

Algebraic-diagrammatic construction propagator approach to molecular response properties

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Abstract

A polarization propagator method, referred to as algebraic-diagrammatic construction (ADC), is extended to the treatment of static and dynamic response properties of molecules. The recent intermediate state representation (ISR) concept of the ADC theory, giving direct access to excited states wave functions and properties, allows us to derive simple closed-form expressions for linear and higher response functions. The use of the band-Lanczos algorithm is proposed to evaluate efficiently the resolvent type ADC expressions. The performance of the method is tested in computations of static and dynamic polarizabilities of several small molecules at the second-order (ADC(2)) level of the theory. The ADC(2) results are compared with those of full configuration interaction (FCI), coupled cluster (CC), and SOPPA (second-order polarization propagator approximation) treatments.

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1. Introduction

The linear and non-linear response of ground-state molecules to static and dynamic (time- or frequency-dependent) perturbations, e.g. external electric fields, is of paramount importance for a variety of fields. The frequency-dependent polarizability [1], describing the linear response to an electric field, determines optical properties such as refractive indices, dielectric constants, Verdet constants, and Raman intensities, as well as dispersion coefficients of long-range intermolecular interaction. Response properties involving external magnetic fields and internal nuclear magnetic moments are magnetizabilities, NMR shielding constants, and nuclear spin–spin coupling constants [2,3]. Beyond the linear regime, hyperpolarizabilities, second hyperpolarizabilities, etc., form the basis for describing a wealth of non-linear optical (NLO) phenom-

ena, such as second harmonic generation (SHG), the electro-optic Pockels effect (EOPE), electric-field induced second-harmonic generation (EFISH), and the electro-optic Kerr effect (EOKE) [4].

In view of the importance of molecular response properties, great efforts have been directed towards establishing adequate means of a theoretical description. As long as only static properties are concerned one can recur to finite field techniques and determine the response properties through numerical or, preferably, analytical derivatives. This means that one can essentially use the well-developed arsenal of quantum chemical ground state methods such as the self-consistent field (SCF), many-body perturbation theory (MBPT), configuration interaction (CI), and coupled cluster (CC) treatments. In this context the coupled Hartree–Fock (CHF) method [5,6], associated with the molecular response at the SCF level, has played (and still plays) a key role.

When one proceeds to time- or frequency-dependent response, one is confronted with the necessity to deal with

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the (electronic) excitations, where presently the quantum chemical methods are less satisfactory than those used in the treatment of ground-states. At the SCF level the time-dependent (TD) generalization of the CHF leads to the TDHF method, which is equivalent to the famous random-phase approximation (RPA) [7–9]. Being the only method initially available, the RPA method has been widely used to calculate frequency-dependent response properties (see for example Refs. [10,11]). But the overall accuracy afforded by the RPA method is hardly satisfactory, as the error in the excitation energies and transition moments is of second-order in the electron repulsion [12].

A variety of more elaborate methods has been developed until now. A distinct step beyond the TDHF level was achieved by time-dependent MBPT methods as worked out by Rice and Handy [13] and by Hättig and Hess [14]. Another important development is the response theory for multiconfiguration self-consistent field (MCSCF) wave functions formulated by Olsen and Jørgensen [15]. Recently, also the time-dependent extension of density functional theory (DFT) has been applied to calculate polarizabilities and hyperpolarizabilities [16,17]. From a formal point of view the TDDFT method is quite similar to the RPA, which means that the numerical expense is similarly modest. CI approaches have been suggested as well [18,19], and seemingly very accurate polarizability results for small atoms and molecules have been obtained by Spelsberg and Meyer [18] using a large-size CI treatment.

Certainly, the most important theoretical development in the treatment of molecular response properties is based on the coupled cluster (CC) approach to excited states. Here, three similar formulations have been pursued, namely the CC-LR (coupled cluster linear response) theory [20], the EOM-CC (equation-of-motion coupled cluster) method [21], and the SAC-CI (symmetry adapted cluster CI) approach [22]. The CC-LR approach was formulated from the outset as a response theory for CC ground states, and was immediately applied in response property computations [23]. Computer implementations of linear response functions have been reported for the hierarchy of CCs, CC2, CCSD, and CC3 coupled cluster models [24,25] and also higher CC response functions have been derived [26]. The development of an EOM-CC approach to frequency-dependent molecular polarizabilities was reported by Stanton and Bartlett [27] and Rozyczko et al. [28].

As is well known, there is a close relationship between linear response functions and the polarization propagator [29]. A propagator approach that has been used for a long time to calculate polarizabilities and other linear response functions, is the second-order polarization propagator approximation (SOPPA) [30–32]. In particular, the SOPPA method has been applied very successfully to the treatment of nuclear spin–spin coupling constants (see, for example, Refs. [33,34]). Recently, the SOPPA method could be extended to quadratic and higher response functions by Olsen et al. [35] using a more general derivation scheme

based on time-dependent perturbation theory for a multi-configuration reference state.

Another polarization propagator approach, referred to as algebraic-diagrammatic construction (ADC) method [12], has proved useful in the treatment of electronic excitation in molecules [36,37]. The ADC computational procedure combines diagonalization of a Hermitian secular matrix and Rayleigh-Schrödinger (RS) perturbation theory (PT) for the secular matrix elements. At the presently worked out second-order (ADC(2)) [12,36] and third-order (ADC(3)) [38,39] levels the explicit configuration space comprises (generalized) single (S) and double (D) excitations and thus is of the size of the familiar CI-SD or CCSD treatments. Triple excitations are accounted for implicitly through the perturbation expansion of the secular matrix elements.

The original derivation of the ADC approximation schemes [12,38] was based on diagrammatic perturbation theory of the polarization propagator. Owing to this derivation, the ADC approach was previously confined to excitation energies and spectral moments of ground-to-excited state transitions. Recently, this restriction was overcome thanks to a new formulation of the ADC approach in terms of a specific intermediate state representation (ISR) [40–42]. Using the ISR concept the ADC secular matrix can be written as a representation of the Hamiltonian (or shifted Hamiltonian) with respect to a basis set of explicitly correlated states, referred to as (ADC) intermediate states. Together with the ADC eigenvectors, the intermediate states allow for an explicit representation of the excited state wave functions and, thus, for a direct approach to excited states properties. Moreover, transition moments between different excited states can now be treated as well.

Apart from a first trial run [43], the ADC method has not been used so far to compute response properties of molecules. Attempting to fill this gap, the purpose of this paper is to extend the ADC method to response properties and assess its potential here in first computational tests. A specific ADC form of the frequency-dependent response functions can easily be obtained from the response theory for exact states by replacing the (diagonal) sum-over-states (SOS) expressions with the corresponding (non-diagonal) ISR representation. For the numerical evaluation of the resulting ADC expression, being essentially frequency-dependent resolvent matrix elements, the so-called band or block Lanczos (BL) algorithm [44,45] proves to be a practical and efficient method.

In this paper, we report on computations of static and time-dependent polarizabilities at the ADC(2) level for a series of atoms and small molecules, comprising Ne, CO, N₂, HF, H₂O, CH₄, and C₂H₄. For these systems an extensive set of CC results is available, obtained at various levels of the CC hierarchy [46–51]. In the case of Ne and HF even full configuration interaction (FCI) results have been reported [47]. For a stringent comparison the present ADC(2) computations were performed using the basis sets and structural parameters taken from the CC computa-

tions. As expected, the ADC(2) method will be seen to perform essentially as other second-order methods, that is, CC2 and SOPPA. In some cases, however, the ADC(2) errors stand out of the usual margin, indicating that for certain ADC transition amplitudes one must go beyond the second-order perturbation-theoretical expressions used at the strict ADC(2) level.

2. Theory

2.1. ADC method and intermediate state representations: general background

The ADC approach and its reformulation using the intermediate state representation (ISR) concept has been amply presented elsewhere [12,38,39,42]. A brief review of the basic notions will be given in the following.

The ADC approach can be viewed as a specific reformulation of the diagrammatic perturbation series for the polarization propagator. Let us consider an N -electron system with the Hamiltonian \hat{H} , a (non-degenerate) ground-state $|\Psi_0\rangle$, and energy E_0 . The polarization propagator [29]

$$\mathbf{\Pi}(\omega) = \mathbf{\Pi}^+(\omega) + \mathbf{\Pi}^-(\omega) \quad (1)$$

is defined as a matrix of resolvent-type matrix elements

$$\mathbf{\Pi}_{rs,r's'}^+(\omega) = \langle \Psi_0 | c_s^\dagger c_r (\omega - \hat{H} + E_0 + i\eta)^{-1} c_{r'}^\dagger c_{s'} | \Psi_0 \rangle' \quad (2a)$$

$$\mathbf{\Pi}_{rs,r's'}^-(\omega) = \mathbf{\Pi}_{s'r',sr}^+(-\omega) \quad (2b)$$

Here, c_p^\dagger (c_p) denote creation (annihilation) operators of second quantization associated with the ground-state Hartree–Fock (HF) orbitals, φ_p . The prime after the ket on the r.h.s. of Eq. (2a) indicates the subtraction of the undesired contribution

$$\langle \Psi_0 | c_s^\dagger c_r | \Psi_0 \rangle \langle \Psi_0 | c_{r'}^\dagger c_{s'} | \Psi_0 \rangle (\omega + i\eta)^{-1}$$

in the resolvent matrix elements. The positive infinitesimal η , guaranteeing the convergence of the Fourier transforms between time and energy representations, will be dropped whenever unessential. According to Eq. (2b), the two parts, $\mathbf{\Pi}^+(\omega)$ and $\mathbf{\Pi}^-(\omega)$, contain the same physical information, so that it suffices to confine oneself to the former part.

The polarization propagator part $\mathbf{\Pi}^+(\omega)$ can be written in the general algebraic form (ADC form)

$$\mathbf{\Pi}^+(\omega) = \mathbf{f}^\dagger (\omega - \mathbf{M})^{-1} \mathbf{f} \quad (3)$$

by inserting twice the a complete basis set of the so-called intermediate states, $|\tilde{\Psi}_J\rangle$, on the r.h.s. of Eq. (2a). Here, the ADC secular matrix \mathbf{M} is defined as the representation

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

of the (shifted) Hamiltonian $\hat{H} - E_0$ with respect to the intermediate states $|\tilde{\Psi}_I\rangle$, and \mathbf{f} is the matrix of effective transition amplitudes, defined correspondingly by

$$f_{J,rs} = \langle \tilde{\Psi}_J | c_r^\dagger c_s | \Psi_0 \rangle. \quad (5)$$

The intermediate states introduced here will be specified below. The physical information of interest is obtained from the (exact or approximate) ADC matrices \mathbf{M} and \mathbf{f} in an obvious way. The (vertical) excitation energies,

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

are given by the eigenvalues of \mathbf{M} . In a compact matrix notation the eigenvalue problem can be written as:

$$\mathbf{M}\mathbf{X} = \mathbf{X}\mathbf{\Omega}, \quad \mathbf{X}^\dagger \mathbf{X} = \mathbf{1}. \quad (7)$$

Here, $\mathbf{\Omega}$ and \mathbf{X} denote the diagonal eigenvalue matrix and the matrix of eigenvectors, $\underline{X}^{(n)}$, respectively. The excited states can be expanded according to

$$|\Psi_n\rangle = \sum_J X_{Jn} |\tilde{\Psi}_J\rangle \quad (8)$$

in terms of the eigenvector components and the intermediate states, so that transition moments of the type

$$T_n = \langle \Psi_n | \hat{D} | \Psi_0 \rangle \quad (9)$$

are given according to

$$T_n = \underline{X}_n^\dagger \mathbf{F} \quad (10)$$

by the scalar product of the eigenvector $\underline{X}^{(n)}$ and a vector \mathbf{F} of the so-called effective transition moments,

$$F_J = \langle \tilde{\Psi}_J | \hat{D} | \Psi_0 \rangle = \sum_{rs} d_{rs} f_{J,rs} \quad (11)$$

Here, $\hat{D} = \sum d_{rs} c_r^\dagger c_s$ is a (one-particle) transition operator, e.g., a dipole moment operator, with one-particle matrix elements $d_{rs} = \langle \varphi_r | \hat{d} | \varphi_s \rangle$, and $f_{J,rs}$ denotes the effective transition amplitudes defined by Eq. (5).

In the original ADC procedure [12,38] explicit expressions for the matrix elements of \mathbf{M} and \mathbf{f} are obtained without the need to specify the intermediate state representation. The starting point is the observation that these quantities are accessible in the form of perturbation expansions:

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \dots, \quad (12a)$$

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \dots \quad (12b)$$

Note that in previous work the ADC (secular) matrix, \mathbf{M} , has been denoted by $\mathbf{K} + \mathbf{C}$, where $\mathbf{K} = \mathbf{M}^{(0)}$ is the diagonal matrix of zeroth-order (Hartree–Fock) excitation energies. Using these expansions in the ADC form (Eq. (3)) leads to a formal perturbation expansion for the $\mathbf{\Pi}^+$ part of the polarization propagator, which, in turn, can be compared with the original diagrammatic perturbation series. Performing this comparison through a definite order n of perturbation theory, this procedure allows one to determine successively higher-order contributions to \mathbf{M} and \mathbf{f} and, thus, generate in a systematic way a hierarchy of consistent n th-order approximation schemes referred to as ADC(n) approximations.

Of particular interest is the ADC(2) level of theory [12,36]. Here the explicit excitation manifold comprises the p - h and $2p$ - $2h$ excitations; the perturbation expansions

of the secular matrix elements extend through second, first, and zeroth-order in the $p-h$ block (\mathbf{M}_{11}), the $p-h/2p-2h$ coupling block (\mathbf{M}_{12}), and the $2p-2h$ block (\mathbf{M}_{22}), respectively. In a similar way, the $p-h$ and $2p-2h$ parts of the IS transition amplitudes, \mathbf{f}_1 and \mathbf{f}_2 , require expansions through second and first-order, respectively. An extension of the ADC(2) scheme, referred to as ADC(2)- x , is obtained by using the first-order expansion $\mathbf{M}_{22}^{(0)} + \mathbf{M}_{22}^{(1)}$ for the $2p-2h$ block. This improves the treatment of doubly excited states and states with a strong admixture of double excitations. At the third-order (ADC(3)) level [38] the expansion manifold is the same as in second-order, while the perturbation expansions of the matrix elements extend through the next order of PT (that is, 3, 2, and 1, respectively). Explicit expressions for the ADC(n) secular matrix elements, $n = 1, 2, 3$, have been given in Refs. [12,38]; for the f amplitudes of the ADC(2) scheme see Ref. [53].

The intermediate states underlying the ADC approach can explicitly be constructed, affording a direct approach to the ADC matrices \mathbf{M} and \mathbf{f} . The starting point for this construction is the set of the so-called correlated excited states,

$$|\Psi_J^0\rangle = \hat{C}_J |\Psi_0\rangle \quad (13)$$

where

$$\{\hat{C}_J\} \equiv \{c_a^\dagger c_k; c_a^\dagger c_b^\dagger c_k c_l, a < b, k < l; \dots\} \quad (14)$$

denotes the set (physical) excitation operators corresponding to $p-h$, $2p-2p$, ... excitations and $|\Psi_0\rangle$ is the exact ground state. Here, and elsewhere we use the familiar notation, in which the subscripts a, b, c, \dots and i, j, k, \dots refer to unoccupied (virtual) and occupied orbitals, respectively; the subscripts p, q, r, \dots will be used for orbitals of either type. The procedure used to generate the intermediate states is essentially successive Gram–Schmidt orthonormalisation of the $p-h$, $2p-2h$, ... excitation classes. Including here also the exact ground state as a zeroth excitation class one obtains an orthonormal basis set $\{|\tilde{\Psi}_J\rangle\}$, where

$$\langle \tilde{\Psi}_I | \tilde{\Psi}_J \rangle = \delta_{IJ}, \quad \langle \tilde{\Psi}_I | \Psi_0 \rangle = 0, \quad I, J \neq 0 \quad (15)$$

Obviously, the set $\{|\tilde{\Psi}_J\rangle, J > 0\}$ is complete in the space of the (exact) excited states. The Gram-Schmidt procedure leads to formal expansions for the successive classes of intermediate states (becoming rather lengthy for higher classes). Inserting these Gram-Schmidt expansions in the respective sub-blocks of the ISR (or ADC) matrices \mathbf{M} and \mathbf{f} (Eqs. (4) and (5)) one obtains closed-form expressions depending on the exact ground state (and the ground-state energy), which now can be evaluated using RS PT for $|\Psi_0\rangle$ and E_0 . By truncating the IS manifolds and the resulting perturbation expansions in a consistent way, this procedure reproduces the hierarchy of ADC(n) approximations.

The ISR approach to the derivation of explicit ADC expressions becomes quite cumbersome beyond second-order, and here the original diagrammatic derivation is more advantageous. On the other hand, the ISR proce-

dure allows one to determine representations of operators other than the Hamiltonian. Recently, the ADC/ISR representation,

$$D_{IJ} = \langle \tilde{\Psi}_I | \hat{D} | \tilde{\Psi}_J \rangle \quad (16)$$

of an arbitrary one-particle operator

$$\hat{D} = \sum_{r,s} d_{rs} c_r^\dagger c_s \quad (17)$$

was derived at the second-order (ADC(2)) level [42]. As a consequence, one can now calculate properties of excited states according to

$$D_n = \langle \Psi_n | \hat{D} | \Psi_n \rangle = \underline{Y}_n^\dagger \mathbf{D} \underline{Y}_n \quad (18)$$

and, in a similar way, transition moments between excited states,

$$T_{nm} = \langle \Psi_n | \hat{D} | \Psi_m \rangle = \underline{Y}_n^\dagger \mathbf{D} \underline{Y}_m \quad (19)$$

The perturbation-theoretical consistency of the results depends on the excitation class of the considered states. At the ADC(2) level, the properties and transition moments of single excitations are treated consistently through second-order.

A summarizing characterization of the ADC method is as follows: the basic computational procedure consists in the diagonalization of a Hermitian secular matrix using RS type PT to evaluate the secular matrix elements. The explicit configuration spaces of the secular problem are smaller than those of comparable CI expansions, a property referred to as *compactness*. The ADC truncation error resulting from restricting the configuration space to singles and doubles is of fourth-order (for the excitation energies of single excitations) as compared to a second-order truncation error in the CI case. (In that respect the ADC scheme is even superior to the CC methods, where the corresponding truncation error is of order 3.) The ADC equations are *separable* [54], that is, local and non-local excitations are strictly decoupled, and the ADC results both for the energies and for the transition moments (intensities) are *size-consistent* (*size-intensive*).

2.2. ADC formulation of polarizabilities

The ADC formulation of polarizabilities can readily be derived from the exact formulation of time-dependent (td) linear response, as given, for example, by Fetter and Walecka [29]. The td linear response of a property A , associated with a (one-particle) operator \hat{A} , and a td perturbation of the form $\hat{B}f(t)$, where \hat{B} is a time-independent (one-particle) operator and $f(t)$ a td function with $f(t) = 0$ for $t < t_0$, can be written as:

$$\Delta A(t) = \int_{-\infty}^{\infty} R_{AB}(t, t') f(t') dt' \quad (20)$$

where

$$R_{AB}(t, t') = \theta(t - t') \langle \Psi_0 | [\hat{B}(t'), \hat{A}(t)] | \Psi_0 \rangle \quad (21)$$

is referred to as the associated response function. Here, it is supposed that for $t \leq t_0$ the system is in the exact (unperturbed) ground state $|\Psi_0\rangle$ and $\hat{O}(t) = e^{i\hat{H}t}\hat{O}e^{-i\hat{H}t}$ denotes the interaction picture form of the operator \hat{O} . Fourier transform according to

$$R_{AB}(\omega) = \int_{-\infty}^{\infty} e^{i(\omega+i\eta)t} R_{AB}(t, 0) dt \quad (22)$$

leads to the final energy-dependent form of the response function,

$$R_{AB}(\omega) = \langle \Psi_0 | \hat{A}(\omega - \hat{H} + E_0 + i\eta)^{-1} \hat{B} | \Psi_0 \rangle - \langle \Psi_0 | \hat{B}(\omega + \hat{H} - E_0 + i\eta)^{-1} \hat{A} | \Psi_0 \rangle \quad (23)$$

Here, again, η is a positive infinitesimal introduced for the definiteness of the Fourier transforms. The familiar sum-over-states (SOS) form of the response function,

$$R_{AB}(\omega) = \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{A} | \Psi_n \rangle \langle \Psi_n | \hat{B} | \Psi_0 \rangle}{\omega - E_n + E_0 + i\eta} - \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{B} | \Psi_n \rangle \langle \Psi_n | \hat{A} | \Psi_0 \rangle}{\omega + E_n - E_0 + i\eta} \quad (24)$$

is obtained by inserting the resolution of the identity in terms of the exact states $|\Psi_n\rangle$. Note that the contributions associated with $|\Psi_0\rangle\langle\Psi_0|$ cancel. Using the intermediate states $|\tilde{\Psi}_I\rangle$ rather than the exact states in Eq. (23), one arrives at the ADC form

$$R_{AB}(\omega) = \mathbf{F}_A^\dagger(\omega - \mathbf{M})^{-1} \mathbf{F}_B - \mathbf{F}_B^\dagger(\omega + \mathbf{M})^{-1} \mathbf{F}_A \quad (25)$$

where \mathbf{M} is the ADC secular matrix and \mathbf{F}_A denotes the vector of IS transition moments for the operator \hat{A} according to Eq. (11).

Depending on the choice of the operators \hat{A} , \hat{B} the general expressions (24) and (25) allow one to treat various response properties, such as dipole polarizabilities, nuclear magnetic shielding tensors, diamagnetic magnetizabilities and nuclear spin–spin coupling constants. Here, we are interested in dipole polarizabilities,

$$\alpha_{\mu\nu}(\omega) = R_{D_\mu D_\nu}(\omega) \quad (26)$$

where \hat{D}_ν , $\nu = x, y, z$, denotes the dipole operator components, e.g., $\hat{D}_z = e \sum_{i=1}^N z_i$. The special case of a static perturbation is obtained by setting $\omega = 0$:

$$\alpha_{\mu\nu}(0) = -e^2 (\mathbf{F}_{D_\mu}^\dagger \mathbf{M}^{-1} \mathbf{F}_{D_\nu} + \text{c.c.}) \quad (27)$$

In a similar way, the exact expressions for quadratic and higher response can be cast into ADC form. Let us briefly inspect the case of hyperpolarizabilities (quadratic response). Here, one may distinguish a property A and two time-dependent perturbations B and C, being represented by the three (one-particle) operators \hat{A} , \hat{B} , and \hat{C} , respectively. Upon Fourier transformation, a typical hyperpolarizability contribution reads

$$\beta_{ABC}(-\omega_\sigma; \omega_1, \omega_2) = \sum_{n, m \neq 0} \frac{\langle \Psi_0 | \hat{A} | \Psi_m \rangle \langle \Psi_m | \hat{B} | \Psi_n \rangle \langle \Psi_n | \hat{C} | \Psi_0 \rangle}{(\omega_\sigma - \omega_m)(\omega_2 - \omega_n)} \quad (28)$$

where ω_1 and ω_2 are the frequencies of the perturbing (“incoming”) fields and $\omega_\sigma = \omega_1 + \omega_2$ is the frequency of the resulting (“outgoing”) field. The SOS expression (28) can again be transformed in a corresponding ADC form reading

$$\beta_{ABC}(-\omega_\sigma; \omega_1, \omega_2) = \mathbf{F}_A^\dagger(\omega_\sigma - \mathbf{M})^{-1} \mathbf{B}(\omega_2 - \mathbf{M})^{-1} \mathbf{F}_B \quad (29)$$

In addition to the ingredients appearing also in the polarizability expression (25), here the matrix \mathbf{B} comes into play, denoting the intermediate state representation of the operator \hat{B} .

2.3. Improved treatment of second-order transition amplitudes

Certain perturbation-theoretical terms occurring in the ADC schemes sometimes perform rather poorly, and one has to go beyond their strict PT treatment in order to achieve a generally satisfactory description [39,52,53]. Characteristically, these terms involve, in one form or another, matrix elements of the one-particle density,

$$\rho_{rs} = \langle \Psi_0 | c_s^\dagger c_r | \Psi_0 \rangle \quad (30)$$

or, more precisely, some low-order terms, $\rho_{rs}^{(v)}$, of their PT expansions. While in the ADC secular matrix such contributions do not arise before third-order (see Ref. [39]), the effective (ISR) transition amplitudes are already affected at the second-order level. According to Eqs. (A5-A18) in Ref. [53], there are 13 distinct second-order terms $f_{ak,rs}^{(2,m)}$, $m = 1, \dots, 13$. Of these the two terms (A9, A10) contributing to $f_{ak,ij}$ (second index pair: hh) and the two terms (A11, A12) contributing to $f_{ak,bd}$ (second index pair: pp) can be combined, yielding

$$f_{ak,ij}^{(2)} = -\delta_{kj} \rho_{ia}^{(2)}, \quad f_{ak,bd}^{(2)} = \delta_{ab} \rho_{dk}^{(2)} \quad (31)$$

The second-order term, $\rho_{ai}^{(2)}$, being the lowest non-vanishing contribution to the p – h components of the density matrix, is associated with the admixture p – h excitations in the exact ground state, for which, in general, second-order RSPT is not a stable and reliable approximation. In view of this, it is advisable to replace the strict second-order expressions $\rho_{ai}^{(2)}$ in Eq. (31) by an improved representation for the p – h density matrix elements, as provided, for example, by the Dyson expansion method (DEM) [52]. The DEM procedure has been used for a long time in the treatment of the so-called static self-energy contributions, $\Sigma_{pq}(\infty)$, arising in third-order approximations for the electron propagator [55]. For a more detailed discussion the reader is referred to Ref. [53], where also the DEM is reviewed.

It should be noted that in a similar spirit Sauer [56] has introduced an improved SOPPA variant referred to as SOPPA(CCSD) in which the second-order p – h density matrix elements have been replaced by the corresponding CCSD singles amplitudes.

3. Computations

3.1. Block-Lanczos method for polarizabilities

The method of choice for the inversion of the ω -dependent matrices arising in the ADC formulation of the polarizabilities and hyperpolarizabilities (Eqs. (25) and (29)) is the band or block extension of the ordinary Lanczos algorithm (see, for example, Parlett [44] and Meyer and Pal [45]). To explain the numerical procedures let us consider a typical set of resolvent matrix elements

$$I_{ab}(\omega) = \mathbf{F}_a^\dagger (\omega - \mathbf{M})^{-1} \mathbf{F}_b, \quad a, b = 1, \dots, r \quad (32)$$

where \mathbf{M} and \mathbf{F}_a may represent the ADC secular matrix and r transition moment vectors, respectively. The BL algorithm starts by supplying r orthonormal vectors q_i formed, e.g., by a Gram-Schmidt procedure from the set $\{\mathbf{F}_a, a = 1, \dots, r\}$. Each BL step generates an additional set of r Lanczos vectors. In the basis spanned by the Lanczos vectors the projection of the original secular matrix \mathbf{M} becomes a band matrix \mathbf{T} with a bandwidth of $2r + 1$:

$$\mathbf{T} = \mathbf{Q}^\dagger \mathbf{M} \mathbf{Q} \quad (33)$$

Here, \mathbf{Q} denotes the matrix (q_1, \dots, q_{nr}) of the Lanczos vectors generated after n BL steps. Diagonalization of the (small) band matrix \mathbf{T} generates a set of nr approximate eigenvalues $\tilde{\omega}_k$, $k = 1, \dots, nr$ of \mathbf{M} . The corresponding approximate eigenvectors are obtained according to

$$\tilde{\mathbf{Y}}_k = \mathbf{Q} \mathbf{Z}_k \quad (34)$$

where \mathbf{Z}_k is the k th eigenvector of \mathbf{T} . Using the approximate Lanczos eigenpairs $(\tilde{\omega}_k, \tilde{\mathbf{Y}}_k)$ in a spectral representation of an resolvent matrix element (Eq. (32)) yields

$$\tilde{I}_{ab}(\omega) = \sum_{k=1}^{nr} \frac{g_a^{(k)} g_b^{(k)}}{\omega - \tilde{\omega}_k} \quad (35)$$

where

$$g_a^{(k)} = \tilde{\mathbf{Y}}_k^\dagger \mathbf{F}_a = \mathbf{Z}_k^\dagger \mathbf{Q}^\dagger \mathbf{F}_a \quad (36)$$

is the scalar product of the Lanczos eigenvector $\tilde{\mathbf{Y}}_k$ and the transition moment vector \mathbf{F}_a . Relatively, few Lanczos steps suffice to yield a good approximation for the exact resolvent functions, $I_{ab}(\omega)$ for frequencies ω not too close to non-converged energy eigenvalues $\tilde{\omega}_k$. It should be noted that the BL method can be applied to the static limit $\omega = 0$ as well.

An important point for the efficiency of the BL algorithm is the observation that, by construction, the original vectors \mathbf{F}_a , $a = 1, \dots, r$ are orthogonal to all Lanczos vectors with $i > r$. Thus, it suffices to compute and store the r^2 scalar products $q_i^\dagger \mathbf{F}_a$ ($i, a = 1, \dots, r$) in order to determine the residue amplitudes $g_a^{(k)}$ according to Eq. (36). As in all iterative diagonalization routines the basic numerical step in each BL cycle, determining also the scaling behavior, is the *matrix \times vector* product, $\mathbf{M}v \rightarrow v'$.

3.2. Computational details

The H₂O and C₂H₄ molecules were placed in the yz -plane, the molecular axis along the z -axis. The basis sets comprised the cc-pVXZ sets [57], X = D,T,Q, using both the aug- and d-aug-extensions [58]. However, the six-component representation of the Cartesian d-functions had to be used in the present calculations, which will slightly affect the comparability of the CC and ADC results. In the present study static polarizabilities have been computed for Ne, CO, N₂, HF, H₂O, CH₄, and C₂H₄. For Ne and HF also dynamic polarizabilities in the 0.1–0.5 a.u. frequency range are reported. For a stringent comparison with FCI [47] and CC results [46–51], the molecular structures and basis sets used here are as in the latter work. More specifically, the molecular structure data were taken from Ref. [59]: $R(\text{CO}) = 1.12836 \text{ \AA}$; $R(\text{NN}) = 1.09773 \text{ \AA}$; $R(\text{HF}) = 0.916879 \text{ \AA}$; $R(\text{OH}) = 0.957902 \text{ \AA}$, HOH = 104.4°; $R(\text{CH}) = 1.08588 \text{ \AA}$ (CH₄); $R(\text{CC}) = 1.33074 \text{ \AA}$, $R(\text{CH}) = 1.08068 \text{ \AA}$, HCH = 121.4° (C₂H₄). The ADC calculations were performed using the original code [60] interfaced to the GAMESS [61] program package. The strict (not improved) second-order contributions to the \mathbf{f} amplitudes were used in the ADC(2) computations.

The Heidelberg block-Lanczos module [45,62,63] was slightly modified and adapted to the ADC code. In the polarizability computations, typically 500 block-Lanczos iterations were performed to ensure fully converged results. A typical Lanczos convergence pattern is displayed in Table 1.

4. Results and discussion

In Tables 2 and 3 we compare dynamic polarizabilities of Ne and HF at distinct frequencies obtained at the ADC(1) and ADC(2) levels of theory with FCI reference data, the results of various CC schemes [46–51], and recent SOPPA results [64]. The common basis sets used in these

Table 1

Convergence of Lanczos iterations for the lowest eigenvalues of the ADC secular matrix (Hartree) and components of the static polarizability α (a.u.) for CO (ADC(2)/d-aug-cc-pVTZ)^a

Number of Lanczos iterations	Lowest ¹ B ₁ eigenvalue ^b	Lowest ¹ A ₁ eigenvalue ^c	$\alpha_{xx} = \alpha_{yy}$	α_{zz}
30	0.365354	0.477467	11.87908	17.31481
50	0.323858	0.443533	11.88485	17.31763
100	0.320735	0.416355	11.88488	17.31764
300	0.320734	0.406282	11.88488	17.31764
500	0.320734	0.406282	11.88488	17.31764

^a Using C_{2v} spatial symmetry the ADC(2) secular matrices were of the dimensions 125,488 and 138,782 for ¹B₁ and ¹A₁ symmetry, respectively.

^b Converged eigenvalue obtained using Davidson diagonalization 0.320734 Hartree.

^c Converged eigenvalue obtained using Davidson diagonalization 0.406283 Hartree.

Table 2
Dynamic polarizabilities (a.u.) of Ne obtained using TDA, ADC, CC, and SOPPA methods compared to FCI results(d-aug-cc-pVDZ basis set)^{a,b,c}

ω (a.u.)	0.0	0.1	0.2	0.3	0.4	0.5
FCI	2.67	2.70	2.79	2.97	3.31	4.09
<i>Error</i>						
TDA/CIS	-0.10	-0.11	-0.14	-0.18	-0.30	-0.66
ADC(1)	-0.29	-0.30	-0.32	-0.38	-0.51	-0.88
ADC(2)	0.16	0.16	0.18	0.22	0.32	0.85
CCS	-0.23	-0.24	-0.27	-0.32	-0.44	-0.82
CC2	0.15	0.15	0.17	0.20	0.28	0.66
CCSD	0.03	0.04	0.04	0.05	0.07	0.14
CC3	0.00	0.00	0.00	0.01	0.01	0.01
SOPPA	0.15	0.15	0.17	0.21	0.31	0.88

^a FCI and CC results from Ref. [47].

^b SOPPA results from S.P.A. Sauer, Private Communication, 2006.

^c The TDA and ADC calculations were performed using the six-component Cartesian representation of d-functions.

computations are the aug-cc-pVDZ and d-aug-cc-pVDZ sets, where the 6-component rather than the 5-component d-function sets were used in the ADC computations. At the first-order (ADC(1)) level the polarizabilities are smaller than the FCI results, the error being in the order of 10% for small frequencies and 20% for larger frequencies. A modest, though rather systematic improvement can be seen at the ADC(2) level. Here, the error ranges from 5% at small frequencies to 10% at higher frequencies, the ADC results lying now above the FCI values. As has been pointed out in the case of excitation energies and spectral intensities [39], the CCS and CC2 results are essentially equivalent to those of the ADC(1) and ADC(2) methods, respectively, and this observation also applies to polarizabilities. Both with respect to the magnitude and the sign of the errors, the ADC(1) and ADC(2) results in Tables 2 and 3 are quite similar to those of the CCS and CC2 schemes, respectively. One may also note that there is little difference between the ADC(2) and SOPPA results.

Significantly, more accurate results are obtained at the CCSD and CC3 levels. In particular, the CC3 method yields a highly satisfactory description of polarizabilities and may serve as accuracy standard when FCI results are not available. However, the CCSD and CC3 methods scale as N^6 and N^7 , respectively, with the number of basis functions, that is, they are more expensive than the CC2 and ADC(2) methods, both scaling as N^5 . One may note that the simple CIS or Tamm–Dancoff approximation (TDA) performs surprisingly well, yielding better results than those of ADC(1) and CCS in the present examples of Ne and HF. Presumably, this will be largely due to favorable error compensation rather than representing generally valid pattern.

ADC(2) results for the static polarizabilities of Ne, CO, N₂, HF, H₂O, CH₄, and C₂H₄ are given in Table 4 together with experimental data. A relatively large basis set (d-aug-cc-pVTZ) was used in the ADC(2) computations, making a comparison between theory and experiment meaningful. For the isotropic polarizabilities, $\bar{\alpha}$, the error relative to experiment is below 5%, except for CO and HF, where the ADC(2) results exceed the experiment by 9% and 8%, respectively. While such deviations, uncorrected for vibrational effects, may still be in an acceptable range, a less satisfactory situation is found for the polarizability anisotropies, $\Delta\alpha$. Particularly large deviations from experiment are seen in CO and N₂, amounting to almost 2 a.u. in the case of CO. Obviously, the error in the ADC(2) results for different α components is not uniform.

For a closer inspection of the anisotropy problem, we compare in Table 5 various theoretical results for the static polarizabilities of CO and H₂O, where the CC3 results of Christiansen et al. [48] can serve as accuracy benchmark. In both the ADC, CC, and SOPPA [64] computations the d-aug-cc-pVTZ basis set was used. The ADC anisotropy error in CO can clearly be traced to the poor reproduction of the longitudinal (zz) polarizability component. Whereas the ADC(2) result for the orthogonal (xx , yy) components

Table 3
Dynamic polarizabilities (a.u.) of HF obtained using TDA, ADC, CC, and SOPPA methods compared to FCI results (aug-cc-pVDZ basis set)^{a,b,c}

ω (a.u.)	0.0		0.1		0.2		0.3	
	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}
FCI	4.29	6.21	4.39	6.33	4.76	6.74	6.00	7.63
<i>Error</i>								
TDA/CIS	-0.12	0.18	-0.16	0.17	-0.30	0.10	-0.97	-0.08
ADC(1)	-0.47	-0.66	-0.50	-0.69	-0.65	-0.79	-1.33	-1.03
ADC(2)	0.27	0.51	0.30	0.53	0.43	0.62	1.48	0.81
CCS	-0.34	-0.32	-0.38	-0.35	-0.53	-0.44	-1.21	-0.65
CC2	0.29	0.43	0.32	0.44	0.44	0.51	1.24	0.66
CCSD	0.05	0.07	0.06	0.08	0.08	0.09	0.19	0.11
CC3	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.02
SOPPA	0.26	0.43	0.29	0.46	0.44	0.55	1.76	0.78

^a FCI and CC results from Ref. [47].

^b SOPPA results from S.P.A. Sauer, Private Communication, 2006.

^c The TDA and ADC calculations were performed using the six-component Cartesian representation of d-functions.

Table 4

Theoretical (ADC(2)/d-aug-cc-pVTZ) and experimental static polarizabilities α (a.u.), isotropic polarizabilities $\bar{\alpha}^a$ (a.u.) and polarizability anisotropy $\Delta\alpha^b$ (a.u.) of Ne, CO, N₂, HF, H₂O, CH₄, and C₂H₄^c

System	ADC(2)			Experiment			
	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
Ne	2.79	2.79	2.79	2.79		2.67 ^d	
CO	11.89	11.89	17.32	13.70	5.43	13.08 ^e	3.59 ^f
N ₂	10.07	10.07	15.15	11.76	5.08	11.74 ^g	4.45 ^g
HF	5.53	5.53	6.83	5.96	1.30	5.60 ^h	1.33 ⁱ
H ₂ O	9.76	10.40	10.17	10.11	0.56	9.83 ^j	0.67 ^k
CH ₄	16.57	16.57	16.57	16.57		17.27 ^l	
C ₂ H ₄	22.54	24.91	35.35	27.60	11.81	27.82 ^m	11.31 ^m

$$^a \bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}).$$

$$^b \Delta\alpha = \frac{1}{\sqrt{2}}((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2)^{1/2}.$$

^c The aug-cc-pVDZ basis set employed in case of CH₄ and C₂H₄.

^d Ref. [65], as cited in Ref. [51].

^e Ref. [66], as cited in Ref. [51].

^f Ref. [67] for $\lambda = 632.8$ nm, as cited in Ref. [48].

^g Ref. [67], as cited in Ref. [49].

^h Ref. [68], as cited in Ref. [64].

ⁱ Ref. [69], as cited in Ref. [64].

^j Ref. [70], as cited in Ref. [48].

^k Ref. [71], as cited in Ref. [48].

^l Ref. [72], as cited in Ref. [64].

^m Derived from the data of Ref. [73], as cited in Ref. [46] ($\alpha_{xx} = 22.38$, $\alpha_{yy} = 26.02$, $\alpha_{zz} = 35.06$ a.u.).

agrees with the CC3 reference to within 0.06 a.u., there is a discrepancy of 1.8 a.u. for α_{zz} . One will note strikingly different convergence patterns in the xx - and zz -component results with increasing ADC order number (n). While in both cases the behavior is oscillatory, the amplitudes of the results for the longitudinal component are much larger than those of the orthogonal components: the α_{zz} value drops by about 3.8 a.u. when going from the zeroth- (TDA) to the first-order (ADC(1)) level, and rises again by 3.9 a.u. at the second-order (ADC(2)) level. The corresponding changes of the α_{xx} values, being -2.3 and $+0.6$ a.u., respectively, are considerably smaller. It seems that in view of the large oscillations in the case of α_{zz} , the second-order contribution becomes unbalanced and overshoots the acceptable limit. The trend to overestimate the longitudinal component is seen also in the SOPPA and CC2 results, though much less pronounced than in the ADC(2) data. Obviously, the large error in the longitudinal polarizability of CO indicates a serious deficiency of the present ADC(2) version, which is still based on the strict (not improved) second-order expressions for the effective transition amplitudes. We expect that the improved amplitudes according to Section 2.3 will lead to a more satisfactory description in line with the CC2 and SOPPA results.

In H₂O, the second example of Table 5, the polarization anisotropy is relatively small, and the ADC(2) result of 0.56 a.u. is in very good agreement with the CC3 value. Here, the ADC(2) error with respect to the CC3 reference is roughly uniform for all three polarizability components (~ 0.4 – 0.5 a.u.), being even somewhat smaller than the

Table 5

Static polarizabilities α (a.u.), isotropic polarizabilities $\bar{\alpha}$ (a.u.) and polarizability anisotropy $\Delta\alpha$ (a.u.) of CO and H₂O calculated using TDA, ADC, CC and SOPPA schemes in comparison with experimental data^a

	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
CO					
TDA/CIS	13.62		17.17	14.80	3.55
ADC(1)	11.31		13.43	12.02	2.12
ADC(2)	11.89		17.32	13.70	5.43
CIS ^b	13.57		17.19	14.77	3.62
CCS ^c	12.09		15.26	13.15	3.17
CC2 ^c	12.15		16.10	13.47	3.95
CCSD ^c	11.87		15.71	13.15	3.84
CC3 ^c	11.95		15.57	13.16	3.62
SOPPA ^f	11.91		16.49	13.44	4.58
Experimental				13.08 ^d	3.59 ^e
H ₂ O					
TDA/CIS	8.74	10.59	9.75	9.69	1.60
ADC(1)	7.97	9.24	8.48	8.56	1.11
ADC(2)	9.76	10.40	10.17	10.11	0.56
CCS ^c	8.26	9.71	8.97	8.98	1.26
CC2 ^c	10.15	10.52	10.28	10.32	0.33
CCSD ^c	9.35	9.98	9.61	9.65	0.55
CC3 ^c	9.38	9.96	9.61	9.65	0.51
SOPPA ^f	9.83	10.36	10.10	10.10	0.46
Experimental				9.83 ^g	0.67 ^h

^a Theoretical results for the d-aug-cc-pVTZ basis set (the present TDA and ADC calculations performed using Cartesian six-component representation of d-functions).

^b Ref. [51], basis set aug-cc-pVTZ.

^c Ref. [48].

^d Ref. [66], as cited in Ref. [51].

^e Ref. [67] for $\lambda = 632.8$ nm, as cited in Ref. [48].

^f Ref. [64].

^g Ref. [70], as cited in Ref. [48].

^h Ref. [71], as cited in Ref. [48].

CC2 error. The SOPPA results are seen to be in excellent agreement with the ADC(2) results.

In Table 6, the ADC(2) results are given for the static polarizabilities of CO and H₂O using different basis sets of increasing size. In addition to the polarizabilities, also results for the dipole or Thomas–Reiche–Kuhn (TRK) sum rules are given here. A thorough basis set study of CC and FCI results for BH polarizabilities and hyperpolarizabilities has been given by Larsen et al. [47], and their essential findings apply to the present results as well. The cc-pVDZ basis set is clearly insufficient, yielding much too small polarizability values. A large improvement is obtained at the triple- and quadruple-zeta levels of the cc-pVXZ hierarchy. The inclusion of one set of diffuse functions (aug-cc-pVXZ) has a significant effect, being largest at the double-zeta level ($X = D$), whereas adding further diffuse functions (d-aug scheme) appears to be of minor importance beyond the $X = T$ level. The aug-cc-pVTZ basis set may be seen as a good compromise between basis set size and accuracy.

Table 6

Comparison of ADC(2) results for polarizabilities α (a.u.), isotropic polarizabilities $\bar{\alpha}$ (a.u.), dipole sum rule, $S = 2/3(S_1^x + S_1^y + S_1^z)$, for CO and H₂O obtained using different basis sets

	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$2/3S_1^x$	$2/3S_1^y$	$2/3S_1^z$	S	$S(1)$
CO									
cc-pVDZ	8.20		14.69	10.36	3.84		3.87	11.55	11.30
aug-cc-pVDZ	11.62		17.54	13.59	3.50		3.85	10.85	10.54
d-aug-cc-pVDZ	11.94		17.59	13.82	3.52		3.86	10.90	10.60
cc-pVTZ	10.12		16.22	12.15	4.11		4.31	12.53	12.26
aug-cc-pVTZ	11.84		17.30	13.66	4.13		4.45	12.71	12.41
d-aug-cc-pVTZ	11.89		17.32	13.70	4.22		4.49	12.93	12.65
cc-pVQZ	11.06		16.86	12.99	4.56		4.70	13.82	13.57
aug-cc-pVQZ	11.81		17.21	13.61	4.51		4.75	13.77	13.53
H ₂ O									
cc-pVDZ	3.24	7.17	5.42	5.28	3.16	3.02	3.07	9.25	9.13
aug-cc-pVDZ	9.14	10.36	9.64	9.71	2.76	2.81	2.81	8.38	8.21
d-aug-cc-pVDZ	10.09	10.56	10.31	10.32	2.75	2.80	2.79	8.34	8.20
cc-pVTZ	5.90	8.60	7.45	7.32	3.21	3.13	3.16	9.50	9.37
aug-cc-pVTZ	9.55	10.38	9.99	9.97	3.07	3.12	3.11	9.30	9.19
d-aug-cc-pVTZ	9.76	10.40	10.17	10.11	3.11	3.16	3.15	9.42	9.31
cc-pVQZ	7.43	9.33	8.57	8.44	3.38	3.34	3.35	10.07	9.94
aug-cc-pVQZ	9.57	10.28	9.99	9.95	3.23	3.31	3.31	9.85	9.76

The first-order dipole sum expression, $S(1)$, is exact up to the basis set error (see Ref. [36]).

The TRK results for the individual dipole sum components, S_α^z , $\alpha = x, y, z$, in Table 6 may serve as a check for the absence of any directional basis set bias. The results for the (weighted) first-order dipole sum expression, $S(1)$ in Table 6, differing from the electron number N only due to basis set incompleteness (see Ref. [36]), clearly reflect the increasing basis set quality with $X = D, T, Q$. One may note that diffuse functions have only a marginal effect here and their inclusion may even enhance the $S(1)$ error.

5. Concluding remarks

The ADC approach to the polarization propagator has been extended to the treatment of molecular response properties. To demonstrate the performance of the method, static and dynamic polarizabilities were computed for a series of small molecules at the second-order (ADC(2)) level of theory. The comparison with previous FCI, CC, and SOPPA results showed that in most cases the accuracy of the ADC(2) method matches that of the CC2 and SOPPA treatments. However, in the case of the longitudinal static polarizabilities of the CO and N₂ molecules, distinctly larger ADC(2) errors did occur. The reason for this deficiency is seen in the fact that certain second-order contributions to the effective transition amplitudes are poorly described at the strict PT level used in the present ADC(2) version. A systematic improvement should result by correcting the deficient second-order terms as outlined in Section 2.3. The numerical confirmation of this expectation has to be postponed, until the first results of the improved ADC(2) version will be available.

An obvious option for higher accuracy is the third-order ADC(3) approximation, which, however, scales already as N^6 . As a first step, one may combine the ADC(3) secular

matrix with the (corrected) second-order transition amplitudes. Using such a mixed ADC(3/2) version [36,38], very satisfactory results were obtained for the ground-to-excited state transition moments of small molecules [42]. The full ADC(3) level may be more difficult to achieve, because the number of third-order contributions to the effective transition amplitudes is substantial [74].

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Some thirty years ago then-not-yet-professor L.S. Cederbaum (“Lenz”) told an older, somewhat innocent fellow student (J.S.) that propagators would be an extremely challenging and rewarding approach to the many-electron problem in molecules. Three decades later on that track, the magic spell of propagators etc. is still alive, for which this paper may be an indication. So sincere thanks for the initiation, education, and never-ending encouragement over all those years. And on the occasion of the 60th birthday of the mentor and friend, here is the most vital wish for Lenz: Keep propagating!

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