

Correlated calculations of molecular dynamic polarizabilities

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Frequency-dependent molecular polarizabilities of several molecules N_2 , CO , CO_2 , Cl_2 , C_2H_2 , COS , and CS_2 are calculated by the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method. The EOM-CCSD CI-like, linear and quadratic methods for dynamic second-order properties are presented. The importance of electron correlation, the quadratic contribution, and orbital relaxation effects are assessed. London dispersion coefficients are calculated by numerical integration of the EOM-CCSD polarizabilities. © 1997 American Institute of Physics. [S0021-9606(97)01541-9]

I. INTRODUCTION

The frequency-dependent polarizability (FDP), $\alpha(\omega)$, also known as the dynamic dipole polarizability, is a linear response of a system to an external electric field. In addition, for low frequencies, $\alpha(\omega)$ determines Raman intensities,¹⁻⁴ refractive indices, molar refractivity, the Verdet constants (see Ref. 5 for a summary), and scattering cross sections.^{6,7} FDPs find applications in a wealth of nonlinear optical materials research. The excitation energies, the corresponding transition moments, and the van der Waals coefficients, C_6 , of long-range interactions can be calculated by knowing the variation of the dipole polarizability with the frequency of incident radiation.⁸⁻¹⁰

Much effort has been made in recent years to develop analytical methods to calculate molecular properties, in particular second- and higher-order properties.¹¹⁻¹⁶ Analytical methods alleviate limitations caused by the large number of tensor elements or numerical precision problems. Significantly, only analytical methods can be used to evaluate most dynamic properties, including dynamic polarizabilities and hyperpolarizabilities. These include analytical energy derivatives,^{11,17} polarization propagator,¹⁸ and equation-of-motion methods.^{16,19} The uncorrelated methods include the coupled perturbed Hartree-Fock method (CPHF),^{20,21} which in the static limit is identical to the random phase approximation (RPA) or to the (linearized) time dependent Hartree-Fock (TDHF) theory.²² A list of correlated methods includes higher random phase approximation (HRPA), second-order polarization propagator (SOPPA),^{18,23-25} multiconfiguration time-dependent Hartree-Fock (MC-TDHF),²⁶⁻²⁸ coupled cluster singles and double polarization propagator (CCSDPPA),²⁹ coupled cluster (CC) and many-body perturbation theory (MBPT) methods,³⁰⁻³⁴ etc. The general picture that arises from these correlated studies of static molecular polarizabilities is that the electron correlation effects are about 10% of the correlated results, and the calculated results are sensitive to the diffuse character of the atomic basis set.

Although there is much work done on static polarizabilities at both TDHF and correlated levels,³² frequency-dependent calculations for molecules are scarce. Furthermore, little attempt has been made to describe the whole

range of the polarizability curve, including both the real and imaginary frequencies, and the polarizability poles corresponding to excitation energies, for a particular method.

In our group, we have developed the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method to calculate second-order properties.^{16,35,36} The second derivative of the CCSD energy with respect to perturbations of interest will lead to what is called the quadratic EOM-CCSD approach to second-order properties.³⁶ In taking the derivative, orbital relaxation effects are neglected, as they have been shown to be relatively unimportant for CC reference states,^{37,38} although not necessarily unimportant for excited states. The alternative propagator expansion can be employed by taking the EOM-CCSD similarity transformed Hamiltonian as the zeroth-order Hamiltonian. This defines the EOM-CCSD CI-like approximation.¹⁶ The difference between quadratic and CI-like approximations is henceforth referred to as the quadratic contribution. In the third approximation, we take advantage of the fact that all the unlinked contributions in the CI-like expression cancel with the unlinked contributions in the quadratic term and neglect the remaining small linked quadratic contribution. This defines the purely extensive ("linked") EOM-CCSD linear approximation.^{35,39} The formal sum-over-states (SOS) propagator structure of the CI-like approximation is retained in the linear approximation as well.

In this study we employ the above mentioned three EOM-CCSD models to calculate the dynamic polarizabilities at real and imaginary frequencies. The list of molecules includes N_2 , CO , C_2H_2 , Cl_2 , CO_2 , OCS , CS_2 , and finally, trans-butadiene C_4H_6 . A comparison of numerical results obtained by the three different EOM-CCSD models in a consistent basis,^{40,41} and a comparison with other well-established correlated theoretical results and experiment is presented.

II. THEORY

Properties can usually be evaluated from the derivative of the energy associated with a wave function, subject to an external perturbation. For time-independent perturbations

this is straightforward. For example, dipole moments, static polarizabilities, and hyperpolarizabilities are defined as the first-, second-, and third-derivatives of energy which are proportional to the zeroth, first-, and second-order response of a molecule to a static electric field. However, a straightforward extension of energy derivative methods to time-dependent perturbations is not as apparent, because the corresponding energy is not uniquely defined. Hence, the starting point of our derivation is the time-dependent dipole moment, which is well defined and unique.

The time-dependent dipole moment is given by

$$\mu(t) = \langle \Psi(t) | \hat{\mu} | \Psi(t) \rangle, \quad (1)$$

where $|\Psi(t)\rangle$ satisfies the time-dependent Schrödinger equation

$$i \frac{\partial |\Psi(t)\rangle}{\partial t} = \hat{H}(t) |\Psi(t)\rangle, \quad (2)$$

and is assumed to be normalized at time $t=0$, and hence at all times. To define polarizabilities, hyperpolarizabilities, and so forth, let us consider the field-dependent Hamiltonian

$$H(t) = H_0 + \sum_a \int d\omega_a \varepsilon_a(\omega_a) \hat{\mu}_a e^{-i\omega_a t} = H_0 + V(t), \quad (3)$$

where H_0 is the usual molecular Hamiltonian, $\hat{\mu}_a$ denotes the three Cartesian components of the dipole operator, while $\varepsilon_a(\omega_a)$ indicates the respective components of the frequency-dependent field strength. (Every integration, either in time or in frequency, is accompanied by a factor $1/\sqrt{2\pi}$. We absorb this factor in our integral sign to facilitate the notation.) At time $t=0$, we assume that the state $|\Psi(0)\rangle$ is the ground state (or possibly another stationary state) of the field-independent molecular Hamiltonian H_0 . Under these conditions, the polarizability and higher polarizabilities (with respect to the state at time $t=0$) can be defined as the expansion coefficients of the time-dependent dipole moment

$$\begin{aligned} \mu_A(t) = & \mu_A^{(0)} + \sum_a \int d\omega_a \alpha_{Aa}(\omega_a) \varepsilon(\omega_a) e^{-i\omega_a t} \\ & + \frac{1}{2!} \sum_{a,b} \int d\omega_a d\omega_b \beta_{Aab}(\omega_a, \omega_b) \\ & \times \varepsilon(\omega_a) \varepsilon(\omega_b) e^{-i(\omega_a + \omega_b)t} + \dots \end{aligned} \quad (4)$$

Here, we adopt the convention,⁴² using upper case letters for the component under consideration and lower case letters to indicate components that are summed over. For future reference, the Fourier transform of $\mu_A(t)$ reads

$$\begin{aligned} \mu_A(\omega) = & \int_{-\infty}^{\infty} \mu_A(t) e^{i\omega t} dt \\ = & \mu_A^{(0)} \delta(\omega) + \sum_a \int d\omega_a \alpha_{Aa}(\omega_a) \varepsilon_a(\omega_a) \\ & \times \delta(\omega - \omega_a) + \frac{1}{2!} \sum_{a,b} \int_{-\infty}^{\infty} d\omega_a d\omega_b \beta_{Aab}(\omega_a, \omega_b) \\ & \times \varepsilon_a(\omega_a) \varepsilon_b(\omega_b) \delta(\omega - \omega_a - \omega_b) + \dots \end{aligned} \quad (5)$$

It follows that the polarizability can be obtained as

$$\alpha_{AB}(\omega_B) = \int_{-\infty}^{\infty} d\omega \left. \frac{\partial \mu_A(\omega)}{\partial \varepsilon(\omega_B)} \right|_{\mathbf{E}=0}, \quad (6)$$

where \mathbf{E} indicates all components of the field strength. The first hyperpolarizability is given by

$$\begin{aligned} \beta_{ABC}(\omega_B, \omega_C) = & \beta_{ACB}(\omega_C, \omega_B) \\ = & \int_{-\infty}^{\infty} d\omega \left. \frac{\partial \mu_A(\omega)}{\partial \varepsilon_B(\omega_B) \partial \varepsilon_C(\omega_C)} \right|_{\mathbf{E}=0}. \end{aligned} \quad (7)$$

The wave function $|\Psi(t)\rangle$ that defines the time- and frequency-dependent dipole moment satisfies the time-dependent Schrödinger equation corresponding to the complete, field-dependent Hamiltonian. This wave function (and the time-dependent dipole moment) can be expanded in orders of the field, and this will yield expressions for the polarizability and hyperpolarizabilities. If we assume that all eigenstates of the molecular Hamiltonian are known (at least formally), we can obtain in this way the familiar sum over states expressions for the polarizability, and so forth.

Alternatively, we can assume a parameterization for the complete field-dependent wave function, which is then subject to a perturbation expansion. This leads directly to equations for the perturbed amplitudes, which in turn define the quantities of interest. One possible parameterization is, of course, the exponential coupled cluster ansatz, which is the focus of this paper.

The above approach to polarizabilities (or hyperpolarizabilities and so forth) does not apply directly to the coupled cluster formalism, however. The reason is that the time-dependent wave function in the CC formalism is not normalized to unity, but rather satisfies intermediate normalization

$$|\Psi_{CC}(t)\rangle = e^{T(t)} |\Phi_0\rangle \rightarrow \langle \Phi_0 | \Psi_{CC}(t) \rangle = 1. \quad (8)$$

The exact CC wave function is proportional to $|\Psi(t)\rangle$, where the proportionality factor is, in general, complex. Let us write

$$|\Psi(t)\rangle = |\Psi_{CC}(t)\rangle e^{-i\varphi(t)}, \quad (9)$$

where the normalization factor is defined as

$$e^{-i\varphi(t)} = \langle \Phi_0 | \Psi(t) \rangle. \quad (10)$$

Substituting this expression in the time-dependent Schrödinger equation, and multiplying by $e^{i\varphi(t)}$, we obtain

$$i \frac{\partial}{\partial t} |\Psi_{CC}(t)\rangle + \frac{\partial \varphi(t)}{\partial t} |\Psi_{CC}(t)\rangle = H |\Psi_{CC}(t)\rangle. \quad (11)$$

If we multiply in addition by $e^{-T(t)}$, we find

$$i \frac{\partial T}{\partial t} |0\rangle + \frac{\partial \varphi}{\partial t} |0\rangle = \bar{H}(t) |0\rangle, \quad (12)$$

where $\bar{H}(t) = e^{-T(t)} H e^{T(t)}$. It may be appreciated that the equations for T are completely decoupled from the equation for the phase

$$\langle q | \bar{H}(t) - i \frac{\partial T}{\partial t} | 0 \rangle = 0, \quad (13)$$

$$\frac{\partial \varphi}{\partial t} = \langle 0 | \bar{H}(t) | 0 \rangle.$$

The analogy with time-independent CC theory is evident. The quantity $\partial \varphi / \partial t$ is called the quasi-energy, and it has been observed that polarizabilities and so forth can be obtained from differentiating this quantity.^{12,13,42-44} The relation between the quasi-energy and the quantities of interest is not very transparent in our opinion, however, so we prefer not to use the quasi-energy.

The time-dependent dipole moment in terms of the CC wave function is defined as the expectation value,

$$\frac{e^{i\varphi(t)} \langle \Psi_{CC}(t) | \hat{\mu}_A | \Psi_{CC}(t) \rangle e^{-i\varphi(t)}}{e^{i\varphi(t)} \langle \Psi_{CC}(t) | \Psi_{CC}(t) \rangle e^{-i\varphi(t)}} \equiv \langle \tilde{\Psi}_{CC}(t) | \hat{\mu}_A | \Psi_{CC}(t) \rangle. \quad (14)$$

The state

$$\langle \tilde{\Psi}_{CC}(t) | = \frac{\langle \Psi_{CC}(t) |}{\langle \Psi_{CC}(t) | \Psi_{CC}(t) \rangle}, \quad (15)$$

by definition satisfies the normalization condition

$$\langle \tilde{\Psi}_{CC}(t) | \Psi_{CC}(t) \rangle = 1 \quad \forall t, \quad (16)$$

and it can be conveniently parameterized as

$$\langle \tilde{\Psi}_{CC}(t) | = \langle \Phi_0 | (1 + \Lambda(t)) e^{-T(t)}, \quad (17)$$

where $\Lambda(t)$ is a deexcitation operator introduced in analogy with CC derivative theory.^{11,17} The normalization condition is satisfied trivially for all values of the parameters determining the operators $\Lambda(t)$ and $T(t)$. The state $\langle \tilde{\Psi}_{CC}(t) |$ is related to the true Schrödinger bra as $\langle \Psi(t) | = e^{i\varphi(t)} \times \langle \tilde{\Psi}_{CC}(t) |$, and the time evolution of this state is, of course, determined by the Schrödinger equation

$$-i \frac{\partial}{\partial t} \langle \Psi(t) | = \langle \Psi(t) | H. \quad (18)$$

If we substitute the parameterization for $\langle \tilde{\Psi}(t) |$ in the Schrödinger equation, and multiply by $e^{-i\varphi(t)}$ and e^T from the right, we find

$$\langle 0 | (1 + \Lambda(t)) \left[\bar{H}(t) - i \frac{\partial T}{\partial t} - \frac{\partial \varphi}{\partial t} \right] + i \langle 0 | \frac{\partial \Lambda(t)}{\partial t} = 0. \quad (19)$$

Projecting on $|0\rangle$ and $|q\rangle = \hat{q}|0\rangle$, we obtain

$$\begin{aligned} \frac{\partial \varphi}{\partial t} &= \langle 0 | \bar{H}(t) | 0 \rangle + \langle 0 | \Lambda(t) \left[\bar{H}(t) - i \frac{\partial T}{\partial t} \right] | 0 \rangle \\ &= \langle 0 | \bar{H}(t) | 0 \rangle \end{aligned} \quad (20)$$

and

$$\begin{aligned} \langle 0 | (1 + \Lambda(t)) [\bar{H}(t), q] | 0 \rangle + i \langle 0 | \frac{\partial \Lambda}{\partial t} | q \rangle \\ + \langle 0 | (1 + \Lambda(t)) \hat{q} \left\{ \bar{H}(t) - i \frac{\partial T}{\partial t} - \frac{\partial \varphi}{\partial t} \right\} | 0 \rangle = 0. \end{aligned} \quad (21)$$

The last term in this equation vanishes because the CC equations are satisfied (this is true also if T is truncated). Let us summarize our basic equations obtained so far:

$$\begin{aligned} \mu(t) &= \langle 0 | (1 + \Lambda(t)) e^{-T(t)} \hat{\mu} e^{T(t)} | 0 \rangle \\ &= \langle 0 | (1 + \Lambda(t)) \bar{\mu}(t) | 0 \rangle, \end{aligned} \quad (22)$$

$$\langle q | \left(\bar{H}(t) - i \frac{\partial T}{\partial t} \right) | 0 \rangle = 0, \quad (23)$$

$$\langle 0 | (1 + \Lambda(t)) [\bar{H}(t), \hat{q}] | 0 \rangle + i \langle 0 | \frac{\partial \Lambda}{\partial t} | q \rangle = 0. \quad (24)$$

In addition, we have an equation for the phase factor that establishes the connection between our CC states and the true (normalized) wave functions

$$\frac{\partial \varphi}{\partial t} = \langle 0 | \bar{H}(t) | 0 \rangle. \quad (25)$$

However, this quantity will not play any further role in our derivation.

To obtain a perturbation expansion for the time-dependent dipole moment, we assume a perturbation expansion for the cluster operator T and the operator Λ ,

$$T(\kappa, t) = \sum_{n=0}^{\infty} \kappa^n T^{(n)}(t), \quad (26)$$

$$\Lambda(\kappa, t) = \sum_{n=0}^{\infty} \kappa^n \Lambda^{(n)}(t). \quad (27)$$

To keep the notation compact we also introduce an expansion for

$$\bar{H}(t) = \sum_{n=0}^{\infty} \kappa^n \bar{H}^{(n)}(t). \quad (28)$$

The components $\bar{H}^{(n)}$ are defined in terms of H_0 , V , and the various $T^{(m)}$, for example

$$\begin{aligned} \bar{H}^{(0)} &= e^{-T^{(0)}} H_0 e^{T^{(0)}}, \\ \bar{H}^{(1)} &= [\bar{H}^{(0)}, T^{(1)}] + e^{-T^{(0)}} V e^{T^{(0)}}, \\ &\vdots \end{aligned} \quad (29)$$

$$\bar{H}^{(n)} = [\bar{H}^{(0)}, T^{(n)}] + \bar{H}^{(n/n-1)}.$$

For future convenience we have introduced $\bar{H}^{(n/m)}$ to denote all terms in $\bar{H}^{(n)}$ that can be obtained by connecting cluster

operators of order $\leq m$ to $H = H_0 + V$. This notation allows us to write explicit equations for $T^{(n)}$, for $n > 0$,

$$\langle q | [\bar{H}^{(0)}, T^{(n)}(t)] - i \frac{\partial T^{(n)}}{\partial t} | 0 \rangle = - \langle q | \bar{H}^{(n/n-1)}(t) | 0 \rangle. \quad (30)$$

These equations can be solved hierarchically. Similarly, the equations for $\Lambda^{(n)}$ can be written

$$\begin{aligned} \langle 0 | \Lambda^{(n)}(t) [\bar{H}^{(0)}, \hat{q}] | 0 \rangle + i \langle 0 | \frac{\partial \Lambda^{(n)}}{\partial t} | q \rangle \\ = - \langle 0 | (1 + \Lambda^{(0)}) [\bar{H}^{(n)}(t), \hat{q}] | 0 \rangle - \sum_{k=1}^{n-1} \langle 0 | \Lambda^{(k)}(t) \\ \times [\bar{H}^{(n-k)}(t), \hat{q}] | 0 \rangle. \end{aligned} \quad (31)$$

Again, these equations can be solved hierarchically. The equations for $\Lambda^{(n)}$ require the solution of perturbed amplitudes T up to and including $T^{(n)}$.

The zeroth-order equations are the usual time-independent T and Λ equations

$$\langle q | \bar{H}^{(0)} | 0 \rangle = 0 \quad (32)$$

and

$$\langle 0 | \Lambda [\bar{H}^{(0)}, \hat{q}] | 0 \rangle = - \langle 0 | \bar{H}^{(0)} | q \rangle. \quad (33)$$

The higher-order equations are best solved in the frequency domain. If we introduce Fourier transforms

$$T(\omega) = \int e^{i\omega t} T(t) dt, \quad (34)$$

the equation for $T^{(n)}(\omega)$ can be written

$$\langle q | [\bar{H}^{(0)}, T^{(n)}(\omega)] + \omega T^{(n)}(\omega) | 0 \rangle = - \langle q | \bar{H}^{(n/n-1)}(\omega) | 0 \rangle. \quad (35)$$

With the operator $\langle q | [\bar{H}^{(0)}, p] | 0 \rangle + \omega \delta_{pq}$ we associate its inverse, the resolvent $\bar{R}^0(\omega)$, which only acts in the space of excited determinants. Hence we can write

$$\langle q | T^{(n)}(\omega) | 0 \rangle = - \langle q | \bar{R}^0(\omega) \bar{H}^{(n/n-1)}(\omega) | 0 \rangle. \quad (36)$$

The resolvent has the very useful property that when acting on a connected operator to its right, the result is again connected. We will see that the structure of the whole approach will be intrinsically connected.

The quantity

$$\langle q | \bar{H}^{(n/n-1)}(\omega) | 0 \rangle = \int e^{i\omega t} \langle q | \bar{H}^{(n/n-1)}(t) | 0 \rangle dt \quad (37)$$

is in general a complicated expression that involves the Fourier transform of a product of functions of time (T -amplitudes, a time-dependent perturbation, etc.). Each of

these elementary functions has a Fourier transform, and the total transform can be written as a generalized convolution, e.g.,

$$\begin{aligned} \int f(t) g(t) h(t) e^{i\omega t} dt \\ = \int \int \int d\omega_1 d\omega_2 d\omega_3 \\ \times \int f(\omega_1) g(\omega_2) h(\omega_3) e^{i(\omega - \omega_1 - \omega_2 - \omega_3)t} dt \\ = \int \int \int d\omega_1 d\omega_2 d\omega_3 f(\omega_1) g(\omega_2) h(\omega_3) \\ \times \delta(\omega - \omega_1 - \omega_2 - \omega_3). \end{aligned} \quad (38)$$

We note that these types of expressions have precisely the same form as the polarizabilities and so forth, and this will therefore provide an easy connection.

The equation for $\Lambda^{(n)}$ takes the form

$$\begin{aligned} \langle 0 | \Lambda^{(n)}(\omega) [\bar{H}^{(0)}, q] | 0 \rangle - \omega \langle 0 | \Lambda^{(n)}(\omega) | q \rangle \\ = - \langle 0 | (1 + \Lambda^{(0)}) [\bar{H}^{(n)}(\omega), q] | 0 \rangle \\ - \sum_{k=1}^{n-1} \langle 0 | \Lambda^{(k)}(\omega) [\bar{H}^{(n-k)}(\omega), q] | 0 \rangle. \end{aligned} \quad (39)$$

Using the resolvent, the solution can be written

$$\begin{aligned} \langle 0 | \Lambda^{(n)}(\omega) | p \rangle = - \sum_q \sum_{k=0}^{n-1} \langle 0 | (\delta_{k0} + \Lambda^{(k)}(\omega)) \\ \times [\bar{H}^{(n-k)}(\omega), q] | 0 \rangle \bar{R}_{qp}^0(-\omega). \end{aligned} \quad (40)$$

The above equations are not the most convenient for application. One may manipulate further, starting from the expression for the frequency-dependent dipole moment and eliminating the frequency-dependent Λ terms. In the following section, we will consider the dynamic polarizability.

A. The dynamic polarizability in the CC framework

As mentioned before, the dynamic polarizability is related to the first-order term in the dipole moment,

$$\begin{aligned} \alpha_{Aa}(\omega) = \int d\omega_1 \frac{\mu_A^{(1)}(\omega_1)}{\partial \epsilon_a(\omega)} \\ = \langle 0 | (1 + \Lambda^{(0)}) [\bar{\mu}_A^{(0)}, T_a^{(1)}(\omega)] | 0 \rangle \\ + \langle 0 | \Lambda_a^{(1)}(\omega) \bar{\mu}_A^{(0)} | 0 \rangle, \end{aligned} \quad (41)$$

where

$$\langle q | T^{(1)}(\omega) | 0 \rangle = - \langle q | \bar{R}_0(\omega) \bar{\mu}_a^{(0)} | 0 \rangle \quad (42)$$

and

$$\langle 0 | \Lambda_a^{(1)}(\omega) | p \rangle = \langle 0 | (1 + \Lambda^{(0)}) [\bar{H}_a^{(1)}(\omega), q] | 0 \rangle \times \bar{R}_{qp}^0(-\omega). \quad (43)$$

Using

$$\bar{R}^0(-\omega) \bar{\mu}_A^0 | 0 \rangle = T_A^{(1)}(-\omega) \quad (44)$$

and

$$\bar{H}_a^{(1)}(\omega) = \bar{\mu}_a^{(0)} + [\bar{H}^{(0)}, T_a^{(1)}(\omega)], \quad (45)$$

we find

$$\alpha_{Aa}(\omega) = \langle 0 | (1 + \Lambda^{(0)}) [\bar{\mu}_A^{(0)}, T_a^{(1)}(\omega)] | 0 \rangle + \langle 0 | (1 + \Lambda^{(0)}) \times [\bar{\mu}_a^{(0)}, T_A^{(1)}(-\omega)] | 0 \rangle + \langle 0 | (1 + \Lambda^{(0)}) \times [[\bar{H}^{(0)}, T_a^{(1)}(\omega)], T_A^{(1)}(-\omega)] | 0 \rangle, \quad (46)$$

which is a familiar expression for the polarizability in a CC framework.¹⁵

We can rewrite Eq. (45) in the configuration basis³⁵ as

$$\alpha_{Aa}(\omega) = \sum_{l=0}^1 \sum_{k \neq 0} \frac{\langle \tilde{\Psi}_0^{(0)} | \hat{\mu}_A^{(0)} - \langle \hat{\mu}_A^{(0)} | \Psi_k^{(0)} \rangle \langle \tilde{\Psi}_k^{(0)} | \hat{\mu}_A^{(0)} - \langle \hat{\mu}_A^{(0)} | \tilde{\Psi}_0^{(0)} \rangle}{(E_0^{(0)} - E_k^{(0)} + (-1)^l \omega)}, \quad (48)$$

where $\Psi_k^{(0)}$ and $E_k^{(0)}$, $k=0,1,\dots$ are eigenfunctions and eigenvalues of the unperturbed zeroth-order Hamiltonian. The states $\Psi_k^{(0)}$, $\tilde{\Psi}_k^{(0)}$ form a complete biorthogonal set (i.e., $\langle \tilde{\Psi}_k^{(0)} | \Psi_l^{(0)} \rangle = \delta_{kl}$). By using the CC parametrization for the ground and excited states (EOM-CC states), we can rewrite Eq. (48) as

$$\alpha_{Aa}(\omega) = \sum_{l=0}^1 \langle 0 | (1 + \Lambda) | (\bar{\mu}_A^{(0)} - \langle \bar{\mu}_A^{(0)} \rangle) | \mathbf{h} \rangle \times \mathbf{A}^{-1}((-1)^l \omega) \langle \mathbf{h} | \bar{\mu}_A^{(0)} | 0 \rangle, \quad (49)$$

which amounts to exactly the first two terms of Eq. (47). This provides a computationally and conceptually convenient alternative approach to polarizabilities. The EOM-CC has the advantage of providing the $\Psi_k^{(0)}$, $\tilde{\Psi}_k^{(0)}$, and $E_k^{(0)}$, $k=0,1,\dots$ in Eq. (48). From the above development it is clear that this is not the full derivative for a truncated CC method, but it offers an equally valid ‘‘propagator’’ viewpoint that has often been used in SOPPA and CCPPA property calculations.¹⁸ The analogy with an expectation value and the first derivative of the energy relative to a field is apparent. If the (generalized) Hellmann–Feynman⁴⁵ theorem is satisfied, the two forms are identical. If not, different results are obtained. Depending upon your viewpoint, either can be the ‘‘rigorous’’ definition of the property. The same condition applies for second- and higher-order properties. If the higher analog of the Hellmann–Feynman theorem is satisfied, it means that the results from ordinary perturbation theory and derivative theory are identical. Since the deriva-

$$\alpha_{Aa}(\omega) = \sum_{\mu,\nu} \langle 0 | (1 + \Lambda^{(0)}) [\bar{\mu}_A^{(0)} - \langle \bar{\mu}_A^{(0)} \rangle] | \mathbf{h} \rangle \mathbf{A}^{-1}(+\omega) \times \langle \mathbf{h} | \bar{\mu}_a^{(0)} - \langle \bar{\mu}_a^{(0)} \rangle | 0 \rangle + \sum_{\mu,\nu} \langle 0 | (1 + \Lambda^{(0)}) \times [\bar{\mu}_A^{(0)} - \langle \bar{\mu}_A^{(0)} \rangle] | \mathbf{h} \rangle \mathbf{A}^{-1}(-\omega) \langle \mathbf{h} | \bar{\mu}_a^{(0)} - \langle \bar{\mu}_a^{(0)} \rangle | 0 \rangle + \langle 0 | (1 + \Lambda^{(0)}) (\bar{H}^{(0)} - E_0) | \mathbf{f} \rangle \times \langle \mathbf{f} | T_a^{(1)}(\omega) T_A^{(1)}(-\omega) | 0 \rangle, \quad (47)$$

where $\mathbf{A}(\pm\omega) = \langle \mathbf{h} | (\bar{H}^{(0)} - E^{(0)} \pm \omega) | \mathbf{h} \rangle$, where $|\mathbf{h}\rangle$ indicates the manifold of singly and doubly excited determinants. $\langle \bar{\mu}^{(0)} \rangle = \langle 0 | (1 + \Lambda) \bar{\mu}^{(0)} | 0 \rangle$ and $|\mathbf{f}\rangle$ indicate all determinants that are higher than twofold excited. In the limit that the $|\mathbf{h}\rangle$ manifold is complete, the quadratic term in Eq. (47) vanishes, or at the CCSD level the result is equivalent to full CI for two electrons.

Alternatively, we can adopt the ‘‘propagator’’ viewpoint,¹⁶ which defines the polarizability as

itive always introduces the appropriate non-Hellmann–Feynman terms, it should be somewhat superior numerically. The straight ‘‘propagator’’ approach using the EOM-CC states is referred to as the CI-like approximation,¹⁶ as the excited states in EOM-CC are obtained from a CI-like diagonalization procedure of a transformed Hamiltonian based upon a CC ground state. The EOM-CC approximation for excitation energies is not entirely linked⁴⁶ like CI. Second-order properties in EOM-CC are fully linked in the quadratic approximation but not in the CI-like approach. This scarcely affects a single molecule, but if we replicate the molecule many times we would find a numerical problem with the CI-like approximation in the limit.⁴⁷ We can correct this, however, by removing the unlinked terms that remain in the CI-like approximation. Formally, this means we take from the quadratic term that needed to correct the unlinked diagrams in the lead term, and then in the interest of efficiency, neglect the remaining linked quadratic part. This defines a linear linked approximation^{35,39}

$$\alpha_{Aa}(\omega) = \sum_{l=0}^1 \langle 0 | (1 + \Lambda') | (\bar{\mu}_{A,\text{open}}^{(0)} | \mathbf{h} \rangle \mathbf{A}^{-1}((-1)^l \omega) \times \langle \mathbf{h} | \hat{\mu}_a^{(0)} | 0 \rangle. \quad (50)$$

Here

$$\bar{\mu}_{A,\text{open}}^{(0)} = e^{-T} \mu_A e^T - \langle 0 | e^{-T} \mu_A e^T | 0 \rangle, \quad (51)$$

while Λ' is an explicitly connected operator that is defined from a slightly modified Λ equation obtained by equating the usually small matrix elements,

$$\langle 0 | e^{-T} H e^T |_i^a \rangle = F_{ia} + \sum_{j,b} \langle ij || ab \rangle t_j^b, \quad (52)$$

responsible for disconnected contributions in Λ , rigorously to zero. The linear approximation scales properly for any number of molecules, but is no longer “exact” for two-electron systems. However, it retains the convenient “propagator” form, shared by the exact result. In practice we replace Λ' by Λ since this changes the results only very slightly, but it allows us to calculate both the CI-like and the linear approximations in a single calculation. It follows that in the present calculations, if a molecule does not have a permanent dipole moment (due to symmetry) the linear and CI-like approximations yield identical results. In the next section we will also consider the fully linked linear approximation, and we will refer to this as linear' (in accordance with Λ').

Equations (47), (49), and (50) (with $\Lambda' = \Lambda$) summarize the quadratic, CI-like and linear approximations to polarizabilities. In the following we will consider all three approximations numerically.

III. ANALYSIS OF THE EOM-CC LINEAR APPROXIMATION TO POLARIZABILITIES

The difference between the CI-like and linear approximation to the polarizability can succinctly be put as

$$\begin{aligned} \alpha_{Aa}(\omega)^{\text{CI-like}} &= \alpha_{Aa}(\omega)^{\text{Linear}} + (\langle 0 | \bar{\mu}_A | 0 \rangle \\ &\quad - \langle 0 | (1 + \Lambda) \bar{\mu}_A | 0 \rangle) \langle 0 | (1 + \Lambda) \cdot T_a(\omega) | 0 \rangle \\ &\quad + (\langle 0 | \bar{\mu}_a | 0 \rangle - \langle 0 | (1 + \Lambda) \bar{\mu}_a | 0 \rangle) \langle 0 | (1 + \Lambda) \\ &\quad \cdot T_A(-\omega) | 0 \rangle. \end{aligned} \quad (53)$$

Therefore, in general, if the dipole moment of the reference determinant and the correlated CC dipole moment are similar, there is very little difference between the linear and CI-like approximations. For very large systems there is a problem with the CI-like approximation, however, because the term involving the perturbed amplitudes can grow indefinitely. For larger systems, the linear approximation, therefore, offers distinct advantages over the CI-like approximation.³⁹ Most of our calculations are limited to small to medium sized systems, and the difference between the linear and CI-like approximation due to improper scaling of the CI-like approximation is usually negligible.

The other limiting case occurs when there is a large difference between the correlated and Hartree–Fock dipole moments. As an example, we consider the HF molecule at three internuclear distances $R_0 = 1.7328, 3.0$ and 10.0 a.u. At the RHF level the system incorrectly separates into $H^+ + F^-$ fragments, and, correspondingly, carries a large dipole moment. The CCSD calculation brings this back to the proper ground state, separating into neutral fragments, $H + F$ which in the limit does not have a dipole moment. This is illustrated in Table I, where we list the dipole moments for the three distances considered. In Table I we also include the t_1 CCSD amplitudes. These amplitudes are very large at larger separation, indicating again that the Hartree–Fock reference state

TABLE I. Dipole moments of the HF molecule.

$R_{\text{H-F}}$ (a.u.)	μ (SCF)	μ (CCSD)	t_1 coefficients
1.7328(R_e)	0.756 28	0.706 55	0.021
3.90	1.786 78	0.584 05	0.182
10.0	4.035 77	−0.072 91	0.396

is not a good description of the true ground state. If we subsequently calculate the static polarizabilities, we obtain the results presented in Table II. It is obvious that the CI-like and quadratic results agree quite well at all distances, but the linear version does not follow this pattern, and is in fact erroneous. Diagrammatic analysis shows that in the linear approximation, so-called EPV terms are neglected, and the present pathological example highlights these contributions. The situation is similar to the correlation energy. For two-electron systems, CCSD and CISD are exact, and both can be said to include EPV terms. On the other hand, linearized CCSD does not include such contributions, but unlike CISD, it is rigorously size extensive. However, it is not exact for two-electron systems. In fact LCC(S)D usually overshoots the correlation energy. The situation for second-order properties is a little different, because the extra (EPV-related) term in the CI-like approximation is usually very small.

We have also included the fully linked linear' results. Compared to linear, these results deviate further from the more correct quadratic results for larger separations. This can be understood because the disconnected contribution to Λ is quite appreciable (it follows the pattern for t_1^2), and in the linear' approximation we neglect such contributions from Λ , even though the *disconnected* contributions in Λ mainly give rise to *connected* contributions to the polarizability. In this context the extended coupled cluster method (for analysis see Ref. 45), which treats both the right- and left-hand ground state in exponential fashion, is most satisfactory.

We conclude that in the single molecule calculations that are of practical interest to us, the CI-like approximation does not suffer significantly from the size-extensivity error. Due to the inclusion of EPV terms, we actually expect it to be a little more accurate than the extensive linear approximation for some cases of interest. In all of the examples considered in this paper (except the above pathological example), the CI-like and linear approximation yield identical results up to the figures quoted in this paper. This is true exactly if molecules do not have a dipole moment due to symmetry.

Let us emphasize finally that the EOM quadratic model as the derivative is formally most satisfactory, but it loses the convenient propagator form and can become expensive computationally. This is particularly true if we apply partitioning

TABLE II. α_{zz} component of the static polarizability for the HF molecule.

$R_{\text{H-F}}$ (a.u.)	CI-like	Linear	Linear'	Quadratic
1.7328(R_e)	6.568	6.570	6.590	6.498
3.90	28.49	31.38	31.63	28.48
10.0	8.461	9.922	11.21	8.410

techniques to the EOM scheme.^{48–50} We know this is a valid approach to polarizabilities as well as NMR spin–spin coupling constants,⁵⁰ and in the partitioned model we definitely did not want to use the quadratic model, since it would forfeit all time savings obtained by the partitioning.

IV. COMPUTATIONAL DETAILS

In the following we wish to make a survey of several molecules in a consistent basis, rather than the ultimate converged result for one example. Hence, we use experimental geometries and Sadlej's polarizability basis, POL1 (Refs. 40 and 41) which consist of a (14s,10p,4d)/[7s,5p,2d] contraction for S, a (10s,6p,4d)/[5s,3p,2d] contraction for C, N, and O, and a (6s,4p)/[3s,2p] contraction for hydrogen. For trans-butadiene, to be consistent with prior work,^{51,52} we

have used the standard 6-31G basis set augmented by two diffuse *p* and *d* shells with the same exponent $\zeta_p = \zeta_d = 0.05$, which has been previously shown to combine small size with good accuracy for this molecule. Cartesian Gaussian basis functions have been used in all the calculations. All the results reported were obtained by using the ACES II program system.⁵³

The dipole polarizability is a diagonal second-rank tensor. For any linear molecule, two of these three components are identical due to symmetry. The two unique components are commonly referred to as the perpendicular α_{\perp} and parallel α_{\parallel} components with respect to the principal rotational axis. The average polarizability $\langle\alpha\rangle$ and the polarizability anisotropy $\Delta\alpha$ are the quantities most commonly determined experimentally.⁵⁴ They are defined as

$$\langle\alpha\rangle = \frac{\alpha(xx) + \alpha(yy) + \alpha(zz)}{3},$$

$$\Delta\alpha = \frac{[(\alpha(xx) - \alpha(yy))^2 + (\alpha(xx) - \alpha(zz))^2 + (\alpha(yy) - \alpha(zz))^2]^{1/2}}{\sqrt{2}},$$
(54)

which reduces to the simple expressions for molecules possessing a threefold or higher rotation axis (e.g., a linear molecule)

$$\langle\alpha\rangle = \frac{2\alpha_{\perp} + \alpha_{\parallel}}{3},$$
(55)

$$\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp}).$$

All the molecules considered in this study are linear, and hence we report the average polarizability and the polarizability anisotropy (henceforth referred to as $\langle\alpha\rangle$ and $\Delta\alpha$, respectively).

The C_6 dispersion coefficients are calculated from polarizabilities evaluated at selected imaginary frequencies $i\alpha$ using

$$C_6 = \frac{\pi}{3} \int_{-1}^1 f(t) dt,$$
(56)

and Gauss–Legendre quadrature where the function $f(t)$ is defined as

$$f(t) = \frac{2\omega_0}{(1+t)^2} \alpha \left(i\omega_0 \left[\frac{1-t}{1+t} \right] \right)$$
(57)

by means of the substitution

$$\omega = \omega_0 \left[\frac{1-t}{1+t} \right].$$
(58)

ω_0 has been chosen to be 0.1 a.u. as in Amos *et al.*⁵⁵

V. RESULTS AND DISCUSSION

A. Nitrogen, carbon monoxide, and acetylene

In Tables III–V we present the calculated dipole polarizabilities of the N₂, CO, and C₂H₂ molecules at several different frequencies along with the corresponding experimental results. The “CCSD” results are obtained by the finite-field method as the difference of the analytically computed dipole moment³² with orbital relaxation, and are limited to the static values. The TDHF values are from the analytical program of Sekino and Bartlett.⁵⁶ For N₂ and CO we have also included second-order polarization propagator approximation (SOPPA) results,²⁴ while for N₂, there are MC-TDHF results. Both the latter are in different basis sets from the CC results but agree exceptionally well with the EOM-CC results.

As we can see from Tables III–V, the electron correlation effects in general are fairly minor for these molecules; the TDHF and correlated dispersion for the isotropic component of the polarizability agree fairly well for all methods. However, the most notable exception is the dispersion for $\Delta\alpha(\omega)$ of the CO molecule, which is negative (but very small) at the TDHF level, and positive (but small) at the correlated level. This is likely to be related to the well-known sensitivity of the (small) dipole moment of CO, which changes sign upon inclusion of correlation. In the case of acetylene, the agreement is less satisfactory, even for the isotropic parts, while also the discrepancy between TDHF, SOPPA, and the EOM models is more pronounced.

Orbital relaxation effects are very minor, as follows from the comparison between finite-field-CCSD and the

TABLE III. Dynamic polarizabilities of the N₂ molecule.^a

ω (a.u.)	TDHF ^b	SOPPA ^c	MCTDHF ^d	CCSD ^b	EOM-CCSD ^b		exp.
					CI-like	Quadratic	
0.0000	11.42	11.29	11.61	11.61	$\langle\alpha(0)\rangle$		
					11.75	11.60	11.76 ^e
0.0720	0.15	0.15	0.15		$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
					0.15	0.15	0.16 ^f
0.0886	0.23	0.23	...		0.23	0.23	0.25 ^f
0.0934	0.25	0.26	0.26		0.26	0.24	0.27 ^f
0.0995	0.29	0.30	...		0.30	0.29	0.31 ^f
0.0000	5.37	4.07	4.36	4.83	$\Delta\alpha(0)$		
					4.92	4.79	4.45 ^g
0.0720	0.11	0.09			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
					0.08	0.07	0.22 ^h
0.0886	0.17	0.13			0.12	0.11	0.37 ^g
0.0934	0.19	0.14			0.14	0.13	0.40 ^g
0.0995	0.22	0.16			0.16	0.15	0.44 ^g

^aAt the equilibrium experimental bond length $r(NN)=2.074$ a.u. The $\langle\epsilon\rangle$ denotes the mean absolute deviation from experiment. This applies in all the following tables.

^bThe present work.

^cOddershede and Svendsen, Ref. 24.

^dLuo and Jørgensen, Ref. 70.

^eExtrapolated from Ref. 67.

^fReference 67.

^gG. R. Alms *et al.*, Ref. 68.

^hBridge and Buckingham, Ref. 69.

EOM-CC quadratic model for all three molecules. It is well known that CCSD shows remarkable insensitivity to orbital choice,^{37,57} but the EOM-CCSD (or CCSD linear response) will not necessarily be as insensitive. Here, however, the ground state molecular orbital relaxation effects are very small. Finally, the static, absolute values for the CI-like and quadratic EOM-CC models agree quite nicely. Inclusion of correlation improves the agreement with experiment, but TDHF results are already pretty good.

TABLE IV. Dynamic polarizabilities of the CO molecule.^a

ω (a.u.)	TDHF ^b	SOPPA ^c	CCSD ^b	EOM-CCSD ^b		exp.
				CI-like	Quadratic	
.0000	12.23	12.45	12.95	$\langle\alpha(0)\rangle$		
				13.28	13.07	13.08 ^d
.0720	0.22	0.24		$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
				0.27	0.25	0.27 ^e
.0886	0.34	0.37		0.41	0.39	0.41 ^e
.0934	0.38	0.41		0.46	0.43	0.47 ^e
.0995	0.44	0.47		0.52	0.50	0.66 ^e
.0000	3.37	4.45	3.97	$\Delta\alpha(0)$		
				4.39	4.17	3.59 ^f
.0720	-0.01	0.07		$\Delta\alpha(\omega) - \Delta\alpha(0)$		
				0.03	0.02	...
.0886	-0.01	0.10		0.03	0.03	...
.0934	-0.02	0.11		0.03	0.04	...
.0995	-0.02	0.12		0.04	0.04	...

^aAt the experimental equilibrium bond length $R(\text{CO})=2.132$ a.u.

^bPresent work.

^cOddershede and Svendsen, Ref. 24.

^dExtrapolated from Ref. 67.

^eReference 67.

^fBridge and Buckingham, Ref. 69.

B. Chlorine

The calculated dipole polarizabilities of the Cl₂ molecule for several different frequencies and the corresponding experimental values are given in Table VI.

Here there is a substantial difference between the correlated dispersion and that given by TDHF. The EOM CI-like and quadratic model dispersion curves agree very well as before and there is only a minor effect from orbital relaxation. However, correlation effects for Cl₂ are more signifi-

TABLE V. Dynamic polarizabilities of the C₂H₂ molecule.^a

ω (a.u.)	TDHF ^b	CCSD ^b	EOM-CCSD ^b		exp.
			CI-like	Quadratic	
.0000	23.11	22.17	$\langle\alpha(0)\rangle$		
			22.60	22.25	22.67 ^c
.0720	0.65		$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
			0.58	0.57	0.80 ^d
.0886	1.00		0.90	0.89	1.01 ^d
.0934	1.12		1.01	0.99	1.28 ^d
.0995	1.28		1.15	1.13	1.41 ^d
.0000	12.52	12.30	$\Delta\alpha(0)$		
			12.97	12.50	11.84 ^c
.0720	0.34		$\Delta\alpha(\omega) - \Delta\alpha(0)$		
			0.31	0.30	0.54 ^d
.0886	0.52		0.48	0.46	0.74 ^d
.0934	0.58		0.53	0.51	0.88 ^d
.0995	0.66		0.61	0.58	1.08 ^d

^aThe equilibrium experimental bond length $r(\text{CH})=2.004$ and $r(\text{CC})=2.274$ a.u.

^bPresent work.

^cExtrapolated from G. R. Alms *et al.*, Ref. 68.

^dG. R. Alms *et al.*, Ref. 68.

TABLE VI. Dynamic polarizabilities of the Cl₂ molecule.^a

ω (a.u.)	TDHF ^b	SOPPA ^c	CCSD ^b	EOM-CCSD ^b		exp.
				CI-like	Quadratic	
.0000	27.38	24.42	30.48	$\langle\alpha(0)\rangle$		
				31.32	30.86	30.35 ^d
				$\langle\alpha(\omega)\rangle-\langle\alpha(0)\rangle$		
				0.66	0.66	0.72 ^e
				1.04	1.03	1.11 ^e
.0720	0.84	0.47		0.66	0.66	0.72 ^e
.0886	1.31	0.74		1.04	1.03	1.11 ^e
.0934	1.48	0.84		1.18	1.15	1.23 ^e
.0995	1.70	0.98		1.37	1.32	1.41 ^d
.0000	15.22	24.44	16.79	$\Delta\alpha(0)$		
				17.46	16.94	17.56 ^f
				$\Delta\alpha(\omega)-\Delta\alpha(0)$		
				0.58	0.56	...
				0.91	0.85	...
.0720	0.95	0.86		0.58	0.56	...
.0886	1.50	1.29		0.91	0.85	...
.0934	1.69	1.43		1.04	0.95	...
.0995	1.96	1.60		1.20	1.07	...

^aAt the equilibrium experimental bond length $r(\text{ClCl})=3.755$ a.u.

^bPresent work.

^cOddershede and Svendsen, Ref. 24.

^dExtrapolated from Ref. 67.

^eReference 67.

^fBridge and Buckingham, Ref. 69.

cant. For example, the correlation contribution to the static polarizability is 3.10 a.u. [10% of the total correlated (finite-field-CCSD) result] for $\langle\alpha\rangle$ and 1.57 a.u. (0.94% of the total correlated result) for $\Delta\alpha$. The EOM-CCSD CI-like results overestimate the electron correlation effects by almost 1 a.u. compared to experiment, whereas the quadratic results lower the deviation to about 0.5 a.u. The role of correlation (and/or basis set) effects is further demonstrated by the rather poor agreement of SOPPA results with the experimental values.

C. Carbon dioxide, carbon oxysulfide, and carbon disulfide

In Tables VII–IX we present calculated $\langle\alpha\rangle$ and $\Delta\alpha$ values for the CO₂, OCS, and CS₂ molecules for several different frequencies. The results obtained by the TDHF method and experiment are also given for comparison.

It is evident from Tables VII–IX that orbital relaxation effects are very important for these molecules, and this importance increases with the number of sulfurs. The orbital relaxation effect (EOM quadratic – CCSD) for the isotropic component increases as 0.6, 2.3, and 4.1 a.u. in the series CO₂, OCS, CS₂, while for the anisotropic component this effect is enhanced from 1.0, 2.5, to 10.5 a.u. (!). Invariably, inclusion of orbital relaxation effects brings the results closer to experiment. Comparing the EOM CI-like and EOM quadratic models we find that the CI-like version overshoots the experimental results by up to 15 a.u. for the anisotropic component of CS₂. It is clear that for these molecules, derivative techniques will work better than perturbation based methods, but most of the error corresponds to orbital relaxation, which is not included in either method. Interestingly, for $\langle\alpha(0)\rangle$ the TDHF model performs better than the correlated EOM methods for CS₂. Relaxation effects are, of course, precisely what is accounted for in TDHF. This, together with some favor-

TABLE VII. Dynamic polarizabilities of the CO₂ molecule.^a

ω (a.u.)	TDHF ^b	CCSD ^b	EOM-CCSD ^b		exp.
			CI-like	Quadratic	
.0000	15.84	17.44	$\langle\alpha(0)\rangle$		
			18.47	18.00	17.52 ^c
			$\langle\alpha(\omega)\rangle-\langle\alpha(0)\rangle$		
			0.29	0.27	0.27 ^d
			0.44	0.42	0.34 ^e
.0720	0.20		0.29	0.27	0.27 ^d
.0886	0.30		0.44	0.42	0.34 ^e
.0934	0.33		0.49	0.46	0.47 ^e
.0995	0.38		0.56	0.53	0.50 ^e
.0000	12.08	14.43	$\Delta\alpha(0)$		
			16.32	15.40	13.73 ^c
			$\Delta\alpha(\omega)-\Delta\alpha(0)$		
			0.41	0.40	0.54 ^d
			0.63	0.60	0.68 ^e
.0720	0.26		0.41	0.40	0.54 ^d
.0886	0.39		0.63	0.60	0.68 ^e
.0934	0.44		0.71	0.68	0.88 ^e
.0995	0.50		0.80	0.77	0.95 ^e

^aThe experimental equilibrium bond length $r(\text{CO})=2.195$ a.u.

^bPresent work.

^cG. R. Alms *et al.*, Ref. 68.

^dExtrapolated from G. R. Alms *et al.*, Ref. 68.

able, cancellation of errors, is likely to account for the relative accuracy of the TDHF results. Of course, we also assume that the reference experimental values are reliable, even though in many cases these are rather old results.

Dispersion effects in EOM-CC, on the other hand, are in reasonable agreement with experiment and greatly improve upon the Hartree–Fock dispersion curves (see Figs. 1 and 2). We note that the EOM CI-like model performs a little better than the EOM quadratic model compared to experiment, especially for higher frequencies.

From these comparisons, we conclude that if orbital relaxation effects appear to be important, they should be included. The potential importance of orbital relaxation in time-dependent properties is a tricky question. It is certainly

TABLE VIII. Dynamic polarizabilities of the OCS molecule.^a

ω (a.u.)	TDHF ^b	CCSD ^b	EOM-CCSD ^b		exp.
			CI-like	Quadratic	
.0000	32.99	34.69	$\langle\alpha(0)\rangle$		
			36.96	35.71	34.35 ^c
			$\langle\alpha(\omega)\rangle-\langle\alpha(0)\rangle$		
			1.13	1.09	0.67 ^d
			1.70	1.65	1.01 ^d
.0720	0.90		1.13	1.09	0.67 ^d
.0886	1.33		1.70	1.65	1.01 ^d
.0934	1.56		1.91	1.86	1.21 ^d
.0995	1.79		2.20	2.17	1.42 ^d
.0000	24.01	27.55	$\Delta\alpha(0)$		
			32.50	29.97	26.25 ^c
			$\Delta\alpha(\omega)-\Delta\alpha(0)$		
			1.59	1.48	1.62 ^d
			2.42	2.29	2.57 ^d
.0720	1.06		1.59	1.48	1.62 ^d
.0886	1.57		2.42	2.29	2.57 ^d
.0934	1.85		2.78	2.57	2.83 ^d
.0995	2.12		3.19	2.97	3.11 ^d

^aThe experimental bond length for $R(\text{OC})=2.191$ and $R(\text{CS})=2.947$ a.u.

^bPresent work.

^cExtrapolated from G. R. Alms *et al.*, Ref. 68.

^dG. R. Alms *et al.*, Ref. 68.

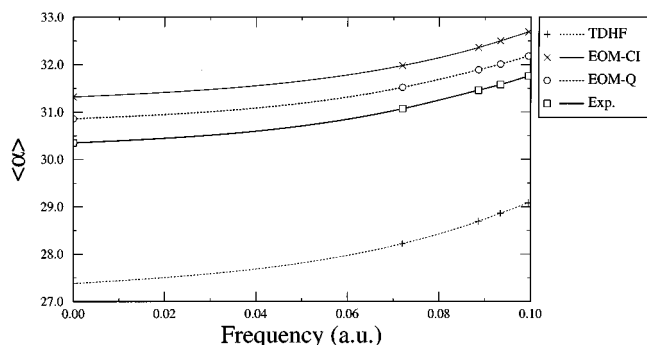
TABLE IX. Dynamic polarizabilities of the CS₂ molecule.^a

ω (a.u.)	TDHF ^b	CCSD ^b	EOM-CCSD ^b		exp.
			CI-like	Quadratic	
.0000	55.18	55.03	$\langle\alpha(0)\rangle$		
			62.10	59.15	55.40 ^c
			$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
.0720	2.50		2.84	2.89	3.24 ^d
.0886	3.93		4.67	4.62	5.27 ^d
.0934	4.42		6.49	5.25	5.94 ^d
.0995	5.10		7.47	6.05	6.82 ^d
.0000	56.58	56.50	$\Delta\alpha(0)$		
			73.74	66.51	58.71 ^c
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	5.03		6.27	6.24	6.41 ^d
.0886	7.97		10.34	10.01	10.66 ^d
.0934	9.00		12.38	11.33	12.28 ^d
.0995	10.44		14.41	13.19	14.31 ^d

^aThe equilibrium experimental bond length for $R(\text{CS})=2.944$ a.u.^bPresent work.^cExtrapolated from G. R. Alms *et al.*, Ref. 68.^dG. R. Alms *et al.*, Ref. 68.

possible to include orbital relaxation by building the correlated calculation on the underlying TDHF solution, just as coupled perturbed Hartree–Fock (CPHF) solutions are essential in analytical gradients and Hessian evaluations for the total energy. In that case orbital relaxation can never be neglected without invalidating the exactness of the critical points. The CCSD and higher methods, though, build in the vast majority of such relaxation effects via $|\phi'\rangle = e^{T_1}|\phi\rangle$,^{32,58} and such flexibility is usually sufficient for other kinds of properties.³⁷ However, when orbital relaxation is as large as found here for CS₂, we have to reconsider whether they should be included in highly accurate calculations. However, to incorporate TDHF relaxation means also introducing artifactual TDHF (RPA) excitation energies (part of the propagator) into the calculation, which is unsatisfactory. Another obvious possibility is to include effects from connected triple and higher excitation operators in the calculation. Until the full CI is reached, though, there are still residual orbital relaxation effects. Here, apparently that effect is numerically significant.

Interestingly, the dispersion is, in all cases considered, well described by the CI-like model in EOM-CCSD. If we

FIG. 1. CO₂ mean polarizabilities.TABLE X. Dynamic polarizabilities of the C₄H₆ molecule.^a

ω (a.u.)	TDHF ^b	CCSD ^b	EOM-CCSD ^b		exp.
			CI-like	Quadratic	
.0000	52.04	48.79	$\langle\alpha(0)\rangle$		
			49.78	49.16	58.31
			$\langle\alpha(\omega)\rangle - \langle\alpha(0)\rangle$		
.0720	2.58		1.87	1.16	
.0886	4.10		2.92	1.97	
.0934	4.63		3.32	2.26	
.0995	5.37		3.79	2.63	
.0000	50.29	35.24	$\Delta\alpha(0)$		
			36.26	35.51	
			$\Delta\alpha(\omega) - \Delta\alpha(0)$		
.0720	5.01		2.60	1.18	
.0886	8.06		4.13	2.20	
.0934	9.14		4.66	2.55	
.0995	10.67		5.41	3.02	

^aThe experimental equilibrium bond length $r(\text{C}_1-\text{C}_2)=2.508$, $r(\text{C}_2-\text{C}_3)=2.768$, $r(\text{C}_1-\text{H}_1)=2.028$, $r(\text{C}_2-\text{H}_3)=2.035$ a.u.^bPresent work.^cIn *Handbook of Chemistry and Physics*, 66th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, 1985), pp. E-70.

combine this with a finite-field CCSD value for the static component (or full second-order analytical CCSD derivative), we may expect to obtain reliable results, even when orbital relaxation effects are important.

D. Trans-butadiene

Table X shows the results of the dynamic polarizability calculation for the trans-butadiene molecule. Polyenes, of which trans-butadiene is a prototypical example, are of substantial interest in NLO materials.⁵⁹ One can notice that TDHF values are much larger than the corresponding EOM values, due to the overestimation of the xx and yy components of α . The dispersion behavior is also very different: the percentage dispersion at $\omega=0.0995$ a.u. is 10.3% at the TDHF level, 7.61% for the EOM CI-like method, and 5.35% for the quadratic scheme. The quadratic correction accounts for up to 2%–3% of the total correlation correction and also slightly changes the dispersion behavior: for the static case the difference between the CI-like and quadratic anisotropy is only 0.75, whereas for the largest computed frequency it amounts to 3.1 a.u. This result suggests that the dispersion of

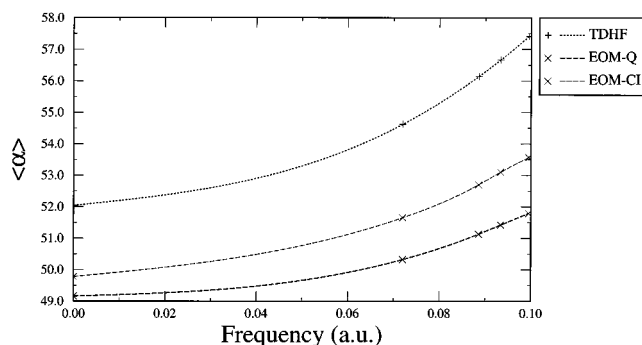
FIG. 2. CS₂ mean polarizabilities.

TABLE XI. C_6 dispersion coefficients for homonuclear interaction.

	TDHF ^a	EOM-CCSD (CI-like) ^b	EOM-CCSD (Quadratic) ^b	exp.
N ₂	71.46	73.63	71.84	73.40 ^c
Cl ₂	...	416.3	405.2	...
C ₂ H ₂	196.6	204.3	196.9	231.4 ^d
CO	63.29	83.51	80.64	81.40 ^c
CO ₂	123.1	173.6	166.4	158.7 ^e
SCO	368.5	453.1	481.4	402.2 ^e
CS ₂	826.0	1182	1079	991.3 ^e

^aM. A. Spackman, Ref. 64.^bPresent work.^cMargoliash and Meath, Ref. 71, and M. A. Spackman, Ref. 64.^dStarkschall and Gordon, Ref. 72.^eFowler *et al.*, Ref. 73.

the dipole polarizability in conjugated hydrocarbons is sensitive to the correlation level. The fact that correlated results have been found to be further from experiment than TDHF^{51,52} has led to the argument⁶⁰ that for butadiene, and indeed linear polyenes in general, TDHF gives a better description of the hyperpolarizabilities than correlated methods. If so, the ultimate correlated methods must regain the TDHF results. However, it is difficult to see how the correlation effects can be neutralized. The extension of the atomic basis set and inclusion of vibrational effects must be considered, as well.

E. Long-range London dispersion coefficients

Table XI lists the C_6 coefficients for the collection of atoms and molecules considered in this study. We use the same procedure previously discussed.⁶¹ The largest errors are for CS₂ and OCS, consistent with our observation of the quality of the calculated polarizability results of the two respective molecules. Inclusion of the quadratic contribution improves the agreement of the calculated results with experiment, and inclusion of orbital relaxation would presumably lead to still further improvements (see previous section).

There are several other correlated theoretical studies of C_6 coefficients of small molecules in the literature,^{61–63} the former using EOM-CCSD. However, the only previous theoretical results of C_6 coefficients for CS₂ and COS are due to Spackman. The first column of Table XI contains C_6 coefficients calculated by Spackman⁶⁴ at the TDHF level using a 6-31G basis set with added polarization functions. There are no previous theoretical or experimental C_6 coefficients for the Cl₂ molecule available in the literature.

VI. CONCLUSIONS

The main focus of the present investigation is to study the variation of the molecular polarizability with frequency (both real and imaginary) and to calculate the dispersion coefficients (C_6) for a series of molecules at a consistent level. For this purpose, we use the recently developed EOM-CCSD CI-like, linear and quadratic approximations to calculate frequency-dependent polarizabilities of several selected small molecules. The EOM-CCSD CI-like approximation,

when combined with Sadlej polarized basis sets, was shown previously to perform well for molecular dynamic polarizabilities.¹⁶ In this paper we also consider orbital relaxation effects on calculated static polarizabilities through finite difference CCSD calculations.

In general, the difference between the EOM CI-like, linear, and quadratic models is found to be minor, both for the net result and the dispersion. Also the results agree reasonably well with experiment. An important exception is the CS₂ molecule, and to a lesser extent OCS. In these cases we found orbital relaxation effects on the calculated static polarizabilities to be very important, implying significant potential effects on the dynamic polarizability. Even in these cases, however, the frequency dependence of the polarizabilities is well described at the EOM-CCSD level. If orbital relaxation is important, a hybrid method like a combination of EOM-CCSD for dispersion and finite-field CCSD (or analytical CCSD second derivatives) for the static component could offer a pragmatic approach.

To better include orbital relaxation, in particular also the contribution to dispersion, the EOM-CCSD model can be extended with an approximate treatment for triples, like EOM-CCSDT-1 or EOM-CCSDT-3.⁶⁵ Such triple contributions have been shown to introduce the most important remaining orbital relaxation terms.³⁷ The numerical effect of triple excitations (in cases in which relaxation effects are not considered very important) on polarizabilities can be assessed from other results,^{32,66} with the general conclusion that it increases the magnitude of the polarizability, but not necessarily the agreement with experiment.

Dispersion at the TDHF level is often a poor representation of the correlated EOM-CC dynamic polarizability in the same basis set. Dispersion at the EOM-CCSD level agrees significantly better with the experimental measurements.

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