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The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties

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A comprehensive overview of the equation of motion coupled-cluster (EOM-CC) method and its application to molecular systems is presented. By exploiting the biorthogonal nature of the theory, it is shown that excited state properties and transition strengths can be evaluated via a generalized expectation value approach that incorporates both the bra and ket state wave functions. Reduced density matrices defined by this procedure are given by closed form expressions. For the root of the EOM-CC effective Hamiltonian that corresponds to the ground state, the resulting equations are equivalent to the usual expressions for normal single-reference CC density matrices. Thus, the method described in this paper provides a universal definition of coupled-cluster density matrices, providing a link between EOM-CC and traditional ground state CC theory. Excitation energy, oscillator strength, and property calculations are illustrated by means of several numerical examples, including comparisons with full configuration interaction calculations and a detailed study of the ten lowest electronically excited states of the cyclic isomer of C_4.

I. INTRODUCTION

In the past two decades, techniques based on the many-body perturbation theory (MBPT) of Brueckner and Goldstone[1] and the related infinite-order generalization known as the coupled-cluster (CC) approximation[2] have been used with much success to study the spectroscopic and thermodynamic properties of molecular systems.[3] This field has witnessed a considerable amount of both theoretical and algorithmic development, with the result that it is now a fairly routine matter to carry out calculations on medium-sized molecules using MBPT through fourth order or with infinite order CC approximations. In addition, studies of potential energy surfaces and molecular properties have been greatly facilitated by the development of methods for calculating derivatives of the MBPT and CC energy analytically.[4-15] Hence, application of MBPT and CC methods to the study of molecules in their ground electronic state is now a relatively mature field.

Quantum chemical treatments of electron correlation within MBPT and CC approximations have traditionally been based on a single Slater determinant that serves as a zeroth-order approximation to the wave function. In practice, this parameterization usually limits applications to molecular ground states or, more precisely, the lowest electronic state of a given symmetry and spin multiplicity. There are a number of reasons for this. First, if one wishes to use a reference state that is a relatively good approximation to the exact wave function, variationally optimal solutions such as self-consistent-field (SCF) determinants are recommended. While such a reference function can be evaluated in a completely straightforward way for electronic ground states, variational collapse of the orbital optimization procedure usually presents problems when ex-

cited states are sought. However, CC methods that include a complete (exponential) treatment of single excitation effects exhibit a characteristic insensitivity to the choice of reference function.[16] By virtue of this property, the use of variationally optimal reference states is not as important for CC as it is for MBPT calculations. Therefore, acceptable reference functions can be constructed for special cases, namely those in which the state of interest is well described by a high-spin single-determinant electronic configuration. Perhaps the most popular and straightforward realization of this idea is the quasirestricted Hartree–Fock (QRHF) procedure advocated by Rittby and Bartlett[17] for the calculation of ionization potentials and subsequently applied to study potential energy surfaces and certain types of symmetry-breaking problems.[14,18] In this scheme, reference functions are constructed from a set of orbitals that have been optimized for a different state of the molecule, which may even differ in the number of electrons. The occupation numbers of the orbitals are then modified as needed to offer an approximation to the state of interest.

While QRHF and related strategies that exploit the approximate orbital invariance of CC theory[19] potentially provide a means to study excited states with many-body methods, applications of these techniques are limited to high-spin open-shell configurations, as mentioned in the preceding paragraph. Since many interesting electronic states do not belong to this category, these approaches do not provide a suitably general theoretical framework for the investigation of excited states. In particular, the vast majority of states accessed by optically allowed transitions from a closed-shell molecule in the ground electronic state are open-shell singlets. Short of an exact calculation, no single-determinant-based MBPT or CC method offers a qualitatively correct description of these systems, since two

determinants having equal weights in the final wave function are needed to properly treat the spin symmetry. Recent advances in Hilbert space multireference CC techniques[20] have led to a framework for performing calculations on open-shell singlets[21] (hereafter referred to as the two-determinant coupled-cluster method), a development that holds great promise for studying specific excited states within the framework of a many-body approach.

Alternatively, the development of direct methods—those in which a spectrum of electronic states is obtained in a single calculation—has been an active area of research in many-body theory for the last decade. For excitation energies, two such approaches are the Fock space multireference coupled-cluster (FSMRCC) approach[22] and the equation-of-motion coupled-cluster (EOM-CC) method.[23-26] In both of these methods, the excited state wave function is generated from some CC reference state [usually the coupled-cluster singles and doubles[27] (CCSD) wave function for the ground state] by the action of a wave operator. With respect to the two-determinant CC (TD-CC) approach of Balkova and Bartlett,[21] these methods have advantages and disadvantages. First, when used in conjunction with a closed-shell reference state, both FSMRCC and EOM-CC provide rigorously spin-adapted final state wave functions, while TD-CC does not. Furthermore, a common set of molecular orbitals is used to describe *all* electronic states in the direct approaches, resulting in considerable computational simplifications. This is particularly true if one is interested in calculating properties other than the energy, which is the principal subject of this paper. Nevertheless, when dynamic correlation effects dominate, the QRHF-type CC and TD-CC approaches are likely to be superior at a given level of truncation, as they focus upon a single electronic state and exploit the full exponential structure of the CC wave operator.[28]

For the most part, many-body based direct approaches have only been applied to the calculation of energy differences.[22,25] The purpose of this paper is to show that the EOM-CC approach may also be used to determine properties and transition probabilities between electronic states, provided one exploits the full structure of the theory. In particular, it will be demonstrated that the biorthogonal representation of the many-body problem afforded by EOM-CC offers a convenient formalism for evaluating properties other than the energy, as it obeys a special type of Hellman–Feynman condition similar to that used in the theory of CC energy gradients.[7-14] An aesthetic merit of the present approach is that it demonstrates an intimate relationship between the normal single-determinant ground state CC approach and EOM-CC, as the former may simply be viewed as a special case of the latter. Indeed, we will show that the equations for properties (in particular the definitions of the associated reduced density matrices) for both ground and excited states are identical.

In the following, a thorough description of the EOM-CC method as applied to the calculation of excitation energies and properties is presented, emphasizing connections to the more familiar single-determinant CC approach where appropriate. Following a discussion of the general theory, computational aspects of the approach are addressed, with particular attention paid to additional steps that are required when properties other than the energy are calculated. Finally, a number of applications of the method are documented, including comparisons with full configuration interaction calculations and representative computational timings. An overall assessment of EOM-CC and its applicability to chemical problems is presented in the final section of this paper.

II. GENERAL THEORY

In EOM-CC as well as many other approaches to excited states, final state wave functions are given by the simple parameterization

$$|\Psi_x\rangle = \mathscr{R}|\Psi_g\rangle, \qquad (1)$$

where the subscripts x and g refer to excited and ground state wave functions, respectively, and $\mathscr{R}$ is a linear (CI-like) excitation operator

$$\mathscr{R} = \mathscr{R}_0 + \mathscr{R}_1 + \mathscr{R}_2 + \mathscr{R}_3 + \cdots, \qquad (2)$$

$$\mathscr{R}_n = \frac{1}{n!^2} \sum r_{ijk\cdots}^{abc\cdots} a^\dagger i b^\dagger j c^\dagger k \cdots. \qquad (3)$$

Above and in the following we adhere to the usual convention that $i,j,k,\ldots$ represent orbitals that are occupied in the Slater determinant reference function, while $a,b,c,\ldots$ refer to unoccupied orbitals. The indices $p,q,r,\ldots$ denote generic orbitals that may be either occupied or unoccupied. In EOM-CC, the ground state wave function is given by the coupled-cluster approximation

$$|\Psi_g\rangle = \exp(T)|\Phi_0\rangle, \qquad (4)$$

where $|\Phi_0\rangle$ is an arbitrary single Slater determinant, usually chosen to be the SCF solution.

Insertion of Eqs. (1) and (4) into the Schrödinger equation yields

$$H\mathscr{R} \exp(T)|\Phi_0\rangle = E\mathscr{R} \exp(T)|\Phi_0\rangle. \qquad (5)$$

Since both $\mathscr{R}$ and T are excitation operators, they necessarily commute and Eq. (5) therefore may be rewritten as

$$\exp(-T)H \exp(T)\mathscr{R}|\Phi_0\rangle = E\mathscr{R}|\Phi_0\rangle, \qquad (6)$$

$$[\exp(-T)H \exp(T) - E]\mathscr{R}|\Phi_0\rangle = 0, \qquad (7)$$

i.e., an eigenvalue problem involving an effective Hamiltonian ($\bar{H}$) obtained from the similarity transformation

$$\bar{H} \equiv \exp(-T)H \exp(T). \qquad (8)$$

At this point, it should be noted that EOM-CC is a formally exact procedure, as transformations of this kind do not change the eigenvalues of the full Hamiltonian. However, in practical calculations, the T and $\mathscr{R}$ operators are necessarily truncated to some tractable level of excitation (usually singly and doubly substituted determinants, which define the EOM-CCSD approximation), thereby compromising the exactness of the method.[29] Nevertheless, it should be evident that EOM-CCSD provides an exact

TABLE I. Explicit equations for matrix elements of the one- and two-body components of the CCSD effective Hamiltonian, $\bar{H}$, in the spin–orbital basis. The amplitudes are given in terms of Fock matrix elements (f_{pq}), antisymmetrized two-electron integrals, and coupled-cluster T_1 and T_2 amplitudes (t_i^a and t_{ij}^{ab}, respectively). The τ quantities are defined by $\tau_{ij}^{ab} \equiv t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a$, and the antisymmetric permutation operator $P(pq)$ is defined by Eq. (33). The two-electron terms in the leftmost column are understood to be antisymmetrized, and the Einstein summation convention is used throughout.

Matrix element	Shorthand notation	Defining equation
$\langle a\|\bar{H}\|i\rangle$	$\mathscr{F}_{ai}$	0
$\langle a\|\bar{H}\|b\rangle$	$\mathscr{F}_{ab}$	$f_{ab} - f_{mb}t_m^a + t_m^f\langle ma\|fb\rangle - \frac{1}{2}\tau_{mn}^{ae}\langle mn\|be\rangle$
$\langle j\|\bar{H}\|i\rangle$	$\mathscr{F}_{ji}$	$f_{ji} + t_i^e f_{je} + t_m^e\langle jm\|ie\rangle + \frac{1}{2}\tau_{im}^{ef}\langle jm\|ef\rangle$
$\langle i\|\bar{H}\|a\rangle$	$\mathscr{F}_{ia}$	$f_{ia} + t_m^e\langle im\|ae\rangle$
$\langle ab\|\bar{H}\|ij\rangle$	$\mathscr{W}_{abij}$	0
$\langle kl\|\bar{H}\|ij\rangle$	$\mathscr{W}_{klij}$	$\langle kl\|ij\rangle + P(ij)t_j^e\langle kl\|ie\rangle + \frac{1}{2}\tau_{ij}^{ef}\langle kl\|ef\rangle$
$\langle ab\|\bar{H}\|cd\rangle$	$\mathscr{W}_{abcd}$	$\langle ab\|cd\rangle - P(ab)t_m^b\langle am\|cd\rangle + \frac{1}{2}\tau_{mn}^{ab}\langle mn\|cd\rangle$
$\langle ai\|\bar{H}\|bc\rangle$	$\mathscr{W}_{aibc}$	$\langle ai\|bc\rangle - t_m^a\langle mi\|bc\rangle$
$\langle ij\|\bar{H}\|ka\rangle$	$\mathscr{W}_{ijka}$	$\langle jk\|ia\rangle + t_i^e\langle jk\|ea\rangle$
$\langle ij\|\bar{H}\|ab\rangle$	$\mathscr{W}_{ijab}$	$\langle ij\|ab\rangle$
$\langle aj\|\bar{H}\|ib\rangle$	$\mathscr{W}_{ajib}$	$\langle aj\|ib\rangle + t_i^e\langle aj\|eb\rangle - t_m^a\langle mj\|ib\rangle$ $-(t_{im}^{ea} + t_i^e t_m^a)\langle mj\|eb\rangle$
$\langle ab\|\bar{H}\|ci\rangle$	$\mathscr{W}_{abci}$	$\langle ab\|ci\rangle + P(ab\cdots$ $+ t_{im}^{ab}\mathscr{F}_{mc} + t_i^e\mathscr{W}$ $- t_{ni}^{be}\langle mn\|ce\rangle]$
$\langle ia\|\bar{H}\|jk\rangle$	$\mathscr{W}_{iajk}$	$\langle ia\|jk\rangle + P(ij)t_{km}^{ae}\langle im\|je\rangle + \frac{1}{2}\tau_{jk}^{ef}\langle ia\|ef\rangle$ $+ t_{jk}^{ae}\mathscr{F}_{ie} + t_m^a\mathscr{W}_{imjk} - P(ij)t_j^e[\langle ia\|ek\rangle$ $- t_{mk}^{af}\langle im\|ef\rangle]$

treatment of two-electron systems, which is considered to be a highly desirable feature of quantum chemical methods.[30] One rather subtle point concerning the similarity transformation is that the wave operator is nonlinear and therefore includes configurations that lie outside the space defined by the truncation of the T operator. As a result, the eigenvalues of $\bar{H}$ within the space of singly and doubly substituted determinants are not the same as those of H, i.e., the configuration interaction singles and doubles (CISD) roots. The nonlinear transformation acts to "fold in" effects of higher excitations, thereby allowing superior results to be obtained in the same determinantal subspace.

The effective Hamiltonian ($\bar{H}$) that contains the EOM-CC energy levels is most conveniently expressed in the spin–orbital basis

$$\bar{H} = \sum_{pq}\mathscr{F}_{pq}p^\dagger q + \frac{1}{4}\sum_{pqrs}\mathscr{W}_{pqrs}p^\dagger q^\dagger sr + \cdots. \qquad (9)$$

The leading terms in the one- and two-body amplitudes ($\mathscr{F}$ and $\mathscr{W}$, respectively) are the corresponding Fock matrix elements and two-electron integrals, with remaining contributions coming from appropriate contractions between the Hamiltonian and the T amplitudes that parametrize $|\Psi_g\rangle$. A complete list of all one- and two-body $\mathscr{F}$ and $\mathscr{W}$ elements is presented in Table I. Note that $\bar{H}$ contains three- and higher-body operators, unlike the bare Hamiltonian itself. In a matrix representation, the effective Hamiltonian assumes the form

$$\bar{H} = \begin{pmatrix} E_{CC} & \cdots & \cdots \\ 0 & \ddots & \cdots \\ 0 & \vdots & \ddots \end{pmatrix}, \qquad (10)$$

where the zero entries follow from the condition that the T amplitudes obey the coupled-cluster equations

$$\langle \Phi_{ij\cdots}^{ab\cdots}|\bar{H}|\Phi_0\rangle = 0. \qquad (11)$$

As a result of this special structure, the ground state coupled-cluster solution is given by one root of $\bar{H}$, namely that for which $\mathscr{R} = \mathscr{R}_0 = 1$. Note that $\bar{H}$ is not Hermitian by virtue of the nonunitary nature of the coupled-cluster wave operator $\exp(T)$. As a result, each root of $\bar{H}$ is associated with two eigenvectors that correspond to distinct bra and ket states

$$\langle\tilde{\Psi}| = \langle\Phi_0|\mathscr{L}\exp(-T), \qquad (12)$$

$$|\Psi\rangle = \exp(T)\mathscr{R}|\Phi_0\rangle. \qquad (13)$$

$\mathscr{L}$ represents the left eigenvector of $\bar{H}$, which is of course a deexcitation operator

$$\mathscr{L} = \mathscr{L}_0 + \mathscr{L}_1 + \mathscr{L}_2 + \mathscr{L}_3 + \cdots, \qquad (14)$$

$$\mathscr{L}_n = \frac{1}{n!^2}\sum l_{abc\cdots}^{ijk\cdots}i^\dagger a j^\dagger b k^\dagger c \cdots. \qquad (15)$$

Due to the non-Hermitian nature of the EOM-CC approach, the bra and ket states are never simply Hermitian conjugates. This is true even in cases where the method is exact (i.e., EOM-CCSD for the hydrogen molecule) because intermediate normalization is used. However, the distinction between bra and ket states is not important if one is only interested in evaluating the excitation energies, as Eq. (7) may be solved directly without any consideration of the bra states.

Nevertheless, properties other than the energy can be evaluated within the framework of EOM-CC theory provided one considers both the bra and ket states. It follows from the general properties of non-Hermitian eigenvalue problems that these two sets of solutions satisfy the property of biorthogonality

$$\langle\tilde{\Psi}^{(i)}|\Psi^{(j)}\rangle = C\delta_{ij}, \qquad (16)$$

although the bra and ket states *are not* orthogonal among themselves. Choosing C to be unity[31] leads to the EOM-CC normalization condition

$$\langle\tilde{\Psi}|\Psi\rangle = 1, \qquad (17)$$

which allows one to write the energy in the illustrative functional form

$$E = \langle\tilde{\Psi}|H|\Psi\rangle \qquad (18)$$

$$= \langle\Phi_0|\mathscr{L}\bar{H}\mathscr{R}|\Phi_0\rangle. \qquad (19)$$

This is a special case of the generalized Hellman–Feynman property,[32] which is satisfied due to the stationary nature of the solutions with respect to variation of the $\mathscr{R}$ or $\mathscr{L}$ vectors

$$\theta = \langle\tilde{\Psi}|\Theta|\Psi\rangle, \qquad (20)$$

TABLE II. Elements of the reduced one-particle EOM-CCSD density matrix, expressed in the basis of spin orbitals. The equations listed below have a one-to-one correspondence with the equivalent diagrammatic expressions in Fig. 1. The expressions are listed in terms of the t amplitudes of the reference state, and the r and l amplitudes of the $\mathcal{R}$ and $\mathcal{L}$ eigenvectors. These equations apply to both the diagonal case ($\mathcal{R}$ and $\mathcal{L}$ correspond to the same state) and to transition densities (where $\mathcal{R}$ and $\mathcal{L}$ correspond to the two states of interest). For the ground state solution, $r_0 = 1$, and all r_i^a and r_{ij}^{ab} vanish. The Einstein summation convention is used.

	Shorthand notation	Defining equation
$\langle i^\dagger j \rangle$	ρ_{ij}	$-r_0[l_i^e t_e^j + \frac{1}{2} l_{fe}^{jm} t_{fe}^{im}] - r_i^e l_e^j - \frac{1}{2} r_{im}^{fe} l_{fe}^{jm} - t_i^f r_{m}^f l_{fe}^{ijm}$
$\langle a^\dagger b \rangle$	ρ_{ab}	$r_0[l_m^b t_a^m + \frac{1}{2} l_{mn}^{eb} t_{ea}^{mn}] + r_m^b l_a^m + \frac{1}{2} r_{mn}^{eb} l_{ea}^{mn} + t_n^b r_m^e l_{ea}^{mn}$
$\langle i^\dagger a \rangle$	ρ_{ia}	$r_0 l_a^i + l_{ae}^{im} r_e^m$
$\langle a^\dagger i \rangle$	ρ_{ai}	$r_0[t_{im}^{ae} l_e^m - t_i^e t_m^a l_e^m - \frac{1}{2} l_{in}^{ef} t_{mn}^{af} - \frac{1}{2} l_{ef}^{ef} t_i^e l_{ef}^{mn}] + r_i^a$
		$+ r_{im}^{ae} l_e^m - r_m^a t_i^e l_e^m - t_i^e r_m^a l_e^m - \frac{1}{2} r_m^{af} l_{ef}^{mn} - \frac{1}{2} t_{in}^{ef} r_m^a l_{ef}^{mn}$
		$- \frac{1}{2} r_{mn}^{af} t_i^e l_{ef}^{mn} - \frac{1}{2} t_{mn}^{ef} r_i^a l_{ef}^{mn} - t_i^e t_m^a r_n^f l_{ef}^{mn} + t_{im}^{ae} r_n^f l_{ef}^{mn}$

where Θ is an arbitrary linear operator. Hence, we may refer to Eq. (20) as a generalized expectation value that permits properties to be calculated in the usual way

$$\theta = \mathrm{Tr}(\rho \Theta) \qquad (21)$$

where ρ is the reduced n-particle density matrix

$$\rho_{pq\cdots rs} = \langle p^\dagger q^\dagger \cdots sr \rangle$$

$$= \langle \Phi_0 | \mathcal{L} \exp(-T) p^\dagger q^\dagger \cdots sr \exp(T) \mathcal{R} | \Phi_0 \rangle \qquad (22)$$

$$= \langle p^\dagger q^\dagger \cdots sr \rangle$$

$$= \langle \Phi_0 | \mathcal{L} [p^\dagger q^\dagger \cdots sr \exp(T)]_c \mathcal{R} | \Phi_0 \rangle. \qquad (23)$$

The subscript c in Eq. (23) means that contractions between the quasiparticle creation and annihilation operators and the T amplitudes are restricted to connected diagrams. Elements of the reduced one-particle density matrix appropriate for calculating one-electron properties are presented in Table II, with the equivalent diagrammatic representations displayed in Fig. 1. In passing, we note that the density matrix is manifestly Hermitian only in the limit that the bra and ket states are adjoints of one another, apart from a multiplicative factor. Since this condition is always satisfied in the exact limit (where both are eigenfunctions of the full Hamiltonian within a given basis set), the non-Hermiticity of the density acts as a measure of the treatment of electron correlation. Some numerical studies of this asymmetry and its use in assessing the quality of calculated results would be desirable.

It should be emphasized that the approach advocated here for calculating properties is *not* equivalent to calculating θ as a response property (by differentiating the energy), as it does not include the contribution of reference state relaxation (the change in the molecular orbitals and the T amplitudes due to interaction with the perturbation). In this sense, the present procedure is similar to the calculation of expectation value properties in configuration interaction approaches, although the numerical impor-
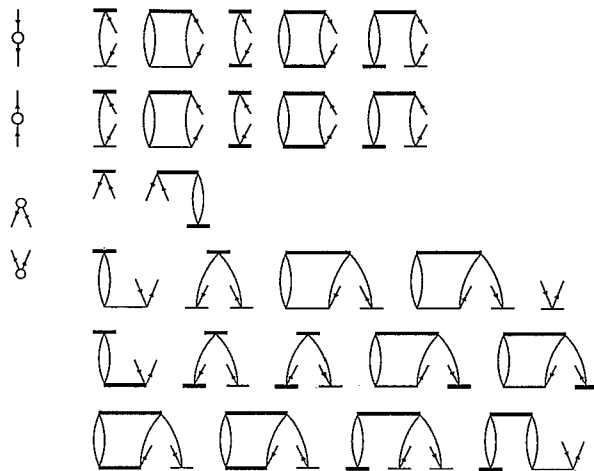
FIG. 1. Complete antisymmetrized diagrammatic expressions for elements of the one-particle reduced EOM-CCSD density matrix. Single- and double-excitation amplitudes of the ground state wave function (T_1 and T_2) correspond to the thin horizontal lines, while the upper and lower thick lines represent elements of the $\mathcal{L}$ and $\mathcal{R}$ vectors, respectively. The ordering of diagrams is consistent with the terms of the algebraic equations listed in Table I, with each diagram corresponding uniquely to one term in the equations.

tance of relaxation is expected to be somewhat less for EOM-CC than it is for CI. This point will be addressed in the next section of this paper.

Due to the non-Hermitian nature of the EOM-CC approach, transition moments are not well defined. Nevertheless, it is the "square" of these quantities that represent experimental observables, and the approach developed here provides a framework for calculations of this type since the product of "left" and "right" transition moments is unambiguous

$$\theta_{gx} \theta_{xg} = \langle \tilde{\Psi}_g | \Theta | \Psi_x \rangle \langle \tilde{\Psi}_x | \Theta | \Psi_g \rangle \qquad (24)$$

$$= \langle \Phi_0 | \mathcal{L}_g [\Theta \exp(T)]_c \mathcal{R}_x | \Phi_0 \rangle$$

$$\times \langle \Phi_0 | \mathcal{L}_x [\Theta \exp(T)]_c \mathcal{R}_g | \Phi_0 \rangle \qquad (25)$$

$$= \mathrm{Tr}(\rho_{g \to x} \Theta) \mathrm{Tr}(\rho_{x \to g} \Theta). \qquad (26)$$

Elements of the transition density matrices are given by equations identical to those in Table II, except that the l and r amplitudes now correspond to the two states under consideration.[33] Perhaps the most interesting quantity of this type is the dipole strength

$$D = \langle \tilde{\Psi}_g | \mu | \Psi_x \rangle \langle \tilde{\Psi}_x | \mu | \Psi_g \rangle, \qquad (27)$$

which is related to the oscillator strength in the dipole length approximation via

$$f_L = \tfrac{2}{3} E_{g \to x} D. \qquad (28)$$

Before concluding, it is instructive to note that the normal coupled-cluster approach typically used to study ground electronic states can be viewed as a special case of the EOM-CC method. As mentioned above, the ground state energy is given by the root of $\bar{H}$ for which $\mathcal{R}_0 = 1$. The bra wave function for the ground state turns out to be

precisely the same as the "lambda" state used in the theory of coupled-cluster properties and energy gradients,[8–15] although the first derivations of energy derivative formulas did not approach the problem from this perspective.[32] In particular, expressions for the reduced one- and two-particle density matrices in EOM-CC theory are identical to those used in normal ground state CC approaches, provided one understands that $\mathscr{R}_0 = 1$ and that $\mathscr{L}_g \exp(-T)$ is the lambda state of CC gradient theory.[34] Thus, the EOM-CC approach provides a unifying theoretical foundation for calculating properties other than the energy for both ground and excited states, as all electronic states represent solutions to a common eigenvalue problem.

III. COMPUTATIONAL CONSIDERATIONS

After the ground state coupled-cluster solution has been obtained, a small number of additional steps are required to obtain the excited state solutions. In the present discussion, we limit consideration to EOM-CCSD calculations. First, the one- and two-particle matrix elements of the effective Hamiltonian ($\bar{H}$) listed in Table I are constructed and written to disk as ordered lists. In our case, this stage of the calculation involves a relatively small amount of work since the factorized intermediates used in our CCSD code[35] are either exactly the $\bar{H}$ matrix elements or terms that are closely related to them. The computational requirements involved in constructing the $\bar{H}$ matrix elements from the CCSD intermediates are discussed in Ref. 13, where special attention is devoted to avoiding steps that scale as the sixth power of the basis set dimension.[36] In our implementation of the CCSD method, integrals and intermediates which have the same type of bra and ket indices ($\mathscr{W}_{abcd}, \mathscr{W}_{aibj}, \mathscr{W}_{ijkl}$) are stored on ordered lists that do not assume that $\mathscr{W}_{pqrs} = \mathscr{W}_{rspq}$.[37] Since the bare Hamiltonian integrals are not required for EOM-CCSD calculations, the corresponding $\bar{H}$ elements can simply overwrite these lists. However, some additional storage space is required for quantities having different bra and ket indices (the $\mathscr{W}_{abci}$ and $\mathscr{W}_{ijka}$ matrix elements[38]).

After the $\bar{H}$ matrix elements have been constructed and processed, the eigenvalues are found. Since the number of singly and doubly excited determinants can be very large, in-core diagonalization of $\bar{H}$ is not a reasonable way to determine the excited state energies and wave functions. Rather, an iterative solution in the spirit of Davidson's algorithm for symmetric matrices[39] should be used. A generalization of the Davidson method has been suggested by Hirao and Nakatsuji,[40] and we have adopted their approach into our computer program. Aside from the need to diagonalize a nonsymmetric matrix, there are only two other features of EOM-CCSD calculations that are not encountered in the more familiar CISD method. First, the non-Hermiticity of $\bar{H}$ must be carefully considered when forming the matrix vector contractions $\bar{H}\mathscr{C}(\mathscr{R})$ and $\mathscr{C}(\mathscr{L})\bar{H}$, where the $\mathscr{C}$ vectors represent elements of the basis that eventually expands to contain the exact eigenvectors. In our vectorized implementation of the EOM-CC method, all contractions are performed with matrix multiplication routines and some care must be exercised regarding whether the matrices of effective Hamiltonian amplitudes should be multiplied as stored on disk or as their transpose. For the $\mathscr{W}_{abci}, \mathscr{W}_{aibc}, \mathscr{W}_{ijka},$ and $\mathscr{W}_{iajk}$ elements, the proper ordered list must be selected. An additional complication involves the three-body contributions to the $\bar{H}\sigma$ products, which could be evaluated as

$$\sum_{me} r^e_m \mathscr{W}_{mabeij} + \frac{1}{2}\left(\sum_{mef} r^{fe}_{im}\mathscr{W}_{ambfej} - \sum_{men} r^{ea}_{mn}\mathscr{W}_{nmbiej} \right) \tag{29}$$

for the right eigenproblem, and

$$\frac{1}{2}\left(\sum_{mef} l^{im}_{fe}\mathscr{W}_{ejfmba} - \sum_{men} l^{mn}_{ea}\mathscr{W}_{ejimbn} \right) \tag{30}$$

for the left-hand solution.[41] If these terms were indeed evaluated according to Eqs. (29) and (30), storage of six-index quantities would be necessary, and the cost of the calculations would scale with the seventh power of the basis set size. Fortunately, both of these undesirable consequences can be avoided by carrying out contractions that involve the T amplitudes and the bare Hamiltonian integrals explicitly:

$$P(ab) \sum_f \left[\left(\sum_{me} r^e_m \langle bm\|fe\rangle \right) t^{af}_{ij} \right.$$
$$\left. - \frac{1}{2}\left(\sum_{men} r^{ea}_{mn}\langle nm\|fe\rangle \right) t^{fb}_{ij} \right],$$
$$-P(ij) \sum_n \left[\left(\sum_{me} r^e_m \langle nm\|je\rangle \right) t^{ab}_{in} \tag{31} \right.$$
$$\left. - \frac{1}{2}\left(\sum_{mef} r^{fe}_{im}\langle nm\|fe\rangle \right) t^{ab}_{jn} \right],$$

and

$$\frac{1}{2}\left[P(ij) \sum_n \left(\sum_{mef} t^{ef}_{mn} l^{im}_{ef} \right) \langle jn\|ba\rangle \right.$$
$$\left. + P(ab) \sum_f \left(\sum_{men} t^{ef}_{mn} l^{mn}_{ae} \right) \langle ij\|fb\rangle \right], \tag{32}$$

which have only a fifth power dependence. The antisymmetric permutation operator $P(qr)$ is defined by its action on a function of its arguments

$$P(qr)\mathscr{S}(\cdots pqrs\cdots) \equiv \mathscr{S}(\cdots pqrs\cdots) - \mathscr{S}(\cdots prqs\cdots). \tag{33}$$

Of course, this approach requires that the T amplitudes be saved after construction of the $\bar{H}$ matrix elements, but this is not a serious limitation due to their small size.

In practice, we find that the nonsymmetric eigenvalue approach of Hirao and Nakatsuji[40] converges in approximately the same number of iterations as the usual Davidson method for symmetric matrices. Typically, the norm of the residuum,

$$\bar{H}\mathscr{R} - \epsilon\mathscr{R}, \tag{34}$$

is converged to $< 10^{-5}$ after 10–15 iterations.

In our implementation, the right eigenvector problem is solved if only excitation energies are sought. When prop-

TABLE III. EOM-CCSD and full configuration interaction excitation energies and dipole strengths for the lowest optically allowed transitions in CH^+ and the beryllium atom. Also listed are the approximate excitation levels (AEL) for each process. The basis sets used in these calculations are discussed in the text.

	Final state	Excitation energy (eV)		Dipole strength (a.u.)		AEL[a]
		EOM-CCSD	FCI	EOM-CCSD	FCI	
Be[b]	$^1P(2s2p)$	5.318	5.314	3.564	3.549	1.07
	$^1P(2s3p)$	7.465	7.460	0.021	0.022	1.06
	$^1P(2s4p)$	8.306	8.300	0.000 102	0.000 121	1.05
CH^+ [c]	$^1\Sigma^+$	9.109	8.549	0.025	0.025	1.96
	$^1\Sigma^+$	13.580	13.525	1.073	1.080	1.03
	$^1\Sigma^+$	17.315	17.217	0.720	0.684	1.13
	$^1\Pi$	3.261	3.230	0.095	0.090	1.03
	$^1\Pi$	14.454	14.127	0.692	0.588	1.24

[a]Approximate excitation level defined by Eq. (37).
[b]FCI results from Ref. 45.
[c]FCI results from Ref. 46.

erties or oscillator strengths are desired as well, additional steps are required. First, the $\mathscr{L}_g$ vectors of the left-hand ground state wave function are formed by our program used for the normal CC property and gradient calculations. Then, after each root and $\mathscr{R}$ vector of the $\bar{H}$ matrix is found, the corresponding bra state must be evaluated. One should note that this corresponds to a linear equation since the eigenvalue corresponding to $\mathscr{L}$ is precisely known. Hence, one need not use an iterative eigenvalue algorithm to determine $\mathscr{L}$, but rather standard procedures for the solution of linear equations.[4,42,43] After the $\mathscr{L}$ and $\mathscr{R}$ states are determined, they must be properly normalized. A good check on the correctness of the implementation is to calculate the overlap of the $\mathscr{R}$ vector with the $\mathscr{L}_g$ vector, which must vanish. To be consistent with the ground state solution, the $\mathscr{R}$ vector is normalized to unity and the left vector is then normalized as

$$\mathscr{L}' = \mathscr{N}\mathscr{L}, \tag{35}$$

where

$$\mathscr{N} = \frac{1}{\langle \mathscr{L} | \mathscr{R} \rangle}. \tag{36}$$

After properly normalized $\mathscr{L}$ and $\mathscr{R}$ vectors have been determined, the reduced density matrices are evaluated according to the equations listed in Table II, and properties and oscillator strengths are calculated as discussed in the preceding section.

A fully vectorized program for performing EOM-CCSD calculations has been written for the ACES II program system,[44] and will be available as part of a future release of the package. Full exploitation of Abelian symmetry is made in the calculations, using algorithms similar to those developed in our group for MBPT and CC calculations.[35] An additional complication arises in the present case, as the $\mathscr{R}$ and $\mathscr{L}$ vectors are in general not totally symmetric quantities. This requires more difficult coding than that needed for standard MBPT and CC energy calculations in which the final and reference states have the same symmetry. Nevertheless, the resulting savings in

CPU time and core memory requirements (both scale with the *square* of the order of the Abelian subgroup) make the extra work worthwhile.

IV. ILLUSTRATIVE CALCULATIONS

A. Comparison with exact results

As a first test of the accuracy of oscillator strengths obtained within the framework presented here, calculations have been carried out on two systems for which full configuration interaction (FCI) results are available—the beryllium atom and the CH^+ molecule—with the same basis sets and C–H bond length that were used in the FCI calculations of Refs. 45 and 46. Table III documents excitation energies and dipole strengths for all optically allowed transitions that were addressed in the FCI calculations.[47] Also included are approximate excitation levels (AEL) that act as a measure of the number of electrons that are excited from the CCSD ground state (i.e., not the SCF orbitals). The AEL is defined by the equation

$$AEL \equiv \tfrac{1}{2} \sum_p | \rho_{pp}^x - \rho_{pp}^g |, \tag{37}$$

where both the ground and excited reduced density matrices are expressed in the quasiparticle (approximate natural orbital) basis that diagonalizes the ground state CC density.[48] It should be clear to the reader that the AEL as defined above is equal to one in the simple particle–hole picture of excitations relative to an SCF reference if correlation effects are not included. For EOM-CCSD, results obtained for transitions to states having an AEL significantly larger than unity should be regarded with a certain amount of suspicion since the parametrization of the excited state wave function is highly constrained for states of significant double replacement character. This is due to the nature of the double-excitation component of the $\mathscr{L}$ and $\mathscr{R}$ vectors, which acts to expand the space available to the wave function beyond that spanned by the singly excited quasiparticle states

$$a^\dagger i \exp(T)|\Psi_g\rangle. \tag{38}$$

This provides important flexibility for describing transitions that are well described by single excitations. However, within the singles and doubles implementation of the EOM-CC method studied here, no such flexibility is available for describing doubly excited states since triple-excitation operators in $\mathscr{L}$ and $\mathscr{R}$ would be required for this purpose.

For beryllium, excitation energies and dipole transition strengths obtained in the present calculations are in nearly perfect agreement with the FCI results. Nevertheless, since the EOM-CCSD method is exact for two electrons, the beryllium atom is an "easy" problem. The processes studied here are essentially single-electron transitions (all AEL values are near 1.05) and the correlation effects in this system are dominated by the two valence electrons.

A more difficult test is provided by the CH^+ molecule, which contains more electrons and exhibits strong nondynamical electron correlation effects in its ground electronic state via interaction of the

$$1\sigma^2 2\sigma^2 3\sigma^2 \tag{39}$$

and

$$1\sigma^2 2\sigma^2 1\pi^2 \tag{40}$$

electronic configurations. Due to this important configuration mixing, one expects some of the low-lying electronic states to have appreciable double-excitation character, as confirmed by the AEL values listed in the rightmost column of Table III. It can be seen that the closest coincidence of FCI and EOM-CCSD results for excitation energies and oscillator strengths occurs for the transitions near 3.2 and 13.5 eV, which both have associated AEL values below 1.1. Differences between FCI and EOM-CCSD dipole strengths for transitions to the third $^1\Sigma^+$ and second $^1\Pi$ state are larger [errors of 5.26% (AEL=1.13) and 17.69% (AEL=1.24), respectively]. The quantitative agreement between FCI and EOM-CCSD for the dipole strength of the nearly pure double excitation at 8.549 eV is clearly fortuitous.

While the limited body of FCI excitation energies and oscillator strengths in the literature prevents us from drawing many conclusions from the present set of calculations, it appears that the EOM-CCSD method gives reliable values for dipole strengths and excitation energies (and, therefore, oscillator strengths) for electronic transitions dominated by single excitations.

B. Excited state properties

Table IV presents dipole moments of water in a number of singlet electronic states, evaluated at the equilibrium geometry of the ground state. Calculations were performed with the polarized (POL) basis of Sadlej,[49] which has been specifically optimized for the calculation of molecular polarizabilities. Two sets of EOM-CCSD values are reported. In the first, dipole moments were calculated as response properties by numerically differentiating energies calculated in the presence of an applied electric field

TABLE IV. Excitation energies and dipole moments of water, calculated with the EOM-CCSD approximation and the polarized basis set of Sadlej. All calculations were performed at the experimental equilibrium geometry of the ground state ($r=0.957$ Å; $\theta=104.5°$.)

State symmetry	Excitation energy (eV)	Dipole moment	
		Energy derivative[a] (a.u.)	Expectation value[b] (a.u.)
$^1A_1$	0.00	0.730	0.724
$^1A_1$	9.82	−0.485	−0.523
$^1A_1$	11.30	1.093	1.096
$^1B_1$	7.40	−0.632	−0.654
$^1B_1$	10.55	2.414	2.428
$^1B_2$	11.57	−0.573	−0.603
$^1B_2$	13.57	0.069	0.052
$^1A_2$	9.16	−0.522	−0.539
$^1A_2$	11.74	0.527	0.513

[a]Fully relaxed value.
[b]Calculated from $Tr(\rho\mu)$.

$$\mu_{\text{response}} = \frac{E_x(\mathscr{E}) - E_x(-\mathscr{E})}{2\mathscr{E}}, \tag{41}$$

where $\mathscr{E}$ is the field strength. In the second set, dipole moments were evaluated according to the generalized expectation value prescription given by Eq. (20). For the ground state, the latter approach is equivalent to differentiating the CCSD energy in the presence of the field but using the zero-field orbitals in all calculations, a procedure that has been previously applied by Salter, Sekino, and Bartlett[16] to study the influence of orbital response on electrical properties. For the excited states, the expectation value procedure corresponds to the energy derivative with a frozen reference state (the zero-field orbitals and T amplitudes must be used). The correctness of our implementation of the equations in Table II was checked by performing such a calculation.

From the results listed in Table IV we can see that perturbation induced relaxation of the reference state does not make a significant contribution to the excited state properties, at least for the eight states of water studied here. While the average relaxation contribution to the dipole moments (0.019 a.u.) is larger than that found for the ground state of water (0.006) and a number of other molecular systems,[16] one should not expect the EOM-CCSD method to be as insensitive to relaxation effects as the normal ground state CC approach, due to the more constrained nature of the wave function parameterization. Nonetheless, the differences observed here are less than those typically found in configuration interaction studies and sufficiently small that use of the generalized expectation value method should provide a useful means for studying properties of excited states.

Since the contribution of state relaxation to molecular properties necessarily vanishes in the limit of an exact calculation, the good agreement between the fully relaxed and unrelaxed dipole moments listed in Table IV represents a necessary, but not sufficient, criterion that must be satisfied by an accurate wave function. It is therefore of interest to

compare properties calculated with the EOM approach to those obtained with other high-level methods. For water, the dipole moment of the lowest $^1B_1$ state has been calculated by Balkova and Bartlett using the two-determinant, TD–CCSD method and the atomic natural orbital (ANO) basis set of Widmark, Malmqvist, and Roos (WMR),[50] truncated to $6s5p3d$ and $2f$ ANOs on oxygen and $4s3p$ and $2d$ ANOs on the hydrogen atoms.[51] In their work, the dipole moment was evaluated as a response property at the minimum energy geometry ($r = 1.070\ 56$ Å; $\theta = 105.124°$), and was found to have a value of 0.417 a.u. Using the same basis set and geometry, the EOM-CCSD dipole moments are 0.439 (expectation value) and 0.414 (energy derivative), which is clearly in excellent agreement with the TD-CCSD results. Thus it appears that the EOM-CCSD method offers a convenient means for studying the properties of a collection of electronic states. A particularly attractive feature of this method is that properties for all states may be obtained in a single calculation.

C. Application to rhombic C_4

In the past decade, a considerable amount of theoretical and experimental work has been devoted to the study of small carbon clusters. One of the more interesting species is C_4, where a number of theoretical studies have predicted that two isomers—a linear triplet and a closed-shell D_{2h} rhombic structure—are thermodynamically competitive.[52–55] In a recent calculation, the CCSD(T) method and an extensive generally contracted basis set of 220 functions was applied to this problem, and the rhombus was found to be approximately 1.5 kcal/mol more stable than the linear triplet.[56] Despite the theoretical consensus regarding the quasidegeneracy of the two isomers, the rhombus has thus far only been tentatively observed in a Coulomb explosion experiment,[57] while the triplet has been characterized in a number of spectroscopic investigations.[58]

While theoretical predictions of the equilibrium geometry and vibrational spectra of the rhombic form of C_4 abound in the chemical literature, relatively little attention has been paid to its excited states and electronic spectrum. Magers, Harrison, and Bartlett calculated transition energies between the ground state of the rhombus and several low-lying singlet and triplet states.[52] In this work, the open-shell singlet states were studied with single-determinant MBPT(4) calculations and an approximate spin projection scheme to account for the resulting spin contamination. Later, two sets of calculations at the configuration interaction singles and doubles (CISD) level[54,59] were reported as well as multireference doubles configuration interaction (MRD-CI) results.[54] Most recently, a multireference restricted active space (RAS) calculation has been reported by Nygren and Petersson.[55] All of these studies agree in predicting a low-lying optically allowed transition to a state of $^1B_{3u}$ symmetry in the vicinity of 2.5 eV. However, these studies have addressed only a small number of states, and only the MRD-CI work of Ref. 54 has also predicted oscillator strengths for the electronic transitions.

TABLE V. Comparison of EOM-CCSD excitation energies and oscillator strengths for rhombic C_4 with other theoretical results. The DZP basis and geometry of Ref. 53 has been used in the EOM-CCSD calculations. Excitation energies are in eV, and oscillator strengths (where available) are listed in parentheses. The molecule is oriented in the xy plane, with the longer diagonal C–C distance coincident with the x axis.

Final state	CISD[a]	CISD[b]	MBPT(4)[c]	MRD-CI[b]	EOM-CCSD
$^1B_{1u}$	2.65	2.63	2.40	2.39(0.025)	2.46(0.016)
$^1B_{2u}$	⋯	⋯	⋯	7.03(0.836)	6.94(0.114)
$^1B_{3u}$	⋯	⋯	⋯	6.88(0.183)	6.90(0.094)
$^1B_{1g}$	⋯	⋯	⋯	⋯	6.36(⋯)
$^1B_{2g}$	⋯	⋯	⋯	⋯	4.68(⋯)
$^1B_{2g}$	⋯	⋯	⋯	⋯	5.18(⋯)
$^1B_{3g}$	2.62	2.61	3.02	2.41	2.48(⋯)
$^1B_{3g}$	⋯	⋯	⋯	⋯	5.91(⋯)
$^1B_{3g}$	⋯	⋯	⋯	⋯	7.26(⋯)
^1A_u	⋯	⋯	⋯	⋯	4.57(⋯)

[a]Reference 59, as cited in Ref. 54.
[b]Reference 54.
[c]Reference 52.

In order to provide more information regarding the electronic states of rhombic C_4, we have studied the ten lowest excited states with EOM-CCSD. First, we have used the optimized CISD geometry and double-zeta plus polarization (DZP) basis set of Ref. 54 in order to make a direct comparison between the EOM-CCSD and MRD-CI results. Following this, the optimized CCSD(T)/PVTZ equilibrium geometry of Ref. 56 has been used in conjunction with the DZP and POL (Ref. 49) basis sets to obtain better estimates of the excitation energies and oscillator strengths. Finally, results near the basis set limit for the important optically allowed transitions were obtained with the WMR basis,[50] truncated to $6s5p4d$ and $3f$ ANOs on each atom. The resulting basis contains 248 Gaussian functions, 244 of which were used in the CCSD and EOM-CCSD energy evaluations. This is one of the largest coupled-cluster calculations performed to date, and the basis is likely to be the most extensive ever used to study excited states with any correlated method. In all calculations, only the spherical harmonic components of the d and f polarization functions were retained, and determinants involving excitations from the four K-shell molecular orbitals were not considered.

From Table V, we see that excitation energies obtained at the EOM-CCSD level with the DZP basis of Ref. 54 are in acceptable agreement with the results of other calculations that were performed with the same or similar basis sets. This suggests that all of these methods (EOM-CCSD, CISD, MRD-CI, and MBPT) provide comparable treatments of differential correlation effects in the ground and excited states of rhombic C_4. The values of the AEL in Table VI also show that all ten transitions are relatively well described by single-excitation processes, so the residual correlation error in the EOM-CCSD results is probably small. However, oscillator strengths calculated at the EOM-CCSD level are uniformly smaller than those obtained in the MRD-CI calculations of Ref. 54, with an extremely large difference [0.836 (MRD-CI) vs 0.116

TABLE VI. Excitation energies of C_4 (in eV) and dipole oscillator strengths, calculated at the EOM-CCSD level with various basis sets.

Final state	DZP basis		POL basis		WMR basis		AEL[a]
	ΔE	f_L	ΔE	f_L	ΔE	f_L	
$^1B_{1u}$	2.388	0.016	2.352	0.014	2.325	0.014	1.09
$^1B_{2u}$	7.153	0.123	7.061	0.128	7.028	0.122	1.10
$^1B_{3u}$	6.975	0.103	6.859	0.123	6.804	0.119	1.09
$^1B_{1g}$	6.314	$\cdots$	6.211	$\cdots$	$\cdots$	$\cdots$	1.10
$^1B_{2g}$	4.598	$\cdots$	4.566	$\cdots$	$\cdots$	$\cdots$	1.08
$^1B_{2g}$	5.375	$\cdots$	5.332	$\cdots$	$\cdots$	$\cdots$	1.08
$^1B_{3g}$	2.493	$\cdots$	2.451	$\cdots$	$\cdots$	$\cdots$	1.10
$^1B_{3g}$	5.876	$\cdots$	5.828	$\cdots$	$\cdots$	$\cdots$	1.14
$^1B_{3g}$	7.356	$\cdots$	7.317	$\cdots$	$\cdots$	$\cdots$	1.09
^1A_u	4.383	$\cdots$	4.366	$\cdots$	$\cdots$	$\cdots$	1.14

[a]Calculated with the DZP basis set.

(EOM-CCSD)] for the $^1A_g \rightarrow {}^1B_{2u}$ transition. The reason for this discrepancy is not clear. Additional calculations using other high-level theoretical methods would be helpful in analyzing this curiosity.

The results in Table VI show that the basis set dependence of the excitation energies and oscillator strengths under investigation is relatively modest. In particular, note that all of the excitation energies change by less than 0.2 eV when the basis is expanded from the relatively small DZP set to the POL or WMR basis sets. This is surprising, since the larger two basis sets have been optimized for studies of molecular polarizabilities and therefore contain a number of diffuse functions. For excited states, one generally expects the effective spatial extent of the electronic wave function to be greater than in the ground state, which will lead to relatively large reductions in the excitation energies as the basis set is expanded. However, that is not the behavior observed here. To explain this phenomenon, second moments of the electron density have been calculated as expectation values and are listed in Table VII along with the spherically averaged values

$$\tfrac{1}{3}[\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle]. \tag{42}$$

For the most part, the values in all 11 states are similar, with more than half of them actually having more compact electron distributions than the ground state. Hence, all states considered here appear to be valence rather than Rydberg type.

The results obtained for the optically allowed transitions with the very large WMR basis set should be near the EOM-CCSD basis set limit. Since the corresponding AEL values are acceptably small (≈ 1.1), the excitation energies and oscillator strengths obtained in this extensive calculation are probably reasonably close to the exact nonrelativistic results for the vertical excitation processes. It is hoped that these theoretical results will be useful to experimentalists in the future.

To conclude this section, computer timings for the calculations on C_4 are presented in Table VIII. On a per root basis, the cost of an EOM-CCSD energy and property calculation is approximately equal to that required for solution of the ground state CCSD equations. Hence, the separate determinations of the $\mathscr{L}$ and $\mathscr{R}$ vectors require roughly half the time of a CCSD energy evaluation. This confirms our expectations since the number of floating point operations in each EOM-CCSD iteration is similar to that of a CISD calculation. CCSD calculations, on the other hand, require about twice as many operations since the T amplitude dependent intermediates must be evaluated in each iteration.[35] Construction of the $\bar{H}$ matrix elements is dominated by the $\mathscr{W}_{abci}$ terms[13] and requires the same amount of CPU time as a few iterations of the CCSD equations. Clearly, this technique provides a feasible means for the calculation of excited state energies and properties as even the massive calculation on C_4 using 244 basis functions required only 2 h of CPU time on a Cray YMP supercomputer.

V. CONCLUSIONS

This paper clearly demonstrates that the equation-of-motion coupled-cluster method[23–26] provides a convenient formalism for the calculation of molecular excitation ener-

TABLE VII. Second moments of the electronic probability distribution (a.u.) for the ground and ten lowest singlet excited states of rhombic C_4, calculated by the expectation value approach. Also listed are the spherically averaged values ($\bar{r}^2$), defined by $(1/3)\mathrm{Tr}\langle r^2 \rangle$. The orientation of the molecule is described in the caption to Table V.

Final state	DZP basis				POL basis			
	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\bar{r}^2$	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\bar{r}^2$
^1A_g[a]	86.76	42.39	15.11	48.08	86.93	42.43	15.61	48.33
$^1B_{1u}$	84.04	42.34	16.42	47.60	83.93	42.41	16.83	47.72
$^1B_{2u}$	88.89	42.28	15.24	48.80	89.06	42.41	15.83	49.10
$^1B_{3u}$	87.09	43.17	15.08	48.45	87.09	44.13	15.86	49.03
$^1B_{1g}$	82.16	46.01	15.06	47.74	82.13	46.65	15.70	48.16
$^1B_{2g}$	85.67	41.46	16.50	47.80	85.87	41.56	16.99	48.14
$^1B_{2g}$	88.23	41.15	16.48	48.62	88.17	41.20	16.94	48.77
$^1B_{3g}$	89.70	38.89	16.44	48.34	89.61	39.00	16.87	48.49
$^1B_{3g}$	85.78	41.84	16.42	48.01	85.72	41.88	16.88	48.16
$^1B_{3g}$	84.84	43.28	16.57	48.23	85.00	43.30	17.09	48.46
^1A_u	80.28	44.61	16.49	47.13	80.43	44.69	17.03	47.38

[a]The electronic ground state.

TABLE VIII. Computational details and timings for EOM-CCSD calculations on rhombic C_4. All timings are in seconds of CPU time and were obtained on the Cray YMP at the Ohio Supercomputer Center with the ACES II program system.

	Basis set		
	DZP	POL	WMR
Basis set dimension[a]	56.0	92.0	244
Integral evaluation	11.0	38.0	786
SCF orbital optimization	1.0	3.0	57
Integral transformation	2.0	11.0	649
Construction of lists	1.0	4.0	376
CCSD ground state calculation	9.0	31.0	751
Formation of $\bar{H}$ elements	2.0	9.0	303
CCSD bra state evaluation	5.0	19.0	630
EOM-CCSD calculation	86.0	359.0	3569
Number of excited state roots	10.0	10.0	3
EOM-CCSD timing per root	8.6	35.9	1190

[a]Number of active orbitals in post-SCF calculations.

gies, oscillator strengths, and excited state properties. By fully considering the biorthogonal nature of the theory, it is possible to define reduced density matrices that are suitable for calculating properties within a generalized Hellman–Feynman expectation value approach. These density matrices are analogous to those used for traditional ground state coupled-cluster approaches. Indeed, for the root of the EOM-CC effective Hamiltonian that corresponds to the CC ground state, the density matrices defined here are equivalent to those previously derived for the normal coupled-cluster approach.[11,14] This connection with traditional single-determinant CC gradient theory is one of the most pleasing aspects of the framework presented here. In the past, other techniques have been used to evaluate properties in coupled-cluster calculations where one assumes that the bra and ket states are Hermitian conjugates. Density matrices are then evaluated by a perturbation expansion.[60] The generalized transition-type expectation value approach that exploits the biorthogonal representation has two distinct advantages over such calculations. First, and most important, the properties calculated by the present method correspond to inserting the perturbation into the infinite series of diagrams summed by the CC approach[61,16] and are therefore identical to what is calculated by an appropriate finite field procedure. Hence, the results are consistent with the wave function in a way that those obtained with the other approach are not.[62] That is, the generalized Hellman–Feynman theorem is satisfied.[33] Second, the density is easily evaluated by a closed form expression and not by truncated approximations to an infinite series of perturbation diagrams.

Although the numerical accuracy of excitation energies obtained with the EOM-CCSD method has been appreciated for some time,[25,47] the numerical results presented in this paper suggest that it is also a reliable method for predicting molecular properties. Particularly gratifying in this regard is the close coincidence of calculated dipole moments for the lowest $^1B_1$ state of water obtained in EOM-CCSD and TD-CCSD calculations. This result, coupled with the satisfactory agreement between expectation

value and energy derivative properties noted for nine electronic states of the water molecule, suggests that the EOM-CCSD approach does an adequate job of introducing orbital relaxation effects in the excited state and provides a good treatment of the electron correlation effects.

We believe that the EOM-CCSD method will be widely used in quantum chemistry. Already, this approach has been applied to resolve a long-standing photochemical dilemma involving the participation of chlorine peroxide in the catalytic destruction of stratospheric ozone.[63] Although chemical applications of this method in the literature are currently limited to that study and the current investigation of rhombic C_4, the simple black box nature of the approach, its future availability in the highly vectorized ACES II program system, and its accurate treatment of properties and energies of singly excited states makes it an attractive method for use in chemical applications. In addition, the method has recently been generalized to treat excited states of open-shell molecules, a development that greatly broadens the scope of its applicability.[64]

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[26] Excitation energies obtained in EOM-CC calculations are equivalent to those calculated using coupled-cluster linear response theory [H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990); H. Koch, H. J. Aa. Jensen, T. Helgaker, and P. Jørgensen, ibid. **93**, 3345 (1990)]. In addition, the EOM-CC approach is similar to Nakatsuji's symmetry adapted cluster method [H. Nakatsuji, Chem. Phys. Lett. **39**, 562 (1978)].

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[28] In cases where nondynamical correlation effects are important, direct methods such as EOM-CCSD and the multireference Fock space CC approach should be more reliable than the single-configuration QRHF-CC and TD-CC methods since the latter approaches are intrinsically biased towards the reference configuration. In direct methods, there is no such bias and these methods therefore provide a more balanced treatment for problems of this type. This point has been discussed in some detail in a recent paper on the Fock space approach [J. F. Stanton, R. J. Bartlett, and C. M. L. Rittby, J. Chem. Phys. **95**, 6224 (1992)].

[29] Strictly speaking, it is only the truncation of the $\mathscr{R}$ vector which causes the method to be inexact.

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[36] In Ref. 13, the $\bar{H}$ matrix elements are designated as $\mathscr{W}$, while the intermediates used in solving the CCSD equations are denoted as $\mathscr{W}$.

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[47] It should be pointed out that partitional EOM (Ref. 25) and the coupled-cluster linear response theory (Ref. 26) has previously been applied to calculate transition energies for these systems. Since the latter gives excitation energies identical to those obtained in the EOM-CC approximation, the energies listed in the first column of Table III have been previously presented in the literature but not the dipole strengths or AEL values.

[48] The ground state CCSD density matrix is of course non-Hermitian, and the approximate natural orbital basis is therefore biorthogonal. Nevertheless, to calculate the AEL values listed in this paper we have simplified matters by symmetrizing the ground and excited state density matrices. This should make essentially no difference to the numerical values of the AEL.

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