Relativistic Theory of the Electric Dipole Moment of an Atom due to the Electric Dipole Moment of an Electron

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The relativistic theory for the electric dipole moment (EDM) of paramagnetic atoms arising from the electric dipole moment of the electron is presented. A novel approach using the relativistic coupled-cluster method that incorporates the residual Coulomb interaction to all orders and a weak parity and time-reversal violating interaction to one order has been employed in Fr to obtain the enhancement of the EDM of that atom compared to the EDM of the electron. Trends of the different correlation effects and leading contributions from different physical states are discussed. Our result in combination with that of the Fr EDM that is currently in progress, has the potential to probe the validity of the Standard Model (SM) of elementary particle physics.

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I. INTRODUCTION

The Standard Model (SM) of elementary particle physics given by Glashow, Weinberg and Salam described by the $SU(3) \times SU(2) \times U(1)$ gauge group satisfactorily explains most of the phenomena observed so far on the fundamental interactions. However, this model is widely believed to be incomplete. Indeed a question of great importance is whether there is any new physics beyond the highly celebrated SM of elementary particles. Any kind of experimental evidence supporting the extensions of the SM like the left-right symmetric model, the multi-Higgs model or supersymmetry models will have a significant impact on our understanding of the fundamental forces between the elementary particles in nature.

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Detailed studies of the fundamental interactions have a bearing on chemical and biological processes as well. For example, the violation of parity is believed to be one of the fundamental reasons behind the "homochirality" of bio-molecules \[7\]. In the same vein, any time reversal symmetry (\(T\)) violation will lead to a certain asymmetry in chemical phenomena whose importance will depend on the actual magnitude of the asymmetry observed in the experiments. A case in point is the emergence of enantiomorphic excess where none is expected from the electromagnetic interaction \[8\]. One can in fact, distinguish between the chirality brought out by \(T\)-invariant and \(T\)-noninvariant enantiomorphism, introducing the concept of "false chirality" in the latter situation. Clearly if the predictions by the SM and those beyond, relating to certain symmetry violations are observed, they will have profound chemical and biological implications. Additionally, if the predictions from the SM and some of its extensions differ, then this will lead to different expected magnitudes of the effect. This may bring observational efficiency to the limit achievable currently. Fixing the limit of observability then depends on the accuracy of electronic structure theories \[8\]. This is why studies on the predictions as defined by the SM and beyond are of immediate interest to chemists.

The EDM (\(D\)) associated with the nondegenerate state of a physical system like an atom can be shown to be proportional to the angular momentum (\(J\)) of that on the basis of the Wigner-Eckart theorem \[9\]. It can be proved that the existence of a nonzero electric dipole moment (EDM) which is the expectation value of operator \(D\) in a given atomic state would imply the violations of the \(T\) invariance and parity (\(P\)) symmetries \[10, 11\]. The SM which conserves the combined transformations of charge conjugation (\(C\)), \(P\) and \(T\) symmetries (known as the CPT theorem \[12\]), predicts \(P\) and \(CP\) violations in weak interactions. A possible observation of a nonzero EDM in an atom would be a direct signature of \(T\) violation. An EDM has not been observed so far for whether in elementary particles or composite systems. The SM predicts an upper limit on the electron EDM of the order of \(10^{-38} e \cdot cm\) \[13, 14\], while other suggested models predict this value almost ten orders of magnitude larger. Therefore, measurements of EDM in atomic systems are necessary to test the SM. Thus, an unambiguous observation of a nonzero EDM of any fundamental particle including the electron will undoubtedly unveil a new arena of physics beyond the SM. A direct measurement of the electron EDM is not possible using accelerator approaches due to the charge of the electron, however it could be obtained by combining the results measurements and calculations of atomic EDMs using the table-top experiments.

In 1963, Schiff \[15\] argued that the permanent EDM of an atom vanishes under the assumption that the constituents of non-relativistic point-like systems interact only electrostatically. It was,
however, put forth by Salpeter [16] and Sachs and Scwebel [17] as early as 1958-1959 that when relativistic effects are included it is possible for an EDM on the electron to give rise to an EDM on the atom as a whole. Later, it was rigorously proved by Sandars [11] that by introducing the correct relativistic form of the interaction Hamiltonian into the Dirac equation in a Lorentz covariant manner, as emphasized by Salpeter, one will get non-zero EDM for the atom when an electron is assumed to have intrinsic EDM.

In principle, an atom being a composite many-body system will have many sources of intrinsic EDMs arising from its constituent particles and their $\mathcal{P}, \mathcal{T}$ violating electron-nucleus interactions. At the elementary particle level; electrons may possess intrinsic EDMs, describing by a coupling constant $d_e$ which may directly contribute to the atomic EDM. The electron EDM can also interact with the central electrostatic field of an atom and can produce an atomic EDM. The interactions between electrons - quarks may manifest at different levels as electrons - nucleons to electrons - nucleus interactions. The $\mathcal{P}$ and $\mathcal{T}$ violating electron-nucleus interactions can either be scalar–pseudo-scalar (S-PS), with a coupling constant $C_s$ or a tensor–pseudo-tensor (T-PT) interaction describing with a coupling constant $C_T$.

The paramagnetic (open-shell) atoms will in general be sensitive to the contribution from the intrinsic EDM of the electrons and their $\mathcal{P}$, and $\mathcal{T}$-violating S-PS interactions with the nucleus whereas, the EDM in diamagnetic (closed-shell) atoms will arise from the EDM of the nucleus and their $\mathcal{P}$, and $\mathcal{T}$-violating T-PT interactions with the electrons. This can be understood as the electron EDM is a spin dependent property, hence it contributes to open-shell atoms because of the unpaired valence electron. However, for a closed-shell atom because of the Fermi exclusion principle, it will add up to zero if hyperfine interactions are excluded. These $\mathcal{P}$- and $\mathcal{T}$-violating electron-nucleus interactions will provide a useful tool in understanding the $CP$ violation from the semi-leptonic sectors. Using the knowledge of $CP$-violation obtained in these atomic EDM experiments one can also constrain different models of $CP$-violation.

It was shown by Sandars that by choosing suitable atoms and favorable electronic states one can get an enhanced EDM for an atom which may even be a few orders of magnitude larger than that of the free electron [18]. In particular, he demonstrated by carrying out relativistic calculations that the atomic EDMs of thallium (Tl) and caesium (Cs) are two orders of magnitude larger than the EDM of the electron. It was this important result which provided the impetus for the first generation of atomic EDM experiments that were carried out in the 1960s [19, 20, 21]. It was realized quickly that the EDM enhancement factor $R$ defined as the ratio of atomic EDM to the electron EDM increases with increase in the nuclear charge ($Z$) and also if there are close lying
states of opposite parity since it is inversely proportional to the difference in their near degenerate energy levels. Hence, heavy rare-earth atoms with anomalously close energy levels of opposite parity, have large EDM enhancement factors. These factors are also fairly large for heavy alkali atoms. The enhancement factor is proportional to

\[ R \propto \frac{Z^3 \alpha^2}{J(J + 1/2)(J + 1)}, \]

where \( \alpha \) is the fine structure constant. This formula for order of magnitude estimate of EDM enhancement factors illustrates the dependence on nuclear charge \( Z \) and the angular momentum \( J \) which implies that \( R \) is large for high \( Z \) and low \( J \).

The ground state EDMs of heavy neutral alkali atoms are of considerable interest to experimentalists, because: (i) the EDMs in these cases are several orders of magnitude larger than that of the electron, unlike in the hydrogen atom where the enhancement factor is large only for the 2s excited state, however, it can be easily perturbed by external electric fields and is therefore not amenable to sensitive experiments, (ii) the availability of commercial lasers whose operating frequencies match with those of the resonant energies needed for causing transitions between the low lying levels and (iii) the large polarizabilities of these atoms.

The EDM of an atom or any other neutral particle is determined experimentally by applying an external static electric field to the atom and measuring its shift in energy that results from the interaction of the EDM with the electric field. Consider an atom which has a permanent EDM as well as a magnetic dipole moment. In the presence of a static electric field \( \vec{E} \) and a magnetic field \( \vec{B} \), the interaction Hamiltonian is given by

\[ H_{\text{int}} = -\vec{D}.\vec{E} - \vec{\mu}.\vec{B}, \]

where \( \vec{D} \) and \( \vec{\mu} \) are, respectively, the electric and magnetic dipole moment operators.

The application of the external fields leads to a precession of the atom. The precession (Larmor) frequency is primarily due to the magnetic dipole moment, but there is also a small contribution from the EDM. The observable in an EDM experiment is the difference in the Larmor frequencies corresponding to parallel and antiparallel configurations of \( \vec{E} \) and \( \vec{B} \) - reversal of \( \vec{E} \) relative to \( \vec{B} \). This change in frequency is

\[ \Delta\omega_E = \frac{2DE}{\hbar}. \]

It corresponds to \( \Delta\omega_E = 10^{-6}\text{Hz} \) for \( D \approx 10^{-25}e - cm \) and \( E = 10KV/cm \). This frequency shift corresponds to a magnetic field of \( 10^{-9}\text{G} \) for a diamagnetic atom and \( 10^{-12}\text{G} \) for a paramagnetic atom.
One of the most important systematic errors in the EDM experiment is the magnetic field that is produced by the motion of the atoms. This field to first order in $\frac{v}{c}$ is given in the moving frame of the atoms as

$$\vec{B}_m = \frac{\vec{v}}{c} \times \vec{E}. \quad (4)$$

For $v = 300 \text{ m/s}$ and $E = 10 \text{ KV/cm}$, the motional magnetic field $\vec{B}_m = 3 \times 10^{-5} \text{G}$. This magnetic field can give rise to a frequency shift which can mimic an EDM. In the Tl experiment, two counter-propagating beams are used to minimize this effect [24]. EDM experiments using optically pumped atoms in a cell have a zero average velocity and are therefore not affected very much by the motional magnetic field [25]. Both the beam and the cell experiments have their advantages and disadvantages. While it is possible to apply larger electric fields in the beam experiments, the coherence times are longer in the cell experiments. The motional magnetic fields often limit the sensitivity of the former, while leakage currents give rise to systematic errors in the latter and they cannot be estimated easily.

EDM experiments based on laser cooled and trapped atoms in principle have the advantages of both the beam and the cell experiments [26, 27, 28, 29, 30]. In these experiments, one can apply large electric fields and the coherence times are long. The leakage current problem can be overcome using a suitable configuration for the laser trap. The systematic error due to the motional magnetic field is virtually non-existent because of the extremely low average velocity of the cold atoms.

The procedure of the atomic EDM measurements with cold atoms is as follows: First, a fast atomic beam from a hot oven is slowed down by using the Zeeman-tuning method. After this pre-cooling stage, the atoms are trapped and cooled by a magneto-optical trap (MOT). A high density and large number of atoms is then loaded into the MOT within several seconds. Then the atomic beam and the magnetic field for the MOT is switched off, the detuning of the trapping laser is increased and its intensity reduced. This results in further cooling to the micro Kelvin region by the polarization-gradient method. The next step is to perform optical pumping to polarize the nuclear spin by the application of a circularly polarized resonant light pulse after completely switching off the laser fields. Finally, a high power laser for a far blue-detuned dipole forced trap and also a high static electric field for the EDM measurement is switched on. A probe laser beam will be used to measure the Larmor precession frequency. The loading and measurement procedure is repeated many times to reduce the statistical uncertainty.

Atomic theory is needed in combination with experiments to extract a variety of T violating coupling constants. Following a series of insightful calculations of atomic EDMs by Sandars in the
1960s and 1970s based on the relativistic central field potential \[11\], a number of relativistic many-body calculations on atoms of experimental interest have been carried out in the last two decades \[31\]. Ingenious experiments were initiated in the 1980s to observe the EDMs of mercury (Hg), Cs and Tl \[24, 25, 32\]. Subsequently systematic errors have been improved in these experiments and today the most accurate results are available in Hg \[33\] for diamagnetic atoms and Tl for paramagnetic atoms \[34\]. Polar molecules seem to be better candidates than heavy atoms for observing EDMs arising from the electron EDM and there have been recent attempts to calculate the observable in some of the molecular EDM experiments \[35, 36, 37\]. However, these calculations are in their infancy. In contrast, it is possible to perform very accurate calculations on alkali atoms. Therefore, to shed light on physics beyond the SM or in fact to observe a nonzero atomic EDM, the heaviest of the alkali atoms, francium (Fr) seems to be another suitable candidate for its relatively simple spectroscopic levels and large enhancement factor. A number of spectroscopic analysis on Fr has been carried out at SUNY Stony Brook using laser trapping technique \[38\] and it has been proposed both for EDM \[39\] and atomic parity violation (APV) \[40\] measurements. In fact, there is a preliminary calculation available for the enhancement factor of Fr using radial integrals for a few matrix elements \[41\]. In the present work, we will demonstrate an approach using the relativistic coupled-cluster method that includes Coulomb interaction among electrons to all orders and \(P\) and \(T\) violating electron-nucleus pseudoscalar interaction due to electron EDM up to first order but involving contributions from continuum and all possible single and double excited states to calculate \(R\) in Fr. In this procedure, we will also demonstrate contribution from important intermediate states and highlight the role of various electron correlation effects.

II. THEORETICAL STUDIES OF ATOMIC EDM

A. General features

The three discrete symmetries - charge conjugation (\(C\)), space inversion or parity (\(P\)) and time-reversal (\(T\)) are related by the well-known CPT theorem \[12\]. According to this theorem, while a physical system described by a local field theory may violate any one of these symmetries independently, it is invariant under the combined operation of all three of them.

The combined operation of \(C\) and \(P\) (\(CP\)) was thought to be a good symmetry till 1964 when Christenson et al observed its violation in the decay of \(K_0\) meson \[42\]. Using the CPT theorem, one arrives at the conclusion that this observation implies \(T\) violation. An observation of an electric
FIG. 1: Violation of $T$ and $P$ symmetries is necessary for a non-zero electric dipole moment.

dipole moment (EDM) of a non-degenerate physical system would be a direct signature of the violations of $T$ as well as $P$ symmetries [43]. Consider a physical system with non-zero angular momentum that has a permanent EDM, $\vec{D}$. The vector $\vec{D}$ like the magnetic dipole moment will be parallel or antiparallel to $\vec{J}$, the angular momentum of the system [18]. Under the action of $T$, $\vec{J} \rightarrow -\vec{J}$ and $\vec{D} \rightarrow -\vec{D}$. Since $\vec{D}$ is proportional to $\vec{J}$, $T$ invariance implies $\vec{D} = 0$. If a transformation is carried out under $P$, $\vec{D} \rightarrow -\vec{D}$ but $\vec{J} \rightarrow \vec{J}$, and this leads to $\vec{D} = 0$ for $P$ invariance. One therefore concludes that $T$ and $P$ must be violated independently for the existence of a non-zero EDM. The above arguments are illustrated in Fig. I

B. Atomic EDM from the electron EDM

In a manner analogous to the anomalous magnetic moment, one can introduce an electric dipole moment for a single electron in an electromagnetic field in a Lorentz covariant manner into the Dirac equation. The only difference is that it contains a pseudo-scalar Dirac operator $\gamma_5$. 
The pseudo-scalar perturbation Hamiltonian for the intrinsic EDM of an electron then reads,

\[ H_{\text{EDM}} = i \frac{d_e}{2} \left( \bar{\Psi} \gamma_5 \gamma_\mu \gamma_\nu \Psi \right) F_{\mu\nu} = -\frac{d_e}{2} \left( \bar{\Psi} \gamma_5 \sigma_{\mu\nu} \Psi \right) F_{\mu\nu} \] (5)

where \( d_e \) is the intrinsic EDM of the electron.

In the Pauli approximation, Eq. (5) reduces, in atomic units, to

\[ H_{\text{EDM}} = -d_e \beta \left( \vec{\sigma} \cdot \vec{E} + i \vec{\alpha} \cdot \vec{H} \right) \] (6)

where \( \vec{\alpha}, \beta \) and \( \vec{\sigma} \) are the Dirac matrices, \( \vec{E} \) and \( \vec{H} \) are the total electric and magnetic fields at the site of the electron. The second term in the rhs of Eq. (6) is much weaker than the first term and hence, we will consider only the latter in the calculation of EDMs of paramagnetic atoms. The non-relativistic limit of this interaction is \( -d_e \vec{\sigma} \cdot \vec{E} \). This form of the interaction produces a zero atomic EDM \[11\], thus as we show below the EDM of a paramagnetic atom due to the intrinsic EDM of the electron is entirely a relativistic effect. Therefore, it is necessary to use a relativistic many-body theory to determine its size. The atomic EDM arising from the intrinsic EDM of the electron is discussed in detail below.

C. Method of calculations

The total Hamiltonian for a many-electron atom, in the absence of any external field, when the electron possesses an intrinsic EDM is given by,

\[ H = H_0 + H_{\text{EDM}} \] (7)

where, \( H_0 \) is the atomic Hamiltonian given by

\[ H_0 = \sum_i \left[ c\alpha \cdot p_i + (\beta - 1)c^2 + V_{\text{nuc}}(r_i) \right] + \sum_{i \geq j} \frac{1}{r_{ij}} \] (8)

due to the electromagnetic interaction and \( H_{\text{EDM}} = -d_e \sum_i \beta \vec{\sigma}_i \cdot \vec{E}^{\text{int}}_i \) with the internal electric field, \( \vec{E}^{\text{int}}_i = -\nabla \left[ V_{\text{nuc}}(r_i) + \sum_{i > j} \frac{1}{r_{ij}} \right] \), exerted by the nucleus (\( V_{\text{nuc}}(r_i) \)) and other electrons (\( \frac{1}{r_{ij}} \)).

The application of external electric field also induces EDM to the atom. Hence, the total perturbed Hamiltonian \( H^{(1)} \) in the presence of an external electric field is given by,

\[ H^{(1)} = H_{\text{EDM}} - d_e \sum_i \beta \vec{\sigma}_i \cdot \vec{E} - e \sum_i \vec{r}_i \cdot \vec{E} \] (9)

In the time-independent perturbation theory, the first order shift in energy is given by,

\[ E^{(1)}_m = \langle \Psi_m^{(0)} | H^{(1)} | \Psi_m^{(0)} \rangle \]

\[ = -\sum_i \left[ \langle \Psi_m^{(0)} | d_e \beta \vec{\sigma}_i \cdot \vec{E}^{\text{int}}_i | \Psi_m^{(0)} \rangle + \langle \Psi_m^{(0)} | d_e \beta \vec{\sigma}_i \cdot \vec{E} | \Psi_m^{(0)} \rangle - \langle \Psi_m^{(0)} | e \vec{r}_i \cdot \vec{E} | \Psi_m^{(0)} \rangle \right] \] (10)
Assuming that the applied field is in the positive z-direction,

\begin{equation}
E_m^{(1)} = \sum_j \left[ -d_e \langle \Psi_m^0 | \beta \sigma_{z,j} \cdot \mathbf{E}^\text{int}_j | \Psi_m^0 \rangle - d_e \langle \Psi_m^0 | \beta \sigma_{z,j} | \Psi_m^0 \rangle | \mathbf{E} \rangle - \langle \Psi_m^0 | e \mathbf{z}_j | \Psi_m^0 \rangle | \mathbf{E} \rangle \right]
\end{equation} (11)

Noting the fact that, the operators in the first and third terms are odd under parity and the expectation value of odd parity operator vanishes in a state of definite parity, the only non-vanishing term (corresponds to the even parity operator) is given by,

\begin{equation}
E_m^{(1)} = -d_e \langle \Psi_m^0 | \beta \sum_j \sigma_{z,j} | \Psi_m^0 \rangle | \mathbf{E} \rangle
\end{equation} (12)

As the strength of the perturbation is sufficiently weak, we consider only up to the first-order perturbation in the wavefunction. The first-order perturbed wavefunction \( |\Psi_m^{(1)} \rangle \) is given by,

\begin{equation}
|\Psi_m^{(1)} \rangle = \sum_{n \neq m} \frac{\langle \Psi_n^0 | H^{(1)} | \Psi_m^0 \rangle}{E_m^0 - E_n^0} |\Psi_n^0 \rangle
\end{equation} (13)

The second order shift in energy due to EDM as a perturbation is given by,

\begin{equation}
E_m^{(2)} = \langle \Psi_m^0 | H^{(1)} | \Psi_m^0 \rangle
\end{equation}

\begin{equation}
E_m^{(2)} = \sum_{n \neq m} \frac{\langle \Psi_n^0 | H^{(1)} | \Psi_n^0 \rangle \langle \Psi_n^0 | e \sum_j z_j | \Psi_m^0 \rangle}{E_m^0 - E_n^0}
\end{equation} (14)

On inserting the expression for \( H^{(1)} \) in the above equation and discarding the terms containing \( d_e^2 \) and \( E^2 \) while expanding, we get those terms which are first order in perturbation and linearly proportional to the applied uniform electric field as below;

\begin{equation}
E_m^{(2)} = \left\{ \sum_{n \neq m} \frac{\langle \Psi_n^0 | H_{EDM} | \Psi_n^0 \rangle \langle \Psi_n^0 | e \sum_j z_j | \Psi_m^0 \rangle}{E_m^0 - E_n^0} + \sum_{n \neq m} \frac{\langle \Psi_n^0 | e \sum_j z_j | \Psi_n^0 \rangle \langle \Psi_m^0 | H_{EDM} | \Psi_n^0 \rangle}{E_m^0 - E_n^0} \right\} |\mathbf{E}| (15)
\end{equation}

Thus, the total shift in energy would be,

\begin{equation}
E_m = E_m^{(1)} + E_m^{(2)}
\end{equation}

\begin{equation}
E_m = \left\{ -d_e \langle \Psi_m^0 | \beta \sum_j \sigma_{z,j} | \Psi_m^0 \rangle + \sum_{n \neq m} \frac{\langle \Psi_n^0 | H_{EDM} | \Psi_n^0 \rangle \langle \Psi_n^0 | e \sum_j z_j | \Psi_m^0 \rangle}{E_m^0 - E_n^0} \right. \left. + \sum_{n \neq m} \frac{\langle \Psi_n^0 | e \sum_j z_j | \Psi_n^0 \rangle \langle \Psi_m^0 | H_{EDM} | \Psi_n^0 \rangle}{E_m^0 - E_n^0} \right\} |\mathbf{E}| (16)
\end{equation}
The coefficient of the linear shift in energy due to the applied electric field is the total electric dipole moment of an atom i.e., 
\[ \varepsilon = \vec{D} \cdot \vec{E} \]. Thus, the total EDM of an atom is given by,

\[
\langle D \rangle = \left\{ d_e \langle \Psi_m^{(0)} | \beta \sum_j \vec{\sigma}_{z,j} | \Psi_m^{(0)} \rangle - \sum_{n \neq m} \frac{\langle \Psi_n^{(0)} | H_{EDM} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e \sum_j \vec{z}_j | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\}
\]

The total atomic EDM given by Eq. (17) can be further simplified to the effective one-electron form given by,

\[
\langle D \rangle = \sum_j \left[ \frac{2i c d_e}{\hbar} \left\{ \sum_{n \neq m} \frac{\langle \Psi_m^{(0)} | \beta \gamma^5 \vec{p}_j^2 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e \sum_j \vec{z}_j | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\} \right] + h.c. \tag{18}
\]

Here, \( \beta \) and \( \gamma^5 \) are the Dirac matrices, \( \vec{p} \) is the 3-momentum, \( \hbar = \frac{h}{2\pi} \) is the modified Planck’s constant, \( E_m^{(0)} \) and \( E_n^{(0)} \) are the zeroth order energies of the states \( m \) and \( n \) respectively, and the abbreviation \( h.c. \) stands for hermitian conjugate. Eq. (18) shows that \( H_{EDM} \) in Eq. (17) reduces to an effective one-body term given by \( H_{EDM}^{eff} = 2i c d_e \sum_j \beta \gamma^5 \vec{p}_j^2 \).

\( H_{EDM}^{eff} \) can be responsible for mixing atomic states of opposite parities. Its strength is sufficiently weak for it to be considered as a first-order perturbation. It is, therefore, possible to write the \( m'th \) state atomic wavefunction as

\[
|\Psi_m \rangle = |\Psi_m^{(0)} \rangle + d_e |\Psi_m^{(1)} \rangle. \tag{19}
\]

Therefore, we have

\[
\langle D \rangle = d_e \frac{\langle \Psi_m^{(0)} | D | \Psi_m^{(1)} \rangle + (\Psi_m^{(1)} | D | \Psi_m^{(0)} \rangle}{\langle \Psi_m^{(0)} | \Psi_m^{(0)} \rangle}, \tag{20}
\]

where \( D \) is the electric dipole (E1) operator.

The above first order perturbed wave functions due to \( H_{EDM}^{eff} \) can be calculated by summing over a few important intermediate states. However, the accuracy of this approach is rather limited. We have developed an approach based on the relativistic coupled-cluster (RCC) theory that can overcome the sum-over-states approach by directly solving the first order perturbed equation

\[
(H^{(0)} - E_m^{(0)}) |\Psi_m^{(1)} \rangle = (E_m^{(1)} - H_{EDM}^{eff}) |\Psi_m^{(0)} \rangle, \tag{21}
\]

where \( E_m^{(1)} \) vanishes since \( H_{EDM}^{eff} \) is an odd parity operator. We present below the formulation of this problem based on RCC theory.
D. RCC theory of atomic EDM

Using RCC theory, the atomic wavefunction \( |\Psi_m^{(0)}\rangle \) for a single valence \( m \) open-shell system is given by \([44, 45]\)

\[
|\Psi_m^{(0)}\rangle = e^{T^{(0)}} \{ 1 + S_m^{(0)} \} |\Phi_m\rangle,
\]

(22)

where we define \( |\Phi_m\rangle = a_m^\dag |\Phi_0\rangle \), with \( |\Phi_0\rangle \) as the Dirac-Fock (DF) state for the closed-shell system. The curly bracket in the above expression represents normal order form.

In the single and double excitations approximation coupled-cluster (CCSD) method, we have

\[
T^{(0)} = T_1^{(0)} + T_2^{(0)},
\]

\[
S_m^{(0)} = S_{1m}^{(0)} + S_{2m}^{(0)},
\]

(23)

where \( T_1^{(0)} \) and \( T_2^{(0)} \) are the single and double particle-hole excitation operators for the core electrons and \( S_{1m}^{(0)} \) and \( S_{2m}^{(0)} \) are the single and double excitation operators for the valence electron, respectively. The amplitudes corresponding to these operators can be determined by solving the relativistic coupled-cluster singles and doubles equations.

These amplitudes are obtained by solving the following equations

\[
\langle \Phi^L | \{ \widehat{H}\widehat{e}^T \} | \Phi_0 \rangle = \delta_{0,L} \Delta E_{\text{corr}}
\]

\[
\langle \Phi_m^L | \{ \widehat{H}\widehat{e}^T \} S_m | \Phi_m \rangle = -\langle \Phi_m^L | \{ \widehat{H}\widehat{e}^T \} | \Phi_m \rangle + \langle \Phi_m^L | 1 + S_m | \Phi_m \rangle \langle \Phi_m | \{ \widehat{H}\widehat{e}^T \} \{ 1 + S_m \} | \Phi_v \rangle
\]

\[
= -\langle \Phi_m^L | \{ \widehat{H}\widehat{e}^T \} | \Phi_m \rangle - \langle \Phi_m^L | \delta_{L,m} + S_m | \Phi_m \rangle \text{IP},
\]

(25)

where the superscript \( L (= 1, 2) \) represents excited states from the corresponding DF states, the wide hat symbol denotes connected terms, \( \Delta E_{\text{corr}} \) and \( \text{IP} \) represents the correlation energy and ionization potential of the valence electron \('m'\), respectively. We consider the Dirac-Coulomb (DC) Hamiltonian in our calculation given by

\[
H = [H_0] + [V_{es}]
\]

\[
= \sum_i \Lambda_i^+ \left[ c\alpha \cdot p_i + (\beta - 1)c^2 + V_{\text{nuc}}(r_i) + U(r_i) \right] \Lambda_i^+
\]

\[
+ \sum_{i>j} \frac{\Lambda_i^+ \Lambda_j^+}{r_{ij}} \Lambda_i^+ \Lambda_j^+ - \sum_i \Lambda_i^+ U(r_i) \Lambda_i^+],
\]

(26)

where \( H_0 \) is the DF Hamiltonian, \( V_{es} \) is the Coulomb residual term in atomic units that is neglected in the DF calculation and \( \Lambda^+ \) are the projection operators on to the positive-energy states of the Dirac Hamiltonian in the nuclear \( (V_{\text{nuc}}(r_i)) \) and DF \( (U(r_i)) \) potentials.
The most important triple excitations have been considered by constructing triple excitation operators\[46\]
\[
S^{\rho qr(0)}_{mbc} = \frac{V_{es}T^2_{2(0)} + V_{es}S^0_{m2}}{\epsilon_b + \epsilon_c - \epsilon_q - \epsilon_r},
\]
where $\epsilon$’s are the orbital energies. The above operators are used to construct single and double open-shell cluster amplitudes by connecting further with the CCSD operators and evaluating contributions to IP which are also involved in the amplitude determining equations. Finally, these amplitudes are solved self-consistently.

In the presence of the EDM, the exact atomic wavefunction can be written as
\[
|\Psi_m\rangle = e^T\{1 + S_m\}|\Phi_m\rangle,
\]
where the cluster amplitudes are given by
\[
T = T^{(0)} + d_e T^{(1)},
\]
\[
S_m = S^{(0)}_m + d_e S^{(1)}_m.
\]
$T^{(1)}$ and $S^{(1)}_m$ are the first order in $d_e$ corrections to the cluster operators $T^{(0)}$ and $S^{(0)}_m$, respectively.
In the CCSD method, we have
\[
T^{(1)} = T^{(1)}_1 + T^{(1)}_2,
\]
\[
S^{(1)}_m = S^{(1)}_{1m} + S^{(1)}_{2m}.
\]

The amplitudes of these operators are solved, keeping up to linear in $d_e$, by the following equations
\[
\langle \Phi^L | \overline{H}^{(0)}_N T^{(1)} + \overline{H}^{eff}_{EDM} | \Phi^0 \rangle = 0,
\]
\[
\langle \Phi^L_m | \overline{H}^{(0)}_N S^{(1)}_m + \overline{H}^{(0)}_N T^{(1)} + \overline{H}^{(0)}_N T^{(1)} S^{(0)}_m + \overline{H}^{eff}_{EDM} + \overline{H}^{eff}_{EDM} S^{(0)}_m | \Phi^0_m \rangle = -\langle \Phi^L_m | S^{(1)}_m | \Phi^0_m \rangle \text{IP}_{32}
\]
where Hamiltonian operators with overline as defined as $\overline{H} = e^{-T^{(0)}} \{H\} e^{T^{(0)}}$. These are computed after determining $T^{(0)}$.

After solving the CCSD amplitudes we determine $\langle D \rangle$ by
\[
R = \frac{\langle D \rangle}{d_e} = \frac{\langle \Phi^L_m | \{S^{(1)}_m + (1 + T^{(1)})S^{(0)}_m\} e^{T^{(0)}} D e^{T^{(0)}} \{1 + T^{(1)}\} S^{(0)}_m + S^{(1)}_m \rangle | \Phi^0_m \rangle}{\langle 1 + N^{(0)}_m \rangle}
\]
In the above expression, we define $\overline{D}^{(0)} = e^{T^{(0)}} D e^{T^{(0)}}$ and $N^{(0)}_m = \langle \Phi^L_m | S^{(0)}_m e^{T^{(0)}} e^{T^{(0)}} S^{(0)}_m | \Phi^0_m \rangle$ for the valence electron ‘$m$’. These terms are evaluated using the generalized Wick’s theorem\[44\] by constructing effective one-body, two-body etc. terms.
As explained in our earlier work on EDM arising from scalar- pseudoscalar interaction in Cs and Tl [47], the important RCC terms in the above expression are $D^{(0)}T_1^{(1)}$, $D^{(0)}S_{1m}^{(1)}$ and $D^{(0)}S_{2m}^{(1)}$. The first term corresponds to the core-correlation effects whereas the second and third terms correspond to the valence correlation effects. Core-polarization and pair-correlation effects arising through the singly excited states are considered through $D^{(0)}S_{1m}^{(1)}$ and important core-polarization effects from the doubly excited states are taken into account through $D^{(0)}S_{2m}^{(1)}$. Important excited states that contribute significantly through these terms are given below.

III. CONSTRUCTION OF BASIS FUNCTIONS

The EDM interactions for both closed and open shell atoms are sensitive to the nuclear region. Therefore, the Gaussian type orbitals (GTOs) that produce good wave functions in the nuclear region can be used to calculate accurate $\langle D \rangle$. For atomic wavefunction calculations, they are given by [48]

$$F_{i,k}(r) = r^k e^{-\alpha_i r^2}, \quad (34)$$

where $k = 0, 1, \ldots$ for s,p,... type orbital symmetries, respectively. For the exponents, we have used

$$\alpha_i = \alpha_0 \beta^i - 1. \quad (35)$$

We consider excitations from all occupied orbitals (holes) in both the DF and RCC calculations. The orbitals are generated on a grid as in the numerical code GRASP [49]. The finite size of the nucleus has been accounted for by considering a two-parameter Fermi nuclear charge distribution approximation given by

$$\rho = \frac{\rho_0}{1 + e^{(r-c)/a}}. \quad (36)$$

We use values of $\rho_0$, $c$ and $a$ as given by Parpia and Mohanty [50].

IV. RESULTS AND DISCUSSIONS

In Table I, we present our enhancement factor calculations to the ground state of Fr. We obtain the final result $R = 894.93$ which agrees fairly well with Byrnes et al. who have obtained 910(46) (error bar is quoted as $\sim 5\%$) [41]. However, this is just a coincidence. Byrnes et al. have used a sum-over-states approach and have only considered singly excited valence states as the intermediate states. They have therefore not taken into account pure core correlation and contributions from
TABLE I: Contributions from important RCC terms to the $R = D_a/d_e$ calculations of the ground state in Fr. c.c represents conjugate terms. Here contributions given by *Norm* and *Others* correspond to normalization corrections higher order terms those are not mentioned in this table, respectively.

| RCC terms                     | $R = D_a/d_e$ |
|-------------------------------|---------------|
| Dirac-Fock (core)             | 25.77         |
| Dirac-Fock (virtual)          | 695.44        |
| $DT_1^{(1)} + \text{c.c.}$    | 43.39         |
| $D(0)S_{1m}^{(1)} + \text{c.c.}$ | 1000.19     |
| $D(0)S_{2m}^{(1)}$           | -64.94        |
| $S_{1m}^{(0)}D(0)S_{1m}^{(1)} + \text{c.c.}$ | -18.07     |
| $S_{2m}^{(0)}D(0)S_{1m}^{(1)} + \text{c.c.}$ | -59.18     |
| $S_{1m}^{(0)}D(0)S_{2m}^{(1)} + \text{c.c.}$ | -2.80     |
| $S_{2m}^{(0)}D(0)S_{2m}^{(1)} + \text{c.c.}$ | 19.26     |
| *Norm*                        | -24.42        |
| *Others*                      | 1.51          |
| **Total**                     | 894.93        |

the doubly excited states. In their calculation, the $7s_{1/2} - 7p_{1/2}$ E1 matrix element was taken from experiment and only $7p_{1/2} - 10p_{1/2}$ discrete states were used in the calculation and the contributions of the continuum states were included in an approximate way. Another limitation in the calculation of Byrnes et al is in their treatment of the internal electric field in their parity and time-reversal violating Hamiltonian. They have considered only the potential that an electron sees from the nucleus but not the other electrons of the atom. We have included contributions from all the core-electrons and all possible single and double excited states through the RCC method in our calculation.

We have also explicitly given the DF contributions from core and virtual orbitals in Table I. It is clear from this that the contributions due to core orbitals are not small in the present system. Our $DT_1^{(1)} + \text{c.c.}$ RCC terms at the lowest order correspond to the above DF core contributions. Comparing contributions at the DF and the RCC levels, it shows that the all order core correlation effects are almost twice as much as the DF contribution. Similarly, our $D(0)S_{1m}^{(1)} + \text{c.c.}$ RCC terms at the lowest order corresponds to the DF results only due to the virtual orbitals. From Table I
it is also clear that the all order correlation effects are significant.

**TABLE II:** Break down of $DT_1^{(1)} + c.c.$ contributions using DF reduced E1 matrix elements from core orbitals.

| $n$ | $\langle 7s_{1/2}||D||np_{1/2}\rangle_{DF}$ | $\langle np_{1/2}||T_1^{(1)}||7s_{1/2}\rangle$ | $R$ |
|-----|------------------------------------------|------------------------------------------|----|
| 2   | $-0.15 \times 10^{-3}$                    | 1.55                                     | 0.19 $\times 10^{-3}$ |
| 3   | $0.88 \times 10^{-3}$                     | $-3.35$                                  | $0.24 \times 10^{-2}$ |
| 4   | $-0.52 \times 10^{-2}$                    | 7.56                                     | $0.32 \times 10^{-1}$ |
| 5   | $0.38 \times 10^{-1}$                     | $-20.31$                                 | 0.63 |
| 6   | 0.54                                      | $-100.01$                                | 44.16 |

Contributions from the doubly excited states arise through the $S_{2m}^{(1)}$ operator. It can be seen from the above table that these states contribute to about 7% of the final result, but with opposite sign. Therefore, the error bar quoted (which is $\sim 5\%$) by Byrnes et al. without considering the doubly excited states contributions does not seem to be correct. Again, the normalization correction ($Norm$) in our calculation is also about 3%, which is a significant contribution, and this appears to be missing in the work of Byrnes et al.

The trends exhibited by the correlation effects in the present work are similar to those in the case of rubidium (Rb) [51], but the amount of core correlation effects are substantially larger for Fr. Interestingly, we observe that the correlation contributions for Rb [51], Cs [51] and Fr are about 24%, 22% and 20%, respectively. This is because of the fact that as the size of the system increases contributions from the doubly excited states increases with opposite sign and hence there are strong cancellations in the heavy systems.

In Table III we present the core orbital contributions combining the reduced matrix element of E1 matrix element obtained using DF method and RCC amplitude obtained using $T_1^{(1)}$ operator. This shows that the upper most $p_{1/2}$ core orbital, i.e. $6p_{1/2}$ orbital, contributes almost through this term and the remaining core orbital contributions are small. This can be understood as the energy difference between the valence orbital, $7s_{1/2}$ and $6p_{1/2}$ core orbital is small and hence it contributes large.

As in the case of the core orbital contributions, we have also investigated the role of various virtual orbitals considering the most dominant operator, $S_{2m}^{(1)}$, and E1 matrix element obtained using DF method. These results are reported in Table III. As seen in this table, $7p_{1/2}$, $8p_{1/2}$ and
TABLE III: Break down of $DS_{1m}^{(1)} + c.c.$ contributions using DF reduced E1 matrix elements from important virtual orbitals.

| $n$  | $\langle 7s_{1/2} | D | np_{1/2} \rangle_{DF}$ | $\langle np_{1/2} | S_{1m}^{(1)} | 7s_{1/2} \rangle$ | $R$    |
|------|---------------------------------|---------------------------------|-------|
| 7    | 5.12                            | 227.26                          | 949.69|
| 8    | $-0.57$                         | $-81.71$                        | 37.79 |
| 9    | 0.18                            | 115.55                          | 16.66 |
| 10   | $0.17 \times 10^{-1}$           | $-91.63$                        | $-1.25$|
| 11   | $-0.53 \times 10^{-1}$          | 45.35                           | $-1.95$|
| 12   | $0.17 \times 10^{-1}$           | $-17.37$                        | $-0.24$|
| 13   | $-0.21 \times 10^{-2}$          | 5.17                            | $-0.87 \times 10^{-2}$ |
| 14   | $-0.29 \times 10^{-3}$          | 2.02                            | $-0.48 \times 10^{-3}$ |

$9p_{1/2}$ orbitals contribute the most. In our DF calculations, the orbitals up to $8p_{1/2}$ are bound and $9p_{1/2}$ orbital onwards as continuum orbitals, respectively. Large contribution from the $7p_{1/2}$ orbital can be understood based on the fact that the energy difference between the valence orbital $7s_{1/2}$ and virtual orbital $7p_{1/2}$ is very small and the overlap of these two orbitals is large at distances close to and far away from the nucleus. Since the density of the continuum orbital $9p_{1/2}$ in the nuclear region is large, it also gives a large contribution.

We have also determined the contributions from the most important doubly excited states by combining the $S_{2m}^{(1)}$ operator with the E1 matrix elements obtained using the DF method and given them in Table IV. As a special condition, our $S_{2m}^{(1)}$ can excite the valence orbital $7s_{1/2}$ to itself (a spectator), but other virtuals may go to the core orbitals by the dipole operator. This is a special type of core-polarization effect and which manifests through doubly excited states. From the above table, we find that virtual orbitals from the $d$ symmetry are contribute significantly through this process.

V. CONCLUSION

We have discussed the relativistic theory of the electric dipole moments of paramagnetic atoms arising from the electric dipole moment of the electron. We have employed the relativistic coupled-cluster method to calculate the atomic wavefunctions to all orders in Coulomb interaction and
TABLE IV: Break down of $DS^{(1)}_{2m} + c.c.$ contributions using DF reduced E1 matrix elements from important doubly excited states. Here indices $m$, $l$ and $k$ represent valence, core and virtual orbitals, respectively.

| $l$ | $k$ | $\langle l||D||k \rangle_{DF}$ | $\langle ml||S^{(1)}_{2m}||mk \rangle_R$ | $R$ |
|-----|-----|-------------------------------|---------------------------------|-----|
| $6p1/2$ | $7s_{1/2}$ | 0.54 | 11.05 | -5.25 |
| $6p1/2$ | $10s_{1/2}$ | 0.54 | 13.78 | -2.22 |
| $6p1/2$ | $9d_{3/2}$ | -1.10 | -11.95 | -2.22 |
| $6p1/2$ | $10d_{3/2}$ | -1.48 | 14.89 | -4.93 |
| $6p3/2$ | $10d_{3/2}$ | -0.74 | -27.17 | -4.09 |
| $6p3/2$ | $7d_{5/2}$ | 1.78 | -25.17 | -10.24 |
| $6p3/2$ | $8d_{5/2}$ | -1.18 | 16.31 | -4.48 |
| $6p3/2$ | $9d_{5/2}$ | -1.80 | 24.87 | -10.55 |
| $6p3/2$ | $10d_{5/2}$ | -2.21 | 27.31 | -14.80 |
| $6p3/2$ | $11d_{5/2}$ | 1.10 | -7.85 | -2.50 |

one order in the $\mathcal{P}$ and $\mathcal{T}$ violating interaction and obtained the EDM enhancement factor for francium; the heaviest of all the alkali atoms. Our result has been compared with the available semi-empirical result and contributions from various correlation effects and important intermediate states have been explicitly given.

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