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Ab initio ground-state correlation calculations for semiconductors with the local ansatz

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Ab initio correlation calculations for different semiconductors performed with the local ansatz are reported. The results include binding energies as well as equilibrium lattice distances and bulk moduli. Furthermore, we investigate how the results are influenced by the use of pseudopotentials. From the detailed correlation functions the strength of the effective local interactions within a bond-orbital model are determined. These vary strongly for the different materials. Comparisons to other correlation schemes are made, and shortcomings of some local-density-approximation results are explained.

I. INTRODUCTION

While for many years the *ab initio* treatment of electronic correlations in solids seemed to be out of reach, the progress in computer technology in the last decade has made this task tractable, several methods having been developed to this end. Starting from computations for the homogeneous electron gas, Green's-function Monte Carlo calculations were performed for simple metals.[1,2] Monte Carlo variational calculations based on a Jastrow ansatz[3] have been done for solids like diamond or graphite.[4,5] We have developed a local ansatz (LA),[6] which starts from a self-consistent-field (SCF) calculation for the system under consideration and subsequently takes correlations into account in a way similar to quantum-chemistry methods. With this approach, we have investigated molecules[7] as well as three-dimensional insulators and semiconductors,[8–11] different one-dimensional systems,[12,13] and even metals.[14]

Here, we shall report on a series of calculations for different semiconductors based on the LA. This investigation has become possible because, on the one hand, the *ab initio* Hartree-Fock program CRYSTAL (Refs. 15 and 16) is now available, which allows us to do SCF calculations with a much higher precision than available so far[17] and, on the other hand, the programs for the LA have been improved substantially.

The paper is organized as follows. First, a short description of the method used is given. The third section contains results for the ground state and binding energies, the fourth section, for equilibrium lattice distances and bulk moduli. In the fifth section, details of the correlation functions are given and model atomic interactions are derived from them. Finally, a comparison with other *ab initio* results is made. Some deficits of methods starting from the homogeneous electron gas can be explained.

II. THE COMPUTATION SCHEME

For the SCF calculations the program CRYSTAL92 (Ref. 16) was used. All-electron calculations were performed for diamond and silicon, while pseudopotential calculations were made for the latter system as well as for germanium and tin. In all cases, the basis sets were of double ζ plus polarization function quality. For the all-electron case, these basis sets were taken from Ref. 18, while the pseudopotentials and the basis sets for the pseudopotential calculations were taken from Ref. 19. In every case, the outer exponents of these basis sets needed to be increased in order to contract the spatial extent of the basis set and to decrease the variance in the eigenvalues of the overlap matrix. This modification was necessary due to the particular way in which the exchange potential is computed in CRYSTAL92. For more details, we refer to the discussion for the case of solid lithium.[14] Table I displays the exponents of the two outermost basis orbitals and the exponents of the polarization functions for the different systems.

The correlations are accounted for by the LA. Within this scheme, one makes the following variational ansatz with the η's as parameters for the correlated ground state:

TABLE I. Outer exponents of the basis sets used.

	C	Si	Ge	Sn
Outer s exponent	0.233	0.120	0.105	0.109
Outer p exponent	0.233	0.120	0.105	0.074
d exponent	0.590	0.350	0.320	0.200

$$|\Psi_{\text{corr}}\rangle = e^{-S}|\Psi_{\text{SCF}}\rangle, \tag{1}$$

$$S = \sum_{\nu} \eta_{\nu} O_{\nu}, \tag{2}$$

$$O_{\nu} = \begin{cases} n_{i\uparrow}n_{i\downarrow}, \\ n_i n_j, \\ \vec{s}_i \cdot \vec{s}_j. \end{cases} \tag{3}$$

Here $n_{i\sigma}$ and $\vec{s}_i$ are density and spin operators for an electron in the local orbital,

$$g_i(\vec{r}) = \sum_j \gamma_{ij} f_j(\vec{r}), \tag{4}$$

where the $f_i(\vec{r})$ represent the basis orbitals. The operators have an obvious meaning. The first operator $n_{i\uparrow}n_{i\downarrow}$, for example, when applied to $|\Psi_{\text{SCF}}\rangle$, projects out all configurations with two electrons in orbital $g_i(\vec{r})$. In connection with the variational parameter η_{ν}, as in Eq. (1), it partially suppresses those configurations. Similarly, the operators $n_i n_j$ describe density correlations between electrons in local orbitals $g_i(\vec{r})$ and $g_j(\vec{r})$. For the homogeneous electron gas, an ansatz with these two kinds of operators leads to the Jastrow function.[3] The operators $\vec{s}_i \cdot \vec{s}_j$ generate spin correlations.

Applying the operators to $|\Psi_{\text{SCF}}\rangle$, one obtains a state that contains, besides two-particle excitations, also the original state and one-particle excitations. Since it is the two-particle excitations that describe the correlations, we want to keep only that part of the operators that generates them. This is achieved by forbidding contractions within the operators when expectation values are computed. The operators then reduce fluctuations in $|\Psi_{\text{SCF}}\rangle$.

The variational parameters η_{ν} are chosen so that the energy

$$E_G = \frac{\langle \Psi_{\text{corr}}|H|\Psi_{\text{corr}}\rangle}{\langle \Psi_{\text{corr}}|\Psi_{\text{corr}}\rangle} \tag{5}$$

$$= \langle \Psi_{\text{corr}}|H|\Psi_{\text{corr}}\rangle_c \tag{6}$$

is optimized. In the last equation, the subscript c indicates that only connected diagram contributions are summed up.[20] This expression cannot be evaluated exactly. The standard approximation is an expansion in powers of η, up to second order, i.e.,

$$E_G = \langle \Psi_{\text{corr}}|H|\Psi_{\text{corr}}\rangle_c$$

$$= E_{\text{SCF}} + E_{\text{corr}}, \tag{7}$$

$$E_{\text{corr}} \simeq -2\sum_{\nu} \eta_{\nu}\langle O_{\nu}H\rangle + \sum_{\nu,\mu} \eta_{\nu}\eta_{\mu}\langle O_{\nu}HO_{\mu}\rangle_c \ . \tag{8}$$

Here, $\langle A\rangle$ means the expectation value of A within $|\Psi_{\text{SCF}}\rangle$. This approximation works only if the correlations are sufficiently weak. It is formally analogous to a particular coupled electron pair approximation (CEPA-0, Ref. 21) or linearized coupled cluster expansion, restricted to doubly excited states (LCCD, Ref. 22) in quantum chemistry but manages with relatively few operators and is thus much less expensive.

What one has still to decide is how to choose the local orbitals in Eq. (4) and how to combine them to correlation operators. Here, knowledge on the physical nature of the correlations can be used to a large extent. Generally, we distinguish between three kinds of correlations, viz. interatomic, intra-atomic, and polarization correlations.

By interatomic correlations, we mean those correlations that arise due to bonding, i.e., due to the delocalization of electrons. They are expressed by the above operators when the local orbitals represent atomic orbitals. For the considered semiconductors, we have chosen atomic hybrids, i.e., an orthogonal hybridization of the atomic valence s and p orbitals in bond directions. The atomic orbitals were uniquely determined by the condition that they are built from basis orbitals on the respective atoms only and that they contain a maximal part of the occupied space. These atomic hybrids were then orthogonalized to each other.

Shorter range correlations are covered by so-called intra-atomic operators. They are built from sets of localized subatomic states that are generated from basis orbitals on a given atom only. Details for their construction can be found in Ref. 6. The possible choices of localized subatomic states depend on the available basis. Within a basis of double ζ plus polarization functions quality, the maximal angular subdivision of the atomic volume is a twelvefold nonorthogonal sp^3d^5 hybridization while the maximal radial subdivision is into three shells, which we call inner, central, and outer. There are a few open parameters connected with the formation of these subatomic states. These were determined by maximizing a partial correlation energy contribution. The operators constructed by these orbitals are connected with individual atoms only.

There is also a set of medium range or polarization operators that need to be added. When atoms come closer to each other, they interact by an induced polarization. Furthermore, when the electrons delocalize, then charge fluctuations on individual atoms are screened by polarizations on the neighbors as well. Polarizations on individual atoms are described by those local orbitals that were constructed for the central shell in the intra-atomic part. Induced polarizations are described by density operators from pairs of polarization orbitals on two neighbor atoms, while polarization screening of charge fluctuations is described by operators formed from pairs consisting of atomic orbitals (hybrids) on one atom and of polarization orbitals on the second atom.

Even though the LA utilizes the local character of correlations, it would be impossible to treat all relevant correlations simultaneously. Therefore, the correlations are taken into account in an incrementational scheme. The correlation energy is expressed as an incremental sum over contributions from different sets of atom clusters,

$$E_{\text{corr}} = \sum_{m=1}^{N} \frac{1}{m!} \times \left\{ \sum_{j_1}^{N}\sum_{j_2}^{N}\cdots\sum_{j_m}^{N} \langle E_{\text{corr}}\,(A_{j_1}A_{j_2}\cdots A_{j_m})\rangle_i \right\}$$
$$\text{with } j_1 \neq j_2 \neq \cdots \neq j_m, \tag{9}$$

where the A_{j_n} denote atoms, on and between which correlation operators are formed and (the index $_i$ meaning "increment")

$$\langle E_{\mathrm{corr}}(A_1A_2)\rangle_i = E_{\mathrm{corr}}(A_1A_2) - E_{\mathrm{corr}}(A_1) - E_{\mathrm{corr}}(A_2), \tag{10}$$

$$\begin{aligned}\langle E_{\mathrm{corr}}(A_1A_2A_3)\rangle_i = {} & E_{\mathrm{corr}}(A_1A_2A_3) - \langle E_{\mathrm{corr}}(A_1A_2)\rangle_i \\ & - \langle E_{\mathrm{corr}}(A_1A_3)\rangle_i - \langle E_{\mathrm{corr}}(A_2A_3)\rangle_i \\ & - E_{\mathrm{corr}}(A_1) - E_{\mathrm{corr}}(A_2) \\ & - E_{\mathrm{corr}}(A_3),\end{aligned} \tag{11}$$

etc., are the energy increments, i.e., the changes of the correlation energy due to overlap effects when correlating all atoms in the cluster.

Translation invariance in a solid allows for further simplifications. In Eq. (9), the sum (j_1) can be replaced by the number of atoms N. This handling has the additional advantage that local symmetry enters in the simplest way. Let us take the case of diamond as an example. In its structure, all atoms are equivalent, so only a single cluster with one atom needs to be treated. Further, there is only a single pair of neighbor atoms, a single pair of next nearest neighbors (and a single three atom cluster which contains the intermediate atom as well) and only one third neighbor pair (plus one three-atom cluster with one intermediate atoms added and one four-atom cluster with two of them), which need to be included making use of the crystal symmetry. Therefore, symmetry maximally reduces the required computations and can be exploited in a very simple way.

When a computation for a particular cluster is performed, then for all single-particle expectation values, the exact expectation values in the solid are taken. However, for the coverage of the interaction part, in principle summations over all interaction matrix elements between the basis orbitals V_{ijkl} in the full environment need to be included. Here, the local nature of the correlation operators allows a drastically simplifying approximation. For the particular correlations on the set of atoms in the cluster, the required matrix elements V_{ijkl} can, to a very good approximation, be restricted to these atoms plus all their nearest neighbors. Restricting the V_{ijkl} in this way makes all required computations easily feasible. Possible corrections due to lacking V_{ijkl} are included in computations extending over larger clusters.

The correlation contributions are further separated into different terms depending on which kind of operators is included on and between the different atoms in the cluster. Again, the notion of increments is used. A first separation is made with respect to interatomic, intra-atomic and polarization correlations,

$$E_{\mathrm{corr}} = E_{\mathrm{corr}}^{\mathrm{inter}} + E_{\mathrm{corr}}^{\mathrm{intra}} + E_{\mathrm{corr}}^{\mathrm{pol}} \ . \tag{12}$$

Here, the second and third terms are defined as incremental gains due to the newly added operators, i.e.,

$$E_{\mathrm{corr}}^{\mathrm{intra}} = E_{\mathrm{corr}}^{\mathrm{inter+intra}} - E_{\mathrm{corr}}^{\mathrm{inter}} \ . \tag{13}$$

The individual contributions to the correlation energy [Eq. (12)] differ in their convergence behavior. The interatomic correlations converge slowest. The corresponding energy separates into contributions originating from operators, which correlate electrons at different distances,

$$E_{\mathrm{corr}}^{\mathrm{inter}} = E_{\mathrm{corr}}^{\mathrm{inter}}(\text{on site}) + \sum_{\text{neighbors}} E_{\mathrm{corr}}^{\mathrm{inter}}(\text{neighbors}). \tag{14}$$

Again, these terms are understood in an incremental way, the energy gained from certain neighbor correlations is the gain obtained with all shorter range correlations included.

All these contributions are determined from a series of cluster calculations. For on-site correlations, the smallest cluster deals with correlations on the respective atom only, while for longer range correlations clusters are needed, which contain at least the two atoms involved. For all semiconductors, it turned out to be sufficient to constrict the interatomic operators between up to next nearest neighbors. Longer range contributions were partly computed, partly estimated. Furthermore, it was found to be sufficient to restrict the set of clusters to up to three-atom clusters, where two atoms are the nearest neighbors to a third atom. Test calculations were performed with a particular four-atom cluster.

By definition, intra-atomic correlations are represented by operators defined for individual atoms only. The dominant contribution therefore arises, when in addition to the interatomic correlations on a single-atom intra-atomic correlations are added. In a first approximation, the total intra-atomic correlation energy is given as a summation over those individual contributions. These correlations on different atoms are not fully separate from each other, however, since the atomic charges show a sizeable overlap. Therefore, overlap corrections need to be determined from calculations where these intra-atomic correlations are included on different atoms. It turned out that overlap corrections between nearest neighbor pairs are very small and that longer range overlap contributions can be fully neglected. Therefore, the intra-atomic correlation energy is given as

$$E_{\mathrm{corr}}^{\mathrm{intra}} = \sum_{A} E_{\mathrm{corr}}^{\mathrm{intra}}(A) + \sum_{\langle A,A'\rangle} E_{\mathrm{corr}}^{\mathrm{ov}}(A,A'). \tag{15}$$

Here, each contribution contains by definition only the incremental gains of the respective correlations. The sum over pairs of atoms is restricted to nearest neighbor pairs.

The last correlation contributions are obtained from polarization correlations. Here, operators between two atoms are constructed from atomic orbitals or polarization hybrids on the different atoms. These corrections are small, and it is sufficient to cover them on the smallest possible level, namely, as a sum over two-atom cluster calculations. Then it holds that

$$E_{\mathrm{corr}}^{\mathrm{pol}} = \sum_{A,A'} E_{\mathrm{corr}}^{\mathrm{pol}}(A,A') \ . \tag{16}$$

Here, the sum cannot be restricted to nearest neighbor distances as was the case for the intra-atomic calculations but usually up to third nearest neighbor contributions need to be added before convergence is reached. Again, these polarization contributions are to be understood as increments obtained due to the newly added operators. It is important that the longer range interatomic correlations between the respective two atoms are always included. When making this separation, the treatment of the polarization correlations can be restricted to the handling of effective two-atom clusters, too.

In Fig. 1, the different clusters treated are represented. Dots indicate the atoms for which only interaction matrix elements are included. Filled circles indicate atoms where only atomic orbitals are generated for correlation purposes and open circles indicate atoms where atomic orbitals and intra-atomic orbitals are generated. As can be seen, the required clusters are very small and pose no problems for the standard quantum-chemistry programs, which are used for the evaluation of the two-particle matrix elements V_{ijkl}.

III. CORRELATION AND BINDING ENERGIES

The individual contributions to the correlation energy of the different systems are presented in Table II. They are given in a.u. or Hartree per unit cell.

As can be seen, interatomic correlations contribute 25% to the correlation energy for diamond but contribute less for the other compounds. Longer range correlations converge quite rapidly. Contributions extending beyond next nearest neighbor (NNN) correlations were estimated.

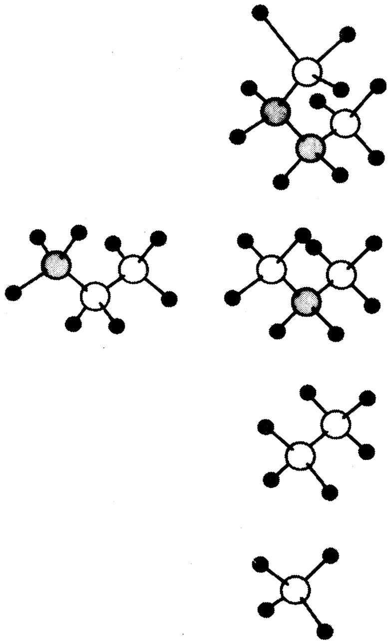

FIG. 1. Schematic representation of the five different clusters for which interaction matrix elements for the basis orbitals V_{ijkl} were generated. For atoms denoted by open circles, atomic and intra-atomic orbitals were constructed, and for atoms denoted by filled circles only atomic orbitals were generated. Dots indicate atoms who contributed only to the V_{ijkl}.

Intra-atomic correlations contribute with roughly the same amount to the correlation energy for the different solids. These contributions are almost perfectly additive, i.e., the overlap corrections are very small. Polarization corrections come out smallest. While there is a sizeable contribution stemming from nearest neighbors, the next nearest neighbor terms add only 2–3 % to the correlation energy.

For two cases, viz. diamond and silicon, these energies can be compared with correlation energies from cluster calculations with standard quantum-chemistry programs.[23,24] There, the correlation energy of the solid was obtained from a series of C_mH_n or Si_mH_n clusters, respectively. This was done in an incremental way, making use of the representation of the occupied orbitals in terms of bond orbitals for these systems. A first set of calculations was performed with a basis set similar to the one used here. The results are represented in Table II as $E_{\rm corr}(S1)$. In the case of diamond, the result of the LA is roughly 12% poorer. This is the same deficit as found before for the case of C_{60}.[25] This shortcoming of the LA results from the strong reduction in correlation operator space and in particular from the restriction to local orbitals constructed from basis functions on single atoms only. For silicon, this deficit is larger. So far we do not know whether this indicates an increased error of the LA or whether possibly the result of the cluster calculation is not yet fully converged. Therefore, we restrict to the deficit of diamond and C_{60}, and assume for each system a relative correction of 12%, which shall compensate the shortcoming of the LA, $\Delta E_{\rm corr}({\rm LA})$, and which leads to the estimate of the exact result for the given finite basis, $E_{\rm corr}({\rm fb})$.

From experience on calculations for small molecules, we make an estimate of the finite basis size correction $\Delta E_{\rm corr}({\rm fb})$, leading to the final estimate of the valence correlation energy in a complete basis set, $E_{\rm corr}({\rm cb})$. This estimate is based on a set of calculations of the correlation energy for two electrons within an $X - X$ bond in X_2H_6, with $X =$C, Si, Ge, Sn, with successively increasing basis sets. The particular correlation energy obtained within the basis used by us increases by 28%, 44%, 40%, and 50%, respectively, when compared with the limiting complete basis result. For more details, we refer to Ref. 26. As can be seen, these finite basis size corrections are significant; they result from the poorly converging description of the very short range correlation cusp with finite basis sets.

The above-mentioned cluster calculations for diamond and silicon could be performed with an increased basis set, namely, with two sets of d orbitals and one set of f orbitals.[23,24] As the results indicate [$E_{\rm corr}(S2)$ in Table II], with such a basis set, more than 90% of the total correlation energy can be obtained.

Let us turn next to the binding energies. They are determined from the differences of the total energies for the solid and the individual atoms. The values are presented in Table III. The SCF binding energy $E_B({\rm SCF})$ is obtained by subtracting the atomic energies, obtained

TABLE II. Contributions to the valence shell correlation energy of the 4th row elemental crystals, (a.u./u.c.), as obtained with the LA. A detailed description of the individual contributions is found in the text. Results of other computations are given for comparison.

	C	Si	Ge	Sn
Interatomic correlations				
$E_{\mathrm{corr}}^{\mathrm{inter}}$(on site)	−0.0798	−0.0336	−0.0339	−0.0273
$E_{\mathrm{corr}}^{\mathrm{inter}}$(NN)	−0.0048	−0.0047	−0.0072	−0.0073
$E_{\mathrm{corr}}^{\mathrm{inter}}$(NNN)	−0.0035	−0.0015	−0.0018	−0.0014
$\Delta E_{\mathrm{corr}}^{\mathrm{inter}}$(longer range)	−0.0015	−0.0006	−0.0008	−0.0006
$E_{\mathrm{corr}}^{\mathrm{inter}}$	−0.0895	−0.0405	−0.0437	−0.0366
Intra-atomic correlations				
$E_{\mathrm{corr}}^{\mathrm{intra}}$	−0.1182	−0.1054	−0.0912	−0.0845
Polarization correlations				
$E_{\mathrm{corr}}^{\mathrm{pol}}$(NN)	−0.0141	−0.0197	−0.0175	−0.0142
$E_{\mathrm{corr}}^{\mathrm{pol}}$(NNN)	−0.0135	−0.0090	−0.0072	−0.0089
$\Delta E_{\mathrm{corr}}^{\mathrm{pol}}$(longer range)	−0.0057	−0.0038	−0.0030	−0.0038
$E_{\mathrm{corr}}^{\mathrm{pol}}$	−0.0333	−0.0325	−0.0247	−0.0269
Total correlation energies				
E_{corr}(LA)	−0.2410	−0.1784	−0.1627	−0.1479
ΔE_{corr}(LA)	−0.0299	−0.0221	−0.0202	−0.0183
ΔE_{corr}(fb)	−0.0750	−0.0890	−0.0733	−0.0830
Total valence correlation energy				
E_{corr}(cb)	−0.3459	−0.2896	−0.2562	−0.2492
Valence correlation energies obtained by other methods				
E_{corr}(Jastrow) (Ref. 5)	−0.294	−0.243		
$E_{\mathrm{corr}}(S1)$ (Refs. 23, 24)	−0.275	−0.215		
$E_{\mathrm{corr}}(S2)$ (Refs. 23, 24)	−0.322	−0.267		

within the original basis[18,19] but without contraction of the outer orbitals from the total energy of the solids. A rough guess is made for the finite basis correction ΔE_B(SCF) leading to the Hartree-Fock (HF) limit of the binding energies, E_B(HF).

For the diamond case, the results presented here are in good agreement with earlier calculations and estimates. We estimate that $\Delta E_B(\mathrm{SCF}) = -0.008 \pm 0.004$ a.u./u.c. For the case of silicon, the results vary with the pseudopotential used. With the one used in the earlier calculation,[10] an SCF binding energy for the same basis of −0.240 a.u./u.c. was obtained. An all electron calculation with carefully selected core orbitals and with a basis of the same quality for the valence electrons led to an energy of −0.228 a.u./u.c.[27] From the latter calculations, it is known that a second set of *d*-basis orbitals increases the

TABLE III. Binding energy contributions to the elemental crystals (a.u./u.c.), obtained by the LA, in comparison to the LDA binding energies and experiment. ϵ_{ZP} indicates the zero-point energy.

	C	Si	Ge	Sn
HF contributions				
E_B(SCF)	−0.398	−0.223	−0.171	−0.154
ΔE_B(SCF)	−0.008	−0.011	−0.011	−0.011
E_B(HF)	−0.406	−0.234	−0.182	−0.165
Correlation contributions				
$E_B(\mathrm{LA}) - E_B(\mathrm{SCF})$	−0.090	−0.038	−0.042	−0.038
ΔE_B(LA)	−0.024	−0.016	−0.014	−0.012
ΔE_B(fb)	−0.030	−0.054	−0.042	−0.039
E_B(cb)	−0.547	−0.342	−0.280	−0.253
E_B(LDA) (Ref. 35)	−0.625	−0.353	−0.265	
E_B(LDA) (Ref. 33)		−0.370		
E_B(LDA) (Ref. 38)		−0.383	−0.330	−0.283
$E_B(\mathrm{exp.}) - \epsilon_{\mathrm{ZP}}$	−0.555	−0.345	−0.285	−0.229

binding energy by -0.007 a.u. for silicon. Therefore, we assume the total basis set deficits for silicon, germanium, and α tin to be $\Delta E_B(\mathrm{SCF}) = -0.011 \pm 0.003$ a.u./u.c. In addition, an uncertainty of the HF binding energy due to the use of different pseudopotentials of ± 0.005 a.u/u.c. arises.

The correlation contribution to the binding energy is obtained by subtracting from the total correlation energy, obtained within the LA, $E_{\mathrm{corr}}(\mathrm{LA})$, given in Table II, the valence correlation energies of the individual atoms, obtained within the LA for the same basis but with the original exponents. It is represented as $E_B(\mathrm{LA}) - E_B(\mathrm{SCF})$ in Table III.

The estimates of the LA shortcomings, $\Delta E_B(\mathrm{LA})$, and the finite basis size corrections, $\Delta E_B(\mathrm{fb})$ are added as well. The explicitly computed correlation contributions make up a sizeable fraction of all correlation contributions to the binding energy for the case of diamond, while for the other systems, they amount to a rather small fraction, and the largest part arises from the error estimates of the LA and of the finite basis. This is connected with the fact that interatomic correlations, which are apparently rather well covered within the LA contribute less to the energy for the heavier elements.

The estimates seem to be reasonable, as can be seen from the final agreement of $E_B(\mathrm{cb})$ and the experimental electronic binding energies $E_B(\exp)$, which represent the experimental values corrected by zero-point vibration energies.

For tin, already the SCF binding energy is relatively large, and a final overestimation of $E_B(\mathrm{cb})$ by -0.03 a.u./u.c. results. We can rule out that this originates from shortcomings in the correlation treatment but cannot decide where on the SCF level it results from. These doubts concerning the SCF calculation of α tin will be affirmed by the discussion of the bulk moduli below.

For silicon, not only a pseudopotential calculation was performed but a second calculation was made with all electrons included. The results for the valence electrons came out to be very similar in both cases. Due to differences in the inner part of the basis sets, partial contributions differed by up to 10% but the resulting valence correlation energy for the all-electron case was above the pseudopotential result only by $+0.0086$ a.u./u.c. or 4% of the LA result. These differences resulted almost completely from differences in the on-site (atomic plus intra-atomic) contributions.

It is known that valence shell correlations are somewhat overestimated when pseudopotentials are used. For the atomic limit, the valence correlation energy in the all-electron case turned out to be 0.0025 a.u. or 3% above the pseudopotential result. This leads to an overestimation of the binding energy for the pseudopotential case of -0.0036 a.u./u.c. or 3% of the total correlation contributions to binding. Altogether, the differences between pseudopotential and all-electron calculations for the valence shell correlations are small compared with other shortcomings of the computations. We cannot tell whether these overestimations result from the differences between the two wave functions close to the nucleus, i.e., the nodes for the all-electron case, or from the virtual availability of core orbitals for correlation purposes in the pseudopotential case.

Finally, a short comparison to earlier computations with the LA shall be made. For the case of diamond, a calculation with the LA was published before.[9] This computation was based on an LDA calculation from which the SCF ground state was obtained. The exchange energy and potential were then separately computed. The resulting SCF energy and binding and the estimated HF limit were in quite good agreement with the values obtained here. The same holds true for the individual contributions to the correlation energy. The results presented here differ only in the explicit inclusion and computation of longer range correlations.

For the case of silicon, a similar calculation had been performed before, too.[10] Here, larger differences showed up. Already on the SCF level, the binding energy was overestimated by -0.02 a.u./u.c. This was in part due to another pseudopotential used, as mentioned before, and in part due to an overestimate of finite basis set corrections. For the correlation treatment, it turned out that all individual correlation contributions that were computed in the old work were systematically 10–20 % too large as compared with the present results. Since in the present calculations the same correlation program was used, this discrepancy can only be connected with an error in the addition of the separately computed exchange potential in the previous computation. These two shortcomings of the old computation led to a surprising closeness of the resulting binding energy to the experimental values in contrast to the new and error free results for silicon presented here.

IV. EQUILIBRIUM LATTICE CONSTANTS AND BULK MODULI

So far, the ground-state calculations were performed for the experimental lattice constants. Next, the dependence of the different energy contributions on the lattice constants is analyzed. For this purpose, the basis set and details of the handling of the intra-atomic correlations are frozen at the values obtained for the computation performed at the experimental lattice constant. The computations are repeated for a set of lattice constants, stepwise extended by 1% each. Smaller lattice constants were not used because they would lead to increasing overlap problems in the SCF calculations. Altogether, energies were computed for five points and a parabola was fitted to these points, leading to the optimal lattice constant, a_0, and a curvature at this extremal point, $c = \frac{\partial^2}{\partial a^2} E(a)|_{a=a_0}$.

The bulk modulus at the experimental lattice constant, $B(a_{\exp})$, was computed from these values as

$$B(a_{\exp}) = \frac{4c}{9a_{\exp}} \left(1 - 2\frac{a_{\exp} - a_0}{a_{\exp}}\right). \tag{17}$$

Table IV contains the results of the optimal lattice constants a_0. When comparing the SCF results to the experimental values, then it can be seen that in every case, the lattice constant is slightly too large. The devi-

TABLE IV. Equilibrium lattice constants a_0 and partial contributions for the elemental crystals (Å), as obtained by the LA, in comparison to other methods and to experiment.

	C	Si	Ge	Sn
HF contributions				
a_0(SCF)	3.580	5.526	5.755	6.517
Correlation contributions				
Δa_0(inter)	+0.076	+0.093	+0.123	+0.124
Δa_0(intra)	−0.039	−0.091	−0.075	−0.054
Δa_0(Polar.)	−0.016	−0.040	−0.043	−0.049
a_0(LA)	3.601	5.488	5.760	6.538
a_0(LDA) (Ref. 35)	3.530	5.408	5.705	
a_0(LDA) (Ref. 36)		5.373	5.569	
a_0(LDA) (Ref. 37)				6.547
a_0(Jastrow) (Ref. 5)	3.54(3)	5.40(4)		
a_0(exp)	3.567	5.431	5.657	6.489

ation amounts to 0.5% for C and Sn, and to 2.0% for Si and Ge. Computations on small molecules indicate that for the cases of silicon and germanium, a finite basis size reduction of 0.5% is to be expected. Furthermore, different pseudopotentials lead to variations in the equilibrium lattice constants of ±0.5%.

When turning to correlation corrections, then continuous changes show up that are easily understood. Interatomic contributions systematically enlarge the lattice constants by 2% in each case. This expansion can be understood to arise from the fact that with interatomic correlations, systematically antibonding orbitals are occupied, while in the SCF ground state only bonding orbitals were occupied. The dominant contributions to these corrections come from the on-site correlations. It is only for the heavier semiconductors with more and more delocalized electrons that the longer range interatomic contributions contribute to this trend, too.

A second set of correlations, namely, the intra-atomic correlations have the opposite trend. They lead to a lattice contraction of 1.2% (diamond, tin) to 1.5% (silicon, germanium). This is due to the inclusion of a short range correlation hole that enables the electrons to avoid each other at small distances more easily. It is plausible that the largest correction shows up for the case of silicon. Here, the unoccupied 3*d* orbitals are close to the Fermi energy and contribute particularly strongly to the short range correlations.

Polarization contributions, finally, lead to a further contraction which is rather small for diamond (0.5%) and considerably larger (1%) for the other systems. In the latter cases, the enhanced polarizability due to the proximity of the unoccupied *d* orbitals to the Fermi energy plays a role.

Contrary to the case of the energies, we did not try to obtain an estimate of the defects in the equilibrium distances originating from either the LA approximation or the finite basis set deficits. As mentioned in the discussion of the correlation energies, only 50% of the short range correlation energy is obtained by the basis sets used. A certain contribution of the error in the final lattice constant, if compared to experiment, may arise from this shortcoming, too. The actual error amounts to between 10% of the intra-atomic contributions for silicon and 50% for germanium. This indicates that the lacking short range contributions must influence the lattice constants to a much smaller relative extent than they do for the energies.

Correlation contributions to the lattice constant altogether apparently cancel each other to a large extent. The largest correction is a 1% contribution for the case of silicon. The accuracy of these investigations is thus eventually dominated by shortcomings of the SCF treatment.

Finally, the results for the bulk modulus at the experimental lattice constant are discussed. The values for the bulk modulus are given in Table V. As can be seen, the SCF calculations overestimate the bulk modulus by between 3% for α tin and 15% for germanium. Correlations reduce the bulk modulus. Here, all different contributions have a similar effect. The only difference is that the interatomic correlations contribute 30% for the case of diamond but very much less for the other cases. The final values are in fair agreement with experiment with exception of the case of α tin. As mentioned above, the SCF calculation for tin still seems to suffer from minor errors. This suspicion is supported by the presented results for the bulk moduli.

As for the equilibrium distances before, we did not try to obtain a guess for possible corrections which care for the shortcomings of the LA or the finite basis. As the numbers indicate, there is not much room for such corrections, indicating that these corrections are not relevant for the bulk moduli.

V. CORRELATION FUNCTIONS

Correlation calculations performed with the LA allow not only compute global quantities like the correlation

TABLE V. Bulk modulus B and partial contributions for the elemental crystals (Mbar), as obtained by the LA, in comparison to other methods and to experiment.

	C	Si	Ge	Sn
HF contributions				
$B_{\text{SCF}}(a_{\text{exp}})$	4.58	1.117	0.868	0.544
Correlation contributions				
$\Delta B_{\text{inter}}(a_{\text{exp}})$	−0.09	−0.018	−0.017	−0.010
$\Delta B_{\text{intra}}(a_{\text{exp}})$	−0.16	−0.099	−0.077	−0.026
$\Delta B_{\text{Polar.}}(a_{\text{exp}})$	−0.00	−0.000	−0.000	−0.000
$B_{\text{LA}}(a_{\text{exp}})$	4.33	1.000	0.774	0.508
$B_{\text{LDA}}(a_{\text{exp}})$ (Ref. 35)	4.90	0.980	0.66	
$B_{\text{LDA}}(a_{\text{exp}})$ (Ref. 36)		0.968	0.762	
$B_{\text{LDA}}(a_{\text{exp}})$ (Ref. 37)				0.509
$B_{\text{Jastrow}}(a_{\text{exp}})$ (Ref. 5)	4.20(50)	1.08(10)		
B_{exp}	4.42	0.988	0.734	0.53

energy, but also particular correlation functions. As has been found several times before in computations with the LA, the correlations in terms of the atomic orbitals, and among them those on the individual atoms, are of largest importance. For the applications presented here, these are most simply described in terms of correlations in single atomic hybrids and between pairs of them on the same atom. This allows us to reduce the atomic correlation description to two quantities, namely, the reduction of charge fluctuations due to correlations within a single hybrid, $\Delta_{ii}(A)$ and in different hybrids i, j, $\Delta_{ij}(A)$ on the same atom A. Spin correlations will be disregarded in the following. Formally, these correlation corrections are given as

$$\begin{aligned}\Delta_{ii} &= \langle\Psi_{\text{corr}}|n_{i\uparrow}n_{i\downarrow}|\Psi_{\text{corr}}\rangle - \langle n_{i\uparrow}n_{i\downarrow}\rangle,\\ \Delta_{ij} &= \langle\Psi_{\text{corr}}|n_{i}n_{j}|\Psi_{\text{corr}}\rangle - \langle n_{i}n_{j}\rangle.\end{aligned} \tag{18}$$

These quantities Δ are given for the different solids in Table VI as obtained from the correlation calculation restricted to interatomic correlations. They depend only slightly on intra-atomic and on longer range polarization correlations as will be discussed later in more detail. It can be seen that the atomic correlation corrections are of similar strength for the different solids although the corresponding correlation energies strongly decrease from diamond to tin; this was discussed above. This difference results from the fact that the correlation functions depend on the ratio of interaction to band energies while the corresponding correlation energies scale like these correlation functions times the interactions. Both energy scales decrease from diamond to tin as will be shown below.

The first correlation correction Δ_{ii} can be directly used to obtain the correlation strength for the atomic orbital i. For the uncorrelated ground state of all these half filled systems it holds that $\langle n_{i\uparrow}n_{i\downarrow}\rangle = \frac{1}{4}$. The corrections therefore reduce the double occupancies by between 15% for diamond and 12% for tin. Thus, all these solids are weakly correlated.

The correlation corrections obtained from this *ab initio* calculation may be used to determine the interaction parameters of a model Hamiltonian. This can simply be done by constructing a model that contains just the relevant degrees of freedom and by mapping particular correlation features of the *ab initio* results to this model.

The simplest model that can be used is a model for the valence electrons only. It is a tight-binding single-particle Hamiltonian with one parameter only which represents the delocalization of the electrons when the atoms form a solid plus an interaction part with two parameters for effective atomic interactions.

The simplest tight-binding model in a bond-orbital approximation (BOA) has a single hopping term between

TABLE VI. Atomic correlation functions Δ_{ij} and parameters for a bond-orbital model Hamiltonian for the elemental crystals, as obtained from the LA.

	C	Si	Ge	Sn
Correlation functions				
Δ_{ii}	−0.0382	−0.0322	−0.0300	−0.0292
Δ_{ij}	−0.0287	−0.0222	−0.0226	−0.0237
Model Hamiltonian parameters (eV)				
t	10.7	6.1	6.1	5.6
U	4.4	1.8	1.8	1.7
J	1.4	0.7	0.65	0.55
$U+2J$	7.2	3.3	3.1	2.8

two directed valence sp^3 hybrids on neighboring atoms 1 and 2, which form a bond orbital.[28,29] Its Hamiltonian reads

$$H_0 = -t \sum_{I\sigma} (a^\dagger_{I1\sigma} a_{I2\sigma} + a^\dagger_{I2\sigma} a_{I1\sigma}) \ , \tag{19}$$

where the index I runs over the different bonds.

In these semiconductors, each atom is surrounded by four neighbors. The single-particle ground state of this model Hamiltonian H_0 is understood in terms of bond orbitals which are formed by the corresponding atomic hybrids pointing at each other. Since there are four electrons per atom, all these bond orbitals are completely occupied. The one-particle ground state is thus written as a superposition of orthogonal bond orbitals, represented by the creation operators $b^\dagger_{I\sigma}$,

$$|\Psi_{\mathrm{SCF}}\rangle = \prod_{I\sigma} b^\dagger_{I\sigma} |0\rangle \ . \tag{20}$$

The latter are defined in terms of the corresponding two orthogonalized atomic hybrids $a^\dagger_{I1\sigma}, a^\dagger_{I2\sigma}$,

$$b^\dagger_{I\sigma} = \frac{1}{\sqrt{2}} (a^\dagger_{I1\sigma} + a^\dagger_{I2\sigma}) \ . \tag{21}$$

Since only atomic correlations are covered, it is sufficient to confine oneself to an interaction part with atomic terms only. With only two independent parameters allowed for, it reads as

$$\begin{aligned} H_1 = & \sum_A (U + 2J) \sum_l n_{Al\uparrow} n_{Al\downarrow} \\ & + \frac{U}{2} \sum_{l \neq l' \sigma\sigma'} a^\dagger_{Al\sigma} a^\dagger_{Al'\sigma'} a_{Al'\sigma'} a_{Al\sigma} \\ & + \frac{J}{2} \sum_{l \neq l' \sigma\sigma'} a^\dagger_{Al\sigma} a^\dagger_{Al'\sigma'} a_{Al\sigma'} a_{Al'\sigma} \ . \end{aligned} \tag{22}$$

Terms which are not biquadratic in l and l' do not contribute to ground-state correlations within BOA, and therefore have been dropped here. Here, a different set of indices is introduced for the atomic hybrids. The indices l, $l' (= 1, \ldots, 4)$ refer to the different sp_3 hybrids on atom A.

The use of the minimal basis of atomic orbitals implies that only interatomic correlations can be covered. Thus, the correlation treatment can be restricted to two sets of operators (spin operators are disregarded again).

$$\begin{aligned} O_1(A, l) &= n_{Al\uparrow} n_{Al\downarrow}, \\ O_2(A, l, l') &= n_{Al} n_{Al'}, \end{aligned} \tag{23}$$

with two variational parameters. Here, $n_{Al} = \sum_\sigma n_{Al\sigma}$. These correlation operators for the model represent the interatomic correlation operators of the *ab initio* calculation. Thus the interaction parameters U and J, in relation to the hopping terms t, are fully determined by requiring that the resulting correlation corrections of the model Δ_{ii} and Δ_{ij} equal those of the *ab initio* calculation. For diamond, the parameters t were taken from an earlier fit to the band structure,[29] and for the other solids they were rescaled according to the changes of the valence bandwidth in comparison to the one of diamond.[30]

The parameters t as well as the resulting values U and J are given in Table VI. As can be seen, the interaction terms U are very much smaller than the known atomic interactions of the bare atoms U_{at}, which are $U_{\mathrm{at}}(\mathrm{C}) =$ 14 eV, $U_{\mathrm{at}}(\mathrm{Si}) =$ 9.2 eV for two representative cases. The interaction terms J, however, are more closely connected to the atomic values J_{at}, which are $J_{\mathrm{at}}(\mathrm{C}) = 1.9$ eV and $J_{\mathrm{at}}(\mathrm{Si}) = 1.3$ eV. For more details, we refer to Ref. 31.

This strong reduction of U is not connected with any screening because all correlations included for the particular *ab initio* result used are explicitly covered in the model as well. Rather, this small U results from the folding of the long range $\frac{1}{r}$ Coulomb interaction into the effective local term. It can be shown that for such a semiconductor model only two terms of a long range interaction contribute, namely, the direct atomic interaction U_0 which due to renormalization effects is actually expected to be somewhat larger than the atomic interaction U_{at} introduced above and the Coulomb interaction V between electrons in hybrids on neighboring atoms. It can be further shown that in the BOA it holds that $U = U_0 - V$.[31] This explains the strongly reduced values of U.

For the interaction J, there is no such large compensation. There is, however, a smaller correction due to differences among the longer range contributions of the Coulomb interaction, which can explain the reduction in comparison to the atomic terms.[31]

When comparing the interactions U for the different semiconductors, then it is seen that they do not scale at all like the quantities t or J but that they are very much smaller for silicon, germanium, and tin than they are for diamond. This is due to the extended cores of the heavier elements. These lead to an increase of the average extension of the atomic orbitals beyond the one due to the increase in the lattice constant alone. This changes U_0 only a little but causes a relatively large change in the difference value U. Let us point out again that this strong reduction of the effective atomic interaction is not due to screening effects or other tricky correlation features but due to a simple folding of the long range Coulomb interaction.

From more complete *ab initio* calculations, it was found that longer range polarization corrections do not at all change the correlation functions Δ. Consequently, they do not lead to modified interactions U either. At a first glance, this finding strongly contradicts the experience that additional charges in a semiconductor are strongly screened by the highly polarizable environment. But considering that the value U represents a difference between interactions, here it just means that these long range polarizations reduce the interaction of two electrons on the same atom, U_0, by (almost) the same total amount as the interaction of two electrons on neighboring atoms, V.

It was further found that very short range intra-atomic correlations have a small effect. When added, they reduce the atomic correlation corrections by 5% in every case. Consequently, the model interactions U and J are reduced by the same relative amount. When considering that these short range correlations were not very well treated (i.e., only half of the correlation energy connected with them was obtained), then the final interactions U and J are by 10 ± 5% smaller than the values given in Table VI.

These findings again indicate that effective interactions for models can be determined with high accuracy from *ab initio* calculations with the LA. For results on other systems we refer to Ref. 32.

VI. COMPARISON WITH DIFFERENT *AB INITIO* CALCULATIONS

Within the discussion of our *ab initio* results, we have already made comparisons to earlier results obtained with the LA and to results obtained from cluster calculations with standard quantum-chemistry methods. In this section, we shall make comparisons to *ab initio* results of very different methods, which correlate the electrons like in homogeneous systems. The one method is the standard *ab initio* method for solids, namely, the local-density approximation (LDA); the other is a Monte Carlo Jastrow computation scheme.

The comparison to LDA results can be made for the binding energies and for equilibrium lattice constants and bulk moduli. All corresponding tables which contain the results of the LA contain results of the LDA, as far as available. The LDA results are from Refs. 33, 34 for diamond and from Refs. 35–38 for the other systems.

As can be seen for the binding energies in Table III, the uncorrected results of the LA, E_B(LA) obtained in the computations presented here, differ roughly by the same amount from the experimental values E_B(exp.) as do the LDA results E_B(LDA). However, the shortcomings of the LA can, due to the intrinsic variational nature of this ansatz, be easily estimated.

The LDA errors for equilibrium lattice constants and bulk moduli are of the same order of magnitude as the LA errors presented here. While for the bulk moduli the LDA errors are not systematic, the equilibrium lattice constants are too small compared with the experiment, except for the case of tin. This is the typical deviation expected for every LDA calculation. Here, one may connect these systematic deviations of between 0.5% and 1% with particular correlation features. As found in our calculations, different correlation contributions influence the lattice constants differently. There are two groups of correlations, which a homogeneous correlation treatment cannot describe well. The first is the group of interatomic correlations. For the homogeneous electron gas, there are no atomic orbitals and therefore no enhanced interatomic correlations. The second is the group of longer range polarization corrections. In a homogeneous system, there is no longer range van der Waals like correlation. The combined effect of these two groups of correlation corrections is in every case a lattice enhancement of roughly 1%, which is of the same size as the LDA deficiency. Here, it shall just be noted that LDA deficits in the treatment of transition metals were connected before with similar interatomic correlation contributions.[39]

Computations with a Jastrow Monte Carlo method were performed for diamond and silicon.[4,5] This variational Monte Carlo scheme assumes the electrons to correlate like they do in a homogeneous system. The optimal variational ansatz for the correlated wave function under this restriction was then found to be the one for an homogeneous electron gas with the density of the valence electrons in the real system. The resulting correlation energies, E_{corr}(Jastrow), are given in Table II, too. They bypass the results of the LA and lack only 15% to the estimated exact result E_{corr}(cb). In comparison to our results, this computation profits from the fair description of the short range part of the correlation hole.

The binding energies determined from these computations are not displayed in Table III, because they contain a minor error. This error is not connected with the correlation treatment, but with the estimated finite-size corrections on the SCF level. For diamond for example, a finite-size SCF binding energy of −0.342 a.u./u.c. was obtained. When including a finite-size correction, a final value for the HF binding energy of −0.436 a.u./u.c. was estimated. This value is much too large as compared to our estimate of the HF binding energy E_B(HF), which is -0.410 ± 0.005 a.u./u.c. A similar shortcoming occurred for silicon.

The equilibrium lattice constants were identically the same ones as for the LDA computations.

It is of interest to connect the deficiencies of the Jastrow results with immanent shortcomings of the homogeneous electron gas like treatment behind the Jastrow ansatz. As for the LDA before, one would not expect a very good coverage of the interatomic and of the longer range polarization correlations. In fact, the slightly short equilibrium distances indicate that the Jastrow ansatz suffers here from the same shortcomings as the LDA. The missing 15% of correlation energy amount to roughly half the combined interatomic and polarization energy contributions for diamond but somewhat more for silicon.

There is in fact conclusive evidence from such a calculation for the C atom that the Jastrow ansatz lacks the proper treatment of correlations in terms of atomic orbitals. For the C atom a particular correlation described by atomic orbitals contributes 17% of the valence correlation energy. This is a two-particle excitation of the $2s$ electrons into the single empty $2p$ orbitals. This correlation is strong because the atomic $2s$ and $2p$ orbitals are almost degenerate. It was found that when adding such a particular correlation to a Jastrow ansatz computation, still 60% of the original correlation energy contribution could be gained.[40] These results indicate that correlations which really differ from correlations in the homogeneous electron gas are not well described by this scheme either. Therefore, this scheme might not really offer an improvement in comparison to LDA when correlations are concerned.

For diamond, a Green's-function Monte Carlo calculation using a local pseudopotential[41] could be performed. It yields a much larger gain in correlation energy in comparison to the Jastrow result for diamond than for the C atom. The improvement of the correlation energy for diamond amounts to −0.025 a.u./u.c., and the correlation contributions to the binding energy increases from -0.126 a.u./u.c. for the Jastrow computation[5] to -0.135 a.u./u.c. Again, a comparison to the interatomic correlation energy is suggestive. The Green's-function error amounts to roughly 20% of this value. This is a similar relative error as found for the C-atom computation with the same scheme. It was found that 30% of the particular correlation in terms of atomic orbitals for the C atom was still gained when this correlation was explicitly added to a Green's-function Monte Carlo computation.[40]

This is the first evidence that even Green's-function Monte Carlo schemes will not be able to perform very well for the particular correlations that arise due to inhomogeneity. Possibly, correlations on the atomic scale must be directly addressed as is done in the LA.

VII. CONCLUSIONS

We have presented in this paper results of *ab initio* calculations for different semiconductors obtained with the local ansatz. We could present results on equilibrium lattice constants and on the bulk moduli, too.

As can be seen from the results obtained by our computations, so far they do not represent a significant quantitative improvement as compared with the LDA results. On the other hand; they allow a quantitative treatment of those correlation contributions that deviate sizeably from the ones of a homogeneous system. Here, even quantitative connections to the deficits of schemes based on homogeneous electron gas ideas like the LDA or Monte Carlo Jastrow calculations could be made.

At present, the LA is the only *ab initio* correlation scheme which can be equally applied to every kind of solid from ionic crystals to metals and to whatever dimension required: molecules, chains, slabs, and solids. In addition, it has the advantage that its computer time expenses are less than one order of magnitude larger than the computation expenses for a preceding Hartree-Fock calculation with the CRYSTAL program.

However, improvements for the LA are required first to reduce its deficits in comparison with a more complete correlation calculation in the same basis. Here, correlation results obtained from different clusters with standard quantum-chemistry methods with which the solid case could be extrapolated serve as a reference case. Next these computations need to be repeated with an enlarged basis set. The cluster calculations just mentioned indicate that more than 90% of the correlation energies and corresponding binding energy contributions can be obtained by a simple extension to basis sets containing two sets of *d* functions and one set of *f* functions. While such a calculation poses no problems for the LA, calculations including *f* functions are not yet possible with the CRYSTAL program package.

In distinction to all schemes developed from homogeneous electron gas ideas, this method properly cares for the inhomogeneity of real systems. Due to its particular use of local operators and due to its segmentation of the total correlation contribution into different parts, it allows a quantitative description of those correlation functions which are of particular relevance for real systems, namely, correlations in terms of atomic orbitals. Here, immediately a connection to model Hamiltonians can be made, and the necessary effective interaction terms for such models can be computed with high precision.

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[1] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[2] D. M. Ceperley and B. J. Alder, Physica **108B**, 875 (1981).

[3] R. Jastrow, Phys. Rev. **98**, 1479 (1955).

[4] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. Lett. **61**, 1631 (1988).

[5] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. B **42**, 3503 (1990).

[6] G. Stollhoff and P. Fulde, J. Chem. Phys. **73**, 4548 (1980).

[7] G. Stollhoff and P. Vasilopoulos, J. Chem. Phys. **84**, 2744 (1986); **85**, 3138 (1986).

[8] B. Kiel, G. Stollhoff, C. Weigel, P. Fulde, and H. Stoll, Z. Phys. B **46**, 1 (1982).

[9] G. Stollhoff and K. P. Bohnen, Phys. Rev. B **37**, 4678 (1988).

[10] M. V. Ganduglia-Pirovano, G. Stollhoff, P. Fulde, and K. P. Bohnen, Phys. Rev. B **39**, 5156 (1989).

[11] M. V. Ganduglia-Pirovano and G. Stollhoff, Phys. Rev. B **44**, 3526 (1991).

[12] G. König and G. Stollhoff, J. Chem. Phys. **91**, 2993 (1989).

[13] G. König and G. Stollhoff, Phys. Rev. Lett. **65**, 1239 (1990).

[14] A. Heilingbrunner and G. Stollhoff, J. Chem. Phys. **99**, 6799 (1993).

[15] R. Dovesi, C. Pisani, and C. Roetti, *Hartree-Fock Ab Initio Treatment of Crystalline Systems*, Lecture Notes in Chemistry Vol. 48 (Springer, Berlin, 1988).

[16] R. Dovesi, V. R. Saunders, and C. Roetti, CRYSTAL92, User Documentation, University of Torino and SERC Daresbury Lab.

[17] W. v. d. Linden, P. Fulde, and K. P. Bohnen, Phys. Rev. B **34**, 1063 (1986).

[18] P. Siegbahn and B. Roos, Theor. Chim. Acta **17**, 209 (1970).

[19] A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuss, Mol. Phys. **80**, 1431 (1993).

[20] P. Horsch and P. Fulde, Z. Phys. B **36**, 23 (1979).

[21] R. Ahlrichs, Comput. Phys. Commun. **17**, 31 (1979).

[22] J. Čižek and J. Paldus, Int. J. Quantum Chem. **3**, 149 (1969); **5**, 359 (1971).

[23] H. Stoll, Phys. Rev. B **46**, 6700 (1992).

[24] H. Stoll, Chem. Phys. Lett. **191**, 548 (1992).

[25] G. Stollhoff and M. Häser, Phys. Rev. B **45**, 13 703 (1992).

[25] G. Stollhoff and M. Häser, Phys. Rev. B **45**, 13 703 (1992).

[26] R. Pardon, Ph.D. thesis, University of Stuttgart, 1993.

[27] C. Pisani, R. Dovesi, and R. Orlando, Int. J. Quantum Chem. **42**, 5 (1992).

[28] W. Harrison *Electronic Structure and the Properties of Solids* (Freeman, San Fransisco, 1980).

[29] W. Borrmann and P. Fulde, Phys. Rev. B **31**, 7800 (1985).

[30] D. A. Papaconstantopoulos, *Handbook of the Bandstructure of Elemental Solids* (Plenum Press, New York, 1986).

[31] P. Fulde and G. Stollhoff, J. Phys. **50**, 2659 (1989).

[32] G. Stollhoff (unpublished).

[33] A. Svane and O. K. Anderson, Phys. Rev. B **34**, 5512 (1986).

[34] A. Svane, Phys. Rev. B **35**, 5496 (1987).

[35] D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980).

[36] V. Fiorentini, Phys. Rev. B **46**, 2086 (1992).

[37] N. E. Christensen and M. Methfessel, Phys. Rev. B **48**, 5797 (1993).

[38] A. Svane (private communication).

[39] G. Stollhoff, A. M. Oleś, and V. Heine, Phys. Rev. B **41**, 7028 (1990).

[40] H. J. Flad, Ph.D. thesis, University of Stuttgart, 1993.

[41] X. P. Li, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **44**, 10 929 (1991).