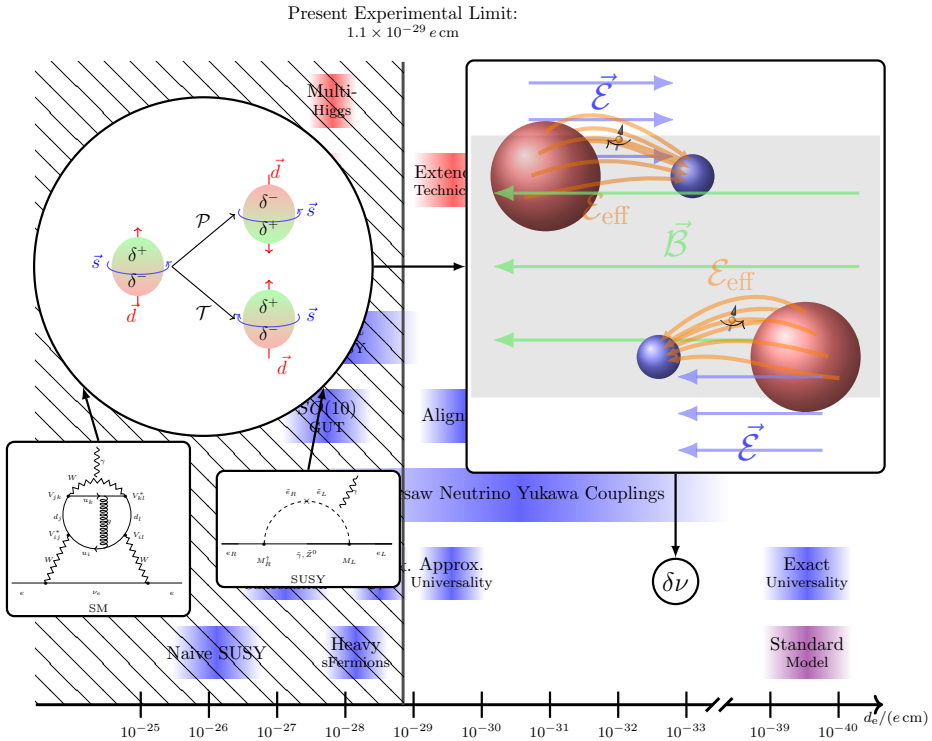

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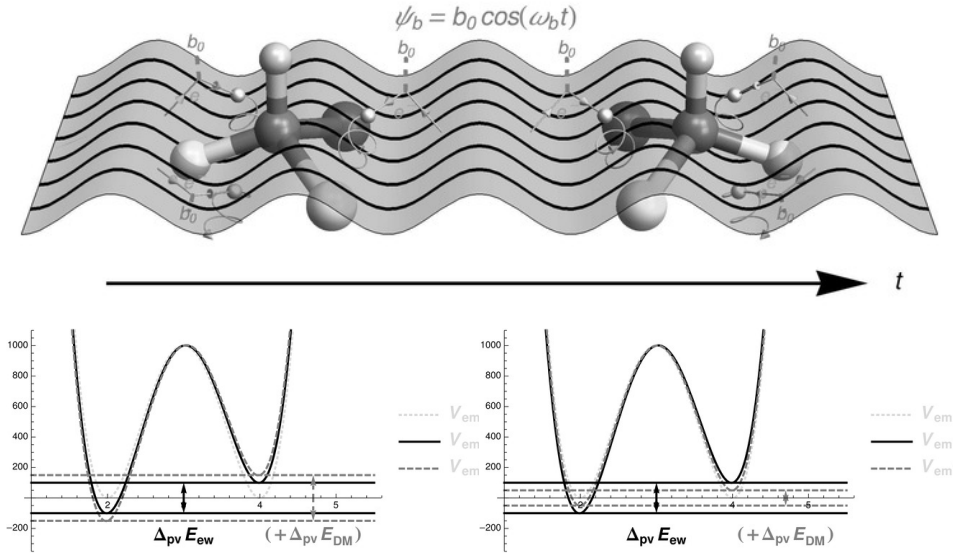
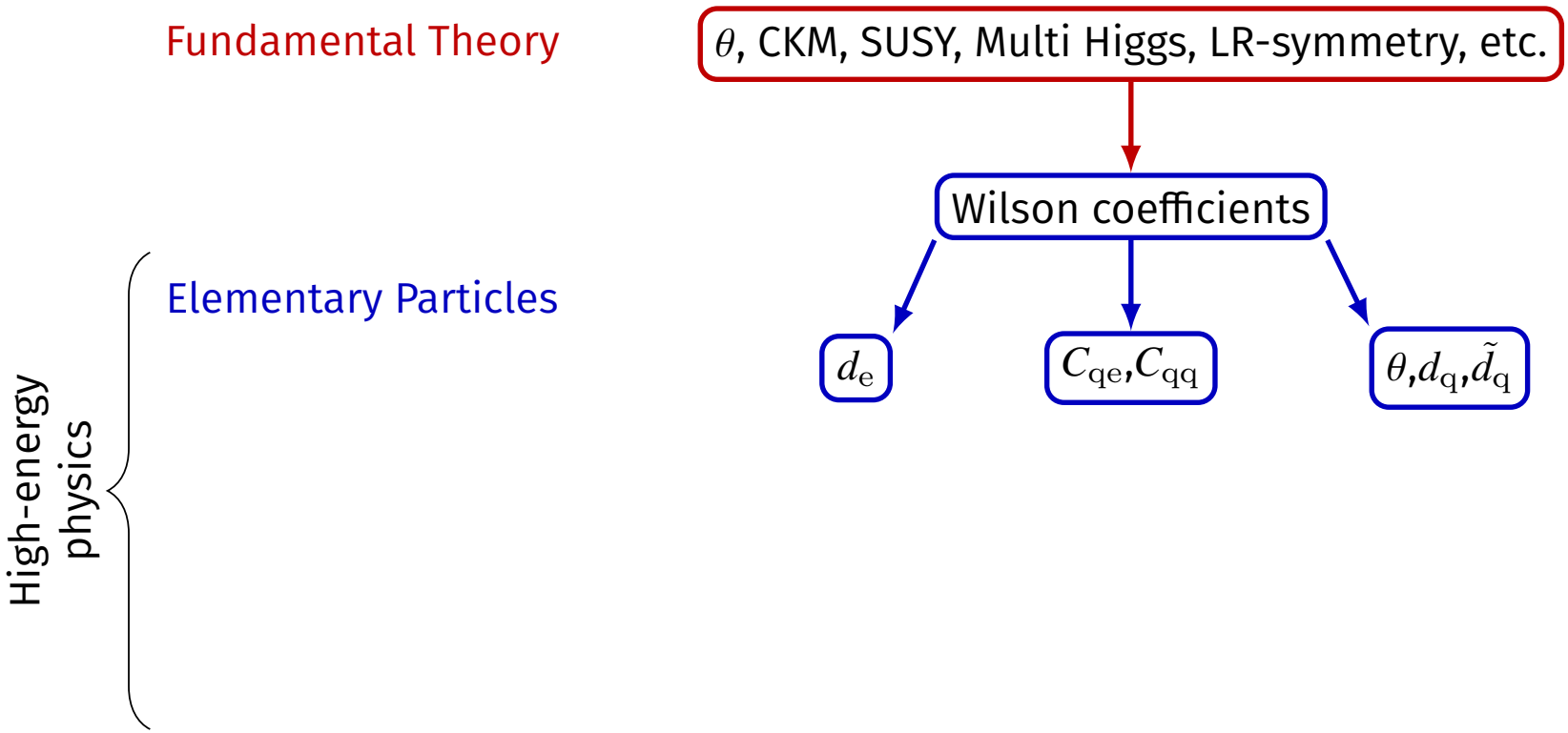


K. Gaul et al., *Phys. Rev. Lett.* **2020**, *125*, 123004, K. Gaul et al., *Phys. Rev. A* **2020**, *102*, 032816.

Sources of $\mathcal{P},\mathcal{T}$-violation in molecules

From elementary particles to atoms and molecules



M. Pospelov, A. Ritz, *Ann. Phys. (N. Y.)* **2005**, *318*, 119 –169, T. E. Chupp et al., *Rev. Mod. Phys.* **2019**, *91*, 015001, W. B. Cairncross, J. Ye, *Nat. Rev. Phys.* **2019**, *1*, 510–521.

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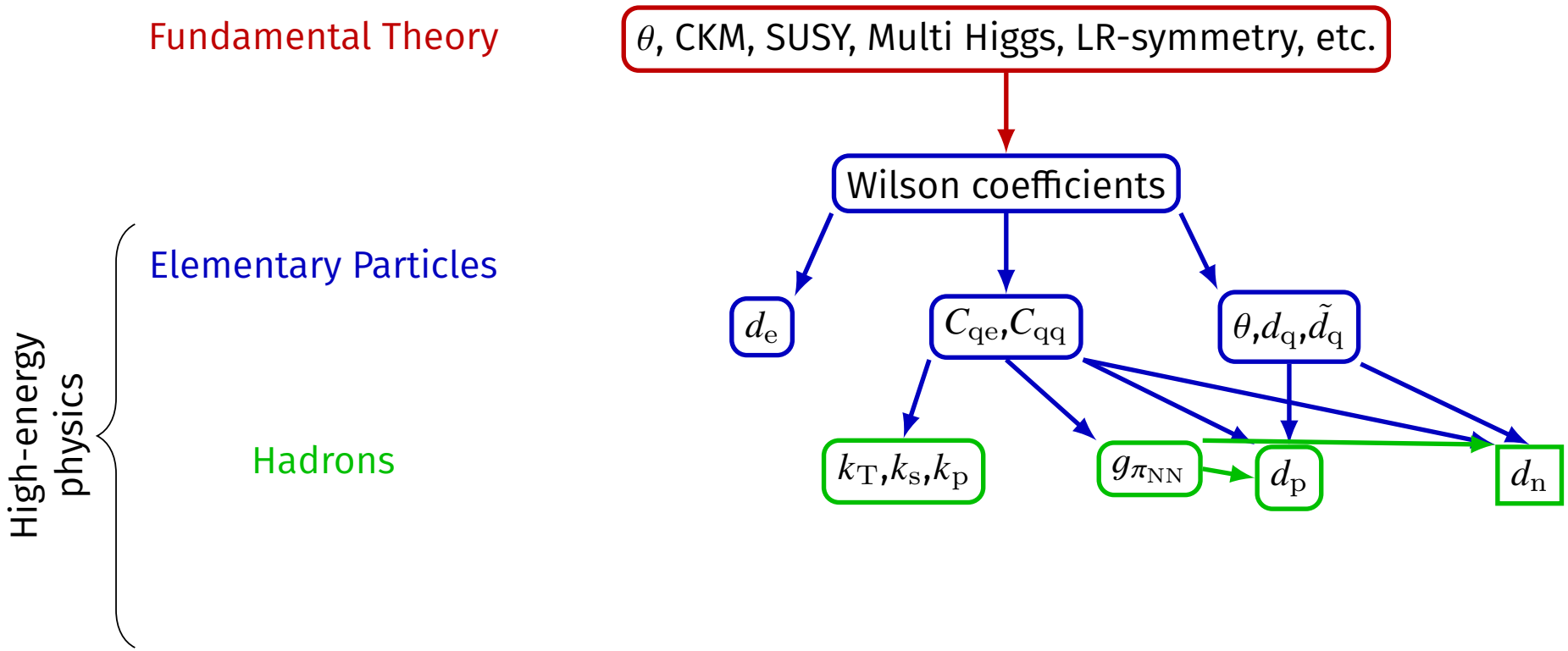

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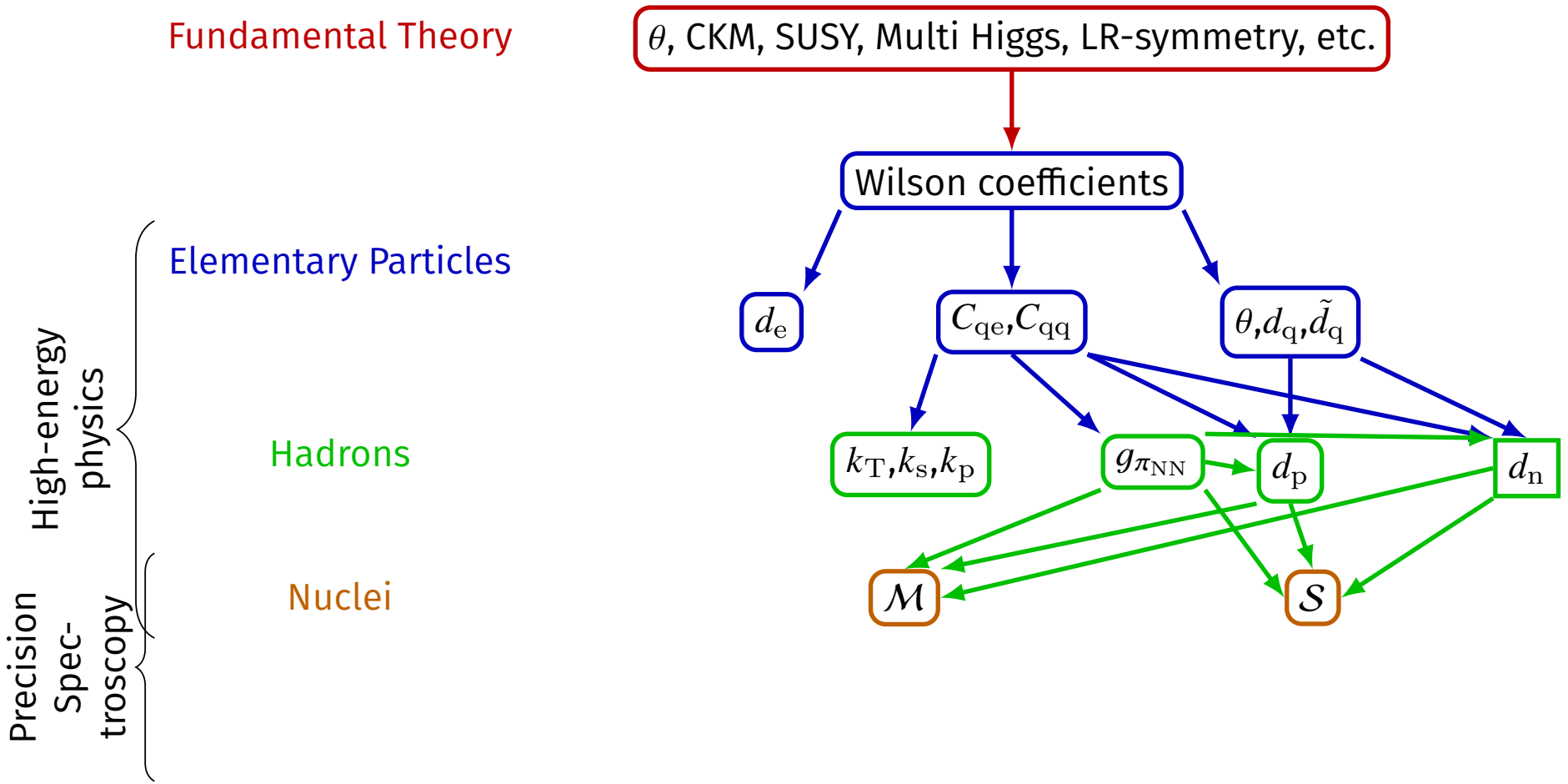

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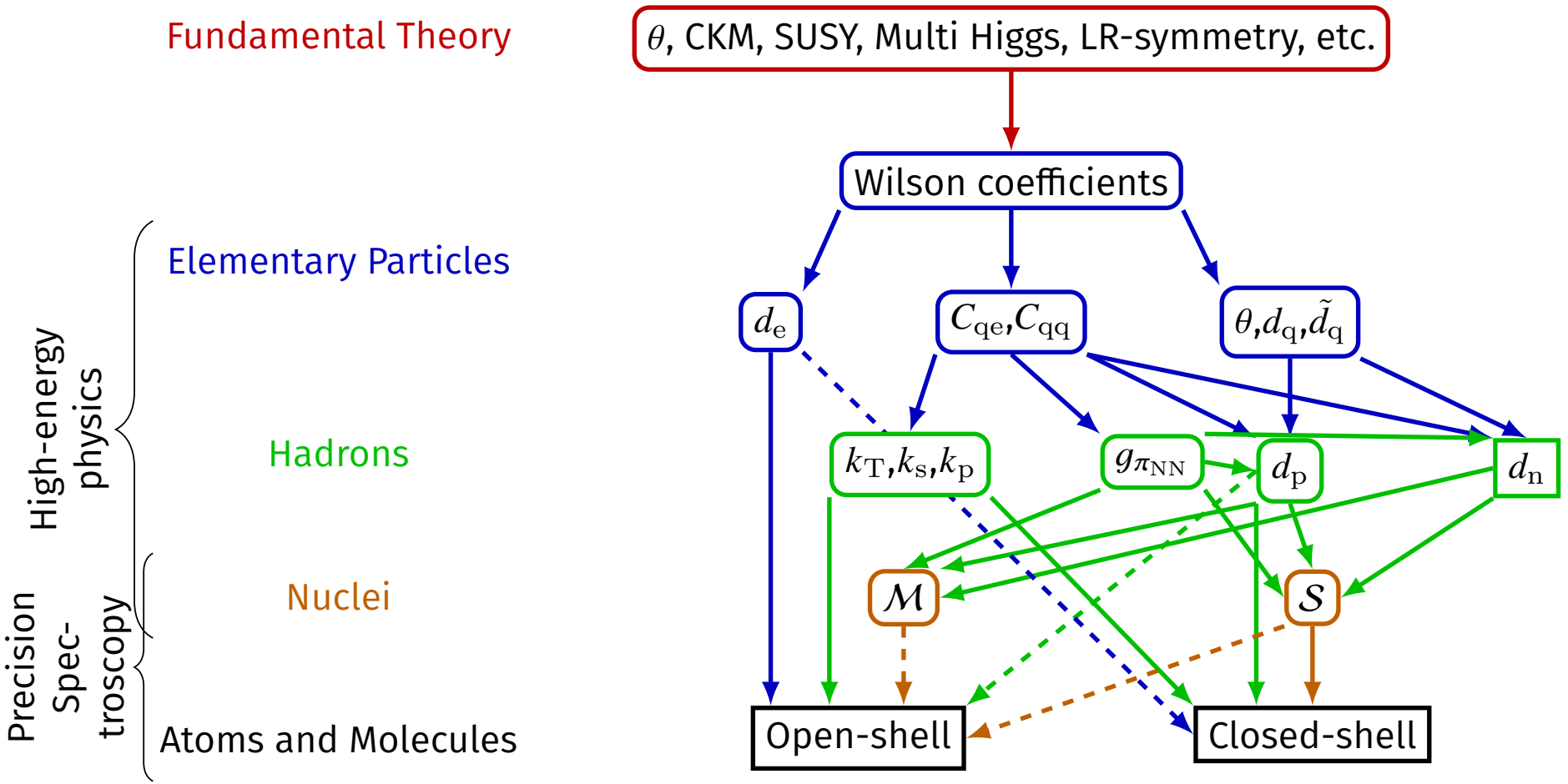

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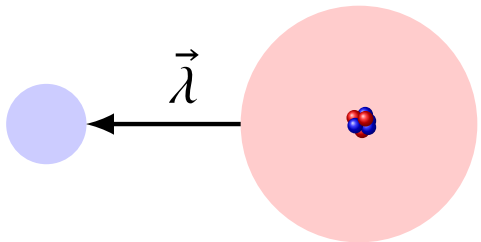
Sources of $\mathcal{P},\mathcal{T}$-violation in molecules

Effective molecular spin-rotational Hamiltonian

Polar linear heavy-elemental molecules
$\Rightarrow$ Strong internal fields
$\Rightarrow$ Easy to polarize



Effective spin-rotational Hamiltonian for heavy nucleus

$$H_{\mathrm{sr}} =$$

M. G. Kozlov, L. N. Labzowsky, *J. Phys. B* **1995**, *28*, 1933–1961, K. Gaul, R. Berger, *J. Chem. Phys.* **2020**, *152*, 044101.

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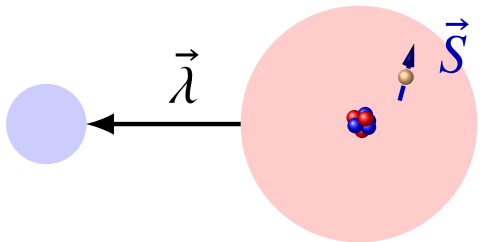

Effective spin-rotational Hamiltonian for heavy nucleus

$$H_{\mathrm{sr}} = \underbrace{\vec{\lambda} \cdot \vec{S}'}_{\Omega} (W_{\mathrm{d}} d_{\mathrm{e}} + W_{\mathrm{s}} k_{\mathrm{s}})$$

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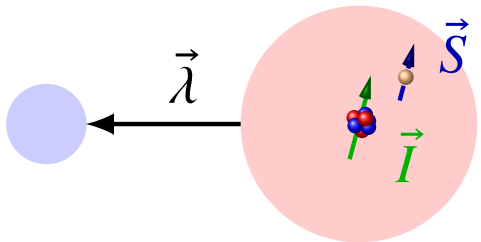

Effective spin-rotational Hamiltonian for heavy nucleus

$$H_{\mathrm{sr}} = \underbrace{\vec{\lambda}\cdot\vec{S}'}_{\Omega}\left(W_{\mathrm{d}}d_{\mathrm{e}} + W_{\mathrm{s}}k_{\mathrm{s}}\right) + \underbrace{\vec{\lambda}\cdot\vec{I}}_{\mathcal{I}}\left(W_{\mathrm{T}}k_{\mathrm{T}} + W_{\mathrm{p}}k_{\mathrm{p}} + W_{\mathrm{s}}^{\mathrm{m}}k_{\mathrm{s}} + W_{\mathcal{S}}\mathcal{S} + (W_{\mathrm{m}} + W_{\mathcal{S}}R)d_{\mathrm{p}} + W_{\mathrm{d}}^{\mathrm{m}}d_{\mathrm{e}}\right)$$

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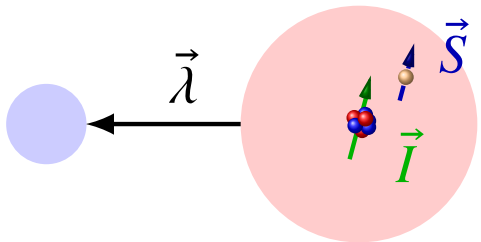

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$$+ \underbrace{\vec{\lambda}\cdot\vec{I}}_{\mathcal{I}}\left(W_{\mathrm{T}}k_{\mathrm{T}} + W_{\mathrm{p}}k_{\mathrm{p}} + W_{\mathrm{s}}^{\mathrm{m}}k_{\mathrm{s}} + W_{\mathcal{S}}\mathcal{S} + (W_{\mathrm{m}} + W_{\mathcal{S}}R)d_{\mathrm{p}} + W_{\mathrm{d}}^{\mathrm{m}}d_{\mathrm{e}}\right)$$

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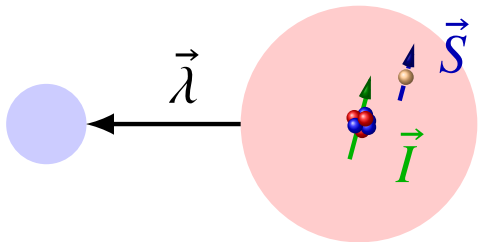

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$\Rightarrow$ **Large effective electronic structure factors W $\Leftrightarrow$ high sensitivity(?)**

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Numerical calculation and analytical models

Molecular ab initio calculations

- Quasi-relativistic Hartree–Fock and DFT calculations
- Sufficiently accurate computation of W (within 10 % for most)
- Can compute arbitrary properties
- Excited states via SCF-MOM

Analytical atomic models

- One-electron atom model
- Laws for *relativistic enhancement*

$\rightarrow$ Scaling with nuclear charge Z

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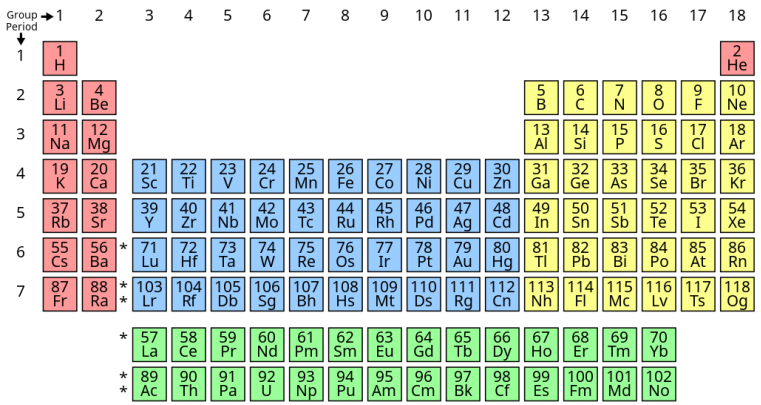
$\longrightarrow$ Scaling with nuclear charge Z

$\Rightarrow$ Periodic trends and selection rules for good candidates



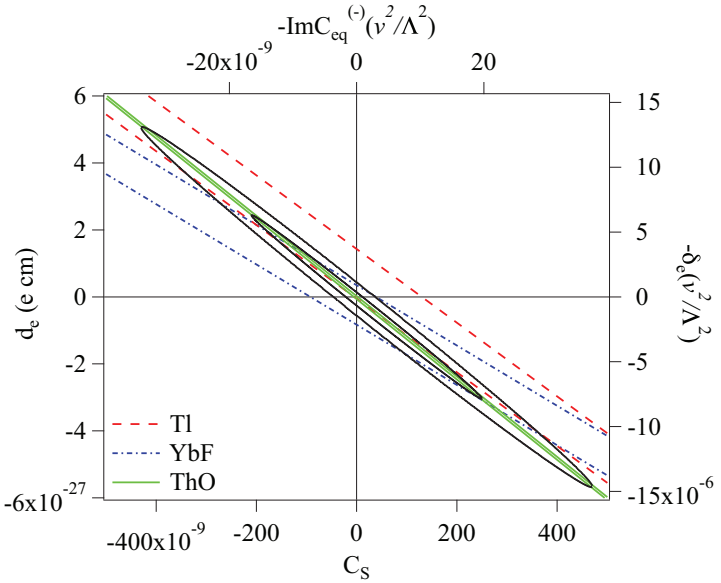
K. Gaul, R. Berger, *J. Chem. Phys.* **2020**, *152*, 044101.

Numerical results for molecules with $\Omega = {}^1/_2, \mathcal{I} = 0$

$$H_{\mathrm{sr}_A} = \Omega \left(W_{\mathrm{d}_A} d_{\mathrm{e}} + W_{\mathrm{s}_A} k_{\mathrm{s}} \right)$$

- electron EDM (eEDM) d_{e}
- scalar-pseudoscalar nucleon-electron current k_{s}

$$h \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \Omega \begin{pmatrix} W_{\mathrm{d},1} & W_{\mathrm{s},1} \\ W_{\mathrm{d},2} & W_{\mathrm{s},2} \end{pmatrix} \begin{pmatrix} d_{\mathrm{e}} \\ k_{\mathrm{s}} \end{pmatrix}$$



$\Rightarrow$ Need **at least two** experiments

T. Chupp, M. Ramsey-Musolf, *Phys. Rev. C* **2015**, *91*, 035502.

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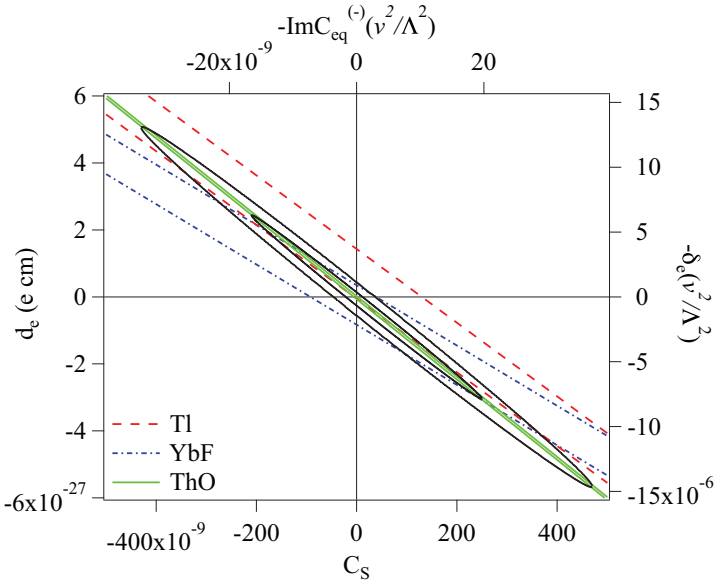

$\Rightarrow$ Need **at least two** experiments

- $\mathcal{P},\mathcal{T}$-violation in diatomic molecules with ${}^2\Sigma_{1/2}$-ground state
  - *Ab initio* calculation of many diatomic molecules vs. atomic models
    $\Rightarrow$ Chemical enhancement
  - Dependence of the coverage area A on Z and chemical influence

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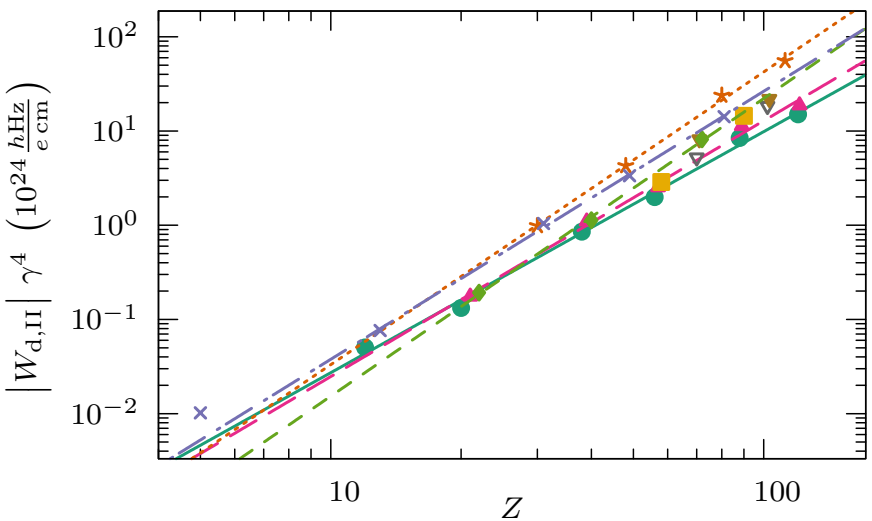
eEDM interactions in ${}^2\Sigma_{1/2}$-ground state molecules

Chemical influence on scaling behavior of eEDM interactions

Empirical atomic model $W_\mathrm{d} \sim \frac{\alpha^2 Z^3}{\gamma^4}$; ZORA-cGKS-B3LYP calculations

$$\log_{10}\left\{|W_\mathrm{d}|\gamma^4 \times 10^{-24}\ \frac{e\mathrm{cm}}{h\mathrm{Hz}}\right\} = b_{\mathrm{d,FS}} + a_{\mathrm{d,FS}} \log_{10}\{Z\}$$



(Mg-E120)F
$10^{-4.12}\ Z^{2.56}$
(Sc-E121)O
$10^{-4.32}\ Z^{2.71}$
(Ce-Th)N
(Yb-No)F
(Lu-Lr)O
(Ti-Hf)N
$10^{-4.97}\ Z^{3.16}$
(Cd-Cn)H
$10^{-4.59}\ Z^{3.11}$
(B-Tl)O
$10^{-4.27}\ Z^{2.85}$

⇒ Chemically suppressed Z-scaling in group 2 and 3
⇒ Chemical enhancement in group 4 and 12

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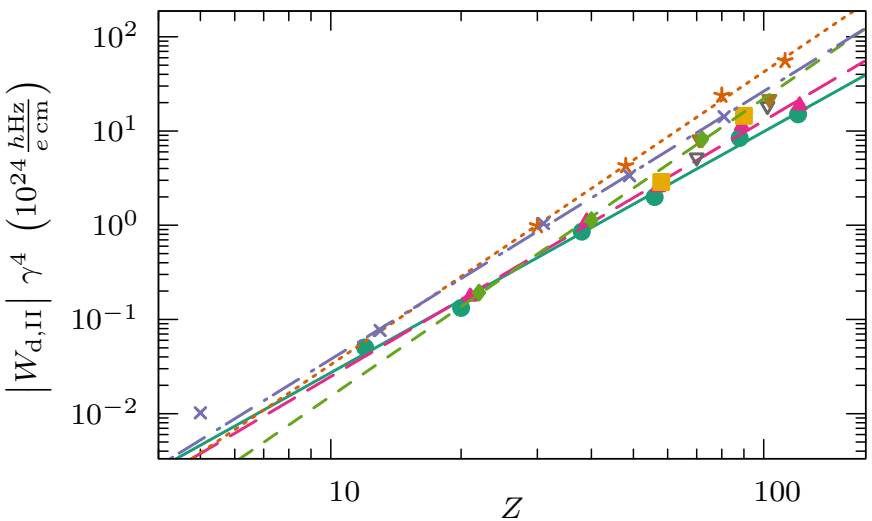

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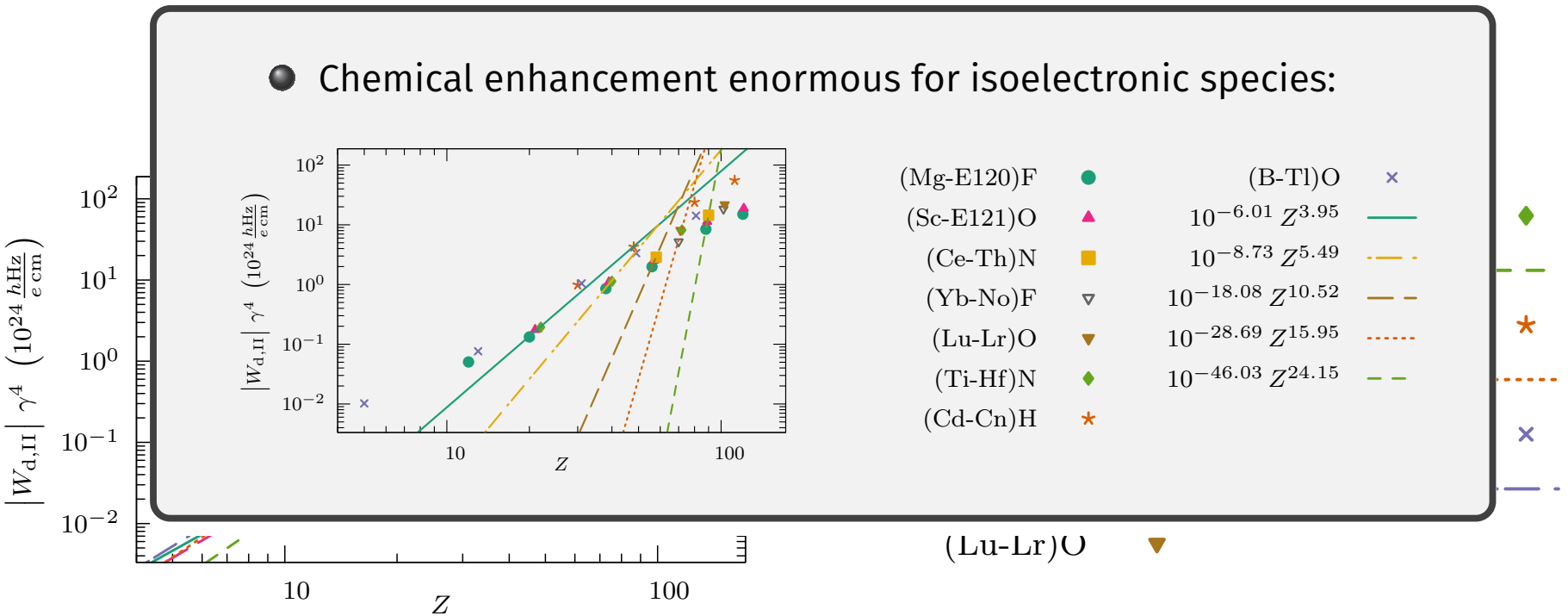
- Chemical enhancement enormous for isoelectronic species:



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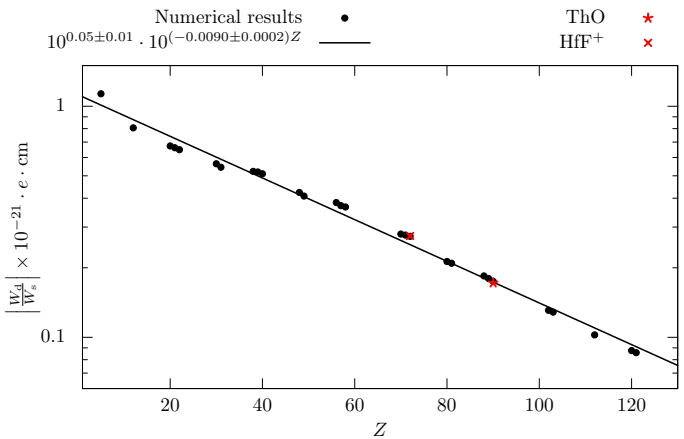
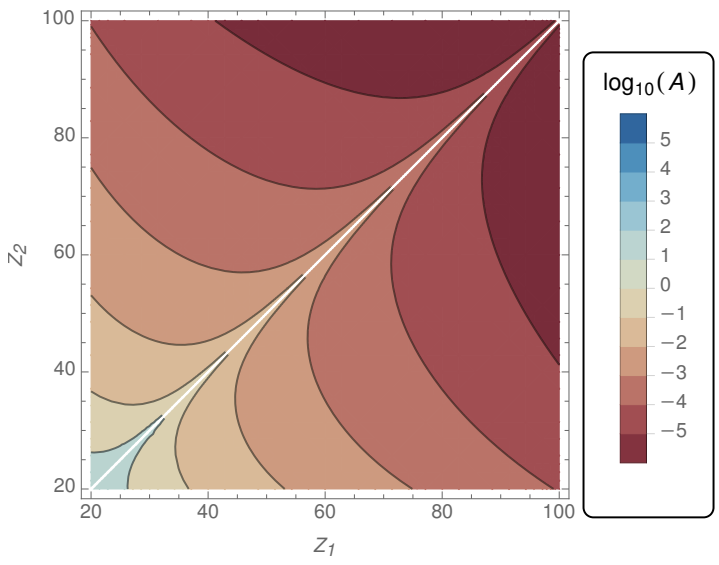
$\mathcal{P}, \mathcal{T}$-odd ratio and coverage region in d_e-k_s parameter space



$$A \sim W_{\mathrm{d},1}^{-1} W_{\mathrm{d},2}^{-1} \left| \frac{W_{\mathrm{s},1}}{W_{\mathrm{d},1}} - \frac{W_{\mathrm{s},2}}{W_{\mathrm{d},2}} \right|^{-1}$$

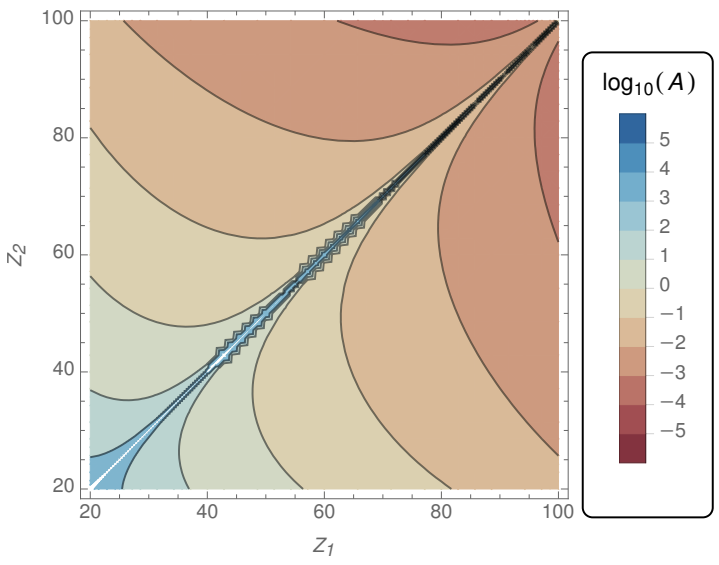
$$A \approx \frac{k_\mathrm{p}^2 \pi |u(\nu_1) u(\nu_2)|}{10^{b_{\mathrm{d},1}+b_{\mathrm{d},2}} \frac{Z_1^{a_{\mathrm{d},1}} Z_2^{a_{\mathrm{d},2}}}{\gamma_1^4 \gamma_2^4} \, 0.9 \cdot \left| 1.02 Z_1 - 1.02 Z_2 \right| \times 10^{27} \, \frac{\mathrm{Hz}^2}{e \cdot \mathrm{cm}}}$$

Analytical atomic model



vs.

Ab initio model: group 2, group 2



K. Gaul et al., *Phys. Rev. A* **2019**, *99*, 032509, T. Fleig, *Phys. Rev. A* **2017**, *96*, 040502, T. Fleig, M. Jung, *J. High Energy Phys.* **2018**, *2018*, 12.

Numerical results for molecules with $\Omega = {}^1/_2, \mathcal{I} = 0$

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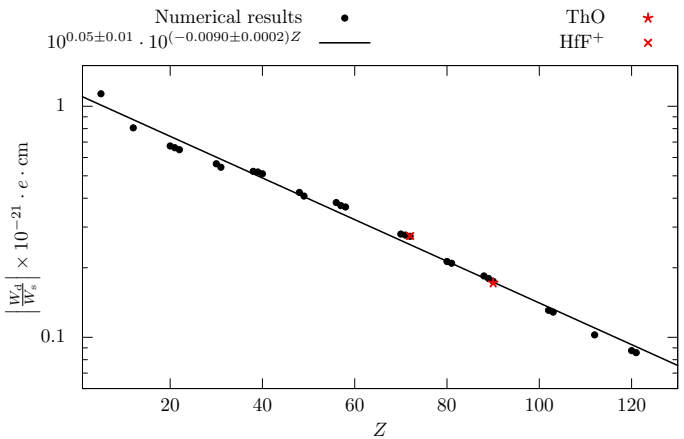
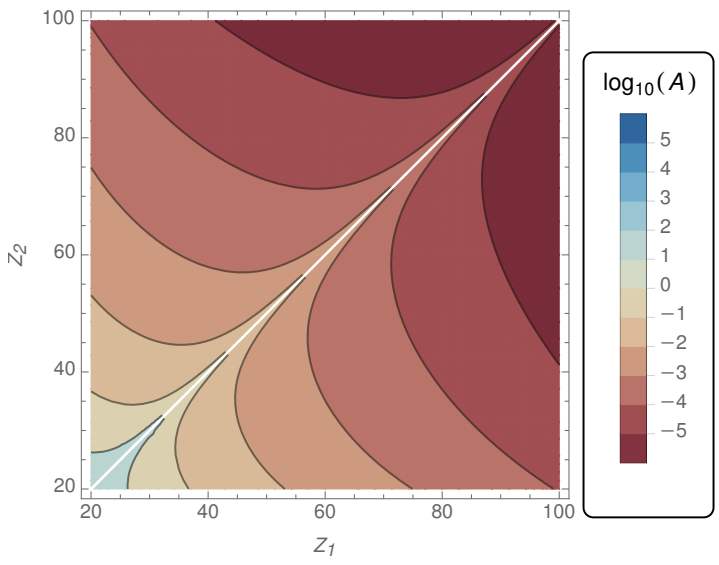


$$A \sim W_{\mathrm{d},1}^{-1} W_{\mathrm{d},2}^{-1} \left| \frac{W_{\mathrm{s},1}}{W_{\mathrm{d},1}} - \frac{W_{\mathrm{s},2}}{W_{\mathrm{d},2}} \right|^{-1}$$

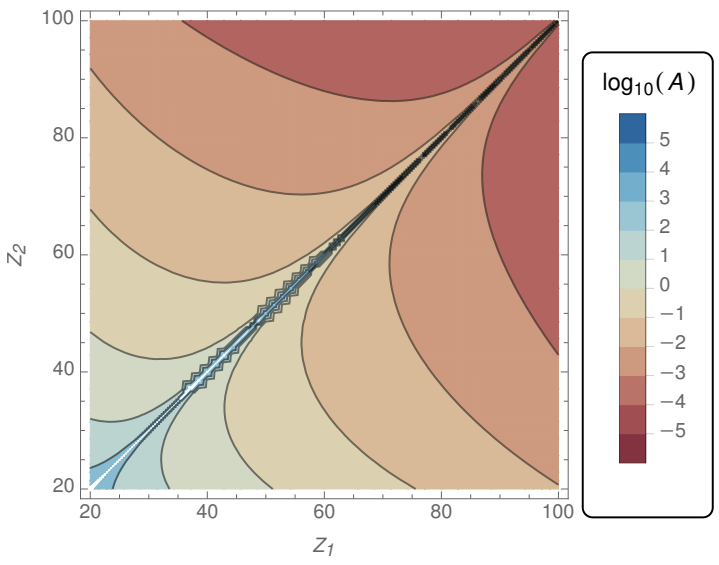
$$A \approx \frac{k_\mathrm{p}^2 \pi |u(\nu_1) u(\nu_2)|}{10^{b_{\mathrm{d},1}+b_{\mathrm{d},2}} \frac{Z_1^{a_{\mathrm{d},1}} Z_2^{a_{\mathrm{d},2}}}{\gamma_1^4 \gamma_2^4} \, 0.9 \cdot \left| 1.02^{Z_1} - 1.02^{Z_2} \right| \times 10^{27} \, \frac{\mathrm{Hz}^2}{e \cdot \mathrm{cm}}}$$

Analytical atomic model



vs.

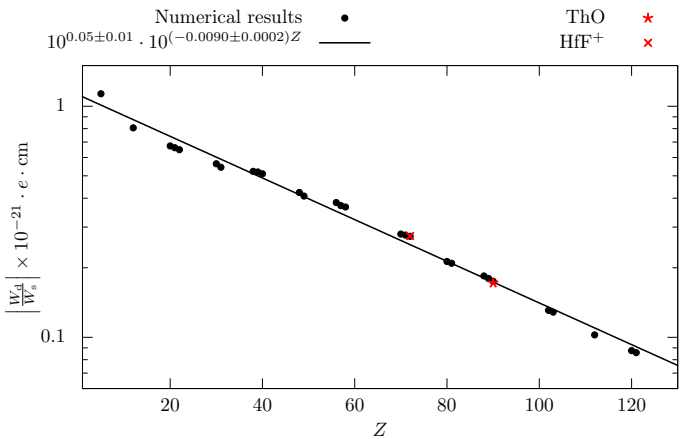
Ab initio model: group 2, group 12



K. Gaul et al., *Phys. Rev. A* **2019**, *99*, 032509, T. Fleig, *Phys. Rev. A* **2017**, *96*, 040502, T. Fleig, M. Jung, *J. High Energy Phys.* **2018**, *2018*, 12.

Numerical results for molecules with $\Omega = {}^1/_2, \mathcal{I} = 0$

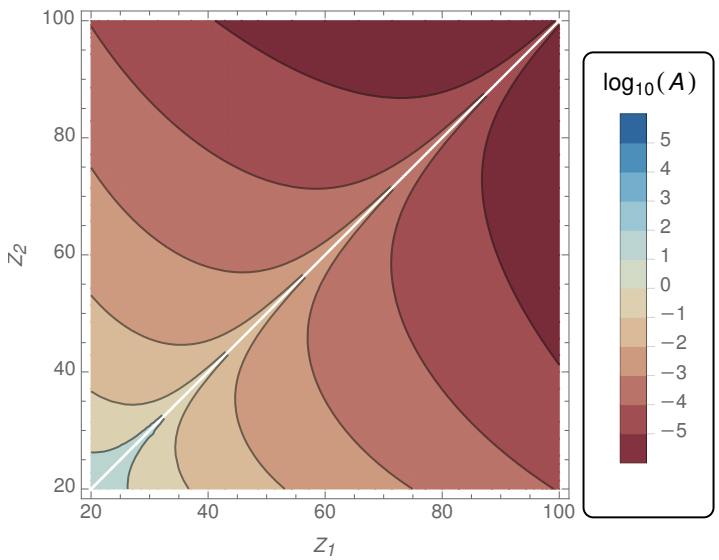
$\mathcal{P},\mathcal{T}$-odd ratio and coverage region in d_e-k_s parameter space



$$A \sim W_{\mathrm{d},1}^{-1} W_{\mathrm{d},2}^{-1} \left| \frac{W_{\mathrm{s},1}}{W_{\mathrm{d},1}} - \frac{W_{\mathrm{s},2}}{W_{\mathrm{d},2}} \right|^{-1}$$

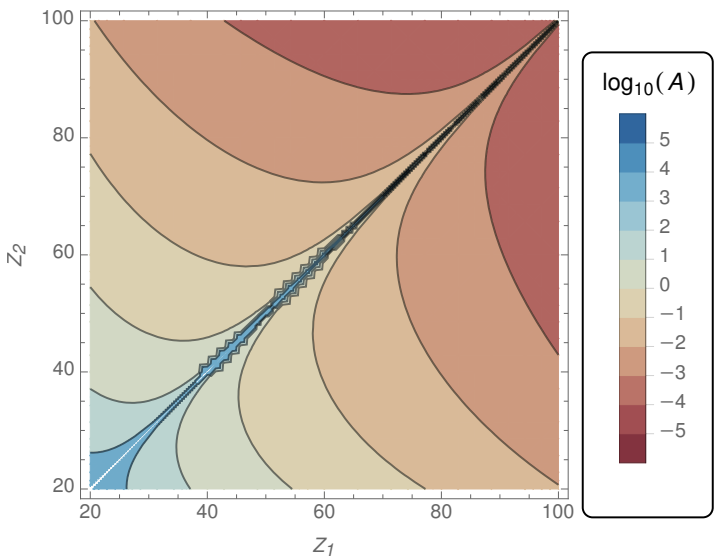
$$A \approx \frac{k_\mathrm{p}^2 \pi |u(\nu_1) u(\nu_2)|}{10^{b_{\mathrm{d},1}+b_{\mathrm{d},2}} \frac{Z_1^{a_{\mathrm{d},1}} Z_2^{a_{\mathrm{d},2}}}{\gamma_1^4 \gamma_2^4} \, 0.9 \cdot \left| 1.02 Z_1 - 1.02 Z_2 \right| \times 10^{27} \, \frac{\mathrm{Hz}^2}{e \cdot \mathrm{cm}}}$$

Analytical atomic model



vs.

Ab initio model: group 12, group 12



K. Gaul et al., *Phys. Rev. A* **2019**, *99*, 032509, T. Fleig, *Phys. Rev. A* **2017**, *96*, 040502, T. Fleig, M. Jung, *J. High Energy Phys.* **2018**, *2018*, 12.

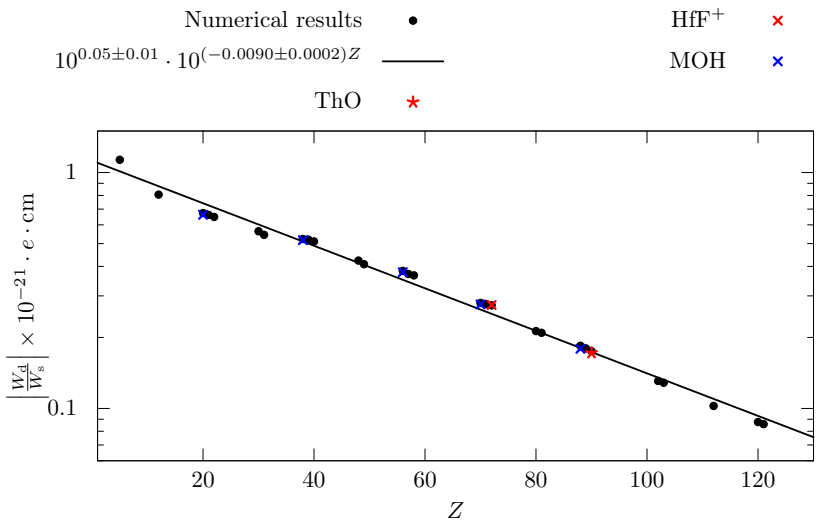
Numerical results for molecules with $\Omega = {}^1/_2, \mathcal{I} = 0$

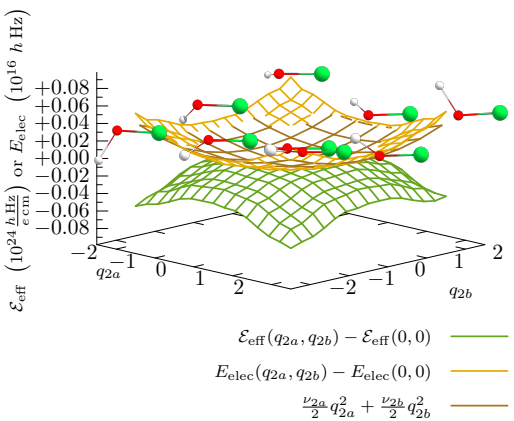
Linear polyatomic molecules: MOH

- W_d, W_s and $\frac{W_\mathrm{s}}{W_\mathrm{d}}$ similar to MF

$\Rightarrow$ No advantages for disentanglement

- **Complementary future searches:**
  - **More complex polyatomic molecules.**
  - **Diamagnetic systems**





H-bending modes in YbOH

Laser-coolable 1st excited vibrational state:

- Experiment: Internal co-magnetometer states
- Calculations: Vibrational corrections to $\mathcal{E}_\mathrm{eff}$ negligible ($< 1\%$)

$\Rightarrow$ Promising candidates for experiment

I. Kozyryev, N. R. Hutzler, *Phys. Rev. Lett.* **2017**, *119*, 133002.

K. Gaul, R. Berger, *Phys. Rev. A* **2020**, *101*, 012508, A. Zakharova, A. Petrov, *Phys. Rev. A* **2021**, *103*, 032819.

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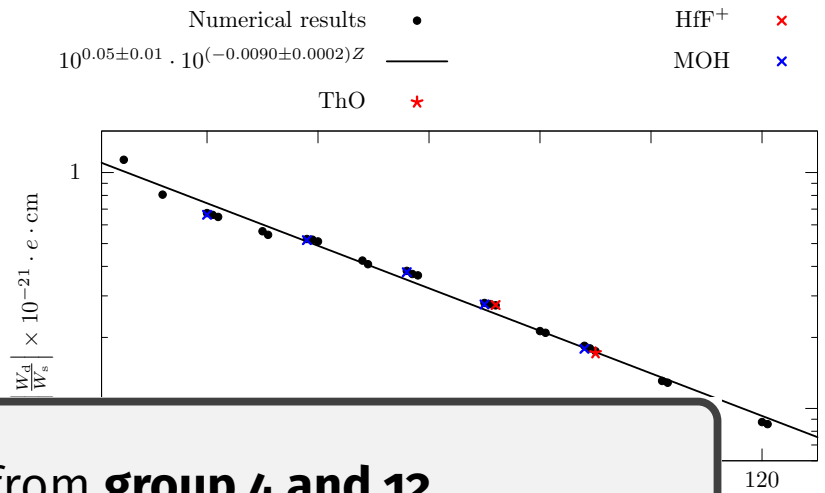
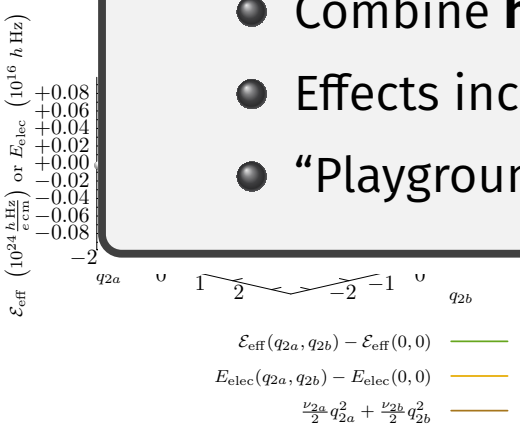


- Largest effects in molecules from **group 4 and 12**
- Combine **heavy** molecules that **differ** in Z
- Effects increase by changing chemical environment
- “Playground” of diatomic/linear molecules restricted ?



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states

$\mathcal{E}_\mathrm{eff}$

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Global $\mathcal{P}, \mathcal{T}$-odd measurement model

- Six relevant *fundamental* parameters in a molecule

$$\hbar\vec{\omega} = \boldsymbol{W}\,\vec{x}_{\mathcal{P},\mathcal{T}}\,,$$

$$\boldsymbol{W} = \begin{pmatrix} & & \\ & & \\ & & \\ & & \\ & & \\ & & \end{pmatrix}$$

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\Omega_2 W_{\mathrm{d},2}+\mathcal{I}_2 W^{\mathrm{m}}_{\mathrm{d},2} & \Omega_2 W_{\mathrm{s},2}+\mathcal{I}_2 W^{\mathrm{m}}_{\mathrm{s},2} & \mathcal{I}_2 W_{\mathrm{T},2} & \mathcal{I}_2 W_{\mathcal{S},2} & \Theta_2 W_{\mathcal{M},2} & \mathcal{I}_2(R_2 W_{\mathcal{S},2}+W_{\mathrm{m},2}) \\
\Omega_3 W_{\mathrm{d},3}+\mathcal{I}_3 W^{\mathrm{m}}_{\mathrm{d},3} & \Omega_3 W_{\mathrm{s},3}+\mathcal{I}_3 W^{\mathrm{m}}_{\mathrm{s},3} & \mathcal{I}_3 W_{\mathrm{T},3} & \mathcal{I}_3 W_{\mathcal{S},3} & \Theta_3 W_{\mathcal{M},3} & \mathcal{I}_3(R_3 W_{\mathcal{S},3}+W_{\mathrm{m},3}) \\
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\Omega_6 W_{\mathrm{d},6}+\mathcal{I}_6 W^{\mathrm{m}}_{\mathrm{d},6} & \Omega_6 W_{\mathrm{s},6}+\mathcal{I}_6 W^{\mathrm{m}}_{\mathrm{s},6} & \mathcal{I}_6 W_{\mathrm{T},6} & \mathcal{I}_6 W_{\mathcal{S},6} & \Theta_6 W_{\mathcal{M},6} & \mathcal{I}_6(R_6 W_{\mathcal{S},6}+W_{\mathrm{m},6})
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IV open-shell molecules with an open-shell nucleus with $\mathcal{I} \geq 1$.

$\Rightarrow$ We need to minimize coverage volume $V = P^3 \frac{\pi^3}{6} \frac{\prod_{i=1}^{6} |u(\omega_i)|}{|\det(\boldsymbol{W})|}$

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- **Radioactive molecules** with long-isotope chains

$\Rightarrow$ **2-4 classes with "one" molecule**

Radioactive molecules for $\mathcal{P},\mathcal{T}$-violation

Radium monofluoride

- RaF has a simple electronic structure
- RaF is laser-coolable
- RaF: Class I (^{226}RaF), [Class II (^{223,225}RaF^{+})], Class III (^{225}RaF) and Class IV (^{223}RaF).
- But no direct sensitivity to d_{p} (no unpaired valence proton)?
- Other candidates: Iso-electronic Actinides

*	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No
*														

T. A. Isaev, R. Berger, *Phys. Rev. A* **2012**, *86*, 062515, R. F. Garcia Ruiz et al., *Nature* **2020**, *581*, 396–400.

Radioactive molecules for $\mathcal{P}, \mathcal{T}$-violation

Actinide molecules for search for $\mathcal{P}, \mathcal{T}$-violation

Nuclear structure effects:

- ^{225,227}Ac, ^{229}Th, ^{229}Pa Supposed to have octupole deformation
- Ac and Pa have an open proton shell.
- Pa possibly has a parity doublet with splitting $\Delta E \sim 60\,\text{eV}$ (^{229}Th has $\Delta E < 130\,\text{keV}$)

$\Rightarrow$ Collective Schiff moment two orders larger than in ^{229}Th

- Embedding ^{229}Pa in a molecule may help to understand nuclear structure!

I. Ahmad et al., *Phys. Rev. Lett.* **1982**, *49*, 1758–1761, V. V. Flambaum, *Phys. Rev. C* **2019**, *99*, 035501.

I. Ahmad et al., *Phys. Rev. C* **2015**, *92*, 024313.

J. T. Singh, *Hyperfine Interact.* **2019**, *240*, 29.

Radioactive molecules for $\mathcal{P}, \mathcal{T}$-violation

Actinide molecules for search for $\mathcal{P}, \mathcal{T}$-violation

Electronic structure:

- ThO most successful eEDM experiment so far, ThF^+ experiment planned
- Large enhancement of eEDM and k_s in AcO and ThN, both may have $^2\Sigma_{1/2}$ ground state (ZORA-cGHF)
- Schiff moment enhancement in AcO ($\sim -5800\,/{a_0}^4$) larger than in RaF ($\sim -4000\,/{a_0}^4$) (in ThN ($\sim -2200\,/{a_0}^4$) smaller)
- Cationic species: AcF^+ (and similar ones), ThO^+
- What about Pa?

V. Andreev et al., *Nature* **2018**, *562*, 355–360.

D. N. Gresh et al., *J. Mol. Spec.* **2016**, *319*, 1–9.

K. Gaul et al., *Phys. Rev. A* **2019**, *99*, 032509.

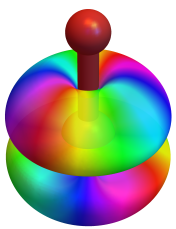
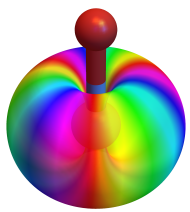
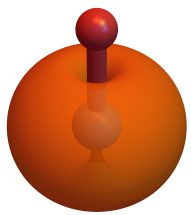
Radioactive molecules for $\mathcal{P},\mathcal{T}$-violation

Protactinium containing molecules?

- No neutral molecules iso-electronic to RaF
- PaN or PaO^+ would be iso-electronic to ThO

$\Rightarrow$ f-electron dominated $\rightarrow$ strongly mixed ground state?

- PaN^+ and PaO^{2+} were experimentally observed
- Theoretical studied of PaO^{2+} by Kovacs *et.al.* (CASPT2)
- $\Omega = 5/2$ ground state with $\sim 80\,\%$ Φ and $\sim 20\,\%$ Δ characterized by a non-bonding f-electron (ZORA-cGKS-B3LYP)

$\psi_\alpha =$  $\psi_\beta =$  $|\psi|^2 =$ 

- Schiff moment strongly enhanced ($W_S \lesssim -11\,000\,/{a_0}^4$)
- Electron spin dependent effects suppressed (f-electron).
- Sympathetic cooling (mass to charge ratio in range of Ba^+)?

M. Santos et al., *J. Phys. Chem. A* **2006**, *110*, PMID: 16640369, 5751–5759.

A. Kovács et al., *Struct. Chem.* **2013**, *24*, 917–925.

Radioactive molecules for $\mathcal{P}, \mathcal{T}$-violation

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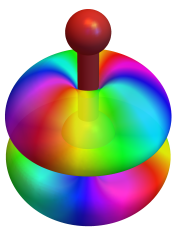
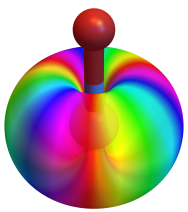
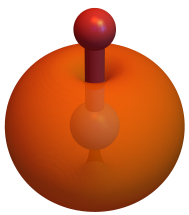
- $\Omega =$ a nor

Continuation follows soon...

$\psi_\alpha =$  $\psi_\beta =$  $|\psi|^2 =$ 

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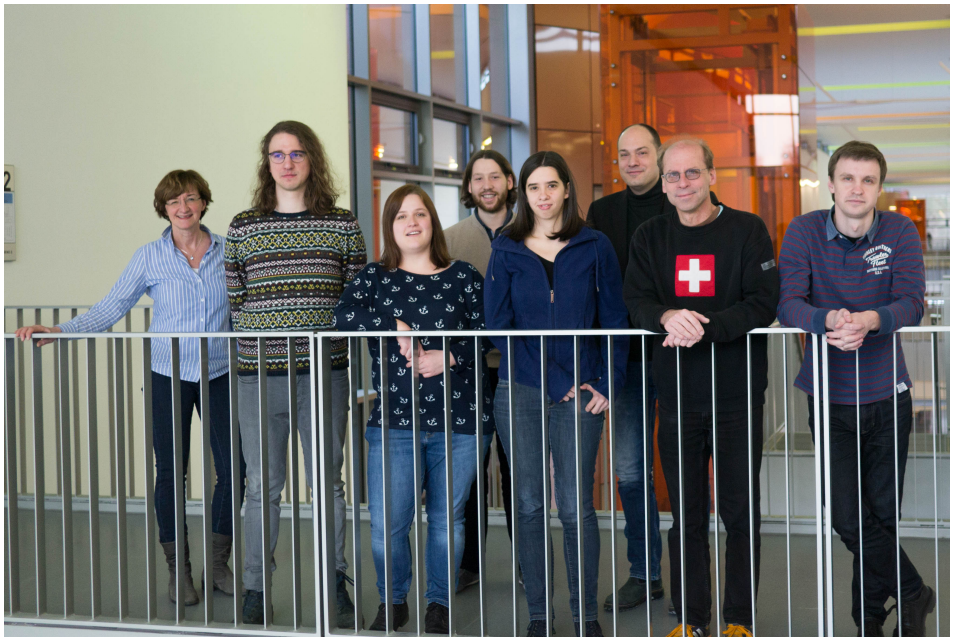
Conclusion

- Many good molecular $\mathcal{P},\mathcal{T}$-violation experiments needed
- Robust bounds on $\mathcal{P},\mathcal{T}$-Violation require molecules with fundamentally different spin-rotational Hamiltonian
  - Many experiments involving non-zero spin nuclei are required

  $\Rightarrow$ Radioactive molecules most interesting here
  - Have to find balance between large enhancement and different ratio of enhancement factors
  - Polyatomic molecules can reduce experimental uncertainty
  - Non-linear polyatomic molecules have a different spin-rotational Hamiltonian!
- PaO^{2+} has potential to be used for precision spectroscopy
- More interesting Pa candidates and a detailed study will follow soon...

Acknowledgments



Group of Robert Berger:

- **Carsten Zülch**
- Anna Hansmann
- Steffen Giesen
- Mira Diekmann
- Oliver Kreuz
- Nityananda Sahu
- Manjinder Kour
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