

Permanent electric dipole moment of strontium monofluoride as a test of the accuracy of a relativistic coupled-cluster method

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The permanent electric dipole moment of the $X^2\Sigma^+$ electronic ground state of the strontium monofluoride molecule is calculated using a relativistic coupled-cluster method. Our result is compared with those of other calculations and that of experiment. Individual contributions arising from different physical effects are presented. The result obtained suggests that the relativistic coupled-cluster method used in the present work is capable of yielding accurate results for the permanent electric dipole moments of molecules for which relativistic effects cannot be ignored.

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I. INTRODUCTION

The relativistic coupled-cluster (RCC) method is considered to be the current gold standard of many-body theory of heavy atoms and diatomic molecules [1,2]. This method has been used extensively to calculate the properties of various atoms, but its applications to the properties of molecules other than their energies have been very limited to date.

The effective electric field in a molecule is required for obtaining an upper limit on the electric dipole moment of the electron, which can provide insights into physics beyond the standard model. Recently, Abe *et al.* applied a RCC method to compute the effective electric field experienced by an electron in the YbF molecule [3]. In addition, they had also obtained the permanent electric dipole moment (pdm) and the magnetic dipole hyperfine coupling constant to assess the accuracy of their calculations. The purpose of this paper is to test the accuracy of a single reference RCC method by using it to calculate the pdm of the strontium monofluoride molecule (SrF), for which the interplay of relativistic and correlation effects is important.

Sr is a moderately heavy atom and, as a result of this, the relativistic effects are more pronounced in SrF, compared to a fluoride of a lighter alkaline earth atom like calcium. We have chosen an alkaline earth monofluoride because it contains only a single valence electron, making it a suitable candidate to test a single reference coupled cluster method. Furthermore, a high precision measurement of the SrF pdm is available for comparison [4].

SrF is the only molecule that has been laser-cooled so far [5]. A knowledge of the pdm would be useful in determining the long-range dipole-dipole interaction [6] for ultracold molecules in optical lattices. The existence of such an interaction will give rise to novel quantum phases, including the elusive supersolid state [7]. Ultracold SrF molecules could also be used for high precision spectroscopy [8,9]. An experiment on the search for parity violation using SrF is currently underway [10].

II. THEORY

The Hamiltonian that we have used is the Dirac-Coulomb Hamiltonian, H_{DC} , which is given by

$$H_{DC} = \sum_i \left[c\boldsymbol{\alpha} \cdot \mathbf{p}_i + \beta mc^2 - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|} \right] + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1)$$

Here, c is the speed of light, $\boldsymbol{\alpha}$ and β refer to the Dirac matrices, and \mathbf{p}_i refers to the momentum of the i th electron. The summation over the electronic coordinates is indicated by i , and that over the nuclear coordinates is indicated by A . \mathbf{r}_i is the position vector from the origin to the site 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 th nucleus.

To obtain the electronic wave function, $|\psi\rangle$, in our calculations, we use a RCC method. The coupled-cluster wave function can be written as

$$|\psi\rangle = e^T |\Phi_0\rangle. \quad (2)$$

Here, $|\Phi_0\rangle$ refers to the Dirac-Fock (DF) wave function of the ground state of the molecule, which is built from single-particle four-component spinors. $|\Phi_0\rangle$ is taken to be a single determinant corresponding to the ionic configuration, Sr:(5s)¹ and F:(2p)⁶, which is an open shell doublet. We can visualize the ionic bonding in SrF by considering the difference in the electronegativities of the constituent atoms. T is the cluster operator. In this work, we use the CCSD (coupled-cluster singles and doubles) approximation, where $T = T_1 + T_2$. Here, T_1 and T_2 are the single (S) and double (D) excitation operators, respectively. They are given by

$$T_1 = \sum_{ap} t_a^p a_p^\dagger a_a, \quad (3)$$

$$T_2 = \sum_{p>q, a>b} t_{ab}^{pq} a_p^\dagger a_q^\dagger a_b a_a. \quad (4)$$

t_a^p and t_{ab}^{pq} are the cluster amplitudes, where a and b refer to holes and p and q refer to particles. $a_p^\dagger a_a$ acting on a state means that a hole “ a ” is destroyed from that state, and a particle “ p ” is created. When $a_p^\dagger a_a$ acts on a model state, which is the Slater determinant in this case, the resulting state is denoted by $|\Phi_a^p\rangle$.

The CCSD amplitude equations are

$$\langle \Phi_a^p | e^{-T} H_N e^T | \Phi_0 \rangle = 0, \quad (5)$$

$$\langle \Phi_{ab}^{pq} | e^{-T} H_N e^T | \Phi_0 \rangle = 0. \quad (6)$$

The term $e^{-T} H_N e^T$ can be written as $\{H_N e^T\}_C$, using the linked cluster theorem [11,12]. The subscript “ C ” means that the term is connected. H_N is the normal-ordered Hamiltonian [13].

The important features of our relativistic CCSD method are that it uses the Dirac-Coulomb approximation, it is size extensive, and the correlation effects are treated to all orders in the residual Coulomb interaction for all possible single and double excitations [3].

In the coupled-cluster method, the expectation value of any operator, O , is given by

$$\begin{aligned} \langle O \rangle &= \frac{\langle \psi | O | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \Phi_0 | e^{T^\dagger} O e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} \\ &= \frac{\langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} + \frac{\langle \Phi_0 | O | \Phi_0 \rangle \langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle}. \end{aligned} \quad (7)$$

Here, in the previous line, we have used the fact that $O = O_N + \langle \Phi_0 | O | \Phi_0 \rangle$ [14].

We now use the expression [15]

$$\frac{\langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} = \langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle_C. \quad (8)$$

Then, the expectation value of the operator O becomes

$$\langle O \rangle = \langle \Phi_0 | e^{T^\dagger} O_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | O | \Phi_0 \rangle. \quad (9)$$

Therefore, pdm of a molecule, d , is given by

$$\begin{aligned} d &= \frac{\langle \psi | D | \psi \rangle}{\langle \psi | \psi \rangle} = \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | D | \Phi_0 \rangle \\ &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | \left(- \sum_i e r_i + \sum_A Z_A e r_A \right) | \Phi_0 \rangle \\ &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | \left(- \sum_i e r_i \right) | \Phi_0 \rangle \\ &\quad + \sum_A Z_A e r_A \langle \Phi_0 | \Phi_0 \rangle \\ &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | \left(- \sum_i e r_i \right) | \Phi_0 \rangle \\ &\quad + \sum_A Z_A e r_A, \end{aligned} \quad (10)$$

where D is the electric dipole moment operator and e is the charge of the electron. We have invoked the Born-Oppenheimer approximation in the fourth line of the equations given above. SrF is a diatomic molecule, with the fluorine atom

chosen to be at the origin. Hence the pdm can be expressed as

$$\begin{aligned} d &= \langle \Phi_0 | e^{T^\dagger} D_N e^T | \Phi_0 \rangle_C \\ &\quad + \langle \Phi_0 | \left(- \sum_i e r_i \right) | \Phi_0 \rangle + Z_{\text{Sr}} e r_e, \end{aligned} \quad (11)$$

where r_e refers to the equilibrium bond length for SrF. The first term captures the electron correlation effects. Note that the leading term in its expansion, namely $\langle \Phi_0 | D_N | \Phi_0 \rangle$, is zero. The second term of the expectation value gives the electronic contribution from the DF calculations. The third part gives the nuclear contribution. It is important to note that the pdm depends on the mixing of orbitals of opposite parity. This is naturally achieved in molecules, since the orbitals are hybridized.

III. METHODOLOGY

The pdm of the ground state of SrF was calculated by combining the well known UTCHEM and DIRAC08 codes [16–18]. The computations for generating the DF orbitals and the transformation of the one and two electron integrals from the atomic orbital to the molecular orbital basis [19] were carried out using the UTCHEM code. The C_8 double group symmetry was used to reduce the computational cost of the calculations [20]. The DIRAC08 code was used to determine the CCSD amplitudes and the one and two electron integrals were taken from UTCHEM. The electronic part of the pdm was then calculated by using only the linear terms in the coupled-cluster wave function, since the dominant contributions come from them [3]. We, hence, evaluate

$$\begin{aligned} &\langle \Phi_0 | (1 + T_1 + T_2)^\dagger \left(- \sum_i e r_i \right)_N (1 + T_1 + T_2) | \Phi_0 \rangle_C \\ &\quad + \langle \Phi_0 | \left(- \sum_i e r_i \right) | \Phi_0 \rangle. \end{aligned} \quad (12)$$

The nuclear contribution is calculated using the experimental value of the bond length and it is then added to the above quantity to obtain the pdm of the molecule.

We performed our calculations with the following choice of uncontracted basis sets: double zeta (dz) level: Sr:(20s, 14p, 9d) [21,22] and F:(9s, 4p, 1d) [23]; triple zeta (tz) level: Sr:(28s, 20p, 13d, 2f) [21,22] and F:(9s, 5p, 2d, 1f) [23].

The basis sets that we used in our calculations were GTOs (Gaussian type orbitals). For Sr, we used the exponential parameters taken from the four-component basis sets obtained by Dyall [21]. We also added to it diffuse and polarization functions from the Sapporo-DKH3 basis sets [22]. We used the exponential parameters of ccpv (correlation consistent-polarized valence) basis sets from the EMSL Basis Set Exchange Library [24,25] for F [23]. We have also imposed the kinetic balance condition [26].

IV. RESULTS

The difference between the CCSD and the DF results gives the correlation contributions. Both these results are given in Table I for the double and triple zeta basis sets.

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

Method	Basis	$T_1 dia$	pdm (D)	% frac
DF	dz		2.83	18.39
DF	tz		2.95	14.93
CCSD	dz	0.01467	2.96	14.64
CCSD	tz	0.01743	3.41	1.66
Expt.			3.4676(10)	

The values of the pdm have been rounded off to the second decimal place. The units are in Debye (D). The experimental bond length of SrF (2.075 Å) [27] was used in all the calculations. The pdm measured from experiment is denoted by “Expt.” in the table. As the size of the basis set increases, the DF values drift towards the experimental result. The results of the CCSD calculations show that the pdm for the triple zeta basis set is closer to the experimental value of pdm than that obtained using double zeta basis sets.

Table I also shows the T_1 diagnostics (denoted in the table as “ $T_1 dia$ ”) for the two runs. They are around 0.01, indicating the stability of the single reference calculations for our choice of basis sets. The last column gives the percentage fractional difference between the calculation and the experiment.

Table II summarizes the results for the pdm of SrF obtained previously by other methods and experiment.

Torrington *et al.* [28] used an ionic model to calculate the pdm of SrF. Ernst *et al.* experimentally determined the pdm to be 3.4676(10) D in their work [4] a year later. The first *ab initio* calculations were performed by Langhoff *et al.* [29]. They employed near Hartree-Fock quality Slater basis sets augmented with diffuse and polarization functions, with Sr:(12s,10p,7d,3f) and F:(6s,5p,4d,2f). They calculated the pdm of the molecule using the single reference CISD (configuration interaction singles and doubles) and the CPF (coupled pair functional) approaches. The former gave a value of 2.523 D, and the latter 3.199 D, and both these results used the experimental value of the bond length (2.075 Å). CISD is not size extensive and, for a given level of excitation, CCSD includes more correlation effects than CISD. This may have led to certain missing terms that could have played a crucial role in cancellations with other terms in the expectation value. The CPF approach is size consistent, and the result is in better agreement with the experimental value. However, SrF

TABLE II. Summary of the pdms of SrF from previous works and this work.

Method	Reference	pdm (D)
Experiment	Ernst <i>et al.</i> [4]	3.4676(10)
Ionic model	Torrington <i>et al.</i> [28]	3.67
SCF	Langhoff <i>et al.</i> [29]	2.579
CISD	Langhoff <i>et al.</i> [29]	2.523
CPF	Langhoff <i>et al.</i> [29]	3.199
EPM	Mestdagh <i>et al.</i> [30]	3.6
Ligand field approach	Allouche <i>et al.</i> [31]	3.7875
FD-HF	Kobus <i>et al.</i> [32]	2.5759
CCSD	This work (TZ)	3.41

is large enough for relativistic effects to be pronounced, but in this paper, the treatment is nonrelativistic. Mestdagh and Vistocot [30] used an electrostatic polarization model (EPM). They used the experimental value of bond length for their calculations, and obtained a value of 3.6 D. Allouche *et al.* [31] used a ligand field approach for their calculations. The largest basis sets they used for Sr had 10 radial functions. The work by Kobus *et al.* [32] was to compare the dipole moments obtained from finite basis set with finite difference Hartree-Fock calculations. We have mentioned the work for completeness. Our fully relativistic calculations gave a result of 3.41 D with Sr:(28s,20p,13d,2f) and F:(9s,5p,2d,1f) basis sets (at the tz level).

We now proceed to focus on the contributions from the individual terms in the pdm given in Eq. (12). We consider the case for the largest basis set that we have used in our calculations, since the SrF wave function built from it is the closest to the actual wave function among the basis sets that we have chosen. We only deal with the electronic contribution to the pdm, because as discussed earlier, the nuclear part is evaluated separately. The ket can be written in terms of either the DF, single-excitation, or double-excitation determinants. The bra can also be expressed similarly. The resulting contributions to the pdm from the nine terms are given below.

In Table III, the first column specifies the different terms in Eq. (12), while the second column gives their respective values (rounded off to two decimal places). The values for the electronic terms are all in Debye. They add up to -375.35 D. The nuclear contribution is 378.76 D. The resulting pdm is, hence, 3.41 D. The electronic contribution from the DF calculations is -375.81 D and, hence, the final value for the pdm at the DF level is 2.95 D. CCSD accounts for the correlations that make up the remaining 0.46 D, which is about 13.5% of the final value of the pdm.

We can see that the dominant contribution is from the DF term. The matrix elements of the pdm operator between the DF and single excitation determinants (and their Hermitian conjugate), which incorporate an important class of pair correlation effects [2], make the largest contribution among the CCSD terms. These correspond to the DT_1 and the $T_1^\dagger D$ terms.

We give in Fig. 1 the Goldstone diagrams that correspond to the terms in Eq. (9).

The possible sources of error could arise from not considering higher-order correlation effects and the choice of basis

TABLE III. Contributions from the individual terms to the pdm.

Term	Contribution
DF	-375.81
DT_1	0.26
DT_2	0.00
$T_1^\dagger D$	0.26
$T_1^\dagger DT_1$	-0.04
$T_1^\dagger DT_2$	0.02
$T_2^\dagger D$	0.00
$T_2^\dagger DT_1$	0.02
$T_2^\dagger DT_2$	-0.06

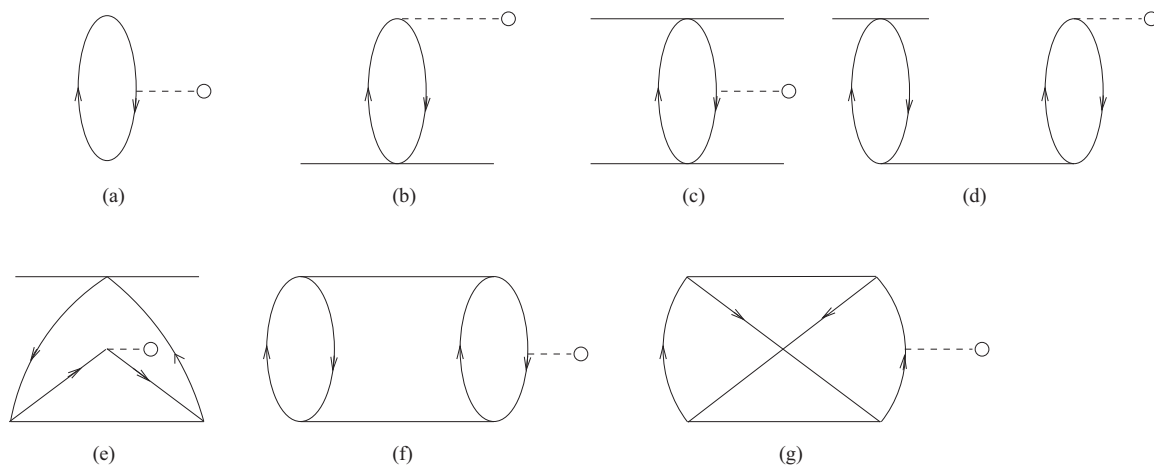


FIG. 1. Goldstone diagrams for pdm: (a) DF term, (b) DT_1 , (c) $T_1^\dagger DT_1$, (d) and (e) direct and exchange diagrams, respectively, of the $T_1^\dagger DT_2$ term, and (f) and (g) direct and exchange diagrams, respectively, of the $T_2^\dagger DT_2$ term.

sets. Apart from the DF term, the DT_1 term, and its conjugate, given in Table III, the rest of the terms add to -0.06 D. It is reasonable to assume that the error from higher-order correlations does not exceed this value. We can roughly state that this error is about ± 0.1 D. For estimating the error due to the choice of basis sets, we evaluated the pdm for SrF, at a preliminary level, using three choices of approximate quadruple zeta (qz) basis functions: (1) Sr:(33s,25p,13d) from Dyall [21], which is optimized but doesn't have diffuse and polarization functions, and F:(12s,6p,3d,2f,1g), which are ccpv-qz basis sets from the EMSL Basis Set Exchange Library [24,25], (2) Sr:(33s,25p,15d,4f,2g) from a combination of Dyall and Sapporo (for diffuse and polarization functions) [21,22], and F:(12s,6p,3d,2f,1g), from the EMSL Basis Set Exchange Library [24,25], and (3) Sr:(23s,17p,13d,4f,2g) and F:(13s,9p,5d,4f,3g) from Sapporo basis [22]. The first choice of basis gave 3.38 D, the second 3.60, and the third 3.58. We took a weighted average, giving 40 wt. % to Dyall, since it is optimized, and 30% to the remaining two choices. We get a weighted average of 3.506 D, and the percentage fraction difference between this estimate and our tz value is about 2.7. Hence we can say that a conservative estimate of the error due to choice of basis is about ± 0.1 D. A ballpark estimate of the error would, hence, be around ± 0.2 D for the pdm of SrF.

V. CONCLUSION

In order to test the accuracy of our RCC method, we have calculated the pdm of SrF, using two kinds of uncontracted Gaussian basis sets, based on the Dyall plus Sapporo (for

diffuse and polarization functions) and ccpv basis sets. Our result for the larger of the two basis sets, i.e., the tz basis with Sr:(28s,20p,13d,2f) and F:(9s,5p,2d,1f), gave a value that is closer to that of experiment than that of the other basis set. The largest contribution to pdm arises from the DF term, and next in importance are the single excitations which embody an important type of pair correlation effect.

Our result for SrF pdm with a high precision measurement of this quantity is in better agreement than those of all the other earlier calculations, and it is a little over one and a half percent of the measured value. With the error in calculation estimated to be ± 0.2 D, we see that the experimental value falls within our estimated error range. This is a testament to the power of the RCC method to account for relativistic and electron correlation effects. Our present work sets the stage for exploring many other properties of molecules using the RCC method.

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