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Orbital magnetism in the density functional theory of superconductors

W. Kohn ⁽¹⁾, E. K. U. Gross ⁽¹⁾ and L. N. Oliveira ⁽²⁾

⁽¹⁾ Department of Physics, University of California, Santa Barbara, CA 93106, U.S.A.

⁽²⁾ Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-São Carlos, SP, Brazil

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Résumé. — Une théorie par la fonctionnelle de la densité de courant est développée pour des supraconducteurs dans un champ magnétique. Le formalisme conduit à un ensemble d'équations de Kohn-Sham auto-cohérentes à résoudre, dans une seconde étape auto-cohérente, avec les équations de Maxwell pour le potentiel vecteur.

Abstract. — A current-density functional theory for superconductors in a magnetic field is developed. The formalism results in a set of self-consistent Kohn-Sham equations to be solved, in a second self-consistency loop, with Maxwell's equations for the vector potential.

Préface. — It is an exceptional pleasure for me to contribute, jointly with my young colleagues, to this scientific celebration of Jacques Friedel. Although we live on different continents and come from rather different backgrounds, Jacques has been one of my closest personal and scientific friends since the early 1950's.

We have witnessed each other's children grow up and establish families of their own. For several years I watched his sons' slow progress, and sometimes lack of it, on a recalcitrant, heavy, old boat which had changed the garage in Palteau into a dry-dock. Jacques' first student, André Blandin, became my close friend and frequent visitor ; his second, Emile Daniel, came to work with me after his thesis. For many years, and still continuing, we have had a regular shuttle service between our groups in California and in Paris. Over this period, spending a few months, or at least, weeks in Paris every few years has grown for me into an almost irresistible need ; and visiting Jacques and Mary in Paris and Palteau, as well as our younger French friends and colleagues in and near Paris, has become for me something like a homecoming.

Almost all of Jacques' scientific work has been of the greatest interest to me and stimulated much of my own thinking. The so-called Kohn phonon anomaly is essentially the Fourier transform of the famous Friedel oscillations in coordinate space. We have shared strong interests in impurities in metals, in properties of alloys, in many body effects in metals, in surfaces, and even in science-planning (of which Jacques has done too much !).

Selecting a suitable subject for this paper was very easy since there are few areas in solid state physics which have not been touched by Jacques' insights. In the fall of 1987, when visiting Santa Barbara, he

proposed some viewpoints concerning the then very new high temperature superconductors, while we began to ask ourselves if density functional theory might have something to offer. The present note is on this latter subject.

Je dédie cette petite œuvre à Jacques et à notre amitié.

1. Introduction.

Traditional superconductivity of pure metals is well described as a phenomenon of *homogeneous* media. Due to the relatively large coherence length (10^2 - 10^4 Å), inhomogeneities on the scale of the lattice constant can be neglected. This statement holds true for both the weak coupling limit (BCS theory [1]) and for the strong coupling case (Eliashberg equations [2]). In the new high- T_c materials, the situation is different. Experimental coherence lengths of the order of 10 Å suggest that inhomogeneities on the scale of the lattice constant have to be taken into account in a proper description of these materials.

Density functional theory (DFT), by its very construction, is a theory of inhomogeneous systems [3]. The basic idea of DFT in its original form is to describe the properties of a normal system in terms of its ground state density [4], or, at finite temperature, in terms of its equilibrium density [5]. The grand canonical potential of such a system is defined as

$$\Omega = -\frac{1}{\beta} \log \text{tr} e^{-\beta \hat{H}_{v-\mu}}, \quad (1)$$

where $\beta = 1/\theta$ denotes the inverse temperature (the Boltzmann constant is set equal to 1), and $\hat{H}_{v-\mu}$ is the grand canonical Hamiltonian

$$\hat{H}_{v-\mu} = \hat{T} + \hat{U} + \int d^3r \hat{n}(r)(v(r) - \mu), \quad (2)$$

with

$$\hat{n}(r) = \sum_{\alpha=\uparrow\downarrow} \psi_{\alpha}^{\dagger}(r) \psi_{\alpha}(r), \quad (3)$$

$$\hat{T} = \sum_{\alpha} \int d^3r \psi_{\alpha}^{\dagger}(r) \left(-\frac{\nabla^2}{2} \right) \psi_{\alpha}(r), \quad (4)$$

and

$$\hat{U} = \frac{1}{2} \sum_{\alpha,\beta} \int d^3r \int d^3r' \psi_{\alpha}^{\dagger}(r) \psi_{\beta}^{\dagger}(r') \frac{1}{|r-r'|} \psi_{\beta}(r') \psi_{\alpha}(r). \quad (5)$$

(Atomic units are used throughout). $v(r)$ is a local external potential and μ denotes the chemical potential of the system. It was shown by Mermin [5] that, for given β , μ , and $v(r)$, there exists a functional of the electron density $n(r)$,

$$\Omega_{v-\mu}[n(r); \beta] \equiv F[n(r); \beta] + \int d^3r (v(r) - \mu) n(r), \quad (6)$$

whose minimum, attained for the correct equilibrium density, is equal to the correct grand potential. Here $F[n(r); \beta]$ is a universal functional of $n(r)$. Based on this variational principle Kohn and Sham [6] (KS) derived a set of temperature dependent single-particle self-consistent equations, having the same structure as the temperature-dependent Hartree

equations, but including many-body effects through an exchange-correlation potential, $v_{xc}(r)$.

Originally developed for normal systems with a local external potential, DFT has since been generalized in many ways. If, e.g., a magnetic field, $\mathbf{B}(r)$, is present, its (Zeeman) coupling to the electron spin can be incorporated by adding the term

$$\hat{H}_B = - \int d^3r \mathbf{B}(r) \cdot \hat{\mathbf{m}}(r) \quad (7)$$

to the basic Hamiltonian $\hat{H}_v - \mu$. Here the operator

$$\hat{\mathbf{m}}(r) = -\mu_0 \sum_{\alpha\beta} \psi_{\alpha}^{\dagger}(r) \boldsymbol{\sigma}_{\alpha\beta} \psi_{\beta}(r)$$

represents the spin magnetization, μ_0 is the Bohr magneton, and $\boldsymbol{\sigma}_{\alpha\beta}$ denotes the vector of Pauli spin matrices. In this case the basic functional F (cf. Eq. (6)) depends on both the density, $n(r)$, and the spin magnetization, $\mathbf{m}(r)$. If orbital magnetic effects are taken into account, F depends, in addition, on the paramagnetic current density $\mathbf{j}_p(r)$ [7, 8].

The most recent development, stimulated by the discovery of the high- T_c materials, has been the DF formulation for superconductors [9]. In this generalization of DFT, the basic functional F depends on a complex valued « anomalous » density $\Delta(r)$, in addition to the normal density, $n(r)$. $\Delta(r)$ is proportional to the order parameter of the Ginzburg-Landau theory [10]. The DFT of superconductors will be briefly summarized in section 2. The purpose of the present note is to incorporate orbital magnetic effects, such as the Meissner effect, into the formalism. The central result will be a set of KS-like equations, generalizing the Bogoliubov-de Gennes equations [11] to incorporate exchange and correlation effects. The derivation of these equations and a detailed proof of their gauge invariance will be presented in section 3.

2. Density functional formalism for superconductors without magnetic field.

Coherence phenomena such as superfluidity and superconductivity are characterized by the presence of « off-diagonal long-range order » (ODLRO) [12, 13]. For superconductors, ODLRO manifests itself in the two-particle density matrix as an exact decoupling of the form

$$\lim_{|r-r'| \rightarrow \infty} \langle \psi_{\downarrow}^{\dagger}(r) \psi_{\uparrow}^{\dagger}(r) \psi_{\uparrow}(r') \psi_{\downarrow}(r') \rangle = \langle \psi_{\downarrow}^{\dagger}(r) \psi_{\uparrow}^{\dagger}(r) \rangle \langle \psi_{\uparrow}(r') \psi_{\downarrow}(r') \rangle \neq 0; \quad (8)$$

(the brackets denote thermal averaging). The « anomalous density »

$$\Delta(r) \equiv \langle \psi_{\uparrow}(r) \psi_{\downarrow}(r) \rangle \quad (9)$$

appearing in equation (8) can be identified [14, 11], in the appropriate limits, with the order parameter of the Ginzburg-Landau theory [10].

In exactly the same fashion as the order parameter, $\mathbf{m}(r)$, of a magnetic system is coupled to an external magnetic field, $\mathbf{B}(r)$ (cf. Eq. (7)), the order parameter $\Delta(r)$ of superconductors is coupled to an external pair potential, $D(r)$, leading to the Hamiltonian

$$\hat{H}_D = - \int d^3r (D^*(r) \psi_{\uparrow}(r) \psi_{\downarrow}(r) + D(r) \psi_{\downarrow}^{\dagger}(r) \psi_{\uparrow}^{\dagger}(r)). \quad (10)$$

More generally, ODLRO holds for the full two-particle density matrix of four different arguments in the form [13]

$$\lim_{|r-r'|\rightarrow\infty} \langle \psi_{\downarrow}^{\dagger}(r_1) \psi_{\uparrow}^{\dagger}(r_2) \psi_{\uparrow}(r_3) \psi_{\downarrow}(r_4) \rangle = \\ = \left\langle \psi_{\downarrow}^{\dagger}\left(r+\frac{s}{2}\right) \psi_{\uparrow}^{\dagger}\left(r-\frac{s}{2}\right) \right\rangle \left\langle \psi_{\uparrow}\left(r'+\frac{s'}{2}\right) \psi_{\downarrow}\left(r'-\frac{s'}{2}\right) \right\rangle \neq 0, \quad (11)$$

where

$$r = (r_1 + r_2)/2, \quad r' = (r_3 + r_4)/2, \\ s = r_1 - r_2, \quad s' = r_3 - r_4.$$

One might therefore consider the *nonlocal* anomalous density,

$$\Delta(r, r') = \langle \psi_{\uparrow}(r) \psi_{\downarrow}(r') \rangle, \quad (12)$$

coupled to an external pair field $D(r, r')$:

$$\hat{H}_D = - \int d^3r (D^*(r, r') \psi_{\uparrow}(r) \psi_{\downarrow}(r') + \text{H.c.}). \quad (13)$$

$D(r, r')$ can be physically realized as a pair field induced by the proximity of an adjacent « given » superconductor [9]. Alternatively the pair field D may be introduced as a mathematical device which is eventually allowed to go to zero. (This scheme is analogous to introducing a weak magnetic field to fix the direction of magnetization of a spontaneous ferromagnet. The same trick is employed in the formal derivation of spin DFT for systems not subject to an external magnetic field).

Logically a DF formalism can be developed either for the local order parameter $\Delta(r)$ or for the nonlocal anomalous density $\Delta(r, r')$ ⁽¹⁾. Although the latter might have more physical significance, we shall concentrate here, for simplicity, on the local gap function $\Delta(r)$. As long as we deal only with Coulomb-induced superconductivity, the total Hamiltonian takes the form

$$\hat{H}_{v-\mu, D} = \hat{H}_{v-\mu} + \hat{H}_D, \quad (14)$$

where $\hat{H}_{v-\mu}$ is given by equation (2). It was demonstrated long ago that the Coulomb repulsion alone *can* give rise to superconductivity [16] and there is a widely held opinion that in the new high- T_c materials the principal pairing mechanism is of purely electronic origin. The formal incorporation of phonon-induced pairing terms in (14) is possible [9], but raises new issues connected with retardation effects and with the universality of the functional F . In the present paper we limit ourselves to purely electronic pairing.

Following Mermin's argument [5], a Hohenberg-Kohn (HK) theorem based on the Hamiltonian $\hat{H}_{v-\mu, D}$ is easily established. The theorem states that, at any given temperature θ , the densities $n(r)$ and $\Delta(r)$ uniquely determine the external potentials $v(r) - \mu$, $D(r)$, so that the grand canonical density operator,

$$\hat{\rho} = e^{-\beta \hat{H}_{v-\mu, D}} / \text{tr} \{ e^{-\beta \hat{H}_{v-\mu, D}} \}, \quad (15)$$

⁽¹⁾ Similarly, DFT of normal systems can be formulated either for the density, $n(r)$, or for the density matrix $\gamma(r, r')$ [15].

and hence the grand potential,

$$\Omega_{v-\mu,D}[\hat{\rho}] = \text{tr} \left\{ \hat{\rho} (\hat{H}_{v-\mu,D} + \theta \log \hat{\rho}) \right\}, \quad (16)$$

become functionals of $n(r)$ and $\Delta(r)$. The latter can be written as

$$\Omega_{v-\mu,D}[n(r), \Delta(r); \beta] = F[n(r), \Delta(r); \beta] + \int d^3r (v(r) - \mu) n(r) - \int d^3r (D^*(r) \Delta(r) + D(r) \Delta^*(r)), \quad (17)$$

where $F[n, \Delta; \beta]$ is a *universal* functional of the densities $n(r)$, $\Delta(r)$, i.e., F does not depend on the external potentials $(v(r) - \mu)$, $D(r)$ of the particular system considered. The functional F is defined as

$$\begin{aligned} F[n, \Delta] &= \text{tr} \left\{ \hat{\rho}[n, \Delta] (\hat{T} + \hat{U} + \theta \log \hat{\rho}[n, \Delta]) \right\} \\ &= T[n, \Delta] + U[n, \Delta] - \theta S[n, \Delta], \end{aligned} \quad (18)$$

where $T[n, \Delta]$, $U[n, \Delta]$ and $S[n, \Delta]$ are, respectively, the functionals for the kinetic energy, the Coulomb energy, and the entropy at temperature $\theta = 1/\beta$. (The explicit dependence of the functionals on β is suppressed for brevity).

Consider now a particular system characterized by the external potentials $(v_0(r) - \mu_0)$, $D_0(r)$. Then, due to the Gibbs principle [5], $\Omega_{v_0-\mu_0,D_0}[n, \Delta]$ is minimized by the equilibrium densities $n_0(r)$, $\Delta_0(r)$ of the system, with $\Omega_{v_0-\mu_0,D_0}[n_0, \Delta_0]$ being the correct equilibrium value of the thermodynamical potential.

A particularly important application of this variational principle is the derivation of a set of KS-like single-particle equations. To this end we define an exchange-correlation free-energy functional $F_{xc}[n(r), \Delta(r)]$ by the equality

$$F[n, \Delta] = F_s[n, \Delta] + \frac{1}{2} \int d^3r \int d^3r' \frac{n(r) n(r')}{|r - r'|} + F_{xc}[n, \Delta], \quad (19)$$

where

$$\begin{aligned} F_s[n, \Delta] &= \text{tr} \left\{ \hat{\rho}_s (\hat{T} + \theta \log \hat{\rho}_s) \right\} \\ &= T_s[n, \Delta] - \theta S_s[n, \Delta]. \end{aligned} \quad (20)$$

$\hat{\rho}_s$, $T_s[n, \Delta]$, and $S_s[n, \Delta]$ denote, respectively, the density operator, the kinetic energy, and the entropy of a noninteracting system subject to potentials $v_s(r)$ and $D_s(r)$, chosen such that its densities $n(r)$ and $\Delta(r)$ are equal to those of the interacting system. The grand canonical Hamiltonian of this system,

$$\hat{H}_s = \sum_{\alpha} \int d^3r \psi_{\alpha}^{\dagger}(r) \left[-\frac{\nabla^2}{2} + v_s(r) - \mu \right] \psi_{\alpha}(r) - \int d^3r [D_s^*(r) \psi_{\uparrow}(r) \psi_{\downarrow}(r) + \text{H.c.}], \quad (21)$$

is diagonalized by the Bogoliubov [17, 18]-Valatin [19] transformation

$$\begin{aligned} \psi_{\uparrow}(r) &= \sum_m [u_m(r) \gamma_{m\uparrow} - v_m^*(r) \gamma_{m\downarrow}^{\dagger}], \\ \psi_{\downarrow}(r) &= \sum_m [u_m(r) \gamma_{m\downarrow} + v_m^*(r) \gamma_{m\uparrow}^{\dagger}], \end{aligned} \quad (22)$$

where the functions $u_m(r)$ and $v_m(r)$ satisfy the eigenvalue equations

$$\begin{aligned} \left[-\frac{\nabla^2}{2} + v_s(r) - \mu - \varepsilon_m \right] u_m(r) &= -D_s(r) v_m(r), \\ \left[-\frac{\nabla^2}{2} + v_s(r) - \mu + \varepsilon_m \right] v_m(r) &= D_s^*(r) u_m(r). \end{aligned} \quad (23)$$

The operators $\gamma_{m\uparrow}^+$ and $\gamma_{m\downarrow}^+$ create quasiparticle excitations above the superconducting ground state. They obey the usual Fermi anticommutation relations, so that

$$\langle \gamma_{m\uparrow}^+ \gamma_{m\uparrow} \rangle = \langle \gamma_{m\downarrow}^+ \gamma_{m\downarrow} \rangle = (1 + e^{\beta \varepsilon_m})^{-1} \equiv f_m^\theta. \quad (24)$$

Using equations (22) and (24), the densities $n(r)$ and $\Delta(r)$ are easily expressed in terms of the functions $u_m(r)$ and $v_m(r)$:

$$n(r) = 2 \sum_m [|u_m(r)|^2 f_m^\theta + |v_m(r)|^2 (1 - f_m^\theta)], \quad (25)$$

$$\Delta(r) = \sum_m v_m^*(r) u_m(r) (1 - 2 f_m^\theta). \quad (26)$$

To determine the effective potentials $v_s(r)$ and $D_s(r)$, we compute $F_s[n, \Delta]$ in terms of the $u_m(r)$, $v_m(r)$ and ε_m , substitute the result in (19) and then minimize the thermodynamic potential (17) with respect to $n(r)$ and $\Delta(r)$. This yields

$$v_s[n, \Delta](r) = v(r) + \int \frac{n(r')}{|r - r'|} d^3 r' + v_{xc}[n, \Delta](r), \quad (27)$$

$$D_s[n, \Delta](r) = D(r) + D_{xc}[n, \Delta](r), \quad (28)$$

where

$$v_{xc}[n, \Delta](r) = \frac{\delta F_{xc}[n, \Delta]}{\delta n(r)}, \quad (29)$$

$$D_{xc}[n, \Delta](r) = -\frac{\delta F_{xc}[n, \Delta]}{\delta \Delta^*(r)}. \quad (30)$$

Since the effective potentials $v_s(r)$ and $D_s(r)$ depend on the densities $n(r)$, $\Delta(r)$, the whole cycle of equations (23), (25)-(30) has to be solved in selfconsistent fashion. This set of KS-like equations is structurally similar to the Bogoliubov-de Gennes equations [11]. However, in contrast to the latter, they contain (in principle exactly) all normal and superconducting many-body effects through the exchange-correlation potentials $v_{xc}(r)$ and $D_{xc}(r)$.

3. Current-density functional theory of superconductors in a magnetic field.

In this section we shall incorporate the coupling of electronic currents to a given vector potential $\mathbf{A}(r)$. This is achieved, as usual, by substituting

$$\hat{T}_A \equiv \sum_\alpha \int d^3 r \psi_\alpha^\dagger(r) \frac{1}{2} \left(-i \nabla + \frac{1}{c} \mathbf{A}(r) \right)^2 \psi_\alpha(r) \quad (31)$$

for the kinetic energy \hat{T} in equations (2) and (14). This leads, after some trivial manipulations, to the total Hamiltonian

$$\hat{H}_{v-\mu, D, \mathbf{A}} = \hat{H}_{v-\mu, D} + \int d^3r \hat{n}(r) \left(\frac{A^2(r)}{2c^2} \right) + \int d^3r \mathbf{j}_p(r) \cdot \frac{\mathbf{A}(r)}{c}, \quad (32)$$

where $\hat{\mathbf{j}}_p$ denotes the paramagnetic current density operator

$$\hat{\mathbf{j}}_p(r) = \frac{1}{2i} \sum_{\alpha} \{ \psi_{\alpha}^{\dagger}(r) \nabla \psi_{\alpha}(r) - [\nabla \psi_{\alpha}^{\dagger}(r)] \psi_{\alpha}(r) \}. \quad (33)$$

The physical current density $\mathbf{j}(r)$ (which satisfies the continuity equation) is related to the paramagnetic current density by the equality

$$\mathbf{j}(r) = \mathbf{j}_p(r) + n(r) \frac{\mathbf{A}(r)}{c}. \quad (34)$$

Following the analysis of section 2, a HK theorem for the Hamiltonian $\hat{H}_{v-\mu, D, \mathbf{A}}$ is easily established : the densities $n(r)$, $\Delta(r)$ and $\mathbf{j}_p(r) = \langle \hat{\mathbf{j}}_p(r) \rangle$ uniquely determine the potentials $v(r) - \mu$, $D(r)$, $\mathbf{A}(r)$, so that the grand canonical potential,

$$\Omega_{v-\mu, D, \mathbf{A}} = -\frac{1}{\beta} \log \text{tr} e^{-\beta \hat{H}_{v-\mu, D, \mathbf{A}}}, \quad (35)$$

becomes a functional of $n(r)$, $\Delta(r)$, and $\mathbf{j}_p(r)$. As before, this functional can be split into a universal part, F , which is defined as in equation (18) (with all functional dependences on $n(r)$ and $\Delta(r)$ being extended to include $\mathbf{j}_p(r)$), and a part that depends on the given potentials :

$$\begin{aligned} \Omega_{v-\mu, D, \mathbf{A}}[n(r), \Delta(r), \mathbf{j}_p(r)] = & F[n(r), \Delta(r), \mathbf{j}_p(r)] + \int d^3r \left(v(r) - \mu + \frac{A^2(r)}{2c^2} \right) n(r) + \\ & + \int d^3r \mathbf{j}_p(r) \cdot \frac{\mathbf{A}(r)}{c} - \int d^3r [D^*(r) \Delta(r) + D(r) \Delta^*(r)]. \end{aligned} \quad (36)$$

Once again, the absolute minimum of this functional, attained for the correct equilibrium densities, equals the correct grand potential at temperature θ .

In order to derive a set of KS-like equations it is assumed ⁽²⁾ that the interacting densities $n(r)$, $\Delta(r)$, $\mathbf{j}_p(r)$ can be obtained as equilibrium densities of some non-interacting system characterized by the Hamiltonian

$$\begin{aligned} \hat{H}_s = \sum_{\alpha} \int d^3r \psi_{\alpha}^{\dagger}(r) \left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \mathbf{A}_s(r) \right)^2 + u_s(r) - \mu \right] \psi_{\alpha}(r) - \\ - \int d^3r [D_s^*(r) \psi_{\uparrow}(r) \psi_{\downarrow}(r) + \text{H.c.}] \end{aligned} \quad (37)$$

⁽²⁾ This assumption corresponds to the usual assumption of « non-interacting v-representability » in ordinary KS theory.

By virtue of the HK theorem, the potentials $u_s(r)$, $D_s(r)$, $A_s(r)$ are *unique* and can be determined from the variational principle. The result is

$$A_s(r) = A(r) + A_{xc}(r), \quad (38)$$

$$D_s(r) = D(r) + D_{xc}(r), \quad (39)$$

$$u_s(r) = v_s(r) + \frac{A^2(r)}{2c^2} - \frac{A_s^2(r)}{2c^2}, \quad (40)$$

where

$$v_s(r) = v(r) + \int \frac{n(r')}{|r - r'|} d^3r' + v_{xc}(r), \quad (41)$$

and

$$\frac{1}{c} A_{xc}(r) = \frac{\delta F_{xc}[n, \Delta, \mathbf{j}_p]}{\delta \mathbf{j}_p(r)}, \quad (42)$$

$$D_{xc}(r) = - \frac{\delta F_{xc}[n, \Delta, \mathbf{j}_p]}{\delta \Delta^*(r)}, \quad (43)$$

$$v_{xc}(r) = \frac{\delta F_{xc}[n, \Delta, \mathbf{j}_p]}{\delta n(r)}. \quad (44)$$

The exchange-correlation functional, F_{xc} , is defined as in equations (19), (20), with all functional dependences on $n(r)$ and $\Delta(r)$ being extended to include $\mathbf{j}_p(r)$.

It should be noted that, in equation (37), the quadratic term $A_s^2(r)/2c^2$, arising from $\frac{1}{2} \left(-i\nabla + \frac{A_s(r)}{c} \right)^2$, cancels with the last term in $u_s(r)$, equation (40). Therefore \tilde{H}_s depends only *linearly* on the exchange-correlation potential $A_{xc}(r)$.

The Kohn-Sham/Bogoliubov-de Gennes equations then take the form

$$\left(\frac{1}{2} \left[-\nabla^2 + A_s(r) \cdot \frac{\nabla}{ic} + \frac{\nabla}{ic} \cdot A_s(r) + \frac{A^2(r)}{c^2} \right] + v_s(r) - \mu - \varepsilon_m \right) u_m(r) = -D_s(r) v_m(r), \quad (45)$$

$$\left(\frac{1}{2} \left[-\nabla^2 - A_s(r) \cdot \frac{\nabla}{ic} - \frac{\nabla}{ic} \cdot A_s(r) + \frac{A^2(r)}{c^2} \right] + v_s(r) - \mu + \varepsilon_m \right) v_m(r) = D_s^*(r) u_m(r), \quad (46)$$

and the densities, expressed in terms of the $u_m(r)$, $v_m(r)$, are given by

$$n(r) = 2 \sum_m [|u_m(r)|^2 f_m^\theta + |v_m(r)|^2 (1 - f_m^\theta)], \quad (47)$$

$$\Delta(r) = \sum_m v_m^*(r) u_m(r) (1 - 2 f_m^\theta), \quad (48)$$

and

$$\mathbf{j}_p(r) = -i \sum_m [\{u_m^*(r) \nabla u_m(r) - u_m(r) \nabla u_m^*(r)\} f_m^\theta + \{v_m(r) \nabla v_m^*(r) - v_m^*(r) \nabla v_m(r)\} (1 - f_m^\theta)]. \quad (49)$$

Equations (38)-(49) are the central result of our analysis. Once a selfconsistent solution of these equations is achieved the thermodynamical potential (36) is easily calculated. We find

$$\Omega_{v-\mu, D, A}[n, \Delta, \mathbf{j}_p] = \Omega_s^\theta - \frac{1}{2} \int \frac{n(r) n(r')}{|r-r'|} d^3r d^3r' - \int n(r) v_{xc}(r) d^3r - \int \mathbf{j}_p(r) \cdot \frac{\mathbf{A}_{xc}(r)}{c} d^3r \\ + \int (D_{xc}^*(r) \Delta(r) + D_{xc}(r) \Delta^*(r)) d^3r + F_{xc}[n, \Delta, \mathbf{j}_p] \quad (50)$$

where $\Omega_s^\theta = -\theta \log \text{tr} \{e^{-\beta \hat{H}_s}\}$ is the grand potential of the non-interacting (KS) system. We now turn to the proof of gauge invariance of the formalism. We consider the gauge transformation

$$\mathbf{A}(r) \rightarrow \mathbf{A}'(r) \equiv \mathbf{A}(r) - \nabla \Lambda(r), \quad (51)$$

$$v(r) \rightarrow v'(r) \equiv v(r), \quad (52)$$

$$\psi(r) \rightarrow \psi'(r) = e^{i\Lambda(r)/c} \psi(r), \quad (53)$$

where $\Lambda(r)$ is an arbitrary function of space coordinates. To ensure gauge invariance of the basic Hamiltonian $\hat{H}_{v-\mu, D, A}$, the external pair potential must transform as

$$D'(r) \equiv e^{2i\Lambda(r)/c} D(r). \quad (54)$$

As a consequence of (53), one finds for the densities

$$n'(r) = n(r), \quad (55)$$

$$\Delta'(r) = e^{2i\Lambda(r)/c} \Delta(r), \quad (56)$$

$$\mathbf{j}'_p(r) = \mathbf{j}_p(r) + \frac{1}{c} n(r) \nabla \Lambda(r). \quad (57)$$

Now let $(u_s(r) - \mu)$, $D_s(r)$, $A_s(r)$ be the set of single-particle potentials leading to KS solutions $u_m(r)$, $v_m(r)$ that reproduce the interacting densities $n(r)$, $\Delta(r)$, $\mathbf{j}_p(r)$ via equations (47)-(49). If $n'(r)$, $\Delta'(r)$, $\mathbf{j}'_p(r)$ are the gauge transformed (interacting) densities then, by virtue of the HK theorem, there exists one and only one set of potentials, $(u'_s - \mu')$, D'_s , A'_s reproducing the densities n' , Δ' , and \mathbf{j}'_p .

Obviously,

$$u'_s(r) - \mu' \equiv u_s(r) - \mu, \quad (58)$$

$$D'_s(r) \equiv e^{2i\Lambda(r)/c} D_s(r), \quad (59)$$

$$A'_s(r) \equiv A_s(r) - \nabla \Lambda(r) \quad (60)$$

do the job: One readily verifies that the solutions $u'_m(r)$, $v'_m(r)$ resulting from the KS equations with the potentials (58)-(60) are given by

$$u'_m(r) = e^{i\Lambda(r)/c} u_m(r), \quad (61)$$

$$v'_m(r) = e^{-i\Lambda(r)/c} v_m(r), \quad (62)$$

which lead to densities $n'(r)$, $\Delta'(r)$, $\mathbf{j}'_p(r)$ satisfying equations (55)-(57). Hence the potentials (58)-(60) constitute the (unique) set of gauge transformed KS potentials leading to the gauge

transformed densities. Equations (58)-(60) together with (53) demonstrate that \hat{H}_s (Eq. (37)) is manifestly gauge invariant.

We conclude this section with an investigation of how the functional F_{xc} and the resulting exchange-correlation potentials behave under the gauge transformation (51)-(54). To this end we first consider the functionals $F[n, \Delta, \mathbf{j}_p]$ and $F_s[n, \Delta, \mathbf{j}_p]$ defined in equations (18) and (20). Since $\hat{H}_{v-\mu, D, A}$ is manifestly gauge invariant the entropic part of $F[n, \Delta, \mathbf{j}_p]$ must be gauge invariant as well. Furthermore, the Coulomb interaction is gauge invariant,

$$\hat{U}' = \hat{U}, \quad (63)$$

while the kinetic energy transforms as

$$\hat{T}' = \hat{T} + \frac{1}{c} \int d^3r \mathbf{j}_p(r) \cdot \nabla \Lambda(r) + \frac{1}{2c^2} \int d^3r \hat{n}(r) |\nabla \Lambda(r)|^2. \quad (64)$$

All this taken together leads to

$$F[n', \Delta', \mathbf{j}_p'] = F[n, \Delta, \mathbf{j}_p] + \frac{1}{c} \int d^3r \mathbf{j}_p(r) \cdot \nabla \Lambda(r) + \frac{1}{2c^2} \int d^3r n(r) |\nabla \Lambda(r)|^2. \quad (65)$$

As demonstrated above, the noninteracting Hamiltonian, \hat{H}_s , is manifestly gauge invariant. Therefore, the non-interacting entropy $S_s[n, \Delta, \mathbf{j}_p]$ must be so too. Furthermore, as a consequence of (64), the noninteracting kinetic energy functional $T_s[n, \Delta, \mathbf{j}_p]$ transforms in exactly the same way as the interacting one since the noninteracting densities are, by construction, identical with the interacting ones.

Hence,

$$F_s[n', \Delta', \mathbf{j}_p'] = F_s[n, \Delta, \mathbf{j}_p] + \frac{1}{c} \int d^3r \mathbf{j}_p(r) \cdot \nabla \Lambda(r) + \frac{1}{2c^2} \int d^3r n(r) |\nabla \Lambda(r)|^2. \quad (66)$$

By inserting (65) and (66) into the defining equation (19) of $F_{xc}[n, \Delta, \mathbf{j}_p]$ one finds that the exchange-correlation functional is gauge invariant,

$$F_{xc}[n', \Delta', \mathbf{j}_p'] = F_{xc}[n, \Delta, \mathbf{j}_p], \quad (67)$$

or, more explicitly,

$$F_{xc}\left[n, e^{2i\Lambda/c} \Delta, \mathbf{j}_p + \frac{1}{c} n \nabla \Lambda\right] = F_{xc}[n, \Delta, \mathbf{j}_p]. \quad (68)$$

Taking the functional derivatives of this equation with respect to $n(r)$, $\Delta^*(r)$, and $\mathbf{j}_p(r)$, one readily verifies that

$$v_{xc}[n', \Delta', \mathbf{j}_p'] = v_{xc}[n, \Delta, \mathbf{j}_p] - \frac{1}{c^2} A_{xc}[n, \Delta, \mathbf{j}_p] \cdot \nabla \Lambda, \quad (69)$$

$$A_{xc}[n', \Delta', \mathbf{j}_p'] = A_{xc}[n, \Delta, \mathbf{j}_p], \quad (70)$$

$$D_{xc}[n', \Delta', \mathbf{j}_p'] = e^{2i\Lambda/c} D_{xc}[n, \Delta, \mathbf{j}_p]. \quad (71)$$

Of course, by inserting these equations, together with (51), (52), and (54) into the defining equations (38)-(41) of u_s , A_s , and D_s , one recovers the transformations (58)-(60).

The gauge invariance of F_{xc} has important consequences for its functional dependence on $\Delta(r)$ and $\mathbf{j}_p(r)$: since equation (68) holds for arbitrary functions $\Delta(r)$, F_{xc} can only depend on $|\Delta(r)|$ and on the curl of the velocity field,

$$\mathbf{v}(r) \equiv \nabla \times \frac{\mathbf{j}_p(r)}{n(r)}, \quad (72)$$

i.e., the exchange-correlation functional can be written as

$$F_{xc}[n, \Delta, \mathbf{j}_p] = \tilde{F}_{xc}[n, |\Delta|, \mathbf{v}]. \quad (73)$$

This implies, e.g., that a local approximation with respect to $\mathbf{j}_p(r)$ is not possible. A local approximation with respect to $\mathbf{v}(r)$ on the other hand can be constructed [8].

In an actual superconducting system placed in a given external field, $\mathbf{A}_{ex}(r)$, supercurrents are set up which act as sources for an induced field, $\mathbf{A}_{in}(r)$, resulting in a total field

$$\mathbf{A}(r) \equiv \mathbf{A}_{ex}(r) + \mathbf{A}_{in}(r). \quad (74)$$

\mathbf{A}_{in} satisfies the Maxwell equation

$$\nabla \times (\nabla \times \mathbf{A}_{in}(r)) = \frac{4\pi}{c} \mathbf{j}(r), \quad (75)$$

where $\mathbf{j}(r)$ is the superconducting current of equation (34). $\mathbf{A}(r)$ must be treated self-consistently with $\mathbf{j}(r)$ by the following procedure:

- 1) a trial form is used for the « given » potential, $A(r)$, in equation (31);
- 2) the analysis described above, equations (31)-(49), is carried through, resulting, in particular, in a corresponding trial supercurrent, $\mathbf{j}(r)$, by equations (34), (47), and (49);
- 3) equation (75) is now solved for $\mathbf{A}_{in}(r)$, with the boundary condition $\mathbf{A}_{in}(r) = 0$ far from the superconductor, resulting in an iterated $\mathbf{A}(r)$ by equation (74);
- 4) this process is repeated until selfconsistency is obtained;
- 5) the total grand potential is obtained by adding to equation (50) the magnetic energy

$$E_{mag} = \frac{1}{8\pi} \int B^2(r) d^3r$$

where $\mathbf{B}(r) = \nabla \times \mathbf{A}(r)$.

In the formalism presented so far, the Zeeman coupling of magnetic fields to the electron spin has been neglected. As indicated in the introduction, such effects are easily incorporated by adding the Hamiltonian \hat{H}_B (Eq. (7)) to the basic Hamiltonian $\hat{H}_{v-\mu, D, A}$. The functional F then depends on $n(r)$, $\Delta(r)$, $\mathbf{j}_p(r)$, and on the spin magnetization $\mathbf{m}(r)$ ⁽³⁾.

The DFT of superconductors presented here provides a *unified* framework to incorporate all normal and « superfluid » many-body effects through the functional $F_{xc}[n, \Delta, \mathbf{j}_p]$. Like all DF methods it is particularly suited for dealing with spatial inhomogeneities. As emphasized in the introduction, the new high- T_c materials are characterized by relatively small coherence lengths. Therefore, inhomogeneities of $\Delta(r)$ can be expected to be important in these materials. Also, an appropriate inclusion of *normal* many-body effects, as achieved by our

⁽³⁾ More complicated couplings involving spin-current densities can also be included following a prescription recently given by Vignale and Rasolt [8] for normal systems.

formulation, is likely to be important for the high- T_c superconductors which appear to be near a Mott-Hubbard transition.

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