# Permanent electric dipole moment of diatomic molecules using relativistic extended-coupled-cluster method

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We employ the four-component relativistic extended-coupled-cluster (ECC) method to compute the permanent electric dipole moment (PDM) of a few open-shell diatomic molecules in their ground electronic state. The computed results are compared with the available results obtained from the experiments and two other coupled-cluster-based methods— Z-vector technique and linear expectation-value approach within the relativistic framework. The study reveals that the relativistic ECC method accurately predicts the PDM of the molecules under consideration and also are in good agreement with these two aforementioned correlated methods.

## I. INTRODUCTION

Single reference coupled-cluster (SRCC) method [1] incorporates dynamical electron-correlation in an efficient manner and thus has been accepted as the method of choice by the quantum chemistry community to evaluate energies and energy derivatives of many-electron systems. To include static correlation of electrons, multi-reference coupled-cluster (MRCC) methods can be chosen. Traditionally, coupled-cluster (CC) theory is known to be non-variational, however, many variational approaches of the theory have also been developed for evaluating energy and properties due to a few additional advantages in comparison to its non-variational traditional approach. Such a variational method, in particular, does have the upper-bound property of energy and satisfy the generalized Hellman-Feynman (GHF) theorem and $(2n+1)$-rule, which states that knowledge up to the $n$th-order amplitude-derivatives is sufficient for evaluating $(2n+1)$th-order energy-derivative. This means that variational approaches of CC theory could save enormous computational effort to calculate the higher-order properties. Unitary coupled-cluster (UCC), expectation-value coupled-cluster (XCC) and extended-coupled-cluster (ECC) approaches are three major variational forms of the CC theory found in literature. In recent times, a number of coupled-cluster-based methods have been extended to relativistic framework and these relativistic *ab initio* methods were used to compute energy and energy-derivatives of many-electron systems [2–18]. Molecular-frame electric dipole moment, also known as the permanent electric dipole moment (PDM), is an important first-order static property. The knowledge of PDM is necessary in the field of cold and ultracold chemistry and physics. The molecular electric dipole moment is useful in the study of long range anisotropic dipole-dipole interactions [19] and thus is important in the field of quantum phase transitions [20], quantum information processing [21], and quantum computing [22]. PDMs become significant in probing fundamental physics with ultracold molecules and in studies that strive to improve understanding of electrostatic bonding. Thus, experimental determination as well as accurate theoretical prediction of PDMs have been an area of cutting-edge research. Alkaline-earth metal halides and hydrides have drawn much attention recently due to their suitability as candidates for high-precision measurement, especially in search of electric dipole moment of the electron [23, 24]. In recent times, a number of studies have been reported on the computation of PDMs of these molecules using various electronic structure methods [25–28]. Relativistic coupled-cluster-based methods were also employed to accurately predict the PDMs of diatomic molecules and the effects of electron-correlation and relativistic motion of electrons in computing molecular PDMs were explored [13–18]. We, in this article, employ a variational many-body method— the relativistic extended-coupled-cluster method within singles and doubles approximation to compute the PDMs of a few moderately heavy alkaline-earth metal halides and hydrides. To examine its reliability for the purpose, the computed results are compared not only with the experimental values but also with results obtained from two other well-studied coupled-cluster-based methods.

The article is organized as follows. We review the theory of the calculated property and brief overview of the methodology in Section II. Computational details of the molecular calculations are presented in Section III followed by a discussion on the results of our study in Section IV. Finally, the concluding remarks of this study is included in Section V.

## II. THEORY AND METHODOLOGY

### A. Permanent dipole moment operator

The electron density is usually distributed unequally between the two nuclei of a heteronuclear diatomic molecule and eventually a finite permanent dipole moment can be observed in such a molecule. Within the Born-Oppenheimer approximation, the molecular PDM is a sum of electronic contribution and nuclear contribution. In such a case, the PDM operator $D$ can be defined as follows:

$$D = -\sum_j e\vec{r}_j + \sum_k Z_k e\vec{r}_k. \tag{1}$$

Where, $e$ is the charge of the electron, $Z_k$ is the atomic number of nucleus $k$, and $\vec{r}_{j(k)}$ is the position vector of $j^{th}$ electron ($k^{th}$ nucleus) from the origin. Thus, the PDM of a diatomic molecule for the electronic state$-$ $\Psi$ can be evaluated as follows:

$$\mu = \frac{\langle\Psi|D|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{2}$$

On the other hand, $\mu$ can also be computed as an energy-derivative. The total energy of a diatomic molecule in presence of an external, weak, static and homogeneous electric field of strength $\lambda$ can be expanded as a Taylor series as given below.

$$E(\lambda) = E^{(0)} + \left(\frac{dE}{d\lambda}\right)_{\lambda=0}\lambda + \frac{1}{2}\left(\frac{d^2E}{d\lambda^2}\right)_{\lambda=0}\lambda^2 + \dots. \tag{3}$$

Molecular dipole moment can be read from the first-order energy-derivative of the above equation as follows.

$$\mu = -\left(\frac{dE}{d\lambda}\right)_{\lambda=0}. \tag{4}$$

### B. Extended-coupled-cluster method

We herein describe the ground electronic state of the considered diatomic molecules by the fully relativistic CC singles and doubles (CCSD) wavefunction, i.e., $|\Psi_{cc}\rangle = e^T|\Phi_0\rangle$. Here $\Phi_0$ is the four-component Dirac-Hartree-Fock wavefunction and $T = T_1 + T_2$, is known as excitation operator which is defined as

$$T_m = \frac{1}{(m!)^2}\sum_{ij\dots ab\dots} t_{ij\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i, \tag{5}$$

where i,j(a,b) indices refer to the occupied (unoccupied) spinors. $t_{ij\dots}^{ab\dots}$ is the cluster amplitude corresponding to $T_m$.

The extended-coupled-cluster (ECC) method is a variational approach and the ECC functional of any operator of interest can be defined as

$$\langle A\rangle = \frac{\langle\Phi_0|e^{T'}Ae^T|\Phi_0\rangle}{\langle\Phi_0|e^{T'}e^T|\Phi_0\rangle}. \tag{6}$$

$T'$ and $T$ in the above equation are the hole-particle (h-p) destruction and creation operator, respectively. Arponen defined a new h-p destruction operator, $T''$ and showed that

$$\frac{\langle\Phi_0|e^{T'}e^T}{\langle\Phi_0|e^{T'}e^T|\Phi_0\rangle} = \langle\Phi_0|e^{T''}. \tag{7}$$

Now, one can write the ECC functional as

$$\langle A\rangle = \langle\Phi_0|e^{T''}e^{-T}Ae^T|\Phi_0\rangle = \langle\Phi_0|e^{T''}(Ae^T)_c|\Phi_0\rangle, \tag{8}$$

where, the subscript $c$ means that only the connected terms survive in the contraction between $A$ and $T$. Although $(Ae^T)_c$ leads to a terminating series, full contraction between a $T''$ with a $T$ vertex may lead to disconnected term in the amplitude equation. This problem can be avoided by following Arponen's recipe where two sets of amplitudes— $t$ and $s$ are defined and the functional is then written as

$$\langle A \rangle = \langle \Phi_0 | e^S (Ae^T)_L | \Phi_0 \rangle_{DL}. \tag{9}$$

Here, $L$ implies that the $T$ operators on the right side of $A$ are linked to the $A$ vertex and $DL$ means that a $S$ operator must be connected to either $A$ or at least two $T$ operators. The $S$ operator with amplitude $s$ can be defined as

$$S = \sum_{ab...ij...} s_{ab...}^{ij...} a_i^\dagger a_j^\dagger \ldots a_b a_a, \tag{10}$$

where a,b(i,j) indices refer to the occupied (unoccupied) spinors.

Now, in presence of an external electric field $O$ of strength $\lambda$, the field-dependent Hamiltonian can be written as

$$H(\lambda) = H + \lambda O, \tag{11}$$

where, $H$ is the field independent (i.e., zeroth order) Hamiltonian. In such a case, ECC functional can be read as

$$E(\lambda) = \langle \Phi_0 | e^{S(\lambda)} (H(\lambda) e^{T(\lambda)})_L | \Phi_0 \rangle_{DL}. \tag{12}$$

For evaluation of the first-order derivative of energy, the zeroth-order $m$-body cluster amplitudes are obtained by solving the following equations.

$$\frac{dE^{(0)}}{dt_m^{(0)}} = 0, \frac{dE^{(0)}}{ds_m^{(0)}} = 0. \tag{13}$$

Although the ECC functional is a terminating series, its natural truncation is computationally expensive due to the presence of very costly terms. We adopt the truncation scheme proposed by Vaval and co-workers [29] to avoid those computationally costly terms. Interested reader can see Refs. [30] for more details.

## III. COMPUTATIONAL DETAILS

We perform our calculations using a locally modified version of DIRAC10 [31, 32] interfaced with our in-house code [30]. We have solved the DHF equation using DIRAC10 program package and generated the one-body and two-body integrals along with the one-electron property integrals, which are used for correlation calculations. The finite-size nuclei modelled by the Gaussian charge distribution, and the default values of the nuclear parameters[33] in DIRAC10 are considered in the present study. Small basis are generated from the large basis using the restricted kinetic balance [34] condition. We remove the negative energy spectrum employing the "no virtual pair approximation" [35, 36]. We consider the metal of the corresponding diatomic molecule at the origin and use the experimental bond length in our calculation. We have correlated all the electrons in the molecular calculations, however, excluded the virtual spinors with energy higher than 500 a.u. The details of bond lengths, basis sets, spinors etc. are given in Table I.

TABLE I. Details of bond lengths, basis sets, virtual cutoffs and spinors used for the diatomic molecules

| Molecule | Bond Length (Å) | Basis Set | Virtual Spinors |
|---|---|---|---|
| CaH | 2.0025 [37] | Ca: Dyall.cv3z [39] H: cc-pCVTZ [40] | 241 |
| CaF | 1.967 [37] | Ca: Dyall.cv3z [39] F: cc-pCVTZ [40] | 303 |
| SrH | 2.1456 [37] | Sr: Dyall.cv3z [39] H: cc-pCVTZ [40] | 295 |
| SrF | 2.07537 [37, 38] | Sr: Dyall.cv3z [39] F: cc-pCVTZ [40] | 357 |

## IV. RESULTS AND DISCUSSION

We herein conduct a relativistic electronic structure study of a few open-shell diatomic molecules to compute molecular-frame dipole moment in their ground electronic configuration state. The aim of this work was to employ the four-component ECC method with singles and doubles approximation for high-precision prediction of PDM of CaH, CaF, SrH and SrF in their ground electronic state. Accordingly, we have calculated the PDMs of the said molecules at triple-zeta quality basis and computed values are compared with available experimental results (denoted as Expt.) in Table II. The units of PDM are expressed in Debye (D). In addition, the relative deviation of the computed results from the experimental values is expressed as

$$\delta\% = \frac{|\mu(Theory) - \mu(Expt.)|}{|\mu(Expt.)|} \times 100\% \tag{14}$$

and shown in Figure 1. From this figure and Table II, one can see that our results obtained with the ECC method have better agreement with experimental results than those of the DHF method. The DHF method incorporating relativistic effects of electrons excludes the effects of electron-correlation and usually results in lower accuracy. The electron-correlation missing out on the DHF level is considered in the ECC method and hence this correlated method yields improved PDM values closer to the experimental one. This shows the importance of electron correlation while calculating PDM. Thus, we can say that ECC can be a suitable method to estimate molecular-frame electric dipole moment of diatomics under consideration. It is noteworthy that Pal and co-workers [2, 3, 13] studied the PDMs of a number of open-shell diatomic molecules using fully relativistic coupled-cluster-based approaches such as Z-vector and linear expectation-value methods and also investigated the effects of basis set size, virtual spinors and hamiltonians on accurate prediction of PDM, which indicates that an increase in the basis set size and correlation space improves accuracy of the computed results. However, we have limited ourselves to calculate the desired molecular property at triple-zeta quality basis set with 500 a.u. as cutoffs for virtual spinors due to computational limitations and thus, there is a scope of improvement in accuracy of our results.
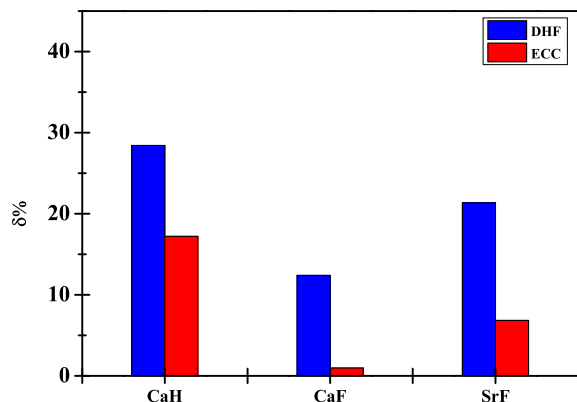


FIG. 1. Relative deviation ($\delta\%$) of computed PDM from experimental results

We further compute the PDMs of the said molecules with two different coupled-cluster-based methods: (a) Z-vector, an energy-derivative approach, and (b) linear expectation-value coupled-cluster (LECC), an expectation-value approach at the same basis set. We present these results in Table III and compare them with our results obtained with

ECC method. We have found that the ECC results are in good agreement with the other two coupled-cluster-based methods, however, the trend in the magnitude of PDMs of fluorides and that of hydrides are found to be different. In the case of hydrides, the PDM values computed by those methods increases as ECC < Z-vector < LECC, whereas the reverse trend is observed for the fluorides. Thus we can comment that the ECC method yields more accurate results of PDMs for CaF and SrF compared to the Z-vector and LECC methods at the considered basis. Das and coworkers [15] also reported PDMs for alkaline-earth metal monohydrides employing the LECC method, the finite-field coupled-cluster singles and doubles (FFCCSD) method and the FFCCSD with partial triples, i.e., FFCCSD(T) method at quadruple-zeta (QZ) basis set. It was observed in their work that inclusion of partial triples, i.e., higher correlation effects reduces the magnitude of PDM. Whatsoever, our results computed at TZ basis shows good agreement with theirs as well.

TABLE II. Molecular frame dipole moment (in Debye), $\mu$ of diatomic molecules

| Molecule | DHF | ECC | Expt. |
|---|---|---|---|
| CaH | 2.1045 | 2.4342 | 2.94(16) [41] |
| CaF | 2.6896 | 3.0403 | 3.07 [42] |
| SrH | 2.4788 | 2.9646 | — |
| SrF | 2.7279 | 3.2303 | 3.4676(10) [43] |

TABLE III. Comparison of ECC results with those of two CC-based methods, viz., Z-vector and LECC methods

| Molecule | $\mu$ (Debye) | | |
|---|---|---|---|
| | ECC | Z-vector | LECC |
| CaH | 2.4342 | 2.4463 | 2.4488 |
| CaF | 3.0403 | 3.0143 | 2.9667 |
| SrH | 2.9646 | 2.9813 | 2.9933 |
| SrF | 3.2303 | 3.2113 | 3.1739 |

## V.   CONCLUSION

We have employed the fully relativistic extended-coupled-cluster (ECC) method within the singles and doubles approximation to predict the permanent electric dipole moments (a first-order molecular property) of CaH, CaF, SrH, and SrF molecules. Good agreement of our results with the available experimental values and those obtained from other widely used coupled-cluster-based methods reflects the reliability of the ECC method. Our study shows that the ECC method predicts the PDM of the studied metal fluorides more accurately than other two coupled-cluster-based methods, *viz.*, Z-vector and LECC methods at the same basis set and cutoff for virtual spinors.

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