Electron or hole binding energy in Cu–O clusters: exact diagonalization of the Emery Hamiltonian

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The ground-state energy of two-dimensional Cu–O clusters consisting of 8 and 12 atoms with various occupation numbers is calculated numerically through an exact diagonalization of the Emery Hamiltonian. It is shown, for the first time, that there is an effective attraction not only for holes [J. E. Hirsh *et al.*, Phys. Rev. **B 39**, 243 (1989)] but also for electrons in these clusters, over a wide range of parameter values. The stability with respect to phase separation is analyzed. The occupation numbers are calculated for the copper and oxygen orbitals. The spin-spin and density-density correlation functions are also calculated. The nature of the disruption of the antiferromagnetic order in the case of an electron doping is the same as in the case of a hole doping: The addition of one electron (or hole) to the insulating state causes a far greater disruption of the antiferromagnetic order than is caused by the subsequent addition of a second electron (or hole). The apparent reason for the attraction of two electrons is, as for holes, a decrease in the size of the regions in which the antiferromagnetic order is disrupted (and a corresponding lowering of the energy of the system) in the case in which the excess electrons (or holes) are close to each other.

INTRODUCTION

Bednorz and Müller's discovery of high T_c superconductivity[1] spurred many suggestions regarding the mechanism for superconductivity in the high T_c superconductors. The high T_c values and the small isotope effect[2] have stimulated very active research on various nonphonon pairing mechanisms. The most popular one today is the Emery model,[3] which incorporates strong electron correlations in the high T_c superconductors. Since CuO_2 planes are a common structural element of all known high T_c superconductors, the usual approach has been to consider only the two-dimensional model:

$$H=-t\sum_{\langle ik\rangle,\sigma}(d_{i\sigma}^{+}p_{k\sigma}+\text{H.a.})+\varepsilon\sum_{k,\sigma}n_{k\sigma}+U_d\sum_{i}n_{i\uparrow}n_{i\downarrow}+U_p\sum_{k}n_{k\uparrow}n_{k\downarrow}+V\sum_{\langle ik\rangle,\sigma,\sigma'}n_{i\sigma}n_{k\sigma'},\qquad(1)$$

where the operators $d_{i\sigma}^{+}$ and $p_{k\sigma}^{+}$ create a hole in the states $d_{x^2-y^2}$ and p_x, p_y, respectively; $\langle ik\rangle$ means a summation over nearest neighbors (i specifies copper sites, and k oxygen sites); $n_{i\sigma}=d_{i\sigma}^{+}d_{i\sigma}$; $n_{k\sigma}=p_{k\sigma}^{+}p_{k\sigma}$; t is the copper-oxygen hopping matrix element; $\varepsilon=\varepsilon_p-\varepsilon_d$ is the difference between the energies of a hole at copper and oxygen sites; and U_d, U_p, and V are the Coulomb repulsion energies of the holes at copper sites, oxygen sites, and between the two, respectively. To go over from the hole representation to the electron representation in (1), we should renormalize the parameter ε, leaving the parameters t, U_d, U_p, and V unchanged.

Even in this simplified form (hops to next-nearest sites, direct oxygen-oxygen hops, etc., are ignored), Hamiltonian (1) is exceedingly difficult to analyze theoretically. The primary difficulty stems from the large value $U_d=6$–10 eV$\gg t\approx 1$ eV (Refs. 4 and 5), which rules out dealing with Coulomb correlations by perturbation theory. On the other hand, U_d is not large enough that one can use the various reduced Hamiltonians which can be found from (1) by expanding in the parameter t/U_d (see the discussion of this question in Ref. 6 for the two-dimensional Hubbard model). Furthermore, it is not possible to carry out an expansion in the parameter t/ε (Refs. 7–9), since we have[4,5] $\varepsilon\approx t$. The large scatter in the values which have been reported for the parameter U_p (0.7–5 eV; Refs. 4 and 5) and also for the parameter V (0–4 eV; Refs. 4, 5, and 10) clouds the choice of parameters for Hamiltonian (1) with considerable uncertainty, and this uncertainty can only complicate the problem. The absence of exact solutions of the Emery model and the difficulties which arise in attempts to find reasonable simplifications of it lead to the use of various untestable approximations, which frequently detract from the results. Because of this situation, there has recently been increased interest in numerical simulation of the electronic structure of small clusters of high T_c superconductors; such simulations can provide exact results in several cases.

In this paper we are reporting a study of the ground state of the Emery Hamiltonian in two-dimensional Cu–O clusters for various carrier densities by an exact diagonalization method. It has been found that the binding energy of the excess carriers added to the system during doping is negative over a wide range of the parameter values of the model, regardless of whether these excess carriers are holes or electrons. In the case of a hole doping, a negative binding energy corresponds to an effective attraction of the holes, while in the case of an electron doping it corresponds to an effective attraction of the electrons. We show that Hamiltonian (1) has a sort of electron-hole symmetry: a symmetric disruption of antiferromagnet correlations in the copper sublattice during hole and electron doping. On the basis of results calculated on the spin correlation functions, it is suggested that the reason for the attraction of electrons is, as for holes,[11] a decrease in the size of the region in which the antiferromagnetic order is disrupted (and in which the energy of the sys-

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tem is correspondingly lowered) in the case in which two excess electrons (or two excess holes) are close to each other. In Sec. 1 we briefly describe the exact diagonalization method and specify the Cu–O clusters to which it can be applied. In Sec. 2, the Emery model is used to study the effective attraction of holes, and in Sec. 3 it is used to study the effective attraction of electrons. Effects which stem from the finite number of atoms in the clusters are examined in Sec. 4 for the particular case of the one-dimensional Hubbard model (a comparison is made with the exact analytic solution in the thermodynamic limit). The results are discussed in Sec. 5.

1. FORMULATION OF THE PROBLEM; THE EXACT DIAGONALIZATION METHOD

Numerical studies of the Emery model generally use the Monte Carlo method and the exact diagonalization method. The Monte Carlo method is capable of dealing with comparatively large clusters, of $N_a = 50$–100 atoms,[12] but the accuracy of the calculations falls off sharply with decreasing temperature, with the result that the most interesting case, $T \lesssim T_c \approx 100$ K, cannot be studied. The exact diagonalization method is free of that shortcoming: It can be used to study both the ground state ($T = 0$) and excited states of the system.[11,13–20] The weak point of the exact diagonalization method is the limitation which is imposed on the size of the clusters by the memory size and the speed of existing computers. Nevertheless, one might expect that it would be sufficient to deal with clusters with $N_a \gtrsim 10$ in order to reach a qualitative understanding of the properties of systems with strong correlations and with a coherence length comparable to the interatomic distances. Caution is advised in using the exact diagonalization method, since the results may depend on the particular choice of boundary conditions and on the particular value of N_a.

Figure 1 shows Cu–O clusters whose ground state has been studied in several places[11,15–20] for various values of the parameters of Hamiltonian (1). Of these four clusters, only one, C, with $N_a = 12$, has the symmetry of a CuO_2 plane and is compatible with periodic boundary conditions. The Cu–O cluster which is next in size, which has a square symmetry, contains $N_a = 24$ atoms.[18] The corresponding $M \times M$ Hamiltonian matrix is too large for the use of the exact diagonalization method (even in an undoped state with $N = 8$ holes, we have $M > 10^8$). We accordingly restrict the study to clusters A and C. For cluster C we use periodic boundary conditions, while for cluster A we use free boundary conditions. The latter approach is equivalent to using periodic boundary conditions for a $(CuO)_4$ chain.

The vacuum for Hamiltonian (1) is the electronic configuration[3] $Cu3d^{10}O2p^6$ (Cu^+O^{2-} valence state). In the undoped insulators La_2CuO_4 and $YBa_2Cu_3O_{7-\delta}$ with $\delta > 0.5$, there is one hole per copper atom in the CuO_2 plane (the $Cu3d^9O2p^6$ electronic configuration; the $Cu^{2+}O^{2-}$ valence state). It is thus necessary to choose $\varepsilon > 0$ in (1). Doping (a partial substitution of Sr^{2+} for La^{3+} in La_2CuO_4 and a decrease in the oxygen deficiency in δ in $YBa_2Cu_3O_{7-\delta}$) increases the hole density in the CuO_2 layers (this is hole doping). It has been shown experimentally[21–23] that "new" holes predominantly fill oxygen orbitals ($3d^9L$, $Cu^{2+}O^-$). The reason lies in the large value of U_d, which makes states

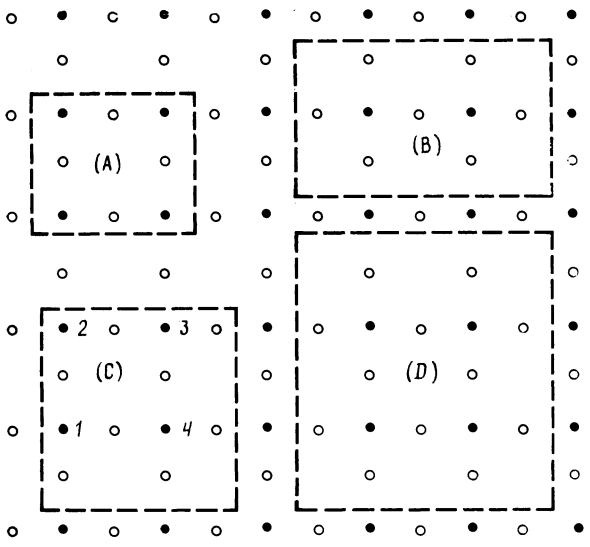

FIG. 1. The clusters used in the exact diagonalization of the Emery Hamiltonian. The numbers of atoms in the clusters are $N_a = 8, 9, 12$, and 16 for A, B, C, and D, respectively. ●—Copper atom; ○—oxygen atom.

with two holes at copper sites unfavorable from the energy standpoint. A different situation arises in the compound Nd_2CuO_4 upon a partial substitution of Ce^{4+} for Nd^{3+} (Refs. 24 and 25) or of F^- for O^{2-} (Ref. 26): The number of holes in copper orbitals decreases, while the oxygen orbitals remain vacant. A decrease in the number of holes is equivalent to an increase in the number of electrons (this is electron doping).

According to the discussion above, the number of holes in undoped Cu–O clusters, N, is equal to the number of copper sites, N_{Cu}. For cluster B (Fig. 1) we have $N_{Cu} = 2$, while for clusters A, C, and D we have $N_{Cu} = 4$. An increase (decrease) in N corresponds to hole (electron) doping of the CuO_2 plane. By studying the ground state of Hamiltonian (1) for various values of N one can trace the changes in the electronic characteristics of the system (the occupation numbers, the correlation functions and so forth) during both hole doping ($N > N_{Cu}$) and electron doping ($N < N_{Cu}$). The interaction of excess holes is characterized by a binding energy (Ref. 11, for example)

$$\Delta_h = E(N_{Cu} + E(N_{Cu} + 2) - 2E(N_{Cu} + 1)\,,$$

where $E(N)$ is the energy of the ground state of a cluster with N holes. The case $\Delta_h < 0$ corresponds to an attraction of two excess holes, while the case $\Delta_h > 0$ corresponds to a repulsion of these holes. Along with Δ_h we consider the electron binding energy

$$\Delta_e = E(N_{Cu} + E(N_{Cu} - 2) - 2E(N_{Cu} - 1);$$

a value $\Delta_e < 0$ corresponds to an attraction, and a value $\Delta_e > 0$ to a repulsion, of two excess electrons. It follows from these definitions that a negative value of Δ_h (Δ_e) corresponds to a situation in which it is favorable from the energy standpoint for the two excess holes (electrons) to be beside each other—within the region bounded by the dimensions of the cluster. In order to distinguish an attraction of holes

TABLE I. The linear dimension M of the Hamiltonian matrix of the Cu–O clusters for various values of N_a (the number of atoms in the cluster), N (the number of holes), and S_z (the projection of the total spin).

N_a	N	S_z	M	N_a	N	S_z	M
8	4	0	784	12	4	0	4 356
8	5	1/2	1568	12	5	1/2	14 520
8	6	0	3136	12	6	0	48 400
9	2	0	81	16	4	0	14 400
9	3	1/2	324	16	5	1/2	67 200
9	4	0	1296	16	6	0	313 600

(electrons) from their condensation in real space, we should verify that the stability condition $d\mu/dN > 0$ holds (μ is the chemical potential). In other words, the addition of a third, fourth, etc., hole (electron) to the same spatial region (cluster) should be disadvantageous in terms of energy. It is thus necessary to test the satisfaction of the conditions

$$\Delta_h' = E(N_{Cu} + E(N_{Cu} + 3) - E(N_{Cu} + 2) - E(N_{Cu} + 1) > 0,$$

$$\Delta_h'' = E(N_{Cu}) + E(N_{Cu} + 4) - 2E(N_{Cu} + 2) > 0,$$

$$\Delta_h''' = E(N_{Cu} + 1) + E(N_{Cu} + 3) - 2E(N_{Cu} + 2) > 0,$$

etc., for holes and the corresponding conditions for electrons:

$$\Delta_e' = E(N_{Cu}) + E(N_{Cu} - 3) - E(N_{Cu} - 22) - E(N_{Cu} - 1) > 0,$$

$$\Delta_e'' = E(N_{Cu}) + E(N_{Cu} - 4) - 2E(N_{Cu} - 2) > 0,$$

$$\Delta_e''' = E(N_{Cu} - 1) + E(N_{Cu} - 3) - 2E(N_{Cu} - 2) > 0,$$

etc. Since the dimensions of our clusters and the permissible number of carriers in them are small, we restrict the study to the conditions actually written out here. Since we have $\Delta''' = \Delta' - \Delta$, under the conditions $\Delta' > 0$ and $\Delta < 0$, we automatically have $\Delta''' > 0$ for both holes and electrons.

We have carried out a systematic study of Δ_h, Δ_h', Δ_h'', Δ_e, Δ_e', and Δ_e'' for $-2 \leqslant \varepsilon \leqslant 4$, $0 \leqslant U_d \leqslant 20$, $0 \leqslant U_p \leqslant 8$, and $0 \leqslant V \leqslant 4$. Here and below, all quantities with the dimensionality of an energy are expressed in units of t ($t = 1$). Our results on Δ_h and Δ_h' agree with results found by other investigators[11,15–19] for various values of ε, U_d, U_p, and V in the specified region of parameter values. To the best of our knowledge, there has been no previous study of electron doping in the Emery model. These are also the first calculations of Δ_h''.

At fixed values of $N = N\uparrow + N\downarrow$ ($N\uparrow$ and $N\downarrow$ are the numbers of holes with spins, respectively, up and down) and of the projection $S_z = (1/2)(N\uparrow - N\downarrow)$ of the total spin, the linear dimension M of the $M \times M$ Hamiltonian matrix which is to be diagonalized is equal to the number of methods by which N holes can be distributed among N_a sites under the restriction of the Pauli principle: $M = C_{N_a}^{N\uparrow} C_{N_a}^{N\downarrow}$. Table I shows M for several values of N_a, N, and S_z (we are interested in the smallest possible values for the given value of N, i.e., $S_z = 0$ for even N or $S_z = 1/2$ for odd N, since these values correspond to a minimum ground-state energy of the Emery Hamiltonian in the clusters under consideration here). With the exception of the nine-site cluster (B) the dimensions of the matrices are such that a complete diagonalization is not possible (it is not possible to find all the eigenvalues and eigenvectors). Incorporating the symmetry under translations and reflections reduces M by a factor of only a few units and thus does not solve the problem. One way out of the difficulty is to make use of the sparse nature of the matrices and to use the Lanczos method,[27] which makes it possible to find the smallest eigenvalue and the corresponding eigenvector (or eigenvectors, in the degenerate case). In our problem, this eigenvalue and this eigenvector correspond to the ground state of Hamiltonian (1).

In the present study we have used an iterative Lanczos algorithm. The dimensionality (m) of the Krylov subspace for the various values of the parameters of the problem and of M was varied over the interval $20 < m < 50$. For the most part, the calculations were carried out for $m = 20$; this value leads to a relative error of 10^{-8} after two to five iterations. Where the convergence was slow (taking ten or more iterations), an increase in m from 20 to 50 made it possible to reduce the overall computation time by a factor of five to ten.

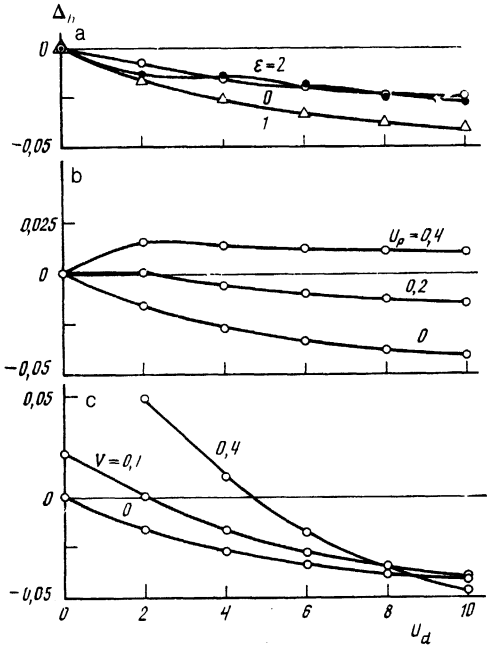

FIG. 2. The hole binding energy Δ_h versus U_d in an 8-site cluster. a—$U_p = V = 0$; b—$\varepsilon = 1$, $V = 0$; c—$\varepsilon = 1$, $U_p = 0$.

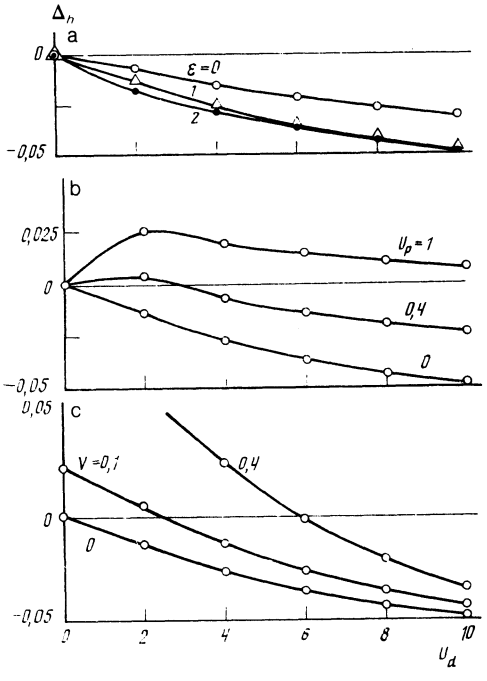

FIG. 3. The same as in Fig. 2, for a 12-site cluster.

2. EXCESS HOLES IN THE EMERY MODEL

Figures 2 and 3 show the hole binding energy Δ_h versus U_d in clusters A and C for various values of ε, U_p, and V. This binding energy is negative, $\Delta_h < 0$, in the case $U_p = V = 0$ with $\varepsilon \lesssim 3$; the absolute value $|\Delta_h|$ increases monotonically with increasing U_d (and then becomes constant at $U_d \gtrsim 20$). At a fixed value of U_d, it goes through a maximum at $\varepsilon \approx 1$–2. A further increase in ε changes the sign of Δ_h at $\varepsilon \approx 3$–4. In clusters A and C, Δ_h becomes positive at $U_p \approx 0.3$ and 0.8, respectively. The apparent reason for the increased sensitivity of Δ_h to U_p in the eight-site cluster is the higher population of the oxygen orbitals in that case.

At $U_d \gtrsim 2$, an increase in V leads to large negative values of the binding energy, and it also results in an instability: $\Delta_h' < 0$ and/or $\Delta_h'' < 0$. Figure 4 illustrates how all three possible states of the system are realized in succession as V increases: a repulsion ($\Delta_h > 0$) an attraction ($\Delta_h < 0$, $\Delta_h' > 0$ and $\Delta_h'' > 0$), and an instability ($\Delta_h < 0$, $\Delta_h' < 0$ or $\Delta_h'' < 0$). The phase diagram in Fig. 5 shows the regions of the various states for $\varepsilon = 1$, $U_p = 0$, $0 \leqslant U_d \leqslant 10$, and $0 \leqslant V \leqslant 4$. The parameter values were deliberately chosen to be the same as in Ref. 11, where the single condition $\Delta_h' > 0$ was used as a stability condition. We see that incorporating the condition $\Delta_h'' > 0$ does no more than cause a very slight contraction of the stability region. The same result (a nearly simultaneous change in the signs of Δ_h' and Δ_h'') was found at other values of ε and U_p.

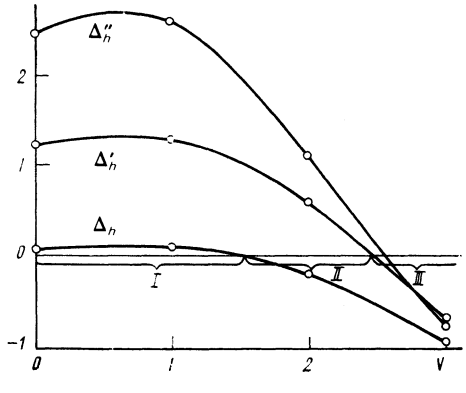

FIG. 4. Δ_h, Δ_h', and Δ_h'' versus V in an 8-site cluster with $\varepsilon = 1$, $U_d = 8$, and $U_p = 1$. Region I—Repulsion; II—attraction; III—instability.

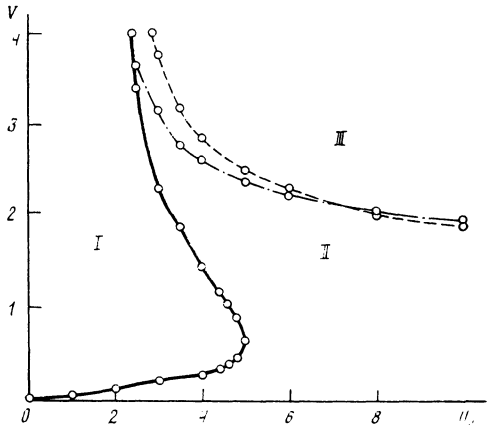

FIG. 5. Phase diagram of an 8-site cluster ($\varepsilon = 1$, $U_p = 0$). Contour lines of (solid line) $\Delta_h = 0$, (dashed line) $\Delta_h' = 0$, and (dot-dashed line) $\Delta_h'' = 0$. Region I—Repulsion; II—attraction; III—instability.

3. EXCESS ELECTRONS IN THE EMERY MODEL

Certain mechanisms which have recently been proposed for the superconductivity of the high T_c superconductors lean heavily on the assumption that the pairing is of a hole nature (see, for example, Ref. 28). On the other hand, we know of high T_c superconductors ($Nd_{2-x}Ce_xCuO_4$, etc., with $T_c \approx 25$ K) in which the carriers are electrons rather than holes.[24,25] It is thus tempting to attempt to explain the "hole" and "electron" versions of high T_c superconductivity in a common model. Our numerical calculations of the electron binding energy Δ_e in Cu–O clusters show that it is possible to find an attraction of not only holes ($\Delta_h < 0$) but also electrons ($\Delta_e < 0$) at the same parameter values in Hamiltonian (1).

Figures 6 and 7 show Δ_e versus U_d in clusters A and C for various values of ε, U_p, and V. The binding energy is negative, $\Delta_e < 0$, at $U_p = V = 0$ with $\varepsilon \lesssim 2$. In contrast with the case of a hole doping, $|\Delta_e|$ does not increase monotonically with increasing U_d. It instead goes through a maximum at $U_d = 4$–10, depending on the ε. For electrons, the optimum values $\varepsilon = 0$–1 are slightly smaller than those for holes. The change in the sign of Δ_e occurs at $U_p \approx 0.2$ and 0.4 in clusters A and C, respectively. The value of Δ_e is very sensitive to the parameter V (Figs. 6c and 7c). We find $\Delta_e > 0$ at large V, in contrast with Δ_h. Interestingly, the state corresponding to an attraction of electrons is always stable: $\Delta_e' >$ and $\Delta_e'' > 0$. We thus see that only two situations arise during electron doping: a repulsion ($\Delta_e > 0$) and an attrac-

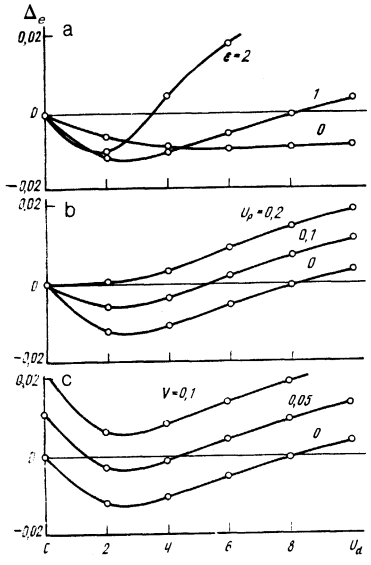

FIG. 6. The electron binding energy Δ_e versus U_d in an 8-site cluster. a—$U_p = V = 0$; b—$\varepsilon = 1$, $V = 0$; c—$\varepsilon = 1$, $U_p = 0$.

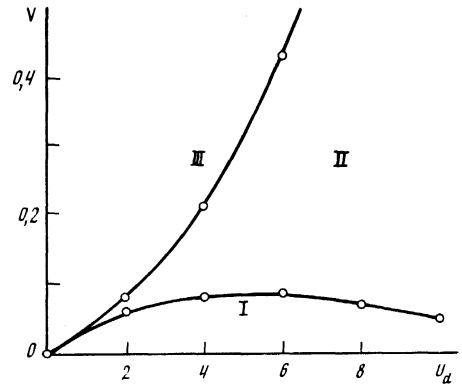

FIG. 8. Phase diagram of a 12-site cluster ($\varepsilon = 1$, $U_p = 0$). I—$\Delta_h < 0$, $\Delta_e < 0$; II—$\Delta_h < 0$, $\Delta_e > 0$; III—$\Delta_h > 0$, $\Delta_e > 0$.

tion ($\Delta_e < 0$, $\Delta_e' > 0$ and $\Delta_e'' > 0$). Figure 8 shows a phase diagram for electrons in comparison with that for holes. We see that the region of attraction for the electrons is smaller than that for the holes.

4. ONE-DIMENSIONAL HUBBARD MODEL; COMPARISON WITH EXACT SOLUTION

A crucial question is how the cluster size affects the results of the numerical analysis. We would like to compare the cluster calculations with analytic results in the limit $N_a \to \infty$ in the example of some model which is amenable to exact solution in the thermodynamic limit. One such model is the one-dimensional, one-band Hubbard model with hopping only to nearest sites.[29] The corresponding Hamiltonian is

$$H = -t \sum_{\langle ik \rangle, \sigma} (C_{i\sigma}^{+} C_{k\sigma} + \text{H.a.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}, \qquad (2)$$

where $C_{i\sigma}^{+}$ ($C_{i\sigma}$) is assumed for definiteness to be the electron creation (annihilation) operator.

We are interested in the energy $E(N)$ of the ground state of Hamiltonian (2) for the case of a half-filled band or an approximately half-filled band, with $N = N_a$, $N_a - 1$, and $N_a - 2$ electrons in a chain. Since the ground state of Hamiltonian (2) is antiferromagnetic with $S_z = 0$, we consider chains with even numbers of sites: $N_a = 4$, 6, 8, and 10, with $S_z = 0$ for even N or $S_z = 1/2$ for odd N. The maximum linear dimension of the $M \times M$ Hamiltonian matrix is $M = 63\,504$, for $N_a = 10$, $N = 10$, and $S_z = 0$. In all cases, periodic boundary conditions were used. The energy is expressed in units of t ($t = 1$). Figure 9 shows the binding energy

$$\Delta = E(N_a) + E(N_a - 2) - 2E(N_a - 1)$$

versus U for $0 \leqslant U \leqslant 100$. Using the expression derived in Ref. 30 for the energy of the ground state of a Hubbard chain with $N_a - L$ electrons, we find $\Delta = 0$ for all U in the limit $N_a \to \infty$. Consequently, Δ vanishes in the thermodynamic limit, despite the circumstance that we have $\Delta < 0$ for $0 < U \lesssim 10$ in chains with $N_a = 4$ and 8 (Fig. 9). For $0 < U \lesssim 20$, the function $\Delta(N_a)$ is oscillatory. These oscillations show that Δ is highly sensitive to the size of the cluster.

At $U \gtrsim 40$, this oscillatory dependence of the electronic characteristics gives way to a monotonic dependence. Figure 10 shows Δ as a function of N_a for $U = 100$. We see that an extrapolation of the binding energies calculated for $N_a \leqslant 10$ to $N_a \to \infty$ leads to zero, in agreement with the exact solution. For $U = \infty$, the problem can be solved exactly for any N_a: $\Delta = 8 \sin^2(\pi/2N_a)$.

In the one-dimensional Hubbard model, there are thus two types of $\Delta(N_a)$ dependence, for various values of U: an oscillatory dependence and a monotonic dependence. In each case we have $\Delta = 0$ in the thermodynamic limit. Consequently, in cluster calculations of Δ_h and Δ_e in the Emery model one must ensure that there are no oscillations or a

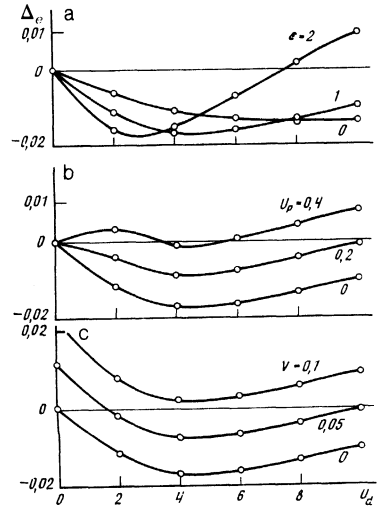

FIG. 7. The same as in Fig. 6, for a 12-site cluster.

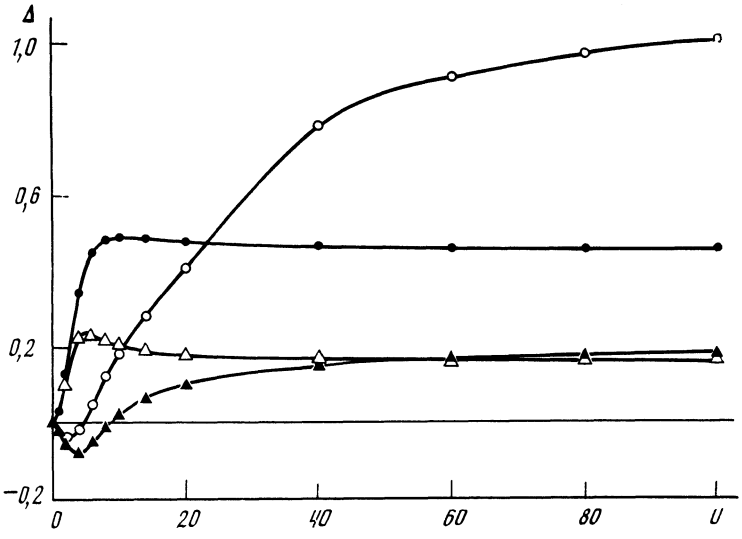

FIG. 9. The one-dimensional Hubbard model: the $\Delta(U)$ dependence for (○) $N_a = 4$, (●) 6, (▲) 8, (△) 10 and $N_a \to \infty$ ($\Delta \equiv 0$).

monotonic tendency of Δ_h and Δ_e toward zero with increasing N_a.

5. DISCUSSION OF RESULTS

It follows from our calculations that in the attraction region the absolute values of the binding energies Δ_h and Δ_e increase as we go from the 8-site cluster to the 12-site cluster. It is difficult to pursue the study of $\Delta_h(N_a)$ and $\Delta_e(N_a)$ further, since cluster C is the largest cluster with square symmetry which can be treated by the exact diagonalization method. Nevertheless, we can cite some reasons why Δ_h and Δ_e should not vanish in the thermodynamic limit. For example, by transforming Hamiltonian (1) through an expansion in the small parameters t/U_d, t/ε, and $t/(U_d - \varepsilon)$, Ogata and Shiba[18] were able to reduce the size of the Hilbert space of states (the occupation of the copper orbitals was fixed) and to calculate Δ_h in clusters with $N_a = 12$, 24, and 30 for the case $U_p = V = 0$. They demonstrated that there are no oscillations of Δ_h with increasing N_a for those values of U_d and ε for which the relation $\Delta_h(N_a = 12) < 0$ holds: $\Delta_h(N_a) \approx \text{const} < 0$. In addition, an increase in N_a leads to an expansion of the region of parameter values with $\Delta_h < 0$ (see Fig. 8 in Ref. 18). It is our belief that, again in the case of the (more realistic) values $\varepsilon \approx 1$ and $U_d \lesssim 10$ of the present study, taking the limit $N_a \to \infty$ would not substantially alter the results found for the 8- and 12-site clusters.

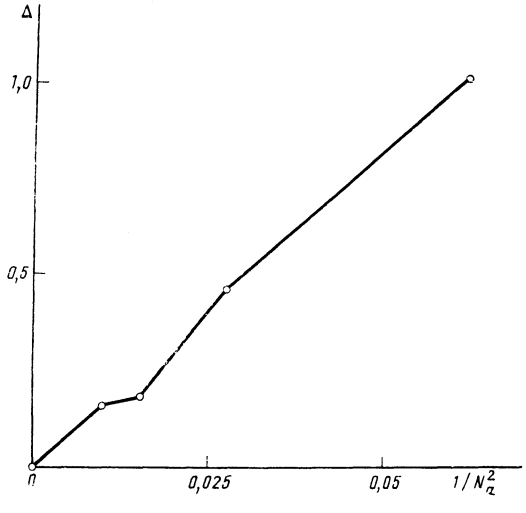

FIG. 10. The one-dimensional Hubbard model: dependence of Δ on $1/N_a^2$ for $U = 100$.

That bound hole states could form in an infinite Cu-O plane in the Emery model was pointed out in Ref. 31—for an insulating ground state of the resonant-valence-bond type (through a construction of wave functions for the plane from the wave functions for clusters of type C)—and Ref. 32—for an antiferromagnetic ground state (by a variation method).

On the phase diagram (Fig. 5; see also Figs. 13 and 14 in Ref. 11) we can distinguish two regions of a stable attraction of holes: at $V \approx 0$ ($|\Delta_h| = 0.01$–0.1) and at $1 \lesssim V \lesssim 3$ ($|\Delta_h| = 0.1$–1). For $U_d \gtrsim 6$, there is no clearly defined boundary between these regions, but it is still reasonable to suggest that the mechanism responsible for the negative values of Δ_h is different at small and large values of V. This conclusion is also implied by the different values of $|\Delta_h|$ and by the proximity of the instability at $V = 2$–3. It can be seen from Fig. 8 that in one of these regions ($V \approx 0$) the electron binding energy Δ_e is also negative. We thus reach the conclusion that there is a large region of parameter values for Hamiltonian (1) in which there is an effective attraction of both excess holes ($\Delta_h > 0$) and excess electrons ($\Delta_e < 0$): $\varepsilon = 0$–2, $U_d = 0$–10, $U_p = 0$–0.5, $V \approx 0$ (we recall that we have adopted $t \approx 1$ eV as the unit of energy). These parameter values correspond to values found in experiments on photoemission[10] and values calculated from first principles[4,5] for high T_c superconductors. Interestingly, the values of $|\Delta_h|$ and $|\Delta_e|$ are $(1$–$5) \cdot 10^{-2} t = 100$–500 K (for $t \approx 1$ eV), in agreement with experimental values of the gap in the high T_c superconductors. In addition, we have $|\Delta_h|/|\Delta_e| = 2$–$4$, in accordance with the higher value of T_C of the hole high T_c superconductors.

Barabanov *et al.*[32] have studied the instability question analytically in the limit U_d, $U_p \to \infty$ and $t \ll \varepsilon$. They showed that a condition for the existence of a bound state of two holes is $V \geqslant V_1 = \varepsilon/3$ and that an instability with respect to

TABLE II. Occupation numbers $\langle n_{Cu}\rangle$ and $\langle n_O\rangle$ and copper-copper correlation functions m_{ij} and ρ_{ij} in cluster C with $\varepsilon = 1$, $U_d = 8$, and $U_p = V = 0$ (the numbering of the sites is shown in Fig. 1; N is the total number of holes in the cluster).

	N				
	2	3	4	5	6
$\langle n_M\rangle$	0,286	0,427	0,567	0,606	0,648
$\langle n_R\rangle$	0,107	0,161	0,216	0,322	0,426
m_{12}	−0,047	−0,062	−0,192	−0,067	−0,052
m_{13}	−0,065	−0,016	0,081	0,003	−0,044
ρ_{12}	0,047	0,153	0,313	0,360	0,414
ρ_{13}	0,065	0,168	0,318	0,363	0,416

the formation of large clusters of holes arises at $V \geqslant V_2 = \varepsilon/2$. With $U_p \neq 0$, our results agree qualitatively with the conclusions of Barabanov *et al.* For example, with $\varepsilon = 1$, $U_d = 8$, and $U_p = 1$ we have $V_1 \approx 1.5$ and $V_2 \approx 2.5$ for cluster A (Fig. 4). On the other hand, we find $V_1 = 0$ at $U_p = 0$ (a decrease in V_1 with decreasing U_p was pointed out in Ref. 33).

Table II shows the results calculated on the occupation numbers of the copper and oxygen orbitals, $\langle n_{Cu}\rangle$ and $\langle n_O\rangle$, and also on the correlation functions (between copper sites)—the spin-spin correlation functions $m_{ij} = 4\langle S_{zi}S_{zj}\rangle$ and the density-density correlation functions $\rho_{ij} = \langle n_i n_j\rangle$—for various numbers of holes, $N = 2$–6, in a 12-site cluster with $\varepsilon = 1$, $U_d = 8$, and $U_p = V = 0$ ($\Delta_h = -0.044$, $\Delta_c = -0.013$). We see that either a hole doping ($N > 4$) or an electron doping ($N < 4$) disrupts the antiferromagnetic order in the copper sublattice. It was pointed out in Ref. 11 that the addition of the first excess hole to a cluster leads to a far greater disruption of the antiferromagnetic order than is caused by the subsequent addition of a second hole. It follows from our data (Table II) that the same picture prevails in the case of electron doping. The reason for the attraction of the two electrons appears to be (as in the case of an attraction of holes) that the dimensions of the region in which the antiferromagnetic order is disrupted are smaller for two electrons (or holes) which are adjacent to each other than for electrons (or holes) which are far apart.

It can be seen from Table II that there is a sort of electron-hole symmetry in the Emery model: a symmetric disruption of the antiferromagnetic order for both electron doping and hole doping. The dimensions of the clusters amenable to exact diagonalization are too small for a more detailed study of the effect of the density of holes (or electrons) on the antiferromagnetic order, since the values $N = 5$ and 6 ($N = 3$ and 2) correspond to $x = 0.25$ and 0.5 in $La_{2-x}Sr_xCuO_4$ ($Nd_{2-x}Ce_xCuO_4$). Experimentally, a comparative study of electron and hole high T_c superconductors has indeed demonstrated that there is an approximate symmetry in the x dependence of their transport and optical properties.[34,35]

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