Electron electric dipole moment searches using ultracold molecules

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Physics with Trapped Atoms, Molecules and Ions

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Outline

- Introduction and motivation.

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- Ongoing work and future prospects.

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- An intrinsic property of the electron (if observed).

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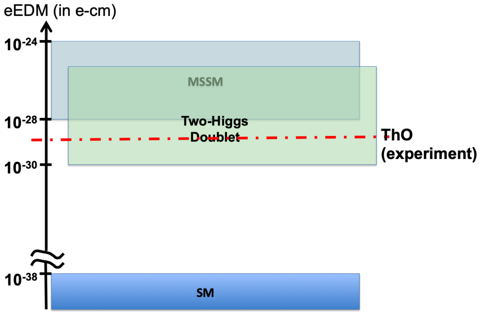

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- $\mathcal{E}_{\text{eff}}$ is a relativistic property, and requires a relativistic quantum many-body treatment. Very compute intensive.

Timeline of electron EDM experiments

Year	d_e bound	System	Ref.
1968	3×10^{-24}	Cs	M. C. Weisskopf et al, PRL, 21, 1645 (1968)
1969	2.5×10^{-23}	Cs	T. S. Stein et al, PRL, 186, 39 (1969)
1970	6×10^{-24}	Tl	H. Gould, PRL, 24, 20 (1970)
1989	1×10^{-26}	Cs	S . A. Murthy et al, PRL 63 , 965 (1989)
1990	2.7×10^{-27}	Tl	K. Abdullah , PRL, 65, 2347 (1990)
2002	1.6×10^{-27}	Tl	B. C. Regan, PRL, 88, 7 (2002)
2011	1.1×10^{-27}	YbF	N. J. Phys., 14 (2012)
2014	8.7×10^{-29}	ThO	Science 343, 269-272 (2014)
2017	1.3×10^{-28}	HfF^+	PRL 119, 153001 (2017)
2018	1.1×10^{-29}	ThO	Nature, 562, 355-360 (2018)
202?	$10^{-29} - 10^{-30}$	ThO,YbF,HfF^+, BaF	U Chicago, Imperial College,
			U C Boulder, U Toronto, U Groningen
?	?	YbOH, HgF?, $\cdots$	CalTech, $\cdots$
?	?	Radioactive molecules	MIT, $\cdots$
?	?	Superheavy molecules	?

An exciting time for electron EDM experiments!

Proposing new molecular candidates for eEDM searches

- Figure of merit for choosing right candidates:

$$\delta d_e \sim \frac{1}{2\pi \mathcal{E}_{\mathrm{eff}} \eta \sqrt{NT\tau}}.$$

[4] T. Ibrahim *et al*, Phys. Rev. D 90, 055006 (2014). Also see Fitch et al, Quantum Sci. Technol. **6**, 014006 (2021).

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- Ultracold laser cooled molecules can promise 2-3 orders of magnitude improvements via better control over some statistical and systematic effects, in both beam and trap experiments.
- Sensitivities $\sim 10^{-32}$ e cm can probe energy scales of $\sim$ 1 PeV (LHC $\sim$ 10TeV) [4]!!

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- $\mathcal{E}_{\mathrm{eff}}$ can be calculated either as an expectation value or as an energy derivative Phys. Rev. A 97, 032515 (2018), and Symmetry 12(5), 811 (2020).

Results for $\mathcal{E}_{\text{eff}}$

ThO: $\approx$ 75 GV/cm [5], HfF^{+} = 22.5 GV/cm [6].

For ongoing experiments with ultracold molecules:

- YbF: 23.1 GV/cm (Phys. Rev. A 90, 022501 (2014)).
- YbOH: 23.80 GV/cm (Phys. Rev. A 99, 062502 (2019)).
- BaF: 6.39 (Symmetry 12(5), 811 (2020)).

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For promising candidates for future electron EDM experiments:

- HgF: 115.42 GV/cm (Phys. Rev. Lett. 114, 183001 (2015)). Plans for experiment underway in China (Phys. Rev. A 99, 032502 (2019)).
- HgLi: GV/cm (Phys. Rev. A 99, 040501(R) (2019)).
- RaH: 80 GV/cm (RaF: 57 GV/cm) (Phys. Rev. A 99, 052502 (2019)).
- LrO: 258.92 GV/cm (Phys. Rev. A 104, 062801 (2021)). Ultracold part unknown yet, but superheavy systems could offer tremendous promise in the future.

[5] L. V. Skripnikov, J. Chem. Phys. 145, 214301 (2016).
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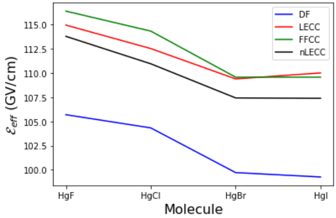
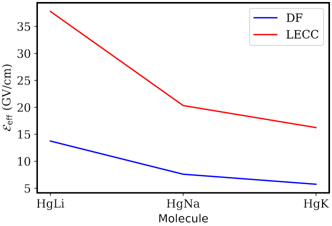
Current understanding, trends, and challenges with heavy systems





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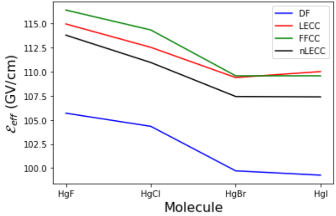

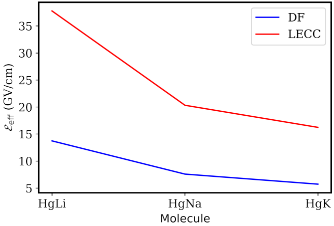

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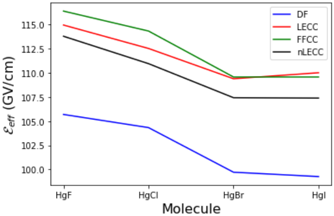

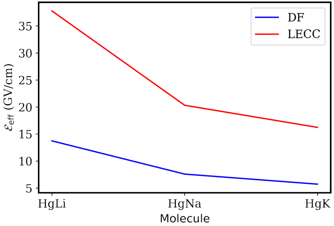

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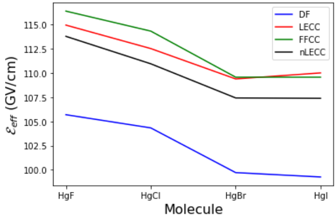

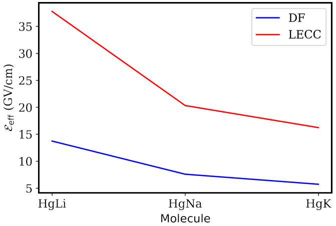

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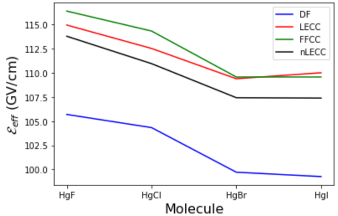

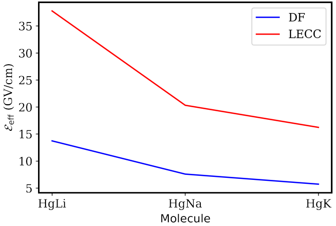

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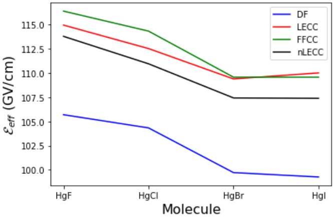

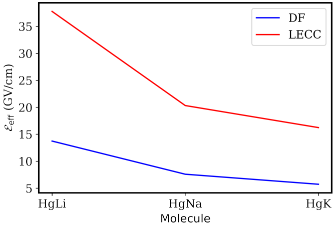

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- In summary, many exciting directions remain to be explored.

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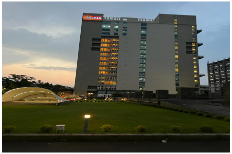
- Future plans: inclusion of multi-configurational effects appropriately in VQE algorithm.
- In the next few years, when $\sim$ 1000 qubits become available (IBM Condor and Pasqual's quantum computers), one can use quantum computers for probing fundamental physics.

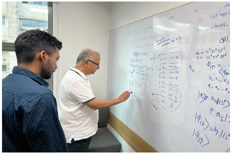
- TCG CREST is a new research institute, with its verticals carrying out research in quantum science and technology, artificial intelligence, sustainable energy, and neuroscience.
- Joint PhD programme with IIT Tirupati. Applications are now open!



Our building

CQuERE entrance

Discussion lobby



Whiteboard discussions

Intelligent classroom

Infinite coffee!

- Please visit https://www.tcgcrest.org/institutes/cquere/ .

Thank You!

Details

- HgX: bond lengths from literature. Dyall's QZ basis for Hg, and cc-pVQZ for halides. All-electron calculations. 1000 au cut-off. At 100 processors (6.5 days vs 2.5 hours), we got the right balance between time and speed-up. Error budget: LECC vs nLECC: about 2.5 percent. Error due to diffuse functions excluded: 2.5 percent. Beyond QZ: at most 10 percent error. Triples etc: 3 percent. Other non-linear terms: 2 percent.
- RaX and RaY (LECC): Dyall's DZ basis for PEC (X2C, or DFT (PBE0 functional)), and also for computations. 80 au cut-off.
- RaH (LECC and FFCC): Dyall's DZ basis for PEC, and QZ basis for computing effective electric field, and all-electron calculations. Error budget: about 5 percent (truncations in LECC, basis set incompleteness, and bond length dependence).
- LrX (nLECC): Dyall's TZ basis and 2000 au cut-off for PECs, and QZ basis for calculating effective electric fields.

A feel for numbers

- Molecular dipole moments, for example, are around 10^{-8} to 10^{-9} e cm. Compare this with the upper bound to eEDM: 10^{-29} e cm!
- Other EDMs? : n $\sim 10^{-26}$, $\mu \sim 10^{-19}$, ... (all in units of e-cm) [7].

[7] Rev.Mod.Phys. 91, 1, 015001 (2019).

A feel for numbers: part 2

- EDM experiment: $\delta E \approx 200 \mu Hz$.
- The highest lab electric fields are of the order of 10^2 kV/cm.
- Value of $n \cdot z$ for YbF: 0.55 [8].
- Motional magnetic fields: for YbF, it is around 5 $\times 10^{-32}$ e cm.
- Typical T values: 500 hours for ThO, for example.
- Typical coherence times $\sim$ 1 ms for neutral beam experiments, and ~ 700 ms for HfF^+, for example (Cairncross, PRL, 2017).

[8] New Journal of Physics 14 (2012) 103051

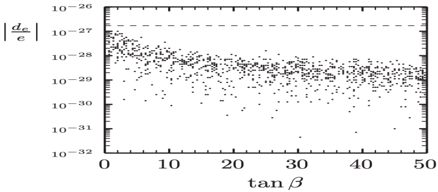
Effective electric field and sensitivity: a feel for numbers

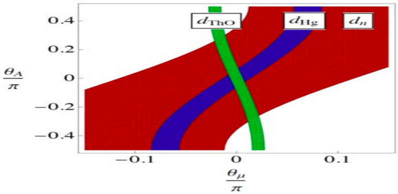
HgX:

- η =0.5, T=10^7s, $\tau = 1$s, and N=10^4.
- 100 GV/cm translates to 1.3×10^{-31} e-cm.
- 110 GV/cm: 1.2×10^{-31} e-cm.
- 120 GV/cm: 10^{-31} e-cm.

HgA:

-
- η =0.13, T=10^7s, $\tau = 1$s, and N=10^4.
- 14 GV/cm: 3.6×10^{-30} e-cm.
- 24 GV/cm: 2×10^{-30} e-cm.
- 35 GV/cm: 1.4×10^{-30} e-cm.





References:
We-Fu Chang, Electric Dipole Moment in (S)SUSY models, INT EDM Workshop (2007).
Adam West, Lepton Dipole Moments, Physics In Collision (2015): arXiV 1607.00925v1.

SUSY, etc

One loop EDM in SUSY:

$$d_e \sim 10^{-23} g^2 sin\phi_{CP} (\frac{100GeV}{M})^2 e - cm$$

Solution:
Smaller CP phase (10^{-2} or smaller), so that the sine is very small, or heavy sfermions, etc.

Aside: Matter-antimatter asymmetry

- Baryon asymmetry coefficient:
  $\eta = \frac{n_b}{n_\gamma} \approx 6.1^{+0.3}_{-0.2} \times 10^{-10}$
- Baryon asymmetry coefficient from SM: $\sim 10^{-18}$.
- Both the eEDM and η require CPV.
- Is there a model that predicts the right amount of CPV to explain both these phenomena?

Aside: Matter-antimatter asymmetry

$$\begin{aligned}
\eta &= \frac{45}{2\pi^2 N_{eff}} \kappa n_F \alpha_W^6 sin^3(2\alpha)\lambda_{CP} \frac{m_t^2 T_c^2}{v_1^3 v_2} \\
d_e &= \frac{m_1^2}{2\sqrt{2}G_F} \frac{(v_2(M^{-2})_{23} + v_1(M^{-2})_{13})}{v_1 v_2 v} 1.3 \times 10^{-26} e - cm
\end{aligned}$$

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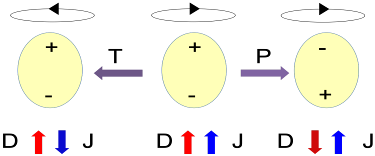
P violation necessary for eEDM



P violation necessary for eEDM

No external electric field, stationary state:

$$\langle d \rangle = \langle \varphi | d | \varphi \rangle \tag{1}$$

$$\begin{aligned} \langle d \rangle &= \langle \varphi | P^\dagger P d P^{-1} P | \varphi \rangle \\ &= -\langle \varphi' | d | \varphi' \rangle \end{aligned} \tag{2}$$

The following equation is satisfied by the stationary state:

$$H|\varphi\rangle = E|\varphi\rangle \tag{3}$$

That is,

$$\begin{aligned} PHP^{-1}P|\varphi\rangle &= EP|\varphi\rangle \\ H|\varphi'\rangle &= E|\varphi'\rangle \end{aligned} \tag{4}$$

Here, it is assumed that the Hamiltonian is invariant under space inversion.
Therefore, both $|\varphi\rangle$ and $|\varphi'\rangle$ describe stationary states whose energies are the same, given by E.
If the energy level is non-degenerate, then $|\varphi'\rangle = c|\varphi\rangle$, where c is an eigenvalue of the parity operator, which means that it is either $+1$ or -1.

P violation necessary for eEDM

$$\begin{aligned} \therefore \langle\varphi|d|\varphi\rangle &= -\langle\varphi'|d|\varphi'\rangle \\ &= -c^2\langle\varphi|d|\varphi\rangle \\ &= -\langle\varphi|d|\varphi\rangle \end{aligned} \tag{5}$$

The above equation is true, only if $\langle d\rangle = 0$.
This means that if the Hamiltonian is invariant under parity, and if the stationary state is non-degenerate, then the EDM=0, for that system. Back to slide

Consider the time dependent Schrodinger's equation:

$$i\hbar\frac{d\psi(\vec{x},t)}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi(\vec{x},t)}{dx^2} + V(\vec{x})\psi(\vec{x},t) \tag{6}$$

For simplicity, V is made dependent on space and spin, but not time. Note that if V is real, then if $\psi(t)$ is a solution, so is $\psi^*(-t)$. This is because on the right hand side, not only does t go to -t, but also i to -i (since T is anti-unitary). However, if V were to be complex, that is, $V = |V|(cos(\phi) + isin(\phi))$, in other words, $V = Ve^(i\phi)$, where ϕ is called the complex phase, then T is violated. We can say that the complex phase, ϕ specifies the degree of T violation in the system, or the degree of CP violation (assuming CPT theorem). It is in a very similar way that complex phases in quantum field theory also imply T violation. The only complex phase associated with the weak sector in the SM is the CKM phase, which occurs in the CKM matrix.

$$\omega_1 = -\mu \cdot B - d \cdot E \quad (7)$$

$$\omega_2 = -\mu \cdot B + d \cdot E \quad (8)$$

$$\Delta\omega = \omega_2 - \omega_1 \quad (9)$$

$$= 2d \cdot E \quad (10)$$

Note that the constants involved in the expression (like $\hbar$) are not explicitly mentioned.
Idea: Apply an electric field, perpendicular to d (same direction as L). This results in a torque, $d \times E$, perpendicular to d and E. But, $\tau = \frac{dL}{dt}$. That is, dL is perpendicular to L. Hence, precession.
If ϕ is the angle between L and the line connecting the tail of L with the head of dL, then: $\omega = \frac{d\phi}{dt} = \frac{dL}{Ldt} = \frac{\tau dt}{Ldt} = \frac{dE}{L}$; L is $h/4\pi$.

Experiment

$$\psi = \frac{|0\rangle + |1\rangle}{\sqrt{2}} \tag{11}$$

$$\psi(t) = \frac{e^{i\phi}|0\rangle + |1\rangle}{\sqrt{2}} \tag{12}$$

$$\tag{13}$$

Polarization factor

- A diatomic in state, $|\psi_\alpha^0\rangle$. External field: E (perturbation; an important approximation).
- $\therefore |\psi_\alpha\rangle = |\psi_\alpha^0\rangle + |\psi_\alpha^1\rangle + \cdots$
- To evaluate: $\langle\psi_\alpha|d \cdot E|\psi_\alpha\rangle$. E is along z, and d along n.
  $\langle\psi_\alpha|d \cdot E|\psi_\alpha\rangle = d^2E^2 \sum_{m\neq\alpha} 2\frac{|\langle\psi_\alpha^0|n.z|\psi_m^0\rangle|^2}{\Delta E}$
  $\therefore \langle\psi_\alpha^0|n.z|\psi_m^0\rangle \equiv \eta = dE \sum_{m\neq\alpha} \frac{|\langle\psi_\alpha^0|n.z|\psi_m^0\rangle|^2}{B}$
- Only the rotational states contribute significantly, since $\Delta E \sim 1GHz$, whereas for vibrational states, $\Delta E \sim 10THz$, and it is $\sim 100THz$ for electronic states.

eEDM Hamiltonian

We start with the magnetic dipole interacting with a spin $1/2$ particle. It takes the form (Bjorken and Drell):

$$H_{M1} = \frac{\kappa\mu}{2}\sigma_{\mu\nu}F^{\mu\nu} \tag{14}$$

Here, κ is some constant, $\sigma_{\mu\nu} = \frac{i}{2}[\gamma^\mu\gamma^\nu]$, and $F^{\mu\nu}$ is the electromagnetic field tensor, given by $\partial^\mu A^\nu - \partial^\nu A^\mu$. Now, using the approach by Salpeter, an EDM can be considered as an odd-parity counterpart of the MDM, that is, $H_{E1} = \gamma^5 H_{M1}$. Also, $\kappa\mu$ is replaced by $-id$, where the 'i' is to ensure that the resulting Hamiltonian is Hermitian.

$$\begin{aligned} H_{E1} &= \frac{id}{2}\gamma^5\sigma_{\mu\nu}F^{\mu\nu} && (15) \\ &= -d\beta(\vec{\sigma}\cdot\vec{E} - i\alpha\cdot\vec{B}) && (16) \end{aligned}$$

Note: $\sigma_{\mu\nu} = \frac{i}{2}[\gamma^\mu\gamma^\nu]$

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Note: $\sigma_{\mu\nu} = \frac{i}{2}[\gamma^\mu\gamma^\nu]$

EDM in non-relativistic case

- We can rewrite the eEDM Hamiltonian as:
  $-e\beta\sigma \cdot E_{intl} = [\beta\sigma \cdot \nabla, H_0] + 2\frac{ic}{\hbar}\sum_j \beta\gamma_5 p_j^2$
- In the expectation value of the above expression, the first term vanishes. This is because the commutator involves two terms, both containing H_0, which implies that both the terms give an energy term corresponding to it (this is because E_{eff} is the expectation value of the unperturbed wave function, which is the eigenstate of the unperturbed Hamiltonian, by definition).
- NR case: $[\sigma \cdot \nabla, H_0] = -e\sigma \cdot E_{intl}$

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CC vs CI

CISD:

$$\begin{aligned} C_1 &= T_1 \quad (17) \\ C_2 &= T_1^2 + T_2 \quad (18) \end{aligned}$$

With the same level of hole-particle excitations, $|\psi_{CCSD}\rangle = e^{(T_1+T_2)}|\Phi_0\rangle$. We see that the CCSD approximation contains all the powers of T_1 and T_2 (due to the exponential nature of ψ_{CC}). Of course, in an actual calculation, we cannot take into account all the terms. Truncated CCM is size extensive.

CC vs MBPT

$$|\psi\rangle = |\psi^0\rangle + |\psi^1\rangle + \cdots \quad (19)$$

$$|\psi^1\rangle = \sum_S C_S^1 |\psi_S\rangle + \sum_D C_D^1 |\psi_D\rangle + \ldots \quad (20)$$

$$|\psi_\alpha^1\rangle = \sum_{n\neq\alpha} \frac{|\psi_n\rangle\langle\psi_n|H'|\psi_\alpha\rangle}{E_\alpha - E_n} \quad (21)$$

$$H' = V - V^{HF} \quad (22)$$

$$If\ |\psi_n\rangle = |\psi_i^a\rangle, then \quad (23)$$

$$\langle\psi_n|H'|\psi_\alpha\rangle = 0 : T_1, C_S^1 \quad (24)$$

$$If\ |\psi_n\rangle = |\psi_{ij}^{ab}\rangle, then \quad (25)$$

$$\langle\psi_n|H'|\psi_\alpha\rangle = \langle ab|v|ij\rangle - Exch : T_2, C_D^1 \quad (26)$$

Similarly, C_S^2 is T_1^2, etc. This also tells us why $T_1 T_2$ is probably more important than T_1^3.

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Jacobi method

Rewrite the CC equations in the form $A(X) \cdot X = -B$.
$A_{11}X_1 + A_{12}X_2 + \cdots + A_{1n}X_n = B_1 \Rightarrow X_1 = (-B_1 - (A_{12}X_2 + \cdots + A_{1n}X_n))/A_{11}$
$A_{21}X_1 + A_{22}X_2 + \cdots + A_{2n}X_n = B_2 \Rightarrow X_2 = (-B_2 - (A_{22}X_2 + \cdots + A_{2n}X_n))/A_{22}$
$\cdots$
$\therefore\ X_i^n = \frac{-B_i - \sum_{j \neq i} A_{ij} X_j^{(n-1)}}{A_{ii}}$
Guess the amplitudes, obtain a new set of amplitudes. Repeat, till convergence.

For the CCSD approximation:

$$\begin{pmatrix} \langle\Phi_i^a|\bar{H}_N|\Phi_i^a\rangle & \langle\Phi_i^a|\bar{H}_N|\Phi_{ij}^{ab}\rangle \\ \langle\Phi_{ij}^{ab}|\bar{H}_N|\Phi_{ij}^{ab}\rangle & \langle\Phi_{ij}^{ab}|\bar{H}_N|\Phi_i^a\rangle \end{pmatrix} \begin{pmatrix} t_i^a \\ t_{ij}^{ab} \end{pmatrix} = \begin{pmatrix} \langle\Phi_i^a|H_N|\Phi_0\rangle \\ \langle\Phi_{ij}^{ab}|H_N|\Phi_0\rangle \end{pmatrix} \tag{27}$$

Mercury halides

Molecule	$\mathcal{E}_{\mathrm{eff}}^{DF}$	$\mathcal{E}_{\mathrm{eff}}$	PDM^{DF}	PDM
HgF	**104.25**	**115.42**	3.96	2.61
HgCl	103.57	113.56	4.23	2.72
HgBr	97.89	109.29	4.40	2.36
HgI	96.85	109.3	**3.91**	**1.64**

Table: Effective electric fields (in GV/cm) and PDMs (in Debyes) of HgX.

- ThO≈75 GV/cm[9], HfF^+ = 22.5 GV/cm [10], YbF=23.1 GV/cm[11], Fr≈9 MV/cm [12], Tl≈6 MV/cm [13], Cs≈1.25 MV/cm [14], $\cdots$ (Atoms: 10 kV/cm field).
- N$> 10^3$, $\tau \sim$ 1s (ThO $\sim$ ms), low polarizing field ($\sim$ 1 kV/cm), etc.
- Laser-cooled HgF trap experiment[15]: predicts 6×10^{-32} e-cm (ThO: 10^{-29} e-cm).

V. S. Prasannaa, A. C. Vutha, M. Abe, and B. P. Das, Phys. Rev. Lett. 114, 183001 (2015), and **V. S. Prasannaa**, M. Abe, B. P. Das, A J Phys, 25, 10, 1259 (2016), and B. P. Das, M. K. Nayak, M. Abe, and **V. S. Prasannaa**, Handbook of Relativistic Quantum Chemistry, Springer-Verlag Berlin Heidelberg (2015).

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$$\mathcal{E}_{\text{eff}}^{DF} = \langle \phi_v | h_{eEDM}^{eff} | \phi_v \rangle = 2 \sum_k \sum_l C_k^{*S} C_l^L \langle \chi_{v,k}^S | p^2 | \chi_{v,l}^L \rangle$$

Atom	Mixing	HgF	HgCl	HgBr	HgI
Hg	$s - p_{1/2}$	**-266.29**	**-263.47**	**-247.98**	**-239.52**
Hg	$p_{1/2} - s$	**371.96**	**367.74**	**345.2**	**335.33**
Hg	$p_{3/2} - d_{3/2}$	32.83	26.63	22.26	21.41
Hg	$d_{3/2} - p_{3/2}$	-34.1	-27.62	-23.25	-22.26
Hg	$d_{5/2} - f_{5/2}$	-0.98	-0.54	-0.4	-0.33
Hg	$f_{5/2} - d_{5/2}$	0.99	0.55	0.4	0.34
X	$s - p_{1/2}$	-2.68	-4.83	-10.31	-16.63
X	$p_{1/2} - s$	2.68	4.89	10.85	19.16
Total		**104.41**	**103.35**	**96.77**	**97.5**
	$s - p_{1/2} + p_{1/2} - s$	**105.67**	**104.27**	**97.22**	**95.81**

Table: Effective electric fields of HgX at DF level of theory. All units are in GV/cm.

V. S. Prasannaa, M. Abe, V. M. Bannur, and B. P. Das, Phys. Rev. A 95, 042513 (2017).

- Which correlation terms contribute the most?
$\langle H^{eff}_{eEDM} \rangle = \langle \Phi_0 | (1 + T_1 + T_2)^\dagger H^{eff}_{eEDM,N} (1 + T_1 + T_2) | \Phi_0 \rangle_C + \langle \Phi_0 | H^{eff}_{eEDM} | \Phi_0 \rangle$

Term	HgF	HgCl	HgBr	HgI
DF	104.25	103.57	97.89	96.85
$HT_1 + cc$	**20.16**	**19.34**	**22.18**	**24.78**
$T_1^\dagger HT_1$	-3.91	-3.58	-4.07	-4.77
$T_1^\dagger HT_2 + cc$	0.44	0.194	-0.2	-0.30
$T_2^\dagger HT_2$	-5.52	-5.96	-6.5	-7.26
Total	115.42	113.56	109.29	109.30

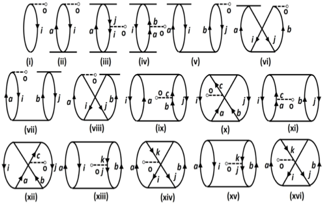
Table: Effective electric fields of HgX: correlation contributions. All units are in GV/cm.

This Table indicates an important theme in such calculations: cancellations between terms.

V. S. Prasannaa, M. Abe, V. M. Bannur, and B. P. Das, Phys. Rev. A 95, 042513 (2017).

HgF	CI [56]	4.15	99.26
	LERCCSD [57]	2.61	
	MRCI [53]		68
	MRCI [54]		95
	DF (This work)	4.11	105.69
	LERCCSD [8]		115.42
	FFCCSD [9]	2.92	116.37
	LERCCSD (This work)	3.25	114.93
	nLERCCSD (This work)	3.45	113.77
HgCl	CI [58]	3.28	
	LERCCSD [57]	2.72	
	LERCCSD [8]		113.56
	FFCCSD [9]	2.96	114.31
	DF (This work)	4.30	104.33
	LERCCSD (This work)	3.26	112.51
	nLERCCSD (This work)	3.45	110.94
HgBr	CI [58]	2.62	
	LERCCSD [57]	2.36	
	LERCCSD [8]		109.29
	FFCCSD [9]	2.71	109.56
	DF (This work)	4.14	99.72
	LERCCSD (This work)	2.62	109.38
	nLERCCSD (This work)	2.94	107.42
HgI	LERCCSD [57]	1.64	
	LERCCSD [8]		109.3
	FFCCSD [9]	2.06	109.56
	DF (This work)	3.61	99.27
	LERCCSD (This work)	1.50	110.00
	nLERCCSD (This work)	2.01	107.38

Molecule		HgF		HgCl		HgBr		HgI	
Term	**Diagram**	**L**	**nL**	**L**	**nL**	**L**	**nL**	**L**	**nL**
DF	Figure 1i	105.69		104.33		99.72		99.27	
AT_1	Figure 1ii	17.09	13.11	17.05	12.21	19.83	14.76	23.85	15.71
$T_1^{\dagger}AT_1$	Figure 1iii	−1.85	−0.28	−2.01	−0.25	−2.65	−0.62	−3.66	−0.41
	Figure 1iv	−1.41	0.16	−1.40	0.28	−1.21	0.47	−1.56	1.16
$T_1^{\dagger}AT_2$	Figure 1v	1.19	0.93	0.65	0.29	0.38	−0.11	0.38	−0.27
	Figure 1vi	0.05	0.08	0.06	0.05	−0.01	−0.07	−0.03	−0.09
	Figure 1vii	0.61	0.58	0.92	0.85	0.66	0.32	0.57	0.19
	Figure 1viii	−1.31	−1.27	−1.24	−1.18	−0.91	−0.63	−1.26	−0.98
$T_2^{\dagger}AT_2$	Figure 1ix	−2.50	−2.46	−2.54	−2.49	−2.68	−2.65	−2.93	−2.89
	Figure 1x	−0.17	−0.17	−0.15	−0.14	−0.14	−0.13	−0.13	−0.11
	Figure 1xi	−1.22	−1.40	−1.50	−1.47	−1.65	−1.85	−1.96	−1.99
	Figure 1xii	−0.17	−0.17	−0.15	−0.14	−0.14	−0.13	−0.13	−0.11
	Figure 1xiii	−1.64	−1.57	−1.67	−1.57	−1.70	−1.58	−1.84	−1.69
	Figure 1xiv	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10
	Figure 1xv	0.77	0.74	0.36	0.37	0.08	0.12	−0.37	−0.21
	Figure 1xvi	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10	−0.10
Total		114.93	113.77	112.51	110.94	109.38	107.42	110.00	107.38



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Mercury alkalis

- N$> 10^4$, $\tau \sim$ 1s, low polarizing field ($\sim$ 10-70 kV/cm), etc.
- Predicted sensitivity of a future trap experiment: $\sim 10^{-30}$ e-cm.
- Challenges: basis set dependence, bond length dependence, and strong correlation effects (OT1 is $\approx$22 vs DF of $\approx$14 GV/cm)!

Molecule	DF	LECC
HgLi	13.74	37.79
HgNa	7.59	20.33
HgK	5.73	16.24

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Mercury hydroxide

Geometry	$\mathcal{E}_{\text{eff}}$		μ	
	DHF	**LECC**	**DHF**	**LECC**
		From this work		
Linear	107.24	109.02	1.57	1.04
Bent	28.01	28.47†	3.67	2.43 †
		From other works		
				1.89 [32]
				1.92 [51]
				1.96 [33]

† Scaled results from the DHF and LECC values of the linear geometry calculations.

Term	$\mathcal{E}_{\text{eff}}$ (GV/cm)	μ (D)
O (DHF)	107.24	1.57
OT_1+h.c.	9.50	−0.42
$T_1^{\dagger}OT_1$	−2.76	−0.15
$T_1^{\dagger}OT_2$+h.c.	−0.38	0.12
$T_2^{\dagger}OT_2$	−4.58	−0.11

Atom	AOs	Linear	Bent
Hg	$s^S_{1/2} - p^L_{1/2}$	378.40	100.11
	$p^S_{1/2} - s^L_{1/2}$	−270.26	−71.81
	$p^S_{1/2} - d^L_{3/2}$	−31.40	−8.07
	$d^S_{3/2} - p^L_{3/2}$	30.19	7.77
	$d^S_{5/2} - f^L_{5/2}$	0.79	0.19
	$f^S_{5/2} - d^L_{5/2}$	−0.78	−0.18
O	$s^S_{1/2} - p^L_{1/2}$	2.78	1.44
	$p^S_{1/2} - s^L_{1/2}$	−2.77	−1.44

Molecule	$\mathcal{E}_{\text{eff}}$	δd_e
ThO	79.9 [12]	1.1×10^{-29}
HfF^+	22.5 [13]	1.3×10^{-28}
YbF	23.1 [10]	1.06×10^{-27}
HgOH	28.47	5×10^{-30}
$HgCH_3$	75.07	2×10^{-30}
$HgCF_3$	60.95	2×10^{-30}

Ytterbium hydroxide

- The polyEDM experiment[16]: aims at $\sim 10^6$YbOH molecules, coherence times (~ 10s coherence time; beams $\sim ms$), and fully polarizable molecules, with co-magnetometer states.
- Spectroscopy known.
- YbOH offers the advantage of a polyatomic with its co-magnetometer states, and that of some special diatomics in laser cooling!
- However, there were no calculations of $\mathcal{E}_{\rm eff}$ at that stage. So, we calculated it, and obtained 23.72 GV/cm!

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[16]polyedm.com, hutzlerlab.com

The finite field method

- Since we have established that HgX are excellent candidates for eEDM search, we need to perform precise calculations of their effective electric fields (higher quality basis sets). We can also improve the result by using a different/modified many-body technique: the finite field method.

- In the finite field coupled cluster method, a property is expressed as an energy derivative, instead of an expectation value problem.

$$H_0|\psi_0\rangle = E_0|\psi_0\rangle \tag{28}$$

$$H(\lambda) = H_0 + H' \tag{29}$$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \tag{30}$$

$$E(\lambda) = E_0 + \lambda E_1 + \cdots \tag{31}$$

$$E_1 = \langle\psi_0|H'|\psi_0\rangle \tag{32}$$

$$E(\lambda) = E_0 + \lambda \frac{\partial E}{\partial \lambda}|_{\lambda=0} + \cdots \tag{33}$$

$$\therefore \frac{\partial E}{\partial \lambda}|_{\lambda=0} \approx \langle\psi_0|H'|\psi_0\rangle \tag{34}$$

- Any first order property can now be defined as an energy derivative.

The finite field method

$E(\lambda) = E^{DF}(\lambda) + \Delta E(\lambda)$
$E^{DF}(\lambda) = \langle \Phi_0 | H(\lambda) | \Phi_0 \rangle$
$= \langle \Phi_0 | H_0 | \Phi_0 \rangle + \lambda \langle \Phi_0 | H' | \Phi_0 \rangle$
Here, $|\Phi_0\rangle$ is the DF wave function of the unperturbed system. Therefore,
$\frac{E(\lambda)-E}{\lambda} = \frac{\Delta E(\lambda) - \Delta E}{\lambda} + \langle \Phi_0 | H' | \Phi_0 \rangle$

Results: LrO, LrF^+, and LrH^+

- Lr has a different configuration in a relativistic treatment [17].

Molecule	$\mathcal{E}_{\rm eff}$ (GV/cm)	W_s (kHZ)	μ (D)	Reference
LrO	258.92	1032.23	4.58	This work
	250.21	938		[18]
	246.5			[19]
LrF^+	246.31	977.37	12.29	This work
LrH^+	343.38	1375.62	11.05	This work
ThO	87	232	4.27	[20]
HgF	115.42	264.7	2.61	[21]

To be submitted.

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- Very large effective electric field expected in certain molecules.
- Experimental side: challenging (low N and τ) and very scarce literature until recently, but lot of progress in the last few years.
- Measurement of ionization energy of Lr [22], lifetimes of Ra ion, branching fractions and transition frequencies of Ra [23], first ever laser-spectroscopy measurements in RaF, at CERN-ISOLDE [24].
- FRIB (USA), TRIUMF (Canada), CERN-ISOLDE (EU), JAEA (Japan), RIKEN (Japan), $\cdots$: a bright future ahead!
- Potential eEDM candidate molecules that contain a superheavy atom are no longer far fetched, and their search is a promising direction to pursue [25]!

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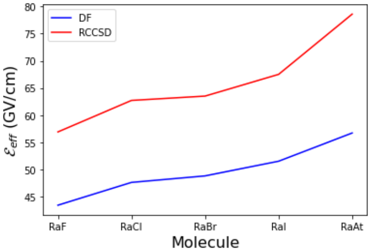
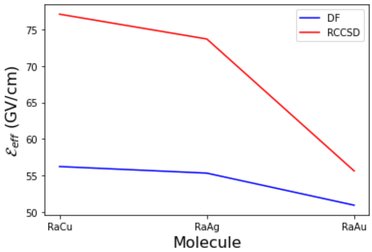
[22] T. K. Sato *et al*, Nature 520, 209 (2015).
[23] Prof. Jayich's talk, New Opportunities for Fundamental Physics Research with Radioactive Molecules, 2021).
[24] Garcia-Ruiz *et al*, Nature 581, 396 (2020).
[25] K. Gaul *et al*, Phys. Rev. A 99, 032509 (2019), C. Zhang *et al*, arXiV 2105.10763 (2021).

Results: RaH, RaX (X=F, Cl, Br, I, and At) , and RaY (Y= Cu, Ag, and Au)

- RaF is a known candidate for future eEDM experiments[26]. RaH: $\mathcal{E}_{\text{eff}}$: 80 GV/cm (RaF: 57 GV/cm). Phys. Rev. A 99, 052502 (2019).





- RaX: $s - p_{1/2}$ hybridization from Ra increases from RaF to RaAt, and the that from X also increases, and is positive.
- RaY: $s - p_{1/2}$ hybridization from Ra is almost constant (in fact, decreases very slowly), and that from Y increases and is negative. Phys Rev A 99, 062506 (2019).

[26] T. A. Isaev *et al*, Phys. Rev. A 82, 052521 (2010).

Results: LrO, LrF^+, and LrH^+

- Lr has a different configuration in a relativistic treatment [27].

[27] T. Naito *et al*, J. Phys. B 53, 21 (2020).

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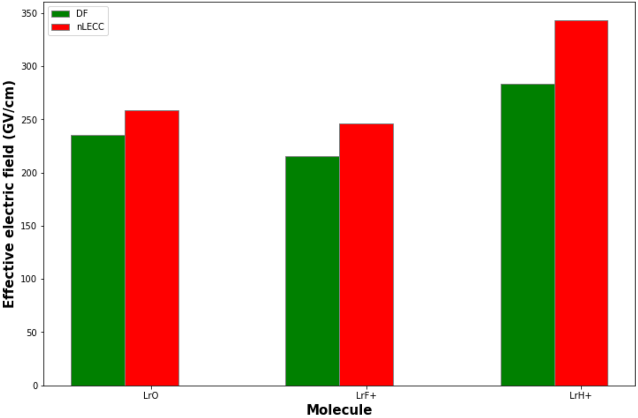

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[27] T. Naito *et al*, J. Phys. B 53, 21 (2020).

Calculating the effective electric field

- $H = H_M + \lambda H_{eEDM}; \lambda = d_e$.
- The expectation value approach:

$$\begin{aligned} \mathcal{E}_{\text{eff}} &= \frac{\langle \Psi | H_{eEDM} | \Psi \rangle}{\langle \Psi | \Psi \rangle} && (35) \\ &= \langle \Phi_0 | e^{T^\dagger} H_{eEDM} e^T | \Phi_0 \rangle_C && (36) \\ &= \langle \Phi_0 | (H_{eEDM} + H_{eEDM} T_1 + \cdots) | \Phi_0 \rangle_C && (37) \end{aligned}$$

Only terms linear in T: linear expectation value coupled cluster (LECC) approach.
Consider as many terms as possible within the intermediate diagram formalism + extensive parallelization: non-linear expectation value coupled cluster (nLECC) method.

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- The energy derivative approach:

$$\mathcal{E}_{\text{eff}} = \left.\frac{\partial E}{\partial \lambda}\right|_{\lambda=0}. \quad (38)$$

We opt for the numerical version, known as the finite field coupled cluster (FFCC) method.
Phys. Rev. A 97, 032515 (2018), and Symmetry 12(5), 811 (2020).