Low Temperature Physics/Fizika Nizkikh Temperatur, 2014, v. 40, No. 4, pp. 414–419

Natural orbital functional theory and pairing correlation effects in electron momentum density

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Received October 31, 2013

Occupation numbers of natural orbitals capture the physics of strong electron correlations in momentum space. A natural orbital density functional theory based on the antisymmetrized geminal product provides these occupation numbers and the corresponding electron momentum density. A practical implementation of this theory approximates the natural orbitals by the Kohn–Sham orbitals and uses a mean-field approach to estimate pairing amplitudes leading to corrections for the independent particle model. The method is applied to weakly doped La_2CuO_4.

PACS: **71.10.–w** Theories and models of many-electron systems;
71.15.–m Methods of electronic structure calculations;
74.72.–h Cuprate superconductors;
71.10.Ca Electron gas, Fermi gas.

Keywords: Fermi surface, pairing correlation, electron momentum density, many-electron systems.

1. Introduction

A key characteristic of an interacting electron system is the electron momentum density (EMD). For metallic systems one can also define the Fermi surface (FS) as the break in the EMD whose presence reveals the existence of quasiparticles and the validity of the Landau–Fermi liquid theory [1]. FS studies are particularly needed in the field of high-temperature superconductivity. Figure 1 shows the calculated FS of the well known $HgBa_2CuO_4$ [2] while Fig. 2 illustrates the evolution of the FS topology with doping of a less known compound studied by Jarlborg *et al*. [3]. One can notice in Fig. 2 a topological transition (also called Lifshitz transition), which does not involve any symmetry breaking [4].

Positron annihilation has been successful for the determination of the FS in many metallic systems, but similar studies of the copper oxide high-temperature superconductors have met difficulties since positrons do not probe well the FS contribution of the Cu–O planes [5]. Another direct probe of FS is the Angular Resolved Photo-Emission Spectroscopy (ARPES) [6]. However, a concern with ARPES is that most of the information of the interacting electron liquid is based on measurements from a surface sensitive technique that can be applied only to a limited number of materials that cleave such as $Bi_2Sr_2CaCu_2O_{8-\delta}$. Thus, a risk is that experimental artifacts may be interpreted as fundamental physics.

At low doping, the FS signal from ARPES breaks up into Fermi arcs [7], which could be part of closed hole pockets [8,9]. The formation of small Fermi pockets in other

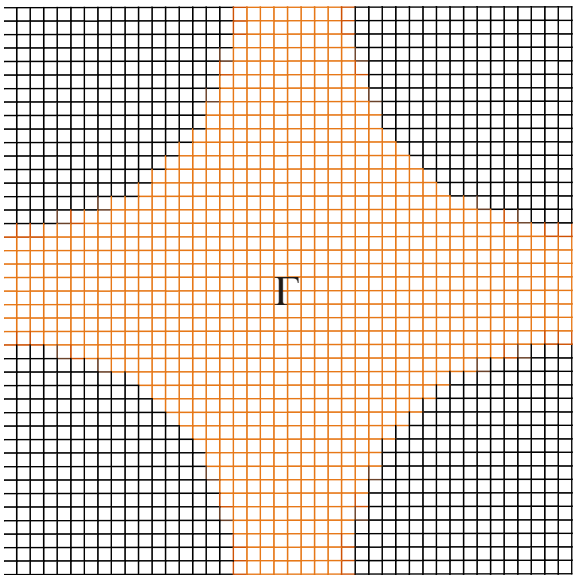

Fig. 1. (Color online) The FS of $HgBa_2CuO_4$ is shown in the first Brillouin zone. It separates the occupied states (yellow grid) from the unoccupied states (black grid).

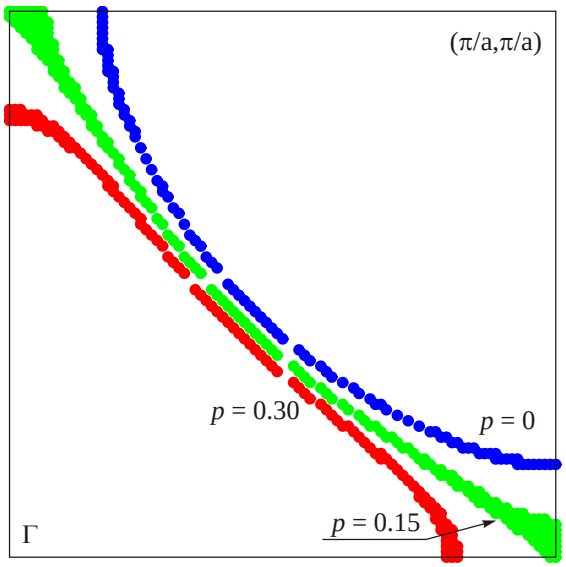

Fig. 2. (Color online) Evolution of the Fermi surface in the $k_z = 0$-plane in Ba_2CuO_3 (where one layer of apical oxygen is missing) as a function of the rigid-band doping for 0, 0.15 and 0.30 holes per unit cell. The FS evolution is almost identical in La_2CuO_4. Only 1/4 of the first Brillouin zone is shown. The momentum units are $1/a$, where a is the lattice constant.

underdoped cuprates also emerges from quantum oscillation (QO) measurements in high magnetic fields [10–14]. These FS pieces seen by QOs could be in fact produced by FS reconstructions when some symmetry is broken [15]. According the theory by Lifshitz and Kosevich (LK) [16,17], a period of QO is linked to an extreme cross-section of the FS. Nevertheless, QOs in the layered and quasi-two-dimensional (2D) conductors may deviate from the LK theory developed for three-dimensional (3D) conventional metals [18,19].

Inelastic x-ray scattering [20,21] in the deeply inelastic limit, can help to clarify the nature of the FS in copper oxide high-temperature superconductors since the corresponding Compton scattering cross-section is well-known to become proportional to the ground state EMD [22]. A Compton scattering study in single crystals of $La_{2-x}Sr_xCuO_4$ has directly imaged in momentum space the character of holes doped into this material [23]. However, improvements in the momentum resolution are still needed to bring Compton scattering into the fold of mainstream probes for the cuprates FS. A recent Compton study of overdoped $La_{2-x}Sr_2CuO_4$ [24] shows the difficulty of extracting details of the FS with the present momentum resolution of about 0.15 a.u. Higher momentum resolution can also allow the study of the FS smearing due to the superconducting energy gap opening [25] and to the breakdown of the Landau–Fermi liquid picture [26]. Surprisingly, Compton scattering experiments even on a simpler material such Li indicate that the EMD of the ground state is not well described by the conventional Landau–Fermi liquid framework since the size of the discontinuity Z at the FS seems to be anomalously small [27–30]. Such deviations from the standard metallic picture can be ascribed to the possible existence of significant pairing correlations in the ground state [26,31,32]. The notion of stabilizing the metallic state through the creation of a resonant valence bond (RVB) state involving the metallic orbitals dates back to the early works of Pauling, who first applied this picture to the Li ground state [33]. In 1987, Anderson proposed the RVB wave function as the natural ground state for the high-temperature superconducting materials [34], arguing that this ansatz is capable of capturing many aspects of the phase diagram of the cuprates [35].

This paper shows how pairing correlation effects modify the electron momentum density distribution [31] by providing an orbital-dependent approach in which the momentum density is constructed using the natural orbitals, and the corresponding occupation numbers are obtained through a variational procedure. The outline of this article is as follows. Section 2 starts with a rigorous expression for the EMD, $\rho(\mathbf{p})$ in terms of the eigenvalues and eigenfunctions of the one-particle density matrix $\hat{\rho}(\mathbf{r},\mathbf{r}')$ [36]. Section 3 discusses the the antisymmetrized geminal product (AGP) and the associated total energy functional [26,31]. A relatively simple practical implementation of the AGP scheme is discussed and applied to La_2CuO_4 in Sec. 4. Finally, Sec. 5 provides the conclusion of this work.

2. Momentum density and natural orbitals

The one-particle density operator $\hat{\rho}$ is a fundamental property of quantum mechanical systems, because it determines the degree of locality of the bonding properties. Inelastic x-ray scattering data are particularly important for determining the density matrix from the experiment. The matrix $\hat{\rho}(\mathbf{r},\mathbf{r}')$ element is defined in terms of the normalized N-particle wavefunction, Ψ, as

$$\hat{\rho}(\mathbf{r},\mathbf{r}') = N\int d\xi\, \Psi^*(\mathbf{r},\xi)\Psi(\mathbf{r}',\xi)\,, \qquad (1)$$

where the integral extends over the coordinates of all other particles. The eigenfunctions and eigenvalues of $\hat{\rho}$ define the natural orbitals, ψ_i, and the associated occupation numbers, n_i [36]. According to the spectral theorem, the density operator $\hat{\rho}$ can then be expanded into projectors $|\psi_i><\psi_i|$ as follows

$$\hat{\rho} = \sum_{i=1}^{\infty} n_i\, |\psi_i><\psi_i|\,. \qquad (2)$$

If one requires the natural orbitals to possess the symmetry of the Hamiltonian, then they constitute a unique decomposition in an orthonormal basis set. Goscinski and Lindner [45] have shown that a canonical orthonormalization of Dyson orbitals [22] yields the natural orbitals.

The EMD is defined as the diagonal part of the density matrix in momentum space

$$\rho(\mathbf{p}) = \frac{1}{8\pi^3}\iint d^3\mathbf{r}d^3\mathbf{r}'\hat{\rho}(\mathbf{r},\mathbf{r}')\exp(-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')). \quad (3)$$

Thus in terms of the natural orbitals ψ_i, the EMD can be cast in the simple form

$$\rho(\mathbf{p}) = \sum_i n_i |<\mathbf{p}|\psi_i>|^2, \quad (4)$$

where $<\mathbf{p}|\psi_i>$ is the momentum transform of ψ_i. If the many body wavefunction is represented by a single determinant, which is true in the case of Hartree Fock or the density functional theory [38], then the density matrix is idempotent $(\hat{\rho} = \hat{\rho}^2)$ and reduces to a summation over the occupied spin-dependent orbitals ψ_i, i.e.,

$$\hat{\rho}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N}\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}'). \quad (5)$$

The EMD in this independent particle model (IPM) is similar to the more general Eq. (2), except that the occupation numbers n_i are now strictly 0 or 1 depending upon whether the state in question is empty or filled. Electron correlations allow these occupied and empty IPM states to mix so that the occupation of states below the Fermi energy, E_F, becomes less than 1, while that of states above E_F becomes non-zero. In a crystal, the one-particle states are Bloch waves, $\psi_{\mathbf{k}\nu}(\mathbf{r})$, where ν is a band index and $\mathbf{k}$ is the crystal momentum which is restricted to the first Brillouin zone (BZ). The associated occupation numbers, $n_{\mathbf{k}}^{\nu}$, possess translational symmetry with respect to the set of reciprocal lattice vectors $\mathbf{G}$ [39]

$$n_{\mathbf{k}}^{\nu} = n_{\mathbf{k}+\mathbf{G}}^{\nu}. \quad (6)$$

According to the Lock, Crisp and West theorem [40]

$$\sum_{\nu} n_{\mathbf{k}}^{\nu} = \sum_{\mathbf{G}}\rho(\mathbf{k}+\mathbf{G}). \quad (7)$$

Therefore, if the EMD originated from a single energy band then the occupation number can be obtained directly by summing the EMD over the reciprocal lattice vectors

$$n_{\mathbf{k}} = \sum_{\mathbf{G}}\rho(\mathbf{k}+\mathbf{G}). \quad (8)$$

3. The antisymmetrized geminal product natural orbital functional theory

The antisymmetrized geminal product [26,31,41–46] is a many-body wavefunction obtained by antisymmetrizing for all possible permutations of particles the simple product of opposite spin electron pairs

$$\Psi = \hat{\mathcal{A}}\left\{\Pi_{i,j=1}^{N/2}\phi(\mathbf{r}_i,\mathbf{r}_j)\right\}, \quad (9)$$

where N is the number of electrons (even in the present case) and $\hat{\mathcal{A}}$ is the antisymmetrization operator. Each pair is described by the same two particle spin singlet function ϕ, which is called *generating geminal*. The function ϕ has a diagonal expansion in the natural orbitals

$$\phi(\mathbf{r}_1,\mathbf{r}_2) = \sum_i g_i\,\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\frac{(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)}{\sqrt{2}}. \quad (10)$$

The ψ_i's and g_i's can be determined by minimizing the total energy functional. In extended systems the coefficients g_i are not particularly convenient, and it is more useful to introduce a new set of coefficients h_i defining a "Cooper pair" function given by

$$C(\mathbf{r}_1,\mathbf{r}_2) = \sum_i h_i\,\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\frac{(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)}{\sqrt{2}}. \quad (11)$$

The total energy functional can then be written as

$$E[h_i,\psi_i] = E_{HF}[\hat{\rho}] + E_{BCS}[h_i,\psi_i] + O(1/N), \quad (12)$$

where E_{HF} is the Hartree-Fock functional and E_{BCS} is a BCS-type functional [31,42,45] given by

$$E_{BCS} = \frac{1}{2}<C|V_{12}|C>, \quad (13)$$

where V_{12} is the electron interaction operator. The normalization of the AGP wavefunction imposes a relationship between the coefficients h_i and the occupation numbers n_i via the condition

$$h_i = \pm\sqrt{n_i(1-n_i)}. \quad (14)$$

Note that for Coulomb interaction the pair potential V_{12} is repulsive, so that energy can be gained only through the exchange part E_{HF} of the Hartree–Fock functional. It can be shown that the amplitudes h_i's must change sign at the so called pseudo-FS [34]. The excitation at the pseudo-FS are called spinons and they correspond to fermions with no charge and spin 1/2 [1]. Energy can also be gained of course through the term E_{BCS} in Eq. (12) by the introduction of lattice dynamics as is the case at the superconducting transition [47].

Several authors [48–55] have considered an approximation to the two-particle density matrix σ which leads to a functional of natural orbitals similar to form (12) discussed here. However, some of these functional are over-correlated. The reason is that σ is varied over a too large a class of functions without the restriction of N-representability. This problem is circumvented in our case since the the AGP functional is N-representable by construction.

4. An efficient approach to extract pairing amplitudes

Our main goal is to gain a handle on the nature of occupation numbers in a correlated electron gas. In this spirit, we start by approximating the natural orbitals by the Kohn–

Sham orbitals [56] for a crystal potential. For the sake of simplicity, we suppose that the eigenvalues are described by a single energy band denoted by $\mathcal{E}_{\mathbf{k}}$ with μ defining the chemical potential. The result for the energy functional minimization gives the occupation numbers

$$n_{\mathbf{k}} = \frac{1}{2}\left(1 - \frac{\mathcal{E}_{\mathbf{k}} - \mu}{E_{\mathbf{k}}}\right), \tag{15}$$

where $E_{\mathbf{k}}$ is given by

$$E_{\mathbf{k}} = \sqrt{(\mathcal{E}_{\mathbf{k}} - \mu)^2 + |\Delta_{\mathbf{k}}|^2}\,. \tag{16}$$

Two self-consistent equations are also involved, one giving $\Delta_{\mathbf{k}}$ [57]

$$\Delta_{\mathbf{k}} = \frac{1}{N}\sum_{\mathbf{k}'} \frac{J_{\mathbf{k}\mathbf{k}'}\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}}}, \tag{17}$$

and the other determining the chemical potential μ

$$N = \sum_{\mathbf{k}} n_{\mathbf{k}}. \tag{18}$$

In order to make progress, one needs to estimate the value of the pairing term $J_{k,k'}$. Since the kinetic energy cost of electron pairing is roughly compensated by the exchange energy, $J_{\mathbf{k}\mathbf{k}'}$ is mostly given by an exchange integral [31]. A useful approximation for $J_{\mathbf{k}\mathbf{k}'}$ is [31,58]

$$J_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'} I_{\mathbf{k}}\,, \tag{19}$$

with

$$I_{\mathbf{k}} = \frac{1}{3}\int d^3\mathbf{r}\,|\psi_{\mathbf{k}}(\mathbf{r})|^4 \frac{v_x(\mathbf{r})}{n(\mathbf{r})}, \tag{20}$$

where $v_x(\mathbf{r}) = 2/\pi\,[3\pi^2 n(\mathbf{r})^{1/3}]$ is the Kohn–Sham exchange potential [56] and $n(\mathbf{r})$ is the electron density. By inserting this approximation in Eq. (17), one obtains

$$\Delta_{\mathbf{k}}^2 = \frac{I_{\mathbf{k}}^2 - 4(\mathcal{E}_{\mathbf{k}} - \mu)^2}{4}. \tag{21}$$

Therefore $\Delta_{\mathbf{k}}$ is different of zero only if $I_{\mathbf{k}} > 2(\mathcal{E}_{\mathbf{k}} - \mu)$.

The evaluation of the EMD follows along the lines of the standard IPM computations, except that the occupation numbers for the correlated electron gas given by Eq. (15) are used. The calculation of the occupation numbers shown in Fig. 3 has been performed within an efficient linear muffin-tin orbital band structure method [59]. The essential parameter which controls the correlation effect in the present scheme is I/ω, where I is the average of $I_{\mathbf{k}}$ and ω denotes the relevant valence electron bandwidth. It is clear that when $\Delta/\omega \sim 1$, and states deep in the Fermi sea are renormalized inducing significant shift of spectral weight from below to above the Fermi energy [31]. In $La_{2-x}Sr_xCuO_4$, the average I is about 1.67 eV. Therefore, at the Fermi

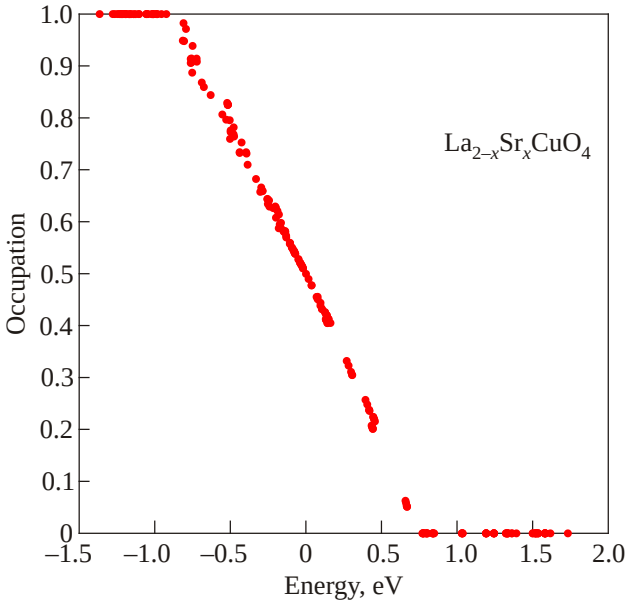

Fig. 3. Occupation number for $La_{2-x}Sr_xCuO_4$ in the limit $x \to 0$ as a function of the Kohn–Sham eigenvalues. The Fermi level is at 0.

energy $\Delta \sim I/2 = 0.83$ eV. The momentum smearing produced by Δ is given by

$$\delta k = \frac{\Delta}{v_F}, \tag{22}$$

where v_F is the Fermi velocity. By taking $\hbar v_F \sim \pi/a$ (where $a = 7.16$ a.u. is the lattice constant) we find $\delta k \sim 0.07$ a.u. This momentum smearing is slightly below the current experimental momentum resolution of 0.15 a.u. available in Compton scattering experiments [24]. A similar δk can be produced by the antiferromagnetic order [60] when $x \to 0$, but the emergence of ferromagnetic fluctuations for $x \sim 0.25$ leads to the destruction of both RVB correlations and of the AF order in the over-doped regime [61].

5. Conclusion

The AGP method has been used to study the occupation numbers of natural orbitals. Strong modification of the occupation numbers due to pairing correlations effects are predicted for $La_{2-x}Sr_xCuO_4$ with $x \to 0$ in an energy window of 0.83 eV around the Fermi energy. This effect produces a smearing of the occupation in momentum space given by $\delta k \sim 0.07$ a.u. The present results demonstrate the suitability of the AGP method in providing a theoretical method for describing correlation effects on the EMD in wide classes of materials. This work is supported by the US Department of Energy, Office of Science, Basic Energy Sciences Contract No. DE-FG02–07ER46352. It has also benefited from Northeastern University's Advanced Scientific Computation Center (ASCC), theory support at the Advanced Light Source, Berkeley, and the allocation of computer time at NERSC through Grant No. DE-AC02–05CH11231.

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