# Theoretical studies of P & T violations in heavy polar molecules

Malaya K. Nayak

Bhabha Atomic Research Centre
Trombay, Mumbai - 400085

Collaborators:
H. S. Nataraj, M. Kallay, and B. P. Das

# Motivation for the study of *P,T*-violations:

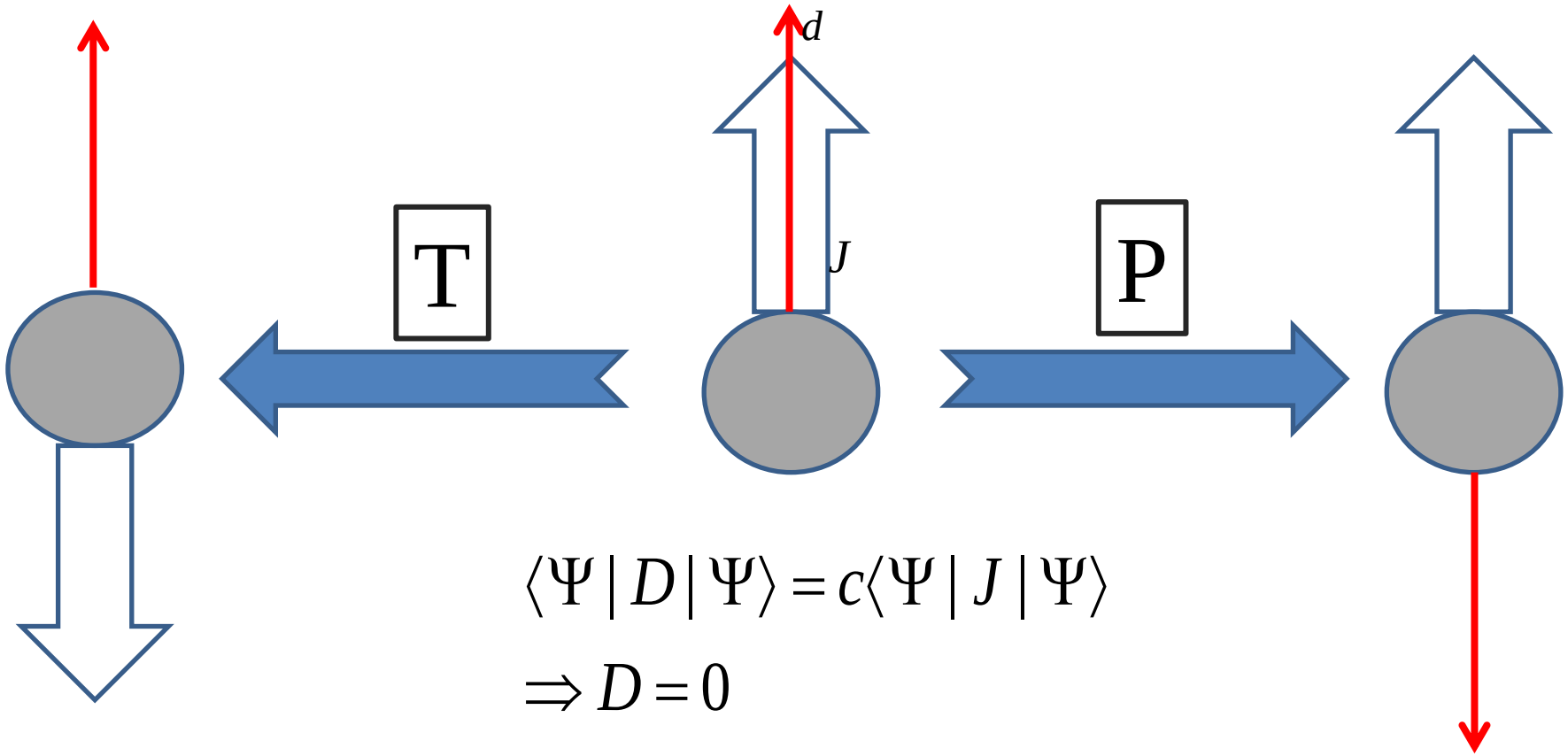
- Conservation of space inversion symmetry (P) was universally accepted for a long time.

- Non-conservation of P was discovered by Wu and co-workers in the β decay of $^{60}Co$, in 1957.

- The combined operation of charge conjugation (C) and space inversion (CP) was thought to be a good symmetry.

- A small violation of CP symmetry was observed in the decay of neutral $K_L$ meson by Christenson *et al.*, in 1964.

- Until now, there are a few experiments where the violations of CP (or T) has been observed.




$$\langle \Psi | D | \Psi \rangle = c \langle \Psi | J | \Psi \rangle$$

$$\Rightarrow D = 0$$

Permanent EDM of a particle VIOLATES both P - & T- invariance
T-violation implies CP-violation via CPT theorem.

# Sources of Atomic or molecular EDM

| Elementary particles | Nucleon | Nucleus | Coupling constant | Atomic or Molecular |
|---|---|---|---|---|
| e ($d_e$) | | | $d_e$ | $D_a$ (open shell) |
| e-q | e-n | e-N | $C_s$ | $D_a$ (open shell) |
| | | | $C_T$ | $D_a$ (closed shell) |
| q ($d_q$) | $d_n$ | $d_N$ | $Q$ | $D_a$ (closed shell) |
| q-q | $d_n$, n-n | $d_N$ | $Q$ | $D_a$ (closed shell) |

Studies of the coupling constants $d_e$ and $C_S$ are very important in open shell atomic or molecular systems. Heavy polar diatomic molecules are best suitable and much more sensitive as compared to atoms.

# Prediction of particle physics models

| 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 | $10^{-25}$ - $10^{-29}$ |

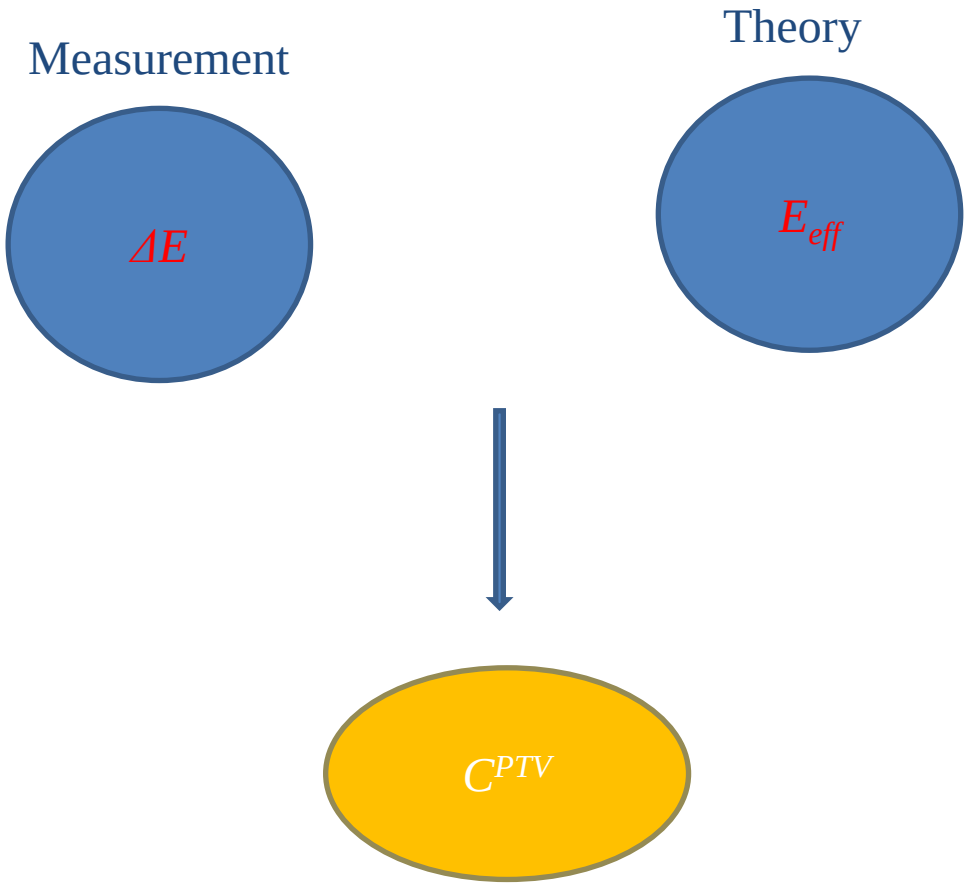
## Measured results:

$d_e \leq 1.6 \times 10^{-27}$ e-cm (Atomic Tl, Regan *et. al.*, 2002)

$d_e \leq 2.0 \times 10^{-27}$ e-cm (Atomic Tl, Nataraj *et. al.*, 2011)

$d_e \leq 1.05 \times 10^{-27}$ e-cm (Molecular YbF, Hudson *et. al.*, 2011)

# How to deduce P,T-violating coupling constant




Here, $C^{PTV}$ stands for either $d_e$ or $C_S$. We need hi precession both in measurement and in theory to obtain reliable limits on these P,T-violating coupling constants

# Molecular EDMs

$$H = H_m - d_e \sum_i \beta_i \vec{\sigma}_i . \vec{E}_i^I \quad \text{where,} \quad \vec{E}_i^I = \vec{E}_N^I + \vec{E}_{i,j}^I$$

and

$$H_m = \sum_i c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i mc^2 - \sum_{i,A} \frac{Z_A e}{r_{i,A}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{A>B} \frac{Z_A Z_B}{r_{AB}}$$

The shift in energy is given by:

$$\Delta E = -\langle \Psi_m \mid d_e \Sigma_i \beta_i \vec{\sigma}_i . \vec{E}_i^I \mid \Psi_m \rangle$$

The effective electric field in certain molecules interacting with the electron EDM can be several orders of magnitude than those in atoms. It can be expressed as

$$E_{eff} = \frac{\Delta E}{d_e} = -\langle \Psi_m \mid \sum_i \beta_i \vec{\sigma}_i \cdot \vec{E}_i^I \mid \Psi_m \rangle = 2ic\langle \Psi_m \mid \beta_i \gamma_i^5 p_i^2 \mid \Psi_m \rangle$$

Note that the approximate one-body form of the EDM operator (LHS) and the exact one-body form of EDM operator (RHS) agrees well within 3% for system like YbF.

Finally the *P,T*-odd interaction constant $W_d$ can be defined as :

$$W_d = \frac{E_{eff}}{\Omega} = \frac{2ic}{\Omega}\langle \Psi_m \mid \beta_i \gamma_i^5 p_i^2 \mid \Psi_m \rangle$$

Where, Ω is the projection of the angular momentum along the molecular axis.

Some of the current molecular EDM experiments that are underway are:

**YbF:** Ed. Hinds, Imperial College, London

**PbO* and ThO* :** DeMille, Yale and Doyle, Harvard

**HfF+:** Cornell, JILA, Colorado

The sensitivity of these experiments could be 2-3 orders of magnitude better than that of the EDM experiment on atomic Tl.

Calculation of effective electric fields in these molecules are currently not very accurate, which needs to be improved significantly.

P,T- violating electron nucleus interaction can also give rise to permanent intrinsic EDMs in atoms and molecules.

The *P,T*-odd Hamiltonian arising from electron-nucleus scalar-pseudoscalar (S-PS) Interaction can be written as:

$$H_s = i\frac{G_F}{\sqrt{2}} Z C_S \sum_i \beta_i \gamma_i^5 \rho_N(r_i)$$

The corresponding *P,T*-odd interaction constant $W_S$ is defined as:

$$W_S = \frac{1}{C_S \Omega} \langle \Psi_m \mid H_s \mid \Psi_m \rangle$$

Where, $C_S$ is a dimension less coupling constant and $\rho_N(r_i)$ is the nuclear charge density normalized to unity.

Some models of particle physics predicts that the effect of e-N S-PS interaction dominates over the electron EDM interaction.

# Calculations of the effective fields using coupled cluster theory

The effective field can be expressed as an expectation value as mentioned in the previous slides.

The molecular wave function is obtained using a state-of-the-art Coupled Cluster (CC) approach.

$$H_m \mid \Psi_m \rangle = E_m \mid \Psi_m \rangle \quad \text{and} \quad \langle \tilde{\Psi}_m \mid H = \langle \tilde{\Psi}_m \mid E_m$$

In CC theory we can expand the wave functions as follows

$$\mid \Psi_m \rangle = e^S \mid \Phi_0 \rangle \quad \text{where} \quad S = S_1 + S_2 + \ldots$$

$$\text{and} \quad S_1 = \sum_{a,p} S_a^p a_p^\dagger a_a ; S_2 = \sum_{ab,pq} S_{ab}^{pq} a_p^\dagger a_q^\dagger a_b a_a$$

$$\langle \tilde{\Psi}_m \mid = \langle \Phi_0 \mid \tilde{S} e^{-S} \quad \text{where} \quad \tilde{S} = 1 + \tilde{S}_1 + \tilde{S}_2 + \ldots$$

$$\text{and} \quad \tilde{S}_1 = \sum_{a,p} \tilde{S}_a^p a_a^\dagger a_p ; \tilde{S}_2 = \sum_{ab,pq} \tilde{S}_{ab}^{pq} a_a^\dagger a_b^\dagger a_q a_p$$

For convenience, we can re-write $S = \sum_{I \neq 0} S_I C_I^\dagger$ and $\tilde{S} = 1 + \sum_{I \neq 0} \tilde{S}_I C_I$

For example, when I = 1: $S_1 = S_a^p$ $C_1^\dagger = a_p^\dagger a_a$

and for I =2: $S_2 = S_{ab}^{pq}$ $C_2^\dagger = a_p^\dagger a_q^\dagger a_b a_a$

Now we can get the CC 'ket' amplitudes by solving the following equation.

$$\langle \Phi_0 \mid C_I e^{-S} H_m e^S \mid \Phi_0 \rangle = 0$$

We get the CC energy for the molecular ground state as:

$$E_m = \langle \Phi_0 \mid e^{-S} H_m e^S \mid \Phi_0 \rangle = \langle \Phi_0 \mid H_m e^S \mid \Phi_0 \rangle$$

After getting the CC 'ket' amplitudes, we can get the CC 'bra' amplitudes by solving the following equation.

$$\langle \Phi_0 \mid \tilde{S} \left( e^{-S} H_m e^S - E_m \right) C_I^\dagger \mid \Phi_0 \rangle = 0$$

Now we can evaluate the expectation value of the effective field as

$$\langle A\rangle = \frac{\langle \tilde{\Psi}_m \,|\, A \,|\, \Psi_m \rangle}{\langle \tilde{\Psi}_m \,|\, \Psi_m \rangle} = \langle \tilde{\Psi}_m \,|\, A \,|\, \Psi_m \rangle$$

It may be noted here that the normalization constant $\langle \tilde{\Psi}_m \,|\, \Psi_m \rangle = 1$

Finally, we get the expectation value of effective field as:

$$\langle A\rangle = \langle \tilde{\Psi}_m \,|\, A \,|\, \Psi_m \rangle = \langle \Phi_0 \,|\, \tilde{S} e^{-S} A e^{S} \,|\, \Phi_0 \rangle$$

where $A = 2ic\sum_i \beta_i \gamma_i^5 p_i^2$ for electron EDM interaction

and $A = i\frac{G_F}{\sqrt{2}}\sum_i \beta_i \gamma_i^5 \rho_N\left(r_i\right)$ for e-N S-PS interaction

# Basis set information

In our earlier calculations of the P,T-odd interaction constants for the ground state of YbF using the restricted active space (RAC) configuration interaction (CI) approach we used an even tempered un-contracted Gaussian basis set for both Yb and F atoms.

**Yb:** 27s, 27p, 12d, 8f and for **F:** 15s, 10p (these basis sets are relatively smaller)

Here we do not consider basis functions for higher angular momentum. So, the results can not be so reliable.

In the present calculations we have improved our basis sets.

We consider Dyall's basis set of valence triple zeta (vTZ) and valence quadruple zeta (vQZ) quality for Yb atom, and a similar quality basis sets for F atom.

**Yb:** 30s, 24p, 18d, 16f, 5g, 2h (dyall.cv3z: un-contracted)
**F:** 12s, 7p, 3d, 1f (cc-pCVTZ: un-contracted)

**Yb:** 35s, 30p, 19d, 19f, 8g, 5h, 2i (dyall.cv4z: un-contracted)
**F:** 15s, 9p, 5d, 3f, 1g (cc-pCVQZ: un-contracted)

# Results for the *P,T*-odd interaction constant $W_d$ and $E_{eff}$ for YbF

| Methods | $W_d$ ($10^{25}$ Hz/e.cm) | $E_{eff}$ GV/cm |
|---|---|---|
| Semiemperical (Kozlov *et. al.*, 1994)<br>Semiemperical (with 4f-correction) (Kozlov, 1997) | -1.5<br>-1.26 | -31.01<br>-26.05 |
| GRECP/SCF (Titov *et. al.*, 1996)<br>GRECP/RASSCF | -0.91<br>-0.91 | -18.81<br>-18.81 |
| Restricted DF (Quiney, 1998)<br>Rescaled restricted DF<br>Restricted DF + Core polarisation | -0.61<br>-1.24<br>-1.20 | -12.61<br>-25.64 |
| Unrestricted DF (Parpia, 1998) (unpaired electron)<br>Unrestricted DF (all electrons) | -0.962<br>-1.203 | -19.89<br>-24.87 |
| GRECP/RASSCF/EO (Mosyagin *et. al.*, 1998)<br>GRECP/RASSCF/EO (with 4f-correction) | -1.206<br>-1.206 | -24.93<br>-24.93 |
| Restricted DF (Nayak *et. al.*, 2006)<br>RASCI+T (small active space) | -0.963<br>-1.088 | -19.91<br>-22.49 |
| MBPT(2) (Nayak *et. al.*, 2007) | -1.043 | -21.56 |
| RASCI (large active space without +T) (Nayak *et. al.*, 2009) | -1.164 | -24.06 |

# Recent results of P,T-odd constant $W_d$ and $E_{eff}$ for YbF

Two sets of calculations are done using the state-of -the-art Couple Cluster approach and improved basis sets of both Yb and F atoms.

The most recent results are as follows:

| Basis set | Number of electrons/virtual orbitals | $W_d$ ($10^{25}$ Hz/e.cm) | $E_{eff}$ GV/cm |
|---|---|---|---|
| Yb: dyall.cv3z<br>F: cc-pCVTZ | 31/160 | -0.89 (DF)<br>-1.03 (CCSD) | -18.42 (DF)<br>-21.29 (CCSD) |
| Yb: dyall.cv4z<br>F: cc-pCVQZ | 31/160 | -0.89 (DF)<br>-1.01 (CCSD) | -18.43 (DF)<br>-20.76 (CCSD) |

We call this as our preliminary results because we need to include some more number of virtual orbitals in our CC calculation.

We may also need to consider partial triple excitations and more correlating electrons in our calculations.

# Results of the *P,T*-odd interaction constant $W_S$ for YbF

| Methods | $W_S$(kHz) |
|---|---|
| Semiemperical (Kozlov *et. al.*, 1994)<br>Semiemperical (with 4f-correction) (Kozlov, 1997) | -48<br>-43 |
| GRECP/SCF (Titov *et. al.*, 1996)<br>GRECP/RASSCF | -33<br>-33 |
| Restricted DF (Quiney, 1998)<br>Rescaled restricted DF<br>Restricted DF + Core polarisation | -22<br>-44<br>-42 |
| Unrestricted DF (Parpia, 1998) (unpaired electron)<br>Unrestricted DF (all electrons) | <br>-44 |
| Restricted DF (Nayak *et. al.*, 2007)<br>RASCI (SD)<br>MBPT (2) (Nayak *et. al.*, 2008) | -34.2<br>-41.2<br>-37.1 |

Results of the *P,T*-odd constant $W_S$ from the recent calculations using CC approach, and improved basis set are yet to obtain.

# Conclusions

- We have performed relativistic Coupled Cluster calculations for the effective field, and got preliminary results.

- The results are showing signs of convergence but calculation on the larger scale will have to be carried out to confirm this trend.

- Electron correlation effects contribute around 13% for vTZ basis set and to around 11% for the vQZ basis set to our calculations of effective field.

- Further improvements of the calculation of the effective electric field are possible using state-of-the-art hi-performance computing techniques.