Permanent Electric Dipole Moments of Closed Shell Atoms

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To My Parents and to

Arti

DECLARATION

I, Mr. Yashpal Singh, S/o Mr. M. P. Singh, resident of Room No. 19 UN Hostel, Physical Research Laboratory, Navrangpura, Ahmedabad, 380009, hereby declare that the research work incorporated in the present thesis entitled, "Permanent Electric Dipole Moments of Closed Shell Atoms" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

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ABSTRACT

Violations under the discrete symmetry transformations, like parity (P), timereversal (T) and combined charged-conjugation-parity (CP) symmetries, have already been observed in nature at the elementary particle level. However, in the composite systems like atoms, P and T-violating (P,T-odd) interactions between its constituent particles could give rise to net intrinsic electric dipole moment (EDM) of the system. Therefore, observation of a non-zero EDM in an atomic system would be a clean signature of violations of both the P- and T- symmetries. In addition, atomic EDMs can also probe CP-violation originating from leptonic, semileptonic and hadronic CP sources. Since last six decades, several attempts have been made by physicists in both the high-energy and low-energy sectors to probe such CP-odd sources.

The EDMs of closed-shell (diamagnetic) atoms (d_A) arise predominantly from the P,T-odd electron-nucleus (e-N) tensor-pseudotensor (T-PT) interactions and interactions between the nuclear Schiff moment (NSM) with the atomic electrons. It is assumed that NSM originates primarily due to the distorted charge distribution inside a finite size nucleus caused by the P,T-odd interactions among the nucleons mediated by the neutral pions (π^0 -mesons) and due to EDMs of the nucleons. Further, at the quantum chromodynamics (QCD) energy scale, the origin of NSM can be viewed as the P,T-odd interactions among the constituent quarks and due to the EDMs and chromo-EDMs of the quarks.

Accurate theoretical evaluations of EDMs require sophisticated many-body methods, which can treat both the electron-correlation effects and the relativistic corrections adequately. In past, several lower-order many-body methods have been employed to study these properties in the atomic systems that are under consideration by the experimentalists to measure their EDMs. Validity of these methods are not well investigated and from the theoretical prospectives, they do not appear to present reliable results. The main objective of this work is to develop more accurate all-order perturbative many-body methods in the relativistic framework so that calculations obtained using these methods can be

combined with the experimental values of the EDMs for different closed-shell atomic systems to infer fundamental quantities that can be used to test possible new physics of elementary particles. In this view, we have developed methods based on the relativistic coupled-cluster (RCC) theory considering full singles and doubles approximation with linear terms (LCCSD method) and including all non-linear terms (CCSD method). To further improve our CCSD results, we perturbatively take into account contributions from the important triple excitations due to the electron-electron repulsion (CCSD(T) method) and along with the P,T-odd interaction ($CCSD_pT$ method). In order to compare our EDM results with the previously reported values we developed a method based on random phase approximation (RPA). In addition to that, we have also developed a third-order many-body perturbation theory (MBPT(3)) and studied trends in the behavior of electron-correlation effects going from one method to another in the evaluation of the property of interest. Before performing EDM calculations, we test the potential of our many-body methods by evaluating electric dipole polarizability (α) of various closed-shell atomic system and comparing these results with the available measurements and other calculations. Since the evaluation of $d_{\rm A}$ and α demands similar angular momentum and parity selection criteria, but accuracies of α s can be tested against their experimental values. This, therefore, can serve as benchmark to determine EDMs reliably. After rigorous testing of our developed many-body methods, we finally evaluate d_A due to T-PT and NSM interactions of the experimentally considered atoms like ¹²⁹Xe, ¹⁹⁹Hg, ²²³Rn and 225 Ra. Till date, the best atomic measurement on d_A is obtained from 199 Hg as $|d_A(^{199}\text{Hg})| < 3.1 \times 10^{-29} |e|$ cm (at 95% confidence level). Large discrepancies among the previously reported calculated results using a variety of many-body methods have been noticed. In this thesis, we aim to explain the reasons for observing such differences by systematically including higher-order corrections to the many-body methods. With above many-body methods in hand we rigorously demonstrate the trends in the electron-correlation effects in determining α and $d_{\rm A}$. We find that non-RPA contributions (pair-correlation effects) which are already there in CCSD are very crucial in achieving better accuracies in these

results. The contributions from important triple excitations to α and d_A were also found to be very significant (sometime 3%). Finally, we present the recommended EDM results from a method that takes into account more physical effects. On combining our recommended EDM results with the measured value of ¹⁹⁹Hg, we obtain limits on the T-PT coupling constant as $C_T < 2.09 \times 10^{-9}$ and on the NSM as $S < 1.45 \times 10^{-12} |e| \text{fm}^3$. Using these values together with the latest nuclear structure and QCD calculations, we get limits for the strong CP parameter as $|\bar{\theta}| < 1.1 \times 10^{-9}$ and for the combined up- and down- quark chromo-EDMs as $|\tilde{d}_u - \tilde{d}_d| < 2.8 \times 10^{-26} |e|$ cm. Experiments to measure EDMs in 129 Xe and 225 Ra are actively underway aiming to improve the precision of the measurements so that the new results can surpass the upper limit set by the Hg experiment. In fact, a research group at Argonne National Laboratory has recently reported their first EDM measurement on ²²⁵Ra atom. Though, their obtained limit is not competitive with Hg at present but from the theoretical and experimental point of view, ²²⁵Ra has the potential to enhance this effects significantly.

In brief, a comprehensive study of closed-shell atomic EDMs is presented in this thesis with a focus on various relativistic many-body methods including the RCC theory. We highlight the importance of non-RPA contributions in determining accurate results of α and d_A in various closed-shell atomic systems. Our obtained limits on various P,T-odd couplings from ¹⁹⁹Hg could constraint various extensions of the standard model (SM) of particle physics. These constraints can further useful for probing new physics beyond-SM.

Keywords: Electric Dipole Moment, CPT Theorem, Dipole Polarizability, Parity, Charge-Conjugation, Time-Reversal, CP-Violation, Tensor-Pseudotensor Interaction, Nuclear Schiff Moment, Many-Body Perturbation Theory, Random Phase Approximation, Relativistic Coupled-Cluster Theory, Standard Model.

LIST OF PUBLICATIONS

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List of Abbreviations

A	Atomic Mass
С	Charge Conjugation
Р	Parity
Т	Time Reversal
T-PT	Tensor-Pseudotensor
HF	Hartree-Fock
DF	Dirac-Fock
DC	Dirac-Coulomb
DK	Douglas-Kroll
GTO	Gaussian Type Orbitals
EDM	Electric Dipole Moment
PNC	Parity Non-Conservation
QCD	Quantum Chromodynamics
QED	Quantum Electrodynamics
DM	Dark Matter
S	Schiff Moment
\mathbf{SM}	Standard Model
SUSY	Super Symmetry
BSM	Beyond Standard Model
SCF	Self Consistent Field
MBPT	Many-Body Perturbation Theory
MDM	Magnetic Dipole Moment
$\mathbf{C}\mathbf{C}$	Coupled-Cluster
RPA	Random Phase Approximation
NCC	Normal Coupled-Cluster
NSM	Nuclear Schiff Moment
ECC	Extended Coupled-Cluster
CI	Configuration Interaction
CPHF	Coupled Perturbed Hartree Fock
TDHF	Time Dependent Hartree-Fock
CCSD	Coupled-Cluster Singles Doubles
LCCSD	Linearized CCSD
CCSD(T)	CCSD with Partial Triples
SE	Self Energy
VP	Vacuum Polarization
RCC	Relativistic CC
WK	WichmannKroll
Z	Atomic Number

Contents

Acknowledgements i			
Abstract iii			iii
List	t of	Publications	vii
List	t of	Abbreviations	ix
Contents xi		xi	
List of Tables xv		xv	
List of Figures xvii		vii	
1 Introduction 1			
	1.1	EDMs of Closed-Shell Atoms	4
		1.1.1 Semileptonic Source: Electron-nucleus T-PT Interactions .	6
		1.1.2 Hadronic Source: Nuclear Schiff Moment	9
		1.1.3 Leptonic Source: Electron EDM (d_{\bullet})	14
	19	Dipole Polarizability as a Benchmark for the Accuracies of EDM	
-	1.2	Studies	15
	19	Concerl Dringiple of FDM Maggurement	10
-	1.0		10
		1.3.1 Difficulties in the EDM Measurements	17
	1.4	Brief History and Current Status of EDM Measurements of Closed-	
		Shell Atoms	19
-	1.5	Thesis Overview	20

2	Rel	ativistic Many-Body Methods for EDM Studies	23
	2.1	Introduction	23
		2.1.1 Dirac-Fock Theory for Closed-Shell Atomic Systems	26
	2.2	Graphical Representations of the Orbitals and Interactions	31
	2.3	Many-Body Perturbation Theory (MBPT)	32
	2.4	Random Phase Approximation (RPA)	38
	2.5	Relativistic Coupled-Cluster (RCC) Theory	40
		2.5.1 Unperturbed RCC Theory to Evaluate $ \Psi_0\rangle$	41
	2.6	Perturbed RCC Theory to Evaluate $ \Psi\rangle$	45
		2.6.1 Perturbative Inclusion of Coupled-Cluster Triple Excitations	47
	2.7	Electric Dipole Moment Calculations from RCC Theory	47
	2.8	Estimation of Uncertainties in the Many-Body Calculations	48
3	Cor	nputational Implementations of RCC Theory	51
	3.1	Introduction	51
	3.2	Solving Unperturbed CCSD Equations	52
	3.3	Solving Perturbed CCSD Equations	57
	3.4	Angular Momentum Selection Rules for the Cluster Operators	58
	3.5	Property Evaluation	66
4	Dip	ole Polarizabilty of Various Closed-Shell Atomic Systems	71
	4.1	Introduction	71
	4.2	Theory of Dipole Polarizability	73
	4.3	Optimization of the Gaussian Basis Functions	75
	4.4	Correlation Trends in α s	80
	4.5	αs of Boron, Carbon, and Zinc Homologous Sequences $\hfill \ldots \hfill \ldots$	88
	4.6	Summary	98
5	ED	M Results and Analysis	L 01
	5.1	Overview	101
		5.1.1 EDM of 129 Xe	103
		5.1.2 EDM of 199 Hg	108

		5.1.3 EDM of 223 Rn	111
		5.1.4 EDM of 225 Ra	115
	5.2	Limits on Hadronic and Semileptonic P- and T-violating Coupling	
		Coefficients	119
	5.3	Summary	122
6	Cor	nclusion and Future Directions	123
	6.1	Work Summary and Conclusion	123
	6.2	Future Directions	126
	6.3	NCC Theory	127
A	Ato	omic Units	129
в	Dira	ac Matrices	131
С	Mat	trix Elements of EDM Interaction Hamiltonians	133
	C.1	Matrix element of $H_{\text{int}}^{\text{TPT}}$	133
	C.2	Matrix element of $H_{\text{int}}^{\text{NSM}}$	135
Bi	bliog	graphy	137
Ρı	ıblic	ations attached with the thesis	xiii

List of Tables

1.1	The ranges and the best values for the coefficients a_i 's	14
1.2	Upper limits on the closed-shell atomic EDMs	20
4.1	GTO parameters of Ne used in the DF calculations	75
4.2	Single particle orbital energies of the bound states of Ne \ldots .	76
4.3	Comparison of the single particle orbital energies of Ne \ldots .	77
4.4	Convergence of α of Ne with the size of the basis sets	78
4.5	SCF energies of Ne with and without Breit contributions	78
4.6	α s of various noble gas elements	79
4.7	α s of various alkaline earth elements $\ldots \ldots \ldots \ldots \ldots \ldots$	79
4.8	α s of singly charged alkali elements $\ldots \ldots \ldots \ldots \ldots \ldots$	80
4.9	α s of doubly charged alkaline earth elements $\ldots \ldots \ldots \ldots$	81
4.10	GTO parameters for various considered closed-shell atoms and ions	82
4.11	The estimated uncertainties to αs from the Breit interaction, QED	
	corrections, finite basis size	83
4.12	αs of various closed-shell atomic systems obtained using different	
	many-body methods	84
4.13	RPA and non-RPA contributions from the MBPT(3) method. $\ .$.	86
4.14	Contributions from various CCSD terms for the evaluations of αs	87
4.15	Universal GTO parameters for B^+ , C^{+2} , Al^+ and Si^{+2}	89
4.16	GTO parameters for Zn, Ga ⁺ , Ge ⁺² , Cd, In ⁺ , Sn ⁺² $\ldots \ldots \ldots$	89
4.17	Comparison of the results of α s of \mathbf{B}^+ , \mathbf{C}^{+2} , \mathbf{Al}^+ , \mathbf{Si}^{+2} and \mathbf{Zn}	
	from different many-body methods	92

4.18	Comparison of the results of α s of \mathbf{Ga}^+ , \mathbf{Ge}^{+2} , \mathbf{Cd} , \mathbf{In}^+ and \mathbf{Sn}^{+2}
	using different many-body methods
4.19	Contributions to the α s of \mathbf{B}^+ , \mathbf{C}^{+2} , \mathbf{Al}^+ , \mathbf{Si}^{+2} , \mathbf{Zn} , \mathbf{Ga}^+ , \mathbf{Ge}^{+2} ,
	Cd , \mathbf{In}^+ and \mathbf{Sn}^{+2} from various $\mathrm{CCSD}_p\mathrm{T}$ terms
5.1	EDM results of ¹²⁹ Xe
5.2	GTO parameters used in the DF calculations of $^{129}\mathrm{Xe}$ 104
5.3	Explicit contributions from various $\text{CCSD}_p T$ terms to the α and
	$d_{\rm A}$ of ¹²⁹ Xe
5.4	Contributions from various matrix elements and from various an-
	gular momentum symmetry groups at the DF, lowest-order RPA
	[denoted by MBPT(l -RPA)
5.5	α and $d_{\rm A}$ results of $^{199}{\rm Hg}$ using different many body methods 109
5.6	Convergence in the $\alpha,d_{\rm A}$ of $^{199}{\rm Hg}$ from different set of basis $~$ 110
5.7	α and $d_{\rm A}$ values of $^{199}{\rm Hg}$ from various CCSD terms $\ . \ . \ . \ . \ . \ . \ . \ . \ . \ $
5.8	α and $d_{\rm A}$ values of $^{211}{\rm Rn}$ using different many-body methods 112
5.9	GTO parameters for the DF calculations of $^{223}\mathrm{Rn}$
5.10	Individual contributions from the non-RPA diagrams to α and d_A
	of ²²³ Rn
5.11	Contributions from RCC terms to α and d_A of ²²³ Rn
5.12	Comparison of the α , $d_{\rm A}$ results for 225 Ra from various many-body
	methods
5.13	Non-RPA contributions through the MBPT(3) diagrams for α and
	$d_{\rm A}$ of ²²⁵ Ra
5.14	Individual contributions to α and $d_{\rm A}$ of 225 Ra from various RCC
	terms
A.1	Conversion Factors from Atomic to S.I Units
A.2	Frequently used Physical Constants and their Numerical Values 129
A.3	The conversion factors for energies in different units. $\dots \dots \dots$

List of Figures

1.1	Pictorial representation of showing existence of intrinsic electric	
	dipole moment implies violation of the P and T symmetry \ldots	2
1.2	A schematic plot of the hierarchy of scales between the CP-odd	
	sources and three generic classes of observable EDMs $\ \ldots \ \ldots$	5
1.3	A Feynman diagram showing P and T-violating interaction be-	
	tween electron and nucleus	6
1.4	General principle of all EDM measurements	16
2.1	Diagram representing excitations of two electrons from core via	
	Coulomb interaction	31
2.2	The graphical representations of the creation and annihilation op-	
	erators	32
2.3	Graphical representations of normal-ordered h_0 and V_N	33
2.4	Few important contributing diagrams of the $MBPT(3)$ method	34
2.5	Graphical representations of the wave operator $\Omega_{\mathrm{RPA}}^{\infty,1}$	40
2.6	Graphical representations of the unperturbed RCC operators	41
2.7	Graphical representations of the perturbed RCC operators $\ . \ . \ .$	45
3.1	Effective one-body P-P, P-H and H-H type diagrams obtained	
	from $ ilde{H_N}$	52
3.2	Effective two-body diagrams from $ ilde{H_{\mathrm{N}}}$	54
3.3		55
3.4	Final CCSD diagrams obtained after contracting effective two-	
	body intermediate diagrams with the $T^{(0)}$ operators $\ldots \ldots \ldots$	56

3.5	Direct contributing diagrams to the singles of the CCSD method .	57
3.6	Direct contributing diagrams to the doubles of the CCSD method	57
3.7	Effective one-body intermediate diagrams obtained from $\overline{H}_{\rm N}$	59
3.8	Effective two-body intermediate diagrams obtained from $\overline{H_{\rm N}}$	61
3.9	The singles diagrams for the A matrix obtained by connecting	
	intermediate one-body and two-body diagrams with $T^{\left(1\right)}$ operators.	61
3.10	The doubles diagrams for the A matrix obtained by connecting	
	intermediate one-body and two-body diagrams with the $T^{(1)}$ op-	
	erators	62
3.11	The singles and doubles diagrams for the B matrix elements ob-	
	tained from \overline{H}_{int}	62
3.12	Perturbed cluster operators showing multi-poles $k1$, $k2$ and rank	
	$\lambda = 1.$	64
3.13	One-body intermediate P-P,H-P and P-H type diagrams obtained	
	from \overline{D}	68
3.14	Example of further dressing-up of effective H-P type diagrams	
	from the effective P-P and H-H type one-body diagrams	69
3.15	The property diagrams	69
4.1	Plots of $(\alpha - \alpha_{DF})/\alpha_{DF}$ results versus atomic numbers from dif-	
	ferent groups of atomic systems	85
4.2	Plots of MBPT(3) and CCSD $(\alpha - \alpha_{DF})/\alpha_{DF}$ results of noble gas,	
	alkali, alkaline-earth metal groups versus atomic numbers	85
4.3	Histogram showing $(\alpha - \alpha_D)/\alpha_D$ (in %) with different many-body	
	methods against the different atomic systems shown above	94
4.4	Few significantly contributing non-RPA type MBPT(3) diagrams.	95
4.5	Trends in the calculations of α s from the employed many-body	
	methods in the singly charged alkali ions	96
4.6	Trends in the calculations of α s from the employed many-body	
	methods in the doubly charged alkaline-earth metal ions	96
5.1	Few important non-RPA diagrams from the MBPT(3) method	105

5.2	Diagram involving effective one-body dipole operator \overline{D} and the
	perturbed wave operator $\Omega^{(1)}$
5.3	Histograms representing for the dominant matrix elements be-
	tween the $7s$ and $6p$ occupied orbitals and the low-lying virtual
	ms and mp orbitals of ²²⁵ Ra

Chapter 1

Introduction

Studying symmetries provide physicists a very powerful and useful tool in exploring fundamental physical laws of nature [1]. In physics, symmetries are broadly classified into two categories

- Continuous internal and space-time symmetries: e.g., spatial-translation, spatial-rotation, time-translation etc., and
- Discrete symmetries: e.g., parity or space inversion symmetry (P), charge-conjugation symmetry (C) and time-reversal or motion-reversal symmetry (T).

All the continuous symmetries are associated with some conservation laws according to the Noether's first theorem, which says "for every continuous symmetry there is a corresponding quantity that is conserved". For example, linear momentum is conserved under spatial translation, angular momentum is conserved under spatial rotation, etc.. There is no such notion of conservation related with the discrete symmetry transformations. In fact, like continuous symmetries, discrete symmetries were also thought of as exact symmetries of the nature. But in 1956, Wu *et al.* [2] reported the first observation of violation of P symmetry in the beta decays of cobalt-60 nucleus, where they found electrons favor a very specific direction during the decay opposite to that of the nuclear spin. Thereafter in 1964, violation of combined CP symmetry (CP-violation) was observed in the decays of neutral K mesons [3]. Since then violation of



Figure 1.1: Pictorial representation of showing existence of intrinsic electric dipole moment implies violation of the P and T symmetry. J is the total angular momentum and δ is the small charge deformation due to which we have dipole moment D of the system.

discrete symmetries have been regularly reported in different sectors of particle physics [4–6].

In a composite system like atom or molecule, the P- and T-violating interactions among the constituent particles or existence of electric dipole moment (EDM) of these constituent particles could give rise to EDM of the system. Since electric dipole operator (\vec{D}) is a polar vector and according to the Wigner-Eckart theorem (projection theorem), any vector pertaining to the system should lie along the direction of total angular momentum (\vec{J}) of the system, i.e. [7]

$$\langle \vec{D} \rangle = \frac{\langle \vec{D}.\vec{J} \rangle}{\langle J^2 \rangle} \langle \vec{J} \rangle. \tag{1.0.1}$$

Now being a polar vector \vec{D} flips its orientation under the parity (P) transformation but under time-reversal (T) operation there should not be any change in \vec{D} . However, the reverse happens for angular momentum operator \vec{J} , which is an axial vector, as shown in Fig. 1.1. If P and T are the exact symmetries of nature than the EDM of the system should be zero, else non-zero EDM would imply simultaneous violations of P and T symmetries. In other words observation of finite EDM in a non-degenerate system like an atom in a relativistic theory is an unambiguous signature of violations of both the P and T symmetries [8,9]. Therefore, EDM observation is a direct test of T-violation; consequently via the CPT theorem T-violation implies CP-violation [10]. Till date, all the observed CP-violation in laboratories are consistent with the predictions of the standard model (SM) of particle physics. There are two sources of CP-violation in the quark sector of the SM. The best understood source is the complex δ phase in the Cabibbo-Kobayashi-Maskawa (CKM) matrix that induces CP-violation by mixing quarks in flavor-changing processes. The second source is the quantum chromodynamic (QCD) vacuum angle $\bar{\theta}$ that parametrizes the P and T-odd interactions between the quarks and gluons [11–13]. In principle, $\bar{\theta}$ would generate large neutron electric dipole moment (EDM) (d_n) of the order of $10^{-16}|e|$ cm while the experimental bound is roughly ten orders in magnitude smaller than that, which strongly limits $\bar{\theta} < 10^{-10}$ [14, 15]. This is the well known strong CP problem of SM where the puzzle is why $\bar{\theta}$ is so tiny or almost equals to zero. The EDMs of the elementary particles predicted by the SM are extremely small. Finite contributions to the lepton EDMs arise via four-loop Feynman diagrams with a closed quark loop [16]. The electron EDM (d_e) in SM is roughly $\approx 10^{-38} |e|$ cm, which is inaccessible with the current experimental techniques [11–13]. There are also many fundamental phenomena which persist in nature that SM do not account for, for example,

- Neutrinos are massless in SM but from the neutrino oscillation experiments it is evident that neutrinos have small masses [17, 18].
- SM does not include gravitational interactions, one of the four fundamental forces.
- SM also fails to explain why there is a huge difference in the strength of fundamental forces ("hierarchy problem"). It also refers to the differences in the masses of leptons in three generations of SM for e.g. muon is 200 times and tau is 3500 times heavier than electron.
- There is no dark matter candidate in SM, however existence of dark matter is now widely accepted. In fact, the best evidence to date come from the gravitational lensing studies of the Bullet Cluster [19].

• The complex phase δ and $\bar{\theta}$ of SM doesn't provide sufficient CP-violation to explain the matter-antimatter asymmetry in the Universe [20, 21], etc..

It is, therefore, widely believed that SM is not a complete theory and there must be additional CP-odd sources which are not discovered yet. In order to search for these additional CP-odd sources many attempts have been made by theorists; mostly by advocating many models as extensions to SM such as, leftright symmetric model, supersymmetric models (SUSY), multi-Higgs models etc.. These extensions predict additional interactions, particles and new sources of CP-violation that can give rise limits on EDMs that are as big as the upper limits established by various atomic and molecular experiments. For example, one of the most celebrated beyond SM is SUSY which relates two basic classes of elementary particles: fermions (particles with half integer spin) and bosons (particle with integer spin). Therefore the number of particles in SUSY are twice of SM such that for every particle we have its heavier superpartner, e.g. electron's super-partner is selectron, photon's superpartner is photino etc.. The doubling of number of particles introduces roughly 100 new parameters and many new CP-odd phases with the breaking of SUSY near the electroweak energy scale of 100GeV. These extra CP-odd phases are responsible for boosting the EDMs of the particles to current experimental range. With the above considerations, enormous efforts to find the non-zero EDMs in leptons, hadrons, nuclei, atoms and molecules are underway at both the theoretical and experimental fronts. Excellent reviews on EDMs can be found elsewhere [13, 22, 23].

1.1 EDMs of Closed-Shell Atoms

Atoms are composite systems and exhibit strong enhancements of the EDMs of its constituent subatomic particles. Depending upon their electronic configurations atomic systems are divided into two categories: open-shell (paramagnetic) and closed-shell (diamagnetic) atoms. The EDM of paramagnetic atoms are sensitive to the intrinsic EDM of an electron (d_e) and P,T-violating pseudoscalar-scalar (PS-S) interactions between the electrons and nucleons which in turn arise from



Figure 1.2: A schematic plot of the hierarchy of scales between the CP-odd sources and three generic classes of observable EDMs. The dashed lines indicate generically weaker dependencies.

the P,T-odd electron-quark and quark-quark interactions at the quantum chromodynamics (QCD) energy scale. However, EDMs of the diamagnetic atoms arise primarily from the following sources :

- Semileptonic Sources: P-,T-odd electron-nucleus (e-N) tensor-pseudotensor (T-PT) interactions and scaler-pseudoscalar (S-PS) interactions.
- Hadronic Source: P,T-odd nuclear Schiff moment (NSM) interacting with electrons [12]. Further at the QCD scale NSM can be further linked with the CP-odd pion-nucleon-nucleon (πnn) coupling constants ($\bar{g}_{\pi nn}$), strong CP parameter $\bar{\theta}$ and chromo-EDMs (d_q) of quarks [23, 24].
- Leptonic source: Electron EDM (d_e) .

A schematic showing various CP-odd sources in the three generic classes of EDM observables against energy scale is shown Fig.1.2 [13]. In this thesis, we study



Figure 1.3: A Feynman diagram showing P and T-violating interaction between electron and nucleus. Red dot represents the P,T-odd coupling.

EDMs of the closed-shell atomic systems arising predominantly from the e-N T-PT and the NSM interactions. In the next three subsections, we will discus these sources in detail and give their corresponding interaction Hamiltonians. At the end, we will also justify why the contributions of the electron EDM (d_e) to the atomic EDM of the closed-shell systems are negligibly small and for which their contributions are not accounted here.

1.1.1 Semileptonic Source: Electron-nucleus T-PT Interactions

The e-N interaction that violates the P and T symmetries can be described by the Feynman diagram shown in Fig. 1.3. The interaction between the nuclear tensor current $\bar{\psi}_n \sigma_{\mu\nu} \psi_n$ and electronic pseudotensor current $\bar{\psi}_e \gamma_5 \sigma_{\mu\nu} \psi_e$ is given by the interaction Hamiltonian

$$H_{\rm int}^{\rm TPT} = \frac{iG_F C_T}{\sqrt{2}} \sum_{n,e} (\bar{\psi}_n \sigma_{\mu\nu} \psi_n) (\bar{\psi}_e \gamma_5 \sigma_{\mu\nu} \psi_e), \qquad (1.1.1)$$

where G_F is the Fermi coupling constant, C_T is the T-PT coupling constant, $\sigma_{\mu\nu} = \frac{i}{2} [\gamma_{\mu}, \gamma_{\nu}]$ with γ 's being the Dirac matrices, ψ_n and ψ_e are the nuclear and electronic wave-function respectively. In order to use the above interaction Hamiltonian in the atomic many-body calculations, we simplify it further using Clifford algebra as given in Appendix B. The tensor part $\gamma_0 \sigma_{\mu\nu}$ belonging to the tensor current of the above Hamiltonian is further simplified as,

$$\gamma_0 \sigma_{\mu\nu} = \gamma_0 \frac{i}{2} [\gamma_\mu, \gamma_\nu] = 0 \quad if \quad \mu = \nu$$
 (1.1.2)

$$= i\gamma_0\gamma_\mu\gamma_\nu \quad if \quad \mu \neq \nu. \tag{1.1.3}$$

The $\mu \neq \nu$ part can be further reduced to

$$i\gamma_{0}\gamma_{\mu}\gamma_{\nu} = i\gamma_{0}[\gamma_{0}\gamma_{i} + \gamma_{i}\gamma_{\nu}]_{(i\neq\nu)}$$

$$= i\gamma_{i} + i\gamma_{0}\gamma_{i}\gamma_{\nu} \quad \text{using} \quad (\gamma_{0}^{2} = I)$$

$$= i(\gamma_{i} + \alpha_{i}\gamma_{\nu})_{(i\neq\nu)} \quad \text{using} \quad (\gamma_{0}\gamma_{i} = \alpha_{i}). \quad (1.1.4)$$

Unlike tensor current, the pseudotensor part of the Hamiltonian contains extra factor γ_5 as $\bar{\psi}_e \gamma_5 \sigma_{\mu\nu} \psi_e = \psi_e^{\dagger} \gamma_0 \gamma_5 \sigma_{\mu\nu} \psi_e$. From the the anti-commutation relation, we get $\gamma_0 \gamma_5 = -\gamma_5 \gamma_0$ and using the simplified form of $\gamma_0 \sigma_{\mu\nu}$ from the above relation, we have

$$\gamma_{0}\gamma_{5}\sigma_{\mu\nu} = -\gamma_{5}\gamma_{0}\sigma_{\mu\nu}$$

$$= -i\gamma_{5}(\gamma_{i} + \alpha_{i}\gamma_{\nu})_{(i\neq\nu)}$$

$$= -i\gamma_{5}(\gamma_{i} + \alpha_{i}\gamma_{0} + \alpha_{i}\gamma_{j})_{(i\neq j)}$$

$$= -i\gamma_{5}(\alpha_{i}\gamma_{j})_{(i\neq j)}.$$
(1.1.5)

Inserting the factors obtained in Eqs. 1.1.3 and 1.1.5 in Eq. 1.1.1, we get the following simplified form of the interaction Hamiltonian

$$H_{\text{int}}^{\text{TPT}} = \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} (\gamma_i + \alpha_i \gamma_{\nu}) \psi_n) (\psi_e^{\dagger} \gamma_5 (\gamma_i + \alpha_i \gamma_{\nu}) \psi_e)_{(i \neq \nu)}$$

$$= \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} \alpha_i \gamma_j \psi_n) (\psi_e^{\dagger} \gamma_5 \alpha_i \gamma_j \psi_e)_{(i \neq j)}$$

$$= \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} \alpha_i \beta \alpha_j \psi_n) (\psi_e^{\dagger} \gamma_5 \beta \alpha_i \beta \alpha_j \psi_e)_{(i \neq j)}$$

$$= \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} \beta \alpha_i \alpha_j \psi_n) (\psi_e^{\dagger} \gamma_5 \beta \alpha_i \alpha_j \psi_e)_{(i \neq j)}. \quad (1.1.6)$$

The $\alpha_i \alpha_j$ in the above equation can be simplified as

$$\begin{aligned}
\alpha_i \alpha_j &= \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix} = \begin{pmatrix} \sigma_i \sigma_j & 0 \\ 0 & \sigma_i \sigma_j \end{pmatrix} = \sigma_i \sigma_j I \\
&= (i\epsilon_{ijk}\sigma^k)_{(i\neq j)} \quad \text{since} \quad (\sigma_i \sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma^k) \quad (1.1.7)
\end{aligned}$$

and

$$\gamma_5 \alpha_k = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} = \sigma_k I.$$

Combining Eqs. 1.1.7 and 1.1.8, we get the following identity

$$\alpha_i \alpha_j = i \epsilon_{ijk} \sigma^k I = i \epsilon_{ijk} \gamma_5 \alpha^k.$$

Further using the above derived relations, we modify our interaction Hamiltonian as follows

$$H_{\text{int}}^{\text{TPT}} = \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} (i\beta \epsilon_{ijk} \sigma_N^k \psi_n) (\psi_e^{\dagger} i\gamma_5 \beta \epsilon^{ijl} \sigma_l \psi_e)$$

$$= \frac{iG_F C_T}{\sqrt{2}} (\psi_n^{\dagger} (\beta \epsilon_{ijk} \sigma_N^k \psi_n) (\psi_e^{\dagger} \beta \gamma_5 \epsilon^{ijl} \sigma_l \psi_e).$$
(1.1.8)

In our calculations, we consider a non-relativistic nucleus and hence spin do not couple with the orbital angular momentum of the system due to which nuclear Pauli matrix (σ_N) will not on act ψ_n and we have

$$H_{\text{int}}^{\text{TPT}} = i \frac{i G_F C_T}{\sqrt{2}} |\psi_n^{\dagger} \psi_n| (\psi_e^{\dagger} \beta^2 \epsilon_{ijk} \epsilon^{ijl} \sigma_N^k \gamma_5 \sigma_l \psi_e) \quad \text{with} \quad \epsilon_{ijk} \epsilon^{ijl} = 2\delta_k^l$$

$$= i \frac{i G_F C_T}{\sqrt{2}} \rho_N(r) (\psi_e^{\dagger} 2\delta_k^l \sigma_N^k \gamma_5 \sigma_l \psi_e)$$

$$= i \sqrt{2} G_F C_T \delta_k^l \begin{pmatrix} \sigma_N^k & 0\\ 0 & \sigma_N^k \end{pmatrix} \begin{pmatrix} 0 & \sigma_k\\ \sigma_k & 0 \end{pmatrix} \rho(r)$$

$$= i \sqrt{2} G_F C_T \begin{pmatrix} 0 & \sigma_N \cdot \sigma\\ \sigma_N \cdot \sigma & 0 \end{pmatrix} \rho(r), \quad (1.1.9)$$
where $\rho(r)$ is the nuclear density, σ_N is the nuclear Pauli matrix and $I = \frac{1}{2}\sigma_N$; with I being the nuclear angular momentum. Now for an N-electron system, our P,T-odd interaction Hamiltonian is given by

$$H_{\rm int}^{\rm TPT} = i2\sqrt{2}G_F C_T \langle I \rangle \gamma \ \rho(r) \ . \tag{1.1.10}$$

We will use the above expression of $H_{\text{int}}^{\text{TPT}}$ for the atomic many-body calculations to evaluate EDMs in the closed-shell atomic systems. On combining our EDM results obtained using $H_{\text{int}}^{\text{TPT}}$ with the available measurements, we can deduce the coupling coefficient C_T . Another source which adds to the atomic EDM is the P,T-odd e-N S-PS interaction but in the closed-shell atoms it contributes along with hyperfine interaction in the third order of perturbation theory. The coupling C_T is related to the e-N S-PS coupling coefficient C_P by the expression [25]

$$C_P \leftrightarrow \frac{5m_p R}{Z\alpha_f} C_T \approx 3.8 \times 10^3 \frac{A^{1/3}}{Z} C_T,$$
 (1.1.11)

where m_p is the proton mass, α_f is the fine structure constant, R is the nuclear radius, Z is the atomic number and A is the nuclear mass of the considered system.

1.1.2 Hadronic Source: Nuclear Schiff Moment

The observation of EDMs in the closed-shell atoms are strongly suppressed by the the screening effect. According to the Schiff's theorem "For a non-relativistic system made up of point, charged particles which interact electro-statically with each other and with an arbitrary external field, the shielding is complete" [26]. Non-relativistically, on application of external electric field the constituent particles in the system orient themselves in such a way that the effective electric field at the site of the nucleus in zero due to which there is no interaction between the applied field and the nuclear-EDM. Therefore, the shielding renders the detection of nuclear EDM impossible. However, there are three effects which cause deviations from the "Schiff Theorem". They are

- **Relativistic effects**: the constituent particles are relativistic; specifically in the heavier systems.
- Volume effect: the constituent particles are not points, but have finite sizes.
- Non-electrostatic interactions: the constituent particles interact via P,T-odd interactions.

The above factors lead to imperfect shielding in the atomic systems which can be exploited to measure EDMs of atoms and molecules. In the closed-shell atoms due to finite size of nucleus, there is a misalignment between the charge and EDM density distributions which give rise to the P,T-odd moments of the nucleus. These moments interact with the electrons and give rise to the atomic EDM and hence, first order energy shift in the measurement. The NSM ($\mathbf{S} = S\mathbf{I}/I$) is the lowest order P,T-odd nuclear moment which arises in the multipole expansion of the nuclear potential when subjected to the electron screening. The NSM produces a P,T-odd potential which mixes the opposite parity states of the electronic wave function and hence, induce EDMs in the closed-shell atomic systems. At the nucleon level, NSM originates primarily from the P,T-odd interactions between the nucleons and due to the intrinsic nucleon-EDMs. The expression for the NSM (S) is obtained by considering the following nuclear electrostatic potential screened by the atomic electrons [27]

$$\phi(\mathbf{R}) = \int \frac{e\rho(r)}{|\mathbf{R} - \mathbf{r}|} d^3r + \frac{1}{Z} (\vec{d} \cdot \nabla) \int \frac{\rho(r)}{|\mathbf{R} - \mathbf{r}|} d^3r, \qquad (1.1.12)$$

where the second term represents screening, $\nabla_i = \partial/\partial_i$, and the P,T-odd nuclear EDM $\vec{d} = \int e\mathbf{r}\rho(r)d^3r = d\frac{\mathbf{I}}{I}$. The second term in Eq. 1.1.12 cancels the longrange dipole electric field in the multipole expansion of $\phi(\mathbf{R})$. We can expand the Coulomb potential $1/|\mathbf{R} - \mathbf{r}|$ in terms of the Legendre polynomials as

$$\frac{1}{|\mathbf{R} - \mathbf{r}|} = \sum_{l} \frac{r_{<}^{l}}{r_{>}^{l+1}} P_{l}(\cos(\theta)), \qquad (1.1.13)$$

where $r_{<}(r_{>})$ is the smaller (larger) value among R and r. Considering the odd harmonics $l = 1, 3, \cdots$ in the above potential, we get P,T-odd part of the potential such that l=1 corresponds to dipole field, l=3 corresponds to the octupole field etc.. The contribution from the octupole field is negligibly small because of its higher rank, it can mix only the orbitals of higher angular momentum symmetries that marginally penetrate the vicinity of the nucleus due to their larger centrifugal barrier. In most of the cases, it is preferred to consider a system with nuclear spin I=1/2, because octupole field is zero in those systems. Here, we are interested only in the selected terms of Eq. 1.1.12 which are first order in the P,T-odd interactions. We consider l = 1 in the first of the Eq. 1.1.12 which corresponds to the distortion in spherical charge distribution due to the P,T-odd interactions. The dominant P,T-odd term in the screening part of the Eq. 1.1.12 is obtained for l = 0, which shows that the spherical charge distribution and P,Todd moment comes from the nuclear-EDM only (\vec{d} contains P,T-odd density). Considering the first term with l = 1 for which $P_1(\cos(\theta)) = \cos(\theta)$, we get

$$\int_{0}^{\infty} \frac{e\rho(r)}{|\mathbf{R} - \mathbf{r}|} d^{3}r = \int_{0}^{R} \frac{e\rho(r)}{|\mathbf{R} - \mathbf{r}|} d^{3}r + \int_{R}^{\infty} \frac{e\rho(r)}{|\mathbf{R} - \mathbf{r}|} d^{3}r$$
$$= \frac{1}{R^{2}} \int_{0}^{R} e\rho(r)r\cos(\theta)d^{3}r + \mathbf{R} \int_{R}^{\infty} \frac{e\rho(r)}{r^{2}}\cos(\theta)d^{3}r$$
$$= \frac{e\mathbf{R}}{R^{3}} \cdot \int_{0}^{R} \mathbf{r}\rho(r)d^{3}r + e\mathbf{R} \cdot \int_{R}^{\infty} \frac{\rho(r)}{r^{2}}d^{3}r.$$
(1.1.14)

In the screening term with l = 0, in which $P_0(\cos(\theta)) = 1$, we get

$$\frac{1}{Z}(\mathbf{d}.\nabla) \int \frac{\rho(r)}{|\mathbf{R}-\mathbf{r}|} d^3r = \frac{1}{Z}(\mathbf{d}.\frac{\partial}{\partial R}) \frac{1}{R} \int_0^R \rho(r) d^3r + \frac{1}{Z}(\mathbf{d}.\frac{\partial}{\partial R}) \int_R^\infty \frac{\rho(r)}{r} d^3r \\
= -\frac{\mathbf{d}\cdot\mathbf{R}}{ZR^3} \int_0^R \rho(r) d^3r + \text{zero} \quad \text{(No derivative w.r.t } R) \\
= -\frac{e\langle\mathbf{r}\rangle\cdot\mathbf{R}}{ZR^3} \int_0^R \rho(r) d^3r. \quad (1.1.15)$$

From Eqs. 1.1.14 and 1.1.15, we get the first order screened electrostatic potential which contains only one order of P,T-odd interaction. Thus,

$$\phi^{(1)}(\mathbf{R}) = \frac{e\mathbf{R}}{R^3} \cdot \int_0^R \mathbf{r}\rho(r) d^3r + e\mathbf{R} \cdot \int_R^\infty \frac{\rho(r)}{r^2} d^3r - \frac{e\langle \mathbf{r} \rangle \cdot \mathbf{R}}{ZR^3} \int_0^R \rho(r) d^3r.$$
(1.1.16)

To simplify it further, we express the limit of integration as $\int_0^R = \int_0^\infty - \int_R^\infty$ and in the limits $\mathbf{R} \to \infty$ the first and the last terms in Eq. 1.1.16 become

$$\frac{e\mathbf{R}}{R^3} \cdot \int_0^\infty \mathbf{r}\rho(r)d^3r = \frac{e\langle \mathbf{r}\rangle\mathbf{R}}{R^3},\tag{1.1.17}$$

and

$$\frac{e\langle \mathbf{r} \rangle \cdot \mathbf{R}}{ZR^3} \int_0^\infty \rho(r) d^3 r = \frac{e\langle \mathbf{r} \rangle \cdot \mathbf{R}}{ZR^3} Z = \frac{e\langle \mathbf{r} \rangle \cdot \mathbf{R}}{R^3}, \qquad (1.1.18)$$

respectively, and cancel each other. With this cancellation Eq. 1.1.16 reduces to

$$\phi^{(1)}(\mathbf{R}) = -\frac{e\mathbf{R}}{R^3} \cdot \int_R^\infty \mathbf{r}\rho(r)d^3r + e\mathbf{R} \cdot \int_R^\infty \frac{\rho(r)}{r^2}d^3r + \frac{e\langle \mathbf{r} \rangle \cdot \mathbf{R}}{ZR^3} \int_R^\infty \rho(r)d^3r$$
$$= e\mathbf{R} \cdot \left[\int_R^\infty \left(\frac{\langle \mathbf{r} \rangle}{ZR^3} - \frac{\mathbf{r}}{R^3} + \frac{\mathbf{r}}{r^3}\right)\rho(r)d^3r\right].$$
(1.1.19)

The charge density outside the nucleus is zero. Therefore, $\rho(r)$ is zero for $r > R_N$. In the non-relativistic limit the matrix element of the Hamiltonian corresponding to the above P,T-odd potential with respect to the *s* and *p* orbitals are non-zero as they give the dominant contributions is given by [28]

$$\langle \psi_s | - e\phi^{(1)}(\mathbf{R}) | \psi_p \rangle = 4\pi e \mathbf{S} \cdot (\nabla \psi_{\mathbf{s}}^{\dagger} \psi_{\mathbf{p}})_{R \to 0}, \qquad (1.1.20)$$

where the nuclear Schiff moment (\mathbf{S}) is defined as

$$\mathbf{S} = \frac{e}{10} \left[\langle r^2 \mathbf{r} \rangle - \frac{5}{3Z} \langle r^2 \rangle \langle \mathbf{r} \rangle \right] = S \frac{\mathbf{I}}{I}.$$
 (1.1.21)

The matrix element in Eq. 1.1.20 is finite for the non-relativistic electrons but for the relativistic electrons it diverges in the limit $\mathbf{R} \to \mathbf{0}$ (for a point nucleus). The problem of divergence is usually solved by a cutoff of the electron wave functions at the nuclear surface (considering the finite size nucleus) and calculating its local dipole moment (LDM) [28]. The approach of LDM, naturally, incorporates relativistic corrections from the electron wave function to the NSM. In the same work, for a finite size nucleus, Flambaum and Ginges [28] generalized the expression for the NSM potential to

$$\phi^{(1)}(\mathbf{R}) = -\frac{3\mathbf{S}.\mathbf{R}}{B_4}\rho(R), \qquad (1.1.22)$$

where $B_4 = \int_0^\infty dR R^4 \rho(R)$. This form of the potential has no singularities and is suitable in the consideration of the relativistic calculations for the atomic systems. The Hamiltonian corresponding to the above potential can be given by

$$H_{\rm int}^{\rm NSM} = -e\phi^{(1)}(\mathbf{R}) = e\frac{3\mathbf{S}.\mathbf{R}}{B_4}\rho(R).$$
(1.1.23)

Till date, the best upper limit on the atomic EDM (d_A) of a diamagnetic system has been obtained from ¹⁹⁹Hg as [29]

$$|d_A| < 3.1 \times 10^{-29} |e| \text{cm}$$
 (with 95% confidence level). (1.1.24)

On combining the experimental data with the accurate many-body atomic calculations considering the $H_{\text{int}}^{\text{NSM}}$, an upper bound on S can be obtained. The value for S can also be obtained from various nuclear structure calculations in terms of the CP-violating pion-nucleon-nucleon (πnn) coupling constants $\bar{g}_{\pi nn}$ as

$$\mathbf{S} = g_{\pi nn} [a_0 \bar{g}^0_{\pi nn} + a_1 \bar{g}^1_{\pi nn} + a_2 \bar{g}^2_{\pi nn}] |e| \text{ fm}^3.$$
(1.1.25)

where $g_{\pi nn}$ is the CP-conserving πnn coupling constant, $\bar{g}^{i}_{\pi nn}$ (i = 0, 1, 2) represent the isospin components of CP-violating πnn couplings and the coefficients a_0, a_1, a_2 parametrize the dependence of S on the P,T-violating interactions. In a recent work, Engel *et al.* [24] considered all the latest nuclear model calculations on atomic nuclei of ¹⁹⁹Hg, ¹²⁹Xe and ²²⁵Ra and found that the parameters a_0 , a_1 , a_2 in operator *S* vary significantly in magnitudes from one to another. Moreover in ¹⁹⁹Hg, parameters differ not only in magnitudes by also in sings. However in the same Ref. [24], they provide a range to these parameters along with their best values for the above atoms as given in Table 1.1. The beyond-SM theories relate

Table 1.1: The ranges and the best values for the coefficients a_i 's predicted from various nuclear models in three nuclei which are used for the EDM analysis of closed-shell atoms.

	Ranges			Best Values		
System	a_0	a_1	a_2	a_0	a_1	a_2
¹²⁹ Xe ¹⁹⁹ Hg ²²⁵ Ra	$\begin{array}{c} 0.005(0.05) \\ 0.0050.05 \\ 1(6) \end{array}$	$\begin{array}{c} 0.003(0.05)\\ 0.03(+0.09)\\ 424 \end{array}$	$\begin{array}{c} 0.005(\ 0.1) \\ 0.010.06 \\ 3(15) \end{array}$	-0.008 0.01 -1.5	$-0.006 \pm 0.02 \\ 6.0$	$-0.009 \\ 0.02 \\ -4.0$

 $\bar{g}_{\pi nn}^0$ to the strong CP parameter of QCD as $\bar{g}_{\pi nn}^0 = -0.018(7)\bar{\theta}$ [23], from where limit on $\bar{\theta}$ can be deduced. Furthermore, chromo-EDMs predicted by beyond SM theories like SUSY and the left-right symmetric models is related to $\bar{g}_{\pi nn}^1$ by the relation $\bar{g}_{\pi nn}^1 = 2 \times 10^{-12} (\tilde{d}_u - \tilde{d}_d)$ [30], where \tilde{d}_u and \tilde{d}_s are the chromo-EDMs for the u and d quarks respectively. Therefore, from the limits on S one can also obtain bounds on the combined $(\tilde{d}_u - \tilde{d}_d)$.

1.1.3 Leptonic Source: Electron EDM (d_e)

The contributions of the d_e in an atomic EDM of the closed-shell system is negligible because of the fact that the electronic angular momentum is zero. The tiny effect which comes from the electron EDM is through higher order perturbations and the first order effect does not contribute. In the ground state of an atom the magnetic field due to the nuclear magnetic moment interacts with d_e to generate possible EDM of the atom which roughly scales as [31]

$$d_A \sim (R_f - 1) Z^2 \alpha_f^2 \frac{m_e}{m_p} d_e,$$
 (1.1.26)

where m_e is the electron mass, m_p is the proton mass, α_f is the fine structure constant and the relativistic factor R_f is given by

$$R_f = \left(\frac{a_0}{2ZR_N}\right)^{2-2\gamma} \frac{4}{[\Gamma(2\gamma+1)]^2}, \quad \gamma = (1-Z\alpha^2)^{1/2}$$
(1.1.27)

with a_0 is the Bohr radius and R_N is the nuclear radius. For the ¹⁹⁹Hg atom, nuclear radius $R_N = 7$ fm which gives the value for $R_f = 8$ and from Eq. 1.1.26, we get $d_A \sim 10^{-3} d_e$. Another effect somewhat more dominant than the previous one through which d_e can contribute to the atomic EDM is through the hyperfine coupling in the third order of perturbation [31]. Combining the above two effects the atomic EDM of ¹⁹⁹Hg is roughly equals to $-0.014d_e$, which shows that contribution of d_e to the atomic EDM is still suppressed by at least two orders in magnitude. Similar calculations for ¹²⁹Xe also shows very high suppression of d_e as $d_A = -0.0008d_e$. Therefore, the contribution of d_e is neglected in most of the calculations and e-N T-PT and NSM interactions are considered as dominant sources of EDMs in the closed-shell atoms.

1.2 Dipole Polarizability as a Benchmark for the Accuracies of EDM Studies

Electric dipole polarizability (α) of any atomic or molecular system is a measure of distortion of the electron cloud when the system is subjected to an external electric field (**E**). In other words α is the measure of rearrangement of the charged particles in a composite system due to the application of an external **E**. The predictive power of any many-body method is judged on the basis of its ability to reproduce the experimental values consistently for different systems. In this thesis, we aim to calculate permanent EDMs due to e-N T-PT and NSM interactions in closed-shell atoms whose experiments are currently underway. To carry out their calculations, we first test validity of the many-body methods that give these quantities reliably. For this purpose, we carry out calculations of α s of atomic systems using these methods. The main reason for determining α s in



Figure 1.4: General principle of all EDM measurements where Larmour spin precession frequencies are measured when electric field **E** is parallel and anti parallel to the magnetic field **B**. The difference in the frequencies $(\omega_1 - \omega_2)$ is the measure of intrinsic EDM.

the atomic systems for the EDM studies is that calculations of both α and EDM require similar numerical accuracies of the atomic wave functions in mid and large r domains and angular momentum selection rules. Again, it is possible to compare the calculated α s with their available experimental results. This would indirectly give some idea about the calculated values of EDMs in the atomic systems by employing the same many-body methods.

1.3 General Principle of EDM Measurement

The basic principle of EDM measurement is easy to follow and the technique is almost similar in all the experiments with an aim to observe the effect of an external electric field on the spin (nuclear or electronic) of the system. Basically, an atomic system is placed in an electric field and just like Zeeman effect shift in the energy levels are measured. The energy shift proportional to the relative orientation of the electron spin and the electric field is the signature of a non-zero EDM. In the experiment, we also have a magnetic field which is aligned parallel or anti-parallel to the electric field. If \vec{d} and $\vec{\mu}$ are the EDM and magnetic moment of the system, respectively, then the electric and magnetic interaction energies are given by $-\vec{d}.\vec{E}$ and $-\vec{\mu}.\vec{B}$ respectively. Now if we consider a closed-shell atom with nuclear spin $\vec{I} = 1/2$ and just two spin states corresponding of $\pm 1/2$, then the total energy of the system subjected to above electromagnetic field is given by

$$\hbar\omega = 2[\mu B + dE],\tag{1.3.1}$$

where \hbar is the reduced Planck's constant and ω is the Larmour spin resonance frequency at which spin precesses about the field axis due to the torque on the electric and magnetic dipoles. In order to extract EDM, ω is measured twice. In the first case electric and magnetic field are kept parallel to each other while in the second case the orientation of the electric field is switched opposite to the of the magnetic field as shown in Fig. 2.1.8. The measured Larmour spin resonance frequencies ω_1 and ω_2 in both the cases are given as

$$\omega_1 = 2[\mu B + dE]/\hbar \tag{1.3.2}$$

and
$$\omega_2 = 2[\mu B - dE]/\hbar.$$
 (1.3.3)

On subtracting Eq. 1.3.3 from Eq. 1.3.2, the magnetic term cancels out and hence, we obtain

$$\Delta \omega = \omega_2 - \omega_1 = \frac{4dE}{\hbar}.$$
(1.3.4)

Since the change in frequency and the strength of the applied electric field are known, the intrinsic EDM can be evaluated from the above expression.

1.3.1 Difficulties in the EDM Measurements

To infer EDM, we need to precisely measure the tiny change in the Larmour frequency. In order to have a rough estimate of how small this change in the frequency is, lets assume EDM $d \approx 10^{-30} |e|$ cm and effective electric field $E_{eff} = 10^5 V/cm$. Substituting in the above equation, we get

$$\Delta \omega = \frac{4(10^{-30}e.cm)(10^5 V/cm)}{6.58 \times 10^{-16} eV.s} \approx 10^{-9} \text{Hz.}$$
(1.3.5)

To measure such a small shift in frequency requires advanced state of art experimental techniques. Moreover, there are many systematic and statistical effects which account for the uncertainty in the experiment. Till date, in all the measurements these uncertainties are larger than the observed value (frequency shift). That is the reason why we have null results so far. The measurements are underway to improve the systematic and statistical sensitivities of the experiments. The two most important sources of systematic effects are

- Leakage current: The magnetic term in Eq. 1.3.1 always dominates because of the fact that the EDM is very tiny. Therefore, the major challenge in the experiment is to keep the magnetic field unchanged specially while reversing the direction of the electric field. The high voltage between plates introduces "leakage" current along any surface connecting between these two plates that generates a stray magnetic field. When the polarity of the plate is reversed, the "leakage" current also reverse its direction. In this process the stray magnetic field introduces error while measuring $\Delta \omega$.
- Motional magnetic field: Atoms moving in the external E experience magnetic field in their rest frame given by B_m = v × E/c. Since B_m is odd under parity, it mimics a false EDM signal.

Apart from systematic effects, statistical uncertainty also plays an important role in obtaining precise measurements. The achievable statistical uncertainty in an EDM experiment can be generically described by the following statistical sensitivity formula

$$\delta d = \frac{\hbar}{\epsilon E \sqrt{N\tau T}},\tag{1.3.6}$$

where ϵ is the efficiency of the experiment, E is the applied electric field, τ is the spin coherence time, N is the number of particles in the observational volume and T is the measurement time. If a measurement run for $T = 10^5$ s with the typical values $\mathbf{E} = 10^5 \text{V/cm}$, $\epsilon = 0.1$, $N = 10^6$ and $\tau = 1$ s, then one gets $\delta d = 10^{-27} |e|$ cm. The improvement in the statistical uncertainties can be achieved by increasing the number of particles and coherence time (for e.g. in ¹²⁹Xe EDM experiment $N = 10^{21}$ and $\tau = 1000$ s).

1.4 Brief History and Current Status of EDM Measurements of Closed-Shell Atoms

The history of the EDM measurement of the closed-shell systems is not very old. There are only a few systems on which EDM measurements have been reported so far, the limits to the d_A obtained from those measurements are presented in Table 1.4.

As mentioned earlier, the best upper limit to the closed-shell atomic EDM is obtained from ¹⁹⁹Hg [29]. It provides an extremely tight bound on various CPviolating sources at the nuclear level. The experiment consisted of a stack of four spin-polarized Hg vapor cells in a common **B** field which drastically improved the statistical sensitivity of the measurement by gaining in larger spin coherence time and reducing the magnetic noise.

In a recent past, an experimental group at Argonne National Laboratory (ANL) has unveiled the first EDM measurement of 225 Ra [32]. Though the limit is not competitive against the limit obtained from 199 Hg, there is a scope for rapid improvement. Theoretically, the octupole deformation in the nucleus of 225 Ra can enhance its EDM by at least two to three orders in magnitude as compared to 199 Hg [27,33]. In addition to that, due to larger Z value EDM enhancement in 225 Ra is large as compared to 199 Hg. The uncertainty due to the superfluous contribution from the octupole moment vanishes in 225 Ra and 199 Hg, owing to their nuclear spin half. On the experimental front, cold-atom techniques that are least sensitive to systematics [34] have been developed to measure the Larmour spin resonance frequency for 225 Ra atoms [35,36]. Moreover, using the facility of rare isotope beam (FRIB) for a measurement time of 100 days, the ANL research group hopes to bring about significant improvement in the statistical uncertainty by increasing number of atoms in the observational volume to 10^6 [37].

In the atomic system ¹²⁹Xe, very first EDM measurement was performed with the spin exchange maser and upper limit to the EDM was obtained as $d_A(^{129}\text{Xe}) < 4.1 \times 10^{-27}|e| \text{ cm } [38]$. The systematics of the measurement were taken into account by using ³He as a co-magnetometer. In order to surpass the

Atoms	Limit $ e $ cm	Laboratory	Reference
129 Xe	$< 4.1 \times 10^{-27} < 3.1 \times 10^{-29} < 5.0 \times 10^{-22}$	University of Michigan	[38]
199 Hg		University of Washington	[29]
225 Ra		Argonne National Laboratory	[32]

Table 1.2: Upper limits on the closed-shell atomic EDMs obtained from three different measurements.

limit set by ¹⁹⁹Hg atom, several proposals to measure EDM in ¹²⁹Xe are underway with advanced techniques such as nuclear spin maser which is a mechanism to sustain the nuclear spin precession for unlimitedly long duration and thereby realizing long measurement times [39–41]. Though Xe has smaller Z compared to Hg but having larger spin coherence time of about 1000 seconds and higher number of particle in observational volume $N > 10^{21}$ makes it quit attractive candidate for the EDM measurement.

The other interesting candidates for the EDM searches are ²²³Rn and ¹⁷¹Yb atoms, just like ²²⁵Ra they also have octupole deformation in their nucleus which naturally enhance the NSM and hence, atomic EDM. So far no EDM measurements in these systems have been reported yet but the experiments are in progress with a quest to find our non-zero EDMs [34, 42, 43].

1.5 Thesis Overview

The rest of thesis is organized as follows:

In Chap. 2, we systematically present various relativistic many-body methods such as many-body perturbation theory (MBPT), random phase approximation (RPA) and relativistic coupled-cluster (RCC) theory at different levels of approximations. These methods are then employed to calculate dipole polarizability (α) and atomic EDM (d_A) in a number of closed-shell atomic systems.

In Chap. 3, we demonstrate a computational procedure to implement our many-body methods described in Chapter 2 to determine α and d_A .

In Chap. 4, we benchmark our many-body methods by studying the behavior of electron correlation effects in determining α of many closed-shell atoms and ions.

In Chap. 5, we employ our many-body methods to finally calculate EDMs due to the T-PT and NSM interactions of experimentally interesting closed-shell atoms. These atoms are ¹²⁹Xe, ¹⁹⁹Hg, ²²⁵Ra and ²²³Rn with zero electronic angular momentum and nuclear spin I = 1/2. In addition to that we also evaluate α in the above systems and compared them with the available experimental results. On combining our Hg EDM results with the most precise measurement, we obtain accurate bounds on C_T , S, $\bar{\theta}$ and chromo-EDMs of quarks.

Finally in Chap. 6, I conclude my thesis by emphasizing on the importance of our obtained results for α and d_A . With the ongoing improvement in the EDM measurement of ²²⁵Ra at Argonne National Laboratory our theoretical results would be very crucial to obtain decisive limits on various P,T-odd couplings.

In order to improve these calculations further, we need more sophisticated many-body methods like normal coupled-cluster (NCC) theory. In this thesis, I also give the working equations of NCC theory.

Chapter 2

Relativistic Many-Body Methods for EDM Studies

2.1 Introduction

An electric dipole moment (EDM) of a closed-shell atom (d_A) is calculated by evaluating the expectation value of the dipole operator (D) which is given by,

$$d_{\rm A} = \frac{\langle \Psi | D | \Psi \rangle}{\langle \Psi | \Psi \rangle},\tag{2.1.1}$$

where $|\Psi\rangle$ is the exact many-body wave function of the considered system. In order to determine d_A precisely, we need to evaluate $|\Psi\rangle$ as accurately as possible for which one need to solve the following many-body Schrödinger's equation

$$H|\Psi\rangle = E|\Psi\rangle, \qquad (2.1.2)$$

where E is the exact energy and H is the Hamiltonian of the considered atomic state. From the basic quantum mechanics, we understand that the Schrödinger's equation of a multi-electron system cannot be solved exactly because of the presence of two-body inter-electronic Coulombic repulsion term in the Hamiltonian [7]. Therefore, in order to determine $|\Psi\rangle$ reliably one has to start with a suitable approximation. Sandars [44] had shown that the EDM of a closed-shell atom scales faster than Z^2 with Z being the nuclear charge. Therefore in experiments heavier systems are preferred for EDM measurements. Now, with larger Z value, relativistic effects become crucial in the atomic calculations. Moreover, as mentioned in the previous chapter, one of the main assumptions of Schiff theorem [26] is that, in the non-relativistic limit atom does not acquire EDM even if its constituent particle does. Thus, one has to consider relativistic theory for the many-body calculations of d_A . In the relativistic theory atoms can be described with the Dirac-Coulomb (DC) Hamiltonian, which in atomic units (au) is given by

$$H_{\rm DC} = \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_n(r_i) + \sum_{j>i}^{N} \frac{1}{r_{ij}} \right],$$

where N is the total number of electrons in the system, c is the velocity of light in vacuum, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the Dirac matrices, V_n denotes the nuclear potential at the site of electron and $1/r_{ij}$ is the Coulombic repulsion between the i^{th} and j^{th} electrons. In this work, we consider the Hamiltonian H of the atomic system given in Eq. 2.1.2 as the sum of H_{DC} and an additional interaction Hamiltonian H_{int} . The H_{int} is either the tensor-pseudotensor (T-PT) or the nuclear Schiff moment (NSM) interaction Hamiltonians which are described in the previous chapter and are given by [25, 28]

$$H_{\rm int}^{\rm TPT} = i2\sqrt{2}G_F C_T \langle I \rangle > \gamma \ \rho(r) \tag{2.1.3}$$

and

$$H_{\rm int}^{\rm NSM} = \frac{3\mathbf{S.r}}{B_4}\rho(r),\tag{2.1.4}$$

respectively, with G_F is the Fermi coupling constant, C_T is the T-PT coupling constant, I is the nuclear spin, γ_i represents the Dirac gamma matrices, $\rho(r)$ is the nuclear density, $\mathbf{S} = S \frac{\mathbf{I}}{I}$ is the NSM and $B_4 = \int_0^\infty dr r^4 \rho(r)$. The H_{int} is odd under parity transformation. Thats why, it mixes the opposite parity states of the atomic systems and give rise to the permanent EDM of the system. The strength of H_{int} is very weak, for which, it is considered as a perturbation in the system such that Eq. 2.1.2 becomes

$$(H_{\rm DC} + \lambda H_{\rm int})|\Psi\rangle = E|\Psi\rangle, \qquad (2.1.5)$$

where λ represents for the strength of the perturbation. In the first step, we evaluate for the unperturbed wave-function $(|\Psi_0\rangle)$ corresponding to $H_{\rm DC}$ by solving the following eigenvalue equation,

$$H_{\rm DC}|\Psi_0\rangle = E_0|\Psi_0\rangle. \tag{2.1.6}$$

Since EDM is the first order effect, in the second step we calculate $|\Psi_0^{(1)}\rangle$ which is the first order correction to $|\Psi_0\rangle$ due to H_{int} . The total wave function of the atomic system in the first order approximation becomes the admixture of opposite parity states given by, $|\Psi\rangle \simeq |\Psi_0\rangle + \lambda |\Psi_0^{(1)}\rangle$. Now the expression for d_A in this approximation is written as

$$d_{\rm A} = \frac{\langle \Psi | D | \Psi \rangle}{\langle \Psi | \Psi \rangle} \approx \frac{\langle \Psi_0 + \lambda \Psi_0^{(1)} | D | \Psi_0 + \lambda \Psi_0^{(1)} \rangle}{\langle \Psi_0 + \lambda \Psi_0^{(1)} | \Psi_0 + \lambda \Psi_0^{(1)} \rangle}.$$
 (2.1.7)

In the above equation, non-zero contribution to d_A will arise only from the terms having matrix elements involving opposite parity states, owing to the odd parity nature of D. Thus, the final expression for d_A by neglecting the λ^2 term in the normalization factor is given by

$$d_{\rm A} \simeq 2 \frac{\langle \Psi_0 | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \tag{2.1.8}$$

As stated earlier it is difficult to solve Eq. 2.1.6 exactly because of the presence of two body operator $1/r_{ij}$ due to which atomic wave function is not separable into single particle wave functions. Again, we cannot consider $1/r_{ij}$ as perturbation because the strength of the Coulomb interaction is not small. Instead of that, the above equation is solved traditionally by approximating $1/r_{ij}$ with an effective one-body mean-field potential such that it includes most of the electron correlation effects from $\frac{1}{r_{ij}}$. The remaining contribution from $\frac{1}{r_{ij}}$ is called as residual Coulomb interaction which is now small enough to be treated as perturbation to evaluate $|\Psi_0\rangle$. In the next section, we describe the Dirac-Fock (DF) mean-field theory which we adopt here as the first step towards the calculations of the atomic many-body wave functions.

2.1.1 Dirac-Fock Theory for Closed-Shell Atomic Systems

In the Dirac-Fock (DF) theory, the issue of non-separable nature of $H_{\rm DC}$ is simplified by an approximation based on the independent particle model. According to this model, we assume that each electron in an atom moves independently and sees an average potential due to interactions among all other electrons. This average potential is an effective one body operator and called as DF mean-field potential ($U_{\rm DF}(r_i)$). On adding and subtracting $U_{\rm DF}(r_i)$ in the $H_{\rm DC}$ we get

$$H_{\rm DC} = \sum_{i}^{N} \left[c \boldsymbol{\alpha}_{i} \cdot \mathbf{p}_{i} + (\beta_{i} - 1)c^{2} + V_{n}(r_{i}) + U_{DF}(r_{i}) \right] + \sum_{j>i}^{N} \frac{1}{r_{ij}} - U_{\rm DF}(r_{i})$$

$$= H_{\rm DF}(r_{i}) + V_{es}, \qquad (2.1.9)$$

with the residual Coulomb interaction given by $V_{es} = \sum_{j>i} (\frac{1}{r_{ij}} - U_{\text{DF}}(r_i))$. The residual interaction V_{es} is small enough to be treated perturbatively over the DF Hamiltonian (H_{DF}) . The eigenvalue equation corresponding to H_{DF} is given by

$$H_{\rm DF}|\Phi_0\rangle = E_{\rm DF}|\Phi_0\rangle, \qquad (2.1.10)$$

where $E_{\rm DF}$ is the DF energy and $|\Phi_0\rangle$ is given by a Slater determinant

$$|\Phi_{0}\rangle = \sqrt{\frac{1}{N!}} \begin{vmatrix} \phi_{a}(r_{1}) & \phi_{a}(r_{2}) & \cdots & \phi_{a}(r_{N}) \\ \phi_{b}(r_{1}) & \phi_{b}(r_{2}) & \cdots & \phi_{b}(r_{N}) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_{c}(r_{1}) & \phi_{c}(r_{2}) & \cdots & \phi_{c}(r_{N}) \end{vmatrix},$$
(2.1.11)

where $\phi(r_i)$ s are the single particle wave functions and $a, b, c \cdots$ represent the orbital indices. This form of many-electron DF wave function is anti-symmetric and obey the Pauli's exclusion principle when the coordinates of any two electrons are exchanged. Now due to the one-body operator $U_{\rm DF}(r_i)$, the DF Hamiltonian is variable separable and can be written as a sum of single particle Hamiltonians $(h_0(r_i))$ as $H_{\rm DF} = \sum_i^N h_0(r_i)$. Considering the above, the single particle DF equation with energy ϵ_a corresponding to orbital $|\phi_a\rangle$ is written as

$$h_0(r)|\phi_a\rangle = [c\boldsymbol{\alpha}_a \cdot \mathbf{p}_a + (\beta_a - 1)c^2 + V_n(r) + U_{\rm DF}(r)]|\phi_a\rangle = \epsilon_a|\phi_a\rangle, \quad (2.1.12)$$

and the potential $U_{\rm DF}(r_i)$ is given by

$$U_{\rm DF}(r_1)|\phi_a(r_1)\rangle = \sum_{b=1}^{occ} [\langle \phi_b(r_2)|\frac{1}{r_{12}}|\phi_b(r_2)\rangle|\phi_a(r_1)\rangle - \langle \phi_b(r_2)|\frac{1}{r_{12}}|\phi_a(r_2)\rangle|\phi_b(r_1)\rangle], \qquad (2.1.13)$$

where *occ* stands for the total number of occupied orbitals, the first and the last terms are called as the *direct* and the *exchange* terms of the DF potential respectively. The above DF equations are solved simultaneously in an iterative manner till the self-consistent results are obtained. Their solutions give us single particle energies and the wave functions for each electron and hence, $E_{\rm DF}$ and $|\Phi_0\rangle$. Further, in the relativistic theory a general single particle orbitals $|\phi_i(r)\rangle$ are expressed in the two components Dirac form as [45]

$$\phi_i(r) = \frac{1}{r} \begin{pmatrix} P_i(r)\chi_{\kappa_i,m_i}(\theta,\phi)\\ iQ_i(r)\chi_{-\kappa_i,m_i}(\theta,\phi) \end{pmatrix}, \qquad (2.1.14)$$

given $P_i(r)$ and $Q_i(r)$ are the large and small components of the radial wave function, $\chi_{\kappa,m}(\theta,\phi)$ are the spin angular functions with the relativistic quantum number κ given by

$$\kappa = -(j + 1/2)a$$
 and $l = j - \frac{1}{2}a$, with $a = \pm 1$ (2.1.15)

for the orbital angular momentum l, the total angular momentum j and the magnetic quantum number m that defines the axis of quantization. The radial components $P_i(r)$ and $Q_i(r)$ are constructed as the linear combinations of sufficiently large number of basis functions. For the atomic many-body calculations most commonly used basis functions are either the Slater type orbitals (STOs) or the Gaussian type orbitals (GTOs) [46,47]. For the precise EDM calculations we need the accurate behavior of the many-body wave functions particularly in the nuclear region. Ishikawa and Coworkers [48] showed that for a finite size nucleus the GTOs can give rise to a natural description of the relativistic wave functions. This is the main reason for considering the GTOs for the DF calculations. The radial components $P_i(r)$ and $Q_i(r)$ are expanded in terms of Gaussian type functions (GTFs), such that the above single particle orbital becomes

$$\phi_i(r) = \frac{1}{r} \left(\frac{\sum_k C_{ik}^L G_k^L(r) \chi_{\kappa_i, m_i}(\theta, \phi)}{\sum_k C_{ik}^S G_k^S(r) \chi_{-\kappa_i, m_i}(\theta, \phi)} \right), \qquad (2.1.16)$$

where $G_k^L(r)$ and $G_k^S(r)$ are the GTOs with coefficients C_{ik}^L and C_{ik}^S corresponding to the large and small components of the wave function. In the shorthand notation, we write

$$|\phi_i(r)\rangle = \sum_k C_{ik} |G_k(r)\rangle.$$
(2.1.17)

The GTFs in our case are given by

$$G_{k,i}^{L}(r) = N^{L} r^{k} e^{-\alpha_{i} r^{2}}$$

and
$$G_{k,i}^{S}(r) = N^{S} \left[\frac{d}{dr} + \frac{k}{r} \right] G_{k,i}^{L}(r), \qquad (2.1.18)$$

where N^L and N^S are the normalization constants for the respective large and small radial components of the GTFs, $k = 0, 1, 2, \cdots$ for $s, p, d \cdots$ type angular momentum symmetries, respectively, and the parameter α_i in the exponent is obtained using the following even tempering (ET) condition

$$\alpha_i = \alpha_0 \beta^{i-1}$$
 where $i = 1, 2, 3 \cdots, n$ (2.1.19)

with the parameters α_0 and β that are defined for each angular momentum symmetry during the calculations.

The radial grid points for the numerical calculations starts from inside of the nucleus at $r_0 = 2 \times 10^{-6}$ a.u. and then defined non-uniformly with a step size $h \simeq 1.61 \times 10^{-2}$ as

$$r_i = r_0 [e^{h(i-1)} - 1]. (2.1.20)$$

The kinetic balance condition imposed on the small radial components of the Dirac wave function given in Eq. 2.1.18 is to avoid variational collapse of the wave function in the continuum [45].

For a finite-size nucleus V_n is described using the Fermi-charge distribution of the nuclear density as given by

$$\rho_{\rm nuc}(r) = \frac{\rho_0}{1 + e^{(r-b)/a}},\tag{2.1.21}$$

where the parameter 'b' is the half-charge radius as $\rho_{\text{nuc}}(r) = \rho_0/2$ for r = b and 'a' is related to the skin thickness which are evaluated by

$$a = 2.3/4(ln3)$$
 and $b = \sqrt{\frac{5}{3}r_{rms}^2 - \frac{7}{3}a^2\pi^2},$ (2.1.22)

with r_{rms} is the root mean square radius of the nucleus. In our calculations, we have taken $a \approx 0.5234$ fm and $b = [5(0.836A^{1/3} + 0.570)^2 - 7\pi^2 a^2/3]^{1/2}$ fm using the Fermi charge distribution for the atomic mass of the system A. By using these values, we determine ρ_0 as

$$\rho_0 = Z \left[\frac{4}{3} \pi b^3 \left(1 + \frac{a^2 \pi^2}{b^2} + \frac{6a^3}{b^3} K_3 \right) \right]^{-1}, \qquad (2.1.23)$$

where Z is the atomic number and $K_n = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^3} e^{-nb/a}$. We consider 1200 grid points, $r_0 = 2 \times 10^{-6}$ au and maximum radial functions up to 500 au with h = 0.016 au in the numerical calculations. This defines 258 grid points within b value to describe the wave functions smoothly both inside and outside the atomic nucleus.

On substituting $|\phi_a(r)\rangle = \sum_k C_{ak} |G_k(r)\rangle$ and multiplying $\langle G_m(r)|$ from the left in the integro-differential equation given in Eq. 2.1.12 we get

$$\sum_{k} \langle G_m(r) | \tilde{h}_0 | G_k(r) \rangle + \sum_{k} \sum_{b} [\langle G_m(r_1) \phi_b(r_2) | \frac{1}{r_{12}} | \phi_b(r_2) \rangle G_k(r_1) \rangle + \langle G_m(r_1) \phi_b(r_2) | \frac{1}{r_{12}} | G_k(r_2) \phi_b(r_1) \rangle] C_{ak} = \epsilon_a \sum_{a} \langle G_m(r) | G_k(r) \rangle C_{ak},$$

where $\tilde{h}_0 = [c \boldsymbol{\alpha}_i \cdot \mathbf{p}_a + (\beta_i - 1)c^2 + V_n(r_a)]$. In a more compact notation, the above equation takes the form

$$\sum_{k} F_{mk} C_{ak} = \epsilon_a \sum_{mk} \langle G_m(r) | G_k(r) \rangle C_{ak}, \qquad (2.1.24)$$

which can be further written in the matrix notation as [49]

$$\tilde{F}\tilde{C} = \epsilon \tilde{S}\tilde{C}, \qquad (2.1.25)$$

where \tilde{F} is the Fock matrix, $\tilde{S} = \langle G_m(r) | G_k(r) \rangle$ is called as the overlap matrix, \tilde{C} 's are eigenvectors and ϵ 's is the eigenvalues. To convert the above matrix into true eigenvalue equation form we multiply it with $\tilde{S}^{-1/2}\tilde{S}^{1/2}$ such that

$$\tilde{F}\tilde{S}^{-1/2}\tilde{S}^{1/2}\tilde{C} = \epsilon \tilde{S}^{1/2}\tilde{S}^{1/2}\tilde{C}$$
$$\tilde{S}^{-1/2}\tilde{F}\tilde{S}^{-1/2}\tilde{S}^{1/2}\tilde{C} = \epsilon \tilde{S}^{1/2}\tilde{C}$$
$$\tilde{F}'\tilde{C}' = \epsilon \tilde{C}', \qquad (2.1.26)$$

where $\tilde{F}' = \tilde{S}^{-1/2} \tilde{F} \tilde{S}^{-1/2}$ and $\tilde{C}' = \tilde{S}^{1/2} \tilde{C}$. This is a symmetric matrix which is diagonalized in order to get energy eigenvalues and eigenvectors for both the occupied and unoccupied orbitals. The above solutions are the mean field solu-



Figure 2.1: Diagram representing excitations of two electrons from core via Coulomb interaction represented by the dashed line.

tions, where, we have neglected the contributions from V_{es} as well as H_{int} . In order to obtain exact solutions of the atomic wave function $|\Psi\rangle$ and energy E, we need to incorporate contributions from these neglected effects. To do so, we consider our atomic mean field wave function $|\Phi_0\rangle$ and energy E_0 as our starting point in a perturbation theory, then we improve them order by order treating V_{es} and H_{int} as the perturbations.

In the next section, we briefly discuss the diagrammatic representations of electron excitation and de-excitation processes which are very useful tools to understand various physical processes more clearly in an atomic system . It also helps in understanding and solving complex many-body equations conveniently [50, 51]. In the rest of this chapter, different relativistic many-body methods such as many-body perturbation theory (MBPT), random phase approximation (RPA) and relativistic coupled-cluster (RCC) theory are explained to evaluate dipole polarizability (α) and d_A . We also study the trends in the electron correlation effects in evaluating these properties for many closed-shell atomic systems.

2.2 Graphical Representations of the Orbitals and Interactions

We will extensively use the graphical approach to represent orbitals and operators [51]. Throughout this thesis we denote occupied (core) orbitals by a, b, c, \cdots , unoccupied (virtual) orbitals by (p, q, r, \cdots) and the unspecified orbitals are shown by i, j, k, \cdots . Graphically, orbitals are represented by the solid arrows where a downward going arrow (hole line) represents a core orbital and the up-



Figure 2.2: The graphical representations of the creation and annihilation operators. The first and the second graphs show the creation of particle in virtuals and the annihilation of a particle in core whereas the third and fourth graph represent creation of hole in virtuals and destruction of hole in core respectively. The dashed line represents the reference state.

ward going arrow (particle line) represents a virtual orbital. The interaction between two electrons are shown by the horizontal line connecting to the electron orbital lines involved in the process. In addition to that the incoming and outgoing arrows with respect to the interaction vertices represent the initial and final states of the process respectively. To make it more clear, we show diagrammatically in Fig. 2.1 a process in which two electrons in core get excited by the Coulomb interaction. The complexity in many-body algebra can be significantly reduced by using the operators expressed in second quantization notation with creation (a^{\dagger}) and annihilation (a) operators [50, 51]. In the many-body calculations all the operators are normal-ordered with respect to the reference state $|\Phi_0\rangle$ [50, 51]. A similar diagrammatic scheme mentioned above is used to represent these general operators where operators a^{\dagger} and a are represented by the lines directed away and towards the vertices respectively, as shown in Fig. 2.2. Now using the above prescription, we present the diagrams of normal-ordered onebody Fock operator (h_0) and the two-body residual Coulomb interaction (V_N) in Fig. 2.3.

2.3 Many-Body Perturbation Theory (MBPT)

The purpose of employing MBPT is to improve the accuracy of the DF wave functions and energies by incorporating perturbations order by order. In this



Figure 2.3: Graphical representations of normal-ordered one-body Fock operator (h_0) and two-body residual Coulomb interaction (V_N) .

theory our target state is $|\Psi_0\rangle$ which satisfies the following equation

$$(H_{\rm DF} + V_{es})|\Psi_0\rangle = E_0|\Psi_0\rangle. \tag{2.3.1}$$

Here $H_{\rm DF}$ is the zeroth-order Hamiltonian and its exact solutions are already obtained earlier in this chapter and V_{es} is considered as a perturbation. The functional space is divided into model space, also called as P space and the orthogonal space also called as Q space. The P space is spanned by the eigenfunctions of the model Hamiltonian $H_{\rm DF}$ and Q space is constructed out of the remaining part of the functional space. The projection operator associated with the model and orthogonal spaces are given by

$$P = \sum_{\eta \in P} |\Phi_0^{\eta}\rangle \langle \Phi_0^{\eta}| \quad \text{and} \quad Q = \sum_{\zeta \notin P} |\Phi_0^{\zeta}\rangle \langle \Phi_0^{\zeta}|, \qquad (2.3.2)$$

respectively such that P + Q = I. The P and Q operators project out of any component of the function that lies in the model space and orthogonal space respectively. Moreover these operators satisfy number of well known relations,



Figure 2.4: Few important contributing diagrams of the MBPT(3) method. The lowest-order contribution is referred as DF result.

such as

$$P = P^{\dagger} = PP \qquad Q = Q^{\dagger} = QQ$$
$$[P, H_{\rm DF}] = [Q, H_{\rm DF}] = 0. \qquad (2.3.3)$$

Kuo *et al* [52] have shown that there is normally one to one correspondence between the eigenfunctions of the target Hamiltonian and their projections onto the model space

$$|\Phi_0\rangle = P|\Psi_0\rangle. \tag{2.3.4}$$

Therefore we define a single wave operator Ω which transform all the model

states into the corresponding target states, i.e.

$$|\Psi_0^a\rangle = \Omega|\Phi_0^a\rangle \qquad a = 1, 2, 3 \cdots, m \tag{2.3.5}$$

where m is the total number of model wave functions. Now on operating P from the left in Eq. 2.3.1 we get

$$(E - H_{\rm DF})|\Phi_0\rangle = PV_{es}|\Psi_0\rangle. \tag{2.3.6}$$

In the above equation, we used Eq. 2.3.4 and the commutation relation of P with H_{DF} . We further multiply Ω from the left in the above equation and use Eq.2.3.5, such that

$$E|\Psi_0\rangle - \Omega H_{\rm DF}|\Phi_0\rangle = \Omega P V_{es} \Omega |\Phi_0\rangle. \tag{2.3.7}$$

On subtracting Eq. 2.3.7 from Eq. 2.3.1, we eliminate E and get

$$(\Omega H_{\rm DF} - H_{\rm DF}\Omega)|\Phi_0\rangle = (V_{es}\Omega - \Omega P V_{es}\Omega)|\Phi_0\rangle, \qquad (2.3.8)$$

which can be written in the iterative form as [53, 54]

$$[\Omega, H_{\rm DF}]P = V_{es}\Omega P - \Omega P V_{es}\Omega P. \qquad (2.3.9)$$

This is called the generalized Bloch equation [55]. Expanding $\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} \cdots + \Omega^{(n)}$, where superscript *n* denotes the order of perturbation V_{es} with $\Omega^{(0)} = 1$. Substituting this expansion in Eq. 2.3.9, we get the recursive form of generalized Bloch equation as

$$[\Omega^{(n)}, H_{\rm DF}]P = QV_{es}\Omega^{(n-1)}P - \sum_{m=1}^{n-1}\Omega^{(n-m)}PV_{es}\Omega^{(m-1)}P \,.$$
(2.3.10)

The above equation can be expanded order by order to evaluate the amplitudes of Ω s operating on model wave function $|\Phi_0\rangle$ for the evaluation of the wave function $|\Psi_0\rangle$. As mentioned earlier, in addition to V_{es} we also consider H_{int} in the perturbation theory by expressing

$$H = H_{\rm DF} + V_{es} + \lambda H_{\rm int}, \qquad (2.3.11)$$

where λ represents order of H_{int} interaction. To incorporate both the perturbation simultaneously, we redefine our wave operator $\Omega^{(n)}$ such that the exact atomic wave function can be written as

$$|\Psi\rangle = \sum_{\beta,\delta} \Omega^{(\beta,\delta)} |\Phi_0\rangle, \qquad (2.3.12)$$

where the superscripts β and δ denote the order of perturbations from V_{es} and H_{int} respectively. In this work, we develop third order MBPT (MBPT(3)) method according to which we consider maximum of two orders of Coulomb interactions ($\beta = 0, 1, 2$) and only one order of H_{int} interaction ($\delta = 1$), owing to the fact that EDM is treat in the first order effect. The calculation of higher orders MBPT with the graphical approach is difficult because there are too many diagrams. In fact, considering beyond two orders in V_{es} , there will be at least eight internal lines (i.e. eight loops in a program) in a typical MBPT diagram which makes it computationally very demanding. The expression for d_A from Eq. 2.1.8 in the MBPT(3) method is given by

$$d_{\rm A} = 2 \frac{\langle \Psi_0 | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = 2 \sum_{\beta=0}^2 \frac{\langle \Phi_0 | \Omega^{\dagger(\beta,0)} D \Omega^{(\beta,1)} | \Phi_0 \rangle}{\langle \Phi_0 | \Omega^{\dagger(\beta,0)} \Omega^{(\beta,0)} | \Phi_0 \rangle}.$$
 (2.3.13)

Expanding the above equation for different values of β such that total perturbation should not exceed beyond three orders with at least one order of H_{int} , we get

$$d_{A} = \frac{2}{\mathcal{N}} \langle \Phi_{0} | [\Omega^{(0,0)} + \Omega^{(1,0)} + \Omega^{(2,0)}]^{\dagger} D [\Omega^{(0,1)} + \Omega^{(1,1)} + \Omega^{(2,1)}] | \Phi_{0} \rangle$$

$$= \frac{2}{\mathcal{N}} \langle \Phi_{0} | D \Omega^{(0,1)} + D \Omega^{(1,1)} + D \Omega^{(2,1)} + \Omega^{(1,0)^{\dagger}} D \Omega^{(0,1)} + \Omega^{(1,0)^{\dagger}} D \Omega^{(1,1)} + \Omega^{(2,0)^{\dagger}} D \Omega^{(0,1)} | \Phi_{0} \rangle, \qquad (2.3.14)$$

with the normalization constant $\mathcal{N} = \langle \Phi_0 | 1 + \Omega^{(1,0)^{\dagger}} \Omega^{(1,0)} | \Phi_0 \rangle$. The importance of various correlation terms in the determination of d_A can be better understood from an explicit analysis of lower-order perturbation calculations, where the contributions from the individual terms can be found explicitly. The lowest order MBPT(1) with $\beta = 0$ corresponds to the DF approximation which is given by

$$d_{\rm A} = 2 \langle \Phi_0 | D\Omega^{(0,1)} | \Phi_0 \rangle, \qquad (2.3.15)$$

and the intermediate MBPT(2) approximation follows with $\beta = 0, 1$ in Eq. 2.3.13 such that total perturbation should not exceed beyond two orders with one order of H_{int} . In this case, Eq. 2.3.13 reduces to

$$d_{\rm A} = \frac{2}{\mathcal{N}} \langle \Phi_0 | D\Omega^{(0,1)} + D\Omega^{(1,1)} + \Omega^{(1,0)^{\dagger}} D\Omega^{(0,1)} | \Phi_0 \rangle, \qquad (2.3.16)$$

with the normalization constant $\mathcal{N} = \langle \Phi_0 | \Phi_0 \rangle$. Few important diagrams corresponding to MBPT(1), MBPT(2) and a MBPT(3) methods are presented in Fig. 2.4. The amplitudes corresponding to the wave operators used in Eqs. 2.3.14,2.3.16 and 2.3.15 are obtained using the following Bloch equations

$$\begin{split} &[\Omega^{(1,0)}, H_{\rm DF}]P = QV_{es}P \\ &[\Omega^{(2,0)}, H_{\rm DF}]P = QV_{es}\Omega^{(1,0)}P - \Omega^{(1,0)}PV_{es}P \\ &\text{and} \\ &[\Omega^{(0,1)}, H_{\rm DF}]P = QH_{\rm int}P \\ &[\Omega^{(1,1)}, H_{\rm DF}]P = QV_{es}\Omega^{(0,1)}P + QH_{\rm int}\Omega^{(1,0)}P \\ &[\Omega^{(2,1)}, H_{\rm DF}]P = QV_{es}\Omega^{(1,1)}P + QH_{\rm int}\Omega^{(2,0)}P - \\ &\Omega^{(1,0)}PV_{es}\Omega^{(0,1)}P - \Omega^{(1,0)}PH_{\rm int}\Omega^{(1,0)}P. \end{split}$$

MBPT is a size-consistent theory which means that the energy scales linearly with the size of the many-body system. However, the major disadvantage with this method is that it is to cumbersome deal with beyond MBPT(3) method.

2.4 Random Phase Approximation (RPA)

Random phase approximation (RPA) is an all order theory where the single particle DF orbitals and energies are directly perturbed by the $H_{\rm int}$ operator. In the first order approximation, we get

$$|\phi_a^0\rangle \to |\phi_a^0\rangle + \lambda |\phi_a^1\rangle \quad \text{and} \quad \epsilon_i^0 \to \epsilon_a^0 + \lambda \epsilon_a^1,$$

$$(2.4.1)$$

where $|\phi_a^1\rangle$ and ϵ_a^1 are the first order corrections to the single particle wave function and energy, respectively. Owing to the fact that H_{int} is an odd parity operator, the first order correction to the energy $\epsilon_a^1 = 0$. Now in the presence of the perturbation source, the DF Eq. 2.1.12 for the single particle wave function yields the form

$$(h_{0} + \lambda H_{int})(|\phi_{a}^{0}\rangle + \lambda |\phi_{a}^{1}\rangle) + \sum_{b}^{occ} (\langle \phi_{b}^{0} + \lambda \phi_{b}^{1} | \frac{1}{r_{12}} | \phi_{b}^{0} + \lambda \phi_{b}^{1} \rangle | \phi_{a}^{0} + \lambda \phi_{a}^{1} \rangle - \langle \phi_{b}^{0} + \lambda \phi_{b}^{1} | \frac{1}{r_{12}} | \phi_{a}^{0} + \lambda \phi_{a}^{1} \rangle | \phi_{b}^{0} + \lambda \phi_{b}^{1} \rangle) = \epsilon_{a}^{0} (|\phi_{a}^{0}\rangle + \lambda |\phi_{a}^{1}\rangle).$$
(2.4.2)

On collecting terms linear in λ , we get

$$(h_0 + U_{\rm DF} - \epsilon_i^0) |\phi_a^1\rangle = (-H_{\rm int} - U_{\rm DF}^1) |\phi_a^0\rangle,$$
 (2.4.3)

where $U_{\rm DF}$ is the DF mean field potential defined earlier in the chapter and $U_{\rm DF}^1$ is the perturbed mean field potential given by

$$U_{\rm DF}^{1} |\phi_{a}^{0}\rangle = \sum_{b}^{occ} (\langle \phi_{b}^{0} | \frac{1}{r_{12}} | \phi_{b}^{1} \rangle | \phi_{a}^{0} \rangle - \langle \phi_{b}^{0} | \frac{1}{r_{12}} | \phi_{a}^{0} \rangle | \phi_{b}^{1} \rangle + \langle \phi_{b}^{1} | \frac{1}{r_{12}} | \phi_{b}^{0} \rangle | \phi_{a}^{0} \rangle - \langle \phi_{b}^{1} | \frac{1}{r_{12}} | \phi_{a}^{0} \rangle | \phi_{b}^{0} \rangle).$$
(2.4.4)

 $|\phi^1_a\rangle$ can be written as a linear combination of $|\phi^0_a\rangle$ which forms a complete basis set as

$$|\phi_a^1\rangle = \sum_{p \neq a} C_a^p |\phi_p^0\rangle, \qquad (2.4.5)$$

where C_a^p s are the expansion coefficients. On substituting Eq. 2.4.5 in Eq.2.4.3 and multiplying by $\langle \phi_p^0 |$ from left we get

$$\sum_{p \neq a} C_a^p \langle \phi_p^0 | (h_0 + U_{\rm DF} - \epsilon_a^0) | \phi_p^0 \rangle = \langle \phi_p^0 | (-H_{\rm int} - U_{\rm DF}^1) | \phi_a^0 \rangle$$
$$C_a^p = \sum_{p \neq a} \left[-\frac{\langle \phi_p^0 | H_{\rm int} | \phi_a^0 \rangle}{(\epsilon_p^0 - \epsilon_a^0)} - \frac{\langle \phi_p | (U_{\rm DF} + U_{\rm DF}^1) | \phi_a^0 \rangle}{(\epsilon_p^0 - \epsilon_a^0)} \right].$$
(2.4.6)

The coefficients C_a^p are obtained by solving the above equation, self-consistently with the initial guess

$$C_a^p = \sum_{p \neq a} -\frac{\langle \phi_p^0 | H_{\text{int}} | \phi_a^0 \rangle}{(\epsilon_p^0 - \epsilon_a^0)}.$$
(2.4.7)

In the Bloch's wave operator representation, we can express

$$\Omega_{\text{RPA}}^{(\infty,1)} = \sum_{p,a} \Omega_{a \to p}^{(\infty,1)} = \sum_{\beta=1}^{\infty} \sum_{pq,ab} \left\{ \frac{[\langle pb | \frac{1}{r_{12}} | aq \rangle - \langle pb | \frac{1}{r_{12}} | qa \rangle] \Omega_{b \to q}^{(\beta-1,1)}}{\epsilon_p^0 - \epsilon_a^0} + \frac{\Omega_{b \to q}^{(\beta-1,1)^{\dagger}} [\langle pq | \frac{1}{r_{12}} | ab \rangle - \langle pq | \frac{1}{r_{12}} | ba \rangle]}{\epsilon_p^0 - \epsilon_a^0} \right\},$$
(2.4.8)

where a, b and p, q are the short hand notation to denote the occupied and unoccupied orbital respectively. In the above equation $a \to p$ means replacement of an occupied orbital a from $|\Phi_0\rangle$ by a virtual orbital p which alternatively refers to a singly excited state with respect to $|\Phi_0\rangle$. This clearly indicates that the RPA method picks-up a certain class of singly excited configurations that corresponds to the core-polarization correlation effects. Using the above RPA wave operator, we evaluate d_A using the following expression

$$d_{A} = 2\langle \Phi_{0} | \Omega^{(0,0)^{\dagger}} D \Omega^{(\infty,1)}_{RPA} | \Phi_{0} \rangle$$

$$= 2\langle \Phi_{0} | D \Omega^{(\infty,1)}_{RPA} | \Phi_{0} \rangle. \qquad (2.4.9)$$

This method evaluates contributions to $|\Psi_0^{(1)}\rangle$ considering infinite orders in V_{es} through a chain of diagrams as shown in Fig. 2.5. Since RPA considers contributions only from the singly excited configurations and hence does not take



Figure 2.5: Graphical representations of the chain of direct diagrams obtained from the wave operator $\Omega_{\text{RPA}}^{\infty,1}$.

into account contributions from the pair-correlation effects. Moreover, in the property evaluation, this method approximates $\langle \Psi_0 |$ with the mean-field wave function $\langle \Phi_0 |$; which is a major drawback of this approach.

2.5 Relativistic Coupled-Cluster (RCC) Theory

The relativistic coupled-cluster (RCC) theory has been successfully used to study a wide range of many-body systems [50, 56, 57]. In fact, it is now considered as the "gold standard" of quantum chemistry. The RCC is an all-order method and it also satisfies the property of size-extensivity according to which the computed energy of the system scales correctly with the size of the system [58, 59]. In the RCC framework, the ground state wave function of a closed-shell system is given by

$$|\Psi\rangle = \Omega |\Phi_0\rangle = e^T |\Phi_0\rangle, \qquad (2.5.1)$$

where $|\Phi_0\rangle$ is the reference state (DF wave function) obtained by solving Eq. 2.1.12 and T is the cluster operator that excites electrons from the reference state. In the RCC method, the eigenvalue equation is given by

$$He^{T}|\Phi_{0}\rangle = Ee^{T}|\Phi_{0}\rangle, \qquad (2.5.2)$$

where the Hamiltonian $H = H_{\rm DC} + \lambda H_{\rm int} = H_{\rm DF} + V_{es} + \lambda H_{\rm int}$ with λ as a perturbation parameter. In order to consider two perturbations into account, we split the cluster operator as $T = T^{(0)} + \lambda T^{(1)}$. The $T^{(0)}$ operator takes care of



Figure 2.6: The unperturbed RCC operators corresponding to single and double excitations. The incoming and outgoing lines represent creation of the hole in the core and creation of particle in the virtuals respectively.

electron correlations effects from the perturbation V_{es} via even parity excitations of the electrons from the reference state $|\Phi_0\rangle$. The cluster operator $T^{(1)}$ considers perturbation H_{int} and excite electrons from the $|\Phi_0\rangle$ into opposite parity states. In this formalism, we will first discuss the evaluation of the unperturbed wave function $|\Psi_0\rangle$ corresponding to the Hamiltonian H_{DC} with V_{es} as a perturbation and then we will consider the perturbation H_{int} in order to improve $|\Psi_0\rangle$ to get the exact wave function $|\Psi\rangle$ corresponding to H.

2.5.1 Unperturbed RCC Theory to Evaluate $|\Psi_0\rangle$

In the RCC approach, the unperturbed wave function is given by

$$|\Psi_0\rangle = e^{T^{(0)}} |\Phi_0\rangle,$$
 (2.5.3)

where the cluster operator $T^{(0)}$ generates all possible even parity excitations and can be written as a sum of single, double, etc.. excitation operators as $T^{(0)} = T_1^{(0)} + T_2^{(0)} + \cdots$, where the operator $T_1^{(0)}$, $T_2^{(0)}$, etc. generate respective singly, doubly, etc. excited configurations with respect to the reference state $|\Phi_0\rangle$. These operators in the second quantization notation are expressed as

$$T_1^{(0)} = \sum_{a,p} a_p^{\dagger} a_a t_a^p \quad \text{and} \quad T_2^{(0)} = \frac{1}{4} \sum_{a,b,p,q} a_p^{\dagger} a_q^{\dagger} a_b a_a t_{ab}^{pq}, \tag{2.5.4}$$

where a, b, \cdots and p, q, \cdots correspond to occupied (core) and unoccupied (virtual) orbitals, respectively, a and a^{\dagger} represent annihilation and creation operators respectively and t_a^p and t_{ab}^{pq} are the cluster amplitudes associated with the single and double excitations respectively. In this thesis, we approximate the cluster operator to singles and doubles excitations only such as $T^{(0)} = T_1^{(0)} + T_2^{(0)}$ (CCSD method). These operators are also shown graphically in Fig. 2.6. In this approach, the eigenvalue equation corresponding to the DC Hamiltonian is given by

$$H_{\rm DC}e^{T^{(0)}}|\Phi_0\rangle = E_0 e^{T^{(0)}}|\Phi_0\rangle. \qquad (2.5.5)$$

On operating both side by $e^{-T^{(0)}}$, we get

$$e^{-T^{(0)}}H_{\rm DC}e^{T^{(0)}}|\Phi_0\rangle = E_0|\Phi_0\rangle.$$
 (2.5.6)

We express DC Hamiltonian into normal-ordered form with respect to the reference state as $H_{\rm DC} = H_{\rm DC} = H_{\rm N} + E_{\rm DF}$, where $E_{\rm DF} = \langle \Phi_0 | H_{\rm DC} | \Phi_0 \rangle$ and $H_{\rm N}$ is called the normal ordered Hamiltonian such that $\langle \Phi_0 | H_{\rm N} | \Phi_0 \rangle = 0$. Now considering the normal-ordered form in Eq. 2.5.6, we get

$$e^{-T^{(0)}}(H_{\rm N}+E_{\rm DF})e^{T^{(0)}}|\Phi_0\rangle = E_0|\Phi_0\rangle.$$
 (2.5.7)

Projecting $\langle \Phi_0 |$ in Eq. 2.5.7, we get

$$\langle \Phi_0 | e^{-T^{(0)}} H_N e^{T^{(0)}} | \Phi_0 \rangle = \Delta E_{\text{corr}},$$
 (2.5.8)

where $\Delta E_{\text{corr}} = E_0 - E_{\text{DF}}$ is known as the correlation energy of the considered closed-shell system. Again projecting $\langle \Phi_0^* |$ which is either singly or doubly excited configurations with respect to the reference state $|\Phi_0\rangle$ in Eq. 2.5.7, we get

$$\langle \Phi_0^* | e^{-T^{(0)}} H_N e^{T^{(0)}} | \Phi_0 \rangle = 0.$$
 (2.5.9)

The similarity transformed normal-ordered Hamiltonian, $e^{-T^{(0)}}H_{\rm N}e^{T^{(0)}}$ is further expanded in the form of nested commutators using the Baker-CampbellHausdorff formula as

$$e^{-T^{(0)}}H_{N}e^{T^{(0)}} = H_{N} + [H_{N}, T^{(0)}] + \frac{1}{2!}[[H_{N}, T^{(0)}], T^{(0)}] + \frac{1}{3!}[[[H_{N}, T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}], T^{(0)}].$$

$$(2.5.10)$$

In the above expansion, we have connected as well as disconnected terms. From the linked-cluster theorem [51], one can show that only the connected terms survive and give non-zero contribution in the above equation. To prove this, we consider the Wick's theorem for the operator product according to which if A and B are arbitrary products of the creation and annihilation operators in normal form then

$$AB = \{AB\} + \{\overline{AB}\}, \qquad (2.5.11)$$

where the first term is the normal form of AB and the second term represents sum of the normal-ordered terms with all possible contractions between operators in A and those in B. Since the first term H_N is already connected, lets consider the second term in the above expansion as

$$[H_{\rm N}, T^{(0)}] = H_{\rm N} T^{(0)} - T^{(0)} H_{\rm N}, \qquad (2.5.12)$$

where on using Eq. 2.5.11, the first and the second terms become

$$H_{\rm N}T^{(0)} = \{H_{\rm N}T^{(0)}\} + \{H_{\rm N}T^{(0)}\}$$
(2.5.13)

and
$$T^{(0)}H_{\rm N} = \{T^{(0)}H_{\rm N}\} + \{\widetilde{T^{(0)}}H_{\rm N}\} = \{H_{\rm N}T^{(0)}\},$$
 (2.5.14)

respectively. On substituting Eqs. 2.5.13 and 2.5.14 in Eq. 2.5.12, we get $[H_{\rm N}, T^{(0)}] = \{H_{\rm N}T^{(0)}\}$. Similarly, the second term in the expansion reduce to

$$[[H_{\rm N}, T^{(0)}], T^{(0)}] = \{ \overbrace{H_{\rm N}}^{\bullet} T^{(0)} T^{(0)} \}$$
(2.5.15)

and so on for other terms. Thus, Eq. 2.5.10 reduces to

$$e^{-T^{(0)}} H_{N} e^{T^{(0)}} = H_{N} + \{H_{N} T^{(0)}\} + \frac{1}{2!} \{H_{N} T^{(0)} T^{(0)}\} + \frac{1}{3!} \{H_{N} T^{(0)} T^{(0)} T^{(0)}\} + \frac{1}{4!} \{H_{N} T^{(0)} T^{(0)} T^{(0)}\} = (H_{N} e^{T^{0}})_{conn}, \qquad (2.5.16)$$

where *conn* stands for the connected terms only. The above series has to terminate at the fourfold commutators because H_N has no more than two-electron operator in it; i.e. maximum of four open lines which can connect to maximum of four $T_1^{(0)}$ operators. Now from Eqs. 2.5.16 and 2.5.8, we express the coupled-cluster (CC) equation for correlation energy as

$$\langle \Phi_0 | (H_{\rm N} e^{T^{(0)}})_{\rm conn} | \Phi_0 \rangle = \Delta E_{\rm corr}, \qquad (2.5.17)$$

and from Eq. 2.5.9, we obtain the CC amplitude equations for the single and double excitations as

$$\langle \Phi_a^p | (H_N e^{T^{(0)}})_{\text{conn}} | \Phi_0 \rangle = 0 \qquad (2.5.18)$$

and
$$\langle \Phi_{ab}^{pq} | (H_{\rm N} e^{T^{(0)}})_{\rm conn} | \Phi_0 \rangle = 0,$$
 (2.5.19)

The above amplitude equations can be written in another form as,

$$\langle \Phi_a^p | [H_N(e^{T^{(0)}} - 1)]_{conn} | \Phi_0 \rangle = \langle \Phi_a^p | H_N | \Phi_0 \rangle \qquad (2.5.20)$$

and
$$\langle \Phi_{ab}^{pq} | [H_{\rm N}(e^{T^{(0)}} - 1)]_{\rm conn} | \Phi_0 \rangle = \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_0 \rangle.$$
 (2.5.21)

In the linearized CCSD approximation (LCCSD method), we omit all the terms containing more than one cluster operators such that the expression for the correlation energy, singles and doubles amplitude equations are given by

$$\langle \Phi_0 | (H_{\rm N} + H_{\rm N} T^{(0)})_{\rm conn} | \Phi_0 \rangle = \Delta E_{\rm corr}, \qquad (2.5.22)$$


Figure 2.7: The perturbed RCC operators corresponding to single and double excitations. k1, k2 are the multi-poles and λ is the rank of the operator.

$$\langle \Phi_a^p | (H_N T^{(0)})_{\text{conn}} | \Phi_0 \rangle = \langle \Phi_a^p | H_N | \Phi_0 \rangle \qquad (2.5.23)$$

and
$$\langle \Phi_{ab}^{pq} | (H_{\rm N} T^{(0)})_{\rm conn} | \Phi_0 \rangle = \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_0 \rangle.$$
 (2.5.24)

The above singles and doubles amplitude equations are coupled with each other and are solved using a special Jacobi iterative procedure. We explain this technique along with the diagrammatic approach to solve these amplitude equations in the following chapter.

2.6 Perturbed RCC Theory to Evaluate $|\Psi\rangle$

In the RCC model, the exact wave function of the atomic system is evaluated by solving the following eigenvalue equation

$$(H_{\rm DC} + \lambda H_{\rm int})e^T |\Phi_0\rangle = Ee^T |\Phi_0\rangle.$$
(2.6.1)

where the cluster operator $T = T^{(0)} + \lambda T^{(1)}$. Similar to the unperturbed case, using $H_{\rm DC} = H_{\rm N} + E_{\rm DF}$ in the above equation, we get

$$(H_{\rm N} + \lambda H_{\rm int})e^T |\Phi_0\rangle = \Delta E_{\rm corr} e^T |\Phi_0\rangle.$$
(2.6.2)

On multiplying by e^{-T} from the left throughout in the above equation and using Baker-Campbell-Hausdorff formula as we did in the previous section, we get

$$[(H_{\rm N} + \lambda H_{\rm int}]e^T)_{\rm conn} |\Phi_0\rangle = \Delta E_{\rm corr} |\Phi_0\rangle.$$
(2.6.3)

On expanding the cluster operator $T = T^{(0)} + T^{(1)}$ in the above equation and restricting $e^{T^{(1)}} = 1 + T^{(1)}$, owing to the fact that evaluation of EDM require only one order of H_{int} interaction, we get

$$[(H_{\rm N} + \lambda H_{\rm int})e^{T^{(0)}}(1 + \lambda T^{(1)}]_{\rm conn}|\Phi_0\rangle = \Delta E_{\rm corr}|\Phi_0\rangle.$$
(2.6.4)

Now from the above equation, we collect terms linear in λ and get

$$(H_{\rm DC}e^{T^{(0)}}T^{(1)})_{\rm conn} + (H_{\rm int})e^{T^{(0)}})_{\rm conn}|\Phi_0\rangle = 0.$$
 (2.6.5)

On projecting $\langle \Phi_0^* |$ in Eq. 2.6.5, we get the amplitude equations for $T^{(1)}$ operators as

$$\langle \Phi_0^* | (H_N e^{T^{(0)}} T^{(1)})_{\text{conn}} | \Phi_0 \rangle = -\langle \Phi_0^* | (H_{\text{int}} e^{T^{(0)}})_{\text{conn}} | \Phi_0 \rangle.$$
(2.6.6)

In the CCSD approximation $T^{(1)} = T_1^{(1)} + T_2^{(1)}$, where $T_1^{(1)}$ and $T_2^{(1)}$ are the single and double excitation operators which are represented in the second quantization notation as

$$T_1^{(1)} = \sum_{a,p} a_p^{\dagger} a_a t_a^{(1)p} \quad \text{and} \quad T_2^{(1)} = \frac{1}{4} \sum_{a,b,p,q} a_p^{\dagger} a_q^{\dagger} a_b a_a t_{ab}^{(1)pq}.$$
(2.6.7)

The graphical representations of these operators are shown in Fig. 2.7. The amplitude equations for the $T_1^{(1)}$ and $T_2^{(1)}$ operators are obtained by projecting the singly and doubly excited determinantal states on both sides of Eq. 2.6.5 such that

$$\langle \Phi_a^p | \overline{H}_N(T_1^{(1)} + T_2^{(1)}) | \Phi_0 \rangle = -\langle \Phi_a^p | \overline{H}_{int} | \Phi_0 \rangle \qquad (2.6.8)$$

and
$$\langle \Phi_{ab}^{pq} | \overline{H}_{N}(T_{1}^{(1)} + T_{2}^{(1)}) | \Phi_{0} \rangle = -\langle \Phi_{ab}^{pq} | \overline{H}_{int} | \Phi_{0} \rangle.$$
 (2.6.9)

with $(H_{\rm N}e^{T^{(0)}})_{\rm conn} = \overline{H}_{\rm N}$. Just like $T^{(0)}$ amplitude equations, the above amplitude equations are also coupled with each other and are solved simultaneously using an iterative procedure. In the next chapter, we will explain the details of the computational procedure to solve the above equations.

2.6.1 Perturbative Inclusion of Coupled-Cluster Triple Excitations

We also include important triple excitations perturbatively in the CCSD calculations to ameliorate the $T^{(0)}$ (referred as CCSD(T) method) and $T^{(1)}$ (referred as CCSD_pT method) amplitudes respectively. The triple excitation operator is constructed by contracting \overline{H}_N with $T_2^{(0)}$ as

$$T_3^{(0),pert} = \frac{1}{3!} \sum_{abc,pqr} \frac{(\overline{H}_N T_2^{(0)})_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r},$$
(2.6.10)

where $\overline{H_{N}} = (H_{N}e^{T^{(0)}})_{\text{conn}}$, ϵ 's are the energies of the occupied (denoted by a, b, c) and unoccupied (denoted by p, q, r) orbitals.

2.7 Electric Dipole Moment Calculations from RCC Theory

The expression for the closed-shell atomic EDM (d_A) in the RCC theory is given by

$$d_{\rm A} = 2 \frac{\langle \Psi_0 | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = 2 \frac{\langle \Phi_0 | e^{T^{\dagger(0)}} D e^{T^{(0)}} T^{(1)} | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^{\dagger(0)}} e^{T^{(0)}} | \Phi_0 \rangle}.$$
 (2.7.1)

Since all the operators in the above expression are in normal-order form and $e^{T^{\dagger(0)}}De^{T^{(0)}}$ is an infinite series, we can express

$$e^{T^{\dagger(0)}} D e^{T^{(0)}} = (e^{T^{\dagger(0)}} e^{T^{(0)}})_{cl} (e^{T^{\dagger(0)}} D e^{T^{(0)}})_{cc}, \qquad (2.7.2)$$

where the subscript cl (cc) means closed (connected and closed) terms [50, 60]. We can then show that

$$d_{A} = 2 \frac{\langle \Phi_{0} | (e^{T^{\dagger(0)}} e^{T^{(0)}})_{cl} (e^{T^{\dagger(0)}} D e^{T^{(0)}} T^{(1)})_{cc} | \Phi_{0} \rangle}{\langle \Phi_{0} | (e^{T^{\dagger(0)}} e^{T^{(0)}})_{cl} | \Phi_{0} \rangle}$$

$$= 2 \frac{\langle \Phi_{0} | (e^{T^{\dagger(0)}} e^{T^{(0)}})_{cl} | \Phi_{0} \rangle \langle \Phi_{0} | (e^{T^{\dagger(0)}} D e^{T^{(0)}} T^{(1)})_{cc} | \Phi_{0} \rangle}{\langle \Phi_{0} | (e^{T^{\dagger(0)}} e^{T^{(0)}})_{cl} | \Phi_{0} \rangle}$$

$$= 2 \langle \Phi_{0} | (\overline{D}^{(0)} T^{(1)})_{cc} | \Phi_{0} \rangle, \qquad (2.7.3)$$

with $\overline{D}^{(0)} = e^{T^{\dagger(0)}} D e^{T^{(0)}}$, is an infinite series. Note that its $(e^{T^{\dagger(0)}} e^{T^{(0)}} T^{(1)})_{cl}$ part will vanish owing to odd-parity of $T^{(1)}$. In the LCCSD method, we get $\overline{D}^{(0)} = D + DT^{(0)} + T^{\dagger(0)} D + T^{\dagger(0)} DT^{(0)}$. To account for contributions from $\overline{D}^{(0)}$ in the CCSD method, we first evaluate terms from $\overline{D}^{(0)}$ that are very unique in the sense that they will not be repeated after connecting with another $T^{(0)}$ or $T^{\dagger(0)}$ operator. Then, the contributions from the other non-linear terms are considered by contracting with another $T^{(0)}$ and $T^{\dagger(0)}$ operators till self-consistent results were achieved. We present these contributions with k numbers of $T^{(0)}$ and/or $T^{\dagger(0)}$ as CCSD^(k) to demonstrate convergence of the results with $k \to \infty$ (which is finally referred to CCSD).

2.8 Estimation of Uncertainties in the Many-Body Calculations

The uncertainties in our many-body calculations are estimated from various neglected sources in our calculation such as

• Incompleteness of basis: In our calculations we consider finite basis size corresponding to each angular momentum symmetry to a certain number for the RCC calculations. To estimate the contributions from the neglected basis, we perform calculations for the property under consideration using the method like RPA for the similar and larger basis and quote their differences as uncertainties.

- We also perform RPA calculations to find the contributions from higher orbitals such as from h- and i- symmetries that are not considered in the RCC calculations.
- Contributions from the neglected higher excitations are estimated from the differences between the results from the CCSD and CCSD_pT or CCSD(T) methods.
- We also estimate uncertainties in the calculations by going beyond the Coulomb approximation for the two-body interactions. We consider the Breit interaction which is mediated by the exchanging transverse photons between two electrons. The mathematical form of the Breit interaction between the i^{th} and j^{th} electron is given by

$$V_{\rm B} = -\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{1}{2} \left[\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} - \frac{(\boldsymbol{r}_{ij} \cdot \boldsymbol{\alpha}_i)(\boldsymbol{r}_{ij}\boldsymbol{\alpha}_j)}{r_{ij}^3} \right], \qquad (2.8.1)$$

where α 's are Dirac matrices and r_{ij} is the distance between two electrons. The first term in the above expression is called the magnetic (or Gaunt) term which dominates in the many-body calculations [61]. The second term is called the retardation term which is sometimes important to obtain high accuracy results [62, 63].

• Contributions from the lower order vacuum polarization effects from the quantum electrodynamics (QED) corrections are also evaluated through the Uehling $(V_{\rm U}(r))$ and Wichmann-Kroll $(V_{\rm WK}(r))$ potentials given by [64,65]

$$V_{\rm U}(r) = -\frac{4}{9c\pi} V_n(r) \int_1^\infty dt \sqrt{t^2 - 1} \left(\frac{1}{t^2} + \frac{1}{2t^4}\right) e^{-2ctr} \qquad (2.8.2)$$

and

$$V_{\rm WK}(r) = -\frac{2}{3} \frac{1}{c\pi} V_N(r) \frac{0.092c^2 Z^2}{1 + (1.62cr)^4}, \qquad (2.8.3)$$

respectively, with Z as the nuclear charge of the considered system.

Chapter 3

Computational Implementations of RCC Theory

3.1 Introduction

In this chapter, we will demonstrate a computational procedure to solve the unperturbed and perturbed amplitude equations for the RCC theory. In the CCSD approximation, we solve the coupled singles and doubles amplitude equations obtained in the previous chapter. These equations are solved simultaneously using an iterative technique till the self-consistent results are achieved. In addition to that we also present an intermediate diagrammatic technique similar to that of Bartlett *et al.* [50] to reduce the computational time of the calculations by breaking the number of loops in the algorithm. This is basically done by splitting the many-body diagrams into intermediate diagrams and the cluster operators whose amplitudes we want to calculate. In this thesis, at the CCSD level we are presenting all the intermediate diagrams and important factors which are important to avoid multiple counting of the same diagram. In this chapter, we also present angular momentum factors and parity selection rules for both the unperturbed and perturbed cluster operators. The property at the CCSD level is evaluated using Eq. 2.7.3 given in the previous chapter. One can notice that there is an infinite series involved in the property equation and for the accurate determination of the property, one has to consider as many terms as possible.



Figure 3.1: Effective one-body P-P, P-H and H-H type diagrams obtained from $\tilde{H_N}$. The broken line represents the Coulomb interaction.

Therefore, in order to consider as many terms as possible from the infinite series, we again adopt the diagrammatic technique in a spirit similar to what we used for the amplitude determination. In the property determination the splitting of diagrams not only reduce the computational time but also helped us in calculating the contributions from certain class of diagrams to infinite loops.

3.2 Solving Unperturbed CCSD Equations

The unperturbed CCSD equations for solving amplitudes of $T_1^{(0)}$ and $T_2^{(0)}$ operators are obtained in Eq. 2.5.21 of the previous chapter and can be rewritten as

$$\langle \Phi_a^p | (\tilde{H}_N T^{(0)})_{\text{conn}} | \Phi_0 \rangle = \langle \Phi_a^p | H_N | \Phi_0 \rangle$$

and $\langle \Phi_{ab}^{pq} | (\tilde{H}_N T^{(0)})_{\text{conn}} | \Phi_0 \rangle = \langle \Phi_{ab}^{pq} | H_N | \Phi_0 \rangle,$ (3.2.1)

where

$$(\tilde{H}_{\rm N}T^{(0)})_{\rm conn} = (H_{\rm N}(e^{T^{(0)}}-1))_{\rm conn} = \left[\left(H_{\rm N} + \frac{1}{2!}H_{\rm N}T^{(0)} + \frac{1}{3!}H_{\rm N}T^{(0)^2} + \frac{1}{4!}H_{\rm N}T^{(0)^3} \right)T^{(0)} \right]_{\rm conn},$$
(3.2.2)

with

$$\tilde{H}_{\rm N} = H_{\rm N} + \frac{1}{2!} H_{\rm N} T^{(0)} + \frac{1}{3!} H_{\rm N} T^{(0)^2} + \frac{1}{4!} H_{\rm N} T^{(0)^3}.$$
(3.2.3)

In the LCCSD method $\tilde{H}_N = H_N$. On expanding $T^{(0)} = T_1^{(0)} + T_2^{(0)}$ in the amplitude equations and rearranging terms, we get

$$\langle \Phi_{a}^{p} | (\tilde{H}_{N} T_{1}^{(0)})_{\text{conn}} | \Phi_{0} \rangle = \langle \Phi_{a}^{p} | H_{N} | \Phi_{0} \rangle - \langle \Phi_{a}^{p} | (\tilde{H}_{N} T_{2}^{(0)})_{\text{conn}} | \Phi_{0} \rangle$$
and $\langle \Phi_{ab}^{pq} | (\tilde{H}_{N} T_{2}^{(0)})_{\text{conn}} | \Phi_{0} \rangle = \langle \Phi_{ab}^{pq} | H_{N} | \Phi_{0} \rangle - \langle \Phi_{ab}^{pq} | (\tilde{H}_{N} T_{1}^{(0)})_{\text{conn}} | \Phi_{0} \rangle$

$$, \qquad (3.2.4)$$

In the LCCSD and CCSD approximation the above equations can be expressed in the matrix form as

$$\begin{pmatrix} \langle \Phi_a^p | H_{\rm N} | \Phi_a^p \rangle & \langle \Phi_a^p | H_{\rm N} | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_{ab}^{pq} \rangle & \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_a^p \rangle \end{pmatrix} \begin{pmatrix} t_a^{p^{(0)}} \\ t_{ab}^{pq^{(0)}} \end{pmatrix} = \begin{pmatrix} \langle \Phi_a^p | H_{\rm N} | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_0 \rangle \end{pmatrix}, \quad (3.2.5)$$

and

$$\begin{pmatrix} \langle \Phi_a^p | \tilde{H}_N | \Phi_a^p \rangle & \langle \Phi_a^p | \tilde{H}_N | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | \tilde{H}_N \rangle | \Phi_{ab}^{pq} \rangle & \langle \Phi_{ab}^{pq} | \tilde{H}_N \rangle | \Phi_a^p \rangle \end{pmatrix} \begin{pmatrix} t_a^{p^{(0)}} \\ t_a^{pq^{(0)}} \end{pmatrix} = \begin{pmatrix} \langle \Phi_a^p | H_N | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | H_N | \Phi_0 \rangle \end{pmatrix}, \quad (3.2.6)$$

respectively, where $t_a^{p^{(0)}}$ and $t_{ab}^{pq^{(0)}}$ are the amplitudes associated with the respective $T_1^{(0)}$ and $T_2^{(0)}$ operators. The above matrix equations can be written more compactly as

$$\mathbf{A}(\mathbf{X}).\mathbf{X} = -\mathbf{B}.\tag{3.2.7}$$



Figure 3.2: Effective two-body diagrams from \tilde{H}_N which are binned in different categories. The broken line represents the Coulomb interaction.



Figure 3.3: Final CCSD diagrams obtained after contracting effective one-body intermediate diagrams with the $T^{(0)}$ operators

The solution for \mathbf{X} which represents $T^{(0)}$ operators in the above coupled nonlinear equations is obtained using a Jacobi iterative procedure expressed as

$$X_{j}^{i} = \frac{-B_{j} - \sum_{k \neq j} A_{kj} X_{k}^{i-1}}{A_{jj}}$$
(3.2.8)

where the index i represents interaction number, j denotes the index for element number, A_{jj} and A_{kj} denotes the diagonal and off-diagonal elements of matrix **A**. B_j and X_j are the j^{th} elements of vector **B** and **X** respectively. In order to evaluate the terms in the amplitude Eqs. 3.2.4, we follow the diagrammatic technique as explained in the last chapter. Our aim is to calculate all the diagrams from $\tilde{H}_{\rm N}T^{(0)}$ which on operating $|\Phi_0\rangle$ give net single and double excitations. To proceed with, we first compute all the effective one-body diagrams from H_N that belonging to the particle-particle (P-P), particle-hole (P-H) and hole-hole (H-H) type excitations as given in Fig. 3.1. Since we don't consider the disconnected diagrams in our calculations, therefore we don't have the hole-particle (H-P) category which on connecting with $T^{(0)}$ operator leads to disconnected diagrams. Similarly, we also evaluate effective two-body diagrams from $H_{\rm N}$ those belonging to six different categories such that on connecting it with $T_1^{(0)}$ or $T_2^{(0)}$ operators we finally get connected diagrams only. We define these classes of diagrams as, PP-PP, HP-PP, HH-PP, HP-PH, HP-HH and HH-HH type diagrams, where P and H stands for particle and hole lines respectively; e.g. in an effective HP-PH type diagram we have incoming hole and outgoing particle line at the first vertex, in the second vertex we have incoming particle line and outgoing hole line. All



Figure 3.4: Final CCSD diagrams obtained after contracting effective two-body intermediate diagrams with the $T^{(0)}$ operators

the two-body intermediate diagrams are given in Fig. 3.2. Since the diagrams (i), (iii), (xxix) and (xxx) are symmetric, we have multiplied a factor of half just to avoid over counting. Whereas, the diagrams (xii), (xvii), (xviii) and (xix) on multiplying with suitable $T^{(0)}$ operators will again become symmetric diagrams thats why we keep half factor with them also to avoid over counting. On connecting these diagrams with the $T_1^{(0)}$ or $T_2^{(0)}$ operators we get our full diagrams as given in Figs. 3.3 and 3.4 which give singly and doubly excited configurations with respect to the reference state $|\Phi_0\rangle$. In our CCSD method some of the diagrams in singles and doubles amplitude equations which are having less number of internal lines are calculated directly without making the use of intermediate diagrams as shown in Figs. 3.5 and 3.6 respectively. In the LCCSD method we have far less numbers of intermediate diagrams to compute. From the intermediate one-body diagrams shown in Fig. 3.1 only diagrams (i) and (viii) will contribute to the LCCSD calculations, where as, diagrams (i), (iv), (xiv), (xxi) and (xxvii) will only contribute from the two-body intermediate diagrams, shown in Fig. 3.2. In addition to that all the direct diagrams shown in Figs. 3.5 and 3.6 will contribute to the amplitude determination in LCCSD method.



Figure 3.5: Direct contributing diagrams to the singles of the CCSD method



Figure 3.6: Direct contributing diagrams to the doubles of the CCSD method

3.3 Solving Perturbed CCSD Equations

The perturbed CCSD singles and doubles amplitude equations obtained in Eq. 2.6.9 of the previous chapter are given by

$$\langle \Phi_a^p | \overline{H}_N(T_1^{(1)} + T_2^{(1)}) | \Phi_0 \rangle = -\langle \Phi_a^p | \overline{H}_{int} | \Phi_0 \rangle$$
(3.3.1)

and
$$\langle \Phi_{ab}^{pq} | \overline{H}_{N}(T_{1}^{(1)} + T_{2}^{(1)}) | \Phi_{0} \rangle = -\langle \Phi_{ab}^{pq} | \overline{H}_{int} | \Phi_{0} \rangle.$$
 (3.3.2)

We express the above equation in the matrix form as

$$\begin{pmatrix} \langle \Phi_a^p | \overline{H}_N | \Phi_a^p \rangle & \langle \Phi_a^p | \overline{H}_N | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | \overline{H}_N | \Phi_{ab}^{pq} \rangle & \langle \Phi_{ab}^{pq} | \overline{H}_N | \Phi_a^p \rangle \end{pmatrix} \begin{pmatrix} t_a^{p^{(1)}} \\ t_{ab}^{pq^{(1)}} \end{pmatrix} = \begin{pmatrix} \langle \Phi_a^p | \overline{H}_{int} | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | \overline{H}_{int} | \Phi_0 \rangle \end{pmatrix}, \quad (3.3.3)$$

where $\overline{H}_N = (H_N e^{T^{(0)}})_{\text{conn}}$, $\overline{H}_{\text{int}} = (H_{int} e^{T^{(0)}})_{\text{conn}}$, $t_a^{p^{(1)}}$ and $t_{ab}^{pq^{(1)}}$ are the amplitudes associated with the respective $T_1^{(1)}$ and $T_2^{(1)}$ operators. In the LCCSD approximation, $\overline{H}_N = H_N$ and $\overline{H}_{int} = H_{\text{int}} + H_{\text{int}}T^{(0)}$ and the above matrix

equation becomes

$$\begin{pmatrix} \langle \Phi_a^p | H_{\rm N} | \Phi_a^p \rangle & \langle \Phi_a^p | H_{\rm N} | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_{ab}^{pq} \rangle & \langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_a^p \rangle \end{pmatrix} \begin{pmatrix} t_a^{p^{(1)}} \\ t_a^{pq^{(1)}} \end{pmatrix} = \begin{pmatrix} \langle \Phi_a^p | H_{\rm int} + H_{\rm int} T^{(0)} | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | H_{\rm int} + H_{\rm int} T^{(0)} | \Phi_0 \rangle \end{pmatrix}.$$

$$(3.3.4)$$

Similar to the unperturbed case, the above non-linear matrix equations can also be written in a more compact notation as

$$\mathbf{A}(\mathbf{X}).\mathbf{X} = -\mathbf{B}.\tag{3.3.5}$$

followed by the Jacobi iterative procedure as explained earlier to obtain the solutions for **X** which represent the $T^{(1)}$ operators in this case. The one-body and two-body intermediate diagrams from $\overline{H}_{\rm N}$ is given in Figs. 3.3 and 3.3. These intermediate diagrams are finally connected with $T_1^{(1)}$ and $T_2^{(1)}$ operators to get the final single and double excitation diagrams as shown in Figs. 3.3 and 3.3 respectively. The diagrams for the B matrix are given in Fig. 3.3.

3.4 Angular Momentum Selection Rules for the Cluster Operators

The cluster operators $T^{(0)}$ and $T^{(1)}$ are associated with the residual Coulomb V_{es} and H_{int} interactions. Therefore, the rank of these interactions must be incorporated into the cluster operators and the diagrams associated with them. The Coulomb interaction between two electrons at position r_1 and r_2 can be expanded in partial waves as [66]

$$\frac{1}{r_{12}} = \sum_{k} \frac{r_{<}^{k}}{r_{>}^{k+1}} P_{k}(\cos\omega), \qquad (3.4.1)$$

where $r_{<}$ is lesser and $r_{>}$ is the greater of two radial distances of electrons, P is the Legendre polynomial which can be further expressed in terms of the products of spherical harmonics depending upon the coordinates of each electron separately



Figure 3.7: Effective one-body intermediate diagrams obtained from $\overline{H_{\rm N}}$ for the evaluation of perturbed CCSD amplitudes. The broken line represents the Coulomb interaction.





Figure 3.8: Effective two-body intermediate diagrams obtained from $\overline{H_{\rm N}}$ for the evaluation of perturbed CCSD amplitudes. The broken line represents the Coulomb interaction.



Figure 3.9: The singles diagrams for the A matrix obtained by connecting intermediate one-body and two-body diagrams with $T^{(1)}$ operators.



Figure 3.10: The doubles diagrams for the A matrix obtained by connecting intermediate one-body and two-body diagrams with the $T^{(1)}$ operators.



Figure 3.11: The singles and doubles diagrams for the B matrix elements obtained from \overline{H}_{int} for the evaluation of perturbed CCSD amplitudes.

as

$$P_k(\cos\omega) = \frac{4\pi}{2k+1} \sum_q Y_q^k(\theta_1, \phi_1) Y_{-q}^k(\theta_2, \phi_2).$$
(3.4.2)

Now on defining C tensors as

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_q^k(\theta,\phi),$$
 (3.4.3)

the Coulomb interaction can be written as [51]

$$\frac{1}{r_{12}} = \sum_{k} \frac{r_{<}^{k}}{r_{>}^{k+1}} C^{k}(1) . C^{k}(2).$$
(3.4.4)

We use the above expression to evaluate the matrix element of the Coulomb operator $1/r_{12}$ as

$$\langle ab|\frac{1}{r_{12}}|cd\rangle = \int \int dr_1 dr_2 [P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)]\frac{r_{<}^k}{r_{>}^{k+1}} \\ \times [P_b(r_1)P_d(r_1) + Q_b(r_1)Q_d(r_1)] \times (A_f),$$
(3.4.5)

where $P_i(r_j)$ and $Q_i(r_j)$ are the large and small components of single particle Dirac wave functions of the i^{th} orbital at a spatial distance r_j , A_f is the angular factor and k is the multi-pole. The angular part of the above equation is given by

$$A_f = \delta(m_a + m_c, m_b + m_d) \sum_k \Pi(\kappa_a, \kappa_c, k) \Pi(\kappa_b, \kappa_d, k)$$
$$\times d^k(j_c m_c j_a m_a,) d^k(j_b m_b, j_d m_d)$$
(3.4.6)

where the relativistic quantum number κ is give in Eq. 2.1.15 and the coefficient $d^k(jm, j'm')$ is defined as

$$d^{k}(jm, j'm') = (-1)^{m+1/2} \frac{[(2j+1)(2j'+1)]^{1/2}}{(2k+1)} C(jj'; \frac{1}{2}, \frac{-1}{2}) C(jj'; -m, m'),$$
(3.4.7)



Figure 3.12: Perturbed cluster operators showing multi-poles k1, k2 and rank $\lambda = 1$.

where m is the magnetic quantum number, j is the total angular momentum of the orbital and C(jj'; -m, m') is known as Clebsch-Gordan (C.G.) or vectorcoupling coefficient. The C.G. coefficients appearing in the above equation ensure the multi-pole k satisfies the following triangular condition of the angular momentum

$$|j_a - j_c| \le k \le (j_a + j_c)$$
 and $|j_b - j_d| \le k \le (j_b + j_d).$ (3.4.8)

In addition, the factor Π appearing in the above equation gives

$$\Pi(\kappa, \kappa', k) = 1 \quad \text{for} \quad l + l' + k = \text{even}$$
$$= 0 \quad \text{for} \quad l + l' + k = \text{odd}, \quad (3.4.9)$$

which restricts the allowed k values by parity conservation. We also define factor Π as

$$\Pi(\kappa, \kappa', k) = \frac{1}{2} [1 - aa'(-1)^{j+j'+k}] \qquad \text{which is 1 for } l+l'+k = \text{even},$$

else 0 (3.4.10)

where l and l' are the orbital angular momentum corresponding to j and j'respectively. For even or odd values of κ the permitted values of k from the parity selection factor change by one unit since $l(-\kappa) = l(\kappa) \pm 1$. The H_{int} operator is a vector, we denote the rank of the cluster operators $T^{(1)}$ by $\lambda = 1$ as shown in Fig. 3.12. The vertex (a, p, λ) of the cluster operator $T_1^{(1)}$ shows the coupling of orbital a and p through λ which corresponds to the matrix element $\langle j_p m_p | T_1^{(1)} | j_a m_a \rangle$. On applying the Wigner-Eckart theorem [51] we get

$$\langle j_p m_p | (T_1^{(1)})_{m_{\lambda}}^1 | j_a m_a \rangle = (-1)^{j_p - m_p} \begin{pmatrix} j_p & 1 & j_a \\ -m_p & m_{\lambda} & m_a \end{pmatrix} \langle j_p | | (T_1^{(1)})^1 | | j_a \rangle$$
(3.4.11)

which must satisfy the triangular condition of the angular momentum as

$$|j_a - 1| \le j_p \le (j_a + 1), \tag{3.4.12}$$

and the constraint on magnetic quantum number as

$$m_a + m_p + m_\lambda = 0. (3.4.13)$$

Since the cluster operator $T^{(1)}$ is a rank one operator, it must be under parity and satisfy one more condition

$$(-1)^{(l_a+l_p)} = -1. (3.4.14)$$

However in the case of cluster operator $T_2^{(1)}$ we have three vertices's and following the similar argument of Wigner-Eckart theorem, we will have three triangular conditions given by

$$|j_a - j_p| \le k_1 \le (j_a + j_p)$$

 $|j_b - j_q| \le k_2 \le (j_b + j_q)$
 $|k_1 - k_2| \le \lambda \le (k_1 + k_2)$

and the parity condition at vertices's (a, p, k_1) and (b, q, k_2) satisfying

$$(-1)^{l_a+l_p} = (-1)(-1)^{l_b+l_q}.$$
(3.4.15)

3.5 Property Evaluation

The expression for the calculation of atomic EDM (d_A) obtained from Eq. 2.7.3 of the previous chapter as

$$d_{A} = 2\langle \Phi_{0} | (\overline{D}^{(0)} T^{(1)})_{cc} | \Phi_{0} \rangle$$

= $2\langle \Phi_{0} | [(\overline{D}^{(0)} (T_{1}^{(1)} + T_{2}^{(1)})]_{cc} | \Phi_{0} \rangle,$ (3.5.1)

with a non-truncative series $\overline{D}^{(0)} = e^{T^{\dagger(0)}} D e^{T^{(0)}}$. To consider most of the dominant terms from this infinite series in the CCSD approximation, we first evaluate unique connected one-body diagrams which are binned in P-P, P-H and H-H type as shown in Fig. 3.5 (H-P diagrams are not shown as they are complex conjugate (cc) terms of P-H type of diagrams). It can be noticed from Fig. 3.5 of the P-H/H-P type diagrams that they contain diagrams (e.g. 1c, 3c, 13cetc.) resembling RPA diagrams along with some of the other non-RPA diagrams which account for the core-polarization effects to all orders. It has been found that their contributions are significant, therefore, we replace the corresponding D operator from the P-H and H-P effective diagrams by the stored contributions from the effective P-P and H-H diagrams. An example is shown in Fig. 3.5 to dress-up the effective H-P/P-H operators for evaluating these contributions more rigorously. We further store diagrams (7c, 8c, 11c, 12c, 13c, 14c and 15c) from P-H type which are then contracted with another P-H type diagram 3c and 4creplacing the D operator. After contraction, the values are stored in a separate P-H type array and again contracted with the diagrams 3c and 4c just like above and the procedure is repeated till we get the self-consistent results. Through this technique we are able to consider most of the dominant RPA and non-RPA type diagrams to infinity orders in the above series. These effective diagrams are then further combined with the $T^{(1)}$ and $T^{(0)}T^{(1)}$ operators to obtain the final contributions as shown in Fig. 3.5.





Figure 3.13: One-body intermediate P-P,H-P and P-H type diagrams obtained from \overline{D} . Wavy line represents the dipole operator D.



Figure 3.14: Example of further dressing-up of effective H-P type diagrams from the effective P-P and H-H type one-body diagrams.



Figure 3.15: The property diagrams obtained on combining intermediate diagrams from $\overline{D} = e^{T^{\dagger(0)}} D e^{T^{(0)}}$ with suitable $T^{(0)}$ and $T^{(1)}$ operator.

Chapter 4

Dipole Polarizabilty of Various Closed-Shell Atomic Systems

4.1 Introduction

The subject of atom-light interactions in atomic clock, optical lattices, quantum information, etc. [67–69] has received considerable attention with the advent of sophisticated techniques to trap and cool atomic systems and measure their properties to a very high precision [70]. This range of applications demand accurate determinations of α s in atomic systems. Precise measurements of α s are challenging and involve using a number of techniques like E-H (electricmagnetic fields) gradient balance method [71–73], deflection of atomic beam by electric field [74], atom interferometry [75,76], cold-atom velocity change [77] et cetera. In fact, the ground state α of many atomic systems are not yet measured very precisely owing to difficulties in eliminating some of the larger systematics. Therefore, accurate theoretical studies of α in atomic systems are of particular interest.

Seminal work on the *ab initio* calculations of α s of the many-electron systems was first introduced by Dalgarno and his co-workers [78, 79] about more than five decades ago. Since then advanced many-body methods and their variants have been developed and applied successfully in the same philosophical procedures to evaluate α as accurately as possible. The primary intent of these

methods are to incorporate electron correlation effects as rigorously as possible at the same time curtailing the computational cost. Examples of few well-known many-body methods that are often employed in the studies of α s are the random phase approximation (RPA), coupled-cluster method in the linear response theory (CCLRT), configuration-interaction (CI) method etc. [80–87]; however many of these methods are developed in the framework of non-relativistic mechanics. In the recent years, Lim and co-workers have employed relativistic coupled-cluster (CC) methods developed for molecular calculations described using the Cartesian coordinates to determine α of many atomic systems. They showed that the relativistic contributions to α , especially in the heavier atomic systems, are large [88,89]. In their CC method, the relativistic effects are accounted by using a two-component Douglas-Kroll Hamiltonian.

In this work, we employ our relativistic many-body methods explained in Chap. 2 to evaluate and study the behavior of electron correlation effects in determining α s of many closed-shell atoms and ions. In our CC method, we consider the Dirac-Coulomb Hamiltonian with the four-component atomic wave functions in the spherical coordinate system to encompass both the correlation and the relativistic effects in the calculations of α . This method has been successfully used in last couple of years to compute α of the ground states for a number of atomic systems [90–95]. In addition to CC, we have employed other methods like the third order many-body perturbation theory (MBPT(3)) and RPA to perceive the passage of the correlation effects at various stages of calculations. In the first part of our study, we determine α of various closed-shell atoms belonging to noble gases and alkaline earth elements. In addition to that, we also evaluate α of singly charged alkali and doubly charged alkaline metals ions. In the second part, we evaluate α of B⁺, C²⁺, Al⁺, Si⁺², Zn, Ga⁺, Ge⁺² Cd, In⁺ and Sn⁺² belonging to atoms and ions in the boron, carbon, and zinc homologous sequences of elements. We also investigate the contributions arising through the non-linear terms constituting the higher order excitation processes and establish accuracies of the results for which the experimental results are unknown. Accurate calculations of α s put premium on the potential of our many-body methods in reproducing physical properties of the closed-shell atomic systems. This is a kind of benchmarking to our methods on their ability to reproduce accurate values of any properties associated with the operators of rank one. In the next chapter we employ these methods to determine permanent electric dipole moments (EDMs) of many closed-shell atoms whose experiments are underway.

4.2 Theory of Dipole Polarizability

The leading second order change in the energy of an atomic state $|\Psi_0^{(0)}\rangle$ when placed in an external weak electric electric field $\vec{\mathcal{E}}$ in given by

$$\Delta E = -\frac{1}{2}\alpha |\vec{\mathcal{E}}|^2, \qquad (4.2.1)$$

where α is known as the static electric dipole polarizability of the state. In the mathematical expression, we can write

$$\alpha = -2 \frac{\langle \Psi_0^{(0)} | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle}, \qquad (4.2.2)$$

with $|\Psi_0^{(0)}\rangle$ and $|\Psi_0^{(1)}\rangle$ are the unperturbed and first-order perturbed ground state wave functions due to the interaction Hamiltonian $\vec{D}.\vec{\mathcal{E}}$ for the dipole operator D. The arduous part of calculating α using the above expression lies in the evaluation of $|\Psi_0^{(1)}\rangle$ which entails mixing of different parity states. On the other hand, it is sometimes easy to use a sum-over-states approach given by

$$\alpha = -\frac{2}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle} \sum_{I \neq 0} \frac{|\langle \Psi_0^{(0)} | D | \Psi_I^{(0)} \rangle|^2}{E_0^{(0)} - E_I^{(0)}}, \qquad (4.2.3)$$

for the *I* representing summation over all allowed intermediate states $|\Psi_I^{(0)}\rangle$, and $E_0^{(0)}$ and $E_I^{(0)}$ are the energies of the ground and the corresponding intermediate states, respectively. The above approach is convenient to use if the electric dipole (*E*1) matrix elements between the ground state and a sufficient number of intermediate states can be calculated to reasonable accuracies. However, it is extremely difficult to determine these matrix elements accurately with confidence because it requires careful handling of a large number of configuration-state functions (CSFs). These contributions are also estimated by dividing the electronic configurations into a core and few valence electrons [96, 97]. This enables us to estimate different contributions separately by using varieties of many-body methods. Obviously, this cannot explain the true behaviors of all the correlation effects in equal footings. In contrast, the present method considers the nuclear V_N potential and treats all the associated correlations among the electrons in the uniform manner.

The other famous approach for determining α is using the finite $\vec{\mathcal{E}}$ perturbation method in which the second order differentiation of the total energy (E_0) of the ground state is estimated in the presence of the electric field (finite field method); i.e.

$$\alpha = -\left(\frac{\partial^2 E_0(|\vec{\mathcal{E}}|)}{\partial |\vec{\mathcal{E}}|\partial |\vec{\mathcal{E}}|}\right)_{|\vec{\mathcal{E}}|=0},\tag{4.2.4}$$

which requires numerical calculations for a smaller arbitrary value of $\vec{\mathcal{E}}$. This is a typical procedure of calculating α using the molecular methods based on the Cartesian coordinate systems where the atomic states do not possess definite parity. In contrast, it is a convoluted procedure of determining α of the atomic systems in the relativistic formalism if we wish to describe the method exclusively in the spherical coordinates.

Our methodology to determine α is to seek the calculation of $|\Psi_0^{(1)}\rangle$ and to supplant the ideology of obtaining it as the solution of the following inhomogeneous equation

$$(H - E_0^{(0)})|\Psi_0^{(1)}\rangle = -D|\Psi_0^{(0)}\rangle$$
(4.2.5)

through the matrix mechanism for the four-component relativistic theory described using the spherical polar coordinate system. By approximating the total

Parameters	8	p	d	f	g
$lpha_0\ eta$	0.00753 2.075	0.00755 2.070	$0.00758 \\ 2.58$	$0.0080 \\ 2.72$	$0.0080 \\ 2.72$

Table 4.1: GTO parameters of Ne used in the DF calculations.

wave function of the ground state as $|\Psi_0\rangle \simeq |\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle$, we have

$$\alpha = 2 \frac{\langle \Psi_0 | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \qquad (4.2.6)$$

where λ is the perturbation parameter and denotes the order of perturbation in D which has to be set as one to determine α .

4.3 Optimization of the Gaussian Basis Functions

The accuracies in the Dirac-Fock (DF) calculations primarily depend on the parameters and the size of the chosen basis functions. Therefore, optimization of those parameters are absolutely necessary to get accurate single particle wave functions. In fact, this is the most important step of many-body calculations that generates our reference state for perturbation calculations. As explained in length in Chap. 2, we use linear combination of Gaussian type orbitals (GTOs) to express the radial part of the large and small components of our single particle wave functions. In general the Gaussian part of the large component is described as

$$G_{k,i}^L(r) \propto r^k e^{-\alpha_i r^2} \tag{4.3.1}$$

where parameter $k = 0, 1, 2, \cdots$ for s, p, d, \cdots denote the respective type orbital symmetry and the parameter α_i in the exponent is obtained using the following

		Orbital Energies			
	Basis Sets	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
(i)	10s9p8d7f6g	19.007	1.1386	0.9948	0.9930
(ii)	14s13p12d11f10g	31.6862	1.8668	0.8630	0.8586
(iii)	20s19p18d17f16g	32.8148	1.9357	0.8528	0.8483
(iv)	26s25p24d23f22g	32.8174	1.9358	0.8528	0.8483
(\mathbf{v})	36s35p34d33f32g	32.8174	1.9358	0.8528	0.8483

Table 4.2: Single particle orbital energies of the bound states of Ne obtained from our <u>DF calculations with different GTOs.</u>

even tempering condition

$$\alpha_i = \alpha_0 \beta^{i-1}, \quad \text{where} \quad i = 1, 2, 3 \cdots, n \tag{4.3.2}$$

with α_0 and β are the arbitrary parameters. These parameters need to be defined properly so that accuracies in the wave functions can be enhanced. In addition to that, we must consider sufficient number of angular momentum symmetries k. In our calculations, we generally take large k as k=5; i.e. up to q symmetry. In this work, we have adopted two ways in which we define values for the parameters α_0 and β : (i) Universal Basis (UB), in which case the values of these parameters are same for every symmetry, (ii) Even-Tempering Basis (ET): in this case parameters α_0 and β are different for each symmetry. The UB type bases are easy in the sense that we have only two parameters to define for the GTOs. Whereas, in the ET bases we have to define different α_0 and β parameters for each symmetry. With the larger parameter space, ET are little complicated as compared to UB basis but at the same time with ET, we have better handle on the single particle wave function. For the atomic systems with closed electronic configurations, we observe that UB and ET basis give almost similar results provided sufficient numbers of GTOs are considered for the calculations. The qualities of the basis parameters are tested by comparing the DF single particle orbital energies calculated using GTOs with different values of α_0 and β against the numerical results obtained from the Fortran package GRASP92 [98]. The parameters whose results are comparable with the numerical results are finally

Table 4.3: Comparison of the single particle orbital energies of Ne obtained using GTOs and GRASP92 method. $|\Delta_R|$ means the absolute values of relative difference in percentage between two results from GTOs and GRASP92.

Orbital	Orbital Energies			
	GRASP92	GTOs	$ \Delta_R $	
$1s_{1/2}$	32.8144	32.8174	0.01	
$2s_{1/2}$	1.9387	1.9358	0.15	
$2p_{1/2}$	0.8523	0.8528	0.06	
$2p_{3/2}$	0.8482	0.8383	1.17	

chosen for further calculations. After obtaining α_0 and β values for an atomic system under consideration, we slowly increase the number of Gaussian basis functions for each symmetry till we get the converged results of the properties. We demonstrate this procedure of optimization on Ne atom, whereas, for other systems we will present the optimized value of these parameters and size of the basis sets used for the beyond DF calculations.

The optimized α_0 and β values in ET basis for Ne atom are given in Table 4.1. With these parameters, we proceed with the DF calculations with different sets of GTOs and present single particle orbital energies in Table 4.2. From the table, we find that the single particle energies become constant as we reach to basis set (iv) and (v). Further, on comparing our results from basis set (v) with the single particles energies obtained from the GRASP92 package as given in Table 4.3, we find they are in good agreement with each other. We also present the relative percentage difference given by $\left(\left|\frac{GRASP92-GTOs}{GRASP92}\right|\right)$ between these two results. For the beyond DF calculations, we only consider finite numbers of single particle orbitals by selecting them during the DF calculations. Now to make sure that we have selected sufficient number of orbitals for the perturbative calculations without compromising on the accuracy of the property of interest, we perform a series of RPA and MBPT(2) calculations with varying number of selected orbitals till the values become consistent. The reasons behind choosing RPA and MBPT(2) methods for these tests are: these methods are not computationally expensive, take less time to execute as compare to the CC calculations and con-

	Basis Sets	α
(i)	6s5p4d3f2q	1.206
(ii)	8s7p6d5f4g	2.344
(iii)	11s10p9d8f7g	2.379
(iv)	13s12p11d10f9g	2.380
(\mathbf{v})	16s15p13d11f11g	2.380

Table 4.4: Convergence of α of Ne with the size of the basis sets.

Table 4.5: SCF energies of Ne with and without Breit contributions.

Atom	Our Work		Oth	ners
	SCF	SCF_B	SCF	SCF_B
He	-2.8618	-2.8617	-2.8618^{*}	-2.8617^{*}
Be	-14.5758	-14.5751	-14.5758^{*}	-14.5751^{*}
Ne	-128.6919	-128.6752	$- 128.6919^{\dagger}$	-128.6752^{\dagger}
Ar	-528.6837	-528.5514	-528.6838^{\dagger}	-528.5514^{\dagger}
Kr	-2788.8052	-2787.3793	-2788.8615^{\dagger}	-2787.4356^{\dagger}
Xe	-7446.8844	-7441.1146	-7446.8880^{\dagger}	-7441.1182^{\dagger}
Hg	-19647.9828	-19625.3493	- 19648.8482 [†]	-19626.2156^{\dagger}

*: Non-relativistic calculations with Breit interaction added perturbatively, Ref. [99].

[†]: Ref. [100].

sider most of the dominant electron correlation effects into account. In Table 4.4, we present the convergences of α s from RPA with different set of selected Gaussian wave functions. We also include contributions from the Breit interaction self-consistently in the DF calculations and compare self-consistent field (SCF) energies of various atomic systems with the earlier calculations [99,100] as given in Table 4.5. Our results for all the considered atoms are in good agreement with each other. Our method is relativistic and the results for He and Be are from non-relativistic calculations where the Breit interaction is added perturbatively, we still get good agreements because of the fact that the relativistic effects are not prominent in these smaller systems

	n ounce works.		
Systems	This Work [90]	Others	Experiments
He	1.360(20)	$1.322 \ [101]$	1.383223(67) $[102, 103]$
		1.383763 $[104]$	1.3838 $[105]$
		1.38376079(23) [106]	1.384 [107]
		1.382(1) [108]	1.383759(13) [109]
Ne	2.652(15)	2.38 [101]	2.670(3) [110]
		2.6648 [104]	2.66110(3) [111]
		2.697 [112]	2.6680 [105]
		$2.665 \ [113] \ 2.6695$	2.663 [107]
		2.668(6) [114], 2.6695 [92]	
Ar	11.089(4)	$10.77 \ [101]$	11.081(5) [110]
		11.084 [104]	$11.091 \ [105]$
		$11.22 \ [112]$	$11.080 \ [107]$
		11.085(6) [115]	11.083(2) [116]
		11.213 [93]	
Kr	16.93(5)	$16.47 \ [101]$	16.766(8) [110]
		16.80 [117]	$16.740 \ [105]$
		16.736 [93]	$16.740 \ [107]$

Table 4.6: α s of various noble gas elements. Estimated uncertainties in our calculations are given in the parentheses. The square brackets refers to the references of other works.

Table 4.7: α s of various alkaline earth elements. Estimated uncertainties in our calculations are given in the parentheses. The square brackets refers to the references of other works.

Systems	This Work [90]	Others	Experiments
Be	37.86(17)	37755[118] 3773(5)[110]	
De	51.00(11)	37.807 [120] 37.29 [121]	
		37.76 [120] $37.80(47)$ [108]	
		37.69 [123]	
Mg	72.54(50)	71.7 [124], 70.90 [125],	
0	()	70.74 [121], 71.35 [123],	
		71.33 [122], $74.9(2.7)$ [126],	
		73.41(2.32) [108]	
Ca	157.03(80)	157 [124], 171.7 [127],	169(17) [72]
		159.4 [123], 158.00 [88],	. ,
		152 [128], 159.0 [122],	
		157.1(1.3) [122], $154.58(5.42)$ [108]	
		156.0 [121]	
Sr	186.98(85)	$201.2 \ [123], \ 198.85 \ [88]$	186(15) [73]
		$190 \ [128], \ 202.0 \ [122],$	
		199.71(7.28) [108]	

Table 4.8: α s of singly charged alkali elements. Estimated uncertainties in our calculations are given in the parentheses. The square brackets refers to the references of other works.

Systems	This Work [90]	Others	Experiments
T •			
Li⊤	0.1913(5)	0.192486 [129, 130], 0.1894 [101]	0.1883(20) [131]
Na^+	0.9984(7)	0.9947 [121]	0.978(10) [132]
		0.9457 [101]	$1.0015(15\ [133]$
		1.00(4) [134], 1.025 [94]	$0.9980(33\ [135]$
K^+	5.522(7)	5.354 [121], 5.457 [101]	5.47(5) [132]
		5.52(4) [134], 5.735 [94]	
Rb^+	9.213(15)	9.076 [101]	9.0 [136]
		9.11(4) [134], 9.305 [94]	

4.4 Correlation Trends in α s

We present our α results of several atomic systems and compare them with the available other calculations and measurements in Tables 4.6, 4.7, 4.8 and 4.9. The α_0 and β parameters used for the optimization of the basis functions for the DF calculations are given in Table 4.10. The uncertainties in our calculations are estimated from the finite size of the basis functions, neglected contributions from the Breit interaction, and QED effects due to the lowest-order vacuum polarization and self-energy corrections [65]. Contributions from the Breit and QED effects are found to be tiny for the property under consideration however it is noticed that the basis is important for the numerical accuracies in the calculations. We also employ the MBPT(3) method to estimate contributions from the Breit and QED interactions by carrying out calculations with these interactions individually along with the DC Hamiltonian. To estimate uncertainties from the choice of basis functions, we followed a two step approach as explained earlier using the DF method: (i) results are obtained for a different sets of optimized Gaussian parameters and (ii) estimating contributions from the inactive orbitals that are not considered in the RCC calculations from the DF method. We present these estimated contributions from the individual source in Table 4.11. Experimental results for the light atomic systems are found to be more accurate than our calculations. However, for heavy systems, the accuracies of our results are
Table 4.9: α s of doubly charged alkaline earth elements. Estimated uncertainties in our calculations are given in the parentheses. The square brackets refers to the references of other works.

Systems	This Work [90]	Others	Experiments
Be^{2+}	0.0521(2)	0.05182 [101], 0.052264 [129, 130]	
Mg^{2+}	0.4852(5)	0.4698 [136], 0.495 [95]	0.489(5) [132]
C-2+	2.007(6)	0.4814 [121]	0.486(7) [137]
Ca ²	3.295(0)	3.254 [101], 3.161 [121] 3.262 [88], 3.387 [95]	3.20(3) [132]
Sr^{2+}	5.877(8)	5.813 [101], 5.792 [88], 5.913 [95]	
$\rm Sc^+$	53.24(20)		
Y^+	72.26(50)		

better than those of experiments and many of the previous calculations.

A variety of many-body methods have been used to calculate α for the atomic systems that we have considered except for Sc^+ and Y^+ . The RCC method we have employed in the present work had been used previously to evaluate these quantities [108, 138, 139]. In those calculations, we had truncated $\overline{D^{(0)}}$ at $\overline{D^{(0)}} = T^{\dagger(0)} D T^{(0)}$ neglecting higher order RPA contributions coming through the $T^{\dagger(0)}D(T^{(0)})^2$ and $(T^{\dagger(0)})^2DT^{(0)}$ CC terms whose contributions in the neutral alkaline-earth atoms, Sc^+ and Y^+ are found to be significant. Recently a similar approach, which had included the normalization of the wave function, had been used for calculating α s of some of the inert gas atoms [92, 93]. In fact, both these works account for nonlinear terms at different levels of approximations resulting in some differences in the results. Another calculation for the inert gas atoms was carried out by Nakajima and Hirao [112], where they have used a scalar relativistic Douglas-Kroll (DK) Hamiltonian to investigate the relativistic effects in α . Moreover Nakajima and Hirao adopted a numerical finite field approach to estimate α from the second-order energy shift due to an arbitrary external electric field whereas, we have evaluated this quantity by calculating the expectation value of the D using the first-order dipole perturbed wave function. It is interesting to see that both the results agree fairly well with each other within the quoted uncertainties.

We compare our α results for the alkaline-earth elements with those of Por-

Table 4.10: GTO parameters for the respective angular momentum symmetries in the calculations of DF wave functions of various considered closed-shell atoms and ions.

System	Parameters	s	p	d	f	g
Не	α_0	0.00075	0.00155	0.00258	0.0560	0.0765
	β	2.075	2.080	2.18	2.30	2.45
Ar	α_0	0.0004	0.0005	0.0040	0.0060	0.0050
	β	2.117	2.130	2.15	2.20	2.30
Kr	$lpha_0$	0.0020	0.0032	0.0042	0.0050	0.0055
	β	2.500	2.650	2.550	2.500	2.550
Be	$lpha_0$	0.0050	0.00615	0.00505	0.0050	0.0048
	β	2.500	2.650	2.550	2.530	2.550
Mg	$lpha_0$	0.00525	0.00525	0.00525	0.00525	0.00525
	β	2.730	2.730	2.730	2.730	2.730
Ca	$lpha_0$	0.00525	0.00525	0.00525	0.00525	0.00525
	β	2.710	2.710	2.710	2.710	2.710
Sr	$lpha_0$	0.00300	0.00330	0.00450	0.00600	0.00520
	β	2.500	2.650	2.550	2.500	2.550
Y^+	$lpha_0$	0.00280	0.00280	0.00280	0.00280	0.00280
	β	2.660	2.660	2.660	2.660	2.660
$\rm Sc^+$	$lpha_0$	0.0004	0.0005	0.0040	0.0060	0.0050
	β	2.117	2.130	2.150	2.200	2.300
Li^+	$lpha_0$	0.0075	0.00755	0.00758	0.00760	0.00765
	β	2.075	2.070	2.580	2.600	2.650
Na^+	$lpha_0$	0.0025	0.00955	0.0070	0.0069	0.0068
	β	2.210	2.125	2.750	2.760	2.770
K^+	$lpha_0$	0.0004	0.0005	0.0040	0.0060	0.0050
	β	2.117	2.130	2.150	2.200	2.300
Rb^+	$lpha_0$	0.0004	0.0005	0.0040	0.0060	0.0050
	β	2.117	2.130	2.150	2.200	2.300
Be^{2+}	$lpha_0$	0.0030	0.00455	0.0055	0.0050	0.0048
	β	2.400	2.550	2.650	2.630	2.500
Mg^{2+}	$lpha_0$	0.00753	0.00755	0.0058	0.0080	0.0082
	eta	2.075	2.070	2.580	2.720	2.800
Ca^{2+}	α_0	0.0040	0.0050	0.0080	0.0060	0.0050
	eta	2.510	2.630	2.750	2.800	2.700
Sr^{2+}	α_0	0.0020	0.00320	0.0042	0.0050	0.0055
	eta	2.500	2.650	2.550	2.500	2.550

System	δ_B	δ_Q	δ_F
He	~ 0.0	~ 0.0	0.0200
Ne	0.0006	~ 0.0	0.1499
Ar	0.0023	0.0002	0.0032
Kr	0.0148	0.0008	0.0478
Be	0.0027	-0.0001	0.1699
Mg	0.1460	-0.0008	0.4782
Ca	-0.1609	-0.0041	0.7836
Sr	-0.1767	-0.0201	0.8312
Li^+	~ 0.0	~ 0.0	0.0005
Na^+	0.0003	~ 0.0	0.0004
K^+	0.0004	0.0001	0.0070
Rb^+	0.00960	0.0002	0.0115
Sc^+	-0.0453	-0.0533	0.1874
Y^+	-0.0631	-0.0089	0.4959
Be^{2+}	~ 0.0	~ 0.0	0.0002
Mg^{2+}	0.0001	~ 0.0	0.0004
Ca^{2+}	0.0005	0.0001	0.0059
Sr^{2+}	0.0061	0.0002	0.0052

Table 4.11: The estimated uncertainties to α s from the Breit interaction (δ_B), QED corrections (δ_Q) and finite basis size (δ_F) in the considered atomic systems.

sev *et al.* [122,140] who had used a hybrid approach combining the configuration interaction (CI) method in the valence space and the MBPT method by scaling the energies and dressing the external electromagnetic field in the RPA framework to evaluate the core-polarization effects. Lim *et al.* [88] had performed the relativistic CC calculations in the finite-field method using the DK Hamiltonian. Our results for most of the atom are in good agreement with them except for Sr which differs significantly. As mentioned in the previous section, we have found that higher-order nonlinear terms, especially those corresponding to RPA, are essential for obtaining accurate results. One probable reason for the discrepancies in the results between our RCC results and those of Porsev *et al.* is the treatment of core correlation effects in the two cases. We have computed these effects by the all order CCSD method, while they have used a finite order MBPT approach. An important difference between our approach and that of Lim *et al.* [88] is that we have used the proper DC Hamiltonian unlike its scalar components in [88]

Atoms	DF=MBPT(1)	MBPT(2)	MBPT(3)	CCSD
He	0.998	1.240	1.215	1.360
Li^+	0.1579	0.1839	0.1851	0.1913
Be^{2+}	0.0453	0.0510	0.0512	0.0521
Ne	1.977	2.254	1.654	2.652
Na^+	0.8337	0.9154	0.8504	0.9984
Mg^{2+}	0.4277	0.4555	0.4371	0.4852
Ār	10.152	9.964	8.005	11.089
K^+	5.466	5.130	4.468	5.522
Ca^{2+}	3.369	3.082	2.568	3.295
Kr	15.82	15.00	10.70	16.93
Rb^+	9.273	8.374	7.103	9.213
Sr^{2+}	6.146	5.388	4.492	5.877
Be	30.53	40.24	38.16	37.86
Mg	54.70	70.72	65.64	72.54
Ca	122.90	151.70	132.80	157.03
Sc^+	50.10	57.17	47.02	53.24
Sr	156.83	188.98	163.13	186.98
Y^+	68.60	75.42	65.10	72.26

Table 4.12: α s obtained using different many-body methods at different level of approximations.

and the polarizabilities are estimated from the second-order corrections to their calculated energies.

We now compare our results for the singly charged alkali and doubly charged alkaline-earth-metal ions, which have electronic configurations similar to that of the noble gas atoms with the results obtained using an another RCC calculation [94, 95] and from the RPA method by Johnson *et. al.* [101]. The method employed in the former calculations have already been referred to in the previous paragraph. The close agreement between the RPA and our RCC results is due to the fact that the dominant correlation effects in the evaluation of α for the closed-shell systems come from the core-polarization effects which are taken to all orders in both the calculations. From the MBPT(3) calculations we find that there is a significant contributions from the non-RPA diagrams in the closed-shell atoms. However, in these ions they cancel out to a large extent and their net contributions are consequently not significant. In another work, Lim *et. al* [134]



Figure 4.1: Plots of $(\alpha - \alpha_{DF})/\alpha_{DF}$ results versus atomic numbers from different groups of atomic systems belonging to noble gas, alkali, alkaline-earth metal groups. α results are obtained using the MBPT(3) and CCSD methods in order to make a comparative study between these two approaches.

have reported α results for the alkali-metal ions considering the scalar relativistic DK Hamiltonian and accounting for the spin-orbit (LS) coupling corrections through the MBPT(2) method using a fully relativistic four-component DF wave functions. In addition to the above-mentioned systems, we have also calculated



Figure 4.2: Plots of MBPT(3) and CCSD $(\alpha - \alpha_{DF})/\alpha_{DF}$ results for the considered atoms and ions belonging to the noble gas, alkali, alkaline-earth metal groups versus atomic numbers.

System	RPA	non-RPA
He	1.274	-0.059
Ne	2.303	-0.649
Ar	9.878	-1.873
Kr	14.980	-4.280
Be	36.788	1.372
Mg	65.074	0.566
Ca	135.459	-2.659
Sr	170.340	-7.210
Li^+	0.1862	-0.0011
Na^+	0.9261	-0.0757
K^+	5.035	-0.567
Rb^+	8.326	-1.223
Sc^+	50.115	-3.095
Y^+	67.181	-2.081
Be^{2+}	0.0513	-0.0001
Mg^{2+}	0.4627	-0.0256
\widetilde{Ca}^{2+}	3.009	-0.441
Sr^{2+}	5.352	-0.860

Table 4.13: RPA and non-RPA contributions from the MBPT(3) method.

 α of the Sc⁺ and Y⁺ ions. There are no other data available for comparison against our results. In this work, we aim to analyze the trends in the electron correlation effects in determining α in the considered systems going from DF to advanced many-body methods. To fulfill our objective, we have carried out a range of many-body calculations using lower-order MBPT to MBPT(3) methods and have presented all the results at different stages in Table 4.12. These results are further compared with our final all-order CCSD calculations in the same table. This clearly demonstrates the significance of the electron correlation effects systematically from lower- to higher-orders in perturbation theory and provide a better understanding of their roles in obtaining accurate results. We present results by grouping the isoelectronic systems together in the same table in order to make a comparative analysis of the correlation effects with increasing atomic number. As can be seen in the table, the DF results of the light noble gas elements are smaller than the MBPT results while this trend changes for the heavier ones. At last, the CCSD results are larger than the DF results

System	$DT_{1}^{(1)}$	$T_1^{(0)\dagger} D T_1^{(1)}$	$T_2^{(0)\dagger} D T_1^{(1)}$	$T_2^{(0)\dagger} D T_2^{(1)}$	Others
He	1.362	0.005	-0.035	0.035	-0.007
Ne	2.613	0.073	-0.099	0.089	-0.024
Ar	11.806	-0.068	-1.143	0.511	-0.017
Kr	18.11	-1.12	-1.82	0.74	1.02
Be	39.45	-1.53	-7.21	3.84	3.31
Mg	75.66	-2.96	-10.16	5.54	4.46
Ca	163.87	-9.24	-24.89	16.05	11.24
Sr	201.90	-12.77	-28.77	15.57	11.05
Li^+	0.1894	~ 0	0.0019	0.0019	-0.0019
Na^+	0.9756	~ 0	-0.0005	~ 0	0.0233
K^+	5.972	-0.038	-0.620	0.211	-0.003
Rb^+	9.971	-0.067	-1.049	0.333	0.025
Sc^+	61.71	-2.16	-8.24	3.84	-1.91
Y^+	83.19	-3.18	-10.68	5.05	-2.12
Be^{2+}	0.0526	~ 0	-0.0007	0.0003	-0.0001
Mg^{2+}	0.4774	~ 0	~ 0	~ 0	0.0078
Ca^{2+}	3.578	-0.019	-0.585	0.117	0.204
Sr^{2+}	6.396	-0.037	-0.689	0.191	0.016

Table 4.14: Contributions from various CCSD terms for the evaluations of α s of the considered atomic systems.

for all the considered atomic systems. From this behavior, we infer that there are strong cancellations between the correlation effects in these atoms and the higher-order correlation effects play an important role in the accurate determination of the final results. A similar trend is also followed by the singly charged alkali and the doubly charged alkaline-earth metal ions. However, the trend for the correlation effects in the neutral alkaline-earth metal atoms is rather different. In this case, the DF results are always smaller than those deduced from MBPT and CCSD methods. In fact, it is also quite interesting to note that the trends in the correlation for Sc⁺ and Y⁺ follow the noble gas elements instead of other isoelectronic alkaline-earth metal atoms. For a quantitative description, we plot $(\alpha - \alpha_{DF})/\alpha_{DF}$ obtained using the MBPT(3) and CCSD methods versus atomic systems belonging to the same group in Fig. 4.1 for the different categories of systems that we have considered. We also plot the same for all the systems together including Sc⁺ and Y⁺ ions in Fig. 4.2 to make a comparative

analysis of the correlation trends among different isoelectronic sequences. To shed light on the role of different types of correlation effects that are crucial in the determination of α and to explain the reasons for their trends in different isoelectronic sequences, we identify diagrams from the MBPT(3) approximation that belong to lower-order RPA. We, then, present MBPT(3) results in Table 4.13 classifying its diagrams as RPA and non-RPA types. It can be seen from Fig. 2.4 that all the diagrams up to MBPT(2) belong to RPA and hence, they are the dominant contributors. However, diagrams shown in Fig. 2.4 (vi-viii) are few examples of non-RPA-type diagrams that also contribute significantly at the third-order level, but they largely cancel out each other in the heavy atomic systems. The final results are the outcome of the interplay between these cancellations which can only be accounted correctly using an all order method like our CCSD method. This is evident from the contributions from different correlation effects represented by the RCC terms in the evaluation of α for different atomic systems. In Table 4.14, we give the individual contribution from the important CCSD terms to α , where the leading term $DT_1^{(1)}$ contains the lowest-order DF result. The next important term is $T_2^{(0)\dagger}DT_1^{(1)}$ and the sign of its contribution is opposite to that of the former resulting in a substantial cancellation between these two largest contributors. In addition to the above two terms, contributions from $T_1^{(0)\dagger}DT_1^{(1)}$ further reduce the final results. Pair excitations contributing through $T_2^{(0)\dagger}DT_1^{(1)}$ and other higher order non-linear terms together take our final results towards the experimental values.

4.5 α s of Boron, Carbon, and Zinc Homologous Sequences

In this part of study, we calculate α of the atoms and ions belonging to group 11, 12 and 13 of the periodic table and present their results in Tables 4.17 and 4.18 along with others calculations and measurements. Among all the methods employed by us our CCSD_pT results for α are found to be more accurate. This may be because of its its capability to include correlation effects. We also

Table 4.15: Universal GTO parameters for all the angular momentum symmetries used in the calculations of DF wave functions of B^+ , C^{+2} , Al^+ and Si^{+2} .

Parameters	B^+	C^{+2}	Al^+	Si^{+2}
$lpha_0\ eta$	$0.00525 \\ 2.73$	$0.00425 \\ 2.67$	$0.00525 \\ 2.72$	$0.00425 \\ 2.67$

Table 4.16: GTO parameters for the respective angular momentum symmetries in the calculations of DF wave functions of Zn, Ga⁺, Ge⁺², Cd, In⁺, Sn⁺².

Parameters	s	p	d	f	g
$lpha_0\ eta$	$0.007 \\ 2.53$	$0.008 \\ 2.55$	$\begin{array}{c} 0.0018\\ 2.66\end{array}$	$0.009 \\ 2.70$	$0.007 \\ 2.77$

provide an estimate of uncertainties associated with our results by considering contributions from the finite basis size, triples excitations, and Breit interactions. These uncertainties are presented in the parentheses alongside the $CCSD_pT$ results in the above Tables. The value that is referred to as the experimental result for Al^+ is not obtained from the direct measurement [126], rather it is estimated by summing over the experimental values of the oscillator strengths and has a relatively large uncertainty compared to some of the reported calculations. There are two high-precision results reported as the experimental values for the Si^{+2} ion [141, 142], however the value reported in [141] is obtained from the analysis of the energy intervals measurement using the resonant Stark ionization spectroscopy (RESIS) technique while the other value [142] is reported by reanalyzing the data of Ref. [141], which is about 0.03% larger than the former value. The only available measurement of the ground state α of Zn is measured using an interferometric technique by Goebel *et al.* [143]. Similarly there is also one measurement of α available for Cd using a technique of dispersive Fourier-transform spectroscopy, but the reported uncertainty in this experimental value is comparatively large [144]. Nevertheless our $CCSD_pT$ results within the reported error bars are in good agreement with all these experimental values except for Cd atom. There are no measurements available for the other consid-

ered ions to compare them against our calculations. However, there are number of theoretical results for α 's are available from many research groups. They used varieties of many-body approaches among which some of them are based on either the lower-order methods or considering the non-relativistic mechanics. In Tables 4.17 and 4.18, we list all these results along with the information about their employed methods. We only discuss about few of these calculations to demonstrate the differences and similarities of the present method with others. An old calculation of α in B⁺ was reported by Epstein *et al* [145] based on the coupled perturbed Hartree-Fock (CHF) method while Cheng et al had employed a configuration interaction method considering a semi-empirical core-polarization potential (CICP) to evaluate it more precisely [146]. Later Safronova et al used a combined CI and LCCSD methods (CI+all order method) to determine α of B^+ ion [147]. However, the $CCSD_pT$ result seems to be larger than all other calculations. From our analysis we infer that the differences in these results are mainly due to inclusion of the pair-correlation effects to all orders in our CC method. In C^{+2} ion, we find only one theoretical result reported by Epstein *et* al using the same CHF method. Our result for C^{+2} is also slightly larger then the value reported by the above calculation. Till date, Al^+ is the most precise ion clock in the world [148] for which a couple of high-accuracy calculations have been reported to determination α of this ion by attempting to push down the uncertainty in the black-body radiation (BBR) shift of the respective ion-clock transition [147, 149, 150]. Among them calculations carried out by Mihaly et al. is based on the relativistic CC method considering up to quadrupole excitations and finite field approach [149]. In addition to that, Mihaly et al. used Cartesian coordinate system in their work with minimizing the energies in the numerical differentiation approach in contrast to the our CCSD_pT method, where the matrix elements of D are evaluated in the spherical polar coordinate system. Calculations reported by Yu *et al* is using the same approach of Ref. [149], but by considering a different set of single particle orbitals [150]. Safronova *et al* have employed the CI+all order approach to calculate α of Al⁺. There are also other theoretical results that have been reported based on varieties of manybody methods such as CCSD, CICP, CI etc. both in the non-relativistic and relativistic mechanics [124, 125, 151]. We find an excellent agreement among all the theoretical results. Some of these methods have also been employed to calculate α of Si⁺² [96, 125, 151] which are in perfect agreement with the experimental results. However, our $CCSD_pT$ value is slightly larger than the experimental result. In fact, our estimated contributions from the Breit interaction using the RPA method, given in Table 4.17 as δ_B , are about 0.02 to 0.03% which are in accordance with the findings by Safronova et al [96]. We found only one more calculation of α in Ga⁺ using the CICP method [97] to compare with our result. Although values from both the calculations are very close but they do not agree within their reported uncertainties. Calculations in Cd are reported by many groups including the latest one by Roos et al who have used the Douglas-Kroll-Hess (DKH) Hamiltonian in their method [152]. Calculations carried out by Ye et al [153] are based on the relativistic formalism in the CICP method. All the theoretical results are consistent and show good agreement with each other suggesting that the experimental result could have been overestimated. Therefore, it is necessary to have an another measurement of the polarizability of Cd to resolve this ambiguity. There has also been an effort made for the precise determination of α in In⁺ to estimate the BBR shift accurately for its proposed atomic clock transition [147]. Our result agrees well with this calculation, but our estimated uncertainty for this result is comparatively larger owing to the fact that contributions from the triples are estimated to be large and the calculations exhibit slight convergence problem with the used finite size basis. As discussed earlier, calculations carried out in [147] are based on the CI+all order method. We could not find any other calculations of α of the ground states of the Ge⁺² and Sn⁺² ions to make comparative analyses with our results.

Method	\mathbf{B}^+	\mathbf{C}^{+2}	\mathbf{Al}^+	\mathbf{Si}^{+2}	Zn
Our work [91]					
DF	8 149	3 989	10 514	0.683	37 317
MBPT(3)	9 720	3.804	21 752	10 482	34 491
RPA	$11 \ 374$	4503	26 289	19.476	50.846
LCCSD	11.875	4.886	26.118	12.410	38 739
CCSD	10.413	4 213	24 299	11 893	38 701
CCSD_T	10.395(22)	4.244(11)	24.26(5)	11.880(28)	38.666(96)
δ_B	0.002	0.001	0.007	0.003	0.056
Others					
CHF	9.448[145]	3.347 [145]			
MP4	[-]	[-]	24.206(2.42) [124]		
DK,CASPT2					38.4 [152]
CI	9.975 [147]		24.12 [125], 24.405 [147]	11.567 [96], 11.75 [125]	L J
CICP	9.64(3) [146]		24.14(12) [151]	11.668 [142]	38.12 [153]
CI+MBPT	9.613 [147]		24.030 [147]	11.502 [96]	
CI+all order	9.624[147]		24.048 [147]	11.670(13) [96]	
CCSD					39.27 [154]
CCSD(T)					39.2(8) [143], 38.01 [154], 37.6 [155]
Expt.			$^{a}24.20(75)$ [126]	$^{b}11.669(9)$ [142], 11.666(4) [141]	38.8(3) [143]

Table 4.17: Comparison of the results of α s of \mathbf{B}^+ , \mathbf{C}^{+2} , \mathbf{Al}^+ , \mathbf{Si}^{+2} and \mathbf{Zn} from different many-body methods listed in the first column and experimental results. Contributions from the Breit interactions are estimated using the RPA method and given as δ_B . Uncertainties in our $\mathrm{CCSD}_p\mathrm{T}$ results are given in the parentheses.

 a Estimated from the measured oscillator strengths.

 b Obtained by reanalyzing data of Ref. [141].

Method	Ga^+	\mathbf{Ge}^{+2}	Cd	\mathbf{In}^+	\mathbf{Sn}^{+2}
Our work [91]					
55			10.01-		
DF'	17.148	10.085	49.647	25.734	16.445
MBPT(3)	15.796	8.884	35.728	18.374	12.095
RPA	21.780	12.011	63.743	29.570	17.941
LCCSD	19.138	11.520	45.086	25.360	15.978
CCSD	18.455	10.890	45.898	24.246	15.537
$\mathrm{CCSD}_p\mathrm{T}$	18.441(39)	10.883(16)	45.86(15)	24.11(51)	15.526(41)
δ_B	0.019	0.006	0.104	0.036	0.019
Others					
DK CASPT2			46.0 [152]		
CI			40.9 [102]	26.27 [147]	
	1705(94) [07]		44.69 [159]	20.27 [147]	
	17.95(34) [97]		44.03 [103]		
CI+MBPT				23.83 [147]	
CI+all order				24.01 [147]	
CCSD			48.09 [154]	24.065(1.70) [150]	
CCSD(T)			$46.25 \ [154], \ 46.8 \ [155]$		
CCSDTQ				24.14(8) [149]	
Expt.			49.65(1.49) [144]		
I	a Fet	imated from th	ne messured oscillator st	rongthe	

Table 4.18: Comparison of the results of α s of \mathbf{Ga}^+ , \mathbf{Ge}^{+2} , \mathbf{Cd} , \mathbf{In}^+ and \mathbf{Sn}^{+2} using different many-body methods listed in the first column and experimental results. Contributions from the Breit interactions are estimated using the RPA method and given as δ_B . Uncertainties in our CCSD_pT results are given in the parentheses.

^b Obtained by reanalyzing data of Ref. [141].



Figure 4.3: Histogram showing $(\alpha - \alpha_D)/\alpha_D$ (in %) with different many-body methods against the different atomic systems shown above.

To comprehend the underlying roles of the electron correlation behavior in the evaluation of the ground state α of the considered systems, we systematically present the calculated values of the α in Tables 4.17 and 4.18 from the DF, MBPT(3), RPA, LCCSD and CCSD methods. The differences between the CCSD results and the values quoted from the $CCSD_{n}T$ method are the contributions from the partial triple excitations. Obviously, these differences are small in magnitudes implying that the contributions from the unaccounted higher order excitations are very small. The lowest order DF results are smaller in magnitudes in the lighter systems but their trends revert in the Cd iso-electronic systems with respect to their corresponding CCSD results. Also, the MBPT(3) results do not follow a steady trend. In the B^+ , C^{+2} , Al^+ and Si^{+2} ions, the correlation effects enhance the α values in the MBPT(3) method from their DF results while the MBPT(3) results are smaller than the DF values in the other systems. It is also found that the electron correlation trends in B^+ and C^{+2} are different than its corresponding iso-electronic neutral Be atom reported by us earlier [90]. For example, the MBPT(3) result of Be is smaller than its DF result, while this trend is other way around in the B^+ and C^{+2} ions. Similar observations are also noticed in the Mg atom and among their iso-electronic Al^+ and Si^{+2} ions. As has been stated earlier RPA is an all order method embracing the core-polarization effects to all orders, but we find that the results are overestimated in this method



Figure 4.4: Few significantly contributing non-RPA type MBPT(3) diagrams.

compared to the CCSD results; more precisely from the experimental values given in Tables 4.17 and 4.18. We understand these differences as the contributions from the pair-correlation effects that are absent in the RPA method, but they are accounted intrinsically to all orders as the integral part of the CCSD method. The role of the pair-correlation effects in the determination of α are verified by examining contributions from the individual MBPT(3) diagrams. The dominant contributing non-RPA diagrams appearing in the MBPT(3) method that take care of the pair-correlation effects are shown in Fig. 4.4. In fact, contributions from these non-RPA diagrams are found to be larger than the differences between the RPA and CCSD results reported in Tables 4.17 and 4.18. This finding advocates that there are large cancellations among the lower order and higher order pair-correlation contributions in the CCSD method bestowing modest size of contributions to α , but they appear to be very significant in the heavier systems to attribute accuracies in the results. To demonstrate the roles of the non-linear terms in yielding high accuracies α values in the considered ions, we have also given the results from the LCCSD method in the above table. Although LCCSD is an all-order perturbative method, but it omits higher



Figure 4.5: Trends in the calculations of α s from the employed many-body methods in the singly charged alkali ions.



Figure 4.6: Trends in the calculations of α s from the employed many-body methods in the doubly charged alkaline-earth metal ions.

order core-polarization and pair-correlation effects that contributes through the non-linear terms involving $T^{(0)}T^{(0)}$ or higher powers of $T^{(0)}$. Consequently, this method also overestimates the results like the RPA method. The LCCSD results in B⁺ and C⁺² are larger than the RPA values, but the LCCSD values are smaller than the RPA results in the other cases. This clearly demonstrates intermittent trends of the correlation effects in the determination of α of the systems belonging to a particular group of elements in the periodic table to another through a given many-body method as well as when they are studied using the methods with different levels of approximations. To manifest contributions from the correlations effects through various many-body methods quantitatively, we

System	$DT_1^{(1)}$ +c.c	$T_1^{(0)\dagger} D T_1^{(1)} + c.c$	$T_2^{(0)\dagger} D T_1^{(1)} + c.c$	$T_2^{(0)\dagger} D T_2^{(1)} + c.c$	Others
B^+	10.848	-0.194	-1.679	0.774	0.646
C^{+2}	4.392	-0.047	-0.668	0.274	0.29
Al^+	25.855	-0.519	-3.166	1.523	0.567
Si^{+2}	12.589	-0.160	-1.475	0.666	0.260
Zn	43.812	-2.458	-5.286	2.047	0.551
Ga^+	20.223	-0.545	-2.409	0.837	0.335
Ge^{+2}	11.846	-0.198	-1.363	0.476	0.122
Cd	52.963	-3.346	-6.985	2.262	0.962
In^+	27.134	-0.882	-3.647	1.064	0.441
Sn^{+2}	17.249	-0.366	-2.286	0.603	0.326

Table 4.19: Contributions to the α s of \mathbf{B}^+ , \mathbf{C}^{+2} , \mathbf{Al}^+ , \mathbf{Si}^{+2} , \mathbf{Zn} , \mathbf{Ga}^+ , \mathbf{Ge}^{+2} , \mathbf{Cd} , \mathbf{In}^+ and \mathbf{Sn}^{+2} from various $\mathrm{CCSD}_p\mathrm{T}$ terms.

portray the results obtained for α in the considered systems using these methods in a histogram as shown in Fig. 4.3. This clearly bespeaks about the lopsided trend in the estimation of α of the considered systems. Again, we also plot the α values of the singly and doubly charged ions separately in Figs. 4.5 and 4.6 in order to make a comparative analysis in the propagation of correlation effects through the employed methods in these elements that belong to two different groups of the periodic table. This figure shows that the contributions from the correlation effects in the singly charged and doubly charged ions do not exactly follow similar trends.

At last, we would like to discuss about the trends in the correlation effects coming through various CCSD_pT terms. We give contributions explicitly from the individual CC terms of linear form and the rest as "Others" in Table 4.19. Clearly, this table shows that the first term $DT^{(1)}$ gives the dominant contributions as it subsumes all the leading order core-polarization and paircorrelation effects along with the DF result. The next dominant contributing term is $T_2^{(0)\dagger}DT_1^{(1)}$ which incorporates some contributions from the correlation effects emanated at the MBPT(2) level and possess opposite signs from the $DT^{(1)}$ contributions causing cancellations among them. It is also worthy to mention that contributions coming from the $T_2^{(0)\dagger}DT_2^{(1)}$ term corresponds to the higher order perturbation and also accounts contributions from the doubly excited intermediate states. As seen from the table, these contributions are non-negligible suggesting that they should also be estimated accurately for accomplishing high precision results and the sum-over-states approach may not be able to augment these contributions suitably in the considered systems. Contributions from the other non-linear CC terms at the final property evaluation level seem to be slender, although the differences between the LCCSD and CCSD results emphasis their importance for accurate calculations of the atomic wave functions in the considered systems.

4.6 Summary

We have employed a variety of many-body methods to evaluate α of many closedshell atoms and ions. Using these methods we study the role of the correlation effects and follow-up their trends to achieve very accurate calculations of the ground state α of many closed shell atomic systems. In the first part we studied correlation trends in α of various atoms and ions belonging specifically to alkali, alkaline and noble gas earth elements The crucial role of correlation effects is highlighted by presenting and comparing the results at different levels of approximations from lower order many-body perturbation theory to the relativistic CCSD method. Correlation trends among the neutral atoms, singly charged ions and doubly charged ions are presented. In the second part of the study we employed our methods to atoms and ions in the boron, carbon, and zinc homologous sequences of elements. We find the patterns in which the correlation effects behave with respect to the mean-field level of calculations are divergent in the individual iso-electronic systems through a particular employed many-body method. Also, our calculations reveal that inclusion of both the core-polarization and pair-correlation effects to all orders are equally important for securing high precision α in the considered systems and the core-polarization effects play the pivotal role among them. Contributions from the doubly excited states are found to be non-negligible implying that a sum-over-states approach

may not be pertinent to carry out these studies. Our results obtained using the singles, doubles and important triples approximation in the coupled-cluster method agree very well with the available experimental values in some of the systems except for Cd. In fact none of the reported theoretical results for Cdagree with the measurement, however there seem to be reasonable agreement among all theoretical results. This urges for further experimental investigation of the Cd result. In few systems, there are no experimental results available yet and the reported precise values in the present work can be served as exemplars for their prospective measurements. Investigation of various correlation effects in evaluating α serve as a benchmark to our many-body methods and it will definitely provide valuable insights into the calculations of atomic electric dipole moments d_A which arises due to parity and time-reversal symmetry violation, owing to the fact that evaluation of α and d_A shares similar parity and angular momentum selection rules. In addition to that our results will also serve as a guide to the future measurements of systems where the experimental values of polarizabilities are not precisely known.

Chapter 5

EDM Results and Analysis

5.1 Overview

In the previous chapter we successfully tested the potential of our many-body methods in calculating dipole polarizabilities (α s) of various closed-shell atoms and ions [90, 91]. Now, we employ these methods to calculate permanent electric dipole moments (EDMs) of the closed-shell (diamagnetic) atoms (d_A) whose experiments are currently underway [29, 32, 39, 42]. The dominant sources of the EDM in a closed-shell atomic system are mainly due to parity (P) and timereversal (T) violating electron-nucleus (e-N) tensor-pseudotensor (T-PT) and nuclear Schiff moment (NSM) interactions; details are given in Chap.1. We consider both the interactions to evaluate EDMs of $^{129}\mathrm{Xe},\,^{199}\mathrm{Hg},\,^{223}\mathrm{Rn}$ and $^{225}\mathrm{Ra}$ atoms. Owing to the fact that the matrix elements of the T-PT and NSM interaction Hamiltonians increase with the atomic number (Z) of the system [156]. Therefore, generally heavier atoms are preferred to get larger enhancements in signals during measurements. In addition to that, all the above mentioned isotopes have nuclear spin I = 1/2 due to which the contributions from the octupole moment vanish. Till date, the most precise EDM measurement has been done on atomic Hg where an upper limit to atomic EDM is obtained as $d_A < 3.1 \times 10^{-29} |e|cm$ (at 95% confidence level) [29]. The next best limit comes from an earlier measurement on ¹²⁹Xe atom as $d_{\rm A} < 4.1 \times 10^{-27} |e| cm$ [38]. Though, ¹²⁹Xe is lightest among all the above considered systems it has some distinct experimental ad-

vantages over the other systems such as: it has larger spin coherence time and can be used in greater densities as compared to other suitable candidates [39]. These advantages could enhance the statistical sensitivity of the measurement by at least about 2 to 3 orders in magnitude. The systems like ²²⁵Ra and ²²³Rn are very interesting because of the fact that they have larger Z values and their nucleus is octupole deformed which brings the opposite parity orbitals closer to each other and hence enhances the EDM signals. In fact, a research group at Argonne National Laboratory (ANL) has recently reported their first EDM measurement of ²²⁵Ra [32] after making a steady progress in the last several years [35, 36, 157]. They infer an upper limit to d_A as $|d_A(^{225}Ra)| < 5.0 \times 10^{-22} |e|$ cm (at 95% confidence). At this moment, their result is not competitive with either of the other two mentioned measurements but the experiment has huge potential to gain in the precision by many orders in magnitude in future [32]. No EDM measurement in $^{223}\mathrm{Rn}$ atom has been reported yet. Along with d_A we also evaluate α in the above mentioned systems and investigate the trends in the behavior of electron correlation effects in determining the above properties, going from lowerto higher-orders in perturbation. The P,T-odd electron-nucleus T-PT and the NSM interaction Hamiltonians are given in Chap. 1 as [25, 28]

$$H_{\rm int}^{\rm TPT} = i\sqrt{2}G_F C_T I \rangle \boldsymbol{\gamma} \ \rho(r), \qquad (5.1.1)$$

and

$$H_{\rm int}^{\rm NSM} = \frac{3\mathbf{S.r}}{B_4}\rho(r),\tag{5.1.2}$$

respectively, with G_F is the Fermi coupling constant, C_T is the T-PT coupling constant, I is the nuclear spin, γ_i represents the Dirac gamma matrices, $\rho(r)$ is the nuclear density, $\mathbf{S} = S \frac{\mathbf{I}}{I}$ is the NSM and $B_4 = \int_0^\infty dr r^4 \rho(r)$. The expression to evaluate d_A is given in Eq. 2.1.8 as

$$d_{\rm A} = 2 \frac{\langle \Psi_{(0)} | D | \Psi_0^{(1)} \rangle}{\langle \Psi_{(0)} | \Psi_{(0)} \rangle}.$$
 (5.1.3)

Method of	This	work []	158]		Others	5	
Evaluation	α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{\mathrm{A}}^{\mathrm{NSM}}$	α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{ m A}^{ m NSM}$	Ref.
DF	26.918	0.447	0.288		0.45	0.29	[25]
$\frac{\text{MBPT}(2)}{\text{MBPT}(3)}$	23.388 18 693	$0.405 \\ 0.515$	$0.266 \\ 0.339$		0.52		[161]
RPA RPA	26.987	0.562	0.375	07 7	0.57	0.38	[25]
LCCSD	27.484	0.608	0.417	27.7	0.564		[162]
CCSD CCSD _n T	27.744 27.782	$0.501 \\ 0.501$	$0.336 \\ 0.337$				
δ	0.050	0.002	0.004				[1.00]
Experiment	27.815(2)	27)					[163]

Table 5.1: α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ in units ea_0^3 , $10^{-20}C_T \langle \sigma \rangle |e|$ cm and $10^{-17} [S/|e|fm^3]|e|$ cm of Xe using different many-body methods. The estimated uncertainties to the CCSD_pT calculations are given as δ .

For the precise determination of $d_{\rm A}$ it is necessary to evaluate atomic wave functions $|\Psi_0\rangle$ and its first order correction due to P,T-odd interactions $|\Psi_0^{(1)}\rangle$ as accurately as possible. The evaluations of $|\Psi_0\rangle$ and $|\Psi_0^{(1)}\rangle$ using different manybody methods considered in this work are given in Chap. 1. On combining our EDM results with the limits obtained from the respective EDM measurements, we get upper bounds on various P and T-violating interactions [158–160]. Our Hg EDM result evaluated using the relativistic CC method in combination with the most precise measurement yield best limits for the P,T-odd couplings associated with the T-PT (C_T) and NSM (S) interactions [159].

5.1.1 EDM of ¹²⁹Xe

In Table 5.1, we present our results for α , d_A^{TPT} and d_A^{NSM} for the ground state of ¹²⁹Xe by the methods explained in Chap. 2 and compare them with the other calculations and measurement. We have used GTOs to generate single particle orbitals with the parameters given in Table 5.2 for each angular momentum symmetry. The most precise measured value of α is reported as 27.815(27) ea_0^3 [163]. From this table we also observe that the DF value of α is close to the experimental result, but when correlation effects are added via the MBPT(2)

Parameters	s	p	d	f	g
$\begin{array}{c} \alpha_0 \\ \beta \\ Basis \end{array}$	$0.0005 \\ 2.20 \\ 19$	0.00073 2.21 18	0.00082 2.22 17	$0.00084 \\ 2.25 \\ 16$	$0.00082 \\ 2.23 \\ 14$

Table 5.2: GTO parameters for the respective angular momentum symmetries in the calculations of DF wave functions of ¹²⁹Xe. The last line presents the active orbitals considered for the perturbative calculations.

and MBPT(3) methods, results become off by more than 6%. However results obtained from the all-order RPA, LCCSD, CCSD and $CCSD_pT$ methods are in good agreement with the measured value, but the $CCSD_pT$ result is more rigorous and accurate method than the other approaches. The motivation for considering the non-linear RCC terms in the singles and doubles approximation supplemented by important triple excitations for the precise evaluation of the ground state properties in Xe atom can be attributed to the significant contributions from the non-RPA diagrams, as have been explicitly demonstrated in our earlier study on the polarizability of the closed-shell atomic systems [90,91]. It is also important to note that d_A due to the T-PT and NSM interactions exhibit different correlation trends than those of α . The results increase steadily from the DF level after the inclusion of the correlation effects in the passage from the finite order MBPT to LCCSD, and after that they decrease at the CCSD level. The uncertainties reported in our calculations are estimated by taking the difference between the results from the CCSD and $CCSD_pT$ methods and from the incompleteness in the basis functions which are given as δ in Table 5.1. The contributions from the QED corrections are estimated by using the Uehling potential $V_{\rm U}(r)$ [64] which is the lowest order modified nuclear potential due to a virtual electron-positron pair given in Eq. 2.8.2. These contributions change $d_{\rm A}^{\rm TPT}$ from 0.501 to 0.503 and $d_{\rm A}^{\rm NSM}$ from 0.337 to 0.338 at the CCSD_pT level.

In Table 5.1, we also present the results from the other calculations with the information on employed methods for α , d_A^{TPT} and d_A^{NSM} [25,161,162]. From the above table one can notice that, we have successfully reproduced the results of the earlier calculations by employing our many-body methods at the same level

Term	α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{\rm A}^{ m NSM}$
$\overline{D}T_1^{(1)} + c.c$	26.246	0.506	0.338
$T_1^{(0)\dagger}\overline{D}T_2^{(1)} + c.c$	0.008	~ 0	~ 0
$T_2^{(0)\dagger}\overline{D}T_2^{(1)} + c.c$	1.395	-0.005	-0.001
Extra	0.095	~ 0	-0.001

Table 5.3: Explicit contributions from various CCSD_pT terms to the α , $d_{\text{A}}^{\text{TPT}}$ and $d_{\text{A}}^{\text{NSM}}$ in units ea_0^3 , $10^{-20}C_T\langle\sigma\rangle|e|\text{cm}$ and $10^{-17}[S/|e|fm^3]|e|\text{cm}$ of Xe.

of approximations. In addition to that, we have gone beyond these approximations for obtaining accurate results. Our results using the MBPT(3), LCCSD, CCSD and $CCSD_pT$ methods provide useful insights into the role of different types of electron-correlation effects. From the MBPT(3) calculations, we find that certain non-RPA type diagrams, for example the diagrams shown in Fig. 5.1.1, contribute significantly with opposite signs to those of the DF values in all the above properties leading to large cancellations in the final results. The above observation undoubtedly give us the reason why the RPA over-estimates the EDM compared to the $CCSD_pT$ method. In fact, like RPA, the LCCSD method also over-estimates these results even though they account for some of the lower order non-RPA contributions because many of these MBPT(3) diagrams correspond to the non-linear terms of the CCSD_pT method. In Table 5.3, we present the contributions from the individual $CCSD_pT$ terms to highlight the importance of various correlation effects. It can be seen in this table that the term $\overline{D}T_1^{(1)}$ is the most dominantly contributing followed by $T_2^{(0)^{\dagger}}\overline{D}T_2^{(1)}$, where \overline{D} is the effective one-body term of $e^{T^{(0)}\dagger}De^{T^{(0)}}$ and the contributions from the



Figure 5.1: Few important non-RPA diagrams from the MBPT(3) method. $H_{\rm int}$ corresponds to either $H_{\rm int}^{\rm TPT}$, $H_{\rm int}^{\rm NSM}$ or D operators in the evaluation of $d_{\rm A}^{\rm TPT}$, $d_{\rm A}^{\rm NSM}$ and α respectively.



Figure 5.2: Diagram involving effective one-body dipole operator \overline{D} and the perturbed wave operator $\Omega^{(1)}$ that accounts for the contributions from the singly excited configurations.

other terms are almost negligible. In order to deeply understand the behavior of electron-correlation effects, we carry out an analysis similar to the one given in [162]. We find the contributions from various orbitals that correspond to various singly excited intermediate configurations for different quantities which are given in Table 5.4. These results are evaluated using the diagrams shown in Fig. 5.2 with the corresponding wave operator $\Omega^{(1)}$ from the many-body methods under consideration such as DF, MBPT(2) which is also called lowest-order RPA denoted by [MBPT(*l*-RPA)] because they are having same number of diagrams , RPA and CCSD_pT . We also present the sum of contributions from the orbitals belonging to a particular category of angular momentum excitations to demonstrate their significance in obtaining the above properties. The information provided in all the three tables together clearly expounds the reasons for the different trends in the electron-correlation effects in the calculations of α , d_A^{TPT} and d_A^{NSM} .

Tabl	le	5.	4:	,

RPA, and CCSD_pT methods to the values of α , d_A , of ¹⁹⁹Xe.]Contributions from various matrix elements and from various angular momentum symmetry groups at the DF, lowest-order RPA [denoted by MBPT(*l*-RPA)], RPA, and CCSD_pT methods to the values of α , d_A^{TPT} and d_A^{NSM} in units ea_0^3 , $10^{-20}C_T \langle \sigma \rangle |e|$ cm and $10^{-17}[S/|e|fm^3]|e|$ cm respectively, of Xe atom. Here the summation indices n and m represent for the occupied and unoccupied orbitals, respectively.

Excitation(s)		DF		М	BPT(<i>l</i> -RI	PA)		RPA			$\mathrm{CCSD}_p\mathrm{T}$	
$(a \rightarrow p)$	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{NSM}$
$5p_{1/2} - 7s$	0.248	0.030	0.007	0.336	0.056	0.016	0.380	0.062	0.016	0.352	0.050	0.014
$5p_{1/2} - 8s$	0.517	0.090	0.022	0.690	0.159	0.045	0.769	0.172	0.045	0.733	0.145	0.039
$5p_{1/2} - 9s$	0.237	0.106	0.025	0.284	0.166	0.044	0.301	0.174	0.044	0.309	0.157	0.041
$5p_{3/2} - 7s$	0.844	~ 0	0.015	1.136	0.005	0.036	1.314	0.007	0.036	1.202	0.001	0.031
$5p_{3/2} - 8s$	1.558	~ 0	0.043	2.056	0.014	0.093	2.351	0.018	0.093	2.261	0.024	0.082
$5p_{3/2} - 9s$	0.583	~ 0	0.044	0.678	0.012	0.081	0.745	0.015	0.081	0.809	0.017	0.076
$5p_{1/2} - 7d_{3/2}$	2.267	~ 0	~ 0	2.200	-0.003	-0.008	2.407	-0.006	-0.008	2.259	-0.011	-0.008
$5p_{1/2} - 8d_{3/2}$	3.454	~ 0	~ 0	2.595	-0.013	-0.020	2.882	-0.022	-0.020	2.925	-0.028	-0.018
$5p_{3/2} - 7d_{5/2}$	5.667	~ 0	~ 0	5.747	-0.027	-0.018	6.365	-0.039	-0.018	5.827	-0.031	-0.018
$5p_{3/2} - 8d_{5/2}$	7.054	~ 0	~ 0	5.749	-0.048	-0.037	6.267	-0.071	-0.037	6.207	-0.057	-0.035
$\sum (ns - mn_{1/2})$	0.013	0 121	0 029	0 049	0.142	0.036	0.046	0 144	0.036	0.046	0.152	0.038
$\sum_{n,m} (ns - mp_{1/2})$	0.010	0.121 ~0	0.025	0.045	0.142	0.000	0.040	0.111	0.000	0.040	0.102	0.048
$\sum_{n,m} (ns - mp_{3/2})$	1.064	0.356	0.030	1 220	0.000	0.042	1 529	0.000	0.042	1 474	0.004	0.040
$\sum_{n,m} (np_{1/2} - ms)$	1.004	0.320	0.078	1.302	0.000	0.130	1.002	0.029	0.150	1.474	0.400	0.122
$\sum_{n,m} (np_{3/2} - ms)$	3.183	~ 0	0.144	4.111	0.036	0.265	4.696	0.046	0.265	4.530	0.057	0.241
$\sum_{n,m} (np_{1/2} - md_{3/2})$	6.293	~ 0	-0.001	4.993	-0.022	-0.033	5.582	-0.038	-0.033	5.539	-0.047	-0.031
$\sum_{n,m} (np_{3/2} - md_{3/2})$	1.545	~ 0	~ 0	1.326	-0.003	-0.006	1.501	0.003	-0.006	1.375	-0.006	-0.007
$\sum_{n,m} (np_{3/2} - md_{5/2})$	13.860	~ 0	~ 0	11.887	-0.082	-0.064	13.428	-0.125	-0.064	12.871	-0.099	-0.060

5.1.2 EDM of ¹⁹⁹Hg

We present our results for α , d_A^{TPT} and d_A^{NSM} along with the other calculations and measurement in Table 5.5. In order to get the converged results with respect to different finite size single particle orbitals such that they are computationally inexpensive for the CCSD calculations within the available resources with us, we first perform RPA calculations for different set of active orbitals. The single particle orbitals at the DF level are expanded using GTOs with UB parameters $\alpha_0 = 0.00625$ and $\beta = 2.53$. Convergence in the results from these orbitals are shown explicitly in Table 5.6. For the computational convenience basis IV is taken in the final calculations. We present all the reported results in the same row so that comparison can be drawn. The results reported by the PRCC method [166, 167] are similar to our CCSD method but they differ in the procedure of determining amplitudes of the CC operators and evaluating Eq. 2.1.8. We also present corrections (shown with + sign) due to the frequency independent Breit interaction and lowest order quantum electrodynamics (QED) effects from RPA to give the final results in the same table. These QED effects include contributions from the Uehling, Wichmann-Kroll and lower-order self-energy correction potentials as have been described in [28]. For the error estimation, we evaluate contributions from the neglected higher excitations using the $T_3^{(0),pert}$ operator as given in Eq. 2.6.10 (given as higher CC in Table 5.5) and contributions from higher orbitals including from h- and i- symmetries that are not considered in the CC calculations (given as basis in Table 5.5). The net errors are estimated by adding these two contributions using the quadrature formula.

The α of ¹⁹⁹Hg has been determined using two different approaches in past among which Pershina *et al.* [165] had evaluated the second-order derivative of the ground state energy with respect to an arbitrary electric field while in the other calculations [164, 166, 167] it is determined from the expectation value of D in the ground state which is an admixture of opposite parity states. Since the DF method gives upper bound to the exact energy, Pershina *et al.* get a large DF value and their CCSD and CCSD(T) methods bring down the results towards the experimental value. Our observation in the triples contribution to α seem to

Table 5.5: α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ in units ea_0^3 , $(10^{-20}C_T \langle \sigma \rangle |e|cm)$ and $(10^{-17}[S/|e|fm^3]|e|cm)$ respectively are presented using different many body methods for the ground state of ¹⁹⁹Hg and compared them with others calculations. Values given in bold fonts are our final results.

Method	,	This Wor	k		Others	
	α	$d_{\rm A}^{ m TPT}$	$d_{ m A}^{ m NSM}$	α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{ m A}^{ m NSM}$
DF	40.95	-2.39	-1.20	40.91 [164] 44.90 [165]	-2.0 [161] -2.4 [25]	$-1.19 [164] \\ -1.2 [25]$
MBPT(2)	34.18	-4.48	-2.30			ĽJ
MBPT(3)	22.98	-3.33	-1.72			
RPA	44.98	-5.89	-2.94	44.92 [164]	-6.0 [161]	-2.8 [164]
					-5.9[25]	-3.0[25]
CI+MBPT				[†] 32.99 [164]	-5.1 [25]	-2.6 [25]
PRCC				33.294 [166]	-4.3 [166]	-5.07 [166]
				33.54 [167]		
PRCC(T)				33.63 [167]		
LCCSD	33.91	-4.52	-2.24			
$\mathrm{CCSD}^{(2)}$	33.76	-3.82	-2.00			
$CCSD^{(4)}$	35.13	-4.14	-2.05			
$\mathrm{CCSD}^{(\infty)}$	34.98	-4.02	-2.00	[165]		
CCSD(T)	33.95	-4.20	-2.08	34.15 [165]		
$\mathrm{CCSD}_p\mathrm{T}$	34.07	-4.30	-2.12			
+ Breit	34.16	-4.29	-2.10			
+QED	34.27	-4.44	-2.16			
		F	Stimated	errors		
Higher CC	0.07	-0.08	-0.02			
Basis	-0.15	-0.03	-0.02			
Net error	0.17	0.09	0.03			
Experiment		33.91(34)	(143]			

agree with Pershina *et al.* To compare the results between our calculations with those reported in [166, 167], we present contributions from different CC terms in the CCSD method for all the evaluated quantities in Table 5.7. However, we learned that due to a phase factor problem the actual values are different than the published results [166]. Nevertheless, comparison between these calculations in Table 5.7 show large differences in the contributions among individual CC terms and from the normalization factor of the wave function, which do not appear in our method. We also noticed that there are significant differences in the contributions from the non-linear terms arising in Eq. 2.1.8 in both the

Table 5.6: Convergence pattern in the α , d_A^T and d_A^S results (in same unit as given in Table 5.5) of ¹⁹⁹Hg from different set of orbitals from various angular momentum symmetries (s, p, d, f and g) using RPA. Ultimately, basis IV is taken in the final calculations.

Basis	s	p	d	f	g	Results		
						α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{ m A}^{ m NSM}$
Ι	10	10	8	6	5	44.66	-4.90	-2.41
II	12	12	11	8	7	44.97	-5.71	-2.84
III	14	14	13	10	9	44.98	-5.87	-2.92
IV	16	16	15	12	11	44.98	-5.89	-2.94
V	18	18	17	14	12	44.98	-5.89	-2.94

Table 5.7: Contributions to α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ values of ¹⁹⁹Hg from various CCSD terms (hermitian conjugate terms are included). Here *norm* represents difference between the contributions after and before normalizing the wave function with normalization factor 1.171 and NA stands for not applicable.

CC terms]	Ref. [167]		
	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α
$DT_{1}^{(1)}$	39.77	-5.00	-2.44	41.927
$T_2^{(0)\dagger} DT_1^{(1)}$	-5.73	1.36	0.62	-2.724
$T_2^{(0)\dagger} D T_2^{(1)}$	1.55	-0.11	-0.06	1.504
$T_1^{(0)\dagger} DT_1^{(1)}$ $T_1^{(0)\dagger} DT_2^{(1)}$	-1.71 -0.12	0.02 -0.08	$\begin{array}{c} 0.02 \\ 0.04 \end{array}$	-1.583 0.091
Extra	1.22	-0.21	-0.18	0.119
norm	NA	NA	NA	-5.74

CC approaches, which are given as Extra in Table 5.7, even though both works consider only the connected diagrams in the calculations. However, as shown in Table 5.5, our α results from DF and RPA are in good agreement with with those reported in [25, 164].

Our main aim in this work is to have more reliable EDM results for ¹⁹⁹Hg, where the previous two calculations using the PRCC method [166] and a hybrid approach of configuration interaction with finite-order many-body perturbation theory (CI+MBPT method) [25] differ substantially as shown in Table 5.5. In the CI+MBPT approach, the initial wave functions are determined using V^{N-2}

potential with N as the total number of electrons and the electron correlation effects are accounted for by dividing the electrons into valence and core electrons. In contrast, both the PRCC method and our calculations are carried out using the V^N potential and correlations among all the electrons are treated on equal footing. We find, like α results, our DF and RPA results for d_A due to the T-PT $(d_{\rm A}^{\rm TPT})$ and NSM $(d_{\rm A}^{\rm NSM})$ interactions match perfectly with [25, 164] and also with another old calculation [161]. The large differences between the results of [166] and [25] may be attributed to the phase factor problem as discussed above in the context of α result. In an earlier calculation, Dzuba *et al.* had also reported α as 32.99 ea_0^3 using the CI+MBPT method along with some corrections from RPA. However, a detailed analysis in [164] demonstrates that individually CI and RPA overestimate α value, however for EDMs in ¹⁹⁹Hg, CI underestimates and RPA overestimates the results. Our final EDM result is the most accurate and differ by about 15-20% from the values given in [25]. It is to be noted that our LCCSD, CCSD⁽²⁾ and final α results are in close agreement with the measured value. However, this is not true for the EDM results due to different behavior of electron correlation effects through the $T_1^{(0)}T_2^{(0)}, \frac{1}{2}T_2^{(0)}T_2^{(0)}, \cdots$ non-linear CC terms corresponding to higher level excitations.

5.1.3 EDM of ²²³Rn

The ²²³Rn isotope is another interesting candidate to search for the permanent EDM in the closed-shell atomic systems because of the octupole deformation in the nucleus which enhances the nuclear Schiff moment significantly. We present the results of our calculations along with others for α , d_A^{TPT} and d_A^{NSM} in Table 5.8. Among these results, we consider the CCSD results to be the most accurate on physical grounds. In our calculations, we use GTOs with ET condition to expand our single particle wave functions at the DF level. The parameters used in the GTOs are given in Table 5.9 along with number of active orbitals used for the beyond DF perturbative calculations. We first discuss our α results for the ground state of Rn. The α for Rn is yet to be measured. The α results reported in [112, 152, 168, 170] are obtained by evaluating the second derivative

Table 5.8: α , d_A^T and d_A^S results (in same unit as given in Table 5.5) of ²²³ Rn using
different many-body methods. "Others" refer to previous results, (Note: †Results
are quoted from basis 2 of [168], ‡ Calculations are for 211 Rn and * estimated using
RPA).

Employed	Thi	s work [1	69]		Others	
method	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α	$d_{\rm A}^{ m TPT}$	$d_{ m A}^{ m NSM}$
DF	34.42	4.485	2.459	34.42 [164]		2.47 [164]
				29.22 [170]	[‡] 4.6 [25]	[‡] 2.5 [25]
				32.81 [112]		
				[†] 33.54 [168]		
MBPT(2)	29.57	3.927	2.356	$28.48 \ [170]$		
				$33.19 \ [112]$		
				32.6 [171]		
MBPT(3)	18.10	4.137	2.398			
RPA	35.00	5.400	3.311	35.00 [164]		3.33 [164]
				$^{\dagger}32.75 [168]$	$^{\ddagger}5.6$ [25]	$^{\ddagger}3.3$ [25]
LCCSD	35.08	5.069	3.055			
CCSD	35.27(9)	4.85(6)	2.89(4)	*34.39 [168]		
				28.61 [170]		
				32.90 [112]		
				35.391 [93]		
				1 /		
m · 1	0.01	0.000	Error bu	dget		
Triples	0.01	-0.003	-0.005			
^QED	0.02	0.053	0.028			
^Breit	0.09	-0.020	-0.033			

of the ground state energy with respect to an arbitrary electric field. However, the calculations carried out in [93, 164] and by us involve the determination of the expectation value of D in the ground state which has a mixed parity wave function due to $H_{\text{int}} \equiv D$. Our results at the DF and RPA levels agree

Table 5.9: GTO parameters for the respective angular momentum symmetries in the calculations of DF wave functions of ²²³Rn. Active orbitals used in perturbative calculations are given in last line.

Parameters	s	p	d	f	g
$\begin{array}{c} \alpha_0 \\ \beta \\ \text{Basis} \end{array}$	0.00715 2.10 18	$0.0067 \\ 2.24 \\ 17$	$0.00715 \\ 2.24 \\ 16$	0.0072 2.57 14	0.0072 2.71 12

Diagram	α	$d_{\rm A}^{ m TPT}$	$d_{ m A}^{ m NSM}$
(i) (ii) (iii)	-4.522	-0.339	-0.241
	-1.166	-0.086	-0.051
	-1.137	-0.053	-0.039

Table 5.10: Individual contributions from the non-RPA diagrams those are shown in Fig. 5.1.1 to α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ of ²²³Rn.

very well with those of Refs. [164]. The agreement between the results of our CCSD and another similar work Ref. [93] is also very good. Our T-PT and NSM EDM results for ²²³Rn at the DF and RPA levels agree with those of Ref. [25, 164]. Our EDM results using the CCSD method which subsumes the DF, RPA and all order non-RPA (the rest apart from RPA) contributions are clearly the most rigorous to date. We also estimate uncertainties to our CCSD results by determining contributions from important triple excitations using a perturbative triple excitation operator ($CCSD_pT$ method), as described in Eq. 2.6.10 of Chap. 2, and using it in perturbed and unperturbed CCSD amplitude equations given in the same chapter as Eqs. 2.5.21 and 2.6.9, from the frequency independent Breit interaction and from the lower order vacuum polarization effects from the QED corrections through the Uehling $(V_{\rm U}(r))$ and Wichmann-Kroll $(V_{WK}(r))$ potentials given in Eqs. 2.8.1, 2.8.2 and 2.8.3. Contributions from the Breit and QED interactions are estimated using RPA and they are given in Table 5.8 towards the bottom under the error budget. Although these contributions for EDMs cancel out, we have added them using the quadrature formula to find out the net uncertainties of all the quantities that are given in the parentheses alongside the CCSD results.

It can be seen from Table 5.8 that the correlation trends for α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ are different. The possible reason for this is that, in the d_A evaluation contributions from the matrix elements of the $s_{1/2}$ and $p_{1/2}$ orbitals are maximum, while the matrix elements of the other higher symmetry orbitals also contribute significantly in the α evaluation. The trends for both the T-PT and NSM interactions seem to be qualitatively similar, but the relative sizes of the correlation

CC		LCCSD CCSD)	
terms	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$	α	$d_{\rm A}^{ m TPT}$	$d_{ m A}^{ m NSM}$
$DT_{1}^{(1)}$	37.747	4.881	2.960	37.492	4.630	2.774
$T_1^{(0)\dagger} D T_1^{(1)}$	-0.166	0.015	0.007	-0.319	0.005	-3×10^{-4}
$T_2^{(0)\dagger} D T_1^{(1)}$	-3.827	0.248	0.099	-4.166	0.308	0.132
$T_1^{(0)\dagger} D T_2^{(1)}$	-0.052	0.004	0.002	-0.074	0.002	0.001
$T_2^{(0)\dagger} D T_2^{(1)}$	1.380	-0.079	-0.013	1.400	-0.087	-0.014
Others				-0.093	-0.005	-0.001

Table 5.11: Contributions from RCC terms to α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ (with same units as in Table 5.8) from the LCCSD and CCSD methods.

contributions are different for the two cases.

The following conclusions can be drawn from Table 5.8: (i) The lower order RPA effects are appreciable in magnitude and they reduce the MBPT(2) and MBPT(3) results relative to that of the DF values. Their higher order counterparts are collectively large and this is reflected in the final RPA results for our α and EDM calculations. (ii) There are significant cancellations between the all order RPA and the all-order non-RPA contributions at the CCSD level for the EDMs. The inclusion of the non-RPA terms which first appear in MBPT(3) in a perturbative theory framework, is therefore crucial. (iii) There are cancellations between the linear and non-linear CCSD terms for the EDMs. It is, therefore, imperative to use an all order approach like the CCSD method to capture the above mentioned effects. In order to identify which non-RPA diagrams take part in the cancellations, we give a few of these diagrams in Fig. 5.1.1 at the MBPT(3) level and their contributions explicitly in Table 5.10.

The differences in the LCCSD and CCSD results given in Table 5.8 highlight the importance of including the non-linear correlation terms such as $T_1^{(0)}T_2^{(0)}$, $\frac{1}{2}T_2^{(0)}T_2^{(0)}$, \cdots , which correspond to the contributions from higher level excitations such as triples, quadruples, etc. A detailed analysis of our calculations reveal that the role of the non-linear effects are more significant when included in the wave functions rather than in the exponential terms in Eq. 2.1.8. This can be observed from the contributions of the linear CC terms in the LCCSD and CCSD methods in Table 5.11. Results given as "Others" from the CCSD method are the nonlinear contributions from the exponential terms in the expectation value given in Eq. 2.1.8.

Finally, we give the results of our CCSD calculations as our recommended values for ²²³Rn EDMs, i.e. $d_{\rm A}^{\rm TPT} \leq 4.853 \times 10^{-20} \langle \sigma \rangle C_T |e| \, cm$ and $d_{\rm A}^{\rm NSM} \leq$ $2.892 \times 10^{-17} S/(|e| \, fm^3)$. They are both about 9 times larger than the results for ¹²⁹Xe that we had reported recently [158]. Our Schiff moment calculation could be combined with the future measured value of ²²³Rn EDM to give limits for the EDMs and chromo-EDMs of quarks and the θ_{QCD} parameter that would be competitive with those obtained from a few other heavy closed shell atoms. These limits have the potential to provide a wealth of information on new physics beyond the SM. Our ground state polarizability result of the Rn atom will be useful in the context of the EDM studies of ²²³Rn and its experimental verification.

5.1.4 EDM of ²²⁵Ra

In Table 5.12, we present the results for α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ of ²²⁵Ra using our many-body methods. The single particle orbitals are obtained by solving DF equation using the GTOs as the basis functions with universal parameters $\alpha_0 =$ 0.00525 and $\beta = 2.25$. In the above table, for the comparison purpose, we also present the previously reported results from different methods. Among these, calculations using the CI+MBPT method with some corrections from RPA by Dzuba and coworkers [25,164] were presumed to be more rigorous. We have already explained the technique of CI+MBPT method and its merits and demerits while discussing our EDM results for ¹⁹⁹Hg atom. Since this hybrid method do not include the correlation effects from all the electrons in equal footing which is essential for the strongly interacting atom like ²²⁵Ra. In fact, Dzuba and coworkers [25,164] and Latha and Amjith [162] have independently employed RPA with V^N potential to report α , $d_A^{\rm TPT}$ and $d_A^{\rm NSM}$ for this atom. From the above table we can see that the DF and RPA results, among all these calculations, agree quite well with each other. In order to test the potential of

Table 5.12: Comparison of the α , d_A^{TPT} and d_A^{NSM} (with same units as in Table 5.8) results for ²²⁵Ra from various calculations. The CCSD(T) results are the converged values from our calculations and the RPA values for the Breit interaction (δ_B), QED correction (δ_{QED}) and truncated basis (δ_{basis}) are given in the end.

Method of	This work [160]			Others		
Evaluation	α	$d_{\rm A}^{ m TPT}$	$d_{\mathrm{A}}^{\mathrm{NSM}}$	α	$d_{\mathrm{A}}^{\mathrm{TPT}}$	$d_{\mathrm{A}}^{\mathrm{NSM}}$
DF	204.13	-3.46	-1.85	204.2 [25]	-3.5[25]	-1.8 [25]
				$\begin{array}{c} 200.6 \ [162] \\ 293.4^{\circledast} \ [172] \end{array}$		
MBPT(2)	230.67	-11.00	-5.48			
MBPT(3)	189.53	-10.59	-5.30			
RPA	296.85	-16.66	-8.12		-17 [25]	-8.3 [25]
				$291.4 \ [162]$	-16.59 [162]	
				297.0^{\otimes} [164]		-8.5^{\otimes} [164]
CI+MBPT					-18 [25]	-8.8 [25]
				229.9^{\otimes} [164]		
LCCSD	251.88	-13.84	-8.40			
$\mathrm{CCSD}^{(2)}$	253.04	-10.40	-6.94			
$CCSD^{(4)}$	242.02	-9.49	-6.52			
$\mathrm{CCSD}^{(\infty)}$	247.76	-10.04	-6.79	251.8^{*} [172]		
$\operatorname{CCSD}(T)$	241.40	-10.01	-6.79	242.8^{*} [172]		
δ_B	0.19	0.06	0.06			
δ_{QED}	-0.43	-0.16	-0.07			
δ_{basis}	-0.03	-0.08	-0.05			

[®] Corrections from the Gaunt term incorporated.

 $^{\otimes}$ Corrections from RPA included.

the employed many-body methods [25,158,159,164,166,169], α is often evaluated together with d_A and compared with its experimental value owing to their same angular momentum and parity selection criteria required for their determination, notwithstanding their different radial behavior. The α in ²²⁵Ra is yet to be measured, but a few calculations using variants of CC methods report its value among which the latest calculations by Borschevsky *et al.* present DF, CCSD and CCSD(T) results [172] and make comparative analysis with the previous calculations. They use the DC Hamiltonian with the Gaunt term in a finite field approach, and get a large DF value whereas their CC results, as seen in Table 5.12, converges towards a value similar to our CC results.
Table 5.13: Non-RPA contributions through the MBPT(3) diagrams shown in Fig. 5.1.1 along with their exchange parts for α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ (with same units as in Table 5.8).

Contributions	α	$d_{\rm A}^{ m TPT}$	$d_{\rm A}^{ m NSM}$
Diagram (i) Diagram (ii) Diagram (iii)	-52.19 -25.98 -14.77	$2.01 \\ 1.29 \\ 0.49$	$0.97 \\ 0.62 \\ 0.20$

Table 5.14: Individual contributions to α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ (in same units as of Table 5.12) of ²²⁵Ra from various LCCSD, CCSD and CCSD(T) terms. "Extra" correspond to the leftover terms.

Method	$DT_{1}^{(1)}$	$T_1^{(0)\dagger} D T_1^{(1)}$	$T_2^{(0)\dagger} D T_1^{(1)}$	$T_2^{(0)\dagger} D T_2^{(1)}$	Extra	
	(3)					
LCCSD	277.57	-22.09 $\frac{\alpha}{2}$	-30.17	24.17	2.40	
CCSD	273.09	-20.14	-32.83	30.60	-2.96	
CCSD(T)	269.08	-22.60	-30.47	30.19	-2.80	
		$d_{\rm A}^{ m TPT}~(10^{-2}$	$^{20}C_T\langle\sigma_n angle e cm$	n)		
LCCSD	-16.62	0.01	3.54	-0.41	-0.36	
CCSD	-13.37	-0.08	3.32	-0.19	0.28	
CCSD(T)	-13.34	-0.09	3.33	-0.20	0.29	
$d_{\rm A}^{\rm NSM}~(10^{-17}[S/ e fm^3] e cm)$						
LCCSD	-9.37	0.06	1.63	-0.75	0.03	
CCSD	-7.76	0.02	1.59	-0.83	0.19	
CCSD(T)	-7.77	0.02	1.59	-0.83	0.21	



Figure 5.3: Histograms representing for the dominant matrix elements between the 7s and 6p occupied orbitals and the low-lying virtual ms and mp orbitals of ²²⁵Ra, with the corresponding principle quantum number m, to $DT^{(1)}$ of the CCSD(T) method. Plots for (i) α , (ii) the 7s \leftrightarrow mp matrix elements of d_A , and (iii) the 6p \leftrightarrow ms matrix elements of d_A .

We also estimate uncertainties from the neglected effects, such as corrections due to the truncated basis (δ_{basis}), Breit interaction (δ_B) and quantum electrodynamic (QED) effects (δ_{QED}), in our calculations by using RPA in a similar manner as explained while discussing previous EDM results. These values are quoted at the end of Table 5.12. Accounting differences between the CCSD(T) and CCSD results from our calculations as the largest possible contributions from the omitted higher level excitations and the above corrections, we estimate uncertainties in our CCSD(T) to be less than 2%.

The present study also highlights that the behavior of electron correlation effects in ²²⁵Ra is different from the other closed-shell atoms like ¹²⁹Xe [158], ²²³Rn [169] and ¹⁹⁹Hg [159] for the EDM studies. For example, RPA is estimating EDMs within reasonably accuracies in ¹²⁹Xe [158] and ²²³Rn [169] while the CCSD method and the CI+MBPT approach of Dzuba and coworkers give almost similar results for ¹⁹⁹Hg [159]. As seen from Table 5.12, the CCSD(T) values for α , $d_{\rm A}^{\rm TPT}$ and $d_{\rm A}^{\rm NSM}$ distinctly differ by 5% (increased), 45% (reduced) and 23% (reduced), respectively, from the CI+MBPT results in ²²⁵Ra. The main reason for these large differences is because of the contributions from significant non-RPA and core correlation effects in the considered properties. This is apparent from the differences between the MBPT(2) and MBPT(3) results and the LCCSD and CCSD⁽²⁾ results given in Table 5.12, since MBPT(2) corresponds

to the lower order RPA whereas the non-RPA contributions start appearing at MBPT(3). For a quantitative substantiation, we present few important non-RPA contributions (that are depicted diagrammatically in Fig. 5.1.1 from MBPT(3)) in Table 5.13. We also give contributions from the LCCSD, CCSD and CCSD(T)methods in Table 5.14 to affirm about the importance of different electronic configurations in the accurate evaluation of the above properties. As seen, $DT_1^{(1)}$ yields the largest contributions in all the cases alluding to careful inclusion of the singly excitation configurations in the calculations for achieving accurate results in ²²⁵Ra. Nevertheless, doubly excited contributions through $T_2^{(1)}$ are also found to be crucial. Comparing the LCCSD and CCSD(T) results, we observe that singly excitation amplitudes are modulated in the calculation of d_A while the doubly excited amplitudes are altered substantially in the evaluation of α . We also investigate proportionate contributions to $DT^{(1)}$ in the CCSD(T) method from different matrix elements of the P,T-odd interaction Hamiltonians and E1 operator between the core and virtual orbitals using which the dominant contributions to α and d_A are shown by histograms in Fig. 5.3. This clearly exhibits uneven contributions to α , d_A^{TPT} and d_A^{NSM} from different matrix elements between the low-lying orbitals of 225 Ra.

5.2 Limits on Hadronic and Semileptonic P- and T-violating Coupling Coefficients

So far there are only three closed-shell atoms on which EDM measurements have been performed and their reported results are given in Table 1.4. Among those, the most precise measurement is done on ¹⁹⁹Hg atom from which an upper bound on the d_A is extracted as [29] $d_A < 3.1 \times 10^{-29}$. On combining our final results of ¹⁹⁹Hg with the above measurement, we get upper limits on T-PT and NSM coupling constants as [159]

$$S < 1.45 \times 10^{-12} |e| \text{fm}^3 \text{ and } C_T < 2.09 \times 10^{-9}.$$
 (5.2.1)

At present these are the most accurate bounds on these couplings. Using Eq. 1.1.11, it yields $C_P < 5.8 \times 10^{-7}$ and from the relation $S = (1.9d_n + 0.2d_p \text{ fm}^2 [173])$, an upper bound on neutron (d_n) and proton (d_p) EDMs can be extracted as

$$d_n < 7.6 \times 10^{-26} |e| \text{cm} \text{ and } d_p < 7.3 \times 10^{-25} |e| \text{cm}.$$
 (5.2.2)

Although our obtained limit on d_n is not better than the limit obtained directly from the measurement [174], however the limit on d_p is slightly better than the previous value [29].

The next best limit on d_A is obtained from ¹²⁹Xe EDM measurement [38] as $d_A < 4.1 \times 10^{-27} |e|$ cm. This limit in combination with our RCC results for d_A^{TPT} and d_A^{NSM} , we obtain an upper bound on TPT and NSM coupling constants as $C_T < 1.6 \times 10^{-6}$ and $S < 1.2 \times 10^{-9} |e| fm^3$ respectively. These limits are not competitive with the limits extracted from ¹⁹⁹Hg [25, 159, 166], which are about three orders of magnitude lower. However, the experiments on ¹²⁹Xe with advanced experimental techniques [39–41] that are underway have the potential to surpass the current sensitivity by about three to four orders of magnitude. It therefore seems very likely that the best limits for both C_T and S could be obtained by combining our calculated values presented above and the results of the new generation of experiments for ¹²⁹Xe when they come to fruition.

The first EDM measurement on ²²⁵Ra has been recently reported [32] with an upper limit $d_A < 5.0 \times 10^{-22}$. The precision of this measurement is not competitive at this moment against the previous experiments. However with ²²⁵Ra, there are many experimental and theoretical advantages, see Chap. 1, on the basis of which it is expected that there will be a tremendous improvement in the sensitivity of the measurement in near future. If we combine our RCC results with the current limit we obtain an upper bound on NSM coupling constants as $S < 7.4 \times 10^{-6} |e| \text{fm}^3$. Similarly with the knowledge of $\langle \sigma_N \rangle$ in ²²⁵Ra from nuclear calculation, an upper bound on C_T can be predicted.

From Eq. 1.1.25, we find that the NSM can be written in terms of the CP-violating pion-nucleon-nucleon (πnn) coupling constants $\bar{g}_{\pi nn}$ with suitable

parameters (a_i) as given in Chap. 1. In a recent review [24], it has been pointed out that all the nuclear calculations available till date based on different nuclear models for ¹⁹⁹Hg predict different parameters. The calculations disagree with each other not only in magnitudes but in signs also. However as can be seen from Table 1.1, Ref. [24] provides the best value for S in terms of pion-nucleonnucleon (πNN) couplings (\bar{g}_i) as

$$S = 13.5[0.01\bar{g}_0 + (\pm 0.02)\bar{g}_1 + 0.02\bar{g}_2] |e| \text{ fm}^3.$$
 (5.2.3)

Combining this with our limit on S obtained from ¹⁹⁹Hg, we infer bounds as $|\bar{g}_0| < 1.2 \times 10^{-11}$ and $|\bar{g}_1| < 5.6 \times 10^{-12}$. Furthermore, using the relations $\bar{g}_0 = -0.018(7)\bar{\theta}$ [23] and $\bar{g}_1 = 2 \times 10^{-12}(\tilde{d}_u - \tilde{d}_d)$ [30], we extract the upper limit on the combined up- and down- quarks chromo-EDMs as $|\tilde{d}_u - \tilde{d}_d| < 2.8 \times 10^{-26} |e|$ cm and the limit on the strong CP-odd parameter as $|\bar{\theta}| < 1.1 \times 10^{-9}$. In fact, it is also possible to infer more stringent limits on the above quantities from our given limit on S provided the uncertainties in the nuclear calculations are reduced further. Similarly two sophisticated nuclear calculations have been carried out using the octupole deformed Wood-Saxon potential [27] and odd-A Skyrme mean field theory [175] to describe the P,T-odd interactions in ²²⁵Ra in terms of \bar{g}_i . Using the best value from the Table 1.1 for S from these two calculations as [24]

$$S = 13.5[-1.5\bar{g}_0 + 6.0\bar{g}_1 - 4.0\bar{g}_2] |e| \text{ fm}^3, \qquad (5.2.4)$$

where $\bar{g}_{i=0,1,2}$ are the isospin components of the P,T-odd π NN coupling constants. We infer bounds as $|\bar{g}_0| < 3.6 \times 10^{-7}$ and $|\bar{g}_1| < 9.1 \times 10^{-8}$ using the above result with our extracted limit on S. Again from the relations $|\bar{g}_0| = 0.018(7)\theta_{QCD}$ [23] and $|\bar{g}_1| = 2 \times 10^{-12} (\tilde{d}_u - \tilde{d}_d)$ [30], we put the upper limits as $|\theta_{QCD}| < 2.0 \times 10^{-5}$ and $|\tilde{d}_u - \tilde{d}_d| < 4.6 \times 10^{-22} |e|$ cm.

5.3 Summary

To summarize, we present the trends in the electron correlation effects to the calculations of EDMs of ¹²⁹Xe, ¹⁹⁹Hg, ²²³Rn and ²²⁵Ra. Combing our results with the most precise measurement available till date for ¹⁹⁹Hg, we are able to put bounds on NSM and T-PT coupling constant as $S < 1.45 \times 10^{-12} |e| fm^3$ and $C_T < 2.09 \times 10^{-9}$ respectively. Moreover, combining the Schiff moment obtained from our study with the latest nuclear calculation, the upper limits yield on the combined up- and down- quarks chromo-EDMs as $|\tilde{d}_u - \tilde{d}_d| < 2.8 \times 10^{-26} |e| cm$ and on the strong CP-odd parameter as $|\bar{\theta}| < 1.1 \times 10^{-9}$. We also present EDM calculations using CC methods on ¹²⁹Xe, ²²³Rn and ²²⁵Ra atoms. On combining our EDM results with the measurement on 129 Xe and 225 Ra, we also obtain limits on the above mentioned parameters. Though these bounds are not competitive at present against the limits obtained from the ¹⁹⁹Hg EDM study, the limits can become more stringent when our results will be combined with the anticipated improved measurement on ¹²⁹Xe and ²²⁵Ra atoms. Our reported atomic calculations in combination with the upcoming EDM measurements in the considered closed-shell systems involving more advanced experimental techniques would constrain to the values of the above coupling constants further. These limits are certainly very useful and significant to shed lights on new physics beyond the SM of particle physics.

Chapter 6

Conclusion and Future Directions

6.1 Work Summary and Conclusion

The search for the existence of permanent electric dipole moments (EDMs) in composite systems like atoms has a long history [8, 13, 65]. If EDM exists in such systems then it would be a clean signature of violations of both the parity (P) and time-reversal (T) symmetries. In fact, it is a direct test to observe T-violation in nature which also imply CP-violation from the CPT theorem [10]. The most celebrated standard model (SM) of particle physics inherit CP-violation in the form of a complex phase in the Cabibbo-Kobayashi-Maskawa (CKM) matrix that mixes different flavors of quarks. The observed CP-violation in the decays of neutral K [3] and B [4-6] mesons are well within the predictions of the SM. However, CKM mechanism is insufficient to account for the observed baryon asymmetry of the Universe. Therefore, searches for new sources of CP-violation are of profound interest. In the atomic systems the major contributor to EDMs are the P- and T-violating (P,T-odd) interactions among the constituent particles. Thus, studying atomic EDMs would provide a powerful probe to search for the CP-violation emanating from the leptonic, semileptonic, and hadronic CP sources. In this thesis, we focused on the EDMs of the closed-shell (diamagnetic) atoms, which predominantly arise from the P- and T-violating electron-nucleus (e-N) tensor-

pseudotensor (T-PT) and the interactions of nuclear Schiff moment (NSM) with the atomic electrons [12]. In order to estimate the strengths of the couplings associated with these interactions, we not only require precise EDM measurements but also reliable theoretical calculations. Further, at the fundamental level, NSM can be linked with the strong CP parameter $\bar{\theta}$ and (chromo)-EDMs of quarks [23, 24, 30]. Therefore, accurate knowledge of NSM can be very helpful to gain information on the above mentioned parameters. Till date, there are only three systems on which EDM measurement have been reported so far (see Table 1.4). Among which, measurement by Griffith *et al.* yields the best upper limit to the ¹⁹⁹Hg EDM as $d_{\rm A}(^{199}\text{Hg}) < 3.1 \times 10^{-29} |e|$ cm with 95% confidence level [29]. Advanced experimental techniques have been proposed for the other diamagnetic atoms, particularly ¹²⁹Xe, with the expectations to improve the sensitivity of the measurement by a few orders in magnitude [39–41]. Recently a research group at Argonne National Laboratory (ANL) [32] reported their first EDM measurement on ²²⁵Ra atom. Though, their obtained limit is not competitive with the other earlier EDM measurements but their experiment has a potential to surpass the sensitivity of the Hg EDM experiment.

We have developed a variety of relativistic many-body methods to compute the dipole polarizabilities (α s) and the EDMs of many closed-shell (diamagnetic) atomic systems. Our methods include third-order many-body perturbation theory (MBPT(3) method), random phase approximation (RPA) and relativistic coupled-cluster (RCC) theory considering singles and doubles approximation at the linearized (LCCSD method) and non-linearized (CCSD method) levels. In order to achieve better accuracies in our CCSD results, we have included contributions from a set of leading order triple excitations in both the unperturbed (CCSD(T) method) and perturbed (CCSD_pT method) RCC equations. We first verified the potential of the above many-body methods by evaluating α s of many closed-shell atoms and ions belonging to, alkali, alkaline and noble gas earth elements [90]. We also highlight about the crucial roles of the electron correlation effects to reproduce the experimental result by presenting and comparing the results at different levels of approximations. Correlation trends among the neutral atoms, singly and doubly charged ions are presented. In addition to that, we also employed our methods to evaluate α s of the boron, carbon, and zinc homologous sequences of elements [91]. We find a divergent patterns in the behavior of the electron correlation effects with respect to the mean-field level of calculations in the individual iso-electronic systems through a particular employed many-body method. Also, our calculations revel that the RPA and LCCSD methods generally overestimate α . The large value of RPA result is due to the absence of certain non-RPA diagrams as shown in Fig. 5.1.1 which contribute significantly with negative signs. However, in the LCCSD method similar to RPA certain negatively contributing diagrams are absent such as diagram (i) in Fig. 5.1.1. These absent diagrams are very important in achieving high accuracies in results. We also report contributions from few of those diagrams from the MBPT(3)method to ascertain our findings. In other words, both the core-polarization and pair-correlation effects to all-orders are equally important for achieving high accuracies in α in the considered systems and the core-polarization effects play the important role among them. Contributions from the doubly excited states are found to be non-negligible implying that a sum-over-states approach may not be pertinent to carry out these studies. Our results obtained using the CCSD(T) and $CCSD_nT$ methods agree very well with the available experimental values in some of the systems except for Cd. In few systems, there are no experimental results available in the literature and the reported accurate values in the present work can be served as benchmarks for their prospective measurements.

The evaluation of α and EDM share similar angular momentum and parity selection criteria despite of fact that their radial dependencies are different. After successfully testing our many-body methods for α , we evaluated EDMs due to NSM and T-PT i interactions of the closed-shell atoms, ¹²⁹Xe, ¹⁹⁹Hg, ²²³Rn and ²²⁵Ra whose experiments are currently under consideration. On combining our ¹⁹⁹Hg EDM results with the most precise measurement till date, we were able to put accurate bounds on NSM and T-PT coupling constants as $S < 1.45 \times$ $10^{-12}|e|fm^3$ and $C_T < 2.09 \times 10^{-9}$ respectively [159]. We also combined our obtained limit on S with the latest nuclear structure calculations [23] to get an upper bound on combined up- and down- quarks chromo-EDMs as $|\tilde{d}_u - \tilde{d}_u|$ $\tilde{d}_d| < 2.8 \times 10^{-26} |e|$ cm and on the strong CP-odd parameter as $|\bar{\theta}| < 1.1 \times 10^{-9}$ [159]. These are the most reliable calculations at the moment which accounts the electron correlation effects more rigorously. Further, we also present the first EDM calculations using our CC methods for ¹²⁹Xe, ²²³Rn and ²²⁵Ra atoms [158, 160, 169]. The limits obtained on combining our EDM results for ¹²⁹Xe and ²²⁵Ra with their respective measurements are not competitive against the limit obtained from Hg atom [158, 160]. However, ongoing efforts to improve the precisions in the EDM experiments particularly on 129 Xe and 225 Ra are very promising. It therefore seems very likely that the best limits on the couplings associated with T-PT and NSM interactions could be obtained by combining our EDM results presented in this thesis with the results of the new generations of experiments for 129 Xe and 225 Ra when they come to fruition. Now from the nuclear physics point of view, it has now become absolutely necessary to improve the nuclear calculations for the NSM which are varying not only in magnitudes but also in signs [24]. Accurate knowledge of NSMs from the nuclear physics can be combined with the limits on S obtained above to put stringent bounds on the strong CP parameter, EDMs and chromo-EDMs of quarks. The origin of the above mentioned P,T-odd couplings are not accounted in the Standard Model (SM) of particle physics. Therefore, accurate information of the above couplings can definitely shed light on beyond-SM particle physics theories that predict new sources of CP-violations.

6.2 Future Directions

The improvement in our CC calculations can be enhanced further by considering full triple, quadrupole etc. excitations, but it demands for huge computational resources. Even CCSD method for a heavy system like Ra with sufficient number of basis generates large number of integrals associated with the Coulomb and additional interactions which not only consumes lots of memory but also computational time. Such issues with memory and computational time can be reduced by implementing group parallelization techniques and by using a string based algorithm to handle higher levels of excitations [176]. One of the main shortcomings of our employed CCSD method comes at the property level where we encounter with an infinite series. To address this issue at the same level of approximation, a normal couple-cluster (NCC) theory would be appropriate [177,178]. In NCC, ket and bra states are parametrized independently due to which they loss their hermitian adjoint relationship but it has many advantages such as: (i) they lead to explicit expectation value of the functional (here dipole operator D) [178], (ii) they are compatible with Hellmann-Feynman theorem [179] and (iii) they are derivable from variational principle.

6.3 NCC Theory

In the NCC theory the ket state is defined by the same ansatz as described in our usual CC theory, whereas, the bra state is parametrized by two different operators. In the NCC model, the ket and the bra states are defined as

$$|\Psi\rangle = e^T |\Phi_0\rangle$$
 and $\langle \tilde{\Psi} | = \langle \Phi_0 | (1+\Lambda)e^{-T},$ (6.3.1)

such that $\langle \tilde{\Psi} | \Psi \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1$ and Λ is the de-excitation operator. The Schrödinger's equation for the bra state is given by

$$\langle \Phi_0 | (1+\Lambda) e^{-T} (H_{\rm DC} + \lambda H_{\rm int}) = \langle \Phi_0 | (1+\Lambda) e^{-T} E.$$
 (6.3.2)

On multiplying e^T from right hand side and considering $H_{DC} = H_N + E_{DF}$, one get

$$\langle \Phi_0 | (1+\Lambda) e^{-T} (H_{\rm N} + \lambda H_{\rm int}) e^T = \langle \Phi_0 | (1+\Lambda) \Delta E_{\rm corr} \\ \langle \Phi_0 | (1+\Lambda) ((H_{\rm N} e^T)_{\rm conn} + \lambda (H_{\rm int} e^T)_{\rm conn}) = \Delta E_{\rm corr} \langle \Phi_0 | (1+\Lambda).$$
(6.3.3)

In order to obtain unperturbed and perturbed amplitude equations, one can split Λ operator as $\Lambda = \Lambda^{(0)} + \lambda \Lambda^{(1)}$ just like $T = T^{(0)} + \lambda T^{(1)}$. In the unperturbed case,

 $\lambda = 0$ and on projecting singly and doubly excited configurations with respect to the reference state $|\Phi_0\rangle$ from right, we get unperturbed amplitude equations as

$$\langle \Phi_0 | \Lambda^{(0)} \overline{H}_N | \Phi_a^p \rangle = -\langle \Phi_0 | \overline{H}_N | \Phi_a^p \rangle$$

$$\langle \Phi_0 | \Lambda^{(0)} \overline{H}_N | \Phi_{ab}^{pq} \rangle = -\langle \Phi_0 | \overline{H}_N | \Phi_{ab}^{pq} \rangle, \qquad (6.3.4)$$

where $\overline{H}_N = (H_N e^{T^{(0)}})_{\text{conn}}$. To consider the first order effect, one can take only terms with λ^1 and get the singles and doubles amplitude equations for operator $\Lambda^{(1)}$ as

$$\langle \Phi_0 | \Lambda^{(1)} \overline{H}_N | \Phi_a^p \rangle = -\langle \Phi_0 | \overline{H}_N T^{(1)} + \overline{H}_{int} + \Lambda^{(0)} \overline{H}_N T^{(1)} + \Lambda^{(0)} \overline{H}_{int} | \Phi_a^p \rangle$$
$$\langle \Phi_0 | \Lambda^{(1)} \overline{H}_N | \Phi_{ab}^{pq} \rangle = -\langle \Phi_0 | \overline{H}_N T^{(1)} + \overline{H}_{int} + \Lambda^{(0)} \overline{H}_N T^{(1)} + \Lambda^{(0)} \overline{H}_{int} | \Phi_{ab}^{pq} \rangle.$$
(6.3.5)

After obtaining amplitudes associated with the T operators using our usual RCC method one can then make use of Eqs. 6.3.4 and 6.3.5 to evaluate the amplitudes of $\Lambda^{(0)}$ and $\Lambda^{(1)}$ operators respectively.

The atomic EDM (d_A) is the expectation value of the dipole operator D which in the NCC framework is given by

$$d_{\rm A} = \frac{\langle \tilde{\Psi} | D | \Psi \rangle}{\langle \tilde{\Psi} | \Psi \rangle} = \langle \Phi_0 | (1 + \Lambda) e^{-T} D e^T | \Phi_0 \rangle.$$
(6.3.6)

The above series terminates automatically with finite number of terms and the normalization factor is equal to one here. Due to the presence of de-excitation operators, the number of terms in the property evaluations are finite. Therefore, with this method one can gain considerably in the accuracies of the considered properties as compared to our usual RCC method.

Appendix A

Atomic Units

Atomic units (au or a.u.) form a system of natural units in which fundamental physical constants e(electronic charge), \hbar (reduced Planks constant), m_e (mass of electron) and $\frac{1}{4\pi\epsilon_0}$ (permittivity of free space) become unity by definition i.e.

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1. \tag{A.0.1}$$

Atomic unit	SI value	Name (symbol)
(base units)		
Mass (m_e)	$9.10938291 \times 10^{31} \text{ kg}$	Mass of electron
Charge (e)	$1.602176565(35) \times 10^{19} \mathrm{C}$	Electronic Charge
Angular Momentum (\hbar)	$1.054571726(47) \times 10^{19} J.s$	Planck's constant/ 2π
Energy $(m_e e^4/\hbar^2)$	$4.35974417(75) \times 10^{19} J$	Hartree (H)
Length $(\hbar^2/m_e e^2)$	$5.2917721092(17) \times 10^{11} \mathrm{m}$	Bohr radius (a_0)
Speed of light $(1/\alpha)$	≈ 137	Fine structure constant inverse
Time $(\hbar^3/m_e e^4)$	$2.418884326505(16) \times 10^{17} s$	Jiffy
EDM $(\hbar^2/m_e e)$	$8.47835326(19) \times 10^{30}$ C.m	2.541765 Debye (D) units
MDM $(e\hbar/2m_e)$	$9.27402 \times 10^{24} \text{ J/T}$	Bohr magneton (μ_B)

Table A.1: Conversion Factors from Atomic to S.I Units

 Table A.2: Frequently used Physical Constants and their Numerical Values.

Speed of light (c)	$299\ 792\ 458\ m/s$
Planck's constant (h)	$6.626\ 069\ 57(29) \times 10^{34}\ J.s$
Planck's constant, reduced (\hbar)	$1.054571726(47) \times 10^{34} J.s$
Fermi coupling constant $(G_F/(\hbar c)^3)$	$1.166 \ 378 \ 7(6) \times 10^5 \ \mathrm{GeV}^{-2}$
	2.22×10^{14} a.u

Joule	$kJ.mol^{-1}$	${ m eV}$	a.u.	\mathbf{cm}^{-1}	Hz
1 Joule=1	6.022×10^{18}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{33}
$1 \text{ kJ.mol}^{-1} = 1.661 \times 10^{-21}$	1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
$1 \text{ eV} = 1.602 \times 10^{-19}$	96.48	1	3.675×10^{-2}	8065	2.418×10^{14}
1 a.u. = 4.359×10^{-18}	2625	27.21	1	2.195×10^5	6.580×10^{15}
$\begin{array}{c} 1 \ \mathbf{cm}^{-1} \\ = 1.986 \times 10^{-23} \end{array}$	1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1	2.998×10^{10}
$ \begin{array}{c} 1 \text{ Hz} \\ = 6.626 \times 10^{-34} \end{array} $	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

Table A.3: The conversion factors for energies in different units.

Appendix B

Dirac Matrices

The Dirac matrices α_i and β , where i = 1, 2, 3 in the 2 × 2 format are given by

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{B.0.1}$$

with

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (B.0.2)$$

These matrices satisfy the following anti-commutation relations

$$\{\alpha_i, \alpha_j\} = 0, \quad \{\alpha_i, \beta\} = 0 \quad \text{with} \quad \alpha_i^2 = \beta^2 = 1.$$
 (B.0.3)

The Dirac and the gamma matrices are related to each other by the relations

$$\gamma_i = \beta \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix}$$
 and $\gamma_0 = \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$, (B.0.4)

such that the commutation and anti-commutation relations of γ matrices are given by

$$\{\gamma_{\mu}, \gamma_{\nu}\} = 2g_{\mu,\nu}I \quad \text{and} \quad \frac{i}{2}[\gamma_{\mu}, \gamma_{\nu}] = \sigma_{\mu\nu}, \tag{B.0.5}$$

where I is an identity matrix, indices μ, ν runs as 0,1,2,3 and $g_{\mu\nu}$ is the Minkowski metric. In addition to above, we also have another metric γ_5 which is defined as

$$\gamma_5 = i\gamma_0\gamma_1\gamma_2\gamma_3 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}, \tag{B.0.6}$$

with the following relations

$$\{\gamma_5, \gamma_\mu\} = 0$$
 and $\gamma_5^2 = I.$ (B.0.7)

In the non-relativistic representation gamma matrices are given by

$$\gamma_i = \begin{pmatrix} 0 & -i\sigma_i \\ i\sigma_i & 0 \end{pmatrix}, \quad \gamma_0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \text{ and } \gamma_5 = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}.$$
 (B.0.8)

Appendix C

Matrix Elements of EDM Interaction Hamiltonians

C.1 Matrix element of $H_{\text{int}}^{\text{TPT}}$

The electron-nucleus P,T-odd tensor-pseudotensor (T-PT) interaction Hamiltonian is given by

$$H_{\rm int}^{\rm TPT} = i2\sqrt{2}G_F C_T \langle I \rangle \gamma \rho(r). \qquad (C.1.1)$$

Ignoring the constant term form the $H_{\text{int}}^{\text{TPT}}$ and considering z-axis as the axis of quantization, the single particle matrix element of the above interaction Hamiltonians given by

$$\langle \phi_a | H_{\text{int}}^{TPT} | \phi_b \rangle = \langle \phi_a | i \gamma_z \rho(r) | \phi_b \rangle.$$
 (C.1.2)

where $|\phi_a\rangle$ and $\phi_b\rangle$ are the single particle wave functions of the considered atomic system. In the position basis, the wave functions $|\phi_a\rangle$ and $|\phi_b\rangle$ can be represented in the two component Dirac wave function as

$$\phi_a(r) = \frac{1}{r} \begin{pmatrix} P_a(r)\chi_{\kappa_a,m_a}(\theta,\phi) \\ iQ_a(r)\chi_{-\kappa_a,m_a}(\theta,\phi), \end{pmatrix}$$
(C.1.3)

and

$$\phi_b(r) = \frac{1}{r} \begin{pmatrix} P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi) \\ iQ_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi), \end{pmatrix}$$
(C.1.4)

where P(r) and Q(r) are the large and small components of the radial wave functions, $\chi_{\kappa,m}(\theta,\phi)$ s are the angular functions with the relativistic quantum number $\kappa = -(j + 1/2)a$ and $l = j - \frac{1}{2}a$, where $a = \pm 1$ [45] Considering the above Dirac wave functions and $\gamma_z = \begin{pmatrix} 0 & \sigma_z \\ -\sigma_z & 0 \end{pmatrix}$ in Eq.C.1.2 we get

$$\langle \phi_a | H_{\text{int}}^{\text{TPT}} | \phi_b \rangle = \int \frac{1}{r^2} \left(P_a(r) \chi_{\kappa_a, m_a}^{\dagger}(\theta, \phi) - iQ_a(r) \chi_{-\kappa_a, m_a}^{\dagger}(\theta, \phi) \right)$$

$$\begin{pmatrix} 0 & \sigma_z \\ -\sigma_z & 0 \end{pmatrix} \begin{pmatrix} P_b(r) \chi_{\kappa_b, m_b}(\theta, \phi) \\ iQ_b(r) \chi_{-\kappa_b, m_b}(\theta, \phi) \end{pmatrix} i\rho(r) r^2 dr d\Omega$$

$$= \int \left(P_a(r) \chi_{\kappa_a, m_a}^{\dagger}(\theta, \phi) - iQ_a(r) \chi_{-\kappa_a, m_a}^{\dagger}(\theta, \phi) \right) \begin{pmatrix} i\sigma_z Q_b(r) \chi_{-\kappa_b, m_b}(\theta, \phi) \\ -\sigma_z P_b(r) \chi_{\kappa_b, m_b}(\theta, \phi) \end{pmatrix}$$

$$\times i\rho(r) dr d\Omega$$

$$= -\int ([P_a(r)\chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi)\sigma_z Q_b(r)\chi_{-\kappa_b,m_b}(\theta,\phi)] + [Q_a(r)\chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi)\sigma_z P_b(r)\chi_{\kappa_b,m_b}(\theta,\phi)]) \times \rho(r)drd\Omega.$$

On separating the radial and the spin integral part, the above equation can be rewritten as

$$\begin{aligned} \langle \phi_a | H_{\text{int}}^{\text{TPT}} | \phi_b \rangle &= -\int P_a(r) Q_b(r) \rho(r) dr \int \chi^{\dagger}_{\kappa_a, m_a}(\theta, \phi) \sigma_z \chi_{-\kappa_b, m_b}(\theta, \phi) d\Omega \\ &- \int Q_a(r) P_b(r) \rho(r) dr \int \chi^{\dagger}_{-\kappa_a, m_a}(\theta, \phi) \sigma_z \chi_{\kappa_b, m_b}(\theta, \phi) d\Omega. \end{aligned}$$

Now using the Wigner Eckart theorem the above equation can be written as a product of Clebsch-Gordan coefficient and the m independent reduced matrix

element [7]. The reduced matrix element for $H_{\rm int}^{\rm TPT}$ is given by

$$\begin{aligned} \langle \phi_a || H_{\text{int}}^{\text{TPT}} || \phi_b \rangle &= -\int \rho(r) dr [P_a(r) Q_b(r) \langle \kappa_a || \sigma_z || - \kappa_b \rangle \\ &+ Q_a(r) P_b(r) \langle -\kappa_a || \sigma_z || \kappa_b \rangle], \end{aligned}$$

where the general expression of the reduced matrix element of σ is given by

$$\langle \kappa_a ||\sigma||\kappa_b \rangle = \delta_{l_a l_b} (-1)^{(l_a + j_a - 1/2)} \sqrt{[j_a, j_b]} \sqrt{6} \begin{cases} 1 & j_a & j_b \\ l_a & 1/2 & 1/2 \end{cases}.$$
(C.1.5)

C.2 Matrix element of $H_{\text{int}}^{\text{NSM}}$

The P,T-odd interaction between the nuclear Schiff moment (NSM) and the atomic electrons is given by the following Hamiltonian

$$H_{\text{int}}^{\text{NSM}} = 3\frac{\mathbf{S.r}}{B_4}\rho(r). \qquad (C.2.1)$$

The single particle matrix element of the $H_{\rm int}^{\rm NSM}$ between the states $|\phi_a\rangle$ and $|\phi_b\rangle$ is given by

$$\langle \phi_a | H_{\text{int}}^{\text{NSM}} | \phi_b \rangle = 3 \frac{S}{B_4} \langle \phi_a | \mathbf{r} \rho(r) | \phi_b \rangle.$$
 (C.2.2)

Considering the above Dirac wave functions given in Eqs. C.1.3 and C.1.4 in Eq.C.2.2 we get

$$\begin{split} \langle \phi_a | H_{\text{int}}^{\text{NSM}} | \phi_b \rangle &= 3 \frac{S}{B_4} \int \frac{1}{r^2} \left(P_a(r) \chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi) - iQ_a(r) \chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi) \right) \\ & r C_1(\theta,\phi) \rho(r) \begin{pmatrix} P_b(r) \chi_{\kappa_b,m_b}(\theta,\phi) \\ iQ_b(r) \chi_{-\kappa_b,m_b}(\theta,\phi) \end{pmatrix} r^2 dr d\Omega \\ &= 3 \frac{S}{B_4} \int ([P_a(r) \chi^{\dagger}_{\kappa_a,m_a}(\theta,\phi) C_1(\theta,\phi) P_b(r) \chi_{\kappa_b,m_b}(\theta,\phi)] \\ & + [Q_a(r) \chi^{\dagger}_{-\kappa_a,m_a}(\theta,\phi) C_1(\theta,\phi) Q_b(r) \chi_{-\kappa_b,m_b}(\theta,\phi)]) \times r \rho(r) dr d\Omega \end{split}$$

On separating the radial and spin integral parts, the above equation reduce to

$$\begin{split} \langle \phi_a | H_{\text{int}}^{NSM} | \phi_b \rangle &= 3 \frac{S}{B_4} \int dr r \rho(r) [P_a(r) P_b(r) + Q_a(r) Q_b(r)] \\ & \times \int d\Omega \chi^{\dagger}_{\kappa_a, m_a}(\theta, \phi) C_1(\theta, \phi) \chi_{\kappa_b, m_b}(\theta, \phi). \end{split}$$

Again, using the Wigner-Eckart theorem the above matrix element can be written as a product of Clebsch-Gordan coefficient and the m independent reduced matrix element [7]. The reduced matrix element of the above interaction Hamiltonian is given by

$$\langle \phi_a || H_{\text{int}}^{\text{NSM}} || \phi_b \rangle = 3 \frac{S}{B_4} \langle \kappa_a || C_1 || \kappa_b \rangle \int r \rho(r) [P_a(r) P_b(r) + Q_a(r) Q_b(r)] dr$$

The general expression for the reduced matrix element of C_1 tensor is given in Eq. C.1.5

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Publications attached with the thesis

- Correlation trends in the ground-state static electric dipole polarizabilities of closed-shell atoms and ions,
 Yashpal Singh, B. K. Sahoo and B. P. Das, Phys. Rev. A 88, 062504 (2013).
- Correlation trends in the polarizabilities of atoms and ions in the boron, carbon, and zinc homologous sequences of elements,
 Yashpal Singh and B. K. Sahoo, Phys. Rev. A 90, 022511 (2014).
- Ab initio determination of the P- and T-violating coupling constants in atomic Xe by the relativistic-coupled-cluster method,
 Yashpal Singh, B. K. Sahoo and B. P. Das, Phys. Rev. A 89, 030502(R) (2014).
- 4. Rigorous limits on the hadronic and semi-leptonic CP-violating coupling constants from the electric dipole moment of ¹⁹⁹Hg,
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