

CALCULATION OF PROPERTIES USING RELATIVISTIC COUPLED CLUSTER THEORY FOR ATOMS AND MOLECULES

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In Chemical Sciences



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DECLARATION

I hereby declare that the thesis entitled “**Calculation of Properties Using Relativistic Coupled Cluster Theory for Atoms and Molecules**” submitted for the degree of Doctor of Philosophy in Chemical Sciences to the Academy of Scientific & Innovative Research (AcSIR), has been carried out by me at the Physical Chemistry Division of CSIR-National Chemical Laboratory, Pune under the supervision of Prof. Sourav Pal and Dr. Nayana Vaval. Such material as has been obtained by other sources has been duly acknowledged in the thesis. The work is original and has not been submitted in part or full by me for any other degree or diploma to any other Institution or University.

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Ph. D candidate

*To
my family*

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Abstract

The complex interplay between relativistic and electron correlation effects always comes in the way in accurate determination of the spectroscopic properties of heavy atomic or molecular systems [1]. However, there have been remarkable advances in recent years in the high-performance computing techniques and extension of the several well established non-relativistic theories to the relativistic realm, such calculations are no longer invincible. The Dirac-Hartree-Fock method is an elegant choice to include the effect of relativity in a single determinantal theory. On the other hand, the performance of the coupled-cluster theory is well tested for the treatment of dynamic part of the electron correlation [2]. However, in dealing with open-shell configurations where nondynamic correlation has a significant contribution, single-reference coupled-cluster method is inadequate for the comprehensive treatment of electron correlation [3].

The first successful attempt to develop a relativistic coupled-cluster theory for the purpose of simultaneous treatment of both relativistic and electron correlation effects is done by Kaldor and co-workers. They implemented Fock-space multi-reference coupled-cluster (FSMRCC) theory for the cause, and applied to both atomic and molecular systems [4–7]. However, the problem of intruder states [8], which leads to the failure in convergence, is associated with the effective Hamiltonian variant of the FSMRCC theory [9–11].

Alternatively, the equation-of-motion coupled-cluster (EOMCC) method [12–15] is an elegant choice to tackle the problem of intruder. The EOMCC method is conceptually very simple and works within a single-reference description to address the complex multi-configurational wave function. Hirata *et al.* [16] put forward the first step to implement the EOMCC method in the relativistic domain. They used two component valence spinors along with a relativistic effective core potential (RECP) [17] which was augmented by the spin-orbit interaction [18] and the electron correlation is treated using a low rank version of the EOMCC method. Therefore, neither the effect of relativity nor the treatment of electron correlation is comprehensive in their approach which motivates us to implement the relativistic EOMCC methods with the rigorous treatment of both relativistic and electron correlation effects.

The thesis deals with the development of the EOMCC method for the purpose of relativistic calculations of both atomic and molecular systems to address various electronic structure problems. We have considered Dirac-Coulomb Hamiltonian in all our calculations.

The thesis is organized as follows:

CHAPTER 1: The questions, why it is so important to consider the effects of relativity in a many-body calculation, what are the various choices to incorporate relativistic effects at different levels of the theory, and how it can be done is being addressed in subsequent sections of the chapter. Concise description of a few of the electron correlation methods, those are very popular in the non-relativistic domain, and can be a potential method in the relativistic framework are explained in brief. Why we have opted for the equation-of-motion coupled cluster method over the other available correlation methods, and what has been done previously in the relativistic equation-of-motion coupled cluster domain, have been addressed.

CHAPTER 2: The chapter considers the implementation of the relativistic equation-of-motion coupled-cluster method (EOMCC) for the calculation of ionization potentials of closed-shell atomic systems. The Dirac-Coulomb Hamiltonian is used to generate one-body and two-body matrix elements required for the correlation calculation, and the reference wave function is constructed using coupled-cluster method considering single- and double- excitation approximation. The Fermi-charge distribution of the nuclear density is considered to take care of the effect of finite size nucleus. The calculated results are compared with the values from the National Institute of Science and Technology database and our results are found to be in good agreement with the standard values. Further, we have done two intermediate calculations in the EOMCC framework to understand the role of electron correlation at different levels of approximation.

CHAPTER 3: Here, we report our successful implementation of the double-ionization equation-of-motion coupled-cluster (DI-EOMCC) method. The implemented method is applied to calculate valence double-ionization potential values of closed-shell atomic systems and the calculated results are compared with the values from NIST database and other theoretical methods. We also present results using the second-order many-body perturbation theory and the random-phase approximation in the equation-of-motion framework, and all these results are compared with the DI-EOMCC results.

CHAPTER 4: In the present chapter, we consider the implementation of relativistic equation-of-motion coupled-cluster (EOMCC) method at the level of single- and double- excitation approximation to calculate the ionization potential of molecular systems. Four-component Dirac spinors

are used in the calculations, and the Dirac-Coulomb Hamiltonian is used to evaluate one- and two-electron integrals. The vertical ionization potentials of the molecules XH (X = F, Cl, Br, I) along with Cl₂ and Br₂ are calculated. We have also presented intermediate results considering first order perturbed wave function for the construction of ground state wave function in the EOMCC framework, in order to understand the role of electron correlation. The results of our calculation are compared with the available experimental results and it is observed that EOMCC results are in good agreement with the experimental values. The relative deviation of less than 1% is achieved for all the considered systems.

CHAPTER 5: The relativistic equation-of-motion coupled cluster method for the electron attachment problem (EA-EOMCC) applicable to both atomic and molecular systems is implemented and presented in chapter 5. The implemented relativistic EA-EOMCC method is employed to calculate ionization potential values of alkali metal atoms (Li, Na, K, Rb, Cs, Fr) and the vertical electron affinity values of LiX (X=H, F, Cl, Br), NaY (Y=H, F, Cl) starting from their closed-shell configuration. The computed atomic results are compared with the available values from the NIST database to test the performance of the newly implemented relativistic EA-EOMCC method. We are successful in achieving an accuracy of $\sim 0.6\%$ with the standard NIST values.

CHAPTER 6: The relativistic equation-of-motion coupled-cluster (EOMCC) method using open-shell reference wave function is successfully implemented with the consideration of single- and double- excitation approximation. As a first attempt, the implemented method is employed to calculate ionization potential values of heavy atomic (Ag, Cs, Au, Fr, Lr) and molecular (HgH, PbF) systems, where the effect of relativity does really matter to obtain highly accurate results. Not only the relativistic effect, but also the effect of electron correlation is crucial in these heavy atomic and molecular systems. To justify the fact, we have taken two further approximations in the four-component relativistic EOMCC framework to quantify how the effect of electron correlation plays a role at different levels of approximation. All these calculated values are compared with corresponding experimental values as well as with other theoretically calculated values to judge the extent of accuracy obtained in our calculation. A nice agreement is achieved for all the considered systems, which validates the performance of the open-shell reference relativistic EOMCC method.

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List of Publications

1. A. K. Dutta, J. Gupta, **H. Pathak**, N. Vaval, and S. Pal, “Partitioned EOMEA-MBPT(2): An Efficient N^5 Scaling Method for Calculation of Electron Affinities”, *J. Chem. Theory Comput.* **10**, 1923 (2014).
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7. **H. Pathak**, B K Sahoo, T. Sengupta, B. P. Das, N. Vaval and S. Pal, “A relativistic equation-of-motion coupled- cluster investigation of the trends of single and double ionization potentials in the He and Be isoelectronic systems”, *J. Phys. B: At. Mol. Opt. Phys.* **48**, 115009 (2015).
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13. S. Sasmal, **H. Pathak**, M. K. Nayak, N. Vaval, and S. Pal, “Relativistic coupled-cluster study of RaF as a candidate for parity and time reversal violating interaction”, (under revision Phys. Rev. A).

Chapter 1

General introduction and the scope of the thesis

The questions, why it is so important to consider the effects of relativity in a many-body calculation, what are the various choices to incorporate relativistic effects at different levels of the theory, and how it can be done is being addressed in subsequent sections of the chapter. Concise description of a few of the electron correlation methods, those are very popular in the non-relativistic domain, and can be a potential method in the relativistic framework are explained in brief. Why we have opted for the equation-of-motion coupled cluster method over the other available correlation methods, and what has been done previously in the relativistic equation-of-motion coupled cluster domain, have been addressed.

1.1 Introduction

The accurate calculations of spectroscopic properties of heavy atomic and molecular systems are challenging since it requires simultaneous incorporation of both the effects of relativity and electron correlation as there is a strong intricate coupling between these two effects [1, 2]. However, recent advances in the high-performance computing techniques and with the extension of the several well established non-relativistic theories to the relativistic domain, such calculations are no longer invincible. The studies of parity nonconservation (PNC) and permanent electric dipole moments (EDMs) due to the violation of parity and time-reversal symmetries demand the development of a highly sophisticated relativistic many-body method [3, 4].

The wavefunction constructed using a non-relativistic theory is not adequate for the accurate description of the energy spectrum of highly charged ions [1] those are of immense interest in diverse areas of physics, starting from x-ray space astronomy, plasma physics and laser physics [5, 6]. Therefore, a relativistic description is imperative in such cases. On the other hand, consideration of the effects of relaxation along with the electron correlation effects is essential for explaining multiple ionization processes precisely. Therefore, calculations based on the lower order many-body theories are not reliable enough and may not be able to complement to describe the quality of results that are anticipated from the sophisticated experiments [7].

The electronically excited molecules or atoms relax through various radiationless mechanisms by emitting electrons. The precise values of the ionization potentials (IPs) and double-ionization potentials (DIPs) are important to analyze these relaxation processes and to understand the excited states of the emitter [8]. Therefore, relativistic calculations are essential for the spectral properties of heavy atomic and molecular systems as well as for highly stripped ions. It is therefore desirable to have a theory which can simultaneously treat the electron correlation and the effects of relativity on equal footing due to their non-additive nature.

1.2 The Relativistic Hamiltonian

The relativistic effects play an important role in the determination of the electronic structure of heavy atomic and molecular systems. The effect is more profound towards the core orbitals and

practically important for all the elements. The effects of relativity are incorporated in the electronic structure calculations by the choice of the Hamiltonian.

The relativistic effects are introduced in the quantum theory by the Dirac equation, which is of the form for a single electron in the vicinity of a potential V_N ,

$$\hat{H}_D \Psi = E \Psi \quad (1.1)$$

here

$$\hat{H}_D = \beta mc^2 + c \boldsymbol{\alpha} \cdot \mathbf{p} + V_N \quad (1.2)$$

The $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are defined in such a way that they follow anticommutation relationship with each other. This can be achieved by expressing them in terms of 4×4 matrices.

$$\boldsymbol{\alpha} = \begin{pmatrix} 0_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0_2 \end{pmatrix} \quad \beta = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix} \quad (1.3)$$

with the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ defined as

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.4)$$

Therefore, the wavefunction must be a 4×1 vector which is the consequence of the above discussion. It is usually represented in a group of two two-component wavefunction as

$$\Psi = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} \quad (1.5)$$

where, Ψ^L and Ψ^S are the large and the small component of the wavefunction. The Dirac equation with an attractive potential V_N has both positive energy and negative energy solutions. The continuum states exist above mc^2 and below $-mc^2$, and is graphically presented in Fig. 1.1. The presence of the negative energy solution is interpreted as the positronic spectrum of the Dirac Hamiltonian. The Dirac equation is usually scaled by subtracting free electron rest mass energy as

$$\begin{pmatrix} V_N & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & V_N - 2mc^2 \end{pmatrix} \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = E \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} \quad (1.6)$$

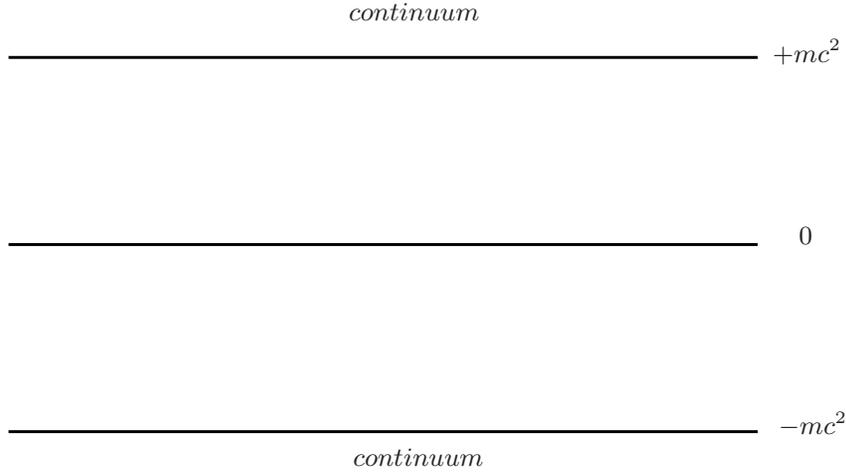


Figure 1.1: The positive and negative energy solution.

The effects of relativity have greater influence on the one-electron part of the interactions. However, the two-electron interactions are also changed by relativity though the effect is small as compared to the one-electron part. There are two kinds of two-body interactions possible to the lowest order approximation; Coulomb and the Breit interaction. The Coulomb part is the dominant one and its expression is same as that in the non-relativistic theory.

$$V(r_{jl}) = V_C(r_{jl}) + V_B(r_{jl}) \quad (1.7)$$

where

$$V_C(r_{jl}) = \frac{1}{|r_{jl}|}, \quad \text{and} \quad V_B(r_{jl}) = -\frac{1}{2|r_{jl}|} \left(\alpha_j \cdot \alpha_l + \frac{(\alpha_j \cdot \mathbf{r}_{jl})(\alpha_l \cdot \mathbf{r}_{jl})}{|r_{jl}|^2} \right). \quad (1.8)$$

with $r_{jl} = r_j - r_l$. The Breit interaction has two parts; unretarded part and the retarded part. The major part of the Breit interaction can be taken care with the inclusion of the unretarded part, which is known as the Gaunt interaction.

$$G_{jl} = -\frac{\alpha_j \cdot \alpha_l}{|r_{jl}|} \quad (1.9)$$

The consideration of Dirac-Coulomb Hamiltonian is most common in the relativistic electronic structure calculations using four-component wavefunction, where two-body Coulomb interaction

operator is added to the Dirac Hamiltonian (\hat{H}_D). Although, the form of the Coulomb operator is same as in the non-relativistic theory, however, the physical content is different as it takes care of the spin-same orbit interaction. This type of truncation in the two-body interaction does not effect much for most of the chemical purposes [9]. However, for very accurate studies of molecular spectra including fine structure, the inclusion of spin-other-orbit interaction and spin-spin interaction are required, which can be done with the full inclusion of the Breit part. The Gaunt term can take care of the spin-other-orbit interaction, whereas inclusion of the retarded part of the Breit interaction is necessary for the spin-spin interaction [10].

The first relativistic calculations using four-component wavefunction in a finite basis set [11, 12] were unsuccessful since the coupling between the large component and small component was not considered [13, 14]. It can be done with the imposition of the kinetic balance condition [15].

$$\lim_{c \rightarrow \infty} \Psi^S = \frac{1}{2mc} (\sigma \cdot p) \Psi^L \quad (1.10)$$

However, this limit is only works for $|E^+ - V| \ll 2mc^2$, and a non-singular nuclear potential. This singularity in the nuclear potential can be avoided by considering a finite charge distribution of the nucleus. A further motivation for the consideration of a finite size nuclear model over the point charge nucleus is that the electronic wavefunction becomes singular at the nucleus for a point nucleus.

The imposition of kinetic balance condition leads to the transformation of the Dirac equation as [16, 17],

$$\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & \frac{1}{2mc} (\sigma \cdot p) \end{pmatrix} \begin{pmatrix} \Psi^L \\ \Phi^L \end{pmatrix} \quad (1.11)$$

where Φ^L is the pseudo-large component and the final equation become [18]

$$\begin{pmatrix} V_N & T \\ T & W_0 - T \end{pmatrix} \begin{pmatrix} \Psi^L \\ \Phi^L \end{pmatrix} = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & \frac{1}{2mc} (\sigma \cdot p) \end{pmatrix} \begin{pmatrix} \Psi^L \\ \Phi^L \end{pmatrix} E \quad ; \quad (1.12)$$

$$T = \frac{p^2}{2m}; \quad W_0 = \frac{1}{4m^2c^2} (\sigma \cdot p) V_N (\sigma \cdot p) \quad (1.13)$$

The term W_0 in the above equation is not a 2×2 diagonal matrix. Therefore, this term is responsible for the spin-dependence. It is interesting to note that W_0 can be separated into two parts, spin

dependent and independent using Dirac identity relation

$$(\sigma \cdot p)V_N(\sigma \cdot p) = pV_N \cdot p + i\sigma \cdot (pV_N \times p). \quad (1.14)$$

If the second term of the above equation is discarded, then it will lead to the spin-free form of the Dirac equation. However, this can further be introduced after the self-consistent field (SCF) part of the calculation. An interesting point to note that in the modified equation speed of light remain as an inverse power contrary to the parent equation, which allows to achieve the non-relativistic limit without blowing up the operator.

The relativistic calculations using four-component wavefunction are very expensive from the computational perspective. A lot of effort has been made to simplify the equations. The calculation of the small component of the wavefunction is the most challenging part of the computation. If a basis set is expressed in terms of contracted Gaussian functions, then the number of required primitive Gaussian functions for the small component is about twice the number of the large component with the imposition of the kinetic balance condition. On the other hand, the small component has a very minor contribution in the calculated values, therefore, it makes sense to look for an approximation. There are a number of one-electron Hamiltonians in between the scalar non-relativistic and four-component relativistic ones. However, the inclusion of the spin-orbit interaction requires at least a two-component description, though it will essentially increase the computational cost due to the appearance of complex algebra in place of real algebra. Nevertheless, the generation of a two-component Hamiltonian from the parent four-component Hamiltonian is the most preferred choice for the purpose which includes the spin-orbit interaction with a lesser cost as compared to the four-component Hamiltonian. The central idea behind the generation of a two-component Hamiltonian is that it should reproduce the positive-energy spectrum of the parent Hamiltonian. Foldy and Wouthuysen [19] proposed an idea to decouple the large and small component by a unitary transformation of the four-component Hamiltonian,

$$\hat{h}_{bd} = U^\dagger \begin{pmatrix} \hat{h}_{LL} & \hat{h}_{LS} \\ \hat{h}_{SL} & \hat{h}_{SS} \end{pmatrix} U = \begin{pmatrix} \hat{h}_{++} & 0 \\ 0 & \hat{h}_{--} \end{pmatrix} \quad (1.15)$$

Another well known approach is the elimination of the small component from the wavefunction. However, these two approaches are equivalent [20].

There are various choices to perform the reduction from a four-component to a two-component approach like Douglas-Kroll-Hess (DKH) method [21, 22], the normalized Elimination of the small component (NESC) [23], the infinite-order two-component (IOTC) method [24, 25], and the exact two-component approach (X2C) [26]. The detailed description of the various two-component methods can be found in [27]. Therefore, computational cost can be reduced by transforming the Hamiltonian from four-component to a two-component form. However, care must be taken while calculating the observable. The same unitary transformation matrix has to be used to transform the property operator

$$\Omega_{2c} = [\hat{U}^\dagger \Omega_{4c} \hat{U}]_{++}, \quad (1.16)$$

Otherwise, it will incorporate a significant amount of error if the approximate relation is used,

$$\Omega_{2c} \approx [\Omega_{4c}]_{LL}, \quad (1.17)$$

and this is known as the picture change error (PCE). The PCE is large in the vicinity of nuclei, however, it has little effect for the valence electrons [28–30]. Therefore, a two-component approach can be used for the relativistic calculations without losing much accuracy with a lesser computational cost for the valence spectra.

Within the Born-Oppenheimer approximation, all the relativistic Hamiltonian can be represented as

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_N \quad (1.18)$$

where \hat{h} and \hat{g} are the one-electron and two-electron operator, respectively. Therefore, it is possible to apply various non-relativistic methods available in the market to the relativistic domain, though it requires possible adaptations.

1.3 The Dirac-Hartree-Fock method

Due to the presence of two-body term in the Hamiltonian, it is not possible to have an exact solution. Therefore, an approximate method is required, which can be done by averaging out the

two-body electron-electron interaction by a one-body potential term. This assumption is known as independent particle approximation in the literature of many-body theory.

The relativistic Hamiltonian including the two-body interactions is given by

$$\hat{H} = \sum_j [c\alpha \cdot p_j + (\beta - 1_4)c^2 + V_N(r_j)] + \sum_{j<l} V(r_{jl}) \quad (1.19)$$

To generate the single particle orbitals, the relativistic Hartree-Fock (Dirac-Fock (DF)) Hamiltonian is represented as

$$\begin{aligned} H_{DF} &= \sum_j [c\alpha \cdot p_j + (\beta - 1_4)c^2 + V_N(r_j) + U(r_j)] \\ &= \sum_j h_0(r_j) \end{aligned} \quad (1.20)$$

where h_0 is the single particle Fock operator.

The residual interaction is given by

$$V_{es} = \sum_{j<l} V(r_{jl}) - \sum_j U(r_j) \quad (1.21)$$

The self-consistent solution of the following equation obtain the single particle orbitals

$$h_0(r_j)|\phi_j\rangle = (f(r_j) + U(r_j))|\phi_j\rangle = \epsilon_j|\phi_j\rangle, \quad (1.22)$$

where

$$f_j = c\alpha \cdot p_j + (\beta - 1_4)c^2 + V_N(r_j) \quad (1.23)$$

and the DF potential, $U|\phi_j\rangle$ is

$$U|\phi_j\rangle = \sum_{a=1}^{occ} \langle \phi_a | \frac{1}{r_{ja}} | \phi_a \rangle |\phi_j\rangle - \langle \phi_a | \frac{1}{r_{aj}} | \phi_j \rangle |\phi_a\rangle \quad (1.24)$$

The residual interaction, V_{es} can be incorporated by the correlation treatment.

1.4 Correlation energy and correlation methods

The major part of the exact ground state energy of atoms and molecules is recovered by the Dirac-Hartree-Fock (DHF) treatment. The DHF method is the best suited method for the treatment

of effect of relativity using a single Slater determinantal wavefunction. The energy difference between the DHF energy and the exact energy of a state in the limit of basis set tending towards the completeness is defined as the correlation energy of the state [31]. The difference arises since the DHF method is an effective one-particle method and cannot fully account for the instantaneous repulsion between the electrons. In order to understand optical and chemical properties of atoms and molecules the treatment electron correlation is necessary. There are various methods known for the treatment of electron correlation. These methods are either variational or based on the treatment of perturbation or it can neither be variational nor perturbative or even both. In the next section a concise description of a few of the most known correlation methods are briefly explained.

1.5 The configuration interaction method

The configuration interaction (CI) method [31–33] is known to be most simplest among the correlation methods. The CI wavefunction (Ψ) is expanded in terms of the excited determinants generally with respect to the SCF determinant (Φ_0) as expressed below,

$$\Psi = \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{j<i \\ b<a}} C_{ij}^{ab} \Phi_{ij}^{ab} + \dots \quad (1.25)$$

Here, $i, j(a, b)$ represents occupied (virtual) orbitals in reference determinant (Φ_0) and Φ_i^a and Φ_{ij}^{ab} are the singly and doubly excited determinants. The linear variation method is employed to determine the expansion coefficients ($C_{i,\dots}^{a,\dots}$). The linear variation method in the determination of expansion coefficients results in eigenvalue problem which is equivalent to the diagonalization of the Hamiltonian matrix in the determinantal space. The Slater-Condon rules are applied to evaluate the matrix elements of the Hamiltonian between any two states. It is worth to note that if all possible determinants for a given basis are included, then the method is referred as Full-CI method. The lowest eigenvalue of the full-CI Hamiltonian matrix corresponds to the ground state while rest represents all other excited states. However, in practical situation in a reasonable basis inclusion of all possible determinants are not feasible. Therefore, some kind of truncation scheme is followed. However, any truncation poorly represents the excited states. The most common truncation scheme is to restrict excited determinants up to single and double excitation (CISD) with respect to the reference determinant. This is the best truncation scheme in terms of accuracy

due to the fact that the electronic Hamiltonian is two-body in nature. The CISD scheme is best suited to the states where reference determinant is dominant in the expansion of many-electron wavefunction and the calculated correlation energy is quite accurate. The truncated CI method is incapable of fulfilling two important criteria of an approximate many-body method, namely, size consistency and the size extensivity [34–36]. The size consistency deals with the proper description of the energy at the dissociation limit, whereas extensivity is associated with the scaling of energy with respect to the size of the system.

1.6 Many-body perturbation theory

The perturbation theory is an alternative choice to incorporate the effect of electron correlation [37–41]. In this approach, the exact Hamiltonian (\hat{H}) is partitioned into two parts known as the zeroth order Hamiltonian (\hat{H}_0) and the perturbation (\hat{H}').

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (1.26)$$

The perturbation matrix elements, $\langle \Phi_I | H' | \Phi_J \rangle$ and the stationary states $\{\Phi_I\}$, and energies $\{E_I\}$, of the zeroth-order Hamiltonian are assumed to be known. Therefore, the stationary states and energies of the exact Hamiltonian are expressed in terms of these known quantities with the assumption that there is a one-to-one correspondence between the stationary states and the energies of the (\hat{H}_0) and (\hat{H}). A parameter, λ which varies between 0 to 1 and connects the eigenvalues and eigenvectors of zeroth-order Hamiltonian (H_0) and the exact Hamiltonian (\hat{H}). In perturbation theory a Taylor series expansion of these quantities is done at the limit of $\lambda = 0$. It is further assumed that the zeroth-order Hamiltonian (H_0) is very close to the \hat{H} which makes the perturbation very small. This will make the Taylor series to a convergent one. In practice such criteria can only be followed in the calculation of the ground state of the closed-shell systems.

The difference between the exact ground state energy, ϵ_0 and zeroth-ordered ground state can be written as

$$\epsilon_0 - E_0 = \Delta\epsilon_0 = \langle \Phi_0 | \hat{H}' | \Psi_0 \rangle, \quad (1.27)$$

where intermediate normalization between the zeroth-order ground state and the corresponding exact state is assumed.

In perturbation theory, $\Delta\epsilon_0$ and Ψ_0 can be expressed as

$$\Delta\epsilon_0 = \Delta\epsilon_0^{(1)} + \Delta\epsilon_0^{(2)} + \Delta\epsilon_0^{(3)} + \cdots + \Delta\epsilon_0^{(n)} \quad (1.28)$$

$$\Psi_0 = \Phi_0 + \Psi_0^{(1)} + \Psi_0^{(2)} + \Psi_0^{(3)} + \cdots + \Psi_0^{(n)} \quad (1.29)$$

$$\Delta\epsilon_0^{(n)} = \langle \Phi_0 | \hat{H}' | \Psi_0^{(n-1)} \rangle \quad (1.30)$$

Here, $\Delta\epsilon_0^{(n)}$ and $\Psi_0^{(n)}$ are n^{th} order correction to the energy and wavefunction for the ground state. The explicit expressions for $\Delta\epsilon_0^{(n)}$ and $\Psi_0^{(n)}$ differs in different variants of the perturbation theory, but the basic idea always remains the same. The problem with the perturbation theory is its slow converging nature. It is therefore necessary to include higher order terms, but such inclusion of higher terms through the conventional techniques is challenging due to the rapid escalation in the number of terms. However, diagrammatic technique allows partial summation to alleviate the problem and diagrams contributing to different perturbation order can be summed to infinite order. This technique provides much accurate correlation energy than the order-by-order summation, which eventually leads to the coupled cluster theory.

1.7 The coupled cluster theory

The coupled cluster (CC) method is known to be the most popular and elegant approach to construct the correlated wavefunctions. The concept of CC theory was first introduced by Cöester and Kümmel to deal with the problems in the area of nuclear physics [42, 43]. However, the pair correlation theory of Sinanoğlu [44, 45] and Nesbet [46] laid the foundation of CC method in the electronic structure theory. The exact ground state wavefunction can be represented in an exponential form for a many-electron system and it was shown by Hubbard [47] by applying the concept of diagrammatic techniques of many-body perturbation theory. Cizek and Paldus [48–51] are the pioneer in introducing the CC theory to address quantum chemical problems.

The ground state wavefunction in the CC method is defined as

$$|\Psi_0\rangle = e^T |\Phi_0\rangle. \quad (1.31)$$

here, Φ_0 is the reference wavefunction, which is generally but not necessarily the Hartree-Fock (DHF) determinant. The exponential structure of the CC operator takes care of the dynamic part of the electron correlation. T is the cluster operator and it is of the form in terms of second quantization representation,

$$T = T_1 + T_2 + \dots = \sum_n^N T_n. \quad (1.32)$$

with

$$T_n = \sum_{\substack{a_1 < a_2 \dots < a_n \\ i_1 < i_2 \dots < i_n}}^M t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} a_1^\dagger i_1 a_2^\dagger i_2 \dots a_n^\dagger i_n, \quad (1.33)$$

where $i, \dots (a, \dots)$ corresponds to the strings of creation and annihilation operators acting on the reference determinant of M numbers of occupied electrons and stands for the hole and particle indices, respectively. The n -body cluster operator T_n , produces a linear combination of n -tuply hole-particle excited determinants by acting on the $|\Phi_0\rangle$.

It is interesting to note that the exponential structure of the CC operator makes the method both size consistent as well as extensive which are the two key criteria for an approximate many-body methods. Since, the reference wavefunction is consists of a single determinant, therefore, this method is known as the single-reference coupled cluster (SRCC) method.

The Schrödinger equation with normal ordered Hamiltonian (H_N) is of the following form

$$H_N e^T |\Phi_0\rangle = E_{corr} e^T |\Phi_0\rangle. \quad (1.34)$$

The above equation can be projected onto the Φ_0 and other excited determinants to obtain the correlation energy and the cluster amplitudes.

$$\langle \Phi_0 | H_N e^T | \Phi_0 \rangle = E_{corr} \langle \Phi_0 | e^T | \Phi_0 \rangle \quad (1.35)$$

$$\langle \Phi_{ij\dots}^{ab\dots} | H_N e^T | \Phi_0 \rangle = E_{corr} \langle \Phi_{ij\dots}^{ab\dots} | e^T | \Phi_0 \rangle. \quad (1.36)$$

If we expand the right hand side of the eqn 1.35, the term which does not contain T will only survive due to the imposition of intermediate normalization condition. Therefore, correlation energy will obtain as $\langle \Phi_0 | H_N e^T | \Phi_0 \rangle = E_{corr}$. By applying Wick's theorem and the fact that e^T is normal-ordered the above sets of equations can be represented by diagrammatic techniques. The expression for the correlation energy is represented by closed-connected diagrams in which cluster

operator is being connected to the vertex of the Hamiltonian. There are unlinked terms in both sides of the amplitude equation, however these diagrams exactly cancel to each other. Therefore, the left hand side of the amplitude equation contain only linked open diagrams,

$$\langle \Phi_{ij\dots}^{ab\dots} | H_N e^T | \Phi_0 \rangle_{\text{open, linked}} = 0 \quad (1.37)$$

The disconnected terms of the above equation for a particular hole-particle excitation disappear due to presence of the equation corresponding to lower hole-particle excitations. There are no disconnected terms for the single excitation. However, the product of a connected single excitation term with t_i^a amplitude give rise to disconnected terms for the double excitation which disappears since $\langle \Phi_i^a | H_N e^T | \Phi_0 \rangle_{\text{open, connected}} = 0$. Therefore, the CC equations become fully connected

$$E_{corr} = \langle \Phi_0 | H_N e^T | \Phi_0 \rangle_{\text{closed, connected}} \quad (1.38)$$

$$\langle \Phi_{ij\dots}^{ab\dots} | H_N e^T | \Phi_0 \rangle_{\text{open, connected}} = 0 \quad (1.39)$$

The contraction between the cluster operators is not possible due to their commutation relation. Therefore, the cluster operators can only be connected to the Hamiltonian vertex. The electronic Hamiltonian considers two-electron interaction, therefore, a maximum of four contraction with the cluster operator is feasible and the non-linear coupled equations are at most quadratic in nature.

On the other hand, similarity transformation technique is an alternative approach to get the CC equations since similarity transformation of an eigenvalue equation does not change its eigenvalues. The multiplication of Schrödinger equation from the left with e^{-T} gives the following equation

$$e^{-T} H_N e^T = E_{corr} | \Phi_0 \rangle \quad (1.40)$$

which on projection on to the reference $\langle \Phi_0 |$ and excited determinants $\langle \Phi^* |$ gives the modified equations for the correlation energy as well as the cluster amplitudes,

$$\langle \Phi_0 | e^{-T} H_N e^T | \Phi_0 \rangle = E_{corr}, \quad \langle \Phi^* | e^{-T} H_N e^T | \Phi_0 \rangle = 0 \quad (1.41)$$

The resulting amplitude equation is completely decoupled from the energy equation and the similarity transformed Hamiltonian can be represented as a linear combination of nested commutators

of H_N and T according to Campbell-Baker-Hausdorff (CBH) formula,

$$\begin{aligned}
 e^{-T} H_N e^T &= H_N + [H_N, T] + \frac{1}{2!} [[H_N, T], T] + \frac{1}{3!} [[[H_N, T], T], T] \\
 &+ \frac{1}{4!} [[[[H_N, T], T], T], T]
 \end{aligned}
 \tag{1.42}$$

This is an infinite series, however, depending on the nature of the Hamiltonian the series truncates naturally. For the electron Hamiltonian, only first five terms of the series survive since the second quantization form of the Hamiltonian has two creation and two annihilation operator string and the truncation is independent of the choice of approximation in the cluster operator. The connectedness of the diagrams comes from the commutator structure.

SRCC method [52–54] is very successful for the treatment of the effect of electron correlation in closed-shell systems where a single determinant is sufficient to provide a good zeroth order description. However, in addressing open-shell states a multi-reference zeroth order description becomes essential for the treatment of non-dynamic part of the electron correlation [55–69]. There are three categories of the existing multi-reference theories: (i) Fock space [55, 56] or the valence universal (VU) (ii) Hilbert space or the state universal [63, 65–69] and (iii) state selective methods [64, 70–73]. The valence-universal (VUMRCC) or the Fock-space variant (FSMRCC), is suitable for the computation of spectroscopic quantities those are based on differences in energy between states having same or different number of electrons like ionization potential, electron affinity and excitation energies. On the other hand, the state-universal (SUMRCC) or the Hilbert-space variant (HSMRCC), is suitable for the description of potential energy surfaces.

In this thesis, we are more concerned about the spectroscopic properties like ionization potential, double ionization potential and the electron affinities of both atomic and molecular systems starting from a closed-shell as well as open-shell reference wave function. The equation-of-motion coupled-cluster method in which we are interested have a nice correspondence with the FSMRCC approach. Therefore, a concise description of a few of the variant of FSMRCC method are briefly explained in the further sections.

1.8 The effective Hamiltonian formalism of the FSMRCC theory

In FSMRCC theory an effective Hamiltonian is constructed with the help of the Bloch-Lindgren equation which extracts a few of the roots of interest from the whole eigenspectrum of the Hamiltonian matrix [57–59]. The entire correlation space is divided into two parts: model space and the orthogonal space [74, 75]. The model space is constructed by taking linear combination of suitable active configuration and the choice is based on the energetic criteria. The correlation contribution of the orthogonal space is included with the help of the wave operator which is the tool to construct the effective Hamiltonian. Finally, the effective Hamiltonian matrix is diagonalized in the model space which includes the correlation contribution of the model space and results in the desired eigenspectrum. The model space is chosen in such a way that the linear combination of the determinants can provide a good zeroth order description of the eigenstates which are of interest. The closely lying valence occupied and virtual orbitals are chosen to construct the model space and the idea of the molecular orbital picture is behind for such a selection. The model space configuration is generated by distributing a certain number of electrons in these orbitals. If the model space contains all the configuration generated by distributing the valence electrons in the entire valence orbitals in all possible way, then the constructed model space is complete otherwise is incomplete. It is worth to note that in the case of incomplete model space the equations are modified, but the basic qualitative idea remains unchanged.

In this approach the configuration space is divided into two parts; model space (M) and the orthogonal space (M_{\perp}) and the projection operators of these two mutually orthogonal space are denoted as P_M and Q_M . The effective Hamiltonian approach is diagrammatically represented in the following figure.

The Schrödinger equation for the m^{th} eigenstates is as

$$H_N \Psi_m = \Delta E_m \Psi_m \quad (1.43)$$

where H_N is the normal-ordered Hamiltonian. The projection operator P_M acts on the exact eigenstates and it generates the model wavefunction (Ψ_m^0) which is defined within the model space:

$$P_M \Psi_m = \Psi_m^0 \quad (1.44)$$

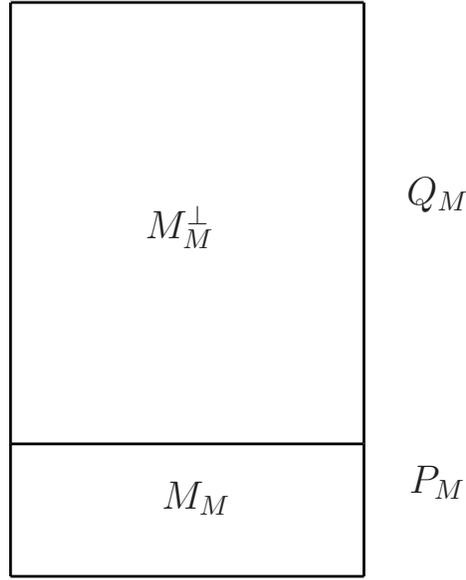


Figure 1.2: Diagrammatic representation of the effective Hamiltonian approach.

The model wavefunction is transformed into the exact eigenstates by the action of the wave operator (Ω) on the model space.

$$\Psi_m = \Omega \Psi_m^0 \quad (1.45)$$

An operator $H_{N,\text{eff}}$ is defined in such a way that it follows the following eigenvalue equation

$$H_{N,\text{eff}} \Psi_m^0 = \Delta E_m \Psi_m^0 \quad (1.46)$$

Therefore, by applying the definition of Ω , P_M , the Bloch-Lindgren equation be obtained as

$$H_N \Omega P_M = \Omega H_{N,\text{eff}} P_M \quad (1.47)$$

Finally, the above equation left projected to the P_M and Q_M determinantal space to obtain the following equations,

$$Q_M (H_N \Omega - \Omega H_{N,\text{eff}}) P_M = 0 \quad (1.48)$$

$$P_M (H_N \Omega - \Omega H_{N,\text{eff}}) P_M = 0 \quad (1.49)$$

The set of equations are coupled to each other and $H_{N,\text{eff}}$ can not be expressed in terms of Ω . However, with the imposition of the intermediate normalization condition, it can be expressed as a function of Ω . Therefore, eq. 1.49 can be expressed as

$$P_M H_N \Omega P_M = P_M H_{N,\text{eff}} P_M \quad (1.50)$$

Finally, the diagonalization of the $H_{N,\text{eff}}$ in the model space results in the desired eigenvalues as

$$H_{N,\text{eff}} C = C E \quad (1.51)$$

$$\tilde{C} H_{N,\text{eff}} = E \tilde{C} \quad (1.52)$$

$$\tilde{C} C = C \tilde{C} = 1 \quad (1.53)$$

here, $C(\tilde{C})$ is the square matrix containing the eigenvectors of the effective Hamiltonian matrix, $H_{N,\text{eff}}$ and E is the diagonal matrix containing the eigenvalues. The wave operator, Ω is defined as

$$\Omega = \{e^{\tilde{S}^{(i,j)}}\} P_M \quad (1.54)$$

in the Fock space MRCC approach, where $\tilde{S}^{(i,j)}$ is of the following form,

$$\tilde{S}^{(i,j)} = \sum_{i=0}^{i=m} \sum_{j=0}^{j=n} S^{(i,j)}. \quad (1.55)$$

However, the problem of intruder states which leads to the failure in convergence [76–78] is associated with a reduced dimension effective Hamiltonian. The intermediate Hamiltonian variant of the FSMRCC (IHFSMRCC) theory [79–81] is a solution to address such problem of intruder. The eigenvalue independent partitioning technique (EIP) of Mukherjee [82] in the Fock-space multi-reference coupled-cluster (EIP-MRCC) framework is also a choice to take care of the intruder state problem. In the next couple of sections, we will briefly describe the IHFSMRCC and the EIP-MRCC approach.

1.9 Intermediate Hamiltonian formalism of the FSMRCC theory

The convergence difficulty is one of the major concern in the effective Hamiltonian based FSMRCC approach. This arises when model space configurations (P_M) are energetically not well

spaced from that of the complementary space (P_Q). The use of intermediate Hamiltonian based approach is a solution to address such a problem. The concept of intermediate Hamiltonian approach was first introduced by Malrieu [79] to handle the problem associated with the degenerate perturbation theory. In this approach, the configuration space is sub-divided into three parts, namely, main, intermediate, and the outer space with the corresponding projection operators P_M , P_I and Q_0 , respectively. The intermediate space behaves as a buffer in between the main space and outer space. The main space is the same as that of the model space of the effective Hamiltonian theory. It is the complementary space which is divided into two parts. However, the obtained roots are identical in both the approaches. The intermediate Hamiltonian approach is graphically presented in Fig. 1.3.

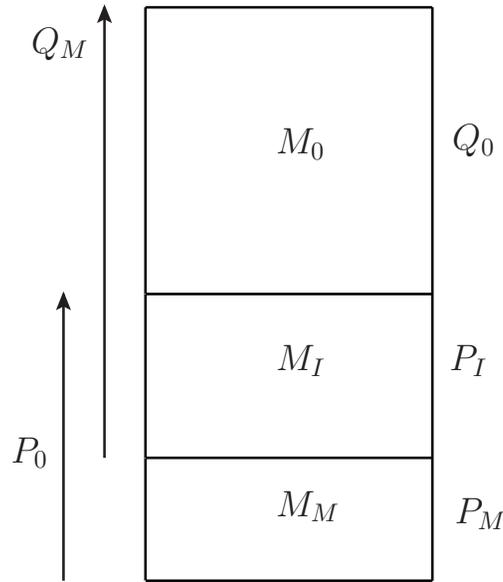


Figure 1.3: Diagrammatic representation of the intermediate Hamiltonian approach.

The final working equation of FSMRCC can be written for the intermediate space as

$$P_I(\bar{H}_N\{e^s\} - \{e^s\}H_{N,\text{eff}})P_M = 0 \quad (1.56)$$

$$H_{N,\text{eff}} = P_M\bar{H}_N\{e^s\}P_M \quad (1.57)$$

An operator X is introduced which is of the form

$$X = \{e^s - 1\}P_M \quad (1.58)$$

and it satisfies

$$X = Q_M X P_M \quad , \quad X^2 = 0 \quad (1.59)$$

The eq. 1.56 and 1.57 can be expressed in terms of X as

$$P_I(1 - X)\bar{H}_N(1 + X)P_M = 0 \quad (1.60)$$

$$P_M(1 - X)\bar{H}_N(1 + X)P_M = H_{N,\text{eff}} \quad (1.61)$$

From the above two equations eq. 1.60 and 1.61 it is evident that the overall process is a two step process: (i) solution of the quadratic equation of X and (ii) is the diagonalization of $H_{N,\text{eff}}$ to obtain the desired roots. The same number of roots can be obtained by diagonalization of the $(1 - X)\bar{H}_N(1 + X)$ in the $P_0 = P_M + P_I$ space if the eq. 1.56 is satisfied. Therefore, the two step process can be replaced by a single process in the following manner.

$$X = Y + Z \quad (1.62)$$

where Y and Z are of the following form

$$Y = Q_0 X P_M \quad , \quad Z = P_I X P_M \quad (1.63)$$

and

$$Q_M = P_I + Q_0 \quad (1.64)$$

Therefore, the operator $(1 - X)\bar{H}_N(1 + X)$ can be expressed as

$$(1 - X)\bar{H}_N(1 + X) = (1 - Z)(1 - Y)\bar{H}_N(1 + Y)(1 + Z) \quad (1.65)$$

It is clear from the definition of X that

$$(1 - X) = (1 + X)^{-1} \quad (1.66)$$

which is also true for the Y and Z . It is clear from above discussion that If eq. 1.60 is satisfied then desired number of roots can be obtained by the diagonalization of $(1 - X)\bar{H}_N(1 + X)$ within $P_0 - P_0$

space since these two operators are interconnected through similarity transformation. Finally, the intermediate Hamiltonian can be defined in the following way

$$H_I = P_0(1 - Y)\bar{H}_N(1 + Y)P_0 \quad (1.67)$$

Since the P_M , P_I , and Q_0 are the projection operators of mutually orthogonal space, therefore, the eq. 1.67 can be finally expressed as

$$H_I = P_0\bar{H}_N(1 + Y)P_0 = P_0\bar{H}_NP_0 + P_0\bar{H}_NY P_M \quad (1.68)$$

This above discussed variant of the intermediate Hamiltonian formulation is proposed by Meissner [80] and several others practiced [83–88]. Kaldor and coworkers [81, 89] also proposed and practiced a variant of intermediate Hamiltonian method.

1.10 The Eigenvalue-independent partitioning technique in Fock-space

The eigenvalue-independent partitioning technique in the multi-reference coupled-cluster (EIP-MRCC) framework is an elegant approach to take care of the problem of intruder state [82, 90–92]. The non-linear FSMRCC equations for a arbitrarily chosen model space are transformed into a set of linear CI-like non hermitian eigenvalue equations. The solution can be obtained by solving one root at a time and the norm of the corresponding eigenvector is preserved in the process. This makes EIP-MRCC free from the problem of intruder and a faster convergence is achieved as compared to the effective Hamiltonian based FSMRCC approach. This approach can be regarded as a specific variant of the intermediate Hamiltonian theory.

Lets say, we are interested in the determination of M_P ($M_P \ll M$) number of roots from the entire set $\{\lambda_i\}$ and the corresponding eigenvectors $\{C_i\}$ of a $M \times M$ non-symmetric matrix H such that the subspace of dimension M_P has a reasonable contribution to the vectors.

The chosen subspace is denoted by the projector P and the complementary space is characterized by the projector Q . The union of the projector P and Q constitutes the entire space. Therefore,

the corresponding eigenproblem can be written as

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} X_{PP} \\ X_{QP} \end{pmatrix} = \begin{pmatrix} X_{PP} \\ X_{QP} \end{pmatrix} (\Lambda_P) \quad (1.69)$$

where Λ_P is a $M_P \times M_P$ diagonal matrix of eigenvalues. The X_{PP} and X_{QP} (dimension $M \times M_P$) are the components of the matrix of vectors \mathbf{C} in the P and Q spaces respectively.

A partitioning-matrix, Σ is introduced, which is defined by

$$\Sigma = X_{QP}X_{PP}^{-1}, \quad (1.70)$$

It is worth to note that the partitioning matrix Σ exists whenever X_{PP} is nonsingular. Therefore, the eq. 1.69 can be written as

$$H_{PP} + H_{PQ}\Sigma = H_{\text{eff}}, \quad (1.71)$$

$$H_{QP} + H_{QQ}\Sigma = \Sigma H_{\text{eff}}, \quad (1.72)$$

where H_{eff} is a $M_P \times M_P$ matrix and is defined as

$$H_{\text{eff}} = X_{PP}\Lambda_P X_{PP}^{-1} \quad (1.73)$$

A set of coupled quadratic equations are obtained from Eq. 1.72 for the elements of Σ , the quadratic term coming from the right-hand side through the expression for H_{eff} from eq. 1.71. Eq. 1.71 gives H_{eff} after Σ is solved from eq. 1.72, which upon diagonalization generates $\{\lambda_i\}$

$$X_{PP}^{-1}H_{\text{eff}}X_{PP} = \Lambda_P \quad (1.74)$$

Therefore, in the process the eq. 1.69 is reduced into eqns. 1.71 and 1.72 and H_{eff} does not have parametric dependence on the eigenvalues $\{\lambda_i\}$. That is why this approach is known as eigenvalue-independent partitioning (EIP) technique. Alternatively, any two sets of equation of the form of eqs. of 1.71 and 1.72 can be cast into a single eigenproblem as in eq. 1.69.

From the above discussion it appears that the multi-reference theories are not straight forward, conceptually difficult and lot of complication is associated with those methods. However, there are methods like method of moment (MMCC) [93] coupled-cluster linear response

theory (CCLRT) [94–98], symmetry-adapted cluster configuration interaction (SAC-CI) [99–101], equation-of-motion coupled cluster method (EOMCC) [102, 103], similarity transformed EOMCC (ST-EOMCC) [104–107] and spin flip EOMCC (SF-EOMCC) [108]. are capable of handling quasi-degenerate situation with a single reference description. Among these methods we have opted for the EOMCC method, which is conceptually very easy to understand and elegant in addressing various electronic structure problem, to extend to the relativistic domain for the accurate calculations of spectroscopic properties.

1.11 Equation of motion coupled cluster method

Monkhorst and coworkers [94, 95] were first to show that excitation energies can be obtained from the poles of the time-dependent form of the coupled cluster response functions. This method is known in the literature as the coupled cluster linear response theory (CCLRT). Mukherjee and coworkers [98, 123, 124] extended the idea to the time-independent form and several other groups [96, 102, 125–127] used for various purposes. Harris [128] introduced a closely related time independent approach and integrate with the concept of equation-of-motion of Rowe [129] to calculate excitation energy. In his approach, the excited state wavefunction is generated by the action of an exponential operator on the coupled cluster ground state wavefunction,

$$|\Psi_\nu\rangle = e^S e^T |\Phi_0\rangle. \quad (1.75)$$

Later, Bartlett and coworkers [130] replaced the exponential operator by a linear CI like operator, R to parametrize the excited state wavefunction.

The EOMCC method [102, 103, 109–120] is a very handy technique since the difference of energy is calculated in a direct manner. A two step procedure is followed in actual practice to solve the EOMCC amplitude equations as ground state amplitudes are decoupled from that of the excited states; (i) solution of the reference wavefunction and (ii) the step engages in the diagonalization of the constructed effective Hamiltonian matrix in the desired Fock-space sector. The idea of diagonalization of the effective Hamiltonian matrix elements is some how associated with the multi-reference theories but EOMCC works within a single reference description to tackle complex wavefunction which is multi-configurational in nature. In principle, the secondary states can also

be obtained as a by-product, which have key role in explaining various photo-ionization spectra. It is worth to note that EOMCC is a size consistent method but the calculated transition energy is extensive only for the principal valence sector whereas the secondary roots are size intensive. We can say that the EOMCC is a configurational interaction (CI) method using coupled-cluster similarity transformed Hamiltonian matrix elements. Therefore, the convergence difficulty is not of concern due to structural resembles with the CI method, which is always an integral part of any multi-root theories.

Another important aspect of EOMCC is that it directly gives the eigenstates in contrast to the propagator based approaches [121, 122] although these methods also have equation-of-motion (EOM) structure. It is worth to note that the transition energies calculated using CCLRT and EOMCC are identical. On the other hand EOMCC/CCLRT produces identical results with the effective Hamiltonian variant of FSMRCC and EIP-MRCC for a single electron attachment or detachment problem. Choudhuri *et. al.* have done extensive work in the relativistic CCLRT framework to calculate ionization potentials and related phenomena for closed-shell atomic systems [131–136]. Symmetry adapted cluster expansion configuration interaction (SAC-CI) [99–101] is a correlation method which is very similar to EOMCC. However, these two methods differ in the description of the ground state wavefunction.

The Schrödinger equation for the reference state and the ν^{th} excited state can be represented as

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (1.76)$$

$$H|\Psi_\nu\rangle = E_\nu|\Psi_\nu\rangle, \quad (1.77)$$

The excited state wavefunction can be described as

$$|\Psi_\nu\rangle = R_\nu|\Psi_0\rangle \quad (1.78)$$

Left multiplication of the Eqn. with R_ν and subtraction from Eqn. will lead to the following expression

$$[H, R_\nu]|\Psi_0\rangle = \Delta E_\nu R_\nu|\Psi_0\rangle \quad (1.79)$$

Here, ΔE_ν is the energy difference between the reference state and the excited states.

With proper definition of the R_ν operator, excited states of electron detached, attached or even excited electron states can be obtained. The reference wavefunction in the EOMCC method is not necessarily the ground state wavefunction but we have chosen coupled-cluster ground state wavefunction as the reference state. The coupled-cluster ground state wavefunction is defined as

$$|\Psi_0\rangle = e^T|\Phi_0\rangle \quad (1.80)$$

The R_ν and T operator commutes among themselves since they are constructed of same quasi-particle creation operator. Therefore, we can represent Eqn. 1.79 as

$$[\bar{H}, R_\nu]|\Phi_0\rangle = \Delta E_\nu R_\nu|\Phi_0\rangle \quad \forall \nu, \quad (1.81)$$

here, $\bar{H} = e^{-T}He^T$ is the effective Hamiltonian. That is why this approach is called EOMCC in analogy to the Heisenberg's equation of motion for the excitation operator R_ν . The above equation is projected onto the set of excited determinants to get the desired energy difference (ΔE_ν). Since \bar{H} is non-Hermitian in nature, therefore, there exists left eigenstates which are not identical to that of the right eigenstates but they form a bi-orthogonal set, $\langle\Phi_0|L_\mu R_\nu|\Phi_0\rangle = \delta_{\mu\nu}$. These eigenstates can be obtained by diagonalizing \bar{H} matrix. Both the left hand solution and the right hand solution leads to same eigenvalues. The right eigenvectors are connected to \bar{H} due to their commutator relationship and left eigenvectors are not necessarily connected. It is worth to note that for the calculation of energy, solution of any of the eigenstates is sufficient. However, left eigenstates are required along with the right eigenstates for the calculation of properties in EOMCC framework or to construct density matrix.

Hirata *et al.* [137], were the first to implement relativistic EOMCC method for the purpose of molecular calculations. They combined different electron correlation methods, basis set, and relativistic treatment to make a composite method. They have considered two-component valence spinors along with a relativistic effective core potential (RECP) which was supplemented by the spin-orbit (SO) interaction. The dynamic part of the electron correlation is taken care by constructing the ground wavefunction at the second order perturbation theory level and employed various basis sets to enable complete basis set extrapolation. The non dynamical correlation is treated using EOMCC method with a small basis set. Finally, the spin-orbit effect is added as the energy difference between the RECP+SO with RECP calculated using a low rank correlated method. This

approach cancels some of the errors associated with the RECP methods. The approach of Hirata *et al.*, is clearly not a rigorous description of the relativistic effects and the treatment of correlation is not comprehensive. We would therefore call Hirata *et al.* treatment as a good compromise of the different many-body effects to get reasonable results. This approach does not address the complex interplay between the relativistic and correlation effects, which motivates us to implement EOMCC method using four-component single particle wavefunction and the Dirac-Coulomb Hamiltonian.

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Chapter 2

Relativistic equation-of-motion coupled-cluster method: Application to closed-shell atomic systems

The chapter deals with the successful implementation of the relativistic equation-of-motion coupled-cluster (EOMCC) method. The implemented method is employed to compute the principal ionization potentials (IPs) of closed-shell rare-gas atoms, He-like ions, Be-like ions, along with Na^+ , Al^+ , K^+ , Be, and Mg. Four-component Dirac spinors are used in the calculations, and the one- and two-electron integrals are evaluated using the Dirac-Coulomb Hamiltonian. The computed results of our calculations are in excellent agreement with available measurements, which are taken from the National Institute of Science and Technology database. The accuracies of the calculations are estimated to be within one half of a percent for He-like and Be-like ions and 1% for the heavier systems. We also present results using the second-order many-body perturbation theory and random-phase approximation in the EOMCC framework. These results are compared with those of EOMCC at the level of single and double excitations in order to assess the role of the electron correlation effects in the intermediate schemes considered in our calculations.

2.1 Introduction

High precision calculations of the spectroscopic properties of heavy atomic and molecular systems are challenging due to the complex interplay between relativistic and correlation effects [1]. However, with the extension of several well established non relativistic many-body methods to the relativistic regime and the recent advances in high performance computing techniques, such calculations are no longer insurmountable. Studies of atomic parity non-conservation (PNC) and permanent electric dipole moments (EDMs) due to the violation of parity and time reversal symmetries [2, 3], the requirement of very accurate atomic properties for a precise estimate of systematic effects in atomic clock experiments [4–6], the determination of nuclear moments [7], calculations of coefficients that are sensitive to relativistic effects to probe the variation of the fine structure constant [8–10], etc. require the development of powerful relativistic many-body methods. The spectra of multicharged ions are of immense interest in many areas of physics, particularly x-ray space astronomy, plasma physics and laser physics [11, 12]. Accurate values of ionization potentials (IPs), double ionization potentials (DIPs), and excitation energies (EEs), especially from the deep-core orbitals, are required for setting up the probe and its tunability of the ionizing beam in experiments like e - $2e$, e - $3e$, γ - $2e$, double Auger decay, etc. [13, 14].

Among the various wave-function-based methods, the coupled-cluster (CC) theory within the single- and double- excitation (CCSD) approximation is the most elegant way of calculating the energy or energy differences of atoms and molecules in the ground state as well as in the excited states [15]. Green's function and propagator techniques [16, 17] are the two traditional approaches to calculate direct energy differences. In the propagator approaches, the ground and excited states are treated simultaneously, and due to the cancellation of common correlation effects, these approaches provide satisfactory results of these energy differences in a direct manner. In the CC domain, the Fock-space multireference CC (FSMRCC) [18–24], and the equation-of-motion coupled-cluster (EOMCC) method [25–27], are the two most familiar variants for the calculation of direct energy differences. Many nonrelativistic calculations of IPs, and DIPs in both the FSMRCC [28] and EOMCC [29, 30] frameworks are available, but full-fledged relativistic counterparts are far fewer for the former method and there are none for the latter.

Relativistic calculations are necessary for the spectral properties of heavy atoms and molecules

as well as for highly charged heavy ions. It is therefore desirable in such cases to have a theory which can simultaneously treat the electron correlation and the effects of relativity on the same footing as they are non-additive in nature. Kaldor and coworkers were the first to develop a relativistic coupled-cluster theory for this purpose. They applied the relativistic FSMRCC method to atoms as well as molecules [31–34]. The effective Hamiltonian formalism of the FSMRCC theory, based on the Bloch equation, acts within a model space [35, 36]. It uses a common vacuum with respect to which holes and particles are defined. The holes and particles are further classified as active and inactive depending on the requirements of the problem. While an increase in the size of the model space can target more states, it can lead to convergence problems, which is well known in the literature as the intruder-state problem [37, 38]. The EOMCC method is basically single reference in nature and is closely related to the CC linear response theory (CCLRT) [39–41]. Chaudhuri *et al.* applied the relativistic CCLRT to the ionization problem [42]. Hirata *et al.* [43] employed the relativistic EOMCC method using two-component valence spinors along with a relativistic effective core potential (RECP) which was supplemented by the spin-orbit interaction [44]. The approach of Hirata *et al.* is clearly not a rigorous description of the relativistic effects, which can be taken into account by using four-component orbitals and the Dirac-Coulomb Hamiltonian.

In the present chapter, we consider the implementation of EOMCC method in the four component relativistic framework within the single- and double- excitation approximation (EOM-CCSD) to calculate IPs by removing one electron from a closed-shell atomic system. This EOMCC method for the ionization problem is size consistent and is equivalent to the (0,1) sector of the FSMRCC theory [45, 46]. It is capable of providing the principal as well as shake-up IP values. The (0,1) sector FSMRCC theory does not address the shake-up states. Although the EOM-CCSD method is a size-extensive method for the principal valence sector [47, 48], it is not so for the shake-up states. The error due to the size extensivity is reduced due to the presence of the two-hole–one-particle (2h-1p) block. Being an eigenvalue problem, it is not affected by numerical instabilities due to the intruder states, which are very common in the FSMRCC method. Two intermediate calculations are employed to assess the effects of electron correlation. We refer to these as the EOM-MBPT(2) and EOM-RPA methods, which are the second-order many-body perturbation theory [MBPT(2)] and random phase approximation (RPA) in the EOMCC framework. The former uses a first-order

perturbed ground-state wave function which corresponds to the MBPT(2) energy as the ground-state energy, and in the latter, the EOM matrix elements are constructed in the one-hole (1h-0p) space.

The chapter is organized as follows. A brief discussion of the relativistic method used to obtain the single-particle orbitals is presented in Sec. 2.2. This is followed by a description of the EOMCC theory of the ionization problem, and the computational details are presented in Sec. 2.3. In Sec. 2.4, we give our results and discuss them before making our concluding remarks in Sec 2.5.

2.2 Generation of relativistic orbitals

The Dirac-Coulomb (DC) Hamiltonian is given by

$$H = \sum_i \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_{nuc}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \right], \quad (2.1)$$

where $\boldsymbol{\alpha}_i$ and β_i are the usual Dirac matrices, $V_{nuc}(r_i)$ is the nuclear potential and $\frac{1}{r_{ij}} = \frac{1}{|\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_j|}$ is the electron-electron repulsion potential. Subtraction of the identity operator from β means that the energies are scaled with reference to the rest mass energy of the electron. The nuclear potential is evaluated using the Fermi-charge distribution of the nuclear density, which is given by

$$\rho_{nuc}(r) = \frac{\rho_0}{1 + e^{(r-b)/a}} \quad (2.2)$$

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

$$a = 2.3/4(\ln 3) \quad (2.3)$$

$$\text{and } b = \sqrt{\frac{5}{3}r_{rms}^2 - \frac{7}{3}a^2\pi^2} \quad (2.4)$$

with r_{rms} is the root-mean-square radius of the nucleus.

In relativistic quantum mechanics, the four-component single particle electron orbital is given by

$$\phi(r) = \frac{1}{r} \begin{pmatrix} P(r) & \chi_{\kappa,m}(\theta, \phi) \\ iQ(r) & \chi_{-\kappa,m}(\theta, \phi) \end{pmatrix} \quad (2.5)$$

where $P(r)$ and $Q(r)$ are the large and small components of the wave function and the angular functions are given by

$$\chi_{\kappa,m}(\theta, \phi) = \sum_{\sigma=\pm\frac{1}{2}} C(l\sigma j; m - \sigma, \sigma) Y_l^{m-\sigma}(\theta, \phi) \phi_\sigma \quad (2.6)$$

with $C(l\sigma j; m - \sigma, \sigma)$ being the Clebsch-Gordan (Racah) coefficient, $Y_l^{m-\sigma}(\theta, \phi)$ representing the normalized spherical harmonics, ϕ_σ being the Pauli two-component spinors, and the relativistic quantum number $\kappa = -(j + \frac{1}{2})a$ satisfying the condition for the orbital angular momentum $l = j - \frac{a}{2}$, where j is the total angular momentum.

To generate the single-particle orbitals, we use the relativistic Hartree-Fock (Dirac-Fock (DF)) Hamiltonian given by

$$\begin{aligned} H_{DF} &= \sum_j [c \vec{\alpha} \cdot \vec{p}_j + (\beta - 1)c^2 + V_{nuc}(r_j) + U(r_j)] \\ &= \sum_j h_0(r_j) \end{aligned} \quad (2.7)$$

where h_0 is the single-particle Fock operator with the DF potential

$$U|\phi_j\rangle = \sum_{a=1}^{occ} \langle \phi_a | \frac{1}{r_{ja}} | \phi_a \rangle |\phi_j\rangle - \langle \phi_a | \frac{1}{r_{aj}} | \phi_j \rangle |\phi_a\rangle \quad (2.8)$$

for all the occupied orbitals occ and the residual interaction $V_{es} = \sum_{j<l} \frac{1}{r_{jl}} - \sum_j U(r_j)$, which is incorporated through the EOMCC method.

To retain the atomic spherical symmetry property in our calculations, the matrix form of the Coulomb interaction operator using the above single-particle wave function is expressed as

$$\begin{aligned} \langle \phi_a \phi_b | \frac{1}{r_{12}} | \phi_c \phi_d \rangle &= \sum_k \int dr_1 [P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)] \\ &\times \int dr_2 [P_b(r_2)P_d(r_2) + Q_b(r_2)Q_d(r_2)] \\ &\times \frac{r_{<}^k}{r_{>}^{k+1}} \times Ang, \end{aligned} \quad (2.9)$$

with the multipole k determined by $|j_a - j_c| \leq k \leq j_a + j_c$ and $|j_b - j_d| \leq k \leq j_b + j_d$. The angular momentum factor of the above expression is given by

$$\begin{aligned} Ang &= \delta(m_a - m_c, m_d - m_b) \sum_k \Pi^e(\kappa_a, \kappa_c, k) \\ &\times \Pi^e(\kappa_b, \kappa_d, k) d^k(j_c m_c, j_a m_a) d^k(j_b m_b, j_d m_d), \end{aligned} \quad (2.10)$$

where the coefficient $d^k(jm, j'm')$ is defined as

$$d^k(jm, j'm') = (-1)^{m+\frac{1}{2}} \frac{[(2j+1)(2j'+1)]^{\frac{1}{2}}}{(2k+1)} \times C(jk j'; \frac{1}{2}, -\frac{1}{2}) C(jk j'; -m, m') \quad (2.11)$$

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

The DF single-particle orbitals, $|\phi_{n,\kappa}(r)\rangle$ s, with principal quantum number n and angular quantum number κ are initially constructed as linear combination of Gaussian type of orbitals (GTOs) by writing

$$\phi_{n,\kappa}(r) = \frac{1}{r} \sum_{\nu} \begin{pmatrix} C_{n,\kappa}^L N_L f_{\nu}(r) & \chi_{\kappa,m} \\ iC_{n,-\kappa}^S N_S \left(\frac{1}{dr} + \frac{\kappa}{r}\right) f_{\nu}(r) & \chi_{-\kappa,m} \end{pmatrix}, \quad (2.12)$$

where $C_{n,\kappa}$ s are the expansion coefficients, $N_{L(S)}$ is the normalization constant for the large (small) component of the wave function, α_{ν} is a suitably chosen parameter for orbitals of different angular momentum symmetries and $f_{\nu}(r) = r^l e^{-\alpha_{\nu} r^2}$ is a GTO. For the exponents, we use the even-tempering condition $\alpha_{\nu} = \alpha_0 \beta^{\nu-1}$ with two parameters α_0 and β . It can be noticed in the above expression that the large and small components of the wave function satisfy the kinetic balance condition. The orbitals are finally obtained after solving the matrix eigenvalue form of the DF equation by a self-consistent procedure.

2.3 Method of calculation: EOM-CCSD

In the CC method, the ground-state wave function of a closed-shell atomic system is defined as

$$|\Psi_0\rangle = e^T |\Phi_0\rangle, \quad (2.13)$$

where $|\Phi_0\rangle$ is the DF wave function. The excited states are defined as

$$H|\Psi_{\mu}\rangle = E_{\mu}|\Psi_{\mu}\rangle = E_{\mu}R_{\mu}|\Psi_0\rangle \quad (2.14)$$

for a linear excitation operator R_{μ} .

The operators R_{μ} commute with T as they are strings of quasiparticle creation operators (but not necessarily particle conserving). Premultiplying the above equation with the nonsingular operator e^{-T} leads to

$$[\overline{H}, R_{\mu}]|\Phi_0\rangle = \Delta E_{\mu}R_{\mu}|\Phi_0\rangle \quad (2.15)$$

where ΔE_μ is the energy change associated with the ionization process. and $\overline{H} = e^{-T} H e^T - \langle \phi_0 | e^{-T} H e^T | \phi_0 \rangle$ is a non-Hermitian operator. This approach is usually known as EOM method for the excitation operators in analogy to the Heisenberg's equation of motion. In the EOM-MBPT(2) and EOM-RPA approaches, the matrix elements of the effective Hamiltonian \overline{H} are replaced appropriately in the above equation.

In the EOM-CCSD method, the cluster operators are defined as

$$T = T_1 + T_2 = \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{a<b} \sum_{i<j} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j, \quad (2.16)$$

and

$$R_\mu = R_{1\mu} + R_{2\mu} = \sum_i r_i a_i + \sum_{i<j} \sum_a r_{ij}^a a_a^\dagger a_i a_j, \quad (2.17)$$

where indices i, j are used for the occupied and a, b are used for the virtual orbitals.

The matrix elements of the effective Hamiltonian for the present ionization problem are constructed in the (1h-0p) and (2h-1p) space and diagonalized to get the desired roots. The Davidson algorithm [49] has been implemented for the diagonalization of \overline{H} . This is an iterative diagonalization scheme through which eigenvalues and eigenvectors are obtained. It avoids computation, storage and diagonalization of the full matrix. The EOM-CC method can be regarded as the diagonalization of the coupled-cluster similarity-transformed Hamiltonian in configuration space.

2.4 Results and discussion

To test the performance of our newly implemented four-component relativistic EOM-CCSD method, we present numerical results of principal ionization potentials. The calculations are performed for the closed-shell rare-gas atoms (He through Rn), beryllium-like ions (B through Ar and Kr), helium-like ions (Li, Ne, Na, Ar, Kr) along with Na^+ , Al^+ , K^+ , Be and Mg. These calculations are compared with the results obtained using the EOM-MBPT(2) and EOM-RPA approaches to assess the role of electron correlation. All these results are compared with those of the measurements, which are taken from the National Institute of Science and Technology (NIST) database [50], where many are measured values and a few are the results of calculations based on different theoretical approaches.

Table 2.1: The α_0 and β parameters of the even-tempered basis used in calculations.

Atom	<i>s</i>		<i>p</i>		<i>d</i>		<i>f</i>		<i>g</i>	
	α_0	β								
He	0.00075	2.075	0.00155	2.080	0.00258	2.180	0.00560	2.300	0.00765	2.450
Li	0.00750	2.075	0.00755	2.070	0.00758	2.580	0.00760	2.600	0.00765	2.650
Be	0.00500	2.500	0.00615	2.650	0.00505	2.550	0.00500	2.530	0.00480	2.500
Ne	0.00753	2.075	0.00755	2.070	0.00758	2.580	0.00800	2.720	0.00800	2.720
Na	0.00250	2.210	0.00955	2.215	0.00700	2.750	0.00710	2.760	0.00715	2.765
Mg	0.02950	1.630	0.09750	1.815	0.00750	2.710	0.00780	2.730	0.00800	2.750
Ar	0.09850	1.890	0.00720	2.965	0.00700	2.700	0.00700	2.690	0.00700	2.696
K	0.00550	2.250	0.00995	2.155	0.00690	2.550	0.00700	2.600	0.00700	2.600
Kr	0.00020	2.022	0.00720	2.365	0.00700	2.550	0.00700	2.695	0.00700	2.695
Xe	0.00010	2.022	0.00720	2.365	0.00700	2.550	0.00700	2.695	0.00700	2.695
Rn	0.00010	2.280	0.00671	2.980	0.00715	2.720	0.00720	2.710	0.00720	2.695

For the construction of the single-particle orbitals, we have used both even-tempered (ET) and universal-basis (UB) functions depending on the convergence of the results. For Be-like systems, we use UB basis with $\alpha_0 = 0.004$ and $\beta = 2.23$. We have used ET basis for other atomic systems in the calculation of ionization potential. The corresponding α_0 and β parameters for ET basis for different atomic systems are given in Table 2.1. The use of total number of orbitals generated at the SCF level is impractical in the CC calculations; as the contributions from the high-lying orbitals are very small in the present calculations owing to their large energy values, we consider only the orbitals that are significant of the calculations, and they are termed as the active orbitals. In Table 2.2, we present (SCF) energy which is our zeroth energy (E_{DF}^0) and the correlation energies from the MBPT(2) (E_{corr}^2) and CCSD ($E_{\text{corr}}^{\text{CCSD}}$) methods along with the number of active orbitals of different symmetries used in the calculations.

All the Gaussian-type of functions generated at the SCF level are not important for the correlation calculations. To investigate this, we have studied the convergence pattern of ionization potential as a function of basis set through a series of calculations. The Be atom is chosen for the convergence study. We started our calculations with the 91 GTOs and gradually increased them to 145 GTOs. It is found that the IP value of the $2s$ orbital changes by 8×10^{-4} when the number of basis functions increases from 91 to 145. The change is more for the $1s$ orbital and it is found to be 1.89×10^{-2} , which is also in the accuracy range of 0.01%. We have also investigated our results by increasing the number of diffuse s and p functions by decreasing the exponent α_0 . It is observed that the $2s$ ionization-potential value remains almost unchanged with more diffuse s and p functions, whereas maximum change for the $1s$ orbital is found to be 0.0529 eV. The deviation from the NIST value increases when more diffuse s and p functions are included. The inclusion of higher-order relativistic effects becomes relevant for inner-core orbitals. As we are more interested in the valence ionization potential in the present work, an active space of a similar basis set is sufficient to construct the orthogonal space for the inclusion of the correlation effects for all the systems without compromising the desired accuracy. The results are given in Table 2.3.

We present the IP values of the helium like ions in Table 2.4. All the results are sub-1% accurate; the result for Li^+ is the most accurate, and the least accurate is 0.15% for Kr^{34+} . Table 2.4 shows that EOM-MBPT(2) results are always less than those of EOM-CCSD, whereas the

EOM-RPA method over estimates them. Also, the differences in the results between the EOM-MBPT(2) and EOM-CCSD are less than those of EOM-RPA and EOM-CCSD. The reason why the EOM-RPA calculations may be over estimating is that the 2h-1p block, which is the major source of nondynamical correlations, is not taken into account in this approach. The ground-state wave function at the CCSD level is responsible for the major source of the dynamical correlations for which the EOM-MBPT(2) method seems to be a more valid approximation than the EOM-RPA method. This suggests that the nondynamical correlations are also important for the calculations of the excited states. It is worth mentioning that the calculated EOM-CCSD IP results are larger than the NIST [50] values for Ne^{8+} onwards and the deviations are larger in the heavier systems.

In Table 2.5, we give the IP results for the beryllium-like systems. The $2s$ valence IPs of these systems are in excellent agreement with the NIST values. Our results for the $1s$ orbital match reasonably well with the NIST data. We find that the relative average deviation of the IP values of beryllium-like systems ($\sim 0.03\%$) are less than helium like (0.05%) systems with reference to the the NIST data. A relatively larger deviation is found for the highly charged ions, which also increases with an increase in the ionic charge of the atom. The QED effects are non-negligible for the highly charged ions, where the effects of relativity is greater and increases with increase in the ionic charge.

Table 2.2: SCF energy (E_{DF}^0) and correlation energies from the MBPT(2) ($E_{\text{corr}}^{(2)}$) and CCSD ($E_{\text{corr}}^{(\text{ccsd})}$) methods, along with the numbers of active orbitals from various symmetries taken in the calculations for different atoms.

Atom	No. of active orbitals					E_{DF}^0	$E_{\text{corr}}^{(2)}$	$E_{\text{corr}}^{(\text{ccsd})}$
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>			
He	16	14	12	9	7	-2.8618	-0.0365	-0.0415
Li ⁺	15	14	10	9	8	-7.2372	-0.0395	-0.0430
Ne ⁸⁺	16	15	11	9	8	-93.9827	-0.0421	-0.0434
Na ⁹⁺	16	15	13	10	9	-114.4158	-0.0414	-0.0426
Ar ¹⁶⁺	14	11	11	10	8	-314.1995	-0.0409	-0.0417
Kr ³⁴⁺	22	13	11	10	9	-1296.1641	-0.0237	-0.0240
Be	13	11	11	9	8	-14.5758	-0.0742	-0.0924
B ⁺	15	14	10	9	8	-24.2451	-0.0824	-0.1062
C ²⁺	15	13	11	10	9	-36.4251	-0.0924	-0.1215
N ³⁺	15	14	13	10	9	-51.1144	-0.1026	-0.1369
O ⁴⁺	15	14	12	10	9	-68.3143	-0.1089	-0.1487
F ⁵⁺	15	14	13	10	9	-88.0271	-0.1168	-0.1621
Ne ⁶⁺	16	15	13	10	9	-110.2559	-0.1237	-0.1744
Na ⁷⁺	15	14	11	10	9	-135.0042	-0.1266	-0.1829
Mg ⁸⁺	15	14	13	11	9	-162.2763	-0.1352	-0.1966
Al ⁹⁺	15	14	13	10	9	-192.0767	-0.1404	-0.2072
Si ¹⁰⁺	15	14	13	11	9	-224.4105	-0.1461	-0.2177
P ¹¹⁺	15	14	13	11	10	-259.2833	-0.1513	-0.2278
S ¹²⁺	15	14	13	11	10	-296.7011	-0.1561	-0.2374
Cl ¹³⁺	15	14	13	11	9	-336.6703	-0.1606	-0.2466
Ar ¹⁴⁺	15	14	13	11	10	-379.1979	-0.1650	-0.2554
Kr ³²⁺	16	15	14	11	10	-1593.0492	-0.2316	-0.3630
Ne	17	17	13	11	10	-128.6919	-0.3736	-0.3732
Na ⁺	17	15	11	10	9	-161.8958	-0.3691	-0.3715
Mg	20	14	11	10	8	-199.9350	-0.4074	-0.4174
Al ⁺	15	14	13	10	9	-242.1290	-0.3951	-0.4065
Ar	14	11	11	10	8	-528.6657	-0.6513	-0.6640
K ⁺	15	14	12	10	8	-601.3780	-0.6664	-0.6799
Kr	22	13	11	9	8	-2788.8492	-1.5247	-1.4622
Xe	23	13	12	9	7	-7446.8108	-2.1180	-2.0009
Rn	21	13	12	10	9	-23595.8070	-3.7880	-3.4583

Table 2.3: Convergence pattern of ionization potentials of Be atom (in eV) as a function of the active orbitals using the EOM-CCSD method.

No of active orbitals	IP values	
	1s	2s
91(13s,11p,11d,9f,8g)	124.6463	9.3247
100(14s,12p,12d,10f,9g)	124.6565	9.3248
109(15s,13p,13d,11f,10g)	124.6620	9.3249
116(16s,14p,13d,12f,11g)	124.6639	9.3249
118(16s,14p,14d,12f,11g)	124.6639	9.3248
125(17s,15p,15d,12f,12g)	124.6630	9.3249
132 ^a (20s,17p,15d,12f,12g)	124.6991	9.3249
135 ^b (21s,18p,15d,12f,12g)	124.6992	9.3250
141(17s,15p,15d,12f,12g,8h)	124.6632	9.3255
145(17s,15p,15d,12f,12g,10h)	124.6652	9.3255
145 ^b (23s,20p,16d,13f,12g)	124.6992	9.3250

^aThe α_0 for the *s* and *p* orbitals are taken as 0.00050 and 0.000615 respectively.

^bThe α_0 for the *s* and *p* orbitals are taken as 0.00020 and 0.000415 respectively.

Table 2.4: Ionization potentials (IPs) of helium (He) like systems (in eV) using MBPT(2), RPA and CCSD methods in the EOM procedure.

Atom	MBPT(2)	RPA	CCSD	NIST [50]
Li ⁺	75.5517	77.1594	75.6399	75.6400
Ne ⁸⁺	1196.1770	1197.7308	1196.2113	1195.8078
Na ⁹⁺	1465.6073	1467.1611	1465.6401	1465.1344
Ar ¹⁶⁺	4123.5442	4125.1003	4123.5661	4120.6654
Kr ³⁴⁺	17323.3995	17324.9869	17323.4104	17296.4200

Table 2.5: Ionization potentials (IPs) of Be-like systems (in eV) using MBPT(2), RPA and CCSD methods in the EOM procedure.

Ion	MBPT(2)		RPA		CCSD		NIST	[50]
	1s	2s	1s	2s	1s	2s		
B ⁺	218.7753	24.6024	223.7170	25.4690	218.6932	25.1510	217.8827	25.1548
C ²⁺	340.5912	47.1763	345.3340	48.1961	340.5074	47.8838		47.8877
N ³⁺	489.5193	76.6082	494.3701	77.7833	489.3987	77.4732		77.4735
O ⁴⁺	665.8043	112.8779	670.6873	114.2098	665.6751	113.9003		113.8990
F ⁵⁺	869.6607	155.9937	874.4161	157.4809	869.5295	157.1714		157.1631
Ne ⁶⁺	1100.7242	205.9558	1105.5077	207.5972	1100.5835	207.2874	1098.7791	207.2710
Na ⁷⁺	1359.1193	262.7653	1363.9246	264.5608	1358.9780	264.2504	1357.1716	264.1920
Mg ⁸⁺	1644.9936	326.4618	1649.9248	328.4010	1644.8387	328.0902		327.9900
Al ⁹⁺	1958.6549	397.0176	1963.3552	399.1102	1958.5119	398.7986	1955.7950	398.6500
Si ¹⁰⁺	2299.5858	474.4895	2304.3242	476.7141	2299.4367	476.4017	2296.5894	476.1800
P ¹¹⁺	2668.1363	558.8627	2672.8963	561.2228	2667.9846	560.9095	2664.7632	560.6200
S ¹²⁺	3064.3424	650.1586	3069.1229	652.6532	3064.1883	652.3391	3059.9469	651.9600
Cl ¹³⁺	3488.2444	748.3994	3493.0728	751.0246	3488.0867	750.7090		750.2300
Ar ¹⁴⁺	3941.3783	853.6104	3944.8161	856.3589	3941.4781	856.0432	3934.7226	855.4700
Kr ³²⁺	16934.9486	3972.1671	16939.9718	3976.0698	16934.8134	3975.7297	16902.8643	3971.0000

Table 2.6: IPs of noble-gas atoms (in eV) using the MBPT(2), RPA and CCSD methods in the EOM procedure.

Atom	Orbital	MBPT(2)	RPA	CCSD	NIST [50]
He	$1s_{1/2}$	24.4560	26.1086	24.5802	24.5870
Ne	$2p_{3/2}$	21.4439	25.5832	21.4503	21.5642
	$2p_{1/2}$	21.5499	25.7096	21.5560	21.6613
	$2s_{1/2}$	48.5478	54.3474	48.6207	48.4746
Ar	$1s_{1/2}$	872.6377	894.5355	872.3581	
	$3p_{3/2}$	15.8278	18.0023	15.7951	15.7594
	$3p_{1/2}$	16.0152	18.2136	15.9817	15.9369
	$3s_{1/2}$	30.0706	36.3317	30.0656	29.2390
	$2p_{3/2}$	250.1420	261.8999	249.7786	
	$2p_{1/2}$	252.3757	264.2143	252.0114	
Kr	$4p_{3/2}$	14.1339	15.8840	13.9963	13.9996
Xe	$5p_{3/2}$	12.3916	13.7572	12.1294	12.1298
Rn	$6p_{3/2}$	10.8604	11.9900	10.5847	10.7485

The results for the rare-gas atoms are given in Table 2.6. For the Kr, Xe, and Rn atoms, we have calculated only the outer valence IPs. The most accurate EOM-CCSD result we obtain among them is for Xe atom. The $2p_{3/2}$ valence ionization energy for the Ne atom differs from the experimental result by 0.1139 eV. The differences are 0.0357 eV, 0.0033 eV and 0.0004 eV for the Ar, Kr and Xe atoms, respectively, for their valence orbitals. The reason for these differences could be due to the possible double-excitation character of the p orbitals and the difference decreases along the group. The IPs of the EOM-CCSD method predominantly account for contributions from the single excitations and, to some extent, from the double excitations. The discrepancies could be mitigated by the inclusion of the triple excitations in the ground and excited states, which is computationally very expensive for the relativistic calculations, so they are not incorporated in the present implementation. The deviation is 1.54% for the Rn atom, which is expected as higher-order relativistic effects are non-negligible for heavy elements and also because of the finite size of the basis sets.

In Table 2.7, we present the results for Na^+ , Al^+ , K^+ , Be and Mg. The largest deviation is found in the $2p_{3/2}$ state of Na^+ and is about to be 0.33%. This could be due to the possible dominance of the double excitations. In the case of K^+ it is reduces to 0.05% and for Mg it is 0.06%.

Table 2.7: IPs of Na⁺, Al⁺, K⁺, Be and Mg (in eV) using the MBPT(2), RPA and CCSD methods in the EOM procedure.

Atom	Orbital	MBPT(2)	RPA	CCSD	NIST [50]
Na ⁺	2p _{3/2}	47.1177	51.2511	47.1286	47.2863
	2p _{1/2}	47.3000	51.4556	47.3105	47.4557
	2s _{1/2}	79.9745	85.4228	80.0303	80.0741
Al ⁺	1s _{1/2}	1090.5239	1112.3845	1090.3169	
	3s _{1/2}	18.6480	19.1227	18.8248	18.8285
	2p _{3/2}	92.0692	97.8533	91.9647	91.7116
	2p _{1/2}	92.5141	98.3291	92.4092	92.1604
	2s _{1/2}	137.4759	143.6488	137.4202	
K ⁺	1s _{1/2}	1582.3139	1605.2003	1582.0885	
	3p _{3/2}	31.6687	33.9023	31.6434	31.6249
	3p _{1/2}	31.9497	34.2071	31.9232	31.8934
	3s _{1/2}	48.4814	55.1066	48.4795	47.8182
	2p _{3/2}	309.0471	320.6904	308.7081	
Be	2p _{1/2}	311.9336	323.6745	311.5935	
	2s _{1/2}	8.9442	9.6603	9.3247	9.3226
Mg	1s _{1/2}	124.7175	129.7139	124.6463	123.6344
	3s _{1/2}	7.5057	7.9519	7.6508	7.6462
	2p _{3/2}	58.3976	64.1697	58.2235	57.5603
	2p _{1/2}	58.6898	64.4875	58.5154	57.7983
	2s _{1/2}	98.3383	104.1001	98.2824	

In order to quantify the errors in our calculations, we take into account the close agreement of our EOM-MBPT(2) and EOM-CCSD results, the convergence obtained using the basis sets in our calculations and the omitted higher-order relativistic and correlation effects. We estimate the uncertainties in the results of the He-like ions reported in Table 2.4 to be below one half of a percent based on the above-mentioned factors. It has been found recently that the dominant contributions to the IPs of the Be-like ions given in Table 2.5 come from electron correlation effects at the DC level, which have been taken into account in this work to all orders via the EOM-CCSD method, and contributions from the QED effects are reported to be below one half of a percent [51]. We therefore assign a conservative uncertainty estimate of 0.5% to the IPs of the He-like systems that we have calculated. Unlike the highly charged ions, correlations effects play a dominant role in the evaluations of the atomic properties of the neutral and singly charged atomic systems. Our EOM-CCSD method is capable of accounting for the correlation effects very accurately for light

and medium-size atoms and ions, but triple and other higher order excitations could become non-negligible as the system gets heavier. It would therefore be reasonable to estimate the errors in these calculations for such systems to be within one percent.

2.5 Conclusion

The present work describes the four-component relativistic implementation of the equation-of-motion coupled-cluster method at the level of single and double excitations for the ionization problem in closed-shell atomic systems. To test the reliability of this method, we have computed the ionization potentials of atomic systems from different groups in the periodic table. The calculations are performed using EOM-MBPT(2) and EOM-RPA in addition to EOM-CCSD to understand the role of electron correlation at all three levels of approximation. The second-order many-body perturbation method is found to underestimate the results, while the random-phase approximation overestimates them. The EOM-CCSD results are in excellent agreement with the NIST data wherever available, and we estimate the errors to be within one half of a percent and 1% for the light and heavy systems, respectively.

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Chapter 3

Relativistic equation-of-motion coupled-cluster method for the double-ionization potentials of closed-shell atoms

We report the implementation of the relativistic equation-of-motion coupled-cluster method to calculate the double-ionization spectra (DI-EOMCC) of the closed-shell atomic systems. This method is employed to calculate the principal valence double-ionization potential values of He and alkaline-earth-metal (Be, Mg, Ca, Sr, and Ba) atoms. Our results are compared with the results available from the NIST database and other ab initio calculations. We have achieved an accuracy of $\sim 0.1\%$, which is an improvement over the first-principles T-matrix calculations [Y. Noguchi et al., *J. Chem. Phys.* **123**, 144112 (2005)]. We also present results using the second-order many-body perturbation theory and the random-phase approximation in the equation-of-motion framework, and these results are compared with the DI-EOMCC results.

3.1 Introduction

Recent advances in the experimental techniques, such as the x-ray free-electron laser of Linac Coherent Light sources of SLAC [1, 2] and attosecond pulses [3, 4], have enabled studies of multi-ionization processes. The double photo-ionization of atoms in which two electrons are ejected to continuum orbitals is a three-body quantal problem.

The complex interplay between the relativistic effects and the electron correlation is of central importance in the accurate description of these processes [5]. The generation of attosecond pulses is an important milestone in the development of ultrafast laser spectroscopy. It can be used to study the dynamics of correlated electrons in double ionization processes in atoms and molecules [6, 7]. One of the outstanding theoretical problems in these studies is to explain the simultaneous double-ionization mechanisms [8], which are different than the sequential ionization events. There has been experimental progress in the direction of attosecond tracing of the correlated electron emissions in the nonsequential double-ionization processes in atomic systems which requires a suitable theory that could describe the effects of the dynamical electron corrections adequately [9]. To complement the sophisticated experimental techniques, it is desirable to have accurate theoretical methods to treat the double-ionization continua.

Attempts have been made using the T -matrix [10, 11], Δ self-consistent-field [12], and the four-component two-particle propagator methods [13, 14]. It is well known that not only the electron correlation, but also the relaxation effects play a significant role in the accurate description of atomic states. Therefore measurements and calculations based on the lower-order many-body methods do not agree with each other [15].

The equation-of-motion coupled-cluster (EOMCC) method [16–29] provides a balanced treatment of the electron correlation and relaxation effects to determine the atomic states and to also calculate differences of the energies in a direct manner. It uses a large configurational space constructed from the occupied and virtual spinors that takes into account both the static and dynamic correlations simultaneously. The wave functions and energies of all the states of interest are obtained through the diagonalization of a similarity-transformed Hamiltonian, which in a sense is associated with the multireference theory, but the EOMCC is operationally single reference in nature. The (0,1) sector Fock space multireference (FSMRCC) [30–41] theory is equivalent to the

EOMCC method for the single-ionization problem [42], but this is not the case for the (0,2) sector FSMRCC and the double-ionization EOMCC (DI-EOMCC) methods. The FSMRCC theory uses the amplitude equations of all the lower sectors along with the amplitudes of that particular sector, whereas EOMCC requires the amplitudes of the sector of interest and those of the (0,0) sector.

The electronically excited molecules or atoms relax through various radiationless mechanisms by emitting electrons. The precise values of the ionization potentials (IPs) and double-ionization potentials (DIPs) are important to analyze these relaxation processes and to understand the excited states of the emitter [43]. Furthermore, these processes play significant roles in designing efficient radio oncology schemes, which can be used as powerful tools to investigate the genotoxic effects on living tissues [44]. Bartlett and co-workers were the first to implement the EOMCC method to calculate DIPs [45]; however, their work was in the nonrelativistic regime. Recently, we have implemented the relativistic EOMCC method and used it to calculate IPs of various atomic systems [46]. In this work, we extend the idea of single electron ionization using the relativistic EOMCC method to the domain of the double-ionization spectra by considering simultaneous removal of two electrons from the closed-shell atomic systems.

To the best of our knowledge, no prior numerical results are available for the double ionization spectra of atomic systems using any variant of the relativistic coupled cluster theory. Development of the relativistic DI-EOMCC method is a step forward as it can be used for studying various photoionization spectra, highly energetic electron scattering processes, and various electronic decay processes, especially the Auger spectra in the atomic systems. The alkaline-earth-metal atoms are well suited for studying the double-ionization spectra, as the outer valence electrons are well separated from the rest of the electrons. The He atom is also similar to these atoms, though they have different radial structures of the ns orbitals. As a first application of our relativistic DI-EOMCC method, we have calculated the valence DIPs of He, Be, Mg, Ca, Sr, and Ba atoms. The computed results are compared with the values from the NIST database and with the available calculations based on the first-principles T -matrix approach [11]. We would also like to mention that, though we have calculated valence DIPs of the closed-shell atoms, the implemented DI-EOMCC method is applicable to both closed-shell and open-shell atomic and molecular systems having any number of valence electrons.



Figure 3.1: Diagrammatic form of the R_2 , R_3 operators. The circled arrow is just to represent a detached occupied orbital.

We also present results using two intermediate schemes at the second-order many-body perturbation theory [MBPT(2)] and the random-phase approximation (RPA) level in the EOMCC framework to assess the roles of the electron correlation effects. The former uses first-order perturbed wave function, which corresponds to MBPT(2) energy as the ground state energy. For the latter, the effective Hamiltonian matrix elements are constructed only in the two hole (2h) space. It is clear that in both these approaches, the electron correlation effects are not treated as comprehensively as they are in the four-component all-electron DI-EOMCC approach.

The chapter is organized as follows. A brief discussion of the EOMCC method for the double-ionization potential is described in Sec. 3.2 and the details of the computation consideration are given in Sec. 3.3. We have presented our results and discuss them in Sec. 3.4 before final remark in Sec. 3.5.

3.2 Theory

The starting point for the EOMCC calculations is the single reference CC wave function $|\Psi_0\rangle$, which is of the form

$$|\Psi_0\rangle = e^{\hat{T}_n} |\Phi_0\rangle, \quad (3.1)$$

where $|\Phi_0\rangle$ is the Dirac-Hartree-Fock (DF) reference determinant and the cluster operators are of the form

$$\hat{T}_n = \sum_{\substack{a_1 < a_2 \dots < a_n \\ i_1 < i_2 \dots < i_n}}^M t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} a_1^+ i_1 a_2^+ i_2 \dots a_n^+ i_n, \quad (3.2)$$

where $i, \dots (a, \dots)$ corresponds to the strings of creation and annihilation operators acting on the reference determinant of M numbers of occupied electrons and stands for the hole and particle

indices, respectively. Projection onto the excited determinants

$$|\Phi_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}\rangle = a_1^+ i_1 a_2^+ i_2 \dots a_n^+ i_n |\Phi_0\rangle, \quad (3.3)$$

we get the simultaneous nonlinear algebraic equations for the correlation energy, defined as $\Delta E_{corr} = E_g - E_{DF}$ for the ground state E_g of the state $|\Psi_0\rangle$ and DF energy E_{DF} of the state $|\Psi_0\rangle$, and also for the unknown cluster amplitudes of any order of excitations

$$\langle \Phi_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} | \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle_c = E \delta_{n,0}, \quad (n = 0, \dots, k), \quad (3.4)$$

In the above equation, subscript c means connected, n is the level of excitations from the DF state, and $\hat{H}_N = \hat{H} - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ is the normal ordered form of the Dirac-Coulomb Hamiltonian (\hat{H}) which is given by

$$\hat{H} = \sum_i \left[c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1) c^2 + V_{nuc}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \right], \quad (3.5)$$

where $\boldsymbol{\alpha}_i$ and β_i are the usual Dirac matrices, $V_{nuc}(r_i)$ is the nuclear potential and $\frac{1}{r_{ij}}$ is the electron-electron repulsion potential. The single particle energies are evaluated with respect to the rest mass energy ($-c^2$) of the electron. In our calculations, we only consider single and double excitations ($n = 2$), which is referred to as the CCSD method.

In DI-EOMCC approach the wave-function for the μ^{th} state of the doubly ionized system ($M - 2$ electron) can be written as

$$|\Psi(\mu)\rangle = R^{M-2}(\mu) |\Psi_0\rangle, \quad \mu = 1, 2, \dots, \quad (3.6)$$

The $R^{M-2}(\mu)$ is a linear operator and it is of the form

$$\begin{aligned} R^{M-2}(\mu) &= R_2 + R_3 + \dots \\ &= \sum_{i<j} r_{ij}(\mu) j i + \sum_{i<j<k,a} r_{ijk}^a(\mu) a^+ k j i + \dots \end{aligned} \quad (3.7)$$

In our approximation, we considered up to the R_2 and R_3 operators which are diagrammatically shown in Fig. 3.1.

The difference ($\Delta E_\mu = E_\mu - E_g$) between the energies of the ground and the doubly ionized states (E_μ) are calculated by solving

$$[\bar{H}_N, \hat{R}^{M-2}(\mu)]|\Phi_0\rangle = \Delta E_\mu \hat{R}^{M-2}(\mu)|\Phi_0\rangle \quad \forall \mu, \quad (3.8)$$

on projecting onto the basis of excited determinants ($|\Phi_{i_1 i_2}\rangle$ and $|\Phi_{i_1 i_2}^{\alpha_1}\rangle$) with respect to $|\Phi_0\rangle$, yields the matrix form,

$$\bar{H}_N R = R \Delta E, \quad (3.9)$$

Here, $\bar{H}_N = (\hat{H}_N e^T)_c$ is the similarity-transformed effective Hamiltonian.

3.3 Computational details

The orbital basis sets were generated using the proper kinetic balance between the large and small component of the wave function, where the large component of the wave function is constructed using the linear combinations of the Gaussian-type of orbitals (GTOs)

$$g_{kp}^L(r) = C_{ki}^L r^{n_\kappa} e^{-\alpha_p r^2}, \quad (3.10)$$

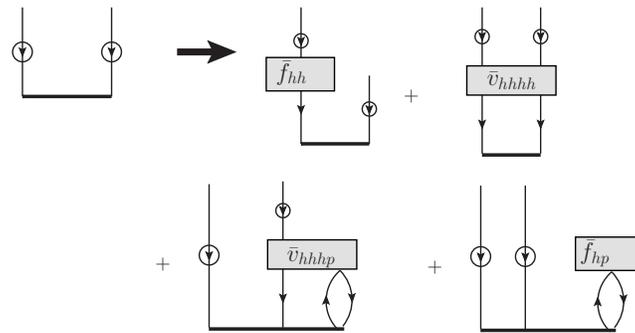
with the imposed condition

$$\alpha_p = \alpha_0 \beta^{p-1}, \quad (3.11)$$

where $p = 0, 1 \dots k$ with k number of GTOs. The corresponding α_0 and β parameters for all the atoms along with the number of GTOs generated at the DF level are given in Table 3.1. The orbital basis is constructed by taking into account primitive functions up to g -harmonics. It is impractical to use of all the orbitals generated in the DF method in a correlation calculation. Therefore, we have considered all the occupied orbitals, and for the virtual orbitals a certain threshold energies, since the contributions from the high-lying orbitals is rather small owing to their large energy values. These orbitals are referred to as the active orbitals. The two-parameter finite-size Fermi charge density distribution nuclear model

$$\rho_{nuc}(r) = \frac{\rho_0}{1 + e^{(r-b)/a}}, \quad (3.12)$$

is used to evaluate the nuclear potential; here ρ_0 is the average nuclear density, b is the half-charge radius, and a is related to skin thickness.

Figure 3.2: Diagrams contributing to the $2h$ block.

In our present implementation of DI-EOMCC method, the matrix elements of the \bar{H}_N matrix are constructed in the $2h$ and $3h-1p$ space and diagonalized to obtain the desired eigenvectors and eigenvalues. The antisymmetrized diagrams contributing to the $2h$ and $3h-1p$ block are presented in Fig. 3.2 and Fig. 3.3, respectively.

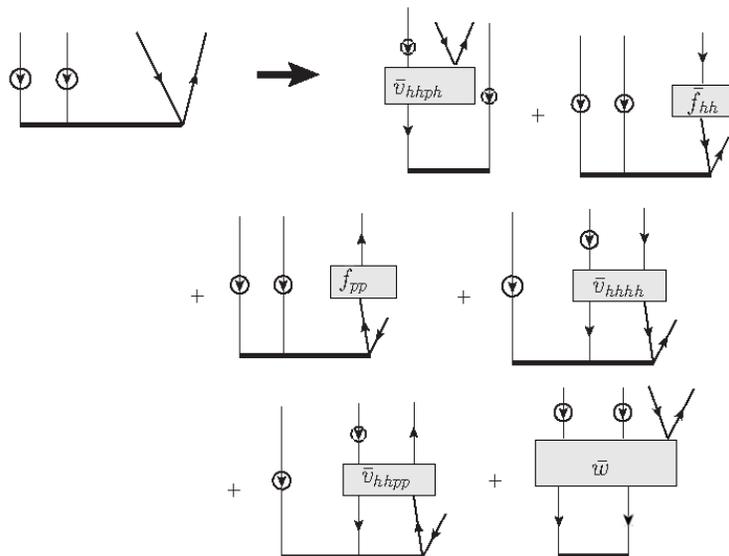
Figure 3.3: Diagrams contributing to the $3h-1p$ block.

Table 3.1: The number and the α_0 and β parameters used for the GTOs to generate single particle orbitals at the DF level.

Atom	Number of orbitals	<i>s</i>		<i>p</i>		<i>d</i>		<i>f</i>		<i>g</i>	
		α_0	β								
He	(36 <i>s</i> ,35 <i>p</i> ,34 <i>d</i> ,33 <i>f</i> ,32 <i>g</i>)	0.00075	2.075	0.00155	2.080	0.00258	2.180	0.00560	2.300	0.00765	2.450
Be	(36 <i>s</i> ,35 <i>p</i> ,34 <i>d</i> ,33 <i>f</i> ,32 <i>g</i>)	0.00500	2.500	0.00615	2.650	0.00505	2.550	0.00500	2.530	0.00480	2.500
Mg	(35 <i>s</i> ,34 <i>p</i> ,33 <i>d</i> ,32 <i>f</i> ,31 <i>g</i>)	0.02950	1.630	0.09750	1.815	0.00750	2.710	0.00780	2.730	0.00800	2.750
Ca	(35 <i>s</i> ,34 <i>p</i> ,33 <i>d</i> ,32 <i>f</i> ,31 <i>g</i>)	0.00895	2.110	0.00815	2.150	0.00750	2.500	0.00700	2.550	0.00690	2.600
Sr	(35 <i>s</i> ,34 <i>p</i> ,33 <i>d</i> ,32 <i>f</i> ,30 <i>g</i>)	0.01850	2.030	0.04750	2.070	0.00910	2.090	0.00950	2.100	0.00950	2.300
Ba	(35 <i>s</i> ,34 <i>p</i> ,33 <i>d</i> ,32 <i>f</i> ,31 <i>g</i>)	0.00925	2.110	0.00975	2.040	0.00995	2.010	0.01015	2.035	0.01035	2.038

The diagrams corresponding to the $2h$ block is responsible for the RPA calculations. These diagrams are evaluated with the help of one-body, two-body, and three-body intermediate diagrams. The evaluation of the intermediate diagrams requires the solution of the CCSD equations. The intermediate diagrams are constructed by contracting one-body and two-body part of the Hamiltonian with the converged T_1 and T_2 amplitudes. The one-body intermediate diagrams are inserted in Fig. 3.2 and 3.3 as \bar{f}_{hh} , \bar{f}_{pp} , and \bar{f}_{hp} . There are four distinct types of two-body intermediate diagrams required for the construction of \bar{H}_N matrix elements for the DI-EOMCC calculations. These are also \bar{v}_{hhhh} , \bar{v}_{hhhp} , and \bar{v}_{hhph} and \bar{v}_{hhpp} in the above two figures. The three-body intermediate diagram is also shown in Fig. 3.3 as \bar{w} .

The dimension of the \bar{H}_N matrix is very large ($nh^2 + nh^3np$, $nh^2 + nh^3np$) and it is not amenable to a full diagonalization scheme. Here nh and np denote the number of holes and particles, respectively. We have, therefore, used the Davidson algorithm [48], which is an iterative scheme, to diagonalize the \bar{H}_N matrix. It avoids computation, storage and diagonalization of the full matrix. The Davidson algorithm performs reasonably well for the whole spectrum, but we have solved only for the root corresponding to the lowest eigenvalue.

Table 3.2: SCF energy (E_{DF}^0), correlation energies from the MBPT(2) ($E_{corr}^{(2)}$) and CCSD ($E_{corr}^{(ccsd)}$) along with number of active orbitals used in the EOMCC calculations.

Atom	No. of active orbitals					E_{DF}^0	$E_{corr}^{(2)}$	$E_{corr}^{(ccsd)}$
	s	p	d	f	g			
He	17	15	13	9	7	-2.8618	-0.0365	-0.0416
Be	14	12	12	10	10	-14.5758	-0.0748	-0.0929
Mg	20	14	12	11	10	-199.9350	-0.4097	-0.4195
Ca	16	15	12	11	10	-679.7100	-0.7515	-0.7648
Sr	16	13	13	12	10	-3178.0797	-1.6530	-1.5922
Ba	16	15	14	12	9	-8135.6428	-2.2556	-2.1258

Table 3.3: Double-ionization energy values of alkaline earth metal atoms (Be, Mg, Ca, Sr, Ba) along with He in eV.

Atom	MBPT(2)	RPA	EOMCC	T -matrix [11]	NIST [47]	$\delta\%$
He	78.8596		79.0092		79.0051	0.005
Be	27.0949	27.5595	27.5421	27.7900	27.5338	0.030
Mg	22.4369	22.7655	22.6624	22.9700	22.6815	0.084
Ca	17.9007	18.0893	17.9992	17.8200	17.9848	0.080
Sr	16.7119	16.8502	16.7370		16.7251	0.071
Ba	15.2950	15.3546	15.2356		15.2154	0.132

3.4 Results and Discussion

We present numerical results of our calculations to test the performance of the newly implemented DI-EOMCC method. We have chosen alkaline earth-metal atoms along with He for the study of valence double ionization potentials. Three different sets of calculation are done for all the considered atomic systems, namely EOMCC using CCSD ground state wave function as a reference, MBPT(2) ground state wave function as a reference and RPA calculation on top of CCSD ground state wave function. All the calculated results are compared with the values from NIST database and the calculations based on first principles T -matrix method. These calculations in the four-component EOMCC framework will help us to understand the role of electron correlation in the calculated double-ionization potential values.

In Table 3.2, we present the DF energy (E_{DF}^0) and the correlation energies from the MBPT(2) (E_{corr}^2) and the CCSD (E_{corr}^{CCSD}) methods along with the number of active orbitals corresponding to each symmetry used in the calculations. In Table 3.3, we present the results for the valence DIPs of the He, Be, Mg, Ca, Sr, and Ba atoms. In fact, the formulation of the present method is valid even for determining DIPs of the states including inner occupied orbitals; however, they require larger dimensional space and special care on account of the higher-order correlation effects in the considered systems, and are left for a future work. All these results are compared with the tabulated values of the NIST database [47] and with the available results from the first-principles T -matrix calculations [11]. The differences between the DI-EOMCC (given in the table as EOMCC) results and the NIST data are plotted as δ (in percent) in Fig. 3.4. All the calculated DIPs are in

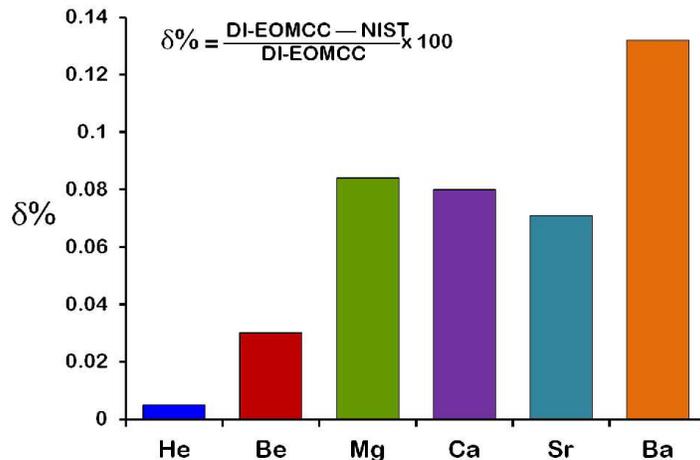


Figure 3.4: Relative % deviation from the NIST values.

excellent agreement with those of the NIST data. The DI-EOMCC values differ by about 0.01-0.02 eV from the NIST values except for the He atom, where the agreement is even better. It is found that MBPT(2) underestimates the values of the DIPs relative to the DI-EOMCC as the dominant part of the dynamic correlation is missing in this scheme. RPA, on the other hand, overestimates them. The $3h - 1p$ block, which is the major source of the nondynamical correlation effects, is missing in the RPA scheme. Our DI-EOMCC results are more accurate than those obtained using the first-principles T -matrix method. The results of the latter differ from the NIST values by about 0.2-0.3 eV.

3.5 Conclusion

In conclusion, we have successfully implemented the relativistic EOMCC method to calculate the double-ionization spectra. As a first application, we have calculated the valence DIPs of the alkaline-earth-metal atoms along with the He atom. We have achieved an accuracy of $\sim 0.1\%$, which is better than all previous DIP calculations. We have also compared the results of our MBPT(2) and RPA calculations with those of DI-EOMCC to highlight the role of correlation effects to attain high-precision results.

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Chapter 4

Relativistic equation-of-motion coupled-cluster method for the ionization problem: Application to molecules

We report the implementation of the four-component spinor relativistic equation-of-motion (EOM) coupled-cluster method within the single- and double- excitation approximation to calculate ionization potential of molecules. We have applied this method to calculate vertical ionization potentials of the molecules XH ($X=F, Cl, Br, I$) along with Cl_2 and Br_2 in their closed-shell configuration. We have also presented intermediate results using the second-order many-body perturbation theory level in the EOM framework to understand the role of electron correlation. All the calculated values are compared with the available experimental results. Our results are found to be in good agreement with the sophisticated experiments, and relative deviation of less than 1% is achieved for all the considered systems.

4.1 Introduction

It is always a hard task for the theoretical physicists to come up with a method that can depict the atomic and molecular spectroscopic properties very precisely. The effects of electron correlations as well as relativistic effects have to be taken care simultaneously, as they are intertwined [1]. The Dirac-Hartree-Fock method in its four-component formalism is the best possible way to include the effects of the relativity within a single determinantal description. On the other hand, coupled-cluster theory is known to be the most elegant to effectuate the electron correlation [2, 3]. It is, therefore, the combination of these two methods will surely be the solution to the problem.

The first step put forward in this direction is by Kaldor and coworkers. They implemented relativistic counterpart of the Fock-space multi-reference coupled cluster theory (FSMRCC) for the cause and applied it extensively to both atomic and molecular systems [4–8]. The original idea of FSMRCC theory is based on the construction of an effective Hamiltonian using the Bloch-Lindgren equation to extricate some of the roots of the Hamiltonian matrix from the set of the entire eigen spectrum [9–15]. The effective Hamiltonian variant of FSMRCC theory works within a reduced dimensional space, called model space, which is the part of the correlation space chosen to construct the effective Hamiltonian, and the rest of the space is known as orthogonal space. The linear combination of suitably chosen active configurations based on energetic criteria is used to construct the model space. An operator, called wave operator is defined through which the contribution of orthogonal space included, is the tool to construct the effective Hamiltonian. Finally, the diagonalization of the effective Hamiltonian matrix includes the correlation contribution of the model space and results into the set of desired eigenvalues. The problem associated with a reduced dimension effective Hamiltonian is the problem of intruder state, which leads to the failure in convergence. It appears that the effective Hamiltonian formalism of the FSMRCC theory is not straight forward, conceptually difficult, and lot of complicacy is associated with it.

An alternative elegant approach to tackle the problem is to use the equation-of-motion variant of the coupled-cluster theory (EOMCC) [16–21]. The EOMCC is operationally a two step process: (i) solution of the coupled-cluster equation for N electron determinant and (ii) construction and diagonalization of the effective Hamiltonian matrix in the $(N - 1)$ electron determinantal space to get the desired set of eigenvectors and eigenvalues. As EOMCC simultaneously treats two Hilbert

space (N and $N - 1$ electron space) in a single problem; the effect of relaxation is also taken into consideration, which plays a key role in the accurate description of the electronic states. The dynamic part of the electron correlation is taken care by the exponential structure of the CC operator, whereas non-dynamical part comes through the diagonalization of the effective Hamiltonian in the configuration space. We must admit that the EOMCC method for the single ionization problem is equivalent to the (0,1) sector FSMRCC theory and produces identical results for the principal peaks [22, 23]. The superiority of the EOMCC method over FSMRCC theory is that the numerical instability due to the problem of intruder states in FSMRCC does not arise in EOMCC, as it is an eigenvalue problem. The EOMCC is capable of giving shake-up states, which play important role in explaining various photo-ionization spectra [24].

The EOMCC can be viewed as a multi-state approach where multiple states are obtained in a single calculation and are treated on equal footing. It works within a single reference description to describe the complex multi-configurational wave function. It is pertinent to say that EOMCC behaves properly at the non-interacting limit but not rigorously size extensive [25, 26]. The error due to the size extensivity is reduced due to the presence of a higher order block. Furthermore, the eigenstates in EOMCC method are obtained directly contrary to the propagator approaches, though both the methods are of EOM structure [27, 28].

Recently, we stepped into the domain of fully four- component relativistic EOMCC and employed it to calculate single-ionization and double-ionization potentials, but that was for the atomic systems in their closed-shell configuration [29–31]. The molecular relativistic calculations are always more tedious than the atomic ones. The spherical symmetry can be exploited in the atomic case, which allows the separation of the radial and angular part to use the reduced matrix elements. The evaluation of radial integrals can be done using the numerical integration. It reduces computational scaling. However, the method is less straightforward, as each of the radial integral has to be multiplied by the corresponding angular factor. The use of antisymmetrized quantities (two-body matrix elements) are common in molecular calculations, but is not suitable for the spherical implementation in the atomic case as different angular factors will arise for the direct and exchange part of the radial integrals. The complexity associated with the atomic calculations is more than compensated by the need to solve only for the radial equations. This allows the use of a very large

basis set and correlation of more electrons with numerically evaluated radial integrals to achieve better accuracy of results.

The relativistic effective core potential (RECP) is routinely used in molecular relativistic calculations [32]. In RECP, only valence and some outer-core electrons are treated explicitly, and rest of the electrons are replaced by an effective RECP operator. This includes the simulating interaction of explicitly treated electrons with those, which are excluded from the RECP calculation. There are a variety of RECPs depending on how the RECPs are optimized [33]. Among the various RECPs, the RECP with spin-orbit (SO) interaction is the most popular one. This is generally done on the basis of separation of the electrons into core and valence and between the scalar and spin-orbit relativistic effects according to the energy. It allows exclusion of a large number of chemically inert electrons from the self-consistent field (SCF) calculations, which eventually reduces the computational costs for the correlation calculation as compared to the all electron two-component and four-component calculation. The problem associated with this approach is the lack of control over accuracy.

Hirata *et al.* was first to implement relativistic EOMCC for the purpose of molecular calculations [34]. They combined different electron correlation methods, basis set, and relativistic treatment to make a composite method. The dynamic part of the electron correlation is taken care of with a low rank method including the scalar relativistic effect and employed various basis sets to enable complete basis set extrapolation. The nondynamical correlation is treated using EOMCC method with a small basis set. Finally, the SO effect is added as the energy difference between the RECP+SO with RECP calculated using a low rank correlated method. This approach cancels some of the errors associated with the RECP methods. We would rather call Hirata *et al.*'s treatment a good compromise of the different many-body effects to get reasonable results. This approach does not address the complex interplay between the relativistic and correlation effects, which has been taken into account using the four-component single-particle wave function, and the Dirac-Coulomb Hamiltonian along with the correlation treatment are done by the EOM-CCSD method.

In this chapter, we consider the implementation of fully four-component relativistic EOMCC

method to calculate ionization potentials of molecular systems within the single- and double- excitation approximation (the EOM-CCSD method). Pilot calculations of molecular ionization potential using EOM-CCSD method are presented. We have also presented results by constructing the ground state wave function at the first order perturbation theory level, which corresponds to the second order perturbation energy as the ground- state energy. We call this EOM-MBPT(2). These results are compared with the EOM-CCSD results to understand the role of electron correlation.

The chapter is organized as follows. A brief description of the EOMCC theory for the ionization potential is given in Sec. 4.2, and the computational details are presented in Sec. 4.3. We have presented results and discuss on them in Sec. 4.4, before making our final remarks in Sec. 4.5.

4.2 Theory

The starting point for the EOMCC calculation for the ionization problem is the solution of the reference wave function, which is the N electron CC closed-shell ground state wave function. The ground state wave function in the CC method is defined as $|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle$, Where $|\Phi_0\rangle$ is the single slater determinant, which is the closed-shell N electron Dirac-Hartree-Fock reference determinant in our case. \hat{T} is the cluster operator, within the CCSD approximation is represented as

$$T = T_1 + T_2 = \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{\substack{a<b \\ i<j}} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \quad (4.1)$$

The $i, j(a, b)$ are the indices for the occupied (virtual) spinors. The cluster operators are solved by the following simultaneous non-linear algebraic equations.

$$\langle \Phi_i^a | e^{-T} \hat{H} e^T | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | e^{-T} \hat{H} e^T | \Phi_0 \rangle = 0. \quad (4.2)$$

where, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$ are the singly and doubly excited determinant with reference to the N electron closed-shell Dirac-Hartree-Fock determinant. Finally, the ground state energy is obtained by solving the equation for the energy: $E_{ccsd} = \langle \Phi_0 | e^{-T} \hat{H} e^T | \Phi_0 \rangle$, where, \hat{H} is the Dirac-Coulomb Hamiltonian, which is

$$\hat{H}_{DC} = \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + \beta_i m_0 c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} 1_4. \quad (4.3)$$

α and β are the usual Dirac matrices. V_{iA} stands for potential-energy operator for the i th electron in the field of nucleus A. m_0c^2 is the free-electron rest mass energy, where c is the speed of light.

In the EOMCC approach for the single electron ionization problem, the wave function for the k th target state is created by the action of a linear operator ($R(k)$) on the single reference coupled-cluster wave function $|\Psi_0\rangle$, $|\Psi_k\rangle = R(k)|\Psi_0\rangle$. Within the CCSD approximation $R(k)$ is also approximated to

$$R(k) = R_1 + R_2 = \sum_i r_i a_i + \sum_{i < j}^a r_{ij}^a a_a^\dagger a_j a_i, \quad (4.4)$$

The diagrammatic representation of the R_1 and R_2 operator is presented in Fig. 4.1 and are one rank higher than the CC operators. The energy of the k th ionized state is determined by the

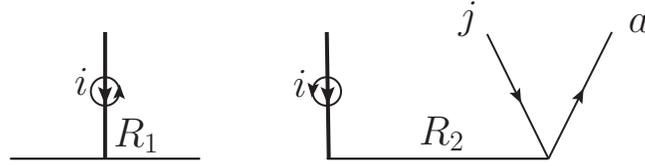


Figure 4.1: Diagrammatic representation of R_1 and R_2 operator.

equation

$$e^{-T} H R e^T |\Phi_0\rangle = e^{-T} H e^T R |\Phi_0\rangle = \bar{H} R |\Phi_0\rangle = E R |\Phi_0\rangle, \quad (4.5)$$

It is assumed that the e^T and R commute, as they are the strings of same quasi-particle creation operator. Here, $\bar{H} = e^{-T} H e^T$ is the effective Hamiltonian and E , which is the energy of the ionized state, is the sum of the E_{ccsd} and the corresponding ionization potential. Subtraction of E_{ccsd} from the eq. 4.5 takes the form as

$$[\bar{H}, \hat{R}(k)] |\Phi_0\rangle = \Delta E_k \hat{R}(k) |\Phi_0\rangle, \quad \forall k. \quad (4.6)$$

That is why this approach is called EOMCC in analogy to the Heisenberg's equation of motion for the excitation operator $R(k)$. A correlated determinantal space of $|\phi_i\rangle$ and $|\phi_{ij}^a\rangle$ ($1h$ and $2h - 1p$) with respect to $|\Phi_0\rangle$ is chosen to project the above equation to get the desired ionization potential values, ΔE_k :

$$\langle \phi_i | \bar{H}, R(k) | \phi_0 \rangle = \Delta E_k R_i \quad , \quad \langle \phi_{ij}^a | \bar{H}, R(k) | \phi_0 \rangle = \Delta E_k R_{ij}^a, \quad (4.7)$$

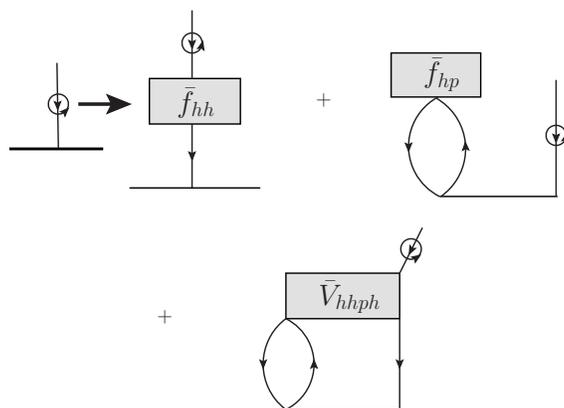


Figure 4.2: Diagrams contributing to the 1h block.

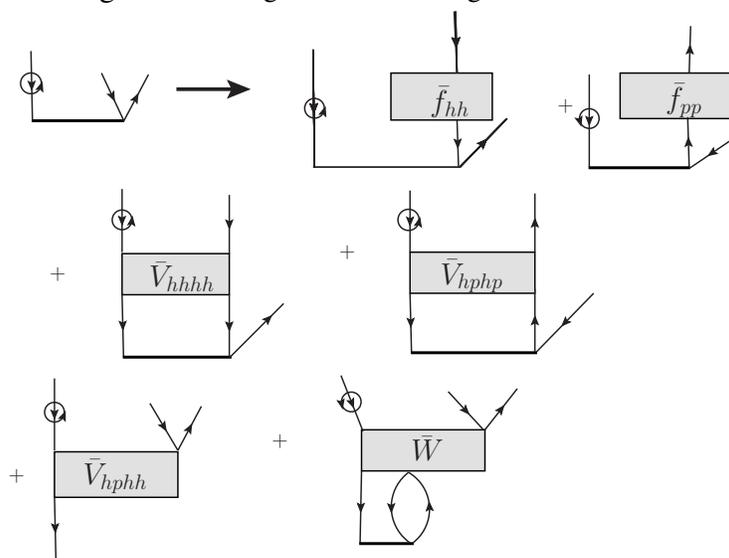


Figure 4.3: Diagrams contributing to the 2h-1p block.

The above equations can be represented in the matrix form as $\bar{H}R = R\Delta E_k$. The anti-symmetrized diagrams contributing to the $1h$ and $2h - 1p$ block are presented in the Fig. 4.2 and Fig. 4.3 respectively. The evaluation of these diagrams is done by constructing one-body, two-body and three-body intermediate diagrams. This requires the solution of the coupled-cluster ground-state amplitude equations. With the converged T_1 and T_2 amplitudes from CC ground-state calculations, these intermediate diagrams are constructed by contracting one-body and two-body parts of the effective Hamiltonian matrix elements. There are three distinct types (three one-body, four two-body and one three-body) of intermediate diagrams, which are required for the calculation of

Table 4.1: Bond length(in A^0), SCF energy (E_{DF}^0), correlation energies from the MBPT(2) ($E_{corr}^{(2)}$) and CCSD ($E_{corr}^{(ccsd)}$) methods for different systems.

Molecule	Bond Length[42]	E_{DF}^0	$E_{corr}^{(2)}$	$E_{corr}^{(ccsd)}$
HF	0.9168	-100.1604	-0.3649	-0.3646
HCl	1.2750	-461.5644	-0.6228	-0.6382
HBr	1.4140	-2605.6330	-1.6500	-1.5873
HI	1.6090	-7116.3860	-2.0049	-1.9134
Cl ₂	1.9870	-921.9144	-1.2180	-1.2404
Br ₂	2.2810	-5210.0830	-2.9822	-2.8543

ionization potential using the EOM-CCSD method. We denote these as \bar{f}_{hh} , \bar{f}_{pp} , \bar{f}_{hp} , \bar{v}_{hphh} , \bar{v}_{hhhh} , \bar{v}_{hhph} , \bar{v}_{hhph} , and \bar{W} . Here \bar{f} , \bar{v} and \bar{W} stand for one-body, two-body and three-body intermediates, respectively. The algebraic expression as well as diagrammatic of the intermediate diagrams can be found in [35]. All these intermediate diagrams are inserted in-between the diagrams contributing to the $1h$ and $2h - 1p$ block. A circled arrow represents a detached occupied orbital.

The dimension of the \bar{H} matrix is quite large ($nh + nh^2np, nh + nh^2np$) for the relativistic calculations in a reasonable basis. Therefore, following a full diagonalization scheme is not at all a good idea. Here nh and np represent the number of hole and particle, respectively. The Davidson algorithm [36], which is an iterative diagonalization scheme, is implemented for the diagonalization purpose of \bar{H} to get the desired set of eigenvalues ΔE_k and the corresponding eigenvectors. This avoids computation, storage, and diagonalization of the full matrix. The EOMCC can be regarded as the diagonalization of the coupled-cluster similarity transformed Hamiltonian in the configuration space. This makes the EOMCC a hybrid method of coupled-cluster and configuration interaction.

4.3 Computational details

The one-body and two-body matrix elements are generated with the help of DIRAC10 program package [37]. The finite atomic orbital basis consists of scalar real Gaussian functions. The large components of the basis set are contracted, and the small components are in uncontracted

Table 4.2: Vertical IPs (in eV) of (XH(X=F, Cl, Br, I)), Cl₂ and Br₂ using EOM-CCSD methods.

Molecule	Ionizing State	EOM-MBPT(2)	EOM-CCSD	Experiment
HF	5 Π	16.1709	16.1380	16.1200 [43]
	4 Π	16.2109	16.1777	
	3 Σ	20.0648	20.0667	19.8900 [43]
	2 Σ	39.5239	39.5802	39.6500 [43]
	1 Σ	697.0884	696.6777	694.0000[43]
HCl	9 Π	12.8248	12.8079	12.7450 [44]
	8 Π	12.9090	12.8917	12.8300[44]
	7 Σ	16.8321	16.8230	
	6 Σ	25.8646	25.8799	
HBr	18 Π	11.8294	11.6977	11.6450 [45]
	17 Π	12.1693	12.0343	11.9800[45]
	16 Σ	15.9093	15.8169	15.6500[45]
HI	27 Π	10.6763	10.4229	10.3880 [46]
	26 Π	11.3628	11.0998	11.047[46]
Cl ₂	17 Π	11.6842	11.6679	11.5900 [47]
	16 Π	11.7774	11.7604	
	15 Π	14.6353	14.4969	14.4000 [47]
	14 Π	14.7138	14.5751	
Br ₂	35 Π	10.5681	10.4370	10.5180 [48]
	34 Π	10.9252	10.7897	10.8670 [48]

except for the Br₂ molecule, where both the large and small component are uncontracted in nature. The small component of the basis set is generated by imposing a restricted kinetic balance (RKB) condition with the large components. This RKB is done by the preprojection in the scalar basis, and the unphysical solutions are removed by diagonalizing the free particle Hamiltonian. The DIRAC10 uses Gaussian charge distribution for the nuclear potential. The nuclear parameters used in our calculations are all default values. We adopted cc-pVQZ basis set [38] for H atom in all the calculations. In the calculation of HF and HCl molecule, the basis set chosen both for F and Cl atom is aug-cc-pCVQZ [39, 40]. The dyall.acv4z [41] basis is chosen for Br and I for the calculations of HBr and HI. The basis sets chosen for Cl and Br atom are aug-cc-pCVQZ [40] and dyall.cv3z [41], respectively in the calculation of Cl₂ and Br₂. We have taken into account C_{2v} symmetry to generate the single-particle orbitals and two-body matrix elements in all the calculations, and none of the electrons are frozen for the correlation calculations. The matrix elements of

the intermediate diagrams are stored setting a cutoff of 10^{-12} to save storage requirements as the contribution of the matrix elements beyond 12 decimal places is much less. To debug our newly implemented relativistic EOM-CCSD code, we benchmarked our results with the Fock-space MRCC code of DIRAC10 for the ionization problem with same basis, same convergence criteria and equal number of DIIS subspace, as these two methods in principle are supposed to produce identical results. We have achieved identical results for the MBPT(2) correlation energy, ten-digit agreement for the CCSD correlation energy and eight-digit agreement for ionization potential values. This agreement is achieved independent of the choice of molecules as well as of the basis sets. The discrepancy beyond this limit could be due to the different convergence algorithm and the use of a cutoff in the construction of the intermediate diagrams. The experimental bond length used in our calculations are taken from the ref [42]. In our calculations we have used 10^{-6} as a convergence cutoff for the Davidson algorithm and 10^{-10} for the ground state coupled cluster equations. The numerical labeling of the ionized states are done from the inner to the outer.

4.4 Results and Discussion

We present numerical results of our calculations using the four-component EOM-CCSD method developed by us for the calculation of ionization potentials of molecular systems by removing an electron from their closed-shell configuration. We also present results using an intermediate scheme, EOM-MBPT(2) which uses a first-order perturbed wave function for the construction of a ground-state wave function. We applied both these methods to HF, HCl, HBr, HI, Cl₂ and Br₂ molecule.

In Table 4.1, we present the equilibrium bond length used in the calculations of considered diatomic molecules and also the SCF energy (E_{DF}^0), correlation energy from the second-order perturbation theory ($E_{corr}^{(2)}$) and CCSD method ($E_{corr}^{(ccsd)}$). The reported SCF results are calculated using the DIRAC10 and correlation calculations are done with the relativistic code developed by us for the purpose of ground-state energy calculations within the single- and double- excitation approximation.

In Table 4.2, we present results of the vertical ionization potential of diatomic molecules using EOM-CCSD and EOM-MBPT(2) method. The results of our calculation of ionization potentials

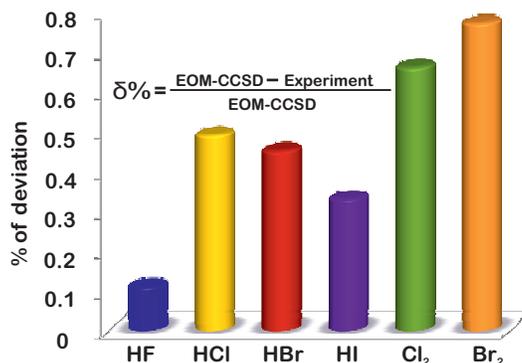


Figure 4.4: Relative deviations in % from the experimental values.

are compared with the available experimental values. Our EOM-CCSD results for the valence orbitals show good agreement with the experimental values, and the difference is less than 0.1 eV. The difference is slightly more for the inner orbitals; it is expected that the extent of accuracy will definitely be less as compared to the valence orbitals, as we have used Dirac-Coulomb Hamiltonian in our calculations. The higher-order relativistic effects, especially the Breit interactions for the neutral molecules have significant contribution for the inner orbitals. On the other hand, the deviation for the EOM-MBPT(2) is more as a dominant part of the dynamic correlation is missing in the scheme. We present the deviation of valence ionization calculations as $\delta\%$ in Fig. 4.4. In all the calculated systems we have achieved an accuracy of less than 1% with the standard values. The maximum deviation is for the Br₂ molecule, which is 0.77% and the minimum for HF, which is 0.11%. One possible reason for the deviation in Br₂ molecule could be that the basis employed is not adequate for the exact description of the ionized states.

4.5 Conclusion

We have successfully implemented the four-component spinor relativistic equation-of-motion coupled-cluster method (EOM-CCSD) to calculate ionization potential of molecular system in their closed-shell configuration. We presented numerical results of our calculation using both EOM-CCSD and EOM-MBPT(2) method. Our results are found to be in excellent agreement with the experimental values.

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Chapter 5

Relativistic equation-of-motion coupled-cluster method for the electron attachment problem

The chapter considers the successful implementation of relativistic equation-of-motion coupled cluster method for the electron attachment problem (EA-EOMCC) at the level of single- and double- excitation approximation. The Dirac-Coulomb Hamiltonian is used to generate the single particle orbitals and two-body matrix elements. The implemented relativistic EA-EOMCC method is employed to calculate ionization potential values of alkali metal atoms (Li, Na, K, Rb, Cs, Fr) and the vertical electron affinity values of LiX (X=H, F, Cl, Br), NaY (Y=H, F, Cl) starting from their closed-shell configuration. We have taken C₂ as an example to understand what should be the nature of the basis and cut off in the orbital energies that can be used for the correlation calculations without losing a considerable amount of accuracy in the computed values. Both four-component and X2C calculations are done for all the opted systems. To test the performance of the newly implemented EA-EOMCC method, we have compared our atomic results with the values from the NIST database and our results are found to be well within 0.6% with the standard NIST values. Therefore, by looking at the accuracy in the atomic results, we can conclude that the accuracy in the molecular calculations will also be fair enough and these computed values can be used as a reliable standard to benchmark the capability of other theoretical methods.

5.1 Introduction

A considerable growing interest is noticed in recent years in the study of negative ions as negative ions have significance in many areas of physics like in astrophysics, plasma physics and surface physics [1–4]. The electron affinity (EA) is an important quantity of these ions. The precise measurement of EA of atomic or molecular systems is always a challenge as the resulting negative ion is difficult to handle. Despite of the complexity in the measurement, there have been significant advances in the experimental techniques like laser photodetachment electron spectroscopy (LPES), laser photodetachment threshold spectroscopy (LPTS), accelerator mass spectroscopy (AMS) and photodetachment microscopy, et cetera are capable of precise measurements of EA of an atomic system [5–8]. However, the situation is inappreciative in achieving such an extent of accuracy in the molecular systems due to the possibility of structural change on attachment of an extra electron. Therefore, it is an outstanding challenge for the computational physicists to complement these atomic measurements as well as for new predictions for the future purpose.

The computational prediction of EA is difficult due to the absence of long-range Coulomb field outside of a neutral precursor. Therefore, an extra electron is solely bound through correlation with other electrons [9, 10]. Moreover, most of the theoretical calculations are based on the quantum chemical basis set methods, the finite size of the basis and unbalanced treatment of electron correlation in the atomic or molecular system and in the resulting ion are the sources of error [11, 12]. It is an established fact that not only the electron correlation but also the effect of relativity play a definite role in accurate description of the eigenstates [13]. It is, therefore, in such a case a highly correlated many-body method, capable of simultaneous treatment of relativity and electron correlation is required due to the intricate coupling between these two effects [14–16].

The four-component relativistic equation-of-motion coupled cluster (EOMCC) method is an elegant choice to fulfill the purpose. The performance of the fully four-component EOMCC has already been established for both atomic and molecular systems for the single ionization and double ionization problem [17–19]. The idea of EOMCC [20–26, 57, 58] is conceptually very simple and it is operationally a two step process: (i) solution of the N electron closed-shell determinant and (ii) construction and diagonalization of the effective Hamiltonian matrix for the Fock-space sector of interest in the configuration space. The simultaneous treatment of two Hilbert space

(N and $N + 1$ electron determinantal space in the case of EA problem) ensures the inclusion of relaxation effects, which also have an important role in proper description of the eigenstates. It takes into account of both the dynamic and non dynamic part of the electron correlation. The exponential structure of the coupled cluster operator takes care of the dynamic part of the electron correlation and non dynamic part is included by means of diagonalization of the effective Hamiltonian matrix in the configurational space. The diagonalization of effective Hamiltonian, by and large is associated with the multi-reference theories, whereas EOMCC works within a single reference description to tackle the complex multi-configurational wave function. The multiple roots can be addressed in a single calculation and each of the states are treated with equal weightage. The EOMCC method behaves properly at the non-interacting limit but not rigorously extensive (only for the core-core and core-valence interactions) due to the linear structure of the EOM operator [27].

The EOMCC is in close kinship with the coupled cluster linear response theory (CCLRT) [28, 29] and symmetry adapted cluster expansion configuration interaction (SAC-CI) method [30, 31]. Besides these two methods, effective Hamiltonian variant of Fock space multi-reference (FSMRCC) theory [32–37] always comes in the discussion on EOMCC as these two methods produce identical results for the one valence problem. The amplitudes of all the lower sector including the sector of interest is involved in the FSMRCC theory. On the other hand, EOMCC deals with the amplitudes of the (0,0) sector and the sector of interest. Therefore, both the approaches are eventually the same for the one electron attachment or detachment problem. The superiority of EOMCC over FSMRCC is the capability in addressing the shake-up states [38]. The EOMCC is free from the problem of intruder due to its CI (configuration interaction method) like structure, which is associated with the effective Hamiltonian variant of the FSMRCC theory.

Recently, Blundell implemented relativistic EOMCC method for the electron affinity problem and applied to calculate fine-structure splittings in high-lying states of rubidium atom [39]. The implemented version of Blundell is applicable only for the atomic calculations. Ours is a general one, applicable to both atoms as well as molecules starting from their closed-shell ground state configuration. The spherical implementation, which is very common in atomic systems allows the separation of radial and angular parts. Therefore, evaluation of radial integrals is only required and

the angular part will add up to it as a multiplier. The radial integrals can be evaluated numerically. A separation of that kind is not possible in the molecular case since evaluation of two-body matrix elements for molecular calculations are done in Cartesian coordinate system due to the absence of spherical symmetry. Furthermore, the anti-symmetrized two-body matrix elements are used in molecular relativistic calculations, which is not possible in the atomic calculations as angular factor will be different for the direct and exchange part of the two body matrix element. It appears that the spherical implementation is much more complex than that of the molecular calculations, but it is favorable from the computational point of view as it requires only the solution of radial integrals. Therefore, atomic calculations are computationally easy, which allows to correlate more number of electrons and amenable to use huge basis for the correlation calculation to achieve a better accuracy.

In this chapter, we report the implementation of relativistic EOMCC method for the electron affinity problem applicable to both atomic and molecular systems. The implemented EA-EOMCC method is employed to calculate ionization potential of open-shell atomic systems starting from their singly positive closed-shell configuration. Further, the vertical EA values of molecular systems are also calculated. Both four-component and exact two component (X2C) calculations are done for all the considered systems.

The present chapter is organized as follows. The EOMCC theory of the electron attachment problem is briefly described in Sec. 5.2, and the computational details of our calculations are presented in Sec. 5.3. We have discussed our results in Sec. 5.4 and finally made concluding remarks in Sec. 5.5.

5.2 Theory

In the EOMCC method the k^{th} target excited state of single electron attached state is defined as

$$|\Psi_k\rangle = R_k^{N+1}|\Psi_0\rangle, k = 1, 2, \dots \quad (5.1)$$

Here, the R_k^{N+1} is a linear operator, which on acting on the single reference coupled cluster (SRCC) ground state wave function $|\Psi_0\rangle$, generates the k^{th} excited state wave function $|\Psi_k\rangle$. The R_k^{N+1}

operator takes the form in the coupled cluster single-double (CCSD) approximation as

$$R_k^{N+1} = R_1 + R_2 = \sum_a r^a a_a^\dagger + \sum_{b < a} \sum_j r_j^{ba} a_a^\dagger a_b^\dagger a_j \quad (5.2)$$

The R_1 and R_2 operator are diagrammatically represented in Fig. 5.1. The R_1 is a one particle ($1p$) creation operator and R_2 is a two-particle and one-hole ($2p-1h$) creation operator. The circled arrow is just to represent that overall it is a one electron attachment process.

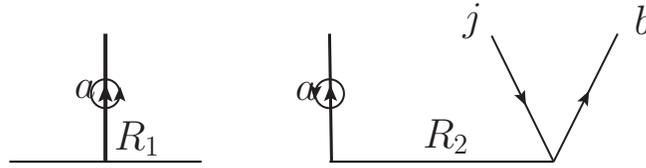


Figure 5.1: Diagrammatic representation of R_1 and R_2 operator.

The Schrödinger equation for the ground state ($k=0$) is

$$H_N |\Psi_0\rangle = \Delta E_0 |\Psi_0\rangle, \quad (5.3)$$

The electron attached states ($k=1,2,\dots$) is written as

$$H_N R_k |\Psi_0\rangle = \Delta E_k R_k |\Psi_0\rangle \quad (5.4)$$

The above equation on multiplication with a non-singular operator e^{-T} (where T is the coupled cluster excitation operator) in the course it is assumed that R_k commute with T (as strings of same quasi-particle creation operator) with some mathematical manipulation leads to equation-of-motion with respect to the R_k operator,

$$[\bar{H}_N, R_k] |\Phi_0\rangle = \Delta E_k R_k |\Phi_0\rangle \quad \forall k. \quad (5.5)$$

In the above equation, ΔE_k is the energy change associated with the electron attachment process and $\bar{H}_N = e^{-T} H e^T - \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle$ is the similarity transformed normal ordered effective Hamiltonian. In our case it is the Dirac-Coulomb Hamiltonian, which is given by

$$\hat{H}_{DC} = \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + (\beta - 1_4)c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} 1_4, \quad (5.6)$$

where α_i and β are the usual Dirac matrices, V_{iA} is the nuclear potential and $\frac{1}{r_{ij}}$ is the electron-electron repulsion potential. The orbital energies are scaled with respect to the free electron rest mass energy (c^2), which is zero in the non-relativistic case. We have chosen a correlated determinantal space of $|\Phi^a\rangle$ and $|\Phi_j^{ab}\rangle$ ($1p$ and $2p-1h$) with respect to the Dirac-Hartree-Fock determinant ($|\Phi_0\rangle$) to project the above equation to get the desired electron affinity values, ΔE_k .

$$\langle \Phi^a[\bar{H}_N, R_k]|\Phi_0\rangle = \Delta E_k R^a, \quad \langle \Phi_j^{ab}[\bar{H}_N, R_k]|\Phi_0\rangle = \Delta E_k R_j^{ba}, \quad (5.7)$$

The matrix form of the above equations is as $\bar{H}R = R\Delta E_k$. The effective Hamiltonian matrix is constructed in $1p$ and $2p-1h$ space and diagonalized. In Figs. 5.2 and 5.3, the contributing diagrams for the $1p$ and $2p-1h$ space are presented, respectively. The evaluation of these diagrams requires the solution of the coupled-cluster amplitude equations. The converged T_1 and T_2 amplitudes are contracted with the two-body matrix elements of the Hamiltonian matrix to construct one-body, two-body and three-body intermediate diagrams. The intermediate diagrams are categorized into \bar{f}_{pp} , \bar{f}_{hp} , \bar{f}_{hh} , \bar{V}_{hppp} , \bar{V}_{pppp} , \bar{V}_{phph} , \bar{V}_{ppph} and \bar{W} . Here \bar{f} 's, \bar{V} 's and \bar{W} stands for one-body, two-body, and three-body intermediates, respectively. We have followed a recursive intermediate factorization scheme as described in Ref. [40] to evaluate these intermediate diagrams. The factorization scheme in the construction of intermediate diagrams saves enormous computational resources. The matrix elements corresponding to the three-body intermediate diagram are not stored rather computed on the fly. The programmable algebraic expression for the diagrams corresponding to $1p$ block and $2p-1h$ block are presented in Eq. 5.8 and 5.9, respectively. We have used the standard notation ($\bar{f}(\text{out}, \text{in})$) and (\bar{V} (left out, right out, left in, right in)) for one-body and two-body intermediate matrix element. In Eqn 5.8 and 5.9, $i, j, \dots (a, b, \dots)$ stands for hole (particle) index. \hat{P} is a permutation operator and any odd permutation introduces a negative sign. The constructed effective Hamiltonian matrix is iteratively diagonalized using Davidson algorithm [41] to get the desired set of eigenvalues and eigenvectors.

$$\Delta E_k R^a = \sum_b \bar{f}_{pp}(a, b) r^b + \sum_{j,b} \bar{f}_{hp}(j, b) r_j^{ba} + 0.5 \sum_{j,b,c} \bar{V}_{hppp}(j, a, b, c) r_j^{bc} \quad \forall a \quad (5.8)$$

$$\begin{aligned} \Delta E_k R_j^{ba} &= \hat{P}(ab) \sum_c \bar{f}_{pp}(b, c) r_i^{ca} - \sum_j \bar{f}_{hh}(j, i) r_j^{ba} + 0.5 \sum_{cd} \bar{V}_{pppp}(a, b, c, d) r_i^{dc} \\ &\quad - \hat{P}(ab) \sum_{ck} \bar{V}_{phph}(a, k, c, i) r_k^{bc} + \sum_c \bar{V}_{ppph}(a, b, c, j) r^c \\ &\quad - 0.5 \sum_{k,l,c,d} \bar{V}_{hhpp}(k, l, c, d) r_k^{cd} t_{lj}^{ab} \quad \forall (i, b < a) \end{aligned} \quad (5.9)$$

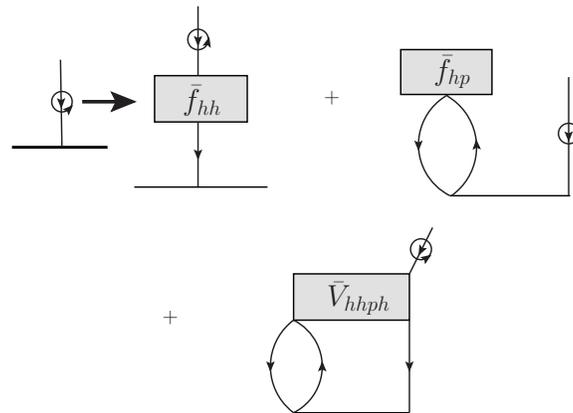


Figure 5.2: Diagrams contributing to the $1p$ block.

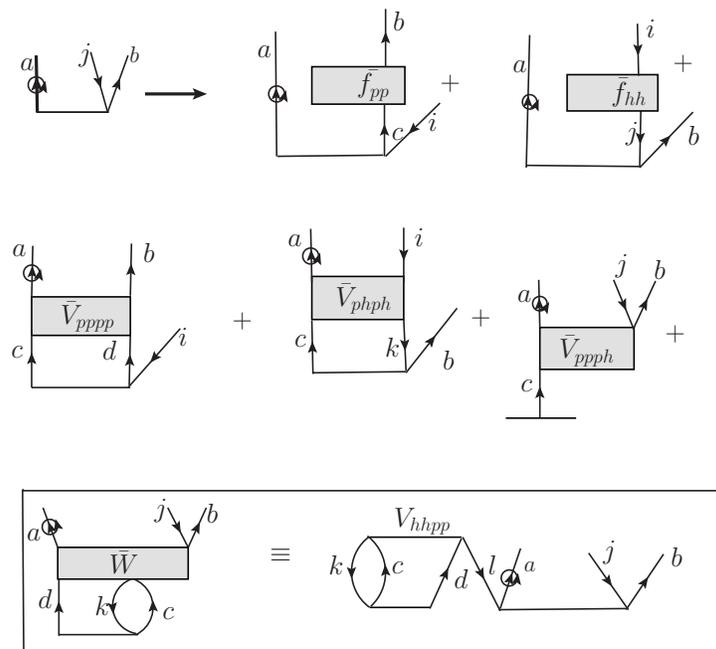


Figure 5.3: Diagrams contributing to the $2p-1h$ block.

Table 5.1: SCF (E_{DF}^0) and correlation energy from MBPT(2) and CCSD of alkali metal ions.

Atom	X2C			4C		
	SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
Li ⁺	-7.237045	-0.038520	-0.042313	-7.237174	-0.038490	-0.042284
Na ⁺	-161.885871	-0.352072	-0.355824	-161.895637	-0.351504	-0.355258
K ⁺	-601.317915	-0.655371	-0.669654	-601.378197	-0.654132	-0.668419
Rb ⁺	-2979.125369	-1.603877	-1.544953	-2979.693217	-1.600533	-1.541667
Cs ⁺	-7784.579785	-1.746204	-1.654556	-7786.643511	-1.740037	-1.648569
Fr ⁺	-24296.910671	-1.635291	-1.468312	-24308.061505	-1.634768	-1.467783

Table 5.2: Bond length(in Å), SCF (E_{DF}^0) and correlation energy from MBPT(2) and CCSD of LiX(X=H, F, Cl, Br) and NaY(H, F, Cl).

Molecule	Bond Length [52]	X2C			4C		
		SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
LiH	1.5957	-7.987794	-0.069223	-0.080955	-7.987928	-0.069191	-0.080923
LiF	1.5939	-107.078887	-0.400341	-0.399171	-107.084024	-0.400097	-0.398927
LiCl	2.0207	-468.469738	-0.606016	-0.622235	-468.511539	-0.605515	-0.621738
LiBr	2.1704	-2612.134924	-1.465099	-1.404927	-2612.603993	-1.463721	-1.403588
NaH	1.8874	-162.602176	-0.385821	-0.397925	-162.611952	-0.385251	-0.397357
NaF	1.9259	-261.676902	-0.694456	-0.691459	-261.691677	-0.694011	-0.691018
NaCl	2.3608	-623.077913	-0.846128	-0.861815	-623.129354	-0.845488	-0.861179

5.3 Computational Details

The DIRAC program package [42, 43] is used to evaluate the required one-body and two-body matrix elements for the correlation calculation. Both the X2C and four-component calculations are done by using uncontracted finite atomic basis, which consists of scalar real gaussian functions. The small component of the basis is linked with the large component of the basis through the restricted kinetic balance (RKB) condition. The RKB condition represents the kinetic energy properly in the non-relativistic limit and avoids the variational collapse [44]. This is achieved by pre-projecting in scalar basis and unphysical solutions are removed by diagonalizing the free particle Hamiltonian. The RKB condition generates the positronic solution and electronic solution in 1:1 manner. The DIRAC program package uses Gaussian distribution nuclear model to take care of the finite size of the nucleus. The used nuclear parameters are taken as default values from DIRAC package [45]. We adopted aug-cc-pCVQZ basis for Li^+ [46] and Na^+ [48] atom and all the generated orbitals are taken into consideration for the correlation calculations. Dyall.cv4z [49] basis is opted for K^+ and Rb^+ . We have neglected the virtual orbitals whose energy is more than 500 a.u. for the K^+ and Rb^+ atom. The Cs^+ and Fr^+ are calculated using dyall.cv3z basis [49]. The cutoff used for Cs^+ atom is 1000 a.u. whereas for Fr^+ atom, we have taken the orbitals having energy in between -25 a.u. to 100 a.u. in our correlation calculations. In the molecular calculations of LiF, LiCl, LiBr, we have chosen aug-cc-pCVTZ basis for Li atom [46] and cutoff of 100 a.u. for the virtual orbitals. The calculations of F and Cl are done using aug-cc-pCVQZ [46, 48] basis and for Br, dyall.cv4z [50] basis is used. In LiH we have chosen aug-cc-pCVQZ basis [46] for Li and aug-cc-pVTZ [46] for the H atom and none of the electrons are frozen for the correlation calculations. Aug-cc-pCVTZ basis is opted for both Na [48] and Cl [47] in the calculations of NaCl and a cutoff of 100 a.u. is used for the virtual orbitals. The single particle orbitals and two-body matrix elements are generated by taking account of C_{2v} symmetry. Both X2C and four-component calculations of Rb and LiBr are done with the DIRAC14 version and rest of the calculations are done using DIRAC10. The implemented version of X2C SCF [51] in DIRAC10 is capable of taking up to g harmonics but the opted basis for Rb and LiBr require up to h harmonics to express the large component of the wave function. Therefore, these two calculations are done using DIRAC14 version. We have fixed a cutoff of 10^{-12} to store the matrix elements for the intermediate diagrams

Table 5.3: Convergence pattern of electron affinity (in eV) of the C₂ (R=1.243 Å, Ref [52]) as a function of basis set.

Basis	Spinor	Electron affinity	Expt.[53]
cc-pVDZ	88	2.649364	
cc-pCVDZ	104	2.664512	
aug-cc-pVDZ	124	3.189648	
aug-cc-pCVDZ	140	3.194913	
cc-pVTZ	152	3.114016	
cc-pCVTZ	192	3.128478	
aug-cc-pVTZ	216	3.331555	3.30±0.1
cc-pVQZ	252	3.274313	
aug-cc-pCVTZ	256	3.341214	
cc-pCVQZ	316	3.285165	
aug-cc-pCVQZ	416	3.384036	
aug-cc-pCVQZ ^a	488	3.385261	

^a All the virtual orbitals are used for the EOMCC calculation.

Table 5.4: Ionization potential values (in eV) of alkali metal atoms.

Atom	X2C	4C	NIST [54]
Li	5.389401	5.389455	5.391714
Na	5.110412	5.110662	5.139076
K	4.341902	4.342264	4.340663
Rb	4.174975	4.175704	4.177128
Cs	3.886082	3.887077	3.893905
Fr	4.057888	4.060236	4.072740

as two-body matrix elements contributed negligibly beyond this limit. The convergence of 10^{-10} is fixed for the solution of SRCC amplitude equations and 10^{-5} for the Davidson algorithm in the EOMCC part. A direct inversion in the iterative subspace (DIIS) of 6 is used in the solution of ground state amplitudes for all the calculations. The newly implemented relativistic EOMCC code is tested by comparing EA-EOMCC results with the (1,0) sector FSMRCC code implemented in the DIRAC package as these two theories are supposed to produce identical results for one electron attachment process. The MBPT(2) correlation energy is identical whereas CCSD correlation

energy and the EA value are matching upto ten-digit and eight-digit, respectively. The test is performed with identical convergence cut off, equal number of DIIS space and without any cutoff in the intermediate diagrams. We have done the test over a series of atoms and molecules with various basis sets and successful in achieving similar agreement for all the considered system, independent of the choice of basis set.

5.4 Results and discussion

We have reserved this section of our manuscript to present numerical results of our calculations and to interpret the outcome of these calculations. The four-component and exact two component (X2C) EOMCC calculations are performed for all the considered atomic and molecular systems starting from their closed-shell configuration.

In Tables 5.1 and 5.2, we present numerical results of our SCF and correlation energy from MBPT(2) and CCSD calculation of singly positive alkali metal atomic systems (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+) and molecular systems (LiX ($\text{X}=\text{H}$, F , Cl , Br) and NaY ($\text{Y}=\text{H}$, F , Cl)) in their closed-shell configuration. The bond length of the molecular systems is also compiled in Table 5.2. For atomic systems (Table 5.1), we noticed that the difference between MBPT(2) and CCSD correlation energies for both X2C and four component calculation keep on increasing as we go down the group. This trend is expected as the effect of correlation increases as the number of electron in the system increases.

We have done a series of calculations to understand how the electron affinity value changes with the nature of basis set and cut off in the orbital energies can be used without losing considerable amount of accuracy as EOMCC calculations for the EA problem are computationally costly. We have chosen C_2 as an example system for which experimental vertical EA value is reported in the literature. We have started our calculation with cc-pVDZ, which is a very small basis as it generates only 88 spinor for the beyond SCF calculations using a cutoff of 100 a.u. for the virtual orbitals. A few more calculations are also done by improving the nature of the basis functions. The EA value as well as the number of generated spinor in different basis are tabulated in Table 5.3. We have taken 1.243 Å as bond length for the C_2 molecule, which is the experimentally reported bond length. The reported experimental value is 3.30 ± 0.1 eV, whereas our calculation yields 3.384036

Table 5.5: Vertical EA (in eV) values of LiX (X=H, F, Cl, Br) and NaY (Y=H, F, Cl).

Molecule	X2C	4C	Others [56]
LiH	0.296759	0.296757	0.247
LiF	0.354954	0.354964	0.340
LiCl	0.552586	0.552595	0.551
LiBr	0.614757	0.614773	
NaH	0.321751	0.321740	0.319
NaF	0.484822	0.484863	0.485
NaCl	0.672601	0.672653	0.672

eV for aug-cc-pCVQZ basis with a cut off of 100 a.u. in the virtual orbital energy. On the other hand, without using any cut off, the result is 3.385261 eV. Therefore, a cutoff of 100 a.u. for virtual orbital energies and similar basis set can be used without losing much accuracy for all other calculations to achieve a good agreement with the experiment. It will save enormous computational time without losing a significant amount of accuracy as contribution from the high energy virtual orbitals is very less in the correlation calculations. The reported experimental uncertainty is in the first digit after the decimal point. Therefore, it is hard to comment on the accuracy of our calculated results. It can be said that our results is also spanning same range starting from a reasonable basis.

In Table 5.4, we report the calculated ionization potential values of atomic systems using both X2C and four-component EA-EOMCC method. We have started our calculations from singly positive alkali metal ions and applied EA-EOMCC method. The negative of the computed values are reported as ionization potential values of the open-shell atomic systems. These computed ionization potential values are compared with the values from the National Institute of Standards and Technology (NIST) database. A nice agreement with NIST values is achieved for all the considered systems. The maximum deviation is obtained for the Na atom, which is also in the accuracy of $\sim 0.6\%$ with the NIST value. The difference between the X2C with four-component results is in the fifth digit after the decimal for Li atom whereas the difference is about 0.01 eV for Fr atom.

In Table 5.5, we present the results of our calculations of vertical EA of molecular systems

using both X2C EA-EOMCC and four-component EA-EOMCC method. Further, we have compared our result with the theoretical results calculated by Gutsev *et al* [56]. They also employed EA-EOMCC method for correlation treatment to calculate the vertical EA values of the molecular systems. In their calculation, Gutsev *et al* misses the effect of relativity, which is included in our calculation in its four-component formalism. We have achieved a nice agreement for the atomic results and also for the vertical EA value of C_2 molecule. Therefore, it can be said that our calculated results for the molecular systems are also quite accurate though there is no reliable experimental data or any other values calculated using any variant of relativistic coupled cluster theory to compare with. However, the accuracy of the molecular calculations will not be that much accurate as compared to the atomic results. The reason behind this is due to the possibility of structural change on attachment of an extra electron to the neutral molecule depending on the polarity of the molecule.

5.5 Conclusion

The relativistic EOMCC method for the electron attachment problem applicable to both atomic and molecular systems is successfully implemented. To test the performance of the EA-EOMCC method, we applied to calculate ionization potential values of alkali metal atoms starting from a closed-shell configuration. We have compared our calculated ionization potential values with the values from NIST database. We are successful in achieving about 0.6% agreement with the NIST values. We have also presented molecular EA values of LiX ($X=H, F, Cl, Br$) and NaY ($Y=H, F, Cl$) using our relativistic EOMCC methods.

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Chapter 6

Relativistic equation-of-motion coupled-cluster method using open-shell reference wavefunction

The open-shell reference relativistic equation-of-motion coupled-cluster method within its' four-component description is successfully implemented with the consideration of single- and double- excitation approximation. The one-body and two-body matrix elements required for the correlation calculation are generated using Dirac-Coulomb Hamiltonian. As a first attempt, the implemented method is employed to calculate ionization potential values of heavy atomic (Ag, Cs, Au, Fr, Lr) and molecular (HgH, PbF) systems, where the effect of relativity does really matter to obtain highly accurate results. Not only the relativistic effect, but also the effect of electron correlation is crucial in these heavy atomic and molecular systems. To justify the fact, we have taken two further approximations in the four-component relativistic equation-of-motion framework to quantify how the effect of electron correlation at different level of approximation play role in the calculated values. All these calculated values are compared with the experimental values as well as with other theoretically calculated values to judge the extent of accuracy obtained in our calculations. A nice agreement is achieved for all the considered systems, which validates the performance of the open-shell reference relativistic equation-of-motion coupled-cluster method.

6.1 Introduction

The accurate calculations of the transition energies, especially for the heavier atomic and molecular systems require simultaneous incorporation of both the effect of relativity and electron correlation as there is a sinuous ally between these two effects [1]. The Dirac-Hartree-Fock (DHF) method is the best suited recipe to include the effect of relativity in a single determinant wave function based theory using four-component Dirac spinor. In the DHF technique, the complicated many-electron problem is converted into sum of many one-electron problems and an average interaction between the electrons is assumed in the due course. Therefore, the instantaneous interaction between the electrons having opposite spin or the electron correlation is missing in such a treatment. On the other hand, equation-of-motion coupled-cluster (EOMCC) method is very successful in the non-relativistic theory for the treatment of electron correlation. The performance of the method is well tested for the calculations of ionization potential, electron affinity and excitation energy starting from both closed-shell as well as open-shell reference wave function [2–14] but the full fledged extension of the EOMCC method to the relativistic realm is far fewer for the former [15–17] and none for the latter.

The EOMCC method is a very handy technique since the difference of energy is calculated in a direct manner. A two step procedure is followed in actual practice to solve the EOMCC amplitude equations as ground state amplitudes are decoupled from that of the excited states; (i) solution of the N electron reference wave function and (ii) the step engages in the diagonalization of the constructed effective Hamiltonian matrix in the $(N-1)$ electron determinantal space for the single electron ionization problem. Therefore, the method is taking account of two Hilbert space simultaneously, which fortifies the inclusion of relaxation effect. Relaxation effect have definite role in assigning the ionized states precisely but it shows greater relevance in ionization of an inner orbital electron as compared to the valence electrons. The idea of diagonalization of the effective Hamiltonian matrix elements is some how associated with the multi-reference theories but EOMCC works within a single reference description to tackle complex wave function which is multi-configurational in nature. In principle, the secondary ionized states or the indirect excitation energies can also be obtained as a by-product, which have key role in explaining various photoionization spectra. It is worth to note that EOMCC is a size consistent method but the calculated

transition energy is extensive only for the principal valence sector whereas the secondary roots are size intensive [18–20]. We can say that the EOMCC is a configurational interaction (CI) method using coupled-cluster similarity transformed Hamiltonian matrix elements. Therefore, the convergence difficulty is not of concern due to structural resembles with the CI method, which is always an integral part of any multi-root theories. Although there are ways to deal with such a problem, a brief overview of various options can be found in Ref. [21]

The Fock-space multi-reference coupled-cluster method (FSMRCC) [22–27] is an alternative approach to calculate transition energies between an arbitrary chosen ground state and several other final states. Operationally, this approach is divided into various “sectors” depending on the number of electron added to or removed from the system. In the FSMRCC approach for a given sector (x,y) depends upon all (a,b) ; $a \leq x$ and $b \leq y$, sector amplitude equations. Therefore, this advocates for a hierarchical solution. On the other hand, the EOMCC method deals only with the amplitudes of the reference sector and that of the target Fock space sector of interest. Therefore, these two approach eventually produces identical results for the single electron ionization or attachment problem but different for the excitation of electron from an occupied orbital to a virtual orbital and in multi-electron ionization or attachment processes. It appears that FSMRCC theory is conceptually difficult in contrast to the EOMCC method which is very easy to understand. Therefore, it can be used in a “black box” way to address various electronic structure problems which motivates us to focus in the EOMCC domain. A detail comparative discussion in the context of performance between these two methods can be found in Ref. [28]. Stanton and co-workers [29] implemented FSMRCC theory for general single determinant reference wave function and applied to calculate ionization potential values of molecules starting from a high spin ground state configuration but their approach lacks the consideration of relativistic motion of the electrons. On the other hand, Kaldor and co-workers [30–33] have done extensive work in the relativistic FSMRCC framework but they always starts from a closed-shell reference wave function. As for example, they applied $(1,0)$ sector FSMRCC theory to a mono-cationic closed-shell reference state and negative of the obtained value is reported as the ionization potential value of the open-shell atomic or molecular systems. We have also followed such an idea in a recent work using EOMCC method

[34]. The problem with such an approach is that either (1,0) sector FSMRCC theory or the electron attached (EA) EOMCC method require four particle intermediate H_{eff} matrix elements. The size of those matrix element and required computational time due to its scaling is enormous for a relativistic calculation. Therefore, it is not at all a good idea to follow such an approach from the computational perspective, specially in the relativistic domain. On the other hand, starting from an open-shell reference wave function is more realistic choice particularly when large non-dynamic electron correlation effects are present.

The most common practice in a molecular relativistic calculations is the use of relativistic effective core potential (RECP) with the inclusion spin-orbit coupling (SOC) [35, 36]. The SOC is the dominant part of the relativistic effect and play significant role specially for the heavy p-block elements and also for the moderate heavy molecular systems when highly accurate results are sought. Due to the SOC different degenerate electronic configuration mixed with each other leads to significant change in the wave function, energetics and spectra. Hirata *et al.* [37] made the first attempt to include SOC with RECP in the EOMCC framework. They made a composite method by taking consideration of different electron correlation methods, basis set, and a part of the relativistic effect is added. The ground state wave function is constructed at the second order perturbation theory level to take care of the dynamic part of the electron correlation with the addition of scalar relativistic effect and extrapolated it to the complete basis set limit. The EOMCC calculation is done to take care of the non-dynamic part of the electron correlation using a very small basis set. The SOC effect is quantified as the energy difference between RECP+SOC with RECP using the low rank method employed to take care of the dynamic part. The applied strategy cancels some of the errors associated with the RECP method. The RECP is generally build upon the separation of the electrons according to the energy with classification of electron into core and valence. The valence including the few outer-core electrons are treated explicitly and an effective RECP operator is defined to replace the other electrons. This RECP operator takes care of the interaction between the explicitly treated electrons with the other excluded electrons. Therefore, a large number of less contributing electrons are excluded from the calculations and reduces the computational cost as compared to all electron relativistic treatment. However, the approach can not grantee high accurate results as all the electrons are not treated explicitly. Therefore, neither

the effect of electron correlation nor the relativistic effect is comprehensive in their approach. In a recent work Epifanovsky *et al.* [38] did perturbative treatment to include SOC with explicit treatment of all the electrons using Breit-Pauli Hamiltonian with zeroth-order non-relativistic wave functions in different variant of EOMCC method and applied to very small molecular systems where effect of relativity does not have much role to play. Li *et al.* [39] included SOC only in the EOM part to calculate ionization potential of molecular system but they have taken N electron closed-shell coupled cluster wave function as a reference. The perturbative treatment of SOC is not reliable for heavy atomic and molecular systems. Therefore, a fully relativistic description is necessary to address such effects. The solution based on Dirac-Hamiltonian naturally takes care of the SOC effect [40]. The effect is more prominent for the open-shell systems as compared to the closed-shell atomic or molecular systems which motivates us to implement EOMCC method starting from a open-shell reference wavefunction using four-component Dirac spinors with the explicit treatment of all the electrons in the SCF calculations and to apply for the treatment of heavy atomic and molecular systems.

In the present chapter, discussion is only restricted to implementation of relativistic EOMCC method in the context of single electron ionization problem starting from a open-shell reference wave function, though it can be generalized to any other Fock-space sector of interest by defining an appropriate EOM operator. The ground state wave function in the EOMCC method is taken as the single reference coupled-cluster wave function. We have constructed the coupled-cluster ground state wave function considering up to single- and double- excitation (CCSD) from N electron Dirac-Hartree-Fock (DHF) reference wave function. The EOM matrix is constructed in the 1h and 2h-1p space and diagonalized to get the principal peaks. Beside the effect of relativity, correlation effects also have important role in the heavier systems. We, therefore, followed two intermediate scheme in the four-component relativistic EOMCC framework to understand the effect of electron correlation in the calculated ionization potential values. We call these as EOM-MBPT(2) and EOM-RPA. In the EOM-MBPT(2) scheme the ground state wave function is constructed using first order perturbed wave function, which corresponds to the second order perturbation (MBPT(2)) energy. On the other hand, in the EOM-RPA scheme the ground state wave function is constructed at the CCSD level but the EOM matrix is constructed and diagonalized only in the 1h space.

Therefore, in the EOM-MBPT(2) scheme part of the dynamic correlation is missing whereas in the EOM-RPA scheme dominant part of the non-dynamic correlation, since contribution from the 2h-1p block is absent which contributes significantly to the non-dynamic part of the electron correlation. Finally, all these results are compared with the values calculated using other theoretical methods and with the values from experiment. These three calculations will help us to understand how the effect of electron correlation at different level of approximation is equally important for the heavier systems. We have taken few representative example of heavy atomic (Ag, Cs, Au, Fr, Lr) and molecular (HgH, PbF) systems where both relativistic effect and electron correlation have a larger role in getting ionization potential values accurately.

The chapter is organized as follows. A brief overview of the EOMCC method in the context of single electron ionization problem is discussed in Sec. 6.2. Sec. 6.3 and Sec. 6.4 are reserved for details of the computational consideration and discussion of the obtained results in our calculations, respectively. Finally we made our concluding remark in Sec. 6.5.

6.2 Method

In the following section we present a brief overview of the EOMCC method in the context of ionization of a single electron from the N electron ground state wave function and the final algebraic equations are represented in their spinor form. In the EOMCC method a linear operator (R) acts on the reference wave function to generate the excited state determinants. We have consistently used $i, j(a, b)$ indices to represent the occupied (virtual) spinors.

The Schrödinger equation for the reference state and the ν^{th} excited state can be represented as

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (6.1)$$

$$H|\Psi_\nu\rangle = E_\nu|\Psi_\nu\rangle, \quad (6.2)$$

The excited state wave function can be described as $|\Psi_\nu\rangle = R_\nu|\Psi_0\rangle$ Left multiplication of the Eqn. 6.1 with R_ν and subtraction from Eqn. 6.2 will lead to the following expression

$$[H, R_\nu]|\Psi_0\rangle = \Delta E_\nu R_\nu|\Psi_0\rangle \quad (6.3)$$

Here, ΔE_ν is the energy difference between the reference state and the excited states. With proper definition of the R_ν operator, excited states of electron detached, attached or even an electron excited state can be obtained. In the case of ionization problem the expression of the R_ν operator is like

$$R_\nu^{IP} = R_1 + R_2 + \dots = \sum_i r_i a_i + \sum_{i < j}^a r_{ij}^a a_a^\dagger a_j a_i + \dots, \quad (6.4)$$

The reference wave function in the EOMCC method is not necessarily the ground state wavefunction but we have chosen coupled-cluster ground state wave function as the reference state. The coupled-cluster ground state wave function is defined as $|\Psi_0\rangle = e^T |\Phi_0\rangle$ Here, T is the cluster operator and $|\Phi_0\rangle$ is the N electron DHF eigenstate. The cluster operator T is represented in second quantization form as

$$T = T_1 + T_2 + \dots = \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{\substack{a < b \\ i < j}} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots \quad (6.5)$$

The following simultaneous non-linear algebraic equations are iteratively solved to get the cluster amplitudes

$$\langle \Phi_i^a | e^{-T} H e^T | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | e^{-T} H e^T | \Phi_0 \rangle = 0. \quad (6.6)$$

where, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$ are the singly and doubly excited determinant with reference to the DHF determinant. Finally, the ground state energy is obtained by solving the equation for the energy,

$$E_{ccsd} = \langle \Phi_0 | e^{-T} \hat{H} e^T | \Phi_0 \rangle, \quad (6.7)$$

where, \hat{H} is the Dirac-Coulomb Hamiltonian which is,

$$H_{DC} = \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + (\beta - 1_4)m_0c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} 1_4, \quad (6.8)$$

here, α and β are the known Dirac matrices. V_{iA} is the potential energy operator for the i^{th} electron in the field of nucleus A. m_0c^2 is the rest mass energy of the free electron, where c stands for the speed of light.

The R_ν and T operator commutes among themselves since they are constructed of same quasi-particle creation operator. Therefore, we can represent Eqn. 6.3 as

$$[\bar{H}, R_\nu] |\Phi_0\rangle = \Delta E_\nu R_\nu |\Phi_0\rangle \quad \forall \nu, \quad (6.9)$$

Here, $\bar{H} = e^{-T} H e^T$ is the effective Hamiltonian. The above equation is projected onto the set of excited determinants ($|\Phi_i\rangle$) and ($|\phi_{ij}^a\rangle$) to get the desired ionization potential values (ΔE_ν).

$$\langle \phi_i | [\bar{H}, R_\nu] | \phi_0 \rangle = \Delta E_\nu R_i, \quad (6.10)$$

$$\langle \phi_{ij}^a | [\bar{H}, R_\nu] | \phi_0 \rangle = \Delta E_\nu R_{ij}^a, \quad (6.11)$$

The matrix form of the above equations is as $\bar{H}R = R\Delta E_\nu$. The algebraic expression of the left hand sides of Eqn. 6.10 and Eqn. 6.11 are as follows

$$\Delta E_\nu R_i = - \sum_j \bar{f}_{hh}(j, i) r_j + \sum_{j,a} \bar{f}_{hp}(j, a) r_{ji}^a - 0.5 \sum_{j,k,a} \bar{V}_{hhhp}(j, k, i, a) r_{kj}^a \quad \forall i \quad (6.12)$$

$$\begin{aligned} \Delta E_\nu R_{ji}^a &= -\hat{P}(ij) \sum_k \bar{f}_{hh}(k, i) r_{ji}^a - \sum_k \bar{V}_{hphh}(k, a, i, j) r_k + \sum_b \bar{f}_{pp}(a, b) r_{ji}^b \\ &\quad + \hat{P}(ij) \sum_{k,c} \bar{V}_{phhp}(a, k, j, c) r_{ki}^c + \sum_{k,l} \bar{V}_{hhhh}(k, l, i, j) r_{lk}^c \\ &\quad + 0.5 \sum_{k,l,c,d} V_{hhpp}(k, l, c, d) r_{kl}^c t_{ij}^{db} \quad \forall (a, j < i) \end{aligned} \quad (6.13)$$

Here \bar{f} , \bar{V} and $V_{hhpp}(k, l, c, d) t_{ij}^{db}$ stands for one-body, two-body and three-body intermediate diagrams. The diagrams are evaluated by applying intermediate factorization scheme and a detail description can be found in Ref [41]. Since \bar{H} is non-Hermitian in nature, therefore, there exists left eigenstates which are not identical to that of the right eigenstates but they form a bi-orthogonal set, $\langle \Phi_0 | L_\mu R_\nu | \Phi_0 \rangle = \delta_{\mu\nu}$. These eigenstates can be obtained by diagonalizing \bar{H} matrix. Both the left hand solution and the right hand solution leads to same eigenvalues. It is worth to note that for the calculation of energy, solution of any of the eigenstates is sufficient. In relativistic calculation the dimension of the effective Hamiltonian matrix is huge. Therefore, it is not a good idea to follow a full diagonalization scheme. Therefore, we have implemented Davidson algorithm [42] to diagonalize \bar{H} matrix for the right hand solution. However, left eigenstates are required along with the right eigenstates for the calculation of properties in EOMCC framework or to construct density matrix. Convergence is always of concern in the case of open-shell atomic and molecular systems. Therefore, Direct Inversion of Iterative Space (DIIS) method is implemented to achieve a faster convergence for the solution of ground state amplitude equations.

In the case of EOM-MBPT(2), the ground state wave function is characterized at the MBPT(2) level, which require nothing but the first order perturbed wave function. In this scheme the CCSD

amplitudes are approximated at the MBPT(2) level. These amplitudes can be written as

$$T_i^{a'} = \frac{f_{ia}}{\epsilon_i - \epsilon_a}, \quad T_{ij}^{ab'} = \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (6.14)$$

with these non-iterative T' amplitudes one can calculate modified effective \bar{H} . These reduces computational scaling to a non-iterative N^5 instead of iterative N^6 , where N is the number of basis function.

6.3 Computational considerations

In this section, we address some computational aspects of the relativistic EOMCC method in the context of ionization potential. The spinor based EOMCC method as described in the previous section as listed in Eqn. 6.12 and Eqn. 6.13 has been coded as matrix multiplication, which results in a fully vectorized program for these ionization potential calculations. We have generated one-body and two-body matrix elements required for the correlation calculations using DIRAC10 program package [43]. Finite size nucleus is considered in all our calculations. The charge density of the finite size nucleus is defined using Gaussian distribution model. All the parameters for the Gaussian distribution nuclear model is taken as default of DIRAC10 [44]. The scalar, real Gaussian functions are used to construct the finite atomic orbital basis. The wave function in the four-component relativistic theory consists of both large and small component. The small component of the basis is generated by imposing restricted kinetic balance condition (RKB). It generates both the large and small component of the wave function in equivalent amount. The employed RKB scheme properly represents the kinetic energy (KE) solution in the non-relativistic limit and variational collapse is avoided which occurs due to the presence of both electronic and positronic solution [45]. As a results of which real finite eigen spectrum is achieved. In the process free particle Hamiltonian is diagonalized to remove the unphysical solution. The uncontracted basis function better represents the relativistic wave function. Therefore, we have taken the large component of the basis function in un-contracted form and small component is uncontracted in nature by default in DIRAC10. We adopted dyall.ae4z [46] basis for Ag and Au atom in our calculations. In the calculations of Cs [47], Fr [47], and Lr [48] atom we have chosen dyall.cv4z basis. The high energy virtual orbitals contributes very less in a correlation calculation as energy difference

between the virtual orbitals and occupied orbitals appears in the denominator in coupled-cluster method. Therefore, we have fixed a limit of 500 a.u. for the virtual orbital energies in the correlation calculation of Ag and Cs atom. None of the core electrons are frozen for these two atoms. For Au, Fr, and Lr we have frozen 36 inner core electrons and a cutoff of 70 a.u., 26 a.u. and 10 a.u. is fixed for the virtual orbitals, respectively. Besides these atomic systems we have calculated ionization potentials of PbF and HgH. In the case of HgH, we have chosen dyall.cv4z basis for the Hg [47] atom and cc-pCVQZ basis for the H atom [49]. All the orbitals in between -50 a.u. and 40 a.u. is taken into consideration for the correlation calculation. Dyall.cv3z basis is opted for the Pb atom [50] and cc-pCVTZ basis for F [49] and 36 core electrons are frozen for PbF molecule and cutoff of 1700 a.u. is fixed for the virtual orbital energy. We have taken experimental bond length 2.0585 Å for PbF and 1.7660 Å for HgH molecule from Ref. [51]. A cutoff 10^{-12} is fixed while storing the two-body matrix elements required for the ground state energy calculation as contribution of the two-body matrix elements beyond 12 digit after the decimal point is negligible for the correlation calculation. A convergence of 10^{-9} is fixed for the solution of coupled cluster amplitude equation and 10^{-5} in the EOM part. A DIIS space of 6 is used for the solution of ground state amplitude equations.

6.4 Results and Discussion

The numerical results of our calculation are presented to judge the accuracy obtained in our newly implemented open-shell reference relativistic EOMCC method for the single electron ionization problem. We have chosen heavy atomic (Ag, Cs, Au, Fr, Lr) and molecular (HgH, PbF) systems where both the effect of electron correlation and relativistic effects are important to obtain high accurate results. Three different sets of calculation are done for all the considered atomic and molecular systems, viz EOMCC using CCSD ground state wave function as reference, MBPT(2) ground state wave function as reference and RPA calculation on top of CCSD ground state wave function. All these calculated results are compared with the experimental values and with the calculations based on other theoretical means. The intermediate calculation in the four-component EOMCC framework will help us to understand how effect of correlation play role to get good agreement with the sophisticated experiments.

Table 6.1: Basis information and correlation energies in a.u. unit

Atom/ Molecule	Basis	Cutoff (a.u.)	Spinor		Correlation Energy	
			Occupied	Virtual	MBPT(2)	CCSD
Ag	dyall.ae4z	-5000.0, 500.0	47	455	-2.26210408	-2.15131109
Cs	dyall.cv4z	-5000.0, 500.0	55	405	-1.97593327	-1.87228643
Au	dyall.ae4z	-20.0, 70.0	43	389	-2.32397837	-2.06391155
Fr	dyall.cv4z	-30.0, 26.0	51	313	-1.55222794	-1.41702529
Lr	dyall.cv4z	-50.0, 10.0	67	387	-2.01017854	-1.68749396
HgH	Hg : dyall.cv4z H : cc-pCVQZ	-50.0, 40.0	53	399	-2.23826797	-2.00274790
PbF	Pb : dyall.cv3z F : cc-pCVTZ	-25.0, 1700.0	57	417	-1.99440949	-1.79400780

Table 6.2: Experimental and theoretical IP values (in eV) in MBPT(2), RPA and CCSD approximation

System	MBPT(2)	RPA	CCSD	Others	Experiment
Ag	7.5103	7.8180	7.5103	7.5411 [52] 7.2368 [53] 7.3600, 7.4610 [54]	7.5762 [55]
Cs	3.8963	3.9564	3.8996	3.8984, 3.8983, 3.7497 [56] 3.8795 [57, 58]	3.8939 [55]
Au	9.3481	9.7965	9.2138	9.1010, 9.0860, 6.9810 [59] 9.0340, 9.1230 [54]	9.2255 [55]
Fr	4.0822	4.1579	4.0734	4.0715, 3.6041 [56]	4.0727 [55]
Lr	5.2781	6.0437	4.8381	4.8870 [60] 4.8931, 4.8936 [61] 4.9340 [62] 4.963(15) [63]	4.96 ^{+0.08} _{-0.07} [63]
HgH	8.2703	9.2900	8.2618	7.8350, 7.8660, 7.9600 [64]	8.60 ± 0.43 [65]
PbF	7.7491	8.6091	7.5464	6.7756 [66]	7.54(1) [67]

In Table 6.1, we have provided information regarding the basis set employed, cutoff used in the orbital energies for the correlation calculation and the dimension of the determinantal space constructed from number of occupied and virtual orbitals used in the correlation calculation for all the considered atomic and molecular systems. Further, we have reported the correlation energies from both second-order perturbation theory level (MBPT(2)) and using coupled-cluster single- and double- excitation approximation (CCSD) method. It is worth to note that CCSD correlation energy from our calculation is matching up to 7-digit after the decimal place with DIRAC10 irrespective of the choice basis set and the system of study. The discrepancy beyond this limit could be due to the use of different convergence algorithm and the use of cutoff in storing two-body matrix elements.

The calculated ionization potential values of the considered atomic and molecular systems using different approximation scheme in the EOMCC framework are reported in Table 6.2. A comparison of these calculated values is made with the values calculated using other theoretical methods. Finally all these values are compared with the experimental values to judge how different many-body effects play role in getting accurate results in the considered systems.

6.4.1 Ag atom

Ag is a moderate heavy atomic system. Therefore, relativistic treatment is necessary to obtain accurate result. There is a single electron outside of the closed-shell core and the ground state configuration of Ag is $[\text{Kr}]4d^{10}5s^1$. The ionization potential calculated using EOMCC method with CCSD as the ground state reference wave function is 7.5103 eV. The MBPT(2) EOMCC results are identical upto fourth digit after the decimal place with the CCSD results. Therefore, missing dynamic correlation does not have much effect in the calculated ionization potential values of the Ag atom. On the other hand, RPA result is much higher than the CCSD results, since in the RPA scheme, construction and diagonalization of the EOM matrix is done only in the 1-h space, therefore, a major part of the non-dynamic electron correlation is missing. Thus, it can be said that the non-dynamic part of the electron correlation is more important than the dynamic part for Ag atom. Neogrady *et al.* [54] have done ionization potential calculation of Ag atom with $4s^2 4p^6 4d^{10} 5s^1$ shell is used for the correlation calculation and spin free Douglas-Kroll (D-K) Hamiltonian is used for the purpose of relativistic treatment. Two different sets of calculation are done; one with CCSD ground state wave function and other with the consideration of partial triples. There is a difference of 0.1 eV. in these two employed schemes. Therefore, it can be said that consideration of partial triples is important which is evident from Neogrady *et al.*'s calculation. Safronova *et al.* [53] also calculated ionization potential of Ag atom at the level of third order perturbation theory (MBPT(3)) with the consideration of relativistic effect using Dirac-Coulomb-Breit Hamiltonian and the correction due to the Lamb shift is also included. Therefore, the relativistic treatment is far more comprehensive than any other approach but the calculated result is poor in comparison to any other calculation as the effect of electron correlation is not considered using high level of correlated theory. Nayak *et al.* [52] used valence-universal or the Fock space multi-reference coupled cluster theory in their calculation using closed-shell reference CCSD ground state wave function. Their result is 0.03 eV better than our calculated result. They have used 36s30p28d15f primitive GTOs in their calculations whereas we have used dyall.ae4z basis which uses 33s25p17d10f6g3h primitive GTOs. Nayak *et al.* did not used any cutoff for the virtual orbital energies in their calculation but considered Fermi distribution nuclear model to take care of the finite size of the nucleus and exploited spherical symmetry. The spherical implementation allows the separation of

the radial and angular part to use the reduced matrix elements. The calculations based on reduced matrix elements are easy from computational point of view as it only requires evaluation of the radial integrals and the angular part is add up to as a multiplier. The difference between our calculated ionization potential value using CCSD reference wave function with National Institute of Standards and Technology (NIST) database is about 0.06 eV which is in the error limit of 0.9 %.

6.4.2 Cs atom

The alkali metal, Cs has the ground state electronic configuration $[Xe]6s^1$. The effect of relativity will not be that much as compared to Ag atom as there is a single electron outside of a noble gas core, whereas there are ten d-electrons outside of the Kr core in Ag atom. The effect of relativity has much larger influence on the d orbitals than on p orbitals. We have done three sets of calculation for Cs atom and compared with the values calculated by using other theoretical methods and with experimental values. Eliav *et al.* [56] have done three different sets of calculation for Cs atom. They have used both Dirac-Coulomb and Dirac-Coulomb-Breit Hamiltonian in their calculations and one calculation at the non-relativistic limit taking speed of light as 10^5 and the correlation treatment is done using FSMRCC theory starting from a closed-shell CCSD reference wave function. The results calculated using DC Hamiltonian and DCB Hamiltonian is 0.0001 eV. Therefore, the result of their calculation justifies that higher order relativistic effect specially the Breit interaction does not have much effect in the calculated ionization potential value of Cs atom. The difference between non-relativistic and relativistic calculation is only about 0.15 eV. They followed a strategy like $M^+(0, 0) \rightarrow M(0, 1) \rightarrow M^-(0, 2)$ to calculate ionization potential, excitation energy, and electron affinity value of the open-shell system using effective Hamiltonian based relativistic FSMRCC method. Therefore, such an approach is not healthy from the computational point of view. They have correlated ns,(n-1)s,(n-1)p, and (n-1)d orbitals and a cutoff of 100-150 a.u. for the virtual orbital energies whereas we have used 500 a.u. as cutoff and correlated all the electron. Our results calculated using EOMCC method with CCSD reference wave function and the Eliav's results are almost similar. Therefore, deep core orbitals of the alkali metals can be frozen for the correlation calculation as these electrons does not have much influence in the calculated ionization potential values. If we look into our calculated results the MBPT(2) results are very

close to the CCSD results than RPA results but the effect of non-dynamic correlation is not that much what we observed in the case of Ag atom as there is only 0.05 eV. difference between CCSD and RPA results. It can be said that MBPT(2) is better approximation than the RPA for the case of Cs atom also. Blundell and coworker [57, 58] also done ionization potential calculation using a linear version of relativistic CC theory considering single-, double-, and important subset of triple excitation. The difference between their result and the NIST value is about 0.15 eV. Therefore, it can be concluded that non-linear terms have significant contribution to the calculated ionization potential values.

6.4.3 Au atom

The relativistic effect of Au is a well known phenomenon. The non-relativistic calculation of Au shows incorrect results even it results in the reversal the order of first two excited states. Therefore, a relativistic description is must required for calculation of ionization potential of Au atom. The electronic configuration of Au in the ground state is $[Xe]4f^{14}5d^{10}6s^1$. We have done three sets of calculation for the Au atom which is previously mentioned. All these results are compared with the results calculated by Eliav and coworkers [59] and Neogrady *et al.* [54]. Neogrady *et al.* employed spin-free D-K Hamiltonian in their calculations and there is a difference about 0.08 eV. in CCSD and CCSD(T) calculations. Therefore, it can said that triple excitation have significant contribution to the calculated ionization potential value of Au atom. They have considered only the $5p^65d^{10}6s^1$ shell for beyond SCF calculation. If we look at the Eliav *et al.*'s results, the non-relativistic result is totally out of track. There is a difference of about 2 eV. with the experiment. The difference between calculation based on DC Hamiltonian and DCB Hamiltonian is about 0.02 eV, therefore higher order relativistic effect have role in the calculated values. Eliav *et al.* used same strategy in the FSMRCC framework as mentioned in the discussion of Cs atom and used a rather small basis consists of only 21s17p11d7f GTOs. If we look into our calculated results, it can be observed that the non-dynamic part of the electron correlation has larger influence than the dynamic part as the difference between MBPT(2) result and EOMCC is about 0.13 eV whereas it is 0.6 eV for CCSD and RPA. We have achieved a better accuracy using our open-shell reference EOMCC method than the calculation based on FSMRCC by Eliav and coworkers. The error in our

calculation is 0.1 % in comparison to the experimental value.

6.4.4 Fr atom

Fr is heavier than the Au atom but effect of relativity is not that much as the difference between relativistic results and non-relativistic result is about 0.5 eV. in comparison to 2 eV. in the case of Au atom which is obtained from Eliav *et al.* [56] calculations. They employed effective Hamiltonian formalism of the FSMRCC theory to calculate ionization potential values of Fr atom starting from a closed-shell reference ground state wave function. From the reported result of Cs, it is evident that higher order relativistic effects specially the Breit interaction does not have much effect in the case of alkali metal atoms. Eliav *et al.* used well tempered s-basis consists of 36s26p21d15f10g primitive GTOs for the Fr atom. The atomic orbitals having same l value but with different k quantum numbers are expanded using same set of basis functions. The outer orbitals and (n-1)s,(n-1)p, (n-1)d orbitals are correlated and a cutoff 100-150 a.u. is used. The calculated EOMCC results are almost identical to that of FSMRCC results. In our EOMCC calculations it is observed that the difference between MBPT(2) and CCSD results is about 0.01 eV. On the other hand the difference is 0.07 eV for RPA and CCSD. The calculated result justifies that the missing 2h-1p block in the RPA scheme does not have much effect in the calculated ionization potential value of Fr in comparison to what we observe in Ag and Au atom. The accuracy achieved in our EOMCC calculation is 0.02 %.

6.4.5 Lr atom

The effect of relativity play a decisive role in the determination of electronic structure of the heavy elements in the sixth row of the periodic table. This effect is profoundly increases in the seventh row including the actinides. The effect is such that it even alter the ground state electronic configuration. The $s_{1/2}$ and $p_{1/2}$ are stabilized whereas $p_{3/2}$, $d_{5/2}$, $d_{7/2}$ and $f_{7/2}$, $f_{9/2}$ orbitals are destabilized which makes their ground state configuration different from the lighter elements of the same group. The ground state electronic configuration of Lr was debatable for years. A recent successful measurement and theoretical calculation confirmed $[Rn]5f^{14}7s^27p^1$ ground state configuration in contrast to $[Xe]4f^{14}6s^25d$ of its homologue Lu. There are various theoretically calculated value

available for the ionization potential of Lr atom using different variants of relativistic correlated theories. Eliav *et al.* [60] applied effective Hamiltonian variant of the FSMRCC theory to calculate ionization potential value of Lr starting from a closed-shell reference ground state wave function and the relativistic treatment is done using DCB Hamiltonian. They have correlated 5df6spd7sp shell and rest of the inner electrons are frozen. A cutoff of 100 a.u. is used for the virtual orbital energies and they got 4.8870 eV. as ionization potential value of Lr. Borschevsky *et al.* [61] applied intermediate Hamiltonian variant of the FSMRCC theory using a larger model space using DCB Hamiltonian. The inclusion of QED effect does not have much effect in the calculated ionization potential value as there is a change of 0.0005 eV. with inclusion of the QED effects. The QED effects are important for the highly charged ion rather than neutral or mono-cationic ions. They used universal basis set with even-tempered Gaussian type of orbitals (37s, 31p, 26d, 21f, 16g, 11h, and 6i orbitals) in uncontracted fashion with a cutoff of 200 a.u. for the virtual orbital energies and correlated only 43 outer electrons in their calculation and got 4.8931 eV. as the valence ionization potential value. Dzuba *et al.* [62] applied CI+all order method to calculate ionization potential of Lr atom. In this approach ground state wave function is constructed using linearized version of the CCSD method. The correlation between valence electrons are treated with CI while core-valence electron correlation is taken care by the linearized version of CCSD method. The relativistic effect is taken care using DCB Hamiltonian with inclusion of QED effect and 4.9340 eV. is obtained as the ionization potential value. The approach can be regarded as the Hilbert space analogue of the EOMCC method which is a Fock space approach. If we look into our results, the difference between EOMCC result and that of the latest experiment is about 0.13 eV. This difference could be reduced with the inclusion of larger correction space as we have only taken 10 a.u. as virtual orbital energy cutoff, missing Breit interaction, triple excitation or the finite size of the basis. Although it is difficult blame any of the effect as all these effects are intricately coupled to each other. There is a difference of more than 1 eV. between CCSD and RPA values but MBPT(2) result is more accurate than RPA though effect is quite high. Therefore, it can be inferred that both dynamic and non-dynamic correlation effect have greater role in Lr.

The best result in accordance to the measured value is obtained using delta CCSD(T) method with DC Hamiltonian plus the Breit correction and Lamb Shift [63]. The Breit correction (-12

meV) and the Lamb shift (16 meV) does not have much effect on the calculated IP value. Two different calculation are done, one for the neutral atom and one for the mono-cationic ion and the difference is reported as the IP value of Lr atom. The EOMCC approach due to its CI like structure is capable of taking care of non-dynamic electron correction elegantly and performs better in comparison to Δ CC approach. However, the treatment of dynamic correlation is inferior with CCSD ground state wave function since a complete treatment of doubly excited configuration relative to the reference determinant require at least a part of the T_3 operator. Lr is very heavy atomic system, therefore there is a huge contribution of the relaxation effect in the computed ionization potential value and the Δ based methods are capable of taking account of the relaxation effect much better than any energy difference method.

6.4.6 HgH

The results for HgH using all three variant of the relativistic EOMCC method using open-shell reference wave function is compiled in Table 6.2. We have compared our calculated results with the values from experiment and other theoretically calculated values. The outcome of our calculation shows that MBPT(2) results are very close to CCSD result on the other hand, RPA result is differing about 1 eV with CCSD results. Our calculated CCSD results are in best agreement with the experiment though there is a huge uncertainty in the measured value. Häussermann *et al* [64] calculated IP of HgH using quasi-relativistic pseudo-potential method with correlation treatment is done using CISD, MRCI and CASSCF+MRCI with the addition of QED effects. It is true that there is not much effect of QED in neutral molecule. The result of their calculation lacks both proper relativistic treatment and electron correction. As a result of which the calculated results in all three approach are not in accordance with the experimental value.

6.4.7 PbF

PbF has the ground state term $^2\Pi_{1/2}$, that means the unpaired electron is in the π orbital. We have calculated valence IP value of PbF using different approximation scheme in the relativistic EOMCC framework starting from a open-shell reference wave function and presented the result in Table 6.2 along with other atomic or molecular systems. We have compared our results with

Kozlov *et al.*'s [65] result and with the experimentally reported value. Our CCSD result is found to be more accurate than them. The MBPT(2) result is very close to the CCSD result whereas RPA results are very poor. Therefore, it can be inferred that non-dynamic electron correlation is dominant in PbF than that of dynamic part. Our CCSD result is in the accuracy of 0.1 %.

6.5 Conclusion

We have successfully implemented relativistic equation-of-motion coupled cluster method using Dirac-Coulomb Hamiltonian to calculate ionization potential values of open shell atomic and molecular systems. The calculated results are found to be in nice agreement with the experimental values. The calculated MBPT(2) results are much closer to the CCSD results than RPA results. Therefore, it can be inferred that non-dynamic correlation have greater effects than the missing dynamic part in the computed ionization potential values of the heavier systems.

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Chapter 7

Summary of the Thesis

The main goal of the thesis was to develop a highly correlated relativistic method applicable to both atomic and molecular systems starting from a closed-shell as well as open-shell reference wave function for the purpose of accurate calculations of spectroscopic properties. We have successfully implemented and applied relativistic equation-of-motion coupled-cluster (EOMCC) for the calculations of ionization potential, double-ionization potential, and electron affinity of atoms and molecules using four-component Dirac spinors. The consideration of Dirac-Coulomb Hamiltonian is sufficient for the inclusion of the effects of relativity for most of the chemical purposes. Therefore, we have employed Dirac-Coulomb Hamiltonian for the generation of one-body and two-body matrix elements required for the correlation calculations. On the other hand, the performance of the (EOMCC) method is well tested for the treatment of electron correlation effects in the non-relativistic domain. In EOMCC method the reference wave function is generally constructed using single-reference coupled-cluster method which is very elegant for the treatment of dynamic part of the electron correlation. Therefore, we have considered coupled-cluster single- and double- excitation approximation (CCSD) for the construction of reference wave function. We even constructed ground state wave function using first-order perturbed wave function, which corresponds to the second-order perturbation energy (MBPT2) as the ground state energy, and also taken approximation in the EOM part to understand the role of electron correlation.