Electron correlations for ground state properties of group IV semiconductors

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Abstract

Valence energies for crystalline C, Si, Ge, and Sn with diamond structure have been determined using an ab-initio approach based on information from cluster calculations. Correlation contributions, in particular, have been evaluated in the coupled electron pair approximation (CEPA), by means of increments obtained for localized bond orbitals and for pairs and triples of such bonds. Combining these results with corresponding Hartree-Fock (HF) data, we recover about 95 \% of the experimental cohesive energies. Lattice constants are overestimated at the HF level by about 1.5 \%; correlation effects reduce these deviations to values which are within the error bounds of this method. A similar behavior is found for the bulk modulus: the HF values which are significantly too high are reduced by correlation effects to \( \sim 97\% \) of the experimental values.

71.45.Nt, 31.20.Tz, 71.55.Cn

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I. INTRODUCTION

Several methods are presently available for performing *ab initio* calculations for solids. Most frequently used is the density-functional method, with a local-density approximation (LDA) for the exchange and correlation contributions to the total energy. This method yields good results for solid-state properties, on average, but a systematic improvement is difficult. In the past few years it has become possible to determine self-consistent-field (SCF) calculations for solids using the exact non-local Hartree-Fock (HF) exchange. While the results are often inferior to LDA because electron correlations are neglected, it has the advantage of yielding a well-defined mean-field wave-function, which can be used as a starting point for treating many-body effects. In the Quantum Monte Carlo (QMC) approach, one multiplies a mean field function (Slater determinante) by a Jastrow factor which explicitly introduces inter-electronic coordinates. Another approach of incorporating electron correlation is the local ansatz (LA), where local operators acting on the SCF wave-function are used to admix suitable one- and two-particle excitations to the mean-field ground state. A method closely related to the ideas of the LA is the incremental expansion of the correlation energy; here information on local excitations in clusters is made use of, which are accessible to an accurate quantum-chemical configuration interaction (CI) treatment. This way $\sim 85\%$ of the correlation contribution to the cohesive energy $E_{\text{coh}}$ has been recovered for diamond and crystalline silicon. In the present paper we extend the application of the method of increments to two more systems – germanium and grey tin – and to other properties beside $E_{\text{coh}}$: we determine, for all of the group IV semiconductors, the influence of electron correlation on the lattice constant $a$ and the bulk modulus $B$.

In order to discuss the influence of correlation, we need reliable HF values for the ground state properties of these solids. We supplement the results of the Torino group by cluster calculations which are described in Section 2. In Section 3, we sketch the method of increments and report on computational details of the correlation treatment. The results for group IV semiconductors are discussed and compared with experiment and other calculations.
in Section 4. Conclusions follow in Section 5.

II. HARTREE-FOCK CALCULATIONS

Obtaining accurate HF energies for solids is still a difficult computational task. The Torino group of Pisani and co-workers developed a method which enables one to perform SCF-LCAO (linear combination of atomic orbitals) calculations for periodic systems\textsuperscript{2}. However, as a certain drawback of their program package CRYSTAL\textsuperscript{3} convergency problems are encountered, if one uses Gaussian functions with small exponents as normally contained in molecular basis sets; moreover, higher polarization functions than \textit{d} are presently not available.

Another possibility for obtaining information on solids are cluster calculations. They do not account for the infinite extension of the solid, but one can use standard quantum chemical program packages for achieving high accuracy, without any restriction with regard to the basis set. In this paper, we use a cluster method in conjunction with an energy partitioning approach which was developed for diamond\textsuperscript{7} and is here extended to silicon, germanium and grey tin. The systems considered in this scheme are fragments of the diamond lattice, with dangling bonds saturated by hydrogen atoms. More specifically, one chooses clusters with closed structure where each of the \textit{X} atoms (\textit{X} = C, Si, Ge, Sn) has at least two neighbouring \textit{X} atoms. The smallest one which meets this condition is \textit{X}_6\textit{H}_{12}, the biggest one which was accessible in our calculations is \textit{X}_{35}\textit{H}_{36}. (All clusters of the present SCF study are shown in Fig. 1.) The \textit{X}-\textit{X} distances were taken from the solid (\textit{r}_{CC}=1.544 Å, \textit{r}_{SiSi}=2.352 Å, \textit{r}_{GeGe}=2.460 Å, \textit{r}_{SnSn}=2.810 Å)\textsuperscript{9}, for the \textit{X}-H bond lengths those of the corresponding \textit{XH}_4 molecule were used (\textit{r}_{CH}=1.102 Å, \textit{r}_{SiH}=1.480 Å, \textit{r}_{GeH}=1.525 Å, \textit{r}_{SnH}=1.711 Å)\textsuperscript{10}. For carbon the correlation-consistent polarized valence double-zeta (pvdz) basis set (9s4p1d)/[3s2p1d] of Dunning\textsuperscript{11} was selected. For Si, Ge and Sn we employed 4-valence-electron pseudopotentials simulating the atomic cores, together with the corresponding optimized basis sets of double-zeta quality (dz) (4s4p)/[3s3p] for the valence
electrons; we added one d-function in each case whose exponent was optimized in CI calculations for XH_4 and X_2H_6 (Si: 0.40; Ge: 0.32; Sn: 0.23). For hydrogen we chose Dunning’s double zeta basis (4s)/[2s], without polarization function. We calculated the total HF energy \( E_{\text{total}} \) for each cluster, using the direct SCF program package TURBOMOLE of Ahlrichs and co-workers. In order to obtain an estimate of that part of \( E_{\text{total}} \) which can be attributed to a ‘solid-like’ X atom of the cluster, surrounded only by X atoms, we employed the energy partitioning method of Refs. 7, 14–16: \( E_{\text{total}} \) is approximated by a sum of energy contributions of the bare X atom, XH and XH_2 groups

\[
E_{\text{total}} = n_X E_X + n_{\text{XH}} E_{\text{XH}} + n_{\text{XH}_2} E_{\text{XH}_2}
\]  

(1)

where \( n_X \) (\( n_{\text{XH}} \), \( n_{\text{XH}_2} \)) are the numbers of atoms in the cluster with zero (one, two) neighbouring H atoms. We determined the quantities \( E_X \), \( E_{\text{XH}} \), and \( E_{\text{XH}_2} \) by adjustment to the SCF results \( E_{\text{total}} \) of the three largest clusters (\( \text{X}_{22}\text{H}_{28} \), \( \text{X}_{26}\text{H}_{30} \) and \( \text{X}_{35}\text{H}_{36} \)). We checked the resulting values for the group energies using the total SCF energies of the other clusters: the quantity \( \sigma \) in Table 1 is the (average) difference of these energies to the values evaluated from the group contributions according to (1). Finally, the HF cohesive energy of the solid per unit cell was calculated from

\[
E_{\text{coh}} = n_{\text{uc}} (E_X - E_{\text{atom}})
\]  

(2)

where \( E_{\text{atom}} \) is the SCF energy of the free atom determined at the same level as \( E_X \) (i.e. using the same basis set), and \( n_{\text{uc}} \) is the number of atoms per unit cell (2 for the diamond lattice). The results for \( E_{\text{coh}} \) of the group IV semiconductors are listed in Table 1. The error \( \sigma \) gives an estimate for the finite size effect; it is 3% for Sn and smaller for the other compounds. Hartree-Fock results from literature, calculated with CRYSTAL, are in good agreement (to \( \sim 1\% \)) with our values for diamond and silicon (although smaller primitive basis sets were used in Ref. 3), but there is a difference of 7% for Ge.

III. CORRELATION-ENERGY INCREMENTS
A. Formalism

In the following we give a derivation of the incremental expansion for the correlation energy which supplements the one given in Refs. 5, 6; it is similar to the one proposed in Ref. 18. The present derivation is more formal, but it shows clearly that the method applies to infinite solids and should not be considered as being merely related to calculations for finite systems. We use thereby the CEPA-0 (see e.g. Ref. 13) which is particularly suitable for our purpose.

We start from a Hamiltonian $H$ which can be divided into two parts

$$H = H_0 + H_1.$$  \hspace{1cm} (3)

The ground state of $H_0$ is supposed to be known; in our case it is the HF ground state with the corresponding wave-function $\Phi_0$. We define a product of two operators $A$ and $B$ in the Liouville space as follows:

$$(A|B) = \langle \Phi_0| A^\dagger B|\Phi_0 \rangle^c = \langle A^\dagger B \rangle^c$$ \hspace{1cm} (4)

The upper script $c$ indicates that the cumulant of the expectation value is taken, which is given by

$$\langle A \rangle^c = \langle A \rangle$$ \hspace{1cm} (5)

$$\langle AB \rangle^c = \langle AB \rangle - \langle A \rangle \langle B \rangle$$ \hspace{1cm} (6)

etc.

For further details see Ref. 21. By using (4) we may write the exact ground-state energy $E$ in the following way:

$$E = (H|\Omega) = E_{HF} + (H_1|\Omega),$$ \hspace{1cm} (7)

where $\Omega$ plays the role of the wave operator which describes the transformation from the HF ground state to the exact ground state.
If we have a solid with well-defined bonds, we can express the HF ground state $\Phi_0$ in terms of localized orbitals and label those orbitals by a bond index $i$. We define operators $A_i$, where $i$ should be considered as a compact index which includes the bond $i$ as well as the one and two particle excitations of bond $i$, and $A_{ij}$, which describes the two particle excitations where one excitation is out of bond $i$ while the other is out of bond $j$. Within the restricted operator subspace spanned by $A_i$ and $A_{ij}$ we make for $\Omega$ an ansatz of the form

$$|\Omega\rangle = |1 + \sum_i n_i A_i + \sum_{ij} n_{ij} A_{ij}\rangle.$$  

(8)

This choice represents the coupled electron pair approximation at level zero (CEPA-0)\textsuperscript{22}. The parameters $n_i$ and $n_{ij}$ are determined from the set of equations $(A_i|H\Omega) = 0$ and $(A_{ij}|H\Omega) = 0$\textsuperscript{20}. With (8) this implies

$$0 = (A_k|H) + \sum_i n_i (A_k|HA_i) + \sum_{ij} n_{ij} (A_k|HA_{ij})$$

(9)

The method of increments provides a scheme, in which this set of equations and hence the correlation energy is evaluated in a hierarchical order.

a) First all electrons are kept frozen except for the ones e.g. in bond $i$. The operators $A_i$ describe the corresponding excitations of these two electrons and Eq. (9) reduce to

$$0 = (A_i|H) + n_i^{(1)} (A_i|HA_i).$$

(10)

Within this approximation the $n_i^{(1)}$ are independent of each other and the correlation energy becomes

$$E_{\text{corr}}^{(1)} = \sum_i \epsilon_i$$

(11)

with

$$\epsilon_i = n_i^{(1)} (H_1|A_i).$$

(12)
b) In the next step we correlate the electrons in two bonds, e.g. $i$ and $j$. The corresponding $n^{(2)}$ parameters are determined from the coupled equations

$$
0 = (A_i | H) + n_i^{(2)} (A_i | HA_i) + n_j^{(2)} (A_j | HA_j) + n_{ij}^{(2)} (A_i | HA_{ij}) \\
0 = (A_j | H) + n_i^{(2)} (A_j | HA_i) + n_j^{(2)} (A_j | HA_j) + n_{ij}^{(2)} (A_j | HA_{ij}) \\
0 = (A_{ij} | H) + n_i^{(2)} (A_{ij} | HA_i) + n_j^{(2)} (A_{ij} | HA_j) + n_{ij}^{(2)} (A_{ij} | HA_{ij})
$$

(13)

Again, the increments $\delta n_i = n_i^{(2)} - n_i^{(1)}$ and $\delta n_j = n_j^{(2)} - n_j^{(1)}$ are treated as independent of each other in this approximation, and we have

$$
E^{(2)}_{\text{corr}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{i \neq j} \Delta \epsilon_{ij}
$$

(14)

where

$$
\Delta \epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j).
$$

(15)

and

$$
\epsilon_{ij} = (H_1 | n_i^{(2)} A_i + n_j^{(2)} A_j + n_{ij}^{(2)} A_{ij}).
$$

(16)

c) Analogously we calculate the three bond energy increment, which is defined as

$$
\Delta \epsilon_{ijk} = \epsilon_{ijk} - (\Delta \epsilon_i + \Delta \epsilon_j + \Delta \epsilon_k) - (\Delta \epsilon_{ij} + \Delta \epsilon_{jk} + \Delta \epsilon_{ik}).
$$

(17)

The correlation energy $\epsilon_{ijk}$ is that obtained when all electrons are kept frozen except those in bond $i,j$ and $k$. Again, the increments $\Delta \epsilon_{ijk}$ are treated as being independent of each other.

The total correlation energy within this approximation is the sum of all increments.

$$
E^{\text{solid,corr}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{i \neq j} \Delta \epsilon_{ij} + \frac{1}{6} \sum_{i \neq j \neq k} \Delta \epsilon_{ijk} + ...
$$

(18)
It is obvious that by calculating higher and higher increments the exact correlation energy within CEPA-0 is obtained.

The method just described is only useful if the incremental expansion is well convergent, i.e. if increments up to, say, triples are sufficient, and if increments become rapidly small with increasing distance between localized orbitals. These conditions were shown to be well met in the case of diamond and silicon\cite{5,6}, but have to be checked again for germanium and grey tin here. Ideally the increments should be local entities not sensitive to the surroundings. We use this property to calculate the energy increments in finite clusters. If they can be proven to be well transferable even between finite clusters, such cluster calculations may be extrapolated to the corresponding solid state quantities.

B. Computational Details

In this section we give computational details characterizing our \textit{ab initio} calculations for the correlation energies of group IV semiconductors with diamond structure.

First we select suitable fragments of the diamond lattice, and, as in the SCF calculations, we saturate the dangling bonds with hydrogen. We have to take much smaller clusters, however, for the correlation treatment (see Fig. 2) than in the SCF case, because CI calculations for clusters as large as $X_{35}H_{36}$ would be prohibitive.

As a second step we perform, for each cluster, a standard SCF calculation (using the program package \textsc{Molpro}{\textcopyright}) and localize the bond orbitals, applying the Foster-Boys criterion\cite{24}, within the occupied valence space in $C_1$ symmetry. Following that we calculate CEPA-0 energy increments by successively correlating more and more of the localized $X$-$X$ bond orbitals (LMO) as described in the previous subsection.

Two different basis sets are used: Basis set A is the same as in the SCF calculations. An extended basis set B has been generated by replacing the single $d$ function of basis set A by a $2d1f$ polarization set with an optimized $f$ exponent (C: $d$: 1.0970, 0.318; $f$: 0.76; Si: $d$: 0.8, 0.23; $f$: 0.35; Ge: $d$: 0.6, 0.15; $f$: 0.43; Sn: $d$: 0.45, 0.12; $f$: 0.30). In order to check
the quality of the basis sets we performed test calculations for the one-bond increment $\Delta \epsilon_i$ of the Ge$_2$H$_6$ cluster (Table 2). One sees that the $sp$ basis set is well chosen; enlarging the $d$ space and adding an additional $f$ function yields an enhancement of about 25%, supplying a polarisation set 3d2f1g adds another 20%.

Next we have to check the transferability and the convergence of the increments. We will discuss them for Sn since this is the most critical case. The correlation energy increments obtained for Sn are listed in Table 3 together with the weight factors appropriate for the solid. We observe the following:

a) The convergence of the incremental expansion is quite rapid both with respect to the number of the bonds involved (e.g. cluster 4: $\epsilon_2 \approx 2.5\Delta \epsilon_{23} \approx 300\Delta \epsilon_{123} \approx 1500\Delta \epsilon_{1234}$) and with respect to the distance between the bonds (e.g. cluster 4: $\Delta \epsilon_{12} \approx 10\Delta \epsilon_{13} \approx 50\Delta \epsilon_{14}$). In view of these findings, we restrict the energy increments up to the third order for adjacent bonds and up to the second order for next nearest through third nearest neighbours.

b) The transferability of the increments is reasonably good. There are changes of $1 \cdot 10^{-3}$ a.u. for one-bond increments between the smallest (Sn$_2$H$_6$) and the largest (Sn$_6$H$_{14}$) clusters considered. For the most important two-bond increment the difference between Sn$_3$H$_8$ and Sn$_6$H$_{14}$ is about $1 \cdot 10^{-4}$ a.u.. As these changes are of different sign, the total effect on the cohesive energy of the solid is not larger than $3 \cdot 10^{-3}$ a.u. per unit cell.

Finally, in order to test the quality of the CEPA-0 results, we performed calculations for Ge$_3$H$_8$ at different levels of correlation treatment (Table 4). We tried CEPA-1 and CEPA-2 as well as the coupled cluster method with single and double excitations (CCSD) and even with additional triple excitations included in a perturbative way (CCSD(T)). The effect on the one-bond increment is of the order of $3 \cdot 10^{-4}$ a.u., and $\sim 2 \cdot 10^{-4}$ a.u. for the two-bond increment. Thus, the errors are of the same order of magnitude as those caused by lack of transferability.
It is clear, from these remarks, that the accuracy of our method has its limitations, in practical applications. On the other hand, there are formal arguments why errors due to the truncation of the incremental expansion should be small: higher than two-bond increments involve triple excitations which do not directly couple to the Hartree-Fock ground state; two-bond increments between localized orbitals at large distances are of the van-der-Waals type, with a rapid decrease as $\frac{1}{r^6}$. Moreover, there are means for numerically controlling these errors: the $\frac{1}{r^6}$ law just mentioned, e.g., lends itself to an approximate summation of neglected two-bond increments; energy variations between different finite clusters allow for an easy estimate of transferability defects of individual local increments.

Summarizing these considerations, one may conclude that the greatest remaining error of the results, to be discussed in the next section, is due to limitation of the one-particle basis sets.

**IV. RESULTS AND DISCUSSION**

Applying the method of increments as described in the preceding section, we have determined correlation contributions to cohesive energies, lattice constants, and bulk moduli for all of the group IV semiconductors. The increments were always taken from the largest possible cluster (cf. Table 3 and Fig. 2).

The correlation contributions to the cohesive energies were obtained as $E_{\text{coh}}^{\text{corr}} = E_{\text{solid}}^{\text{corr}} - 2E_{\text{atom}}^{\text{corr}}$ per unit cell of the diamond lattice. The results for the two different basis sets are shown in Table 5. For basis set A we obtain about 65 % of the ‘experimental’ correlation energies (defined here as the differences between the experimental cohesive energies and the corresponding HF values of Sect. 2). The larger basis set B yields a substantial improvement, to about 85 %. Combining the HF results with the correlation contributions we recover about 95 % of the experimental cohesive energies. (The experimental values in Table 5 have been corrected for the phonon zero point energies $\frac{9}{8}k_B\Theta_D$ derived from the Debye model (C: 1860 K; Si: 625 K; Ge: 360 K; Sn: 260 K).)
For comparison, we have also listed in Table 5 results from the literature which have been obtained with other methods. The Local Ansatz (LA) which also uses a CEPA-0 scheme yields smaller cohesive energies for all compounds. The LA values in Table 5 have been obtained by adding the correlation contributions to $E_{\text{coh}}$ calculated in Ref. 29 to the SCF values of the present work (Sect. 2). Our basis set A is comparable with the basis used in LA, but still the correlation contributions differ by about 1 eV for Si, Ge and Sn. LDA overestimates the cohesive energies by $\sim$15%. The QMC result for diamond is excellent and also very good for silicon (with an accuracy of 4%); note, however, that in both cases the HF cohesive energy of Ref. 17 is lower by $\sim$1 eV than that of Ref. 30 and of this work.

In the next step we evaluate lattice constants (Table 6). They have been determined by varying the X-X distances both in the HF and in the CEPA-0 calculations. More specifically, to obtain the HF lattice constant we varied all X-X distances of the largest cluster $X_{35}H_{36}$ and minimized the SCF energy with respect to the interatomic distance. At the HF level, the lattice constant is larger than in the experiment, except for diamond. Our results are in fair agreement here with the CRYS\textsc{tal} SCF calculations by Causa and Zupan: the deviations are $\sim$0.5% for C and Si, but $\sim$1% for Ge, see Table 6. By using pseudopotentials for the core electrons in the present work, any effects of the latter beyond the frozen-core approximation are excluded from the outset. However, calculations for small molecules show that core polarization is very important for bond lengths of Ge and Sn compounds. We simulated, therefore, this effect using a core polarization potential (CPP) and studied the influence on the X-X distance for different clusters. We find that the changes are nearly independent of the cluster size. By transferring these changes to the solid we obtain the results listed in row b) of Table 6. The influence of core polarization is seen to significantly increase within the group Si, Ge and Sn. Valence correlations affect the lattice constant in two different ways. Correlation contributions calculated with a minimal basis set (‘inter-atomic correlations’) enlarge the lattice constant. The increase for diamond is mostly due to them. Intra-atomic correlations, on the other hand, decrease the lattice constant; extended basis sets with many polarization functions are needed to describe them accurately. The total influence of valence
correlation seems to become less important when going from Si to Ge and Sn. The final values are within the error bounds of the pseudopotential and CPP (≈ 0.02 Å), and within the error of the limited basis set which can be roughly estimated from the difference between basis sets A and B to be ≤ 0.02 Å. The LA overestimates the lattice constant, since with the small basis set used in Ref. 29 the intra-atomic correlations could not be described very well. The LDA yields lattice constants which are systematically too small by about 1%. The QMC result is again excellent for diamond, slightly less good for silicon, but still reaching the experimental value within their error bounds.

As a last property, we consider the bulk modulus \( B = V \left( \frac{\partial^2 E}{\partial V^2} \right) \), which describes the response of the solid to a homogeneous pressure. For the diamond structure one can easily derive the following expression

\[
B = \left( \frac{4}{9a} \frac{\partial^2}{\partial a^2} - \frac{8}{9a^2} \frac{\partial}{\partial a} \right) E_{\text{coh}}(a).
\]  

We evaluate the bulk modulus at the experimental lattice constant \( a \), so that the second term in (19) is small but not zero. We obtain the HF bulk modulus again from the largest possible cluster. Compared with experiment (see Table 7) all values are too high. The core-polarization effect has been taken from smaller clusters, which causes an uncertainty of about 3%, but the total effect of the CPP is much greater so that one can justify this approximation: for Sn, it reduces \( B \) by 14%. Valence correlation reduces the bulk modulus, too, especially for Ge. Overall, we obtain results for the bulk modulus which are a little too small but still within few percents of the experimental data.

V. CONCLUSIONS

We have determined ground state properties (cohesive energy, lattice constant and bulk modulus) of group IV semiconductors, both at the HF and the CEPA-0 levels. The HF results have been obtained using a cluster method and an energy-partitioning ansatz which works well for solids with covalent bonds as those considered here. Electronic correlations at
the CEPA-0 level are described with the method of local intra- and inter-bond increments, which allows for a systematic improvement of accuracy towards the fully correlated solid-state limit. The results show that this method works well for all solids with diamond structure, with the transferability only slightly deteriorating down the fourth column of the Periodic Table. Not only the cohesive energy $E_{\text{coh}}$, but also the lattice constant $a$, and the bulk modulus $B$, have been calculated with quantum chemical accuracy, to about 5% for $E_{\text{coh}}$, 0.5% for $a$, and 3% for $B$. Work is underway in our laboratory to apply the methods presented in this paper to solids with zinkblende structure, such as GaAs.

VI. ACKNOWLEDGMENTS

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### TABLE I. Hartree-Fock cohesive energies per unit cell (in a.u.), with average deviations $\sigma$ in parentheses (cf. text)

|      | C   | Si   | Ge   | Sn   |
|------|-----|------|------|------|
| this work | -0.3947 | -0.2273 | -0.1560 | -0.1323 |
|       | (0.0036) | (0.0032) | (0.0034) | (0.0044) |
| Ref.$^{17}$ | -0.3984 | -0.2253 | -0.1672 | — |

### TABLE II. Test calculations for the Ge basis set: the SCF energy, $E_{\text{SCF}}$, and the one-bond CEPA-0 correlation-energy increment, $\Delta\epsilon_i$, for Ge$_2$H$_6$ (in a.u.)

| basis set | $E_{\text{SCF}}$ | $\Delta\epsilon_i$ |
|-----------|----------------|------------------|
| A         | -10.831779     | -0.01845         |
| B         | -10.836493     | -0.02265         |
|           | -10.836633     | -0.02301         |
|           | -10.838324     | -0.02317         |
|           | -10.841788     | -0.02750         |
TABLE III. Correlation-energy increments for Sn (in a.u), determined at the CEPA-0 level using basis set A. For the numbering of the source clusters and bonds involved, see Fig. 2.

| Source cluster/bond orbitals | Increment | Weight factor for the solid |
|-----------------------------|-----------|----------------------------|
| $\epsilon_i$                |           |                            |
| 1/1                         | -0.018526 | 4                          |
| 2/1                         | -0.018257 |                            |
| 4/2                         | -0.017966 |                            |
| 8/1                         | -0.017476 |                            |
| $\Delta \epsilon_{ij}$      |           |                            |
| 2/1,2                       | -0.006794 | 12                         |
| 4/2,3                       | -0.006738 |                            |
| 8/1,2                       | -0.006905 |                            |
| 4/1,3                       | -0.000701 | 12                         |
| 8/2,5                       | -0.000715 |                            |
| 7/1,3                       | -0.000575 | 24                         |
| 8/2,4                       | -0.000553 |                            |
| 4/1,4                       | -0.000142 | 12                         |
| 5/1,4                       | -0.000104 | 48                         |
| 6/1,4                       | -0.000111 | 24                         |
| 7/1,4                       | -0.000194 | 12                         |
| $\Delta \epsilon_{ijk}$     |           |                            |
| 8/1,2,3                     | 0.000475  | 8                          |
| 8/1,2,5                     | -0.000038 | 12                         |
| 4/1,2,3                     | -0.000055 |                            |
| 8/1,2,4                     | 0.000055  | 24                         |
| $\Delta \epsilon_{ijkl}$    |           |                            |
| 4/1,2,3,4                   | -0.000011 |                            |
TABLE IV. Test calculations for the one-bond increment $\epsilon_i$ and the two-bond increment $\Delta \epsilon_{ij}$ between nearest neighbours, at various levels of correlation treatment, for Ge$_3$H$_8$ (a.u.)

| Method     | $\epsilon_i$ | $\Delta \epsilon_{ij}$ |
|------------|---------------|--------------------------|
| CEPA-0     | -0.01824      | -0.00651                 |
| CEPA-1     | -0.01798      | -0.00631                 |
| CEPA-2     | -0.01798      | -0.00650                 |
| CCSD       | -0.01798      | -0.00613                 |
| CCSD(T)    | -0.01798      | -0.00645                 |

TABLE V. Cohesive energies per unit cell (in a.u.); deviations from experimental values (in percent) are given in parentheses

|         | C      | Si     | Ge     | Sn     |
|---------|--------|--------|--------|--------|
| this work, basis set A | -0.5077 | -0.2996 | -0.2346 | -0.1979 |
|         | (92 % ) | (87 % ) | (82 % ) | (86 % ) |
| this work, basis set B | -0.5276 | -0.3248 | -0.2565 | -0.2230 |
|         | (96 % ) | (94 % ) | (90 % ) | (97 % ) |
| exp. (sec 26) | -0.555  | -0.345  | -0.285  | -0.229  |
| LA (sec 29) | -0.475  | -0.259  | -0.192  | -0.164  |
| LDA (sec 30) | -0.634  | -0.389  | -0.333  | —       |
| QMC (sec 16) | -0.5475 | -0.3587 | —       | —       |
TABLE VI. Lattice constants in Ångström a) this work, SCF level, basis set A; b) this work, core polarization included, basis set A; c) this work, valence correlation included, basis set B – in comparison to experimental and other theoretical results. Deviations from experimental values are given in parentheses.

|     | C      | Si     | Ge     | Sn     |
|-----|--------|--------|--------|--------|
| a)  | 3.5590 | 5.4993 | 5.7516 | 6.6001 |
|     | (-0.2 %) | (+1.2 %) | (+1.7%) | (+1.7%) |
| b)  | —      | 5.4662 | 5.6653 | 6.4549 |
|     | (+0.6 %) | (+0.2%) | (-0.5%) |
| c)  | 3.5833 | 5.4256 | 5.6413 | 6.4443 |
|     | (+0.5 %) | (-0.1 %) | (-0.3%) | (-0.7%) |
| exp. (see 9) | 3.5657 | 5.4317 | 5.6575 | 6.4892 |
| HF (see 17)   | 3.58   | 5.49   | 5.81   | —      |
| LA (see 29)   | 3.601  | 5.488  | 5.760  | 6.538  |
| LDA (see 30)  | 3.53   | 5.38   | 5.57   | —      |
| QMC (see 3)   | 3.543  | 5.404  | —      | —      |
TABLE VII. Bulk moduli (in Mbar) a) this work, SCF level, basis set A; b) this work, core polarization included, basis set A; c) this work, valence correlation included, basis set B – in comparison to experimental and other theoretical results. Deviations from experimental values are given in parentheses.

|     | C    | Si   | Ge   | Sn   |
|-----|------|------|------|------|
| a)  | 4.815| 1.038| 0.961| 0.638|
|     | (+9 %)| (+5 %)| (+31%)| (+20%)|
| b)  | —    | 1.009| 0.889| 0.562|
|     | (+2 %)| (+21%)| (+6%)|
| c)  | 4.196| 0.979| 0.711| 0.510|
|     | (-5 %)| (-1 %)| (-3%)| (-4%)|
| exp (see 9) | 4.42| 0.99| 0.734| 0.531|
| HF (see 17)   | 4.80| 1.10| 0.85| —   |
| LA (see 29)   | 4.332| 1.001| 0.774| 0.509|
| LDA (see 30)  | 4.90| 0.97| 0.75| —   |
| QMC (see 3)   | 4.205| 1.081| —   | —   |
FIGURES

FIG. 1. $X_nH_m$ clusters treated at the SCF level (H-atoms are not drawn).

FIG. 2. The X-skeletons of the clusters treated at the CEPA-0 level (big numbers designate clusters, small numbers the bonds in each cluster).
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