

# Relaxation of atomic orbitals and electron-electron interactions in crystals

B. A. Volkov and S. V. Sharov

*P. N. Lebedev Institute of Physics, USSR Academy of Sciences*

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We consider the effect of relaxation of atomic orbitals associated with the intra-atomic Coulomb interactions between valence electrons. We show that inclusion of this effect within the framework of the single-band approximation leads to the appearance of a term  $f a_{i,\sigma}^+ a_{j,\sigma} (\hat{n}_{i,-\sigma} + \hat{n}_{j,-\sigma})$  in the Hamiltonian. The magnitude of the parameter  $f$  is determined by the Hubbard matrix element  $U$  and the overlap integral  $S$ , and its sign coincides with the sign of the amplitude of single-particle interatomic transitions. We discuss certain properties of the resulting Hamiltonian.

## 1. INTRODUCTION

At this time, ongoing discussions of various aspects of high-temperature superconductivity have lent a special urgency to the study of the detailed structure of the Coulomb electron-electron interaction in crystals. This interaction determines the insulating and magnetic properties of the compounds  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , which within the framework of standard band theory should be metals;<sup>1</sup> it is in fact the basis of Anderson's hypothesis regarding resonating valence bonds;<sup>2</sup> and finally, according to Hirsch,<sup>3</sup> it can lead to a phononless mechanism for superconductivity in hole-based metals according to the BCS scheme.

The simplest model used to describe the properties of interacting electrons is the Hubbard model.<sup>4</sup> This model treats the case of a hypothetical nondegenerate band containing  $n$  electrons per atom ( $n \leq 2$ ) which interact only when they are located on the same lattice site in the crystal. In its standard form, the Hubbard Hamiltonian can be written

$$\hat{H} = \sum_{i,j,\sigma} t_{ij} c_{i,\sigma}^+ c_{j,\sigma} + U \sum_{i,\sigma} \hat{n}_{i,\sigma} \hat{n}_{i,-\sigma}, \quad (1)$$

where  $c_{i,\sigma}^+$  ( $c_{j,\sigma}$ ) are creation (annihilation) operators for an electron at the  $i$ th site with spin  $\sigma$  ( $\sigma = \pm 1/2$ ), and  $\hat{n}_{i,\sigma} = c_{i,\sigma}^+ c_{j,\sigma}$  is the number operator for electrons at the  $i$ th site with spin  $\sigma$ . The matrix elements  $t_{ij}$  and  $U$  are calculated using atomic wave functions;<sup>4</sup> the former, which are amplitudes for intersite transitions, are matrix elements of the crystal potential, while

$$U = \langle i, \sigma; i, -\sigma | \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} | i, \sigma; i, -\sigma \rangle$$

is the matrix element of the intrasite Coulomb electron-electron interaction.

Usually, the Hubbard Hamiltonian is sufficient to describe dielectric and magnetic properties or resonating valence bonds. However, Hirsch<sup>3</sup> has shown that including the matrix elements of the electron-electron interaction in the form

$$V_H = \langle i, i | \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} | i, j \rangle$$

can lead to a qualitatively new effect. The Hirsch correction to the Hamiltonian (1) can be written in the form

$$\sum_{i,j,\sigma} V_H (\hat{n}_{i,-\sigma} + \hat{n}_{j,-\sigma}) c_{i,\sigma}^+ c_{j,\sigma}. \quad (2)$$

Such a term in the Hamiltonian describes a change in the amplitude of the intercenter transition ( $i \rightleftharpoons j$ ) due to the action of the Coulomb potential created by electrons that already occupy these centers. It is important that the Coulomb potential is repulsive, whereas the amplitude of the direct intersite transition  $t_{ij}$  is calculated from the attractive crystal potential. From this it follows that interactions of the form (2) interfere with  $t_{ij}$ , leading to a decrease in the total amplitude of the intercenter transitions, and consequently to a shrinking of the band as the electron density increases. From similar considerations it follows that the energies of electronic states located in the top half of the band will decrease with increasing electron density. This fact also led Hirsch to the conclusion that in a hole-based metal there exists a Coulomb mechanism for electron-electron interactions which can lead to an instability of Cooper type without phonons.

In this paper we wish to discuss an effect which leads to a new type of electron-electron interaction. The essence of this effect may be described as follows. Because of the Coulomb repulsion, the energy of valence electrons at a given crystal lattice site depends on their number, i.e., the more electrons found on a given site, the higher their energies and consequently the larger the radii of the wave functions of these electrons. This broadening of the wave functions in turn implies that there is an increase in the overlap integrals for electron wave functions on neighboring sites; consequently, the tunneling probability for these sites increases. From this we see that the amplitude of intersite transitions depends on the occupation numbers of these sites. We see here a certain similarity between this effect and the effect described by Hirsch. However, in our case the energy band widens. In what follows we will show that for the case of a sufficiently narrow band the effect of broadening of the orbitals dominates, thanks to the exponential dependence of the matrix elements for intercenter transitions on the orbital radius.

It is necessary to emphasize that this effect is wholly due to the intra-atomic interaction, and therefore is determined by the Hubbard matrix element  $U$ . Nevertheless, it cannot be obtained within the framework of the representations developed in Refs. 3 and 4, i.e., from investigating the various matrix elements for electron-electron scattering, which are determined by the atomic wave functions.

The goal of this paper is to include the effect of orbital relaxation in terms of second quantization operators, and also to discuss several properties of the Hamiltonian (13). We note that the authors of Refs. 5 and 6 did indicate the importance of including changes in the wave functions when electrons are added or subtracted. However, these authors did not discuss effects associated with changes in the wave function overlaps of neighboring atoms.

Our subsequent discussions will be based on a many-body Hamiltonian for interacting valence electrons moving in a periodic pseudopotential field. In order to clarify the physics of this situation, and also to obtain quantitative results, we will first investigate the case of a one-dimensional crystal with a pseudopotential in the form of a set of  $\delta$ -functions. The results obtained in this way are easily generalized to the case of a nondegenerate band in a three-dimensional lattice.

The plan of this article is as follows: in Sec. 2 we describe the pseudopotential model, and discuss the properties of the single-particle spectrum. In Sec. 3, we consider the interaction and set up the second-quantized Hamiltonian. In Sec. 4, the results we obtain are generalized to the case of a simple three-dimensional lattice. Section 5 is devoted to a discussion of several properties of the new Hamiltonian.

## 2. MODEL PSEUDOPOTENTIAL AND PROPERTIES OF THE SINGLE-PARTICLE SPECTRUM

As we have already said, correlations caused by orbital relaxation effects are not described by matrix elements of the Coulomb interaction determined by a set of atomic wave functions from different sites. Generally speaking, in order to include this effect properly it is necessary to use exact wave functions for all values of the energy. Therefore, it is convenient to begin with a model in which the states and the spectrum of the Hamiltonian can be calculated exactly. We will investigate the model of a one-dimensional crystal with pseudopotentials for the atomic states in the form of  $\delta$ -functions. Note that the model with  $\delta$ -function-like potentials can be solved exactly in the three-dimensional case as well.<sup>7</sup> The Schroedinger equation for the valence electrons has the form

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + D \sum_{l=-\infty}^{\infty} \delta(x-la) \Psi = E\Psi, \quad (3)$$

where  $D < 0$  characterizes the depth of the pseudopotential well, and  $a$  is the spacing between neighboring wells. It is convenient to rewrite (3) in the following form:

$$\frac{d^2\Psi}{dx^2} + g \sum_l \delta(x-la) \Psi = -\varepsilon \Psi, \quad (4)$$

where

$$g = -\frac{2m}{\hbar^2} D > 0, \quad \varepsilon = \frac{2m}{\hbar^2} E.$$

Since the bound state of a  $\delta$ -function potential has the form  $\exp(-\kappa|x|)$ , we seek the wave function in the form of a superposition of such bound states:

$$\Psi_k(x) = \sum_{l=-\infty}^{\infty} \exp(ikla) \exp(-\kappa|x-la|), \quad (5)$$

where  $\kappa$  is determined from the condition that the function (5) satisfy Eq. (4). Despite a superficial similarity between  $\Psi_k(x)$  and the wave function which follows from the tight-binding method, there is a significant difference between them: in this case,  $\kappa$  depends on  $k$ . Substituting (5) into (4), we obtain

$$\varepsilon = -\kappa^2, \quad (6)$$

$$\kappa = g \left[ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(kla) \exp(-\kappa la) \right].$$

For large  $a$  such that  $ga \gg 1$  (the case of a narrow band), Eq. (6) can be solved by the method of successive approximations. In the zeroth approximation we have  $\kappa = g/2$ ,  $\varepsilon = -g^2/4$ , while in the first approximation we have

$$\kappa = g \left[ \frac{1}{2} + \exp\left(-\frac{ga}{2}\right) \cos ka \right], \quad (7)$$

$$\varepsilon = -\frac{g^2}{4} - g^2 \exp\left(-\frac{ga}{2}\right) \cos ka.$$

Equation (7) corresponds to the tight-binding approximation. We limit ourselves to this order of accuracy; the wave functions corresponding to energies  $\varepsilon > 0$  can be obtained from (5) by analytic continuation of  $\kappa$  onto the imaginary axis. Substituting these functions into (4), we obtain the following dispersion relation:

$$\varepsilon = \kappa^2, \quad (8)$$

$$2\kappa (\cos \kappa a - \cos ka) = g \sin \kappa a.$$

It is easy to see that (8) is obtained from (6) if we make the replacement  $\kappa \rightarrow i\kappa$  in the latter. Equation (6) gives a set of energy bands; the allowed bands are determined from the condition

$$|2\kappa \cos \kappa a - g \sin \kappa a| \leq |\kappa|.$$

The expressions given above imply that for sufficiently large values of the parameter  $ga$  the wave function of the lowest band is given by Eq. (5) with  $\kappa$  a real quantity for all  $k$  ( $|k| \leq \pi/a$ ). However, if  $ga < 1$  holds, for  $k$  larger than a certain  $k_0$  the quantity  $\kappa$  becomes imaginary. This implies that the energy  $\varepsilon = 0$  now lies in the lowest band. From (8) it is easy to obtain an equation for  $k_0$ :

$$ga/4 = \sin^2(k_0 a/2).$$

From this it is clear that for  $ga/4 > 1$  the energy of the lowest band is always negative, and  $\kappa$  is a real quantity for all  $k$ . The properties of electrons from this band will be of interest to us in what follows.

Let us now incorporate the Coulomb interaction between electrons. Since electrons moving in a narrow band spend a large part of their time on sites of the crystal lattice, while the Coulomb potential is strongly overscreened, we can assume that the electrons interact only when they are located on the same site. Such an interaction can be treated within the mean-field theory, if we introduce the following effective potential into (3):

$$\bar{U} \langle n \rangle \sum_l \delta(x-la),$$

where  $\langle n \rangle$  is the average number of electrons with opposite

spin on a given site. Now it is easy to trace how the energy spectrum changes as we vary  $\tilde{U}$ . The introduction of this effective potential implies that  $g$  in Eq. (4) changes by an amount  $u\langle n \rangle$ , where  $u = (2m/\hbar^2)\tilde{U}$ . Then for  $u \ll g$  we obtain from (7)

$$\begin{aligned} \varepsilon &= -\frac{(g-u\langle n \rangle)^2}{4} - (g-u\langle n \rangle)^2 \exp\left(-\frac{ga}{2}\right) \exp\left(\frac{u\langle n \rangle a}{2}\right) \cos ka \\ &\approx -\frac{g^2}{4} + \frac{g}{2} u\langle n \rangle - g^2 \exp\left(-\frac{ga}{2}\right) \\ &\quad \times \left(1 - \frac{2u}{g}\langle n \rangle + \frac{u}{2g}\langle n \rangle ga\right) \cos ka. \end{aligned} \quad (9)$$

This equation implies first of all that the average electron energy is increased by  $1/2gu\langle n \rangle$ , and secondly that the width of the band becomes equal to

$$g^2 \exp\left(-\frac{ga}{2}\right) \left(1 - \frac{2u}{g}\langle n \rangle + \frac{u}{2g}\langle n \rangle ga\right).$$

Since  $ga \gg 1$  holds for a narrow band, the width of the band increases. Eq. (9) provides a striking illustration of the two competing tendencies mentioned in the Appendix: the width of the band is determined both by the pre-exponential factor and the overlap integral. On the one hand, the interaction leads to a decrease in the pre-exponential factor; on the other hand, it increases the overlap integral. For a sufficiently narrow band the second tendency will always dominate (irrespective of the dependence on the magnitude of the interaction energy).

### 3. THE TWO-PARTICLE POINT INTERACTION WITHIN THE MODEL OF A ONE-DIMENSIONAL CRYSTAL

Let us now turn to a more correct treatment of the electron-electron interaction. For the reasons described above, we can assume that the electrons interact only when they are located on one and the same site in the crystal. Therefore we can introduce the following two-particle potential for the Coulomb repulsion:

$$\hat{H}_{int} = \frac{U}{2} \sum_{a \neq b} \sum_{m=-\infty}^{+\infty} \delta(x_a - ma) \delta(x_b - ma). \quad (10)$$

Here  $a$  and  $b$  take on values from unity up to  $N_0$ , where  $N_0$  is the number of valence electrons. Let us write the interaction operator (10) in second-quantized representation. In the quasimomentum representation, the matrix elements have the form

$$\begin{aligned} V_{k_1 k_2 k_3 k_4} &= \frac{1}{2} \int dx_1 dx_2 \Psi_{k_1}^*(x_1) \Psi_{k_2}^*(x_2) V(x_1, x_2) \Psi_{k_3}(x_1) \Psi_{k_4}(x_2), \end{aligned} \quad (11)$$

where

$$V(x_1, x_2) = U \sum_m \delta(x_1 - ma) \delta(x_2 - ma).$$

Then using the condition

$$\Psi_k(ma) = \exp(ikma) \Psi_k(0),$$

we find

$$V_{k_1 k_2 k_3 k_4} = \frac{1}{2} UN \delta(k_1 + k_2 - k_3 - k_4) \Psi_{k_1}^*(0) \Psi_{k_2}^*(0) \Psi_{k_3}(0) \Psi_{k_4}(0). \quad (12)$$

The interaction operator is conventionally divided into three groups of operators. In the first group we include operators that describe transitions within the lowest band, in the second operators which mix the states of the upper bands, and in the third operators corresponding to transitions from the lowest band to the upper bands and conversely. The corresponding groups have the form

$$\begin{aligned} \hat{H}_1 &= \frac{UN}{2} \sum_{\substack{k_1, k_2, k_3, k_4 \\ \sigma, \sigma'}} \delta(k_1 + k_2 - k_3 - k_4) \\ &\quad \times \Psi_{0k_1}^*(0) \Psi_{0k_2}^*(0) \Psi_{0k_3}(0) \Psi_{0k_4}(0) \\ &\quad \times a_{k_1, \sigma}^+ a_{k_2, \sigma'}^+ a_{k_3, \sigma} a_{k_4, \sigma'} \end{aligned} \quad (13)$$

$$\begin{aligned} \hat{H}_2 &= \frac{UN}{2} \sum_{\substack{k_1, k_2, k_3, k_4 \\ n_1, n_2, n_3, n_4 \\ \sigma, \sigma'}} \delta(k_1 + k_2 - k_3 - k_4) \Psi_{n_1 k_1}^*(0) \Psi_{n_2 k_2}^*(0) \\ &\quad \times \Psi_{n_3 k_3}(0) \Psi_{n_4 k_4}(0) \\ &\quad \times c_{n_1 k_1, \sigma}^+ c_{n_2 k_2, \sigma'}^+ c_{n_3 k_3, \sigma} c_{n_4 k_4, \sigma'} \end{aligned} \quad (14)$$

$$\begin{aligned} \hat{H}_3 &= \frac{UN}{2} \sum_{\substack{k_1, k_2, k_3, k_4 \\ \sigma, \sigma'}} \delta(k_1 + k_2 - k_3 - k_4) \\ &\quad \times \left\{ \sum_n (\Psi_{0k_1}^*(0) \Psi_{0k_2}^*(0) \Psi_{0k_3}(0) \Psi_{nk_4}(0) \right. \\ &\quad \times a_{n k_1, \sigma}^+ a_{n k_2, \sigma'}^+ c_{n k_3, \sigma} a_{n k_4, \sigma'} + \Psi_{0k_1}^*(0) \Psi_{0k_2}^*(0) \Psi_{n k_3}(0) \Psi_{0k_4}(0) a_{n k_1, \sigma}^+ a_{n k_2, \sigma'}^+ \\ &\quad \times a_{n k_3, \sigma} c_{n k_4, \sigma'} + \text{h.c.}) + \sum_{n, n'} \Psi_{0k_1}^*(0) \Psi_{0k_2}^*(0) \Psi_{n k_3}(0) \Psi_{n' k_4}(0) \\ &\quad \times a_{k_1, \sigma}^+ a_{k_2, \sigma'}^+ c_{n' k_4, \sigma} c_{n k_3, \sigma'} + \dots \left. \right\}. \end{aligned} \quad (15)$$

Here  $a^+(a)$ ,  $c_n^+(c_n)$  are operators for creation (annihilation) of electrons in the lowest band and in the  $n$ th upper band, respectively.

We assume that there are  $n < 2$  valence electrons per atom of the crystal. Then in the absence of interactions the upper bands are found to be empty, and the lower band is only partly filled. Therefore, if the interaction energy  $U$  is small compared to the size of the forbidden band, to first order in  $U$  we can neglect the admixture to the wave function of states from the upper bands. This implies that in a first approximation we should set  $\hat{H}_3 = 0$ . Nevertheless, it is clear from Eq. (9) that there is a contribution to the energy of the lowest band associated with the effect of broadening of the orbitals even to first order in the interaction energy. Consequently, in including this effect it is sufficient to consider the intraband transitions described by the operator  $\hat{H}_1$ .

Let us calculate the matrix elements of these transitions using the exact wave functions (5). It is important that the matrix elements are determined by normalized wave functions. The corresponding normalization constants have the form

$$c_k^2 = \frac{1}{N} \left[ S(0) + 2 \sum_m S(m) \cos kma \right]^{-1}, \quad (16)$$

where

$$S(m) = \int_{-\infty}^{\infty} dx \exp[-\kappa(k)|x|] \exp[-\kappa(k)|x - ma|].$$

For the case of a narrow band, i.e., neglecting all the  $S(m)$

with  $m \geq 2$ , we obtain the following expression for  $\Psi_{0k}(0)$ :

$$\Psi_{0k}(0) = \frac{2}{g} \frac{x^h(k)}{N^{1/2} \{1 + 2[1 + \kappa(k)a] \exp[-\kappa(k)a] \cos ka\}^{1/2}}. \quad (17)$$

Then the matrix elements for the intraband transitions have the form

$$V_{k_1 k_2 k_3 k_4} = \frac{U}{2N} \left(\frac{2}{g}\right)^4 \times \prod_{i=1}^4 \frac{x^h(k_i) \delta(k_1 + k_2 - k_3 - k_4)}{\{1 + 2[1 + \kappa(k_i)a] \exp[-\kappa(k_i)a] \cos k_i a\}^{1/2}}. \quad (18)$$

Calculating  $V_{k_1 k_2 k_3 k_4}$  to order  $[\exp(-ga/2)]^2$  [see (7)], we obtain

$$V_{k_1 k_2 k_3 k_4} = \frac{U}{8N} g^2 \delta(k_1 + k_2 - k_3 - k_4) \times \left[1 + \left(2 - \frac{ga}{2}\right) \exp\left(-\frac{ga}{2}\right) \sum_{i=1}^4 \cos k_i a\right]. \quad (19)$$

In what follows it will be convenient to change from the quasi-momentum representation to the site representation. The matrix elements are related in the following way:

$$V_{ijkl} = \frac{1}{N^2} \sum_{k_1 k_2 k_3 k_4} V_{k_1 k_2 k_3 k_4} \exp[i(k_1 x_i + k_2 x_j - k_3 x_l - k_4 x_k)], \quad (20)$$

where  $x_i = ia$ , etc.

As a final result, we obtain the following expression for the operator  $\hat{H}_1$ :

$$\hat{H}_1 = \frac{Ug^2}{8} \sum_{i\sigma} \hat{n}_{i,\sigma} \hat{n}_{i,-\sigma} + \frac{Ug^2}{4} \left(1 - \frac{ga}{4}\right) \exp\left(-\frac{ga}{2}\right) \times \sum_{i\sigma} (a_{i+1,\sigma}^+ a_{i,\sigma} \hat{n}_{i,-\sigma} + \hat{n}_{i+1,-\sigma} + \text{h.c.}). \quad (21)$$

The first term in (21) corresponds to the Hubbard interaction, while the second describes intercenter transitions mediated by the Coulomb repulsion. In this case, the amplitude of these transitions consists of two contributions. The positive contribution  $(Ug^2/4) \exp(-ga/2)$  we associate with the processes investigated by Hirsch in Ref. 3. However, the negative contribution

$$(-1) \frac{Ug^2}{4} \frac{ga}{4} \exp\left(-\frac{ga}{2}\right)$$

reflects the fact that the Coulomb repulsion at one center increases the overlap integral with the wave functions of the neighboring atoms. Since  $ga \gg 1$  holds for the case of a narrow band, the sign of the total amplitude is negative. This interpretation of the various terms becomes especially obvious if we examine the resulting Hamiltonian within Hartree-Fock theory. Replacing the operator  $n$  by its average value, and taking into account that

$$u = \frac{Ug}{2} = \frac{g}{2} \int \exp\left(-\frac{g|x|}{2}\right) U \delta(x) \exp\left(-\frac{g|x|}{2}\right) dx,$$

we obtain the following expression for the width of the band

$$g^2 \exp\left(-\frac{ga}{2}\right) \left(1 - \frac{2u}{g} \langle n_{-\sigma} \rangle + \frac{u}{2g} \langle n_{-\sigma} \rangle ga\right),$$

which coincides exactly with (9).

The matrix elements entering into the single-band Hamiltonian (21) must be regarded as bare electron-electron scattering amplitudes. Inclusion of transitions to the upper bands leads to their renormalization; it then follows from the results obtained in Sec. 2 that the amplitude corresponding to orbital relaxation takes the form

$$g^2 \exp\left(-\frac{ga}{2}\right) [1 - \exp(gUa)].$$

This behavior is due to the exponential dependence of the overlap integral on energy. The change in the other components of the total scattering amplitude is insignificant.

In concluding this section, let us discuss why the orbital relaxation effect was not included by the authors of Refs. 3 and 4. The fact is that the approximations used in these papers by the authors to calculate the bare matrix elements were too crude; to be specific, the exact Wannier functions were replaced by atomic orbitals in these calculations. Here, however, we have in fact included the difference between Wannier functions and atomic wave functions. In fact, if we neglect the dependence of  $\kappa$  on  $k$  ( $ga \rightarrow \infty$ ), the wave function will have the form

$$\Psi_{0k}(x) = \left(\frac{g}{2N}\right)^{1/2} \Gamma \left[1 + ga \exp\left(-\frac{ga}{2}\right) \cos ka\right]^{-1/2} \times \sum_m \exp(ikma) \exp\left(-\frac{g}{2}|x - ma|\right). \quad (22)$$

Even in this case,  $\Psi_k(x)$  differs from the wave function given by the tight-binding method due to the additional dependence on the quasimomentum  $k$ . To order  $[\exp(-ga/2)]^2$ , the Wannier function has the form

$$\Phi(x) = \frac{1}{N^{1/2}} \sum_k \Psi_k(x) \approx \left(\frac{g}{2}\right)^{1/2} \left\{ \exp\left(-g \frac{|x|}{2}\right) - \frac{ga}{4} \exp\left(-\frac{ga}{2}\right) \left[ \exp\left(-\frac{g}{2}|x-a|\right) + \exp\left(-\frac{g}{2}|x+a|\right) \right] \right\}, \quad (23)$$

i.e., it differs from the atomic function  $(g/2)^{1/2} \exp(-1/2g|x|)$ .

#### 4. GENERALIZATION OF THE RESULTS TO THE CASE OF A THREE-DIMENSIONAL LATTICE

All the results obtained above are specific to the simplest model of a one-dimensional crystal with a special type of atomic pseudopotential and a special type of interaction between the electrons. In this section, however, we consider the case of a nondegenerate band in a cubic crystal, and we assume that the interaction between valence electrons is the usual Coulomb interaction.

The matrix element for the Coulomb interaction in the site representation has the form

$$\begin{aligned} \langle i, j | V(\mathbf{r}_1 - \mathbf{r}_2) | kl \rangle &= \int \Phi^*(\mathbf{r}_1 - \mathbf{R}_i) \Phi^*(\mathbf{r}_2 - \mathbf{R}_j) V(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &\times \Phi(\mathbf{r}_1 - \mathbf{R}_k) \Phi(\mathbf{r}_2 - \mathbf{R}_l) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (24)$$

where  $\Phi(\mathbf{r})$  is the Wannier function for that band and  $\mathbf{R}$  is a translation vector.

Thus, in order to calculate the matrix elements it is necessary to determine the corresponding Wannier functions. This is easy to do within the approximation discussed above. Specifically, let us assume that the overlap integrals between neighboring atoms are small, and use a representation of the wave functions analogous to (22). Then the Wannier function has the form

$$\Phi(\mathbf{r}) = \Psi(\mathbf{r}) - S \sum_{\mathbf{R}_1} \Psi(\mathbf{r} - \mathbf{R}_1), \quad (25)$$

where  $\Psi(\mathbf{r})$  is a normalized atomic wave function,

$$S = \int \Psi^*(\mathbf{r}) \Psi(\mathbf{r} - \mathbf{R}_1) d\mathbf{r}$$

is the overlap integral between orbitals of nearest neighbors, and  $\mathbf{R}_1$  is a translation vector to a nearest-neighbor site. Substituting Eq. (25) into Eq. (24), we obtain the relation between the site matrix element and the atomic matrix element. Then the Hubbard matrix element acquires the form

$$\begin{aligned} \langle i, i | V(\mathbf{r}_1 - \mathbf{r}_2) | i, i \rangle = & \int |\Psi(\mathbf{r}_1)|^2 V(|\mathbf{r}_1 - \mathbf{r}_2|) |\Psi(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ & - 2S \left( \sum_{\mathbf{R}_1} \int \Psi(\mathbf{r}_1 - \mathbf{R}_1) \Psi^*(\mathbf{r}_1) V \right. \\ & \left. \times (|\mathbf{r}_1 - \mathbf{r}_2|) |\Psi(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 + \text{c.c.} \right). \quad (26) \end{aligned}$$

Here we have omitted terms of higher order in  $S$ . However, it should be noted that the second term in (26) is of order  $S^2$ , since the integral entering into it contains an additional factor of the orbital overlap. Consequently, this term may be neglected. It is easy to verify that there is only one matrix element that contains a correction linear in  $S$ . It has the form

$$\langle i, i | V(\mathbf{r}_1 - \mathbf{r}_2) | i, j \rangle,$$

where  $i$  and  $j$  are nearest-neighbor sites. In fact, to order  $S^2$  we have

$$\begin{aligned} \langle i, i | V(\mathbf{r}_1 - \mathbf{r}_2) | i, j \rangle = & \int |\Psi(\mathbf{r}_1)|^2 V(|\mathbf{r}_1 - \mathbf{r}_2|) \Psi^*(\mathbf{r}_2) \Psi(\mathbf{r}_2 - \mathbf{R}_1) d\mathbf{r}_1 d\mathbf{r}_2 \\ & - S \int |\Psi(\mathbf{r}_1)|^2 |\Psi(\mathbf{r}_2 - \mathbf{R}_1)|^2 V(|\mathbf{r}_1 - \mathbf{r}_2|) d\mathbf{r}_1 d\mathbf{r}_2 \\ & - S \int |\Psi(\mathbf{r}_1)|^2 V(|\mathbf{r}_1 - \mathbf{r}_2|) |\Psi(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2. \quad (27) \end{aligned}$$

The integral entering into the second term on the right side of (27) contains an additional small factor due to the falloff in the Coulomb potential over a lattice period. Therefore, this term can be omitted. Discarding all higher-order terms in the same way, and picking the function  $\Psi(\mathbf{r})$  to be real, we obtain the following Hamiltonian:

$$\begin{aligned} \hat{H} = & \varepsilon_0 \sum_{i,\sigma} \hat{n}_{i,\sigma} + t \sum_{\langle ij \rangle, \sigma} (a_{i,\sigma}^\dagger a_{j,\sigma} + \text{h.c.}) + U \sum_{i,\sigma} \hat{n}_{i,\sigma} \hat{n}_{i,-\sigma} \\ & + V \sum_{\substack{\langle ij \rangle \\ \sigma, \sigma'}} \hat{n}_{i,\sigma} \hat{n}_{j,\sigma'} + (V_H - SU) \sum_{\langle ij \rangle, \sigma} (a_{i,\sigma}^\dagger a_{j,\sigma} (\hat{n}_{i,-\sigma} + \hat{n}_{j,-\sigma}) + \text{h.c.}), \quad (28) \end{aligned}$$

where  $\varepsilon_0$  is the nondegenerate atomic level,

$$t = \int \Delta u \Psi(\mathbf{r}) \Psi(\mathbf{r} - \mathbf{R}_1) d\mathbf{r},$$

$\Delta u$  is a pseudopotential created by all the atoms except the one at  $\mathbf{r} = 0$ ,  $U$  is the intra-atomic Coulomb interaction energy,  $V$  is the matrix element for Coulomb interactions between neighboring atoms, and

$$V_H = \int |\Psi(\mathbf{r}_1)|^2 V(|\mathbf{r}_1 - \mathbf{r}_2|) \Psi(\mathbf{r}_2) \Psi(\mathbf{r}_2 - \mathbf{R}_1) d\mathbf{r}_1 d\mathbf{r}_2,$$

where  $S$  is the overlap integral.

We note that, generally speaking, we have  $SU > V_H$ , since  $V_H$  contains an additional small factor due to the decay of the Coulomb potential over an interatomic spacing. Therefore the sign of the total amplitude for intersite transitions due to the Coulomb repulsion coincides with the sign of  $t$  ( $\Delta u < 0$ ). Furthermore, inclusion of the upper bands must lead to enhancement of the contribution with the same sign as  $t$ . Let us estimate this contribution. We assume that the atomic wave function falls off at large distances like  $\exp(-r/r_0)/r_0$ , where  $r_0$  is a characteristic scale of the decay. Then we have the following estimate:

$$t \sim (r_0/a) \overline{\Delta u} \exp(-a/r_0), \quad S \sim \exp(-a/r_0),$$

where  $a$  is the interatomic spacing and  $\overline{\Delta u}$  is the pseudopotential averaged over a scale  $r_0$ . From this it follows that

$$S \sim t \frac{a}{r_0} \frac{1}{\Delta u}.$$

The term of interest to us is

$$f = SU \sim t \frac{a}{r_0} \frac{U}{\Delta u}.$$

Inclusion of higher orders of perturbation theory with respect to the parameter  $U/\overline{\Delta u}$  leads to the function

$$f \sim t \left[ \exp\left(\frac{U}{\Delta u} \frac{a}{r_0}\right) - 1 \right].$$

Then for values of  $U$  that are not too small we have  $f \gg V_H$ , and the contribution  $V_H$  to the total amplitude can be neglected in general.

## 5. DISCUSSION OF RESULTS

In this paper we have shown that the interaction corresponding to the effect of orbital relaxation has the form

$$-|f| a_{i,\sigma}^\dagger a_{j,\sigma} (\hat{n}_{i,-\sigma} + \hat{n}_{j,-\sigma}).$$

For cases where the band is narrow enough, or the intra-center repulsion strong enough, that multiband effects become important, the magnitude of this term exceeds the contribution of the term described by Hirsch, which is analogous but has a different origin (and a different sign). It is obvious that these results can be generalized without difficulty to the case of degenerate bands.

Let us now consider certain physical consequences of this interaction. First of all, it follows from Eq. (28) that the interaction leads to an increase in the effective width of the energy bands as the electron density increases. The absolute value of the amplitude for intersite transitions  $t$  is increased by an amount  $|f|/n$ . This assertion has a precise meaning only in the case where a single unoccupied state is present in

the band. Then the energy of a hole has the form

$$\varepsilon = \varepsilon_0 + U(N-1) + 2z(N-1)V + (|t| + 2|f|) \sum_{\mathbf{R}_i} \exp(i\mathbf{k}\mathbf{R}_i),$$

where  $N$  is the number of sites in the lattice and  $z$  is the number of neighbors. Secondly, this interaction can lead to a Cooper instability when there is less than one electron per atom. In fact, the corresponding amplitude in the quasimomentum representation has the form

$$V_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} = -|f|N\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \times \sum_{i=1}^4 (\cos k_{ix}a + \cos k_{iy}a + \cos k_{iz}a).$$

From this it is clear that the interaction will be attractive when the momentum of the electrons is not too large (in contrast to Ref. 3, where the electrons attract in antibonding states). Finally, let us touch briefly on the magnetic properties of the system. We discuss the case of a half-filled band and a situation where  $U \gg f \gtrsim t$ . Then to zeroth order in  $f$  and  $t$  we can assume that each atom is occupied by one electron. Such a system is infinitely degenerate with respect to the direction of spins. Taking into account transitions by adjacent atoms leads to magnetic (antiferromagnetic) ordering. The effective Hamiltonian corresponding to treating  $t$  and  $f$  via perturbation theory has the form<sup>8</sup>

$$\hat{H} = \frac{Vz}{2}N + \frac{2(|t| + |f|)^2}{U - V} \sum_{\langle ij \rangle} \left( \mathbf{S}_i \mathbf{S}_j - \frac{1}{4} \right), \quad (29)$$

where  $\mathbf{S}_{i,j}$  is the spin operator. From this it is clear that an increase in the amplitude of the intersite transitions leads to an increase in the antiferromagnetic exchange energy in the Heisenberg Hamiltonian (29). Furthermore, since it is

necessary to include the difference between the true amplitude  $f$  and the bare amplitude, the exchange energy can depend on  $U$  in a nonmonotonic fashion. In fact, the condition for it to be an increasing function of  $U$  has the form

$$\frac{2U}{\Delta u} \frac{a}{r_0} > 1,$$

while the condition for applicability of the expansion (29) is

$$t + f \sim t \exp\left(\frac{Ua}{\Delta u r_0}\right) \ll U.$$

It is obvious that this condition can be satisfied.

If in this situation we add or subtract one electron, we obtain an excitation of electron or hole type, respectively, whose energies are separated by the Hubbard gap  $U$ . However, in this case the electronic excitations have a smaller effective mass than the hole excitations. This asymmetry in the properties of the electrons and holes leads in turn to an asymmetry in the regions of ferromagnetic and antiferromagnetic ordering on the phase diagram  $U/t$  versus  $n = \langle n_i \rangle$  with respect to the line  $n = 1$ . The curve that separates these regions has the form  $1 - n \propto t/U$  for holes and  $n - 1 \propto (t + f)/U$  for electrons.

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