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# Permanent Electric Dipole Moments of Alkaline Earth Monofluorides: Interplay of Relativistic and Correlation Effects

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The interplay of the relativistic and correlation effects in the permanent electric dipole moments of the  $X^2\Sigma^+$  electronic ground states of the alkaline earth monofluorides (BeF, MgF, CaF, SrF and BaF) has been studied using a relativistic coupled cluster method. The calculations were carried out using double, triple and quadruple zeta basis sets, and with no core orbitals frozen. The results are compared with those of other calculations available in the literature and with experiments. The correlation trends in the permanent electric dipole moments of these molecules are discussed in detail. This information will be useful in throwing light on the interplay between relativistic and correlation effects of other properties that are relevant to fundamental physics.

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## I. INTRODUCTION

This paper is a sequel to our earlier work [1], where we had considered SrF, and shown that a relativistic coupled cluster method (RCCM) is sufficiently accurate to calculate the permanent electric dipole moments (PDMs) of molecules with a single valence electron. We extend our calculations to the PDMs of the alkaline earth monofluorides (BeF, MgF, CaF, SrF and BaF), using the same method. We elucidate the trends in the correlation effects in the PDMs, as the molecules become progressively heavier, and consequently the relativistic effects get more pronounced, in order to understand the interplay between relativistic and correlation effects. To the best of our knowledge, such a study has not been performed earlier for molecules.

Similar to the PDM, the effective electric field ( $E_{eff}$ ) and the coupling constant of the nuclear anapole moment (NAM),  $\kappa_A$ , depend on the degree of hybridization of the orbitals. Hence, there are similarities in the correlation trends for these properties [2].  $E_{eff}$  is necessary for determining the electric dipole moment of the electron (eEDM), which is currently one of the most important probes of new physics beyond the Standard Model [3]. Furthermore,  $E_{eff}$  arises entirely from relativistic interactions [2, 4–6] in a molecule. Our present work on the interplay between relativistic and correlation effects should be useful in the context of theoretical studies for  $E_{eff}$ , and also  $\kappa_A$ , which is enhanced by relativistic effects. Alkaline earth monofluorides are of special interest, since PDMs of this family of molecules are important for various applications. SrF was the first molecule to be laser cooled [7], and high precision spectroscopy experiments, including a parity violation experiment [8], have been planned for the molecule. Experiments to laser cool CaF are underway, and subsequently, various high precision experiments will be performed on it [9]. BaF

was identified as a suitable candidate for probing the NAM [10, 11]. In their work, DeMille et al used diatomic molecules to probe NAM, since they could apply accessible laboratory magnetic fields to get opposite parity rotational states close together in energy. When two opposite parity rotational levels in a molecule are tuned to near degeneracy using the Zeeman effect, the degree of parity violation is enhanced. They chose ground state molecules, since they had a longer lifetime, and hence better resolution in their experiments. They considered a few such molecules that could be important for NAM, that included SrF and BaF. They concluded by mentioning that they plan on implementing the technique that they discussed, with BaF as their first candidate. Their group, in 2014, brought two opposite parity rotational levels to  $10^{-11}$  eV of each other, in BaF [12].

Moreover, the PDMs have been calculated earlier using different approaches for this class of molecules [1, 13–21] and high precision experimental data are available for some of these molecules [22–24].

A knowledge of PDMs, which play a vital role in the long range dipole-dipole interactions for ultracold molecules in optical lattices, are also useful in the search of elusive quantum phases, like the supersolid phase. The supersolid phase is characterized by the simultaneous existence of the superfluid and the density wave (periodic in nature) phases. It can arise due to long range dipole-dipole (PDM-PDM) interactions between trapped molecules [25, 26]. PDMs also play a role via a polarizing electric field,  $E_{pol}$  [27], in the sensitivity of eEDM search experiments. For molecular eEDM candidates for which no experimental measurements of the PDMs are available, we must employ many-body techniques, which capture the interplay of relativistic and correlation effects accurately, to compute PDMs. This, in turn, will provide us with an estimate of the sensitivity of an eEDM experiment with these molecules.

## II. THEORY

We discuss briefly the underlying ideas of the PDM of a molecule and the coupled cluster method. The details of both of these topics are discussed in detail elsewhere [1]. The PDM of a molecule,  $d$ , is given by:

$$\begin{aligned}
 d &= \frac{\langle \psi | D | \psi \rangle}{\langle \psi | \psi \rangle} \\
 &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | D | \Phi_0 \rangle \\
 &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | (-\sum_i e \mathbf{r}_i + \sum_A Z_A e \mathbf{r}_A) | \Phi_0 \rangle \\
 &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | (-\sum_i e \mathbf{r}_i) | \Phi_0 \rangle \\
 &+ \sum_A Z_A e \mathbf{r}_A \langle \Phi_0 | \Phi_0 \rangle \\
 &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | (-\sum_i e \mathbf{r}_i) | \Phi_0 \rangle \\
 &+ \sum_A Z_A e \mathbf{r}_A \tag{1}
 \end{aligned}$$

where  $|\psi\rangle$  is the electronic wavefunction of the molecule, which is expressed as  $e^T|\Phi_0\rangle$ , in the coupled cluster method.  $|\Phi_0\rangle$  is the model state, the Dirac-Fock (DF) wavefunction of the ground state of the molecule, which is built from single particle four-component spinors.  $T$  is the cluster operator. In the coupled cluster singles and doubles (CCSD) approximation, which we work with,  $T = T_1 + T_2$ , where  $T_1$  and  $T_2$  are the single and double excitation operators respectively. The occupied orbitals in the Slater determinant are called holes, and those excited into virtual space by the cluster operators are called particles. The  $T_1$  operator includes all possible one hole and one particle excitations from the Slater determinant,  $T_2$  includes all two hole-two particle excitations, and so on.  $D$  is the electric dipole moment operator,  $e$  is the charge of the electron, summation over the electronic coordinates is indicated by  $i$ , and that over the nuclear coordinates by  $A$ .  $\mathbf{r}_i$  is the position vector from the origin to the coordinate of an electron, and  $\mathbf{r}_A$  is the position vector from the origin to the coordinate of a nucleus.  $Z_A$  is the atomic number of the  $A^{\text{th}}$  nucleus. The subscript ‘C’ means that each term in that expression is connected [28, 29], and ‘N’ refers to the normal ordered form of that operator [30]. A term is said to be connected when all the operators in that term are fully contracted. Diagrammatically, it means that the Goldstone diagram corresponding to that term has no open lines. A normal ordered form of an operator is obtained by using anti-commutation relations of the creation and annihilation operators, and arranging hole creation and particle annihilation operators to the right. Note that we have invoked the Born-Oppenheimer approximation in the fifth line of the equations given above.

The important aspects of our relativistic CCSD method are that we use the Dirac-Coulomb Hamiltonian,

and correlation effects have been taken into account to all orders in the residual Coulomb interaction for the one and two hole-particle excitations. The coupled cluster method is size extensive, unlike the truncated configuration interaction (CI) method [31].

For all the molecules considered in the present work, the origin is chosen to be the fluorine atom, and hence the PDMs can be expressed as

$$\begin{aligned}
 d &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C \\
 &+ \langle \Phi_0 | (-\sum_i e \mathbf{r}_i) | \Phi_0 \rangle + Z_A e r_e \tag{2}
 \end{aligned}$$

where  $r_e$  refers to the equilibrium bond length for the molecule AF, with A=Be, Mg, Ca, Sr or Ba. The first term captures the electron correlation effects, while the second is the electronic contribution from the DF calculations. The third gives the nuclear contribution. We shall define the first two terms as the electronic terms, and the third as the nuclear term. The PDM depends on the mixing of orbitals of opposite parity. This is naturally achieved in polar molecules, as their orbitals are hybridized.

## III. METHODOLOGY

The molecular PDMs in the present work were calculated by combining the well known UTChem and DIRAC08 codes [32–34]. The DF calculations to generate the orbitals at the Self Consistent Field (SCF) level and the atomic orbital to molecular orbital integral transformations [35] were carried out using the UTChem code. The  $C_8$  double group symmetry was used to reduce the computational cost [36]. The CCSD calculations were carried out in the DIRAC08 code, using the one and two electron integrals from UTChem. The electronic part of the PDM was calculated by using only the linear terms in the coupled cluster wavefunction, since their contributions are the largest [2]

$$\begin{aligned}
 &\langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | (-\sum_i e \mathbf{r}_i) | \Phi_0 \rangle \\
 &= \langle \Phi_0 | (1 + T_1 + T_2)^\dagger D_N (1 + T_1 + T_2) | \Phi_0 \rangle_C \\
 &\quad + \langle \Phi_0 | (-\sum_i e \mathbf{r}_i) | \Phi_0 \rangle \tag{3}
 \end{aligned}$$

In the above expression, the cluster amplitudes are obtained by solving the full CCSD equations containing the linear and the nonlinear terms. We add the nuclear contribution to the electronic part of the PDM, using the experimental value for the bond length, wherever available. The values of the bond lengths used for BeF, MgF, CaF, SrF and BaF are 1.361, 1.75, 1.967, 2.075 [15, 37] and 2.16 [16, 38] Angstrom respectively.

The details of the basis sets used for our computations are given below in Table I. We used uncontracted Gaussian type basis sets (GTOs) in all our calculations. We also imposed the kinetic balance [39] condition for all the basis sets.

For Sr and Ba, we used the exponential parameters taken from the four-component basis sets obtained by Dyall [40], and added to it diffuse and polarization functions from the Sapporo-DKH3 [41] basis sets. We used the exponential parameters of cc-pV (correlation consistent-polarized valence) basis sets from the EMSL Basis Set Exchange Library [42, 43] for Be, Mg, Ca and F.

Since basis sets optimized at the Hartree-Fock level may not be suitable for calculations involving correlations, we use correlation consistent basis sets. We add polarization functions, in order to account for one orbital being polarized due to another, for example, the s orbital being polarized due to p, etc [44]. We add diffuse functions to the basis of Sr and Ba to account for far nuclear region properties. The basis sets for Be, Mg, and Ca contain polarization functions, but not diffuse functions. This is because aug-cc-pV basis sets ('aug' adds diffuse functions to cc-pV) are not available for Ca. For Be and Mg, we decided to look for the difference in the PDMs at the QZ level between cc-pV and the aug-cc-pV basis sets for the alkaline earth atom. Adding diffuse functions to BeF makes almost no difference, both at DF (using cc-pV:1.3D, aug-cc-pV: 1.3D) and at the CCSD (1.1 and 1.12 for cc-pV and aug-cc-pV respectively) levels. For MgF, the DF PDM remained almost the same (3.16 and 3.17D for cc-pV and aug-cc-pV respectively), while the CCSD PDM changes by around 2 percent (3.07 and 3.13D respectively for cc-pV and aug-cc-pV). Hence, at least for the lighter elements, diffuse functions do not seem to change the PDMs much. We find that for CaF, adding diffuse functions to Ca via a combination of Dyall and Sapporo basis gives a PDM different from that obtained by using cc-pVQZ (no diffuse functions) only by 2.2 percent. However, diffuse functions become important from SrF. The PDM of SrF changes by over 6 percent when we add diffuse functions [45]! Note that we have not added diffuse functions to F, that is, we use cc-pV and not aug-cc-pV basis sets, since adding diffuse functions to F does not really change the PDM significantly [45].

#### IV. RESULTS AND DISCUSSIONS

Table II gives the results of our calculations of energies of the molecules and their PDMs, at the DF and CCSD levels. The values for the PDMs have been rounded off to the second decimal place.

We observe that the absolute value of the correlation energy increases as the molecules get heavier, that is, as the relativistic effects get more pronounced. In each of the molecules BeF, MgF, and CaF, the PDMs decrease

Atom	Basis
Be	cc-pVDZ: 9s, 4p, 1d cc-pVTZ: 11s, 5p, 2d, 1f cc-pVQZ: 12s, 6p, 3d, 2f, 1g
Mg	cc-pVDZ: 12s, 8p, 1d cc-pVTZ: 15s, 10p, 2d, 1f cc-pVQZ: 16s, 12p, 3d, 2f, 1g
Ca	cc-pVDZ: 14s, 11p, 5d cc-pVTZ: 20s, 14p, 6d, 1f cc-pVQZ: 22s, 16p, 7d, 2f, 1g
Sr	Dyall+Sapporo: 20s, 14p, 9d Dyall+Sapporo: 28s, 20p, 13d, 2f Dyall+Sapporo: 33s, 25p, 15d, 4f, 2g
Ba	Dyall+Sapporo: 25s, 19p, 13d Dyall+Sapporo: 31s, 25p, 15d, 2f Dyall+Sapporo: 37s, 30p, 18d, 3f, 2g
F	cc-pVDZ: 9s, 4p, 1d cc-pVTZ: 10s, 5p, 2d, 1f cc-pVQZ: 12s, 6p, 3d, 2f, 1g

TABLE I: Details of the basis sets used

at the DF level as we move from DZ through the QZ basis sets, while for BaF, the PDMs oscillate.

For a given molecule, the CCSD values of this quantity increase progressively as the size of the basis set is enlarged. This can be partially understood by rewriting the terms in equation 4. We shall only do this for the DF and the  $\langle\Phi_0|D_N T_1|\Phi_0\rangle_C$  (called the  $DT_1$  term hereafter) terms, since we shall soon see that these are the terms that contribute the most to the PDM. The DF term is rewritten as:

$$d^{DF} = \langle\Phi_0|D|\Phi_0\rangle = \sum_m \langle\varphi_m|d|\varphi_m\rangle \quad (4)$$

$$= \sum_m \sum_{k,l} C_{m,k}^{*L} C_{m,l}^{*L} \langle\chi_{mk}^L|d|\chi_{ml}^L\rangle + \sum_m \sum_{k,l} C_{m,k}^{*S} C_{m,l}^{*S} \langle\chi_{mk}^S|d|\chi_{ml}^S\rangle \quad (5)$$

The summation m is over the molecular orbitals, and the summations k and l are over the atomic orbitals.  $\varphi_m$  refers to the  $m^{th}$  molecular orbital.  $\chi$  refers to an atomic orbital. The superscripts L and S refer to the large and small components respectively.

Similarly, we can rewrite the  $DT_1$  term in the following way (dropping the subscript, 'C', it is implied that each term is connected):

$$\begin{aligned} \langle\Phi_0|D_N T_1|\Phi_0\rangle &= \sum_{i,a} t_i^a \langle\varphi_i|d_N|\varphi_a\rangle \\ &= \sum_{i,a} \sum_{k,l} t_i^a C_{i,k}^{*L} C_{a,l}^{*L} \langle\chi_{ik}^L|d|\chi_{al}^L\rangle \\ &+ \sum_{i,a} \sum_{k,l} t_i^a C_{i,k}^{*S} C_{a,l}^{*S} \langle\chi_{ik}^S|d|\chi_{al}^S\rangle \quad (6) \end{aligned}$$

Molecule	Method	Basis	$E(\text{au})$	PDM(D)
BeF	DF	DZ	-114.07	1.32
	DF	TZ	-114.23	1.31
	DF	QZ	-114.26	1.30
	CCSD	DZ	-114.38	0.93
	CCSD	TZ	-114.59	1.06
	CCSD	QZ	-114.67	1.10
	Expt	-	-	-
MgF	DF	DZ	-299.51	3.21
	DF	TZ	-299.52	3.21
	DF	QZ	-299.57	3.16
	CCSD	DZ	-299.96	2.84
	CCSD	TZ	-300.02	3.02
	CCSD	QZ	-300.11	3.07
	Expt	-	-	-
CaF	DF	DZ	-779.31	2.89
	DF	TZ	-779.33	2.82
	DF	QZ	-779.37	2.77
	CCSD	DZ	-780.09	3.01
	CCSD	TZ	-780.21	3.13
	CCSD	QZ	-780.31	3.16
	Expt	-	-	3.07(7)
SrF	DF	DZ	-3277.67	2.83
	DF	TZ	-3277.70	2.95
	DF	QZ	-3277.74	3.01
	CCSD	DZ	-3278.85	2.95
	CCSD	TZ	-3279.01	3.42
	CCSD	QZ	-3279.13	3.60
	Expt	-	-	3.4676(1)
BaF	DF	DZ	-8235.25	2.42
	DF	TZ	-8235.27	2.28
	DF	QZ	-8235.31	2.65
	CCSD	DZ	-8236.55	2.69
	CCSD	TZ	-8236.71	3
	CCSD	QZ	-8236.82	3.40
	Expt	-	-	3.170(3)

TABLE II: Summary of the calculated results of the present work

The final value of PDM depends on the cancellations between these terms, since some would be positive and others negative. When the basis is changed from DZ to TZ, and then to QZ, the number of  $\chi$ s for a particular MO increase. In the alkaline earth monofluorides, after cancellations, the overall PDM, at the CCSD level, increases, with increase in basis size. In general, the quality of the molecular wavefunction improves as the basis set gets larger, and consequently the properties also improve. In our present work, we find that our CCSD results for the PDMs converge, that is, the difference between the PDM values for the QZ and the TZ basis sets are less than those between TZ and DZ, except for BaF. This may either be due to the correlation being inadequate or due to insufficient optimization of the basis sets. The PDMs increase from BeF to SrF, that is, the PDMs increase as the systems become more relativistic. However, from SrF to BaF, the PDM decreases. We also see that the absolute value of the correlation effects monotonically increase as we go to more relativistic systems, with MgF being an exception. The effect of correlation is 0.2 D for

BeF, whereas it is 0.75 for BaF.

The  $T_1$  diagnostic is defined by:

$$T_1 = \sqrt{\frac{t_1 \cdot t_1}{N}} \quad (7)$$

where the numerator refers to the vector of single excitation amplitudes of the CCM, and N is the number of independent correlated electrons. This diagnostic is a test of the validity of whether the coupled cluster wave function, for a particular system, can be expressed in terms of a single reference determinantal state. In the present work, the value of this diagnostic is about 0.02 for all molecules, except BaF, for which it is even smaller (about 0.01). This clearly suggests that all the molecules, on which we have performed our calculations, can be described by a single reference determinantal state [46, 47].

Our calculated values of the PDMs at the QZ level differ from experiment by about 3, 4 and 7 percent for CaF, SrF and BaF respectively.

We tabulate the electronic (at the CCSD level, with QZ basis) and nuclear contribution to the PDMs for the five molecules in Table III.

Molecule	Electronic terms	Nuclear term
BeF	-25.05	26.15
MgF	-97.80	100.87
CaF	-185.81	188.97
SrF	-375.16	378.76
BaF	-577.64	581.04

TABLE III: Electronic (at the CCSD level, with QZ basis sets) and nuclear contributions to the PDMs for all the alkaline earth monofluorides

The nuclear term depends on the atomic number and the equilibrium bond length of a molecule. It is easy to understand that as we go from BeF to BaF, this term increases. The electronic terms depend on the method employed, and this changes, depending on how much correlation a given method can capture, as well as on the choice of basis sets.

Writing the PDM of a molecule as the sum of its electronic and nuclear terms also hints at why the PDMs increase from BeF to SrF, and reduces for BaF. If we take the difference in the electronic terms for two successive molecules, and the difference in the nuclear terms for the same two molecules, and then compare the two, we observe that the latter is larger. Since the effect of the nuclear term is to increase the PDM (because it is positive), the PDM increases from BeF to SrF. However, it is the difference in the electronic terms that dominates between SrF and BaF, and hence the PDM decreases corresponding to this magnitude, for BaF.

Although we see from Table III that the absolute values of the electronic and the nuclear terms increase with the size of the molecules, their ratio can give us a sense of which term ‘grows’ faster among the two. Their absolute values, from BeF to BaF are 0.96, 0.97, 0.98, 0.99 and



0.99 respectively. The ratio for BaF is higher than that for SrF, with the difference occurring in the third decimal place. The electronic term hence ‘grows’ faster than the nuclear term with  $Z$ , and since the nuclear term changes as  $Z$ , the electronic terms may be a slightly more sensitive function of  $Z$ .

To understand correlation trends, we consider the contributions from each of the terms in Eq. 3. When we expand equation 3, we get a total of 10 terms. The last term is simply the DF contribution. Note that the  $\langle \Phi_0 | D_N T_2 | \Phi_0 \rangle_C$  (which we shall call  $DT_2$ , and so on for the other terms) as well as the  $T_2^\dagger D$  terms are zero, due to the Slater-Condon rules [30] and  $D$  being a one-body operator. Also, the very first term, which is  $\langle \Phi_0 | D_N | \Phi_0 \rangle_C$  is zero, since the expectation value of a normal ordered operator between Slater determinants is zero. This can be understood from the fact that we cannot create a hole or destroy a particle from the Slater determinant.

Term	BeF	MgF	CaF	SrF	BaF
DF	-24.85	-97.72	-186.20	-375.75	-578.39
$DT_1$	-0.08	-0.02	0.21	0.31	0.4
$DT_2$	0	0	0	0	0
$T_1^\dagger D$	-0.08	-0.02	0.21	0.31	0.4
$T_1^\dagger DT_1$	-0.02	-0.02	-0.02	-0.03	-0.05
$T_1^\dagger DT_2$	0.02	0.01	0.02	0.02	0.02
$T_2^\dagger D$	0	0	0	0	0
$T_2^\dagger DT_1$	0.02	0.01	0.02	0.02	0.02
$T_2^\dagger DT_2$	-0.06	-0.04	-0.05	-0.04	-0.04

TABLE IV: Contributions from the individual terms to the PDMs for all the alkaline earth monofluorides

We observe that the largest contribution to the PDM of a given molecule comes from the DF term. The  $DT_1$  term, which embodies important pair correlation effects [48] contributes the most, among the correlation terms, in the heavier molecules, starting from CaF, and increases from CaF to BaF. It is, however, not significant for BeF and MgF. In fact, for MgF, it is the  $T_2^\dagger DT_2$  term that dominates, among the correlation terms. Mathematically, the  $DT_1$  term is the off-diagonal matrix element between the model state, and a state, where one electron is excited by the electron-electron Coulomb repulsion. Physically, this can be visualized as a one hole and one particle excitation in all orders of residual Coulomb interaction, and the particle falling back to a hole due to interaction with the electric dipole moment operator. This can be easily seen from the diagrammatic representation of this term [1].  $DT_1$  increases monotonically from BeF to BaF. This strongly influences the correlation trend in the three heavier molecules. Also, the term changes sign as it increases with the size of the molecule. The second most important correlation contribution comes from the  $T_2^\dagger DT_2$  term (except in the case of MgF). The physical meaning of this term can, again, be understood in a way that is similar to that of the  $DT_1$  term. Just like in  $DT_1$ , this too can be seen from the diagrammatic representation of the term. The  $T_2^\dagger DT_2$

term follows no specific trend, but is always negative, and hence always reduces the PDM. It is also almost the same for all of the molecules considered, that is, it appears to have a rather weak  $Z$  dependence, as compared to the  $DT_1$  term.

Furthermore there are cancellations between the various correlation effects. The fractional contributions of the correlation effects increase from lighter to heavier elements, except in the case of BeF. It is largest in the case of BaF for which the value is 0.22.

It is worth noting that the PDM depends on how different the nuclear term is from the electronic terms. Among the electronic terms, the DF term dominates. Its effect is to ‘cancel out’ a large part of the nuclear contribution. The correlation terms may cancel or enhance the PDM though (This can be seen from Table IV; the correlation terms add to -0.2 for BeF, and 0.75 for BaF). For the lighter molecules BeF and MgF, it is the former, while for the heavier ones, it is the latter.

We have given below the comparison of our results with previous calculations and experiment.

We first mention briefly the semi-empirical models and experimental work, and then proceed to compare in detail our work with the ab initio calculations. The first calculations on the PDMs of some of the alkaline earth monofluorides were carried out by Topping et al [13]. They used an ionic model to calculate the PDMs of MgF, CaF, SrF and BaF. They compare their results with the Rittner model [51] and experiment (wherever available) in their work. Childs et al experimentally determined the PDM of CaF to be 3.07(7) D in their work [22] in the same year. In 1985, the PDM of SrF was measured, using a molecular beam microwave double resonance method [24]. Rice et al [14] used the Ligand field approach (LFA) to obtain a value of 3.01 D for CaF, later that year. The PDM of BaF was measured to be 3.170 (3) by Ernst et al in the subsequent year [23]. Mestdagh et al [16] used an electrostatic polarization model (EPM) for calculating the PDMs of MgF, CaF, SrF and BaF, among other molecules. Allouche et al [18] extended the LFA of Rice et al, in 1993, to calculate the PDMs, among other properties, of Ca, Sr and Ba monohalides.

The first ab initio calculations on select alkaline earth monofluorides were performed by Langhoff et al [15]. They computed the PDMs, among other properties, of many molecules, which include the alkaline earth monofluorides BeF, MgF, CaF and SrF. We compare our results with those that they computed at the experimental value of bond lengths (Table III in their work). They employed extended Slater basis sets augmented with diffuse and polarization functions. They used the following basis sets: Be: (6s, 4p, 1d), Mg: (8s, 6p, 4d, 2f), Ca: (10s, 8p, 4d, 2f), Sr: (12s, 10p, 7d, 3f), and F: (6s, 5p, 4d, 2f). Our largest basis sets, which also contain in them diffuse and polarization functions, are bigger than theirs, and hence probably better. They employed the single reference configuration interaction singles and doubles (CISD) and the coupled pair functionals (CPF)

<i>Molecule</i>	<i>Work</i>	<i>Method</i>	<i>PDM(D)</i>
BeF	Langhoff et al [15]	CPF	1.086
	Buckingham et al [19]	MP2	1.197
	Kobus et al [20]	FD-HF	-1.2727
	This work (QZ)		1.10
	Expt	-	-
MgF	Torrington et al [13]	Ionic model	3.64
	Langhoff et al [15]	CPF	3.077
	Mestdagh et al [16]	EPM	3.5
	Buckingham et al [19]	MP2	3.186
	Kobus et al [20]	FD-HF	-3.1005
	This work (QZ)		3.06
Expt	-	-	
CaF	Torrington et al [13]	Ionic model	3.34
	Rice et al [14]	LFA	3.01
	Langhoff et al [15]	CPF	3.06
	Mestdagh et al [16]	EPM	3.2
	Bundgen et al [17]	MRCI	3.01
	Allouche et al [18]	LFA	3.55
	Buckingham et al [19]	MP2	3.19
	Kobus et al [20]	FD-HF	-2.6450
	This work (QZ)		3.16
	Expt [22]		3.07(7)
	SrF	Torrington et al [13]	Ionic model
Langhoff et al [15]		CPF	3.199
Mestdagh et al [16]		EPM	3.59
Allouche et al [18]		LFA	3.79
Kobus et al [20]		FD-HF	-2.5759
Prasanna et al [1]		CCSD	3.41
Sasmal et al [21]		Z-vector	3.4504
This work (QZ)			3.60
Expt [24]			3.4676(1)
BaF	Torrington et al [13]	Ionic model	3.44
	Mestdagh et al [16]	EPM	3.4
	Allouche et al [18]	LFA	3.91
	This work (QZ)		3.40
	Expt [23]		3.170(3)

TABLE V: Comparison of present work with previous calculations and experiment

methods. The CISD method does not take into account certain higher order correlation effects that are present in the CCSD method (due to its exponential structure) [29]. The authors also conclude that their CPF values are in better agreement with experiment. So, we only quote their CPF results for comparison. The CPF approach is a size extensive version of CISD (CISD is not size extensive [29]). Although both the CCSD and the CPF approaches are size extensive, the treatment in their work is non-relativistic. Also, not all the electrons are correlated in these calculations. We therefore expect that our work, with a larger basis, a method that takes into account higher order correlations within a level of truncation, and a fully relativistic, all-electron calculation is an improvement over their results.

Bundgen et al [17] employed the multireference-configuration interaction (MRCI) approach, with the singles and doubles excitations taken into account, to compute the PDM of the ground state of CaF, among other properties and those properties for low lying excited

states of the molecule. They computed the PDM at a value of bond length slightly lesser than the value that we used. They used contracted Gaussian basis sets: Ca: [8s, 7p, 3d, 1f] and F: [5s, 4p, 1d]. A total of 17 electrons were correlated in their calculations. We use a larger basis, do not freeze any of the core orbitals, and also employ a fully relativistic method in our work. Also, our method is size extensive, while MRCI singles and doubles is not.

Buckingham et al [19] used Second order Moller-Plesset perturbation theory (MP2) to calculate PDMs of BeF, MgF and CaF, among other properties. The PDMs were computed from their calculated bond lengths. The basis sets used were Gaussian, contracted ones: Be: [5s, 3p, 1d], Mg: [6s, 5p, 3d], Ca: [9s, 6p, 3d], and F: [5s, 4p, 2d]. The method is size extensive, like the CCSD method. However, MP2 is actually upto second order in energy, and hence first order in wave function. So, the method captures single and double excitations, but only to the first order of perturbation in the residual Coulomb interaction (difference between the exact Coulomb interaction and the Hartree-Fock interaction). In CCSD, the single and double excitations to all orders of perturbation are accounted for. Hence, MP2 is subsumed in the CCSD method. Also, their calculations are non-relativistic.

The work by Kobus et al [20] involved comparing the electric moments obtained from finite basis set with finite difference Hartree-Fock (FD-HF) calculations. The magnitude of their PDMs get less accurate as the molecules get heavier. This is probably due to the fact that they work within the domain of Hartree-Fock theory, which does not account for correlations. Therefore, the part of PDM which is due to the missing correlations is absent. Also, since the correlation effects get more pronounced as we go to heavier alkali earth monofluorides, the PDM that one obtains for them is probably less accurate.

In an earlier work [1], we had tested the accuracy of our RCCM by computing the PDM of the SrF molecule. Since the purpose was to test a method, the result is only for SrF, and at the TZ level. Sasmal et al [21] improved upon our result of SrF in their work, which involved implementing the Z-vector approach in an RCCM.

The possible sources of errors in our calculations stem from the higher order terms neglected, and the choice of basis sets. If we add up the individual terms that make the PDM (other than the DF,  $DT_1$  and its conjugate), we see that the highest sum is from BaF, which is -0.05 D. It is reasonable to assume that the neglected higher order terms do not exceed this value, and we set a conservative estimate of  $\pm 0.1$  D.

The error from the choice of basis sets can be estimated by taking the difference between the QZ and the TZ PDMs. They are 0.04, 0.05, 0.03 and 0.18 for the first four alkaline earth monofluorides. We set a conservative error of  $\pm 0.1$  D for BeF, MgF and CaF, and  $\pm 0.2$  D for SrF. The PDM doesn't converge at the QZ level for BaF, so we cannot determine the error due to incompleteness of the basis here. However, we can roughly estimate the error to be about 0.2 D, based on comparison with a pre-

liminary investigation that has been carried out using a larger basis based on the same method that we have used in our calculations [52].

For SrF and BaF, we have used a combination of Dyllal's and Sapporo's basis for Sr and Ba. These contain in them diffuse and polarization functions, just as Be, Mg and Ca had these functions via cc-pV. In order to study the trends across the alkaline earth monofluorides, we have to assume that the results do not change significantly, whether we use cc-pV basis or a combination of Dyllal and Sapporo basis. The error from this assumption is tested using CaF at the QZ level, since Ca is the only atom in the candidate molecules for which both Dyllal and cc-pV basis sets were available. We obtain a PDM of 2.84 and 3.23 D at the DF and the CCSD levels, respectively, when we use Dyllal plus Sapporo basis for CaF. Earlier, we obtained, using cc-pVQZ for Ca, 2.77 and 3.16 D at the DF and CCSD levels, respectively. The difference is about 2.5 percent at DF and 2.2 at CCSD. Since we can't tell how this may vary for the heavier molecules, we can conservatively set an error percentage of about 5, due to the change in the choice of basis sets for the molecules.

## V. CONCLUSIONS

We calculated the PDMs of the alkaline earth monofluorides, up to BaF, using a RCCM, with no core orbitals frozen in our calculations. We used uncontracted cc-pV

and Dyllal+Sapporo basis sets for our calculations. We reported the DF and CCSD energies and the PDMs. Our results, using QZ basis sets, are in good agreement with the experimental results, wherever available. We have examined the electronic and nuclear contributions to the PDMs for all the molecules considered, as well as the importance of the individual correlation terms. The results we obtained suggest that as the molecules get heavier, that is, as the relativistic effects increase, the correlation effects get larger in size. We also provided a rough estimate of the errors in our calculations, caused by ignoring higher order terms and from the basis sets. We also give a rough estimate of the error in comparing the PDMs as we move from BeF through BaF, due to the choice of basis sets being different for the two heaviest monofluorides.

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- [1] V. S. Prasanna, M. Abe, and B. P. Das, *Phys. Rev. A* **90**, 052507 (2014).
- [2] M. Abe, G. Gopakumar, M. Hada, B. P. Das, H. Tatewaki, and D. Mukherjee *Phys. Rev. A* **90**, 022501 (2014).
- [3] Norval Fortson, Patrick Sandars, and Stephen Barr. The search for a permanent electric dipole moment. *Phys. Today*, 56(6):33739, 2003.
- [4] L. I. Schiff, *Phys. Rev.* **132**, 2194 (1963).
- [5] P G H Sandars, *J. Phys. B: At. Mol. Phys.*, Volume 1 Number 3, 511 (1968).
- [6] B. P. Das, in *Aspects of Many-Body Effects in Molecules and Extended Systems*, edited by D. Mukherjee (Springer, Berlin, 1989), p. 411.
- [7] E. S. Shuman, S. F. Barry, D. DeMille, *Nature* **467**, 820-823 (2010).
- [8] Joost van den Berg, Using cold molecules to detect molecular parity violation, SSP2012, Groningen, URL <https://www.kvi.nl/ssp2012/material/107?berg,vanden/slides/107?1?praatjeSSP2012.pdf>.
- [9] Ed Hinds, private communication.
- [10] Malaya K. Nayak and B. P. Das, *Phys. Rev. A* **79**, 060502(R) 2009.
- [11] D. DeMille, S. B. Cahn, D. Murphree, D. A. Rahmlow, and M. G. Kozlov, *Phys. Rev. Lett.* **100**, 023003 2008.
- [12] DeMille, *Physics Today* **68**(12), 34 (2015); doi: 10.1063/PT.3.3020.
- [13] T. Topping, W. E. Ernst, and S. Kindt, *The Journal of Chemical Physics* **81**, 4614 (1984).
- [14] Steven F. Rice, Hans Martin, and Robert W. Field, *The Journal of Chemical Physics* **82**, 5023 (1985).
- [15] Stephen R. Langhoff, Charles W. Bauschlicher Jr., Harry Partridge, and Reinhart Ahlrichs, *The Journal of Chemical Physics* **84**, 5025 (1986).
- [16] J. M. Mestdagh and J. P. Visticot, *Chemical Physics* **155**, 79-89 (1991).
- [17] Peter Bundgen, Bernd Engels, and Sigrid D. Peyerimhoff, *Chemical Physics Letters* Volume 176, number 5 (1991).
- [18] A. R. Allouche, G Wannous and M. Aubert-Frecon, *Chemical Physics* **170**, 11-22 (1993).
- [19] A. D. Buckingham, and R. M. Olegario, *Chemical Physics Letters* Volume 212, number 3,4 (1993).
- [20] J. Kobus, D. Moncrieff, S. Wilson, *Physical Review A*, Volume 62, 062503 (2000).
- [21] Sudip Sasmal, Himadri Pathak, Malaya K. Nayak, Nayana Vaval, and Sourav Pal *Phys. Rev. A* **91**, 030503(R) (2015).
- [22] W. J. Childs, L. S. Goodman, U. Nielsen, and V. Pfeufer, *J. Chem. Phys.* **80**, 2283-2287 (1984).
- [23] W. E. Ernst, J. Kandler and T. Topping, *J. Chem. Phys.* **84**, 4769 (1986).
- [24] W.E. Ernst, J. Kandler, S. Kindt, T. Topping, Volume 113, Issue 4, Pages 351-354 (1985).



- [25] C. Trefzger, C. Menotti, B. Capogrosso-Sansone, and M. Lewenstein, *J. Phys. B: At. Mol. Opt. Phys.* **44**, 193001 (2011).
- [26] T. Mishra, R. V. Pai, S. Ramanan, M. S. Luthra, and B. P. Das, *Phys. Rev. A* **80**, 043614 (2009).
- [27] V.S. Prasanna, A.C. Vutha, M. Abe, and B.P. Das, *Phys. Rev. Lett.* **114**, 183001 (2015).
- [28] Kvasnicka et al., *Phys. Rep.* **90**, 159 (1982).
- [29] R. F. Bishop, in *Microscopic Quantum Many-Body Theories and their Applications* (Springer-Verlag, Berlin, 1998), Chap. 1.
- [30] Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).
- [31] M. Abe, G. Gopakumar, M. Hada, B. P. Das, H. Tatewaki, D. Mukherjee, submitted (2014); T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular Electronic Structure Theory* (John Wiley and Sons Ltd., Chichester, 2000).
- [32] UTChem 2004: Yanai, T.; Kamiya, M.; Kawashima, Y.; Nakajima, T.; Nakano, H.; Nakao, Y.; Sekino, H.; Paulovic, J.; Tsuneda, T.; Yanagisawa, S.; Hirao, K.
- [33] REL4D: Abe, M.; Iikura, H.; Kamiya, M.; Nakajima, T.; Paulovic, J.; Yanagisawa, S.; Yanai, T.
- [34] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC08 (2008), written by L. Visscher, H. J. Aa. Jensen, and T. Saue, with new contributions from R. Bast, S. Dubillard, K. G. Dyall, U. Ekstrom, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Ilias, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Salek, and J. Sikkema.
- [35] M. Abe, T. Yanai, T. Nakajima, and K. Hirao, *Chem. Phys. Lett.* **388**, 68 (2004).
- [36] T. Yanai, R. J. Harrison, T. Nakajima, Y. Ishikawa, and K. Hirao, *Int. J. Quantum Chem.* **107**, 1382 (2007).
- [37] *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, edited by K. P. Huber and G. Herzberg (Van Nostrand Reinhold, New York, 1979).
- [38] Ch. Ryzlewicz and Topping, *Chemical Physics* **51**, 329 (1980).
- [39] K. G. Dyall and K. Faegri, Jr., *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, New York, 2006), p. 176.
- [40] K. G. Dyall, *J. Phys. Chem. A* **113**, 12638 (2009).
- [41] T. Noro, M. Sekiya, and T. Koga, *Theor. Chem. Acc.* **131**, 1124 (2012).
- [42] Basis Set Exchange: A Community Database for Computational Sciences Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., and Windus, T.L. *J. Chem. Inf. Model.*, **47**(3), 1045-1052, 2007, doi:10.1021/ci600510j.
- [43] The Role of Databases in Support of Computational Chemistry Calculations Feller, D., *J. Comp. Chem.*, **17**(13), 1571-1586, 1996.
- [44] Basis Sets in Quantum Chemistry, C. David Sherrill, URL: <http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/basis-sets.pdf>.
- [45] Permanent Electric Dipole Moment of Strontium Monofluoride in its ground State Using a Relativistic Coupled Cluster Method: Basis Set Dependence, V S Prasanna, M Abe, and B P Das (manuscript under preparation).
- [46] Lee, Timothy J., Taylor, Peter R., A diagnostic for determining the quality of single-reference electron correlation methods, *Int. J. Quantum Chem.*, volume 36, issue S23, John Wiley and Sons, Inc., <http://dx.doi.org/10.1002/qua.560360824>, 199-207, 1989.
- [47] Coupled cluster theory: Fundamentals, Wim Klopper and David P. Tew, C4 Tutorial, Zurich, 24 October 2006, URL: <http://www.ipc.kit.edu/theochem/download/Kapitel3.pdf>.
- [48] E. Eliav, U. Kaldor, and Y. Ishikawa, *Int. J. Quantum Chem.* **52**, 205 (1994); H. S. Nataraj, B. K. Sahoo, B. P. Das, and D. Mukherjee, *Phys. Rev. Lett.* **101**, 033002 (2008).
- [49] Sten Salomonson and Per Oster, *Phys. Rev. A* **41**, 4670, 1990.
- [50] S. Raouafi, G. -H. Jeung, and Ch. Jungen, *The Journal of Chemical Physics* **115**, 7450 (2001).
- [51] E. S. Rittner, *J. Chem. Phys.*, **19**, 1030, 1951.
- [52] A. Sunaga, 2015 (unpublished).
- [53] P.F. Bernath and S. McLeod, "DiRef, A Database of References Associated with the Spectra of Diatomic Molecules", *J. Mol. Spectrosc.*, **207**, 287 (2001).