

# **Recent Theoretical Results From The Electron and Nuclear Electric Dipole Moments**

**Bhanu Pratap Das**

**International Education and Research Centre of Science  
Department of Physics,  
Tokyo Institute of Technology,  
Tokyo, Japan**

**Collaborators:**

V. S. Prasanna, M. Abe, A. Sunaga, B. K. Sahoo, and Y. Singh

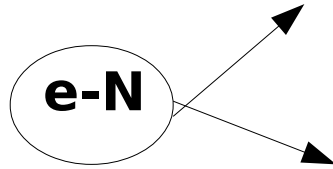
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# Outline of the talk

- Brief comments on EDM searches in atoms and molecules.
- Brief introduction to some theoretical methods used in the EDM calculations.
- Relativistic coupled cluster method and its applications to EDM searches in atoms and molecules.
- Recent results for the electron and nuclear EDMs.

# Sources of Atomic and Molecular Electric Dipole Moments

Elementary Particles	Nucleon	Nucleus	Coupling constant	Atomic
$e$ ( $d_e$ )			$d_e$	$D_a$ ( <i>open shell</i> )
$e-q$	$e-n$	$e-N$	$C_S$	$D_a$ ( <i>open shell</i> )
$q$ ( $d_q$ )	$d_n$	$d_N$	$C_T$	$D_a$ ( <i>closed shell</i> )
$q-q$	$d_n, n-n$	$d_N$	$Q$	$D_a$ ( <i>closed shell</i> )



Atoms and Molecules are excellent Systems for Studying T or CP Violation

# eEDM in the Standard Model (SM) & some of the theories beyond SM

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Particle Physics Model	Electron EDM (e-cm)
Standard Model	$< 10^{-38}$
Super-symmetric Model	$10^{-24} - 10^{-28}$
Left-Right Symmetric Model	$10^{-25} - 10^{-30}$
Multi-Higgs Model	$10^{-25} - 10^{-29}$

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# The effective electric field on an electron

- An electric field (internal or external) in an atom or a molecule causes a shift,  $\Delta E = -\mathbf{d}_e \cdot \mathbf{E}$ .

- Atoms:**  $\Delta E = -\mathbf{d}_A \cdot \mathbf{E}_{\text{external}} = R d_e \mathbf{E}_{\text{external}} = d_e \mathbf{E}_{\text{eff}}$ . Here,

$\mathbf{E}_{\text{eff}} = R \mathbf{E}_{\text{external}}$ .  $D_A$  arises due to  $H_{eEDM}$ :

$$H_{eEDM} = -d_e \sum_{i=1}^{N_e} \beta \vec{\sigma}_i \cdot \vec{E}_{int}$$

- Molecules:**

$$\begin{aligned} \Delta E &= \langle \psi | H_{eEDM} | \psi \rangle \\ &= -d_e \sum_{i=1}^{N_e} \langle \psi | \beta \vec{\sigma}_i \cdot \vec{E}_{int} | \psi \rangle \\ &= -d_e E_{eff} \end{aligned}$$

## Effective electric field:

The electric field experienced by an electron in an atom or a molecule.

$$\therefore E_{eff} = \sum_{i=1}^{N_e} \langle \psi | \beta \vec{\sigma}_i \cdot \vec{E}_{int} | \psi \rangle$$

# eEDM: Combination of experiment and theory

- $\Delta E_{\text{expt}}$  is measured in experiment.
- The effective electric field,  $E_{\text{eff}}$ , is calculated from theory.

- **Atoms:**  $\Delta E_{\text{expt}} = - d_e R E_{\text{external}}$

Therefore,  $d_e = \Delta E_{\text{expt}} / R E_{\text{external}}$

- **Molecules:**

$$\Delta E_{\text{expt}} = - d_e E_{\text{eff}} \eta (\mathbf{E}_{\text{external}})$$

$$\Rightarrow d_e = - \Delta E_{\text{expt}} / (E_{\text{eff}} \eta (\mathbf{E}_{\text{external}}));$$

- Here,  $\eta$  refers to the polarization factor. It is a known quantity in experiment, since it is a function of the applied external electric field.
- Calculate effective field, measure  $\Delta E$ ,  $\eta$  is known, hence obtain  $d_e$ .

# Why are Molecules Better than Atoms?

- **Atoms:**  $\Delta E = f(\mathbf{E}_{\text{external}})$

$$\mathbf{E}_{\text{external}} \sim 10\text{kV/cm}$$

- **Molecules:**  $\Delta E = f(\mathbf{E}_{\text{internal}}, \mathbf{E}_{\text{external}})$

$$\mathbf{E}_{\text{internal}} \sim \text{MV/cm}$$

- $\Delta E$  is greater for molecules than atoms.

# Calculation of the effective electric field

**Atoms:**  $E_{\text{eff}} = \mathcal{R} E_{\text{external}}$

$$\mathcal{R} = 2 \frac{\langle \Psi_0^{(0)} | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle}$$

$|\Psi_0^{(0)}\rangle$  is the unperturbed state, and

$|\Psi_0^{(1)}\rangle$  is the perturbed state, due to the eEDM.

**Molecules:** 
$$E_{\text{eff}} = \sum_{i=1}^{N_e} \langle \psi | \beta \vec{\sigma}_i \cdot \vec{E}_{\text{int}} | \psi \rangle$$

The wavefunctions are calculated using a suitable many-body method.

Relativistic treatment is necessary. This is because for the non-relativistic case, the effective electric field is zero (Sandars, 1964, 1966, and 1968).

Note that in the non-relativistic case, the electron still has its EDM, but it is due to all the interactions in the atom/ molecule treated non-relativistically that one gets the effective field to be zero.



# Dirac-Fock (DF) method

- The relativistic version of the Hartree-Fock or Mean Field method.
- The wave function of the atom/ molecule is given by a many-electron wavefunction known as the Slater Determinant.  $|\Phi_0\rangle = \text{Det } \varphi_1\varphi_2\varphi_3 \dots$
- $H_0 |\Phi_0\rangle = E_0 |\Phi_0\rangle$ ;  $H_0 = T + V_N + V_{DF}$ ;  $V_{DF}$  is an average
- Potential experienced by every electron due to all other electrons.
- A single particle orbital:

$$\varphi_i = \begin{pmatrix} \varphi_1^L \\ \varphi_2^L \\ \varphi_3^S \\ \varphi_4^S \end{pmatrix} = \begin{pmatrix} v \\ w \end{pmatrix}$$

# Dirac-Fock (DF) method

$$t|\varphi_i\rangle + V_{DF}|\varphi_i\rangle = E_i|\varphi_i\rangle;$$

$$V_{DF}|\varphi_i\rangle = \sum_{b=1}^{N_c} \langle \varphi_b | v | \varphi_b \rangle |\varphi_i\rangle - \sum_{b=1}^{N_c} \langle \varphi_b | v | \varphi_i \rangle |\varphi_b\rangle$$

$$\text{If } F \equiv t + V_{DF}$$

$$F|\varphi_i\rangle = E_i|\varphi_i\rangle$$

$$\text{Let } |\varphi_i\rangle = \sum_n C_{in} |\chi_n\rangle$$

$$FC = ESC$$

- The DF equations are solved iteratively, to get the coefficients, C.
- $\chi$  : basis sets. The choice of basis is one of the factors that determines the precision of the calculations. The other important factor that determines the precision is electron correlations.

# Electron Correlation

- The physical effects beyond those embodied in the mean field approximation.
- $E_{\text{corr}} = E - E_{\text{DF}}$ ;  $E$  is the exact energy,  $E_{\text{DF}}$  is the Dirac-Fock energy, and  $E_{\text{corr}}$  is the correlation energy.

Examples of many-electron theories that take electron correlation into account are: Configuration interaction (CI), Multi-Configuration Hartree-Fock/Dirac-Fock (MCHF/ DHF), Many-Body Perturbation Theory (MBPT), and Coupled Cluster Methods (CCM).

# Configuration Interaction: Non-relativistic and relativistic (CI)

- If the wave function be made up of two configurations, then

$$|\psi\rangle = c_1|\Phi_1\rangle + c_2|\Phi_2\rangle$$

- Using the variational principle, i.e., minimizing the energy functional,  $\varepsilon$ , with respect to the coefficients, and keeping the orbitals fixed, we get:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$
$$\varepsilon = \langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle$$

- Generalizing the above result to N configurations:

$$|\psi\rangle = c_0|\Phi_0\rangle + \sum_S c_S|\Phi_S\rangle + \sum_D c_D|\Phi_D\rangle + \dots$$

Single excitations

Double excitations

**MCHF/MCDF:** Energy functional is minimized by varying the orbitals and the mixing coefficients. The equations for the orbitals and the coefficients are then solved self consistently.

# Many-Body Perturbation Theory: non-relativistic and relativistic (MBPT)

- The difference between the actual  $1/r_{ij}$  potential and the MF potential is the perturbation to the Hamiltonian.

$$H_0|\Phi_0\rangle = E_0|\Phi_0\rangle;$$

$$H_0 = \sum_i t_i + \sum_i V_i^{DF}$$

$$H|\psi\rangle = E|\psi\rangle;$$

$$H = \sum_i t_i + \sum_{ij} \frac{1}{r_{ij}}$$

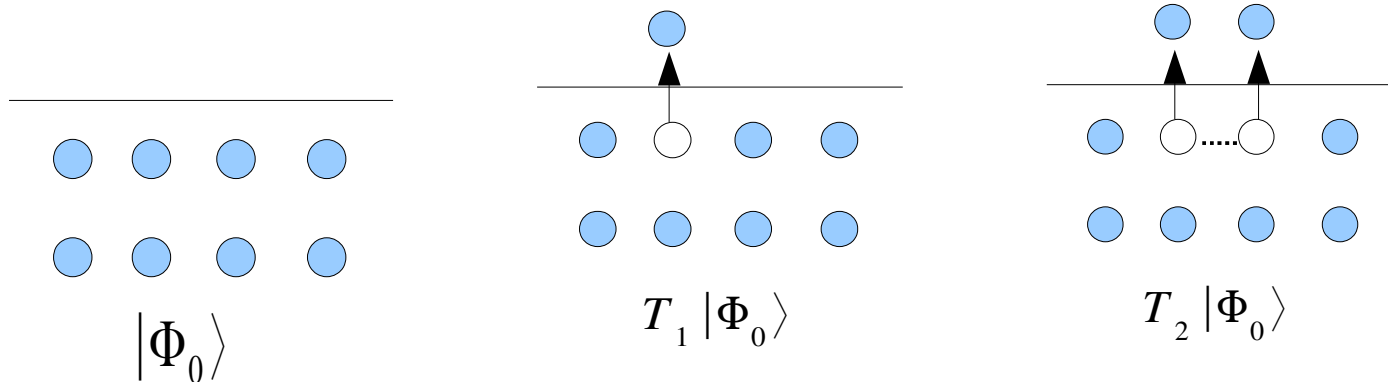
$$\therefore H' = H - H_0$$

$$= \sum_{ij} \frac{1}{r_{ij}} - \sum_i V_i^{DF}$$

$$\text{And, } |\psi\rangle = |\Phi_0\rangle + |\Phi_0^{(1)}\rangle + |\Phi_0^{(2)}\rangle + \dots$$

# Coupled Cluster Method: non-relativistic and relativistic

$$|\Phi_0\rangle = \text{Det} \{ \phi_1 \phi_2 \cdots \phi_N \} \quad (\text{Relativistic Dirac-Fock wavefunction})$$



$$T_1 = \sum_{a,p} t_{ap} a^\dagger_p a_a$$

$$T_2 = \sum_{a,b,p,q} t_{abpq} a^\dagger_p a^\dagger_q a_b a_a$$

$$T = T_1 + T_2 + \cdots$$

Relativistic Coupled-cluster (CC) wavefunction;  $|\Psi^{(0)}\rangle = \exp(T) |\Phi_0\rangle$  and  $H_0 |\Psi^{(0)}\rangle = E_0 |\Psi^{(0)}\rangle$

CC wfn. has electron correlation to all-orders of perturbation theory for any level of excitation.

In presence of EDM,  $|\Psi\rangle = |\Psi^{(0)}\rangle + d_e |\Psi^{(1)}\rangle = \exp\{T + d_e T^1\} |\Phi_0\rangle$

First-order EDM Perturbed RCC wfn. satisfies:  $(H_0 - E_0) |\Psi^{(1)}\rangle = -H_{PTV} |\Psi^{(0)}\rangle$

T and  $T^1$  can be obtained from the unperturbed and the perturbed equations.  
For molecules, only the t amplitudes are computed.

The atomic EDM,  $D_a = \langle \Psi^{(0)} + \Psi^{(1)} | D | \Psi^{(0)} + \Psi^{(1)} \rangle$

# CCM vs CI

Consider the CI-SD approximation scheme:

$$C_1 = T_1$$
$$C_2 = T_1^2 + T_2$$

On the other hand, with the same level of hole-particle excitations,  $|\Psi_{\text{CCSD}}\rangle = e^{(T_1+T_2)}|\Phi_0\rangle$ . We see that the CCSD approximation contains all the powers of  $T_1$  and  $T_2$ . This is due to the exponential nature of the CCSD wave function. Of course, in an actual calculation, we cannot take into account all these higher order terms.

Also, CCSD is size consistent and size extensive, any truncated version of CI isn't.

# CCM vs MBPT

$$\begin{aligned}
 |\psi\rangle_{MBPT} &= |\Phi_{0,\alpha}\rangle + |\Phi_\alpha^{(1)}\rangle + |\Phi_\alpha^{(2)}\rangle + \dots \\
 |\Phi_\alpha^{(1)}\rangle &= \sum_S (C_S^{(1)} + C_D^{(1)} + \dots) |\Phi_{0,\alpha}\rangle \\
 |\Phi_\alpha^{(2)}\rangle &= \sum_S (C_S^{(2)} + C_D^{(2)} + \dots) |\Phi_{0,\alpha}\rangle \\
 &\quad \dots
 \end{aligned}$$

Single excitations to all orders  
in residual Coulomb interaction

Likewise, double excitations

First order correction:

$$|\Phi_\alpha^{(1)}\rangle = \sum_{n \neq \alpha} \frac{|\Phi_n\rangle \langle \Phi_n | H' | \Phi_{0,\alpha}\rangle}{E_\alpha - E_n}$$

$$H' = v - v^{HF}$$

**CCSD**

If  $|\Phi_n\rangle = |\Phi_i^a\rangle$ , then the matrix element is like a t1 amplitude. Specifically, it is that part of t1 amplitude contained in  $C_S^{(1)}$ .

If  $|\Phi_n\rangle = |\Phi_{ij}^{ab}\rangle$ , then we get the part of t2 that is contained in  $C_D^{(1)}$ .

Second order correction:

$$|\Phi_\alpha^{(2)}\rangle = \sum_{m,n \neq \alpha} \frac{|\Phi_n\rangle \langle \Phi_n | H' | \Phi_m\rangle \langle \psi_m | H' | \Phi_{0,\alpha}\rangle}{(E_\alpha - E_n)(E_\alpha - E_m)}$$

If  $\Phi_n$  is a two hole two particle Slater determinant, and if  $\Phi_m$  is one-hole one-particle excitation, then both the matrix elements look like T1 each, and therefore the entire term is like the part of  $T_1^2$ , which is contained in  $C_D^{(2)}$ . This can be repeated for all other terms.



# Linear expectation value approximation

1. Solve the Dirac Fock (DF) equations, get the DF orbitals.



2. Solve the CCSD equations, get t amplitudes.



3. Solve expectation value problem.

$$\langle O \rangle = \frac{\langle \psi | O | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\langle O \rangle = \langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | O | \Phi_0 \rangle \quad \text{This expression is due to Cizek (1969).}$$

Truncation required!

We consider only the linear terms in  $e^T$  in the expectation value for  $E_{\text{eff}}$ .

$$\mathcal{E}_{\text{eff}} = \frac{1}{d_e} \langle \Phi_0 | (1 + T_1 + T_2)^\dagger (H_{\text{EDM}}^{\text{eff}})_N (1 + T_1 + T_2) | \Phi_0 \rangle_c + \frac{1}{d_e} \langle \Phi_0 | H_{\text{EDM}}^{\text{eff}} | \Phi_0 \rangle$$

# The Finite Field Coupled Cluster Method (FFCC)

The basic idea is that we can evaluate a property by either an expectation value expression or an energy derivative. We do not need to truncate if we use this approach!

$$H_0|\psi^0\rangle = E_0|\psi^0\rangle$$

$$H(\lambda) = H_0 + \lambda H'$$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$$

$$E(\lambda) = E_0 + \lambda E_1 + \dots; E_1 = \langle\psi^0|H'|\psi^0\rangle$$

$$\text{Also, } E(\lambda) = E_0 + \lambda \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} + \dots$$

$$\left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} = \frac{E(\lambda) - E}{\lambda}$$

Comparing the two expressions:

$$E_1 = \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0}$$

$\lambda$  is  $d_e$  for eEDM, and  $E_1 = -d_e E_{\text{eff}}$ . The method can also be applied to other first order properties, like the molecular electric dipole moment (PDM).

# The Analytical Derivative Approach

The analytical counterpart of FFCC.

$$\begin{aligned}H_0|\psi^0\rangle &= E_0|\psi^0\rangle \\ \text{where } |\psi^0\rangle &= e^T|\Phi_0\rangle \\ H(\lambda)|\psi(\lambda)\rangle &= E(\lambda)|\psi(\lambda)\rangle \\ \text{where } H(\lambda) &= H + \lambda H' \\ E(\lambda) &= E_0 + \lambda E_1 + \dots \\ |\psi(\lambda)\rangle &= e^{T(\lambda)}|\Phi_0\rangle \quad \text{where } T(\lambda) = T + \lambda T^{(1)} \\ &= e^T e^{\lambda T^{(1)}}|\Phi_0\rangle\end{aligned}$$

Equating terms of order lambda:

$$\begin{aligned}\langle\Phi_0|([H, T^{(1)}] + H'e^T)_C|\Phi_0\rangle &= E_1 \\ \langle\Phi_0^*|(e^{-T}H_N e^T T^{(1)})_C|\Phi_0\rangle &= 0\end{aligned}$$

These are the energy and amplitude equations, to be solved, to obtain  $E_1$ . Note that before solving these equations, one must solve the usual CC equations.

The effective electric field can be obtained, once we know  $E_1$ , since it is a first order property. In this case,  $H'$  is the eEDM operator.

# Normal CCM (NCCM)

The bra and the ket are treated on different footings:

$$\begin{aligned} H|\psi\rangle &= E|\psi\rangle \\ \langle\tilde{\psi}|H &= \langle\tilde{\psi}|E \end{aligned}$$

where

$$\begin{aligned} |\psi\rangle &= e^T|\Phi_0\rangle; T = \sum_{I \neq 0} T_I C_I^+ & \longrightarrow & \text{Has excitation operators} \\ \langle\tilde{\psi}| &= \tilde{T}e^{-T}\langle\Phi_0|; \tilde{T} = \sum_{I \neq 0} 1 + \tilde{T}_I C_I^- & \longrightarrow & \text{Has de-excitation operators} \end{aligned}$$

$$\langle\Phi_0|C_I^+ e^{-T} H e^T |\Phi_0\rangle = 0$$

Ket equation; identical to CC

$$\langle\Phi_0|\tilde{T}e^{-T} [H, C_I^+] e^T |\Phi_0\rangle = 0$$

Bra equation

Arponen (1983), Arponen and Bishop (1985).

# Normal CCM (NCCM)

Expectation value of an operator, A:

$$\begin{aligned}\langle A \rangle &= \frac{\langle \tilde{\psi} | A | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \frac{\langle \Phi_0 | \tilde{T} e^{-T} A e^T | \Phi_0 \rangle}{\langle \Phi_0 | \tilde{T} | \Phi_0 \rangle}\end{aligned}$$

where

$$\begin{aligned}\langle \Phi_0 | \tilde{T} | \Phi_0 \rangle &= \langle \Phi_0 | (1 + \tilde{T}_1 + \tilde{T}_2) | \Phi_0 \rangle \\ &= 1\end{aligned}$$

since

$$\begin{aligned}\langle \Phi_0 | 1 | \Phi_0 \rangle &= 1 \\ \langle \Phi_0 | \tilde{T}_1 | \Phi_0 \rangle &= \langle \Phi_0 | t_a^i i^\dagger a | \Phi_0 \rangle \\ &= 0\end{aligned}$$

*Likewise,*  $\langle \Phi_0 | \tilde{T}_2 | \Phi_0 \rangle = 0$

Therefore,

$$\langle A \rangle = \langle \Phi_0 | \tilde{T} e^{-T} A e^T | \Phi_0 \rangle$$

**This series terminates!  
NCCM better than CCM.**

If A is the eEDM operator, then the resulting quantity is the effective field.

# Results for $E_{\text{eff}}$ in YbF

The best limit comes from ThO, but an improved result from YbF is expected soon.

The limit on eEDM from YbF is:  $d_e < 10.5 \times 10^{-28}$  e-cm (90% confidence limit), Hudson et al, Nature, 2011.

We obtain a value of 23.1 GV/cm for  $E_{\text{eff}}$  in YbF with an estimated error of less than 10% (M Abe et al, Phys. Rev. A 90, 022501 (2014)).

Improved upper limit on eEDM using YbF:  $d_e < 11.8 \times 10^{-28}$  e-cm.

# Results for $E_{\text{eff}}$ in YbF

Basis set type	Method	Total energy (a.u.)	$T_1$ diagnostic	$E_{\text{eff}}$ (GV/cm)	DM <sup>a</sup>	$A_{\parallel}$ (MHz)
DZ	DF	-14167.289602		17.9	3.21	
TZ	DF	-14167.321791		18.2	3.21	
QZ	DF	-14167.323266		18.2	3.21	6239
DZ	49e-CCSD(197)	-14169.344299	0.0432	21.4	3.37	
TZ	49e-CCSD(255)	-14169.899971	0.0588	21.1	3.46	
QZ	49e-CCSD(293)	-14170.080575	0.0397	22.7	3.59	
QZ	49e-CCSD(303)	-14170.026999	0.0339	22.8	3.59	
QZ	69e-CCSD(293)	-14170.501826	0.0334	23.1	3.60	
QZ	79e-CCSD(293)	-14170.522807	0.0311	23.1	3.60	7913
Expt.					3.91(4) <sup>b</sup>	7424(81) <sup>c</sup>

<sup>a</sup>The direction of the dipole moment is taken as the molecular axis from the fluorine to the ytterbium atom.

# Results for $E_{\text{eff}}$ in YbF

Our first calculation was based on the relativistic CCSD method. All the occupied orbitals were excited, and a fairly large basis was used (Yb: 35s,30p,19d,13f,5g,3h,2i, F: 13s,10p,4d,3f). The results were obtained by only taking into account the linear terms in the expectation value expression.

We overcome this limitation in finite field approach, since the effective field can be considered as the derivative of energy, with respect to eEDM. There is no truncation here.

Previous calculations on YbF were based on the Dirac-Fock approximation (F A Parpia, J Phys B, 1998), effective core potential methods (Titov et al, Phys Rev Lett, 1996), and the CI-SD method (Nayak and Chaudhuri, Chem Phys Lett, 2006).

We used basis sets that were optimized differently than for the previous calculations, for both Yb and F. No occupied orbitals were frozen.

Using FFCC, we obtain 23 GV/cm.



# Why HgX?

- Commonly accepted heuristic:  $E_{\text{eff}}$  is proportional to  $Z^3$ , where  $Z$  refers to the atomic number of the heavier atom.
- However,  $E_{\text{eff}}^{\text{RaF}}=54$  GV/cm, while  $E_{\text{eff}}^{\text{HgF}}=115$  GV/cm (using linear expectation value CCSD approach).
- This can be attributed to poor screening effect of  $(n-1)d$  electrons in Hg, as compared to Ra (A Sunaga et al, manuscript under preparation).

# HgX as Promising Candidates

- Choice of a candidate depends on:
  1. Large effective electric field ( $E_{\text{eff}}$ ).
  2. Large coherence time per measurement ( $\tau$ ).
  3. Number of molecules (N).

$$\delta d_e \sim \frac{1}{2\pi E_{\text{eff}} \sqrt{NT\tau}}$$

# Results for HgX using linear expectation value CCSD

Molecule	Method	Basis	$T_{1,\text{dia}}$	$\mathcal{E}_{\text{eff}}$ (GV/cm)
HgF	DF	Hg:22s,19p,12d,9f,1g F:9s,4p,1d	-	104.25
HgCl	DF	Hg:22s,19p,12d,9f,1g Cl:12s,8p,1d	-	103.57
HgBr	DF	Hg:22s,19p,12d,9f,1g Br:14s,11p,6d	-	97.89
HgI	DF	Hg:22s,19p,12d,9f,1g I:8s,6p,6d	-	96.85
HgF	CCSD	Hg:22s,19p,12d,9f,1g F:9s,4p,1d	0.0268	115.42
HgCl	CCSD	Hg:22s,19p,12d,9f,1g Cl:12s,8p,1d	0.0239	113.56
HgBr	CCSD	Hg:22s,19p,12d,9f,1g Br:14s,11p,6d	0.0255	109.29
HgI	CCSD	Hg:22s,19p,12d,9f,1g I:8s,6p,6d	0.0206	109.30

# DF results for HgX

The DF contribution can be rewritten as:  $\sum_{k=1}^q \sum_{l=q+1}^{2q} C_k^{*S} C_l^L \langle \chi_{v,k}^S | p^2 | \chi_{v,l}^L \rangle$

Atom	Mixing	HgF	HgCl	HgBr	HgI
Hg	$s - p_{1/2}$	-266.29	-262.07	-249.39	-242.34
Hg	$p_{1/2} - s$	373.37	367.74	349.42	339.56
Hg	$p_{3/2} - d_{3/2}$	31.22	25.22	21.84	20.99
Hg	$d_{3/2} - p_{3/2}$	-32.26	-26.35	-22.48	-21.84
Hg	$d_{5/2} - f_{5/2}$	-0.91	-0.51	-0.39	-0.33
Hg	$f_{5/2} - d_{5/2}$	0.92	0.52	0.4	0.33
X	$s - p_{1/2}$	-2.78	-4.85	-10.58	-17.19
X	$p_{1/2} - s$	2.79	4.92	11.17	19.87
Total:		106.06	104.62	99.99	99.05
DF		105.47	104.03	99.55	98.99
	$s - p_{1/2}$ and $p_{1/2} - s$	107.08	105.67	100.03	97.22

# Results for HgX using FFCC

Molecule	CCSD	FFCC
HgF	115.42	116.37
HgCl	113.56	114.305
HgBr	109.29	109.56
HgI	109.3	109.56

For the FFCC approach, we used a two point and six point central difference formula to evaluate the derivative. We used the following values of lambda:  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$ .

# Limits for $d_e$ : Present Status and Future Prospects

Limit from YbF:

$$d_e < 10.5 \times 10^{-28} \text{ e-cm (90\% confidence limit)}$$

Hudson et al, Nature, 2011

New result expected soon.

Limit for ThO:

$$d_e < 0.87 \times 10^{-28} \text{ e-cm (90\% confidence limit) : Current best limit for } d_e$$

Baron et al, Science, 2014

$E_{\text{eff}} = 80 \text{ GV/cm}$  (Skripnikov),  $75 \text{ GV/cm}$  (Fleig). Several experiments have been proposed using neutral molecules and molecular ions to search for the electron EDM. Examples are  $\text{HfF}^+$  (Cornell, JILA), WC (Leanhardt, U Michigan).

New proposal: Hg halides (Prasanna, Vutha, Abe and Das, PRL 2015);  $E_{\text{eff}} \sim 115 \text{ GV/cm}$ .

# Superheavy Elements

- Superheavy elements appear very promising for future EDM searches, due to recent advances on the experimental side. Example: ionization potential of Lawrencium (Sato et al, Nature, 2015).
- Molecules like  $\text{LrF}^+$ ,  $\text{LrO}$ ,  $\text{CnF}$ , and  $\text{NoF}$  could be suitable eEDM search candidates.

# Atomic EDM due to nuclear Schiff moment

The relativistic atomic Hamiltonian (in atomic units),  $H_A$ :

$$\sum_i \{ c\alpha_i \cdot p_i + \beta c^2 + V_i^{Nuclear} \} + \sum_{i>j} 1/r_{ij}$$

$$H_S = 3 \frac{\mathbf{S} \cdot \mathbf{r}}{B} \rho_n(r)$$

$\mathbf{S} = S \frac{\mathbf{I}}{I}$

$\int_0^\infty dr r^4 \rho_n(r)$

Nuclear Schiff moment  
 Nuclear density

Treating  $H_S$  as a first-order perturbation, the atomic wave function is given by  $|\psi\rangle = |\psi^0\rangle + S|\psi^1\rangle$

The atomic EDM is given by:  $R = \frac{D_a}{S} = \frac{\langle \psi^0 | D | \psi^1 \rangle + \langle \psi^1 | D | \psi^0 \rangle}{\langle \psi^0 | \psi^0 \rangle}$



# Results for the Nuclear Schiff Moment of $\text{Xe}^{129}$

$$R = \frac{D_a}{S/|e|fm^3}$$

$$R_{DF} = 0.288 \times 10^{-17}$$

$$R_{CCSD} = 0.336 \times 10^{-17}$$

$$R_{CCSD_pT} = 0.337 \times 10^{-17}$$

$R=0.38 \times 10^{-17}$ , using RPA (Dzuba et al, Phys Rev A, 80, 032120 (2009))  
Y Singh, B K Sahoo, B P Das, Phys Rev A (R) 89, 030502(2014)

*Combining this with the experimental result  $S < 1.2 \times 10^{-9} efm^3$*

(Rosenberry and Chupp. PRL, 86, 22 (2001))

All occupied orbitals were excited.

A large single particle basis was used.

Briet interaction and some higher order QED effects were included.

Experiments on Xe EDM are in progress at RIKEN, Japan, TU Munich,  
and, JGU Mainz.

# Results for the Nuclear Schiff Moment of Hg<sup>199</sup>

• $R_{DF} = -1.2 \times 10^{-17}$

(Sahoo, PRD, 95, 013002 (2017))

• $R_{CCSD} = -1.78 \times 10^{-17}$

(Sahoo, PRD, 95, 013002 (2017))

• $R_{CI+MBPT} = -2.6 \times 10^{-17}$

(V.A. Dzuba et al, Phys. Rev. A 80, 032120 (2009).)

• $R_{PRCC} = -2.46 \times 10^{-17}$

(Latha, et al., Phys. Rev. Lett. 103, 083001 (2009) 115, 059902(E) (2015))

• $R_{MCDF} = -2.22 \times 10^{-17}$

(L. Radziute et al, Phys. Rev. A 93, 062508 (2016))

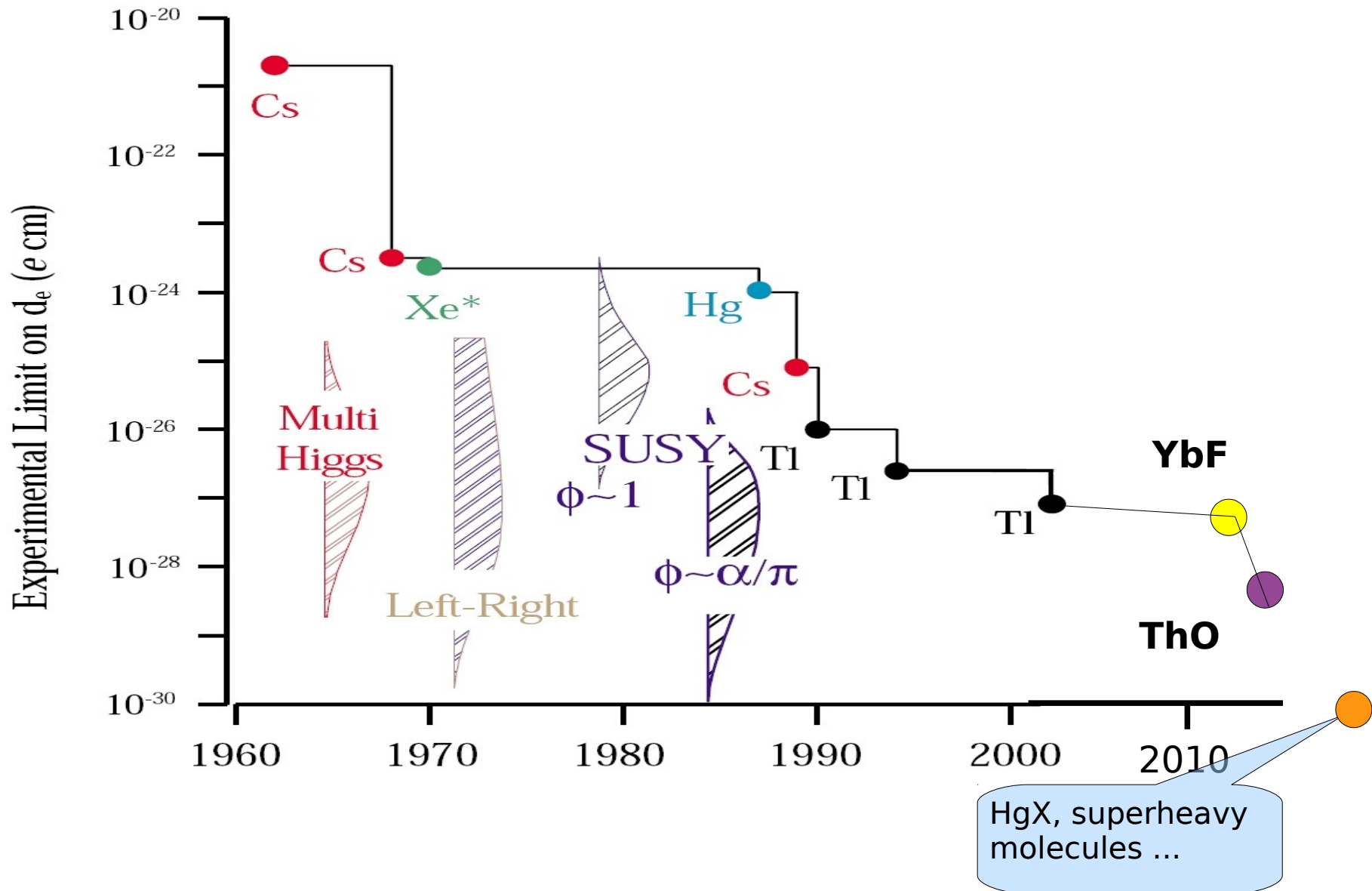
• $R_{NCCM} = -1.68 \times 10^{-17}$

(Sahoo and Das)

# Extracting Limits

- Experimental limit on Hg EDM is the best till date.  
 $D_a^{\text{expt}} < 7.4 \times 10^{-30} \text{ e cm}$  (Phys Re Lett, 116, 161601 (2016)).
- Our calculations:  $S < 4.2 \times 10^{-13} |e| \text{ fm}^3$ .
- Nuclear calculations:  $S = [1.9d_n + 0.2d_p]$  (Phys Rev Lett, 91, 212303 (2003)).  
and  $S = 13.5[0.01g_{\pi NN}^{(0)} \pm 0.02g_{\pi NN}^{(1)} + 0.02g_{\pi NN}^{(2)}] |e| \text{ fm}^3$  (Prog. Part. Nucl. Phys., 71, 21 (2013)).
- In combination:  $|\vec{d}_u - \vec{d}_d| < 2.7 \times 10^{-27} \text{ e cm}$ .  
 $d_n < 3 \times 10^{-27} \text{ e cm}$ .  
 $d_p < 2.1 \times 10^{-26} \text{ e cm}$ .
- $|\theta| < 1.1 \times 10^{-10}$  (Phys Rev D, 95, 013002 (2017)).

# Status of eEDM Searches



# Conclusions

- Atomic and molecular relativistic many-body theory are indispensable in searches of electron and nuclear EDMs.
- Relativistic coupled cluster theory is well suited for the EDM searches mentioned above. It would be necessary to develop different variants of the theory for this purpose.
- With a new result expected for the electron EDM experiment in YbF soon and further improvements in the measurement of EDMs of diamagnetic atoms in the near future, improvements in relativistic many-body calculations of EDMs in atoms and molecules are desirable.

"The electric dipole moments of neutrons and atoms seem to me to offer one of the most exciting possibilities for progress in particle physics. Experiments here move very slowly but there has been a lot of progress recently in calculating EDMs with results that are encouraging for future experiments."

Steven Weinberg,

Conference Summary, XXVI International Conference on High Energy Physics, Dallas, 1992

"I am personally interested in the EDM tests, since I first proposed them and began looking for them 56 years ago, as tests of P, then T, and then CP. Originally I wanted to be the first person to discover an EDM, but now I at least want to know the answer. I have therefore personally established the time limited " Ramsey Prize of \$5000 for the first person, or group, during my lifetime to announce the convincing discovery of a non zero electric dipole moment for any elementary particle or atomic nucleus." Since I am now 91 years old, please hurry. "

Norman Ramsey

International Conference on Atomic Physics, 2006, Innsbruck

**Aside**



**Table 16.** Calculated values of  $\mathcal{R}$  due to both T-PT (given as  $\mathcal{R}^{TPT}$  in  $\times 10^{-20} \langle \sigma | e | \text{cm} \rangle$ ) and NSM (given as  $\mathcal{R}^{NSM}$  in  $\times [10^{-17} / |e| \text{fm}^3] |e| \text{cm}$ ) interactions in the  $^{199}\text{Hg}$  and  $^{225}\text{Ra}$  diamagnetic atoms. The final recommended values with uncertainties are given as “Best value” for the respective quantities.

Method	$^{199}\text{Hg}$				$^{225}\text{Ra}$			
	This work		Others		This work		Others	
	$\mathcal{R}^{TPT}$	$\mathcal{R}^{NSM}$	$\mathcal{R}^{TPT}$	$\mathcal{R}^{NSM}$	$\mathcal{R}^{TPT}$	$\mathcal{R}^{NSM}$	$\mathcal{R}^{TPT}$	$\mathcal{R}^{NSM}$
DF	-2.39	-1.20	-2.0 [447] -2.4 [443] -7.29 [457] <sup>a</sup>	-1.19 [450] -1.2 [443] -2.86 [457] <sup>a</sup>	-3.46	-1.86	-3.5 [443]	-1.8 [443]
MBPT(2)	-4.48	-2.30			-11.00	-5.48		
MBPT(3)	-3.33	-1.72			-10.59	-5.30		
RPA	-5.89	-2.94	-6.0 [447] -5.9 [443]	-2.8 [450] -3.0 [443]	-16.66	-8.12	-17 [443] -16.59 [448]	-8.3 [443] -8.5 [450]
CI+MBPT			-5.1 [443]	-2.6 [443]			-18 [443]	-8.8 [443]
PRCC			-4.3 [449]	-2.46 [449]				
MCDF			-4.84 [457] <sup>a</sup>	-2.22 [457] <sup>a</sup>				
LCCSD	-4.52	-2.24			-13.84	-8.40		
CCSD <sup>(3)</sup>	-3.82	-2.00			-10.40	-6.94		
CCSD <sup>(5)</sup>	-4.02	-2.00			-10.01	-6.79		
CCSD <sup>(∞)</sup>	-3.38	-1.78			-9.926	-6.215		

**Table 17.** Breakdown of contributions to the  $\mathcal{R}$  values from the CCSD method due to the T-PT interaction (in  $\times 10^{-20} \langle \sigma | e | \text{cm} \rangle$ ) in the considered diamagnetic atoms.

CC term	$^{129}\text{Xe}$	$^{223}\text{Rn}$	$^{199}\text{Hg}$	$^{225}\text{Ra}$
$DT_1^{(1)}$	0.459	4.345	-4.400	-13.10
$T_1^{(0)\dagger} DT_1^{(1)}$	-0.001	0.005	0.027	-0.100
$T_2^{(0)\dagger} DT_1^{(1)}$	0.039	0.333	1.224	3.303
$T_1^{(0)\dagger} DT_2^{(1)}$	-0.006	-0.069	-0.058	-0.086
$T_2^{(0)\dagger} DT_2^{(1)}$	-0.009	-0.108	0.107	0.778
Extra	-0.007	-0.047	-0.28	-0.721

**Table 18.** Breakdown of contributions to the  $\mathcal{R}$  values from the CCSD method due to the NSM interaction (in  $\times [10^{-17} / |e| \text{fm}^3] |e| \text{cm}$ ) in the considered diamagnetic atoms.

CC term	$^{129}\text{Xe}$	$^{223}\text{Rn}$	$^{199}\text{Hg}$	$^{225}\text{Ra}$
$DT_1^{(1)}$	0.313	2.695	-2.388	-7.577
$T_1^{(0)\dagger} DT_1^{(1)}$	-0.001	-0.004	0.018	0.008
$T_2^{(0)\dagger} DT_1^{(1)}$	0.023	0.134	0.607	1.557
$T_1^{(0)\dagger} DT_2^{(1)}$	0.0002	-0.006	0.011	0.046
$T_2^{(0)\dagger} DT_2^{(1)}$	0.004	0.020	-0.026	-0.594
Extra	-0.006	-0.057	-0.002	0.345

# METHOD OF CALCULATION

. . . Dirac - Fock Theory

For a relativistic N-particle system, we have a **Dirac-Fock equation** given by,

$$H_0 = \sum_I \{ c \vec{\alpha}_I \cdot \vec{p}_I + (\beta_I - 1) m c^2 + V_N(r_I) \} + \sum_{I < J} \frac{e^2}{r_{IJ}}$$

We represent the ground state wave function  $\Phi$  as an N×N **Slater determinant**,

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \phi_1(x_3) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \phi_2(x_3) & \cdots & \phi_2(x_N) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \phi_N(x_1) & \phi_N(x_2) & \phi_N(x_3) & \cdots & \phi_N(x_N) \end{vmatrix}$$

The single particle wave functions  $\phi_i$ 's expressed in Dirac form as,

$$\phi_a = \frac{1}{r} \begin{pmatrix} P_a(r) \chi_{\kappa_a, m_a} \\ iQ_a(r) \chi_{-\kappa_a, m_a} \end{pmatrix}$$

## . . . Coupled Cluster Theory

The **coupled cluster wave function** for a closed shell atom is given by,

$$|\Psi_0\rangle = e^{T^{(0)}} |\Phi_0\rangle$$

Since the system considered here has only one valence electron, it reduces to

$$|\Psi_v\rangle = e^{T^{(0)}} \{1 + S^{(0)}\} |\Phi_v\rangle$$

Where,  $T^{(0)} = T_1^{(0)} + T_2^{(0)} + \dots$  and  $S^{(0)} = S_1^{(0)} + S_2^{(0)} + \dots$

The RCC operator amplitudes can be solved in two steps; first we solve for **closed shell amplitudes** using the following equations:

$$\langle \Phi_0 | \bar{H}_0 | \Phi_0 \rangle = E_g \quad \text{and} \quad \langle \Phi_0^* | \bar{H}_0 | \Phi_0 \rangle = 0$$

Where,  $\bar{H}_0 = e^{-T^{(0)}} H_0 e^{T^{(0)}}$

The **open shell operators** can be obtained by solving the following two equations :

$$H_{EDM}^{eff} = 2 i c d_e \beta \gamma_5 p^2$$

$$\langle \Phi_v^* | \bar{H}_{op} \{ 1 + S_v^{(0)} \} | \Phi_v \rangle = -\Delta E_v \langle \Phi_v^* | \{ S_v^{(0)} \} | \Phi_v \rangle$$

Where,  $\Delta E_v$  is the negative of the ionization potential of the valence electron  $v$ .

The total atomic Hamiltonian in the presence of **EDM as a perturbation** is given by,

$$|\Psi_v\rangle = e^{(T^{(0)} + d_e T^{(1)})} \{ 1 + S_v^{(0)} + d_e S_v^{(1)} \} |\Phi_v\rangle$$

The effective ( one-body ) **perturbed EDM operator** is given by,

$$\langle \Phi_v | \bar{H}_{op} \{ 1 + S_v^{(0)} \} | \Phi_v \rangle = -\Delta E_v$$

Thus, the modified atomic wave function is given by,

$$H = H_0 + H_{EDM}$$

The **perturbed cluster amplitudes** can be obtained by solving the following equations self consistently :

$$\langle \Phi_0^* | \bar{H}_N^{(0)} T^{(1)} + \bar{H}_{EDM}^{eff} | \Phi_0 \rangle = 0$$

$$\langle \Phi_v^* | (\bar{H}_N^{(0)} - \Delta E_v) S_v^{(1)} + (\bar{H}_N^{(0)} T^{(1)} + \bar{H}_{EDM}^{eff}) \{1 + S_v^{(0)}\} | \Phi_v \rangle = 0$$

Where,  $H_N = H_0 - \langle \Phi_0 | H_0 | \Phi_0 \rangle$

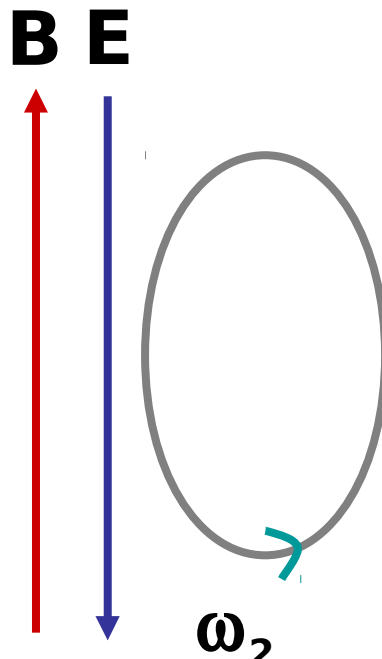
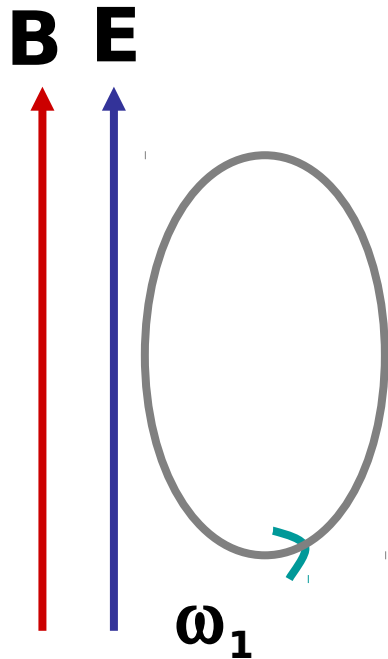
The atomic EDM is given by,

$$\langle D_a \rangle = \frac{\langle \Psi_v | D_a | \Psi_v \rangle}{\langle \Psi_v | \Psi_v \rangle}$$

# EXPERIMENTS ON ATOMIC EDM

... Principle of Measurement

$$H_I = -\vec{D}_a \cdot \vec{E} - \vec{\mu} \cdot \vec{B}$$



$$\omega_1 = \frac{2\mu \cdot B + 2D_a \cdot E}{\hbar}$$

$$\omega_2 = \frac{2\mu \cdot B - 2D_a \cdot E}{\hbar}$$

$$\Delta\omega = \omega_1 - \omega_2 = \frac{4D_a \cdot E}{\hbar}$$

If the atomic EDM  $D_a \sim 10^{-26}$  e-cm and  $E = 10^5$  V/cm;

$\Delta\omega \sim 10^{-5}$  Hz

Major source of error:  $B_m = \frac{v \times E}{c^2}$

# EDM of an Atom

Consider an external electric field  $E$  that is applied to an atom. Only those terms in the expression for energy shift ( $\Delta\varepsilon$ ) of an atomic state that are first order in the external electric field and in  $d_e$  are considered.

$$\begin{aligned}
 H &= H_0 + H' \\
 &= H_0 - d_e \beta \sigma \cdot E_{int} - D_{induced} \cdot E - d_e \beta \sigma \cdot E \\
 &= H_0 - d_e \beta \sigma \cdot E_{int} - ezE - d_e \beta \sigma_z E \\
 \Delta\varepsilon^{(1)} &= \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle \\
 &= -d_e \langle \psi_n^{(0)} | \beta \sigma_z | \psi_n^{(0)} \rangle E \\
 \Delta\varepsilon^{(2)} &= \langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle \\
 \Delta\varepsilon^{(2)} &= -d_e \left[ \frac{\sum_{m \neq n} \langle \psi_n^{(0)} | \beta \sigma \cdot E_{int} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | (-ez) | \psi_n^{(0)} \rangle}{E_m - E_n} \right. \\
 &\quad \left. + \frac{\sum_{m \neq n} \langle \psi_n^{(0)} | (-ez) | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \beta \sigma \cdot E_{int} | \psi_n^{(0)} \rangle}{E_m - E_n} \right] E \\
 \Delta\varepsilon &= -d_e \left[ \langle \psi_n^{(0)} | \beta \sigma_z | \psi_n^{(0)} \rangle \right. \\
 &\quad - \left( \frac{\sum_{m \neq n} \langle \psi_n^{(0)} | \beta \sigma \cdot E_{int} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | (-ez) | \psi_n^{(0)} \rangle}{E_m - E_n} \right. \\
 &\quad \left. + \frac{\sum_{m \neq n} \langle \psi_n^{(0)} | (-ez) | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \beta \sigma \cdot E_{int} | \psi_n^{(0)} \rangle}{E_m - E_n} \right) \Big] E \\
 &= -D_a E
 \end{aligned}$$



# Results for $E_{\text{eff}}$ of mercury monohalides

- We have tested the accuracy of the relativistic CCSD method for molecules by determining the permanent electric dipole moment (pdm) of SrF.

Phys. Rev. A 90, 052507, 2014.

- Our calculations were performed without freezing any of the core orbitals.
- We used the following bond lengths (in nm) for our calculations: HgF (0.200686), HgCl (0.242), HgBr (0.262), HgI (0.281).
- We used Dyall's c2v for Hg and I, and ccpvdz for F, Cl, and Br.
- All-electron four-component Dirac-Coulomb Hamiltonian, the effective operator  $p^2$  including  $E_{\text{int}}$  by both nuclei and electrons, fully solved CCSD but approximated to linear order in the expectation value.

# Results for $E_{\text{eff}}$ of mercury monohalides

- Contributions from individual terms at dz level:

$$\langle O \rangle = \langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | O | \Phi_0 \rangle$$

Term	HgF	HgCl	HgBr	HgI
DF	104.25	103.57	97.89	96.85
$H_{\text{EDM}}^{\text{eff}} T_1$	10.08	9.67	11.09	12.39
$H_{\text{EDM}}^{\text{eff}} T_2$	0	0	0	0
$T_1^\dagger H_{\text{EDM}}^{\text{eff}}$	10.08	9.67	11.09	12.39
$T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_1$	-3.91	-3.58	-4.07	-4.77
$T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_2$	0.22	0.097	-0.1	-0.15
$T_2^\dagger H_{\text{EDM}}^{\text{eff}}$	0	0	0	0
$T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_1$	0.22	0.097	-0.1	-0.15
$T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_2$	-5.52	-5.96	-6.5	-7.26