Density-Functional Theory for Superconductors

L. N. Oliveira,[a] E. K. U. Gross, and W. Kohn
Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106
(Received 7 January 1988)

A density-functional theory for superconductors at arbitrary temperature is described. It leads to equations of the Kohn-Sham type, which incorporate exchange and correlation effects into the Bogoliubov–de Gennes equations for an inhomogeneous superconductor. Further, this formalism yields exchange-correlation corrections to Eilenberger's expression for the thermodynamic potential of a superconductor, and the Ginzburg-Landau equation. Practical aspects of the application of the formalism are discussed.

PACS numbers: 71.10.+x, 74.20.−z, 74.50.+r

We present a density-functional formulation[1] for superconductors. The central results are formally exact self-consistent equations generalizing the Bogoliubov–de Gennes equations[2] for inhomogeneous superconductors, as well as a formally exact generalization of Eilenberger's[3] expression for the thermodynamic potential, which in turn leads to Ginzburg-Landau–type equations.

The formalism easily accommodates very general pairing interactions; to be definite, we write in standard notation and atomic units the grand-canonical Hamiltonian for a superconductor in an external potential $v(r)$ as

$$\hat{H}_v=\int \psi^\dagger(r)\left[\frac{-\nabla^2}{2}-\mu+v(r)\right]\psi(r)dr+\tfrac{1}{2}\int \psi^\dagger(r)\psi^\dagger(r')\frac{1}{|r-r'|}\psi(r')\psi(r)dr\,dr'$$
$$-\int \psi_\uparrow^\dagger(r_1')\psi_\downarrow^\dagger(r_1)w(r_1',r_1,r_2,r_2')\psi_\uparrow(r_2)\psi_\downarrow(r_2')dr_1\,dr_1'\,dr_2\,dr_2', \quad (1)$$

where $\psi^\dagger(r)\psi(r)$ is a shorthand for $\sum_\alpha \psi_\alpha^\dagger(r)\psi_\alpha(r)$. The kernel w is a (generally nonlocal) pairing interaction. Particular cases are the BCS form,[4] $w(r_1',r_1,r_2,r_2')=w(r_1-r_1',r_2-r_2')$, and the Gorkov form,[5]

$$w(r_1',r_1,r_2,r_2')=w_0\delta(r_1-r_1')\delta(r_1-r_2)\delta(r_1-r_2').$$

More realistically, we expect the kernel to be nonlocal but short ranged, i.e., $w(r_1',r_1,r_2,r_2')\to 0$ for $|r_1-r_1'|$, $|r_1-r_2|$, or $|r_1-r_2'|\gg$ lattice parameter. To be brief, we have omitted vector-potential contributions to $\hat{H}_v$; following a recent prescription for the normal state,[6] however, we have also been able to introduce magnetic fields into the formalism (to be published).

In a superconductor, both the normal density operator, $\psi^\dagger(r)\psi(r)$, and the anomalous density operator, $\psi_\uparrow(r)\psi_\downarrow(r)$, have finite expectation values, which we denote by $n(r)$ and $\Delta(r)$. This suggests that, in analogy with the external normal potential $v(r)$, we also introduce an anomalous pair potential[7] $D(r)$ into H_v:

$$\hat{H}_{v,D}\equiv\hat{H}_v-\int[D^*(r)\psi_\uparrow(r)\psi_\downarrow(r)+\text{H.c.}]dr. \quad (2)$$

As we shall see in an example below, it is useful to introduce instead of the local $\Delta(r)$ the *nonlocal* gap function[8] $\Delta(r,r')\equiv\langle\psi_\uparrow(r)\psi_\downarrow(r')\rangle$, coupled to the nonlocal pair potential $D(r,r')$. This leads to

$$\hat{H}_{v,D}\equiv\hat{H}_v-\int[D^*(r,r')\psi_\uparrow(r)\psi_\downarrow(r')+\text{H.c.}]dr\,dr', \quad (2')$$

instead of Eq. (2). In the example below the integral in (2′) acquires physical significance. However, even when $D(r,r')\equiv 0$, we shall see that it is convenient to keep a finite small $D(r,r')$ until, at the end, the limit $D(r,r')\to 0$ is taken.

The first step in the density-functional formulation, a Hohenberg-Kohn theorem for $\hat{H}_{v,D}$, is easily established. This theorem states that, at the temperature $\theta=1/\beta$, the densities $n(r)$ and $\Delta(r,r')$ determine uniquely the density operator $\hat{\rho}=e^{-\beta\hat{H}_{v,D}}/\text{Tr}\,e^{-\beta\hat{H}_{v,D}}$, which minimizes[9] the thermodynamic potential

$$\Omega_{v,D}[\hat{\rho}']=\text{Tr}\{\hat{\rho}'\hat{H}_{v,D}+\theta\hat{\rho}'\ln\hat{\rho}'\}.$$

The proof is a straightforward adaptation of Mermin's[9] argument. From the theorem, it follows[1,9] that the thermodynamic potential $\Omega_{v,D}$ can be written as a functional of $n'(r)$ and $\Delta'(r,r')$:

$$\Omega_{v,D}[n',\Delta']=F[n',\Delta']+\int n'(r)v(r)dr-\int[D^*(r,r')\Delta'(r,r')+\text{c.c.}]dr\,dr', \quad (3)$$

where $F[n',\Delta']$ is a universal functional. Moreover, the inequality

$$\Omega_{v,D}[n',\Delta']>\Omega_{v,D}[n,\Delta]\ \text{ for }\ [n'(r),\Delta'(r,r')]\neq[n(r),\Delta(r,r')]$$

provides a variational principle to determine the densities $n(r)$ and $\Delta(r,r')$ associated with the Hamiltonian $\hat{H}_{v,D}$.

Next, we define the exchange-correlation free-energy functional $F_{xc}[n'(r),\Delta'(r,r')]$ by the equality

$$F[n',\Delta'] = T_s[n',\Delta'] - \theta S_s[n',\Delta'] - \mu N + \frac{1}{2}\int \frac{n'(r)n'(r')}{|r-r'|}dr\,dr' - \int \Delta'^*(r_1,r_1')w(r_1',r_1,r_2,r_2')\Delta'(r_2,r_2')dr_1\,dr_1'\,dr_2\,dr_2' + F_{xc}[n',\Delta'], \quad (4)$$

where $T_s[n',\Delta']$ and $S_s[n',\Delta']$ denote the kinetic energy and the entropy of a noninteracting system subject to potentials $v_s(r)$ and $D_s(r,r')$ chosen such that its densities $n'(r)$ and $\Delta'(r,r')$ are equal to those of the interacting system. The grand-canonical Hamiltonian for the noninteracting system,

$$\hat{H}_s = \int \psi^\dagger(r)\left[\frac{-\nabla^2}{2} - \mu + v_s(r)\right]\psi(r)dr - \int [D_s^*(r,r')\psi_\uparrow(r)\psi_\downarrow(r') + \text{H.c.}]dr\,dr', \quad (5)$$

is diagonalized[2] by the Bogoliubov transformation

$$\psi_\uparrow(r) = \sum_m [u_m(r)\phi_{1m} - v_m^*(r)\phi_{2m}^\dagger], \quad \psi_\downarrow(r) = \sum_m [u_m(r)\phi_{2m} + v_m^*(r)\phi_{1m}^\dagger]. \quad (6)$$

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

$$\begin{aligned}\left[\frac{-\nabla^2}{2} - \mu + v_s(r) - \epsilon_m\right]u_m(r) &= -\int D_s(r,r')v_m(r')v_m(r')dr',\\ \left[\frac{-\nabla^2}{2} - \mu + v_s(r) + \epsilon_m\right]v_m(r) &= \int D_s^*(r,r')u_m(r')dr',\end{aligned} \quad (7)$$

and the fermionic operators ϕ_{1m} and ϕ_{2m} obey the usual anticommutation relations[2] and annihilate the ground state of the noninteracting system, so that

$$\langle\phi_{1m}^\dagger\phi_{1m}\rangle = \langle\phi_{2m}^\dagger\phi_{2m}\rangle = (1+e^{\beta\epsilon_m}) \equiv f_m^\theta.$$

As functions of the $u_m(r)$ and the $v_m(r)$, the densities are given by

$$n(r) = 2\sum_m [|u_m(r)|^2 f_m^\theta + |v_m(r)|^2(1-f_m^\theta)], \quad \Delta(r,r') = \sum [v_m^*(r')u_m(r)(1-f_m^\theta) - v_m^*(r)u_m(r')f_m^\theta]. \quad (8)$$

To determine the potentials $v_s(r)$ and $D_s(r,r')$, we compute the kinetic energy and the entropy of the noninteracting system in terms of the $u_m(r)$, $v_m(r)$, f_m^θ, and ϵ_m, substitute the result in (4), and then minimize the thermodynamic potential with respect to variations in $n(r)$ and $\Delta(r,r')$. This yields

$$\begin{aligned}v_s[n,\Delta](r) &= v(r) + \int \frac{n(r')}{|r-r'|}dr' + v_{xc}[n,\Delta](r),\\ D_s[n,\Delta](r,r') &= D(r,r') + \int w(r',r,r_1,r_1')\Delta(r_1,r_1')dr_1\,dr_1' + D_{xc}[n,\Delta](r,r'),\end{aligned} \quad (9)$$

where $v_{xc}[n,\Delta](r) = \delta F_{xc}[n,\Delta]/\delta n(r)$, and $D_{xc}[n,\Delta](r,r') = -\delta F_{xc}[n,\Delta]/\delta\Delta^*(r,r')$. With $D(r,r') \to 0$, Eqs. (9) complete the cycle of the self-consistent equations (7)-(9). This cycle solved, the thermodynamic potential (3) can be computed. We find

$$\Omega_{v,D}[n,\Delta] = \Omega_s^\theta - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}dr\,dr' - \int n(r)v_{xc}(r)dr + \int \Delta^*(r_1,r_1')w(r_1',r_1,r_2,r_2')\Delta(r_2,r_2')dr_1\,dr_1'\,dr_2\,dr_2' + \int [D_{xc}^*(r,r')\Delta(r,r') + \text{c.c.}]dr\,dr' + F_{xc}[n,\Delta]. \quad (10)$$

Here $\Omega_s^\theta = -\theta\ln\text{Tr}\{e^{-\beta\hat{H}_s}\}$ is the thermodynamic potential for the noninteracting system.

Equations (7)-(10) constitute our main formal results. By neglecting the exchange-correlation and the Coulomb terms, we recover the Bogoliubov-de Gennes equations[2] from Eqs. (7)-(9) and Eilenberger's formula[3] from Eq. (10).

We now discuss the physical significance of the pairing field $D(r,r')$ for the case of a normal-superconducting junction. We consider two media, one superconducting and one normal, occupying the half-spaces $x<0$ and $x>0$, respectively, described by the Hamiltonian

$$\hat{H}_s' = \int \psi^\dagger(r)\left[\frac{-\nabla^2}{2} - \mu + v_s(r)\right]\psi(r)dr + \int [D_s^*(r,r')\psi_\uparrow(r)\psi_\downarrow(r') + \text{H.c.}]dr\,dr' + \int_{x'<0;x>0} [t_s(r,r')\psi^\dagger(r)\psi(r') + \text{H.c.}]dr\,dr'.$$

This generalization of Eq. (5) includes a tunneling matrix element $t_s(r,r')$ between the two media. $\hat{H}_s'$ is diagonalized by a Bogoliubov transformation involving functions $u_m(r)$ and $v_m(r)$ that, for $x<0$, satisfy the Bogoliubov-de Gennes equations

$$\begin{aligned}&\left[\frac{-\nabla^2}{2} - \mu + v_s(r) - \epsilon_m\right]u_m(r) + \int_{x'>0} t_s(r,r')u_m(r')dr' = -\int D_s(r,r')v_m(r')dr',\\ &\left[\frac{-\nabla^2}{2} - \mu + v_s(r) + \epsilon_m\right]v_m(r) + \int_{x'>0} t_s(r,r')v_m(r')dr' = \int D_s^*(r,r')u_m(r')dr',\end{aligned} \tag{11}$$

and for $x>0$, the equations

$$\begin{aligned}&\left[\frac{-\nabla^2}{2} - \mu + v_s(r) - \epsilon_m\right]u_m(r) + \int_{x'<0} t_s(r,r')u_m(r')dr' = 0,\\ &\left[\frac{-\nabla^2}{2} - \mu + v_s(r) + \epsilon_m\right]v_m(r) + \int_{x'<0} t_s(r,r')v_m(r')dr' = 0.\end{aligned} \tag{12}$$

Now let $\tilde{u}_l(r)$, $\tilde{v}_l(r)$, and $\tilde{\epsilon}_l$ be the eigenfunctions and eigenvalues of Eqs. (11) for $t_s(r,r')\equiv 0$. For $x<0$, these functions constitute a complete basis in which we expand the $u_m(r')$ and $v_m(r')$ in the integrals on the left-hand sides of Eqs. (12). The Bogoliubov-de Gennes equations for the normal side ($x>0$) then become[10]

$$\begin{aligned}&\left[\frac{-\nabla^2}{2} - \mu + v_s(r) - \epsilon_m\right]u_m(r) = -\int D_m(r,r')v_m(r')dr',\\ &\left[\frac{-\nabla^2}{2} - \mu + v_s(r) + \epsilon_m\right]v_m(r) = \int D_m^*(r,r')u_m(r')dr',\end{aligned} \tag{13}$$

where $D_m(r,r')$ is a proximity-induced anomalous potential given by

$$D_m(r,r') = \int t_s(r,r_1)\sum_l \left[\frac{\tilde{v}_l^*(r_1)\tilde{u}_l(r_1')}{\tilde{\epsilon}_l - \epsilon_m} + \frac{\tilde{u}_l(r_1)\tilde{v}_l^*(r_1')}{\tilde{\epsilon}_l + \epsilon_m}\right] t_s(r_1',r')dr_1\,dr_1'. \tag{14}$$

At temperatures θ much smaller than the gap $\tilde{D}$ on the superconducting side ($x<0$), these potentials become independent of m [i.e., $D_m(r,r')\to D(r,r')$], since $\epsilon_m \approx \theta \ll \tilde{D} \leq \tilde{\epsilon}_l$. The field introduced in Eq. (2′) thus describes proximity effects,[11] making the normal-superconducting junction a potentially interesting application of our formalism.

Like conventional density-functional theory, the formalism requires practical approximations to be useful. For weak pairing interactions one may set $F_{xc}[n,\Delta]\to F_{xc}[n]$. Substitution in (10) introduces normal-state exchange and correlation in Eilenberger's formula[3]; a gradient expansion of $\Omega_{v,D}[n,\Delta]$, currently under study, leads to a generalization of the Ginzburg-Landau equation.

For strong electron-phonon interactions, we have obtained encouraging results for an effective time-independent electron-electron interaction, which—again with the substitution $F_{xc}[n,\Delta]\to F_{xc}[n]$—would allow treatment of such systems by the present density-functional formalism.

For a given pairing interaction, the task of finding more general approximations for $F_{xc}[n,\Delta]$ remains a challenge (in principle, one might even explore the possibility of a unified theory featuring a universal exchange-correlation functional applicable to all inhomogeneous superconductors).

The density-functional theory of this paper is alternative to the Green's-function theory of superconductors (especially the Eliashberg theory[12]), just as normal density-functional theory is an alternative to normal many-body Green's-function theory. Density-functional theory is specifically able to deal conveniently with spatially inhomogeneous systems.

For normal systems, a connection between the density-functional and the Green's-function approaches was pointed out by Sham and Schlüter.[13] Following their procedure, the matrix of exchange-correlation potentials

$$\hat{U}_{xc}(r,r')=\begin{bmatrix} v_{xc}(r)\delta(r-r') & D_{xc}(r,r') \\ D^*_{xc}(r,r') & -v_{xc}(r)\delta(r-r') \end{bmatrix}$$

can be expressed in terms of the Green's-function matrix $\hat{G}(r,r';\omega)$ and its noninteracting Kohn-Sham counterpart $\hat{G}_s(r,r',\omega)$ as

$$\int \hat{G}_s(r,r_1;\omega)\hat{U}_{xc}(r_1,r_1')\hat{G}(r_1',r;\omega)d\omega\, dr_1\, dr_1' = \int \hat{G}_s(r,r_1;\omega)\hat{\Sigma}_{xc}(r_1,r_1';\omega)\hat{G}(r_1',r;w)d\omega\, dr_1\, dr_1', \tag{15}$$

where $\hat{\Sigma}_{xc}(r,r';\omega)$ denotes the electron self-energy matrix excluding the Hartree term. Given an approximation for $\hat{\Sigma}_{xc}$, the integral equation (15) determines $\hat{U}_{xc}$.

Certain properties of the high-T_c superconductors suggest that the present formalism may be pertinent to them. Density-functional theory is well suited for the treatment of *inhomogeneities* due to crystalline defects, which strongly affect the properties of these materials.[14] More importantly, the energy gaps' becoming comparable to the Fermi energy and the relatively small coherence length[15] suggest that a unified treatment of normal and superconducting aspects (band structure, densities, gap function, etc.) may be necessary, e.g., to explain the 5% drop[16] in the positron lifetime at the transition temperature of ceramic samples of $YBa_2Cu_3O_{6.8}$.

We thank W. Clinton for a discussion which stimulated our interest in this project. This work was supported by the National Science Foundation under Grant No. DMR87-03434. One of us (E.K.U.G.) gratefully acknowledges a Heisenberg Fellowship of the Deutsche Forschungsgemeinschaft.

[a]On leave from the Instituto de Física e Química de São Carlos of the University of São Paulo, São Paulo, Brazil.

[1]For a review of density-functional theory, see W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), p. 79.

[2]P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[3]G. Eilenberger, Z. Phys. **182**, 427 (1965).

[4]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[5]L. P. Gorkov, Zh. Eksp. Teor. Fiz. **34**, 735 (1958) [Sov. Phys. JETP **7**, 505 (1958)].

[6]G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).

[7]Anomalous densities and pair potentials appear in the Hartree-Fock-Bogoliubov equations, studied for nuclei [see, e.g., R. Bengtsson and P. Schuck, Phys. Lett. **89B**, 321 (1980)] and superconductors [see, e.g., W. L. Clinton, Int. J. Quantum Chem. Symp. **7**, 479 (1973)].

[8]Normal density-functional theory has also been developed in a nonlocal version by T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975), but found little practical application. Logically, both normal and superconducting density-functional theory can be developed in either local or nonlocal versions.

[9]N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[10]In Eqs. (13) and (14) we have neglected a nonlocal normal potential $v_m(r,r')$, much smaller than $D_m(r,r')$ for $\epsilon_m \ll \tilde{D}$.

[11]G. Deutscher and P. G. de Gennes, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), p. 1005. For recent work, see E. V. Thuneberg and V. Ambegaokar, Phys. Rev. Lett. **60**, 365 (1988), and references cited.

[12]G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [Sov. Phys. JETP **11**, 696 (1960)].

[13]L. J. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).

[14]G. Deutscher and K. A. Müller, Phys. Rev. Lett. **59**, 1745 (1987).

[15]See, e.g., T. K. Worthington, W. J. Gallagher, and T. R. Dinger, Phys. Rev. Lett. **59**, 1160 (1987).

[16]Y. C. Jean, S. J. Wang, H. Nakanishi, W. N. Hardy, M. E. Hayden, R. Kiefl, R. L. Meng, H. P. Hor, J. Z. Huang, and C. W. Chu, Phys. Rev. B **36**, 3994 (1987); see also S. Ishibashi, A. Yamaguchi, Y. Suzuki, M. Doyama, H. Kumakura, and K. Togano, Jpn. J. Appl. Phys. **26**, L688 (1987).