## 

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

by

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Under the guidance of

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## Declaration

I hereby declare that this PhD thesis titled "Application of Relativistic Coupled-Cluster Method to Study  $\mathcal{P}, \mathcal{T}$ -odd Properties in Heavy and Superheavy Molecules" is carried out by me to fulfil the requirement of PhD degree at *Atomic, Molecular and Optical Physics Division* under the supervision of Prof. Bijaya Kumar Sahoo. All information and facts provided in this thesis are correct to the best of my knowledge. I also declare that wherever I have borrowed any ideas or results of someone else, I have properly cited to the original sources. No part of this thesis has formed the basis for award of any other degree in any university or institution.

Signature: Ramanuj Mitra IITGN Roll No: 17330024 AMOPH Division Physical Research laboratory, Ahmedabad. India Date: 29 July, 2022

# Certificate

It is certified that the work contained in this thesis titled "Application of Relativistic Coupled-Cluster Method to Study  $\mathcal{P}, \mathcal{T}$ -odd Properties in Heavy and Superheavy Molecules", submitted by Ramanuj Mitra (Roll No. 17330024) to the Indian Institute of Technology Gandhinagar, is a record of bona fide research work carried out under my supervision and has not been submitted elsewhere for a degree. I have read this dissertation and in my opinion, it is fully adequate, in scope and quality, for the degree of Doctor of Philosophy.

Signature: Prof. Bijaya Kumar Sahoo AMOPH Division Physical Research laboratory, Ahmedabad. India Date: 29 July, 2022

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# List of publications

#### A. <u>Included in thesis</u>:

1 "Comparative analysis of nonrelativistic and relativistic calculations of electric dipole moments and polarizabilities of heteronuclear alkali-metal dimers", **R. Mitra**, V. S. Prasannaa, and B. K. Sahoo, Phys. Rev. A **101**, 012511 (2020).

2 "Study of HgOH to assess its suitability for electron electric dipole moment mearches", **R. Mitra**, V. S. Prasannaa, B. K. Sahoo, N. R. Hutzler, M. Abe, and B. P. Das, Atoms **9**, 7 (2021).

3 "Towards *CP*-violation studies on superheavy molecules: Theoretical and experimental perspectives ", **R. Mitra**, V. S. Prasannaa, R. F. Garcia Ruiz, T. K. Sato, M. Abe, Y. Sakemi, B. P. Das, and B. K. Sahoo, Phys. Rev. A **104**, 062801 (2021).

4 "Electric dipole moments and static dipole polarizabilities of alkali–alkaline-earth molecules: non-relativistic versus relativistic coupled-cluster theory analyses", R. Mitra, B. K. Sahoo, and V. S. Prasannaa, Phys. Rev. A 105, 062811 (2022).

#### B. <u>Not included in thesis</u>:

5 "Reappraisal of P, T-odd parameters from the improved calculation of electric dipole moment of <sup>225</sup>Ra atom ", V. S. Prasannaa, **R. Mitra** and B. K. Sahoo, J. Phys. B **53**, 195004 (2020).

# Contents

1	Intr	oduction	1
	1.1	Electric dipole moment (EDM) of a system	1
	1.2	P, T-odd phenomena and EDM of a system	3
	1.3	General features of elementary particle physics	8
	1.4	The SM and BSM sources to the eEDM	10
	1.5	Molecules for eEDM searches	11
	1.6	Current limits on eEDM from molecular studies	12
	1.7	Manifestation of eEDM in molecules	12
	1.8	Typical principles of molecular EDM experiments	14
	1.9	Criteria for searching suitable molecules for eEDM searches	17
	1.10	The eEDM and matter-antimatter asymmetry	19
	1.11	Nucleus-electron scalar-pseudoscalar interaction	20
	1.12	Motivation of the work	21
	1.13	Outline of thesis	22
2	Mol	ecular Many-Body Theory	29
	2.1	Introduction	29
	2.2	Born-Oppenheimer approximation	30
	2.3	Challenges involved with $H_e^{BO}$	32
	2.4	Variational method	36
	2.5	The HF method	37
		2.5.1 Roothaan's equation	41

	2.6	The DF method	45
	2.7	Kinetic balance condition	50
		2.7.1 Brillouin's theorem	52
	2.8	Electron correlation effects	53
	2.9	Many-body perturbation theory	54
	2.10	CI method	55
	2.11	The (R)CC method	57
		2.11.1 The BCH expansion formula	60
		2.11.2 The LCT	62
		2.11.3 (R)CC energy and amplitude equations	67
		2.11.4 CC energy and amplitudes in singles and doubles approximation	67
		2.11.5 CC expectation value expression	71
		2.11.6 Truncated CC vs CI methods	72
		2.11.7 Comparison between the CC and MBPT methods	76
3	PDI	Ms and Static Electric Dipole Polarizabilities of Alkali-Dimers	81
	3.1	Introduction	81
	3.2	Theory and methodology	87
	3.3	Results and discussion	89
		3.3.1 Results for PDMs	90
		3.3.2 Results for polarizabilities	96
		3.3.3 Importance of relativistic effects	106
1	וחס	Ms and Static Floctric Dipole Polarizabilities of Open Shell Alkali-Alkaline	
4	For	th Moloculos	- 191
	<b>La</b>	Introduction	121
	4.1	Methodology	121
	4.2	Regulta and diagonation	120
	4.3	4.2.1   Deculta for DDMa	128
		4.0.1 Results for relaxizabilities	128
		4.3.2 Results for polarizabilities	131
		4.3.3 Reliability tests of the results	132

		4.3.4 A simple empirical relation between PDM and average polarizability	137
		4.3.5 Recommended values	143
5	Tria	atomic HgOH Molecule for EDM Study	147
	5.1	Introduction	147
	5.2	Why triatomic molecules?	148
	5.3	Theory	150
	5.4	Ground state geometry optimization	151
	5.5	Method of calculation	151
	5.6	Results and discussion	152
		5.6.1 Other prospective polyatomic molecules for EDM measurements	160
6	The	poretical and Experimental Perspectives of Superheavy Distomic Melecule	
		corectical and Experimental Perspectives of Superneavy Diatomic Molecule	S
	for	Probing eEDMs	es 167
	<b>for</b> 6.1	Probing eEDMs Introduction	<b>167</b> 167
	for 6.1 6.2	Probing eEDMs         Introduction	<b>167</b> 167 167
	for 6.1 6.2 6.3	Probing eEDMs         Introduction         Why superheavy systems?         Lr containing molecules	<b>167</b> 167 167 168
	for 6.1 6.2 6.3 6.4	Probing eEDMs         Introduction         Why superheavy systems?         Lr containing molecules         Theoretical aspects	<b>167</b> 167 167 168 169
	for 6.1 6.2 6.3 6.4 6.5	Probing eEDMs         Introduction         Why superheavy systems?         Lr containing molecules         Theoretical aspects         Method of calculation	<b>167</b> 167 167 168 169 171
	for 6.1 6.2 6.3 6.4 6.5 6.6	Probing eEDMs         Introduction         Why superheavy systems?         Lr containing molecules         Theoretical aspects         Method of calculation         Results and discussion	<b>167</b> 167 167 167 168 169 171 171
7	for 6.1 6.2 6.3 6.4 6.5 6.6 Sum	Probing eEDMs         Introduction         Why superheavy systems?         Lr containing molecules         Theoretical aspects         Method of calculation         Results and discussion         nmary and Outlook	<ul> <li>167</li> <li>167</li> <li>167</li> <li>168</li> <li>169</li> <li>171</li> <li>171</li> <li>187</li> </ul>

## List of Figures

- 1.1 Tree-level and loop-level (1-, 2-, 3-, and 4- loop) diagrams representing electroweak interactions in the SM. As can be seen, the first non-zero contribution to eEDM arises at the 4-loop level electroweak diagram of the SM.
  10
- 3.2 Plots comparing the CCSD(T) and RCCSD(T) values of μ (in a.u.) for the heteronuclear alkali dimers belonging to the (a) Li-, (b) Na-, (c) K-, (d) Rb-, and (e) Cs-families against the atomic number Z<sub>A</sub>.
  96
- 3.3 Graphs illustrating the differences between the CCSD(T) and RCCSD(T) values of the parallel components of polarizabilities (in a.u.) of (a) Li-, (b) Na-, (c) K-, (d) Rb-, and (e) Cs-families of heteronuclear alkali dimers against the atomic number  $Z_A$ .

97

3.4	Graphs showing the departure between the values of perpendicular components of	
	polarizabilities (in a.u.) obtained from the $CCSD(1)$ and $RCCSD(1)$ calculations of different families of beterenueleer alkeli dimers. The sub-figures (a) shows the	
	of different families of neteronuclear arkan different. The sub-figures (a) shows the transfer in the Li fermilie milit $(h)$ $(e)$ $(d)$ and $(e)$ compared to Ne IV. Discussion	
	trends in the Li family, while (b), (c), (d), and (e) correspond to Na, K, Rb, and	0.0
	Cs families, respectively.	98
3.5	Plots depicting the fork between the average dipole polarizabilities (in a.u.) in	
	the (a) Li-, (b) Na-, (c) K-, (d) Rb-, and Cs-families from the CCSD(T) and	
	RCCSD(T) methods.	99
3.6	Plots highlighting the variation of relativistic effects in the polarizability aniso-	
	tropies (in a.u.) of the heteronuclear alkali dimers belonging to (a) Li-, (b) Na-,	
	(c) K-, (d) Rb-, and (e) Cs-families using the $CCSD(T)$ and $RCCSD(T)$ methods.	100
3.7	The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ (commonly denoted by X, and given in a.u.) are plotted	
	against volume (in a.u.). In the legend, 'NR' refers to the CCSD(T) results while	
	'Rel' denotes to the $\operatorname{RCCSD}(T)$ values	101
4.1	Plots demonstrating relative percentage changes in the values of $\mu$ in the Alk-AlkE	
	molecules due to (a) the electron correlation effects ( $\delta_{\mu}^{corr}$ ) and (b) the relativistic	
	effects $(\delta_{\mu}^{rel})$ through the four-component spinfree Hamiltonian in the RCCSD(T)	
	method. The x-axis shows atomic number of the alkaline-earth atoms	125
4.2	Schematic figures showing relative percentage changes in (a) the $\bar{\alpha}$ values and (b)	
	the $\Delta \alpha$ values of the Alk-AlkE molecules due to the electron correlation effects at	
	the RCCSD(T) method. The values in y-axis are given in % while x-axis shows	

- atomic number of the alkaline-earth atom for a given alkali atom family. . . . . 129
- 4.3 Schematic figures showing relative percentage changes in (a)  $\delta_{\bar{\alpha}}^{rel}$ , and (b)  $\delta_{\Delta\alpha}^{rel}$  in the Alk-AlkE molecules using the RCCSD(T) method. The x-axis provides atomic number of the alkaline-earth atom, as in the previous figure. . . . . . . 130

- 4.4(a) Plot showing the agreement between average polarizabilities calculated using the RCCSD(T) method (in blue) and our empirical relation (in red). The dominant part of the empirical relation is shown in green. We find that the red and the blue curves agree to within 10 percent for each of the points, whereas the green curve deviates from the blue one for heavier systems. The shaded background regions have been given to distinguish between families. Sub-figures (b) and (c) show the same plots, but for alkali-alkali molecules and alkaline-earth-monofluorides, respectively. The RCCSD(T) values of PDM and  $\bar{\alpha}$  given in sub-figure (b) were taken from our previous work [19], whereas the ab initio values of PDM and  $\bar{\alpha}$  in sub-figure (c) were taken from Ref. [20] and Ref. [21], respectively. . . . . . . . 1385.1Pictorial representation of the bent geometry of the ground state of HgOH. Our finding shows  $\theta_{Hg-O-H} = 104.83^{\circ}$ . 1495.2The ground electronic state PEC of the hypothetical linear geometry of HgOH in the DF, RCCSD, and RCCSD(T) approximations using the exact two-component (X2C) Hamiltonian, with a double-zeta basis. In the plot, R is the Hg-O bond-

# List of Tables

1.1	Projected statistical uncertainties to $d_e \ (\delta d_e^{stat})$ of the currently proposed (on the	
	basis of theoretical analyses) molecules for EDM experiments. All the values are	
	given in units of e-cm.	12
3.1	Values of PDM ( $\mu$ ) (in a.u.) for LiNa, LiK, LiRb, LiCs and NaK from both re-	
	lativistic and non-relativistic calculations. We compare these values from various	
	previous calculations and available experimental results. Our results from both	
	the non-relativistic and the relativistic methods are given separately. The errors	
	are quoted within the parentheses.	109
3.2	Values of PDM ( $\mu$ ) (in a.u.) for NaRb, NaCs, KRb, KCs and RbCs from both re-	
	lativistic and non-relativistic calculations. We compare these values from various	
	previous calculations and available experimental results. Correlation effects are	
	added through both the (R)CCSD and (R)CCSD(T) methods. Our results from	
	both the non-relativistic and the relativistic methods are given separately	110
3.3	A comparative analysis of parallel component of the dipole polarizabilities, $\alpha_{\parallel}$	
	(in a.u.) of LiNa, LiK, LiRb, LiCs and NaK, between the non-relativistic and	
	relativistic calculations. We also present results from the earlier studies for the	
	comparative purpose.	111
3.4	A comparative analysis of parallel components of the dipole polarizabilities, $\alpha_{\parallel}$	
	(in a.u.) of NaRb, NaCs, KRb, KCs and RbCs, between the non-relativistic and	

relativistic calculations. We also present results from the earlier studies. . . . . 111

3.5	The values of perpendicular components of dipole polarizability, $\alpha_{\perp}$ (in a.u.), both	
	from the non-relativistic and relativistic methods. We have also added results that	
	are obtained in the previous works for comparing with our calculations	112
3.6	The average values of dipole polarizability, $\bar{\alpha}$ (in a.u.), of the alkali-dimers from	
	both our and previous calculations. We have also given experimental values for	
	the comparison.	112
3.7	The non-relativistic and relativistic values of dipole polarizability anisotropy, $\Delta \alpha$	
	(in a.u.), reported at different levels of (R)CC theory and other methods. A list	
	of previous works are added to the table for comparison with our results	113
3.8	Demonstration of changes in the $\alpha_{\parallel}$ , $\alpha_{\perp}$ , $\bar{\alpha}$ , $\Delta \alpha$ , and $\mu$ values of NaCs molecule at	
	different virtual energy level cut-offs using the RCCSD(T) method. Calculations	
	were performed using the TZ basis functions. All the quantities are specified in	
	a.u	113
3.9	Values of isotropic $C_6$ coefficients (in a.u.) of LiNa, LiK, LiRb, LiCs, and NaK by	
	combining our estimated $C_6^{ind}$ and $C_r^{rot}$ contributions with the $C_6^{disp}$ contributions	
	borrowed from Ref. [29]. We have also compared these results with the previously	
	reported two non-relativistic calculations. The differences between our results	
	with other calculations demonstrate importance of relativistic calculations in the	
	determination of the $C_6$ coefficients	114
3.10	Values of isotropic $C_6$ coefficients (in a.u.) of NaRb, NaCs, KRb, KCs, and	
	RbCs by combining our estimated $C_6^{ind}$ and $C_r^{rot}$ contributions with the $C_6^{disp}$	
	contributions borrowed from Ref. [29]. We have also compared these results with	
	the previously reported two non-relativistic calculations.	115
4.1	Values of PDMs (in a.u.) of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and	
	NaSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T)	
	methods	123
4.2	Values of PDMs (in a.u.) of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and	
	RbSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T)	
	methods	124

- 4.3 Values of different components of the electric dipole polarizabilities ( $\alpha_{\parallel}$  and  $\alpha_{\perp}$ ) as well as average polarizability ( $\bar{\alpha}$ ) and polarizability anisotropy ( $\Delta \alpha$ ) of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and NaSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods. All units are in a.u. 126
- 4.4 Values of different components of the electric dipole polarizabilities ( $\alpha_{\parallel}$  and  $\alpha_{\perp}$ ) as well as average polarizability ( $\bar{\alpha}$ ) and polarizability anisotropy ( $\Delta \alpha$ ) of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and RbSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods. All units are in a.u.. 127
- 4.5 The values of PDM and parallel components of polarizabilities of the LiBe, KBe, and RbBe molecules using different approximations in Hamiltonian from the RCCSD(T) method. All units are in a.u..
  133
- 4.6 The values of PDM and polarizability of four representative molecules (LiBe, KBe, RbBe, and RbSr) with basis sets of increasing cardinal number (DZ to QZ) in the RCCSD(T) method, and with the four-component spinfree relativistic Hamiltonian. We also give results from a CBS extrapolation scheme. All units are in a.u..

- 4.9 Our final recommended results for  $\mu$ ,  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ ,  $\bar{\alpha}$ , and  $\Delta \alpha$  of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and NaSr from the RCCSD(T) calculations, along with the estimated uncertainties that are quoted in the parentheses. We have also compared our results with the previously reported values using the MRCI and CCSD(T) methods.  $\bar{\alpha}$  and  $\Delta \alpha$  are rounded-off to the nearest whole number, given that fact that they have large values. All the results are given in a.u.. 140

4.10	Our final recommended results for $\mu$ , $\alpha_{\parallel}$ , $\alpha_{\perp}$ , $\bar{\alpha}$ , and $\Delta \alpha$ of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and RbSr from the RCCSD(T) calculations, along with the estimated uncertainties that are quoted in the parentheses. We have also compared our results with the previously reported values using the MRCI and CCSD(T) methods. $\bar{\alpha}$ and $\Delta \alpha$ are rounded-off to the nearest whole number, given their large values. All the results are given in a.u.	141
5.1	List of the optimized geometry of the ground electronic state and three low-lying excited states of HgOH from various works. The unit of bond-lengths is angstrom (Å), while that of the bond angle is degrees.	153
5.2	A comparative analysis of the calculated $\mathcal{E}_{eff}$ (in GV/cm) and $\mu$ (in D) values in HgOH by assuming its hypothetical linear and the actual bent geometry ground state using the DF and RCCSD methods. We also give $\mu$ values from the previous calculations using DFT.	155
5.3	Contributions from the individual RCC terms to $\mathcal{E}_{\text{eff}}$ (in GV/cm), $\mu$ (in D), and $W_s$ (in kHz) from both the linear and bent geometries of HgOH. $O$ denotes the operator corresponding to the properties. Note that for the PDM, the term corresponding to the DF contribution also accounts for the nuclear contribution in it.	157
5.4	Contributions from different atomic orbital (AO) mixing to the DF value of $\mathcal{E}_{eff}$ (in GV/cm), where the AO in the left hand side is a small component AO and that in the right hand side is a large component AO. Non-zero contributions may come only from odd-parity AO mixings $\langle (AO)_1^S   \hat{O}   (AO)_2^L \rangle$ , where superscript $S$ , and $L$ stand for small component and large component AOs respectively. Results are given for both the linear and the actual bent geometry HgOH molecule	158
5.5	Comparison of measured and projected sensitivities offered by different molecules for EDM experiments. For molecules where measurements are not available, the sensitivity is estimated with to projected $N, T, \tau$ , and $\eta$ values. The unit chosen for $\delta d_{\sigma}$ is e-cm.	160

- 6.1 Calculated values of  $\mathcal{E}_{\text{eff}}$ ,  $W_s$  (with  $M_A = 256$ ) and  $\mu$  for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> using the RCCSD method, and comparison with literature values wherever they are available. We also compare these values with calculations of the corresponding quantities for other molecules and atoms (see the text for further details).

170

xxviii

## List of acronyms

- EDM ..... Electric Dipole Moment
- eEDM ..... Electron's Electric Dipole Moment
- ${\bf SM}$  ..... Standard Model
- BSM ..... Beyond Standard Model
- CKM ...... Cabibo-Kobayashi-Masakawa Matrix
- PDM ..... Permanent Electric Dipole Moment
- ${\bf S-PS}$  ..... Scalar-Pseudoscalar
- **QED** ..... Quantum Electrodynamics
- HF ..... Hartree-Fock
- $\mathbf{DF}$  ..... Dirac-Fock
- CC ..... Coupled-Cluster
- RCC ..... Relativistic Coupled-Cluster
- CCSD ..... Coupled-Cluster Singles Doubles
- CCSD(T) ..... Coupled-Cluster Singles Doubles and Perturbative Triples
- a.u. ..... atomic units
- LECC ..... Linear Expectation Value Coupled-Cluster
- **KBC** ..... Kinetic Balance Condition
- $\mathbf{LCT}$  ..... Linked-Cluster Theorem
- CI ..... Configuration Interaction

- MRCI ...... Multi-Reference Configuration Interaction
- KRCI ...... Kramers Restricted Configuration Interaction
- MBPT ..... Many-Body Perturbation Theory
- $\mathbf{DZ}$ ..... Double-Zeta
- $\mathbf{TZ}$ ..... Triple-Zeta
- $\mathbf{Q}\mathbf{Z}$ ..... Quadruple-Zeta
- ccpv ...... Correlation-Consistent Polarized Valence
- ccpcv ...... Correlation-Consistent Polarized Core Valence
- BCH ..... Baker Campbell Haussdorf
- AO ..... Atomic Orbital
- ${\bf MO}$  ..... Molecular Orbital
- SOMO ..... Single Occupied Molecular Orbital
- h.c. ..... hermitian conjugate
- ${\bf FF}$  ..... Finite-Field
- PEC ..... Potential Energy Curve
- DFT ..... Density Functional Theory
- **CASPT** ..... Complete Active Space Perturbation Theory
- BKPT ..... Bishop-Kirtman Perturbation Theory
- ${\bf CASSCF}$  ...... Complete Active Space Self Consistent Field
- $\mathbf{ECP}$  ..... Effective Core Potential
- NR ..... Non-Relativistic

## Abstract

Atoms and molecules are called the natural laboratories to probe electron-electron, electronproton, electron-neutron, proton-proton, proton-neutron, and neutron-neutron interactions. Except for the electron-electron interactions, other interactions originate at the quarks levels. There have been immense interest to probe the nature of all possible phenomena involving these interactions. Direct probes of interactions involving electrons and quarks demand very large energy facilities like the Large Hadron Collider (LHC) at CERN owing to Heisenberg's uncertainty principle. However, using atoms or molecules, one can indirectly probe these interactions. These probes sometimes include evaluation of certain properties of fundamental particles, which can have further implications in fields like cosmology. One of the biggest cosmological mysteries in the present universe is the riddle of matter-antimatter asymmetry. According to Sakharov's conditions, it requires sufficient amount of CP (C: charge conjugation, P: parity) violation to properly explain the matter-antimatter asymmetry. Although there are a few known signatures of CP violation in the electro-weak interaction sector, those are insufficient to explain the matter-antimatter asymmetry. Therefore, it is imperative to search for new sources of CP violation. The electric dipole moment of electron (electron's EDM or eEDM,  $d_e$ ) being a P, T-odd (T: time-reversal) property, is one such CP violating phenomenon which is yet to be observed. Therefore, the eEDM, if detected, would be regarded as a direct signature of CP violation and it can throw light into explaining matter-antimatter asymmetry.

Probing eEDM through accelerator method with a single isolated electron is impractical, as it demands huge amount of energy that is currently beyond the capacity of existing as well as projected laboratory set ups. However, in non-accelerator probes, many-electron systems like paramagnetic atoms or molecules are used as proxies in EDM experiments. Due to their better experimental sensitivities, heavy polar molecules have historically become superior choices over atoms for EDM experiments. Within an atom or a molecule, an electron with EDM experiences an internal electric field due to other electrons and nuclei. For molecules, this electric field can be viewed as an effective electric field ( $\mathcal{E}_{\text{eff}}$ ), a large value of which would imply a better sensitivity in EDM experiments.  $\mathcal{E}_{\text{eff}}$  of a molecule is completely a relativistic phenomenon and cannot be measured in experiments, thus requiring a fully relativistic framework to perform theoretical calculations. Combination of relativistic many-body calculation of  $\mathcal{E}_{eff}$  and experimentally measured molecular energy shift can together put a stringent bound to  $d_e$ . The best experimental upper limit on  $d_e$  comes from a heavy diatomic molecule, ThO, which is about ten orders larger than the upper bound predicted by the Standard Model (SM) of particle physics. Experimentally set upper limit to  $d_e$  may constrain theories beyond the SM (BSM) which predict larger values of eEDM. An improvement in the upper bound to  $d_e$  through molecular EDM experiments and relativistic many-body calculations could guide us to reach near to the actual value of eEDM. In this thesis work, we mainly focus on exploring new molecular candidates for EDM experiments to obtain better sensitivity by means of our theoretical analyses. For this purpose, we employ the relativistic coupled-cluster (relativistic CC or RCC) method to carry out theoretical calculations relevant to EDM searches.

Before employing RCC theory to calculate molecular properties pertaining to high-precision EDM experiments, it is essential to test the potential of the RCC method to produce accurate results. As we do not have the option to compare our RCC results of properties related to EDM studies of new molecular candidates with existing literature, we employ the RCC method to calculate a few molecular properties for a couple of systems for which previous theoretical studies and/or experimental results are available. To serve this purpose, we calculate static dipole polarizabilities and permanent electric dipole moments (PDMs) of closed shell heteronuclear alkali-dimens for which experimental values are available. We discuss in detail the relativistic and correlation effects in both the properties. We compare our results from relativistic calculations with existing non-relativistic results as well as experimental data. We observe that our results obtained from RCC calculations agree well with experimental results and improves upon existing non-relativistic results. As open-shell paramagnetic molecules are considered for EDM experiments, similar exercise of testing the RCC theory needed to be performed with openshell molecules also. For that matter, we considered open-shell alkali-alkaline earth (Alk-AlkE) molecules to calculate their PDMs and static dipole polarizabilities using the RCC method. Experimental results of PDMs and polarizabilities of these systems are not available. Therefore, we had to settle by comparing our RCC results with non-relativistic results from our calculations as well as from other works available in literature. We observe that our RCC calculations of PDMs of Alk-AlkE systems significantly improve over the non-relativistic estimates, while the relativistic effects in dipole polarizabilities become prominent for heavier systems. After checking the capability of the RCC method, we employ it to assess the suitability of new molecular candidates for EDM searches.

Diatomic heavy polar molecules have been very popular for both theoretical and experimental studies of eEDM. However, it is recently shown by Kozyrev *et al.* [Phys. Rev. Lett. 119, 133002] that due to the presence of internal comagnetometer states in triatomic molecules, they could offer extra advantages over diatomic molecules in EDM experiments. We know that HgF possesses the largest  $\mathcal{E}_{eff}$  among the theoretically proposed molecules. Keeping this in mind, we chose HgF's triatomic isoelectronic counterpart HgOH for conducting theoretical analyses to assess its suitability in EDM experiment. Based on our RCC calculations and several experimental considerations, we provide the projected sensitivity of HgOH, which is better than the current best experimental limit set by the ThO experiment. We also explored feasibility of HgOH for different types EDM experiments.

As  $\mathcal{E}_{\text{eff}}$  is a purely relativistic property, we expect its value to get enhanced for molecules which exhibit relativistic effects more prominently. Superheavy molecules are generally anticipated to exhibit larger relativistic effects than the non-superheavy ones. Therefore, in our next endeavour, we selected three superheavy molecules, namely LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> to assess their prospects in EDM experiments. Using RCC calculations, we obtained the equilibrium bond-lengths of the molecules at their ground states from the minima of the corresponding potential energy curves (PEC). Once we found that stable bound state formation is quite possible for the considered Lr molecules, we employed the RCC theory to calculate  $\mathcal{E}_{\text{eff}}$  and PDM of the chosen molecules. We observe that the values of  $\mathcal{E}_{\text{eff}}$  for all the three molecules are almost 3 to 4 times larger than that of the current best theoretically proposed candidate HgF and experimentally considered molecule ThO. RCC values of PDM are also found to be quite large for the aforementioned systems. In superheavy molecules, along with the eEDM, another *P*, *T*-odd phenomenon that may significantly contribute to the molecular energy shift during an EDM experiment is the nucleus-electron scalar-pseudoscalar (S-PS) interaction. In the S-PS interaction, the properties analogous to  $d_e$  and  $\mathcal{E}_{\text{eff}}$  are S-PS coupling coefficient  $k_s$  and S-PS enhancement factor  $W_s$ , respectively. Calculated values of  $W_s$  using RCC method for the chosen superheavy molecules are observed to be almost four to five times larger than that of HgF and ThO. We also provide a pathway to produce Lr atoms in larger numbers, which is crucial in the formation of Lr molecules during EDM experiments. Enhanced values of  $\mathcal{E}_{\text{eff}}$  and PDMs of the chosen Lr molecules make them interesting for future EDM experiments. Our precise calculations of the molecular PECs and PDMs could also guide other future experiments with these molecules.

## Chapter 1

## Introduction

## 1.1 Electric dipole moment (EDM) of a system

Electric dipole moment (EDM,  $\vec{d}$ ) is the measure of charge separation within a system. For composite systems made of discrete charges, EDM is given by

$$\vec{d} = \sum_{i} q_i \vec{r_i},\tag{1.1}$$

where  $q_i$  stands for the charge of  $i^{th}$  particle and  $\vec{r_i}$  is the position of  $i^{th}$  particle with respect to a chosen origin. For a continuous charge distribution of charge density  $\rho(\vec{r})$ , EDM is defined as

$$\vec{d} = \int \vec{r} \rho(\vec{r}) d\tau, \qquad (1.2)$$

where the integral is calculated within the total volume of the charge distribution. Composite systems like atoms do not possess any EDM because of their spherical charge distribution. On the other hand, molecules do not have spherical charge distribution and possess intrinsic electric dipole moment (not induced by any external electric field), which is generally referred to as permanent electric dipole moment (PDM).

If treated as point-like particles, elementary particles (electrons, quarks etc.) cannot have any EDM. But, according to quantum field theory (QFT), an elementary particle is surrounded by a cloud of virtual particles, and the charge distribution of the cloud may give rise to an EDM. In our work, we mainly focus on the EDM of an electron (eEDM). The eEDM arises due to the simultaneous violations of two discrete symmetries, namely parity (P) and time-reversal (T) symmetries. Therefore, eEDM is a P, T-odd phenomenon. Moreover, according to the CPT theorem [1], T violation implies CP violation. Hence eEDM is a CP violating property. The eEDM is yet to be observed in experiments. Therefore, if detected, eEDM would be considered to be an intrinsic property of an electron and it would be a direct signature of CP violation in nature.

The Standard Model (SM) of particle physics sets a very tiny upper bound to eEDM,  $d_e < 10^{-38}$  e-cm. Several theories that explains physics beyond the Standard Model (BSM) predict much larger value of eEDM as compared to the SM bound. Direct measurement of eEDM with a single electron is impractical owing to its tiny size, which necessitates the use of very high energy accelerator facilities (as a consequence of Heisenberg's uncertainty principle), which are beyond our reach in near future. That is why many-body systems like atoms and molecules are used as proxies for conducting EDM experiments, where the relevant signals can be enhanced by many orders of magnitude. The model independent eEDM bounds obtained by combining atomic or molecular experiments with the corresponding theoretical many-body calculations have already constrained the parameter space of BSM physics to a reasonable extent and have thrown some light into the long standing problem of matter-antimatter asymmetry [2] in the universe.

Historically, heavy polar molecules have been proven to be better choices over atoms for EDM experiments. However, several challenges are posed regarding the choice of candidate molecules in terms of the experimental sensitivities that they promise to offer. Therefore, search for new molecular candidates for EDM experiments becomes necessary to improve upon the experimental bound to eEDM. The primary objective of this thesis work is to propose new molecular candidates suitable for EDM experiments based on our theoretical calculations and several experimental considerations.
## **1.2** *P*, *T*-odd phenomena and EDM of a system

As mentioned above, eEDM is an outcome of simultaneous violations of P and T symmetries (hereafter referred as P, T-odd for convenience). Here we justify this statement for its better understanding. Symmetry transformations play a huge role in our current understanding of nature. In quantum mechanics, if a physical property or operator remains unaltered under some physical or mathematical transformation, we consider that transformation as a symmetry transformation to the system. Under a symmetry transformation, the quantum mechanical operator remains invariant, and its eigenvalue also remains constant in time. Symmetry operations are broadly classified into two categories, namely discrete and continuous symmetries. A continuous symmetry operation is described by a continuous group (e.g. Lie group) which is labelled by a continuous parameter. A discrete symmetry operation involves non-continuous transformation of a system, and described by finite groups (e.g. point groups). There are mainly three different types of discrete symmetry operations in quantum mechanics: parity (P), time-reversal (T), and charge conjugation (C). The operators corresponding to these symmetry transformations are expressed as either unitary or anti-unitary operators. Parity is the operation of space inversion. Under P transformation, the position operator  $(\vec{r})$  changes its sign:  $P\vec{r}P^{-1} = -\vec{r}$ . The P operator is a linear operator with eigenvalues  $\pm 1$ .

The dipole operator  $(\vec{d})$  of any atomic or molecular system undergoes parity transformation as:  $P\vec{d}P^{-1} = -\vec{d}$ . In the absence of an external electric field, a stationary state  $|\Psi\rangle$  would possess a non-zero PDM given by

$$\langle \vec{d} \rangle = \langle \Psi | \vec{d} | \Psi \rangle. \tag{1.3}$$

Using the unitarity of parity operator P (i.e.,  $PP^{\dagger} = P^{\dagger}P = I$ , and  $P^{\dagger} = P^{-1}$ ) we can rewrite Eq. (1.3) as

$$\langle \vec{d} \rangle = \langle \Psi | P^{\dagger} P \vec{d} P^{\dagger} P | \Psi \rangle$$

$$= \langle \Psi | P^{\dagger} P \vec{d} P^{-1} P | \Psi \rangle$$

$$= -\langle P \Psi | \vec{d} | P \Psi \rangle$$

$$= -\langle \Psi' | \vec{d} | \Psi' \rangle,$$

$$(1.4)$$

where  $P|\Psi\rangle = |\Psi'\rangle$ .

Now we need to find out  $|\Psi'\rangle$ , i.e., how parity transformation impacts the stationary state wave function  $|\Psi\rangle$ . Schrödinger equation is satisfied by  $|\Psi\rangle$ 

$$H|\Psi\rangle = E|\Psi\rangle,\tag{1.5}$$

where H is the Hamiltonian of the system, and E is the energy eigenvalue. In general, the Hamiltonian can be assumed to remain invariant under parity transformation [3]:

$$PHP^{-1} = H, (1.6)$$

which leads to

$$H|\Psi\rangle = E|\Psi\rangle$$
  

$$\Rightarrow PH|\Psi\rangle = EP|\Psi\rangle$$
  

$$\Rightarrow PHP^{-1}P|\Psi\rangle = EP|\Psi\rangle$$
  

$$\Rightarrow HP|\Psi\rangle = EP|\Psi\rangle$$
  

$$\Rightarrow H|\Psi'\rangle = E|\Psi'\rangle.$$
(1.7)

Therefore from Eq. (1.3) and Eq. (1.7), it is evident that both  $|\Psi\rangle$  and  $|\Psi'\rangle$  describe stationary states with same energy eigenvalue E. If  $|\Psi\rangle$  and  $|\Psi'\rangle$  are non-degenerate, they cannot be

independent eigenvectors, and they must have a relation of following kind:

$$P|\Psi\rangle = p|\Psi\rangle,\tag{1.8}$$

$$\Rightarrow \langle \Psi | P^{\dagger} P | \Psi \rangle = | p |^{2} \langle \Psi | \Psi \rangle$$
(1.9)

$$\Rightarrow \langle \Psi' | \Psi' \rangle = |p|^2 \tag{1.10}$$

$$\Rightarrow |p|^2 = 1 \tag{1.11}$$

$$\Rightarrow p = \pm 1, \tag{1.12}$$

where p is a constant, and must be equal to one of the eigenvalues of parity operator, i.e.,  $p = \pm 1$ . Now combining this with Eq. (1.4), we get

$$\langle \Psi | \vec{d} | \Psi \rangle = -\langle \Psi' | \vec{d} | \Psi' \rangle = -p^2 \langle \Psi | \vec{d} | \Psi \rangle = -\langle \Psi | \vec{d} | \Psi \rangle.$$
(1.13)

From Eq. (1.13), we can infer that if the Hamiltonian is parity invariant and if the stationary state is non-degenerate, the system cannot possess a non-zero spontaneous EDM.

The time-reversal operation (T) is analogous to motion reversal and under this transformation, the temporal component (t) of the four-position changes its sign:  $TtT^{-1} = -t$ . The momentum operator also undergoes a sign change under T transformation. Unlike the P operator, the Toperator is a anti-linear operator with properties:

$$Tc|\Psi\rangle = c^*T|\Psi\rangle,\tag{1.14}$$

where  $c^*$  refers to the complex conjugate of the constant c.

If the Hamiltonian of a system is invariant under some unitary rotation, it should commute with the generators of rotation, i.e., components of the angular momentum operator  $(\vec{J})$ . The eigenvectors of H,  $\vec{J} \cdot \vec{J}$ , and  $J_z$  form a complete set denoted as  $|E, j, m\rangle$ . Now, we make an assumption that the only degeneracy arises from the (2j + 1) values of m. Invoking the WignerEckart theorem [4] to the irreducible rank 1 tensor EDM operator  $\vec{d}$ , we get

$$\langle E, j, m | \vec{d} | E, j, m \rangle = C_{E,j} \langle E, j, m | \vec{J} | E, j, m \rangle, \qquad (1.15)$$

where  $C_{E,j}$  is a scalar coefficient independent of m.

For any two functions  $|u\rangle$  and  $|v\rangle$ , if

$$T|u\rangle = |u'\rangle$$
 and  $T|v\rangle = |v'\rangle$ , (1.16)

it can be shown that [3]

$$\langle u'|v'\rangle = \langle u|v\rangle^*. \tag{1.17}$$

Let us choose  $|u\rangle = |\Psi\rangle$ , and  $|v\rangle = d_{\alpha}|\Psi\rangle$  with  $d_{\alpha}$  being one of the components of the EDM operator. Therefore,  $|u'\rangle = |\Psi'\rangle = T|\Psi\rangle$  and  $|v'\rangle = Td_{\alpha}|\Psi\rangle = d_{\alpha}T|\Psi\rangle = d_{\alpha}|\Psi'\rangle$ , where we used the fact that T commutes with  $d_{\alpha}$ . Combining these, we get

$$\langle \Psi' | d_{\alpha} | \Psi' \rangle = \langle \Psi | d_{\alpha} | \Psi \rangle^*.$$
(1.18)

As  $d_{\alpha}$  is a hermitian operator (hence possesses real eigenvalues), Eq. (1.18) can be written as

$$\langle \Psi' | \vec{d}_{\alpha} | \Psi' \rangle = \langle \Psi | \vec{d}_{\alpha} | \Psi \rangle. \tag{1.19}$$

Generalising, it yields

$$\langle \Psi' | \vec{d} | \Psi' \rangle = \langle \Psi | \vec{d} | \Psi \rangle. \tag{1.20}$$

Instead of using  $d_{\alpha}$ , the same exercise can be done using  $\vec{J}$ , which can give rise to

$$\langle \Psi' | \vec{J} | \Psi' \rangle = -\langle \Psi | \vec{J} | \Psi \rangle, \qquad (1.21)$$

where the reason behind the negative sign in Eq. (1.21) is that T anticommutes with  $\vec{J}$ , i.e.,  $TJ_{\alpha} = -J_{\alpha}T$ . From the definition we know

$$J_{z}|E, j, m\rangle = m|E, j, m\rangle \text{ (In atomic units (a.u.), } \hbar = 1.)$$

$$TJ_{z}|E, j, m\rangle = mT|E, j, m\rangle$$

$$TJ_{z}T^{-1}T|E, j, m\rangle = mT|E, j, m\rangle$$

$$J_{z}(T|E, j, m\rangle) = -m(T|E, j, m\rangle). \tag{1.22}$$

With the aforementioned assumption for restricting degeneracy to only (2j+1), the eigenvector  $T|E, j, m\rangle$  can differ from  $|E, j, -m\rangle$  by only a phase factor. Therefore, for  $|\Psi\rangle = |E, j, m\rangle$  and  $|\Psi'\rangle = T|E, j, -m\rangle$ , we obtain from Eq. (1.20) that

$$\langle E, j, -m | \vec{d} | E, j, -m \rangle = \langle E, j, m | \vec{d} | E, j, m \rangle, \qquad (1.23)$$

and from Eq. (1.21) we get

$$\langle E, j, -m | \vec{J} | E, j, -m \rangle = -\langle E, j, m | \vec{J} | E, j, m \rangle.$$
(1.24)

If we replace m to -m in Eq. (1.15), we achieve

$$\langle E, j, -m | \vec{d} | E, j, -m \rangle = C_{E,j} \langle E, j, -m | \vec{J} | E, j, -m \rangle.$$

$$(1.25)$$

Using Eq. (1.23) and Eq. (1.24) in Eq. (1.25) leads to

$$\langle E, j, m | \vec{d} | E, j, m \rangle = -C_{E,j} \langle E, j, m | \vec{J} | E, j, m \rangle.$$
(1.26)

Now combining Eq. (1.15) and Eq. (1.26), we see that

$$\langle E, j, m | \vec{d} | E, j, m \rangle = 0. \tag{1.27}$$

Therefore, we observe that under the assumption of rotational invariance, time-reversal invariance and degeneracy restricted to arise only from 2j + 1 values of m, the average spontaneous EDM of a state vanishes. This is a generalised proof and not only restricted to EDM of an electron, but also valid for EDM of other fundamental particles and composite systems.

#### **1.3** General features of elementary particle physics

Subatomic particles which are not composed of other particles are called elementary or fundamental particles. The SM of particle physics, by far the most celebrated model in physics, describes the phenomena of these fundamental particles well. However, the SM is an effective manifestation of a complete unknown theory that needs to be unearthed. The SM successfully describes the three (electromagnetic, weak and strong) interactions of the four existing fundamental forces in the universe and classifies the known elementary particles as matter (six quarks and six leptons), force carriers (photon, gluon, W boson, and Z boson) and the Higgs boson. The SM has been precisely verified through numerous accelerator based high energy experiments. The SM is based on a non-Abelian gauge theory [5] that belongs to  $SU(3)_c \times SU(2)_L \times U(1)_Y$  symmetry group, and it contains twelve gauge bosons (photon, three weak bosons, and eight gluons). All the three fundamental forces described by the SM are invariant under  $SU(3)_c \times SU(2)_L \times U(1)_Y$ transformation. With the venture to unify these three fundamental forces with gravity, the SM serves as an intermediate stage which unifies the electromagnetic and weak forces. Recent discovery of the Higgs boson (2012) in A Toroidal LHC ApparatuS (ATLAS) and Compact Muon Solenoid (CMS) experiments conducted at Large Hadron Collider (LHC) further strengthened the basis of the SM. Though the SM successfully explains most of the elementary particle physics, there are certain phenomena in physics that cannot be explained by the SM. A few examples of limitations of the SM are listed below:

(a) The formulation of the SM is based on QFT, while the origin of gravity is explained by theory of general relativity. If QFT is applied to general relativity, it leads to divergences [6].

(b) Only 5% of the total cosmic energy budget is made of baryonic matter, interactions (ex-

cept gravitational) of which are explained by the SM. Cosmological observations assert that 26% of the energy budget should be constituted by dark matter. Dark matter interacts only through gravitational interactions and does not interact with electromagnetic forces, thus making it impossible to probe with light or electromagnetic pulses. Hence, the prefix 'dark' is associated with dark matter. Fundamental particles present in the SM are not good dark matter candidates.

(c) The remaining 69% energy budget of the universe is believed to be comprised of dark energy. Dark energy is presumed to be responsible for the expansion of the universe. Dark energy is hypothesised as a constant energy density of the vacuum. However, the value of vacuum energy density in the SM calculated using QFT is off by 120 orders of magnitude relative to the observed one [7]. Therefore, the SM cannot successfully address the reason for the existence of dark energy.

(d) In the SM, neutrinos are considered as massless particles. However, the neutrino oscillation experiment [8] established that neutrinos have mass. To address this inadequacy, mass information has to be added to the SM by hand explicitly, thus indicating an incompleteness in the SM.

(e) One of the biggest mysteries in cosmology is the riddle of matter-antimatter asymmetry (baryon asymmetry), i.e., the asymmetry in the number of baryons and their anti-baryons in our observable universe. The SM cannot sufficiently explain this anomaly. Russian physicist Andrei Sakharov proposed three necessary conditions, known as Sakharov's conditions [9], for explaining matter-antimatter asymmetry :

- (i) baryon number (B) violation,
- (ii) sufficient amount of C and CP (C: charge conjugation, P: parity) violation, and
- (iii) interactions out of thermal equilibrium.

Baryon number is a conserved quantity in the SM, with one possible exception of the hypothetical Adler–Bell–Jackiw [10, 11] anomaly in quantum electrodynamics (QED). CP symmetry is conserved in QED but it is violated in electroweak interactions. The CP violating interactions in the SM are insufficient to adequately address the matter-antimatter asymmetry. Therefore,



Figure 1.1: Tree-level and loop-level (1-, 2-, 3-, and 4- loop) diagrams representing electroweak interactions in the SM. As can be seen, the first non-zero contribution to eEDM arises at the 4-loop level electroweak diagram of the SM.

search for additional sources of CP violation is necessary to unravel the mystery behind the baryon asymmetry.

As mentioned earlier, eEDM  $(d_e)$  arises due to P, T-odd interactions and its observation would amount to be another signature of CP violation in nature, which would in turn help throw light into the matter-antimatter asymmetry. The SM imposes a very small upper limit to eEDM  $(d_e < 10^{-38}\text{e-cm})$ , while several BSM frameworks (e.g. left-right symmetric model, supersymmetric model, multi-Higgs model etc.) predict much larger value for eEDM than the SM limit, which we shall discuss later in this chapter.

#### 1.4 The SM and BSM sources to the eEDM

If an electron is regarded as a point particle, i.e., all of its charge is contained in a point, it cannot possess an EDM. However, from a QFT point of view, an electron is always surrounded by a cloud of several virtual particles. The asymmetry in this electron cloud is responsible for the concept of eEDM. In the SM, CP symmetry is conserved in electromagnetic interactions. The first non-zero contribution to eEDM appears from the 4-loop electroweak diagrams in SM (Fig. 1.1). As a 4-loop correction corresponds to the fourth order perturbation, eEDM in the SM is predicted to be very small (<  $10^{-38}$  e-cm) as it is proportional to the fourth power of the weak interaction parameter  $\alpha_w$  ( $\mathcal{O}(10^{-6})$ ) [5]. Several BSM frameworks predict eEDM much larger than the aforementioned SM limit. For example, the minimal supersymmetric model (MSSM) predicts an eEDM  $\mathcal{O}(10^{-26})$  e-cm, which is several orders larger than the SM bound. The reason behind this is that in the MSSM, the first non-vanishing contribution to eEDM appears at the first loop level itself. This is because unlike the SM, the complex CP violating phases involved in absorption and emission of virtual particles need not be same in the MSSM. The MSSM allows several CP violating phases in contrast to only one CP violating phase (the phase appears in the Cabibo-Kobayashi-Masakawa (CKM) matrix) allowed in the SM.

#### **1.5** Molecules for eEDM searches

Despite the bounds to eEDM set by different models, any experimental detection of eEDM is yet to be confirmed in the accelerator based experiments. However, non-accelerator based experiments using atoms or molecules in combination with theoretical many-body calculations, can put a stringent bound on eEDM, which in turn can constrain or rule out (up to certain level of confidence) some of the BSM scenarios that predict larger value of eEDM. The current best limit to eEDM set by an atomic experiment comes from the thallium (Tl) EDM experiment  $(d_e < 20 \times 10^{-28}$  e-cm), while even better eEDM bounds come from three molecular EDM experiments [12, 13, 14]. By far, the best upper limit to eEDM arises from the ThO [12] EDM experiment ( $d_e < 1.1 \times 10^{-29}$  e-cm with 90% level of confidence). Several other molecules have also been considered for the EDM experiments. Of them, the HfF<sup>+</sup> experiment [13] provides an eEDM bound of  $1.3 \times 10^{-28}$  e-cm and the YbF EDM experiment [14] sets an eEDM bound of  $10.5 \times 10^{-28}$  e-cm. EDM experiments with BaF molecule are underway [15, 16]. On the theoretical front, there are a plethora of proposed molecular candidates for the EDM experiments with even higher projected sensitivity. YbOH is the current best theoretically proposed molecular candidate for the EDM measurement with a projected statistical sensitivity  $\mathcal{O}(10^{-32})$  e-cm. One of the main goals of this thesis work is to find even better molecular candidates for EDM experiments on the grounds of several theoretical and experimental considerations.

#### 1.6 Current limits on eEDM from molecular studies

Table 1.1: Projected statistical uncertainties to  $d_e$  ( $\delta d_e^{stat}$ ) of the currently proposed (on the basis of theoretical analyses) molecules for EDM experiments. All the values are given in units of e-cm.

Molecule	$\delta d_e^{stat}$ (e-cm)
<b>TT T t [</b> 0]	1 2 4 2 20
HgLi [9]	$1.3 \times 10^{-30}$
HgNa [9]	$2.5 \times 10^{-30}$
HgK [9]	$3.1 \times 10^{-30}$
YbOH [17]	$2.76 \times 10^{-32}$
RaH [18]	$1.63\times10^{-29}$
HgF [19, 20]	$6 \times 10^{-32}$
RaF [21]	$2.49\times10^{-29}$
YbF [22]	$1.06 \times 10^{-27}$

Only a handful of molecules have been considered so far for the EDM experiments. EDM experiments were conducted with ThO [12], HfF<sup>+</sup> [13], and YbF [14] molecules. The race is on to find better molecular candidates that would promise higher statistical sensitivity and in turn help improve upon the currently existing experimental eEDM bound. In Table 1.1 we enlist the projected statistical sensitivities of some of the theoretically proposed molecules. Among the listed molecules, YbOH offers the highest projected statistical sensitivity.

#### 1.7 Manifestation of eEDM in molecules

The EDM interaction Hamiltonian due to eEDM manifested at the molecular level can be expressed as [23]

$$H_{eEDM} = -d_e \sum_{i=1}^{N_e} \beta \Sigma_i \cdot E_i^{int}, \qquad (1.28)$$

where  $\beta$  is the one of the of Dirac matrices ( $\gamma^0$ ),  $N_e$  is the total number of electrons in the molecule,  $\Sigma$  is the four-component Pauli spin matrix, and  $E_i^{int}$  is the internal electric field

experienced by the  $i^{th}$  electron due to presence of other electrons and nuclei, and is given by

$$E_{i}^{int} = -\nabla \left[ V_{Ne}(r_{i}) + \frac{1}{2} \sum_{j \neq i} \frac{1}{r_{ij}} \right], \qquad (1.29)$$

where  $V_{Ne}$  is the nucleus-electron attractive Coulomb potential, and the second term inside the square bracket corresponds to the Coulombic electron-electron repulsion potential. The first-order shift in energy due to the EDM interaction Hamiltonian is given by

$$E^{(1)} = \langle \Psi | H_{eEDM} | \Psi \rangle$$
  
=  $-d_e \sum_{i=1}^{N_e} \langle \Psi | \beta \Sigma_i \cdot E_i^{int} | \Psi \rangle$   
=  $-d_e \mathcal{E}_{eff},$  (1.30)

where

$$\mathcal{E}_{\text{eff}} = \sum_{i=1}^{N_e} \langle \Psi | \beta \Sigma_i \cdot E_i^{int} | \Psi \rangle$$
(1.31)

is called the *effective electric field* of the molecule and  $|\Psi\rangle$  is the total unperturbed wave function of the molecule which actually is a Slater determinant wave function made of molecular orbitals  $|\phi_k\rangle$ s. Eq. (1.31) can be written as a sum of one-body operator [24]

$$\mathcal{E}_{\text{eff}} = -\frac{1}{d_e} \frac{\langle \Psi | H_{eEDM} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 2ic \sum_{i=1}^{N_e} \langle \phi_i | \beta \gamma_5 p_i^2 | \phi_i \rangle.$$
(1.32)

It can be shown that in Eq. (1.32), only the matrix element corresponding to the valence molecular orbital would survive (see Appendix A for details). Hence, for closed-shell molecules, the value of  $\mathcal{E}_{\text{eff}}$  would be zero in the first order approximation. Only molecular systems having one or more unpaired electrons would possess non-zero  $\mathcal{E}_{\text{eff}}$ , thus making them apt for the eEDM search experiments. The signature of eEDM in an open-shell molecular system is effectively manifested only upon the valence shell electron. It is also noteworthy that in a non-relativistic framework,  $\mathcal{E}_{\text{eff}} = 0$  due to Schiff's theorem [25]. Thus one has to undertake only a relativistic theory to calculate  $\mathcal{E}_{\text{eff}}$ . This has been shown explicitly in the later part of the thesis.

#### 1.8 Typical principles of molecular EDM experiments

From Heisenberg uncertainty principle, we know that

$$\Delta p \Delta x \sim \frac{\hbar}{2},\tag{1.33}$$

where  $\Delta p$  and  $\Delta x$  represent uncertainties in momentum and position, respectively. Due to the tiny dimension of electron,  $\Delta x$  is very small, thus leading to very large  $\Delta p$ . Therefore, the typical energy required,  $\frac{(\Delta p)^2}{2m}$ , to trap an electron would also be very high. Thus, trapping a single electron requires a huge amount of electric field which is beyond the reach of current experimental facilities. However, EDM measurements of composite systems like molecules are possible. There are two broad types of molecular EDM experiments, namely, beam experiment and trap experiment. Hence, instead of a single electron, atomic or molecular systems with one or more unpaired electrons are used as proxies in the EDM experiments.

In a beam EDM experiment, an atomic or molecular beam is passed through a chamber where it subject to external electric field  $(\vec{E}_{ext})$  and magnetic field  $(\vec{B}_{ext})$ . Due to the application of external magnetic field, the energy of the atom or molecule would shift due to Larmour precession, as atomic or molecular electrons with magnetic dipole moment  $(\mu_{mag})$  would experience a torque, given by

$$\vec{\tau} = \frac{d\vec{J}}{dt} = \vec{\mu}_{mag} \times \vec{\mathcal{B}}_{ext} = \gamma \vec{J} \times \vec{\mathcal{B}}_{ext}.$$
(1.34)

Here  $\vec{J}$  is the total angular momentum vector,  $\gamma$  is the gyromagnetic ratio defined as  $\gamma = g_e \frac{\mu_B}{\hbar} = g_e \mu_B$  (in a.u.)  $\mu_B$  is the Bohr magneton expressed as  $\mu_B = \frac{e\hbar}{2m_e} = \frac{1}{2}$  (in a.u., both the electron charge and mass are unity). The torque in Eq. (1.34) would try to align the magnetic moment,  $\vec{\mu}_{mag}$ , towards the direction of  $\vec{\mathcal{B}}_{ext}$ . As  $\vec{\mu}_{mag} \propto \vec{J}$ ,  $\vec{J}$  would also be affected by the magnetic field in the same manner as  $\vec{\mu}_{mag}$ . From Eq. (1.34), it is evident that torque or the rate of change of angular momentum is perpendicular to  $\vec{J}$ . This leads to the precession of  $\vec{J}$  around the direction of  $\vec{\mathcal{B}}_{ext}$ .

Now, if we invoke a time-reversal operation, i.e., if we run the entire process backward in time, the Larmour precession also should flip its direction. Therefore, if an EDM experiment can be set up in such a manner that it is analogous to running the whole experimental procedure backward in time, and if the precession gets its direction reversed (and the time-reversed precessional frequency is different from the original frequency of precession), it would be a test of T violation. But, the magnetic field also switches direction under the transformation  $t \to -t$ . Therefore, we cannot distinguish between the precessions before and after the time-reversal. The electric field does not flip under time-reversal. Thus, we can implement this idea in experiments by measuring the precession of spin of the unpaired electron of a molecule in an electric field. In a typical beam EDM experiment, along with an external electric field ( $\vec{E}_{ext}$ ), an external magnetic field ( $\vec{B}_{ext}$ ) is also applied as a carrier signal. The idea behind using carrier signal is to amplify the signal. The effect of the external magnetic field is balanced out by performing two experiments, one with  $\vec{E}_{ext}$  and another with  $\vec{E}_{ext}$  flipped. The shifts in energy in a molecule before and after electric field flip are respectively given by

$$E_1 = \omega_1 = -\vec{d_e} \cdot \vec{E_{ext}} - \vec{d_e} \cdot \vec{\mathcal{E}_{eff}} + \vec{\mu} \cdot \vec{E_{ext}} - \vec{\mu_{mag}} \cdot \vec{\mathcal{B}_{ext}}$$
(1.35)

and

$$E_2 = \omega_2 = -\vec{d_e} \cdot \vec{E_{ext}} + \vec{d_e} \cdot \vec{\mathcal{E}_{eff}} + \vec{\mu} \cdot \vec{E_{ext}} - \vec{\mu_{mag}} \cdot \vec{\mathcal{B}_{ext}}.$$
 (1.36)

Here, we denote the PDM of the molecule as  $\vec{\mu}$ . Electric dipole moments tend to align towards the direction of externally applied static electric field to attain the minimum energy configuration (as energy:  $E_{dip} = -\vec{D} \cdot \vec{E}_{ext}$ , where  $\vec{D}$  is a general notation for electric dipole moment). Therefore, when the direction of  $\vec{E}_{ext}$  is reversed, both the electric dipole moments  $\vec{\mu}$  and  $\vec{d}_e$ would flip their orientation. As  $\mathcal{E}_{eff}$  is an internal property of the molecule, it is not affected due to the reversal of the external electric field. Atomic units (a.u.) are used both in Eq. (1.35) and (1.36).

The difference between the two energy shifts is measured in experiments in terms of frequency

shift  $\Delta \omega = \omega_1 - \omega_2$ . This energy shift difference is given by

$$\Delta E = E_2 - E_1 = \omega_2 - \omega_1 = \Delta \omega = 2\vec{d_e} \cdot \vec{\mathcal{E}}_{\text{eff}}.$$
(1.37)

In Eq. (1.37),  $\Delta E$  or  $\Delta \omega$  is measured in experiments, while  $\mathcal{E}_{\text{eff}}$  is not a measurable quantity, and therefore must be calculated using relativistic quantum many-body theory [26]. Combining these two results (experimental, and theoretical) one infers the  $d_e$  value. Since thus far all the measurements of  $\Delta E$  have much larger uncertainties than their magnitudes, we can only assign to the  $d_e$  value.

Now, we proceed to give a brief overview of trap EDM experiments. Although by far the most accurate eEDM bound comes from a beam experiment with ThO [12], beam experiments are constrained by very low coherence times (~  $\mathcal{O}(1-10 ms)$ ). As eEDM sensitivity is directly proportional to the coherence times, beam experiments give very low coherence times which fall short to improve the sensitivity. Whereas, EDM experiments with trapped molecules can achieve much longer coherence time (~  $\mathcal{O}(1 s)$ ) [27] and thus could improve the sensitivity of eEDM by several orders. One of the popular techniques to trap molecules in an EDM experiment includes direct laser cooling of cryogenic buffer gas beams (CBGBs) followed by trapping in a magneto-optical trap (MOT). CBGBs produce molecular beams with high brightness and low velocity. Cooling and trapping procedures of a proposed EDM experiment with YbOH molecules have been discussed thoroughly in Ref. [10]. Another trapping mechanism, called EDM<sup>3</sup> [28, 29] experiment, has been introduced recently. In this procedure, molecules are trapped inside a solid-state inert gas (e.g. Ar, He etc.) matrix (crystal). It is possible to trap a large number of polar molecules  $[\mathcal{O}(10^{10} - 10^{16})]$  inside these solid inert gas matrices, while the typical value of number of molecules per second (N), is at most  $\mathcal{O}(10^5)$  in the beam experiments. Capability of trapping a large number of molecules and with a large coherence time of 1 s make the  $EDM^3$  technique a lucrative option to conduct future EDM experiments, as it could lead to obtain  $\delta d_e \sim 10^{-35} - 10^{-37}$  e-cm [28]. The influence of the transparent inert gas matrices on the molecules is very negligible, which permits similar state preparation and detection mechanisms used in beam experiments. In this method, polar molecules are embedded inside a solid state inert-gas matrix and fully oriented with the help of an external electric field of strength 1-3 MV/ cm [30] generated by the ice-film nanocapacitors [31].

# 1.9 Criteria for searching suitable molecules for eEDM searches

The figure of merit for the choice of a suitable molecular candidate for experiments to probe eEDM depends upon several factors. The statistical sensitivity offered by a molecule in a beam EDM experiment is given by [32]

$$\delta d_e^{stat} \sim \frac{1}{2\pi \mathcal{E}_{\text{eff}} \sqrt{NT\tau}\eta} \tag{1.38}$$

where N is the rate of production of number of molecules, T is the total integration time of the experiment,  $\tau$  is the coherence time of the molecular state of interest, and  $\eta$  ( $0 \le \eta \le 1$ ) is the polarization factor which depends on external electric field strength ( $E_{ext}$ ) and the PDM of the molecule. It is given by,

$$\eta(E_{ext}, D) \propto \langle \hat{n} \cdot \hat{z} \rangle,$$
 (1.39)

where  $\hat{z}$  is chosen to be the direction of applied electric field and  $\hat{n}$  is the direction of the internuclear axis. In an ideal case,  $\eta$  is unity, i.e., molecule is said to be fully polarized. From Eq. (1.38) we see that  $\delta d_e^{stat}$  is inversely proportional to  $\mathcal{E}_{eff}$ . Therefore, the larger the value of  $\mathcal{E}_{eff}$ of a molecule, more suitable it is for the EDM experiment. Hence, once a molecule appears to be reasonably suitable, based on experimental factors, one needs to calculate  $\mathcal{E}_{eff}$  by employing relativistic many-body theory.

From an experimental point of view, polarization factor modifies the energy shift due to eEDM

in a molecule by a factor

$$\Delta E = -d_e \mathcal{E}_{\text{eff}} \eta \tag{1.40}$$

We shall briefly analyze the expression in Eq. (1.39) to understand our objective better. We basically intend to justify here how a molecule has advantage over atoms to be considered for eEDM measurement. In a polar molecule, one can obtain a very large  $\mathcal{E}_{\text{eff}}$  value compared to atoms as orbitals are highly polarized in the molecule. Further,  $\eta$  can be enhanced dramatically in molecules compared to atoms with a small application of electric field owing to the presence of rotational spectra. This can be shown by writing down the wave function of a diatomic molecule in the presence of an external electric field as

$$|\Psi_{\alpha}\rangle = |\Psi_{\alpha}^{(0)}\rangle + |\Psi_{\alpha}^{(1)}\rangle + |\Psi_{\alpha}^{(2)}\rangle + \cdots, \qquad (1.41)$$

where  $|\Psi_{\alpha}^{(0)}\rangle$ ,  $|\Psi_{\alpha}^{(1)}\rangle$ ,  $|\Psi_{\alpha}^{(2)}\rangle$  etc. are the zeroth, first, second etc. order wave functions. The polarizing factor  $\eta$  is given by

$$\eta = \langle \Psi_{\alpha} | \hat{n} \cdot \hat{z} | \Psi_{\alpha} \rangle, \qquad (1.42)$$

where  $\hat{n}$  is the unit vector of the electric field and  $\hat{z}$  is the electric vector of the electric dipole operator. Keeping only terms up to first-order wave function, we can get

$$\eta = 2\langle \Psi_{\alpha}^{(0)} | \hat{n} \cdot \hat{z} | \Psi_{\alpha}^{(1)} \rangle. \tag{1.43}$$

Here only the rotational states contribute significantly because for the energy denominator from rotational states are ~ 1 GHz, whereas for vibrational states it is ~ 10 THz, and for electronic states it is ~ 100 THz. Since interaction due to the electric field mixes rotational states under the selection rule  $\Delta J_r = \pm 1$  for the rotational quantum number  $J_r$ , we can thus write

$$\eta = DE_{ext} \sum_{\beta \neq \alpha} \frac{|\langle J_{\alpha} | \hat{n} \cdot \hat{z} | J_{\beta} \rangle|^2}{B_r}, \qquad (1.44)$$

One should note here that, the matrix element of  $\hat{n} \cdot \hat{z}$  between rotational states  $J_{\alpha} = 0$  and  $J_{\beta} = 0$  is zero, as  $J_r = 0 \rightarrow 0$  is a forbidden rotational transition. In the above expression,  $B_r$  is the rotational constant of the molecule that depends on the reduced mass and the equilibrium bond-length  $(R_e)$  of the molecule. In our case, we have considered ground state with  $J_{\alpha} = 0$  so the intermediate states will have  $J_{\beta} = 1$ . The energy denominator becomes  $2B_r$  when  $J_r = 0$  and  $J_r = 1$  states are considered.

We observe that for achieving an optimal sensitivity in the experiment, the polarization factor has to be close to unity, which depends on the PDM,  $R_e$ , and the reduced mass of the molecule, and the the external field. Therefore, one needs to calculate the PDM and equilibrium bondlength of the molecule to get an estimate of  $\eta$ . The information of PDM (mu) is useful not only to calculate  $\eta$ , but also to estimate the polarizing electric field ( $E_{pol} = 2\frac{B_r}{\mu}$ ). After theoretically evaluating  $R_e$ ,  $\mathcal{E}_{\text{eff}}$ , PDM,  $\eta$ , and providing a reasonable estimate of N, T, and  $\tau$ , one can decide on the suitability of a molecule for eEDM search experiments. In this thesis, we shall focus on the proposal of a few new molecular candidates such as triatomic molecular candidate HgOH and superheavy lawrencium (Lr) molecular systems for eEDM search experiments.

#### **1.10** The eEDM and matter-antimatter asymmetry

As mentioned earlier in this chapter, eEDM, by the virtue of being a CP violating property can help throw light on understanding the matter antimatter asymmetry in the universe. In their 1992 work [33], Kazarian, Kuzmin and Shaposhnikov used the framework of two Higgs doublet model to correlate the magnitude of CP violation ( $\lambda_{CP}$ ) to  $d_e$ , and showed that their estimate of eEDM is close to the then best experimental limit to eEDM available from the Cs atomic EDM experiment. Therefore, any molecular EDM experiment with better experimental sensitivity on eEDM would help to impose a better constraint on  $\lambda_{CP}$  value. Thus, molecular EDM experiments might improve the limits of magnitudes of CP violation.

#### 1.11 Nucleus-electron scalar-pseudoscalar interaction

In an EDM experiment, another source of P, T-odd contribution arises from the nucleus-electron scalar-pseudoscalar (S-PS) interaction. The net energy shift due to both the eEDM and S-PS P, T-odd interactions in an EDM experiment can be given by

$$\Delta E_{P,T-\text{odd}} = -d_e \mathcal{E}_{\text{eff}} + k_s W_s, \qquad (1.45)$$

where  $k_s$  is the S-PS coupling coefficient and  $W_s$  is the S-PS enhancement factor. Just like  $\mathcal{E}_{\text{eff}}$ ,  $W_s$  also must be calculated using relativistic many-body theory. In Eq. (1.45), there are two unknown quantities, namely,  $d_e$  and  $k_s$ . Therefore, at least two sets of EDM experiments (i.e. EDM experiments with two molecules) are necessary to be performed to infer about  $d_e$  and  $k_s$ independently. Once  $\mathcal{E}_{\text{eff}}$  and  $W_s$  are obtained from theoretical calculations and energy shifts are measured in experiments, values of  $d_e$  and  $k_s$  can be achieved.

The S-PS interaction Hamiltonian in a molecule with N number of nuclei and  $N_e$  number of electrons can be expressed as [24, 34]

$$H_{S-PS} = \sum_{A=1}^{N} H_{S-PS,A}, \qquad (1.46)$$

where 
$$H_{S-PS,A} = i \frac{G_F}{\sqrt{2}} k_{s,A} M_A \sum_{j=1}^{N_e} \beta \gamma_5 \rho_A(r_{A_j}).$$
 (1.47)

In Eq. (1.47),  $H_{S-PS,A}$  is the S-PS Hamiltonian corresponding to the  $A^{th}$  nucleus,  $G_F = 2.219 \times 10^{-14}$  a.u. is the Fermi constant,  $M_A$  is mass number of the  $A^{th}$  nucleus with  $M_A = Z_A + N_A$  ( $Z_A$  is the atomic number of the  $A^{th}$  nucleus and  $N_A$  is the number of neutrons in the  $A^{th}$  nucleus),  $k_{s,A}$  stands for the S-PS coupling coefficient of the corresponding nucleus and  $\rho_A$  denotes the  $A^{th}$  nucleus charge distribution. The quantity of theoretical interest pertaining to nucleus-electron S-PS interaction is  $W_s$  and can be evaluated from the expectation value of S-PS Hamiltonian

$$W_s = \frac{1}{k_s} \frac{\langle \Psi | H_{S-PS} | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$
(1.48)

## 1.12 Motivation of the work

The prime objective of this thesis work is to probe P, T-odd molecular properties based on theoretical many-body analyses. The P, T-odd phenomenon that we mainly focus on is the eEDM through molecular EDM. The SM predicts a very tiny upper bound to eEDM but it is yet to be experimentally verified. Due to very small value of eEDM, it is very challenging to detect in experiment. Combination of theoretical calculation with low-energy atomic or molecular experimental result can place a bound on eEDM. As mentioned earlier, the current best upper bound to  $d_e$  is  $1.1 \times 10^{-29}$  e-cm [12]. An improved upper limit to  $d_e$  through molecular EDM experiments and many-body calculations could help to reach closer to the actual eEDM value. New upper limit to  $d_e$  could discard (with certain level of confidence) several BSMs which predict larger values of eEDM and suggest for modification of parameter spaces of those BSMs. As eEDM is a CP violating property, a new bound to it may lead to improvement over our current understanding about matter-antimatter asymmetry which requires ample amount of CP violation to be explained. To improve upon the current bound on  $d_e$ , we need to look for new molecular candidates which could offer better experimental sensitivity over the already proposed molecules. As mentioned earlier, heavy polar molecules possess larger  $\mathcal{E}_{\text{eff}}$  than other lighter molecules, thus becoming solicited candidates for EDM experiments. In our work, we aim to theoretically explore the suitability of new molecular candidates for EDM experiments depending upon the values of their parameters ( $\mathcal{E}_{eff}$ , PDM etc.) and other possible experimental considerations.

Although a few heavy polar diatomic molecules have been proved to be suitable for eEDM searches, efforts to find even more appropriate polyatomic molecules are underway. It has been realized that polyatomic molecules exhibit similar advantages to a diatomic molecule, along with other additional features like the presence of internal comagnetometer states. The triatomic YbOH [35] molecule offers a projected sensitivity to  $d_e$  of  $2.8 \times 10^{-32}$  e-cm, which is by far the best among the proposed molecular candidates. YbOH is the triatomic isoelectronic counterpart of YbF. Both YbF and YbOH offer almost similar values of  $\mathcal{E}_{\text{eff}}$ . Whereas, the HgF molecule possesses an  $\mathcal{E}_{\text{eff}}$  almost five times larger than YbF or YbOH. Therefore, it motivates

us to anticipate that HgOH, the triatomic isoelectronic counterpart of HgF, could also offer a large  $\mathcal{E}_{\text{eff}}$  and an improved projected sensitivity. We examine the potentiality of the triatomic HgOH molecule for EDM experiment [12].

We have stated earlier that  $\mathcal{E}_{\text{eff}}$  is a purely relativistic property. Therefore, it is fairly logical to expect that  $\mathcal{E}_{\text{eff}}$  should be sufficiently large for heavier molecules, as relativistic effects are more prominent in the heavier systems. We explore the suitability of superheavy Lr molecules (LrX; X=O, F<sup>+</sup> and H<sup>+</sup>) for eEDM searches [39].

We use the RCC theory to calculate molecular properties related to eEDM searches. It is essential to test the potential of the RCC method to produce accurate results in the molecular systems before employing them for calculations pertaining to eEDM probes. To do so, we carry out the calculations of static dipole polarizabilities and PDMs of heteronuclear alkali-dimers [36]. Expectation value of dipole polarizability has functional resemblance with that of  $\mathcal{E}_{\text{eff}}$ . On the other hand, PDM is a property that is also relevant to eEDM searches. Therefore it is prudent to calculate these properties using the RCC methods and compare our theoretical results with the previous theoretical and experimental results to assert the capability of the RCC theory. We also demonstrate how relativistic effects play important roles in determining the above properties by carrying out calculations using non-relativistic CC theory and comparing with our RCC calculations.

#### 1.13 Outline of thesis

This thesis is organized in the following manner. In Chapter 2, we discuss in detail on quantum many-body theory (both relativistic and non-relativistic) in the context of molecular physics. We introduce the Hartree-Fock (HF) method as a mean field approach. Then we put emphasis on adding electron correlation effects on top of mean field calculations. Among the several available techniques to account for the correlation effects, we mainly elaborate on the CC theory that we use extensively for our calculations.

For calculating properties pertaining to EDM searches, we need to adapt a reliable technique to obtain an accurate wave function. It is therefore necessary to demonstrate the accuracy of the RCC methods that we employ for calculations. Properties like  $\mathcal{E}_{\text{eff}}$  and  $W_s$  cannot be measured through experiments. Hence, we do not have the choice to directly compare the calculated values of these properties with experimental data. Therefore, we choose to calculate PDMs and static dipole polarizabilities for some systems for which previous theoretical as well as experimental results are available. In Chapter 3, we discuss on our fully relativistic calculations of PDMs and static dipole polarizabilities of heteronuclear alkali-alkali-dimers, as demonstrated in Ref. [36]. Most of the previous calculations were done in a non-relativistic framework or adding relativistic effects partially. We compare our relativistic results with the non-relativistic results and also with the literature data. We make a thorough analysis of the correlation effects at different levels of theory. While analyzing these quantities, we show that the implication of relativistic calculations of PDMs and polarizabilities greatly improve the estimation of van der Waals  $C_6$ coefficients. This clearly indicates the importance of considering a relativistic theory for high accuracy calculations of molecular properties. We also provide a meticulous error estimation procedure for the calculated properties.

Since alkali-dimers are closed-shell molecules, the next logical step for proceeding is to check whether the results obtained for open-shell molecules are as accurate as in the case of the closedshell ones. In Chapter 4, on the basis of Ref. [37], we discuss on the fully relativistic calculations of PDMs and static dipole polarizabilities of open-shell alkali-alkaline earth molecules. We make an in depth analyses of trends in the relativistic and correlation effects in the values of static polarizability and PDM of alkali-alkaline earth molecules. We compare our relativistic results with the existing non-relativistic calculations. We also establish an empirical formula to relate average static polarizability of a molecule with the constituent atomic polarizabilities and verify the functional form of the formula for a couple of systems. In these calculations also, we make a detailed error analysis.

After verifying the reliability of the RCC theory through the calculations of PDMs and static dipole polarizabilities for a number of molecular systems, we are in a firm ground to start our venture of probing eEDM through molecules. In Chapter 5, we discuss in detail on the suitability of HgOH molecule for an EDM experiment, as described in Ref. [38]. We optimize the ground state geometry of the molecule, which affirms to be having a bent configuration. For conducting a beam EDM experiment, one of the prerequisites is a slow molecular beam for avoiding systematic effects. The kinetic energy of the molecules in a beam can be reduced by cooling them down to mK temperatures. For trap EDM experiments also, one needs to cool the molecules down to  $\mu K$  temperature before trapping. That is why it becomes necessary to check out the cooling prospects of HgOH. We scrutinized the laser cooling possibilities of HgOH by calculating the Franck-Condon factors between different vibrionic states. At the end, weighing upon some realistic assumptions about possible experimental scenarios we provide a projected sensitivity offered by HgOH for the EDM experiment.

In Chapter 6, the discussion is based on Ref. [39], where we scrutinize the prospect of three superheavy lawrencium molecules (LrO, LrF<sup>+</sup>, and LrH<sup>+</sup>) as EDM experimental candidates. To ensure the formation of a stable state of the molecules, we find out the equilibrium bond-lengths of the molecules from the minima of their corresponding PECs. Then, we carry out relativistic calculations to find out their  $\mathcal{E}_{\text{eff}}$  and PDM. We also probe another P, T-odd interaction, namely the S-PS interaction which has significant impact on the molecular energy change due to in the EDM experiments. We calculate the S-PS enhancement factor  $W_s$  and show its dependence on nuclear charge distribution of Lr nucleus. We also comment on favourable experimental set ups for each molecule. At first, we begin with the geometry optimization of the molecules. After that, we calculate  $\mathcal{E}_{\text{eff}}$ , PDM and  $W_s$  of the aforementioned molecules by employing the RCC theory. We also propose suitable experimental set ups for each of these molecules.

In Chapter 7, we draw an overall conclusion to this PhD thesis work. We also provide an insight about the future course of actions on the above studies.

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# Chapter 2

# Molecular Many-Body Theory

## 2.1 Introduction

Quantum many-body theory is a branch of quantum mechanics that deals with systems having two or more constituent quantum particles. It is applicable to various branches of physics, e.g. atomic physics, molecular physics, condensed matter physics, nuclear physics etc.. In this chapter, we shall discuss quantum many-body theory in the context of molecular physics. For molecules with two or more electrons, the Schrödinger equation cannot be solved exactly and one needs to adopt approximation methods to achieve a near accurate wave function for determining molecular properties. For more accurate calculations, it is imperative to apply quantum many-body methods in the relativistic framework. Accurate calculations of molecular properties to study EDMs due to P, T-odd interactions also require use of a reliable many-body method. Relativistic effects are quite significant in the heavier molecules and ions owing to the fact that electrons close to the nucleus can move at relativistic speeds. Again, it is not possible to consider a covariant form of relativistic Hamiltonian for the calculation of molecular properties due to complexity involved in handling it and none of the existing computers will be able to solve it. As a result, we consider Dirac Hamiltonian and non-relativistic form for nuclear potential and electron-electron interactions in defining the total molecular Hamiltonian to determine molecular spectroscopic properties. If necessary, corrections due to the Breit interactions to account for the contributions due to exchange of transverse photons among the electrons and lower-order

quantum electrodynamics (QED) effects can be included to improve accuracy of the molecular calculations. However, these higher-order corrections do not contribute significantly in our analyses of the interested molecular properties; hence neglected in this thesis work. Furthermore, we are interested only in the electronic properties of a molecular system. So we freeze the nuclear degrees of freedom in the calculations by invoking Born-Oppenheimer approximation throughout the calculations. Also, it is being considered that interaction among two electrons is itself too much to solve exactly the equation-of-motion of a system. Thus, it is a challenge to take into account Coulomb interactions due to electrons in a molecular system exactly because of which approximated many-body methods are being applied in our analyses. A perturbative approach cannot be useful for us to produce molecular properties with reasonable accuracy. Therefore, we employ an all-order perturbative theory in the RCC method framework to carry out the calculations. For this purpose, we begin with a mean-field approximation in the HF (referred as Dirac-Fock (DF) in the relativistic form) procedure to consider the Coulomb interactions among the electrons as an average potential, and then the residual interactions are treated to all-order perturbation through the RCC methods. In this chapter, we discuss these procedures briefly for the general understanding of calculating molecular properties. We have also performed calculations for a few cases using non-relativistic Hamiltonian, and compared results from both the approximations in order to demonstrate the importance of relativistic effects in the investigated spectroscopic properties.

### 2.2 Born-Oppenheimer approximation

Let us consider a molecule with N number of nuclei and  $N_e$  number of electrons. The total Hamiltonian (in a.u.) of the molecule can, then, be written as

$$H_{tot} = \sum_{A=1}^{N} \frac{P_A^2}{2M_A} + \sum_{i=1}^{N_e} \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{i,A} \frac{Z_A e^2}{|\mathbf{R}_A - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.1)

$$= -\sum_{i=1}^{N} \frac{\nabla_{A}^{2}}{2M_{I}} - \sum_{i=1}^{N_{e}} \frac{\nabla_{i}^{2}}{2} + \frac{1}{2} \sum_{A \neq B} \frac{Z_{A} Z_{B}}{\mathbf{R}_{A} - \mathbf{R}_{B}} - \sum_{i,A} \frac{Z_{A}}{\mathbf{R}_{A} - \mathbf{r}_{i}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \quad (2.2)$$

$$= T_N(\mathbf{R}) + T_e(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{rR}) + V_{ee}(\mathbf{r})$$
(2.3)

where the first two terms are the kinetic energy operators of the nuclei and electrons respectively, the third term accounts for the nucleus-nucleus Coulomb repulsions, the fourth corresponds to the electron-nucleus Coulomb interactions and the last term involves the electron-electron repulsive Coulomb interactions. In Eq. (2.1),  $P_A$  and  $p_i$  denote the momentum operators of  $A^{th}$ nucleus and  $i^{th}$  electron, respectively,  $M_A$  and  $m_i$  are masses of  $I^{th}$  nucleus and electron, respectively. Nuclear coordinates are defined as **R** and electronic coordinates are given as **r** and  $Z_A$  is the atomic number of the  $A^{th}$  nuclei.

The Hamiltonian in Eq. (2.1) satisfies the Schrödinger equation

$$H_{tot}|\Psi(\mathbf{r},\mathbf{R})\rangle = E_{tot}|\Psi(\mathbf{r},\mathbf{R})\rangle,$$
(2.4)

where the wave function  $|\Psi(\mathbf{r}, \mathbf{R})\rangle$  carries information about the nuclei and electrons of a molecule. Since we shall be dealing with mostly diatomic molecules, number of nuclei present in our case is two and for some situations it is three where we work with triatomic molecules. Solving the Schrödinger equation for the total wave function with the above Hamiltonian is still a cumbersome job as it includes  $3(N + N_e)$  coordinates. Since we are interested only in electronic properties in this study, we invoke a pragmatic approximation, known as Born-Oppenheimer (BO) approximation [1], to decouple electronic and nuclear wave functions. The basic idea behind this approximation lies in the fact that the nuclei are heavier than the electrons by three orders of magnitude, and thus there exists a strong separation of time scales between the nuclear and electronic motions. Therefore, nuclear positions can be regarded as fixed (clamped-nuclei) and nuclear wave functions are considered to be highly localized to the nuclei positions. This can be exploited by using the quasi-separable ansätz

$$|\Psi\rangle = |\Psi_N(\mathbf{R})\rangle \otimes |\Psi_e(\mathbf{r}, \mathbf{R})\rangle.$$
(2.5)

Under the BO approximation, the kinetic energy term of nuclei  $(T_N(\mathbf{R}))$  can be neglected as it is smaller than  $T_e(\mathbf{R})$  by a factor  $\frac{M}{m_e}$ . As the inter-nuclear separation  $\mathbf{R}$  is a constant in BO approximation, the nuclear-nuclear interaction term  $V_{NN}(\mathbf{R})$  is also a constant and can be left out of the electronic Hamiltonian and its contribution can be added later by hand to the calculated properties. Hence, after invoking the BO approximation, the electronic Hamiltonian takes the form

$$H_e^{BO}(\mathbf{r}, \mathbf{R}) = T_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}), \qquad (2.6)$$

which follows the electronic Schrödinger equation

$$H_e^{BO}|\Psi_e(\mathbf{r},\mathbf{R})\rangle = E_e|\Psi_e(\mathbf{r},\mathbf{R})\rangle, \qquad (2.7)$$

where  $E_e$  is the eigenvalue of  $H_e^{BO}$  and it gives the total molecular energy when added with  $V_{NN}$ . Eq. (2.7) represents the clamped-nuclei Schrödinger equation.

In the BO approximation, electrons are assumed to be pulled towards the heavier nucleus with almost no relaxation time and thus follow the nuclear motions adiabatically. There can be systems with the presence of non-adiabatic effects which do not allow electrons to move in this instantaneous manner. This adiabatic approximation is valid and widely employed in most of the systems of our interest.

# 2.3 Challenges involved with $H_e^{BO}$

Let us consider the simplest molecular ion, the  $H_2^+$  ion. The electronic Hamiltonian under BO approximation can be expressed as

$$H_e^{BO} = \frac{p^2}{2m} - \sum_{I=1}^2 \frac{1}{|\mathbf{R}_I - \mathbf{r}|},$$
(2.8)

where the first term denotes the kinetic energy of the electron and the second term corresponds to the nucleus electron attractive potential.  $R_I$  and r represent the nuclear and electronic positions, respectively. It can be easily shown that exact solution of the above equation can be easily obtained in the analytical approach, but one needs to choose a suitable coordinate system (i.e. elliptic coordinate) [2] to achieve this. However, it becomes strenuous when another electron is added to the system; i.e. for the  $H_2$  molecule. The electronic Hamiltonian for the  $H_2$  molecule contains the extra two-body term of electron-electron repulsive Coulomb potential and is given by

$$H_{e}^{BO} = \underbrace{\sum_{i=1}^{2} \frac{p_{i}^{2}}{2m_{i}} - \sum_{i,I=1}^{2} \frac{1}{|\mathbf{R}_{I} - \mathbf{r}_{i}|}}_{h_{1}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}}_{h_{2}}, \qquad (2.9)$$

$$= \sum_{i=1}^{2} h_1(\vec{x}_i) + \frac{1}{2} \sum_{i \neq j} h_2(\vec{x}_i, \vec{x}_j), \qquad (2.10)$$

where  $h_1$  and  $h_2$  represent the one-body and two-body terms respectively with  $\vec{x}_i$ s being the generalised coordinates. Due to the presence of the two-body potential term in Eq. (2.9), the Schrödinger equation cannot be exactly solved for H<sub>2</sub> molecule. For the same reason, exact solution to Schrödinger is not possible for molecules having more electrons. In such scenarios, we need to solve the Schrödinger equation using approximation methods but their solutions should tend towards the exact values for producing accurate theoretical results. The exactness of the results can be assumed by comparing calculated theoretical results with the experimental values of some physical observables.

Since electrons are fermions, the total electronic wave function  $|\Psi\rangle$  for a molecule is a Slater determinant. For example, for the H<sub>2</sub> molecule it can be given by

$$\Psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_1(\vec{x}_2) \\ \phi_2(\vec{x}_1) & \phi_2(\vec{x}_2) \end{vmatrix}$$
(2.11)

where  $\phi_i$ s correspond to the molecular orbitals (MO). It can be generalised to a molecule with  $N_e$  number of electrons. The electronic BO-Hamiltonian of such a molecule in the absence of

any external perturbation can be written in the following form

$$H = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \qquad (2.12)$$

$$=\sum_{i=1}^{N_e} \underbrace{\left(-\frac{\nabla_i^2}{2} - \sum_I \frac{Z_I}{|\mathbf{R}_{\mathbf{I}} - \mathbf{r}_{\mathbf{i}}|}\right)}_{h_1(\vec{x}_i)} + \frac{1}{2} \sum_{i \neq j} \underbrace{\frac{1}{|\mathbf{r}_{\mathbf{i}} - \mathbf{r}_{\mathbf{j}}|}}_{h_2(\vec{r}_i, \vec{r}_j)},$$
(2.13)

where all the notations are already defined earlier and we have dropped the suffices from the notation of the electronic Hamiltonian for simplicity. In Eq. (2.12) it is clear that the first two terms are sums of single particle (one-body) operators while the last term is a sum of two electron (two-body) operators. To calculate the molecular ground state energy from the Hamiltonian in Eq. (2.13), we need to evaluate the following integral

$$\langle \Psi | H | \Psi \rangle = \langle \Psi | \sum_{i} h_1(\vec{x}_i) | \Psi \rangle + \langle \Psi | \frac{1}{2} \sum_{i \neq j} h_2(\vec{x}_i, \vec{x}_j) | \Psi \rangle.$$
(2.14)

In this case the total electronic wave function is a Slater determinant composed of different molecular orbital with dimension of the determinant as  $N_e \times N_e$ ; i.e.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_1(\vec{x}_2) & \cdots & \phi_1(\vec{x}_{N_e}) \\ \phi_2(\vec{x}_1) & \phi_2(\vec{x}_2) & \cdots & \phi_2(\vec{x}_{N_e}) \\ \vdots & \ddots & \vdots \\ \phi_{N_e}(\vec{x}_1) & \phi_{N_e}(\vec{x}_2) & \cdots & \phi_{N_e}(\vec{x}_{N_e}) \end{vmatrix}.$$
(2.15)

To evaluate the one-body integral  $\langle \Psi | \sum_i h_1(\vec{x}_i) | \Psi \rangle$  and the two-body integral  $\langle \Psi | \frac{1}{2} \sum_{i \neq j} h_2(\vec{x}_i, \vec{x}_j) | \Psi \rangle$ in Eq. (2.14), there exists a convenient recipe to boil down the integrals containing the Slater determinant wave function to sum of integrals involving individual molecular orbitals. These set of rules are called *Slater-Condon* (SC) rules [3, 4] and are outlined below

(i) For a one-body operator F in an N particle system defined as a sum of individual operators,

 $F = \sum_{i=1}^{N} f(\vec{x}_i)$ , it can follow

an

(a) 
$$\langle \Psi | \sum_{i} f(\vec{x}_{i}) | \Psi \rangle = \sum_{i} \langle \phi_{i} | f(\vec{x}_{i}) | \phi_{i} \rangle,$$
 (2.16)

(b) 
$$\langle \Psi | \sum_{i} f(\vec{x}_{i}) | \Psi_{i}^{a} \rangle = \langle \phi_{i} | f(\vec{x}_{i}) | \phi_{a} \rangle,$$
 (2.17)

and (c) 
$$\langle \Psi | \sum_{i} f(\vec{x}_{i}) | \Psi_{i,j,\cdots}^{a,b,\cdots} \rangle = 0.$$
 (2.18)

(ii) For a two-body operator (G) in an N particle system, defined as  $G = \frac{1}{2} \sum_{i \neq j} g(\vec{x}_i, \vec{x}_j)$ , we have

$$(a) \quad \langle \Psi | \frac{1}{2} \sum_{i,j} g(\vec{x}_{i}, \vec{x}_{j}) | \Psi \rangle = \frac{1}{2} \sum_{i,j} (\langle \phi_{i} \phi_{j} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{i} \phi_{j} \rangle - \langle \phi_{j} \phi_{i} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{i} \phi_{j} \rangle) (2.19)$$

$$(b) \quad \langle \Psi | \frac{1}{2} \sum_{i \neq j} g(\vec{x}_{i}, \vec{x}_{j}) | \Psi_{i}^{a} \rangle = \sum_{j} (\langle \phi_{i} \phi_{j} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{a} \phi_{j} \rangle - \langle \phi_{i} \phi_{j} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{j} \phi_{a} \rangle) (2.20)$$

$$(c) \quad \langle \Psi | \frac{1}{2} \sum_{i \neq j} g(\vec{x}_{i}, \vec{x}_{j}) | \Psi_{i,j}^{a,b} \rangle = \langle \phi_{i} \phi_{j} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{a} \phi_{b} \rangle - \langle \phi_{i} \phi_{j} | g(\vec{x}_{i}, \vec{x}_{j}) | \phi_{b} \phi_{a} \rangle, \quad (2.21)$$

$$(d) \quad \langle \Psi | \frac{1}{2} \sum_{i \neq j} g(\vec{x}_{i}, \vec{x}_{j}) | \Psi_{i,j,\cdots}^{a,b,\cdots} \rangle = 0. \quad (2.22)$$

In the following discussions, we shall make use of these relations.

Applying the SC rules in Eq. (2.14), the integral takes the form

$$\langle \Psi | \sum_{i} h_{1}(\vec{x}_{i}) + \frac{1}{2} \sum_{i \neq j} h_{2}(\vec{x}_{i}, \vec{x}_{j}) | \Psi \rangle = \sum_{i} \langle \phi_{i} | h_{1}(\vec{x}_{i}) | \phi_{i} \rangle + \frac{1}{2} \sum_{i,j} \left( \langle \phi_{i} \phi_{j} | h_{2}(\vec{x}_{i}, \vec{x}_{j}) | \phi_{i} \phi_{j} \rangle - \langle \phi_{j} \phi_{i} | h_{2}(\vec{x}_{i}, \vec{x}_{j}) | \phi_{i} \phi_{j} \rangle \right).$$

$$(2.23)$$

As the molecular orbitals are constructed from finite number of atomic basis functions, energy obtained from solving Eq. (2.23) iteratively does not guarantee to yield the ground state energy. Here comes the necessity to apply the variational principle to Eq. (2.23) in order to obtain the ground state energy. In the next section we shall introduce the variational principle and the variational method to obtain the ground state wave function and energy of a molecule.

## 2.4 Variational method

The variational method is a way to obtain the lowest energy eigenstate (ground state) of a system for which we do not know the exact wave function. This method employs the variational principle to achieve the lowest energy eigenstate from an approximate (trial) wave function. [5]

Assume that H is the Hamiltonian of such a system and  $|\Psi_0\rangle$  is the exact (but unknown) ground state wave function. Then,

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \qquad (2.24)$$

where  $E_0$  is the exact ground state energy of the system given by

$$E_0 = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}.$$
(2.25)

If  $|\Psi'\rangle$  is an arbitrary wave function and E is the corresponding energy

$$E = \frac{\langle \Psi' | H | \Psi' \rangle}{\langle \Psi' | \Psi' \rangle},\tag{2.26}$$

then the variational principle states that  $E \geq E_0$ .

**Proof:** As the exact unknown eigenfunctions  $(|\psi_n\rangle)$  form a complete set, the approximate state can be written in terms of linear combination of them

$$|\Psi'\rangle = \sum_{n} C_n |\psi_n\rangle, \qquad (2.27)$$

with 
$$H|\psi_n\rangle = E_n|\psi_n\rangle$$
 (2.28)

Assume that the eigenfunctions are orthonormalized:  $\langle \psi_m | \psi_n \rangle = \delta_{mn}$ .

The normalization of  $|\Psi\rangle$  leads to

$$\langle \Psi' | \Psi' \rangle = 1 \tag{2.29}$$

$$\Rightarrow \sum_{m,n} C_m^* C_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} = 1$$
(2.30)

$$\Rightarrow \sum_{n} |C_n^2| = 1. \tag{2.31}$$

The expectation value of the Hamiltonian in the approximate state is

$$\langle \Psi'|H|\Psi'\rangle = E = \sum_{m,n} C_m^* C_n \langle \psi_m | H | \psi_n \rangle$$
 (2.32)

$$= \sum_{m,n} C_m^* C_n E_n \langle \psi_m | \psi_n \rangle$$
(2.33)

$$= \sum_{n} E_n |C_n^2|. \tag{2.34}$$

But, by definition, the energy of the ground state  $(E_0)$  is the lowest. Therefore,  $E_0 \leq E_n$ . Invoking this in Eq. (2.34) we get

$$\langle \Psi' | H | \Psi' \rangle \ge E_0 \sum_n |C_n^2| \tag{2.35}$$

$$\langle \Psi' | H | \Psi' \rangle \stackrel{=}{\geq} E_0. \tag{2.36}$$

Therefore, from Eq. (2.36) it is evident that the energy expectation value using the approximate wave function must be minimized, with respect to the variation of some parameter, to obtain the ground state wave function.

### 2.5 The HF method

The variational technique we shall follow does not include minimization of energy with respect to coefficients of the basis functions, instead we conduct the minimization with respect to the basis functions themselves. In this variational approach, we assume that the functional differentiation of the expectation value in change in Eq. (2.23) due to any infinitesimal change in  $|\phi\rangle$  is zero,

i.e.,

for 
$$|\phi_k\rangle \to |\phi_k\rangle + \delta |\phi_k\rangle$$
,  $\delta \langle \Psi | H | \Psi \rangle = 0.$  (2.37)

Moreover, we demand that the  $|\phi_i\rangle$ 's would remain orthogonal throughout the process of minimization

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}. \tag{2.38}$$

If both the conditions in Eq. (2.37) and Eq. (2.38) are satisfied, we can connect the two equations through Lagrange's undetermined multipliers  $(\lambda_{ij})$ 

$$\delta F = \delta \left[ \langle \Psi | H | \Psi \rangle - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \right] = 0, \qquad (2.39)$$

$$\delta\left[\langle\Psi|\sum_{i}h_{1}(\vec{x}_{i})+\frac{1}{2}\sum_{i\neq j}h_{2}(\vec{x}_{i},\vec{x}_{j})|\Psi\rangle-\sum_{ij}\lambda_{ij}(\langle\phi_{i}|\phi_{j}\rangle-\delta_{ij})\right] = 0.$$
(2.40)

In Eq. (2.39), we set  $F = \langle \Psi | H | \Psi \rangle - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij})$ . It is evident from Eq. (2.40) that the number of Lagrange's undetermined multipliers is  $N_e^2$ . We demand that first-order derivatives of Eq. (2.40) with respect to all the  $\lambda_{ij}$ 's vanish. At first, we shall look at the variation of the one-body term in Eq. (2.40) due to any infinitesimal change in orbital  $|\phi_k\rangle$ 

$$\delta\langle\Psi|\sum_{i}h_{1}(\vec{x}_{i})|\Psi\rangle = \delta\left[\sum_{i}\langle\phi_{i}|h_{1}(\vec{x}_{i})|\phi_{i}\rangle\right]$$
(2.41)

$$= \langle \delta \phi_k | h_1(\vec{x}_i) | \phi_k \rangle + \langle \phi_k | h_1(\vec{x}_i) | \delta \phi_k \rangle$$
(2.42)

$$= \langle \delta \phi_k | h_1(\vec{x}_i) | \phi_k \rangle + \langle \delta \phi_k | h_1(\vec{x}_i) | \phi_k \rangle^*, \qquad (2.43)$$
where the symbol '\*' in the second term is used to denote hermitian conjugate (h.c.). Similarly, the variation of the two-body term in Eq. (2.40) can also be simplified as

$$\delta \langle \Psi | \frac{1}{2} \sum_{i \neq j} h_2(\vec{x}_i, \vec{x}_j) | \Psi \rangle = \delta \frac{1}{2} \sum_{i \neq j} (\langle \phi_i \phi_j | h_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | h_2 | \phi_i \phi_j \rangle)$$

$$= \frac{1}{2} \sum_i (\langle \phi_i \delta \phi_k | h_2 | \phi_i \phi_k \rangle + \langle \phi_i \phi_k | h_2 | \phi_i \delta \phi_k \rangle - \langle \delta \phi_k \phi_i | h_2 | \phi_i \phi_k \rangle)$$

$$- \langle \phi_k \phi_i | h_2 | \phi_i \delta \phi_k \rangle) + \frac{1}{2} \sum_j (\langle \delta \phi_k \phi_j | h_2 | \phi_k \phi_j \rangle + \langle \phi_k \phi_j | h_2 | \delta \phi_k \phi_j \rangle)$$

$$- \langle \phi_j \delta \phi_k | h_2 | \phi_k \phi_j \rangle - \langle \phi_j \phi_k | h_2 | \delta \phi_k \phi_j \rangle) \qquad (2.44)$$

Invoking the identity

$$\langle \phi_1 \phi_2 | A | \phi_3 \phi_4 \rangle = \langle \phi_2 \phi_1 | A | \phi_4 \phi_3 \rangle$$

in Eq. (2.44) for any two-body hermitian operator A, we get

$$\delta \langle \Psi | \frac{1}{2} \sum_{i \neq j} h_2(\vec{x}_i, \vec{x}_j) | \Psi \rangle = \sum_i (\langle \phi_i \delta \phi_k | h_2 | \phi_i \phi_k \rangle + \langle \phi_i \delta \phi_k | h_2 | \phi_i \phi_k \rangle - \langle \delta \phi_k \phi_i | h_2 | \phi_i \phi_k \rangle - \langle \delta \phi_k \phi_i | h_2 | \phi_k \phi_i \rangle), \qquad (2.45)$$

where we exploited the dummy nature of the indices i and j in Eq. (2.45). Combining Eq. (2.43) and Eq. (2.45) we can write

$$\delta F = \langle \delta \phi_k | h_1 | \phi_k \rangle + \langle \delta \phi_k | h_1 | \phi_k \rangle^* + \sum_i (\langle \phi_i \delta \phi_k | h_2 | \phi_i \phi_k \rangle + \langle \phi_i \delta \phi_k | h_2 | \phi_i \phi_k \rangle^* - \langle \delta \phi_k \phi_i | h_2 | \phi_i \phi_k \rangle - \langle \delta \phi_k \phi_i | h_2 | \phi_i \phi_k \rangle^*) - \sum_i (\lambda_{ik} \langle \delta \phi_k | \phi_i \rangle^* + \lambda_{ki} \langle \delta \phi_k | \phi_i \rangle).$$
(2.46)

Terms in Eq. (2.46) written in their integral form would read, for example,

$$\langle \delta \phi_k \phi_i | h_2 | \phi_i \phi_k \rangle = \int \int \delta \phi_k^*(\vec{x}_1) \phi_i^*(\vec{x}_2) h_2(\vec{x}_1, \vec{x}_2) \phi_i(\vec{x}_1) \phi_k(\vec{x}_2) d\vec{x}_1 d\vec{x}_2.$$
(2.47)

Now, we shall evaluate the variation of F with respect to  $|\phi_k\rangle^*$ ,

$$\frac{\delta F}{\delta \phi_k^*} = \delta \phi_k^* h_1 \phi_k(\vec{x}_1) + \sum_i \left[ \int \phi_i^*(\vec{x}_2) h_2(\vec{x}_1, \vec{x}_2) \phi_i(\vec{x}_2) \phi_k(\vec{x}_1) d\vec{x}_2 - \int \phi_i^*(\vec{x}_2) h_2(\vec{x}_1, \vec{x}_2) \phi_k(\vec{x}_2) \phi_i(\vec{x}_1) d\vec{x}_2 \right] \\
- \sum_i \lambda_{ki} \phi_i = 0,$$
(2.48)

which can be written as

$$\left[h_1 + \sum_i (J_i - K_i)\right]\phi_k = \sum_i \lambda_{ki}\phi_i,$$
(2.49)

where the  $J_i$  is the direct term and  $K_i$  is the exchange term and defined as

$$J_i \phi_k(\vec{x}_1) = \left[ \int \phi_i(\vec{x}_2)^* h_2(\vec{x}_1, \vec{x}_2) \phi_i(\vec{x}_2) d\vec{x}_2 \right] \phi_k(\vec{x}_1),$$
(2.50)

$$K_i \phi_k(\vec{x}_1) = \left[ \int \phi_i^*(\vec{x}_2) h_2(\vec{x}_1, \vec{x}_2) \phi_k(\vec{x}_2) d\vec{x}_2 \right] \phi_k(\vec{x}_1).$$
(2.51)

From Eq. (2.50) it is evident that the direct term is the classical Coulomb interaction averaged over  $\phi_i$  and the exchange term is an integral operator with no classical analogue and is a result of the antisymmetric nature of the wave function.

The left hand side of Eq. (2.49) is called the Fock operator:  $\mathcal{F} = h_1 + \sum_i (J_i - K_i)$ . Then Eq. (2.49) takes the form

$$\mathcal{F}\phi_k = \sum_i \lambda_{ki}\phi_i. \tag{2.52}$$

Several solutions to Eq. (2.52) are possible for different choices of  $\lambda_{ki}$ . However, we have the liberty to focus on those values of  $\lambda_{ki}$  which satisfy the following condition

$$\lambda_{ki} = \delta_{ki} \epsilon_k, \tag{2.53}$$

where  $\epsilon_k$  is a new Lagrange's multiplier. With this special choice of  $\lambda_{ki}$ , Eq. (2.52) assumes the

following form

$$\mathcal{F}\phi_k = \epsilon_k \phi_k. \tag{2.54}$$

Eq. (2.54) is called the HF equation [6] where  $\epsilon_k$ s are the eigenvalues of the Fock operator.

#### 2.5.1 Roothaan's equation

The HF equation can conveniently be written in terms of a mean-field potential  $(V_{HF})$  as follows

$$h_1|\phi_k\rangle + V_{HF}|\phi_k\rangle = \epsilon_k |\phi_k\rangle. \tag{2.55}$$

The HF potential  $V_{HF}$  is given by

$$V_{HF}|\phi_k\rangle = \sum_{i=1}^{N_e} \left[ \langle \phi_i | \frac{1}{r_{12}} | \phi_i \rangle | \phi_k \rangle - \langle \phi_k | \frac{1}{r_{12}} | \phi_i \rangle | \phi_i \rangle \right].$$
(2.56)

In Eq. (2.56), the summation over the orbital indices run from 1 to total number of core electrons  $(N_e)$ , not  $(N_e - 1)$ . However, both the cases would lead to same expression as when i = k, the right hand side of Eq. (2.56) vanishes. The above set of equations are for core orbitals. If we consider a virtual orbital  $|\phi_a\rangle$ ,

$$h_1|\phi_a\rangle + V_{HF}|\phi_a\rangle = \epsilon_a|\phi_a\rangle, \qquad (2.57)$$

$$V_{HF}|\phi_a\rangle = \sum_{i}^{N_e} \left[ \langle \phi_i | \frac{1}{r_{12}} | \phi_i \rangle | \phi_a \rangle - \langle \phi_a | \frac{1}{r_{12}} | \phi_i \rangle | \phi_i \rangle \right]$$
(2.58)

where  $V_{HF}$ , in this case, is a  $V^{N-1}$  potential as discussed above. Under a  $V^{N-1}$  potential an electron experiences a mean potential due to the presence of N-1 electrons. Eq. (2.56) and (2.58) can be combined and written for a generalised orbital  $|\phi_p\rangle$  as

$$h_1|\phi_p\rangle + V_{HF}|\phi_p\rangle = \epsilon_p|\phi_p\rangle, \qquad (2.59)$$

$$V_{HF}|\phi_p\rangle = \sum_{i=1}^{N_e} \left[ \langle \phi_i | \frac{1}{r_{12}} | \phi_i \rangle | \phi_p \rangle - \langle \phi_p | \frac{1}{r_{12}} | \phi_i \rangle | \phi_i \rangle \right].$$
(2.60)

To solve Eq. (2.59), let us write  $\mathcal{F} = t_1 + V_{HF}$ 

$$\mathcal{F}|\phi_p\rangle = \epsilon_p |\phi_p\rangle. \tag{2.61}$$

For atoms, the single particle orbital orbital  $|\phi_p\rangle$  can be written as a linear combination of atomic basis functions  $(|\chi\rangle)$ 

$$|\phi_p\rangle = \sum_n C_{pn} |\chi_n\rangle.$$
(2.62)

Using Eq. (2.62) in Eq. (2.61) we get

$$\mathcal{F}\sum_{n} C_{pn} |\chi_n\rangle = \epsilon_p \sum_{n} C_{pn} |\chi_n\rangle$$
(2.63)

$$\sum_{n} \langle \chi_m | \mathcal{F} | \chi_n \rangle C_{pn} = \epsilon_p \sum_{n} \langle \chi_m | \chi_n \rangle C_{pn}$$
(2.64)

$$\sum_{n} \mathcal{F}_{mn} C_{pn} = \epsilon_p \sum_{n} S_{mn} C_{pn}, \text{ where } \mathcal{F}_{mn} = \sum_{n} \langle \chi_m | \mathcal{F} | \chi_n \rangle, \ S_{mn} = \langle \chi_m | \chi_n \rangle. (2.65)$$

Eq. (2.65) can be written in a matrix form

$$\mathcal{F}C = \epsilon SC \tag{2.66}$$

$$\mathcal{F}S^{-1/2}S^{1/2}C = \epsilon S^{1/2}S^{1/2}C \tag{2.67}$$

$$S^{-1/2}\mathcal{F}S^{-1/2}S^{1/2}C = \epsilon S^{1/2}C \tag{2.68}$$

$$\mathcal{F}'C' = \epsilon C', \tag{2.69}$$

where  $\mathcal{F}' = S^{-1/2} \mathcal{F} S^{-1/2}$  and  $C' = S^{1/2} C$ . Eq. (2.69) is an eigenvalue equation and solved self consistently. This equation is solved for C' and hence C while the information about  $|\chi\rangle$ s are given as inputs. To solve the HF equation in a matrix formulation, one needs to construct the Fock matrix  $\mathcal{F}$  given by

$$\mathcal{F} = h_1 + V_{HF} \tag{2.70}$$

$$\mathcal{F}_{mn} = (h_1)_{mn} + (V_{HF})_{mn}, \tag{2.71}$$

where  $\mathcal{F}_{mn} = \langle \chi_m | \mathcal{F} | \chi_n \rangle$ ,  $(h_1)_{mn} = \langle \chi_m | h_1 | \chi_n \rangle$ , and  $(V_{HF})_{mn} = \langle \chi_m | V_{HF} | \chi_n \rangle$ . Now, we shall simplify Eq. (2.71). We have,

$$V_{HF}|\phi_p\rangle = \sum_{i} \left[ \langle \phi_i | \frac{1}{r_{12}} | \phi_i \rangle | \phi_p \rangle - \langle \phi_i | \frac{1}{r_{12}} | \phi_p \rangle | \phi_i \rangle \right]$$
(2.72)

$$\phi_i \rangle = \sum_n C_{in} |\chi_n \rangle, \ |\phi_p \rangle = \sum_l C_{pl} |\chi_l \rangle.$$
 (2.73)

$$\therefore V_{HF} \sum_{l} C_{pl} |\chi_l\rangle = \sum_{i} \left[ \sum_{kln} C_{in}^* C_{ik} \langle \chi_n | \frac{1}{r_{12}} |\chi_k\rangle C_{pl} |\chi_l\rangle - C_{in}^* C_{pl} \langle \chi_n | \frac{1}{r_{12}} |\chi_l\rangle |\chi_k\rangle C_{ik} \right] (2.74)$$

For a given value of p,

$$\sum_{l} \langle \chi_{m} | V_{HF} | \chi_{l} \rangle C_{l} = \sum_{i} \left( \sum_{kln} C_{l} C_{in}^{*} C_{ik} \langle \chi_{m} \chi_{n} | \frac{1}{r_{12}} | \chi_{k} \chi_{l} \rangle - \sum_{kln} C_{l} C_{in}^{*} C_{ik} \langle \chi_{m} \chi_{n} | \frac{1}{r_{12}} | \chi_{l} \chi_{k} \rangle \right).$$

$$(2.75)$$

For a known value of l,

$$\langle \chi_m | V_{HF} | \chi_l \rangle = \sum_i \left( \sum_{kn} C_{in}^* C_{ik} \langle \chi_m \chi_n | \frac{1}{r_{12}} | \chi_k \chi_l \rangle - \sum_{kn} C_{in}^* C_{ik} \langle \chi_m \chi_n | \frac{1}{r_{12}} | \chi_l \chi_k \rangle \right)$$
(2.76)

$$= \sum_{kn} \rho_{nk} \left( \langle mn | \frac{1}{r_{12}} | kl \rangle - \langle mn | \frac{1}{r_{12}} | lk \rangle \right), \qquad (2.77)$$

where density matrix  $\rho_{nk} = \sum_{i} C_{ik}^* C_{ik}$ , and for simplicity we have used the notation  $|\chi_m\rangle = m$ ,  $|\chi_n\rangle = n$  and so on. We solve the HF equation for these  $\rho$ s. From the density matrix elements we can calculate the coefficients (Cs) and ultimately obtain the HF wave function.

So far, we described the procedure of solving the HF equation for atoms. However the case is slightly different for molecules. Unlike the construction of atomic single particle orbitals, construction of molecular single particle orbitals is a two-fold process. For the molecular case, at first atomic orbitals (AO) are generated from atomic basis functions ( $|\chi\rangle$ s) and thereafter linear combinations of the atomic orbitals construct the molecular orbitals (MO). The process of construction of MOs is as follows

$$|AO_l\rangle = \sum_n C_{ln} |\chi_n\rangle, \qquad (2.78)$$

$$\underbrace{|\phi_p\rangle}_{p^{th}MO} = \sum_l C_{pl}|AO_l\rangle = \sum_l \sum_n C_{pl}C_{ln}|\chi_n\rangle.$$
(2.79)

Using Eq. (2.79) in Eq. (2.61) we get

$$\mathcal{F}\sum_{l}\sum_{n}C_{pl}C_{ln}|\chi_{n}\rangle = \epsilon_{p}\sum_{l}\sum_{n}C_{pl}C_{ln}|\chi_{n}\rangle, \qquad (2.80)$$
$$|\chi_{m}\rangle \text{ on both sides,} \qquad (2.81)$$

and taking inner product with  $|\chi_m\rangle$  on both sides,

$$\sum_{l} \sum_{n} \underbrace{C_{pl}C_{ln}}_{\mathfrak{C}_{pln}} | \underbrace{\langle \chi_m \mathcal{F}\chi_n \rangle}_{\mathcal{F}_{mn}} = \epsilon_p \sum_{l} \sum_{n} \underbrace{C_{pl}C_{ln}}_{\mathfrak{C}_{pln}} \underbrace{\langle \chi_m | \chi_n \rangle}_{S_{mn}}.$$
(2.82)

$$\sum_{l,n} \mathcal{F}_{mn} \mathfrak{C}_{pln} = \epsilon_p \sum_{l,n} \mathfrak{C}_{pln} S_{mn}.$$
(2.83)

In matrix form,

$$\mathcal{F}\mathfrak{C} = \epsilon \mathfrak{C}S. \tag{2.84}$$

Our aim is now to determine the matrix element  $\mathcal{F}_{mn} = (h_1)_{mn} + (V_{HF})_{mn}$ . This requires the knowledge of the matrix element  $V_{HF}$ , which can be determined in the following way. By expanding the MOs using basis functions and inserting in Eq. (2.72), we get

$$V_{HF} \sum_{ln} C_{pl} C_{ln} |\chi_n\rangle = \sum_{i} \left[ \sum_{\alpha\beta} \sum_{qr} \sum_{ln} C^*_{i\alpha} C^*_{\alpha\beta} C_{iq} C_{qr} \langle \chi_\beta | \frac{1}{r_{12}} |\chi_r\rangle C_{pl} C_{ln} |\chi_n\rangle - \sum_{\alpha\beta} \sum_{ln} \sum_{qr} C^*_{i\alpha} C^*_{\alpha\beta} C_{pl} C_{ln} \langle \chi_\beta | \frac{1}{r_{12}} |\chi_n\rangle |C_{iq} C_{qr} |\chi_r\rangle \right].$$

$$(2.85)$$

For a given value of l, Eq. (2.85) takes the form

$$\sum_{n} C_{p}C_{n}\langle\chi_{m}|V_{HF}|\chi_{n}\rangle = \sum_{i} \left[\sum_{\alpha\beta} \sum_{qr} \sum_{n} C_{i\alpha}^{*}C_{\alpha\beta}^{*}C_{iq}C_{qr}\langle\chi_{m}\chi_{\beta}|\frac{1}{r_{12}}|\chi_{r}\chi_{n}\rangle C_{p}C_{n} - \sum_{\alpha\beta} \sum_{qr} \sum_{n} C_{i\alpha}^{*}C_{\alpha\beta}^{*}C_{p}C_{n}\langle\chi_{m}\chi_{\beta}|\frac{1}{r_{12}}|\chi_{n}\chi_{r}\rangle C_{iq}C_{qr}\right].$$
(2.86)

For a known value of p and n, Eq. (2.86) can be expressed as

$$\langle \chi_m | V_{HF} | \chi_n \rangle = \sum_i \left[ \sum_{\alpha\beta} \sum_{qr} C^*_{i\alpha} C^*_{\alpha\beta} C_{iq} C_{qr} \langle \chi_m \chi_\beta | \frac{1}{r_{12}} | \chi_r \chi_n \rangle - \sum_{\alpha\beta} \sum_{qr} C^*_{i\alpha} C^*_{\alpha\beta} C_{iq} C_{qr} \langle \chi_m \chi_\beta | \frac{1}{r_{12}} | \chi_n \chi_r \rangle \right].$$

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### 2.6 The DF method

HF theory is based on the Schrödinger equation which is not invariant under Lorentz transformation. Any theory which does not obey Lorentz invariance is deemed to be incompatible for relativistic calculations, as Lorentz invariance is a necessary condition for the inclusion of special relativity. Therefore, for performing relativistic calculations one needs to undertake a theory which is consistent with special relativity. In 1928, Paul Dirac introduced the Dirac equation which is consistent with both quantum mechanics and special relativity. Dirac equation successfully describes the properties of spin 1/2 massive particles (electrons, quarks). The Dirac equation for a molecular system under Coulomb potential reads

$$H_{DC}|\Psi\rangle = \left[\sum_{i} (\alpha_{i}p_{i} + \beta + V_{i}^{nuc}) + \sum_{i>j} \frac{1}{r_{ij}}\right]|\Psi\rangle = E|\Psi\rangle, \qquad (2.88)$$

where  $H_{DC}$  is the Dirac-Coulomb Hamiltonian,  $\alpha_i$ s and  $\beta$  are four component Dirac matrices:

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \ \beta = \begin{pmatrix} 1_{2 \times 2} & 0 \\ 0 & -1_{2 \times 2} \end{pmatrix},$$
(2.89)

where  $\sigma_i$  is the  $i^{th}$  Pauli spin matrix. A single particle orbital  $|\phi\rangle$  can be written as a fourcomponent one-particle wave function [7]

$$\phi = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} = \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m} \\ iQ_{n\kappa}(r)\chi_{-\kappa m} \end{pmatrix}$$
(2.90)

where  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  correspond to the large component and small component of the single particle orbital wave function, respectively.  $\kappa = -a(j + \frac{1}{2})$ , where  $a = 2(j - l) = \pm 1$  serves as a sign factor (j and l are total and azimuthal angular momentum quantum number, respectively). The spin angular function  $\chi_{\kappa m}$  is given by

$$\chi_{\kappa m} = \frac{1}{\sqrt{2l+1}} \begin{pmatrix} a\sqrt{l+\frac{1}{2}+am} Y_l^{m-1/2} \\ \sqrt{l+\frac{1}{2}-am} Y_l^{m+1/2} \end{pmatrix}.$$
 (2.91)

When a = 1, i.e., j = l + 1/2,

$$\chi_{\kappa m} = \frac{1}{\sqrt{2l+1}} \begin{pmatrix} \sqrt{l+m+\frac{1}{2}} Y_l^{m-1/2} \\ \\ \sqrt{l-m+\frac{1}{2}} Y_l^{m+1/2} \end{pmatrix}.$$
 (2.92)

When a = -1, i.e., j = l - 1/2,

$$\chi_{\kappa m} = -\frac{1}{\sqrt{2l+1}} \begin{pmatrix} \sqrt{l-m+\frac{1}{2}} \ Y_l^{m-1/2} \\ \\ \sqrt{l+m+\frac{1}{2}} \ Y_l^{m+1/2} \end{pmatrix}.$$
 (2.93)

In this relativistic treatment, we use the same form of the mean-field equations but with the relativistic Dirac-Coulomb Hamiltonian with orbitals becoming four-component spinors. As mentioned above, the orbitals can be broken into large (L) and small (S) components in the relativistic approach

$$\phi_i = \begin{pmatrix} \phi^L \\ \phi^S \end{pmatrix}. \tag{2.94}$$

We solve the DF equation for each of these components and find out the coefficients. Therefore, if there exists N coefficients for the non-relativistic case, there would be 2N coefficients in the relativistic scenario. Hence, the computational cost shoots up for the relativistic case.

The Dirac Hamiltonian for a many electron system with a potential V is given by

$$H_D = c(\alpha \cdot p) + \beta mc^2 + V. \tag{2.95}$$

The rest mass subtracted form of the Hamiltonian is

$$H'_D = H_D - mc^2. (2.96)$$

The total energy E becomes

$$E' = E - mc^2. \tag{2.97}$$

The rest mass subtracted time-independent Dirac equation takes the form

$$(V-E)\phi^L + c(\sigma \cdot p)\phi^S = 0 (2.98)$$

and 
$$c(\sigma \cdot p)\phi^L + (V - E - 2mc^2)\phi^S = 0.$$
 (2.99)

Let us expand the large and small components in terms of 2-spinors  $\{\chi^L_\mu, \chi^S_\mu\}$ 

$$\phi^{L} = \sum_{\mu=1}^{N_{L}} \mathbf{a}_{\mu}^{L} \chi_{\mu}^{L}, \ \phi^{S} = \sum_{\mu=1}^{N_{S}} \mathbf{a}_{\mu}^{S} \chi_{\mu}^{S},$$
(2.100)

where  $N_L$  and  $N_S$  need not be the same.

Substituting the values of  $\phi^L$  and  $\phi^S$  from Eq. (2.100) in Eq. (2.98) and Eq. (2.99), we get

$$(V-E)\sum_{\mu=1}^{N_L} \mathbf{a}_{\mu}^L \chi_{\mu}^L + c(\sigma \cdot p)\sum_{\mu=1}^{N_S} \mathbf{a}_{\mu}^S \chi_{\mu}^S = 0, \qquad (2.101)$$

$$c(\sigma \cdot p) \sum_{\mu=1}^{N_L} \mathbf{a}_{\mu}^L \chi_{\mu}^L + (V - E - 2mc^2) \sum_{\mu=1}^{N_S} \mathbf{a}_{\mu}^S \chi_{\mu}^S = 0.$$
 (2.102)

Eq. (2.101) and (2.102) can together be written in the following matrix form after taking the inner product with the matrix  $\sum_{\nu} (\chi_{\nu}^L \chi_{\nu}^S)$ 

$$\begin{pmatrix} V^{LL} - ES^{LL} & c\Pi^{LS} \\ c\Pi^{SL} & V^{SS} - (E + 2mc^2)S^{SS} \end{pmatrix} \begin{pmatrix} a^L \\ a^S \end{pmatrix} = 0,$$
(2.103)

where the elements of  $V^{LL}$ ,  $V^{SS}$ ,  $\Pi^{LS}$ ,  $\Pi^{SL}$ ,  $S^{LL}$ , and  $S^{SS}$  matrices are given by  $V^{LL}_{\mu\nu} = \langle \chi^L_{\mu} | V | \chi^L_{\nu} \rangle$ ,  $V^{SS}_{\mu\nu} = \langle \chi^S_{\mu} | V | \chi^S_{\nu} \rangle$ ,  $\Pi^{LS}_{\mu\nu} = \langle \chi^L_{\mu} | \sigma \cdot p | \chi^S_{\nu} \rangle$ ,  $\Pi^{SL}_{\mu\nu} = \langle \chi^S_{\mu} | \sigma \cdot p | \chi^L_{\nu} \rangle$ ,  $S^{LL}_{\mu\nu} = \langle \chi^L_{\mu} | \chi^L_{\nu} \rangle$ , and  $S^{SS}_{\mu\nu} = \langle \chi^S_{\mu} | \chi^S_{\nu} \rangle$ , respectively. It should be noted that  $\Pi^{LS}_{\mu\nu} = \Pi^{SL^{\dagger}}_{\nu\mu}$ , so that

$$\Pi = \begin{pmatrix} 0 & \Pi^{LS} \\ \Pi^{SL} & 0 \end{pmatrix}$$
(2.104)

is a Hermitian matrix. Now, we have obtained a two-body integrals in a 2- spinor form like

$$\langle p^{L}q^{L}|\frac{1}{r_{12}}|r^{L}s^{L}\rangle = \sum_{\mu\nu\kappa\lambda} C^{*L}_{\mu p} C^{*L}_{\nu q} C^{L}_{\kappa r} C^{L}_{\lambda s} \langle \chi^{L}_{\mu} \chi^{L}_{\nu}|\frac{1}{r_{12}}|\chi^{L}_{\kappa} \chi^{L}_{\lambda}\rangle, \qquad (2.105)$$

where we have followed the notation:  $|\phi_p\rangle = |p\rangle$ . Other combinations also holds similar kind of expressions. Here, we shall introduce the density matrix P given by

$$P = \begin{pmatrix} P^{LL} & P^{LS} \\ P^{SL} & P^{SS} \end{pmatrix}, \qquad (2.106)$$

where  $P^{LL} = C_L^* C_L$  and so on.

In the relativistic case, the Fock matrix F is given by

$$F = \begin{pmatrix} F^{LL} & F^{LS} \\ F^{SL} & F^{SS} \end{pmatrix}$$
(2.107)

with the components are given by

$$F_{\mu\nu}^{LL} = V_{\mu\nu}^{LL} + \sum_{\kappa\lambda}^{LL} P_{\kappa\lambda}^{LL} [\langle \chi_{\mu}^{L} \chi_{\nu}^{L} | \frac{1}{r_{12}} | \chi_{\kappa}^{L} \chi_{\lambda}^{L} \rangle - \langle \chi_{\mu}^{L} \chi_{\nu}^{L} | \frac{1}{r_{12}} | \chi_{\lambda}^{L} \chi_{\kappa}^{L} \rangle] + \sum_{\kappa\lambda} P_{\kappa\lambda}^{SS} [\langle \chi_{\mu}^{L} \chi_{\nu}^{L} | \frac{1}{r_{12}} | \chi_{\kappa}^{S} \chi_{\lambda}^{S} \rangle],$$

$$F_{\mu\nu}^{LS} = F_{\mu\nu}^{SL} = c \Pi_{\mu\nu}^{LS} - \sum_{\kappa\lambda} [P_{\kappa\lambda}^{SL} \langle \chi_{\mu}^{L} \chi_{\nu}^{S} | \frac{1}{r_{12}} | \chi_{\kappa}^{S} \chi_{\lambda}^{L} \rangle] \text{ and}$$

$$F_{\mu\nu}^{SS} = V_{\mu\nu}^{SS} - 2c^{2} S_{\mu\nu}^{SS} + \sum_{\kappa\lambda} P_{\kappa\lambda}^{LL} \langle \chi_{\mu}^{S} \chi_{\nu}^{S} | \frac{1}{r_{12}} | \chi_{\kappa}^{L} \chi_{\lambda}^{L} \rangle + \sum_{\kappa\lambda} P_{\kappa\lambda}^{SS} [\langle \chi_{\mu}^{S} \chi_{\nu}^{S} | \frac{1}{r_{12}} | \chi_{\kappa}^{S} \chi_{\lambda}^{S} \rangle - \langle \chi_{\mu}^{S} \chi_{\nu}^{S} | \frac{1}{r_{12}} | \chi_{\lambda}^{S} \chi_{\kappa}^{S} \rangle].$$

Therefore, in the matrix representation, as mentioned in Eq. (2.108), the DF equation resembles its non-relativistic form, i.e.

$$FC = \epsilon SC. \tag{2.109}$$

# 2.7 Kinetic balance condition

Earlier efforts to solve the DF equations sometimes did not lead to convergence to a lowest bound state. [8] The obtained energy often came out to be very low due to the negative energy continuum. The root of this problem lies in the fact that each of the four components of the spinor was permitted to vary independently, which basically means that each component used to be treated with its corresponding independent basis without paying attention to the interdependence of the large and small components of an orbital. This hurdle was finally overcome by inspecting the non-relativistic limit of the Dirac equation, and establishing the relation between the small and large components. This relation is known as the "kinetic balance" condition (KBC) [9].

**Derivation of KBC:** The matrix equation in Eq. (2.103) can be written as a sum of two coupled matrix equations

$$(V^{LL} - ES^{LL})a^{L}c\Pi^{LS}a^{S} = 0 (2.110)$$

and 
$$c\Pi^{SL} \mathbf{a}^L + [V^{SS} - (E + 2mc^2)S^{SS}]\mathbf{a}^{SS} = 0.$$
 (2.111)

Our objective is to find the solutions for energies above the negative energy continuum limit, i.e. for  $E > -2mc^2$ . In most of the cases  $V^{SS}$  is negative definite for atoms or molecules. The two aforementioned conditions of  $E > -2mc^2$  and  $V^{SS} < 0$  together allow to invert the matrix in square bracket in Eq. (2.111). This gives

$$\mathbf{a}^{S} = [(E + 2mc^{2})S^{SS} - V^{SS}]^{-1}c\Pi^{SL}\mathbf{a}^{L}.$$
(2.112)

Now we eliminate the small component expansion coefficient from Eq. (2.110)

$$(V^{LL} - ES^{LL})\mathbf{a}^{L} + c\Pi^{LS}[(E + 2mc^{2})S^{SS} - V^{SS}]^{-1}c\Pi^{SL}\mathbf{a}^{L} = 0.$$
(2.113)

Using the relation for any two matrices A and B

$$(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1},$$
(2.114)

we can expand the square bracket term in Eq. (2.113) where we set  $A = 2mc^2 S^{SS}$  and  $B = V^{SS} - ES^{SS}$ . Thus we rewrite Eq. (2.113) as

$$(V^{LL} - ES^{LL})a^{L} + \frac{1}{2m}\Pi^{LS} \{ [S^{SS}]^{-1} + [S^{SS}]^{-1} (V^{SS} - ES^{SS}) [(E + 2mc^{2})S^{SS} - V^{SS}]^{-1} \} \Pi^{SL} a^{L} = 0$$

Keeping terms of order  $c^0$  in the left hand side and order  $c^{-2}$  or lower in the right hand side of the equation, we get

$$[V^{LL} - ES^{LL} + \frac{1}{2m}\Pi^{LS}[S^{SS}]^{-1}\Pi^{SL}]a^{L} = \frac{1}{2m}\Pi^{LS}[S^{SS}]^{-1}(V^{SS} - ES^{SS})[V^{SS} - (E + 2mc^{2})S^{SS}]^{-1}\Pi^{SL}$$

With the application of the non-relativistic limit  $c \to \infty$ , the right hand side of the above equation vanishes and we are left with

$$[V^{LL} - ES^{LL} + \frac{1}{2m}\Pi^{LS}[S^{SS}]^{-1}\Pi^{SL}]a^{L} = 0.$$
(2.115)

Now drawing analogy with the non-relativistic case [note that for non-relativistic case the kinetic energy operator  $T = \frac{1}{2m} (\sigma \cdot p) (\sigma \cdot p)$ ], we can claim that the third term in the left hand side of the equation correspond to the kinetic energy operator, T, expressed as

$$T = \frac{1}{2m} \Pi^{LS} [S^{SS}]^{-1} \Pi^{SL}.$$
 (2.116)

The matrix element of  $T^{LL}$  in Eq. (2.116) can explicitly be written as

$$T_{\mu\nu}^{LL} = -\frac{\hbar^2}{2m} \sum_{\kappa\lambda} \langle \chi_{\mu}^L | \sigma \cdot \nabla | \chi_{\kappa}^S \rangle \underbrace{\langle \chi_{\kappa}^S | [S^{SS}]^{-1} | \chi_{\lambda}^S \rangle}_{=[S^{SS}]_{\kappa\lambda}^{-1}} \langle \chi_{\lambda}^S | \sigma \cdot \nabla | \chi_{\nu}^L \rangle \tag{2.117}$$

$$= -\frac{\hbar^2}{2m} \sum_{\kappa\lambda} \langle \chi^L_{\mu} | \sigma \cdot \nabla | \underbrace{\chi^S_{\kappa}}_{\kappa\lambda} [S^{SS}]^{-1}_{\kappa\lambda} \langle \chi^S_{\lambda} | \sigma \cdot \nabla | \chi^L_{\nu} \rangle.$$
(2.118)

The underlined part of Eq. (2.118) acts as an inner projection operator onto the small component basis space. Therefore, the small component is sometimes called as a mathematical glue connecting the two momentum operators. Under the constraint where small component basis function spans the space of the momentum operators in the large component space,  $\{\sigma \cdot \nabla \chi^L_{\mu}\}$ , the inner projection just becomes the identity and we retrieve the non-relativistic version of Eq. (2.118) as

$$T_{\mu\nu} = -\frac{\hbar^2}{2m} \langle \chi^L_{\mu} | (\sigma \cdot \nabla) (\sigma \cdot \nabla) | \chi^L_{\nu} \rangle = -\frac{\hbar^2}{2m} \langle \chi^L_{\mu} | \nabla^2 | \chi^L_{\nu} \rangle, \qquad (2.119)$$

which resembles the kinetic energy term in a pure non-relativistic framework. Hence, at the outset of performing a relativistic calculation, if we set the constraint

$$\chi^S_\mu = (\sigma \cdot p)\chi^L_\mu, \tag{2.120}$$

we would recover the accurate non-relativistic limit. Under this constraint of the KBC given by Eq. (2.120) solutions would no longer collapse to energies lower than  $-2mc^2$ . Moreover, when calculations are performed with finite basis sets, the common problem of variational collapse [9] appears. This is because the Dirac equation permits negative energy continuum in its energy spectrum which leads to large negative energy of the single particle states during numerical calculations. Application of the KBC resolves the problem of variational collapse, but throws an error of the order of  $c^{-4}$  to the total DF energy [10]. We make use of the KBC in our relativistic calculations.

#### 2.7.1 Brillouin's theorem

**Statement:** For a given HF wave function  $|\Phi_0\rangle$ , the matrix element of the Hamiltonian between the ground state wave function and the singly excited state wave function  $(|\Phi_i^a\rangle)$  vanishes

$$\langle \Phi_0 | H | \Phi_i^a \rangle = 0. \tag{2.121}$$

**Proof:** 

$$\langle \Phi_0 | H | \Phi_i^a \rangle = \langle \phi_i | h_1 | \phi_a \rangle + \sum_j (\langle \phi_i \phi_j | \frac{1}{r_{12}} | \phi_a \phi_j \rangle - \langle \phi_i \phi_j | \frac{1}{r_{12}} | \phi_j \phi_a \rangle).$$
(2.122)

Eq. (2.122) can be written as [11]

$$\langle \Phi_0 | H | \Phi_i^a \rangle = \langle \phi_i | h_1 | \phi_a \rangle + \sum_j (\langle \phi_i | (2J_j - K_j) | \phi_a \rangle), \qquad (2.123)$$

which can be identified as an off-diagonal matrix element  $\langle \phi_i | \mathcal{F} | \phi_a \rangle$  of the Fock matrix. But, the HF wave function  $|\Phi_0\rangle$  was achieved by diagonalizing the Fock matrix. Therefore, for an optimized wave function  $|\Phi_0\rangle$ , the off-diagonal matrix element in Eq. (2.123) is indeed zero. We shall use this fact while calculating wave functions using beyond HF/DF methods.

# 2.8 Electron correlation effects

The underlying approximation in the HF/DF method is that a part of electron-electron interactions is included in the mean-field approach leaving out a gross amount of dynamic electron correlation effects in the calculations. In other words, the interaction between electrons are treated in the HF/DF method in an averaged manner rather than a instantaneous way. For accurate estimate of spectroscopic properties, particularly EDM enhancement factors, in the molecular systems, roles of the neglected residual Coulomb interactions can be crucial. This problem can be understood as follows.

The HF/DF Hamiltonian for a many-body system can be written in a compact form as

$$H_{HF} = \sum_{i} h_1(\vec{x}_i) + \sum_{i} (V_{HF})_i, \qquad (2.124)$$

which is basically a mean-field Hamiltonian and satisfies the following relation

$$H_{HF}|\Phi_0\rangle = E_{HF}|\Phi_0\rangle, \qquad (2.125)$$

where  $|\Phi_0\rangle$  is the mean-field wave function and  $E_{HF}$  is the HF energy.

The actual Hamiltonian of a many-body system is given by

$$H = \sum_{i} h_1(\vec{x}_i) + \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}}$$
(2.126)

$$= \underbrace{\sum_{i} h_{1}(\vec{x}_{i}) + \sum_{i} (V_{HF})_{i}}_{i} + \underbrace{\frac{1}{2} \sum_{ij} \frac{1}{r_{ij}} - \sum_{i} (V_{HF})_{i}}_{ij}$$
(2.127)

$$=H_{HF} = V_{res}$$

$$= H_{HF} + V_{res}, \qquad (2.128)$$

where  $V_{res}$  is called the residual Coulomb potential. From Eq. (2.128) we can see that the total Hamiltonian is comprised of the HF Hamiltonian along with the residual Coulomb potential. This means that the HF method does not account for  $V_{res}$ , which is a part of the actual Hamiltonian. The physical effects that arise due to this residual Coulomb interaction are referred to as electron correlation effects, which are beyond the reach of the mean-field calculations.

The actual energy of a state can be obtained using the equation

$$H|\Psi\rangle = E|\Psi\rangle,\tag{2.129}$$

where  $|\Psi\rangle$  is the total wave function the many-body system. The actual quantity that is calculated using many-body methods is  $E_{corr} = E - E_{HF}$ , defined as the correlation energy, as  $E_{HF}$ can be evaluated with the knowledge of HF/DF wave function. The commonly employed manybody methods for molecular calculations are the many-body perturbation theory, configuration interaction (CI) method, CC method etc. and their relativistic counterparts.

### 2.9 Many-body perturbation theory

Many-body perturbation theory (MBPT) is an another tool to take into account the electron correlation effects perturbatively. In MBPT method the residual Coulomb potential,  $V_{res}$ , as

defined in Eq. (2.127) is treated as perturbation. The MBPT wave function is written as

$$|\Psi\rangle_{MBPT} = |\Phi_0^{(0)}\rangle + |\Phi_0^{(1)}\rangle + |\Phi_0^{(2)}\rangle + \cdots, \qquad (2.130)$$

where  $|\Phi_0^{(i)}\rangle$  is the  $i^{th}$  order correction to the HF/DF wave function due to the perturbation  $V_{res}$ with  $|\Phi_0^{(0)}\rangle = |\Phi_0\rangle$  and  $|\Phi_0^{(n)}\rangle$ . Some of the popular MBPT theories include Rayleigh-Schrödinger perturbation theory, Brillouin-Wigner perturbation theory, Moller-Plesset perturbation theory etc.. Relativistic MBPT techniques use the Dirac-Coulomb Hamiltonian instead of the nonrelativistic Hamiltonian and the wave function becomes a four-component one.

## 2.10 CI method

CI method is one of the many-body theories that takes into account electron correlation effects to all orders. The CI wave function of a molecule with N electrons can be written as a linear combination of Slater determinants made of any occupation of HF orbitals. Let us start with the simplest configuration of a CI wave function which is a linear combination of two such Slater determinants

$$|\Psi\rangle = c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle, \qquad (2.131)$$

where  $c_1$  and  $c_2$  are two unknown real coefficients which we have to solve for and  $|\Phi_1\rangle$  and  $|\Phi_2\rangle$ are known and they follow the orthonormal condition

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij}, \tag{2.132}$$

i.e.,  $\langle \Phi_1 | \Phi_2 \rangle = 0$ . Therefore the energy functional (F') that has to minimized is

$$F' = \langle \Psi | H | \Psi \rangle - E \langle \Psi | \Psi \rangle.$$
(2.133)

First term in the left hand side of Eq. (2.133) can be elaborated as

$$\langle \Psi | H | \Psi \rangle = (c_1 \langle \Phi_1 | + c_2 \langle \Phi_2 |) H(c_1 | \Phi_1 \rangle + c_2 | \phi_2 \rangle)$$
(2.134)

$$= c_1^2 \langle \Phi_1 | H | \phi_1 \rangle + c_1 c_2 \langle \Phi_1 | H | \Phi_2 \rangle + c_1 c_2 \langle \Phi_2 | H | \Phi_1 \rangle + c_2^2 \langle \Phi_2 | H | \phi_2 \rangle$$
(2.135)

$$= c_1^2 \langle \Phi_1 | H | \phi_1 \rangle + 2c_1 c_2 \langle \Phi_1 | H | \Phi_2 \rangle + c_2^2 \langle \Phi_2 | H | \phi_2 \rangle, \text{ [as } H \text{ is Hermitian] (2.136)}$$

$$= c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}, (2.137)$$

where  $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$ . Now applying the variational principle (i.e.  $\frac{\delta F'}{\delta c_i} = 0$ ) to Eq. (2.133) we get

$$\frac{\delta F'}{\delta c_1} = 2c_1 H_{11} + 2c_2 H_{12} - 2c_1 E = 0, \qquad (2.138)$$

$$\Rightarrow c_1 H_{11} + c_2 H_{12} = c_1 E \tag{2.139}$$

$$\frac{\delta F'}{\delta c_2} = 2c_1 H_{12} + 2c_2 H_{22} - 2c_2 E \qquad (2.140)$$

$$\Rightarrow c_1 H_{12} + c_2 H_{22} = c_2 E. \tag{2.141}$$

Eq. (2.139) and Eq. (2.141) can conveniently be written in a matrix form

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \qquad (2.142)$$

which is actually an eigenvalue equation. One needs to solve this matrix equation to find the unknown coefficients  $c_1$  and  $c_2$ .

The above exercise can be extended to any number of configurations and in general Eq. (2.142) takes the form

$$HC = EC. (2.143)$$

The generalised CI wave function is expressed as

$$|\Psi\rangle_{CI} = c_0|\Phi_0\rangle + \sum_{i,a} c_i^a |\Phi_i^a\rangle + \sum_{i,j,a,b} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \cdots$$
(2.144)

$$= c_0 |\Phi_0\rangle + \sum_{i,a} c_i^a a^{\dagger} i |\Phi_0\rangle + \sum_{i,j,a,b} c_{ij}^{ab} a^{\dagger} b^{\dagger} i j |\Phi_0\rangle + \cdots$$
(2.145)

$$= (c_0 + \sum_{i,a} c_i^a a^{\dagger} i + \sum_{i,j,a,b} c_{ij}^{ab} a^{\dagger} b^{\dagger} i j) |\Phi_0\rangle)$$
(2.146)

$$= (c_0 + \boldsymbol{C_1} + \boldsymbol{C_2} + \cdots) |\Phi_0\rangle, \qquad (2.147)$$

where  $|\Phi_0\rangle$  is the HF wave function,  $i, j \cdots$  denote the occupied orbitals and a, b define the virtual orbitals, and the excitation operators take the form  $C_1 = \sum_{i,a} c_i^a a^{\dagger} i$ ,  $C_2 = \sum_{i,j,a,b} c_{ij}^{ab} a^{\dagger} b^{\dagger} i j$ , and so on. The creation operators  $a^{\dagger}$ ,  $b^{\dagger}$  correspond to the virtual orbitals a and b respectively and the annihilation operators i and j correspond to occupied orbitals i and j.

The entire formulation of CI method can be carried out for the relativistic case in a similar way but with the Dirac-Coulomb Hamiltonian and using four-component wave functions.

## 2.11 The (R)CC method

The CC method is the state-of-art theory for quantum chemistry calculations to include correlation effects to all-orders like the CI method, but its truncated versions have several advantages over the truncated CI methods. Basically approximated CC methods obey size-consistency and size-extensivity properties, and they include more physical effects compared to approximated CI methods at a given level of approximation. This is why the CC theory is considered to be the gold standard of modern quantum chemistry calculations. The CC theory was first introduced in the context of calculating ground state energies of atomic nuclei [12]. In this method, the wave function of a many-body quantum system is described in terms of virtual excitation operators corresponding to the excitation of clusters consisting of one or more than one particles. In the molecular physics, after calculating the mean field wave function, one employs the CC theory to incorporate the correlation effects to estimate the accurate wave function. According to the CC ansatz, the wave function of a many-body system is expressed as [13]

$$|\Psi\rangle = e^T |\Phi_0\rangle, \tag{2.148}$$

where  $|\Phi_0\rangle$  is the mean field (HF/DF) wave function, T is called the 'cluster-operator' which is responsible for the virtual excitations of electrons from occupied orbitals to virtual orbitals due to  $V_{res}$ . To understand the concept of cluster excitations, we explain first classification of electron orbitals as the occupied and virtual orbitals through an example. Let us take the example of neon (Ne) atom. The electronic configuration of Ne at its ground state is  $1s^22s^2sp^6$ , i.e., 1s, 2s, 2p orbitals are occupied with electrons and called occupied orbitals. Whereas, the orbitals 3s, 3p, 3d, 4s etc. are unoccupied and referred to as virtual orbitals. The virtual excitation operators operate on the occupied states (e.g. 1s, 2s, 2p for Ne) to excite the occupied electrons to virtual states (3s, 3p, 3d,  $4s \cdots$  etc. for Ne). Occupied states are often called holes and virtuals states are called particles, as it is conveniently viewed as the excitations leave a hole in the occupied states and creates new particles in the virtual states. Excitations from the occupied to virtual orbitals may happen in multi fold ways: single excitation, double excitation,  $\cdots N$ -tuple excitation due to the residual Coulomb interactions in an N-electron molecular system.

We discuss about the single excitations at first. In a single excitation process, one electron from an occupied orbital is excited to a virtual orbital. This type of excitations are also known as one hole-one particle excitations, as during this process one hole and one particle is created as a result of the excitation. Mathematically speaking, in a single excitation event, fermionic annihilation operator acts on an occupied state to destroy one electron in that state and a fermionic creation operator acts on a virtual state to create a particle in that state. The wave function of a many-body system after a single excitation is given as [14]

$$|\Phi_i^a\rangle = a_a^{\dagger}a_i|\Phi_0\rangle = a^{\dagger}i|\Phi_0\rangle \tag{2.149}$$

where  $a_i$  is the annihilation operator corresponding to an occupied orbital i and  $a_a^{\dagger}$  is the creation operator corresponding to a virtual orbital a. For simplicity, we make use of the notation a instead of  $a_a$  and i in the place of  $a_i$ . In our notation, the occupied orbitals are denoted as  $i, j, k \cdots$  and virtual orbitals are described as  $a, b, c \cdots$ . Eq. (2.149) tells that the excitation creates a hole at the occupied orbital i and a particle at the virtual orbital a leading to a state  $|\Phi_i^a\rangle$ .

Not all the single excitations are equally likely happen. To describe this let us choose lithium (Li) atom at its ground state configuration  $1s^22s^1$ . The excitation from 1s to 4s is less probable than the excitation from 2s to 4s in Li atom. This is the reason why we should attach a weight factor while estimating the probability amplitude of a single excitation. For a single excitation from i to a, let us call the weight factor as  $t_i^a$ . Taking into account all the possible single excitations, the total amplitude reads

$$\sum_{i,a} t_i^a |\Phi_i^a\rangle. \tag{2.150}$$

Similarly, the amplitude corresponding to all possible double excitations can be written as

$$\sum_{i>j,a>b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle, \qquad (2.151)$$

where  $t_{ij}^{ab}$  corresponds to the excitation from occupied orbitals *i* and *j* to virtual orbitals *a* and *b*, respectively. Amplitudes corresponding to triple, quadruple,  $\cdots$ , *N*-tuple excitations can also be expressed likewise.

Another possible scenario may appear if two single or double or  $\cdots$  *n*-tuple excitations occur simultaneously. In case of two single excitations occurring simultaneously, the amplitude is given by

$$\sum_{i>j,a>b} t_i^a t_j^b |\Phi_{ij}^{ab}\rangle = \frac{1}{2!} T_1^2 |\Phi_0\rangle, \qquad (2.152)$$

where the factor  $\frac{1}{2!}$  appears to avoid double counting. Taking into account these type of excitations, one would get amplitude terms like  $\frac{1}{2!}T_2^2$ ,  $\frac{1}{2!}T_3^2$ ,  $\cdots$ ,  $\frac{1}{2!}T_N^2$ . Similarly, terms like  $\frac{1}{3!}T_1^3$ ,  $\frac{1}{3!}T_3^3$ ,  $\cdots$ ,  $\frac{1}{4!}T_1^4$ ,  $\frac{1}{4!}T_2^4$ ,  $\frac{1}{4!}T_3^4$ ,  $\cdots$  would also appear. There can also be composite singles

and doubles excitations leading to terms like  $T_1T_2$ ,  $T_1^2T_2$ ,  $T_1T_2^2$  and so on. All other types of possible composite excitations would also come into picture. Therefore, taking into account all possible combinations of excitations, the total probability amplitude can be written in terms of an exponential operator

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{i,a} t_i^a |\Phi_i^a\rangle + \sum_{i>j,a>b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots + \sum_{i>j,a>b} t_i^a t_j^b |\Phi_{ij}^{ab}\rangle + \sum_{i>j,k>l,a>b,c>d} t_{ij}^{ab} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle + \dots$$

$$(2.153)$$

$$= |\Phi_0\rangle + T_1|\Phi_0\rangle + T_2|\Phi_0\rangle + \dots + \frac{1}{2!}T_1^2|\Phi_0\rangle + \frac{1}{2!}T_2^2|\Phi_0\rangle + \dots$$
(2.154)

$$|\Psi\rangle = e^T |\Phi_0\rangle, \qquad (2.155)$$

where the cluster operator is given by

$$T = T_1 + T_2 + T_3 + \dots + T_N. \tag{2.156}$$

The CC method is equally applicable for relativistic calculations. In the RCC theory, the single particle wave functions of  $|\Phi_0\rangle$  are four-component ones  $|\Phi_0\rangle$  is a four component one and the Hamiltonian is the Dirac-Coulomb Hamiltonian.

Next, we would proceed to discuss about how to obtain the amplitudes of the T-operators. For that matter, we need to introduce the CC amplitude equations. Before deriving the CC amplitude equations, one needs to have a prerequisite knowledge about certain techniques to tactfully handle the algebra of second quantization operators. For that, we discuss the Baker-Campbell-Hausdorff (BCH) formula and the linked cluster theorem (LCT) in the two subsequent subsections.

#### 2.11.1 The BCH expansion formula

Assume two operators A and X. The BCH formula is a tool to expand the expression  $e^{-X}Ae^{X}$ . Let us choose a parameter  $\lambda$  and consider the  $\lambda$  dependent expression  $A'(\lambda) = e^{-\lambda X}Ae^{\lambda X}$ , where  $A'(\lambda)$  is the transformed operator A. Considering the differential of A' with respect to  $\lambda$ , we get

$$\frac{dA'(\lambda)}{d\lambda} = -Xe^{-\lambda X}Ae^{\lambda X} + \underbrace{e^{-\lambda X}\frac{dA}{d\lambda}e^{\lambda X}}_{=0} + e^{-\lambda X}AXe^{\lambda X}$$
(2.157)

$$= -e^{-\lambda X} X A e^{\lambda X} + e^{-\lambda X} A X e^{\lambda X}$$
(2.158)

$$= e^{-\lambda X} [A, X] e^{\lambda X}.$$
(2.159)

Similarly, the second-order differential can be written as

$$\frac{d^2 A'(\lambda)}{d\lambda^2} = -X e^{-\lambda X} [A, X] e^{\lambda X} + e^{-\lambda X} [A, X] X e^{\lambda X}$$
(2.160)

$$= e^{-\lambda X}[[A, X], X]e^{\lambda X}.$$
(2.161)

In a similar way it can be shown that

$$\frac{d^3 A'(\lambda)}{d\lambda^3} = e^{-\lambda X}[[[A, X], X], X]e^{-\lambda X}, \qquad (2.162)$$

and so on.

Expanding  $A'(\lambda)$  in a Taylor series, it yields

$$A'(\lambda) = A'(0) + \lambda \frac{dA'}{d\lambda}|_{\lambda=0} + \frac{1}{2!} \lambda^2 \frac{d^2 A'}{d\lambda^2}|_{\lambda=0} + \cdots$$
(2.163)

$$= A + \lambda[A, X] + \frac{1}{2!}\lambda^{2}[[A, X], X] + \cdots$$
 (2.164)

$$A'(1) = A + [A, X] + \frac{1}{2!}[[A, X], X] + \cdots$$
(2.165)

$$A'(1) = e^{-X}Ae^{X} = A + [A, X] + \frac{1}{2!}[[A, X], X] + \cdots$$
(2.166)

$$e^{-X}Ae^X = \sum_{n=0}^{\infty} \frac{1}{n!} [A, X]^{(n)},$$
 (2.167)

whre  $[A, X]^{(n)} = [[A, X]^{(n-1)}, X]$ . Eq. (2.167) is known as the BCH formula [15].

### 2.11.2 The LCT

LCT is a useful recipe to deal with a string of creation and annihilation operators. At first, let us consider a string of creation and annihilation operators  $ABC \cdots$ . The normal product of this string of second quantization operators is defined as  $\{ABC \cdots\}$ , such that, all the hole creation operators  $(i^{\dagger}, j^{\dagger}, \cdots)$  and particle annihilation operators  $(a, b, \cdots)$  are to the right of the other operators. Hence, the expectation value of the string is zero:

$$\langle \Phi_0 | \{ ABC \cdots \} | \Phi_0 \rangle = 0. \tag{2.168}$$

The expectation value in Eq. (2.168) vanishes because the hole creation operators are at the right of the string and no further hole can be created at the Fermi vacuum state  $|\Phi_0\rangle$ .

Now we define a operation called contraction. The contraction of a general creation operator  $p^{\dagger}$  and an annihilation operator q is defined as

$$\widehat{p^{\dagger}q} = p^{\dagger}q - \{p^{\dagger}q\}.$$
(2.169)

Different cases arising from different choices of p and q are discussed below:

• Case 1: Both p and q represent particles. One such combination is  $ba^{\dagger}$ .

$$\therefore \ ba^{\dagger} = ba^{\dagger} - \{ba^{\dagger}\}. \tag{2.170}$$

From the anticommutation relations of fermionic second quantization operators we know

$$[a^{\dagger}, b]_{+} = \delta_{ab} \tag{2.171}$$

$$a^{\dagger}b + ba^{\dagger} = \delta_{ab} \tag{2.172}$$

$$ba^{\dagger} = -a^{\dagger}b + \delta_{ab} \tag{2.173}$$

Plugging Eq. (2.173) in Eq. (2.170) we get

$$\widehat{ba^{\dagger}} = -a^{\dagger}b + \delta_{ab} - \underbrace{\{ba^{\dagger}\}}_{=-a^{\dagger}b}$$

$$(2.174)$$

$$\widehat{ba^{\dagger}} = -a^{\dagger}b + \delta_{ab} + a^{\dagger}b = \delta_{ab}.$$
(2.175)

• Case 2: Another combination where p and q both represent particles could be  $a^{\dagger}b$ .

$$\widehat{a^{\dagger}b} = a^{\dagger}b - \{a^{\dagger}b\}.$$
(2.176)

By definition  $\{a^{\dagger}b\} = a^{\dagger}b$ . Hence, Eq. (2.176) can be rewritten as

$$\widehat{a^{\dagger}b} = 0. \tag{2.177}$$

• Case 3: p and q both correspond to holes. One such combination is  $i^{\dagger}j$ .

$$\widehat{i^{\dagger}j} = i^{\dagger}j - \{i^{\dagger}j\}.$$
 (2.178)

By definition  $\{i^{\dagger}j\} = -ji^{\dagger}$ , therefore, from Eq. (2.178) we get

$$\widehat{i^{\dagger}j} = i^{\dagger}j + ji^{\dagger} = \delta_{ij}.$$
(2.179)

• Case 4: p and q both are holes and another combination of this kind could be  $ij^{\dagger}$ . Therefore,

$$\widehat{ij^{\dagger}} = ij^{\dagger} - \underbrace{\{ij^{\dagger}\}}_{=ij^{\dagger}} = ij^{\dagger} - ij^{\dagger} = 0.$$
(2.180)

After explaining the process of contraction of string of creation and annihilation operators, we explain the usefulness of the Wick's theorem [16].

#### Wick's theorem

If  $ABC \cdots$  is a string of creation and annihilation operators,

$$ABC \cdots = \{ABC \cdots\} + \sum_{\text{single contractions}} \widehat{AB} CDE \cdots + \sum_{\text{double contractions}} \widehat{AB} \widehat{CD} E \cdots + \cdots$$

$$(2.181)$$

Therefore, the expectation value of such a string of operators is given by

$$\langle \Phi_0 | ABC \cdots | \Phi_0 \rangle = \sum_{\text{full contractions}} \langle \Phi_0 | \overrightarrow{ABC} \cdots | \Phi_0 \rangle.$$
 (2.182)

Now, we introduce the normal product form of an operator A as

$$A_N = A - \langle \Phi_0 | A | \Phi_0 \rangle. \tag{2.183}$$

Hence the Hamiltonian H can also be decomposed as

$$H = H_N + \langle \Phi_0 | H | \Phi_0 \rangle, \tag{2.184}$$

where  $H_N$  is the normal ordered Hamiltonian.  $H_N$  can be written in terms of second quantization operators [17]

$$H_N = \sum_{pq} f_{pq} \{p^{\dagger}q\} + \frac{1}{2} \sum_{pqrs} \langle pq | | rs \rangle \{p^{\dagger}q^{\dagger}sr\}, \qquad (2.185)$$

where  $f_{pq}$  is a matrix element of the Fock operator and given by

$$f_{pq} = \langle p|F|q \rangle \tag{2.186}$$

and the Mulliken's notation  $\langle pq | | rs \rangle = \langle pq | \frac{1}{r_{12}} | rs \rangle - \langle pq | \frac{1}{r_{12}} | sr \rangle$ . Now, we define what is called an object. An operator that contains same number of creation and annihilation operators. Suppose,

A and B are two objects. Therefore, from the generalised Wick's theorem

$$AB = \{AB\} + \widehat{AB} \tag{2.187}$$

and 
$$BA = \{BA\} + \widehat{BA}$$
. (2.188)

As AB and BA consist of same number of creation and annihilation operators,  $\{AB\} = \{BA\}$ . Hence, the commutation of A and B is given by

$$[A,B] = AB - BA = \overrightarrow{AB} - \overrightarrow{BA}.$$
(2.189)

The Schrödinger equation says

$$H|\Psi\rangle = E|\Psi\rangle \tag{2.190}$$

$$\Rightarrow He^T |\Psi_0\rangle = Ee^T |\Phi_0\rangle \tag{2.191}$$

$$\Rightarrow e^{-T}He^T = E|\Phi_0\rangle. \tag{2.192}$$

From the BCH formula, we can write

$$e^{-T}He^{T} = \sum_{n=0}^{\infty} \frac{1}{n!} [H, T]^{(n)}.$$
 (2.193)

The first term of the right hand side of Eq. (2.193) is H, which is connected. While, the second term is  $[H,T] = \widehat{HT} - \widehat{TH}$ . Again,

$$H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle, \qquad (2.194)$$

$$H_N = H - \overbrace{H}^{\sim}. \tag{2.195}$$

$$\therefore \widehat{H} = \langle \Phi_0 | H | \Phi_0 \rangle. \tag{2.196}$$

Similarly, the second term in Eq. (2.196) can be written as

$$\widehat{TH} = \langle \Phi_0 | TH | \Phi_0 \rangle = 0.$$
(2.197)

The left hand side of Eq. (2.197) vanishes as particle annihilation operator(s) of  $T^{\dagger}$  acting on the Fermi vacuum state gives a zero. Therefore, only one term survives in the expression of [H, T], i.e.

$$[H,T] = \widehat{HT} \,. \tag{2.198}$$

Similarly, the third term in Eq. (2.193) can be written as

$$[H,T]^{(2)} = [[H,T],T]$$
(2.199)

$$= [\widehat{HT}, T] = \widehat{HT} T - T \widehat{HT} = \widehat{HT} T, \qquad (2.200)$$

where we used the fact that the contraction between T and T is zero, making the second term in the right hand side of the equation vanish. Following the same analogy we can write

$$[H,T]^{(n)} = \overbrace{HT\cdots T}^{(n)}.$$
(2.201)

Therefore, invoking the above relation in Eq. (2.193) we get

$$e^{-T}He^{T} = (He^{T})_{c},$$
 (2.202)

where the subscript states that all the terms are connected. This form of Eq. (2.202) is referred as the LCT.

### 2.11.3 (R)CC energy and amplitude equations

The Schrödinger equation is given by

$$H|\Psi\rangle = E|\Psi\rangle \tag{2.203}$$

$$(H - E_{HF/DF})|\Psi\rangle = (E - E_{HF/DF})|\Psi\rangle \text{ where } (E_{DF} = \langle \Phi_0 | H | \Phi_0 \rangle)$$
(2.204)

$$H_N e^T |\Phi_0\rangle = \Delta E e^T |\Phi_0\rangle \tag{2.205}$$

$$e^{-T}H_N e^T |\Phi_0\rangle = \Delta E |\Phi_0\rangle \tag{2.206}$$

$$\Delta E = \langle \Phi_0 | e^{-T} H_N e^T | \Phi_0 \rangle \tag{2.207}$$

$$\Delta E = \langle \Phi_0 | (H_N e^T)_c | \Phi_0 \rangle, \qquad (2.208)$$

where  $\Delta E = E - E_{HF/DF}$  is the measure of correlation energy. Eq. (2.208) is known as CC energy equation. To obtain the CC amplitudes  $(t_i^a, t_{ij}^{ab}, \text{ etc.})$ , one solves the CC amplitude equations

$$\langle \Phi_{ij\cdots}^{ab\cdots} | (H_N e^T)_c | \Phi_0 \rangle = 0.$$
(2.209)

# 2.11.4 CC energy and amplitudes in singles and doubles approximation

In CC method, the cluster operator, T, is defined as the sum of single, double,  $\cdots$ , N-tuple excitations (see Eq. (2.156)). Also, due to the exponential form of the CC wave functions, the CC amplitude equations would include non-linear terms. Therefore, with a limited computational facility, it is very difficult to include all the non-linear terms as well as all possible virtual excitations while solving the CC amplitude equations for heavy molecules. This is the reason that one needs to consider only important excitations at a reasonable level of approximation and only a certain non-linear terms depending on the problem to be solved. In most of the important problems single and double excitations give rise to the largest contributions. Therefore, the CC singles and doubles (CCSD) method have been extensively used in a large number of calculations.

In the CCSD method, the CC wave function is approximated as

$$|\Psi_{CCSD}\rangle = e^{(T_1+T_2)}|\Phi_0\rangle \tag{2.210}$$

$$= (1 + T_1 + T_2 + \frac{1}{2!}T_1^2 + \frac{1}{2!}T_2^2 + T_1T_2 + \frac{1}{2!}T_1^2T_2 + \cdots)|\Phi_0\rangle, \qquad (2.211)$$

where we can see that non-linear terms like  $T_1^2$ ,  $T_2^2$ ,  $T_1T_2$ ,  $T_1^2T_2$ , and so on. From Eq. (2.211) it is visible that the CCSD wave function includes disconnected triple excitations in the form of  $T_1T_2$ along with additional disconnected quadruple excitations in the form of  $T_1^2T_2$  and many more higher excitations in disconnected form. Therefore, it is evident that the CCSD formalism not only takes into account full contributions from single and double excitations, but also includes other higher order excitations in a disconnected form.

Now we shall derive the CCSD energy equations. In CCSD approximation, Eq. (2.208) takes the form

$$\Delta E_{CCSD} = \langle \Phi_0 | (H_N e^{(T_1 + T_2)})_c | \Phi_0 \rangle.$$
(2.212)

If we expand the right hand side of Eq. (2.212), the first term  $\langle \Phi_0 | H_N | \Phi_0 \rangle$  comes out to be zero. This is obvious from the fact that the hole creation and particle annihilation operators at the right of  $H_N$  gives zero while operating on the Fermi vacuum state  $|\Phi_0\rangle$ . Terms containing  $T_2^2$  or higher powers of  $T_2$  and  $T_1^3$  and higher powers of  $T_1$  would not contribute in the estimation of  $\Delta E_{CCSD}$ , as there would remain unconnected second quantization operators causing the matrix elements vanish. With all these considerations the CCSD energy equation can be written as

$$\Delta E_{CCSD} = \langle \Phi_0 | (H_N T_1 + H_N T_2 + \frac{1}{2!} H_N T_1^2) | \Phi_0 \rangle.$$
(2.213)

To get a more specific form of Eq. (2.213), we use the form of the normal-ordered Hamiltonian  $H_N$  from Eq. (2.186), which gives

$$\Delta E = \sum_{ia} f_{ia} t^a_i + \frac{1}{4} \sum_{a>b,i>j} \langle ij||ab \rangle t^{ab}_{ij} + \frac{1}{2} \sum_{a>b,i>j} \langle ij||ab \rangle t^a_i t^b_j$$
(2.214)

Now we would like to obtain the CCSD amplitude equations. The CCSD singles amplitude equation contains the terms:

$$\sum_{c} f_{ac}t_{i}^{c} - \sum_{k} f_{ki}t_{k}^{a} + \sum_{kc} \langle ka||ci\rangle t_{k}^{c} + \frac{1}{2} \sum_{kcd} \langle ka||cd\rangle t_{ki}^{cd} - \frac{1}{2} \sum_{kcl} \langle kl||ci\rangle t_{kl}^{ca} + \sum_{kcd} \langle ka||cd\rangle t_{k}^{c}t_{i}^{d} - \sum_{kcl} \langle kl||ci\rangle t_{k}^{c}t_{l}^{a} - \sum_{klcd} \langle kl||cd\rangle t_{k}^{c}t_{i}^{d}t_{l}^{a} + \sum_{klcd} \langle kl||cd\rangle t_{k}^{c}t_{l}^{da} - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd}t_{l}^{a} - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd}t_{l}^{a} - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd}t_{l}^{a} = 0.$$

$$(2.215)$$

Similarly, the CCSD doubles amplitude equation contains the terms:

$$\begin{split} \sum_{e} \langle ab | |cj\rangle t_{i}^{e} &= \sum_{e} \langle ab | |cj\rangle t_{i}^{e} &= \sum_{k} \langle kb | |ij\rangle t_{k}^{ab} + \sum_{k} \langle ka | |ij\rangle t_{k}^{b} + \sum_{e} f_{be} t_{ij}^{ce} &= \sum_{e} f_{ac} t_{ij}^{be} \\ &= \sum_{k} f_{k} f_{ijk}^{ab} + \sum_{k} f_{kl} t_{ijk}^{ab} + \frac{1}{2} \sum_{kl} \langle kl | |ij\rangle t_{k}^{ab} + \frac{1}{2} \sum_{cl} \langle ab | |cd\rangle t_{ij}^{ce} + \sum_{kc} \langle kb | |ci\rangle t_{ik}^{ac} \\ &= \sum_{kc} \langle kb | |ci\rangle t_{ijk}^{ac} - \sum_{kc} \langle ka | |cj\rangle t_{ik}^{b} + \sum_{kc} \langle ka | |ci\rangle t_{jk}^{cb} + \sum_{kc} \langle ka | |ci\rangle t_{ijk}^{cd} + \sum_{kc} \langle kb | |ci\rangle t_{ijk}^{ac} \\ &= \sum_{kc} \langle kb | |ci\rangle t_{ijk}^{ac} + \sum_{kc} \langle ka | |cj\rangle t_{ik}^{b} + \sum_{kc} \langle ka | |ci\rangle t_{ijk}^{cd} + \frac{1}{2} \sum_{cl} \langle kb | |cl\rangle t_{ijk}^{cd} \\ &= \sum_{kc} \langle kb | |ic\rangle t_{k}^{a} t_{j}^{c} + \sum_{kc} \langle kb | |jc\rangle t_{k}^{a} t_{i}^{c} + \sum_{kc} \langle ka | |ci\rangle t_{k}^{b} t_{j}^{c} - \sum_{kc} \langle ka | |ci\rangle t_{ijk}^{cd} + \frac{1}{2} \sum_{cl} \langle kl | |cd\rangle t_{ijk}^{cd} t_{ij}^{cd} \\ &= \sum_{kc} \langle kb | |ic\rangle t_{k}^{a} t_{j}^{c} + \sum_{kc} \langle kb | |cc\rangle t_{k}^{a} t_{i}^{c} + \sum_{kc} \langle ka | |cd\rangle t_{ik}^{cd} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{cd} t_{ij}^{cd} \\ &= \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \sum_{kc} \langle ka | |cd\rangle t_{ik}^{b} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{cd} t_{ij}^{cd} \\ &= \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{b} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{b} t_{ij}^{cd} \\ &= \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} \\ &= \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} \\ &= \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} \\ &= \frac{1}{2} \sum_{kled} \langle kl | |cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | | cd\rangle t_{ik}^{a} t_{ij}^{cd} + \frac{1}{2} \sum_{kled} \langle kl | | cd\rangle t_{ik}^{a} t_{ij}^{cd} \\ &=$$

$$-\frac{1}{2}\sum_{kcld}\langle kl||cd\rangle t_{j}^{c}t_{i}^{d}t_{kl}^{ab} + \frac{1}{2}\sum_{kcld}\langle kl||cd\rangle t_{k}^{a}t_{l}^{b}t_{l}^{cd} - \frac{1}{2}\sum_{kcld}\langle kl||cd\rangle t_{k}^{b}t_{l}^{a}t_{ij}^{cd} - \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{a}t_{ij}^{db} + \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{d}t_{lj}^{ab} - \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{d}t_{lj}^{b} + \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{d}t_{lj}^{ab} - \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{d}t_{lj}^{ba} + \sum_{kcld}\langle kl||cd\rangle t_{k}^{c}t_{k}^{d}t_{lj}^{cb} - \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{d}t_{lj}^{bb} - \sum_{kcld}\langle kl||cd\rangle t_{i}^{c}t_{k}^{b}t_{lj}^{da} = 0.$$

$$(2.216)$$

For relatively heavier systems, sometimes it becomes very challenging to cope with the non-linear terms even at the CCSD level, for which often one settles with considering only the linear terms of the CCSD wave function, in which we approximate as  $e^T \approx 1 + T_1 + T_2$ .

### 2.11.5 CC expectation value expression

Following the CC wave function  $|\Psi\rangle = e^T |\Phi_0\rangle$ , the expectation value of any physical operator  $\hat{O}$  is given by

$$\langle \hat{O} \rangle = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$(2.217)$$

$$= \frac{\langle \Phi_0 | e^{T^{\dagger}} \hat{O} e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^{\dagger}} e^T | \Phi_0 \rangle} \tag{2.218}$$

$$= \frac{\langle \Phi_0 | [1+T^{\dagger} + \frac{1}{2!}(T^{\dagger})^2 + \frac{1}{3!}(T^{\dagger})^3 + \cdots] \hat{O}[1+T + \frac{1}{2!}T^2 + \frac{1}{3!}T^3 + \cdots] | \Phi_0 \rangle}{\langle \Phi_0 | [1+T^{\dagger} + \frac{1}{2!}(T^{\dagger})^2 + \frac{1}{3!}(T^{\dagger})^3 + \cdots] [1+T + \frac{1}{2!}T^2 + \frac{1}{3!}T^3 + \cdots] | \Phi_0 \rangle}, (2.219)$$

where the expansions of  $e^{T^{\dagger}}$  and  $e^{T}$  terminate individually if the total excitation level of the product of excitation operators in any term exceeds the total number of electrons in the system. Because of the large number of excitation operators involved in the expectation value expression, the process of evaluating the numerator and denominator followed by the division of numerator by denominator would require huge computational cost. However, Cizek [18] showed that the numerator can actually be factorized such that the denominator becomes one of the factors. Under this prescription, the numerator takes the following form

$$\langle \Phi_0 | e^{T^{\dagger}} \hat{O}_N e^T | \Phi_0 \rangle = \langle \Phi_0 | e^{T^{\dagger} e^T} | \Phi_0 \rangle \langle \Phi_0 | e^{T^{\dagger}} \hat{O}_N e^T \Phi_0 \rangle_c, \qquad (2.220)$$

where the subscript c denotes that all the terms are connected. Now, invoking Eq. (2.220) in (2.218) we get the final form of the CC expectation value

$$\langle \hat{O} \rangle = \langle \hat{O}_N \rangle + \langle \Phi_0 | \hat{O} | \Phi_0 \rangle$$
 (2.221)

$$= \langle \Phi_0 | e^{T^{\dagger}} \hat{O}_N e^T \Phi_0 \rangle_c + \langle \Phi_0 | \hat{O} | \Phi_0 \rangle.$$
(2.222)

This way of expressing the expectation value significantly simplifies the calculation. However, one still requires to truncate the two infinite series in the numerator. Under CCSD approximation, the expectation value of an operator  $\hat{O}$  takes the following form

$$\langle \hat{O} \rangle_{CCSD} = \frac{\langle \Phi_0 | e^{(T_1 + T_2)^{\dagger}} \hat{O} e^{(T_1 + T_2)} | \Phi_0 \rangle}{\langle \Phi_0 | e^{(T_1 + T_2)^{\dagger}} e^{(T_1 + T_2)} | \Phi_0 \rangle}$$
(2.223)

In our calculations, we choose  $\hat{O} = H_{eEDM}$  for calculating  $\mathcal{E}_{eff}$ ,  $\hat{O} = D$  to determine PDM,  $\hat{O} = H_{S-PS}$  to evaluate  $W_s$  and so on.

Sometimes, for saving computational cost,  $e^T$  is approximated as 1 + T at the time of calculating expectation value of some property. This approach of obtaining expectation value of a property is known as linearized expectation value coupled-cluster (LECC) method.

#### 2.11.6 Truncated CC vs CI methods

Both CC and CI method take into account electron correlation effects and untruncated CC is equivalent to full CI. However, these two techniques have certain subtle differences when they are truncated at a certain level, which make each of them distinct than the other. As mentioned earlier, the CCSD wave function contains not only upto double excitation operators but also higher disconnected higher excitation terms. Similarly the coupled-cluster singles, doubles, and triples (CCSDT) wave function is expressed as [19, 20]

$$|\Psi_{CCSDT}\rangle = e^{T_1 + T_2 + T_3} |\Phi_0\rangle = |\Psi_{CCSD}\rangle + (T_3 + T_1T_3 + T_2T_3 + T_3^2/2 + \cdots) |\Phi_0\rangle.$$
(2.224)

It is evident from Eq. (2.224) that the CCSDT wave function also includes higher order excitation terms. If we continue upto n-tuple excitations, we would get the full CI (FCI) wave function

$$|\Psi_{FCI}\rangle = (1+C)|\Phi_0\rangle \tag{2.225}$$

$$= (1 + C_1 + C_2 + C_3 + \cdots) |\Phi_0\rangle.$$
 (2.226)

If we compare between FCI and untruncated CC wave function, we would get [21]

$$\boldsymbol{C}_1 = \boldsymbol{T}_1 \tag{2.227}$$

$$C_2 = \frac{1}{2}T_1^2 + T_2 \tag{2.228}$$

$$C_3 = \frac{1}{3!}T_1^3 + T_1T_2 + T_3$$
(2.229)

$$C_{4} = \frac{1}{4!}T_{1}^{4} + \frac{1}{2}T_{1}^{2}T_{2} + \frac{1}{2}T_{2}^{2} + T_{1}T_{3} + T_{4}$$

$$\vdots$$
(2.230)

From the above set of equations we see that in CI singles and doubles (CISD) method, terms that correspond to more than double excitations do not appear, unlike in the case of CCSD. Similar trend is found for CISDT (CISD triples), CISDTQ (CISD triples, quadruples) and so on. Hence, at the same level of truncation, the truncated CC method would include more excitations than the truncated CI method. We know that the more possible excitations are taken into account, the more accuracy in result is obtained. Thus, truncated CC method would yield more accurate result over truncated CI method if the level of truncation is the same.

Size-extensivity: Another aspect that is crucial in understanding the nature of a manybody method is the size-extensivity property. A property of a uniformly distributed system is said to be size extensive if its value is proportional to the size of the system. A quantum mechanical computation method is called size extensive if the energy of a many-body system computed via that method scales properly with the size of the system. For example, we consider He gas with N non interacting He atoms. For size-extensivity, the energy of N He atoms together should be equal to the energy of a single He atom multiplied (or scaled) by a factor of N. But for a truncated CI method, namely CI doubles (CID), the correlation energy can be expressed as [17]

$$\Delta E = E - E_0 \propto \sqrt{N} \Delta \epsilon, \qquad (2.231)$$

where  $\Delta \epsilon$  is the correlation energy of a single He atom computed through CID method. From Eq. (2.231) we see that the CID method is not size extensive as the total correlation energy  $\Delta E$ scales with  $\sqrt{N}$ , instead of N. Similar trend can be seen for all other truncated CI methods. Therefore, truncated CI is not size extensive. However, in CC doubles (CCD) method, the total energy of an N non-interacting He atom system is given by [17]

$$E = N\epsilon, \tag{2.232}$$

where  $\epsilon$  is the CCD energy of a single He atom. From Eq. (2.232) it is visible that the total energy of the N particle system scales with N, proving the size-extensivity of truncated CC method. Hence, truncated CC theory holds the upper hand over truncated CI in terms of size-extensivity.

Size-consistency: Another broad distinction between the truncated CC and truncated CI methods arises from the qualitative point of view of size-consistency. Truncated CC is size-consistent, whereas truncated CI is not. To explain this, at first, we introduce size-consistency. Consider two non-interacting atoms A and B far apart from each other (at dissociation limit) composing a system  $A \cdots B$ . At the dissociation limit, the Hamiltonian of the composite system is equal to the sum of the Hamiltonians of the sub-systems, i.e.

$$H(A \cdots B) \rightarrow H_A + H_B$$
 (2.233)

and 
$$[H_A, H_B] = 0.$$
 (2.234)

A many-body method is said to be size-consistent if the total wave function of the composite system  $A \cdots B$  is separable and the energy of the composite system  $A \cdots B$  calculated through
that method is equal to the sum of the energies of A and B calculated separately:

$$|\Psi(A\cdots B)\rangle = |\Psi(A)\rangle \otimes |\Psi(B)\rangle \tag{2.235}$$

and 
$$E(A \cdots B) = E(A) + E(B).$$
 (2.236)

Both Eq. (2.236) and Eq. (2.235) are necessary conditions for size-consistency. Assume that the reference wave function of the composite system is separable, i.e.

$$|\Phi_0(A\cdots B)\rangle = |\Phi_0(A)\rangle \otimes |\Phi_0(B)\rangle \tag{2.237}$$

Consider the CCSD method as an example of a truncated CC method. In the CCSD method

$$|\Psi(A\cdots B)\rangle = e^T |\Phi_0(A\cdots B)\rangle \tag{2.238}$$

$$= e^{T^A + T^B} |\Phi_0(A \cdots B)\rangle \tag{2.239}$$

$$= e^{T_1^A + T_2^A + T_1^B + T_2^B} |\Phi_0(A \cdots B)\rangle$$
(2.240)

$$= e^{T_1^A + T_2^A + T_1^B + T_2^B} |\Phi_0(A)\rangle \otimes |\Phi_0(B)\rangle \text{ (using Eq. (2.237))}$$
(2.241)

$$= e^{T_1^A + T_2^A} |\Phi_0(A)\rangle \otimes e^{T_1^B + T_2^B} |\Phi_0(B)\rangle$$
(2.242)

$$= |\Psi(A)\rangle \otimes |\Psi(B)\rangle \tag{2.243}$$

Therefore, one of the two conditions of size-consistency is met by the CCSD method. Next, we inspect if CCSD method holds the second condition also. The separability of the wave functions would lead to the additive nature of the energies. Consider the equation

$$H(A\cdots B)|\Psi(A\cdots B)\rangle = (H_A + H_B)|\Psi(A\cdots B)\rangle$$
(2.244)

$$\Rightarrow E(A \cdots B) |\Psi(A \cdots B)\rangle = (H_A + H_B) |\Psi(A)\rangle |\Psi(B)\rangle$$
(2.245)

$$= (H_A|\Psi(A)\rangle)|\Psi(B)\rangle + (H_B|\Psi(B)\rangle)|\Psi(A)\rangle \qquad (2.246)$$

$$= (E(A) + E(B))|\Psi(A)\rangle|\Psi(B)\rangle \qquad (2.247)$$

$$= (E(A) + E(B))|\Psi(A \cdots B)\rangle$$
(2.248)

$$E(A \cdots B) = (E(A) + E(B)).$$
 (2.249)

We see that CCSD also fulfills the energy additivity property. Hence, the truncated CC is sizeconsistent. Now we turn our attention to CISD as one of the truncated CI methods. CISD wave function of the system  $A \cdots B$  is given by

$$|\Psi(A\cdots B)\rangle = (1 + \boldsymbol{C}_1 + \boldsymbol{C}_2)|\Phi_0(A\cdots B)\rangle$$
(2.250)

$$= (1 + C_1^A + C_2^A + C_1^B + C_2^B)(|\Phi_0(A)\rangle \otimes |\Phi_0(B)\rangle).$$
(2.251)

Now,

$$\begin{aligned} |\Psi(A)\rangle \otimes |\Psi(B)\rangle &= (1 + \boldsymbol{C}_{1}^{A} + \boldsymbol{C}_{2}^{A}) |\Phi_{0}(A) \otimes \rangle (1 + \boldsymbol{C}_{1}^{B} + \boldsymbol{C}_{2}^{B}) |\Phi_{0}(B)\rangle & (2.252) \\ &= (1 + \boldsymbol{C}_{1}^{A} + \boldsymbol{C}_{2}^{A} + \boldsymbol{C}_{1}^{B} + \boldsymbol{C}_{2}^{B} + \boldsymbol{C}_{1}^{A} \boldsymbol{C}_{1}^{B} \\ &+ \boldsymbol{C}_{1}^{A} \boldsymbol{C}_{2}^{B} + \boldsymbol{C}_{2}^{A} \boldsymbol{C}_{1}^{B} + \boldsymbol{C}_{2}^{A} \boldsymbol{C}_{2}^{B}) (|\Phi_{0}(A)\rangle \otimes |\Phi_{0}(B)\rangle). \end{aligned}$$

From Eq. (2.251) and Eq. (2.253) we can see that CISD wave function does not meet the separability of wave function criterion. Therefore, unlike the truncated CC method, truncated CI method is not size-consistent.

Variational property: One common criticism received by the truncated CC method is that it is not variationally consistent. This is due to the fact that unlike a variational theory, the truncated CC energy is not calculated as an upper bound to the exact energy. However, we can view this from a rational point of view. We know that FCI method is variational and energy obtained from FCI calculation is exactly equal to that from full CC calculation. Moreover, truncated CC methods like CCSD, CCSDT etc. are considered to be considerably good approximations to full CC. Therefore, we can expect that the energy obtained from truncated CC methods would be close to the energy calculated using full CC method. Therefore, truncated CC methods, though being non-variational, would provide reliable estimates of energies.

### 2.11.7 Comparison between the CC and MBPT methods

We know that a full CC calculation is equivalent to an all-order MBPT calculation [22]. We try to examine the qualitative difference between the truncated CC and truncated MBPT methods.

In the MBPT method, the residual Coulomb interaction is considered as a perturbation:

$$H' = \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}} - \sum_{i} (V_{HF})_i = V_{res}.$$

So that we can express the molecular wave function as

$$|\Psi_{MBPT}\rangle = |\Phi_{\alpha}^{(0)}\rangle + |\Phi_{\alpha}^{(1)}\rangle + |\Phi_{\alpha}^{(2)}\rangle + |\Phi_{\alpha}^{(3)}\rangle + \cdots, \qquad (2.254)$$

where  $|\Phi_{\alpha}^{(i)}\rangle$  is the *i*<sup>th</sup> order perturbative correction to the wave function.

The first-order correction to the wave function in the MBPT method is given by

$$|\Phi_{\alpha}^{(1)}\rangle = \sum_{n \neq \alpha} \frac{|\Phi_n\rangle \langle \Phi_n | H' | \Phi_{\alpha}^{(0)} \rangle}{E_{\alpha}^{(0)} - E_n}.$$
(2.255)

If  $|\Phi_n\rangle = |\Phi_i^a\rangle$  and  $|\Phi_\alpha^{(0)}\rangle = |\Phi_0\rangle$ , the matrix element in the numerator would represent a  $T_1$  excitation, which is specifically the part of  $T_1$  that is contained in  $C_S^{(1)}$ .

Similarly, the second-order correction to the wave function in MBPT is given as

$$|\Phi_{\alpha}^{(2)}\rangle = \sum_{m,n\neq\alpha} \frac{|\Phi_n\rangle\langle\Phi_n|H'|\Phi_m\rangle\langle\Phi_m|H'|\Phi_{\alpha}^{(0)}\rangle}{(E_{\alpha}^{(0)} - E_n)(E_{\alpha}^{(0)} - E_m)}.$$
(2.256)

When  $|\Phi_n\rangle = |\Phi_{ij}^{ab}\rangle$ , the matrix element in the numerator of Eq. (2.255) becomes

$$\langle \Phi_{ij}^{ab} | H' | \Phi_{\alpha}^{(0)} \rangle = \langle ab | \frac{1}{r_{12}} | ij \rangle - \langle ab | \frac{1}{r_{12}} | ji \rangle.$$

$$(2.257)$$

This matrix element represents a  $T_2$  excitation, more specifically, the part of  $T_2$  excitation that is contained in  $C_D^{(2)}$ . Therefore, we can rewrite these corrections to the wave functions in an order as a sum over single, double, triple,  $\cdots$  excitations. i.e.

$$|\Phi_{\alpha}^{(1)}\rangle = \sum_{S} (C_{S}^{(1)} + C_{D}^{(1)} + \cdots) |\Phi_{\alpha}^{(0)}\rangle$$
 (2.258)

$$|\Phi_{\alpha}^{(2)}\rangle = \sum_{S} (C_{S}^{(2)} + C_{D}^{(2)} + \cdots) |\Phi_{\alpha}^{(0)}\rangle, \qquad (2.259)$$

From the above equations it is clear that a truncated CC method like CCSD contains single and double excitations to all-orders of perturbation. If, in Eq. (2.256),  $|\Phi_n\rangle$  is a doubly excited state and  $|\Phi_m\rangle$  is a singly excited state, both the matrix elements in the numerator would represent  $T_1$  excitation each, and the entire term would represent that part of  $T_1^2$  which is contained in  $C_D^{(2)}$ . Also, when  $|\Phi_n\rangle$  is a singly excited state and  $|\Phi_m\rangle$  is a doubly excited one, the numerator would represent a  $T_1T_2$  like excitation. This procedure of mapping between the MBPT and CC methods can be repeated for other excitations too. This approach of looking at the CC method helps us intuitively identify the important excitations which will give more significant contributions to the energy calculations. For example, both  $T_1$  and  $T_2$  appear in the first-order perturbation, while  $T_1^2$  appears in the second-order and so on. In perturbation theory, the second-order correction is usually supposed to be smaller than the first-order one. Therefore, in view of the above rationale,  $T_1$  and  $T_2$  are anticipated to contribute more than  $T_1T_2$  excitations in the evaluation of CC energy.

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# Chapter 3

# PDMs and Static Electric Dipole Polarizabilities of Alkali-Dimers

## 3.1 Introduction

For inferring  $d_e$  from molecular EDM experiments, reliable calculations of  $\mathcal{E}_{\text{eff}}$  are very important. General perception is that while intending to establish existence of  $d_e$ , accuracy of  $\mathcal{E}_{\text{eff}}$ is not essential. However, this understanding is not correct because of two reasons. First, at times mean-field calculation of a property can have opposite sign than the final result (observed experimentally or obtained from a rigorous calculation). In such a scenario, the result may misguide the experimentalists to carry out measurements. Second, even though a finite value of  $d_e$  cannot be inferred sooner from the combined experimental and theoretical results, but more precise value of measurement of Larmour precession and accurate calculation of  $\mathcal{E}_{\text{eff}}$  can put stringent limit on  $d_e$  that would help us in ruling out CP violating phenemona of certain energy scale. From this point of view, it is necessary to verify reliability of the many-body method employed to determine  $\mathcal{E}_{\text{eff}}$  in the molecular systems. We had also demonstrated in Chapter I, why it is imperative to apply a relativistic version method to calculate  $\mathcal{E}_{\text{eff}}$ . In this thesis, we have employed the RCC theory to evaluate  $\mathcal{E}_{\text{eff}}$  of different molecular systems. Due to computational complexity in molecular systems, it is not possible to apply full RCC method. Also, a reasonable accuracy of our calculations of  $\mathcal{E}_{\text{eff}}$  would serve our purpose. The traditionally considered RCCSD method can be sufficient enough to incorporate electron correlation effects in the evaluation of  $\mathcal{E}_{\text{eff}}$ . The RCCSD results can be further improved by adding correlation effects through partial triple excitations (RCCSD(T) method) perturbatively. In order to demonstrate reliability of the RCCSD and RCCSD(T) methods for molecular property calculations, we determine PDMs and electric dipole polarizabilities of molecules using the above methods and compare them with the literature values. Since earlier calculations for these properties were performed for the alkali-dimers, we first study PDMs and electric dipole polarizabilities of these molecules. Apart from the necessity of employing a relativistic method to determine  $\mathcal{E}_{\text{eff}}$  of a molecule, it is also essential to use a relativistic theory to improve the accuracy of molecular calculations in heavier molecules where relativistic effects are prominent. To demonstrate the role of relativistic effects in improving the results, we also present non-relativistic calculations of PDMs and electric dipole polarizabilities using CCSD and CCSD(T) methods. The other reason for investigating these quantities in the context of molecular EDM studies can be understood from the following discussions.

The expression of  $\mathcal{E}_{\text{eff}}$  as mentioned in Eq. (1.31) can be expressed as

$$\mathcal{E}_{\text{eff}} = -\frac{1}{d_e} \sum_{i} \langle 0|d_e \beta \Sigma_i E^{int}|0\rangle = -\frac{1}{d_e} \sum_{i} \langle 0|D'_i E^{int}_i|0\rangle$$
(3.1)

$$= -\frac{1}{d_e} \sum_{i} \sum_{n \neq 0} \langle 0|D'_i|n\rangle \langle n|E^{int}_i|0\rangle, \qquad (3.2)$$

where  $D' = d_e \beta \Sigma$ .

On the other hand, the static dipole polarizability expression of a molecule is given by

$$\alpha = \sum_{n \neq 0} \frac{\langle 0|D|n \rangle \langle n|D|0 \rangle}{E_n^{(0)} - E_0^{(0)}},$$
(3.3)

where the dipole operator  $D = -\sum_{i} r_i + \sum_{A} Z_A R_A$  with  $Z_A$  is the atomic number corresponding to the  $A^{th}$  nuclei. We can see from Eq. (3.2) and Eq. (3.3) that for both the cases we have to calculate the matrix element  $\langle 0|D|n\rangle$ . Again, both D and  $E_i^{int}$  are one-body operators with odd-parity. Therefore, obtaining accurate result for  $\alpha$  using RCC method would in turn assert on the reliability of the approach for calculating  $\mathcal{E}_{\text{eff}}$ . Unlike  $\mathcal{E}_{\text{eff}}$ ,  $\alpha$  is a measurable quantity and RCC calculations of  $\alpha$  can be verified with the existing experimental results. PDM is another measurable quantity that plays a role in determining the sensitivity of EDM experiments. A larger PDM of a molecule means that a small amount of polarizing electric field ( $E_{pol} = \frac{B_r}{2\mu}$ ,  $B_r =$ rotational constant) would be sufficient to polarize the molecules, which would help in reducing the systematic uncertainty associated with an EDM experiment. Keeping this rationale in the back of mind, we decided to calculate  $\alpha$  and  $\mu$  for a set of molecules having a range of potential applications in ultracold physics. As we know that the molecules adapted for EDM experiments are also needed to be cooled down to low temperatures, it is necessary to conduct the test of RCC method with cold or ultracold molecules.

We would like to give a brief overview on other applications of PDMs and static dipole polarizabilities of ultracold alkali dimers apart from using them to test the potential of the RCC method. For the last few decades, enormous interest has grown in the field of ultracold molecules for their wide array of applications [1, 2] which include exciting possibilities to probe fundamental constants [3]. A significant molecular property that plays a crucial role in most of these applications as well as in molecular EDM experiments is the PDM ( $\mu$ ) of a molecule. A large value of molecular PDM would enable one to polarize the molecules with a small amount of external electric field, which would help to reduce systematic effects like motional magnetic field  $\vec{B}_{mot} = \frac{\vec{E}_{ext} \times \vec{v}}{c^2}$  with  $\vec{v}$  being the molecular beam velocity. On the other hand, molecules which possess large PDMs find their application in various fields of ultracold physics. Molecules with fairly large PDMs give rise to long-range and anisotropic dipole-dipole interactions that can be controlled by external electric fields [4]. To realise the dipole-dipole interactions, molecules with large values PDM enable us to align them with comparatively low external electric field [5]. Moreover, a knowledge of PDM helps understand the dipole interaction strengths for a specified density of trapped molecules [6]. Electric dipole-dipole interactions are extensively utilised in the emerging field of quantum phase transitions [7]. One of the salient features of these interactions is that they could couple qubits described as molecular electric dipoles aligned along or opposite to an external electric field, thus indicating possibilities for quantum computation with trapped

polar molecules [8, 9, 10]. The PDM plays an important role in chaining of polar molecules [11], during the process of molecular chaining in a one-dimensional optical lattice, the interaction strengths for this chaining process are directly proportional to the square of the molecular PDM.

As already stated, evaluation formula of  $\alpha$  has resemblance with the expression of  $\mathcal{E}_{\text{eff}}$ . Therefore, accurate estimation of  $\alpha$  using a many-body method ((R)CC in our case) would be a intriguing test of the quality of its wave functions before conducting theoretical calculations of  $\mathcal{E}_{\text{eff}}$ for prospective EDM candidate molecules. Besides, the information of static dipole polarizability is crucial in the context of laser cooling and molecular trapping too. The restoring force of a trapping laser beam inside an optical tweezer is proportional to the static dipole polarizability of the molecule [12]. Therefore, larger the value of static dipole polarizability, more suitable the molecule for laser cooling and trapping. For a molecule trapped inside a far-off resonance optical trap, the static dipole polarizability helps predict the depth of the trap depending on the intensity of the laser fields [6]. Knowledge of polarizability also finds importance in the field of femtosecond spectroscopy, especially in laser-induced impulsive alignment of molecules [13]. So, in view of the above discussions, knowledge of both PDMs and static dipole polarizabilities are crucial for studying ultracold molecules trapped in laser fields [14]. For example, authors in Ref. [15] studied three-body interactions in polar molecules and took LiCs molecule for investigation because of its large PDM. Actually, prospects of orienting and aligning alkali-dimers can be viewed in terms of their PDMs and polarizabilities, respectively [16]. The significance of PDMs and polarizabilities, especially in the case of alkali-dimens, are further elaborated in Ref. [17].

There are only a handful number of experimental values for PDMs of the alkali-dimers that are available in literature [18, 19, 20, 21, 22, 23, 24, 25]. Experimental results for dipole polarizabilities of alkali-dimers are even more rare [20, 18]. In contrast, there are numerous theoretical works, applying different variants of many-body theory, available in literature on evaluating PDMs of alkali-dimers, from as early as 1970s (e.g., see Ref. [26]) until very recently [27, 16, 28, 29, 30]. However, static dipole polarizabilities of alkali-dimers have not been explored as much in theoretical sector, but a few studies have been conducted on this property [31, 16, 29]. Most of these calculations were carried out by employing non-relativistic framework, with some works included lower-order relativistic corrections [16, 27, 29, 30, 32]. Molecular orbitals get deformed more prominently due to the relativistic effects in heavier alkali-dimers. Therefore, we anticipate significant departures from the non-relativistic to relativistic values for the PDMs and static dipole polarizabilities of heavier systems. Previously, static dipole polarizabilities of homonuclear alkali-dimers have been investigated by Lim *et al* [33], and it was found that relativistic effects become significant for the heavier dimers. They made use of the scalar 2-component Douglas-Kroll (DK) Hamiltonian to take into account the relativistic effects.

We scrutinize the roles of relativistic effects in the values of PDMs and dipole polarizabilities of heteronuclear alkali-dimers, comprised of Li, Na, K, Rb and Cs. In view of the aforementioned purpose, in this chapter (based on Ref. [34]), we perform calculations of PDM and dipole polarizabilities by employing a non-relativistic Hamiltonian as well as 4-component Dirac-Coulomb Hamiltonian in the RCC theory. We have undertaken the finite field (FF) approach to evaluate the first-order and the second-order perturbed energies of the ground states of the above mentioned heteronuclear alkali-dimers (LiNa, LiK, LiRb, LiCs, NaK, NaRb, NaCs, KRb, KCs, RbCs), by varying an weak external electric field. From these energies, values of the PDMs and dipole polarizabilities are inferred. Mean field level results are first calculated using HF and DF methods. Once the mean field results are obtained, correlation effects are then systematically added by employing the (R)CCSD method, followed by the (R)CCSD(T) method. We compare our results with the previously reported non-relativistic calculations as well as those obtained using a 2-component scalar relativistic DK Hamiltonian. We also compare our results of PDM and polarizabilities with the existing experimental results, wherever available. In this process, we investigate the reason behind the discrepancy observed earlier between the theoretical and experimental results in the PDM of LiNa, and attempt to explain the disparity. To validate the accuracy our polarizability calculations, we verify the variation of the components of polarizability with the volume of the molecule using our relativistic results. We perform detailed error analyses taking into account all possible sources of errors. Finally, we throw some light into the effect of relativity in determining the isotropic  $C_6$  coefficients of the intermolecular van der Waals potential, where we show to which extent the values of  $C_6$  coefficients change if relativistic



Figure 3.1: Demonstration of extrapolation procedure of the PDM values (in a.u.) using complete basis set for LiNa, calculated using the CCSD(T) and the RCCSD(T) methods. The former is shown as a dashed red line with the results from the double, triple and the quadruple zeta basis functions marked by circles, while the latter is a solid blue line, with the results from the double, triple and the quadruple zeta basis functions marked by triangles. The green dotted line is the experimental value. N in the x axis of the plot defines the quality of the N-zeta basis; N = 2for double-zeta basis, N = 3 for triple-zeta basis, N = 4 for quadruple-zeta basis, and so on.

PDMs are used instead of non-relativistic values.

This chapter is structured as follows: Sec. 3.2 describes the theory of PDMs and static dipole polarizabilities in a FF approach, and after giving a brief introduction of (R)CC method (already discussed in Chapter 2), we present the details of the tools of our calculation. In Sec. 3.3 we present our results and thoroughly analyze them. We then examine the trends observed for the considered properties, with emphasis on relativistic and correlation effects. We also made a comparative study of our obtained values with the results available in the literature. Thereafter, we briefly demonstrate the variation of the components of polarizability with volume in both relativistic and non-relativistic frameworks. Next we present a detailed error analysis covering almost all possible sources and quote the estimated uncertainties. In the last sub-section, we report the values of  $C_6$  coefficients of the alkali-dimers due to the inclusion of relativistic effects. At the end, we conclude our work in Sec. 4.3. We use a.u. as our default unit system throughout this exercise, unless mentioned otherwise. We made use of the conversion factors of 1 Debye = 0.3934 a.u. and 1 Å<sup>3</sup> = 6.7483 a.u.<sup>3</sup> while comparing our results with other literature works which do not use a.u..

## **3.2** Theory and methodology

We employ the FF approach to calculate  $\mu$  and  $\alpha$  of heteronuclear alakli-dimers, in which the properties are calculated using energy derivative technique. We elaborate the basic idea of FF method here. In the FF method, an  $n^{th}$  order molecular property can be expressed as a  $n^{th}$ order derivative of energy with respect to a perturbation parameter, which is a weak external electric field for our case. In the presence of a weak, static, and homogeneous electric field of strength  $\mathcal{E}$ , the ground state energy  $(E_0)$  of a molecule can be expressed as

$$E_0 = E_0^{(0)} + \mathcal{E}E_0^{(1)} + \mathcal{E}^2E_0^{(2)} + \cdots, \qquad (3.4)$$

where  $E_0^{(0)}$ ,  $E_0^{(1)}$ ,  $E_0^{(2)}$  etc. are the zeroth-order, first-order, second-order etc. contributions to the total energy, respectively. In traditional form, it can be written as

$$E_0 = E_0^{(0)} - \mu_i \mathcal{E}_i - \frac{1}{2} \alpha_{ij} \mathcal{E}_i \mathcal{E}_j + \cdots, \qquad (3.5)$$

where the indices *i* and *j* run from 1 to 3, while  $\mu_i$  and  $\alpha_{ij}$  are the components of the vector PDM ( $\mu$ ) and rank-two dipole polarizability tensor ( $\alpha$ ), respectively. Now, invoking the Taylor series expansion, it yields

$$E_0 = E_0^{(0)} + \frac{\partial E_0}{\partial \mathcal{E}_i} \bigg|_{\mathcal{E}_i = 0} \mathcal{E}_i + \frac{1}{2!} \frac{\partial^2 E_0}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \bigg|_{\substack{\mathcal{E}_i = 0, \\ \mathcal{E}_j = 0}} \mathcal{E}_i \mathcal{E}_j + \cdots .$$
(3.6)

Comparing Eqs. (3.5) and (3.6), we get

$$\mu_i = -\frac{\partial E_0}{\partial \mathcal{E}_i} \bigg|_{\mathcal{E}_i = 0} \tag{3.7}$$

and

$$\alpha_{ij} = -\frac{\partial^2 E_0}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \bigg|_{\substack{\mathcal{E}_i = 0, \\ \mathcal{E}_j = 0}}.$$
(3.8)

Using these components, the average dipole polarizability  $(\bar{\alpha})$  of a polar molecule is defined as

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{1}{3}(\alpha_{zz} + 2\alpha_{xx}).$$
(3.9)

Here, the quantization axis is assumed along the bond-length and is in the z- direction. Therefore, it follows that  $\alpha_{xx} = \alpha_{yy}$ , leading to the last part of the above equation. It is common to denote  $\alpha_{zz}$  as  $\alpha_{\parallel}$ , and  $\alpha_{xx}$  and  $\alpha_{yy}$  as  $\alpha_{\perp}$ , for such diatomic systems. Hence,

$$\bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}). \tag{3.10}$$

We will use this notation hereafter. Further, one defines polarizability anisotropy as the difference between the parallel and perpendicular components of the polarizability tensor, and is given by

$$\Delta \alpha = \alpha_{\parallel} - \alpha_{\perp}.$$

We chose  $\mathcal{E} = 0.0001$  a.u., for all our FF calculations. At first, we calculated the ground state energies of the molecules using both non-relativistic and relativistic theory. After calculating the mean field energies using HF (DF) method, we took into account the correlation effects by employing the (R)CCSD and (R)CCSD(T) methods. We evaluated the energy derivatives numerically using a three-point central difference formula for our FF calculations of PDMs and static dipole polarizabilities.

In our work, we used a Gaussian charge distribution for the nucleus [35]. We chose the same bond-lengths as in Refs. [16, 29] for the alkali-dimers, and they are 5.4518 a.u. for LiNa, 6.268 a.u. for LiK, 6.5 a.u. for LiRb, 6.93 a.u. for LiCs, 6.61 a.u. for NaK, 6.88 a.u. for NaRb, 7.27 a.u. for NaCs, 7.688 a.u. for KRb, 8.095 a.u. for KCs, and 8.366 a.u. for RbCs. We used Dyall's triple zeta (TZ) basis sets [36] for heavier nuclei (K, Rb, and Cs) and for lighter elements (Li and Na), we opted for augmented correlation-consistent polarized core valance triple zeta (aug-cc-pCVTZ) basis functions [37]. We used Dirac16 program [38] to carry out all the property calculations related to this work.

For heavier molecules, to reduce our computational cost, we imposed a cut-off to electron excitations to high-lying virtuals as their contributions are almost negligible. For NaCs, a cut-off of 2000 a.u. was imposed, while for the KRb, KCs and RbCs molecules, we cut-off all the orbitals possessing energies above 1000 a.u..

# 3.3 Results and discussion

In this section, we discuss our results for the PDMs and then polarizabilities, followed by a detailed error analysis. We discuss in detail the trends observed for the PDMs, based on Table 3.1 and Table 3.2. We then proceed to compare our results with previous works. Fig. 3.1 presents our accurately calculated relativistic  $\mu$  values for LiNa, obtained at complete basis set (CBS) limit, and its excellent agreement with experiment. In Tables 3.3, 3.4 and 3.5, we present our results for  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ . This is followed by discussions on the average polarizabilities and polarizability anisotropies, with the corresponding data presented in Table 3.6 and Table 3.7, respectively. Table 3.9 and Table 3.10 illustrate the importance of relativistic calculations for the isotropic Van der Waals  $C_6$  coefficients in molecule-molecule interactions, while Fig. 3.7 shows the linear variation of the components of polarizabilities with volume. We then present detailed error estimates, one of which is shown explicitly in Table 3.8. In order to determine the reliability of our numerical technique, we systematically tested our FF results by comparing them with results from a five-point central difference scheme.

In the paragraph below, we discuss our calculated results on PDMs and polarizabilities of the considered molecules along with their trends that we observe from our calculations. We then proceed to compare our values with the available ones from literature, for each property. While reporting the trends, we do so within a family (for example, Li family refers to LiA; A=Na, K, Rb, and Cs) and between them, rather than look for trends by arranging the molecules in the increasing order of the number of electrons. This is because two molecules that are next to each other in the number of electrons could be very different, as one may possess a combination of light-heavy nuclei and other moderate-moderate nuclei. We will see in the subsequent paragraphs that ordering molecules in this manner, i.e., by family, provides better insights in trends. A useful quantity to define for the following discussions is the percentage fraction change, F, given by the magnitude of  $\left(\frac{Rel-NR}{Rel} \times 100\right)$  for a property; with 'Rel' and 'NR' being the respective relativistic and non-relativistic values from a given approach. Basically, F quantifies the corrections due to the relativistic effects in a molecule, for that property.

#### 3.3.1 Results for PDMs

Here, we analyze the trends in the PDMs (whose results are provided in Table 3.1 and Table 3.2), starting with the Li family. In this paragraph, we first examine the effects of correlations on the PDMs including the roles of partial triples, followed by a detailed report on relativistic effects. We adopt this order of discussing results for the polarizabilities too. By comparing the three methods that we have employed, we observe that for a given molecule in a family, the inclusion of correlation effects steadily decreases the value of  $\mu$ , in both the non-relativistic and relativistic cases. We find that partial triples in the (R)CCSD(T) methods reduce the values of PDM as compared to those from the (R)CCSD methods. This effect could be as large as 17 percent, as in the case of KRb. We now move on to investigating the roles of relativistic effects. When we inspect the data for the Li family and calculate F, we notice that the differences between the non-relativistic and relativistic results widens as a molecule becomes heavier, but from LiK through LiCs. LiNa displays more percentage fraction change in its PDM with the inclusion of relativistic effects than LiK, in all the three methods (in the HF, CCSD and CCSD(T) methods as well as in the DF, RCCSD and RCCSD(T) methods). We also observe that relativity decreases the PDM of LiCs at the RCCSD(T) level of correlation by about 18 percent, which is clearly not negligible. The trends in the Na family are qualitatively similar to those in the Li family. Again, with the exception of LiNa, we witness a monotonic increase in F, with relativistic effects accounting for as high as about 21 percent for NaCs. In the K family, it is seen that the first deviation from monotonic behaviour as the PDMs decrease from KLi to KRb, and then increase from KRb to KCs. We come across similar trends with the Rb

family as well. In the Cs family, we report a monotonic decrease in the values of PDM. Also, we see that the relativistic effects play significant roles starting from the K family, with F being about 50 percent for KRb, KCs, and RbCs. In light of the significance of relativistic effects for these systems, our RCCSD(T) calculations for the heteronuclear alkali-dimer molecules are the most accurate, to the best of our knowledge. Lastly, we comment on the importance of triple excitations, at the CCSD(T) and RCCSD(T) levels. We also compare our results with some of the recent works on the PDMs of alkali-dimers, and compare their results with ours below.

#### •LiNa

There are a number of calculations on the PDM of LiNa; for example, see Refs. [26, 39, 40, 41, 42, 43]. Most of these earlier works were carried out by employing non-relativistic methods, and some of the results were at odds with the experimental values. We focus on and compare here our results with experiments, and the more recent theoretical studies.

Dagdigian *et al* [21], in 1971, reported the PDM of LiNa to be 0.18(1) a.u.. In the experiment, the measured quantity is actually  $\mu^2/B$ , where *B* is the rotational constant of the molecule. Then, *B* was obtained by using Badger's rule, which required the knowledge of the then-existing literature values for the spectroscopic constants of the molecule. In a subsequent work [22], they improved their value for *B*, and obtained a PDM of 0.1822(7) a.u., with much lesser uncertainty. A third work from the same group [18] found the quantity to be 0.1822(8) a.u., by performing a molecular beam resonance experiment. A fourth experimental result was obtained in 1982, as 0.1777(2) a.u. [25], using laser-induced fluorescence spectra. They too obtained *B*, and hence the PDM. A PDM of 0.18 a.u. was reported by Tarnowsky *et al* [20]. They estimated the property from the empirically derived formula  $\mu_{XY} = C(\bar{\alpha}_{X_2} - \bar{\alpha}_{Y_2})$ , where  $\mu_{XY}$  corresponds to the PDM of a molecule made of atoms *X* and *Y*, and  $\alpha_{X_2}$  corresponds to the average polarizability of a homonuclear dimer of type  $X_2$ , and likewise for  $\alpha_{Y_2}$ . The PDM,  $\mu_{XY}$ , was computed by the authors with a fitting procedure, which in turn required their measured homonuclear polarizabilities of Li<sub>2</sub> and Na<sub>2</sub> as well as their PDMs taken from the then-recent literature.

As a survey of literature described above shows that five different measurements give almost the same value, the experimental result of about 0.18 a.u. itself is very reliable. However, we note that there is a strong tension in results between experiment and theory, as seen from Table 3.1. In fact, for a specified method employed by a work on alkali-dimers, the agreement between experiment and theory is the least for LiNa among other reported alkali-dimers. One such example is Ref. [43], where the authors have employed the CI method to find this issue. We proceed now with discussion of the results obtained from more recent calculations. The work by Urban and Sadlej [31] considers the electron correlation contribution due to the next-to-valence electrons of the two atoms forming a dimer, and reported a PDM of 0.17 a.u.. They employed the CCSD(T) method and added relativistic corrections due to mass-velocity and Darwin (MVD) terms. A subsequent work [44] employed CI in the singles and doubles approximation considering correlations only among ten electrons to obtain 0.19 a.u.. Aymar and Dulieu [27] had employed a full valence CI approach with pseudo-potentials (PP). The PPs included relativistic effects via MVD terms for the heavier Rb and Cs atoms. They took core polarization into account via an l-dependent effective core potential (ECP) due to the sensitivity of the PDM to this effect. They considered three different basis sets, which we denote in the Table 3.1 as Basis A, B, and C. They obtained 0.221 a.u. and 0.218 a.u., by using basis sets A and B, respectively. Mabrouk and Berriche [32] obtained 0.228 a.u. using their CI approach involving the perturbation of a multi-configuration wave function selected iteratively, in a PP approach. Core-polarization and core-valence interactions were partially considered by using *l*-dependent core-polarization potentials. Zuchowski et al [29] computed the PDM of LiNa to be 0.19 a.u., using the CCSD(T) method, and employed a cc-pCV5z basis, augmented with diffuse functions. They also used small-core type ECPs in their calculations. We obtain  $\mu=0.22$  a.u., using the RCCSD(T) approach, with aug-cc-pCVTZ basis sets. Our result is in excellent agreement with that reported in Federov et al (0.21 a.u.) [30]. They employ the the CCSDT method, include scalar relativistic effects, and use the cc-pCVQZ basis. Below, we try to investigate possible reasons due to which results from both our works match well. There are three major differences among these calculations: consideration of relativistic effects, basis functions, and the approximations in the correlation effects due to triple excitations. We observe from Table I that our

RCCSD(T) result is less than the non-relativistic one by about 4.5 percent. Since Federov et al perform their calculations at the scalar-relativistic level while ours uses the DC Hamiltonian, we check the extent to which the difference in relativistic effects affects the final value of PDM. We perform four-component spin-free calculations [45] and show that spin-dependent effects are negligible. For completeness, we have also verified that including Gaunt interaction (which adds the spin-other orbit interaction to the DC Hamiltonian) in our relativistic calculations does not alter the PDM, both at the TZ and QZ levels of basis functions. Therefore, the difference in relativistic effects between the two works leaves the PDM unaltered. The results from both our work as well as from Ref. [30] indicate that as we go to a higher quality basis, the value of PDM decreases. Therefore, we anticipate our PDM obtained at the TZ level of basis to be slightly higher based on this observation. In order to further verify this aspect, we perform RCCSD(T)calculations with aug-ccpCVQZ basis sets, and indeed found that our PDM reduces to 0.197 a.u.. At this point, we verify the importance of diffuse functions in the basis, as the authors of Ref. [30] do not include them. However, we find that diffuse functions hardly change the final results, while core functions (which were employed in both our work as well as Ref. [30]) significantly modifies the PDM. This is in agreement with the findings in Ref. [30]. Next, we observe from our results that as we go from DF to RCCSD(T), correlation effects seem to reduce the value of PDM. However, a careful look shows that the drop in the value of PDM is sharper from RCCSD to RCCSD(T) method. Based on the comparison of the QZ results from our work as well as from Ref. [30], and the facts that a scalar relativistic and a fully relativistic approach gives the same value of PDM, and inclusion of diffuse functions does not change the PDM, we conclude that the missing triples contributions increase the PDM value of LiNa by around 4.5 percent. This analysis also provides an indicator of the importance of choice of basis, scalar relativistic effects, and the importance of higher-order excitations.

We improve our value for the PDM of LiNa further by using the two-point scheme by Helgaker for CBS extrapolation, which is known to be simple and accurate [46, 47]. Fig. I shows our relativistic results (as a solid blue line, with the double, triple and the quadruple zeta results shown as triangles), and we obtain a CBS value that is very close to experiment, at 0.178 a.u.. Our result is in very good agreement with the CBS value from Ref. [30], which employs the CCSD method for this purpose. This indicates that the contributions that could have otherwise occurred from partial triples to the PDM of LiNa is offset by basis extrapolation. Also, we observe from Fig. (3.1) that the non-relativistic CBS curve (as a dashed red line, with the corresponding double, triple and quadruple zeta values indicated by circles) yields a PDM of 0.189 a.u., as compared to the relativistic value of 0.178 a.u., which is different by about 6 percent.

#### •LiX; X = K, Rb, and Cs

Our results for LiK and LiRb are in excellent agreement with experimental results from Dagdigian et al [22], and are well within the error bars. However, the other experimental result presented in Ref. [19] that is available for LiK provides a slightly higher value. Since Ref. [19] uses an improved value for B as compared to that used in Ref. [21], we expect the former to be more accurate. We anticipate that calculations with an even higher quality basis than ours could account for this gap of about 1.5 percent between our work and experiment. For the heavier LiRb and LiCs molecules, even though our calculations and the existing theoretical works agree closely, we expect our all-electron calculations which go beyond the scalar relativistic effects to be an improvement over the existing theoretical works (we did not find any experimental result for LiCs for comparison). The most recent calculation by Federov *et al* [30] employs a higher quality 5Z basis for the lighter Li as compared to our TZ basis. However, they correlate only 9 occupied electrons (one valence electron from the outermost s orbital, and 8 from the next inner sp-shell) of K, Rb, and Cs in their work. We do not make any such approximations, and we correlate all electrons besides not cutting-off any virtuals in our RCCSD(T) calculations with a TZ basis for the LiX molecules. The importance of relativistic effects is especially evident from the difference between our non-relativistic and relativistic results for LiCs.

#### •The Na family

Tarnovsky *et al* [20] reported a PDM of 1.34 a.u. for NaK using an approach that combines measurement with an empirical rule, as discussed under Sec. IIIA of their paper. The work in Ref. [22] found the PDM to be 1.09(4) a.u., using their *B* value, which in turn was obtained from an extrapolation of Badger's rule. Our result is within 2 percent of both the experimental value as well as the most recent theoretical work [30]. The experimental values for NaRb and NaCs were obtained too with their respective *B* values computed using an extrapolation of Badger's rule [22]. Our results agree well with both experiment and recent calculations from other groups [30, 29].

#### •The K and Rb families

The last three molecules that we consider, viz. KRb, KCs, and RbCs, are made solely of relatively heavier atoms. Experimental values exist for KRb and RbCs, and our PDMs differ from the experimental results by about 8 percent and 4 percent, respectively. At this point, it is worth noting that the most recent scalar relativistic calculation on the heavy KRb system using relativistic ECP, done in Ref. [30], differs from experiment by about 17 percent. We now examine if the difference of 0.02 a.u. between our results and those from Ref. [30] is due to relativistic effects beyond those included in the latter. We find that in the case of KRb, we had obtained 0.24 a.u. with our RCCSD(T) calculations, while performing four-component spin-independent calculations give us 0.25 a.u., which is closer to the 0.26 a.u. obtained by Ref. [30]. Therefore, the differences in results between our RCCSD(T) calculations and Ref. [29] are, in part, due to spin-dependent effects such as spin-orbit coupling, while the rest could be due to level of relativity, that is, the use of ECP in Ref. [30] as against an all-electron four-component calculations in the current work. For the heaviest system, RbCs, there is no change in the PDM when we ignore spin-dependent effects. Therefore, we conclude that like KRb, the difference in our RbCs results as compared to those obtained from Ref. [30] are possibly due to our all-electron calculations.

The trends of relativistic effects in PDM in different families are pictorially demonstrated in Fig. 3.2, where we have plotted the CCSD(T) and RCCSD(T) level values of PDM against the atomic number ( $Z_A$ ) of the other constituent nuclei of the molecules under a single family. From the figure it is evident that relativistic effects in PDM increase from lighter to heavier systems in each family, except for Cs family. In Cs family, the relativistic effects become prominent from



Figure 3.2: Plots comparing the CCSD(T) and RCCSD(T) values of  $\mu$  (in a.u.) for the heteronuclear alkali dimers belonging to the (a) Li-, (b) Na-, (c) K-, (d) Rb-, and (e) Cs-families against the atomic number  $Z_A$ .

the lightest molecule of the family, LiCs.

#### 3.3.2 Results for polarizabilities

We now turn to discussing parallel component results of polarizability. The  $\alpha_{\parallel}$  values from our calculations, as well as those from previous works and experiments, are shown in Table 3.3 and Table 3.4. It can be observed from this table that the effects of electron correlations are increasing the  $\alpha_{\parallel}$  values from their HF and DF values, except in the cases of KRb, KCs, and RbCs. This is opposite to the trend that we observed for the PDM, where we found that inclusion of correlation effects lowered their magnitudes. We see that for KRb, KCs, and RbCs, the inclusion of partial triples increases  $\alpha_{\parallel}$  in the non-relativistic calculations, while in the relativistic calculations, we observe a non-uniform trend where it increases  $\alpha_{\parallel}$  values for KCs, and reduces it for



Figure 3.3: Graphs illustrating the differences between the CCSD(T) and RCCSD(T) values of the parallel components of polarizabilities (in a.u.) of (a) Li-, (b) Na-, (c) K-, (d) Rb-, and (e) Cs-families of heteronuclear alkali dimers against the atomic number  $Z_A$ .

KRb and RbCs. However, unlike in the case of PDM, the contribution from partial triples to  $\alpha_{\parallel}$  is quite small, with NaCs differing the most between the (R)CCSD and (R)CCSD(T) results, at about 4 percent. Relativistic effects themselves do not become important for the molecules up to KRb, with F being less than 2 percent throughout (at the CCSD(T) level of theory). However, the relativistic corrections result in a slightly higher F of about 4.5 and 6.5 percent for KCs and RbCs, respectively.

We now briefly discuss the previous works on the  $\alpha_{\parallel}$  values of alkali-dimers. There are no measurements of individual  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  components; experiments obtain average polarizability and polarizability anisotropy. We could only find limited works in literature that report calculation of  $\alpha_{\parallel}$ , and with the exception of Ref. [29], the other works discuss the polarizabil-



Figure 3.4: Graphs showing the departure between the values of perpendicular components of polarizabilities (in a.u.) obtained from the CCSD(T) and RCCSD(T) calculations of different families of heteronuclear alkali dimers. The sub-figures (a) shows the trends in the Li family, while (b), (c), (d), and (e) correspond to Na, K, Rb, and Cs families, respectively.

ities of only one or a few alkali-dimers. In Ref. [31], Urban and Sadlej reported  $\alpha_{\parallel}$  for LiNa, LiK, LiRb, NaK, NaRb, and KRb, using the CCSD(T) method (along with MVD corrections), with the electron correlations accounted from the valence and next-to-valence shells only. The authors in Ref. [48], on the other hand, employed a Numerov-Cooley (NC) scheme in their semi-numerical approach. They reported their results for  $\alpha_{\parallel}$  of LiK in this approach by using Complete Active Space Self-Consistent Field (CASSCF) approach and second-order Complete Active Space Perturbation Theory (CASPT2). They also perform CASSCF in combination with Bishop-Kirtman perturbation theory (BKPT), besides calculating vibrational corrections to  $\alpha_{\parallel}$ . Merawa *et al* [49] calculated  $\alpha_{\parallel}$  of LiNa to be 350.6 a.u., by using the CCSD(T) method, and exciting all the electrons in their calculations. They also obtained this property to be 352.3 a.u., using a time-dependent gauge invariant (TDGI) method. The most recent work by Deiglmayr



Figure 3.5: Plots depicting the fork between the average dipole polarizabilities (in a.u.) in the (a) Li-, (b) Na-, (c) K-, (d) Rb-, and Cs-families from the CCSD(T) and RCCSD(T) methods.

et al [16] employed the CI approach by perturbing the multi-configuration wave function, and had performed calculations on all the alkali-dimers. We find that our RCCSD(T) results are in excellent agreement with their results up to NaCs (the differences are less than 2 percent), after which we observe a sharp deviation of up to 10 percent for KCs. We expect that the differences are not only because of relativity, but also due to correlation effects, recalling our observation that the electron correlations *reduce* this quantity from the HF or DF to the (R)CCSD(T) methods only for these last three heavier molecules. To verify this hunch further, we performed four-component spin-independent calculations [45] for the heavier KRb, NaCs, KCs, and RbCs. We reported that spin-dependent effects such as SOC add to only about 0.1 percent to both parallel as well as perpendicular components of polarizability. A full valence CI treatment in Ref. [16] could be superior to our single reference treatment, but there could also have been a difference due to their ECP versus our all-electron calculations and their CISD against our



Figure 3.6: Plots highlighting the variation of relativistic effects in the polarizability anisotropies (in a.u.) of the heteronuclear alkali dimers belonging to (a) Li-, (b) Na-, (c) K-, (d) Rb-, and (e) Cs-families using the CCSD(T) and RCCSD(T) methods.

RCCSD(T) level of excitations. A reasonable check without expending computational resources is to compare the calculated average polarizabilities from both the works, which is constructed from the parallel and perpendicular components, with experiment. The only available experimental result is from Ref. [20] for KCs, and we find that our result is in better agreement with experiment (within 1 percent) than the result from Ref. [16] (about 5 percent). We do note that these differences are well within our quoted error bars of 10 percent, but based on our observations above, it is very likely that our calculations are more accurate. For the ease of understanding, we present the relativistic effects in  $\alpha^{\parallel}$  for each family of alkali-dimers in Fig. 3.3.

Proceeding with the discussions on the results for  $\alpha_{\perp}$ , we find that these values consistently decrease with the inclusion of electron correlation effects in both the non-relativistic and relativ-



Figure 3.7: The values of  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  (commonly denoted by X, and given in a.u.) are plotted against volume (in a.u.). In the legend, 'NR' refers to the CCSD(T) results while 'Rel' denotes to the RCCSD(T) values.

istic calculations, as shown in Table 3.5, contrary to  $\alpha_{\parallel}$ , and similar to PDM. Relativistic effects are also found to decrease  $\alpha_{\perp}$ . Examining F values reflect that relativistic effects become more important as a molecule in a family gets heavier, with the exception of LiRb. Also, similar to  $\alpha_{\parallel}$ , F is the largest for RbCs, and is about 7 percent. The effect of partial triples is slightly higher for  $\alpha_{\perp}$ , and is about 4.5 percent for RbCs (see Fig. 3.4). In the previous paragraph, we had compared our calculated values for  $\alpha_{\parallel}$  with those from earlier literature. All of those references also computed  $\alpha_{\perp}$  (with the exception of Ref. [48]), and therefore, we will not discuss their methods again in this paragraph.

We see from Table 3.6 that for the non-relativistic as well as the relativistic cases, the average polarizability value decreases from mean-field to (R)CCSD(T) methods, with the exception of LiNa. This can be understood from the fact that for LiNa, the parallel component increases more due to correlation than the decrease in the perpendicular component. This is not the case for all of the other molecules. In fact, the change in perpendicular components even dominates over that of parallel components for the heavier molecules. Relativity, as seen by comparing the CCSD(T) and RCCSD(T) results, further reduces  $\bar{\alpha}$  results. Again, relativistic effects do not alter the average values of polarizabilities significantly, as they do not do so for the individual components. Examining the trends in  $\bar{\alpha}$  at the (R)CCSD(T) level by family, we observe that the relativistic effects within each family become increasingly important as the non-family atom (for example, in the Li family, it could be Na, K, Rb, or Cs) becomes heavier, with the exception of LiCs (see Fig. 3.5). The effect of partial triples is seen to be unimportant for  $\bar{\alpha}$  from Table 3.6. Our results also agree very well with the available experimental values, and are within the error bars of the measured values for NaK and KCs that are reported by Tarnovsky et al [20]. These experimental results for NaK and KCs are obtained by combining measurements of average effective polarizabilities with the then-available PDM values taken from Igel-Mann et al [43], at an average temperature of 612 K and 494 K for NaK and KCs, respectively. When we replaced the PDMs from Igel-Mann *et al* [43] with ours, we observed negligible difference in  $\bar{\alpha}$  that Tarnovsky et al obtained. However, to estimate  $\bar{\alpha}$  for the other alkali-dimers, the work by Tarnovsky et al combines their measured homonuclear dimer polarizabilities with an empirical formula, thereby possibly introducing fairly large errors in some of their results. Regarding temperature dependency, we do not expect that our T = 0 K results would differ significantly from the measurements carried out at the aforementioned temperatures, based on the earlier mentioned work by Muller and Meyer on homonuclear alkali-dimers [50]. In these rigorous studies, Muller and Meyer had shown that the dependency of average polarizability on a wide range of temperatures (between 0 and 1000 K) are not going to change the results significantly, and the maximum variation is anticipated to be about 10 percent from the values obtained at the zero temperature.

For completeness, we discuss the experimental results briefly for  $\bar{\alpha}$  of LiNa from Ref. [22], where the authors have first measured polarizability anisotropy,  $\Delta \alpha$ , by determining Stark frequencies at some value of external electric field. They have combined this information with their knowledge of PDM (which is in turn obtained by measuring the rotational constant, as discussed in the previous paragraphs), to get  $\bar{\alpha}$ , as prescribed in Ref. [21]. At this point, it is worthwhile to mention that all of the current theoretical values underestimate the average polarizability when compared with the experimental results for LiNa (we add that all of these theoretical values are within or very close to the error bars from experiment). This observation holds in spite of the theoretical results agreeing very well with their measurement for the anisotropy. However, since only one known experimental work exists (both for average polarizability and polarizbility anisotropy of LiNa), more detailed calculations and further experiments are possibly required, before arriving at further conclusions.

The trends in  $\Delta \alpha$  (listed in Table 3.7) stem from those in parallel and perpendicular components of polarizability, as  $\Delta \alpha$  is the difference between  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ . For example, since relativistic effects increase  $\alpha_{\parallel}$  while they decrease  $\alpha_{\perp}$  for LiCs, we observe that relativistic effect matters the most for the molecule (about 5 percent) (see Fig. 3.6). Also, partial triples in  $\Delta \alpha$  become more important than in  $\bar{\alpha}$ , with NaCs and LiCs accounting for 8 and 9 percent, respectively. We are not discussing here the  $\Delta \alpha$  results of Ref. [22] as it has already been done in the previous paragraph.

#### •Volume effects

Next, we examine the dependence of components of polarizability on molecular volume. This aspect has been addressed by using models in the past, for example, see Refs. [51, 52]. It has also been discussed in Ref. [16], where the volume, V, is defined as  $\frac{4}{3}\pi r_e^3$ , with  $r_e$  denoting the equilibrium bond-length. We plot the components of polarizabilities, both from non-relativistic and relativistic calculations, against volume in Fig. 3.7. From the figure, we see that a linear fit to our relativistic calculations gives 0.36V + 104.26 for  $\alpha_{\parallel}$ , and 0.17V + 66.7 for  $\alpha_{\perp}$ . We find that the ratio of the slopes of  $\alpha_{\parallel}$  versus V to  $\alpha_{\perp}$  versus V from our relativistic calculations agree well with the non-relativistic ones, and we obtain a value of about 2 for the ratio. This is in agreement with the slope obtained by Deiglmayr *et al* [16] from their calculations. The linear polarizability-volume relationship could be viewed as an effective elliptic charge distribution for a dimer at a specified  $r_e$  [16]. Although relativistic and non-relativistic results for the lighter systems are very close to each other, we observe that the linear fits between the two cases deviate further as we go to the heavier molecules, while continuing to preserve the ratio of the slopes.

#### •Error Analysis

We discuss the possible sources of uncertainties in our calculations of PDMs and polarizabilities of the considered alkali-dimers. We assume our RCCSD(T) values are the most accurate among other methods in literature and therefore the uncertainties are estimated for these results. Since we have adopted the FF approach, it is essential to choose the perturbation parameter,  $\mathcal{E}$ , carefully in order to obtain reliable results. Our choice of  $\mathcal{E} = 10^{-4}$  a.u. is consistent with those from the previous works that had determined PDMs and polarizabilities using the FF procedure. However, we had also verified consistencies in the results by performing calculations of PDMs as well as polarizabilities by using the following values of  $\mathcal{E}$ , namely  $10^{-3}$ ,  $5 \times 10^{-4}$ , and  $10^{-4}$  a.u.. For this purpose, and in view of minimizing the computational cost, we chose only the Li family as a representative case, and repeated the non-relativistic calculations due to the choice of  $\mathcal{E}$ . We also anticipate similar trends with the relativistic calculations and in other heavier alkali-dimers. We found that the PDM values hardly change, while the parallel and perpendicular components of polarizability smoothly change in the first decimal place for LiNa and LiK, and within 3 a.u. for LiRb and LiCs. Also, the truncation errors that could result from numerical differentiation schemes have been taken care of by comparing our results using three-point as well as five-point formulae and we found that the results in both those approaches are identical.

It is imperative to ensure that there is negligible uncertainty involved due to cut-off of virtual orbitals in our relativistic RCCSD(T) calculations for the heavier alkali-dimers. Therefore, we chose NaCs, a moderately heavy molecule where relativistic effects are sufficiently important and yet practical for multiple computations, for this purpose. The results with different set of virtual orbitals are tabulated in Table 3.8. It shows that the PDM values remain identical, while the components of polarizability change in the second decimal place, which are much smaller than the level of accuracy intended to achieve in the present work.

We check the error due to performing calculations on a single geometry instead of vibrational averaging. We have estimated these uncertainties for PDMs as well as parallel and perpendicular components of polarizabilities for the Li family, using the CFOUR program [53, 54]. We employed the CCSD(T) method, and the same basis sets as in our single point calculations. We find that the values of PDM and  $\alpha_{\perp}$  change by less than 1 percent for the Li dimers, while the parallel components change by about 1 percent. We do not expect the error due to neglecting vibrational averaging to exceed a conservative estimate of 2 percent for all of the three properties in alkali-dimers.

Next, we proceed to discuss on the most traditional uncertainties due to neglected effects in our calculations. It is beyond the scope of this work to estimate contributions due to the full Breit and quantum electrodynamics interactions. However, it is expected that these higher-order relativistic corrections will not exceed 0.5% in all the considered molecules. Uncertainties could also arise because of neglecting contributions from higher level excitations in the (R)CC theory and use of incomplete basis functions. The percentage fraction difference in our relativistic results from RCCSD to RCCSD(T) methods indicate that higher-level excitations should not contribute beyond 5 percent to the PDMs. A similar analysis provides us with an error estimate of about 3 percent for  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ . We now analyse the error due to incompleteness in basis. We had employed a TZ basis for our relativistic calculations, and included diffuse functions, wherever available. We could not, however, perform relativistic calculations using a QZ basis, as they are forbiddingly expensive, even for moderately heavy systems like KRb. Therefore, we resort to an approximation, where we first perform extensive CBS calculations for the alkalidimers using the CCSD(T) method. We employed the two-point scheme by Helgaker [46, 47] for CBS, which was mentioned earlier. We then approximate the relativistic CBS value of  $\mu$ and  $\alpha$  (commonly denoted here as O for ease in notation) by  $O_{CBS}^{Rel} \approx (O_{CBS}^{NR}/O_{TZ}^{NR})O_{TZ}^{Rel}$ , where the subscripts refer to the basis and the superscripts indicate whether the property has been obtained using an non-relativistic calculation or a relativistic one. With this approximation, we obtain a percentage fraction difference of less than 2 percent for the PDMs of the alkali-dimers, with the exceptions of NaK and NaRb, as the PDMs for these systems do not converge from DZ through quadruple-zeta (QZ) basis, hence making a CBS extrapolation not possible. However, we do not expect the errors to be beyond 2 percent in these cases too. A similar exercise was also carried out for  $\alpha_{\parallel}$ , and we found that the fraction difference was less than 4 percent for all the alkali-dimers, except for LiRb. We also verified our approximate formula for  $O_{CBS}^{Rel}$ , by explicitly performing RCCSD(T) calculations for the PDM and  $\alpha_{\parallel}$  of NaCs (with aug-cc-pCVTZ for Na and Dyall's 4Z basis for Cs), and obtained exactly the same PDM as that from  $O_{CBS}^{Rel}$ , while  $\alpha_{\parallel}$  differed from the  $O_{CBS}^{Rel}$  estimate by just 0.6 percent. We would expect an error percentage that is similar to that in  $\alpha_{\parallel}$  for the perpendicular components of polarizabilities too, which is at most 4 percent. Finally, we linearly add the errors and estimate that the uncertainties in our relativistic calculations are about 10 percent for the PDMs, as well as for the parallel and perpendicular components of polarizabilities.

#### **3.3.3** Importance of relativistic effects

In this section, we intend to discuss on the implications of our relativistic calculations in a property which is crucial in understanding inter-molecular interactions. For this, we have chosen the van der Waals coefficient  $C_6$ , whose values are very sensitive to the relativistic effects even in the lighter dimers.

As known, when two heteronuclear alkali-dimer molecules interact via a long-range van der Waals interaction, its dominant potential is given by  $-C_6/r^6$  [17, 29, 55]. Here, r is the intermolecular separation and  $C_6$  is known as van der Waals coefficient. For molecules,  $C_6$  can be expressed as [17, 29, 55]

$$C_6 = C_6^{disp} + C_6^{ind} + C_6^{rot}, (3.11)$$

where the three terms on the right hand side are known as the dispersion (denoted by superscript, 'disp'), the induction (denoted by superscript, 'ind'), and the rotational (denoted by superscript, 'rot') contributions, respectively. We estimate the induced contribution, using the expression [29]

$$C_6^{ind} = 2\mu^2 \bar{\alpha},\tag{3.12}$$

by substituting our calculated PDM and  $\bar{\alpha}$  values. Similarly, we determine the rotational contributions using the expression given by [17, 29, 55]

$$C_6^{rot} = \frac{\mu^4}{6B}.$$
 (3.13)

Due to the fourth-power dependence on PDM, the rotational term dominates over the sum of the other two terms by at least an order of magnitude in the evaluation of  $C_6$  values for molecules with large PDMs [17]. This is indeed the case for eight of the ten alkali-dimers with the exceptions LiNa and KRb, owing to their small PDMs and larger *B* value of LiNa. This dependence on accurate calculations of  $C_6$  coefficients become more relevant for molecules such as LiCs and KCs, for which experimental values of PDM do not exist. For estimating *B* values, we consider the <sup>7</sup>Li, <sup>23</sup>Na, <sup>41</sup>K, <sup>87</sup>Rb, and <sup>133</sup>Cs bosonic isotopes.

We, however, have borrowed the most accurately calculated results for the dispersion terms from Ref. [29]. This is done keeping in mind that the dispersion contributions are at least one order lesser than the rotational ones for most of the alkali-dimers. We tabulate all these contributions and the final results of  $C_6$  for various heteronuclear dimens in Table 3.9 and Table 3.10. It can be clearly seen from this table that use of revised  $C_6^{ind}$  and  $C_6^{rot}$  contributions change the final results of  $C_6$  significantly than the values reported in Ref. [29]. In fact, the results become substantially different compared to pure non-relativistic calculations of Ref. [55], which are also quoted in the above table for the comparison. We see from the table that the isotropic  $C_6$  coefficient can vary as much as 7 percent for LiCs, when compared to that from Ref. [29], while it can be about 20 percent for LiK and 15 percent for LiRb with respect to Ref. [55], when relativistic effects are included in obtaining the PDM and polarizabilities. We also observe that there are significant differences between our results and those obtained from the recent calculations in Ref. [56], and are over 25 percent for LiK, LiRb, LiCs, and KCs. At this point, we would also like to draw attention to the fact that although PDM values from Ref. [29] are in close agreement with ours, the differences in our results are still sufficiently large to lead to a non-negligible change in  $C_6$  values owing to the  $\mu^4$  dependence. This clearly highlights the crucial roles that accurate calculations of PDM play in determining the  $C_6$  coefficients of alkalidimers.

With the above discussion it is evident that the many-body theory, i.e. RCC theory, that we have employed gives very reliable estimates of permanent electric dipole moments and polarizabilities of heteronuclear alkali-dimers which are in very good agreement with previous theoretical as well as experimental results.

Table 3.1: Values of PDM ( $\mu$ ) (in a.u.) for LiNa, LiK, LiRb, LiCs and NaK from both relativistic and non-relativistic calculations. We compare these values from various previous calculations and available experimental results. Our results from both the non-relativistic and the relativistic methods are given separately. The errors are quoted within the parentheses.

Method	LiNa	LiK	LiRb	LiCs	NaK				
	_								
PDM results									
This work									
HF	0.26	1.65	2.09	2.92	1.41				
CCSD	0.25	1.49	1.88	2.70	1.19				
$\operatorname{CCSD}(T)$	0.23	1.39	1.75	2.54	1.09				
DF	0.25	1.62	1.96	2.61	1.39				
RCCSD	0.24	1.45	1.72	2.33	1.16				
$\mathrm{RCCSD}(\mathrm{T})$	0.22	1.36	1.59	2.16	1.07				
$\operatorname{RCCSD}(T)$ : QZ	0.197								
$\mathrm{RCCSD}(\mathrm{T})$ : CBS	0.178								
Previous calcula	ations								
CCSD(T) [31]	0.17	1.36	1.71		1.12				
CI [44]	0.19								
CI [27]: Basis A	0.22	1.40	1.64	2.17	1.09				
CI [32]	0.23								
CCSD(T) [29]	0.19	1.34	1.57	2.12	1.07				
CCSDT [30]	0.21	1.34	1.60	2.11	1.05				
Experiment									
Ref. [21]	0.18(1)								
Ref. [22]	0.1822(7)	1.36(4)	1.57(4)		1.09(4)				
Ref. [18]	0.18								
Ref. [25]	0.1777(2)								
Ref. [19]		1.381(2)							
*Ref. [20]	0.18	1.52	1.59	2.48	1.34				

\*The values given for a molecule XY that is made of atoms X and Y are actually obtained by employing an empirical rule, which requires a combination of experimental values of polarizabilities of the homonuclear  $X_2$  and  $Y_2$  molecules, and the values of PDM from the then-recent literature. Table 3.2: Values of PDM ( $\mu$ ) (in a.u.) for NaRb, NaCs, KRb, KCs and RbCs from both relativistic and non-relativistic calculations. We compare these values from various previous calculations and available experimental results. Correlation effects are added through both the (R)CCSD and (R)CCSD(T) methods. Our results from both the non-relativistic and the relativistic methods are given separately.

Method	NaRb	NaCs	KRb	KCs	RbCs				
	חד		ta						
This work									
THIS WOLK									
HF	1.88	2.75	0.50	1.46	0.98				
CCSD	1.57	2.39	0.42	1.28	0.87				
$\operatorname{CCSD}(\mathrm{T})$	1.43	2.21	0.36	1.14	0.77				
DF	1.75	2.42	0.37	1.10	0.73				
RCCSD	1.43	2.02	0.28	0.90	0.61				
$\mathrm{RCCSD}(\mathrm{T})$	1.29	1.83	0.24	0.78	0.53				
Previous calculations									
CCSD(T) [31]	1.43		0.43						
CI [27]: Basis A	1.30	1.82	0.24	0.75	0.49				
CCSD(T) [29]	1.30	1.82	0.24	0.78	0.52				
CCSDT [30]	1.29	1.78	0.26	0.75	0.48				
Experiment									
Ref. [22]	1.22(12)	1.87(8)							
*Ref. [20]	1.38	2.31	0.08	1.02	0.94				
Ref. [24]			0.2227(8)						
Ref. [23]			. /		0.51(4)				

\*The values given for a molecule XY that is made of atoms X and Y are actually obtained by employing an empirical rule, which requires a combination of experimental values of polarizabilities of the homonuclear  $X_2$  and  $Y_2$  molecules, and the values of PDM from the then-recent literature.
Method	LiNa	LiK	LiRb	LiCs	NaK	
		<b>T</b> ].	1-			
		I fils wo	ork			
$\operatorname{HF}$	301.98	425.92	470.95	525.74	502.15	
CCSD	341.02	470.47	512.88	563.86	522.24	
$\operatorname{CCSD}(\mathrm{T})$	344.78	482.64	530.04	594.94	531.01	
DF	301.63	425.52	465.38	529.48	500.20	
RCCSD	340.55	470.06	507.80	577.23	519.73	
$\mathrm{RCCSD}(\mathrm{T})$	344.29	481.94	523.26	604.40	528.01	
		Previous v	vorks			
CCSD(T) [31]	352.26	484.53	591.83		537.16	
CASSCF/NC [48]		532.00				
CASSCF/BKPT [48]		532.00				
CASPT2/NC [48]		512.90				
TDGI [49]	350.6					
CCSD(T) [49]	352.3					
CI [16]	347.6	489.7	524.3	597.0	529.2	

Table 3.3: A comparative analysis of parallel component of the dipole polarizabilities,  $\alpha_{\parallel}$  (in a.u.) of LiNa, LiK, LiRb, LiCs and NaK, between the non-relativistic and relativistic calculations. We also present results from the earlier studies for the comparative purpose.

Table 3.4: A comparative analysis of parallel components of the dipole polarizabilities,  $\alpha_{\parallel}$  (in a.u.) of NaRb, NaCs, KRb, KCs and RbCs, between the non-relativistic and relativistic calculations. We also present results from the earlier studies.

Method	NaRb	NaCs	KRb	KCs	RbCs					
This work										
$\operatorname{HF}$	553.93	625.42	816.33	955.87	1084.57					
CCSD	574.12	653.41	792.99	929.26	1023.90					
$\operatorname{CCSD}(T)$	587.90	685.49	794.12	942.39	1025.35					
$\mathrm{DF}$	549.97	621.75	808.95	932.45	1034.89					
RCCSD	567.46	648.24	783.30	900.21	971.17					
$\mathrm{RCCSD}(\mathrm{T})$	578.50	672.12	780.48	902.22	962.85					
		Previo	us works							
CCSD(T) [31]	606	110010	8/2 10							
CU[16]	579.0	670 7	740 7	0 <u>00</u> 0	004.0					
	572.0	070.7	(48.7	822.3	904.0					

Table 3.5: The values of perpendicular components of dipole polarizability,  $\alpha_{\perp}$  (in a.u.), both from the non-relativistic and relativistic methods. We have also added results that are obtained in the previous works for comparing with our calculations.

Method	LiNa LiK	LiRb	LiCs	NaK	NaRb	NaCs	KRb	KCs	RbCs	
	This work									
$\operatorname{HF}$	203.04282.32	306.98	347.67	321.88	352.61	402.27	516.23	605.67	681.61	
CCSD	187.67249.42	264.58	294.69	284.17	307.90	346.94	424.52	489.13	541.42	
$\operatorname{CCSD}(T)$	186.98247.27	266.80	293.37	280.06	303.41	343.51	410.83	473.24	519.76	
$\mathrm{DF}$	202.67280.92	301.20	335.69	319.57	344.86	385.81	501.11	571.87	628.52	
RCCSD	187.33248.31	262.50	287.97	282.08	300.90	333.43	412.41	463.20	505.76	
$\mathrm{RCCSD}(\mathrm{T})$	186.44246.13	260.10	286.01	277.90	296.02	328.84	398.58	446.81	484.38	
			Previe	ous worl	ks					
CCSD(T)[31]	$188.8\ 246.6$	268.7		268.7	303.2		411.5			
CCSD(T) [49]	187.7									
TDGI [49]	183.1									
$\operatorname{CI}[16]$	$181.8\ 236.2$	246.5	262.5	262.3	280.3	304.2	382.9	425.62	492.3	

Table 3.6: The average values of dipole polarizability,  $\bar{\alpha}$  (in a.u.), of the alkali-dimers from both our and previous calculations. We have also given experimental values for the comparison.

Method	LiNa	LiK	LiRb	LiCs	NaK	NaRb	NaCs	KRb	KCs	RbCs
					This work					
$_{ m HF}$	236.02	330.19	361.64	407.03	381.97	419.72	476.65	616.26	722.40	815.93
CCSD	238.79	323.10	347.35	384.41	363.53	396.64	449.10	547.34	635.84	702.25
$\operatorname{CCSD}(T)$	239.58	325.72	354.55	393.90	363.71	398.24	457.50	538.59	629.62	688.29
DF	235.64	329.12	355.93	400.29	379.78	413.23	464.46	603.72	692.06	763.98
RCCSD	238.40	322.23	344.27	384.39	361.30	389.75	438.37	536.04	608.87	660.90
$\mathrm{RCCSD}(\mathrm{T})$	239.06	324.73	347.82	392.14	361.27	390.01	443.27	525.88	598.61	643.87
				P	revious works					
Experiment										
Ref. [18]	269.93(33.7)	4)								
Ref. [20]		-)			344.16(26.99)				600.60(42.24)	
Ref. [20]*	249.69	377.91	384.65	465.63	391.40	398.15	479.13	526.37	607.35	614.10
Theory										
CCSD(T) [31]	243.23	326.00	365.20		365.57	404.23		555.13		
CI [16]	237.0	320.7	339.1	374.0	351.3	377.5	426.4	504.8	571.1	602.8
CCSD(T) [29]	237.7	324.2	347.2	391.9	358.1	387.1	439.3	523.5	596.0	638.6

\*These values are not strictly experimental, as they are obtained by combining measured homonuclear polarizability with an empirical rule. The rule may not always hold, as evident from the difference in their results that they arrived at by using this approach as compared to their experimental value, for NaK.

Table 3.7: The non-relativistic and relativistic values of dipole polarizability anisotropy,  $\Delta \alpha$  (in a.u.), reported at different levels of (R)CC theory and other methods. A list of previous works are added to the table for comparison with our results.

Mathad	I:No	I :IZ	I:DL	LiCa	NeV	NaDh	NaCa	<b>VD</b> L	VC <sub>a</sub>	DhCa	
Method	Lina	LIK	LIKD	LIUS	nan	Nand	NaOs	KRD	KUS	RDUS	
				This w	ork						
$_{ m HF}$	98.94	143.60	163.97	178.07	180.27	201.05	223.15	300.10	350.20	402.96	
CCSD	153.35	221.05	248.30	269.17	238.07	266.22	306.47	368.48	440.13	482.48	
CCSD(T)	157.80	235.37	263.24	301.57	250.95	284.49	341.98	383.29	469.15	505.59	
DF	98.96	144.60	164.18	193.79	180.63	205.11	235.94	307.84	360.58	406.37	
RCCSD	153.22	221.75	245.30	289.26	237.65	266.56	314.81	370.89	437.01	465.41	
$\mathrm{RCCSD}(\mathrm{T})$	157.85	235.81	263.16	318.39	250.11	282.48	343.28	381.90	455.41	478.47	
			I	Previous	works						
Experiment											
Ref. [18]	161.96(13.5)										
	( )										
Theory											
CCSD(T) [31]	163.3	238.2	289.5		2579	303.1		430.9			
CCSD(T) [29]	156.3	234.5	262.0	317.8	247.2	279.2	339.4	367.6	436.1	462.1	
CI [16]	165.8	253.5	277.8	334.5	266.9	291.7	366.5	365.8	436.7	491.7	

Table 3.8: Demonstration of changes in the  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ ,  $\bar{\alpha}$ ,  $\Delta \alpha$ , and  $\mu$  values of NaCs molecule at different virtual energy level cut-offs using the RCCSD(T) method. Calculations were performed using the TZ basis functions. All the quantities are specified in a.u..

Cut-off	Method	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$	$\mu$
1000	$\mathrm{DF}$	621.78	385.80	464.46	235.98	2.42
1000	RCCSD	648.26	335.48	439.74	312.78	2.02
1000	$\mathrm{RCCSD}(\mathrm{T})$	672.15	331.56	445.09	340.59	1.82
2000	$\mathrm{DF}$	621.75	385.81	464.46	235.94	2.42
2000	RCCSD	648.24	333.43	438.37	314.81	2.02
2000	RCCSD(T)	672.12	328.84	443.27	343.28	1.82
5000	$\mathrm{DF}$	621.78	385.81	464.47	235.97	2.42
5000	RCCSD	648.26	333.43	438.37	314.83	2.02
5000	$\mathrm{RCCSD}(\mathrm{T})$	672.15	328.93	443.34	343.22	1.82

Table 3.9: Values of isotropic  $C_6$  coefficients (in a.u.) of LiNa, LiK, LiRb, LiCs, and NaK by combining our estimated  $C_6^{ind}$  and  $C_r^{rot}$  contributions with the  $C_6^{disp}$  contributions borrowed from Ref. [29]. We have also compared these results with the previously reported two non-relativistic calculations. The differences between our results with other calculations demonstrate importance of relativistic calculations in the determination of the  $C_6$  coefficients.

Molecule	Reference	$C_6$ value
LiNa	Ref. [55]	3 880
	Ref. [56]	3583
	Ref. [29]	3  709
	This work	3 807
LiK	Ref. [55]	524  000
	Ref. [56]	$570 \ 190$
	Ref. [29]	411 682
	This work	$434 \ 316$
LiRb	Ref. [55]	$1\ 070\ 000$
	Ref. [56]	$1\ 252\ 300$
	Ref. [29]	884  705
	This work	$929\ 144$
LiCs	Ref. [55]	$3\ 840\ 000$
	Ref. [56]	4 585 400
	Ref. [29]	$3\ 409\ 406$
	This work	$3\ 664\ 836$
NaK	Ref. [56]	$561 \ 070$
	Ref. [29]	516 606
	This work	$518 \ 370$

Table 3.10: Values of isotropic  $C_6$  coefficients (in a.u.) of NaRb, NaCs, KRb, KCs, and RbCs by combining our estimated  $C_6^{ind}$  and  $C_r^{rot}$  contributions with the  $C_6^{disp}$  contributions borrowed from Ref. [29]. We have also compared these results with the previously reported two non-relativistic calculations.

Molecule	Reference	$C_6$ value
NaRb	Ref. [56]	$1 \ 524 \ 900$
	Ref. [29]	$1 \ 507 \ 089$
	This work	$1 \ 457 \ 076$
NaCs	Ref. [56]	$7 \ 323 \ 100$
	Ref. [29]	$6 \ 946 \ 696$
	This work	$7\ 086\ 877$
KRb	Ref. [56]	15  972
	Ref. [29]	17 720
	This work	17  542
KCs	Ref. [56]	345  740
	Ref. [29]	$469\ 120$
	This work	469  769
RbCs	Ref. [56]	$147 \ 260$
	Ref. [29]	$180 \ 982$
	This work	190 442

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## Chapter 4

# PDMs and Static Electric Dipole Polarizabilities of Open-Shell Alkali–Alkaline-Earth Molecules

## 4.1 Introduction

With a view to examining the potential of the RCC method we use, in the preceding chapter we have discussed on the relativistic effects in the determination of PDMs and static dipole polarizabilities of heteronuclear alkali-dimers. Our theoretical RCC results for PDMs and polarizabilities agreed reasonably well with the literature values wherever available. One can assert that the RCC method is fairly accurate, at least to produce accurate wave functions in the heteronuclear alkali-dimers. But, the alkali-dimers are closed-shell molecules. Only open-shell molecules are sensitive to eEDM in the EDM experiments. Therefore, we are interested to find out accurate wave functions for one-valence molecular systems using RCC theory in order to apply the method to search for eEDM studies. In view of this, our next rational step forward is to study PDMs and static electric dipole polarizabilities of the open-shell laser coolable molecules. We extend our RCC calculations to the hetoeronuclear molecules consisting of alkali (Alk) and alkaline-earth metal (AlkE) atoms. Successful cooling of the the Alk [1] and AlkE atoms [2] to ultracold temperatures opens up the opportunity to produce Alk-AlkE molecules. In this chapter, we shall discuss about the relativistic effects in PDMs and static dipole polarizabilities of open-shell Alk-AlkE molecules along with other useful aspects. The Alk-AlkE molecules promise similar potential applications like alkali-dimers along with some advantageous features due to the possession of non-zero magnetic dipole moments. Non-zero magnetic moments of Alk-AlkE molecules would enable us to control and manipulate them with external magnetic fields. Bauschlicher et al. [3] had carried out one of the first theoretical studies on Alk-AlkE molecular bond-lengths and PDMs. Kotochigova et al. [4] had investigated the electronic properties of Li-AlkE molecules employing non-relativistic CC theory. In Ref. [5], ground state properties for eight Alk-AlkE molecules (Alk: Li, Na, K, Rb, and AlkE: Ca, Sr) were calculated using CCSD(T) method. Roles of relativistic effects were not investigated in these studies. In an another recent work [6], electronic and spectroscopic properties of sixteen Alk-AlkE molecules (Alk: Li, Na, K, Rb and AlkE: Be, Mg, Ca, Sr) were investigated using multi-reference CI (MRCI) method. In our work, we consider sixteen Alk-AlkE molecules made from the combination of four Alk atoms (Li, Na, K, Rb) and four AlkE atoms (Be, Mg, Ca, Sr). We compare results obtained from both the non-relativistic (NR) and relativistic (Rel) calculations of  $\mu$  and  $\alpha$  of the chosen molecules in their ground state  $(^{2}\Sigma^{+})$ . In this work too, we adopt the FF approach to estimate the PDMs and polarizabilities from the ground state energies of the molecules calculated at different levels of theory (HF/DF, (R)CCSD, and (R)CCSD(T) methods). The theory of estimating PDM and polarizability in the FF approach has been already discussed in the previous chapter. We also analyze the correlation effects in great detail as done for the alkali dimers in the previous chapter. The discussions that follow in this chapter include studying the associated uncertainties of our results, establishing empirical relationship between average molecular polarizability and constituent atomic polarizabilities, and lastly comparing our results with those available in literature.

This chapter is organised as follows: In Sec. 4.2, we briefly describe the basis sets used in our calculations, cut-offs imposed on high-lying virtual orbitals, and other important parameters crucial to our calculations. In Sec. 4.3, we present our results and discuss about their trends.

Molecule	Method	Non-relativistic	Relativistic
LiBe	$\mathrm{HF}/\mathrm{DF}$	2.04	2.04
	(R)CCSD	1.39	1.39
	(R)CCSD(T)	1.33	1.33
LiMg	$\mathrm{HF}/\mathrm{DF}$	0.33	0.34
	(R)CCSD	0.36	0.35
	(R)CCSD(T)	0.41	0.40
LiCa	$\mathrm{HF}/\mathrm{DF}$	0.85	0.84
	(R)CCSD	0.47	0.44
	(R)CCSD(T)	0.43	0.40
LiSr	$\mathrm{HF}/\mathrm{DF}$	0.30	0.23
	(R)CCSD	0.18	0.13
	(R)CCSD(T)	0.16	0.11
NaBe	HF/DF	0.09	0.12
	(R)CCSD	0.70	0.76
	(R)CCSD(T)	0.85	0.86
NaMg	HF/DF	0.25	0.25
	(R)CCSD	0.25	0.24
	(R)CCSD(T)	0.31	0.30
NaCa	$\mathrm{HF}/\mathrm{DF}$	0.09	0.06
	(R)CCSD	0.45	0.42
	(R)CCSD(T)	0.46	0.43
NaSr	$\mathrm{HF}/\mathrm{DF}$	0.09	0.08
	(R)CCSD	0.28	0.21
	(R)CCSD(T)	0.26	0.20

Table 4.1: Values of PDMs (in a.u.) of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and NaSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods.

Molecule	Method	Non-relativistic	Relativistic
KBe	$\mathrm{HF}/\mathrm{DF}$	0.33	0.32
	(R)CCSD	0.58	0.57
	(R)CCSD(T)	0.76	0.75
KMg	$\mathrm{HF}/\mathrm{DF}$	0.47	0.46
	(R)CCSD	0.25	0.24
	(R)CCSD(T)	0.37	0.35
KCa	$\mathrm{HF}/\mathrm{DF}$	0.05	0.08
	(R)CCSD	0.66	0.61
	(R)CCSD(T)	0.76	0.70
KSr	$\mathrm{HF}/\mathrm{DF}$	0.16	0.13
	(R)CCSD	0.57	0.44
	(R)CCSD(T)	0.64	0.51
RbBe	$\mathrm{HF}/\mathrm{DF}$	0.45	0.40
	(R)CCSD	0.49	0.46
	(R)CCSD(T)	0.69	0.64
$\operatorname{RbMg}$	$\mathrm{HF}/\mathrm{DF}$	0.54	0.49
	(R)CCSD	0.23	0.21
	(R)CCSD(T)	0.37	0.33
RbCa	$\mathrm{HF}/\mathrm{DF}$	0.09	0.09
	(R)CCSD	0.69	0.60
	(R)CCSD(T)	0.81	0.70
RbSr	$\mathrm{HF}/\mathrm{DF}$	0.04	0.14
	(R)CCSD	0.60	0.50
	(R)CCSD(T)	0.72	0.58

Table 4.2: Values of PDMs (in a.u.) of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and RbSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods.



Figure 4.1: Plots demonstrating relative percentage changes in the values of  $\mu$  in the Alk-AlkE molecules due to (a) the electron correlation effects ( $\delta_{\mu}^{corr}$ ) and (b) the relativistic effects ( $\delta_{\mu}^{rel}$ ) through the four-component spinfree Hamiltonian in the RCCSD(T) method. The x-axis shows atomic number of the alkaline-earth atoms.

## 4.2 Methodology

We employ both the CC and RCC theories to calculate PDMs and static dipole polarizabilities of the Alk-AlkE molecules in the FF approach. We consider both the (R)CCSD and (R)CCSD(T) approximations to carry out these calculations.

We have used the equilibrium bond-lengths of the Alk-AlkE molecules from Ref. [6], where the authors had employed the MRCI method to obtain the ground state energies of the chosen molecules, and obtained the equilibrium bond-lengths from the minima of the corresponding PECs. For lighter elements (Li, Be, Na, Mg), we used correlation-consistent polarized corevalance quadruple zeta (cc-pCVQZ) basis sets [7, 8], and for the heavier ones (K, Ca, Rb, Sr), we used Dyall's quadruple zeta (QZ) [9] basis functions. We chose a reasonably small static electric field perturbation parameter  $\epsilon = 10^{-4}$  a.u. for the property calculations. For the reduction of computational cost, at both the (R)CCSD and (R)CCSD(T) levels, we have cut-off virtual orbitals having energies greater than 1000 a.u. for the relatively heavier molecules (NaSr, KSr, RbBe, RbMg, RbCa and RbSr). All the computations were carried out using the DIRAC program [10].

Table 4.3: Values of different components of the electric dipole polarizabilities ( $\alpha_{\parallel}$  and  $\alpha_{\perp}$ ) as well as average polarizability ( $\bar{\alpha}$ ) and polarizability anisotropy ( $\Delta \alpha$ ) of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and NaSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods. All units are in a.u..

			Non-rel	ativistic			Relat	ivistic	
Molecule	e Method	$lpha_\parallel$	$\alpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$	$lpha_\parallel$	$lpha_{\perp}$	$\bar{lpha}$	$\Delta \alpha$
LiBe	HF'/DF	211.36	88.52	129.46	122.84	212.06	88.56	129.73	123.5
	(R)CCSD	373.58	111.54	198.87	262.04	374.13	111.6	199.11	262.53
	(R)CCSD(T)	376.55	114.42	201.78	262.13	376.9	114.12	201.91	262.48
LiMg	$\mathrm{HF}/\mathrm{DF}$	557.42	197.55	317.51	359.87	553.14	197.66	316.15	355.48
	(R)CCSD	497.42	169.19	278.6	328.23	495.95	169.37	278.23	326.58
	(R)CCSD(T)	481.64	166.64	271.64	315	480.63	166.84	271.44	313.79
LiCa	$\mathrm{HF}/\mathrm{DF}$	445.36	252.82	317	192.54	455.26	250.32	318.63	204.94
	(R)CCSD	559.03	231.68	340.8	327.35	563.01	229.97	340.98	333.04
	(R)CCSD(T)	580.16	229.88	346.64	350.28	584.28	228.08	346.81	356.2
LiSr	HF/DF	504.27	332.4	389.69	171.87	464.91	296.6	352.7	168.31
	(R)CCSD	597.14	283.13	387.8	314.01	560.36	268.63	365.78	291.73
	(R)CCSD(T)	622.61	276.08	391.59	346.53	620.03	268.5	385.68	351.53
NaBe	$\mathrm{HF}/\mathrm{DF}$	532.87	153.96	280.26	378.91	536.96	147.47	277.3	389.49
	(R)CCSD	396.7	144.08	228.27	252.62	402.3	140.48	227.75	261.82
	(R)CCSD(T)	390.48	137.79	222.02	252.69	392.99	140.2	224.46	252.79
NaMg	HF/DF	490.11	220.49	310.36	269.62	485.25	219.52	308.1	265.73
-	(R)CCSD	446.77	186.06	272.96	260.71	442.72	185.37	271.15	257.35
	(R)CCSD(T)	441.11	183.04	269.06	258.07	437.29	182.39	267.36	254.9
NaCa	HF/DF	743.08	276.5	432.03	466.58	730.78	274.73	426.75	456.05
	(R)CCSD	605.78	246.26	366.1	359.52	600.19	245.06	363.44	355.13
	(R)CCSD(T)	590.94	243.6	359.38	347.34	585.93	242.25	356.81	343.68
NaSr	HF/DF	816.5	325.57	489.21	490.93	784.82	316.82	472.82	468
	(R)CCSD	666.07	299.65	421.79	366.42	648.63	284.99	406.2	363.64
	(R)CCSD(T)	652.97	296.04	415.02	356.93	636.1	280.9	399.3	355.2

Table 4.4: Values of different components of the electric dipole polarizabilities ( $\alpha_{\parallel}$  and  $\alpha_{\perp}$ ) as well as average polarizability ( $\bar{\alpha}$ ) and polarizability anisotropy ( $\Delta \alpha$ ) of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and RbSr molecules from the HF, DF, CCSD, RCCSD, CCSD(T), and RCCSD(T) methods. All units are in a.u..

		Non-rela	ativistic		Relativistic			
Method	$lpha_{\parallel}$	$lpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$	$lpha_{\parallel}$	$lpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$
$\mathrm{HF}/\mathrm{DF}$	763.69	433.35	543.46	330.34	745.42	424.52	531.49	329.9
(R)CCSD	646.62	276.35	399.77	370.27	628.81	271.91	390.88	356.9
(R)CCSD(T)	638.91	250.30	379.84	388.61	621.5	246.63	371.59	374.87
$\mathrm{HF}/\mathrm{DF}$	764.42	451.98	555.86	312.84	749.44	443.96	545.79	305.48
(R)CCSD	671.65	315.14	433.98	356.51	657.19	310.20	425.86	346.99
(R)CCSD(T)	658.97	295.79	416.85	363.18	644.47	291.31	409.03	353.16
$\mathrm{HF}/\mathrm{DF}$	1209.95	462.82	711.86	747.13	1171.9	468.66	703.07	703.24
(R)CCSD	956.7	347.2	550.37	609.5	931.75	350.76	544.42	580.99
(R)CCSD(T)	909.43	330.71	523.62	578.72	888.38	334.4	519.06	553.98
$\mathrm{HF}/\mathrm{DF}$	1339.52	505.45	783.47	834.07	1249.65	498.21	748.69	751.44
(R)CCSD	1026.44	388.06	600.85	638.38	975.42	387.44	583.43	587.98
(R)CCSD(T)	971.74	372.68	572.37	599.06	928.23	372.13	557.5	556.1
HF/DF	819 56	554 86	643 09	$264 \ 7$	$773 \ 14$	507 91	576 32	265 23
$(\mathbf{R})\mathbf{CCSD}$	697 67	333.56	454 93	364.11	648 61	312.05	494 94	336.56
(R)CCSD(T)	692 69	295.00	427.6	397.64	644 08	278.14	400 12	365.94
HF/DF	862.3	567.18	665.55	295.12	806.75	523.44	617.88	283.31
(R)CCSD	740.42	366.43	491.09	373.99	684.47	343.39	457.08	341.08
(R)CCSD(T)	720.48	335.83	464.05	384.65	667.39	316.44	433.42	350.95
HF/DF	1372.88	567.82	836.17	805.06	1260.82	533.44	775.9	727.38
(R)CCSD	1072.62	393.68	619.99	678.94	986.42	380.38	582.39	606.04
(R)CCSD(T)	1015.59	368.26	584.04	647.33	939.92	357.71	551.78	582.21
HF/DF	1526.59	599.47	908.51	927.12	1349.35	562.62	824.86	786.73
(R)CCSD	1150.27	438.2	675.56	712.07	1027.13	407.66	614.25	619.77
(R)CCSD(T)	1080.95	414.26	636.49	666.69	970.25	385.59	580.48	584.66
	Method HF/DF (R)CCSD (R)CCSD(T) HF/DF (R)CCSD (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T) HF/DF (R)CCSD(T)	Method $\alpha_{\parallel}$ HF/DF         763.69           (R)CCSD         646.62           (R)CCSD(T)         638.91           HF/DF         764.42           (R)CCSD         671.65           (R)CCSD(T)         658.97           HF/DF         1209.95           (R)CCSD         956.7           (R)CCSD(T)         909.43           HF/DF         1339.52           (R)CCSD(T)         9071.74           HF/DF         1339.52           (R)CCSD(T)         971.74           HF/DF         819.56           (R)CCSD(T)         697.67           (R)CCSD(T)         692.69           HF/DF         862.3           (R)CCSD(T)         720.48           HF/DF         1372.88           (R)CCSD(T)         1015.59           HF/DF         1526.59           (R)CCSD(T)         1015.59           HF/DF         1526.59           (R)CCSD(T)         105.27           (R)CCSD(T)         1080.95	Method $\alpha_{\parallel}$ $\alpha_{\perp}$ HF/DF         763.69         433.35           (R)CCSD         646.62         276.35           (R)CCSD(T)         638.91         250.30           HF/DF         764.42         451.98           (R)CCSD         671.65         315.14           (R)CCSD(T)         658.97         295.79           HF/DF         1209.95         462.82           (R)CCSD(T)         956.7         347.2           (R)CCSD(T)         909.43         330.71           HF/DF         1339.52         505.45           (R)CCSD(T)         971.74         372.68           HF/DF         819.56         554.86           (R)CCSD(T)         692.69         295.05           HF/DF         862.3         567.18           (R)CCSD(T)         692.69         295.05           HF/DF         862.3         567.18           (R)CCSD(T)         720.48         335.83           HF/DF         1372.88         567.82           (R)CCSD(T)         1015.59         368.26           (R)CCSD(T)         1015.59         368.26           (R)CCSD(T)         1015.59         599.47	Method $\alpha_{\parallel}$ $\alpha_{\perp}$ $\bar{\alpha}$ HF/DF763.69433.35543.46(R)CCSD646.62276.35399.77(R)CCSD(T)638.91250.30379.84HF/DF764.42451.98555.86(R)CCSD671.65315.14433.98(R)CCSD(T)658.97295.79416.85HF/DF1209.95462.82711.86(R)CCSD956.7347.2550.37(R)CCSD(T)909.43330.71523.62HF/DF1339.52505.45783.47(R)CCSD1026.44388.06600.85(R)CCSD(T)971.74372.68572.37HF/DF819.56554.86643.09(R)CCSD(T)697.67333.56454.93(R)CCSD(T)692.69295.05427.6HF/DF862.3567.18665.55(R)CCSD(T)720.48335.83464.05HF/DF1372.88567.82836.17(R)CCSD(T)1015.59368.26584.04HF/DF1526.59599.47908.51(R)CCSD(T)1015.59368.26584.04HF/DF1526.59599.47908.51(R)CCSD(T)1015.59368.26584.04HF/DF1526.59599.47908.51(R)CCSD(T)1080.95414.26636.49	Method $\alpha_{\parallel}$ $\alpha_{\perp}$ $\bar{\alpha}$ $\Delta \alpha$ HF/DF         763.69         433.35         543.46         330.34           (R)CCSD         646.62         276.35         399.77         370.27           (R)CCSD         646.62         276.35         399.77         370.27           (R)CCSD         646.42         451.98         555.86         312.84           (R)CCSD         671.65         315.14         433.98         356.51           (R)CCSD(T)         658.97         295.79         416.85         363.18           HF/DF         1209.95         462.82         711.86         747.13           (R)CCSD         956.7         347.2         550.37         609.5           (R)CCSD(T)         909.43         330.71         523.62         578.72           HF/DF         1339.52         505.45         783.47         834.07           (R)CCSD         1026.44         388.06         600.85         638.38           (R)CCSD(T)         971.74         372.68         572.37         599.06           HF/DF         819.56         554.86         643.09         264.7           (R)CCSD(T)         692.69         295.05 <td><math display="block">\begin{array}{ c c c c c c c c c c c c c c c c c c c</math></td> <td>Method         <math>\alpha_{\parallel}</math> <math>\alpha_{\perp}</math> <math>\bar{\alpha}</math> <math>\Delta \alpha</math> <math>\alpha_{\parallel}</math> <math>\alpha_{\perp}</math>           HF/DF         763.69         433.35         543.46         330.34         745.42         424.52           (R)CCSD         646.62         276.35         399.77         370.27         628.81         271.91           (R)CCSD(T)         638.91         250.30         379.84         388.61         621.5         246.63           HF/DF         764.42         451.98         555.86         312.84         749.44         443.96           (R)CCSD         671.65         315.14         433.98         356.51         657.19         310.20           (R)CCSD         658.97         295.79         416.85         363.18         644.47         291.31           HF/DF         1209.95         462.82         711.86         747.13         1171.9         468.66           (R)CCSD         956.7         347.2         550.37         609.5         931.75         350.76           (R)CCSD(T)         909.43         330.71         523.62         578.72         888.38         34.4           HF/DF         1339.52         505.45         783.47         834.07         1249.65</td> <td><math display="block">\begin{array}{ c c c c c c c c c c c c c c c c c c c</math></td>	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Method $\alpha_{\parallel}$ $\alpha_{\perp}$ $\bar{\alpha}$ $\Delta \alpha$ $\alpha_{\parallel}$ $\alpha_{\perp}$ HF/DF         763.69         433.35         543.46         330.34         745.42         424.52           (R)CCSD         646.62         276.35         399.77         370.27         628.81         271.91           (R)CCSD(T)         638.91         250.30         379.84         388.61         621.5         246.63           HF/DF         764.42         451.98         555.86         312.84         749.44         443.96           (R)CCSD         671.65         315.14         433.98         356.51         657.19         310.20           (R)CCSD         658.97         295.79         416.85         363.18         644.47         291.31           HF/DF         1209.95         462.82         711.86         747.13         1171.9         468.66           (R)CCSD         956.7         347.2         550.37         609.5         931.75         350.76           (R)CCSD(T)         909.43         330.71         523.62         578.72         888.38         34.4           HF/DF         1339.52         505.45         783.47         834.07         1249.65	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

### 4.3 Results and discussion

We investigate the trends of relativistic effects as well as electron correlation effects by analyzing results from the HF/DF, (R)CCSD and (R)CCSD(T) methods in the undertaken properties of the Alk-atom family-wise. Which means is that, for example, Li-family refers to LiX molecules, where X could be Be, Mg, Ca, or Sr atom. The rationale behind categorizing the chosen molecules as families rather than looking for trends based on electron number is due to the fact that two molecules that are next to each other in the periodic table can display very dissimilar trends, since one molecule may contain a combination of light-heavy nuclei, while the other could contain moderate-moderate combination of nuclei. There is no particularly strong reason to provide our results based on Alk-atom family rather than AlkE-atom family, and therefore when certain trends are easier to see with the latter, we have appropriately discussed them in the main text. For the purpose of analyzing the trends, we use two quantities in the subsequent subsections – one for correlation effects and the other for relativistic ones. For the former, we define  $\delta_P^{corr} = \left(\frac{P_{(R)CC} - P_{DF/HF}}{P_{DF/HF}} \times 100\right)$  that signifies the relative percentage of correlation contributions to the property, P. For the latter, we define  $\delta_P^{rel} = \left(\frac{P_{Rel} - P_{NR}}{P_{NR}} \times 100\right)$ .

#### 4.3.1 Results for PDMs

In Table 4.1, we present the values of PDM for all the considered systems from both the NR and Rel calculations. To demonstrate the roles of electron correlation effects explicitly, we give values from the HF/DF, (R)CCSD, and (R)CCSD(T) methods for all the molecules. We observe from the table that electron correlation effects play significant roles in determining the quality of the final values. These effects are largest in the RCCSD(T) values for NaCa (where the percentage fraction correlation is about 620), KCa (775), and RbCa (680). In the LiX family, the magnitudes of the PDM decrease gradually from the HF method to the CCSD(T) method, except in the case of LiMg, which shows the opposite behaviour. However, this trend changes for NaX family, where the values increase from the HF method to the CCSD(T) method, with two exceptions – NaSr, where the PDM increases from HF to CCSD, but decreases slightly (within error margins) in the CCSD(T) method, and NaMg, where the relativistic results decrease ever so slightly (again within error margins) from the HF to CCSD methods, and then show a clear



Figure 4.2: Schematic figures showing relative percentage changes in (a) the  $\bar{\alpha}$  values and (b) the  $\Delta \alpha$  values of the Alk-AlkE molecules due to the electron correlation effects at the RCCSD(T) method. The values in y-axis are given in % while x-axis shows atomic number of the alkaline-earth atom for a given alkali atom family.

increase in the magnitude of the PDM. For both the KX and RbX families, the values increase from the HF method to the CCSD(T) method gradually, except for KMg and RbMg. In a nutshell, for non-Mg containing molecules, we observe from our results for PDM that except for the lightest Li family, where correlation effects decrease the PDM, the general tendency of electron correlation is to increase the value of the property. For those chosen molecules that contain Mg, correlation effects increase the PDM in the lighter Li and Na families, whereas for the heavier K and Rb families, correlation decreases the PDM. Fig. 4.1(a), which plots the related quantity,  $\delta_{\mu}^{corr}$  for the relativistic case for the four families, shows these observed trends. An interesting observation that arises from the distribution of  $\delta_{\mu}^{corr}$  for the Mg family in the figure is that  $|\mu_{corr}/\mu_{HF}|$  is almost a constant, especially relative to the same quantity for the other families.

Having discussed trends of correlation effects, we now compare the results for PDMs between the non-relativistic and relativistic methods, from the data presented in Table 4.1, Table 4.2 and Fig. 4.1(b), with the figure plotting percentage fraction difference due to relativity at the (R)CCSD(T) level of theory. The first observation that we can draw from our results is that the effect of relativity is usually small in the evaluation of PDM values in most of the cases. The only exceptions are the lightest LiBe, where there is practically no difference between NR and Rel



Figure 4.3: Schematic figures showing relative percentage changes in (a)  $\delta_{\bar{\alpha}}^{rel}$ , and (b)  $\delta_{\Delta\alpha}^{rel}$  in the Alk-AlkE molecules using the RCCSD(T) method. The x-axis provides atomic number of the alkaline-earth atom, as in the previous figure.

values, and NaBe, where relativistic effects are around 1 percent. This is reflected in Fig. 4.1(b), where for each of the families, the slope is negative. The figure also shows that in each family, the importance of relativity increases with the atomic number of the AlkE atom. However, the rate of change is non-trivial, with crossings observed between families. We also note that the importance of relativistic effects is most pronounced in the heaviest molecules considered of each family, with the PDM of LiSr changing the most with the inclusion of relativistic effects (31 percent). In summary, while the PDM is lowered when one switches to a relativistic framework from a non-relativistic one, the degree to which the quantity decreases increases with the atomic number of a given AlkE atom. Note that this is not directly obvious visually from Fig. 4.1(b), since the x-axis is not linear.

Relativistic effects impact the results both at the mean-field level and after inclusion of correlation effects in the RCC theory. In the former, we see that relativity accounts for as much as 250 percent for RbSr, but also note that this is an exception; they are at most about 33 percent in the the rest of the molecules. In the correlation sector, inclusion of relativity can decrease the correlation value by as large as 35 percent for RbSr.

#### 4.3.2 Results for polarizabilities

In Tables 4.3 and 4.4, we present values of  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ ,  $\bar{\alpha}$ , and  $\Delta \alpha$ , both from NR and Rel calculations, and in each of these cases, we provide results at the mean-field, CCSD, and CCSD(T) levels of theory. We note that the individual values as well as the trends for  $\bar{\alpha}$  and  $\Delta \alpha$  are obviously influenced by those in  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ . Therefore, in view of the former two quantities being the ones that are obtained in experiment, we focus on the individual values and trends of these properties. Otherwise, the discussion of the flow of results in this sub-section will be very similar to that from the previous one.

We begin with a discussion on correlation effects, based on data from Table 4.3, Table 4.4 and Fig. 4.2. We expect the trends in polarizabilities to be at least somewhat different from those in PDMs not only because the quantities are intrinsically different, but also because the stress would not be on  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , but rather on  $\bar{\alpha}$  and  $\Delta \alpha$ . We observe that electron correlation influences the results significantly, with the largest percentage fraction difference between the RCCSD(T) and DF results occurring for the lightest LiBe molecule (about 60 percent for  $\bar{\alpha}$  and about 110 percent for  $\Delta \alpha$ ). However, it is not as striking as in the case of PDMs, where we encountered changes as large as about 775 percent. Trend-wise, the plots in sub-figures 2(a) and 2(b) display an almost monotonic trend for each of the families, with the molecules containing Be in each family being an exception, unlike in the case of PDMs. Note that in the non-relativistic case, the correlation trends are similar for  $\Delta \alpha$ , but are slightly different in the case of  $\bar{\alpha}$ . One can also observe from sub-figures 2(a) and 2(b) that with the exception of the Li family, the correlation trends vary relatively mildly for the rest of the families for  $\bar{\alpha}$ , whereas for  $\Delta \alpha$ , we see more variation. This indicates that accurate determination of the values of  $\Delta \alpha$  for the Alk-AlkE systems would be more sensitive to proper inclusion of the electron correlation effects. We observe similar signs of the peculiarity seen in the Mg family of Fig. 4.1 in our relativistic results, and in this case, we find that  $|\Delta \alpha_{corr}/\Delta \alpha_{HF}|$  varies within around 30 percent, which is not small but still significantly smaller relative to other families. The same quantity constructed for  $\bar{\alpha}$ also varies within 30 percent across the Mg family, which is again much less than the maximum variation seen in each of the other families. To summarize, we find that correlation effects play

a very important role in determining  $\bar{\alpha}$  and  $\Delta \alpha$ , but not as extreme as in the case of PDMs. We also observe that the trends for both  $\bar{\alpha}$  and  $\Delta \alpha$  are smoother than the trend found for the PDMs. Lastly, we see a similar behaviour in  $|P_{corr}/P_{HF}|$  for the Mg family as it was for PDMs.

We now turn our attention to the importance of relativistic effects in polarizabilities. From Fig. 4.3(a), we immediately notice that the effect of relativity decreases the value of  $\bar{\alpha}$  in each of the families, with the Li family being an exception. On the other hand, relativity increases the value of  $\Delta \alpha$  for six out of the sixteen systems considered (see Fig. 4.3(b)). The trends are a reflection of those in  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , as  $\bar{\alpha}$  involves a sum of these quantities, while  $\Delta \alpha$  is constructed from the differences among them. When we compare the importance of relativistic and correlation effects, we find that while the former can be as large as 10 percent and therefore not negligible in their own right, the latter is more pronounced, and is as large as 120 percent for LiBe. Thus, the relativistic trends in  $\bar{\alpha}$  and  $\Delta \alpha$  are not as clear as in the case of PDM, and relativistic effects are not as dominant as correlation effects, while being non-negligible.

#### 4.3.3 Reliability tests of the results

In order to present our recommended values along with their uncertainties from our calculations, we first assess the reliability of our results in the form of multiple precision checks. The precision of a calculation would depend on the choice of approximations in the Hamiltonian and the wave functions. The choice of wave function entails selecting the single particle basis as well as the quantum many-body theory to employ. Further, since we adopt the FF approach, we also need to check the dependence of the precision in our results on the choice of perturbing parameter. We will address each of these aspects very briefly in the next few paragraphs, in order to arrive at a reasonable estimate for the recommended values of the properties for the chosen molecules. Note that choosing a better stencil than our simplest central difference scheme would have little effect on results given that the perturbing parameter,  $\epsilon$ , is already small. For carrying out these reliability tests, we choose three representative systems, which include the lightest LiBe, the slightly heavier KBe, and the moderately heavy RbBe. In view of the steep computational cost,

Table 4.5: The values of PDM and parallel components of polarizabilities of the LiBe, KBe, and RbBe molecules using different approximations in Hamiltonian from the RCCSD(T) method. All units are in a.u..

Molecule	$\mu$	$lpha_{\parallel}$			
	Dirac-Coulomb				
LiBe	1.33	376.96			
KBe	0.75	621.64			
RbBe	0.64	644.01			
	4-comp	onent spinfree			
LiBe	1.33	376.9			
KBe	0.75	621.5			
RbBe	0.64	644.08			
	Spinfree-X2C				
LiBe	1.32	376.86			
KBe	0.75	621.76			
RbBe	0.64	644.58			
	DKH2				
LiBe	1.32	376.99			
KBe	0.72	620.31			
RbBe	0.64	644.87			
	Non-relativistic				
LiBe	1.32	376.55			
KBe	0.76	638.91			
RbBe	0.69	692.69			

Molecule	Basis	$\mu$	$lpha_\parallel$	$\alpha_{\perp}$	$\bar{lpha}$	$\Delta \alpha$
LiBe	DZ	1.1	387.33	114.73	205.6	272.6
	TZ	1.27	378.12	114.06	202.08	264.06
	QZ	1.33	376.9	114.12	201.91	262.48
	CBS	1.37	376.01	114.69	201.8	261.32
KBe	DZ	0.35	555.73	257.82	357.12	297.91
	TZ	0.65	608.5	248.04	368.19	360.46
	QZ	0.75	621.5	246.63	371.59	374.87
	CBS	0.81	630.99	245.6	374.06	385.39
RbBe	DZ	0.27	577.9	289.86	385.87	288.04
	TZ	0.55	627.78	279.22	395.41	348.56
	QZ	0.64	644.08	278.14	400.12	365.94
	CBS	0.71	655.97	277.34	403.55	378.63
RbSr	DZ	0.26	915.82	387.95	563.91	527.87
	TZ	0.52	957.48	384.35	575.39	573.13
	QZ	0.58	970.25	385.59	580.48	584.66
	CBS	0.62	979.56	386.49	584.18	593.07

Table 4.6: The values of PDM and polarizability of four representative molecules (LiBe, KBe, RbBe, and RbSr) with basis sets of increasing cardinal number (DZ to QZ) in the RCCSD(T) method, and with the four-component spinfree relativistic Hamiltonian. We also give results from a CBS extrapolation scheme. All units are in a.u..

we did not choose the heavier systems for reliability tests.

The first of our precision checks is on the influence of the choice of Hamiltonian. For this analysis, we assume that our RCCSD(T) values are the more accurate results compared to those from the RCCSD method due to the fact that the former takes into account more physical effects. We consider a hierarchy of Hamiltonians in terms of physical effects included as well as the resources that they consume. They include the computationally very expensive four-component Dirac-Coulomb Hamiltonian, the four-component spinfree Hamiltonian that we used for all our main results, an exact two-component Hamiltonian (spinfree X2C) [11], an approximate twocomponent Hamiltonian (we choose second-order Douglas-Kroll-Hess [12, 13, 14] Hamiltonian for this purpose), and finally the non-relativistic Hamiltonian. Note that the four-component Dirac-Coulomb Hamiltonian (DCH) does not include the Coulomb integrals of the type SSSS (where S stands for small component), but rather replaced by interatomic corrections [15, 16]. This approximation is known to be very accurate, and save lots of computational time. In spite of this approximation, the DCH is very expensive. In view of this situation, we only test the dependence of results on the choice of Hamiltonian for  $\mu$  and  $\alpha_{\parallel}$ , and assume that the difference in results between any two chosen Hamiltonians would be comparable for  $\alpha_{\perp}$  too. The results in Table 4.5 show that the PDM of the considered systems are practically unchanged between the DCH and our four-component spinfree calculations. We observe a similar behaviour for  $\alpha_{\parallel}$ . This indicates that the effect of spin-orbit coupling is negligible in these systems, and we expect a similar behaviour to hold for the other Alk-AlkE molecules. We see that the results agree very well with the spinfree X2C Hamiltonian. Note that spinfree X2C Hamiltonian, which is a twocomponent Hamiltonian, still contains in it relativistic effects (excluding spin-orbit coupling). We see no noteworthy deviations when we compare our results with DKH2 Hamiltonian. We take this a step further by carrying out calculations of the PDM and  $\alpha_{\parallel}$  for the heaviest RbSr molecule with spinfree X2C Hamiltonian, and find that the PDM remains unchanged while  $\alpha_{\parallel}$ changes well within 1 percent.

Another important test of reliability of our calculations is to analyze the basis set dependence of the results. To that end, we have performed calculations using the four-component spinfree

Molecule	$\epsilon$	$\mu$	$\bar{\alpha}$	$\Delta \alpha$
LiBe	0.00005	1.33	203.77	259.68
	0.0001	1.33	201.91	262.48
	0.0005	1.32	201.29	263.92
KBe	0.00005	0.75	370.42	376.64
	0.0001	0.75	371.59	374.87
	0.0005	0.75	372.08	372.98
RbBe	0.00005	0.64	404.22	359.91
	0.0001	0.64	400.12	365.94
	0.0005	0.64	399.18	366.73

Table 4.7: The PDMs and dipole polarizabilities (all in atomic units) of the LiBe, KBe, and RbBe molecules with different choices of the perturbing parameter,  $\epsilon$ .

relativistic Hamiltonian in the RCCSD(T) method with Dyall's triple-zeta (TZ) and double-zeta (DZ) basis functions. Again, we have considered LiBe, KBe and RbBe as representative molecules. Further, we carry out a two-point complete basis set (CBS) [17, 18] extrapolation with our TZ and QZ results upto  $\zeta = 50$ . We enlist the RCCSD(T) values of  $\mu$ ,  $\bar{\alpha}$  and  $\Delta \alpha$  using the aforementioned basis sets in Table 4.6. The table shows that  $\mu$  increases and converges systematically from cardinal numbers 1 through 50. However, we see a relatively strong dependence of PDMs on basis, as the results change from QZ to the CBS limit by about 4% for LiBe, 8% for KBe, and 11% for RbBe. We extended our analysis to the heaviest RbSr molecule in view of this dependence being important, and found that the percentage fraction difference between results using QZ basis and with CBS extrapolation is 7.5%. We carry out the same analysis for polarizabilities too, and we find that the QZ basis is reasonably good, with the percentage fraction differences between QZ and CBS extrapolation being utmost 1% for  $\bar{\alpha}$  and 4% for  $\Delta \alpha$ .

The other possible source of uncertainty in our calculation could stem from the contributions from high-lying orbitals that are not considered to account for electron correlation effects in the RCCSD(T) method. To carry out the calculations with the available computational resources, we have imposed a cut-off to virtual orbitals having more than energies at 1000 a.u. for relatively heavier systems. To get an estimate of error arising from the neglected higher virtual orbitals, we calculate PDMs and polarizabilities for RbBe, by considering all the generated virtual orbitals in the QZ basis. We found that the changes in the values are insignificant and within the precision of the present interest. This further assured us about the precision in the calculations.

We now consider the error due to the missing triple excitations in the CC method. Since CCSD(T) is widely regarded as a gold standard for molecular property calculations, we expect that the error due to missing triple excitations from RCCSD(T) would be much lesser than the percentage fraction difference between the RCCSD and the RCCSD(T) values, and assume that it would be roughly half its magnitude or lower. We find that the percentage fraction difference between the RCCSD and the RCCSD(T) methods is at most about 6 percent for  $\bar{\alpha}$ , and is within 7 percent for  $\Delta \alpha$ , except in the case of LiSr, where it is significant at about 17 percent. However, for the PDM, we find that the percentage fraction difference is well over 15 percent for some of the chosen systems, and is as large as 57 percent in the case of RbMg. We therefore expect that while the error due to missing higher order excitations are usually reasonably small for polarizabilities, the PDM is much more sensitive to this factor. Hence, we defer detailed analysis to a future study and conservatively set an error estimates in the PDM as mentioned in the beginning of this paragraph.

Another factor that needs to be taken into account in determining the precision of our results is the dependence on the choice of  $\epsilon$ . We again choose our representative molecules LiBe, KBe and RbBe. We check the change in our results in the neighborhood of  $\epsilon = 10^{-4}$  a.u., as shown in Table 4.7, and find that the results are stable in that range, with negligible variation.

## 4.3.4 A simple empirical relation between PDM and average polarizability

In this subsection, we seek to explore interesting connections between  $\mu$  and  $\bar{\alpha}$  just to understand how both the quantities behave. Such knowledge may be useful to estimate one property qualitatively from value of other in other molecules. Previous works have sought such empirical



Figure 4.4: (a) Plot showing the agreement between average polarizabilities calculated using the RCCSD(T) method (in blue) and our empirical relation (in red). The dominant part of the empirical relation is shown in green. We find that the red and the blue curves agree to within 10 percent for each of the points, whereas the green curve deviates from the blue one for heavier systems. The shaded background regions have been given to distinguish between families. Sub-figures (b) and (c) show the same plots, but for alkali-alkali molecules and alkaline-earthmonofluorides, respectively. The RCCSD(T) values of PDM and  $\bar{\alpha}$  given in sub-figure (b) were taken from our previous work [19], whereas the ab initio values of PDM and  $\bar{\alpha}$  in sub-figure (c) were taken from Ref. [20] and Ref. [21], respectively.

Table 4.8: The estimated  $\bar{\alpha}$  values (in a.u.) of the considered Alk-AlkE molecules using the empirical relation given by Eq. (4.1). In the table, the entry in the first row and third column of the results, for example, corresponds to LiCa.

AlkE Alk	Be	Mg	Ca	Sr
Li	$218.41 \\ 216.81 \\ 344.42 \\ 375.47$	250.69	348.71	374.54
Na		250.82	353.17	386.97
K		381.07	495.26	544.84
Rb		412.58	527.57	583.29

relationships, but they usually give complicated functions; for example, the authors in Ref. [6] find such a function connecting PDM and average atomic polarizabilities. We intend to find a relatively simple relation,  $\bar{\alpha} = f(\mu, Z_{Alk}, Z_{AlkE}, \bar{\alpha}_{at})$ , whose predictions for  $\bar{\alpha}$  should agree reasonably well with our RCCSD(T) results. Here,  $Z_{Alk}$  and  $Z_{AlkE}$  are the atomic numbers of the alkali and alkaline earth atoms, and  $\bar{\alpha}_{at}$  is the average atomic polarizability, given by  $\bar{\alpha}_{at} = (\alpha_{Z_{Alk}} + \alpha_{Z_{AlkE}})/2$ . We find that  $\bar{\alpha}$  predicted by the empirical relation

$$\bar{\alpha} = [a\bar{\alpha}_{at} + \pi ln(Z_{Alk}) + b\mu Z_{AlkE}]/c, \qquad (4.1)$$

with a = 2, b = 2.5, and c = 1. This agrees reasonably well with our RCCSD(T) results of  $\bar{\alpha}$ . We note that the dominant contribution comes from the first term, that is, the term containing average atomic polarizability. However, as Fig. 4.4(a) shows, using just the first term does not reproduce the RCCSD(T) results for  $\bar{\alpha}$  well for heavier systems in each family. The next two terms play an important role in improving the predictability of the empirical relation. Within those two terms, the result is not strongly influenced by the term containing the atomic number of the alkali atom, owing to the *log* dependence. An interesting occurrence in the expression is the presence of  $\pi$ . We have used the  $\bar{\alpha}_{at}$  values from Ref. [22] in our analyses. In Table 4.8, we have listed  $\bar{\alpha}$  estimated using the above relation. By comparing these results with the corresponding values from Table 4.3 and Table 4.4 it is clear that the relation predicts  $\bar{\alpha}$  well within 10 percent of the RCCSD(T) values. It is worth commenting at this point that we have made a conscious choice to exclude the dependence of the function on electronegativity differences, as the PDMs that we obtained do not follow the straightforward and simplistic dependence on

Table 4.9: Our final recommended results for  $\mu$ ,  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ ,  $\bar{\alpha}$ , and  $\Delta \alpha$  of LiBe, LiMg, LiCa, LiSr, NaBe, NaMg, NaCa, and NaSr from the RCCSD(T) calculations, along with the estimated uncertainties that are quoted in the parentheses. We have also compared our results with the previously reported values using the MRCI and CCSD(T) methods.  $\bar{\alpha}$  and  $\Delta \alpha$  are rounded-off to the nearest whole number, given that fact that they have large values. All the results are given in a.u..

Molecule	$\mu$	$lpha_{\parallel}$	$lpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$	Method	Reference
LiBe	1.33(18)	376.9	114.12	202(3)	263(11)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	1.32	376.55	114.42	201.78	262.13	$\operatorname{CCSD}(T)$	This work
	1.36	365				MRCI	[6]
LiMg	0.40(7)	480.63	166.84	271(6)	314(19)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	0.41	481.64	166.64	271.64	315	$\operatorname{CCSD}(T)$	This work
	0.46	470				MRCI	[6]
LiCa	0.40(6)	584.28	228.08	347(6)	356(26)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	0.43	580.16	229.88	346.64	350.28	$\operatorname{CCSD}(T)$	This work
	0.43	594	230	352	364	$\operatorname{CCSD}(T)$	[5]
	0.47	588				MRCI	[6]
LiSr	0.11(2)	620.03	268.5	386(14)	352(44)	RCCSD(T)	This work
	0.16	622.61	276.08	391.59	346.53	CCSD(T)	This work
	0.12	621	271	395	372	CCSD(T)	[5]
	0.11	653				MRCI	[6]
NaBo	0.86(15)	302 00	140.2	994(4)	253(15)	BCCSD(T)	This work
NaDe	0.85	300 48	140.2 137.70	224(4)	250(10)	CCSD(T)	This work
	0.00	390.40 307	101.19	222.02	202.09	MBCI	[6]
NoMa	0.92 0.20(7)	127 20	189.20	967(5)	955(11)	PCCSD(T)	[ <b>U</b> ] This work
Ivalvig	0.30(7)	407.29	102.09	207(3)	253(11)	CCSD(T)	This work
	0.31	441.11 429	100.04	209.00	238.07	MPCI	
$N_{0}C_{0}$	0.34 0.42(5)	402 585 02	949 95	257(5)	244(97)	PCCSD(T)	[ <b>U</b> ] This work
NaCa	0.43(3)	500.95	242.20	250.28	344(21) 247.24	CCSD(T)	This work
	0.40	590.94 591	240.0	254	261	CCSD(T)	
	0.39	577	240	004	301	MPCI	[J] [6]
NoCr	0.40 0.90(2)	011 626 1	<u> </u>	200(7)	255(10)	DCCSD(T)	[ <b>U</b> ] This work
ICBNI	0.20(3) 0.26	030.1 652.07	200.9 206.04	399(7) 415 09	256 02	CCSD(T)	This work
	0.20	002.97 699	290.04 291	410.02 200	250.93 250	CCSD(T)	I IIIS WOLK
	0.19	000 626	201	999	392	MPCI	[0] [6]
	0.20	050				MINUI	U

Table 4.10: Our final recommended results for  $\mu$ ,  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ ,  $\bar{\alpha}$ , and  $\Delta \alpha$  of KBe, KMg, KCa, KSr, RbBe, RbMg, RbCa, and RbSr from the RCCSD(T) calculations, along with the estimated uncertainties that are quoted in the parentheses. We have also compared our results with the previously reported values using the MRCI and CCSD(T) methods.  $\bar{\alpha}$  and  $\Delta \alpha$  are rounded-off to the nearest whole number, given their large values. All the results are given in a.u..

Molecule	$\mu$	$lpha_{\parallel}$	$lpha_{\perp}$	$\bar{\alpha}$	$\Delta \alpha$	Method	Reference
KBe	0.75(20)	621.5	246.63	372(13)	375(24)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	0.76	638.91	250.30	379.84	388.61	$\operatorname{CCSD}(T)$	This work
	0.87	628				MRCI	[6]
KMg	0.35(12)	644.47	291.31	409(12)	353(17)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	0.37	658.97	295.79	416.85	363.18	$\operatorname{CCSD}(T)$	This work
	0.42	656				MRCI	[6]
KCa	0.70(13)	888.38	334.4	519(17)	554(36)	$\mathrm{RCCSD}(\mathrm{T})$	This work
	0.76	909.43	330.71	523.62	578.72	$\operatorname{CCSD}(T)$	This work
	0.64	892	326	515	566	$\operatorname{CCSD}(T)$	[5]
	0.83	869				MRCI	[6]
KSr	0.51(10)	928.23	372.13	558(18)	556(38)	$\operatorname{RCCSD}(T)$	This work
	0.64	971.74	372.68	572.37	599.06	$\operatorname{CCSD}(T)$	This work
	0.50	942	367	559	574	$\operatorname{CCSD}(T)$	[5]
	0.60	925				MRCI	[6]
RbBe	0.64(20)	644.08	278.14	400(15)	366(29)	RCCSD(T)	This work
	0.69	692.69	295.05	427.6	397.64	CCSD(T)	This work
	0.78	631				MRCI	[6]
RbMg	0.33(13)	667.39	316.44	433(16)	351(19)	RCCSD(T)	This work
	0.37	720.48	335.83	464.05	384.65	CCSD(T)	This work
	0.41	664				MRCI	[6]
RbCa	0.70(14)	939.92	357.71	552(20)	582(35)	RCCSD(T)	This work
	0.81	1015.59	368.26	584.04	647.33	CCSD(T)	This work
	0.68	961	357	558	604	CCSD(T)	[5]
	0.86	922				MRCI	[6]
RbSr	0.58(11)	970.25	385.59	581(22)	585(41)	RCCSD(T)	This work
	0.72	1080.95	414.26	636.49	666.69 <sup>´</sup>	CCSD(T)	This work
	0.55	1009	394	599	615	CCSD(T)	[5]
	0.64	972				MRCI	[6]

electronegativity differences.

We take the applicability of the empirical relation a step further, and check if we can reproduce the correct value of molecular polarizability of LiBa, given its PDM. For this purpose, we use the RCCSD(T) results for the PDM, and find that the average polarizability thus obtained using our empirical relation (459.09 a.u.) matches remarkably well with the RCCSD(T) result for the same quantity (443.69 a.u.), to within 4 percent.

Lastly, we check if the functional form given in Eq. (4.1) can reliably predict  $\bar{\alpha}s$  for at least a few other diatomic molecules. For this purpose, we choose two other systems that find important applications, heteronuclear Alk-Alk (see Fig. 4.4(b)) and AlkE-F (see Fig. 4.4(c)) molecules. For the former, the empirical relation that agrees reasonably well (within 15 percent) with results from RCCSD(T) calculations (both PDM and  $\bar{\alpha}$  have been taken from Ref. [19]) is with a = 1.5, b = 2.5, and c = 1. i.e.

$$\bar{\alpha} = 1.5\bar{\alpha}_{at} + \pi \ln(Z_{Alk1}) + 2.5\mu Z_{Alk2}.$$
(4.2)

Here, Alk2 can be Li, Na, K, or Rb. For a given Alk2, Alk1 is either Li, Na, K, or Rb. We also test the quality of the results obtained from the above mentioned equation for homonuclear alkali-alkali molecules. We borrow the values of average polarizabilities from Deiglmayr *et al* [23] for comparison, and find that Eq. (4.2) gives results that are in reasonable agreement (within 10 percent, except in the case of Li<sub>2</sub>, which gives 20 percent).

A similar empirical equation is found to give reasonably good agreement (within 15 percent) with *ab initio* theory for AlkE-F molecules when a = 2, b = 2.5, and c = 2. i.e.

$$\bar{\alpha} = \left[2\bar{\alpha}_{at} + \pi \ln(Z_F) + 2.5\mu Z_{AlkE}\right]/2. \tag{4.3}$$

For this purpose, we chose the PDMs from our previous work [20], and  $\bar{\alpha}$ s from Ref. [21]. The former work uses RCCSD method, while the latter employs Kramers Restricted CI (KRCI) method. It is worth noting that in spite of the values of  $\mu$  and  $\bar{\alpha}$  being taken from different relativistic many-body methods, the empirical data generated from Eq. (4.3) agrees well with theory. This is not very surprising, as the KRCI results for the PDMs agree well with the corresponding RCCSD results for these systems. The causes behind the seemingly unreasonable effectiveness of the simple functional form based on Eq. (4.1) are unclear, and future studies on these aspects with more systems may shed light on the rationale behind these observations. Nonetheless, we assume that  $\bar{\alpha}$  of other heavier Alk-AlkE molecules, which are not considered here, will obey our above suggested empirical relation.

#### 4.3.5 Recommended values

After performing the reliability test of our results and finding out possible uncertainties in their evaluation using the RCCSD(T) method, we would like to provide now their final values for their possible applications in the future. From the above discussions, it is clear that the uncertainties to our calculated values of  $\mu$ ,  $\bar{\alpha}$  and  $\Delta \alpha$  come mainly from the dependence on basis functions and missing higher order CC excitations. From our CBS extrapolation results in an earlier section, we conservatively assign a maximum uncertainty in the PDMs of about 11%, about 1% uncertainties to  $\bar{\alpha}$ , and about 4% to  $\Delta \alpha$ . The uncertainties due to the neglected electron correlation effects are calculated for each of the molecules and are added linearly to the error arising from incompleteness of basis, and are quoted in Table 4.9 and Table 4.10 in brackets next to our recommended values, which are our RCCSD(T) results. In the same table, we also give the previously calculated values of some of the above quantities that are obtained using the MRCI method [6] and non-relativistic CCSD(T) method [5]. Our RCCSD(T) values and the MRCI values for the PDMs mostly agree within our quoted uncertainties, thus reinforcing our error estimates. It can be noted that the values of  $\mu$  from the CCSD(T) calculations in Ref. [5] differ from the present CCSD(T) results listed in Table 4.1 and Table 4.2. This may be due to the fact that different basis functions (their ANO-RCC contracted bases versus our cc-pCVQZ and Dyall bases) are used in both the works. Moreover, we carry out all-electron calculations, and we expect that to have a non-negligible bearing on the precision of our results, whereas the authors in Ref. [5] freeze inner orbitals. We did not find any other calculations of the  $\bar{\alpha}$  and  $\Delta \alpha$  values apart from the CCSD(T) calculations in Ref. [5].

In this chapter, we saw that our RCC calculations improved the values of PDMs and polarizabilities reported earlier using non-relativistic CC and other many-body methods. Therefore, in view of the preceding and current chapters, it can be safely concluded that the RCC theory is an accurate as well as reliable relativistic method for calculating first-order and second-order molecular properties. This, in turn, gives us the liberty to employ the RCC theory for precise calculations of properties pertaining to eEDM searches in the upcoming chapters.

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# Chapter 5

# Triatomic HgOH Molecule for EDM Study

## 5.1 Introduction

This chapter and the next one are more relevant to the main objective of this thesis work. In both the chapters, we explore the suitability of new molecular candidates for future experiments to search for eEDM with the help of relativistic many-body calculations. In the current chapter, we shall analyze in detail the prospects of using heavy polar mercury hydroxide (HgOH) molecule for EDM experiment to infer the value of  $d_e$  more precisely.

Selection of a new molecule for an eEDM study is based on the statistical uncertainty expression mentioned in Eq. (1.38), which is the figure of merit for the suitability of a molecule for an EDM experiment. It is evident from the expression for sensitivity that a large value of the molecule-specific effective electric field ( $\mathcal{E}_{eff}$ ) promises better experimental sensitivity. Historically, it is observed that certain heavy polar molecules can possess much larger  $\mathcal{E}_{eff}$  in comparison with atoms [1, 2, 3, 4], thus making heavy polar molecules the favourable choice for EDM experiments over atoms. For the past few decades, there have been tremendous developments on both experimental and theoretical sectors in the exploration for eEDM searches using diatomic polar molecules. On the theoretical front, several interesting proposals have been made to identify suitable polar molecules and molecular ions for EDM experiments, including PtH<sup>+</sup>, HfH<sup>+</sup> [3], YbRb, YbCs, YbSr<sup>+</sup>, YbBa<sup>+</sup> [5], WC [6], RaF [7], TaN [8], HgX (X=F, Cl, Br, and I) [2], HgA (A=Li, Na, and K) [9], and RaH [10]. Among these candidates, the diatomic polar HgX molecules have the edge in terms of possessing significantly larger  $\mathcal{E}_{\text{eff}}$  than other proposed systems. As eEDM is yet to be confirmed from the molecular EDM experiments due to very large uncertainties associated with the measurements, further search for favourable molecules with suppressed errors and improved sensitivity is necessary.

### 5.2 Why triatomic molecules?

Despite all the favourable prospects of heavy polar diatomic molecules for EDM experiments, the quest for suitable polyatomic molecules has also begun due to several reasons. Polyatomic molecules can offer similar advantages of a diatomic molecule, along with other features such as full polarization with small external electric fields and the ability to gain good control over systematic effects by exploiting their internal co-magnetometer states (low-lying opposite parity doublets) [11]. Additionally, molecules like YbOH possess additional desirable features such laser coolability [11, 12]. In the works [13, 14, 15, 16], it has been shown that if an EDM experiment is conducted with a large number of YbOH molecules prepared in the low-lying (010) vibrational state of the ground electronic state, and are trapped in an optical lattice, it promises a sensitivity to eEDM that is four orders of magnitude better than the current best limit obtained using the ThO molecule; *albeit* YbOH possesses three times smaller  $\mathcal{E}_{\text{eff}}$  than ThO.

It is noted from Ref. [1, 15] that YbF and its isoelectronic triatomic counterpart YbOH have almost comparable values of  $\mathcal{E}_{\text{eff}}$ . On the other hand, HgF molecule possesses 5 times larger  $\mathcal{E}_{\text{eff}}$ than YbF. HgOH is an isoelectronic triatomic counterpart of HgF. Heuristically, one may expect that HgOH would also possess as large an  $\mathcal{E}_{\text{eff}}$  as HgF. However, studies on HgOH spectroscopy are very limited and the molecule has not received significant attention in previous works, unlike in the case of YbOH. In fact, we come across the mention of HgOH in literature mainly in the realm of atmospheric physics while studying Hg removal processes in the atmosphere [17]. It is only in this context that limited information on the geometry of the molecule and properties exist in literature [18, 19]. However, HgOH is yet to be considered in laboratory for carrying out



Figure 5.1: Pictorial representation of the bent geometry of the ground state of HgOH. Our finding shows  $\theta_{Hg-O-H} = 104.83^{\circ}$ .

any spectroscopic measurements.

In this chapter, we scrutinize the candidature of HgOH for a future EDM experiment to infer  $d_e$  with better limit, based on the aforementioned considerations. Since not much information on the structure and/or spectroscopic properties of HgOH are available in literature, our primary task is to find out its bond formation. Thus, we chose to optimize the ground state geometry of the molecule by employing density functional theory (DFT), and inferred its bond-lengths and bond angle. We then calculated  $\mathcal{E}_{\text{eff}}$  and PDM of HgOH at the DF level. Next, we proceeded to analyze the potentiality of the molecule for future EDM measurements in plausible experimental conditions. This included the investigation of laser-cooling possibilities in HgOH, for which we calculate the Franck-Condon factors (FCF) between pairs of vibrational states across two electronic states. To serve this purpose, we optimized the geometries of higher excited states of HgOH. The lowest vibrational level of the ground state was chosen for carrying out the proposed EDM measurements.

The schematic structure of HgOH with a bent geometry that has been optimized with the

help of potential energy curve (PEC) as depicted in Fig. 5.1. We enlist the optimized parameters of ground state and other excited state geometries in Table 5.1. To examine the departure of the values of  $\mu$  and  $\mathcal{E}_{\text{eff}}$  from a linear geometry to a bent one, we also carried out the calculations of the aforementioned properties for a fictitious linear geometry HgOH after obtaining its equilibrium bond-length in a linear configuration (Fig. 5.2). In Table 5.2, we show the results of  $\mu$  and  $\mathcal{E}_{\text{eff}}$ calculated at different levels of theory. We inspected the contributions of different RCC terms to the value of  $\mathcal{E}_{\text{eff}}$  as given in Table 5.3. We also analyzed to see how the different AO-mixings contribute to  $\mathcal{E}_{\text{eff}}$  at the DF level as demonstrated in Table 5.4. In Table 5.5, we presented the projected statistical sensitivity offered by HgOH in EDM experiments and compared it with those of other theoretically proposed and experimentally considered molecules. We also extended our study to Hg containing polyatomic molecules like HgCH<sub>3</sub> and HgCF<sub>3</sub>, and estimated their projected sensitivities based on our mean-field calculations.

#### 5.3 Theory

Among the properties relevant to EDM experiments, we have already introduced  $\mathcal{E}_{\text{eff}}$  in Chapter 1 of this thesis. Another relevant molecular property that is crucial in finding sensitivity of the EDM experiment is the molecular PDM and is given by

$$\mu = \frac{\langle \Psi | D | \Psi \rangle}{\langle \Psi | \Psi \rangle},\tag{5.1}$$

where  $D = -\sum_{i=1}^{N_e} r_i + \sum_{A=1}^{N_{nuc}} Z_A r_A$  (in atomic units (a.u.)) for the position vector  $r_i$  of the  $i^{th}$  electron from origin,  $r_A$  is the site of the  $A^{th}$  nucleus, and  $Z_A$  is the atomic number of the  $A^{th}$  nucleus. For the sake of simplicity, we choose the oxygen atom as our origin and we work with the BO approximation. Therefore, in the expression for PDM,  $r_A$  are simply the chosen values of bond-lengths in the molecule.

### 5.4 Ground state geometry optimization

In order to obtain the aforementioned properties of HgOH, it is necessary to evaluate its manybody wave function. In the relevant equations to be solved, the ground state equilibrium geometry of the molecule is a crucial input. It includes the equilibrium bond-lengths,  $R_{Hg-O}$  and  $R_{O-H}$ , and the bond angle,  $\theta_{Hg-O-H}$ , which is the angle formed between Hg-O and O-H, as shown in Fig. 5.1. As stated earlier, we used the DFT method in order to optimize the geometry of the molecule. We chose the  $\omega$ B97xD functional, which is known to perform well in obtaining equilibrium geometries [20], and opted for the LANL2DZ [21, 22, 23] basis sets for Hg, while we choose cc-pVTZ [24] functions for O and H. We performed these calculations using the Gaussian 16 software [25]. We took utmost care to avoid saddle points, and among those optimized geometries without negative frequencies, we selected the equilibrium bond-lengths and bond angle from the configuration with the lowest energy.

In order to assess the laser coolability of HgOH, we also optimized three excited electronic states. We used time-dependent DFT for the excited state optimizations. We then calculated the FCFs using the parallel approximation between the ground state and each of the four excited electronic states. The FCF for a transition from a vibrational state  $|\Psi_v(\tau_n)\rangle$  to another vibrational state  $|\Psi'_v(\tau_n)\rangle$  is given by

$$FCF = \langle \Psi'_{v}(\tau_{n}) | \Psi_{v}(\tau_{n}) \rangle, \qquad (5.2)$$

where the integral is taken over the nuclear coordinates (denoted by  $\tau_n$ ). We used the ezSpectrum 3.0 software [26] to calculate the FCF matrix elements for the transitions between the ground state and the excited states. A highly diagonal FCF matrix is a good indicator of laser coolability of a molecule.

# 5.5 Method of calculation

Once the equilibrium geometry was obtained, the next step was to calculate the wave function of the ground state. In this work, we made use of the RCC theory for this purpose. In the previous two chapters, we had studied PDMs and electric dipole polarizabilities of the alkali dimers and alkali–alkaline-earth metal molecules extensively to demonstrate its capability for producing reliable results.

The Dirac-Coulomb Hamiltonian was chosen to describe the molecular interactions in this work. We invoked the BO approximation to the total Hamiltonian to separate out the electronic part of the Hamiltonian. We start with HgOH having a hypothetical linear geometry and calculate the values of  $\mu$  and  $\mathcal{E}_{\text{eff}}$  to extrapolate from the linear one the correlation effects in its bent counterpart. Understanding the roles of electron correlation effects in the relevant properties of HgOH in a linear geometry using RCC theory allowed us to extrapolate values of different properties with a bent geometry by only performing calculations using the mean-field theory. For calculating the PEC (see Fig. 5.2) of the hypothetical linear geometry, we employed the RCCSD(T) method. The calculation of molecular ground state energies to obtain the PEC of the hypothetical linear HgOH was performed using the Dirac16 program [27]. In order to reduce the computational cost, we restricted ourselves to only considering those virtual orbitals with energies not more than 1000 a.u. The DF calculations of  $\mathcal{E}_{\text{eff}}$  and  $\mu$  and the AO to MO integral transformations were carried out using the UTChem program [28, 29], while the RCCSD calculations of the aforementioned properties were conducted on the Dirac08 software [30]. We used here the expectation value approach (Eq. (2.219)) to calculate  $\mathcal{E}_{\text{eff}}$  and  $\mu$ . First, we carried out the calculations using the RCCSD method, keeping only the terms that are linear in T and  $T^{\dagger}$  (both of them are treated independently) of the expression in Eq. (2.219) and the results from this approximation are quoted under LECC abbreviation. Then, contributions from the non-linear terms were included using intermediate steps to obtain the final recommended RCC values.

#### 5.6 Results and discussion

For performing an electron EDM experiment on HgOH, it is imperative to show that it possesses a bound ground state. Since HgOH is a triatomic molecule, its ground state geometry need not be linear. This required us to perform geometry optimization to find out its equilibrium bond-

Table 5.1: List of the optimized geometry of the ground electronic state and three low-lying excited states of HgOH from various works. The unit of bond-lengths is angstrom (Å), while that of the bond angle is degrees.

State	$R_{\text{Hg-O}}$	$R_{O-H}$	$\theta_{Hg-O-H}$
Ground	2.2294	0.9633	104.83
First-excited Second-excited Third-excited	3.1458 2.0766 3.5482	$\begin{array}{c} 0.9563 \\ 0.9615 \\ 1.0095 \end{array}$	180 102.5 81.93

lengths and the bond angle. We followed the procedure outlined in the previous section, and found that the molecule has a bent structure in its ground electronic state (<sup>2</sup>A' state), unlike in the case of YbOH [15]. Although one may expect a metal-hydroxide molecule to be linear on grounds of the ionic nature of its bonding, a bent structure for HgOH indicated that the bond may possess a hint of covalent nature too, similar to the case of ZnOH [31, 32]. We determined the optimized  $R_{Hg-O}$  to be 2.2294 Åand  $R_{O-H}$  to be 0.9633Å, with the HgOH bond angle  $(\theta_{Hg-O-H})$  being 104.83°. These results are presented in Table 5.1, along with the optimized values that we obtained for some of the excited states as well. Our DFT results of geometry optimization have been obtained using the  $\omega$ B97xD functional and with the LAN2LDZ basis for Hg and cc-pVTZ basis sets for O and H.

We also determined the PEC for the hypothetical linear ground state geometry in the RCCSD(T) method using the two-component X2C Hamiltonian [33], by varying  $R_{Hg-O}$  and keeping fixed  $R_{O-H}$  at 0.922 Å. Further details can be found in Ref. [34]. As described earlier, the purpose of carrying out this exercise is to extrapolate the results from the linear geometry calculations to the actual bent geometry of the ground state of HgOH. In principle, it is possible to perform the RCC calculations using the bent geometry itself. However, it demands large computational resources. As we will demonstrate later, the roles of the electron correlation effects are not significant in determining the values of  $\mathcal{E}_{\text{eff}}$  and PDM ( $\mu$ ) of HgOH. Therefore, it is acceptable to evaluate the results using the hypothetical linear geometry and then estimate results for the bent geometry by scaling the RCCSD results from the linear geometry for the



Figure 5.2: The ground electronic state PEC of the hypothetical linear geometry of HgOH in the DF, RCCSD, and RCCSD(T) approximations using the exact two-component (X2C) Hamiltonian, with a double-zeta basis. In the plot, R is the Hg-O bond-length. The DF energy has been shifted by -2.9 units, in order to make it easier to compare the three curves.

purposes of present work. If necessary, more accurate calculations can be performed wif the experiment were to be realized.

The result for our linear geometry calculation, presented in Table 5.2, gives an  $\mathcal{E}_{\text{eff}}$  of 108.9 GV/cm. This value is somewhat similar to that of HgF [2], which is about 115 GV/cm. We also note that while correlation effects account for about 9 percent in HgF, it is less than 2 percent for HgOH in its linear geometry. This implies that it is not necessary to employ a more sophisticated method for calculating  $\mathcal{E}_{\text{eff}}$  at this stage. The PDM of HgOH is 1 D, which is much smaller than that of HgF. This is possibly due to reasons similar to that which explains YbOH having a much smaller PDM than YbF [15]. At the DF level of calculation (which is the dominant contribution to the total value of  $\mathcal{E}_{\text{eff}}$ ),  $\mathcal{E}_{\text{eff}}$  is about 3.83 times smaller than that in a hypothetical linear geometry. This gives a scaled RCC value of 28.44 GV/cm, as compared to the DF value of 28.01 GV/cm. In contrast, the PDM value increases from the DF method to the RCC calculation. After scaling the values from linear geometry to the bent geometry, we got its value to be 2.43 D. Comparing this value with the previous works, we find that our estimate  $\mu$  value is relatively large. This could be due to two main reasons: We have used a double-zeta (DZ) quality basis sets [35, 36] and our calculations are based on relativistic methods whereas the previous calculations

Geometry	$\mathcal{E}_{ ext{eff}}$			$\mu$		
	DF	LECC	RCC	DF	LECC	RCC
	From	this work	<u> </u>			
Linear	107.24	109.02	108.9	1.57	1.04	1.00
Bent	28.01	$28.47^{\dagger}$	$28.44^{\dagger}$	3.67	$2.43^{\dagger}$	$2.34^{\dagger}$
	From o	ther worl	<u>KS</u>			1 80 [37]
						1.09[01] 1.02[38]
						1.52 [50] 1.06 [20]
						1.90 [39]

Table 5.2: A comparative analysis of the calculated  $\mathcal{E}_{\text{eff}}$  (in GV/cm) and  $\mu$  (in D) values in HgOH by assuming its hypothetical linear and the actual bent geometry ground state using the DF and RCCSD methods. We also give  $\mu$  values from the previous calculations using DFT.

<sup>†</sup>Scaled results from the DF and LECC values of the linear geometry calculations.

were carried using non-relativistic methods. We expect that maximum error in the estimated value of  $\mathcal{E}_{\text{eff}}$  to be within 10 percent, while the error in the PDM is expected can be slightly higher.

Table 5.3 gives the contributions to  $\mathcal{E}_{\text{eff}}$  and  $\mu$  from each of the terms of the RCCSD method in the LECC approximation for the linear geometry. We note that of the nine resulting terms in the LECC approximation,  $OT_2$  and its h.c. do not contribute, due to the Slater-Condon rules. We now discuss the contributions from different individual terms to  $\mathcal{E}_{\text{eff}}$ . It can be seen from the above table that the dominant correlation contributions come from  $OT_1$  and its h.c. terms, and there are strong cancellations of correlations effects through different RCC terms. As a result, there is a very small difference between the DF and RCCS values. For PDM too,  $OT_1$  term and its h.c. gives dominant correlation contributions. There is an important difference between the correlation contributions to  $\mathcal{E}_{\text{eff}}$  and  $\mu$  in that in the former quantity, they cancel out whereas in  $\mu$ , they add up to give a reduced value than the DF result.

Since the DF term contributes the most to  $\mathcal{E}_{eff}$ , we intend to analyze contributions from various single particle orbitals (especially from the heavier Hg and O atoms) to it in both the

linear and bent geometry configurations. In our calculation, the DF value is computed by

$$\mathcal{E}_{\text{eff}}^{DF} = \langle \Phi_0 | H_{eEDM} | \Phi_0 \rangle \tag{5.3}$$

$$= -4ic \sum_{j=1}^{N_B} \sum_{k=N_B+1}^{2N_B} C_j^{*S} C_k^L \langle \chi_{n,j}^S | p^2 | \chi_{n,k}^L \rangle, \qquad (5.4)$$

where the summations are over large (denoted by superscript L) and small (denoted by superscript S) component basis functions,  $N_B$  is the total number of large component basis functions,  $C_j$  and  $C_k$  are the MO coefficients,  $h_{eEDM}$  is the single particle effective eEDM Hamiltonian operator, and  $\chi$  is the atomic orbital basis function, with the subscript n denoting the singly occupied molecular orbital. The results of this analysis are presented in Table 5.4. We have not provided the results for terms that arise from mixings between other orbital combinations, as they are well below error margins, and are almost zero. The table shows that the DF term is dominated by the contributions that arise from the mixing of the s and  $p_{1/2}$  orbitals of Hg. The rest of the terms almost completely cancel out in pairs. While the s and  $p_{1/2}$  mixing accounts for nearly 108.14 GV/cm for the linear case, we see that it contributes only 29.30 GV/cm for the bent geometry. We also observed that although the values of the other contributions are different between the linear and bent cases, their differences turn out to be very similar. Thus, the major deciding factor for the effective electric field between the linear and bent cases is the mixing between the s and  $p_{1/2}$  orbitals.

We propose that the EDM experiment to be performed on the lowest vibrational level of the ground state of HgOH. We note that in YbOH, the chosen EDM measurement state is the low-lying (010) vibrational state of the ground electronic state. This was necessary for YbOH, as it is in a linear geometry. The choice of a bent mode allows to make use of the closelyspaced doublets of opposite parity as internal co-magnetometer states [11]. In such a case, there is no need to flip the external electric field in order to perform electron EDM measurements, and this feature, therefore, helps to avoid systematic effects associated with reversing electric fields. Since HgOH is permanently bent in its ground electronic state unlike YbOH, it would have these relevant parity doublets even in its ground vibrational state. We now estimate the

Table 5.3: Contributions from the individual RCC terms to  $\mathcal{E}_{\text{eff}}$  (in GV/cm),  $\mu$  (in D), and  $W_s$  (in kHz) from both the linear and bent geometries of HgOH. *O* denotes the operator corresponding to the properties. Note that for the PDM, the term corresponding to the DF contribution also accounts for the nuclear contribution in it.

Term	$\mathcal{E}_{\rm eff}({\rm GV/cm})$	$\mu(D)$
$O(\mathrm{DF})$	$107 \ 94$	1 57
$OT_1$ +h.c.	9.50	-0.42
$T_1^{\dagger}OT_1$	-2.76	-0.15
$T_1^{\dagger}OT_2$ +h.c.	-0.38	0.12
$T_2^{\dagger}OT_2$	-4.58	-0.11

size of such a doublet for HgOH, which is an asymmetric top. Using the computed values for the rotational constants, 623.56714, 6.39027, and 6.32545 (in GHz), we estimate the size of the K-doublet [40, 41] to be 30 MHz, which is comparable to that of YbOH ( $\sim 10$  MHz) [11].

We then conducted a preliminary survey of the possible experimental schemes for an EDM measurement using the HgOH molecule. We began with the statistical sensitivity of an electron EDM experiment with HgOH. If we were to propose a trap experiment, a preliminary requirement would be laser cooling of the molecules, as typical 'non-perturbative' traps are  $\sim mK$  deep. We used the data from Table 5.1 to calculate FCFs from the ground electronic state to each of the four low-lying excited electronic states. We found that the diagonal FCFs are negligibly small, thus, rendering HgOH unsuitable for a trap experiment. This result suggested us that albeit one may naively expect HgOH to possess highly diagonal FCFs based on its isoelectronic counterpart, HgF, it need not be the case. A possible reason for this observation may be the presence of inner (n-1)d orbitals, unlike in the case of YbOH. The (n-1)d orbitals possibly led to a strong coupling between electronic and vibrational degrees of freedom, thus, allowing for off-diagonal excitations. However, the precise mechanism of the (n-1)d orbitals in substantially lowering the diagonal nature of FCFs is unclear. A reasonable understanding of this mechanism is useful for qualitatively predicting the laser coolability of other polyatomic systems in the future.

Table 5.4: Contributions from different atomic orbital (AO) mixing to the DF value of  $\mathcal{E}_{\text{eff}}$  (in GV/cm), where the AO in the left hand side is a small component AO and that in the right hand side is a large component AO. Non-zero contributions may come only from odd-parity AO mixings  $\langle (AO)_1^S | \hat{O} | (AO)_2^L \rangle$ , where superscript *S*, and *L* stand for small component and large component AOs respectively. Results are given for both the linear and the actual bent geometry HgOH molecule.

Atom	AOs	Linear	Bent
Hg	$\begin{array}{c} s^S_{1/2} - p^L_{1/2} \\ p^S_{1/2} - s^L_{1/2} \\ p^S_{1/2} - d^L_{3/2} \\ d^S_{3/2} - p^L_{3/2} \\ d^S_{5/2} - f^L_{5/2} \\ f^S_{5/2} - d^L_{5/2} \end{array}$	378.40 -270.26 -31.40 30.19 0.79 -0.78	100.11 -71.81 -8.07 7.77 0.19 -0.18
0	$\begin{array}{c} s^S_{1/2} - p^L_{1/2} \\ p^S_{1/2} - s^L_{1/2} \end{array}$	2.78 -2.77	1.44 -1.44

We shift our focus now to a beam EDM experiment. The figure of merit for statistical sensitivity of a beam experiment is given in Eq. (1.38). We attempted to roughly estimate the statistical sensitivity of HgOH molecule by projecting the values of N, T,  $\tau$  and  $\eta$  based on some practical considerations in combination with the calculated value of  $\mathcal{E}_{\text{eff}}$ . We anticipated that the  $\mathcal{E}_{eff}$  in the ground vibrational state will be very close to the calculated value in the absolute ground state. Photoassociation of laser cooled Hg and magnetically trapped OH [42] to produce HgOH molecules may be a possibility [2]. Based on other optimized beam sources, we expect that we can produce  $10^9$  molecules in a single pulse for a slow beam. Assuming the detection area of radius  $\sim 1$  cm to be 1 m away, and using a slow beam divergence of 1 sr, we expect a total of  $\sim 10^{5-6}$  molecules. One can also increase the number of molecules by magnetic or electrostatic guiding [43, 44]. There are also possibilities that the molecular production can be chemically enhanced [45]. A distinct advantage over ThO is that HgOH is not limited by radiative decay. With a slow beam [46] of buffer gas-cooled HgOH molecules, one can hope to achieve  $\tau \sim 10$  ms. Combining these estimates with an  $\mathcal{E}_{\text{eff}}$  of 28.47 GV/cm and  $T \sim 10^7$ , the projected statistical sensitivity is about  $5 \times 10^{-30}$  e-cm, which is an improvement over ThO, the system that has set the current best limit for electron EDM.

We also examined the possibility of an EDM experiment with HgOH using the EDM<sup>3</sup> proposal [47]. In this class of experiments, a molecule of interest to eEDM searches is embedded in an inert gas matrix, while retaining the measurement schemes of a beam experiment. Since the molecules are embedded in a matrix, one can achieve large values of N and long coherence times,  $\tau$ . Given that the molecules are already embedded, a laser cooling scheme gives no specific advantage. Since the FCFs are unfavourable for laser cooling in HgOH, we consider the possibility of employing HgOH in an EDM<sup>3</sup> experiment. A reasonably large PDM in its ground state facilitates orienting the molecule in a relatively low applied electric field. Moreover, our preliminary DFT calculations showed that HgOH possesses very large PDM of around 7 D in an excited  $^{2}\Sigma$  state. A large difference between PDMs of the ground and an excited electronic state offers promise in state selective detection [47]. However, from a comagnetometry point of view, it is unclear if parity doublets can arise, in view of HgOH interacting with the inert gas atoms in the lattice. With the possible absence of this advantage, HgOH in itself may not offer any distinct advantage in an EDM<sup>3</sup> experiment over HgF, although in principle, an EDM<sup>3</sup> measurement with HgOH is very much possible. HgOH may offer some advantage in a clock-state EDM experiment [48] due to its polarizability, though the advantages of that approach would be most notable in a trap experiment. Hence, we conclude from our preliminary survey that a beam experiment is best suited for HgOH, given its spectroscopic properties. Moreover, we forecast that as the co-magnetometer states in polyatomic species aid extensively in controlling systematics, one can extract parameters from the BSM theories with very stringent constraints, with possible combinations like YbOH and HgOH. The more the number of such systems, the tighter the bounds. To that end, we discuss next other natural extensions of HgF and HgOH for EDM experiments.

Table 5.5: Comparison of measured and projected sensitivities offered by different molecules for EDM experiments. For molecules where measurements are not available, the sensitivity is estimated with to projected  $N, T, \tau$ , and  $\eta$  values. The unit chosen for  $\delta d_e$  is e-cm.

Molecule	$\delta d_e$	Reference(s)
HgLi	$1.3 \times 10^{-30}$	Ref. [9]
$\operatorname{HgNa}$	$2.5 \times 10^{-30}$	Ref. [9]
$_{ m HgK}$	$3.1 \times 10^{-30}$	Ref. [9]
RaH	$1.63 \times 10^{-29}$	Ref. [10]
YbOH	$2.76 \times 10^{-32}$	Refs. [11, 15, 56]
$\mathrm{ThO}$	$1.1 \times 10^{-29}$	Ref. [51]
$\mathrm{HfF}^+$	$1.3\times10^{-28}$	Ref. [52]
YbF	$1.06\times10^{-27}$	Ref. [53]
$\mathrm{HgF}$	$6 \times 10^{-32}$	Ref. [54]
$\operatorname{RaF}$	$2.49\times10^{-29}$	Ref. [55]
HgOH	$5 \times 10^{-30}$	This work
$\mathbf{HgCH}_3$	$2 \times 10^{-30}$	This work
$HgCF_3$	$2 \times 10^{-30}$	This work

# 5.6.1 Other prospective polyatomic molecules for EDM measurements

We now briefly look into two other molecular candidates that are natural extensions to HgF and HgOH, namely HgCH<sub>3</sub> and HgCF<sub>3</sub>. These systems are expected to preserve the features of K-doublets, with the additional advantage that these splittings will be even smaller [11]. We chose our geometry for HgCH<sub>3</sub> from Refs. [49, 50]. We obtained 75.07 GV/cm for  $\mathcal{E}_{eff}$  at the DF level of theory, which is almost comparable to that of ThO, thereby giving this system an edge over HgOH. We do not expect the effective electric field to change beyond 10 percent when we include electron correlation effects. We found that the PDM of HgCH<sub>3</sub> is about 0.47 D at the DF level of theory and 0.44 D using DFT. This low value for PDM can be explained by observing the fact that the difference in electronegativity is very less for CH<sub>3</sub>. We expect that this issue will be alleviated when CH<sub>3</sub> is replaced by CF<sub>3</sub>. Indeed, we observed that the value of  $\mathcal{E}_{eff}$  for HgCF<sub>3</sub> is 60.95 GV/cm, while its PDM is 3.33 D. The projected eEDM sensitivities from HgCH<sub>3</sub> and HgCF<sub>3</sub> were found out to be  $2 \times 10^{-30}$  e-cm and  $2 \times 10^{-30}$  e-cm, respectively.

Table 5.5 presents the sensitivities of several ongoing and proposed EDM experiments to eEDM, and compares the projected sensitivities of Hg-containing polyatomics that have been considered in this work, with them. We see immediately that the projected eEDM sensitivities from HgOH, HgCH<sub>3</sub>, and HgCF<sub>3</sub> are better than RaH and RaF, and comparable to mercury al-kalis. The estimated sensitivities for HgCH<sub>3</sub> and HgCF<sub>3</sub> assume that they are not laser coolable. Given the stark contrast in FCFs between HgF and HgOH, it is not inconceivable that HgCH<sub>3</sub> and HgCF<sub>3</sub> may offer prospects for cooling. In such a case, a trap experiment could provide much higher sensitivities to eEDM compared to YbOH.

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# Chapter 6

# Theoretical and Experimental Perspectives of Superheavy Diatomic Molecules for Probing eEDMs

### 6.1 Introduction

In pursuit of searching for appropriate candidate molecules for EDM experiments, several heavy polar molecules have been considered so far [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. In the previous chapter, we have discussed the suitability of triatomic HgOH molecule for carrying out an EDM experiment to infer eEDM. In this chapter, we explore the prospects of some superheavy molecules (molecules containing superheavy atoms with atomic number  $\geq 100$ ) for future EDM searches.

# 6.2 Why superheavy systems?

Paramagnetic molecules with heavy nuclei have become popular choices for EDM experiments over atoms due to their enhanced sensitivities to eEDM. Enhancements of this type were elaborated in Ref. [14] from the atomic perspective, and Ref. [15] for diatomic molecular point of view. eEDM enhancement factors ( $\mathcal{R}$ ) in heavy atoms scale as the third power of corresponding atomic numbers (Z) [16], such that,  $\mathcal{R} = Z^3 R(Z\alpha)$ , where  $R(Z\alpha)$  is the relativistic factor which depends on both Z and the fine structure constant  $\alpha$ . Therefore, nuclei with large Z are preferable for high-precision EDM experiments, as the enhancement factor increases with the cubic power of Z. With the increasing value of Z of a nucleus, relativistic effects become more prominent owing to the fact that the electrons in a heavier atom move at relativistic speeds, therefore giving rise to significant orbital deformation. The Z dependence of the sensitivity of an atom to CP-violating nucleus-electron scalar-pseudoscalar interaction is also discussed in Ref. [17]. Based on the aforementioned rationales, it is reasonable to expect that the superheavy atoms could offer better sensitivities to eEDM in the EDM experiments due to their large Z and highly relativistic nature. It is also prudent to anticipate that similar advantages of a superheavy atom will be qualitatively retained in a superheavy molecule along with other advantages. Superheavy molecules are expected to exhibit a substantial enhancement in their effective electric field,  $\mathcal{E}_{\text{eff}}$ . Indeed, effective electric fields of CnH [18, 19], CnF [20], LrO, NoF, RfN, E120F, and E121O [21] have been calculated, which assert the above statement. However, so far no experiment has been conducted with superheavy systems to probe EDM. Spectroscopic results from studies of superheavy elements have recently been reported. In view of these developments, it is desirable to investigate EDMs of molecules with superheavy atoms. Our experimental knowledge of such rare molecules is in its infancy, and theoretical developments are critical to motivate and guide the experimental progress [22, 23]. These developments motivate us to consider diatomic molecules containing superheavy atoms for EDM studies.

### 6.3 Lr containing molecules

A purified single ion-beam of <sup>256</sup>Lr, synthesized in the <sup>249</sup>Cf (<sup>11</sup>B, 4*n*) reaction, has been recently produced by using the ISOL (Isotope Separator On-Line) system at the Tandem accelerator facility of Japan Atomic Energy Agency (JAEA) [24]. Success in producing Lr atom in experiment opens up the possibility of artificial formation of Lr molecules. In this work, we focus our studies on diatomic molecules containing Lr atoms, i.e. LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> to assess their feasibility for EDM experiments. There are fourteen different isotopes of Lr, of which we propose to employ <sup>256</sup>Lr (half-life  $\approx 27$  s), which has been used in several studies of atomic properties.



Figure 6.1: Potential energy curves (PEC) of neutral LrO (sub-figure (a)), as well as LrF<sup>+</sup> (sub-figure (b)), and LrH<sup>+</sup> (sub-figure (c)) molecular ions with a range of typical molecular bond-lengths (R) using the RCCSD(T) method. The plot shows that LrO can form a stable molecule around the equilibrium bond-length  $R_e \simeq 3.46$ , while both the ions possess their minima around  $R_e \simeq 3.56$ . All the values are given in a.u.

Because of short half-lives and the low production rates, superheavy elements, including Lr, need to be handled on a single-atom scale. We explore a possible alternative scheme to produce Lr atoms. Our work also aims to extend the studies of molecular ions, which could enable precision measurements with just a single molecular ion [25, 26, 27].

#### 6.4 Theoretical aspects

At the outset, it is crucial to find if the chosen Lr molecules can form stable bound states. At first, we calculate the PEC for each molecule and obtain  $R_e$  from corresponding PEC minimum. After ensuing the bound state formation, we calculate  $\mu$  and  $\mathcal{E}_{\text{eff}}$  of the molecules using RCC theory. A fully relativistic approach becomes especially crucial here, as theoretical calculations have predicted that the Lr atom would have a configuration different from that expected by a non-relativistic treatment,  $[\text{Rn}]5f^{14}6d^{1}7s^{2}$ , due to strong relativistic effects [28]. The  $[\text{Rn}]5f^{14}7s^{2}7p_{1/2}$  configuration would be most probable for the Lr atom according to the measurement of the first ionization potential [24]. Since LrO,  $\text{LrF}^{+}$  and  $\text{LrH}^{+}$  have one unpaired electron each, these molecules are sensitive to both the eEDM and nucleus-electron scalar-pseudoscalar (S-PS) interactions [29]. Thus, these P, T-odd sources can induce energy shifts (approximated to first order) in the ground state, as already shown in Eq. (1.45).  $W_s$ , being the analogue of  $\mathcal{E}_{\text{eff}}$ ,

Table 6.1: Calculated values of  $\mathcal{E}_{\text{eff}}$ ,  $W_s$  (with  $M_A = 256$ ) and  $\mu$  for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> using the RCCSD method, and comparison with literature values wherever they are available. We also compare these values with calculations of the corresponding quantities for other molecules and atoms (see the text for further details).

Molecule	$\mathcal{E}_{ ext{eff}}$	Ws	$W_s/\mathcal{E}_{\rm eff}$	$W_s/\mathcal{E}_{ ext{eff}}$	μ	Reference
	(GV/cm)	(kHZ)	(kHz-cm/GV)	$(\times 10^{-21} \text{ e-cm})$	(D)	
LrO	258.92	2565.54	9.91	41.03	4.58	This work
	250.21	2367.77	9.46	39.16		[21]
	246.5					[30]
$\rm LrF^+$	246.31	2445.83	9.93	41.11	12.29	This work
$\rm LrH^+$	343.38	3402.36	9.91	41.03	11.05	This work
ThO	87	300.24	3.45	14.29	4.27	Ref. $[2]$
HgF	115.42	668.37	5.79	23.97	3.96	Ref. $[8, 20]$
$\mathrm{HfF}^+$	22.5	49.41	2.20	9.11		[31]
YbF	23.2	100.67	4.34	17.97	3.91	[32]
Atom	$\mathcal{R}$	$\mathcal{S} (\times 10^{-18} \text{ e-cm})$		$\mathcal{S}/\mathcal{R}~(\times 10^{-21} \text{ e-cm})$	-	Reference
$\mathbf{Cs}$	120.53	0.80	-	6.64	-	[33, 34]
Tl	558	6.77	-	12.13	-	[35]
Rb	25.74	0.11	-	4.27	-	[33]
Fr	812.19	10.62	-	13.08	-	[36]

Note: In the literature values given in the table for molecules, the authors use  $Z_A$  in place of  $M_A$  in the definition of  $W_s$ , and we have multiplied by  $M_A/Z_A$  to rescale those values to be consistent with the definition adopted in the present work.

is the quantity of theoretical interest pertaining to S-PS interactions. The expression of  $W_s$  is described in Eq. (1.48). The calculation of  $\mathcal{E}_{\text{eff}}$  and  $W_s$ , in combination with the measured value of  $\Delta E$ , can provide upper bounds on  $d_e$  and  $k_s$ . It is worth mentioning that we only consider the S-PS interaction involving Lr nucleus, as we expect that the major contribution to the molecular energy shift due to S-PS interaction would come from the superheavy nucleus. Therefore, we actually calculate  $W_{s,Lr}$  instead of total  $W_s$ . For the sake of brevity, we use  $W_s$  instead of  $W_{s,Lr}$ throughout this work.

# 6.5 Method of calculation

The PEC of the molecules are obtained from calculations of energies by varying the bond-lengths. We calculate the molecular ground state energies using the RCCSD(T) method. Once the ground state equilibrium geometry is obtained, we calculate wave functions of the molecules using the Dirac-Coulomb Hamiltonian under the BO approximation. Then, we evaluate the properties of interest, i.e.  $\mu$ ,  $\mathcal{E}_{\text{eff}}$ , and  $W_s$  by adopting the expectation value approach in the RCCSD method.

### 6.6 Results and discussion

The ground electronic state energies at several bond-lengths were calculated to construct the PEC of each molecule. We then identified the minimum of the PEC, whose corresponding bondlength provided the molecular  $R_e$ . We carried out this procedure for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> (see Fig. 6.1), while ensuring that for each molecule, we choose more grid points around the minimum, to pin-point  $R_e$  to an accuracy of two decimal places in a.u.. We employed the RCCSD(T) method, using the Dirac18 package [37, 38] to perform the calculations. We used Dyall's triplezeta (TZ) v3z [39] basis sets to generate the single particle orbital wave functions. For reducing the computational requirements with little loss in accuracy, we cut-off the high-lying virtual orbitals with energies above 2000 a.u.. The value of  $R_e$  for LrO was found to be 3.46 a.u., while that of LrF<sup>+</sup>, and LrH<sup>+</sup> were found to be 3.56 a.u.. The PEC of each of the molecule exhibited a smooth trend with a clear global minimum (see Fig. 6.1).

After finding the equilibrium bond-lengths of the investigated molecules, we calculated other properties of interest. For this purpose, we used Dyall's quadruple-zeta (QZ) v4z [39] basis sets. We employed the UTChem [40, 41] package for the DF calculations and for atomic orbital to molecular orbital integral transformations, and in tandem, use the Dirac08 package for RCC calculations [42]. We finally used our expectation value code to evaluate the values of the properties [43]. We present the calculated values of  $\mathcal{E}_{\text{eff}}$ ,  $W_s$ , their ratios, and  $\mu$  of LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> from the DF and RCCSD methods in Table 6.1. We also compare our results for LrO with the only available values in literature from Refs. [21, 30]. In Ref. [21], the authors had

Term	$\mathcal{E}_{ ext{ef}}$	<sub>f</sub> (GV/cr	n)		$W_s \; (\mathrm{kHz})$			$\mu$ (D)	
	LrO	$\rm LrF^+$	$\rm LrH^+$	LrO	$\rm LrF^+$	$\rm LrH^+$	LrO	$\rm LrF^+$	$\rm LrH^+$
0	235.16	215.20	283.59	2346.95	2149.75	2821.54	-898.40	-828.32	-919.79
$OT_1$ +h.c.	65.02	35.52	76.06	632.20	348.28	746.75	-1.62	-0.56	-0.72
$T_1^{\dagger}OT_1$	-26.28	-2.24	-9.56	-262.64	-22.42	-96.71	-0.59	-0.09	-0.14
$T_1^{\dagger} O T_2 + \text{h.c.}$	-8.11	-2.87	0.95	-82.72	-29.38	-81.92	0.58	0.14	0.12
$T_2^{\dagger}OT_2$	-8.54	-1.70	-8.21	-85.57	-17.05	9.27	-0.48	-0.14	-0.14
Others	1.67	2.4	-0.45	17.32	16.65	3.43	-0.44	0.08	0.02
Nuclear term	_	_	_	_	_	_	905.56	841.27	931.73
Total	258.92	246.31	343.38	2565.54	2445.83	3402.36	4.58	12.29	11.05

Table 6.2: Contributions from the individual terms of the expectation value expression in the RCCSD method to  $\mathcal{E}_{\text{eff}}$ ,  $W_s$  and  $\mu$  for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup>. The table shows the trends in different contributions between  $\mathcal{E}_{\text{eff}}$  and  $W_s$ .

used (37s, 34p, 14d, and 9f) uncontracted Gaussian type functions for Lr, and a decontracted atomic natural orbital (ANO) basis set of TZ quality for O. They performed their calculations by employing complex generalised Hartree-Fock (cGHF) as well as complex generalised Kohn-Sham (cGKS) theories. They obtained an  $R_e$  of 3.51 a.u. and 3.53 a.u. with cGHF and the cGKS approaches, respectively, which is in reasonably close proximity to our estimated value of 3.46 a.u.. The value of  $\mathcal{E}_{\text{eff}}$  using cGHF method came out to be 322.58 GV/cm, while the cGKS method yielded 250.21 GV/cm. Our calculation, using the RCCSD method and with Dyall's QZ bases for Lr: (37s, 34p, 24d, and 14f) and O: (18s and 10p), give an  $\mathcal{E}_{\text{eff}}$  of 258.92 GV/cm, which is in better agreement with their results from the cGKS method than the cGHF approach.

In Ref. [30], the authors used analytic first derivatives for X2C (exact 2-component) CCSD and CCSD(T) methods, and employed TZ quality basis sets. Further, they froze several of the occupied orbitals in their computations, and obtain an effective electric field of 263.9 GV/cm with CCSD and 246.5 GV/cm with the CCSD(T) approaches. Although their CCSD results are in reasonable agreement with our CCSD results obtained using all-electron fully relativistic CCSD calculations and with a QZ basis, it could be fortuitous. This is evident from the disagreement in the correlation trends in Ref. [30], where the DF result is greater than that CCSD counterpart. In Table 6.1, we have also compared our results with the corresponding values of ThO, where the most accurate EDM measurement is available, and HgF, which possesses the largest  $\mathcal{E}_{\text{eff}}$  estimated thus far for non-superheavy systems. The Lr molecules were found to have values of  $\mathcal{E}_{\text{eff}}$  that are 3-4 times larger than ThO and HgF [2, 8]. Similarly, the values of  $W_s$  for LrO and LrF<sup>+</sup> were found to be about 4 times larger than that for HgF. The table also provides the values for these quantities for other leading candidates, HfF<sup>+</sup> and YbF [31, 32]. Table 6.1 also provides data on the ratio of  $W_s$  and  $\mathcal{E}_{\text{eff}}$ . The significance of the quantity is related to the fact that one needs to perform two experiments to extract both the electron EDM and the S-PS interaction, as seen from Eq. (1.45). We have also presented  $\mathcal{R}$ ,  $\mathcal{S}$ , and their ratios for the leading atomic candidates, Cs, Tl, Rb, and Fr in Table 6.1 [33, 34, 35, 36] from the literature.

In Table 6.2, we present contributions to the values of  $\mathcal{E}_{\text{eff}}$ ,  $W_s$  and  $\mu$  for LrO, LrF<sup>+</sup>, and  $LrH^+$  from different terms of the RCCSD method, given in Eq. (2.219). The first term corresponds to the DF value, while other terms represent correlation contributions. As the table shows,  $OT_1$ +h.c. terms contribute the most to the correlation effects. We note at this point that  $OT_1$  primarily contains in it correlation effects arising from interaction of pairs of electrons.  $T_1^{\dagger}OT_1$  also contains effects involving pairs of electrons, but the interplay between the EDM and Coulomb interactions are more complex. The next leading-order contributions arise from  $T_1^{\dagger}OT_1$ . Albeit the terms related to  $T_2$  operator give comparatively small contributions, they are non-negligible. In fact, for LrO, a sizeable amount of the contributions from  $OT_1$ +h.c. terms are cancelled out by the other terms that are linear in T. The row denoted as 'Others' show that the non-linear terms are negligible even for the considered superheavy systems. Comparisons between the ratios of the magnitudes of  $OT_1$ +h.c. and DF values of  $\mathcal{E}_{eff}$ ,  $W_s$ , and  $\mu$  in LrO, which come out to be  $\approx 0.28$ ,  $\approx 0.27$  and  $\approx 0.23$ , respectively, indicate that the electron correlation effects are almost equally important in all these quantities. Similarly, for  $\mathcal{E}_{\text{eff}}$ ,  $W_s$ , and  $\mu$ , we find these ratios as  $\approx 0.16$ ,  $\approx 0.16$  and  $\approx 0.27$ , respectively, for LrF<sup>+</sup>, and  $\approx 0.27$ ,  $\approx 0.17$  and  $\approx 0.26$ , respectively, for LrH<sup>+</sup>. These results suggest that the electron correlation trends are almost similar in both molecular ions.

We now briefly comment on the molecular orbital information in the chosen systems. We

expected that the singly occupied molecular orbital (SOMO) electron is localized in the *s* orbital of Lr from the following reasoning: as Lr has  $7s^27p^1$  configuration, while O, H<sup>+</sup>, and F<sup>+</sup> are expected to pull two electrons towards themselves owing to their larger electronegativity, thus leading to Lr  $7s^1$ . We verified this reasoning explicitly by examining the atomic components of the SOMO for all three systems, and indeed found that the atomic orbitals from Lr provide the dominant contributions. We also carried out population analysis, and found that in LrF<sup>+</sup>, for example, the SOMO is predominantly made out of the *s* function of Lr (0.86), followed by its *d* (0.09) and *p* functions (0.0388).

As seen in Table 6.2, the major contributions to the properties of interest in this work come from the DF part. Therefore, we take a closer look at the DF contribution, in order to understand the possible reasons for observing large values of  $\mathcal{E}_{\text{eff}}$  and  $W_s$  in the studied superheavy molecules, as compared to other systems. Typically, in these molecules, the heavier atom provides most of the contributions to  $\mathcal{E}_{\text{eff}}$  and  $W_s$ . Due to the short-range and odd-parity nature of the scalar interaction Hamiltonians, the  $s_{1/2}$  and  $p_{1/2}$  orbitals generally contribute predominantly to  $\mathcal{E}_{\text{eff}}$ and  $W_s$ . It is known that relativistic effects deform the inner core orbitals,  $s_{1/2}$  and  $p_{1/2}$ , strongly in the heavier atomic system. Thus, it is anticipated that these orbitals can strongly influence the  $\mathcal{E}_{\text{eff}}$  and  $W_s$  values in LrO, LrF<sup>+</sup>, and LrH<sup>+</sup>. We explicitly verified this argument by decomposing the DF contribution to  $\mathcal{E}_{\text{eff}}$  (we do not repeat the analysis for  $W_s$ , as we expected for it similar trends as the effective electric field) for all the three systems as

$$\mathcal{E}_{\text{eff}}^{DF} = \frac{1}{d_e} \langle \Phi_0 | H_{EDM} | \Phi_0 \rangle 
= \frac{1}{d_e} \sum_j \langle \phi_j | h_{EDM} | \phi_j \rangle 
= \frac{1}{d_e} \langle \phi_v | h_{EDM} | \phi_v \rangle 
= \frac{1}{d_e} \sum_k \sum_l C_k C_l \langle \chi_{v,k} | h_{EDM} | \chi_{v,l} \rangle.$$
(6.1)

In above expression, the sum over all MO contributions boils down to only the valence molecular orbital (SOMO, denoted as v in the above set of equations) term due to the fact that



Figure 6.2: Bar plots showing effective electric fields of LrO,  $LrF^+$ , and  $LrH^+$  at three levels: the  $s - p_{1/2}$  mixing contributions from Lr at the DF level of theory (as red bars), the DF values themselves (as green bars), and the total values (in blue). All units are in GV/cm.

contributions from the orbitals with opposite spin components of the closed-shell configuration cancel out each other. In Eq. (6.1), we have expanded the valence molecular orbital as the sum of atomic orbitals (AOs),  $|\chi_{v,i}\rangle$ , where *i* can be *l* or *k*. Further details about this decomposition of SOMO to AOs can be found in, for example, Ref. [44]. Note that the SOMO contains contributions from both the constituent atoms of a molecule. Of all the terms in Eq. (6.1), the contributions from the *s* and  $p_{1/2}$  orbitals of Lr dominates, and accounts for about 232, 214, and 281 GV/cm, for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup>, respectively, as shown in Fig. 6.2. Note that the DF values for these systems are 235, 215, and 284 GV/cm for LrO, LrF<sup>+</sup>, and LrH<sup>+</sup>, respectively. The other contributions, such as those from  $p_{3/2}$  and  $d_{3/2}$  of Lr, *s* and  $p_{1/2}$  of the lighter atom etc., are less than 1 GV/cm. It is also worth noting that while the DF values of LrO and LrH<sup>+</sup> themselves are different only by about 50 GV/cm, the total effective electric fields are apart by over 80 GV/cm. This is attributed to the significant cancellation between the  $OT_1$  + h.c. and the  $T_1^{\dagger}OT_1$  terms in LrO, as shown in Table 6.2.

We would like to mention here that the above calculations were carried out by assuming

Gaussian nuclear charge distribution. Since Gaussian type functions are used for constructing the MOs, it was convenient to consider the Gaussian nuclear charge distribution in the calculations [45]. Because Lr is a superheavy radioactive element, its nuclear charge distribution may be explained more accurately by using a more realistic nuclear charge distribution such as Fermi [46] or the Woods-Saxon charge distribution [47, 48]. In order to get an impression about how the results differ by considering different nuclear charge distribution models in the Lr isotopes, we investigated below the EDM enhancement factors,  $\mathcal{R}$  and  $\mathcal{S}$ , in two isolated isotopes of Lr due to  $d_e$  and  $k_s$ , respectively, using various forms of nuclear charge distributions and potentials.

In the point-like nuclear model, the nuclear density is  $\rho_A(0) = 0$  and the nuclear potential takes the form

$$V(r) = -\frac{Z_A}{r}.$$
(6.2)

In the simplest case, one can assume uniform nuclear charge density in which the nuclear density and potential are given by

$$\rho_A(r) = \rho_0 \Theta\left(1 - \frac{r}{R_A}\right),\tag{6.3}$$

and

$$V(r) = \begin{cases} -\frac{3Z_A}{2R_A^{rms}} \left(1 - \frac{1}{3} \left(\frac{r}{R_A^{rms}}\right)^2\right) & \text{for } r \le R_A^{rms} \\ -\frac{Z_A}{r}, & \text{for } r > R_A^{rms} \end{cases},$$
(6.4)

where  $\rho_0 = 3Z_A/4\pi R_A^3$  is the normalization constant,  $R_A$  is the radius of an arbitrary sphere in which nuclear charges are distributed and  $R_A^{rms}$  is root mean squared (rms) radius of the  $A^{th}$ nucleus.  $\Theta$  is the Heaviside step function. We have determined  $R_A = r_0 M_A^{1/3}$  with  $r_0 = 1.2 \ fm$ and atomic mass  $M_A$ , and  $R_A^{rms} = \sqrt{(3/5)}R_A$ . In the Gaussian nuclear charge distribution model, the nuclear density is given by

$$\rho_A(r) = \left(\frac{\eta_A}{\pi}\right)^{\frac{3}{2}} e^{-\eta_A r^2} \tag{6.5}$$

with  $\eta_A = \frac{3}{2} (R_A^{rms})^{-2}$ , where  $R_A^{rms}$  is the rms nuclear charge radius of the  $A^{th}$  nucleus. This leads to the expression for nuclear potential observed by an electron as

$$V(r) = -\frac{Z_A}{r} \operatorname{erf}\left(\sqrt{\eta}r\right).$$
(6.6)

Similarly, the Fermi nuclear charge distribution is given by

$$\rho_A(r) = \frac{\rho_0}{1 + e^{(r-c)/a}},\tag{6.7}$$

where  $\rho_0$  is the normalization constant, c is the half-charge radius and a = 2.3/4ln(3) is known as the skin thickness. The expression for the nuclear potential in this case is given by [49]

$$V(r) = -\frac{Z_A}{\mathcal{N}r} \times \left\{ \begin{array}{l} \frac{1}{c} \left(\frac{3}{2} + \frac{a^2\pi^2}{2c^2} - \frac{r^2}{2c^2} + \frac{3a^2}{c^2} P_2^+ \frac{6a^3}{c^2r} (S_3 - P_3^+) \right) & \text{for } r_i \le c \\ \frac{1}{r_i} \left(1 + \frac{a62\pi^2}{c^2} - \frac{3a^2r}{c^3} P_2^- + \frac{6a^3}{c^3} (S_3 - P_3^-) \right) & \text{for } r_i > c, \end{array} \right.$$
(6.8)

where the factors are

$$\mathcal{N} = 1 + \frac{a^2 \pi^2}{c^2} + \frac{6a^3}{c^3} S_3$$
  
with  $S_k = \sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^k} e^{-lc/a}$   
and  $P_k^{\pm} = \sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^k} e^{\pm l(r-c)/a}.$  (6.9)

In the Woods-Saxon model, the nuclear charge density is again given by using a uniform charge distribution but using different rms radii for protons and neutrons as

$$\rho_n(r) = \rho_0^n \Theta\left(1 - \frac{r}{R_n}\right),\tag{6.10}$$

with the corresponding normalization constant  $\rho_0 = 3Z_A/4\pi R_n^3$  for  $R_n = r_0^n M_A^{1/3}$ . We have taken  $r_0^n = 1.275 \ fm$  and  $r_0^n = 1.347 \ fm$  for protons and neutrons respectively [50]. Therefore, the Coulomb potential due to this charge distribution can be given by

$$V_C^n(r) = \begin{cases} -\frac{3Z_A}{2R_n^{rms}} \left(1 - \frac{1}{3} \left(\frac{r}{R_n^{rms}}\right)^2\right) & \text{for } r \le R_n^{rms} \\ -\frac{Z_A}{r}, & \text{for } r > R_n^{rms} \end{cases}.$$
(6.11)

In addition to the Coulomb interaction, the Woods-Saxon model takes care of corrections to nuclear potential due to diffuse surface  $(V_{ds})$  and spin-orbit  $(V_{ls})$  interactions. This results in a net nuclear potential given by [48, 47]

$$V(r) = V_C^n(r) + V_{ds}^n(r) + V_{ls}^n(r), (6.12)$$

where  $V_{ds}^{n} = V_{0} f_{ds}^{n}(r)$  with a' = 0.65 fm,  $R_{n}^{rms} = r_{0}^{n} M_{A}^{1/3} fm$  and

$$f_{ds}^{n}(r) = \begin{cases} \frac{1}{1 + e^{(r - R_{n}^{rms})/a'}} & \text{for } r \le R_{n}^{rms} \\ 0, & \text{for } r > R_{n}^{rms} \end{cases},$$
(6.13)

and

$$V_{ls}^n(r) = V_{ls}^c r^{n_0^2} \mathbf{L} \cdot \mathbf{S} \frac{1}{r} \frac{df_{ls}^n(r)}{dr}$$
(6.14)

for the orbital angular momentum operator  ${\bf L},$  spin operator  ${\bf S},$   $V_{ls}^c=0.44V_0^n$  and

$$f_{ls}^{n}(r) = \begin{cases} \frac{1}{1 + e^{(r - R_{n}^{ls})/a'}} & \text{for } r \le R_{n}^{ls} \\ 0, & \text{for } r > R_{n}^{ls} \end{cases}$$
(6.15)

with  $R_n^{ls} = r_{ls}^n M_A^{1/3}$ . We have taken  $r_{ls}^n = 0.932 \ fm$  and  $r_{ls}^n = 1.280 \ fm$  for protons and neutrons respectively [50]. In the above expressions,  $V_0^n$  are chosen as  $V_0^n = 51 + 33(N_A - Z_A)/(N_A + Z_A)$ MeV and  $V_0^n = 51 - 33(N_A - Z_A)/(N_A + Z_A)$  MeV for protons and neutrons, respectively.

Though we have suggested earlier to consider <sup>256</sup>Lr in the experiment, but we consider here

Table 6.3: The enhancement factors of the isolated Lr isotopes,  ${}^{253}Lr$  and  ${}^{255}Lr$ , due to  $d_e$  and  $k_s$  by considering various nuclear charge density distributions, using the DF method. In the Woods-Saxon model, results quoted under 'Coulomb' refer to Coulomb interaction contributions, while revised values after adding corrections due to diffuse surface and spin-orbit interactions are given as '+Surface diffuse' and '+LS', respectively.

Model	$\mathcal{R}$	$\mathcal{S} (\times 10^{-18} \text{ e-cm})$				
	252					
In case	of $^{253}$ Lr iso	otope				
Point-like	-2091.39	0.0				
Uniform	-1628.51	-31.74				
Gaussian	-1638.11	-33.18				
Fermi	-1631.06	-32.28				
Woods-Saxon:						
Coulomb	-1608.66	-31.20				
+Surface diffuse	-1420.18	-15.18				
+LS	-1403.27	-15.45				
In case	of $^{255}$ Lr iso	otope				
Point-like	-2091.39	0.0				
Uniform	-1627.66	-31.71				
Gaussian	-1637.35	-33.40				
Fermi	-1630.29	-32.48				
Woods-Saxon:						
Coulomb	-1607.79	-31.17				
+Surface diffuse	-1420.40	-15.18				
+LS	-1414.60	-15.25				

the <sup>253</sup>Lr and <sup>255</sup>Lr odd-isotopes to analyze the spin-orbit effects. This is not going to affect the  $\mathcal{E}_{\text{eff}}$  value estimation much. However, considering odd isotopes is helpful to analyze spin-orbit effects conveniently. It can be noticed that other contributions, except the spin-orbit interactions, from the aforementioned models will be almost similar in the calculations of  $\mathcal{R}$  and  $\mathcal{S}$ . According to shell-model configurations, these isotopes have odd-proton in the valence orbitals (in the  $f_{7/2}$  orbital for <sup>253</sup>Lr) and (in the  $p_{1/2}$  orbital for <sup>255</sup>Lr) [51]. The dependencies of these charge distribution models to the estimation of  $\mathcal{E}_{\text{eff}}$  comes indirectly through V(r), while evaluation of  $W_s$  depends both directly and indirectly from it. Since this exercise is carried out to demonstrate influence in the results due to choice of different nuclear distribution models, we have employed the DF method for this purpose and the results are given in Table 6.3. As can be seen from this table, there is a significant differences in the results when finite size nucleus is

considered over the point nucleus. The results do not differ substantially when different nuclear charge distribution models are considered, but a large effect is seen when diffuse surface interaction is introduced. The results do not change significantly due to the spin-orbit interactions. Also, differences between the results for the <sup>253</sup>Lr and <sup>255</sup>Lr isotopes are negligibly small. This analysis suggests that the  $W_s$  values of the considered molecules may reduce approximately by ~ 40% if the calculations are carried out by introducing diffuse potential, which we defer to the future work.

Using the values of PDM and bond-length of a molecule, we estimate the polarizing electric field for that system, which is given by  $E_{pol} = \frac{2B}{\mu}$ , with B being the rotational constant. The  $E_{pol}$  of LrO is 18.38 kV/cm, while they are 5.79 kV/cm and 101.03 kV/cm in LrF<sup>+</sup> and LrH<sup>+</sup>, respectively. The  $E_{pol}$  required to polarize LrO and LrF<sup>+</sup> are practically achievable in the laboratory. The larger, and thus less desirable, value of  $E_{pol}$  in LrH<sup>+</sup> can be attributed to its smaller reduced mass. Therefore, LrH<sup>+</sup> may not be as suitable as the other two considered candidates, but it can also be considered in an experiment if any alternative suitable technique to measure EDM in this ion can be found.

We now turn our attention to estimating the production rates of Lr molecules for an EDM experiment. We propose to use the RIKEN heavy-ion linear accelerator (RILAC) facility because a high intensity ion beam is readily available to produce atoms of interest. As for <sup>256</sup>Lr production, we propose the <sup>209</sup>Bi(<sup>48</sup>Ca, 1n) reaction as a possible candidate, where a production cross-section of 60 nanobarns (nb) has been reported [52], although it is necessary to have a prospect of stable supply of <sup>48</sup>Ca. As explained in Ref. [53], the <sup>249</sup>Cf(<sup>11</sup>B, 4n) reaction was employed in the single ion beam production of <sup>256</sup>Lr at JAEA due to its relatively high cross-section of 122 nb. The <sup>249</sup>Cf target material is, however, radioactive, and too rare to prepare a sufficiently large target, which can be applied to a beam from the RILAC. On the other hand, <sup>209</sup>Bi is stable and easy to handle to make a target with a large area. A typical target thickness is 300  $\mu gcm^{-2}$  [54]. The RILAC facility can typically provide a 3 –  $p\mu A$  <sup>48</sup>Ca beam. Under the situation, Lr atoms can be produced with a rate of one atom per second. In the case that GARIS (GAs-filled Recoil Ion Separator) is applied to mass-separation and single ion beam production, a transparent efficiency

of 50% is expected [55]. In addition, in preliminary experiments at JAEA, about 20% of Lr can be converted to LrO. Thus, we estimate N  $\approx 0.1$  molecules per second. It means only about one-atom-per-minute molecular beam could be produced, which presents major challenges for experiments with neutral molecules. On the other hand, molecular ions such as LrF<sup>+</sup> and LrH<sup>+</sup> can be efficiently guided and trapped by electromagnetic fields, enabling experiments even with just a single molecular ion.
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#### Chapter 7

#### Summary and Outlook

In this chapter, we summarize the work carried out in this thesis in a nutshell. First, we have performed four-component relativistic finite-field coupled-cluster calculations of permanent electric dipole moments and different components of static dipole polarizabilities of heteronuclear alkali-dimers (in their ground states) and compared these results with the non-relativistic calculations at the same level of approximations in the theory. We find from our observations that the relativistic effects become very prominent in the evaluation of permanent electric dipole moments, especially in the heavier alkali-dimers. We attempt to explain the mismatch between the experimental value of permanent electric dipole moment of LiNa with previous theoretical calculations and resolve the discrepancy by invoking the complete basis set extrapolation technique. We briefly discuss the trends in electron correlation effects in the calculated properties of alkali-dimers by grouping them into different family of molecules. We compare our calculated values with the previous experimental and theoretical works from literature. We verify the linear variation of the components of static electric dipole polarizability with molecular volume. We report the uncertainties to the calculated properties arising from several possible sources. At the next step, we illustrate the importance of incorporating relativistic effects in the evaluation of the permanent electric dipole moments and static dipole polarizabilities, by using them to determine the van der Waals  $C_6$  coefficients of the considered alkali-dimers. It is evident from our calculations that the relativistic coupled-cluster theory that we have employed gives very reliable estimates of permanent electric dipole moments and static dipole polarizabilities of heteronuclear alkali-dimers, which are in very good agreement with the previous theoretical as well as experimental results.

Then, we have investigated the roles of relativistic and electron correlation effects in the determination of the permanent electric dipole moments and static electric dipole polarizabilities of the alkali-alkaline earth heteronuclear dimers. For this purpose, we employed finite-field coupled-cluster theory in the singles, doubles and perturbative triple excitation approximation in both non-relativistic and relativistic frameworks. We find that electron correlation effects can have significant impact on the final values of the permanent electric dipole moments of some of the considered molecules. Trend-wise, we observe that while correlation effects decrease the permanent electric dipole moments of the Li-family, they increase it for the rest of the families, with Mg-containing molecules being exceptions. We also find that for molecules containing Mg, the ratio of the correlation contributions to the permanent dipole moments to their mean-field values are almost constant. We find that relativistic effects decrease the magnitudes of permanent dipole moments in most cases. The importance of relativistic effects increases from the lighter to the heavier molecules in each family, as expected. Correlation effects play important roles and are pronounced in the determination of polarizabilities too, but not as much as in the case of permanent electric dipole moments. Moreover, the observed correlation trends in evaluation of polarizability anisotropies indicate that this property is likely more sensitive to correlation effects than the average polarizabilities. Relativistic effects in polarizabilities are found to be non-negligible but are much less prominent than in the case of permanent electric dipole moments. The analyses of relativistic and correlation effects are followed by tests of precision in our results, where we find that the errors due to spin-orbit coupling are negligible. We also test the stability of our numerical results by varying the perturbing parameter in the neighborhood of the chosen value for this work. We observe that the uncertainties due to the choice of basis sets and missing higher-level excitations of coupled-cluster theory are the dominant error sources. We find a simple and interesting empirical functional form that connects average molecular polarizabilities with constituent atomic polarizabilities reasonably well and does so consistently, not only for the considered alkali-alkaline earth molecules, but also for homonuclear as well as heteronuclear alkali-alkali systems and for alkaline earth-fluorine molecules. We finally provide recommended

relativistic values of permanent dipole moments and polarizabilities of the alkali-alkaline earth systems using coupled-cluster singles, doubles and perturbative triple excitation method, and compare them with the available literature values as well as with our non-relativistic calculations. In this work, we saw that our relativistic calculations improve the values of permanent electric dipole moments and polarizabilities over the reported values using the non-relativistic methods in the literature. Therefore, in view of the preceding and current chapters, it can be safely concluded that the relativistic coupled-cluster theory is an accurate as well as reliable recipe for calculating first-order and second-order molecular properties. This analysis allows us to employ relativistic coupled-cluster theory for precise estimations of molecular properties relevant to electron electric dipole moment probes.

After studying permanent electric dipole moments and electric dipole polarizabilities of a number of molecules with closed-shell and one-valence configurations, we investigate the feasibility of using triatomic molecules over traditional diatomic molecules for electron electric dipole moment studies. For that purpose, we analyzed the suitability of HgOH molecule as a plausible candidate for experiments to measure electric dipole moment of an electron. To that end, we have evaluated the effective electric field and permanent electric dipole moment of the HgOH molecule. We have also calculated the Franck-Condon factors of HgOH among the lowest and other higher vibrational levels of the ground state. Very negligible values of the Franck-Condon factors indicate that HgOH is not laser coolable, unlike its isoelectronic diatomic counterpart HgF. The aspect of laser non-coolability of HgOH makes a trap experiment with the molecule very challenging. We closely inspect the possible experimental scenarios with HgOH based on some reasonable guess estimates of different parameters. We have also pointed out that HgOH may not provide specific advantages in other experimental schemes such as the EDM<sup>3</sup>, except a possibility of state selective detection. We reached at a conclusion that HgOH molecule is best suited for a beam experiment as it offers a statistical sensitivity of  $5 \times 10^{-30}$  e-cm, which is an improvement over ThO, which sets the current best limit on the upper bound of the electron electric dipole moment. Moreover, we have conducted preliminary analyses on HgCH<sub>3</sub> and  $HgCF_3$  and find that these two molecules could offer statistical sensitivities of the same order as that of HgOH.

After analyzing the suitability of the heavy polar triatomic HgOH molecule for electron electric dipole moment searches, we turn our attention to the combined search of electron electric dipole moment and the nucleus-electron scalar-pseudoscalar coupling constant in the *superheavy* LrF<sup>+</sup>, LrH<sup>+</sup>, and LrO molecules. We find that bound states with a stable minima do occur in the chosen molecular systems. We reported calculations of effective electric fields, scalarpseudoscalar enhancement factors, and permanent electric dipole moments for the aforementioned molecules, using the relativistic coupled-cluster method. We analyze the importance of correlation effects for the properties in these three systems. We observe that the values of effective electric fields for the three superheavy molecules are about three to four times larger than other molecules on which electron electric dipole moment experiments have been performed or proposed to be performed. Similarly, the values of the scalar-pseudoscalar enhancement factors are found to be about eight times larger than ThO (experimentally undertaken best molecule so far) and about three to four times larger than the current best theoretically proposed molecule HgF. By analysing the Woods-Saxon model to account for the nuclear charge density distribution, we found that the calculated scalar-pseudoscalar interaction coefficients are very sensitive to the diffuse surface interactions in the superheavy Lr nucleus and need to be accounted for, for accurate estimate of the scalar-pseudoscalar interaction constants for the Lr-containing molecules. We discuss a feasible pathway to produce Lr atoms, which are necessary for the creation of superheavy molecules containing these atoms. We also study the properties of LrF<sup>+</sup> and LrH<sup>+</sup> molecules and their potentials for future single ion experiments. Our precisely estimated bondlengths and permanent electric dipole moment values of the LrF<sup>+</sup>, LrH<sup>+</sup>, and LrO molecules can also be useful to guide other experimental setups using these superheavy molecules.

Our overall findings in this thesis work are listed in bullet points as follows

• From the calculations of permanent electric dipole moments and static dipole polarizabilities of alkali-dimers, we come to the conclusion that our relativistic coupled-cluster theory is very efficient in precisely calculating molecular properties that agree very well with experimental results. • We also observed that electron correlation effects can play significant roles in the determination of the calculated molecular properties, which justifies the usage of the sophisticated relativistic coupled-cluster theory over mean-field methods to estimate enhancement factors associated with the electron electric dipole moment and scalar-pseudoscalar interaction.

• We observe that relativistic effects become prominent in the evaluation of permanent electric dipole moments in the heavier alkali-dimers, which suggests that one needs to perform a relativistic calculation to obtain an accurate permanent electric dipole moments of heavy polar paramagnetic molecules in general as well as for the considered molecules for electron electric dipole moment experiments in particular.

• In our second work, which can be viewed as a sequel to our first, we calculated permanent electric dipole moments and static dipole polarizabilities of the paramagnetic alkali-alkaline earth molecules.

• As paramagnetic molecules are essential for electric dipole moment searches, it was a necessary check to see whether the relativistic coupled-cluster theory is able to produce reliable results for these molecules. In this exercise too, we found that electron correlation effects become important for the evaluation of permanent electric dipole moments, thus necessitating the use of the state-of-art non-relativistic and relativistic coupled-cluster theory to account for the electron correlation effects.

• We also observe that the relativistic effects in permanent electric dipole moments of the open-shell alkali-alkaline earth molecules can be as large as 32 percent (for LiSr). This further suggests that employing a relativistic theory is essential for calculating permanent dipole moments of heavier paramagnetic molecules that are chosen for theoretical studies involving electron electric dipole moment searches.

• After analyzing the potential of the relativistic coupled-cluster theory and getting an in-

sight of correlation effects in paramagnetic molecules, we began to work on theoretical proposals for new molecular candidates for electron electric dipole moment experiments.

• We chose the heavy polar triatomic HgOH molecule to investigate its feasibility for future electron electric dipole moment search experiments using the relativistic coupled-cluster theory.

• We found that the effective electric field of HgOH is not as large as its diatomic isoelectronic counterpart, HgF. The reason behind the comparatively smaller value of effective electric field can be back-traced to the bent geometry of the HgOH molecule. A reasonable value of the molecule's permanent electric dipole moment at the actual bent geometry suggests that the molecule can be easily polarized during an electron electric dipole moment experiment. From our theoretical estimates of Frank-Condon Factors for transitions between the lowest vibrational level of the ground state and other higher vibrational levels of low-lying excited electronic states, we conclude that HgOH is not laser coolable, thus discarding the possibility of a trap electron electric dipole moment experiment with the molecule.

• Based on several experimental considerations, we conclude that HgOH is best suited for a beam electron electric dipole moment experiment, with its projected statistical sensitivity promising to be an order of magnitude improvement over the ThO experiment, which gives the current best experimental limit to the electron electric dipole moment.

• Depending on our preliminary calculations at the Dirac-Fock level and other projected experimental scenarios, we found that the polyatomic HgCH<sub>3</sub> and HgCF<sub>3</sub> molecules also offer similar sensitivity to electron electric dipole moment experiments. Further studies on these two systems using relativistic many-body theories, which include correlation effects, could improve upon the estimated sensitivities.

• In the next work, we consider superheavy LrO, LrF<sup>+</sup>, and LrH<sup>+</sup> molecules to carry out a theoretical study to assess their applicability in electric dipole moment experiments. We have explicitly shown that the formation of these superheavy molecules are actually possible, as we obtained their equilibrium bond-lengths employing the relativistic coupled-cluster theory with singles, doubles and triples excitations approximation. These estimates of bond-lengths can prove to be useful for any future experiments using these molecules. With the ground state equilibrium bond-lengths at our disposal, we calculated effective electric fields, scalar-pseudoscalar interaction constants, and permanent electric dipole moments of these molecules. As anticipated, we have observed that the values of effective electric fields and scalar-pseudoscalar enhancement factors get heavily amplified for these superheavy systems, when compared with other nonsuperheavy molecules that are either theoretically proposed or experimentally considered.

• The polarizing electric fields of LrO and LrF<sup>+</sup> are found to be quite achievable in conventional experimental setups.

• Along with our theoretical calculations, we also propose a possible technique to produce Lr atoms in laboratories. Further progress in the experimental sector to produce Lr atoms (followed by Lr-containing molecules) in large numbers could make the considered molecules very exciting candidates for future electron electric dipole moment experiments.

In the voyage of probing eEDM with molecules through theoretical calculations using the RCC method, we would like to give a brief sketch about the future direction of our work. After theoretically surveying the prospects for HgOH, HgCH<sub>3</sub>, and HgCF<sub>3</sub> for EDM experiments, we can extend our exploration to several other triatomic/ polyatomic paramagnetic molecules.

As the three considered superheavy Lr-molecules showed enhanced values of  $\mathcal{E}_{\text{eff}}$ , PDM, and  $W_s$ , it would be appropriate to explore more superheavy molecular systems (containing Cf, Es, No, Cn etc.) for their suitabilities in EDM experiments.

### Appendix A

# Contributions to $\mathcal{E}_{\text{eff}}$ from Only Valence Orbitals Survive

As stated earlier in Chapter I, only valence MOs contribute to the final expression of  $\mathcal{E}_{\text{eff}}$ . This happens because contributions from all other MOs cancel out. One can realise this as follows. Consider the numerator of Eq. (1.32) and expand it in terms of MOs of a single valence molecule with N electrons:

$$\langle \Psi | H_{eEDM} | \Psi \rangle = \sum_{i}^{N} \langle \phi_i | h_{eEDM} | \phi_i \rangle,$$
 (A.1)

where  $h_{eEDM} = -2icd_e\beta\gamma_5 p^2$  is the one-body eEDM interaction Hamiltonian. Invoking Kramer's symmetry [1], we can decompose the right hand side of Eq. (A.1) as

$$\sum_{i}^{N} \langle \phi_{i} | h_{eEDM} | \phi_{i} \rangle = \sum_{i'}^{(N-1)/2} \langle \phi_{i'} | h_{eEDM} | \phi_{i'} \rangle + \sum_{\bar{i'}}^{(N-1)/2} \langle \phi_{\bar{i'}} | h_{eEDM} | \phi_{\bar{i'}} \rangle + \langle \phi_{v} | h_{eEDM} | \phi_{v} \rangle, \qquad (A.2)$$

where the first two terms in the right hand side correspond to the doubly occupied Kramer's pair orbitals  $|\phi_{i'}\rangle$  and  $|\phi_{\bar{i}'}\rangle$ . The Kramer's pair orbitals  $|\phi_{i'}\rangle$  and  $|\phi_{\bar{i}'}\rangle$  are connected by the

time-reversal operator:

$$|\phi_{i'}\rangle = T|\phi_{\bar{i}'}\rangle \text{ and } |\phi_{\bar{i}'}\rangle = -T|\phi_{i'}\rangle.$$
 (A.3)

Invoking the above relations we get

$$\langle \phi_{\bar{i}'} | h_{eEDM} | \phi_{\bar{i}'} \rangle = \langle \phi_{i'} | T^{\dagger} h_{eEDM} T | \phi_{i'} \rangle. \tag{A.4}$$

Next, we find how  $h_{eEDM}$  converts under time-reversal operation. Time-reversal operator has the following form for spin-1/2 particles such as electron [1]

$$T = -i\Sigma_y \tau_0,\tag{A.5}$$

where  $\Sigma_y$  is the four-component counterpart of Pauli spin matrix  $\sigma_y$ , i.e.  $\Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}$ ,  $\tau_0$  is the complex conjugation operator. The *T* operator takes the form

$$T = \underbrace{\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}}_{=M} \tau_0 = M \tau_0.$$
(A.6)

Therefore,

$$\langle \phi_{i'} | T^{\dagger} h_{eEDM} T | \phi_{i'} \rangle = \langle \phi_{i'} | \tau_0^{\dagger} M^{\dagger} h_{eEDM} M \tau_0 | \phi_{i'} \rangle.$$
(A.7)

Property of complex conjugation operator tells  $\langle \phi_{i'} | \tau_0^{\dagger} = \langle \phi_{i'} |$  and  $\tau_0 | \phi_{i'} \rangle = | \phi_{i'}^* \rangle = | \phi_{i'} \rangle$  (as MOs are real). Inserting these relations in Eq. (A.7) we get

$$\langle \phi_{i'} | T^{\dagger} h_{eEDM} T | \phi_{i'} \rangle = \langle \phi_{i'} | \tau_0^{\dagger} M^{\dagger} h_{eEDM} M \tau_0 | \phi_{i'} \rangle.$$
(A.8)

Now, we simplify the operator  $M^{\dagger}h_{eEDM}M$ . We know

$$h_{eEDM} = -2icd_e\beta\gamma_5 p^2 = -2icd_e p^2 \underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}}_{=\beta} \underbrace{\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}}_{=\gamma_5 = i\gamma_0\gamma_1\gamma_2\gamma_3}$$
(A.9)

$$= -2icd_e \begin{pmatrix} 0 & 0 & p^2 & 0\\ 0 & 0 & 0 & p^2\\ -p^2 & 0 & 0 & 0\\ 0 & -p^2 & 0 & 0 \end{pmatrix}$$
(A.10)

$$\Rightarrow \underbrace{\tau_0^{\dagger} M^{\dagger} h_{eEDM} M \tau_0}_{T^{\dagger} h_{eEDM} T} = 2icd_e \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}}_{M^{\dagger}} \begin{pmatrix} 0 & 0 & p^2 & 0 \\ 0 & 0 & 0 & p^2 \\ -p^2 & 0 & 0 & 0 \\ 0 & -p^2 & 0 & 0 \end{pmatrix} \underbrace{\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}}_{=M}$$
(A.11)  
$$= 2icd_e \begin{pmatrix} 0 & 0 & p^2 & 0 \\ 0 & 0 & 0 & p^2 \\ -p^2 & 0 & 0 & 0 \\ 0 & -p^2 & 0 & 0 \end{pmatrix} = -h_{eEDM}$$
(A.12)

$$\Rightarrow T^{\dagger} h_{eEDM} T = -h_{eEDM}. \tag{A.13}$$

Inserting this result in Eq. (A.4) we get

$$\langle \phi_{\bar{i}'} | h_{eEDM} | \phi_{\bar{i}'} \rangle = -\langle \phi_{i'} | h_{eEDM} | \phi_{i'} \rangle. \tag{A.14}$$

Using this relation in Eq. (A.2) we see that the first two terms are cancelling out, which gives

$$\sum_{i}^{N} \langle \phi_i | h_{eEDM} | \phi_i \rangle = \langle \phi_v | h_{eEDM} | \phi_v \rangle, \qquad (A.15)$$

$$\Rightarrow \mathcal{E}_{\text{eff}} = -\frac{1}{d_e} \frac{\sum_i^N \langle \phi_i | h_{eEDM} | \phi_i \rangle}{\langle \Psi | \Psi \rangle} = -\frac{1}{d_e} \frac{\langle \phi_v | h_{eEDM} | \phi_v \rangle}{\langle \Psi | \Psi \rangle}.$$
(A.16)

From Eq. (A.16) it is evident that only valence molecular orbital contributes to  $\mathcal{E}_{\rm eff}$ .

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