TIME-INDEPENDENT COUPLED-CLUSTER THEORY OF THE POLARIZATION PROPAGATOR

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

A novel, time-independent formulation of the coupled-cluster theory of the polarization propagator is presented. This formulation, unlike the equation-of-motion coupled-cluster approach, is fully size-extensive and, unlike the conventional time-dependent coupled-cluster method, is manifestly Hermitian, which guarantees that the polarization propagator is always real for purely imaginary frequencies and that the resulting polarizabilities exhibit time-reversal symmetry (are even functions of frequency) for purely real or purely imaginary perturbations. This new formulation is used to derive compact expressions for the three leading terms in the Møller–Plesset expansion for the polarization propagator. The true and apparent correlation contributions to the second-order term are analyzed and separated at the operator level. Explicit equations for the polarization propagator at the non-perturbative, singles and doubles level (CCSD) are presented.

Keywords: Linear-response theory; Polarization propagator; Coupled clusters; CCSD; Møller–Plesset expansion; Wave functions; Quantum chemistry.

The response of a system (an atom or a molecule) to external perturbations is described by response functions. This response may be interpreted as the result of the process in which the system is perturbed at some initial time, the perturbation is propagated, and the state of the system is examined at some later time. The linear, quadratic, etc. response functions are defined by expanding the response, quantified by expectation values of relevant operators, as a power series in external perturbations. Many physical observables are either response functions themselves or can be derived from the response functions for some particular choices of the external perturbations. In particular, electric properties such as dynamic multipole polarizabilities are linear response functions corresponding to external multipolar fields. The response functions represent also a very useful tool in the

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theory of intermolecular forces. For instance, fundamental components (including the three-body ones) of the interaction energy such as the induction or dispersion energies can be expressed through the response functions of monomers[1,2]. In particular, the asymptotics of the interaction energy at large intermolecular separations R can be described in terms of the static and dynamic multipole polarizabilities[3].

The concept of response functions was first introduced in statistical physics by Zubarev[4] and very soon showed its utility in the field of molecular physics[5]. Among various response functions, the linear response is of primary importance. It describes the (leading) first-order response of the system to an external perturbation. In practical applications it is much more convenient to work in the frequency representation, which is the Fourier transform of the time-dependent response function. The frequency-dependent linear response function is often referred to as the polarization propagator[5,6] and we shall use this terminology in the present work.

Quite a few computational techniques have been proposed in the literature which can be used to calculate the polarization propagator with a different degree of accuracy. The simplest approach, referred to as the random phase approximation (RPA), is equivalent to the time-dependent Hartree–Fock approach[7] and, consequently, neglects the correlation of the electronic motion. The electron correlation has been initially included using the perturbation theory[8,9], the so-called higher RPA methods[9], or the multi-configurational Hartree–Fock technique[10,11]. Somewhat later the time-dependent Møller–Plesset methods were introduced in the non-relaxed[12] and relaxed[13] approach. It should be noted that the latter approach can be formulated in different, nonequivalent ways[14–16], depending on the way the quasi-energy is differentiated with respect to the frequencies of the applied perturbations.

Interestingly enough, the conceptually more subtle and potentially more accurate time-dependent coupled-cluster approach to the polarization propagator was already formulated in 1977 by Monkhorst[17]. One year later, similar formulations appeared in the nuclear[18] and solid-state physics[19]. A slightly improved presentation of the original Monkhorst theory was published in the general physics literature by Dalgaard and Monkhorst[20]. Initially, the Monkhorst theory met with little interest (see, however, applications to the excitation energies from the Bartlett[21] and Paldus[22] groups). Large-scale applications started to appear only after Koch and Jørgensen[23] showed how to efficiently eliminate the second-order cluster amplitudes using the powerful time-dependent Lagrangian technique. Since then, Monkhorst theory found numerous applications in calculations of frequency-dependent polarizabilities and excitation energies (see, e.g., ref.[24] for a recent application to excitation energies and transition dipole moments of weakly interacting atoms). Current state of the art involves not only the singles and doubles (CCSD) level of theory[25] but also an approximate (CC3)[26–28] and complete (CCSDT)[29] treatment of triple excitation effects.

In Monkhorst theory[17,20] the polarization propagator is defined as the time average (over one period of oscillation) of the quasi-energy. The propagator itself, as precisely defined in the next section, is a time-independent object and one can think of obtaining it from a potentially simpler time-independent theory. One may recall here that the development of time-independent approach to the many-fermion theory[30] contributed significantly to the spread of the many-body techniques (developed originally in the time-dependent context[31,32]) in the field of quantum chemistry and paved the way for the success the coupled-cluster theory enjoys today in molecular applications. In fact, a time-independent coupled-cluster theory of the polarization propagator has already been presented in the literature[33,34]. The corresponding polarization propagator expression[34], derived within the framework of the equation-of-motion coupled-cluster (EOM-CC) theory[21,35,36], however, contains a disconnected contribution which leads to size-inconsistent behavior of the resulting polarizabilities[25].

In this paper we present a time-independent coupled-cluster theory of the polarization propagator which does not suffer from this problem. Our propagator is expressed exclusively in terms of commutators (like the polarization propagator of the Monkhorst theory) which guarantees the extensivity of the resulting polarizabilities. It differs, however, from the Monkhorst propagator by exhibiting the correct symmetries resulting from

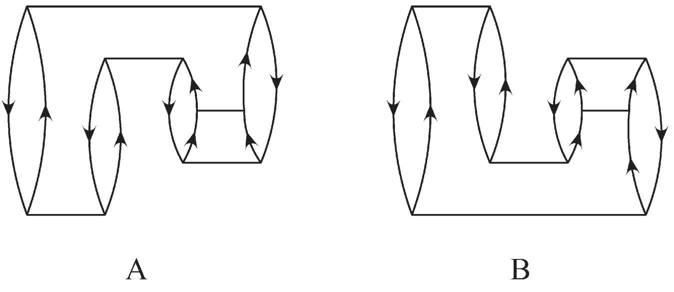

FIG. 1
The fifth–order CCD diagram (A) and its complex conjugate diagram (B) included only at the CCSDTQ level of coupled-cluster theory

the real nature of the molecular Hamiltonian. In particular the dynamic polarizability tensors predicted by our theory exhibit the time-reversal symmetry when the cluster operator is arbitrarily truncated, the feature which does not hold in Monkhorst's theory.

It is well known that in the conventional (projective) coupled-cluster theory[37] the energy is not manifestly real when the cluster operator T is truncated at some excitation level. In terms of diagrams this means that some diagrams are included, but their complex conjugates (obtained by drawing the diagrams upside down and performing the particle-hole conjugation) are not. In particular the diagram A in Fig. 1 is included in the coupled-cluster doubles (CCD) model but its complex conjugate, diagram B, is not. Diagram B would be included only when the quadruple excitations were taken into account[38], i.e., at the CCSDTQ level or in a variational coupled-cluster doubles (VCCD) theory[39]. It should be noted that taking the real part of the coupled-cluster energy expression, as advocated in refs.[40,41], does not solve the problem. Both diagrams A and B of Fig. 1 would then be included but with a wrong coefficient of 1/2. The fact that the set of coupled-cluster diagrams corresponding to a specific truncation of T is not closed under the complex conjugation does not cause difficulties in ground-state energy calculations since for real orbitals the cluster coefficients are always real. The violation of the Hermitian symmetry has more serious consequences in the conventional time-dependent coupled-cluster theory[17,20,23], since it leads to polarizability tensors that do not exhibit the time reversal symmetry, i.e., are not even functions of frequency for purely real or purely imaginary perturbations. The approach presented by us in this paper is Hermitian in the sense that any restriction of the excitation space in the coupled-cluster Ansatz for the wave function does not break the correct symmetry of the polarization propagator under complex conjugation and does not lead to a violation of the time-reversal symmetry. All final equations of our theory are written exclusively in terms of commutators which ensures the connectedness and, consequently, the size extensivity of the resulting propagators.

THEORY

General Definitions

The polarization propagator $\langle\langle A;B\rangle\rangle_\omega$ for a non-degenerate N-electron system described by the Hamiltonian H is defined by the expression (see, e.g., ref.[6])

$$\langle\langle A;B\rangle\rangle_\omega = -\langle\Psi_0|B\frac{Q}{H-E_0+\omega}A\Psi_0\rangle - \langle\Psi_0|A\frac{Q}{H-E_0-\omega}B\Psi_0\rangle \qquad (1)$$

where Ψ_0 is the normalized ground-state wave function, $E_0 = \langle\Psi_0|H\Psi_0\rangle$ is the ground-state energy, Q is the projection on the space spanned by all excited states, and ω is interpreted as a (generally complex) frequency. The operators A and B can be arbitrary although usually only one-particle Hermitian operators are considered. The polarization propagator describes a linear response of the system to the perturbation (A or B) oscillating with the frequency ω and is usually derived within the time-dependent perturbation theory[42]. The expression on the right-hand side of Eq. (*1*) can also be taken as a definition of $\langle\langle A;B\rangle\rangle_\omega$ without any reference to the time-dependent derivation and then applied in different contexts to obtain, e.g., the excitation energies, transition moments, or various contributions to interatomic and intermolecular interaction energies. From now on we shall assume that the operators A and B are Hermitian. This assumption does not result in any loss of generality because the definition of Eq. (*1*) is separately linear in A and B, and any non-Hermitian operator can be written as a linear combination of Hermitian ones.

The propagator $\langle\langle A;B\rangle\rangle_\omega$ exhibits the following Hermitian symmetry

$$\langle\langle A;B\rangle\rangle_\omega^* = \langle\langle A;B\rangle\rangle_{-\omega^*} \qquad (2)$$

valid if the perturbations A and B (and the Hamiltonian H) are Hermitian. For pure imaginary frequencies (which are of special importance for intermolecular forces) $\omega^* = -\omega$, and, consequently,

$$\langle\langle A;B\rangle\rangle_\omega^* = \langle\langle A;B\rangle\rangle_\omega \qquad (\text{for } \omega^* = -\omega) \qquad (3)$$

i.e., the propagator is real for any operators A and B. The second term in Eq. (*1*) is then a complex conjugate (c.c.) of the first one and does not have to be separately computed. This simplification does not occur for other frequencies (including the real ones). In the general case the second term in Eq. (*1*) can be obtained by computing the first one for the frequency $-\omega^*$ and by taking the complex conjugation. This operation, reducing to the usual c.c. operation for pure imaginary frequencies, will be referred to as the generalized complex conjugation and will be denoted by g.c.c.

For real frequencies and for purely real or purely imaginary perturbations (and a real Hamiltonian), Eq. (*2*) reduces to

$$\langle\langle A;B\rangle\rangle_{\omega} = \langle\langle A;B\rangle\rangle_{-\omega} \tag{4}$$

which reflects the time-reversal symmetry. As a result of the Schwartz reflection principle Eq. (*4*) holds also for arbitrary complex frequencies. As mentioned in the introduction the symmetry relations given by Eqs. (*2*)–(*4*) are not fulfilled in the conventional time-dependent coupled-cluster theory of the polarization propagator[17,20,23].

The result of an action of the resolvent $R_\omega = Q(H - E_0 + \omega)^{-1}$ on $A\Psi_0$, needed to evaluate Eq. (*1*), cannot be easily represented by a cluster Ansatz since $R_\omega A\Psi_0$ is orthogonal to Ψ_0, a condition impossible to fulfill automatically by a cluster expansion. Therefore, instead of the function $R_\omega A\Psi_0$ we consider a modified first-order wave function

$$\Psi^{(1)}(\omega) = c(\omega)\Psi_0 - R_\omega A\Psi_0 \tag{5}$$

where $c(\omega)$ is a certain frequency dependent constant different from zero. The constant $c(\omega)$ will be fixed later by assuming that $\Psi^{(1)}(\omega)$ fulfills the orthogonality condition consistent with the coupled-cluster Ansatz employed to represent $\Psi^{(1)}(\omega)$. It is easy to see that $\Psi^{(1)}(\omega)$ satisfies the conventional first-order perturbation equation

$$(H - E_0 + \omega)\Psi^{(1)}(\omega) = [\omega c(\omega) + \overline{A} - A]\Psi_0 \tag{6}$$

where

$$\overline{A} = \langle\Psi_0 | A\Psi_0\rangle\ . \tag{7}$$

Using the definition (*5*) we can express the polarization propagator $\langle\langle A;B\rangle\rangle_\omega$ by the following formula

$$\langle\langle A;B\rangle\rangle_{\omega} = \langle\Psi_0|(B-\overline{B})\Psi^{(1)}(\omega)\rangle + \text{g.c.c.} \tag{8}$$

valid for an arbitrary value of $c(\omega)$. Equations (*6*) and (*8*) will be used as a starting point in deriving our coupled-cluster representation of the polarization propagator.

Coupled-Cluster Representation of the Zeroth- and the First-Order Wave Functions

To obtain a coupled-cluster hierarchy of approximations to Eq. (*8*), we represent the wave function Ψ_0 using a renormalized form of the conventional exponential Ansatz

$$\Psi_0 = \langle \mathrm{e}^T \Phi | \mathrm{e}^T \Phi \rangle^{-1/2} \, \mathrm{e}^T \Phi \tag{9}$$

where Φ is the Hartree–Fock determinant, and the cluster operator T is defined as

$$T = \sum_{n=1}^{N} T_n \,, \qquad T_n = (n!)^{-2} \, t^{\alpha_1 \ldots \alpha_n}_{\rho_1 \ldots \rho_n} \, e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} \tag{10}$$

with $e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n}$ denoting the product of the annihilation (a_α) and creation ($a^\dagger_\rho$) operators: $a^\dagger_{\rho_1} a^\dagger_{\rho_2} \ldots a_{\alpha_2} a_{\alpha_1}$. Summation over repeated lower and upper indices is implied throughout this paper. We shall always assume that the indices λ, κ refer to all spinorbitals, while α and ρ label exclusively occupied and virtual spinorbitals, respectively. We assume that T is known from the conventional coupled-cluster calculations involving a specific truncation of the excitation structure of T.

For the first-order wave function $\Psi^{(1)}(\omega)$ we employ the following coupled-cluster-like Ansatz

$$\Psi^{(1)}(\omega) = \langle \mathrm{e}^T \Phi | \mathrm{e}^T \Phi \rangle^{-1/2} \, \Omega(\omega) \, \mathrm{e}^T \Phi \tag{11}$$

where $\Omega(\omega)$ is a cluster operator of the form

$$\Omega(\omega) = \sum_{n=1}^{N} \Omega_n(\omega) \,, \qquad \Omega_n = (n!)^{-2} \, \Omega^{\alpha_1 \ldots \alpha_n}_{\rho_1 \ldots \rho_n} \, e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} \;. \tag{12}$$

Substituting Eq. (*11*) into Eq. (*6*) we obtain

$$([H,\Omega(\omega)] + \omega\Omega(\omega) + A - \omega c(\omega) - \overline{A})\,\mathrm{e}^{T}\Phi = 0\ . \tag{13}$$

Multiplying Eq. (*13*) with e^{-T} and projecting against $e^{\rho_1\dots\rho_n}_{\alpha_1\dots\alpha_n}\Phi$ and Φ, we find an explicitly connected (i.e., involving only commutator products of operators) equation for the operator $\Omega(\omega)$

$$\langle e^{\rho_1\dots\rho_n}_{\alpha_1\dots\alpha_n} \,|[\mathrm{e}^{-T}H\mathrm{e}^{T},\Omega(\omega)] + \omega\Omega(\omega) + \mathrm{e}^{-T}A\mathrm{e}^{T}\rangle = 0 \tag{14}$$

and an expression for the constant $c(\omega)$

$$c(\omega) = \frac{1}{\omega}[\langle H\Omega_2(\omega)\rangle + \langle HT_1\Omega_1(\omega)\rangle + \langle A\rangle + \langle AT_1\rangle - \overline{A}]\ . \tag{15}$$

In Eqs. (*14*) and (*15*) and in the ensuing text we use the following shorthand notation for scalar products and expectation values

$$\langle X|Y\rangle = \langle X\Phi|Y\Phi\rangle \quad \text{and} \quad \langle X\rangle = \langle\Phi|X\Phi\rangle\ . \tag{16}$$

The constant $c(\omega)$ does not enter Eq. (*14*) and is not needed to compute $\langle\langle A;B\rangle\rangle_\omega$. It should be noted that our equation for the first-order cluster amplitudes is the same as that appearing in the theory of Monkhorst[17,20] or in the EOM-CC approach[21,35].

Explicitly Connected Expression for the Polarization Propagator

Inserting Eqs. (*9*) and (*11*) into Eq. (*8*) leads to a complicated expression involving numerous disconnected terms. To eliminate these nonphysical terms we shall make use of the commutator expansion of the expectation value of an operator developed in ref.[39]

$$\overline{A} = \frac{\langle \mathrm{e}^{T}|A\mathrm{e}^{T}\rangle}{\langle \mathrm{e}^{T}|\mathrm{e}^{T}\rangle} = \langle \mathrm{e}^{S}|\mathrm{e}^{-T}A\mathrm{e}^{T}\rangle = \langle \mathrm{e}^{S^\dagger}\mathrm{e}^{-T}A\mathrm{e}^{T}\mathrm{e}^{-S^\dagger}\rangle \tag{17}$$

where S is an excitation operator

$$S = \sum_{n=1}^{N} S_n \ , \qquad S_n = (n\,!)^{-2}\, S^{\alpha_1 \dots \alpha_n}_{\rho_1 \dots \rho_n}\, e^{\rho_1 \dots \rho_n}_{\alpha_1 \dots \alpha_n} \tag{18}$$

uniquely defined by the equation

$$\mathrm{e}^{S}\Phi = \frac{1}{\langle \mathrm{e}^{T} | \mathrm{e}^{T} \rangle}\, \mathrm{e}^{T^\dagger}\, \mathrm{e}^{T}\Phi\,. \tag{19}$$

It was shown in ref.[39] that the operator S is connected and satisfies a linear equation which contains only finite powers of T and which can easily be solved by iterations. The S operator plays a similar role to that of the $\Lambda^\dagger$ operator used in the coupled-cluster gradients theory[43,44] but, unlike $\Lambda^\dagger$, it is connected. When $T = T_1 + T_2$, the only truncation level we shall consider in this work, then up to $O(T^3)$ terms we have[39]

$$S = T + \hat{\mathcal{P}}_1([\,T_1^\dagger\,, T_2\,]) + O(T^3) \tag{20}$$

where $\hat{\mathcal{P}}_n$ is the superoperator projecting on the space spanned by excitation operators

$$\hat{\mathcal{P}}_n(X) = (n\,!)^{-2}\, \langle e^{\alpha_1 \dots \alpha_n}_{\rho_1 \dots \rho_n}\, X \rangle\, e^{\rho_1 \dots \rho_n}_{\alpha_1 \dots \alpha_n} \ . \tag{21}$$

Using the coupled-cluster representations for $\Psi^{(1)}(\omega)$ and for Ψ_0, the first term on the right-hand side of Eq. (*8*) can be rewritten as

$$\langle \Psi_0 | (B - \overline{B}) \Psi^{(1)}(\omega) \rangle = \frac{\langle \mathrm{e}^{T} | B\Omega(\omega)\, \mathrm{e}^{T} \rangle}{\langle \mathrm{e}^{T} | \mathrm{e}^{T} \rangle} - \overline{B}\, \frac{\langle \mathrm{e}^{T} | \Omega(\omega)\, \mathrm{e}^{T} \rangle}{\langle \mathrm{e}^{T} | \mathrm{e}^{T} \rangle}\,. \tag{22}$$

Making use of the definition of the operator S one can transform the first term on the right-hand side of Eq. (*22*) as follows

$$\frac{\langle B\mathrm{e}^{T} | \Omega(\omega)\, \mathrm{e}^{T} \rangle}{\langle \mathrm{e}^{T} | \mathrm{e}^{T} \rangle} = \langle \mathrm{e}^{T^\dagger} B \mathrm{e}^{-T^\dagger} \mathrm{e}^{S} | \Omega(\omega) \rangle = \langle \mathrm{e}^{-S} \mathrm{e}^{T^\dagger} B \mathrm{e}^{-T^\dagger} \mathrm{e}^{S} | \mathrm{e}^{S^\dagger}\, \Omega(\omega)\, \mathrm{e}^{-S^\dagger} \rangle\,. \tag{23}$$

When deriving the above equation we used the fact that $\mathrm{e}^{-T}\Omega(\omega)\mathrm{e}^{T} = \Omega(\omega)$, and that $\mathrm{e}^{-S^\dagger}\Phi = \Phi$. The ket on the right-hand side of Eq. (*23*) can be transformed using the identity

$$X\Phi = \langle X\rangle\Phi + \hat{\mathcal{P}}(X)\Phi \tag{24}$$

where $\hat{\mathcal{P}}(X) = \hat{\mathcal{P}}_1(X) + \hat{\mathcal{P}}_2(X) + \ldots + \hat{\mathcal{P}}_N(X)$, valid for an arbitrary operator X. Setting $X = \mathrm{e}^{S^\dagger}\Omega(\omega)\,\mathrm{e}^{-S^\dagger}$ and using Eq. (*24*), one obtains

$$\begin{aligned}\frac{\langle \mathrm{e}^{T}\,|\,B\Omega(\omega)\,\mathrm{e}^{T}\,\rangle}{\langle \mathrm{e}^{T}\,|\mathrm{e}^{T}\,\rangle} &= \langle \mathrm{e}^{-S}\mathrm{e}^{T^\dagger}B\mathrm{e}^{-T^\dagger}\,\mathrm{e}^{S}\,\rangle\,\langle \mathrm{e}^{S^\dagger}\,\Omega(\omega)\mathrm{e}^{-S^\dagger}\,\rangle + \\ &+ \langle \mathrm{e}^{-S}\mathrm{e}^{-T^\dagger}B\mathrm{e}^{T^\dagger}\,\mathrm{e}^{S}\,|\hat{\mathcal{P}}|\,\mathrm{e}^{S^\dagger}\,\Omega(\omega)\,\mathrm{e}^{-S^\dagger}\,\rangle\;.\end{aligned} \tag{25}$$

The first term on the right-hand side of Eq. (*25*) is equal to the unlinked term

$$\overline{B}\,\frac{\langle \mathrm{e}^{T}\,|\,\Omega(\omega)\,\mathrm{e}^{T}\,\rangle}{\langle \mathrm{e}^{T}\,|\mathrm{e}^{T}\,\rangle} \tag{26}$$

in Eq. (*22*) and cancels out exactly when the subtraction in Eq. (*22*) is carried out. Thus, only the second term in Eq. (*25*) makes a contribution and we find that the polarization propagator is given by a finite series of nested commutators:

$$\langle\langle A;B\rangle\rangle_\omega = \langle \mathrm{e}^{-S}\mathrm{e}^{T^\dagger}B\mathrm{e}^{-T^\dagger}\,\mathrm{e}^{S}\,|\hat{\mathcal{P}}|\,\mathrm{e}^{S^\dagger}\,\Omega(\omega)\,\mathrm{e}^{-S^\dagger}\,\rangle + \text{g.c.c.} \tag{27}$$

where $\langle X|\hat{\mathcal{P}}|Y\rangle \equiv \langle X|\hat{\mathcal{P}}(Y)\rangle$. Equation (*27*) is the main result of this paper. It shows how the polarization propagator can be expressed in terms of the cluster operators T, S, and $\Omega(\omega)$. Equation (*14*) and the nested commutator expansion of S in terms of T, given in ref.[39], show that the operators S and $\Omega(\omega)$ are connected. Since the commutator of two connected second-quantized operators contains only connected diagrams, the polarization propagator of Eq. (*27*) must be connected. The response functions computed using our theory must therefore be size-extensive. This feature of theory, holding for arbitrary truncations of cluster operators T and Ω, simplifies the perturbation (Møller–Plesset) expansion of the polarization propagator and allows for a considerable flexibility in performing infinite-order size-extensive summations of selected classes of diagrams.

MØLLER–PLESSET EXPANSION OF THE POLARIZATION PROPAGATOR

To show the merits of our coupled-cluster formulation we present here the Møller–Plesset (MP) expansion of the polarization propagator and present a compact form of all terms through the second-order in the Møller–Plesset perturbation W. The MP expansion for the T operator[45] can be most easily obtained by iterating the operator equation for T, given in ref.[39],

$$T_n = \hat{\mathcal{R}}_n(e^{-T} W e^{T}) \tag{28}$$

where the resolvent superoperator $\hat{\mathcal{R}}_n$ is defined[46] as

$$\hat{\mathcal{R}}_n(X) = (n!)^{-2}(\varepsilon_{\alpha_1} + \ldots + \varepsilon_{\alpha_n} - \varepsilon_{\rho_1} - \ldots - \varepsilon_{\rho_n})^{-1} \langle e^{\alpha_1 \ldots \alpha_n}_{\rho_1 \ldots \rho_n} X \rangle e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} \tag{29}$$

ε_κ being the orbital energy associated with the spinorbital ϕ_κ. It is easy to verify that

$$[F, \hat{\mathcal{R}}_n(X)] + \hat{\mathcal{P}}_n(X) = 0 \tag{30}$$

where $F = H - W$ is the Fock operator and $\hat{\mathcal{P}}_n(X)$ the projection superoperator of Eq. (*21*).

Iterating Eq. (*28*) immediately gives the following expressions for the first- and second-order terms $T^{(1)}$ and $T^{(2)}$ in the expansion of T in powers of W

$$T^{(1)} = T_2^{(1)} = \hat{\mathcal{R}}_2(W) \tag{31}$$

$$T_m^{(2)} = \hat{\mathcal{R}}_m([W, T_2^{(1)}]), \quad m = 1, 2, 3 . \tag{32}$$

Higher-order terms in this expansion are given in ref.[39], where the perturbation expansion for the operator S is also considered in more detail. Here, suffice it to observe that, in view of Eq. (*20*), the S and T operators are identical through the second order in W, i.e.,

$$S^{(1)} = T_2^{(1)}, \quad S_m^{(2)} = T_m^{(2)}, \quad m = 1, 2, 3 . \tag{33}$$

To derive the MP perturbation expansion of the cluster operator $\Omega(\omega)$, we transform Eq. (*14*) by substituting $F + W$ for H and using the identity $e^{-T}[F, \Omega(\omega)]\, e^{T} = [F, \Omega(\omega)]$:

$$\langle e^{\rho_1 \dots \rho_n}_{\alpha_1 \dots \alpha_n} | [F, \Omega(\omega)] + \omega\Omega(\omega) + \mathrm{e}^{-T} A \mathrm{e}^{T} + [\mathrm{e}^{-T} W \mathrm{e}^{T}, \Omega(\omega)] \rangle = 0 \,. \tag{34}$$

An analogue of Eq. (*28*) can be easily obtained if we note that for any operator X the equation

$$\langle e^{\rho_1 \dots \rho_n}_{\alpha_1 \dots \alpha_n} | [F, Y_n] + \omega Y_n + X \rangle = 0 \tag{35}$$

has a solution $Y_n = \hat{\mathcal{R}}_{n,\omega}(X)$, where $\hat{\mathcal{R}}_{n,\omega}$ is the ω-dependent superoperator defined by

$$\hat{\mathcal{R}}_{n,\omega}(X) = (n!)^{-2} (\varepsilon_{\alpha_1} + \dots + \varepsilon_{\alpha_n} - \varepsilon_{\rho_1} - \dots - \varepsilon_{\rho_n} - \omega)^{-1} \langle e^{\alpha_1 \dots \alpha_n}_{\rho_1 \dots \rho_n} X \rangle \, e^{\rho_1 \dots \rho_n}_{\alpha_1 \dots \alpha_n} \,. \tag{36}$$

Note that $\hat{\mathcal{R}}_{n,0} = \hat{\mathcal{R}}_n$ and that $\hat{\mathcal{R}}_{n,\omega}(X)$ satisfies the operator equation

$$[F, \hat{\mathcal{R}}_{n,\omega}(X)] + \omega \hat{\mathcal{R}}_{n,\omega}(X) + \hat{\mathcal{P}}_n(X) = 0 \tag{37}$$

similar to Eq. (*30*). Using $\hat{\mathcal{R}}_{n,\omega}$ to solve Eq. (*34*) gives

$$\Omega_n(\omega) = \hat{\mathcal{R}}_{n,\omega}(\mathrm{e}^{-T} A \mathrm{e}^{T} + [\mathrm{e}^{-T} W \mathrm{e}^{T}, \Omega(\omega)]) \,. \tag{38}$$

Iterating Eq. (*38*) we easily find that the first three terms $\Omega^{(0)}(\omega)$, $\Omega^{(1)}(\omega)$, and $\Omega^{(2)}(\omega)$ in the MP expansion of $\Omega(\omega)$ are given by

$$\Omega^{(0)}(\omega) = \Omega^{(0)}_1(\omega) = \hat{\mathcal{R}}_{1,\omega}(A) \tag{39}$$

$$\Omega^{(1)}_n(\omega) = \hat{\mathcal{R}}_{n,\omega}([A, T^{(1)}_2] + [W, \Omega^{(0)}_1(\omega)]) \tag{40}$$

$$\begin{aligned} \Omega^{(2)}_n(\omega) = \hat{\mathcal{R}}_{n,\omega}([A, T^{(2)}_1 + T^{(2)}_2] + [W, \Omega^{(1)}_1(\omega) + \Omega^{(1)}_2(\omega)] + \\ + [[W, T^{(1)}_2], \Omega^{(0)}_1(\omega)]) \end{aligned} \tag{41}$$

where $n = 1, 2$ in Eq. (*40*) and $n = 1, 2, 3$ in Eq. (*41*).

The three leading terms, $\langle\langle A;B\rangle\rangle_\omega^{(k)}$, $k = 0, 1, 2$, in the MP expansion of the polarization propagator are easily found by substituting the MP expansions for T and $\Omega(\omega)$ into Eq. (*27*) and collecting terms of appropriate order in W. Through the second order in W one gets

$$\langle\langle A;B\rangle\rangle_\omega^{(0)} = \langle B|\Omega^{(0)}(\omega)\rangle + \text{g.c.c.} \tag{42}$$

$$\langle\langle A;B\rangle\rangle_\omega^{(1)} = \langle B|\Omega_1^{(1)}(\omega)\rangle + \langle [B,T_2^{(1)}]|\Omega_1^{(0)}(\omega)\rangle + \text{g.c.c.} \tag{43}$$

$$\begin{aligned}\langle\langle A;B\rangle\rangle_\omega^{(2)} &= \langle B|\Omega_1^{(2)}(\omega)\rangle + \langle [B,T_2^{(1)}]|\Omega_1^{(1)}(\omega)\rangle + \langle [B,T_2^{(1)}]|\Omega_2^{(1)}(\omega)\rangle + \\ &+ \langle [B,T_1^{(2)}]|\Omega_1^{(0)}(\omega)\rangle + \langle [B,T_2^{(2)}]|\Omega_1^{(0)}(\omega)\rangle - \langle [[B,T_2^{(1)\dagger}],T_2^{(1)}]|\Omega_1^{(0)}(\omega)\rangle + \text{g.c.c.}\end{aligned} \tag{44}$$

Note that the triple excitation operators T_3 and $\Omega_3(\omega)$ do not contribute at this level. Using the Wick theorem[30], the contraction theorem[47], or one of the codes for symbolic manipulations of second-quantized expressions, one can easily expand the commutators appearing in Eqs. (*42*)–(*44*) in terms of molecular integrals and orbital energies.

SEPARATION OF THE APPARENT AND TRUE CORRELATION CONTRIBUTIONS

Similarly as in the theory of molecular polarizabilities[48]; the MP corrections $\langle\langle A;B\rangle\rangle_\omega^{(k)}$ contain the apparent and true correlation contributions, the former defined as those taken into account by the RPA theory and the latter representing the remaining part of each MP correction. Since RPA calculations are nowadays rather routine, the apparent correlation can easily be taken into account by the RPA method and the perturbation theory can be used to obtain only the true correlation part of the polarization propagator. For this purpose the apparent correlation effects should be separated from each MP correction. This separation can be performed[12,49] at the level of final expressions, containing only molecular integrals and orbital energy differences, by using some algebraic identities involving sums of rational functions. In the first order this is relatively easy[50]. The second-order correction, however, comprises over fifty terms, and performing such a reduction would require a rather lengthy algebra. Below we show how such a separation can be performed at the operator level.

It is obvious that the zeroth-order correction $\langle\langle A;B\rangle\rangle_{\omega}^{(0)}$ contains no correlation, either true or apparent. The first-order correction depends on the $T_2^{(1)}$ cluster operator, cf. Eq. (*43*), and involves two-electron denominators; so one could think that it takes account of some true correlation. This is not the case, however, since the $T_2^{(1)}$ operator can be entirely eliminated from the expression for $\langle\langle A;B\rangle\rangle_{\omega}^{(1)}$. To demonstrate this we expand the right-hand side of Eq. (*43*) using Eq. (*40*) and obtain

$$\begin{aligned}\langle\langle A;B\rangle\rangle_{\omega}^{(1)} &= \langle \hat{\mathcal{R}}_{1,\omega^*}(B) | A T_2^{(1)}\rangle + \langle B T_2^{(1)} | \Omega_1^{(0)}(\omega)\rangle + \\ &+ \langle \hat{\mathcal{R}}_{1,\omega^*}(B) | [W, \Omega_1^{(0)}(\omega)]\rangle + \text{g.c.c.}\end{aligned} \tag{45}$$

where we made use of the “Hermicity” of the resolvent superoperator,

$$\langle X | \hat{\mathcal{R}}_{\omega}(Y)\rangle = \langle \hat{\mathcal{R}}_{\omega^*}(X) | Y\rangle \tag{46}$$

and of the fact that the commutators in the first two terms can be replaced by products.

The third term in Eq. (*45*), corresponding to diagram A in Fig. 2, contains only one-electron denominators and appears in the RPA theory. This term and its g.c.c. counterpart, represented by diagram B in Fig. 2, account thus for the apparent correlation effect. To examine the remaining terms we consider the sum of the first term and the g.c.c. counterpart of the second term in Eq. (*45*), i.e., the contribution

$$C = \langle A\hat{\mathcal{R}}_{1,\omega^*}(B) + B\hat{\mathcal{R}}_{1,-\omega^*}(A) | T_2^{(1)}\rangle \, . \tag{47}$$

The two selected terms, corresponding to diagrams C and D from Fig. 2, contain long, two-electron denominators which originate from the presence of the $T_2^{(1)}$ cluster operator. To eliminate this operator we use the identity

$$[F, \hat{\mathcal{R}}_{1,-\omega}(A)\hat{\mathcal{R}}_{1,\omega}(B)] = -\hat{\mathcal{R}}_{1,-\omega}(A)\hat{\mathcal{P}}_1(B) - \hat{\mathcal{P}}_1(A)\hat{\mathcal{R}}_{1,\omega}(B) \tag{48}$$

resulting directly from Eq. (*37*). Employing Eq. (*24*) one can easily find that the operators A and B in Eq. (*47*) play the role of single-excitation operators and can be replaced by their projections $\hat{\mathcal{P}}_1(A)$ and $\hat{\mathcal{P}}_1(B)$. An obvious application of Eq. (*48*) gives then

$$C = -\langle [F, \hat{\mathcal{R}}_{1,-\omega^*}(A)\hat{\mathcal{R}}_{1,\omega^*}(B)] | T_2^{(1)} \rangle = -\langle \hat{\mathcal{R}}_{1,-\omega^*}(A)\hat{\mathcal{R}}_{1,\omega^*}(B) | [F, T_2^{(1)}] \rangle \,. \quad (49)$$

In view of Eqs. (*31*) and (*30*) we can write $[F, T_2^{(1)}] = -\hat{P}_2(W)$ and, consequently,

$$C = \langle \hat{\mathcal{R}}_{1,-\omega^*}(A)\hat{\mathcal{R}}_{1,\omega^*}(B) | W \rangle \quad (50)$$

where we also made use of the obvious Hermicity of the projection superoperator $\hat{\mathcal{P}}_n$

$$\langle X | \hat{\mathcal{P}}_n(Y) \rangle = \langle \hat{\mathcal{P}}_n(X) | Y \rangle \,. \quad (51)$$

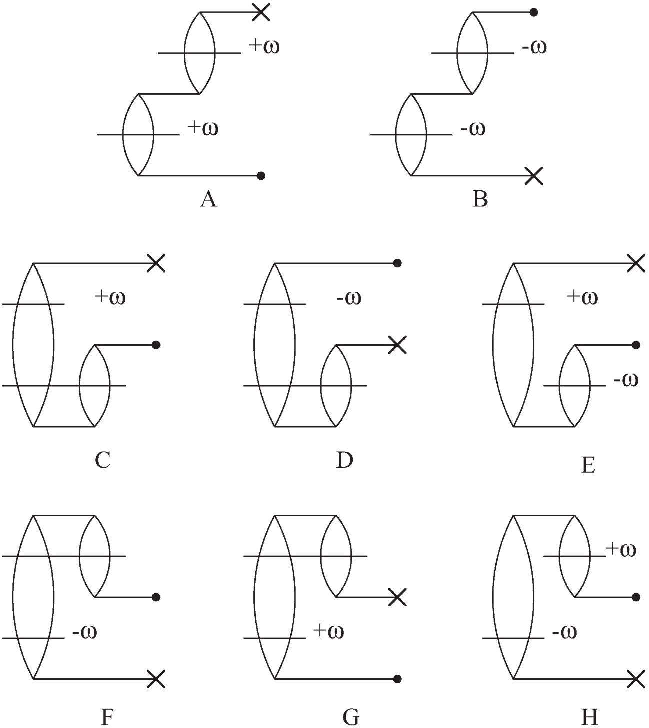

FIG. 2
First-order diagrams contributing to the polarization propagator. The dot and cross vertices represent the *A* and *B* operators, respectively

The expression on the right-hand side of Eq. (*50*), corresponding to diagram E in Fig. 2, contains only local, one-electron denominators and is taken into account by the RPA theory. The g.c.c. counterpart of the terms included in C is represented by diagrams G and F, or, alternatively by the single RPA diagram H. The final, alternative expression for $\langle\langle A;B\rangle\rangle_\omega^{(1)}$, corresponding to diagrams A, B, E, and H in Fig. 2, can now be written as

$$\langle\langle A;B\rangle\rangle_\omega^{(1)} = \langle W|\tilde{\Omega}_1^{(0)}(-\omega)\,\Omega_1^{(0)}(\omega)\rangle + \langle\tilde{\Omega}_1^{(0)}(\omega^*)|[W,\Omega_1^{(0)}(\omega)]\rangle + \text{g.c.c.} \tag{52}$$

where $\tilde{\Omega}_1^{(0)}(\omega) \equiv \hat{\mathcal{R}}_{1,\omega}(B)$. We see that the polarization propagator of the first order in W is fully included in the RPA and represents the apparent correlation effect.

The true correlation contributions, containing ring-type diagrams, appear starting from the second order. Using the technique presented above, one can show that the second-order polarization propagator can be split into two distinct parts, representing the apparent (a) and the true (t) correlation

$$\langle\langle A;B\rangle\rangle_\omega^{(2)} = \langle\langle A;B\rangle\rangle_\omega^{(2)}(\mathrm{a}) + \langle\langle A;B\rangle\rangle_\omega^{(2)}(\mathrm{t})\,. \tag{53}$$

The apparent correlation terms, appearing in the second order of the MP expansion of the RPA propagator, are given by

$$\begin{aligned}\langle\langle A;B\rangle\rangle_\omega^{(2)}(\mathrm{a}) = {} & \langle X_B^{(1)}(\omega^*)|[W,\Omega_1^{(0)}(\omega)]\rangle + \langle W|X_B^{(1)}(-\omega)\Omega_1^{(0)}(\omega)\rangle + \\ & + \langle W|X_A^{(1)}(\omega)\tilde{\Omega}_1^{(0)}(-\omega)\rangle + \langle Y_B^{(1)}(-\omega)\Omega_1^{(0)}(-\omega^*)|W\rangle + \text{g.c.c.}\end{aligned} \tag{54}$$

where $X_C^{(1)}(\omega) \equiv \hat{\mathcal{R}}_{1,\omega}([W,\hat{\mathcal{R}}_{1,\omega}(C)])$, $C = A, B$, and $Y_B^{(1)}(\omega) \equiv -\hat{\mathcal{R}}_{1,-\omega}([W,\hat{\mathcal{R}}_{1,\omega}^{\dagger}(B)])$. The diagrams representing the four consecutive terms in Eq. (*54*) are given in Fig. 3.

The true correlation part of the second-order polarization propagator has the form

$$\begin{aligned}\langle\langle A;B\rangle\rangle_\omega^{(2)}(\mathrm{t}) = {} & \langle[B,T_2^{(1)}]|\Omega_2^{(1)}(\omega)\rangle + \langle[B,T_1^{(2)}]|\Omega_1^{(0)}(\omega)\rangle + \langle\tilde{\Omega}_1^{(0)}(\omega^*)|[A,T_1^{(2)}]\rangle + \\ & + \langle\tilde{\Omega}_1^{(0)}(\omega^*)|[W,\Omega_2^{(1)}(\omega)]\rangle + \langle[[W,\tilde{\Omega}_1^{(0)}(\omega^*)],\Omega_1^{(0)}(-\omega^*)]|T_2^{(1)}\rangle + \\ & + \langle T_2^{(1)}|[[\mathrm{B},T_2^{(1)}],\Omega_1^{(0)}(\omega)]\rangle - \langle[[W,\Omega_1^{(0)\dagger}(\omega)],\tilde{\Omega}_1^{(0)}(\omega^*)]|T_2^{(1)}\rangle + \text{g.c.c.}\end{aligned} \tag{55}$$

In Fig. 4 we present the (non-oriented) diagrams representing all the terms written out on the right-hand side of Eq. (*55*). The first term is represented by diagrams A, B, C, and D, the second term by diagrams E, and F, the third term by diagrams G, and H, the fourth term by diagrams I, J, K, and L, the fifth term by diagram M, and the sixth and seventh term by diagrams N and O, respectively. The g.c.c. counterparts of these diagrams can be obtained by turning the diagrams up-side down and substituting $-\omega$ for ω.

Wormer and collaborators[12,49] reported a diagrammatic analysis of the correlation contributions to the frequency-dependent polarizability in the second-order perturbation theory. Starting from the standard time-dependent perturbation theory expressions they derived all Hugenholtz diagrams corresponding to the second-order perturbation theory, including the disconnected diagrams corresponding to unlinked terms, and after a tedious algebra they obtained workable expressions in terms of molecular integrals and orbital energies. It should be noted that a proper cancellation

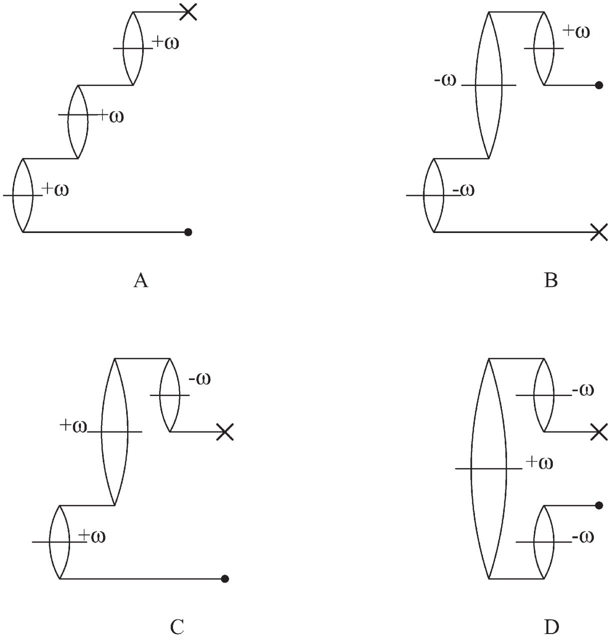

FIG. 3
Second-order RPA diagrams contributing to the polarization propagator

of the unlinked terms that appear in the second-order perturbation expression required explicit inclusion of the triple-excitation terms in the first-order wave function. Although the long, three-particle denominators cancel out, this cancellation was not performed in the original presentation of the theory[12], but only in the subsequent work of Wormer and Hettema[49]. It should also be mentioned that the diagrammatic analysis of ref.[49] was not entirely unique since the ambiguity resulting from the presence of the so-called exclusion principle violating (EPV) diagrams was not resolved, and two versions of the final expressions for the second-order perturbation

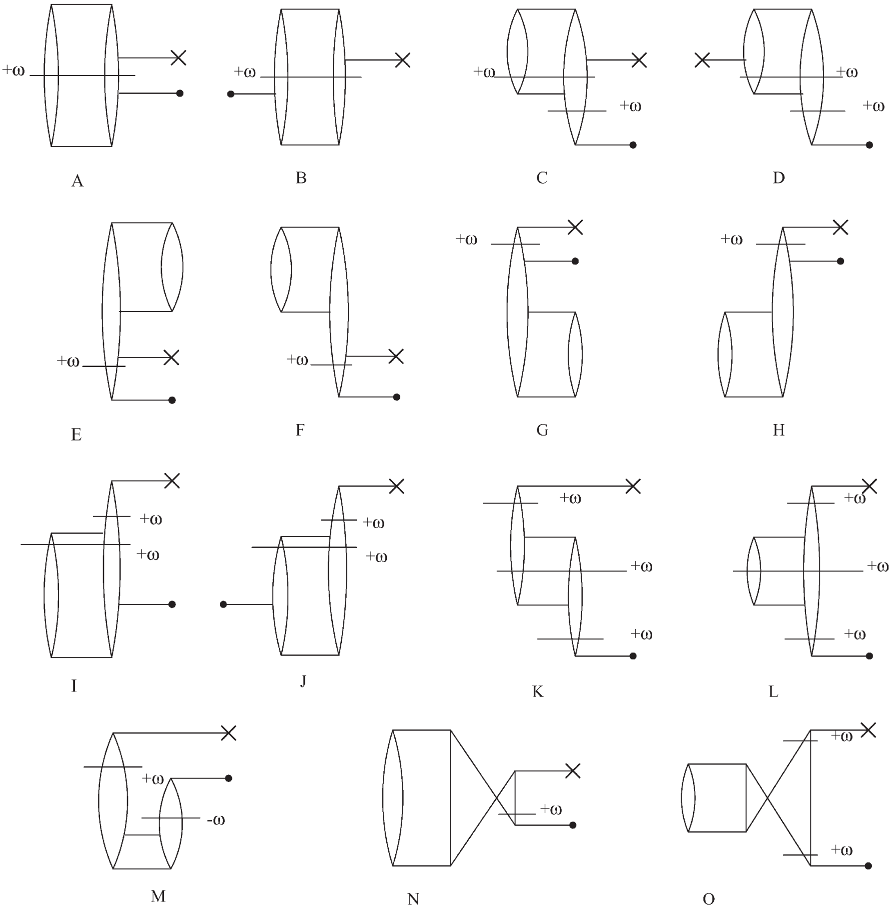

FIG. 4
Second-order non-oriented diagrams representing the true correlation part of the polarization propagator

contribution were reported in ref.[49]. Our derivation based on the commutator expressions appears to be simpler and unique. The elimination of the long, non-local denominators is not completely trivial, but does not require considering dozens of diagrams with all possible time orientations, and energy denominators. Since our propagator expression, Eq. (*27*), contains only connected quantities, no unlinked terms appear in the derivation. In particular triply-excited contributions do not appear at the second order in W. Let us mention finally that the derivation of the third-order perturbation contribution to the polarization propagator is quite feasible although, obviously, substantially more complex than in the second order.

NON-PERTURBATIVE APPROXIMATION SCHEMES

The second-order Møller–Plesset approximation for the correlation contribution to the polarization propagator is quite effective for complex frequencies[12,49] and has been extensively employed to compute dispersion interaction energies using the POLCOR package developed by Wormer and collaborators[51]. In some cases, however, the Møller–Plesset expansion may converge slowly or may even diverge. In such situations, or when accuracy higher than the second-order MP treatment is needed, we have to resort to a nonperturbative approach, i.e. to an iterative coupled-cluster procedure. The theory presented by us is quite flexible as far as a specific design of such a procedure. The corresponding computational scheme consists of four entirely independent steps, each can be implemented with different level of accuracy and computational cost.

The first step is the calculation of the ground-state cluster operator T. Any of the available hierarchy of coupled-cluster approximations to T can be used. The only requirement is that T must be connected so that the final propagator expression remains size-extensive. Since equations for T are highly nonlinear, this step is iterative and is usually expensive.

The second step is the solution of Eq. (*14*), i.e., the calculation of the Ω operator. Within the $T = T_1 + T_2$, $\Omega = \Omega_1 + \Omega_2$ approximation, this is now a standard procedure used to compute coupled-cluster gradients[43,44,52]. A complete inclusion of Ω_3 has also been recently implemented[29,53]. For large basis sets the computation of Ω is an iterative procedure and can be expensive.

The third step, specific for our method, is the calculation of the S operator. This operator satisfies a linear equation, given in ref.[39], containing very high (although finite) powers of T, see Eq. (*23*) of ref.[39]. Some approximation is needed to eliminate this high nonlinearity in T. We propose to neglect the fourth and higher combined powers of S and T and to compute S_1 and S_2 by solving the system of linear equations $\mathcal{H}_n(S) = I_n$, $n = 1, 2$, with the homogeneous part

$$\mathcal{H}_n(S) = \langle e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} | nS_n - 2[T_1^\dagger, S_2] - [[T^\dagger, T], S_1] - 2[[T^\dagger, T], S_2]\rangle \qquad (56)$$

and the inhomogeneity

$$I_n = \langle e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} | nT_n - [T_1^\dagger, T_2] - \frac{1}{2}[[T_1^\dagger, T], T] - [[T_2^\dagger, T], T]\rangle . \qquad (57)$$

The quartic terms, neglected in Eqs. (*56*) and (*57*), would give a contribution in the fifth order in the MP expansion of the polarization propagator. It should be emphasized that even if T is restricted to single and double excitations the S_3 and higher S_n operators do not vanish. The neglect of S_3 and higher S_n operators leads in this case to a fifth-order error in the MP theory, so we did not consider these terms in Eqs. (*56*) and (*57*). One may also consider omitting the cubic terms in these equations which amounts to the neglect of some fourth-order terms in the MP expansion of the propagator. One may easily see that the resulting equations for S_1 and S_2

$$\langle e^{\rho_1 \ldots \rho_n}_{\alpha_1 \ldots \alpha_n} | nS_n - nT_n - 2[T_1^\dagger, S_2] + [T_1^\dagger, T_2]\rangle = 0 \qquad (58)$$

uncouple and have a simple, "closed-form" solution $S_1 = T_1 + \hat{\mathcal{P}}_1([T_1^\dagger, T_2])$, $S_2 = T_2$, fully consistent with Eq. (*20*).

The iterations needed to solve the linear equations for S can be avoided if S is approximated by a direct expansion in powers of T, derived in ref.[39]. The cubic terms $S_n^{[3]}$ in this expansion, not written explicitly in Eq. (*20*), are given by

$$S_1^{[3]} = \frac{1}{2}\mathcal{P}_1([[T_1^\dagger, T_1], T_1]) + \mathcal{P}_1([[T_2^\dagger, T_2], T_1]) \qquad (59)$$

$$S_2^{[3]} = \frac{1}{2}\mathcal{P}_2([[T_2^\dagger, T_2], T_2]) + \mathcal{P}_2([[T_1^\dagger, T_2], T_1]) \qquad (60)$$

$$S_3^{[3]} = \frac{1}{2}\mathcal{P}_3([[T_1^\dagger, T_2], T_2]) \qquad (61)$$

where the $S_3^{[3]}$ operator is given here to show only that it does not vanish. Approximating S using the noniterative Eqs. (*59*) and (*60*) leads to the polarization propagator accurate through the fourth order in the Møller–Plesset perturbation W.

The last step of the whole calculation is the evaluation of the formula (*27*). Since the nested commutator expansion of Eq. (*27*) involves terms of rather high order (the seventh order when $\Omega = \Omega_1 + \Omega_2$) this expansion must be truncated for practical reasons. We propose to expand it through the combined third power of T and S. The successive terms in the resulting expansion, denoted by $\langle\langle A;B\rangle\rangle_\omega^{[k]}$, $k = 0, 1, 2, 3$, are given by

$$\langle\langle A;B\rangle\rangle_\omega^{[0]} = \langle B\Omega_1(\omega)\rangle + \text{g.c.c.} \tag{62}$$

$$\langle\langle A;B\rangle\rangle_\omega^{[1]} = \langle S|[B,\Omega(\omega)]\rangle + \langle [B,S_2]|\Omega_1(\omega)\rangle + \text{g.c.c.} \tag{63}$$

$$\begin{aligned}\langle\langle A;B\rangle\rangle_\omega^{[2]} = &-\langle[[B,T^\dagger],S]|\Omega(\omega)\rangle + \langle[B,S]|[S_1^\dagger,\Omega_2(\omega)]\rangle + \\ &+\frac{1}{2}\langle[[B,S],S]|\Omega(\omega)\rangle + \text{g.c.c.}\end{aligned} \tag{64}$$

$$\begin{aligned}\langle\langle A;B\rangle\rangle_\omega^{[3]} = &-\frac{1}{2}\langle[[[B,T^\dagger],S],S]|\Omega(\omega)\rangle - \langle[[B,T^\dagger],S]|[S_1^\dagger,\Omega_2(\omega)]\rangle + \\ &+\frac{1}{2}\langle[[[B,T_1^\dagger],T_1^\dagger],S_2]|\Omega_1(\omega)\rangle + \frac{1}{2}\langle[[B,S_1],S_1]|[S_1^\dagger,\Omega_2(\omega)]\rangle + \text{g.c.c.}\end{aligned} \tag{65}$$

Equations (*62*)–(*64*) correspond to the singles and doubles level of the coupled-cluster theory i.e., to the CCSD propagator. The expansion of the commutator expressions in Eqs. (*62*)–(*64*) in terms of one-electron molecular integrals and cluster amplitudes is straightforward and will not be discussed here. It may be noted that the last three terms in Eq. (*65*) give contributions of, successively, the fifth, fifth and seventh order in the Møller–Plesset perturbation W and are likely to be negligible. The last two terms in Eq. (*64*) and the first term in Eq. (*65*) are of the fourth order in W and probably can also be neglected in many cases. The final propagator evaluation via Eqs. (*62*)–(*64*) is a noniterative process and is expected to be much less time-consuming than the first two steps involving the standard coupled-cluster calculation of the T_1, T_2, Ω_1 and Ω_2 operators. Inclusion of T_3 and Ω_3 generates additional terms but only a few of them must be included to obtain the propagator which is accurate through the third order of the Møller–Plesset theory.

It should be noted that approximating Eq. (*27*) by Eqs. (*62*)–(*64*) leads to a small (high-order in W) violation of the operator exchange symmetry $\langle\langle A;B\rangle\rangle_{\omega} = \langle\langle B;A\rangle\rangle_{-\omega}$ of the propagator. This symmetry could be fulfilled exactly if the g.c.c. operation in Eq. (*27*) were replaced by the operator exchange operation $(A,\omega) \leftrightarrow (B,-\omega)$. This replacement would result, however, in a loss of Hermitian symmetry of the theory and a small violation of the time-reversal symmetry of the propagator approximated via Eqs. (*62*)–(*64*). Therefore we did not follow this option.

One may ask what is the simplest coupled-cluster approximation to $\langle\langle A;B\rangle\rangle_{\omega}$, which is accurate through the second order in W. Such an approximation can be obtained by setting $S = T$ and computing the propagator from the formula

$$\begin{aligned}\langle\langle A;B\rangle\rangle_{\omega} &= \langle B\Omega_1(\omega)\rangle + \langle T|[B,\Omega(\omega)]\rangle + \langle [B,T_2]|\Omega_1(\omega)\rangle - \\ &- \langle [[B,T^{\dagger}],\mathrm{T}]|\Omega(\omega)\rangle + \text{g.c.c.}\end{aligned} \tag{66}$$

where T is the ground state CCSD operator and $\Omega(\omega)$ is obtained from Eq. (*14*). Once the T and Ω operators are known, the evaluation of Eq. (*66*) is a very simple one-step noniterative procedure, which gives a propagator accounting for all diagrams in Figs. 3 and 4 and for an infinite set of high-order diagrams resulting from the coupled-cluster treatment of T and Ω operators.

CONCLUSIONS

We presented a novel approach to the coupled-cluster calculation of the polarization propagator. Our approach is fully time-independent and appears to be conceptually much simpler than the conventional time-dependent approaches. The resulting propagator is exactly size-extensive and exhibits the correct Hermitian and time-reversal symmetries. The computational procedure is the same as in the conventional coupled-cluster gradient calculations, except for additional two simple noniterative steps.

Using the proposed approach one can easily obtain an explicitly connected purely algebraic formulation of the Møller–Plesset expansion for the polarization propagator. We have outlined a general procedure of separating the apparent correlation (RPA) terms from this expansion.

The polarization propagators obtained from our theory are particularly useful for applications to the theory of intermolecular forces. The resulting dynamic polarizabilities can be directly applied to obtain the large R

asymptotics of the suitably defined coupled-cluster approximation to the dispersion energy[54]. It should be noted that the dispersion energy predicted by the conventional coupled-cluster approach[55] does not have this feature and is not related to the dynamic polarizabilities of the time-dependent coupled-cluster theory.

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