

June 10th, 2025, 07:40 pm – 08:00 pm
15th Conference on the Intersections of Nuclear and Particle Physics
University of Wisconsin Madison
Pan Hellenic
Parallel 9: Tests of Symmetries and the Electroweak interaction



FRIB

The FRIB-EDM3 Experiment: Designing a measurement protocol for CP-violation searches using radioactive molecules in solids

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This work is supported by the U.S. DOE, Office of Science, Office of Nuclear Physics, under contracts DE-SC0025679 and DE-SC0019015 and by the U.S. DOE, Office of Science, Office of High Energy Physics, under contract DE-SC0022299.



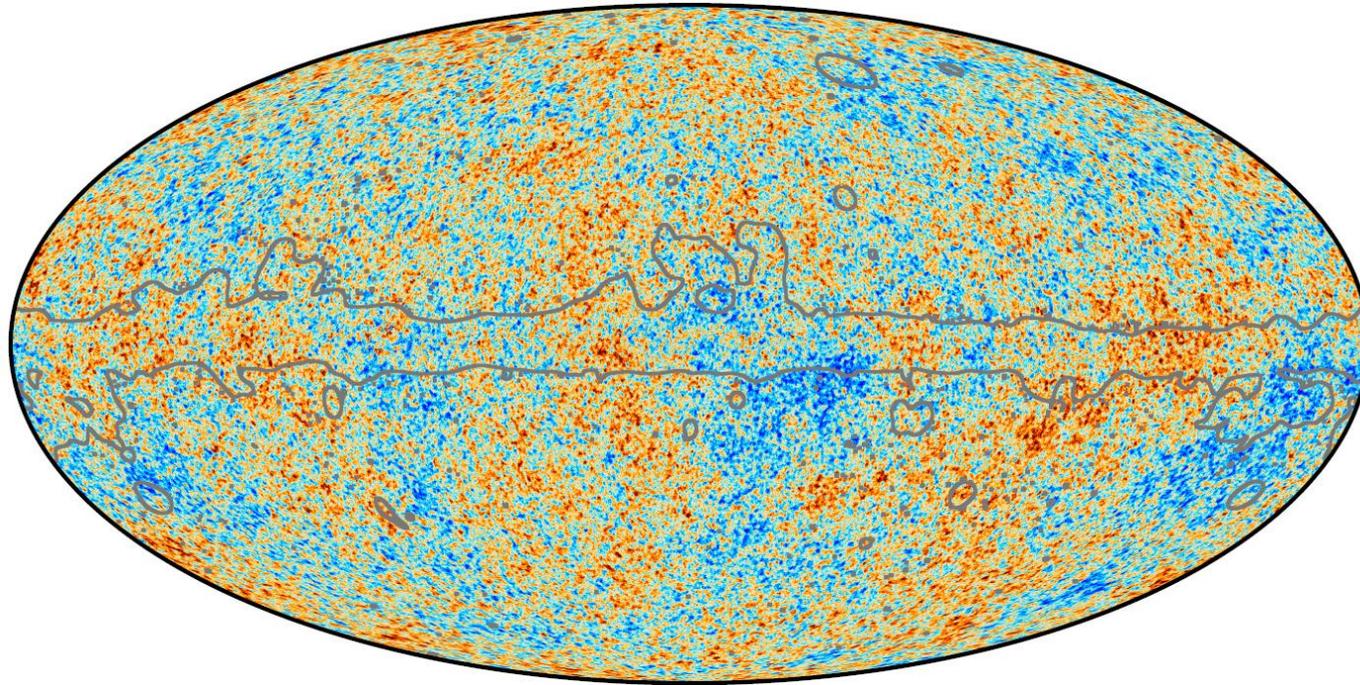
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Science

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Nuclear Physics and used resources of the Facility for Rare Isotope Beams (FRIB) Operations, which is a DOE Office of Science User Facility under Award Number DE-SC0023633.

There is no visible antimatter in the universe



-300  300 μK

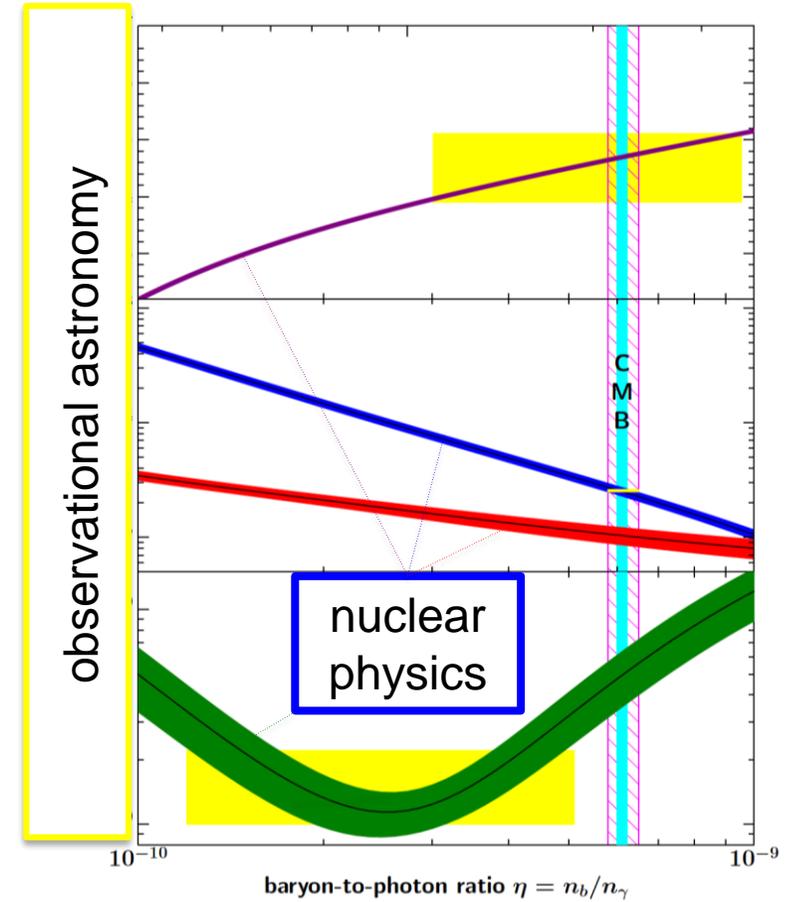
Planck (2018) <https://www.cosmos.esa.int/web/planck/picture-gallery>

$$\eta = \frac{\text{matter} - \text{antimatter}}{\text{relic photons}} \propto \sin(\delta)$$

$\delta = CP$ -violating “phase”

$$\eta_{\text{exp}} \approx 10^{-9} \quad \text{PDG2024}$$

$$\eta_{\text{CKM}} \approx 10^{-26} \quad \text{Huet \& Sather Phys. Rev. D 51:379 (1995)}$$



Permanent Electric Dipole Moments are a signature of CP-Violation

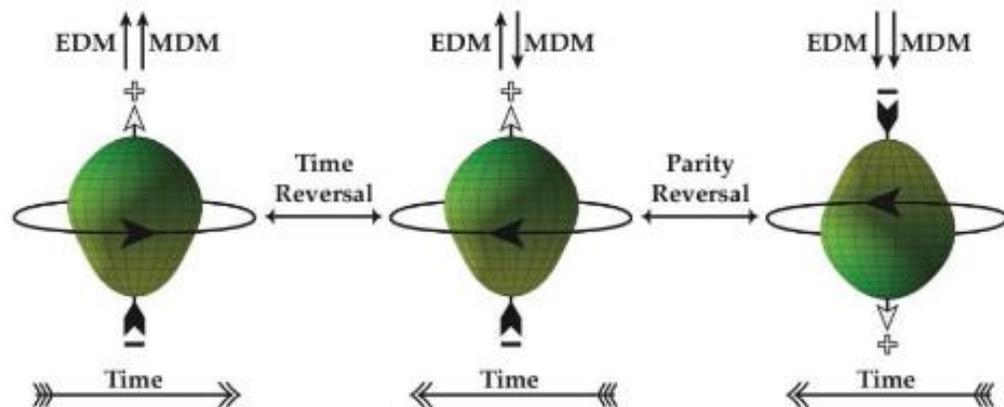
| Quantity | P (Parity) | T (Time-reversal) |
|-------------------------|------------|-------------------|
| \vec{J} | Even (+) | Odd (-) |
| \vec{B} | Even (+) | Odd (-) |
| \vec{E} | Odd (-) | Even (+) |
| $\vec{J} \cdot \vec{B}$ | Even (+) | Even (+) |
| $\vec{J} \cdot \vec{E}$ | Odd (-) | Odd (-) |

EDMs measure a separation of charge

$$\vec{d} = \int \vec{r} \rho_Q d^3r = d \frac{\langle \vec{J} \rangle}{J}$$

$$\mathcal{H} = -(\vec{\mu} \cdot \vec{B} + \vec{d} \cdot \vec{E}) = -\frac{(\mu \vec{J} \cdot \vec{B} + d \vec{J} \cdot \vec{E})}{J}$$

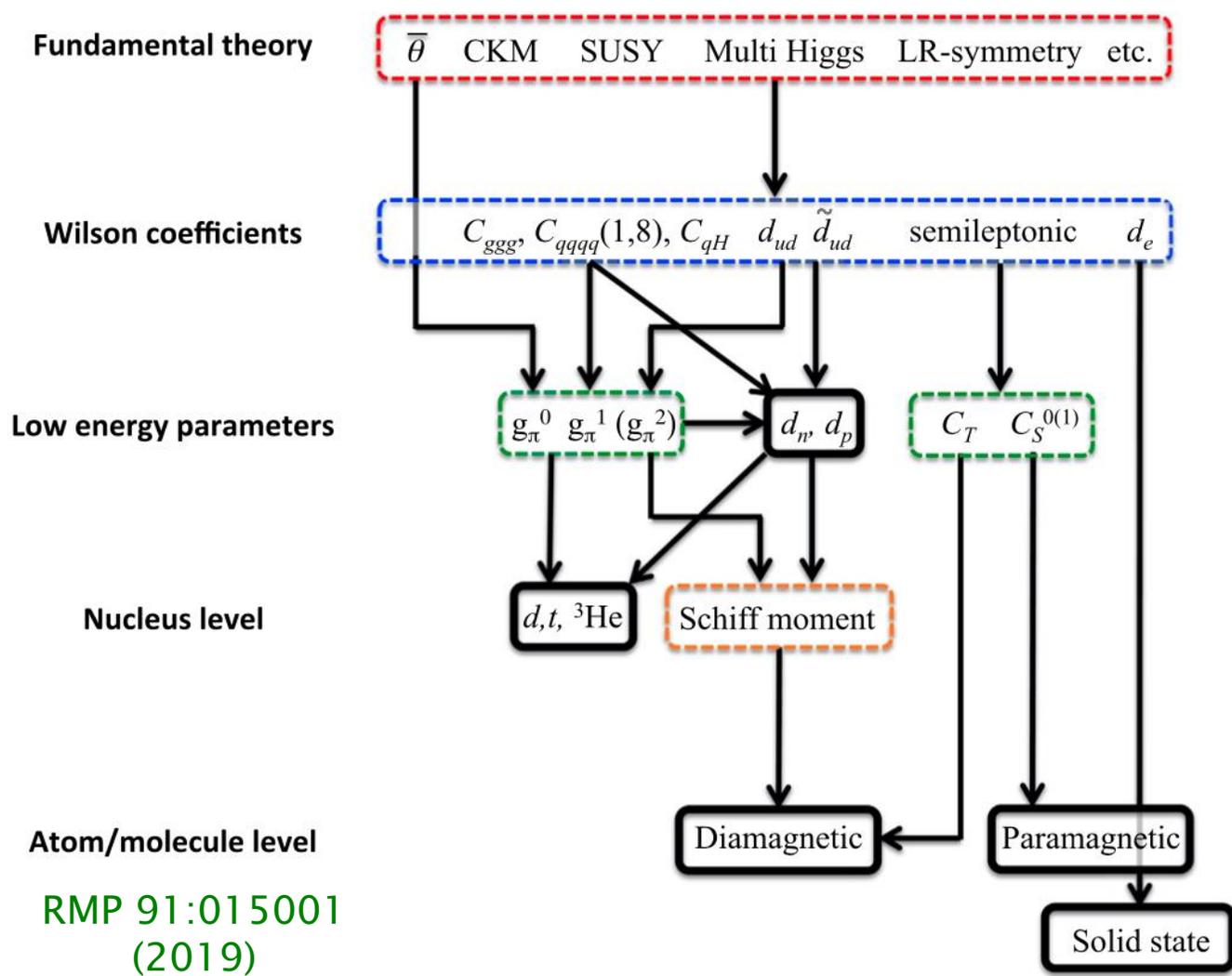
| | |
|----------|------------------------|
| J | Total angular momentum |
| B | Magnetic field |
| E | Electric field |
| d | Electric dipole moment |
| μ | Magnetic dipole moment |
| ρ_Q | Charge Distribution |



CPT Theorem: T-Violation = CP-Violation

Measurements in many systems are needed to fully constrain sources of CP-violation (“new physics”)

- There are many proposed sources of CP violation
 - There are two in the standard model alone
- EDMs in various systems have multiple sources
- To properly constrain multiple sources, need multiple independent measurement types



RMP 91:015001 (2019)

- Sources of CP-violation**
- Particle Physics Theory
 - Effective Field Theory
 - Lattice QCD Theory
 - Nuclear Structure Theory
 - + Experiment
 - Atomic Theory
 - + Atomic Experiment
 - Molecular Theory
 - + Molecular Experiment

EDMs are screened in atomic systems resulting in nuclear Schiff moments

Neutral diamagnetic atoms: all electrons are paired

- Shielding in diamagnetic atoms
 - Schiff Phys. Rev. 132:2194 (1963)

$$\vec{S} = \frac{\langle er^2 \vec{r} \rangle}{10} - \frac{\langle r^2 \rangle \langle e\vec{r} \rangle}{6}$$

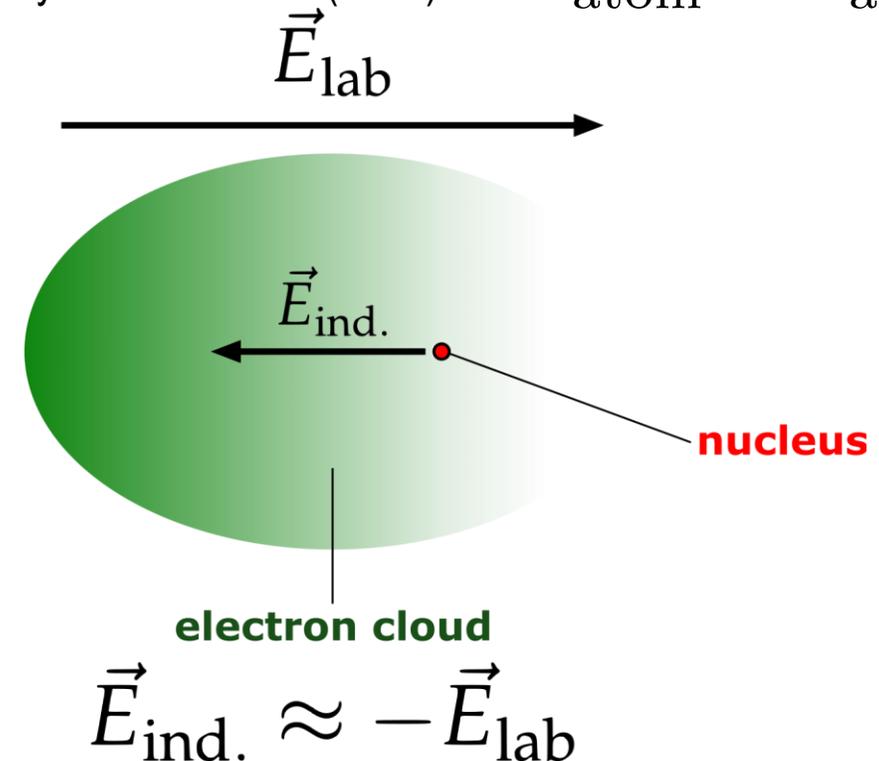
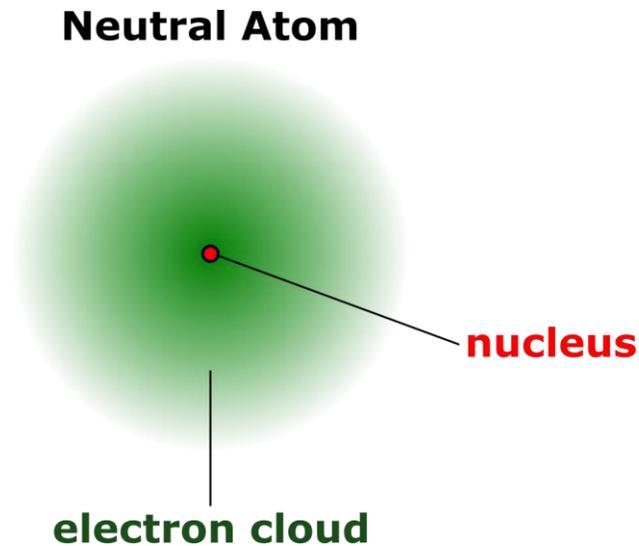
Schiff Moment

Relativistic atoms: Sandars-Bouchiat Z^3 scaling

- Shielding imperfect, leaving residual T-violating observable
- Atomic parity violating effects scale like Z^3
 - Sandars Phys. Lett. 14:194 (1965), Bouchiat and Bouchiat Phys. Lett. B 2:111 (1974)

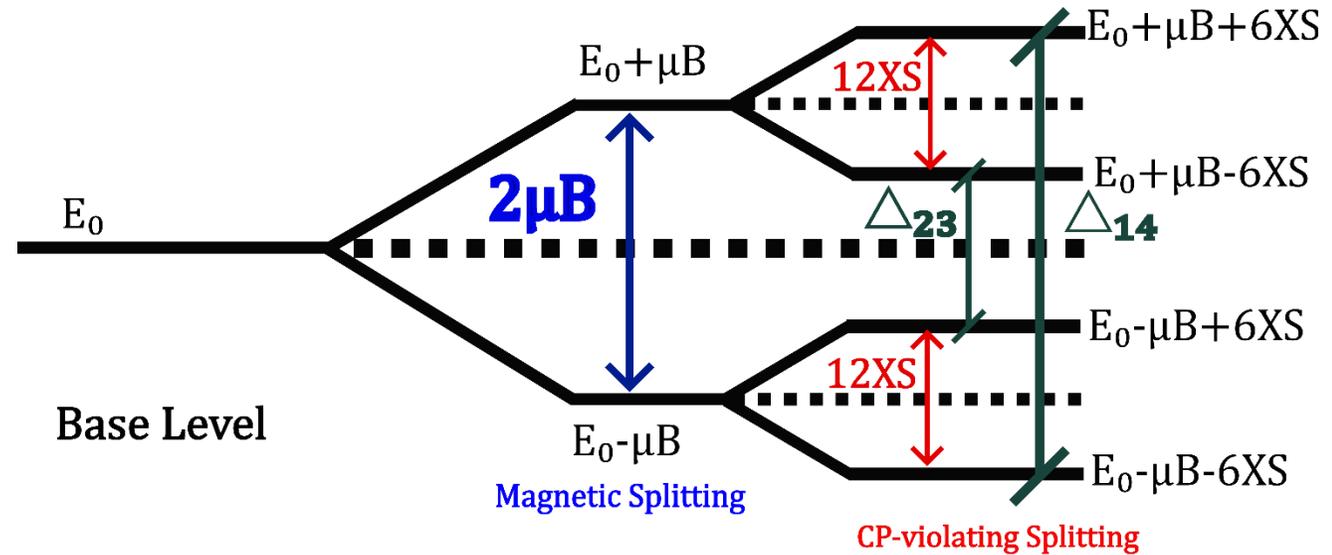
Sushkov et al. Zh. Eksp. Teor. Fiz 87:1521 (1984)

$$\vec{d}_{\text{atom}} = \kappa_{\text{atom}} Z^3 \vec{S}$$



Searching for CP-violating moments: Measure A Frequency Shift

- The most precise measurements are of frequencies/energy shifts
- Thus, we want to set up our system so that there's an energy shift proportional to our CP-violating Nuclear Schiff Moment
 - Typically apply a combination of magnetic and electric fields to set up this energy shift
 - Turns out we specifically will only need a magnetic field
- Measure population oscillations between pairs of states to measure an energy shift
 - For technical reasons, want easier to measure a nonzero shift
 - Thus, we're looking for a different size of the energy shift in "aligned" and "anti-aligned" pairs of states



Want to take combinations so that the difference only depends on the CP-violating splitting $12XS$

** Note: Not to scale, $2\mu B \gg 12XS$

$$\frac{\sigma_S}{\sqrt{N_m}} = \frac{\hbar}{12X \sqrt{\epsilon N_p T \tau}}$$

↓
↓
↓
↓
↓

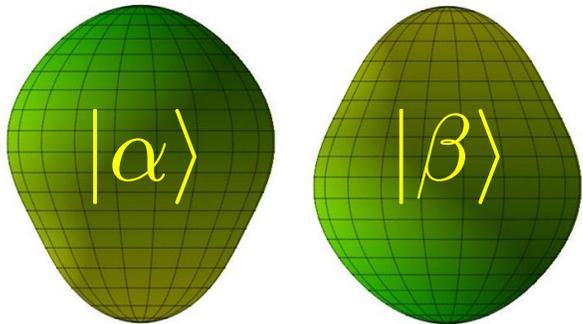
Number of measurements Molecular enhancement factor Number of particles Integration time Spin coherence time

CP-Violating observable strongly enhanced by pear-shaped nuclei

$$S_z = \frac{\langle er^2 z \rangle}{10} - \frac{\langle r^2 \rangle \langle ez \rangle}{6}$$

$$S \equiv \langle \Psi_0 | S_z | \Psi_0 \rangle = \sum_{k \neq 0} \frac{\langle \Psi_0 | S_z | \Psi_k \rangle \langle \Psi_k | V_{\text{PT}} | \Psi_0 \rangle}{E_0 - E_k} + \text{c.c.}$$

Ex: ^{225}Ra Parity Doublet



55 keV

$$|\Psi_1\rangle = \frac{|\alpha\rangle - |\beta\rangle}{\sqrt{2}}$$

$$|\Psi_0\rangle = \frac{|\alpha\rangle + |\beta\rangle}{\sqrt{2}}$$

- **Nearly degenerate parity doublet**

Haxton & Henley PRL 51:1937 (1983)

- **Large intrinsic Schiff moment due to octupole deformation**

Auerbach, Flambaum, & Spevak PRL 76:4316 (1996)

Total Enhancement Factor: EDM (^{225}Ra) / EDM (^{199}Hg)

| Skyrme Model | Isoscalar | Isovector |
|--------------|-----------|-----------|
| SIII | 300 | 4000 |
| SkM* | 300 | 2000 |
| SLy4 | 700 | 9000 |

^{225}Ra : Dobaczewski & Engel PRL 94:232502 (2005)

^{199}Hg : Ban et al. PRC 82:015501 (2010)

Polar molecules as ultrasensitive tools for CP-violation searches

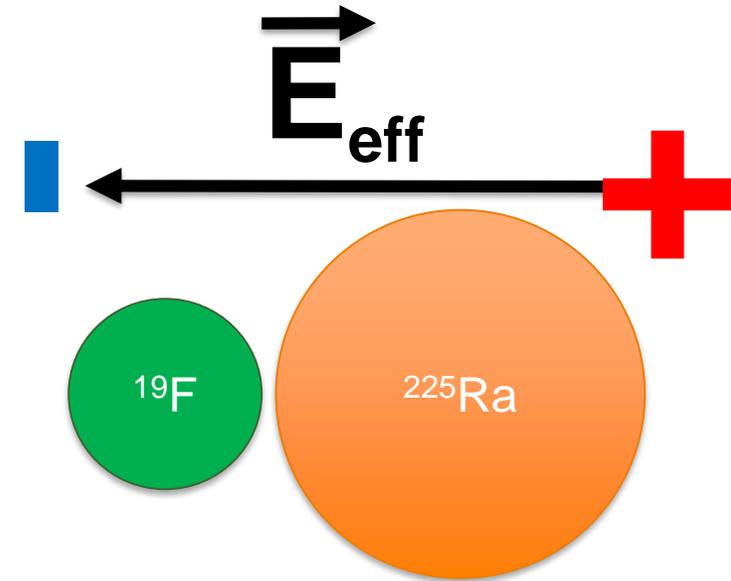
- Diatomic polar molecules have large effective electric fields (\sim GV/cm for electrons, \sim 100 MV/cm for nuclei)

A. D. Kudashov et al, PRA 87:020102 (2013)

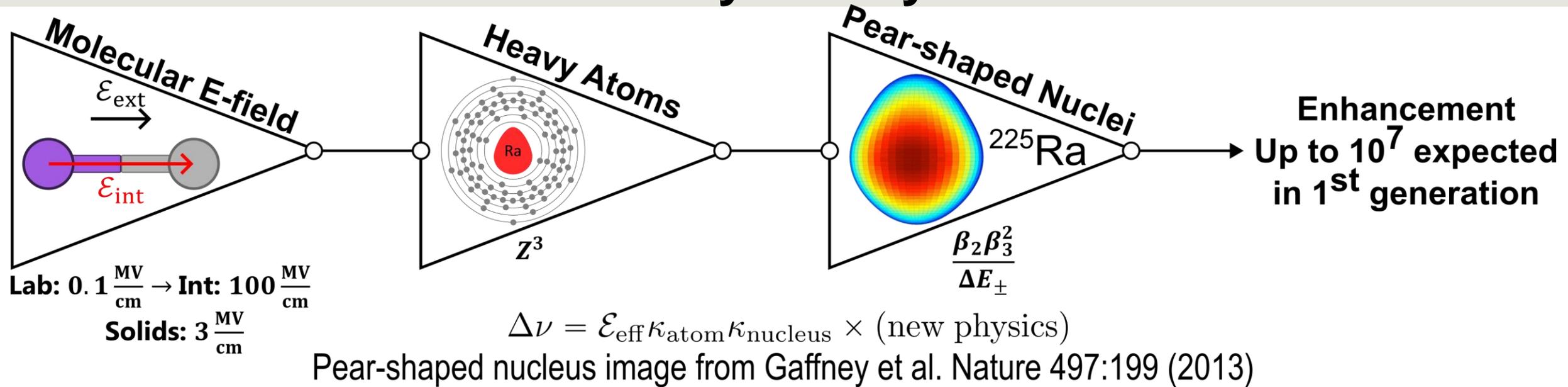
A. D. Kudashov et al, PRA 90:052513 (2014)

- This is many orders of magnitude larger than can be achieved in-lab.
 - For comparison, largest laboratory fields are \sim 0.3 MV/cm
- R. Ready et al, NIMA 165738 (2021)

- Molecules have many internal degrees of freedom, allowing for
- Well established for electron EDM
 - Roussy et. al. *Science* 381:6653 (2023)
 - Andreev et al. *Nature* 562:7727 (2018)
- Many efforts to make use of this in the hadronic sector



Radioactive polar molecules with pear-shaped nuclei: enhanced sensitivity and systematic control



- Polar molecules have been demonstrated as an ultrasensitive tool for electron EDM searches
 - Easy to align molecule dipole moment with applied field
 - Molecule dependent co-magnetometry via energy splittings
 - Large internal fields produce larger splittings

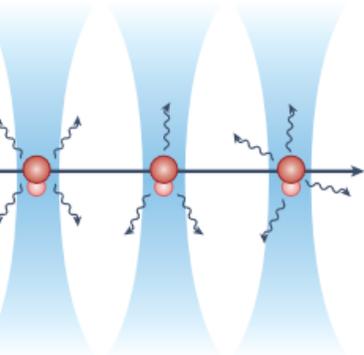
- Polar molecules to be implemented in upcoming hadronic searches
 - CeNTREX: ^{205}TlF (Stable)
 - RaX: ^{225}RaF and $^{225}\text{RaOH}$ (Pear-shaped, not stable)
 - FrAg: $^{223}\text{FrAg}$ (Pear shaped, not stable)
 - FRIB-EDM³: $^{225}\text{RaF}:\text{Ar}$
- Radioactive polar molecules challenging to use
 - Creation and handling of short-lived isotopes
 - How do we efficiently form molecules with these isotopes?

Contemporary techniques for EDM searches using molecules

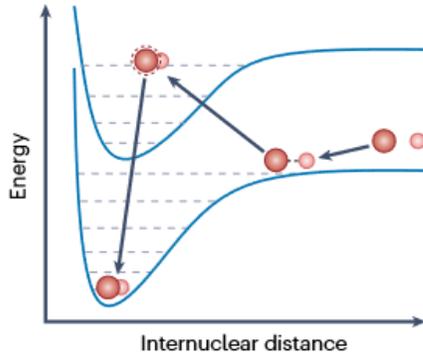
DeMille et al. Nature Physics 20:741 (2024)

Neutral Laser Traps

Direct cooling

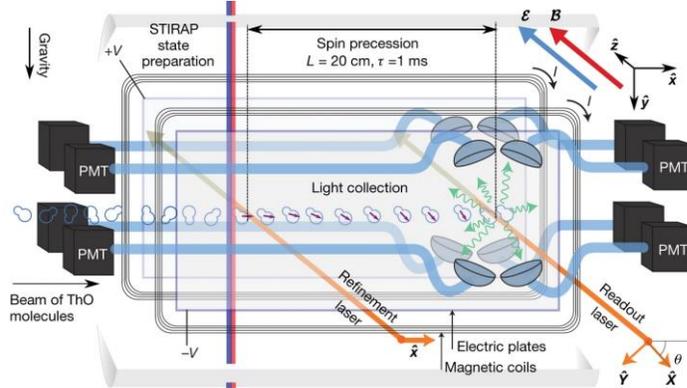


Ultracold assembly



- Direct: RaX (Ronald Ruiz, John Doyle, Nick Hutzler)
- Ultracold Assembly: FrAg (Dave DeMille)

Molecular Beams

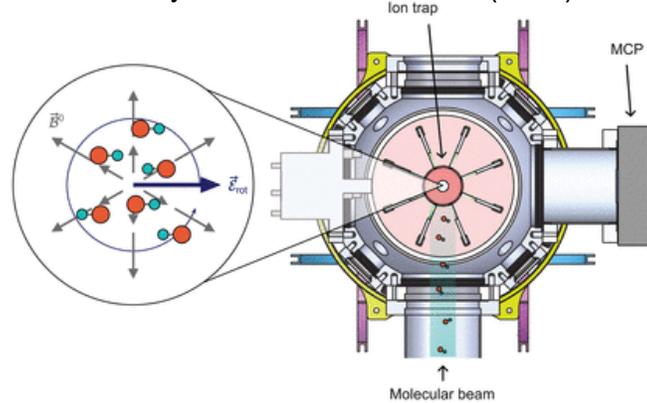


Panda (Harvard PhD Thesis, 2018)

- ACME (Xing Wu)
- CeNTREX (Dave DeMille)

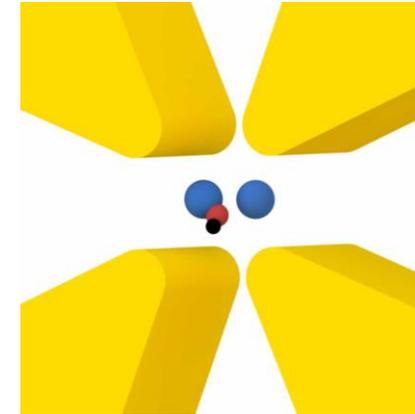
Ion Trapping

Roussy et al. Science 381:46 (2023)



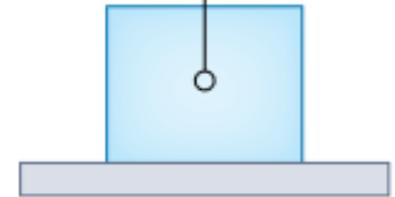
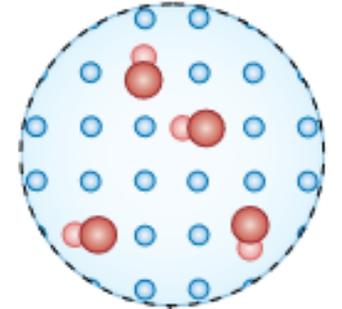
- Rotating Ion Trap: JILA Collaboration (Eric Cornell), Xing Fan, TRIUMF

Arrowsmith-Kron et al. Rep. Prog. In Phys. 87:084301 (2024)



- Quantum Logic Spectroscopy: Andrew Jayich

Embedding In Solids



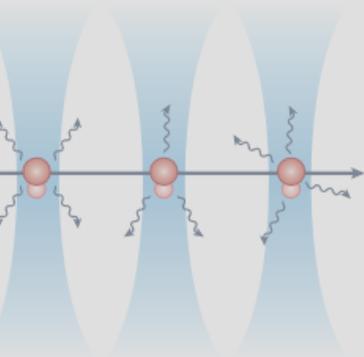
- EDM3: Amar Vutha, Eric Hessels, Jaideep Taggart Singh & Spinlab
- Optical crystals: Jaideep Taggart Singh

Contemporary techniques for EDM searches using molecules

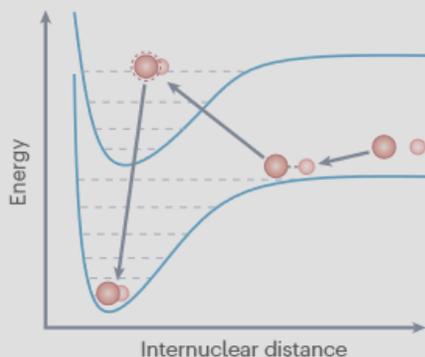
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Neutral Laser Traps

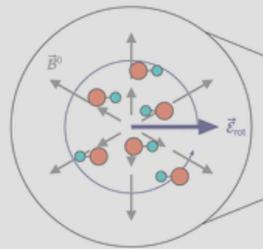
Direct cooling



Ultracold assembly



Roussy et al.



Rotating Ion
Collaboration
Xing Fan,

- Direct: RaX (Ronald Ruiz, John Doyle, Nick Hutzler)
- Ultracold Assembly: FrAg (Dave DeMille)

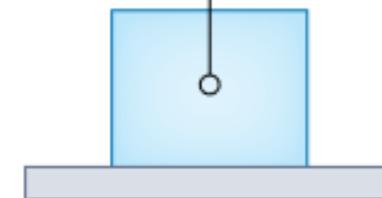
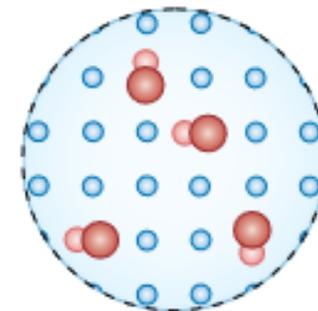
Opportunities

- High trapping efficiencies achievable
- Capable of trapping a wide variety of species
- Large number of molecules (10^{13}) can be trapped in a small volume (1mm^3)
- Stable, chemically inert confinement
- Optically transparent, growth techniques well established

Challenges

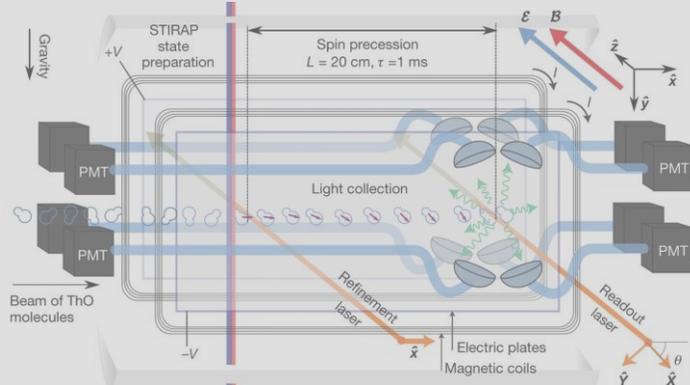
- High molecular production efficiency desired
- Pure molecular beam needed to ensure purity in medium
- Inhomogeneities and broad linewidths may obscure sensitivity

Embedding In Solids



- EDM3: Amar Vutha, Eric Hessels, Jaideep Taggart Singh & Spinlab
- Optical crystals: Jaideep Taggart Singh

Molecular Beams

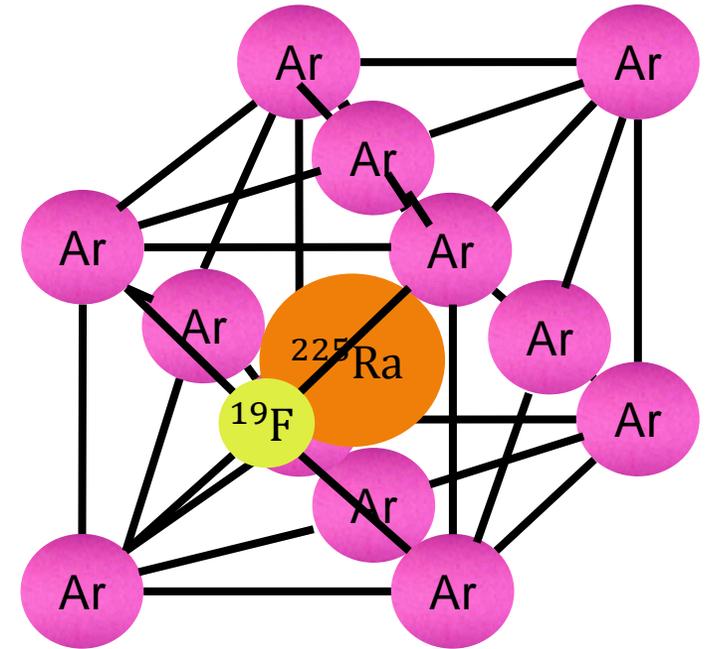


- ACME (Xing Wu & QuE)
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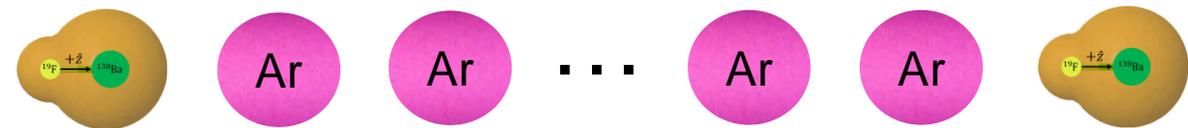
Panda (Harvard PhD Thesis, 2018)

Orientation locking with a noble gas matrix provides many advantages for molecular CP-violation searches

- Noble gas matrices lock orientation of certain guest polar molecules
 - Measured in BaF:Ne in Li et al, NJP 25, 082001 (2023)
 - Predicted for BaF:Ar in Vutha, Horbatsch, Hessels, PRA 98, 032513, (2018)
 - Don't need an externally applied electric field because the molecules have an internal one and are oriented by the matrix
 - Can use nearby molecules as comagnetometers
 - » Should help provide near-perfect electric field reversal
 - Possibility to control for systematic effects, such as
 - » Electric field stability
 - » Magnetic field stability
 - » Perfect reversal of electric and/or magnetic fields
- Noble gases are chemically inert
- Matrix is optically transparent, allowing for
 - use laser control of quantum state
 - fluorescence measurements
- Matrix isolates guest molecules, allowing for high density



Cartoon of ^{225}RaF embedded in an Argon matrix



Even at an enormous guest density of $10^{13}/\text{mm}$, there still will be many Argon atoms ($\sim 10^2$) separating guest molecules

Orientation locking of Barium Monofluoride molecules has been observed in Neon

- S J Li *et al*, *New J. Phys.* 25 082001 (2023)
- Observed clear evidence of orientation locking using a magnetic field to separate aligned and antialigned populations
- Also observed hyperfine structure in-medium using a combination of lasers and RF
- Observed smaller-than-expected shifts and broadening

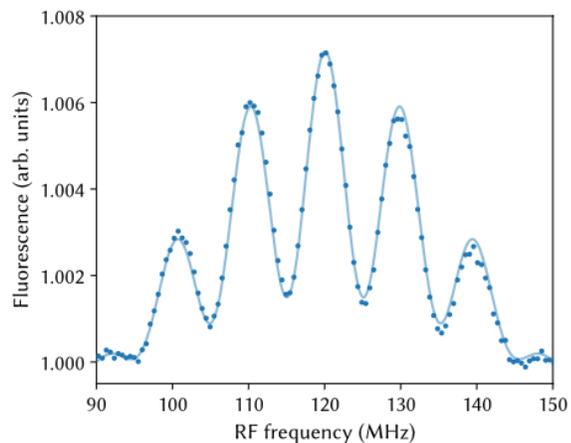


Figure 6. Optically-detected hyperfine line. For this measurement the σ_+ -polarized D1 laser was pulsed on and off at 20 kHz, and two 30-ns-long rf pulses with a separation of 100 ns were applied during the dark phase. The data points show how the fluorescence after the first optical pumping pulse revives due to the rf transition. The solid line is a fit to a Ramsey lineshape, which yields an uncertainty of 10 kHz in the resonance frequency of the hyperfine transition.

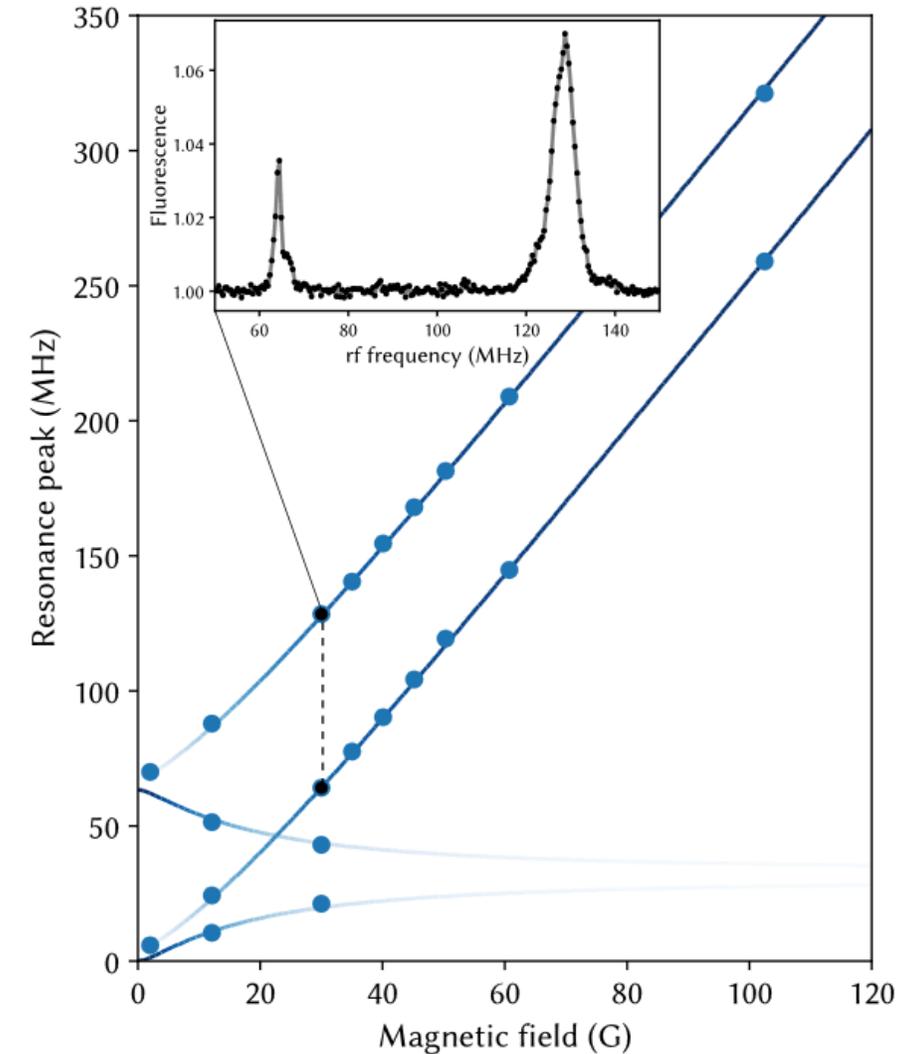


Figure 5. Resonances in the hyperfine spectrum for various values of the static B -field. Data points are the measured peak positions (uncertainties smaller than the symbol size). Lines through the data points are the calculated hyperfine transition frequencies for BaF molecules oriented parallel to the substrate, from the effective Hamiltonian described in the text. The boldness of the lines indicates the calculated transition strength. The inset shows a section of the optically-detected hyperfine spectrum at $B_z = 30$ G.

The EDM³ method

- Adapted from a technique developed for eEDM searches by our collaborators at York University and University of Toronto

Vutha, Horbatsch, Hessels, PRA 98, 032513, (2018)

- Aim to search for Nuclear Schiff moments
 - Sensitive to CP violation in nucleus
 - Using RaF, are also sensitive to eEDM
- Electric Dipole/Schiff moment searches
 - Measure difference of frequencies with internal electric field and magnetic field aligned and then anti-aligned
 - Change in precession frequency \propto CP violation
- Basic idea
 - Form radioactive molecules
 - Embed them in solid noble gas matrix
 - Use lasers and RF to initialize quantum state
 - Use laser induced fluorescence to read out quantum state

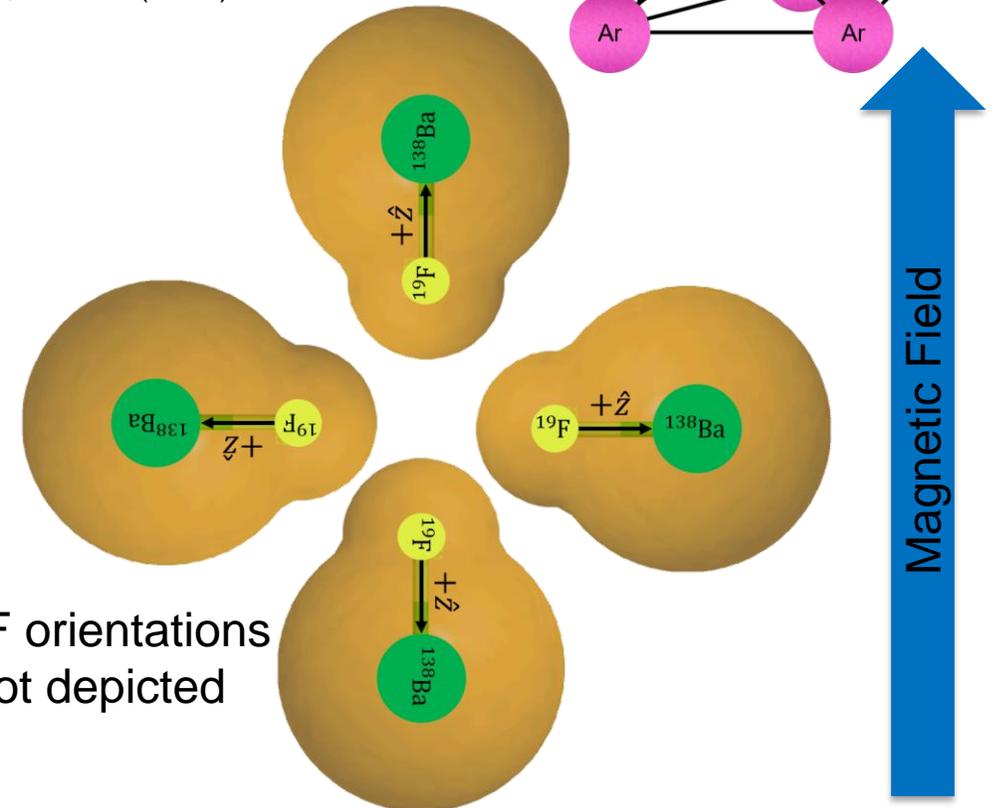
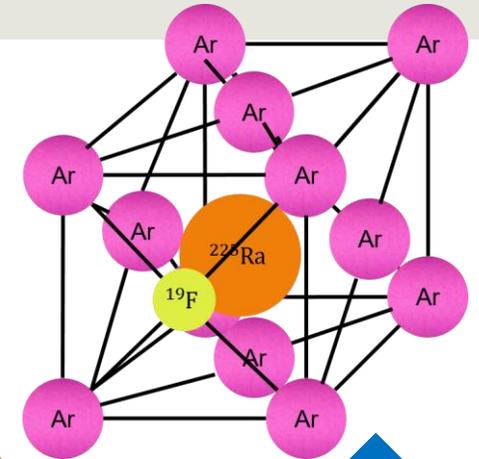
See also:

Singh, Hyp Int 240, 29 (2019)

Koyanagi *et al* JMS 391, 111736 (2023)

Ramachandran *et al*, PRA 108, 012819 (2023)

Li *et al* NJP 25, 082001 (2023)

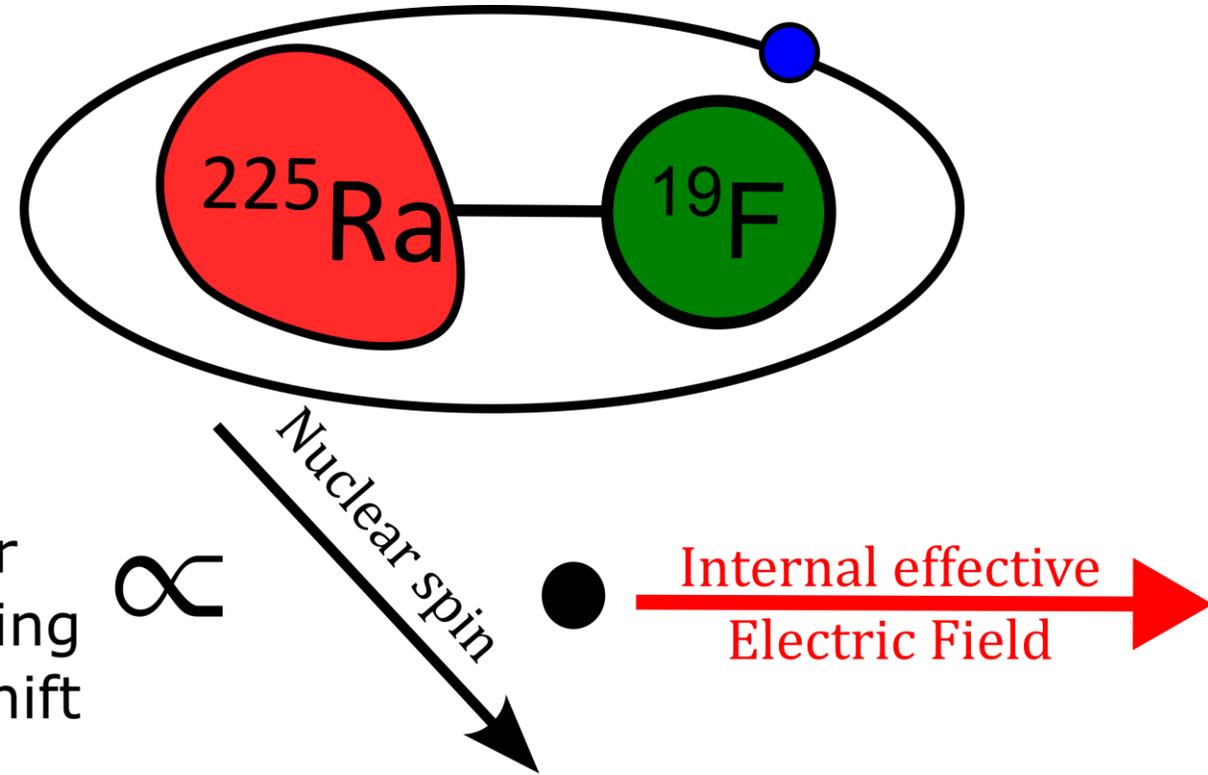


BaF/RaF orientations
(in/out not depicted
here)

These images of molecules were generated using jmol: <https://www.jmol.org/>

The CP-violating shift produced by a nuclear Schiff moment

- Recap: a nuclear Schiff moment can induce CP-violating energy shifts between pairs of states
- We need to know what pairs of molecular states have the largest CP-violating energy shifts
- What parts of the quantum state are most relevant?
- This shift involves:
 - Nuclear spin \rightarrow hyperfine structure
 - The internal effective electric field: this points along the intramolecular axis, which defines the molecular orientation \rightarrow rotational structure
- Thus we need to investigate the rotational-hyperfine structure of ^{225}RaF embedded in medium

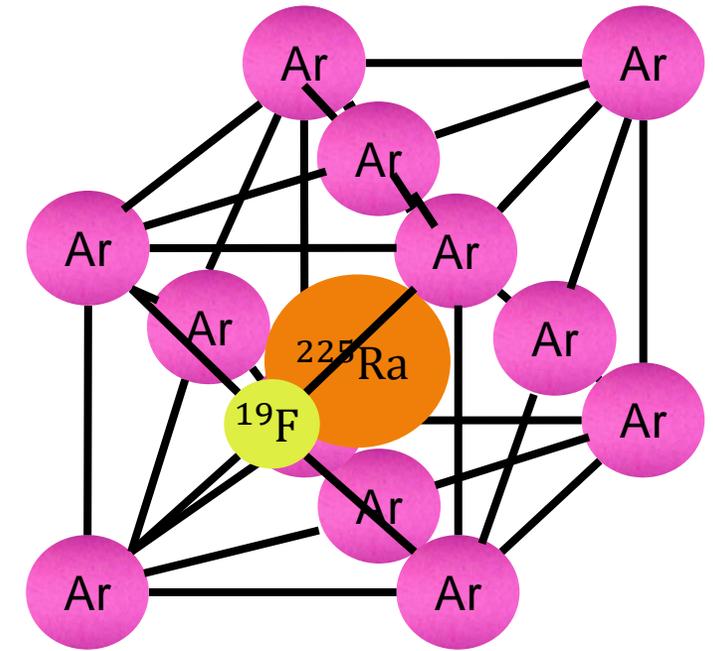


Nuclear
CP-violating
energy shift

Calculating the Rotational-Hyperfine Structure of ^{225}RaF and ^{138}BaF

$$\underbrace{H(N, J, F_1, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{\text{rot}}(N, J) + H_{\text{hfs}}(\vec{I}_{\text{Ra}}, \vec{I}_{\text{F}}, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{\text{stk}}(N, J, F_1, F, M_F, E_{\text{lab}})}_{\text{External Field}} + \underbrace{H_{\text{Dev}}(N, J, F_1, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}} + \underbrace{H_{\text{CPV}}}_{\text{CP-violating physics}}$$

- Recap: need to calculate the rotational-hyperfine structure of ^{225}RaF in-medium
- “That’s easy”™, right, “Just”:
 - Write down the analytic form of each term
 - Compute the matrix elements of Hamiltonian/relevant operators
 - Numerically diagonalize the Hamiltonian to get the energy eigenstates
 - Evaluate energy differences and matrix elements of interest

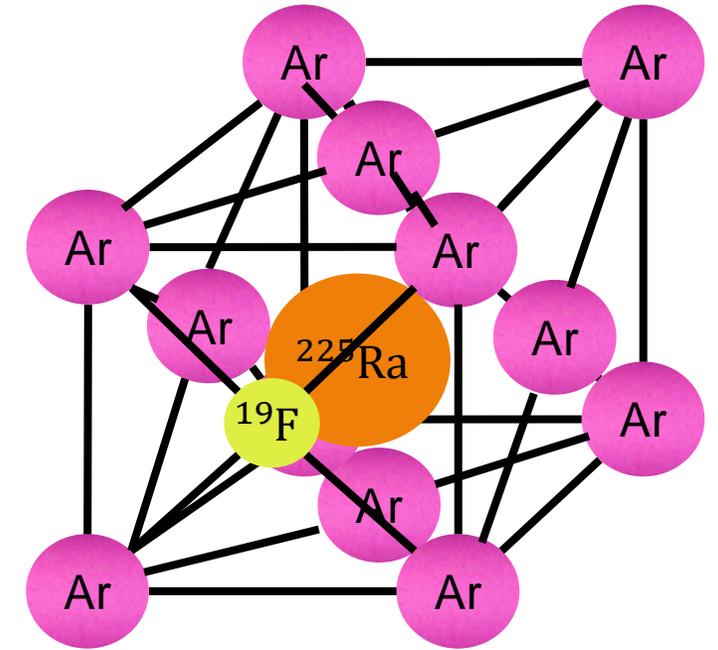


Cartoon of ^{225}RaF embedded in an Argon matrix

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 - Also, needed to write my own code: DOI [10.5281/zenodo.14037068](https://doi.org/10.5281/zenodo.14037068)

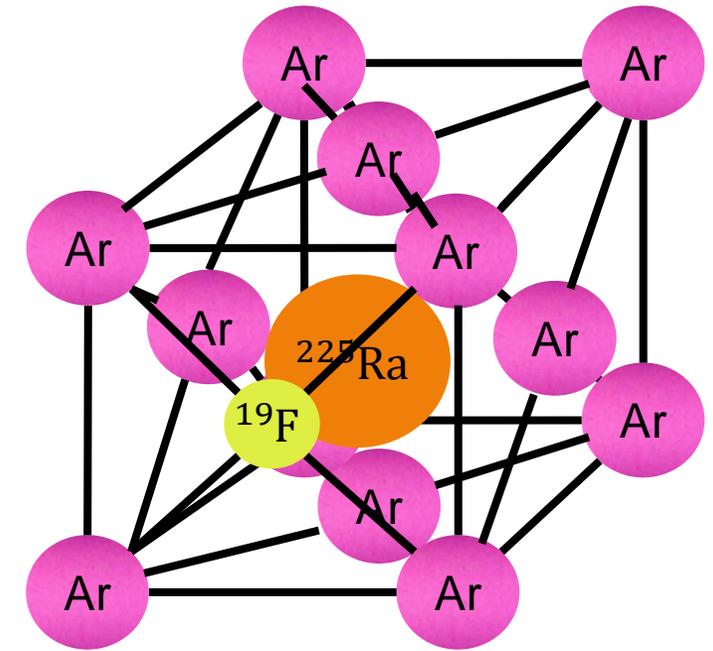


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- Also, the first measurements of ^{225}RaF ’s hyperfine structure in vacuum were published a little over a year and a half ago (after we started this)
Wilkins et al. arXiv:2311.04121 (2023)

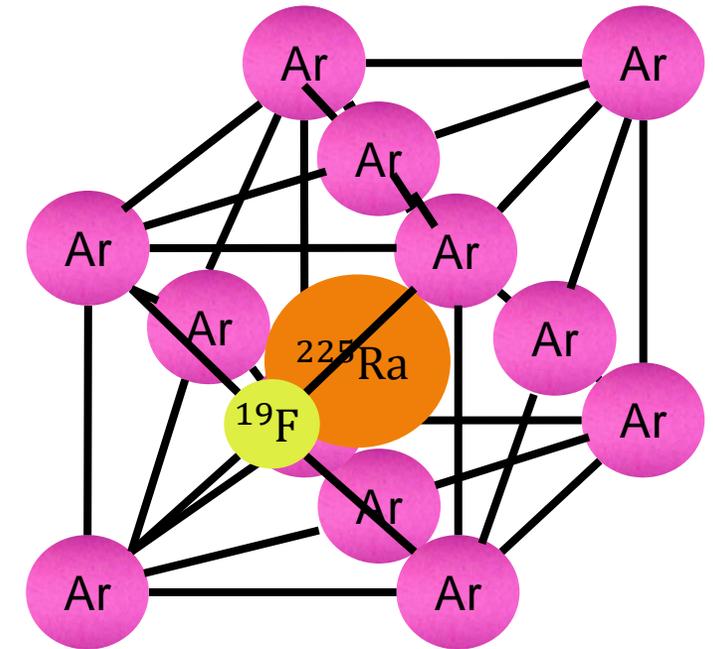


Cartoon of ^{225}RaF embedded in an Argon matrix

Calculating the Rotational-Hyperfine Structure of ^{225}RaF and ^{138}BaF

$$\underbrace{H(N, J, F_1, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{\text{rot}}(N, J) + H_{\text{hfs}}(\vec{I}_{\text{Ra}}, \vec{I}_{\text{F}}, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{\text{stk}}(N, J, F_1, F, M_F, E_{\text{lab}})}_{\text{External Field}} + \underbrace{H_{\text{Dev}}(N, J, F_1, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}} + \underbrace{H_{\text{CPV}}}_{\text{CP-violating physics}}$$

- Recap: need to calculate the rotational-hyperfine structure of ^{225}RaF in-medium
- “That’s easy”™, right, “Just”:
 - Write down the analytic form of each term
 - Compute the matrix elements of Hamiltonian/relevant operators
 - Numerically diagonalize the Hamiltonian to get the energy eigenstates
 - Evaluate energy differences and matrix elements of interest
- Actually somewhat complicated:
 - Also, needed to write my own code: DOI [10.5281/zenodo.14037068](https://doi.org/10.5281/zenodo.14037068)
- Also, the first measurements of ^{225}RaF ’s hyperfine structure in vacuum were published a little over a year and a half ago (after we started this)
Wilkins et al. arXiv:2311.04121 (2023)
- For these reasons, decided to start with a chemically similar but simpler molecule ^{138}BaF
 - Hyperfine structure known both in vacuum (Ruzlewicz et al. Chem. Phys. 71:389 (1982)) and in-medium (Vutha et al. Phys. Rev. A 98:032513 (2018) – our collaborators)

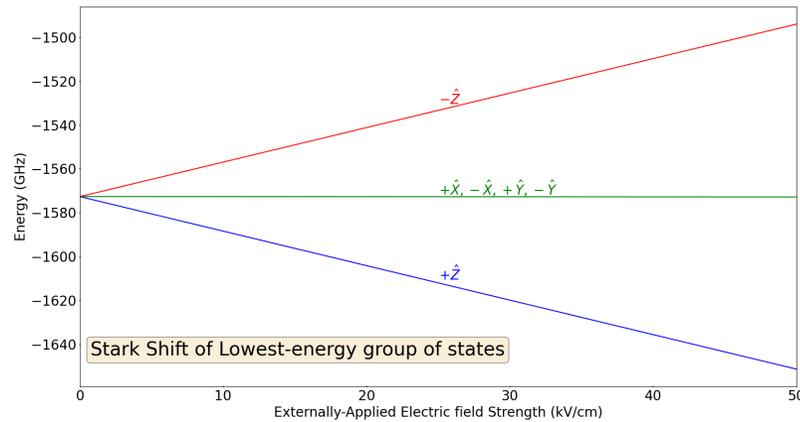


Cartoon of ^{225}RaF embedded in an Argon matrix

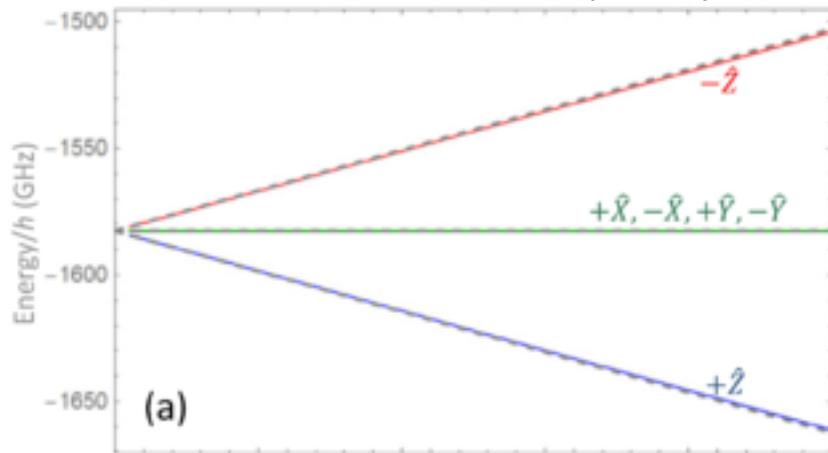
Calculated stark shift of molecules embedded in solid matches the literature

$$\underbrace{H(N, J, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{rot}(N, J) + H_{hfs}(\vec{I}_F, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{Stk}(N, J, F, M_F, \vec{E}_{lab})}_{\text{External Field}} + \underbrace{H_{Dev}(N, J, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}}$$

This work



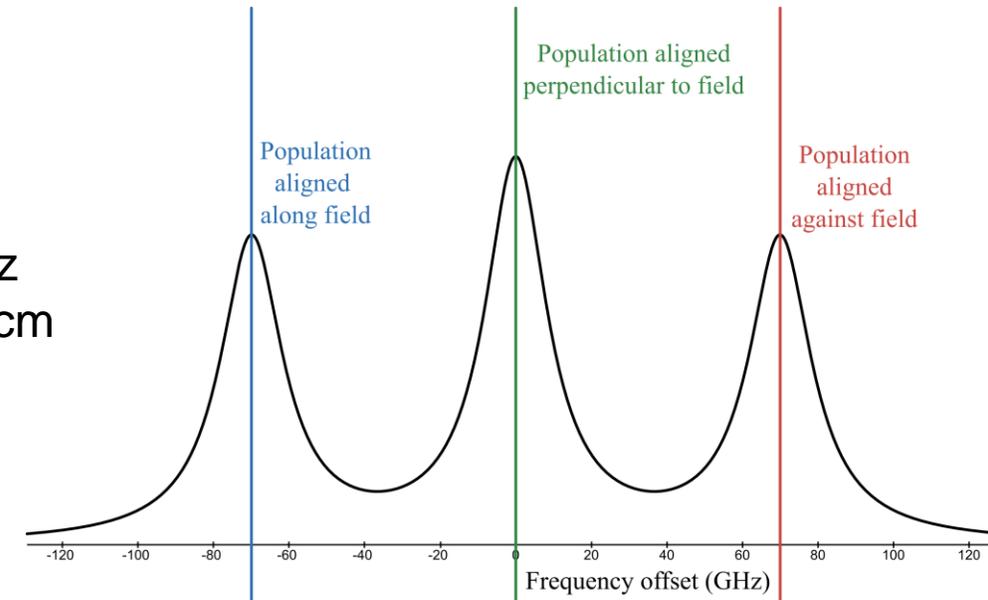
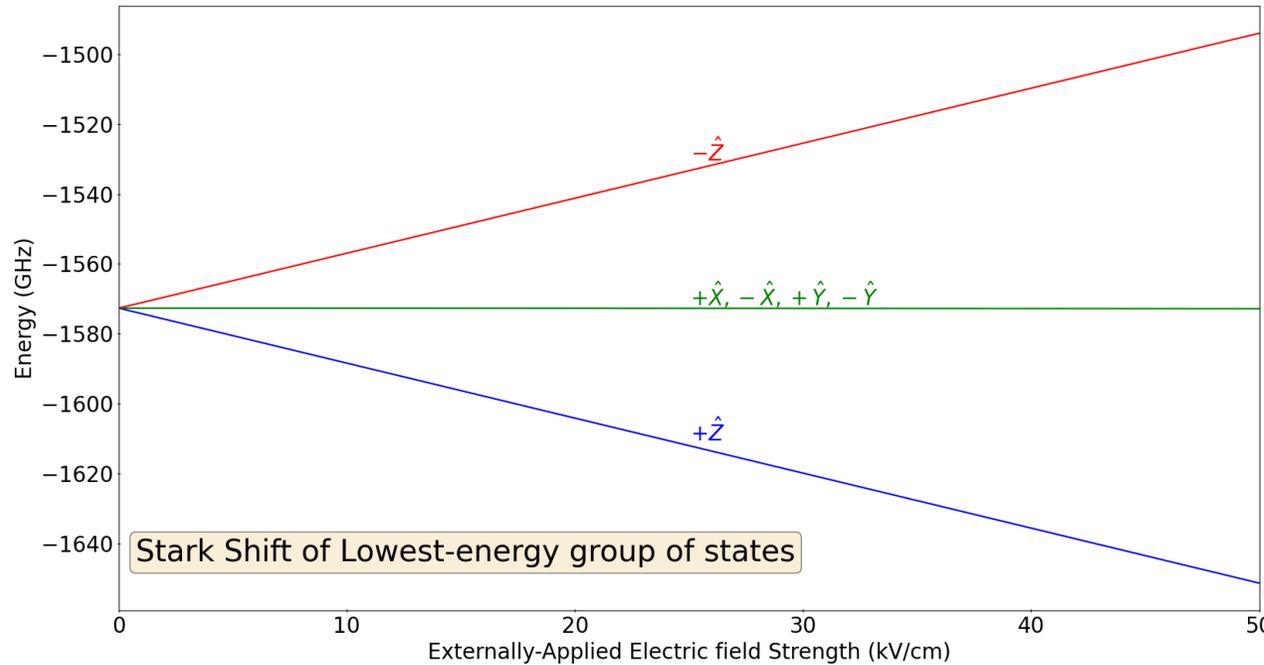
PRA 98, 032513 (2018)



- Can use an externally-applied electric field to spectroscopically distinguish 3 populations
 - Oriented along field
 - Oriented against field
 - Oriented perpendicular to field
- States oriented along/against field → possible science states
- States oriented perpendicular to field → may be useful in controlling systematics
- Orientations have been verified by calculating the expectation value of the axis pointing from F to Ba

The presence of multiple ensembles offers possibilities for control over systematics

$$\underbrace{H(N, J, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{rot}(N, J) + H_{hfs}(\vec{I}_F, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{Stk}(N, J, F, M_F, \vec{E}_{lab})}_{\text{External Field}} + \underbrace{H_{Dev}(N, J, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}}$$

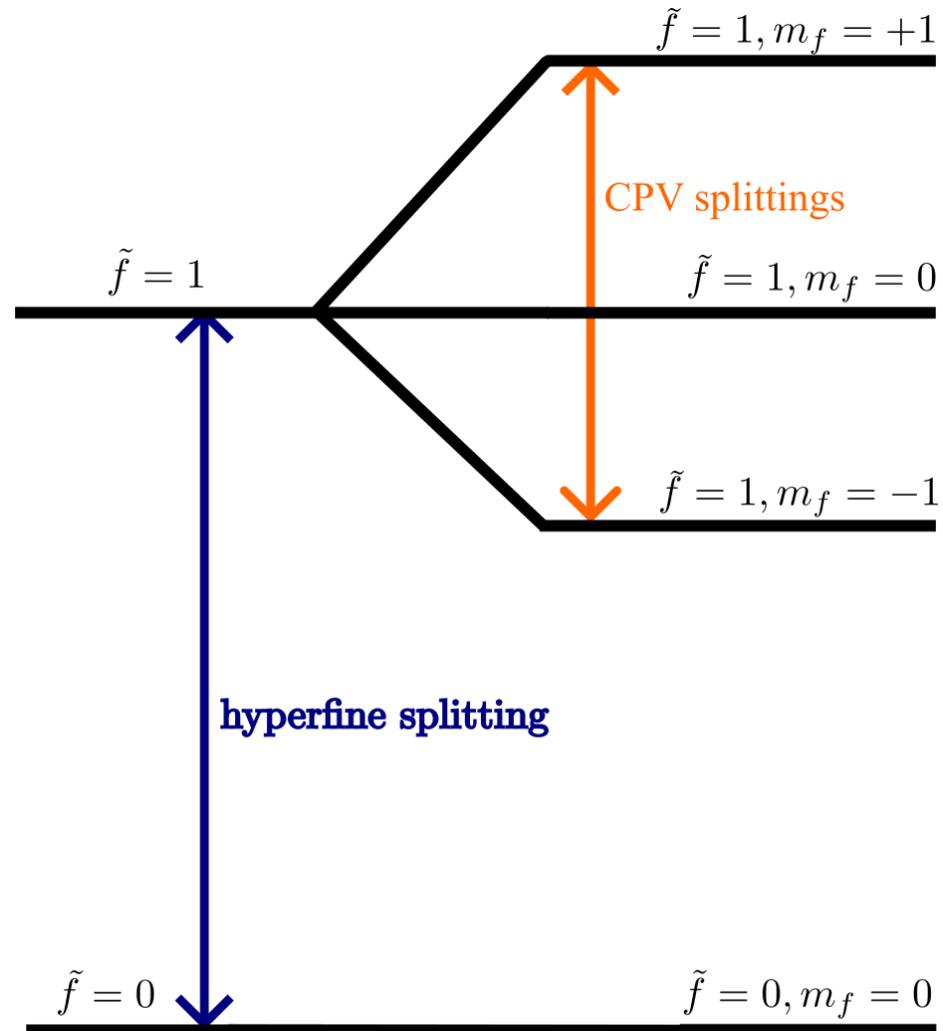


■ Caveats:

- Want single crystal
 - » In polycrystalline material, crystal axes of various grains will not be aligned

Calculations show a nonzero CP-violating energy shift along the Z-axis

$$\underbrace{H(N, J, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{rot}(N, J) + H_{hfs}(\vec{I}_F, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{Stk}(N, J, F, M_F, \vec{E}_{lab})}_{\text{External Field}} + \underbrace{H_{Dev}(N, J, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}} + \underbrace{H_{CPV}}_{\text{CP-violating physics}}$$

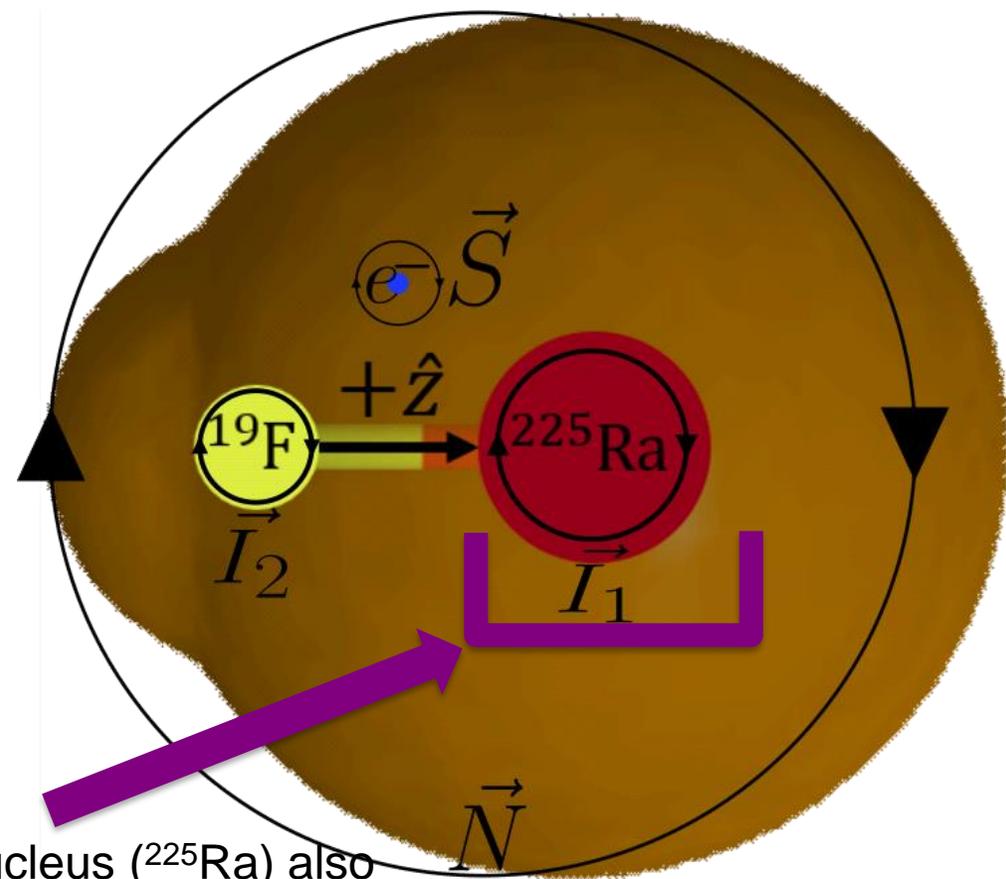


- We want the CP-violating energy shifts
 - Write down and evaluate the CP-violating part of the Hamiltonian
- Since H_{CPV} is very small, use perturbation theory to evaluate it
 - There are technical complications
- Gas-phase: reproduces known splitting patterns (see e.g.: Nature 473, 493-496 (2011))
- Embedded in medium: confirms expectations of PRA 98, 032513 (2018)
 - This confirms that there are states aligned and anti-aligned with the Z-axis that have a nonzero CP-violating relative energy shift
 - Possible science states

Extension to molecules with hyperfine structure on the heavy nucleus (e.g. ^{225}RaF)

$$\underbrace{H(N, J, F, M_F)}_{\text{Molecular Hamiltonian}} = \underbrace{H_{\text{rot}}(N, J) + H_{\text{hfs}}(\vec{I}_F, \vec{S})}_{\text{Intrinsic to Molecule}} + \underbrace{H_{\text{stk}}(N, J, F, M_F, E_{\text{lab}})}_{\text{External Field}} + \underbrace{H_{\text{Dev}}(N, J, F, M_F)}_{\text{Model of matrix effects (Devonshire potential)}} + \underbrace{H_{\text{CPV}}}_{\text{CP-violating physics}} + \underbrace{H_{\text{heavy}}}_{\text{Modifications for nuclear spin of heavy atom}}$$

- ^{225}Ra has a nonzero nuclear spin
- Structure of ^{225}RaF is very similar to ^{138}BaF with extra terms as a result of ^{225}Ra 's having a nuclear spin
 - Form of extra terms well known, for example, see Chem Phys 71, 389 (1982)
- Extra terms include
 - Hyperfine structure of ^{225}Ra
 - Interaction between ^{225}Ra and ^{19}F nuclear spins
 - Nuclear Schiff moment of ^{225}Ra
- Coefficients not well known
 - First measurements made recently: [Nature Physics 20, 202 \(2024\)](#)
- Extension of the existing codebase is nearly complete – in process of verifying additions



The heavy nucleus (^{225}Ra) also has hyperfine structure here

Summary / Future Goals

- EDM³ method holds great promise for precision BSM searches
 - Large density of guest molecules (up to $\sim 10^{13}/\text{mm}^3$)
 - Large effective E-field $\sim 300\times$ lab fields
 - Orientation locking, if realized, suppresses systematic effects and allows for co-magnetometry
- Near Future:
 - Finish extension of rohyperfine structure calculations to molecules with nuclear spin on both atoms (e.g. ^{225}RaF)
 - Finalize design of and construct nanoelectrospray source
- Perform spectroscopy needed to develop measurement scheme
 - Need details on how the noble gas matrix affects guest molecule energy levels
 - Need to experimentally verify orientation-locking of guest molecules in RaF:Ar



Special thanks to:

Jochen Ballof, Sebastian Miki-Silva, Oscar Naviliat Cuncic, Tom-Erik Haugen, Mia Au, Peyton Lalain, Sebastian Rothe, Ben Arend, Brandon Ewert, Patrick Glennon, Eric Hessels, Greg Koyanagi, David Leimbach, Ryan Ringle, Stefan Schwarz, Amar Vutha

Spinlab @ MSU: Yousuf Alishan, Gordon Arrowsmith-Kron, Aiden Boyer, Rashawn Carter, Aesen Copeland, Myles Daugherty, Lindsey Hickman, Nick Koester, Tanusree Makwana, Graham Malone, Skylar Milne, Nicholas Nusgart, Jaideep Taggart Singh, Erin White

... and to our collaborators

at CERN, York University and University of Toronto





BACKUP SLIDES



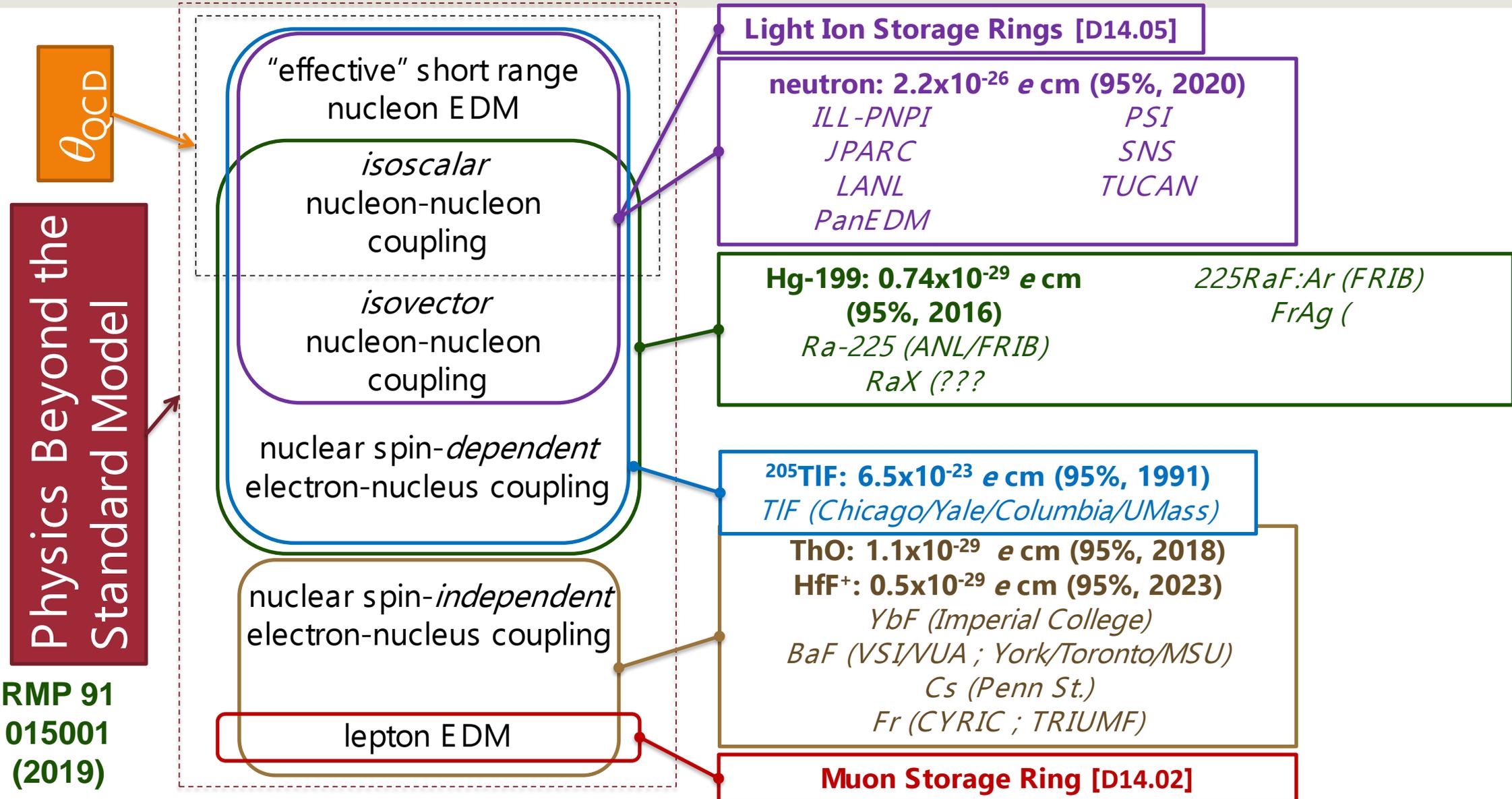
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of **ENERGY** | Office of
Science

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Nuclear Physics and used resources of the Facility for Rare Isotope Beams (FRIB) Operations, which is a DOE Office of Science User Facility under Award Number DE-SC0023633.

Different Sources of Violation of EDM of Different Systems



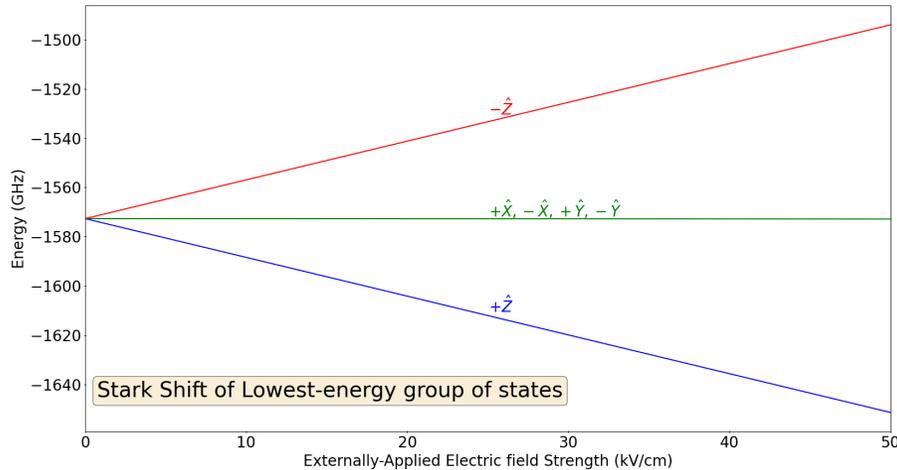
Physics Beyond the Standard Model

θ_{QCD}

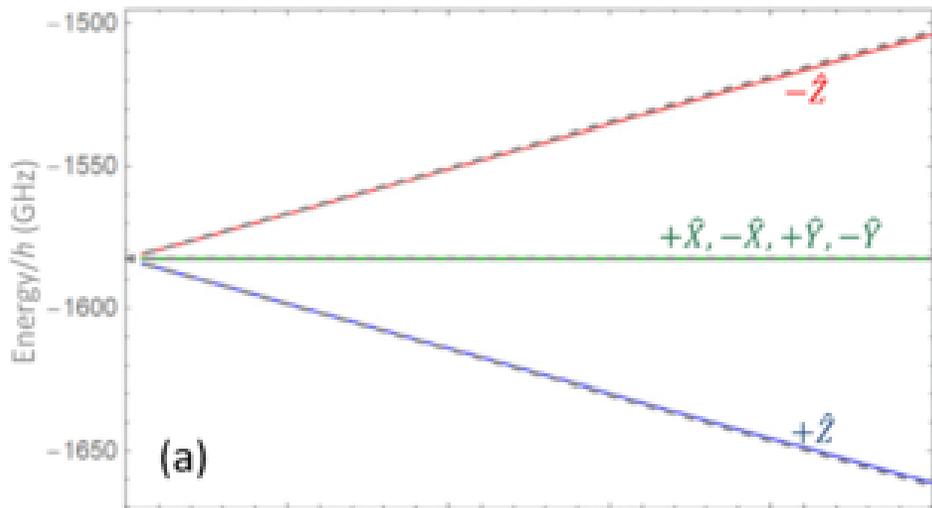
RMP 91
015001
(2019)

Our results for ^{138}BaF in-medium match prior literature

Our work



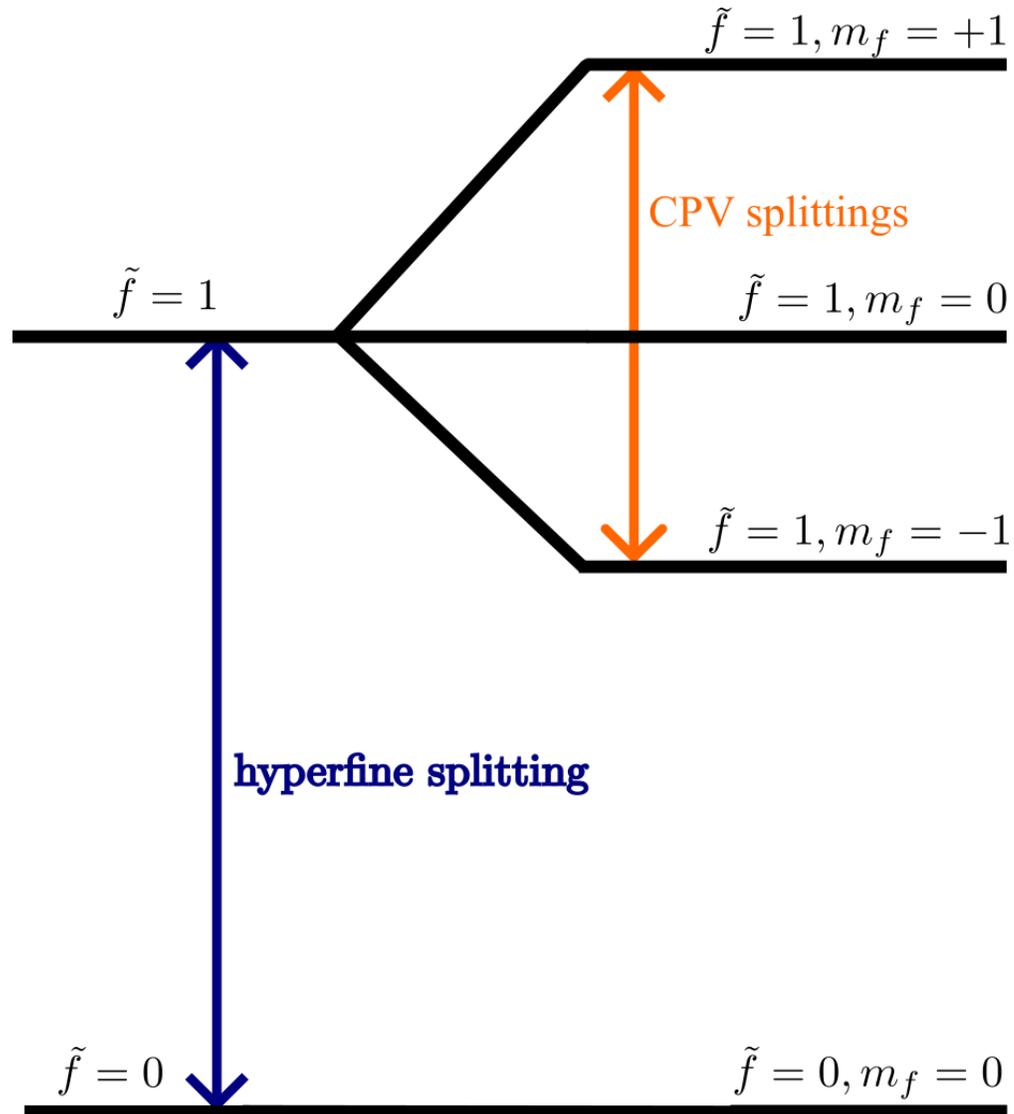
PRA 98, 032513 (2018)



- Can use an externally-applied electric field to spectroscopically distinguish 3 populations
 - Oriented along field
 - Oriented against field
 - Oriented perpendicular to field
- This corresponds to “orientation locking”
 - The noble gas matrix holds the orientation of certain guest molecules fixed
 - Allows one to omit the externally-applied electric field during the spin precession phase
- States oriented along/against field → possible science states
 - Some of states these have CP-violating energy shifts
- States oriented perpendicular to field → may be useful in controlling systematics
 - These don't have CP-violating energy shifts

Calculations of the CP-violating energy shifts in ^{138}BaF

In-medium example CP-violating energy shifts



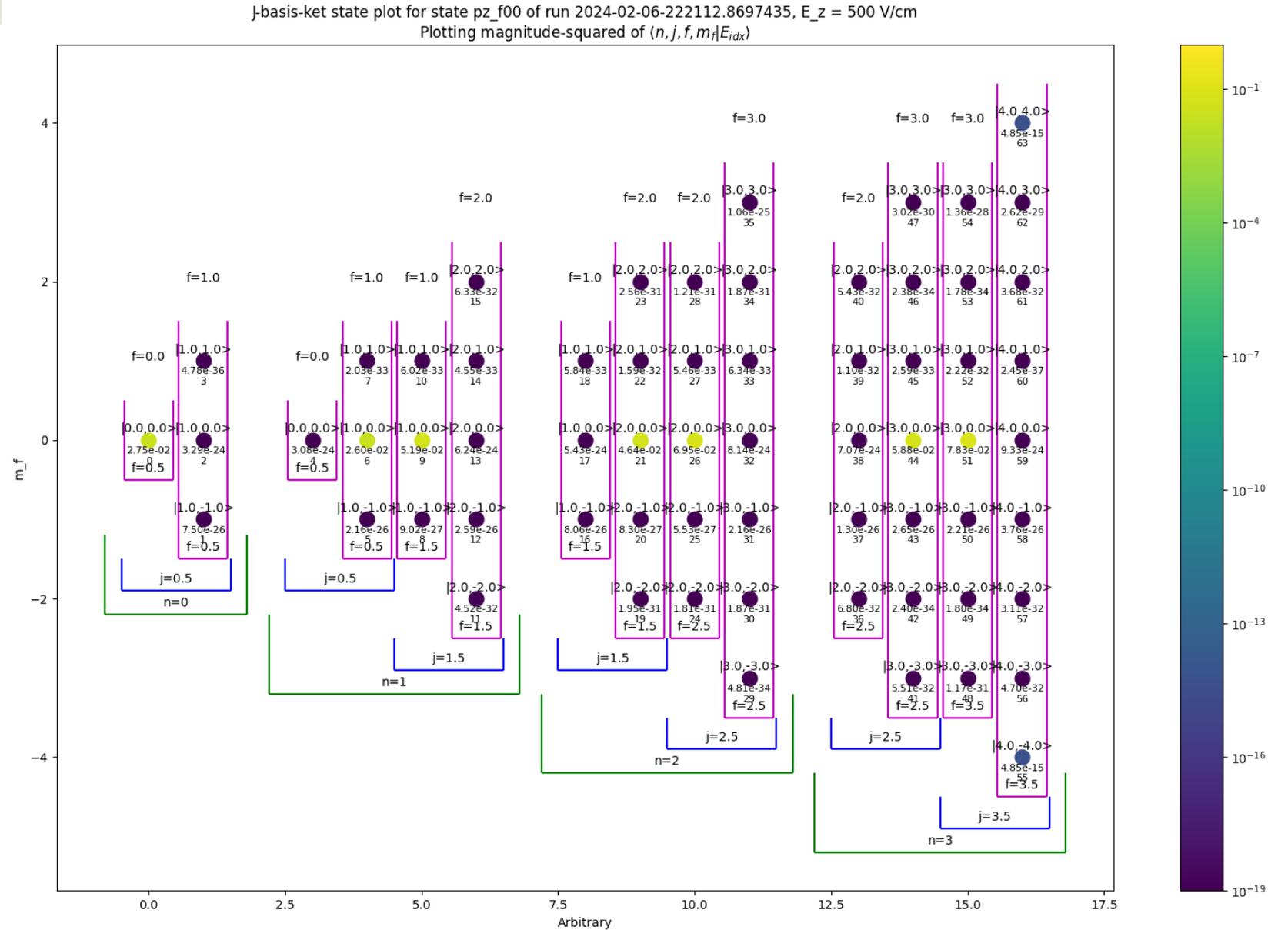
- Have also directly calculated shifts proportional to the CP-violating energy shifts
 - We don't know the BSM CP-violating physics, so we can't calculate the exact size of the shifts
- Calculate the shifts using perturbation theory
- Gas-phase: reproduces known splitting patterns (see Hudson et al. Nature 473:493 (2011))
- Embedded in medium: confirms expectations of Vutha *et al.* Phys. Rev. A 98:032513 (2018)
 - This confirms that there are states aligned and anti-aligned with the Z-axis that have a nonzero CP-violating relative energy shift
 - Possible science states

225RaF code test plan

- Critical note: this code will work for any molecule sufficiently similar to 225RaF – any molecule that:
 - Is a diatomic molecule with ground state $X^2\Sigma^+$
 - » i.e. with exactly one unpaired electron and no net electronic orbital angular momentum
 - And doesn't have any nuclear spin $> \frac{1}{2}$
 - But, the Hund's case *does not* need to match
- Phase 1: matching the ^{138}BaF code
 - Set coefficients of terms involving heavy nuclear spin to 0
 - Then set the rest of the coefficients to match ^{138}BaF
 - Results should be the same as the 138BaF code
- Phase 2: testing the new additions
 - Unfortunately, no stable Ba isotope has $I=\frac{1}{2}$ → can't compare with data
 - ^{171}Yb is stable, has $I=\frac{1}{2}$, and ^{171}YbF 's rotational structure is known (Glassman et al, JMS 300, 7-11 (2014))
- Then, since code should work for any sufficiently similar molecule, set coeffs to match look at ^{171}YbF

J-Basis plot

- This is essentially a plot of what j-basis states make up



“ H_{heavy} ” – modifications to the molecular hamiltonian

- H_{heavy} includes both new terms, and a few modifications to existing terms

$$H(N, J, F_1, F, M_F) = H_{\text{rot}}(N, J) + H_{\text{hfs}}(N, J, F_1, F) + H_{\text{Stk}}(N, J, F, F, M_F) + H_{\text{Dev}}(N, J, F_1, F, M_F)$$

$$H_{\text{rot}} = B\vec{N}^2 - D\vec{N}^4 + \gamma\vec{N} \cdot \vec{S} + \delta\vec{N}^2 \vec{N} \cdot \vec{S}$$

$$H_{\text{hfs}} = b_{225}{}_{Ra} \vec{I}_1 \cdot \vec{S} + b_{19}{}_F \vec{I}_1 \cdot \vec{S} + c_{Ra} I_{1,z} S_z + c_F I_{2,z} S_z + c_I \vec{I}_1 \cdot \vec{I}_2 + \dots$$

$$H_{\text{Stk}} = -m\vec{u}_E \cdot \vec{E}_{\text{ext}} = -\mu_E \varepsilon_Z \cos(\theta)$$

$$H_{\text{Zeeman}} = -m\vec{u}_B \cdot \vec{B} = -\mu_S \vec{S} \cdot \vec{B} - \mu_{Ra} \vec{I}_1 \cdot \vec{B} - \mu_F \vec{I}_2 \cdot \vec{B} - \mu_R \vec{N} \cdot \vec{B}$$

$$H_{\text{Dev}} = -\frac{K}{3} \left[\sqrt{\frac{10}{7}} (\mathbf{T}_4^4 + \mathbf{T}_{-4}^4) + \sqrt{4\pi} \mathbf{T}_0^4 \right]$$

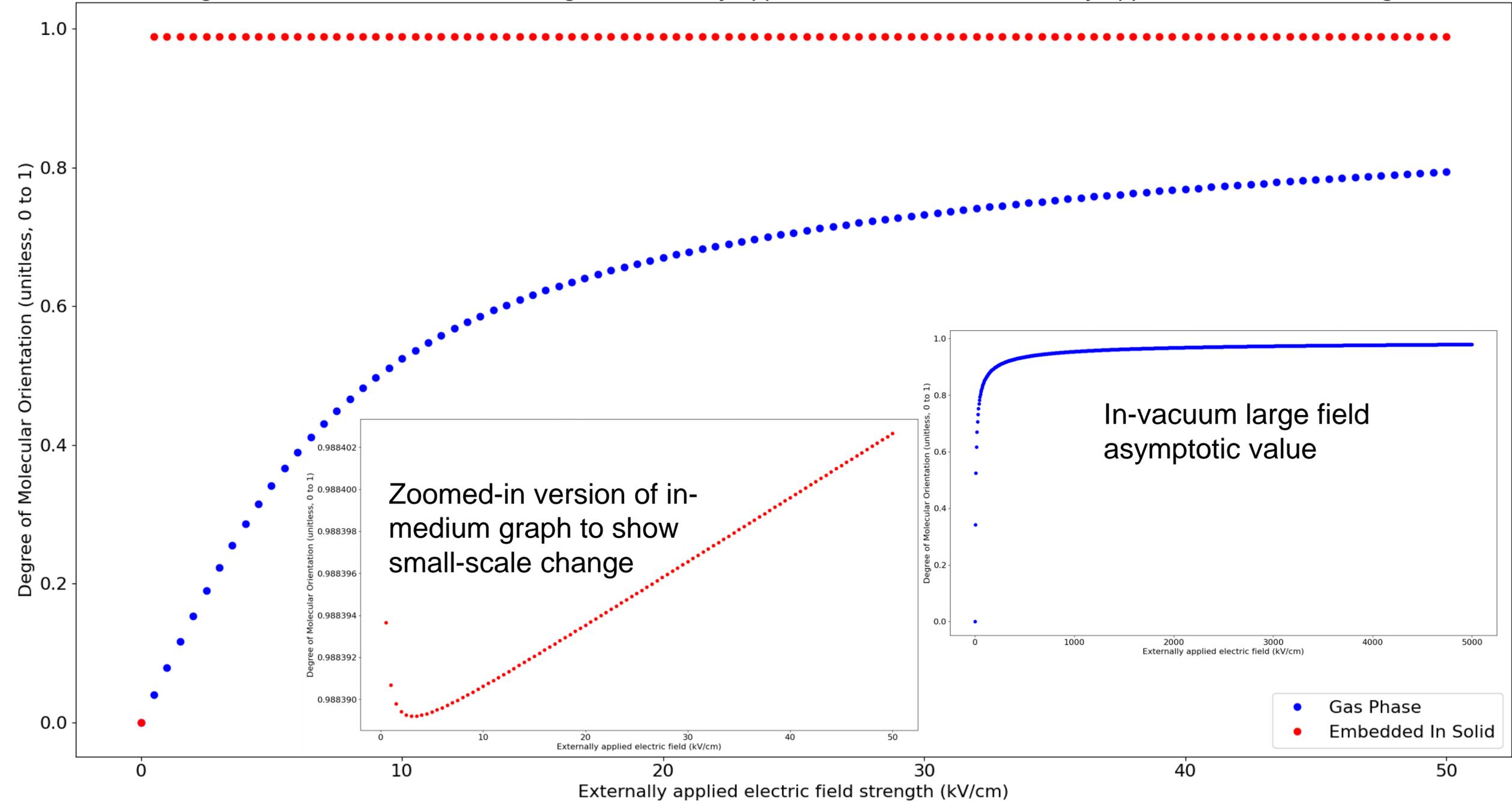
- For detailed matrix elements:

- Rotation: $E_{\text{rot}} = Bn(n+1) - D(n(n+1))^2 + (\gamma + \delta n(n+1)) \frac{j(j+1) - n(n+1) - s(s+1)}{2}$

- HFS: see Chem Phys 71, 389 (1982)

- Stark, Zeeman, Devonshire: See Brown, Carrington, *Rotational Spectroscopy of Diatomic Molecules*, Cambridge Molecular Science (Cambridge University Press, 2003) for details

Degree of Molecular Orientation along the externally-applied electric field vs Externally-applied electric field strength

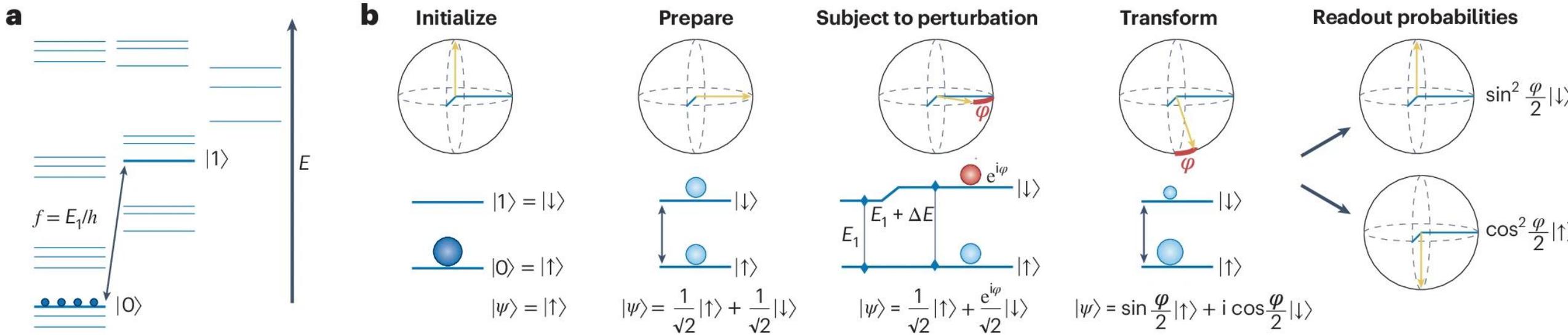


Calculating the CP-violating energy shifts

- Two basic kinds of CP-violating effects are relevant here
 - electron Electric Dipole Moment (eEDM)
 - » Also includes unpolarized CP-violating nucleus-electron interactions
 - Nuclear Schiff Moment
 - » Also includes polarized CP-violating nucleus-electron interactions
 - Note: can only calculate operators proportional to the “true” energy shifts because the un
- ^{138}BaF CP-violating effects
 - Electron-EDM-type:  Implemented
 - » Dominant CP-violating effect in ^{138}BaF
 - NSM of ^{19}F →  Implemented
 - » Negligible because of low Z and no enhancement
 - » Enables use to control for systematic effects
 - ^{138}Ba doesn't have an NSM because it has zero nuclear spin
- ^{225}RaF
 - Has the same CP-violating operators
 - » code is in progress
 - Also has ^{225}Ra 's NSM – relatively large because of large Z and enhancement factor
 - » This is the desired measurable
 - » Code also in-progress

Precision Measurement with Molecules

Nat Phys 20, 741-749 (2024)



■ “Always measure frequency”

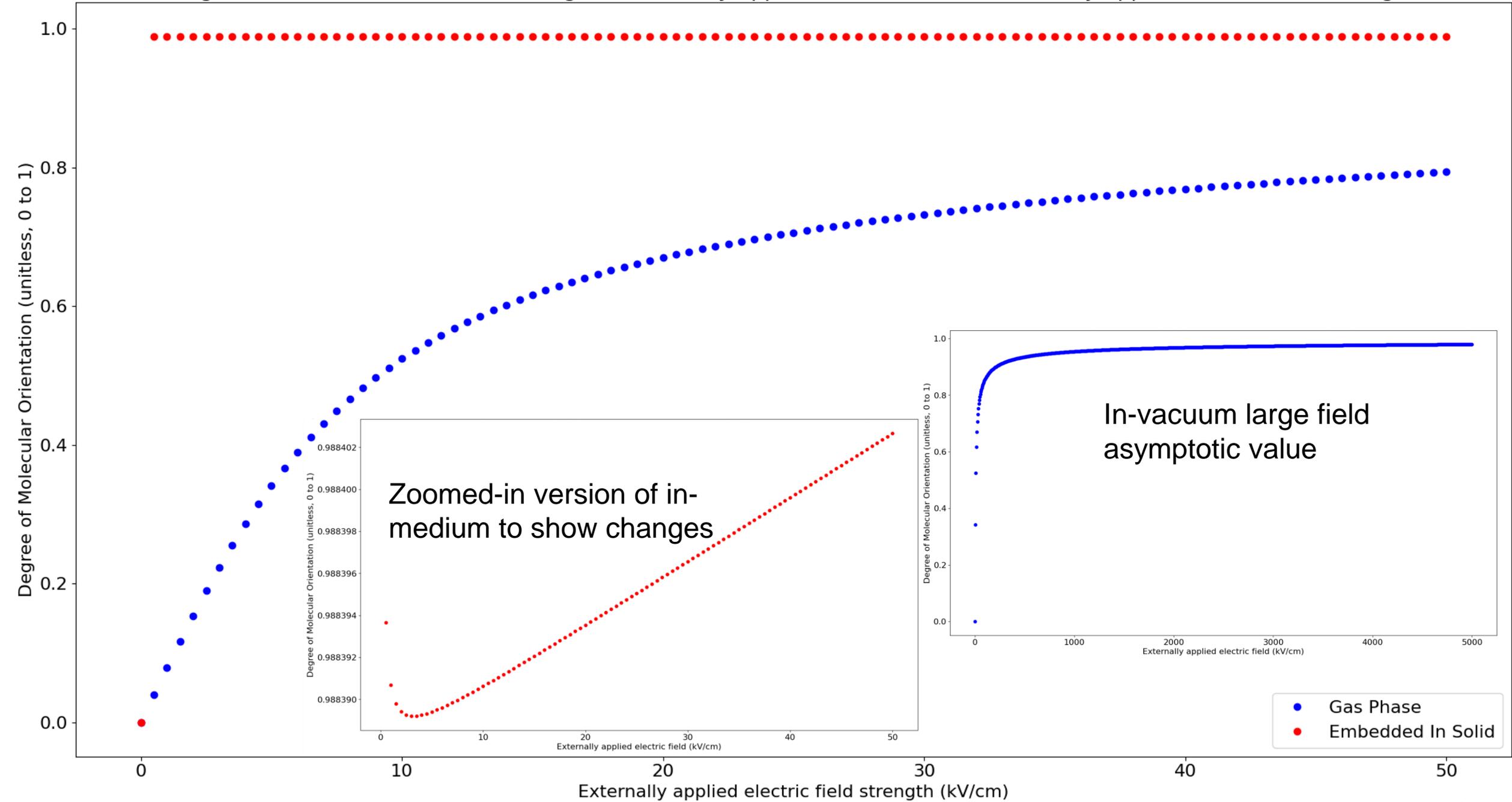
■ Want to find transitions whose frequency/energy difference depends on the observable of interest

■ The large number of states molecules offer often enable greater control of systematics

- Classic example: lambda-doublets as co-magnetometers

- Also, small energy splittings can greatly enhance sensitivity to desired observables

Degree of Molecular Orientation along the externally-applied electric field vs Externally-applied electric field strength

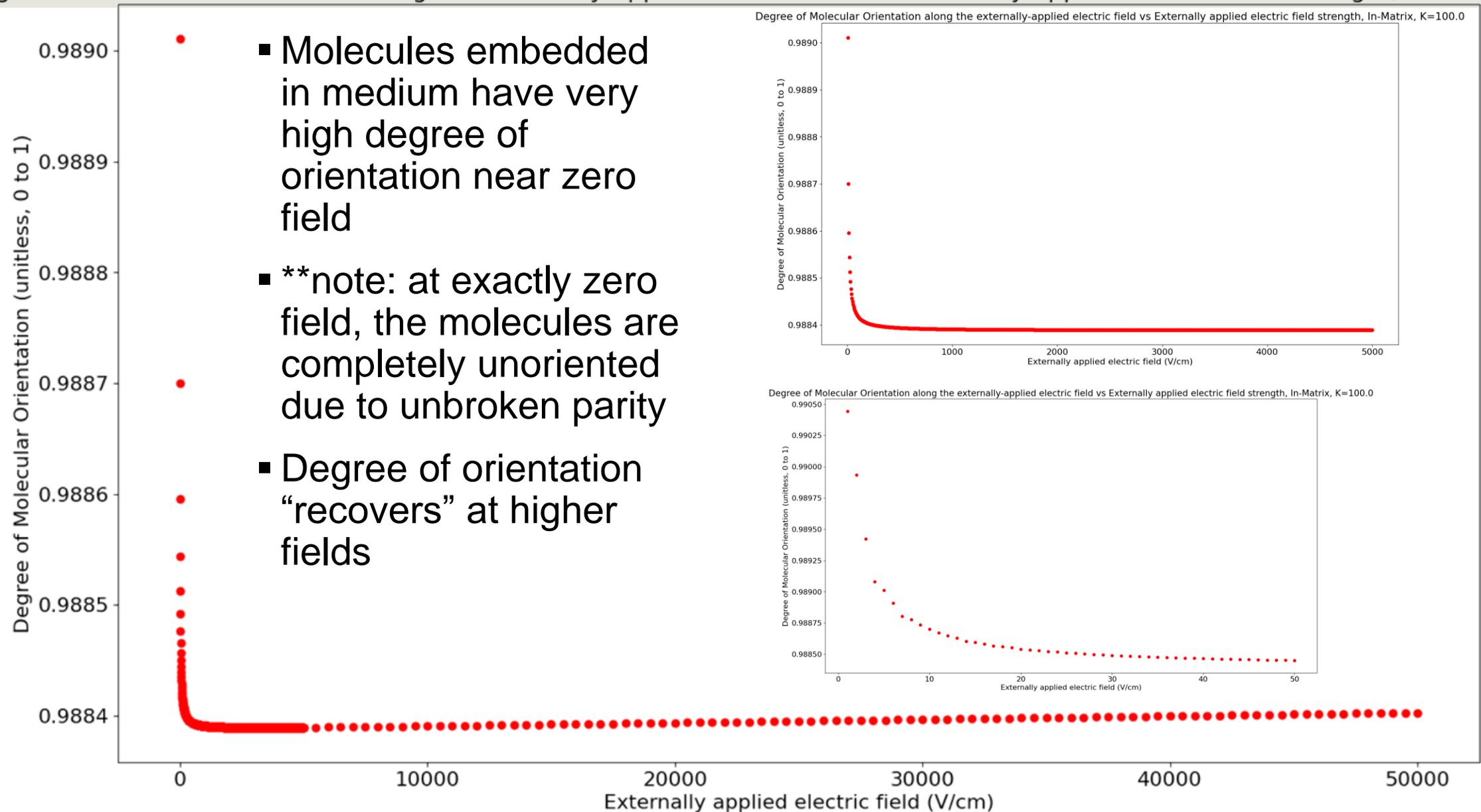


Extension to calculating CP-violating effects

- Two basic kinds of CP-violating effects relevant here
 - electron Electric Dipole Moment (eEDM)
 - » Also includes unpolarized CP-violating nucleus-electron interactions
 - Nuclear Schiff Moment
 - » Also includes polarized CP-violating nucleus-electron interactions
- ^{138}BaF
 - Dominant CP-violating effect: eEDM
 - Negligible: NSM of fluorine-19 – low Z , no enhancement \rightarrow negligible NSM, can be used to help control for systematic effects
 - ^{138}Ba doesn't have an NSM because it has zero nuclear spin
- ^{225}RaF
 - Has the same CP-violating operators
 - Also has ^{225}Ra 's NSM – relatively large because of large Z and enhancement factor

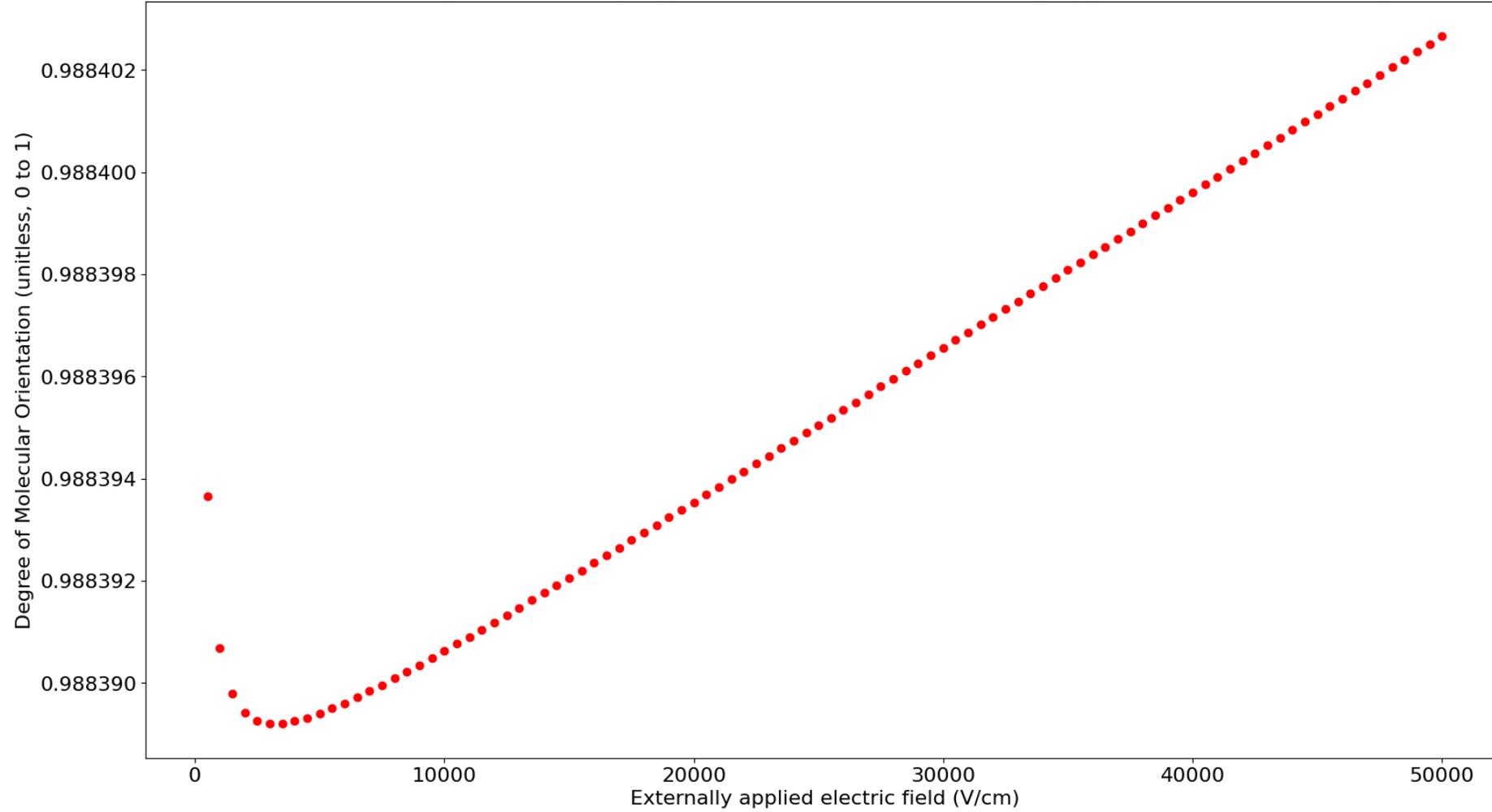
Strange Orientation patterns at low-to-Intermediate electric field strengths embedded in medium

Degree of Molecular Orientation along the externally applied electric field vs Externally applied electric field strength, In-Matrix, K=100.0



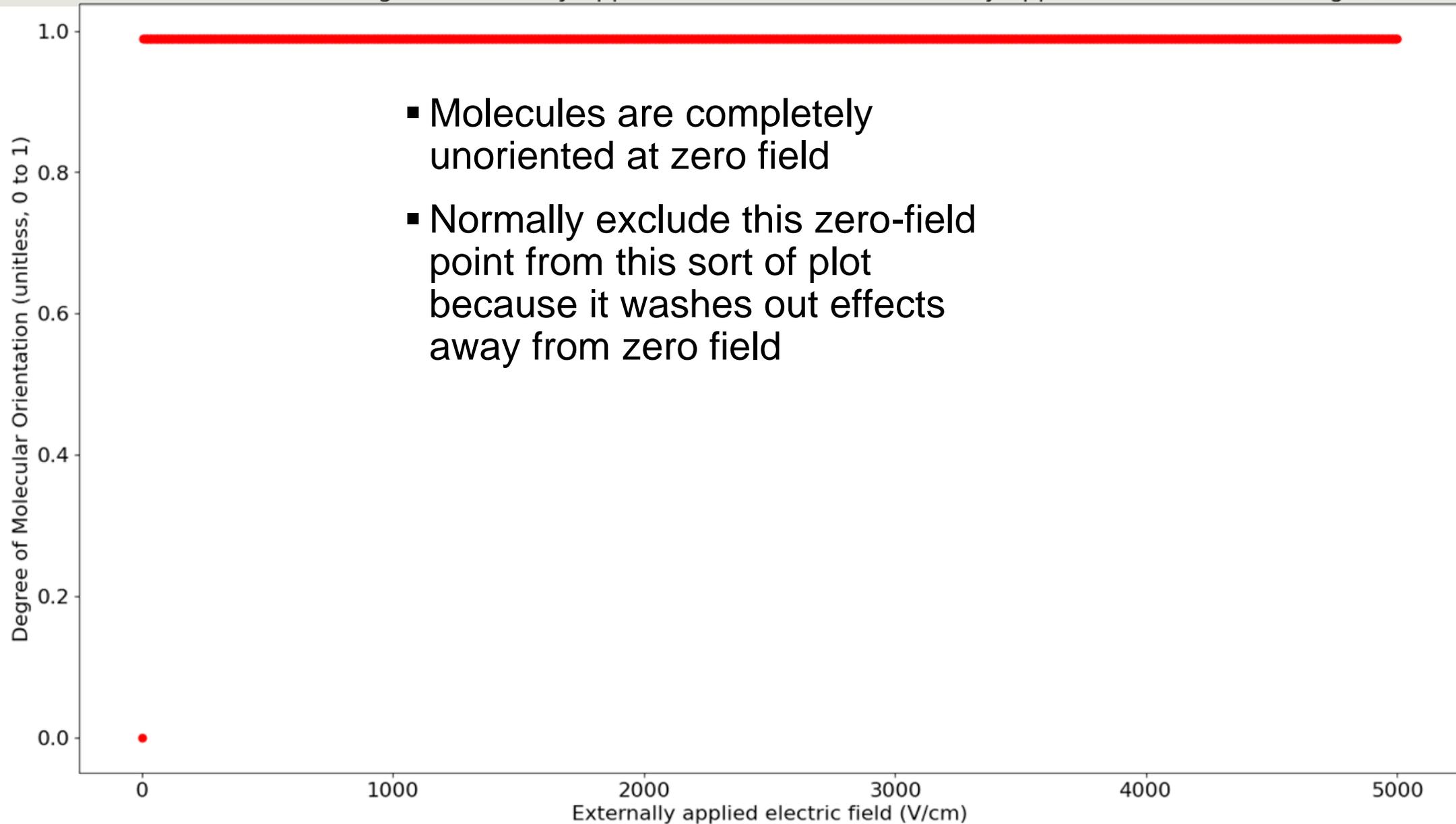
Degree of Molecular Orientation

Degree of Molecular Orientation along the externally-applied electric field vs Externally applied electric field strength, In-Matrix, K=100.0



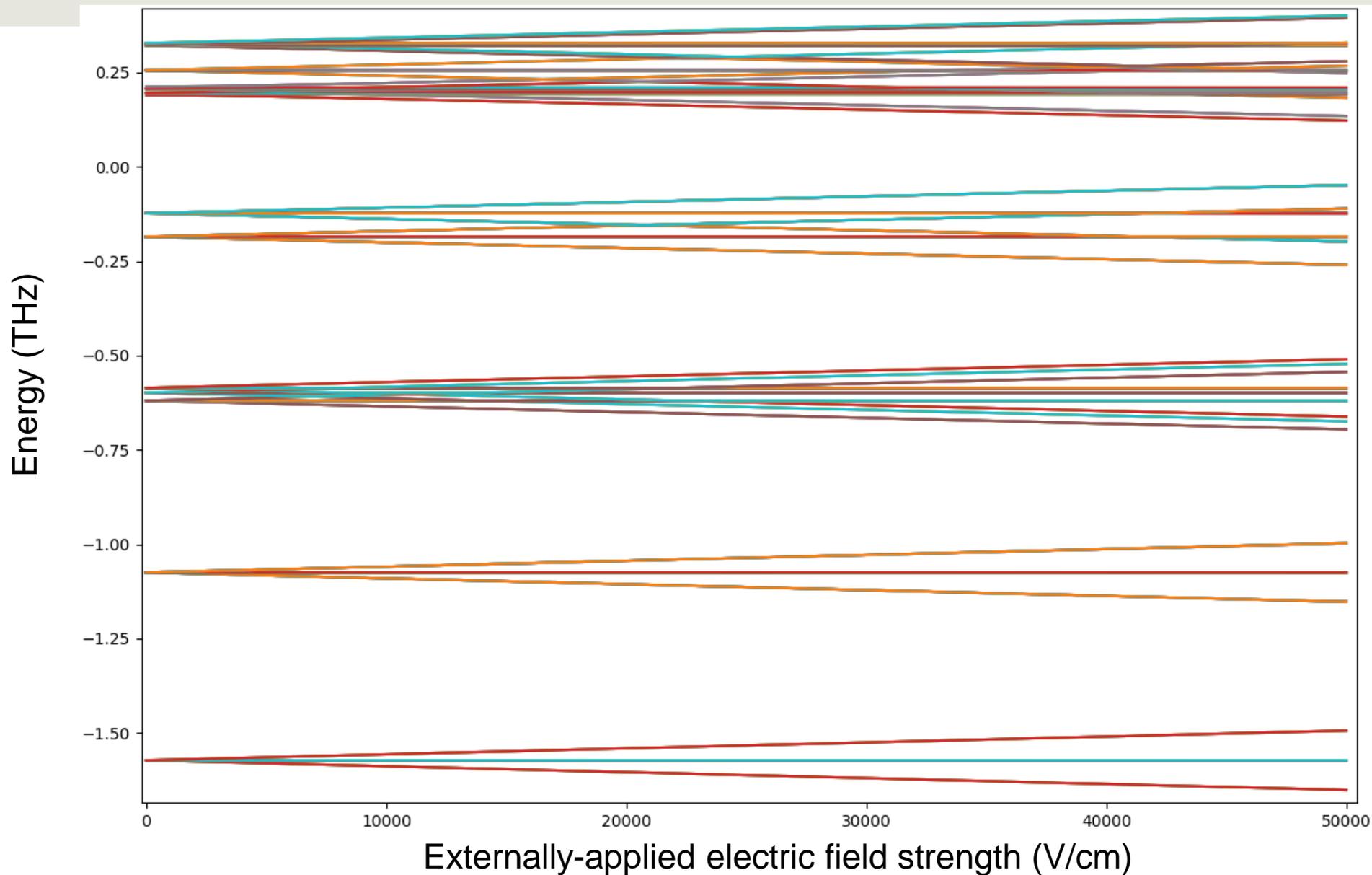
Degree of Molecular Orientation including zero externally-applied electric field embedded in medium

Degree of Molecular Orientation along the externally-applied electric field vs Externally applied electric field strength, In-Matrix, $K=100.0$



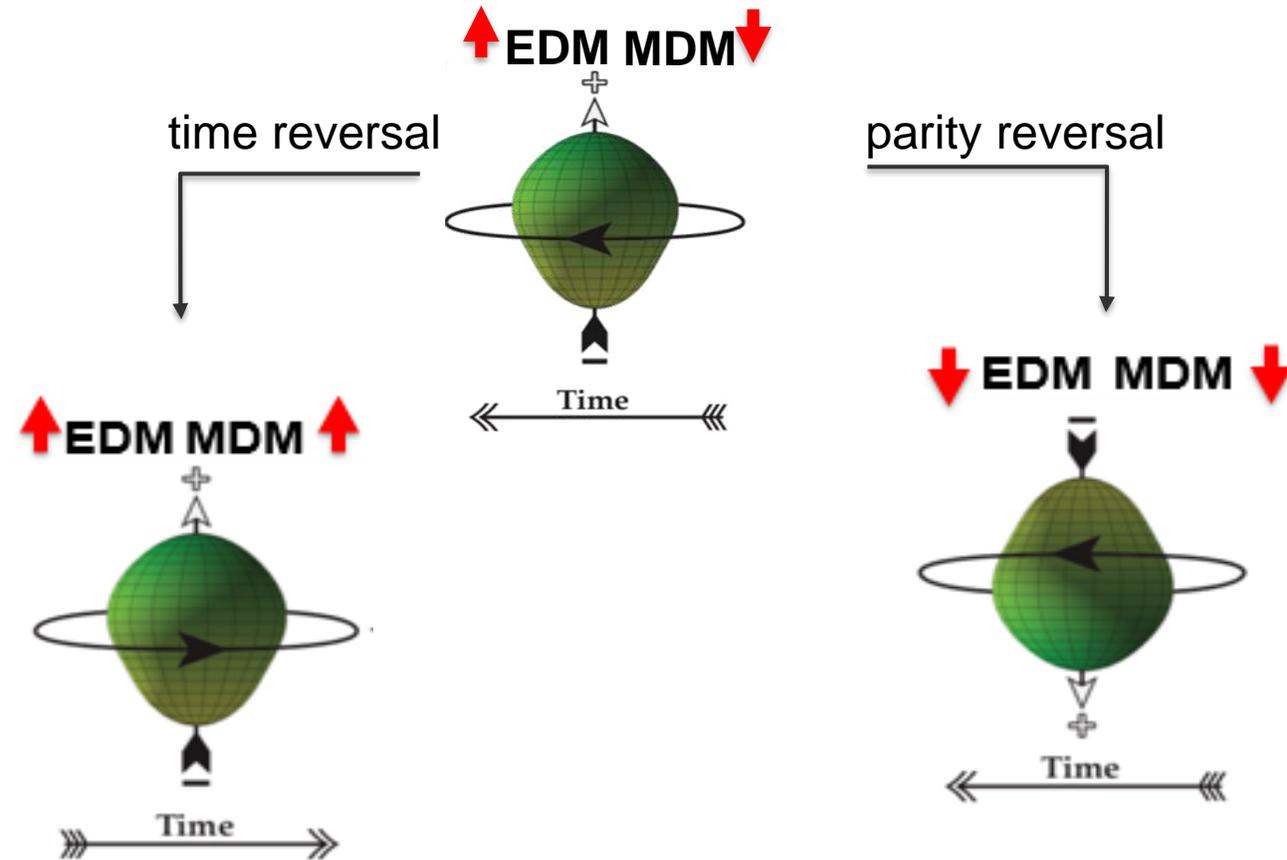
Energies of the lowest energy states vs Externally-applied Electric field In-Medium

- Shows ~360 states of 6724
 - Most are too closely separated to distinguish here
- States separated into distinct groups, the nth lowest energy group has $24 \cdot n$ states for the lowest few groups
- The 5 lowest groups are shown here



How to find charge-parity violation?

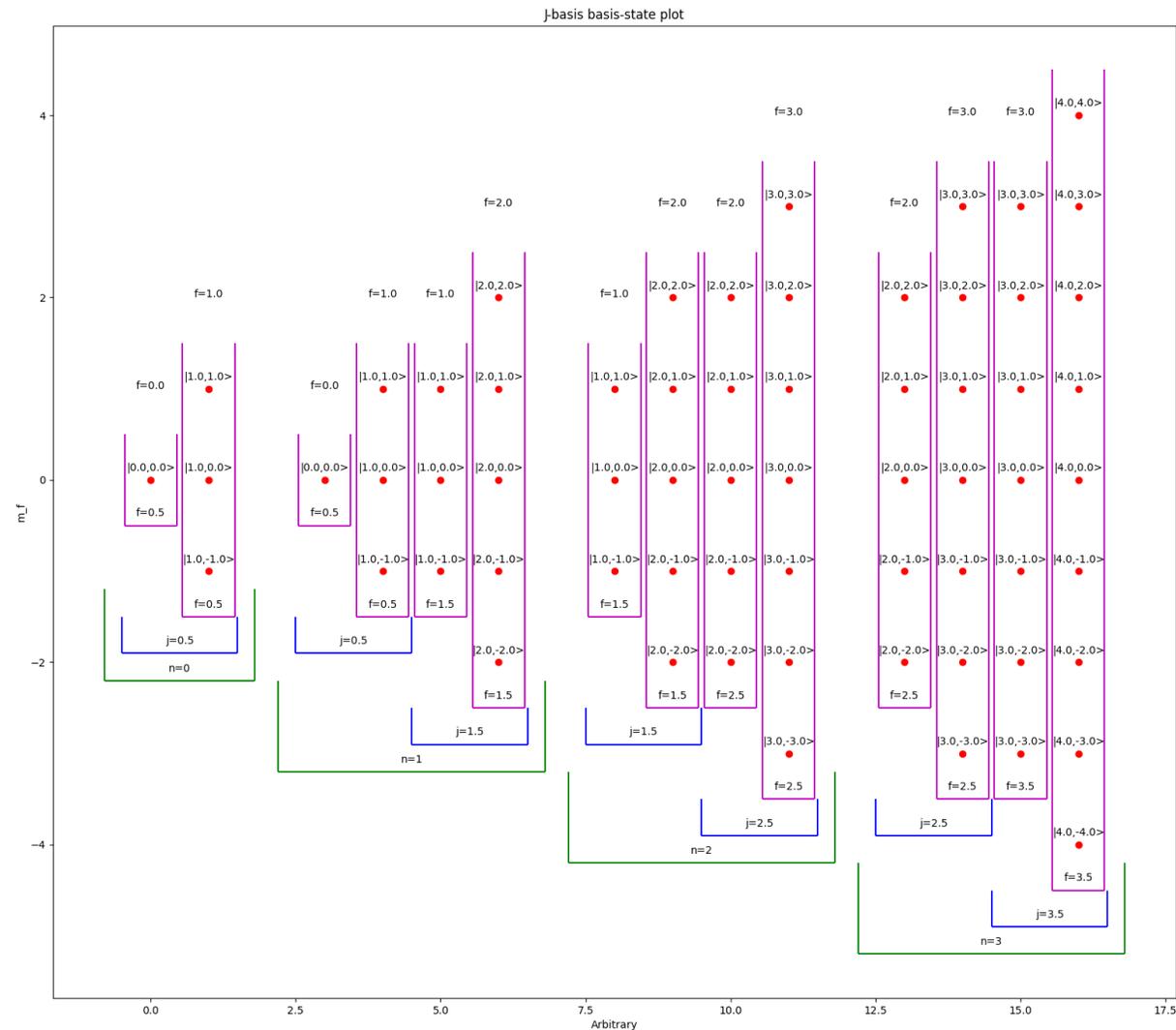
- CPT theorem: CP violation == T violation
 - Many signatures of CP violation are actually signatures of T violation
 - This does assume Lorentz invariance
- Need to find measurable observables:
 - CP violating decays/branching ratios
 - Pro: actually has been done
 - Need to measure differences
 - Ex: rate of $K_{0L} \rightarrow \pi^- e^+ \nu_e >$ rate of $K_{0L} \rightarrow \pi^+ e^- \bar{\nu}_e$
 - CP violating static observables
 - Any nonzero value --> found
 - Limited by systematics
 - Ex: Electric dipole moments/nuclear Schiff moments



adapted from J. T. Singh

The “J”-basis for ^{138}BaF

- In its ground electronic and vibrational state ^{138}BaF can be modeled as three coupled angular momenta
 - \vec{N} : rotational angular momentum of molecule
 - \vec{S} : net electron spin
 - \vec{I} : ^{19}F nuclear spin
 - Note that there is zero net electron angular momentum and zero
- Coupling
 - Purely rotational part of the Hamiltonian is largest
 - Next largest is spin-rotational coupling
- This suggests a coupled basis we call the “j-basis”
 - Couple N to S giving J, then to I giving F
 - In-vacuum, when no field applied, j-basis states are nearly eigenstates of Hamiltonian (hyperfine mixing)



Rotational Hamiltonian

$$H_{rot} = B\vec{N}^2 - D\vec{N}^4 + \gamma\vec{N} \cdot \vec{S} + \delta\vec{N}^2\vec{N} \cdot \vec{S}$$

$$\langle H_{rot} \rangle = Bn(n+1) - D(n(n+1))^2 + \frac{j(j+1) - n(n+1) - s(s+1)}{2}(\gamma + \delta n(n+1))$$

- Both BaF and RaF correspond to Hund's case (b) since $L = 0$
- Three effects are included here
 - The rotational energy of the molecule about its center of mass
 - The centrifugal stretching of the molecule
 - Rotational-electron spin coupling
- The J-basis basis kets are eigenstates of the rotational Hamiltonian
- Note that the BN^2 term dominates
 - In the absence of the Devonshire potential, this is the largest term in the overall Hamiltonian for the electric fields modeled here
 - With the Devonshire potential included, this is the second largest term for $n \lesssim 12-15$ and the largest term for $n \gtrsim 12-15$

| Coefficient | Value (MHz) |
|-------------|-------------|
| B | 6743.9586 |
| D | 0.0055296 |
| γ | 80.954 |
| δ | 0.000111 |

Hyperfine Hamiltonian for ^{138}BaF

- The hyperfine Hamiltonian for ^{138}BaF consists of two parts

- A scalar fermi contact interaction
- A rank-2 tensor dipolar spin-spin interaction

does not conserve n , but does conserve the parity of n

$$H_{hfs} = b\vec{I} \cdot \vec{S} + cI_z$$

| Coefficient | Value (MHz) |
|-------------|-------------|
| b | 63.509 |
| c | 8.224 |

$$H_{hfs} = (b + \frac{1}{3}c)T_0^0(H_{hfs}) + cT^2(H_{hfs})$$

$$\langle njfm_f | T_0^0(H_{hfs}) | njfm_f \rangle = \frac{3}{4}(b + \frac{c}{3})\xi'_{j,j'} \left(\begin{matrix} \frac{1}{2} & \frac{1}{2} & 0 \\ n & f & j' \end{matrix} \right)_{6j} \begin{matrix} \frac{1}{2} & \frac{1}{2} & 0 \\ n & f & j \end{matrix} \Bigg|_{6j} - \begin{matrix} \frac{1}{2} & \frac{1}{2} & 1 \\ n & f & j' \end{matrix} \Bigg|_{6j} \begin{matrix} \frac{1}{2} & \frac{1}{2} & 1 \\ n & f & j \end{matrix} \Bigg|_{6j} \right) \delta_{n,n'} \delta_{f,f'}$$

$$\langle njfm_f | T_2^0(H_{hfs}) | njfm_f \rangle = \frac{3}{2}c\sqrt{\frac{10}{3}}\xi'_{n,n'}\xi'_{j,j'}(-1)^{(1+n+i+j'+f)} \begin{matrix} n' & 2 & n \\ 0 & 0 & 0 \end{matrix} \Bigg|_{3j} \begin{matrix} f & j' & \frac{1}{2} \\ 1 & \frac{1}{2} & j \end{matrix} \Bigg|_{6j} \begin{matrix} n & n' & 2 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ j & j' & 1 \end{matrix} \Bigg|_{9j}$$

Stark Hamiltonian for ^{138}BaF

$$H_{St} = -\vec{\mu}_E \cdot \vec{E}$$

$$|\vec{\mu}_E| = 3.170 \text{ MHz/D}$$

$$\langle njf m_f | H_{St} | n' j' f' m'_f \rangle = \delta_{m_f m'_f} \mu_e \varepsilon_Z (-1)^{1-m_f} \xi_{ff'} \xi_{jj'} \xi_{nn'}^* \\ \begin{pmatrix} f & 1 & f' \\ -m_f & 0 & m_f \end{pmatrix}_{3j} \begin{pmatrix} n & 1 & n' \\ 0 & 0 & 0 \end{pmatrix}_{3j} \begin{Bmatrix} f & 1 & f' \\ j' & \frac{1}{2} & m_f \end{Bmatrix}_{6j} \begin{Bmatrix} j & 1 & j' \\ n' & \frac{1}{2} & n \end{Bmatrix}_{6j}$$

Devonshire Hamiltonian for ^{138}BaF

- Simple models of the effects of the matrix
 - May be completely wrong
 - This will need to be experimentally tested
- Octahedral symmertry

$$H_{Dev} = -\frac{K}{3} \left[\sqrt{\frac{10}{7}} (T_4^4 + T_{-4}^4) + \sqrt{4\pi} T_0^4 \right]$$

$$K = 100\text{K} \approx 2.048\text{THz}$$

$$K \xi_{ff'} \xi_{jj'} \xi_{nn'} * \left(\sqrt{\frac{5}{14}} \begin{pmatrix} f & 4 & f' \\ -m_f & 4 & m'_f \end{pmatrix}_{3j} + \sqrt{\frac{5}{14}} \begin{pmatrix} f & 4 & f' \\ -m_f & -4 & m'_f \end{pmatrix}_{3j} + \begin{pmatrix} f & 4 & f' \\ -m_f & 0 & m'_f \end{pmatrix}_{3j} \right) \langle njfm_f | H_{St} | n'j'f'm'_f \rangle =$$

$$\times \begin{Bmatrix} f & 4 & f' \\ j' & \frac{1}{2} & j \end{Bmatrix}_{6j} \begin{Bmatrix} j & 4 & j' \\ n' & \frac{1}{2} & n \end{Bmatrix}_{6j}$$