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Calculation of excited-state properties using general coupled-cluster and configuration-interaction models

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Using string-based algorithms excitation energies and analytic first derivatives for excited states have been implemented for general coupled-cluster (CC) models within CC linear-response (LR) theory which is equivalent to the equation-of-motion (EOM) CC approach for these quantities. Transition moments between the ground and excited states are also considered in the framework of linear-response theory. The presented procedures are applicable to both single-reference-type and multireference-type CC wave functions independently of the excitation manifold constituting the cluster operator and the space in which the effective Hamiltonian is diagonalized. The performance of different LR-CC/EOM-CC and configuration-interaction approaches for excited states is compared. The effect of higher excitations on excited-state properties is demonstrated in benchmark calculations for NH_2 and NH_3 . As a first application, the stationary points of the S_1 surface of acetylene are characterized by high-accuracy calculations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805494]

I. INTRODUCTION

The properties of excited states of atoms and molecules play an important role in chemistry and physics. Important spectroscopic and analytic techniques are based on transitions between different electronic states. Many reactions can be initialized by electronic excitation or proceed via the excited state of the reactants. Therefore, the theoretical study of excited states is important and the ability to provide a balanced description for both ground and excited states is desirable for all quantum chemical methods.

Single-reference (SR) coupled-cluster (CC) theory¹ provides an accurate description of electron correlation for atomic and molecular ground states. However, generalization of CC theory to excited states—unlike for configuration interaction (CI) methods—is not trivial. Though higher solutions of CC equations can be obtained in special cases for the lowest states of a given symmetry or excited states dominated by a single Slater determinant,² most excited states require the extension of the usual SRCC theory.

One of the CC approaches developed for excited states is linear-response (LR) CC theory which is equivalent to the equation-of-motion coupled-cluster (EOM-CC) method for excitation energies. It was first derived by Monkhorst from time-dependent linear-response theory.^{3,4} Later it was observed^{5,6} that the equations for transition energies can also be derived from an equation-of-motion approach^{7,8} using the CC wave function for the ground state and postulating a linear *Ansatz* for the excitation operator. Sekino and Bartlett reported the first implementation of such an EOM-CC model at the coupled-cluster singles and doubles (CCSD) level imposing additional approximations on the two-particle excitations. Mukherjee and co-workers^{5,9,10} applied a time-independent formalism of linear-response theory for the

evaluation of excitation energies. A linear excitation operator was also employed by Emrich¹¹ and Paldus *et al.*¹² while Harris proposed an exponential form for the excitation operator.¹³ The symmetry adapted cluster CI method of Nakatsuji and Hirao and co-workers^{14–16} is also closely related to and—under certain conditions—identical with the EOM-CC approach. Takahashi and Paldus combined an orthogonally spin-adapted formalism with time-dependent CC linear-response theory and implemented it on the approximative singles and doubles level for semiempirical Hamiltonians.¹⁷

The CC response functions were later rederived by Koch and Jørgensen in a simplified way¹⁸ exploiting a generalization of the Hellmann–Feynman theorem (GHF).¹⁹ Computationally tractable formulas were also presented for response properties¹⁸ and coded for excitation energies at the closed-shell CCSD level.^{20–22} Later the EOM- and LR-CCSD theories were also extended to open-shell states.^{23,24} Concerning higher-than-double excitations, excitation energies for arbitrary EOM-CC methods are available^{25–27} by means of determinant-based full CI (FCI) codes. Recently implementations of the closed-shell EOM-CC singles, doubles, and triples (EOM-CCSDT) were also reported.^{28–30}

Several iterative and noniterative approximative schemes were suggested including also higher excitations.^{22,23,31–38} From our point of view, the *Ansatz* advocated by Kowalski and Piecuch is the most significant.^{37,28} In their EOM-CCSDt approach the whole set of single and double excitations are treated while triple substitutions are selected via an active space—an idea put forward originally by Adamowicz and co-workers for ground state CC wave functions.^{39,40} The CC_n family of methods proposed by the Århus group also offers a consistent hierarchy for calculating ground and—via response theory—excited-state properties.^{41,42}

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There exist other coupled-cluster approaches which are also capable of describing excited states. Such methods are, e.g., the “genuine” multireference (MR) CC *Ansätze*, which are classified into Fock-space^{43–46} and Hilbert space^{47–49} categories. We should also mention the CC polarization propagator approach of Geertsen and Oddershede⁵⁰ as well as CC Green’s function theory.⁵¹

For the first time, implementation of excited-state properties at the EOM-CCSD level was reported by Stanton and Bartlett.²¹ These authors evaluated first-order one-electron properties and transition moments via a generalized expectation value approach which, however, is equivalent to response theory only in the exact limit. Subsequently Stanton published the theory for calculating EOM-CC analytic first derivatives⁵²—which are equivalent to LR-CC derivatives—employing thereby the Dalgarno and Stewart interchange theorem⁵³ (popularly known as the *Z*-vector method⁵⁴). EOM-CCSD (or equivalently LR-CCSD) analytic first derivatives were implemented somewhat later by Stanton and Gauss.^{55,56} A more straightforward derivation of the EOM-CC analytic derivatives was presented by Szalay⁴⁹ by applying the GHF theorem, that is, using Lagrange multipliers. LR-CCSD transition moments and excited states one-electron properties were later implemented using response theory by Koch and Christiansen and co-workers.^{57,58}

In contrast to coupled-cluster approaches, treatment of excited states is less complicated by CI methods since the same theory is applicable to both ground and excited states. Theory and implementation of CI analytic gradients is well documented for several types of CI wave functions including single-reference^{59,60} and multireference CI methods^{60–62} as well as FCI.⁶⁰ Transition moments are available for MRCI and for its approximately size-extensive variants^{62,63} and for FCI.^{64–67} For further references on CC and CI analytic gradients see Refs. 60 and 68.

In recent years the general implementation of many-body methods has reached an advanced stage.^{60,69–74} These developments were motivated by the increasing interest in high-accuracy calculations and MRCC schemes. Due to the complexity of the corresponding equations, implementation of high-order many-body methods is hardly feasible without automatized tools. The first attempt at the general implementation of CC, EOM-CC, and CI methods was made in 2000 in three different groups by simple modification of FCI algorithms.^{25–27,75,76} Since the scaling of these procedures were not optimal, they were mainly applicable only to benchmark studies. However, it has been shown shortly thereafter that it is possible to solve arbitrary CC and CI problems with the desired scaling by combined string-based and many-body techniques.⁶⁹ The developed algorithms were also applied to CC and CI wave functions including a selected excitation manifold.⁷⁰ Recently, implementation of analytic first⁶⁰ and second⁷¹ derivatives have been reported for general CC and CI models. Alternative procedures for automatized CC and CI methods have been considered by other authors. Olsen has coded a string-based algorithm^{72,73} while Hirata has elaborated a method for the automatic generation of program codes of many-body methods.⁷⁴

In the aforementioned studies less attention has been paid to excited states. Although general EOM-CC excitation energies were presented already at the early stage,^{25–27} an optimally-scaling versions have not been implemented so far and excited-state properties have not been considered at all. The principal purpose of this paper is to report an implementation of excitation energies and excited-state analytic gradients for CC methods together with oscillator strengths for one-photon transitions between the ground and excited states computed via linear-response theory.

Algorithms for the evaluation of general (MR)CI energies and properties has already been discussed.^{60,69–71} These procedures can be adapted without modification for excited states. The only new result in this area is the implementation of transition moments for arbitrary CI wave functions.

II. THEORY

The coupled-cluster wave function is expressed by an exponential wave operator acting on a single Slater determinant $|0\rangle$:

$$|\Psi_{CC}\rangle = e^{\hat{T}}|0\rangle \quad \hat{T} = \sum_K t_K \hat{O}_K. \quad (1)$$

Here t_K is a cluster amplitude to be determined and \hat{O}_K is an excitation operator of type $a^+ i^-$, $a^+ i^- b^+ j^-$, \dots , etc. where the usual convention applies, that is, i, j, k, \dots (a, b, c, \dots) refer to occupied (virtual) orbitals in the Fermi-vacuum $|0\rangle$. If the type of the orbital is immaterial, letters p, q, r, \dots are used. The cluster operator \hat{T} is frequently decomposed according to the level of excitation as

$$\hat{T} = \sum_{k=1}^n \hat{T}_k, \quad (2)$$

where \hat{T}_k generates k -fold excitations. In the present study two types of cluster operators are considered. In SRCC theory all excitations up to a given level n are incorporated in the cluster operator, i.e., \hat{T}_k reads as

$$\hat{T}_k = \sum_{\substack{a_1 < a_2 \dots < a_k \\ i_1 < i_2 \dots < i_k}} t_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} a_1^+ i_1^- a_2^+ i_2^- \dots a_k^+ i_k^-. \quad (3)$$

In the case of the other, multireference-type *Ansatz*, which was proposed originally by Oliphant and Adamowicz³⁹ and developed by others,^{40,70,77} restrictions are imposed on the excitation manifold. A complete active space (CAS) including the reference determinant is selected and the set of orbitals is divided into an active and an inactive part. Excitations carrying at most N_i inactive particle or hole labels are allowed in the cluster operator. If $n = N_i + N_a$ -fold excitations are included, where N_a is the maximal excitation level in the active space, the arising excitation manifold corresponds to the configurations employed in a conventional MRCI calculation (provided that excitations out of the symmetry forbidden reference functions are allowed). However, the present many-body formalism is more flexible and allows us to define new types of selection schemes, for example,

different N_i s can be chosen for each \hat{T}_k (denoted by N_i^k hereafter), given \hat{T}_k clusters can be deleted, etc. This selection results in new MR-type wave functions, which may be more advantageous than the conventional ones in particular cases.⁶⁰ However, a disturbing feature of this method is that it is dependent on the choice of the Fermi-vacuum which may be ambiguous if the weight of two or more determinants in the active space is similar. However, this *Ansatz* combined with the LR-CC approach may be well suited for the description of excited states of molecules characterized by a SR ground state.

Inserting the $|\Psi_{CC}\rangle$ *Ansatz* into the Schrödinger equation, premultiplying by $e^{-\hat{T}}$ and projecting onto the Fermi-vacuum $\langle 0|$, and the set of excited determinants $\langle \Psi_K| = \langle 0|\hat{O}_K^\dagger$ we arrive at the CC equations:

$$\langle 0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = E, \quad (4)$$

$$\langle \Psi_K|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = 0. \quad (5)$$

In the following the concept of the $\hat{\Lambda}$ operator,^{60,78}

$$\hat{\Lambda} = \sum_K \lambda_K \hat{O}_K^\dagger, \quad (6)$$

well-known from ground-state CC gradient theory plays an important role. This operator consists of the deexcitation operators corresponding to the excitation operators in cluster operator \hat{T} multiplied by Lagrangian multipliers which were introduced to make the CC energy functional, Eq. (4), stationary with respect to the variation of the wave function parameters and thus, to enable the efficient calculation of energy derivatives.

In order to extend the coupled-cluster theory to excited states we invoke response-theory. Equations for CC excitation energies can be derived by taking the poles of the coupled-cluster linear-response function,⁵⁸

$$\begin{aligned} \langle \langle \hat{A}, \hat{X} \rangle \rangle_{\omega_x} = & \frac{1}{2} \hat{P}(\omega_x) (\langle 0|(1 + \hat{\Lambda})[e^{-\hat{T}}\hat{A}e^{\hat{T}}, \hat{T}^{\omega_x}]|0\rangle \\ & + \langle 0|\hat{\Lambda}^{\omega_x}e^{-\hat{T}}\hat{A}e^{\hat{T}}|0\rangle). \end{aligned} \quad (7)$$

Here \hat{X} is a perturbation operator oscillating with frequency ω_x . The linear response of the observable related to operator \hat{A} to the perturbation \hat{X} is determined by the response function. \hat{T}^{ω_x} and $\hat{\Lambda}^{\omega_x}$ are the first-order responses of operators \hat{T} and $\hat{\Lambda}$, respectively, and the operator $\hat{P}(\omega)$ symmetrizes a function $f(\omega)$ with respect to complex conjugation and reversal of the sign of the frequency as $\hat{P}(\omega) f(\omega) = f(\omega) + f(-\omega)^*$. For derivation of the response function and for the basics of response theory we refer to Refs. 18, 58, and 79.

Excitation energies are obtained by determining the eigenvalues of the CC Jacobian, $\langle \Psi_K|[e^{-\hat{T}}\hat{H}e^{\hat{T}}, \hat{O}_L]|0\rangle$. Introducing the linear operator

$$\hat{R} = \sum_K r_K \hat{O}_K, \quad (8)$$

where the summation runs over the same excitations as in the cluster operator, the corresponding right-hand eigenvalue equations read as

$$\langle \Psi_K|[e^{-\hat{T}}\hat{H}e^{\hat{T}}, \hat{R}]|0\rangle = \omega r_K. \quad (9)$$

Note that the CC linear-response function has originally been constructed for SRCC models;¹⁸ however, that derivation can be adapted for selected excitation manifolds meaning that Eq. (9) is valid also for MR-type *Ansätze*.

The above eigenvalue equation was also derived within the equation-of-motion approach.^{7,8} A wave operator $\hat{\Omega}$ is defined which transforms the ground-state wave function into the excited-state one and is supposed to satisfy the “equation-of-motion”

$$[\hat{H}, \hat{\Omega}] = \omega \hat{\Omega} \quad (10)$$

with ω being the corresponding excitation energy. In EOM-CC theory the wave operator $\hat{\Omega}$ is parametrized similarly to Eq. (8).⁸⁰ It is not mandatory but we consider here only such wave operators where the excitation manifold corresponds to the cluster operator, that is, $\hat{\Omega} = \hat{R}$. Multiplying Eq. (10) by $|\Psi_{CC}\rangle$ from the right and by $e^{-\hat{T}}$ from the left and projecting onto the space of excited determinants, utilizing that quasicreation operators \hat{T} and \hat{R} commute, we recover the LR-CC equations, Eq. (9).

The LR/EOM-CC excited-state total energy is defined as the sum of the CC total energy and the excitation energy:

$$E_x = E + \omega. \quad (11)$$

The excited-state total energy is not rigorously size extensive because disconnected diagrams occur in the equations. However, an important feature of the excitation energy defined by Eq. (9) is the size intensivity which means that we obtain the transition energies of the subsystems in a calculation on a system consisting of the subsystems at infinite separation. This statement was proven by Koch *et al.* for CC models containing excitations through a certain level.²⁰ It can be easily checked that this proof is valid for CC approaches including selected excitation manifold. Hence excitation energies determined by these methods are also size intensive.

There exists another derivation of the EOM-CC equations. We can insert the $\hat{R}|\Psi_{CC}\rangle$ wave function directly into the Schrödinger equation. After premultiplying by $e^{-\hat{T}}$ and projecting by the excited determinants⁸¹ we end up with the

$$\langle \Psi_K|e^{-\hat{T}}\hat{H}e^{\hat{T}}\hat{R}|0\rangle = E_x r_K \quad (12)$$

equation which is equivalent to Eq. (9) under certain conditions. To prove it let us insert the resolution of identity between operators \hat{R} and $e^{-\hat{T}}$ in the second term of the commutator in Eq. (9):

$$\langle \Psi_K|\hat{R}e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = \sum_L \langle \Psi_K|\hat{R}|\Psi_L\rangle \langle \Psi_L|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle. \quad (13)$$

The matrix element $\langle \Psi_L|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle$ vanishes for each L excitation included in the cluster operator while it equals the CC total energy for $L=0$. When L lies out of the excitation

space defining the particular CC model we need to show that $\langle \Psi_K | \hat{R} | \Psi_L \rangle = 0$, i.e., the product of an “in-space” and an “out-of-space” excitation operator is always an out-of-space one. This relation is trivially satisfied for SRCC methods, but not automatic for selected excitation manifolds. It can easily be seen that this condition holds in the latter case, e.g., if (i) all \hat{T}_k clusters are included and (ii) $N_i^{k+1} \leq N_i^k$ for each k which is not a serious restriction on the structure of the cluster operator.

We note that other variants of the EOM-CC equations arise if the premultiplication by $e^{-\hat{T}}$ is omitted from the derivation of Eq. (9) or Eq. (12). These equations are equivalent to Eqs. (9) and (12) if the aforementioned restrictions are imposed and may be useful in certain cases.²⁵ In the following the first form [Eq. (9)] of the LR/EOM-CC equations is employed which seems to be the most advantageous for our purpose.

Since the CC Jacobian defined in Eq. (9) is non-Hermitian, its left and right eigenvectors are different. If properties other than energy are desired, the solution of the left-hand eigenvalue equations,

$$\langle 0 | \hat{L} [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{O}_k] | 0 \rangle = \omega l_k \quad (14)$$

is required where operator \hat{L} includes the deexcitations corresponding to the excitations in \hat{T} :

$$\hat{L} = \sum_K l_K \hat{O}_K^\dagger. \quad (15)$$

Note that operator \hat{L} corresponds to $(1 + \hat{\Lambda})$ for the electronic ground state and Eq. (14) is reduced in that case to the Λ equation of CC gradient theory with the excitation energy ω being zero.

The left and right eigenvectors are biorthogonal among themselves as a consequence of the non-Hermitian nature of the eigenvalue problem. In practice, it is advantageous to fix their norm. The right-hand eigenvector is usually normalized to unity and the norm of its left-hand pair is chosen to satisfy the normalization condition

$$\langle 0 | \hat{L} \hat{R} | 0 \rangle = 1. \quad (16)$$

Relying on this expression the excitation energy can be written in the illustrative form

$$\omega = \langle 0 | \hat{L} [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{R}] | 0 \rangle. \quad (17)$$

To calculate the derivatives of the excited-state total energy the existence of an energy functional that is stationary with respect to the variation of the wave function parameters is desirable. Since the energy functional defined by Eqs. (11), (4), and (17) does not satisfy this criteria, the technique of Lagrange multipliers is invoked.^{19,49} The coupled-cluster equations, Eq. (5), and the normalization condition, Eq. (16), are added to the excited-state total energy E_x resulting in the Lagrangian

$$\tilde{E}_x = E_x + \sum_K \zeta_K \langle \Psi_K | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle + \varepsilon (1 - \langle 0 | \hat{L} \hat{R} | 0 \rangle) \quad (18)$$

with ζ_K and ε being the corresponding Lagrangian multipliers. To facilitate the following discussion we introduce the \hat{Z} deexcitation operator as

$$\hat{Z} = \sum_K \zeta_K \hat{O}_K^\dagger. \quad (19)$$

Using this notation the energy functional can be recast as

$$\begin{aligned} \tilde{E}_x = & \langle 0 | \hat{L} [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{R}] | 0 \rangle + \langle 0 | (1 + \hat{Z}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle \\ & + \varepsilon (1 - \langle 0 | \hat{L} \hat{R} | 0 \rangle). \end{aligned} \quad (20)$$

The stationary conditions for the l_K and r_K coefficients lead to the right and left eigenvalue equations, Eqs. (9) and (14), respectively, and we identify ε as the excitation energy ω . By imposing stationarity with respect to the Lagrange multipliers ζ_K and ε the CC amplitude equations, Eq. (5), and the normalization condition (16) are recovered, respectively. Differentiation of the energy functional with respect to the CC amplitudes results in new equations,

$$\begin{aligned} \frac{\partial \tilde{E}_x}{\partial t_K} = & \langle 0 | \hat{L} [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{O}_K] | 0 \rangle \\ & + \langle 0 | (1 + \hat{Z}) [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{O}_K] | 0 \rangle \\ = & 0, \end{aligned} \quad (21)$$

which are referred to as the zeta equations. These equations are the analogue of the Λ equations⁷⁸ of the ground-state CC gradient theory and ensure that only one perturbation-independent set of equations has to be solved for the computation of gradients in addition to the ground-state amplitude as well as the left-, and right-hand eigenvalue equations.

After solving all of these equations, the derivative of the excited-state total energy with respect to a perturbation x can simply be expressed as

$$\begin{aligned} \frac{\partial \tilde{E}_x}{\partial x} = & \langle 0 | \hat{L} \left[e^{-\hat{T}} \frac{\partial \hat{H}}{\partial x} e^{\hat{T}}, \hat{R} \right] | 0 \rangle \\ & + \langle 0 | (1 + \hat{Z}) e^{-\hat{T}} \frac{\partial \hat{H}}{\partial x} e^{\hat{T}} | 0 \rangle. \end{aligned} \quad (22)$$

In this expression, all contributions due to orbital relaxation are included in the Hamiltonian, hence its treatment is independent of the particular method. The theory and implementation of the orbital relaxation is well established and we refer to the literature for details.^{82,61,83} The calculation of energy derivatives and molecular properties usually proceed through the construction of (effective) density matrices.^{84,85} For the LR-CC approach, for instance, the one-particle reduced density matrix reads as

$$\begin{aligned} D_{pq} = & \langle 0 | \hat{L} [e^{-\hat{T}} \{p^+ q^-\} e^{\hat{T}}, \hat{R}] | 0 \rangle \\ & + \langle 0 | (1 + \hat{Z}) e^{-\hat{T}} \{p^+ q^-\} e^{\hat{T}} | 0 \rangle \end{aligned} \quad (23)$$

and a corresponding formula applies to the two-particle one. Using the density matrices, the gradient and properties can be evaluated simply by contracting them with the corresponding derivative integrals.

The formulas of analytic EOM-CC gradients were presented for the first time by Stanton using the Z -vector

method to eliminate the perturbed wave function parameters from the equations.⁵² Later these expressions were rederived by Szalay employing the technique of Lagrange multipliers.⁴⁹ The common feature of these derivations are that both authors start from the second form, Eq. (12), of the EOM-CC equations. This choice leads to slightly different equations, namely, in Eqs. (20), (21), (22), and (23), the second term of the commutator involving operator \hat{R} in the first matrix element and the identity operator in second matrix element are missing. Though the definition of the ζ coefficients is different, the two formulations result in identical density matrices and derivatives, provided that the Eqs. (9) and (12) forms of the EOM-CC equations are equivalent. However, we prefer the above derivation, because it is consistent with both EOM-CC and response theory even if the equivalence of the two EOM-CC equations does not hold. Moreover, as we shall see, the presence of the commutator in the working equations highly facilitates the implementation of excited-state CC gradients.

Transition properties for coupled-cluster models are most conveniently evaluated by means of response theory. From the residue analysis of the CC linear-response function, Eq. (7), transition strengths for ground to excited-state transitions are obtained.⁵⁸ To avoid the solution of perturbation-dependent equations for the response of the cluster amplitudes the perturbation-independent equations,

$$\langle 0|(1+\hat{\Lambda})[[e^{-\hat{T}}\hat{H}e^{\hat{T}},\hat{O}_K],\hat{R}]|0\rangle + \langle 0|\hat{M}[e^{-\hat{T}}\hat{H}e^{\hat{T}},\hat{O}_K]|0\rangle + \omega\mu_K = 0 \quad (24)$$

are solved where \hat{M} is a deexcitation operator of the form of Eq. (19) with coefficients μ_K . After solving these equations the “left,”

$$\rho_{pq}^{o \rightarrow x} = \langle 0|(1+\hat{\Lambda})[e^{-\hat{T}}\{p^+q^-\}e^{\hat{T}},\hat{R}]|0\rangle + \langle 0|\hat{M}e^{-\hat{T}}\{p^+q^-\}e^{\hat{T}}|0\rangle \quad (25)$$

and “right,”

$$\rho_{pq}^{x \rightarrow o} = \langle 0|\hat{L}e^{-\hat{T}}\{p^+q^-\}e^{\hat{T}}|0\rangle \quad (26)$$

transition density matrices are built and the transition strength is evaluated as

$$S^{o \rightarrow x} = \frac{1}{2} \{ \text{Tr}(\rho^{o \rightarrow x}\hat{A})\text{Tr}(\rho^{x \rightarrow o}\hat{X}) + [\text{Tr}(\rho^{o \rightarrow x}\hat{X})\text{Tr}(\rho^{x \rightarrow o}\hat{A})]^* \} \quad (27)$$

for arbitrary \hat{A} and \hat{X} operators.

A remarkable property of the transition strengths defined by Eq. (27) is the size intensivity, as it was shown by Koch *et al.*⁵⁷ for SR CC methods. Their proof can be as well applied to the present MR-type *Ansätze* meaning that transition properties, as excitation energies, computed by these methods are size intensive.

We mention that there is another possibility to calculate excited-state properties and transition strengths in EOM-CC theory. Stanton and Bartlett suggested evaluating excited-state properties via a generalized expectation value approach,²¹ that is, calculating the matrix element of an op-

erator associated with the property between the left- and right-hand EOM-CC states. This approach is equivalent to calculating properties as energy derivatives only in the exact limit since it does not include the change of molecular orbitals and t amplitudes due to the perturbation. Transition probabilities were evaluated similarly by forming the matrix element of the given operator with the corresponding ground and excited-state left and right eigenvectors. This method is equivalent to the above response theory formulation only in the exact case; its disadvantage is the lack of size intensivity.

Previously it has been shown that energy, gradients, and molecular properties can be efficiently implemented for arbitrary ground-state CC models employing string-based algorithms.^{60,69,70} Recently these algorithms have been extended to analytic second derivatives.⁷¹ In this formalism term “string” means an ordered sequence of spin-orbital indices. The main idea behind employing strings is that it permits one to implement quantum chemical methods in a general way, independently of the excitation level. In our procedures the working formulas are automatically derived in terms of antisymmetrized diagrams represented by sequences of integer numbers. They are factorized and evaluated as successive contractions of intermediates and wave function parameters. The reusable intermediates are also recognized. The wave function parameters and intermediates are stored in terms of strings and the contractions are performed by string-based algorithms. For details of the string-based formalism we refer to our previous publications.^{60,69–71} Here we demonstrate that CC excitation energies and first-order excited-state and transition properties can conveniently be implemented relying upon this infrastructure.

Since the structure of the new operators \hat{R} , \hat{L} , \hat{Z} , and \hat{M} , is the same as that of operators \hat{T} , $\hat{\Lambda}$, and their derivatives they can be stored and processed in terms of strings too. This also holds for the intermediates containing them. Furthermore, similarities between the equations of ground and the excited-state theories can be identified. Apparently several new types of matrix elements emerge in our working equations, Eqs. (9), (14), (21), (23), (24), (25), and (26). However, all these terms are closely related to a certain matrix element appearing in ground-state CC derivative theory. Programming of these equations requires only the reorganization of the CC first and second derivative codes. Special attention must be paid only to the storage of the intermediates and to the different spatial symmetry of the new parameters.

The structure of the CC Jacobian (or the EOM-CC matrix) in Eq. (9) is identical to that for one of the terms in the so-called perturbed amplitude equations which are solved when calculating CC second derivatives [cf. the second term of Eq. (11) in Ref. 71]. Consequently this matrix element is simply evaluated by replacing the derivatives of the cluster amplitudes by the r coefficients. As we have already mentioned, the left-hand eigenvalue equations correspond to the Λ equations of the CC gradient theory in the ground state limit,⁶⁰ therefore they are easily solved by substituting $1 + \hat{\Lambda}$ by \hat{L} and subtracting ωl_K from the equations. Note that the left eigenvalue equations are solved as a linear system of equations since the excitation energy ω is already known.

The first term of the zeta equations is very similar to one of the constant terms of the so-called perturbed Λ equations of CC second derivative theory [cf. the third term of Eq. (12) in Ref. 71]. Here operators \hat{L} and \hat{R} have to be used instead of $1 + \hat{\Lambda}$ and the perturbed t amplitudes, respectively. The same conclusion applies to the first matrix element of the reduced density matrix, Eq. (23), which can be derived by the same modifications from one of the terms of the perturbed density matrix entering a second derivative calculation [see the second term of Eq. (14) in Ref. 71]. The second matrix element in Eq. (23) corresponds to the ground state CC density matrix.⁶⁰ The structure of Eq. (24) and the transition density matrices, Eqs. (25) and (26), is reminiscent of the zeta equations and the excited-state density matrices, hence they can be implemented by straightforward modification of the corresponding terms.

Note that if the second form of the EOM-CC equations, Eq. (12) was taken as a starting point of our implementation, we would have encountered additional disconnected diagrams due to the absence of the commutator. The implementation of these diagrams would have required further coding effort.

In high-order CC derivative methods, special attention must be paid to the efficient organization of the processing of the intermediates.⁷¹ While solving the equations, intermediates which can be reused at several places are saved. Since the overall size of these intermediates may exceed, sometimes by an order of magnitude, that of the wave function parameters, care must be taken so that only the necessary intermediates will be stored. Taking into account this aspect, an excited-state CC gradient calculation is organized as follows. First the ground-state CC amplitude equations, Eq. (5), are solved and the intermediates which can be later reused are stored. In the next step the right [Eq. (9)] and left [Eq. (14)] eigenvalue equations are iterated until convergence, respectively, and the first term of Eqs. (21) and (23) are constructed. These are the matrix elements which contain the l and r coefficients which implicates that these coefficients and intermediates including them may be dropped. Subsequently the zeta equations are solved and the reduced density matrices are built according to Eq. (23).

Evaluation of transition strengths is slightly more complicated. In this case the solution of the CC amplitude [Eq. (5)], the Λ (see Ref. 60) and the right-hand eigenvalue equations [Eq. (9)] are determined initially. Thereafter the first term of Eqs. (24) and (25) are computed. Since there is no need to store λ coefficients and the right-hand eigenvector as well as the corresponding intermediates, they are erased. In the next step the left-hand eigenvalue equations are solved and the right transition density matrix [Eq. (26)] is evaluated. Subsequently the l coefficients and intermediates incorporating them are deleted. Finally Eq. (24) is solved and the remaining part of the left transition density matrix [Eq. (25)] is calculated.

For the calculation of orbital relaxation contribution to the (effective) density matrices, existing procedures are utilized.^{61,82,83} For this purpose our code has been interfaced with the ACESII (Ref. 86) and the COLUMBUS (Ref. 87) suite of programs for Hartree-Fock (HF) self-consistent field

TABLE I. Equilibrium bond lengths R , bond angles $\langle(\text{H}\text{N}\text{H})$, energies E , and dipole moments μ for the ground 2B_1 state of the NH_2 radical using the aug-cc-pVDZ basis set (frozen core). Distances in angstroms, angles in degrees, and energies and dipole moments in atomic units.

Method	R	$\langle(\text{H}\text{N}\text{H})$	E	μ
CCSD	1.035 79	102.516	-55.747 919	0.699 30
CCSDT	1.038 13	102.296	-55.752 428	0.691 39
CCSDTQ	1.038 37	102.277	-55.752 680	0.691 05
CC(5)	1.038 39	102.275	-55.752 690	0.691 03
CC(6)	1.038 39	102.275	-55.752 691	0.691 03
CISD	1.032 50	102.704	-55.741 398	0.703 91
CISDT	1.034 64	102.506	-55.745 912	0.697 10
CISDTQ	1.038 13	102.291	-55.752 406	0.691 51
CI(5)	1.038 33	102.278	-55.752 628	0.691 09
CI(6)	1.038 39	102.275	-55.752 690	0.691 04
MRCC/3	1.038 19	102.280	-55.751 998	0.691 12
MRCC/4	1.038 42	102.262	-55.752 223	0.690 80
MRCC/5	1.038 43	102.260	-55.752 234	0.690 78
MRCC/6	1.038 44	102.260	-55.752 234	0.690 78
MRCC	1.038 44	102.260	-55.752 234	0.690 78
MRCI/3	1.034 71	102.493	-55.745 474	0.696 71
MRCI/4	1.038 22	102.280	-55.750 983	0.691 95
MRCI/5	1.038 38	102.267	-55.751 131	0.691 68
MRCI/6	1.038 43	102.265	-55.751 176	0.691 66
MRCI	1.038 43	102.265	-55.751 177	0.691 66
FCI	1.038 39	102.275	-55.752 691	0.691 03

(SCF) and for general multiconfigurational SCF (MCSCF) orbitals, respectively.

For the solution of the non-Hermitian eigenvalue equation we adapted a modified Davidson-type approach⁸⁸ as well as our previous diagonalization procedure²⁵ designed for large expansion spaces. It is also worth mentioning here that we employ a partially spin-adapted formalism⁶⁹ which allows for handling the singlet and triplet excited states separately for closed-shell reference functions.

Previously we have implemented gradients for general CI methods.⁶⁰ These algorithms are of course applicable to excited states without any modification. Here we report the development of transition strengths for arbitrary CI models. CI transition strengths are usually calculated by simply evaluating the transition expectation value of the corresponding operator with two different CI eigenvectors. This approach is also consistent with response theory.⁷⁹ In our implementation we follow a density-matrix-based route. Transition density matrices can be constructed by trivial modification of the density matrix code. Note that CI transition strengths—in contrast to CC which requires for this purpose quadratic-response theory⁸⁹—can be employed for characterizing transitions between excited states, too.

III. BENCHMARK CALCULATIONS

To monitor the convergence of excited-state and transition properties with the level of correlation we have performed benchmark calculations for the lowest excited states of the amino radical and the ammonia molecule.

In the following our previous simplified notation is taken over for general CC, CI methods.^{25,60,69-71} CC(n) and

TABLE II. Equilibrium bond lengths R , bond angles $\langle(\text{HNH})$, dipole moments μ , adiabatic ω_a , and vertical ω_v excitation energies, and dipole strengths θ for the first excited 2A_1 state of the NH_2 radical using the aug-cc-pVDZ basis set (frozen core). Distances in angstroms, angles in degrees, excitation energies in eV, and dipole strengths in atomic units.

Method	R	$\langle(\text{HNH})$	μ	ω_a	ω_v^a	θ^a
LR-CCSD	1.006 28	143.570	0.270 28	1.434	2.201	0.033 98
LR-CCSDT	1.007 70	144.046	0.264 62	1.431	2.199	0.033 19
LR-CCSDTQ	1.007 86	144.103	0.264 44	1.432	2.199	0.033 13
LR-CC(5)	1.007 86	144.105	0.264 46	1.432	2.199	0.033 13
LR-CC(6)	1.007 87	144.105	0.264 46	1.432	2.199	0.033 13
CISD	0.994 59	143.234	0.279 69	3.966	4.774	0.030 07
CISDT	1.004 48	144.002	0.268 17	1.476	2.256	0.033 52
CISDTQ	1.006 83	144.037	0.265 23	1.478	2.248	0.033 00
CI(5)	1.007 79	144.100	0.264 52	1.432	2.200	0.033 13
CI(6)	1.007 86	144.104	0.264 46	1.432	2.199	0.033 13
LR-MRCC/3	1.007 53	144.330	0.266 70	1.443	2.221	0.033 09
LR-MRCC/4	1.007 68	144.380	0.266 58	1.444	2.221	0.033 04
LR-MRCC/5	1.007 68	144.381	0.266 58	1.444	2.221	0.033 04
LR-MRCC/6	1.007 68	144.381	0.266 58	1.444	2.221	0.033 04
LR-MRCC	1.007 68	144.381	0.266 58	1.444	2.221	0.033 04
MRCI/3	1.004 06	144.300	0.270 03	1.501	2.262	0.034 62
MRCI/4	1.006 45	144.349	0.267 51	1.508	2.261	0.034 58
MRCI/5	1.007 36	144.415	0.267 04	1.470	2.221	0.034 72
MRCI/6	1.007 42	144.417	0.267 04	1.470	2.221	0.034 72
MRCI	1.007 42	144.417	0.267 04	1.470	2.220	0.034 73
FCI	1.007 87	144.105	0.264 46	1.432	2.199	0.033 13

^aCalculated at the ground state, FCI-optimized geometry, see Table I.

$\text{CI}(n)$ will denote CC and CI models which include up to n -fold excitations, respectively. LR-CC(n) will stand for the LR-CC approach which was achieved by applying the above linear-response formalism to the CC(n) wave function. For instance, LR-CC(2) denotes LR-CCSD, LR-CC(3) is equivalent to LR-CCSDT, etc. We also introduce the notation LR-MRCC for the LR-CC method where the linear-response formalism is adapted for the corresponding MRCC approach.

In our calculations Dunning's (aug-)cc-p(C)VXZ basis set hierarchies were used⁹⁰⁻⁹² (here X stands for the cardinal number of the basis set). The frozen-core approximation was employed with the (aug-)cc-pVXZ basis sets while all electrons were correlated in the core-valence bases. Single-reference methods used restricted (open-shell) Hartree-Fock orbitals throughout.

Transition strengths are calculated in the dipole length approximation, that is, both \hat{A} and \hat{X} operators in Eq. (27) are the electric dipole moment operator.

A. The 2B_1 and 2A_1 states of NH_2

The amino radical is a popular target for benchmark calculations.^{24,60,71,76,93} Its ground state is 2B_1 while its lowest-lying excited state is totally symmetric (2A_1). Both the static and dynamic correlation are moderate for these states. The equilibrium bond lengths, bond angles, dipole moments and adiabatic excitation energies have been computed for both states with the aug-cc-pVDZ basis set. In addition we report vertical excitation energies and dipole

strengths evaluated at the ground state, FCI-optimized geometry. The results are compiled in Tables I and II.

We carried out calculations by all SR methods up to full CI in the (LR-)CC(n) and CI(n) sequences and by the (LR-)MRCCSD and MRCISD approaches. As mentioned in the previous section, the present many-body formalism permits one to impose further restrictions on MR-type wave functions. The resulting selection schemes may be more advantageous in certain cases than the conventional MR approaches because excitations, which are irrelevant to the problem can be deleted thus reducing the cost of the calculation. To demonstrate this we also performed (LR-)MRCC and MRCI calculations where the excitation manifold was truncated at n -tuple excitations with respect to the Hartree-Fock determinant. These methods are denoted by (LR-)MRCC/ n and MRCI/ n , respectively.

In the MR calculations an eight orbital-seven electron CAS was employed including the $2-5a_1 1-3b_2 1b_1$ orbitals. Molecular orbitals were obtained at the MCSCF level using the same CAS space. For (LR-)MRCC approaches, to be consistent with the response theory picture, the orbitals were always optimized for the ground state. In contrast, MRCI geometries, total energies and dipole moments were computed using orbitals optimized for the particular state while vertical excitation energy and transition moment calculations used state-averaged MCSCF orbitals which were obtained by applying equal weights for the two states. This choice provides usually the most optimal orbitals for MRCI calculations. In the (LR-)MRCC calculations the $(1a_1)^2 (2a_1)^2$

$(3a_1)^2 (1b_2)^2 (1b_1)^1$ determinant was chosen as Fermi-vacuum.

Concerning the convergence of the single-reference CC hierarchy, we can draw similar conclusions as previously for energies, geometrical parameters, first-order properties, and harmonic vibrational frequencies.^{25,60,69,71} The convergence of the studied properties is mostly monotonic, only excited-state dipole moments, and adiabatic transition energies oscillate slightly. The error of the (LR-)CC(n) results with respect to the FCI is lower by an order of magnitude than that of the preceding member of the CC sequence. Higher excitations results in longer bond lengths, but decrease the value of dipole moments, excitation energies, and dipole strengths. It is interesting to note that the bond angle increases in the 2A_1 state with the level of excitation but the opposite trend is observed for the ground state.

All the studied properties converge with pentuple excitations to the accuracy given in the Tables, however, the error is already negligible at the CCSDTQ (CC singles, doubles, triples and quadruples) level. The absolute errors of bond distances, angles, and dipole moments are about 0.002–0.003, 0.0002–0.0003, 0.000 01–0.000 02 Å, 0.2–0.5, 0.02–0.06, 0.02 deg; and 0.006–0.008, 0.0002–0.0004, 0.000 02 a.u.; for (LR-)CCSD, (LR-)CCSDT, and (LR-)CCSDTQ, respectively. It suggests that consideration of at least triple excitations is needed even for this simple system if an accuracy of 0.001 Å and 0.1 deg is desired. The description of the ground and excited states is balanced, the magnitude of the errors of geometries and dipole moments is similar for both states. This fact is further evidenced by the rapid convergence of transition properties. Dipole strengths practically converge with triple excitations while FCI-quality transition energies are obtained already at the LR-CCSD level.

As usual, the convergence of the SR CI series is slower—especially for the excited state—than that of CC methods. The error of a CI(n) method is approximately comparable to and in most cases falls behind that for the ($n - 1$)th member of the CC hierarchy. For the ground state the error roughly decreases by one order of magnitude upon increasing the level of excitation except the CISD→CISDT step where the factor is lower than 2. The convergence of excited-state properties is even slower for the first three members of the CI hierarchy and the error is significantly diminished only by pentuple excitations. The large error of CI excitation energies, which is a consequence of the different quality of the treatment of ground and excited states, is conspicuous.

The quality of the MRCC results is somewhat better than that of the CCSDT ones. For the excited states, the error of LR-MRCC is roughly by an order of magnitude greater than that for the corresponding MRCC method, hence the performance of LR-MRCC for geometry and dipole moment falls between LR-CCSD and LR-CCSDT. Though the LR-MRCC transition moments are accurate, the relatively large error of transition energies is disturbing and reveals the less balanced description of the two states. The accuracy of (LR-)MRCC is not significantly better than that of MRCI. (LR-)MRCC provides superior results for ground state energies and dipole

TABLE III. Equilibrium bond lengths R , adiabatic excitation energies ω , and dissociation energies ΔE for the S_1 state of ammonia. Distances in angstroms, excitation energies in eV, and dissociation energies in kJ/mol.

Method	R	ω	ΔE
LR-CCSD	1.052 39	5.716	−98.0
LR-CCSDT	1.057 61	5.707	−93.6
LR-CCSDTQ	1.058 13	5.722	−94.7
LR-CC(5)	−94.9 ^a
CISD	1.043 70	9.187	−441.6
CISDT	1.050 42	5.937	−126.1
CISDTQ	1.055 78	5.820	−105.0

^aSingle-point calculation at the estimated LR-CC(5) geometry, $R = 1.058\ 18$ Å.

moments as well as for excited-state bond length, vertical excitation energies and dipole strengths. As to the other properties, no substantial difference can be observed. On the other hand, truncated (LR-)MRCC expansions obviously converge faster. Practically the MR method truncated after the quadruple excitations is sufficiently close to the conventional (LR-)MRCC approach. The resulting (LR-)MRCC/4 method, which is significantly cheaper than CCSDT and conventional MRCC and MRCI, may be a cost-effective approximation for higher-order effects for systems with weak static correlation. However, the present results suggest that MR methods including single and double excitations out of the reference determinants do not outperform—at least for single-reference states—high-order SRCC methods if high-accuracy is required.

B. Stationary points on the S_1 surface of NH_3

The lowest singlet excited surface of ammonia is a typical example for the photodissociation of a molecule proceeding via its excited state. The surface is well characterized both experimentally⁹⁴ and theoretically.^{62,95–99} The molecule dissociates from the planar D_{3h} equilibrium structure (${}^1A_1'$) through a C_{2v} saddle point (1B_1) into NH_2 (2B_1) and H (2S). The surface is challenging for theoreticians since it has significant Rydberg character near the equilibrium while it becomes more compact under dissociation.⁹⁵

We report optimized geometries, dipole moments, adiabatic excitation energies for the stationary points of the S_1 surface as well as barrier heights and (using the above results for the amino radical) dissociation energies (see Tables III and IV). Ground-state geometries, dipole moments, and total energies are also presented in Table V. Due to the Rydberg character of the excited state, diffuse functions are indispensable, hence we employed the aug-cc-pVDZ basis set. Since FCI and higher-order CC and CI calculations are currently not feasible with this basis set, we performed calculations including up to quadruple excitations, only a single-point LR-CC(5) calculation is reported at the highly symmetric excited-state equilibrium geometry.

For the convergence of ground-state properties, excited-state geometries, excitation energies and barrier heights the same conclusions apply as has been found in the previous section. The error of excited state properties is larger by usually a factor of 2–3 than that for the corresponding ground-state property. Exceptions are the $R(NH^*)$ bond length (H^*

TABLE IV. Bond lengths R , bond angles $\langle(H^*NH)$, dipole moments μ , adiabatic excitation energies ω , and barrier heights for the predissociative transition state on the S_1 surface of the ammonia molecule using the aug-cc-pVDZ basis set (frozen core). Distances in angstroms, angles in degrees, dipole moments in atomic units, and excitation energies and barrier heights in eV. The asterisk denotes the hydrogen which lies on the C_2 axes.

Method	$R(NH^*)$	$R(NH)$	$\langle(H^*NH)$	μ	ω	Barrier
LR-CCSD	1.358 01	1.044 44	124.272	1.119 91	6.075	0.360
LR-CCSDT	1.318 29	1.050 63	123.913	1.138 33	5.971	0.264
LR-CCSDTQ	1.314 03	1.051 26	123.860	1.015 05	5.976	0.254
CISD	1.289 28	1.031 29	123.078	1.183 43	9.441	0.255
CISDT	1.323 40	1.042 01	123.961	1.114 09	6.234	0.296
CISDTQ	1.313 09	1.048 41	123.813	1.038 55	6.082	0.262

denotes the dissociating hydrogen atom) and dipole moment of the transition state (TS) whose error with respect to CCSDTQ is greater by about one and two orders of magnitude, respectively, indicating the difficulty in describing this state. The accuracy of the (LR-)CCSDTQ bond lengths and angles is probably better than 0.0001 Å and 0.01 deg except for the $R(NH^*)$ parameter of the saddle point which requires quintuple excitations to reach this accuracy. It is also interesting to note that this distance gets longer when increasing the excitation level in contrast to the lengths of “real” chemical bonds. The accuracy of the computed transition energies and barrier heights is satisfactory already at the LR-CCSD level, though the error is larger by an order of magnitude at the TS. The remaining error of LR-CCSDTQ may be smaller than 0.005 eV. The dissociation energies go through a maximum at the LR-CCSDT level which is a consequence of the similar behavior of the excited-state total energies. The accuracy of the LR-CCSD dissociation energy is already better than the definition of “chemical accuracy” (1 kcal/mol), however, quadruple excitation are required to reduce the error under 1 kJ/mol.

Recently the ground-state FCI geometry of ammonia has been determined with cc-pVDZ basis.⁶⁰ Relying on these results our estimates for the FCI geometry with the present basis set are 1.02402 Å and 105.900 deg. Although there are no FCI data available for excited states, we may give a reasonable estimate by adjusting our LR-CCSDTQ geometries by a tenth of the corresponding LR-CCSDTQ–LR-CCSDT difference (note that the error of LR-CCSDT with respect to LR-CCSDTQ is smaller by about a factor of 10 than that for LR-CCSD and this tendency is likely to continue for higher-

order methods as discussed in the previous section). This procedure results in $R=1.05818$ Å as well as $R(NH^*)=1.3136$ Å, $R(NH)=1.05132$ Å, and $\langle(H^*NH)=123.855$ deg for the equilibrium and TS geometries, respectively.

The size of the applied basis set is not sufficient to compare with experiment, but it is instructive to compare our geometries with previous theoretical results.^{62,95–99} In general, a fair agreement can be established apart from the H^*NH angle of the TS. The value computed by MR methods^{62,97} (~ 112 deg) is smaller by more than 10 deg than the present estimates. In Ref. 62 the aug-cc-pVDZ basis was used augmented with an additional diffuse function. In order to check whether this discrepancy is caused by the diffuse function, we have performed LR-CCSD and LR-CCSDT geometry optimizations with this basis, however, only a marginal effect (≤ 0.1 deg) has been observed. Since the treatment of correlation seems to be converged in our calculations, this discrepancy might be attributed to the shortcomings of the MR approach.

IV. APPLICATION TO ACETYLENE

The first singlet excited state of acetylene has been a subject of several experimental and theoretical studies^{100–102} (for an extensive bibliography see, e.g., Refs. 101 and 102). The experimentally observed equilibrium geometry is not linear, but rather has a *trans*-bent structure. Quantum chemical calculations supported this observation, however, a *cis* and a vinylidene minimum have also been localized on the potential energy surface with the latter being the global minimum.¹⁰¹ The vinylidene isomer is unlikely to be formed via excitation of the ground-state acetylene due to its high activation barrier. Though the formation of *cis* isomer is kinetically allowed, it has not been detected in experiments so far. In this section, to demonstrate the applicability of the developed methods, we provide high-accuracy geometries and excitation energies for the *trans* and *cis* isomer as well as for the *trans*→*cis* transition state.

Geometries of the stationary points have been optimized by (LR-)CC methods up to (LR-)CCSDTQ with different basis sets. For (LR-)CCSD calculations the aug-cc-pCVXZ (C)/cc-pVXZ (H) basis set combination was employed which is denoted—for the sake of simplicity—by the APCVXZ acronym. Higher-order (LR-)CC calculations used the

TABLE V. Equilibrium bond lengths R , bond angles $\langle(HNH)$, energies E , and dipole moments μ for the ground state of the ammonia molecule using the aug-cc-pVDZ basis set (frozen core). Distances in angstroms, angles in degrees, and energies and dipole moments in atomic units.

Method	R	$\langle(HNH)$	E	μ
CCSD	1.021 55	106.171	−56.419 964	0.609 79
CCSDT	1.023 77	105.918	−56.425 844	0.606 02
CCSDTQ	1.024 00	105.903	−56.426 201	0.605 84
CISD	1.017 97	106.403	−56.410 156	0.611 81
CISDT	1.019 71	106.192	−56.415 401	0.608 76
CISDTQ	1.023 60	105.932	−56.425 626	0.606 24

TABLE VI. Equilibrium bond lengths R and total energies E for the ground state of the acetylene molecule. Distances in angstroms and energies in atomic units.

Basis	Method	R_{CC}	R_{CH}	E
PVDZ	CCSD	1.222 77	1.077 58	-77.099 264
	CCSDT	1.228 53	1.078 93	-77.111 241
	CCSDTQ	1.229 47	1.078 94	-77.112 234
PVTZ	CCSD	1.203 26	1.062 02	-77.171 184
	CCSDT	1.209 27	1.063 55	-77.187 692
APCVDZ	CCSD	1.221 68	1.076 56	-77.184 892
APCVTZ	CCSD	1.200 85	1.061 99	-77.275 684
APCVQZ	CCSD	1.197 37	1.060 44	-77.301 869
APCV5Z	CCSD	1.196 35	1.059 96	-77.309 367
	Corrected ^a	1.203 30	1.061 50	
	Experimental ^b	1.203 56	1.061 66	

^aCCSD/APCV5Z-optimized geometry corrected with CCSDTQ-CCSDT/PVDZ and CCSDT-CCSD/PVTZ differences.

^bEmpirical equilibrium geometry from Ref. 106.

cc-pVXZ hierarchy which is referred to as PVXZ in the following. Note that the S_1 surface of acetylene is basically of valence-type, therefore basis sets without diffuse functions are sufficient for the description of this state. The results for the excited state are collected in Tables VII–IX, while ground-state geometries are reported in Table VI for reference.

The convergence of the geometries with the level of excitation is monotonic but slow and exhibits a significant state-dependence. The excited-state stationary points, especially the *cis* and *trans* forms require higher level of correlation. The error of the C–C distance is about three times larger for the excited state than for the ground state and reduced only by factors of about three and six for these states, respectively, when going from LR-CCSD to LR-CCSDT. The remaining error due to neglect of higher-than-quadruples may be about 0.0002 and 0.001 Å, respectively. The convergence of C–H bond lengths, bond angles, and excitation energies is somewhat faster, the contribution of

pentuple and higher excitations may be smaller than 0.0001 Å, 0.1 deg and 0.01 eV, respectively. Relying on the differences of PVDZ and PVTZ triples contributions we can give a rough estimate of the basis set error of higher-order corrections. The average difference of the triples contributions calculated with PVDZ and PVTZ basis sets is better than 20%. The maximum errors are about 0.001 Å, 0.0004 Å, 0.4 deg, and 0.02 eV for the C–C and C–H distances, bond angles and excitation energies, respectively. Hence conservative estimates for the basis-set error of triples effect are 0.0005 Å, 0.0002 Å, 0.2 deg, 0.01 eV, respectively. For the basis-set error of the quadruples contribution, supposing an error of 20%, we arrive at error bars of 0.001 Å, 0.0007 Å, 0.1 deg and 0.01, respectively.

The basis set convergence of (LR-)CCSD geometrical parameters and excitation energies is smooth and mostly independent of the state. The errors with respect to the APCV5Z basis set are reduced roughly by a factor of 5 upon increasing the cardinal number of the basis. Exceptions are the C–H distances when going from APCVDZ to APCVTZ as well as the bond angles where the convergence is faster. The errors of the double-, triple-, and quadruple- ζ quality basis sets are about 0.03, 0.005, and 0.001 Å for the C–C bond lengths; 0.02, 0.002, and 0.0005 Å for the C–H distances; 0.3–2, 0.04–0.5, and 0.01–0.1 deg for the bond angles; and 0.2, 0.05, and 0.01 eV for the transition energies, respectively. Supposing that the tendency is similar with larger basis sets, the basis-set error of the APCV5Z basis set is estimated to be 0.0004 Å, 0.0002 Å, 0.02 deg, and 0.003 eV for the aforementioned parameters, respectively. Fortunately, the errors of the basis set and the correlation treatment are of opposite sign and of same order of magnitude, hence they cancel each other to some extent.

In high-accuracy calculations it is also usual to consider relativistic and adiabatic effects. In a previous study,¹⁰³ however, it has been found that post-Born-Oppenheimer effects have negligible impact on geometries. Furthermore, relativistic effects are not sensitive to small changes of geometries, hence can also be safely ignored.

TABLE VII. Equilibrium bond lengths R , bond angles $\langle(HCC)\rangle$, and adiabatic excitation energies ω for the S_1 *trans*-acetylene. Distances in angstroms, angles in degrees, and excitation energies in eV.

Basis	Method	R_{CC}	R_{CH}	$\langle(HCC)\rangle$	ω
PVDZ	LR-CCSD	1.377 39	1.112 19	122.121	5.451
	LR-CCSDT	1.393 00	1.114 90	120.742	5.203
	LR-CCSDTQ	1.397 56	1.115 23	120.456	5.156
PVTZ	LR-CCSD	1.359 31	1.093 10	123.563	5.545
	LR-CCSDT	1.373 94	1.096 25	122.107	5.319
APCVDZ	LR-CCSD	1.375 81	1.108 35	122.683	5.310
APCVTZ	LR-CCSD	1.354 85	1.091 59	124.115	5.534
APCVQZ	LR-CCSD	1.351 07	1.089 76	124.356	5.577
APCV5Z	LR-CCSD	1.350 01	1.089 23	124.399	5.591
	Corrected ^a	1.369 20	1.092 71	122.657	
	Experimental ^b	1.375	1.097	122.48	

^aLR-CCSD/APCV5Z-optimized geometry corrected with LR-CCSDTQ-LR-CCSDT/PVDZ and LR-CCSDT-LR-CCSD/PVTZ differences.

^bExperimental r_0 geometry from Ref. 107. Note that our estimate cannot directly be compared to this geometry without making corrections for vibrational effects.

TABLE VIII. Equilibrium bond lengths R , bond angles $\langle(\text{HCC})\rangle$, and adiabatic excitation energies ω for the S_1 *cis*-acetylene. Distances in angstroms, angles in degrees and excitation energies in eV.

Basis	Method	R_{CC}	R_{CH}	$\langle(\text{HCC})\rangle$	ω
PVDZ	LR-CCSD	1.339 41	1.115 10	134.466	5.866
	LR-CCSDT	1.356 86	1.117 92	132.323	5.621
	LR-CCSDTQ	1.361 60	1.118 18	131.821	5.575
PVTZ	LR-CCSD	1.325 57	1.095 37	134.966	5.923
	LR-CCSDT	1.341 32	1.098 79	132.891	5.697
APCVDZ	LR-CCSD	1.341 44	1.111 61	133.697	5.731
APCVTZ	LR-CCSD	1.323 48	1.094 10	135.028	5.904
APCVQZ	LR-CCSD	1.320 55	1.092 09	135.081	5.938
APCV5Z	LR-CCSD	1.319 72	1.091 52	135.064	5.951
	Corrected ^a	1.340 21	1.095 20	132.487	

^aLR-CCSD/APCV5Z-optimized geometry corrected with LR-CCSDTQ-LR-CCSDT/PVDZ and LR-CCSDT-LR-CCSD/PVTZ differences.

To achieve our final estimates for the geometrical parameters, the (LR-)CCSD/APCV5Z-optimized geometries have been corrected by triple and quadruple contributions measured by the (LR-)CCSDT–(LR-)CCSD/PVTZ and (LR-)CCSDTQ–(LR-)CCSDT/PVDZ differences, respectively. The computed geometry for the ground state, where experimental data are attainable, is in good agreement with the experimental results. According to the above discussion we attach error bars of 0.002 Å, 0.0008 Å, and 0.4 deg to the C–C, H–H bond lengths and bond angles, respectively.

To compare our excitation energies directly to the experimental ones we performed the following single-point calculations at the corrected geometries displayed in Tables VI–IX. The Hartree-Fock energies have been extrapolated to the basis set limit by an exponential function¹⁰⁴ using APCVTZ, APCVQZ, and APCV5Z results (denoted by APCV(T,Q,5)Z hereafter) while an $A + B/X^3$ -type extrapolation formula has been applied to APCVQZ and APCV5Z (LR-)CCSD correlation energies.¹⁰⁵ The obtained complete basis set (LR-)CCSD energies have been adjusted by higher-order, relativistic and vibrational corrections. The effects of triple and quadruple excitations have been estimated by the (LR-)CCSDT–(LR-)CCSD and (LR-)CCSDTQ–(LR-)CCSDT differences computed with the PVTZ and PVDZ

basis sets, respectively. First-order Darwin and mass-velocity relativistic corrections have been calculated at the (LR-)CCSD level in the APCVQZ basis. The harmonic vibrational frequencies have been determined with the APCVQZ basis via analytic CCSD second derivatives for the ground state and numerical differentiation of analytically evaluated LR-CCSD energy gradients for excited states. Our harmonic frequencies are (in cm^{-1}): 659 (π_g), 769 (π_u), 2060 (σ_g), 3437 (σ_u), and 3533 (σ_g) for the ground state; 637 (a_u), 732 (b_u), 1085 (a_g), 1499 (a_g), 3087 (b_u), and 3108 (a_g) for the *trans* form; 452 (b_2), 736 (a_2), 802 (a_1), 1672 (a_1), 3000 (b_2), and 3056 (a_1) for the *cis* conformer; and 818i (a'), 777 (a''), 839 (a'), 1516 (a'), 2824 (a'), and 3422 (a') for the TS.

The evaluated contributions and the corrected values of transition energies are collected in Table X. Since the corrections do not strongly depend on the state, the separation of different conformers is qualitatively correct already at the (LR-)CCSD level. The largest correction to extrapolated (LR-)CCSD values originates from the contribution of triple excitations followed by vibrational effects which have to be considered to meet an accuracy goal of 0.1 eV while qua-

TABLE IX. Bond lengths R , bond angles $\langle(\text{HCC})\rangle$, and adiabatic excitation energies ω for the *trans*→*cis* transition state on the S_1 surface of acetylene. Distances in angstroms, angles in degrees, and excitation energies in eV.

Basis	Method	R_{CC}	R_{CH_1}	R_{CH_2}	$\langle(\text{H}_1\text{CC})\rangle$	$\langle(\text{H}_2\text{CC})\rangle$	ω
PVDZ	LR-CCSD	1.364 86	1.135 44	1.082 25	117.183	179.315	6.050
	LR-CCSDT	1.371 93	1.138 24	1.083 41	118.363	179.580	5.877
	LR-CCSDTQ	1.374 66	1.138 25	1.083 56	118.425	179.576	5.845
PVTZ	LR-CCSD	1.345 55	1.112 17	1.066 53	119.386	178.310	6.094
	LR-CCSDT	1.353 08	1.115 36	1.068 08	120.191	178.822	5.935
APCVDZ	LR-CCSD	1.363 56	1.128 09	1.082 95	117.868	177.998	5.905
APCVTZ	LR-CCSD	1.340 62	1.109 16	1.066 80	120.383	177.686	6.066
APCVQZ	LR-CCSD	1.336 74	1.106 99	1.065 06	120.773	177.654	6.102
APCV5Z	LR-CCSD	1.335 62	1.106 33	1.064 58	120.865	177.646	6.115
	Corrected ^a	1.345 88	1.109 53	1.066 28	121.732	178.154	

^aLR-CCSD/APCV5Z-optimized geometry corrected with LR-CCSDTQ-LR-CCSDT/PVDZ and LR-CCSDT-LR-CCSD/PVTZ differences.

TABLE X. Calculated contributions to the vertical excitation energies (in eV) for the *trans* and *cis* local minima as well as the *trans*→*cis* transition state on the S_1 surface of acetylene.

	<i>trans</i>	<i>cis</i>	TS	Source
LR-CCSD	5.613	5.977	6.129	APCV(T,Q,5)Z SCF+ APCV(Q,5)Z LR-CCSD
LR-CCSDT	-0.229	-0.238	-0.162	PVTZ
LR-CCSDTQ	-0.043	-0.043	-0.030	PVDZ
Scalar relativistic	-0.003	-0.001	-0.001	APCVQZ
Zero-point energy	-0.108	-0.134	-0.155	APCVQZ, harmonic freq.
Corrected	5.230	5.561	5.781	Sum of all contributions
Experiment	5.232			^a

^aReference 100.

druples are required for higher accuracy. Relativistic effects are obviously negligible.

Our estimate for the excitation energy of the *trans* state is in excellent agreement with the experimental value. However, we think that this transition energy benefits from error cancellation and the errors for the other states may be somewhat larger, because the following sources of errors have still to be considered. The largest error may come from the imperfections of the applied basis sets. It may amount to 0.005, 0.01, and 0.01 eV at the (LR-)CCSD, (LR-)CCSDT, and (LR-)CCSDTQ levels, respectively. Other sources of error may be the neglect of the pentuple excitations, vibrational anharmonicity in zero-point energies and due to post-Born-Oppenheimer effects. The contributions of these corrections may be as large as 0.01, 0.005, and 0.005 eV, respectively. Since the basis-set error of (LR-)CCSD calculations partly cancels with error arising from the correlation treatment, we believe that an estimate of 0.04 eV for the uncertainty of the computed excitation energies is reasonable and perhaps even conservative.

V. CONCLUDING REMARKS

We have implemented excitation energies, transition moments, and excited state analytic gradients for general coupled-cluster models by means of CC response theory. It has been demonstrated that the previously developed string-based technique^{60,69–71} enables us to implement many-body methods of any complexity with a moderate programming effort and without loss of computational efficiency. Since contractions of any many-index quantities appearing in many-body approaches are evaluated by a couple of prewritten routines,^{60,69} implementation of new methods is only a matter of formula generation and straightforward rearrangement of the program code.

The effect of higher excitations on excited-state and transition properties has been studied for the amino radical as well as the ammonia and acetylene molecules. As expected, accurate calculation of excited state geometries generally requires higher level of correlation than the corresponding treatment of the ground state even for the present, relatively simple excited states which are characterized by promotion of a single electron. The error of the LR-CCSDT method may be as large as 0.005 Å and consideration of quadruple excitations is necessary in most cases if an accuracy of better

than 0.001 Å is desired. The transition properties benefit much from error cancellation and may be very accurate at a lower level of theory in particular cases. In general, however, the maximum error of LR-CCSD and LR-CCSDT may exceed 0.5 and 0.04 eV, respectively, and LR-CCSDTQ calculations are recommended if quantitative accuracy is aimed at.

Note added in proof. In a recent paper,¹⁰⁸ Hirata reported the implementation of EOM-CC excitation energies up to the CCSDTQ level together with transition moments and dipole moments by using a CI-like expectation value expression.

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