

Searches for Fundamental Symmetry Violations with Atoms and Molecules

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Notes About the Content

- We will focus mostly on CP-violation searches (EDMs) in atoms and molecules
 - Mainly because this is what I do and what I know!
 - Many of the ideas and techniques are directly applicable to a wide range of atomic/molecular science, and relevant for a very wide range of research, from HEP to QIS to Chemistry
- I am an atomic/molecular/optical (AMO) experimentalist
- This is not a review, but I have many to suggest
- Please feel free to get in touch any time!
- Ask lots of questions!



Part I: Motivation and Background

Why are we interested in CP-violation at low energy? How are atoms and molecules used for these searches?

An Asymmetric Universe

- There is a large imbalance between matter and anti-matter in the universe
 - Baryon Asymmetry of the Universe (BAU)
- How can we explain this?
- One model: an undiscovered particle which preferentially decays into matter
- Sakharov conditions:
 - B-violating processes
 - Departure from thermal equilibrium

 - Must be outside Standard Model





Low Energy Observables

- New CPV physics with SM couplings generically gives rise to CPV electromagnetic moments in SM objects
 - Fundamental particles:
 - Electric dipole moment (EDM)
 - Nuclei:
 - Nuclear Schiff moment (NSM)
 - Magnetic quadrupole moment (MQM)
- Moments must lie along intrinsic spin (no internal other vectors!)
- $\vec{d} \propto \vec{s} \rightarrow$ problem
 - \vec{d} is P-odd, T-even
 - \vec{s} is P-even, T-odd





EDMs violate P, T, CP*

(*Assuming conservation of CPT...)

Electron EDM

- Generically sensitive to CPV particles and forces coupling to the electron
 - One loop ~ 10-50 TeV
 - Two loop ~ 0.5-2 TeV
- "Background free"
 - SM value is small
 - |d_e| < 10⁻³⁸ e cm
 - Arises from CKM @ 4 loops
- For specific models, energy reach can be even higher (or lower!)



 $|d_e| \sim 1 \times 10^{-29}$ e cm (current experimental limit)

Many complementary approaches



Shading shows progress since 2013 (LHC, ACME, nEDM, ¹⁹⁹Hg)

"All of the constraints shown are merely indicative and are subject to significant loopholes and caveats." –J. Feng

Adapted and updated from J. Feng, Ann. Rev. Nuc. Part. Sci. 63, 351 (2013) with help from D. DeMille

An Idealized EDM Experiment









Sensitivity

 Experimental observable is angle φ (phase),

$$\varphi = d\mathcal{E}\tau/\hbar$$

Repeated measurements:



Internal Fields

- Basic idea: Atoms/molecules have extremely large fields
 - $e/4\pi\epsilon_0 a_0^2 \sim \text{GV/cm}$
 - Up to ~100 GV/cm for heavy species
 - Much larger than "maximum" lab field of ~100 kV/cm
- Permanent EDM causes splitting of energy levels
 - Amplified by internal fields
- This simple picture has several caveats



Polarization

- First "internal field" picture caveat – electrons and nucleus experience zero average field!
 - Always the case: eigenstates have well-defined parity, so $\vec{\mathcal{E}}_{lab}$ $\langle \psi | \vec{\mathcal{E}} | \psi \rangle \propto \langle \psi | \vec{r} | \psi \rangle = 0$

Solution: polarize

- Apply lab field to polarize atom/molecule
- Interaction no longer averages to zero



 $\vec{d} \cdot \vec{\mathcal{E}}_{int} \! > \! 0$

 $\langle \vec{d} \cdot \vec{\mathcal{E}}_{int} \rangle = 0$

 $\langle \vec{d} \cdot \vec{\mathcal{E}}_{int} \rangle \neq 0$

Polarizing atoms and molecules

+

i d. É = D

Actual shift Linear shift

+

 $P \approx 0$

+

Energy

Δ

- Atoms/molecules are symmetric in zero field
- Electric field mixes opposite parity states
- Must overcome energy splitting ∆ between the states to polarize
 - Therefore an induced dipole moment
- EDM sensitivity is ∝ P, fractional polarization
- Nothing has a permanent EDM
 - H₂O, NaCl, H (n=2), ...
 - Except from CP-violation!



Atoms vs. molecules

Atoms

- $\Delta \sim 100$ THz (electronic)
- *P* ~ 10⁻³ @ 100 kV/cm

Molecules

- $\Delta \sim 10$ GHz (rotational)
 - Sometimes even smaller, more on that later
- *P* ~ 𝒴(1) @ 10 kV/cm
- "Molecules are 1000x more sensitive"



 $\begin{array}{c} \textbf{Atoms} \\ \Delta \sim 100 \text{ THz} \end{array}$



Molecules $\Delta \sim 10 \text{ GHz}$

Schiff Shielding

- Second "simple internal field" picture caveat electrons and nuclei experience zero average field even when polarized
 - Schiff's Theorem
 - Basic idea: Atoms/molecules do not accelerate in static electric fields. Therefore, $\langle F_i \rangle = q_i \langle E_i \rangle = 0$ in steady state.
 - Charged particles move to a point where they see zero average field
 - Charges are "shielded" or "screened"
- This is true! But there are evasions:
 - Electrons move relativistically
 - Nuclei have complex shape

Relativistic Effects

- Dipole moment \vec{d} experiences Lorentz contraction
- Correlation of velocity, position relative to nucleus
- \vec{d} is not a constant in the atom
- $\langle \vec{E} \rangle = 0$ but "effective field" is not zero, $\left\langle \vec{d} \cdot \vec{E} \right\rangle = d_e \mathcal{E}_{eff} \neq 0$
- Depends on very short-range electronic wavefunction near nucleus – very relativistic quantum mechanics
 - Requires core-penetrating electron orbitals
- "Purely relativistic effect"
- Scales roughly as $\mathcal{E}_{eff} \propto Z^3$

Commins et al., Am. J. Phys. 75, 532 (2007)

Nuclear Schiff Moments

- What about nuclear EDMs? Nuclear motion is definitely not relativistic...
- Evasion: charge (only p) and EDM (p, n, ...) distributions *need not* overlap
- Gives rise to a Nuclear Schiff Moment (NSM)
 - Depends on mismatch between charge and mass distributions in nucleus
 - Looks like an E field correlated with nuclear spin (CPV)
 - Mixes opposite parity, core-penetrating electron orbitals
 - Enhanced in high Z nuclei
 - Requires nuclear spin >0
- Can be significantly enhanced in highly deformed (non-spherical) nŭclei



N. Auerbach, V. V. Flambaum, and V. Spevak, PRL 76, 4316 (1996) V. V. Flambaum and J. S. M. Ginges, PRA 65, 032113 (2002)

Octupole Deformations

- Schiff Moments (NSMs) enhanced by ~100-1,000 in nuclear with octupole deformation
 - Heavy, spinful, deformed species are short-lived
- Combines with molecular enhancements → 10⁵⁻⁶ sensitivity gain vs. atoms with spherical nuclei
- Truly exotic nuclei like ²²⁹Pa offer another factor of 100-1000 (maybe)



Neutron Number N



Nuclear Magnetic Quadrupole Moments

- Another evasion of Schiff shielding: magnetic effects
- Nuclear magnetic quadrupole moments (MQM) are not screened
 - Intuitive origin: orbiting nucleon with EDM creates an MQM $\sim \vec{I}$
 - Violates T, P, CP
- Need $I \ge 1$
- Enhanced in high Z nuclei
- Quadrupole deformation (β₂) enhances MQM



Rotating EDM produces MQM



EDM vs. NSM vs. MQM shifts



 $|\downarrow\downarrow\rangle$

 $|\downarrow\uparrow\rangle$

 $|M_I M_S\rangle$

- Very similar methods, requirements, approaches
- These are often all just called "EDM Experiments"
- All shifts are proportional to polarization

Field + Nuclear Enhancements

	Internal Field Enhancement	Nuclear Enhancement		
Atom	~1,000			
Molecule	~1,000,000			
Quadrupole nucleus (MQM)		~10	Both NSM, MQM potentic	
Octupole nucleus (NSM)		~1,000	enhancement in ²²⁹ Pa	



Summary: Structure Requirements

Feature	eEDM	NSM	MQM	Reason
Large Z?	Yes!	Yes!	Yes!	Gives large atomic/molecular enhancement
Core-penetrating s/p-like electrons?	Yes!	Yes!	Yes!	Depends on short-distance electronic wave function (for different reasons)
Quadrupole nucleus?	Not necessary	Yes!	Yes!	Collective nuclear enhancement
Octupole nucleus?	Not necessary	Yes!	Not necessary	Collective nuclear enhancement
Open shell?	Necessary	Not necessary	Necessary	Electron spin density near nucleus
Nuclear spin?	Not necessary	$I \ge 1/2$	$I \ge 1$	Need nuclear spin to define moments

Many Sources q e qEDM eEDM πNN Leptonic Hadronic q e-N q **CEDM NEDM**

We <u>need</u> experiments in multiple systems (eEDM, NSM, MQM, nucleons, ...) !!





We <u>need</u> broad theory input!



Part II: Selected Contemporary Experiments

Not a review, but instead using them as a vehicle to explain modern experimental methods, and motivate ongoing and future improvements.

We will not discuss all ongoing EDM experiments!

¹⁹⁹Hg EDM

- University of Washington
- ¹⁹⁹Hg in a vapor cell
- I = 1/2 due to valence *n*
 - Spherical nucleus → no "nuclear enhancement"
- Heavy nucleus, highly relativistic electrons
 - Large "atomic enhancement"
 - Sensitive to NSM
- Very high count rates (vapor cell) + very long coherence times (minutes)
 → extremely good frequency resolution
 - ~0.1 nHz (!!)
- Sensitive primarily to hadronic CPV
 - Example: $\theta_{QCD} < 1.5 \times 10^{-10}$ (single source assumption)
- ¹²⁹Xe EDM experiments are similar, but use different techniques





B. Graner, Y. Chen, E. G. Lindahl, and B. R. Heckel, PRL 116, 161601 (2016) Photo from Y. Chen FRIB Presentation, 2019 https://indico.frib.msu.edu/event/13/

²²⁵Ra EDM

- Argonne National Lab
- 225 Ra, I = 1/2
 - Large atomic enhancement
 - Large static octupole deformation, ~1,000x more intrinsic (nuclear) NSM sensitivity vs. Hg
 - Challenges: t_{1/2} ~ 2 weeks, no vapor cells
- Laser-coolable
 - Trap in gas phase at ultracold temperatures
 - Low temperature → highly coherent
- ¹⁷¹Yb @ USTC
 - "Test bed" for ²²⁵Ra
 - Similar structure, not radioactive
 - Recently demonstrated some advanced quantum methods for EDM measurement
 - arXiv: 2207.08140



Ra EDM @ ANL R. H. Parker, et al., PRL 114, 233002 (2015)

YbF

- Imperial College London
- ¹⁷⁴YbF has single unpaired valence electron, no nuclear spin
 - Sensitive to eEDM
- Spin precession in pulsed supersonic beam
- First to beat atomic experiments
 - Berkeley, Tl, 2002
- |d_e| < 1.1 × 10⁻²⁷ e cm (2011)
 - Statistics limited
- Being upgraded (more later)



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

ThO

- ACME Collaboration (Harvard, Chicago, Northwestern)
- Spin precession in cryogenic beam

Current most sensitive limit

- |d_e| < 8.7 × 10⁻²⁹ e cm (2014)
- |d_e| < 1.1 × 10⁻²⁹ e cm (2018)
- Being upgraded
 - Demonstrated improvements for ~10x improvement in next few years





Beam Experiments



Beam Experiments



Beam Experiments



Photo of ACME Gen I



Cryogenic Buffer Gas Beams

- These molecules are free radicals with low vapor pressure – challenging
- Use inert gas in cryogenic environment to cool via collisions
 - CBGB Cryogenic buffer gas beam
- "Works for anything"
- Cold, slow, high flux
- First step for molecular laser cooling as well (more on that later)



NRH, H. Lu, and J. M. Doyle, Chem. Rev. 112, 4803 (2012) 35

Parity Doublets

- Certain molecules have parity doublets
 - Each rotational state is split into a doublet of opposite parity states, split by <100 MHz
 - Small splittings mean high polarization in ~100 V/cm
- Gives rise to two, fullypolarized states with opposite alignment of internal fields
- Change EDM shift without changing external fields – just tune lasers to address different states
- Very powerful for rejection of systematic errors



 $\overline{\mathcal{E}}_{lab}$

An Idealized EDM Experiment











HfF⁺

- JILA and CU Boulder
- Spin precession in molecular ion trap
 - Rotating electric field prevents charged ions from escaping
- Molecular structure with parity doublets
 - Critical can't reverse electric field! Trap → Anti-trap
- Long coherence time
- |d_e| < 1.3 × 10⁻²⁸ e cm (2017)
- Being upgraded!
 - Demonstrated order of magnitude improvement, result in next ~year





W. B. Cairncross, D. N. Gresh, M. Grau, K. C. Cossel, T. S. Roussy, Y. Ni, Y. Zhou, J. Ye, and E. A. Cornell, Phys. Rev. Lett. **119**, 153001 (2017)



Part III: Selected Ongoing and Future Developments

Not a review, but instead using them as a vehicle to explain experimental methods under development

We will not discuss all ongoing and future developments!



Laser cooling

Motivation for molecular laser cooling

- Beam experiments (ThO, YbF) limited by time of flight, τ ~ few ms
- Can extend by slowing and compressing beam
- Trapping can yield orders of magnitude improvement
 - Critical for long coherence time of HfF⁺, Ra experiments
- Neutral species require ultracold temperatures <1 mK
- \rightarrow Laser cooling
- Also highly relevant for atomic searches (Cs, Fr, Ra, ...)



10⁶ molecules 100 s coherence time Heavy, deformed nucleus Quantum control Robust error rejection Two weeks integration



~PeV-scale CP-violating physics @ 1 loop ~100 TeV-scale CP-violating physics @ 2 loops Both leptonic and hadronic sectors Extreme precision, $\theta_{QCD} \lesssim 10^{-14}$ ~10 year time scales

> Future orders-of-magnitude improvements from quantumenhanced metrology, highly exotic nuclei, ... + ~5-10 year time scale?

Laser cooling molecules

- Apply forces by photon scattering
- Requires many (~10⁵) cycles of absorption, spontaneous decay
- Decay to other states stops the cooling process
- Internal vibrational, rotational levels are excited in decay
- For certain molecules, this is *manageable*





Laser cooling molecules

- Able to scatter sufficient photons for stop, trap, cool molecules to ~uK
 - Requires one laser per vibrational repump
 - Each laser needs "sidebands" to address spin-rotation, hyperfine
- Four species so far: SrF, CaF, YO, CaOH
 - SrF first in 2014!
 - Decades behind atoms, but moving rapidly
- Starts with cryogenic buffer gas beam (CBGB)





Intuition for Needed Structure

- Need to find molecules where valence electrons "don't participate in chemical bond"
 - Excitation won't change chemical bond





E. Hudson, Science 369, 1304 (2020)

Electronic Structure for Laser Cooling

- Generally works for molecules with single, metal-centered s electron
 - Alkaline-earth (s²)
 - Single bond to halogen (F)
 - Metal-centered electron
- Hybridization of s, p-like orbitals
 - Pushes electron away from bond
 - Decouples electron
- These electrons have significant s character – good for CPV searches
 - s-like electrons penetrate the nuclear core, experience relativistic effects
- Works for polyatomics (more later)



Three Examples







YbF

- eEDM @ Imperial College London
- Laser cooling, other upgrades demonstrated
- X. Alauze *et al.*, Q. Sci. & Tech. 6, 044005 (2021)
- N. J. Fitch *et al.*, Q. Sci. & Tech. 6, 014006 (2021)

BaF

- NL-eEDM Collaboration
- Advanced deceleration techniques
- P. Aggarwal et al., Eur. Phys. J. D 72, 197 (2018).
- P. Aggarwal *et al.*, PRL 127, 173201 (2021)

TIF

- CeNTREX Collaboration
- TI Schiff moment (~proton EDM)
- O. Grasdijk *et al.*, Q. Sci. & Tech. 6, 014006 (2021)

Several more laser cooling examples later



- Additional degrees of freedom to engineer desirable properties
 - Electric and magnetic field interactions
 - High polarizability
 - Species in ligand
 - Frequencies of rotation and vibration
 - •
- Review: 2008.03398

50



Adapted from Eric Hudson, Science 369, 1304 (2020)



- Many bonding partners "bond similarly"
 - $-F \approx -OH$, --CCH, $-OCH_3$, ...
 - Not in general, but for s² atoms it typically holds
 - Ca, Sr, Ba, Yb, Ra
 - Since electron wavefunction is metal-centered, ligand matters much less
- Similar electronic structure implies similar:
 - Laser cooling/photon cycling
 - CPV sensitivity
 - Measurement methods
- ... but with the possibility of engineering other features





T. A. Isaev and R. Berger, PRL 116, 063006 (2016) T. A. Isaev, A. V. Zaitsevskii, and E. Eliav, J. Phys. B 50, 225101 (2017) M. V. Ivanov, F. H. Bangerter, and A. I. Krylov, Phys. Chem. Chem. Phys. 21, 19447 (2019)

- Polyatomics generically have parity doublets
 - (>3 atoms)
 - Arise from symmetrylowering mechanical modes
 - As opposed to diatomics, which rely on "exotic" electronic structure
 - Generically realize high polarizability and systematic robustness advantages
- Useful Laser-coolable diatomic molecules don't have parity doublets!
- Available for any atomic species

Three Examples



CaOH/SrOH/YbOH

- Combine laser cooling, high polarizability
- PolyEDM: eEDM search, NRH, Doyle, Steimle, Vutha
- ¹⁷³YbOH MQM @ Caltech
- I. Kozyryev and NRH, PRL 119, 133002 (2017)

MgNC

- Engineer magnetic field interactions for PV
- E. B. Norrgard, et al, Nat.
 Comm. Phys. 2, 77 (2019)



RaOCH₃⁺

- Combines deformed nucleus with ion trapping
- Other molecules as well, ex. PaF³⁺ [2203.10333]
- M. Fan et al., PRL 126, 023002 (2021)
 P. Yu and NRH, PRL 126, 023003 (2021)

... Many, many more!

Versatile Platform



Symmetry Violation



High-Fidelity, Scalable QC



Quantum Simulation



Dark Matter Quantum Sensing



Robust Qubit Encoding



Controlled Quantum Chemistry

All of these have very similar requirements

- Ultracold temperatures for good coherence
- Efficient preparation and readout
- Good quantum control

Laser cooling molecules has many applications!



Deformed Nuclei

Octupole Deformations

- Heavy, octupole-deformed nuclei combine large nuclear and field enhancements
 - ~10⁶ intrinsic sensitivity gain
- Spinful, heavy, deformed nuclei are rather limited
 - Fr, Ra, Ca, Th, Pa, ...
 - Half-lives between thousands of years and several minutes



L. P. Gaffney et al., Nature 497, 199 (2013)

87 ² S _{1/2}	88 ¹ S ₀	89 ² D _{3/2}	90 ³ F ₂	91 ⁴ K _{11/2}
Fr	Ra	Ac	Th	Pa
Francium	Radium	Actinium	Thorium	Protactinium
(223)	(226)	(227)	232.0381	231.03588
[Rn]7s	[Rn]7s ²	[Rn]6d7s ²	[Rn]6d ² 7s ²	[Rn]5f ² 6d7s ²
4.0727	5.2784	5.17	6.3067	5.89

Radium

Ra is highly versatile

- Ra has well-understood octupole deformation
- Ra, Ra⁺, Ra molecules can be laser cooled
- Venue to combine laser cooling, polyatomics, ion trapping, deformed nuclei
- Ra Laser-cooled, trapped EDM experiment @ ANL
- RaF Laser-coolable [Isaev et al., PRA 82, 052521 (2010)] Recent high-resolution spectroscopy
- RaAg Assemble from laser-coolable atoms T. Fleig and D. DeMille, NJP 23, 113039 (2021)
- RaOCH₃⁺ Trapped, cooled/controlled with co-trapped Ra⁺ [Fan et al., PRL 126, 023002 (2021)] Single ion could reach frontiers of hadronic CPV [P. Yu and NRH, PRL 126, 023003 (2021)]
- RaOH, Laser coolable, high polarizability RaOCH₃, T. A. Isaev, et al., J. Phys. B 50, 225101 (2017) ... I. Kozyryev and NRH, PRL 119, 133002 (2017)



Ra EDM @ ANL R. H. Parker, et al., PRL 114, 233002 (2015)



High-resolution RaF spectroscopy R. F. Garcia Ruiz *et al.*, Nature 581, 396 (2020)

Molecules with Exotic Nuclei

- How do we design/engineer molecules tailored to the experimental methods?
- Example: ion trapping
 - JILA EDM has proven the power of this method
 - Highly sensitive due to long coherence times
 - Well-suited for "small quantities" – ideal for shortlived species
- Radium molecules in an ion trap sound great, but...



W. B. Cairncross *et al.*, PRL 119, 153001 (2017)

Radium Molecular Ions

- RaF⁺ → Not highly polarizable
 - No parity doubling
 - True for any RaX⁺ diatomic
- Radium polyatomics
 - High polarizability due to symmetry-lowering motions
 - Ability to tune properties to match experimental needs
 - Quantum logic, clock measurement, spin precession
- Already created and trapped in Jayich Lab @ UCSB
- A single trapped molecular ion could probe the frontiers of symmetry violation

P. Yu and NRH, PRL 126, 023003 (2021) M. Fan *et al.,* PRL126, 023002 (2021)





Part IV: Outlook

Progress in the last ~year



Creation, trapping, cooling, control of radioactive molecular ions



Electron spin precession in opticallytrapped polyatomic molecules



Precision spectroscopy of radioactive molecules



Atomic EDM searches with long coherence times in optical traps

Fan *et al.*, PRL 126, 023002 (2021) Doyle Group @ Harvard PolyEDM Collaboration Udrescu *et al.*, PRL 127, 033001 (2021) Zheng *et al.*, arXiv:2207.08140 (2022)

A Positive Outlook



Similar gains in a very broad range of areas – hadronic CPV, ultralight DM, precision electroweak, ...

From Snowmass EDM whitepaper, arXiv:2203:08103

WOULD YOU LIKE TO KNOW MORE?

Precision measurements in atoms/molecules

- M. S. Safronova et al., Rev. Mod. Phys. 90, 025008 (2018)
- N. R. Hutzler, Quantum Sci. Technol. 5, 044011 (2020)

EDMs

- T. E. Chupp, et al., Rev. Mod. Phys. 91, 015001 (2019)
- W. B. Cairncross and J. Ye, Nat. Rev. Phys. 1, 510 (2019)
- Snowmass 2021 EDM white paper: arXiv:2203.08103

Interpretation of EDM limits

- See Safronova, Chupp, Snowmass reviews
- J. Engel et al., Prog. Part. Nucl. Phys. 71, 21 (2013)

Email me!



Thank you!