Density-Functional Theory for Superconductors

L. N. Oliveira, E. K. U. Gross, and W. Kohn

Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106

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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.

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We present a density-functional formulation for superconductors. The central results are formally exact self-consistent equations generalizing the Bogoliubov-de Gennes equations for inhomogeneous superconductors, as well as a formally exact generalization of Eilenberger's 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

\[
\hat{H}_e = \int \psi^\dagger(r) \left( -\frac{\nabla^2}{2} - \mu + V(r) \right) \psi(r) dr + \frac{1}{2} \int \psi^\dagger(r) \psi^\dagger(r') \frac{1}{|r - r'|} \psi(r') \psi(r) dr dr' - \int \psi^\dagger(r) \psi^\dagger(r_1 \cdots r_n) \psi(r_1) \cdots \psi(r_n) dr_1 \cdots dr_n,
\]

where \( \psi^\dagger(r) \psi(r) \) is a shorthand for \( \sum_a \psi_a^\dagger(r) \psi_a(r) \). The kernel \( W \) is a (generally nonlocal) pairing interaction. Particular cases are the BCS form, \( W(r_1, r_2; r_1, r_2) = W(r_1 - r_2, r_2 - r_1) \), and the Gorkov form, \( W(r_1, r_1, r_2, r_2) = W_0 \delta(r_1 - r_2) \delta(r_1 - r_2) \delta(r_1 - r_2) \).

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 \( |r_1 - r_2|, |r_1 - r_2|, |r_1 - r_2| \gg \text{lattice parameter} \). To be brief, we have omitted vector-potential contributions to \( \hat{H}_e \); following a recent prescription for the normal state, 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, \( \psi^\dagger(r) \psi^\dagger(r) \), 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 \( \Delta(r) \) into \( \hat{H}_e \):

\[
\hat{H}_{e,D} \equiv \hat{H}_e - \int [D^*(r) \psi^\dagger(r) \psi^\dagger(r) + \text{H.c.}] dr.
\]

As we shall see in an example below, it is useful to introduce instead of the local \( \Delta(r) \) the nonlocal gap function

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

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

\[
\Omega_{e,D}(n, \Delta) > \Omega_{e,D}(n, \Delta) \text{ for } (n'(r), \Delta'(r, r')) \equiv (n(r), \Delta(r, r'))
\]

is satisfied.
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

\[
F[n',\Delta'] = T_S \left[ n'[n',\Delta'] \right] - \theta S_S \left[ n'[n',\Delta'] \right] - \mu N + \frac{1}{2} \int \frac{n'(r)n'(r')}{|r-r'|} dr dr' - \int \Delta^*(r_1,r_2)w(r_1,r_1,r_2,r_2)\Delta'(r_2,r_2)dr_1 dr_2 dr_3 dr_4 + F_{xc}[n',\Delta'],
\]

where \( T_S \left[ n'[n',\Delta'] \right] \) and \( S_S \left[ n'[n',\Delta'] \right] \) denote the kinetic energy and the entropy of a noninteracting system subject to potentials \( \nu_s(r) \) 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,

\[
\hat{H}_s = \int \psi^*(r) \left[ \frac{-\nabla^2}{2} - \mu + \nu_s(r) \right] \psi(r) dr - \int \left[ D_s^*(r,r')\psi_1(r)\psi_1(r') + \text{H.c.} \right] dr dr',
\]

is diagonalized\(^2\) by the Bogoliubov transformation

\[
\psi_1(r) = \sum_m [u_m(r)\phi_{1m} - v_m^*(r)\phi_{2m}], \quad \psi_1(r) = \sum_m [u_m(r)\phi_{2m} + v_m^*(r)\phi_{1m}].
\]

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

\[
\left[ \frac{-\nabla^2}{2} - \mu + \nu_s(r) - \epsilon_m \right] u_m(r) = - \int D_s(r,r')v_m(r')v_m(r') dr',
\]

\[
\left[ \frac{-\nabla^2}{2} - \mu + \nu_s(r) + \epsilon_m \right] v_m(r) = \int D_s^*(r,r')u_m(r') dr',
\]

and the fermionic operators \( \phi_{1m} \) and \( \phi_{2m} \) obey the usual anticommutation relations\(^2\) and annihilate the ground state of the noninteracting system, so that

\[
\langle \phi_{1m}\phi_{2m} \rangle = \langle \phi_{2m}\phi_{1m} \rangle = (1 + e^{\epsilon_m}) \equiv f_m.
\]

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

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

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

\[
u_s[n,\Delta](r) = \nu(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}[n,\Delta](r),
\]

\[
D_s[n,\Delta](r,r') = D(r,r') + \int w(r',r,r_1,r_2)\Delta(r_1,r_2)dr_1 dr_2 + D_{xc}[n,\Delta](r,r'),
\]

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

\[
\Omega_{e,D}[n,\Delta] = \Omega_s^0 - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' - \int n(r)v_{xc}(r)dr + \int \Delta^*(r_1,r_2)w(r_1,r_1,r_2,r_2)\Delta(r_2,r_2)dr_1 dr_2 dr_3 dr_4
\]

\[
+ \int [D_{xc}^*(r,r')\Delta(r,r') + \text{c.c.}] dr dr' + F_{xc}[n,\Delta].
\]

Here \( \Omega_s^0 = -\theta \ln \text{Tr} [e^{-\beta \hat{H}_s}] \) 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\(^3\) 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 \( x > 0 \), respec-
tively, described by the Hamiltonian

$$
\hat{H}_i' = \int \psi^*(r) \left[ -\frac{\nabla^2}{2} - \mu + v_i(r) \right] \psi(r) dr + \int [D_i^*(r,r') \psi_i(r') \psi_i(r') + \text{H.c.}] dr \, dr',
$$

This generalization of Eq. (5) includes a tunneling matrix element $t_i(r,r')$ between the two media. $\hat{H}_i'$ 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

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) - \epsilon_m \right] u_m(r) + \int_{x > 0} t_i(r,r') u_m(r') dr' = -\int D_i(r,r') v_m(r') dr',
$$

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) + \epsilon_m \right] v_m(r) + \int_{x < 0} t_i(r,r') v_m(r') dr' = \int D_i^*(r,r') u_m(r') dr',
$$

and for $x > 0$, the equations

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) - \epsilon_m \right] u_m(r) + \int_{x < 0} t_i(r,r') u_m(r') dr' = 0,
$$

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) + \epsilon_m \right] v_m(r) + \int_{x > 0} t_i(r,r') v_m(r') dr' = 0.
$$

Now let $\tilde{u}_i(r)$, $\tilde{v}_i(r)$, and $\tilde{\epsilon}_i$ be the eigenfunctions and eigenvalues of Eqs. (11) for $t_i(r,r') \equiv 0$. 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

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) - \epsilon_m \right] u_m(r) = -\int D_m(r,r') v_m(r') dr',
$$

$$
\left[ -\frac{\nabla^2}{2} - \mu + v_i(r) + \epsilon_m \right] v_m(r) = \int D_m^*(r,r') u_m(r') dr',
$$

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

$$
D_m(r,r') = \int t_i(r,r') \sum \left[ \frac{\tilde{\epsilon}_i^*(r) \tilde{u}_i(r')}{\tilde{\epsilon}_i - \epsilon_m} + \frac{\tilde{\epsilon}_i(r) \tilde{v}_i^*(r')}{\tilde{\epsilon}_i + \epsilon_m} \right] t_i(r',r') dr' dr'.
$$

At temperatures $\theta$ much smaller than the gap $\tilde{D}$ on the superconducting side ($x < 0$), these potentials become independent of $m$ [i.e., $D_m(r,r') \rightarrow D(r,r')$], since $\epsilon_m = \theta \ll \tilde{D} \approx \tilde{\epsilon}_i$. The field introduced in Eq. (2) thus describes proximity effects, \(^1\) 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 $F_{xc}[n,\Delta] \rightarrow F_{xc}[n]$. Substitution in (10) introduces normal-state exchange and correlation in Eilenberger's formula\(^1\), a gradient expansion of $\Omega_{e,D}[n,\Delta]$, 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 $F_{xc}[n,\Delta] \rightarrow F_{xc}[n]$—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 den-
sity-functional and the Green’s-function approaches was pointed out by Sham and Schütter. 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 \( \hat{G}_0(r, r'; \omega) \) as

\[
\int \hat{G}_0(r_1, r_1'; \omega) \hat{U}_{xc}(r_1, r_1') \hat{G}(r_1, r_1'; \omega) dw dr_1 dr_1' = \int \hat{G}_0(r, r_1; \omega) \hat{\Sigma}_{xc}(r, r_1; \omega) \hat{G}(r_1, r; w) dw dr_1 dr_1',
\]

where \( \hat{\Sigma}_{xc}(r, r_1; \omega) \) 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. More importantly, the energy gaps’ becoming comparable to the Fermi energy and the relatively small coherence length 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 in the positron lifetime at the transition temperature of ceramic samples of \( \text{YBa}_2\text{Cu}_3\text{O}_{6.8} \).

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