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Correlated ground state of diamond reexamined

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New *ab initio* correlation calculations for the correlated ground state and the binding energy of diamond are presented. As a starting point, we use an improved self-consistent-field ground state. It is obtained from a calculation within the local-density approximation (LDA). The correlation calculation is performed with the help of the local ansatz of Stollhoff and Fulde. Recent improvements in the correlation treatment are included. The resulting estimate of the binding energy obtained is considerably better than the LDA results. This variational scheme treats the short-range correlations very efficiently. The computations for diamond are, therefore, no more time consuming than comparable variational calculations for a small molecule like ethane.

I. INTRODUCTION

A quantitative understanding of electronic correlations is a necessary contribution to accurate *ab initio* calculations for solids. Here, short-range electron correlations play an especially important role. Only if they are well accounted for can good binding energies be obtained, for example. Other properties which are strongly influenced by these correlations are the properties of transition metals[1] as well as valence-fluctuating or heavy-fermion systems.[2]

These short-range correlations are well understood only in two limiting cases: first, for small molecules, and second, for the homogeneous electron gas. For the first case, a large number of quantum-chemistry methods exist which allow treatment of these small molecules with high accuracy.[3,4] For the case of the homogeneous electron gas, different methods exist too. There are coupled-cluster schemes[5,6] which compare with specific quantum-chemistry methods. There are Jastrow methods which recently could be extended to systems anisotropic in one dimension.[7,8] Finally, there are Monte Carlo methods which at present allow for the most accurate treatment of the homogeneous electron gas.[9] This last method is the only one which has been generalized to a few anisotropic solids,[10] although at considerable computation expenses. Neither the coupled-cluster schemes nor quantum-chemistry methods could be used for anisotropic solids yet. A reason is that both schemes are of purely numeric origin. Therefore, they run over a complete class of orthogonal excitations. This orthogonality requirement prevents an efficient coverage of the short-range part of the electronic correlations and requires a detailed inclusion of essentially all of these excitations. Long-range correlations on the other hand are covered for the homogeneous electron gas by any of the above-mentioned methods in a very simple fashion. It is expected that their treatment for anisotropic solids does not lead to major problems no matter which scheme is used.

Correlations are therefore usually included in computations for solids only within a specific approximation, namely the local approximation to the density-functional method (LDA).[11,12] There, one restricts to the solution of an one-particle Hamiltonian where electrons only "see" an effective correlation potential. The correlation potential as well as the exchange potential at a given point are assumed to be those of the homogeneous electron gas with an electronic density corresponding to the actual one on this site. This approximation allows for very efficient computations. Many physical properties could be explained by calculations within the LDA. There are shortcomings, however, caused by this rough approximation. Binding energies come out wrong by typically 1 eV for semiconductors, as will be discussed below. More serious problems arise for transition metals as far as details of the understanding of itinerant magnetism are concerned.[1,13] It seems at present as if there is no way to improve systematically beyond this approximation.[14]

We have developed a local ansatz (LA) of the treatment of electronic correlations which takes into account from the beginning the local character of the correlation hole.[15–17] Within this approach a computation of correlations within a solid is not much more expensive than within a molecule. It can be seen as a generalized Jastrow ansatz applied to anisotropic systems. We have tested this approach successfully on small molecules.[17,18] Correlations are treated variationally within given one-particle basis sets in analogy to quantum-chemistry methods. Although we include only a very small subset of excited states, namely those states which represent local correlation corrections, we obtain more than 95% of the complete energy available for the given one-particle basis set.[15–18]

Due to the drastic reduction in correlation space, it was possible to perform a first variation-like *ab initio* computation for a solid, namely for diamond.[19] There it turned out that the correlation calculations do not lead to any numerical problems. The preceding self-consistent-field (SCF) calculation, however, was less easy to handle. This first computation was handicapped by a rather poor SCF ground state and by poorly converged matrix elements. These shortcomings led to rather large uncertainties on the one-particle level and excluded careful checks of the convergence of the correlation calculation itself. Recently, progress has been made as far as SCF computations are concerned. A better SCF ground state could be computed and all one-particle matrix elements could be obtained with high precision.[20] This enabled us to repeat the correlation computations with much better accuracy. Furthermore we included all improvements which have been developed recently on calculations for small molecules.[18] The local ansatz of Stollhoff and Fulde will be discussed in Sec. II. Section III contains details of the actual computation as well as the results for the total and binding energy of diamond. Section IV then gives details about the convergency of these calculations and about the computational expenses. Section V deals with the pair correlation functions. Conclusions are drawn and further possible improvements and fields of applicability are discussed in Sec. VI.

II. THE CALCULATION OF ELECTRONIC CORRELATIONS WITHIN THE LOCAL ANSATZ

As with most quantum-chemical methods, this approach has been developed specifically for variational-like calculations within a given finite one-particle space of Gaussian-type orbitals (GTO's) $f_i(r)$, which are centered at different atoms. The corresponding creation and annihilation operators are called $\hat{a}^{\dagger}_{i\sigma},\hat{a}_{i\sigma}$. Within the Hilbert space spanned by them, the Hamiltonian is written as

$$H=\sum_{i,j,\sigma}\varepsilon_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+\frac{1}{2}\sum_{i,j,k,l,\sigma,\sigma'}V_{ijkl}a^{\dagger}_{i\sigma}a^{\dagger}_{k\sigma'}a_{l\sigma'}a_{j\sigma}\ , \tag{1}$$

where

$$\varepsilon_{ij}=\int d^3r\, f_i^{*}(r)[-\tfrac{1}{2}\Delta+V(r)]f_j(r)\ ,$$

$$V_{ijkl}=\int d^3r\int d^3r'\, f_i^{\dagger}(r)f_j(r)\times\frac{1}{|r-r'|}f_k^{*}(r')f_l(r')\ .$$

$V(r)$ is the single-electron potential due to the nuclei. The operators $a_i^{\dagger},a_i$ are adjoint to the operators $\hat{a}^{\dagger}_{i\sigma},\hat{a}_{i\sigma}$. For the anticommutation relations it holds that

$$\{a_{i\sigma},a^{\dagger}_{j\sigma'}\}=S_{ij}^{-1}\delta_{\sigma\sigma'}$$

with the overlap matrix

$$S_{ij}=\langle f_i\,|\,f_j\rangle\ .$$

Through a self-consistent field (SCF) calculation, the SCF ground state $|\psi_{\rm SCF}\rangle$ is obtained. It is determined by the one particle eigenstates of the effective one-particle Hamiltonian

$$H_0=\sum_{i,j,\sigma}(\varepsilon_{ij}+V_{\mathrm{Coul}\,ij}+V_{\mathrm{excl}\,ij})a^{\dagger}_{i\sigma}a_{j\sigma}\ , \tag{2}$$

where the Coulomb($V_{\mathrm{Coul}\,ij}$) and exchange ($V_{\mathrm{exch}\,ij}$) potentials are determined self-consistently.[17]

For the correlated ground state, the following ansatz is made:[15–17]

$$|\psi_c\rangle=e^{-S}|\psi_{\rm SCF}\rangle \tag{3}$$

with

$$S=\sum_n\eta_nO_n\ .$$

The operators O_n take the three forms

$$O_n=\begin{cases}n_{i\uparrow}n_{i\downarrow}\\ n_in_j=\sum_{\sigma,\sigma'}n_{i\sigma}n_{j\sigma'}\\ \mathbf{S}_i\cdot\mathbf{S}_j\ .\end{cases} \tag{4}$$

The $n_{i\sigma}$ are occupation number operators and the $\mathbf{S}_i$ are spin operators for electrons in the state i. The states i are described by localized functions $g_i(r)$ which are defined as

$$g_i(r)=\sum_j\gamma_{ij}f_j(r)\ . \tag{5}$$

The first two kinds of operators O_n, when applied to $|\psi_{\rm SCF}\rangle$, project out those parts of it in which two electrons are in the same or in neighboring states at the same time. They therefore reduce local charge fluctuations. The third kind of operator correlates the spins of electrons on neighboring sites. Within the actual computations these operators are not chosen in the original form as Eq. 4. The original operators, when applied to $|\psi_{\rm SCF}\rangle$ create a state which is not orthogonal to $|\psi_{\rm SCF}\rangle$ and include contributions which describe one-particle excitations of $|\psi_{\rm SCF}\rangle$. In the following, only those parts of the above operators will be kept which describe two-particle excitations. This formally implies that no contractions of fermion operators belonging to the same correlation operator are allowed when expectation values are calculated. For more details see Ref. 17. These parts of the projection operators represent the fluctuations in charge or spin around the mean values in $|\psi_{\rm SCF}\rangle$. It is these fluctuations which need to be suppressed when they arise for charges and eventually increased when spin ordering comes into play.

The variational parameters η_n of the correlated ground state are determined by optimizing its energy

$$E=\langle\psi_c\,|H|\,\psi_c\rangle_c\ . \tag{6}$$

The subscript c to the angular brackets means that only connected diagrams are to be included for the evaluation of E.[21]

The variational computation cannot be performed exactly. An approximate solution is a variational expansion. There, E is expanded in powers of η

$$E = E_{\mathrm{SCF}} - 2\sum_{n} \eta_n \langle O_n \tilde{H} \rangle + \sum_{n,m} \eta_n \eta_m \langle O_n \tilde{H} O_m \rangle \tag{7}$$

with

$$\tilde{H} = H - E_{\mathrm{SCF}} \ .$$

Here $\langle A \rangle$ means $\langle \psi_{\mathrm{SCF}} | A | \psi_{\mathrm{SCF}} \rangle$. The optimization of Eq. (7) immediately leads to

$$E = E_{\mathrm{SCF}} - \sum_{n,m} \langle O_n \tilde{H} \rangle (\langle O \tilde{H} O \rangle)^{-1}_{nm} \langle O_m \tilde{H} \rangle \ . \tag{8}$$

This expansion is equivalent to the so called CEPA-0 variant of coupled cluster schemes in quantum chemistry, with the advantage, however, that it is performed within a very small subspace of two-particle excitations, namely those defined in Eq. (4).

Note that second-order perturbation expansion is obtained by replacing $\langle O\tilde{H}O \rangle$ by $\langle O\tilde{H}_0 O \rangle$ in Eq. (8). The result of Eq. (8) contains all corrections up to third order. It does not diverge for long-range correlations in metals.[21] The derivation of this result as well as the calculation of the matrix elements $\langle O\tilde{H} \rangle$, $\langle O\tilde{H}O \rangle$ are described in detail in Refs. 17 and 21.

The proper choice of the functions g_i (or the γ_{ij}) Eq. (5) is of prime importance for an effective correlation calculation. Experience gained from calculations for small molecules suggests the following procedure.

A first choice of local functions is that of atomic orbitals or atomic hybrids. With hybrids we mean orbitals obtained by a hybridization of the s and p atomic orbitals for diamond which point into the bond directions. For diamond these atomic orbitals are obtained from the bond orbitals of the SCF ground state. Details will be given below. All these atomic orbitals are orthogonalized to the core states and to each other. The operators constructed with these atomic functions have a special meaning. They describe mostly correlations which arise due to bonding. We have called them therefore "interatomic." The bonding leads immediately to charge fluctuations. The operator $n_{i\uparrow}n_{i\downarrow}$ now allows for reducing the probability to find two electrons in the same atomic hybrid at the same time. Additional important contributions come from the operators where the states i,j are on the same atom. The operators $n_i n_j$ allow reduction of the charge fluctuations on an atom. These global fluctuations are only partially suppressed by the diagonal terms $n_{i\uparrow}n_{i\downarrow}$. The operators $\mathbf{S}_i \cdot \mathbf{S}_j$ finally allow the electrons on a given atom to align their spins and therefore to obey Hund's rule at least partially on that site. Operators with pairs of states on different atoms need to be chosen, too. They describe the longer-range correlations. In metallic systems they are important and screen the long-range charge fluctuations. For the case of diamond, they only lead to a van der Waals polarization between more distant bonds.

These interatomic correlations are quite strong. They cannot be described by second-order perturbation expansion only. For these correlations, Eq. (8) needs to be computed without further approximations.

The interatomic operators describe a significant part of the changes in the pair correlation function due to correlations but the energy gain due to these correlations is only a fraction of the total correlation energy. The largest contributions to this energy come from "intra-atomic correlations" as we call them. They describe the strong variations in the short-range part of the correlation hole around each electron. This correlation hole even has a cusp at the electron position. These correlations are present for the solid as well as for individual atoms. They contribute to the binding energy too since the mean electron density within a solid is higher than that within an individual atom and since often the occupation of the atomic states changes within a solid due to hybridization effects.

When described within the LA, the local states $g_i(r)$ are therefore to be defined as small subregions of the atomic orbitals. The computations are restricted to a finite one-particle basis for each atom, though. Therefore, only a finite subdivision of the atomic volume with such local states is possible; the mesh of local regions in fact has to be of the same dimension as the basis size. The correlations are to be averaged within the volume of each subregion. This restriction is a global shortcoming of correlation calculations within finite basis sets. Due to the strong variation of the correlation hole on very-short-range distances, such calculations always miss a non-negligible part of the correlation energy, its convergence with basis-size dimension being rather slow. Therefore, a larger basis needs to be chosen for the correlation calculations than for the SCF calculations themselves. The specific method how to construct localized states from the basis set will be discussed later. Here it is sufficient to mention that there are essentially two degrees of freedom for such constructions: first a separation of the atomic volume into shells, and second, an angular separation of these shells into hybrids. It is important to note that all these states are defined by basis orbitals on the corresponding atom only. The operators constructed by these states on a single atom describe the short-range correlations there. Furthermore, correlations connecting subatomic regions on neighbor atoms need to be included. They lead to small corrections.

This definition of very localized operators has an immediate consequence. It is evident that short-range correlations on separate parts of the solid do not interact with each other. In fact, it turned out that these short-range correlations influence each other only as long as there is a significant overlap of these regions. The computation therefore splits into the following independent sets of calculations: (1) SCF calculation within a sufficiently good basis set [for example double ζ—this means two sets of (contracted) GTO's for each atomic orbital]; (2) inclusion of interatomic correlations within the whole solid—this computation needs to be performed only within the basis set of the SCF calculation; and (3) addition of further basis functions on single atoms and computation of the additional intra-atomic correlations on these atoms. The dominant part of the total intra-atomic correlation energy is obtained by adding these contributions from all atoms independently. In the case of diamond only a single calculation with correlations on a specific C atom needs to be performed. There are finally small corrections to be computed. These are (4) computations which simultaneously take into account the intra-atomic correlations on two neighboring atoms within the increased basis sets and add correlations between regions on both atoms. In this step an overlap correction is made to step (3) since otherwise specific correlations in the region in between both atoms might be counted twice by the individual and independent computations there. Further, new operators for short-range correlations between both atomic sites are added. In the case of diamond this means that a single further computation is performed which covers correlations on two neighbor atoms. It turned out that the corrections of step (4) are very small as compared with the result of step (3). Besides, corrections due to overlap effects of non-neighbor atoms can be neglected.[17]

Another approximation made possible by the separation into interatomic and intra-atomic correlations is that intra-atomic correlations when orthogonalized to the interatomic correlations can be treated in second-order perturbation expansion. This facilitates the correlation computations even more.

III. NUMERICAL APPLICATION FOR DIAMOND

The correlation calculation for diamond is based on a SCF calculation by von der Linden, Fulde, and Bohnen.[20] We will repeat here the relevant details of this work. The SCF calculation was performed within the same double-ζ basis set as used in the calculation by Kiel *et al.*[19] The basis set consists of 4*s* orbitals, contracted from seven GTO's and two sets of *p* orbitals, contracted from three GTO's.[22] This SCF calculation differed completely from the one used in Ref. 19. It was performed by a program developed for self-consistent calculations within the LDA (Ref. 23) for GTO basis sets. This way, a one-particle ground state was obtained which is defined by its density matrix P_{ij}, and the effective one-particle Hamiltonian H'_{0ij}. The latter includes exactly the one-particle part and the Coulomb potential but adds an approximate exchange-correlation potential. The outcoming one-particle ground state was then taken as a trial ground state for the computation of the exact exchange potential. This potential and the exchange energy needed to be calculated by a separate program. They replace the corresponding LDA contributions. The outcoming total energy is -75.656 a.u./(unit cell). When compared to the energy of the SCF ground state of a C atom, obtained within the same contracted basis, -37.653 a.u.,[24] a SCF binding energy of -0.349 a.u./(unit cell) is obtained.[25]

In order to reach the Hartree-Fock (HF) limit of the binding energy, two corrections play an important role. First, the state as obtained self-consistently within the LDA is not the SCF ground state. From calculations on the C atom, it is known that the exact energy of this state is 0.0075 a.u. above the HF ground-state energy.[14] Assuming that this shortcoming is present already for the finite basis set and that this defect does not change for diamond, the SCF binding energy needs to be increased by 0.015 a.u./(unit cell).

Second, the binding energy comes out too small due to the finite basis set within which these calculations are performed. While additional *s* and *p* functions only add to the energy of the atoms and of the solid in the same way and therefore do not contribute to the binding energy anymore, *d* functions as well as higher polarization functions contribute to the solid only. From molecular calculations it is known that already a single set of *d* functions contributes with an energy of 0.015 a.u. for each bound carbon atom. This energy does not depend on the nature of these bonds or on the size of the molecules.[26] A reasonable guess is that all further polarization functions when added lead to an additional correction of roughly a third to one half of this first contribution.[18]

Altogether, the binding energy as obtained from this calculation needs to be corrected by 0.060 ± 0.01 a.u./(unit cell). The error bar indicates the uncertainty connected with these estimates. The estimated HF limit for the binding energy is then -0.409 ± 0.01 a.u./(unit cell).

It is possible to obtain most of these corrections explicitly by a self-consistent calculation within an enlarged basis set. It turned out, however, that already the single computation of the exchange energy within the small double-ζ basis set was the most expensive part within the whole computation.[21] A further gain in efficiency needs to be obtained before such computations are justifiable. It is much easier to include these corrections via single-particle excitations which are added to the correlation treatment. It will be a future task to program such a correlation program based on the LA which includes single-particle excitations and calculates the corrections which have been estimated above.

The results of the above one-particle calculations, namely the density matrix and the one-particle Hamiltonian with the exact exchange added, provide the necessary input for the correlation calculations.

In a first step, information about the atomic orbitals is extracted from the density matrix. In principle, the valence-band states as solutions of the one-particle Hamiltonian can be transformed into localized bond orbitals by a Wannier transformation for diamond. Even atomic orbitals might be obtained when localizing properly admixed valence and conduction band states. Such a transformation is not unique anymore, however. Details of the long-range tails of these orbitals are not of much interest either for ground-state calculations. Therefore, a simple scheme has been chosen which leads to atomic orbitals in a good approximation. First bond orbitals are obtained by perturbing the density matrix and looking at its eigenvalues. When transforming it into that of an orthogonalized basis $\tilde{P}=S^{1/2}PS^{1/2}$, the eigenvalues of $\tilde{P}$ are degenerate and either 1 or 0. Setting all elements of $\tilde{P}$ outside a certain cluster to zero, only those states which are not influenced much by this cutoff retain eigenvalues close to 1. This way localized occupied states can be obtained. They converge well with increasing cluster size. To obtain a good approximation for a core state, a cluster including just one atom is sufficient. To obtain the contribution of one atom to bond orbitals, a cluster of this atom together with all neighbor atoms is sufficient. When represented in the original basis orbitals, then only the contributions of this central atom to the four bonds are kept, leading to a set of four $(2s,2p)$ atomic hybrids. These states are orthogonalized to all $1s$ states first. Finally they are orthogonalized to each other. With them we construct operators which describe the interatomic correlations of the valence electrons.

The original nonorthogonal atomic orbitals which are described by orbitals on the respective atom only are used to determine the orbitals for the intra-atomic correlations. As mentioned above, the atomic volume is subdivided into different shells and each shell is then subdivided into different angular parts. The double-ζ basis set as used for the SCF calculation is extended to include one set of d functions with exponent $\alpha_d=0.6$. Such a basis set is exhausted by a subdivision into three shells. For each shell, one set of s and p orbitals is constructed. These orbitals are generated from the atomic orbitals by a cutoff procedure. There, the contributions of the outer basis orbitals to the atomic orbitals are partially reduced or removed. For each s and p orbital in each shell this cutoff is described by a single parameter. These parameters have been optimized before in a calculation for a small molecule, namely CH_4.[19] Here they are chosen as in the computation of Ref. 19. Having fixed the respective s and p orbitals for the inner, central and outer shells, they are then orthogonalized to the core states and hybridized within each shell. For the inner and outer shell only the s and p orbitals are hybridized to form sp^3-like states while for the central shell a sp^3d^5 hybridization into 12 nonorthogonal states is performed. Details of this hybridization are given in Ref. 17. There is a set of additional parameters connected with these hybridizations. Since usually the resulting intra-atomic states are orthogonal to each other neither within nor in between the different shells, different weights for the individual sets of orbitals are introduced. The weights have been optimized before.[19] For this diamond calculation, we reoptimized a few parameters. This results in an increase of the total correlation energy by almost 3%. For the central shell, the cutoff parameter of the s orbital changes to -0.4, that of the p orbital to 0.10. The anisotropy in the d_{e_g} and $d_{t_{2g}}$ weight factors is removed; the resulting average d weight factor is 0.71. For the outer shell, the s cutoff parameter increases to -2.8, while the s weight factor shrinks to -0.5. This change within the outer shell leads to a surprisingly large improvement as compared with previous molecular computations, which were rather insensitive to changes there.

In this way all atomic orbitals and intra-atomic states are fixed. Since the basis set for the correlation calculation is extended, a few additional matrix elements dealing with the new d orbitals need to be calculated. Matrix elements for the overlap matrix S_{ij} and for the one-particle part of the Hamiltonian H'_{0ij} without exchange are generated easily with the LDA-GTO program. The missing terms of the exchange potential $V_{\mathrm{excl}\,ij}$ are determined by a modified version of the program which computes the exchange potential for the one-particle calculations. Here only relatively few matrix elements going up to second neighbors need to be included. These are roughly 50 terms whose exclusive use in the correlation calculations demands also much less accuracy. With all matrix elements S_{ij}, H_{0ij}, P_{ij} and the transformation γ_{mi} available, all modified one-particle matrix elements derived in Ref. 17 are calculated exactly without further approximation. The calculation of the matrices $\langle O_n H \rangle$ and $\langle O_n H O_m \rangle$ converges within a finite cluster. For this purpose, interaction matrix elements V_{ijkl} in terms of basis orbitals need to be calculated only within a cluster of eight atoms. These are two neighbor atoms and all their nearest neighbors. Only for the two central atoms is the basis size extended by additional d functions. Details of the convergence behavior will be demonstrated below. The calculation of the matrix elements V_{ijkl} is performed within the POLYATOM program package.[27]

Next, the results for the correlation energy of the valence electrons and for the corresponding binding energy contributions are discussed. The different contributions to the correlation energy are given in Table I together with the corresponding values for the C atoms as obtained within the same basis set.

The interatomic correlations are separated into three parts. The dominant contribution comes from the operators defined on single atoms. Further, density correlations between neighbor atoms are calculated. Here, the atomic hybrids describing the bond between these atoms are not included. These terms describe therefore van der Waals polarizations of next nearest bonds. Finally, from these neighbor correlations all longer-range polarizations are estimated. If it is assumed that these correlation energies behave like $1/R^6$ with increasing distance R, these terms should add less than half of the correlation energy as obtained from nearest-neighbor contributions alone.[19] The typical uncertainty of this estimate should not be larger than 50% of its value. A more precise computation might be performed but is not very meaningful since larger uncertainties enter later. When added up, all interatomic correlations lead to a correlation energy of -0.0925 a.u./(unit cell). These correlations need to be compared with a specific correlation for the C atom which can be described by atomic orbitals there, namely a two-particle excitation of the occupied $2s$ states into the empty $2p$ states. The contribution of the interatomic correlations to the binding energy then amounts to -0.058 a.u.(unit cell). This is only 40% of the total correlation contributions.

The intra-atomic correlations are calculated stepwise. First they are treated on single atoms only; the results on different atoms are added. The resulting intra-atomic correlation energy needs to be corrected in a next step by overlap effects. These corrections are very small although not negligible. They reduce the intra-atomic correlation energy by less than 3% only. Correlations between neighbor atoms are finally added which are described by intra-atomic states on both atoms. Here all states within the central shells of both atoms need to be correlated with each other. Inner shell states on the one atom correlated with central shell states on the neighbor add an additional small amount. None of the individual contributions dominates. Their importance increases

TABLE I. Valence electron correlation energies and energy differences.

	Diamond [a.u./(unit cell)]	C atom (a.u.)	Binding-energy contributions [a.u./(unit cell)]
	Interatomic correlations		
Single-site operators	−0.0865	−0.0175	
Neighbor-atom operators	−0.004		
Longer-range correlations	−0.002 ±0.001		
	−0.0925±0.001		−0.0575±0.001
	Intra-atomic correlations		
Single-site operators	−0.1130	−0.0580[a]	
Overlap corrections	+ 0.0030		
Different site corrections	−0.0252		
	−0.1352		−0.020
	Total correlation energies		
Result (LA)	−0.228 ±0.001	−0.0755[a]	−0.077 ±0.001
Correction (LA)	−0.010 ±0.003	−0.0025[a]	−0.005 ±0.003
Correction (finite basis)	−0.086 ±0.005	−0.021	−0.044 ±0.005
Estimated experimental values	−0.324 ±0.006	−0.099	−0.126 ±0.006

[a] The result within the LA for the C atom has been guessed. The exact value for the finite basis set in this case is known.

when the states on the neighbor atoms are close to each other. This behavior is very similar to corresponding findings for these correlations in small hydrocarbon molecules.[18] Furthermore outer shell states on each atom need to be correlated with central shell states on the neighbors. These corrections did not play a role for the small molecules treated so far but contribute with almost 30% to the different site corrections as obtained for diamond.

All these intra-atomic correlations add to −0.1352 a.u./(unit cell). They are to be compared with the corresponding intra-atomic correlations for the individual C atom. There, only the exact value for this basis set is known, namely −0.0605 a.u.[28] Since a program within the LA does not exist for open-shell cases yet, we have estimated from results for the Ne atom that the shortfall of such a LA calculation should be roughly 0.0025 a.u. Comparing the values for the correlation energy of the C atom obtained this way with the result for diamond reveals a correlation contribution to the binding energy which amounts to 60% of the final value.

To obtain a good estimate of the experimental limit of the correlation energy, the following two shortcomings need to be corrected for. The first is a correction of the LA result towards the exact result obtainable within the same basis set. As it turned out for calculation on atoms and small molecules,[16–18] this approach rather constantly underestimates the correlation energy by 4–5 % due to the severe restriction of the excitation space. This correction is, in the case of diamond, roughly −0.010±0.003 a.u./(unit cell). The second correction is the larger one and results from the finite basis set used. It is known that this deficit amounts to −0.021 a.u. for the correlation energy of each separate C atom. For molecular calculation within a similar basis set, it is known that this deficit increases by (110±10)% as compared with the atomic value.[18] These corrections do not depend much on the actual nature of the bonds around the C atoms. By choosing this empirical renormalization the finite basis size correction for the correlation energy of diamond can be estimated to be −0.086±0.005 a.u./(unit cell).

With these correlations added, the correlation contributions to the binding energy amount to −0.126±0.006 a.u./(unit cell). The error bar results mostly from uncertainties in the estimate of the finite-basis-size effect. When added to the HF binding energy −0.409±0.01 a.u./(unit cell), then a total binding energy of −0.535±0.013 a.u. arises, the numerical uncertainty coming mostly from the one-particle part of the calculations. This value needs to be compared with the electronic contributions to the experimental binding energy. The latter is known to be −0.542 a.u./(unit cell). With zero-point energies for the nuclei of −0.013 a.u./(unit cell) added, the former comes out to be −0.555 a.u./(unit cell). The value obtained is too small as compared with this experimental value by almost twice the error bar connected with the uncertainties in the estimates.

The only plausible explanation for this deviation is a shortcoming in the estimate of the finite-basis-size effect. This estimate has been taken from calculations on small molecules. As compared with the atomic limit, the electronic densities are slightly higher there. Furthermore, a redistribution of charge from the *s* into *p* atomic orbitals due to hybridization takes place. It has long been known that electrons within *p* orbitals correlate more strongly than within *s* orbitals in the atomic limit.[29,30] These two changes lead to an increased weight of very-short-range correlations and, therefore, to the strongly increased basis-size dependency as mentioned above. The diamond crystal is distinct from small molecules in that the charge density renormalizes more strongly and that there is no spherical atomlike outer low-density domain anymore. The latter is contracted instead into holes with low density within the open diamond structure. Outer-shell correlations which cover the outer regions for small molecules apparently are of no use anymore in the case of diamond. This explains the sizably smaller contributions of single-site operators to the intra-atomic correlation energy as compared with the atom (Table I). For molecules with comparable bonds, these contributions were by more than 10% larger than the atomic values.[18] In addition, in the diamond case, these outer regions are strongly reparametrized, indicating that the corresponding operators now cover within a first, probably poor attempt, correlations within the low-density areas. This way, the large additional contributions of intersite operators with outer shell states can be explained, too. Apparently, the basis set chosen for diamond is not able to cover these correlations within the low-density areas as well as the correlations closer to the atoms. An improvement could be obtained within an extended basis either by adding more delocalized atomic orbitals, especially an additional set of d functions, or by choosing an additional basis set for the holelike domains so that the electrons can be directly correlated in these regions. We will investigate these extensions in the future.

It is of interest to compare these binding energies with those obtained within the LDA. There, the most reasonable values published give a binding energy of -0.625 a.u./(unit cell). These results have been obtained by a calculation within the atomic sphere approximation.[31] It has been possible to correct part of the approximations made there.[32,33] These corrections lead to an estimated LDA binding energy of -0.645 ± 0.01 a.u./(unit cell).

A LDA calculation in a GTO basis set with only s and p functions included led to a binding energy of -0.589 a.u./(unit cell).[34] Its deviation from the estimated LDA binding energy may result partly from the lack of higher polarization functions which should contribute with a similar energy as within the HF calculations. Other pseudopotential computations originally gave results close to the experimental binding energy[35] but moved more recently toward this estimated limit.[34]

As compared with our old computation, Ref. 19, we have obtained stable and well-converged results. The uncertainties connected with the error estimates decreased by a factor of 3. In the former computation, the results came out qualitatively similar. The intra-atomic correlations due to single-site operators have been overestimated there. The different site correlations are new; they were completely neglected the last time. It is only this time that new features in the basis-size dependencies show up.

IV. CONVERGENCE OF THE CORRELATION CALCULATIONS

As mentioned above, none of the computational steps which deal with one-particle matrices is very time consuming. These calculations can be handled with ease until numerical convergence is achieved. For diamond, it turned out that restricting these matrices to next-nearest-neighbor terms leads to a typical failure of 1% for the correlation energy while the inclusion of all third-neighbor terms leads to well-converged results.

When dealing with the interaction part of the Hamiltonian (1), a more restrictive treatment is necessary. Each atom has 4 nearest, 12 next-nearest and 24 third-nearest neighbors. Suppose an operator is defined for a given atom; then going straightforwardly up to third-nearest neighbors would suggest calculation of the matrix elements V_{ijkl} within a cluster of 41 atoms. Although this cluster is of high symmetry, such a computation goes beyond the limits of today's quantum-chemistry methods. As we will demonstrate, however, the actual convergence is much better.

The matrix elements V_{ijkl} are needed for two sets of expectation values, namely $\langle O_n\tilde{H}\rangle$ for all operators O_n and $\langle O_n H' O_m\rangle$ for the interatomic operators O_n and O_m only. H' here means the residual part of the interaction within (1), which is not contracted into Coulomb and exchange potentials.[17] Due to orthogonalization tails, the convergence behavior of the interatomic correlations is expected to be poorer than that of the intra-atomic correlations. We will in the following therefore restrict ourselves to these terms and especially to the most important contributions, namely to the correlations described by on-site operators. When calculating their matrix elements, then certainly the nearest-neighbor contributions around the atom where the individual operators are defined need to be included. In a next step, selected next-nearest-neighbor contributions can be added. For a specific atomic hybrid these are either next-nearest neighbors in the bonding direction or in nonbonding directions. These contributions are obtained from a calculation within a cluster of eight atoms, consisting of one atom with all neighbors and the three next-nearest-neighbors in one bonding direction. For all operators the expectation values $\langle O_n\tilde{H}\rangle$ and $\langle O_n\tilde{H}O_m\rangle$ are calculated first within a cluster of five atoms. Next the correction of three next-nearest neighbors are added depending on whether they are in direction of (one of) the atomic hybrids or not. In Table II, these values are given for a few expectation values. It is seen that next-nearest-neighbor corrections cannot be neglected. The contributions in hybrid direction change the expectation values by typically 10%, but already contributions of next-nearest neighbors in nonhybrid directions are negligible. Third-nearest-neighbor corrections are certainly smaller than the latter contributions so that there is not need to include them any more. The converged result of the interatomic correlations with all single-site operators included is therefore obtained from calculations within this small cluster only. Longer-range correlations which describe polarizations of next-nearest-neighbor bonds can be computed in a first step within this cluster too. For these terms we expect that complete convergence is not reached within such a cluster. These correlations effects are so small, however, that even errors of 10% can be tolerated.

Table III contains the correlation energies as obtained from the single-site interatomic correlations within different approximations. The first column contains the final results. Presented are the energies obtained with the operators $n_{i\uparrow}n_{i\downarrow}$ only, with density correlations added and finally with spin correlations included.

TABLE II. Expectation values $\langle O_n\tilde{H}\rangle$ and $\langle O_n\tilde{H}O_m\rangle$ for interatomic operators as obtained for different cluster sizes. All values are in a.u.

	Central atom plus four nearest neighbors	Three next-nearest neighbors In (one) hybrid direction	In no hybrid direction	Final result
$\langle n_{i\uparrow}n_{i\downarrow}\tilde{H}\rangle$	0.043 53	−0.005 57	+0.000 01	0.037 99
$\langle n_in_j\tilde{H}\rangle$	0.036 82	0.001 86	−0.000 07	0.040 40
$\langle \mathbf{S}_i\mathbf{S}_j\tilde{H}\rangle$	−0.004 96	−0.000 13	+0.000 03	−0.005 16
$\langle n_{i\uparrow}n_{i\downarrow}\tilde{H}n_{i\uparrow}n_{i\downarrow}\rangle$	0.105 45	0.009 80	0.000 14	0.115 67
$\langle n_in_j\tilde{H}n_in_j\rangle$	0.064 51	0.004 95	0.000 09	0.074 69
$\langle \mathbf{S}_i\mathbf{S}_j\tilde{H}\mathbf{S}_i\mathbf{S}_j\rangle$	0.491 66	0.015 20	0.000 03	0.522 12

The second column contains results as obtained with matrix elements gained from the five-atom cluster calculation only. This way, the correlation energy is overestimated by 15%, the largest error coming from the operators $n_{i\uparrow}n_{i\downarrow}$.

The last column contains the results as obtained in second-order perturbation expansion. The matrix $\langle O_n\tilde{H}O_m\rangle$ is then replaced by $\langle O_n\tilde{H}_0O_m\rangle$. There the total correlation energy decreases by 20%. Even worse, different contributions behave differently. The energy gain due to correlations within single bonds decreases by 20% while the density correlations between different states are not affected. The spin correlations effects, however, shrink to 30% of their correct values. This seemingly paradoxical behavior can be understood easily. The corrections $\langle O_nH'O_m\rangle$ have different consequences. For diagonal terms $\langle O_n\tilde{H}O_n\rangle$ they partially cancel the interaction effects included in the dispersion of the energy bands by the exchange potential. This cancellation is rather effective. For the operators $n_{i\uparrow}n_{i\downarrow}$, 85% of the exchange potential is quenched by these terms, for example. This explains the main shortcomings of the correlation energy for the operators $n_{i\uparrow}n_{i\downarrow}$. Another effect of these corrections is an interaction between different operators $\langle O_nH'O_m\rangle$. Where density correlations are concerned, the nondiagonal terms cause a mutual dependence of all operators on each other. This way, the different correlations screen each other. This screening effect is missing in second-order perturbation expansion, causing a considerable overestimate by simply adding individual correlation contributions. For the density correlations in diamond, both corrections apparently compensate each other. In the case of spin correlations, the role of these nondiagonal corrections is reversed. While in a second-order perturbation expansion the energy gain due to spin correlations competes alone with the kinetic energy loss caused by them, the coupling terms allow for corrections due to the stronger density correlations and facilitate Hund's rule correlations. In this case both corrections add up and explain this big change. A second-order perturbation expansion treatment of these correlations on the atomic scale leads therefore to unreliable results even for weakly correlated systems like diamond. This shortcoming is more evident for stronger correlated systems like transition metals.[1,36]

Contrary to these interatomic correlations, the intra-atomic ones can be treated mostly in second-order perturbation expansion. Since these corrections deal essentially with very short range correlations an even better convergence with respect to the size of the cluster treated is expected. It is therefore sufficient to restrict to a global treatment for all these terms. In a first step the intra-atomic correlations on one atom are calculated. The smallest meaningful cluster again contains five atoms, namely the one where these correlation operators are located and its nearest neighbors. Within this calculation, the basis size of the central atom is expanded. To test the convergence, in a next calculation step three-next-nearest neighbors in one of the neighbors direction are added. The outcoming intra-atomic correlation energy for the small cluster is −0.0555 a.u. in second-order perturbation theory. The correction due to the three further atoms added is −0.000 13, or little more than 0.1%. Going beyond the second-order perturbation expansion increases this value by 0.0004 a.u. This leads to a final result of −0.0565 a.u. for the intra-atomic correlation energy for each C atom as given in Table I.

For the last step within the correlation treatment, namely an intra-atomic correlation calculation for two neighboring atoms, a computation within the same cluster of eight atoms needs to be performed, but this time with an extended basis size on both central atoms. Since

TABLE III. Interatomic correlation energies due to single site operators [in a.u./(unit cell)].

	Final result	Restriction to nearest neighbor V_{ijkl}	Second-order perturbation expansion
$n_{i\uparrow}n_{i\downarrow}$	−0.0556	−0.0719	−0.0441
$+n_in_j$	−0.0798	−0.0935	−0.0675
$+\mathbf{S}_i\mathbf{S}_j$	−0.0865	−0.1039	−0.0695

the overlap effect and the short-range correlations between neighbor atoms are very small we dispensed with any further convergency checks for these terms too. Corrections there should not be larger than these for the intra-atomic correlations on single sites themselves. Furthermore, we treated these corrections in second-order perturbation expansion only.

This cluster of eight atoms used in the final calculation is the largest cluster for which all interaction matrix elements V_{ijkl} needed to be computed. Only for the two central atoms is an extended basis set needed. The expense of this step corresponds to that necessary for a correlation calculation for the molecule ethane with similar quality. Such a computation is a very simple task for present day quantum-chemistry computer programs.

V. PAIR CORRELATION FUNCTIONS

As discussed above, the interatomic correlations play a special role in anisotropic systems. Already the need to treat them better than in second-order perturbation expansion indicates that they are rather strong. Here we will discuss their strength in a little more detail and compare them with correlations as they arise for molecules as well as for the homogeneous electron gas.

The atomic correlation functions which change most are

$$\langle \psi_c \mid n_{i\uparrow} n_{i\downarrow} \mid \psi_c \rangle = \langle n_{i\uparrow} n_{i\downarrow} \rangle - \Delta_{ii}$$

and

$$\langle \psi_c \mid n_i n_j \mid \psi_c \rangle = \langle n_i n_j \rangle - \Delta_{ij} \ , \tag{9}$$

where n_i describes the occupation operator of the atomic hybrid i. The correction terms Δ_{ij} are only calculated to dominating order, namely

$$\Delta_{ij} \cong -2 \sum_n \eta_n \langle O_n n_i n_j \rangle \ . \tag{10}$$

For the orthogonalized atomic hybrids it holds that $\langle n_{i\uparrow} n_{i\downarrow} \rangle \cong 0.25$ and $\langle n_i n_j \rangle \cong 1.0$.

The reduction of the fluctuation within the bond is $\Delta_{ii} = 0.040$ or roughly 16%. The nondiagonal charge suppression is $\Delta_{ij} = 0.027$. Both values are comparable to corresponding correlations on the atomic hybrid positions of the C atoms in C_2H_6.[18]

Of further interest is a calculation of the total charge fluctuation on a C atom in diamond in one-particle approximation $\tilde{\Delta} n^2_{\mathrm{HF}}$ and for the correlated ground state $\tilde{\Delta} n^2 c$. There it holds that

$$\begin{aligned} \tilde{\Delta} n^2_{\mathrm{HF}} &= \langle n^2 \rangle - \langle n \rangle^2 \cong 2.0 \ , \\ \tilde{\Delta} n^2_c &= \tilde{\Delta} n^2_{\mathrm{HF}} - 2 \sum_i \Delta_{ii} - \sum_{\substack{i,j \\ (i \neq j)}} \Delta_{ij} \\ &= 1.36 \ . \end{aligned} \tag{11}$$

This reduction of the charge fluctuations by 32% is very close to that in a C atom in C_2H_6 again. The nondiagonal correlations together are of the same size as the diagonal terms.

All other corrections within the pair correlation function are of minor weight. Longer-range correlations are quite small. They are described as bond polarizations and decrease as $\sim R^{-6}$. Short-range corrrelations are significant but only in a small volume around the actual electronic position. Their integrated weight is much smaller than that of the correlations on the atomic scale.

This structure of the correlation function differs strongly from that of the homogeneous electron gas. There, the long-range correlations are of very different origin and are much stronger. The very-short-range correlations there might compare with the very-short-range correlations in the diamond case for comparable local densities. The outstanding size of the correlations on the atomic scale, on the other hand, cannot be obtained within a homogeneous system. It is very doubtful whether generalizations of such a scheme based on gradient expansions beyond the homogeneous case will be able to deal more properly with these correlations caused by the anisotropic nature of solids. Experimental evidence for these dominant corrections of the pair correlation function on an atomic scale does not exist yet for diamond. In more strongly correlated systems, namely the transition metals, there is, however, evidence from Compton scattering that correlations as they arise in a homogeneous system cannot explain the experimental situation,[37] while strong correlations on an atomic scale lead to a better description.[38]

To conclude, the electronic correlation pattern of the electrons in diamond has much more similarity with that of molecules with comparable binding than with that of the homogeneous electron gas.

VI. SUMMARY AND OUTLOOK

The results of the preceding sections demonstrate the accuracy which can now be reached for *ab initio* ground-state calculations of solids with the help of the local ansatz. The quality of quantum-chemistry methods can be transferred this way to solids. The estimate for the binding energy of diamond made by this scheme deviates from the exact result by roughly 0.3 eV/atom. It is therefore better by a factor of 4 than the current best *ab initio* results as obtained within the LDA. These results give a deviation of 1.2–1.3 eV/atom.

Due to the fast convergence of the correlation calculations, the computational expenses for the correlation part in the case of diamond are not larger than those for the original GTO-LDA calculation. The only really expensive part therefore is still the accurate calculation of the exchange energy for the one-particle ground state of the LDA calculation. Its costs are at present two orders of magnitude larger than those of the original LDA calculations. This exchange energy program, however, has not really been optimized either for the computation of the individual interaction matrix elements or with respect to an efficient use of convergence within the summation of the single contributions. Such an optimization should reduce the computation cost by up to two orders of magnitude. It is worth mentioning here that other HF programs have been developed recently which are considerably more efficient but have not been applied yet to calculations in basis sets of the quality needed here.[39] Therefore, while the correlation part already poses no more problems, we hope for the same as far as the exchange part is concerned.

Another interesting topic is an eventual increase of accuracy for the individual energy contributions. We could improve considerably beyond the shortcomings of the first computations. Now all energy contributions which can be computed for the part of the Hilbert space available to the calculation scheme are converged. The remaining errors are connected with the estimates of effects of the parts of *N*-particle Hilbert space not covered yet. At present the greatest shortcomings arise for the one-particle ground state obtained from the LDA calculation. Its defects have been discussed in detail in Sec. III. As mentioned there, it should be possible to improve considerably beyond the present state. A further non-negligible shortcoming is connected with the finite one-particle basis set used for the correlation calculation. At the present level we have to estimate the relatively large defect from known corrections for molecules. It is possible to repeat this correlation calculation with a larger basis set which includes for example two additional sets of *d* functions and one of *f* functions. Then roughly half of the missing contribution will be obtained by such a calculation while the remaining part hopefully can be estimated with much better accuracy from this additional calculation alone and not from results for molecular calculations. In this way we will also be able to describe the differences in the dependence of the correlation calculations for a solid on the basis functions as compared with that for atoms and small molecules. The final correction which needs to be estimated is that caused by the local ansatz itself. There are different ways to improve on this field. One is to optimize numerically the intra-atomic states. First successful attempts in this direction have just been finished.[40] Another is to include all excitations on an atom exactly instead of restricting to a very small excitation space described by the intra-atomic states.

This discussion demonstrates that there are no objections in principle against a further continuous improvement of the local ansatz. At present we are only restricted by the difficulties of the HF calculation itself. Since there is a steady progress on this field, different kinds of solids will become accessible to a proper many-body treatment. Our presentation of the pair correlation function as well as details and accuracy of the calculations indicate the importance of a good understanding of many-body effects in anisotropic systems.

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