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Correlated electronic ground state of the molecule C_{60}

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Ab initio correlation calculations for the C_{60} molecule are reported. Details are compared with those of similar calculations on diamond and graphite. It is found that the binding energy of the molecule is smaller by 0.45 eV/atom than that of the solids. The correlation pattern is very similar to the one for graphite.

I. INTRODUCTION

A detailed understanding of electron correlations in the fullerene molecule C_{60} (Ref. 1) is of significance. It was recently found that C_{60} compounds become superconducting at temperatures that are large in comparison with related compounds such as doped graphite.[2] Therefore it seems to be worthwhile to investigate whether there are differences in the electronic many-body effects in these systems. If they exist, then they might give a hint for a superconducting mechanism caused by the direct Coulomb interaction of the electrons.

This aim is pursued by an *ab initio* correlation calculation for the neutral molecule. For this purpose, the local ansatz is used, a scheme which was developed using calculations for small molecules[3] and has been applied to two other allotropic forms of carbon, namely diamond[4] and graphite.[5] From the calculations not only ground-state energies but also correlation patterns can be taken. Here, we start from a Hartree-Fock (HF) self-consistent-field (SCF) calculation which was performed with the direct SCF program in the program package TURBOMOLE.[6]

Correlation calculations for large molecules or solids can be performed within the local ansatz because this scheme is restricted to relatively few correlation operators which all have a definite purpose. In this respect, the scheme differs from standard quantum-chemistry approaches which all cover complete sets of operators. This leads to computation costs that have so far made calculations for solids too expensive to be performed.

Such a selection of correlation operators within the local ansatz has a disadvantage, though. A certain amount of correlation energy is lost when the resulting energy is compared with the one of a complete coverage of the correlation space. Such comparisons have been made in the past for atoms and small molecules. There a loss of 5–8 % was observed.[3,7] The computations for the C_{60} molecule offer a comparison for a larger system, since recently a standard correlation calculation could be performed although only in second-order many-body perturbation expansion (MP2).[8] In this way, experience about the shortcomings of the local ansatz may be gained. Such information will be relevant for future solid calculations.

The next section contains a short introduction into the calculation scheme. Within the third section, the partial contributions to the correlation energy are discussed and a comparison between results of the local ansatz when restricted to MP2 and the correct MP2 energy for the same basis set are made. The fourth section contains some details of the correlation patterns and a comparison with other carbon representations.

II. THE COMPUTATION SCHEME

The SCF calculation was performed by the program TURBOMOLE.[6] As a basis set, the same set of (contracted) Gaussians was taken as was used before for the calculations for diamond and graphite. It is of double-ζ plus polarization function quality.[9] As compared with the original basis set, the outer s and p orbitals were contracted to 0.23. The exponent for the d orbitals was set to 0.6. The molecule is completely described by the two different neighbor distances. Here, the optimal values for the SCF ground state were taken, namely $a_1 = 1.37$ Å and $a_2 = 1.45$ Å. a_1 is the axis connecting two hexagons while a_2 connects a pentagon and a hexagon. MP2 calculations and experiments indicate that the difference between these distances as obtained using the SCF approximation is a factor of 2 too large compared with the real difference.[8]

Correlations are included by the local ansatz. Within this scheme, the following variational ansatz is made for the correlated ground state:

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

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

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

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

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

where the $f_i(\mathbf{r})$ represent the basis orbitals. The operators have a transparent meaning. The first operator $n_{i\uparrow}n_{i\downarrow}$, for example, when applied to $|\Psi_{\mathrm{SCF}}\rangle$, picks out all configurations with two electrons in orbital $g_i(\mathbf{r})$. When applied with a variational parameter η_ν, as in Eq. (3), it partially suppresses those configurations. Similarly, the operators n_in_j introduce density correlations between electrons in local orbitals $g_i(\mathbf{r})$ and $g_j(\mathbf{r})$. The wave function with these two sets of operators, when chosen for the homogeneous-electron-gas problem, is the Jastrow function.[10] The operators $\mathbf{s}_i\cdot\mathbf{s}_j$ generate spin correlations.

All operators, when applied to $|\Psi_{\mathrm{SCF}}\rangle$, create states which are not orthogonal to $|\Psi_{\mathrm{SCF}}\rangle$. Besides, these states include one-particle excitations in addition to the two-particle excitations from $|\Psi_{\mathrm{SCF}}\rangle$. We want to keep only the two-particle excitation parts of these states. Therefore, we require that contractions within the operators are forbidden when expectation values are computed. The operators then reduce fluctuations in $|\Psi_{\mathrm{SCF}}\rangle$.

The variational parameters η_ν are chosen so that the energy

$$E_g=\frac{\langle\Psi_c|H|\Psi_c\rangle}{\langle\Psi_c|\Psi_c\rangle} \tag{5}$$

is optimized. Such a computation cannot be performed exactly. The standard approximation is an expansion in powers of η, e.g.,

$$\begin{aligned} E_G&=\langle\Psi_c|H|\Psi_c\rangle_c\\ &=E_{\mathrm{SCF}}+E_{\mathrm{corr}}\ , \end{aligned} \tag{6}$$

$$E_{\mathrm{corr}}\simeq-2\sum_\nu\eta_\nu\langle O_\nu H\rangle+\sum_{\nu,\mu}\eta_\nu\eta_\mu\langle O_\nu HO_\mu\rangle_c\ . \tag{7}$$

Here, $\langle A\rangle$ means the expectation value of A within $|\Psi_{\mathrm{SCF}}\rangle$. The subscript $\langle\ \rangle_c$ indicates that only connected diagram contributions are added.[11] This approximation works only if the correlations are sufficiently weak. It is equivalent to a specific coupled electron pair approximation called CEPA-0 in quantum chemistry[12] but is restricted to relatively few operators.

An MP2 calculation within the subspace of the operators O_ν is performed when the matrix $\langle O_\nu HO_\mu\rangle_c$ in Eq. (7) is replaced by the matrix $\langle O_\nu H_0O_\nu\rangle_c$, where H_0 represents the HF one-particle Hamiltonian for the problem. For both approximate calculation schemes it holds that correlation energy is lost if the space of correlation operators is restricted.

So far everything except the local orbitals [Eq. (4)] and the sets of operators built by them is fixed. A first choice within the treatment is to restrict ourselves to the so-called interatomic correlations. These correlations 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. There is no unique way to determine atomic orbitals from a SCF ground state. Here, they were obtained in the following way. First, the density matrix in terms of Löwdin orthogonalized basis orbitals was restricted to a small cluster around a specific atom. Next, only the eigenstates of this density matrix closest to 1 were kept, representing occupied states localized to this cluster. From these, contributions from the basis orbitals on the central atom were taken and averaged. This led to a core state, and to information about the representation of average atomic $2s$ and $2p$ valence orbitals on this atom. From these valence orbitals, a π orbital in center direction and three sp_2 hybrids in the direction of a neighbor atom each were generated. Such orbitals were constructed on every atom and Löwdin orthogonalized to each other. They were used as atomic orbitals for the interatomic calculation and represent more than 99% of the total electronic charge. With them, correlations on individual atoms as well as longer-range correlations between different atoms were treated. Such a calculation can only be performed when the energy converges sufficiently fast with respect to operators describing long-range correlations. It turned out that for the actual calculation, operators describing correlations between atomic orbitals up to second nearest atoms had to be included. The corresponding calculations were performed without further approximation, leading to the interatomic correlation energy $E_{\mathrm{corr}}^{\mathrm{inter}}$.

Shorter-range correlations are covered by so-called intra-atomic operators. They are built from sets of localized subatomic orbitals that are generated from basis orbitals on a given atom each. Details for their construction can be found in Ref. 3. The choice of localized subatomic orbitals depends 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 one into three shells. For them, sets of parameters had to be determined. These were taken from an optimization calculation on the molecule CH_4 computed in the same basis set. The same parameter sets have been used before for calculations in diamond[4] and graphite.[5] Neither here nor in the cases before did a reoptimization lead to a sizable energy gain. The operators constructed by these orbitals are connected with individual atoms only. For each atom A, a gain in correlation energy $E_{\mathrm{corr}}^{\mathrm{intra}}(A)$ is obtained when these operators on atom A are added to the interatomic operators. In a first approximation, the total correlation energy consists of the interatomic energy and the sum of all these terms. There is a correction to be made, however: a set of calculations in which intra-atomic correlations on neighbor atoms A and A' are added at the same time has to be performed and leads to an overlap correction $E_{\mathrm{corr}}^{\mathrm{ov}}(A,A')$, since these short-range correlations on the two atoms are not orthogonal to each other.

There is also a set of medium-range operators that need to be added. Such operators were constructed from subatomic orbitals on nearest-neighbor atoms before and were thought to describe short-range correlations in the volume between the two respective atoms.[7] From the calculations for C_{60} presented here, it turned out that similar operators needed to be included for next nearest neighbors as well. Therefore, a more appropriate interpretation of these operators is made. When atoms come closer, they interact by an induced polarization. Furthermore, when the electrons delocalize, charge fluctuations on individual atoms are screened by polarizations on the neighbors as well. Polarizations on individual atoms are described by local orbitals that represent superpositions of atomic orbitals and the appropriate polarization functions. In order to be able to describe polarizations in each required direction, the set of atomic orbitals is hybridized with the complete set of polarization functions. For the C atom this means a (nonorthogonal) twelvefold sp^3d^5 hybridization. It turned out in the calculations that no new local orbitals needed to be generated but that a specific twelvefold hybridized set could be taken that was used for intra-atomic correlations on an individual atom before. When constructing the operators for the induced polarizations, the polarization orbitals on two neighbor atoms are coupled by density operators, while polarizations due to charge fluctuations are described by operators formed from pairs consisting of atomic orbitals on one atom and of polarization orbitals on the second atom. These operators are included into the calculations in an incremental fashion. For pairs of atoms A and A', intra-atomic correlations are added to the interatomic correlations and then the polarization operators are included as well. This leads to an energy gain which is called $E_{\text{corr}}^{\text{pol}}(A, A')$.

The total correlation energy is therefore

$$E_{\text{corr}} = E_{\text{corr}}^{\text{inter}} + \sum_{A} E_{\text{corr}}^{\text{intra}}(A) + \sum_{\langle A, A' \rangle} [E_{\text{corr}}^{\text{ov}}(A, A') + E_{\text{corr}}^{\text{pol}}(A, A')] \ . \quad (8)$$

Similarly, other properties are computed. This way, a segmentation of the correlation treatment for larger systems is available which applies independent of details of the delocalization of electrons. It is crucial that the interatomic correlations which in fact do depend on the details of bonding are treated separately. They do not show such a perfect separability as the intra-atomic terms and the polarization contributions.

This computation scheme allows us to include symmetry in a very efficient way. For the molecule C_{60}, there exists only one kind of C atom. Therefore, there was only need for a single calculation leading to $E_{\text{corr}}^{\text{intra}}(\text{C})$. Furthermore, there were only two calculations for different nearest-neighbor C atoms necessary—the one dealing with two atoms on a line connecting two hexagons, the other on a line connecting a hexagonal and a pentagon. For next nearest neighbors there exist only two types as well—the one describing a second neighbor on a pentagon and the second describing a second neighbor on a hexagon.

The largest computer time expenses come into the calculations from the generation of the required interaction matrix elements between basis orbitals on different atoms, V_{ijkl}. It is self-evident that for operators on the atoms A and A' basis orbitals on these atoms need to be included. Additional matrix elements are only needed due to the delocalization of the SCF ground state. It turned out that only matrix elements from basis orbitals on further atoms needed to be included that are nearest neighbors to these two atoms. Actually, all polarization functions for these additional atoms may be left out without changing sizably the results because these orbitals contribute very little weight to the SCF ground state. Figure 1 represents the three clusters for which interaction matrix elements had to be calculated. The atoms represented by filled dots require a complete basis set while the ones given by open circles require only the smaller basis. These clusters are big enough to determine all intra-atomic and polarization contributions described above. Cluster 3 actually enables one to compute a specific third-neighbor polarization as well. Besides, these clusters were large enough to determine all matrix elements needed for the interatomic correlation calculation. On the other hand, they were small enough to make the generation of the V_{ijkl} a simple task for standard quantum-chemistry programs and to guarantee that the following calculations within the local ansatz program scheme were not time consuming either.

III. CORRELATION AND BINDING ENERGIES

The individual contributions to the correlation energy of the molecule C_{60} are presented in Table I for the complete solution of Eq. (7) (called CEPA-0) and for the ap-

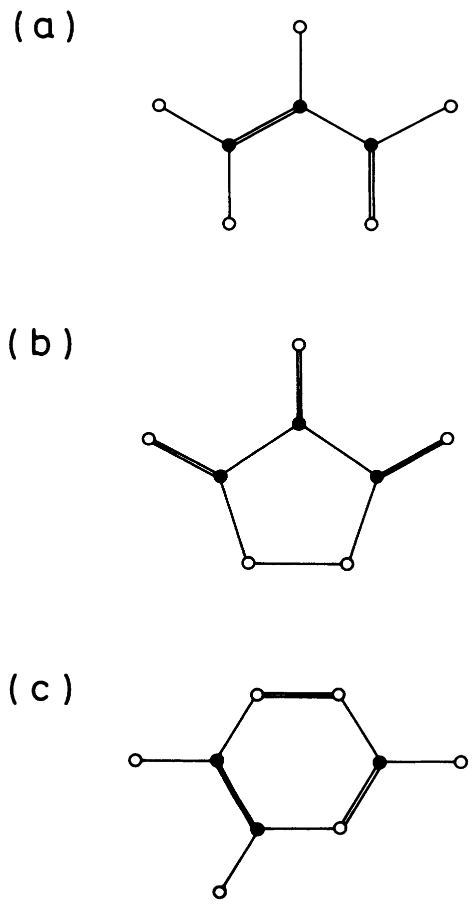

FIG. 1. Schematic representation of the three different clusters for which interaction matrix elements for the basis orbitals were generated. Double lines denote the shorter distances a_1.

TABLE I. Contributions to the valence-shell correlation energy of C_{60}, as obtained in two different approximations. Quantities are expressed in a.u./2 C atoms.

	CEPA-0	MP2
	Interatomic correlations	
Single-site operators	−0.0898	−0.0717
Neighbor-atom operators	−0.0175	−0.0165
NNN-atom operators	−0.0058	−0.0046
Longer-range correlations	−0.0040±0.0020	−0.0040±0.0020
Total interatomic contributions	−0.1171±0.0020	−0.0968±0.0020
	Intra-atomic correlations	
Single-site operators	−0.1092	−0.1088
Overlap corrections	+0.0028	+0.0028
Total intra-atomic contribution	−0.1064	−0.1060
	Polarization correlations	
Nearest-neighbor atoms	−0.0140	−0.0171
NNN atoms	−0.0054	−0.0067
Opposite hexagon atoms	−0.0004	−0.0006
Total polarization contributions	−0.0198	−0.0244
	Total correlation energies	
Result LA	−0.2433±0.0020	−0.2272±0.0020
Exact result		−0.257

proximate solution in MP2. For the latter approximation, the result obtained for the local ansatz can be compared to the exact result for the same basis set. Actually, the latter result was obtained after a first calculation within the local ansatz without longer-range polarization contributions was performed. As can be seen, the local ansatz loses almost 12% of the correlation energy. This is a significantly larger error than found before for calculations on atoms and small molecules. When comparing the results obtained there[3,7] with results obtained with standard programs,[13] a loss of 4–6 % for atoms and 6–9 % for small molecules was observed.

Before addressing the origin of this defect, details of the results shall be discussed briefly. As can be seen, interatomic correlations contribute almost half of the correlation energy. Longer-range correlations converge quite fast. Contributions extending beyond next-nearest-neighbor (NNN) correlations were estimated. A few of them were explicitly computed. When calculated using MP2, the single-site terms are strongly underestimated. Such a behavior was found before for other systems and is well understood.[7,4] It is known that MP2 strongly overestimates longer-range correlations in metals. For a three-dimensional metal, this even leads to a divergence of the correlation energy. Here it can be seen that longer-range results come closer to the CEPA-0 results but up to second-neighbor distances do not overestimate them.

Intra-atomic correlations contribute with roughly the same amount to the correlation energy as do the interatomic correlations. Note that these contributions are almost perfectly additive, i.e., the overlap corrections are very small, and that almost the same result is obtained within MP2. Polarization corrections come out smallest. While there is a sizeable contribution stemming from nearest neighbors, the newly added NNN terms add only 2–3 % to the correlation energy. A specific set of third nearest neighbors adds only a negligible amount of polarization contributions. These polarization contributions are systematically overrated by 20% in MP2.

We now return to the question where correlations get lost due to the restrictions of the local ansatz. We do not trace the source of the discrepancy to the longer-range correlations since the operators, which are expected to describe the dominant long-range contributions, were explicitly included, and the resulting contributions seem to be well converged. What must have been handled not well enough are the intra-atomic contributions and the on-site and neighbor contributions to the interatomic correlation energy. Possibly, neighbor polarizations will necessitate a better treatment too. In fact, the size of the defect for C_{60} can be estimated from trends in the defects of small molecules.

Let us turn next to the binding energy of C_{60}. Knowing the corresponding energies for the free atom and the molecule within the same finite-basis set, one may calculate the individual contributions to the binding energy. The values are presented in Table II. The SCF binding energy is obtained by subtracting the atomic energies, obtained within the original basis[9] but corrected for the double-ζ contraction of the s orbitals, from the total energy of the molecule. The latter is −2270.191 a.u., while the first is −37.653 a.u. A rough estimate is made for the finite-basis correction leading to the HF limit of the binding energy. The correlation contribution to the binding energy is obtained by subtracting from the total correlation energy, obtained within the local ansatz for C_{60} (Table I) the valence correlation energies of the individual

TABLE II. Binding-energy contributions to C_{60} (a.u./2 C atoms).

HF contributions	
SCF result	−0.367
Finite-basis corrections	0.010±0.005
Correlation contributions	
Local ansatz	0.093±0.002
Corrections to the LA	−0.025
Finite-basis corrections	0.034±0.008
Final estimate	0.528±0.010

atoms, obtained within the local ansatz for the same basis but with the original exponents. The latter value is −0.075 a.u.[14]

There are two corrections that need to be made in order to estimate the experimental binding energy. The first is an estimate of the shortcoming of the local ansatz. The exact valence shell correlation energy for the C atom in the actual basis is known to be −0.078 a.u.[13] An estimate for C_{60} is made by assuming that the relative error of the result in the CEPA-0 approximation is the same as in MP2. The resulting correction is sizeable.

The second correction is connected with the finite basis used for the correlation calculation. An estimate of the shortcomings of the basis was obtained from a comparison of results for such a basis and experimental information in the case of small molecules. Here, it is assumed that the finite-basis error is the same as for small organic molecules. The error bar connected with this estimate represents variations in the finite-basis defects for different molecules.[7]

The resulting electronic contribution to the binding energy is sufficiently smaller than the corresponding values for diamond or two-dimensional graphite (−0.555 a.u./unit cell) as deduced from the experimental binding energies. From calculation performed using techniques such as the local-density approximation (LDA) and density-functional theory, a binding energy of 0.561 a.u./2 C atoms for the molecule was obtained.[15] This binding energy is certainly too large, probably due to the well-known shortcomings of the LDA.

Similar correlation calculations to those performed here for C_{60} have been performed for two-dimensional graphite.[5] A more accurate estimate of the metastability of C_{60} can therefore be made by directly comparing the values of the two calculations. For graphite, a SCF binding energy of −0.398 a.u./unit cell was obtained. In the SCF approximation, C_{60} is by 0.015 a.u./atom less stable than graphite. This loss in binding represents the costs of the bending of the plane. The valence-shell correlations of graphite are very similar of those of C_{60}. The correlation energy amounts to −0.244 a.u./unit cell when including the same sets of operators. Therefore, a further loss in energy of 0.0005 a.u./atom is found. Altogether, this leads to a loss of energy of 0.016 a.u. or 0.45 eV per atom for C_{60}.

There is no reason to assume that finite-basis effects or shortcomings of the local ansatz should result in differences in between C_{60} and graphite. The energy difference discussed above should therefore represent well the metastability of the molecule C_{60}. A certain correction is expected from an optimization of the ground-state geometry. When assuming that the difference between the two neighbor distances for C_{60} was overestimated by a factor of 2, then this is connected with a loss of binding energy of 0.10 eV per atom.

IV. CORRELATION FUNCTIONS

The detailed correlation energy contributions of C_{60} turned out to be very similar to those of graphite. Therefore the correlation behavior is expected to be very similar too. Details of the correlation functions shall be investigated in the following. As it turned out in all calculations done so far, the dominant corrections to the pair-correlation functions of the HF ground state are connected with interatomic correlations.

Here, the following correlation functions will be investigated. The first one describes the probability to find two electrons in the same atomic orbital. Since each atomic orbital is half filled, this probability is 0.25 for the uncorrelated case. In this case, the correlation strength or relative reduction of charge fluctuations is defined as

$$\begin{aligned}\xi_i &= \frac{1}{0.25}(0.25 - \langle \Psi_c | n_{i\uparrow} n_{i\downarrow} | \Psi_c \rangle) \\ &= 8 \sum_{\nu} \eta_\nu \langle O_\nu n_{i\uparrow} n_{i\downarrow} \rangle \ . \end{aligned} \tag{9}$$

Here, only linear corrections in the variational parameters η_ν were included. Table III contains the values for the correlation strength ξ_i, where i represents the π orbital and the σ orbitals in the different directions. For comparison, analogous values for diamond and graphite are added. As can be seen, correlations of the valence electrons in C_{60} are very similar to the ones in graphite.

From the values of the correlation strength, it may be deduced that the π electrons in C_{60} are weakly correlated. Correlations are not expected to reduce the mobility of the electrons by more than 5%. Theories of strong correlations or resonant-valence-bond theories will therefore not work when they are applied to intramolecular interactions in C_{60}. This notion is supported by the close agreement between the experimental equilibrium geometry of the molecule and the theoretical result obtained from MP2 calculations.[8]

The correlation strength obtained from this *ab initio* calculation may be used to fix the interaction parameters of a model Hamiltonian. When choosing a Hamiltonian

TABLE III. Correlation strength ξ and atomic charge fluctuation Δn^2(C) for different C representations.

	ξ_π	ξ_σ	Δn_c^2(C)
C_{60}	0.18	0.14	1.27
		0.12	
Diamond		0.16	1.36
Graphite	0.17	0.14	1.28

with neighbor hopping t for the π electrons and with on-site interaction U, then the following ratio holds: $U/t=2.0$.[16]

The second correlation function considered is the total atomic charge fluctuation on atom C, called $\Delta n^2(\mathrm{C})$. For a state Ψ_l, it is defined as

$$\begin{aligned}\Delta n_l^2(\mathrm{C}) &= \langle \Psi_l | \Delta n^2(\mathrm{C}) | \Psi_l \rangle \\ &= \langle \Psi_l | n^2(\mathrm{C}) | \Psi_l \rangle - \langle \Psi_l | n(\mathrm{C}) | \Psi_l \rangle^2 \ . \end{aligned} \tag{10}$$

For the SCF ground state of C_{60}, it holds that $\Delta n^2_{\mathrm{SCF}}(\mathrm{C})=2.0$. For the correlated ground state, it holds in lowest order in η_ν,

$$\Delta n_c^2(\mathrm{C}) = \Delta n^2_{\mathrm{SCF}}(\mathrm{C}) - 2 \sum_{i,j\in C} \sum_{\nu} \eta_\nu \langle O_\nu n_i n_j \rangle \ . \tag{11}$$

The charge fluctuation for the correlated ground state is given in Table III, too. As can be seen, the atomic charge fluctuations are as strongly reduced in C_{60} as they are in graphite.

V. CONCLUSIONS

This investigation had two aims: first to gain additional information about the electronic structure of the neutral molecule C_{60}, and second to learn about advantages and limitations of the theoretical method applied, i.e., the local ansatz.

Let us address the first question, namely a better understanding of C_{60}. Here, it could be demonstrated that electrons in C_{60} are weakly correlated. Actually, the correlation of the most relevant π electrons is almost identical to the case of graphite. There is not the slightest evidence of any peculiarity in intramolecular electronic interactions. When addressing the problem of superconductivity, these electronic interactions should at most enter via renormalizations of electron-lattice coupling.[17]

Next, we were able to give a first estimate of the binding energy of C_{60}. As compared with diamond or two-dimensional graphite, this molecule is rather unstable. An energy of 0.4–0.5 eV per atom is lost. Very recently, a total-energy calculation, performed within density-functional theory, has been carried out where a direct comparison between the energies of diamond and C_{60} was made.[18] There, an energy loss of 0.3 ± 0.1 eV was deduced.

As far as the second question is concerned, it was demonstrated that a detailed understanding of correlations does arise from these calculations. Specifically, it could be demonstrated which parts of correlations dominate the correlation energy and which ones are relevant for other correlation effects. Besides, it was shown that correlations are short ranged and hence well behaved as far as real-space convergence is concerned.

A disadvantage of every variational treatment is that only specific contributions are accounted for which are explicitly included in the ansatz for the ground state. Here, we compared a result for the local ansatz with a complete result for a large system. The shortcomings turned out to be bigger than originally anticipated. The defect in correlation energy was larger than 10%, and therefore larger than originally estimated from results obtained for small molecules. It is encouraging, though, that this error is probably not caused by a poor treatment of long-range correlations but has its origin in an incomplete coverage of shorter-range contributions. It means that the principal idea behind the local ansatz will not have to be changed in order to improve it, but a better understanding of short-range correlations has to be obtained.

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