

### Pairing of holes in a tight-binding model with repulsive Coulomb interactions

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We consider a tight-binding model with two orbitals per site and purely repulsive Coulomb interactions. It is shown rigorously that in this model there exists a parameter regime in which pairing of hole carriers occurs. It is argued that the model is not totally unrealistic.

Although many proposals for superconductivity originating in electronic-pairing mechanisms exist,<sup>1</sup> it has never been shown rigorously that pairing can occur in a model with purely repulsive Coulomb interactions and no coupling to bosonic degrees of freedom. The purpose of this paper is to discuss such a model. It contains two atomic orbitals per site,  $s$  and  $s'$ , with destruction operators  $c_{i\sigma}$  and  $c'_{i\sigma}$  for electrons in  $s$  and  $s'$  orbitals at site  $i$ , respectively. The Hamiltonian is

$$H = \sum_i H_0^i + H_1, \tag{1a}$$

with the interatomic term  $H_1$  a purely kinetic-energy term for the electrons in  $s$  orbitals,

$$H_1 = -t_0 \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.C.}), \tag{1b}$$

and the atomic Hamiltonian given by (we omit the site index on the right, as it is the same for all operators)

$$H_0^i = U n_{\uparrow} n_{\downarrow} + U' n'_{\uparrow} n'_{\downarrow} + V n n' + \epsilon n' - t'(c_{\sigma}^\dagger c'_{\sigma} + \text{H.c.}), \tag{1c}$$

with  $n = \sum_{\sigma} n_{\sigma}$ ,  $n_{\sigma} = c_{\sigma}^\dagger c_{\sigma}$ , and similarly for the primed operators. The  $s'$  orbital is higher in energy than the  $s$  orbital, hence  $\epsilon > 0$ . It is also more extended in space, so that the Coulomb repulsion for two electrons in it,  $U'$ , is smaller than that for two electrons in the  $s$  orbital,  $U$ . We may think of these orbitals roughly as  $1s$  and  $2s$  orbitals in a hydrogen atom, for example.  $V$  is the repulsion between one electron in the  $s$  and another electron in the  $s'$  orbital, and  $t'$  a small hybridization between  $s$  and  $s'$  orbitals. The reason why we use orbitals that do not diagonalize the single-particle part of the atomic Hamiltonian is to avoid inclusion of off-diagonal matrix elements of the Coulomb interaction in the starting Hamiltonian, which would make the discussion less clear.

The Coulomb interaction between electrons in arbitrary two-particle states should be repulsive,<sup>2</sup> which for the Hamiltonian Eq. (1) requires that

$$U > 0, \tag{2a}$$

$$U' > 0, \tag{2b}$$

$$V > 0. \tag{2c}$$

In addition, the Coulomb interaction should lead to a

positive self-energy for an arbitrary charge distribution.<sup>3</sup> For the Hamiltonian Eq. (1), this requires that the matrix

$$V_{\text{Coul}} = \begin{pmatrix} U & V \\ V & U' \end{pmatrix} \tag{3}$$

has positive eigenvalues. This leads to the constraint

$$UU' > V^2. \tag{4}$$

The conditions Eqs. (2) and (4) should be satisfied in order for the Hamiltonian Eq. (1) not to violate fundamental physical constraints.

We assume the following ordering of parameter values,

$$U' + \epsilon < V < U - \epsilon, \tag{5}$$

which leads to the ordering of two-electron atomic energy states shown in Fig. 1 for  $t'=0$ . The essential point is that two electrons prefer to occupy the higher single-particle level because their Coulomb repulsion in it is smaller than it would be otherwise.

To lowest order in  $t'$ , the ground state for one electron of spin  $\sigma$  with the atomic Hamiltonian Eq. (1c) and  $\epsilon > 0$  is

$$|\bar{\sigma}\rangle = (c_{\sigma}^\dagger + \delta c'_{\sigma}{}^\dagger)|0\rangle, \tag{6}$$

and the ground state for two electrons of opposite spin under the condition Eq. (5) is

$$|\bar{\uparrow}\bar{\downarrow}\rangle = [c'_{\uparrow}{}^\dagger c'_{\downarrow}{}^\dagger + \delta'(c_{\uparrow}^\dagger c'_{\downarrow}{}^\dagger - c'_{\downarrow}{}^\dagger c_{\uparrow}^\dagger)]|0\rangle, \tag{7}$$

where  $|0\rangle$  is the atomic state with no electrons in  $s$  and  $s'$  orbitals, and

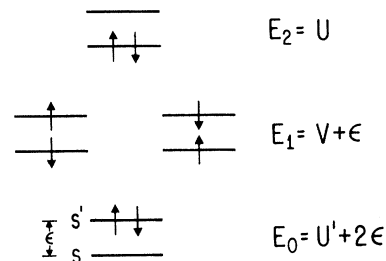


FIG. 1. Two-particle states of atomic Hamiltonian, with  $t'=0$ . We assume parameters so that  $E_0 < E_1 < E_2$  [Eq. (5)].

$$\delta = \frac{t'}{\varepsilon}, \quad (8a)$$

$$\delta' = \frac{t'}{V - U' - \varepsilon}. \quad (8b)$$

We assume that  $\delta, \delta' \ll 1$ , so that the forms Eqs. (6) and (7) are accurate. Next we define an intra-atomic fermion operator  $\tilde{c}_\sigma^\dagger$  that creates electrons in these low-lying states:

$$\tilde{c}_\sigma^\dagger |0\rangle = |\bar{\sigma}\rangle, \quad (9a)$$

$$\tilde{c}_\sigma^\dagger |-\bar{\sigma}\rangle = \pm |\hat{\uparrow}\downarrow\rangle, \quad (9b)$$

where the  $+$  ( $-$ ) sign corresponds to  $\sigma = \uparrow$  ( $\sigma = \downarrow$ ). The original fermion operator  $c_\sigma$  may be expressed in terms of the fermion operator  $\tilde{c}_\sigma$  as

$$c_\sigma = \tilde{c}_\sigma [1 + (S-1)\tilde{n}_{-\sigma}], \quad (10)$$

with  $\tilde{n}_\sigma = \tilde{c}_\sigma^\dagger \tilde{c}_\sigma$  and

$$S = \delta\delta'. \quad (11)$$

We now project the original Hamiltonian Eq. (1) onto the subspace spanned by these low-lying atomic states and obtain the following effective single-band Hamiltonian:

$$H_{\text{eff}} = -t_0 \sum_{\langle ij \rangle} (\tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} + \text{H.c.}) [1 - (1-S)(\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma}) + (1-S)^2 \tilde{n}_{i,-\sigma} \tilde{n}_{j,-\sigma}] + U_{\text{eff}} \sum_i \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}, \quad (12)$$

with

$$U_{\text{eff}} = U' \quad (13)$$

to lowest order in  $t'$  (it will be reduced with higher-order corrections). The kinetic-energy part of the Hamiltonian Eq. (12) has the following meaning: the hopping amplitude for an electron when there are no other electrons at the two sites involved, i.e., in the process

$$|\bar{\sigma}\rangle |0\rangle \leftrightarrow |0\rangle |\bar{\sigma}\rangle, \quad (14a)$$

is

$$t(0) = t_0; \quad (14b)$$

if there is one other electron at the sites involved,

$$|\bar{\uparrow}\rangle |\bar{\downarrow}\rangle \leftrightarrow |0\rangle |\hat{\uparrow}\downarrow\rangle, \quad (15a)$$

the hopping amplitude is

$$t(1) = t_0 S; \quad (15b)$$

and if there are two other electrons at the sites involved,

$$|\hat{\uparrow}\downarrow\rangle |\bar{\downarrow}\rangle \leftrightarrow |\bar{\downarrow}\rangle |\hat{\uparrow}\downarrow\rangle, \quad (16a)$$

the hopping amplitude is

$$t(2) = t_0 S^2. \quad (16b)$$

Since we have assumed that  $\delta, \delta' \ll 1$ , this implies that  $S \ll 1$  and hence

$$t(0) \gg t(1) \gg t(2). \quad (17)$$

This reduction in the hopping rate as more electrons are added occurs because of the change in the state of the first electron at a site from state  $s$  to state  $s'$  when a second electron goes into that site, leading to a reduced overlap factor.

Next we rewrite the Hamiltonian Eq. (12) in terms of hole operators, using the transformation

$$\tilde{c}_{i\sigma} \rightarrow (-1)^i \tilde{c}_{i\sigma}^\dagger \quad (18)$$

(assuming a bipartite lattice) and obtain

$$H_{\text{eff}}^h = -t_0 S^2 \sum_{\langle ij \rangle} (\tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} + \text{H.c.}) \left[ 1 + \left[ \frac{1}{S} - 1 \right] (\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma}) + \left[ \frac{1}{S} - 1 \right]^2 \tilde{n}_{i,-\sigma} \tilde{n}_{j,-\sigma} \right] + U_{\text{eff}} \sum_i \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}, \quad (19)$$

where the operator  $\tilde{c}_{i\sigma}^\dagger$  now creates a hole (i.e., destroys an electron) in an atom with two electrons. From Eq. (19), the hopping rate for a hole when there are no other holes in the two sites involved is  $t_0 S^2$ , when there is one other hole involved it is  $t_0 S$ , and when there are two other holes involved it is  $t_0$ —in agreement with Eqs. (14)–(16).

Consider now two holes of opposite spin in a filled band governed by the Hamiltonian Eq. (19). The last term in the kinetic energy does not act in this case. The “hopping interaction” given by the second term in Eq. (19),

$$\Delta t = t_0 S (1 - S), \quad (20)$$

favors pairing of the holes, while the on-site repulsion  $U_{\text{eff}}$  opposes it. Exact solution of the Schrödinger equation leads to the condition<sup>4</sup>

$$1 > C(d) \left[ S^2 + \frac{U_{\text{eff}}}{2zt_0} \right]^{1/2} \quad (21)$$

for the two holes to pair in a singlet state with zero center-of-mass momentum. Here,  $z$  is the number of nearest neighbors to a site, and  $C(d)$  a constant that depends on dimensionality  $d$ :

$$C(1)=C(2)=1, \quad (22a)$$

$$C(3)=1.713. \quad (22b)$$

[Equation (22b) assumes a simple cubic lattice]. In terms of the single-hole bandwidth,

$$D_h = 2zt_0S^2, \quad (23)$$

the condition Eq. (21) is (assuming  $d=2$  or  $d=1$ )

$$1 > S \left[ 1 + \frac{U_{\text{eff}}}{D_h} \right]^{1/2}, \quad (24)$$

which for small  $S$  can be satisfied even if the hole-hole repulsion is larger than the hole bandwidth. Equation (24) is also the condition to obtain a nonzero  $T_c$  in the dilute-hole-concentration regime in any dimension within BCS theory.<sup>4</sup>

We next review the conditions to be satisfied for our analysis to be valid. To obtain the desired ordering of atomic energy levels required that  $\varepsilon > 0$  and that the condition Eq. (5) be fulfilled. In order for the mapping to an effective single-band model to be accurate, we require that

$$t_0 \ll \varepsilon, \quad (25a)$$

$$t_0 \ll V - U' - \varepsilon, \quad (25b)$$

so that the excited atomic states can be neglected. The lowest-order perturbative treatment of the atomic problem required that

$$\delta \ll 1, \quad (26a)$$

$$\delta' \ll 1, \quad (26b)$$

with  $\delta, \delta'$  given in Eq. (8). This condition also implies that  $S \ll 1$ , which is the favorable condition for pairing to occur in our model. The condition Eq. (21) requires that

$$t_0 \gtrsim \frac{U'}{z}, \quad (27)$$

which does not contradict Eq. (25). Finally, we require positivity of the Coulomb interaction as expressed by conditions (2) and (4). It is clear that this set of conditions is not mutually exclusive; in particular, we can take  $U$  arbitrarily large and  $t'$  arbitrarily small to help satisfy them. Thus, a parameter range clearly exists in which our Hamiltonian leads to pairing with purely repulsive interactions.

It is also clear that some of these conditions can be somewhat relaxed by extending the analysis presented here, with no essential change in the results: the intra-atomic Hamiltonian can be diagonalized exactly rather than in perturbation expansion in  $t'$ , and the second-order contribution in  $t_0$  to the effective Hamiltonian can be easily computed by taking into account virtual transitions to the excited atomic states. The form of the effective Hamiltonian and the essential physics remain unchanged.

The model discussed here is closely related to the phenomenological model for hole pairing discussed in Ref. 5. There, a pseudospin degree of freedom was introduced to describe the relaxation of the "background" when holes were added to a filled shell: the first hole caused a large disruption in this background due to the contraction of the orbitals of the remaining electrons in the shell, while the second hole caused essentially no change. This is the same physics contained in the model discussed here. Elimination of the background degree of freedom led to a Hamiltonian similar to Eq. (19),<sup>6</sup> except that the last term in the kinetic energy was omitted; we expect this last term, however, to be irrelevant in the regime of interest for this model, for low hole concentration. The advantage of the model discussed here is that it contains only electronic degrees of freedom; on the other hand, the phenomenological Hamiltonian of Ref. 5 is somewhat more general, as the pseudospin can be interpreted to describe the collective state of all the electrons in the outer shell.

We believe that the model discussed here (and in Ref. 5) bears some semblance to reality. An essential feature of it is the ordering of energy scales assumed

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$$\text{Intra-atomic Coulomb repulsion} \gg \text{intra-atomic level spacing} \gg \text{interatomic hopping} \quad (28)$$

(i.e.,  $U, V \gg \varepsilon \gg t_0$  in the notation of the present model). This is, of course, what occurs in nature and follows simply from the length scales involved: the first part of this inequality from the fact that orbiting electrons are closer to each other than to the nucleus, and the second part from the larger interatomic compared with intra-atomic distances. The first part of this inequality implies that it is not in principle possible to deal with single-band tight-binding models originating from a given fixed atomic orbital, since the intra-atomic Coulomb repulsion will mix in other orbitals depending on the electronic occupation; the second part implies that the intra-atomic states relax

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much faster than it takes for an electron to hop from site to site, leading to instantaneous, rather than retarded, interactions. Both inequalities together imply, as shown in this paper, that a single-band tight-binding model can still be a useful concept, provided that one keeps in mind that the orbitals in it are not fixed but change with electronic occupation and takes this into account in computing the interactions in the model.

It is well known that when electrons are added to an atomic shell the shell expands due to electron-electron repulsion,<sup>7</sup> and in the expanded orbit the repulsion is reduced, as assumed in the present model ( $U' < U$ ). How-

ever, more specifically the model discussed here required the ordering

$$U' < V < U, \quad (29)$$

so that, in particular, the repulsion of two electrons in the expanded orbit ( $U'$ ) should be less than between one in the expanded and one in the unexpanded one ( $V$ ). This can be justified assuming that it is easier for atomic electrons to avoid each other (i.e., to set up angular correlations) if they are in the same "radial" orbital rather than in different ones. In an (oversimplified) classical picture, we would describe this effect as follows: in the expanded orbital both electrons can orbit at the same rate and be always  $180^\circ$  out of phase to minimize their Coulomb repulsion, while in different orbitals the electrons will transverse their orbits with different periods and come close every now and then, therefore experiencing greater repulsion.

The model discussed here can be made somewhat more realistic by including nearest-neighbor hoppings between  $s$  and  $s'$  orbitals and between two  $s'$  orbitals,  $t_1$  and  $t_2$ , respectively. An analysis similar to the one given above

yields for the dominant contributions to the hoppings when one, two, and three electrons are in the sites involved:

$$t(0) = t_0, \quad (30a)$$

$$t(1) = t_1(\delta + \delta'), \quad (30b)$$

$$t(2) = t_2(\delta + \delta')^2. \quad (30c)$$

As long as  $t_1$  and  $t_2$  are not much larger than  $t_0$ , with  $\delta, \delta' \ll 1$  the ordering given by Eq. (17) will continue to hold, leaving the physics discussed above unchanged. [It is, of course, only the second inequality in Eq. (17) that is the crucial one for pairing of holes to occur.] One can also generalize the model by including nearest-neighbor Coulomb repulsions as well as contributions to the hopping interaction from the nearest-neighbor "hybrid" matrix element of the Coulomb interaction.<sup>8</sup> The essential physics remains the same.

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<sup>1</sup>See, for example, *Electronic Structure and Mechanisms for High Temperature Superconductivity*, Proceedings of the Miami Workshop, January, 1991, edited by J. Ashkenazi and G. Vezzoli (Plenum, New York, in press).

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<sup>5</sup>J. E. Hirsch, *Phys. Lett. A* **134**, 451 (1989); J. E. Hirsch and S. Tang, *Phys. Rev. B* **40**, 2179 (1989); *Solid State Commun.* **69**,

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<sup>6</sup>J. E. Hirsch and F. Marsiglio, *Phys. Rev. B* **41**, 2049 (1990). In this reference, the mapping to the effective Hamiltonian was performed to second order in the intersite coupling, which can also be done for the model discussed here.

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<sup>8</sup>J. E. Hirsch, *Physica C* **158**, 326 (1989).