

## Why holes are not like electrons. II. The role of the electron-ion interaction

J. E. Hirsch

*Department of Physics, University of California, San Diego, La Jolla, California 92093-0319, USA*

(Received 1 September 2004; revised manuscript received 30 November 2004; published 31 March 2005)

In recent work, we discussed the difference between electrons and holes in energy band in solids from a many-particle point of view, originating in the electron-electron interaction, and argued that it has fundamental consequences for superconductivity. Here we discuss the fact that there is also a fundamental difference between electrons and holes already at the single particle level, arising from the electron-ion interaction. The difference between electrons and holes due to this effect parallels the difference due to electron-electron interactions, *holes are more dressed than electrons*. We propose that superconductivity originates in “undressing” of carriers from *both* electron-electron and electron-ion interactions, and that both aspects of undressing have observable consequences.

DOI: 10.1103/PhysRevB.71.104522

PACS number(s): 74.20.-z, 71.10.Fd

### I. INTRODUCTION

Hamiltonians used to describe many-body phenomena in solids are usually electron-hole symmetric (by electrons and holes it is meant the charge carriers at the Fermi energy when the Fermi level is near the bottom and near the top of the band, respectively). Instead, in the first paper of this series<sup>1</sup> and other recent work<sup>2</sup> we have argued that holes are fundamentally different from electrons, due to the different effect of electron-electron interaction for carriers at the bottom and the top of a band. We have proposed a class of model Hamiltonians, “dynamic Hubbard models,” to describe this physics, and argued that this physics plays a fundamental role in superconductivity.<sup>3,4</sup> These electron-hole *asymmetric* Hamiltonians describe quasiparticles that become increasingly dressed by the electron-electron interaction as the Fermi level rises from the bottom to the top of the band, and give rise to superconductivity driven by quasiparticle “undressing.”<sup>5</sup> They also display many characteristic features that are observed in high  $T_c$  cuprates.

In these Hamiltonians, the electron-electron interaction breaks electron-hole symmetry, however the single particle part of the Hamiltonians is still electron-hole symmetric. In this paper we point out that in real solids a fundamental electron-hole asymmetry already exists at the single-electron level, which parallels the electron-hole asymmetry arising from electron-electron interactions. This physical effect is *also* missing in the tight binding Hamiltonians commonly used to describe correlated electrons in solids. Just as quasiparticles in real solids are increasingly dressed by *electron-electron* interactions as the Fermi level rises in the band,<sup>1</sup> we point out here that they are also increasingly dressed by the *electron-ion* interaction as the Fermi level rises. Furthermore we argue that because when holes pair the band becomes locally less full, undressing from *both* the electron-electron interaction *and* the electron-ion interaction will take place. Remarkably, as we will discuss, experimental evidence that undressing from the electron-ion interaction takes place upon the transition to the superconducting state has been known, even if not fully appreciated, for a long time. The fact that electrons undress from the electron-ion interaction when they pair has also fundamental consequences for superconductivity.<sup>6</sup>

The central character in this paper is in fact not the hole, but the “invisible” antibonding electron, the electron at the Fermi level when the Fermi level is near the top of the band. Using the language of “holes” rather than “electrons” in fact obscures the essential physics since these antibonding electrons are the ones that undress and carry the supercurrent (as electrons, not as holes) in the superconducting state.

### II. TIGHT BINDING ELECTRONIC ENERGY BANDS

The tight binding Hamiltonians usually considered such as the Hubbard model have a single-particle part of the form

$$H_0 = - \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}, \quad (1)$$

where  $c_{i\sigma}^\dagger$  creates an electron in Wannier orbital  $\varphi_i(r)$  centered at lattice site  $i$ . This Hamiltonian may or may not be electron-hole symmetric. However if we restrict ourselves to nearest neighbor hopping on a hypercubic lattice as is usually done,

$$H_0 = -t \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) \quad (2)$$

then the Hamiltonian is electron-hole symmetric, as can be seen from the fact that the canonical transformation

$$c_{i\sigma} = (-1)^i d_{i\sigma}^\dagger \quad (3)$$

leaves it invariant. The band energy is

$$\epsilon_k = -2t \sum_{\nu=1}^d \cos k_\nu a \quad (4)$$

with  $a$  the lattice spacing and  $d$  the dimensionality. The effective mass for carriers at the bottom of the band is independent of direction and given by

$$m^* = \left[ \frac{1}{\hbar^2} \left( \frac{\partial^2 \epsilon_k}{\partial k_x^2} \right)_{k=0} \right]^{-1} = \frac{\hbar^2}{2ta^2} \quad (5)$$

and the effective mass at the top of the band has the same magnitude as Eq. (5) and opposite sign.

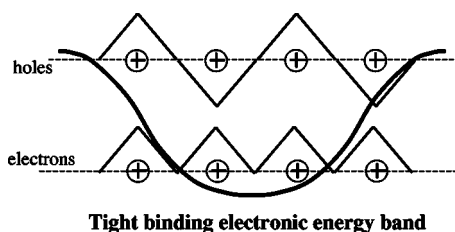


FIG. 1. Electronic states in a tight binding band. The states at the top of the band and those at the bottom of the band are related by a canonical transformation. This will be the case if they are Bloch sums of *nonoverlapping* Wannier orbitals with wave vector  $k$  and  $\pi-k$ , respectively.

When one includes electron-electron interactions that do not break electron-hole symmetry, e.g., in an extended Hubbard model,

$$H = H_0 + \sum_{ij} V_{ij} n_i n_j \quad (6)$$

or electron-phonon interactions as in the Holstein or Su-Schrieffer-Heeger models, or electron-spin interactions as in the Kondo lattice model, the Hamiltonian retains electron-hole symmetry and hence the properties of the system are identical for band filling  $n_e$  and  $2-n_e$ , with  $n_e$  the number of electrons per site. Instead, adding a correlated hopping term<sup>7</sup> or electron-boson interactions of particular forms as in dynamic Hubbard models<sup>3,4</sup> breaks electron-hole symmetry and leads to qualitatively new physics.

Here however we want to focus on the fact that in writing down the noninteracting Hamiltonian Eq. (2) we have already eliminated an important source of electron-hole asymmetry, arising from the electron-ion interaction. The electron-hole transformation Eq. (3) says that the wave function of an electron at the bottom of the band is essentially the same (except for a phase factor) as the one for an electron at the top of the band. Note also that the Wannier orbitals used to define the Hamiltonian Eq. (2) need to be orthogonal to each other. Schematically, this can be represented by the wave functions shown in Fig. 1. Here indeed the states at the bottom and the top of the band are equivalent, since one can be transformed into the other by the operation  $\varphi_i(r) \rightarrow (-1)^i \varphi_i(r)$ . However in fact the real situation is very different and no such electron-hole symmetry exists even at the single particle level.

### III. REAL ELECTRONIC ENERGY BANDS

Real electronic energy bands can be obtained from band structure calculation schemes, and the eigenstates certainly do not look like the states depicted in Fig. 1. Here we wish to focus on what we believe is the key universal aspect that differentiates the states at the bottom and the top of any electronic band.

The essential physics can be illustrated clearly with a diatomic molecule. If  $\varphi_i(r)$  is an atomic orbital at atom  $i=1, 2$ , the bonding and antibonding atomic orbitals in a linear combination of atomic orbitals (LCAO) scheme are given by

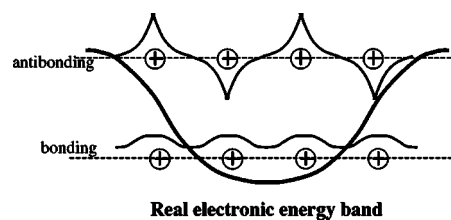


FIG. 2. Electronic states in a real band. The states at the bottom (bonding) have a high density of charge in between the ions, and a smooth wave function. The states at the top (antibonding) have a node in the charge density between the ions and a spiky wave function.

$$\phi_{b,a} = \frac{\varphi_1(r) \pm \sigma \varphi_2(r)}{[2(1 \pm \sigma S)]^{1/2}}, \quad (7a)$$

$$S = (\varphi_1, \varphi_2), \quad (7b)$$

$$\sigma = S/|S| \quad (7c)$$

with the upper (lower) sign corresponding to bonding (antibonding) states. For  $s$  orbitals, the sign of the overlap matrix element is positive and the *even* linear combination gives the lowest energy molecular orbital, the bonding orbital, and the odd linear combination gives the high energy antibonding orbital. For  $p$  orbitals  $S$  is negative and the situation is reversed. However the key point is that the lowest molecular orbital is always the linear combination that yields high electronic charge density between the ions, and the other one has a node in the electronic wave function at the midpoint between the ions. Conversely, the low energy bonding orbital has always lower charge density at the ion site than the antibonding orbital.

For an energy band we argue that the electronic states look qualitatively as shown in Fig. 2, independent of which atomic orbital gave rise to the band. The point is that the states at the bottom of the band have lowest energy (by definition), which is achieved by piling up electronic charge density in the region where it can most benefit from the electron-ion potential, namely in the interstitial region between ions; at the same time, due to normalization, the charge density at the ionic site is reduced compared to the free atom situation, and the resulting smooth wave function also has a low kinetic energy. Instead, the states at the top of the band are constrained by the fact that they must be orthogonal to the states below them. This causes the wave function to have a node in the region between the ions, and a higher amplitude at the ionic site than for the isolated ion; as a consequence, these states have a high potential energy, since they do not take maximal advantage of the electron-ion potential, and a high kinetic energy because the wave function is spiky rather than smooth.

Because the wave function at the bottom of the band is more smooth, it resembles more the free electron plane-wave function, which gives rise to a uniform electronic density. The wave functions at the top of the band give rise to a nonuniform charge density, quite unlike free electron wave functions. Furthermore the effective mass defined by Eq. (5)

will be positive near the bottom of the band, as the free electron mass, and negative near the top of the band. We conclude that quite generally the single-particle electronic states near the bottom of the band are more free-electron-like than those near the top of the band.

We argue that these are universal physical differences between electronic states at the bottom and top of electronic energy bands, determined by the facts that states at the bottom have low energy and states at the top have high energy, and by the exclusion principle. These are real physical differences that cannot be eliminated away by canonical transformations. For  $s$  orbitals the energy versus  $k$  relation looks like that in Fig. 2, while for  $p$  orbitals it is inverted, with the lowest states at  $k \sim \pi$  and the highest states at  $k \sim 0$ . In both cases the electronic wave function looks qualitatively as in Fig. 2 in the region between the ions, except that for a band deriving from  $p$  orbitals the wave function has an additional node exactly at the ionic site for all states in the band. The same considerations apply to bands originating in other orbitals.

The physical difference between states at the bottom and top of the band is also embodied in their name, bonding and antibonding, respectively. The high interstitial electronic density of the bonding orbitals gives rise to an attractive interaction between ions, binding the solid together; instead, the vanishing electronic charge density between ions of the antibonding electrons causes a repulsive interaction between ions, which tends to break the solid apart. This is why lattice instabilities are associated with the presence of antibonding states at the Fermi energy, i.e., with bands that are almost full. As is well known, superconductivity is also often associated with the presence of lattice instabilities nearby in the phase diagram,<sup>8</sup> indicating a connection between antibonding states and superconductivity.

#### IV. WEAK COUPLING

It was noted already by Bloch that the very different tight binding and weak binding starting points for the description of electronic states in solids give complementary and very similar pictures. The fact that electrons at the bottom of the band are more similar to free electrons than those at the top of the band discussed in the last section is very evident from the weak coupling point of view. Perturbation theory in the electron-ion potential  $U_K$  yields for the band energy

$$\epsilon_k = \epsilon_k^0 + \sum_K \frac{|U_K|^2}{\epsilon_k^0 - \epsilon_{k-K}^0} \quad (8)$$

with  $\epsilon_k^0 = \hbar^2 k^2 / 2m_e$  the free electron energy ( $m_e$  = free electron mass) and  $K$  reciprocal lattice vectors. Starting from the state at  $k=0$  energy denominators are large, so the second term in Eq. (8) is small and the energy versus  $k$  relation is almost free-electron-like. The wavelength  $\lambda = 2\pi/k$  is large and the electronic wave function

$$\varphi_k = \varphi_k^0 + \sum_K \frac{U_K}{\epsilon_k^0 - \epsilon_{k-K}^0} \varphi_{k-K}^0 \quad (9a)$$

is almost the free-electron plane wave

$$\varphi_k^0 = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}. \quad (9b)$$

The effective mass tensor is given by

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_k}{\partial k_i \partial k_j} = \frac{1}{m_e} \delta_{ij} + \frac{1}{\hbar^2} \frac{\partial^2}{\partial k_i \partial k_j} \sum_K \frac{|U_K|^2}{\epsilon_k^0 - \epsilon_{k-K}^0} \quad (10)$$

and is almost isotropic and free-electron-like for small  $k$  since the second term in Eq. (10) is small.

As the Fermi level rises electrons at the Fermi surface become increasingly dressed by the electron-ion interaction, the wave vector  $k$  increases, the energy denominators in Eqs. (8)–(10) decrease and the electronic energy, wave function, and effective mass increasingly deviate from the free electron values, as the second terms in Eqs. (8)–(10) become increasingly important compared to the first terms. Qualitatively, as the wavelength  $\lambda$  decreases, the electrons become increasingly aware of the existence of the discrete ionic potential due to the fact that the wavelength of the electronic wave function becomes closer to that of the ionic potential.

Consider for definiteness a simple cubic lattice. The perturbative expressions Eqs. (8)–(10) break down when the wave vector  $k$  approaches one half of the smallest reciprocal lattice vectors  $\vec{K} = (2\pi/a)\hat{l}$ , with  $\hat{l}$  one of the three principal axis, i.e., when the wave vector approaches the edge of the Brillouin zone, or the electronic wavelength approaches twice the ionic charge wavelength. Then, nearly degenerate perturbation theory yields for the state near the top of the band

$$\epsilon_k = \frac{\epsilon_k^0 + \epsilon_{k-K}^0}{2} - \sqrt{\left(\frac{\epsilon_k^0 - \epsilon_{k-K}^0}{2}\right)^2 + |U_K|^2}, \quad (11a)$$

$$\varphi_k = \frac{\varphi_k^0 + \varphi_{k-K}^0}{\sqrt{2}}, \quad (11b)$$

$$\frac{1}{m^*} = \frac{1}{m_e} - \frac{\hbar^2}{4m_e^2} \frac{K^2}{|U_K|}. \quad (11c)$$

The wave function  $\varphi_k(r) \sim \cos(kr)$ ,  $k \sim \pi/a$  is zero at the midpoint between the atoms, just as the tight binding picture also predicts. Because the ionic potential has broken the degeneracy with the other linear combination of free electron wave functions,  $\varphi'_k(r) \sim \sin(kr)$ , the charge density associated with the states at the top of the band is nonuniform unlike the free electron case. Beyond lowest order perturbation theory these wave functions get modified by the ionic potential that pulls the electronic charge closer to the regions of positive charge. The dependence of energy on wave vector is very different from the free electron case, and in particular the effective mass Eq. (11c) is negative for small  $|U_K|$  which is the regime where these expressions are valid.

These facts are of course well known.<sup>9</sup> However it is not usually stressed that they reflect a fundamental physical difference between states at the bottom and the top of electronic energy bands, i.e., between bonding and antibonding elec-

trons, or equivalently between electrons and holes.

For the lowest band in a solid these considerations then imply that electronic states at the bottom of the band are not very different from free-electron states, and in particular that the electronic density is nearly uniform and not strongly modulated by the ionic potential. The electron-ion interaction has an increasing effect in modifying the electronic density and the energy-momentum relation from the free-electron values as the states approach the top of the band. We argue that the same physics will be true for other bands. Let us first consider the results of the perturbation theory discussed above for the second band. The wave function  $\varphi'_k(r) \sim \sin(kr)$  at the bottom of the second band has a node at the ionic site but is smooth in the interstitial region, as free-electron wave functions are. The effective mass at the bottom of the second band is given by Eq. (11c) with a positive sign for the second term, hence is positive as for free electrons. Even though it is smaller than the free-electron mass, second order contributions of the form Eq. (8) will increase its value towards the free-electron mass. For example, the dominant contribution in second order for  $k \sim \pi/a$  comes from  $K' = 4\pi/a$  in Eq. (8) and yields

$$\frac{1}{m^*} = \frac{1}{m_e} \left( 1 + \frac{\hbar^2 \pi^2}{m_e a^2 |U_K|} - \frac{a^4 m_e^2 |U_{K'}|^2}{2 \pi^4 \hbar^4} \right) \quad (12)$$

and contributions from other  $K$  values will increase it further. At the top of the second band, i.e., at  $k=2\pi/a$ , degenerate perturbation theory with  $K=4\pi/a$  again yields negative effective mass. More generally, we know from pseudopotential theory<sup>10</sup> that one can find an effective description of conduction bands in solids that is similar to the lowest band discussed above. In pseudopotential theory the conduction band energy is to second order

$$\epsilon_k = \epsilon_k^0 + \langle k|W|k \rangle + \sum_K \frac{\langle k|W|k-K \rangle \langle k-K|W|k \rangle}{\epsilon_k^0 - \epsilon_{k-K}^0}, \quad (13)$$

where the pseudopotential  $W$  is an operator rather than a local function of position. The pseudopotential is chosen to give a smooth pseudo-wave-function to optimize the convergence, and it is found that its matrix elements are small and the second order expression Eq. (13) is adequate except near Bragg planes, as in the simple case discussed above.<sup>10</sup> Equation (13) yields an additional contribution to the effective mass from the first order perturbation term that is absent in Eq. (8), however that term is generally found to be small.<sup>10</sup> Consequently the considerations made above for the lowest band still apply. The pseudo-wave-functions (linear combination of orthogonalized plane waves) give a smooth charge distribution in the interstitial regions near the bottom of the band,<sup>10</sup> as free electrons do. Finally, quite generally it is true that the effective mass is positive, hence closer to the free electron value, near the bottom of a band, and negative, hence more different from the free electron value, near the top of a band.

## V. PHYSICAL DIFFERENCES BETWEEN ELECTRONS AND HOLES DUE TO THE ELECTRON-ION INTERACTION

In the preceding sections we have discussed the difference in wave function, resulting charge density, and energy-wave-vector relation between states at the bottom of a band (electrons) and states at the top of a band (holes), and argued that states near the bottom of the band are free-electron-like and those near the top of the band are not. A tight binding model of the form Eq. (2) does not reflect the physical difference between bonding and antibonding electrons. Yet these differences have concrete observable consequences, as discussed in what follows.

### A. Momentum transfer to the lattice

When a force is applied to an electron inside a metal, both the electron and the lattice change their momentum,

$$\vec{F} = \frac{\Delta \vec{p}}{\Delta t} = \frac{\Delta \vec{p}_{\text{el}} + \Delta \vec{p}_{\text{latt}}}{\Delta t}. \quad (14)$$

Semiclassical transport theory relates the change in total momentum to the change in the electronic *crystal momentum*

$$\Delta \vec{p} = \hbar \Delta \vec{k} \quad (15)$$

while the change in electronic momentum is given by

$$\Delta \vec{p}_{\text{el}} = m_e \Delta \vec{v}_{\text{el}} = m_e \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_k}{\partial k^2} \hbar \Delta \vec{k} = \frac{m_e}{m^*} \Delta \vec{p} \quad (16)$$

(assuming isotropic effective mass for simplicity) so that the momentum transferred to the lattice is

$$\Delta \vec{p}_{\text{latt}} = \left( 1 - \frac{m_e}{m^*} \right) \Delta \vec{p}. \quad (17)$$

For electrons near the bottom of the band,  $m^*$  is close to  $m_e$  and practically all the momentum is transferred to the electron and none to the lattice. Instead, for electrons near the top of the band the change in the electron momentum is opposite to the transferred momentum since  $m^*$  is negative, and the lattice needs to pick up both the externally transferred momentum and the negative of the momentum change of the electron. We may quantify the dressing of the free electron by the momentum transferred to the lattice when an external force attempts to change the electronic momentum; it is clear then that the electron-ion interaction increasingly dresses the bare electron at the Fermi level as the Fermi level rises in the band.

### B. Conduction of electricity

When an electric potential difference is applied to a metal, electric current flows from the higher to the lower potential side of the metal. However, the behavior is very different for electrons near the bottom and near the top of the band. The change in velocity of an electron upon application of an electric field  $\vec{E}$  is



$$\Delta \vec{v} = \frac{1}{m^*} e \vec{E} \tau \quad (18)$$

with  $\tau$  the collision time. Electrons in the lower half of the band have  $m^* > 0$  and hence change their velocity in the direction that contributes to the flow of electricity (i.e., opposite to  $\vec{E}$  since  $e < 0$ ); instead, electrons in the upper half of the band change their velocity in direction that opposes the flow of electric current, and as the band becomes filled the two contributions exactly cancel and zero current results. Hence the dressing of the antibonding electron by the electron-ion potential causes it to oppose, rather than contribute, to the conduction of electricity as a free electron would.

### C. Optical conductivity

The integrated optical conductivity from *intraband* transitions, when the Fermi level is close to the bottom of the band, is given by

$$\frac{2}{\pi e^2} \int_{\text{intraband}} d\omega \sigma_1(\omega) = \frac{n_e}{m^*} \quad (19)$$

with  $n_e$  the number of electrons in the band. Hence electrons near the bottom of the band each contribute a positive amount to the low frequency optical conductivity, which is close to the contribution of a free electron if  $m^*$  is close to  $m_e$ . Instead, when the Fermi level is close to the top of the band the integrated intraband optical conductivity is

$$\frac{2}{\pi e^2} \int_{\text{intraband}} d\omega \sigma_1(\omega) = \frac{n_h}{|m^*|} = \frac{2 - n_e}{|m^*|} \quad (20)$$

and each antibonding electron added to the nearly full band *decreases* rather than increases the intraband optical conductivity. The difference between the Drude weight Eq. (19) and the Drude weight that would arise from free electrons,  $n_e/m_e$ , also quantifies the amount of dressing, and this difference increases as the Fermi level rises from the bottom to the top of the band. The global conductivity sum rule

$$\frac{2}{\pi e^2} \int_0^\infty d\omega \sigma_1(\omega) = \frac{n_e}{m_e} \quad (21)$$

implies that this missing spectral weight is transferred from low intraband frequencies to high interband frequencies due to the electron-ion interaction.

### D. Hall effect

As a final physical manifestation of the difference between electrons at the bottom and at the top of electronic energy bands we mention the Hall effect.<sup>11</sup> Electrons near the bottom of the band respond to crossed electric and magnetic fields as free electrons would, namely they traverse cyclotron orbits in the direction consistent with the negative charge of the free electron. Instead, the strong dressing of the free electron by the electron-ion potential for electrons near the top of the band causes them to respond as if they had a charge of opposite sign, reflecting the positive charge of the ionic lattice that dresses them.

### E. Summary

In summary, we have discussed in this section various observable manifestations of the physical difference between electrons at the bottom and at the top of electronic energy bands, which arise due to the electron-ion interaction. Electrons near the bottom of the band resemble free electrons with a nearly uniform charge density, and are largely unaffected by the presence of the discrete ionic lattice potential. When perturbed by external probes they respond very much like free electrons. Instead, electrons near the top of energy bands (antibonding electrons) have a wave function that changes rapidly over interatomic distances as shown in Fig. 2, are tightly coupled to the discrete ionic lattice, and their charge density is very nonuniform and hence different from the free electron case. The antibonding electrons are strongly dressed by the electron-ion interaction. When perturbed by external probes, this tight coupling between antibonding electrons and positive ionic charge causes them to respond very differently from free electrons.

## VI. DRESSING FROM ELECTRON-ELECTRON INTERACTIONS

In previous work we have discussed the different effect of the electron-electron interaction for electrons at the bottom and the top of bands.<sup>1-3</sup> Just as the electron-ion interaction discussed in the preceding sections, we showed that the electron-electron interaction increasingly dresses the quasiparticle as the Fermi level goes up in the band. Dressing due to the electron-electron interaction does not change the sign of the effective mass but increases its magnitude. It also causes another effect that goes beyond single-particle physics, it reduces the quasiparticle weight in the single particle spectral function and gives rise to incoherent spectral weight at higher energies. For the optical conductivity, *both* the dressing from electron-ion and from electron-electron interaction cause spectral weight to be pushed up from the low-frequency intraband range to higher frequencies.

In summary, both the electron-ion and the electron-electron interaction cause electrons in a metal to become dressed, i.e., different from free electrons. The dressing from both of these sources becomes increasingly important as the Fermi level goes up in the band, and is largest when the Fermi level is close to the top of the band. We adopt then as a basic principle: *higher concentration of electrons in a band leads to higher dressing of the quasiparticles at the Fermi energy.*

## VII. SUPERCONDUCTIVITY FROM UNDESSING

When the Fermi level is close to the top of the band, the carriers at the Fermi energy, antibonding electrons, are most highly dressed. Furthermore, the kinetic energy of electrons at the Fermi energy is highest, and they do not benefit from the crystal ionic potential because their charge density in the region between ions is small. If these electrons were able to occupy states that are lower in the band their energy would be lowered. However, those lower states are occupied by other electrons (bonding electrons) and the Pauli principle

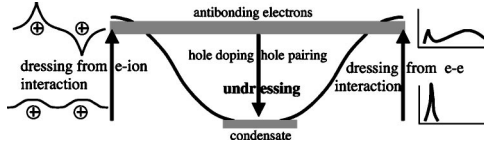


FIG. 3. As the Fermi level rises in a band, electrons at the Fermi energy become dressed due to electron-electron interactions which modify the free particle spectral function (as shown schematically on the right-hand side of the figure), and due to electron-ion interactions which modify the free-electron wave function (as shown on the left-hand side of the figure). Pairing effectively lowers the position of the Fermi level and causes the carriers at the Fermi energy to undress and become free-electron-like.

prevents other fermions from occupying those states. In the absence of electron-electron interactions, the antibonding electrons have no choice but to remain in the unfavorable antibonding states, and to pay the high price in both kinetic and potential energy in doing so.

However, electrons do interact with each other, and states at the Fermi energy can be modified by electronic correlations. When the Fermi level is close to the top of the band, pairing of holes leads locally to a higher hole concentration, hence to a lower electron concentration. According to the basic principle enunciated above, this should lead to undressing of carriers at the Fermi energy. Since both the dressing by electron-electron and by electron-ion interactions increase with band filling, a local decrease in band filling should lead to undressing from both the electron-electron and the electron-ion interactions, as shown schematically in Fig. 3. A Cooper pair behaves as a boson rather than a fermion, and these arguments indicate that the members of a Cooper pair will bear a closer resemblance to free undressed electrons than the unpaired antibonding electrons.

The phenomenology of undressing from the electron-electron interaction is described mathematically by dynamic Hubbard models<sup>3</sup> and by their low energy effective counterpart, the Hubbard model with correlated hopping.<sup>7</sup> The quasiparticle weight is given by<sup>5</sup>

$$z(n_e) = \left(1 - (1 - S) \frac{n_e}{2}\right)^2 \quad (22)$$

with  $0 \leq n_e \leq 2$  and  $S < 1$  a parameter that depends on the nature of the ion.<sup>1</sup> The effective mass is given by  $m^* = m_e / z(n_e)$ . As the band filling  $n_e$  decreases,  $z(n_e)$  increases and  $m^*$  decreases.

Experimentally, undressing from electron-electron interaction is seen as an increase in the coherent response in photoemission experiments,<sup>12</sup> reflecting increase in the quasiparticle weight, and transfer of optical spectral weight from high to low frequencies, reflecting decrease in the quasiparticle mass and decrease in the kinetic energy.<sup>13</sup> In the following we discuss experimental evidence for undressing from the electron-ion interaction upon onset of superconductivity.

### VIII. UNDRRESSING FROM THE ELECTRON-ION INTERACTION

There are several experiments that indicate that in the transition to superconductivity undressing from the electron-ion interaction also takes place.

(1) *Hall effect*: As discussed earlier, the Hall coefficient is negative for electrons near the bottom of the band that are undressed from the electron-ion interaction and is positive for electrons near the top of the band that are dressed by the electron-ion interaction. Hence undressing from the electron-ion interaction should be signaled by a change in sign of the Hall coefficient from positive to negative. Indeed, empirical evidence shows that superconductivity is associated with a positive Hall coefficient in the normal state in the vast majority of cases,<sup>14,15</sup> indicating that the carriers at the Fermi energy are dressed antibonding electrons. Furthermore, it is found in both high  $T_c$  (Ref. 16) and low  $T_c$  materials (Ref. 17) that the Hall coefficient changes its sign from positive to negative at temperatures slightly below  $T_c$ , which indicates that carriers change from holelike to electronlike.

(2) *Bernoulli potential*: Because the superfluid carriers in superconductors carry kinetic energy one expects that an electric field should exist in regions where there is a spatial variation of the superfluid velocity, according to the relation

$$\vec{E} = \frac{1}{e} \vec{\nabla} \frac{1}{2} m_e v_s^2. \quad (23)$$

This was first discussed by London for a free electron model,<sup>18</sup> and the resulting potential is termed Bernoulli potential. As discussed by Adkins and Waldram,<sup>19</sup> within BCS theory the sign of the effect should correspond to the sign of the charge carriers in the normal state. Experiments to measure this effect have been performed with samples of Pb, Nb, PbIn, and Ta, and in all cases the sign of the effect measured corresponds to the superfluid carriers having *negative charge*.<sup>20–22</sup> Note that the Hall coefficient in the normal state is *positive* for all these cases. Furthermore the magnitude of the effect measured is consistent with the mass in Eq. (23) being the *free-electron-mass*.<sup>22</sup>

(3) *Rotating superconductor*: A superconducting body rotating with angular velocity  $\vec{\omega}$  develops a uniform magnetic field in its interior.<sup>23</sup> This can be understood as follows: as the ions start rotating, a time-dependent magnetic field is generated which in turn induces an azimuthal electric field according to Faraday's law

$$\oint \vec{E} \cdot d\vec{l} = - \frac{1}{c} \frac{d}{dt} \int \vec{B} \cdot d\vec{s} \quad (24)$$

so that if the magnetic field is uniform the electric field at position  $\vec{r}$  from the axis of rotation is

$$\vec{E} = \frac{1}{2c} \vec{r} \times \frac{d\vec{B}}{dt}. \quad (25)$$

Now semiclassical transport theory relates the electric field to the time derivative of the wave vector of the carrier

$$\hbar \frac{d\vec{k}}{dt} = e\vec{E} \quad (26)$$

while the time derivative of the velocity of the carrier is given by (for an isotropic case)

$$\frac{d\vec{v}}{dt} = \frac{d}{dt} \left( \frac{1}{\hbar} \frac{\partial \epsilon}{\partial \vec{k}} \right) = \frac{1}{m^* \hbar} \frac{d\vec{k}}{dt}, \quad (27)$$

so that

$$\frac{d\vec{v}}{dt} = \frac{e}{m^*} \vec{E} = \frac{e}{2m^*c} \vec{r} \times \frac{d\vec{B}}{dt}. \quad (28)$$

In steady state the superfluid in the interior rotates together with the lattice<sup>23</sup> so that  $\vec{v} = \vec{\omega} \times \vec{r}$  and from integration of Eq. (28),

$$\vec{\omega} = - \frac{e}{2m^*c} \vec{B}. \quad (29)$$

If the superfluid carriers were dressed by the electron-ion interaction the effective mass in Eq. (29) would be dependent on the particular material and in particular  $\vec{B}$  would point antiparallel to  $\vec{\omega}$  if the carriers are holelike. Instead, it is found experimentally that for all superconductors where it has been measured (including high  $T_c$  cuprates and heavy fermion materials)<sup>24</sup>

$$\vec{B} = - \frac{2m_e c}{e} \vec{\omega} \quad (30)$$

with  $m_e$  the *free-electron mass*. The fact that the magnetic field always points parallel and never antiparallel to the angular velocity indicates that the superfluid carriers have *negative* charge. The fact that the magnitude of the magnetic field is given by Eq. (30) for all materials, with  $m_e$  the *bare* electron mass, indicates that the carriers in the superconducting state are undressed free electrons. This means that the dressed carriers at the top of the Fermi distribution in the band depicted in Fig. 3, with antibonding wave function that knows about the discrete ionic potential, condense to the bottom of the Fermi distribution with a smooth long wavelength wave function that is insensitive to the short wavelength ionic potential. Physically the magnetic field Eq. (30) arises because the negative electrons near the surface of the superconductor lag behind and rotate at slightly smaller angular velocity than the body, as shown schematically in Fig. 4.

(4) *Gyromagnetic effect*: A related effect occurs if a magnetic field is suddenly applied to a superconductor at rest. The supercurrent that develops to nullify the magnetic field in the interior (Meissner effect) carries angular momentum, and for the total angular momentum of the superconducting body to be unchanged the body must start rotating with angular momentum in the opposite direction. If the superfluid carriers have negative charge, the body will start rotating with angular velocity antiparallel to the applied field, which is indeed what is observed.<sup>25</sup>

### IX. KINETIC ENERGY LOWERING, WAVELENGTH EXPANSION, AND PHASE COHERENCE

An effect associated with having an increasing number of electrons in a band is of course an increase in the kinetic energy of the electrons at the Fermi energy. This is true both

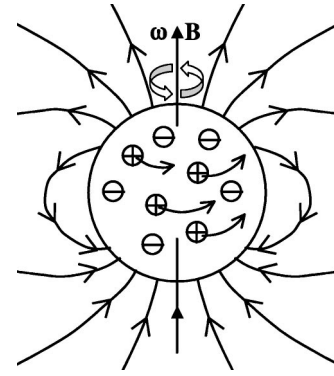


FIG. 4. Experimental proof that electrons undress from the electron-ion interaction when they become superconducting. The *magnitude* of the magnetic field generated in a rotating superconductor Eq. (30) reflects relative motion of superfluid electrons with *bare* mass  $m_e$ . The *sign* of the magnetic field generated reflects slowing down of superfluid *negative* charge.

for band electrons as well as for free electrons. The kinetic energy associated with a spatial variation of the wave function in a region of linear dimension  $\lambda$  is

$$T \sim \frac{\hbar^2}{2m_e \lambda^2}. \quad (31)$$

$\lambda$  can be thought of as the wavelength of the electronic wave function in a  $k$ -space picture, or equivalently as the linear dimension of the region occupied by each electron, i.e., the mean distance between electrons, in a real space picture. In a free-electron model,  $\lambda \sim k_F^{-1}$ . For a single electron in an empty band  $\lambda$  in Eq. (31) is the linear dimension of the sample. As more electrons are added to a band the wavelength of the electronic wave function decreases, or equivalently the size of the region occupied by each electron decreases and the wave function becomes more spatially confined, which leads to an increase of kinetic energy. To the extent that superconductivity is associated with kinetic energy lowering<sup>13,26</sup> it is natural to expect that this will occur when the electrons at the Fermi level have highest kinetic energy in the normal state, which corresponds to the case of an almost full band, which also corresponds to the smallest spatial extent of the electronic wave function, with  $\lambda$  of order the interatomic spacing  $a$ . If the kinetic energy Eq. (31) decreases as the system goes superconducting it implies that the wavelength of the electronic wave function increases so that it no longer sees the short wavelength ionic potential and becomes free-electron-like, and  $\lambda$  in Eq. (31) becomes again the linear macroscopic dimension of the sample, as for the empty band.

We can also understand the origin of diamagnetism in superconductors from this point of view. The diamagnetic response of a normal metal (Landau diamagnetism) can be understood as arising from induced Ampere circular currents of radius given by  $r \sim \lambda \sim k_F^{-1}$ , the interelectronic spacing or equivalently the wavelength of the electronic wave function. In a free-electron model

$$\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}} = -\frac{1}{3}\mu_B^2 g(\epsilon_F) \quad (32)$$

with  $\mu_B = e\hbar/2m_e c$  the Bohr magneton and  $g(\epsilon_F) = 3n/2\epsilon_F$  the density of states, with  $n$  the number of electrons per unit volume. The Larmor diamagnetic response from  $n$  atoms per unit volume is

$$\chi_{\text{Larmor}} = -\frac{e^2 n}{6m_e c^2} \langle r^2 \rangle \quad (33)$$

with  $\langle r^2 \rangle$  the spatial extent of the electronic wave function. Equations (32) and (33) are the same for  $\langle r^2 \rangle = 3/(2k_F^2) \sim \lambda^2$ . When the metal goes superconducting the Meissner currents extend over the entire sample, and the wavelength  $\lambda$  becomes  $R$ , the macroscopic dimension of the sample. Using Eq. (33) for the atomic susceptibility yields perfect diamagnetism when  $\langle r^2 \rangle$  becomes macroscopic.<sup>27</sup> Hence we can interpret the change from Landau diamagnetic response to London diamagnetic response as a wavelength expansion from  $\lambda \sim k_F^{-1} \sim a$  ( $a$ =lattice spacing) for the electrons at the top of the Fermi distribution in Fig. 3 to  $\lambda \sim R \sim k^{-1}$ , i.e., the bottom of the band in Fig. 3 where the free-electron states are.

Furthermore the concept of wavelength expansion provides a qualitative understanding of the phase coherence in superconductors. The carriers near the top of the band, having wavelength of order of a lattice spacing, undergo of order  $10^8$  changes in the sign of their phase from one end to the other of a macroscopic sample of size 1 cm. It is intuitively clear that maintaining phase coherence of such a rapidly oscillating wave is impossible. As the antibonding electrons at the top of the band condense into the  $k \sim 0$  state at the bottom of the band their wavelength becomes the size of the sample and their phase maintains the same sign across the macroscopic sample dimension, thus allowing for the existence of phase coherence over macroscopic length scales which is the hallmark of superconductivity.

Finally if we interpret  $\lambda \sim k_F^{-1}$  as the size of the electronic wave function, the fact that it expands and reaches the boundaries of the macroscopic sample in the transition to superconductivity suggests that negative charge will flow from the interior towards the boundaries of the sample as the normal metal becomes superconducting.<sup>28</sup>

## X. HISTORICAL PRECEDENTS

There were many attempts to understand superconductivity before BCS theory. Some of these early attempts focused on physics closely related to what we discuss in this paper.

(1) The idea that superconductivity would occur only when the normal state carriers are holes, i.e., when the band is almost full, was discussed in early theoretical work by Papapetrou.<sup>29</sup> He argued that electrons at the top of the Fermi distribution would become metastable if the Fermi level was close to a zone boundary. That the band should be almost full was also deemed to be essential in the theory of Born and Cheng.<sup>30</sup>

(2) The idea that the superconducting electrons are not sensitive to the discrete ionic potential was discussed by

Kronig.<sup>31</sup> He proposed that electron-electron interaction effects would dominate over electron-ion effects, and that the ionic lattice should be replaced by a continuum positive background for the description of superconductivity. In the review by Smith and Wilhelm<sup>32</sup> it is also stated that the superconducting electrons, in order to move freely, may experience some binding with the lattice as a whole rather than with particular atoms. Note how different this is to BCS theory, where coupling of electrons not only to the discrete ions but even to their deviation from equilibrium position is deemed essential.

(3) Brillouin<sup>33</sup> postulated that the energy versus  $k$  relation in superconductors may show secondary minima *near the Brillouin zone boundary* (in a band where the minimum is at the zone center), and that electrons in those states would not be sensitive to scattering.

(4) Schafroth<sup>34</sup> proposed that electrons at the top of the Fermi distribution would pair into a resonant state of *negative* binding energy, however such that their combined energy would be less than twice the Fermi energy of single particles, so they would not be able to break up into single particles due to the Pauli principle. This idea obviously requires that the Fermi level be high in the band, or at the very least not near the bottom of the band. It also foreshadows the concept of kinetic energy driven pairing.

(5) Bardeen in early work<sup>35</sup> suggested that superconducting electrons would have a much smaller effective mass than normal electrons. However he abandoned this concept in BCS theory.

(6) Meissner wondered whether superconductivity is carried by the same electrons that carry the normal state current or by different ones.<sup>36</sup> He favored the latter alternative, based on the observation that atoms with only one valence electron outside a closed shell do not form superconductors. This is in agreement with the ideas discussed here, since the antibonding electrons do not carry electric current in the normal state, in fact they do precisely the opposite.

(7) London<sup>37</sup> pointed out that diamagnetism could be understood if electrons in superconductors behave as electrons in giant atoms. A natural extension of London's idea is that the charge distribution in superconductors will also be inhomogeneous as in real atoms, with more positive charge near the center and more negative charge near the boundaries.<sup>6,28</sup>

## XI. THE CUPRATES, CONVENTIONAL SUPERCONDUCTORS, AND THE PAIRING MECHANISM

It is generally agreed that conventional superconductors are described by BCS-electron-phonon theory, and that an unconventional mechanism applies to the cuprates. There is no general agreement on which is the right mechanism for the cuprates, with proposals ranging from purely electronic to magnetic to electron-phonon interactions of unconventional type.<sup>38,39</sup> However the considerations in this paper should apply to all superconductors, conventional or otherwise, because they relate to fundamental aspects of the band theory of solids.

The predominance of hole carriers in the normal state of conventional and unconventional superconductors has been



pointed out repeatedly elsewhere.<sup>14,15,29,30,40</sup> For the cuprates, we have proposed that the hole carriers of interest are those at the top of the band formed by overlap of planar oxygen  $p\pi$  orbitals pointing in direction perpendicular to the Cu-O bond.<sup>41</sup> For  $\text{MgB}_2$ , the holes in the nearly full bands formed by overlap of planar boron  $p\sigma$  orbitals are generally believed to be the dominant carriers driving superconductivity, and there are also electronlike carriers at the Fermi level from other bands.<sup>42</sup> Calculations for a two-band model, one with holelike and one with electronlike carriers at the Fermi energy,<sup>41</sup> yield results for tunneling characteristics that resemble experimental observations in  $\text{MgB}_2$ , with hole (electron) carriers giving rise to a large (small) gap.<sup>43</sup> For electron-doped cuprates, the existence of hole carriers in the regime where they become superconducting has been established experimentally.<sup>44</sup>

We do not address here the question whether specific mechanisms unrelated to the physics discussed here play or do not play a role in different classes of materials. However the following two points necessitate discussion: first, is it *possible* that undressing is the driving force for superconductivity in any or in all materials? We have shown elsewhere that within a class of models (dynamic Hubbard models) pairing leads to lowering of kinetic energy and that as a consequence the low temperature phase is superconducting, in the absence of electron-phonon interactions.<sup>3,4</sup> At the same time in these models pairing gives rise to increased quasiparticle weight and transfer of optical spectral weight from high to low frequencies.<sup>5</sup> Hence at least in these models pairing and superconductivity may be said to be driven by quasiparticle undressing. Instead, in other models with different pairing mechanisms undressing may be a *consequence* of the transition to superconductivity. The physics that is reflected in dynamic Hubbard models is not specific to one class of materials but is generic to electrons and ions in solids as discussed in Ref. 1.

Second, the electron-phonon interaction is known to lead to an isotope effect in  $T_c$  in most conventional materials<sup>45</sup> and to an isotope effect on the London penetration depth in the cuprates.<sup>46</sup> How can this be related to the physics discussed here? First it is clear that the electron-phonon interaction generally will modify electronic-related properties, e.g., band gaps, due to ionic zero-point motion.<sup>47</sup> For dynamic Hubbard models we have shown that the ionic zero-point motion leads to enhancement of the correlated hopping term in the Hamiltonian and as a consequence to a positive isotope shift in  $T_c$ .<sup>48</sup> Now the London penetration depth can be written as

$$\frac{1}{\lambda_L^2} = \frac{4\pi n_s e^2}{m^* c^2}. \quad (34)$$

Note that only the combination  $n_s/m^*$  enters this expression, with  $n_s$  the density of superfluid carriers and  $m^*$  the superfluid carrier's effective mass. Within the dynamic Hubbard model Hamiltonian, a reduction in  $\lambda_L$  would be expected due to lowering of the pair effective mass caused by ionic zero-point motion.<sup>48,49</sup> This may appear to be incompatible with the argument in this paper that the superfluid carriers com-

TABLE I. Different properties of the carriers at the Fermi energy when the Fermi level is near the bottom (bonding electron) and near the top of the band (antibonding electron).

Bonding electron at the Fermi energy	Antibonding electron at the Fermi energy
Undressed	Dressed
Low kinetic energy	High kinetic energy
Long wavelength	Short wavelength
Small effective mass	Large effective mass
Uniform charge density	Nonuniform charge density
Moves in direction of force	Moves opposite to force
Conducts electricity	Anticonducts electricity
Contributes to Drude weight	Anticontributes to Drude weight
Detached from lattice	Transfers momentum to lattice
Large quasiparticle weight	Small quasiparticle weight
Coherent conduction	Incoherent conduction
Large Drude weight	Small Drude weight
Negative Hall coefficient	Positive Hall coefficient
Good metals	Bad metals
Stable lattices	Unstable lattices
Ions attract each other	Ions repel each other
Carriers repel each other	Carriers attract each other
Normal metals	Superconductors

pletely undress from the electron-ion interaction and respond to perturbations as if they had the free electron mass. However the two points of view can be reconciled if one interprets the superfluid weight  $n_s/m^*$  as  $n_s^{\text{eff}}/m_e$  and ascribes its enhancement by larger ionic zero-point motion to an enhancement of the effective superfluid density  $n_s^{\text{eff}}$ .

Table I summarizes the different properties of electrons at the Fermi energy when the Fermi level is near the bottom and near the top of the band and some resulting properties of the solid. Within conventional BCS-electron-phonon theory, these properties do not play an important role in superconductivity, and superconductivity can occur with either bonding or antibonding electrons at the Fermi energy. Instead, independent of what role the electron-phonon interaction may play in superconductivity we propose that only when a solid has at least some carriers with the characteristics listed in the right-hand column can superconductivity occur, and that when it does the normal state carriers of the right-hand column adopt characteristics of the carriers in the left-hand column. In simple and noble metals and any other metal where only carriers of the type described by the left-hand column exist at the Fermi energy superconductivity would not occur according to our theory, no matter how strong the electron-phonon interaction.

## XII. DISCUSSION

In this paper we have continued our analysis of the differences between electrons and holes in energy bands and its implications for the understanding of superconductivity. Our

earlier work<sup>1-5</sup> centered on the differences between electrons and holes arising from the electron-electron interaction. Here we have focused on the even more basic aspects of electron-hole asymmetry that arise from the electron-ion interaction.

It is interesting that the effects of electron-electron interaction and electron-ion interaction related to electron-hole asymmetry are qualitatively similar. Both effects lead to spectral weight transfer from low frequencies to high frequencies as the carriers evolve from electronlike to holelike as the Fermi level rises in the band. Both effects lead to a decrease in the electrical conductivity per carrier as the Fermi level rises, electron-electron interactions because the carriers become heavier, and electron-ion interaction because Bragg scattering causes the antibonding electrons to move in direction opposite to the applied force. Fundamentally, both effects lead to dressing of the quasiparticle as the Fermi level rises in the band, where we define dressing loosely as what makes the quasiparticle different from the bare particle, the free electron.

If dressing impairs the electrical conductivity, and if superconductors are perfect conductors of electricity, it is natural to conclude that superconductivity must be associated with undressing. The fact that pairing of hole carriers effectively shifts the Fermi level to a region lower in the band where the carriers are less dressed supports this point of view. Furthermore it is natural to conclude in view of these considerations that undressing will affect both the dressing originating in the electron-electron interaction and that originating in the electron-ion interaction. Experiments support this interpretation.

What is however not obvious is that carriers will undress *completely* when the transition to superconductivity takes place, and respond as if they had the bare mass and the bare charge of the free electron, as the experimental evidence indicates. The dynamic Hubbard models<sup>3</sup> as well as the Hubbard model with correlated hopping<sup>7</sup> predict that the hopping amplitude increases upon pairing, hence the effective mass decreases, but they *do not* predict that the effective mass becomes the free-electron mass. Furthermore the magnitude of effective mass decrease predicted by the models depends on parameters in the models and on band filling.

The superfluid electrons in the superconducting state have a wave function that extends coherently over the macroscopic dimensions of the sample. As a consequence they no longer see the discrete nature of the electron-ion potential that varies over microscopic scales, instead they see an average smooth background of positive charge. In other words, the wave function is smooth over interatomic distance scales: the carriers have undressed from the electron-ion potential and they can no longer transfer momentum to the ionic lattice. For this scenario to be possible, electrons at the Fermi energy must pair, as it is the pairing that gives rise to superconductivity and to undressing and allows the electrons to circumvent the Pauli principle. Beyond the pairing correlations, superfluid electrons will resemble free electrons in a smooth positive background, a "Thomson atom."<sup>6</sup>

The point of view discussed here also highlights the important role of the electronic confinement of electrons near

the top of the band in the normal state, which raises their kinetic energy, and of their deconfinement upon the transition to the superconducting state, which lowers their kinetic energy. This is especially clear when one considers the lowest band in a solid within the weak electron-ion approximation, but should also apply more generally. The wavelength of electrons at the bottom of the band is macroscopic and becomes gradually smaller as the Fermi level rises, finally being of the order of the lattice spacing for the Fermi level near the top of the band. The wave function deconfines and the wavelength goes from microscopic to macroscopic as the antibonding electrons at the Fermi energy condense into the  $k \sim 0$  superconducting state. In metals where the wavelength of electrons at the Fermi energy is large in the normal state (bonding electrons), no tendency to superconductivity will exist.

In the conventional BCS-Fermi liquid theory quasiparticles are fixed objects that develop special correlations when the transition to superconductivity occurs but do not change their intrinsic nature. Our previous work on undressing from the electron-electron interaction instead had proposed that quasiparticles do change intrinsic properties, their quasiparticle weight and the magnitude of their effective mass, when the transition to superconductivity occurs.<sup>5</sup> Here we have argued that this change in intrinsic properties is even more radical: quasiparticles also change the *sign* of their effective mass from negative to positive and their wavelength from microscopic to macroscopic, when they condense into the superconducting state.

Note that in ordinary Bose condensation for pointlike bosons the phase transition as function of increasing density occurs when the interparticle distance becomes comparable to the boson de Broglie wavelength. Analogously here, the onset of superconductivity as function of increasing band occupation occurs when the Fermi level is high enough in the band such that the de Broglie wavelength of electrons at the Fermi level becomes comparable to the *interatomic* distance. As in ordinary Bose condensation, the transition is to a state with macroscopic de Broglie wavelength.<sup>50</sup>

In ordinary metals, charge inhomogeneity occurs at the level of a single unit cell. If the superfluid electrons do not see the discrete ionic lattice, the unit cell becomes the entire sample and consequently charge inhomogeneity can occur at a macroscopic level in superconductors. Just as in the metallic unit cell bonding electrons lower their kinetic energy by expanding their wave function from one atom to its neighbor, in the superconductor to lower the kinetic energy the electronic wave function will expand towards the outer boundaries of the sample. Indeed, as discussed in other work<sup>6,28,51</sup> we expect superfluid electrons to have a tendency to go near the surface of the sample, giving rise to an excess of negative charge in that region and to experimentally observable consequences.<sup>52,53</sup> Furthermore we suggest that this expansion of the electronic wave function to the boundary of the macroscopic unit cell and beyond is likely to be relevant to the understanding of the superconducting proximity effect.

- <sup>1</sup>J. E. Hirsch, Phys. Rev. B **65**, 184502 (2002).
- <sup>2</sup>J. E. Hirsch, Phys. Lett. A **134**, 451 (1989); Chem. Phys. Lett. **171**, 161 (1990); Phys. Rev. B **48**, 3327 (1993); J. E. Hirsch and F. Marsiglio, Phys. Rev. B **41**, 2049 (1990).
- <sup>3</sup>J. E. Hirsch, Phys. Rev. Lett. **87**, 206402 (2001); Phys. Rev. B **65**, 214510 (2002); **66**, 064507 (2002); **67**, 035103 (2003).
- <sup>4</sup>F. Marsiglio, R. Teshima, and J. E. Hirsch, Phys. Rev. B **68**, 224507 (2003).
- <sup>5</sup>J. E. Hirsch, Physica C **201**, 347 (1992); **364–365**, 37 (2001); Phys. Rev. B **62**, 14487 (2000); **62**, 14498 (2000).
- <sup>6</sup>J. E. Hirsch, Phys. Lett. A **309**, 457 (2003).
- <sup>7</sup>J. E. Hirsch and F. Marsiglio, Phys. Rev. B **39**, 11515 (1989).
- <sup>8</sup>The connection between lattice instabilities and superconductivity was repeatedly emphasized by B. Matthias, who wrote in 1973 “From now on, I shall look for systems that should exist, but won’t—unless one can persuade them.” B. T. Matthias, Physica (Amsterdam) **69**, 54 (1973).
- <sup>9</sup>C. Kittel, *Introduction to Solid State Physics*, 7th ed. (Wiley, New York, 1996).
- <sup>10</sup>W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).
- <sup>11</sup>R. E. Peierls, Phys. Z. **30**, 273 (1929).
- <sup>12</sup>H. Ding, J. R. Engelbrecht, Z. Wang, J. C. Campuzano, S. C. Wang, H. B. Yang, R. Rogan, T. Takahashi, K. Kadowaki, and D. G. Hinks, Phys. Rev. Lett. **87**, 227001 (2001).
- <sup>13</sup>H. J. A. Molegraaf, C. Presura, D. van der Marel, P. H. Kes, and M. Li, Science **295**, 2239 (2002); A. F. Santander-Syro, R. P. S. M. Lobo, N. Bontemps, Z. Konstantinovic, Z. Z. Li, and H. Raffy, Europhys. Lett. **62**, 568 (2003).
- <sup>14</sup>I. Kikoin and B. Lasarev, Nature (London) **129**, 57 (1932); Zh. Eksp. Teor. Fiz. **3**, 44 (1933); Phys. Z. Sowjetunion **3**, 351 (1933).
- <sup>15</sup>I. M. Chapnik, Sov. Phys. Dokl. **6**, 988 (1962).
- <sup>16</sup>M. Galffy and E. Zirngiebl, Solid State Commun. **68**, 929 (1988); S. J. Hagen, C. J. Lobb, R. L. Greene, M. G. Forrester, and J. H. Kang, Phys. Rev. B **41**, 11630 (1990); C. C. Almasan, S. H. Han, K. Yoshiara, M. Buchgeister, D. A. Gajewski, L. M. Paulius, J. Herrmann, M. B. Maple, A. P. Paulikas, Chun Gu, and B. W. Veal, *ibid.* **51**, 3981 (1995).
- <sup>17</sup>H. Van Beelen, J. P. Van Braam Houckgeest, H. M. Thomas, C. Stolk, and R. De Bruyn Ouboter, Physica (Amsterdam) **36**, 241 (1967); C. H. Weijzenfeld, Phys. Lett. A **28**, 362 (1968); N. Usui, T. Ogasawara, K. Yasukochi, and S. Tomoda, J. Phys. Soc. Jpn. **27**, 574 (1969); K. Noto, S. Shinzawa, and Y. Muto, Solid State Commun. **18**, 1081 (1975).
- <sup>18</sup>F. London, *Superfluids* (Wiley, New York, 1950), Vol. 1.
- <sup>19</sup>C. J. Adkins and J. R. Waldram, Phys. Rev. Lett. **21**, 76 (1968).
- <sup>20</sup>J. Bok and J. Klein, Phys. Rev. Lett. **20**, 660 (1968).
- <sup>21</sup>T. D. Morris and J. B. Brown, Physica (Amsterdam) **55**, 760 (1971).
- <sup>22</sup>Y. N. Chiang and O. G. Shevchenko, Low Temp. Phys. **22**, 513 (1996).
- <sup>23</sup>R. Becker, F. Sauter, and C. Heller, Z. Phys. **85**, 772 (1933).
- <sup>24</sup>A. F. Hildebrand, Phys. Rev. Lett. **8**, 190 (1964); N. F. Brickman, Phys. Rev. **184**, 460 (1969); J. Tate, S. B. Felch, and B. Cabrera, Phys. Rev. B **42**, 7885 (1990); A. A. Verheijen, J. M. van Ruitenbeek, R. de Bruyn Ouboter, and L. J. de Jongh, Physica B **165–166**, 1181 (1990); Nature (London) **345**, 418 (1990); M. A. Sanzari, H. L. Cui, and F. Karwacki, Appl. Phys. Lett. **68**, 3802 (1996).
- <sup>25</sup>I. K. Kikoin and S. W. Gubar, J. Phys. (USSR) **3**, 333 (1940); R. H. Pry, A. L. Lathrop, and W. V. Houston, Phys. Rev. **86**, 905 (1952); R. Doll, Z. Phys. **153**, 207 (1958).
- <sup>26</sup>J. E. Hirsch, Science **295**, 2226 (2002).
- <sup>27</sup>W. L. Ginsburg, Fortschr. Phys. **1**, 88 (1953).
- <sup>28</sup>J. E. Hirsch, Phys. Rev. B **68**, 184502 (2003).
- <sup>29</sup>A. Papapetrou, Z. Phys. **92**, 513 (1934).
- <sup>30</sup>M. Born and K. C. Cheng, Nature (London) **161**, 1017 (1948).
- <sup>31</sup>R. de L. Kronig, Z. Phys. **78**, 744 (1932); **80**, 203 (1933).
- <sup>32</sup>H. G. Smith and J. O. Wilhelm, Rev. Mod. Phys. **7**, 237 (1935).
- <sup>33</sup>L. Brillouin, J. Phys. Radium **4**, 677 (1933).
- <sup>34</sup>M. R. Schafroth, Phys. Rev. **96**, 1442 (1954).
- <sup>35</sup>J. Bardeen, Phys. Rev. **81**, 829 (1951).
- <sup>36</sup>W. Meissner, Ergeb. Exakten Naturwiss. **11**, 219 (1932).
- <sup>37</sup>F. London, Nature (London) **140**, 793 (1937).
- <sup>38</sup>P. Brusov, *Mechanisms of High Temperature Superconductivity* (Rostov State University Publishing, Rostov on Don, 1999).
- <sup>39</sup>V. Z. Kresin, H. Morawitz, and S. A. Wolf, *Mechanisms of Conventional and High Tc Superconductivity* (Oxford University Press, New York, 1993).
- <sup>40</sup>J. E. Hirsch, Phys. Rev. B **55**, 9007 (1997).
- <sup>41</sup>J. E. Hirsch and S. Tang, Solid State Commun. **69**, 987 (1989); J. E. Hirsch and F. Marsiglio, Phys. Rev. B **43**, 424 (1991).
- <sup>42</sup>J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
- <sup>43</sup>R. S. Gonnelli, D. Daghero, G. A. Ummarino, V. A. Stepanov, J. Jun, S. M. Kazakov, and J. Karpinski, Phys. Rev. Lett. **89**, 247004 (2002).
- <sup>44</sup>Wu Jiang, S. N. Mao, X. X. Xi, Xiuguang Jiang, J. L. Peng, T. Venkatesan, C. J. Lobb, and R. L. Greene, Phys. Rev. Lett. **73**, 1291 (1994); M. Suzuki, S. Kubo, H. Ishiguro, and K. Haruna, Phys. Rev. B **50**, 9434 (1994); Z. Z. Wang, T. R. Chien, N. P. Ong, J. M. Tarascon, and E. Wang, *ibid.* **43**, 3020 (1991); M. A. Crusellas, J. Fontcuberta, S. Piol, M. Cagigal, and J. L. Vicent, Physica C **210**, 221 (1993); P. Fournier, X. Jiang, W. Jiang, S. N. Mao, T. Venkatesan, C. J. Lobb, and R. L. Greene, Phys. Rev. B **56**, 14149 (1997).
- <sup>45</sup>P. B. Allen, Nature (London) **335**, 396 (1988).
- <sup>46</sup>Guomeng Zhao, K. K. Singh, A. P. B. Sinha, and D. E. Morris, Phys. Rev. B **52**, 6840 (1995); J. Hofer, K. Conder, T. Sasagawa, Guo-meng Zhao, M. Willemin, H. Keller, and K. Kishio, Phys. Rev. Lett. **84**, 4192 (2000).
- <sup>47</sup>P. B. Allen, Philos. Mag. B **70**, 527 (1994); C. Parks, A. K. Ramdas, S. Rodriguez, K. M. Itoh, and E. E. Haller, Phys. Rev. B **49**, 14244 (1994).
- <sup>48</sup>J. E. Hirsch, Phys. Lett. A **282**, 392 (2001), Sec. V.
- <sup>49</sup>J. E. Hirsch and F. Marsiglio, Phys. Rev. B **45**, 4807 (1992).
- <sup>50</sup>J. M. Blatt, *Theory of Superconductivity* (Academic, New York, 1964).
- <sup>51</sup>J. E. Hirsch, Phys. Lett. A **281**, 44 (2001).
- <sup>52</sup>J. E. Hirsch, Phys. Rev. Lett. **92**, 016402 (2004).
- <sup>53</sup>J. E. Hirsch, Phys. Rev. B **69**, 214515 (2004).