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Correlation energy of diamond

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The correlation energy of diamond is determined by means of increments obtained in *ab initio* calculations for localized C-C bond orbitals and for pairs and triples of such bonds. The resulting correlation contribution to the cohesive energy is -0.129 a.u., which is approximately 85% of the experimental value.

I. INTRODUCTION

Quantum-chemical *ab initio* self-consistent-field (SCF) calculations can be routinely performed nowadays for quite large molecules (using direct SCF programs[1,2]), and even for solids (using the newly developed CRYSTAL program of Pisani and co-workers[3]). With respect to the post-Hartree-Fock treatment, the situation is less favorable, however: the need for large one-particle basis sets, the high-level correlation treatment needed for quasidegenerate cases, and the size-extensivity requirement restrict conventional *ab initio* methods to systems of much smaller size than in the Hartree-Fock (HF) case.

A way to (partially) overcome these difficulties is by using local operators to restrict both the virtual space and the number of correlated pairs (and/or the level of correlation treatment), cf. e.g., Refs. 4–8. When, in addition, translational symmetry is exploited [as in the "local ansatz" (LA) (Ref. 9)], one may even treat electron correlation in solids. In contrast to density-functional-type methods, i.e., those methods which are most often used in solid-state calculations presently, it is possible with LA (as with quantum-chemical *ab initio* methods in general) to systematically improve results towards the exact ones. Unfortunately, the actual LA results which have been obtained so far for diamond (0.47 a.u. for the cohesive energy, E_{coh}, per unit cell[9]) exhibit errors of similar magnitude as the local-density ones [0.63 a.u. (Refs. 10 and 11); the experimental value is 0.553 a.u. (Ref. 12)]. The correlation contribution to the diamond E_{coh}, in particular, is only 50% of the exact value (0.077 vs $\sim$0.15 a.u.), in the LA calculations. Responsible for these deficiencies are most probably limitations of the one-particle basis set as well as of the configuration selection procedure.

As an attempt to improve on the above results, I want to discuss the possibility, in this paper, to combine the idea of local correlation with that of evaluating properties by means of increments. For diamond, specifically, this means correlating a single localized C-C bond orbital first and then determining "two-body" and "three-body" corrections, etc., by simultaneously correlating pairs, triples, etc., of C-C bonds. This way, the number of orbitals to be correlated at a time can be kept to a minimum. Moreover, provided that there is a good transferability of the increments, the latter can be determined for small molecules using standard quantum-chemical *ab initio* programs and large basis sets. Of course, the usefulness of such a method depends on the good convergence of the "many-body" expansion for the increments. It will be shown to be quite rapid for diamond, in this paper, but further experience for other covalent (and ionic) solids is clearly needed.

The idea to evaluate properties by means of local increments has a long tradition in chemistry, especially for hydrocarbons, cf. e.g., Refs. 13–16 [and has been even used for the "intra-atomic" part of the correlation energy of solids, within the LA (Ref. 9)]. I therefore first consider a simple estimate of the diamond correlation energy, which is in the spirit of this old chemical tradition,[15,16] in Sec. II. In Secs. III and IV this estimate will be refined and put on a more solid basis; in addition, the transferability, the basis-set dependency, and the convergency of the increments (with respect to the distance of the C-C bonds) will be investigated. The conclusions follow in Sec. V.

II. A SIMPLE ESTIMATE

The following argument has been used by a number of workers, cf. e.g., Refs. 15 and 16, in the context of molecules, but it can be easily applied to a solid like diamond, too: Let $E_{\text{at}}(\text{CH}_4)$ and $E_{\text{at}}(\text{C}_2\text{H}_6)$ be the atomization energies of the respective molecules; then we can attribute to each of the localized C-H bonds in CH_4 an energy contribution

$$\Delta E(\text{CH}) = \tfrac{1}{4} E_{\text{at}}(\text{CH}_4) \; ; \tag{1}$$

assuming the contribution per C-H bond to be the same in C_2H_6 as in CH_4, we can estimate the energy of the C-C single bond as

$$\Delta E(\text{CC}) = E_{\text{at}}(\text{C}_2\text{H}_6) - 6\Delta E(\text{CH}) \; . \tag{2}$$

In diamond, there are four C-C bonds per unit cell, so the cohesive energy can be readily calculated from Eq. (2):

$$E_{\text{coh}} = 4\Delta E(\text{CC}) \; . \tag{3}$$

Of course, Eq. (3) may be evaluated either from experimental or theoretical data, and, in the latter case, either at the HF or at correlated levels, using various basis sets, thus yielding detailed estimates of different contributions to E_{coh}.

Let us see what we get this way. From the values listed in Table I, it is apparent that the SCF estimate of E_{coh} converges to ~ 0.39 a.u., with increasing basis-set quality. The latter value is quite close to the most recent SCF result of 0.396 a.u., obtained for E_{coh} in calculations for the diamond crystal.[17] Two observations may be made concerning the correlation contribution to E_{coh}: Firstly, the basis-set dependency of our estimate is considerably larger than in the SCF case; even with multiple polarization functions (*2d1f*) at the C atom, there is a 10% underestimation with respect to the (estimated) basis-set limit. Secondly, even in the basis-set limit, there is a significant underestimation with respect to experiment: The total E_{coh} for diamond is 0.553 a.u. per unit cell (measured value extrapolated to $T = 0$ K, corrected for zero-point vibration[12]); subtracting an HF value of ~ 0.40 a.u. yields an "experimental" correlation contribution of ~ 0.15 a.u. which is to be compared to the value of 0.130 a.u. from Table I. However, although Eq. (3) works less well in the correlated than in the SCF case, it should be noted that even there it is competitive with sophisticated solid-state calculations: With the local ansatz, a correlation contribution to E_{coh} of 0.077 a.u. has been directly determined for diamond, and (estimated) corrections for limitations in the one- and many-particle basis sets yield a final value of 0.126 a.u.;[9] a variational quantum Monte Carlo (QMC) calculation for diamond covering correlation by means of a Jastrow factor leads to a correlation contribution of 0.118 a.u.[11]

In view of these results, we have to answer two questions: (a) Why does the simple estimate Eq. (3) work so surprisingly well for diamond, although it is derived from data on the two most simple hydrocarbon compounds and apparently includes information on a single C-C bond only? (b) Which correlation effects are still missing in this estimate? The answers will evolve from a more detailed and rigorous treatment of correlation energy increments for CH_4 and C_2H_6 which will be considered in the next section. This treatment, moreover, shall give us a lead on how to evaluate the diamond correlation energy by means of a well-defined incremental expansion.

TABLE I. Estimate of the cohesive energy of diamond according to Eq. (3). SCF and correlation contributions, $E_{\mathrm{coh,SCF}}$ and $E_{\mathrm{coh,corr}}$, are listed separately. (All energies in atomic units.)

	$E_{\mathrm{coh,SCF}}$	$E_{\mathrm{coh,corr}}$
DZP[a]	0.379	0.096[b]
TZ2P[c]	0.383	0.113[d]
TZ2P-ANO[e]		0.117[f]
limit[g]	0.387	0.130[h]

[a] Valence double-ζ basis set $(9s4p1d)/[3s2p1d]$ for C, $(4s1p)/[2s1p]$ for H (Ref. 21).

[b] Correlation level: CEPA-0; $1s^2$ cores of the C atoms frozen.

[c] Valence triple-ζ basis set $(10s5p2d1f)/[4s3p2d1f]$ for C, $(5s2p1d)/[3s2p1d]$ for H (Ref. 21).

[d] Correlation level: CEPA-0; $1s^2$ cores of the C atoms frozen.

[e] Value derived from correlated data of Refs. 26 and 27 [an atomic natural orbital (ANO) basis set of triple-ζ quality was employed], subtracting our TZ2P SCF result (second row, first entry).

[f] Correlation level: modified coupled-pair functional.

[g] Values derived using HF limits from Refs. 15 and 28 and experimental data from Refs. 26 and 27 (and references cited therein).

[h] Experimental data corrected for zero-point energies minus HF limit values.

III. WHY IT WORKS

In order to see why the simple estimate considered in the preceding section yields quite reliable results, we systematically calculated correlation energy increments for CH_4 and C_2H_6, i.e., for the two molecules which the estimate is derived from. All calculations were done with the MOLPRO SCF-CMRCI (where CMRCI denotes internally contracted multiconfiguration-reference configuration interaction) *ab initio* program package.[18,19] Standard bond lengths for C-H and C-C single bonds [$r_{\mathrm{CH}} = 1.102$ Å, $r_{\mathrm{CC}} = 1.544$ Å (Ref. 20)] and tetrahedral bond angles were used; the staggered geometry was chosen for C_2H_6. The valence double-ζ plus polarization (DZP) correlation-consistent basis sets for C and H by Dunning[21] ($(9s4p1d)/[3s2p1d]$ for C, $(4s1p)/[2s1p]$ for H) were employed. SCF calculations were first performed, and the resulting valence orbitals were localized according to Foster and Boys,[22] yielding C-H and C-C bond orbitals, respectively. We then performed a series of size-extensive linearized-coupled-cluster (CEPA-0) (where CEPA denotes coupled electron pair approximation) calculations (cf. e.g., Ref. 23), correlating 1,2,3,... bond orbitals at a time and keeping the rest of the localized molecular orbitals (LMO) inactive in each case. From the resulting correlation energies we determined increments: the "one-body" contributions $\Delta\epsilon_i$ directly as the correlation energies for a single bond orbital i; the "two-body" corrections $\Delta\epsilon_{ij}$ by subtracting, from the correlation energy obtained when simultaneous excitations from two bond orbitals i,j are allowed for, the sum of one-body terms $\Delta\epsilon_i + \Delta\epsilon_j$; the "three-body" correction $\Delta\epsilon_{ijk}$ analogously, by subtracting, from the correlation energy of the triple i,j,k of bond orbitals, the sum of one- and two-body terms $\Delta\epsilon_i + \Delta\epsilon_j + \Delta\epsilon_k + \Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ki}$, etc. The increments evaluated this way are compiled in Table II.

The following observations can be made: (a) While three-body increments are very small (non-negligible only for three adjacent bonds), two-body increments are of the same order of magnitude as the one-body values; (b) two-body increments for next-nearest neighbors are by about an order of magnitude smaller than those for an adjacent pair; (c) corresponding increments in CH_4 and C_2H_6 are practically identical (to ~ 1 %); (d) the increments for C-C and C-H bonds are quite similar (to ~ 10–20 %). It is clear from these observations that an expansion of the correlation energy of saturated hydrocarbons by means of increments makes sense indeed: The expansion is rapidly convergent, and the increments themselves have a very good transferability. The total correlation energies for

TABLE II. Correlation energy increments (in atomic units) for localized bond orbitals in CH_4 and C_2H_6 (cf. text).

CH_4	Bond orbitals	Increment
$\Delta\epsilon_i$	C-H	−0.030 119
$\Delta\epsilon_{ij}$	C-H,C-H	−0.012 608
$\Delta\epsilon_{ijk}$	C-H,C-H,C-H	0.001 472

C_2H_6	Bond orbitals	Increment
$\Delta\epsilon_i$	C-H	−0.030 293
	C-C	−0.025 613
$\Delta\epsilon_{ij}$	C-H,C-H[a]	−0.012 497
	C-H,C-C	−0.011 934
	C-H,C-H[b]	−0.001 099
	C-H,C-H[c]	−0.000 973
$\Delta\epsilon_{ijk}$	C-H,C-H,C-H[d]	0.001 420
	C-H,C-H,C-C[d]	0.001 339
	C-H,C-C,C-H[b]	−0.000 006
	C-H,C-C,C-H[c]	0.000 089

[a] Adjacent bonds.

[b] Nonadjacent C-H bonds, *trans* position.

[c] Nonadjacent C-H bonds, *gauche* position.

[d] Bonds with common vertex.

CH_4 and C_2H_6 obtained by correlating all valence orbitals are $-0.190\,346$ and $-0.349\,883$ a.u., respectively; with a sum of one-body increments (with appropriate weight factors) one gets 63% and 59% of these values, including two-body increments yields 103% and 104%, and truncating the expansion after the three-body terms gives $\sim 100\%$ in both cases.

Turning back now to the simple estimate of the preceding section, we may conclude that the quantities $\Delta E(\mathrm{CH})$ and $\Delta E(\mathrm{CC})$ defined there cannot be considered as properties of a single bond; they contain large interbond contributions, at least as far as their correlation part, ΔE_{corr}, is concerned. In fact, inserting our incremental expansion for $\Delta E_{\mathrm{corr}}(\mathrm{CH})$ and $\Delta E_{\mathrm{corr}}(\mathrm{CC})$ into Eqs. (1) and (2), we find that $\Delta E_{\mathrm{corr}}(\mathrm{CC})$ would even assume the wrong sign, if two- and three-body increments were neglected. As all the interbond contributions for CH_4 and C_2H_6 are more or less related to C-H bonds, the near equality of increments for C-H bonds with analogous ones for C-C bonds, which is apparent from Table II (cf. also Tables III–V below), is crucial for the success of the estimate Eq. (3). In fact, assuming this equality to hold exactly, it is easy to show that then (and only then) we get an expression for the diamond cohesive energy with Eq. (3) which contains all the two- and three-body increments up to next-nearest neighbors with just the right weight factors, i.e., those appropriate for diamond. Increments for more distant bonds are not accounted for, however, not even approximately, by Eq. (3); as will be shown in the next section, this may be the main source for the underestimation of the correlation contribution to E_{coh} in Table I.

IV. A SYSTEMATIC MANY-BODY EXPANSION

In view of the fact that the "many-body" expansion in terms of (intra- and inter-) bond increments is quite successful for CH_4 and C_2H_6, as shown by the results of Sec. III, we now try to apply it directly to the determination of the correlation energy for diamond. The best way, of course, would be to extract the relevant data from solid-state calculations, but since the increments exhibit excellent transferability (cf. results in Table II; further support is given by Tables III and IV below), we felt justified to determine them from calculations for suitable hydrocarbon molecules; the obvious advantage was that we could use standard quantum-chemical programs for that purpose. We performed calculations using the SCF-CMRCI program package MOLPRO (Refs. 18 and 19) for C_2H_6 (ethane), C_3H_8 (propane), C_4H_{10} (*n*-butane), various conformers of C_5H_{12} (*n*-pentane), C_6H_{12} (cyclohexane), and C_6H_{14} (2,3-dimethylbutane). Standard geometries were used in all cases ($r_{\mathrm{CC}}=1.544$ Å, $r_{\mathrm{CH}}=1.102$ Å,[20] tetrahedral angles). The basis sets employed in the calculations were of DZP quality for C ($(9s4p1d)/[3s2p1d]$) and of DZ quality for H ($(4s)/[2s]$);[21] polarization functions were omitted for H, because no C-H bonds needed to be correlated; for investigating the basis-set dependency of the C-C bond increments, we also performed calculations for C_3H_8 with a $(10s5p2d1f)/[4s3p2d1f]$ basis set of valence triple-ζ quality (TZ2P) for C.[21] Using Foster-Boys[22] LMO, various CEPA-0 calculations were made for the above molecules, correlating single C-C bond orbitals, pairs, triples, etc. of them, while allowing no excitations from other LMO; no restrictions, on the other hand, were introduced in the virtual space. The intra- and interbond increments were then determined from the resulting correlation energies by much the same procedure as described in Sec. III, i.e., for determining a "three-body" increment, e.g., the correlation energy for simultaneous excitations from a chosen triple of C-C orbitals was used, and the sum of relevant one- and two-body increments involving that triple was subtracted. The increments obtained this way are compiled in Tables III–V.

It is seen again that the increments are excellently transferable; differences between values from the various source molecules are $<10^{-4}$ a.u. The main contributions ($>10^{-2}$ a.u.) come from the one-body term and the two-body correction between nearest-neighbor bonds. Further two-body terms up to third-nearest-neighbor bonds

TABLE III. C-C intrabond increment, $\Delta\epsilon_i$, from CEPA-0 calculations with DZP basis. (Atomic units are used throughout.)

Increment	Source molecule; C-C bond involved	Weight factor for diamond
−0.025 208	C_2H_6	4
−0.025 241[a]	C_3H_8	
−0.025 272	$C_4H_{10}^{b,c}$	
−0.025 290	$C_6H_{14}^{d,c}$	

[a] Corresponding value using TZ2P basis set is −0.030 524.

[b] All C-C bonds in a single plane.

[c] Increment refers to central C-C bond.

[d] $(CH_3)_2CH\text{-}CH(CH_3)_2$, with the hydrogens of the CH groups in *trans* position.

TABLE IV. C-C interbond increments, $\Delta\epsilon_{ij}$, from CEPA-0 calculations with DZP basis. (Atomic units are used throughout.)

Increment	Source molecule; C-C bonds involved	Weight factor for diamond
−0.011 042[a]	C_3H_8	12
−0.011 031	C_4H_{10}[b,c]	
−0.011 006	C_6H_{14}[d,e,c]	
−0.000 941	C_4H_{10}[b,f]	12
−0.000 932	C_6H_{14}[d,f]	
−0.000 837	C_6H_{12}[g,h]	24
−0.000 847	C_6H_{14}[d,h]	
−0.000 211	C_5H_{12}[b,i]	12
−0.000 180	C_5H_{12}[j,i]	48
−0.000 185	C_5H_{12}[k,i]	24
−0.000 319	C_6H_{12}[g,i]	12

[a] TZ2P value is −0.013 106.

[b] All C-C bonds in a single plane.

[c] Adjacent bonds correlated.

[d] $(CH_3)_2CH\text{-}CH(CH_3)_2$, with the hydrogens of the CH groups in *trans* position.

[e] Central C-C bond involved.

[f] Second-nearest-neighbor bonds, *trans* position.

[g] $(CH_2)_6$ ring.

[h] Second-nearest-neighbor bonds, *gauche* position.

[i] Third-nearest-neighbor bonds.

[j] One of the outer C-C bonds out-of-plane.

[k] Plane of the first two C-C bonds orthogonal to that of the remaining two.

contribute with values between 10^{-3} and 10^{-4} a.u. Of the three-body terms, only a single one, that between adjacent bonds, surpasses 10^{-4} a.u. Basis effects are significant; changing from the DZP to the TZ2P basis enhances the magnitude of the increments by ~20%. Only minor effects come from the correlation method: switching from CEPA-0 to CEPA-1,[24] e.g., reduces the increments by ~2%.

Let us see now what we get employing these increments in a many-body expansion for the diamond correlation energy and its contribution to the cohesive energy (cf. Table VI). We evaluated these quantities at two levels of accuracy; firstly, by taking increments obtained with the smaller basis set (DZP) throughout, neglecting increments of magnitude $<10^{-4}$ a.u.; and secondly, replacing the largest increments ($\Delta\epsilon_i$, and $\Delta\epsilon_{ij}$ for adjacent bonds) as well as the atomic reference energy (for the evaluation of the cohesive energy) by their analogs obtained with the larger basis set (TZ2P). It is seen that the basis-set effect which is large in absolute value (0.05 a.u.) for $E_{\rm corr}$ is much smaller (0.015 a.u.), as expected, for a differential quantity like the cohesive energy. The effect of the correlation level on the cohesive energy may be assessed again by switching from CEPA-0 to CEPA-1; the resulting change is of the order ~0.001 a.u.

At the DZP level, a comparison with results from calculations using the local ansatz is possible, where a basis set of comparable quality was employed.[9] The correlation effects obtained there are substantially lower than in our calculation. Part of the difference is due to the neglect of the contributions from third-nearest neighbors in Ref. 9 (which were estimated by using a minimal basis set there), but the major part seems to come from the LA configuration selection procedure. At the TZ2P level, we get a larger correlation energy for diamond (and, incidentally, also a larger correlation contribution to the cohesive energy) than in all previous calculations using explicitly correlated wave functions (i.e., calculations with the local ansatz[9] and quantum Monte-Carlo calculations).[20] Our contribution to $E_{\rm coh}$ is smaller, on the other hand, than with the density-functional based correlation energy expression by Perdew,[17,25] which yields $E_{\rm coh,corr}=0.153$ a.u. [Note, however, that with a simple local-density-functional approximation for both exchange

TABLE V. C-C interbond increments, $\Delta\epsilon_{ijk}$, from CEPA-0 calculations with DZP basis. (Atomic units are used throughout.)

Increment	Source molecule; C-C bonds involved	Weight factor for diamond
0.001 096	C_6H_{14}[a,b]	8
−0.000 020	C_6H_{14}[a,c]	12
0.000 065	C_6H_{14}[a,d]	24
−0.000 020	C_5H_{12}[e,f]	24

[a] $(CH_3)_2CH\text{-}CH(CH_3)_2$, with the hydrogens of the CH groups in *trans* position.

[b] Three bonds with common vertex.

[c] Three bonds including the central one, with the outer ones in *trans* position.

[d] Three bonds including the central one, with the outer ones in *gauche* position.

[e] All C-C bonds in a single plane.

[f] Three bonds, one of them nonadjacent to the others.

TABLE VI. Correlation energy, $E_{\rm corr}$, per unit cell and correlation contribution to cohesive energy, $E_{\rm coh,corr}$, for diamond. (Atomic units are used throughout.)

	$E_{\rm corr}$	$E_{\rm coh,corr}$
DZP[a]	−0.275[b]	0.114
TZ2P[c]	−0.322	0.129
Local ansatz (calculated)[d]	−0.228	0.077
Local ansatz (estimated)[e]	−0.324	0.126
Quantum MC[f]	−0.300	0.118
Experiment[g]		~0.15

[a] This work; $(9s4p1d)/[3s2p1d]$ basis set[21] for C; the CEPA-0 energy of the C atom with this basis set is −0.080 501 a.u.

[b] Three-body expansion, using CEPA-0 increments of magnitude $>10^{-4}$ a.u. from Tables III–V; the entry referring to the largest calculated source molecule is taken for each increment.

[c] This work: $\Delta\epsilon_i$ and $\Delta\epsilon_{ij}$ for adjacent bonds replaced by their values with $(10s5p2d1f)/[4s3p2d1f]$ basis set[21] for C (cf. footnotes to Tables III and IV); also, the CEPA-0 energy for the C atom with this basis (−0.096 433 a.u.) is used.

[d] Reference 9.

[e] Reference 9.

[f] Reference 11.

[g] Reference 12.

and correlation, the diamond cohesive energy is considerably overestimated, by ~0.1 a.u. (Refs. 10 and 11).] Interestingly, our TZ2P results are quite close to values estimated in Ref. 9 on the basis of LA calculations, but as indicated a strict comparison is not appropriate here. Compared to experiment, our result for the correlation contribution to E_{coh} is still on the low side. There are two obvious reasons for this remaining deficiency. Firstly, there are basis-set effects: From the values based on the simple estimate of Sec. I (cf. Table I), we may conclude that the remaining error with our TZ2P basis is of the order 0.01–0.02 a.u. (Note, incidentally, how closely the values of Table I parallel those of Table VI, for the DZP and TZ2P basis sets.) A similar estimate comes from molecular calculations by Bauschlicher and coworkers;[26,27] there, the error of breaking a C-H or C-C single bond in a hydrocarbon molecule, with a basis set of TZ2P quality, was found to be ~2 kcal/mol; using this estimate, the cohesive energy for diamond with 4 C-C bonds per unit cell should be too small by ~0.013 a.u. Another error, of probably the same magnitude, may be connected to the neglect of increments beyond third-nearest neighbors: The third-nearest-neighbor contribution to E_{corr} (and $E_{\mathrm{coh,corr}}$) is 0.019 a.u.; these van der Waals like increments should decrease by a $1/R^6$ law approximately.

V. CONCLUSIONS

The expansion into intra- and interbond increments provides a both simple and reliable means of calculating the correlation energy of diamond: The expansion is rapidly convergent, both with respect to the number of bonds involved and to the distance between bonds; the individual increments are, to a very good approximation, transferable and may even be calculated for small molecules using standard quantum-chemical program packages. Whether these favorable features persist when calculating other than energetic properties and/or applying the method to other than well-localizable solids like diamond, remains to be seen; investigations along these lines are currently underway in our laboratory.

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