PHYSICAL REVIEW B VOLUME 43, NUMBER 4 1 FEBRUARY 1991

Electronic structure and correlations of high-temperature superconducting compounds

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(Received 25 June 1990)

Calculations on negatively charged planar Cu_nO_m clusters are reported. Starting from a self-consistent-field calculation within a good Gaussian-type-orbital basis set, correlations are included using the local ansatz. A charge analysis reveals a Cu 3d occupation in close agreement with calculations in the local-density approximation. The electrons in the formal $Cu^{2+}{}_nO^{2-}{}_m$ entities are delocalized between Cu and O sites and strongly correlated. Our findings do not agree with the assumption of localized Cu^{2+} spins which is often made in models for these compounds. Spin correlations indicate strong short-range antiferromagnetic order even if electrons are removed. For them, there is no difference between O and Cu sites.

I. INTRODUCTION

A detailed understanding of the electronic structure of the novel high-T_c superconductors is of prime importance. It is generally accepted that such an understanding is needed for the quantitative description of these compounds' superconductivity; moreover, there are also many speculations that this understanding would reveal a new electronic mechanism for superconductivity.

In the beginning of such investigations even the repulsive interaction in a single-band Hubbard model was transferred into a short-range attraction.[1] It could be demonstrated on a simple model that such a transfer occurred incorrectly as an artifact due to the approximate treatment of the conditional hopping, while the interaction remained repulsive in a correct treatment.[2] Lately more elaborate models have been favored in which delocalized electrons interact with localized spins on the Cu atoms,[3] leading to effective attractions and/or nonfermion statistics, and eventually to a new mechanism of superconductivity.[4] Such speculations are based on the claim that the Cu 3d occupation n_d is very close to $n_d=9$.

The only *ab initio* calculations performed for solids, however, that have been done within the local-density approximation (LDA) led to occupations $n_d=9.4$.[5] They gave a fair description of lattice vibrations, but could not account for the magnetic properties of these systems. Therefore, especially the resulting 3d-orbital occupations have been questioned. Constrained LDA calculations have been performed in which specific partial charges on the Cu and O positions were frozen.[6,7] The charge distributions of model Hamiltonians built with parameters extracted from these constrained computations led to the values $n_d=9.2$.[6,7]

For small clusters, *ab initio* calculations have been performed in computations not restricted to LDA. A first example was a set of generalized valence-bond calculations that can be understood as an *ab initio* self-consistent-field (SCF) calculation including a minimal amount of correlation degrees of freedom. These computations, performed in a rather poor basis, gave Cu 3d occupations of roughly $n_d=9.0$.[8] More recently, more extended but still very much simplified correlation calculations with use of better basis sets have been published, but no charge analysis has been made.[9,10]

The aim of this paper is to report on some *ab initio* calculations for (Cu_mO_n) clusters. It will be demonstrated that with them conclusive results for charge distributions and details of short-range correlations are obtained. In order to fullfill this aim, those calculations are done within good basis sets of Gaussian orbitals. Details of the choice of clusters, basis sets, and pseudopotentials used are given in Sec. II. While the SCF calculations could be performed by standard quantum-chemistry (QC) programs, the subsequent correlation calculations were performed within the local ansatz.[11] This approach compares with standard QC correlation schemes in quality, but allows a much more efficient treatment of many-body effects as well as a detailed representation of electronic correlations. Its quality and applicability have been demonstrated on many computations for molecules[11,12] and solids.[13-16] Here the ansatz is used in a form generalized by one-particle corrections so that charge distributions may be modified as compared with the SCF computations. This guarantees an optimal charge distribution of the correlated ground state. The correlation scheme is introduced in Sec. III. Section IV contains the results of the different calculations. First, charge distributions and their dependencies on the details of the choice of the clusters are discussed. Next, the strength of the detailed correlations is presented. Finally, a detailed discussion of the spin correlations is given. Section V contains a comparison of all these *ab initio* results to results of LDA computations and of speculative models as well as to experimental findings.

Parts of this work have already been published in a short note.[17]

II. CHOICE OF CLUSTERS, BASIS SETS, AND PSEUDOPOTENTIALS

The actual calculations were performed for almost planar CuO_4, Cu_2O_7, Cu_3O_{10}, and Cu_4O_{13} clusters. They are formally described as linear $(CuO_3)_nO$ chains. The atomic positions were chosen so that they represent a part of the buckled CuO_2 plains in $YBa_2Cu_3O_7$.[18] The largest cluster is schematically drawn in Fig. 1. The charges of clusters were chosen to be $(-2-4n)$. This corresponds to a formal charge of $+2$ for each Cu and of -2 for each O atom, representing the so-called half-filled case for the crystal with one hole per Cu atom. In addition, a few calculations with one less electron were done. The situation with one less electron corresponds to the existence of additional holes in the crystal case. In order to get stable results for these highly negatively charged clusters, the positively charged environment needed to be included explicitly. The surrounding was approximated by point charges on all neighbor atom positions. The values were chosen so that the total cluster was neutral. Figure 2 gives such a typical surrounding for the smallest cluster treated here. The positions of the point charges were chosen according to the crystal structure of $YBa_2Cu_3O_7$.[18] For the smallest cluster [Fig. 2(b)], point charges of $+0.6$ for Y, $+0.4$ for Ba, $+0.25$ for the in-plane Cu, $+0.4$ for out-of-plane Cu, and -0.4 for O were chosen. As is usually done when Madelung sums are computed, we restricted to those part of the charges on the environment atoms which keep the cluster neutral. Therefore, for larger clusters, larger point charges (especially for Y and Ba) were chosen. It was found that the charge distribution between the Cu $3d$ orbitals and the O $2p$ orbitals did not depend sensitively on different point charges, and that nearest-neighbor point charges as the upper O atoms in Fig. 2(b) had no influence on the electronic properties of the cluster. Actually, it turned out that the largest error of this approximate treatment of the out-of-plane environment is connected with the O atoms below the planar Cu positions. Here a few tests were made for the cluster with two Cu atoms. The point charges on these O positions were replaced first by Na pseudopotentials to roughly reproduce the effects of the electrons on them. As value for the core charge on this pseudopotential, the original value of the O point charge was taken. Next, the electrons on these atoms were explicitly included.

Pseudopotentials were chosen that include for Cu the $3s$ and $3p$ states[19] and for O the $1s$ state.[20] A test was made by alternatively using a $2s,2p$ pseudopotential for Cu.[21]

For the valence shell of O, a double-ζ basis set was chosen,[20] while for the $3d$ orbitals of Cu an extended triple-ζ basis set was taken.[21] It turned out that the results depended strongly on a good choice of the $3d$ basis set. The $4s$ and $4p$ states were added in different basis sets. Here severe restrictions needed to be made. In general, an artifact of such a negatively charged cluster computation is that the electrons are pushed to the surface, since the pressure of the outside electrons is missing. With diffuse basis orbitals available, the electrons would populate these, because the upper occupied eigenstates in our computations turned out to be not bound in a SCF approximation. To avoid such an effect, the basis orbitals for the $4s$ and $4p$ orbitals of Cu were restricted to usually only a single contracted orbital each. Part of the computations were done without any of these orbitals. The detailed basis sets are represented in Table I. The basis dimensions for these calculations were large. For the biggest cluster they amounted to 155, thus requiring the extensive use of pseudopotentials as they have been introduced above.

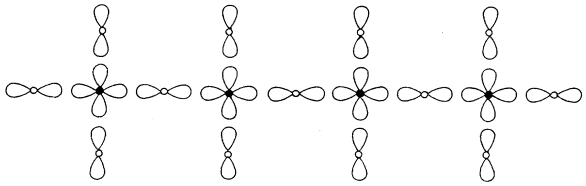

FIG. 1. Schematic representation of the largest cluster (Cu_4O_{13}) for which computations were done. Solid circles represent Cu atoms, while open circles represent O atoms.

III. TREATMENT OF CORRELATIONS BY THE LOCAL ANSATZ

The SCF calculations for the clusters as defined above were performed with the Karlsruhe version of the Columbus program package.[22] The correlation calculations were performed with the local ansatz.[11] Here the following variational ansatz is made for the correlated ground state $|\Psi_c\rangle$:

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

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

$$O_\nu = \left\{ \begin{array}{l} n_{i\uparrow}n_{i\downarrow} \\ n_i n_j \\ \mathbf{s}_i \cdot \mathbf{s}_j \\ n_i \end{array} \right. \ . \tag{3}$$

The $n_{i\sigma}$ and $\mathbf{s}_i$ are density and spin operators for an elec-

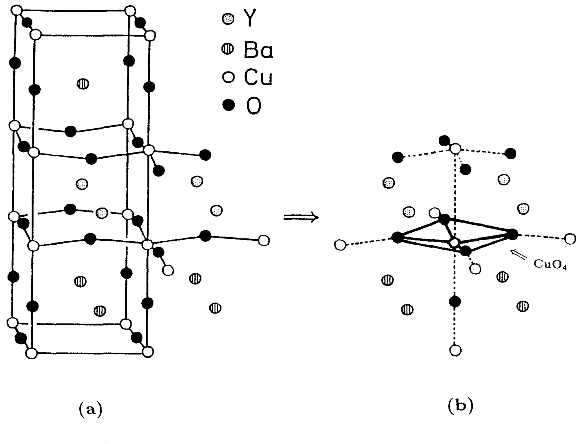

FIG. 2. Schematic drawing of the surrounding of the smallest cluster as treated here in comparison to the experimental structure of Ref. 18. Here open circles represent Cu atoms, while solid circles represent O atoms.

tron in the local state

$$b_{i\sigma}^{\dagger}=\sum_{j}\gamma_{ij}a_{j\sigma}^{\dagger} , \tag{4}$$

where the $a_{i\sigma}^{\dagger}$ represent the basis orbitals. The operators have a transparent meaning. The first operator $n_{i\uparrow}n_{i\downarrow}$, for example, when applied to $|\Psi_{\rm SCF}\rangle$, picks out all configurations with two electrons in the orbital $g_i(\mathbf{r})$. When applied with a variational parameter η_ν, as in Eq. (2), it partially suppresses those configurations. Similarly, the operators $n_i n_j$ 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.[23,24] The operators $\mathbf{s}_i\cdot\mathbf{s}_j$ generate spin correlations. The last operator n_i has been newly added to the computation scheme.[25] It allows one to change the charge distribution explicitly as compared with $|\Psi_{\rm SCF}\rangle$. All operators, when applied to $|\Psi_{\rm SCF}\rangle$, create states which are not orthogonal to $|\Psi_{\rm SCF}\rangle$. Besides, the two-particle operators do include one-particle excitations in addition to the two-particle excitations out of $|\Psi_{\rm SCF}\rangle$. We want to keep only the two-particle excitations for the two-particle operators and the one-particle excitations for the operators n_i. Therefore, we require that contractions within the operators are forbidden when expectation values are computed. The two-particle operators have then the meaning of reducing fluctuations in $|\Psi_{\rm SCF}\rangle$, while the one-particle operators guarantee an adjustment of charge.

TABLE I. Basis sets for Cu and O.

Function type	Exponent	Contraction coefficient	Atomic orbitals
Basis set for Cu atom with Ar-core pseudopotential: $(6s5p6d)/[2s2p3d]$			
s_1	13.738 109 00	0.224 265 40	
	2.208 020 30	−0.732 766 00	
	0.848 466 10	−0.401 078 00	0.1996
s_2	0.920 522 75	−0.097 117 30	
	0.102 556 37	0.561 040 80	
	0.036 490 45	0.519 203 10	1.0000
p_1	5.994 236 00	0.246 450 00	
	2.536 875 00	0.792 024 00	−0.5686
p_2	0.920 522 75	−0.097 117 30	
	0.102 556 37	0.561 040 80	
	0.036 490 45	0.519 203 10	1.0000
d_1	41.225 006 00	0.044 694 00	
	12.343 250 00	0.212 106 00	
	4.201 920 00	0.453 423 00	
	1.379 825 00	0.533 465 00	1.0000
d_2	0.383 450 00	1.000 000 00	0.4159
d_3	0.100 000 00	1.000 000 00	−0.1283
Basis set for O atom with He-core pseudopotential: $(3s7p)/[1s2p]$			
Function type	Exponent	Contraction coefficient	
s_1	6.609 000 0	−0.147 200 00	
	0.921 000 0	0.649 700 00	
	0.285 200 0	0.466 400 00	
p_1	26.967 137 0	0.017 206 40	
	8.333 864 9	0.075 084 60	
	4.766 000 0	0.083 000 00	
	2.981 165 4	0.072 276 20	
	1.128 403 1	0.372 558 30	1.000
p_2	0.421 673 7	0.398 584 20	
	0.150 590 5	0.183 206 00	0.2788

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.,

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

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

Here $\langle A\rangle$ means the expectation value of A within $|\Psi_{\rm SCF}\rangle$. The subscript $\langle\ \rangle_c$ indicates that only connected diagram contributions are added.[24] This approximation works only if the correlations are sufficiently weak. For stronger correlations, it is restricted to cases where the low concentration limit applies; i.e., the occupation of the states $\langle n_{i\sigma}\rangle$ used for the operators is either close to 0 or close to 1. To test whether for the computations performed here the results of this approximation are reasonable, a few computations were repeated within another approximation. In it, $|\Psi_c\rangle$ is approximated by

$$|\Psi_c\rangle\simeq\left[1-\sum_{\nu}\eta_\nu O_\nu\right]|\Psi_{\rm SCF}\rangle , \tag{8}$$

but the expectation value of this variational state is computed exactly. This is a so-called configuration interaction (CI) ansatz. For its energy, it holds that

$$E_{\rm corr}^{\rm CI}=\frac{E_{\rm corr}}{1+\sum_{\nu,\mu}\eta_\nu\eta_\mu\langle O_\nu O_\mu\rangle} . \tag{9}$$

As a variational ansatz, the total energy is always an upper limit to the exact energy. Such an ansatz is exact for a two-electron (or two-hole) problem, but fails for large systems due to its size inconsistency. However, this approximation enables one to compare the results of Eq. (7) with that of Eq. (9) for small clusters under specific constraints and so to get information about the validity of the energy expansion.

So far, everything except the local states [Eq. (4)] is fixed. A first choice within this treatment is to restrict ourselves to so-called interatomic correlations. With this, correlations are meant that arise due to bonding. They are expressed by the above operators when as local states the atomic orbitals are chosen. The atomic orbitals are obtained in the following way. They are deduced from the occupied molecular orbitals by separating these into the individual basis orbital contributions on each atom. An average is then made for each of the atomic orbitals which represent the $2s,2p$ states of O and the $3d,4s,4p$ states of Cu. Finally, these atomic orbitals are orthogonalized. This procedure is made in two steps. First, the $3d$, $2s$, and $2p$ orbitals are Löwdin orthogonalized onto each other. Then the $4s$ and $4p$ states are orthogonalized to them and among each other. This procedure was chosen to have a better comparison for different calculations. Roughly 99% of the total electronic charge is covered by these states so that they are well suited for a charge distribution analysis.

We have done more detailed calculations for these clusters and included shorter-range intra-atomic correlations as well as longer-range polarization or breathing corrections. In both cases, additional local states were generated. With one exception, none of these additions changed sizably any of the results which we will discuss. Therefore, we will restrict ourselves in the following to the results of the interatomic correlation calculations.

When restricted to interatomic correlations, only atomic orbitals play a role. When contributions of the Cu $4s$ and $4p$ states are neglected for the moment, then for the 2-Cu cluster only two electrons are lacking as compared with a complete filling of the $3d$ and $2p$ shells. The correlation treatment within the one-particle space of these atomic orbitals can therefore be seen as a two-hole problem. Thus it is exactly solvable by a CI computation as defined above. From this 2-Cu computation, we gain information about the validity of Eq. (7). The computations for the 3-Cu or 4-Cu clusters cannot be performed exactly anymore because up to four-particle excitation operators would be needed.

IV. RESULTS OF CLUSTER COMPUTATIONS

A. Charge distributions

Of prime interest is the distribution of the electronic charge onto the atomic orbitals. In these clusters, the $2p$ and $3d$ shells are almost completely filled. First, results of calculations will be presented in which no basis orbitals for the Cu $4s$ and $4p$ atomic orbitals were included. Under such conditions, all atomic $3d$ and $2p$ orbitals are completely filled except the $3d_{x^2-y^2}$ orbitals on Cu and the $2p$ orbitals in Cu direction on the O atoms (p_b). As mentioned above, roughly 1% of the total charge is lost when described in terms of the atomic orbitals. Complete filling means, therefore, filling up to 1%. Table II represents the electronic charge distribution within those orbitals which are not completely filled for different cluster sizes and hole occupations in the SCF approximation and with interatomic correlations added. The values for the correlated cases were obtained using the energy expansion. Similarly as the energy, the charge distributions of the correlated ground states were obtained by an expansion

$$\langle \Psi_c | n_{i\sigma} | \Psi_c \rangle = \langle n_{i\sigma} \rangle - 2 \sum_{\nu} \eta_\nu \langle O_\nu n_{i\sigma} \rangle + \sum_{\nu\mu} \eta_\nu \eta_\mu \langle O_\nu n_{i\sigma} O_\mu \rangle_c \, . \tag{10}$$

Here we have averaged over different Cu occupations and over different O occupations within the CuO chain, O_c, and the out-of-chain positions, O_s. As can be seen, the electrons in this strongly negatively charged system prefer to stay on the outer O atoms whose orbitals are almost completely occupied. For the cluster with a single Cu atom, this leads to a Cu $3d_{x^2-y^2}$ occupation close to 1. As soon as inner O positions are available, however, their occupation reduces strongly, leading to an average Cu $3d_{x^2-y^2}$ occupation of roughly 1.66 in the SCF approximation and of 1.57 in the correlated case. The effect of correlations on the charge distribution is apparently small. For an ideal planar $(CuO_2)_n$ system, this implies a $2p_b$ charge on O of -1.66 or -1.72, respectively. Our finite clusters have relatively more O atoms than required in the ideal case. This defect is compensated, however, by the fact that most of the O atoms in the finite clusters are on the outside positions and are therefore strongly negative charged. Indeed, the average charge in the $2p_b$ orbitals of the O_c atoms is close to this ideal limit for the largest cluster, as seen in Table II. The correlation calculations could only be performed for those cases where there was an even number of electrons in the respective cluster (this corresponds to a so-called closed-shell system). Because of the same restriction, no computation of a quadratic cluster with four Cu atoms could be performed. There, a fourfold-degenerate level is occupied with two electrons only.

The small change in charge distributions due to correlations seems surprising at a first glance. In this context,

TABLE II. Average occupations of the $3d_{x^2-y^2}$ atomic orbitals on Cu and the $2p_b$ atomic orbitals on the O atoms within the CuO chain (O_c) and on the outside positions (O_s) for different (Cu_nO_{3n+1}) clusters and different hole numbers n_h in the SCF approximation and with correlations included.

n	n_h	Cu $d_{x^2-y^2}$	O_c p_b	O_s p_b
		SCF		
1	1	1.09	1.95	1.95
1	2	0.88	1.76	1.76
2	2	1.61	1.71	1.86
3	3	1.60	1.68	1.90
3	4	1.53	1.55	1.88
4	4	1.66	1.62	1.83
		Correlated		
1	2	1.0	1.73	1.73
2	2	1.47	1.76	1.88
3	4	1.44	1.59	1.90
4	4	1.57	1.62	1.94

it is important to note that the dominant scale of energy is the total d- and p-band width for the solid or level spacing of the corresponding molecular-orbital energies, respectively. Without contributions due to the nonlocal exchange, this scale is of the order of 10 eV. It must be compared with defects of the Hartree-Fock (HF) approximation. In the HF approximation, too large charge fluctuations occur. An error in the charge distributions arises when these fluctuations cause different costs at different atoms. The difference in the bare atomic Coulomb energies on Cu and O sites is, however, smaller than 5 eV and should not lead to drastically modified charge distributions. It is easy to understand why SCF calculations have a trend to overestimate the population of the Cu $3d$ orbitals. These orbitals are less filled than O $2p$ orbitals. In the SCF approximation, fluctuations appear that rise quadratically with the number of electrons (holes) and are largest for half-filling. Taking charges out of the O $2p$ orbitals and putting them into Cu $3d$ orbitals reduces these artificial fluctuations on the Cu sites more than it increases them on the O sites. The energy gained this way in the SCF approximation causes a small charge redistribution.

Short-range correlations which have not been included in the interatomic correlation calculations should more effectively correlate electrons in d orbitals due to the higher density there and lead to an increase in the d-orbital population. Such trends could be seen when adding intra-atomic operators, but they led to very small corrections only.

For the 2-Cu cluster, a few extended computations were done. First, the O point charges on top of the Cu positions were replaced by Na pseudopotentials. This did not lead to changes of the atomic charge distributions that amounted to more than 1%. Second, the electrons on these atoms were included explicitly. The charge of the resulting cluster was again chosen so that it corresponded to a formal O^{2-} and Cu^{2+} filling. It turned out that all additional electrons populated the added O atoms, leading to a charge of 2^- on each of them. There was a small redistribution of charge in the planar orbitals. The occupation of the atomic $d_{x^2-y^2}$ orbitals reduced by 0.06 in the SCF approximation and by 0.10 with correlations included. Within the SCF computation, this charge went to the outside O atoms. With correlations added, half of the electron loss of the Cu atoms was recovered in the O atoms of the central chain (0.04 on each of them). When assuming that all the other environmental effects may lead to corrections of similar magnitude, then the following charge distribution arises: Cu $3d_{x^2-y^2}^{1.47\pm0.1}$, O $2p_b^{1.77\pm0.05}$. Within a final computation, $4s$ and $4p$ orbitals on the Cu atoms were added. These orbitals are weakly occupied. The $4s$ occupation is 0.2, the $4p$ occupation 0.1. This charge is taken from the so far completely occupied orbitals $3d_{z^2}$ whose occupation reduces to 1.9, further from the O $2p_b$ orbitals whose average charge reduces by 0.03 and with minor contributions from all other orbitals. The $3d_{x^2-y^2}$ occupation is not sizably changed. This leads to a final occupation of Cu $3d^{9.4\pm0.1}\,4s^{0.2}\,4p^{0.1}$ and O $2p_b^{5.65\pm0.1}$. These data are given in Table III in detail.

The partial occupations displayed in Table II contain information where electrons originate from when they are taken out of the half-filled systems. These charge distributions are determined by comparing the SCF results for the clusters with one and three Cu atoms each with different numbers of holes. As can be seen, 20% of the charge removed originate in both cases from the Cu atoms, while 80% come from the O atoms. Correlations do not lead to changes in this ratio. Their influence cannot be computed directly, but is estimated indirectly by comparing the 3-Cu four-hole state with the 4-Cu four-hole state. In both cases, correlations lead to almost exactly the same changes in occupation as compared with the SCF results. From these cluster calculations, it is concluded that electrons when taken from the so-called half-filled system originate dominantly from the O atoms.

B. Correlation strength

Having determined the charge distributions, the next step is to obtain the strength of correlations (Σ). This correlation strength gives the relative reduction of charge fluctuations in the correlated ground state for an atomic orbital i with occupation $\bar{n}_i$. n_i represents the density operator for this state. The fluctuation of occupations can be given easily for two limiting cases. The first is the uncorrelated case. Then it holds for the fluctuations at site i that

$$\langle|(\Delta n_i)^2|\rangle = 2\times\frac{\bar{n}_i}{2}\left[1-\frac{\bar{n}_i}{2}\right], \qquad (11)$$

with $\bar{n}_i=\langle n_i\rangle$. The second is the completely correlated case (Ψ_{cc}). In this case there exist only fluctuations due to variations in charge in between the two integer occu-

TABLE III. Average charge distributions obtained within different basis sets and environments.

	Cu				O
	$3d_{x^2-y^2}$	$3d_{z^2}$	$4s$	$4p$	$2p$
Without $4s$,$4p$ orbitals, without out-of-plane atoms	1.57	2.0	0.0	0.0	5.72
Without $4s$,$4p$ orbitals, with out-of-plane atoms	1.47	2.0	0.0	0.0	5.77
With $4s$,$4p$ orbitals, and with out-of-plane atoms	1.47	1.90	0.2	0.1	5.67

pations encircling $\bar{n}_i$, with $\bar{n}_i = \langle \Psi_{cc}|n_i|\Psi_{cc}\rangle$. When assuming that $\bar{n}_i$ is in between 1 and 2, it then holds that

$$\langle \Psi_{cc}|(\Delta n_i)^2|\Psi_{cc}\rangle = 2(\bar{n}_i - 1)\left[1-\frac{\bar{n}_i}{2}\right] . \quad (12)$$

For the actual correlated states, the charge fluctuation is numerically computed in analogy to the density [Eq. (10)]

$$\langle \Psi_c|(\Delta n_i)^2|\Psi_c\rangle = \langle(\Delta n_i)^2\rangle - 2\sum_{\nu} \eta_\nu \langle O_\nu (\Delta n_i)^2\rangle_c + \sum_{\nu,\mu}\eta_\nu\eta_\mu\langle O_\nu(\Delta n_i)^2 O_\mu\rangle_c , \quad (13)$$

when performing a computation using the variational expansion, or with additional corrections when performing a CI computation. The correlation strength as the relative reduction of the actual fluctuations compared with the limiting cases is then defined as

$$\Sigma = \frac{\langle \Psi_c|(\Delta n_i)^2|\Psi_c\rangle - \langle(\Delta n_i)^2\rangle}{\langle \Psi_{cc}|(\Delta n_i)^2|\Psi_{cc}\rangle - \langle(\Delta n_i)^2\rangle} . \quad (14)$$

The correlation strength defined this way gives a direct measure of the reduction of unfavorable occupations, i.e, for $\bar{n}_i$ in between 1 and 2 the contributions with zero occupation. Be aware that usually the occupation $\bar{n}_i$ is different for a correlated and an uncorrelated ground state. The correlation strength is in this case meaningful only when comparing the fluctuations with those of a fictitious uncorrelated state and a similar completely correlated state with the same occupation as in the correlated state. Table IV gives the correlation strength for the $d_{x^2-y^2}$ and p_b orbitals for different clusters, averaged over different positions within each cluster calculated.

Although the electrons in the partially filled $3d_{x^2-y^2}$-$2p_b$ band are strongly fluctuating, as can be seen from the charge distribution, they are strongly correlated. The probability of finding a Cu d^8 occupation is reduced by typically 85%, and the one to find an O $2p^4$ occupation is reduced by 75% as compared with the uncorrelated case. These values were obtained with an uncertainty of 10%. Because of the specific definition of the correlation strength, the latter depends on the actual occupation. It is weakest when the corresponding orbital is half-filled. A typical example is the cluster with one Cu atom and two holes. From the latter result, it may be concluded that interactions and band energy contributions are of comparable size.

At this point, it seems necessary to explain why we were able to handle the correlation calculations although the electrons are strongly correlated. As explained above, a trial correlation calculation for a 2-Cu cluster omitting 4*s* and 4*p* orbitals and restricted to operators covering $d_{x^2-y^2}$ and p_b states may serve as a test case. Here it turned out that the correlation energy as obtained from Eq. (7) was only 10% larger than the one obtained from Eq. (9). This leads to values for η_ν which are in the average 10% larger, too. The correlation strength from the variational expansion was 25% larger as the exact one from the CI calculation, 10% originating from the larger η_ν, and the remaining part originating from an additional renormalization due to the denominator. The reason for the small deviations is the following. The $d_{x^2-y^2}$ as well as the p_b states each are far from half-filled. For the extreme limit of almost completely filled bands, the variational expansion [Eq. (7)] contains all dominating highest-order terms in the hole concentration, i.e., all relevant contributions to a Kanamori *t*-matrix representation in the subspace of correlation operators included here. For the actual case, the deviations of all orbitals from complete filling is not so large that the correlation calculations may run into problems. A large system with half-filled orbitals and a correlation strength as found for the only case where the Cu $d_{x^2-y^2}$ orbital is half-filled, namely, the 1-Cu two-hole cluster could eventually not be handled anymore by Eq. (7). It should be pointed out that the shortcomings of the variational expansion [Eq. (7)] always lead to an overestimate of the correlation energies and correlation strength.

TABLE IV. Correlation strength Σ for electrons in the $d_{x^2-y^2}$ atomic orbitals on Cu and in the bonding p_b orbitals on O in the chain direction (O_c) or outside positions (O_s) for different (Cu_nO_{3n+1}) clusters and specific hole numbers n_h, when restricted to interatomic correlations.

n	n_h	Cu $d_{x^2-y^2}$	O_c p_b	O_s p_b
1	2	0.50	0.79	0.79
2	2	0.84	0.76	0.97
3	4	0.84±0.08	0.64±0.06	0.88±0.09
4	4	0.88±0.09	0.72±0.07	0.81±0.08

When dealing with the two four-hole cases, it turned out that the energies of the two calculations differed by 25%. It is plausible to assume that as for the 2-Cu cluster, 10% originate from the overestimate of Eq. (7), while 15% originate from the lack of size consistency of the CI calculation, i.e., the lack of four-particle excitations in Eq. (8). The correlation strength within the variational expansion was twice as large as in the CI result. A reasonable estimate for a correction of the variational expansion results is to compute it with η_ν that are reduced by 10% and add a further correction of 20% in analogy to the 2-Cu cluster. These corrections are chosen with an uncertainty of ±10%. While a change of 10% for the η_ν plays no role for the small charge redistribution, and Table II contains the values obtained by variational expansion, for the correlation strength such a more careful handling was necessary. The direct results of a variational expansion gave sometimes values very close to 100% and even larger than that. For these larger clusters, Table IV contains values of the variational expansion [Eq. (7)] but reduced by 30% as discussed before.

Although the electrons are strongly correlated, they cannot be seen as localized spins. Since occupations are far from integer values, the strongly correlated electrons have kept more than half of their band energy. They are still delocalized, and occupations are strongly fluctuating.

This correlation strength turned out to depend somewhat on further details of the correlation calculations. We went beyond a correlation treatment with atomic orbitals only. First, an attempt was made to include intra-atomic correlations for the individual atoms. With intra-atomic correlations, shorter than atomic range correlations can be included so that, for example, two electrons on the same atom can stay away from each other. Because of shortcomings of the double- (triple-) ζ basis, the correlation energy obtained should amount to only 30% of the total intra-atomic correlation energy obtainable in a fictitious complete basis. These corrections should effectively reduce the atomic interactions and should allow for increased fluctuations. The corresponding correlation strength, however, decreased only by in between 1% and 3%.

Next, explicit density correlations between (orthogonalized and alternatively unorthogonalized) $3d$ and $4s$ and $4p$ orbitals on Cu were included. This way screening of $3d$ fluctuations due to $4s$ and $4p$ occupations can be modeled. Such an effect has been proposed for transition metals by Herring[26] and is thought to strongly reduce the effective d-d electronic interactions there. Here it leads to a reduction of the correlation strength of only 5%. Finally, for the Cu atoms, the eventual screening due to polarization of the neighboring O atoms has been investigated. For this purpose, a set of additional polarization functions on the O sites within the planes has been included. This led to sizable corrections of the order of 15%. Additional contributions of similar magnitude are expected from the out-of-plane O atoms. Restriction to atomic correlations, therefore, overestimates the correlation strength by probably 25–30 % for Cu.

C. Spin correlations

Finally, we report on a specific correlation function in terms of atomic orbitals, namely, the spin correlations along the central chain in these clusters. Here we are restricted to the discussion of the two systems with four holes, i.e., the ones with four and three Cu atoms. We are not able yet to correlate the three-hole cases, and the two-hole cases would only give a description of the exchange hole. Actually, we compute the relative spin-correlation functions between atomic orbitals. The diagonal terms are renormalized by the on-site autocorrelation function of a spin in the correlated case:

$$f_{ij}^{(N)}=\frac{\langle\Psi_N|\mathbf{s}_i\cdot\mathbf{s}_j|\Psi_N\rangle}{\langle\Psi_N|(2-n_i)|\Psi_N\rangle\langle\Psi_N|(2-n_j)|\Psi_N\rangle}-\delta_{ij}\frac{\langle\Psi_c|\mathbf{s}_i\cdot\mathbf{s}_j|\Psi_c\rangle}{\langle\Psi_c(2-n_i)|\Psi_c\rangle\langle\Psi_c|(2-n_j)|\Psi_c\rangle}\ . \quad (15)$$

The function $f^{(N)}$ is given for the correlated state ($\Psi_N=\Psi_c$) in Figs. 3 and 4. These spin-correlation functions are first discussed for the 4-Cu cluster in Fig. 3. They are drawn with the one index i fixed to the O sites as well as to the Cu sites. As can be seen, a strong antiferromagnetic correlation pattern develops. It has been discussed above that the on-site correlation is almost perfect. Here there is further evidence of a nearest-neighbor repulsion, leading to nearest-neighbor values slightly reduced from the uncorrelated limit. Strong antiferromagnetic correlations build up to the next-nearest-neighbors, weaker ferromagnetic correlation, and then again antiferromagnetic correlations arise to more distant atomic orbitals. There is no difference in this ordering with respect to O or Cu positions. These findings indicate that the four holes—although very mobile—develop a strong short-range antiferromagnetic order. When switching to the four-hole 3-Cu atom case (Fig. 4), it can be seen that this correlation pattern stays qualitatively the same. However, the length scale of the antiferromagnetic order contracts. Figure 5 contains selected examples of the two earlier figures to facilitate this comparison. Here, the spin-correlation functions for $\psi_N=\psi_{\mathrm{SCF}}$ are added, too. They represent only the autocorrelation functions or exchange holes of the delocalized electrons. This whole correlation pattern can best be understood by a picture of electrons (or holes) delocalized over Cu and O atomic orbitals which show strong short-range (itinerant) order, but are compressible.

The spin correlations caused another problem, however. While on-site correlations as well as density correlations could be computed with an uncertainty of only 10%, this did not hold true for spin correlations any more. The energy gained when spin correlations were included differed by a factor of 2 when computed within the expansion [Eq. (7)] as compared to the CI computation [Eq .(9)]. The strength of the spin correlations can therefore only be given with an uncertainty of 30%, after having corrected the CI results for the well-known finite-

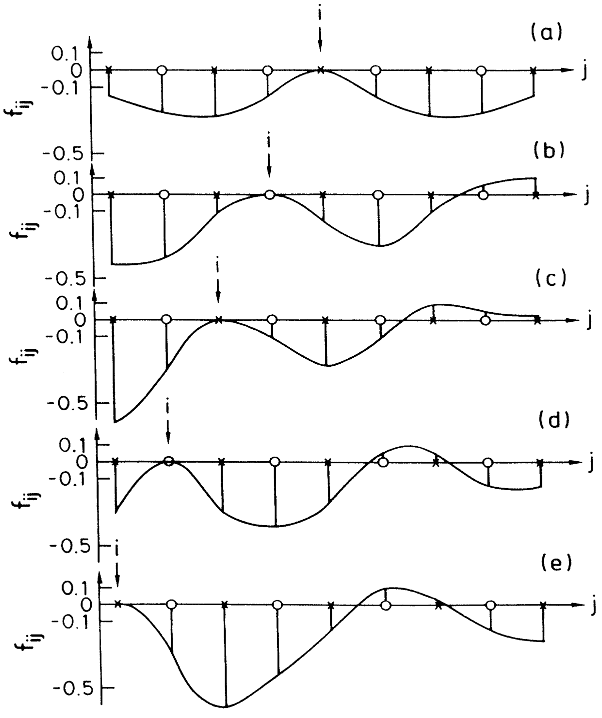

FIG. 3. Spin-correlation functions f_{ij} [Eq. (15)] for the correlated ground state of the 4-Cu cluster, with one index i fixed (a) to the central O atom, (c) to an out-of-center, and (e) to an outer O atom, as well as to (b) inner and (d) outer Cu atoms within the central chain.

size-effect contributions and the variational expansion results for the overestimates known to be present for the other operators. This deficiency can be understood in the following fashion: The spin correlations show strong tendencies for ordering in what corresponds to the upper half-filled band in these clusters, i.e., ordering in the delocalized Wanier orbitals built by an antibonding superposition of Cu $d_{x^2-y^2}$ and O p_b atomic orbitals. We will investigate whether these correlations features can be explained by a model Hamiltonian for these (delocalized) Wanier orbitals which contains as the only interaction a diagonal Hubbard interaction, i.e., by a single-band Hubbard model.

V. COMPARISON WITH EXPERIMENTS AND OTHER COMPUTATIONS

Within Sec. IV, we have collected a set of ground-state data for (CuO) clusters that should be of significance for the high-temperature superconducting materials. None of the ground-state properties obtained for these clusters—charge distributions, correlation strength, and equal-time spin-correlation functions—can at present be measured directly. A few indirect comparisons can be made, however. The first is the experimental magnetic moment, found for these compounds. Neutron scattering indicates that it should be described mostly by Cu 3*d* contributions[27] and that its magnitude is $(0.4-0.6)\mu_B$ within the Cu planes.[28,29] We did not obtain any information about an ordered state because we were restricted to finite-size clusters. These computations show tendencies for strong antiferromagnetic order, however. The maximal moment that can be obtained for each Cu atom with a 3*d* occupation of 9.4 ± 0.1 and a *g* value of 2.2 is $(0.67\pm0.1)\mu_B$ and does not disagree with experiments. Our results do not leave much space for reductions due to spin fluctuations within the strongly anisotropic system, though.

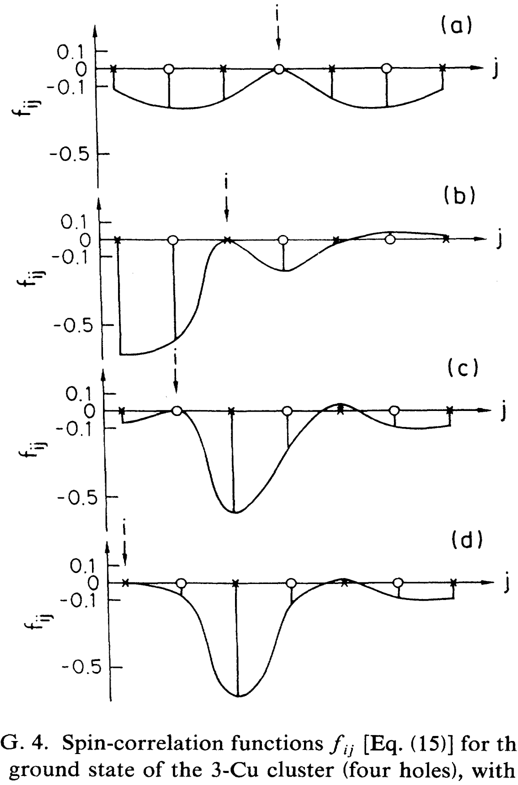

FIG. 4. Spin-correlation functions f_{ij} [Eq. (15)] for the correlated ground state of the 3-Cu cluster (four holes), with one index *i* fixed (a) to the central and (c) to an outer Cu atom and to the (b) inner and (d) outer O atoms within the central chain.

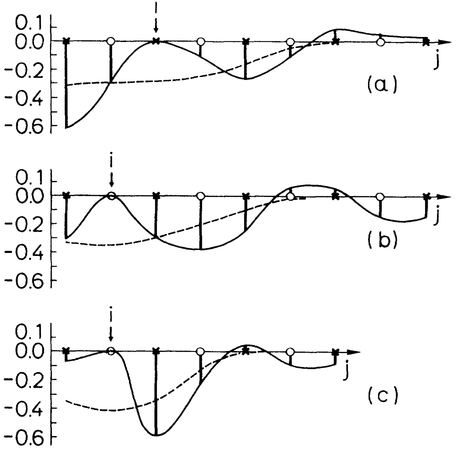

FIG. 5. Spin-correlation functions f_{ij} [Eq. (15)] for the correlated ground state (solid lines) and SCF ground state (dotted lines) (a) and (b) of the 4-Cu cluster and (c) of the 3-Cu cluster. Hereby, for the index *i*, positions (a) on an O atom and (b) and (c) on Cu atoms were selected.

For the extreme limit of two dimensions, i.e., the Heisenberg model, it is known that the moment deduced from the long-range correlation function is reduced to 60% of its maximal value.[30] While it is plausible to assume that this value does not increase for two-dimensional itinerant electrons, the real system is not two dimensional, but has a high transition temperature. A three-dimensional coupling can be modeled by a staggered field in a two-dimensional system. There are indications that already the limiting moment obtained when a small field is added to the two-dimensional Heisenberg model is not equivalent to the moment deduced from the correlation function,[31,32] but increases to 72% of the maximal value.[31] Nothing is known about the moment in a staggered field that amounts to roughly 10% of the planar coupling as needed for the high transition temperature. A reduction of the moment to 80% of its maximal size would not lead to disagreement between our results and experiment. Besides, the large moments measured within the (1-2-3) compounds[29] may partly originate from O positions, too.

As far as spin correlations are concerned, the equal-time spin correlation found here should be obtained from neutron-scattering experiments when integrating over energies up to an energy which corresponds to the bandwidth of the upper half-filled band (i.e., roughly 1 eV). Neutron-scattering experiments have been done, however, only for energies up to 0.02 eV. For a half-filled band system above the magnetic transition temperatures[33] and for non-half-filled systems,[34] inelastic neutron scattering was found that showed relatively sharp structures which differed. While the former case could be connected with large two-dimensional order parameter fluctuations,[33] the latter case could not be explained. There, the structures seen in the momentum dependence of the scattering function $S(\mathbf{q},\omega)$ were shifted with respect to $\mathbf{q}$ in dependence of band filling and did not depend sizably on the energy transfer. One might speculate that if there is no dependence on energy up to energies of the order of 1 eV, these structures might be explained by short-range order of the kind as found here. As has been discussed above, the length scale of this order does in fact depend on the number of holes.

Next, results of other computations shall be discussed. LDA computations led to charge distributions in almost perfect agreement with the values found here.[5] In contrast, the values obtained by constrained LDA computations[6,7] did not agree with our results. Therefore, it is questionable whether constrained LDA offers any improvement as compared with the original LDA results. There has been independent evidence justifying the original LDA results. The first is the close agreement of phonon modes obtained by LDA frozen phonon calculations for these compounds with experiments;[5,35] the second is the agreement with LDA results and experiments for nuclear electric-field gradients.[36] There is further indirect experimental evidence that the Cu $3d_{x^2-y^2}$ occupation as found here is correct. When fitting a model Hamiltonian so that core spectroscopic data are reproduced, this is optimally done for $n_{d_{x^2-y^2}}=1.4$.[37] Photoemission experiments do not give conclusive data about charge distributions. While they can be fitted by values of $n_{d_{x^2-y^2}}=1.1-1.3$,[38] an interpretation using values of $n_{d_{x^2-y^2}}=1.4-1.5$ works too.[39] Inverse photoemission experiments require unoccupied $3d_{x^2-y^2}$ states. These states as well as the relation of unoccupied $3d_{x^2-y^2}$ to $3d_{z^2}$ states as found in experiments[40] come out nicely in the present calculations, too.

Finally, we turn to model Hamiltonians proposed in the literature and discuss whether they offer a valid description of the high-temperature superconductors. Our findings indicate that a three-band Hubbard Hamiltonian can be taken as a good starting point for further approximations. All electronic degrees of freedom which are of relevance are covered by it. The charge analysis of our *ab initio* calculation, however, indicates that the limit which is often chosen for this Hamiltonian does not apply. Usually, it is assumed that the energy difference between a $d^{10}p^5$ configuration and a d^9p^6 configuration is larger than the hopping, leading to a charge close to d^9 for Cu (or actually close to $d^1_{x^2-y^2}$ for the model). Approximate models are therefore often constructed that start from localized Cu spin and delocalized O holes.[3,4] While these models may be extended to values $n_{d_{x^2-y^2}}\sim 1.2$, they fail for charge distributions as found here. Therefore, our results falsify all applications using such models. A typical example is the claim of Aharony *et al.*[41] that there is a short-range frustration of magnetic order between nearest-neighbor positions when electrons are taken out of the half-filled system. As demonstrated above, there is no frustration of short-range order due to a change in occupation for the delocalized electrons.

These conclusions depend on a careful interpretation of the complete spin-correlation functions. If one is restricted to correlation functions between the Cu sites only, then one might obtain the false impression that there is a frustration effect since these correlations decrease when a hole is added.[38] If one further looks at the correlation pattern around a hole when it is on an O site, then the antiferromagnetic correlation to each of the neighbor Cu sites implies at least a tendency for ferromagnetism between them. This should not be interpreted as an indication for frustration either. The most simple counterargument is that these same correlations exist independent of filling in the half-filled case, too. In the delocalized picture, it just means that next-nearest-neighbor holes have ferromagnetic order, and that there is a finite probability to have three holes in direct neighbor positions. Results of three-band Hubbard models that, in fact, are in fair agreement with our results[42] should be interpreted this way.

Partial information about charge distributions and correlation strength have been obtained before from semiempirical computations.[43] Taking into account the uncertainties connected with the choice of model Hamiltonian parameters for such methods, there is a fair agreement with our *ab initio* values. Details of the correlations were in good agreement with our *ab initio* results if the charge distribution was chosen not too different from the one found here.[44,45]

Computations based on semiempirical schemes as well as LDA data were done in order to understand the dependence of magnetism on band filling in these compounds. None of these attempts succeeded. Either the magnetic moment was too small or the domain of stable magnetism as function of band filling was too large.[46] Here our findings offer a solution, too. It is suggestive to argue that a system with strong short-range spin correlations like those found here will freeze very fast into an ordered state with large moment once the Stoner criterion is fulfilled due to nesting conditions. The Stoner parameter $I(\mathbf{k})$ within such a criterion should depend sizably on $\mathbf{k}$ and should be largest for a momentum $\mathbf{k}$ in agreement with the intrinsic short-range order. In none of the computations done so far were short-range spin correlations added. Therefore, no Stoner parameter was used that really depended on $\mathbf{k}$.

To conclude, we have presented detailed information about the electronic structure of high-temperature superconducting compounds. We did not contribute directly to the explanation of high-temperature superconductivity, but eliminated a few speculative models that were built with the specific aim to lead to a new and exotic mechanism for superconductivity. Our results will hopefully improve the detailed understanding of the electronic properties of the novel materials and restrict speculations in the future. They give a good example of how accurately *ab initio* computations can be performed today.

ACKNOWLEDGMENTS

We are indebted to H. Stoll for his help when selecting the appropriate basis sets and pseudopotentials, and thank P. Fulde for his valuable support and K. P. Becker, O. Gunnarsson, P. Horsch, J. Tranquada, and J. Zaanen for stimulating discussions.

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