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Electron Pairing Mediated by Coulomb Repulsion in a Periodic Potential

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Abstract

It is shown that the binary Coulomb repulsion between two electrons can lead to spatially localized pair states (preformed pairs) in the periodic potential of a crystalline solid. These composite bosonic states, residing in the erstwhile forbidden gaps, could further our understanding of the solid state, in particular, of the high temperature superconducting state.

The single most important concept in all microscopic theories of superconductivity is that of an electron pair [1-4]. In the far reaching and highly successful theory of Bardeen, Cooper and Schrieffer (BCS) [4], the pair formation is due to the attractive electron-phonon interaction. The electrons, forming a Cooper pair, though highly correlated in momentum, are rather loosely bound in physical space with spatial extensions $\simeq 10^{-4} - 10^{-5}$ cm. On the other hand, the primary constituent of the models inspired by Schafroth [5,1-3] is a highly localized (in space) pair of electrons forming a composite, spin-zero boson. For want of a physical mechanism for creating localized pairs however, these latter models have remained dormant.

With the advent of high temperature superconductivity (HTSC) [6], with exciting new phenomenology generated at a feverish pace, and with experiments indicating that highly localized pairs may actually exist in superconductors [1,6], it is imperative that the theories based on localized pairs be re-examined. It is even more important to discover the generic mechanism(s) which could lead to such pairing.

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The idea of two mutually repelling particles forming a spatially compact pair seems paradoxical. In fact the Coulomb repulsion (shielded by the lattice ions) between the electrons, strong as it is, has always been considered to be a serious impediment to pair formation mediated by other effectively 'attractive' interactions. In the periodic potential of a lattice, however, this very Coulomb repulsion, under suitable conditions, can conspire to bind two electrons. The periodic potential breaks up the electron energy spectrum into allowed bands separated by forbidden gaps, although in some cases the bands 'overlap' and there may be no gaps. Assuming the existence of gaps, the energy of the proposed bound pair of mutually repelling electrons will reside precisely in this gap forbidden to a noninteracting (i.e., Coulomb repulsion switched off) duo of electrons. In comparatively simpler settings, the repulsive potential-generated gap states are known in solid state [impurity or surface states] as well as in plasma physics [Toroidal Alfvén Eigenmodes [7]].

For simplicity of exposition we restrict our analysis to a single spatial dimension. Although the analysis can be extended to higher dimensions, the solutions cannot be readily obtained in analytic form. The quantum mechanics of two electrons a, b interacting with each other via a mutual repulsive potential $V_r(|x_a - x_b|)$ in the presence of an external periodic potential $V_p(x + d) = V_p(x)$ is described by the steady-state Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x_a^2} - \frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x_b^2} + [V_p(x_a) + V_p(x_b) + V_r(|\, x_a - x_b\,|)]\,\Psi = E\Psi(x_a, x_b)\ . \tag{1}$$

In the absence of either V_p or V_r, this equation may be solved to yield non-square integrable solutions corresponding respectively to 'Bloch states' ($V_r = 0$) or 'scattering states' ($V_p = 0$). For a short-ranged (e.g., screened coulomb) repulsive potential V_r we now show that Eq. (1) admits solutions that are Bloch-like $\sim e^{iKx}\,W(x, y)$ in the center of mass coordinate $x = (x_a + x_b)/2$ [$W(x, y)$ is periodic in x with the lattice period d], and localized in the relative coordinate $y = x_a - x_b$. These eigensolutions are nondegenerate and are labelled by K, the center-of-mass 'wavenumber'. Thus the wave function $\Psi(x_a, x_b, K)$ has a character-

istic energy $E(K)$. The proof given below applies to any reasonable periodic potential and to any purely repulsive potential which is sufficiently short-ranged. The pair states will be constructed in terms of one electron Bloch states $\Phi = \Phi(k,n,x) \equiv \exp(ikx)U_{k,n}(x)$ [$U_{k,n}(x)$ is periodic in x] obeying

$$\left[-(\hbar^2/2m)(\partial^2/\partial x^2) + V_p(x)\right] \Phi(k,n,x) = \epsilon(k,n)\Phi(k,n,x) \ , \tag{2}$$

with the normalization $2\pi\delta(k-k')\delta_{n,n'} = \int_{-\infty}^{+\infty} \varphi^*(k,n,x)\varphi(k',x',x)dx$, where $\epsilon(k,n)$ is the eigenenergy and where we have used the reduced zone scheme in which k is the reduced zone wavenumber $-\pi/d \leq k \leq \pi/d$, and n is the band index. In the rest of this paper we will use ξ as a composite symbol for k and n with $\int_\xi \equiv \sum_{n=1}^{\infty} \int_{-\pi/d}^{\pi/d}(dk/2\pi)$ denoting integration over the allowed bands.

The two-electron wave function can be readily expanded in terms of the complete set of product Bloch states,

$$\Psi(x_a,x_b) = \int_{\xi_a} \int_{\xi_b} \Phi(\xi_a,x_a)\Phi(\xi_b,x_b)\widehat{\Psi}(\xi_a,\xi_b) \tag{3}$$

which, when substituted in Eq. (1) yields the following integral equation for the amplitude $\widehat{\Psi}$,

$$(2\pi)^2 \left[E - \epsilon(\xi_a) - \epsilon(\xi_b)\right] \widehat{\Psi}(\xi_a,\xi_b) = \int_{\xi'_a} \int_{\xi'_b} P(\xi_a,\xi_b|\xi'_a,\xi'_b)\widehat{\Psi}(\xi'_a,\xi'_b) \tag{4}$$

with [$\Delta_{a(b)} \equiv [U'_k(x)\, U^*_k(x)]_{a(b)}$ are periodic in $x_{a(b)}$]

$$P \equiv P(\xi_a,\xi_b|\xi'_a,\xi'_b) = \iint dx_a\, dx_b\, \Delta_a\, \Delta_b\, V_r(|x_a - x_b|) \exp[i(k'_a - k_a)x_a + i(k'_b - k_b)x_b] \ . \tag{5}$$

Transforming to the center of mass x and the relative coordinate y [$x_a = x + y/2, x_b = x - y/2$, $dx_a\, dx_b \equiv dx\, dy$], exploiting the periodicity of the Bloch functions, and using the well-known identity $\sum_{n=-\infty}^{n=+\infty} \exp[in\theta] = 2\pi\delta(\theta)$ for $-\pi \leq \theta \leq \pi$, Eq. (5) can be manipulated to yield [$\widehat{P}(\xi_a,\xi_b|\xi'_a,\xi'_b) \equiv \widehat{P}$]

$$P = (2\pi/d)\delta(k'_a + k'_b - k_a - k_b)\widehat{P} \ ,$$
$$\widehat{P} = \int dy\, V_r(|y|) \exp[-iy(k'_a - k_a)] \int_{-d/2}^{d/2} dx\, \Delta(x + y/2)\Delta(x - y/2) \tag{6}$$

where the explicit appearance of the delta function allows us to define a conserved center of mass momentum $K = k_a + k_b = k'_a + k'_b$. In our manipulations, we have used the fact that in the reduced zone scheme $-\pi/d \leq K \leq \pi/d$.

Enormous simplification follows by the realization that Eqs. (4)–(6) admit a solution of the form $\widehat{\Psi}(\xi_a, \xi_b) = \delta(K - k_a - k_b)F(k_a, K - k_a, n_a, n_b)$ with F satisfying

$$[E - \epsilon(\xi_a) - \epsilon(\xi_b)]\, F(k_a, n_a, n_b) = (2\pi d)^{-1} \sum_{n'_a n'_b} \int \widehat{P}\, F(k'_a, n'_a, n'_b) dk'_a \ , \tag{7}$$

and k'_a lying in the range $-\pi/d \leq K - k'_a \leq \pi/d$; this range is a consequence of the k'_b integration using one of the delta functions. Since both $|K|$ and $|k'_a|$ are limited to π/d, the integration interval has to be properly determined for finite K.

Equation (7), essentially a one-dimensional integral equation on a finite interval, is general, rigorous and exact, and can serve as the starting point for detailed work. The primary object of this letter, however, is to expose the basic physics underlying the pair-formation phenomenon. Therefore we simplify the analysis by putting Bloch functions equal to unity, by modelling the repulsive potential by $V_r = V_0 d\delta(y)$ leading to $\widehat{P} = V_0 d^2$, and by restricting the k integration only to the two relevant bands $n = 1, 2$.

Defining new dimensionless variables $k = kd/2\pi$, $K = Kd/2\pi (-1/2 \leq k, K < 1/2)$, $u = k - K/2$, and remembering the constraints on k'_a integration, Eq. (7) becomes [$i, j = 1, 2, K > 0$. For $K < 0$, similar expressions pertain]

$$[E - \epsilon_i(u + K/2) - \epsilon_j(u - K/2)]\, F_{ij}(u, K) = 2V_0 \sum_{i',j'} \int_0^{(1-K)/2} du'\, F_{i'j'}(u', K) \tag{8}$$

leading to the dispersion relation

$$\frac{1}{2V_0} = \sum_{i,j} \int_0^{(1-K)/2} \frac{du}{E - \epsilon_i(u - K/2) - \epsilon_j(u + K/2)} \equiv \sum_{i,j} I_{ij} \tag{9}$$

which can be solved if the single-particle energy spectrum in the periodic potential V_p is known. For Eq. (9) to represent a true [not quasi or unstable] pair eigenstate, i.e., to yield a real energy E (for real V_0), all four of the energy denominators $D_{ij} = [E - \epsilon_i - \epsilon_j]$ must remain nonzero in the range of integration.

This very condition insures the spatial (in y) localization of the pair wave function [derived from Eqs. (3)–(8) with x and y measured in d]

$$\psi(x,y) = C \exp[i2\pi Kx] \sum_{i,j} \int_0^{(1-K)/2} du\, D_{ij}^{-1}(u,K,E) \cos(2\pi yu) \ , \tag{10}$$

which (for nonzero D_{ij}) vanishes as $|y| \to \infty$ by Riemann-Lebesgue theorem. Indeed, from Parseval's formula, it follows that $\int_{-\infty}^{+\infty} |\Psi(x,y)|^2 dy < |C|^2$. Notice that keeping the Bloch functions [which are nonsingular] in the integrand does not alter the conclusion. The exact behavior for large $|y|$ depends upon the details of D_{ij}. Thus to demonstrate the existence of localized pair states, we must show that for typical crystalline periodic potentials, D_{ij}'s can be nonzero for some choice(s) of E.

We sketch the argument for the $K = 0$ case. Similar considerations apply for $K > 0$. Since the one-particle spectrum is assumed to have a gap ($\epsilon_2(1/2) > \epsilon_1(1/2)$), D_{11}, D_{22} are nonzero in $2\epsilon_1(1/2) < E < 2\epsilon_2(1/2)$ and the corresponding integrals, I_{11}, I_{22} are well defined, the former being positive. It is obvious that we must choose E to be outside the range of $\epsilon_{12}(u) \equiv \epsilon_1(u) + \epsilon_2(u)$ for $I_{12}(= I_{21})$ to be defined. When $\epsilon_{12}(u)$ is decreasing, clearly all the denominators of the dispersion integral are nonzero in the interval, $2\epsilon_1(1/2) < E < \epsilon_{12}(1/2)$. If, in addition, the range of ϵ_{12} does not overlap that of $2\epsilon_2(u)$ (i.e., $\epsilon_{12}(0) < 2\epsilon_2(1/2)$), there is a second, higher energy solution in the interval, $\epsilon_{12}(0) < E < 2\epsilon_2(1/2)$.

Since the dispersion integral is a monotonic decreasing function of E varying between $-\infty$ and $+\infty$ in its intervals of definition, there is a unique solution corresponding to each gap. The lower energy solutions always exist (for decreasing ϵ_{12}) and are called 'lower gap' pairs. The upper solutions exist if the periodic potential is strong enough. A third possibility

where $\epsilon_{12}(u)$ is increasing and overlaps with $2\epsilon_{11}$ could occur if the range of $\epsilon_1(u)$ is wider than that of ϵ_2. In this case the upper gap pairs necessarily exist but not the lower ones.

For an explicit demonstration, we display numerical solutions based on the one-particle dispersion relation $\cos 2\pi\epsilon^{1/2} + (\sin 2\pi\epsilon^{1/2}/2\pi\epsilon^{1/2})Q_0 = \cos 2\pi k$ corresponding to the well-known Kronig-Penney potential $V_p(x) = Q_0(\hbar^2/md)\sum_{n=-\infty}^{n=\infty}\delta(x-nd)$, $Q_0 = (md/\hbar^2)Qb$, where $Q(b)$ is the strength (range) of the potential. Here we present a typical strong potential ($Q_0 = 5$) example (possibly relevant to materials exhibiting high T_c superconductivity) for which the gap size is comparable to the band size.

In Fig. 1, the lower, the middle, and the upper curves respectively represent (for $K = 0$) the functions $\epsilon_1(k)$ [lower band], $\epsilon_2(k)$ [upper band] and $[\epsilon_1(k) + \epsilon_2(k)]/2$. For finite K, all the curves in Fig. 1 will be a little different. The precise location of the energy eigenvalue $E(K)$ (in the allowed range) will depend on the strength of the repulsive potential V_0. For $V_0 = 0.5$ (a typical value when the screened Coulomb potential is approximated by a delta function), Fig. 2 gives a plot of $E(K)/2$ as a function of K revealing extremely slow K variation with $E(K)_{\min}$ very close to $K = 1/2$. Thus the lower-gap pairs are more tightly bound for $K = 1/2$ as compared to $K = 0$.

In Fig. 3 we display a plot of the relative probability density $|\Psi(x,y)|^2/|\Psi(x,0)|^2 = \rho(y)$ [Eq. (10)] as a function of y (measured in d) for the most tightly bound $K = 1/2$ state. The probability density falls rapidly implying a highly localized pair of size $\Delta y \sim d$, the lattice period. The pair size remains between $1 - 10d$ for all reasonable values of Q_0 and V_0.

It is now evident that the localized pairs owe their existence to the mutual Coulomb repulsion (which is always there) between the constituent electrons, and the gaps in the one-electron energy spectrum created by the periodic potential. In higher dimensions, the dispersion integral will be multidimensional, and the energy denominators will be more complicated due to the vectorial nature of $\mathbf{k}$. However, as long as there are gaps in the three-dimensional energy spectrum, there will always be room for the localized pairs, the

singlet as well as the higher energy triplet states. These latter states will also have physically interesting consequences.

The existence of these pair states forces us to redraw the electronic picture of a solid. In the conventional picture, the electrons in a solid move as independent Fermi particles in the periodic lattice potential due to both the ions and the smoothed-out Hartree-Fock contribution of the electron gas (mean field theory). The residual binary screened Coulomb potential is totally neglected. The independent particle model leads to the well-known band structure, and the electrons are arranged to occupy these allowed states in conformity with Fermi-Dirac statistics. Let us consider solids in which the dynamically interesting valence and conduction bands have a definite gap separating them (non-overlapping bands). Typically, the valence band is filled and the conduction band is partially so in a metallic solid. Let us now switch on the binary short-ranged Coulomb repulsion. Although there will be some quantitative changes in the erstwhile one-electron states, the most significant consequence is the creation of a new continuum of pair-states [with energy $E(K)$, K is continuous] in the gap. These pair states, with energies decidedly lower than that of any duo of electrons in the conduction band, must be occupied before the electrons (after filling the valence band) find their way to the conduction band. If pair-pair interaction is neglected, then there is nothing to prevent all those electrons (which would have occupied the conduction band in the absence of binary repulsion) from preferentially populating the pair states as long as the temperature is less than the gap size. Since the spatial wave function of the pair is symmetric in the relative coordinate $y = x_a - x_b$, Pauli principle demands that its spin wave function be antisymmetric (singlet). The pairs will, therefore, constitute a weakly interacting spin-zero gas of bosons with charge $(-2e)$, and whose energy E is a very slowly varying function of the momentum K. It seems that we have just supplied the missing element in the theory of superconductivity due to Schafroth and coworkers!

The consequence of a Bose gas of highly localized electron-pairs have been worked out in

great detail [1-3,5]. For this letter, we enumerate only the most relevant ones: (1) The Bose Einstein condensation temperature T_c in degree Kelvin (the transition temperature for the superconducting state) is given by $T_c = 3 \times 10^{-11}\, n^{2/3}\ (m/M_{\text{eff}})$, where n is the density and M_{eff} is the effective mass of the pair states. Much care is needed to calculate the density as well as the effective mass of the pair states. Making quite bold extrapolations from our 1D calculation [M_{eff} is calculated from $E(K)$ versus K curve], we estimate that T_c can be as high as 500° K for values of Q_0 and V_0 in the range expected for HTSC materials. Better and more accurate estimates will be presented later. It seems hopeful that this mechanism could lead to high temperature (even room temp.) superconductivity quite naturally, (2) assuming a standard energy spectrum for the Bose gas, Schafroth and Blatt have shown that the Meissner-Ochsenfeld effect occurs at the Bose-Einstein condensation temperature, and that the material behaves like an extreme type II superconductor. All the relevant electrodynamic properties can be readily calculated.

The linchpin of this alternative (to BCS) route to superconductivity (maybe the only route to high T_c superconductivity), the highly localized electron-pair is fundamentally different from the Cooper-pair. Firstly, it is strongly localized in space while the Cooper-pair is enormously extended. Secondly, the Cooper-pairs form (due to an attractive electron-phonon interaction) at the Fermi surface; the band structure plays no part in their formation. The Coulomb mediated localized pairs, on the other hand, live in the gaps between allowed bands; their existence and properties (e.g., localization distance, effective mass M_{eff}) are fundamentally controlled by the band structure. Thirdly, unlike the Cooper pairs, which disappear above the critical temperature, the localized pairs will exist at higher temperatures also; they will start breaking up when the temperature becomes comparable to the gap-size. Finally, the localized pairs and Cooper pairs could exist simultaneously. For materials with overlapping bands (where the pair states will be unstable resonances), the BCS mechanism is likely to be dominant. Also the isotope-effect can enter the new mechanism only indirectly

through the weakening of the Coulomb repulsion by electron-phonon interaction.

There does exist some evidence [6] that such preformed pairs with charge $(-2e)$ might have been seen in materials exhibiting high T_c superconductivity. The experimental observation that high T_c superconductivity can occur in materials near the metal-insulator transition (i.e., when nearly all the electrons are in the valence band) is also compatible with the localized-pair (formed near the top edge of the valence band) route to superconductivity.

From simple quantum mechanics, we have shown that under the influence of their binary short-range Coulomb repulsion, electrons in a solid (with non-overlapping bands) can form pair states (spin zero bosons) of charge $(-2e)$. These pair states will constitute a new dynamic element in the solid state, and below their Bose-Einstein condensation temperature, may be the effective carriers of superconducting currents in strong type II superconductors.

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Figure Captions

[1] Single particle dispersion relations, a plot of $\epsilon_1(k)$ (lower band), $\epsilon_2(k)$ (upper band) and $\epsilon_1(k) + \epsilon_2(k)/2$ as a function of k for $Q_0 = 5, U_0 = 0.5$ and $K = 0$. Allowed range for E is indicated.

[2] Pair energy eigenvalue $E(K)$ as a function of K for $Q_0 = 5, V_0 = 0.5$.

[3] The highly localized pair probability density $\rho(y)$ as a function of the relative distance y for $Q_0 = 5, V_0 = 0.5$, and $K = 0.5$.

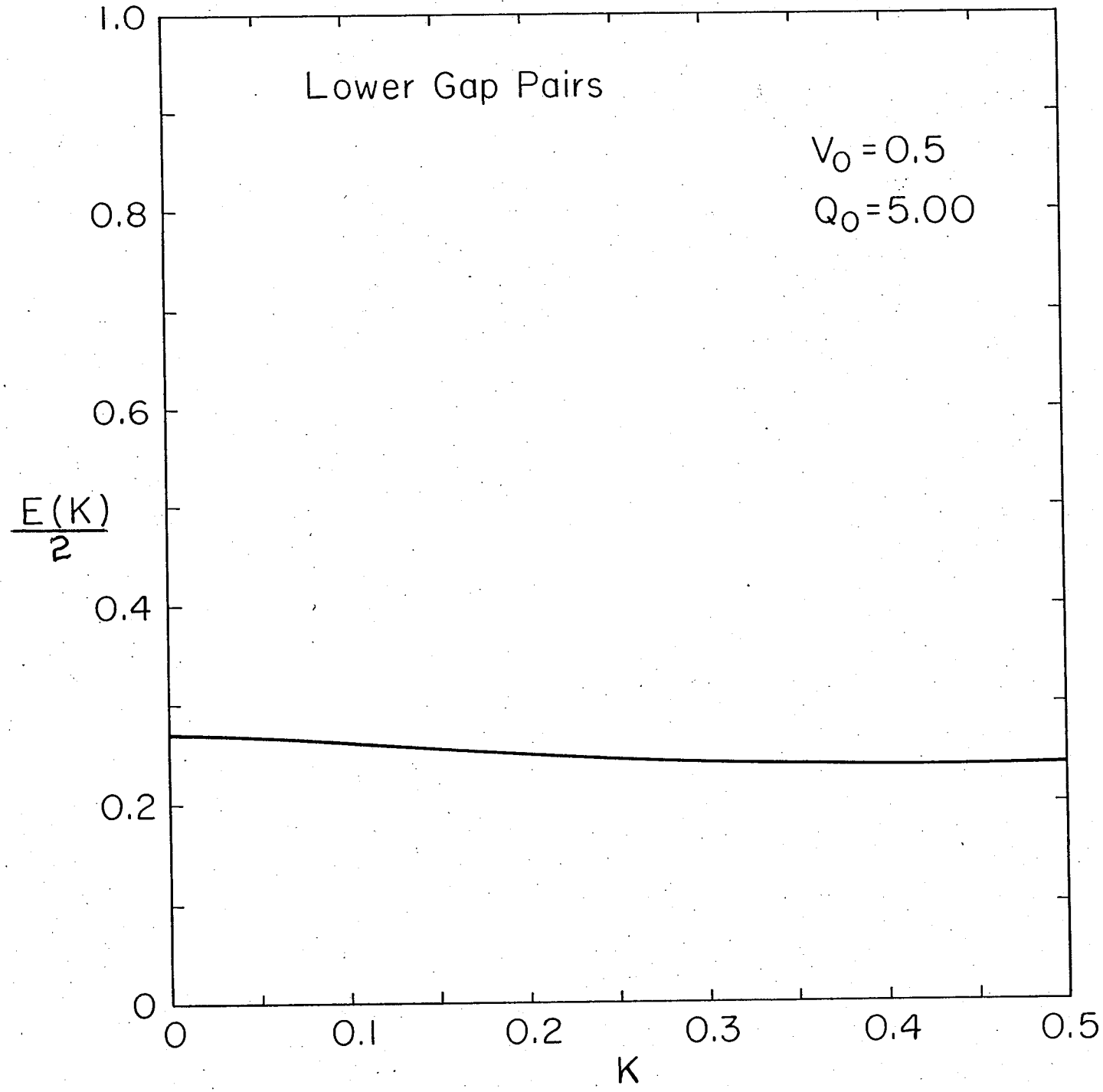
Lower Gap Pairs
$V_0 = 0.5$
$Q_0 = 5.00$
$\frac{E(K)}{2}$
1.0
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
K

Fig 2.

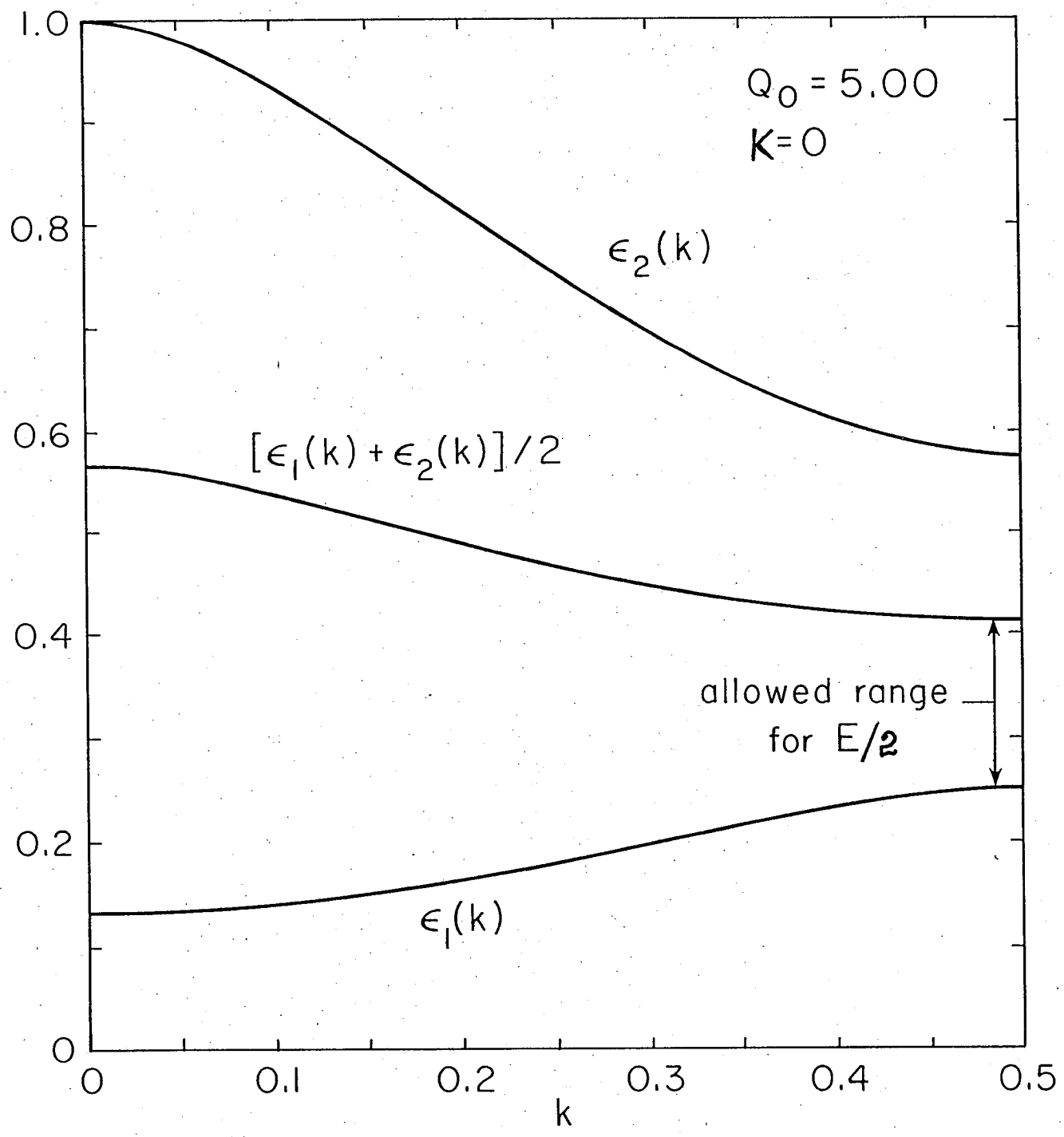
1.0
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
k
$Q_0 = 5.00$
$K = 0$
$\epsilon_2(k)$
$[\epsilon_1(k) + \epsilon_2(k)]/2$
allowed range
for $E/2$
$\epsilon_1(k)$

Fig 1

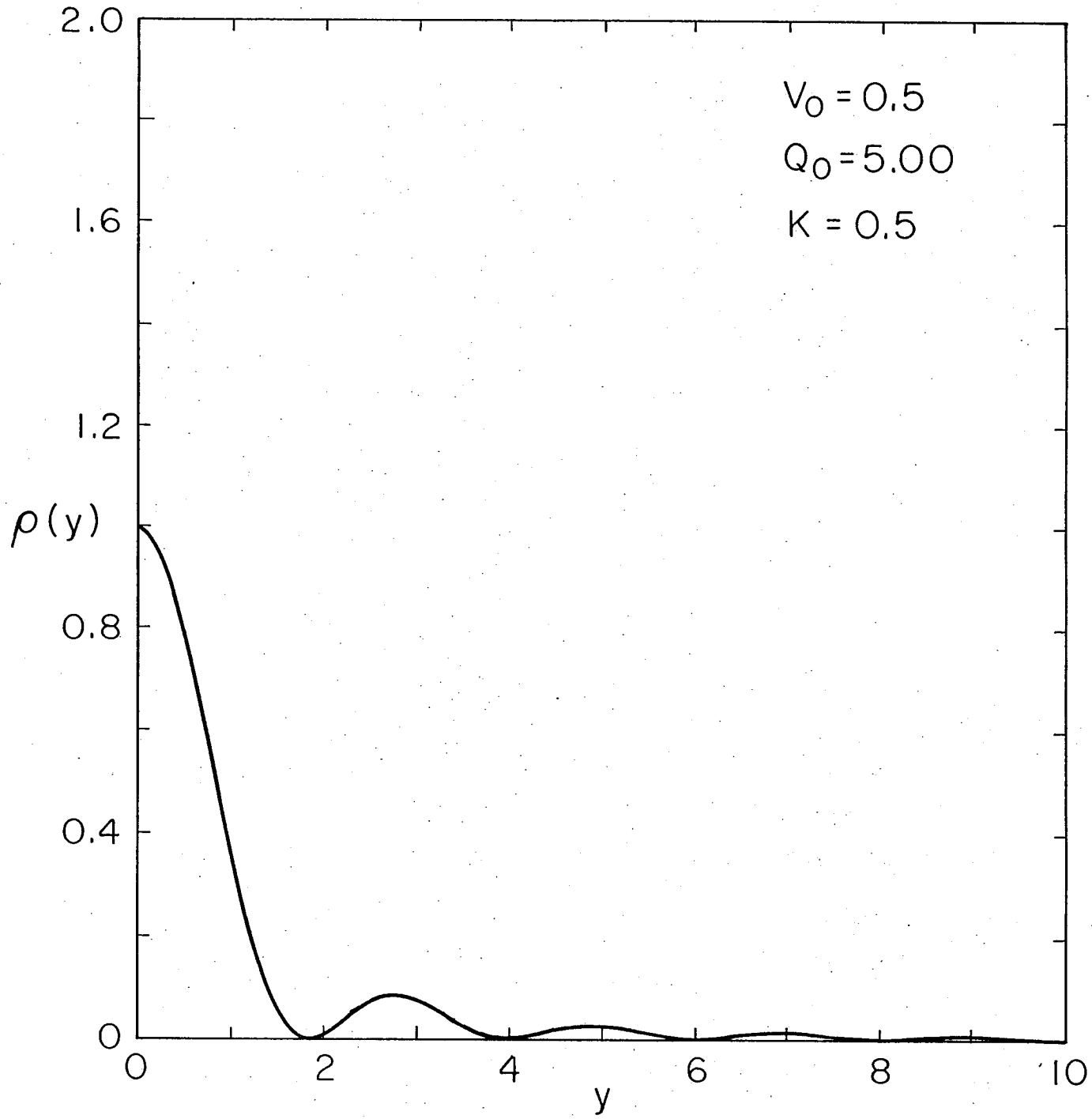

Fig. 3