

Using Polyatomic Molecules in eEDM Searches

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Bachelor Thesis Presentation

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Introduction: Problems in the Standard Model

- Only accounts for 4% of the energy content in the universe
- Cannot explain the existence of dark matter and dark energy
- Matter-antimatter imbalance ←



New Beyond the Standard Model Theories are needed



Matter-antimatter imbalance

In the early universe the amount of matter and antimatter was almost equal, matter being slightly more abundant. However in the present time matter dominates the universe.



How do we explain this time reversal (T) violating effect?



Look for source of T-violation



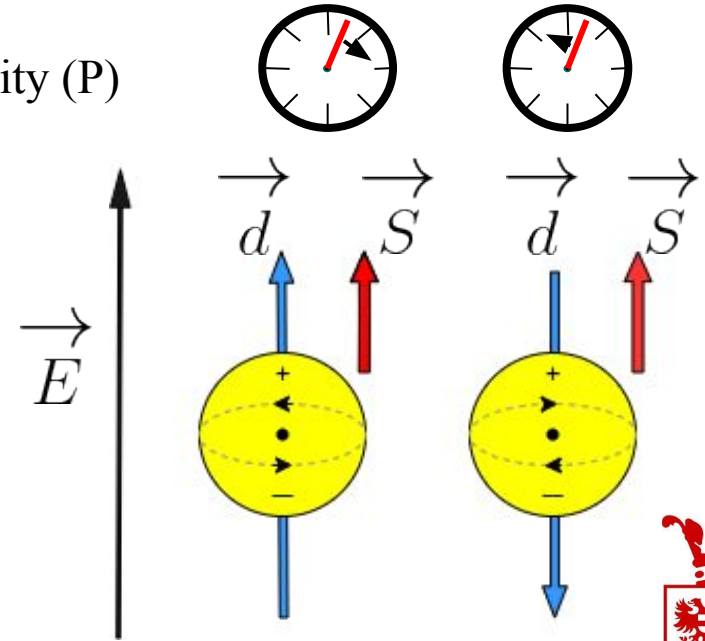
Electron Electric Dipole Moment (eEDM)

- The eEDM violates both time reversal (T) and parity (P) symmetries

- It is still to be measured

SM predicted value: $d_e \sim 10^{-38} ecm$

BSM predicted value: $d_e \sim 10^{-25} - 10^{-33} ecm$



Measuring Technique

Direct measurement on electrons is not feasible and experiments are performed on polar molecules instead:

- E_{eff} amplifies the eEDM signal
- Most experiments use polar diatomic molecules
- Upper limit on eEDM se at $|d_e| < 4.1 \times 10^{-30} ecm$ with HfF+



Higher Sensitivity

All experiments give zero value, the upper limit arises due to statistical uncertainty:

$$\sigma_d = \frac{\hbar}{e 2|P| E_{eff} \tau \sqrt{\dot{N} T}}$$

e : electron charge

P : polarization

τ : coherence time

T : measurement time

\dot{N} : detection rate

- Goal: increase the coherence interaction time without decreasing the detection rate.
- Possible with laser cooling
- Problem: Diatomics with opposite parity states do guarantee being laser cooling amendable



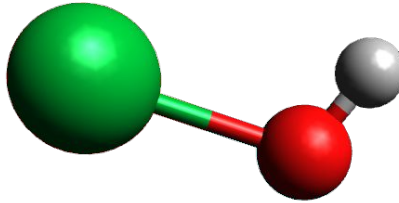
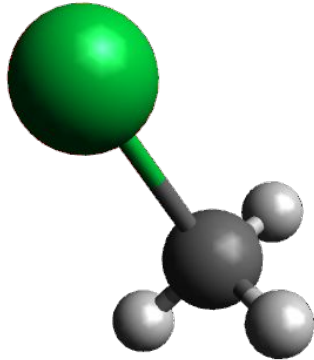
Polyatomic Molecules

- Similar eEDM sensitivity to diatomics
- Opposite parity states do not depend on electronic structure
- Laser coolable
- Source of parity doubling: nuclear angular momentum



Molecule Characteristics

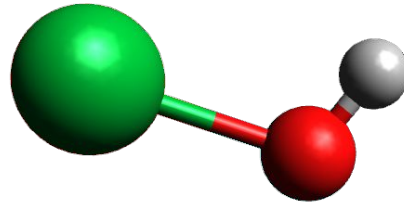
- Posses a molecular dipole moment
- Contain at least one heavy nucleus $W_d \propto Z^3$
- Paramagnetic
- Bend geometry in the ground state



Goal of this study:

Determine the eEDM enhancement W_d factor of PbOH and PoOH through ab initio quantum chemistry calculations

Both molecules are linear triatomics



$$\frac{e Hz}{h cm}$$




Theory

$$d_e = \Delta E / E_{eff}$$

$$\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$$

$$\hat{H}_{eff}^{eEDM} = 2icd_e \sum_i^n \gamma^5 \beta \mathbf{p}_i^2$$

$$\beta = \begin{bmatrix} 1_{2 \times 2} & \emptyset_{2 \times 2} \\ \emptyset_{2 \times 2} & -1_{2 \times 2} \end{bmatrix}$$

 First order perturbation model: $\hat{H} = \hat{H}^{(0)} + \lambda \frac{\hat{H}_{eff}^{eEDM}}{d_e}$

$\hat{H}^{(0)}$: Unperturbed Hamiltonian

λ : field strength

\mathbf{p}_i : momentum of electron i



Theory

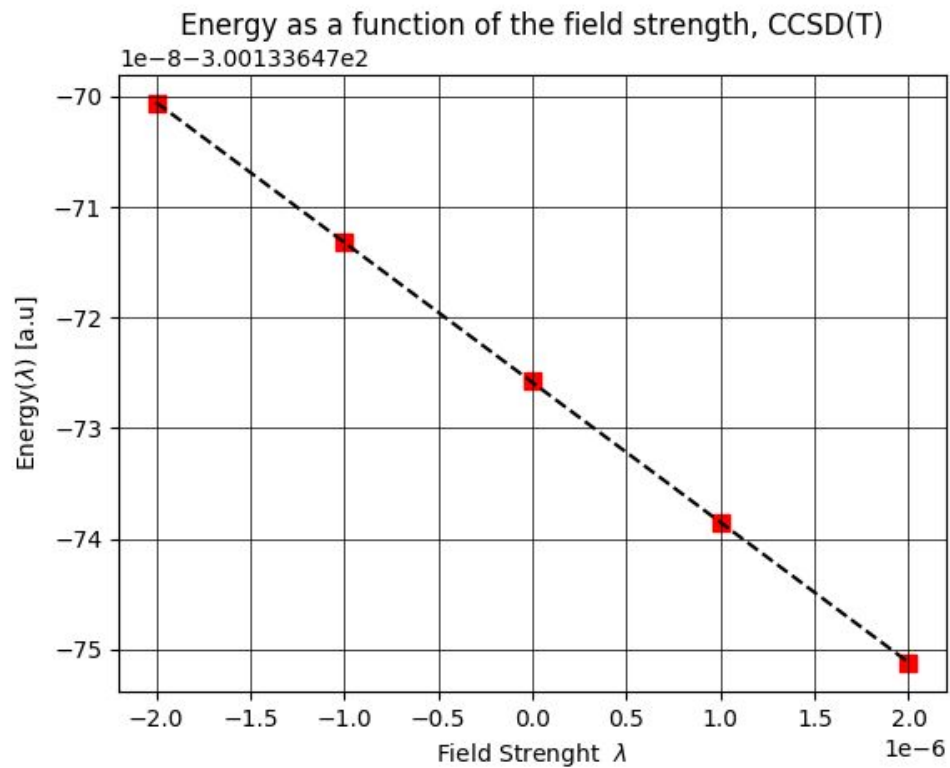
$$\hat{H} = \hat{H}^{(0)} + \lambda \frac{\hat{H}_{eff}^{eEDM}}{d_e} \quad \longrightarrow \quad E_{\Omega} = E_{\Omega}^{(0)} + \lambda E_{\Omega}^{(1)} + \mathcal{O}(\lambda^n)$$

$$\longrightarrow \quad W_d = \left. \frac{1}{\Omega} \frac{dE_{\Omega}}{d\lambda} \right|_{\lambda=0} = \frac{E_{eff}}{\Omega} \approx \frac{1}{\Omega} \frac{E(\lambda) - E(-\lambda)}{2\lambda}$$

Ω : Electronic angular momentum projected along the internuclear axis



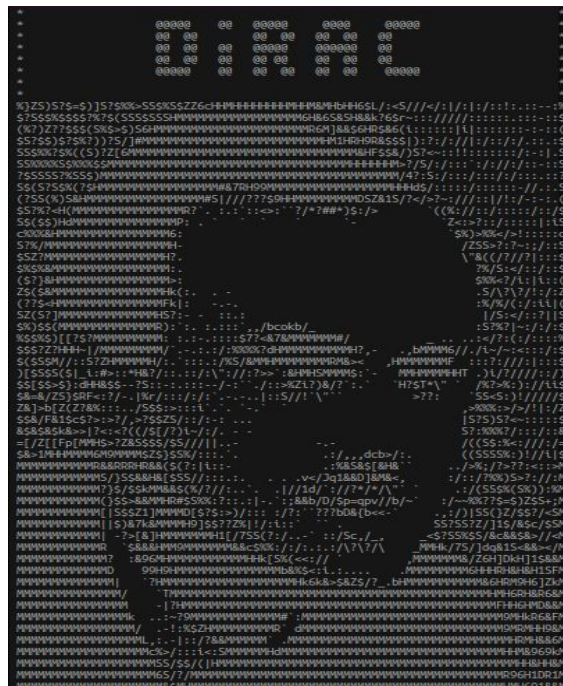
Theory



Computational Methods and Considerations

The value of the enhancement factor will be calculated using relativistic ab initio quantum chemistry DIRAC19 software.

- Dirac-Hartree–Fock (DHF)
- Couple Cluster (CC)
- Møller–Plesset perturbation theory (MP2)
- Density Functional Theory (DFT)



Molecular Hamiltonian

$$\hat{H}_{mol} = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{R}) + V_{Ne}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R})$$

\mathbf{R} : nuclear coordinates

\mathbf{r} : electronic coordinates



Born-Oppenheimer Approximation

- The nuclei are much heavier than the electrons.
- Electrons move much faster than nuclei.
- Nuclear coordinates are assumed to be fixed.

$$V_{Ne}(\mathbf{r}, \mathbf{R}) \rightarrow V_{Ne}(\mathbf{r}; \overset{\blacktriangleleft}{\mathbf{R}})$$

$$\hat{H}_{mol} = \underbrace{\hat{T}_e(\mathbf{r}) + V_{Ne}(\mathbf{r}; \mathbf{R}) + V_{ee}(\mathbf{r})}_{\hat{H}_e} + \underbrace{V_{NN}(\mathbf{R}) + \hat{T}_N(\mathbf{R})}_{\hat{H}_N} = \hat{H}_e + \hat{H}_N$$



Born-Oppenheimer Approximation

The final form of the Hamiltonian can be given as:

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN} \quad ; \quad V_{NN} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}}$$

$\hat{h}(i)$: one-electron operator, contains \hat{T}_e and V_{Ne}

$\hat{g}(i, j)$: two-electron operator, represents the electron-electron repulsion



MO-Theory and Basis Sets

Molecular orbitals as a linear combination of atomic orbitals:

$$\psi = \sum_A^N c_A \Phi_A$$

Atomic orbitals are approximated by Slater type orbitals (STO):

$$\Phi_{abc}^{STO}(x, y, z) = N x^a y^b z^c e^{-\zeta r}$$

N : normalization constant

a, b, c : control angular momentum, ($L = a + b + c$)

ζ : controls the width of the orbital

$$r = \sqrt{x^2 + y^2 + z^2}$$



Gaussian Type Orbitals (GTO)

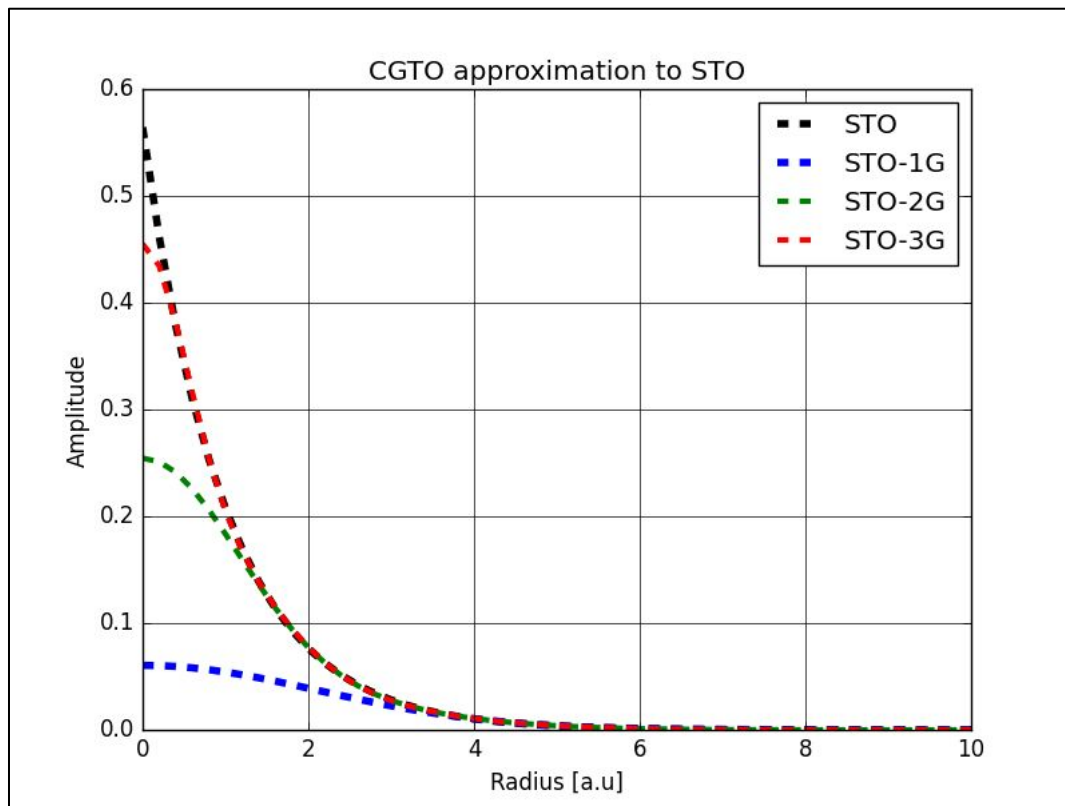
$$\Phi_{abc}^{GTO}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2}$$

- GTOs are computationally less demanding.
- STOs give more accurate results
- Use linear combination of GTOs
- Cardinality: number of basis functions used (Tz, Dz, Qz,...)

Contracted Gaussian Types Orbitals, (CGTO):
$$\Phi_{abc}^{CGTO} = N \sum_{j=1}^K c_j x^a y^b z^c e^{-\zeta_j r^2}$$



Gaussian Type Orbitals (GTO)



Dirac-Hartree-Fock (DHF)

- In HF electrons are described by a single particle function and treat the other electrons as an average charge distribution.
- Variational method
- First wave function approximation:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_n(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_n) & \chi_2(\mathbf{x}_n) & \cdots & \chi_n(\mathbf{x}_n) \end{vmatrix} = |12\dots n\rangle$$

$$\text{Spin Orbitals: } \chi(\mathbf{x}) = \phi(\mathbf{r})\alpha(w) ; \quad \mathbf{x} = \{\mathbf{r}, w\}$$

Dirac-Hartree-Fock (DHF)

- Hartree-Fock energy:

$$E_{HF} = \langle \Psi | \hat{H}^{(0)} | \Psi \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} ([ii|jj] - [ij|ji])$$

One-electron integral: $\langle i | \hat{h} | i \rangle = \int \chi_i^*(\mathbf{x}_1) \hat{h}(i) \chi_j(\mathbf{x}_1) d\mathbf{x}_1$

Two-electron integral: $[ij|kl] = \int \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{ij}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$

Dirac-Hartree-Fock (DHF)

- Hartree-Fock equation:

$$\left[\hat{h}(\mathbf{x}_1) + \sum_{j \neq i}^n [\mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)] \right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \longrightarrow \hat{f}(\mathbf{x}_1) \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

Energy eigenfunction of spin orbit $\chi_i(\mathbf{x}_1) : \epsilon_i$

$$\text{Coulomb operator: } \mathcal{J}_j(\mathbf{x}_1) = \int \frac{|\chi_j(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_2$$

$$\text{Exchange operator: } \mathcal{K}_j(\mathbf{x}_1) \chi_i(\mathbf{x}_1) = \left[\int \frac{\chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \chi_j(\mathbf{x}_1)$$

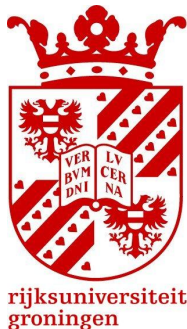
Dirac-Hartree-Fock

- Why is it called Dirac?

$$\hat{h}_D = \beta mc^2 + c(\boldsymbol{\alpha} \cdot \hat{\mathbf{p}}) + V_{eN} \quad \boldsymbol{\alpha} = \begin{bmatrix} \emptyset_{2 \times 2} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \emptyset_{2 \times 2} \end{bmatrix}$$

In the relativistic regime there is a mass term added to the one-electron operator:

Contains positive and negative energy solutions: $4c, X2c$



Electron Correlation (EC)

- The motion of the electron is influenced by the presence of the other electrons.
- HF does not account for EC.
- The difference between HF energy and the real energy is termed correlation energy.
- Post-HF methods are used in order to account for it.



Coupled Cluster (CC)

- Post-HF method.
- Perturbative method.
- Includes EC
- Based on exponential operator: $\Psi = e^{\hat{T}} \Phi_0$

Cluster operator, \hat{T} : $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n$

$$\hat{T}_1 \Phi_0 = \sum_{r,k} t_r^k D_r^k \quad ; \quad \hat{T}_2 \Phi_0 = \sum_{\substack{r>s \\ k>l}} t_{rs}^{kl} D_{rs}^{kl}$$



Coupled Cluster (CC)

$$\exp \left[\hat{T} \right] = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots$$

$$\longrightarrow \Psi = \left[1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \right] \Phi_0$$



Coupled Cluster (CCSD)

If we only take in to account one and two-particle excitation operators:

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

$$\Psi = \left[1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \right] \Phi_0$$

$$\longrightarrow \Psi = e^{\hat{T}} \Phi_0 = e^{(\hat{T}_1 + \hat{T}_2)} \Phi_0 = \left[1 + \hat{T}_1 + \hat{T}_2 + \frac{(\hat{T}_1 + \hat{T}_2)^2}{2!} + \dots \right] \Phi_0$$

$$\hat{T}_1 \Phi_0 = \sum_{r,k} t_r^k D_r^k \quad ; \quad \hat{T}_2 \Phi_0 = \sum_{\substack{r>s \\ k>l}} t_{rs}^{kl} D_{rs}^{kl}$$



Coupled Cluster (CCSD)

- If we add the three particle excitation operators, $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$, we obtain the CCSDT method.
- Computationally heavy
- There exist other methods that approximate CCSDT like CCSD(T) or CCSD-T



Current Results

Geometry Optimization: first the geometry of the molecule needs to be determined

Search the literature → Run geometry in DIRAC → Test different methods

Methods:

- DFT
- CCSD

Basis Sets:

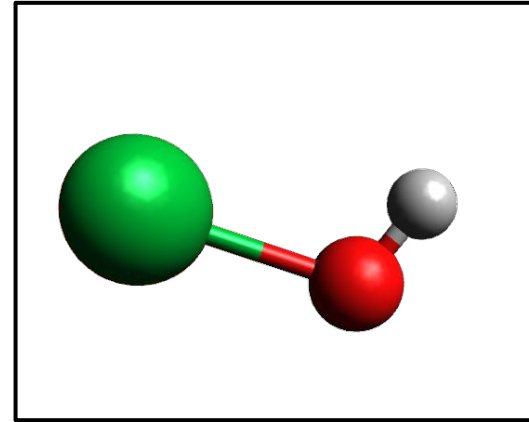
- Dyall.v2z
- Dyall.v3z

Hamiltonian:

- 4c
- X2c

We used a space cut off energy of -30 a.u to +30 a.u,
correlating a total of 61 electrons

1 a.u = 27.211324570273 eV



Geometry of PoOH

CCSD

Basis	Hamiltonian	R (Po-O) [Å]	R (O-H) [Å]	Angle [degrees]
Dyall.v2z	4c	2.156052	0.967499	105.904
Dyall.v3z	4c	2.100646	0.958618	107.840
Dyall.v2z	X2c	2.156044	0.967511	105.910
-	1c	-	-	-

Literature values	R (Po-O) [Å]	R (O-H) [Å]	Angle [degrees]
DFT	2.0644	0.9610	106.89



Geometry of PbOH

1 A = 10×10^{-10} m

CCSD

Basis	Hamiltonian	R (Pb-O) [A]	R (O-H) [A]	Angle [degrees]
Dyall.v2z	4c	2.112572	0.964580	113.764
Dyall.v3z	4c	-	-	-
Dyall.v2z	X2c	2.111954	0.964043	113.769
-	1c	-	-	-

Initial Calculation	R (Pb-O) [A]	R (O-H) [A]	Angle [degrees]
DFT	2.111954748375	0.964242722369	113.79373244



Following Calculations

- Use the obtained geometries for the enhancement factor calculations
- Calculate the enhancement factor varying the electron correlation
- Calculate the enhancement factor using DHF and varying CCSD methods
- Calculate the enhancement factor varying the Hamiltonian



The End



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Thank you for your attention