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Electron correlations in the ground state of covalent semiconductors

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We describe a simple and transparent method for studying electronic correlations in the ground state of covalent semiconductors. The starting point is a single-determinantal ground-state wave function in the bond-orbital approximation. Electronic correlations are taken into account by applying a variational ansatz. Analytical expressions are obtained for the interatomic or bond correlation energy as well as for the pair-correlation function. Both are discussed in detail. The intra-atomic correlation energy is estimated in two different ways which give identical results. One is based on an "atoms in solids" method which requires a population analysis of the ground-state wave function, while the other is based on an analysis of the correlation energies of hydrocarbon molecules. The theory is applied to diamond, Si, Ge, and α-Sn. The correlation-energy contributions to the cohesive energy and the radial force constant are discussed and compared with experimental data. By using a diagrammatic representation, a comparison is made with ground-state correlation-energy calculations which use the "*GW* approximation" of Hedin [Phys. Rev. **139**, A796 (1965)].

I. INTRODUCTION

A qualitative and quantitative understanding of electronic correlations in semiconductors remains a challenging problem. This holds true for the ground state, which will be the subject of the present paper, as well as for the excited states. For example, it is well known that the cohesive energy[1] and the size of the band gap[2,3] are strongly influenced by electronic correlations. Therefore the one-electron approximation is inadequate for their determination.

Various attempts have been undertaken to obtain estimates for the correlation energy contributions to the cohesive energy of diamond[4,5] and zinc blende.[6] The calculations were done by constructing a two-electron wave function for each bond and introducing an ionic state correction into the Heitler-London wave function. Such a description includes intrabond correlations. More recent estimates of the total correlation energy of diamond and its contribution to the cohesive energy have been obtained by using the local-density approximation.[7]

Recently it was demonstrated that for the ground state[8] as well as for the excited states[9] of diamond accurate self-consistent field (SCF) and correlation-energy calculations can be performed on an *ab initio* level. Thereby a local approach (LA) to the correlation problem was used. The LA is a variational method which can be applied both to molecules[10] and solids. Although the underlying physical picture of that approach is simple and the formalism is straightforward, actual calculations are far from being trivial. This is mainly due to the fact that they require a SCF calculation as a starting point which poses in itself an elaborate problem.

In order to give a simple and transparent picture of the electronic correlations in the ground state some approximations have to be made. First of all we will assume that a SCF calculation has been performed and that we know the corresponding localized atomic-like (sp^3) hybrid functions from that calculation. These can always be obtained from the SCF eigenstates. Using these hybrid functions we adopt the bond-orbital approximation (BOA)[11] to construct our approximated SCF ground state. This will enable us to calculate analytically the interatomic correlation energy by means of the LA. The *interatomic* correlations consist of the correlations within the bonds (intrabond correlations) and the correlations between different bonds (interbond correlations); therefore interatomic correlations can also be called bond correlations. In addition to the interatomic or bond correlations we must also consider the *intra-atomic* correlations. The intra-atomic correlations, however, are not contained in this calculation which is formulated within a minimal basis set. For their *ab initio* description the use of a larger basis set is necessary. The approach taken here relies on the observations that intra-atomic correlations on different atomic sites do not influence each other[8,10] and that inter- and intra-atomic correlations are independent to a very good approximation.[12,13] This enables us to employ, e.g., an "atoms in solids" method to estimate the intra-atomic correlation energy which makes use of some ideas developed by Verhaegen and co-workers.[13,14]

Although the present theory deals with a many-body problem, it is conceptually, and also computationally, of comparable simplicity as the one-electron theories of Harrison and co-workers[11,15,16] and Levin,[17] which are on the level of an extended Hückel theory.

The present paper is organized as follows. In Sec. II, we define the Hamiltonian for the present calculations and we set up the correlated ground-state wave function. A simple expression for the interatomic or bond correlation energy is derived in Sec. III by means of the LA and a physical interpretation of it is provided. This section also contains an investigation of the pair correlation function. Furthermore, a brief discussion of the extended bond-orbital approximation (EBOA) as well as an extension of the theory to polar semiconductors is given. The intra-atomic correlations are discussed in Sec. IV. Here also the charge fluctuations at an atomic site are studied in detail. Numerical results for interatomic as well as intra-atomic correlation energies are presented in Sec. V. Their contributions to the cohesive energy and to the radial force constant are evaluated. A summary is given in Sec. VI. Appendix A contains a discussion of the applicability of the GW approximation of Hedin[18] (with G the Green's function and W the screened, spin-independent electron-electron potential) to the calculation of ground-state energies of semiconductors. In Appendix B, the relation of the present theory to perturbation theoretical treatments, e.g., the perturbative configuration interaction using localized orbitals (PCILO) method[19–21] is studied.

II. DESCRIPTION OF METHOD

We are interested in a simple description of the effects of electronic correlations on the ground-state properties of semiconductors. For that purpose we will use the BOA for the SCF ground-state wave function.

Consider a diamond lattice structure which is built up by localized atomic-like (sp^3) hybrids. Their optimal form can be determined by a SCF calculation. We assume that such a calculation has been performed and that the hybrids have been Löwdin orthogonalized with respect to each other. We denote these orthogonalized functions by $h_i(\underline{r})$. The corresponding electron creation and annihilation operators are $a_{i\sigma}^\dagger$ and $a_{i\sigma}$. They fulfill the relations

$$[a_{i\sigma},a_{j\sigma'}^\dagger]_+=\delta_{ij}\delta_{\sigma\sigma'},\ldots . \tag{1}$$

From the two hybrids $h_{I1}(\underline{r})$ and $h_{I2}(\underline{r})$, which point into bond I, we form bonding and antibonding wave functions

$$\begin{aligned} B_{I\sigma}^\dagger &= 2^{-1/2}(a_{I1\sigma}^\dagger + a_{I2\sigma}^\dagger) , \\ A_{I\sigma}^\dagger &= 2^{-1/2}(a_{I1\sigma}^\dagger - a_{I2\sigma}^\dagger) . \end{aligned} \tag{2}$$

This construction applies to the elemental semiconductors which will be primarily considered. An extension of the theory to heteropolar semiconductors is discussed in Sec. III.

The transformation from the hybrid functions to bonding and antibonding functions is essential in order to present a simple picture of the electronic correlations in semiconductors or any closed-shell system. It can be made irrespective of whether a BOA is made or not.

The simplifications of the BOA come in when the ground-state wave function $|\Phi_{\text{SCF}}\rangle$ is derived. In that case it has the simple form

$$|\Phi_{\text{SCF}}\rangle = \prod_{I,\sigma} B_{I\sigma}^\dagger |0\rangle , \tag{3}$$

where $|0\rangle$ is the vacuum state. The one-particle density matrix is then of the simple diagonal form,

$$\langle a_{i\sigma}^\dagger a_{j\sigma'}\rangle = \begin{cases} \frac{1}{2}\delta_{\sigma\sigma'}, & i,j \in I \\ 0, & \text{otherwise.} \end{cases} \tag{4}$$

Here and in the following

$$\langle \cdots \rangle = \langle \Phi_{\text{SCF}} | (\cdots) | \Phi_{\text{SCF}}\rangle .$$

This diagonal form which is a direct consequence of the BOA will simplify the correlation-energy calculations decisively.

For the following we need the Hamiltonian H expressed in terms of the $a_{i\sigma}^\dagger$, $a_{i\sigma}$,

$$\begin{aligned} H &= H_0 + H_{\text{int}} \\ &= \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l,\\ \sigma,\sigma'}} V_{ijkl} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma} . \end{aligned} \tag{5}$$

Here

$$t_{ij} = \int d\underline{r}\, h_i^*(\underline{r}) \left[-\frac{1}{2m}\Delta + V(\underline{r}) \right] h_j(\underline{r}) \tag{6}$$

is the bare hopping matrix element between hybrids i and j where $V(\underline{r})$ is the electrostatic potential from the nuclei and core electrons, and

$$V_{ijkl} = \int d\underline{r}\, d\underline{r}'\, h_i^*(\underline{r}) h_j(\underline{r}) \frac{e^2}{|\underline{r}-\underline{r}'|} h_k^*(\underline{r}') h_l(\underline{r}') \tag{7}$$

are the interaction matrix elements. For convenience we will use in the following the abbreviations

$$\left.\begin{aligned} U &= V_{iiii} \\ K &= V_{iijj} \\ J &= V_{ijji} \end{aligned}\right\} i \neq j,\ i,j \in I \tag{8}$$

for the relevant interaction matrix elements in a bond. Later we will also need the interaction expressed in terms of the bonding and antibonding functions instead of the hybrids. We shall denote these matrix elements by $\tilde{V}_{A_I B_J A_K B_L}$, etc., in obvious notation, i.e., with $h_i(\underline{r}), h_j(\underline{r})$ replaced by the bonding and antibonding functions.

For the following discussion it is advantageous to divide H into a self-consistent field part H_{SCF} and a residual interaction part H_{res},

$$H = H_{\text{SCF}} + H_{\text{res}} . \tag{9}$$

It follows that

$$H_{\text{SCF}} = \sum_{i,j,\sigma} f_{ij} a_{i\sigma}^\dagger a_{j\sigma} , \tag{10}$$

where the Fock matrix is

$$f_{ij} = t_{ij} + \sum_{k,l,\sigma'} (V_{ijkl} - \tfrac{1}{2} V_{ilkj}) \langle a_{k\sigma'}^\dagger a_{l\sigma'}\rangle \tag{11}$$

and

$$H_{\text{res}} = H_{\text{int}} - \frac{1}{2} \sum_{\substack{i,j,k,l\\ \sigma,\sigma'}} (V_{ijkl} - \delta_{\sigma\sigma'} V_{ilkj}) \langle a_{k\sigma'}^\dagger a_{l\sigma'}\rangle a_{i\sigma}^\dagger a_{j\sigma} . \tag{12}$$

Having defined the Hamiltonian and the SCF ground state we make the following ansatz for the correlated ground-state wave function[22]

$$|\psi_0\rangle = \exp(S) |\Phi_{\text{SCF}}\rangle . \tag{13}$$

The operator S is of the form

$$S = -\sum_{m,n} \eta_{mn} O_{mn} , \tag{14}$$

where the η_{mm} are variational parameters and the O_{mn} are written as

$$O_{mn}=O'_{mn}-\langle O'_{mn}\rangle \ . \tag{15}$$

This ensures that, when applied on $|\Phi_{\rm SCF}\rangle$ they generate a state which is orthogonal to it. The O'_{mn} are of the form

$$O'_{mn}=\sum_{\sigma,\sigma'} n_{m\sigma}n_{n\sigma'} \ , \tag{16}$$

where $n_{n\sigma}=a^\dagger_{n\sigma}a_{n\sigma}$.

Generally, $O_{mn}|\Phi_{\rm SCF}\rangle$ contains one-particle as well as two-particle excitations of $|\Phi_{\rm SCF}\rangle$. For simplicity we shall neglect the former. They lead to small density changes as a secondary effect of the electron correlations. We do this by requiring that contractions within the O_{mn} operators are forbidden when expectation values are calculated of quantities containing them. The form (16) for O'_{mn} neglects Hund's rule correlations. Including them would require additional operators O'_{mn}, which are products of spin instead of density operators.

The parameters η_{mn} are determined by minimizing

$$E_0=\frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \ . \tag{17}$$

After applying a linked-cluster theorem[22] this expression can be written as

$$E_0=\langle e^SHe^S\rangle_c \ , \tag{18}$$

where the subscript c implies that only "connected" contractions are taken into account. For more details we refer to the original Ref. 22. Equation (18) is evaluated by making the replacement $\exp(S)\simeq 1+S$, which turns out to be a good approximation for not too strongly correlated systems such as semiconductors. An explicit expression for E_0 is written below.

The main effect of applying $\exp(S)$ on $|\Phi_{\rm SCF}\rangle$ is to reduce large density fluctuations in the system. The simplest way to see that is to consider a bond which is formed by the hybrids 1 and 2. Then

$$O_{11}=2n_{1\uparrow}n_{1\downarrow} \ . \tag{19}$$

Here we have dropped a term $(n_{1\uparrow}+n_{1\downarrow})$ which generates one-particle excitations only. The state

$$|\psi\rangle=\exp(-\eta_{11}O_{11})|\Phi_{\rm SCF}\rangle; \quad \eta_{11}>0 \tag{20}$$

has the charge fluctuations in the chosen bond diminished because the probability is reduced of finding two electrons simultaneously in hybrid 1. Similar considerations hold for charge fluctuations in different bonds.

An equivalent point of view is the following. Imagine a decomposition of $|\Phi_{\rm SCF}\rangle$ into a sum of products of different atomic configurations. The application of $\exp(S)$ on $|\Phi_{\rm SCF}\rangle$ decreases the weight of all those configurations in which there are too many or too few electrons on different atomic sites. We call these configurations "unfavorable" because the electron-electron interaction energies are very large for them. In return the relative weight of "favorable" configurations is enhanced. These are configurations in which the atomic occupational numbers are close to the average number of valence electrons, i.e., four. An example of both types of configurations is shown in Fig. 1.

In the BOA, in which the one-particle density matrix has the simple form (4), the O'_{mn} simplify considerably. In that case there are always two electrons within a bond. Therefore we need to consider only *one* hybrid per bond when the O'_{mn} are constructed [see Eq. (16)]. A reduction of the double occupancy within one hybrid implies automatically a reduction of the double occupancy of the other hybrid in the same bond. An analogous statement holds true for correlations between electrons in different bonds. In the following we shall choose that particular hybrid of a given bond which enters with a positive sign when the antibonding function of that bond is constructed. With these simplifications we can write Eq. (14) in the form

$$S=-\eta_0\sum_I S_I-\eta_1\sum_{\langle IJ\rangle}S_{IJ}-\cdots \ , \tag{21}$$

where I and J are *bond* (not hybrid) indices. $S_I(=S_{II})=O_{ii}$ describes correlations in bond I while $S_{IJ}=O_{ij}$ describes those between nearest-neighbor bonds, indicated by $\langle IJ\rangle$, etc. The indices i,j refer to hybrids which are chosen according to the above description. We are now able to write E_0 [see Eq. (18)] in the following form:

$$\begin{aligned}E_0&=\langle H\rangle+2\langle SH_{\rm res}\rangle_c+\langle SHS\rangle_c\\&=\langle H\rangle-2\eta_0\sum_I\langle S_IH_{\rm res}\rangle_c-2\eta_1\sum_{\langle IJ\rangle}\langle S_{IJ}H_{\rm res}\rangle_c\\&\quad+\eta_0^2\sum_{I,I'}\langle S_IHS_{I'}\rangle_c+\eta_1^2\sum_{\langle IJ\rangle}\sum_{\langle KL\rangle}\langle S_{IJ}HS_{KL}\rangle_c\\&\quad+2\eta_0\eta_1\sum_I\sum_{\langle KL\rangle}\langle S_IHS_{KL}\rangle_c \ .\end{aligned} \tag{22}$$

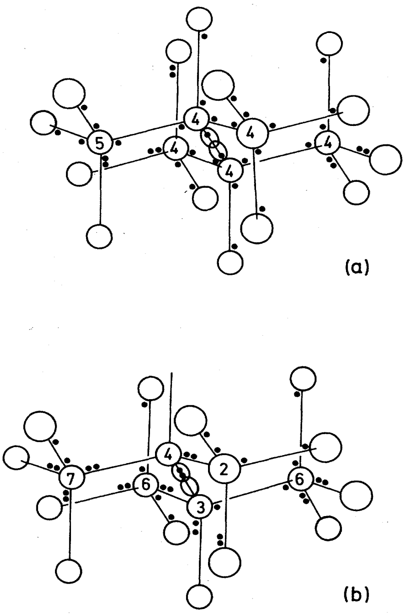

FIG. 1. Two configurations which are contained in the SCF ground state; (a) is called favorable and (b) is called unfavorable. The positions of valence electrons in the bonds are indicated by dots. The numbers of valence electrons at different atomic sites are also indicated.

Here use has been made of $\langle S_{IJ} H_{\mathrm{SCF}} \rangle_c = 0$. From this expression for E_0 the correlation energy $E_{\mathrm{corr}} = E_0 - \langle H \rangle$ will be calculated in the following. Because of the minimal basis set used here, E_{corr} is an interatomic or bond correlation energy.

III. INTERATOMIC CORRELATION ENERGY

In order to evaluate E_{corr} one has to evaluate the various expectation values which appear in Eq. (22). Because of the BOA it is possible to express all interactions in the bond representation. One finds

$$\langle S_{IJ} H_{\mathrm{res}} \rangle_c = \widetilde{V}_{A_I B_I A_J B_J} - \tfrac{1}{2} \widetilde{V}_{A_I B_J A_J B_I} \, . \qquad (23)$$

The corresponding expression for $\langle S_I H_{\mathrm{res}} \rangle_c$ follows by setting $J = I$. Equation (23) represents the van der Waals interaction between dipoles in bonds I and J. The second term on the right-hand side (rhs) compensates for the self-interaction when $I = J$. It is missing in the so-called GW approximation,[18] which has been originally deviced for the homogeneous electron gas but is also widely used in band-structure calculations for semiconductors and insulators.[23–26] For more details we refer to Appendix A.

The evaluation of $\langle S_{IJ} H S_{KL} \rangle_c$ is given in Appendix A [see Eqs. (A1) and (A2)]. The expectation value $\langle S_{IJ} H_{\mathrm{SCF}} S_{KL} \rangle_c$ is proportional to $T_0 = -f_{12}$ which is half the energy splitting between the bonding and antibonding states in the SCF approximation, 1 and 2 denote the two hybrids forming a bond. From Eq. (11) one finds

$$T_0 = t_0 + \tfrac{1}{2}(K - 3J) \, , \qquad (24)$$

where $t_0 = -t_{12} > 0$ is the bare intrabond hopping matrix element or half the bare splitting between the bonding and antibonding states. In Eq. (24) we have neglected V_{1112} and those V_{ijkl} which depend on at least three different hybrids because their values are very small compared to J. In diamond it is $K = 13.3$ eV and $J = 0.3$ eV.[8,27]

The term $K/2$ is the contribution of the electron-electron interaction to the effective intrabond hopping in the SCF approximation, arising because of the nonlocal exchange interaction. It is this term, K, which is responsible for the overly large energy gaps between the conduction and valence bands of semiconductors and insulators in the SCF approximation.[28,29] This feature is missing in any treatment in which the exact exchange interaction is replaced by a local exchange potential $V_{\mathrm{ex}}(\underline{r})$.

In the following we want to restrict ourselves to the correlations within a bond and between neighboring bonds. Correlations between bonds which are further apart contribute only insignificantly to the correlation energy. The reason for this is simply that correlations between bonds are due to van der Waals interactions with an interaction energy falling off as r^{-6} with increasing distance r between bonds.

We determine next the various sums which appear in Eq. (22). One finds from Eq. (23),

$$N_c^{-1} \sum_I \langle S_I H_{\mathrm{res}} \rangle_c = 2 \widetilde{V}_{A_I B_I A_I B_I} = (U - K) = 2 V_0^D \, , \qquad (25)$$

where N_c is the number of unit cells, each containing four bonds. The remaining sums which involve operators within one bond only are

$$N_c^{-1} \sum_I \langle S_I H_{\mathrm{SCF}} S_I \rangle_c = 4 T_0 \, ,$$
$$N_c^{-1} \sum_I \langle S_I H_{\mathrm{res}} S_I \rangle_c = -2(K - 3J) \, , \qquad (26)$$

where use has been made of Eqs. (A1) and (A2). Similarly one can evaluate the terms in Eq. (22) which involve operators acting on neighboring bonds. For that purpose we abbreviate [see Eq. (23)]

$$\langle S_{IJ} H_{\mathrm{res}} \rangle_c = V_1^D \qquad (27)$$

when I and J are neighboring bonds.[30] One finds

$$N_c^{-1} \sum_{\langle IJ \rangle} \sum_{\langle KL \rangle} \langle S_{IJ} H_{\mathrm{SCF}} S_{KL} \rangle_c = 48 T_0 \, , \qquad (28a)$$

$$N_c^{-1} \sum_{\langle IJ \rangle} \sum_{\langle KL \rangle} \langle S_{IJ} H_{\mathrm{res}} S_{KL} \rangle_c = 24[V_0^D + 4V_1^D - (K - J)] \, . \qquad (28b)$$

There are 12 pairs of neighboring bonds per unit cell. The term $96 V_1^D$ results from $J = L$ but $I \neq K$. It describes local field corrections. A dipole fluctuation in bond I induces dipoles in bonds J and K. The dipole in bond K contributes to the local electric field in bond J and therefore to the dipole which is formed there. The remaining terms in Eq. (28b) describe the influence of the electron interactions on the polarizability of a bond. Stated differently, the induction of a dipole in a bond is different in the presence and absence of electron correlations.

Finally one finds

$$N_c^{-1} \sum_I \sum_{\langle KL \rangle} \langle S_I H_{\mathrm{res}} S_{KL} \rangle_c = 24 V_1^D \, , \qquad (29)$$

which describes the mutual influence of correlations within a bond and between neighboring bonds. The correlation energy per unit cell then becomes

$$E_{\mathrm{corr}} = -4\eta_0 V_0^D + 4\eta_0^2 t_0 - 48\eta_1 V_1^D + 48\eta_1^2 t_0 \alpha + 48\eta_0\eta_1 V_1^D \, , \qquad (30)$$

where the abbreviation

$$\alpha = 1 + \frac{V_0^D}{2t_0} + \frac{2V_1^D}{t_0} \qquad (31)$$

has been introduced.

It should be noticed that the bare hopping element t_0 enters into E_{corr} instead of the SCF hopping matrix element T_0. The intrabond hopping t_0 is the only hybrid hopping matrix element which appears in the expression for the correlation energy. Therefore E_{corr}, as given by Eq. (30), is ultimately connected with the formation of the bonds and is an interatomic or bond correlation energy.

The variational parameters η_0 and η_1 are determined from $\partial E_{\mathrm{corr}} / \partial \eta_{0(1)} = 0$, respectively. This yields the coupled equations

$$\eta_0^{\mathrm{st}} = \frac{V_0^D}{2t_0} - \frac{6V_1^D}{t_0}\eta_1^{\mathrm{st}} ,$$
$$\eta_1^{\mathrm{st}} = \frac{V_1^D}{2t_0\alpha}(1-\eta_0^{\mathrm{st}}) \tag{32}$$

for the stationary values η_i^{st}. When set into Eq. (30) the latter can be simplified to the form

$$E_{\mathrm{corr}} = -2V_0^D\eta_0^{\mathrm{st}} - 24V_1^D\eta_1^{\mathrm{st}} . \tag{33}$$

A discussion of Eq. (33) with respect to perturbation theoretical results is given in Appendix B. It is instructive to consider correlations within a bond only, i.e., to set $\eta_1 = 0$. In that case $\eta_0^{\mathrm{st}} = \eta_0^{(0)}$ with

$$\eta_0^{(0)} = \frac{V_0^D}{2t_0} , \tag{34a}$$

and

$$E_{\mathrm{corr}}^{(0)} = -\frac{(V_0^D)^2}{t_0} . \tag{34b}$$

As a side remark we mention that making the GW approximation would increase $E_{\mathrm{corr}}^{(0)}$ by a factor of 2 (see Appendix A).

In practice it turns out to be quite a good approximation to replace Eqs. (32) by

$$\eta_0^{\mathrm{st}} = \eta_0^{(0)}, \quad \eta_1^{\mathrm{st}} = \frac{V_1^D}{2t_0\alpha}(1-\eta_0^{(0)}) . \tag{35}$$

We repeat that in obtaining Eq. (33), spin-spin correlations have been neglected completely as well as density-density correlations beyond nearest-neighbor bonds. Both contributions are estimated to be very small in the systems we study here[8,31] (≈ -0.1 eV in diamond).

A. Polar semiconductors

At this stage we want to discuss briefly the extension of the present theory to polar semiconductors. In these systems, a new characteristic parameter, the polarity α_p of a bond, enters into the calculations.[11] By considering how the interaction and hopping matrix elements depend on α_p one finds that

$$E_{\mathrm{corr}}(\alpha_p) \approx (1-\alpha_p^2)^{5/2} E_{\mathrm{corr}}(0) . \tag{36}$$

In Eq. (36), $E_{\mathrm{corr}}(0)$ is the interatomic or bond correlation energy of a (fictitious) covalent semiconductor ($\alpha_p = 0$) of the same bond length as the polar semiconductor under consideration. For GaAs, which has nearly the same bond length as Ge, we obtain, therefore,

$$E_{\mathrm{corr}}(\mathrm{GaAs}) \approx \tfrac{1}{2} E_{\mathrm{corr}}(\mathrm{Ge}) ,$$

where $\alpha_p(\mathrm{GaAs}) = \frac{1}{2}$ has been used.

This shows that in a polar semiconductor the interatomic or bond correlations are not as important as in covalent semiconductors. In particular one expects that the bond correlation energy tends to zero as the system becomes purely ionic ($\alpha_p = 1$). A more accurate determination of $E_{\mathrm{corr}}(\alpha_p)$ will be the subject of a separate investigation.

B. Pair correlation function

It is instructive to calculate the pair correlation function in the correlated ground state

$$g_{ij} = \langle \psi_0 | n_i n_j | \psi_0 \rangle_c , \tag{37}$$

and to compare it with the one in the SCF ground state $g_{ij}^{\mathrm{SCF}} = \langle n_i n_j \rangle$. In the following we identify the index i with the arbitrarily chosen hybrid 1. The results are shown in Fig. 2. When we label the hybrids as indicated in the inset of that figure it is found that $g_{11} = (1-\eta_0^{\mathrm{st}})/2$, $g_{12} = (1+\eta_0^{\mathrm{st}})/2$, $g_{13} = 1+\eta_1^{\mathrm{st}}$, $g_{14} = 1-\eta_1^{\mathrm{st}}$, $g_{1\bar{3}} = 1-\eta_1^{\mathrm{st}}$, $g_{1\bar{4}} = 1+\eta_1^{\mathrm{st}}$, etc. The correlation contributions $\delta g_{ij} = g_{ij} - g_{ij}^{\mathrm{SCF}}$ are due to the polarization fluctuations in the bonds. Therefore they fall off very fast, i.e., as r^{-3} if r is the distance between the bonds. In the ground state the SCF pair correlation function is changed appreciably only on a length scale which is less than three bond lengths (see Fig. 2).

It is easy to see that E_{corr}, as given by Eq. (33), can be rewritten as

$$E_{\mathrm{corr}} = \sum_{i,j=1}^{I} V_{iijj}\,\delta g_{ij} + 6 \sum_{i=1}^{I} \sum_{k=1}^{K} (V_{iikk} - \tfrac{1}{2} V_{ikki})\,\delta g_{ik} \tag{38}$$

where I and K denote neighboring bonds with hybrids $i(j)$ and k. This equation shows explicitly within our approach the connection between the changes $\delta g_{ij} = g_{ij} - g_{ij}^{\mathrm{SCF}}$ in the pair correlation function and the correlation energy.

It should be pointed out that δg_{ij} looks very different when i refers to an additional electron or hole added to the system, as in a calculation of the quasiparticle band structure. In this case the correlation contributions δg_{ij} to the pair correlation function as well as to the quasiparticle band structure are due to the long-ranged polarizations of the bonds around the extra particle.[9,28,32]

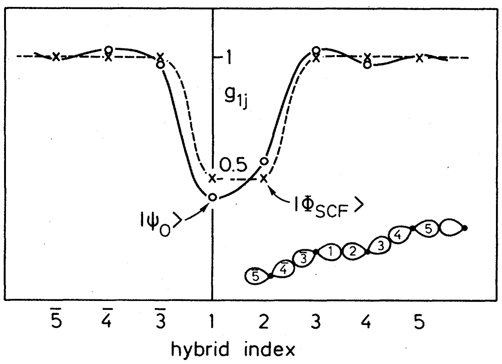

FIG. 2. Pair correlation functions g_{1j}^{SCF} and g_{1j} along a zigzag chain of carbon atoms, as indicated in the inset. The lines serve as guides to the eye.

C. Extended bond-orbital approximation (EBOA)

Finally, we would like to mention the modifications which arise when the BOA is replaced by the EBOA. This approximation allows for charge fluctuations between different bonds which are excluded in the BOA. In distinction to the BOA, a Wannier function $W_{I\sigma}^{\dagger}$ also contains admixtures of antibonding functions from neighboring bonds, i.e.,

$$W_{I\sigma}^{\dagger}=N^{-1}\left[B_{I\sigma}^{\dagger}+\sum_{J\,(\neq I)}\lambda_{IJ}A_{J\sigma}^{\dagger}\right] . \tag{39}$$

N is a normalization factor. The coupling parameter $\lambda=|\lambda_{IJ}|$ is usually small for semiconductors, i.e., $\lambda \lesssim 0.1$.[28] It turns out that the correlation-energy correction due to λ is of order λ^2. With $V_1^D/V_0^D \cong 0.4$, the correction factor for the correlation energy $E_{\text{corr}}^{(0)}$ [see Eq. (34)] is approximately $(1-6\lambda^2)$, and therefore can be safely neglected. The same holds true for the correlation energy between different bonds. This demonstrates again that the correlation energy of a system is relatively insensitive to small changes in the ground-state wave function.

IV. INTRA-ATOMIC CORRELATION ENERGY

In addition to the interatomic or bond correlations one must consider the intra-atomic correlations, because they also contribute to the cohesive energy and other physical properties of the solid. An accurate calculation of the intra-atomic correlation energy in a solid would require the use of a very large basis set, containing high angular-momentum functions. Such type of calculations, however, are very elaborate and have been started only recently.[8]

To obtain an estimate for the intra-atomic correlation energy we first will use an atoms in solids method which is based on some work of Verhaegen and co-workers,[13,14] to which we refer for more details. The basic idea is demonstrated in the following for diamond (C_x).

An isolated carbon atom has four valence electrons in the configuration s^2p^2, the ground state of which is given by the term ^3P according to Hund's rule. The situation is different for a carbon atom in diamond. Due to the covalent bonding the number n of valence electrons varies between $0 \le n \le 8$. We denote by $P_n(\text{C})$ the probability of finding n valence electrons at a given site in the ground state $|\psi_0\rangle$ of the crystal. The probability distribution of finding different configurations i when n is fixed is called $w_n(i)$. We will assume that the probabilities for different terms within a configuration are according to their respective degeneracies. The total intra-atomic correlation energy (per unit cell) of diamond is then approximated by

$$E_{\text{corr}}^{\text{intra}}(\text{C}_x)=2\sum_n P_n(\text{C})\epsilon_n(\text{C}) , \tag{40a}$$

$$\epsilon_n(\text{C})=\sum_i w_n(i)\epsilon_n^{\text{at}}(i) . \tag{40b}$$

Here $\epsilon_n^{\text{at}}(i)$ is the correlation energy of an isolated carbon atom (ion) characterized by n and i with different terms weighted according to their degeneracies. It can be obtained therefore from atomic calculations.

In writing Eq. (40a) one assumes that interatomic and intra-atomic correlations are independent of each other. This has been shown to be a good approximation[8,10] and we assume that it also holds true here. Calculating $\epsilon_n(\text{C})$ in the way described underestimates the weight of the Hund's rule state within each configuration. Therefore the correlation energy may be overestimated somewhat. Another implicit assumption made in writing Eq. (40b) is that renormalization effects are unimportant. They can result from the different spatial extent of the electronic wave functions when the atom is free or part of a solid.

For the $w_n(i)$ we use the same values as have been calculated for a carbon atom in CH_4 or C_2H_6.[33] We believe that this is a good approximation because we know from a number of molecular calculations[33] that this distribution is very insensitive to the atomic surroundings as long as one is dealing with σ bonds. By using the numerical values for $\epsilon_n^{\text{at}}(i)$ for the carbon atom as given in Ref. (13) the correlation energies $\epsilon_n(\text{C})$ can be calculated. They are listed in Table I. The corresponding energies for Si, Ge, and Sn are not known, unfortunately.

It should be mentioned that a theory of the above form works quite well for the calculation of the intra-atomic correlation energy of hydrocarbon molecules without π bonds.[33]

Finally, it is instructive to compare the correlated ground state $|\psi_0\rangle$ and the SCF ground state $|\Phi_{\text{SCF}}\rangle$ with respect to a population analysis. In $|\Phi_{\text{SCF}}\rangle$ the probability of finding n valence electrons at an atomic site is given by a binomial distribution P_n^{SCF}. This function can be easily calculated in the BOA and is tabulated in Table I. P_n^{SCF} has its maximum value for $n=4$. For the parameter

$$\beta_{\text{SCF}}=\langle(\Delta n)^2\rangle , \tag{41}$$

which is related to the charge fluctuation $\Delta n = n-4$, the BOA yields a value $\beta_{\text{SCF}}=2$. We now compare this result with the charge fluctuations at a carbon atom in the correlated ground state $|\psi_0\rangle$. We label with a,b two hybrids of one atom and make use of

$$\begin{aligned}\langle\psi_0|n_{a\uparrow}n_{a\downarrow}|\psi_0\rangle_c&=\tfrac{1}{4}(1-\eta_0) ,\\ \langle\psi_0|n_a n_b|\psi_0\rangle_c&=1-\eta_1 ,\end{aligned} \tag{42}$$

to find

$$\beta_{\text{corr}}=\langle\psi_0|(\Delta n)^2|\psi_0\rangle_c=2(1-\eta_0-6\eta_1) . \tag{43}$$

For diamond this gives a value of $\beta_{\text{corr}}=1.25$ as compared with $\beta_{\text{SCF}}=2$. It is seen that the charge fluctuations are considerably reduced in the correlated ground state. Numerical values for $P_n^{\text{corr}}(\text{C})$ are given in Table I. It has been assumed that P_n^{corr} is given by a Gaussian distribution,[34]

$$P_n^{\text{corr}}=(2\pi\beta_{\text{corr}})^{-1/2}\exp\left[-\frac{1}{2\beta_{\text{corr}}}(n-4)^2\right] . \tag{44}$$

This expression will be used in Eq. (40a) when the intra-atomic correlation energy is calculated.

This completes the description of the atoms in solids method. We show next how the intra-atomic correlation energy of diamond can be approximately determined from

TABLE I. Atomic correlation energies ϵ_n (including core electrons) in eV as defined in the text and probabilities P_n of finding n valence electrons on a carbon atom in diamond (for the SCF and correlated ground state, respectively).

n	0	1	2	3	4	5	6	7	8
$-\epsilon_n$	1.2	1.4	2.2	3.4	4.9	6.6	8.1	9.7	11.2
$2^8 P_n^{\mathrm{SCF}}$	1	8	28	56	70	56	28	8	1
$2^8 P_n^{\mathrm{corr}}$	0.15	2.5	18.5	61.2	91.3	61.2	18.5	2.5	0.15

an analysis of the correlation energies of some simple hydrocarbon molecules. From such an analysis one obtains the intra-atomic correlation energy $E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C})$ of a carbon atom in a molecule. One can use then the same value for diamond. In our opinion this is a good approximation because we will see in Sec. V that $E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C})$ is the same in all (hydrocarbon) alkane molecules $\mathrm{C}_n\mathrm{H}_{2n+2}$ which we will investigate. Therefore we do not expect that $E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C})$ will be much different when we move on to diamond.

We start from the expression

$$E_{\mathrm{corr}}^{\mathrm{total}}(\mathrm{C}_n\mathrm{H}_{2n+2}) = E_{\mathrm{corr}} + (2n+2)E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{H}) + nE_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C}) \qquad (45)$$

for the total correlation energy of simple hydrocarbon molecules which involve σ bonds only. Here E_{corr} is the interatomic or bond correlation energy of the molecule. Values for E_{corr} are taken from numerical calculations for a number of molecules. The second term on the right-hand side is the intra-atomic correlation energy of the $(2n+2)$ hydrogen atoms in the molecule. For the intra-atomic correlation energy of one hydrogen atom we use $E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{H}) = -0.25$ eV. This value has been obtained from an *ab initio* calculation of CH_4.[10] It is insensitive to the particular form of the molecule.[10,35] The last term on the right-hand side is the intra-atomic correlation energy of the n carbon atoms in the molecule. From Eq. (45) $E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C})$ can be calculated if the other energies are known. This is done in Sec. V.

V. NUMERICAL RESULTS

We present in the following some numerical results for the inter- and intra-atomic correlation energies per unit cell of C, Si, Ge, and α-Sn. Let us begin with the interatomic correlations. In order to compute them we must know the numerical values for t_0, V_0^D, and V_1^D for each substance. Since they are available only for diamond we must estimate them for Si, Ge, and α-Sn by a scaling procedure.

The SCF calculations for diamond of Kiel *et al.*[8,27] yield the values

$$V_0^D(C_x) = 4.6 \text{ eV}, \quad V_1^D(C_x) = 1.1 \text{ eV} . \qquad (46)$$

For $t_0(C_x)$ we have chosen a value of 10.7 eV. This value was extracted from a fit to *ab initio* Hartree and Hartree-Fock band structures for diamond,[28,36] using the BOA. With these parameter values, one finds for diamond $\eta_0^{(0)} = 0.21$ and $E_{\mathrm{corr}}^{(0)} = -2.0$ eV. When Eqs. (32) and (33) are used one finds that $\eta_0^{\mathrm{st}} = 0.20$, $\eta_1^{\mathrm{st}} = 0.029$, and

$$\begin{aligned} -2\eta_0^{\mathrm{st}} V_0^D &= -1.8 \text{ eV (intrabond correlations)} , \\ -24\eta_1^{\mathrm{st}} V_1^D &= -0.8 \text{ eV} \\ &\quad \text{(nearest-neighbor interbond correlations)} . \end{aligned} \qquad (47)$$

When one adds an estimated -0.1 eV for correlations between more distant bonds[8,31] one obtains

$$E_{\mathrm{corr}}(C_x) = -2.7 \text{ eV} . \qquad (48)$$

The numerical values from SCF calculations for the parameters t_0, V_0^D, and V_1^D are not known for Si, Ge, α-Sn. Therefore we use scaling relations in order to derive them from those of diamond. We scale according to

$$t_0^{\xi} = t_0^{C_x}(d_{C_x}/d_{\xi})^{1.8} , \qquad (49a)$$

$$V_0^{D,\xi} = V_0^{D,C_x}(d_{C_x}/d_{\xi})^{1.4} , \qquad (49b)$$

$$V_1^{D,\xi} = V_1^{D,C_x}(d_{C_x}/d_{\xi})^{1.4} , \qquad (49c)$$

where d denotes the bond length. The index C_x stands for diamond and ξ for Si, Ge, α-Sn. A relation of the form of Eq. (49a) is found in Ref. 28 (see Ref. 36). The relation (49b) was obtained as follows. The interaction matrix elements U,K can be calculated easily[37] for nonorthogonal hybrids constructed from atomic s and p functions by using the results of atomic Hartree-Fock calculations. The latter have been tabulated by Mann[38] for the entire Periodic Table. In order to obtain the matrix elements for the orthogonalized atomic hybrids the Mulliken approximation[39] was made. It was found that $(\mathrm{U}\text{-}\mathrm{K})_{\mathrm{atomic}}$ scales with $d^{-1.4}$, d being the bond length. The assumption is made that the same scaling property holds when instead of the atomic hybrids the required SCF hybrids in the solid are used. Since $V_0^D = (\mathrm{U}\text{-}\mathrm{K})/2$, this yields immediately the relation (49b). The Eq. (49c) was assumed to be valid without further justification.

The resulting numerical values for t_0, V_0^D, and V_1^D are shown in Table II. The variational parameters $\eta_0^{\mathrm{st}}, \eta_1^{\mathrm{st}}$ can now be determined according to Eq. (32). They are listed in Table III. One notices that the η parameters become larger in going from diamond to Si, Ge, and α-Sn. This is due to the fact that the bare hopping matrix element t_0 changes more rapidly than the interaction matrix elements V_0^D and V_1^D. The bond correlation energy per unit cell E_{corr} is listed in Table IV together with its decomposition into intrabond and interbond contributions. As expected the intrabond contributions exceed the interbond contributions. The results are relatively insensitive to moderate changes in the exponent of the scaling laws for V_0^D, V_1^D.

TABLE II. Numerical values for the parameters t_0, V_0^D, V_1^D (in eV).

	C	Si	Ge	α-Sn
t_0	10.7	5.0	4.7	3.6
V_0^D	4.6	2.5	2.4	2.0
V_1^D	1.1	0.6	0.6	0.5

TABLE IV. Calculated interatomic or bond correlation energy per unit cell (in eV).

	C	Si	Ge	α-Sn
$-2\eta_0^{\mathrm{st}}V_0^D$	1.8	1.2	1.2	1.1
$-24\eta_1^{\mathrm{st}}V_1^D$	0.8	0.4	0.4	0.4
$-E_{\mathrm{corr}}$	2.6	1.6	1.6	1.5

Next we discuss the intra-atomic correlation energies. As pointed out before the fluctuations in the number of valence electrons at an atomic site are drastically reduced in the correlated ground state. We list in Table V the values for $\beta_{\mathrm{corr}} = \langle \psi_0 | (\Delta n)^2 | \psi_0 \rangle_c$ for the four systems under consideration. They have to be compared with $\beta_{\mathrm{SCF}} = 2$.

In the following we shall consider diamond only, because the required atomic calculations are available for the carbon atom only. We will attempt below a rough extrapolation to the other systems.

By combining the energies $\epsilon_n(\mathrm{C})$ listed in Table I with the Gaussian distribution (44) one obtains

$$E_{\mathrm{corr}}^{\mathrm{intra}}(C_x) = -10.0 \text{ eV} . \tag{50}$$

Nearly the same result (-10.1 eV) is obtained when the SCF population is used. This demonstrates that the result is insensitive with respect to an accurate determination of P_n.

Next we use the second method described in Sec. IV to calculate the intra-atomic correlation energy (per unit cell) of diamond. We use for the interatomic or bond correlation energies of CH_4, C_2H_6, and C_3H_8 the values -1.9, -3.5, and -5.1 eV,[10,33,35] respectively. For the total correlation energies of these molecules, we use the numbers -8.0, -15.0, and -22.0 eV,[40] respectively. From Eq. (45) we finally obtain for the intra-atomic correlation energy of one carbon atom

$$E_{\mathrm{corr}}^{\mathrm{intra}}(\mathrm{C}) = -5.0 \text{ eV} . \tag{51}$$

This leads to the same result for the intra-atomic correlation energy of diamond as in Eq. (50).

In order to compute the contribution of the intra-atomic correlation energy $\Delta E_{\mathrm{intra}}^{\mathrm{coh}}$ to the cohesive energy of diamond, one must subtract from Eq. (50) the correlation energy for two isolated carbon atoms,[41] i.e.,

$$E_{\mathrm{corr}}(2\mathrm{C}) = -8.4 \text{ eV} . \tag{52}$$

This results in

$$\Delta E_{\mathrm{intra}}^{\mathrm{coh}}(C_x) = 1.6 \text{ eV} \tag{53}$$

and a total correlation contribution to the cohesive energy of

$$\Delta E_{\mathrm{corr}}^{\mathrm{coh}}(C_x) = 4.3 \text{ eV} . \tag{54}$$

Although the total correlation energy $E_{\mathrm{corr}}^{\mathrm{tot}}(C_x) = -12.7$ eV is only a very small fraction ($<1\%$) of the ground-state energy of diamond, it contributes considerably (28%) to the cohesive energy which is $E_{\mathrm{exp}}^{\mathrm{coh}}(C_x) = 15.2$ eV. Whereas the total correlation energy $E_{\mathrm{corr}}^{\mathrm{tot}}(C_x) = -12.7$ eV is dominated by the intra-atomic correlation energy $E_{\mathrm{corr}}^{\mathrm{intra}}(C_x) = -10.0$ eV it is the interatomic or bond correlation energy which dominates the correlation contribution to the cohesive energy. Intra-atomic and interatomic correlations contribute to the cohesive energy in the ratio $\gamma = \frac{3}{5}$.

We want to mention that the estimated value of -12.1 eV,[7] for $E_{\mathrm{corr}}^{\mathrm{tot}}(C_x)$, agrees very well with the value of -12.7 eV calculated in our approach. From the *ab initio* calculation of Ref. 8 an estimated limit of -11.8 ± 0.5 eV for the total correlation energy (per unit cell) of diamond is obtained. Using the result given by Cremer[40] for the correlation energy of a carbon-carbon bond in simple hydrocarbon molecules one obtains an estimate of -12.2 eV for $E_{\mathrm{corr}}^{\mathrm{tot}}(C_x)$. All the results for $E_{\mathrm{corr}}^{\mathrm{tot}}(C_x)$ are in very good agreement.

As has been pointed out before, appropriate numerical data for the calculation of the intra-atomic correlation energies for Si, Ge, and Sn is not available. Therefore nothing rigorous can be said about the contributions of the intra-atomic correlations to the cohesive energy in these systems. But when one assumes that also in Si, Ge, and Sn the ratio γ is approximately the same as in diamond the results for the correlation contributions to the cohesive energy look reasonable. They are listed in Table VI together with the experimental values for the cohesive energies. One may use the values given in that Table VI for an estimate of the SCF contribution to the cohesive energy in diamond, Si, Ge, and α-Sn. For diamond the value $E_{\mathrm{SCF}}^{\mathrm{coh}}(C_x) = 10.9$ eV agrees very well with an estimate of 11.0 eV, which is based on an *ab initio* SCF calculation.[45]

Finally we want to discuss the contributions of the in-

TABLE III. Calculated values for η_0^{st} and η_1^{st}.

	C	Si	Ge	α-Sn
η_0^{st}	0.20	0.24	0.25	0.27
η_1^{st}	0.029	0.030	0.032	0.034

TABLE V. Square deviation $\beta_{\mathrm{corr}} = \langle \psi_0 | (\Delta n)^2 | \psi_0 \rangle_c$ in the number of valence electrons at an atomic site in the correlated ground state $|\psi_0\rangle$ ($\beta_{\mathrm{SCF}} = 2$).

	C	Si	Ge	α-Sn
β_{corr}	1.25	1.14	1.10	1.03

TABLE VI. Experimental cohesive energy (taken from Refs. 42—44) per unit cell $E^{\text{coh}}_{\text{exp}}$ (corrected for zero-point motion) and contribution $\Delta E^{\text{coh}}_{\text{corr}}$ of electronic correlations (in eV).

	C	Si	Ge	α-Sn
$E^{\text{coh}}_{\text{exp}}$	15.2	9.5	7.9	6.3
$\Delta E^{\text{coh}}_{\text{corr}}$	4.3	2.6	2.6	2.4

teratomic correlations to the radial force constant C_0. We assume that the intra-atomic correlations contribute much less to C_0 so that we can discard them. C_0 is given by

$$C_0 = \frac{d^2}{4}\left[\frac{\partial^2 E^{\text{coh}}}{\partial x^2}\right]\Bigg|_{x=d} . \tag{55}$$

The radial force constant is directly related to the bulk modulus.

In order to calculate the correlation contribution C_0^{corr} from Eq. (55) we have to know the dependence of the various matrix elements in Eq. (33) on small changes of the bond length. We assume t_0 to vary as $1/x^2$. Furthermore we assume that the on-site Coulomb matrix elements remain constant and that the other Coulomb matrix elements vary as $1/x$. This should be a reasonable approximation because the dominant Coulomb matrix elements for the hybrid functions entering V_0^D and V_1^D are of the form V_{iijj}.

We obtain then the following estimate

$$C_0^{\text{corr}} = -\frac{U^2}{8t_0} . \tag{56}$$

In Eq. (56) a small contribution due to the electronic correlations between different bonds has been neglected. C_0^{corr} is dominated ($\geq 90\%$) by the intrabond correlations. For diamond, U=22.5 eV (Ref. 27) and $C_0^{\text{corr}} = -5.9$ eV. The experimental value is $C_0 = 70$ eV.[46] We do not expect C_0^{corr} to be much different for Si, Ge, and α-Sn because t_0 varies from one substance to the other as $1/d^{1.8}$ and U should scale roughly as $1/d$.

It should be noted that the correlation contribution to the radial force constant is negative. This means that the corresponding SCF force constant is weakened. This observation is in agreement with findings from SCF calculations on various molecules[47,48] and also on diamond.[49,50]

VI. SUMMARY

We have presented a simple variational scheme for determining the various contributions to the ground-state correlation energy of covalent semiconductors. The calculations demonstrated that the variational parameters η_i have an easy to grasp physical meaning. The correlation corrections to the SCF ground state with respect to charge fluctuations as well as the pair correlation function can be easily expressed in terms of these parameters.

Due to the BOA, the one-particle density matrix simplifies so much that the interatomic or bond correlation-energy calculations could be done analytically. We believe that the results are not very sensitive to find details of the wave function (see the discussion on the EBOA). It has been shown that the bond correlation energy as well as the correlation corrections to the pair correlation function are due to the short-ranged van der Waals interactions between bonds. Whereas in the ground state the polarization fluctuations are important it is the long-ranged polarization of the bonds around an extra particle which determines the influence of the electronic correlations on the quasiparticle band structure.

The intra-atomic correlation energies are not contained within the minimal basis set in terms of which the BOA was formulated. For their determination, an atoms in solids method has been used as well as an analysis of the correlation energies of some hydrocarbon molecules. The approximations involved were discussed in detail. We believe that the value of -5.0 eV for the intra-atomic correlation energy of a carbon atom in diamond is a rather accurate one. Due to the lack of appropriate numerical data the values given for Si, Ge, and Sn should be taken only as rough estimates.

In any case the present approach provides a simple and transparent way of understanding the various correlation corrections to the ground-state energy as well as the large amount (around 25%) of the correlation contribution to the cohesive energy. There is no difficulty in extending the local approach to the calculation of excited states of covalent semiconductors. This will be the subject of a separate publication. We believe that calculations of this type will help to clarify our understanding of the electronic properties in a class of materials which have been viewed for a long time as good candidates for a one-electron description.

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APPENDIX A: DIAGRAMMATIC REPRESENTATION AND *GW* APPROXIMATION

In the following we want to relate the various contributions to the expectation values $\langle SH_{\text{res}}\rangle_c$ and $\langle SHS\rangle_c$ to a corresponding diagrammatic representation. The general rules for the construction of such diagrams can be found in Ref. 9. The diagrams have the advantage of making transparent the origin of the various terms in the above expectation values.

The expectation value $\langle SH_{\text{res}}\rangle_c$ has two corresponding diagrams which are shown in Fig. 3 [diagrams (1a) and (1b)]. The operator to the right (here H_{res}) appears always at the bottom of a diagram with the other operators following in the same sequence in the diagram as they appear in the expectation value. The two diagrams (1a) and (1b) correspond to the two terms in Eq. (23).

Corresponding to $\langle SH_{\text{SCF}}S\rangle_c$ are the two diagrams (2a) and (2b). The one-electron operator H_{SCF} is represented by a cross. The resulting expression is

$$\langle S_{IJ} H_{\mathrm{SCF}} S_{KL} \rangle_c = 2T_0 \delta_{IK} (\delta_{JL} - \tfrac{1}{2} \delta_{KL} \delta_{IJ}) \ . \tag{A1}$$

From Eq. (A1) one obtains $\langle S_I H_{\mathrm{SCF}} S_{KL} \rangle_c = 0$. This means that H_{SCF} does not couple intra- and interbond correlations.

The diagrams (3a)—(3h′) represent the various contributions to the expectation value $\langle S H_{\mathrm{res}} S \rangle_c$, which is given by the following equation:

$$\begin{aligned} \langle S_{IJ} H_{\mathrm{res}} S_{KL} \rangle_c = {} & 2\delta_{JL} (\widetilde{V}_{A_I B_I A_K B_K} - \tfrac{1}{2} \widetilde{V}_{A_I A_K B_K B_I}) - \delta_{JL} \delta_{JK} (\widetilde{V}_{A_I B_I A_J B_J} - \tfrac{1}{2} \widetilde{V}_{A_I A_J B_J B_I}) \\ & - \delta_{JL} \delta_{IL} (\widetilde{V}_{A_L B_L A_K B_K} - \tfrac{1}{2} \widetilde{V}_{A_L A_K B_K B_L}) - \delta_{JK} \delta_{IL} (\widetilde{V}_{A_I A_I B_J B_J} - \tfrac{1}{2} \widetilde{V}_{A_I B_J A_I B_J}) \\ & + \tfrac{1}{2} \delta_{JK} \delta_{IL} (\widetilde{V}_{A_I A_I A_J A_J} - \tfrac{1}{2} \widetilde{V}_{A_I A_J A_J A_I}) + \tfrac{1}{2} \delta_{JK} \delta_{IL} (\widetilde{V}_{B_I B_I B_J B_J} - \tfrac{1}{2} \widetilde{V}_{B_I B_J B_J B_I}) \ . \end{aligned} \tag{A2}$$

The diagrams (3a) and (3b) correspond to the first line on the rhs of that equation. The second and third line correspond to (3c) and (3d) and (3c′) and (3d′), while those in the fourth line are represented by diagrams (3e) and (3f) and those in fifth and sixth line by (3g) and (3h) and diagrams (3g′) and (3h′), respectively.

When the energy is calculated due to correlations within a bond the diagrams (3a)—(3d′) cancel and only (3e)—(3h′) remain. On the other hand, to the correlation energy between different bonds only diagrams (3a)—(3d′) contribute while (3c)—(3h′) cancel each other. This is easily verified from Eq. (A2).

Next we discuss the GW approximation of Hedin.[18] It corresponds to taking into account only (1a), (2a), (3a), (3b), (3c), and (3c′). First let us consider correlations within the bonds only (i.e., $\eta_1 = 0$). In that case one finds

$$E^{(0)}_{\mathrm{corr},GW} = -4\eta_0 (2V_0^D) + 4\eta_0^2 (2T_0 - W) \ , \tag{A3}$$

where

$$W = \widetilde{V}_{A_I A_I B_I B_I} \approx \tfrac{1}{2} (\mathrm{U} + \mathrm{K}) \ . \tag{A4}$$

The contributions from the diagrams (3a), (3c), and (3c′) compensate each other. Minimizing Eq. (A3) results in

$$\begin{aligned} \eta_0^{(0)} &= \frac{V_0^D}{2t_0} \frac{1}{1 - V_0^D/(2t_0)} \ , \\ E^{(0)}_{\mathrm{corr},GW} &= -\frac{(V_0^D)^2}{t_0} \frac{2}{1 - V_0^D/(2t_0)} \ . \end{aligned} \tag{A5}$$

The last expression must be compared with Eq. (34b). It is seen that the GW approximation results in an increase of the intrabond correlations by more than a factor of 2. For example, for diamond, $E^{(0)}_{\mathrm{corr},GW} \cong -5.0$ eV instead of -2.0 eV.

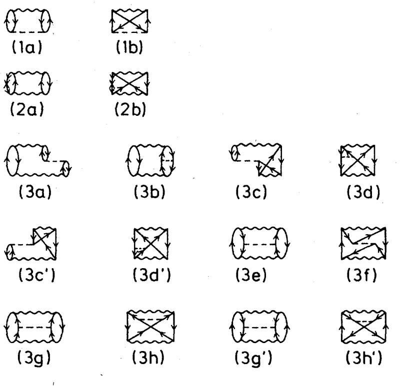

FIG. 3. Diagrams (v) contributing to the ground-state correlation energy. One can distinguish three classes of matrix elements, i.e., first-order matrix elements containing (1) the residual interaction H_{res}, second-order matrix elements arising from H_{SCF} (2), and (3) the interaction energy H_{res}. The wavy line corresponds to the operator S, the dashed line represents H_{res}, and the cross is associated with H_{SCF}.

The simplest way of realizing the shortcomings of the GW approximation when applied to a covalent semiconductor is to consider intead the H_2 molecule in a Hubbard model description. It can be considered as a rough simulation of a bond. In that case,

$$E_{\mathrm{corr},GW}(H_2) = -\frac{\mathrm{U}^2}{8t_0} - \frac{\mathrm{U}^3}{32t_0^2} \tag{A6}$$

while in the exact result the first term on the rhs should be multiplied by $\frac{1}{2}$ and the second term should be absent altogether (the next highest order term is proportional to U^4).

This incorrect description of the intrabond correlations is due to the neglect of the exchange diagrams, such as (1b), which correspond to vertex corrections in the spirit of the GW approximation.

The correlations between different bonds are treated in a reasonable way by the GW approximation. This is due to the fact that in this case the neglected exchange integrals (between functions of different bonds) are only of minor importance.

APPENDIX B: RELATION TO PERTURBATION THEORY

By expanding Eq. (33) for E_{corr} to second order in the electron-electron interaction, we obtain

$$E_{\mathrm{corr},2} = -\frac{(V_0^D)^2}{t_0} - 12 \frac{(V_1^D)^2}{t_0} \ . \tag{B1}$$

The same result is obtained by considering the bare Hamiltonian H_0 of Eq. (5) as unperturbed part and by treating H_{int} as a perturbation. Second-order Rayleigh-Schrödinger (RS) perturbation theory leads to Eq. (B1), which can also be written in the form

$$E_{\mathrm{corr},2}=-\frac{1}{4t_0}\langle(H_{\mathrm{int}}-\langle H_{\mathrm{int}}\rangle)^2\rangle \tag{B2}$$

when the BOA is used.[31] Equation (B2) explicitly shows the connection between the correlation energy and the fluctuation of the electron-electron interaction in the SCF ground state.

The computation of the interatomic or bond correlation energy within the BOA reminds one of the PCILO (perturbative configuration interaction using localized orbitals) method,[19–21] which is well known in quantum chemistry.

The difference is that the LA is a variational method and, more important, it can be easily extended to excited state calculations of infinite systems.[9,28,32]

In the PCILO method H_{SCF}, and not H_0, is treated as unperturbed Hamiltonian. In this case, second-order RS perturbation theory leads to

$$E_{\mathrm{corr},2}=-\frac{(V_0^D)^2}{T_0}-12\frac{(V_1^D)^2}{T_0}\ . \tag{B3}$$

Instead of the bare hopping matrix element t_0, the SCF hopping matrix element T_0 [see Eq. (24)] enters into the expression for the correlation energy. The same result is obtained within the LA, if the term $\langle SH_{\mathrm{res}}S\rangle_c$ in the correlation-energy calculation is neglected. In this case we have

$$E_{\mathrm{corr},2}=-4\eta_0V_0^D+4\eta_0^2T_0-48\eta_1V_1^D+48\eta_1^2T_0\ , \tag{B4}$$

which, after minimization, leads to Eq. (B3).

For diamond Eq. (B1) leads to $E_{\mathrm{corr},2}(C_x)=-3.3$ eV while Eq. (B3) gives $E_{\mathrm{corr},2}(C_x)=-2.1$ eV. The more accurate result obtained within the LA is $E_{\mathrm{corr}}(C_x)=-2.6$ eV (see Sec. V).

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$$V_1^D=[\langle\Phi_{\mathrm{SCF}}|H_{\mathrm{res}}|\psi_{\sigma,-\sigma}\rangle+\langle\Phi_{\mathrm{SCF}}|H_{\mathrm{res}}|\psi_{\sigma,\sigma}\rangle]/2\ .$$

The spin-spin correlations, on the other hand, are proportional to the difference $\langle\Phi_{\mathrm{SCF}}|H_{\mathrm{res}}|\psi_{\sigma,-\sigma}\rangle-\langle\Phi_{\mathrm{SCF}}|H_{\mathrm{res}}|\psi_{\sigma,\sigma}\rangle$, which, however, is very small in the systems studied here.

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