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Electron excitation energies using a consistent third-order propagator approach: Comparison with full configuration interaction and coupled cluster results

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A recently developed consistent third-order propagator method for the treatment of electronic excitation in molecules is tested in first applications. The method referred to as third-order algebraic-diagrammatic construction [ADC(3)] extends the existing second-order approximation and aims at a more accurate computation of excitation energies and transition moments than afforded at the second-order level. For a stringent test of the method we compare the ADC(3) energies for over 40 singlet and triplet vertical transitions in H₂O, HF, N₂, and Ne with the results of recent full configuration interaction (FCI) and coupled cluster (CC) computations. The ADC(3) results reflect a substantial and uniform improvement with respect to the second-order description. The mean absolute deviation of the single excitation energies from the FCI results is below 0.2 eV. Although this does not equal the accuracy of the third-order CC3 model, the ADC(3) method, scaling as N⁶ with the number of orbitals, may be viewed as a good compromise between accuracy and computational cost. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504708]

I. INTRODUCTION

An adequate theoretical description of electronic excitations in molecules is a basic requirement for the understanding of photophysical and photochemical processes. In spite of the ongoing growth of computer capabilities and impressive methodological advances, the present state of the art here is much less satisfactory than in the treatment of the ground state, and it is still an urgent concern to improve existing computational schemes or to develop new methods.

In recent years substantial efforts have been directed to the development of methods extending the successful coupled cluster (CC) parametrization of the ground state to the treatment of excited states. Such developments comprise the coupled cluster linear-response (CCLR)^{1–3} and the essentially equivalent equation-of-motion CC methods (EOMCC).^{4–6} Another method of that type is the symmetry-adapted cluster configuration interaction (SACCI) approximation,^{7–9} which has been used for a long time in studies of excited molecules. The CC approach establishes a framework in which one can formulate a hierarchy of successively more accurate computational schemes, including at present the CCS, CC2, CCSD, CC3, and CCSDT models. Here the acronyms S, D, and T denote the increasing configuration space of single, double, and triple excitations, respectively, with respect to the ground-state Hartree–Fock (HF) reference state. The CC2 and CC3 methods can be viewed as approximations to the CCSD and CCSDT methods, respectively. The CC methods yield size-consistent results for excitation energies, thus being, by principle, superior to a (limited) configuration interaction (CI) treatment. Due to the

size-consistency property and their potential to be used as “black-box” applications, the CC methods have rapidly established themselves as standard tools for the treatment of electronic excitation in molecules. As constituent parts they are included in major quantum chemistry program packages.

Among the more traditional methods for treating electronically excited states, one has to name the multireference configuration interaction (MRCI) method.¹⁰ The MRCI method can successfully be used for small molecules. However, in the application to larger molecules one encounters problems due to the rapidly increasing configuration space and, more on principle, due to the violation of size consistency.¹¹ Another important approach is based on the multiconfiguration self-consistent field (MCSCF) treatment. Combining the so-called complete active space (CAS) SCF version of MCSCF with second-order perturbation theory (PT), Roos and collaborators^{12,13} have established the CASPT2 method as a useful and versatile tool in excited state electronic structure calculations. However, the CASPT2 method can hardly be applied as a black-box method, since a careful choice of the active orbitals is crucial for reliable results. It should also be noted that the originally claimed accuracy standard has recently been challenged by very accurate CC3 computations.^{14,15}

For a long time also methods deriving from propagator theory have been used successfully in the computation of molecular excitation spectra. Most notable examples of propagator methods beyond the first-order or random-phase approximation level are the second-order polarization propagator approach (SOPPA),^{16–18} and the second-order

algebraic-diagrammatic construction [ADC(2)] method.^{19–21} These methods allow for a direct determination of excitation energies and transition moments, and they share with the CC methods the property of size consistency. While both the SOPPA and ADC(2) methods are quite practical and efficient, they are restricted to a consistent second-order treatment of the single excitations, and the accuracy thereby afforded is only modest: The results for (single) excitation energies are typically in error by ± 0.5 eV. Aiming at a more accurate description, the ADC method has recently been extended to the level of third-order consistency [ADC(3)].²² In the following we report on the implementation and first numerical tests of the ADC(3) method in applications to several small systems such as H₂O, HF, N₂, and Ne. For these systems an extensive set of data for both singlet and triplet states has been generated recently based on CCS, CCSD, CC2, CC3, and full configuration interaction (FCI) computations^{23–26} using reasonably large basis sets. The repetition of these computations at the ADC(3) level allows for stringent comparisons and a reliable evaluation of the accuracy. As will be seen, the ADC(3) results indicate a substantial and uniform improvement with respect to the second-order treatment, the mean deviations from the FCI (single) excitation energies being below 0.2 eV.

II. THEORY

A. ADC(3) method

In the following we give a brief review of the ADC(3) computational scheme and its properties. While the ADC approach was derived originally within the context of propagator methods, a more convenient and direct way of presentation is afforded by the concept of intermediate state representations (ISR). For more details the reader is referred to Refs. 22 and 27.

In the ADC method the exact excited states $|\Psi_n\rangle$ are expanded according to

$$|\Psi_m\rangle = \sum_J X_{Jm} |\tilde{\Psi}_J\rangle \quad (1)$$

in terms of so-called intermediate states $|\tilde{\Psi}_J\rangle$ generated by a specific orthonormalization procedure from the correlated excited states,

$$|\Psi_J^0\rangle = \hat{C}_J |\Psi_0\rangle. \quad (2)$$

Here $|\Psi_0\rangle$ denotes the exact N -electron ground state, and \hat{C}_J denote “physical” excitation operators of particle-hole (p - h), two-particle-two-hole ($2p$ - $2h$),... type:

$$\{\hat{C}_J\} = \{c_a^\dagger c_k; c_a^\dagger c_b^\dagger c_k c_l, a < b, k < l; \dots\}. \quad (3)$$

The operators $c_p^\dagger(c_p)$ of second quantization correspond to (spin) orbitals as provided, e.g., by a ground-state Hartree–Fock (HF) calculation; the subscripts a, b, c, \dots and i, j, k, \dots label unoccupied (virtual) and occupied orbitals, respectively. The intermediate states establish a representation of the Hamiltonian \hat{H} or of the shifted Hamiltonian $\hat{H} - E_0$,

$$M_{IJ} = \langle \tilde{\Psi}_I | \hat{H} - E_0 | \tilde{\Psi}_J \rangle, \quad (4)$$

and the associated secular equations take the form of a Hermitian eigenvalue problem,

$$\mathbf{M}\mathbf{X} = \mathbf{X}\mathbf{\Omega}, \quad \mathbf{X}^\dagger \mathbf{X} = \mathbf{1}, \quad (5)$$

where $\mathbf{\Omega}$ and \mathbf{X} denote the diagonal matrix of eigenvalues and the eigenvector matrix, respectively. Obviously, the eigenvalues are the excitation energies,

$$\Omega_n = E_n - E_0, \quad (6)$$

while the eigenvector components are the expansion coefficients in the ISR [Eq. (1)] of the excited states. The transition moments

$$T_n = \langle \Psi_n | \hat{D} | \Psi_0 \rangle, \quad (7)$$

for a given (one-particle) operator

$$\hat{D} = \sum_{r,s} d_{rs} c_r^\dagger c_s \quad (8)$$

are obtained as

$$T_n = \sum_{I,rs} X_{In}^* f_{I,rs} d_{rs}, \quad (9)$$

where the quantities

$$f_{I,rs} = \langle \tilde{\Psi}_I | c_r^\dagger c_s | \Psi_0 \rangle \quad (10)$$

are referred to as intermediate state (or effective) transition amplitudes.

Approximation schemes based on the ISR are obtained by truncating the IS configuration space and by using consistent perturbation expansions for the IS secular matrix elements and transition amplitudes:

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \dots, \quad (11a)$$

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \mathbf{f}^{(2)} + \dots. \quad (11b)$$

The explicit perturbation expansions for \mathbf{M} and \mathbf{f} can in principle be derived by using the familiar Rayleigh–Schrödinger perturbation theory (RSPT) for the ground state and the ground-state energy in the closed-form expressions for the intermediate states.²⁸ A more practical approach, however, consists in the algebraic-diagrammatic construction (ADC) operating on the diagrammatic perturbation expansion for the polarization propagator.¹⁹ The ADC procedure, used previously in the derivation of the ADC(2) equations,¹⁹ could recently be extended to the third-order level.²² Figure 1 shows schematically the block structure of \mathbf{M} and \mathbf{f} and the required orders of perturbation theory for the respective blocks at the ADC(n) levels, $n=1, 2, 3$. The explicit ADC(3) expressions for the secular matrix elements have been given in Appendix C of Ref. 22; the third-order extensions for the IS transition amplitudes²⁹ are to be published in the near future. The ADC(3) expressions extend the ADC(2) secular matrix by third-, second-, and first-order contributions in the p - h diagonal block, the p - $h/2p$ - $2h$ coupling block, and the $2p$ - $2h$ diagonal block, respectively. For further reference we note that the first-order [ADC(1)] secular matrix is obtained as the

	$p-h$	$2p-2h$	ph	hp	pp	hh
$p-h$	$\mathbf{M}_{11}^{(\mu)}$	$\mathbf{M}_{12}^{(\nu)}$	$\mathbf{f}_{1,rs}^{(\kappa)}$			
$2p-2h$	<i>h.c.</i>	$\mathbf{M}_{22}^{(\lambda)}$	$\mathbf{f}_{2,rs}^{(\gamma)}$			
	(a)		(b)			

Scheme	μ	ν	λ	κ	γ
ADC(3)	0-3	1-2	0-1	0-3	1-2
ADC(2)-E	0-2	1	0-1	0-2	1
ADC(2)	0-2	1	0	0-2	1
ADC(1)	0-1	-	-	0-1	-
TDA (CIS)	0-1	-	-	0	-

(c)

FIG. 1. Block structure of the secular matrix \mathbf{M} (a) and of the effective transition amplitudes \mathbf{f} (b); order of perturbation-theoretical expansions for the matrix elements in the ADC(3) and lower-level ADC schemes (c).

representation of $\hat{H} - E_0(1)$ with respect to single excitations, where $E_0(1)$ is the HF ground-state energy.

The ADC methods combine the eigenvalue problem (diagonalization) of a Hermitian secular matrix and perturbation theory for the secular matrix elements. The eigenvalue problem of the ADC(2) and ADC(3), with an explicit configuration space of $p-h$ (single) and $2p-2h$ (double) excitations, is of the size of the familiar CI singles and doubles (SDCI) treatment. The (finite) perturbation expansions used for the matrix elements behave with respect to convergence like the Rayleigh-Schrödinger (RS) perturbation series for the ground-state energy and wave function, respectively. At the ADC(3) level, the single and double excitations are treated consistently through third and first order, respectively. In general, the truncation error (for single excitations) due to restricting the explicit ADC configuration space to the μ lowest excitation classes $p-h, 2p-2h, \dots, \mu p - \mu h$ is of the order 2μ (*compactness property*). This is a consequence of the “canonical” order relations²⁷ holding for the ADC (or ISR) secular matrices. Another basic property is the *separability* of the ADC secular matrices:³⁰ For a system consisting of two noninteracting parts A and B, the ADC secular equations for local excitations, say on A, are strictly decoupled from local excitations on B and from nonlocal excitations (on A and B). This property guarantees size-consistent (size-intensive) excitation energies and transition moments, which is a crucial requirement for the application to large systems.

B. Improved treatment of one-particle densities

For certain contributions to the secular matrix elements the finite perturbation expansions are not always satisfactory, and one has to go beyond the strict third-order expressions in

order to achieve a systematical improvement. This is the case for contributions to \mathbf{M} which can be written in terms of (ground-state) one-particle density-matrix elements. For example, the latter quantities do appear in the form of the so-called static self-energy matrix elements,³¹

$$\Sigma_{pq}^{(\infty)} = \sum_{r,s} V_{pr[qs]} \rho_{sr}^c, \quad (12)$$

where

$$\rho_{sr}^c = \langle \Psi_0 | c_r^\dagger c_s | \Psi_0 \rangle - \langle \Phi_0 | c_r^\dagger c_s | \Phi_0 \rangle \quad (13)$$

are the matrix elements of the correlation density, that is, the difference $\rho^c = \rho - \rho^{(0)}$ between the exact ground-state one-particle density matrix and the HF density matrix, $\rho_{rs}^{(0)} = n_r \delta_{rs}$, and $V_{pr[qs]} = V_{prqs} - V_{prsq}$ denote antisymmetrized Coulomb integrals in the “1212” notation. Contributions of that type and the concomitant problems in their adequate treatment are well known in the third-order one-particle Green’s-function (electron propagator) computations of valence electron ionization.^{32,33} The diagonal elements $\Sigma_{kk}^{(\infty)}$ have an obvious physical meaning: they account for the ground-state correlation effect in the electrostatic interaction between the electron in the orbital k and the valence electron charge distribution. As the zero- and first-order contributions to ρ^c vanish, the static self-energy matrix elements arise for the first time in third order, however, in general being not well approximated at that level. As the method of choice for an improved treatment of the one-particle density matrix and the static self-energy matrix elements the so-called Dyson expansion method has proved successful in previous valence ionization applications. The method has been amply described in Ref. 32 and more recently in Sec. V of Ref. 34, where the reader is referred to for details. In brief, the method is based on the third-order approximation for the electron propagator and the related self-energy. It provides a consistent description of the one-particle density and the static self-energy through third and fourth order, respectively, and represents, moreover, an infinite, though incomplete, summation of higher-order terms.

In the present case static self-energy terms arise in the $p-h$ diagonal block of the secular matrix \mathbf{M} , more specifically in the contributions Eqs. (C17)–(C20) of Ref. 22, which can be collected in the form

$$\sum_{\mu=9}^{12} C_{ak,a'k'}^{(3,\mu)} = -\delta_{aa'} \Sigma_{k'k}^{(3)}(\infty) + \delta_{kk'} \Sigma_{aa'}^{(3)}(\infty). \quad (14)$$

An inspection of the remaining third-order terms shows, that also the contributions (C24), (C25), (C27), and (C28) of Ref. 22 can be expressed in terms of density matrix elements as follows:

$$\sum_{\mu=16,17,19,20} C_{ak,a'k'}^{(3,\mu)} = \sum_i V_{ik'[a'k]} \rho_{ai}^{(2)} + \sum_c V_{k'a[ca']} \rho_{ck}^{(2)} + \text{h.c.} \quad (15)$$

According to the preceding discussion, it is recommended to replace the strict perturbation-theoretical expressions for

$\Sigma(\infty)$ and ρ in the right-hand side of Eqs. (14) and (15), respectively, by the corresponding results of the Dyson expansion method. A numerical test of the improvement afforded by the Dyson expansion method is presented in Sec. IV.

C. Comparison with coupled cluster methods

Since we will compare in Sec. IV ADC and CC results, a brief survey of the CC methods for electronic excitation (see Refs. 2, 3, and 6) should be in order. Also the CC methods can be viewed as specific intermediate state representations of the shifted Hamiltonian $\hat{H} - E_0$ using two different set of states, namely the correlated excited states in the form $|\Psi_J^0\rangle = \hat{C}_J e^{\hat{T}} |\Phi_0\rangle$ and the corresponding biorthogonal states $\langle\Psi_I^+| = \langle\Phi_0| \hat{C}_I^\dagger e^{-\hat{T}}$. Here $|\Psi_0\rangle = e^{\hat{T}} |\Phi_0\rangle$ with $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$ is the CC parametrization of the ground-state. The secular matrix of the resulting biorthogonal coupled cluster (bCC) representation

$$M_{IJ}^{cc} = \langle\Psi_I^+| \hat{H} - E_0 | \Psi_J^0\rangle \quad (16)$$

is non-Hermitian, giving rise to a right- and left-hand eigenvalue problem,

$$\mathbf{M}^{cc} \mathbf{X} = \mathbf{X} \mathbf{\Omega}, \quad \mathbf{Y}^\dagger \mathbf{M}^{cc} = \mathbf{\Omega} \mathbf{Y}^\dagger, \quad \mathbf{Y}^\dagger \mathbf{X} = \mathbf{1}. \quad (17)$$

The CC model hierarchy is obtained by extending the configuration space (S, SD, SDT) and by introducing approximations to the CC amplitudes and secular matrix elements. The simplest approximation, CCS, is identical to other first-order methods, such as the ADC(1) or Tamm-Dancoff approximation (TDA), and may be seen essentially as a CIS approach. Both the CC2 and CCSD models extend the explicit configuration space to the double ($2p-2h$) configurations, yielding a consistent second-order treatment of singly excited states. Due to the use of first-order expressions for the \hat{T}_2 amplitudes the CC2 and ADC(2) methods are essentially equivalent. Some differences, being of third order though, arise from the use of the \hat{T}_1 transformed Hamiltonian in the CC2 model. As a consequence of the less stringent order relations of the bCC secular matrix (see Refs. 27 and 35), the CC configuration space must comprise the triple excitations in order to have third-order consistency for the singly excited states. This is the case in the CC3 approximation to the full CCSDT method. The third-order consistency of the CC3 model (for singly excited states) is shared by the less expensive ADC(3) method. However, the explicit consideration of the double excitations in the CC3 configuration space allows for a better, namely, a consistent second-order treatment of the doubly excited states, which at the ADC(3) level are treated consistently through first order only. In view of the importance of the admixture of double excitations in singly excited states, one has to expect that, in general, the ADC(3) results will be less accurate than those of a CC3 (or CCSDT) treatment. A compilation of the characteristics of the CC and ADC hierarchies is given in Table I.

TABLE I. Characteristics [explicit configuration space, perturbation-theoretical consistency for ground- (E_0) and excited-state (E_n) energies, and scaling property] of members of the ADC and CC method hierarchies.

Method	Configuration space ^a	E_n^a			Scaling
		E_0	S	D	
ADC(1)/CCS	S	1	1	-	N^4
ADC(2)	SD	2	2	0	N^5
CC2	SD	2	2	0	N^5
ADC(2)-E	SD	2	2	1	N^6
CCSD	SD	3	2	1	N^6
ADC(3)	SD	3	3	1	N^6
CC3	SDT	4	3	2	N^7

^aS, D, and T, denote single, double, and triple excitations, respectively.

III. COMPUTATIONS

A. Implementation of the ADC(3) method

The ADC(3) code used in the present study has been written as an extension of the existing ADC(2) program.²⁰ The required additions comprise third-order terms in the p - h diagonal block (\mathbf{M}_{11}) and second-order terms in the p - h / $2p$ - $2h$ coupling blocks (\mathbf{M}_{12}); the first-order $2p$ - $2h$ diagonal block (\mathbf{M}_{22}) was already available from the so-called extended second-order [ADC(2)-E] variant (see Fig. 1). The most demanding task was the coding of third-order terms of \mathbf{M}_{11} involving four- and fivefold summations over orbital indices. As a measure for reliability, the coding of the ADC(3) extension was performed independently by two of the authors, so that the two versions could be tested against one another. Generally, the emphasis in the design of the present code was laid on an utmost secure and error-free realization. The development of a program version optimized with respect to computational efficiency will be aimed at in a successive step.

The explicit expressions for the ADC(3) secular matrix, as given in Ref. 22, are formulated with respect to electron configurations in the spin-orbital form, referred to as ‘‘primitive’’ excitations. For an efficient computer code it is necessary to generate spin-free working equations for the final-state spin values of interest, that is, $S=0$ and 1. This can be achieved in a most straightforward way using standard angular momentum algebra techniques operating on the general (spin-orbital) expressions. Basically, one forms spin-adapted excitations as suitable linear combinations of the primitive excitations and applies the corresponding unitary transformations to the original secular matrix. This leads to decoupled secular equations of smaller size for $S=0$ and 1. The original primitive configuration space (for $M_S=0$) is reduced roughly by a factor of 1/3 and 1/2 for the singlet ($S=0$) and triplet ($S=1$) cases, respectively. Ensuing to the decoupling step, one can perform the spin summations in the general perturbation-theoretical expressions for the matrix elements, yielding the desired spin-free expressions that involve only spatial two-electron integrals and orbital energies. The task of generating the spin-free expressions has been performed in a semiautomatic way with the help of a specially devised computer program. The spatial symmetry of a molecule is

exploited in the present code only to the extent of Abelian groups or subgroups, having only one-dimensional irreducible representations.

The present prototypical ADC(3) implementation still follows the conventional strategy, in which one first computes and stores the nonvanishing secular matrix elements and then, in a second step, performs the (iterative) diagonalization. This procedure results in an unfavorable N^8 scaling with the number N of orbitals, since N^8 operations are required to compute the third-order contributions in the p - h block of the secular matrix.²² A more advantageous technique, which has been used for a long time in the CC codes,³⁶ consists in forming intermediate quantities along with the matrix-vector multiplication in the iterative diagonalization. To be more specific, let us consider the procedure for one of the second-order terms [Eq. (C7) of Ref. 22],

$$M_{ak,a'k'}^{(C)} = \sum_{c,i} v_{k'ia'c} v_{acik} \times \left(\frac{1}{2}(\varepsilon_k + \varepsilon_{k'} - \varepsilon_a - \varepsilon_{a'}) + \varepsilon_i - \varepsilon_c \right), \quad (18)$$

where

$$v_{abij} = \frac{V_{ab[ij]}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}.$$

Obviously, the computation of these contributions for the entire p - h block scales as N^6 , whereas the vector-matrix product

$$\bar{Z}_{ak} = \sum_{a'k'} M_{ak,a'k'}^{(C)} Z_{a'k'} \quad (19)$$

for this part requires N^4 operations. The form of the contributions [Eq. (18)] suggests to compute the N^2 intermediates

$$Y_{ic} = \sum_{a'k'} v_{k'ia'c} Z_{a'k'} \quad (20a)$$

and

$$Y'_{ic} = \sum_{a'k'} v_{k'ia'c} \frac{1}{2}(\varepsilon_{k'} - \varepsilon_{a'}) Z_{a'k'} \quad (20b)$$

from which the final contributions to the “target” vector can be obtained according to

$$\bar{Z}_{ak} = \sum_{c,i} v_{acik} \{ Y'_{ic} + Y_{ic} \left[\frac{1}{2}(\varepsilon_k - \varepsilon_a) + \varepsilon_i - \varepsilon_c \right] \}. \quad (21)$$

Both partial steps require N^4 operations, so that the overall scaling reduces from N^6 to N^4 . The inspection of the ADC(3) equations shows that using these techniques one can reduce the overall scaling behavior to N^6 . The corresponding scaling potential of the ADC(2) method is N^5 . In Table I we compare the operation count characteristics for the ADC and CC methods.

B. Computational details

In the present study the H₂O, HF, N₂, Ne, CH₂, and BH systems have been considered. For the ground and the lowest

excited states of these systems the results of a new generation of FCI calculations using cc-pVDZ basis sets augmented with diffuse functions, as well as CC results are available.^{23–26} For the sake of comparison we used in each case the same input data (basis set, geometry and “frozen” 1s orbitals) as in the FCI work. Except for HF, the singlet excitations were computed as described in Refs. 23 and 24, the triplet excitations as in Refs. 25 and 26. The HF singlet and triplet computations were performed according to Ref. 25. The compliance with the previous work implies slightly different input data for singlet and triplet excitations in the case of Ne, CH₂, and BH. The ADC calculations were performed using the new ADC code interfaced to the MOLCAS program package.^{37,38} For the conversion to eV the conversion factor 1 hartree = 27.211 606 eV has been used throughout.

The consistency of our input data with those used in the FCI calculations was controlled by checking the HF ground-state energies, as far as they were available,^{23,24,26} or by inspecting the CIS energies in the case of Ne, HF, and BH.²⁵ Here our HF ground-state energies are $-128.496\,350$, $-100.033\,466$ and $-25.126\,476$ hartree, respectively. We could not reproduce the HF ground-state energy of $-38.884\,254$ hartree reported for CH₂ in Ref. 26 (our result is $-38.884\,244$ hartree). This inconsistency affects the CIS energies to the order of 0.01 eV. Similar discrepancies occur in the CIS energies of BH. In the case of CH₂ we note a confusion between the B_1 and B_2 irreducible representations of the C_{2v} point group in the assignment of excited states. In Refs. 24 and 26 the B_1 and B_2 labels should be interchanged, in order to be consistent with the established nomenclature for the CH₂ ground state, which is 3B_1 rather than 3B_2 (see, for example, Ref. 39 and the literature cited therein). A similar problem occurs for the singlet excited states of H₂O.²⁵ Finally, it appears that the CCS results for 1^3S and 1^3D states of Ne in Table 1 of Ref. 25 should be interchanged.

IV. RESULTS AND DISCUSSION

In Table II we compare the ADC(1), ADC(2), and ADC(3) results for the lowest singlet and triplet excitations energies in H₂O, HF, N₂, and Ne with the corresponding results obtained using full CI (FCI) and coupled cluster methods.^{23–26} We here refrain from comparing the computed excitation energies to experiment (for experimental data the reader is referred to Refs. 20, 24, and 25 and references therein). To get an idea of the quality of the FCI description one may compare the experimental value of the lowest singlet excitation in Ne (16.84 eV) with the FCI result of 16.40 eV. Altogether Table II contains 43 transitions, of which 41 transitions are considered in the evaluation of statistical quantities. The two exempted data sets correspond to inner-shell transitions in Ne.

At the first-order approximation level the CC and ADC methods for the excitation energies are identical, so that the CCS and ADC(1) results are listed under the same heading in Table II. Obviously, the accuracy here is rather poor: The mean absolute error (for the sample of 41 transitions considered in Table II) amounts to 1.16 eV, the maximal deviation

TABLE II. FCI, ADC, and CC results for vertical excitation energies (eV) of H₂O, HF, N₂, and Ne. The ADC and CC results are given relative to the FCI values. The last two lines give the mean absolute error ($\bar{\Delta}_{\text{abs}}$) and the maximum absolute error (Δ_{max}), respectively, relative to FCI^a (eV).

Transition	FCI ^b	ADC(1)/CCS	ADC(2)	ADC(3)	CC2 ^b	CCSD ^b	CC3 ^b
H ₂ O 1 ¹ A ₁ →							
2 ¹ A ₁	9.87	1.11	-0.50	0.14	-0.42	-0.07	-0.02
1 ¹ B ₁	7.45	1.22	-0.50	0.13	-0.41	-0.07	-0.02
1 ¹ B ₂	11.61	1.03	-0.64	0.18	-0.56	-0.09	-0.02
1 ¹ A ₂	9.21	1.15	-0.63	0.17	-0.55	-0.09	-0.02
1 ³ B ₁	7.06	0.95	-0.45	0.09	-0.37	-0.08	-0.02
1 ³ A ₂	9.04	0.99	-0.58	0.14	-0.50	-0.08	-0.02
1 ³ A ₁	9.44	0.70	-0.44	0.10	-0.36	-0.08	-0.01
2 ³ A ₁	10.83	0.61	-0.35	0.01	-0.29	-0.11	-0.01
2 ³ B ₁	11.05	0.93	-0.48	0.11	-0.40	-0.09	-0.01
1 ³ B ₂	11.32	0.58	-0.55	0.13	-0.47	-0.08	-0.01
HF 1 ¹ Σ ⁺ →							
1 ¹ Π	10.44	1.32	-0.81	0.18	-0.62	-0.14	-0.02
2 ¹ Π	14.21	1.27	-0.87	0.19	-0.68	-0.15	-0.02
2 ¹ Σ ⁺	14.58	0.84	-0.67	0.10	-0.48	-0.11	-0.01
1 ¹ Δ	15.20	1.18	-0.74	0.12	-0.53	-0.17	-0.01
1 ¹ Σ ⁻	15.28	1.09	-0.74	0.12	-0.54	-0.18	-0.01
3 ¹ Π	15.77	1.47	-0.85	0.23	-0.67	-0.18	-0.02
3 ¹ Σ ⁺	16.43	1.41	-1.10	0.37	-0.85	-0.14	-0.04
1 ³ Π	10.04	1.02	-0.75	0.14	-0.56	-0.15	-0.02
1 ³ Σ ⁺	13.54	0.05	-0.49	0.05	-0.33	-0.13	0.00
2 ³ Π	14.01	1.17	-0.87	0.19	-0.69	-0.16	-0.02
2 ³ Σ ⁺	14.46	0.78	-0.66	0.07	-0.49	-0.21	-0.01
1 ³ Δ	14.93	0.96	-0.70	0.10	-0.52	-0.19	-0.01
1 ³ Σ ⁻	15.25	1.12	-0.73	0.12	-0.54	-0.18	-0.01
3 ³ Π	15.57	1.34	-0.85	0.22	-0.67	-0.19	-0.02
N ₂ 1 ¹ Σ _g ⁺ →							
1 ¹ Π _g	9.58	0.49	0.17	-0.17	0.14	0.08	0.03
1 ¹ Σ _u ⁻	10.33	-1.68	0.29	-0.33	0.34	0.14	0.01
1 ¹ Δ _u	10.72	-1.49	0.45	-0.37	0.52	0.18	0.01
1 ¹ Π _u	13.61	2.51	0.95	-0.23	0.93	0.40	0.18
1 ³ Σ _u ⁺	7.90	-1.53	0.41	-0.19	0.44	-0.02	-0.03
1 ³ Π _g	8.16	-0.11	0.17	-0.29	0.15	0.06	0.02
1 ³ Δ _u	9.19	-1.72	0.33	-0.27	0.36	0.07	0.00
1 ³ Σ _u ⁻	10.00	-1.35	0.54	-0.29	0.58	0.19	0.03
1 ³ Π _u	11.44	0.59	0.29	-0.19	0.28	0.10	0.07
Ne 1 ¹ S→							
1 ¹ P	16.40	1.69	-0.78	0.17	-0.66	-0.24	0.01
1 ¹ D	18.21	1.74	-0.92	0.18	-0.80	-0.25	0.02
2 ¹ P	18.26	1.72	-0.92	0.18	-0.80	-0.25	0.02
2 ¹ S	18.48	1.93	-1.05	0.27	-0.92	-0.24	0.01
3 ¹ S	44.05	3.73	-0.49	0.35	-0.25	-0.17	-0.10
1 ³ P	18.70	1.25	-0.71	0.13	-0.50	-0.24	-0.01
1 ³ S	19.96	0.94	-0.74	0.10	-0.55	-0.26	0.00
1 ³ D	20.62	1.17	-0.79	0.13	-0.58	-0.23	0.00
2 ³ P	20.97	1.30	-0.83	0.13	-0.61	-0.24	-0.01
2 ³ S	45.43	3.04	-0.32	0.40	-0.13	-0.10	-0.04
$\bar{\Delta}_{\text{abs}}$		1.16	0.64	0.17	0.53	0.15	0.02
Δ_{max}		2.51	1.10	0.37	0.93	0.40	0.18

^aTransitions to the 2^{1,3}S (2s¹2p⁶3s¹) inner-shell excited states of Ne are exempted.

^bResults from Refs. 23–26.

being 2.51 eV. It should be noted that double excitation are not considered at all at the first-order level.

A distinctly better description is obtained using the second-order methods. The mean absolute errors are reduced to 0.64 and 0.53 eV in the ADC(2) and CC2 treatments, respectively. Besides the similarity of the mean errors, one finds good agreement also for the individual ADC(2) and CC2 results, especially distinct in the case of N₂. The similarity of the results reflects, of course, the essential equivalence of the two methods. The small remaining discrepancies

arise from third-order contributions due to the use of the T_1 similarity-transformed Hamiltonian in the CC2 method.

A distinct, uniform improvement with respect to the second-order description is achieved at the ADC(3) level. The mean absolute error here is below 0.2 eV, the largest deviation being 0.37 eV. The quality of the ADC(3) results for the excitation energies, as inferred from the present computations, is comparable to the established accuracy standard of ± 0.2 eV in the related third-order electron propagator methods for electron ionization. A most impressive accuracy

TABLE III. Comparison of different ADC schemes for HF and N₂. The individual ADC results, the mean absolute error ($\bar{\Delta}_{\text{abs}}$), and the maximum absolute error (Δ_{max}) are given relative to the FCI vertical excitation energies (eV).

Transition	FCI ^a	ADC(1)	ADC(2)	ADC(2)-E	ADC(3)		
					Strict	$\Sigma(\infty)^b$	Full ^c
HF 1 ¹ Σ ⁺ →							
1 ¹ Π	10.44	1.32	-0.81	-0.96	0.52	0.20	0.18
2 ¹ Π	14.21	1.27	-0.87	-0.94	0.53	0.21	0.19
2 ¹ Σ ⁺	14.58	0.84	-0.67	-0.81	0.42	0.13	0.10
1 ¹ Δ	15.20	1.18	-0.74	-0.91	0.45	0.14	0.12
1 ¹ Σ ⁻	15.28	1.09	-0.74	-0.92	0.44	0.12	0.12
3 ¹ Π	15.77	1.47	-0.85	-0.98	0.58	0.26	0.23
3 ¹ Σ ⁺	16.43	1.41	-1.10	-1.09	0.70	0.38	0.37
1 ³ Π	10.04	1.02	-0.75	-0.92	0.46	0.15	0.14
1 ³ Σ ⁺	13.54	0.05	-0.49	-0.67	0.26	0.00	0.05
2 ³ Π	14.01	1.17	-0.87	-0.93	0.51	0.20	0.19
2 ³ Σ ⁺	14.46	0.78	-0.66	-0.87	0.36	0.05	0.07
1 ³ Δ	14.93	0.96	-0.70	-0.90	0.40	0.09	0.10
1 ³ Σ ⁻	15.25	1.12	-0.73	-0.91	0.44	0.12	0.12
3 ³ Π	15.57	1.34	-0.85	-0.98	0.56	0.24	0.22
$\bar{\Delta}_{\text{abs}}$		1.07	0.77	0.91	0.47	0.16	0.16
Δ_{max}		1.47	1.10	1.09	0.70	0.38	0.37
N ₂ 1 ¹ Σ _g ⁺ →							
1 ¹ Π _g	9.58	0.49	0.17	-0.70	-0.14	-0.15	-0.17
1 ¹ Σ _u ⁻	10.33	-1.68	0.29	-0.10	-0.48	-0.49	-0.33
1 ¹ Δ _u	10.72	-1.49	0.45	-0.05	-0.47	-0.49	-0.37
1 ¹ Π _u	13.61	2.51	0.95	-1.26	-0.17	-0.20	-0.23
1 ³ Σ _u ⁺	7.90	-1.53	0.41	0.07	-0.38	-0.40	-0.19
1 ³ Π _g	8.16	-0.11	0.17	-0.55	-0.23	-0.25	-0.29
1 ³ Δ _u	9.19	-1.72	0.33	-0.03	-0.44	-0.45	-0.27
1 ³ Σ _u ⁻	10.00	-1.35	0.54	-0.01	-0.43	-0.45	-0.29
1 ³ Π _u	11.44	0.59	0.29	-0.93	-0.15	-0.20	-0.19
$\bar{\Delta}_{\text{abs}}$		1.27	0.40	0.41	0.32	0.34	0.26
Δ_{max}		2.51	0.95	1.26	0.48	0.49	0.37

^aResults of Refs. 23–26.^bDyson expansion method for third-order self-energy terms only (see Sec. III B).^cDyson expansion method for all terms with density-matrix elements (see Sec. III B).

record is seen for the CC3 results in Table II, yielding a mean absolute error of only 0.02 eV with 0.18 eV maximal deviation (for the ¹Π_u state in N₂). In comparing the two third-order methods one should, however, keep in mind that the CC3 method is considerably more expensive than the ADC(3) method. The explicit CC3 configuration space extends to the 3*p*-3*h* (triple) excitations, which leads to an overall *N*⁷ scaling of the method as compared to the *N*⁶ scaling of the ADC(3) scheme. The CCSD energies in Table II seem to lie systematically between the CC2 and CC3 results. Both with respect to the mean absolute error and the size of the maximal deviation the CCSD and ADC(3) results are quite similar. Nevertheless, one finds considerable discrepancies for the individual excitation energies.

For most of the transitions in Table II one sees a typical oscillatory convergence pattern with increasing order of the method. The ADC(1) or CCS excitation energies (for low-lying single excitations) are too large as the coupling to the energetically higher 2*p*-2*h* (double) excitations is not taken into account. At the second-order level the *p*-*h*/2*p*-2*h* coupling comes into play, leading to a substantial and usually overshooting lowering of the excitation energies, which in turn is corrected at the third-order level by an improved de-

scription of the *p*-*h*/2*p*-2*h* coupling and of the 2*p*-2*h* energies.

According to the discussion in Sec. II B, for two distinct types of contributions to the *p*-*h* block of the secular matrix the evaluation of the strict perturbation-theoretical ADC(3) expressions has to be replaced by an improved treatment using the so-called Dyson expansion method for one-particle density-matrix elements and the related matrix elements of the static self-energy. To demonstrate the effect of these modifications we compare in Table III the results of several ADC variants for HF and N₂. A typical behavior is seen in the case of HF, where the major improvement with respect to the strict ADC(3) version results from the use of the Dyson expansion method for the static self-energy terms, while the second amendment concerning the one-particle densities in Eq. (15) has almost no effect. The overall improvement due to the Dyson expansion method is reflected by the distinct reduction of the mean absolute error by about 0.3 eV. A less typical example is N₂. Here the improvement of the static self-energy terms does not change much, but the improved one-particle densities play a role. The overall improvement of the N₂ results is significant, though not as large as in HF.

Table III allows also for a comparison of the standard

TABLE IV. Comparison of FCI, ADC, and CC results for systems with “none-RSPT” character in the ground state: CH₂ and BH. The ADC and CC results are given relative to the FCI vertical excitation energies (eV). Only transitions with dominant single-excitation character have been considered in the determination of the mean absolute error ($\bar{\Delta}_{\text{abs}}$) and the maximum absolute error (Δ_{max}) (eV).

Transition	FCI ^a	ADC(1)/CCS	ADC(2)	ADC(3)	CC2 ^a	CCSD ^a	CC3 ^a
CH ₂ 1 ¹ A ₁ →							
2 ¹ A ₁ ^b	4.66			-1.10		1.46	0.47
3 ¹ A ₁	6.51	0.44	-0.09	-0.31	-0.10	-0.01	-0.01
4 ¹ A ₁	8.48	0.38	-0.20	-0.29	-0.21	-0.02	-0.01
1 ¹ B ₂	7.70	0.41	-0.11	-0.24	-0.13	0.01	0.02
2 ¹ B ₂ ^b	8.02			-1.10		1.60	0.52
1 ¹ B ₁	1.79	-0.15	-0.14	-0.55	-0.13	-0.01	-0.01
2 ¹ B ₁ ^b	8.91			-0.61		1.80	0.57
3 ¹ B ₁ ^b	10.55			-0.53		1.82	0.61
1 ¹ A ₂	5.85	0.22	0.04	-0.42	0.04	0.01	0.01
2 ¹ A ₂ ^b	9.41			0.00		2.42	1.17
1 ³ A ₁	6.39	0.30	-0.12	-0.31	-0.11	-0.01	-0.01
2 ³ A ₁	8.23	-0.11	-0.16	-0.38	-0.17	-0.03	-0.01
3 ³ A ₁	9.84	0.34	-0.12	-0.31	-0.11	0.01	0.00
1 ³ B ₂ ^b	6.41			-1.13		-1.84	-0.65
2 ³ B ₂	7.70	0.17	-0.19	-0.31	-0.18	-0.06	0.01
1 ³ B ₁	-0.01	-0.49	-0.16	-0.61	-0.15	-0.03	-0.01
2 ³ B ₁	8.38	0.39	-0.09	-0.41	-0.08	0.01	0.01
1 ³ A ₂	4.79	-0.13	-0.01	-0.44	0.00	0.00	0.00
$\bar{\Delta}_{\text{abs}}$		0.29	0.12	0.38	0.12	0.02	0.01
Δ_{max}		0.49	0.20	0.61	0.21	0.06	0.02
BH 1 ¹ Σ ⁺ →							
1 ¹ Π	2.94	-0.10	-0.09	-0.61	-0.08	0.02	0.01
1 ¹ Δ ^b	5.88			-1.19		0.79	0.31
2 ¹ Σ ⁺	6.38	-0.01	-0.08	-0.43	-0.09	0.04	0.02
3 ¹ Σ ⁺ ^b	7.00			-1.54		0.39	0.18
2 ¹ Π	7.47	-0.10	-0.12	-0.51	-0.13	0.04	0.01
4 ¹ Σ ⁺	7.56	-0.16	-0.20	-0.54	-0.21	0.19	0.05
3 ¹ Π	8.24	-0.12	-0.13	-0.50	-0.14	0.04	0.02
1 ³ Π	1.31	-0.76	-0.29	-0.62	-0.28	-0.01	0.00
1 ³ Σ ⁻ ^b	4.69			-1.19		0.89	0.39
1 ³ Σ ⁺	6.26	-0.24	-0.12	-0.47	-0.13	0.03	0.01
2 ³ Σ ⁺	7.20	-0.35	-0.19	-0.49	-0.20	0.02	0.01
2 ³ Π	7.43	-0.22	-0.18	-0.51	-0.18	0.00	-0.01
3 ³ Σ ⁺	7.62	-0.22	-0.08	-0.52	-0.09	0.05	0.02
3 ³ Π	7.92	-0.15	0.00	-0.45	-0.01	0.08	0.05
$\bar{\Delta}_{\text{abs}}$		0.22	0.13	0.51	0.14	0.05	0.02
Δ_{max}		0.76	0.29	0.62	0.28	0.19	0.05

^aResults from Refs. 23–26.

^bTransitions with strong or dominant double-excitation character.

ADC(2) method and the so-called extended version [ADC(2)-E], in which the $2p$ - $2h$ diagonal block of the secular matrix is expanded through first order. While this leads to an improved treatment of the doubly excited states, the effect for the single excitations rather seems to be inconsistent and a change to the worse. Particularly large individual energy changes can be seen in the case of N₂.

The systems considered so far have in common that their ground-states can fairly well be treated in terms of RS perturbation theory, which also is the precondition for the applicability of the ADC methods. In Table IV we take a look at the performance of the method in cases such as CH₂ and BH, where that requirement is not fulfilled. Both systems are of quasi-open-shell type, lacking a distinct energy gap between occupied and virtual orbitals, which is reflected by unusually low excitation energies. Due to the choice of the ¹A₁ state as the reference state in the case of CH₂, one even has a negative excitation energy with respect to the true ¹B₁

ground state. The ADC(2) and CC2 second-order results for the single excitations are surprisingly good; the mean absolute error is below 0.14. However, the nonregular behavior in both CH₂ and BH becomes apparent in the deterioration of the results at the third-order ADC level, where the mean absolute error jumps to 0.38 and 0.51 eV, respectively; for the double excitations the deviations from FCI are in the order of -1 eV.

V. SUMMARY AND CONCLUSIONS

The numerical tests of the recently derived ADC(3) method presented here have shown a significantly improved accuracy for the excitation energies of single excitations with respect to the previous second-order [ADC(2)] treatment. The mean absolute error, as calibrated versus the FCI results for 41 singlet and triplet transitions, has been found to be smaller than 0.2 eV. The quality of the results seems to be

comparable or even superior to that of the CCSD method, not fully qualifying for third-order consistency, but it does not match the impressive accuracy of the CC3 computations, which, however, are substantially more expensive. At the second-order level, the present results confirm the essential equivalence of the ADC(2) and CC2 methods.

Let us reiterate that the computational concept of the ADC(3) method is simple. It combines diagonalization of a Hermitian secular matrix with perturbation theory for the matrix elements. The explicit configuration space, spanned by p - h and $2p$ - $2h$ excitations, is of the size of the SDCI treatment. As a consequence of the so-called *compactness* property, the ADC(3) results for the single excitations are consistent through third order in the residual electronic repulsion. The ADC(3) secular matrix is *separable*, which leads to size-intensive results both for excitation energies and transition moments. In principle, the method scales as N^6 with the number of molecular orbitals, yet that potential is not exhausted in the present prototypical ADC(3) computer code. As discussed in Sec. II B, an essential factor in the performance of the ADC(3) method is the improved treatment of one-particle density contributions using the Dyson expansion method. Like the CC methods the ADC(3) allows for black-box computations avoiding adjustments for individual states or groups of states, which may be the source of unbalances.

Of course, the use of perturbation theory causes limitations to the applicability of the method. The perturbation expansions for the secular matrix elements behave essentially like the corresponding RS ground-state and ground-state energy expansions, which means that whenever the ground state RSPT fails, e.g., in the case of large “static” correlation, the ADC methods can no longer reasonably be applied. This restriction also applies to systems with degenerate (open-shell) ground states. Similar limitations also affect the usual CC methods.

In the present study we have not considered transition moments, as the full third-order consistency here does not appear to be of utmost importance. Rather we recommend to combine the ADC(3) eigenvectors with the ADC(2) intermediate state transition moments. The performance of the latter quantities at the consistent ADC(2) level has been demonstrated in Ref. 20. It should be emphasized that the ADC size-consistency property and truncation error characteristics apply as well to the transition moments. Moreover, let us note that the method is not restricted to the treatment of excitation energies and transition moments. The ISR formulation, as outlined in Sec. II A, allows one to exploit the full potential of a wave-function approach: the method can readily be extended to the computation of excited-state properties and excited-state transition moments.⁴⁰

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