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Christopher E. Smith, Rollin A. King, and T. Daniel Crawford



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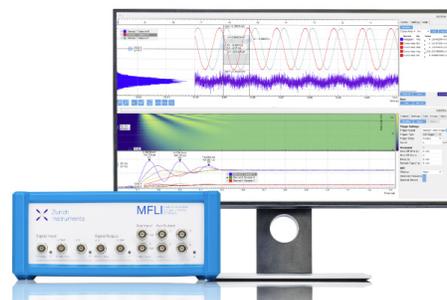
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# Coupled cluster methods including triple excitations for excited states of radicals

Christopher E. Smith

*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061*

Rollin A. King

*Department of Chemistry, Bethel University, St. Paul, Minnesota 55112*

T. Daniel Crawford

*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061*

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We report an extension of the coupled cluster iterative-triples model, CC3, to excited states of open-shell molecules, including radicals. We define the method for both spin-unrestricted Hartree–Fock (UHF) and spin-restricted open-shell Hartree–Fock (ROHF) reference determinants and discuss its efficient implementation in the PSI3 program package. The program is streamlined to use at most  $\mathcal{O}(N^7)$  computational steps and avoids storage of the triple-excitation amplitudes for both the ground- and excited-state calculations. The excitation-energy program makes use of a Löwdin projection formalism (comparable to that of earlier implementations) that allows computational reduction of the Davidson algorithm to only the single- and double-excitation space, but limits the calculation to only one excited state at a time. However, a root-following algorithm may be used to compute energies for multiple states of the same symmetry. Benchmark applications of the new methods to the lowest valence  ${}^2B_1$  state of the allyl radical, low-lying states of the CH and  $\text{CO}^+$  diatomics, and the nitromethyl radical show substantial improvement over ROHF- and UHF-based CCSD excitation energies for states with strong double-excitation character or cases suffering from significant spin contamination. For the allyl radical, CC3 adiabatic excitation energies differ from experiment by less than 0.02 eV, while for the  ${}^2\Sigma^+$  state of CH, significant errors of more than 0.4 eV remain. © 2005 American Institute of Physics. [DOI: 10.1063/1.1835953]

## I. INTRODUCTION

A variety of *ab initio* methods for computing molecular properties in electronically excited states have been developed over the last fifteen years, with a wide range of expected accuracy and computational expense. The simplest such approach is configuration interaction singles (CIS) or the Tamm–Dancoff approximation, in which the electronic Hamiltonian is diagonalized within the space of all singly excited determinants.<sup>1</sup> Although CIS excitation energies are often significantly in error relative to experiment, the corresponding wave functions can sometimes provide a reasonable starting point for higher-level corrections, including the (D) correction for excited-state electron correlation effects.<sup>2–5</sup> The random-phase approximation (RPA) [also known as time-dependent Hartree–Fock (TDHF)]<sup>6</sup> is similar to CIS in that it provides an approximate set of Hartree–Fock-type excited states, but is often viewed as incorporating the response into the orbitals while maintaining the single-determinant form of the wave function.<sup>5</sup> Among more advanced methods, the recently developed time-dependent density-functional theory (TDDFT) has had the greatest immediate impact.<sup>7</sup> TDDFT’s formulation is similar to that of RPA, but its predictions for singly excited valence states are far superior. On the other hand, modern functionals such as B3LYP are notorious in their failures for “delocalized” excitations, such as diffuse Rydberg and charge-transfer

states.<sup>8,9</sup> Among wave-function-based models that include electron correlation, second-order perturbation theory built upon a complete active space reference (CASPT2) has proved to be very useful for many applications.<sup>10</sup> A disadvantage of this approach, however, is the nonsystematic selection of active spaces and the steep (factorial) scaling of the CAS wave function with system size. Excited states are also accessible via coupled cluster theory,<sup>11–14</sup> one of the most reliable quantum chemical methods, through its equation-of-motion (EOM-CC) or linear-response (LRCC) variants.<sup>15,16</sup> For many organic molecules, the singles and doubles truncation of the method (EOM-CCSD) has been shown to reproduce experimental excitation energies for single-excitation-dominated states to within 0.2 eV.<sup>17</sup>

Unfortunately, the reliability and accuracy of most excited-state methods does not generally extend to radicals because of increases in both spin contamination and double-excitation character of excited-state wave functions. These problems are illustrated by the nine  $M_S = \frac{1}{2}$  determinants shown in Fig. 1 for three electrons distributed among nine spin-orbitals. Ignoring spatial symmetry, and given a doublet ground state described by the single Slater determinant shown in Fig. 1(a), the “closed-shell” determinants given in Fig. 1(b) and Fig. 1(c) are all eigenfunctions of the  $\hat{S}^2$  spin operator and may be classified as single- and double-excitations, respectively. As noted above, for excited states dominated by the singly excited determinants, methods such

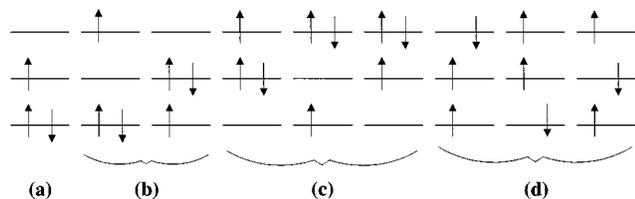


FIG. 1. Schematic diagram of the nine  $M_S = \frac{1}{2}$  Slater determinants arising from the distribution of three electrons in three spatial orbitals (six spin-orbitals): (a) The ground doublet state, used as a reference determinant; (b) two “closed-shell” doublet determinants, both classified as single excitations relative to (a); (c) three “closed-shell” doublet determinants classified as double excitations relative to (a); and (d) three “low-spin” determinants that contribute to both doublet and quartet states, one of which is a double excitation relative to (a).

as EOM-CCSD perform admirably, but for those dominated by the doubly excited determinants, at least triple excitations are required to properly account for electron correlation effects within pairs of electrons that are both excited relative to the reference configuration. In addition, as noted by Szalay and Gauss,<sup>18</sup> the “low-spin” determinants in Fig. 1(d) contribute to both doublet and quartet excited states. If an approximate excited-state wave function fails to include these determinants in a spin-adapted manner, large spin contamination effects may result, potentially rendering the computed properties meaningless. Indeed, Maurice and Head-Gordon designed the extended CIS (XCIS) method specifically to deal with such cases,<sup>4</sup> and the spin-restricted coupled cluster (SR-CC) method recently developed by Szalay and Gauss includes such effects explicitly.

Coupled cluster treatments of the properties of excited states including the effects of triple excitations have been explored by several researchers. The first was reported in the mid-1990s by Watts and Bartlett<sup>19–21</sup> who implemented an approximate EOM-CCSDT model (with a restriction to two-body elements in the triples blocks of the similarity-transformed Hamiltonian),<sup>19</sup> iterative EOM-CCSDT-1 and noniterative EOM-CCSD(T) models,<sup>20</sup> and iterative EOM-CCSDT-3 and noniterative EOM-CCSD( $\bar{T}$ ).<sup>21</sup> They applied these methods to a variety of singlet and triplet excited states from closed-shell reference states and found significant improvement over EOM-CCSD for states with significant double-excitation character. At around the same time, Christiansen, Koch, Jørgensen, and co-workers introduced the CC3 model,<sup>22–24</sup> which, like its EOM-CCSDT-1 and EOM-CCSDT-3 counterparts, is iterative and does not require explicit storage of triple-excitation amplitudes, but incorporates orbital relaxation effects through inclusion of singles at zeroth order (*vide infra*). The CC3 method has been applied to excitation energies out of closed-shell ground-states,<sup>22,23,25</sup> as well as to a variety of ground-state properties, including dipole moments<sup>26</sup> and both static- and frequency-dependent polarizabilities<sup>23,27–29</sup> and hyperpolarizabilities.<sup>30</sup> These same researchers have also developed a noniterative method triples method known as CCSDR(3), which is closely related to the CC3 approach.<sup>31</sup> In 2001, Kucharski and co-workers<sup>32</sup> and Kowalski and Piecuch<sup>33,34</sup> independently implemented the first full EOM-CCSDT method. In addition, Stanton and

Saeh developed a variant of the EOMIP-CCSD method (EOM-CCSD for ionized states) that is applicable to radicals and implicitly includes triple-excitation effects,<sup>35</sup> and Musial, Kucharski, and Bartlett developed the EOMIP-CCSDT method which explicitly includes triples,<sup>36</sup> though these methods have not been used to explicitly calculate excitation energies. Finally, we note that Piecuch and co-workers have extended the method of moments coupled cluster approach<sup>37</sup> to excited states, including corrections for triple and quadruple excitations.<sup>38–40</sup>

The purpose of the present work is to develop an open-shell version of the CC3 method and to benchmark its effectiveness in describing excited states of radicals. As noted above, such states often present greater difficulty than their closed-shell counterparts, and thus we anticipate that triple excitations should have even greater impact on the computed transition energies. We have implemented this method for both spin-unrestricted Hartree–Fock (UHF) and spin-restricted open-shell Hartree–Fock (ROHF) reference determinants and have applied it to a number of small molecules, including the allyl and nitromethyl radicals. This is the first time that an equation-of-motion (linear response) CC method for excitation energies that includes any treatment of connected triple excitations has been implemented for open-shell systems.

## II. THEORY

The CC3 model is an approximation to the full coupled cluster singles, doubles, and triples (CCSDT) approach defined based on a perturbation breakdown of the CCSDT amplitude equations that requires that single excitations are treated as zeroth order and triple excitations as second order in the perturbation potential.<sup>24</sup> The first requirement stems from the fact that single excitations, while second order in a standard many-body perturbational analysis of the correlation energy, become first order in the perturbation potential in the case of non-Hartree–Fock orbitals, and zeroth order in an external (e.g., electric or magnetic field) potential. In addition, the desired pole structure of frequency-dependent response functions motivates the development of methods in which orbital response contributions are ignored to avoid artifactual poles introduced by the Hartree–Fock reference function itself. Thus, the singles play a pivotal role as orbital relaxation parameters, and thus should be included without truncation. The second requirement is motivated by efficiency considerations; assignment of triples to second-order leads to amplitude equations in which the triples do not couple into themselves. As a result, although the CC3 amplitudes must be determined iteratively, explicit storage of the complete set of triples amplitudes in each iteration is not necessary. In addition, the algebraic equations scale nominally as  $O(N^7)$  at most, similar to the popular noniterative triples approximation, CCSD(T), and the closely related iterative CCSDT- $n$  methods of Bartlett and co-workers.<sup>41–43</sup>

As discussed by Christiansen *et al.*,<sup>23</sup> CC3 excitation energies are obtained as the eigenvalues of a nonsymmetric matrix (the “Jacobian”), which is an approximation to the CCSDT similarity-transformed Hamiltonian:

$$\bar{\mathbf{H}}_{\text{CC3}} = \begin{pmatrix} \langle S | [\hat{H} + (\hat{H}T_2)_c] | S \rangle & \langle S | \hat{H} | D \rangle & \langle S | \hat{H} | T \rangle \\ \langle D | [\hat{H} + (\hat{H}T_2)_c + (\hat{H}T_3)_c] | S \rangle & \langle D | [\hat{H} + (\hat{H}T_2)_c] | D \rangle & \langle D | \hat{H} | T \rangle \\ \langle T | (\hat{H}T_2)_c | S \rangle & \langle T | \hat{H} | D \rangle & \langle T | \hat{H} | T \rangle \end{pmatrix}, \quad (1)$$

where  $S$ ,  $D$ , and  $T$  are all singly, doubly, and triply excited determinants, respectively,  $F$  is the one-electron spin-orbital Fock operator, and  $T_n$  denotes the  $n$ th excited cluster operator obtained by solving the ground-state CC3 amplitude equations (see Refs. 23 and 24). In addition,  $\hat{H}$  is the  $T_1$ -similarity-transformed operator,

$$\hat{H} = \exp(-T_1)H \exp(T_1), \quad (2)$$

and the subscript  $c$  indicates that only connected diagrams are included. Note that the equation above for  $\bar{\mathbf{H}}_{\text{CC3}}$  implicitly includes only those matrix elements for which the Hamiltonian is connected (in the diagrammatic sense) to the excited determinant on the right (*vide infra*).

Because we are generally interested only in the lowest few eigenvalues of the above matrix, these could be obtained by straightforward application of the Davidson algorithm, which involves repeated application of  $\bar{\mathbf{H}}_{\text{CC3}}$  to a set of guess vectors,  $\mathbf{C}$ ,

$$\sigma = (\bar{\mathbf{H}}_{\text{CC3}}\mathbf{C})_c. \quad (3)$$

Such an approach is computationally inefficient, however, because it would require explicit storage of the triples components of the  $\sigma$  and  $\mathbf{C}$  vectors. Instead, as noted by Christiansen *et al.*,<sup>23</sup> one may adopt a Löwdin-type partitioning of the CC3 eigenvalue equation,

$$\begin{pmatrix} \mathbf{H}_{PP} & \mathbf{H}_{PQ} \\ \mathbf{H}_{QP} & \mathbf{H}_{QQ} \end{pmatrix} \begin{pmatrix} \mathbf{C}_P \\ \mathbf{C}_Q \end{pmatrix} = \omega \begin{pmatrix} \mathbf{C}_P \\ \mathbf{C}_Q \end{pmatrix}, \quad (4)$$

where  $P$  denotes the direct sum of the singles and doubles spaces and  $Q$  denotes the triples space. This leads to a pair of matrix-vector equations:

$$\mathbf{H}_{PP}\mathbf{C}_P + \mathbf{H}_{PQ}\mathbf{C}_Q = \omega\mathbf{C}_P \quad (5)$$

and

$$\mathbf{H}_{QP}\mathbf{C}_P + \mathbf{H}_{QQ}\mathbf{C}_Q = \omega\mathbf{C}_Q. \quad (6)$$

Solving the second set of equations for  $\mathbf{C}_Q$  and inserting the result into the first set leads to a new eigenvalue equation in only the  $P$  space:

$$[\mathbf{H}_{PP} + \mathbf{H}_{PQ}(\omega\mathbf{1}_{QQ} - \mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP}]\mathbf{C}_P = \omega\mathbf{C}_P, \quad (7)$$

where  $\mathbf{1}_{QQ}$  denotes the identity matrix in the  $Q$  space. The matrix inverse appearing in Eq. (7) is trivial to evaluate as long as  $\mathbf{H}_{QQ} = \langle T | F | T \rangle$  is diagonal, which is the case for canonical Hartree-Fock or semicanonical non-Hartree-Fock orbitals. One repercussion of the use of Eq. (7) to determine the eigenvalue  $\omega$  is that, because the  $P$ -space matrix on the left-hand side of the equation depends on the eigenvalue itself, one may use the Davidson algorithm to determine only one excited state at a time. This is discussed in more detail below.

Using Eq. (1) and Eq. (7), the CC3 sigma singles and doubles equations become

$$\sigma_1^{\text{CC3}} = \sigma_1^{\text{CCSD}} + \langle S | (HX_3)_c | 0 \rangle + \langle S | (HY_3)_c | 0 \rangle \quad (8)$$

and

$$\begin{aligned} \sigma_2^{\text{CC3}} = & \sigma_2^{\text{CCSD}} + \langle D | (\hat{H}X_3)_c | 0 \rangle + \langle D | (\hat{H}Y_3)_c | 0 \rangle \\ & + \langle D | ([HC_1]_c T_3)_c | 0 \rangle, \end{aligned} \quad (9)$$

respectively. In Eqs. (8) and (9) above,  $\sigma^{\text{CCSD}}$  refers to the corresponding EOM-CCSD equations, which have been given several times in the literature (see, for example, Ref. 16). The five additional terms involve the effective triple excitations,  $X_3$ ,  $Y_3$ , and  $T_3$ , which may be written as

$$D_3(\omega)X_3 = \langle T | (\hat{U}'T_2)_c | 0 \rangle, \quad (10)$$

$$D_3(\omega)Y_3 = \langle T | (\hat{U}C_2)_c | 0 \rangle, \quad (11)$$

and

$$D_3(0)T_3 = \langle T | (\hat{U}T_2)_c | 0 \rangle, \quad (12)$$

where  $\hat{U}$  is the  $T_1$ -similarity-transformed two-electron component of the Hamiltonian,  $\hat{U}' = (\hat{U}C_1)_c$ , and  $D_3(\omega)$  is a three-electron orbital-energy denominator, shifted by the current guess at the eigenvalue,  $\omega$ . All three of these classes of triples may be represented by the antisymmetrized diagrams shown in Fig. 2(a), with appropriate substitutions for the two-electron and double-excitation vertices. (See Ref. 11 for a detailed explanation of how to interpret such diagrams algebraically.) Similarly, the contributions of these triples to Eqs. (8) and (9) are shown in the generalized diagrams in Figs. 2(b) and 2(c), respectively. We note that these diagrams are identical in structure to those required for the well-known (T) correction.

Each  $X_3$ ,  $Y_3$ , and  $T_3$  triples amplitude depends on six orbital indices, three occupied and three virtual. To avoid explicit storage of these amplitudes, we follow the same strategy used by Rendell, Lee, and Kormornicki and compute batches of amplitudes for fixed combinations of the occupied orbitals.<sup>44</sup> Furthermore, as the diagrams in Fig. 2 suggest, our implementation of Eqs. (8)–(12) makes use of general functions for constructing these batches and then determining their contributions to  $\sigma_1$  and  $\sigma_2$  on the fly. Specifically, in each iteration of the Davidson algorithm, we carry out the following steps:

- (1) Compute the necessary  $\hat{U}'$  and  $(HC_1)_c$  intermediates using the current single-excitation guess vector,  $C_1$ .
- (2) Loop over all combinations of three unique occupied indices.

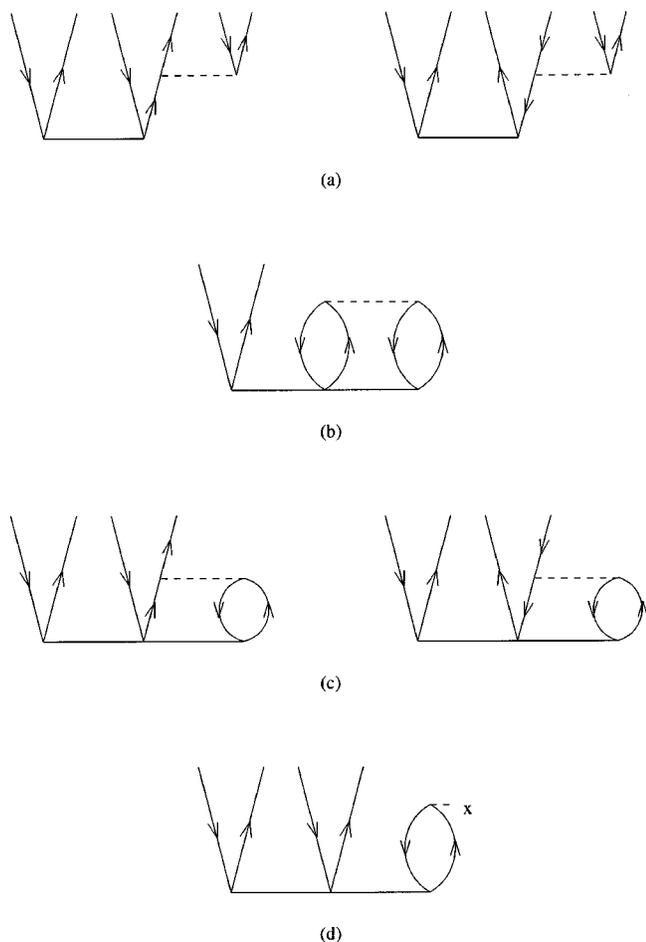


FIG. 2. Generalized antisymmetrized diagrammatic representations of expressions for (a)  $X_3$ ,  $Y_3$  and  $T_3$  triples given in Eqs. (10), (11), and (12); (b) triples contributions to Eq. (8); (c) triples contributions to Eq. (9) from two-electron intermediates; (d) triples contributions to Eq. (9) from the occupied-virtual block of the Fock matrix for non-Hartree-Fock references (e.g., ROHF).

- (3) Compute all  $X_3$  amplitudes for the given occupied-index combination using  $\hat{U}'$  and the ground-state  $T_2$  amplitudes in Eq. (10) and determine their contributions to Eqs. (8) and (9).
- (4) Compute all  $Y_3$  amplitudes for the given combination using  $\hat{U}$  and the current  $C_2$  guess vector in Eq. (11) and add their contributions to Eqs. (8) and (9).
- (5) Compute the ground-state  $T_3$  amplitudes for the given combination using  $\hat{U}$  and the ground-state  $T_2$  amplitudes in Eq. (12) and determine their contributions to Eq. (9).
- (6) Return to step (2) for the next combination of occupied orbitals.

Once  $\sigma_1$  and  $\sigma_2$  have been computed for the current guess vector, the remaining steps of the Davidson algorithm proceed as usual for EOM-CCSD calculations. Because the value of  $\omega$  changes in each iteration, if  $\sigma$  vectors from previous iterations are used, the Davidson subspace Hamiltonian (referred to as the  $G$  matrix in the literature<sup>45</sup>) will be comprised of dot products involving  $\sigma$  vectors corresponding to different values of  $\omega$ . As the number of  $\sigma$  vectors increases, the procedure can become unstable or converge to

an energy with significant error. This problem of reusing  $\sigma$  vectors is corrected by periodic “collapse” of the set of guess vectors to a single guess, with recomputation of the corresponding  $\sigma$  vector. We have found that for the excited states studied in this work, collapse after every eight iterations works efficiently.

We have also implemented a root-following algorithm to converge the solutions of excited states which are not the lowest of their spatial symmetry. At each iteration of the Davidson algorithm, the eigenvectors of the  $G$  matrix are used to construct the current best-guesses for the eigenvectors of  $\bar{\mathbf{H}}_{\text{CC3}}$  (constructed only within the singles and doubles space). The desired eigenvector of  $G$  is chosen to be the one with maximum overlap with the converged EOM-CCSD eigenvector of the desired state.

We have implemented Eqs. (8)–(12) in the open-source PSI3 program package<sup>46</sup> using a spin-factored/spin-orbital approach that is useful for applications to excited-states of open-shell systems with either UHF or ROHF reference wave functions. The method is directly comparable to that described by Watts, Gauss, and Bartlett for the CCSD(T) method, for example.<sup>47</sup> For UHF orbitals, the implementation is straightforward and requires no special considerations beyond those described above. For ROHF orbitals, however, three complications should be noted. First, because the spin-orbital expression for the Fock operator appearing in Eq. (1) is not diagonal in the occupied–occupied and virtual–virtual blocks, we first semicanonicalize the ROHF orbitals,<sup>47,48</sup> resulting in an UHF-like reference determinant (though it remains an eigenfunction of  $\hat{S}^2$ ). This allows a noniterative construction of the triples amplitudes, thus avoiding their explicit storage. This same approach is used in a number of ROHF-CCSD(T) implementations.<sup>47,49</sup> Second, unlike for UHF orbitals, the occupied-virtual block of the Fock matrix is nonzero in a ROHF orbital basis, giving rise to additional  $\mathcal{O}(N^6)$  terms in Eq. (9) of the form shown in Fig. 2(d). (Similar terms also arise in the ground-state CC3 amplitude equations, and these are included in our ROHF-CC3 implementation.)

Third, we note a potential complication in the fundamental definition of CC3 for ROHF reference wave functions. In the perturbational analysis used to develop CC3 in Refs. 23 and 24, the zeroth-order Hamiltonian was taken to be the Fock operator, a typical approach for RHF- or UHF-based many-body perturbation theory (MBPT). For ROHF reference determinants, however, one could instead choose to shift the non-zero occupied-virtual blocks of  $F$  into the perturbation, thus defining ROHF-CC3 in direct analogy to the ROHF-MBPT and ROHF-CCSD(T) schemes of Bartlett and co-workers.<sup>47,48,50</sup>

However, as mentioned earlier, the CC3 method was also defined to include single-excitation contributions at zeroth order in the perturbation potential because of their unique role as orbital relaxation parameters. This suggests instead that the occupied-virtual blocks of the Fock matrix, which are the leading contributions to the singles amplitudes equations in a ROHF orbital basis, should instead be treated as zeroth order. Such an approach would require a term that

TABLE I. CCSD and CC3 vertical and adiabatic excitation energies (in eV) of the valence  ${}^2B_1$  state of the allyl radical, computed at the CCSD/cc-pVDZ optimized  $C_{2v}$  geometry for the ground state (vertical) and the cc-pVDZ/EOM-CCSD optimized geometry for the excited state (adiabatic). The experimental UV absorption maximum reported in Ref. 71 is 3.05 eV.

	ROHF						UHF					
	CCSD			CC3			CCSD			CC3		
	Vertical	$T_e$	$T_0$									
cc-pVDZ	3.427	3.171	3.110	3.387	3.085	3.023	3.634	3.457	3.395	3.440	3.172	3.111
aug-cc-pVDZ	3.378	3.125	3.064	3.342	3.042	2.980	3.580	3.400	3.339	3.393	3.123	3.062
cc-pVTZ	3.400	3.201	3.140	3.351	3.099	3.037	3.634	3.518	3.456	3.402	3.187	3.125

couples  $T_3$  into itself be included in the amplitude equations, namely,

$$D_3 T_3 \leftarrow \langle T | (FT_1 T_3)_c | 0 \rangle. \quad (13)$$

As a result, either explicit storage of the triples amplitudes or an iterative  $\mathcal{O}(N^8)$  algorithm would be required, thus rendering the method essentially useless.<sup>51</sup>

Given this choice between two variants of ROHF-CC3—one that scales similarly to its UHF-CC3 counterpart, but does not include occupied-virtual Fock contributions in zeroth-order vs one that includes all such terms but requires dramatically greater storage or computational time—we have chosen to *define* the ROHF-CC3 method such that the term in Eq. (13) is ignored. It is likely that this term will have little to no numerical impact on ground-state energies or excitation energies, though for response properties it could be more significant due to the presence of  $T_1$  (which will become a perturbed  $T_1$  in the response function) in Eq. (13).

### III. BENCHMARK CALCULATIONS

We have performed numerical tests of the ROHF- and UHF-CC3 excitation energy approach described above using a number of representative open-shell systems, including the CH and  $\text{CO}^+$  diatomics, the lowest valence  ${}^2B_1$  state of the allyl radical, and three low-lying states of the nitromethyl radical. Each of these cases involves, to varying degrees, the double-excitation and/or spin-contamination complications described in the Introduction. Unless otherwise specified, all calculations were carried out using the PSI3 program package.<sup>46</sup>

#### A. The valence ${}^2B_1$ state of the allyl radical

The excited states of the allyl radical provided our initial motivation for developing the UHF- and ROHF-CC3 approaches described above because of their interesting challenges to excited-state methods. The absorption maximum in the experimental UV spectrum occurs at 3.05 eV, but EOM-CCSD methods predict considerably higher values (*vide infra*). The three valence allyl  $\pi$  molecular orbitals transform as the  $b_1$  (doubly occupied),  $a_2$  (singly occupied), and  $b_1$  (unoccupied) irreducible representations of the  $C_{2v}$  point group to which the  ${}^2A_2$  ground-state equilibrium structure corresponds. As first shown by Yamaguchi, however, the  ${}^2B_1$  excited state breaks symmetry by twisting the end methylene groups, leading to a  $C_2$ -symmetric excited-state structure (properly labeled  ${}^2B$  symmetry).<sup>52</sup> The corresponding verti-

cal excitation is dominated by the two determinants shown in Fig. 1(b), both of which are singles relative to the reference state and are thus well described at the EOM-CCSD level. However, two of the three doubly excited determinants shown in Fig. 1(c) also contribute significantly and at least triple excitations are required to treat them adequately. We note that the third determinant in Fig. 1(c) and none of the “low-spin” determinants in Fig. 1(d) contribute to the  ${}^2B_1$  state due to symmetry constraints.

Table I summarizes the CCSD and CC3 excitation energies (vertical and adiabatic) computed using the Dunning correlation-consistent polarized-valence double- and triple-zeta basis sets (cc-pVDZ and cc-pVTZ, respectively) as well as the cc-pVDZ basis augmented with diffuse  $s$ ,  $p$ , and  $d$ -type functions (aug-cc-pVDZ).<sup>53–55</sup> The adiabatic excitation energies were computed using ground- and excited-state optimized structures obtained at the CCSD and EOM-CCSD levels of theory with the aug-cc-pVDZ basis set using analytic energy gradients<sup>56,57</sup> in the ACESII program package.<sup>58</sup> Zero-point energies were determined at these same levels of theory using harmonic vibrational frequencies computed using analytic energy second derivatives at the CCSD level for the ground state<sup>59,60</sup> and finite-differences of analytic energy first derivatives<sup>57</sup> in the excited state.

We first note that the basis set has only a small impact on the computed excitation energy (less than 0.06 eV in all cases), suggesting that the Rydberg character of the  ${}^2B_1$  state is small. However, the ROHF-CCSD and UHF-CCSD excitation energies differ by more than 0.2 eV for all three basis sets, indicative of significant spin-contamination in the latter. At the CC3 level, however, these differences are mostly removed, with both ROHF- and UHF-CC3 predicting a vertical excitation energy of 3.35–3.40 eV. [We note that “spin-flip” EOM-CCSD (Ref. 61) and QRHF-EOM-CCSD calculations<sup>16,62,63</sup> for this state, performed at the same geometry with a 6-31++G\*\* basis set give vertical excitation energies of 3.387 and 3.48 eV, in good agreement with these results.<sup>64</sup>] The adiabatic excitation energies,  $T_e$  and  $T_0$ , shift significantly downward ( $\approx 0.2$ – $0.3$  eV) relative to the vertical transitions because of the substantial geometry change upon excitation. While the UHF-CCSD values of  $T_e$  and  $T_0$  are too high (approximately 0.3–0.4 eV above experiment), the corresponding UHF-CC3 values are in superb agreement with the experimental absorption maximum. The ROHF-CCSD adiabatic excitation energies, on the other hand, differ

TABLE II. CCSD and CC3 vertical excitation energies (in eV) of  $\text{CO}^+$  and CH radicals with ROHF and UHF reference determinants.<sup>a</sup>

State	CCSD		CC3		MRCI <sup>b</sup>	Expt. <sup>c</sup>	
	UHF	ROHF	UHF	ROHF			
$\text{CO}^+$	$^2\Pi$	3.532	3.229	3.330	3.290	3.30	3.264
	$^2\Sigma^+$	6.192	6.002	5.811	5.725	5.88	5.819
CH	$^2\Delta$	3.221	3.215	3.173	3.160	2.96	2.880
	$^2\Sigma^-$	4.404	4.230	3.643	3.576	3.31	...
	$^2\Sigma^+$	5.312	5.199	4.517	4.472	4.03	3.943

<sup>a</sup>Calculations performed at the experimental ground-state geometries of  $r(\text{C}-\text{O})=1.115 \text{ \AA}$  and  $r(\text{C}-\text{H})=1.1198 \text{ \AA}$ . Core orbitals were held frozen in the CCSD and CC3 calculations.

<sup>b</sup>MRCI results from Ref. 18.

<sup>c</sup>Experimental results as reported in Ref. 4.

little from their ROHF-CC3 counterparts, again indicative of reduced spin contamination in the ROHF-based calculations.

## B. The CH and $\text{CO}^+$ radicals

The CH and  $\text{CO}^+$  radicals have been considered previously by Maurice and Head-Gordon with the ROCIS and XCIS methods<sup>4</sup> and by Szalay and Gauss for the SR-CCSD method.<sup>18</sup> Table II summarizes CCSD and CC3 excitation energies for several low-lying states of both molecules using the Sadlej-pVTZ basis set<sup>55,65</sup> for comparison to MRCI data reported in Ref. 18 and the extrapolated experimental results reported in Ref. 4.

For  $\text{CO}^+$ , the large difference between the UHF-CCSD and ROHF-CCSD excitation energies (0.2–0.3) is indicative of significant spin contamination in the former, as noted by Szalay and Gauss. At the CC3 level, this difference is mostly eliminated, suggesting that the spin contamination is greatly reduced by the inclusion of triples, as one would expect. The comparison between CC3 and the MRCI excitation energies is excellent, with differences of less than 0.1 eV for both states of  $\text{CO}^+$  considered.

The CH radical presents a considerably more difficult test of the CC3 method. The  $^2\Delta$  state is dominated by “low-spin” determinants analogous to the first two shown in Fig. 1(d). It is therefore reasonably well described even at the CCSD level, and the corresponding CC3 excitation energies shift downward by only about 0.05 eV, all in agreement with the 2.96 eV MRCI excitation energy. For the  $^2\Sigma^-$  state, however, the third determinant in Fig. 1(d), which is a double excitation relative to the reference, contributes significantly. Thus, the UHF- and ROHF-CCSD excitation energies differ from the MRCI value of 3.31 eV by approximately 1.0 eV. The CC3 approach improves the comparison with MRCI considerably, though the error remains  $\approx 0.3$  eV. (We note that both the  $^2\Delta$  and  $^2\Sigma^-$  states were computed as  $A_2$  states in  $C_{2v}$  symmetry with our codes.) For the  $^2\Sigma^+$  state, another double excitation contribution becomes important, analogous to the second determinant shown in Fig. 1(c). The CCSD results are essentially useless, with errors relative to MRCI of 1.2–1.3 eV. CC3 again improves upon this result, but the discrepancy is still approximately 0.5 eV. It is likely that a

TABLE III. CCSD and CC3 vertical excitation energies (in eV) of three low-lying states of the nitromethyl radical relative to the  $^2B_1$  ground state.<sup>a</sup> ROCIS, XCIS, and G2 results from Ref. 4.

State	CCSD		CC3		ROCIS <sup>b</sup>	XCIS <sup>b</sup>	G2	Expt.
	UHF	ROHF	UHF	ROHF				
$^2B_2$	2.403	2.401	2.048	2.033	4.557	2.607	1.990	...
$^2A_2$	2.624	2.627	2.418	2.407	6.183	1.512	2.476	1.591 <sup>b</sup>
$^2A_1$	2.880	2.870	2.545	2.533	4.688	2.928	2.473	...
$^2B_1$	5.508	5.482	5.296	5.278	...	...	...	4.25 <sup>c</sup>

<sup>a</sup>Computed at the UMP2/6-31++G( $d,p$ ) optimized geometry using the Sadlej-pVTZ basis set with core orbitals frozen.

<sup>b</sup>Computed using a 6-31+G( $d$ ) basis set at the MP2/6-31++G( $d,p$ ) geometry.

<sup>c</sup>Reference 66.

<sup>d</sup>Reference 67.

full treatment of triple excitations at the EOM-CCSDT level will be necessary to reduce the error to less than 0.2 eV.

## C. Low-lying doublet states of the nitromethyl radical

Very little is known experimentally about the excitation spectrum of the nitromethyl radical. In the early 1990s, Metz, Cyr, and Neumark examined the ground  $^2B_1$  and excited  $^2A_2$  states using photoelectron spectroscopy of the  $\text{CH}_2\text{NO}_2^-$  anion and *ab initio* calculations and determined that the  $^2A_2$  state lies 1.591 eV above the ground state with a geometry similar in structure to the anion.<sup>66</sup> Later, Cyr and co-workers reported a photodissociation of nitromethyl following its production from the anion,<sup>67</sup> and tentatively estimated that the second  $^2B_1$  state lies  $\approx 4.25$  eV above the ground state based on earlier estimates of the dissociation threshold from matrix isolation studies by Jacox.<sup>68</sup> Later, Maurice and Head-Gordon used the nitromethyl radical as a benchmark case for the ROCIS and XCIS methods, though they made no comparison between their results and the limited experimental data.<sup>4</sup>

We have computed vertical excitation energies of  $\text{CH}_2\text{NO}_2$  relative to its  $^2B_1$  ground state at the CCSD and CC3 levels of theory using the Sadlej-pVTZ basis.<sup>65</sup> For comparison to the work of Maurice and Head-Gordon, all computations were carried out at the MP2/6-31++G( $d,p$ ) optimized geometry.<sup>4,66</sup> Core orbitals of the C, N, and O atoms were held frozen in all coupled cluster calculations.

Table III summarizes the CCSD and CC3 vertical excitation energies for comparison to the ROCIS, XCIS, and G2 results of Maurice and Head-Gordon.<sup>4</sup> For all four states, the choice of reference determinant makes little difference at either the CCSD or CC3 levels, suggesting that spin contamination in these states is minimal. However, the difference between CCSD and CC3 results is large, up to 0.37 eV for the  $^2B_2$  state, indicating that some double-excitation character is present in all four states. This is further supported by the ROCIS and XCIS results of Maurice and Head-Gordon. The ROCIS method gives poor results off by up to several eV, and the XCIS method, while a significant improvement over ROCIS, is still significantly in error for the  $^2B_2$ ,  $^2A_2$ , and  $^2A_1$  states. Interestingly, none of the methods compares well to the experimental result of 1.591 eV for the  $^2A_2$  state,

except for the XCIS method whose good agreement of 0.08 eV is likely fortuitous. It is likely that optimization of the excited state geometry would lower the CC3 result of 2.4 eV, though it is not clear that this would be sufficient to bring accord to theory and experiment for this state.

#### IV. CONCLUSIONS

We have developed an open-shell variant of the CC3 method for computing excitation energies of open-shell systems. The method is defined for both UHF and ROHF reference determinants, and we have implemented it in the open-source PS3 program package. The implementation is streamlined to use at most  $\mathcal{O}(N^7)$  computational steps and avoids storage of the triple-excitation amplitudes for both ground and excited states. The excitation-energy program makes use of a Löwdin projection formalism (comparable to that of earlier implementations) that allows computational reduction of the Davidson algorithm to only the single- and double-excitation space, but limits the calculation to only one excited state at a time.

Benchmark applications of the new methods to the lowest valence  ${}^2B_1$  state of the allyl radical, low-lying states of the CH and  $\text{CO}^+$  diatomics, and the nitromethyl radical show substantial improvement over ROHF- and UHF-based EOM-CCSD excitation energies for states with strong double-excitation character or cases suffering from significant spin contamination. Our future development efforts will focus on transition properties (such as oscillator strengths) and excited-state properties, including analytic energy gradients.

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