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# Hole pairing within an extended Anderson impurity model applicable to the high-$T_c$ cuprates

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We calculate the binding energy of a hole pair within the extended Anderson Hamiltonian for the high-$T_c$ cuprates including a Cu impurity and an oxygen-derived band. The results indicate that stable hole pairs can be formed for intra-atomic and interatomic Coulomb repulsion strengths larger than 6 and 3.5 eV, respectively. It is also shown that the total hybridization strength between the Cu $3d$ and oxygen $p$ band should be less than 2.5 eV. The hole pairing takes place primarily within the oxygen-derived $p$ band. The range of parameter values for which hole pairing occurs is also consistent with the earlier photoemission results from these cuprates.

Ever since the discovery of high-temperature superconductivity in copper-oxygen-based systems, there have been several theoretical attempts to explain the phenomenon in these compounds. At this stage it seems apparent that the electron-phonon mechanism operative in the more conventional superconductors cannot explain the unusually high transition temperatures observed in these systems. This is supported by the near absence of isotope effects in these compounds.[1,2] Therefore, search for a suitable theory of high-$T_c$ superconductivity based on electron-electron interactions alone has assumed great importance. Various theories have been proposed involving only the large intra-atomic Coulomb repulsion $U_{dd}$ between the copper $3d$ electrons.[3-5] However, numerical calculations involving exact diagonalization and Monte Carlo methods indicate that $U_{dd}$ alone is not sufficient to give rise to the formation of Cooper pairs.[6] It was pointed out in another work[7] that besides the on-site interaction, interatomic interaction $U_{dp}$ between one electron at the Cu site and the other at the O site may play an important role in the high-temperature superconductivity of these compounds. In this context it has been suggested[8] that nearest-neighbor electron-electron interactions alone in a nearly quarter-filled band can lead to pairing. This claim has been substantiated by calculations on finite-size systems.[9] Using an extended Hubbard Hamiltonian for small clusters, Hirsch *et al.*[10] have recently shown that pairing of holes indeed takes place within a two-dimensional $CuO_2$ layer, provided both $U_{dd}$ and $U_{dp}$ are sizable. Besides these large $U$'s, these authors also obtain the charge transfer excitation energy ($\varepsilon_d$-$\varepsilon_p$) to be nearly zero as a precondition for pairing of holes. It has been pointed out[10] that if this mechanism is true, the hole occupancy at the Cu site should decrease (instead of increasing) with an increase in the level of doping of the system.

From our photoemission experiments[11,12] combined with calculations within the Anderson impurity Hamiltonian,[12,13] we have found indications of increasing $Cu^{1+}$ formation concomitant with evidence for increasing proportions of holes in these systems upon lowering the temperature. Encouraged by this evidence, we have further calculated the core-level photoemission spectra of these compounds based on an extended Anderson impurity Hamiltonian, where we have included the intersite interaction term.[14] The results obtained from these calculations show that the various parameter strengths, namely $U_{dd}$ and $U_{dp}$, that are compatible with the core-level spectra are very similar to those obtained by Hirsch *et al.*[10] and consistent with the condition of hole pairing. Furthermore, the analysis of core-level spectra of $La_{2-x}Sr_xCuO_4$ (Ref. 15) by the extended Anderson Hamiltonian[14] indicates that the Cu site hole occupancy indeed decreases with increasing $x$ in conformity with the prediction of Hirsch *et al.*[10] While such similarities in conclusions concerning parameter strengths based on very different considerations are indeed encouraging, the calculations performed by Hirsch *et al.*[10] were based only on a small cluster formed from two Cu and seven O atoms. Moreover, even at the cluster level, the oxygen-oxygen direct interactions were not taken into account, besides neglecting the band effects. In our calculation within the Anderson impurity Hamiltonian,[14] the oxygen $p$ band is included via a tight-binding calculation of the oxygen sublattice. On the other hand, the use of Cu as a single impurity (Ref. 14) implies that we are considering a nearly filled band. This is not a serious limitation since all experiments point towards local pairing of holes in these systems. Thus, the main difference between our approach and that of Hirsch *et al.* is that we consider a single Cu impurity in an oxygen band[14] while Hirsch *et al.* use approximately the right number of Cu atoms per oxygen atom without any oxygen-oxygen interaction.[10] It should, however, be noted that Hirsch *et al.*[10] claim that the effect of oxygen-oxygen interaction as well as that of larger cluster size, in general, make the conditions for pairing less stringent.

Since we have obtained a very satisfactory description of the core-level photoemission spectra and have also arrived at interesting conclusions concerning the electronic structure of these compounds with the extended Anderson impurity model,[14] we have carried out an investigation of the possibilities of hole pairing within this model. Our calculations show that the ranges of parameter values that do indeed lead to hole pairing are compatible with those obtained from the spectroscopic data.[14]

The method of calculation closely follows that of Ref. 14, using the oxygen unit cell shown in Fig. 1. Here, we give only a brief description of the model. The extended Anderson impurity Hamiltonian is given by

$$H=\sum_{i,\mathbf{k},\sigma}\varepsilon_{\mathbf{k}}^{i}n_{i\mathbf{k}\sigma}+\sum_{\sigma}\varepsilon_d n_{d\sigma}+\sum_{i,\mathbf{k},\sigma}(\mathrm{V}_{d\mathbf{k}}^{i}\,\mathrm{a}_{d\sigma}^{\dagger}\,\mathrm{a}_{i\mathbf{k}\sigma}+\mathrm{H.c.})+U_{dd}n_{d\uparrow}n_{d\downarrow}+U_{dp}n_dn_p$$

with the usual notation. Including the $p_x$ and $p_y$ orbitals at the oxygen sites in the square sublattice, we obtain the two energy bands $\varepsilon_{\mathbf{k}}^{1}$ and $\varepsilon_{\mathbf{k}}^{2}$ in terms of $V_\sigma$ and $V_\pi$. The hybridization matrix elements $V_{d\mathbf{k}}^{i}$ are given by the matrix element $\langle d_{x^2-y^2}|H|\psi^i(\mathbf{r},\mathbf{k})\rangle$, where $\psi^i(\mathbf{r},\mathbf{k})$ are the band eigenstates. Thus, we obtain

$$\mathrm{Re}[V_{d\mathbf{k}}^{1}]=(\sqrt{3}/2\sqrt{2})V_{pd\sigma}[-1-\cos k_a+\cos k_b+\cos(k_a+k_b)]\,,$$

$$\mathrm{Re}[V_{d\mathbf{k}}^{2}]=(\sqrt{3}/2\sqrt{2})V_{pd\sigma}[-1+\cos k_a-\cos k_b+\cos(k_a+k_b)]\,.$$

To avoid working with the two-band and two-continuum ($k_a$ and $k_b$) indices we make the usual transformation[16]

$$|V(\varepsilon)|^2=\sum_{i,\mathbf{k}}|V_{d\mathbf{k}}^{i}|^2\delta(\varepsilon-\varepsilon_{\mathbf{k}}^{i})\,,$$

and rewrite the Hamiltonian as

$$H=\sum_{i,\sigma}\varepsilon_{i\sigma}n_{i\sigma}+\sum_{\sigma}\varepsilon_d n_{d\sigma}+\sum_{i,\sigma}[V(\varepsilon_i)a_{d\sigma}^{\dagger}a_{i\sigma}+\mathrm{H.c.}]$$
$$+U_{dd}n_{d\uparrow}n_{d\downarrow}+U_{dp}n_dn_p\,.$$

Here, we have further replaced the continuum index $\varepsilon$ by a set of $N$ discrete levels $\varepsilon_i$. This procedure with large but finite $N$ ($>6$) is known to give essentially the infinite $N$ results when $|V|^2=\sum_i|V(\varepsilon_i)|^2$ is preserved.[17] We have explicitly checked this point from test calculations using $N=20$, 25, and 30. The results presented here are, however, obtained with $N=20$. Here, we work with the full basis set which corresponds to $\binom{2N+2}{p}$ configurations, where $p$ is the number of holes. The stoichiometric compound in absence of any hole doping corresponds to the existence of one hole within the filled oxygen band and $3d^{10}$ configuration of Cu, with an energy $E(1)$. The energy of one extra hole doping then is given by $E(2)$ and that of two hole doping by $E(3)$. The pairing energy $\Delta$ is given by[10]

$$\Delta=E(1)+E(3)-2E(2)\,.$$

We compute $\Delta$ exactly by direct diagonalization of the Hamiltonian which is represented as a matrix whose dimension is the dimension of the Hilbert space spanned by the Hamiltonian. The largest dimension of 37 820 occurs for $N=30$ and 3 holes.

In what follows, we have used $V_\sigma=1.0$ eV and $V_\pi=-0.2$ eV for direct oxygen-oxygen interaction giving a total $p$-band width of 4.8 eV.[14] To investigate the effect of the intersite electron-electron repulsion term $U_{dp}$ on the pairing energy, we have calculated $\Delta$ as a function of $U_{dp}$ with $U_{dd}=9.5$ eV, $\varepsilon_d=-2.0$ eV, and the total hybridization $V=-2.3$ eV. The result is shown in Fig. 2 from where it is found that the pairing of holes can be stabilized for $U_{dp}>3.5$ eV. The variation of $\Delta$ with $U_{dd}$, using $U_{dp}=4$ eV, $\varepsilon_d=-2.0$ eV, and $V=-2.3$ eV is also shown in Fig. 2. From this figure it is seen that a hole pair is stable for $U_{dd}>6$ eV. Therefore, to understand the dependence of the hole-pairing energy $\Delta$ on $\varepsilon_d$ and $V$, we have used $U_{dd}=9.5$ eV and $U_{dp}=4.0$ eV. With these parameter values, we have calculated $\Delta$ as a function of $\varepsilon_d$ for different values of the hybridization strength $V$; the results are shown in Fig. 3. The plots in Fig. 3 provide the range of $\varepsilon_d$, $V$ values for which a hole pair can be stabilized in these systems; we have shown this phase diagram of pair stability in a $\varepsilon_d$-$V$ plot in Fig. 4. In the same plot

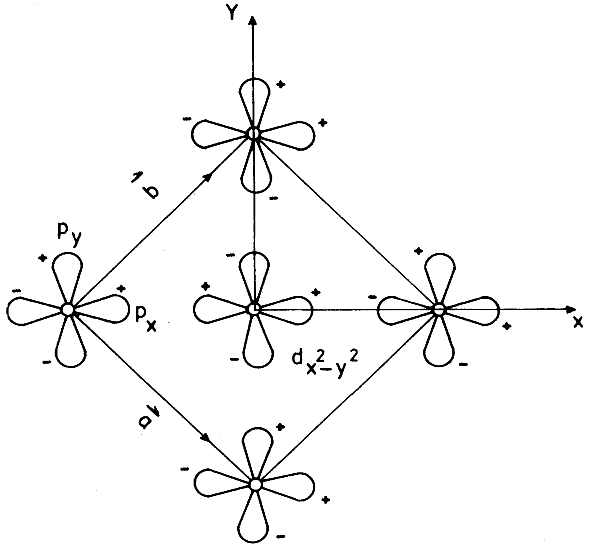

FIG. 1. Schematic representation of the square lattice formed by the oxygens with $p_x$ and $p_y$ orbitals and a copper impurity with $d_{x^2-y^2}$ orbital.

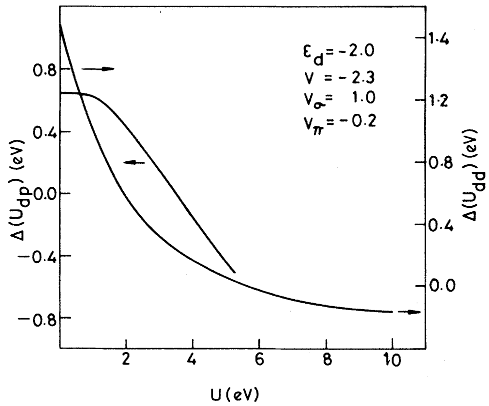

FIG. 2. The binding energy $\Delta$ of a hole pair as a function electron-electron interaction energies, $U_{dp}$ and $U_{dd}$, with other energies as shown in the figure. All values are in eV.

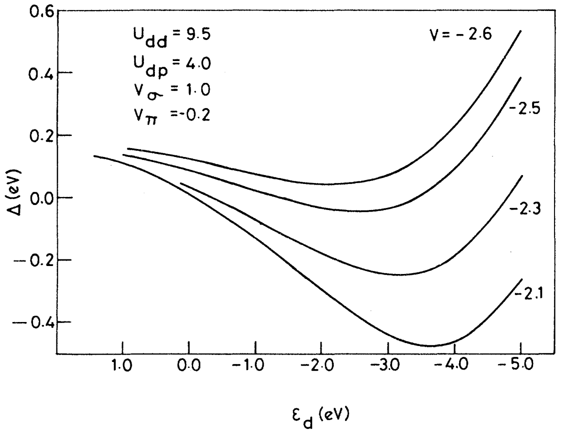

FIG. 3. The binding energy $\Delta$ of a hole pair as a function of $\varepsilon_d$ for various values of the total hybridization strength $V$ and other parameter values as shown in the figure. All values are in eV.

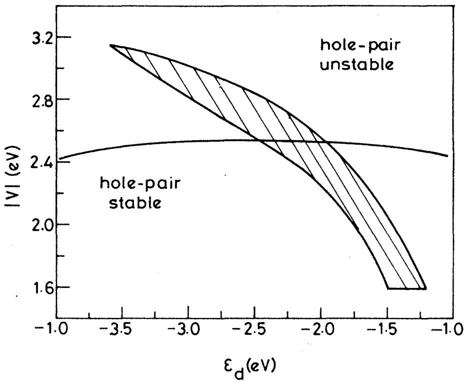

FIG. 4. The solid line divides the $\varepsilon_d$-$V$ space in terms of the stability of the hole pair. The shaded enclosed region is the $\varepsilon_d$-$V$ space that is compatible with the core photoemission spectra from the cuprates (from Ref. 14).

we also show the range of values of $\varepsilon_d$, $V$ that is compatible with the core-level photoemission data for the same Hamiltonian.[14] Comparing these two phase diagrams, we find that pairing occurs when $|V| < 2.5$ eV and $\varepsilon_d > -2.4$ eV. This estimate of upper limit of the hybridization strength is consistent with that estimated from the valence-band photoemission spectra.[18] While the valence-band photoemission spectra also indicate that $\varepsilon_d$ is small,[15,18] the present estimate places it within the oxygen $2p$-derived valence band. It has been shown earlier[14] that while the $3d_{x^2-y^2}$ energy falls within the O $2p$-derived band, the ground state of the stoichiometric compound (e.g., $La_2CuO_4$) corresponds to a mixed-valent insulator due to a localized level that splits off from the band due to strong covalent mixing. Analyzing the ground-state wave functions for the one-hole (stoichiometric compound), two-hole, and three-hole systems, we find that the stability of the hole pairing is provided by the partial removal of the hole occupancy at the Cu site due to the intersite repulsion $U_{dp}$, in accordance with the analysis of Hirsch *et al.*[10] The ground state for the one-hole case has about 9.5 $d$ electrons for typical parameter values ($\varepsilon_d = -2.0$, $V = -2.2$, $U_{dd} = 9.5$, $U_{dp} = 4.0$). Upon doping the system to introduce one more hole, the $d$ occupancy increases to ~9.8 electrons. Thus, the doped hole induces a transition locally to a weakly mixed valent metal with mainly oxygen $2p$ character. The ground state of the three-hole system has approximately ~9.9 $d$ electrons, making the system even more weakly mixed valent.

In conclusion, we have shown within the extended Anderson Hamiltonian that the hole pairing can be stabilized for large values of $U_{dd}$ ($> 6$ eV) and sizable values of $U_{dp}$ ($> 3.5$ eV) in the high-$T_c$ superconducting cuprates. The ranges of $\varepsilon_d$, $V$ values leading to a stable hole pair is also calculated. Comparison of the $\varepsilon_d$ vs $V$ phase diagram for the stability of hole pairs compared with the $\varepsilon_d$ and $V$ values consistent with the experimental photoemission data shows that the Cu $3d$ level is either very close to or within the oxygen $p$ band. It is also shown that the hole pairing takes place primarily within the oxygen $p$ band.

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