

Effect of Triples to Dipole Moments in Fock-Space Multireference Coupled Cluster Method

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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 multireference coupled cluster (Λ -FSMRCC) response method. We have implemented a specific scheme of noniterative triples, in addition to singles and doubles schemes, 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.

I. 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 onward. So far a different version of the SRCC method with full or partial inclusion of triples with increasing precision has been developed^{19–24} for energy. The noniterative 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-workers²¹ 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 (quasidegenerate) to the exact wave function, i.e., bond-breaking situations in the ground or excited states, where SRCC fails. The restricted open (RO) shell-based CC method,²⁶ which uses a linear operator have been successful in describing the quasidegenerate cases. Though in single reference framework, selected triple and quadruple level excitations^{27,28} have been considered for quasidegenerate cases,^{29,30} multideterminantal or multireference coupled cluster (MRCC) methods have emerged as the methods of choice to take into account the quasidegenerate molecular systems.³¹ Among the multireference methods, the effective Hamiltonian-based^{32–34} 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.^{39–44} 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) studies³¹ and situations involving curve crossing. However for PES, the 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 electrons 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-based³³ formulation both in Fock^{47,48} as well as Hilbert spaces.^{49,50}

The important feature of both the multireference formulations is their size extensivity. On the other hand, equation of motion (EOMCC)^{51–57} or linear response CC (CCLR) methods^{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-state⁵¹ 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 multireference 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 quasidegenerate 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 noniterative triples for ionization potential^{68,69} and excitation energies,⁷⁰ within a FSMRCC scheme, and Bartlett and co-workers included full triples correction for excitation energies.⁷¹ The full triples correction to excitation energies in intermediate Hamiltonian FSCC has been pursued

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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 noniterative perturbative triples correction to the spin-flip EOMCC (SF-EOMCC) method for excitation energies.⁸³ The noniterative energy corrections to MMCC for excitation energy has been achieved by Piecuch et al.⁸⁴

Formulation of energy derivatives using multiroot CC methods is a challenging task. The response theory has been a valuable theoretical tool to study molecular properties.^{85,86} Along the lines of nonvariational CC (NVCC) response approach of Monkhorst, a response approach was developed for FSMRCC 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-space⁹¹ as well as Fock-space⁹² 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 Szalay⁹⁴ independently formulated similar approach based on Lagrange multipliers for the FSMRCC 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 moment⁹⁶ and polarizability⁹⁷ of the doublet radicals as well as excited states⁹⁸ 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 Stanton¹⁰⁰ and implemented by Stanton and Gauss.^{101,102} Nooijen and co-workers implemented gradients in STEOMCC,^{103,104} using Lagrange multipliers. Analytic gradients for SF-EOMCC models at the 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 toward 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 the linear response CC method for excited-state properties was studied iteratively.¹¹¹

In this paper, we present the first implementation of partial triples corrections to the response properties for Lagrange-based formulation within Λ -FSMRCC for the 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 Section II, we start with a brief review of the FSMRCC method and the Lagrange approach for energy derivatives. Section III deals with the perturbative analysis of triples amplitude in Λ -FSMRCC for energy and dipole moments. We discuss the results in Section IV.

II. REVIEW OF FSMRCC

The FSMRCC theory^{38,40–42,44} and the Lagrangian formulation within FSMRCC have been described in detail in various articles.^{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 restricted Hartree–Fock (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

$$|\Psi_{(0)\mu}^{(m,n)}\rangle = \sum_i C_{\mu i}^{(m,n)} |\Phi_i^{(m,n)}\rangle \quad (1)$$

where, $C_{\mu i}^{(m,n)}$ is the model space coefficient. The correlated wave function for the μ^{th} state can be written as

$$|\Psi_{\mu}^{(m,n)}\rangle = \Omega |\Psi_{(0)\mu}^{(m,n)}\rangle \quad (2)$$

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

$$\Omega = \{e^{\tilde{T}^{(m,n)}}\} \quad (3)$$

The curly bracket denotes normal ordering of the operators within it.¹¹² The cluster operator $\tilde{T}^{(m,n)}$ can be expressed as

$$\tilde{T}^{(m,n)} = \sum_{k=0}^m \sum_{l=0}^n T^{(k,l)} \quad (4)$$

$T^{(k,l)}$ 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 quasidegenerate states as

$$H|\Psi_{\mu}^{(0,1)}\rangle = E_{\mu}|\Psi_{\mu}^{(0,1)}\rangle \text{ which leads to } H\Omega(\sum_i C_{\mu i}^{(0,1)}|\Phi_i^{(0,1)}\rangle) = E_{\mu}\Omega(\sum_i C_{\mu i}^{(0,1)}|\Phi_i^{(0,1)}\rangle) \quad (5)$$

Projection operator for model space is defined as

$$P^{(0,1)} = \sum_i |\Phi_i^{(0,1)}\rangle\langle\Phi_i^{(0,1)}| \quad (6)$$

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

equation:

$$\begin{aligned} P^{(0,1)}(H\Omega - \Omega H_{\text{eff}}^{(0,1)})P^{(0,1)} &= 0 \\ Q^{(0,1)}(H\Omega - \Omega H_{\text{eff}}^{(0,1)})P^{(0,1)} &= 0 \end{aligned} \quad (7)$$

Because of normal ordering, the contractions among 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 upward. This is also known as the subsystem embedding (SEC) condition.

Similar to the Lagrange formulation of linear response approach of SRCC, Szalay⁹⁴ 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) is satisfied for a specific μ^{th} state:

$$\begin{aligned} \mathcal{J} = & \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{\text{eff}})_{ij}^{(0,1)} C_{j\mu}^{(0,1)} \\ & + \sum_{ji} \Lambda_{ji}^{(0,1)} \langle \phi_j^{(0,1)} | (H\Omega - \Omega H_{\text{eff}}) | \phi_i^{(0,1)} \rangle \\ & + \sum_{\alpha} \sum_i \Lambda_{\alpha i}^{(0,1)} \langle \phi_{\alpha}^{(0,1)} | (H\Omega - \Omega H_{\text{eff}}) | \phi_i^{(0,1)} \rangle \\ & + \sum_{ji} \Lambda_{ji}^{(0,0)} \langle \phi_j^{(0,0)} | H\Omega | \phi_i^{(0,0)} \rangle \\ & + \sum_{\alpha} \sum_i \Lambda_{\alpha i}^{(0,0)} \langle \phi_{\alpha}^{(0,0)} | H\Omega | \phi_i^{(0,0)} \rangle - E_{\mu} (\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1) \end{aligned} \quad (8)$$

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 of which the closed part of the Lagrangian multipliers vanishes. Thus, the second and fourth terms of eq 8 vanish, simplifying Lagrangian to

$$\begin{aligned} \mathcal{J} = & \sum_{ij} \tilde{C}_{\mu i}^{(0,1)} (H_{\text{eff}})_{ij}^{(0,1)} C_{j\mu}^{(0,1)} \\ & + \sum_{\alpha} \sum_i \Lambda_{\alpha i}^{(0,1)} \langle \phi_{\alpha}^{(0,1)} | (H\Omega - \Omega H_{\text{eff}}) | \phi_i^{(0,1)} \rangle \\ & + \sum_{\alpha} \sum_i \Lambda_{\alpha i}^{(0,0)} \langle \phi_{\alpha}^{(0,0)} | H\Omega | \phi_i^{(0,0)} \rangle \\ & - E_{\mu} (\sum_{ij} \tilde{C}_{\mu i}^{(0,1)} C_{j\mu}^{(0,1)} - 1) \end{aligned} \quad (9)$$

Differentiation of eq 9 with respect to Λ results in the 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 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 , Ω , and Λ 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 refs 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 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 noniterative 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 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 nonrelaxed 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 noniteratively 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 equations updates the CCSD equations. Even though $VT_3^{(0,0)}$ term is third order, considering the term in a $T_3^{(0,0)}$ 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 and $VT_2^{(0,0)}T_2^{(0,0)}$ 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 ($\bar{H} = \exp(-T^{(0,0)})H\exp(T^{(0,0)})$) 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

$$\begin{aligned} H_{\text{eff}} = & P^{(0,1)}(\bar{F} + \bar{F}T_1^{(0,1)} + \bar{V}T_2^{(0,1)} \\ & + \bar{F}T_2^{(0,1)} + \bar{V}T_3^{(0,1)})P^{(0,1)} \end{aligned} \quad (10)$$

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

$$\begin{aligned} Q_1^{(0,1)}(\bar{F} + \bar{F}T_1^{(0,1)} + \bar{V}T_2^{(0,1)} \\ + \bar{F}T_2^{(0,1)} + \bar{V}T_3^{(0,1)} - T_1^{(0,1)}H_{\text{eff}})P^{(0,1)} = 0 \end{aligned} \quad (11)$$

$$\begin{aligned} Q_2^{(0,1)}(\bar{V} + \bar{F}T_2^{(0,1)} + \bar{V}T_1^{(0,1)} + \bar{V}T_2^{(0,1)} \\ + \bar{W}T_2^{(0,1)} + \bar{V}T_3^{(0,1)} + \bar{F}T_3^{(0,1)} - T_2^{(0,1)}H_{\text{eff}})P^{(0,1)} = 0 \end{aligned} \quad (12)$$

$$\begin{aligned} Q_3^{(0,1)}(\bar{W} + \bar{W}T_2^{(0,1)} + \bar{F}T_3^{(0,1)} + \bar{V}T_2^{(0,1)} - T_3^{(0,1)}H_{\text{eff}})P^{(0,1)} \\ = 0 \end{aligned} \quad (13)$$

Table 1. Dipole Moments of $^2\Pi$ OH Radical^a

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	—	—

^a Results in au and $R_{eq} = 1.85104 a_0$. ^b See ref 96. ^c See ref 113.

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 eqs 11 and 12 are first solved fully excluding the terms which involve $T_3^{(0,1)}$ amplitude, which is the CCSD approximation. Using these amplitudes eq 13 is solved noniteratively. 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 $T_3^{(0,1)}\bar{F}$. After solving $T_3^{(0,1)}$, we again solve the eqs 11 and 12 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, 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

$$\begin{aligned} \mathcal{J} = & SD + \bar{V}T_3^{(0,1)}C\bar{C} + \Lambda_3^{(0,1)}\bar{V}T_2^{(0,1)} + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,1)} \\ & + \Lambda_3^{(0,1)}\bar{F}T_3^{(0,1)} + \Lambda_2^{(0,1)}\bar{V}T_3^{(0,1)} + \Lambda_2^{(0,1)}\bar{F}T_3^{(0,1)} \\ & - \Lambda_2^{(0,1)}T_2^{(0,1)}(\bar{V}T_3^{(0,1)}) + \Lambda_1^{(0,1)}\bar{V}T_3^{(0,1)} + \Lambda_3^{(0,0)}VT_2^{(0,0)} \\ & + \Lambda_2^{(0,0)}VT_3^{(0,0)} + \Lambda_1^{(0,0)}VT_3^{(0,0)} + \Lambda_3^{(0,0)}FT_3^{(0,0)} \\ & + \Lambda_3^{(0,1)}\bar{W}T_2^{(0,0)} + \Lambda_3^{(0,1)}VT_3^{(0,0)} + \Lambda_3^{(0,1)}VT_2^{(0,0)} \quad (14) \end{aligned}$$

The \bar{C} and C are left and right eigen vectors of the H_{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:

$$\begin{aligned} \langle P^{(0,1)} | \bar{V}C\bar{C} + \Lambda_3^{(0,1)}\bar{F} - \Lambda_2^{(0,1)}T_2^{(0,1)}\bar{V} + \Lambda_1^{(0,1)}\bar{V} \\ + \Lambda_2^{(0,1)}\bar{V} | Q^{(0,1)} \rangle = 0 \quad (15) \end{aligned}$$

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

$$SD + \langle P^{(0,1)} | \Lambda_3^{(0,1)}\bar{V} + \Lambda_3^{(0,1)}\bar{W} | Q^{(0,1)} \rangle = 0 \quad (16)$$

The eq 15 is solved noniteratively 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 $\bar{V}C\bar{C}$, $\Lambda_2^{(0,1)}\bar{V}$, $\Lambda_1^{(0,1)}\bar{V}$, and $\Lambda_2^{(0,1)}T_2^{(0,1)}\bar{V}$. These contribute at the first, second, and third orders, 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 $\Lambda_3^{(0,1)}$ 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 14 with respect to $T_3^{(0,0)}$. The terms appear after the differentiation with respect to $T_3^{(0,0)}$ are given in eq 17:

$$\langle P^{(0,0)} | \Lambda_3^{(0,0)}F + \Lambda_2^{(0,0)}V + \Lambda_1^{(0,0)}V + \Lambda_3^{(0,1)}V | Q^{(0,0)} \rangle = 0 \quad (17)$$

The equation for $\Lambda_2^{(0,0)}$ is obtained from differentiating eq 14 with respect to $T_2^{(0,0)}$. The $\Lambda_2^{(0,0)}$ equation with triples correction is given by

$$SD + \langle P^{(0,0)} | \Lambda_3^{(0,0)}V + \Lambda_3^{(0,1)}V + \Lambda_3^{(0,0)}VT_2^{(0,0)} | Q^{(0,0)} \rangle = 0 \quad (18)$$

The eq 17 is solved noniteratively 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 $\Lambda_3^{(0,1)}VT_3^{(0,0)}$ appears 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 18 is solved fully by taking in to account of $\Lambda_3^{(0,0)}$ terms calculated above. Finally, the triples contribution to $E^{(1)}$ is given in eq 19, where \hat{O} is the explicit derivative of Hamiltonian with respect to external field:

$$E_{triples}^{(1)} = \Lambda_2^{(0,1)}\hat{O}T_3^{(0,1)} + \Lambda_2^{(0,0)}\hat{O}T_3^{(0,0)} \quad (19)$$

These triples corrected Λ and T amplitudes are used for the evaluation of dipole moments in (0,0) and (0,1) sectors. The term $VT_2^{(0,0)}T_2^{(0,0)}$ in $T_3^{(0,0)}$ equation will thus have a higher effect on the dipole moment, while the other triples correcting terms will affect the dipole moment at the 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.

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 nonrelaxed finite field approach. The systems studied are OH, OOH, HCOO, CN, and CH.

A. OH Radical. We report the dipole moment of hydroxy radical at the equilibrium geometry in Table 1. We start with the closed-shell configuration of OH[−] anion as a vacuum. The highest occupied molecular orbital (HOMO) of OH[−] is two-

Table 2. Dipole Moments of $^2\Sigma^+$ State of CN Radical^a

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 \pm 0.001	
exp ^e			0.57 \pm 0.03	

^a Results in au and $R_{\text{eq}} = 2.21512 a_0$. ^b Results obtained from ACES II package. ^c Relaxed finite-field values. ^d See ref 114. ^e See ref 116.

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 the hydroxy radical. In Table 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 show 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) toward the FCI value of 0.663 au.¹¹³ Though triples exceeds the FCI dipole moment, the qualitative trend toward 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 2. 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^{114,115} to achieve the experimental accuracy. In Table 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 restricted open-shell Hartree–Fock (ROHF)-CC and FSMRCC within singles and doubles approximation as well as with partial triples. The values presented in parentheses 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 2. It has been observed so far that only beyond the double- ζ with augmentation, the dipole moment close to CBS limit (0.559 \pm 0.001 au)¹¹⁴ and experimental (0.57 \pm 0.03 au)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 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 the same in both the basis sets, i.e., triples correction increases 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 a finite field relaxed FSMRCC

calculation. Here too, we get the same trend as we obtained from the analytic nonrelaxed 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 Radicals. The dipole moments for the nonlinear molecules, such as hydroperoxy and formyloxy radical, at the equilibrium geometry were studied using the double- ζ basis set of Huzinaga–Dunning^{117,118} with a set of uncontracted polarized functions. The description of the geometries for these radicals is given in Appendix I. The center of mass coordinates is used, and the molecules are kept along the X,Y direction. The dipole moments for each direction are obtained and presented in Table 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], $3a_1^2, 4a_1^2, 5a_1^2, 1a_2^2, 6a_1^2, 7a_1^2, 2a_2^2$.

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 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*) method.

The dipole moments of the first two low-lying near-degenerate states of the formyloxy radical at the equilibrium geometry are given in Table 3. We start with the RHF of formate anion as vacuum. Removal of an electron from the formate anion results in formyloxy radical, the near degenerate low-lying states of which have the electronic configuration: [core], $3a_1^2, 2b_2^2, 4a_1^2, 5a_1^2, 3b_2^2, 1b_1^2, 1a_2^2, 6a_1^2, 4b_2^2$ and [core], $3a_1^2, 2b_2^2, 4a_1^2, 5a_1^2, 3b_2^2, 1b_1^2, 1a_2^2, 6a_1^2, 4b_2^2$. The dipole moments along the H–C bond axis for these states, denoted by 2B_2 and 2A_1 have been reported. The EOMCC result¹⁰¹ 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 3, 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^+ , $1\sigma^2 2\sigma^2 3\sigma^2$ is chosen as a vacuum. The degenerate lowest unoccupied molecular orbitals (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 reports the results for the CH radical in cc-pVDZ¹¹⁹ and Sadlej¹²⁰ 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 experimental¹²¹ 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 toward the FCI value of 0.074 au. This

Table 3. Dipole Moments of OOH and HCOO Radical^a

state	direction	Λ -FSMRCCSD(T*)	Λ -FSMRCCSD	FF-FSMRCCSD(T*)	EOMCCSD ^b
OOH					
² A ₂	X	−0.588	−0.557	−0.571	
	Y	−0.713	−0.669	−0.692	
total		0.924	0.870	0.897	
¹ A ₂					
	X	−0.402	−0.369	−0.387	
	Y	−0.717	−0.676	−0.694	
total		0.822	0.770	0.795	
HCOO					
² B ₂	Y	0.965	0.909	0.979	1.004
² A ₁	Y	0.835	0.786	0.842	—

^b See ref 101. ^a Results in au.Table 4. Dipole Moments of CH Radical^a

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 ^b				0.57 ± 0.023
cc-pVDZ	R_{dis}	0.061	0.100	0.074
Sadlej	R_{dis}	0.084	0.111	—

^a Results in au, $R_{eq} = 2.11648 a_0$, and $R_{dis} = 3.1660 a_0$. ^b See ref 121.Table 5. Dipole Moments of PO Radical^a

basis	ROHF ^b		Λ -FSMRCC	
	CCSD	CCSD(T)	CCSD	CCSD(T*)
cc-pVDZ	0.777	0.726	0.708	0.750
exp ^c				0.740 ± 0.028

^a Results in au and $R_{eq} = 2.78357 a_0$. ^b Results obtained from the ACES II package. ^c See ref 122.

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 toward 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 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 5, is slightly overestimated. However, inclusion of triples improves the accuracy toward 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 the ACES-II package.¹²³ Finite field calculations using large basis sets are reported for this radical at ROHF-CCSD(T) level by Urban et al.¹¹⁵ 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 a 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 Λ -FSMRCCSD(T*) performs better than Λ -FSMRCCSD and tends toward FCI. In particular, when the dipole moments of 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 that of the Λ -FSMRCCSD results. At stretched geometries, where the multireference description is required, inclusion of the triples provides better results. From the dipole moment of OH radical using cc-pVDZ, TZ, and 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 overestimated, compared to the FCI it gives qualitatively correct trend. Also, the nonrelaxed EOMCCSD shows a 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 a 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 noniterative 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 analyzed the importance of triples excitation is PO. We observe that the triples excitation

Table 6. Geometries in au

molecule	atom	X	Y	Z
ÖOH	H	−1.60075	−1.66668	0.00000
	O	1.27888	−0.01807	0.00000
	O	−1.17802	0.12308	0.00000
HCOÖ	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

improves the results for cc-pVDZ basis. ROHF-based CCSD and CCSD(T) calculations are performed to analyze the way triples improve the dipole moment for CN and PO radicals. It has been observed that the way the triples contributes to the 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.

APPENDIX I

Geometries in au are summarized in Table 6.

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