

UNIVERSITY OF GRONINGEN

BACHELOR THESIS

Using Polyatomic Molecules for eEDM Searches

Author:
Pablo CAPARRÓS CALLE (S3695778)

First Examiner:
prof. dr. ANASTASIA BORSHEVSKY

Second Examiner:
prof. dr. STEVEN HOEKSTRA

Daily Supervisor:
dr. LUKÁŠ FÉLIX PAŠTEKA

Date:
July 2023

Using Polyatomic Molecules for eEDM Searches

Measuring the enhancement factor W_d for untested polyatomic molecules
PbOH and PoOH

Pablo Caparrós Calle

Abstract

Current electron electric dipole (eEDM) searches are investigating the use of previously untested polyatomic molecules in order to overcome limitations presented by diatomic molecules. Calculating the eEDM sensitivity of these proposed polyatomics is then key for such eEDM searches. The determination of such sensitivity to an eEDM must be calculated through ab initio computational methods. In this work the enhancement factor W_d for PbOH and PoOH is calculated using Hartree-Fock, coupled cluster methods and Møller-Plesset perturbation theory. Optimized geometries of the mentioned molecules are determined as well in the process. Triple and double basis sets are utilized in the geometry optimization of the molecules. For W_d only double zeta basis sets are utilized due to time limitations. The treatment of relativity is addressed by performing the calculations with a four component Dirac Hamiltonian. In all calculations core orbitals were frozen and the maximum electron correlation treated in the paper is done at a space cut off of 30 a.u of energy for the geometry optimization and of 5 a.u. for the enhancement factor calculations. For PoOH the final value was of $W_d = 8.402 \times 10^{24} \frac{e}{h} \frac{Hz}{cm}$, calculated using the CCSD(T). For PbOH the final value was $W_d = 9.031 \times 10^{24} \frac{e}{h} \frac{Hz}{cm}$ and it was determined using MP2 methods instead.

Contents

1	Introduction	3
2	Theory	5
2.1	eEDM Hamiltonian	5
2.2	First-order Perturbation on Model Hamiltonian	5
3	Computational Methods and Considerations	7
3.1	Born-Oppenheimer Approximation	7
3.1.1	One-Electron Operator	8
3.1.2	Two-Electron Operator	9
3.1.3	Further Relativistic Considerations	9
3.2	Molecular Orbital Theory	10
3.2.1	Basis Sets	10
3.2.2	Dyall Basis Sets	11
3.3	Computational Methods	12
3.3.1	Hartree-Fock	12
3.3.2	Restricted and Unrestricted Hartree-Fock	14
3.3.3	Dirac-Hartree-Fock	14
3.3.4	Electron Correlation Methods	15
3.3.5	Coupled Cluster	15
3.3.6	Møller-Plesset Perturbation Theory	16
4	Results	18
4.1	Geometry Optimization	18
4.2	Calculations for the Enhancement Factor \mathbf{W}_d	20
4.3	Results for the Enhancement Factor \mathbf{W}_d	21
5	Discussion	23
5.1	Uncertainty	23
5.2	Comparison with the Literature	24
6	Conclusion	25
7	Acknowledgements	26
8	References	27

1 Introduction

The Standard Model (SM) of particle physics describes the behaviour of all elementary particles ever discovered and predicts some of their properties with incredible accuracy [1]. Even if some of the predictions achieved by the SM are extremely impressive, the reality is that all the elementary particles contained in it account only for 4 percent of the energy content of the universe [1]. It is then not surprising to know that there are still some aspects of our universe that cannot be explained through the SM. The phenomena causing the biggest conflict can be divided in to three categories. First is the matter-antimatter imbalance observed in the universe, next is the existence of dark matter and dark energy which account for 96 percent of the energy content in the universe [1] and at last the inability to merge gravity with the SM framework. In this circumstances Beyond the Standard Model (BSM)¹ theories are required in order to explain these discrepancies between empirical data and the SM. Some of these BSM theories consist of supersymmetric models or extradimensional theories [3]. It is crucial to determine which of these BSM theories yields the most accurate representation of nature and a possible way of achieving this is by measuring specific experimental quantities for which different BSM theories will have differing predictions.

A quantity being currently searched for is the theorized but yet undetected electron electric dipole moment (eEDM). If the electron was to possess this property, it would violate both parity (P) and time reversal (T) symmetries. The CPT theorem then states that every relativistic quantum field theory has a symmetry that simultaneously reverses charge (C)², reverses parity (P), and reverses the direction of time[4]. If CPT is conserved in the SM, T violation is equivalent to CP violation meaning an eEDM would violate CP symmetry equivalently [5]. In the SM the eEDM value is predicted to be extremely small ($d_e \simeq 10^{-38} \text{ ecm}$)[6] and remains undetected due to the current experimental limitations. This is where new-physics or BSM theories come in to play as they predict values for the eEDM orders of magnitude bigger ($10^{-25} - 10^{-33} \text{ ecm}$)[7], making it fall within the experimental reach. This increase of the eEDM is caused by a higher degree of CP violation, which is required to explain the matter-antimatter asymmetry in the universe [8].

The search for the eEDM is carried out through high precision experiments carried out in molecules as direct measurements on the electron are not feasible. This because in order to detect an eEDM, an electric field has to be applied resulting in an energy shift. Electrons are charged and exposing one to a field would cause it to accelerate away. This problem is solved by using polar molecules because the electron remains inside the molecule and the internal molecular electric field caused by the molecular dipole can act as the effective electric field E_{eff} interacting with the electron. The small energy shifts caused by these electromagnetic moments can be found in the spectrum of the molecule under test [9]. The eEDM sensitivity of a molecule is determined by its E_{eff} and normally is calculated by finding the eEDM enhancement factor W_d through numerical calculations. This enhancement factor W_d is equivalent to E_{eff} only differing by an omega factor. The energy shift in the particles will be minute, so a large W_d is needed. Until recently most measurements have been conducted using polar diatomic molecules such as YbF[10], HfF+[11], BaF[12] and ThO[13]. The upper limit was set at $|d_e| < 10^{-29} \text{ ecm}$ in experiments with ThO[13] but has been recently surpassed with HfF⁺ molecular ions giving an upper limit of $|d_e| < 4.1 \times 10^{-30} \text{ ecm}$. All experiments have only given zero-valued measurements and the limit previously mentioned arises due to the statistical uncertainty σ_d in the eEDM measurement [14]:

$$\sigma_d = \frac{\hbar}{e} \frac{1}{2|P|E_{eff}\tau\sqrt{\dot{N}T}} \quad (1)$$

where e is the electron charge, P is the molecular polarization, τ is the coherence interaction time, \dot{N} the detection rate of the molecules and T the measurement time. For future experiments it is vital to increase the coherence interaction time without decreasing the detection rate. This can be effectuated

¹BSM can refer to physical phenomena established experimentally but not accommodated by the SM, deeper explanations accommodated to the SM that serve as extensions to the theory or maybe new-physics theories [2].

²C stands for charge conjugation

by using laser cooled molecules. Another way to isolate systematic effects mimicking the sought-for shift is by using molecules with nearly degenerate opposite parity states structure, like the Ω -double levels in diatomics [15]. In diatomics this source of parity doubling is derived from the electron orbital angular momentum (electronic structure)[9]. This means there is no guarantee diatomics molecules will allow for laser coolability as it depends on electronic structure too [9]. However, in polyatomic molecules³ such parity doublets can be obtained irrespective of the electronic structure of the selected polyatomic species [16]. This is because in polyatomics the source of parity doubling is due to nuclear orbital angular momentum in vibrational bending modes (l -doubling) and so it is decoupled from the source of laser coolability (electronic structure) [9]. Furthermore, it has also been shown in [14] that polyatomics YbOH and BaOH offer the same eEDM sensitivity as their isoelectronic diatomic counterparts YbF and BaF but with the advantage of being laser coolable, offer full polarization in small fields and the ability to obtain good control over systematic error effects using internal co-magnetometer states [17].

As previously said the eEDM enhancement factor W_d is required to be as large as possible. There are multiple key characteristics that give rise to a large W_d and the molecule under test must combine all of them in order to be able to give measurable energy shifts. The eEDM enhancement factor is proportional to the atomic number cubed and molecules with at least one heavy atom drastically increase W_d [9]. Furthermore, W_d is proportional to the polarization of the molecule, so the chosen molecule should be made of atoms with unequal electronegativities. The molecule in question must also be paramagnetic and hold an unpaired electron in the groundstate in order for the electron to be sensitive to the E_{eff} .

At the moment most theory proposals for eEDM experiments with polyatomics incorporate either a linear triatomic molecule consisting of a heavy element with an OH ligand (YbOH[14, 18, 19], BaOH[14], HgOH[20], RaOH[21], AcOH⁺[22]) or a symmetric top formed out of CH₃/OCH₃ ligands (YbCH₃[23], BaCH₃[23], HgCH₃[20], HgCF₃[20], YbOCH₃[21], RaOCH₃[24], BaOCH₃[21]). The diversity of the heavy elements used is somewhat scarce, most experiments carried out have been done with lanthanides like Yb or with alkaline earths like Ba or Ra. Some actinides like No or Lr [21] and transition metals like Hg have also been studied. The number of possible molecules still to be tested is quite extensive and there are still a substantial amount of different elements that can be utilized. When exploring the literature, it comes to our attention that the group composed of p-block metals has not been examined yet even though there are suitable elements that could give promising results. In this work the enhancement factor W_d for polonium hydroxide (PoOH) and for lead hydroxide (PbOH) will be calculated for the first time through ab initio calculations.

These molecules are made out of atoms with a high atomic number which implies a high enhancement factor. Both molecules have an odd number of electrons, ensuring they possess an unpaired electron in its valence shell. This single unpaired electron will be able to interact with the E_{eff} of the molecules and give an energy splitting.

³three atoms or more

2 Theory

2.1 eEDM Hamiltonian

The interaction of the eEDM with an electric field causes an experimental energy shift ΔE in the molecule. The value for the eEDM (d_e) can then be known by obtaining the experimental energy shift and the effective electric field [14]:

$$d_e = \Delta E / E_{eff} \quad (2)$$

This energy shift is described by the following Hamiltonian [25]:

$$\hat{H}^{eEDM} = -d_e(\gamma^0 \boldsymbol{\Sigma} \cdot \mathbf{E} + i\boldsymbol{\gamma} \cdot \mathbf{B}) \quad (3)$$

where \mathbf{E} is the total electric field⁴, \mathbf{B} is the total magnetic field, $\gamma^\mu = \{\gamma^0, \boldsymbol{\gamma}\}$ are the Dirac gamma matrices and $\boldsymbol{\Sigma}$ is the vector of Pauli spin matrices given by:

$$\boldsymbol{\Sigma} = \begin{bmatrix} \boldsymbol{\sigma} & \emptyset_{2 \times 2} \\ \emptyset_{2 \times 2} & \boldsymbol{\sigma} \end{bmatrix}, \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (4)$$

In equation 3 the second term originating from the magnetic field interaction with the eEDM is negligible in comparison with the first term originating from the electric field interaction with the eEDM [26]. As a consequence the eEDM Hamiltonian can be rewritten effectively as a one-body operator in the following form [27]:

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

where n is the total number of electrons in the system, \mathbf{p}_i is the momentum of electron i and $\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$. At last β is a Dirac matrix specified as:

$$\beta = \begin{bmatrix} 1_{2 \times 2} & \emptyset_{2 \times 2} \\ \emptyset_{2 \times 2} & -1_{2 \times 2} \end{bmatrix} \quad (6)$$

2.2 First-order Perturbation on Model Hamiltonian

The eEDM Hamiltonian discussed in the previous section can be treated as a first order perturbation to an unperturbed Hamiltonian $\hat{H}^{(0)}$. This gives the total Hamiltonian in the following form:

$$\hat{H} = \hat{H}^{(0)} + \lambda \frac{\hat{H}_{eff}^{eEDM}}{d_e} \quad (7)$$

where λ is the field strength and $\hat{H}^{(0)}$ is the relativistic Dirac-Coulomb Hamiltonian given by [27]:

$$\hat{H}^{(0)} = \sum_i^n [\beta_i m c^2 + c\boldsymbol{\alpha}_i \cdot \hat{\mathbf{p}}_i - V_{eN}(r_i)] + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{r_{ij}} \quad (8)$$

where m is the electron's mass, V_{eN} is the Coulomb potential generated by the nucleus, r_i is the distance of electron i from the nucleus and r_{ij} is the distance between electron i and electron j . The term β is the Dirac matrix specified in equation 6 and $\boldsymbol{\alpha}$ is another Dirac matrix of the form:

$$\boldsymbol{\alpha} = \begin{bmatrix} \emptyset_{2 \times 2} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \emptyset_{2 \times 2} \end{bmatrix} \quad (9)$$

Perturbation theory is employed in this method and the introduction of λ in equation 7 allows for the energy to be expanded as a Taylor series around $\lambda = 0$:

$$E_\Omega = E_\Omega^{(0)} + \lambda E_\Omega^{(1)} + \mathcal{O}(\lambda^n) \quad (10)$$

⁴includes both the applied external electric field and the internal electric fields

E_Ω is the total energy of the electronic state and $E_\Omega^{(1)}$ is proportional to the eEDM energy shift with a factor d_e . The last term $\mathcal{O}(\lambda^n)$ stands for higher order terms and λ is chosen such that this higher order terms vanish [27]. This means the final expression for the energy is:

$$E_\Omega = E_\Omega^{(0)} + \lambda E_\Omega^{(1)} \quad (11)$$

Consequently the eEDM enhancement factor can be obtained numerically, according to the Hellmann-Feynman theorem, from the first derivative of the energy with respect to λ [14]:

$$W_d = \frac{1}{\Omega} \frac{dE_\Omega}{d\lambda} \Big|_{\lambda=0} = \frac{E_{eff}}{\Omega} \approx \frac{\langle \hat{H}_{eff}^{eEDM} \rangle}{\Omega} \quad (12)$$

the proportionality factor between W_d and E_{eff} is Ω , the electronic angular momentum projected along the internuclear axis.

3 Computational Methods and Considerations

Solving the full Dirac or Schrödinger equation will yield the exact solution for the energy of the system but unfortunately solving such equation for systems like molecules is too computationally costly. This means some approximations have to be made, the results will yield a lower accuracy but in return the computational cost and time will be reduced. In this research all calculations will be carried out with the relativistic ab initio quantum chemistry DIRAC19 software. This program is capable of calculating various molecular properties using the Dirac-Hartree-Fock (HF), Møller-Plesset perturbation theory (MP2), density functional theory (DFT), configuration interaction (CI) and coupled cluster (CC) electronic structure theories. In this work only HF, CC and MP2 methods will be explained, the derivation of these types of methods will be looked in detail in the Computational Methods section 3.3.

3.1 Born-Oppenheimer Approximation

The general expression for a molecular Hamiltonian has the following form [28]:

$$\hat{H}_{mol} = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{R}) + V_{Ne}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) \quad (13)$$

Where the \hat{T} operators are the kinetic terms for the electrons and nuclei in the molecule respectively, V_{Ne} is the attraction potential between nuclei and electrons and the last two potential terms correspond the repulsion between electrons (V_{ee}) and the repulsion between nuclei (V_{NN}). All these terms are functions dependent either on electronic coordinates \mathbf{r} or nuclear coordinates \mathbf{R} . Now our goal is to solve the Schrödinger equation for this Hamiltonian ($\hat{H}_{mol}\Psi = E_{mol}\Psi$) but a problem arises if we do this. The Schrödinger equation can only be solved exactly for the hydrogen atom [29], anything more complex can only be solved using an approximation. This approximation is the Born-Oppenheimer (BO) approximation and is based on the fact that electrons are thousands of time lighter than nuclei. This means electrons move much faster than their nuclear counterparts and so from their perspective it seems like the nuclei are static and do not change their spatial coordinates. Now, how does this help in solving the Schrödinger equation?

In quantum mechanics, if the Hamiltonian can be separated as a sum of terms each depending on different variables ($\hat{H} = \hat{H}_1(\mathbf{r}_1) + \hat{H}_2(\mathbf{r}_2)$) then the wavefunction can be expressed as a product of functions with different variables ($\Psi = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$). If the molecular Hamiltonian could be expressed as a sum of nuclear and electronic Hamiltonians, then the molecular wavefunction would consist of a product of two separate functions:

$$\hat{H}_{mol}\Psi = E_{mol}\Psi \rightarrow [\hat{H}_e(\mathbf{r}) + \hat{H}_N(\mathbf{R})] \psi_e(\mathbf{r})\psi_N(\mathbf{R}) = E_{mol}\psi_e(\mathbf{r})\psi_N(\mathbf{R}) \quad (14)$$

Now there is a problem with the Hamiltonian in equation 13, it does not satisfy the condition for a Hamiltonian consisting on separable Hamiltonians because the term for the electron-nucleus attraction V_{Ne} depends both on \mathbf{r} and \mathbf{R} [28]. Here is where the BO approximation comes in to play. Treating the nuclei as being static in the electrons frame will allow for the wavefunction to be expressed in a similar form to the one previously mentioned:

$$\Psi = \psi_e(\mathbf{r}; \mathbf{R})\psi_N(\mathbf{R}) \quad (15)$$

where the ; symbol in the argument of the electronic part means that we are treating the nuclear coordinates no longer as a variable but as a parameter that is fixed. This type of separation allows us to separate as well the Hamiltonian in the following way:

$$\hat{H}_{mol} = \overbrace{\hat{T}_e(\mathbf{r}) + V_{Ne}(\mathbf{r}; \mathbf{R}) + V_{ee}(\mathbf{r})}^{\hat{H}_e} + \overbrace{V_{NN}(\mathbf{R}) + \hat{T}_N(\mathbf{R})}^{\hat{H}_N} = \hat{H}_e + \hat{H}_N \quad (16)$$

Then we know that the electronic Hamiltonian will give the electronic energies if we solve the electronic Schrödinger equation:

$$\hat{H}_e\psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\psi_e(\mathbf{r}; \mathbf{R}) \quad (17)$$

where the electronic energy depends on the parameter \mathbf{R} . Then if we solve for the total molecular energy we obtain the following expression:

$$E_{mol} = \langle \Psi | \hat{H}_{mol} | \Psi \rangle = E_e + \frac{\hat{H}_N \psi_N(\mathbf{R})}{\psi_N(\mathbf{R})} \quad (18)$$

It must be noticed that in this derivation of the molecular energy expression, the action of the nuclear kinetic term \hat{T}_N on the electronic part of the wavefunction vanishes due to the BO approximation. This is because \hat{T}_N is an operator that applies differentiation with respect to the nuclear coordinates \mathbf{R} and our electronic wavefunction treats \mathbf{R} as a parameter that remains fixed⁵. Knowing this, the nuclear Schrödinger equation can be written:

$$\overbrace{\left(\hat{T}_N(\mathbf{R}) + V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) \right)}^{\hat{T}_N(\mathbf{R}) + U(\mathbf{R})} \psi_N(\mathbf{R}) = E_{mol} \psi_N(\mathbf{R}) \quad ; \quad U(\mathbf{R}) = V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) \quad (19)$$

The new term $U(\mathbf{R})$ is known as the internuclear potential for a given \mathbf{R} [28]. This internuclear potential can be expressed in Hamiltonian form as [30]:

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN} \quad ; \quad V_{NN} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \quad (20)$$

where this time the Hamiltonian is expressed in terms of one-electron and two-electron operators, ($\hat{h}(i)$ and $\hat{g}(i, j)$ respectively). The one-electron operator will contain the kinetic term of the electron and the electron-nucleus interaction. The two-electron operator represents the electron-electron repulsion interaction term. Even though the nuclear kinetic term is neglected, the BO approximation still takes in to account the variation in the position of the nuclei when determining the electronic energy. This contribution comes from the V_{NN} term in equation 20.

3.1.1 One-Electron Operator

The form of the Hamiltonian in the BO approximation can vary depending on the type of one-electron operator chosen for the calculation. In the non-relativistic framework the one-electron operator is a one component (1c) scalar. On the other hand, in the relativistic regime the expression for the energy of a relativistic free particle gives both positive and negative energy solutions [31], implying the existence of both particles and antiparticle [32]. This results in the one-electron operator becoming a four component (4c) operator describing both particle and antiparticle with their corresponding spins included.

The 4c Hamiltonian can be computationally too heavy for big systems containing several electrons. The antiparticle part of the Hamiltonian can be frozen in order to obtain a two component Hamiltonian (2c), where the spin-orbit interaction between the spin of the electron and the magnetic field originating from the nuclear motion in the electrons frame is well described. Nonetheless, the 4c operator will still give the most accurate results for relativistic effects. In order to reduce computational costs, new types of Hamiltonian like the exact two component Hamiltonian (X2c)⁶ have been developed. The DIRAC program will always work with 4c operators [33].

In equation 20 the one-electron operator is split in to a relativistic free-electron Dirac Hamiltonian $\hat{h}^{(0)}$ and an electric potential V_{eN} addressing the electron-nucleus interaction [33]:

$$\hat{h}_D = \hat{h}^{(0)} + V_{eN} = \beta m c^2 + c(\boldsymbol{\alpha} \cdot \hat{\mathbf{p}}) + V_{eN} \quad (21)$$

In the non-relativistic case the free-electron Hamiltonian only contains a kinetic term but in the relativistic regime a mass term is added aswell. In general \hat{h}_D is the Dirac-Hamiltonian in a bare nuclear field [30].

⁵Differentiation with respect to a constant always yields zero so in this case $\nabla_N^2(\mathbf{R})\psi_e(\mathbf{r}; \mathbf{R}) \approx 0$.

⁶This Hamiltonian yields the same results as the 4c Hamiltonian for for positive energy solutions[31]

3.1.2 Two-Electron Operator

For the non-relativistic case the two-electron operator $\hat{g}(i, j)$ has the form:

$$\hat{g}^{Coulomb}(i, j) = \frac{1}{r_{ij}} \quad (22)$$

When using this approximation one can notice that we obtain the previously mentioned Dirac-Coulomb Hamiltonian in equation 8 [31]. However, this means that the Dirac-Coulomb Hamiltonian is not fully relativistic as it considers the Coulomb interaction to be instantaneous. In order to obtain the full relativistic picture, the two-electron operator has to be modified so it includes magnetic interactions as well as retardation effects. In order to obtain the two-electron operator in the relativistic framework, a Taylor expansion around c^{-1} up to c^{-2} is performed [34]. The instantaneous Coulomb-interaction is then the zeroth-order term of the expansion and first-order correction to the overall Coulomb interaction is given by the Breit term [31]:

$$\hat{g}^{Breit}(i, j) = -\frac{c\alpha_i \cdot c\alpha_j}{2c^2 r_{ij}} - \frac{(c\alpha_i \cdot \mathbf{r}_{ij})(c\alpha_j \cdot \mathbf{r}_{ij})}{2c^2 r_{ij}^3} \quad (23)$$

The Breit term can be rearranged and split in to two terms, the Gaunt term and the gauge term [30]:

$$\hat{g}^{Breit}(i, j) = \hat{g}^{Gaunt}(i, j) + \hat{g}^{gauge}(i, j) = -\frac{c\alpha_i \cdot c\alpha_j}{c^2 r_{ij}} - \frac{(c\alpha_i \cdot \nabla_i)(c\alpha_j \cdot \nabla_j) r_{ij}}{2c^2} \quad (24)$$

So the expression for the total relativistic Coulomb interaction is give by:

$$\begin{aligned} \hat{g}(i, j) &= \hat{g}^{Coulomb}(i, j) + \hat{g}^{Breit}(i, j) \\ &= \hat{g}^{Coulomb}(i, j) + \hat{g}^{Gaunt}(i, j) + \hat{g}^{gauge}(i, j) \\ &= \frac{1_{4 \times 4}}{r_{ij}} - \frac{c\alpha_i \cdot c\alpha_j}{c^2 r_{ij}} - \frac{(c\alpha_i \cdot \nabla_i)(c\alpha_j \cdot \nabla_j) r_{ij}}{2c^2} \end{aligned} \quad (25)$$

where the overall expression consists of a charge-charge interaction $\hat{g}^{Coulomb}$, a current-current interaction \hat{g}^{Gaunt} and a gauge term \hat{g}^{gauge} [30, 31]. Even though the Coulomb term is in non-relativistic form, it describes also the spin-same orbit interaction. The Gaunt term describes the spin-other-orbit as well as orbit-orbit and spin-spin interactions. The gauge term contributes only to the spin-free (scalar) interaction and is usually less relevant. The Gaunt term is a magnetic interaction (spin) while the other terms represents retardation effects[34].

3.1.3 Further Relativistic Considerations

A feature of key importance is to include relativity when analyzing the electronic molecular structure of the system as electrons surrounding the nuclei can reach extremely fast speeds. The velocity of the electron will increase with heavier nuclei (larger atomic number Z) due to a stronger electric field being present. As it was previously said in the introduction, the enhancement factor W_d increases with atomic number. An estimate of this dependence is given by [35]:

$$W_d \approx -\frac{4}{3} \frac{Z^3 \alpha^2 \kappa}{\gamma^4} \quad (26)$$

we can see a cubic dependence on Z , which means heavy nuclei will be favorable for a large eEDM enhancement factor W_d . In this case γ is the Lorentz factor, $\alpha \approx \frac{1}{137}$ is the fine structure constant and κ is a constant that depends on the electronic structure.

3.2 Molecular Orbital Theory

Molecular Orbital theory (MO) is the most popular method used for the description of the electronic structure of molecules. Unlike Valence bond theory, in MO electrons are not assigned to an individual chemical bond in the molecule. Instead, each electron is influenced by all atomic nuclei in the molecule in varying degrees. Molecular orbitals are constructed as a linear combination of all atomic orbitals forming the molecule (LCAO-MO) [29]:

$$\psi = \sum_A^N c_A \Phi_A \quad (27)$$

where ψ is the molecular orbital, ϕ is the atomic orbital and c_A is the linear coefficient assigned to the atomic orbital ϕ_A .

3.2.1 Basis Sets

In order to describe this molecular orbitals first the atomic orbitals have to be specified. The general expression for an atomic orbital is give by the expression:

$$\Phi_{nlm}(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi) \quad (28)$$

where the atomic orbital is divided in two parts, the radial part $R_n(r)$ and the angular part $Y_{lm}(\theta, \phi)$. The radial part can be described by basis functions, the combination of these basis functions will form a basis set. Basis functions can be divided in two types, Slater type orbitals (STO) and Gaussian type orbitals (GTO) [36]:

$$\Phi_{abc}^{STO}(x, y, z) = Nx^a y^b z^c e^{-\zeta r}, \quad \Phi_{abc}^{GTO}(x, y, z) = Nx^a y^b z^c e^{-\zeta r^2} \quad (29)$$

they are given in Cartesian coordinates. N is a normalization constant and a, b, c control angular momentum ($L = a + b + c$). The parameter ζ controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function) [36] and at last $r = \sqrt{x^2 + y^2 + z^2}$. The use of L for the specification of the angular momentum instead of spherical harmonics is justified because using spherical harmonics is in computational terms too complicated. Both STO and GTO have similar form, only differing in the argument of the exponent. The STO gives a more accurate description of the actual orbital than the GTO but it is computationally more demanding. A solution to this problem is to use a linear combination of GTOs to emulate the behaviour of an STO. This technique will be less computationally heavy and it will give a good approximation of the STO. This linear combination of GTOs is defined as a contracted Gaussian type orbital (CGTO), where the terms in the linear combination are now called primitive Gaussian type orbitals (PGTO):

$$\Phi_{abc}^{CGTO} = N \sum_{j=1}^K c_j x^a y^b z^c e^{-\zeta_j r^2} \quad (30)$$

where K is the number of PGTOs per CGTO. A combination of n PGTOs used to mimic an STO is called "STO-nG". The larger the number of PGTO, the more it will resemble the actual STO. In figure 1 the quality of the STO-nG functions is shown for varying n , it is clear that a larger number of PGTO in a CGTO will give a more precise description of the STO

If only one basis function (STO, GTO or CGTO) is used in the description of each atomic orbital then the basis set is called a minimal basis set. When two basis functions are used for the atomic orbital then it is called a double zeta (Dz) basis sets and three basis functions per atomic orbital is a triple zeta (Tz) basis set. This can be extrapolated to a larger number of basis set (quadruple, quintuple etc.). The number of basis functions used per orbital gives the cardinality of the basis set. A larger basis set increases both the accuracy and the computational cost of the calculation. For an infinite number of basis functions per atomic orbital, the basis set is said to be a complete basis set (CBS).

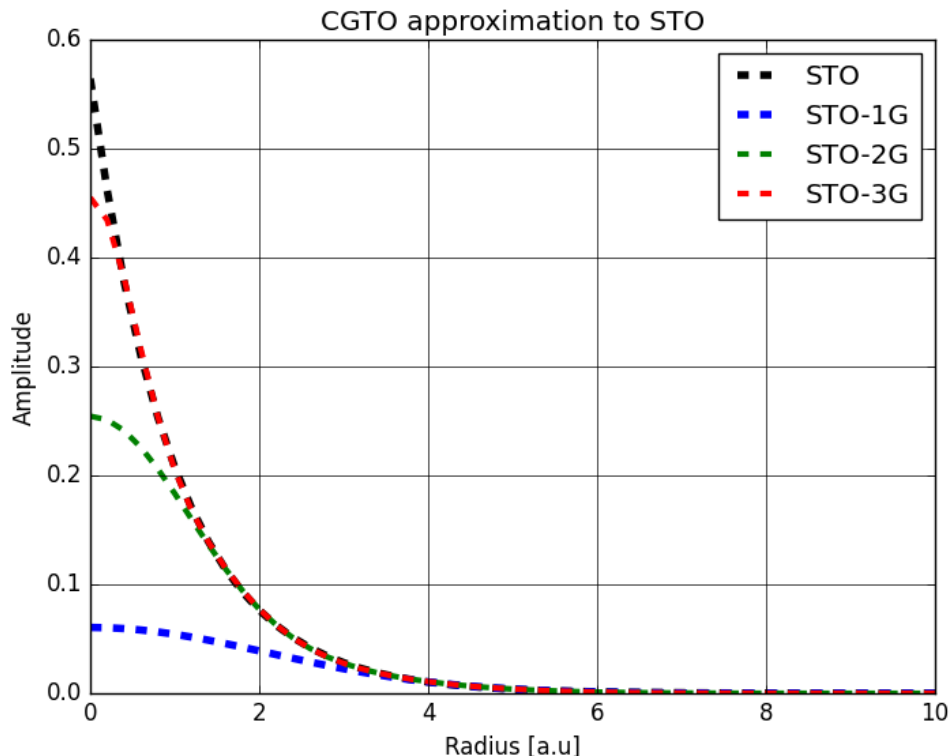


Figure 1: Comparison of the quality of the STO obtained from CGTO at the STO-1G, STO-2G, STO-3G level. The equation used for the CGTOs is given in radial form instead of using the Cartesian format given in equation 30. The values for the coefficients c_j and the parameters ζ are given in [37].

Other variations of basis sets can be used like split valence basis sets (vXz) which use a minimal basis for core orbitals and a larger basis for valence orbitals [36]. In this basis sets the X specifies the cardinality of the basis.

Depending on the system being studied, either tight or diffuse basis functions can be used in order to get a more accurate description. Tight functions have high values for ζ and they describe with high accuracy the behaviour of the orbital near the origin. On the other hand diffuse functions have a low ζ and they decay less rapidly than tight ones. This types of functions increase the quality of the description of the atomic orbital near the outer regions. They are usually used in systems were an electron is held far away from the nucleus like anions⁷.

3.2.2 Dyall Basis Sets

The types of basis sets discussed in the previous section were designed to give good results and convergence for HF methods but they are not suitable for post-Hartree-Fock calculation where electron correlation is taken in to account [36]. In order to solve this problem, Dunning developed the correlation consistent basis sets which are labelled cc-pVXZ. The "cc-" in front stands for correlation consistent and the letter p stands for the addition of polarization functions.

Polarization functions address the behaviour of an atomic orbital when another atom is approaching. The electric field of an approaching atom can cause a shift on the electron density of the other atom. If for example an s orbital is approached by an atom that repels electrons, the electron density in the

⁷Anions are negatively charged ions.

symmetric s orbital will move away from the approaching atom. The final electron density will resemble more the shape of a p orbital than of an s orbital, making it look polarized. This is what polarization functions do, they add higher order angular momentum functions to the already existing ones in order to take in to account electron correlation and polarization.

In the DIRAC program there is a wide variety of GTOs available for use, where the main ones are the ones developed by Dyall and coworkers. This type of basis sets follow the correlation consistent methodology introduced by Dunning. Dyall basis sets include electron correlation functions for valence, outer core and inner core orbitals. They add as well diffuse functions [38] for s, p and d block elements [33]. The main characteristic of the Dyall basis sets is that they are designed to be suitable for relativistic calculations.

The relativistic Hamiltonian 21 is a four component Hamiltonian that requires a four component spinor on which to act. This four component spinor is normally represented as two component object:

$$\Psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \quad (31)$$

where each of the components is a two component object itself. The values ψ^L and ψ^S are the large and small components of the four component spinor respectively. The large component would stand for the positive energy solutions and the small component for the negative energy solutions. This components can be expressed in terms of each other and for an electron in a hydrogen like atom the small component can be expressed in terms of the large component as follows [39]:

$$\psi^S = (2mc^2 + \epsilon - V)^{-1} c\sigma\hat{p}\psi^L \quad (32)$$

where V is the potential, ϵ the eigenvalue and \hat{p} is the momentum. Any basis set used to resolve the four component Dirac Hamiltonian must satisfy this coupling for the coupling between small and large component. When this coupling is taken to the non-relativistic limit for positive energy orbitals then we obtain what is called as kinetic balance [33]. This means that the small and big components of the basis sets must satisfy the following relation [39]:

$$\chi^S = \frac{1}{2mc} \sigma\hat{p}\chi^L \quad (33)$$

3.3 Computational Methods

3.3.1 Hartree-Fock

Hartree-Fock (HF) theory posits that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons, instead every electron sees all the other electrons as a average charge distribution with which it can interact. This method is a type of variational method⁸ and derives a set of N-coupled equations for the N spin orbitals. A solution to these equations will yield the HF wave function and energy of the system. The following derivation for HF theory will be based on the notes provided by David Sherrill [40], the Hartree atomic units ($\hbar = e = a_0 = me = 1$) will be used in the following sections. The goal of this method is to solve the electronic Schrödinger equation that results from the time-independent Schrödinger equation (non-relativistic case) after invoking the BO approximation:

$$\hat{H}_{el}^{NR}|\Psi(\mathbf{r}, \mathbf{R})\rangle = \left[-\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_{A,i}^{N,n} \frac{Z_A}{r_{Ai}} + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}^n \frac{1}{r_{ij}} \right] |\Psi(\mathbf{r}, \mathbf{R})\rangle = E_{el}|\Psi(\mathbf{r}, \mathbf{R})\rangle \quad (34)$$

⁸Variational methods are based on the variational principle which states that if an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy. It implies that, if the coefficients in the trial wavefunction are varied until the lowest energy is obtained, then those coefficients will be the best for that particular form of trial function [29].

where $|\Psi(\mathbf{r}, \mathbf{R})\rangle$ is the electronic wave function depending on the electronic and nuclear coordinates (\mathbf{r} and \mathbf{R} respectively). Furthermore, N is the total number of nuclei, n is the total number of electrons, Z_X is the atomic number of nuclei X , r_{Ai} is the distance between nuclei A and electron i , r_{ij} is distance between electrons i and j and at last R_{AB} is the distance between nuclei A and B . Another way of expressing this equation is in term of kinetic and potential terms:

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \right] |\Psi(\mathbf{r}, \mathbf{R})\rangle = E_{el} |\Psi(\mathbf{r}, \mathbf{R})\rangle \quad (35)$$

As we are making use of the BO approximation, it is possible to rewrite equation 34 in terms of one and two electron operators like in equation 20:

$$\hat{H}_{el}^{NR} = \sum_i^n \hat{h}(i) + \frac{1}{2} \sum_{i<j}^n \hat{g}(i, j) + V_{NN} \quad (36)$$

where the one-electron operator has the form:

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A^N \frac{Z_A}{r_{Ai}} \quad (37)$$

In this case the one-electron operator does not have a mass term like equation 21 and the two-electron operator does not contain any of the Breit terms. This is due to the fact that we are treating the BO approximation in the non-relativistic case for this derivation.

In the HF method, a first approximation to the wavefunction is done by assuming that the electrons in the system do not interact with each other. In this case the overall wavefunction can be separated and treated as the product of all spin-orbitals involved in the system:

$$\Psi_{HF}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) \dots \chi_n(\mathbf{x}_n) \quad (38)$$

this type of wavefunction is the Hartree product. The spin-orbital for electron i is $\chi_i(\mathbf{x}_i)$ and is dependent on \mathbf{x} which is the set of spin-space coordinates with the form $\mathbf{x} = \{\mathbf{r}, w\}$. The spin-space coordinates are formed from combining spatial coordinates \mathbf{r} with generic spin coordinates w ($w = \alpha$ for spin up and $w = \beta$ for spin down). So the spin-orbitals usually can be expressed as a product of a spatial orbital with a spin function, $\chi(\mathbf{x}) = \phi(\mathbf{r})\alpha(w)$.

This type of wavefunction does not satisfy *Pauli's antisymmetry principle* which states that a wavefunction describing fermions should be antisymmetric when interchanging any set of space-spin coordinates [41]. This shortcoming can be solved by using the linear combination of spin-orbitals given by the Slater determinant. For n spin-orbitals the Slater determinant has the form:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_n(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_n) & \chi_2(\mathbf{x}_n) & \dots & \chi_n(\mathbf{x}_n) \end{vmatrix} = |12\dots n\rangle \quad (39)$$

Now that the form for the Hamiltonian and of the wavefunction are known, the total energy of the system can be found by:

$$E_{HF} = \langle \Psi | \hat{H}_{el}^{NR} | \Psi \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} ([ii|jj] - [ij|ji]) \quad (40)$$

where the term in angle brackets is the one-electron integral:

$$\langle i | \hat{h} | i \rangle = \int \chi_i^*(\mathbf{x}_1) \hat{h}(i) \chi_i(\mathbf{x}_1) d\mathbf{x}_1 \quad (41)$$

and the term in square brackets is the two-electron integral:

$$[ij|kl] = \int \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{ij}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2 \quad (42)$$

The HF method assumes that the wavefunction can be approximated by a single Slater determinant made up of one spin orbital per electron. Now the goal is to minimize the Hartree-Fock energy expression with respect to changes in the orbitals $\chi_i \rightarrow \chi_i + \delta\chi_i$. The spin-orbitals are assumed to be orthonormal ($\langle i|j \rangle = \delta_{ij}$) and the variational procedure should also leave them orthonormal. This can be accomplished by Lagrange's method of undetermined multipliers. The end result is the HF equation:

$$\left[\hat{h}(\mathbf{x}_1) + \sum_{j \neq i}^n [\mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)] \right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \quad (43)$$

from this equation we obtain the energy eigenvalues ϵ_i for the spin orbital i . The two new terms introduced are the Coulomb operator \mathcal{J}_j and the exchange operator \mathcal{K}_j . The Coulomb operator gives the average local potential at point \mathbf{x}_1 due to the charge distribution at \mathbf{x}_2 from the electron in orbital j :

$$\mathcal{J}_j(\mathbf{x}_1) = \int \frac{|\chi_j(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_2 \quad (44)$$

The exchange operator does not have a simple classical analog like the Coulomb operator and it is the result from the antisymmetry requirement of the wavefunction. It exchanges spin orbitals χ_i and χ_j , it can be defined by its action on an arbitrary spin orbital χ_i :

$$\mathcal{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \left[\int \frac{\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \chi_j(\mathbf{x}_1) \quad (45)$$

In equation 43 the action on the spin-orbital χ_i can be treated as a single *Fock operator*:

$$\hat{f}(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1), \quad \hat{f}(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_j^n [\mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)] \quad (46)$$

The solutions to these equations are found by guessing an initial trial orbital wavefunction, calculating the Fock operator. Solving the HF equation then results in a new orbital wavefunctions. Next, these new orbitals are used for further calculations and this process is repeated until reaching convergence. This iterative procedure is called a self-consistent-field (SCF) approach.

3.3.2 Restricted and Unrestricted Hartree-Fock

The HF method derived above assumes that the spatial part of the spin orbital is the same for both spin up α and spin down β . This assumption follows from the fact that only orbitals which are fully occupied by two electrons are allowed. This is because having an equal amount of spin up and spin down electrons guarantees that the interaction between electrons of equal spin is equal for both spin up and spin down. This case for fully occupied orbitals is called the restricted Hartree-Fock (RHF).

In the case of having a system consisting of an unequal number of spin up and spin down orbitals, the spatial part of their spin-orbitals should be different. This gives a pair of coupled equations, this method is called the spin unrestricted Hartree-Fock (UHF).

3.3.3 Dirac-Hartree-Fock

The whole procedure discussed in the previous section was done under the non-relativistic framework. The one-electron operator only contains a kinetic term and no mass terms are added. If the HF procedure is done taking relativity in to account, then the free electron Dirac Hamiltonian is used as the one-electron operator. In this case the method is called the Dirac-Hartree-Fock (DHF) method.

3.3.4 Electron Correlation Methods

The HF method generates solutions to the Schrodinger equation where the actual electron–electron interaction is replaced by an average mean field interaction. In a large basis set, the HF wave function might be able to account for 99 percent of the total energy, but the remaining 1 percent is still very important for describing chemical phenomena [34]. The difference in energy between the HF and the lowest possible energy in the given basis set is called the Electron Correlation (EC) energy. This EC energy arises from Coulomb correlation interactions and Fermi correlation interactions. The first one correlates electrons with opposite spin and the second one electrons with the same spin. The Coulomb correlation will occur more frequently as it is present for both the electrons in the same orbital and for electrons in different orbitals.

In HF methods only one single Slater determinant is used where electrons in the same spin-orbital have a spatial overlap of one but with opposite spin. On the other hand for electrons in different spin-orbitals the spatial overlap will be zero [34]. This means that Coulomb correlation is fully ignored by the HF method because the wave function takes into account the interelectronic repulsion only in an average way [42]. This interaction may be better addressed by using dynamic correlation methods which address electron excitation.

3.3.5 Coupled Cluster

Coupled cluster (CC) is one of the most common use methods out of several post-Hartree–Fock ab initio quantum chemistry methods. The CC method is an approach that solves the problem of electron correlation that we encounter in HF theories [42]. In this section we will follow the derivation from A.A. Hasanein and M.W. Evans in [42]. The CC method is based on an exponential operator:

$$\Psi = e^{\hat{T}} \Phi_0 \quad (47)$$

which is added to the Slater determinant Φ_0 . The argument in the exponent \hat{T} is an operator that creates excitations from an independent particle model wave function Φ_0 . It can stand for either a closed shell (RHF) or open shell (UHF) single determinant formed out of molecular spin-orbitals. The operator \hat{T} is called the cluster operator and it has the following form:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n \quad (48)$$

where \hat{T}_1 is the one-particle excitation operator and \hat{T}_2 is the two-particle excitation operator. The letter n stands for the number of electrons in the molecule. The action of the first two operators is given by:

$$\hat{T}_1 \Phi_0 = \sum_{r,k} t_r^k D_r^k \quad ; \quad \hat{T}_2 \Phi_0 = \sum_{\substack{r>s \\ k>l}} t_{rs}^{kl} D_{rs}^{kl} \quad (49)$$

where the letters p, q, r, s... stand for the occupied orbitals and the letters i,j,k,l,...stands for the unoccupied virtual orbitals. The terms t_{rs}^{kl} ...etc, are the operator coefficients which give the amplitude of the transition. D_r^k is a singly excited determinant and D_{rs}^{kl} is a doubly excited determinant. The single excitation operator excites the electron from orbital r to the virtual orbital k as described by D . The equation for the rest of operators is similar to the the ones shown above, they are formed out of a linear combination of excited determinants. The maximum amount of excited electrons that can exist in the system is n so \hat{T}_n is the last operator available.

The term in exponential form in equation 47 can expanded through Taylor expansion to get:

$$\exp\{\hat{T}\} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \quad (50)$$

and equation 47 obtains the form:

$$\Psi = \left[1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \right] \Phi_0 \quad (51)$$

Now, equation 48 for the overall cluster operator is inserted in to equation 51 with the corresponding expression 49 for each operator of \hat{T} . Performing this operation would resemble the full CI calculation and it would give the exact wavefunction and correlation energy of the system [42]. Normally the full CI calculations are not carried out as they require a lot of computational cost. It is more common to truncate the expression for the cluster operator and only use the first couple of operators in equation 48. If only \hat{T}_1 and \hat{T}_2 are utilized, then it is called the CC singles and doubles (CCSD) method. When utilizing this method we use the following expression for the wavefunction:

$$\Psi = e^{\hat{T}} \Phi_0 = e^{(\hat{T}_1 + \hat{T}_2)} \Phi_0 = \left[1 + \hat{T}_1 + \hat{T}_2 + \frac{(\hat{T}_1 + \hat{T}_2)^2}{2!} \right] \Phi_0 \quad (52)$$

where we get double excitation determinants originating both by a two-particle excitation operator \hat{T}_2 and by the product of two consecutive one-particle operator $\frac{1}{2!} \hat{T}_1^2$. Although they both will give double excitation orbitals, the amplitude for the latter case will be given by a product of two separate coefficients $t_r^k t_s^l$ instead of a single amplitude coefficient t_{rs}^{kl} . The terms consisting of both one and two-particle excitation operators $\frac{1}{2!} \hat{T}_1 \hat{T}_2$ will resemble triple excitations. Ultimately, the square of the two-particle operator will address the case for quadruple excitations.

Although used extensively, the coupled cluster singles and doubles (CCSD) method is not sufficient when highly accurate results are required [43]. The CCSDT which includes the three-particle excitation operator \hat{T}_3 gives results in excellent agreement with those obtained with full CI, but the cost of CCSDT is high enough to severely restrict its application. A computationally cheaper approximation to CCSDT can be done by introducing a perturbative estimate of the connected triple excitations, this is done in methods such like CCSD(T) [44]. This method includes perturbations up to fifth order in the expansion of $\exp\{\hat{T}_1 + \hat{T}_3 + \hat{T}_3\}$. Other methods only introduce new perturbations up to fourth order like the CCSD+T [44]. All these CC methods guarantee size extensivity⁹ and size consistency¹⁰ but they are not variational like HF. [45].

3.3.6 Møller-Plesset Perturbation Theory

Møller-Plesset (MP) perturbation theory is another of the theories addressing the problem of electron correlation faced in HF methods. It is a perturbation method like CC but this time the perturbation is applied on the Hamiltonian. The basic idea behind perturbation theory is that if the description of a simple system is known, then a more complex version of this system can be treated mathematically as an altered (perturbed) version of the simple one [46]. This section is based on the derivation of C.J.Cramer [47]. In perturbation theory, the overall Hamiltonian is described as:

$$\hat{H} = \hat{H}^{(0)} + \lambda V \quad (53)$$

where we have an unperturbed Hamiltonian with a perturbing term V parameterized by λ . In MP the unperturbed Hamiltonian is taken as the sum of one-electron Fock operators:

$$\hat{H}^{(0)} = \sum_{i=1}^n \hat{f}_i \quad (54)$$

where n is the number of basis functions. The zeroth-order eigenvalue for the unperturbed Hamiltonian is given then by:

$$\hat{H}^{(0)} \Psi^{(0)} = \sum_i^{occ} \epsilon_i \Psi^{(0)} \quad (55)$$

⁹Means that the energy should grow linearly with the number of electrons in the system.

¹⁰Property that guarantees the consistency of the energy behaviour when the interaction between the involved molecular system is nullified.

where we are summing over the occupied orbitals and $\Psi^{(0)}$ is the HF wavefunction. The perturbation term V is given in the following expression as:

$$V = \sum_i^{\text{occ}} \sum_{i>j}^{\text{occ}} \frac{1}{r_{ij}} - \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left(\mathcal{J}_{ij} - \frac{1}{2} \mathcal{K}_{ij} \right) \quad (56)$$

where we are summing over MO orbitals instead of AO orbitals. Now we can compute the first-order correction to the zeroth-order energy by finding the expectation value, which will give the HF energy:

$$E^{(0)} + E^{(1)} = \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | V | \Psi^{(0)} \rangle = E_{HF} \quad (57)$$

If only the first-order correction is applied to the energy then the method is known as MP1. No electron correlation has been added until now. In order to account for it, it is necessary to compute the second order energy correction also which is given by:

$$E^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | V | \Psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_j^{(0)}} \quad (58)$$

If this expression for the second-order correction is further derived using the Condon–Slater rules and Brillouin’s theorem¹¹, then the final form for $E^{(2)}$ is:

$$E^{(2)} = \sum_i^{\text{occ}} \sum_{j>i}^{\text{occ}} \sum_a^{\text{vir}} \sum_{b>a}^{\text{vir}} \frac{[(ij|ab) - (ia|jb)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (59)$$

where in this case the indices a and b stand for virtual orbitals. Combining all this corrections in a sum we obtain the MP2 method. Additional energy correction can be added to the total energy, if energy corrections up to n -order are counted then the method is termed MP n . In the case of MP2 the final energy would be:

$$E_{MP2} = E^{(0)} + E^{(1)} + E^{(2)} \quad (60)$$

MP2 methods do not take a lot of computational time and can be efficiently evaluated. They scale with N^5 where N is the number of basis functions.

¹¹Integrals involving the singly excited determinants will all be zero [47].

4 Results

As it was mentioned in the introduction, the molecules of interest for eEDM searches must be polyatomic in order to overcome the limitations encountered with diatomics (not laser coolable). The molecule must contain a heavy atom with a high atomic number Z so relativistic enhancements can amplify the eEDM signal and it should also possess a dipole moment acting as a E_{eff} . The molecule must also contain an unpaired electron in its groundstate so it can interact with the E_{eff} .

In the literature most of the polyatomic molecules utilized consist of a heavy metal atom bonded to a OH ligand, other types of molecule like symmetric tops (CH_3 ligand) have been proposed as well. This types of molecular structures have been studied several times, varying the type of heavy atoms in them. Lanthanides and alkaline earth metals have been utilized as the heavy atom but no elements in the p-metal group of the periodic table have been used. This overlook of the p-metal group comes to our attention as there are promising candidates like Pb or Po that could give a high eEDM enhancement factor. That is why in this work the proposed molecules for study are PbOH and PoOH, they follow a similar structure to the literature consisting of an OH ligand but they contain at the same time new untested elements that could give interesting results. The chosen molecules have the previously mentioned qualities that are needed so in theory they should give good eEDM sensitivity.

4.1 Geometry Optimization

Before doing a proper calculation for W_d , it is crucial to have a sensible description of the geometry of the molecule. The molecules under study are linear triatomics with a bend geometry, a schematic of this types of molecules is shown in figure 2.

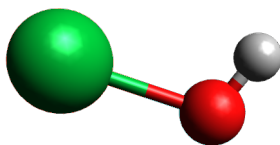


Figure 2: Schematic of the type of geometry that PoOH and PbOH possess. The nucleus in green corresponds to the heavy element (Pb or Po) and the other two atoms are the ligand OH. This image was created using the AVOGADRO software [48].

An accurate description of the bond lengths and bond angles must be found, this can be achieved by performing a geometry optimization. A geometry optimization works by using an initial geometry as an input to the program which then varies the bond lengths and angles until it finds the geometry with the lowest energy state. This process takes several iterations before it converges on one value.

As it was mentioned previously, all the calculations performed for the derivation of the molecular properties were carried out with the DIRAC19 program. The first guess for the geometry used as the input for the optimization was found in the literature for PoOH. For PbOH the geometry found in the literature [49] did not converge in the calculations so instead an alternative initial geometry was calculated.

For the alternative calculation of PbOH, first a optimization using the auto optimize tool in AVOGADRO was done. This optimization uses a default universal force field (UFF) to find the geometry [48]. This UFF geometry is then used as an input for a second geometry optimization, this time performed with the ORCA program. This ORCA calculation was carried out at the DFT level, using the functional form B3LYP and basis sets def2-TZVP. This DFT method uses similar math to the one found in HF but it

includes as well a certain amount of correlation energy through exchange correlation potential. This final geometry found in ORCA was then used as the input for the calculations in DIRAC.

On the other case, the geometry found in the literature for PoOH converged when being used as the initial input. This geometry found in the literature was also calculated using DFT methods and treated relativistic effects with RECP [50]. The initial geometries are shown in the table below:

Molecule	R_{M-O} [Å]	R_{O-H} [Å]	α [°]
PoOH [50]	2.0644	0.9610	106.89
PbOH	2.1119	0.9642	113.79

Table 1: Initial input geometries for the CCSD geometry optimization, bond lengths are given in Angstrom ($1\text{Å} = 1 \times 10^{-10}\text{m}$ [51]). Both calculations were done using the DFT, for PbOH the B3LYP functional was used and for PoOH the PBE0 functional was utilized instead

These initial geometries were further optimized using the CCSD method. Triple excitations (CCSD(T), CCSD-T, CCSD+T) were not utilized in this section in order to save computational time. For this calculations the basis sets were varied in cardinality, where Tz and Dz basis sets were used. In specific, the basis sets utilized in this work are the relativistic Dyall.v2z and Dyall.v3z basis sets. Calculations were also performed varying the type of Hamiltonian. A set of calculations was done using the relativistic 4c Hamiltonian and another with the X2c Hamiltonian. The non-relativistic 1c Hamiltonian was tested as well in order to see how important the effects of relativity are in this calculations. The results for PoOH are given in table 2:

Basis	Hamiltonian	R_{Po-O} [Å]	R_{O-H} [Å]	α [°]
Dyall.v2z	4c	2.156052	0.967499	105.904
Dyall.v2z	X2c	2.156044	0.967511	105.910
Dyall.v3z	4c	2.100646	0.958618	107.840
Dyall.v2z	1c	1.934903	1.000172	171.874

Table 2: Optimized geometry for PoOH at the CCSD level of theory. The space cut-off was set in an energy range of -30a.u to +30a.u, this corresponds to 61 correlated electrons.

The final geometries given by CCSD have longer bond lengths than the one that was initially used. Another interesting observation that comes to mind is the difference in bond length between the different basis sets used. Assuming that the Tz basis is more accurate, we can conclude that the Dz basis overestimates the bond lengths for both the Po-O and the O-H bonds. We can notice as well a slight difference in the bond angle, this time being underestimated in the Dz case.

In the case were the Hamiltonian was changed from 4c to X2c there appeared to be no significant differences, the bond lengths in both calculations agreed up to three decimal places. For the angle, the difference is again minimal and can be considered to be negligible. On the other hand for the 1c Hamiltonian we see that it clearly deviates from its relativistic counterparts. Bond lengths are altered when ignoring relativity, but more importantly is the effects this has on the bond angle. The bond angle increases drastically and it seems like the molecule is trying to reach a fully straight linear geometry.

The results for PbOH are given in table 3. For PbOH no measurements for with v3z have been performed and only the Hamiltonian has been varied.

Again we observe that the choice of relativistic Hamiltonian (4c or X2c) does not alter the values significantly like in the case of PoOH. For the 1c Hamiltonian we see again that the geometry changes severely. It is curious to see how for both PoOH and PbOH the bond angle increases considerably but the bond length between the p-metal and the oxygen atom decreases PoOH while for PbOH it increases. Apart

Basis	Hamiltonian	R_{Pb-O} [Å]	R_{O-H} [Å]	α [°]
Dyall.v2z	4c	2.112572	0.964580	113.764
Dyall.v2z	X2c	2.111954	0.964043	113.769
Dyall.v2z	1c	2.295624	1.116204	158.382

Table 3: Optimized geometry for PbOH at the CCSD level of theory. The space cut-off was set in an energy range of -30a.u to +30a.u, this corresponds to 61 correlated electrons.

from the non-relativistic case, the geometry of PbOH remains virtually the same in both the CCSD optimization and the original DFT optimization. It seems like PoOH is more sensitive to the change of computational method which might mean that PoOH is also affected more by how electron correlation is treated.

The geometry for the calculations of W_d will be chosen based on the accuracy of the method used to determine it. So for PoOH the geometry given by the CCSD calculation, using the Dyall.v3z basis and 4c Hamiltonian will be the one used. For PbOH, the geometry that will be used will be one determined with CCSD, a 4c Hamiltonian and Dyall.v2z basis sets.

4.2 Calculations for the Enhancement Factor W_d

As it was mentioned in the theory, in order to obtain a value for the enhancement factor W_d we have to compute the derivative or gradient of the energy of the molecule with respect to the applied field strength λ . So in order to find such gradient, the energy of the molecule is calculated when being exposed to different field strengths. This applied field strength will range from $-\lambda$ to λ , which means it will be reversed.

A correct order of magnitude for the field strength has to be found as well, because it is crucial to have a linear fit between the molecular energy and the field strength. If this is the case then we can approximate the derivative of the energy with respect to λ in the following way:

$$W_d = \left. \frac{1}{\Omega} \frac{dE_\Omega}{d\lambda} \right|_{\lambda=0} \approx \frac{1}{\Omega} \frac{E(\lambda) - E(-\lambda)}{2\lambda} \quad (61)$$

With a linear fit it is then possible to find the enhancement factor by determining the numerical gradient of the graph. In order to quantify the strength of the linear relationship between energy and λ , the correlation coefficient¹² r was computed for the calculated energies. The values for the correlation coefficients and of the gradient of the plotted energies were obtained using the stats.linregress command in Python from the Scipy package.

The optimal order of magnitude for the field strength was found to be of $\lambda \sim 10^{-8}$. The field strength at this value gave the best linear fits for the energy in terms of λ , an example of such a fit is shown in figure 3 for PbOH. The r value for such graph is nearly equal -1 so the requisite of having a linear dependence is satisfied¹³, the obtained linear fit is shown by the dashed line.

The molecular energies calculated in this paper will be given in atomic energy units¹⁴, the units of the actual effective electric field E_{eff} will be given GVcm^{-1} and the unit of W_d will be in $\text{h} \frac{e}{h} \frac{\text{Hz}}{\text{cm}}$ where e is the electron charge and h is the Planck constant¹⁵. In addition, a factor of 10^{24} will be added to the units of W_d in order to increase readability. Then the final expression relating the W_d and the numerical

¹²It varies from 1 to -1 depending if the relationship is negative or positive, if the r value is 0 then both variables are not correlated at all.

¹³The actual correlation coefficient of figure 3 is $r=-0.9999996707181451$

¹⁴1a.u. = $5.142\,206\,747\,63 \cdot 10^{11} \text{ V m}^{-1}$ [52].

¹⁵ $h = 4.135\,667\,696 \cdot 10^{15} \text{ Hz eV}^{-1}$ [53].

gradient of the graph is given as:

$$W_d \left[10^{24} \frac{e \text{ Hz}}{h \text{ cm}} \right] = \frac{5.14220674763}{4.135667696} \frac{1}{\Omega} \frac{E(\lambda) - E(-\lambda)}{2\lambda} = 1.24338006 \frac{1}{\Omega} \frac{E(\lambda) - E(-\lambda)}{2\lambda} \quad (62)$$

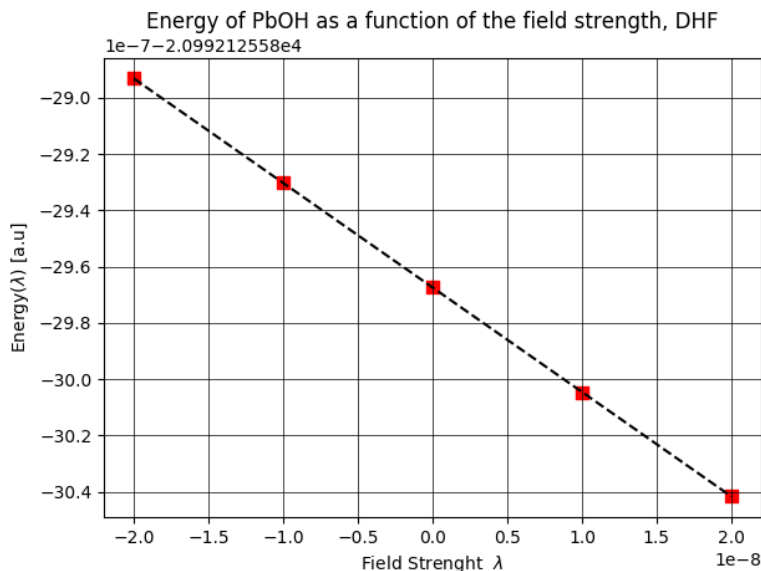


Figure 3: Graph showing the linear dependence of the molecular energy in terms of the field strength λ for PbOH. The energy is computed with DHF,4c Hamiltonian, Dyall.cv2z and an occupied and virtual space cut-off of ± 5 a.u.

4.3 Results for the Enhancement Factor W_d

In this section the results obtained for the enhancement factor of PbOH and PoOH will be shown. As it can be observed in the figure 3, the field strength λ was varied from -2×10^{-8} to 2×10^{-8} . These calculations of the energy were performed with the core-valence Dyall.cv2z basis sets. These basis sets are similar to the Dyall.v2z basis sets used in the geometry optimization but they add as well tight functions to the basis sets in order to improve the description of the AO near the nucleus and the core electrons [36]. These core-valence basis sets include the (n-2) shell for the s elements, the (n-1) shell for the p elements, the (n-1) shell for the d elements, and nothing extra for the f elements [33]. At last, in order to account for relativity the Hamiltonian used was the Dirac 4c-Hamiltonian.

The geometries used as the input for the calculations were the ones found in the previous section of the geometry optimization. Molecules were positioned with the M-O bond axis (M stands for the corresponding p-metal) pointing in the z-direction, parallel to the field strength in order to increase the eEDM signal.

Finally, the results shown in the calculation for PbOH were computed using DHF and MP2 methods. No results calculated using CCSD or CCSD with triple excitations will be shown for PbOH due to the fact that they gave extremely high values for E_{eff} which does not correspond at all with other similar molecules found in the literature. This inconsistency found in the CC method might be arising from the symmetry of the molecule and the multireference character of this one. On the other hand, for PoOH the CC methods gave reasonable results while DHF gave underestimated values for E_{eff} that were too low to take in to consideration. Table 4 and table 5 show the results obtained for E_{eff} and W_d corresponding to PoOH and PbOH respectively.

Mehtod	E_{eff} [GVcm ⁻¹]	W_d [$10^{24} \frac{e}{h} \frac{Hz}{cm}$]
MP2	8.882	4.295
CCSD	20.582	9.952
CCSD(T)	17.378	8.402
CCSD-T	17.668	8.542

Table 4: Effective electric field and the corresponding enhancement factor for PoOH. Calculations were done with Dyall.cv2z basis set, a 4c Hamiltonian and an occupied and virtual space cut-off of ± 5 a.u.

Mehtod	E_{eff} [GVcm ⁻¹]	W_d [$10^{24} \frac{e}{h} \frac{Hz}{cm}$]
MP2	18.678	9.031
DHF	19.087	9.229

Table 5: Effective electric field and the corresponding enhancement factor for PbOH. Calculations were done with Dyall.cv2z basis set, a 4c Hamiltonian and an occupied and virtual space cut-off of ± 5 a.u.

In table 5 we can see that for PbOH the enhancement factor W_d does not vary too much with the change of method as the MP2 value only differs by 2 per cent from the DHF value . On the other hand in table 4 PoOH seems to be more sensitive to the method as it is noticeable how the enhancement decreases drastically for MP2, being approximately half of the value calculated with CC methods. We can see as well that when triple excitations are added to CCSD, the enhancement factor decreases slightly with respect to CCSD by 16 per cent for CCSD(T) and by 14 percent for CCSD-T.

The final values recommended for W_d will be chosen taking in consideration the most accurate method used for the calculation. In the case of PbOH the chosen final value will be the one obtained with MP2 as it is the only method for PbOH that takes electron correlation in to consideration up to some degree. Now, for PoOH several methods that account for electron correlation where performed so deciding which one to chose requires more deliberation.

MP2 is based on perturbation theory, and these types o theories work best with small perturbations in order for the Taylor expansion to converge quickly [47]. The problem is that in MP2 the perturbation originates from the electron-electron repulsion which can be a large contributor to the total energy so the electron correlation given by this method is not expected to be very accurate [47]. That is why one of the CCSD methods with triple excitations must be chosen instead. The final value for W_d of PoOH will be the one calculated with CCSD(T), following the reasoning in [14]. The final values can be found in table 6:

Molecule	E_{eff} [GVcm ⁻¹]	W_d [$10^{24} \frac{e}{h} \frac{Hz}{cm}$]
PoOH	17.378	8.402
PbOH	18.678	9.031

Table 6: Final values for the effective electric field E_{eff} and enhancement W_d .

5 Discussion

5.1 Uncertainty

The values determined in this research have to be taken with a grain of salt. A big part missing in this study is the corresponding uncertainty analysis required for this values that were just determined. Due to the lack of time, no further calculations were carried out for W_d . If any future studies are carried for this molecules, a rigorous uncertainty analysis must be carried out in order to asses the values given in here.

The first source of uncertainty that may arise in this calculations corresponds to the low electron correlation that was taken in to account. The virtual and occupied space cut-off was of ± 5 a.u. which represents only 27 correlated electrons for both PbOH and PoOH. This space cut-off corresponds only to an electron correlation of 0.297 for PbOH and of 0.290 for PoOH¹⁶. It is recommended to perform a several calculations varying the electron correlation and as well with a full electron correlation. This way it will be possible to asses how this computational parameter affects the enhancement factor value. Due to a lack of time, only calculations with a certain type of electron correlation were performed.

A second source of uncertainty is the choice of basis set. In this study the basis sets were only varied for the geometry optimization. For the enhancement factor only v2z basis sets were used as they are computationally less demanding and take less time than the v3z basis. More calculations should be carried out with higher cardinality in the basis sets as a means to determine the effect of this computational parameter in the enhancement factor. Apart from the cardinality, it should also be studied what are the effects of adding diffuse and tight functions to the to the basis sets. In this work only cv2z basis sets were used for W_d , calculations should be carried out with no tight functions to see if the final values vary considerably with this change in the description of the orbitals.

The third computational parameter that needs to be considered is the treatment of relativity. In this paper relativity was accounted for by using the 4c Hamiltonian. Even though this is a good description of the system, it only accounts for the one-electron operator part of the overall total Hamiltonian. The two-electron operator still got a classical treatment. In this types calculations for the enhancement factor, relativity plays a crucial role as it enhances the eEDM signal. A better description of relativity could be obtained by implementing the Gaunt term in the 4c Hamiltonian. Other sources of uncertainty would still be present as one part of the Breit term is still missing, the gauge term. DIRAC has at the moment no way of implementing this gauge term so the Gaunt term must suffice at the moment.

The last source of uncertainty is the geometry of the molecule. Even though a geometry optimization was performed for both molecules, there still some uncertainty in the values found for the bond lengths and bond angles. A way of addressing how this uncertainty affects the final enhancement factor of the molecules could be done by varying slightly the bond angles and bond lengths when performing the W_d calculations. Seeing how changing the bond length and bond angles affects the final W_d value could give some insight on how reliable the values obtained are.

In addition to the sources of uncertainty listed above, an explanation for the drastic change of effective electric field when varying the method needs explanation. It was observed that the for PbOH, the E_{eff} increased drastically when it was calculated through CC methods. On the other hand for PoOH, CC methods gave reasonable results while DHF underestimated E_{eff} unlike PbOH. This behaviour of the molecules is unusual to say the least, as they are both similar molecules with nearly equal number of electrons in their heavy atom.

It should also be mentioned that in eEDM experiments the measured energy shift of the molecule is not only due to the eEDM. A second interaction known as the scalar-pseudoscalar interaction (S-PS) also contributes to the energy shift experienced by the molecule. In order to obtain an accurate magnitude for the eEDM, the effects of this S-PS interaction should also be determined by calculating its corresponding

¹⁶electron correlation given by $\frac{N_{correlated}}{N_{total}}$

enhancement factor W_s . Knowing both enhancement factors allows for disentanglement of the effects corresponding to the eEDM from the overall energy shift.

5.2 Comparison with the Literature

In order to know if the molecules chosen for study are promising candidates, they must be compared with the already studied molecules in the literature. In table 7 we can see the effective electric field E_{eff} for the molecules in this paper compared to some polyatomics with similar geometry found in the literature. The value for ThO (molecule used to determine the eEDM upper limit) is displayed as well

Molecule	E_{eff} [GVcm ⁻¹]
PoOH	17.378
PbOH	18.678
RaOH [24]	48.866
HgOH [20]	28.470
YbOH [14]	23.4
BaOH [14]	6.650
ThO [54]	84

Table 7: Effective electric field for different monohydroxide molecules found in the literature and for PoOH and PbOH

It must be taken in to account that the computational methods and considerations used for these molecules in these other works are different than the ones used in this paper.

At first glance the effective electric field or enhancement factor W_d of PoOH and PbOH is not very high compared to other tested molecules like HgOH which contains a similar number of electrons in its heavy atom. RaOH is another molecule that possesses a way higher enhancement factor than the tested molecules in this paper, which means that the molecules PbOH and PoOH may not be the most sensitive molecules towards the eEDM.

We can see as well that all these monohydroxide polyatomics found in the literature are less sensitive to the eEDM than the diatomic ThO, which almost doubles the E_{eff} of the most sensitive MOH molecule (RaOH) found in the literature. This does not mean that polyatomics are not suitable to eEDM searches, as they offer more advantages apart from their eEDM sensitivity, (Laser coolability). Other factors like practical limitations need to be taken in to account, all the values listed in the table above were determined with theoretical computational methods and no practical considerations of their actual experimental applicability were considered.

6 Conclusion

In this work the enhancement factor W_d for PbOH and PoOH was calculated using Hartree-Fock, coupled cluster methods and Møller-Plesset perturbation theory. Optimized geometries of the mentioned molecules were determined as well in the process at the CCSD level of theory. No triple excitations were added in this calculations in order to save computational time. Relativistic Dyall triple and double basis sets were utilized in the geometry optimization of the molecules as well.

For W_d only double zeta basis sets are utilized due to time limitations. The treatment of relativity was addressed by performing the calculations with a 4c Dirac Hamiltonian. In all calculations core orbitals were frozen and the maximum electron correlation treated in the paper was done at a space cut off of 30 a.u. of energy for the geometry optimization (correlating 61 electrons) and of 5 a.u. (correlating 27 electrons) for the enhancement factor calculations. For PoOH the final value was of $W_d = 8.402 \times 10^{24} \frac{e}{h} \frac{Hz}{cm}$, calculated using the CCSD(T). For PbOH the final value was $W_d = 9.031 \times 10^{24} \frac{e}{h} \frac{Hz}{cm}$ and it was determined using MP2 methods instead.

The values obtained lack of an uncertainty analysis which is required in order to do a proper assessment of the values obtained in this research. Further calculations varying the electron correlation, type of basis set, treatment of relativity and molecular geometry are required. Calculation of the scalar-pseudoscalar enhancement factor W_s is required as well, as this interaction plays also a role in the energy shift of the molecule in eEDM experiments.

The final values for the PbOH and PoOH for the enhancement factor do not seem to be specially high in comparison to other monohydroxide molecules found in the literature. Still, further computations for PbOH and PoOH are suggested to be carried with a higher level of theory and with higher electron correlation. As well, the Gaunt term should be taken in to consideration in order to evaluate more precisely the effects of relativity on W_d .

7 Acknowledgements

I would like to thank first of all my supervisor Anastasia Borschevsky for giving me the opportunity of working on such an interesting project and also for helping me with the theoretical aspects of the study which I did not fully grasp. This thesis also allowed me to learn about many different topics that were previously unknown to me and that now allow me to have a better understanding of many aspects studied during my bachelors . Next I would like to thank Lukáš Félix Pašteka for the help given with the computational aspect of the thesis and for answering all my emails with questions regarding to the DIRAC program and the Habrok cluster. I would also like to thank Yuly A. Chamorro Mena for helping with the enhancement factor calculations and for checking if the calculations were carried out in the correct way. At last, the bachelor thesis by J. D. Polet [55] has been a very helpful source of guidance and has given me an idea on how to proceed with the research carried out in this field.

8 References

- [1] B. Allanach, “Beyond the standard model lectures,” *arXiv preprint arXiv:1609.02015*, 2016.
- [2] J. D. Lykken, “Beyond the standard model,” *arXiv preprint arXiv:1005.1676*, 2010.
- [3] A. S. Cornell, “Some theories beyond the standard model,” in *Journal of Physics: Conference Series*, vol. 645, no. 1. IOP Publishing, 2015, p. 012002.
- [4] H. Greaves and T. Thomas, “On the cpt theorem,” *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics*, vol. 45, pp. 46–65, 2014.
- [5] W. B. Cairncross and J. Ye, “Atoms and molecules in the search for time-reversal symmetry violation,” *Nature Reviews Physics*, vol. 1, no. 8, pp. 510–521, 2019.
- [6] M. Pospelov and A. Ritz, “Electric dipole moments as probes of new physics,” *Annals of physics*, vol. 318, no. 1, pp. 119–169, 2005.
- [7] Van-Swinderen-Institute, “electron-edm,” <https://www-rug-nl.proxy-ub.rug.nl/research/vsi/newtopics/edm?lang=en>, (Accessed 28 May 2021).
- [8] M. Safronova, D. Budker, D. DeMille, D. F. J. Kimball, A. Derevianko, and C. W. Clark, “Search for new physics with atoms and molecules,” *Reviews of Modern Physics*, vol. 90, no. 2, p. 025008, 2018.
- [9] B. L. Augenbraun, “Methods for direct laser cooling of polyatomic molecules,” Ph.D. dissertation, Harvard University, 2021.
- [10] J. J. Hudson, D. M. Kara, I. Smallman, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, “Improved measurement of the shape of the electron,” *Nature*, vol. 473, no. 7348, pp. 493–496, 2011.
- [11] W. B. Cairncross, D. N. Gresh, M. Grau, K. C. Cossel, T. S. Roussy, Y. Ni, Y. Zhou, J. Ye, and E. A. Cornell, “Precision measurement of the electron’s electric dipole moment using trapped molecular ions,” *Physical review letters*, vol. 119, no. 15, p. 153001, 2017.
- [12] N. eEDM collaboration, P. Aggarwal, H. L. Bethlem, A. Borschevsky, M. Denis, K. Esajas, P. A. Haase, Y. Hao, S. Hoekstra, K. Jungmann *et al.*, “Measuring the electric dipole moment of the electron in baf,” *The European Physical Journal D*, vol. 72, pp. 1–10, 2018.
- [13] D. V Andreev, “Improved limit on the electric dipole moment of the electron,” *Nature*, vol. 562, no. 7727, 2018.
- [14] M. Denis, P. A. Haase, R. G. Timmermans, E. Eliav, N. R. Hutzler, and A. Borschevsky, “Enhancement factor for the electric dipole moment of the electron in the baoh and yboh molecules,” *Physical Review A*, vol. 99, no. 4, p. 042512, 2019.
- [15] S. Eckel, P. Hamilton, E. Kirilov, H. Smith, and D. DeMille, “Search for the electron electric dipole moment using ω -doublet levels in pbo,” *Physical Review A*, vol. 87, no. 5, p. 052130, 2013.
- [16] B. L. Augenbraun, L. Anderegg, C. Hallas, Z. D. Lasner, N. B. Vilas, and J. M. Doyle, “Direct laser cooling of polyatomic molecules,” *arXiv preprint arXiv:2302.10161*, 2023.
- [17] I. Kozyryev and N. R. Hutzler, “Precision measurement of time-reversal symmetry violation with laser-cooled polyatomic molecules,” *Physical review letters*, vol. 119, no. 13, p. 133002, 2017.
- [18] V. Prasanna, N. Shitara, A. Sakurai, M. Abe, and B. Das, “Enhanced sensitivity of the electron electric dipole moment from yboh: The role of theory,” *Physical Review A*, vol. 99, no. 6, p. 062502, 2019.
- [19] A. Petrov and A. Zakharova, “Sensitivity of the yboh molecule to p t-odd effects in an external electric field,” *Physical Review A*, vol. 105, no. 5, p. L050801, 2022.

- [20] R. Mitra, V. S. Prasanna, B. K. Sahoo, N. R. Hutzler, M. Abe, and B. P. Das, “Study of hgho to assess its suitability for electron electric dipole moment searches,” *Atoms*, vol. 9, no. 1, p. 7, 2021.
- [21] C. Zhang, X. Zheng, and L. Cheng, “Calculations of time-reversal-symmetry-violation sensitivity parameters based on analytic relativistic coupled-cluster gradient theory,” *Physical Review A*, vol. 104, no. 1, p. 012814, 2021.
- [22] A. V. Oleynichenko, L. V. Skripnikov, A. V. Zaitsevskii, and V. V. Flambaum, “Laser-coolable acoh⁺ ion for cp-violation searches,” *Physical Review A*, vol. 105, no. 2, p. 022825, 2022.
- [23] Y. Chamorro, A. Borschevsky, E. Eliav, N. R. Hutzler, S. Hoekstra, and L. F. Pašteka, “Molecular enhancement factors for the p, t-violating electric dipole moment of the electron in bach 3 and ybch 3 symmetric top molecules,” *Physical Review A*, vol. 106, no. 5, p. 052811, 2022.
- [24] A. Zakharova, “Rotating and vibrating symmetric-top molecule raoch 3 in fundamental p, t-violation searches,” *Physical Review A*, vol. 105, no. 3, p. 032811, 2022.
- [25] A.-M. Mårtensson-Pendrill and P. Öster, “Calculations of atomic electric dipole moments,” *Physica Scripta*, vol. 36, no. 3, p. 444, 1987.
- [26] E. Lindroth, B. Lynn, and P. Sandars, “Order α^2 theory of the atomic electric dipole moment due to an electric dipole moment on the electron,” *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 22, no. 4, p. 559, 1989.
- [27] P. A. Haase, D. J. Doeglas, A. Boeschoten, E. Eliav, M. Iliaš, P. Aggarwal, H. L. Bethlem, A. Borschevsky, K. Esajas, Y. Hao *et al.*, “Systematic study and uncertainty evaluation of p, t-odd molecular enhancement factors in baf,” *The Journal of Chemical Physics*, vol. 155, no. 3, p. 034309, 2021.
- [28] J. T. Oden, *An introduction to mathematical modeling: a course in mechanics*. John Wiley & Sons, 2011.
- [29] P. Atkins, P. W. Atkins, and J. de Paula, *Atkins’ physical chemistry*. Oxford university press, 2014.
- [30] W. Liu, “Ideas of relativistic quantum chemistry,” *Molecular Physics*, vol. 108, no. 13, pp. 1679–1706, 2010.
- [31] T. Saue, “Relativistic hamiltonians for chemistry: A primer,” *ChemPhysChem*, vol. 12, no. 17, pp. 3077–3094, 2011.
- [32] D. Tong, *Quantum Field Theory*. University of Cambridge Part III Mathematical Tripos, 2006, <https://www.damtp.cam.ac.uk/user/tong/qft/qft.pdf>.
- [33] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC19 (2019), written by A. S. P. Gomes, T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from I. A. Aucar, V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, B. Heimlich–Paris, T. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, J. M. H. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. di Remigio, K. Ruud, P. Sałek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (available at <http://dx.doi.org/10.5281/zenodo.3572669>, see also <http://www.diracprogram.org>).
- [34] F. Jensen, *Introduction to computational chemistry*. John wiley & sons, 2017.
- [35] K. Gaul, S. Marquardt, T. Isaev, and R. Berger, “Systematic study of relativistic and chemical enhancements of p, t-odd effects in polar diatomic radicals,” *Physical Review A*, vol. 99, no. 3, p. 032509, 2019.

- [36] C. D. Sherrill, "Basis sets in quantum chemistry," *School of Chemistry and Biochemistry, Georgia Institute of Technology*, 2017.
- [37] M. A. Mahmood, B. H. Adil, and K. H. Al Bayati, "33application of gaussian wave functions for 1s states in helium and helium like atoms," *Al-Nahrain Journal of Science*, vol. 16, no. 3, pp. 98–103, 2013.
- [38] T. Saue, R. Bast, A. S. P. Gomes, H. J. A. Jensen, L. Visscher, I. A. Aucar, R. Di Remigio, K. G. Dyall, E. Eliav, E. Fasshauer *et al.*, "The dirac code for relativistic molecular calculations," *The Journal of chemical physics*, vol. 152, no. 20, p. 204104, 2020.
- [39] J. Styszyński, "Atoms and molecules in relativistic quantum mechanics," in *Journal of Physics: Conference Series*, vol. 104, no. 1. IOP Publishing, 2008, p. 012025.
- [40] C. D. Sherrill, "An introduction to hartree-fock molecular orbital theory," *School of Chemistry and Biochemistry Georgia Institute of Technology*, 2000.
- [41] V. Magnasco, *Methods of molecular quantum mechanics: An introduction to electronic molecular structure*. John Wiley & Sons, 2009.
- [42] A. A. Hasanein and M. W. Evans, *Computational methods in quantum chemistry*. World Scientific, 1996, vol. 5.
- [43] J. F. Stanton, "Why ccSD (t) works: a different perspective," *Chemical Physics Letters*, vol. 281, no. 1-3, pp. 130–134, 1997.
- [44] L. Visscher, T. J. Lee, and K. G. Dyall, "Formulation and implementation of a relativistic unrestricted coupled-cluster method including noniterative connected triples," *The Journal of chemical physics*, vol. 105, no. 19, pp. 8769–8776, 1996.
- [45] I. N. Levine, D. H. Busch, and H. Shull, *Quantum chemistry*. Pearson Prentice Hall Upper Saddle River, NJ, 2009, vol. 6.
- [46] E. G. Lewars, "Computational chemistry," *Introduction to the theory and applications of molecular and quantum mechanics*, vol. 318, 2011.
- [47] C. J. Cramer, F. Bickelhaupt *et al.*, "Essentials of computational chemistry," *ANGEWANDTE CHEMIE-INTERNATIONAL EDITION IN ENGLISH-*, vol. 42, no. 4, pp. 381–381, 2003.
- [48] Avogadro Chemistry, "Avogadro." [Online]. Available: <http://avogadro.cc/>
- [49] A. T. Benjelloun, A. Daoudi, and H. Chermette, "Interaction of lead atom with atmospheric hydroxyl radical. an ab initio and density functional theory study of the resulting complexes pboh and hpbo," *The Journal of chemical physics*, vol. 121, no. 15, pp. 7207–7221, 2004.
- [50] A. Van Yperen-De Deyne, K. Rijpstra, M. Waroquier, V. Van Speybroeck, and S. Cottenier, "Binary and ternary po-containing molecules relevant for lbe cooled reactors at operating temperature," *Journal of Nuclear Materials*, vol. 458, pp. 288–295, 2015.
- [51] Wikipedia, "Angstrom," <https://es.wikipedia.org/wiki/%C3%81ngstrom>, (Accessed 9 June 2023).
- [52] C. Value, "Value: atomic unit of electric field." <https://physics.nist.gov/cgi-bin/cuu/Value?auelfd>, (2018).
- [53] —, "Value: Planck constant in eV/hz," <https://physics.nist.gov/cgi-bin/cuu/Value?hev>, (2018).
- [54] L. Skripnikov, A. Petrov, and A. Titov, "Communication: Theoretical study of the electron electric dipole moment search," *The Journal of chemical physics*, vol. 139, no. 22, 2013.
- [55] J. Polet, "High accuracy calculations of the eEDM enhancement factor w_d in ybcu, ybag & ybau," Ph.D. dissertation, 2022.