STUDY OF MAGNETIC PROPERTIES OF MOLECULES USING COUPLED-CLUSTER THEORY

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University of Pune
for the Degree of

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Chemsitry

By

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CERTIFICATE

CERTIFIED THAT the work done in the thesis entitled,

Study of magnetic properties of molecules using coupled-cluster theory

submitted by **R. Lalitha** was carried out by the candidate under my supervision in the Physical Chemsitry Division, National Chemical Laboratory, Pune 411008, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date:
Place:

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(Research Superviser)

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Date:
Place:

Dr. Nayana Vaval
(Research co-superviser)

DECLARATION

I hereby declare that the work incorporated in the thesis entiled

Study of magnetic properties of molecules using coupled-cluster theory

submitted by me to **University of Pune** for the degree of Doctor of Philosophy is original and has not been submitted to this or other University or Institution for the award of Degree or Diploma. Such material, as has been obtained from other sources has been duly acknowledged.

R. Lalitha

for my parents

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"Knowledge is in the end based on acknowledgement"

-Ludwig Wittgenstein

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Lalitha

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Abstract

Coupled cluster(CC) [1] method has evolved as the most accurate and reliable computational method for energy and energy derivatives. The first main focus of this thesis is to develop and implement the coupled cluster(CC) method for the accurate calculation of magnetic properties of molecules. Second focus is on the implementation of higher order correction in Λ-FSMRCC method for first order property.

The single reference coupled cluster(SRCC) method has been successful in describing energy, gradients and molecular properties around equilibrium geometry [2–5]. The method is non-variational and it has built in size-extensivity and size-consistency property. However, SRCC gives accurate energy even at the truncated level, most often we are interested in obtaining the energy differences and derivatives. The analytic response approach for energy derivatives in SRCC context was developed first by Monkhorst [5]. The non-variational SRCC response approach did not have a (2n+1) rule [6] inherent in it. As a result, the evaluation of the energy derivatives turns complicated, that is the expression for the first order energy derivative involves the derivative of the first order wave function. However, the dependence of derivative amplitudes with respect to different perturbation can be avoided with the help of an additional perturbation independent amplitudes. This is known as Z-vector approach, which was first introduced in configuration interaction (CI) method by Handy and Schaefer [7]. Later this technique was implemented in the context of CC by Bartlett and coworkers [3]. Z-vector technique simplified the CC response approach, in particular for gradients. However, extension of this technique to higer derivatives is tedious. On the other hand, Jorgensen et al [4] proposed a conceptually different approach called constrained variational approach(CVA). In CVA, the Lagrangian is constructed with SRCC equations as constraints. The form of the Lagrangian is

$$\Im(\Theta) = \langle\phi_0|e^{-T}\hat{H}e^{T}|\phi_0\rangle + \sum_{q\neq 0}\lambda_q\langle\phi_q|e^{-T}\hat{H}e^{T}|\phi_0\rangle. \quad (1)$$

The variation of Lagrangian with respect to Lagrange multipliers (λ_q) gives SRCC amplitude equations, while variation with respect to cluster amplitudes gives equations for Lagrange multipliers. It is known that both the approaches are equivalent. A major advantage of CVA is, being variational it satisfies (2n+1) rule for cluster amplitudes and (2n+2) rule for Lagrange multipliers. This approach can easily be extended for higher order properties.

The thrid approach is a fully variational approach. This was implemented for energy derivatives by Bartlett and coworkers and Pal and coworkers. In this approach, form of the functional is very important. Various functionals exists in literature namely, expectation value CC (XCC) [8], Unitary CC (UCC) [9] and extended CC (ECC) [10]. XCC and UCC were studied for energy and energy derivatives. Pal and coworkers implemented variational response approach with XCC and ECC functionals [11, 12]. Among these ECC method proposed by Arponen [10] is based on the double similarity transformation and has been very efficient for molecular property evaluation of closed shell molecules. The functional form of ECC is

$$E = \langle \phi_0 | e^{\tilde{\Sigma}} e^{-\tilde{T}} \hat{H} e^{\tilde{T}} e^{-\tilde{\Sigma}} | \phi_0 \rangle_{DL}. \tag{2}$$

The double similarity transformed energy functional leads to double linking of the functional after the additional transformation on the right vectors. The double linking of the left vectors and the connectedness of the Hamiltonian to the right vector ensures natural termination of the series and the size-extensivity in the equation of the cluster amplitudes. The amplitudes are obtained by varying energy functional with respect to right and left vectors. Despite being size-extensive, ECC is not quite useful for energy. This is because it contains double the number of coupled cluster amplitudes as well as number of equations as compared to single reference CC. But due to its variational nature, Hellmann-Feynman theorem holds and (2n+1) rule is applied for evaluating response properties. The response properties in ECC are pursued extensively by Pal and coworkers [12].

The single reference based methods despite of being size-extensive and size-consistent,

fails to describe the quasi-degenerate situations such as potential energy surfaces at bond-breaking/bond-stretching regions, open shell atomic states and low-lying excited states of molecules has led to the multi reference(MR) based theories [13, 14]. The multi-determinantal or multi-reference based methods well describe quasi-degeneracy through the pre-chosen model space consisting of important determinants. Among the multi-reference methods, effective Hamiltonian based MRCC methods, provide multiple roots via diagonalization of the effective Hamiltonian within the model space. This subclass mainly spans two approaches: namely the Hilbert space (HS) MRCC [13] and Fock-space (FS) MRCC [14]. Both differ in the nature of ansatz used for the wave-operator and both the methods are size-extensive, and hence are suitable for different types of situations. FSMRCC is based on the concept of a common vacuum and assumes a valence universal wave operator to describe the various states, which are generated by addition and/or removal of electron to/from the common vacuum, usually the closed-shell RHF configuration. FS methods are suitable for the difference energy calculations and thus describe ionized, electron-attached, or excited states of a closed-shell system [15].

A response approach similar to Monkhorst's non-variational CC is developed and implemented for FSMRCC method by Pal [16]. This was not pursued because of the explicit dependence of the first order derivative cluster amplitudes in the first order property. To solve this problem, a Z-vector type approach was attempted by Ajitha and Pal [17], but this proved satisfactory in eliminating wave-function derivatives only in limited cases. Along the lines of SRCC, the constrained variation approach based on Lagrange multipliers has been developed in MRCC framework (Λ-MRCC) [18]. This was also pursued independently by Szalay and coworkers [19]. Though in principle Szalay's approach can be used for general model spaces, this was implemented only for complete model spaces. But the one proposed by Pal and coworkers has been applicable for general incomplete model spaces. The Λ-FSMRCC method was implemented successfully for electric based properties of doublet states as well as the excited states of molecules [20].

It is well known that triple excitations in SRCC contribute to the energy from fourth order onwards. So far different version of the SRCC method with full or partial inclusion of triples with increasing precision have been developed for energy [21]. The non-iterative triples are routinely used for high accuracy with an economical treatment of triples. The full inclusion of triples is expensive, though in the SRCC it has been implemented by Bartlett and co-workers for energy. The perturbative treatment of the quadruple excitations has also been attempted in single reference context [22]. There are several implementations of the full and partial inclusion of the triples within the Fock space MRCC [23]. Pal and co-workers included non-iterative triples for ionization potential and excitation energies, within Fock space MRCC scheme and Bartlett and co-workers included full triples correction for excitation energies. However, to improve the accuracy of the molecular properties of the outer valence as well as some of the inner valence states, it is important to include the effect of triples. However, inclusion of full triples is computationally expensive. This limits the applicability of the method to small molecules or to moderate basis sets. The non-iterative triples based on perturbative order, does not guarantee the improvement of molecular properties towards the Full CI (FCI), due to oscillatory nature of the perturbation series.

As we know, many important molecular properties are defined as the derivatives of the molecular energy [24]. The second derivative of energy with the magnetic field is termed as the molecular susceptibility. The second derivative of the molecular energy with the nuclear magnetic moment and the magnetic field is termed as the nuclear magnetic resonance(NMR) shielding constant.

The evaluation of magnetic properties are not straight forward like electric based properties because of two factors. First, the nature of the magnetic field is purely imaginary and hence the finite-difference procedures using the complex wavefunction for calculating the magnetic properties are highly undesirable. We need the analytical method for magnetic properties calculation. The method should efficiently include the fact that the matrix representation of the imaginary quantities is antisymmetric. Secondly, the

electric field interacts with the charged particles (electron and nuclei) and adds a scalar potential to the Hamiltonian operator. However, magnetic field interacts with the magnetic moments generated by the movement of the charged particles and hence adds a vector potential to the Hamiltonian. A vector potential is a vector function from which the magnetic field is derived. This vector potential is not uniquely defined since the gradient of any arbitrary scalar function may be added to the vector potential and leave the field unchanged (gauge invariance). Hence a proper gauge should be chosen or the gauge independent atomic orbitals(GIAO) [25] should be used to eliminate this problem.

The motivation of this thesis is to evaluate the magnetizabilities and NMR shielding constants using these highly effecient methods for closed and open-shell molecules. The first attempt of GIAO in ECC method is also presented. Along with this, the new implementation of partial triples for the dipole moment of doublet radicals in Lagrangian formulation of FSMRCC (Λ-FSMRCC) response method has also been presented.

The thesis is organized as follows:

CHAPTER I : This chapter includes a brief overview of many-body methods starting from Hartree-Fock approach. Eventually, in this chapter evaluation of magnetic properties using various correlated methods are presented in details. This involves the insight of the coupled-cluster methods both single reference based and multi-reference based and its energy derivatives. We also discuss the correlated methods used in the literature for magnetic properties evaluation such as perturbation theory, linearized coupled cluster(L-CC), multiconfigurational self-consistent-field (MCSCF), CCSD, CCSD(T) and equation of motion CC (EOMCC).

CHAPTER II : This chapter presents calculation of the nuclear magnetic shielding constant using ECC approach. We present the results for the HF, BH, CO and N_2 molecules using standard atom-centered Gaussian basis functions and choosing proper gauge as origin. The results reflect the importance of correlation corrections for the shielding constant.

CHAPTER III : This chapter deals with the details of the FSMRCC method and

Lagrangian technique method for properties. Along with the details, first implementation of the recently developed FSMRCC response approach for magnetizabilities is discussed. The FSMRCC treats dynamic and static correlation in a very extensive manner. We report pilot application of the dia-magnetizability of NO, NO_2, OH and BH_2 radicals. We also report preliminary applications of the paramagnetic magnetizability of the NO radical. Standard atom-centered Gaussian basis functions have been used and this allowed us to study the gauge-dependence of the magnetizabilities.

CHAPTER IV : This chapter says the importance of triples correction to the FSMRCC method. The new implementation of partial triples for the dipole moment of doublet radicals in Lagrangian formulation of FSMRCC (Λ-FSMRCC) response method has been presented. We have implemented a specific scheme of non-iterative triples, in addition to singles and doubles scheme, which accounts for the effects appearing at least at the third order in dipole moments. The method is applied to the ground states of OH, OOH, HCOO, CN, CH, NH_2 and PO radicals.

CHAPTER V : In this chapter we present implementation of GIAO-ECC method. The test results are presented for HF, BH and N_2 molecules. The shielding tensors obtained with and without GIAO are presented and compared. The summary of the present thesis is presented. The future perspective in this field is given, which will lead the pavement for the evaluation of other properties.

References

[1] F. Coester, *Nucl. Phys.* **7**, 421 (1958); F. Coester and H. Kummel, *Nucl. Phys.* **17**, 477 (1960); J. Cizek, *Adv. Chem. Phys.* **14**, 35 (1969); J. Cizek, *J. Chem. Phys.* **45**, 4256 (1966); J. Cizek and J. Paldus *Int. J. Quantum Chem.* **5**, 359 (1971); J. Paldus, J. Cizek and I. Shavitt *Phys. Rev. A* **5**, 50 (1972).

[2] R. J. Bartlett, *Ann. Rev. Phys. Chem.* **32**, 359 (1981); R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jorgensen, J. Simons, (Reidel, Dordrecht, The Netherlands, 1986), pp. 3561. A. C. Scheiner , G. E. Scuseria, J. E. Rice, T.J. Lee and H. F. Schaefer, *J. Chem. Phys.* **87**, 5361 (1987); R. J. Bartlett, *Modern Electronic Structure Theory*, Vol 2 edited by D. R. Yarkony, (World Scientific, Singapore, 1995) pp. 1047.

[3] L. Adamowicz, W. D. Laidig and R. J. Bartlett, *Int. J. Quantum Chem.* **S18**, 245 (1984); E. A. Salter, G. W. Trucks and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989)

[4] T. Helgaker and P. Jorgensen, *Adv. Quantum Chem.* **19**, 183 (1988); H. Koch, H. J. Aa. Jensen, P, Jorgensen, T. Helgaker, G. E. Scuseria and H. F. Schaefer, *J. Chem. Phys.* **92**, 4924 (1990).

[5] H. J. Monkhorst, *Int. J. Quantum Chem.* **S11**, 421 (1977).

[6] S. T. Epstein, *The Variation principle in Quantum Chemistry* (Academic, New york, 1974).

[7] N. Handy and H. F. Schaefer, *J. Chem. Phys.* **81**, 5031 (1984).

[8] R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988).

[9] W. Kutzelnigg, *Theor. Chim. Acta* **80**, 349 (1991).

[10] J. Arponen, *Ann. Phys.* **151**, 311 (1983).

[11] K. Ghose, P. Nair and S. Pal, *Chem. Phys. Letts.* **211**, 15 (1993); N. Vaval, K. Ghose, P. Nair and S. Pal, *Proc. Indian. Acad. Science* **106**, 387 (1994).

[12] N. Vaval and S. Pal, *Phys. Rev. A* **54**, 250 (1996); N. Vaval, A. B. Kumar and S. Pal, *Int. J. Mol. Sci.* **2**, 89 (2001).

[13] B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1982); A. Balkova, S. A. Kucharski, L. Meissner and R. J. Bartlett, *J. Chem. Phys.* **95**, 4311 (1991).

[14] I. Lindgren and D. Mukherjee, *Phys. Rep.* **151**, 93 (1987); D. Mukherjee, R. K. Moitra and A. Mukhopadhyay, *Mol. Phys.* **30**, 1861 (1975); W. Kutzelnigg *J. Chem. Phys.* **77**, 3081 (1982);

[15] D. Mukherjee and S. Pal, *Adv. Quantum Chem.* **20**, 291 (1989).

[16] S. Pal, *Phys. Rev. A.* **39**, 39 (1989); S. Pal, *Int. J. Quantum Chem.* **41**, 443 (1992).

[17] D. Ajitha and S. Pal, *J. Chem. Phys.* **111**, 3832 (1999).

[18] K. R. Shamasundar, S. Asokan and S. Pal, *J. Chem. Phys.* **120**, 6381 (2004).

[19] P. Szalay, *Int. J. Quantum Chem.* **55**, 151 (1995).

[20] P. U. Manohar, N. Vaval and S. Pal, *J. Mol. Struct.* THEOCHEM, **91**, 768 (2006); P. U. Manohar and S. Pal, *Chem. Phys. Lett.* **438**, 321 (2007); A. Bag, P. U. Manohar, N. Vaval and S. Pal, *J. Chem. Phys.* **131**, 024102 (2009).

[21] M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985); J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989); S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 5243 (1998).

[22] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990). Y. J. Bomble, J. F. Stanton, M. Kallay and J. Gauss, *J. Chem. Phys.* **123**, 054101 (2005).

[23] S. Pal, M. Rittby, R. J. Bartlett, *Chem. Phys. Lett.* **160**, 212 (1989); N. Vaval, K. B. Ghose, S. Pal and D. Mukherjee, *Chem. Phys. Lett.* **209**, 292 (1993); N. Vaval, S. Pal and D. Mukherjee, *Theor. Chem. Acc.* **99**, 100 (1998); M. Musial, and R. J. Bartlett, *J. Chem. Phys.* **129**, 244111 (2008).

[24] C. Dykstra, in *Ab initio calculation of the structures and properties of molecules* (Elsevier Science Publiser, B. V., 1988); P. Atkins and R. Friedman, in *Molecular quantum mechanics*, fourth edition, (Oxford University Press, 2005); W. Kutzelnigg, *J. Mol. Struct.* THEOCHEM, **202**, 11 (1989).

[25] F. London, *J. Phys. Radium.* **8**, 397 (1937); R. Ditchfield, *Mol. Phys.* **27**,789 (1974); *J. Am. Chem. Soc.* K. Wolinski, J. F. Hinton and P. Pulay, **112**, 8251 (1990).

List of Publications

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Chapter 1

A brief Overview: Ab-initio methods and molecular magnetic properties

1.1 Introduction

Chemistry is the science dealing with construction, transformation and properties of molecules. Theoretical chemistry is the subfield where mathematical methods are combined with fundamental laws of physics to study processes of chemical relevance. Theoretical chemistry has attained significant improvements in past few decades. A very important conceptual advance in theoretical field was achieved by the exploitation of the variation principle, which led to the formulation of Hartree-Fock(HF) equations. The HF method gives 99$\%$ of the total energy, and still not accurate enough to describe many chemical phenomena or properties of interest. This paved the way for "many electron" methods like configuration interaction(CI), many body perturbation theory(MBPT) and coupled cluster (CC) methods [1]. All these methods are grouped as single-reference methods(SR). Among all these, coupled cluster [2, 3] method has gained a special attention due to its size-extensivity, size-consistency and the correct treatment of electron correlation effects. The double similarity transformed single reference based CC known as extended CC (ECC) has been extensively developed and used for molecular properties. However, for quasi-degenerate cases SR methods fails. The restricted open-shell (RO)- based CC methods, which uses linear operator have been successful in describing the quasi-degenerate cases. Though in single reference framework, selected triples and quadruple level excitations have been considered for quasi-degenerate cases, multi-determinantal or multi-reference coupled cluster (MRCC) [4–10] methods have emerged as the method of choice to take into account the quasi-degenerate molecular systems. Analytical evaluation of accurate properties using this method is more demanding due to the successive evaluation of higher derivatives. In this thesis we present the analytical evaluation of magnetic properties using CC method.

Unlike the electric properties, the evaluation of magnetic properties is not so straightforward. Hamiltonian of the system in the presence of external magnetic field depends on the gauge of the magnetic vector potential [11, 12]. Various attempts were made earlier at self-consistent field (SCF) [13] level as well as correlated levels [14] to eliminate the problem of gauge-variance of magnetic properties to some extent by using extended basis set of field-independent atomic orbitals, so that the results are almost gauge-invariant at the complete basis set limit. However, computationally this approach is quite time consuming, since the basis set required for reasonably accurate results is quite big even for small molecules. To eliminate the gauge problem various other studies have been proposed by making use of field-dependent orbitals. This starts with the work of Kutzelnigg on individual gauge for localized orbitals (IGLO) [15]. For several reasons the gauge-including atomic orbitals (GIAO) approach [16, 17] has become the standard method for quantum chemical applications. This solution to the gauge problem was first advocated by London [16] in the context of magnetic susceptibilities and later used by Hameka [18], Ditchfield [19] and others for chemical shifts [20].

The aim of the present chapter is to give a brief over-view of ab-initio methods and their development for properties. In particular, the literature towards chemical shieldings and susceptibilities are discussed. A brief discussion on importance and developments of higher order amplitudes are also presented.

1.2 Basis of quantum Chemistry

Electronic structure of atoms and molecules are studied by solving time-independent Schrödinger equation proposed in 1926. In Dirac notation Schrödinger equation is written as

$$H|\psi\rangle = E|\psi\rangle. \tag{1.1}$$

In this form it is easy to demonstrate that the expectation value of the above Hamiltonian gives energy. For a system of interacting electrons and nuclei, $\hat{H}$ in au is [1]

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \frac{1}{2}\sum_A \frac{1}{M_A}\nabla_A^2 - \sum_i\sum_A \frac{Z_A}{r_{iA}} + \sum_i\sum_{j>i}\frac{1}{r_{ij}} + \sum_A\sum_{B>A}\frac{Z_A Z_B}{R_{AB}}. \tag{1.2}$$

Where *i* indexes the electrons, *A* indexes the nuclei. By introducing Born-Oppenheimer(BO) approximation [21], the above Hamiltonian is simplified. Born-Oppenheimer approximation states that, since the nuclei are approximately 1800 times as massive as electrons, they can be considered as stationary points, and electrons move in their constant potential field. Under this the second term in eq.1.2 is zero, since the nuclei have no kinetic energy, and the last term is constant, since the distance between the nuclei will not change. Thus eq.1.2 is reduced to

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i\sum_A \frac{Z_A}{r_{iA}} + \sum_i\sum_{j>i}\frac{1}{r_{ij}}. \tag{1.3}$$

$$H = \sum_i h(i) + \sum_{j>i} g(ij) \tag{1.4}$$

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}; g(ij) = \sum_i \frac{1}{r_{ij}} \tag{1.5}$$

where $h(i)$ is one electron term and $g(ij)$ is two electron term. If the two-electron terms $g(ij)$ were absent, H would be a sum of terms each depending only on the coordinates of one electron. Then H would be additively separable. Its eigenfunctions would be just products of eigenfunctions of the one-particle Hamiltonian $h(i)$ and its eigenvalues are sums of eigenvalues of $h(i)$. Unfortunately, H contains the two-electron repulsion terms $g(ij)$ and they are by no means small and cannot be simply neglected.

1.3 Many-electron wave function and molecular Hamiltonian

Another technique used to simplify Schrödinger equation is called the orbital approximation, where the many-electron wave function is written as the product of one-electron wave functions. Many-electron wave function for N electron system is written as

$$\Psi = \Psi_1(1)\Psi_2(2)\Psi_3(3)...\Psi_N(N). \tag{1.6}$$

This product form is known as Hartree [22] product and Ψ_i is called spacial orbital. According to Born interpretation of the wave function, the spacial probability density is $|\Psi|^2 d\tau$, where $d\tau$ is an element of volume. If the wave function is written as a Hartree product, then this probability density must be the product of the squares of the individual orbitals. According to probability theory, this can only be true if the probability represented by the individual orbitals are independent of one another. Hartree product is also known as the independent-electron wave function.

1.4 Antisymmetry and the Slater method

According to Pauli's exclusion principle, no two electrons in an atom can have the same set of quantum numbers. Since electrons have spin quantum number of $\pm 1/2$, this means each orbital can have two electrons with one up-spin and one down-spin. This condition arises naturally, if we assume the nature of the wave function to be antisymmetric i.e., the wave function changes sign when the two electronic coordinates are interchanged

$$\Psi(x_1, ..., x_i, ..., x_j, ..., x_N) = -\Psi(x_1, ..., x_j, ..., x_i, ..., x_N). \tag{1.7}$$

It is apparent from the Hartree form of the wave function 1.6 that it is not antisymmetric. Although various ways to expand the antisymmetric wave function are available, ubiquitous in quantum chemistry is the expansion in terms of Slater determinant.

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \parallel \chi_i(x_1), \chi_j(x_2), ..., \chi_k(x_N) \parallel \tag{1.8}$$

where χ_i's are spin orbitals. Here the rows are labeled by electrons and columns are labeled by spin orbital. Slater determinant incorporates exchange correlation, which means that the motion of two electrons with parallel spins is correlated. This is known as *Fermi hole*. The concept of Fermi hole emerges from the Fermi-Dirac statistics obeyed by electrons and according to this, probability of finding two electrons with parallel spin at the same point in space is zero. This is an important feature of many-electron wave function. Another feature is the presence of coulomb hole. The concept of *coulomb hole* emerges from the coulombic repulsion of electrons, which leads to probability of finding two electrons at the same point in space is zero. Within the single determinant description, the motion of electrons with parallel spins is correlated but the motion of electrons with opposite spins is not. However, the Fermi hole also includes the corresponding Coulomb hole to some extent.

1.5 Glimpse of Hartree-Fock method

If it was possible to write the Hamiltonian in eq.1.3, as the sum of one-electron terms, then the solution of the Schrödinger's equation would be a simple task by separation of variables. As the Hamiltonian depends on $\frac{1}{r_{ij}}$, which means that we must know the instantaneous relative positions of two electrons. Therefore, the full Hamiltonian cannot be written as the sum of one-electron Hamiltonians. However, the best solution within the class of simple independent particle model wave function can be obtained by a spherical averaging of inter electronic interactions. This is known as the Hartree Fock potential.

$$H_{approx} = \sum_i [\frac{1}{2}\nabla_i^2 + V(i)] \tag{1.9}$$

where, $V(i)$ is some average potential resulting from the field of other electrons from the system. As written, this approximate Hamiltonian does not explicitly include electron correlation, which is the instantaneous interaction of pairs of electrons. This $V(i)$ includes the classical coulomb and exchange potentials. The N-electron expectation value of this Hamiltonian with antisymmetrized single determinant in eq.1.8 gives

$$\langle\Psi|H|\Psi\rangle = \sum_i^N \langle i|h|i\rangle + \frac{1}{2}\sum_{i\neq j}^N [\langle ij|ij\rangle - \langle ij|ji\rangle]. \tag{1.10}$$

where the following one- and two-electron integrals occur. One-electron integral is

$$\langle i|h|i\rangle = \int \chi_i^*(1)h(1)\chi_i(1)d\tau. \tag{1.11}$$

The two-electron Coulomb-integral part is

$$\langle ij|ij\rangle = \int \chi_i^*(1)\chi_j^*(2)\frac{1}{r_{12}}\chi_i(1)\chi_j(2)d\tau. \tag{1.12}$$

The two-electron exchange-integral part is

$$\langle ij|ji\rangle = \int \chi_i^*(1)\chi_j^*(2)\frac{1}{r_{12}}\chi_j(1)\chi_i(2)d\tau. \tag{1.13}$$

Coulomb-integral corresponds exactly to the classical Coulomb interaction between two charge distributions. The exchange interaction has no classical analogue and is a consequence of the antisymmetry requirement to the quantum mechanical wave function.

To find the best spin orbital, one has to apply variation principle to the wave function and vary the energy expectation value in eq.1.10 with Ψ as a functional of the occupied orbitals χ_i. This is achieved through minimization of the Lagragian defined as,

$$\pounds = \langle\Psi|H|\Psi\rangle + \sum_{i,j} \varepsilon_{ij}[\langle\chi_i|\chi_j\rangle - \delta_{ij}] \tag{1.14}$$

with respect to the spin orbitals χ_i. The minimum of this functional is obtained by varying the spin orbitals χ_i. The coefficients ε_{ij} is the Lagragian multipliers. By performing variation, one arrives at the following one-particle pseudo eigenvalue equation

$$\hat{f}|\chi_i\rangle = \varepsilon_i|\chi_i\rangle. \tag{1.15}$$

Here, $\chi_i; i = 1, 2..., N$ are orthonormal set of spin orbitals, ε_i is orbital energy and $\hat{f}$ is the effective one-electron operator called as Fock operator.

$$\hat{f}(1) = h(1) + \sum_j^N [J_j(1) - K_j(1)] \tag{1.16}$$

Where J_j and K_j are coulomb and exchange terms

$$J_j(1)\chi_i(1) = \int \chi_j^*(2)\chi_j(2)\frac{1}{r_{12}}\chi_i(1)dx_2 \tag{1.17}$$

$$K_j(1)\chi_i(1) = \int \chi_j^*(2)\chi_i(2)\frac{1}{r_{12}}\chi_j(1)dx_2 \tag{1.18}$$

The equation 1.15 is the Hartree-Fock(HF) equation which plays the role of a one-electron Schrödinger equation for the orbitals χ_i. The main features of the HF equation is follows. The HF equation is an integro-differential equation. Since the Coulomb and exchange operators have to be determined by solving HF equation, iterative procedure called Self-consistent field method(SCF) is used to solve HF equation. The ground state of the N electron system is obtained if the energetically lowest HF orbitals are occupied in Ψ. Generally, one distinguishes between occupied orbitals as those orbitals occupied in Ψ, which are used to construct J and K operators and virtual orbitals which are not occupied in Ψ. The virtual orbitals are not optimized orbitals, since the energy expectation value does not depend on them at all. They are however frequently used for electronically excited states. The eigenvalues ε_i of the HF equation are called orbital energies. The orbital energies of the occupied orbitals can be identified by the *Koopmans theorem* The Koopmans' theorem states that the orbital energy of the i-th occupied orbital is equal to the negative value of the energy necessary to remove one-electron from orbital (Ionization potential). Likewise, electron affinities can be related to energies of unoccupied orbitals.

If all the electrons are paired in the HF determinant, the corresponding method is referred to as closed-shell or restricted HF (RHF) method. If there are one or more unpaired electrons, it is referred to as restricted open-shell Hartree-Fock (or ROHF) method. On the other hand, use of unrestricted set of orbitals results in unrestricted HF (UHF) method. The RHF theory has few shortcomings. First, it can not always provide the proper dissociation of molecules. For example, the dissociation of the H_2 molecule, where "dissociation catastrophe" occurs because the separated hydrogen atoms cannot be described using doubly occupied orbitals. Because in this case H_2 tends to dissociate in H^+ and H^-. This problem does not occur in the UHF method. However, this has the disadvantage that it does not give pure spin states. Second, the HF wave functions takes care of Fermi hole, but not able to account the Coulomb hole. This can be taken care of by higher level theories, which includes electron correlation.

The essence of HF approximation is that it involves replacement of the complicated many-electron problem by an effective one-electron problem in which electron repulsion is treated in an average way. This leads to a simple picture of molecular orbital (MO) theory with electrons occupying different orbitals. HF theory is a common starting point for many more advanced theoretical methods, some of them are outlined in the next section.

1.6 Correlation energy and configuration interaction

The Hartree-Fock method is an approximation to the exact solution of the Schrödinger equation. In many cases, for yielding accurate results one has to go beyond the HF method. All effects beyond the HF level are called as *"correlation"* effects. It arises due to the fact that HF method is still an effective one-particle (or mean-field) method and can not fully account for instantaneous electron repulsion. The correlation energy of a system as defined by Lowdin [23] is the difference between the exact energy eigenvalue of the N-electron Hamiltonian and the SCF energy

$$E_{corr} = E - E_{SCF}. \tag{1.19}$$

The conceptually simplest method to account for correlation effects is the method of *configuration interaction* (CI).

Here the main idea is based on the lemma, that the N-electron wave function is constructed as linear combination of Slater determinants.

$$\Psi(x_1, x_2, ..., x_N) = \sum_{I=1}^{\infty} C_I \phi_I(x_1, x_2, ..., x_N) \tag{1.20}$$

where C_I's are linear coefficients, which are determined by the variational optimization(linear variation) of the expectation value of the energy

$$\frac{\partial}{\partial C_I} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 0. \tag{1.21}$$

It is possible to rewrite Eq.1.20 in terms of the reference ϕ_0 and different excited determinants obtained from systematically replacing increasing number of occupied orbitals in ϕ_0 by virtual orbitals.

$$\Psi = \phi_0 + \sum_{a,r} C_a^r \phi_a^r + \sum_{a>b, r>s} C_{ab}^{rs} \phi_{ab}^{rs} + ... \tag{1.22}$$

This is the form of the CI wave function. Here the orbital labels $a, b...$ refer to occupied orbitals and $r, s, ...$ refer to unoccupied orbitals in the reference determinants. $\phi_a^r, \phi_{ab}^{rs}, ...$ are singly, doubly etc, excited determinants. They differ from the lowest energy spin orbital ϕ_0 by single, double etc excitations. These excitations are obtained by replacing the spin orbital χ_a by χ_r for singly excited determinants and χ_a, χ_b by χ_r, χ_s for doubly excited determinants etc. The orbitals used in the above expansion are often chosen to be HF orbitals, and reference determinant ϕ_0 is then the corresponding HF determinant. Although such a choice is not necessary, it is convenient and leads faster convergence in cases where the HF determinant is really dominant one. The restriction on the summation takes care of the appearance of the given excited determinant once in the function. Here the intermediate normalization convention $\langle\Psi|\phi_0\rangle = 1$ has been used.

These linear variation method for evaluating coefficients are equivalent to an eigenvalue problem for the coefficients and the energy.

$$HC = EC \tag{1.23}$$

where H is the Hamiltonian matrix with the elements $H_{ij} = \langle i|\hat{H}|j\rangle$, and C is the coefficent matrix. When all possible excited determinants within a given basis set are included, it is referred to as the Full-CI(FCI) method. The eq.1.23 corresponds to a standard Hermitian eigenvalue problem of linear algebra. This is therefore solved by diagonalizing the Hamiltonian matrix in the usual manner. Since we are interested in only few of its lowest eigenvalues, the complete diagonalization of the Hamiltonian matrix is not required. Selected eigenvalues of the Hamiltonian can be determined by iterative methods. Several authors used Davidson's [24] iterative diagonalization scheme to compute few lower lying eigenvalues and eigenvectors of CI matrix. This method bypasses the need of complete diagonalization of FCI matrix by using matrix-vector product of the Hamiltonian with a trial vector.

If this expansion in eq.1.22 is carried out to all possible excitations (FCI), leads to an exact solution of Schrödinger's equation in the space spanned by the basis set. For FCI wave functions, the number of excited determinants increases rapidly with the number of electrons and with the number of orbitals. Hence for practical calculations it is not possible to include all excitations as the FCI becomes quickly intractable with the increase in number of electrons. A useful approximations can be obtained by truncating at the different levels. Due to *Brillouins theorem*, the singly excited configurations alone cannot improve the ground state of the wave function, although, they can lead to excited states. The most common truncations of CI are double excitations (CID), and single and double excitations (CISD). These are specially suited for states where the reference determinant is dominant(ground state), and recovers a significant portion of its correlation energy within the given basis set.

Apart from the large configurational space problem, truncated CI suffers from two important criteria namely *size consistency* and *size extensivity* which any quantum mechanical method should satisfy. The *size consistency* signifies the proper description at dissociation limit and size extensivity is related to the proper scaling of energy with respect to the size of the system. These two concepts are discussed in detail in the next section.

1.7 Size-consistency and size-extensivity

As stated earlier, any approximate many body method should satisfy two important criteria, namely size consistency and size extensivity [1, 25–27]. As defined by Pople and coworkers [25], a method is size consistent if energy of a molecule is the sum of energies of its fragments at non-interacting limit. In other words, if a system has N non-interacting monomers with energy e_i, its total energy will be Ne_i. This means, if a system consists of two non-interacting fragment A and B, (or if AB molecule dissociates in to A and B at infinite separation) then the energy should be additively separable

$$E_{AB} = E_A + E_B, \tag{1.24}$$

and the wave function should be multiplicatively separable

$$\Psi_{AB} = \Psi_A \Psi_B. \tag{1.25}$$

The concept of size extensivity is related to size consistency. It accounts proper scaling of the energy with the number of particle i.e. with the size of the system. Unlike size consistency, which is a property of infinite separation of the fragments of the system, size extensivity is a more general mathematical concept that hold at any situation. If a method is not size extensive, the error in calculated energy will scale as N^m, where m is either less than 1 or greater than 1 and N is the number of particles present in the system.

In the former case, the correlation energy per particle decreases as the number of particle N increases and becomes zero as $N \to \infty$. In the later case, the correlation energy per particle becomes infinity as $N \to \infty$. Therefore, it results unphysical behavior in energy calculations. It can be easily shown that the wave functions obtained from any truncated CI calculations are not multiplicatively separable and hence the energies of the fragments are not additively separable.

1.8 Perturbation Theory

A different systematic procedure for finding the correlation energy, which is not variational is perturbation theory (PT). Since the correlation energy can be considered as a small perturbation on the HF energy, the full Hamiltonian can be written in the following way:

$$H = H_0 + \lambda H^{(1)} \tag{1.26}$$

where H_0 is zeroth order Hamiltonian, λ is an ordering parameter which varies between zero and unity, and $H^{(1)}$ is the perturbation.

Among the various perturbation approaches e. g. Rayleigh-Schrödinger perturbation theory(RSPT) [1, 28], Brillouin-Wigner perturbation theory (BWPT) [28] and Van-Vleck perturbation theory [29], the conceptually simplest one is RSPT. Since the Hamiltonian depends on perturbation, the eigenfunctions and eigen vaules also becomes perturbation dependent. The exact eigenfunctions and eigenvalues of a non-degenerate state are expanded as Taylor series expansions around $\lambda = 0$

$$\Psi_i(\lambda) = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \frac{\lambda^2}{2!}\Psi_i^{(2)} + ... + \frac{\lambda^n}{n!}\Psi_i^{(n)} + ... \tag{1.27}$$

$$E_i(\lambda) = E_i^{(0)} + \lambda E_i^{(1)} + \frac{\lambda_i}{2!}E_i^{(2)} + ... + \frac{\lambda_n}{n!}E_i^{(n)} + ... \tag{1.28}$$

By substituting the above expressions in the corresponding Schrödinger equation and equating the co-efficients of λ one gets the perturbation corrections to energy order by order. The zeroth order energy is expectation value of the zeroth order Hamiltonian over the unperturbed function

$$E_i^{(0)} = \langle \Psi_i^{(0)} | H_0 | \Psi_i^{(0)} \rangle. \tag{1.29}$$

At first order in the perturbation, BWPT and RSPT theories are equivalent. However, BWPT extends more easily to higher orders, and avoids the need for separate treatment of non-degenerate and degenerate levels. For each unperturbed eigen state a pair of complimentary projection operators are defined as $P_0 = |\Psi_0\rangle\langle\Psi_0|$ and $Q_0 = 1 - P_0$. A little manipulation of Schrödinger equation with these operators leads to following BWPT expression for energies

$$E_i^{(1)} = \langle \Psi_i^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle \tag{1.30}$$

$$E_i^{(2)} = \langle \Psi_i^{(0)} | H^{(1)} R H^{(1)} | \Psi_i^{(0)} \rangle. \tag{1.31}$$

Where R is the resolvent

$$R = \frac{Q_0}{E - H_0} \tag{1.32}$$

Equations 1.30 and 1.31 contains the unknown exact energy in the denominator and hence iterative method is adopted to solve these equations.

In RSPT the unknown energy in the denominators of the BWPT expansion is avoided and this enables a size-consistent theory. The resolvent is $R_0 = \frac{Q_0}{E_i^{(0)} - H_0}$. The corrections in the energy are,

$$E_i^{(1)} = \langle \Psi_i^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle \tag{1.33}$$

$$E_i^{(2)} = \langle \Psi_i^{(0)} | H^{(1)} R_0 H^{(1)} | \Psi_i^{(0)} \rangle \tag{1.34}$$

$$E_i^{(2)} = \sum_{n \neq i} \frac{\langle \Psi_i^{(0)} | H^{(1)} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}} \tag{1.35}$$

The efficiency and convergence of the perturbation series depends on the choice of zeroth order Hamiltonian H_0. For the quick convergence of the perturbation series one needs a wise choice of H_0 and the small H^1. Different perturbation theory differ in explicit expressions for $E_i^{(n)}$ and $\Psi_i^{(n)}$. If H_0 is chosen as the sum of Fock operators, i.e.,

$H_0 = \sum_i \hat{f}(i)$ in the RSPT, the partitioning is known as Moller-Plesset (MP) partitioning scheme. In this case, $\Psi_0^{(0)}$ (the HF wave function) is the zeroth order function for the ground state, $E_0^{(0)}$ is the zeroth order energies which is the sum of energies of the occupied HF orbitals, and $\Psi_n^{(0)}, n \neq 0$ are the different excited determinants as in CI expansion. The Second-order MPPT (also known as MP2 method) for energy recovers considerable fraction of correlation energy for closed-shell atoms and molecules.

The main idea behind the Van Vleck PT [29] is that a unitary transformation U is applied in order to construct an effective Hamiltonian which exhibits, to a certain order in the perturbation, the same eigen energies as the original Hamiltonian but only connects almost degenerate levels. Originally the Van Vleck PT is used to treat modifications on diatomic molecules caused by vibrations and rotations of the nuclei [29]. Since then the formalism has found many applications in both chemistry and physics and experienced various modifications [30].

1.9 Second quantization

Second quantization method was first introduced by Dirac in his treatment of quantization of radiation field. This method takes care of the antisymmetry of electronic wave functions in a more elegant way than the Slater method. It is very useful for explaining the coupled cluster and related many-body methods. In the second quantization formalism the expansion of a determinant into $N!$ terms is bypassed. Instead, the antisymmetry is taken care of by defining creation operators $a_i^\dagger$ and annihilation operators a_i.

The creation operator $a_k^\dagger$ creates an electron on the spin orbitals χ_k. An annihilation operators a_i annihilates or removes an electron from the spin orbital χ_i if the later was occupied. So, if a creation operator $a_i^\dagger$ operating on the N electron determinant without the spin orbital χ_i creates $N + 1$ electron state:

$$a_i \dagger |\chi_j, \chi_k, \chi_l\rangle = |\chi_i, \chi_j, \chi_k, \chi_l\rangle \tag{1.36}$$

An annihilation operator a_i annihilates an electron from the N electric state which contains spin orbital χ_i generates $N-1$ electron state:

$$a_i|\chi_i, \chi_j, \chi_k, \chi_l\rangle = |\chi_j, \chi_k, \chi_l\rangle \tag{1.37}$$

The creation-annihilation operator shares the adjoint relation $a_k = (a_k\dagger)\dagger$. The creation and annihilation operators satisfies the various algebraic properties. The anti-commutation relation between them is given below:

$$a_i^\dagger a_k^\dagger + a_k^\dagger a_i^\dagger \equiv [a_i^\dagger, a_k^\dagger]_+ = 0 \tag{1.38}$$

$$a_i a_k + a_k a_i \equiv [a_i, a_k]_+ = 0 \tag{1.39}$$

$$a_i^\dagger a_k + a_k a_i^\dagger \equiv [a_i^\dagger, a_k]_+ = \delta_{ik} \tag{1.40}$$

Let us define the concept of an abstract mathematical entity called vacuum state. It is the state that contains no electron and is denoted by $|vac\rangle$. The vacuum state is normalized to unity $\langle vac|vac\rangle = 1$ and orthogonal to any other state. Any N electron state can be obtained by acting creation operators on vacuum. *Fock space* is a linear vector space spanned by determinants with different number of electrons. This can also be visualized as the direct sum of *Hilbert spaces* with different number of electron. Any N electron Fock space can be constructed as $a_i^\dagger a_j^\dagger ... a_N^\dagger|vac\rangle$.

In second quantization, the Hamiltonian is expressed in terms of these creation-annihilation operators and hence the dependence on number of electrons is eliminated. The expectation values of such operator between functions of a Fock space are determined by applying the concept of normal ordering and Wick's theorem [31]. The concept of normal ordering is used to evaluate the matrix elements of second quantized operators between any two Fock space determinants. The *generalized Wick's theorem* states that any time order operator string can be written as normal ordered form plus sum of all possible contractions. In normal ordering, all annihilation operators are placed at the right of the creation operators. When a commutation/anti-commutation is performed between a pair of creation and annihilation operators, two terms arise. One that doest not contain the pair of creation-annihilation operators is known as contraction term. In the second term the creation and annihilation operator pair is commuted/anti-commuted. The states of many particle system between which the expectation values to be calculated are written as a string of creation-annihilation operators acting on the vacuum. The above expressed correlation methods e.g. CI, MBPT are re-expressed in terms of second quantization. The diagrammatic technique was introduced by Feynman [32] in the context of quantum field theory and later on applied to many electron problem. The diagrammatic representation of the Wick theorem bypasses the cumbersome algebraic formulation of many-body methods. The diagrammatic representation of the corresponding energy terms and amplitude equations not only simplify the formulation but monitor the size extensivity.

1.10 Coupled cluster

The coupled cluster (CC) methods form another popular approach to the problem of constructing correlated wave functions. The CC theory has been employed for decades in the physics community, particularly in the area of nuclear physics by Cöester and Kümmel [2] to deal with double magic atomic nuclei. It was originally introduced into the quantum chemistry community by $\check{C}\acute{i}\check{z}$ek and Paldus [3] in the late 1960's. These early formulations used Feynman-like diagrams and the notation of second quantization to aid in the derivation of programmable CC equations. Both Feynman diagrams and second quantization concepts were alien to quantum chemists, it was Hurley [33] to present derivation of CC theory in terms accessible to chemists. Despite Huley's derivation, the use of second quantization and diagrammatic theory is still beneficial in the efficient derivation of CC equations. The use of these efficient derivation tools is so important to CC theory because, unlike CI theory in which the core problem is the diagonalization of the Hamiltonian matrix with elements given by Slater's rules and in which individual methods only differ in the basis functions used to construct this matrix, standard CC theory requires the iterative solution of algebraic equations which must be re-derived with each change in method.

There are many differences between CI and CC theory. In CI theory, the wave function may be written as a linear combination of all excited states relative to a chosen reference configuration eq.1.22. Using the second quantization operators, the operator $\hat{C}_n$ can be written which, when acted on the reference, generates a linear combination of all possible n-tuply excited configurations:

$$\hat{C}_n = (\frac{1}{n!})^2 \sum_{ij...ab...}^{n} c_{ij...}^{ab...} a_a^\dagger a_b^\dagger ... a_j a_i \tag{1.41}$$

The $c_{ij...}^{ab...}$ coefficients are the CI coefficients for the configurations produced by the action of the string of creation and annihilation operators on the reference. Making use of these excitation operators, the CI wave function is given by equation

$$\Psi_{CI} = (1 + \hat{C})|\phi_0\rangle. \tag{1.42}$$

where

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + ... = \sum_{n}^{N} \hat{C}_n. \tag{1.43}$$

In this notation, it is possible to construct any CI wave function which is truncated solely on the basis of excitation level by including only the desired C_n excitation operators in C. The CC method employs an excitation operator $\hat{T}$ which is identical in form to the $\hat{C}$ operator of CI theory,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + ... = \sum_{n}^{N} \hat{T}_n. \tag{1.44}$$

with

$$\hat{T}_n = (\frac{1}{n!})^2 \sum_{ij...ab...}^{n} t_{ij...}^{ab...} a_a^\dagger a_b^\dagger ... a_j a_i \tag{1.45}$$

but instead of acting on the reference in a linear fashion, the $\hat{T}$ operator of CC theory acts exponentially:

$$\Psi_{CC} = e^{\hat{T}}|\Phi_0\rangle. \tag{1.46}$$

The $t_{ij\cdots}^{ab\cdots}$ coefficients in the $\hat{T}_n$ operators are known as cluster amplitudes. Analogous to CI theory, an excitation truncated CC method may be constructed by including only the desired excitation operators within $\hat{T}$. For example, the popular CCSD method is realized when only the $\hat{T}_1$ and $\hat{T}_2$ operators are included within $\hat{T}$. There are various theoretical basis for employing the exponential formalism instead of remaining with the linear ansatz of CI theory. The interesting thing is that the exponential approach produces a method which is both size consistent and size extensive, provided the reference function possesses these qualities, even when $\hat{T}$ is truncated at a chosen excitation level.

Having established that the CI and CC formalisms differ primarily in the method in which the excitation operators $\hat{C}$ and $\hat{T}$ operate on the reference, linearly for CI and exponentially for CC, the next step is to examine how one derives the working CC equations. Beginning from the universal starting point, the Schrdinger equation, one substitutes in the form of the CC wave function given by eq 1.46 and finds

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle. \tag{1.47}$$

Projecting through on the left by the reference, $|\Phi_0\rangle$, one can obtain an expression for the energy

$$\langle\Phi_0|\hat{H}e^{\hat{T}}|\Phi_0\rangle = E\langle\Phi_0|e^{\hat{T}}|\Phi_0\rangle = E, \tag{1.48}$$

provided one employs the technique of intermediate normalization and sets the overlap between the reference and the CC wave function i.e., $\langle\Phi_0|\Psi_{CC}\rangle$ equal to unity. Obtaining an energy expression is only the first step, however one must also determine all of the cluster amplitudes which define the wave function with this energy. In order to accomplish this, one must left-project eq 1.48 by the excited determinants produced by the action of the $\hat{T}$ operator:

$$\langle\Phi_{ij\cdots}^{ab\cdots}|\hat{H}e^{\hat{T}}|\phi_0\rangle = E\langle\Phi_{ij\cdots}^{ab\cdots}|e^{\hat{T}}|\Phi_0\rangle. \tag{1.49}$$

For example, one can produce an equation for the specific amplitude t_{ij}^{ab} by left-projecting by the $|\Phi_{ij}^{ab}\rangle$ excited determinant. The resulting equation is non-liner and depends upon other cluster amplitudes. However, these equations are exact, and if one were able to solve them with the full $\hat{T}$ operator, one would indeed obtain the full CI energy and wave function.

The CC method depends upon the action of the exponential excitation operator $e^{\hat{T}}$ on the reference. The excitation operator is expanded as the power series

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots . \tag{1.50}$$

As a matter of fact, the equivalence of $e^{\hat{T}}$ and this power series is commonly used in the various arguments employed to justify the exponential ansatz. From eq.1.48 one get

$$E = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}T|\Phi_0\rangle + \langle\Phi_0|\hat{H}\frac{\hat{T}^2}{2!}|\Phi_0\rangle + \langle\Phi_0|\hat{H}\frac{\hat{T}^3}{3!}|\Phi_0\rangle + \cdots \tag{1.51}$$

from which one can find another benefit of the exponential formalism. The Hamiltonian operator only includes one- and two- particle operators, and thus, according to Slater's rules, matrix elements of the Hamiltonian between determinants which differ by more than two spin orbitals must vanish. Therefore, the fourth and subsequent terms in the above expansion, in which the $\hat{T}$ operator is raised to the third or higher power and can thus produce only triply or higher excited determinants when operated upon the reference, must also vanish and the energy expression is truncated to

$$E = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}T|\Phi_0\rangle + \langle\Phi_0|\hat{H}\frac{\hat{T}^2}{2!}|\Phi_0\rangle. \tag{1.52}$$

This is a natural truncation of the CC equations due to the nature of the Hamiltonian and also applies to the amplitude equations, although the exact range of allowed powers of $\hat{T}$ will vary from that seen for the energy expression. Therefore, in practical CC derivations, theorists exploit a bit of mathematical experience and multiply eq 1.48 through on the left by $e^{-\hat{T}}$. Subsequent left-projection by the reference and excited determinants produces the following new set of energy and amplitude equations:

$$E = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle \tag{1.53}$$

$$\langle\Phi_{ij\cdots}^{ab\cdots}|e^{-\hat{T}}\hat{H}^{\hat{T}}|\Phi_0\rangle = E\langle\Phi_{ij\cdots}^{ab\cdots}|e^{-\hat{T}}e^{\hat{T}}|\Phi_0\rangle = E\langle\Phi_{ij\cdots}^{ab\cdots}|\Phi_0\rangle = 0 \tag{1.54}$$

respectively. Notice that the introduction of the $e^{-\hat{T}}$ operator cancels out its $e^{\hat{T}}$ counterpart in the amplitude equations and guarantees that the right hand side vanishes, taking any dependence of the amplitudes on the energy with it. The similarity transformed Hamiltonian, $e^{-\hat{T}}\hat{H}e^{\hat{T}}$, employed in the above energy and amplitude equations is not a Hermitian operator; therefore, the energy equation does not satisfy any variational conditions where the energy is derived from the Average Value Theorem. Despite this disadvantage, which is considered to be small by a number of theorists, the use of this similarity transformed Hamiltonian has as a second benefit which makes this formulation of the CC equations both practical and desirable. The $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ operator may be expanded as a linear combination of nested commutators

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{4!}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}] + \cdots \tag{1.55}$$

according to the Campbell-Baker-Hausdorff formula.

While the expansion of the similarity transformed Hamiltonian given above in equation 1.55 may not, at first glance, appear to be simple but the sequence of nested commutators naturally truncates due to the structure of the electronic Hamiltionian. The second quantized form of the Hamiltonian includes strings containing at most a total of four general-index creation and annihilation operators. When one evaluates the commutator between the Hamiltonian and the $\hat{T}$ operator, one replaces one of these operators by a Kronecker delta function. This reduces the number of available general-index operators in the Hamiltonian by one. Thus, the sequence of nested commutators in eq.1.55 must truncate after the five terms explicitly written. Using this truncated Hausdorff expansion, it is possible to obtain analytic expressions for the commutators which may be inserted into both the energy and amplitude equations. Finally, these equations may then be reduced into expressions that depend only on the amplitudes and the known one- and two-electron integrals.

1.11 Different cluster approximations

The method which uses the cluster operator in eq.1.44 is known as full CC (FCC) and is equivalent to FCI. Obviously the number of cluster operators are same as CI operators. However, the simplicity of CI is lost due to the exponential nature of CC function and hence it is never used in practice. Unlike truncated CI, CC is known to be size-consistent and size-extensive at any level of truncation because of its exponential nature. The most commonly used CC ansatz is to define $T = T_1 + T_2$ leading to singles and doubles (SD) approximation by Purvis and Bartlett [34]. This model consider the effect of disconnected triple excitations, but it neglects the connected triple excitations. The importance of connected triples is demonstrated by the complete fourth-order MBPT calculations [35] for energy, chemical reactivity and molecular properties. The inclusion of connected triples within the CC scheme is considered very early after the introduction of the CC approach by Paldus, Cizek, and Shavitt [36]. There are various models like CCSDT-1a, CCSDT-1b, CCSDT-2, CCSDT-3 are developed to reach full CCSDT model [37]. The details of all these models are compared in reference [38]. The main goal of the approximate model is to obtain the results closer to FCI with a computational efforts that is as small as possible. The non-approximated coupled cluster models only provide a feasible hierarchy for small systems due to their fast increasing computational cost: CCSD(N^6), CCSDT(N^8), etc., where the number in parentheses denotes the scaling with the number of orbitals. The perturbative correction in the CCSD(T) model [39] is used successfully in obtaining static molecular properties. CCSD(T) scales as N^7. The quadruple excitations are also taken care perturbatively CCSDT(Q) and fully CCSDTQ [40]. There are methods which emphasizes only on molecular properties rather than the total energies because the accuracy of total energies does not assure accuracy of molecular properties. The second order CC model known as CC2 [41] is an approximation to CCSD and CC3 [42] is an approximation to CCSDT.

The complexity of the implementation of CC methods grows rapidly with the excitation rank of the cluster operator. At most pentuple excitations are derived and coded in a “traditional way” [43]. However, the implementations of higher excitations with proper computational scaling is developed in two ways. One involves an automatic generation of Fortran (or other language) code for each particular case, which is then compiled and linked into the final program [44]. Second way is the string-based CC approach, which implements contractions of tensors with arbitrary number of indices within one (human-written) code [45]. Both approaches are able to achieve proper computational scaling and take advantage of the antisymmetry of amplitudes and spin symmetry for any CC excitation level. Approximate non-iterative schemes of general order and analytic gradients using the string approach are implemented by Kally and coworkers [46].

1.12 Alternate single reference(SR) CC approaches

The traditional CC method just discussed is known as normal coupled cluster (NCC) method. The implicit formulation of this method is non-variational. In this version the proof of size extensivity is more transparent. The nonvariational CC has been extensively applied for the calculation of electronic energies. However, the nonvariational nature makes it computationally unattractive for energy derivatives. Alternate way to simplify the problem is to solve the CC ansatz variationally. The advantage of variational CC is that, here, Hellmann-Feynman theorem and $(2n + 1)$ rule holds. This makes the method attractive for higher energy derivative. These stationary methods includes expectation value functional (XCC), unitary CC (UCC) and extended CC (ECC). We will review these mothods in the following subsections.

1.12.1 Expectation value and Unitary coupled cluster ansatz

One of the attempt in formulating the stationary theory is via the expectation value type hermitian functional

$$E = \frac{\langle\Phi_0|e^{T^\dagger}He^{T}|\Phi_0\rangle}{\langle\Phi_0|e^{T^\dagger}e^{T}\Phi_0\rangle} \tag{1.56}$$

This functional is referred as expectation value coupled cluster (XCC) [47, 48]. The T operators are hole-particle creation operators like in NCC, the $T^\dagger$ being conjugate of T, indicate hole-particle destruction. The practical implementation of this functional is impossible because both the numerator and denominator are infinite series in $T^\dagger$ and T. Moreover, this functional does not exhibit the connected nature of energy as in NCC. Pal et al. [48] used linked cluster theorem and showed that the numerator can be decomposed into a connected term multiplied by a disconnected term. The disconnected term exactly cancels the denominator. Therefore, the connected form of the functional which is suitable for carrying out the variation is

$$E = \langle\Phi_0|e^{T^\dagger}He^{T}|\Phi_0\rangle_{conn}. \tag{1.57}$$

It can be seen that the functional is a nonterminating, but hermitian series in cluster amplitudes and thus has to be truncated for any practical application. Various truncation schemes were employed in the literature to truncate this functional. Pal et. al. [47] used polynomial truncation based on fixed power of $T^\dagger$ and T . Bartlett and co-workers [49] used perturbative arguments for the truncation.

An another stationary CC scheme proposed by Kutzelnigg [50] following Van Vleck [51] and Primas [52] formalism is based on the unitary ansatz, referred as unitary CC (UCC). The exact correlation function has the form

$$\Psi = e^{\sigma}|\phi_0\rangle. \tag{1.58}$$

where σ is anti hermitian $\sigma = -\sigma^\dagger$. The special choice of σ is $\sigma = T - T^\dagger$. With this wave function, the energy functional becomes,

$$E = \langle\phi_0|e^{-\sigma}He^{\sigma}|\phi_0\rangle \tag{1.59}$$

This functional is connected due to BCH expansion of $e^{-\sigma}He^{\sigma}$. However, the expansion leads to an infinite series and need to be truncated for practical implementations. Pal et. al. [47] showed that the UCC functional in eq.1.58 is identical with the XCC functional in eq.1.57.

These stationary CC methods, however, were not pursued extensively due to some inherent drawbacks. Unlike the standard variational methods, these truncated energy functional does not lead to any upper bound of calculated energy. Although the energy functional is connected, the differentiations of this functional with respect to cluster amplitudes lead to disconnected terms in the amplitude equations. Consequently, the disconnected terms bring in an inherent error of size-extensivity into the theory.

1.12.2 Extended coupled cluster

Extended coupled cluster (ECC) proposed by Arponen [53] is an alternate stationary coupled cluster method which uses the double similarity transformation in the energy functional

$$E = \langle\phi_0|e^{\Sigma}e^{-T}He^{T}e^{-\Sigma}|\phi_0\rangle. \tag{1.60}$$

Here, Σ is an deexcitation operator and $e^{\Sigma}|\Phi_0\rangle = 0$. This functional terminates naturally depending of the rank of the T and Σ operators. This functional can be variationally optimized with respect to cluster operators Σ and T. However, it generates some disconnected terms in the amplitude equations while differentiations leading to size-inextensivity in the energy value. Arponen and Bishop [54] arrive at double linked type functional by transforming T

$$E = \langle\phi_0|e^{\Sigma}e^{-\tilde{T}}He^{\tilde{T}}e^{-\Sigma}|\phi_0\rangle_{DL}. \tag{1.61}$$

Here *DL* means double linking which means that $\tilde{T}$ is linked to Hamiltonian due to BCH ($e^{-\tilde{T}}He^{\tilde{T}}$), Σ operator is connected to either at least with one Hamiltonian vertex or with two distinct $\tilde{T}$ vertex. Alternately, eq.1.61 can be expressed as

$$E = \langle\phi_0|e^{\Sigma}[He^{\tilde{T}}]_L|\phi_0\rangle_{DL}. \tag{1.62}$$

$$\frac{\partial E}{\partial \sigma} = 0; \frac{\partial E}{\partial \tilde{t}} = 0. \tag{1.63}$$

The equations of Σ and $\tilde{T}$ are obtained by making the energy stationary with respect to $\tilde{t}$ and σ. The double linking ensures the connectedness of terms in the equations of Σ and $\tilde{T}$, there by ensuring the size-extensivity. Piecuch [55] and Gordon and co-workers [56] used the method to study the molecular bond breaking. Piecuch and Bartlett [55] tested size-extensivity of ECCM.

1.13 Equations of motion CC

The equation of motion CC (EOMCC) provides a straightforward and general path to calculate energy differences. In EOMCC formalism, Rowe's [57] equation is solved for excitation operators Ω_k. The electronic states, different from ground (or reference) state are parameterized in a linear fashion as

$$\Psi_k = \Omega\Psi_0 = \Omega_k e^T \Psi_0, \tag{1.64}$$

where Ω_k is a linear operator. The method is also called as the coupled cluster linear response theory (CCLRT). The Ω_k may change the number of particles, and by making different choices for the set of Ω_k, different sectors of Fock space are made accessible. The operator Ω_k is a sum of operators with odd number of electron creation and destruction operators such that the final state is $N \pm 1$ electron state. In case of excitation energy (EE) the excitation operator is formed from a set of equal number of creation and annihilation operators. The eigenvalue equation obtained in EOMCC is

$$[\bar{H}, \Omega_k]_c|0\rangle = \omega_k \Omega_k |0\rangle. \tag{1.65}$$

Here, $\bar{H} = e^{-T} H e^T$ and $\omega_k = E_k - E_0$. As mentioned above EOMCC gives the energy difference directly by solving the EOMCC eigenvalue equation of $\bar{H}$ i.e.diagonalization of $\bar{H}$ in the excited manifold generated by Ω_k . Bartlett et. al. [58] proposed EOMCC for the calculation of difference energies. Since the equations are not fully linked, the corresponding excitation energies are not size extensive. The second drawback of EOMCC method is that since it diagonalizes a non-Hermitian Hamiltonian $\bar{H}$, one may encounter complex eigenvalues in the eigenvalue spectrum. The EOM-CC methods and are now, very commonly used for ionisation potential, electron affinity and EE calculations [59–61]. Recently Nooijen et. al. [62] proposed a similarity transformed EOMCC method to over come the size-extensivity problem in EOMCC. For one valence problem EOMCC and FSMRCC are equivalent. However, such equivalence breaks down for excited state. EOMCC contains certain unlinked diagrams which are associated with charge-transfer separability [63]. The spin-flip EOMCC method has also been introduced as a clever way to describe the multi reference states [64].

1.14 Static and Dynamic correlation

In the design of the configuration spaces smaller than that of FCI, it is important to distinguish between static and dynamic correlation. *Static correlation* or *nondynamical* is treated by retaining, in the dominant configurations in FCI expansion as well as those configurations that are nearly degenerate with the dominant configurations. These configurations selected for an adequate description of static correlation are referred to as the *reference configurations* of the CI wave function. The configuration space spanned by the reference configurations are called the *reference space*. *Dynamical correlation* is subsequently treated by adding the wave function configurations generated by excitations out of the reference space to the dominant configuration.

1.15 Quasidegeneracy and multi-reference methods

The SR methods are suitable for the description of closed-shell atomic states and near equilibrium ground states of closed-shell molecules where the single determinant dominates Φ. A major portion of electron correlation in such states is accounted in the mean-field description used for finding this dominant determinant. The remaining part of short range electron correlation is referred as dynamical or external correlation. The dynamical

[65] correlation arises due to somewhat weak interaction of various excited determinants with this dominant determinant and contributes to correlation energy of the state. There are many cases in chemistry are dominated by several determinants. The cases such as degenerate or quasi-degenerate systems (excited states of molecules and potential energy surfaces, bond breaking processes, reactive chemical phenomena, and so on) involves more than one configurations or multi-configurations (MR). A quasi-degenerate state is characterized by a significant amount of non-dynamical electron correlation arising due to strong interaction between the dominant determinants.

The first MR correlated method to be implemented was MRCI [66, 67] (due to its conceptual simplicity) but it has still not been devoid of the size-consistency problem that is inherent to all variational approaches. Therefore, in the past decade, there has been much effort involved to develop MR MBPT [68, 69] and MR CC [7] methods that are assumed to treat electron correlation from the secondary space more effectively than CI methods do. The common obstacles of both MR approaches are (i) the choice of an appropriate reference space and (ii) the problem of intruder states.

1.15.1 Multi-reference configuration interaction (MRCI)

The MRCI method is the straightforward extension to the SR-CI method. This method has been implemented first by Buenker and Peyerimhoff [66]. In this method the reference is taken as the linear combination of several interacting dominant configurations known as model space. The MRCI wave-function is constructed as a linear combinations of all distinct excited determinants generated by carrying out excitations on each determinant within the model space. The MRCI-SD wave function is written as the combination of excited determinants obtained from the set of reference functions ϕ_R. The normalized reference and MRCI wave functions for state n is

$$\Psi_{ref}^{(n)} = \sum_R C_{Rn}\phi_R \tag{1.66}$$

$$\Psi_{MRCI-SD} = \sum_{R} C_{Rn}\phi_R + \sum_{S} C_S\phi_S + \sum_{D} C_D\phi_D. \tag{1.67}$$

Here ϕ_S and ϕ_D are singly and doubly excitations obtained out from the set of reference functions $\{\phi_R\}$. Solving MRCI is also similar to SRCI. The combining coefficients in eq.1.67 are determined by applying the variational principle leading to diagonalization of the Hamiltonian matrix evaluated between different determinants. The problem of size inconsistency of truncated CI-methods is not solved by taking more references.

The modern MRCI treatments make use of spin-adapted configuration state functions (CSF) in place of determinants along with the efficient rules developed for evaluation of coupling coefficients entering the Hamiltonian matrix elements. To achieve efficiency, they further employ the direct CI method proposed by Roos [70] in combination with the graphical methods of unitarty and symmetric group approaches. The works by various authors Meyer [71] and Knowles and coworkers [72, 73] and Werner and coworkers [73, 74] uses internally contracted configurations. Various methods like multireference averaged coupled-pair functional (MR-ACPF) method of Gdanitz and Ahlrichs [75], the multireference averaged quadratic coupled cluster (MR-AQCC) method of Szalay and Bartlett, [76] and the multireference self-consistent self-consistent CI (MR-SCSCCI) method of Malrieu and coworkers [77] emerged to fulfill the size-consistency requirement.

1.15.2 Multiconfigurational self consistent field (MCSCF)

In MCSCF the wave function [78] is written as a linear combination of determinants, whose expansion coefficients are optimized along with molecular orbitals.

$$|\Psi\rangle = \sum_{i} C_i\phi_i \tag{1.68}$$

The MCSCF wave function is well suited for the system involving degenerate or nearly degenerate configurations, where static correlation is important. Such states are usually encountered in the description of reaction process involving bond breaking, even sometimes in ground state geometry. Unlike RHF wave function, the MCSCF wave function gives a balanced description of the potential energy surfaces of ground state hydrogen atoms. The most difficult part in handling the MCSCF wave function is in the addition of configuration spaces. That has been elegantly taken care in the generalized form of MCSCF called complete active space SCF (CASSCF).

Aanother MCSCF model is based on a partitioning of the subspace of active orbitals. This is known as restricted active space (RAS) SCF. Here the active orbitals are partitioned into three subgroups [79]. In the first subspace, usually called RAS1, the number of electron holes is restricted, in the second subspace (RAS2), all occupations are allowed, in the third subspace (RAS3), the number of electrons is restricted. RASSCF function may provide a good approximation to the corresponding CASSCF function using a much smaller set of configurations. More frequently, it is applied to provide a coarse description of dynamical correlation effects by including extended set of active orbitals in the RAS3 subspace.

1.15.3 CASSCF

The CASSCF wave-function as zeroth-order reference function was developed and successfully applied by Roos and coworkers [80]. In CASSCF the basic quantity of interest is the molecular orbitals. The starting point is an orthonormal orbital space $\phi_i(r); i = 1, ..., m$. The MO's are obtained as expansion in a set of atom-centered basis function (the linear combination of atomic orbitals)(LCAO method), m being the number of such functions. The MO space is further divided into the inactive, active and external orbitals. The inactive and active subspaces constitute the occupied spaces, while the external orbitals are unoccupied. The CASSCF wave function is formed as a linear combination of configuration state functions(CSF). The configuration state functions are constructed by considering doubly occupied orbitals as inactive orbitals and the remaining electrons occupy the active orbitals. Using these electrons and orbitals, a full list of CSF's which have the required spin and space symmetry is constructed. The CASSCF wave function is written as a linear combination of all these CSF's, comprising a complete expansion in the active orbital subspace.

Unlike CI method, in CASSCF the energy is optimised with respect to expansion coefficients and MO's. During the optimization the core orbitals are kept frozen. This reduces the computational effort. By replacing the core electrons by effective core potential (ECP), CASSCF can be extended to systems containing several heavy atoms. When active space comprises all the orbitals in the system, the FCI wave function is recovered. For the case of empty active space the MCSCF reduces to HF. The MCSCF model may be regarded as a combination of HF model and FCI model.

There are cases where a larger number of active orbitals are needed. In such cases the restricted form of the CASSCF wave function may be used.

1.15.4 Multi-reference perturbation theory (MRPT)

The MRPT is classified in to two categories. In the first one the perturbative effective Hamiltionian is constructed over the defined model spaces. The diagonalisation of this Hamiltionian yields approximate energies and approximate wave-functions of one or more states having their zeroth-order components within the model space. They are commonly known as perurb-then-diagonalise type of approaches and also known as quasi-degenerate perturbation theory (QDPT) by Brandow [68]. The second category is the straight extension of the SR perturbation theory where the zeroth order wave function qualitatively describing the desired state is first constructed by diagonalizing the Hamiltonian over the model space, usually through a multi-configuration self-consistent field (MCSCF) calculation. This is then used to construct the zeroth order Hamiltonian, which then defines perturbation. The perturbative expansion over zeroth order wave function is used to obtain the corrections to the wave function and energies at various order. This is a state-specific approach (one state at a time), usually referred to as diagonalize- then-perturb approach by Wolinski [69]. Of course, the diagonalize then perturb approach or the perturb then diagonalize approach will yield the same result at infinite order but the results at low order may differ significantly.

The so called 'perturb then diagonalize' approaches involve works by Robb and coworkers [81], Freed and coworkers [82], Nakano [83], Davidson [84], Malrieu and coworkers [85], works by Mukherjee and coworkers [86], Finley [87], Angeli et al. [88] and others. There are schemes developed without an effective operator by several authors Davidson [89], PT formulations worked out by Wolinski, Pulay, Murphy and Messmer [90], the complete active space second-order PT (CASPT2) methodology by Roos and coworkers [91], studies by Werner, Dyall and Mitrushenkov [92], the multi reference Moller-Plesset (MRMP) methodology of Hirao and coworkers [93], works by Rosta and Surjan [94], the n-electron valence state perturbation theory (NEV-PT) framework of Angeli et al. [95] and the recent multi configuration perturbation theory (MCPT) [96] and several others.

An another approach called as generalized Van Vleck PT (GVVPT) [97] is a subspace-specific variant of multireference perturbation theory. This approach is contrast to most computationally feasible MRPTs or QDPTs which accounts for the interaction of the perturbed model space functions of interest with the unperturbed complementary states. Perhaps most importantly, GVVPT avoids completely the notorious intruder state problem, even when considering excited electronic states. As a consequence, GVVPT potential energy surfaces of both ground and excited states are rigorously continuous. Recently, analytical evaluation of dipole moments is acheived through Lagrangian technique by Pal, Hoffmann and coworkers [98].

A main difficulty of MRPT lies in the choice of the zeroth-order Hamiltonian In multi-reference cases, the zeroth-order Hamiltonian is in general non-diagonal. As a result, a set of linear equations have to be solved to determine the first-order wave function. The issue of zeroth-order Hamiltonian in diagonalize-then-perturb type of MRPT approaches has been a subject of numerous detailed studies. This is also related to the size-consistency aspects of the method.

1.15.5 Multi-reference CC methods (MRCC)

The single reference based approach is well suited for nondegenerate or closed shell systems and only in limited cases for quasidegenerate situations. The ground states of open shell radicals are described by SRCC based on the restricted open shell HF determinant. Similarly in some cases excited states are described accurately by the SRCC method. On the other hand, to introduce nondynamical correlations systematically in the wave function, a general solution is to start from a multideterminantal model space consisting of dominant determinants. Subsequent introduction of dynamical correlation through the exponential wave operator is the basis of the class of multireference CC methods (MRCC) [4–8]. In recent years, this class of methods are studied for the description of excited states, ionized states, and potential energy surfaces (PES), where the nondynamical correlation is likely to be important. The traditional MRCC uses an effective Hamiltonian route [99], which is investigated extensively in recent years. The effective Hamiltonian is constructed within a model space (corresponding states of interest). The effect of orthogonal complement to the model space is folded into the model space through the wave operator for the construction of an effective Hamiltonian. The standard and commonly used effective Hamiltonian is the Bloch effective Hamiltonian. The effective Hamiltonian method can provide the energies of multiple states at a time and this advantage can be exploited in many situations. The effective Hamiltonian methods can be further classified into *valence-universal or Fock space* (FS) [4, 106, 107] and *valence-specific or Hilbert space* types (HS) [109, 110]. The valence universal type is based on a common vacuum with respect to which holes and particles are defined. These holes and particles are further subdivided into active and inactive subsets. The active subset is the one that contained in the model space determinants. This approach works well when the model space determinants contain a small number of active holes and particles. This class is well suited for ionized or low lying excited states. However, for the PES, the model space determinants usually do not satisfy this feature and the valence specific type, where each determinant acts separately as vacuum, is more suitable for PES calculations. This is called as HSMRCC. However, for a general problem of PES, the effective Hamiltonian method, which provides the energies of a multiple of states still suffers from the intruder state problem. The *state specific MR* (SSMR) theory by Malrieu and co-workers [100], Mukherjee and co-workers [101, 102], and Masik et al. [103], pertaining to the description of a single state (i.e, one state at a time) has emerged as a more attractive formulation to take care of intruder state problem. The state-specific multi-reference CC (SS-MRCC) method of Mahapatra et al. [102] uses CAS and it is rigorously size-extensive. SS-type approaches are classified into those that employ genuine MR CC equations, represented primarily by MkCC (Mukherjee et al. MR CC [101, 102]), KB-MRCC (using Kucharski and Bartlett coupling [104]), and by the BW-MRCC (Brillouin Wigner MR CC [105]) methods, as well as by a large group of approaches that are essentially of a SR-type, but employ some MR CC ideas in accounting for higher-than-pair clusters.

1.16 Fock-space multi-reference coupled-cluster method

The FSMRCC theory was originally formulated by Kutzelnigg [106], Mukherjee [4] and Lindgren [107], and applications to atoms were made by Kaldor and co-workers [8]. First molecular applications of FSMRCC theory at singles and doubles level were presented in a few important papers published in the late 1980's [5, 6, 108].

In the Fock-space, the model space determinants contain h-holes and p-particles distributed within a set of what are termed as active holes and active particles, usually around the fermi level. We denote the above p-active particle, h-active hole model space determinant by $\{\Phi_i^{(p,h)}\}$. Thus, the model space of a (p,h) valence Fock-space is written as

$$|\Psi_{(0)\mu}^{(p,h)}>=\sum_i C_{i\mu}^{(p,h)}|\Phi_i^{(p,h)}> \tag{1.69}$$

The projection operator for model space is defined as

$$P^{(p,h)} = \sum_i |\Phi_i^{(p,h)} >< \Phi_i^{(p,h)}| \tag{1.70}$$

The orthogonal component of the model space, i.e. the virtual space is defined as

$$Q = 1 - P \tag{1.71}$$

The dynamical electron correlation arises due to comparatively weak interactions of the model space configurations with the virtual space configurations. This interaction is brought in through a universal wave operator Ω which is parameterized such that the states generated by its action on the reference function satisfy the Schrödinger equation. To generate the exact states for the (p, h) valence system, the wave operator must generate all valid excitations from the model space. Subsequently, Ω should contain cluster operators $\tilde{T}^{(p,h)}$ which are defined as follows

$$\tilde{T}^{(p,h)} = \sum_{k=0}^{p} \sum_{l=0}^{h} T^{(k,l)} \tag{1.72}$$

The superscripted bracket in the right hand side of the above expression indicates that the cluster operator T is capable of destroying exactly k active particles and l active holes, in addition to creation of holes and particles. The $\tilde{T}^{(p,h)}$ operator subsumes all such lower $T^{(k,l)}$ operators. Using these operators, the Ω is defined as follows.

$$\Omega = \{e^{\tilde{T}^{(p,h)}}\} \tag{1.73}$$

The brace-bracket in eq.1.73 indicates normal ordering of the cluster-operators. The Schrödinger equation for the manifold of quasi-degenerate states can be written as

$$H|\Psi_i^{(p,h)} > \;=\; E_i|\Psi_i^{(p,h)} > \tag{1.74}$$

which leads to,

$$H\Omega(\sum_i C_{i\mu}^{(p,h)} \Phi_i^{(p,h)}) \;=\; E_\mu \Omega(\sum_i C_{i\mu}^{(p,h)} \Phi_i^{(p,h)}) \tag{1.75}$$

The effective Hamiltonian for (p, h) valence system can be defined such that

$$\begin{aligned} \sum_j (H_{eff}^{(p,h)})_{ij} C_{j\mu} &= E_\mu C_{i\mu} \\ (H_{eff}^{(p,h)})_{ij} &= \langle \phi_i^{(k,l)} | \Omega^{-1} H \Omega | \phi_j^{(k,l)} \rangle \end{aligned} \tag{1.76}$$

which can be written as

$$H_{eff}^{(p,h)} = P^{(p,h)} \Omega^{-1} H \Omega P^{(p,h)}. \tag{1.77}$$

The form of the inverse of Ω, in general may not be well defined. Hence, above definition is seldom used to obtain the effective Hamiltonian. Instead, the Bloch-Lindgren approach is commonly used to define the effective Hamiltonian. The Bloch equation is just the generalized form of Schrödinger equation.

$$H\Omega P = \Omega H_{\mathit{eff}} P \tag{1.78}$$

The Bloch-Lindgren approach not only eliminates the requirement of Ω^{-1}, but also provides an important criterion the effective Hamiltonian must fulfill. The effective Hamiltonian is, in general, non-hermitian. The Bloch projection approach is used to obtain Ω and the effective Hamiltonian. This involves left projection of above equation by P and Q.

$$\begin{aligned} P^{(k,l)}(H\Omega - \Omega H_{\mathit{eff}}^{(k,l)}) P^{(k,l)} &= 0 \\ Q^{(k,l)}(H\Omega - \Omega H_{\mathit{eff}}^{(k,l)}) P^{(k,l)} &= 0 \\ ; \forall k = 0, \ldots, p; l = 0, \ldots, h & \end{aligned} \tag{1.79}$$

The normalization condition is specified indirectly through parameterization of Ω. In case of complete model spaces (CMS), the intermediate normalization is commonly employed i.e. $P\Omega P = P$.

The diagonalization of the effective Hamiltonian within the P space gives the energies of the corresponding states and the left and the right eigen vectors.

$$H_{\mathit{eff}}^{(p,h)} C^{(p,h)} = C^{(p,h)} E$$

$$\tilde{C}^{(p,h)}H_{\mathit{eff}}^{(p,h)} = E\tilde{C}^{(p,h)} \tag{1.80}$$

$$\tilde{C}^{(p,h)}C^{(p,h)} = C^{(p,h)}\tilde{C}^{(p,h)} = 1 \tag{1.81}$$

Because of normal ordering, the contractions amongst different cluster operators within the exponential are avoided, leading to partial hierarchical decoupling of cluster equations. This is commonly referred to as sub-system embedding condition (SEC). The lower valence cluster equations are completely decoupled from the higher valence cluster equations because of SEC. Hence, the Bloch equations (1.79) are solved progressively from the lowest valence $(0,0)$ sector upwards up to (p,h) valence sector.

The applications of FSMRCC were done using a model space of 1-active hole and 1-active particle, which automatically included the lower one-valence FS sectors of 1-active hole (0,1) or 1-active particle (1,0) sectors. These one valence sectors, by definition are complete model spaces. However, 1h-1p sector denoted as (1,1) sector is not CMS. However it was shown that this is a special case of quasi-complete model space [5, 111]. For general model space, it was shown by Mukherjee [112] that valence-universality of the wave operator was sufficient to guarantee the linked cluster theorem, but it was important that the condition of intermediate normalization need to be relaxed. Thus, the P-space projection equation explicitly involved $P\Omega P$ term. However, for the special case of (1,1) sector, $P\Omega P$ term effectively behaves as a model space projector only and thus the (1,1) sector equations behave as CMS equations. This was a simplification which was exploited in actual calculations.

It was important to recognize that for (1,1) sector, starting with the ground state RHF as vacuum, the wave function contained $T^{(1,1)}$ operator, which generates the RHF determinant. However, as an additional simplification, the excitation energy calculations did not involve the calculation of $T^{(1,1)}$ amplitudes [5].

1.17 Linear response method for molecular properties

Molecular properties are specific for a given electronic state which is described as the "response" of the molecular system to an external perturbation. In the presence of small time-independent perturbation ζ, the Hamiltionian is a function of this perturbation and which can be expanded as a Taylor series of ζ. However, for small perturbation the higher order derivatives of Hamiltionian are negligible. Hence the Hamiltonian is a linear function of ζ

$$\hat{H}(\zeta) = \hat{H}^{(0)} + \zeta\hat{O} \tag{1.82}$$

where $\hat{H}^{(0)}$ is a total electronic Hamiltonian in the absence of perturbation and $\hat{O}$ is a proportionality constant. The resulting method of obtaining derivative eigenfunctions and eigenvalues is referred as "Linear response" (LR).

In the presence of perturbation, the wave function and the energy parameters becomes dependent on perturbation and can be expressed in terms of Taylor series expansion. Hence the properties are obtained as the derivatives of energy. For the case of electric field as perturbation, the first order quantity is called as dipole moment, second order quantity is polarizability etc. For chemists, certainly NMR shieldings and spin-spin coupling constants are of greater interest. However, theory also allows calculation of magnetizabilities, spin-rotation constants, rotational g tensors [113] as well as parameters that can be obtained from ESR spectroscopy [114]. All these properties are expressed in terms of second derivatives, arises from magnetic field as perturbation.

In principle, derivatives of the energy can be computed in a rather straightforward manner using finite-differentiation or finite-field (FF) technique (numerically). In FF method, the Schrödinger equation for the system of interest at various field values are obtained.

$$\frac{dE}{dx} \approx \frac{E(\Delta x) - E(-\Delta x)}{2\Delta x} \tag{1.83}$$

where Δx is an approximate chosen step size. This method requires very accurate evaluation of wave function and energy, although, no computational developments are required. Furthermore, it is very difficult to use FF for higher derivatives and also handling of magnetic properties is less straightforward, as the computation requires the capability of dealing with complex wave function parameters. The alternative to numerical differentiation is analytical differentiation. This means that first an analytic expression for the corresponding derivative is deduced and then implemented within a computer code for the actual computation of the corresponding property. It is known that the exact wave function follows the Hellmann-Feynman theorem (HFT). The Hellmann-Feynman theorem states the identity of the derivative and expectation value expression for first order properties:

$$\frac{dE}{d\zeta} = \langle\Psi|\frac{\partial H}{\partial\zeta}|\Psi\rangle. \tag{1.84}$$

The theorem can be generalized for higher order derivatives. The generalized Hellmann-Feynman theorem says that with the knowledge of wave function and its derivatives up to n-th order, one can obtain analytically, the response properties up to $(2n+1)$-th order. This is the famous $(2n+1)$-rule used in the context of analytical response properties. For a general non-exact wave function, the HFT and its generalized form are not applicable. However, if the wave function is obtained variationally, it can be easily shown that the wave function obeys the generalized HFT. Hence, in electronic structure theories, emphasis is given on stationarity of the wave functions. HFT does not hold for approximate wave functions with which we are generally dealing in quantum chemistry. However, it holds for a few special cases such as, for example, in HF theory at the complete basis set limit. For approximate wave functions the derivative expressions are usually the preferred choice.

1.18 Linear response in SRCC theory

The linear response approach to SRCC was initiated by Monkhorst [115]. In the presence of uniform external field (ζ) the SRCC energy and amplitude T becomes perturbation dependent and expanded in terms of Taylor series expansion. The expressions for the derivatives of energy and wave functions are obtained by differentiating eq.1.53 and 1.54 with respect to ζ up to desired order. Without the orbital relaxation, the expressions for first derivatives of correlation energy and cluster amplitudes are respectively,

$$E_0^{corr(1)} = \langle\phi_0|[(\hat{O}e^T)_c + (H_N e^T T^{(1)})_c]|\phi_0\rangle \tag{1.85}$$

$$0 = \langle\phi_I|[(\hat{O}e^T)_c + (H_N e^T T^{(1)})_c]|\phi_0\rangle \tag{1.86}$$

From eq.1.85, it is apparent that for getting energy derivative, response of the amplitudes $T^{(1)}$ is required. This is obtained by solving the eq.1.86. This needs to be solved for every mode of perturbation, which is a clear disadvantage. This disadvantage arises due to the fact that SRCC theory is non-variational (or non-stationary) theory, and it does not have advantages of the generalized Hellmann-Feynman theorem and $(2n+1)$-rule of variational theories.

To circumvent this problem of the dependence of wave function derivative in the energy derivative expression, Bartlett and co-workers [116] introduced Z-vector technique in SRCC context. This is based on Dalgarno's interchange theorem [117]. The idea of Z-vector was taken from Handy and Schaefer who used the technique for analytical derivatives of CI method. The eq.1.85 and eq.1.86 are written in a different from

$$E_0^{corr(1)} = Y^T T^{(1)} + Q(\hat{O}) \tag{1.87}$$

$$0 = AT^{(1)} + B(\hat{O}) \tag{1.88}$$

where,

$$\begin{gathered} Y^T T^{(1)} = \langle\phi_0|(H_N e^T T^{(1)})_c|\phi_0\rangle \\ Q(\hat{O}) = \langle\phi_0|(\hat{O}e^T)_c|\phi_0\rangle \\ AT^{(1)} = \langle\phi_I|(H_N e^T T^{(1)})_c|\phi_0\rangle \ ; B(\hat{O}) = \langle\phi_I|(\hat{O}e^T)_c|\phi_0\rangle \end{gathered}$$

We introduce a perturbation independent vector Z^T as

$$Z^T A = Y^T. \tag{1.89}$$

Substitution of eq.1.88 and eq.1.89 in eq.1.87 leads to

$$E_0^{corr(1)} = Z^T B(\hat{O}) + Q(\hat{O}), \tag{1.90}$$

which is independent of wave function derivative. Thus, one has to solve only one extra set of perturbation independent amplitudes, i.e. the Z-vectors, defined by eq.1.89, in addition to the cluster amplitudes, making the procedure of obtaining first derivatives of energy more efficient.

An another attractive method to eliminate the dependence of $T^{(1)}$ is pursued by Jorgensen and co-workers [118–120] for SRCC derivatives which automatically incorporates the benefits of Z-vector technique to all orders. This approach, known as constrained variation approach, involves construction of a functional with undetermined Lagrange multipliers λ_q corresponding to SRCC equations as follows.

$$\Im(\zeta) = \langle\phi_0|e^{-T}\hat{H}e^{T}|\phi_0\rangle + \sum_{q\neq 0}\lambda_q\langle\phi_q|e^{-T}\hat{H}e^{T}|\phi_0\rangle. \tag{1.91}$$

Optimization of the above functional leads to the same equations as SRCC equations and with λ_q equations similar to Z-vector in eq.1.89. In this formulation, obtaining derivative expressions for higher order is quite transparent. While the cluster amplitude derivatives obey the $(2n+1)$-rule, the derivatives of Lagrange multipliers obey $(2n+2)$-rule [118, 121]. Koch and coworkers have used this approach to obtain efficient expressions for up to third-order molecular properties [121].

1.19 Linear response to stationary CC

As we discussed, the stationary CC method enjoys the advantage of being variational and hence HFT holds. This makes the evaluation of higher derivatives simple. The response approach in XCC and UCC framework was developed by Pal [122] and extensively used for obtaining static properties [123–125] of molecules. Here the energy functional and the response of the functional is expressed in terms of the CC amplitudes and their derivatives. These amplitudes and derivatives are obtained by imposition of the stationarity of the functional and functional derivatives. This stationarity ensures that in the final formula of the first derivative of energy, the first derivative amplitudes do not appear.

The energy functional and cluster amplitudes in the presence of external fields can be expressed as Taylor's series around the external field. The different derivatives of the functional and the cluster operators are denoted as $E^{(i)}$ and $T^{(i)}$. The equations to determine the cluster amplitudes and their derivatives are defined by making $E(i)$ stationary with respect to $T^{(j)}$ amplitudes in general for $i \geq j$. Pal and coworkers showed [122–124] that, if cluster amplitudes and their derivatives are truncated to uniform degree then $\frac{\partial E^{(i)}}{\partial t^{(j)}} = 0$, provides identical set of equations for a fixed value of (i-j). Hence, the following set of equations

$$\frac{\partial E^{(i)}}{\partial t^{(0)}} = 0; i = 1, 2, 3... \tag{1.92}$$

are sufficient to calculate all the cluster amplitudes and their derivatives. While, the XCC and UCC functionals suffer from loss of size-extensivity due to disconnected terms in cluster equations, the double-linked form of ECC functional ensures the size-extensivity even for the energy derivatives. ECC has therefore, emerged as a state-of-the-art method for obtaining molecular properties. Pal and co-workers extensively used ECCSD response for molecular electric properties [126, 127]. Recently, Pal and coworkers attempted ECC response for obtaining magnetizabilities [128]. In this thesis we attempted the ECC response for obtaining molecular shielding constants, which is discussed in chapter II.

1.20 Linear response to FSMRCC

Naturally the energy derivatives of the FSMRCC was the next important development in quantum theory. The essential difference in implementing energy derivatives in FSMRCC, a opposed to the SRCC, arises from the fact that the FSMRCC is an effective

Hamiltonian approach providing multiple roots via diagonalization. Initial developments by Pal and co-workers involved explicit differentiation of Bloch equation with respect to uniform external field. In presence of time-independent uniform external field, the parameters $\Upsilon = \{H_{\mathit{eff}}^{(p,h)}, C^{(p,h)}, \tilde{C}^{(p,h)}, E, \Omega\}$ become perturbation dependent and can be expanded in Taylor series of ζ.

$$\Upsilon(\zeta) = \Upsilon^{(0)} + \zeta\Upsilon^{(1)} + \frac{1}{2!}\zeta^2\Upsilon^{(2)} + \frac{1}{3!}\zeta^3\Upsilon^{(3)} + \ldots \tag{1.93}$$

The differentiation of the Bloch equations following left projections by model space and virtual space configurations with respect to ζ yields the equations for wave function derivatives and the derivative effective Hamiltonian.

$$\begin{aligned} P^{(k,l)}(H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)} - \Omega^{(1)}H_{\mathit{eff}}^{(k,l)^{(0)}} - \Omega^{(0)}H_{\mathit{eff}}^{(k,l)^{(1)}})P^{(k,l)} &= 0 \quad (1.94) \\ Q^{(k,l)}(H^{(1)}\Omega^{(0)} + H^{(0)}\Omega^{(1)} - \Omega^{(1)}H_{\mathit{eff}}^{(k,l)^{(0)}} - \Omega^{(0)}H_{\mathit{eff}}^{(k,l)^{(1)}})P^{(k,l)} &= 0 \quad (1.95) \\ ;\forall k = 0,\ldots,p; l = 0,\ldots,h & \end{aligned}$$

The equations are linear in the perturbation dependent quantities. It is interesting to note that the homogeneous parts of the Ω derivative equations are identical to the linear homogeneous part of the undifferentiated cluster equations. The SEC transparently holds at every order. The method provides multiple roots of derivative effective-Hamiltonian which can be obtained simultaneously by solving following equations.

$$\sum_i \{(H_{\mathit{eff}}^{(1)})_{ji}C_{i\mu}^{(0)} + (H_{\mathit{eff}}^{(0)})_{ji}C_{i\mu}^{(1)}\} = E_\mu^{(1)}C_{j\mu}^{(0)} + E_\mu^{(0)}C_{j\mu}^{(1)} \tag{1.96}$$

However, due to its non-variational nature, the method does not obey the generalized Hellman-Feynman theorem for energy derivatives. Therefore, the evaluation of n^{th} order energy derivatives demands the knowledge of cluster amplitudes and their derivatives up to n^{th} order and is thus not a practicable approach.

In lines of Z-vector formalism in SRCC, Pal and co-workers proposed Z-vector technique for FSMRCC response [129]. Ajitha and Pal [129] proposed a perturbation independent set of amplitudes Z such that for every $Q^{(p,h)}T^{(p,h)}P^{(p,h)}$ sector amplitude, there is a corresponding $P^{(p,h)}Z^{(p,h)}Q^{(p,h)}$ amplitude and the derivative effective Hamiltonian equation can be written in terms of these Z vectors using Dalgarno's interchange theorem. However this worked only in the case of diagonal assumption of the effective Hamiltonian. In the lines of SRCC, the Lagrange approach for energy derivatives was introduced in FSMRCC context by Szalay [130] and was applicable for CMS. Later, Pal and co-workers [131] independently formulated a conceptually simple Lagrange variation based approach for general incomplete model spaces (IMS) and showed that the functional simplifies to the one proposed by Szalay if applied for CMS and QMS. The above method of Pal and co-workers provides response of a specific root of the multiple roots of FSMRCC. One has to project a single desired state (root of effective Hamiltonian) for doing constrained variation. In FSMRCC context, the energy of a specific state of the (p,h) FS sector is given by

$$E_\mu = \sum_{ij} \tilde{C}^{(p,h)}_{\mu i} (H_{\mathit{eff}})^{(p,h)}_{ij} C^{(p,h)}_{j\mu} \tag{1.97}$$

We construct the Lagrangian to minimize the energy expression given above, with the constraint that the MRCC equations [Eqs (1.79,1.81)] are satisfied for the state μ.

$$\begin{aligned} \Im &= \sum_{ij} \tilde{C}^{(p,h)}_{\mu i} (H_{\mathit{eff}})^{(p,h)}_{ij} C^{(p,h)}_{j\mu} \\ &+ \sum_{k=0}^{p} \sum_{l=0}^{h} \{ P^{(k,l)} \Lambda^{(k,l)} P^{(k,l)} P^{(k,l)} [H\Omega - \Omega H^{(k,l)}_{\mathit{eff}}] P^{(k,l)} \\ &+ P^{(k,l)} \Lambda^{(k,l)} Q^{(k,l)} Q^{(k,l)} [H\Omega - \Omega H^{(k,l)}_{\mathit{eff}}] P^{(k,l)} \} \\ &+ E_\mu [\sum_{ij} \tilde{C}^{(p,h)}_{\mu i} C^{(p,h)}_{j\mu} - 1] \end{aligned} \tag{1.98}$$

The Λ's in the above equation are the undetermined Lagrange multipliers obtained by applying stationarity condition on the Lagrangian $\Im$ with respect to the cluster amplitudes of the corresponding sectors. The stationarity condition on $\Im$ with respect to the Λ vectors yields the MRCC equations for the cluster amplitude. Obviously, the cluster-amplitudes are completely decoupled from the Λ vectors. The Λ vectors follow the partial sector wise decoupling exactly in the reverse SEC, i.e., the Λ vectors of the highest sector are totally decoupled from the lowest ones. The lowest sector Λ vectors are coupled with the Λs of all the higher sectors through the inhomogeneous part of the linear equations. The eigen vectors and effective Hamiltonian can be obtained by applying stationarity condition on the $\Im$ with respect to each other. In case of CMS and IMS, since the effective Hamiltonian can be explicitly defined in terms of the cluster amplitudes, the above method simplifies to the one proposed by Szalay.

The Lagrangian defined in eq.(1.98) can be differentiated with respect to the field ζ to obtain the Lagrangians at different order. The energy derivatives follow $(2n+1)$ rule with respect to the Ω amplitudes and $(2n+2)$ rule with respect to Λ amplitudes. There is a $(2n+1)$ rule for the eigen vectors $\tilde{C}^{(0,1)}$ and $C^{(0,1)}$ for evaluation of energy derivatives. The first order properties can thus be obtained simply with the knowledge of Ω and Λ amplitudes only. For second order properties, we differentiate the Lagrangian (eq.1.98) twice with respect to the external field. However, the expensive evaluation of wave-function derivatives for each mode of perturbation is avoided in Λ-FSMRCC. This feature becomes more prominent while obtaining higher order properties like polarizability and first hyper-polarizability. The electric properties using Λ-FSMRCC method was successfully implemented for the dipole moment [132] and polarizability [133] of the doublet radicals as well as excited states [134] of molecules.

It may be pertinent to note that studies have been carried out to compute energy derivatives using methods which are related to MRCC. EOMCC derivatives for property calculation was initiated and implemented first by Stanton [135] and then by Stanton and Gauss [136, 137]. Analytic energy derivatives for ionized states were described by Stanton and Gauss [137] in EOMCC formalism. Subsequently, analytic second derivative for excited state was also introduced by Stanton and Gauss [136]. Gradients using STEOM-CC were implemented by Nooijen and coworkers [138] using Lagrange undetermined multipliers. In STEOMCC method, two more Z-vector like quantities are required to be evaluated for the response of the $S^{\pm}$ coefficients to the perturbation along with the

Lagrange multipliers (Λ). The role of Λ is equivalent in both cases. In this thesis we discussed the Λ-FSMRCC for magnetic properties in chapter-III. Further triples correction to this method is discussed in chapter-IV.

1.21 Motivation behind molecular magnetic property study

Although quantum chemists have spent most of their effort in searching for good wave function and energies, the aim of a quantum chemical calculations is often neither the wave function nor the energy, but rather some physical properties or to phrase it more physically, the response of a system to an external perturbation [11, 12]. The perturbation can be external electric field, magnetic field or nuclear displacement. Depending on the field type properties are characterized. For the case of magnetic field as perturbation one obtains magnetizabilities, NMR shieldings, spin-spin coupling constants etc [11]. The evaluation of magnetic properties are not straight forward like electric based properties because of two factors. First, the nature of the magnetic field is purely imaginary and hence the finite-difference procedures using the complex wave function for calculating the magnetic properties are highly undesirable. We need the analytical method for magnetic property calculations. The method should efficiently include the fact that the matrix representation of the imaginary quantities is antisymmetric. Secondly, the electric field interacts with the charged particles (electron and nuclei) and adds a scalar potential to the Hamiltonian operator. However, magnetic field interacts with the magnetic moments generated by the movement of the charged particles and hence adds a vector potential to the Hamiltonian. This thesis is focused on magnetic properties because of the challenges posed by it and also less available studies for the evaluation of these properties. The closed shell method ECC, which is very useful for higher order property evaluation is used for magnetic property studies, also the FSMRCC method is used for the studying open-shell system property evaluation. These two highly efficient methods should be able to handle various situations involving magnetic field. In the following subsections we will discuss the above mentioned issues and some already available methods for the magnetic property evaluation.

1.21.1 Magnetic properties as energy derivatives

The electronic energy in the presence of an external magnetic field B and nuclear magnetic moment M_K, around zero field and and zero magnetic moments is expressed as

$$E(B, M) = E_0 + \frac{1}{2} B E^{(20)} B + \frac{1}{2} \sum_K B E_K^{(11)} M_K + \cdots \tag{1.99}$$

where

$$E^{(20)} = \frac{d^2 E(B, M)}{dB^2}|_{B=0, M=0} \rightarrow \xi \tag{1.100}$$

is the representation of the magnetizability (ξ) and

$$E_K^{(11)} = \frac{d^2 E(B, M)}{dB dM_K}|_{B=0, M=0} \rightarrow \sigma \tag{1.101}$$

is the representation of the shielding tensor (σ). These properties have two contributions, one is dia magnetic and another is from para magnetic contributions. For linear and symmetric top molecules the isotropic shielding constants are defined by

$$\bar{\sigma} = \frac{1}{3}(\sigma_{\parallel} + 2\sigma_{\perp}) \tag{1.102}$$

where $\sigma_{\parallel}$ refers to the component along the major molecular axis and $\sigma_{\perp}$ is the component in the direction perpendicular to it. Anisotropies are given by

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}. \tag{1.103}$$

All these properties are second order quantities. Other properties like spin-spin rotation constant, g-tensors etc, also be expressed using energy derivatives (Chapter V). In this thesis we are focused on the magnetizability and shielding constants.

1.21.2 Molecular Hamiltonian in magnetic field

Unlike electric perturbation, magnetic perturbation is associated with a change in momentum in the kinetic energy part of Hamiltonian H [12].

$$p \rightarrow \pi = p + \frac{e}{c}A \tag{1.104}$$

where e is elementary charge, c is speed of light and A is vector potential. All quantities are in Gaussian system of units. The vector potential A, is the vector function from which the field is derived. The magnetic field is uniquely defined through A

$$B = \nabla \times A. \tag{1.105}$$

The vector potential is not uniquely defined since the gradient of any scalar function(f) may be added and leave the field unchanged ($\nabla \times \nabla f \equiv 0$). It is convention to select it as

$$A = \frac{1}{2} B \times r. \tag{1.106}$$

The vector potential shown above satisfy the Coulomb gauge condition ($\nabla.A = 0$). With eq.1.104 the H is

$$H = \frac{p^2}{2m} + \frac{e}{mc}A.p + \frac{e^2}{2mc^2}A^2 + V(r). \tag{1.107}$$

The Hamiltonian differ from the true Hamiltonian by the presence of two terms, one is first order in magnetic induction B (via A), the second is second order (viaA^2). Inserting the explicit form of vector potential in eq.1.106, the H is

$$H = -\frac{\hbar}{2m}\nabla^2 - \frac{ie\hbar}{2mc}B.(r \times \nabla) + \frac{e^2}{8mc^2}[(B.B)(r.r) - (B.r)(B.r)] + V(r). \tag{1.108}$$

Here, the first term is the unperturbed kinetic energy term.

1.21.3 The gauge origin problem

The problem of gauge invariance (gauge-origin independence) arises in the magnetic properties calculation because of the use of vector potential A for the description of the magnetic interactions in the Hamiltonian. The Hamiltonian in the presence of the magnetic field does not contain the field B directly, but rather its vector potential. If A is given B can be constructed eq.1.105. However the converse is not true. The reason is the ∇ operator in eq.1.105 which allows to add the gradient of any scalar function to A without changing the corresponding magnetic field. If A satisfies eq.1.105 with a given B, then A' with an arbitrary scalar function χ,

$$A' = A + \nabla\chi \tag{1.109}$$

also satisfies eq.1.105. Hence A is determined up to the gradient of an arbitrary 'gauge function'. All physical observables should be independent of gauge function. The major problem in quantum chemical calculation of magnetic properties, as pointed out by Kutzelnigg [139] is that the exact solution to the Schrödinger equation satisfies the requirement of gauge invariance. The gauge invariance is not necessarily ensured for approximate solutions of the Schrödinger equation.

The main problem with the gauge-dependence of the results which are computed is that they are no longer uniquely defined. The computed values for magnetic properties depend on a parameters which can be chosen in an arbitrary manner. In all practical calculations the results are gauge independent only when a complete basis is used. The choice of gauge is very important for calculations. For an external homogeneous magnetic field of strength B, a possible choice of the vector potential is

$$A(r) = \frac{1}{2}B \times (r - R) \tag{1.110}$$

where R is a fixed point in space, called the *'gauge origin'*. For atoms there is a *'natural'* gauge origin namely $R = (X, Y, Z) = 0$. In molecules there is, however, no natural gauge origin and it is very important to choose the proper gauge origin. One can have unique results by simply fixing the gauge origin to the center of mass of the considered molecule. Of course, such a choice would guarantee unique results, but on the other hand it does not resolve the fundamental problem connected with the gauge problem in the computation of magnetic properties. There are methods developed to eliminate the gauge dependence in the magnetic property calculations, which are discussed in the following sections.

1.21.4 Local gauge origin methods

In local gauge origin methods or distributed gauge origin methods, the gauge invariance is eliminated by using more than one gauge origin for the external magnetic field. In this method the molecule is partitioned into local fragments and for each fragment the gauge origin is individually chosen in an optimal way. If the local fragments is assigned to the various atoms in the molecule, the corresponding nuclear position is good choice for local origin. For understanding local gauge origins, it is important to introduce gauge transformations. A shift of gauge origin from R_o to R'_o is achieved via gauge transformation. The corresponding equations for one electron system are

$$\Psi \rightarrow \Psi' = exp(-\Lambda(r))\Psi \tag{1.111}$$

$$\hat{H} \rightarrow \hat{H}' = exp(-\Lambda(r))\hat{H}exp(\Lambda(r)) \tag{1.112}$$

The gauge factor is defined by

$$\Lambda(r) = \frac{ie}{2c\hbar}[(R'_o - R_o) \times B].r. \tag{1.113}$$

Expansion of the Hamiltonian H' using Hausdorff formula $H' = H + [H, \Lambda] + \frac{1}{2}[[H, \Lambda], \Lambda] +$ ... shows that H' is indeed the Hamiltonian with the gauge origin at R'_o instead of R_o. Local gauge origins are introduced by the more general gauge transformations of the following kind

$$\sum_A exp(\Lambda_A(r))\hat{P}_A \tag{1.114}$$

where $\hat{P}_A$ is a suitable projector on the local fragment A and $exp(\Lambda_A(r))$ a gauge transformation to the origin chosen for A. The above eq.1.114 is suitable to define the local fragment at the one electron level. The individual gauge for localized orbitals

(IGLO) [15, 140] by Kutzelnigg and Schindler, and local origin (LORG) [141] scheme of Bouman and Hansen are based on individual gauges for molecular orbitals. However, standard HF orbitals are usually delocalized, they are not well suited for local origin approach. Therefore Kutzelnigg [15] introduced localized orbitals and defined individual gauges for them.

1.21.5 The GIAO ansatz

Having seen that localized orbitals are not more suitable choice, it is more natural to work with atomic orbitals(AOs) and to assign each of them an individual gauge origin. This choice of local gauge origins leads to what is nowadays known as the gauge-including atomic orbital approach (GIAO) [16, 18–20]. This is sometimes called as London atomic (LAO) approach.

In GIAO ansatz, local gauge origins for atomic orbitals $|\chi_\mu\rangle$ is chosen. The meaning of this is that the corresponding nucleus at which the atomic orbital is centered is chosen as the “natural” gauge origin. Within the concept of local gauge origins, the GIAO ansatz is based on the following gauge transformation

$$\sum_\mu exp(\Lambda_\mu(r))\hat{P}_\mu. \tag{1.115}$$

The projector on $|\chi_\mu\rangle$ defined by $\hat{P}_\mu = \sum_\mu |\chi_\nu\rangle S^{-1}_{\mu\nu}\langle\chi_\nu|$. The gauge factor given by

$$\Lambda_\mu(r) = \frac{ie}{2c\hbar}[(R_\mu - R_o) \times B].r \tag{1.116}$$

where R_o is the initial gauge origin in the Hamiltionian and R_μ is the center of the basis function $|\chi_\mu\rangle$. This gauge factor given above shifts the gauge origin from R_o to R_μ.

It is convenient to attach the additional phase factors to the AO’s to describe GIAO ansatz. The calculation of magnetic properties are carried out with the following perturbation dependent basis functions

$$|\chi_\mu(B)\rangle = exp(-\frac{ie}{2c\hbar}(B \times [R_\mu - R_o]).r|\chi_\mu\rangle \tag{1.117}$$

instead of the usual field independent functions $|\chi_\mu(0)\rangle$. This field dependent basis functions are represented as gauge-including atomic orbitals or London orbitals. There are various advantages involved in GIAO. This first provides unique results and ensures the fast basis set convergence, as for each AO the corresponding optimal gauge is used. When AO's depend on perturbation, the corresponding coefficients are also depend on perturbation. One need to solve coupled-perturbed HF for obtaining coefficent derivatives.

1.22 Coupled-Perturbed HF

Although a calculation of the wave function response can be avoided for the first derivative, it is necessary for higher derivative. The first derivatives of the coefficients are obtained by solving *Coupled Perturbed Hartree-Fock* equations [142]. For HF wave function, an equation of the change in the MO coefficients may also be formulated from the HF equation

$$F^{(0)}C^{(0)} = S^{(0)}C^{(0)}\varepsilon^{(0)}. \tag{1.118}$$

The superscript (0) here denotes the unperturbed system. Expanding F, C, S and ε, matrices in terms of a perturbation parameter (e.g. $F = F^{(0)} + \lambda F^{(1)} + \lambda^2 F^{(2)} + \cdots$) and collecting all the first order terms gives first order CPHF equations,

$$(F^{(0)} + S^{(0)}\varepsilon^{(0)})C^{(1)} = (F^{(1)} + S^{(0)}\varepsilon^{(1)} + S^{(1)}\varepsilon^{(0)})C^{(0)}. \tag{1.119}$$

The orthonormality condition becomes

$$C^{\dagger(1)}S^{(0)}C^{(0)} + C^{\dagger(0)}S^{(1)}C^{(0)} + C^{\dagger(0)}S^{(0)}C^{(1)} = 0. \tag{1.120}$$

The $F^{(1)}$ in eq.1.119 is given as

$$F^{(1)} = h^{(1)} + G^{(1)}D^{(0)} + G^{(0)}D^{(1)} \tag{1.121}$$

where h is the one-electron(core) matrix, D is the density matrix and G is the tensor containing the two-electron integrals. The $S^{(1)}$, $h^{(1)}$ and $G^{(1)}$ quantities are (first) derivatives of overlap, one- and two-electron integrals over basis functions. When the Fock matrix is diagonal, then the derivatives of Fock matrix are also diagonal.

The density matrix is given as a product of MO coefficients

$$D^{(0)} = C^{\dagger(0)}C^{(0)}; D^{(1)} = C^{\dagger(1)}C^{(0)} + C^{\dagger(0)}C^{(1)} \tag{1.122}$$

The stationary orbitals, in the presence of a perturbation, is given by a unitary transformation of the unperturbed orbitals

$$C^{(1)} = C^{(0)}U^{(1)}. \tag{1.123}$$

On simplifying the eq.1.119, using $C^{\dagger(0)}S^{(0)}C^{0)} = 1$ and $C^{\dagger(0)}F^{(0)}C^{0)} = E$ one obtains

$$EU^{(1)} - U^{(1)}E = C^{\dagger(0)}S^{(1)}C^{(0)}E - C^{\dagger(0)}F^{(1)}C^{(0)} + E^{(1)} \tag{1.124}$$

This equation is a CPHF equation in matrix form. The CPHF equations are linear and can be determined by standard matrix operations. The size of the U matrix is the number of occupied orbitals times the number of virtual orbitals, which is generally quite large. Solving the CPHF equation requires U matrix, which in turn used for the construction of derivative Fock matrix. Hence CPHF equations are normally solved by iteratively [143]. The CPHF equations may be formulated either in an atomic orbital or molecular orbital basis. Although the latter has computational advantages in certain cases, the former is more suitable for use in connection with direct methods (where the atomic integrals are calculated as required). There will be one CPHF equation to be solved for each perturbation. If it is an electric or magnetic field, there will in general be three components (F_x, F_y, F_z), if it is a geometry perturbation there will be 3N (actually only 3N-6 independent) components, N being the number of atoms.

The CPHF procedure may be generalized to higher order. Extending the expansion to second-order allows derivation of an equation for the second-order change in the MO coefficients, by solving a second-order CPHF equation etc. Pople and coworkers [144] developed an efficient method for solving CPHF equations, which made second derivative calculations practicable for SCF and unrestricted SCF wave functions. The CPHF method is extended to restricted openshell HF cases also[145]. The CPHF method is equivalent to the random phase approximation (RPA) [146] or the Time-dependent Hartree-Fock (TDHF) [147] for static calculations within a given basis.

1.23 Coupled-Perturbed MCSCF

The *Coupled-Perturbed MCSCF* (CPMCSCF) have been formulated [148] and MCSCF second derivatives are applied by various groups [149]. The CPMCSCF simultaneous equations provide the derivatives of both MO and CI coefficients with respect to perturbations. The equations are obtained by differentiating the variational conditions on both the CI and MO spaces.

The MCSCF wave function is written as,

$$|MC\rangle = \sum_{\mu} C_{\mu}^{(0)} |\mu\rangle \tag{1.125}$$

satisfies the condition

$$E_{MC}^{(0)} = \frac{\langle MC|\hat{H}|MC\rangle}{\langle MC|MC\rangle} =_{\mu,C}^{Min} \frac{\langle \mu, C|H|\mu, C\rangle}{\mu, C|\mu, C\rangle}. \tag{1.126}$$

with respect to the MO and CI coefficients. Expressions for the MCSCF molecular properties are

$$E_{MC}^{(0)} = \langle MC|\hat{H}^{(0)}|MC\rangle \tag{1.127}$$

$$E_{MC}^{(1)} = \langle MC|\hat{H}^{(1)}|MC\rangle \tag{1.128}$$

$$\begin{aligned} E_{MC}^{(2)} &= \langle MC|\hat{H}^{(2)}|MC\rangle + \langle MC|[\mu^{(1)}, \hat{H}^{(1)}]|MC\rangle && (1.129) \\ &\quad +2\langle MC|\hat{H}^{(1)}|C^{(1)}\rangle - 2E_{MC}^{(1)}\langle MC|C^{(1)}\rangle. && (1.130) \end{aligned}$$

The normalization of the wave function $\langle MC|MC\rangle = 1$ is assumed. The first order CPMCSCF equations are required for constructing second order CPMSCF equations.

There are methods developed for the calculation of shielding constants at the MCSCF level. The two approaches mainly developed are GIAO [150] and IGLO [151] approximations. For the identical MCSCF references, the results obtained in the MCSCF-GIAO and IGLO approaches are similar.

1.24 Magnetic properties from CC method

In common gauge origin calculation for ξ, the only needed integrals are

$$\frac{\partial h_{\mu\nu}}{\partial B_\alpha} = \frac{1}{2}\langle\chi_\mu|((r-R_o)\times p)_\alpha|\chi_\nu\rangle \tag{1.131}$$

and

$$\frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial B_\beta} = \frac{1}{4}\langle\chi_\mu|\delta_{\alpha\beta}(r-R_o)^2-(r-R_o)_\beta(r-R_o)_\alpha|\chi_\nu\rangle. \tag{1.132}$$

The gauge-origin independence is achieved by using the following explicitly magnetic field dependent basis functions:

$$\chi_\mu(B) = exp(-\frac{i}{2}(B\times(R_\mu-R_o)).r)\chi_\mu(0) \tag{1.133}$$

where $\chi_\mu(0)$ is standard field-independent basis functions, R_μ is center of the basis function χ_μ, R_o as the global gauge origin and r as the coordinates of the electron.

A general formula for σ_N can be obtained by first differentiating the energy E with respect to m_N and then with respect to B. A computationally convenient expression for σ_N is

$$\sigma_N(CCSD) = \sum_{\mu\nu} D_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu}\frac{\partial D_{\mu\nu}}{\partial B_i}\frac{\partial h_{\mu\nu}}{\partial m_{Nj}} \tag{1.134}$$

where μ, ν are atomic orbital indices, $D_{\mu\nu}$ is one-particle density of CC gradient theory,

$$D_{\mu\nu} = \sum_{p,q} C^*_{\mu p} D_{pq} C_{\nu q} \tag{1.135}$$

The elements of $D_{\mu\nu}$ are determined by the t amplitudes that are solutions of the usual CCSD equations. The $D_{\mu\nu}$ has two two contributions, one is from amplitude part and the second is from orbital response part. The most computationally demanding requirement is a knowledge of the perturbed density matrix. Since the derivative of the density matrix (amplitude part) involves derivative of coefficient, one need to solve CPHF equations to obtain U matrices. The orbital response part of the perturbed density is obtained from the first order Z-vector equations.

1.25 Brief overview on available methods for the calculation of magnetic susceptibilities and NMR shieldings

The use of London orbitals in *ab initio* calculations are pioneered by Hameka [152] in the 1950s and 1960s and by Ditchfield [153] in the 1970s. Efficient implementations are presented, first for self-consistent field (SCF) shieldings by Wolinski, Hinton, and Pulay [154]. The use of London orbitals has now become widespread, and Hiker et al. presented a direct program for the calculation of nuclear shielding constants [155]. The correlated shieldings are calculated by Gauss et. al. [156] at the second-order Moller-Plesset (MP2) and MP3 level and by Ruud et al. [157] at the multiconfigurational self-consistent field (MCSCF) level. Stanton and Gauss [158] calculated shielding at CCSD, CCSD(T) and CCSDt-n levels. Using various density functional theory (DFT) approximations, the NMR parameters are studied by Salsbury and Haris [159], Cheeseman et al [160] and by various authors [161]

Ruud, Helgaker, and co-workers have presented calculations of magnetizabilities at the SCF [162] and MCSCF levels. The multi-configuration IGLO is proposed and studied by Kutzelnigg et al [163]. Cybulski and Bishop reported, set of small molecules, large-scale magnetizability calculations at MP2 and MP3 levels as well as using the linearized CC doubles model (L-CCD) [164]. Magnetizabilities of some hydrocarbons are done using IGLO calculations [165]. GIAO MCSCF program is able to calculate magnetizabilities of relatively large molecules accurately with modest basis sets [166]. Magnetizabilities calculations using CC level theory is achieved by Gauss et al. [167].

The magnetizability is studied using DFT method considering various functionals and its performance also argued by many authors [168].

1.26 Objective and Scope of the thesis

The ECC and FSMRCC methods are well studied for electric properties. Our plan of this thesis is to develop these methods for the magnetic based properties calculation. We also implement a non-iterative triples correction to FSMRCC method for dipole moment. The ECC method is used here to study the nuclear magnetic shielding. The proper gauge as origin and standard atom centered basis functions are chosen to carry out the study. Considering small molecules as a study, the analysis are done, which is included in the chapter-II. The shielding values obtained are carefully compared with the CASSCF method, choosing reasonably larger active spaces. In this thesis FSMRCC method for magnetizability study of radicals is implemented. The FSMRCC method, which is suitable for doublet radicals are tested for few small radicals. The standard atom centered basis functions are used along with the proper choice of gauge origin. The calculations are performed in two different gauge origins. From our calculations, it is reflected that the center of mass is a more suitable gauge for magnetic properties studies. The results obtained are compared against the CASSCF values. In chapter-III the details of magnetizability calculations are given. Along with the magnetic properties study we have also presented a partial triples correction to FSMRCC method for properties. The triples are taken order wise and amplitudes up to third order are considered. The dipole moment obtained from this method is correct up to third order. This method has been tested with some radicals. The results are compared against the FCI and finite-field approaches. The details and results are presented in chapter-IV. In the last chapter we give the future perspective in the field of magnetic properties using these methods and higher order corrections to other properties. We also give the importance of including GIAO's for chemical shieldings under ECC method.

References

[1] A. Szabo and N. S. Ostlund, in *Modern Quantum Chemistry*, (McGraw-Hill, New York, 1989).

[2] F. Cöester, *Nucl. Phys.* **7**, 421 (1958); F. Cöester and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).

[3] J. $\check{C}\acute{i}\check{z}$ek, *J. Chem. Phys.* **45**, 4256 (1966); J. $\check{C}\acute{i}\check{z}$ek, *Adv. Chem. Phys.* **14**, 35 (1969); J. $\check{C}\acute{i}\check{z}$ek and J. Paldus, *Int. J. Quantum Chem.* **5**, 359 (1971).

[4] D. Mukherjee, *Pramana* **12**, 203 (1979).

[5] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha and D. Mukherjee, *J. Chem. Phys.* **88**, 4357 (1988).

[6] D. Mukherjee and S. Pal, *Adv. Quantum Chem.* **20**, 291 (1989); D. Mukherjee, R. K. Moitre and A. Mukhopadhyay, *Pramana* **4**, 247 (1975); *ibid. Mol. Phys.* **30**, 1861 (1975); **33**, 955 (1977); A. Mukhopadhyay, R. K. Moitra and D. Mukherjee, *J. Phys. B* **12**,1 (1979).

[7] B. Jeziorski and J. Paldus, *J. Chem. Phys.* **8**, 5673 (1988).

[8] U. Kaldor and M. A. Haque, *Chem. Phys. Lett.* **128**, 45 (1986); A. Haque and U. Kaldor, *Chem. Phys. Lett.* **117**, 347 (1985); *ibid.* 120, 261 (1985).

[9] J. Pittner, *J. Chem. Phys.* **118**, 10876 (2003).

[10] X. Li and J. Paldus, *J. Chem. Phys.* **119**, 5320 (2003).

[11] C. Dykstra, in *Ab initio calculation of the structures and properties of molecules* (Elsevier Science Publiser, B. V, 1988).

[12] P. Atkins and R. Friedman, *Molecular quantum mechanics*, fourth edition, (Oxford University Press, 2005).

[13] D. M. Bishop and S. M. Cybulski, *Mol. Phys.* **80**, 199 (1993);
R. M. Stevens, R. M. Pitzer and W. N. Lipscomb , *J. Chem. Phys.* **38**, 550 (1963).

[14] D. M. Bishop and S. M. Cybulski, *Mol. Phys.* **80**, 209 (1993); S. M. Cybulski and D. M. Bishop, *Chem. Phys. Lett.* **250**, 471 (1996); S. M. Cybulski and D. M. Bishop *J. Chem. Phys.* **106**, 4082 (1997).

[15] W. Kutzelnigg, *Isr. J. Chem.* **19**, 193 (1980); M. Schindler and W. Kutzelnigg, *J. Chem. Phys.* **76**, 1919 (1982).

[16] F. London, *J. Phys. Radium.* **8**, 397 (1937); F. London, *Z. Naturwiss.* **15**, 187 (1982).

[17] J. A. Pople, *J. Chem. Phys.* **37**, **53**, 60 (1962).

[18] H. F. Hameka, *Mol. Phys.* **1**, 203 (1958); *ibid.* **2**, 64 (1959).

[19] R. Ditchfield, *Mol. Phys.* **27**, 789 (1974).

[20] K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990).

[21] M. Born and J. R. Oppenheimer, *Ann. Phys.* **84**, 457 (1927).

[22] D. R. Hartree, *Proc. Camb. Phil. SOC.* **24**, 89, 111 426 (1928).

[23] P. O. Lowdin, *Adv. Chem. Phys.* **2**, 207 (1959)

[24] E. R. Davidson, *J. Comput. Phys.* **17**, 87 (1975).

[25] J. A. Pople, J. S. Binkley and R. Seeger, *Int. J. Qunatum Chem.* **S10**, 1 (1977).

[26] R. Choudhary, D. Mukherjee and M. D. Prasad, in *Aspects of Many-body Effects in Molecules and Extended Systems*, edited by D. Mukherjee (Springer-Verlag, Heidelberg, 1989), Vol. 50, pp.3.

[27] M. Nooijen, K. R. Shamasundar and D. Mukherjee, *Mol. Phys.* **103**, 2277 (2005).

[28] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, (Springer- Verlag, Berlin, 1982, ch. 9).

[29] J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929).

[30] B. Kirtman, *J. Chem. Phys.* **49**, 3890 (1968); P. R. Certain and J. O. Hirschfelder, *J. Chem. Phys.* **52**, 5977 (1970); I. Shavitt and L. T. Redmon, *J. Chem. Phys.* **73**, 5711 (1980); B. Kirtman, *J. Chem. Phys.* **75**, 798 (1981); E. C. Kemble, in *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill, New York, 1937).

[31] G. C. Wick, *Phys. Rev.* **80**, 268 (1950).

[32] R. P. Feynman, *Phys. Rev.* **76**, 749 (1949); *ibid.* **76**, 769 (1949).

[33] A. C. Hurley, in *Electron Correlation in Small Molecules* (Academic Press, London, 1976).

[34] G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).

[35] M. I. Frisch, R. Krishnan, and J. A. Pople, *Chem. Phys. Lett.* **75**, 66 (1980); R. Krishnan, M. I. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980); S. Wilson and Y. R. Saunders, *J. Phys. B* **12**, L403 (1979); M. F. Guest and S. Wilson, *Chem. Phys. Lett.* **73**, 607 (1980); Y. Kvasnicka, Y. Laurinc, and S. Biskupic, *ibid.* 67, 81 (1979); V. Kello, M. Urban, J. Noga, and G. H. F. Diercksen, *J. Am. Chem. Soc.* **106**, 5864 (1984); R. J. Bartlett, H. Sekino, and G. D. Purvis, *Chem. Phys. Lett.* **98**, 66 (1983); M. Urban, I. Cernusak, and V. Kello, *Chem. Phys. Lett.* **105**, 625 (1984); R. Krishnan, M. I. Frisch and J. A. Pople, *Chem. Phys. Lett.* **75**, 66 (1980); M. J. Frisch, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.* **81**, 1882 (1984).

[36] J. Paldus, J. $\check{C}\acute{i}\check{z}$ek, and I. Shavitt, *Phys. Rev. A* **5**, 50 (1972).

[37] J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); G. E. Scuseria and H. F. Schaefer III, *Chem. Phys. Lett.* **152**, 382 (1988); M. R. Hoffmann and H. F. Schaefer III, *Adv. Quantum Chem.* **17**, 207 (1986).

[38] M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *J. Chem. Phys.* **83**, 8 (1985).

[39] K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

[40] J. Noga, S. A. Kucharski and R. J.Bartlett, *J. Chem. Phys.* **80**, 3399 (1989); J. D. Watts, I. Cernusak, J. Noga, R. J. Bartlett, C. W. Bauschlicher, T. J. Lee, A. P. Rendell and P. R. Taylor, *J. Chem. Phys.* **93**, 8875 (1990); P. Piecuch, S. A. Kucharski and K. Kowalski, *Chem. Phys. Lett.* **344**, 176 (2001); S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **97**, 4282 (1992).

[41] O. Christiansen, H. Koch and P. Jorgensen, *Chem. Phys. Lett.* **243**, 409 (1995).

[42] O. Christiansen, J. Gauss and J. F. Stanton, *Chem. Phys. Lett.* **292**, 437 (1998).

[43] M. Musial, S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **116**, 4382 (2002).

[44] S. Hirata, *J. Phys. Chem. A* **107**, 9887 (2003); P. Piecuch, S. Hirata, K. Kowalski, P. D. Fan and T. L. Windus, *Int. J. Quantum Chem.* **106**, 79 (2005); S. Hirata, P. D. Fan, A. A. Auer, M. Nooijen and P. Piecuch, *J. Chem. Phys.* **121**, 12197 (2004); S. Hirata, *J. Chem. Phys.* **122**, 094105 (2005); A. A. Auer, G. Baumgartner, D. E. Bernholdt, A. Bibireata, V.

Choppella, D. Cociorva, X. Gao, R. Harrison, S. Krishnamoorthy, S. Krishnan, C. C. Lam, Q. Lu, M. Nooijen, R. Pitzer, J. Ramanujam, P. Sadayappan and A. Sibiryakov, *Mol. Phys.* **104**, 211 (2006).

[45] M. Kallay and P. R. Surjan, *J. Chem. Phys.* **113**, 1359 (2000); M. Kallay and P. R. Surjan, *J. Chem. Phys.* **115**, 2945 (2001); J. Olsen, *J. Chem. Phys.* **113**, 7140 (2000).

[46] M. Kallay, J. Gauss and P. G. Szalay, *J. Chem. Phys.* **119**, 2991 (2003); *ibid.* **120**, 6841 (2004); *ibid.* **123**, 214105 (2005); *ibid.* **129**, 144101 (2008).

[47] S. Pal, M. D. Prasad and D. Mukherjee, *Pramana* **18**, 261 (1982). *ibid. Theor. Chim. Acta.*, **62**, 523 (1983); *ibid.* **66**, 311 (1984).

[48] S. Pal, *Theor. Chim. Acta.* **66**, 151 (1984); J. Noga and M. Urban, *Theor. Chim. Acta.* **73**, 523 (1989).

[49] R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988); R. J. Bartlett, S. A. Kucharski and J. Noga, *Chem. Phys. Lett.* **155**, 133 (1989).

[50] W. Kutzelnigg, in *Methods in Electronic Structure Theory*, edited by H. F. Schaefer III, (Plenum, New York, 1977), pp. 129.

[51] J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929).

[52] H. Primas, *Helv. Phys. Acta* **34**, 331 (1961).

[53] J. Arponen, *Ann. Phys.* **151**, 311 (1983).

[54] J. Arponen and R. F. Bishop and E. Pajanne, *Phys. Rev. A* **36**, 2519 (1987); J. Arponen and R. F. Bishop and E. Pajanne, *Phys. Rev. A* **36**, 2539 (1987).

[55] P. Piecuch and R. J. Bartlett, *Adv. Quantum Chem.* **34**, 295 (1999).

[56] S. R. Gwaltney, E. F. C. Byrd, T. Van Voorhis and M Head-Gordon, *Chem. Phys. Lett.* **353**, 359 (2002); T. Van Voorhis and M. Head-Gordon, *Chem. Phys. Lett.* **330**, 585 (2000); E. F. C. Byrd, T. Van Voorhis and M. Head-Gordon, *J. Phys. Chem. B* **106**, 8070 (2002).

[57] D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).

[58] J. Geertsen, M. Rittby and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989); J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993); M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995).

[59] R. J. Bartlett and J. F. Stanton, *in Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. 5, pp. 65.

[60] J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993); J. Stanton, J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).

[61] M. Wladyslawski and M. Nooijen, in *Low-lying potential energy surfaces*, edited by M.R. Hoffmann and K.G. Dyall (ACS,2002), Vol. 828, pp. 65-92; M. Tobita, S. A. Perera, M. Musial, R. J. Bartlett, M. Nooijen and J. S. Lee, *J. Chem. Phys.* **119**, 10713 (2003).

[62] M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **106**, 6441 (1997); *ibid.* **106**, 6449 (1997).

[63] M. Nooijen, R. J. Bartlett, *J. Chem. Phys.* **106**, 6441 (1997).

[64] A. I. Krylov, *Chem. Phys. Lett.* **338**, 375 (2001)

[65] P. Knowles, M. Schutz, and H. J. Werner, *Modern Methods and Algorithms of Quantum Chemistry Proceedings*, Second Edition, edited by J. Grotendorst (Neumann Institute of Computing Series, Julich, 2000) , Vol 3.

[66] R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974).

[67] P. E. M. Siegbahn, *Int. J. Quantum Chem.* **18**, 1229 (1980); J. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, *Int. J. Quantum Chem.* **S15**, 91 (1981); V. R. Saunders, and J. H. van Lenthe, *Mol. Phys.* **48**, 923 (1983).

[68] B. H. Brandow, *Rev. Mod. Phys.* **39**, 771 (1967).

[69] K. Wolinski, H. Sellers and P. Pulay, *Chem. Phys. Lett.* **140**, 225 (1987).

[70] B. O. Roos, *Chem. Phys. Lett.* **15**, 153 (1972); B. O. Roos and P. E. M. Siegbahn, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III, (Plenum, New York, 1977), pp. 277

[71] W. Meyer, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III, (Plenum, New York, 1977), pp. 413

[72] P. J. Knowles, and H. J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).

[73] H. J. Werner, and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).

[74] H. J. Werner and E. A. Reinsch, *J. Chem. Phys.* **76**, 3144 (1982).

[75] R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988).

[76] P. G. Szalay and R. J. Bartlett, *Chem. Phys. Lett.* **214**, 481 (1993); *ibid. J. Chem. Phys.* **103**, 3600 (1995).

[77] J. P. Daudey, J. L. Heully and J. P. Malrieu, *J. Chem. Phys.* **99**, 1240 (1993); J. P. Malrieu, J. P. Daudey and R. Caballol, *J. Chem. Phys.* **101**, 8908 (1994).

[78] A. C. Wahl and G. Das, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977) pp. 51.

[79] J. Olsen, B. O. Roos, P. Jorgensen and H. J. A. Jensen, *J. Chem. Phys.* **89**, 2185 (1988); R. Shepard, *Adv. Chem. Phys.* **69**. 1 (1987).

[80] B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987); B. O. Roos, P. Linse, P. E. M. Siegbahn and M. R. A. Blomberg, *Chem. Phys.* **66**, 197 (1982); K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990); K. Andersson, and B. O. Roos, *Chem. Phys. Lett.* **191**, 507 (1992); *ibid. Int. J. Quantum Chem.* **45**, 591 (1993); K. Andersson, B. O. Roos, P. A. Malmqvist and P. O. Widmark, *Chem. Phys. Lett.* **230**, 391 (1994).

[81] J. J. W. McDouall, K. Peasleyand and M. A. Robb, *Chem. Phys. Lett.* **148**, 183 (1988).

[82] M.G. Sheppard and K. Freed, *J. Chem. Phys.* **75**, 4507 (1981).

[83] H. Nakano, *J. Chem. Phys.* **99**, 7983 (1993).

[84] P. M. Kozlowski and E. R. Davidson, *J. Chem. Phys.* **100**, 3672 (1994).

[85] A. Zaitevskii and J. P. Malrieu, *Theor. Chim. Acta* **96**, 269 (1997).

[86] U. S. Mahapartra, B. Datta and D. Mukherjee, *Chem. Phys. Lett.* **299**, 42 (1999); U. S. Mahapartra, B. Datta and D. Mukherjee, *Chem. Phys. Letters* **301**, 206, (1999); S. Chattopadhyay, U. S. Mahapatra and D. Mukherjee, *J. Chem. Phys.* **111**, 3820 (1999); P. Ghosh, S. Chattopadhyay, D. Jana and D. Mukherjee, *Int. J. Mol. Sci.* **3**, 733 (2002).

[87] J. Finley, *J. Chem. Phys.* **109**, 7725 (1998).

[88] C. Angeli, S. Borini, M. Cestari, and R. Cimiraglia, *J. Chem. Phys.* **121**, 4043 (2004).

[89] E. R. Davidson and C. F. Bender, *Chem. Phys. Lett.* **59**, 369 (1978); R. J. Cave and E. R. Davidson, *J. Chem. Phys.* **88**, 5770 (1993); F. Chen, E. R. Davidson, and S. Iwata, *Int. J. Quantum Chem.* **86**, 256 (2002).

[90] K. Wolinski and P. Pulay, *J. Chem. Phys.* **90**, 3647 (1989); R. B. Murphy and R. P. Messmer, *J. Chem. Phys.* **97**, 4170 (1992).

[91] B.O. Roos, K. Andersson, M.P. Fulscher, P. A. Malmqvist, L. Serrano-Andreas, K. Pierloot, and M. Merchan, *Adv. Chem. Phys.* **93**, 219 (1996).

[92] H. J. Werner, *Mol. Phys.* **89** 645 (1996); K. G. Dyall, *J. Chem. Phys.* **102**, 4909 (1995); A.O. Mitrushenkov, *J. Chem. Phys.* **105**, 10487 (1996).

[93] Y. K. Choe, H. A. Witek, J. P. Finley, and K. Hirao, *J. Chem. Phys.* **114**, 3913 (2001).

[94] E. Rosta and P. R. Surjan, *J. Chem. Phys.* **116**, 878 (2002).

[95] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J. P. Malrieu, *J. Chem. Phys.* **114**, 10252 (2001).

[96] Z. Rolik, A. Szabados, and P. R. Surjan, *J. Chem. Phys.* **119**, 1922 (2003).

[97] M. R. Hoffmann, *Chem. Phys. Lett.* **195**, 127 (1992); Y. G. Khait and M. R. Hoffmann, *J. Chem. Phys.* **108**, 8317 (1998); Y. G. Khait, J. Song and M. R. Hoffmann, *J. Chem. Phys.* **117**, 4133 (2002).

[98] D. Theis, Y. G. Khait, S. Pal and M. R. Hoffmann, *Chem. Phys. Lett.* **487** 116 (2010).

[99] P. Durand and J. P. Malrieu, *Adv. Chem. Phys.* **67**, 321 (1987); J. P. Malrieu, P. Durand and J. P. Daudey, *J. Phys. A* **18**, 809 (1985); V. Hurtubise and K. F. Freed, *Adv. Chem. Phys.* **83**, 465 (1993).

[100] I. Nebot-Gil, J. Sanchez-Marin, J. Malrieu, J. L. Heully and D. J. Maynau, *J. Chem. Phys.* **103**, 2576 (1995); J. Meller, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **104**, 4068 (1996).

[101] S. Chattopadhyay, U. S. Mahapatra and D. Mukherjee, *J. Chem. Phys.* **111**, 3820 (1999); S. Chattopadhyay, U. S. Mahapatra, P. Ghosh and D. Mukherjee, *Low-Lying Potential Energy Surfaces*, edited by M. R. Hoffmann and K. G. Dyall, (ACS Symposium Series, No. 828, Washington, DC, 2002).

[102] U. S. Mahapatra, B. Datta, B. Bandyopadhyay and D. Mukherjee, *Advances in Quantum Chemistry*, edited by D. Hanstrop and H. Persson, (Academic Press Inc., San Diego, 1998) Vol. 30; U.S. Mahapatra, B. Datta and D. Mukherjee, *Mol. Phys.* **94**, 157 (1998); U.S. Mahapatra, B. Datta and D. Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999).

[103] J. Masik and I. Hubac, *Quantum Systems in Chemistry and Physics: Trends in Methods and Applications*, edited by R. McWeeny, et al. (Kluwer Academic, Dordrecht, 1997); J. Masik, I. Hubac and P. Mach, *J. Chem. Phys.* **108**, 6571 (1998).

[104] S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **95**, 8227 (1991).

[105] I. Hubac, in *New Methods in Quantum Theory*, edited by A. Tsipis, V. S. Popov, D. R. Herschbach and J. S. Avery (Kluwer, Dordrecht, 1996) (NATO ASI Series 3: High Technology), Vol. 8, pp. 183-202;
J. Masik and I. Hubac, *Adv. Quantum Chem.* **31**, 75 (1998).

[106] H. Reitz and W. Kutzelnigg, *Chem. Phys. Lett.* **66**, 111 (1979).

[107] I. Lindgren and D. Mukherjee, *Phys. Rep.* **151**, 93 (1987).

[108] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha and D. Mukherjee, *Chem. Phys.*

Lett. **137**, 273 (1987); M. Rittby, S. Pal and R. J. Bartlett, *J. Chem. Phys.* **90**, 3214 (1989).

[109] B. Jezioroski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1982);

[110] A. Balkova, S. A. Kucharski, L. Meissner and R. J. Bartlett, *J. Chem. Phys.* **95**, 4311 (1991).

[111] N. Vaval and S. Pal, *Chem. Phys. Lett.* **300**, 125 (1999).

[112] D. Mukherjee, *Chem. Phys. Lett.* **125**, 207 (1986).

[113] W. H. Flygare, in *Molecular structure and dynamics* (Prentice-Hall, Englewood Cliffs, 1978).

[114] W. Weltner, Jr, in *Magnetic Atoms and Molecules* (Dover, New York, 1989)

[115] H. J. Monkhorst, *Int. J. Quantum Chem.* **S11**, 421 (1977).

[116] E. A. Salter, G. Trucks and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989); E. A. Salter and R. J. Bartlett, *J. Chem. Phys.* **90**, 1767 (1989); L. Adamowicz, W. D. Laidig and R. J. Bartlett, *Int. J. Quantum Chem.* **S18**, 245 (1984); G. Fitzgerald, R. J. Harrison and R. J. Bartlett, *J. Chem. Phys.* **85**, 5143 (1986); R. J. Bartlett, *in Geometrical Derivatives of Energy Surface and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht, 1986), pp. 35.

[117] A. Dalgarno and A. L. Stewart, *Proc. R. Soc. London A* **238**, 269 (1957).

[118] T. Helgaker and P. Jorgensen, in *Methods in Computational Molecular Physics*, NATO ASI Series B, edited by S. Wilson and G.H.F. Dierckson (Plenum, New York, 1992).

[119] T. Helgaker and P. Jorgensen, *Adv. Quantum Chem.* **19**, 183 (1988).

[120] P. Jorgensen and T. Helgaker, *J. Chem. Phys.* **89**, 1560 (1988).

[121] H. Koch, H. J. Aa. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria and H. F. Schaefer III, *J. Chem. Phys.* **92**, 4924 (1990).

[122] S. Pal, *Theor. Chim. Acta* **66**, 207 (1984); *ibid.* **68**, 379 (1985).

[123] S. Pal, *Phys. Rev. A* **33**, 2240 (1986); *ibid.* **39**, 2712 (1989).

[124] S. Pal and K. B. Ghose, *Phys. Rev. A* **45**, 1518 (1992).

[125] S. Pal and K. B. Ghose, *Current Sci.* **63**, 667 (1992); K. B. Ghose, P. Nair and S. Pal, *Chem. Phys. Lett.* **211**, 15 (1993); N. Vaval, K. B. Ghose, P. Nair and S. Pal, *Proc. Ind. Acad. Sci.* **106**, 387 (1994).

[126] N. Vaval and S. Pal, *Phys. Rev. A* **54**, 250 (1996); A. B. Kumar, N. Vaval and S. Pal, *Chem. Phys. Lett.* **295**, 189 (1998); N. Vaval, A. B. Kumar and S. Pal, *Int.J. Mol. Sci.* **2**, 89 (2001); S. Pal and N. Vaval, *Recent Res. Devel. Phys. Chem.* **6**, 527 (2002).

[127] N. Vaval and S. Pal, *Chem. Phys. Lett.* **398**, 194 (2004).

[128] P. U. Manohar, N. Vaval and S. Pal, *Chem. Phys. Lett.* **387**, 442 (2004).

[129] D. Ajitha and S. Pal, *J. Chem. Phys.* **111**, 3832 (1999).

[130] P. Szalay, *Int. J. Quantum Chem.* **55**, 151 (1995).

[131] K. R. Shamasundar, S. Asokan, and S. Pal, *J. Chem. Phys. 120*, 6381 (2004).

[132] P. U. Manohar, N. Vaval and S. Pal, *J. Mol. Struct.* THEOCHEM, **91**, 768 (2006).

[133] P. U. Manohar and S. Pal, *Chem. Phys. Lett.* **438**, 321 (2007).

[134] A. Bag, P. U. Manohar, N. Vaval and S. Pal, *J. Chem. Phys.* **131**, 024102 (2009).

[135] J. F. Stanton, *J. Chem. Phys.* **99**, 8840 (1993).

[136] J. F. Stanton and J. Gauss, *J. Chem. Phys.* **103**, 88931 (1995).

[137] J. F. Stanton and J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).

[138] S. R. Gwaltney, R. J. Bartlett and M. Nooijen, *J. Chem. Phys.* **111**, 58 (1999).

[139] W. Kutzelnigg, *J. Mol. Struct.* THEOCHEM. **202**, 11 (1989).

[140] W. Kutzelnigg, U. Fleischer, M. Schindler, in *The IGLO-Method: Ab Initio Calcula- tion and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities*, (Springer-Verlag, Heidelberg, 1990) Vol. 23.

[141] A. E. Hansen and T. D. Bouman, *J. Chem. Phys.* **82**, 5035 (1985).

[142] J. Gerratt and I. M. Mills, *J. Chem. Phys.* **49**, 1719 (1968); J. Gerratt, *J. Chem. Phys.* **49**, 1730 (1968).

[143] C. E. Dykstra and P. G. Jasen, *Chem. Phys. Lett.* **104**, 388 (1984).

[144] J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, *Int. J. Quantum Chem.* **S13**, 225 (1979).

[145] P. Saxe, Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.* **77**, 5647 (1982); Y. Osamura, Y. Yamaguchi, P. Saxe, M. A. Vincent, J. F. Gaw and H. F. Schaefer III, *Chem. Phys.* **73**, 131 (1982).

[146] D. J. Thouless, *Quantum Mechanics of Many Body Systems* (Academic, New York, 1961).

[147] J. Linderberg, Y. Ohrn, *Propogators in Quantum chemistry* (Academic Press, London, 1974); A. Dalgarno and G. A. Victor, *Proc. R. Soc. London Ser. A*, **291**, 291 (1966).

[148] Y. Osamura, Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.* **77**, 385 (1982).

[149] P. Pulay, *J. Chem. Phys.* **78**, 5043 (1983); P. Jorgensen and J. Simons, *J. Chem. Phys.* **79**, 334 (1983); J. Almof and P. R. Taylor, *Int. J. Quantum Chem.* **27**, 743 (1985); Y. Yamaguchi, Y. Osamura, G. Fitzgerald and H. F. Schaefer III, *J. Chem. Phys.* **78**, 1607 (1983).

[150] K. Ruud and T. Helgaker, *Chem. Phys. Lett.* **264**, 17 (1997).

[151] C. Van Wullen and W. Kutzelnigg, *J. Chem. Phys.* **104**, 2330 (1996).

[152] H. F. Hameka, *Z. Naturforsch A*, **14**, 599 (1959); H. F. Hameka, *Rev. Mod. Phys.* **34**, 87 (1962); H. F. Hameka, *Physica* **25**, 626 (1959).

[153] R. Ditchfield, *J. Chem. Phys.* **56**, 5688 (1972).

[154] K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990).

[155] M. Hiser, R. Ahlrichs, H. P. Baron, P. Weis and H. Horn, *Theor. Chim. Acta* **83**, 455 (1992).

[156] J. Gauss, *Chem. Phys. Lett.* **191**, 614 (1992); J. Gauss, *J. Chem. Phys.* **99**, 3629 (1993); J. Gauss, *Chem. Phys. Lett.* **229**, 198 (1994).

[157] K. Ruud, T. Helgaker, R. Kobayashi, P. Jorgensen, K. L. Bak and H. J. A. Jensen, *J. Chem. Phys.* **100**, 8178 (1994); T. Helgaker, M. Jaszuski and K. Ruud, *Chem. Rev.* **99**, 293 (1999)

[158] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **102**, 251 (1995); *ibid.* **103**, 3561 (1995); *ibid.* **104**, 2574 (1996); J. Gauss and J. F. Stanton, *Phys.Chem. Chem. Phys.* **2**, 2047 (2000).

[159] F. R. Salsbury. Jr. and R. A. Harris, *Chem. Phys. Lett.* **279**, 247 (1997); *J. Chem. Phys.* **107**, 7350 (1997).

[160] J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys.* **104**, 5497 (1996).

[161] A. M. Lee, N. C. Handy and S. M. Colwell, *J. Chem. Phys.* **103**, 10095 (1995); G. Rauhut, S. Puyear, K. Wolinski and P. Pulay, *J. Phys. Chem.* **100**, 6310 (1996); L. Olsson and D. Cremer, *J. Chem. Phys.* **105**, 8995 (1996); idib **100**, 16881 (1996).

[162] K. Ruud, T. Helgaker, K. L. Bak, P. Jorgensen and H. J. A. Jensen, *J. Chem. Phys. 99*, 3847 (1993); K. Ruud, T. Helgaker, P. Jorgensen and K. L. Bak, *Chem. Phys. Lett.* **223**, 12 (1994).

[163] C. Van Wullen and W. Kutzelnigg, *Chem. Phys. Lett.* **205**, 563 (1993).

[164] S. M. Cybulski and D. M. Bishop, *Mol. Phys.* **76**, 1289 (1992); *ibid. J. Chem. Phys.* **100**, 2019 (1994); *ibid. J. Chem. Phys.* **106**, 4082 (1997).

[165] M. Schindler and W. Kutzelnigg, *J. Am. Chem. Soc.* **105**, 1360 (1983).

[166] K. Ruud, H. Skaane, T. Helgaker,K. L. Bak and P. Jorgensen, *J. Am. Chem. Soc.* **116**, 10135, (1994).

[167] J. Gauss, K. Ruud and M. Kallay, *J. Chem. Phys.* **127**, 74101 (2007).

[168] P. J. Wilson, R. D. Amos and N. C. Handy, *Mol. Phys.* **9**, 757 (1999); O. B. Lutnaes, A. M. Teale, T. Helgaker, D. J. Tozer, K. Ruud, and J. Gauss, *J.*

Chem. Phys. **131**, 144104 (2009); M. P. Johansson and M. Swart, *J. Chem. Theory Comput.* **6**, 3302 (2010).

Chapter 2

Chemical shielding of closed-shell molecules using Extended Coupled-cluster theory

In this chapter we report calculation of the nuclear magnetic shielding constant using extended coupled cluster response approach. We present the results for the HF, BH, CO and N_2 *molecules. These results show importance of correlation corrections for the shielding constant.*

2.1 Introduction

The single-reference coupled-cluster (SRCC) theory [1–7] is one of the most accurate and widely used electronic structure method for studying ground state energy, properties and spectroscopy of closed-shell molecules at the equilibrium geometry [6, 8–10, 10–16]. Due to its in-built size-extensivity and size-consistency property SRCC has been accepted as the state-of-the-art method for electronic structure and properties of atoms and molecules. Energy derivatives obtained through analytic response approach were first developed by Monkhorst [8]. Traditional CC response approach based on non-variational method did not have a $(2n + 1)$- rule inherent in it. As a result, the expression for the first order energy derivative involves the first derivative of the wave function with respect to the external perturbation. This means one needs to evaluate wave function derivatives with respect to all modes of perturbation for the first order property. This problem was overcome by Bartlett and co-workers [16, 20]. They implemented the idea of algebraic Z-vector method introduced by Handy and Schaefer [18] based on Dalgarno's interchange theorem [19]. The method is known as the Z-vector technique. This development made the non-variational CC method viable for the computation of energy derivatives, using only one extra set of perturbation-independent variables, solved through a linear equation. This and the subsequent developments by Bartlett and coworkers [15, 16, 20] substantially facilitated efficient implementation of molecular energy gradients for SRCC, and significantly contributed to its success in quantum chemistry. However, Z-vector type of approach turned out to be a tedious job for higher-order properties such as Hessian's, polarizabilities, etc. On the other hand, a conceptually different approach, using a constrained variation method (CVM), proposed by Jørgensen and coworkers [21, 22] was more useful. This approach is based on the formation of Lagrangian functional which is easily applicable to higher order energy derivatives [23–25]. Constrained variation approach involves recasting of the standard SRCC equation in a stationary framework by introducing an extra set of de-excitation amplitudes. It was shown that this method includes the Z-vector method as a zeroth-order result and transparently extends its benefits to higher-order properties. Parallel to these developments, Pal [26] proposed a fully stationary response approach. In this approach choice of the energy functional is very important. Initial implementation was based on the expectation-value (XCC) functional [27–29]. The XCC functional, however, is a non-terminating series and the stationary equations resulting from the functional were truncated to a fixed power in cluster amplitudes contain disconnected terms. Bartlett and co-workers [30, 31] used the truncation scheme based on the order of perturbation for the XCC and Unitary CC (UCC) functional. This scheme of truncation leads to connected series, however, it is computationally expensive to implement this approach beyond third order of perturbation.

Extended coupled cluster (ECC) functional based on a double-similarity transformation of the Hamiltonian is other energy functional implemented by Pal and co-workers [32–34]. The ECC functional developed by Arponen and co-workers [35–37], uses bi-orthogonal vectors and is shown by Arponen to have a special double-linking structure. Linear form of the left amplitudes gives SRCC equations when differentiated with respect to the left amplitudes. This double linking structure of the bi-orthogonal or ECC functional not only ensures natural termination of the series, but also provides fully connected amplitude equations, even when truncated to a fixed power in number of cluster amplitudes. Being variational, method enjoys the advantage of $(2n + 1)$-rule i.e. it satisfies Hellmann Feynman theorem. The natural termination of the functional occurs at high order and for the practical purpose needs to be truncated. CC response approach is extensively used for the electric properties [30–34], however, there are not many reports on magnetic properties [25, 38]. Magnetic response property calculations are not straight forward like electric response properties. The Hamiltonian of the system in the presence of external magnetic field depends on the gauge of the magnetic vector potential. Proper gauge origin should hence be chosen for the evaluation of the magnetic properties [39].

Various attempts were made earlier at the SCF level [39–43] as well as correlated levels [44–50] to eliminate the problem of gauge-variance of magnetic properties to some extent. Recently Manohar *et al* [38], reported the ECC response for magnetizability of the closed shell molecules. GIAO-based techniques have been implemented for the coupled-cluster singles and doubles (CCSD) [51] method as well as for the CCSD(T) approach [49] in which triple excitation effects are approximated based on perturbative guidelines. Coupled-cluster calculations of NMR shifts have been very successful in achieving experimental accuracy especially when partial triples are included. While CCSD and CCSD(T) appear to be the best approaches for highly accurate calculations in most cases but it is computationally very expensive. However, when system is dominated by non-dynamic correlation, it is important to use multi-determinantal based theory like multi-configurational SCF (MCSCF) [44, 45].

In this chapter we report the shielding constant for the closed shell molecules using extended coupled cluster response approach. In the following sections we discussed the theory of the shielding constant and CC response approach, results and discussion and conclusion of this work.

2.2 Theory

The theory of nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) [25, 52] parameters is the study of an atom or a molecule in external homogeneous magnetic field of different origin. Inclusion of electron correlation effects is very important for the accurate prediction of nuclear magnetic shielding constants and the related NMR chemical shifts. At least for molecular calculations with atom-centered basis functions, center of mass represents the preferred choice of gauge origin. Nuclear magnetic shielding tensor is a mixed second-order energy derivative. Calculation of NMR chemical shifts thus requires evaluation of a second derivative of the energy with respect to the magnetic field and nuclear magnetic moment. The perturbation involved is a imaginary perturbation, transforming the real wave function of the unperturbed molecule into complex field-dependent wave-function. Thus, magnetic properties, unlike electric properties and other second-order quantities, cannot be computed easily using numerical differentiation techniques. Hence, development of analytic response approach for the calculation of magnetic properties was necessary and represented the main bottleneck in the development of correlated schemes for the calculation of chemical shifts.

The Hamiltonian in the presence of a magnetic field can be written as

$$\begin{aligned} H &= H_0 + \sum_j \frac{\partial H}{\partial B_j} B_j + \sum_N \sum_i \frac{\partial H}{\partial m_i^N} m_i^N + \\ & \sum_N \sum_i \sum_j \frac{\partial^2 H}{\partial B_j \partial m_i^N} B_j m_i^N + \cdots \end{aligned} \tag{2.1}$$

H_0 is the usual field-free, non-relativistic Hamiltonian of a molecule and the perturbation contributions are given by

$$\frac{\partial H}{\partial B_j} = \frac{1}{2} \sum_k ((r_k - R_o) \times P_k) \tag{2.2}$$

$$\frac{\partial H}{\partial m_i^N} = \alpha^2 \sum_k ((r_k - R_N) \times P_k)_i / \mid r_k - R_N \mid^3 \tag{2.3}$$

$$\frac{\partial^2 H}{\partial B_j \partial m_i^N} = \frac{\alpha^2}{2} \sum_k (r_k - R_o)(r_k - R_N)\delta_{ij} - (r_k - R_o)_i (r_k - R_N)_j / \mid r_k - R_N \mid^3 \tag{2.4}$$

Here r_k and p_k are the position and momentum operators for the k^{th} electron, R_o is the gauge origin, R_N represents the position of the Nth nucleus and α is fine structure constant.

The tensor element of NMR shielding constant can be computed as the corresponding second derivative of the electronic energy

$$\sigma_{ij}^N = \left(\frac{\partial^2 E}{\partial m_i^N \partial B_j} \right)_{B=0; m_i^N=0} \tag{2.5}$$

Similar to the magnetizability, shielding constant also has diamagnetic and paramagnetic component. In the case of closed shell molecule the diamagnetic nuclear spin -electron orbit operator contributes to the shielding constant. Diamagnetic contribution can be obtained through expectation value approach. For the paramagnetic shielding constant we need the response of the wave function. Thus, we need to get the derivative of the CC cluster amplitudes with respect to the nuclear magnetic moment first, then we evaluate the derivative of the cluster amplitudes with respect to the magnetic field. Only, after having obtained both the derivative cluster amplitudes we can get the paramagnetic contribution for the shielding constant. For the calculation of NMR shielding we have used fully variational CC response approach based on extended coupled cluster functional. Variational methods satisfy Hellman -Feynman theorem which is very useful for the higher order properties. This Means, with the help of first order response wave-function we can calculate the properties up to third order. The form of the energy functional in ECC is

$$E_0 = \langle \phi_0 \mid e^S (He^T)_L \mid \phi_0 \rangle_{DL} \tag{2.6}$$

where, *L* means linked and *DL* is double linked. This makes functional naturally terminating and we never end up with disconnected diagrams for the amplitude equations. Thus the properties obtained using this functional are size-extensive. Though the functional is naturally terminating it terminates at quite high order and needs truncation for the practical application. We have used the singles and doubles (CCSD) approximation. Thus, within CCSD approximation we have included all the terms for the one and two body $\bar{H} = ((He^T)_{conn,open}$)in the energy as well as derivative energy functional. We can see that we have two set of amplitudes S and T. Thus, the price one pays to get terminating series is double the number of amplitudes as well as double the number of equations.

To get the equation for the cluster amplitudes we differentiate energy expression with respect to t as well as s. For the derivative amplitude equations we differentiate derivative energy expression with respect to the unperturbed t and s amplitudes only. For the details of the ECC response see refs. [32–34].

The cluster amplitudes of S and T operators as well as those of the derivative $S^{(1)}$ and $T^{(1)}$ operators are obtained using a stationary condition. The double-linked nature of the functional guarantees that the terms generated by the deletion of a vertex from the energy/energy derivative diagram remains connected. Thus, the stationary equations resulting from the variation of the functional with respect to the cluster amplitudes are themselves connected. This yields the equations for the amplitudes of the cluster operators S and T, denoted as $s^{(0)}$ and $t^{(0)}$. The following set of equations are solved to obtain the above amplitudes: (2.7)

$$\frac{\delta E}{\delta t^{(0)}} = 0; \frac{\delta E}{\delta s^{(0)}} = 0$$

The functional, at the stationary point, E_{stat} , has a simplified structure, due to the stationary condition of cluster amplitudes. To obain the derivative amplitude equations, one makes the derivative energy functional $E^{(1)}$ stationary with respect to the ground state $s^{(0)}$ and $t^{(0)}$ amplitudes. This explicit derivative functional depends on the amplitudes $s^{(0)}$,$t^{(0)}$, $s^{(1)}$ and $t^{(1)}$. Thus, the equations

$$\frac{\delta E^{(1)}}{\delta t^{(0)}} = 0; \frac{\delta E^{(1)}}{\delta s^{(0)}} = 0 \tag{2.7}$$

provide us with the equation for $s^{(1)}$ and $t^{(1)}$ amplitudes. The double-linked structure of the $E^{(1)}$ leads to the connectivity of the terms in the equations for derivative cluster amplitudes. The resulting higher order properties (up to first hyper-polarizability) are thus fully size-extensive.

2.3 Results and Discussion

In this section we report the shielding constants for some closed shell molecules using extended coupled cluster method. The nuclear magnetic shielding constant σ can be defined as the second derivative of the energy with respect to the external magnetic field *B* and a nuclear magnetic moment m_N. In the perturbation formulation, the shielding constant can be written in terms of a diamagnetic and paramagnetic contribution, where the former is calculated as an expectation value of the diamagnetic shielding operator (DS) while the latter is calculated as a response property of the paramagnetic spin-orbit (PSO) and orbital Zeeman (LG) operators. It is known that electron correlation and basis set plays an important role in the accurate determination of nuclear magnetic shielding constants. Here, absolute values of shielding constants are reported. In particular, for magnetic properties it is very important to have large basis sets to counter gauge origin problem. Thus, a basis of at least valence triple zeta quality is chosen. It is interesting to study the shielding constants for molecules with multiple bond. Nitrogen and carbon monoxide are interesting systems for the study of magnetic shielding constants. In this section shielding constants for HF, BH, N_2 and CO molecules are reported. For BH and N_2, the cc-pVXZ (X=QZ,5Z) basis without g and h functions are used. For Hydrogen fluoride and carbon monoxide molecules the cc-pVTZ and cc-pVQZ basis sets are used for our studies. The results are compared with the MCSCF values obtained using the DALTON program [53]. Also the results are compared against the available experimental values.

2.3.1 Boron hydride

For boron hydride cc-pVQZ and cc-pV5Z basis without g and h functions are used for the calculations. The bond distance of $1.2328\mathring{A}$ is used. The MCSCF calculations in the same basis using 4 electrons and 15 active orbitals as our CAS space are performed. In Boron, the effect of electron correlation is large for the paramagnetic component

Table 2.1: Nuclear magnetic shielding constants values BH

Basis		Method	σ^d_{xx}	σ^d_{zz}	σ^p_{xx}	$\bar{\sigma}$
cc-pVQZ	^{11}B	SCF	214.01	198.81	-708.31	-263.26
		ECC	214.03	199.53	-625.08	-207.52
		MCSCF	214.09	199.71	-570.47	-171.02
cc-pV5Z	^{11}B	SCF	214.01	198.82	-713.08	-266.43
		ECC	214.01	199.50	-634.66	-213.03
		MCSCF	214.09	199.71	-573.88	-173.30
		FCI [a]				-170.08
		Extrapolated FCI				-183.08
cc-pVQZ	^{1}H	SCF	17.77	33.63	2.53	24.75
		ECC	18.19	33.66	2.15	24.90
		MCSCF	18.28	33.69	2.33	24.97
cc-pV5Z	^{1}H	SCF	17.72	33.64	2.83	24.90
		ECC	18.11	33.65	2.41	24.89
		MCSCF	18.22	33.69	2.60	25.12
		FCI [a]				24.60
		Extrapolated FCI				24.90

Results in ppm

[a] see Ref.[54]

of shielding than the diamagnetic shielding component. For the case of Boron in BH molecule, in comparison with SCF, electron correlation reduces paramagnetic component of the shielding constant by 11% in ECC and almost by 20% in MCSCF method. For BH the full configuration interaction (FCI) results available for triple zeta plus basis as well as extrapolated FCI value [54] are reported. These results are obtained using a large basis set. Though, the FCI results are not in the basis we have used but it can be used to get the qualitative trend of the correlated shielding values compared to SCF. The coupled cluster level calculation overestimates the shielding constant compared to FCI value. With larger basis it is enhanced. The same trend is observed for FCI as well as MCSCF. Table-2.1 reports the results for the shielding constant of ^{11}B and ^{1}H in BH. For ^{1}H we observed that the ECC values are in good agreement with the MCSCF as well as extrapolated FCI values.

2.3.2 Hydrogen fluoride

Hydrogen fluoride is an another system studied for the shielding constant. Here, cc-pVTZ and cc-pVQZ basis is used without any g functions. In Table-2.2, the results for the diamagnetic and paramagnetic components of the shielding constants of Fluorine as well as Hydrogen in HF are reported. Here too the results are compared with the experimental [55, 56] as well as MCSCF results obtained using 4 electrons and 10 orbitals. With increase in basis set paramagnetic component of the shielding is reduced and total shielding constant value is in good agreement with the experimental shielding constant. The CC results are in good agreement with the MCSCF results. For ^{1}H in hydrogen fluoride good results are obtained compared to experimental value [57] for both the basis sets. For hydrogen, change in shielding constant is very small as basis set convergence is almost reached.

Table 2.2: Nuclear magnetic shielding constants values of HF

Basis		Method	σ^d_{xx}	σ^d_{zz}	σ^p_{xx}	$\bar{\sigma}$
cc-pVTZ	^{1}H	SCF	8.77	44.13	12.04	28.59
		ECC	8.88	44.46	12.29	28.93
		MCSCF	9.82	44.44	12.14	29.45
cc-pVQZ	^{1}H	SCF	8.48	44.07	11.67	28.13
		ECC	9.49	44.34	11.80	28.98
		MCSCF	9.49	44.37	11.73	28.96
	^{1}H	Expt[a]				28.5±0.2
cc-pVTZ	^{19}F	SCF	481.88	481.75	-112.36	406.93
		ECC	481.90	481.52	-115.07	405.06
		MCSCF	481.98	481.74	-111.84	407.03
cc-pVQZ	^{19}F	SCF	481.81	481.69	-104.21	412.29
		ECC	481.89	481.48	-106.91	410.64
		MCSCF	481.97	481.81	-104.04	412.99
	^{19}F	Expt[b]				410±6

Results in ppm

[a] see Ref. [55]

[b] see Ref. [56]

Table 2.3: Nuclear magnetic shielding constants values of N_2

Basis		Method	σ^d_{xx}	σ^d_{zz}	σ^p_{xx}	$\bar{\sigma}$
cc-pVQZ	^{15}N	SCF	362.67	338.70	-681.46	-99.62
		ECC	363.02	339.56	-591.47	-39.11
		MCSCF	362.96	339.30	-618.42	-57.21
cc-pV5Z	^{15}N	SCF	361.89	338.71	-639.82	-108.38
		ECC	362.77	339.57	-588.77	-37.48
		MCSCF	362.73	339.31	-621.60	-59.48
	^{15}N	Exp[a]				-61.6±2

Rsults in ppm

[a] see Ref.[57]

2.3.3 Nitrogen dioxide

The ^{15}N shielding is studied in cc-pVQZ and cc-pV5Z basis without any g and h functions. The MCSCF results are obtained using rather small active space of 4 electrons and 6 orbitals. It can be seen that the paramagnetic component of the shielding constant is reduced considerably by electron correlation in coupled cluster method for both the basis sets, whereas in MCSCF it is not so. In fact, as we go from cc-pVQZ to cc-pV5Z basis coupled cluster reduces the paramagnetic component of the shielding, although in MCSCF it increases. Compared to experiment, coupled cluster underestimates the shielding constant, whereas MCSCF value is in good agreement with the experiment. Discrepancy of the CC could be attributed to the relaxation missing at the CCSD level. Inclusion of partial triples may improve results. MCSCF introduces relaxation which may be the reason why MCSCF despite of using a smaller space in calculations, provides a closer values to the experimental results.

2.3.4 Carbon monoxide

In Table-2.4 shielding constants for ^{13}C and ^{17}O in cc-pVTZ and cc-pVQZ basis without any g functions are reported. The results are compared with the MCSCF results obtained using 10 electrons and 12 active orbitals. It can be seen from the Table-2.4, that the paramagnetic component of the shielding for ^{13}C is reduced in both the basis sets by almost 10% due to electron correlation. ECC as well as MCSCF predicts positive shielding constant, whereas SCF gives negative shielding constant. Thus, effect of electron correlation is seen to be important for ^{13}C. However, neither ECC nor MCSCF is closer to the experimental results. For the ^{17}O shielding constant is reduced in ECC and MCSCF compared to SCF, which is considerably emphasizing on the effect of electron correlation.

Table 2.4: Nuclear magnetic shielding constants values of CO

Basis		Method	σ^d_{xx}	σ^d_{zz}	σ^p_{xx}	$\bar{\sigma}$
cc-pVTZ	^{13}C	SCF	297.77	271.10	-459.78	-17.64
		ECC	298.13	272.66	-417.48	11.32
		MCSCF	298.30	272.74	-413.48	13.52
cc-pVQZ	^{13}C	SCF	297.12	271.03	-461.58	-7.77
		ECC	298.28	272.62	-422.65	7.97
		MCSCF	299.68	272.63	-419.55	9.05
	^{13}C	Expt[a]				0.6±0.9
cc-pVTZ	^{17}O	SCF	430.54	410.46	-754.65	-74.25
		ECC	430.93	410.08	-681.87	-30.60
		MCSCF	430.98	410.00	-689.43	-36.11
cc-pVQZ	^{17}O	SCF	431.95	410.48	-760.49	-83.50
		ECC	430.47	410.18	-682.94	-31.58
		MCSCF	430.45	410.24	-639.30	-39.07
	^{17}O	Expt[a]				-42.3±17.2

Results in ppm

[a] see Ref.[58]

[b] see Ref.[59]

2.4 Conclusion

In this chapter we report the shielding constants for the Hydirdes BH and HF along with multiple bonded systems N_2 and CO. Accuarate calculation of shielding constant is by far more challenging as values for the shielding are very sensitive to the basis set chosen and electron correlation effects. We see that for the ^{1}H in HF and BH basis set limit is almost reached and hence shielding constant is closer to the experimental or FCI value. However, for other cases we have not reached the basis set limit. In particular, for multiple bonded systems it might be useful to choose basis sets with more tight S functions. Partial inclusion of triples might improve results.

References

[1] J. $\check{C}\acute{i}\check{z}$ek, *J. Chem. Phys.* **45**, 4256-4266 (1966).

[2] J. Paldus and J. $\check{C}\acute{i}\check{z}$ek, *in Energy, Structure and Reactivity* D. W. Smith, Mcrae. Ed. Wiley, NY 1973.

[3] F. Cöester *Nucl. Phys.* **7**, 421 (1958).

[4] F. Cöester and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).

[5] R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359-402 (1981).

[6] H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem* **S18**, 255 (1984).

[7] R. J. Bartlett, in *Modern Electronic Structure Theory* edited by D. R. Yarkony (World Scientific Singapore, 1995) pp. 1047.

[8] H. Monkhorst, *Int. J. Quantum Chem* **S11**, 421-427 (1977).

[9] P. Pulay, *Mol. Phys.* **17**, 197-204 (1969).

[10] E. Salter and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).

[11] S. Pal, M. D. Prasad and D. Mukherjee, *Theor. Chim. Acta.* **62**, 523 (1983).

[12] R. J. Bartlett and Noga, *Chem. Phys. Lett.* **150**, 29 (1988).

[13] J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **99**, 5178 (1993).

[14] M. Kally and J. Gauss, *J. Mole. Struct.* THEOCHEM, **768**, 71 (2006).

[15] L. Adamowicz, W. D. Laidig and R. J. Bartlett, *Int. J. Quantum Chem* **S18**, 245 (1984).

[16] G. B. Fitzgerald, R. J. Harrison, *Int. J. Quantum Chem* **85**, 5143 (1986).

[17] H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem* **S18**, 255 (1984).

[18] N. C. Handy and H. F Schaefer III, *J. Chem. Phys.* **81**, 5031 (1984).

[19] A. Dalgarno, A. L. Stewart, *Proc. R. Soc. London, Ser. A* **238**, 269 (1957).

[20] E. A. Salter and R. J. Bartlett, *J. Chem. Phys.* **90**, 1767 (1989).

[21] T. Helgaker and P. Jørgensen, *Adv. Quantum Chem.* **19**, 183 (1988).

[22] H. Koch, H. J. A. Jensen, P. Jørgensen, T. Helgaker, G. E. Scuseria and H. F. Schaefer III, *J. Chem. Phys.* **92**, 4924 (1990).

[23] P. Jørgensen and Helgaker, *J. Chem. Phys.* **89**, 1560 (1988).

[24] T. Helgaker and P. Jørgensen, *Theor. Chim. Acta.* **75**, 111 (1989).

[25] T. Helgaker, M. Jaszunski and K. Ruud, *Chem. Rev.* **99**, 293 (1999).

[26] S. Pal, *Theor. Chim. Acta.* **66**, 151 (1984); *ibid Phys. Rev.A* **42**, 4385 (1990); *ibid* **34**, 2682 (1986).

[27] S. Pal and K. B. Ghose, *Curr. Sci.* **63**, 667 (1992).

[28] K. B. Ghose, P. G. Nair and S. Pal, *Chem. Phys. Lett.* **211**, 15 (1993).

[29] N. Vaval, K. B. Ghose, P. G. Nair and S. Pal, *Proc. Ind. Acad. Sci.* **106**, 387 (1994).

[30] R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29-36 (1988).

[31] R. J. Bartlett, S. A. Kucharshi and J. Noga, *Chem. Phys. Lett.* **155**, 133-140 (1989).

[32] N. Vaval, K. B. Ghose and S. Pal, *J. Chem. Phys* **101**, 4914 (1994).

[33] N. Vaval and S. Pal, *Phys. Rev. A* **54**, 250 (1996).

[34] N. Vaval, A. B. Kumar and S. Pal, *Int. J. Mol. Sci.* **2**, 89 (2001).

[35] J. Arponen, *Ann. Phys.* **151**, 311-382 (1983).

[36] J. Arponen, R. F. Bishop and E. Pajanne, *Phys. Rev. A* **36**, 2519 (1987).

[37] R. F. Bishop, J. Arponen and E. Pajanne, *Phys. Rev. A* **36**, 2539 (1987).

[38] P. U. Manohar, N. Vaval and S. Pal, *Chem. Phys. Lett.* **387**, 442 (2004).

[39] F. J. London, *Phys. Radium* **8**, 397 (1937).

[40] R. Ditchfield, *J. Chem. Phys.* **56**, 5688 (1972).

[41] R. Ditchfield, *J. Chem. Phys.* **27**, 789 (1974).

[42] H. Hameka, *Mol. Phys.* **1**, 203 (1958).

[43] J. Kussmann and C. Ochsenfelda, *J. Chem. Phys.* **127**, 054103 (2007).

[44] W. Kutzelnigg, W. C. van Wüllen, U. Fleischer, R. Franke and T. V. Mourik,, in *Nuclear Magnetic Shieldings and Molecular Structure*, edited by J. A. Tossell (NATO ASI series, Plenum, New York, 1993).

[45] S. Coriani, M. Jaszunski, A. Rizzo and K. Ruud, *Chem. Phys. Lett.* **287**, 677 (1998).

[46] J. Gauss, *Chem. Phys. Lett.* **229**, 198 (1994).

[47] J. Gauss *Chem. Phys. Lett.* **191**, 614 (1992).

[48] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **104**, 2574 (1996).

[49] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **102**, 251 (1995).

[50] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **103** 3561 (1995).

[51] J. Gauss, *J. Chem. Phys.* **99**, 3629 (1993).

[52] M. Kaupp, M. Bühl and V. G. Malkin, in *Calculation of NMR and EPR Parameters: Theory and Applications* (Wiley-VCH 2004).

[53] Dalton 2.0 C. Angeli, K. L. Bak, V. Bakken, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Httig, K. Hald, A. Halkier, H. Heiberg, T. Helgaker, H. Hettema, a H. J. Aa. Jensen, D. Jonsson, P. Jrgensen, S. Kirpekar, W. Klopper, R. Kobayashi, H. Koch, A. Ligabue, O. B. Lutns, K. V. Mikkelsen, P. Norman, J. Olsen, M. J. Packer, T. B. Pedersen, Z. Rinkevicius, E. Rudberg, T. A. Ruden, K. Ruud, P. Salek, A. Sanchez de Meras, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras, D. J. Wilson, and H. Agren,

[54] J. Gauss and K. Ruud, *Int. J. Quantum Chem.* **S29**, 437 (1995).

[55] W. T. Raynes, *Nucl. Magn. Reson.* **7**, 1 (1978).

[56] D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.* **48**, 4148 (1968).

[57] C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. Burrell and J. Mason, *J. Chem. Phys.* **81**, 74 (1981).

[58] A. K. Jameson, C. J. Jameson, *Chem. Phys. Lett.* **134**, 461 (1987).

[59] R. E. Wasylishen, S. Mooibroek and J. B. Macdonald, *J. Chem. Phys.* **81**, 1057 (1984).

Chapter 3

Magnetizability of doublet radicals using Fock space multi-reference coupled cluster method

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In this chapter we report the first implementation of the recently developed Fock-space multi-reference coupled cluster (FSMRCC) response approach for magnetizabilities. The FSMRCC treats dynamic and static correlation in a very extensive manner. We report pilot application of the dia-magnetizability of NO, NO_2, OH and BH_2 radicals. We also report preliminary applications of the paramagnetic magnetizability of the NO radical. Standard atom-centered Gaussian basis functions have been used and this allowed us to study the gauge-dependence of the magnetizabilities.

3.1 Introduction

Single reference coupled cluster (SRCC) [1–4] has been accepted as the state-of-the-art method for the electronic structure calculations. It has been successfully implemented for the energy, energy gradients [5, 6], molecular properties [7–9] and for potential energy surfaces. In general, SRCC very successfully introduces dynamic electron correlation, which keeps electrons apart. However, for cases where several configurations are likely to make nearly equal contribution to the exact wave-function i.e bond breaking situations or in excited states, single reference CC fails. Multi-reference based CC (MRCC) [10–12] have been regarded as the methods of choice in such situations to take care of non-dynamic electron correlation in an effective manner. Among the MR based methods, effective Hamiltonian methods [13, 14] provide multiple solutions at a time. Effective Hamiltonian is defined over a small primary space of interest in such a way that diagonalization of it gives the exact eigen-values and the associated eigen-functions are the zeroth order approximation for the exact eigen functions. This space is known as reference space or model space. This class of methods can be further sub-divided into two variants as Hilbert space (HS) [15, 16] and Fock Space (FS) [17–19] methods. Choice of model space and the wave operator play a central role in MR based methods. Hilbert space MRCC assumes different vacuum for different configurations in the model space. A cluster operator T_μ is associated for each of the model space determinant ϕ_μ acting as a vacuum. The Fock space is based on the concept of a common vacuum, which is usually a closed-shell restricted Hartree-Fock determinant. With respect to this vacuum, holes and particles are defined, which are further sub-divided into active and inactive holes and particles. Fock space method is suitable for the difference energy calculations and thus describes ionized, electron-attached or excited states of a closed shell system, whereas Hilbert space based method is suitable for the potential energy surface calculations. In addition to the effective Hamiltonian-based methods, state-selective multi-reference CC methods [20] have also been developed, which are appropriate for potential energy surface calculations.

SRCC based methods like Equation of motion (EOM) CC [21, 22], symmetry adapted cluster expansion configuration interaction (SACCI) [23, 24] method restricted open-shell (RO) based CC methods [25] have also been successful in describing some quasi degenerate problems. For one valence problem, EOMCC, SACCI and FSMRCC are equivalent. However, for higher valence this equivalence no longer holds.

Each of the above methods has its own merit and demerit which gives different window for their applicability in real problems. It is well known that the intruder state problem is one of the major drawbacks for the effective Hamiltonian based methods. To avoid the problem of intruder states incomplete or quasi complete model spaces can be used. Independent partitioning technique [13]. is another way to get rid of intruder states problem. Within a complete model space, this can be avoided with the proper choice of the active orbital. FSMRCC, EOMCC and SACCI have been successfully used for the difference energy calculations [26, 27]. However, for the linear response there are very few implementations. The initial linear response in SRCC was proposed by Monkhorst [28] and subsequently made more efficient by Bartlett and co-workers using Z-vector technique [7, 29]. Around the same time, Jorgensen and co-workers [30] implemented constrained variational approach to obtain the same response equations. Pal and co-workers [31, 32] used the fully variational approach using different functionals. However, the variation based multi-reference variants for the response approach have been developed only recently. The derivatives using EOM-CC based methods, which are equivalent for one valence problem to the FSMRCC, were developed by Stanton and Gauss [33]. Initially, Pal and co-workers [34] implemented Z-vector method for the Fock space based coupled cluster. Later, Pal and co-workers [35, 36] proposed a more efficient constrained variational approach for Fock space as well as Hilbert space for a single root at a time for a general model space. Szalay [37] also proposed a constrained variational approach for a complete model space within FSMRCC framework. For a complete model space both the approaches are equivalent. Pal and co-workers [38, 40] implemented Lagrangian based FSMRCC linear response approach for dipole moment and polarizability for the doublet radicals of one valence problem as well as excited states more recently.

Though the response approach was tested for electric properties of closed and open shell molecules there are very few applications for the magnetic properties [41, 42]. The imaginary perturbation and the gauge-dependence of the properties make it complicated to implement. Gauss and co-workers [43] have recently implemented gauge-independent magnetizabilities using CC for closed shell molecules. Pal and co-workers [44] used extended coupled cluster method to calculate the magnetizabilities of the closed shell molecules without any gauge dependence. In this chapter, we report pilot applications of the dia-magnetic magnetizability of the ground states of NO, NO_2, BH_2 and OH doublet radicals and perpendicular component of the paramagnetic magnetizability of the NO radical using different gauges.

3.2 Review of FSMRCC Response Theory

The FSMRCC theory [10, 12, 17, 26] and the Lagrangian formulation within FSMRCC have been described in detail in various articles [36, 38, 40]. However, for the completeness of the chapter, we briefly discuss the FSMRCC theory here. The FSMRCC method is based on the concept of a common vacuum. We choose an N-electron RHF as a vacuum. With respect to this vacuum, holes and particles are defined, which are further divided into active and inactive space. Thus, a general model space contains *m*-active particles and *n*-active holes. The model space function can be written as

$$|\Psi^{(m,n)}_{(0)\mu}>=\sum_i C^{(m,n)}_{\mu i}|\Phi^{(m,n)}_i> \tag{3.1}$$

where, $C^{(m,n)}_{\mu i}$'s are the model space coefficients. The correlated wave function for the μ^{th} state can be written as

$$|\Psi^{(m,n)}_{\mu}>=\Omega|\Psi^{(m,n)}_{(0)\mu}> \tag{3.2}$$

The universal wave operator Ω is such that the states generated by its action on the reference space satisfy Bloch equation. The wave operator is defined as

$$\Omega = \{e^{\tilde{T}^{(m,n)}}\} \tag{3.3}$$

The curly bracket denotes normal ordering of the operators within it [39]. The cluster operator $\tilde{T}^{(m,n)}$ can be expressed as

$$\tilde{T}^{(m,n)} = \sum_{k=0}^{m} \sum_{l=0}^{n} T^{(k,l)} \tag{3.4}$$

$T^{(k,l)}$ is capable of creating holes and particles in addition to destroying specifically *k*-active particles and *l*-active holes. Thus, $\tilde{T}^{(m,n)}$ amplitudes contain all the lower valence amplitudes and give additional flexibility to the theory. For a specific problem of zero active particle and one active hole, we write the Schrodinger equation for the quasi-degenerate states as

$$\begin{aligned} H|\Psi_\mu^{(0,1)}> &= E_\mu|\Psi_\mu^{(0,1)}> \\ &\text{which leads to} \\ H\Omega(\sum_i C_{\mu i}^{(0,1)}|\Phi_i^{(0,1)}) > &= E_\mu\Omega(\sum_i C_{\mu i}^{(0,1)}|\Phi_i^{(0,1)}) > \end{aligned} \tag{3.5}$$

Projection operator for model space is defined as

$$P^{(0,1)} = \sum_i |\Phi_i^{(0,1)} >< \Phi_i^{(0,1)}| \tag{3.6}$$

The complementary space operator Q is $1 - P$. The effective Hamiltonian(H_{eff}) is defined commonly through the Bloch equation.

$$\begin{aligned} P^{(0,1)}(H\Omega - \Omega H_{\mathit{eff}}^{(0,1)})P^{(0,1)} &= 0 \\ Q^{(0,1)}(H\Omega - \Omega H_{\mathit{eff}}^{(0,1)})P^{(0,1)} &= 0 \end{aligned} \tag{3.7}$$

Because of normal ordering, the contractions amongst different cluster operators within the exponential are not possible. This leads to decoupling of the equations of different sectors. The equations for the cluster amplitudes are solved, starting from the lowest valence sector upwards. This is also known as subsystem embedding(SEC) condition.

Similar to the Lagrange formulation of linear response approach of SRCC, Szalay [37] developed a response approach for the multi-reference methods. Though this approach can in principle, be applied for general model space, this has been implemented to complete model spaces. In this approach response of a specific root out of multiple roots of the effective Hamiltonian is targeted. Thus, one has to project a single desired root of the H_{eff} out of various roots for variation. We construct the Lagrangian and minimize the energy expression with the constraint that the MRCC(i.e. Bloch equations) are satisfied for a specific μ^{th} state.

$$\begin{aligned}
\Im \;=\; & \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} (H_{eff})^{(0,1)}_{ij} C^{(0,1)}_{j\mu} \\
& + \sum_{ji} \Lambda^{(0,1)}_{ji} < \phi^{(0,1)}_{j} | (H\Omega - \Omega H_{eff}) | \phi^{(0,1)}_{i} > \\
& + \sum_{\alpha} \sum_{i} \Lambda^{(0,1)}_{\alpha i} < \phi^{(0,1)}_{\alpha} | (H\Omega - \Omega H_{eff}) | \phi^{(0,1)}_{i} > \\
& + \sum_{ji} \Lambda^{(0,0)}_{ji} < \phi^{(0,0)}_{j} | H\Omega | \phi^{(0,0)}_{i} > + \sum_{\alpha} \sum_{i} \Lambda^{(0,0)}_{\alpha i} < \phi^{(0,0)}_{\alpha} | H\Omega | \phi^{(0,0)}_{i} > \\
& - E_{\mu} \left(\sum_{ij} \tilde{C}^{(0,1)}_{\mu i} C^{(0,1)}_{j\mu} - 1 \right) \qquad (3.8)
\end{aligned}$$

Where $\phi_i^{(0,1)}$, $\phi_j^{(0,1)}$, $\phi_i^{(0,0)}$ and $\phi_j^{(0,0)}$ are the functions in P space. $\phi_\alpha^{(0,1)}$ and $\phi_\alpha^{(0,0)}$ are functions in Q space. $\Lambda_{ji}^{(0,1)}$ and $\Lambda_{ji}^{(0,0)}$ are the Lagrange multipliers defined within P-space for the (0,1) and (0,0) sectors respectively. Similarly, $\Lambda_{\alpha i}^{(0,1)}$ and $\Lambda_{\alpha i}^{(0,0)}$ are the Lagrange multipliers from P to Q-space for the (0,1) and (0,0) sectors respectively. However, in case of complete model space (CMS), effective Hamiltonian has an explicit expression in terms of cluster operators. As a result, the closed part of the Lagrangian multipliers vanishes. Thus, the second and fourth terms of eq (3.8) vanish, simplifying Lagrangian to:

$$
\begin{aligned}
\Im &= \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} (H_{eff})^{(0,1)}_{ij} C^{(0,1)}_{j\mu} \\
&+ \sum_{\alpha} \sum_{i} \Lambda^{(0,1)}_{\alpha i} < \phi^{(0,1)}_{\alpha} | (H\Omega - \Omega H_{eff}) | \phi^{(0,1)}_{i} > \\
&+ \sum_{\alpha} \sum_{i} \Lambda^{(0,0)}_{\alpha i} < \phi^{(0,0)}_{\alpha} | H\Omega | \phi^{(0,0)}_{i} > \\
&- E_{\mu} \left(\sum_{ij} \tilde{C}^{(0,1)}_{\mu i} C^{(0,1)}_{j\mu} - 1 \right)
\end{aligned}
\tag{3.9}
$$

Differentiation of eq 3.9 with respect to Λ results in expression for cluster amplitudes, i.e., the Bloch equation. Differentiation of eq 3.9 with respect to the T amplitudes leads to equation for Lagrange multipliers. It is seen that the equation for cluster amplitudes is decoupled from the Λ amplitude equation. The Λ equations are however coupled with those of the cluster amplitudes T. In the presence of the external field, the Lagrangian and the parameters $H_{eff}, C, \tilde{C}, E, \Omega, \Lambda$ become perturbation dependent. The differentiation of the Lagrangian with respect to unperturbed cluster amplitude leads to equation for the Lagrangian multipliers. Similarly differentiation of the Lagrangian with respect to unperturbed Lagrange multipliers leads to equation for cluster amplitudes. Cluster amplitudes follow $(2n+1)$ rule whereas Lagrange multipliers satisfy $(2n+2)$ rule. Thus with the help of first derivative of cluster amplitudes and Lagrange multipliers , one can obtain energy derivatives up to second order i.e. polarizability. Lagrangian for the first and second order properties for one valence hole are presented in references [40] and [38] under singles and doubles approximation. Along similar line, the one valence particle problem can be solved.

3.3 Computational details

The diamagnetic magnetizability is obtained as expectation values of the second moment integrals. The corresponding operator is written as

$$\chi^d_{\alpha\beta} = -\frac{1}{4}\sum_i [(r_i - R_G)]^2\delta_{\alpha\beta} - (r_{i\alpha} - R_{G\alpha})((r_{i\beta} - R_{G\beta}). \tag{3.10}$$

The magnetic moment operator for a closed shell molecule is defined as

$$\mu^m_\alpha = \frac{1}{2}\sum_i \hat{l}_{i\alpha} \tag{3.11}$$

where, $l_{i\alpha}$ is the α^{th} component of the angular momentum operator for the i^{th} electron. Then, energy can be written as

$$E(B) = E_0 - \frac{1}{2}B.\chi^p.B - \frac{1}{2}B.\chi^d.B + ... \tag{3.12}$$

where χ^d and χ^p are diamagnetic and paramagnetic magnetizability tensors, respectively. The diamagnetic susceptibility is obtained as

$$\chi^d_{\alpha\beta} = Tr(H^d_{\alpha\beta}D_0) = \langle\phi_0|\hat{\chi}^d_{\alpha\beta}|\phi_0\rangle \tag{3.13}$$

and

$$\chi^p_{\alpha\beta} = Tr[H^p_\alpha D(\mu^m_\beta)] \tag{3.14}$$

where D_0 and D^m_μ are the perturbed and unperturbed densities, respectively. We obtain the density using field-independent cluster amplitudes, Lagrange multipliers, and model space coefficients and then calculate the diamagnetic magnetizability as trace of the product of density with the second moment operator. However, for the paramagnetic susceptibilities, we need the derivative of the cluster amplitudes and effective Hamiltonian. We have, however, included only the orbital response part in our implementation and not the spin contribution. In the present application, we have used singles and doubles truncation of the Lagrange multipliers and cluster amplitudes.

In the presence of the magnetic field, Hamiltonian of the system is not uniquely defined. Because of complex potential and gauge dependence of the Hamiltonian, computation of the magnetic properties is not so simple. However, the problem of gauge can be partially taken care by using the proper gauge origin, i.e., center of mass coordinates. There are various attempts at SCF and correlated level to eliminate the problem of gauge dependence using large basis set, so that we get nearly complete basis limit results. However, this is not computationally feasible. Methods are developed for the evaluation of gauge-independent properties. Gauge including atomic orbital (GIAO) approach by London [45], individual gauge for localized orbitals (IGLO) by Van Wulen and Kutzelnigg [46], and second-order polarization propagator (SOPPA) of Geertsen [47] are some of the methods. Recently, Kollwitz and Gauss [48] have implemented GIAO at the coupled cluster singles and doubles level for the calculation of magnetizability and nuclear shielding of closed-shell molecules. However, there is no report of calculation of magnetic properties of open-shell molecules. In the next section, we report the study of the diamagnetic magnetizabilities of various radicals using moderate basis sets. The RHF configuration of the cation/anion of the radical is chosen as vacuum. With respect to the vacuum, we have defined a few active particles/holes and the model space of the radicals consists of one particle/hole FS. To compare our results, we performed a relatively more extensive complete active space (CAS) SCF calculation in the same basis as well as at the same gauge origin using DALTON code [49]. We will describe the CAS for each application later.

3.4 Results and discussion

The Λ-FSMRCC method is used successfully for studying magnetizabilities. The magnetizabilities of NO_2, OH, BH_2 and NO radicals and perpendicular component of the paramagnetic part are studied and compared against the CASSCF method. The details are given in following sections.

3.4.1 NO_2 radical

To study the magnetizabilities of NO_2 doublet radical, we choose RHF of NO_2 as our vacuum and thus the radical is studied as electron attached state of NO_2. With respect to this vacuum, we chose two active particles which are close lying in energies of our

Table 3.1: Diamagnetic magnetizabilities of NO_2 radical

Basis	Gauge	Method	X	Y	Z
cc-pVTZ	CM	Λ-FSMRCC	-6.56	-24.43	-23.34
		CASSCF	-6.60	-24.44	-23.36
	N atom	Λ-FSMRCC	-6.87	-24.64	-23.53
		CASSCF	-7.01	-24.85	-23.36
cc-pVDZ	CM	Λ-FSMRCC	-6.51	-24.44	-23.34
		CASSCF	-6.55	-24.45	-23.36
	N atom	Λ-FSMRCC	-6.90	-24.83	-23.35
		CASSCF	-6.96	-24.86	-23.36
Results in au					

interest. Here center of mass is one of the gauge, and the other gauge was chosen to be at N atom. The molecule lies in the XZ plane. For the gauge at the N atom, we placed N along the Z-axis at 0.8875 au, whereas the two oxygen atoms are placed along the X-axis at ±2.0814 au For the center of mass as gauge, coordinates were chosen accordingly so that the center of mass is at the origin. The ground-state electronic structure of the nitrogen dioxide is $[core]3a_1^2 2b_2^2 4a_1^2 3b_2^2 1b_1^2 5a_1^2 1a_2^2 4b_2^2 6a_1^0$. We have studied the diamagnetic components of the NO_2 radical using cc-pVDZ and cc-pVTZ basis sets. For cc-pVTZ basis, we have chosen five electrons and eight orbitals as our active space. On the other hand, for the cc-pVDZ basis, we chose five electrons and six orbitals as active space. The Table-3.1 gives the results for the NO_2. We can see that all the three components of the diamagnetic magnetizability of NO_2 are in good agreement with CASSCF results for center of mass as gauge. However, there is some slight deviation between FSMRCC and CASSCF when we chose nitrogen as our gauge.

Table 3.2: Diamagnetic magnetizabilities of OH radical

Basis	Gauge	Method	X	Y	Z
aug-cc-pVTZ	CM	Λ-FSMRCC	-2.84	-2.80	-2.34
		CASSCF	-2.63	-2.87	-2.29
	O atom	Λ-FSMRCC	-2.88	-2.85	-2.34
		CASSCF	-2.87	-2.90	-2.29
aug-cc-pVDZ	CM	Λ-FSMRCC	-2.75	-3.03	-2.41
		CASSCF	-2.63	-2.87	-2.27
	N atom	Λ-FSMRCC	-2.79	-3.07	-2.41
		CASSCF	-2.66	-2.90	-2.27
Results in au					

3.4.2 OH radical

For OH radical, the bond distance of 0.97953 $\AA$ was considered. The coordinates were chosen such that in one case, center of mass is at the origin, while for second gauge molecule is symmetrically places around the origin. We start with RHF of hydroxide anion as vacuum and choose the degenerate π HOMOs as active orbitals. Electron detachment from these active orbitals results in doublet $^2\Pi$ state of OH radical. We have studied this radical using aug-cc-pVDZ as well as aug-cc-pVTZ basis. The gauge origin was chosen at the center of mass and at the oxygen atom. Table-3.2 gives the results for the OH radical. We compare our results with the CASSCF results obtained with the CAS space of five electrons and nine active orbitals. It can be seen that for a given gauge with the better basis set diamagnetic magnetizability value enhances. It is observed that in a given basis, there is a marginal change in the diamagnetic magnetizability of this radical with the gauge origin.

Table 3.3: Diamagnetic magnetizabilities of BH_2 radical

Basis	Gauge	Method	X	Y	Z
aug-cc-pVDZ	CM	Λ-FSMRCC	-5.72	-4.86	-3.36
		CASSCF	-5.72	-4.85	-3.32
	Origin[a]	Λ-FSMRCC	-6.54	-4.86	-4.82
		CASSCF	-6.54	-4.84	-4.14

[a] Origin is at the mid point of the H-O-H bond
Results in au

3.4.3 BH_2 radical

In Table-3.3, we report the results for the BH_2 radical. To obtain the diamagnetic magnetizability of BH_2, we start with BH_2^+ as a vacuum. Hence, the model space of BH_2 can be expressed as one particle FS. In the case of BH_2 molecules for both the gauge choices, molecule was placed in the YZ plane. For the choice of the gauge at the origin, boron atom is placed along the Y-axis at 0.924714 au and the two hydrogens are placed along the Z-axis at ±2.02910 au. For the gauge at the center of mass, we choose the coordinates such that center of mass is at the origin. The ground-state electronic structure of BH_2 is $1a_1^2 2a_1^2 1b_2^2 3a_1^1$. With respect to the vacuum, we choose two active particles for our study. We have studied this radical in aug-cc-pVDZ basis in two different gauges. One of the gauges is the center of mass, whereas the other one is at the origin of the molecule. In case of Λ-FSMRCC, the magnetizability is enhanced as we go from center of mass to gauge origin to molecular origin. The CASSCF results obtained with three active electrons in three active orbitals. Our results are in good agreement with the CASSCF results.

Table 3.4: Diamagnetic magnetizabilities of NO radical

Basis	Gauge	Method	X	Y	Z
aug-cc-pVTZ	CM	Λ-FSMRCC	-8.41	-8.40	-3.79
		CASSCF	-8.42	-8.41	-3.78
	N atom	Λ-FSMRCC	-13.42	-13.44	-3.80
		CASSCF	-13.46	-13.45	-3.78
aug-cc-pVDZ	CM	Λ-FSMRCC	-8.35	-8.57	-3.85
		CASSCF	-8.51	-8.36	-3.80
	N atom	Λ-FSMRCC	-13.55	-13.38	-3.85
		CASSCF	-13.56	-13.40	-3.80

Results in au

3.4.4 NO radical

The ground-state electronic structure of the nitrous oxide is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^1$. The basis sets used are aug-cc-pVTZ and aug-cc-pVDZ. We have studied the molecule using center of mass and the N atom as gauges. The bond distance of $1.15077\mathring{A}$ is used for the NO radical. The coordinates are chosen in a way that the center of mass is at the origin in one case, whereas for the second gauge center of the molecule is at the origin. To study the NO radical, we start with NO$^+$ as our vacuum. For , NO$^+$ the sigma orbital in the virtual space is comparable in energy with the doubly degenerate π orbital (LUMO). Therefore, we choose σ and π as active orbitals. With respect to this vacuum, NO radical can be seen as one active particle problem. Table-3.4 gives magnetizabilities of NO doublet radical in two different basis sets at both the gauge origins. We observe that for a given basis, diamagnetic susceptibility along the molecular axis, i.e., Z direction is invariant to the gauge. It can be seen that the absolute values of the magnetizability are enhanced as we go from center of mass gauge to nitrogen atom

Table 3.5: Paramagnetic magnetizabilities of NO radical

Basis	Gauge	Method	X	Y
aug-cc-pVTZ	CM	Λ-FSMRCC	3.98	8.25
		CASSCF	5.88	6.93
	N atom	Λ-FSMRCC	9.60	8.25
		CASSCF	10.52	11.58
aug-cc-pVDZ	CM	Λ-FSMRCC	4.65	1.91
		CASSCF	6.33	7.52
	N atom	Λ-FSMRCC	9.60	5.60
		CASSCF	8.75	9.92
Results in au				

as our gauge origin. We have chosen three electrons as active electrons and 11 orbitals as active once for our calculation of CASSCF results for comparison. In aug-cc-pVTZ basis, the FSMRCC and CASSCF results are in good agreement for both the gauges. However, for the aug-cc-pVDZ basis, center of mass gauge has some discrepancy between CASSCF and FSMRCC. This could be because of the poor basis set. In general, there is a good agreement between the FSMRCC and CASSCF results.

Table-3.5 reports the perpendicular component of the paramagnetic magnetizability of the NO radical. To obtain the paramagnetic magnetizability of the NO radical, we use NO^+ as our vacuum. The NO^+ being a closed-shell system and we do not have the spin component in the magnetic moment. However, because NO is a linear molecule, we expect that the spin component of the magnetic moment will align itself along or opposite direction to the magnetic field. Thus, only the z-component of the paramagnetic magnetizability will be affected by the spin part of the magnetic moment. We do not expect the contribution of spin magnetic moment to be large compared with the orbital contribution in the perpendicular direction. Hence, we report only the perpendicular component of the paramagnetic magnetizability, which is obtained using only orbital part of the magnetic moment. Although the basis is not good enough for the paramagnetic properties, it is only for preliminary application we are presenting. From the table, it appears that N atom as a gauge is more reliable for paramagnetic properties.

3.5 Conclusion

In this chapter, we have studied the diamagnetic magnetizabilities of doublet radicals using the recently developed stationary FSMRCC method. We have studied NO, NO_2, OH and BH_2 radicals starting from their corresponding cation/anion as a vacuum. We compare our results with the MCSCF results obtained with a CAS space, which is relatively larger than the corresponding model space for the FSMRCC. We have studied each of the molecules in two different gauges. Except, for the NO radical, we observe that the gauge does not change the magnetizability values much for other radicals. We observe that FSMRCC results obtained with a relatively smaller model space are in good agreement with the MCSCF results for most of the molecules. For comparison, the MCSCF method is used

References

[1] J. Cizek, *Adv. Quantum Chem.* **14**, 35 (1969); J. Cizek, *J. Chem. Phys.*, **45**, 4256 (1966); J. Cizek and J. Paldus, *Int. J. Quantum Chem.* **5**, 359 (1971).

[2] R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981); R. J. Bartlett, *J. Phys. Chem.* **93**, 1697 (1989).

[3] F. Coester, *Nucl. Phys.* **7**, 421 (1958); F. Coester and H. Kummel, *Nucl. Phys.*, **17**, 477 (1960).

[4] R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony, (World Scientific, Singapore, 1995) pp. 1047.

[5] L. Adamowicz, W. D. Laidig and R. J. Bartlett, *Int. J. Quantum Chem.* **S18**, 245 (1984).

[6] G. B. Fitzgerald, R. J. Harrison and R. J. Bartlett, *Int. J. Quantum Chem.* **85**, 5143 (1986).

[7] E . Salter, G. Trucks and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989); H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem.* **S18**, 255 (1984)

[8] J. Noga and R. J. Bartlett, *J. Chem. Phys.* **96**, 7041 (1987).

[9] H. J. Monkhorst, *Int. J. Quantum Chem.* **S11**, 421 (1977).

[10] D. Mukherjee and S. Pal, *Adv. Quantum Chem.* **20**, 291 (1989)

[11] J. Paldus, in *Methods of Computational Molecular Physics* edited by S. Wilson, G. H. F. Dierckson, NATO ASI series B, (Plenum Publishing Corporation, New York, 1992) Vol. 293, pp 99.

[12] W. Kutzelnigg, *J. Chem. Phys.* **77**, 3081 (1981); ibid, **80**, 822 (1984); W. Kutzelnigg and S. Koch, *J. Chem. Phys.* **79**, 4315 (1983).

[13] P. Durand and J. P. Malreiu, *Adv. Chem. Phys.* **67**, 321 (1987).

[14] V. Hurtubise and K. F. Freed, *Adv. Chem. Phys.* **83**, 465 (1993).

[15] B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A.* **24**, 1968 (1982).

[16] B. Jeziorski and J. Paldus, *J. Chem. Phys.* **90**, 2714 (1989); L. Meissner, *J. Chem. Phys.* **103**, 8014 (1995).

[17] D. Mukherjee, R. K. Moitra and A. Mukhopadhyay, *Mol. Phys.* **33**, 955 (1977).

[18] D. Mukherjee, *Pramana* **12**, 203 (1979); D. Mukherjee, R. K. Moitra and A. Mukhopadhyay, *Indian. J. Pure. Appl. Phys.* **15**, 613 (1977).

[19] R. K. Moitra and D. Mukherjee, *J. Phys. B* **12**, 1 (1979); M. A. Haque and D. Mukherjee, *J. Chem. Phys.* **80**, 5058 (1984); R. Offermann, W. Ey and H. Kummel, *Nucl. Phys. A.* **273**, 349 (1976); R. Offermann, *Nucl. Phys. A.* **273**, 368 (1976); W. Ey, *Nucl. Phys. A.* **296**, 189 (1978)

[20] S. Das, N. Bera, S. Ghosh and D. Mukherjee, *J. Mol. Struct.* (THEOCHEM) **771**, 79 (2006); U. S. Mahapatra, B. Datta, B. Bandyopadhyay and D. Mukherjee, *Adv. Quantum Chem.* **30**, 163 (1998); U. S. Mahapatra, B. Datta and D. Mukherjee, *Mol. Phys.* **94**, 157 (1998).

[21] M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995); S. R. Gawlitsky, M. Nooijen and R. J. Bartlett, *Chem. Phys. Lett.* **248**, 189 (1996); J. Geertsen, M. Rittby and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989); J. F. Stanton and R. J. Bartlett, *J. Chem. Phys* **98**, 7029 (1993); D. C. Comeau, and R. J. Bartlett, *Chem. Phys. Lett.* **207**, 414 (1993).

[22] M. Nooijen, and R. J. Bartlett, *J. Chem. Phys.* **106**, 6441 (1997); ibid, **106**, 6449 (1997); ibid, **107**, 6812 (1997).

[23] H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); ibid, **67**, 329 (1979); M. Ehara and H. Nakatsuji, *J. Chem. Phys.* **99**, 1952 (1992).

[24] H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978); ibid, **68**, 4279 (1978).

[25] M. Urban, P. Neogrady, and I. Hubac, in *Recent Advances in Coupled-cluster Methods*, editted by R. J. Bartlett, (World Scientific, Singapore, (1997)), pp. 275.

[26] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, *J. Chem. Phys.* **88**, 4357 (1988); ibid, *Chem. Phys. Lett.* **137**, 273 (1987); ibid, **142**, 575 (1987).

[27] N. Vaval, K. B. Ghose, S. Pal, and D. Mukherjee, *Chem. Phys. Lett.* **209**, 292 (1993); N. Vaval, S. Pal and D. Mukherjee, *Theor. Chem. Acc.* **99**, 100 (1998).

[28] N. C. Handy, and H. F. Schaefer III, *J. Chem. Phys.* **81**, 5031 (1984).

[29] G. Fitzgerald, R. J. Harrison and R. J. Barlett, *J. Chem. Phys.* **85**, 5143 (1986); **90**, 1752 (1989).

[30] T. Helgaker and P. Jorgensen, *Adv. Quantum. Chem.* **19**, 183 (1988); H. Koch, H. J. A. Jensen, P. Jorgensen, T. Helgaker, G. E. Scuseria and H. F. Schaefer III, *J. Chem. Phys.* **92**, 4924 (1990).

[31] S. Pal, M. D. Prasad and D. Mukherjee, *Pramana* **18**, 261 (1982); S. Pal, M. D. Prasad and Mukherjee, *Theor. Chim. Acta.* **62**, 523 (1983); ibid, **66**, 311 (1984); S. Pal, *Theor. Chim. Acta.* **66**, 151 (1984); S. Pal and K. B. Ghose, *Curr. Sci.* **63**, 667 (1992); K. B. Ghose, P. G. Nair and S. Pal, *Chem. Phys. Lett.* **211**, 15 (1993); N. Vaval, K. B. Ghose, P. G. Nair and S. Pal, *Proc. Indian. Acad. Sci.* **106**, 387 (1994).

[32] N. Vaval, K. B. Ghose and S. Pal, *J. Chem. Phys.* **101**, 4914 (1994); N. Vaval and S. Pal, *Phys. Rev. A.* **54**, 250 (1996); N. Vaval, A. B. Kumar and S. Pal, *Int. J. Mol. Sci.* **2**, 89 (2001); N. Vaval, *Chem. Phys. Lett.* **318**, 168 (2000).

[33] J. F. Stanton and J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).

[34] D. Ajitha and S. Pal, *Phys. Rev. A.* **56**, 2658 (1997); D. Ajitha, N. Vaval and S. Pal, *J. Chem. Phys.* **110**, 2316 (1999); D. Ajitha and S. Pal, *Chem. Phys. Lett.* **309**, 457 (1999); ibid, *J. Chem. Phys.* **114**, 3380 (2001).

[35] K. R. Shamsundar and S. Pal, *J. Mol. Sci.* **3**, 710 (2002).

[36] K. R. Shamsundar, S. Asokan and S. Pal, *J. Chem. Phys.* **120**, 6481 (2004).

[37] P. G. Szalay, *Int. J. Quantum Chem.* **55**, 151 (1994).

[38] P. U. Manohar, N. Vaval and S. Pal, *J. Mol. Struct.* THEOCHEM, **768**, 91 (2006).

[39] I. Lindgren, *Int. J. Quantum Chem.* **S12**, 33 (1979).

[40] P. U. Manohar, and S. Pal, *Chem. Phys. Lett.* **438**, 321 (2007).

[41] T. Helgaker, M. Jaszunski and K. Ruud, *Chem. Rev.* **99**, 293 (1999); J. Gauss and J. F. Stanton, *J. Chem. Phys.* **104**, 2574 (1996); K. Ruud, T. Helgaker, K. L. Bak, P. Jorgensen and H. J. A. Jensen, *J. Chem. Phys.*, **99**, 3847 (1993).

[42] T. Helgaker and P. Jorgensen, *J. Chem. Phys.* **95**, 2595 (1991); K. Ruud, T. Helgaker, K. L. Bak, P. Jorgensen and Olsen, *J. Chem. Phys.* **192**, 157 (1995).

[43] J. Gauss, K. Ruud and M. Kallay, *J. Chem. Phys.* **127**, 74101 (2007).

[44] P. U. Manohar, N. Vaval and S. Pal, *Chem. Phys. Lett.* **387**, 442 (2004).

[45] F. London, *J. Phys. Radium.* **8**, 397 (1937).

[46] C. Van Wulen and W. Kutzelnigg, *Chem. Phys. Lett.* **205**, 563 (1993).

[47] J. Geertsen, *Chem. Phys. Lett.* **188**, 326 (1992).

[48] M. Kollwitz and J. Gauss, *Chem. Phys. Lett.* **260**, 639 (1996).

[49] T. Helgaker, H. J. Aa Jensen, P. Jorgensen, J. Oslen, K. Ruud, H. Agren, A. A. Auer, K. L. Bak, V. Bakken, O. Christiansen, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Hattig, A. Hald, A. Halkier, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpeker, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. B. Pedersen, T. A. Ruden, A. Sanchez, T. Saue, S. P. A. Sauer, B. Schimmelpfenning, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras, *DALTON a molecular electronic structure program, Release 1.2, (2001).*

Chapter 4

Effect of triples to dipole moments in Fock-space multi-reference coupled cluster method

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In this chapter, we present the new implementation of partial triples for the dipole moment of doublet radicals in Lagrangian formulation of Fock-space Multi-reference coupled cluster (Λ-FSMRCC) response method. We have implemented a specific scheme of non-iterative triples, in addition to singles and doubles scheme, which accounts for the effects appearing at least at the third order in dipole moments. The method is applied to the ground states of OH, OOH, HCOO, CN, CH, NH_2 and PO radicals.

4.1 Introduction

Single reference coupled cluster (SRCC) [1–7] has been accepted as the state-of-the-art method for the electronic structure calculations. It has been successfully implemented for the energy, gradients, molecular properties and potential energy surfaces [8–18]. In general, SRCC introduces dynamic electron correlation, which keeps electrons apart. It is well known that triple excitations in SRCC contribute to the energy from fourth order onwards. So far different version of the SRCC method with full or partial inclusion of triples with increasing precision have been developed [19–24] for energy. The non-iterative triples are routinely used for high accuracy with a economical treatment of triples. The full inclusion of triples is expensive, though in the SRCC it has been implemented by Bartlett and co-workers [21] for energy. The perturbative treatment of the quadruple excitations has also been attempted [23, 25] in single reference context. However there are cases which involve several configurations which make nearly equal contribution(quasi-degenerate) to the exact wave function, i.e., bond breaking situations of the ground state or in excited state, where single reference CC fails. The restricted open-shell (RO)- based CC methods [26], which uses linear operator have been successful in describing the quasi-degenerate cases. Though in single reference framework, selected triples and quadruple level excitations [27, 28] have been considered for quasi-degenerate cases [29, 30], multi-determinantal or multi-reference coupled cluster (MRCC) methods have emerged as the methods of choice to take into account the quasi-degenerate molecular systems [31]. Among the multi-reference methods, the effective Hamiltonian [32–34] based MRCC methods provide multiple roots via diagonalization of the effective Hamiltonian within the model space. This subclass mainly spans two approaches: namely the Hilbert space (HS) MRCC [35–37] and Fock-space (FS) MRCC [38–44]. HSMRCC assumes different vacua for different configurations in the model space with same number of electrons and a state-universal wave operator to introduce the model space to virtual space excitations. The method is suitable for potential energy surface (PES) studies [31] and the situations involving curve crossing. However for PES, state selective MRCC method developed by Mukherjee and co-workers [45, 46] has been found to be more attractive in recent years from the point of view of circumventing the problem of intruder states. The FSMRCC theory was originally formulated by Kutzelnigg [38], Mukherjee [39–41] and Lindgren [42], and applications to atoms were made by Kaldor and co-workers [43]. The FSMRCC applications to molecules were performed by Pal et al [44]. FSMRCC is based on the concept of a common vacuum and assumes a valence universal wave operator to describe the various states, which are generated by addition and/or removal of electron to/from the common vacuum, usually the closed-shell RHF configuration. FS methods are suitable for the difference energy calculations and thus describe ionized, electron-attached, or excited states of a closed-shell system. However, both these methods suffer from the problem of intruder states. This problem can be avoided with the help of intermediate Hamiltonian [33] based formulation both in Fock space [47, 48] as well as Hilbert space [49, 50].

The important feature of both the multi-reference formulations is their size-extensivity. On the other hand, in equation of motion(EOMCC) [51–57] or linear response CC(CCLR) method [58–60] use a linear operator for an excited state, but an exponential operator for the ground state. The EOMCC method has been extensively developed for ionized [53, 54], electron attached [55] and excited state [51] problems. The similarity transformed EOMCC method (STEOMCC) which is size extensive was developed by Nooijen and co-workers [61, 62]. For one valence problem EOMCC and FSMRCC are equivalent. However, such equivalence breaks down for excited state. EOMCC contains certain unlinked diagrams which are associated with charge-transfer separability [61]. The spin-flip EOMCC method has also been introduced as a clever way to describe the multi reference states [63]. The symmetry-adapted cluster expansion configuration interaction (SACCI) [64, 65] and method of moments coupled cluster(MMCC) [66, 67] have also been successful in describing some quasi-degenerate problems. There are several implementations of the full and partial inclusion of the triples within the Fock space

[68–71] MRCC. Pal and co-workers included non-iterative triples for ionization potential [68, 69] and excitation energies [70], within Fock space MRCC scheme and Bartlett and co-workers included full triples correction for excitation energies [71]. The full triples correction to excitation energies in intermediate Hamiltionian Fock space CC has been pursued currently by Musial et al [72]. The inclusion of iterative and non-iterative triples in EOMCC [73–77] and state-selective approaches [78, 79] for energy calculations has also been attempted. The perturbative triples corrections to EOM-IP-CCSD was introduced by stanton and Gauss [80]. Recently, perturbative triples correction to EOM-EA-CCSD has been done by Manohar et al [81]. The selected set of triples defined through the active orbitals in EOMCCSD (EOMCCSDt) has also been attempted [82]. Recently, Krylov et al. employed the non-iterative perturbative triples correction to spin flip EOMCC (SF-EOMCC) method for excitation energies [83]. The non-iterative energy corrections to MMCC for excitation energy has been achieved by Piecuch et al [84].

Formulation of energy derivatives using multi-root CC methods is a challenging task. The response theory has been a valuable theoretical tool to study molecular properties [85, 86] . Along lines of non variational CC (NVCC) response approach of Monkhorst, a response approach was developed for Fock-space MRCC formulation [87, 88] and implemented for FSMRCC based dipole moments of various ionized/electron attached states as well as excited states. This method explicitly calculates the first derivatives of all cluster amplitudes [89, 90] and thus was not a satisfactory approach. Extending the idea of the Lagrange multipliers for the specific root of the effective Hamiltonian, Pal and co-workers developed the response approach within the MRCC framework Λ-MRCC). This approach was formulated for the Hilbert space [91] as well as Fock space [92] MRCC methods. This formulation is very general and can be implemented in any method. Recently this was implemented for the Generalized van Vleck perturbation approach [93]. Szalay [94] independently formulated similar approach based on Lagrange multipliers for the Fock space MRCC method. Though in principle, Szalay's approach can be used for general model spaces, this was implemented only for complete model spaces [95]. Λ-FSMRCC method was successfully implemented for the dipole moment [96] and polarizability [97] of the doublet radicals as well as excited states [98] of molecules. The initial implementation was within singles and doubles (Λ-FSMRCCSD) approximation. Response theory for molecular properties has been pursued by Jorgensen et. al in LR-CC formalism [99]. Theory for analytic energy derivatives in EOMCC method was proposed by Stanton [100] and implemented by Stanton and Gauss [101, 102]. Nooijen and coworkers implemented gradients in STEOMCC [103, 104], using Lagrange multipliers. Analytic gradients for SF-EOMCC model at singles and doubles level has also been proposed recently [105].

However, to improve the accuracy of the molecular properties of the outer valence as well as some of the inner valence states, it is important to include the effects of triples. However, inclusion of full triples is computationally expensive. This limits the applicability of the method to small molecules or to moderate basis sets. Hence, partial inclusion of the triples is more practicable and this has been implemented in this work. Since, triples are added on the basis of perturbative order, it does not guarantee that inclusion of triples will improve molecular properties towards the Full CI (FCI), due to oscillatory nature of the perturbation series. Analytical derivatives for CCSD with various levels of triples excitations has been analyzed long ago [106, 107]. Gauss et al [108] implemented analytical gradients for the CCSDT model. Recently, parallel calculation of CCSD(T) has been achieved for analytic first and second derivatives [109]. In the context of SRCC, the importance of triples to the dipole moment has also been analyzed [110]. Triples excitation in linear response CC method for excited state properties were studied iteratively [111].

The FSMRCC theory [38, 40–42, 44, 112] and the Lagrangian method in FSMRCC [92, 96, 97] are given in details in the introduction of this thesis. The review of the above are also discussed in chapter 3 of this thesis. With this beginning, let us move on to the triples correction to FSMRCC first order properties. In this chapter, we present the first implementation of partial triples corrections to the response properties for Lagrange based formulation within Fock space multi-reference coupled cluster method (Λ-FSMRCC) for first order electric property. We have implemented the terms coming from triples whose contribution is at the fourth order in energy and at least up to third order in dipole moment.

4.2 Implementation of the partial triples in Λ-FSMRCC method

In this section, we will present the contribution of triples to the dipole moment, whose origin is beyond the singles and doubles approximations in FSMRCC scheme. Here we will discuss the first implementation of non-iterative triples in T and Λ-amplitudes to the dipole moment in FSMRCC response. The triples amplitudes are generated as and when used. Since there are several schemes for the inclusion of triples in the literature for SRCC, first we will discuss the specific scheme implemented in this chapter for (0,0) sector. The approach implemented here uses canonical orbitals and the orbitals are not allowed to change with the perturbation and hence this approach is a non-relaxed approach. We solve $T_1^{(0,0)}$ and $T_2^{(0,0)}$ amplitudes excluding $VT_3^{(0,0)}$ in a completely iterative manner, which is CCSD approximation. Using these amplitudes of $T_1^{(0,0)}$ and $T_2^{(0,0)}$, $T_3^{(0,0)}$ amplitude is calculated non-iteratively from $VT_2^{(0,0)}$ and $VT_2^{(0,0)}T_2^{(0,0)}$. The $T_1^{(0,0)}$ and $T_2^{(0,0)}$ amplitudes are solved iteratively including the term $VT_3^{(0,0)}$. The inclusion of $VT_3^{(0,0)}$ term in singles and doubles amplitude equation updates the CCSD equations. Even though $VT_3^{(0,0)}$ term is third order, considering the term in $T_3^{(0,0)}$ equation will make the method iterative. Hence, this term is not included in this scheme. The term $VT_2^{(0,0)}$ contributes at the second order, $VT_2^{(0,0)}T_2^{(0,0)}$ contributes at the third order in perturbation.

In the implementation of the MRCCSD(T*)/CCSD(T*) approximation, we construct an intermediate operator $\bar{H}$ given by $\bar{H} = exp(-T^{(0,0)})Hexp(T^{(0,0)}))$ and truncate up to one($\bar{F}$), two($\bar{V}$) and three body($\bar{W}$) parts. For the construction of $\bar{H}$ we use CCSD approximation without including the amplitudes of triples i.e. $T_3^{(0,0)}$. H_{eff} under this approximation is

$$H_{eff} = P^{(0,1)}(\bar{F} + \bar{F}T_1^{(0,1)} + \bar{V}T_2^{(0,1)} + \bar{F}T_2^{(0,1)} + \bar{V}T_3^{(0,1)})P^{(0,1)} \tag{4.1}$$

The Fock space Bloch equations for the $T_1^{(0,1)}$, $T_2^{(0,1)}$ and $T_3^{(0,1)}$ amplitudes are as below

$$Q_1^{(0,1)}(\bar{F} + \bar{F}T_1^{(0,1)} + \bar{V}T_2^{(0,1)} + \bar{F}T_2^{(0,1)} + \bar{V}T_3^{(0,1)} - T_1^{(0,1)}H_{eff})P^{(0,1)} = 0 \tag{4.2}$$

$$Q_2^{(0,1)}(\bar{V}+\bar{F}T_2^{(0,1)}+\bar{V}T_1^{(0,1)}+\bar{V}T_2^{(0,1)}+\bar{W}T_2^{(0,1)}+\bar{V}T_3^{(0,1)}+\bar{F}T_3^{(0,1)}-T_2^{(0,1)}H_{eff})P^{(0,1)} = 0 \tag{4.3}$$

$$Q_3^{(0,1)}(\bar{W} + \bar{W}T_2^{(0,1)} + \bar{F}T_3^{(0,1)} + \bar{V}T_2^{(0,1)} - T_3^{(0,1)}H_{eff})P^{(0,1)} = 0 \tag{4.4}$$

It can be seen that $\bar{V}T_3^{(0,1)}$ is the only term contributing to the singles and doubles amplitude equation along with H_{eff}. It is easy to see that $\bar{W}$ cannot contribute to H_{eff}. The equations 4.2 and 4.3 are first solved fully excluding the terms which involve $T_3^{(0,1)}$ amplitude, which is CCSD approximation . Using these amplitudes eq 4.4 is solved non-iteratively. In eq 4.4, we want to be accurate up to third order. Hence we include in the term $T_3^{(0,1)}H_{eff}$ only $T_3^{(0,1)}\bar{F}$. After solving $T_3^{(0,1)}$, we again solve the equations 4.2 and 4.3 iteratively. Here the effect of $T_3^{(0,1)}$ appears via $\bar{V}T_3^{(0,1)}$ and $\bar{F}T_3^{(0,1)}$.

We now consider the triples correction to the Λ amplitudes and then to the overall dipole moment. The Λ equations are like the conjugates of the T amplitude equations and hence the terms in T equations appear in Λ equations also. It should be mentioned here, that unlike in T amplitude equations, here we first solve for the (0,1) sector and then for the (0,0) sector due to reverse decoupling in Λ equations.

First, the Λ amplitudes in singles and doubles approximation are solved iteratively for both (0,1) and (0,0) sector. With these Λ amplitudes the Lagrangian for triples is constructed. During the construction, the singles and doubles(SD) terms remain as such.

The Lagrangian with the triples correction is given by,

$$\begin{aligned} \Im \;=\;& SD + \bar{V}T_3^{(0,1)}C\tilde{C} + \Lambda_3^{(0,1)}\bar{V}T_2^{(0,1)} + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,1)} + \Lambda_3^{(0,1)}\bar{F}T_3^{(0,1)} + \Lambda_2^{(0,1)}\bar{V}T_3^{(0,1)} \\ & + \Lambda_2^{(0,1)}\bar{F}T_3^{(0,1)} - \Lambda_2^{(0,1)}T_2^{(0,1)}(\bar{V}T_3^{(0,1)}) + \Lambda_1^{(0,1)}\bar{V}T_3^{(0,1)} \\ & \Lambda_3^{(0,0)}VT_2^{(0,0)} + \Lambda_2^{(0,0)}VT_3^{(0,0)} + \Lambda_1^{(0,0)}VT_3^{(0,0)} + \Lambda_3^{(0,0)}FT_3^{(0,0)} + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,0)} \\ & + \Lambda_3^{(0,1)}VT_3^{(0,0)} + \Lambda_3^{(0,1)}VT_2^{(0,0)} \end{aligned} \tag{4.5}$$

The $\tilde{C}$ and C are left and right eigen vectors of the H_{eff}. The Lagrangian in eq 4.5 is differentiated with respect to $T_3^{(0,1)}$ to get the equation for $\Lambda_3^{(0,1)}$. The equation defining the $\Lambda_3^{(0,1)}$ amplitude is given in eq 4.6.

$$< P^{(0,1)}|\bar{V}C\tilde{C} + \Lambda_3^{(0,1)}\bar{F} - \Lambda_2^{(0,1)}T_2^{(0,1)}\bar{V} + \Lambda_1^{(0,1)}\bar{V} + \Lambda_2^{(0,1)}\bar{V}|Q^{(0,1)} >= 0 \tag{4.6}$$

The Lagrangian in eq 4.5 is differentiated with respect to $T_2^{(0,1)}$ to get the equation for $\Lambda_2^{(0,1)}$. The $\Lambda_2^{(0,1)}$ equation is given by

$$SD + < P^{(0,1)}|\Lambda_3^{(0,1)}\bar{V} + \Lambda_3^{(0,1)}\bar{W}|Q^{(0,1)} >= 0 \tag{4.7}$$

The eq 4.6 is solved non-iteratively to obtain $\Lambda_3^{(0,1)}$. The connected terms in $\Lambda_3^{(0,1)}$ amplitude equation are considered in this approximation. Thus, $\Lambda_3^{(0,1)}$ amplitude is obtained from the terms $\bar{V}C\tilde{C}$, $\Lambda_2^{(0,1)}\bar{V}$, $\Lambda_1^{(0,1)}\bar{V}$ and $\Lambda_2^{(0,1)}T_2^{(0,1)}\bar{V}$. These contribute at the first order, second order and third order respectively. The $\Lambda_3^{(0,1)}$ amplitude is also obtained from the second order $\bar{F}$ containing term $\Lambda_3^{(0,1)}\bar{F}$. After obtaining $\Lambda_3^{(0,1)}$, its effect on $\Lambda_2^{(0,1)}$ appears through the third order terms $\Lambda_3^{(0,1)}\bar{V}$ and $\Lambda_3^{(0,1)}\bar{W}$. The equation for $\Lambda_2^{(0,1)}$ amplitude, eq 4.7 is solved fully by taking in to account the $\Lambda_3^{(0,1)}$ terms calculated above.

For solving (0,0) sector $\Lambda_3^{(0,0)}$ amplitude is obtained first. Here too the equation for $\Lambda_3^{(0,0)}$ is obtained by differentiating the Lagrangian in eq 4.5 with respect to $T_3^{(0,0)}$. The terms appear after the differentiation with respect to $T_3^{(0,0)}$ are given in eq 4.8.

$$< P^{(0,0)}|\Lambda_3^{(0,0)}F + \Lambda_2^{(0,0)}V + \Lambda_1^{(0,0)}V + \Lambda_3^{(0,1)}V|Q^{(0,0)} >= 0 \tag{4.8}$$

The equation for $\Lambda_2^{(0,0)}$ is obtained from differentiating eq 4.5 with respect to $T_2^{(0,0)}$. The $\Lambda_2^{(0,0)}$ equation with triples correction is given by

$$SD+ < P^{(0,0)}|\Lambda_3^{(0,0)}V + \Lambda_3^{(0,1)}V + \Lambda_3^{(0,0)}VT_2^{(0,0)}|Q^{(0,0)} >= 0 \tag{4.9}$$

The eq 4.8 is solved non-iteratively to obtain $\Lambda_3^{(0,0)}$. $\Lambda_3^{(0,0)}$'s are obtained by taking the direct contribution from the second order term $\Lambda_2^{(0,0)}V$ and the third order terms $\Lambda_1^{(0,0)}V$ and $\Lambda_3^{(0,1)}V$. Also F containing term $\Lambda_3^{(0,0)}F$ contributes to $\Lambda_3^{(0,0)}$ equation at second order. It should be noted that due to reverse decoupling $\Lambda^{(0,1)}$ involving terms $\Lambda_3^{(0,1)}VT_2^{(0,0)}$ and $\Lambda_3^{(0,1)}VT_3^{(0,0)}$ appear in $\Lambda^{(0,0)}$. After obtaining $\Lambda_3^{(0,0)}$, its effect on $\Lambda_2^{(0,0)}$ equation is incorporated through the third order terms $\Lambda_3^{(0,0)}V$, $\Lambda_3^{(0,1)}V$ and $\Lambda_3^{(0,0)}VT_2^{(0,0)}$. The eq 4.9 is solved fully by taking in to account of $\Lambda_3^{(0,0)}$ terms calculated above. Finally, the triples contribution to $E^{(1)}$ are given in eq 4.10, where $\hat{O}$ is the explicit derivative of Hamiltonian with respect to external field.

$$E^{(1)}_{triples} = \Lambda_2^{(0,1)}\hat{O}T_3^{(0,1)} + \Lambda_2^{(0,0)}\hat{O}T_3^{(0,0)} \tag{4.10}$$

These triples corrected Λ and T amplitudes are used for the evaluation of dipole moments in (0,0) and (0,1) sector. The term $VT_2^{(0,0)}T_2^{(0,0)}$ in $T_3^{(0,0)}$ equation will thus have higher effect on the dipole moment, while the other triples correcting terms will affect the dipole moment at third order. The third order terms which appear in the dipole moment are $\Lambda_2^{(0,1)}\hat{O}T_3^{(0,1)}$ and $\Lambda_2^{(0,0)}\hat{O}T_3^{(0,0)}$. Hence the final dipole moment is corrected at least up to third order in triples.

4.3 Results and discussion

We have implemented the contribution of triples partially to the FSMRCC singles and doubles scheme (FSMRCCSD(T*)). To test our code we chose small systems as a case study. We present our results and discussion on them in this section. The code is tested against the non-relaxed finite field approach. The systems studied are OH, OOH, HCOO, CN, CH, PO and NH_2 radicals.

Table 4.1: Dipole moments of $^2\Pi$ OH radical

BASIS	Λ-FSMRCCSD(T*)	Λ-FSMRCCSD	EOMCCSD(unrelaxed) [b]	Full CI [c]
cc-pVDZ	0.682	0.634	0.639	0.663
cc-pVTZ	0.682	0.645	...	...
cc-pVQZ	0.684	0.645	...	...

Results in au
[a] $R_{eq} = 1.85104\, a_0$
[b] see Ref.[96]
[c] see Ref.[113]

4.3.1 OH radical

We report the dipole moment of hydroxy radical at the equilibrium geometry in Table-4.1. We start with the closed shell configuration of OH^- anion as a vacuum. The HOMO of OH^- is two fold degenerate in nature. The degenerate HOMO's are chosen as active holes of the Fock space (0,1) sector. The removal of an electron from one of these HOMO's lead to degenerate doublet $^2\Pi$ of hydroxy radical. In Table-4.1 we report the dipole moment of hydroxy radical in cc-pVXZ(X=D,T,Q) basis. The calculated FCI and available EOMCCSD dipole moments in cc-pVDZ basis are also presented. The Λ-FSMRCCSD values shows that the dipole moment is converged from cc-pVDZ to cc-pVQZ. Whereas, the Λ-FSMRCCSD(T*) produces a marginal change in dipole moment. It is observed that the Λ-FSMRCCSD dipole moment in cc-pVDZ basis is 0.634 au, whereas the Λ-FSMRCCSD(T*) increases the dipole moment (0.682 au) towards the FCI value of 0.663 au [113]. Though triples exceeds the FCI dipole moment, the qualitative trend towards FCI dipole moment is obtained. With the higher order triples it may improve further.

4.3.2 CN radical

The dipole moments of the CN radical are presented in the Table-4.2. We start with the cyanide anion which is closed shell with the ground state geometry $^2\Sigma^+$. Removal of

Table 4.2: Dipole moments of $^2\Sigma^+$ state of CN radical

BASIS	ROHF[b]		Λ-FSMRCC	
	CCSD	CCSD(T)	CCSD	CCSD(T*)
cc-pVDZ	0.522	0.476	0.427 (0.437)[c]	0.497 (0.489)[c]
aug-cc-pVDZ			0.510	0.558
CBS LIMIT [d]			0.559 ± 0.001	
Exp[e]			0.57 ± 0.03	

Results in au

[a] R_{eq} = 2.21512 a_0

[b] Results obtained from ACES II package

[c] Relaxed finite-field values

[d] see Ref.[114]

[e] see Ref.[116]

an electron from the cyanide anion gives CN radical. The studies are carried out with one active hole. Since the dipole moment of the CN radical is important in astrophysics, there are various theoretical calculations [114, 115] to achieve the experimental accuracy. In Table-4.2 we report the dipole moment obtained using our method in cc-pVDZ and aug-cc-pVDZ basis sets. For cc-pVDZ basis we also report the finite field dipole moment values using ROHF CC and FSMRCC within singles and doubles approximation as well as with partial triples. The values presented in parenthesis denote the finite field FSMRCC results. Observation of the various levels of theory [114, 115] says that it is necessary to have augmented basis sets for the dipole moment calculations of CN radical, which is clearly reflected in the Table-4.2. It has been observed so far that only beyond the double zeta with augmentation, dipole moment close to CBS limit (0.559 ± 0.001 au) [114] and experimental(0.57 ± 0.03au) [116] value is attained. In our method, as we go from cc-pVDZ basis to aug-cc-pVDZ basis, Λ-FSMRCCSD gives dipole moment values of 0.427 au and 0.510 au respectively. Thus, with augmented basis at the CCSD level is close to the reported CBS limit as well as experimental dipole moment. The inclusion of triples improves the dipole moment values to 0.497 au for cc-pVDZ basis and

Table 4.3: Dipole moments of OOH and HCOO radical

STATE	DIRECTION	Λ-FSCCSD(T*)	Λ-FSCCSD	FF-FSCCSD(T*)	EOMCCSD ^{a}
$\dot{O}OH$					
$^2A_2$	X	-0.588	-0.557	-0.571	
	Y	-0.713	-0.669	-0.692	
Total		0.924	0.870	0.897	
$^1A_2$	X	-0.402	-0.369	-0.387	
	Y	-0.717	-0.676	-0.694	
Total		0.822	0.770	0.795	
$HCO\dot{O}$					
$^2B_2$	Y	0.965	0.909	0.979	1.004
$^2A_1$	Y	0.835	0.786	0.842	...

Results in au
^{a} see Ref.[101]

0.558 au for aug-cc-pVDZ basis respectively. It can be seen that the qualitative trend remains same in both the basis sets i.e triples correction increase the dipole moment values. However, in ROHF-CC approach the trend is opposite to that of Λ-FSMRCC. ROHF-CC results are obtained using finite field approach which inlcudes relaxation effects. To test the effect of relaxation we have done finite field relaxed FSMRCC calculation. Here too, we get the same trend as we obtained from the analytic non-relaxed approach. Thus the difference in trends of dipole moment in Λ-FSMRCC and ROHF-CC may arise due to combination of the way triples are included and the treatment of dynamic correlation.

4.3.3 OOH and HCOO radical

The dipole moments for the non-linear molecules such as hydroperoxy and formyloxy radical at the equilibrium geometry

were studied using the double zeta basis set of Huzinaga Dunning [117, 118] with a set of uncontracted polarized functions. The description of the geometries for these radicals are given in appendix A. The center of mass coordinates are used and the molecules are kept along the X,Y direction and the dipole moments for each direction is obtained and presented in Table-4.3. Since there is no FCI or experimental dipole moment available for these systems, we report the relaxed finite field FSMRCC(FF-FSMRCC) dipole moments. We start with the RHF of hydroperoxide anion as vacuum. The electronic configuration of RHF of hydroperoxide anion is

[core], $3{a_1}^2, 4{a_1}^2, 5{a_1}^2, 1{a_2}^2, 6{a_1}^2, 7{a_1}^2, 2{a_2}^2$

Removal of an electron from one of the two highest occupied orbitals results in near-degenerate states ($^2A_2$ and $^2A_1$) of hydroperoxy radicals. The dipole moments of the radical along two orthogonal directions (X and Y) have been presented in Table-4.3. We also report the FF-FSMRCC calculations for the system. In this case, the Λ-FSMRCCSD(T*) predicts the lower dipole moment than one obtained from the FF-FSMRCCSD(T*).

The dipole moments of the first two low-lying near-degenerate states of formyloxy radical at the equilibrium geometry are given in Table-4.3. We start with the RHF of formate anion as vacuum. Removal of an electron from the formate anion results in formyloxyl radical, the near degenerate low-lying states of which, have the electronic configuration

[core], $3{a_1}^2, 2{b_2}^2, 4{a_1}^2, 5{a_1}^2, 3{b_2}^2, 1{b_1}^2, 1{a_2}^2, 6{a_1}^2, 4{b_2}^1$

and

[core], $3{a_1}^2, 2{b_2}^2, 4{a_1}^2, 5{a_1}^2, 3{b_2}^2, 1{b_1}^2, 1{a_2}^2, 6{a_1}^1, 4{b_2}^2$

The dipole moments along the H-C bond axis for these states, denoted by $^2B_2$ and $^2A_1$ have been reported. The EOMCC result [101] for the ground state has also been reported. We have also mentioned the finite field dipole moment obtained by the FF-FSMRCCSD(T*) in Table-4.3, which stays close to the dipole moment obtained from the Λ-FSMRCCSD(T*) method.

Table 4.4: Dipole moments of CH radical

BASIS		Λ-FSMRCCSD(T*)	Λ-FSMRCCSD	Full CI
cc-pVDZ	R_{eq}	0.575	0.582	0.548
Sadlej	R_{eq}	0.547	0.540	...
Exp[a]				0.57±0.023
cc-pVDZ	R_{dis}	0.061	0.100	0.074
Sadlej	R_{dis}	0.084	0.111	...

Results in au

[a] see Ref.[121].

R_{eq} = 2.11648 a_0.

R_{dis}=3.1660 a_0.

4.3.4 CH radical

The CH radical can be considered as the electron attached state of the corresponding cation CH$^+$. The RHF configuration of CH$^+$, $1\sigma^2 2\sigma^2 3\sigma^2$ is chosen as a vacuum. The degenerate LUMO's are chosen as active particles. For CH$^+$ we report the dipole moment at the equilibrium as well as at the stretched geometry i.e., at 1.5 R_e. Table-4.4 reports the results for the CH radical in cc-pVDZ [119] and Sadlej [120] basis along the direction of molecular axis. We compare the dipole moment obtained from cc-pVDZ basis with the FCI dipole moment and the dipole moment obtained from Sadlej basis with experimental [121] value. At the equilibrium geometry the dipole moment value is reduced in Λ-FSMRCCSD as well as in Λ-FSMRCCSD(T*) as we go from cc-pVDZ to Sadlej basis. However, at the stretched geometry, the dipole moment is increased with the basis set. In cc-pVDZ basis, at the equilibrium geometry the Λ-FSMRCCSD dipole moment value is 0.582 au, which is reduced by the triples correction (0.575 au). The Λ-FSMRCCSD(T*) dipole moment (0.575 au) is closer to the FCI(0.548 au) value. At the stretched geometry the Λ-FSMRCCSD gives 0.100 au, the inclusion of the triples reduces it to 0.061 au, which is approaching towards the FCI value of 0.074 au. This emphasizes the importance of inclusion of the triples for the calculation of dipole moment at the stretched geometry. Similar trend is observed for the Sadlej basis too. However, even

Table 4.5: Dipole moments of PO radical

BASIS	ROHF [b]		Λ-FSMRCC	
	CCSD	CCSD(T)	CCSD	CCSD(T*)
cc-pVDZ	0.777	0.726	0.708	0.750
Exp [d]				0.740±0.028

Results in au

[a] R_{eq} = 2.78357a_0

[b] Results obtained from ACES II package

[d] see Ref.[122]

at the equilibrium geometry with the inclusion of partial triples the dipole moment value approaches towards FCI. This shows the importance of the triples even at the equilibrium geometry.

4.3.5 PO radical

The dipole moment of PO radical, which is difficult to be predicted by the single reference method, has been studied using FSMCCSD and FSMRCCSD(T*). The RHF configuration of PO^- has been taken as the vacuum. The calculations are carried out with one active hole. The dipole moment value of PO radical obtained using cc-pVDZ basis in FSMRCCSD is 0.708 au and FSMRCCSD(T*) is 0.750 au. The dipole moment obtained from the FSMRCCSD(T*) method, as can be seen from the Table-4.5, is slightly over estimated. However, inclusion of triples improves the accuracy towards the experimental value of 1.88±0.07 debye [122](0.740±0.028 au). The finite filed relaxed ROHF-CCSD and ROHF-CCSD(T) are performed in the same basis using ACES-II package [123]. The opposite trend in the inclusion of triples is observed for ROHF based CCSD and CCSD(T). This difference in trends in the inclusion of dipole moment of triples in Λ-FSMRCC and ROHF-CC could be due to combination of the way triples are included and the treatment of dynamic correlation.

Table 4.6: Dipole moments of NH_2 radical

BASIS	Method	X	Z	Total	Full CI	Exp [a]
DZV	SD	1.199	0.947	2.146	2.428	1.82(5)
	SD(T*)	1.262	0.993	2.255		
cc-pVDZ	SD	0.930	0.734	1.663		
	SD(T*)	1.026	0.979	2.005		
cc-pVTZ	SD	0.970	0.767	1.737		
	SD(T*)	1.051	0.822	1.873		
aug-cc-pVDZ	SD	0.615	0.486	1.101		
	SD(T*)	0.653	0.520	1.173		

Results in au, [a] see Ref.[124]

4.3.6 NH_2 radical

The Λ-FSMRCCSD(T*) method discussed above is used to study the ground state dipole moment of an important doublet radical NH_2. We performed the calculations using four different basis, DZV, cc-pVDZ, cc-pVTZ and aug-cc-pVDZ. The dipole moments obtained are presented in Table-4.6. We compared our results with experimental dipole moment of NH_2 radical [124]. We observed that for cc-pVDZ and cc-pVTZ basis results are better with Λ-FSMRCCSD(T*) than Λ-FSMRCCSD and close to experimental value. For DZV basis set the dipole moment is away from experimental value. We performed FCI calculation using this basis and we observed that the dipole moment with triple correction is close to FCI value(2.428 *debye*). The Λ-FSMRCCSD dipole moment is away from the FCI in this case.

In the case of aug-cc-pVDZ basis, as can be seen that the Λ-FSMRCCSD(T*) dipole moment is quite off from the experimental value. However, the results improve with triples than Λ-FSMRCCSD. Thus all the results emphasize the importance of triples for the accurate calculation of the dipole moment of the doublet radicals.

Table 4.7: Dipole moments of ClO radical in Debye

BASIS	Λ-FSMRCC		ROHF Non-relaxed[b]		ROHF Relaxed[b]	
	CCSD	CCSD(T*)	CCSD	CCSD(T*)	CCSD	CCSD(T*)
cc-pVDZ	1.051	1.418	1.160	1.166	1.131	1.153
cc-pVTZ	1.081	1.147	1.148	1.152	1.112	1.150
Exp						1.297 D
MRCI						1.275 D

[a] Cl-O bond distance is 3.1898 Bohr

[b] Obtained from ACES II

Table 4.8: Dipole moments of SF radical in Debye

BASIS	Λ-FSMRCC		ROHF Non-relaxed[b]		ROHF Relaxed[b]	
	CCSD	CCSD(T*)	CCSD	CCSD(T*)	CCSD	CCSD(T*)
cc-pVDZ	1.027	1.127	1.046	1.049	1.128	1.062
cc-pVTZ	0.892	1.064	0.895	0.878	0.895	0.878
Exp						0.87±0.05 D
CISD						1.106 D
CEPA-3(SD)						0.968 D

[a] S-F bond distance is $1.600575\AA$

[b] Obtained from ACES II

4.4 ClO and SF radicals

The dipole moment values for the ClO radical in Table-4.7, shows that the inclusion of partial triples i.e. Λ-FSMRCCSD(T*) converge the dipole moment values toward the experimental value, hence the inclusion of triples lead to more accurate results. Even though in case of the cc-pVDZ basis the triples correction goes beyond the predicted experimental value, its basic trend is in the right direction. ROHF also predicts the same trend in the triples correction. On the other hand, in case of the SF radical in Table-4.8, the CCSD value of 0.892D is already in good agreement with the experimental value of 0.87D. On including the partial triples it overestimates the dipole moment value to 1.064D. The triples correction in the ROHF calculation is seen to match fairly well with the predicted experimental dipole moment. However, the CISD and CEPA-3(SD) results are in better agreement with that of Λ-FSMRCCSD(T*). In case of the SF radical, it is seen that the ROHF and FSMRCC triples addition follow opposite trend. A probable reason could be the way, the effect of triples have been implemented in both the methods and the different manner in which the dynamical correlation has been taken into account.

4.5 Conclusions

In this chapter we presented the implementation and the results for the recently developed Lagrange based Fock-space multi-reference coupled cluster response approach with the inclusion of partial triples for electric properties of the doublet radicals. The results for the $\dot{O}H$, $\dot{C}H$ and NH_2 radical indicate that the Λ-FSMRCCSD(T*) perform better than Λ-FSMRCCSD and tend towards FCI. In particular, when the dipole moments of the Λ-FSMRCCSD and Λ-FSMRCCSD(T*) are compared at the $1.5R_e$ for the CH radical, we can observe that the inclusion of triples leads to more accurate results than the Λ-FSMRCCSD results. At stretched geometries, where the multi-reference description is required, inclusion of the triples provides better results. From the dipole moment of OH radical using cc-pVDZ, TZ, QZ basis sets, it is observed that at the Λ-FSMRCCSD level dipole moment saturates at 0.645 au whereas with the inclusion of triples it is 0.684 au which tends to the FCI dipole moment of 0.663 au. Though it is slightly over estimated, compared to the FCI it gives qualitatively correct trend. Also, the non-relaxed EOMCCSD shows dipole moment of 0.639 au which is closer to the Λ-FSMRCCSD value. The results of the analytic Λ-FSMRCCSD(T*) are compared with the finite field dipole moments for OOH and HCOO molecules. In both the cases, it is observed that the analytic Λ-FSMRCCSD(T*) shows qualitatively correct trend as does the finite field dipole moment. However, it should be mentioned here that the finite field method has explicit relaxation through the orbital rotation whereas the analytic method implemented does not include the explicit relaxation effects. The calculations are performed for CN radical using cc-pVDZ and aug-cc-pVDZ basis sets. Augmented basis set helps to get the results closer to the basis set limit. Inclusion of the non-iterative triples improves dipole moment by about 9%. The inclusion of the triples indicates the dipole moment closer to the experimental as well as basis set limit value. Another radical where we have analysed the importance of triples excitation is PO. We observe that the triples excitation found to improve the result for cc-pVDZ basis. ROHF based CCSD and CCSD(T) calculations are performed to analyse the way triples improve the dipole moment for CN and PO radicals. It has been observed that the way the triples contributes to dipole moment is opposite to that of the FSMRCC method. This can be due to the different way the triples are taken in FSMRCCSD(T*) method and the different treatment of the dynamic correlation. Thus, all the results emphasize the importance of triples for the accurate calculation of the dipole moment for the doublet radicals.

References

[1] J. Cizek, *Adv. Chem. Phys.* **14**, 35 (1969).

[2] J. Cizek, *J. Chem. Phys.* **45**, 4256 (1966).

[3] J. Paldus, J. Cizek and I. Shavitt *Phys. Rev. A* **5**, 50 (1972).

[4] R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).

[5] F. Coester, *Nucl. Phys.* **1**, 421 (1958).

[6] H. Kummel, *Nucl. Phys.* **17**, 477 (1960).

[7] R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Vol. 2, pp. 1047.

[8] R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht, The Netherlands, 1986), pp. 3561.

[9] L. Adamowicz, W. D. Laidig and R. J. Bartlett, *Int. J. Quantum Chem.* **18**, 245 (1984).

[10] A. C. Scheiner, G. Scuseria,T. J. Lee, J. Rice and H. F. Schaefer III, *J. Chem. Phys.* **87**, 5361 (1987).

[11] F. Wang and J. Gauss, *J. Chem. Phys.* **129**, 174110 (2008).

[12] M. Kallay, J. Gauss and P. G. Szalay, *J. Chem. Phys.* **119**, 2991 (2003).

[13] H. J. Monkhorst, *Int. J. Quantum Chem.* **S11**, 421 (1977).

[14] E. A. Salter, G. Trucks and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).

[15] T. Helgaker and P. Jorgensen, *Adv. Quantum. Chem.* **19**, 183 (1988).

[16] O. Christiansen, A. Koch and P. Jorgensen, *Chem. Phys. Lett.* **243**, 409 (1995).

[17] H. Koch, O. Christiansen, P. Jorgensen, A. S. de Meras and T. Helgaker, *J. Chem. Phys.* **106**, 1808 (1997).

[18] M. Medved, M. Urban and J. Noga, *Theor. Chem. Acc.* **98**, 75 (1997).

[19] G. E. Scuseria and H. F. Schaefer III, *Chem. Phys. Lett.* **146**, 23 (1988).

[20] J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987).

[21] S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 5243 (1998).

[22] K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

[23] R. J. Bartlett, J. D. Watts, S. A. Kucharski and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).

[24] M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985).

[25] Y. J. Bomble, J. F. Stanton, M. Kallay and J. Gauss, *J. Chem. Phys.* **123**, 054101 (2005).

[26] M. Medved, M. Urban, V. Kello and G. H.F. Diercksen, *J. Mol. Struct.* THEOCHEM, **547**, 219 (2001).

[27] P. Piecuch and L. Adamowicz, *J. Chem. Phys.* **100**, 5857 (1994).

[28] N. Oliphant and L. Adamowicz, *J. Chem. Phys.* **94**, 1229 (1991).

[29] N. Oliphant and L. Adamowicz, *J. Chem. Phys.* **96**, 3739 (1992).

[30] K. B. Ghose, P. Piecuch, S. Pal and L. Adamowicz, *J. Chem. Phys.* **104**, 6582 (1996).

[31] L. Meissner, K. Jankowski and J. Wasilewski, *Int. J. Quantum Chem.* **34**, 535 (1988).

[32] V. Hurtubise and K. F. Freeds, *Adv. Chem. Phys.* **83**, 465 (1993).

[33] P. Durand and J. P. Malrieu, *Adv. Chem. Phys.* **67**, 321 (1987).

[34] S. Evangelisti, J. P. Daudey and J. P. Malrieu, *Phys. Rev. A* **35**, 4930 (1987).

[35] B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).

[36] J. Paldus, L. Pylypow and B. Jeziorski, in *Many-body Methods in Quantum Chemistry, Lecture Notes in Chemistry* edited by Kaldor, Vol. 52, pp.151 (1989).

[37] A. Balkova S. A. Kucharski, L. Meissner R. J. Bartlett, *J. Chem. Phys.* **95**, 4311 (1991).

[38] W. Kutzelnigg, *J. Chem. Phys.* **77**, 2081 (1982).

[39] D. Mukherjee, R. K. Moitre and A. Mukhopadhyay, *Mol. Phys.* **30**, 1861 (1975).

[40] D. Mukherjee, *Pramana* **12**, 203 (1979).

[41] D. Mukherjee and S. Pal, *Adv. Quantum Chem.* **20**, 292 (1989).

[42] I. Lindgren and D. Mukherjee, *Phys. Rep.* **151**, 93 (1987).

[43] M. Haque and U. Kaldor, *Chem. Phys. Lett.* **117**, 347 (1985).

[44] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha and D. Mukherjee, *J. Chem. Phys.* **88**, 4357 (1988).

[45] S. Chattopadhyay, U. S. Mahapatra, B. Datta and D. Mukherjee, *Chem. Phys. Lett.* **357**, 426 (2002).

[46] S. Chattopadhyay, U. S. Mahapatra and D. Mukherjee, *J.Chem. Phys.* **111** 3820 (1999).

[47] L. Meissner, *J. Chem. Phys.* **108**, 9227 (1998).

[48] L. Meissner, *Chem. Phys. Lett.* **255**, 244 (1996).

[49] A. Landau, E. Eliav, Y. Ishikawa and U. Kaldor, *J. Chem. Phys.* **121**, 6634 (2004).

[50] E. Eliav, A. Borschevsky, K. R. Shamasundar, S. Pal U. Kaldor, *Int. J. Quantum Chem.* **109**, 2909 (2009).

[51] J. Geertsen, M. Rittby and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989).

[52] J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).

[53] R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz, D. B. Boyd, (VCH, New York, 1994) Vol. 5, p. 65.

[54] P. A. Pieniazek, S. A. Arnstein, S. E. Bradforth, A. I. Krylov and C. D. Sherrill, *J. Chem. Phys.* **127**, 164110 (2007).

[55] M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995).

[56] K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **347**, 237 (2001).

[57] M. Wladyslawski and M. Nooijen, in *Low-lying potential energy surfaces*, ACS symposium series, edited by M. R. Hoffmann and K. G. Dyall (ACS, 2002) Vol. 828, pp.65.

[58] D. Mukherjee and P. K. Mukherjee, *Chem. Phys.* **39**, 325 (1979).

[59] H. Koch and P. Jorgensen, *J. Chem. Phys.* **93**, 3333 (1990).

[60] H. Koch, H. J. Aa.Jensen, P. Jorgensen and T. Helgaker, *J. Chem. Phys.* **93**, 3345 (1990).

[61] M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **106**, 6441 (1997).

[62] M. Nooijen and R. J. Bartlett, *J. Chem.Phys.* **106**, 6449 (1997).

[63] A. I. Krylov, *Chem. Phys. Lett.* **338**, 375 (2001).

[64] H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).

[65] M. Ehara and H. Nakatsuji, *J. Chem. Phys.* **99**, 1952 (1993).

[66] P. Piecuch, K. Kowalski, I. S. O. Pimienta and S. A Kucharski, in *Low-Lying Potential Energy Surfaces* (ACS Symposium Series.) edited by M.R. Hoffmann and K.G. Dyall (American Chemical Society, Washington, D.C, 2002) Vol. 828, pp. 31.

[67] P. Piecuch, K. Kowalski, I. S. O. Pimienta, P. D. Fan, M. Lodriguito, M. J. McGuire, S. A. Kucharski, T. Kus and M. Musial, *Theor. Chem. Acc.* **112**, 349 (2004).

[68] S. Pal, M. Rittby and R. J. Bartlett, *Chem. Phys. Lett.* **160**, 212 (1989).

[69] N. Vaval, K. B. Ghose, S. Pal and D. Mukherjee, *Chem. Phys. Lett.* **209**, 292 (1993).

[70] N. Vaval, S. Pal and D. Mukherjee, *Theor. Chem. Acc.* **99**, 100 (1998).

[71] M. Musial and R. J. Bartlett, *J. Chem. Phys.* **129**, 244111 (2008).

[72] M. Musial and R. J. Bartlett, *J. Chem. Phys.* **129**, 044101 (2008).

[73] K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 8490 (2000).

[74] P. A. Pieniazek, S. E. Bradforth and A. I. Krylov, *J. Chem. Phys.* **129**, 074104 (2008).

[75] M. Kallay and J. Gauss, *J. Chem. Phys.* **121**, 9257 (2004).

[76] M. Kamiya and S. Hirata, *J. Chem. Phys.* **125**, 074111 (2006).

[77] M. Musial, S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **118**, 1128 (2003).

[78] K. Kowalski and P. Piecuch, *J. Chem. Phys.* **116**, 7411 (2002).

[79] F. A. Evangelista, E. Prochnow, J. Gauss and H. F. Schaefer III, *J. Chem. Phys.* **132**, 074107 (2007).

[80] J. F. Stanton and J. Gauss, *Theor. Chim. Acta* **93**, 303 (1996).

[81] P. U. Manohar, J. F. Stanton and A. I. Krylov, *J. Chem. Phys.* **131**, 114112 (2009).

[82] K. Kowalski and P. Piecuch, *J. Phys. Chem.* **115**, 643 (2001).

[83] P. U. Manohar and A. I. Krylov, *J. Chem. Phys.* **129**, 194105 (2008).

[84] K. Kowalski and P. Piecuch, *J. Chem. Phys.* **115**, 2966 (2001).

[85] P. Jorgensen and J. Simons, in*Second Quantization Based Methods in Quantum Chemistry*, (Academic Press, New York, 1981).

[86] J. Olsen and P. Jorgensen, *J. Chem. Phys.* **82**, 3235 (1985).

[87] S. Pal, *Phys. Rev. A* **39**, 39 (1989).

[88] S. Pal, *Int. J. Quantum Chem.* **41**, 443 (1992).

[89] D. Ajitha and S. Pal, *J. Chem. Phys.* **114**, 3380 (2001).

[90] D. Ajitha, N. Vaval and S. Pal, *J. Chem. Phys.* **110**, 2316 (1999).

[91] K. R. Shamasundar and S. Pal, *J. Chem. Phys.* **114**, 1981 (2001).

[92] K. R. Shamasundar, S. Asokan and S. Pal, *J. Chem. Phys.* **120**, 6381 (2004).

[93] D. Theis, Y. G. Khait, S. Pal and M. R. Hoffmann, *Chem. Phys. Lett.* **487**, 116 (2010).

[94] P. Szalay, *Int. J. Quantum Chem.* **55**, 151 (1995).

[95] D. Ajitha and K. Hirao, *Chem. Phys. Lett.* **341**, 121 (2001).

[96] P. U. Manohar, N. Vaval and S. Pal, *J. Mol. Struct.* THEOCHEM, **768**, 91 (2006).

[97] P. U. Manohar and S. Pal, *Chem. Phys. Lett.* **438**, 321 (2007).

[98] A. Bag, P. U. Manohar, N. Vaval and S. Pal, *J. Chem. Phys.* **131**, 024102 (2009).

[99] O. Christiansen, P. Jorgensen and C. Hattig, *Int. J. Quantum Chem.* **68**, 1 (1998).

[100] J. F. Stanton, *J. Chem. Phys.* **99**, 8840 (1993).

[101] J. F. Stanton ans J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).

[102] J. F. Stanton and J. Gauss, *J. Chem. Phys.* **103**, 88931 (1995).

[103] M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **107**, 6812 (1997).

[104] S. R. Gwaltney, Bartlett, R. J.; Nooijen, M. *J. Chem. Phys.* **111**, 58 (1999).

[105] S. V. Levchenko, T. Wang and A. I. Kyrlov, *J. Chem. Phys.* **122**, 224106 (2005).

[106] G. E. Scuseria, *J. Chem. Phys.* **94**, 442 (1991).

[107] J. Gauss and J. F Stanton, *Chem. Phys. Lett.* **276**, 70 (1997).

[108] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **116**, 1773 (2002).

[109] M. E. Harding, T. Metzroth and J. Gauss, *J. Chem. Theory Comput.* **4**, 64 (2008)

[110] K. L. Bak, J. Gauss, T. Helgaker, P. Jorgensen and J. Olsen, *Chem. Phys. Lett.* **319**, 563 (2000).

[111] K. W. Sattelmeyer, J. F. Stanton, J. Olsen and J. Gauss, *Chem. Phys. Lett.* **347**, 499 (2001).

[112] Lindgren, I. *Int. J. Quantum Chem.* **S12**, 33 (1979).

[113] M. Kallay, J. Gauss and P. Szalay, *J. Chem. Phys.* **119**, 2991 (2003).

[114] P. Neogrady, M. Medved, I. Cernusak and M. Urban, *Mol. Phys.* **100**, 541 (2002).

[115] M. Urban, P. Neogrady, J. Raab and G. H. F. Diercksen, *Collect. Czech. Chem. Commun.* **63**, 1409 (1998).

[116] R. Thomson and F. F. Dalby, *Can. J. Phys.* **46**, 2815 (1968).

[117] S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

[118] T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).

[119] T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).

[120] A. J. Sadlej, *Theor. Chim. Acta.* **79**, 123 (1991).

[121] D. H. Phekps and F. W. Dalby, *Phys. Rev. Lett.* **16**, 3 (1966).

[122] H. Kanata, S. Yamamoto, S. Saito, *J. Mol. Spectroscopy* **131**, 89 (1988).

[123] ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: J.F. Stanton, J. Gauss, S.A. Perera, J.D. Watts, A.D. Yau, M. Nooijen, N. Oliphant, P.G. Szalay, W.J. Lauderdale, S.R. Gwaltney, S. Beck, A. Balkova, D.E. Bernholdt, K.K. Baeck, P. Rozyczko, H. Sekino, C. Huber, J. Pittner, W. Cencek, D. Taylor, and R.J. Bartlett. Integral packages included are VMOL (J. Almlof and P.R. Taylor); VPROPS (P. Taylor); ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jorgensen, J. Olsen, and P.R. Taylor); HONDO/GAMESS (M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery).

[124] J. M. Brown, S. W. Chalkley and F. D. Wayne, *Mol. Phys.* **38**, 1521 (1979).

Chapter 5

GIAO-ECC and Future aspects

In this chapter we present the implementation of the gauge including atomic orbital ansatz in extended coupled cluster method (GIAO-ECC) for the shielding constants. The preliminary results are presented for HF, BH and N_2 molecules. Along with this the future direction on the present thesis work is also presented.

5.1 Introduction

The main goal of this thesis is to develop coupled cluster based method to study molecular magnetic properties. Much of the interest in the field of molecular magnetic properties focuses on the parameters encountered in magnetic resonance [1, 2]. These parameters include nuclear magnetic resonance (NMR) shielding constants, gyromagnetic ratio or $g-$values, spin-spin coupling constants and hyperfine coupling constants. All these properties are second-order quantities. Among all these, the importance of the NMR shielding constants is wide spread due to its importance in the chemical applications. Generally, the magnetic properties evaluation is not so straightforward mainly because of two reasons [3]. First, due to the imaginary character of the magnetic perturbation magnetic properties cannot be treated in a trivial manner. Second difficulty in the accurate evaluation of molecular magnetic properties stems from the fact that, in general, the use of approximate wave functions leads to an unphysical dependence on the so called gauge origin of the magnetic vector potential A. The magnetic field B appears in the Hamiltonian in the form of the vector potential A whose origin is called gauge origin, which is not fixed. The results are independent of the gauge origin only when the complete basis sets are used. But, in most of the cases, we use finite basis for the calculation.

Various attempts have been employed at the SCF and correlated levels to eliminate this gauge dependence. However, computationally this approach is quite expensive, due to the basis set required for reasonably accurate results is quite big even for small molecules. Various other approaches have been extensively studied to eliminate the gauge-dependence of the magnetic properties by making use of field dependent orbitals. This includes the 'individual gauge for localized orbitals (IGLO)' method of Kutzelnigg [4], 'second-order polarization propagator approximation (SOPPA)' of Geertsen [5] and other approaches like local origin method (LORG) [6] and random phase approximation [7].

A satisfactory approach to treat gauge origin problem was proposed by London [8] imposing gauge-origin independence in his study of molecular diamagnetism by attaching field-dependent complex phase factor to the atomic orbitals (AO's). This method is known as *gauge-including atomic orbital (GIAO) ansatz*, widely used for NMR chemical shieldings [9–11]. The use of these orbitals for the calculation of NMR chemical shift via electron correlation is now widespread [12–18] and often preferred due to the more rapid convergence of the properties with respect to the size of basis employed.

These GIAO or London orbitals are used by Hameka for calculating the magnetic susceptibility and shielding constants of H_2 [9]. Ditchfield employed London orbitals in *ab initio* calculations of shielding constants [10]. The GIAO method has been incorporated at self-consistent field (GIAO-SCF) level by Wolinski et al. [19] and Haser et al. [20]. The electron correlation effects are important for the accurate prediction of nuclear magnetic shielding constants and chemical shifts. Gauss formulated and implemented GIAO in second order many-body perturbation theory (GIAO-MBPT(2)) [21] and Cybulski and Bishop presented conventional MBPT(2) calculations for chemical shifts and magnetic susceptibilities [22]. The electron correlation effects of the nuclear magnetic chemical shifts using GIAO-MBPT(3) are investigated by Gauss [23]. The multi-configuration level (GIAO-MCSCF) chemical shift calculations are carried out by Ruud et al. [24, 25]

Among the various methods, the coupled cluster (CC) method [26, 27] emerged as the most promising tool to treat electron correlation, due to its size-extensivity. In the single reference framework, the GIAO-CC is developed successfully by Gauss et al. at the singles and doubles (CCSD) [28] and triples level [29–31]. The CC calculations on NMR shielding have been very successful in achieving experimental accuracy especially when the partial triples are included [31].

Arponen and Bishop developed [32] the extended coupled cluster functional (ECC) which uses the bi-orthogonal vectors. Arponen showed that the special double linking structure of the energy functional leads to natural truncation of the series. However, the natural truncation of the series occurs at higher order and for the practical purpose needs to be truncated. Due to its double linking structure of the functional, the amplitude equations are connected even when truncated to a fixed power in number of cluster amplitudes. Variational nature of ECC enjoys the advantage of (2n+1)-rule. The shielding tensor is formally a second order property. The ECC method, with inbuilt (2n+1)-rule, takes care of second order property evaluation naturally. The ECC response approach is extensively used for the electric properties [33, 34]. However, not many reports on magnetic properties. Recently, ECC method is used for evaluating susceptibility [35] and chemical shielding tensors [36] with atom centered Gaussian orbitals. In this chapter, we present the first implementation of GIAO's in ECC method for shielding constants. In section 5.2, the GIAO-ECC theory and its implementation are presented. The results and conclusions are given.The future direction of this thesis work is outlined at the end of the chapter.

5.2 GIAO-ECC Theory

The work implemented in this section uses the GIAO's for ECC method. The GIAO ansatz for calculating NMR parameter uses the following field-dependent basis functions

$$\chi_\mu(B) = exp[-\frac{i}{2c}(B \times R_\mu).r]\chi_\mu(0) \tag{5.1}$$

where, $\chi_\mu(0)$ is the usual field-independent AO's, R_μ is their center and c is speed of light. The nuclear magnetic shielding tensor σ of a nucleus N is defined by the mixed second-order energy derivative with respect to the magnetic field B and nuclear magnetic moment m_N

$$\sigma^N_{ji}(SCF) = (\frac{d^2E_{(SCF)}}{dB_i dm_{Nj}}). \tag{5.2}$$

A general formula for σ^N can be obtained by first differentiating the energy E with respect to m_N

$$\frac{\partial E}{\partial m_{N_j}} = \sum_{\mu\nu} D^{(SCF)}_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial m_{N_j}} \tag{5.3}$$

where, $D_{\mu\nu}$ are elements of an effective one-particle density matrix and $h_{\mu\nu}$ the one-electron part of the Hamiltonian. The final expression for σ^N is obtained by differentiating eq.5.3 with respect to B

$$\sigma^N_{ji}(SCF) = \sum_{\mu\nu} D^{(SCF)}_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D^{(SCF)}_{\mu\nu}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}. \tag{5.4}$$

The labels μ, ν, ... mention the AO's. From the above expression, we can observe that the knowledge of both the unperturbed and perturbed one particle densities are needed for the evaluation of the shielding tensor.

In eq.5.4, the first term provides the diamagnetic contribution and part of the paramagnetic contribution to the shielding tensor. The second term provides exclusively the paramagnetic contribution to the shielding. The derivatives of the one-electron Hamiltonian integrals in eq. 5.4 includes the derivatives of h and contributions due to the derivatives of the AO basis functions with respect to the external field

$$\frac{\partial \langle \mu | h | \nu \rangle}{\partial B_i} = \langle \frac{\partial \chi_\mu}{\partial B_i} | h | \nu \rangle + \langle \mu | \frac{\partial h}{\partial B_i} | \nu \rangle + \langle \mu | h | \frac{\partial \chi_\nu}{\partial B_i} \rangle \tag{5.5}$$

with

$$\frac{\partial \chi_\mu}{\partial B_i} = -\frac{i}{2c} (R_\mu \times r)_j \chi_\mu(0) \tag{5.6}$$

The derivatives of the one-electron Hamiltonian h are defined as

$$\frac{\partial h}{\partial B_i} = -\frac{i}{2c} (r \times \nabla)_j \tag{5.7}$$

$$\frac{\partial h}{\partial m_{Nj}} = -\frac{[(r - R_N)\nabla]_j}{|r - R_N|^3} \tag{5.8}$$

and

$$\frac{\partial^2 h}{\partial B_i \partial m_{Nj}} = \frac{1}{2c^2} \frac{r.(r - R_N)\delta_{ij} - r_i (r - R_N)_j}{|r - R_N|^3} \tag{5.9}$$

where, R_N is the coordinates of the nucleus N.

The magnetic perturbation is imaginary in character, due to which the first derivative integrals are imaginary and therefore antisymmetric with respect to the bra-ket permutations. The second derivative integrals are real and have the same symmetry as the undifferentiated integrals, except that in the two-electron integrals we cannot permute the labels of each electron independently. The two-electron derivative integrals are antisymmetric only with respect to a simultaneous permutation of the two labels of each electron. The symmetry of two-electron derivative integrals in Mulliken notation is

$$(\mu\nu|\rho\sigma)^{(1)} = (\rho\sigma|\mu\nu)^{(1)} = -(\nu\mu|\sigma\rho)^{(1)} = -(\sigma\rho|\nu\mu)^{(1)}.$$

The symmetry of two-electron derivative integrals in Dirac notation is

$$\langle\mu\rho|\nu\sigma\rangle^{(1)} = \langle\rho\mu|\sigma\nu\rangle^{(1)} = -\langle\nu\sigma|\mu\rho\rangle^{(1)} = -\langle\sigma\nu|\rho\mu\rangle^{(1)}.$$

Therefore, the derivative two-electron integrals have a lower permutational symmetry than the corresponding undifferentiated integrals.

The density at SCF level is given by,

$$D^{(SCF)}_{\mu\nu} = \sum_{p,q} c^*_{\mu p} D_{pq} c_{\nu q}. \tag{5.10}$$

The density times the integral in eq.5.9 gives the diamagnetic part of the shielding. The density times the integral in eq.5.7 gives the part of paramagnetic shielding, which is coming from the derivative Hamiltonian. For obtaining another part of paramagnetic contribution, the derivative of the density is needed. The construction of the derivative density at the SCF level requires the derivative of the coefficients, which is obtained from the coupled-perturbed Hartree-Fock equations (CPHF). The derivative of density is defined as

$$\frac{\partial D_{\mu\nu(SCF)}}{\partial B_i} = \sum_p \sum_i (U^{B_i *}_{pi} c^*_{\mu p} c_{\nu i} + c^*_{\mu i} c_{\nu p} U^{B_i}_{pi}) \tag{5.11}$$

where, the MO coefficients are parameterized using $U^{B_i}_{pi}$'s

$$\frac{\partial c_{\mu p}}{\partial B_i} = \sum_q U^{B_i}_{pq} c_{\mu q}. \tag{5.12}$$

The occupied-virtual block U^{Bi}_{ai} is obtained as solution of the CPHF equations, while the occupied-occupied and virtual-virtual blocks are chosen though the overlap matrix i.e,

$$U^{Bi}_{ij} = -1/2 S^{Bi}_{ij} \tag{5.13}$$

and

$$U_{ab}^{Bi} = -1/2 S_{ab}^{Bi}. \tag{5.14}$$

Using this, the one-electron derivative density is constructed. The derivative of the density with field B and the angular momentum integral in eq.5.8 gives another part of shielding contribution.

In GIAO-ECC method, the form of energy functional in ECC method is

$$E_{(ECC)} = \langle \phi_0 | e^S (He^T)_L | \phi_0 \rangle_{DL} \tag{5.15}$$

where, *L* means linked and *DL* is double linked. In the presence of magnetic field perturbation (λ), the functional and the amplitudes t and s depends on the perturbation,

$$E(\lambda) = \langle \phi_0(\lambda) | e^{S(\lambda)} (H(\lambda) e^{T(\lambda)})_L | \phi_0(\lambda) \rangle_{DL} \tag{5.16}$$

The ECC shielding tensor is obtained by differentiating ECC energy with respect to B and m_N

$$\sigma_{ji}^N(ECC) = \sum_{\mu\nu} D_{\mu\nu}^{(ECC)} \frac{\partial^2 H_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}^{(ECC)}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}. \tag{5.17}$$

The $c_{\mu i}$'s are molecular orbital (MO) coefficients. The main difference between the GIAO-SCF and GIAO-ECC lies in the definition of the density matrix. In general, density D_{pq} is separated in to two parts. One is response of the amplitude part $D_{pq}^{(amp)}$ and the other is orbital relaxation effect from response of the orbitals $D_{pq}^{(orb)}$.

The amplitude part of the density is obtained by solving the ECC equations. The stationary equations resulting from the variation of the functional with respect to the cluster amplitudes are themselves connected. This yields the equations for the amplitudes of the cluster operators S and T, denoted as $s^{(0)}$ and $t^{(0)}$. The following sets of equations are solved to obtain the amplitudes

$$\frac{\partial E}{\partial t} = 0; \frac{\partial E}{\partial s} = 0. \tag{5.18}$$

The density at the ECC level is constructed using these s and t amplitudes. The occupied-occupied and virtual-virtual block of density is given as

$$D_{ij}^{(ECC)} = \sum_{a} t_i^a s_a^j + \sum_{k}\sum_{a,b} t_{ik}^{ab} s_{ab}^{jk} + \sum_{k}\sum_{a,b} t_{ik}^{ab} s_a^j s_b^k + \sum_{k}\sum_{a,b} t_i^a t_k^b s_{ab}^{jk} \tag{5.19}$$

and

$$D_{ab}^{(ECC)} = \sum_{i} t_i^b s_a^i + \sum_{c}\sum_{i,j} t_{ij}^{bc} s_{ac}^{ij} + \sum_{c}\sum_{i,j} t_{ij}^{ac} s_a^i s_c^j + \sum_{c}\sum_{i,j} t_i^b t_j^c s_{ac}^{ij} \tag{5.20}$$

The second derivative integrals $\partial^2 h_{\mu\nu}/\partial B_i \partial m_{Nj}$ are immediately multiplied with $D_{\mu\nu}^{ECC}$ to give the diamagnetic contribution of σ^d. The first derivative integral eq.5.7 multiplied with $D_{\mu\nu}^{ECC}$ to give a part of paramagnetic shielding tensor σ^p. This part is coming from the derivative of the Hamiltonian i.e kinetic energy term eq.1.108. We are adding it to paramagnetic part of the shielding tensor. The required integrals are extracted from the Hondoplus package of version-5 [37].

For obtaining the other part of σ^p, the derivative of the density at the ECC level is needed. Hence, the derivative of the amplitudes $s^{(1)}$ and $t^{(1)}$ are required. The cluster amplitudes of S and T operators as well as their derivative $S^{(1)}$ and $T^{(1)}$ operators are obtained using a stationary condition. To obtain the derivative amplitude equations, one makes the derivative energy functional $E^{(1)}$ stationary with respect to $s^{(0)}$ and $t^{(0)}$ amplitudes

$$\frac{\partial E^{(1)}}{\partial t^{(0)}} = 0; \frac{\partial E^{(1)}}{\partial s^{(0)}} = 0. \tag{5.21}$$

Because of the field dependence of the Hamiltonian in eq.5.16, the one, two- particles integrals and also the coefficients depend on the field. In $E^{(1)}$ the CPHF contribution is taken care. The amplitude contribution to the derivative density $D^{(1)(amp)}$ for occupied-occupied, virtual-virtual, occupied-virtual and virtual-occupied blocks are constructed using S, T, $S^{(1)}$ and $T^{(1)}$. The perturbed amplitude part of the density matrix $D^{(1)(amp)}$ at ECC level is obtained from the solution of CPHF-ECC equations. The perturbed off-diagonal part of the density i.e. occupied-virtual and virtual-occupied blocks contributes to orbital relaxation part $D^{(1)(orb)}$. The occupied-virtual and virtual-occupied blocks $D_{ia}^{(1)(ECC)}$ and $D_{ai}^{(1)(ECC)}$ are obtained by the solution of the first order Z-vector equations,

$$\sum_{me} D_{me}^{(1)(orb)}[2\langle ma|ei\rangle - \langle ma|ie\rangle + \delta_{im}\delta_{ea}(f_{ae} - f_{mi})] - D_{me}^{(1)}[2\langle ae|im\rangle - \langle ae|mi\rangle] = -X_{ia}, \tag{5.22}$$

$$\sum_{me} D_{em}^{(1)(orb)}[2\langle ie|am\rangle - \langle ie|ma\rangle + \delta_{im}\delta_{ea}(f_{ea} - f_{im})] - D_{em}^{(1)}[2\langle im|ae\rangle - \langle im|ea\rangle] = -X_{ai}, \tag{5.23}$$

where, f_{pq} are matrix elements of the Fock operator and $\langle pq|rs\rangle$ are two-electron integrals. The quantities X_{ia} and X_{ai} are interpreted as the gradients of the energy with respect to rotations amongst the molecular orbitals and are defined as

$$\begin{aligned} X_{ai}^{(1)} &= \sum_{mne}\Gamma^{ae}_{mn}(-2\langle ie|mn\rangle + \langle ie|nm\rangle) + 2\sum_{efm}\Gamma^{ef}_{im}\langle ef|am\rangle - \Gamma^{ef}_{mi}\langle ef|am\rangle \\ &\quad + \sum_{me} D_{me}(2\langle im|ae\rangle - \langle im|ea\rangle) + \sum_{me} D^{*}_{em}(2\langle ie|am\rangle - \langle ie|ma\rangle), \end{aligned} \tag{5.24}$$

$$\begin{aligned} X_{ia}^{(1)} &= \sum_{mef}\Gamma^{fe}_{im}(2\langle ma|ef\rangle - \langle ma|fe\rangle) + \sum_{mne}\langle mn|ie\rangle(-2\Gamma^{ae}_{mn} + \Gamma^{ae}_{nm}) \\ &\quad + \sum_{me} D_{me}(2\langle ma|ei\rangle - \langle ma|ie\rangle) + \sum_{me} D^{*}_{em}(2\langle ae|im\rangle - D^{*}_{em}\langle ae|mi\rangle). \end{aligned} \tag{5.25}$$

The total $D^{(1)(ECC)}$ is obtained by adding the amplitude derivative density part with orbital derivative density part

$$D^{(1)(ECC)} = D^{(1)(amp)} + D^{(1)(orb)} \tag{5.26}$$

Thus, the obtained $D^{(1)(ECC)}$ is multiplied by the angular momentum integrals to get the σ^{p} shielding tensor at the ECC level. The implemented GIAO-ECC ensures the results do not depend on the choice of the gauge origin.

Table 5.1: The calculated absolute shieldings (σ in ppm) using GIAO-ECC ansatz in cc-pVDZ basis

MOLECULE	ATOM	SCF^a	CCSD^a	ECC	EXPσ_0 ^{b}	EXPσ_e ^{c}	FCI ^{d}
HF	H	29.5	30.4	32.7	28.5 ± 0.2	29.2 ± 0.5	
	F	423.5	427.0	419.2	410 ± 6	419.7± 6	
BH	H	24.5	24.8	23.3			24.60
	B	-257.3	-167.3	-229.8			-170.08
N_2	N	-79.5	-22.0	-26.3	-61.6 ±0.5	-59.6 ±1.5	

[a] obtained using cfour program package
[b] The experimental σ_0 from Ref. [38] for HF, Ref. [39] for N_2
[c] σ_e using ro-vibrational corrections [38]
[d] Ref. [40]

5.3 Results and discussions

In this section the absolute shieldings, shielding anisotropy and the comparison of our methodology without GIAO is presented.

5.3.1 Absolute shieldings

The preliminary test results of GIAO-ECC shielding constants are presented for HF, BH and N_2 in Table 5.1. The cc-pVDZ basis is used for the calculations. For HF molecule the equilibrium bond distance of 0.9169 $\AA$ is chosen. The shielding obtained for H atom by GIAO-ECC method is 32.7 ppm. This is quite large compared to the experimental value without ro-vibrational corrections (28.5 ± 0.5) as well as with ro-vibrational corrections (29.2 ± 0.5) [38]. It is observed from the calculation that the correlation for H must be small, because SCF itself is able to predict the shielding closer that the experimental value. Further, the CCSD and ECC are overestimating the shielding for H atom. The shielding constant for F atom obtained by GIAO-ECC is 419.2 ppm. This is close to the experimental value with ro-vibrational corrections (419.7 $\pm$ 6 ppm). The CCSD and SCF shielding values are 427.0 ppm [38] and 423.5 ppm respectively. For F atom the importance of correlation is very clear from the values presented. The results shows that the CCSD is not improving towards the experimental value, but ECC does improve towards the experimental limit.

Our second case study is BH molecule. The B-H bond distance of 1.2328 $\AA$ is chosen. The GIAO-ECC shielding value is 23.3 ppm for H atom. The CCSD and SCF values for this atom are 24.8 and 24.5 ppm respectively. For B atom, we find that the GIAO-ECC shielding value is -229.8 ppm , whereas, the SCF and the CCSD shielding values are -257.3 and -167.3 ppm. The full CI (FCI) shielding constant [40] for B and H are -170.08 and 24.60 ppm respectively.

We also implemented our methodology to study the shielding value of multiple bonded system N_2 using cc-pVDZ basis. The N-N bond distance of 1.0943 $\AA$ is used. The GIAO-ECC shielding value is -26.3 ppm, whereas, the experimental value is -61.6 $\pm$ 0.5 ppm [39]. The SCF and CCSD values are -79.5 and -22.0 ppm respectively. The results indicate that for multiple bonded systems, the cc-pVDZ basis is not good enough to predict the shielding.

In Table 5.2 we presented the basis set convergence study of shielding constant for HF molecule. We started with DZ basis and added polarization functions for the construction of DZP basis. For constructing DZ+(2p,2d), we added 2p functions to H atom and 2d functions to F atom in DZ basis. Similarly, the TZ+(2p,2d) is also constructed. The polarization functions are given in appendix A. For H atom with DZ basis, the shielding constant obtained is 32.1 ppm. It can be seen from the results that, with the addition of p function, shielding constant for H atom is reduced to 29.8 ppm. However, with the addition of further p and d functions, the shielding of H is increased to 30.8ppm. Triple zeta basis reduced the value to 31.61 ppm. Here too, further addition of p and d

Table 5.2: GIAO-ECC shielding constants of H and F in HF (in *ppm*)

BASIS	H	F
DZ	32.1	368.9
DZP	29.8	411.20
DZ+(2p,2d) [a]	30.8	397.1
TZ	31.61	365.1
TZ+(2p,2d) [a]	33.1	412.3
Exp[b]	29.2±0.5	419 ±6

[a] Pople (2d,2p) polarization is taken.
[b] The experimental σ_0 obtained from Ref. [38].

functions to TZ, increases the values to 33.1 ppm, which is away from the experimental values of 29.2±0.5 ppm. Thus we see that shielding constant has a oscillatory behavior with increasing the basis set.

In the case of F also we observe oscillating behavior of shielding constant as we go from DZ, DZ+p and to DZ+(2p,2d) basis. From DZ to TZ basis, shielding constant is reduced from 368.9 ppm to 365.1 ppm. Further addition of 2p+2d function increases it to 412.3 ppm. Thus, we do not have any definite conclusion for the convergence of shielding constant, we plan to do more extensive study in the future.

5.3.2 The shielding anisotripies

The shielding anisotropies ($\Delta\sigma$) for HF in cc-PVDZ basis are presented in table 5.3. We observed that for H, the anisotropy by ECC is 16.7 ppm, whereas, the CCSD gives anisotropy value of 21.1 ppm. The anisotropy of F atom is 94.8 ppm by ECC. The anisotropy obtained by CCSD for this case is 82.2 ppm. The experimental value is 93.8

Table 5.3: The calculated shielding anisotropies ($\Delta\sigma$ in ppm) using GIAO-ECC ansatz in cc-pVDZ basis

MOLECULE	ATOM	SCF^d	CCSD^d	ECC	EXP
HF	H	21.9	21.1	16.7	
	F	88.1	82.2	94.8	93.8^a
BH	H	13.7	13.2	15.5	
	B	684.2	550.2	642.9	
N_2	N	627.8	542.7	534.0	601.3^b, 603 ±28^c

[a] Ref. [38]
[b] Ref. [41]
[c] Ref. [42]
[d] obtained using cfour program package

ppm [38]. We found satisfactory shielding and anisotropy value for F atom.

The anisotropy obtained by ECC for N atom in N_2 case is 534.0 ppm. The SCF and CCSD values are 627.8 and 542.7 ppm respectively. The experimental anisotropy in this case is 601.3 [41]/603 ±28[42]. For this system, the CCSD and ECC underestimates the anisotropy, when compared to experimental value. This may be due to the fact that the basis is not good for triply bonded system. For the case of H atom in BH molecule, the GIAO-ECC anisotropy is 15.5 ppm compared to the SCF value 13.7 ppm and the CCSD value 13.2 ppm. For the B atom in BH, the anisotropy is 642.9 ppm compared to the SCF value 627.8 ppm and CCSD value 542.7 ppm. Since, there is no benchmark is available for BH anisotropy, we cannot conclude its behavior with our methodology.

Table 5.4: The calculated absolute ECC shieldings in cc-pVDZ with and without GIAO ansatz

MOLECULE	ATOM	GAUSSIAN'S	GIAO ANSATZ	EXP[b]	FCI[c]
HF	F	391.5	419.2	419±6	
	H	28.6	32.7	29.2±0.5	
BH	H	25.9	23.3		24.60
	B	-72.4	-229.8		-170.08

[a] all results are in ppm

[b] σ_0 obtained from Ref. [38].

[c] Ref.[40]

5.3.3 Comparison of the ECC shieldings with and without GIAO ansatz

We compared the absolute shielding obtained using the standard atom centered Gaussian with our recently implemented GIAO-ECC methodology. The calculations are carried out using the cc-pVDZ basis. For the calculations without GIAO, the center of mass is chosen as the Gauge origin. The results are presented in Table-5.4. The results for H with and without GIAO in HF shows, the shielding value of 419.2 ppm and 391.5 ppm are obtained. With GIAO ansatz, the results are close to the experimental value of 419±6 ppm [38]. For H atom, the shielding with GIAO is 32.7 ppm, whereas, without GIAO it is 28.6 ppm. The experimental value for H is 29.2±0.5 ppm [38] . The another case study is BH molecule in cc-pVDZ basis. Here, The shielding tensor for H atom using GIAO ansatz is 23.3 ppm, whereas without GIAO is 25.9 ppm. The FCI value is 24.60 ppm [40]. For B atom, without GIAO, the shielding value is surprisingly low with this basis (-72.4 ppm), whereas in GIAO ansatz, the shielding tensor is -229.8 ppm. The

FCI value for B is -170.08 ppm [40]. This study actually proves the statements made in the chapter II, that larger basis sets and center of mass is the preferred choice for the calculations without GIAO.

5.4 Conclusion

In conclusion, the GIAO-ECC method has been implemented in this chapter. The code is tested for few molecular systems in cc-pVDZ basis. The results are compared with the SCF, CCSD and the experimental values. The results are quite satisfactory. Ideally, for getting better shieldings and anisotropies, one should go for larger basis sets. Particularly, a very good basis should be chosen for multiple bonded systems. The comparison of the ECC shielding with and without GIAO methodology is performed. The presented values prove the importance of GIAO ansatz for the shielding calculations. The results presented for HF, BH and N_2 in this chapter are only preliminary results. Because of the constraints in the software we are using for the integrals, currently, we are not able to include F functions. A more extensive study will be performed on this in future.

Future direction of the thesis

In this thesis, we studied the susceptibility and magnetic shielding by using the common Gauge origin with atom centered Gaussian orbitals. This has been quite satisfactory for small systems. To take care of the so called Gauge origin problem, magnetic shielding tensors using GIAO ansatz have been studied. To incorporate the importance of the higher order excitations in FSMRCC method, the partial triples have been done for dipole moments. However, the present thesis work put forth the following future research.

- The GIAO-ECC method presented in the above section can be used for the evaluation of magnetic susceptibilities.

- Properties other than NMR are less used and the development on these properties are current field. Methods to evaluate $g-$ tensors are less because of the less available methods for the study of open-shell properties. The $\Lambda-$FSMRCC method which have used for predicting open-shell susceptibilities can be used for $g-$tensors. The $g-$tensors is

  $$g = \frac{1}{\mu_B}(\frac{\partial^2 E}{\partial B \partial S})_{B;S=0}. \tag{5.27}$$

  The theoretical clue for the evaluation of $g-$tensors, as proposed by Gauss et. al [43], is

  $$g = g_e I + \Delta g_{pso} + \Delta g_{dso} + \Delta g_{rms} \tag{5.28}$$

  where, the $g-$tensors is split in to various components, like free electron value(g_e), paramagnetic spin-orbit (Δg_{pso}), diamagnetic spin-orbit (Δg_{dso}) and relativistic mass correction (Δg_{rms}) terms. The quantum chemical calculation of the electronic g-tensor requires the evaluation of one true second-order contribution (Δg_{pso}) and of two first-order contributions (Δg_{dso} and Δg_{rms}) for which the perturbed Hamiltonian is second order.

- In chapter-IV we studied triples correction to the first order properties. In the same spirit the inclusion of triples excitations can be pursued in FSMRCC for the calculation of the higher order properties. For getting the higher order property, say, polarizability or second order magnetic properties, the derivative of the amplitudes at the $T^{(0,0)}$ and $T^{(h,p)}$ level is needed. Since we have included triples excitation in $T^{(0,1)}$ and $T^{(1,0)}$ amplitudes, the excited state properties need only the triples contribution from $T^{(1,1)}$ sector.

References

[1] W. H. Flygare, *Molecular Structure and Dynamics*, (Prentice-Hall, Englewood Cliffs, 1978).

[2] W. Weltner, Jr, *Magnetic Atoms and Molecular*, (Dover, New York, 1989).

[3] W. Kutzelnigg, *J. Mol. Struct. (THEOCHEM)*, **202**, 11 (1989).

[4] C. van Wullen and W. Kutzelnigg, *Chem. Phys. Lett.* **205**, 563 (1993).

[5] J. Geertsen, *Chem. Phys. Lett.* **188**, 326 (1992).

[6] A. E. Hansen, T. D. Bouman, *J. Chem. Phys.* **82**, 5035 (1985).

[7] J. Geertsen, *J. Chem. Phys.* **90**, 4892 (1989).

[8] F. London, *J. Phys. Radium* **8**, 397 (1937).

[9] H. Hameka, *Mol. Phys.* **1**, 203 (1958); *Z. Naturforsch. A: Phys. Sci.* **14**, 599 (1959); *Rev. Mod. Phys.* **34**, 87 (1962).

[10] R. Ditchfield, *J. Chem. Phys.* **56**, 5688 (1972); R. Ditchfield, *Mol. Phys.* **27**, 789 (1974).

[11] F. R. Prado, C. Giessner-Prettre, J. P. Daudey, A. Pullmann, F. Young, J. F. Hinton, and D. Harpool, *J. Magn. Reson.* **37**, 431 (1980); H. Fukui, K. Miura, H. Yamazaki, and T. Nosaka, *J. Chem. Phys.* **82**, 1410 (1985).

[12] T. Helgaker and P. Jorgensen, *J. Chem. Phys.* **95**, 2595 (1991).

[13] J. Gauss, *Chem. Phys. Lett.* **191**, 614 (1992); J. Gauss, *J. Chem. Phys.* **99**, 3629 (1993); J. Gauss, *Chem. Phys. Lett.* **229**, 198 (1994).

[14] H. Fukui, T. Baba, H. Matsuda, and K. Miura, *J. Chem. Phys.* **100**, 6609 (1994).

[15] K. Ruud, T. Helgaker, R. Kobayashi, P. Jorgensen, K. L. Bak, and H. J. Aa. Jensen, *J. Chem. Phys.* **100**, 8178 (1994).

[16] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **102**, 251 (1995); J. Gauss and J. F. Stanton, *J. Chem. Phys.* **103**, 3561 (1995).

[17] O. Christiansen, J. Gauss, and J. F. Stanton, *Chem. Phys. Lett. 266*, **53** (1997).

[18] G. Schreckenbach and T. Ziegler, *J. Phys. Chem.* **99**, 606 (1995); G. Rauhut, S. Puyear, K. Wolinski, and P. Pulay, *J. Phys. Chem.* **100**, 6310 (1996); J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, *J. Chem. Phys.* **104**, 5497 (1996); A. M. Lee, N. C. Handy, and S. M. Colwell, *J. Chem. Phys.* **103**, 10095 (1995); T. Helgaker, P. J. Wilson, R. D. Amos, and N. C. Handy, *J. Chem. Phys.* **113**, 2983 (2000).

[19] K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990); P. Pulay, *Adv. Chem. Phys.* **69**, 241 (1987).

[20] M. Haser, R. Ahrichs, H. P. Baron, P. Weiss and H. Horn, *Theor. Chim. Acta* **83**, 455 (1992); R. Ahrichs, M. Bar, M. Haser, H. Horn and C. Kolmol, *Chem. Phys. Lett.* **162**, 165 (1989).

[21] J. Gauus, *Chem. Phys. Lett.* **191**, 614 (1992).

[22] S. M. Cybulski and D. M. Bishop, *J. Chem. Phys.* **98**, 8057 (1993).

[23] J. Gauss, *J. Chem. Phys. 99*, 3629 (1993).

[24] K. Ruud, T. Helgaker, R. Kobayashi, P. Jorgensen, K. L. Bak, and H. J. Aa. Jensen, *J. Chem. Phys.* **100**, 8178 (1994).

[25] T. Helgaker, M. Jaszuski and K. Ruud, *Chem. Rev.* **99**, 293 (1999).

[26] J. Cizek, *J. Chem. Phys.* **45**, 4256 (1996); J. Cizek, *Adv. Chem. Phys.* **14**, 35 (1969).

[27] F. Coester, *Nucl. Phys.* **7**, 421 (1958). F. Coester and H. Kummel, *Nucl. Phys.* **17**, 477 (1960).

[28] J. Gauss, *J. Chem. Phys.* **116**, 4773 (2002).

[29] J. Gauss and J. F. Stanton, *Phys. Chem. Chem. Phys.* **2**, 2047 (2000).

[30] J. Gauss, *J. Chem. Phys.* **116**, 4773 (2002).

[31] J. Gauss and J. F. Stanton, *J. Chem. Phys.* **104**, 2574 (1996).

[32] J. Arponen, *Annals. Phys.* **151**, 311 (1983); J. Arponen and R. F. Bishop and E. Pajanne, *Phys. Rev. A* **36**, 2519 (1987); J. Arponen, R. F. Bishop and E. Pajanne, *Phys. Rev. A* **36**, 2539 (1987).

[33] N. Vaval, K. B. Ghose and P. G. Nair and S. Pal, *Prc. Ind. Acad. Sci.* **106**, 387 (1994); N. Vaval, K. B. Ghose and S. Pal, *J. Chem. Phys.* **101**, 4914 (1994); N. Vaval, A. B. Kumar and S. Pal, *Int. J. Mol. Sci.* **2**, 89 (2001); N. Vaval and S. Pal, *Phys. Rev. A* **54**, 250 (1996).

[34] R. J. Bartlett, S. A. Kucharshi and J. Noga, *Chem. Phys. Lett.* **155**, 133 (1989); R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988).

[35] P. U. Manohar, N. Vaval and S. Pal, *Chem. Phys. Lett.* **387**, 442 (2004).

[36] L. Ravichandran, S. Joshi and N. Vaval, *Recent Adavances in Spectroscopy; Theoritical, Astrophysical and Expermental Perspectives, Astrophysics and Space Science Proceedings* edited by R. K. Chaudhuri, M. V. Mekkaden, A. V. Raveendran and A. Satya Narayanan, (Springer-Verlag, Berlin, 2010).

[37] M. Dupuis, A. Marquez, and E.R. Davidson, HONDO 99.6, 1999, based on HONDO 95.3, M. Dupuis, A. Marquez, and E.R. Davidson, *Quantum Chemistry Program Exchange (QCPE)*, Indiana University, Bloomington, In 47405.

[38] D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.* **48**, 4142 (1968).

[39] C. J. Jameson, A. K. Jameson, S. Wille and P. M. Burrell, *J. Chem. Phys.* **74**, 853 (1981).

[40] J. Gauss and K. Ruud, *Int. J. Quantum Chem. Symp.* **29**, 437 (1995).

[41] C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell and J. Mason, *J. Chem. Phys.* **74**, 81 (1981).

[42] L. M. Ishol and T. A. Scott, *J. Magn. Reson.* **27**, 23 (1977).

[43] J. Gauss, M. Kallay and F. Neese, *J. Chem. Phys.* **113**, 11541 (2009).

“We ought to consider the present state of this universe as the effects of its previous state and as the cause of that which is to follow. An intelligence that, at a given instant, could comprehend all the forces by which nature is animated and the respective situation of the beings that make it up, if moreover it were vast enough to submit these data to analysis, would encompass in the same formula the movements of the greatest bodies of the universe and those of the lightest atoms. For such an intelligence nothing would be uncertain, and the future, like the past, would be open to its eyes.”

- Pierre Simon De Laplace

(1814)

The Geometries

All the geometries reported here are in atomic units.

Molecule	Atom	X	Y	Z
OH	H	0.00000	0.00000	1.85104
	O	0.00000	0.00000	0.00000
OOH	H	-1.60075	-1.66668	0.00000
	O_1	1.27888	-0.01807	0.00000
	O_2	-1.17802	0.12308	0.00000
HCOO	H	0.00000	2.96725	0.00000
	C	0.00000	0.88855	0.00000
	O_1	-1.98007	-0.42700	0.00000
	O_2	1.98007	-0.42700	0.00000

Pople polarization functions

(p,d)

```
HYDROGEN
    P       1
            1   1.000000    1.000000

 FLOURINE
    P       1
            1  0.0740000    1.000000
    D       1
            1  0.9000000    1.000000
```

(2p,2d)

```
HYDROGEN
    P       1
            1   1.500000    1.000000
    P       1
            1   0.375000    1.000000

 FLOURINE
    D       1
            1  2.3960000    1.000000
    D       1
            1  0.8750000    1.000000
```