

Second-Order Polarization Propagator Calculations of Dynamic Dipole Polarizabilities and C_6 Coefficients

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Abstract

The frequency-dependent dipole polarizability, $\alpha(E)$, is calculated using the second-order polarization propagator approximation (SOPPA). We have shown how to express $\alpha(E)$ as a function of E^2 and thus obtained a form of $\alpha(E)$ that can be used to compute C_6 -coefficients without invoking complex arithmetic. For He we find that SOPPA recovers a large fraction of the correlation contribution for all frequencies, whereas for H_2 where the correlation contributions are much smaller and also basis set-dependent, we find a less definite trend of SOPPA relative to RPA.

1. Introduction

The sum-over-states or Kramers–Heisenberg expression for the ground-state, energy (E)-dependent dipole polarizability tensor is

$$\alpha^L(E) = 2 \sum_n' \frac{\langle 0|\mathbf{r}|n\rangle \langle n|\mathbf{r}|0\rangle}{E_{n0}^2 - E^2} E_{n0} \quad (1)$$

in the dipole length formulation. Here $|0\rangle$ is the ground state and the sum extends over all excited states $|n\rangle$, different from $|0\rangle$. Thus,

$$E_{n0} = E_n - E_0 \quad (2)$$

are the excitation energies of the system. It is only feasible to compute all excitation energies and transition moments either in simple models [1] or for small systems [2] and thus to obtain $\alpha^L(E)$ directly from Eq. (1).

The most common approach to the calculation of polarizabilities consists of a direct evaluation of $\alpha(E)$ as the response of the system to an external electric field. This is the basis for the finite-field method [3] in which $\alpha(E)$ is obtained either as the linear response (the induced dipole moment) or as the quadratic response (of the total energy) to a finite, but small external field [4]. In practice, however, the finite-field method is limited to the calculation of static polarizabilities, and for dynamic polarizabilities, other methods will have to be used [5–10].

Among these methods are the random-phase-like approximations (RPA) where we find an explicit analytic expression for $\alpha(E)$ in terms of one- and two-electron integrals in the SCF representation [1, 8, 9, 11] by formally solving for the response function, i.e., the RPA-like methods are the analytic counterparts to the numerical finite-field method. In the RPA method itself, the unperturbed state is the self-consistent field (SCF) ground state of the system, and for static polarizabilities, RPA is identical to the coupled Hartree-Fock method. The random-phase approximation is the first-order polarization propagator approximation [12]. Some years ago we derived a method (SOPPA) that is the extension of RPA consistent through second order in the electronic fluctuation potential [13]. Since then, this method has been shown to give considerable improvements over RPA both for spectra and second-order electric and magnetic properties of molecules. This is to be expected for triplet response properties, but also for singlet properties, like the paramagnetic spin-orbit contribution to indirect nuclear spin-spin coupling constants [14], we do sometimes find rather large differences between SOPPA and RPA results.

The purpose of the present communication is twofold. First, we wish to investigate the accuracy of the second-order polarization propagator method for systems where the full CI results in large basis sets [10], as well as nearly exact results [15], are known for frequency-dependent second-order properties. Thus, we have calculated the dynamic dipole polarizability and C_6 coefficients for He and H₂. Second, we derive expressions for the polarizabilities in SOPPA that are functions of E^2 (and not just E), which, in contrast to our earlier formulation [13], is very convenient when we calculate C_6 coefficients via the Casimir-Polder formula [16]:

$$C_6 = -\frac{3}{\pi} \int_0^\infty \alpha^a(iE) \alpha^b(iE) dE, \quad (3)$$

where α^a and α^b are the invariants of the polarizability tensors for the two species a and b . When $\alpha(E)$ is a function of E^2 , we do not need to use complex arithmetic in the calculation of C_6 .

2. Theory

Realizing that we may write Eq. (1) as

$$\alpha^L(E) = -Re \lim_{\eta \rightarrow 0^+} \sum_n' \left\{ \frac{\langle 0|\mathbf{r}|n\rangle \langle n|\mathbf{r}|0\rangle}{E - E_{n0} + i\eta} - \frac{\langle 0|\mathbf{r}|n\rangle \langle n|\mathbf{r}|0\rangle}{E + E_{n0} + i\eta} \right\}, \quad (4)$$

we see that

$$\alpha^L(E) = -Re \langle \langle \mathbf{r}, \mathbf{r} \rangle \rangle_E, \quad (5)$$

where $\langle \langle \mathbf{r}, \mathbf{r} \rangle \rangle_E$, defined by Eqs. (4) and (5), is the energy representation of the retarded polarization propagator [17] or linear response function [18] for a perturbing electric field. Thus, except for a sign change, the dynamic polarizability tensor is the $\langle \langle \mathbf{r}; \mathbf{r} \rangle \rangle_E$ polarization propagator. We have shown [13] that, consistent through second order in the fluctuation potential (Hamiltonian minus the Fock

potential), this propagator can be written as

$$\langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_E = \{\mathbf{T}(\mathbf{r}, E), -\mathbf{T}(\mathbf{r}, -E)\} \mathbf{P}^{-1}(E) \begin{Bmatrix} \tilde{\mathbf{T}}(\mathbf{r}, E) \\ -\tilde{\mathbf{T}}(\mathbf{r}, -E) \end{Bmatrix} + \mathbf{W}_4(E), \quad (6)$$

where

$$\mathbf{P}(E) = \begin{pmatrix} E\mathbf{S} - \mathbf{A} - \tilde{\mathbf{C}}(E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} & -\mathbf{B} \\ -\mathbf{B} & -E\mathbf{S} - \mathbf{A} - \tilde{\mathbf{C}}(-E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} \end{pmatrix}, \quad (7)$$

$$\mathbf{T}(\mathbf{r}, E) = (\mathbf{r}|\mathbf{q}^+) + (\mathbf{r}|\mathbf{q}^+\mathbf{q}^+)(E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C}, \quad (8)$$

and

$$\mathbf{W}_4(E) = (\mathbf{r}|\mathbf{q}^+\mathbf{q}^+)((E\mathbf{1} - \mathbf{D})^{-1} + (-E\mathbf{1} - \mathbf{D})^{-1})(\mathbf{q}^+\mathbf{q}^+|\mathbf{r}). \quad (9)$$

The matrices \mathbf{A} , \mathbf{B} , \mathbf{C} , \mathbf{D} , and \mathbf{S} are weighted sums of two-electron integrals (RPA) or products of two-electron integrals (SOPPA). A tilde symbolizes the transposed matrix. The parentheses indicate the superoperator binary product [19]:

$$(\mathbf{r}|\mathbf{q}^+) = \langle 0|[\mathbf{r}^+, \mathbf{q}^+]|0\rangle, \quad (10)$$

where $\mathbf{q}^+ = \{a_m^+ a_\alpha\}$ is the set of particle-hole excitation operators and $\mathbf{q}^+\mathbf{q}^+$ are the corresponding two-particle, two-hole ($2p - 2h$) excitation operators. The actual expressions for all the matrices in terms of SCF molecular two-electron integrals and orbital energies are given in appendix C of Ref. 17.

Expressions equivalent to Eq. (6) for the dynamic dipole polarizability in the mixed (\mathbf{r}, \mathbf{p}) representation [13]*:

$$\alpha^M(E) = -iE^{-1}\langle\langle \mathbf{p}; \mathbf{r} \rangle\rangle_E, \quad (11)$$

and in the dipole velocity representation*:

$$\alpha^V(E) = -E^{-2}\{i(\mathbf{r}|\mathbf{p}) - \langle\langle \mathbf{p}; \mathbf{p} \rangle\rangle_E\}, \quad (12)$$

may be derived from Eq. (4) by successive applications of the relation

$$[\mathbf{r}, H] = i\mathbf{p}, \quad (13)$$

where H is the Hamiltonian of the system. The $\langle\langle \mathbf{r}; \mathbf{p} \rangle\rangle_E$ and $\langle\langle \mathbf{p}; \mathbf{p} \rangle\rangle_E$ polarization propagators are determined from relations like Eq. (6) as well, the only changes being that $-\mathbf{T}(\mathbf{r}, -E)$ and $-\tilde{\mathbf{T}}(\mathbf{r}, -E)$ are replaced by $\mathbf{T}(\mathbf{p}, E)$ and $\tilde{\mathbf{T}}(\mathbf{p}, E)$ for the $\langle\langle \mathbf{p}; \mathbf{p} \rangle\rangle_E$ propagator, whereas for the $\langle\langle \mathbf{r}; \mathbf{p} \rangle\rangle_E$ propagator, only the sign on $\tilde{\mathbf{T}}$ is changed. In the mixed case, we also need to change the sign[†] on the last term in Eq. (9), that is, the inner matrix becomes $(E\mathbf{1} - \mathbf{D})^{-1} - (-E\mathbf{1} - \mathbf{D})^{-1}$.

We know from Eq. (1) that it is possible to express $\alpha^V(E)$ as a function of E^2 rather than E as it might appear from inspection of Eq. (6). This can be accom-

*There is a sign error in the expression for $\alpha^M(E)$ and a factor of i missing in the expression for $\alpha^V(E)$ in Eqs. (50) and (51) of Ref. 13.

[†]This sign change is missing in Eq. (52) of Ref. 13.

plished using

$$\frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (14)$$

Inserting the unit matrix as a factor on both sides of $\mathbf{P}(E)$ in Eq. (6), we find

$$\begin{aligned} \alpha^L(E) = -2 & \left\{ (-EQ'(-E\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C}, \mathbf{P}' - \mathbf{Q}'\mathbf{D}(-E\mathbf{1} + \mathbf{D}^2)^{-1}) \right. \\ & \times \begin{pmatrix} -\mathbf{A} - \mathbf{B} + \tilde{\mathbf{C}}\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} & E\mathbf{S} + E\tilde{\mathbf{C}}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \\ E\mathbf{S} + E\tilde{\mathbf{C}}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} & -\mathbf{A} + \mathbf{B} + \tilde{\mathbf{C}}\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \end{pmatrix}^{-1} \\ & \times \begin{pmatrix} -EQ'(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \\ \mathbf{P}' - \mathbf{Q}'\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \end{pmatrix} - \mathbf{Q}'\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\tilde{\mathbf{Q}}' \left. \right\}, \quad (15) \end{aligned}$$

where we have introduced the notation

$$\mathbf{P}' = (\mathbf{r}|\mathbf{q}^+) \quad (16)$$

$$\mathbf{Q}' = (\mathbf{r}|\mathbf{q}^+\mathbf{q}^+). \quad (17)$$

Partitioning [20] of the 2×2 inverse matrix in Eq. (15) gives us the final form of the polarizability tensors that are quadratic in E

$$\begin{aligned} \alpha^L(E) = -2 & \{ E^2 \widehat{\mathbf{Q}'\mathbf{C}} - (\mathbf{M}_1 \widehat{\mathbf{Q}'\mathbf{C}} - \mathbf{M}_2(\mathbf{P}' - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{C}})) \\ & - (\mathbf{P}' - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{C}})(E^2\mathbf{M}_3 \widehat{\mathbf{Q}'\mathbf{C}} - \mathbf{M}_4(\mathbf{P}' - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{C}})) \\ & - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{Q}'} \}, \quad (18) \end{aligned}$$

$$\begin{aligned} \alpha^M(E) = 2i & \{ (\mathbf{P}^p - \widehat{\mathbf{Q}^p\mathbf{D}\mathbf{C}})(\mathbf{M}_1 \widehat{\mathbf{Q}'\mathbf{C}} - \mathbf{M}_2(\mathbf{P}' - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{C}})) \\ & - \widehat{\mathbf{Q}^p\mathbf{C}}(E^2\mathbf{M}_3 \widehat{\mathbf{Q}'\mathbf{C}} - \mathbf{M}_4(\mathbf{P}' - \widehat{\mathbf{Q}'\mathbf{D}\mathbf{C}})) \\ & + \widehat{\mathbf{Q}^p\mathbf{C}^r} \}, \quad (19) \end{aligned}$$

$$\begin{aligned} \alpha^V(E) = -2 & \left\{ \frac{i}{E^2} \mathbf{P}^p \mathbf{P}^p + (\mathbf{P}^p - \widehat{\mathbf{Q}^p\mathbf{D}\mathbf{C}})(E^{-2}\mathbf{M}_1(\mathbf{P}^p - \widehat{\mathbf{Q}^p\mathbf{D}\mathbf{C}}) - \mathbf{M}_2 \widehat{\mathbf{Q}^p\mathbf{C}}) \right. \\ & \left. - \widehat{\mathbf{Q}^p\mathbf{C}}(\mathbf{M}_3(\mathbf{P}^p - \widehat{\mathbf{Q}^p\mathbf{D}\mathbf{C}}) - \mathbf{M}_4 \widehat{\mathbf{Q}^p\mathbf{C}}) - E^{-2} \widehat{\mathbf{Q}^p\mathbf{D}\mathbf{Q}^p} \right\}, \quad (20) \end{aligned}$$

where

$$\begin{aligned} \mathbf{M}_1 = & \{ -\mathbf{A} - \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}} - E^2(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}})(-\mathbf{A} + \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}})^{-1} \\ & \times (\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}}) \}^{-1} \quad (21) \end{aligned}$$

$$\begin{aligned} \mathbf{M}_2 = & \{ E^2(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}}) - (-\mathbf{A} + \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}})(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}})^{-1} \\ & \times (-\mathbf{A} - \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}}) \}^{-1} \quad (22) \end{aligned}$$

$$\begin{aligned} \mathbf{M}_3 = & \{ E^2(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}}) - (-\mathbf{A} - \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}})(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}})^{-1} \\ & \times (-\mathbf{A} + \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}}) \}^{-1} \quad (23) \end{aligned}$$

$$\begin{aligned} \mathbf{M}_4 = & \{ -\mathbf{A} + \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}} - E^2(\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}})(-\mathbf{A} - \mathbf{B} + \widehat{\mathbf{C}\mathbf{D}\mathbf{C}})^{-1} \\ & \times (\mathbf{S} + \widehat{\mathbf{C}\mathbf{C}}) \}^{-1} \quad (24) \end{aligned}$$

and where we have used the abbreviated symbols

$$\widehat{\mathbf{CC}} = \tilde{\mathbf{C}}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \quad (25)$$

$$\widehat{\mathbf{CDC}} = \tilde{\mathbf{C}}\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \quad (26)$$

$$\widehat{\mathbf{QC}} = \mathbf{Q}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \quad (27)$$

$$\widehat{\mathbf{QDC}} = \mathbf{Q}\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\mathbf{C} \quad (28)$$

$$\widehat{\mathbf{QQ}} = \mathbf{Q}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\tilde{\mathbf{Q}} \quad (29)$$

$$\widehat{\mathbf{QDQ}} = \mathbf{Q}\mathbf{D}(-E^2\mathbf{1} + \mathbf{D}^2)^{-1}\tilde{\mathbf{Q}}. \quad (30)$$

The matrices \mathbf{P}^p and \mathbf{Q}^p appearing in Eqs. (19) and (20) are defined as in Eqs. (16) and (17) with \mathbf{r} replaced by \mathbf{p} . Equations (19) and (20) are derived using the reformulation in Eq. (15) of the propagators defined in Eqs. (11) and (12), taking into account the sign change discussed after Eq. (13).

3. Applications

We have calculated the frequency-dependent polarizability for He and H_2 . For both systems, we have used the basis sets given by Jaszunski and Roos [10], and we can thus compare our results with their full CI calculation in the same basis sets. Both basis sets were uncontracted, consisting of [16s12p6d2f], i.e., 108 CGTOs, for He and of [9s6p3d], i.e., 90 CGTOs, for H_2 . This means that we have not excluded the s -function from the Cartesian d -GTO, nor have we excluded the p -function from the Cartesian f -GTO. The calculation of atomic integrals, the integral transformation, as well as the generation of the polarization propagator matrices were done using the MUNICH program system [21], whereas the frequency-dependent polarizabilities were computed using the new FRYDA program [22] that is part of the MUNICH program system. The ground SCF total energies are -2.861675 a.u. for He and -1.13360684 a.u. for H_2 at $R = 1.40$ a.u., which are 1.56 ppm [23] and 20.0 ppm [24] larger than the Hartree-Fock limits, respectively. Another check on the completeness of the basis set can be obtained by comparing the Thomas-Reiche-Kuhn (TRK) sum rule with the number of electrons in the system. We know that the TRK sum rule must be fulfilled exactly in RPA for a complete basis set [25]. We find that sum rule gives 2.0000 (length and mixed) for both He and H_2 at $R = 1.40$ a.u.

Several other basis sets were tested by Jaszunski and Roos [10], and they concluded that modifications of the present basis sets result in changes of the dipole polarizability by a small fraction of a percent. Hence, the comparison between our calculated dynamic polarizabilities and the full CI results would be expected to be basis-set independent and give a correct picture of the electronic correlation effects.

The results for $\alpha(E)$ of He are given in Table I and plotted in Figure 1. We have also included our previously [26] reported values for the dynamic polarizability of He, calculated with a basis set consisting of 48 Slater-type orbitals. The nearly exact agreement between the two RPA calculations substantiates the completeness of the basis set. In our previous calculation, we did not include the

TABLE I. The frequency-dependent polarizability $\alpha(E)$ of He (in atomic units).

E(a.u.)	RPA			SOPPA			
	Length		Mixed (this calc.)	Length		Mixed (this calc.)	Full ci ^b
	[26] ^a	This calc.		[26] ^a	This calc.		
0.0000	1.322	1.3222	1.3222	1.328	1.3641	1.3674	1.3835 ±0.00076
0.0500	1.325	1.3257	1.3257	1.332	1.3678	1.3712	1.3872 ±0.00077
0.1000	1.336	1.3363	1.3363	1.343	1.3792	1.3826	1.39898 ±0.00078
0.1500	1.354	1.3543	1.3543	1.361	1.3987	1.4022	1.41912 ±0.00080
0.2000	1.380	1.3806	1.3806	1.389	1.4272	1.4307	1.44851 ±0.00083
0.2500	1.416	1.4163	1.4163	1.426	1.4659	1.4695	1.48853 ±0.00087
0.3000	1.462	1.4630	1.4630	1.475	1.5167	1.5205	1.54119 ±0.00093
0.3500	1.522	1.5232	1.5232	1.538	1.5826	1.5866	1.60956 ±0.00100
0.4000	1.600	1.6008	1.6008	1.620	1.6679	1.6722	1.6983 ±0.0011
0.4500	1.701	1.7013	1.7014	1.727	1.7795	1.7840	1.8145 ±0.0013
0.5000	1.834	1.8342	1.8343	1.870	1.9284	1.9334	1.9705 ±0.0015
0.5500	2.015	2.0155	2.0155	2.068	2.1346	2.1402	2.1875 ±0.0018
0.6000	2.275	2.2759	2.2759	2.359	2.4375	2.4441	2.5091 ±0.0023
0.6500	2.683	2.6837	2.6837	2.834	2.9299	2.9380	3.0391 ±0.0034
0.7000	3.434	3.4345	3.4345	3.782	3.9061	3.9173	4.1184 ±0.0073
0.7500	5.486	5.4854	5.4854	7.177	7.2667	7.2889	8.1640 ±0.0761
0.7900	25.032	25.2284	25.2284	-16.704	-24.4963	-24.5807	-14.56 ±0.21
0.8000	-51.740	-49.5019	-49.5016	-5.665	-7.3629	-7.3901	-5.66 ±0.09
0.8050	-17.262	-16.8312	-16.8310	-3.609	-4.7413	-4.7597	-3.75 ±0.09

^aUsing a 48 Slater-type orbital basis set. Without the second-order correction to the transition moments included in SOPPA (see text).
^bRef. 10.
^cRef. 15.

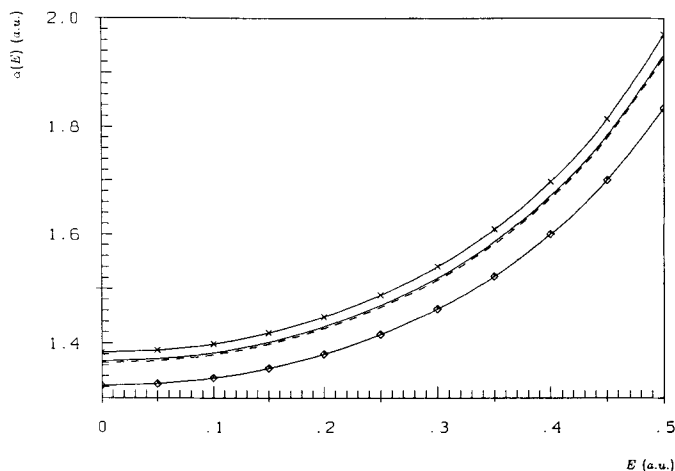


Figure 1. The frequency-dependent dipole polarizability of He (---) (SOPPA, length); (—) (SOPPA, mixed); (\diamond) RPA (length and mixed); and (\times) from Glover and Weinhold [15].

second-order corrections to the transition moments correctly. In fact, $T(\mathbf{r}, E)$ in Eq. (8) was just the zeroth-order part of $(\mathbf{r}|\mathbf{q}^+)$. Furthermore, the metric matrix S was set equal to 1. Later we showed [13] that in a consistent second-order approach $\alpha(E)$ must have the form given in Eqs. (6)–(9). From Table I we see that the second-order corrections to the transition moments are more important than are all of the rest of the second-order corrections. This is particular for polarizabilities [13]. For other properties, these terms are in most cases only a small fraction of the total second-order correction [14, 27].

From Figure 1 (and Table I), we see that a SOPPA calculation recovers most of the difference between RPA and the full CI [10] or exact results of Glover and Weinhold [15]. The latter have upper and lower bounds on $\alpha(E)$. Thus, going through second order in the electronic correlation we have included nearly 70% of the total correlation contribution for most frequencies.

The main differences between the various calculations appear at frequencies close to the asymptotes of $\alpha(E)$, that is, at the excitation energies of He. Table II lists a comparison of the calculated $1s \rightarrow 2p$ excitation energy, and we see that lists a comparison of the calculated $1s \rightarrow 2p$ excitation energy, and we see that the RPA excitation energy is too large, in agreement with the results in Table I.

The parallel behavior of α^L and α^M as a function of E , both in RPA and SOPPA, shows that the basis-set effects are the same at all frequencies.

The C_6 coefficients were calculated from Eq. (3) using a numerical procedure outlined by Amos et al. [29] and using a program written by P.W. Fowler. Since $\alpha(E)$ is only a function of E^2 [see Eqs. (18)–(30)], we can perform the calculations using real arithmetic. The results are shown in Table III. The trends are the same as for $\alpha(E)$ with SOPPA recovering a major part of the total electronic correlation.

TABLE II. The $1s \rightarrow 2p$ excitation energy of He (in eV).

RPA	SOPPA	Full CI ^a	Experiment ^b
21.69	21.33	21.20	21.22

^aRef. 10 using a basis set without f -functions.

^bRef. 28.

TABLE III. The C_6 coefficient for He₂ (in atomic units).

	RPA	SOPPA	MCRRRA ^a	Exact ^b
Length	1.3756	1.4326	1.456	1.4597 \pm 0.0055
Mixed	1.3756	1.4394		

^aRef. 8.

^bRef. 30.

In Tables IV and V, we have compared the two components of the dynamic polarizability of H₂ at the equilibrium internuclear separation with the full CI calculations of Jaszunski and Roos [10] within the same basis set. The percent difference between the RPA and the full CI results are much smaller for H₂ than for He, and the sign of the correlation contribution is also different. We find that SOPPA only gives a small fraction of the total correlation contribution, and only for $\alpha_{\perp}(E)$ does the SOPPA calculation represent an improvement over RPA.

From the disagreement between the length and mixed results in SOPPA compared with the rather good agreement in RPA, we can also conclude that third and higher order terms in the electronic fluctuation potential are important. This we know from the fact that RPA gives exact agreement between the length and the mixed form, whereas in SOPPA, there will be disagreement in third order,

TABLE IV. The perpendicular component of the frequency-dependent polarizability $\alpha_{\perp}(E)$ of H₂ at $R = 1.40$ a.u. (in atomic units).

E(a.u.)	RPA		SOPPA		Full CI ^a
	Length	Mixed	Length	Mixed	
0.0000	4.6107	4.6102	4.6003	4.5968	4.577
0.1045	4.7797	4.7791	4.7685	4.7648	4.745
0.1979	5.2913	5.2908	5.2772	5.2727	5.250
0.3000	6.6361	6.6355	6.6087	6.6024	6.573
0.4000	11.0042	11.0035	10.8483	10.8350	10.784

^aRef. 10.

TABLE V. The parallel component of the frequency-dependent polarizability $\alpha_{\parallel}(E)$ of H_2 at $R = 1.40$ a.u. (in atomic units).

E(a.u.)	RPA		SOPPA		Full α^a
	Length	Mixed	Length	Mixed	
0.0000	6.4495	6.4492	6.4594	6.5055	6.399
0.1045	6.7323	6.7319	6.7448	6.7927	6.681
0.1979	7.6069	7.6065	7.6285	7.6820	7.544
0.3000	10.0440	10.0435	10.0939	10.1629	9.948
0.4000	19.5619	19.5610	19.6940	19.8202	19.192

^aRef. 10.

even for a complete basis set [25]. For He, the RPA and SOPPA length-mixed agreements were not as different.

The basis set for H_2 is probably not fully saturated. It was stated by Jaszunski and Roos [10] that variations in the present basis set only gave a change in $\alpha(E)$ for H_2 by a fraction of a percent, which is in agreement with our calculations. However, the total correlation contribution is less than 1%, and we find that the correlation contribution itself varies quite dramatically with the choice of basis set. In Tables VI and VII, we have compared results of two basis-set calculations with the very best calculation on H_2 by Rychlewski [31]. In addition to the basis set of Jaszunski and Roos [10], we have used another basis set (basis B) taken from Geertsen et al. [32] with exactly the same composition but *slightly* larger

TABLE VI. The perpendicular component of the frequency-dependent polarizability $\alpha_{\perp}(E)$ of H_2 at $R = 1.40$ a.u. in two different basis sets^a (in atomic units).

E(a.u.)	Basis A ^b		Basis B ^c		Rychlewski [31]
	RPA	SOPPA	RPA	SOPPA	
0.0000	4.6107	4.6003	4.6093	4.5676	4.5786
0.0720	4.6892	4.6785	4.6878	4.6445	4.6562
0.0834	4.7167	4.7059	4.7154	4.6715	4.6834
0.1045	4.7797	4.7685	4.7783	4.7331	4.7457
0.1363	4.9070	4.8952	4.9057	4.8576	4.8715
0.1535	4.9941	4.9818	4.9927	4.9427	4.9576
0.1979	5.2913	5.2772	5.2901	5.2328	5.2503
0.2354	5.6479	5.6311	5.6468	5.5800	5.6017
0.2500	5.8221	5.8038	5.8211	5.7493	5.7739
0.3000	6.6361	6.6087	6.6357	6.5367	6.5713
0.3500	8.0425	7.9912	8.0437	7.8834	7.9320
0.3748	9.1889	9.1053	9.1915	8.9633	9.0182
0.4000	11.0042	10.8483	11.0085	10.6421	10.6930
0.4500	22.2767	20.9144	22.2124	20.0551	19.4400

^aDipole length results.^bJaszunski and Roos [10]; a [9s6p3d], 90 CGTO basis set.^cGeertsen et al. [32]; a [9s6p3d], 90 CGTO basis set.

TABLE VII. The parallel component of the frequency-dependent polarizability $\alpha_{\parallel}(E)$ of H_2 at $R = 1.40$ a.u. in two different basis sets^a (in atomic units).

E(a.u.)	Basis A^b		Basis B^c		Rychlewski [31]
	RPA	SOPPA	RPA	SOPPA	
0.0000	6.4495	6.4594	6.4495	6.4495	6.3873
0.0720	6.5805	6.5916	6.5805	6.5812	6.5164
0.0834	6.6266	6.6381	6.6266	6.6276	6.5618
0.1045	6.7323	6.7448	6.7322	6.7338	6.6660
0.1363	6.9473	6.9620	6.9473	6.9501	6.8777
0.1535	7.0953	7.1115	7.0953	7.0990	7.0235
0.1979	7.6069	7.6285	7.6068	7.6136	7.5257
0.2354	8.2333	8.2618	8.2332	8.2437	8.1412
0.2500	8.5445	8.5766	8.5444	8.5568	8.4481
0.3000	10.0440	10.0939	10.0438	10.0649	9.9160
0.3500	12.8215	12.9067	12.8212	12.8558	12.6126
0.3748	15.2762	15.3839	15.2759	15.3084	14.9610
0.4000	19.5619	19.6940	19.5616	19.5639	18.9847
0.4500	66.0705	63.6686	66.0665	62.0977	54.3276

^aDipole length results.
^bJaszunski and Roos [10]; a [9s6p3d], 90 CGTO basis set.
^cGeertsens et al. [32]; a [9s6p3d], 90 CGTO basis set.

exponents. We see that the SOPPA polarizabilities are different in the two basis sets (with basis B results being closest to Rychlewski's calculation), whereas in RPA, we find nearly the same polarizabilities.

Diercksen et al. [33] have shown that the contributions from MBPT2 and MBPT3 to $\alpha_{\parallel}(0)$ have different signs and are of similar magnitudes, whereas both orders in the perturbation theory give negative contributions to $\alpha_{\perp}(0)$. Even though not all third-order terms are included in SOPPA, we would expect $\alpha_{\perp}(E)$ to be smaller in SOPPA than in RPA. For $\alpha_{\parallel}(E)$, it is difficult to make a prediction and both signs of the correction terms would, in principle, be possible. These conclusions are in agreement with the results in Tables IV and V. In general, it appears that much of what can be said about importance of correlation contributions in the static limit also applies to the frequency-dependent polarizabilities.

The position of the low-energy asymptotes for $\alpha(E)$ are as good for H_2 as they are for He as can be seen from a comparison of Tables II and VIII. The C_6 coefficients for the H_2-H_2 interaction and for the H_2-He interaction are expressed in terms of the C , Γ , and Δ constants of Langhoff et al. [36]. The results in Table IX show good agreement with other accurate calculations [8, 37]. Because of the small difference between $\alpha(E)$ of H_2 in RPA and in SOPPA, the correlation effects on C_6 coefficients are also small and only SOPPA values are given. As for $\alpha(E)$ of H_2 , we see a relatively large difference between the coefficients calculated in the length and mixed forms, respectively.

TABLE VIII. The vertical excitation energies of H_2 at $R = 1.40$ a.u. (in eV)^a.

	RPA	SOPPA	Full CI ^b	Exact ^c
$X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$	12.67	12.71	12.74	12.76
$X^1\Sigma_g^+ \rightarrow C^1\Pi_u$	13.10	13.21	13.22	13.22

^aUsing the basis set of Ref 10.^bRef. 10.^cRefs. 34 and 35.TABLE IX. Dispersion force coefficients^a (in atomic units).

Pairs	Method	C	Γ	Δ
H_2-H_2	SOPPA, length	11.381	0.099	0.010
	SOPPA, mixed	11.397	0.103	0.011
	CI ^b	11.40	0.10	
	MCRPA ^c	11.39	0.100	
H_2-He	SOPPA, length	3.877	0.091	
	SOPPA, mixed	3.896	0.094	
	CI ^b	3.904	0.093	
	MCRPA ^c	3.907	0.093	

^aFor a definition of C , Γ , and Δ , see Ref. 36.^bRef. 37.^cRef. 8.

4. Summary

We have reformulated the polarization propagator expression for the frequency-dependent dipole polarizability $\alpha(E)$ through second order in the fluctuation potential (SOPPA) such that $\alpha(E)$ is a function of E^2 rather than E , as was the case earlier [13]. The present form is more convenient for calculation of dispersion coefficients via the Casimir–Polder formula [16], Eq. (3), since it avoids complex arithmetic.

Comparison with a full CI calculation [10] in a large basis set shows that about 70% of the total electronic correlation contribution to $\alpha(E)$ is obtained for He, independent of E . We also find that a major part of the electronic correlation comes from the second-order contributions to the transition moments, i.e., from the non-zeroth-order terms in Eq. (8).

For H_2 , where the total correlation contribution to the dipole polarizability is smaller than for He, SOPPA does not result in any improvement over RPA using the basis set of Jaszunski and Roos [10]. We find, however, that the electronic correlation is rather basis-set dependent and that we get much better agreement with the best calculation [31] of $\alpha(E)$ if we use another basis set [32] that has exactly the same composition of s , p , and d functions as the Jaszunski–Roos basis set but with slightly increased orbital exponents. The TRK sum rule was found to be ful-

filled to the same accuracy in the two basis sets. We thus conclude that, even though the total change in $\alpha(E)$ is only a fraction of a percent, the electronic correlation is still rather basis-set dependent for H_2 using a basis set consisting of 90 CGTOS.

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Bibliography

- [1] P. H. S. Martin, W. H. Henneker, and V. McKoy, *J. Chem. Phys.* **62**, 69 (1975).
- [2] A. L. Ford and J. C. Browne, *Phys. Rev. A* **7**, 418 (1973).
- [3] H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34 (1965).
- [4] G. H. F. Diercksen, B. O. Roos, and A. J. Sadlej, *Chem. Phys.* **59**, 29 (1981).
- [5] R. Kamikawai, J. Watanabe, and A. Amemiya, *Phys. Rev.* **184**, 303 (1969).
- [6] D. M. Bishop and L. M. Cheung, *J. Chem. Phys.* **72**, 5125 (1980); *Adv. Quantum Chem.* **12**, 1 (1980).
- [7] H. P. Kelly, *Adv. Chem. Phys.* **14**, 129 (1969); *Phys. Rev. A* **1**, 274 (1970).
- [8] M. Jaszunski and R. McWeeny, *Mol. Phys.* **46**, 863 (1982).
- [9] F. Visser, P. E. S. Wormer, and P. Stam, *J. Chem. Phys.* **79**, 4973 (1983).
- [10] M. Jaszunski and B. O. Roos, *Mol. Phys.* **52**, 1209 (1984).
- [11] J. Oddershede, P. Jørgensen, and N. H. F. Beebe, *J. Chem. Phys.* **63**, 2996 (1975).
- [12] J. Oddershede and P. Jørgensen, *J. Chem. Phys.* **66**, 1541 (1977).
- [13] E. S. Nielsen, P. Jørgensen, and J. Oddershede, *J. Chem. Phys.* **73**, 6238 (1980).
- [14] J. Geertsen, J. Oddershede, and G. E. Scuseria, *J. Chem. Phys.* **87**, 2138 (1987).
- [15] R. M. Glover and F. Weinhold, *J. Chem. Phys.* **65**, 4913 (1976).
- [16] H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).
- [17] J. Oddershede, P. Jørgensen, and D. L. Yeager, *Compt. Phys. Rep.* **2**, 33 (1984).
- [18] J. Olsen and P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
- [19] O. Goscinski and B. Lukman, *Chem. Phys. Lett.* **7**, 573 (1970).
- [20] P. O. Löwdin, *J. Mol. Spectrosc.* **10**, 12 (1963).
- [21] G. H. F. Diercksen and W. P. Kraemer, MUNICH reference manual, special technical report, Max-Planck-Institut für Physik und Astrophysik, Munich (1981).
- [22] S. P. A. Sauer, Diplomarbeit, Ludwig-Maximilians Universität, Munich (1981).
- [23] J. Styszynski and J. Karwowski, *J. Phys. B: Atom. Mol. Opt. Phys.* **21**, 2389 (1988).
- [24] L. Laaksonen, P. Pyykkö, and D. Sundholm, *Compt. Phys. Rep.* **4**, 313 (1986).
- [25] P. Jørgensen and J. Oddershede, *J. Chem. Phys.* **78**, 1898 (1983).
- [26] P. Jørgensen, J. Oddershede, P. Albertsen, and N. H. F. Beebe, *J. Chem. Phys.* **68**, 2533 (1978).
- [27] J. Geertsen and J. Oddershede, *Chem. Phys.* **104**, 67 (1986).
- [28] C. E. Moore, *Natl. Bur. Stand., Circl. No. 267* (Government Printing Office, Washington, DC, 1949).
- [29] R. D. Amos, N. C. Handy, P. J. Knowles, J. E. Rice, and A. J. Stone, *J. Phys. Chem.* **89**, 2186 (1985).
- [30] R. M. Glover and F. Weinhold, *J. Chem. Phys.* **66**, 191 (1977).
- [31] J. Rychlewski, *J. Chem. Phys.* **78**, 7252 (1983).
- [32] J. Geertsen, J. Oddershede, and J. R. Sabin, *Phys. Rev. A* **34**, 1104 (1986).

- [33] G. H. F. Diercksen, M. Jaszunski, and A. J. Sadlej, *Chem. Phys.* **71**, 105 (1982).
- [34] W. Kolos and J. Rychlewski, *J. Mol. Spectrosc.* **62**, 109 (1976).
- [35] W. Kolos and L. Wolniewicz, *Can. J. Phys.* **53**, 2189 (1975).
- [36] P. W. Langhoff, R. G. Gordon, and M. Karplus, *J. Chem. Phys.* **50**, 2535 (1969).
- [37] W. Meyer, *Chem. Phys.* **17**, 27 (1976).

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