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Evaluation of electronic correlation contributions for optical tensors of large systems using the incremental scheme

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A new method is developed to calculate the optical tensors of large systems based on available wave function correlation approaches (e.g., the coupled cluster ansatz) in the framework of the incremental scheme. The convergence behaviors of static first- and second-order polarizabilities with respect to the order of the incremental expansion are examined and discussed for the model system $\text{Ga}_4\text{As}_4\text{H}_{18}$. The many-body increments of optical tensors originate from the dipole-dipole coupling effects and the corresponding contributions to the incremental expansion are compared among local domains with different distances and orientations. The weight factors for increments of optical tensors are found to be tensorial in accordance with the structural symmetry as well as the polarization and the external electric field directions. The long-term goal of the proposed approach is to incorporate the sophisticated molecular correlation methods into the accurate wave function calculation of optical properties of large compounds or even crystals. © 2007 American Institute of Physics. [DOI: 10.1063/1.2759201]

I. INTRODUCTION

Nonlinear optical (NLO) properties of materials (e.g., crystals) are of exceptional importance in laser science and technology. Obviously, a deep understanding of the mechanism of NLO effects in crystals helps to search for or even design new NLO crystals more efficiently. Several theoretical attempts, including semiempirical methods such as the bond charge model^{1–3} and the anionic group theory^{4,5} as well as first-principles approaches based on density functional theory (DFT),^{6–8} have been made to obtain a correlation between the microstructures of crystals and their NLO responses.

Both the bond charge model and the anionic group theory assume that the macroscopic tensor element of the NLO polarizability of a crystalline material is obtained by appropriately summing up the microscopic tensor elements from all constituent domains, i.e., the chemical bonds or the anionic groups. The microscopic tensor elements can be calculated using molecular first-principles quantum chemistry methods. However, neither of these two methods can be successful for those cases where the couplings between bonds or anionic groups are too strong to be neglected, and the simple sum rules for microscopic polarizabilities fail. The first-principles approaches are becoming more favorable to study the NLO properties of materials⁴ since the 1960's and impressive achievements have been made recently.^{7,9–11} Although the first-principles methods provide a systematic way with high predictive power, the electronic correlation effects are usually accounted for by DFT, particularly local density approximation (LDA) and generalized gradient approximation (GGA) schemes, for large and periodic systems. It is well known that in most cases LDA and GGA greatly under-

estimate the band gap and therefore lead to significantly overestimated optical coefficients, whereas a systematic improvement over DFT band structure calculations using wavefunction-based *ab initio* approaches is only possible for very simple crystals^{12–18} and optical responses of molecular systems^{19,20} so far.

In this paper, we propose a formalism which allows to perform the indirect *ab initio* calculation of optical tensors for large systems by using the available efficient correlation methods such as coupled cluster (CC) theory in the framework of the incremental scheme. In the present work, we explore a simple model system to demonstrate how the convergence of the incremental expansion of static optical tensors can be achieved by truncating the series, and what problems have to be handled for the accurate calculation of optical tensors within this approach. The entire simple system still can be dealt with at the coupled cluster single and double excitations (CCSD) correlation level, which thus can be used to gauge the accuracy of the incremental expansion.

II. INCREMENTAL EXPANSION OF OPTICAL TENSORS

In order to accurately account for the electronic correlation effects for large and nonmetallic periodic systems by using available wavefunction-based correlation methods, one may resort to the so-called incremental scheme originally proposed by Stoll in 1992.^{21–23} The incremental scheme is very general and in principle exact to recover the correlation energy within the invoked correlation approach. It is easily parallelizable and, due to its use of the local nature of electron correlation, is particularly efficient for large and periodic compounds. The incremental scheme in connection with the wave function correlation methods has achieved remarkable progress in successfully deriving the cohesive properties (e.g., lattice constant, cohesive energy, and bulk modulus) of

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various periodic compounds including Van der Waals systems (e.g., rare-gas crystals), hydrogen-bonded systems, ionic systems (e.g., LiF, MgO), covalent systems (e.g., group III, V, and IV cubic semiconductors) and even the delocalized systems (e.g., Li_g, C₆₀, and Hg) with strong correlations.^{24,25}

Given a group D of local domains m accurately derived from local Hartree-Fock (HF) orbitals, the correlation energy for a system can be expanded in Eq. (1) as the sum of so-called n -body increments (e.g., one, two, three, ..., n body):

$$E_{\text{corr}} = \sum_{m \in D} \varepsilon_m + \sum_{m < n \in D} \Delta\varepsilon_{mn} + \sum_{m < n < o \in D} \Delta\varepsilon_{mno} + \dots \quad (1)$$

If ε_m denotes the correlation energy of domain m , ε_{mn} the one of the united domains m and n , etc., the increments in Eq. (1) are defined as

$$\begin{aligned} \Delta\varepsilon_{mn} &= \varepsilon_{mn} - \varepsilon_m - \varepsilon_n, \\ \Delta\varepsilon_{mno} &= \varepsilon_{mno} - \Delta\varepsilon_{mn} - \Delta\varepsilon_{no} - \Delta\varepsilon_{om} - \varepsilon_m - \varepsilon_n - \varepsilon_o, \end{aligned} \quad (2)$$

...

The local domains can be a set of localized orbitals at different atomic/ionic sites in ionic systems or of different localized bond orbitals in covalent systems, or arise from other definitions. Numerous successful applications of the scheme to calculate correlation contributions to total energies appeared in literature so far^{24,25,27} and a fully automatized version of the approach has recently been implemented.²⁶

The optical coefficients, i.e., the first-order linear optical polarizability $\chi_{ij}^{(1)}$, the second- and third-order nonlinear hyperpolarizabilities $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$, etc., can be evaluated via the following partial differentiations of the total energy with respect to the strengths of the applied electric fields F_i in the Cartesian direction i .

$$\begin{aligned} \chi_{ij}^{(1)} &= - \left(\frac{\partial^2 E}{\partial F_i \partial F_j} \right)_0, \\ \chi_{ijk}^{(2)} &= - \left(\frac{\partial^3 E}{\partial F_i \partial F_j \partial F_k} \right)_0, \\ \chi_{ijkl}^{(3)} &= - \left(\frac{\partial^4 E}{\partial F_i \partial F_j \partial F_k \partial F_l} \right)_0, \end{aligned} \quad (3)$$

If the total energy is written as the sum of the HF and the correlation energy,

$$E = E_{\text{HF}} + E_{\text{corr}}, \quad (4)$$

Equations (3) read

$$\begin{aligned} \chi_{ij}^{(1)} &= \chi_{ij,\text{HF}}^{(1)} + \chi_{ij,\text{corr}}^{(1)}, \\ \chi_{ijk}^{(2)} &= \chi_{ijk,\text{HF}}^{(2)} + \chi_{ijk,\text{corr}}^{(2)}, \\ \chi_{ijkl}^{(3)} &= \chi_{ijkl,\text{HF}}^{(3)} + \chi_{ijkl,\text{corr}}^{(3)}, \\ &\dots \end{aligned} \quad (5)$$

Considering Eqs. (1)–(4), the correlation contributions in Eqs. (5) for optical tensors are thereby obtained in the incremental many-body expansions,

$$\begin{aligned} \chi_{ij,\text{corr}}^{(1)} &= \sum_m \chi_{ij,m}^{(1)} + \sum_{m < n} \Delta\chi_{ij,mn}^{(1)} + \sum_{m < n < o} \Delta\chi_{ij,mno}^{(1)} + \dots, \\ \chi_{ijk,\text{corr}}^{(2)} &= \sum_m \chi_{ijk,m}^{(2)} + \sum_{m < n} \Delta\chi_{ijk,mn}^{(2)} + \sum_{m < n < o} \Delta\chi_{ijk,mno}^{(2)} \\ &\quad + \dots, \\ \chi_{ijkl,\text{corr}}^{(3)} &= \sum_m \chi_{ijkl,m}^{(3)} + \sum_{m < n} \Delta\chi_{ijkl,mn}^{(3)} + \sum_{m < n < o} \Delta\chi_{ijkl,mno}^{(3)} \\ &\quad + \dots, \\ &\dots \end{aligned} \quad (6)$$

Here for every correlation contribution to the N th order polarizability $\chi_{ijk\dots,corr}^{(N)}$, the correlation increments can in turn be calculated by

$$\begin{aligned} \Delta\chi_{ijk\dots,mn}^{(N)} &= \chi_{ijk\dots,mn}^{(N)} - \chi_{ijk\dots,m}^{(N)} - \chi_{ijk\dots,n}^{(N)}, \\ \Delta\chi_{ijk\dots,mno}^{(N)} &= \chi_{ijk\dots,mno}^{(N)} - \Delta\chi_{ijk\dots,mn}^{(N)} - \Delta\chi_{ijk\dots,no}^{(N)} \\ &\quad - \Delta\chi_{ijk\dots,om}^{(N)} - \chi_{ijk\dots,m}^{(N)} - \chi_{ijk\dots,n}^{(N)} - \chi_{ijk\dots,o}^{(N)}, \\ \Delta\chi_{ijk\dots,mnop}^{(N)} &= \chi_{ijk\dots,mnop}^{(N)} - \Delta\chi_{ijk\dots,mno}^{(N)} - \Delta\chi_{ijk\dots,nop}^{(N)} \\ &\quad - \Delta\chi_{ijk\dots,opm}^{(N)} - \Delta\chi_{ijk\dots,pmn}^{(N)} - \Delta\chi_{ijk\dots,mn}^{(N)} \\ &\quad - \Delta\chi_{ijk\dots,no}^{(N)} - \Delta\chi_{ijk\dots,op}^{(N)} - \Delta\chi_{ijk\dots,pm}^{(N)} \\ &\quad - \Delta\chi_{ijk\dots,mo}^{(N)} - \Delta\chi_{ijk\dots,np}^{(N)} - \chi_{ijk\dots,m}^{(N)} - \chi_{ijk\dots,n}^{(N)} \\ &\quad - \chi_{ijk\dots,o}^{(N)} - \chi_{ijk\dots,p}^{(N)}, \\ &\dots \end{aligned} \quad (7)$$

The one-body increment tensor $\chi_{ijk\dots,m}^{(N)}$ for the local domain m is calculated by allowing excitations from the local orbitals inside m but entirely freezing those from others outside m at the correlated level. The two-body increment tensor $\Delta\chi_{ijk\dots,mn}^{(N)}$ can be understood as the correction to the one-body increment tensor due to the two-body coupling effect between the local domains m and n ; for each $\Delta\chi_{ijk\dots,mn}^{(N)}$, $\chi_{ijk\dots,mn}^{(N)}$ is obtained by exciting from local orbitals inside both domains m and n but freezing all other local orbitals outside m and n . The three-body increment tensor $\Delta\chi_{ijk\dots,mno}^{(N)}$ is essentially the correction due to the three-body coupling effect among the local domains m , n , and o , and it can be calculated in an analogous way. This interpretation can be generalized for higher order increment tensors until, in principle, all increments are included in the expansion (6). By

taking into account all corrections for the entire coupling effects, the sum rule in Eqs. (6) gives the exact value of optical tensors with no approximations made for the incremental expansion within the wave-function-based first-principles approach. The semiempirical methods, i.e., bond charge model and anionic group theory, actually correspond to the first-order approximation by summing only one-body increments, whereas the interactions between different bonds or anionic groups are totally ignored.

Generally, the number of terms which need to be evaluated for a system with a number of D local domains is

$$C_D^1 + C_D^2 + C_D^3 + \cdots + C_D^D = 2^D - 1$$

For a periodic compound, D goes to infinity and the incremental expansion becomes an infinite series. Although the incremental series (6) offers us the exact result of optical tensors within the correlation approach, the complete inclusion of the coupling effects among all local domains is only possible for small finite systems. Two approximations are introduced in order to make the expansion (6) for optical tensors work in practice. First of all, this series has to be truncated at a certain possibly low expansion order. In order to do so, the series (6) must exhibit a good convergence, i.e., up to, say, the three-body increments. Second, the sum $\sum_{m < n < \dots}$ is carried out only for the nearby local domains so that the coupling effects for those local domains which are spatially distant to each other can be neglected. The above two approximations have been already shown to be well fulfilled in the case of various systems for correlation energies^{24,25} by using localized-orbital-centered domains. In this paper, we examine the behaviors of the two approximations for the calculations of static optical first- and second-order polarizabilities and how the accuracy can be controlled by the series truncation.

III. COMPUTATIONAL DETAILS

The above formalism was applied to the $\text{Ga}_4\text{As}_4\text{H}_{18}$ model system. $\text{Ga}_4\text{As}_4\text{H}_{18}$ was truncated from the cubic GaAs crystal with the hydrogen atoms saturating the dangling bonds. The Ga–H and As–H distances, respectively, are 1.621 and 1.525 Å, which were optimized by Paulus *et al.*²⁷ for GaAsH_6 clusters at the CCSD level. In order to demonstrate how the convergence of incremental expansions depends on the local domains, we have defined three different local domain spaces, i.e., the domain space A for five local domains (cf. the top in Fig. 1) with active localized hydrogen orbitals Ga–H and As–H, the domain space B for three local domains (cf. the middle in Fig. 1), and the domain space C for seven local domains (cf. the bottom in Fig. 1) with frozen localized hydrogen bond orbitals. The multicenter groups of nine As–H and Ga–H bonds are labeled as A1 and A5 only in the domain space A, respectively; the four-center groups of three side As–Ga1 and Ga–As5 bonds are labeled as A2 and A4 in the domain space A as well as B1 and B3 in the domain space B, respectively; the two-center group of the central Ga1–As5 bond is labeled as A3, B2, and C3 in the domain spaces A, B, and C, respectively; the two-center

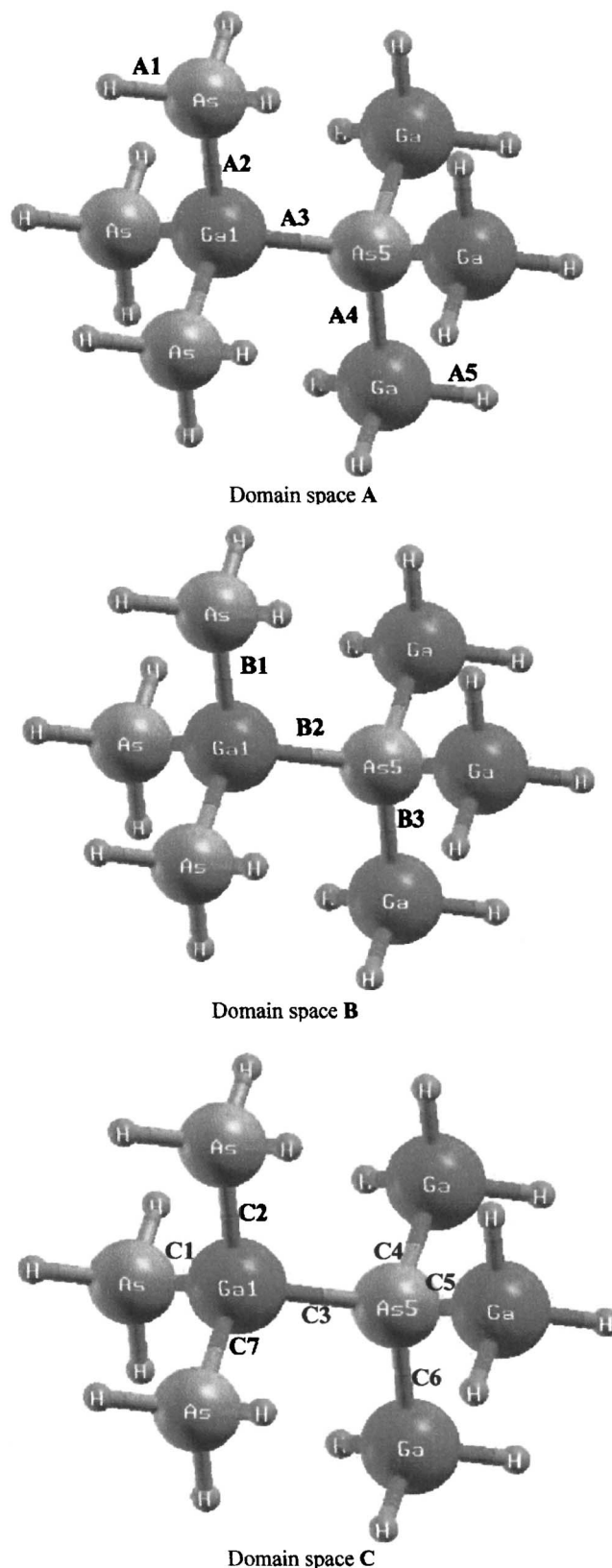


FIG. 1. The structure of $\text{Ga}_4\text{As}_4\text{H}_{18}$ and definitions of three different local domain spaces from A to C. The definitions of A, B, and C can be found in Sec. III.

groups of each single side As–Ga1 and As5–Ga bonds are labeled as C1, C7, C4, C5, and C6 in the domain space C.

The large-core relativistic energy-consistent pseudopo-

TABLE I. The incremental expansion for the correlation energy, first- and second-order polarizabilities within the local domain space A (in a.u.). The percentage listed for the expansion up to n -body increments is taken with respect to the CCSD reference value.

n -body (domain A)	Correlation energies	$\chi_{XX}^{(1)}$	$\chi_{ZZ}^{(1)}$ [$\chi_{ZZ}^{(1)}$]	$\chi_{XXX}^{(2)}$	$\chi_{ZZZ}^{(2)}$ [$\chi_{ZZZ}^{(2)}$]	$\chi_{YYY}^{(2)}$
1	-0.62218 78.9%	249.71 87.6%	238.56 99.0%	2462.00 79.5%	526.55 76.9%	83.37 72.1%
2	-0.17122 100.6%	30.86 98.4%	0.49 99.2%	1017.46 112.4%	189.76 104.7%	14.79 84.9%
3	0.00509 99.9%	3.04 99.4%	2.50 100.2%	-269.88 103.7%	-18.79 101.9%	29.84 110.7%
4	-0.00016 99.9%	1.44 99.9%	-0.59 99.9%	-111.93 100.0%	-14.34 99.8%	-11.78 100.5%
5	0.00001 100.00%	0.15 100.0%	0.06 100.0%	-1.02 100.0%	1.19 100.0%	-0.55 100.0%
CCSD	-0.78850	285.20	241.03	3096.66	684.38	115.66
HF	...	254.57	219.87	1516.52	314.97	-11.78

tential valence model Hamiltonian (ECP-28MWB) (Refs. 28 and 29) was applied to both Ga with a $4s^2 4p^1$ valence configuration and As with a $4s^2 4p^3$ valence configuration in association with $(4s4p)/[2s2p]$ basis sets²⁹ augmented by the energy-optimized d -orbital exponents of 0.1867 for Ga and 0.2851 for As. A library 6-31G basis set^{30,31} was used for the hydrogen atoms. We have noted that the size of these basis sets is too small to sufficiently account for the correlation effect for the optical polarizabilities and hyperpolarizabilities at the CCSD level; however, since one goal of our paper is a comparison of truncated incremental expansion results to the exact CCSD results in the given basis sets we have to limit the basis sets in order to be able to derive the latter. All the HF and CCSD energy calculations were carried out by the code DALTON.³² The CCSD calculations were performed by using the localized reference orbitals generated from both the HF canonical doubly occupied orbitals in the Foster-Boys localization scheme.³³ The static first- and second-order polarizabilities for increment tensors were evaluated by the linear and quadratic response approaches implemented in DALTON.

IV. RESULTS AND DISCUSSIONS

A. Incremental convergence for static first- and second-order polarizabilities

The calculated results of CCSD increments for the domain spaces A, B, and C are listed in Tables I–III, respec-

tively. Obviously the electronic correlation effects have significant contributions to the optical coefficients as it is apparent from the CCSD and HF values listed in Table I. It can be seen that, for either of these domain spaces, the linear polarizabilities achieve much faster convergence against the expansion order than the nonlinear ones. For example, in the domain space A (cf. Table I), at the level of two-body increment corrections, the deviations for the first-order polarizabilities stay within 2% compared to the CCSD reference values, whereas those for the second-order polarizabilities are much larger at about 5%–15%. Including three-body increment corrections in the domain space A, the deviations for the linear polarizabilities further drop to less than 0.6%, whereas much larger overestimations occur for the YYY components of the second-order polarizabilities at about 11%. Finally, at the four-body increment corrections, the linear polarizabilities deviate from the CCSD reference value within 0.05%, and the nonlinear ones still differ from the CCSD reference value by up to 0.5% (cf. Table I).

We have found that the convergence behavior of these numbers also depends on how the domain space is defined. In the case studied here, it is apparent from Figs. 2–4 that the domain space A has obtained the most rapid convergence of optical tensors, particular of the nonlinear hyperpolarizabilities, with respect to the expansion order. Strong oscillatory structures are found for the second-order polarizabilities especially for the $\chi_{YYY}^{(2)}$ component in the domain space C (cf.

TABLE II. As in Table I, but for the local domain space B (in a.u.).

n -body (domain B)	Correlation energies	$\chi_{XX}^{(1)}$	$\chi_{ZZ}^{(1)}$ [$\chi_{ZZ}^{(1)}$]	$\chi_{XXX}^{(2)}$	$\chi_{ZZZ}^{(2)}$ [$\chi_{ZZZ}^{(2)}$]	$\chi_{YYY}^{(2)}$
1	-0.16534 78.5%	99.91 82.1%	102.30 110.4%	934.828 116.4%	142.26 123.8%	-43.11 -559.9%
2	-0.04604 100.4%	21.55 99.8%	-10.76 98.8%	74.389 125.7%	-25.51 101.6%	54.64 149.7%
3	0.00084 100.0%	0.28 100.0%	1.13 100.0%	-206.05 100.0%	-1.84 100.0%	-3.83 100.0%
CCSD	-0.21054	121.74	92.67	803.16	114.90	7.70
HF	...	110.74	86.61	489.80	36.16	-58.10

TABLE III. As in Table I, but for the local domain space C (in a.u.).

n -body (domain C)	Correlation energies	$\chi_{XX}^{(1)}$	$\chi_{YY}^{(1)}$ [$\chi_{ZZ}^{(1)}$]	$\chi_{XXX}^{(2)}$	$\chi_{YYY}^{(2)}$ [$\chi_{ZZZ}^{(2)}$]	$\chi_{YY}^{(2)}$
1	-0.12314	105.58	95.47	753.67	179.86	26.50
	58.5%	86.7%	103.0%	93.8%	156.5%	344.2%
2	-0.09477	29.49	4.04	896.89	59.11	-27.92
	103.5%	111.0%	107.4%	205.5%	208.0%	-18.4%
3	0.00706	-10.74	-8.92	-817.91	-158.18	25.34
	100.0%	102.1%	97.8%	103.7%	70.3%	310.7%
4	0.00058	-5.01	1.78	-191.61	7.26	-29.67
	100.4%	98.0%	99.7%	79.8%	76.6%	-74.7%
5	-0.00036	2.52	0.47	170.27	36.94	17.44
	100.6%	100.1%	100.2%	101.0%	108.8%	151.8%
6	0.00010	-0.11	-0.18	-8.38	-11.16	-4.44
	100.6%	99.9%	99.9%	99.9%	99.1%	94.2%
7	-0.00001	0.00	0.02	0.24	1.07	0.45
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
CCSD	-0.21054	121.74	92.67	803.16	114.90	7.70
HF	...	110.74	86.61	489.80	36.16	-58.10

Fig. 4). In the domain space A, the derivations of the tensors $\chi_{XXX}^{(2)}$, $\chi_{YYY}^{(2)}$, and $\chi_{YY}^{(2)}$ corrected by the three-body increments stay within 10%, while in the domain space C, one needs to go to the five-body incremental correction for $\chi_{XXX}^{(2)}$ and $\chi_{YYY}^{(2)}$, and even the six-body terms for $\chi_{YY}^{(2)}$. This unpleasant result obtained for the domain space C implies that these individual bonds may undergo strong couplings with each other which slows down the convergence of the series. Such couplings may occur through the canonical virtual orbitals, which have not yet been localized in the present approach of the incremental scheme, particularly for the excited properties including optical coefficients. The higher order optical tensors (e.g., $\chi_{ijk}^{(2)}$) may show a slower convergence with respect to the incremental expansion order than the lower order ones (e.g., $\chi_{ij}^{(1)}$) since the former involves a larger number of delocalized electric transition dipole moments between canonical excited states than the latter. Therefore it appears necessary to utilize localized virtual orbitals in future implementations of the incremental scheme for evaluating optical tensors.

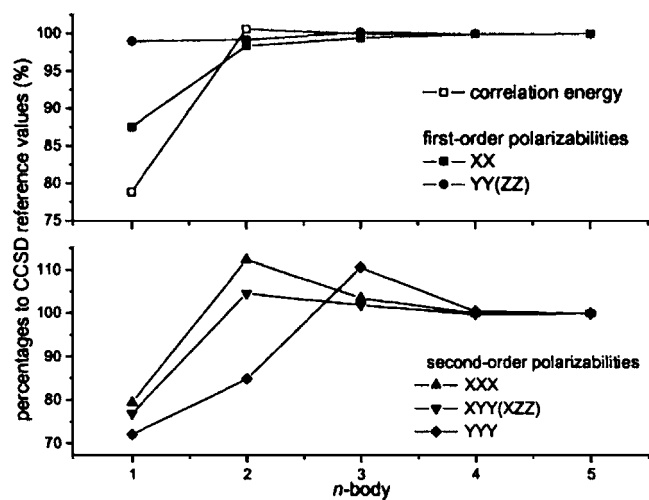


FIG. 2. The deviation of the optical tensor values at the n -body increment contribution from the CCSD reference value within the domain space A.

It is also interesting to see that the correlation energy converges within 1% up to two-body incremental corrections for the two domain spaces A and B and up to only three-body incremental corrections for the domain space C. From this point of view, the problem of how to define suitable domains seems much more severe for the evaluation of optical tensors, especially for the nonlinear components, than for the correlation energy. Just as Lin *et al.* has commented,³⁴ “...the second-order polarizability of most NLO crystals arises from basic structural units with delocalized regions of valence electron orbitals belonging to more than two atoms, rather than from regions localized around two atoms connected by a simple σ -type bond.” Therefore these “basic structural units” need to be grouped into the local domain so that although these optical polarizabilities and hyperpolarizabilities are nonlocal within these basic structural units, they can still be regarded as fairly good local quantities so that the contribution of the coupling between the local domains is small.

One may have already noted in Tables I–III that both of the HF and CCSD polarizabilities are quite different between the local domain spaces A and B (or C). As a matter of fact, in the local domain spaces B and C, since all bonds involving hydrogen are frozen, no contributions of these bonds to the polarizabilities and hyperpolarizabilities have been yet accounted for. According to the bond charge model,^{1–3} the optical polarizabilities are scaled to the difference of atomic sizes forming a bond, i.e., larger atomic sizes often lead to larger polarizabilities. Therefore in the case of $\text{Ga}_4\text{As}_4\text{H}_{18}$, these H–Ga and H–As bonds contribute large portions to the total polarizabilities of the entire system due to the large size difference between H and Ga/As atoms in the local domain space A.

The convergence of the incremental expansion was also studied with larger triple- ζ -quality $(14s10p2d)/[3s3p2d]$ basis sets for the Ga and As atoms.^{28,35} The results are shown in Table IV. A comparison with the double- ζ -quality $(4s4p1d)/[2s2p1d]$ results listed in Table I reveals similar

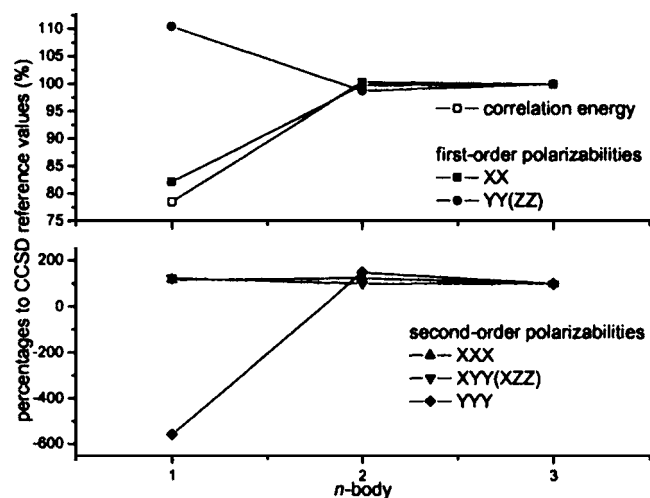


FIG. 3. As in Fig. 2, but for the domain space B.

rates of convergence of the incremental expansions for both cases. Due to the quite small CCSD reference value of $\chi_{YYY}^{(2)}$ at the triple- ζ level the convergence in terms of percentages is deteriorated.

Therefore based on the above comparisons of the convergences for the local domain spaces A, B, and C, it is wise in treating extended systems, as a rule of thumb, to define a multicenter domain (e.g., grouping triple local bond orbitals) in order to avoid relatively strong couplings for many-body increments between local bond orbitals in two-center domains. In addition, the implementation of the incremental scheme for the evaluation of optical tensors is less straightforward than its implementation for the evaluation of correlation energies. Some problems and principle ideas are raised and will be discussed in the following sections.

B. Domain distances and orientations

In the usual evaluation of the correlation energy in the incremental scheme, the coupling effects among spatially separated local domains are small enough so that their contribution to the total correlation energy can be neglected without a significant loss of accuracy. This principle needs to

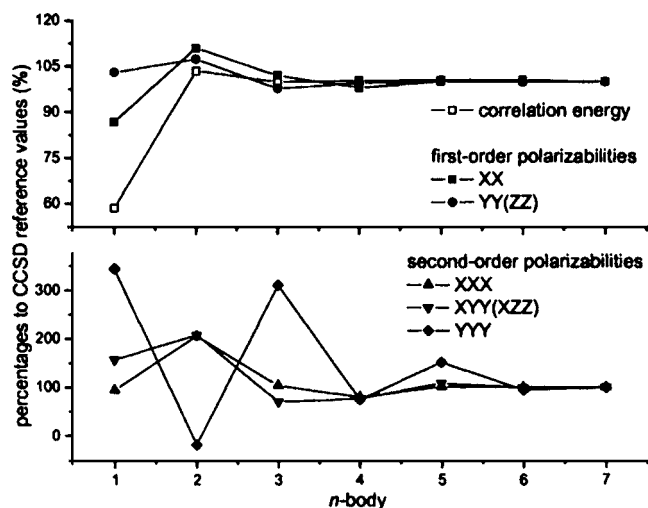


FIG. 4. As in Fig. 2, but for the domain space C.

be reconsidered in the case of optical properties. In the present study, it is found that, unlike the scalar quantity correlation energy, the many-body increments of optical tensors are not always monotonously decreasing with respect to the increasing distance between the local domains. We explain the observed feature as the consequence that the coupling effects for optical tensors among local domains are essentially determined by the interactions among the dipole vectors individually located at these local domains. For example, the two-body increment of the linear polarizability between the local domains D1 and D2 can be expressed as

$$\Delta\chi_{ij,D1D2}^{(1)} = \left[\frac{\partial(p_{12,i} - p_{1,i} - p_{2,i})}{\partial F_j} \right]_0 = \left(\frac{\partial\Delta p_{12,i}}{\partial F_j} \right)_0 \quad (8)$$

In Eq. (8), in the Cartesian direction i , $p_{1,i}$ is the component of the dipole \mathbf{p}_1 at the local domain D1 by freezing other local orbitals outside D1, $p_{2,i}$ the component of the dipole \mathbf{p}_2 at the local domain D2 by freezing other local orbitals outside D2 and $p_{12,i}$ the component of the united dipole \mathbf{p}_{12} at the combined local domain D1-D2 by freezing other local orbitals outside D1-D2.

TABLE IV. As in Table I, but for the larger (14s10p2d)/[3s3p2d] basis sets for Ga and As in the local domain space A (in a.u.).

n -body (domain A)	Correlation energies	$\chi_{XX}^{(1)}$	$\chi_{YY}^{(1)}$ [$\chi_{ZZ}^{(1)}$]	$\chi_{XXX}^{(2)}$	$\chi_{YYY}^{(2)}$ [$\chi_{ZZZ}^{(2)}$]	$\chi_{YYY}^{(2)}$
1	-0.68183 78.1%	274.56 88.5%	266.18 100.9%	2510.76 83.2%	436.70 89.6%	-11.21 223.4%
2	-0.19644 100.6%	33.12 99.2%	-4.57 99.2%	1031.43 117.4%	130.60 116.3%	-6.52 353.3%
3	0.00594 99.9%	0.86 99.5%	3.04 100.3%	-409.58 103.9%	-54.73 105.1%	26.35 -172%
4	-0.00025 100.0%	1.52 100.0%	-0.92 100.0%	-107.68 100.3%	-24.16 100.2%	-12.97 86.6%
5	0.00001 100.00%	0.13 100.0%	0.07 100.0%	-9.09 100.0%	-0.75 100.0%	-0.67 100.0%
CCSD	-0.87256	310.19	263.80	3015.84	487.67	-5.02
HF	—	274.77	240.19	1450.56	172.64	-87.11

TABLE V. The domain distance and the two-body increments of the correlation energy $\Delta\varepsilon_{mn}$ as well as the optical tensors for the local domains m and n within the domain space C (in a.u.).

Local domain pairs (m, n)	$\Delta\varepsilon_{mn}$	$\Delta\chi_{XX,mn}^{(1)}$	$\Delta\chi_{YY,mn}^{(1)}$ [$\Delta\chi_{ZZ,mn}^{(1)}$]	$\Delta\chi_{XXX,mn}^{(2)}$	$\Delta\chi_{YYY,mn}^{(2)}$ [$\Delta\chi_{XZZ,mn}^{(2)}$]	$\Delta\chi_{YYY,mn}^{(2)}$
(C2, C3)	-0.00454	2.66	1.48	-70.8	22.74	62.45
(C2, C4)	-0.00056	0.94	-0.81	1.89	-2.74	7.99

The dipole variation $\Delta p_{12,i}$ has a complicated angular dependence between \mathbf{p}_1 and \mathbf{p}_2 , since there are two dipoles, each one of which can be oriented in any direction. The potential energy of the dipole \mathbf{p}_2 in the electric field \mathbf{E}_1 produced by \mathbf{p}_1 depends on the angular position of \mathbf{p}_2 relative to \mathbf{p}_1 and their relative orientations. Therefore the maximum interaction is achieved if \mathbf{E}_1 is parallel to \mathbf{p}_2 and the interaction vanishes if they are orthogonal to each other. Although the electronic dipole-dipole interactions are short-range effects, the two-body increment between two relatively apart local domains may be larger than the one between two nearby local domains if the former domains are angularly much more favorable for the dipole-dipole interaction than the latter. However, the coupling effects to many-body increments of optical tensors can be varied small and even null among nearby local domains if those local domains are angularly unfavorable, say, orthogonal to each other, and thus their nonadditive contribution could be safely neglected.

As one example in the present study, we compare the two-body increments with respect to both the domain distance (cf. Table V) and orientation (cf. Table VI) in the domain space C. The two-body increments of $\Delta\chi_{XX,mn}^{(1)}$ and $\Delta\chi_{YY,mn}^{(2)}$ between two nearby local domains C2 and C3 (cf. Fig. 1) are 2.66 and 22.74 a.u. (cf. Table V), which are substantially larger than the ones between two farther apart local domains C2 and C4, since the relative angular orientation of C2 and C3 is similar to that of C2 and C4. Meanwhile in Table V, the increment $\Delta\varepsilon_{C2C3}$ is much larger than $\Delta\varepsilon_{C2C4}$ (i.e., by almost one order of magnitude), which is regularly expected in the usual incremental expansion of correlation energies. The angular dependence of two-body increments is shown in Table VI by considering domains with a similar spacing. The much larger two-body increments of, e.g., $\Delta\chi_{XX,mn}^{(1)}$ and $\Delta\chi_{YY,mn}^{(2)}$, occur for the parallel domains between C2 and C6 than for the domains between C2 and C4 as well as C2 and C5. It is also noted in Table VI that the two-body increments of the correlation energies are comparably small for $\Delta\varepsilon_{C2C6}$ (-0.00081 a.u.) and $\Delta\varepsilon_{C2C4}$ (-0.00056 a.u.). Therefore the increments of optical tensors have a far more pronounced angular dependence on local domains with spatial orientations than those of correlation energies.

TABLE VI. The domain distance and the two-body increments of the correlation energy $\Delta\varepsilon_{mn}$ as well as the optical tensors for the local domains m and n within the domain space C (in a.u.).

Local domain pairs (m, n)	$\Delta\varepsilon_{mn}$	$\Delta\chi_{XX,mn}^{(1)}$	$\Delta\chi_{YY,mn}^{(1)}$ [$\Delta\chi_{ZZ,mn}^{(1)}$]	$\Delta\chi_{XXX,mn}^{(2)}$	$\Delta\chi_{YYY,mn}^{(2)}$ [$\Delta\chi_{XZZ,mn}^{(2)}$]	$\Delta\chi_{YYY,mn}^{(2)}$
(C2, C6)	-0.00081	1.99	0.16	42.39	15.16	10.66
(C2, C4)=(C2, C5)	-0.00056	0.94	-0.81	1.89	-2.74	7.99

C. Weight factors for increments of optical tensors

In view of the tensorial properties of the increments of optical coefficients, the weight factors in the incremental expansion, i.e., the prefactors weighting the equivalent increments, need to be calculated with care. The weight factors for the increments of correlation energies may not be applicable to those of optical tensors without redistributions. The reason is that the increments of optical tensors can show a varied symmetry different from those of correlation energies. Let us give one example in the case of the domain space C of the $\text{Ga}_4\text{As}_4\text{H}_{18}$ cluster. According to the C_3 rotational point symmetry along the principal axis containing the Ga1-As5 bond, the contribution of one- and two-body increments of correlation energies adds up as follows:

$$\sum_{m \in D} \varepsilon_m = 3\varepsilon_{C1} + \varepsilon_{C3} + 3\varepsilon_{C4}, \quad (9)$$

$$\sum_{m < n \in D} \Delta\varepsilon_{mn} = 3\Delta\varepsilon_{C1,C2} + 3\Delta\varepsilon_{C1,C3} + 3\Delta\varepsilon_{C1,C5} + 6\Delta\varepsilon_{C1,C4} + 3\Delta\varepsilon_{C3,C4} + 3\Delta\varepsilon_{C4,C5}. \quad (10)$$

For scalar correlation energies, the two-body domain of C1-C2 is identical to C1-C7 and C2-C7, C1-C3 to C2-C3 and C7-C3, C1-C5 to C2-C6 and C7-C4, C1-C4 to C1-C6, C2-C4, C2-C5, C7-C5 and C7-C6, C3-C4 to C3-C5 and C3-C6, and C4-C5 to C4-C6 and C5-C6. However, if the increments of optical tensors are considered, say, for the linear coefficients $\sum_{m < n \in D} \Delta\chi_{XX,mn}^{(1)}$ and $\sum_{m < n \in D} \Delta\chi_{YY,mn}^{(1)}$, and if the X axis is in line with the C3 bond (i.e., the principal axis) and the Y axis lies in the C2-C3-C6 mirror plane (cf. Fig. 1) in the Cartesian coordinate system, the corresponding one- and two-body increments are in turn expressed as

$$\sum_{m \in D} \chi_{XX,m}^{(1)} = 3\chi_{XX,C1}^{(1)} + \chi_{XX,C3}^{(1)} + 3\chi_{XX,C4}^{(1)}, \quad (11)$$

$$\sum_{m \in D} \chi_{YY,m}^{(1)} = 2\chi_{YY,C1}^{(1)} + \chi_{YY,C2}^{(1)} + \chi_{YY,C3}^{(1)} + \chi_{YY,C6}^{(1)} + 2\chi_{YY,C4}^{(1)}, \quad (12)$$

$$\begin{aligned} \sum_{m < n \in D} \chi_{XX, mn}^{(1)} &= 3\Delta\chi_{XX, C1C2}^{(1)} + 3\Delta\chi_{XX, C1C3}^{(1)} + 3\Delta\chi_{XX, C1C5}^{(1)} \\ &+ 6\Delta\chi_{XX, C1C4}^{(1)} + 3\Delta\chi_{XX, C3C4}^{(1)} \\ &+ 3\Delta\chi_{XX, C4C5}^{(1)}, \end{aligned} \quad (13)$$

$$\begin{aligned} \sum_{m < n \in D} \Delta\chi_{YY, mn}^{(1)} &= 2\Delta\chi_{YY, C1C2}^{(1)} + \Delta\chi_{YY, C1C7}^{(1)} + 2\Delta\chi_{YY, C1C3}^{(1)} \\ &+ \Delta\chi_{YY, C2C3}^{(1)} + 2\Delta\chi_{YY, C2C4}^{(1)} + \Delta\chi_{YY, C2C6}^{(1)} \\ &+ 2\Delta\chi_{YY, C1C4}^{(1)} + 2\Delta\chi_{YY, C1C5}^{(1)} \\ &+ 2\Delta\chi_{YY, C1C6}^{(1)} + 2\Delta\chi_{YY, C3C4}^{(1)} \\ &+ \Delta\chi_{YY, C3C6}^{(1)} + 2\Delta\chi_{YY, C4C6}^{(1)} + \Delta\chi_{YY, C4C5}^{(1)}. \end{aligned} \quad (14)$$

The expansions at the higher order increments of higher order polarizabilities can be similarly generated and will not be discussed here. For the increments of the XX component of linear polarizabilities, since the C_3 rotational invariance still holds, the same weight factors and distributions in Eqs. (11) and (13) are expected as those of correlation energies in Eqs. (9) and (10). However, the external electric field applied along the Y direction essentially breaks the C_3 rotational invariance and leaves only the mirror operation resting in the plane determined by $C2$, $C3$, and $C6$ local domains, and the domains of $C1$ ($C7$) and $C2$ thus become nonequivalent. The same nonequivalence also applies to the domains of $C4$ ($C5$) and $C6$. The weight factors for the increments of YY components in Eqs. (12) and (14) are thereby significantly redistributed compared to those of correlation energies in Eqs. (9) and (10).

Therefore the correct weight factors for the increments of optical tensors must be obtained by reclassifying the local domains according to the polarization direction and the electric field direction in association with the total structural symmetry. For one particular increment of different optical tensors, there may be sets of weight factors due to their varied symmetric properties. Therefore these weight factors turn out to be tensorial with the same symmetry as optical tensors at the same rank. For example, the first-rank weight factors can be defined in a first-rank weight factor matrix, say, $W_{d_1 d_2 d_3 \dots d_n}^{(1)}$ for the linear polarizabilities within the n -body local domains $\{d_1, d_2, d_3, \dots, d_n\}$,

$$W_{d_1 d_2 d_3 \dots d_n}^{(1)} = \begin{pmatrix} w_{XX}^{d_1 d_2 d_3 \dots d_n} & w_{XY}^{d_1 d_2 d_3 \dots d_n} & w_{XZ}^{d_1 d_2 d_3 \dots d_n} \\ w_{YX}^{d_1 d_2 d_3 \dots d_n} & w_{YY}^{d_1 d_2 d_3 \dots d_n} & w_{YZ}^{d_1 d_2 d_3 \dots d_n} \\ w_{ZX}^{d_1 d_2 d_3 \dots d_n} & w_{ZY}^{d_1 d_2 d_3 \dots d_n} & w_{ZZ}^{d_1 d_2 d_3 \dots d_n} \end{pmatrix}. \quad (15)$$

The weight factor matrices for higher order polarizabilities have the same structures as the corresponding optical tensors. In the present case of the $\text{Ga}_4\text{As}_4\text{H}_{18}$ cluster with C_{3v} point group symmetry, the first-rank weight factor matrix for the linear polarizabilities is written as follows:

$$W_{d_1 d_2 d_3 \dots d_n}^{(1)} = \begin{pmatrix} w_{XX}^{d_1 d_2 d_3 \dots d_n} & 0 & 0 \\ 0 & w_{YY}^{d_1 d_2 d_3 \dots d_n} & 0 \\ 0 & 0 & w_{YY}^{d_1 d_2 d_3 \dots d_n} \end{pmatrix}. \quad (16)$$

For the one-body local domains $C1$, $C2$, $C3$, $C4$, $C5$, $C6$, and $C7$, the weight factor matrices are

$$\begin{aligned} W_{C1}^{(1)} = W_{C7}^{(1)} = W_{C4}^{(1)} = W_{C5}^{(1)} &= \begin{pmatrix} 3 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \\ W_{C2}^{(1)} = W_{C6}^{(1)} &= \begin{pmatrix} 3 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad W_{C3}^{(1)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned} \quad (17)$$

For the two-body local domains $C1C2$, $C1C3$, $C1C4$, $C1C5$, $C1C6$, and $C1C7$, the weight factor matrices are

$$\begin{aligned} W_{C1C2}^{(1)} = W_{C1C3}^{(1)} = W_{C1C5}^{(1)} &= \begin{pmatrix} 3 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \\ W_{C1C4}^{(1)} = W_{C1C6}^{(1)} &= \begin{pmatrix} 6 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad W_{C1C7}^{(1)} = \begin{pmatrix} 3 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned} \quad (18)$$

We finally note that the consideration of nonscalar weight factors will be crucial for the extension of the scheme to crystals.

V. CONCLUSIONS

A wave-function-based efficient correlation method in the framework of the incremental scheme to calculate optical tensors aiming at large systems has been proposed. The test calculations on the model system $\text{Ga}_4\text{As}_4\text{H}_{18}$ show that the incremental expansion of the first-order polarizabilities is well convergent with respect to the expansion order. The convergence of the second-order hyperpolarizabilities is more critical than for the first-order polarizabilities and depends on the definition of local domains. The many-body increments due to the coupling effects for the studied optical tensors among the local domains have the dependence on the relative orientation and distance of dipoles located at the local domains. The many-body corrections to the incremental expansion can be only minor if the relative orientation of corresponding local domains is unfavorable for dipole-dipole interactions. Unlike the scalar quantity of weight factors for increments of correlation energies, the weight factors for the n -body increments of optical tensors need to be reevaluated and show the same tensorial properties as optical coefficients with respect to the polarization and electric field directions. The weight factor matrices for one- and two-body increments of linear polarizabilities are formulated for the model system $\text{Ga}_4\text{As}_4\text{H}_{18}$ with C_{3v} point group symmetry.

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