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On the correlation energy of graphite

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The correlation energy per atom of a graphite layer is determined by means of increments obtained in *ab initio* calculations for aromatic molecules with various numbers of correlated localized σ and π orbitals. The resulting correlation contribution to the cohesive energy, evaluated with a double-zeta plus polarization basis set is 0.050 a.u. per C atom, which is smaller by 0.007 a.u. than the corresponding value for diamond.

I. INTRODUCTION

In two preceding papers,^{1,2} I described a simple quantum-chemical method, to be used in conjunction with *ab initio* self-consistent-field (SCF) calculations for solids,³ for determining correlation energies of crystalline systems. This method is based on local increments which are evaluated by correlating small numbers of electron pairs in localized orbitals. I have shown for diamond and crystalline silicon that using basis sets of triple-zeta quality including two sets of polarization functions (TZ2P), a fairly large portion ($\sim 85\%$) of the correlation contribution to the cohesive energy can be obtained this way. It turned out that the expansion of the correlation energy in terms of local increments is rapidly convergent in these cases, both with respect to the number of electron pairs to be correlated simultaneously and with respect to the spatial distance of localized orbitals from which simultaneous excitations have to be considered. Moreover, the individual increments proved to be well transferable quantities. Thus, few cluster calculations using standard quantum-chemical program packages were sufficient in order to get reliable estimates of the aforementioned quantities.

Of course, diamond and silicon are solids with well localizable covalent bonds and favourable features similar to those just described must not be anticipated for other systems, in particular for solids with intrinsically delocalized electrons. An example of such a system is graphite, where localized two-center σ bonds coexist with a half-filled delocalized π band. One might well ask whether the determination of local increments makes sense at all for the π band of graphite. But even if it does, slow convergence might render the concomitant incremental expansion unsuitable for practical applications. In this paper, I want to deal with these issues by performing calculations for graphite which are closely analogous to those done previously for diamond in Ref. 1. Since experimental⁴ as well as *ab initio* SCF data^{3,5,6} are available for the cohesive energy of both diamond and graphite, a critical assessment of the respective calculated correlation contributions to these quantities is possible.

In Sec. II, I give a short sketch of the method, together with computational details. Section III is devoted to the determination of local correlation-energy increments in aromatic molecules with results given separately for the intrasystem (σ as well as π) and intersystem (σ - π) pieces of

the correlation energy. The use of these values in an incremental expansion for the total correlation energy per atom of a graphite layer (2D graphite) is also discussed in Sec. III, and a comparison to corresponding results for diamond is made. The conclusions follow in Sec. IV.

II. METHOD AND COMPUTATIONAL DETAILS

Ab initio calculations using the self-consistent field, multireference configuration interaction (SCF/MRCI) program package MOLPRO^{7,8} have been performed for C_2H_4 (as the prototype of an unsaturated hydrocarbon molecule with a π bond) and a series of the simplest "graphite-like" aromatic molecules with one, two, and three rings, respectively [benzene (C_6H_6), naphthalene ($C_{10}H_8$), and phenanthrene ($C_{14}H_{10}$)]. The CC bond lengths were fixed at the experimental graphite equilibrium distance [1.421 Å (Ref. 9)]; for the CH bond lengths, the experimental C_6H_6 value was used [1.084 Å (Ref. 10)]. The "correlation-consistent" double zeta + polarization (DZP) basis set of Dunning¹¹ was employed for C; a corresponding basis set¹¹ was taken for H, but the p polarization function was left out here (if not stated otherwise), since only the correlation of CC bonds was of interest in this work. [For the largest molecule considered ($C_{14}H_{10}$), I also left out the d polarization function at those C atoms which were not directly involved in the localized orbitals contributing to a given correlation-energy increment (cf. below).] Standard SCF calculations were performed first and the resulting canonical SCF orbitals were transformed to a localized representation. Localization of the σ system (in C_s symmetry; valence electrons only) was achieved by means of the Foster-Boys¹² procedure. For the π system, I had to use a different scheme, since Foster-Boys is not unique here; bonding linear combinations of p_z atomic orbitals (AOs) (with equal coefficients) for every second pair of adjacent C atoms were projected onto the occupied SCF space [yielding for C_6H_6 , e.g., three localized " π bonds" (cf. also Fig. 1)] and the resulting nonorthogonal orbitals, spanning the occupied π space, were symmetrically orthogonalized. Size-consistent linearized-coupled-cluster [CEPA-0 (cf., e.g., Ref. 13)] calculations [any other size-extensive correlation method would have done just as well; CEPA-0 was chosen in order to facilitate comparison with other calculations for graphite and diamond (Refs. 1, 14, and 15)] were then performed in the following

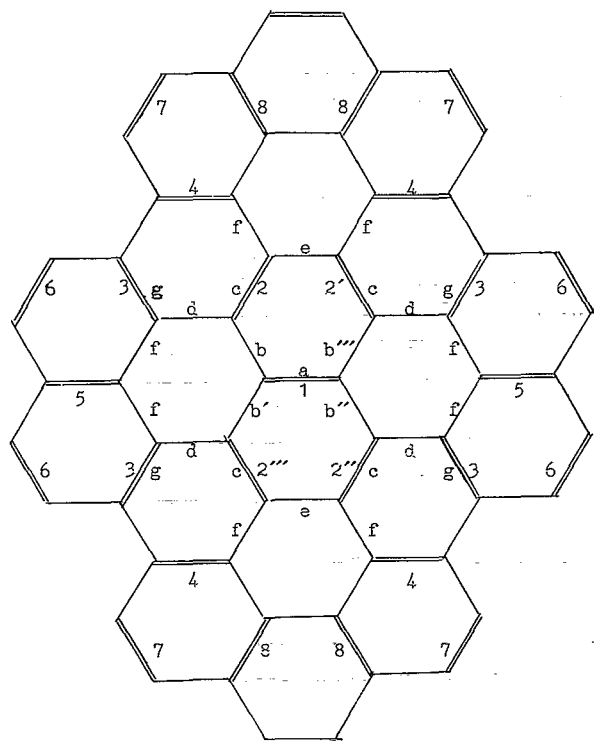


FIG. 1. Labels of localized π and σ orbitals (for use in Tables I–III). Each pair of C atoms defining the localization centers for a π LMO according to the prescription in Sec. II is marked by a double-bond line. Letters denote σ orbitals, numbers denote π orbitals.

way: in the first stage, only two electrons in a single localized orbital were correlated, while keeping all the other orbitals inactive; this yields intrabond correlation-energy increments $\Delta\epsilon_i$ for each (σ or π) bond i . Second, corresponding calculations were performed allowing for (all single and double) excitations of a four-electron “cluster” occupying a pair of localized bond orbitals with the remaining bond orbitals kept frozen again; if there were no interaction between bond orbitals i and j , the resulting correlation energy ϵ_{ij} would be a sum of the intrabond correlation energies $\Delta\epsilon_i$ and $\Delta\epsilon_j$; from the nonadditive contribution to ϵ_{ij} , we define the interbond correlation-energy increment $\Delta\epsilon_{ij} = \epsilon_{ij} - (\Delta\epsilon_i + \Delta\epsilon_j)$. Third, higher-order increments can be obtained in an analogous way; for the three-bond increment $\Delta\epsilon_{ijk}$, e.g., one has to subtract, from the correlation energy ϵ_{ijk} for six electrons in bond orbitals i , j , and k , the sum of intrabond ($\Delta\epsilon_i + \Delta\epsilon_j + \Delta\epsilon_k$) and interbond terms ($\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ki}$). Using the increments just defined, the total correlation energy can be written in the form

$$\epsilon_{\text{corr}} = \sum_i \Delta\epsilon_i + \sum_{i < j} \Delta\epsilon_{ij} + \sum_{i < j < k} \Delta\epsilon_{ijk} + \dots \quad (1)$$

Of course, such an incremental expansion makes sense only if the number of nonnegligible terms is sufficiently small, i.e., if the number of bonds to be treated simultaneously for determining nonadditive corrections is, say, three at most, and if the magnitude of all these corrections decreases rapidly with increasing spatial distance between

the bonds. This condition is met for diamond and silicon, as shown in previous work,^{1,2} but has to be checked again for unsaturated hydrocarbons. Here problems could arise not only with the long-range tails of the localized π orbitals, but also due to the fact that these orbitals occupy the same region of space as the σ bonds. While the former problem will be dealt with in Sec. III, a comparison of C_2H_4 and C_2H_6 may be useful at this point with respect to the latter problem. For C_2H_4 (calculated with a DZP basis set for both C and H), the intrabond terms $\Delta\epsilon_i$ are of the order of $\sim 3 \times 10^{-2}$ a.u. (0.030 a.u. for the CH bond, 0.022 a.u. for the CC σ bond, and 0.041 a.u. for the CC π bond); their sum, with the appropriate weight factors, yields $\sim 56\%$ of the total C_2H_4 correlation energy. The interbond increments $\Delta\epsilon_{ij}$ are of very different magnitudes—the interbond increment between the σ and the π components of the double bond (0.032 a.u.) is comparable to the intrabond ones, but those between next-nearest-neighbor (CH) bonds are $< 1 \times 10^{-3}$ a.u.; including the $\Delta\epsilon_{ij}$ in expansion (1), there is some overshooting (105%) of the C_2H_4 correlation energy. Three-bond increments are $< 3 \times 10^{-3}$ a.u., and accounting for them, one obtains 99.7% of $E_{\text{corr}}(\text{C}_2\text{H}_4)$ now with Eq. (1). Increments involving the π bond are found to be consistently larger than corresponding ones for the σ bond, but the ratio, at the three-bond level, of the largest increments for C_2H_4 and C_2H_6 is not more than 2, and, indeed, the convergence of the incremental expansion for C_2H_6 [59%, 104%, and 100.5%, at the one-, two-, and three-bond levels, respectively (cf. Ref. 1)] is not very different from that for C_2H_4 .

Let me now come to another critical point of the present work, which concerns the use of increments determined for small molecules in applications for solids. How good is the transferability of the increments from small molecules and clusters to solids? How sensitive are they with respect to “surface” effects? I have shown in Refs. 1 and 2 that the transferability is excellent in the case of diamond and nearly as good for silicon, but now we have to consider π bond orbitals with nonnegligible tails at neighboring atoms instead of the well-localizable σ bonds. It is clear that in order to account for these tails, the clusters used should be thus large (and the increments derived from them chosen in such a way) that the π bond orbitals involved are “inner” orbitals, with inclusion of at least the four next-neighbour C atoms to the two atoms acting as “localization centers.” As this condition is only partially met with the small aromatic molecules of this work, we have to study carefully, in Sec. III, the concomitant transferability defects.

III. RESULTS AND DISCUSSION

A. σ correlation energy

Local increments determined for CC σ bonds according to the prescription of the previous section are listed in Table I (cf. also Fig. 1). When for a given increment various choices are possible in one of the source molecules, that one was selected where the σ orbital (or pair/triple of such orbitals) was most graphite-like, i.e., had the largest

TABLE I. Correlation-energy increments for σ bonds and the resulting estimate for the contribution of the σ system to the correlation energy per atom E_{corr} of 2D graphite. (All quantities are in atomic units.)

Orbitals ^a	Weight ^b	C ₂ H ₄ ^c	C ₆ H ₆ ^c	C ₁₀ H ₈ ^c	C ₁₄ H ₁₀ ^c
<i>a</i>	1.5	-0.021 178	-0.022 040	-0.022 526	-0.022 690
<i>a,b</i>	3.0	...	-0.008 725	-0.009 007	-0.008 939
<i>a,c</i>	3.0	...	-0.000 687	-0.000 695	-0.000 701
<i>a,d</i>	3.0	-0.000 692	(-0.000 692) ^d
<i>a,e</i>	1.5	...	-0.000 259	-0.000 263	(-0.000 263) ^d
<i>a,f</i>	6.0	-0.000 115	(-0.000 115) ^d
<i>a,g</i>	3.0	-0.000 119	(-0.000 119) ^d
<i>a,b,b'</i>	1.0	0.000 354	0.000 344
$E_{\text{corr},1}$ ^e		-0.031 767	-0.033 060	-0.033 789	-0.034 035
$E_{\text{corr},2}$ ^f		...	-0.061 685	-0.066 413	-0.066 473
$E_{\text{corr},3}$ ^g		-0.066 059	-0.066 129

^aOrbital(s) involved in a given increment (for labeling, cf. Fig. 1).^bWeight factor of the increments in the expansion of the correlation energy per atom of 2D graphite.^cSource molecule used for determining the increment.^dValues in parentheses taken from C₁₀H₈, since expected changes $\sim 1 \times 10^{-5}$ a.u.^eTruncation of the incremental expansion after intrabond terms.^fTruncation of the incremental expansion after two-bond terms.^gTruncation of the incremental expansion after three-bond terms.

number of surrounding bonds. Included in the table are interbond increments up to third-nearest neighbors; the magnitude of the latter is, with $\sim 1 \times 10^{-4}$ a.u., by two orders smaller than that of the leading intrabond term ($\sim 2 \times 10^{-2}$ a.u.). Of the three-bond increments, only a single one, that between three adjacent σ bonds (with a common vertex) surpasses 10^{-4} a.u. Thus, the incremental expansion of the correlation energy for σ bonds is (at least) as rapidly convergent as in the case of diamond,¹ although the hybridization (sp^2 vs sp^3) is different in the two cases. The transferability of the increments, i.e., their dependence on the source molecules from which they were extracted is slightly worse than for diamond, but can still be considered as very good. Changes of some 10^{-4} a.u. arise for the intrabond term and the interbond one for adjacent bonds when going from C₆H₆ to C₁₄H₁₀, while changes in the other increments are below 10^{-4} a.u.

Estimates for the σ piece of the correlation energy per atom of a two-dimensionally infinite graphite layer (2D graphite) obtained by inserting the σ bond increments discussed above, with the appropriate weight factors into the incremental expansion (1) are also listed in Table I. Results are given separately for truncating the expansion at the intrabond, two-bond, and three-bond levels, respectively, and for the various source molecules which were used for deriving the increments. Note that changes between these values arise from the fact that not all the relevant increments are defined for the smaller molecules. From considering the values for the larger source molecules (C₁₀H₈ and C₁₄H₁₀), however, one finds that the σ correlation energy of graphite can be estimated, with an uncertainty of a few parts in 10^{-4} a.u., to -0.0661 a.u.

B. π correlation energy

The pattern of localized π orbitals, chosen for spanning the occupied Hartree-Fock (HF) space, is depicted by means of double-bond lines in Fig. 1. Increments for

(and between) such bonds have been determined (cf. Table II) again for various source molecules. As in Sec. III A, the most graphite-like possibility was chosen in any case. It is seen that the magnitude of the intrabond contribution is much the same as in the σ case and the convergence pattern of the interbond terms is also quite similar, i.e., including increments up to third-nearest neighbors is sufficient for an accuracy of $\sim 10^{-4}$ a.u. (with respect to individual terms). This looks surprising, at first glance, considering the fact that the π orbitals are much less well-localized than the two-center σ bonds. The explanation is, of course, that the distances between corresponding bond midpoints (centers of orbital charge) are different in the two cases. σ bonds exist between every pair of C atoms, while the localized π orbitals for the half-filled π band center only around every second pair of neighboring C atoms. Thus, the weaker localization of the π orbitals is compensated effectively by their larger interorbital distances. It is clear, on the other hand, that inclusion of increments up to third-nearest neighbors means larger clusters for the π than for the σ case, i.e., the computational effort to determine them in quantum-chemical calculations for finite source molecules is larger. There is another unpleasant feature here (already indicated in Sec. II)—the transferability of the π increments from one source molecule to another one is definitely worse than for σ increments. The number of C atoms surrounding the two atoms acting as localization centers for a given localized π orbital seems to play a decisive role here. The π intrabond increment changes by a factor of 1.8 when going from C₂H₄ (no neighbors) to C₆H₆ (two neighbors): the change is smaller (a factor of 1.25) from C₆H₆ to C₁₀H₈ (four neighbors), and is near zero (a factor of 1.05 or $\sim 1 \times 10^{-3}$ a.u. in absolute magnitude) from C₁₀H₈ to C₁₄H₁₀, where the inner π orbital has the “correct” number of nearest

TABLE II. Correlation-energy increments for localized π orbitals and the resulting estimate for the contribution of the π system to the correlation energy per atom E_{corr} of 2D graphite. (All quantities are in atomic units.)

Orbitals ^a	Weight ^b	C ₂ H ₄ ^c	C ₆ H ₆ ^c	C ₁₀ H ₈ ^c	C ₁₄ H ₁₀ ^c
1	0.5	−0.040 746	−0.022 513	−0.017 985	−0.018 860
1,2	1.0	...	−0.015 157	−0.010 377	−0.007 075
1,3	1.0	−0.001 420	−0.001 041
1,4	1.0	−0.001 327	−0.000 896
1,5	0.5	−0.000 362
1,6 ^d	2.0	−0.000 230
1,7	1.0	−0.000 268
1,2,2'	0.333	...	−0.002 201	−0.000 864	−0.000 441
$E_{\text{corr},1}$ ^e		−0.020 373	−0.011 257	−0.008 993	−0.009 430
$E_{\text{corr},2}$ ^f		...	−0.026 414	−0.022 117	−0.019 351
$E_{\text{corr},3}$ ^g		...	−0.027 147	−0.022 405	−0.019 498

^aOrbital(s) involved in a given increment (for labeling, cf. Fig. 1).

^bWeight factor of the increments in the expansion of the correlation energy per atom of 2D graphite.

^cSource molecule used for determining the increment.

^dEquivalent to increment 1,8 for symmetry reasons.

^eTruncation of the incremental expansion after intrabond terms.

^fTruncation of the incremental expansion after two-bond terms.

^gTruncation of the incremental expansion after three-bond terms.

neighbors (four as in 2D graphite) in both cases and differences arise with respect to second-nearest neighbors only.

As a consequence of such transferability defects, which do not only arise for the intrabond increment but for the interbond ones as well, the π piece of the correlation energy of 2D graphite obtained by means of the incremental expansion (1) changes still by 3×10^{-3} a.u. (truncation after three-bond terms) when replacing C₁₀H₈ by C₁₄H₁₀ as a source molecule for the derivation of the individual increments. On the other hand, we expect the C₁₄H₁₀ value to be accurate to $\sim 1 \times 10^{-3}$ a.u., since here the two most important increments (the intrabond one and the interbond one between adjacent bonds) were determined from π orbitals with the correct nearest-neighbor surroundings. Another indication supporting the above estimate of accuracy of our final value (0.0195 a.u.) for the π correlation energy of graphite is the following: in a delocalized system, such as the π system of aromatic molecules (and graphite), the total correlation energy should scale linearly with the number of atoms involved. In fact, evaluating the total molecular π correlation energy per atom, we get 0.0204 a.u. for C₂H₄, 0.0192 a.u. for C₆H₆, and 0.0198 a.u. for C₁₀H₈, i.e., quite stable values which differ by $\sim 1 \times 10^{-3}$ a.u. only, from each other and from the value obtained with the incremental expansion discussed above.

C. σ - π correlation energy

For determining the σ - π intersystem piece of the graphite correlation energy, it is necessary to evaluate increments between a given σ bond orbital (or bond-orbital pair, etc.; cf. *a* or *a,b*,... in Fig. 1) and all combinations of π bond orbitals (1,2,... in Fig. 1). Since the overlap between localized σ and π orbitals is smaller than that between two π 's, the convergence of such a series of increments is expected to be more rapid than that found in the

previous subsection. In fact, as shown in Table III (for the C₁₄H₁₀ source molecule, e.g.), the σ - π interbond increments between third-nearest neighbors turn out to be of the order of 10^{-5} a.u. only. The single-site term involving a σ and a π bond orbital between the same C atoms (*a* and 1 in Fig. 13), on the other hand, is larger than either the corresponding pure σ or π intrabond terms.

This already gives an indication of the importance of the σ - π intersystem correlation energy for graphite, and indeed, inserting the increments together with the appropriate weight factors into the incremental expansion (1), we obtain a value of 0.0451 a.u. (per atom), which is nearly double that of the π correlation-energy piece; it is smaller, on the other hand, than the σ piece, since interbond increments between nearest neighbors play a much larger role in the latter case (0.009 vs 0.002 a.u.).

D. Total correlation energy

Table IV lists the sum of the σ , π , and σ - π contributions discussed above to the correlation energy (per atom) of 2D graphite; again the values are given for various truncation levels of the incremental expansion (1) [including up to single-site, two-, or three-site terms, respectively (here "site" refers to the midpoints of the bonds)] and for the various source molecules used for determining the individual increments. The near equality of the values for the C₆H₆ and C₁₀H₈ sources is partly fortuitous, since there is a cancellation between the increasing number of increments which can be derived for C₁₀H₈ (while not being defined in C₆H₆) and the decreasing values of individual increments when a localized π orbital with the correct number of neighboring C atoms (four instead of two) becomes available. Since all of the relevant increments are included and the most important ones (the intrabond increment as well as the interbond one between adjacent bonds) are evaluated with such graphite-like π localized

TABLE III. Correlation-energy increments involving σ as well as π LMOs and the resulting estimate for the σ - π intersystem contribution to the correlation energy per atom E_{corr} of 2D graphite. Classification of the individual increments according to the number of sites (i.e., CC pairs acting as localization centers). (All quantities are in atomic units.)

Orbitals ^a	Weight ^b	C ₂ H ₄ ^c	C ₆ H ₆ ^c	C ₁₀ H ₈ ^c	C ₁₄ H ₁₀ ^c
<i>a</i> ,1	1.5	−0.031 815	−0.027 441	−0.025 815	−0.026 271
<i>a</i> ,2	6.0	...	−0.002 757	−0.002 187	−0.001 859
<i>a</i> ,3	6.0	−0.000 305	−0.000 241
<i>a</i> ,4	6.0	−0.000 207	−0.000 140
<i>a</i> ,5	3.0	−0.000 105
<i>a</i> ,6	6.0	−0.000 055
<i>a</i> ,7	6.0	−0.000 040
<i>a</i> ,8	6.0	−0.000 028
<i>a</i> ,1,2	6.0	...	0.000 814	0.000 623	0.000 574
<i>a</i> , <i>b</i> ,1	3.0	...	0.001 928	0.001 776	0.001 766
<i>a</i> , <i>b</i> ,2 nd	3.0	0.000 109	0.000 091
<i>a</i> , <i>b</i> , <i>b</i> ',1 ^c	1.0	−0.000 171	−0.000 179
$E_{\text{corr},1}$ ^f		−0.047 723	−0.041 162	−0.038 723	−0.039 407
$E_{\text{corr},2}$ ^g		...	−0.047 036	−0.045 851	−0.045 158
$E_{\text{corr},3}$ ^h		−0.045 695	−0.045 064

^aOrbitals involved in a given increment (for labeling, cf. Fig. 1); the choice of the LMOs in a given source molecule is made so as to maximize the number of nearest-neighbor C atoms for the π LMO(s).

^bWeight factor of the increments in the expansion of the correlation energy per atom of 2D graphite.

^cSource molecule used for determining the increment.

^dMagnitude of increments *a*,2,2', and *a*,*b*,2 below 10^{-4} a.u.

^eMagnitude of increments *a*,1,2,2' and *a*,*b*,1,2 below 10^{-4} a.u.

^fTruncation of the incremental expansion after single-site terms.

^gTruncation of the incremental expansion after two-site terms.

^hTruncation of the incremental expansion after three-site terms.

molecular orbitals (LMOs) when C₁₄H₁₀ is used as a source molecule, we do not expect changes of more than $\sim 2 \times 10^{-3}$ a.u. for the corresponding estimate of the graphite correlation energy (0.131 a.u.) when going to larger source molecules.

Let us compare this result with that for diamond. With the same method, the same basis set, and the same criteria for truncating the incremental expansion (1), I obtained a correlation energy of 0.138 a.u. per atom for diamond. Subtracting the corresponding value for the atomic correlation energy (0.081 a.u.), we get correlation-energy contributions to the cohesive energy per atom of 0.050 a.u. for 2D graphite and 0.057 a.u. for diamond. This yields a differential correlation effect of 0.007 a.u. in favor of diamond. There is qualitative agreement between this result and density-functional calculations of the Torino group⁶ using various correlation-energy density functionals—that of Colle and Salvetti¹⁶ yields a differential effect of 0.008 a.u., those of Perdew^{17,18} give 0.012 a.u. Calculations with the “local Ansatz” of Stollhoff and Fulde^{14,19} seem to go to

the opposite side: here, graphite is found to have a correlation energy per atom larger in magnitude by 0.009 a.u. than obtained previously for diamond,¹⁵ but note that the treatment is not entirely comparable in the two cases. No comparison is possible with the quantum Monte Carlo (QMC) results for diamond and graphite of Louie and co-workers²⁰ since no Hartree–Fock energy for graphite was given there.

Let us now come to the comparison with experiment. The experimental cohesive energies for 3D graphite and diamond are nearly the same, i.e., 0.271 and 0.270 a.u./atom, respectively.⁴ Accounting for zero-point vibrational energies,²¹ the numbers are 0.277 a.u./atom in both cases. SCF cohesive energies are 0.203 and 0.199 a.u./atom, respectively.⁶ Thus, the “experimental” correlation contributions are 0.074 a.u./atom for graphite and 0.078 a.u./atom for diamond. With our calculated numbers, we recover 68% and 73% of these values. The percentages are relatively low in both cases. The main reason for that is the relatively small DZP basis set used. It has been shown^{1,2} that extension to basis sets of triple-zeta quality with two sets of *d* and one set of *f* polarization functions (TZ2P) leads to considerably higher percentages (85% in the case of diamond). Our DZP calculation yields a lower percentage for graphite than for diamond, but the deviation is so small in absolute value (0.004 a.u./atom) that it may well be caused by SCF and post-SCF basis-set errors as well as uncertainties mentioned above for the incremental expansion of the correlation energy. Note, moreover, that the experimental (and SCF) data refer to 3D graphite, while

TABLE IV. Total correlation energy per atom of 2D graphite (in atomic units) from an expansion in terms of increments including (a) single-site terms; (b) up to two-site terms; (c) up to three-site terms.

	C ₂ H ₄ ^a	C ₆ H ₆ ^a	C ₁₀ H ₈ ^a	C ₁₄ H ₁₀ ^a
(a)	−0.052 140	−0.085 478	−0.081 504	−0.082 872
(b)	−0.099 863	−0.135 134	−0.134 380	−0.130 981
(c)	...	−0.135 867	−0.134 158	−0.130 690

^aSource molecule used for determining the increment.

our calculations concern a single graphite layer; thus, the (unknown) correlation piece of the interlayer binding energy [the total effect is 0.002 a.u./atom (Ref. 22)] also contributes to the above deviation.

IV. CONCLUSIONS

The expansion of the correlation energy into local increments has proven to be a reliable means of calculating correlation energies, even in a case where such an expansion would not be expected to work *a priori*, i.e., for a solid with delocalized electrons such as graphite with its half-filled π band. The resulting correlation contribution to the cohesive energy, evaluated for a graphite layer using a basis set of double-zeta quality with a (single) d polarization function, is with 0.050 a.u./atom in reasonable agreement with the "experimental" value for the graphite crystal (0.074 a.u./atom). The near equality of the experimental correlation contributions in graphite and diamond is well reproduced in our calculations ($\Delta E_{\text{corr}} = 0.007$ vs 0.004 a.u./atom, in both cases in favor of diamond).

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