Searches for Fundamental Symmetry Violations with Atoms and Molecules

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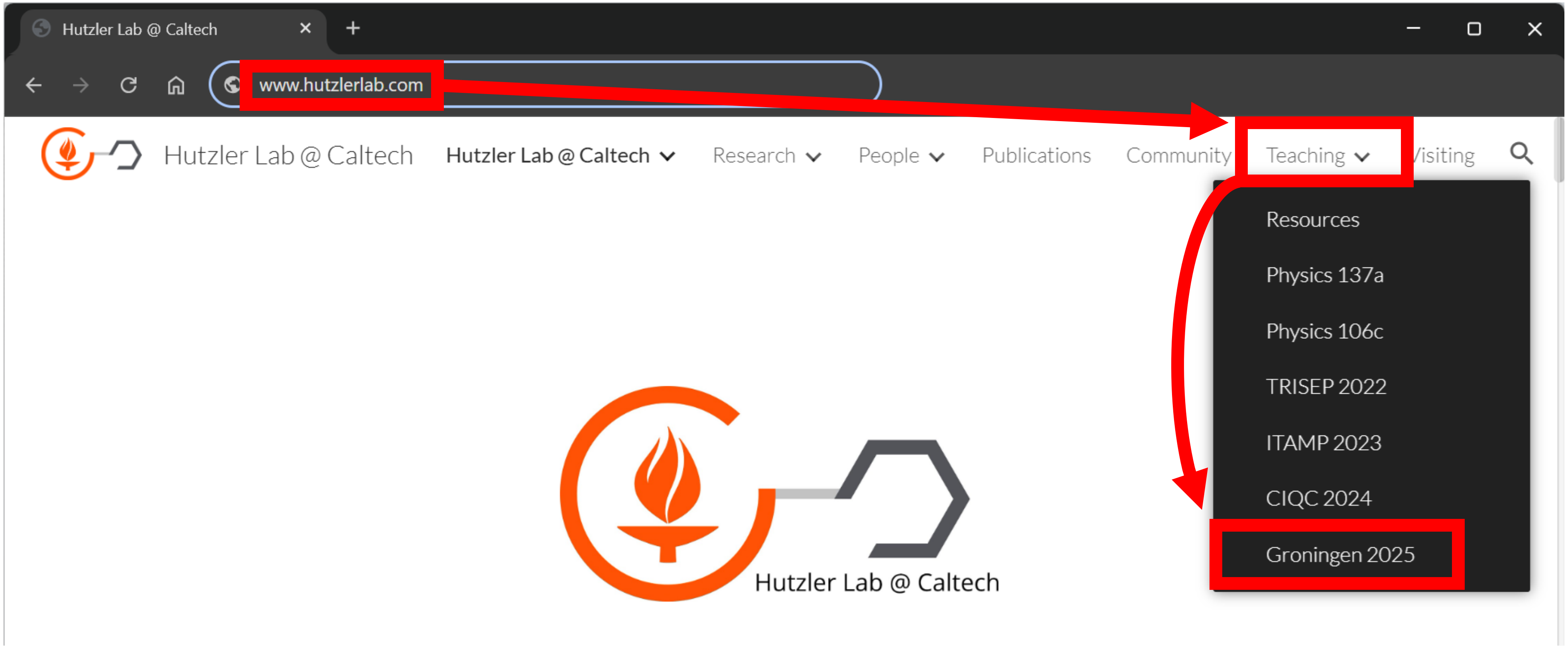
Finding the slides online



- Other summer/winter school presentations too!
  - TRISEP → More emphasis on particle physics
  - ITAMP → More emphasis on experimental aspects
  - CIQC → More emphasis on molecules and chemistry

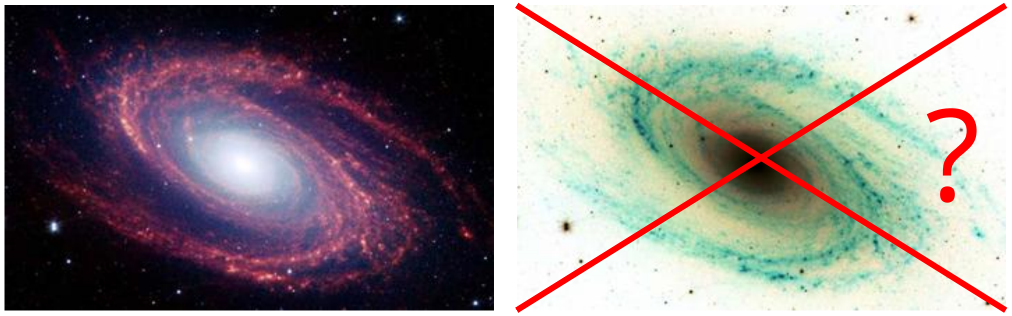
Part I: Motivation and Background

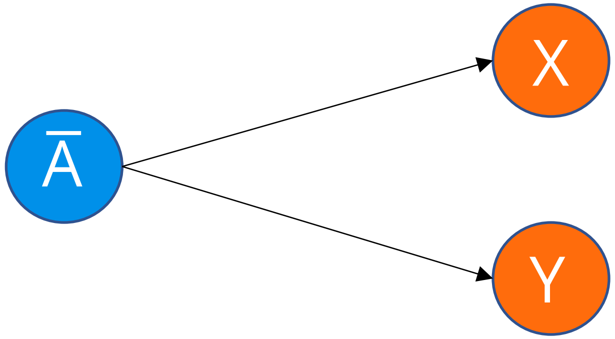
Why are we interested in symmetry violation at low energy?

How are atoms and molecules used for these searches?

An Asymmetric Universe

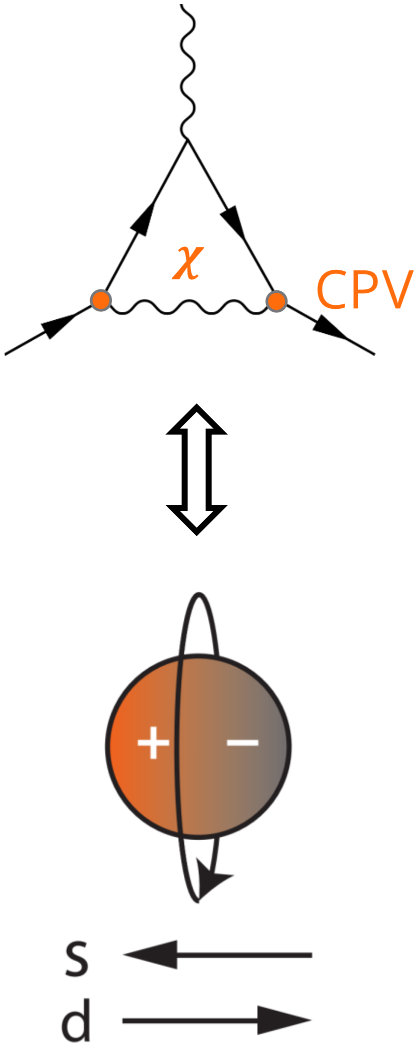
- Why is the universe full of matter but no anti-matter?
    - Baryon Asymmetry of the Universe (BAU)
- How can we explain this?
- One model: an undiscovered particle which preferentially decays into matter
- Requires physics which violates charge-parity (CP) symmetry
    - C: Matter ↔ anti-matter
    - P: mirror reflection
- Motivates search for CP-violating (CPV) physics
    - Note: CP = T (time-reversal) so I will switch between these



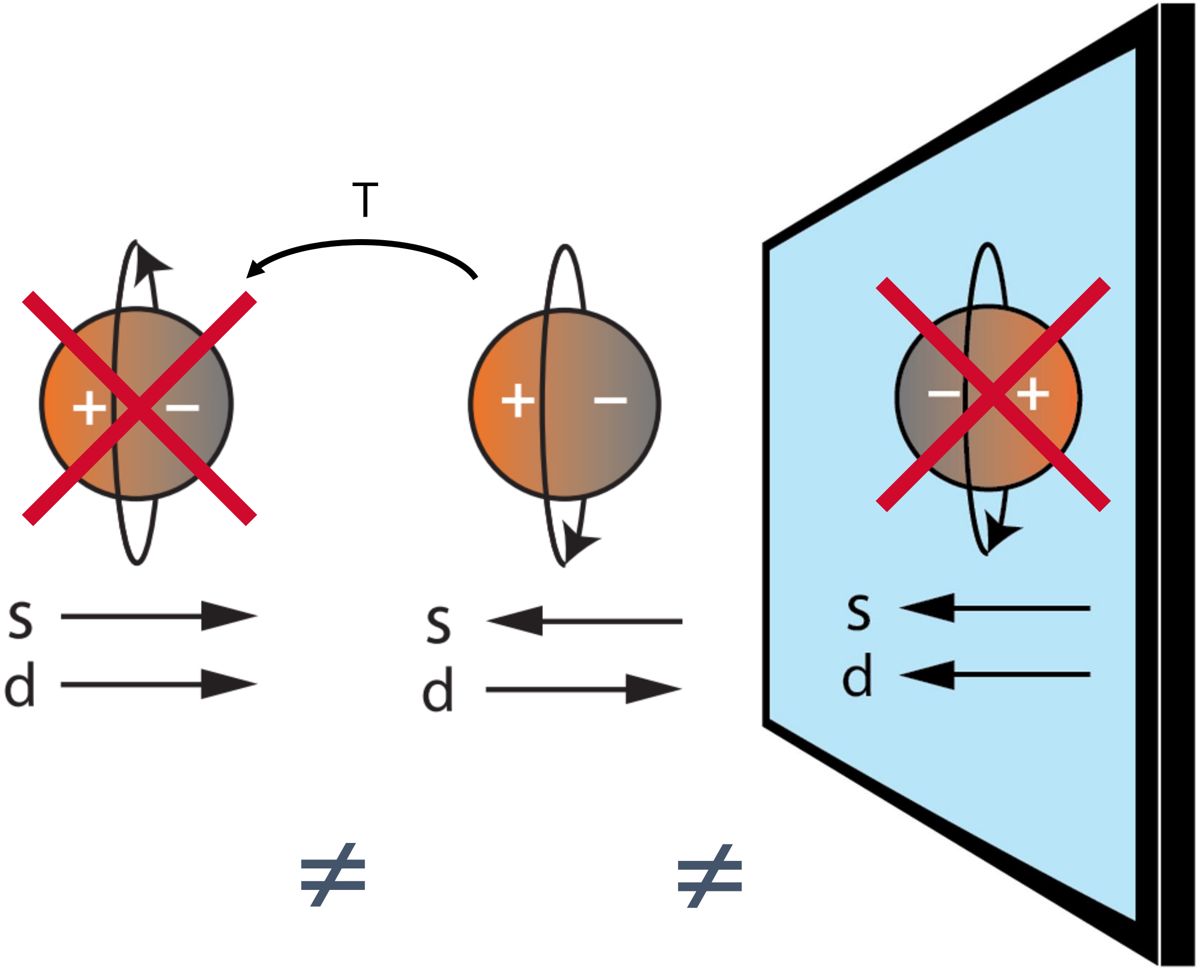


Low Energy Observables

- 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!)
- $\vec{d} \propto \vec{s}$ → problem
  - $\vec{d}$ is P-odd, T-even
  - $\vec{s}$ is P-even, T-odd



EDMs violate symmetries

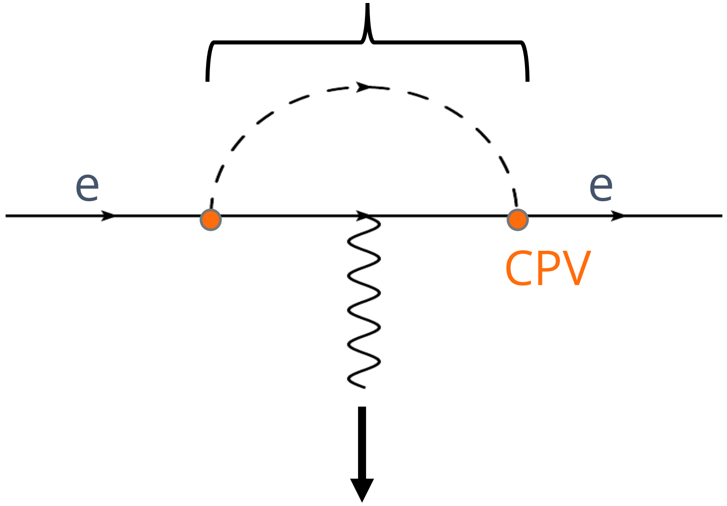


EDMs violate P, T, CP

Electron EDM

- Generically sensitive to CPV particles and forces coupling to the electron
    - One loop ~ 15-75 TeV
    - Two loop ~ 1-3 TeV
- "Background free"
    - SM value is small
    - $|d_e| < 10^{-38}$ e cm
- For specific models, energy reach can be even higher (or lower)
- Orders of magnitude of untapped potential – unique opportunity to explore extremely high energy scales

$\varphi_{CP} \sim 1$, $M \sim 75$ TeV



$|d_e| \sim 4\times10^{-30}$ e cm
(current experimental limit)

Sensitivity

- Experimental observable is angle φ (phase),

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

- Repeated measurements:

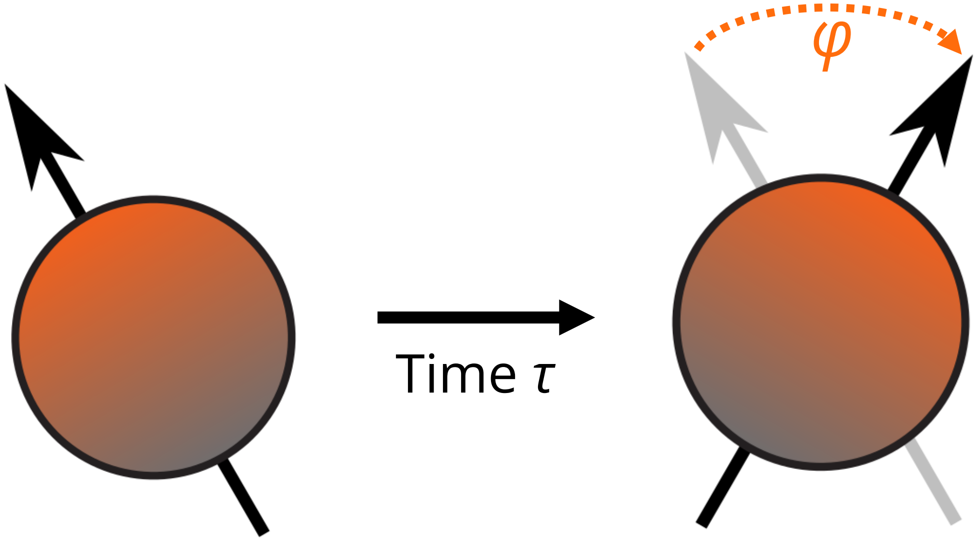
$$\delta d = \hbar/\mathcal{E}\tau\sqrt{N}$$

Total measurements

Coherence time

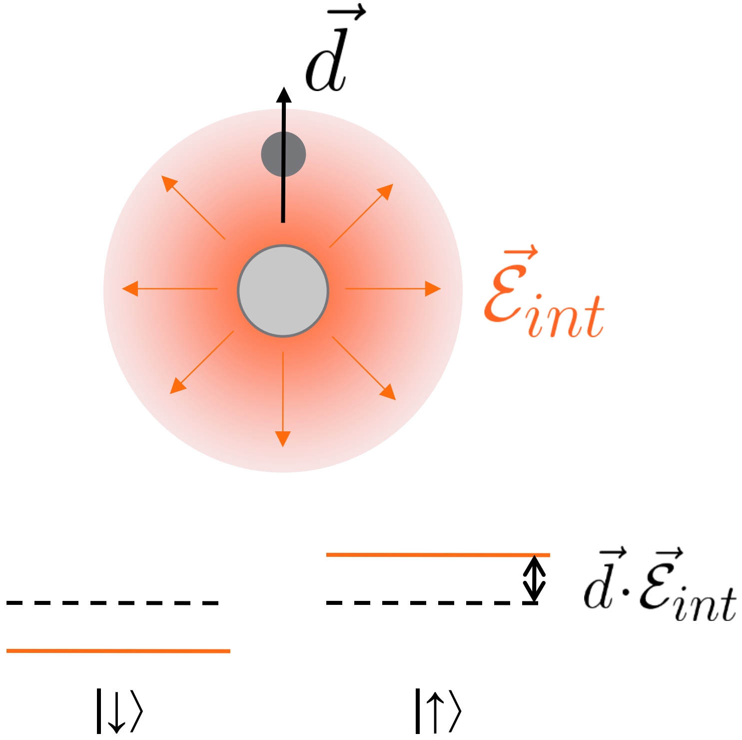
Effective electric field

Make these large!



Internal Fields

- Atoms/molecules have extremely large fields
  - $e/4\pi\epsilon_0 a_0^2 \sim$ GV/cm
  - Heavy species ~10-100 GV/cm
  - Much larger than “maximum” lab field of ~100 kV/cm over macroscopic volumes
- Permanent EDM causes splitting of energy levels
  - Amplified by internal fields
- This simple picture has several caveats
  - Polarization
  - Schiff shielding

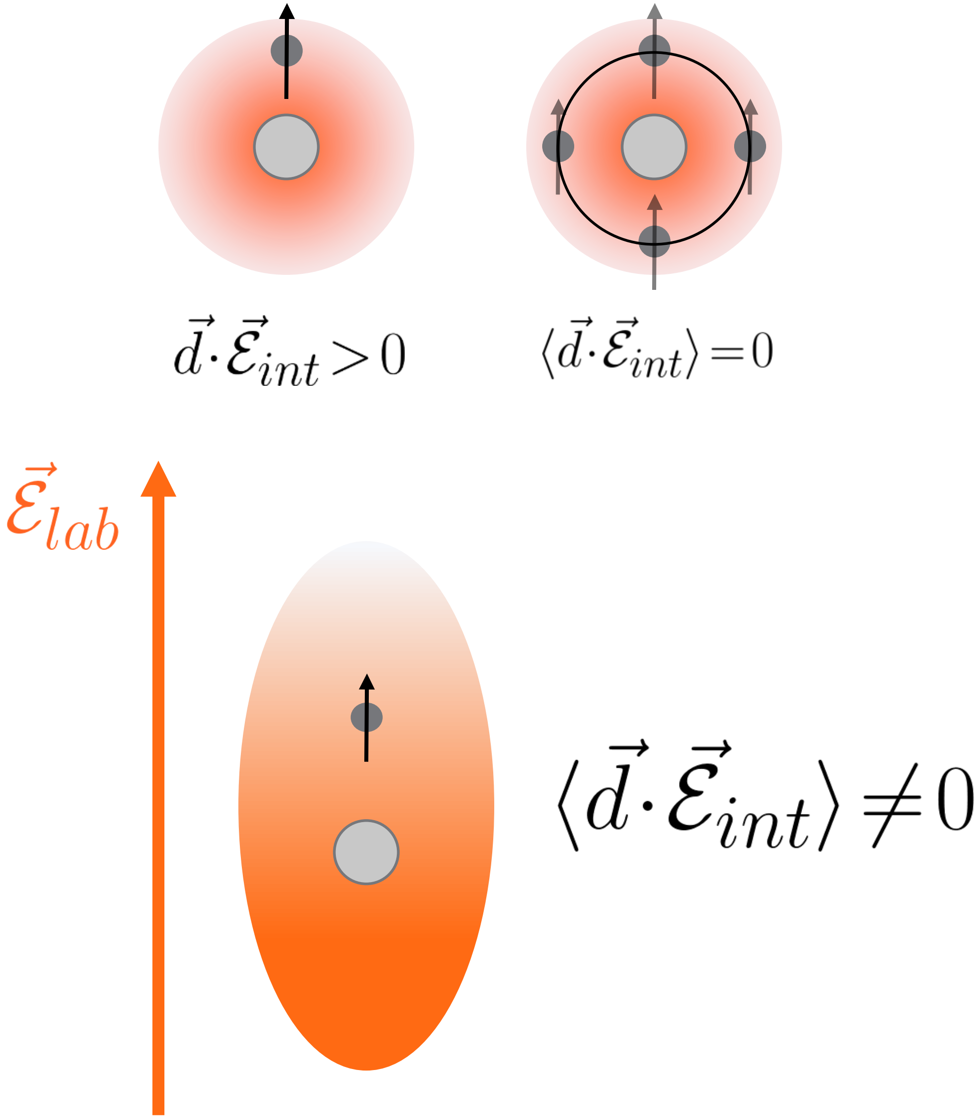


Polarization

- First “internal field” picture caveat – electrons and nucleus experience zero average field
- Always the case:

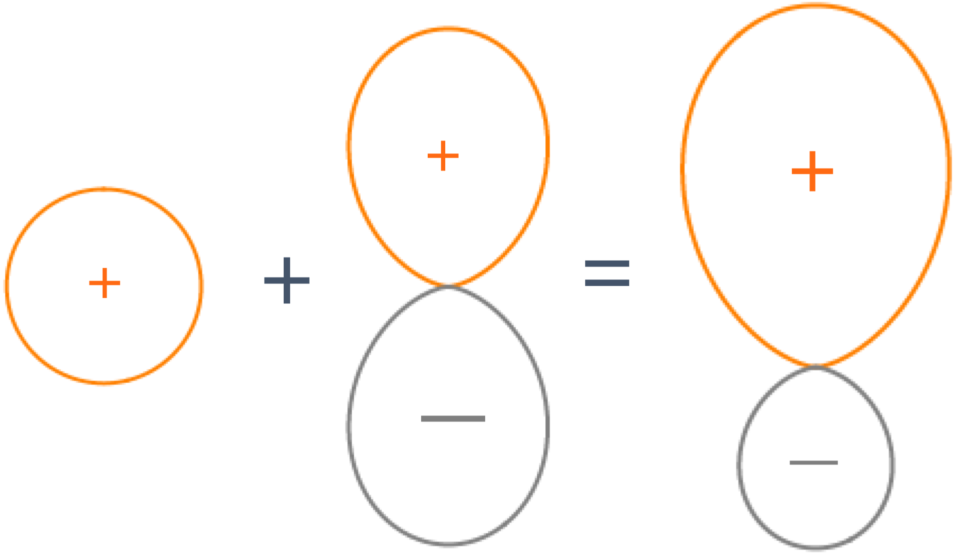
$$
\begin{aligned}
\langle\psi|\vec{\mathcal{E}}|\psi\rangle \propto \langle\psi|\vec{r}/r^3|\psi\rangle &= \int |\psi|^2\vec{r}r^{-3}\,d^3r \\
&= 0
\end{aligned}
$$

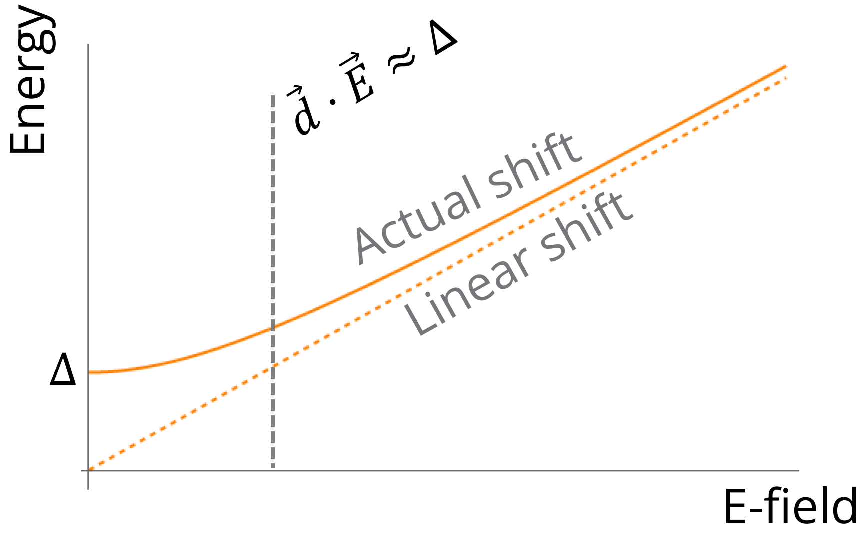
  since $\psi(-\vec{r}) = \pm\psi(\vec{r})$
- Solution: polarize
  - Apply lab field to polarize atom/molecule



Polarizing atoms and molecules

- Atoms/molecules are symmetric in zero field
- Electric field mixes opposite parity states
- Must overcome energy splitting Δ between the states to polarize
  - → induces dipole
- *Nothing* has a permanent EDM (including water)
  - (except from CP-violation)





Polarizing atoms and molecules

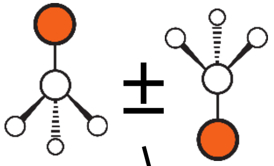
- Consider a system with just two levels *e,g* split by energy $\hbar\Delta$. The Hamiltonian from an applied E field is

$$H_S = -\vec{d}\cdot\vec{\mathcal{E}} = -\mathcal{E}\begin{pmatrix}\langle g|d|g\rangle & \langle e|d|g\rangle \\ \langle g|d|e\rangle & \langle e|d|e\rangle\end{pmatrix} = \begin{pmatrix} 0 & -d\mathcal{E} \\ -d\mathcal{E} & 0\end{pmatrix}$$

  where we used that the states have well defined parity so $\langle g|d|g\rangle = e\langle g|r|g\rangle = 0$ as before (same for state *e*)
  - Defined $d = \langle e|d|g\rangle = e\int \vec{r}\psi_e^*(\vec{r})\psi_g(\vec{r})$
  - $d =$ transition dipole matrix element (TDM)
  - Apologies for the overuse of *e,d*…
  - Note e, g cannot have same parity, otherwise $\psi_e^*(\vec{r})\psi_g(\vec{r})$ is an even function and $d = e\int \vec{r}\psi_e^*(\vec{r})\psi_g(\vec{r}) = 0$
- The total Hamiltonian is therefore

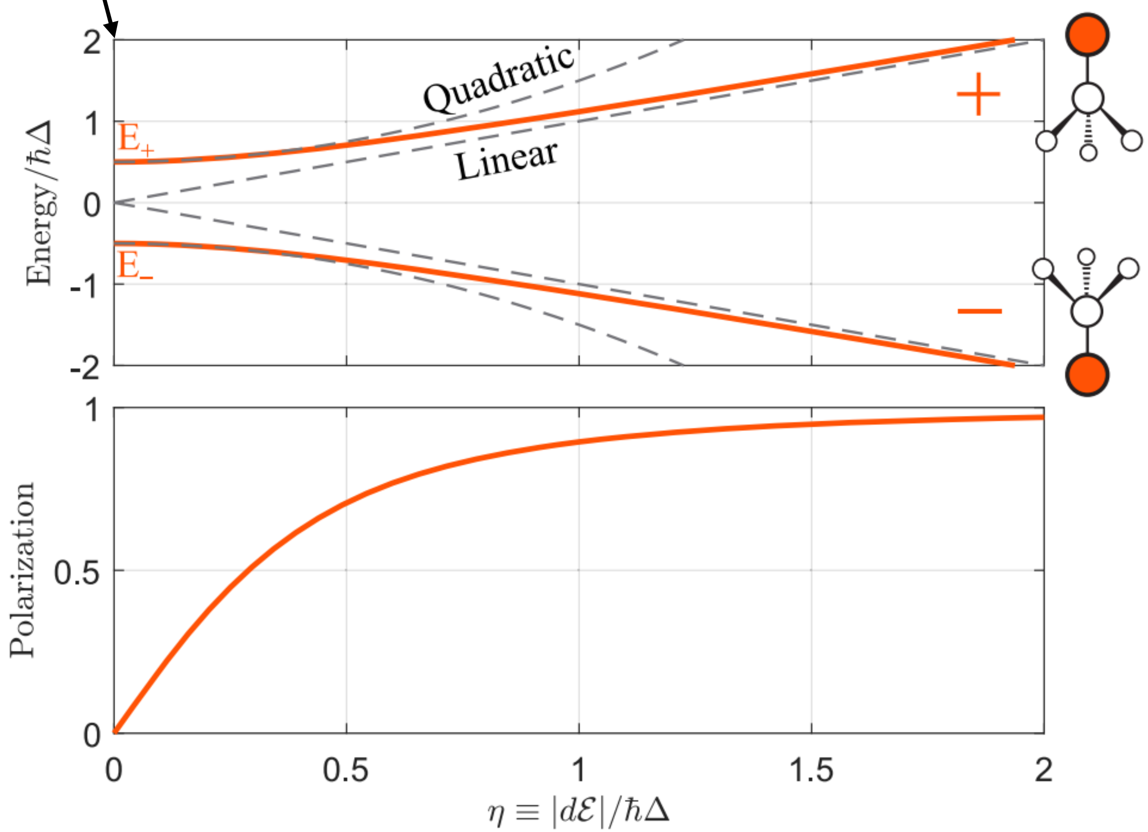
$$H = \begin{pmatrix} -\hbar\Delta/2 & -d\mathcal{E} \\ -d\mathcal{E} & +\hbar\Delta/2\end{pmatrix}$$

Polarizing atoms and molecules



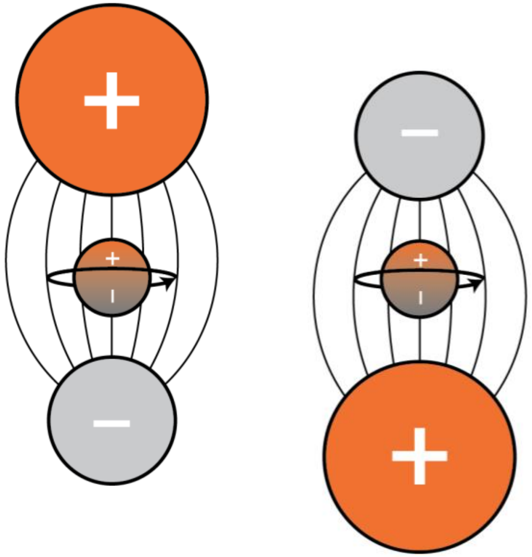
$$H = \begin{pmatrix} -\hbar\Delta/2 & -d\mathcal{E} \\ -d\mathcal{E} & +\hbar\Delta/2 \end{pmatrix}$$

- Diagonalize
  - $E_{\pm} = \pm\frac{1}{2}\hbar\Delta[1 + 4\eta^2]^{1/2}$
  - $\eta \equiv |d\mathcal{E}|/\hbar\Delta$
- High field limit, $\eta \gg 1$
  - Linear shifts, $\Delta E_{\pm} \approx \pm d\mathcal{E}$
  - Eigenstates $|\pm\rangle \approx (|e\rangle + |g\rangle)/\sqrt{2}$
  - “Fully polarized” or “fully mixed”
- Low field limit, $\eta \ll 1$
  - Quadratic shifts, $\Delta E_{\pm} \approx d^2\mathcal{E}^2/\hbar\Delta$
  - Induced dipole, $d \propto \mathcal{E}$
  - Eigenstates $|e\rangle, |g\rangle = (|+\rangle \pm |-\rangle)/\sqrt{2}$
  - *Mixtures of polarized states*
  - Necessary – polarized states are not parity eigenstates!
- Need $\eta \sim 1, |d\mathcal{E}| \sim \hbar\Delta$ to polarize
- Polarization $0 \leq P < 1$ is what fraction of the eigenstates are the fully-polarized states $|\pm\rangle$
  - $P = |\partial E_{\pm}/\partial(d\mathcal{E})|$



Polarization and EDM Sensitivity

- Electron spin can be easily aligned in the lab frame with magnetic fields
  - $\langle \vec{S} \rangle \propto \hat{z}$
- Internal fields require alignment of molecular dipole moment in the lab
  - $\vec{\mathcal{E}}_{eff} \propto \hat{n} \propto \vec{d}_{mol}$
  - $\hat{n}$ = molecular axis
- EDM Shifts ∝ polarization
  - $\Delta E_{EDM} = \langle \vec{S} \cdot \hat{n} \rangle \propto \langle \vec{S} \cdot \hat{z} \rangle \langle \hat{n} \cdot \hat{z} \rangle$
  - $P = |\langle \hat{n} \cdot \hat{z} \rangle|$ Polarization
- True for other CPV shifts

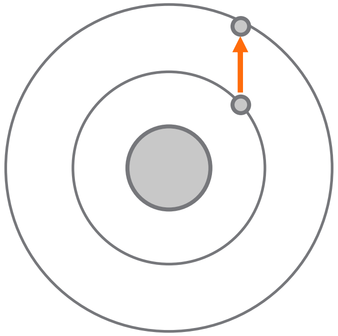


Polarized, $P = 1$

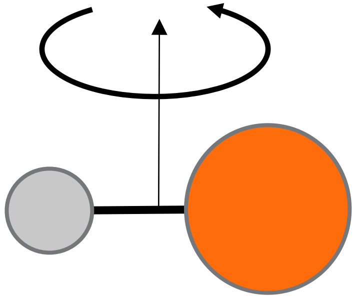
$\Delta E_{EDM} = \pm d_e \mathcal{E}_{eff}$

Atoms vs. molecules

- Atoms
  - $\Delta \sim 100$ THz (electronic)
  - $P \sim 10^{-3}$ @ 100 kV/cm
- Molecules
  - $\Delta \sim 10$ GHz (rotational)
    - Sometimes even smaller, more on that later
  - $P \sim \mathcal{O}(1)$ @ 10 kV/cm
- “Molecules are 1000x more sensitive”



Atoms
$\Delta \sim 100$ THz



Molecules
$\Delta \sim 10$ 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 do not accelerate in static electric fields. Therefore, $\langle F\rangle = q\langle E\rangle = 0$ in steady state.
  - Charged particles move to a point where they see zero average field
- This is true! But there are evasions:
  - Electrons move relativistically
  - Nuclei have complex shape

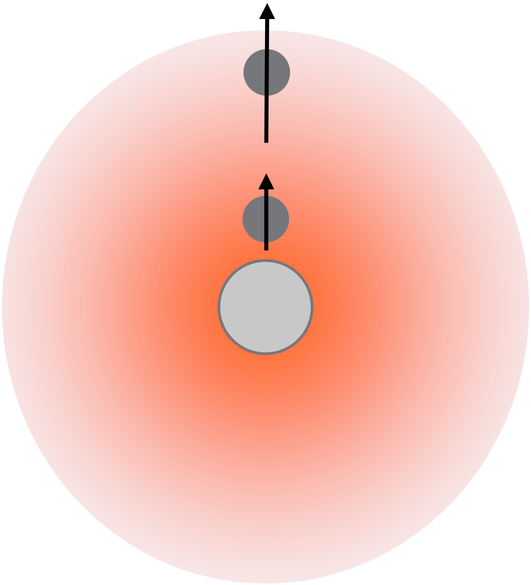
Relativistic Effects

- Dipole moment $\vec{d}$ experiences Lorentz contraction
  - Correlation of velocity and position relative to nucleus
  - $\vec{d}$ is not a constant in the atom
  - $\langle\vec{E}\rangle = 0$ but $\langle\vec{d}\cdot\vec{E}\rangle \neq 0$
  - Most sensitive where contraction is largest – very near the nucleus
  - Depends on very short-range electronic wavefunction near nucleus → needs relativistic atomic/molecular theory
  - Largest for *s* and *p* type electrons
- For Z protons, orbital size ~ a_0/Z,

$$v \sim \frac{p}{m_e} \sim \frac{\hbar Z/a_0}{m_e} \sim Z\alpha c \sim c \times Z/137$$

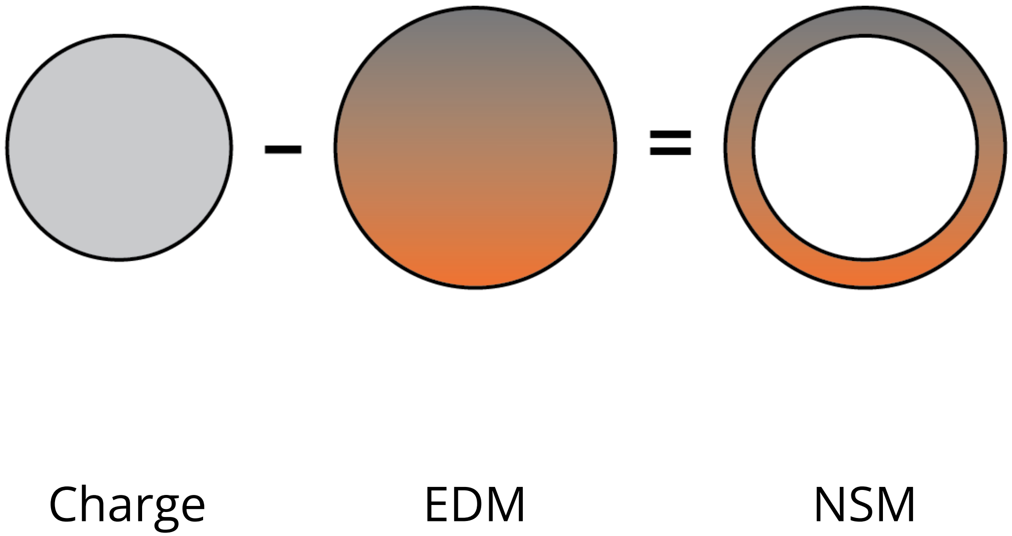
- CPV sensitivity scales roughly as Z^{2-3}

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



Nuclear Schiff Moments

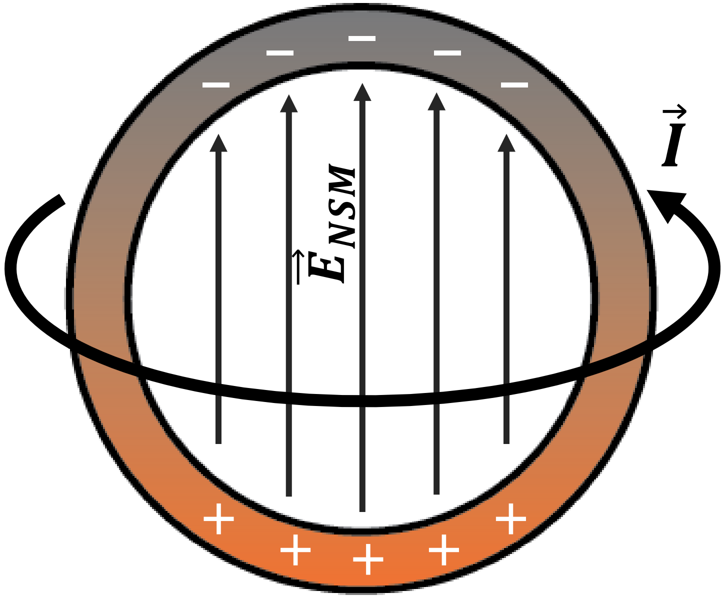
- Nuclear motion is definitely not relativistic
    - Nuclear EDMs unobservable?
- Evasion: charge (only p) and EDM (p, n) distributions *generally don't* overlap
- Gives rise to a Nuclear Schiff Moment (NSM)
    - Depends on mismatch between charge and mass distributions in nucleus
- Can be significantly enhanced in highly deformed (non-spherical) nuclei



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

Nuclear Schiff Moments

- NSM looks like a charged shell with dipole-like distribution
  - Effective, T-violating $\vec{E}_{NSM} \propto \vec{I}$
  - Mixes core-penetrating *s*, *p* electronic orbitals
  - Induces EDM in atom or molecule
- No need for unpaired electron spins – just electron density at the nucleus
  - Often performed in diamagnetic systems (no net electron spin) for reduced magnetic sensitivity
- Since $\propto \vec{I}$, needs $I \geq 1/2$
- Hamiltonian $H \propto \vec{E}_{ext} \cdot \vec{I}$
  - Very analogous to eEDM, so experimental searches are similar
  - Look for splitting of $|\uparrow_I\rangle, |\downarrow_I\rangle$

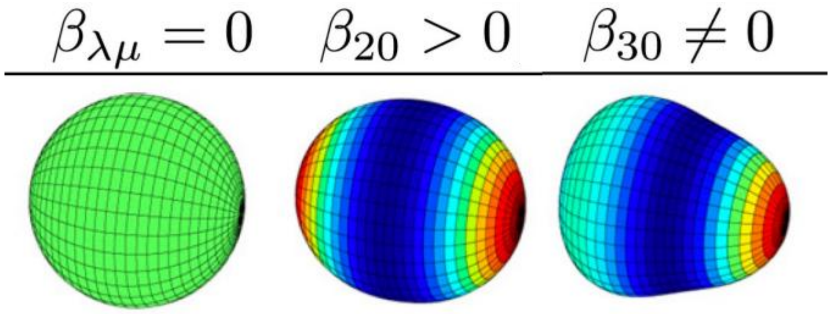


$$\langle S_0 \rangle \propto \sum_p \left(r_p^3 - \frac{5}{3} r_p \overline{r_{ch}^2} \right) z_p$$

V. V. Flambaum and J. S. M. Ginges, PRA 65, 032113 (2002)

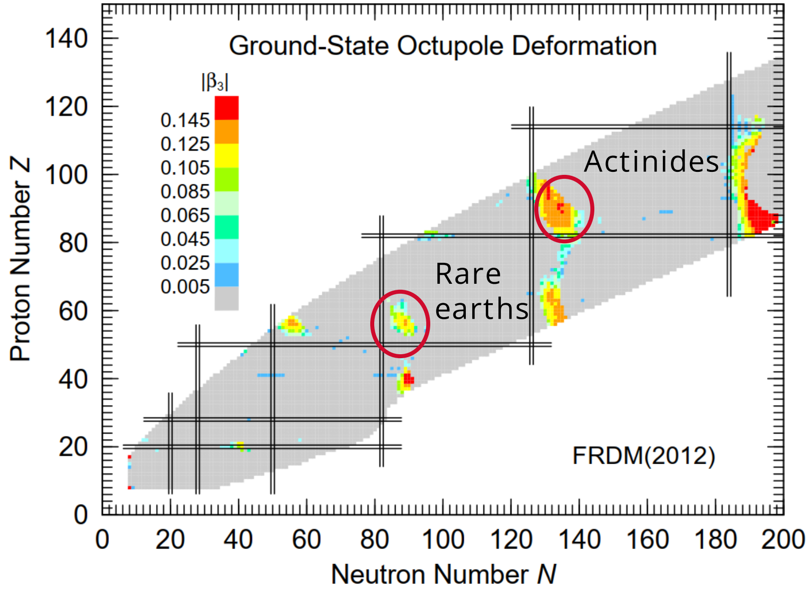
Octupole Deformations

- Schiff Moments (NSMs) enhanced by ~100-1,000 in nuclei with octupole shape deformation
  - $r(\theta) = R_0(1 + \Sigma_{\ell=1}^{\infty} \beta_\ell Y_\ell^0)$
  - Octupole deformation means $\beta_3 \neq 0$
  - Reflection asymmetric
  - Rather rare property
  - Fr, Ra, Ac, Th, Pa, …
  - Heavy, spinful, octupole-deformed species are short-lived
- Combines with molecular enhancements → $10^{5\text{-}6}$ sensitivity gain vs. atoms with spherical nuclei
  - Hg, Xe are highly advanced experiments, hard to beat
  - Many CPV sources → need multiple experiments
- Truly exotic nuclei like ^{229}Pa offer another factor of 100-1000 (maybe)



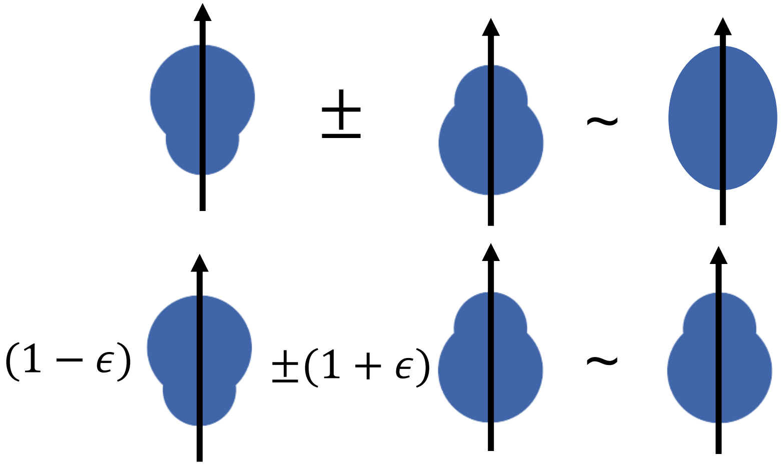
Spherical Quadrupole Octupole

Phys. Scr. 89 054028 (2014)



Why Octupole?

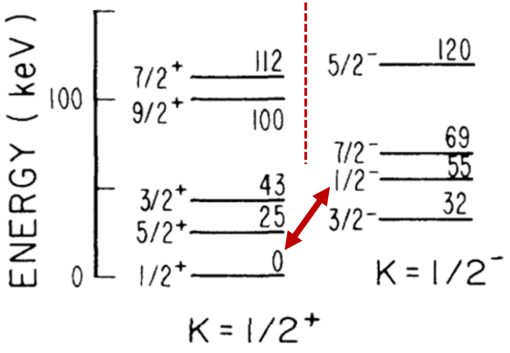
- In absence of symmetry violation, octupole shape averages away
- PV, TV nuclear forces can mix these states
- Large charge, mass mismatch from shape
- Deformed nuclei often have low-lying opposite parity states, $\lesssim$ 100 keV
  - Non-spherical mass → rotational states
  - Dominated by single state
- Pa-229 might have ΔE~60 eV



Can be large, $\sim\boldsymbol{\beta_2\beta_3^2}$

$$S \approx -2\frac{\langle\Psi_0|\hat{S}_0|\bar{\Psi}_0\rangle\langle\bar{\Psi}_0|\hat{V}_{PT}|\Psi_0\rangle}{\Delta E}$$

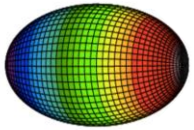
Can be small, rotational

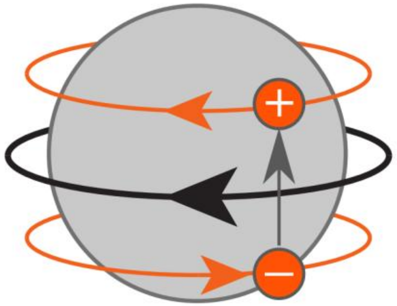


N. Auerbach, V. V. Flambaum, & V. Spevak, PRL 76, 4316 (1996)
J. Dobaczewski, J. Engel, M. Kortelainen & P. Becker, PRL 121, 232501 (2018), J. Engel et al., PRC 35, 1973R (1987)

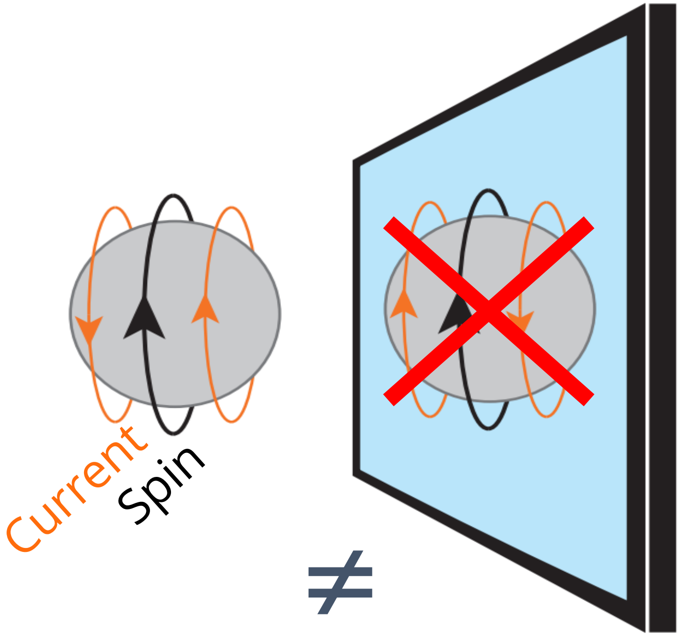
Nuclear Magnetic Quadrupole Moments

- Another evasion of Schiff shielding: magnetic effects
- Nuclear magnetic quadrupole moments (MQM) are not screened
  - Intuitive origin: orbiting nucleon with EDM creates an MQM ~ $\vec{I}$
  - Violates T, P, CP
  - Interacts with electron spin in polarized species to make CPV energy shifts
- Need $I \geq 1$
- Quadrupole deformation (β_2) enhances MQM
  - Collective enhancement via participation of inner shells
  - Typically $\beta_2 Z$ ~ 10
- Experimental approach once again very similar – look for shifts on re-orienting polarization direction, electron spin, and nuclear spin





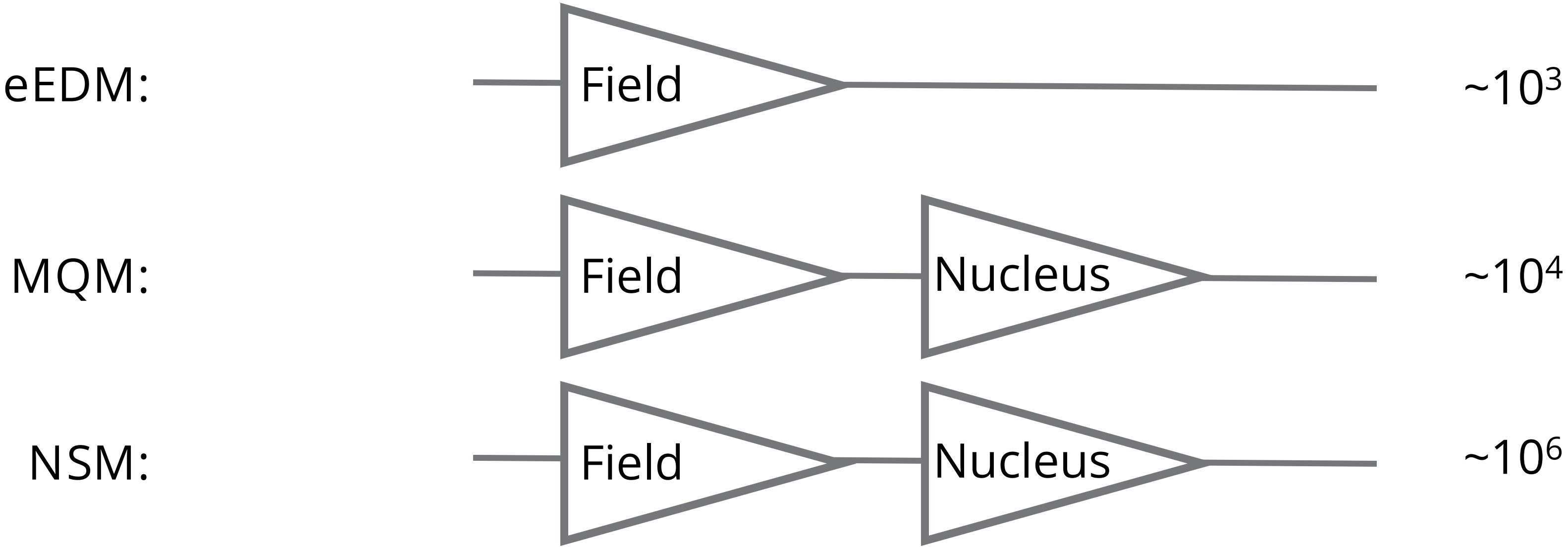
Rotating EDM produces MQM



Field + Nuclear Enhancements

	Internal Field Enhancement	Nuclear Enhancement
Molecule	~1,000	
Quadrupole nucleus (MQM)		~10
Octupole nucleus (NSM)		~1,000

Both NSM, MQM potentially have additional ~1,000x enhancement in ^{229}Pa

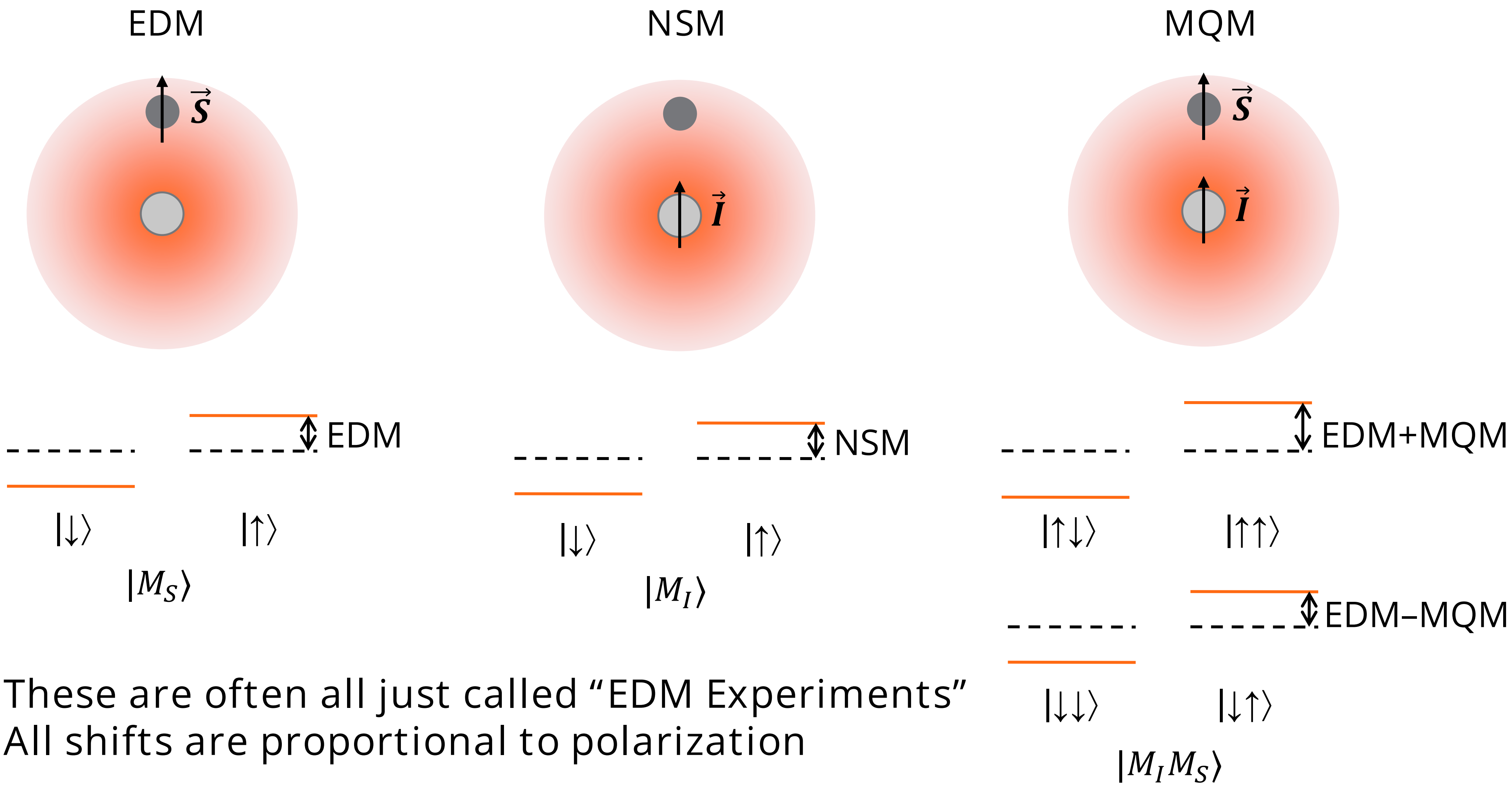


eEDM: Field $\sim 10^3$

MQM: Field Nucleus $\sim 10^4$

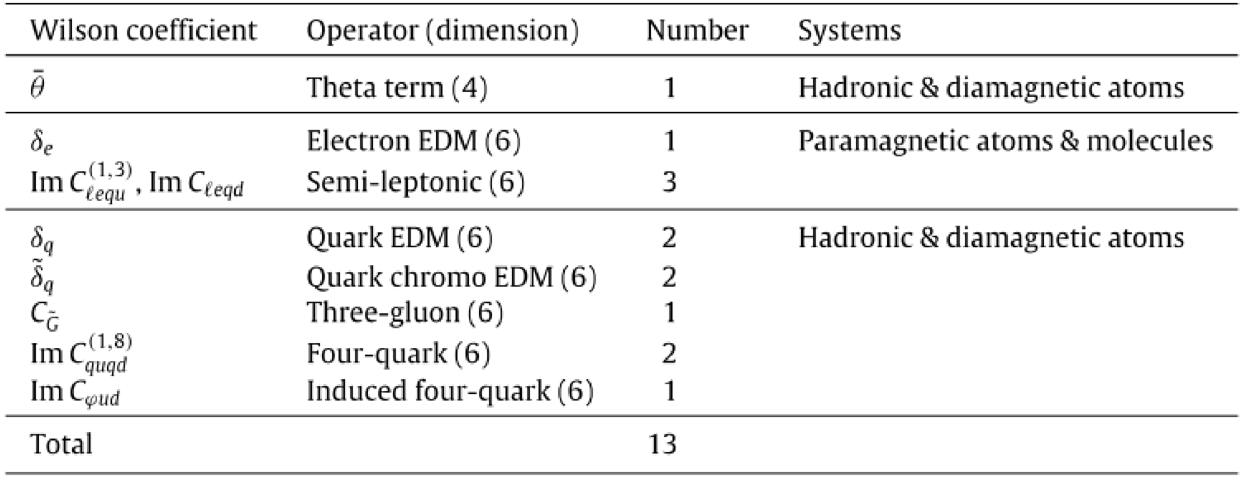
NSM: Field Nucleus $\sim 10^6$

EDM vs. NSM. vs. MQM shifts



- These are often all just called “EDM Experiments”
- All shifts are proportional to polarization

EDM, NSM, MQM – Complementarity

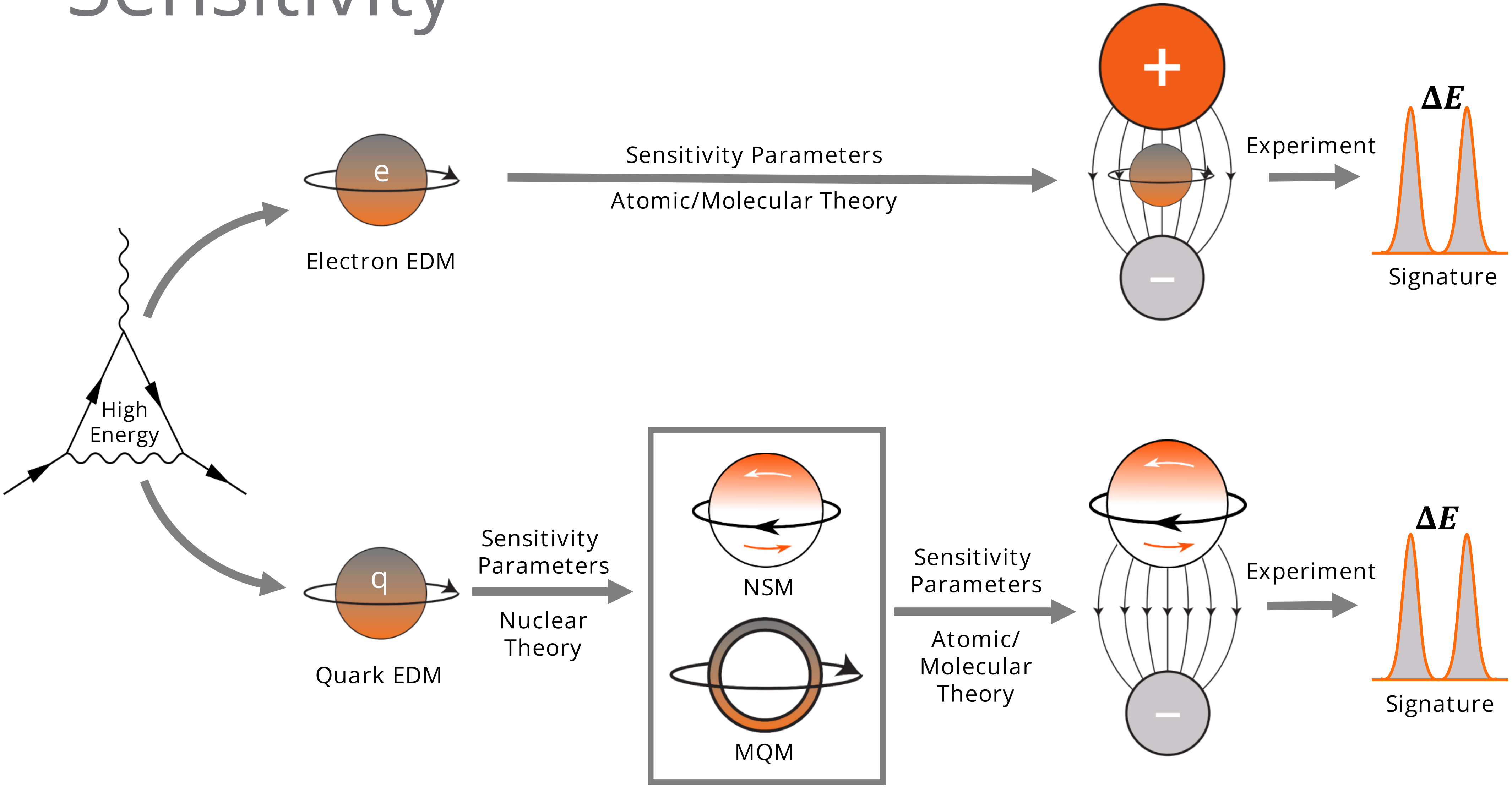


Wilson coefficient	Operator (dimension)	Number	Systems
$\bar{\theta}$	Theta term (4)	1	Hadronic & diamagnetic atoms
δ_e	Electron EDM (6)	1	Paramagnetic atoms & molecules
$\mathrm{Im}\, C_{\ell equ}^{(1,3)}$, $\mathrm{Im}\, C_{\ell eqd}$	Semi-leptonic (6)	3	
δ_q	Quark EDM (6)	2	Hadronic & diamagnetic atoms
$\tilde{\delta}_q$	Quark chromo EDM (6)	2	
$C_{\tilde{G}}$	Three-gluon (6)	1	
$\mathrm{Im}\, C_{quqd}^{(1,8)}$	Four-quark (6)	2	
$\mathrm{Im}\, C_{\varphi ud}$	Induced four-quark (6)	1	
Total		13	

J. Engel, M. J. Ramsey-Musolf, and U. van Kolck, Prog. Part. Nucl. Phys. 71, 21 (2013)

- CPV sector parameter space is complex!
  - “Electron EDM” searches actually sensitivite to electron EDM and CPV electron-nucleon couplings
  - NSM, MQM searches sensitive to hadronic sources (θ_{QCD}, quark EDM and chromo-EDM, CPV nuclear forces, …)
- Multiple sources requires multiple systems to translate measurements into physically meaningful values
- Dependencies are generally complementary

Sensitivity



Fundamental Particles/Forces

Fundamental CPV Moments

Nuclear CPV Moments

Amplification by Molecule

Measurement

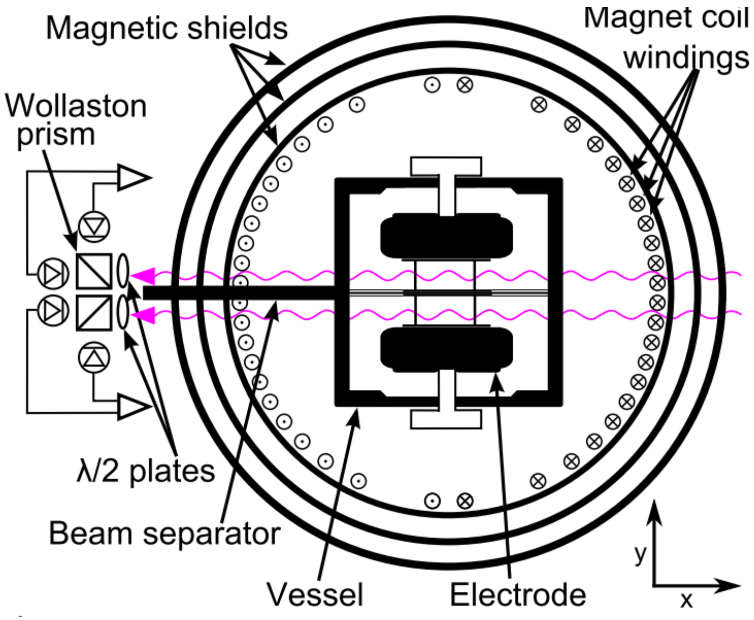
Part II: Select Contemporary Experiments

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!

^{199}Hg EDM

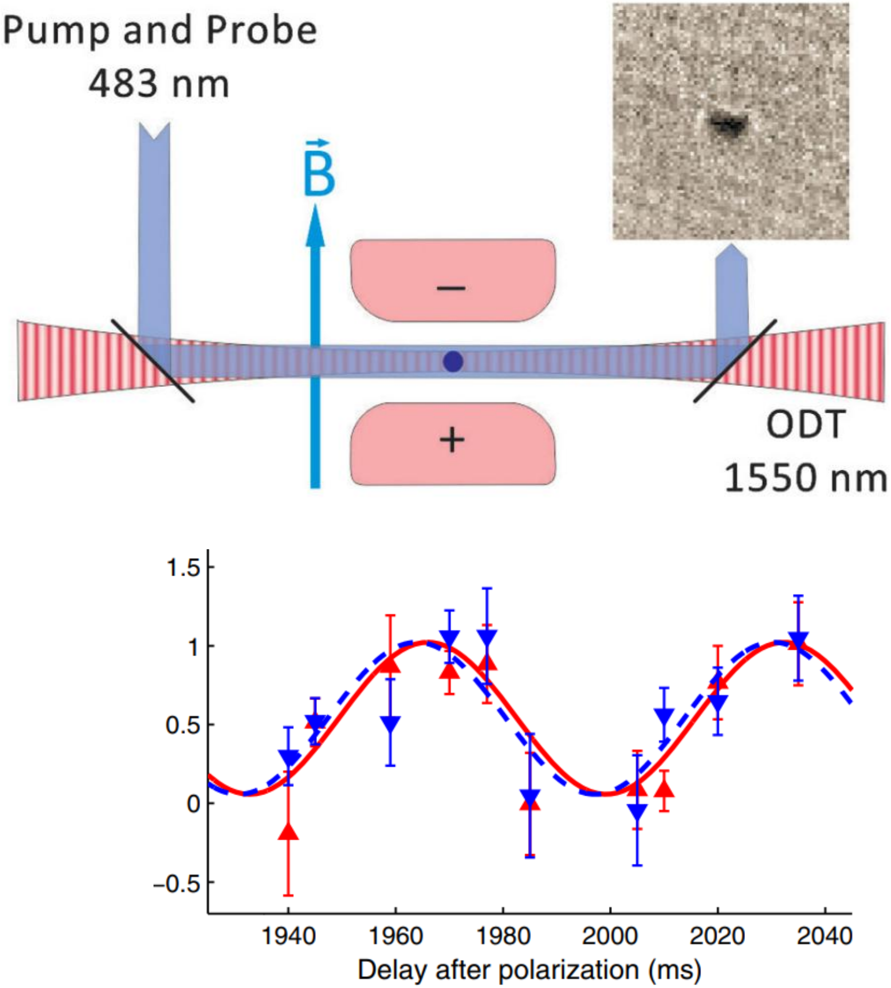
- University of Washington
- ^{199}Hg in a vapor cell
- $I = 1/2$ due to valence *n*
  - Spherical nucleus → no "nuclear enhancement"
- $^1S_0$ (s^2 electron configuration, no net spin or L)
  - Heavy nucleus, highly relativistic electrons → large "atomic enhancement"
  - Electrons are paired off → very small magnetic sensitivity
- 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)
- ^{129}Xe 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/

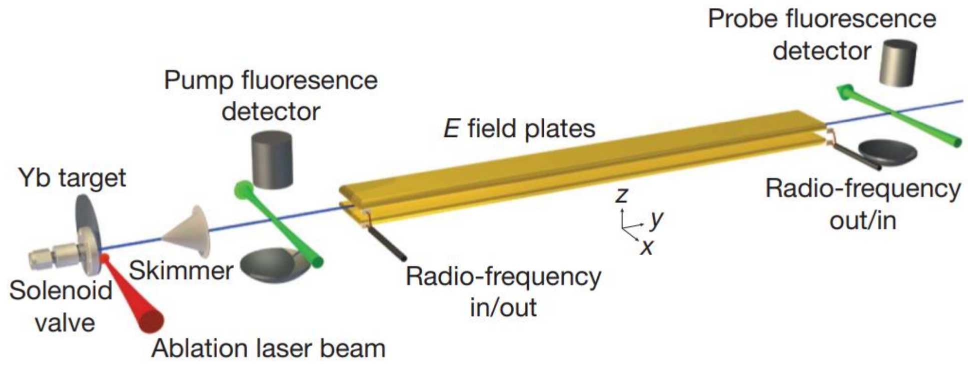
^{225}Ra EDM

- Argonne National Lab
- ^{225}Ra, $I = 1/2\,,\ {}^{1}S_{0}$
    - 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
- Work at USTC with ^{171}Yb using advanced quantum methods
    - PRL 129, 083001 (2022)

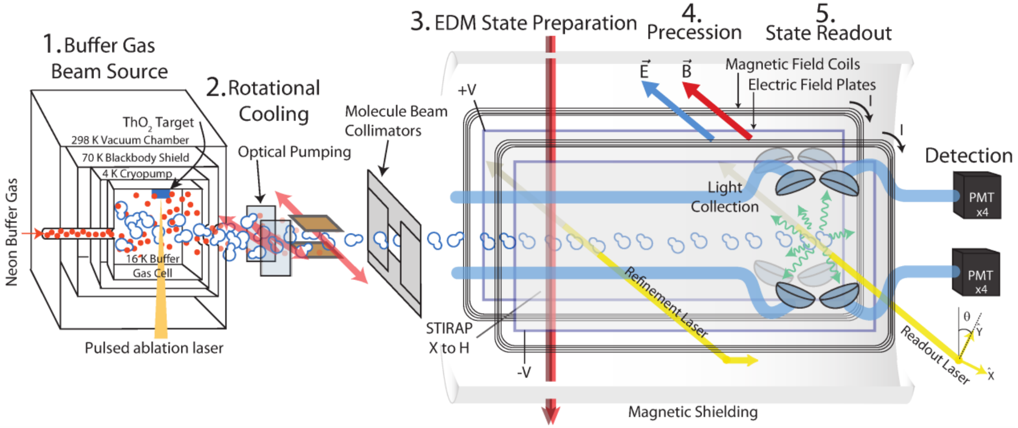


Ra EDM @ ANL
R. H. Parker, et al., PRL 114, 233002 (2015)

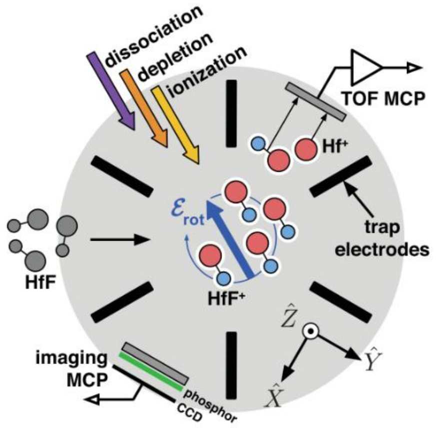
Molecular Experiments



YbF, Imperial
- Spin precession in pulsed supersonic beam
- First to beat atomic Tl limits
- $|d_e| < 1.1 \times 10^{-27}$ e cm (2011)



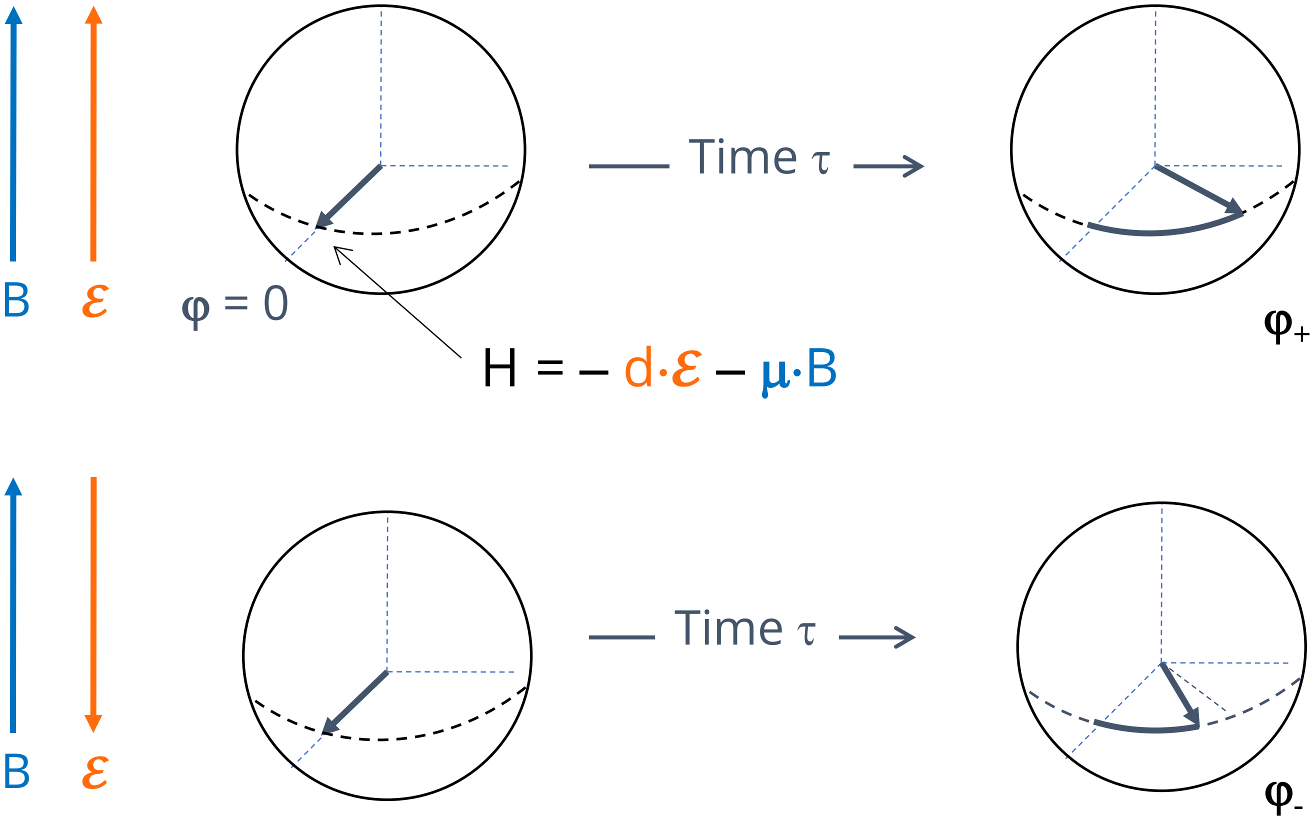
ACME, ThO, Harvard/Chicago/Northwestern
- Spin precession in cryogenic beam
- $|d_e| < 8.7 \times 10^{-29}$ e cm (2014)
- $|d_e| < 1.1 \times 10^{-29}$ e cm (2018)



HfF$^+$, JILA/Boulder
- Spin precession in ion trap
- $|d_e| < 1.3 \times 10^{-28}$ e cm (2017)
- $|d_e| < 4.1 \times 10^{-30}$ e cm (2023)

- ~300x in ~12 years
- Each is being upgraded
- More are under way
- Extending to nuclear CPV
- Will discuss more about these experiments later

An Idealized EDM Experiment



$\varphi = 0$

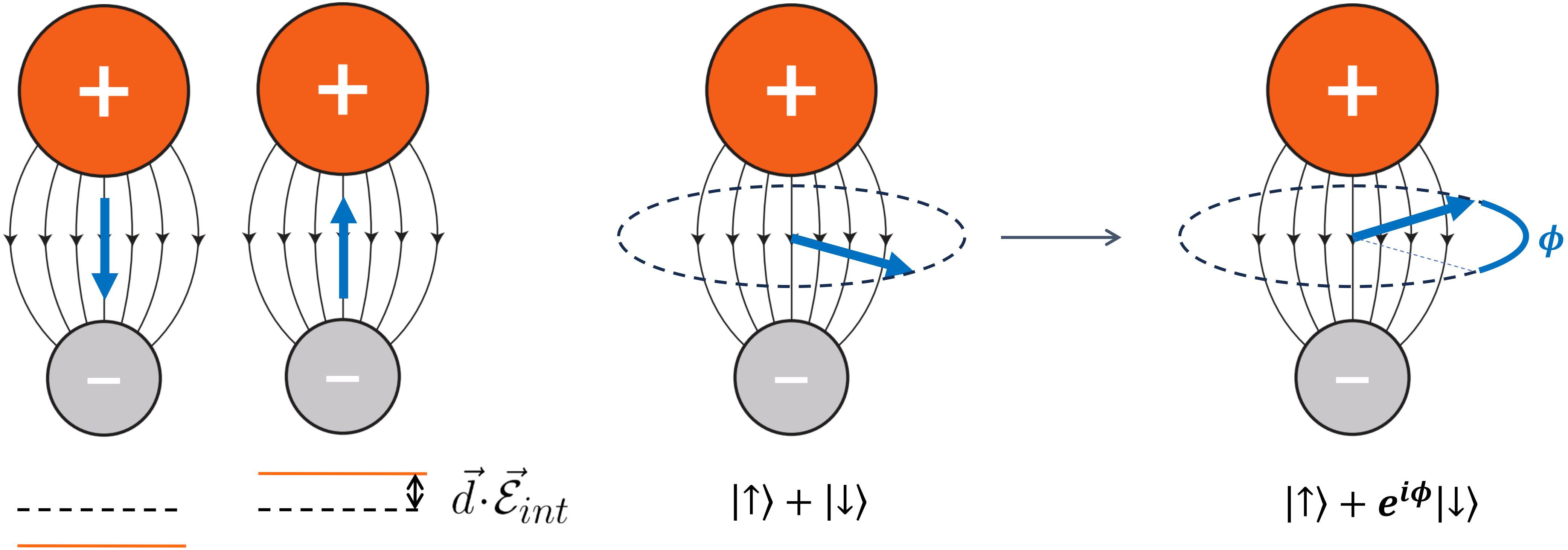
$H = -d\cdot\mathcal{E} - \mu\cdot B$

$\varphi_{+} = \mu B\tau + d\mathcal{E}\tau$

$\varphi_{-} = \mu B\tau - d\mathcal{E}\tau$

$$\boxed{\Delta\varphi \propto d\mathcal{E}\tau}$$

An Idealized EDM Experiment



$\vec{d}\cdot\vec{\mathcal{E}}_{int}$

$|\uparrow\rangle + |\downarrow\rangle$

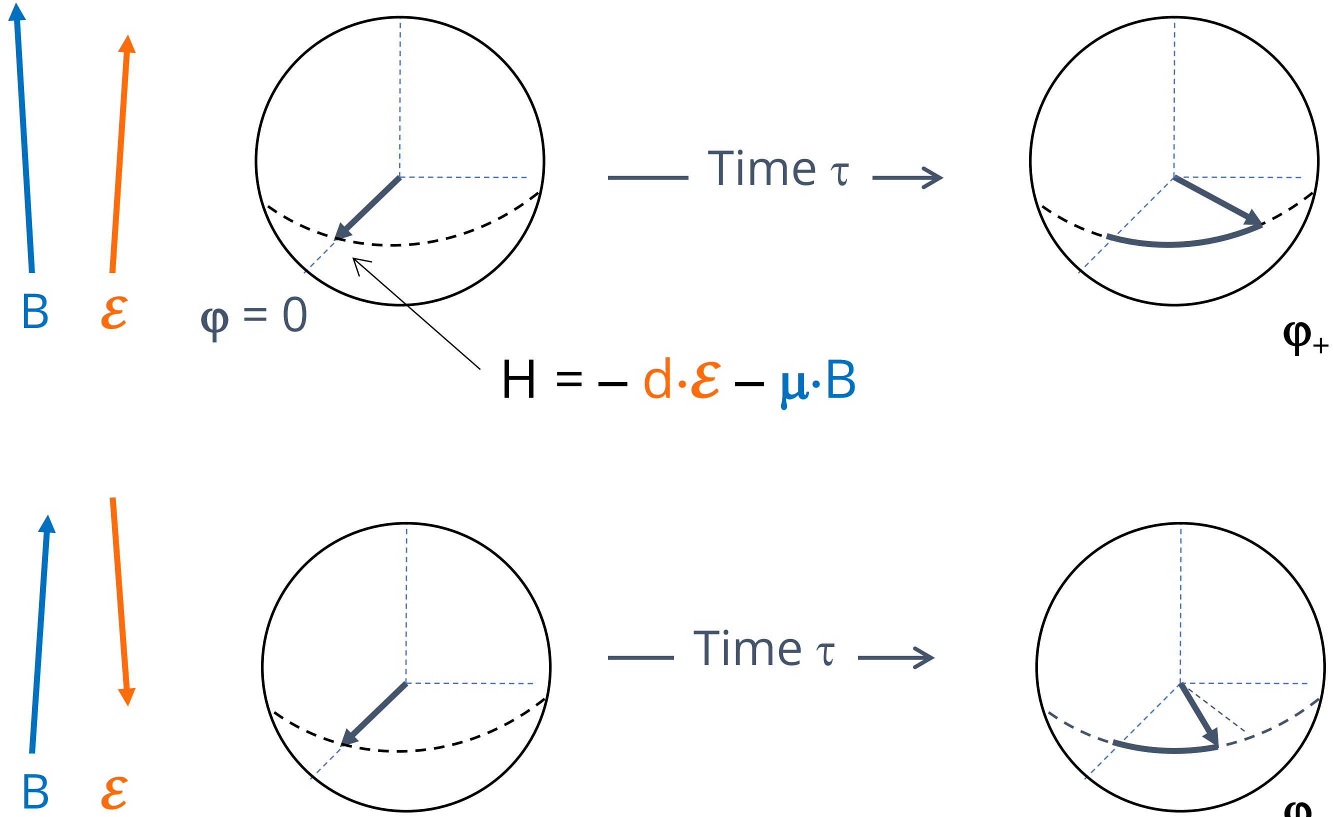
$|\uparrow\rangle + e^{i\phi}|\downarrow\rangle$

$|\downarrow\rangle$ $|\uparrow\rangle$

Electron spin

“Spin Precession”

Nothing is perfect…



$H = -\,d\cdot\mathcal{E} - \mu\cdot B$

$\varphi_+ = \mu B\tau + d\mathcal{E}\tau + ???$

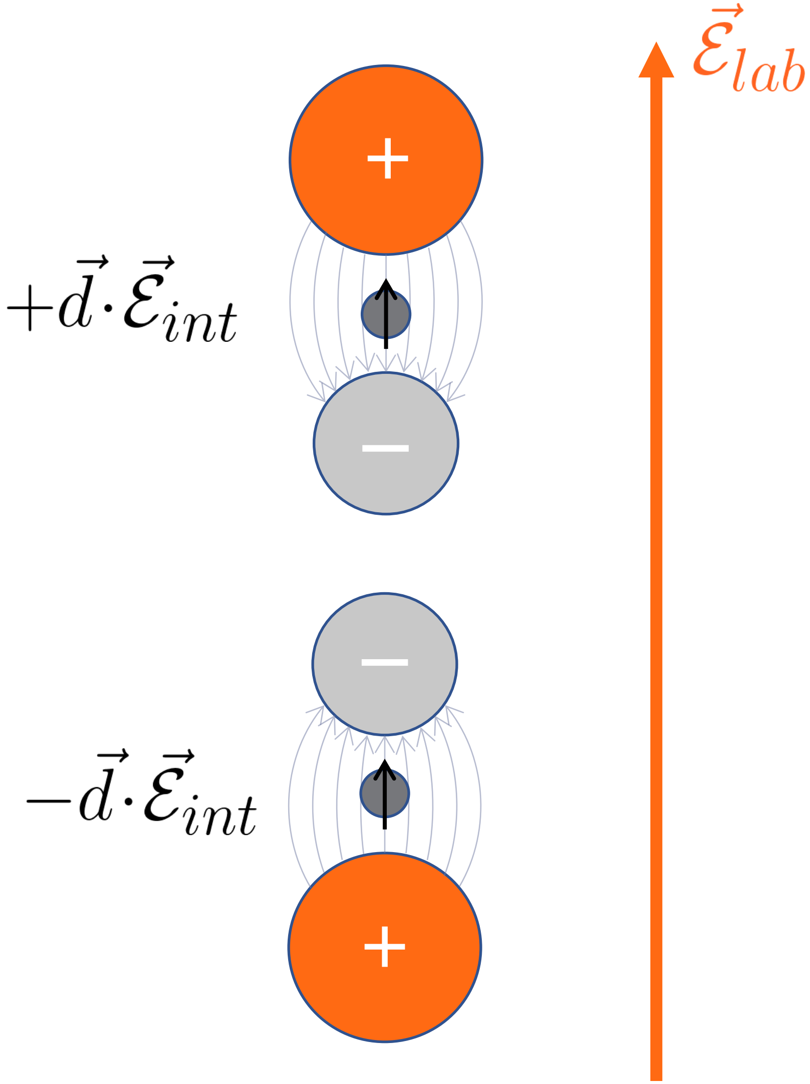
$\varphi_- = \mu B\tau - d\mathcal{E}\tau + ???$

$\boxed{d\mathcal{E} / \mu B < 10^{-6}}$

$\boxed{\Delta\varphi \propto d\mathcal{E}\tau + ???}$

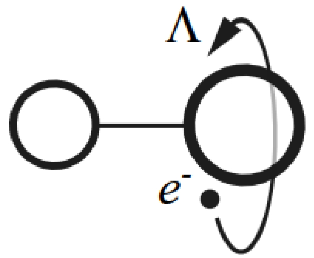
Internal Co-magnetometers

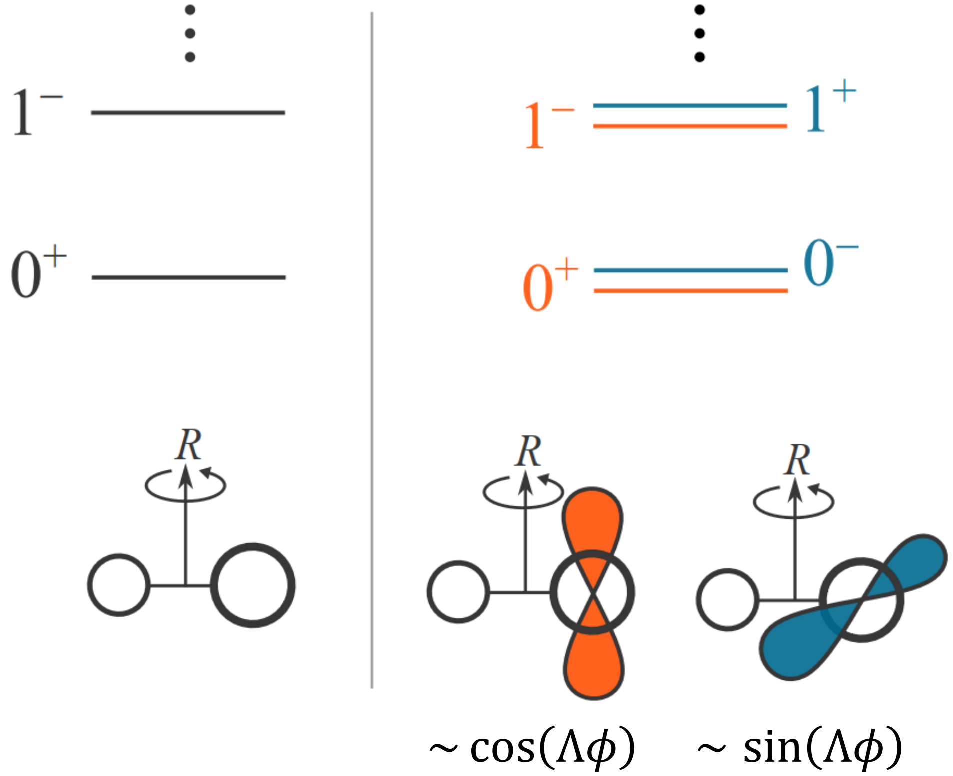
- When a molecule can be fully polarized, we get two states with opposite alignment of internal fields
- EDM see only this internal field, *not* the external field
  - External field is just for polarization
- Change EDM shift without changing external fields – just tune lasers to address different states
- Very powerful for rejection of systematic errors
- “Internal co-magnetometer” – can use the molecule to independently measure B, E fields
  - As opposed to a co-magnetometer species mixed in, such as atomic sodium in atomic thallium experiment



Parity Doublets

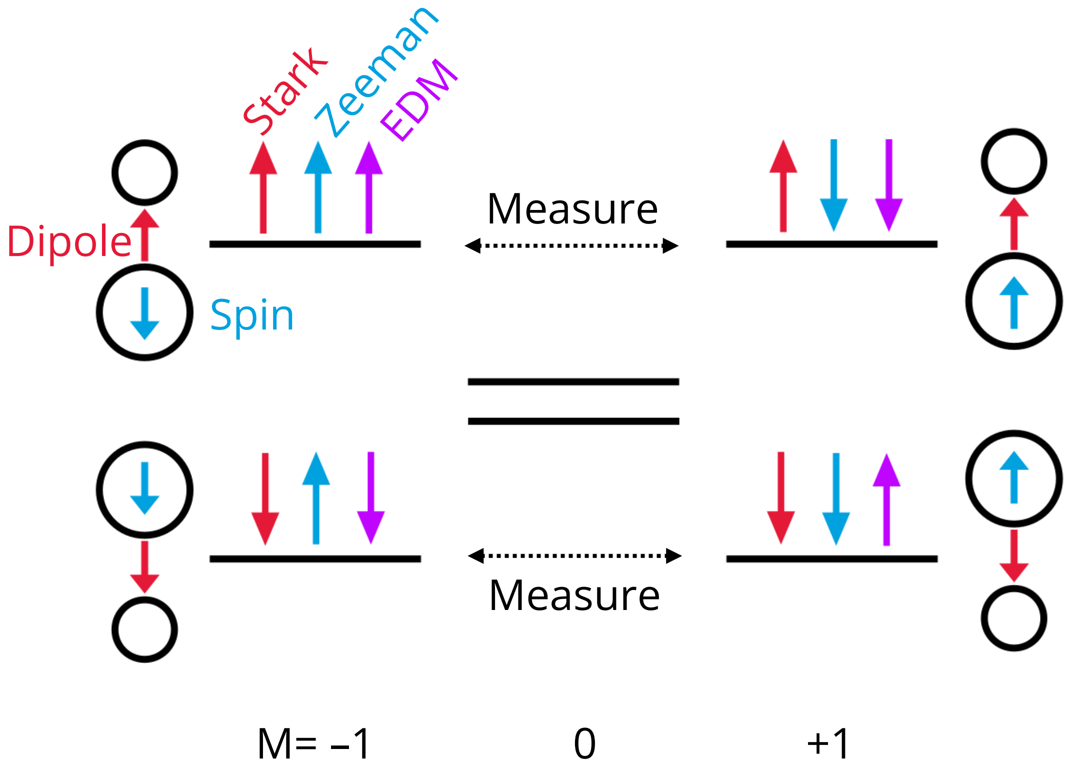
- States with $\Lambda = \vec{L}\cdot\hat{n} \neq 0$ have Λ (or Ω) “parity doublets”
- States with $\pm\Lambda$ are nominally degenerate
  - $\psi_{\pm\Lambda} \sim \exp(\pm i\Lambda\phi)$
- Eigenstates are
$$|\pm\rangle \propto (|+\Lambda\rangle \pm |-\Lambda\rangle)$$
$$\sim \sin(\Lambda\phi)\,,\cos(\Lambda\phi)$$
- States split by molecular rotation
  - Different moments of inertia
  - Each rotational state splits
  - This is a back-of-the-envelope explanation, depends on detailed structure, see for example arXiv:2506.10904
- Can often polarize in ~1 V/cm vs. ~10 kV/cm without parity doublets
- Parity doublets can arise from different mechanisms in polyatomic molecules… more on that later





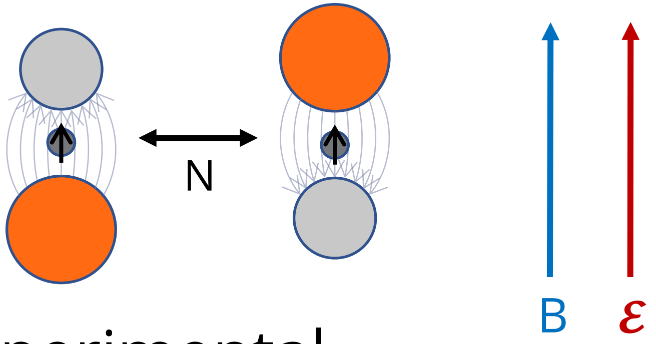
Internal Co-magnetometers

- Polarized parity doublets → two pairs of states for spin precession measurement
- Changes sign of EDM without changing external fields
- Also much smaller E fields needed
- Reversing large E fields is very hard…
- Critical tool in ThO, HfF$^+$
- Somewhat uncommon in diatomics



Isolating the EDM – “Switches”

- All interactions have distinct behavior under reversal of:
  - $\mathcal{E}$ - External electric field
    - Interacts with molecular dipole
  - B - External magnetic field
    - Interactions with electron spin
  - N - Molecule dipole orientation
    - Changes direction of molecular dipole



- Measure spin precession in various experimental configurations and look for correlations

Quantity	$\mathcal{E}$-flip	B-flip	N-flip
Electron EDM	–	+	–
Applied B field	+	–	+
Background B field	+	+	+
Leakage current/v x $\mathcal{E}$/Geometric phases	–	+	+
etc…			

← Limited previous atom experiments

Lecture II: Select Ongoing and Future Developments

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

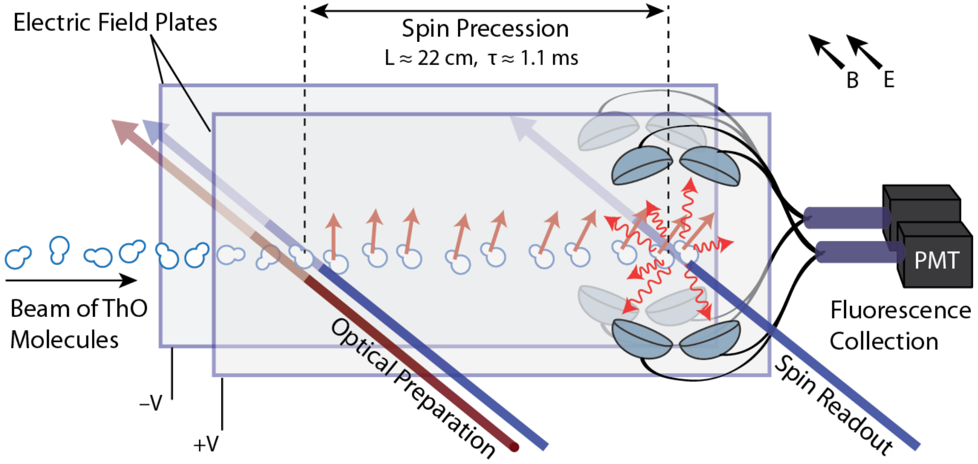
We will not discuss all ongoing and future developments!

Heavily biased towards things that that I work on! Not egotistical, just lazy.

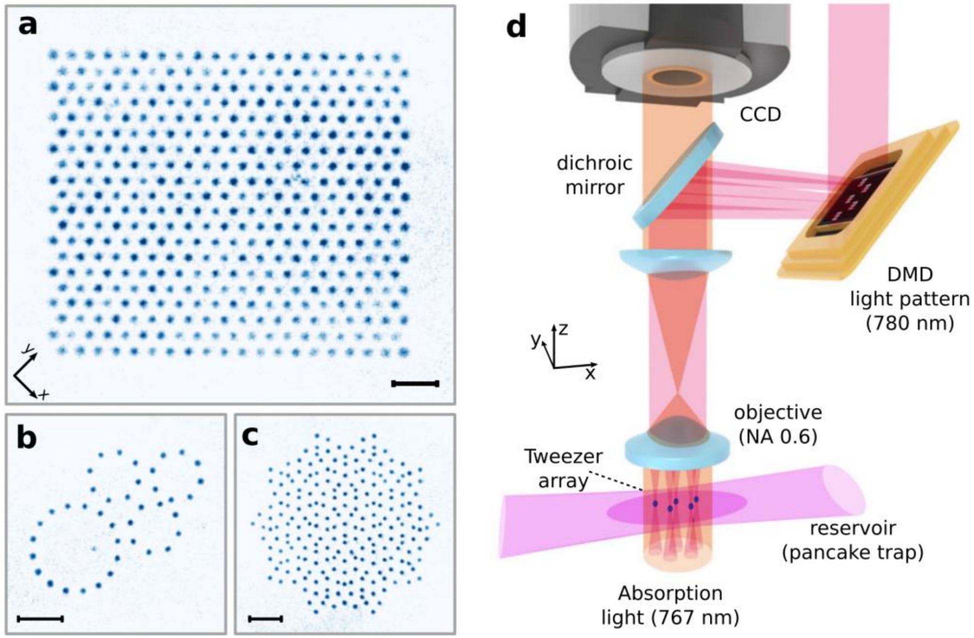
Laser cooling

Motivation for molecular laser cooling

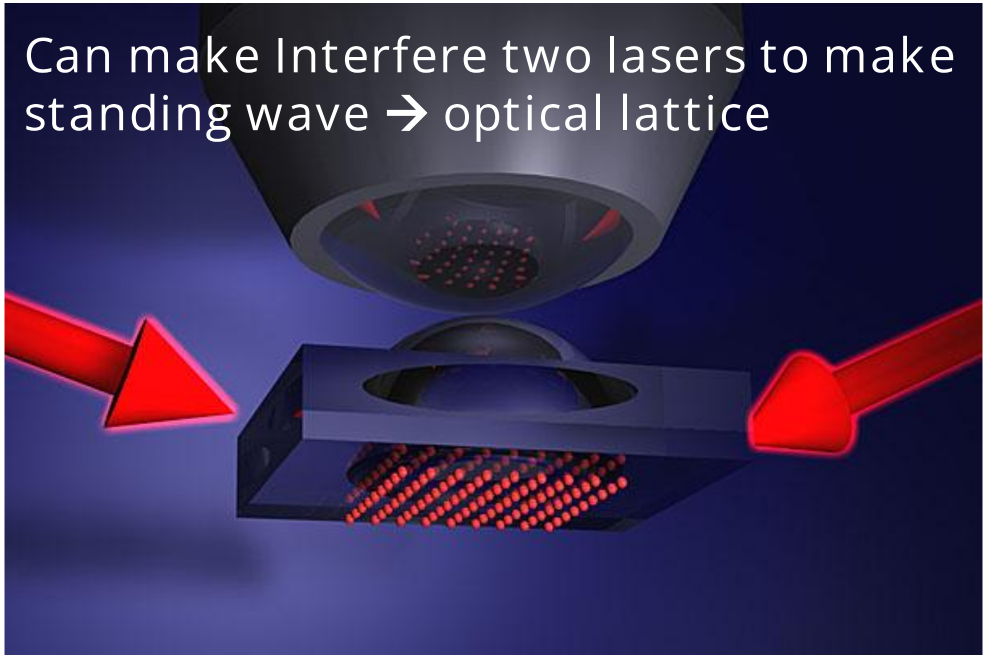
- Beam experiments (ThO, YbF) limited by time of flight, τ ~ few ms
- Can extend by slowing and compressing beam
- Trapping can yield orders of magnitude improvement
  - Critical for long coherence time of HfF^+, Ra experiments
- For neutral species, requires “ultra-cold” temperatures, <1 mK
  - Suitable conservative traps are shallow
  - Free molecules (fountains) must be very slow
- → Laser cooling
- Also highly relevant for atomic searches (Cs, Fr, Ra, …)



Quantum Control with Atoms



Y. Wang *et al.*, npj Quantum Information 6, 54 (2020)



Can make Interfere two lasers to make standing wave → optical lattice

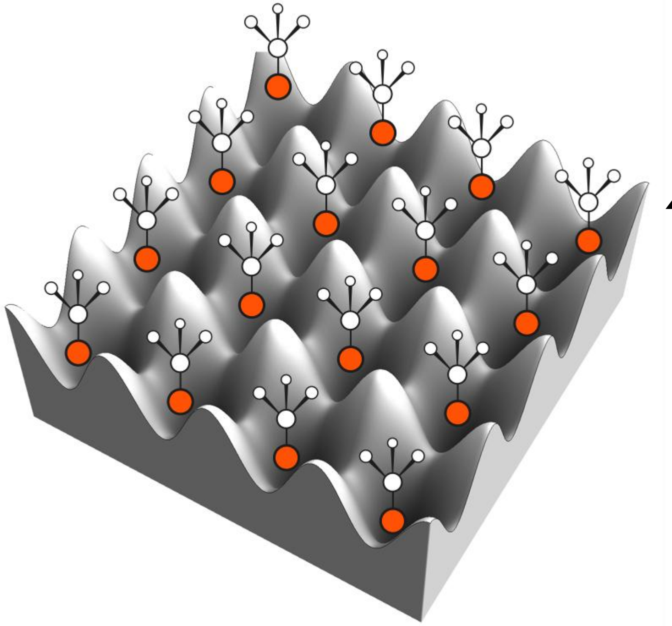
Greiner Lab, Harvard University

- Atomic experiments can realize *extreme* levels of control – internal and external states, environmental couplings, engineered interactions, etc.
- Molecular CPV experiments have not yet benefitted from any of these advances due to complex molecular structure
  - Active area of research, and major advances are coming!

Ultracold CPV Searches

- 10^6 molecules
- 10 s coherence
- Large enhancement(s)
- Robust error rejection
- 1 week averaging

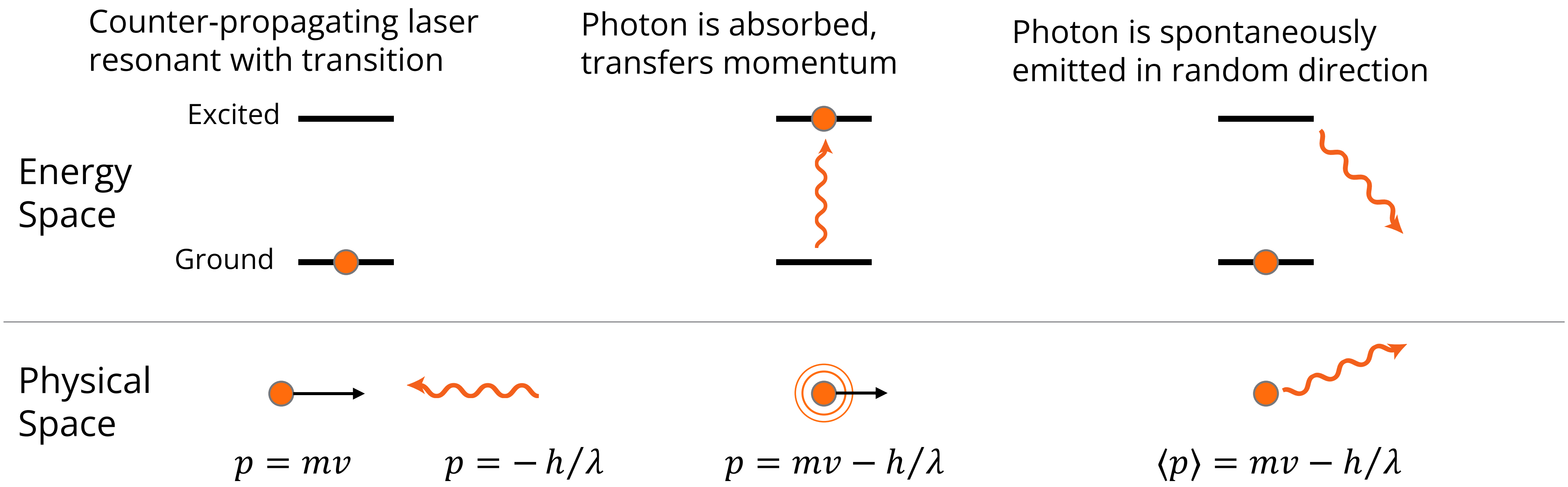
Access to CPV @
1,000 TeV (1-loop)
50 TeV (2-loop)



Heavy, polar molecule
sensitive to new physics

Optical Forces

- Lasers can be used to apply forces to atoms and molecules
    - Including cooling and trapping
    - Major driver of AMO, QIS
- Basic idea: apply forces via (nearly) resonant lasers



Counter-propagating laser resonant with transition

Photon is absorbed, transfers momentum

Photon is spontaneously emitted in random direction

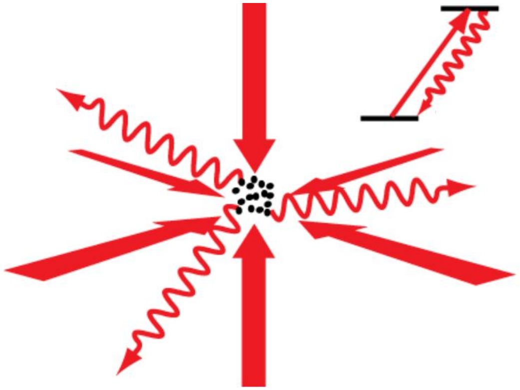
$p = mv$ $\quad p = -h/\lambda$

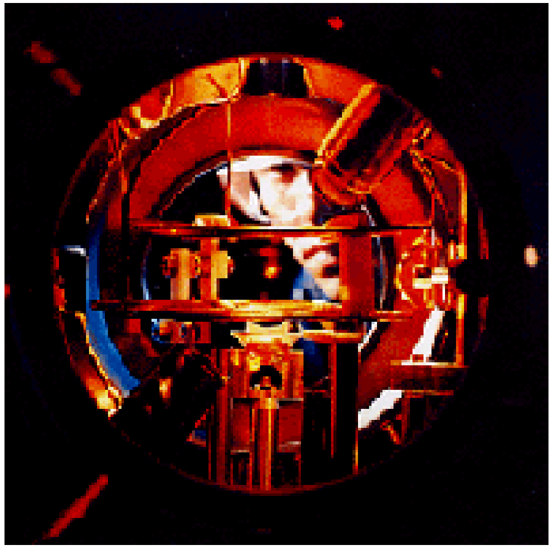
$p = mv - h/\lambda$

$\langle p \rangle = mv - h/\lambda$

Laser cooling/trapping

- These temperatures enable:
  - Quantum coherence
  - Trapping in shallow, “non”-perturbative optical traps
- Critical ingredient in many atomic quantum science experiments
  - Clocks, atom arrays, quantum gases, …
- Why not just laser-cool everything? We shall see…

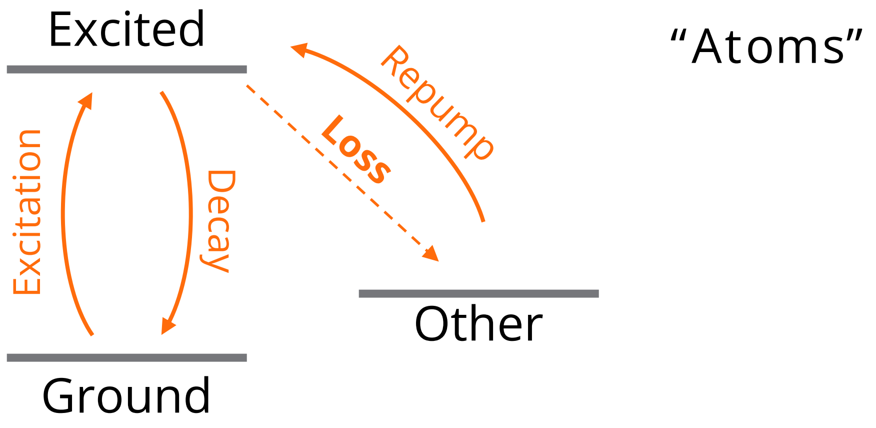


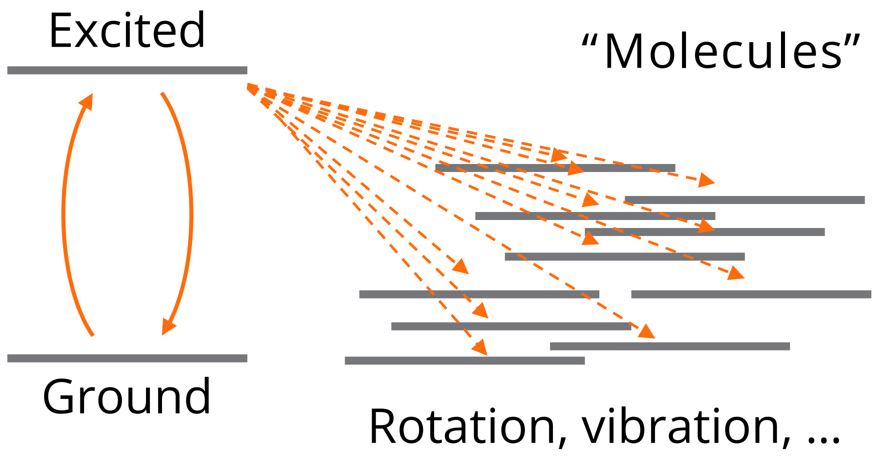


Deceleration of Atoms. NobelPrize.org. Nobel Prize Outreach AB 2022

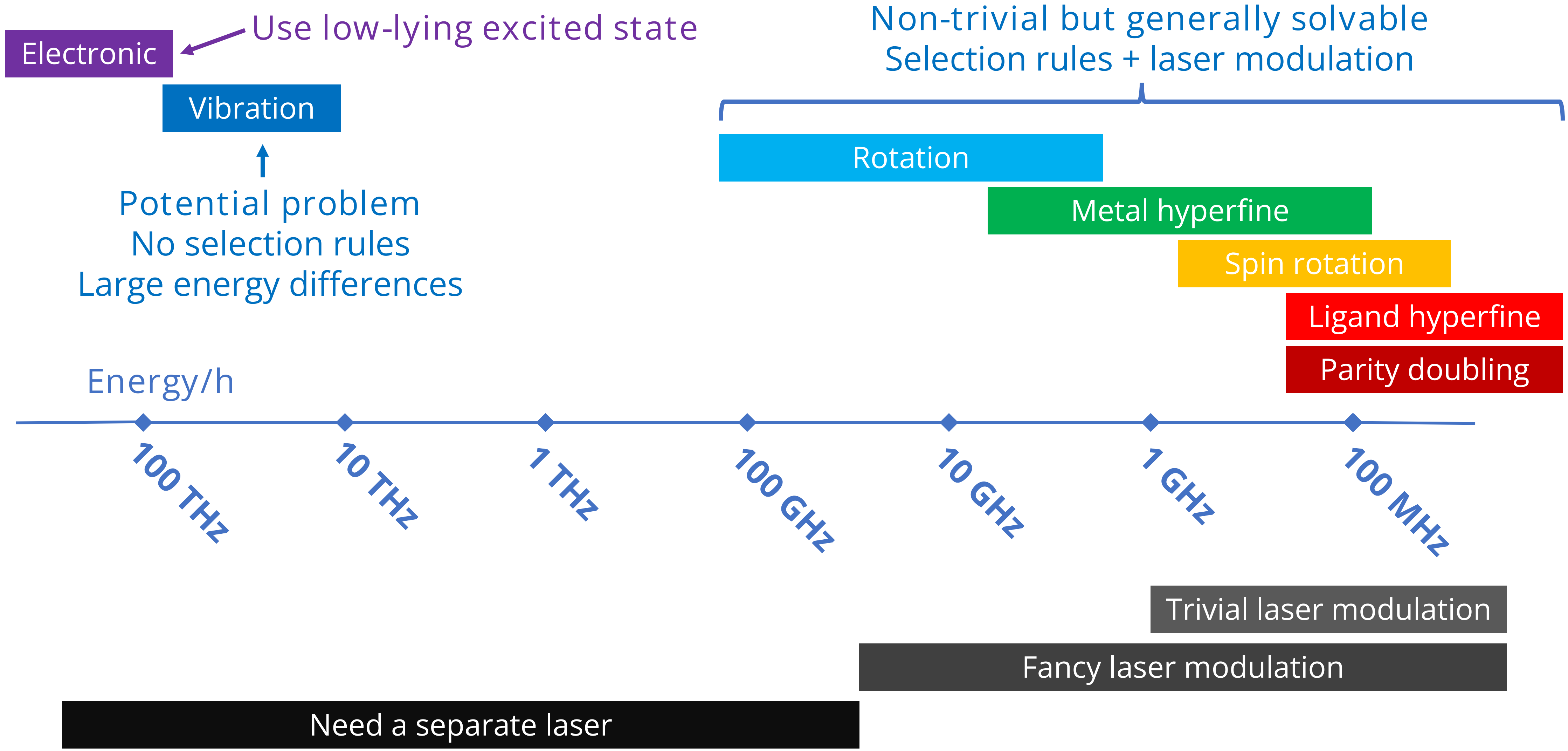
Laser cooling molecules

- Apply forces by photon scattering
- Requires many (~10^5) cycles of absorption, spontaneous decay
  - Photon recoil h/λ
  - $N_{photons} \sim m v_{initial} / (h/\lambda)$
  - $v_{initial} \sim 100\ m/s$ (why? Later…)
  - $N_{photons} \sim M[amu] \times \lambda[nm]$
- Decay to other states stops the cooling process
- Internal vibrational, rotational levels are excited in decay
- For certain molecules, this is *manageable*





Photon cycling in molecules



Electronic

Use low-lying excited state

Vibration

Potential problem
No selection rules
Large energy differences

Non-trivial but generally solvable
Selection rules + laser modulation

Rotation

Metal hyperfine

Spin rotation

Ligand hyperfine

Parity doubling

Energy/h

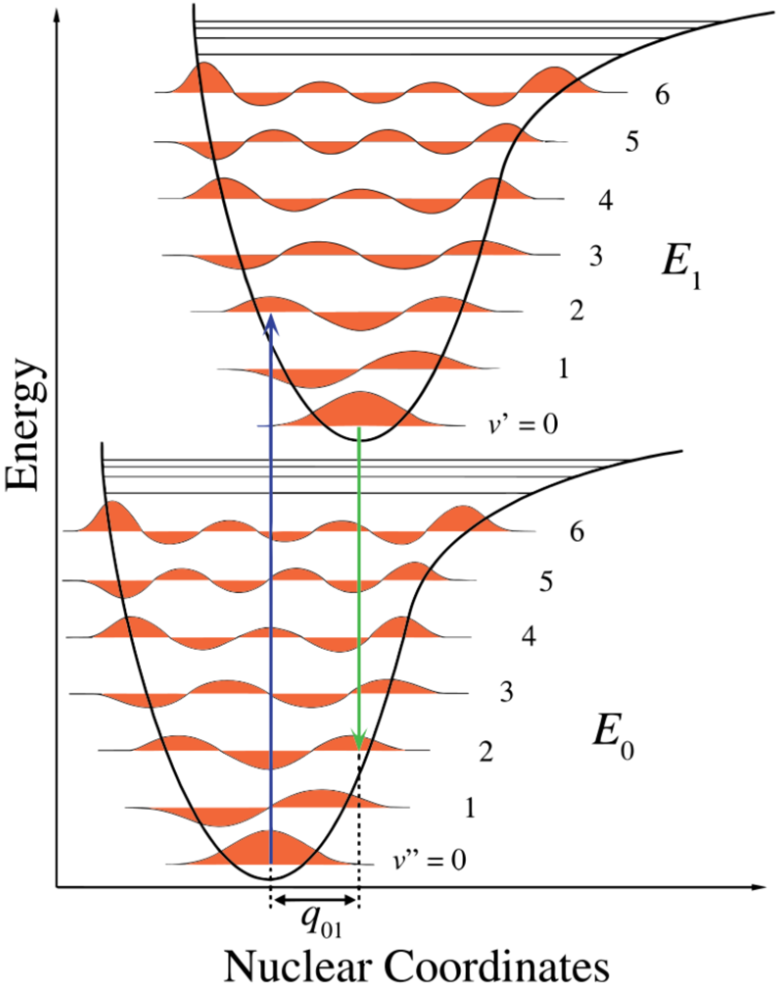
Trivial laser modulation

Fancy laser modulation

Need a separate laser

Vibrational Structure

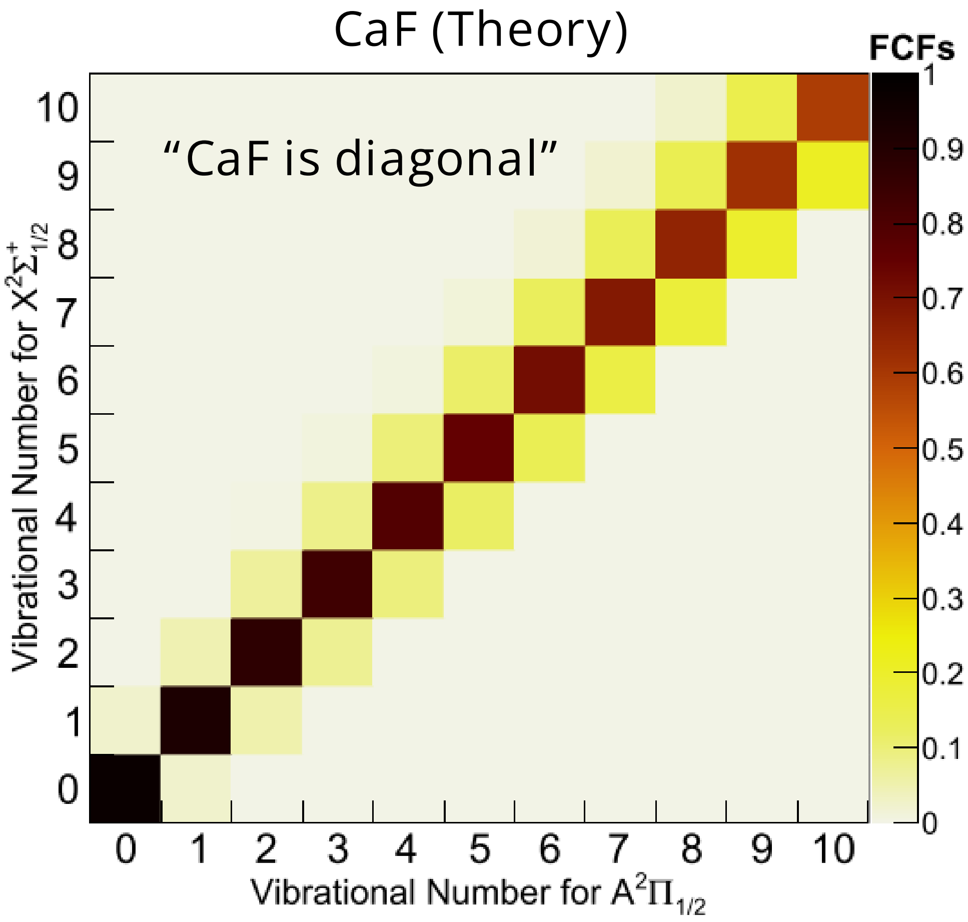
- Biggest challenge: vibration
    - *No selection rules!*
- Each electronic state has a potential energy surface (PES)
    - Energy vs. nuclear distance
    - Vibrational states are eigenstates of this potential
- Born-Oppenheimer: since electron motion is much faster than nuclear motion, electronic transitions instantaneously change the PES
- “Instantaneous perturbation” – vibrational wavefunction unchanged during electronic decay
- Probability for vibrational state change from $i \to j$ is $p_{ij} = \left|\langle \psi_i | \psi_j \rangle\right|^2$
- Franck-Condon Factors (FCFs)



From Chem.LibreTexts.org

“Diagonal” FCFs

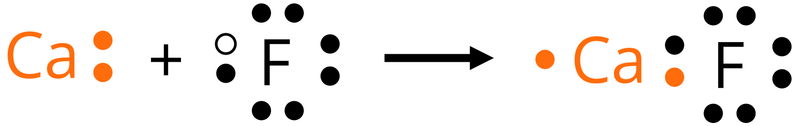
- Ideally, we would like no vibrational change
  - $p_{ij} = \delta_{ij}$
- The matrix p_{ij} would be diagonal – a “diagonal transition”
- Always some chance of “off-diagonal” decays, since $p_{ij} \approx \delta_{ij}$ at best



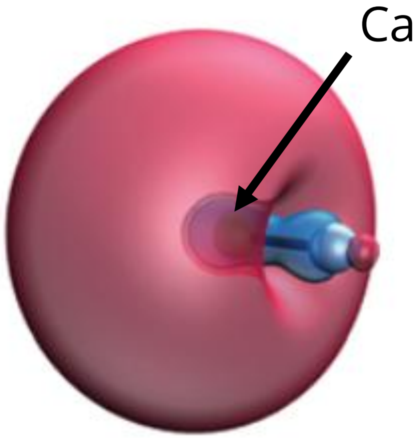
Y. Hao et al., J. Chem. Phys. 151, 034302 (2019)

Example: CaF

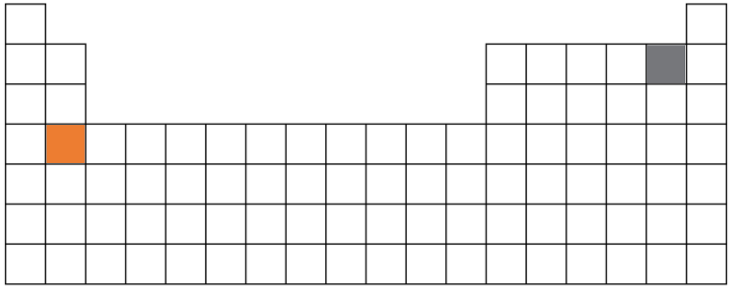
- Intuitive explanation for an important case when this happens – alkaline earth atoms with single ionic bonds
- Ca has two valence electrons (*s^2*)
- F wants one electron



- Result is a single, metal-centered, *s* electron
  - This very simple bonding is unique
  - Bonding electron is deeply bound, hard to excite
  - "Looks like an alkali metal"
- Very similar structure for other [s^2 atom]F molecules
  - CaF, SrF, BaF, RaF, …
  - Yb, Hg have s^2 valence and are similar
  - Also when F → OH, OCH_3, … (later)



Ground state electronic wavefunction of CaF



M. V. Ivanov, T.-C. Jagau, G.-Z. Zhu, E. R. Hudson, and A. I. Krylov, Phys. Chem. Chem. Phys. 22, 17075 (2020)

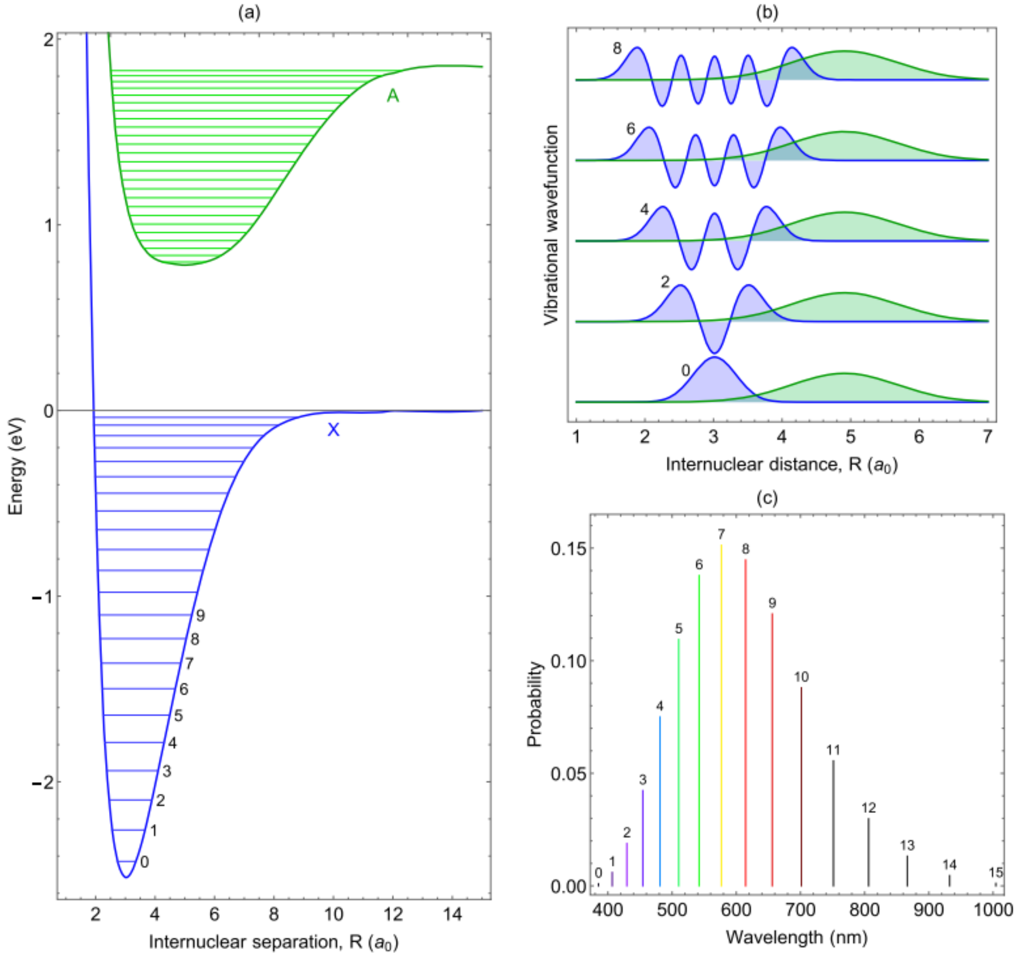
FCFs – Diagonal vs. Non-diagonal

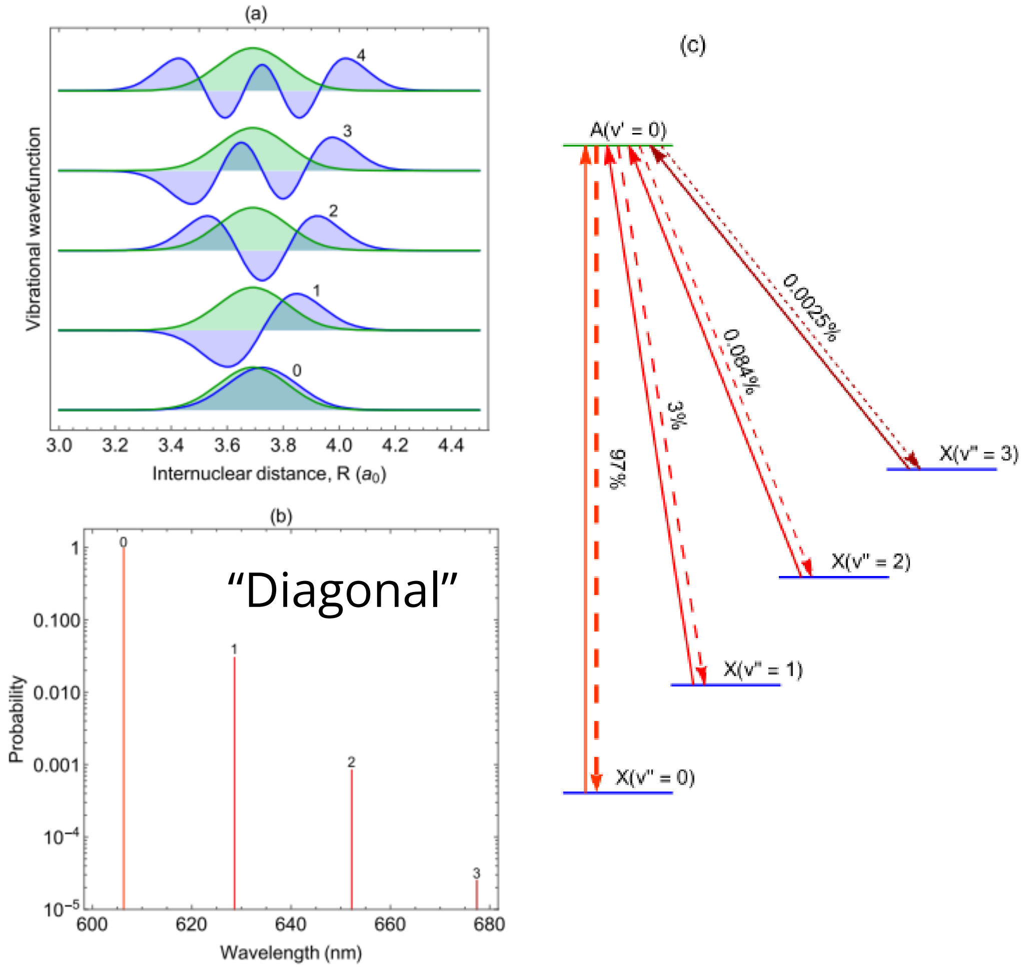
Li : F :

LiF is “not diagonal”

• Ca : F :

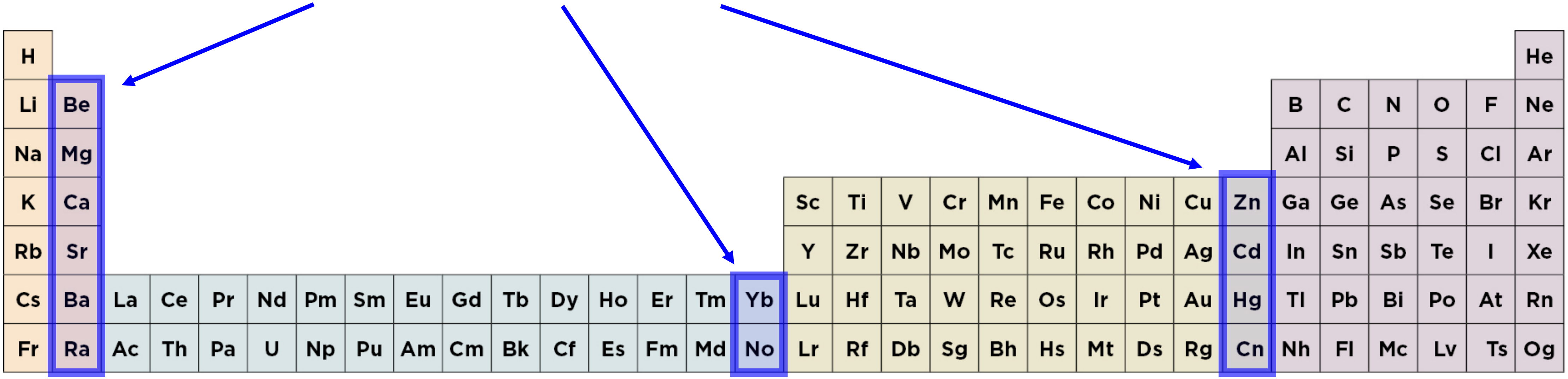
CaF is “diagonal”





M. R. Tarbutt, Contemp. Phys. 59, 356 (2018)

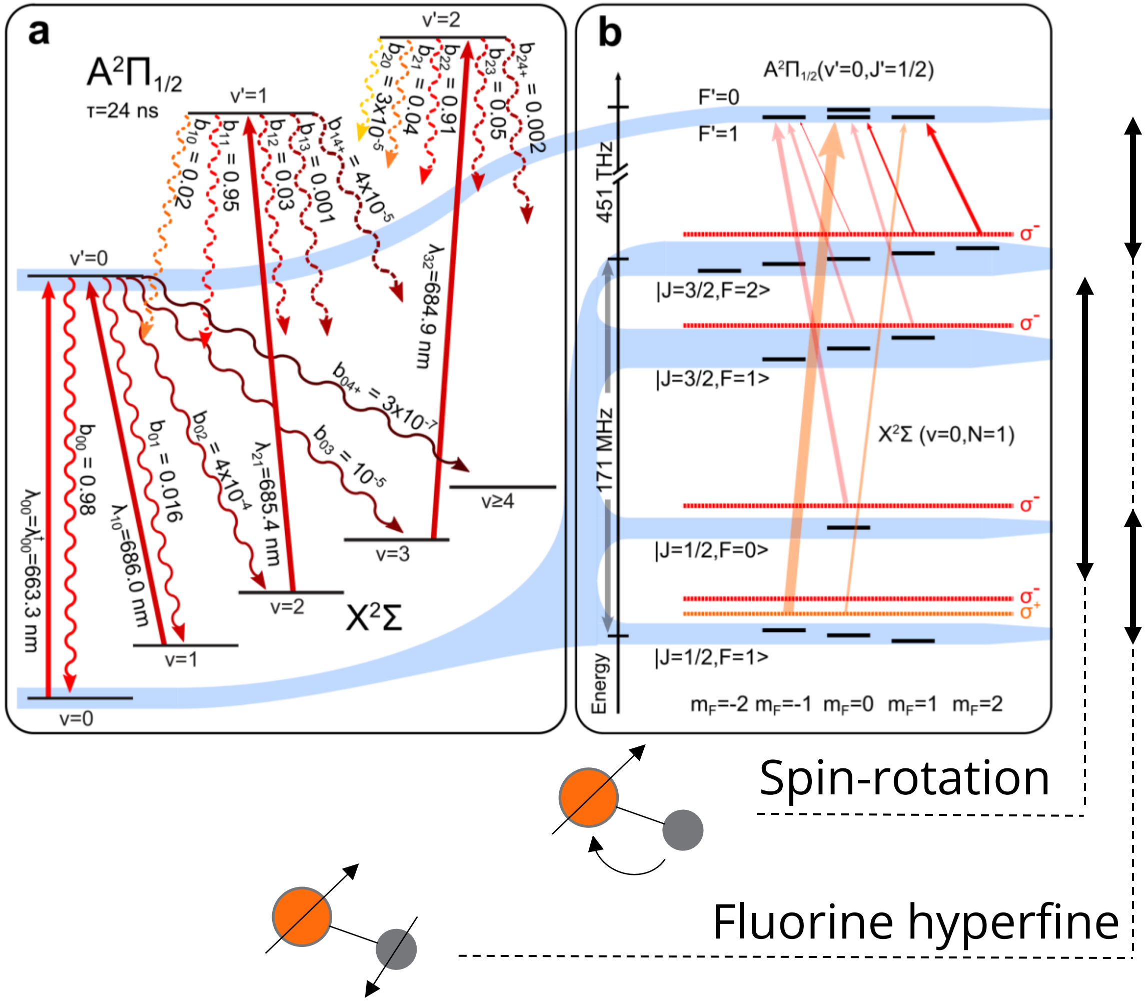
Atoms with s^2 valence configurations



H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca															Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr															Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

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
- SrF, CaF, YO, CaOH, BaF
  - SrF first, in 2014
  - Decades behind atoms, but moving rapidly
- Typically starts with cryogenic buffer gas beam (CBGB)



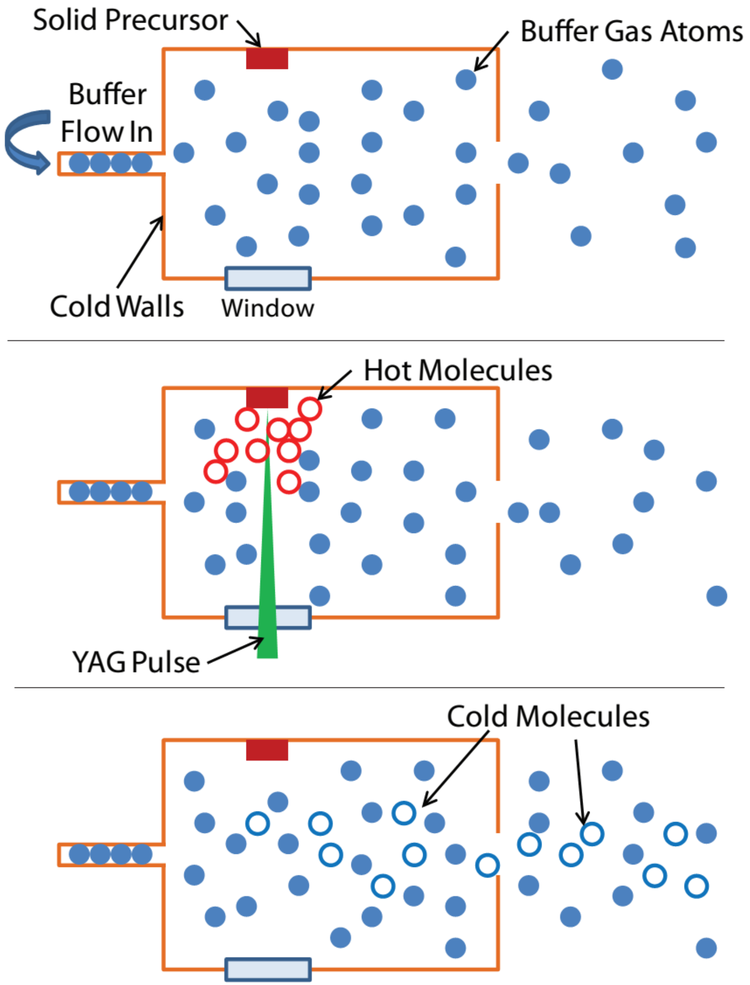
Spin-rotation

Fluorine hyperfine

J. F. Barry, D. J. McCarron, E. B. Norrgard, M. H. Steinecker, and D. DeMille, Nature 512, 286 (2014)

Cryogenic Buffer Gas Beams

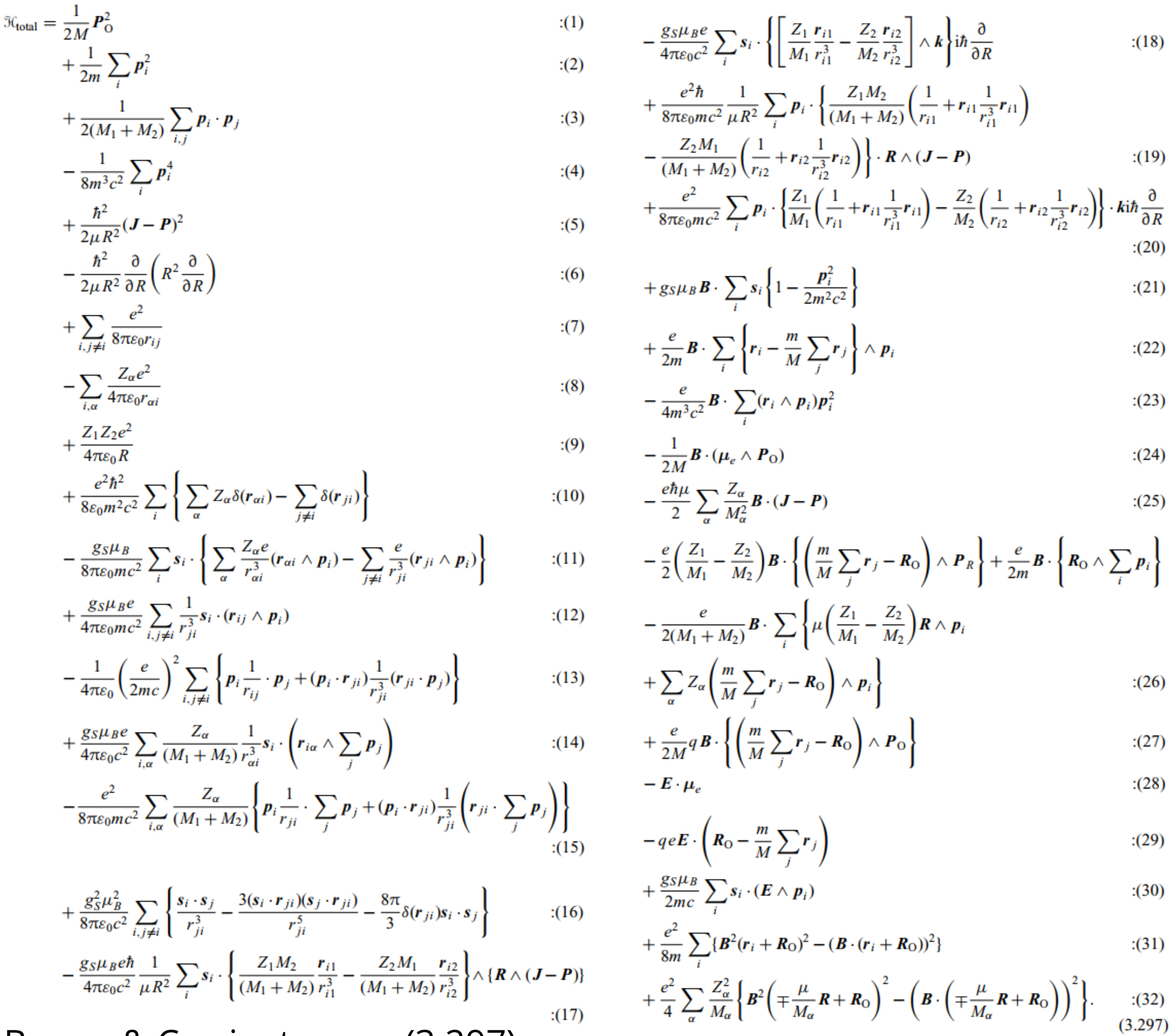
- These molecules are free radicals with low vapor pressure – challenging
- Use inert gas in cryogenic environment to cool via collisions
  - CBGB – Cryogenic buffer gas beam
  - Typically 4 K (He) → 20 K (Ne)
- "Works for anything"
- Cold, slow, high flux
- Concentrates population in lowest few rotational levels
- Used in ACME EDM experiment
- First step for most molecular laser cooling experiments



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

Basic Molecular Structure

- To move beyond simple intuitive picture, need some molecular info
- Molecular structure is a horrifying mess
- Fortunately, will consider “simple” ones whose structure we can write down



$$\mathcal{H}_{\text{total}} = \frac{1}{2M}\boldsymbol{P}_{\mathrm{O}}^2 \qquad :(1)$$

$$+\frac{1}{2m}\sum_i \boldsymbol{p}_i^2 \qquad :(2)$$

$$+\frac{1}{2(M_1+M_2)}\sum_{i,j}\boldsymbol{p}_i\cdot\boldsymbol{p}_j \qquad :(3)$$

$$-\frac{1}{8m^3c^2}\sum_i \boldsymbol{p}_i^4 \qquad :(4)$$

$$+\frac{\hbar^2}{2\mu R^2}(\boldsymbol{J}-\boldsymbol{P})^2 \qquad :(5)$$

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) \qquad :(6)$$

$$+\sum_{i,j\neq i}\frac{e^2}{8\pi\varepsilon_0 r_{ij}} \qquad :(7)$$

$$-\sum_{i,\alpha}\frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{\alpha i}} \qquad :(8)$$

$$+\frac{Z_1Z_2e^2}{4\pi\varepsilon_0 R} \qquad :(9)$$

$$+\frac{e^2\hbar^2}{8\varepsilon_0 m^2c^2}\sum_i\left\{\sum_\alpha Z_\alpha\delta(\boldsymbol{r}_{\alpha i})-\sum_{j\neq i}\delta(\boldsymbol{r}_{ji})\right\} \qquad :(10)$$

$$-\frac{g_S\mu_B}{8\pi\varepsilon_0 mc^2}\sum_i \boldsymbol{s}_i\cdot\left\{\sum_\alpha\frac{Z_\alpha e}{r_{\alpha i}^3}(\boldsymbol{r}_{\alpha i}\wedge\boldsymbol{p}_i)-\sum_{j\neq i}\frac{e}{r_{ji}^3}(\boldsymbol{r}_{ji}\wedge\boldsymbol{p}_i)\right\} \qquad :(11)$$

$$+\frac{g_S\mu_B e}{4\pi\varepsilon_0 mc^2}\sum_{i,j\neq i}\frac{1}{r_{ji}^3}\boldsymbol{s}_i\cdot(\boldsymbol{r}_{ij}\wedge\boldsymbol{p}_i) \qquad :(12)$$

$$-\frac{1}{4\pi\varepsilon_0}\left(\frac{e}{2mc}\right)^2\sum_{i,j\neq i}\left\{\boldsymbol{p}_i\frac{1}{r_{ij}}\cdot\boldsymbol{p}_j+(\boldsymbol{p}_i\cdot\boldsymbol{r}_{ji})\frac{1}{r_{ji}^3}(\boldsymbol{r}_{ji}\cdot\boldsymbol{p}_j)\right\} \qquad :(13)$$

$$+\frac{g_S\mu_B e}{4\pi\varepsilon_0 c^2}\sum_{i,\alpha}\frac{Z_\alpha}{(M_1+M_2)}\frac{1}{r_{\alpha i}^3}\boldsymbol{s}_i\cdot\left(\boldsymbol{r}_{i\alpha}\wedge\sum_j\boldsymbol{p}_j\right) \qquad :(14)$$

$$-\frac{e^2}{8\pi\varepsilon_0 mc^2}\sum_{i,\alpha}\frac{Z_\alpha}{(M_1+M_2)}\left\{\boldsymbol{p}_i\frac{1}{r_{ji}}\cdot\sum_j\boldsymbol{p}_j+(\boldsymbol{p}_i\cdot\boldsymbol{r}_{ji})\frac{1}{r_{ji}^3}\left(\boldsymbol{r}_{ji}\cdot\sum_j\boldsymbol{p}_j\right)\right\} \qquad :(15)$$

$$+\frac{g_S^2\mu_B^2}{8\pi\varepsilon_0 c^2}\sum_{i,j\neq i}\left\{\frac{\boldsymbol{s}_i\cdot\boldsymbol{s}_j}{r_{ji}^3}-\frac{3(\boldsymbol{s}_i\cdot\boldsymbol{r}_{ji})(\boldsymbol{s}_j\cdot\boldsymbol{r}_{ji})}{r_{ji}^5}-\frac{8\pi}{3}\delta(\boldsymbol{r}_{ji})\boldsymbol{s}_i\cdot\boldsymbol{s}_j\right\} \qquad :(16)$$

$$-\frac{g_S\mu_B e\hbar}{4\pi\varepsilon_0 c^2}\frac{1}{\mu R^2}\sum_i\boldsymbol{s}_i\cdot\left\{\frac{Z_1M_2}{(M_1+M_2)}\frac{\boldsymbol{r}_{i1}}{r_{i1}^3}-\frac{Z_2M_1}{(M_1+M_2)}\frac{\boldsymbol{r}_{i2}}{r_{i2}^3}\right\}\wedge\{\boldsymbol{R}\wedge(\boldsymbol{J}-\boldsymbol{P})\} \qquad :(17)$$

$$-\frac{g_S\mu_B e}{4\pi\varepsilon_0 c^2}\sum_i\boldsymbol{s}_i\cdot\left\{\left[\frac{Z_1}{M_1}\frac{\boldsymbol{r}_{i1}}{r_{i1}^3}-\frac{Z_2}{M_2}\frac{\boldsymbol{r}_{i2}}{r_{i2}^3}\right]\wedge\boldsymbol{k}\right\}\mathrm{i}\hbar\frac{\partial}{\partial R} \qquad :(18)$$

$$+\frac{e^2\hbar}{8\pi\varepsilon_0 mc^2}\frac{1}{\mu R^2}\sum_i\boldsymbol{p}_i\cdot\left\{\frac{Z_1M_2}{(M_1+M_2)}\left(\frac{1}{r_{i1}}+\boldsymbol{r}_{i1}\frac{1}{r_{i1}^3}\boldsymbol{r}_{i1}\right)\right.$$

$$\left.-\frac{Z_2M_1}{(M_1+M_2)}\left(\frac{1}{r_{i2}}+\boldsymbol{r}_{i2}\frac{1}{r_{i2}^3}\boldsymbol{r}_{i2}\right)\right\}\cdot\boldsymbol{R}\wedge(\boldsymbol{J}-\boldsymbol{P}) \qquad :(19)$$

$$+\frac{e^2}{8\pi\varepsilon_0 mc^2}\sum_i\boldsymbol{p}_i\cdot\left\{\frac{Z_1}{M_1}\left(\frac{1}{r_{i1}}+\boldsymbol{r}_{i1}\frac{1}{r_{i1}^3}\boldsymbol{r}_{i1}\right)-\frac{Z_2}{M_2}\left(\frac{1}{r_{i2}}+\boldsymbol{r}_{i2}\frac{1}{r_{i2}^3}\boldsymbol{r}_{i2}\right)\right\}\cdot\boldsymbol{k}\mathrm{i}\hbar\frac{\partial}{\partial R} \qquad :(20)$$

$$+g_S\mu_B\boldsymbol{B}\cdot\sum_i\boldsymbol{s}_i\left\{1-\frac{\boldsymbol{p}_i^2}{2m^2c^2}\right\} \qquad :(21)$$

$$+\frac{e}{2m}\boldsymbol{B}\cdot\sum_i\left\{\boldsymbol{r}_i-\frac{m}{M}\sum_j\boldsymbol{r}_j\right\}\wedge\boldsymbol{p}_i \qquad :(22)$$

$$-\frac{e}{4m^3c^2}\boldsymbol{B}\cdot\sum_i(\boldsymbol{r}_i\wedge\boldsymbol{p}_i)\boldsymbol{p}_i^2 \qquad :(23)$$

$$-\frac{1}{2M}\boldsymbol{B}\cdot(\boldsymbol{\mu}_e\wedge\boldsymbol{P}_{\mathrm{O}}) \qquad :(24)$$

$$-\frac{e\hbar\mu}{2}\sum_\alpha\frac{Z_\alpha}{M_\alpha^2}\boldsymbol{B}\cdot(\boldsymbol{J}-\boldsymbol{P}) \qquad :(25)$$

$$-\frac{e}{2}\left(\frac{Z_1}{M_1}-\frac{Z_2}{M_2}\right)\boldsymbol{B}\cdot\left\{\left(\frac{m}{M}\sum_j\boldsymbol{r}_j-\boldsymbol{R}_{\mathrm{O}}\right)\wedge\boldsymbol{P}_R\right\}+\frac{e}{2m}\boldsymbol{B}\cdot\left\{\boldsymbol{R}_{\mathrm{O}}\wedge\sum_i\boldsymbol{p}_i\right\}$$

$$-\frac{e}{2(M_1+M_2)}\boldsymbol{B}\cdot\sum_i\left\{\mu\left(\frac{Z_1}{M_1}-\frac{Z_2}{M_2}\right)\boldsymbol{R}\wedge\boldsymbol{p}_i\right.$$

$$\left.+\sum_\alpha Z_\alpha\left(\frac{m}{M}\sum_j\boldsymbol{r}_j-\boldsymbol{R}_{\mathrm{O}}\right)\wedge\boldsymbol{p}_i\right\} \qquad :(26)$$

$$+\frac{e}{2M}q\boldsymbol{B}\cdot\left\{\left(\frac{m}{M}\sum_j\boldsymbol{r}_j-\boldsymbol{R}_{\mathrm{O}}\right)\wedge\boldsymbol{P}_{\mathrm{O}}\right\} \qquad :(27)$$

$$-\boldsymbol{E}\cdot\boldsymbol{\mu}_e \qquad :(28)$$

$$-qe\boldsymbol{E}\cdot\left(\boldsymbol{R}_{\mathrm{O}}-\frac{m}{M}\sum_j\boldsymbol{r}_j\right) \qquad :(29)$$

$$+\frac{g_S\mu_B}{2mc}\sum_i\boldsymbol{s}_i\cdot(\boldsymbol{E}\wedge\boldsymbol{p}_i) \qquad :(30)$$

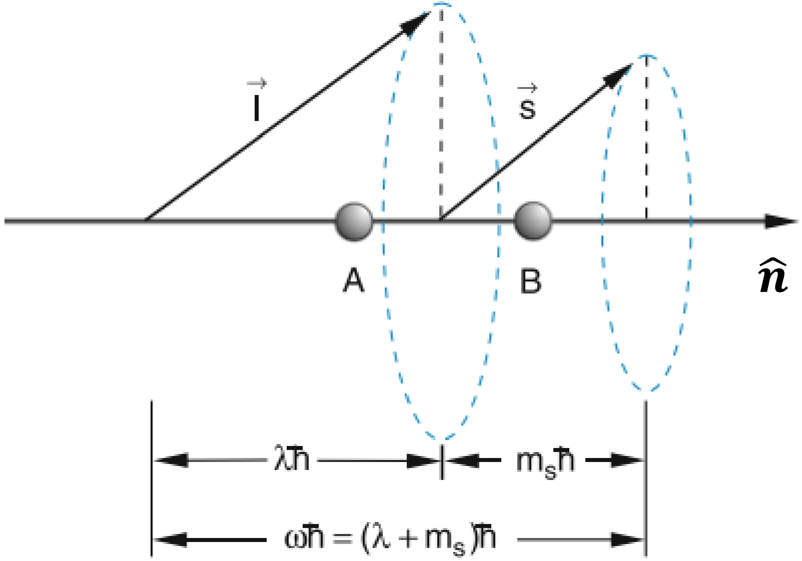
$$+\frac{e^2}{8m}\sum_i\{\boldsymbol{B}^2(\boldsymbol{r}_i+\boldsymbol{R}_{\mathrm{O}})^2-(\boldsymbol{B}\cdot(\boldsymbol{r}_i+\boldsymbol{R}_{\mathrm{O}}))^2\} \qquad :(31)$$

$$+\frac{e^2}{4}\sum_\alpha\frac{Z_\alpha^2}{M_\alpha}\left\{\boldsymbol{B}^2\left(\mp\frac{\mu}{M_\alpha}\boldsymbol{R}+\boldsymbol{R}_{\mathrm{O}}\right)^2-\left(\boldsymbol{B}\cdot\left(\mp\frac{\mu}{M_\alpha}\boldsymbol{R}+\boldsymbol{R}_{\mathrm{O}}\right)\right)^2\right\}. \qquad :(32) \quad (3.297)$$

Brown & Carrington, eq (3.297)
Diatomic molecules only, ignoring nuclear spins and relativity

Single Electron Basis for Molecules

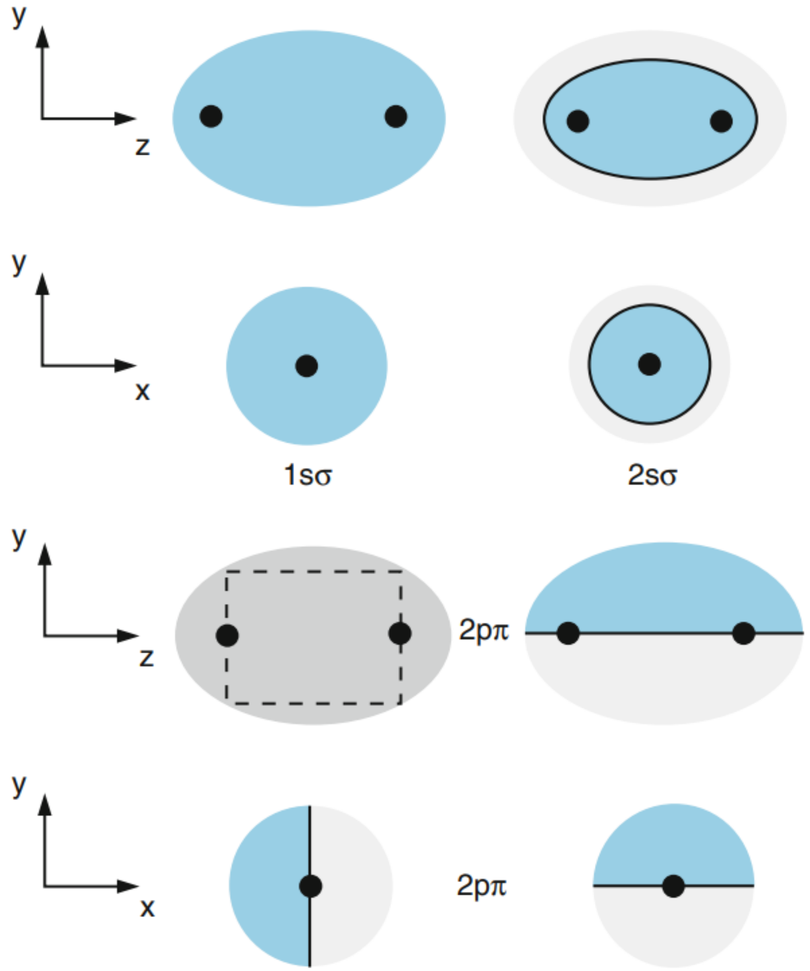
- Based on complete solution of rigid H_2^+ ion
- No spherical symmetry → orbital angular momentum ℓ not a good quantum number
- Cylindrical symmetry about internuclear axis $\hat{n}$
  - $\vec{\ell} \cdot \hat{n}$ is good, $\lambda = \left\langle \vec{\ell} \cdot \hat{n} \right\rangle$
  - ϕ part of wavefunction is $\psi \sim e^{i\lambda\phi}$
- Magnetic field from λ → spin quantized along $\hat{n}$
- Label states by $n\ell\lambda$
  - n = principal quantum number
  - $\ell = s, p, d, \dots, \leq n - 1$
  - $\lambda = \sigma, \pi, \delta, \dots, \leq n - 1$



Demtröder, *Atoms, Molecules, and Photons*

Single Electron Basis for Molecules

- States with well-defined λ have $\psi \sim e^{i\lambda\phi}$ are not parity or time-reversal eigenstates
- Physical eigenstates are superpositions $\propto e^{i\lambda\phi} \pm e^{-i\lambda\phi}$
  $$= \cos(\lambda\phi), \sin(\lambda\phi)$$
- Have λ nodal planes
- Doubly-degenerate except for σ $(\lambda = 0)$

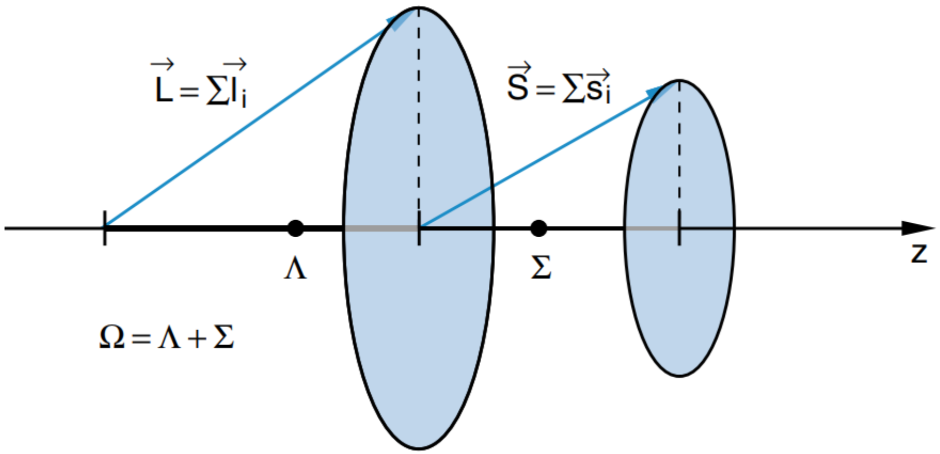


$\mathbf{\Lambda}$-doubling!

Demtröder, *Atoms, Molecules, and Photons*

Multi-Electron Basis for Molecules

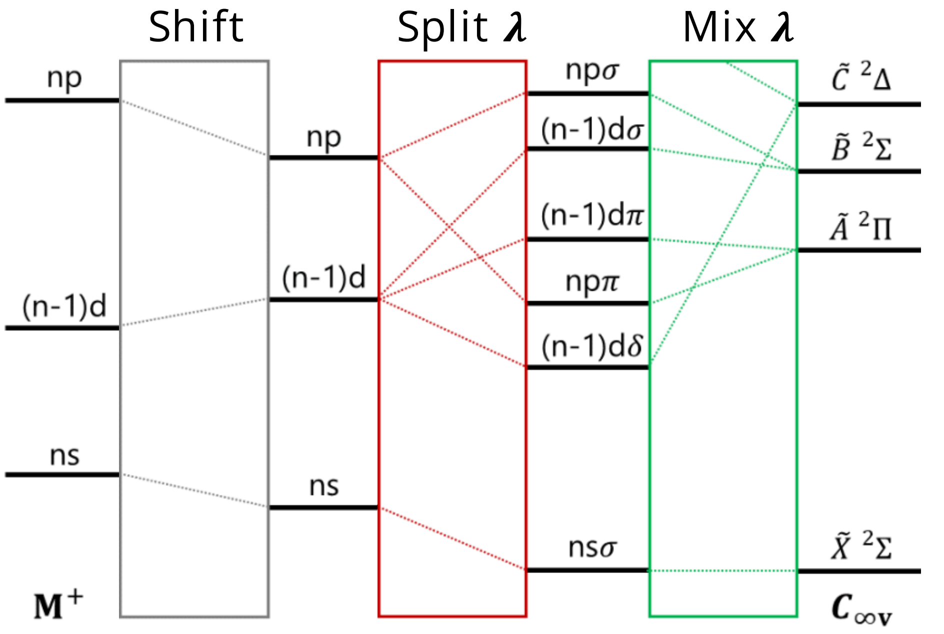
- Like atoms – “just add them up”
- $L = \sum_i \ell_i\,, S = \sum_i s_i\,, J = L + S$
- $\Lambda = \langle \vec{L} \cdot \hat{n} \rangle, \Omega = \langle \vec{J} \cdot \hat{n} \rangle$
- Define a term symbol $^{2S+1}\Lambda_{\Omega}$ where $\Lambda = \Sigma, \Pi, \Delta, \ldots$
- We are interested in a single, metal-centered *s*-type electron
  - Single → S = ½ → 2S+1 = 2
  - s-type → L=0 → Σ
  - State is $^{2}\Sigma$ (omit subscript when $L = 0, S = 1/2$)
- Name electronic states by letter
  - Ground is X
  - Excited A, B, C, …
    - In order of increasing energy… usually
    - ThO: X, H, Q, W, K’, A, B, H’, N’, C, …

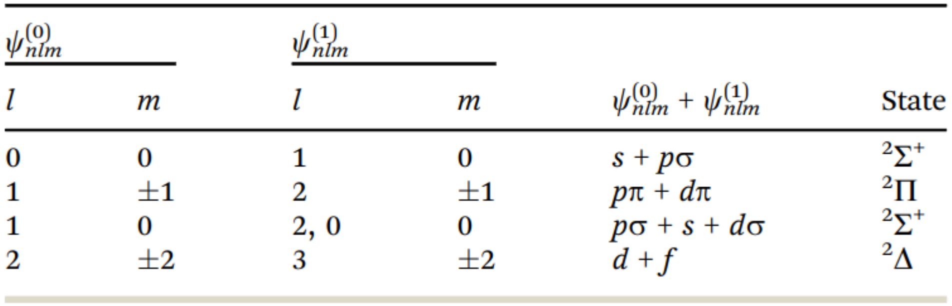


Demtröder, *Atoms, Molecules, and Photons*

Electronic Levels

- Electronic levels arise from M⁺ (s^1) atoms interacting with the ligand's Coulomb field
- This will:
  - Shift overall energy levels
    - Stark effect
  - Split states with by λ
    - Different electron distributions
  - Mix states with same λ
    - Cylindrical symmetry



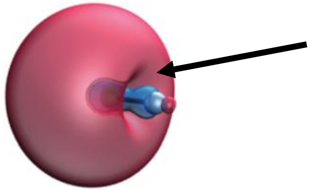


$\psi^{(0)}_{nlm}$		$\psi^{(1)}_{nlm}$			
l	m	l	m	$\psi^{(0)}_{nlm} + \psi^{(1)}_{nlm}$	State
0	0	1	0	$s + p\sigma$	$^2\Sigma^+$
1	±1	2	±1	$p\pi + d\pi$	$^2\Pi$
1	0	2, 0	0	$p\sigma + s + d\sigma$	$^2\Sigma^+$
2	±2	3	±2	$d + f$	$^2\Delta$

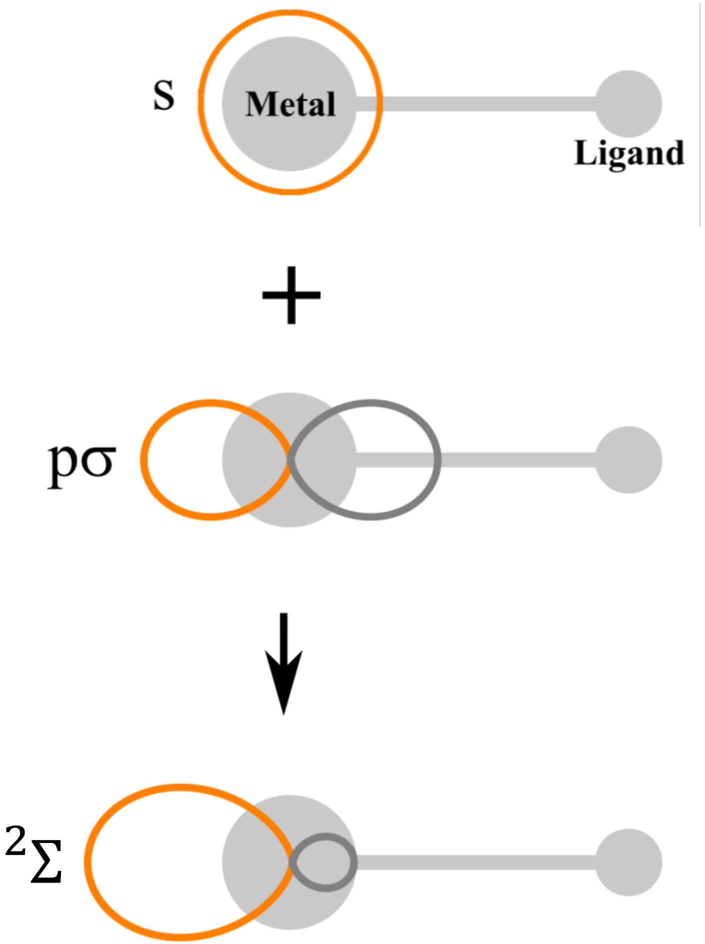
B. L. Augenbraun, L. Anderegg, C. Hallas, Z. D. Lasner, N. B. Vilas, and J. M. Doyle, Adv. At. Mol. Opt. Phys. 72, 89 (2023)
M. V. Ivanov, F. H. Bangerter, and A. I. Krylov, Phys. Chem. Chem. Phys. 21, 19447 (2019)

Electronic Structure for Photon Cycling

- Photon cycling in $^2\Sigma$ states with metal-centered electrons works due to hybridization of *s*, *p*-like orbitals
  - Pushes electron *away* from bond
  - The "dimple" around the F is important – electron avoids bond, decouples excitation
- Works for polyatomics (more on that later)


Valence electron avoids bonding region

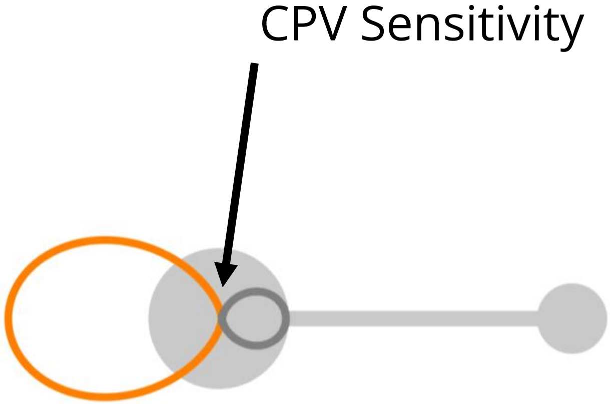
M. V. Ivanov, T.-C. Jagau, G.-Z. Zhu, E. R. Hudson, and A. I. Krylov, Phys. Chem. Chem. Phys. 22, 17075 (2020)



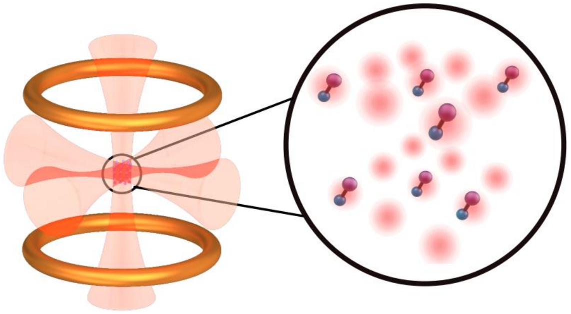
A. M. Ellis, Int. Rev. Phys. Chem. 20, 551 (2001)
T. Isaev and R. Berger, Phys. Rev. Lett. 116, 063006 (2016)

Compatibility with CPV Searches

- *s,p*-like electrons are good for CP violation searches
  - Electron: relativistic enhancement of motion
  - Nuclear: electron wavefunction probes nuclear shape
- Several heavy, laser-coolable molecules
  - Many being actively pursued
- BaF, HgF, RaF, YbF, …
  - $^2\Sigma$, good for eEDM, MQM, NSM
- TlF, …
  - $^1\Sigma$, closed shell, good for NSM
- Also polyatomic analogues

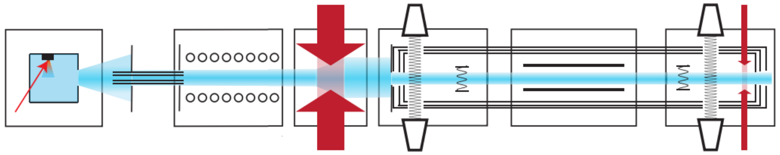


Three Examples



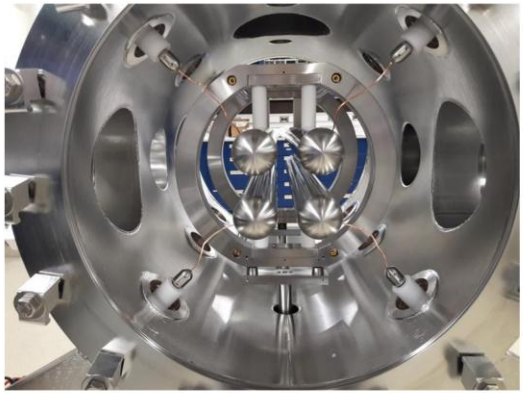
YbF

- 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)



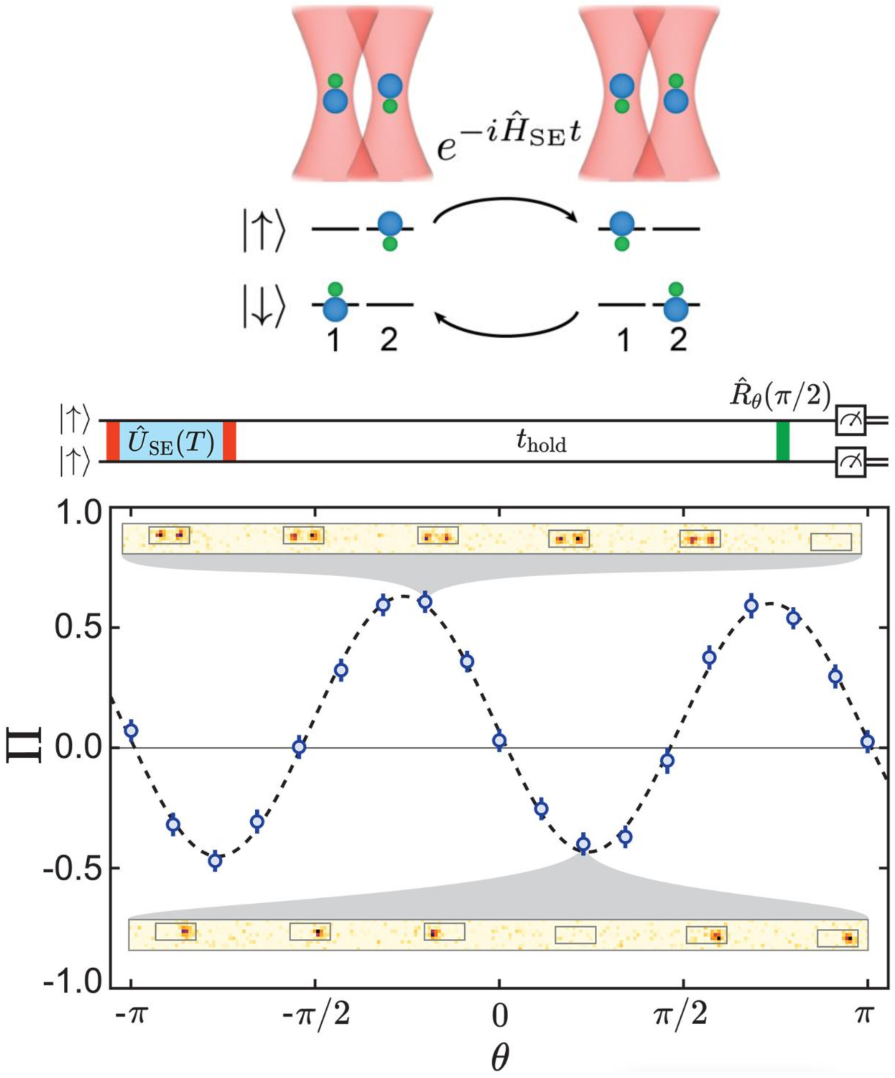
TlF

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

Several more laser cooling examples later

Quantum Control

- In the last few years, many advanced quantum tools from the atom world have been ported over to molecules
- Trapping in arrays, entangling gates, high coherence times, …
- Many groups are working to apply these to CPV searches with molecules!

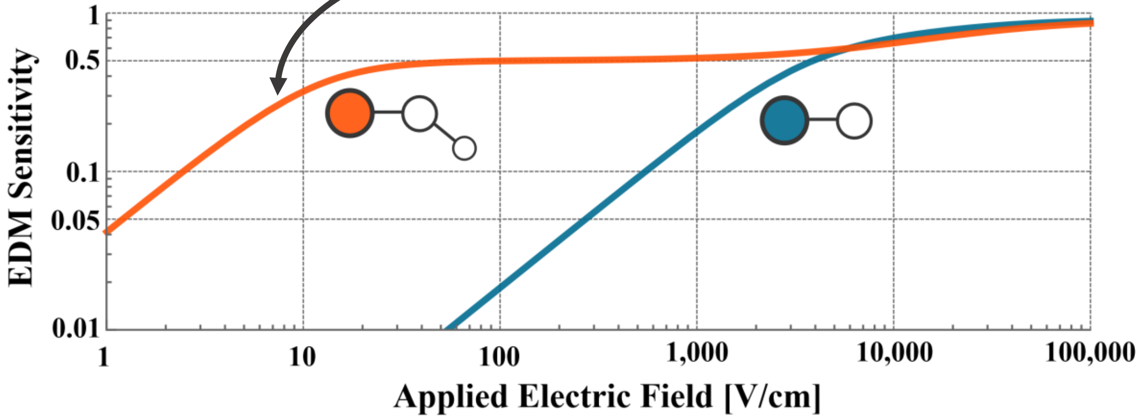


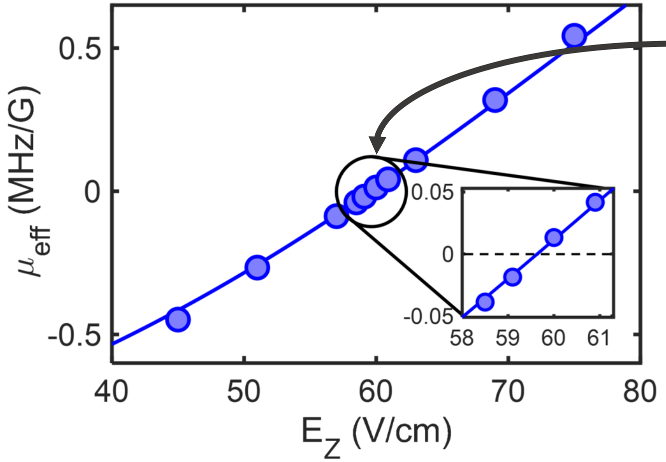
C. M. Holland, Y. Lu, and L. W. Cheuk, Science 382, 1143 (2023), Y. Bao, S. S. Yu, L. Anderegg, E. Chae, W. Ketterle, K.-K. Ni, and J. M. Doyle, Science 382, 1138 (2023)

Polyatomic Molecules

Polyatomics

- Advantages
  - Maintains molecular photon cycling, laser cooling, CPV sensitivity
  - Always have parity doublets
  - Tunable electromagnetic properties
- Disadvantage: more complicated, and diatomics are already rather difficult

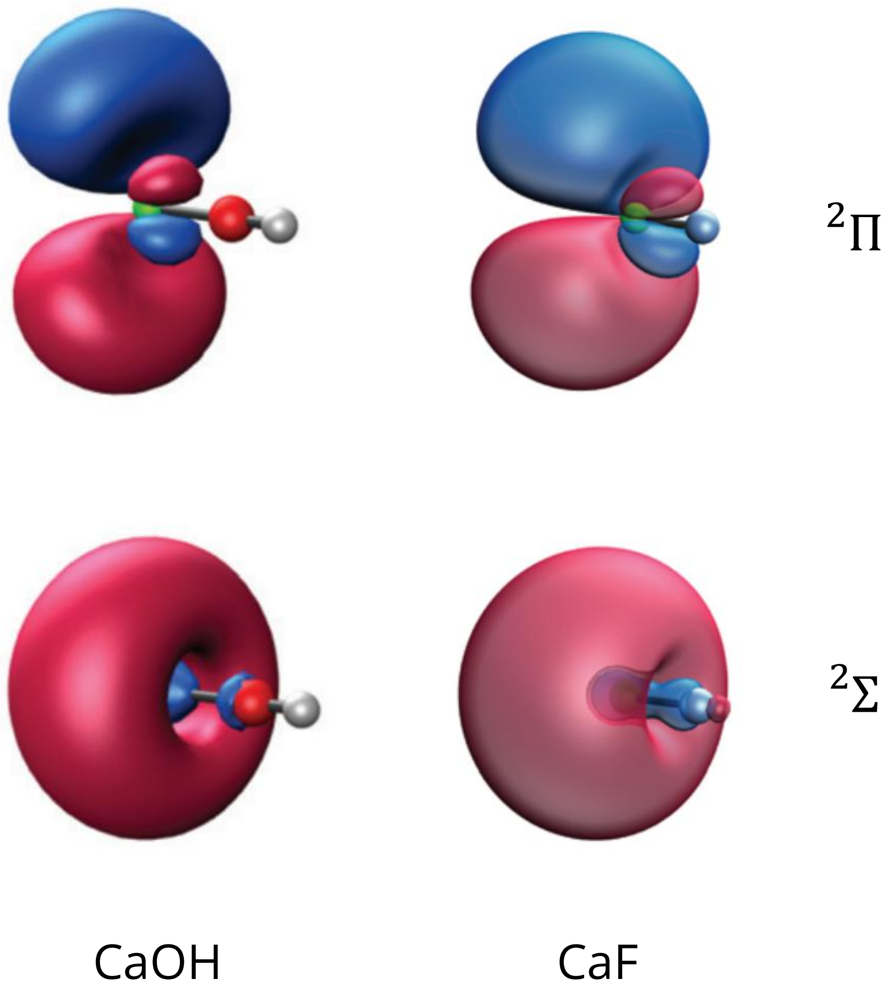

High polarizability in small fields


Magnetically insensitive states

L. Anderegg, N. B. Vilas, C. Hallas, P. Robichaud, A. Jadbabaie, J. M. Doyle, NRH, Science 382, 665 (2023)
Y. Takahashi, C. Zhang, A. Jadbabaie, NRH, PRL 131, 183003 (2023)

Polyatomic Molecules

- Many bonding partners "bond similarly"
  - – F ≈ –OH, – –CCH, – OCH_3, …
    - "A physicists take on chemistry"
  - Not in general, but for these s^2 atoms it typically holds
  - Ca, Sr, Ba, Yb, Ra
  - Probably not Hg though ☹
  - Since electron wavefunction is metal-centered, ligand matters much less
- Similar electronic structure implies similar:
  - Laser cooling/photon cycling
  - CPV sensitivity
  - Measurement methods

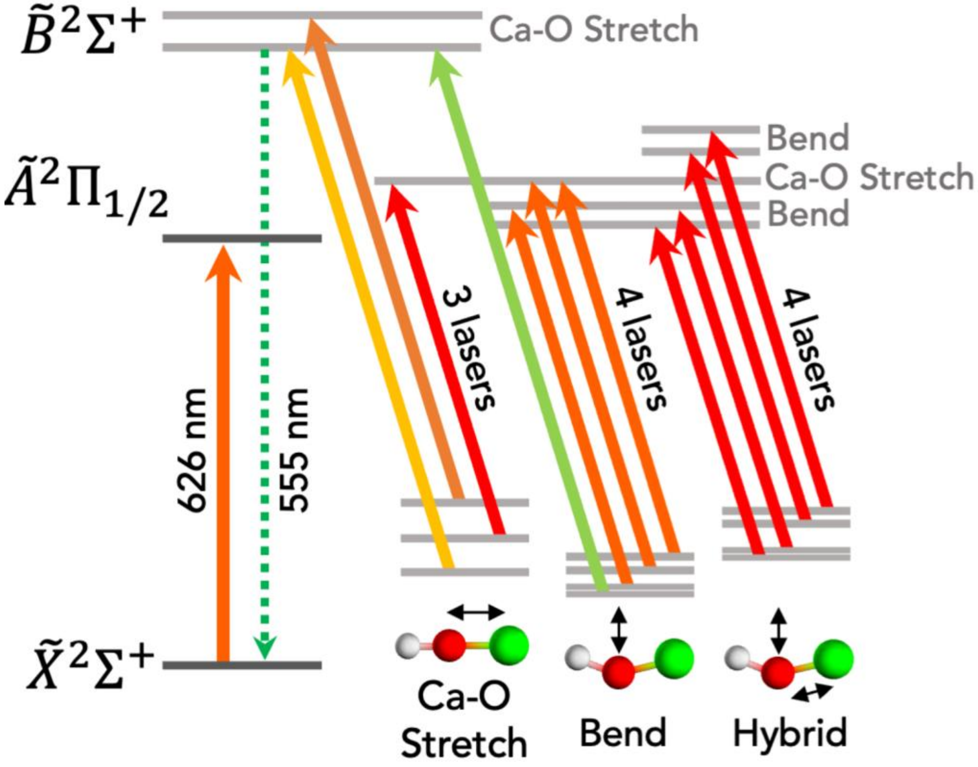


T. A. Isaev and R. Berger, PRL 116, 063006 (2016) T. A. Isaev, A. V. Zaitsevskii, and E. Eliav, J. Phys. B 50, 225101 (2017)
M. V. Ivanov, F. H. Bangerter, and A. I. Krylov, Phys. Chem. Chem. Phys. 21, 19447 (2019)

Polyatomic Laser Cooling

- Laser cooling has been demonstrated in SrOH, CaOH, YbOH, $CaOCH_3$
  - Doyle Group @ Harvard
- Non-trivial, but possible!
  - Requires many distinct, high power, stable, spectrally narrow lasers
  - Solid-state laser technology is increasing making this more practical

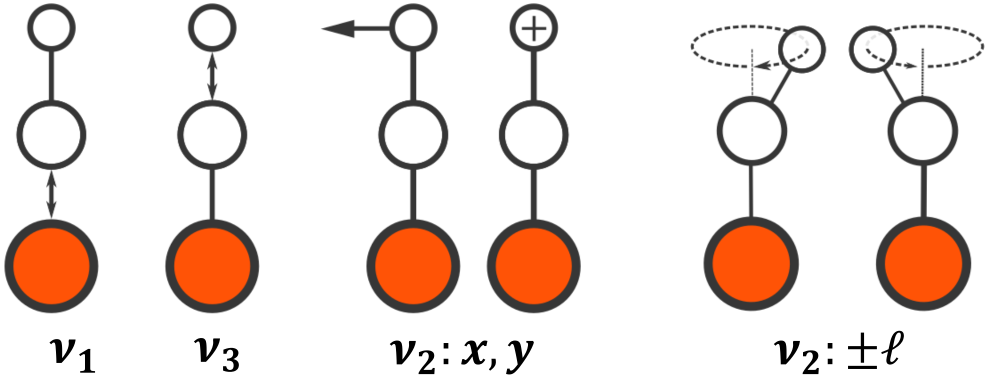
CaOH



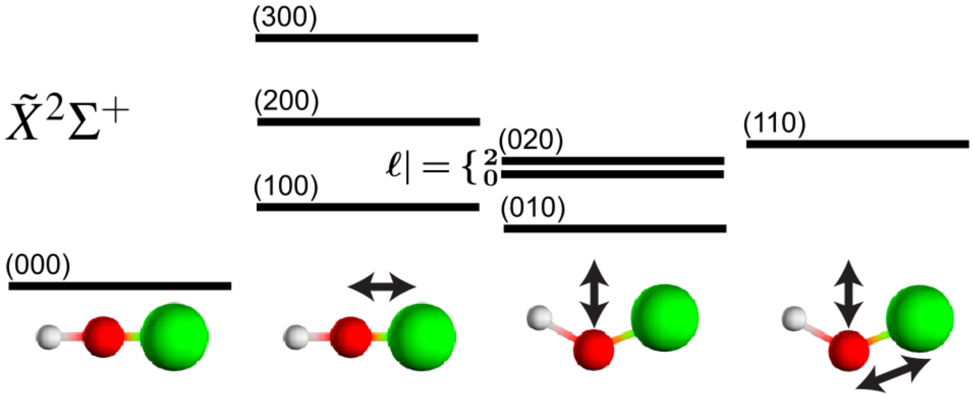
Vilas, N. B., et al., Nature 606, 70 (2022)

Polyatomic Vibrations

- What makes them different?
- Consider a linear triatomic molecule MOH
    - More complex species "conceptually similar"
- Three vibrational modes
    - ν_1 : M-O stretch
    - ν_3 : O-H stretch
    - ν_2 : M-O-H bend
        - ℓ : Projection of bending angular momentum on symmetry axis
- Label states by $\left(\nu_1 \nu_2^{|\ell|} \nu_3\right)$
- Physical eigenmodes are some mixture of these descriptions
    - Valid when $m_M \gg m_O \gg m_H$
- ν_3 (O-H) is basically irrelevant
    - Very decoupled from metal



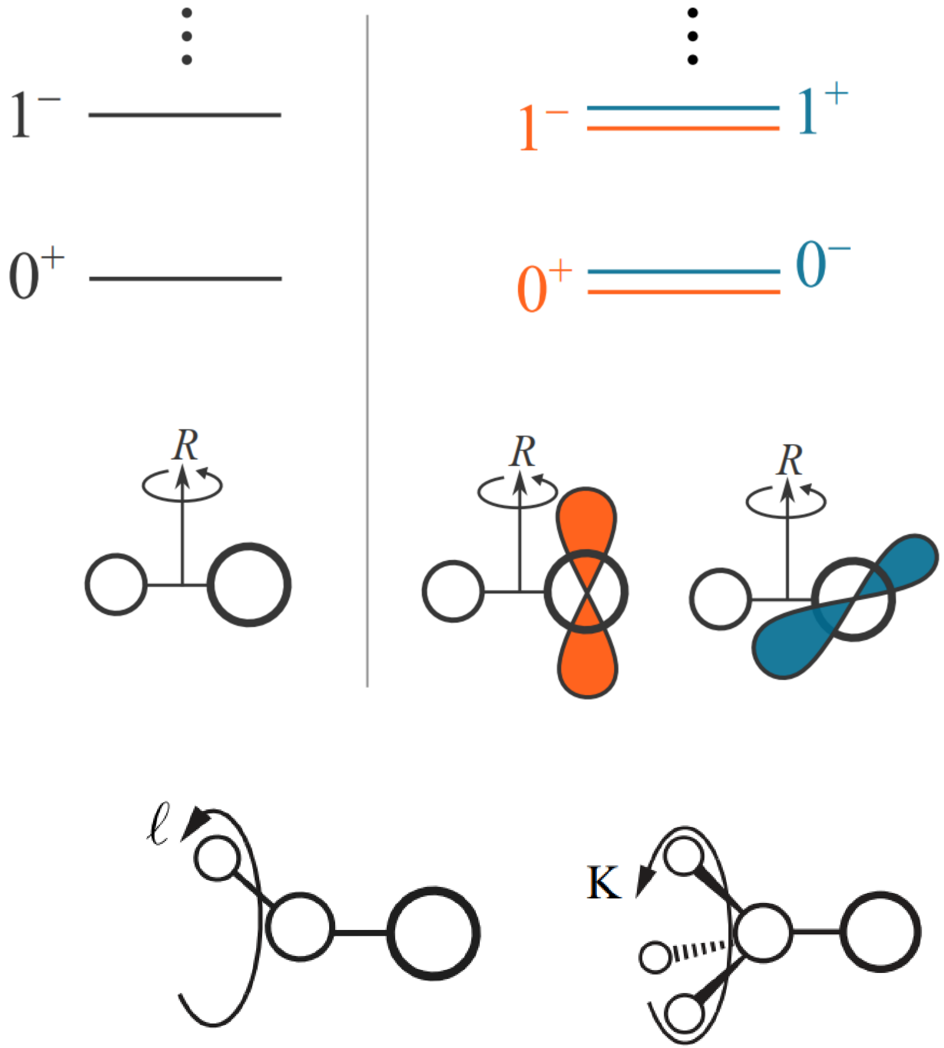
Most relevant levels in SrOH



Z. Lasner, A. Lunstad, C. Zhang, L. Cheng, and J. M. Doyle, PRA 106, L020801 (2022)

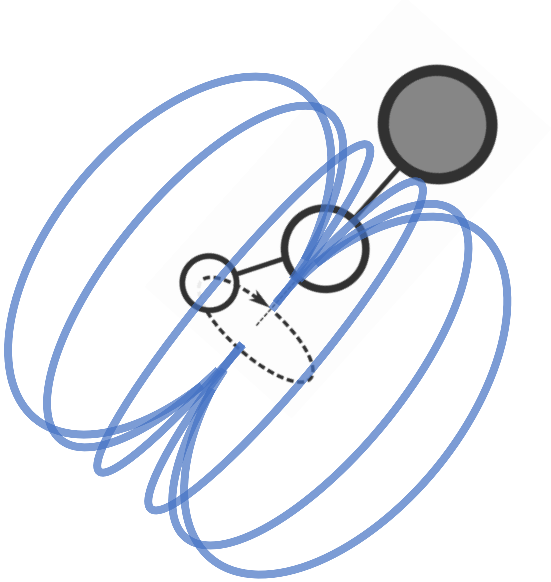
Lower Symmetry

- Polyatomic molecules always have states which lack cylindrical symmetry
- No cylindrical symmetry → breaks moment of inertia degeneracy
- Very analogous to Λ/Ω doubling, but now from mechanical motion
- Independent from electronic state, largely decoupled (usually)
- Laser-coolable $^2\Sigma$ diatomics don't have parity doublets
    - s-electrons → L=0 → $\Lambda = 0$
- Laser-coolable $^2\Sigma$ polyatomics do in states with $\ell, K \neq 0$

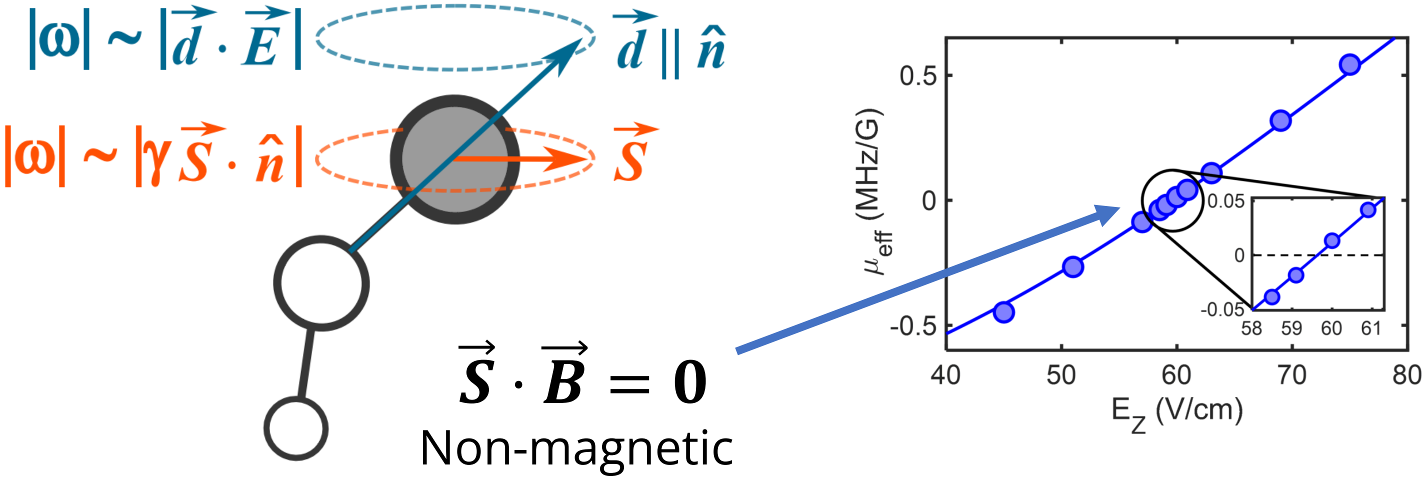


Electromagnetic Control

- Arises due to unique angular momentum couplings
  - $H = -\mu\vec{S}\cdot\vec{B} - \vec{d}\cdot\vec{\mathcal{E}} + \gamma\vec{S}\cdot\vec{\ell}$
  - $\vec{\ell}$ makes internal $\vec{B} \propto \vec{d}$
  - $\vec{\mathcal{E}}$ → control $\vec{d}$ → control $\vec{S}$



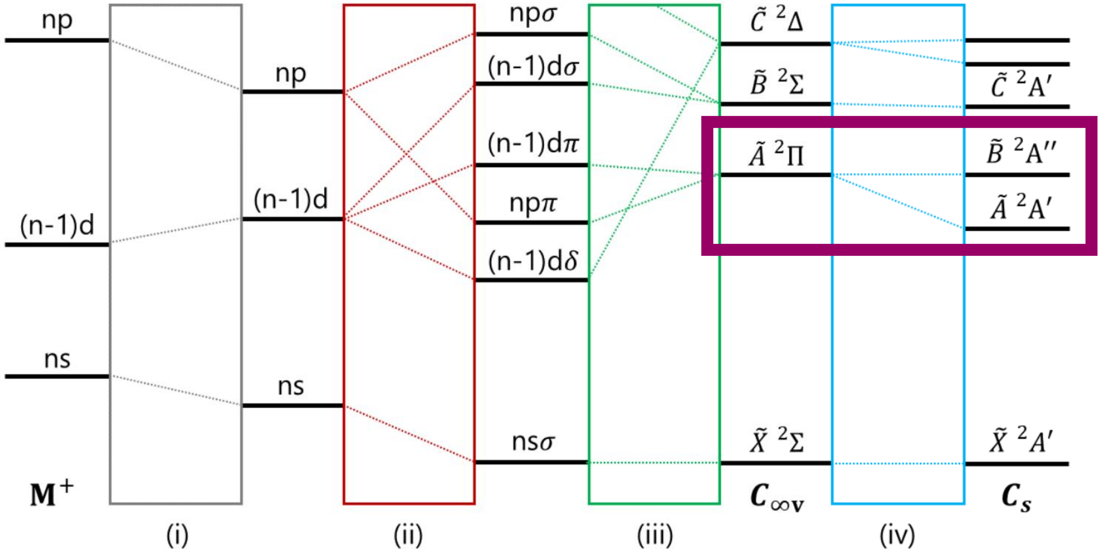
$\vec{B} \propto \vec{\ell}\ ||\ \hat{n} \propto \vec{d}$

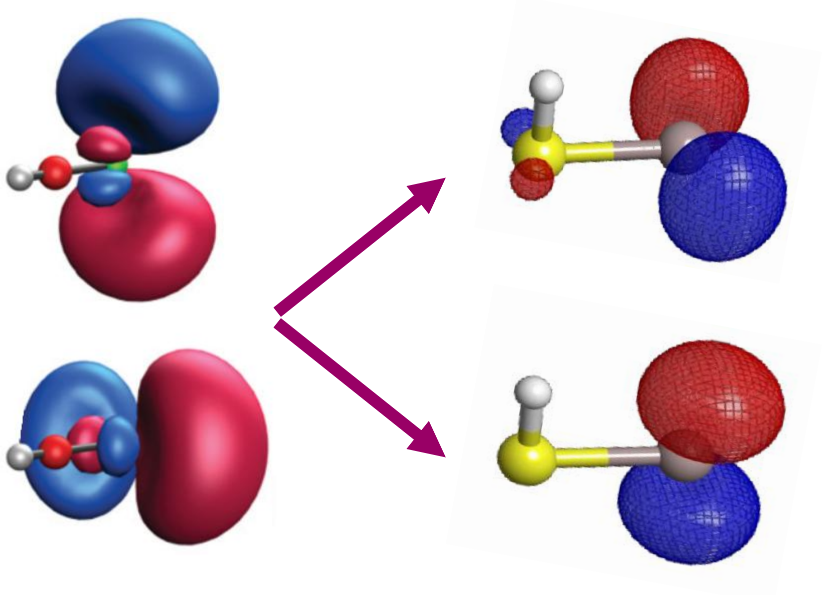


$\vec{S}\cdot\vec{B} = 0$

Non-magnetic

Vibrational Branching





Linear
Degenerate $\mathbf{\Pi}_x, \mathbf{\Pi}_y$

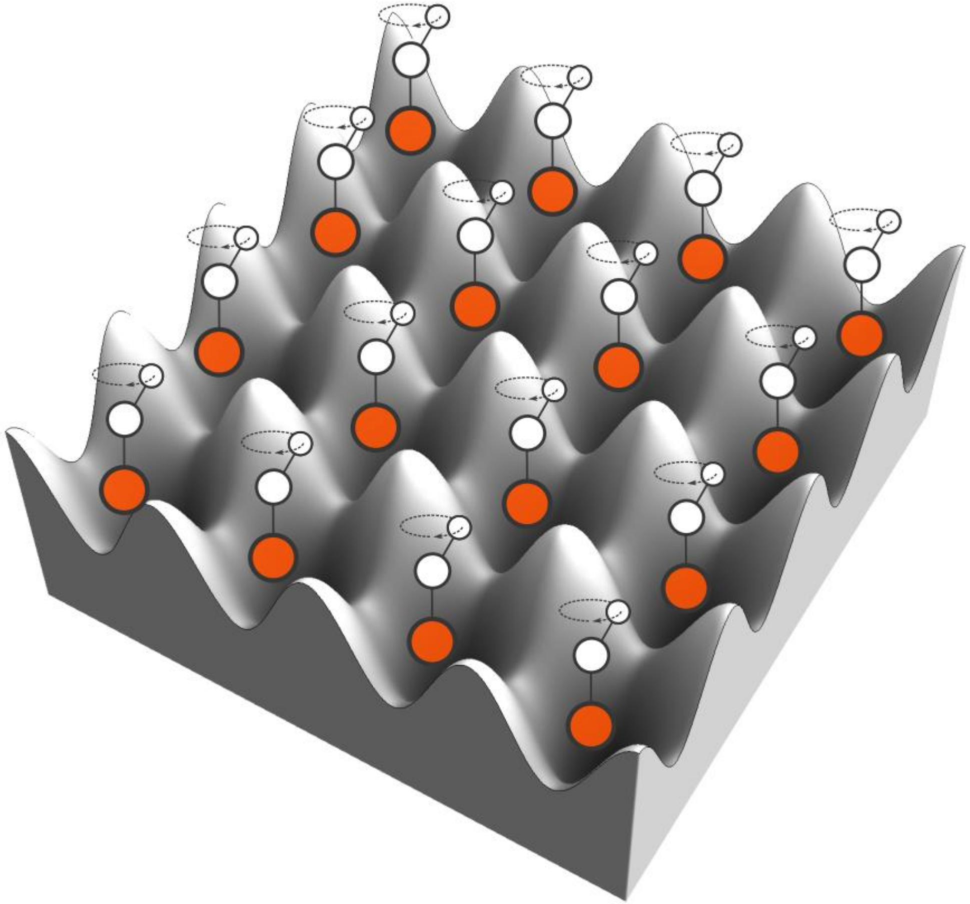
Bent
Splits in/out of plane

- Lower symmetry has other consequences
- Electronic Π state has two lobes
- When bending potential no longer cylindrically symmetric → lifts degeneracy, couples electron and vibration
- More complicated, and remember that electron-vibrational decoupling is good…

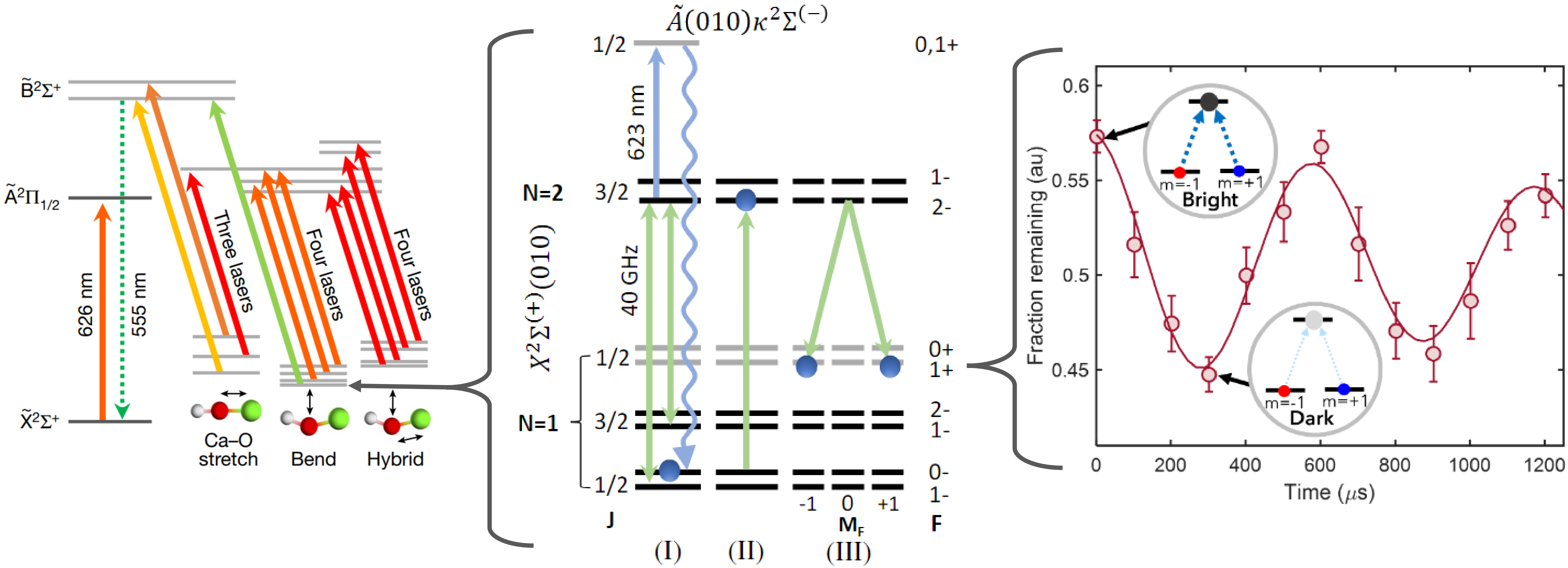
M. V. Ivanov, F. H. Bangerter, and A. I. Krylov, PCCP 21, 19447 (2019), B. L. Augenbraun, et al., Adv. At. Mol. Opt. Phys. 72, 89 (2023), P. Yu, A. Lopez, W. A. Goddard, and NRH, Phys. Chem. Chem. Phys. 25, 154 (2023)

EDM Search : Ultracold Traps

- Ultracold molecules in optical traps offer extreme sensitivity
  - “Modern” quantum tools are so far unused for molecule EDM experiments
- EDMs pose challenges
  - Complex structure
  - Need to apply fields
  - Higher field sensitivity
- PolyEDM Collaboration
  - John M. Doyle, Amar Vutha, Tim Steimle, NRH
  - CaOH eEDM Pathfinder → done
  - SrOH eEDM → underway
  - RaX → underway



Pathfinder EDM in CaOH @ Harvard



- Laser cooling
- Trapping at tens of uK
- Population of EDM state

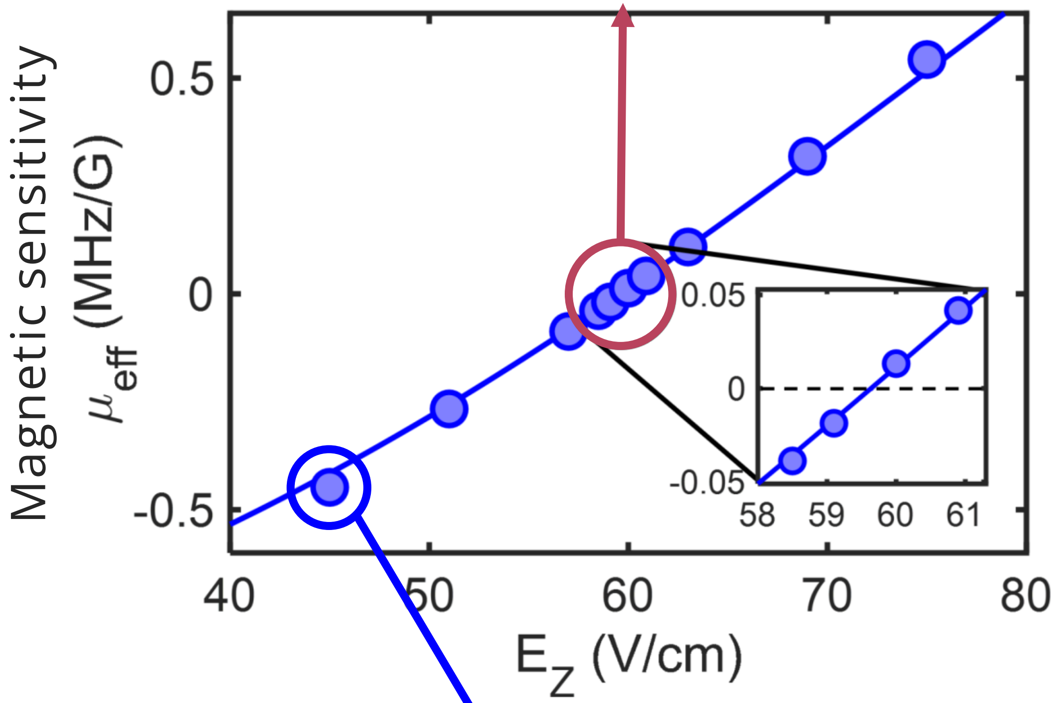
- Full polarization
- Coherent state preparation

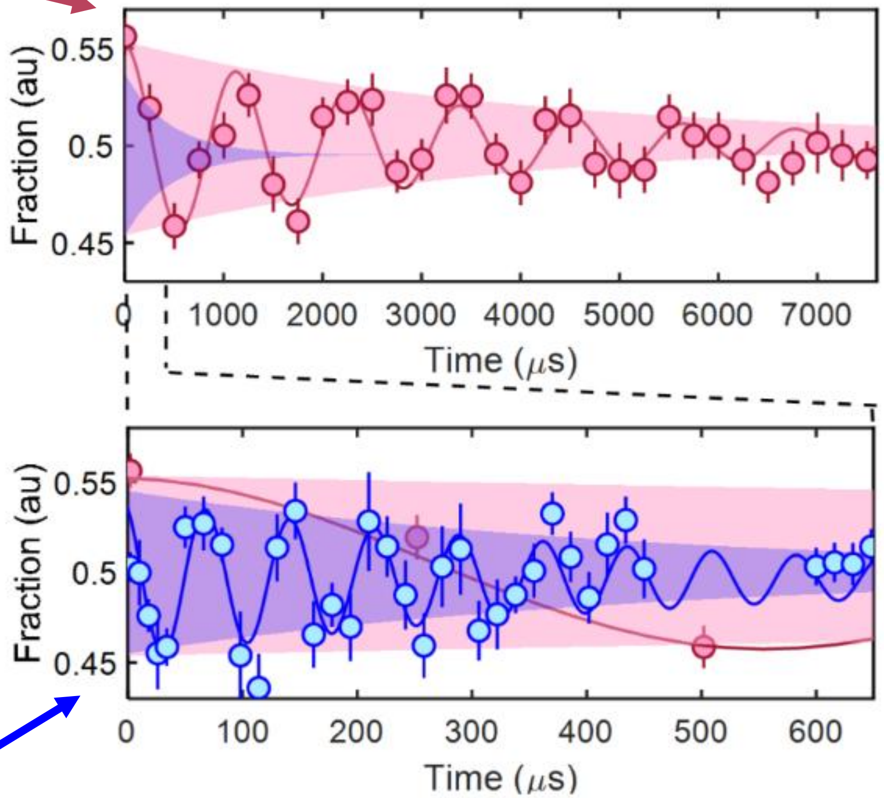
- Coherent evolution
- State readout

L. Anderegg, N. B. Vilas, C. Hallas, P. Robichaud, A. Jadbabaie, J. M. Doyle, NRH, Science 382, 665 (2023)

Electromagnetic Tuning

Long coherence, up to 30 ms
>1s with quieter apparatus
(stainless chamber, no shielding, etc.)



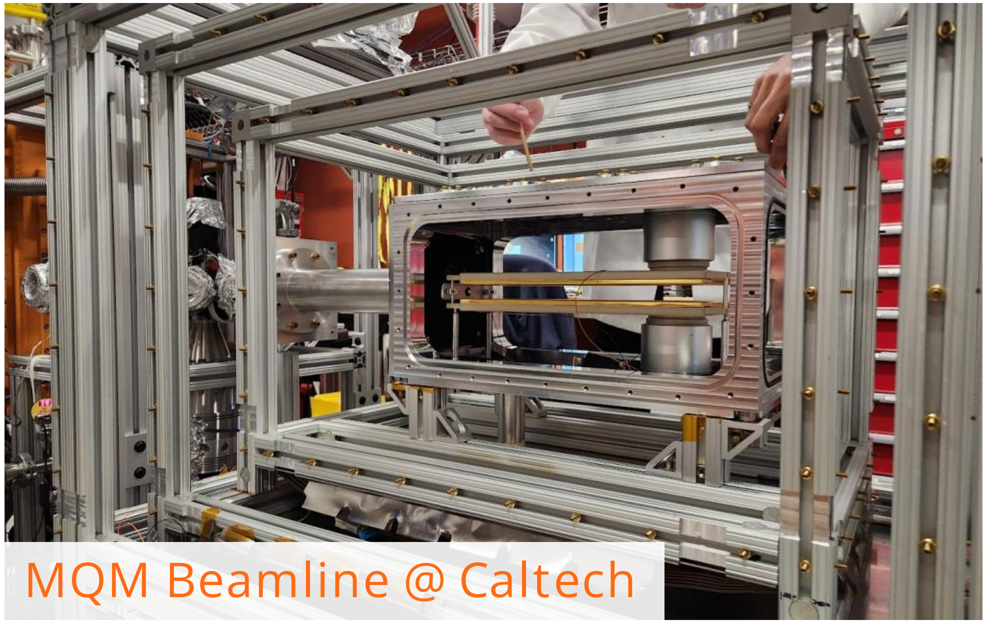


Short coherence, <1 ms

L. Anderegg, N. B. Vilas, C. Hallas, P. Robichaud, A. Jadbabaie, J. M. Doyle, NRH, Science 382, 665 (2023)

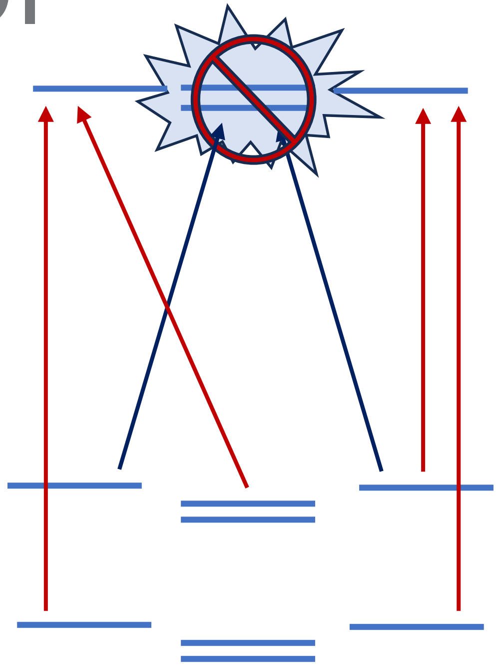
^{173}YbOH NMQM @ Caltech

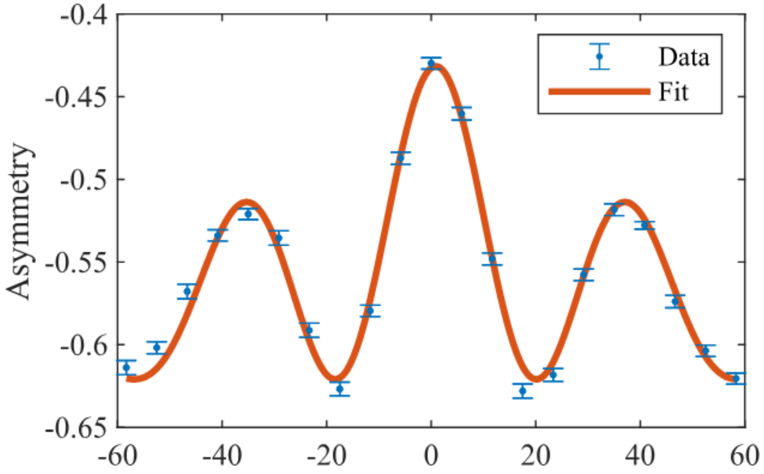
- MQM search in ^{173}YbOH
  - Large quadrupole deformation in Yb
  - Large molecular enhancement
  - Optical control/readout by photon cycling
- Cryogenic molecular beam experiment
- Laser cooling in future generations
- Currently implementing measurement protocol


MQM Beamline @ Caltech

Spin Precession Protocol

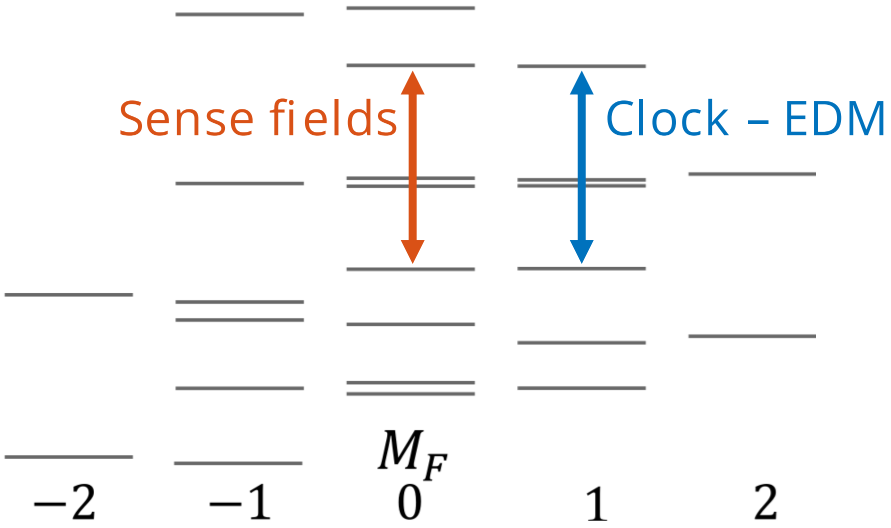
- Problem: $|+M\rangle \pm |-M\rangle$ is hard
  - M is large
    - $I_{Yb} = 5/2, S = 1/2, N = 1, I_H = 1/2$
  - Beam has velocity dispersion and large spatial extent – hard to use microwaves
  - Unresolved excited state hyperfine structure – hard to use lasers
- Solution: Give up
  - Can instead prepare $|M\rangle \pm |M'\rangle$
  - Choose $|M - M'| \leq 2$ to connect with two-photon transition
- This works fine, but has first order Stark and Zeeman shift
  - Large molecular dipole
  - Unpaired electron spin





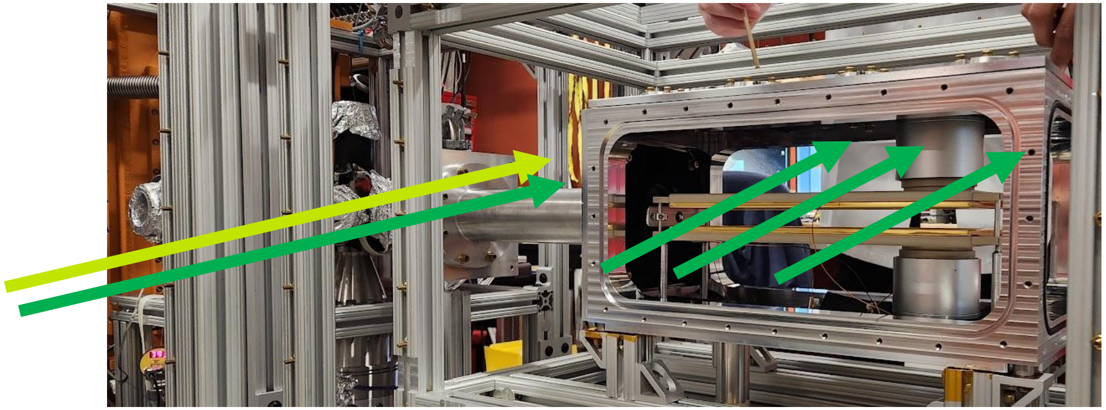
Engineered Clock Transitions

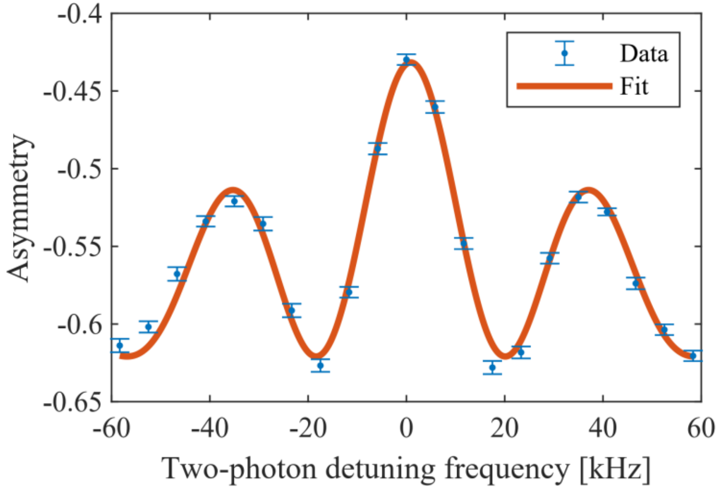
- Engineered molecular clocks
  - Can zero-out field sensitivity
  - Maintains EDM sensitivity
- Can also find environmental sensing transitions
- Exist generically
  - Leverages complexity
  - Especially good in polyatomics
  - Agnostic to molecular details
  - Including complex hyperfine
- Access to *many* measurement states, not just 1 or 2
  - Each for sensing/suppressing a different effect

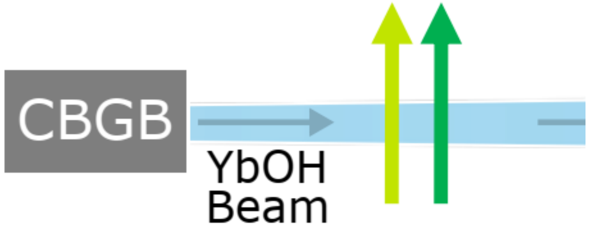


^{174}YbOH "science" state
E ~ 40 V/cm, B ~ 12 mG

Proposal: Y. Takahashi, C. Zhang, A. Jadbabaie, NRH, PRL 131, 183003 (2023)

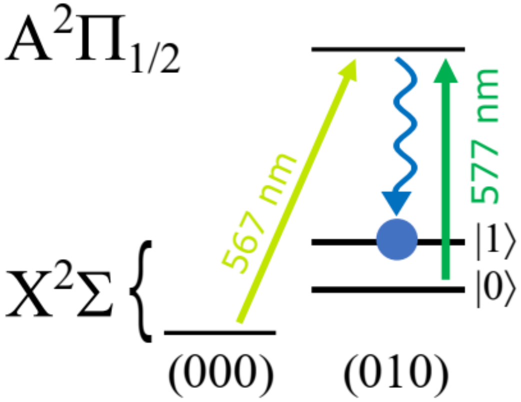






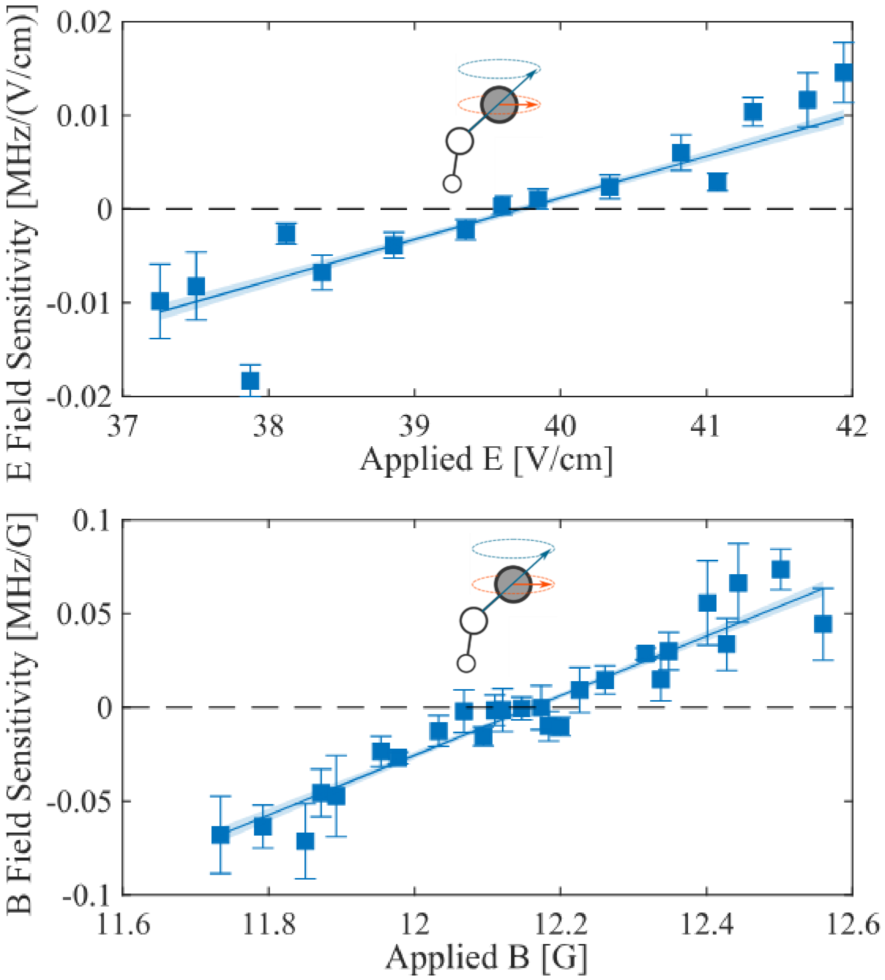
Pumping

$|\psi\rangle = |1\rangle$

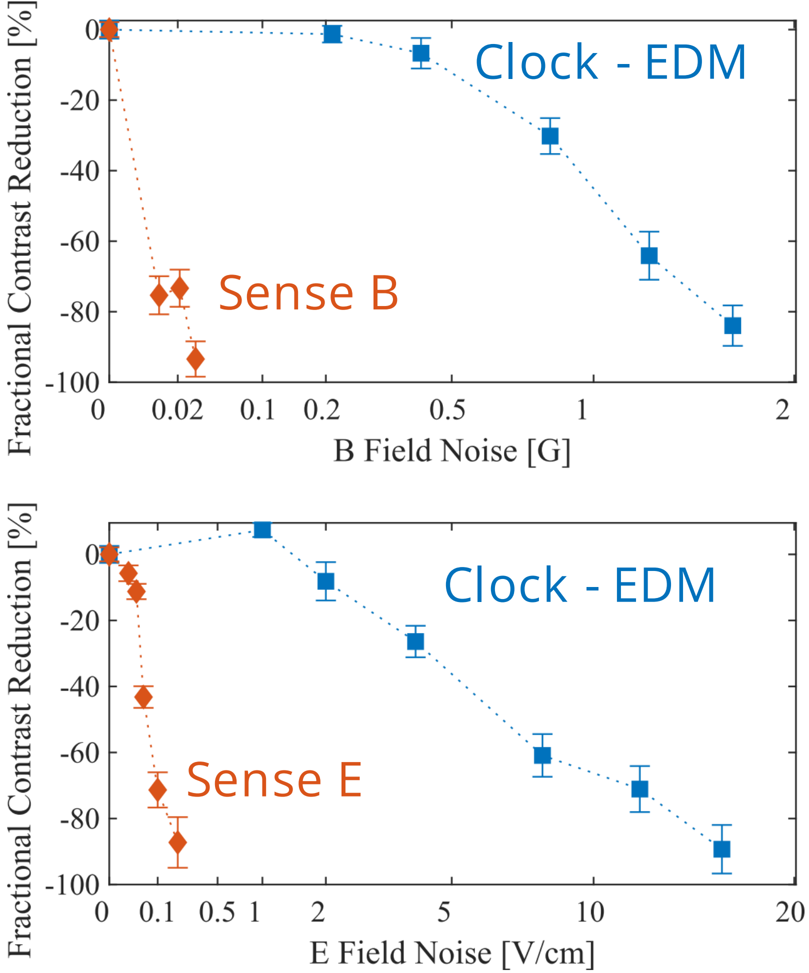


Implementation in ^{174}YbOH

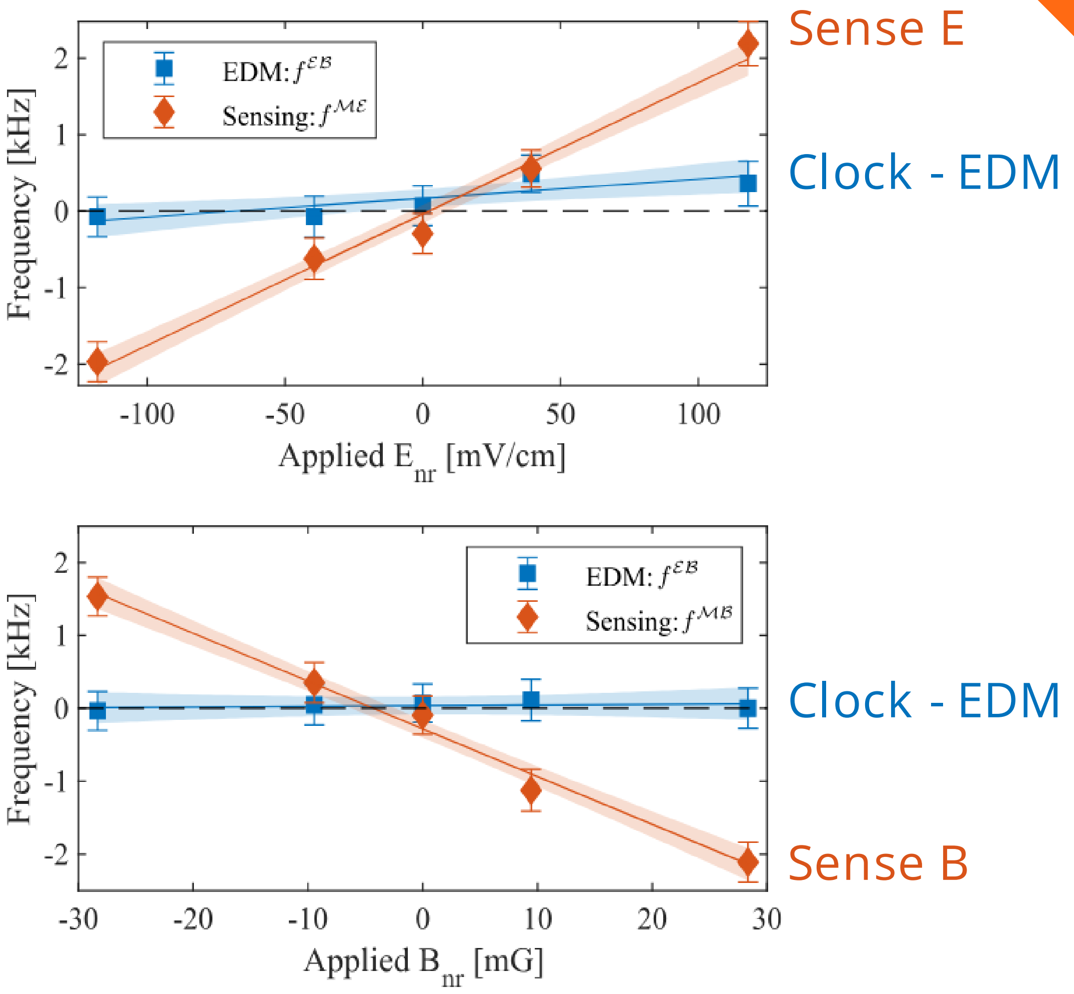
- Recently implemented in ^{174}YbOH science state
  - Electrically polarized symmetry-lowered bending mode
  - $\mathcal{E}_{eff} \approx$ 22 GV/cm @ 40 V/cm
  - Preliminary
- Able to suppress electric, magnetic sensitivity to <1%
  - Measure with spin precession
  - < Few μ_N magnetic sensitivity in a molecule with an unpaired electron
- Demonstrated ability to simultaneously sense fields



Implementation in ^{174}YbOH



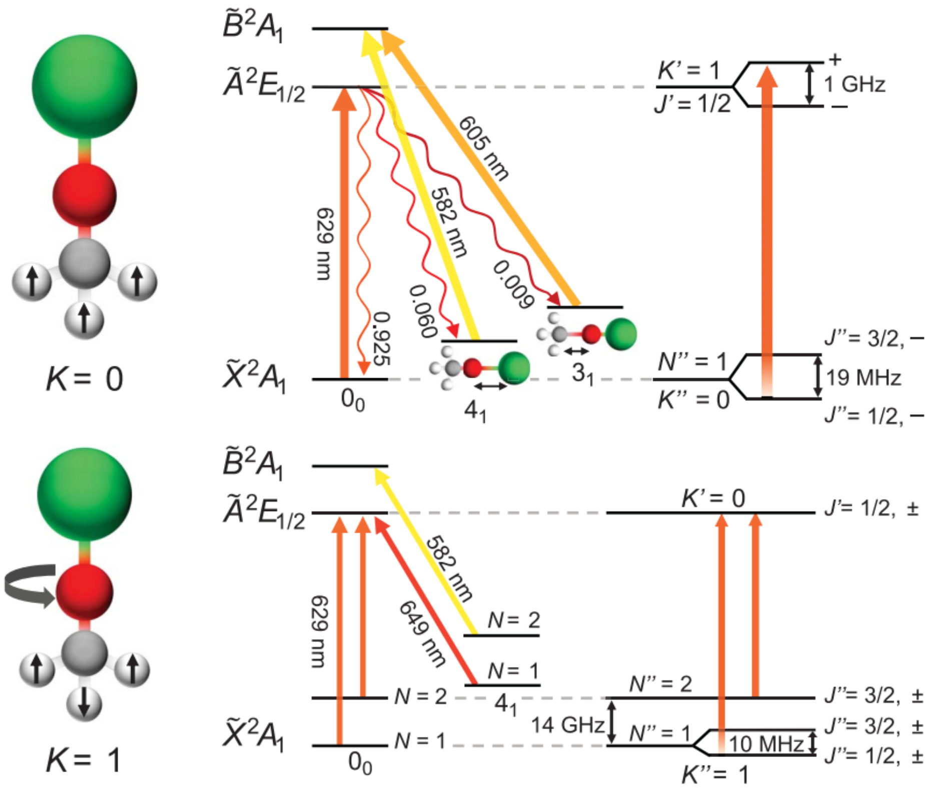
Highly robust against electromagnetic noise



Ability to use field-sensitive transitions to sense fields

Symmetric Tops

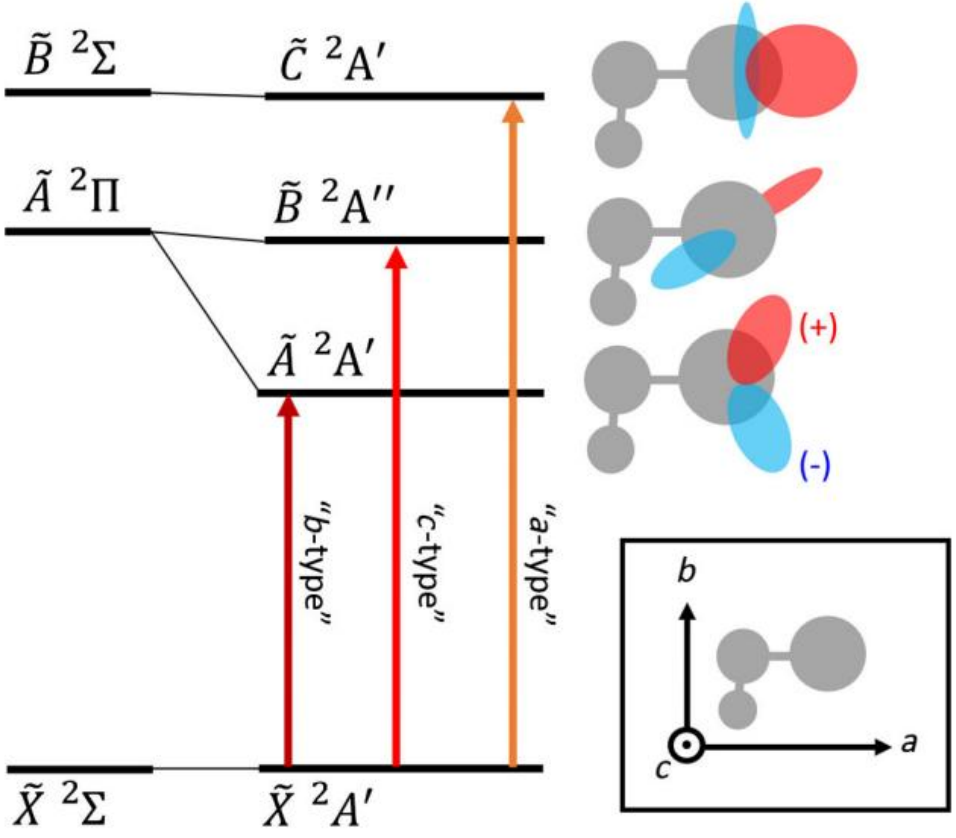
- Symmetric tops like MOCH$_3$ are a similar story, but with key differences
- Parity doubled state is a *rotational* state
  - Rotation of H$_3$ group around symmetry axis
  - K-doubling (K = projection of rotation on symmetry axis)
  - Smaller splittings (~1 MHz or less), basically infinite radiative lifetime
- Different: H$_3$ nuclei must obey Pauli statistics
  - Gives rise to two nuclear spin isomers (singlet, triplet)
  - Need to be addressed individually



D. Mitra, N. B. Vilas, C. Hallas, L. Anderegg, B. L. Augenbraun, L. Baum, C. Miller, S. Raval, and J. M. Doyle, Science 369, 1366 (2020)

Asymmetric Tops

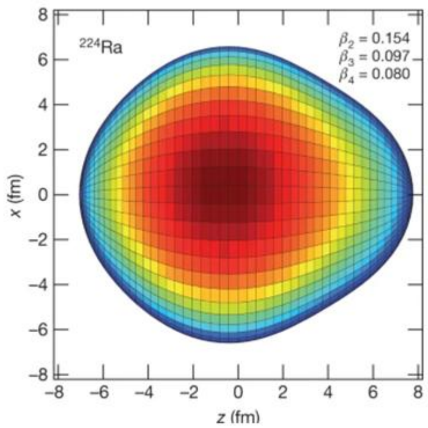
- Asymmetric tops have three distinct moments of inertia
- Very, very complicated
  - Multiple rotational ladders, transitions, mixing
  - In-plane vs. out-of-plane splittings for electronic states
- Surprisingly, appears to maintain laser cooling (theoretically)



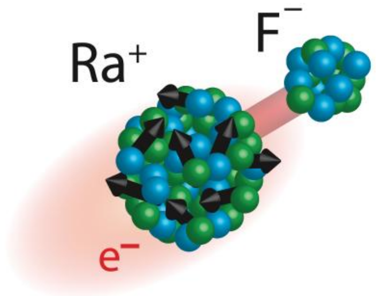
B. L. Augenbraun, J. M. Doyle, T. Zelevinsky, and I. Kozyryev, Phys. Rev. X 10, 031022 (2020)

Radioactive Molecules

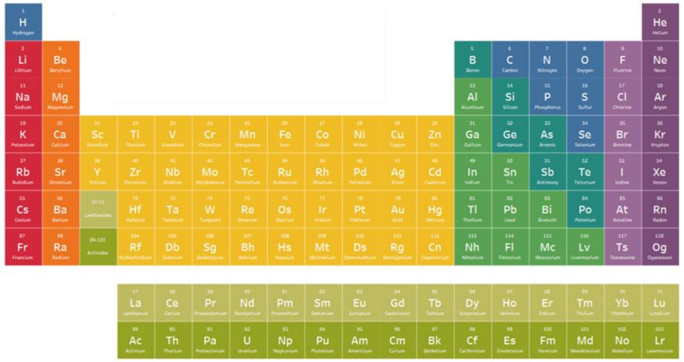
Why Radioactive Molecules?



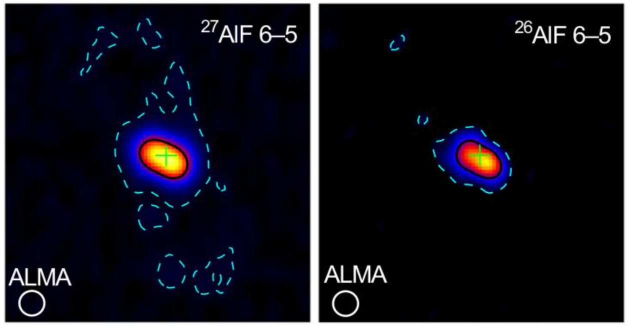
Fundamental symmetries



Nuclear structure



Radiochemistry

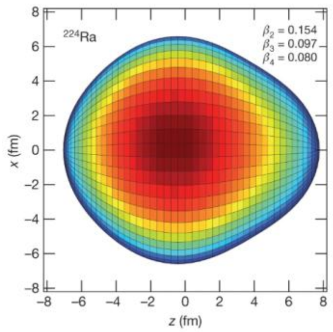


Nuclear astrophysics

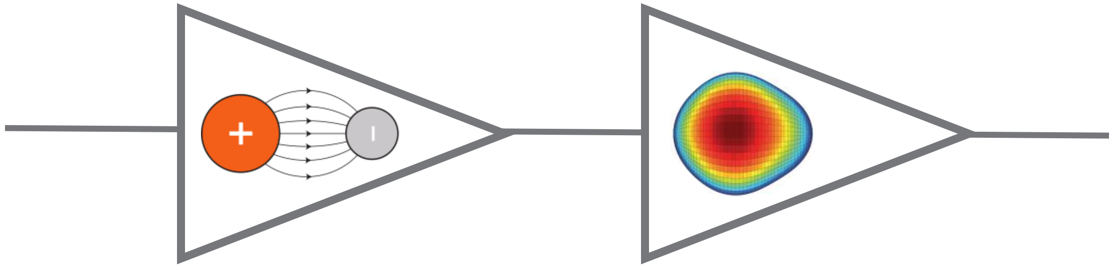
- Molecules containing exotic nuclei have interesting properties [see arXiv:2302.02165]
- Fundamental challenge: adapting many laboratory techniques to trace, short-lived species

Enhanced CPV Sensitivity with Exotic Nuclei

- Nuclear symmetry violations enhanced in heavy, octupole-deformed (pear-shaped) nuclei
  - Combines with molecular sensitivity enhancement



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



CPV Sensitivity

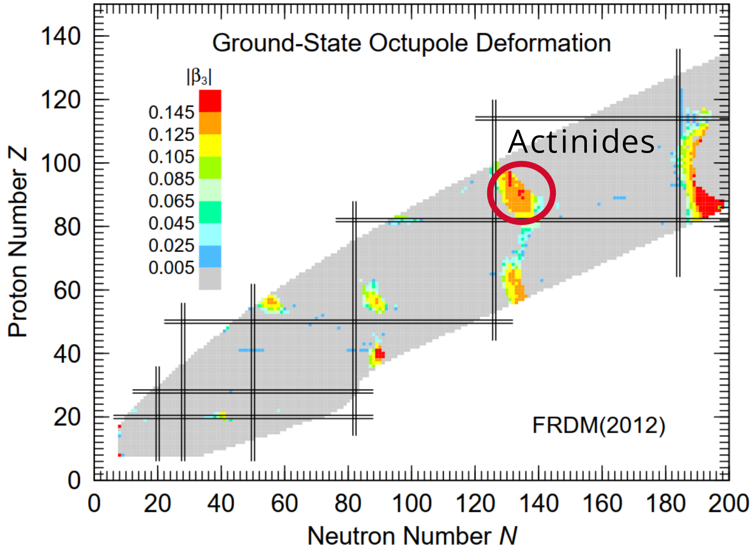
~10^6

~10^3 ~10^3

- Control *one* molecule at a time → hadronic frontier
- Challenge: simply producing radioactive molecules is a research frontier

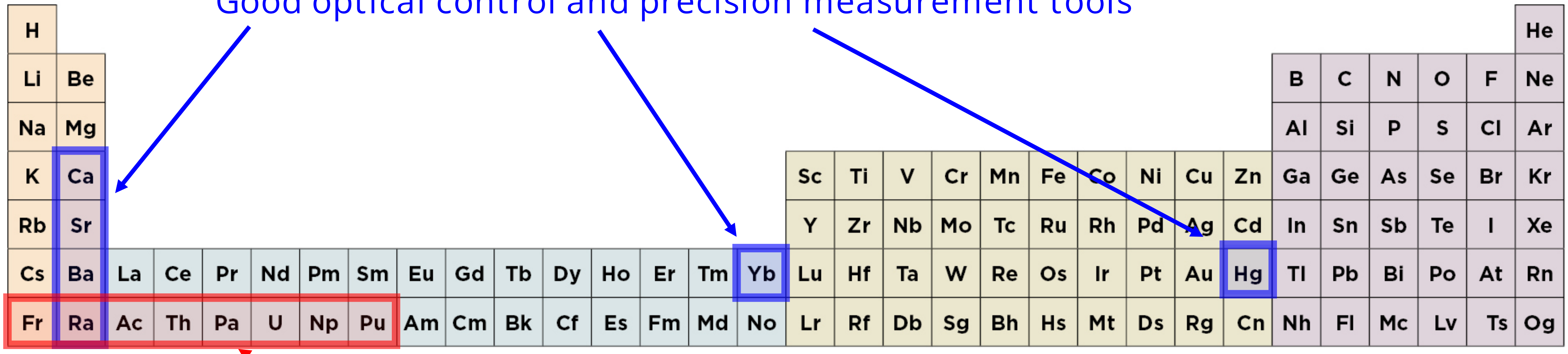
Radioactive Nuclei

- Main challenge: heavy, spinful, octupole-deformed nuclei are radioactive
- Nuclei must be in a molecule amenable to “precision measurement” methods
    - Synthesis, cooling, spectroscopy, measurement protocol, coherent quantum state control, …



Isotope	Half-life
^{223}Fr	22 min
^{225}Ra	15 d
^{223}Ra	11 d
^{227}Ac	22 yr
^{229}Th	7,900 yr
^{229}Pa	2 d

Where to start?



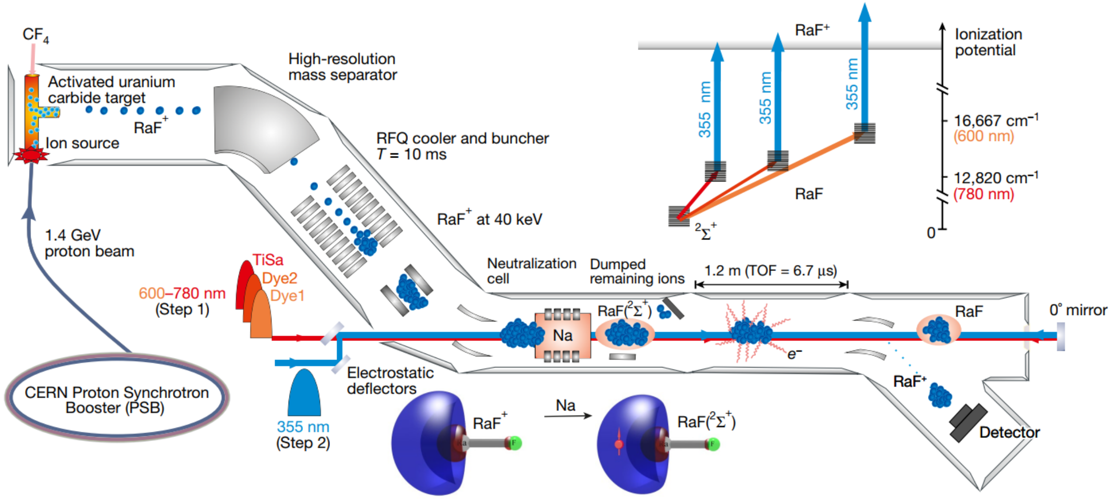
H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca															Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr															Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Good optical control and precision measurement tools

Octupole nucleus

Radium

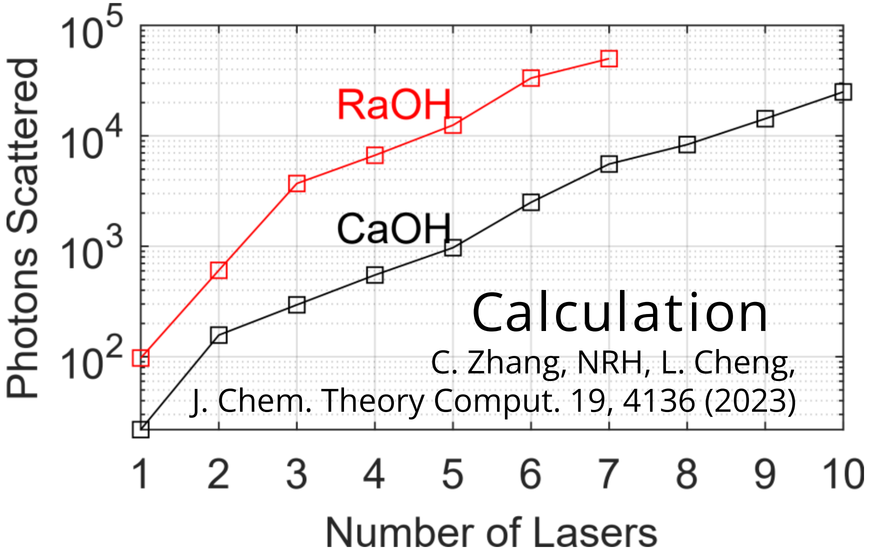
This contributed to motivation
for groundbreaking RaF work



R. F. Garcia Ruiz *et al.*, Nature 581, 396 (2020)
T. A. Isaev, S. Hoekstra, and R. Berger, PRA 82, 052521 (2010)

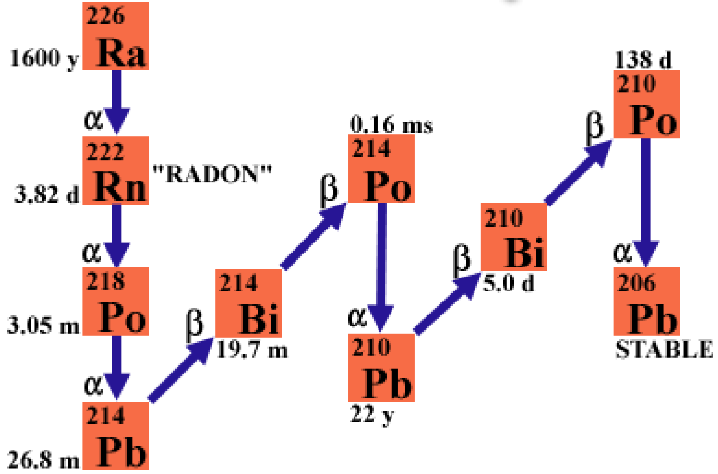
Radium Molecules

- Radium-containing molecules are interesting
- Advantages:
  - Octupole deformed
  - Very good theory support
  - High CPV sensitivity
  - Makes optically-controllable molecules
  - Demonstrated measurement protocols
- Challenges
  - Hard to get
  - Small quantities
  - Biologically hazardous
  - Long-lived radon daughters
  - Large theoretical uncertainties
  - Even “normal” molecules take years to study



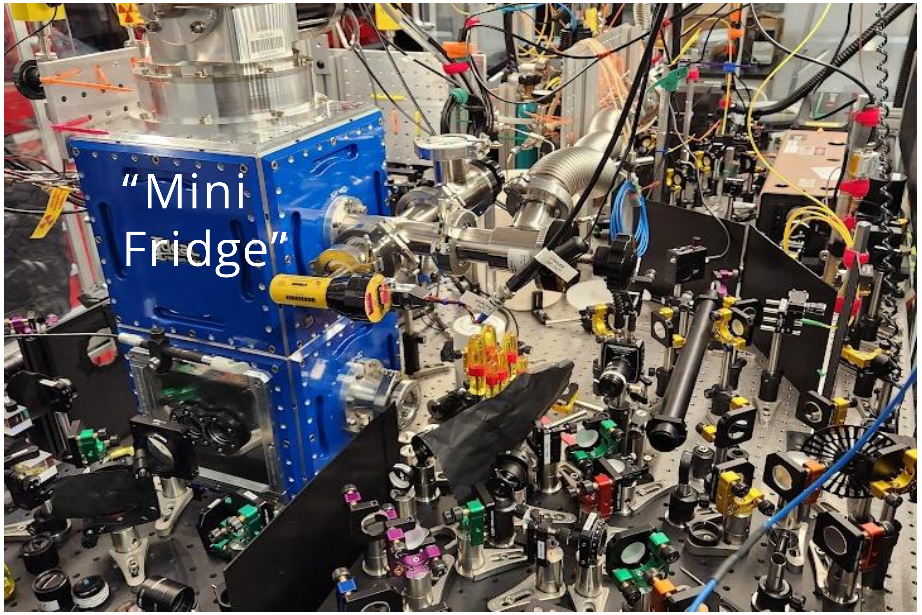
C. Zhang, NRH, L. Cheng, J. Chem. Theory Comput. 19, 4136 (2023)

Radium-226 Decay Chain

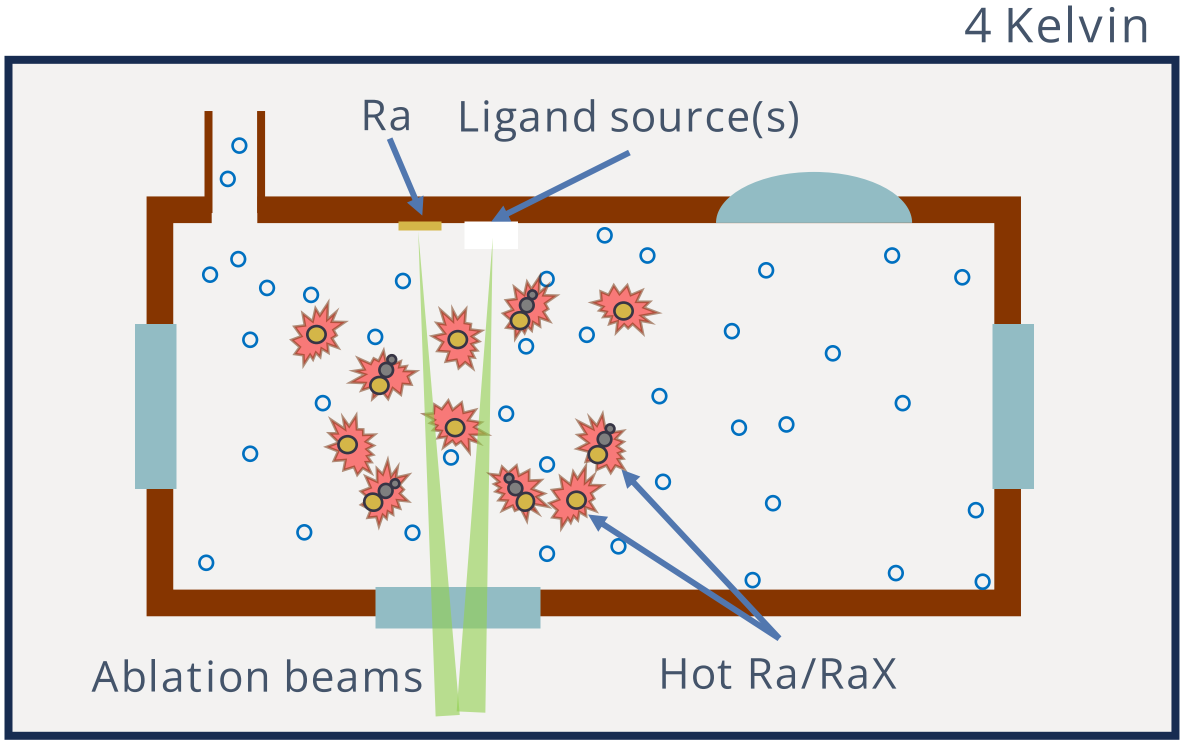


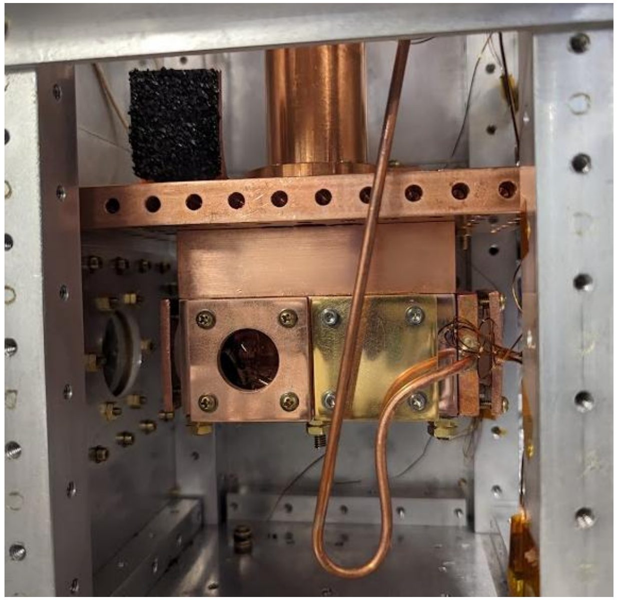
Radium Molecules @ Caltech

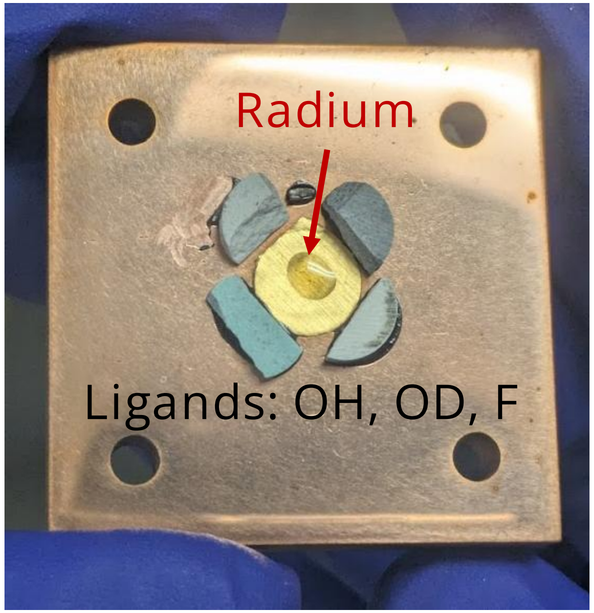
- Fabricate 10-50 μg Ra-226 targets in-house
- Synthesize and cool RaOH
  - Tabletop apparatus
  - 4 K He cooling
  - Molecules are cold, stopped
  - Ready for precision measurement, laser cooling, …
- "Challenges remain"
  - RaX collaboration with John M. Doyle and Ronald Garcia Ruiz to make cold beams
- Method should be applicable to a wide range of rare species



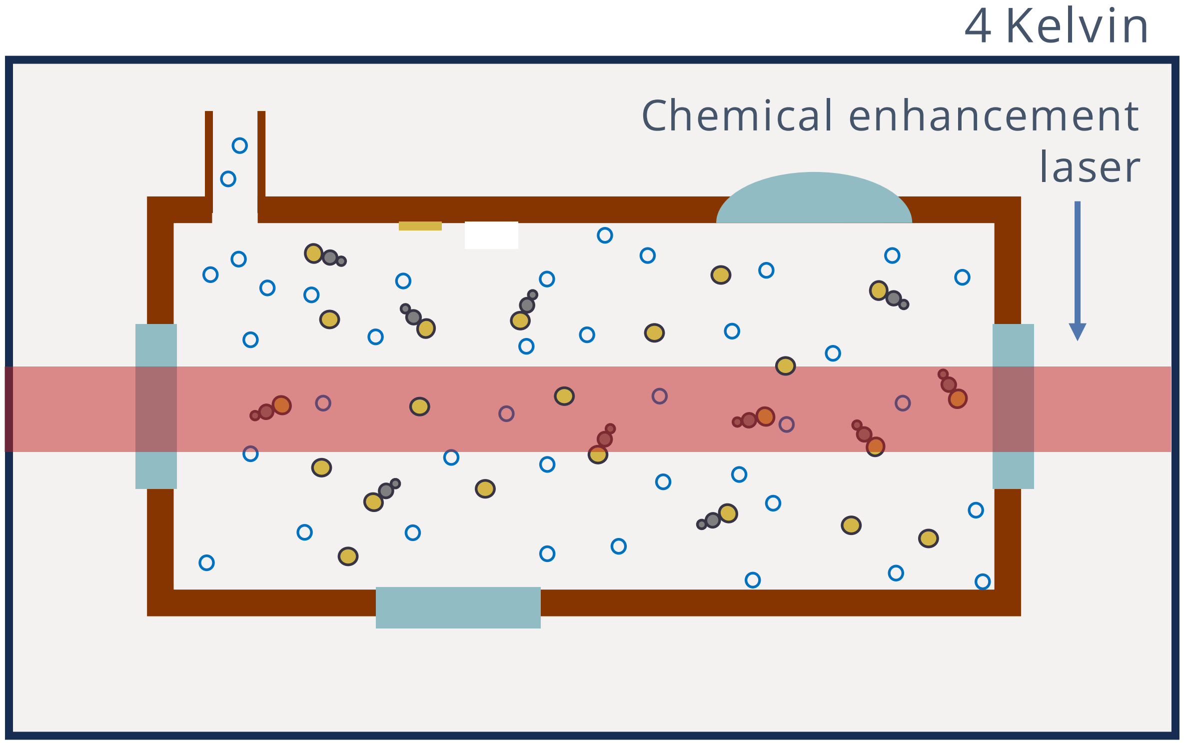
Molecule Production

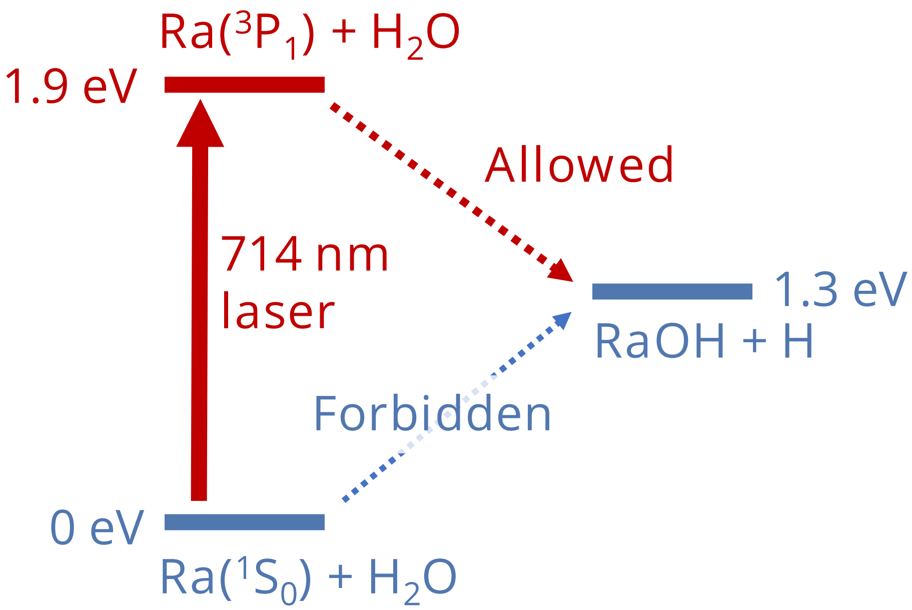






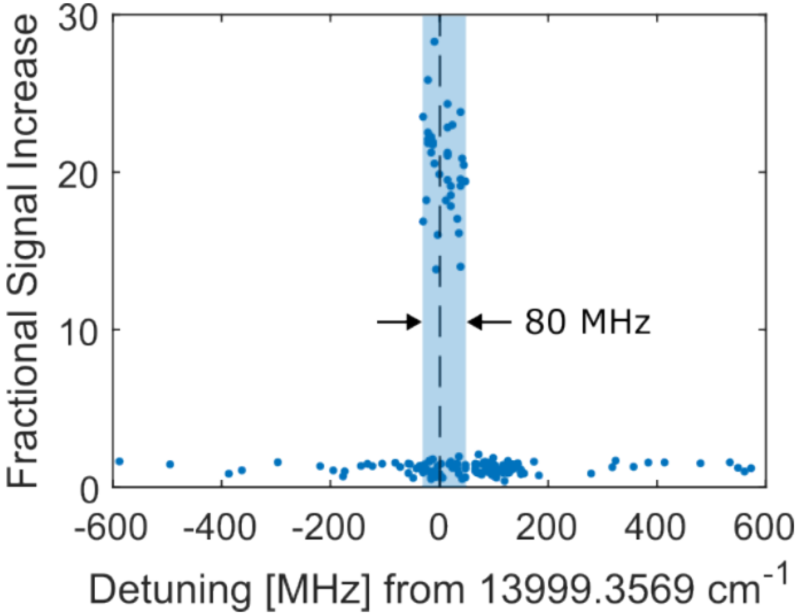
Molecule Production

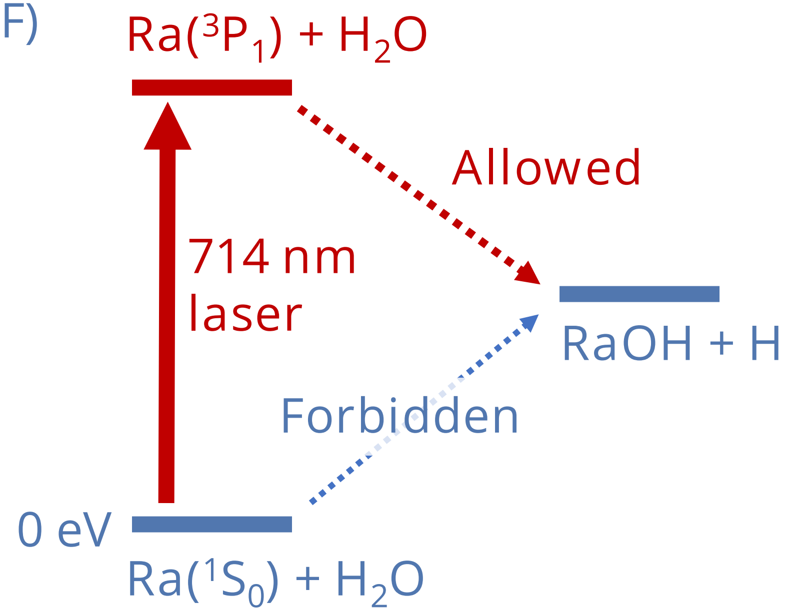




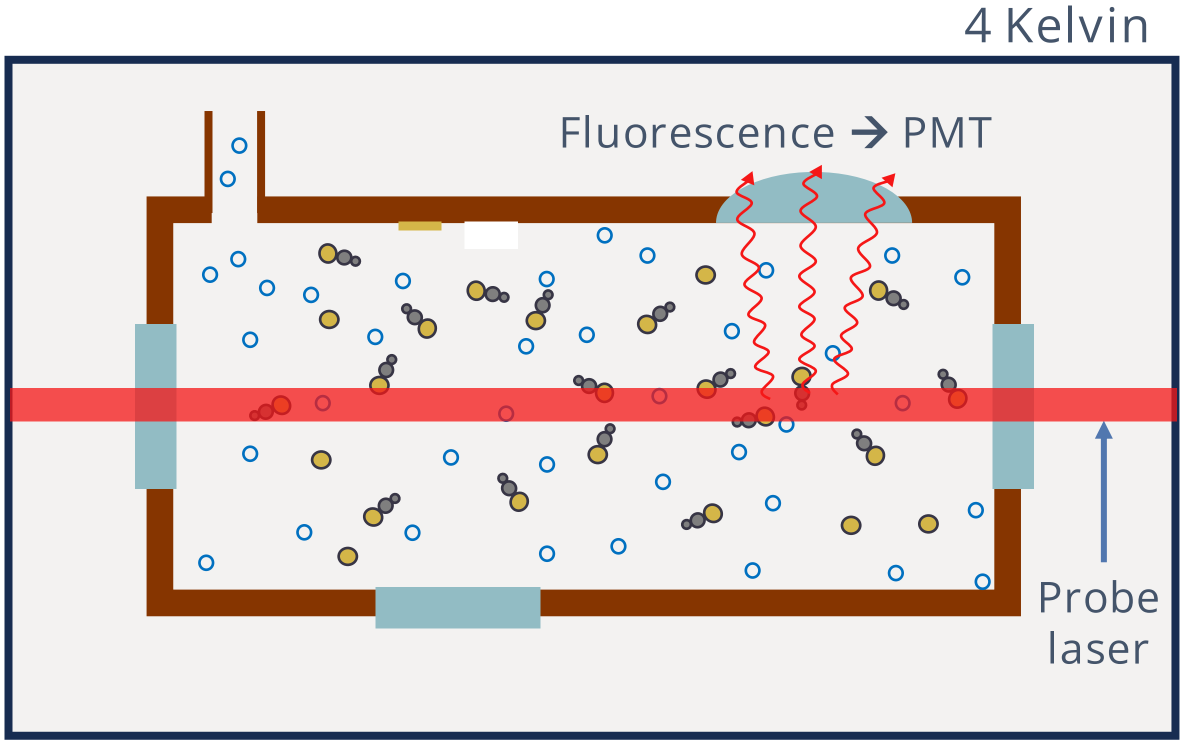
Molecule Production

RaOH production
resonant with Ra excitation
(Also works with RaOD, RaF)

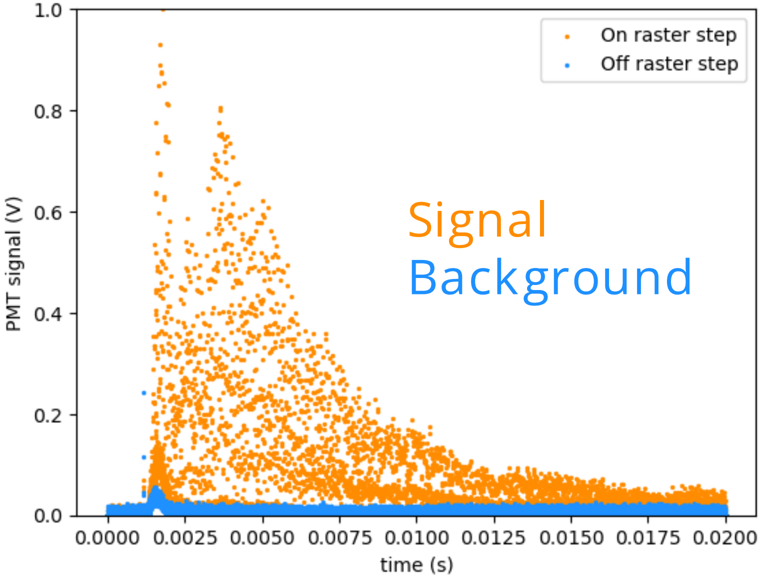




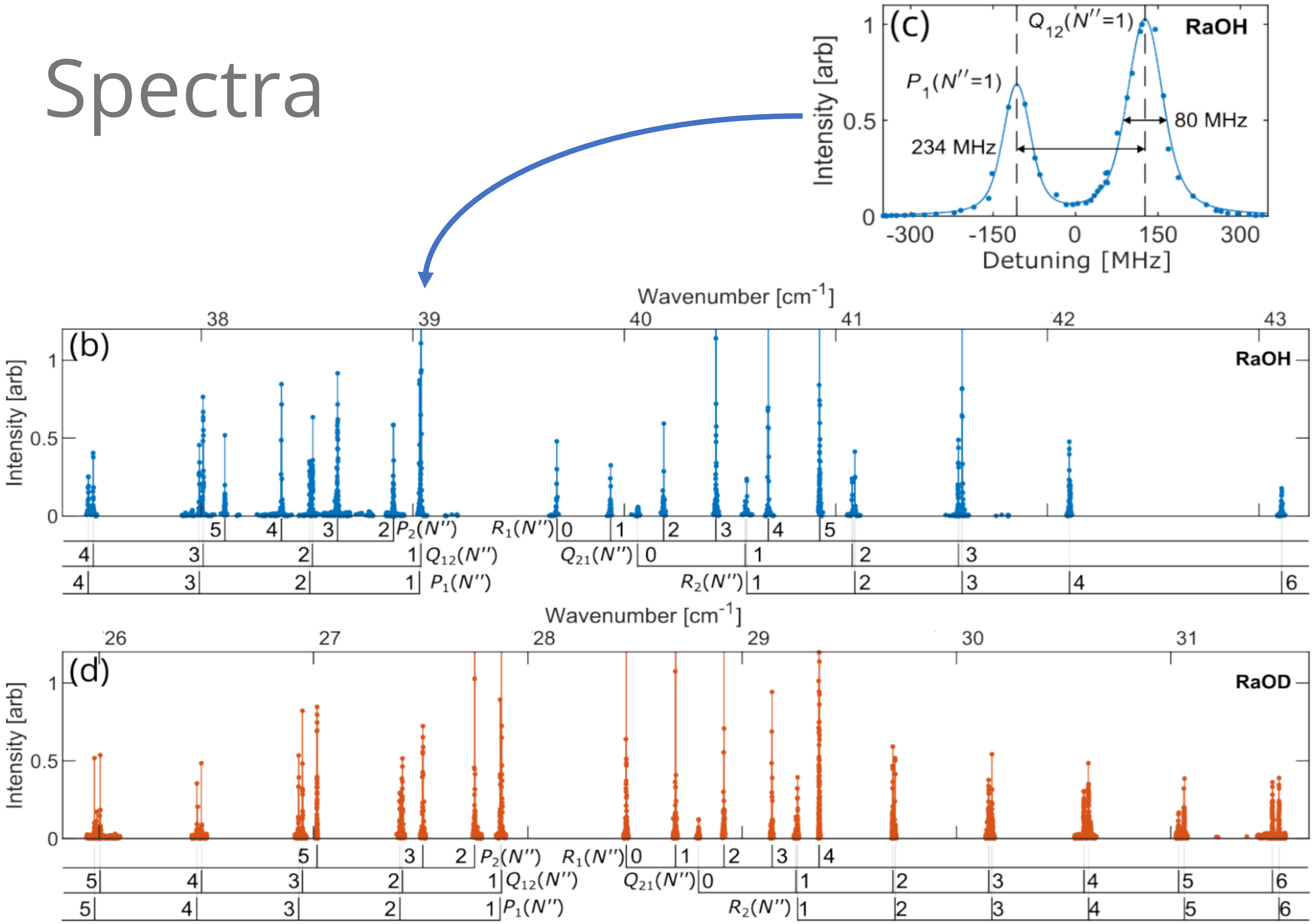
Molecule Detection



Single-shot fluorescence
From 4 K RaF molecules



Spectra

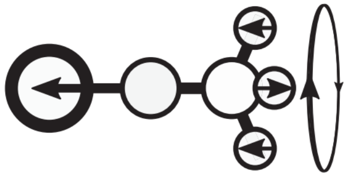

(c)
Q$_{12}$(N''=1)
RaOH
P$_1$(N''=1)
234 MHz
80 MHz
Intensity [arb]
1
0.5
0
-300
-150
0
150
300
Detuning [MHz]
Wavenumber [cm^{-1}]
38
39
40
41
42
43
(b)
RaOH
Intensity [arb]
1
0.5
0
5
4
3
2
P$_2$(N'')
R$_1$(N'')
0
1
2
3
4
5
4
3
2
1
Q$_{12}$(N'')
Q$_{21}$(N'')
0
1
2
3
4
3
2
1
P$_1$(N'')
R$_2$(N'')
1
2
3
4
6
Wavenumber [cm^{-1}]
26
27
28
29
30
31
(d)
RaOD
Intensity [arb]
1
0.5
0
5
3
2
P$_2$(N'')
R$_1$(N'')
0
1
2
3
4
5
4
3
2
1
Q$_{12}$(N'')
Q$_{21}$(N'')
0
1
2
3
4
5
6
5
4
3
2
1
P$_1$(N'')
R$_2$(N'')
1
2
3
4
5
6

RaX Collaboration

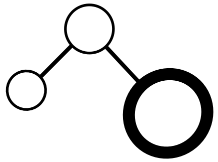
- Cryogenic beam formation for precision measurement is an engineering challenge
- RaX collaboration
  - John M. Doyle @ Harvard
  - Ronald Garcia Ruiz @ MIT
  - NRH @ Caltech
  - Support from FRIB

Radioactive Molecular Ions

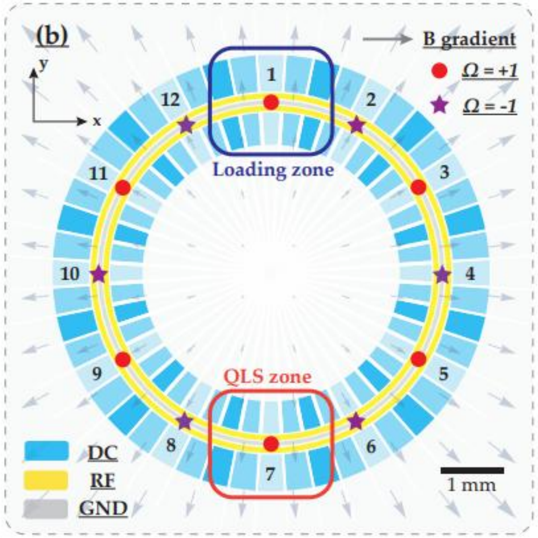
- HfF^+ eEDM gets high sensitivity with small quantities → good match for radioactive species
  - Basically need parity doublets
  - Can't reverse E field since it is used for trapping
- Radium polyatomics
  - Already created and trapped in Jayich Lab @ UCSB
- Thorium polyatomics
  - ThF^+ being pursued at Harvard, TRIUMF, UNLV
- Protactinium
  - PaF^{+++} could benefit from extreme sensitivity of Pa
- Measurement schemes under development



$RaOCH_3^+$



$RaSH^+$



M. Fan *et al.*, PRL126, 023002 (2021), P. Yu and NRH, PRL 126, 023003 (2021)
Zhou et al., PRA 109, 033107 (2024), Zülch *et al.*, arXiv:2203.10333 (2022)

Ultracold Assembled Molecules

- Can coherently associate ultracold atoms into ultracold molecules
  - Offload the difficult cooling steps onto atoms
- Demonstrated for several bi-alkali species
  - Li, Na, K, Rb, Cs
  - … Fr? Heavy, Octupole deformed, laser-cooled
- Problem: bi-alkali molecules have low CPV sensitivity
- Proposed solution: Silver
  - Ag has alkali-like structure, has been laser cooled and trapped
  - Very electronegative
  - FrAg has large CPV sensitivity
  - Under way @ Johns Hopkins (DeMille and collaborators)

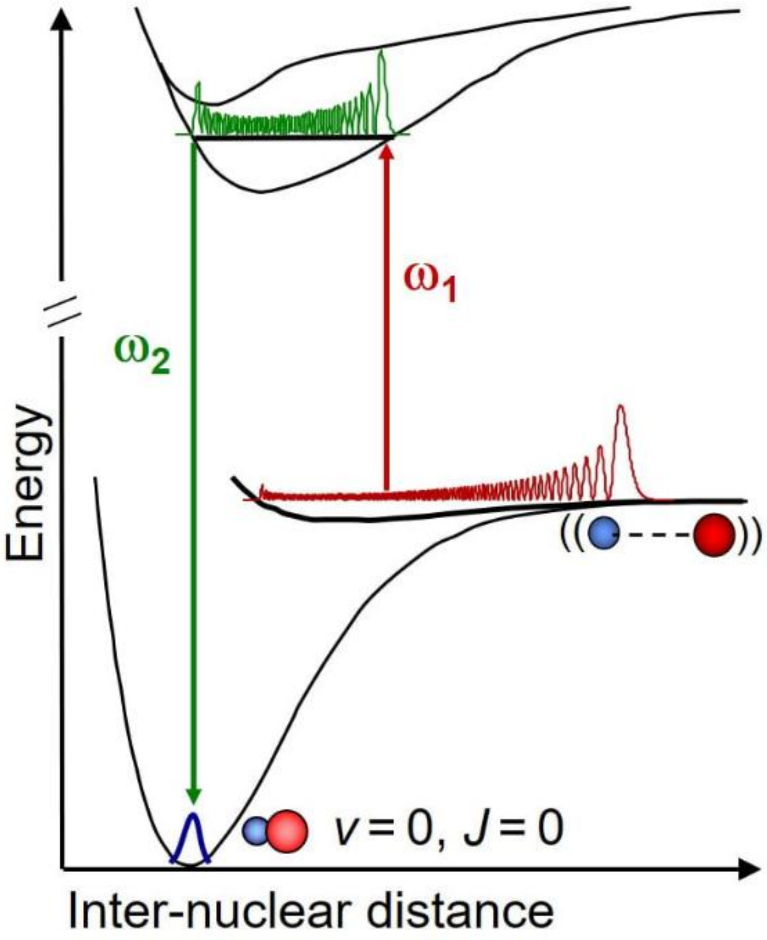
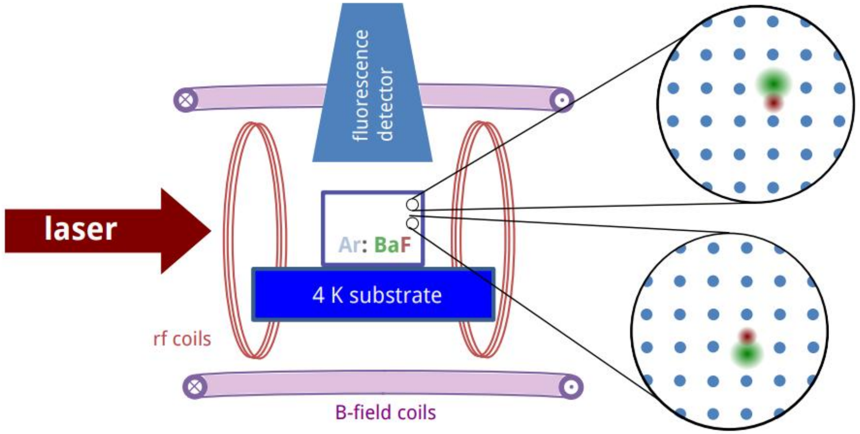


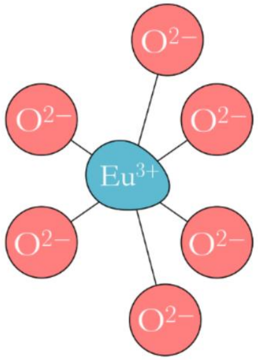
Figure from Dave DeMille

T. Fleig and D. DeMille, New J. Phys. 23, 113039 (2021)

Matrices

- One can trap extremely large numbers of atoms or molecules in solid state environments
    - Noble gas ice (EDM^3, …)
    - Crystals (ONIX, CASPEr, …)
- Can measure optically or with NMR and magnetic pickup loops
- Demonstrated to work well for oscillating EDMs





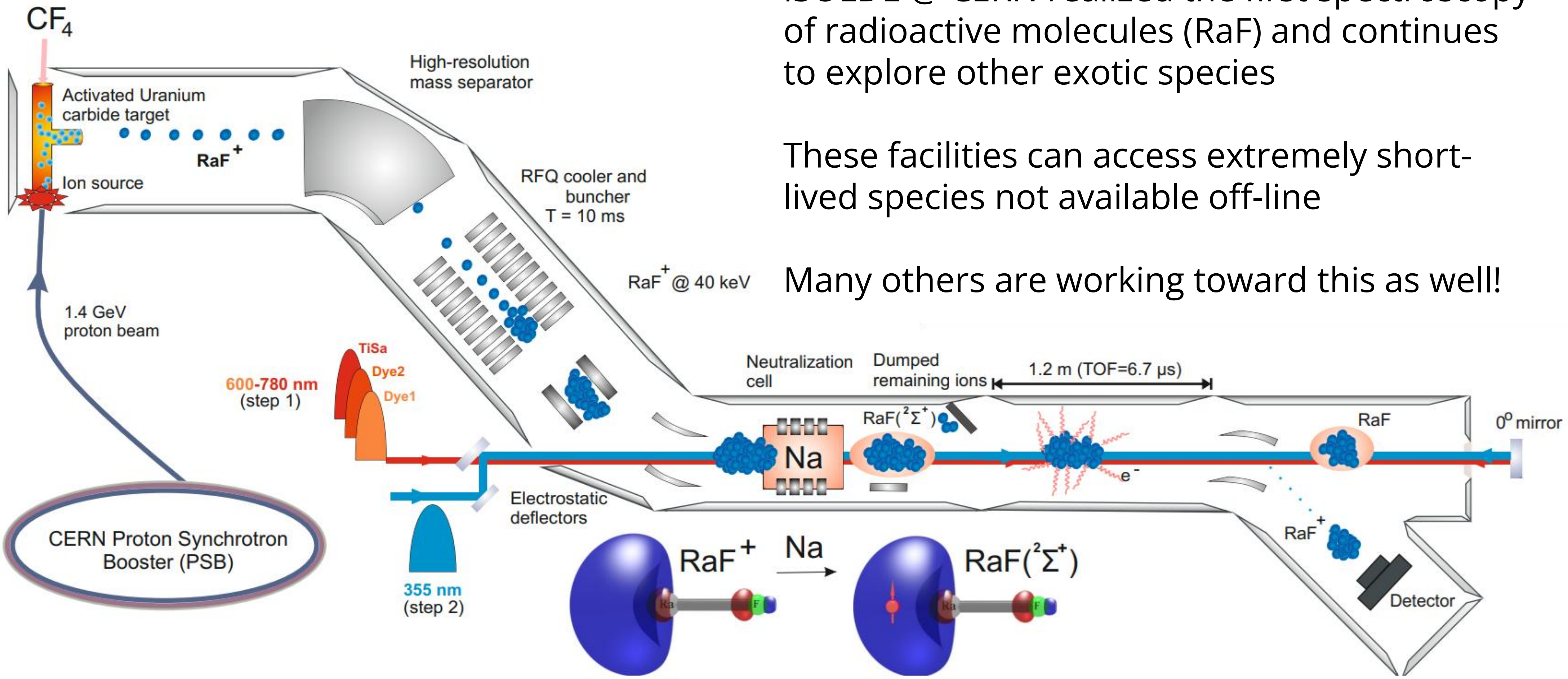
Fan *et al.*, arXiv:2410.02218 (2024), Ramachandran and Vutha, PRA 108 012819 (2023)
D. F. Jackson Kimball *et al.*, arXiv:1711.08999 (2018), Vutha *et al.*, PRA 98 032513 (2018)

Radioactive Beam Facilities

ISOLDE @ CERN realized the first spectroscopy of radioactive molecules (RaF) and continues to explore other exotic species

These facilities can access extremely short-lived species not available off-line

Many others are working toward this as well!



Many Ongoing and Upcoming Opportunities at Facilities!

IGISOL

TRIUMF

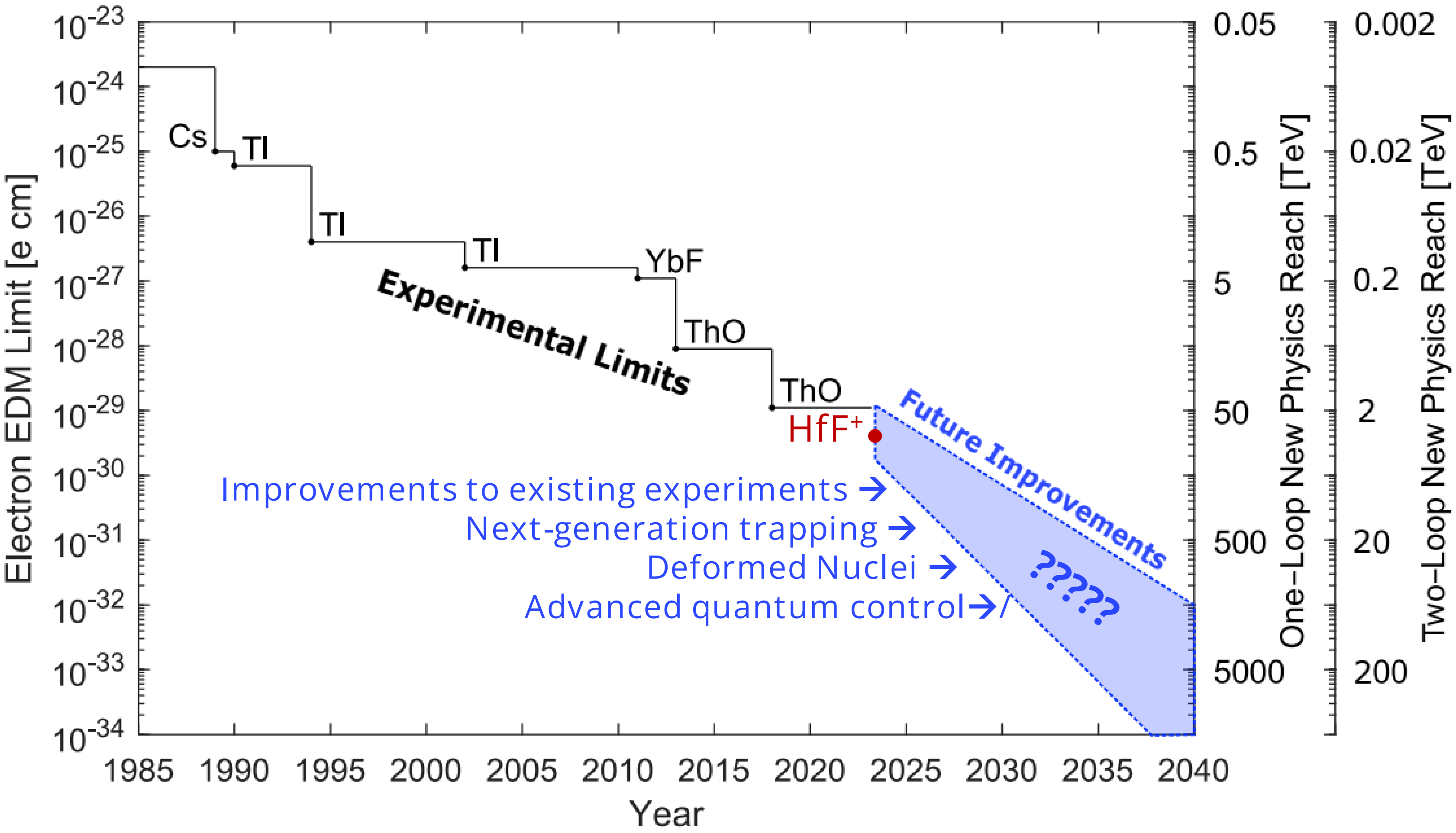
GSI FAIR

RIKEN

FRIB

ISOLDE

Future Improvements



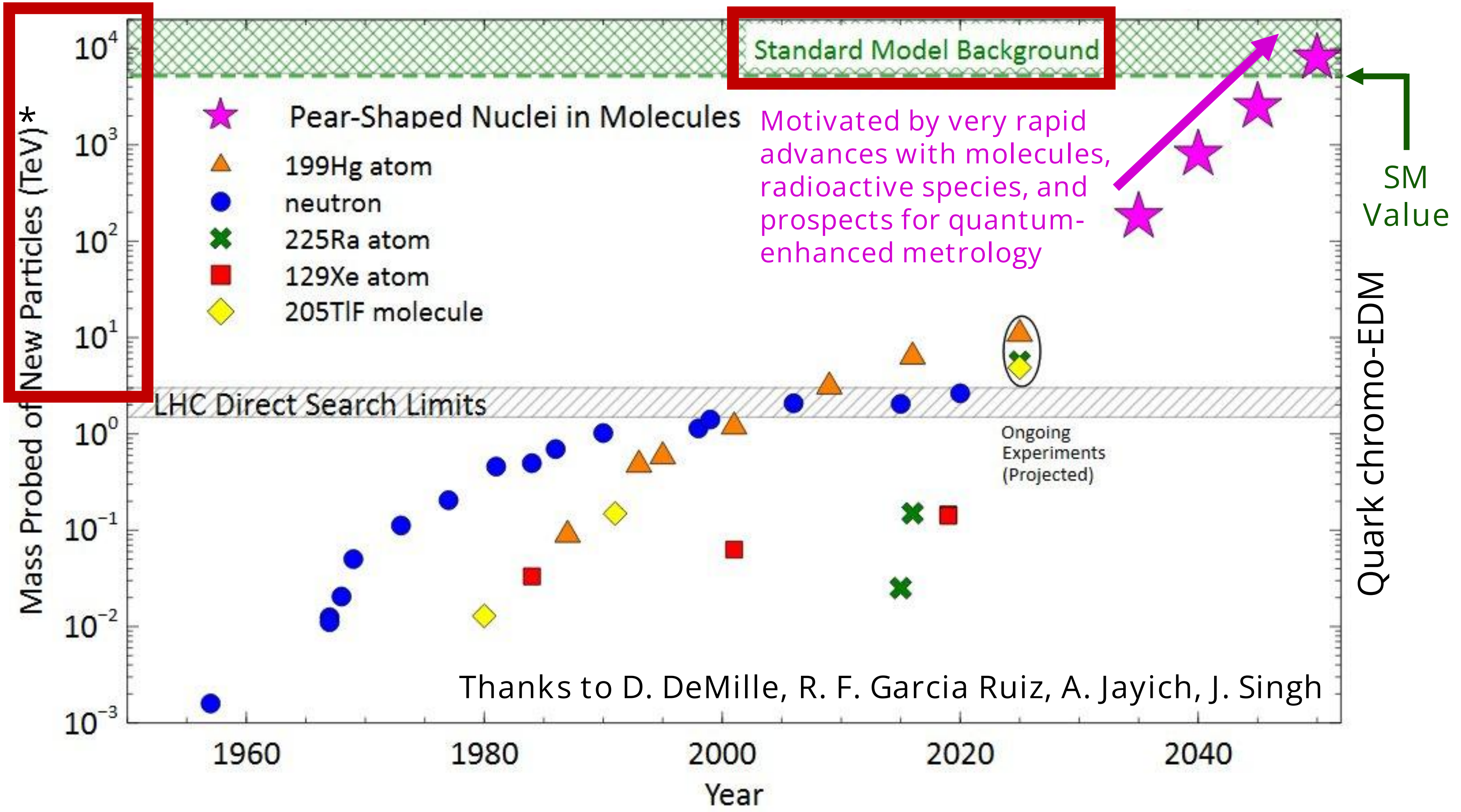
Similar improvements in hadronic CPV are also anticipated

From 2022 Snowmass EDM whitepaper, arXiv:2203:08103 – Updated

Sensitivity Outlook

Pathway to seeing hadronic CKM physics

Pathway to extreme energy scales



Motivated by very rapid advances with molecules, radioactive species, and prospects for quantum-enhanced metrology

SM Value

Thanks to D. DeMille, R. F. Garcia Ruiz, A. Jayich, J. Singh

* One-loop mass reach through quark chromo-EDMs. Different species have different mass reach for different hadronic CPV sources.

10^6 molecules
100 s coherence time
Heavy, deformed nucleus
Quantum control
Robust error rejection

~PeV-scale CP-violating physics @ 1 loop
~100 TeV-scale CP-violating physics @ 2 loops
Both leptonic and hadronic sectors
Extreme precision, $\boldsymbol{\theta_{QCD} \lesssim 10^{-14}}$
Near Standard Model CKM value
~10 – 20 year time scales

Future orders-of-magnitude improvements from quantum-enhanced metrology, highly exotic nuclei, …

The pieces are coming together!
With multiple approaches!