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Relativistic Coupled Cluster (RCC) Computation of the Electric Dipole Moment Enhancement Factor of Francium Due to the Violation of Time Reversal Symmetry[†]

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A relativistic many-body theory for the electric dipole moment (EDM) of paramagnetic atoms arising from the electric dipole moment of the electron is presented and implemented. The relativistic coupled-cluster method with single and double excitations (RCCSD) using the Dirac−Coulomb Hamiltonian and a weak parity and time reversal violating interaction to the first-order of perturbation has been employed to obtain the EDM enhancement factor for the ground state of the Fr atom due to the intrinsic EDM of the electron. The trends of different correlation effects and the leading contributions from different physical states are discussed. Our results in combination with that of the Fr EDM experiment that is currently in progress possess the potential to probe the validity of the standard model (SM) of elementary particle physics.

I. Introduction

The standard model (SM) of elementary particle physics given by Glashow, Weinberg, and Salam described by the SU(3) × SU(2) × U(1) gauge group satisfactorily explains most of the phenomena observed so far on the fundamental interactions.[1−3] 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,[4] the multi-Higgs model,[5] or supersymmetry models[6] will have a significant impact on our understanding of the fundamental forces between the elementary particles in nature.

Detailed studies of the fundamental interactions have a bearing on chemical and biological processes as well. For example, it is believed that the violation of parity could be one of the fundamental reasons[7] behind the "homochirality" of biomolecules.[8−10] Several other possibilities have, of course, also been suggested. In the same vein, any time reversal symmetry ($\mathscr{T}$) 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 enantiomeric excess, where none is expected from the electromagnetic interaction.[11] One can, in fact, distinguish between the chirality brought out by $\mathscr{T}$ -invariant and $\mathscr{T}$-noninvariant enantiomerism, 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.[11] 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 system on the basis of the Wigner−Eckart theorem.[12] 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 both $\mathscr{T}$ invariance and parity ($\mathscr{P}$) symmetry.[13,14] The SM which conserves the combined transformations of charge conjugation ($\mathscr{C}$), $\mathscr{P}$, and $\mathscr{T}$ symmetries (known as the CPT theorem[15]), predicts $\mathscr{P}$ and $\mathscr{CP}$ violations in weak interactions.[45,46] A possible observation of a nonzero EDM in an atom would be a direct signature of $\mathscr{T}$ violation. An EDM has not been observed so far for whether it is in elementary particles or composite systems. The SM predicts an upper limit on the electron EDM on the order of 10^{-38} ecm,[16,17] while other suggested models predict this value to be almost 10 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 of the measurements of atomic EDMs using the tabletop experiments and the calculations of atomic EDM enhancement factors.

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In 1963, Schiff[18] argued that the permanent EDM of an atom vanishes under the assumption that the constituent nonrelativistic point-like particles such as electrons in an atom interact only electrostatically. It was, however, put forth by Salpeter[19] and Sachs and Scwebel[20] 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[14] 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 nonzero 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 $\mathscr{P},\mathscr{T}$ violating electron−nucleus interactions. At the elementary particle level, electrons may possess intrinsic EDMs, described 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 and quarks may manifest at different levels as electrons−nucleons to electrons−nucleus interactions. The $\mathscr{P}$ and $\mathscr{T}$ violating electron−nucleus interactions can either be scalar−pseudoscalar (S−PS), with a coupling constant C_S, or a tensor−pseudotensor (T−PT) interaction, described by 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 $\mathscr{P}$- and $\mathscr{T}$-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 $\mathscr{P}$-, and $\mathscr{T}$-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 Pauli exclusion principle, it will add up to 0 if hyperfine interactions are excluded. These $\mathscr{P}$- and $\mathscr{T}$-violating electron−nucleus interactions will provide a useful tool in understanding the $\mathscr{CP}$ violation from the semileptonic sectors. Using the knowledge of $\mathscr{CP}$ violation obtained in these atomic EDM experiments, one can also constrain different models of $\mathscr{CP}$ 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.[21] In particular, he demonstrated by carrying out relativistic calculations that the atomic EDMs of thallium (Tl) and cesium (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.[22−24] 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[25,26]

$$R \propto \frac{Z^3\alpha^2}{J(J+1/2)(J+1)} \tag{1}$$

where α is the fine-structure constant. This formula given for the order of magnitude estimate of the 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 free 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 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

$$H_{\text{int}} = -\vec{D}\cdot\vec{E} - \vec{\mu}\cdot\vec{B} \tag{2}$$

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

$$\Delta\omega_{\text{E}} = \frac{2DE}{\hbar} \tag{3}$$

It corresponds to $\Delta\omega_{\text{E}} \simeq 10^{-6}$ Hz for $D \approx 10^{-25}$ ecm and $E =$ 10 KV/cm. This frequency shift corresponds to a magnetic field of 10^{-9} G for a diamagnetic atom and 10^{-12} 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 v/c is given in the moving frame of the atoms as

$$\vec{B}_{\text{m}} = \frac{\vec{v}}{c^2} \times \vec{E} \tag{4}$$

For $\vec{v} = 300$ m/s and $\vec{E} = 10$ KV/cm, the motional magnetic field is $\vec{B}_{\text{m}} = 3 \times 10^{-13}$ G. This tiny magnetic field which is proportional to the applied electric field can also give rise to a frequency shift which can mimic a genuine EDM signal. In the Tl experiment, two counterpropagating beams were used to minimize this effect.[27] The 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.[28] 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.

The EDM experiments based on laser-cooled and trapped atoms, in principle, have the advantages of both the beam and the cell experiments.[29−33] In these experiments, one can apply large electric fields, and the coherence times are long. The problems due to the leakage currents can be overcome using a suitable configuration for the laser trap. The systematic error due to the motional magnetic field is virtually nonexistent because of the extremely low average velocity of the cold atoms.

Atomic theory is needed in combination with experiments to extract a variety of $\mathscr{T}$-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,[14] a number of relativistic many-body calculations on atoms of experimental interest have been carried out in the last two decades.[34] Ingenious experiments were initiated in the 1980s to observe the EDMs of mercury (Hg), Cs, and Tl.[27,28,35] Subsequently, systematic errors have been improved in these experiments, and today, the most accurate results are available in Hg[36] for diamagnetic atoms and Tl for paramagnetic atoms.[37] 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.[38−40] However, these calculations are not as advanced as their atomic counterparts. 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 studies on Fr has been carried out at SUNY Stony Brook using the laser trapping technique,[41] and it has been proposed both for EDM[42] and atomic parity violation (APV)[43] measurements. In fact, there is a preliminary calculation available for the enhancement factor of Fr using the sum-over-states approach, where the contributions from the important bound states are included and the contributions of the continuum states are taken in an approximate way.[44] 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 $\mathscr{P}$- and $\mathscr{T}$-violating electron−nucleus scalar−pseudoscalar interactions and intrinsic electron EDM up to first order with the constributions involving all possible single and double excitations from the continuum to calculate R for Fr. In this procedure, we will also demonstrate contribution from important intermediate states and highlight the role of various electron correlation effects.

II. Theory of Atomic EDM

A. 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 pseudoscalar Dirac operator γ_5.

The pseudoscalar perturbation Hamiltonian for the intrinsic EDM of an electron then reads

$$H_{\mathrm{EDM}} = \mathrm{i}\frac{d_{\mathrm{e}}}{2}(\bar{\Psi}\gamma_5\gamma_\mu\gamma_\nu\Psi)F_{\mu\nu} = -\frac{d_{\mathrm{e}}}{2}(\bar{\Psi}\gamma_5\sigma_{\mu\nu}\Psi)F_{\mu\nu} \tag{5}$$

where d_{e} is the intrinsic EDM of the electron, $\sigma_{\mu\nu} = -\mathrm{i}\gamma_\mu\gamma_\nu$ ($\mu \neq \nu$), $F_{\mu\nu}$ is the elecromagnetic field tensor, and the γ_μ's are the Dirac matrices.

In the Pauli approximation, eq 5 reduces, in atomic units, to

$$H_{\mathrm{EDM}} = -d_{\mathrm{e}}\beta(\vec{\sigma}\cdot\vec{E} + \mathrm{i}\vec{\alpha}\cdot\vec{H}) \tag{6}$$

where $\vec{\alpha}$, β, and $\vec{\sigma}$ are the Dirac matrices and the vectors $\vec{E}$ and $\vec{H}$ are the total electric and magnetic fields at the site of the electron. The second term on 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 nonrelativistic limit of this interaction is $-d_{\mathrm{e}}\vec{\sigma}^{\mathrm{P}}\cdot\vec{E}$, where $\vec{\sigma}^{\mathrm{P}}$ is the Pauli spin matrix. This form of the interaction produces a zero atomic EDM;[14] 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.

B. 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

$$H = H_0 + H_{\mathrm{EDM}} \tag{7}$$

where H_0 is the atomic Hamiltonian given by

$$H_0 = \sum_i [c\alpha\cdot p_i + (\beta - 1)mc^2 + V_{\mathrm{nuc}}(r_i)] + \frac{e^2}{4\pi\epsilon_0}\sum_{i\neq j}\frac{1}{r_{ij}} \tag{8}$$

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

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

$$H^{(1)} = H_{\mathrm{EDM}} - d_{\mathrm{e}}\sum_i \beta\vec{\sigma}_i\cdot\vec{E} - e\sum_i \vec{r}_i\cdot\vec{E} \tag{9}$$

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

$$\begin{aligned} E_m^{(1)} &= \langle\Psi_m^{(0)}|H^{(1)}|\Psi_m^{(0)}\rangle \\ &= -\sum_i [\langle\Psi_m^{(0)}|d_{\mathrm{e}}\beta\vec{\sigma}_i\cdot\vec{E}_i^{\mathrm{int}}|\Psi_m^{(0)}\rangle - \\ &\qquad \langle\Psi_m^{(0)}|d_{\mathrm{e}}\beta\vec{\sigma}_i\cdot\vec{E}|\Psi_m^{(0)}\rangle - \langle\Psi_m^{(0)}|e\vec{r}_i\cdot\vec{E}|\Psi_m^{(0)}\rangle] \end{aligned} \tag{10}$$

Assuming that the applied field is in the positive z-direction

$$E_m^{(1)} = \sum_j [-d_{\rm e}\langle\Psi_m^{(0)}|\beta\vec{\sigma}_{z,j}\cdot\vec{E}_j^{\rm int}|\Psi_m^{(0)}\rangle - d_{\rm e}\langle\Psi_m^{(0)}|\beta\vec{\sigma}_{z,j}|\Psi_m^{(0)}\rangle|\vec{E}| - \langle\Psi_m^{(0)}|e\vec{z}_j|\Psi_m^{(0)}\rangle|\vec{E}|] \quad (11)$$

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

$$E_m^{(1)} = -d_{\rm e}\langle\Psi_m^{(0)}|\beta\sum_j\vec{\sigma}_{z,j}|\Psi_m^{(0)}\rangle|\vec{E}| \quad (12)$$

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

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

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

$$\begin{aligned} E_m^{(2)} &= \langle\Psi_m^{(0)}|H^{(1)}|\Psi_m^{(1)}\rangle \\ &= \sum_{n\neq m}\frac{\langle\Psi_m^{(0)}|H^{(1)}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|H^{(1)}|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} \end{aligned} \quad (14)$$

Upon inserting the expression for $H^{(1)}$ into 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

$$E_m^{(2)} = \left\{\sum_{n\neq m}\frac{\langle\Psi_m^{(0)}|H_{\rm EDM}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|e\sum_j\vec{z}_j|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} + \sum_{n\neq m}\frac{\langle\Psi_n^{(0)}|e\sum_j\vec{z}_j|\Psi_m^{(0)}\rangle\langle\Psi_m^{(0)}|H_{\rm EDM}|\Psi_n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}}\right\}|\vec{E}| \quad (15)$$

Thus, the total shift in energy would be

$$\begin{aligned} E_m &= E_m^{(1)} + E_m^{(2)} \\ &= \left\{-d_e\langle\Psi_m^{(0)}|\beta\sum_j\vec{\sigma}_{z,j}|\Psi_m^{(0)}\rangle + \sum_{n\neq m}\frac{\langle\Psi_m^{(0)}|H_{EDM}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|e\sum_j\vec{z}_j|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} + \sum_{n\neq m}\frac{\langle\Psi_n^{(0)}|e\sum_j\vec{z}_j|\Psi_m^{(0)}\rangle\langle\Psi_m^{(0)}|H_{EDM}|\Psi_n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}}\right\}|\vec{E}| \end{aligned} \quad (16)$$

The coefficient of the linear shift in energy due to the applied electric field is the total electric dipole moment of an atom, that is, $\varepsilon = -\vec{D}\cdot\vec{E}$. Thus, the total EDM of an atom is given by

$$\langle D\rangle = \left\{d_{\rm e}\langle\Psi_m^{(0)}|\beta\sum_j\vec{\sigma}_{z,j}|\Psi_m^{(0)}\rangle - \sum_{n\neq m}\frac{\langle\Psi_m^{(0)}|H_{\rm EDM}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|e\sum_j\vec{z}_j|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} - \sum_{n\neq m}\frac{\langle\Psi_n^{(0)}|e\vec{z}|\Psi_m^{(0)}\rangle\langle\Psi_m^{(0)}|H_{\rm EDM}|\Psi_n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}}\right\} \quad (17)$$

In the nonrelativistic case, that is, when $\beta = 1$, coincidentally, the last two terms in the above expression can be simplified to obtain the term which exactly cancels with the first term in the above expression, and thus, one gets a vanishing average atomic EDM, even when the electron is assumed to possess intrinsic EDM. This result was pointed out by Schiff in 1963, who treated electrons as nonrelativistic particles. One can also show that, despite the fact that one considers the relativistic form of H_0, the total atomic EDM effectively vanishes by the similar cancellation of its different terms unless one considers the relativistic form of the interaction Hamiltonian. Therefore, in the present calculation, both H_0 and $H_{\rm EDM}$ are treatd relativistically.

The important role of β in the interaction Hamiltonian has been pointed out by Salpeter (1958), who argued that the interaction of the EDM with the electromagnetic field has to be included into the Dirac equation in a Lorentz covariant manner. Later on, Sandars (1968) also emphasized the fact that the presence of β is the reason why Schiff's general theorem on the absence of effects linear in EDMs does not apply in the relativistic case.

The total atomic EDM given by eq 17 can be further simplified to the effective one-electron form given by[47,48]

$$\langle D\rangle = \sum_j\left[\frac{2icd_{\rm e}}{\hbar}\left\{\sum_{n\neq m}\frac{\langle\Psi_m^{(0)}|\beta\gamma_5 p_j^2|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\vec{z}_j|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}}\right\}\right] + \text{h.c.} \quad (18)$$

Here, β and γ_5 are the Dirac matrices, $\vec{p}$ is the 3-momentum, $\hbar$ ($=h/2\pi$) 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. Equation 18 shows that H_{EDM} in eq 17 reduces to an effective one-body term given by $H_{\mathrm{EDM}}^{\mathrm{eff}} = -(2icd_e/e\hbar)\sum_j \beta\gamma_5 p_j^2$.

$H_{\mathrm{EDM}}^{\mathrm{eff}}$ 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 mth state atomic wave function as

$$|\Psi_m\rangle = |\Psi_m^{(0)}\rangle + \left(\frac{d_e}{ea_0}\right)|\Psi_m^{(1)}\rangle \tag{19}$$

where a_0 is the Bohr radius of the atom.

The above first-order perturbed wave functions due to $H_{\mathrm{EDM}}^{\mathrm{eff}}$ 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

$$(H^{(0)} - E_m^{(0)})|\Psi_m^{(1)}\rangle = (E_m^{(1)} - H_{\mathrm{EDM}}^{\mathrm{eff}})|\Psi_m^{(0)}\rangle \tag{20}$$

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

C. RCC Theory of Atomic EDM. Using RCC theory, the atomic wave function $|\Psi_m^{(0)}\rangle$ for a single valence (m) open-shell system interacting via the DC Hamiltonian is given by[49,50]

$$|\Psi_m^{(0)}\rangle = e^{T^{(0)}}\{1 + S_m^{(0)}\}|\Phi_m\rangle \tag{21}$$

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

In the relativistic coupled-cluster method with single and double excitations of the (RCCSD) method, we have

$$\begin{aligned} T^{(0)} &= T_1^{(0)} + T_2^{(0)} \\ S_m^{(0)} &= S_{1m}^{(0)} + S_{2m}^{(0)} \end{aligned} \tag{22}$$

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. In the case of single valence atoms, the latter excites a valence electron and a core electron together as a pair to the higher virtual states. The amplitudes corresponding to these operators can be determined by solving the relativistic coupled cluster singles and doubles equations. The cluster amplitudes of $T^{(0)}$ for $|\Phi_0\rangle$ are obtained by solving the following set of equations

$$\langle\Phi^L|\{\overbrace{H_N e^{T^{(0)}}}\}|\Phi_0\rangle = 0 \ \forall\Phi^L \notin \Phi_0, \ \forall L = 1,2 \tag{23}$$

where $\langle\Phi^L|$ ($L = 1,2$) are, respectively, the single and double excitations from $\langle\Phi_0|$. The correlation energy for the Φ_0 is given by $\langle\Phi_0|\{\overbrace{H_N e^{T^{(0)}}}\}|\Phi_0\rangle = \Delta E_{\mathrm{corr}}$. In what follows, it is convenient to separate the operator part $\bar{H}_N^0$ of $\overbrace{H_N e^{T^{(0)}}}$ from the number component ΔE_{corr}

$$\overbrace{H_N e^{T^{(0)}}} = \bar{H}_N^0 + \triangle E_{corr} \tag{24}$$

This allows us to write compact working equations for the one-valence cluster amplitudes of both S_m^0 and the correlation energy of the one-valence state $\{1 + S_m^0\}|\Phi_m\rangle$.

The cluster amplitudes of S_m^0 are given by

$$\begin{aligned} \langle\Phi_m^K|\bar{H}_N^0 + \overbrace{\bar{H}_N^0 S_m^0}|\Phi_m\rangle = \langle\Phi_m^K|S_m^0|\Phi_m\rangle\langle\Phi_m|\bar{H}_N^0 + \\ \overbrace{\bar{H}_N^0 S_m^0}|\Phi_m\rangle \ \forall\Phi_m^K, \ \forall K = 1,2 \end{aligned} \tag{25}$$

where $\langle\Phi_m^K|(K = 1,2)$ are the single and double excitations containing the valence orbitals m out of Φ_m. The "energy shift" $\langle\Phi_m|\bar{H}^0 + \overbrace{\bar{H}^0 S_m^0}|\Phi_m\rangle$ is, in fact, just the correlated IP for the state $\{1 + S_m^0\}|\Phi_m\rangle$.

In all of the above equations, $H_{\mathrm{N}} = H - E_{\mathrm{DF}}$; E_{DF} is the Dirac–Fock energy, and the bold denotes connected terms. We consider the positive energy sector of the Dirac–Coulomb (DC) Hamiltonian in our calculation given by

$$\begin{aligned} H^{\mathrm{DC}} &= [H_0] + [V_{\mathrm{es}}] \\ &= \sum_i^N \Lambda_i^+[c\alpha \cdot p_i + (\beta - 1)c^2 + V_{\mathrm{nuc}}(r_i) + \\ &\quad U(r_i)]\Lambda_i^+ + \left[\sum_{i>j}^N \Lambda_i^+\Lambda_j^+\frac{1}{r_{ij}}\Lambda_j^+\Lambda_i^+ - \sum_i^N \Lambda_i^+ U(r_i)\Lambda_i^+\right] \end{aligned} \tag{26}$$

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 Λ^+ are the projection operators onto the positive energy states of the Dirac Hamiltonian in the nuclear ($V_{\mathrm{nuc}}(r_i)$) and DF ($U(r_i)$) potentials.

The most important triple excitations in the absence of the EDM term have been considered by constructing triple excitation operators in a perturbative manner[51]

$$S_{mbc}^{pqr(0)} = \frac{\overbrace{V_{es}T_2^{(0)}} + \overbrace{V_{es}S_{2m}^{(0)}}}{\epsilon_m + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \tag{27}$$

where ϵ's are the orbital energies. The above $S_{3m}^{(0)}$ operators are used to construct single and double open-shell cluster amplitudes by connecting them with the converged amplitudes of the CCSD operators. Further, they are used in evaluating the contributions to the IP of the valence states, through which they also appear in the amplitude-determining equations. Thus, the partial triples are included only in the unperturbed open-shell CC equations.

In the presence of the EDM as the perturbation, the perturbed atomic wave function can be written as

$$|\Psi_m\rangle = e^{\mathrm{T}}\{1 + S_m\}|\Phi_m\rangle \tag{28}$$

where up to the first order of EDM the cluster amplitudes are given by

$$\begin{aligned} T &= T^{(0)} + d_{\mathrm{e}}T^{(1)} \\ S_m &= S_m^{(0)} + d_{\mathrm{e}}S_m^{(1)} \end{aligned} \qquad (29)$$

$T^{(1)}$ and $S_m^{(1)}$ are the perturbed cluster operators, which contain one order in d_{e}, corresponding to $T^{(0)}$ and $S_m^{(0)}$, respectively. In the CCSD method, we have

$$\begin{aligned} T^{(1)} &= T_1^{(1)} + T_2^{(1)} \\ S_m^{(1)} &= S_{1m}^{(1)} + S_{2m}^{(1)} \end{aligned} \qquad (30)$$

The amplitudes of these operators are solved, keeping up to the terms which are linear in d_{e}, by the following equations

$$\langle\Phi^L|\overbrace{\overline{H^{(0)}}T^{(1)}} + \overline{H_{EDM}}|\Phi_0\rangle = 0, \qquad (31)$$

$$\begin{aligned} &\langle\Phi_m^L|\overbrace{\overline{H^{(0)}}S_m^{(1)}} + \overbrace{\overline{H^{(0)}}T^{(1)}} + \overbrace{\overline{H^{(0)}}T^{(1)}S_m^{(0)}} + \overline{H_{EDM}} + \overbrace{\overline{H_{EDM}}S_m^{(0)}}|\Phi_m\rangle \\ &\quad = -\langle\Phi_m^L|S_m^{(1)}|\Phi_m\rangle\langle\Phi_m|H_{eff}|\Phi_m\rangle \end{aligned} \qquad (32)$$

The barred operators $\bar{A}$ are given by $\exp(-T^{(0)})A\exp(T^{(0)})$.

After solving for the unperturbed and perturbed CCSD amplitudes, we determine $\langle D\rangle$ by

$$\begin{aligned} R &= \frac{\langle D\rangle}{d_e} \\ &= \frac{\langle\Phi_m|\{\overbrace{\{1+S_m^{(0)\dagger}\}\tilde{D}^{(0)}\{T^{(1)}+T^{(1)}S_m^{(0)}+S_m^{(1)}\}}\}_1^d + \{\overbrace{\{S_m^{(1)\dagger}+S_m^{(0)\dagger}T^{(1)\dagger}+T^{(1)\dagger}\}\tilde{D}^{(0)}\{1+S_m^{(0)}\}}\}_1^d|\Phi_m\rangle_{conn}}{\langle\Phi_m|e^{T^{(0)\dagger}}e^{T^{(0)}} + S_m^{(0)\dagger}e^{T^{(0)\dagger}}e^{T^{(0)}}S_m^{(0)}|\Phi_m\rangle_{conn}} \end{aligned} \qquad (33)$$

where the entire matrix elements in the numerator and the denominator are fully connected and only the diagonal composites with one valence creation and annihilation operator contribute to these quantities. The proof of this assertion is somewhat involved, and we present it in the Appendix.

In the above expression, we define $\tilde{D}^{(0)} = e^{\mathrm{T}^{(0)\dagger}}De^{\mathrm{T}^{(0)}}$. These terms are evaluated using the generalized Wick's theorem[49] by constructing effective one-body, two-body, and so forth terms.

As explained in our earlier work on EDM arising from scalar−pseudoscalar interaction in Cs and Tl,[52] the important RCC terms in the above expression are $\tilde{D}^{(0)}T_1^{(1)}$, $\tilde{D}^{(0)}S_{1m}^{(1)}$, and $\tilde{D}^{(0)}S_{2m}^{(1)}$. 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 $\tilde{D}^{(0)}S_{1m}^{(1)}$, and important core polarization effects from the doubly excited states are taken into account through $\tilde{D}^{(0)}S_{2m}^{(1)}$. Important excited states that contribute significantly through these terms are given in section III.

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 are used to calculate accurate $\langle D\rangle$. For the atomic wave function calculations, they are given by[53]

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

where $k = 0, 1, \ldots$ for s, p,... orbital symmetries, respectively. For the Gaussian exponents, we have used the even tempering condition[54]

$$\alpha_i = \alpha_0\beta^{i-1} \qquad \text{where } i = 1, 2, \ldots, N_{\mathrm{bas}} \qquad (35)$$

where N_{bas} is the number of basis functions for each symmetry. We have considered 9 relativistic symmetries in the present calculations with 35 basis functions for $s_{1/2}$, 32 for both $p_{1/2}$ and $p_{3/2}$, 30 for $d_{3/2}$ and $d_{5/2}$, and 25 each for $f_{5/2}$, $f_{7/2}$, $g_{7/2}$, and $g_{9/2}$ symmetries. The Gaussian parameters are chosen to be 0.00525 and 2.73 for α_0 and β, respectively, common for all of the symmetries. This approach where the Gaussian exponents are the same for all of the symmetries is termed the Universal Basis. The orbitals are generated on a numerical grid similar to the one used in the numerical code GRASP.[55] The finite size of the nucleus has been accounted for by considering a two-parameter Fermi nuclear charge distribution approximation given by

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

We use values of ρ_0, c, and a as given by Parpia and Mohanty.[56]

For the RCC calculations, we have frozen the outermost virtual orbitals because of their diminishing contributions and have only considered 14s, 13p, 12d, 9f, and 8g number of active orbitals. This includes 9, 7, 6, 3, and 1 number of bound orbitals in s, p, d, f, and g symmetries, respectively. We have considered the excitations from all of the occupied orbitals (holes) to all possible virtual states in our calculations.

IV. Results and Discussions

In Table 1, 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 that of Byrnes et al., who have obtained 910(46) (error bar is quoted as ~5%).[44] 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 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 of the core electrons and all possible single and double excited states through the RCC method in our calculation.0

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

TABLE 1: Contributions from Important RCC Terms to the $R = D_a/d_e$ Calculations of the Ground State in Fr[a]

RCC terms	$R = D_a/d_e$
Dirac–Fock (core)	25.77
Dirac–Fock (virtual)	695.44
$DT_1^{(1)}$ + h.c.	43.39
$\overline{D}^{(0)}S_{1m}^{(1)}$ + h.c.	1000.19
$\overline{D}^{(0)}S_{2m}^{(1)}$ + h.c.	–64.94
$S_{1m}^{(0)\dagger}\overline{D}^{(0)}S_{1m}^{(1)}$ + h.c.	–18.07
$S_{2m}^{(0)\dagger}\overline{D}^{(0)}S_{1m}^{(1)}$ + h.c.	–59.18
$S_{1m}^{(0)\dagger}\overline{D}^{(0)}S_{2m}^{(1)}$ + h.c.	–2.80
$S_{2m}^{(0)\dagger}\overline{D}^{(0)}S_{2m}^{(1)}$ + h.c.	19.26
norm	–24.42
others	1.51
total	894.93

[a] Here, h.c. represents hermitian conjugate terms. The contributions given by *norm* and *others* correspond to the normalization correction and the higher-order terms not shown in this table, respectively.

TABLE 2: Breakdown of $DT_1^{(1)}$ + h.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	-0.15×10^{-3}	1.55	0.19×10^{-3}
3	0.88×10^{-3}	–3.35	0.24×10^{-2}
4	-0.52×10^{-2}	7.56	0.32×10^{-1}
5	0.38×10^{-1}	–20.31	0.63
6	0.54	–100.01	44.16

TABLE 3: Breakdown of $DS_{1m}^{(1)}$ + h.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	0.17×10^{-1}	–91.63	–1.25
11	-0.53×10^{-1}	45.35	–1.95
12	0.17×10^{-1}	–17.37	–0.24
13	-0.21×10^{-2}	5.17	-0.87×10^{-2}
14	-0.29×10^{-3}	2.02	-0.48×10^{-3}

Contributions from the doubly excited states arise through the $S_{2m}^{(1)}$ operator. It can be seen from the Table 1 that these states contribute to about 7% of the final result, but with opposite sign. Therefore, the error bar quoted (which is ~5%) by Byrnes et al. without considering the contributions from the doubly excited states 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),[57] but the amount of core correlation effects is substantially larger for Fr. Interestingly, we observe that the correlation contributions for Rb,[57] Cs,[57] 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 2, we present the core orbital contributions combining the E1 reduced matrix element obtained using the DF method and the RCC amplitude obtained using $T_1^{(1)}$ operator. This shows that the uppermost $p_{1/2}$ core orbital, that is, the $6p_{1/2}$ orbital, contributes almost entirely for the DT_1^1 term, and the remaining core orbital contributions are relatively small. This can be understood as the energy difference between the valence orbital, $7s_{1/2}$, and 6p1/2 core orbital is quite small, and hence, its contribution is 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, $S_{1m}^{(1)}$, and the E1 reduced matrix element obtained using the DF method. These results are reported in Table 3. As seen in this table, $7p_{1/2}$, $8p_{1/2}$, and $9p_{1/2}$ orbitals contribute the most. In our DF calculations, the orbitals up to $8p_{1/2}$ are bound, and the $9p_{1/2}$ and higher orbitals are continuum orbitals. 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

TABLE 4: Breakdown of $DS_{2m}^{(1)}$ + h.c. Contributions Using DF Reduced E1 Matrix Elements from Important Doubly Excited States[a]

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

[a] Here, indices *m*, *l*, and *k* represent valence, core, and virtual orbitals, respectively.

with the E1 matrix elements obtained using the DF method and given in Table 4. 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, which manifests through doubly excited states. From the Table 3, we find that virtual orbitals from the d symmetry contribute significantly through this process.

V. Conclusion

We have presented in some detail the relativistic theory (RCC) of the electric dipole moments of paramagnetic atoms arising from the electric dipole moment of the electron. We have employed the theory method to calculate the atomic wave functions of Fr^+ and Fr, taking into account the orbital relaxation and pair correlations to all orders (RCCSD) in both Fr^+ and Fr cases. For the latter, perturbative inclusion of the three-body cluster operator has also been considered. $\mathscr{P}$- and $\mathscr{T}$-violating interactions have been considered up to the first order, and the EDM enhancement factor was obtained for francium, the heaviest of all of the alkali atoms. Our result has been compared with the available semiempirical result and contributions from various correlation effects, and important intermediate states have been explicitly given.

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Appendix

Expression of the Expectation Value of an Operator for a One-Dimensional One-Valence Model Space. In this appendix, we derive the expression of the expectation value of an operator A, taken with respect to a one-valence exact function $\exp(T)\{1 + S_m^0\}|\Phi_m\rangle$, where *T* corresponds to the vacuum cluster operator and S_m is the valence excitation operator with respect to the one-valence model determinant $|\Phi_m\rangle = a_m^\dagger\Phi$. Although the manipulations that we invoke to arrive at an expression of $\langle A\rangle$ as a ratio of two connected quantities are generally valid for arbitrary open-shell states, we will confine ourselves in this appendix to the specific relevant case of the one-valence particle problem only.

In order to arrive at the appropriate expression for $\langle A\rangle$, it will be useful to introduce the diagonal components of an operator X (either an elementary operator like A or a composite) according to the number of the valence destruction and creation operators. Thus, X_0^d is the diagonal component X^{d} of X. Similarly, X_1^d is the one-valence component of the diagonal part X.

$$X_1^{\mathrm{d}} = x_{1mm}\{a_m^\dagger a_m\} \tag{A1}$$

With this, we can write a simplified expression for A. We have

$$\langle A\rangle = \frac{\langle\Phi_m|\{1 + S_m^\dagger\}\exp(T^\dagger)A\exp(T)\{1 + S_m\}|\Phi_m\rangle}{\langle\Phi_m|\{1 + S_m^\dagger\}\exp(T^\dagger)\exp(T)\{1 + S_m\}|\Phi_m\rangle} \tag{A2}$$

We write both the numerator and the denominator in eq A2 in normal order with respect to Φ as terms with various contractions. The only surviving terms will be the one diagonal composite with no uncontracted lines, that is, the zero-body, and another with just a one-body one-valence operator, taken as expectation values with respect to $|\Phi_m\rangle$.

Let us consider the denominator first. Using Wick's Theorem, we can discern two sets of terms, (a) one set where no $S_m/S_m^\dagger$ operators are connected with A (such terms can be denoted as $[\exp(T^\dagger)A\exp(T)]_{\mathrm{conn}}$, and they are grouped as either zero-body or one-body) and (b) another set where $S_m/S_m^\dagger$ operators are also contracted with A, apart from the arbitrary number of $T^\dagger$ and *T* also connected in the composite; these are necessarily one-valence diagonal operators. Let us denote by the X_T^d the terms with only A and T and by X_{TS}^d terms containing both S and T joined to A. X_T^d and X_{TS}^d are, by construction, connected. Since the maximum valence rank of any expectation value $\langle\Phi_m|...|\Phi_m\rangle$ is one, we may write the numerator of eq A2 as

$$\begin{aligned}\langle\Phi_m|\overbrace{\{1+S_m^\dagger\}exp(T^\dagger)exp(T)\{1+S_m\}}|\Phi_m\rangle X_{0T}^d\langle\Phi_m|exp(T^\dagger)exp(T)|\Phi_m\rangle \\ +\langle\Phi_m|\{\overbrace{exp(T^\dagger)exp(T)\}}_1^d|\Phi_m\rangle X_{1TS}^d\langle\Phi|exp(T^\dagger)exp(T)|\Phi\rangle\end{aligned} \tag{A3}$$

X_{0T}^d and X_{1TS}^d denote respectively the zero-valence and the one-valence components of X_T^d and X_{TS}^d. Hence, eq A2 can be written as

$$\langle A\rangle = \langle\Phi|exp(T^\dagger)Aexp(T)|\Phi\rangle_{conn} + \frac{\langle\Phi_m|\{S_m\}exp(T^\dagger)exp(T)\{S_m\}|\Phi_m\rangle_{conn}}{\langle\Phi_m|[\overbrace{\{S_m\}exp(T^\dagger)exp(T)\{S_m\}}]_1^d|\Phi_m\rangle_{conn} + \langle\Phi_m|\{exp(T^\dagger)exp(T)\}_1^d|\Phi_m\rangle_{conn}} \tag{A4}$$

Thus, $\langle A\rangle$ consists of a contribution from the correlated vacuum (the first term) and a ratio of one-valence connected composites in both the numerator and the denominator. When A is the dipole electric operator D and the Hamiltonian excludes the $\mathscr{CP}$-violating term, $\langle\Phi|\exp(T^\dagger)A\exp(T)|\Phi\rangle_{\mathrm{conn}}$ is 0. All of the other terms start contributing only when the $\mathscr{CP}$-violating term is added to the Hamiltonian, and eq A4 will be nonzero if each of $T/T^\dagger$ and $S_m/S_m^\dagger$ are replaced in turn by the first-order perturbed operator generated by the $\mathscr{CP}$-violating term. This is explicitly demonstrated in the expression for $\langle D\rangle$ in eq 33.

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