Permanent electric dipole moments of alkaline-earth-metal monofluorides: Interplay of relativistic and correlation effects

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(Received 7 October 2015; revised manuscript received 25 January 2016; published 13 April 2016)

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-metal 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.

DOI: 10.1103/PhysRevA.93.042504

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-metal 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 ($E_{\rm eff}$) and the coupling constant of the nuclear anapole moment (NAM), κ_A, depend on the degree of hybridization of the orbitals. Hence, there are similarities in the correlation trends for these properties [2]. $E_{\rm eff}$ 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, $E_{\rm eff}$ 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 $E_{\rm eff}$, and also κ_A, which is enhanced by relativistic effects. Alkaline-earth-metal 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.* [11] 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, is 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, $E_{\rm pol}$ [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

$$\begin{aligned} d &= \frac{\langle\psi|D|\psi\rangle}{\langle\psi|\psi\rangle} = \langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|D|\Phi_0\rangle \\ &= \langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i} + \sum_A Z_A e\boldsymbol{r_A}\right)|\Phi_0\rangle \\ &= \langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i}\right)|\Phi_0\rangle \\ &\quad + \sum_A Z_A e\boldsymbol{r_A}\langle\Phi_0|\Phi_0\rangle \\ &= \langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i}\right)|\Phi_0\rangle \\ &\quad + \sum_A Z_A e\boldsymbol{r_A} \end{aligned} \tag{1}$$

where $|\psi\rangle$ is the electronic wave function 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) wave function 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 and 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 is indicated by A. $\boldsymbol{r_i}$ is the position vector from the origin to the coordinate of an electron, and $\boldsymbol{r_A}$ is the position vector from the origin to the coordinate of a nucleus. Z_A is the atomic number of the Ath 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, this means that the Goldstone diagram corresponding to that term has no open lines. A normal ordered form of an operator is obtained by using anticommutation 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 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

$$d = \langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i}\right)|\Phi_0\rangle + Z_A e r_e \tag{2}$$

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 [32,33]. The DF calculations to generate the orbitals at the self-consistent-field (SCF) level and the atomic orbital to molecular orbital integral transformations [34] were carried out using the UTCHEM code. The C_8 double group symmetry was used to reduce the computational cost [35]. 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 wave function, since their contributions are the largest [2]:

$$\begin{aligned} &\langle\Phi_0|e^{T^\dagger} D_N e^T|\Phi_0\rangle_C + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i}\right)|\Phi_0\rangle \\ &\quad = \langle\Phi_0|(1+T_1+T_2)^\dagger D_N (1+T_1+T_2)|\Phi_0\rangle_C \\ &\quad + \langle\Phi_0|\left(-\sum_i e\boldsymbol{r_i}\right)|\Phi_0\rangle. \end{aligned} \tag{3}$$

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 [15,36], and 2.16 [16,37] Å, respectively.

The details of the basis sets used for our computations are given below in Table I. We used uncontracted Gaussian type basis sets in all our calculations. We also imposed the kinetic balance [38] 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 [39], and added diffuse and polarization functions from the Sapporo-DKH3 [40] basis sets. We used the exponential parameters of cc-pV (correlation consistent polarized valence) basis sets from the EMSL Basis Set Exchange Library [41,42] 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

TABLE I. Details of the basis sets used.

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: $12s,6p,3d,2f,1g$

due to another, for example, the s orbital being polarized due to p, etc. [43]. 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 quadruple zeta (QZ) level between cc-pV and the aug-cc-pV basis sets for the alkaline-earth-metal atom. Adding diffuse functions to BeF makes almost no difference, both at DF (using cc-pV:1.3 D, aug-cc-pV: 1.3 D) 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 3.17 D for cc-pV and aug-cc-pV, respectively), while the CCSD PDM changes by around 2% (3.07 and 3.13 D 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 Saporro bases gives a PDM different from that obtained by using cc-pVQZ (no diffuse functions) only by 2.2% . However, diffuse functions become important from SrF. Significantly, the PDM of SrF changes by over 6% when we add diffuse functions [44]. 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 [44].

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 at the DF level as we move

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

Molecule	Method	Basis	E (a.u.)	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)

from double zeta (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 Eq. (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

$$d^{\mathrm{DF}} = \langle\Phi_0|D|\Phi_0\rangle = \sum_m \langle\varphi_m|d|\varphi_m\rangle \tag{4}$$

$$= \sum_m \sum_{k,l} C^{*L}_{m,k} C^{*L}_{m,l} \langle\chi^L_{mk}|d|\chi^L_{ml}\rangle + \sum_m \sum_{k,l} C^{*S}_{m,k} C^{*S}_{m,l} \langle\chi^S_{mk}|d|\chi^S_{ml}\rangle. \tag{5}$$

The summation m is over the molecular orbitals, and the summations k and l are over the atomic orbitals. φ_m refers to the mth molecular orbital. χ 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):

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

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 triple zeta (TZ), and then to QZ, the number of χs for a particular MO increase. In the alkaline-earth-metal monofluorides, after cancellations, the overall PDM, at the CCSD level, increases, with increase in basis size. In general, the quality of the molecular wave function 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 differences 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 be 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 values 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 D for BaF.

The T_1 diagnostic is defined by

$$T_1 = \sqrt{\frac{\boldsymbol{t}_1 \cdot \boldsymbol{t}_1}{N}} \quad (7)$$

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 determinental 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 determinental state [45,46].

Our calculated values of the PDMs at the QZ level differ from experiment by about 3, 4, and 7% 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.

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.

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

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

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 Eq. (3), we get a total of ten 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.

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 [47], 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

TABLE IV. Contributions from the individual terms to the PDMs for all the alkaline-earth-metal monofluorides.

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

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 (also, refer Table V for the summary).

We first mention briefly the semiempirical 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-metal monofluorides were carried out by Torring *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 [48] 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 and Visticot [16] used an electrostatic polarization model (EPM) for calculating the PDMs of MgF, CaF, SrF, and BaF, among other molecules.

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

Molecule	Work	Method	PDM (D)
BeF	Langhoff *et al.* [15]	CPF	1.086
	Buckingham and Olegario [19]	MP2	1.197
	Kobus *et al.* [20]	FD-HF	−1.2727
	This work (QZ)		1.10
	Expt.		
MgF	Torring *et al.* [13]	Ionic model	3.64
	Langhoff *et al.* [15]	CPF	3.077
	Mestdagh and Visticot [16]	EPM	3.5
	Buckingham and Olegario [19]	MP2	3.186
	Kobus *et al.* [20]	FD-HF	−3.1005
	This work (QZ)		3.06
	Expt.		
CaF	Torring *et al.* [13]	Ionic model	3.34
	Rice *et al.* [14]	LFA	3.01
	Langhoff *et al.* [15]	CPF	3.06
	Mestdagh and Visticot [16]	EPM	3.2
	Bundgen *et al.* [17]	MRCI	3.01
	Allouche *et al.* [18]	LFA	3.55
	Buckingham and Olegario [19]	MP2	3.19
	Kobus *et al.* [20]	FD-HF	−2.6450
	This work (QZ)		3.16
	Expt. [22]		3.07(7)
SrF	Torring *et al.* [13]	Ionic model	3.67
	Langhoff *et al.* [15]	CPF	3.199
	Mestdagh and Visticot [16]	EPM	3.59
	Allouche *et al.* [18]	LFA	3.79
	Kobus *et al.* [20]	FD-HF	−2.5759
	Prasannaa *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	Torring *et al.* [13]	Ionic model	3.44
	Mestdagh and Visticot [16]	EPM	3.4
	Allouche *et al.* [18]	LFA	3.91
	This work (QZ)		3.40
	Expt. [23]		3.170(3)

Allouche *et al.* [18] extended the LFA of Rice *et al.* [14], in 1993, to calculate the PDMs, among other properties, of Ca, Sr, and Ba monohalides.

The first *ab initio* calculations on select alkaline-earth-metal monofluorides were performed by Langhoff *et al.* [15]. They computed the PDMs, among other properties, of many molecules, which include the alkaline-earth-metal 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 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)

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 nonrelativistic. 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 less 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 are not.

Buckingham and Olegario [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 up to 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 (the 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 nonrelativistic.

The work by Kobus *et al.* [20] involved comparing the electric moments obtained from a finite basis set with finite difference Hartree-Fock (FD-HF) calculations. The magnitudes 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 alkaline-earth-metal 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 ± 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-metal monofluorides. We set a conservative error of ± 0.1 D for BeF, MgF, and CaF, and ± 0.2 D for SrF. The PDM does not 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 preliminary investigation that has been carried out using a larger basis based on the same method that we have used in our calculations [49].

For SrF and BaF, we have used a combination of Dyall and Sapporo's basis for Sr and Ba. These contain 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-metal monofluorides, we have to assume that the results do not change significantly, whether we use the cc-pV basis or a combination of Dyall 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 Dyall 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 the Dyall 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% at DF and 2.2% at CCSD. Since we cannot 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-metal monofluorides, up to BaF, using a RCCM, with no core orbitals frozen in our calculations. We used uncontracted cc-pV and Dyall and Saporro 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.

ACKNOWLEDGMENTS

The computational results reported in this work were performed on the high-performance computing facilities of IIA, Bangalore, on the hydra and kaspar clusters. We would

like to acknowledge the help of Anish Parwage, Engineer C, Indian Institute of Astrophysics, Bangalore, for his help in the installation of the codes on the clusters. The DiRef database was extremely useful in searching for literature [50]. This research was supported by Japan Science and Technology Agency, CREST. This work was supported by Japan Society for the Promotion of Science KAKENHI Grant No. 25810007.

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