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# Multireference coupled cluster based analytic response approach for evaluating molecular properties: Some pilot results

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In this paper we present the first results for linear response theory in the multireference Fock space framework. Dipole moments of the open shell radicals hydro peroxy radical, hydroxyl radical, and formyloxyl radical are discussed in this paper. The results obtained from the analytic response are compared with the experimental as well as the finite field results including relaxation of the orbitals and the results suggest that the effects of relaxation are substantial. The Fock space approach enables us to obtain the properties of excited states of these radicals in a single calculation. The dipole moments of the first excited states of the above radicals are also reported. The results of the lower Fock space sector energy derivatives are also presented. © 1999 American Institute of Physics. [S0021-9606(99)30105-7]

## I. INTRODUCTION

In recent years significant progress has been made in the development of analytic energy derivatives using coupled-cluster (CC) methods.<sup>1-7</sup> This progress has been very useful from the point of view of the determination of transition state geometries, vibrational frequencies, and calculation of electric and magnetic properties of molecules. Molecular properties are very sensitive to electron correlation as well as the basis set. The CC method, which takes care of the electron correlation in a very extensive way, has thus emerged as an attractive candidate for the evaluation of molecular energies and energy derivatives. The most standard CC technique is based on the single determinantal model space where the energies are calculated using the nonvariational method of projection. In the response based approach initiated by Monkhorst,<sup>3</sup> the energy derivatives are obtained analytically using the same projection method.

The single reference based approach works well for non-degenerate or closed shell systems and only in limited cases for quasidegenerate situations. The ground states of open shell radicals can be described, for example, by SRCC based on the restricted open shell HF determinant. Similarly in some cases excited states can be 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).<sup>8-12</sup> In recent years, this class of methods has been studied for the description of excited states, ionized states, and potential energy surfaces (PES), where the non-dynamical correlation is likely to be important. The traditional MRCC uses an effective Hamiltonian route,<sup>11</sup> which has been investigated extensively in recent years. The effective Hamiltonian is constructed within a model space corre-

sponding to 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 (Fock space)<sup>8,12</sup> and valence-specific (Hilbert space) types.<sup>9-11</sup> The valence universal type uses 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 subsets are the ones 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. 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. In this context, state-selective MRCC theory pertaining to the description of a single state has emerged as a more attractive formulation, although this class of theory is still at an early stage of development.<sup>13</sup>

Calculation of analytic derivatives using the MRCC wave function is naturally the next stage of development. In recent years one of the present authors developed analytic derivatives of the MRCC energy and wave function with respect to the time-independent electric field.<sup>14</sup> This formulation thus can describe the molecular properties for quasidegenerate systems via an analytic response approach. This was formulated using the effective Hamiltonian valence-universal approach and thus can describe the properties for low-lying ionized and excited states. In the context of the

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SRCC method, the derivatives of the CC amplitudes with respect to all components of fields can be eliminated by the solution of a single linear equation.<sup>15</sup> Such a technique has not been incorporated in the MRCC response theory. But this is not a disadvantage in the evaluation of static properties, particularly for molecules possessing high symmetry. More recently, Ajitha and Pal<sup>16</sup> formulated a general time-dependent version of response of the MRCC wave function and its static limit (i.e., the response to the time-independent field) reduces to the earlier formulation by Pal.<sup>14</sup> The frequency-dependent properties can be evaluated by time integration and were shown to be obtained from the time-independent response equations by shifting the diagonal elements of the matrix of the linear equation by frequency. It may be mentioned in this context that excitation energies and excited state first order properties are also obtained by the linear response of the SRCC state to time-independent fields.<sup>17</sup> In this paper we report the dipole moments of open shell radicals using the response of the MRCC wave function to the time-independent external fields in a Fock space approach. As noted earlier, this method will allow us to describe more than one state from a single calculation, thus enabling us to obtain the dipole moments of the excited states of these radicals from one single calculation. In Sec. II, we present the general theory of the MRCC response to the time-independent field. In Sec. III we present the Fock space version of the MRCC response and in Sec. IV we present the results for the dipole moments of hydroxyl, hydroperoxy, and formyloxyl radicals obtained from our calculation. For comparison we have also obtained the finite field results from the MRCC calculation using a relaxed set of orbitals. These are compared with the EOM CC<sup>18</sup> results for the formyloxyl radical and unitary group algebra based single reference CCSD (UGA-CCSD)<sup>19</sup> results for the hydroxyl radical. As a by-product we also obtain lower Fock space sector results for the corresponding anions treated as vacuum. We discuss the trends of these results.

## II. RESPONSE OF THE OPEN SHELL SYSTEM IN THE MULTIREFERENCE FRAMEWORK

The interacting Hamiltonian in the presence of a time-independent electric field is expressed as

$$H(g) = H + gO, \quad (1)$$

where  $g$  is the strength of the electric field and  $O$  is the dipole moment operator.  $H$  is the Hamiltonian of the system in the absence of the external perturbation. The time-independent Schrödinger equation in the absence of the field is given as

$$H\psi_\mu = E_\mu\psi_\mu, \quad (2)$$

where  $\psi_\mu$  and  $E_\mu$  are the exact states and energies of the system. In the case of quasidegenerate situations, the exact energies corresponding to the model states of interest can be obtained through the effective Hamiltonian constructed within the model space. The eigen function space of the Hartree-Fock Hamiltonian  $H_0$  of the system is partitioned

into a model space consisting of quasidegenerate determinants and its orthogonal component. The projection operator for the model space can be defined as

$$P = \sum |\phi_i\rangle\langle\phi_i|, \quad (3)$$

where  $\{|\phi_i\rangle\}$ 's are the model space determinants. The orthogonal space to the model space is spanned by the projection operator  $Q$ ,  $Q = (1 - P)$ . As the weak field is switched on adiabatically, we assume that the dominant configurations in the model space continue to be the same. However, the model space coefficients are assumed to be weakly dependent on the field strength. The change in the field dependent wave operator incorporates the change in the dynamical correlation in the presence of the field. The generalized Bloch equation in the presence of external weak field  $g$  is given as

$$\begin{aligned} P[H(g)\Omega(g) - \Omega(g)H_{\text{eff}}(g)]P &= 0, \\ Q[H(g)\Omega(g) - \Omega(g)H_{\text{eff}}(g)]P &= 0. \end{aligned} \quad (4)$$

$H_{\text{eff}}$  is the effective Hamiltonian for the problem and  $\Omega$  is the wave operator. Equation (4) describes the wave operator and the effective Hamiltonian. Diagonalization of the effective Hamiltonian gives us the exact energies of the states of interest corresponding to the model space.

The effective Hamiltonian eigen value equation may be written as follows:

$$\sum_i [H_{\text{eff}}(g)]_{ji} C_{i\mu}(g) = E_\mu(g) C_{j\mu}(g), \quad (5)$$

where  $C_{j\mu}(g)$  are the field dependent model space coefficients.

To develop the analytic response of the system, we expand relevant field-dependent quantities as a Taylor series in  $g$ ,

$$\begin{aligned} \Omega(g) &= \Omega^{(0)} + \Omega^{(1)}g + 1/2!\Omega^{(2)}g^2 + \dots, \\ H_{\text{eff}}(g) &= H_{\text{eff}}^{(0)} + H_{\text{eff}}^{(1)}g + 1/2!H_{\text{eff}}^{(2)}g^2 + \dots, \\ E_\mu(g) &= E_\mu^{(0)} + E_\mu^{(1)}g + 1/2!E_\mu^{(2)}g^2 + \dots, \\ C_{j\mu}(g) &= C_{j\mu}^{(0)} + C_{j\mu}^{(1)}g + 1/2!C_{j\mu}^{(2)}g^2 + \dots, \end{aligned} \quad (6)$$

where  $\Omega^{(0)}$ ,  $H_{\text{eff}}^{(0)}$ ,  $E_\mu^{(0)}$ , and  $C_{j\mu}^{(0)}$  are the wave operator, effective Hamiltonian, exact energies, and the model space coefficients of the unperturbed problem, respectively.

The Bloch equation in the absence of any external perturbation is given by

$$P[H\Omega^{(0)} - \Omega^{(0)}H_{\text{eff}}^{(0)}]P = 0, \quad (7)$$

$$Q[H\Omega^{(0)} - \Omega^{(0)}H_{\text{eff}}^{(0)}]P = 0. \quad (8)$$

Analytic response of the Bloch equation at each order in  $g$  may be obtained from the derivatives of the Bloch equation at zero field. For example, the first order response may be obtained from the following equations:

$$\frac{\partial}{\partial g} P[H(g)\Omega(g) - \Omega(g)H_{\text{eff}}(g)]_{g=0} P = 0, \quad (9)$$

$$\frac{\partial}{\partial g} Q[H(g)\Omega(g) - \Omega(g)H_{\text{eff}}(g)]_{g=0} P = 0. \quad (10)$$

These equations describe the analytic response of the wave operator and the effective Hamiltonian to the weak external field. Similarly closed algebraic equations may thus be derived for response at each order in  $g$ . While solving Eqs. (9) and (10), we hold the unperturbed amplitudes obtained from Eqs. (7) and (8) constant. We obtain the first derivative of the effective Hamiltonian from the solution of Eqs. (9) and (10). Finally, the energy derivative is obtained from the derivative of the effective Hamiltonian eigenvalue equation. For example, the first derivative equation is

$$\sum_i \{ (H_{\text{eff}}^{(1)})_{ji} C_{i\mu}^{(0)} + (H_{\text{eff}}^{(0)})_{ji} C_{i\mu}^{(1)} \} = E_{\mu}^{(1)} C_{j\mu}^{(0)} + E_{\mu}^{(0)} C_{j\mu}^{(1)}. \quad (11)$$

Having obtained the  $H_{\text{eff}}^{(0)}$  from Eqs. (7) and (8),  $E_{\mu}^{(0)}$  and  $C_{j\mu}^{(0)}$  are obtained from the eigenvalue equation of the unperturbed effective Hamiltonian. After obtaining  $H_{\text{eff}}^{(1)}$  from Eqs. (9) and (10),  $E_{\mu}^{(1)}$  and  $C_{j\mu}^{(1)}$  are solved from Eq. (11) by applying an auxiliary condition on  $C_{j\mu}^{(1)}$ . If we use the full normalization of the model space at all field strength we can write

$$\sum_i C_{i\mu}^{(0)*} C_{i\nu}^{(0)} = \delta_{\mu\nu}, \quad (12)$$

$$\sum_i C_{i\mu}^{(0)*} C_{i\nu}^{(1)} + \sum_i C_{i\mu}^{(1)*} C_{i\nu}^{(0)} = 0. \quad (13)$$

Equation (13) defines the auxiliary condition on the vector  $C^{(1)}$ . In the next section we describe these response equations for the specific valence universal approach.

### III. THE FOCK SPACE MRCC METHOD

In the Fock space approach,<sup>8,12</sup> a suitable core, usually a single determinantal  $\phi_0$  is chosen as a vacuum with respect to which holes and particles are defined. The model space determinants consist of a subset of the holes and particles, called active holes and active particles. In general, a model space of  $m$  active particles and  $n$  active holes can be written as

$$|\psi_{\mu}^{(0)}(m,n)\rangle = \sum_i C_{i\mu}(g) |\phi_{i(m,n)}\rangle. \quad (14)$$

The configurations  $\{\phi_{i(m,n)}\}$  with  $m$  active particles and  $n$  active holes span the model space. In the presence of time-independent external fields, these  $C_{i\mu}$ 's can be expressed in orders of field strength  $g$  only. The time independent Bloch equation for the perturbed Hamiltonian can be written for all  $g$  as

$$[H(g)\Omega(g) - \Omega(g)H_{\text{eff}}(g)]P = 0. \quad (15)$$

Further, in the Fock space approach, the wave operator is considered to be valence universal and contains cluster operators correlating all lower hole particle sectors,

$$\Omega(g) = \{ \exp[\tilde{T}(g)] \}. \quad (16)$$

The symbol  $\{ \}$  represents the normal ordering of the operator products inside the braces.  $\tilde{T}(g)$  may be written as a Taylor's

series consisting of the derivatives that can destroy all subsets of the active particles and active holes present in the model space. Thus, we can write

$$\tilde{T}_{(m,n)}(g) = \tilde{T}_{(m,n)}^{(0)} + g \tilde{T}_{(m,n)}^{(1)} + \frac{1}{2!} g^2 \tilde{T}_{(m,n)}^{(2)} + \dots, \quad (17)$$

where the unperturbed cluster operator and all derivatives of the cluster operator  $\tilde{T}_{(m,n)}(g)$  may be written in terms of cluster operators of lower number of hole-particle sectors. Thus,

$$\tilde{T}_{(m,n)}^{(0)} = \sum_{k=0}^m \sum_{l=0}^n T_{(k,l)}^{(0)}, \quad (18)$$

$$\tilde{T}_{(m,n)}^{(1)} = \sum_{k=0}^m \sum_{l=0}^n T_{(k,l)}^{(1)}, \quad (19)$$

etc.  $T_{(k,l)}$  destroys exactly  $k$  active particles and  $l$  active holes. Each of these  $T_{(k,l)}$  operators can be written as a sum of different rank operators. The use of one body and two body parts of these operators is known as the MRCCSD scheme. For the specific problem of one hole model space, which is the interest of our present study, we have  $T_{(0,0)}$  and  $T_{(0,1)}$  amplitudes. The one and two body parts of the  $(0,0)$  sector amplitudes are simply the SRCC one and two body hole-particle excitation amplitudes. The one and two body parts of  $T_{(0,1)}$  operators, which destroy one active hole, are given by

$$T_{1(0,1)} = \sum_{i \in ah, j \notin ah} \langle i | t_{(0,1)} | j \rangle i^\dagger j, \quad (20)$$

$$T_{2(0,1)} = \sum_{i \in ah, j, k, a} \langle ia | t_{(0,1)} | jk \rangle i^\dagger a^\dagger k j. \quad (21)$$

To obtain the cluster amplitudes and their derivatives one has to solve the Fock space Bloch equation and its derivative equations.<sup>14,20</sup> First, the amplitudes and the effective Hamiltonian in the absence of external perturbation are obtained by the solution of Eqs. (7) and (8). Because of the valence universal nature of the wave operator, the Bloch equations are solved using subsystem embedding condition (SEC).<sup>8,21</sup> In the SEC approximation the Bloch equation is solved at different Fock space sectors progressively upwards starting from the lowest sector. At each sector the Bloch equation is projected with the model space projector and its orthogonal complement of that particular sector,  $P(k,l)$  and  $Q(k,l)$ , respectively, where  $(k,l)$  denotes the rank of Fock space sector. For example, for a one valence hole model space, we solve for the lowest sector  $(0,0)$  which describes the correlated state of the vacuum. This, by definition, is the SRCC problem. Keeping the amplitudes of the  $(0,0)$  sector fixed, one obtains the amplitudes of the  $(0,1)$  sector by solving the Bloch equation for the  $(0,1)$  sector, i.e., one hole sector.

To obtain the first derivative amplitudes and the first derivative of the effective Hamiltonian, the Bloch equations (9) and (10) are solved with the unperturbed amplitudes obtained from Eqs. (7) and (8) kept fixed. A similar strategy of the SEC for solving the derivative amplitudes at different Fock space sectors is employed to the perturbed Bloch equa-

tion. Thus from the Bloch equation, one obtains the different cluster amplitudes involved and their corresponding derivatives. The  $P$  space projection of the Bloch equation then defines the effective Hamiltonian of the sector of our interest and its derivatives.

As noted earlier, the energies are obtained as eigenvalues of the effective Hamiltonian within the model space. For the unperturbed problem the eigenvalue equation may be written as

$$\sum_i [H_{\text{eff}}^{(0)}]_{ji} C_{i\mu}^{(0)} = E_{\mu}^{(0)} C_{j\mu}^{(0)}. \quad (22)$$

In the construction of the connected part of  $H\Omega^{(0)}$  we first prepare the connected parts of  $H \exp T_{(0,0)}^{(0)}(\bar{H})$ .  $\bar{H}$  has an open part and a closed part. The closed part of  $\bar{H}$  is the energy of the (0,0) sector. Hence if we drop the closed part of  $\bar{H}$  in the construction of the  $H_{\text{eff}}$ , the solution of the above eigenvalue equation (22) directly gives us the ionization potentials. Addition of this ionization potential to the already derived (0,0) sector energy (SRCC energy) gives us the energy of the (0,1) sector. Depending on the number of active holes considered in the model space we get the energy of the different Fock space sector states. For example, we have considered two active holes, so we obtain two ionization potentials and these added to the (0,0) sector energy provides us with the energies of the two states of the (0,1) sector.

Having obtained the  $H_{\text{eff}}^{(0)}$ , its first derivative  $H_{\text{eff}}^{(1)}$  and  $E_{\mu}^{(0)}$  and the  $C_{j\mu}^{(0)}$  from the eigenvalue equation of the unperturbed effective Hamiltonian, one can solve for  $E_{\mu}^{(1)}$  and  $C_{j\mu}^{(1)}$  from Eq. (11) by applying an auxiliary condition on  $C_{j\mu}^{(1)}$  as described by Eqs. (12) and (13). Similar to the strategy used in Eq. (22), if we consider only the open part of the derivative of  $\bar{H}$  in the construction of  $H_{\text{eff}}^{(1)}$  in the solution of the derivative eigenvalue equation, we obtain the derivatives of the ionization potentials, which added to the derivative of the energy of (0,0) sector, will furnish the dipole moments of the states of the (0,1) sector problem. In the Fock space method, we can obtain the first derivatives of energy  $\{E_{\mu}^{(1)}\}$  for multiple states, the initial descriptions of which are included in the model space.

For computational simplicity, we store the open part of the  $\bar{H}$  operator ( $\bar{H}_{\text{op}}$ ). At the next stage connected parts of  $\bar{H} \exp T_{(0,1)}^{(0)}$  are constructed. Similarly in the construction of the derivative of  $H\Omega$  in the present work, we have first constructed the derivative of  $\bar{H}_{\text{op}}$  as an intermediate operator. We note here that  $\bar{H}_{\text{op}}$  as well as the derivative of  $\bar{H}_{\text{op}}$  have more than one and two body parts even in the CCSD approximation. However, for the present study we have truncated  $\bar{H}_{\text{op}}$  and derivative  $\bar{H}_{\text{op}}$  to one and two body parts. Storage of the three and higher body parts adds to the computational complexity. The leading contribution to the three body parts of the  $\bar{H}_{\text{op}}$  comes from the contraction of  $HT_{2(0,0)}^{(0)}$  and thus perturbatively it is at the second order. Apart from the one and two body parts of  $\bar{H}_{\text{op}}$ , only this three body part of  $\bar{H}_{\text{op}}$  contributes to the two body projection of the (0,1) sector of Eq. (8) through the contraction with  $T_{2(0,1)}^{(0)}$ . This term corrects the  $T_{2(0,1)}^{(0)}$  amplitudes at the third order and the

correspondingly the effective Hamiltonian is affected due to the three body part only at the fourth order and this effect should not be significant. Due to this reason the three body part of  $\bar{H}_{\text{op}}$ , requiring large disk space, has been eliminated in the initial application. By the same arguments the three body part of the derivative of  $\bar{H}_{\text{op}}$  has also been neglected.

## IV. RESULTS AND DISCUSSION

This section contains the application of the analytic MRCCSD response theory to evaluate the dipole moment of open shell radicals OOH, OH, and HCOO. We start with anions OOH<sup>-</sup>, OH<sup>-</sup>, and HCOO<sup>-</sup>, respectively, as vacuum and then the open shell radicals are treated as 1 valence hole sectors. The experimental equilibrium geometry of the radicals has been used for the calculation. For comparison, we have also reported the dipole moment obtained by using finite field approach at the MRCCSD level.

### A. Hydroperoxy radical

For the hydroperoxy radical we have reported the dipole moment along two orthogonal directions ( $x$  and  $y$ ) and also the total dipole moment. The coordinate system used for the hydroperoxy radical is as in Ref. 22. For the finite field calculation, the field is applied along the  $x$  and  $y$  direction separately for the hydroperoxy radical. We have calculated energy values at five different field strengths and have reported the interpolated derivative value. The fields with strengths +0.005 a.u., +0.0025 a.u., 0.000 a.u., -0.0025 a.u., and -0.005 a.u. are applied and the energies are obtained using the relaxed Hartree-Fock orbitals. The finite field derivative value has been obtained by the quadratic interpolation method of second order. Table I(a) reports the analytic derivative of the hydroperoxy radical and Table I(b) reports the finite field numbers. We have used the Huzinaga Dunning double zeta basis with a set of uncontracted polarization functions ( $\alpha_d$  for oxygen=1.211 and  $\alpha_p$  for hydrogen=0.6860) for the calculation. The restricted Hartree-Fock orbitals of the OOH<sup>-</sup> show that the two highest occupied orbitals of this anion are quasidegenerate and thus one can infer that the two states of the OOH radical obtained by electron detachment from each of these orbitals of OOH<sup>-</sup> are quasidegenerate and thus have multireference character. We have reported the dipole moment values of OOH<sup>-</sup> and the derivative of the two ionization potentials in both analytic nonrelaxed and finite field relaxed schemes. Naturally the Fock space calculation has been performed with these two active holes in the model space. We thus report the individual dipole moments of the ground and excited state (of  $A$  symmetry) of the hydroperoxy radical in the  $x$  and  $y$  direction using both analytic nonrelaxed and relaxed numerical finite field techniques. The analytic values are reported in Table I(b). Further, in the multireference calculation we have frozen three lowest occupied orbitals and three highest unoccupied orbitals. This is unlikely to affect the quality of results, but results in significant computational gain. We note that the values obtained in these two schemes are quite the same for the closed shell anion but differ significantly for the derivative of both the ionization potentials and correspond-

TABLE I. (a) Dipole moment values<sup>a</sup> using the analytic Fock space multireference coupled cluster approach for the OOH anion and radical.<sup>b</sup> (b) Results<sup>a</sup> using the relaxed finite field approach for the OOH anion and radical.<sup>c</sup>

(a)	Direction of the field	SCF dipole moment OOH anion	Analytic SRCCSD dipole moment OOH anion	Derivative ionization potentials of the OOH anion MRCCSD	Dipole moment of the OOH radical ( <sup>2</sup> Σ) MRCCSD	Total dipole moment of the OOH radical state ( <sup>2</sup> Σ) MRCCSD
	Y	−0.581	−0.533	−0.108 −0.127	−0.642 −0.660	Ground state 0.776
	X	−0.880	−0.897	0.461 0.705	−0.437 −0.192	Excited state 0.922

(b) Field	SRCCSD energy (OOH <sup>−</sup> ) anion	SRCCSD dipole moment (OOH) anion	Ionization potentials of the OOH anion MRCCSD	Derivative ionization potentials of the OOH anion MRCCSD	Finite field dipole moment of the OOH radical ( <sup>2</sup> Σ)	Total finite field dipole moment of the OOH radical ( <sup>2</sup> Σ)
0.005Y	−150.569 11		−0.038 012 1 0.000 785 7			
0.001Y	−150.571 39		−0.038 692 4 0.000 109 5			
0.000	−150.571 93	−0.530	−0.038 857 0 −0.000 055 5	−0.164 −0.164	−0.694 −0.694	
−0.001Y	−150.572 47		−0.039 019 6 −0.000 218 8			
−0.005Y	−150.574 72		−0.039 649 0 −0.000 856 8			Ground state 0.838
0.005X	−150.567 60		−0.040 372 2 −0.002 442 5			Excited state 0.656
0.001X	−150.571 04		−0.039 165 8 −0.000 534 8			
0.000X	−150.571 93	−0.898	−0.038 857 0 −0.000 555 3	0.301 0.480	−0.597 −0.418	
−0.001X	−150.572 78		−0.038 557 0 +0.000 424 7			
−0.005X	−150.576 58		−0.037 368 +0.002 353 8			

<sup>a</sup>All results in a.u.  
<sup>b</sup>The results have been computed at the experimental distance of the OOH radical. The mass weighted coordinate system has been used as in Ref. 22.  
<sup>c</sup>Geometry of the OOH radical is as given in Ref. 22.

ingly the dipole moments of both states of the OOH radical. One can identify this difference as a signature of relaxation effects in this radical.

B. Hydroxy radical

Table II(a) reports the analytic derivatives of the OH radical. Table II(b) reports the finite field energies and dipole moment obtained. The Sadlej’s optimized basis for properties consisting of contracted 5*s*3*p*2*d* functions and oxygen and 3*s*2*p* functions for hydrogen has been used.<sup>23</sup> Since we are interested in the OH radical dipole moment, we start from the RHF of OH<sup>−</sup> obtained at the experimental distance of the OH radical.<sup>24</sup> Again, to make a detailed study, we have reported in each case the results at different stages of the calculation, in particular, at the zero valence Fock space sector for the anion OH<sup>−</sup>. We have chosen the two active holes, which are degenerate 1Π orbitals in the model space of the one hole Fock space sector, and thus we report the doublet Π state of the OH radical which is the ground state. First, we observe that at the (0,0) sector for OH<sup>−</sup> ground

state, the dipole moment for the analytic derivative case is very similar to the finite field results using relaxed orbitals. It may be worth pointing out that the dipole moment of OH<sup>−</sup> depends on the coordinate system used. In this case the co-ordinate system used is given in Table II(b). We see that the results obtained in these two schemes vary for both the OH<sup>−</sup> and OH radical. It shows that the relaxation effects, although not large, are still significant. In the Table II(a) we have also reported the dipole moments of the ground state of the OH radical calculated by Paldus and co-workers using the UGA CCSD (Ref. 19) method using the same basis.

C. Formyloxyl radical

Another system studied is the HCOO radical, the results of which are reported in Table III. We have used the Huzinaga–Dunning double zeta basis set augmented by a set of polarized functions.<sup>25</sup> We have reported both analytical and finite field MRCCSD results. Again the closed shell ground state reference determinants of the anion of the HCOO radical is treated as a vacuum and the radical can thus

TABLE II. (a) Dipole moment values<sup>a</sup> using the analytic Fock space multireference coupled cluster approach for the OH anion and radical.<sup>b</sup> (b) Results<sup>a</sup> using the relaxed finite field approach for the OH anion and radical.<sup>c</sup>

(a) SCF dipole moment OH anion	Analytic SRCCSD dipole moment OH anion	Derivative ionization potential of the OH anion MRCCSD	Dipole moment of the OH radical ( <sup>2</sup> II) MRCCSD	Dipole moment of the OH radical ( <sup>2</sup> II) UGA-CCSD <sup>c</sup>	Dipole moment of the OH radical experimental <sup>d</sup>
0.504	0.441	0.180	0.621	0.641	0.649
(b) Field	SRCCSD energy (OH <sup>-</sup> ) anion	SRCCSD dipole moment (OH) anion	Ionization potential OH anion MRCCSD	Derivative ionization potential of the OH anion MRCCSD	Finite field dipole moment of the OH radical ( <sup>2</sup> II)
0.005	-75.661 39		0.053 78		
0.0025	-75.660 1		0.054 13		
0.000	-75.658 9	0.450	0.054 56	0.190	0.640
-0.0025	-75.657 82		0.055 08		
-0.005	-75.656 88		0.055 68		

<sup>a</sup>All results in a.u.<sup>b</sup>The results have been computed at the experimental distance of the OH radical. The mass weighted coordinate system has been used.<sup>c</sup>See Ref. 19.<sup>d</sup>See Ref. 24.<sup>e</sup>The results have been computed at the experimental distance (0.9697 a.u.) of the OH radical.

be considered as the ionized state of the close shell formylloxyl anion. The dominant configuration of the ground state  $^2B_2$  Formylloxyl radical is given as

$$[\text{core}]3a_1^22b_2^24a_1^25a_1^23b_2^1b_1^1a_2^26a_1^24b_2^1. \quad (23)$$

Distortion of the idealized  $C_{2v}$  symmetry along the coordinate for the asymmetric stretch of the C–O bonds allows the quasidegenerate determinant

$$[\text{core}]3a_1^22b_2^24a_1^25a_1^23b_2^1b_1^1a_2^26a_1^14b_2^2 \quad (24)$$

to mix with the previous configuration. Hence the radical has a multireference character and a MRCC description is appropriate for the radical. Even in the idealized  $C_{2v}$  structure, it is important to introduce the multireference character. With the RHF of the formylloxyl anion as vacuum, the model space of the radical contains two configurations with  $4b_2$  and  $6a_1$  as holes, respectively. Again, the experimental geometry of the HCOO radical has been used. One obtains the energies and properties of the lowest  $2B_2$  and the first excited state  $2A_1$  of the radical. The three core orbitals of the RHF of the anion and three highly virtual orbitals have been frozen during the calculation. The results show that the relaxation effects are

not negligible for this case too. For this case we have not reported the individual values of the Fock space sectors. Also reported in the table is the ground state dipole moments of the HCOO radical obtained by using the EOM-CCSD method.<sup>18</sup>

## V. CONCLUSION

In this paper we have reported the dipole moment of the open shell radicals using an analytic response approach based on the multireference Fock space approach and we have compared the results with the relaxed finite field results at the same level. We see that the effect of relaxation is not negligible for the cases we have investigated for the first order properties. This effect of relaxation can be included in the analytic MRCC response approach by using relaxed orbitals from a coupled perturbed Hartree–Fock approach. Such an approach will include the derivatives of one and two electron integrals over the molecular orbital basis in the response equation. Future developments along this line are in progress.

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