Bound electron pairs in the presence of charge confinement

M. Gulacsi
International School for Advanced Studies, Strada Costiera 11, 34100 Trieste, Italy

Zs. Gulacsi
Institute of Isotopic and Molecular Technology, 3400 Cluj, P.O. Box 700, Romania

(Received 23 February 1990)

The possibility of a bound-electron-pair emergence is investigated in quasi-two-dimensional systems exhibiting charge confinement. The binding energy is calculated considering explicitly the size quantization effect. We prove that the binding energy obtained differs from the three-dimensional isotropic case. The results of this investigation in relation to the high-transition-temperature superconductors are discussed.

Since the breakthrough to higher T_c's by Bednorz and Müller[1] for La-Ba-Cu-O systems, we have witnessed a continuously growing number of newly discovered oxide compounds exhibiting the superconducting phase at high critical transition temperature, such as the Y-Ba-Cu-O,[2] Bi-Sr-Ca-Cu-O,[3] Tl-Ba-(Ca)-Cu-O (Ref. 4) families, or the Pb-Sr-A-Cu-O (Ref. 5) system, where A is a mixture of lanthanide and alkaline-earth elements, and the potassium-doped member of the $BaBiO_3$ compound Ba-K-Bi-O.[6] All of these belong to the class of materials in which the charge carriers are holes or vacancies in the valence band. With the exception of the last mentioned compound, all of the known high-T_c materials have a very strong quasi-two-dimensional character. The states at the Fermi energy are not spread evenly over the unit cell but rather confined to the Cu-O networks in the layer. A large fraction of the density of states lies within a slab no more than 20% of the interplanar separation, i.e., a slab of about 1 Å thickness.[7] But, an additional requirement is also needed that provides an appropriate *electronic environment*[7] to promote superconducting Cu-O layers. This requirement is fulfilled by the Bi-O or Tl-O bands, similar to the cation doping in the La system and the chains in the Y system. These basic properties are also valid in the newly *electronic* superconductors[8] as was confirmed by neutron-diffraction measurements,[9] local-density electronic-structure calculations,[10] and far-infrared spectroscopy.[11] In our discussion we omit the Ba-K-Bi-O system that exhibits bulk superconductivity, the measurements indicating substantial isotope effect,[12] and there exists direct evidence of phonon-mediated coupling.[13] For the other systems, the feature of the electronic normal state distinguishes them from ordinary metals. Therefore it is plausible to assume that the physics may be dominated by a large on-site Hubbard U potential. However, the inverse photoemission spectrum of $Bi_2Sr_2CaCu_2O_8$, the NMR and T_1 data of ^{89}Y in $YBa_2Cu_3O_{6+x}$, or the resonant photoemission spectroscopy of $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_{4-y}$ seem to present direct evidence for the existence of a Fermi liquid.[14] Using the calculated electronic energy bands, by means of the variational principle, many normal-state transport properties of high-T_c oxides can be understood.[15] We could also argue using the classical example of the Pd metal, with significant on-site U, and yet it can be quite well described as a band Fermi liquid.

It is plausible to assume in the following that the details of the host oxide system do not affect the qualitative feature of the superconducting condensate. Only in this way can we explain, for example, the universal correlation between T_c and the carrier density over the effective mass that was found to exist[16] in sixteen different specimens of various high-T_c superconductors. This can occur because of the similarity of the electronic structure in a wide variety of highly complicated and differing oxidic compounds, which in fact, as mentioned previously, consists of electrons confined to the cuprate planes.[7] The electronic density of states in each case contains the free-electron dispersion corresponding to the Cu-O networks.[7] However, if charge confinement indeed exists in the systems this should be reflected also in the physical properties. In this sense (i) the measured[17] critical transition temperature versus the layer thickness [i.e., $\ln T_c/T_0 = \text{const} - (a/a_0)^{2/3}$, where T_0 and a_0 are an arbitrary scale temperature and layer thickness, respectively] is exactly the same as for thin metallic superconducting films;[18] (ii) room-temperature photoemission edge spectra were performed on $Bi_4Ca_3Sr_3Cu_4O_{16+\delta}$ specimens and gold and aluminium overlayers deposited *in situ* on the same specimen without observing any difference;[19] and (iii) the positron-annihilation two-dimensional angular-correlation measurements[20] predict a Fermi surface consisting of four nearly cylindrical sheets oriented to the z axis of Y-Ba-Cu-O, indicating the presence of quasidiscrete energy levels.

Motivated by these results, we will analyze the situation in which the electrons are confined in a thin layer, which gives rise to the so-called, one-dimensional quantum size effect.[21] In this case the state and the energy of the charge carrier are determined by the longitudinal

quasimomenta k_x, k_y and a discrete quantum number n. As a result, quasidiscrete energy levels appear, henceforth called bands.

Interest in quantum size effect in metals started to grow when experiments revealed an increase of the critical superconducting transition temperature in metal films with decreasing thickness.[22] The first experiments were performed on Al films.[23] The increase was independent on the oxide layer on which the metal films were deposited,[24] and it appeared for other elements[25] also. It is interesting to note that the largest increase in T_c was obtained with semiconducting films,[26] where T_c became some hundred times greater than in the bulk (e.g., in Be, it reached a $T_c \sim 8-9$ K, at ~ 10 nm thickness, compared to 0.026 K in bulk; thinner films could not be measured, because of the high tendency to crack).

With respect to these theories, the first attempt made by Blatt and Thompson (Ref. 22) considers the step structure of the total density of states due to the quantum levels. By using BCS-type equation they obtained *shape resonances* in the gap ($\sim T_c$) versus the film thickness dependence. This resonance could also be experimentally seen.[27] Increase in T_c, or an average increase, can be obtained only by considering film boundary effects also.[22,28] However, Tavger and Kresin,[29] argue that even the most favorable choice of boundary conditions cannot explain the growth of the critical transition temperature. They used a method similar to the multiband model for bulk superconductors[30] and obtained a growth of <0.5 K in T_c. The main deficiencies of this model are (i) it does not take into account explicitly the presence of discrete energy levels, just its consequences and (ii) they completely neglected the change in the phonon spectrum due to quantum size effect. This second point will be discussed later, and its crucial importance will become evident. We should also mention that in very thin films T_c decreases,[31] which is known to be related to the *substrate effect*, i.e., metal-insulator boundary.[32]

Recently, it was shown by Trivedi and Ashcroft[33] that in order to analyze quantum size effect in metallic films the discrete energy levels must be explicitly taken into account. Thus, it became clear that under the condition of charge carriers being confined in a slab, the initial Cooper framework,[34] in which the periodic ion potential is replaced by an isotropic box, cannot be applied.

We now consider charge carriers (e.g., electrons) to be confined in a layer (a quasi-two-dimensional box), that extends in the z direction from $z=0$ to $z=a$. Imposing the periodic boundary condition in the x and y direction, with periodicity distance l_x, and l_y, respectively, the basic one-electron wave function will have the form

$$\varphi_{\mathbf{k},n}(\mathbf{r}) = (l_x l_y)^{-1/2} \exp[i(k_x x + k_y y)] u_n(z) \ .$$

The Schrödinger equation can always be separated for the two motions.[35] Considering an infinitely deep quantum well, and the value of $V(z)$ at the bottom of the well as the origin for the energy scale, then $u_n(z) = (2/a)^{1/2} \sin(\pi n z/a)$, which is a well-known form. With eigenvalue spectrum $\varepsilon = \hbar^2 k^2/2m^* + \varepsilon_0 n^2$, $n = 1, 2, \ldots$ and $\varepsilon_0 = \hbar^2 \pi^2/2m^* a^2$ is the zero-point energy (the notations used are similar to those used in Ref. 33). Before passing on to analyzing the binding energy of two particles, let us consider the normal-state transport properties. As was shown in Ref. 33, there is a great difference between in-plane and out-of-plane conductivity. It is found that the in-plane conductivity is given by the well-known Drude formula. We assume that the source of dissipation to which electrons are coupled is the electron-phonon interaction. Then the longitudinal electron-phonon scattering (see Ref. 36, and the references cited therein) will give a linear temperature dependence of the resistivity at high temperatures, as for normal metals and in accordance with the measurements of high-T_c oxides.[37] But, due to the summation over the discrete energy levels, the expression of the out-of-plane conductivity is completely different.[33] In striking contrast to the case of metals, it requires only the knowledge of the value at ε_F of the scattering rate. However, if we want to be realistic concerning the high-T_c oxides, we must consider a stack of layers. Therefore, in the z direction the resistivity will be governed by a tunneling mechanism. Applying a small bias, the net current between two layers i, j, is

$$I_{i\to j} - I_{i\to j} \sim T_\perp \int [f_i(\varepsilon)] g_i(\varepsilon) g_j(\varepsilon) d\varepsilon \ ,$$

where $f(\varepsilon)$ is the Fermi distribution function and $g(\varepsilon)$ is the total density of states in the layer, i.e., $(m^*/2\pi\hbar^2 a)\mathrm{Int}[(\varepsilon/\varepsilon_0)^{1/2}]$ (Ref. 33) (Int denotes the integer part of a number), and $T_\perp$ is the transmission coefficient through a Dirac-delta potential which bounds the layer.[38] We will be concentrating just on the effect caused by the motion of particles in the z direction.[39] For this motion the scaling temperature is $T_0 = \varepsilon_0/k_B$. Considering the numerical values measured[16] for high-T_c oxides, i.e., $m^* \sim 5m_e$ and the average thickness of layers being of ~ 6 Å, $T_0 \sim 2000$ K is obtained. The experimental data[37] taken in the $\sim 100-900$ K temperature range is intermediate between 0 and T_0. Therefore, applying the appropriate approximation,[40] we find in leading order

$$\frac{T_\perp}{2} \left[\frac{2}{\pi}\right]^2 \left[\frac{m^*}{2\pi\hbar^2 a}\right]^2 \frac{n_c + S(n_c)}{a} \frac{|\mathrm{eV}|}{\varepsilon_0^2} k_B T \ , \qquad (1)$$

where[33] $n_c = \mathrm{Int}[k_F a/\pi]$ and

$$S(n_c) = \sum_{n=1}^{n_c} n^2 = n_c(n_c+1)(2n_c+1)/6 \ .$$

From Eq. (1) it can be seen that the resistivity perpendicular to the layers will be inversely proportional to the temperature, as is measured.

To analyze the binding energy, we consider two electrons to be in a layer. For a complete set of states we choose for the wave function (opposite spin case) the production function

$$\varphi_{\mathbf{k}_1,n_1;\mathbf{k}_2,n_2}(\mathbf{r}_1,\mathbf{r}_2) = \varphi_{\mathbf{k}_1,n_1}(\mathbf{r}_1)\varphi_{\mathbf{k}_2,n_2}(\mathbf{r}_2) \ .$$

The superposition of these will give the total wave function

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k_1,k_2}\sum_{n_1,n_2}\chi_{k_1,k_2;n_1,n_2}\times\varphi_{\mathbf{k}_1,n_1;\mathbf{k}_2,n_2}(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{2}$$

where $\chi_{k_1,k_2;n_1,n_2}$ are the coefficients solving the scattering problem.[41] Solving the Schrödinger equation

$$-[\hbar^2(\nabla_1^2+\nabla_2^2)/2m^*-E]\psi(\mathbf{r}_1,\mathbf{r}_2)+H_{\rm int}\psi(r_1,r_2)=0\ ,$$

and integrating over the real space, we obtain

$$(\varepsilon_K+\varepsilon_k+2\varepsilon_0 n^2-E)\chi_{k',k';n',n'}+\sum_{k,n}\chi_{k,k;n,n}\langle\mathbf{k}',\mathbf{K}',n',n'|H_{\rm int}|\mathbf{k},\mathbf{K},n,n\rangle=0\ . \tag{3}$$

A transformation to relative and center-of-mass in-band coordinates was performed, therefore $\varepsilon_K=\hbar^2K^2/4m^*$ and $\varepsilon_k=\hbar^2k^2/m^*$. For details in obtaining Eq. (3), see Ref. 42. For the following discussion which relates to the interaction, let us consider it, for example, to be of phonon type. The basic result of the present calculation is true for any kind of pairing mechanisms. It was realized first by Theil[43] that the presence of confinement will also drastically alter the phonon spectrum. In this sense, low-frequency phonons cannot exist. This low phonon cutoff was applied to the BCS equation for the critical temperature in Ref. 44, obtaining an increase in T_c. However, for the high phonon cutoff, the bulk value was used, which was incorrect.[22] The average phonon frequency becomes lower (see Ref. 22, and the references cited therein) due to the decrease of the force constant. As previously stated, this phonon spectrum change was completely ignored in other theoretical approaches.[22,28,29] The significance of the change in the low-frequency phonon spectrum was shown by molecular-dynamics techniques[45] to be of crucial importance also in the increase of T_c of alternating layered systems.[46]

In a confined system the overwhelming majority of phonons have wave vectors not exactly in the plane of the layer.[35] They must have an energy of at least $\hbar\omega_{\rm min}=\hbar\pi c_t/a$,[44] where c_t is the transverse speed of sound. It is known[47] that the effective electron-electron matrix element will be negative if $|\varepsilon(\mathbf{k})-\varepsilon(\mathbf{k}-\mathbf{q})|<\hbar\omega_{\mathbf{q}}$. We do not know much about the values of the sound velocity, so we will restrict ourselves to a crude evaluation with respect to the wave vectors. In our example the Fermi sphere is cut by a well-defined number (n_c) of planes, which we call bands. These are populated up to a value k_{F_n}, which is the Fermi momentum corresponding to the nth band. k_{F_n} is decreasing with increasing n, and it is related to the three-dimensional Fermi momentum (k_F) by $k_{F_n}^2=k_F^2-(\pi n/a)^2$. In an effective-mass approximation,[47] the maximum value of $|\varepsilon(\mathbf{k})-\varepsilon(\mathbf{k}-\mathbf{q})|$ is $\sim\hbar^2k_{F_1}^2/2m_e$. This value can be small, if a is less than 10 Å because π/a becomes of the same order as k_F, i.e., of the order of the inverse Bohr radius. But, the smallest phonon wave vector is also restricted to π/a. Therefore, it has a well-defined value, as does the related energy accordingly. We conclude, that due to the presence of the bands, and because of the lower phonon cutoff, at very low values of the layer thickness, the matrix elements

$$\langle\mathbf{k}',\mathbf{K}',n',n'|H_{\rm int}|\mathbf{k},\mathbf{K},n,n\rangle$$

can be approximated by $-|\lambda|$, for $0<k'<k_{F_{n'}}$ and $0<k<k_{F_n}$. Where λ is considered a constant. In this way a factorizable potential was achieved,[48] so we can follow the usual procedure.[34] The characteristic equation for the eigenvalues is

$$1+|\lambda|\sum_{k,n}\frac{1}{E-(\varepsilon_K+\varepsilon_k+2\varepsilon_0n^2)}=0\ . \tag{4}$$

The zeros of Eq. (4) fall into two distinct categories. There is an isolated zero (bound state), denoted by E^*, which lies below the quasicontinuum of pair energies. To determine the roots in the quasicontinuum, one can follow the treatment given by Wentzel.[49] The lowest eigenvalue can easily be determined to give $E^*=\varepsilon_K+2\varepsilon_0-\Delta$, where Δ is the binding energy of the pair. The density of the two-particle state in a layer being a constant[50] $\rho=m^*/2\pi\hbar^2a$, we can integrate Eq. (4) easily:

$$\frac{1}{\rho|\lambda|}=\sum_{n=1}^{n_c}\ln\left|\frac{\varepsilon_F+\varepsilon_0(n^2-2)+\Delta}{2\varepsilon_0(n^2-1)+\Delta}\right|\ , \tag{5}$$

where $\varepsilon_F=\hbar^2k_F^2/2m^*$. Maintaining ε_F and Δ in leading order, the gap will have the following form:

$$\Delta=\varepsilon_F e^{-1/n_c\rho|\lambda|}+\varepsilon_0\left[\frac{(n_c+1)(2n_c+1)}{6}-2\right]e^{-1/n_c\rho|\lambda|}\ . \tag{6}$$

Let us consider first, the classical limit of Eq. (6), $a\to\infty$, i.e., $n_c={\rm Int}[k_Fa/\pi]\to\infty$, which corresponds to infinitely many bands populated. The density of states will be $n_c\rho=m^*k_f/2\pi^2\hbar^2\equiv N(0)$, equivalent with that of the three-dimensional one at the Fermi level. Even at finite values of a, the depression of $n_c\rho$ from its bulk value is small. Therefore, in future discussions we will take it to be roughly equal to $N(0)$. In the case of $a\to\infty$, attention must be given to the cutoff. The arguments concerning the change of the phonon spectrum are no longer valid. Varying a continuously, the phonon-mediated interaction will become active at $\varepsilon_F-\varepsilon_0\sim\hbar\omega_D$,

and the cutoff will change to $\frac{4}{3}\varepsilon_F - 2\varepsilon_0 \sim 2\hbar\omega_D$. Thus the classical limit is obtained.

However, as can be seen from Eq. (6), the binding energy is greatly enhanced. If we restrict ourselves to a BCS-type description, this means that the critical transition temperature will also be enhanced considerably. This increase is due mostly to the presence of ε_F, which is of 10^4 K order, while $\exp[-1/N(0)|\lambda|]$, for weak electron-phonon coupling, is of $\sim 10^{-2}$ order, thus giving a T_c of ~ 100 K. The presence of ε_F is crucial for high-T_c superconductors. A linear relation between T_c and n/m^* (i.e., carrier density over effective mass) was measured (see Ref. 16) for sixteen different specimens of various oxides. One possibility to obtain such a behavior is when $T_c \sim \varepsilon_F$, as in our case.

The most striking feature of Eq. (6), however, is the maximum that is obtained versus n_c, i.e., the layer thickness a, at $n_c = 7(\frac{22}{3})$. After which, with the increase of n_c, the critical transition temperature is decreasing, and for $a \to \infty$, as was shown, the bulk value is obtained. This maximum in T_c can also be related to high-T_c superconductors, where it appears versus the level of doping.[51] As was pointed out in Ref. 33, in response to a variation of the density of the carriers the lattice constant along the z direction (i.e., a) will also change, so as to maintain charge neutrality. This lattice-constant variation upon doping was measured in the case of high-T_c materials.[52] Recently it was proved[53] that the suppression of superconductivity due to oxygen removal does not coincide with the orthorhombic-to-tetragonal phase transition, but with a significant charge redistribution. As a consequence, steplike anomalies are observed in some bonding lengths and atomic distances.[53]

Finally, let us analyze the term $\varepsilon_0[(n_c+1)(2n_c+1)/6 - 2]e^{-1/n_c\rho|\lambda|}$ of Eq. (6), the effect of which is to induce a steplike variation of the binding energy (thus T_c), an increase as n_c is raised in the $n_c \in [1,7]$ domain. Such behavior was observed in the case of Tl compounds, where T_c was obtained to grow with the number of Cu-O planes (N) in the unit cell, as 80 K ($N=1$), 108 K ($N=2$), 125 K ($N=3$) (Ref. 7), and 162 K ($N=4$) (Ref. 54). We believe that one Cu-O plane in addition will induce only a small increase in the bulk k_F, that is, in n_c. As stated previously, ε_0/k_B is in the order of ~ 2000 K, thus going from n_c to n_c+1 an increase in T_c of $\sim 20(4n_c+5)/6$ K is obtained.

In conclusion, a simple, easy-to-follow calculation was performed in order to analyze the possible bound states that can appear in quasi-two-dimensional systems. We took two electrons, confined in an infinitely deep quantum well and calculated for the first time the binding energy of the formed pair, taking into consideration explicitly the effect of the size quantization.

It is our pleasure to thank D. Beariswyl, L. N. Bulaevskii, D. C. Johnston, D. I. Khomskii, A. Parola, T. M. Rice, A. E. Ruckenstein, and E. Tosatti for fruitful discussions and valuable comments while this work was in progress. One of the authors (M.G.) wishes to acknowledge the Institute for Scientific Interchange Foundation, Torino, for their kind hospitality.

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[38]Following, for example, M. Bender and S. A. Orszag, *Advanced Methods for Scientists and Engineers* (McGraw-Hill, New York, 1984), p. 526, $T_\perp$ is obtained to be of the form $A^2/1+A^2$, with $A=\pi\hbar^2 n[1+a/2(2m-1)]2/m^*a$, where $z=ma$ is the position of the δ function.

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[42]An analysis of the scattering problem from different n states reveals that the matrix element of the screened interelectron interaction vanishes for transitions between neighboring bands (for details, see Ref. 36). This is caused by the fact that by virtue of the symmetry of the problem, the wave functions in odd bands are symmetrical (antisymmetrical in even bands) relative to reflection from the center ($z=a/2$) plane of the layer. It is further convincing if the layer extends in the z direction from $z=-a/2$ to $z=a/2$, in which case instead of $u_n(z)\cos(\pi nz/a)$ is obtained for odd n and $\sin(\pi nz/a)$ for even n [see also, A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961), Vol. 1, Chap. 3]. We note, however, that the zero result is a consequence of the problem's symmetry and does not depend on the explicit form of the wave functions. Following this line, let us first consider $\langle \ldots,n_i',n_j'|H_{\rm int}|,\ldots,n_i,n_j\rangle$ in-band pairing, i.e., $n_i=n_j=n$. In this case the matrix element is always zero, unless (i) $n_i'=n_j'=n'$; (ii) $n_i'=n'$ and $n_j'=n'+2m$ ($m=1,2,\ldots$); and (iii) $n_i'=n+2m_1$ and $n_j'=n+2m_2$ ($m_1=1,2,\ldots$, $m_2=1,2,\ldots$, $m_1\neq m_2$). From these events, (i) has the highest transition probability (Ref. 36). If we consider intraband pairing, i.e., $n_i=n$ and $n_j=n+1$, then the matrix element again is zero unless (iv) $n_i'=n_i+2m_1$ and $n_j'=n_j+2m_2$ ($m_1=1,2,\ldots$, $m_2=0,1,2,\ldots$). But then again (iv) is much less probable (Ref. 36) than (i). For the same reason as is the case of (ii) and (iii), it involves hopping across two or more bands. Therefore, as in Eq. (3) it is reasonable to consider in-band pairing, which clearly involves time-reversed functions.

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[50]The density per unit volume is

$$\rho=\frac{1}{V}\frac{S}{(2\pi)^2}2\pi k_n dk_n/d\varepsilon(k_n)\ ,$$

with $S=l_x l_y$, $V=aS$ and the subscript n denotes any of the nth band.
[51]This fact was seen immediately after the discovery of the high-transition-temperature superconductors. For a review, see, e.g., the papers presented in *Towards the Theoretical Understanding of High T_c Superconductors,* Proceedings of the Adriatico Research Conference and Workshop, Trieste, Italy, edited by S. Lundqvist, E. Tosatti, M. P. Tosi, and Yu Lu (World Scientific, Singapore, 1988), pp. 599–777.
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