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

Lalitha Ravichandran, Nayana Vaval and Sourav Pal*

Physical Chemistry Division, National Chemical Laboratory, Pune -411008, India

Abstract

In this paper, 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 and PO radicals.

* s.pal@ncl.res.in
I. INTRODUCTION

Single reference coupled cluster (SRCC)\textsuperscript{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\textsuperscript{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\textsuperscript{19–24} for energy. 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\textsuperscript{21} for energy. The perturbative treatment of the quadruple excitations has also been attempted\textsuperscript{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\textsuperscript{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\textsuperscript{27,28} have been considered for quasi-degenerate cases\textsuperscript{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\textsuperscript{31}. Among the multi-reference methods, the effective Hamiltonian\textsuperscript{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\textsuperscript{35–37} and Fock-space (FS) MRCC\textsuperscript{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\textsuperscript{31} and the situations involving curve crossing. However for PES, state selective MRCC method developed by Mukherjee and co-workers\textsuperscript{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\textsuperscript{38}, Mukherjee\textsuperscript{39–41} and Lindgren\textsuperscript{42}, and applications to atoms were made by Kaldor and co-workers\textsuperscript{43}. The FSMRCC applications to molecules
were performed by Pal et al\textsuperscript{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\textsuperscript{33} based formulation both in Fock space\textsuperscript{47,48} as well as Hilbert space\textsuperscript{49,50}.

The important feature of both the multi-reference formulations is their size-extensivity. On the other hand, in equation of motion(EOMCC)\textsuperscript{51–57} or linear response CC(CCLR) method\textsuperscript{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\textsuperscript{53,54}, electron attached\textsuperscript{55} and excited state\textsuperscript{51} problems. The similarity transformed EOMCC method (STEOMCC) which is size extensive was developed by Nooijen and co-workers\textsuperscript{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\textsuperscript{61}. The spin-flip EOMCC method has also been introduced as a clever way to describe the multi reference states\textsuperscript{63}. The symmetry-adapted cluster expansion configuration interaction (SACCI)\textsuperscript{64,65} and method of moments coupled cluster (MMCC)\textsuperscript{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\textsuperscript{68–71} MRCC. Pal and co-workers included non-iterative triples for ionization potential\textsuperscript{68,69} and excitation energies\textsuperscript{70}, within Fock space MRCC scheme and Bartlett and co-workers included full triples correction for excitation energies\textsuperscript{71}. The full triples correction to excitation energies in intermediate Hamiltonian Fock space CC has been pursued currently by Musial et al\textsuperscript{72}. The inclusion of iterative and non-iterative triples in EOMCC\textsuperscript{73–77} and state-selective approaches\textsuperscript{78,79} for energy calculations has also been attempted. The perturbative triples corrections to EOM-IP-CCSD was introduced by Stanton and Gauss\textsuperscript{80}. Recently, perturbative triples correction to EOM-EA-CCSD has been done by Manohar et al\textsuperscript{81}. The selected set of triples defined through the active orbitals in EOMCCSD (EOM-CCSDt) has also been attempted\textsuperscript{82}. Recently, Krylov et al. employed the non-iterative perturbative triples correction to spin flip EOMCC (SF-EOMCC) method for excitation
energies. The non-iterative energy corrections to MMCC for excitation energy has been achieved by Piecuch et al.

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. Along lines of non variational CC (NVCC) response approach of Monkhorst, a response approach was developed for Fock-space MRCC formulation and implemented for FSM-RCC 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 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 (A-MRCC). This approach was formulated for the Hilbert space as well as Fock space 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. Szalay 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. A-FSMRCC method was successfully implemented for the dipole moment and polarizability of the doublet radicals as well as excited states of molecules. The initial implementation was within singles and doubles (A-FSMRCCSD) approximation. Response theory for molecular properties has been pursued by Jorgensen et. al in LR-CC formalism. Theory for analytic energy derivatives in EOMCC method was proposed by Stanton and implemented by Stanton and Gauss. Nooijen and co-workers implemented gradients in STEOMCC, using Lagrange multipliers. Analytic gradients for SF-EOMCC model at singles and doubles level has also been proposed recently.

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\textsuperscript{106,107}. Gauss et al\textsuperscript{108} implemented analytical gradients for the CCSDT model. Recently, parallel calculation of CCSD(T) has been achieved for analytic first and second derivatives\textsuperscript{109}. In the context of SRCC, the importance of triples to the dipole moment has also been analyzed\textsuperscript{110}. Triples excitation in linear response CC method for excited state properties were studied iteratively\textsuperscript{111}.

In this paper, 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. In Sec. II, we start with a brief review of the FSMRCC method and Lagrange approach for energy derivatives. Sec. III deals with the perturbative analysis of triples amplitude in Λ-FSMRCC for energy and dipole moment. We discuss the results in Sec. IV.

II. REVIEW OF FSMRCC

The FSMRCC theory\textsuperscript{38,40–42,44} and the Lagrangian formulation within FSMRCC have been described in detail in various articles\textsuperscript{92,96,97}. However, for the completeness of the paper, 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

\[
|\Psi^{(m,n)}_{(0)\mu}\rangle = \sum_i C^{(m,n)}_{\mu i} |\Phi^{(m,n)}_i\rangle
\]  

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

\[
|\Psi^{(m,n)}_{\mu}\rangle = \Omega |\Psi^{(m,n)}_{(0)\mu}\rangle
\]  

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

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

(3)

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

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

(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 Schrödinger equation for the quasi-degenerate states as

$$H |\Psi^{(0,1)}_{\mu} > = E_{\mu} |\Psi^{(0,1)}_{\mu} >$$

which leads to

$$H \Omega(\sum_{i} C^{(0,1)}_{\mu} |\Phi^{(0,1)}_{i} >) = E_{\mu} \Omega(\sum_{i} C^{(0,1)}_{\mu} |\Phi^{(0,1)}_{i} >)$$

(5)

Projection operator for model space is defined as

$$P^{(0,1)} = \sum_{i} |\Phi^{(0,1)}_{i} > < \Phi^{(0,1)}_{i} |$$

(6)

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

$$P^{(0,1)} (H \Omega - \Omega H_{eff}^{(0,1)}) P^{(0,1)} = 0$$

$$Q^{(0,1)} (H \Omega - \Omega H_{eff}^{(0,1)}) P^{(0,1)} = 0$$

(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\textsuperscript{94} 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 $H_{\text{eff}}$ 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 $\mu^{th}$ state.

$$\Im = \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} (H_{\text{eff}})_{ij}^{(0,1)} C^{(0,1)}_{\mu j}$$

$$+ \sum_{ji} \Lambda^{(0,1)}_{ji} < \phi^{(0,1)}_j | (H\Omega - \Omega H_{\text{eff}}) | \phi^{(0,1)}_i >$$

$$+ \sum_{\alpha} \sum_{i} \Lambda^{(0,1)}_{\alpha i} < \phi^{(0,1)}_i | (H\Omega - \Omega H_{\text{eff}}) | \phi^{(0,1)}_{\alpha} >$$

$$+ \sum_{ji} \Lambda^{(0,0)}_{ji} < \phi^{(0,0)}_j | H\Omega | \phi^{(0,0)}_i > + \sum_{\alpha} \sum_{i} \Lambda^{(0,0)}_{\alpha i} < \phi^{(0,0)}_i | H\Omega | \phi^{(0,0)}_{\alpha} >$$

$$- E_{\mu} \left( \sum_{ij} \tilde{C}^{(0,1)}_{\mu i} C^{(0,1)}_{\mu j} - 1 \right)$$

(8)

Where $\phi^{(0,1)}_i$, $\phi^{(0,1)}_j$, $\phi^{(0,0)}_i$ and $\phi^{(0,0)}_j$ are the functions in P space. $\phi^{(0,1)}_\alpha$ and $\phi^{(0,0)}_\alpha$ are functions in Q space. $\Lambda^{(0,1)}_{ji}$ and $\Lambda^{(0,0)}_{ji}$ are the Lagrange multipliers defined within P-space for the (0,1) and (0,0) sectors respectively. Similarly, $\Lambda^{(0,1)}_{\alpha i}$ and $\Lambda^{(0,0)}_{\alpha i}$ 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 of which the closed part of the Lagrangian multipliers vanishes. Thus, the second
and fourth terms of eq (8) vanish, simplifying Lagrangian to:

\[ \Im = \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{\text{eff}})_{ij}^{(0,1)} C_{\mu j}^{(0,1)} + \sum_{\alpha} \sum_{i} A_{\alpha i}^{(0,1)} < \phi_{\alpha}^{(0,1)} | (H\Omega - \Omega H_{\text{eff}}) | \phi_{i}^{(0,1)} > + \sum_{\alpha} \sum_{i} A_{\alpha i}^{(0,0)} < \phi_{\alpha}^{(0,0)} | H\Omega | \phi_{i}^{(0,0)} > - E_{\mu} \left( \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{\mu j}^{(0,1)} - 1 \right) \]  

(9)

Differentiation of eq 9 with respect to \( \Lambda \) results in expression for cluster amplitudes, i.e., the Bloch equation. Differentiation of eq 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 \( \Lambda \) amplitude equation. The \( \Lambda \) equations are however coupled with those of the cluster amplitudes \( T \). In the presence of the external field, the Lagrangian and the parameters \( H_{\text{eff}}, C, \tilde{C}, E, \Omega, \Lambda \) 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 94 and 95 under singles and doubles approximation. Along similar line, the one valence particle problem can be solved.

III. IMPLEMENTATION OF THE PARTIAL TRIPLES IN \( \Lambda \)-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 \( \Lambda \)-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 paper 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 \( VT_3^{(0,0)} \) 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 \( \tilde{H} \) given by \((\tilde{H} = exp(-T^{(0,0)})Hexp(T^{(0,0)}))\) and truncate up to one(\( \tilde{F} \)), two(\( \tilde{V} \)) and three body(\( \tilde{W} \)) parts. For the construction of \( \tilde{H} \) we use CCSD approximation without including the amplitudes of triples i.e. \( T_3^{(0,0)} \). \( H_{eff} \) under this approximation is

\[
H_{eff} = P^{(0,1)}(\tilde{F} + \tilde{F}T_1^{(0,1)} + \tilde{V}T_2^{(0,1)} + \tilde{F}T_2^{(0,1)} + \tilde{V}T_3^{(0,1)} - T_1^{(0,1)}H_{eff})P^{(0,1)} = 0 \quad \text{(10)}
\]

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

\[
Q_1^{(0,1)}(\tilde{F} + \tilde{F}T_1^{(0,1)} + \tilde{V}T_2^{(0,1)} + \tilde{F}T_2^{(0,1)} + \tilde{V}T_3^{(0,1)} - T_1^{(0,1)}H_{eff})P^{(0,1)} = 0 \quad \text{(11)}
\]

\[
Q_2^{(0,1)}(\tilde{V} + \tilde{F}T_2^{(0,1)} + \tilde{V}T_1^{(0,1)} + \tilde{V}T_2^{(0,1)} + \tilde{W}T_2^{(0,1)} + \tilde{V}T_3^{(0,1)} + \tilde{F}T_3^{(0,1)} - T_2^{(0,1)}H_{eff})P^{(0,1)} = 0 \quad \text{(12)}
\]

\[
Q_3^{(0,1)}(\tilde{W} + \tilde{W}T_2^{(0,1)} + \tilde{F}T_3^{(0,1)} + \tilde{V}T_2^{(0,1)} - T_3^{(0,1)}H_{eff})P^{(0,1)} = 0 \quad \text{(13)}
\]

It can be seen that \( \tilde{V}T_3^{(0,1)} \) is the only term contributing to the singles and doubles amplitude equation along with \( H_{eff} \). It is easy to see that \( \tilde{W} \) cannot contribute to \( H_{eff} \). The equations 11 and 12 are first solved fully excluding the terms which involve \( T_3^{(0,1)} \) amplitude, which is CCSD approximation . Using these amplitudes eq 13 is solved non-iteratively. In eq 13, we want to be accurate up to third order. Hence we include in the term \( T_3^{(0,1)}H_{eff} \) only \( T_3^{(0,1)} \tilde{F} \).

After solving \( T_3^{(0,1)} \), we again solve the equations 11 and 12 iteratively. Here the effect of \( T_3^{(0,1)} \) appears via \( \tilde{V}T_3^{(0,1)} \) and \( \tilde{F}T_3^{(0,1)} \).
We now consider the triples correction to the \( \Lambda \) amplitudes and then to the overall dipole moment. The \( \Lambda \) equations are like the conjugates of the \( T \) amplitude equations and hence the terms in \( T \) equations appear in \( \Lambda \) 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 \( \Lambda \) equations.

First, the \( \Lambda \) amplitudes in singles and doubles approximation are solved iteratively for both \((0,1)\) and \((0,0)\) sector. With these \( \Lambda \) 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,

\[
\mathcal{\mathcal{Z}} = SD + \bar{V}T_3^{(0,1)}C\hat{C} + \Lambda_3^{(0,1)}\bar{V}T_2^{(0,1)} + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,1)} + \Lambda_3^{(0,1)}\bar{F}T_3^{(0,1)} + \Lambda_2^{(0,1)}\bar{V}T_3^{(0,1)} \\
+ \Lambda_2^{(0,1)}\bar{F}T_3^{(0,1)} - \Lambda_2^{(0,1)}T_2^{(0,1)}(\bar{V}T_3^{(0,1)}) + \Lambda_1^{(0,1)}\bar{V}T_3^{(0,1)} \\
+ \Lambda_3^{(0,0)}\bar{V}T_2^{(0,0)} + \Lambda_2^{(0,0)}\bar{V}T_3^{(0,0)} + \Lambda_1^{(0,0)}\bar{V}T_3^{(0,0)} + \Lambda_3^{(0,0)}\bar{F}T_3^{(0,0)} + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,0)} \\
+ \Lambda_3^{(0,1)}\bar{V}T_3^{(0,0)} + \Lambda_3^{(0,1)}\bar{V}T_2^{(0,0)}
\]  

(14)

The \( \hat{C} \) and \( C \) are left and right eigen vectors of the \( H_{\text{eff}} \). The Lagrangian in eq 14 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 15.

\[
< P^{(0,1)}|\bar{V}CC\hat{C} + \Lambda_3^{(0,1)}\bar{F} - \Lambda_2^{(0,1)}T_2^{(0,1)}\bar{V} + \Lambda_1^{(0,1)}\bar{V} + \Lambda_2^{(0,1)}\bar{V}|Q^{(0,1)}> = 0
\]  

(15)

The Lagrangian in eq 14 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

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

(16)

The eq 15 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 \( \bar{V}CC\hat{C} \), \( \Lambda_2^{(0,1)}\bar{V} \), \( \Lambda_1^{(0,1)}\bar{V} \) 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 16 is solved
fully by taking into account the $\Lambda^{(0,1)}_3$ terms calculated above.

For solving (0,0) sector $\Lambda^{(0,0)}_3$ amplitude is obtained first. Here too the equation for $\Lambda^{(0,0)}_3$ is obtained by differentiating the Lagrangian in eq 14 with respect to $T^{(0,0)}_3$. The terms appear after the differentiation with respect to $T^{(0,0)}_3$ are given in eq 17.

$$< P^{(0,0)} | \Lambda^{(0,0)}_3 F + \Lambda^{(0,0)}_2 V + \Lambda^{(0,0)}_1 V + \Lambda^{(0,1)}_3 V | Q^{(0,0)} >= 0$$

The equation for $\Lambda^{(0,0)}_2$ is obtained from differentiating eq 14 with respect to $T^{(0,0)}_2$. The $\Lambda^{(0,0)}_2$ equation with triples correction is given by

$$SD + < P^{(0,0)} | \Lambda^{(0,0)}_3 V + \Lambda^{(0,0)}_2 VT^{(0,0)}_2 | Q^{(0,0)} >= 0$$

The eq 17 is solved non-iteratively to obtain $\Lambda^{(0,0)}_3$. $\Lambda^{(0,0)}_3$’s are obtained by taking the direct contribution from the second order term $\Lambda^{(0,0)}_2 V$ and the third order terms $\Lambda^{(0,1)}_3 V$ and $\Lambda^{(0,0)}_3 V$. Also $F$ containing term $\Lambda^{(0,0)}_3 F$ contributes to $\Lambda^{(0,0)}_3$ equation at second order. It should be noted that due to reverse decoupling $\Lambda^{(0,1)}$ involving terms $\Lambda^{(0,1)}_3 VT^{(0,0)}_2$ and $\Lambda^{(0,1)}_3 VT^{(0,0)}_3$ appear in $\Lambda^{(0,0)}$. After obtaining $\Lambda^{(0,0)}_3$, its effect on $\Lambda^{(0,0)}_2$ equation is incorporated through the third order terms $\Lambda^{(0,0)}_3 V$, $\Lambda^{(0,1)}_3 V$ and $\Lambda^{(0,0)}_3 VT^{(0,0)}_2$. The eq 18 is solved fully by taking into account of $\Lambda^{(0,0)}_3$ terms calculated above. Finally, the triples contribution to $E^{(1)}$ are given in eq 19, where $\dot{O}$ is the explicit derivative of Hamiltonian with respect to external field.

$$E^{(1)}_{\text{triples}} = \Lambda^{(0,1)}_2 \dot{O} T^{(0,1)}_3 + \Lambda^{(0,0)}_2 \dot{O} T^{(0,0)}_3$$

These triples corrected $\Lambda$ and $T$ amplitudes are used for the evaluation of dipole moments in (0,0) and (0,1) sector. The term $VT^{(0,0)}_2 T^{(0,0)}_3$ in $T^{(0,0)}_3$ 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 $\Lambda^{(0,1)}_2 \dot{O} T^{(0,1)}_3$ and $\Lambda^{(0,0)}_2 \dot{O} T^{(0,0)}_3$. Hence the final dipole moment is corrected at least up to third order in triples.
IV. 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 \( \dot{\text{OH}}, \dot{\text{OOH}}, \dot{\text{HCOO}}, \dot{\text{CN}} \) and \( \dot{\text{CH}} \).

A. OH radical

We report the dipole moment of hydroxy radical at the equilibrium geometry in Table-I. We start with the closed shell configuration of \( \dot{\text{OH}}^- \) anion as a vacuum. The HOMO of \( \dot{\text{OH}}^- \) 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-I 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 \( \Lambda \)-FSMRCCSD values shows that the dipole moment is converged from cc-pVDZ to cc-pVQZ. Whereas, the \( \Lambda \)-FSMRCCSD(T*) produces a marginal change in dipole moment. It is observed that the \( \Lambda \)-FSMRCCSD dipole moment in cc-pVDZ basis is 0.634 au, whereas the \( \Lambda \)-FSMRCCSD(T*) increases the dipole moment (0.682 au) towards the FCI value of 0.663 au\(^\text{113}\). 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.

B. CN radical

The dipole moments of the CN radical are presented in the Table-II. We start with the cyanide anion which is closed shell with the ground state geometry \( ^2\Sigma^+ \). Removal of 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\(^\text{114,115}\) to achieve the experimental accuracy. In Table-II 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\textsuperscript{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-II. 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)\textsuperscript{114} and experimental (0.57 ±0.03 au)\textsuperscript{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 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 includes 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.

C. 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\textsuperscript{117,118} with a set of uncontracted polarized functions. The description of the geometries for these radicals are given in appendix I. 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-III. 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

\begin{align*}
&[\text{core}], 3a_1^2, 4a_1^2, 5a_1^2, 1a_2^2, 6a_1^2, 7a_1^2, 2a_2^2
&\end{align*}

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-III. 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-III. 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

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

and

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

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 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-III, which stays close to the dipole moment obtained from the Λ-FSMRCCSD(T*) method.

**D. CH radical**

The CH radical can be considered as the electron attached state of the corresponding cation $CH^+$. The RHF configuration of $CH^+$, $1\sigma^22\sigma^23\sigma^2$ 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-IV 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 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.

E. PO radical

The dipole moment of PO radical, which is difficult to predict by the single reference method, has been studied using FSMSCSD 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-V, is slightly over estimated. However, inclusion of triples improves the accuracy towards the experimental value of 1.88±0.07 debye (0.740±0.028 au). The finite field relaxed ROHF-CCSD and ROHF-CCSD(T) are performed in the same basis using ACES-II package. Finite field calculations using large basis sets are reported for this radical at ROHF-CCSD(T) level by Urban et al. The opposite trend in the inclusion of triples is observed for ROHF based CCSD and CCSD(T). This difference in trends for dipole moment on inclusion of triples in Λ-FSMRCC and ROHF-CC could be due to combination of reasons like the way triples are included and the treatment of dynamic correlation.

V. CONCLUSIONS

In this paper 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 OH and CH 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 1.5Re for the CH radical, we can observe that the in-
clusion 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 improves the results 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.

VI. ACKNOWLEDGMENT

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Science and Technology, India for financial support.
5 Coester, F. Nucl. Phys. 1958, 1, 421.

18
40 Mukherjee, D. Pramana 1979, 12, 203.


<table>
<thead>
<tr>
<th>BASIS</th>
<th>Λ-FSMRCCSD(T*)</th>
<th>Λ-FSMRCCSD</th>
<th>EOMCCSD(unrelaxed)</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pVDZ</td>
<td>0.682</td>
<td>0.634</td>
<td>0.639</td>
<td>0.663</td>
</tr>
<tr>
<td>cc-pVTZ</td>
<td>0.682</td>
<td>0.645</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>cc-pVQZ</td>
<td>0.684</td>
<td>0.645</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

\(\text{a}\) \(R_{eq} = 1.85104 a_0\)
\(\text{b}\) see Ref. 96
\(\text{c}\) see Ref. 113

<table>
<thead>
<tr>
<th>BASIS</th>
<th>ROHF</th>
<th>A-FSMRCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCSD</td>
<td>CCSD(T)</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>0.522</td>
<td>0.476</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>0.510</td>
<td>(0.437) (c)</td>
</tr>
<tr>
<td>CBS LIMIT</td>
<td>Exp (d)</td>
<td>0.559±0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\text{a}\) \(R_{eq} = 2.21512 a_0\)
\(\text{b}\) Results obtained from ACES II package
\(\text{c}\) Relaxed finite-field values
\(\text{d}\) see Ref. 114
\(\text{e}\) see Ref. 116
### TABLE III: Dipole moments of OOH and HCOO radical in \textit{au}

<table>
<thead>
<tr>
<th>STATE</th>
<th>DIRECTION</th>
<th>Λ-FSMRCCSD(T*)</th>
<th>Λ-FSMRCCSD</th>
<th>FF-FSMRCCSD(T*)</th>
<th>EOMCCSD $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A_2$</td>
<td>X</td>
<td>-0.588</td>
<td>-0.557</td>
<td>-0.571</td>
<td></td>
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<tr>
<td></td>
<td>Y</td>
<td>-0.713</td>
<td>-0.669</td>
<td>-0.692</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.924</td>
<td>0.870</td>
<td>0.897</td>
<td></td>
</tr>
<tr>
<td>$^1A_2$</td>
<td>X</td>
<td>-0.402</td>
<td>-0.369</td>
<td>-0.387</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>-0.717</td>
<td>-0.676</td>
<td>-0.694</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.822</td>
<td>0.770</td>
<td>0.795</td>
<td></td>
</tr>
<tr>
<td>$^2B_2$</td>
<td>Y</td>
<td>0.965</td>
<td>0.909</td>
<td>0.979</td>
<td>1.004</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>Y</td>
<td>0.835</td>
<td>0.786</td>
<td>0.842</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$ see Ref. 101

### TABLE IV: Dipole moments of CH radical in \textit{au}

<table>
<thead>
<tr>
<th>BASIS</th>
<th>$R_{eq}$</th>
<th>Λ-FSMRCCSD(T*)</th>
<th>Λ-FSMRCCSD</th>
<th>Full CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pVDZ $R_{eq}$</td>
<td>0.575</td>
<td>0.582</td>
<td>0.548</td>
<td></td>
</tr>
<tr>
<td>Sadlej $R_{eq}$</td>
<td>0.547</td>
<td>0.540</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Exp $^a$</td>
<td></td>
<td></td>
<td></td>
<td>0.57±0.023</td>
</tr>
<tr>
<td>cc-pVDZ $R_{dis}$</td>
<td>0.061</td>
<td>0.100</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>Sadlej $R_{dis}$</td>
<td>0.084</td>
<td>0.111</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ see Ref. 121.

$R_{eq} = 2.11648$ $a_0$.  
$R_{dis} = 3.1660$ $a_0$.  

TABLE V: Dipole moments of PO radical in \textit{au}

<table>
<thead>
<tr>
<th>BASIS</th>
<th>ROHF $^b$</th>
<th>\textit{\Lambda}-FSMRCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-pVDZ</td>
<td>0.777</td>
<td>0.726</td>
</tr>
<tr>
<td>Exp $^d$</td>
<td>0.770</td>
<td>0.708</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.750</td>
</tr>
</tbody>
</table>

$^a R_{eq} = 2.78357 a_0$

$^b$ Results obtained from ACES II package

$^d$ see Ref.\textsuperscript{122}
### Appendix-I

**Geometries in au**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOH</td>
<td>H</td>
<td>-1.60075</td>
<td>-1.66668</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>1.27888</td>
<td>-0.01807</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-1.17802</td>
<td>0.12308</td>
<td>0.00000</td>
</tr>
<tr>
<td>HCOO</td>
<td>H</td>
<td>0.00000</td>
<td>2.96725</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.00000</td>
<td>0.88855</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>O₁</td>
<td>-1.98007</td>
<td>-0.42700</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>1.98007</td>
<td>-0.42700</td>
<td>0.00000</td>
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</tbody>
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