

## Excitonic pairing in high-temperature superconductors

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We study the pairing mechanism within  $MO_2$  ( $M=\text{Cu}$  or  $\text{Bi}$ ) planes of high-temperature superconductors by calculating the binding energy and the character of doped holes within perturbation theory around the atomic limit. We extend the study of Nuñez Regueiro and Aligia [Phys. Rev. Lett. **61**, 1889 (1988)], and show that the interoxygen Coulomb repulsion enhances the pairing in the magnetic regime and that small metal-oxygen repulsion suffices to stabilize pairing both in the bipolaronic and biexcitonic regimes.

The discovery of high-temperature superconductivity in copper-based oxides<sup>1</sup> caused renewed interest in the mechanism of superconductivity of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , with  $T_c \sim 13$  K, discovered already in 1975.<sup>2</sup> The recent discovery of  $\text{Ba}_{1-x}\text{M}_x\text{BiO}_3$  ( $M=\text{K}, \text{Rb}$ ),<sup>3</sup> with  $T_c \sim 30$  K suggests that the Bi-based superconducting oxides must be considered within the same class of high-temperature superconducting perovskites. Numerous similarities between copper- and bismuth-based compounds suggest that a common local pairing mechanism may be present in both types of oxides.<sup>4</sup> Perhaps most importantly: (i) both classes have a similar type of lattice ( $\text{CuO}_2$  and  $\text{BiO}_3$ ) in which doping leads to high values of  $T_c$  with a low number of carriers,<sup>4</sup> and (ii) superconductivity occurs in the proximity of metal-insulator transition. On the other hand, there are some differences: Firstly, Cu-based systems are two-dimensional as opposed to the three-dimensional Bi-based superconductors. Secondly, undoped  $\text{CuO}_2$ -based superconductors are antiferromagnetic insulators,<sup>5</sup> while  $\text{BiO}_3$ -based ones are diamagnetic charge order insulators.<sup>6</sup> It is likely that the superconductivity in these systems is related to local pairing at the effective negative- $U$  centers.<sup>4,7</sup>

In this paper we reconsider a common polarization which may lead to local pairing when the oxygen holes are added either to the antiferromagnetic, or to disproportionated semiconducting states, as proposed by Nuñez Regueiro and Aligia,<sup>6</sup> and by Aligia, Nuñez Regueiro, and Gagliano.<sup>8</sup> Their model is a natural extension of the original idea of Varma, Schmitt-Rink, and Abrahams<sup>9</sup> that the intersite Coulomb repulsion may play a very important role in the pairing mechanism in the oxides. It has been argued recently<sup>10</sup> that the same mechanism may apply as well to the electron-doped systems.

The purpose of the present paper is to extend the perturbation expansion up to  $t^2$  of Ref. 6, where  $t$  is the hopping between the metal ( $M$ ), i.e., copper or bismuth, and oxygen ( $O$ ) sites, and to study the excitonic pairing in three physically different regimes of the same model Hamiltonian: antiferromagnetic, biexcitonic, and bipolaronic. The physical difference between these regimes is discussed in more detail below.

For simplicity we shall consider a two-dimensional (2D)

$MO_2$  structure which will be used as a common generic model both for Cu- and Bi-based high-temperature superconductors. Although the bismuthates are three dimensional (3D), the pairing mechanism is the same in 2D and in 3D, provided that an appropriate renormalization of the hopping is made. As in  $\text{CuO}_2$  planes, a square lattice of metal ions contains oxygen ions between each two  $M$  sites. The Hamiltonian which describes the dynamics of holes within this 2D  $MO_2$  structure is written as follows:<sup>6</sup>

$$H = H_0 + H', \quad (1)$$

$$H_0 = \sum_{ij\sigma} \left( \varepsilon_M + A \sum_{\langle l \rangle} S_l (-1)^{i+j} \right) n_{ij\sigma}^M + \sum_{l\sigma} \varepsilon_p n_{l\sigma}^p + u_M \sum_{ij} n_{i\uparrow}^M n_{j\downarrow}^M + u_p \sum_l n_{l\uparrow}^p n_{l\downarrow}^p + G_p \sum_{\langle ll' \rangle \sigma \sigma'} n_{l\sigma}^p n_{l'\sigma'}^p + \sum_{ij\sigma} \sum_{\langle l \rangle \sigma} [G - \frac{1}{2} A S_l (-1)^{i+j}] n_{ij\sigma}^M n_{l\sigma}^p + \sum_l B S_l^2, \quad (2)$$

$$H' = t \sum_{ij} \sum_{\langle l \rangle \sigma} \left( c_{ij\sigma}^{M\dagger} p_{l\sigma} + \text{H.c.} \right), \quad (3)$$

where  $n_{ij\sigma}^M = c_{ij\sigma}^{M\dagger} c_{ij\sigma}^M$  and  $n_{l\sigma}^p = p_{l\sigma}^\dagger p_{l\sigma}$  are hole number operators at  $M$  site  $ij$  of a 2D lattice and  $O$  site  $l$ , respectively.  $\varepsilon_M$  and  $\varepsilon_p$  are the hole energies at metal and oxygen sites, respectively. The latter energy is renormalized by the term proportional to  $A$  in the case of breathing distortion.  $S_l = 0, \pm 1$  describes three positions for the  $O$  ions (responsible for a distortion in Bi-based oxides). On-site Coulomb interaction elements are  $u_M$  and  $u_p$ ; intersite elements are  $G$  and  $G_p$  for the Coulomb repulsion between two holes located at metal and oxygen or two neighbor oxygen sites, with the corresponding summations over  $\langle l \rangle$  and  $\langle ll' \rangle$ , respectively. It is believed that the interoxygen repulsion,  $G_p$ , is small,<sup>11</sup> but it has been argued that this term is important for the stability of particular excited states and may lead to the pairing.<sup>10,12</sup> Here this extra term is included only in the magnetic regime where it plays an important role as shown below. The metal-oxygen repulsion,  $G$ , is modified by the term proportional to the lattice distortion. As we are interested in the strong coupling regime, the hopping

between metal and oxygen sites,  $t$ , will be considered as a perturbation.

It is straightforward to determine the ground state in the atomic limit,  $t = 0$ , for the undoped systems, i.e., for the filling of one hole per unit cell ( $n = 1$ ). Depending on the values of the electronic structure parameters: the charge-transfer energy,  $\Delta = \varepsilon_p - \varepsilon_M$ , the Coulomb interactions, and the coupling constants  $A$  and  $B$ , it is either antiferromagnetic or exhibits charge order which couples to the lattice disproportionation.

We start with the magnetic regime, represented by the simple case of  $\Delta > 0$  and  $u_M, u_p \rightarrow \infty$ , as the properties of the system are little influenced by the value of  $u_p$ .<sup>12,13</sup> Taking into account the realistic values of microscopic parameters for the Cu-based high- $T_c$  oxides, as determined both from band-structure calculations<sup>11</sup> and experiment,<sup>14</sup> this regime corresponds to the antiferromagnetic ground state without doping. Including the new term  $G_p$ , one obtains the following energies of the states represented in Fig. 1 of Ref. 6:

$$\begin{aligned}
 \text{(a)} \quad E_1 &= \varepsilon_p + 2G + t^2 \left[ \frac{12}{\Delta + G} - \frac{2}{\Delta} - \frac{4}{\Delta + G_p} - \frac{4}{\Delta + G + G_p} \right]; \\
 \text{(b)} \quad E_1 &= \varepsilon_p + 6\Delta + 8G_p + t^2 \left[ \frac{34}{\Delta + G} - \frac{8}{G - 2G_p - \Delta} - \frac{8}{\Delta + G_p} - \frac{2}{2G - 4G_p - \Delta} - \frac{4}{2G - 2G_p - \Delta} - \frac{2}{\Delta + 2G_p} \right]; \\
 \text{(c)} \quad E_2 &= 2\varepsilon_p + 4G + t^2 \left[ \frac{18}{G + \Delta} - \frac{2}{\Delta} - \frac{4}{\Delta + G_p} - \frac{2}{\Delta - G + 2G_p} - \frac{4}{\Delta + G + G_p} - \frac{2}{\Delta + G + 2G_p} \right]; \\
 \text{(d)} \quad E_2 &= 2\varepsilon_p + \Delta + 3G + 2G_p + t^2 \left[ \frac{32}{G + \Delta} - \frac{2}{G - \Delta - 2G_p} - \frac{6}{\Delta + G_p} - \frac{3}{\Delta} - \frac{2}{G - \Delta - G_p} \right. \\
 &\quad \left. - \frac{6}{G + \Delta + G_p} - \frac{1}{G + \Delta + 2G_p} \right]; \\
 \text{(e)} \quad E_2 &= 2\varepsilon_p + 8\Delta + 12G_p + t^2 \left[ \frac{44}{G + \Delta} - \frac{8}{G - 2G_p - \Delta} - \frac{8}{2G - 2G_p - \Delta} - \frac{4}{2G - 4G_p - \Delta} - \frac{8}{\Delta + G_p} - \frac{4}{\Delta + 2G_p} \right].
 \end{aligned} \tag{4}$$

Next we include the interaction between the configurations (c) and (d) in the same way as in Ref. 6. It is believed that the ground state in the atomic limit is the same as presented in Fig. 1 of Ref. 6, as  $G_p < 0.25 G$ ;<sup>11</sup> otherwise (for  $G_p > 0.25 G$ ) such a state is unstable for any  $G$ . The binding energy, of two holes,  $E_b = E_2 - 2E_1$ , where  $E_i = E(N+i) - E(N)$ , and  $E(N+i)$  is the ground-state energy of the system with  $i$  doped holes, is displayed in Fig. 1. The pairing occurs in the atomic limit ( $t = 0$ ) for  $G > 1.1\Delta$ . We find it remarkable that for  $t \neq 0$  the effective attraction between two holes occurs already for small  $G > 0$ . In the weak intersite interaction regime, for  $G/\Delta < 2.8$ ,  $|E_b|$  increases with increasing  $t/\Delta$ . Next, for larger  $G/\Delta$ , the binding energy,  $|E_b|$ , rapidly increases, indicating the charge instability.<sup>15</sup> For  $G/\Delta \rightarrow \infty$  we still observe a slow linear increase of  $|E_b|$  which comes from the terms  $\sim 1/\Delta$  were omitted in the energies which correspond to the configurations of Figs. 1(b) and 1(e) in Ref. 6. By comparing the binding energy shown in Fig. 1 with that of Fig. 2 in Ref. 6, we notice that even small interoxygen repulsion,  $G_p$ , strengthens the pairing mechanism for  $G < 2.8$ . It increases the energy of the state with the copper holes transferred to oxygen sites under doping, shown in Fig. 1(e) of Ref. 6, and thus counteracts the charge instability. In addition, our calculations confirm that local ferromagnetic alignment of copper spins is favored due to second-order terms when holes are added<sup>6,16</sup> which explains the fast disappearance of the antiferromagnetic long-range order under doping.

Next we consider biexcitonic regime for nonmagnetic Bi-based oxides. In this regime the system has a charge-ordered ground state and doped holes go preferentially

on oxygen sites. Formally it is defined by  $\tilde{u} = u_M - 4A'$ ,  $\Delta$ , and  $E_{BP} < 0$ ,<sup>6</sup> where  $A' = 2A - B$ , and  $E_{BP} = u_M - 2\Delta - 4A'$  is the binding energy of bipolaron. It has been pointed out in Ref. 6 that one may introduce the critical values of the intersite repulsion,  $G_1 = (|E_{BP}| - A')/2$  and  $G_2 = (|E_{BP}| - 2A')/4$ , which mark the breaking of a single bipolaron on a Bi ion by one and two added holes, respectively.<sup>6</sup> The respective ground states have been shown in Fig. 3 of Ref. 6. We note, however, that unlike for  $u_p \geq A'$ , discussed in Ref. 6, for  $u_p < A'$  the pairing occurs already for  $G = 0$  at the atomic limit ( $t = 0$ ), with the binding energy of  $E_b = u_p - A'$ . In this case the bipolarons on Bi ions are initially (at small  $G$ ) not influenced by doping and the lowest energy state with two added holes is not the state with two separate holes, presented in Fig. 3(c) of Ref. 6, but a *local* pair with two added holes localized on the *same* oxygen ion. The latter state is stable as long as  $G < G_3 = (|E_{BP}| - A' - u_p)/4$ . For the parameters chosen in Fig. 2 one finds the binding energy of  $E_b = -|\Delta|/2$  for  $G/|\Delta| < 0.25$ , as indicated by the horizontal line at  $t = 0$  for  $0 < G/|\Delta| < 0.25$ . At finite  $t/|\Delta|$  the binding energy is calculated by adding the terms of order  $(H')^2$  to the respective configurations on the lattice. One finds that the resulting binding energy,  $E_b$ , is negative and varies smoothly with  $G/|\Delta|$ , similarly as found in finite-size diagonalizations.<sup>8</sup> A representative example of  $t/|\Delta|=0.5$  is shown in Fig. 2. Furthermore, due to the different number of oxygen neighbors, the pairing in the  $G/|\Delta| \rightarrow \infty$  limit in a 2D model (Fig. 2) is not as strong as in a 3D one [see Fig. 4(a) of Ref. 6].

In order to obtain hole densities we made the same perturbation expansion to obtain the corrected density

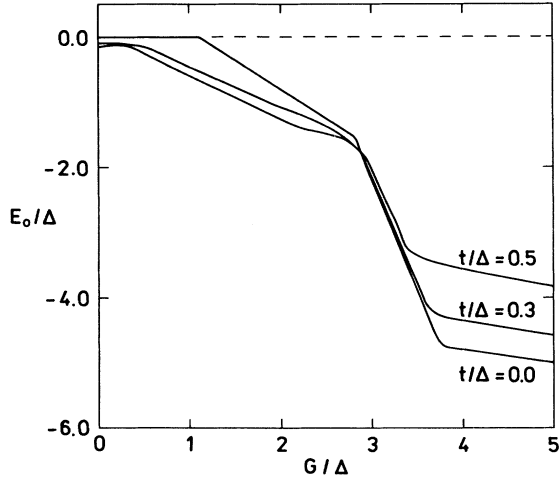


FIG. 1. Binding energy as a function of  $G/\Delta$  for  $u_M, u_p \rightarrow \infty, G_p = 0.05 G$  and for different values of  $t/\Delta$ .

in the ground state up to order  $t^2$ ,<sup>16</sup>

$$\langle n \rangle_{t^2} = \frac{\langle n \rangle^{(0)} + \sum_{k \neq m} \frac{|(k|H'|m)|^2}{(E_k - E_0)^2} \langle n \rangle^{(k)}}{1 + \sum_{k \neq m} \frac{|(k|H'|m)|^2}{(E_k - E_0)^2}}, \quad (5)$$

where  $\langle n \rangle^{(0)}$  and  $\langle n \rangle^{(k)}$  are the densities in one of the degenerate configurations of the ground state at  $t = 0, |m\rangle$ , and in the excited state,  $|k\rangle$ , respectively. The summation includes only excited states which mix up to order  $t$ . For the structure shown in Fig. 3(d) of Ref. 6 for

$$(a) E_1 = \varepsilon_M + 4A' + t^2 \left[ \frac{32}{\Delta + G - u_M + 4A'} - \frac{24}{\Delta + G - u_M + 3A'} - \frac{4}{\Delta + 2G - 3A'} - \frac{8}{\Delta + 2G - u_M + 3A'} \right];$$

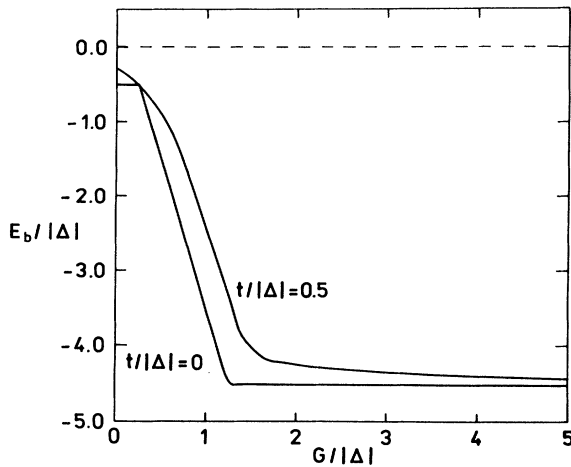


FIG. 2. Binding energy as a function of  $G/|\Delta|$  for  $u_M = 1.5|\Delta|, A' = 2|\Delta|$  and for different values of  $t/|\Delta|$ .

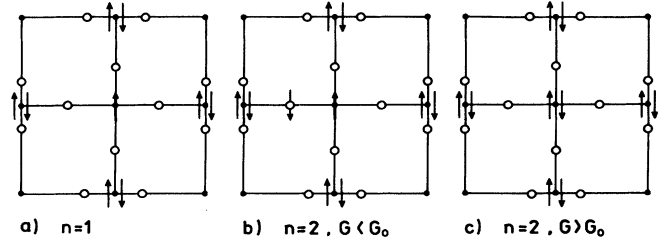


FIG. 3. Schematic representation of the ground state for the Bi oxides with  $n = 1, 2$  added holes for different values of  $G$  and for  $t = 0$ .

$G/|\Delta| = 0.5, t/|\Delta| = 0.75$  and other parameters as in Fig. 2, we found that about 5% of the charge of four oxygen holes goes to the central empty ion  $\text{Bi}^{3+}$  (see Fig. 3(d) of Ref. 6) and only 0.5% goes to the four external  $\text{Bi}^{3+}$  ions. The delocalization of biexciton increases slowly with increasing  $0 < t/|\Delta| < 1.0$ . A more localized character of biexciton was identified for large  $G/|\Delta|$ . For  $G/|\Delta| = 1.0$  and other parameters as given above, only 3% of the total charge of oxygen holes is moved to the nearest-neighbor ions.

Finally, let us consider bipolaronic regime, being a charge-ordered ground state in which doped holes go preferentially on metal (Bi) ion sites. Here  $\Delta > 3A'$  and  $u_M < 4A'$ . For one and two added holes to the system we have the ground states which depend on the value of  $G$  in the atomic limit, as presented in Fig. 3. The transition to the bipolaronic pairing occurs for  $G > G_0$ , where  $G_0 = (u_M - \Delta)/3$ . Energies  $E_i$  of the states represented in Fig. 3 are

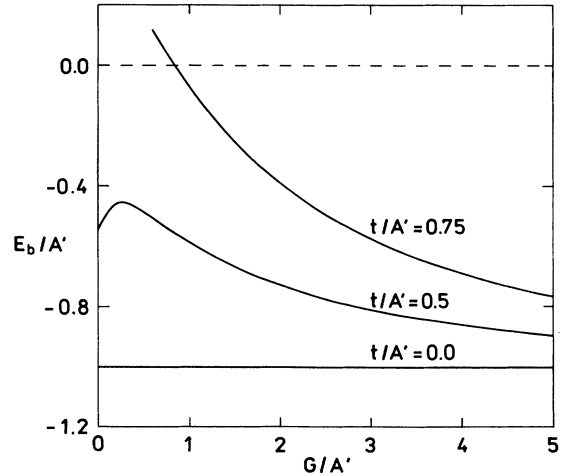


FIG. 4. Binding energy as a function of  $G/A'$  for  $\Delta = 4A', u_M = 3A', u_p = 5A'$ , and for different values of  $t/A'$ .

$$(b) E_2 = 2\varepsilon_M + \Delta + 3G + 4A' + t^2 \left[ \frac{32}{\Delta + G - u_M + 4A'} - \frac{18}{\Delta + G - u_M + 3A'} - \frac{3}{\Delta + G - 2A'} \right. \\ \left. - \frac{2}{-\Delta - 3G + u_M} - \frac{1}{\Delta + G - u_M + u_p + 3A'} - \frac{1}{\Delta + G + u_p - 3A'} \right. \\ \left. - \frac{6}{\Delta + 2G - u_M + 3A'} - \frac{6}{\Delta - u_M + 3A'} \right]; \quad (6)$$

$$(c) E_2 = 2\varepsilon_M + u_M + 4A' + t^2 \left[ \frac{32}{\Delta + G - u_M + 4A'} - \frac{8}{\Delta + 3G - u_M} - \frac{24}{\Delta + G - u_M + 3A'} - \frac{8}{\Delta + 3G - u_M + 3A'} \right].$$

The dependence of binding energy,  $E_b/A'$ , on  $G/A'$  in 2D case is shown in Fig. 4. In general for  $t = 0$ ,  $E_b$  is of the form

$$E_b = \begin{cases} \Delta + 3G - 4A', & \text{if } G < G_0, \\ u_M - 4A', & \text{otherwise.} \end{cases} \quad (7)$$

For the parameters chosen in Fig. 4, which we believe are realistic for bismuthates, one finds  $E_b = -A'$ , independently of  $G$ . For finite  $t$  and small  $G/A'$ ,  $|E_b|$  decreases rapidly when  $t/A'$  increases. For  $G/A' \rightarrow \infty$  we found strong binding almost independently of  $t/A'$  (for  $0 < t/A' < 0.75$ ). This behavior follows from Eqs. (6a)–(6c). Unlike in biexcitonic regime, here added holes go to empty metal sites. The holes break the minimum number of oxygen distortions leading to pairing. For the structure of Fig. 3(c) and for  $t/A' = 0.75$  and other parameters as in Fig. 4, we found that 7% and 3% of the bipolaronic charge goes to the nearest oxygen ions for  $G/A' = 1.0$  and 2.0, respectively. Furthermore, the delocalization of bipolaron increases in the region of  $1.0 < G/A' < 2.0$  and  $0.5 < t/A' < 1.0$  for the increasing  $t/A'$  and decreasing  $G/A'$ .

Summarizing, our study confirms the earlier results of Nuñez Regueiro and Aligia<sup>6</sup> that a similar mechanism

can be responsible for the pairing in Cu- and Bi-based superconducting oxides. It originates from large enough repulsion between nearest-neighbor  $M$  and O orbitals. The regions of  $E_b < 0$  were identified for different characteristic regions of parameters of the model: (i) for the holes of mainly oxygen character in the magnetic regime, with the additional enhancement of the pairing due to the interoxygen repulsion term  $G_p$  and (ii) for the holes either on oxygen or on bismuth in the Bi-O systems, in the biexcitonic and bipolaronic regime, respectively. It is expected that Bi oxides are in the biexcitonic rather than bipolaronic regime, but a continuous transition exists between these two regions and relatively small bismuth-oxygen repulsion stabilizes pairing in both of them. Although the realistic values of parameters describing these systems are likely to be somewhat different from those used in the present study, the qualitative picture is expected to be similar. If the charge transfer mechanism of pairing is indeed responsible for superconductivity in all considered oxides, the order parameter should be of (extended)  $s$ -wave symmetry.

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