Chapter 3

Application of RCC Theory to Atomic EDMs

3.1 Theory of Atomic EDMs

The atoms and molecules, being many particle systems, are the richest laboratories for understanding how different forces operate in Nature. These, in a sense, are the miniature Universe available to us to understand and explore the Nature's unraveling secrets. We shall limit ourselves in this Chapter to investigate one of the very subtle properties of the elementary particles, such as the EDM of the electron.

Let us consider the interaction between an electron and an electromagnetic field. The interaction Hamiltonian is given by,

\[ H_I = -j_\mu A_\mu, \quad \text{where} \quad j_\mu = (j, \rho); \quad A_\mu = (A, i\Phi) \quad \text{and} \quad \mu = 1, 2, 3, 4. \quad (3.1) \]

The current density, \( j = ie(\bar{\psi}\gamma_k\psi) = e(\psi^\dagger \alpha \psi) \), \( \alpha = i\beta\gamma_k \), \( k = 1, 2, 3 \).

The charge density, \( \rho = e(\bar{\psi}\beta\psi) = e(\psi^\dagger \psi) \quad \text{since} \quad \beta^2 = 1. \quad (3.3) \)
On applying a Gordon decomposition rule, we get \( j_\mu = j_\mu^1 + j_\mu^3 \), and correspondingly two terms for the interaction Hamiltonian as,

\[
H_I = H_{I_1} + H_{I_2},
\]

where \( H_{I_2} \) corresponds to anomalous magnetic (Pauli) moment interaction given by,

\[
H_{I_2} = i \frac{k_m}{2} (\bar{\psi} \gamma_\mu \gamma_\nu \psi) F_{\mu\nu} = - \frac{k_m}{2} \left( \bar{\psi} \sigma_{\mu\nu} \psi \right) F_{\mu\nu},
\]

where we have used \( \sigma_{\mu\nu} = -i \gamma_\mu \gamma_\nu (\mu \neq \nu) \); \( F_{\mu\nu} \) is the electromagnetic field tensor and \( k_m \) is the anomalous magnetic moment of the electron.

In a manner analogous to anomalous magnetic moment, one can introduce an electric dipole moment for a single electron in an electromagnetic field into the Dirac equation in a Lorentz covariant manner [1, 2]. The only difference is that the EDM operator contains a pseudo-scalar Dirac operator \( \gamma_5 \).

The pseudo-scalar perturbation Hamiltonian for the intrinsic EDM of an electron in the second quantized notation reads,

\[
H^{SQ}_{EDM} = i \frac{d_e}{2} (\bar{\psi} \gamma_5 \gamma_\mu \gamma_\nu \psi) F_{\mu\nu} = - \frac{d_e}{2} \left( \bar{\psi} \gamma_5 \sigma_{\mu\nu} \psi \right) F_{\mu\nu},
\]

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

In the Pauli approximation, i.e., in the first quantized notation, Eq. (3.6) reduces, in atomic units, to the following:

\[
H^{PQ}_{EDM} = -d_e \beta (\sigma \cdot E + i \alpha \cdot H),
\]

where \( \alpha, \beta \) and \( \sigma \) are the Dirac matrices, \( E \) and \( H \) are the total electric and magnetic fields, respectively, at the site of the electron. The second term in the rhs of Eq. (3.7) is \( \frac{v^2}{2} \) times smaller than that of the first term and it vanishes completely in the non-relativistic limit. Hence, the second term in Eq. (3.7) is dropped usually while calculating the atomic EDM. The EDM Hamiltonian considered further is, therefore,

\[
H_{EDM} = -d_e \beta \sigma \cdot E.
\]
3.1.1 Atomic EDM due to Intrinsic Electron EDM

The EDM of the paramagnetic atom arises mainly in two different ways. The first is due to the intrinsic EDM of the electron which is aligned along the direction of its spin and the second arises through the interaction of the electrons with the nucleus. It is shown in Appendix A that these interactions are odd under both parity \((P)\) and time reversal \((T)\) symmetries. The atomic EDM arising from the intrinsic EDM of the electron and the scalar–pseudo-scalar \(^1\) electron-nucleus interactions are discussed in sufficient detail in the following sections.

3.1.1 Atomic EDM due to Intrinsic Electron EDM

The extensive introduction to the electron EDM has been given in the introductory Chapter of this Thesis. Let us setup the Hamiltonian and derive the working equations for computing the EDM of the single-valence paramagnetic atoms in this section.

The EDM of the electron in the absence of any external field, if it possess any, induces the EDM onto the atom. The intrinsic atomic EDM \((D_{\text{int}})\) in a many-electron case is given by,

\[
D^{\text{int}} = d_e \sum_i \beta \sigma_i,
\]

(3.9)

where \(d_e\) is the magnitude of the electric dipole moment and \(\sigma_i\) is the intrinsic spin of an electron \(i\). The intrinsic EDM of the atom can not be measured directly without the application of an external electric field. The applied field causes the shift in the energy levels. The order of magnitude of this shift is very tiny and hence, it demands state-of-art experimental techniques for its detection. Furthermore, the applied uniform electric field \((E)\) also induces the EDM to an atom which is given by,

\[
D^{\text{ind}} = \sum_i e \cdot r_i.
\]

(3.10)

Hence, one measures only the combined shift in the energy arises due to both the intrinsic and the induced EDMs. The coefficient proportional to the linear shift in energy is the total

\(^1\)The tensor–pseudo-tensor electron-nucleus interactions contribute to the EDM of closed-shell atoms, which is outside the scope of this work.
intrinsic EDM of an atom. The non-degenerate theory with the time-independent perturbative approach is followed, in this Thesis, in order to calculate the energy shift, the procedure for which is described below.

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

$$ H = H_0 - d_e \sum_i \beta \sigma_i \cdot E_{int}^i, \quad (3.11) $$

where $H_0$ is the unperturbed Hamiltonian given in Eq. (2.1).

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

$$ \hat{H}_{EDM} = -d_e \sum_i \beta \sigma_i \cdot E_{int}^i - d_e \sum_i \beta \sigma_i \cdot E - e \sum_i \mathbf{r}_i \cdot \mathbf{E}. \quad (3.12) $$

In the time-independent perturbation theory, the first-order shift in energy for the atomic state $|\Psi_m^{(0)}\rangle$ is given by 2,

$$ E_m^{(1)} = \langle \Psi_m^{(0)} | \hat{H}_{EDM} | \Psi_m^{(0)} \rangle, $$

$$ = - \langle \Psi_m^{(0)} | d_e \beta \sigma \cdot E_{int} | \Psi_m^{(0)} \rangle - \langle \Psi_m^{(0)} | d_e \beta \sigma \cdot E | \Psi_m^{(0)} \rangle = - \langle \Psi_m^{(0)} | e \mathbf{r} \cdot \mathbf{E} | \Psi_m^{(0)} \rangle. \quad (3.13) $$

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

$$ E_m^{(1)} = -d_e \langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_m^{(0)} \rangle - d_e \langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_m^{(0)} \rangle = - \langle \Psi_m^{(0)} | e \mathbf{z} \cdot | \Psi_m^{(0)} \rangle \mathbf{E}. \quad (3.14) $$

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,

$$ E_m^{(1)} = -d_e \langle \Psi_m^{(0)} | \beta \sigma_z \cdot | \Psi_m^{(0)} \rangle \mathbf{E}. \quad (3.15) $$

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,

$$ |\Psi_m^{(1)}\rangle = \sum_{n \neq m} \frac{|\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)} | \hat{H}_{EDM} | \Psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (3.16) $$

\(^2\)The summation over the individual electrons is dropped for the time being.
The second-order shift in energy due to the presence of EDM as a perturbation is given by,

\[ E^{(2)}_m = \langle \Psi_m^{(0)} | \tilde{H}_{EDM} | \Psi_m^{(1)} \rangle, \]

\[ = \sum_{n \neq m} \frac{\langle \Psi_m^{(0)} | \tilde{H}_{EDM} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \tilde{H}_{EDM} | \Psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}}. \] (3.17)

On inserting the expression for \( \tilde{H}_{EDM} \) 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 the perturbation and which are linearly proportional to the applied uniform electric field as below;

\[ E^{(2)}_m = \sum_{n \neq m} \left( \frac{\langle \Psi_m^{(0)} | d_e \beta \sigma_z \cdot E_{int} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} + \frac{\langle \Psi_m^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | d_e \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right), \] (3.18)

\[ \text{i.e., } E^{(2)}_m = d_e \left\{ \sum_{n \neq m} \frac{\langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} + \sum_{n \neq m} \frac{\langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\} |E|. \] (3.19)

Thus, the total shift in energy for the state \( |\Psi_m^{(0)}\rangle \) would be,

\[ E_m = E_m^{(1)} + E_m^{(2)}, \]

\[ = d_e \left\{ - \langle \Psi_m^{(0)} | \beta \sigma_z | \Psi_m^{(0)} \rangle + \sum_{n \neq m} \frac{\langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} + \sum_{n \neq m} \frac{\langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\} |E|. \] (3.20)

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., \( E = -D \cdot E \). Thus, the total EDM of an atom is given by [4],

\[ \langle D \rangle = d_e \left\{ \langle \Psi_m^{(0)} | \beta \sigma_z | \Psi_m^{(0)} \rangle - \sum_{n \neq m} \frac{\langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} - \sum_{n \neq m} \frac{\langle \Psi_n^{(0)} | e \cdot E | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \beta \sigma_z \cdot E_{int} | \Psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\}. \] (3.21)
3.1.2: Atomic EDM due to Electron-Nucleus Interactions

The total atomic EDM given by Eq. (3.21) contains a two-body term through $E_{int}$, however, this can be further simplified to the effective one-body form, the details of which are presented in Appendix C. The effective total atomic EDM is given by,

$$\langle D \rangle_{eff} = \left( \frac{2ic\beta \gamma_5}{e\hbar} \right) \left\{ \sum_{n\neq m} \langle \Psi_m^{(0)} | \sum_i (\beta \gamma_5 \mathbf{p}_i^2) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \sum_i e\mathbf{z}_i | \Psi_m^{(0)} \rangle \right\} + h.c. \text{ (3.22)}$$

Therefore, the effective perturbed atomic Hamiltonian due to the intrinsic EDM of the electron can be written as,

$$H_{edm} = H_{edm}^{eff} = -\left( \frac{2ic\beta \gamma_5}{e\hbar} \right) \sum_i \beta \gamma_5 \mathbf{p}_i^2, \text{ (3.23)}$$

where $\beta$ and $\gamma_5$ are the Dirac matrices, $\mathbf{p}$ is the 3-momentum, $\hbar (= \frac{\hbar}{2\pi})$ 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 acronym $h.c.$ stands for hermitian conjugate i.e., it corresponds to the term in which the positions of $\Psi_1 (e\mathbf{z})$ and EDM ($\beta \gamma_5 \mathbf{p}^2$) operators in Eq. (3.22) are interchanged.

The effective EDM operator is decomposed into radial and angular parts; the radial matrix elements of which are presented in Appendix D.1 and the angular factors are obtained using the Clebsch-Gordan algebra and JLV theorems [3].

3.1.2 Atomic EDM due to Electron-Nucleus Interactions

The $\mathcal{P}$- and $\mathcal{T}$-violating electron-quark interactions at the elementary particle level can manifest at the atomic level as the electron-nucleus interaction. There can be two kinds of $\mathcal{P}$- and $\mathcal{T}$-violating electron-nucleus interactions; one, a scalar–pseudo-scalar (S-PS) interaction and the other a tensor–pseudo-tensor (T-PT) interaction. Although, both are semi-leptonic $\mathcal{CP}$-violating interactions, a $\mathcal{P}$- and $\mathcal{T}$-violating S-PS electron-nucleus interaction will contribute to the EDM of the paramagnetic atoms, whereas, a $\mathcal{P}$- and $\mathcal{T}$- violating T-PT electron-nucleus interaction will contribute to the EDM of the diamagnetic atoms.

We will only consider the S-PS electron-nucleus interaction further, because we are interested only in the EDM of the paramagnetic atoms. Let us consider the pseudo-scalar electron current and a scalar nuclear current, however, the other possibility of considering scalar electron
3.1.2: Atomic EDM due to Electron-Nucleus Interactions

current and pseudo-scalar nuclear current is equally viable. The latter, however, will not affect the forthcoming discussion on the subject.

The Hamiltonian corresponding to the S-PS EDM interaction would be given by,

$$H_{EDM}^{ps} = \frac{iG_F}{\sqrt{2}} \int d^3r \int d^3r_N \sum_N \bar{\Psi}_N \Psi_e \gamma_5 \Psi_e.$$ (3.24)

The summation over $N$ extends from 1 to the total number of nucleons ($Z + N$) in the nucleus, where $Z$ is the number of protons ($p$) and $N$ is the number of neutrons ($n$).

Since the nucleons (protons and neutrons) are very heavy compared to electrons, we treat the nucleons non-relativistically and the electrons relativistically. We know that the covariant relativistic notation, $\bar{\Psi} = \Psi \gamma$. In a non-relativistic case, since $\gamma$ reduces to 1, we obtain, $\bar{\Psi} = \Psi$.

Hence,

$$H_{EDM}^{ps} = \frac{iG_F}{\sqrt{2}} \int d^3r \int d^3r_N \sum_{n=1}^N \Psi_n^\dagger \Psi_n + \sum_{p=1}^Z \Psi_p^\dagger \Psi_p \Psi_e \gamma_5 \Psi_e.$$ (3.25)

We have,

$$\int d^3r \sum_{n=1}^N \Psi_n^\dagger \Psi_n = N \rho_n(r); \quad \int d^3r_p \sum_{p=1}^Z \Psi_p^\dagger \Psi_p = Z \rho_p(r),$$ (3.26)

where $\rho_n$ and $\rho_p$ are the neutron and proton densities respectively, which we assume, to be the same as the nuclear density $\rho_N$.

$$H_{EDM}^{ps} = \frac{iG_F}{\sqrt{2}} \int d^3r \left[ C_{en} N + C_{ep} Z \right] \rho_n(r) \Psi_e^\dagger \beta \gamma_5 \Psi_e.$$ (3.27)

where $C_{en}$ and $C_{ep}$ are the electron-neutron and electron-proton scalar–pseudo-scalar coupling constants. Let us denote, $C_{s-ps} = \frac{[C_{en} N + C_{ep} Z]}{A}$, where $A$ is the mass number.

Thus, the Hamiltonian due to the S-PS electron-nucleus EDM interaction is given by,

$$H_{EDM}^{ps} = \frac{iG_F}{\sqrt{2}} C_{s-ps} A \int d^3r \rho_n(r) \Psi_e^\dagger \beta \gamma_5 \Psi_e.$$ (3.28)

In the first quantized notation, the S-PS EDM operator can be written as,

$$H_{EDM}^{ps} = \frac{iG_F}{\sqrt{2}} C_{s-ps} A \beta \gamma_5 \rho_n(r).$$ (3.29)
The atomic EDM due to S-PS electron-nucleus interactions in a state $|\Psi_m\rangle = |\Psi_m^{(0)}\rangle + |\Psi_m^{(1)}\rangle$, where $|\Psi_m^{(0)}\rangle$ is an unperturbed wavefunction and $|\Psi_m^{(1)}\rangle$ is a first-order perturbed wavefunction, can be written as,

$$(D)_{s-\text{ps}} = \langle \Psi_m^{(0)} | H^{s-\text{ps}}_{\text{EDM}} | \Psi_m^{(1)} \rangle ,$$

$$= \sum_{n\neq m} \frac{\langle \Psi_m^{(0)} | H^{s-\text{ps}}_{\text{EDM}} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e z | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} + \text{h.c.} ,$$

$$= \frac{i G_F}{\sqrt{2}} A C_{s-\text{ps}} \left\{ \sum_{n\neq m} \frac{\langle \Psi_m^{(0)} | \beta \gamma_5 \rho_N(r) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | e z | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \right\} + \text{h.c.} . \quad (3.30)$$

The radial matrix elements of the S-PS EDM operator are presented in Appendix D.2.

Experimentally it is not possible to distinguish between the two EDM contributions of a paramagnetic atom discussed so far i.e., one due to the intrinsic electron EDM and the other due to S-PS electron-nucleus interactions. The measurement of the intrinsic EDM of an atom, the principle of measurement is described in Chapter 1, includes both the contributions. However, we compute the quantity called enhancement factor ($\mathcal{R}$), given by the ratio of the atomic EDM to the intrinsic electron EDM, i.e., $\mathcal{R} = \frac{D}{d_e}$ which is dimensionless and the enhancement factor due to S-PS e-N interactions $\mathcal{S}$, given by the ratio of the atomic EDM to the scalar–pseudo-scalar coupling constant, i.e., $\mathcal{S} = \frac{D}{C_{s-\text{ps}}}$ which carries the unit of $e\text{cm}$.

By combining the measured value of the atomic EDM ($D^{\text{meas}}$) and the theoretical EDM enhancement factor, $\mathcal{R}$, one can extract the electron EDM i.e., from the ratio of the two, one can obtain the limit on the intrinsic EDM of the electron as,

$$d_e = \left( \frac{D^{\text{meas}}}{\frac{D}{d_e^{th}}} \right) . \quad (3.31)$$

Similarly, by combining the measured value of the atomic EDM and the EDM enhancement factor $\mathcal{S}$, one can obtain the coupling constant for the scalar–pseudo-scalar electron-nucleus interaction assuming that the interaction due to the intrinsic EDM of the electron is switched
off. With the knowledge of the atomic EDM measurements and the enhancement factors, both \( \mathcal{R} \) and \( S \) for several atoms, one can in principle separate out these contributions.

Thus, the theoretical determination of the atomic EDM enhancement factors and the experimental measurements of the atomic EDMS compliment one another in obtaining limits on the intrinsic EDM of the electron and the coupling constant for the S-PS electron-nucleus interactions.

### 3.2 RCC Formalism in the presence of EDM as a Perturbation

The total atomic Hamiltonian in the presence of EDM as a perturbation is re-written as,

\[
H = H_0 + \lambda H_{\text{EDM}},
\]

(3.32)

where, \( H_0 \) is the unperturbed Hamiltonian defined in Eq. (2.1) and \( H_{\text{EDM}} \) is the effective perturbed Hamiltonian.

Similarly, the total RCC wavefunction in the presence of EDM as a perturbation can be written as,

\[
|\Psi_v\rangle = |\Psi_v^{(0)}\rangle + \lambda |\Psi_v^{(1)}\rangle.
\]

(3.33)

The cluster operators for calculating the perturbed wavefunction are then given by,

\[
T = T^{(0)} + \lambda T^{(1)},
\]

(3.34a)

and

\[
S_v = S_v^{(0)} + \lambda S_v^{(1)},
\]

(3.34b)

where \( T^{(1)} \) and \( S_v^{(1)} \) are the first order corrections to the cluster operators \( T^{(0)} \) and \( S_v^{(0)} \) operators, respectively, due to the presence of the EDM interaction. Here, the dimensionless

3Note that, here \( H_{\text{EDM}} \) is redefined without the coupling constant \( d_e \) or \( C_{s-\text{ps}} \). In this re-definition, \( H_{\text{EDM}} = - (\epsilon a_0) (\frac{2i\mu}{\epsilon K}) \beta \gamma_5 \mathbf{p}^2 \) for e-EDM. We often use atomic units in which, \( \epsilon = a_0 = \hbar = 0. \)
coupling constant $\lambda$ can either be $\left( \frac{d_m}{e_{\text{a}} a_0} \right)$ for the electron EDM or $C_{\text{e-pS}}$ for the scalar–pseudo-scalar electron-nucleus interaction.

The expectation value of the EDM operator in the state $|\Psi_\nu\rangle$ is given by,

$$\langle D \rangle = \frac{\langle \Psi_\nu | D | \Psi_\nu \rangle}{\langle \Psi_\nu^{(0)} | \Psi_\nu^{(0)} \rangle}.$$  \hfill (3.35)

Now, one can adopt one of the two different approaches described below while applying the RCC method to calculate the EDM enhancement factor.

1. **Sum over intermediate states approach**: Here one considers the all-order contributions from the select few bound intermediate states in addition to the lowest order contributions from the bound core and the continuum virtual orbitals, for both closed- and open-shell systems, with and without EDM as a perturbation, and construct the EDM expression with one order in perturbation.

2. **Mixed parity approach**: Here one considers the all-order contributions from the bound core, higher bound orbitals and the continuum virtual orbitals, for both closed- and open-shell systems, with and without EDM as a perturbation, and construct the EDM matrix elements with one order in perturbation.

The expression for the expectation value of EDM operator in the first approach, using the first order perturbation theory, is given by,

$$\langle D \rangle = \frac{1}{\langle \Psi_\nu^{(0)} | \Psi_\nu^{(0)} \rangle} \sum_I \left\{ \frac{\langle \Psi_\nu^{(0)} | D | \Psi_I^{(0)} \rangle \langle \Psi_I^{(0)} | H_{\text{EDM}} | \Psi_\nu^{(0)} \rangle}{E_\nu - E_I} + \frac{\langle \Psi_\nu^{(0)} | H_{\text{EDM}} | \Psi_I^{(0)} \rangle \langle \Psi_I^{(0)} | D | \Psi_\nu^{(0)} \rangle}{E_\nu - E_I} \right\}.$$  \hfill (3.36)

The drawback of this approach is that the summation can only be performed over a finite set of intermediate bound states which limits the accuracy of the calculations.

Hence, we follow the second approach in the present work which circumvents this problem by solving the first order perturbed equation with the corrected wavefunction. The details of the second method is described for the closed-shell and the single-valence open-shell cases separately in the following sections.
3.2.1 Perturbed RCC Theory for Closed-shell Atoms

The equation of motion for an atom in a state $|\Psi\rangle$ given by,

$$H |\Psi\rangle = E |\Psi\rangle,$$  \hspace{1cm} \text{(3.37)}

where the closed-shell atomic wavefunction, $|\Psi\rangle = e^T |\Phi_0\rangle$, where $T$ is defined in Eq. (3.34a) and the total energy, $E = E_0 + \lambda E^{(1)}$, where $E_0$ is the closed-shell energy in the absence of perturbation.

On substituting the expression for $H$ from Eq. (3.32) we get,

$$(H_0 + \lambda H_{EDM}) e^T |\Phi_0\rangle = (E_0 + \lambda E^{(1)}) e^T |\Phi_0\rangle.$$ \hspace{1cm} \text{(3.38)}

We have $H_0 = H_N + E_{DF}^{(0)}$, where $H_N$ is the normal order form of $H$ and $E_{DF}^{(0)}$ is the DF energy when there is no perturbation. Also, using the fact that $E^{(1)} = 0$, it becomes,

$$(H_N + \lambda H_{EDM}) e^T |\Phi_0\rangle = (E_0 - E_{DF}^{(0)}) e^T |\Phi_0\rangle.$$ \hspace{1cm} \text{(3.39)}

By projecting on the above equation by $e^{-T}$ and using the Hausdorff expansion, we get,

$$e^{-T} (H_N + \lambda H_{EDM}) e^T |\Phi_0\rangle = (E_0 - E_{DF}^{(0)}) |\Phi_0\rangle,$$ \hspace{1cm} \text{(3.40)}

$$\Rightarrow \left( [H_N e^T] + \lambda (H_{EDM} e^T) \right) |\Phi_0\rangle = (E_0 - E_{DF}^{(0)}) |\Phi_0\rangle.$$ \hspace{1cm} \text{(3.41)}

On substituting the expression for $T$ from Eq. (3.34a) in the above equation, we get,

$$\left( [H_N e^{T_0}] + \lambda (H_{EDM} e^{T_0}) \right) |\Phi_0\rangle = (E_0 - E_{DF}^{(0)}) |\Phi_0\rangle.$$ \hspace{1cm} \text{(3.42)}

While expanding, keeping only those terms which are linear in $\lambda$, we get,

$$\left( [H_N e^{T_0}] + \lambda (H_{EDM} e^{T_0}) \right) |\Phi_0\rangle = 0,$$ \hspace{1cm} \text{(3.43)}

$$\Rightarrow (H_N T^{(1)} + H_{EDM}) |\Phi_0\rangle = 0.$$ \hspace{1cm} \text{(3.44)}

By projecting on this, by the excited state determinants $|\Phi^*\rangle$, we get the expression for the perturbed cluster amplitudes, $T^{(1)}$.

$$|\Phi^*| (H_N T^{(1)} + H_{EDM}) |\Phi_0\rangle = 0.$$ \hspace{1cm} \text{(3.45)}

Taking $|\Phi^*\rangle$ as single and double excited determinant, one gets $T^{(1)}_1$ and $T^{(1)}_2$ which correspond to the perturbed singles- and the perturbed doubles- closed-shell coupled-cluster amplitudes, respectively.
3.2.3: Calculation of Atomic EDM due to Intrinsic e-EDM

3.2.2 Perturbed RCC Theory for Single-valence Open-shell Atoms

The equation of motion for an atom in a single-valence state $|\Psi_v\rangle$ is given by,

$$H |\Psi_v\rangle = E_v |\Psi_v\rangle. \tag{3.46}$$

The open-shell atomic wavefunction $|\Psi_v\rangle$ is given by,

$$|\Psi_v\rangle = e^T \{1 + S_v\} |\Phi_v\rangle, \tag{3.47}$$

where $T$ and $S_v$ are defined in Eqns. (3.34a and 3.34b).

On substituting the known definitions in Eq. (3.46), we get,

$$(H_n + \lambda H_{EDM}) e^T \{1 + S_v\} |\Phi_v\rangle = \Delta E_v e^T \{1 + S_v\} |\Phi_v\rangle, \tag{3.48}$$

where $\Delta E_v$ is the negative of the ionization potential for the valence electron $v$.

By projecting on both sides of the above equation by $e^{-T}$, substituting for $T$ and $S_v$ from Eqns. (3.34a and 3.34b) and keeping only those terms which are linear in perturbation during the expansion, i.e., following the procedure similar to the that in the previous section, we obtain,

$$(\overline{H}_N S_v^{(1)} + \overline{H}_N T^{(1)} \{1 + S_v^{(0)}\} + \overline{H}_{EDM} \{1 + S_v^{(0)}\}) |\Phi_v\rangle = \Delta E_v S_v^{(1)} |\Phi_v\rangle. \tag{3.49}$$

On projecting the above equation by the excited state determinant $|\Phi_v^*\rangle$, we obtain the expression for the open-shell perturbed amplitudes $S_v^{(1)}$,

$$\langle \Phi_v^* | (\overline{H}_N - \Delta E_v) S_v^{(1)} + (\overline{H}_N T^{(1)} + \overline{H}_{EDM}) \{1 + S_v^{(0)}\} |\Phi_v\rangle = 0. \tag{3.50}$$

Summarizing the above discussions, the closed-shell and the open-shell perturbed coupled-cluster amplitudes, $T^{(1)}$ and $S_v^{(1)}$ are obtained by solving the following equations in succession, iteratively until the convergence is reached:

$$\langle \Phi_v^* | (\overline{H}_N T^{(1)} + \overline{H}_{EDM}) |\Phi_0\rangle = 0, \tag{3.51}$$

and

$$\langle \Phi_v^* | (\overline{H}_N - \Delta E_v) S_v^{(1)} + (\overline{H}_N T^{(1)} + \overline{H}_{EDM}) \{1 + S_v^{(0)}\} |\Phi_v\rangle = 0. \tag{3.52}$$
3.2.3 Calculation of Atomic EDM due to Intrinsic e-EDM

The expectation value of the EDM operator in the atomic state $|\Psi_e\rangle = |\Psi_e^{(0)}\rangle + \left(\frac{d_e}{\varepsilon_{a_0}}\right) |\Psi_e^{(1)}\rangle$, where $|\Psi_e^{(1)}\rangle$ is the first order perturbed wavefunction, is given by,

$$\langle D \rangle = \frac{\langle \Psi_e | D | \Psi_e \rangle}{\langle \Psi_e^{(0)} | \Psi_e^{(0)} \rangle},$$

(3.53)

where $D = e r$ is the electric dipole operator. It has to be noted that the unperturbed wavefunction $|\Psi_e^{(0)}\rangle$ is normalized.

On substituting the coupled-cluster expressions obtained in the previous sections for the unperturbed and the perturbed wavefunctions, we get,

$$\langle D \rangle = \frac{1}{\langle \Phi_v | e^{T^{(0)^T}} e^{T^{(0)}} + S_v^{(0)^T} e^{T^{(0)}} e_r^{T^{(0)}} | \Phi_v \rangle} \left(\langle \Phi_v | \left\{1 + S_v^{(0)^T}\right\} + \left(\frac{d_e}{\varepsilon_{a_0}}\right) \left\{S_v^{(1)^T}\right\}ight.\left.\left.\left(1 + T^{(1)} + T^{(1)^T} S_v^{(0)} + S_v^{(1)}\right)\right|\Phi_v \rangle\right).$$

(3.54)

Because of the parity selection rule (i.e., As $D$ is odd under parity and the Coulomb excitation operators will not change the parity of the state), the following term which does not contain the EDM perturbation becomes zero.

$$\langle \Phi_v | \left\{1 + S_v^{(0)^T}\right\} e^{T^{(0)^T}} e^{T^{(0)}} \left\{1 + S_v^{(0)}\right\} | \Phi_v \rangle = 0.$$

In addition, because of the smallness of $d_e$, we neglect the terms of order $d_e^2$ and choose only the terms linear in $d_e$.

Thus, we obtain the final expression for the atomic EDM enhancement factor $R = \frac{\langle D \rangle}{d_e}$ to be the following [5, 6],

$$R = \frac{\left(\frac{1}{\varepsilon_{a_0}}\right)}{\langle \Phi_v | e^{T^{(0)^T}} e^{T^{(0)}} + S_v^{(0)^T} e^{T^{(0)}} e_r^{T^{(0)}} | \Phi_v \rangle} \left(\langle \Phi_v | \left\{1 + S_v^{(0)^T}\right\} D^{(0)} \left\{T^{(1)} + T^{(1)^T} S_v^{(0)} + S_v^{(1)}\right\} \left\{1 + S_v^{(0)}\right\} | \Phi_v \rangle\right).$$

(3.55)
3.2.3: Calculation of Atomic EDM due to Intrinsic $e$-EDM

where $\overline{D}^{(0)} = e^{x^{(0)}} \bar{D} e^{x^{(0)}}$ is the dressed EDM operator. The $\overline{D}^{(0)}$ term can be decomposed as the effective one-body, effective two-body etc. terms. By considering the effective one-body terms arising from the $\overline{D}^{(0)}$ term, we have constructed the EDM property diagrams for various terms given in Eq. (3.55). The Goldstone diagrams corresponding to the leading correlation effects such as $\overline{D}^{(0)} T_1^{(1)}$, $\overline{D}^{(0)} S_1^{(1)}$, $\overline{D}^{(0)} S_2^{(1)}$ and $S_0^{(0)} \overline{D}^{(0)} S_0^{(1)}$ are explicitly shown in Fig. (3.1). Also, the diagrams corresponding to the RCC terms $\overline{D}^{(0)} T_1^{(1)} S_0^{(0)}$ and $S_0^{(0)} \overline{D}^{(0)} T_1^{(1)}$ are shown in Fig. (3.2). In Fig. (3.3) the diagrams for the RCC term $S_0^{(0)} \overline{D}^{(0)} T_1^{(1)} S_0^{(0)}$ are shown. Although, the adjoint diagrams for all those diagrams mentioned above are not shown explicitly, they are included in the EDM calculations. The property diagrams using the effective two-body terms arising from the $\overline{D}^{(0)}$ term may also be obtained in the similar fashion. The contributions from the effective two-body terms are also included in our actual calculations. We will discuss the contributions from the various correlation effects to the EDM enhancement factors of different paramagnetic atoms in the forthcoming Chapter.

The similar procedure as explained in Sections §3.2.1 and §3.2.2 is followed in obtaining the perturbed cluster operators $T_1^{(1)}$ and $S_1^{(1)}$ corresponding to the scalar–pseudo-scalar electron-nucleus interactions by taking $\lambda = C_{s-ps}$ and replacing $H_{EDM}$ by $H_{EDM}^{s-ps}$ given by Eq. (3.29) in the perturbed amplitude determining equations. We then define the ratio,

$$ S = \frac{\langle D \rangle_{s-ps}}{C_{s-ps}}, $$

(3.56)

for the EDM enhancement factor due to S-PS EDM interaction. The expression given in Eq. (3.55) for $\mathcal{R}$, with out the factor of $\left( \frac{1}{\epsilon_{\infty}} \right)$, holds for $S$ also if the appropriate perturbed cluster amplitudes are used. The further details on the working equations for the S-PS EDM enhancement factor, $S$ can be obtained from the references [6, 7, 8].

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4The difference in the definition of $\overline{D}^{(0)}$ in comparison to that of $\overline{H}$ defined earlier needs to be noted.
5For convenience, the bold fonted notation $\overline{D}^{(0)}$ would be changed to $\overline{D}^{(0)}$ from here onwards.
Figure 3.1: The Goldstone diagrams corresponding to the RCC terms; $\bar{D}^{(0)} T_1^{(1)}$ (i), $\bar{D}^{(0)} S_{1v}^{(1)}$ (ii), $\bar{D}^{(0)} S_{2v}^{(1)}$ (iii & iv) and $S_{1v}^{(0)} T_1^{(0)}$ (v - xv). The hermitian conjugate terms are not shown here, however, they are included in the calculation.
3.2.3: Calculation of Atomic EDM due to Intrinsic e-EDM

Figure 3.2: The Goldstone diagrams corresponding to the RCC terms; $D^{(0)} T^{(1)} S^{(0)}_e$ (i) and $S^{(0)}_e D^{(0)} T^{(1)}$ (ii - xv). The hermitian conjugate terms are not shown here, however, they are included in the calculation.
3.2.3: Calculation of Atomic EDM due to Intrinsic e-EDM

Figure 3.3: The Goldstone diagrams corresponding to the RCC terms; $S_{\nu}^{(0)} D^{(0)} T^{(1)} S_{\bar{\nu}}^{(0)}$ (i - xi). The hermitian conjugate terms are not shown here, however, they are included in the calculation.
Bibliography


