Metastable electron-pair states in a two-dimensional crystal

G-Q Hai1 and L K Castelano2

1 Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970, São Carlos, SP, Brazil
2 Departamento de Física, Universidade Federal de São Carlos, 13565-905, São Carlos, SP, Brazil

E-mail: hai@ifsc.usp.br

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Abstract
We study possible quantum states of two correlated electrons in a two-dimensional periodic potential and find a metastable energy band of electron pairs between the two lowest single-electron bands. These metastable states result from interplay of the electron–electron Coulomb interaction and the strength of the crystal potential. The paired electrons are bound in the same unit cell in relative coordinates with an average distance between them of approximately one third of the crystal period. Furthermore, we discuss how such electron pairs can possibly be stabilized in a many-electron system.

Keywords: energy band, periodic potential, electron pair

1. Introduction

Electron pairing in a crystal has long been an interesting subject of study in quantum solid-state physics. The most remarkable pairing of electrons is the Cooper pair in superconductors [1], mediated by lattice distortions. Electron pairing may also occur through strong electron–phonon coupling, forming the so-called bipolaron [2–4]. On the other hand, experimental observation of the pairing of ultracold rubidium atoms in an optical lattice [5], where the binding arises from pure quantum interference, has stimulated many theoretical and experimental investigations about bound pairs in strongly correlated systems in periodic potentials. Quantum states of two interacting electrons with short-range interactions and possible electron pairing have been studied both in one-dimensional [6–9] and two-dimensional [10, 11] periodic potentials. Very recently, by a semiclassical analysis of Bloch oscillations of two electrons interacting through a Coulomb potential in a biased crystal lattice, Gaul et al [12] found that they may form a bound pair if the energy of the relative motion exceeds the upper band edge.

In this work, we will study the quantum states of two correlated electrons in a two-dimensional (2D) periodic potential from a different point of view. We observe that, in fact, localized individual electron pairs have been studied in many different quantum units, such as the negative hydrogen ion H− and helium atom [13–15], as well as two-electron quantum dots [16] and negatively charged donor centers (D−) [17] in the solid-state environment. Electron–electron exchange and correlation are essential in the formation of these electron-pair states. The quantum state of an electron pair such as that of H− is different in its nature from the single-electron states of the H atom [15]. The locality of the electron correlation is essential in the H− and D− states, where the correlation of two localized electrons greatly reduces the Coulomb repulsion [14]. The electron-pair state localizes closely to the positive charge of the nucleus and does not form a valence with other atoms. In contrast, bonding (and antibonding) states originating from the single-electron states are fundamental to the formation of a molecule. It is well known that in a crystal the single-electron energy levels of periodically organized individual atoms form energy bands. Then the question is, when those basic quantum units with strongly correlated electron pairs are organized into a periodic structure such as a crystal or a superlattice, where are the corresponding quantum states of the electron pairs? Generally, one believes that, due to strong electron–electron repulsion, these localized states of individual electron pairs cannot survive in a periodic crystal or a superlattice. In the following we show that there may exist a metastable energy
band of electron pairs in a 2D crystal resulting from the electron–electron Coulomb interaction a periodic potential.

2. Theoretical formulation

Our idea is to try to find out the counterpart of the individual H⁻ (or D⁻) electron-pair states in 2D periodic potential. First of all, we should remember that in 2D the energy of a neutral H atom (with a single electron) is \( E_{\text{H}} = -4.8 R_y \) and that of a H⁻ (with two electrons) is \( E_{\text{H}^-} = -4.48 R_y \) \([15, 17]\). It means that an isolated H⁻ is more stable than a single H atom plus one free electron of zero energy (which is the reference for energy). The energy difference of \(-0.48 R_y\) is the binding energy of the H⁻ state in 2D. However, if we consider many H⁻ or many D⁻ centers (for example, periodically organized) in a system, the measure should be the total energy of the system, or equivalently, the average energy per electron. Then the energy difference between the H⁻ and H states in 2D is given by \( E_{\text{H}^-}/2 - E_{\text{H}} = -4.48/2 + 4 = 1.76 R_y \). This indicates that in this case the H⁻ state is of higher energy than the H state.

We intend to calculate the two-electron states in a periodic potential. For simplicity, we consider a 2D periodic potential. For two non-interacting single particles separated by an infinitely large distance, the average energy per electron is finite. Therefore, we intend to solve the relevant two-electron Hamiltonian becomes \( H = -\frac{1}{2} \nabla_r^2 - 2V + 2V_0[\cos(qX) \cos(qY/2)] \). This Hamiltonian is periodic in \( X \) and \( Y \) with period \( \lambda \).

We solve equation (7) as a function of \( \beta \) looking for local minima in the lowest eigenvalue. The parameter \( \beta \) plays an important role when solving this equation because it determines the average distance between the two electrons \( \langle r \rangle \). For fixed \( \beta \) we can obtain a full set of eigenvalues and eigenfunctions. Consequently, the average distance \( \langle r \rangle \) between the two electrons can be calculated. The eigenvalue of equation (7) has to converge upon increasing the size of the matrix up to a maximum \( n = n_{\text{max}} \) and maximum \( l_x = l_y = l_{\text{max}} \). We find that, for fixed period \( \lambda \), the lowest eigenvalue of the two coupled electrons in the 2D periodic

\[
\psi_{l_x, l_y; n, m}(R, r) = \frac{1}{\sqrt{A}} e^{(k + G_l) \cdot R} R_{n, m}(r)\phi_m(\theta),
\]

with

\[
R_{n, m}(r) = \beta c_{n, m}(\beta \lambda r)^m e^{-\beta \lambda r} L_{2m}^m(2\beta \lambda r),
\]

and

\[
\phi_m(\theta) = \frac{1}{\sqrt{\sqrt{\beta^2 m^2 + \lambda^2}}} \cos(m\theta),
\]

where \( n = 0, 1, 2, \ldots, m = 0, 1, 2, \ldots, n \).

Considering the antisymmetry of the electron wavefunctions with spin states, we find that the two-electron wavefunctions of the singlet and triplet states are given by the above expression with the sum over even and odd \( m \) only, respectively. Here we are especially interested in the singlet states.

Using equations (1), (2), and (6) we obtain the matrix eigenvalue equation

\[
\sum_{l_x, l_y} \sum_{n, m} a_{l_x, l_y; n, m}(k) \psi_{l_x, l_y; n, m}(R, r) = E_{\text{pair}}(l_x, l_y; n, m)(k) \]

3. Numerical results and analysis

We solve equation (7) as a function of \( \beta \) looking for local minima in the lowest eigenvalue. The parameter \( \beta \) plays an important role when solving this equation because it determines the average distance between the two electrons \( \langle r \rangle \). For fixed \( \beta \) we can obtain a full set of eigenvalues and eigenfunctions. Consequently, the average distance \( \langle r \rangle \) between the two electrons can be calculated. The eigenvalue of equation (7) has to converge upon increasing the size of the matrix up to a maximum \( n = n_{\text{max}} \) and maximum \( l_x = l_y = l_{\text{max}} \). We find that, for fixed period \( \lambda \), the lowest eigenvalue of the two coupled electrons in the 2D periodic
potential develops a local minimum when $V_0$ is larger than a certain value. Figure 1(a) shows the two lowest eigenvalues of spin singlet states at $\mathbf{k} = 0$ (the $\Gamma$ point) as a function of $\beta$ for $\lambda = 1.5$ a$_0$ and $V_0 = 12$, 15, and 18 R$_0$. These curves converge at $n_{\text{max}} = 8$ and $l_{\text{max}} = 4$ within an error of $10^{-3}$. We have checked the calculations for very large $n$ and the obtained results do not basically change. For small $\beta$ the eigenvalues are almost zero because the two electrons are bound. Upon increasing $\beta$ the eigenvalues are almost zero because the two electrons are pushed into the nearest-neighbor unit cells, as it can be deduced from figure 1(c). In this case a local minimum is found where the two electrons is greatly enhanced. The eigenvalue of the electron pair increases as well. As $\beta$ decreases, the radial probability density becomes broader and the corresponding eigenvalue increases. In contrast, with increasing $\beta$ from $\beta_0$, $\langle r \rangle$ first decreases until a minimum value $\langle r \rangle_{\text{min}}$ is reached, where we obtain the narrowest radial probability density and the Coulomb repulsion between the two electrons is greatly enhanced. The eigenvalue of the electron pair increases as well. As $\beta$ increases further, one of the electrons is pushed into the nearest-neighbor unit cells, as it can be deduced from figure 1(c). In this case a local maximum in the lowest eigenvalue appears where the two lowest eigenvalues approach each other.

![Figure 1](image)

Figure 1. (a) The two lowest eigenvalues of spin singlet states at $\mathbf{k} = 0$ as a function of $\beta$ for $\lambda = 1.5$ a$_0$, $V_0 = 12$, 15, and 18 R$_0$. The solid (dotted) curves indicate the lowest (second lowest) eigenvalue. (b) The average distance $\langle r \rangle$ between the two electrons as a function of $\beta$ for $\mathbf{k} = 0$, $\lambda = 1.5$ a$_0$ and $V_0 = 15$ R$_0$. (c) The electron radial probability densities in relative coordinates for different $\beta$ given in the inset (the corresponding $\langle r \rangle$ are shown in (b) by the dots). (d) A diagram in the ($V_0$, $\lambda$) plane showing where a metastable state of an electron pair exists. $\Gamma$, X and M indicate different points in the first Brillouin zone.

We understand this metastable state as a manifestation in the periodic potential of the electron-pair states existing in some individual atoms or ions, [13, 14], such as the negative hydrogen ion $\text{H}^-$. It is the result of strong electron–electron correlations and local confinement in each unit cell of the 2D crystal potential. The metastable state appears when the potential amplitude $V_0$ is larger than a certain value for a fixed period $\lambda$. In figure 1(d) we show in the ($V_0$, $\lambda$) plane where this metastable electron pair can appear. We find that at the M points ($k_x = \pm q/2$, $k_y = \pm q/2$) this local minimum appears at smaller $V_0$ ($\lambda$) than at the $\Gamma$ point for a fixed $\lambda$ ($V_0$). It means that a pair of short wavelengths is easier to form than that of long wavelengths in the crystal. For smaller $V_0$ (or $\lambda$), this metastable state cannot survive when the Coulomb repulsion

![Figure 1](image)
metastable pair at the 0 point with a separation much less than the lattice period. To the two paired electrons being closely bound in real space, their difference will be shown in the next figure. Similarity between dispersion relations of the single-electron band. Their difference is given by its value divided by two, i.e., the energy per electron. The electron-pair band remains above the lowest single-electron band. Their difference will be shown in the next figure. Similarity between dispersion relations of the electron-pair band and the lowest single-electron band is due to the two paired electrons being closely bound in real space, with a separation much less than the lattice period.

In figure 3(a) we plot the energy per electron of the metastable pair at the $\Gamma$ point ($E_\text{pair}^\text{MP} / 2$) as a function of $V_0$ for different $\lambda$. We also show the maximum energy $E^\text{single}_M$ at the M point of the lowest single-electron band. We define the difference between these two energies as an energy gap, $E_g = E_\text{pair}^\text{MP} / 2 - E^\text{single}_M$, and plot it in figure 3(b). The energy gap $E_g$ is typically a few $R_y$.

### 4. Discussion and summary

So far we have obtained the single-particle states in the system as shown in figure 2, i.e., the single-electron and single-electron-pair states. For a 2D periodic potential of given $V_0$ and $\lambda$, we can obtain the energy and wavefunction of the electron pair, and consequently, the pair–pair and pair–electron (and pair–hole) interaction potential can also be calculated. In the following, we will consider the case in which many electrons are presented in the system. We assume the lowest single-electron band as the valence band with an electron filling factor $n_e$. For $n_e < 1$ we can understand that holes are presented in the valence band with a hole filling factor $n_h = 1 - n_e$. When electrons appear in the electron-pair band, we reach a many-particle system consisting of electron pairs in the $\Gamma$ valley of the electron-pair band and holes in the M valleys of the valence band. Many-particle interactions renormalize the total energy of the system and also reduce the energy gap $E_g$. If the band-gap renormalization due to electron-pair and hole interactions leads to a negative energy gap, in other words, if the renormalized $\Gamma$ valley of the electron-pair band becomes lower than the renormalized M valley of the valence band, the electron pairs in the $\Gamma$ valley can become stable. Band-gap renormalization (BGR) has been extensively studied in nonlinear optics of semiconductors, where one deals with an electron–hole plasma. In this case, the BGR is given by a sum of electron and hole self-energies and is a function of the interparticle distance $r_s$ and temperature [20, 21]. In a 2D electron–hole system at zero temperature, for instance, the BGR is about 8 $R_y$ at $r_s = 1$ [20]. For a high-density electron–hole plasma, the BGR is mainly induced by the Coulomb repulsion among the particles (the Coulomb hole effect). The mechanism of the BGR in our present electron-pair–hole system should be similar. Therefore, we believe that the BGR in our system should be of similar value to that in the electron–hole plasma. The metastable electron pairs can be stabilized in a many-particle system. This is a task for our future study.

On the other hand, the boson–fermion model [2, 3, 22], as well as two-dimensional charged boson fluids [23] with artificially introduced bosons considered as point charges, have been extensively studied over the past few decades. From the electron-pair (boson) states obtained in this work, we can calculate the pair–pair and pair–hole interaction potentials. Consequently, one can study the ground-state properties of the present narrow-gap and multi-valley boson–fermion system with electron pairs and holes. The progress is that now the bosons (i.e., the electron pairs) are obtained from the crystal band structure and are not point charges.

In conclusion, we have obtained an electron-pair energy band in a two-dimensional crystal. The electron-pair states are metastable in the absence of other electrons in the system. The two correlated electrons are bound in the same unit cell in relative coordinates with an average separation of approximately $1/3$ of the period $\lambda$ of the crystal potential. Furthermore, we have discussed the possibility that the electron pairs can be stabilized in a many-particle system with...
electron pairs and holes. From this point of view, the present work could provide an interesting platform for studying 2D charged boson–fermion fluids. The present calculations can also be carried out for a three-dimensional system.

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