Density-Functional Theory of the Superconducting State

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Abstract

A density-functional theory describing the superconducting state of matter is presented. The formalism leads to a set of single-particle equations which are structurally similar to the Bogoliubov-de Gennes equations but (in contrast to the latter) incorporate both normal and superconducting exchange-correlation effects. It is demonstrated via a rigorous decoupling scheme that these single-particle equations are equivalent to a set of normal Kohn-Sham equations, and a BCS-type gap equation to be solved self-consistently with the Kohn-Sham equations.

Key words

Superconductivity, Density-Functional Theory,Bogoliubov-de Gennes equations, BCS model, Kohn-Sham equations

In a recent letter [1] Oliveira, Gross and Kohn (OGK) have presented a density functional theory describing the superconducting state of matter. Similar to the traditional Hohenberg-Kohn theorem [2] , which provides a description of normal-state systems in terms of their ground-state densities, the formalism of OGK ensures that superconductors can be described completely and, in principle, exactly in terms of two "densities": the normal density

$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow\downarrow} < \hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r}) > \tag{1}$$

and the anomalous density

$$\Delta(\mathbf{r},\mathbf{r}') =< \hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}') > . \tag{2}$$

The diagonal $\Delta(\mathbf{r},\mathbf{r})$ can be shown [3] to be identical, in the appropriate limits, with the order parameter of the Ginzburg-Landau theory [4].

OGK consider superconducting systems described by a Hamiltonian of the following form (atomic units are used throughout):

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{U} + \hat{W} + \\ &+ \int (v_{ext}(\mathbf{r}) - \mu)\hat{\rho}(\mathbf{r})\, d^3\mathbf{r} - \int\int (D^*_{ext}(\mathbf{r},\mathbf{r}')\hat{\Delta}(\mathbf{r},\mathbf{r}') + D_{ext}(\mathbf{r},\mathbf{r}')\hat{\Delta}^\dagger(\mathbf{r},\mathbf{r}'))\, d^3\mathbf{r}\, d^3\mathbf{r}'\end{aligned} \tag{3}$$

where $\hat{\rho}$ and $\hat{\Delta}$ are the normal and anomalous density operators whose expectation values are given by (1) and (2). Furthermore

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r}\hat{\psi}^\dagger_\sigma(\mathbf{r}) \left(-\frac{\nabla^2}{2}\right) \hat{\psi}_\sigma(\mathbf{r}) \tag{4}$$

is the kinetic energy of the electrons, $\hat{U}$ denotes their mutual Coulomb repulsion,

$$\hat{U} = \frac{1}{2}\sum_{\sigma,\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}^\dagger_{\sigma'}(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}')\hat{\psi}_\sigma(\mathbf{r}), \tag{5}$$

and $\hat{W}$ is a given phonon-induced electron-electron interaction which, in general, is completely non-local:

$$\hat{W} = -\int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \hat{\psi}^\dagger_\downarrow(\mathbf{r})\hat{\psi}^\dagger_\uparrow(\mathbf{r}') w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}')\hat{\psi}_\uparrow(\mathbf{x})\hat{\psi}_\downarrow(\mathbf{x}'). \tag{6}$$

The hermiticity of (6) requires that

$$w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}') = w^*(\mathbf{x}',\mathbf{x},\mathbf{r}',\mathbf{r}) \tag{7}$$

and spin isotropy implies

$$w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}') = w(\mathbf{r}',\mathbf{r},\mathbf{x}',\mathbf{x}). \tag{8}$$

A simple example is the model interaction of Bardeen, Cooper and Schrieffer (BCS) [5] which depends only on the relative coordinates $(\mathbf{r}-\mathbf{r}')$ and $(\mathbf{x}-\mathbf{x}')$:

$$w_{BCS}(\mathbf{r}-\mathbf{r}',\mathbf{x}-\mathbf{x}') = \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} e^{i\mathbf{q}(\mathbf{x}-\mathbf{x}')} w_{\mathbf{k},\mathbf{q}} \tag{9}$$

with

$$w_{\mathbf{k},\mathbf{q}} = \begin{cases} \lambda & : \text{ if } |\frac{\mathbf{k}^2}{2}-\mu| < \omega_D \text{ and } |\frac{\mathbf{q}^2}{2}-\mu| < \omega_D \\ 0 & : \text{ otherwise} \end{cases} \tag{10}$$

and ω_D being a typical phonon frequency. A more elaborate form for the non-local interaction w has recently been calculated by Wacker and Kümmel [6, 7] on the basis of a one-band model proposed by Schneider, DeRaedt and Frick [8] .

The remaining terms in Eq. (3) represent external potentials : $v_{ext}(\mathbf{r})$ is the Coulomb potential produced, e.g., by a periodic nuclear lattice, and $D_{ext}(\mathbf{r},\mathbf{r}')$ can be viewed as the proximity-induced pair field of an adjacent superconductor.

The central result of the theory of OGK is a set of self-consistent single-particle equations which determine, in principle exactly, the densities $\rho(\mathbf{r})$ and $\Delta(\mathbf{r},\mathbf{r}')$ of the interacting system described by the Hamiltonian (3). At any given inverse temperature β , these single-particle equations have the following form :

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu\right) u_n(\mathbf{r}) + \int D_s(\mathbf{r},\mathbf{r}') v_n(\mathbf{r}')\, d^3\mathbf{r}' = E_n u_n(\mathbf{r}) \tag{11}$$

$$\int D_s^*(\mathbf{r},\mathbf{r}') u_n(\mathbf{r}')\, d^3\mathbf{r}' - \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu\right) v_n(\mathbf{r}) = E_n v_n(\mathbf{r}). \tag{12}$$

In terms of the functions $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$, the densities (1) and (2) are given by

$$\rho(\mathbf{r}) = 2\sum_n \left(|u_n(\mathbf{r})|^2 f_\beta(E_n) + |v_n(\mathbf{r})|^2 f_\beta(-E_n)\right) \tag{13}$$

$$\Delta(\mathbf{r},\mathbf{r}') = \sum_n \left(v_n^*(\mathbf{r}') u_n(\mathbf{r}) f_\beta(-E_n) - v_n^*(\mathbf{r}) u_n(\mathbf{r}') f_\beta(E_n)\right) \tag{14}$$

where f_β denotes the Fermi distribution

$$f_\beta(E) = \frac{1}{1+e^{\beta E}} \; . \tag{15}$$

Both the normal single-particle potential v_s and the effective pair potential D_s in Eqs. (11), (12) consist of a given external part, a Hartree term, and an exchange-correlation (xc) contribution:

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d^3\mathbf{r}' + v_{xc}^{\beta}[\rho,\Delta](\mathbf{r}) \tag{16}$$

$$D_s(\mathbf{r},\mathbf{r}') = D_{ext}(\mathbf{r},\mathbf{r}') + \iint w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}')\Delta(\mathbf{x},\mathbf{x}')\, d^3\mathbf{x}\, d^3\mathbf{x}' + D_{xc}^{\beta}[\rho,\Delta](\mathbf{r},\mathbf{r}'). \tag{17}$$

The xc potentials are formally defined as functional derivatives of an xc-free-energy functional $F_{xc}^{\beta}[\rho,\Delta]$:

$$v_{xc}^{\beta}[\rho,\Delta](\mathbf{r}) = \frac{\delta F_{xc}^{\beta}[\rho,\Delta]}{\delta\rho(\mathbf{r})} \tag{18}$$

$$D_{xc}^{\beta}[\rho,\Delta](\mathbf{r},\mathbf{r}') = -\frac{\delta F_{xc}^{\beta}[\rho,\Delta]}{\delta\Delta(\mathbf{r},\mathbf{r}')}. \tag{19}$$

Since the effective single-particle potentials v_s and D_s depend on the densities ρ and Δ , the whole set of equations (11) - (17) has to be solved self-consistently. The single- particle equations (11), (12) are structurally similar to the Bogoliubov-de Gennes [9] equations. In contrast to the latter, however, the single-particle equations (11) and (12) include xc effects, i.e. the Bogoliubov-de Gennes equations compare to Eqs. (11), (12) just as the ordinary Hartree equations compare to the Kohn-Sham [10] equations. Extensions of the theory of OGK including external vector potentials have been derived by Kohn, Gross, and Oliveira [11] and by Wacker and Kümmel [6] .

In the following we shall derive some exact properties of the single- particle eigenfunctions $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$. On the basis of these properties we will then deduce a rigorous decoupling scheme which transforms the self-consistent equations (11) - (17) into a set of normal Kohn-Sham equations and a BCS-type gap equation.

First, as a matter of convenience, we rewrite Eqs. (11), (12) in matrix form

$$\begin{pmatrix} \left(-\frac{\nabla^2}{2} + v_s - \mu\right) & \hat{D}_s \\ \hat{D}_s^* & -\left(-\frac{\nabla^2}{2} + v_s - \mu\right) \end{pmatrix} \chi_n = E_n \chi_n, \tag{20}$$

where $\hat{D}_s$ is to be interpreted as the integral operator $\int \hat{D}_s(\mathbf{r},\mathbf{r}')...\, d^3\mathbf{r}'$, and χ_n represents the two-component eigenfunction

$$\chi_n(\mathbf{r}) = \begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix}. \tag{21}$$

By inspection of the complex conjugate of Eqs. (11) , (12) , one readily verifies that if

$$\chi_n^{(+)}(\mathbf{r}) \equiv \begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix} \tag{22}$$

is a solution of (20) with energy E_n , then

$$\chi_n^{(-)}(\mathbf{r}) \equiv \begin{pmatrix} v_n^*(\mathbf{r}) \\ -u_n^*(\mathbf{r}) \end{pmatrix} \tag{23}$$

is a solution of (20) with energy $(-E_n)$. In other words, the spectrum is redundant, i.e., for any given set of quantum numbers denoted by "n", there exist two solutions, $(\chi_n^{(+)}, E_n)$ and $(\chi_n^{(-)}, -E_n)$. For each value of n appearing in the summations in Eqs. (13) and (14) one may choose either $(\chi_n^{(+)}, E_n)$ or $(\chi_n^{(-)}, -E_n)$. The structure of Eqs. (13) and (14) is such that the result for $\rho(\mathbf{r})$ and $\Delta(\mathbf{r}, \mathbf{r}')$ does not depend on this choice. The completeness relation, however, must include **all** solutions of Eq. (20) :

$$\sum_n \sum_{s=\pm} \chi_n^{(s)}(\mathbf{r}) \otimes \chi_n^{(s)}(\mathbf{r}')^\dagger = \delta(\mathbf{r} - \mathbf{r}') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \tag{24}$$

Insertion of Eqs. (22) and (23) leads to

$$\sum_n \left[\begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix} \otimes (u_n^*(\mathbf{r}'), v_n^*(\mathbf{r}')) + \begin{pmatrix} v_n^*(\mathbf{r}) \\ -u_n^*(\mathbf{r}) \end{pmatrix} \otimes (v_n(\mathbf{r}'), -u_n(\mathbf{r}')) \right] = \delta(\mathbf{r} - \mathbf{r}') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \tag{25}$$

This yields two independent equations,

$$\sum_n \left[u_n(\mathbf{r}) u_n^*(\mathbf{r}') + v_n^*(\mathbf{r}) v_n(\mathbf{r}') \right] = \delta(\mathbf{r} - \mathbf{r}') \tag{26}$$

and

$$\sum_n \left[u_n(\mathbf{r}) v_n^*(\mathbf{r}') - u_n(\mathbf{r}') v_n^*(\mathbf{r}) \right] = 0. \tag{27}$$

The orthonormality requirement

$$< \chi_n^{(s)} | \chi_{n'}^{(s')} > = \int d^3\mathbf{r} \left(u_n^{(s)*}(\mathbf{r}), v_n^{(s)*}(\mathbf{r}) \right) \begin{pmatrix} u_{n'}^{(s')}(\mathbf{r}) \\ v_{n'}^{(s')}(\mathbf{r}) \end{pmatrix} = \delta_{nn'} \delta_{ss'} \tag{28}$$

yields two further equations :

$$\int d^3\mathbf{r} \left[u_n^*(\mathbf{r}) u_{n'}(\mathbf{r}) + v_n^*(\mathbf{r}) v_{n'}(\mathbf{r}) \right] = \delta_{nn'} \tag{29}$$

and

$$\int d^3\mathbf{r} \left[u_n(\mathbf{r}) v_{n'}(\mathbf{r}) - v_n(\mathbf{r}) u_{n'}(\mathbf{r}) \right] = 0. \tag{30}$$

Relations similar to (26) - (27), (29) - (30) are known [12] for the solutions of the traditional Bogoliubov-de Gennes equations.

An immediate consequence of Eq. (27) is the symmetry relation

$$\Delta(\mathbf{r},\mathbf{r}') = \Delta(\mathbf{r}',\mathbf{r}). \tag{31}$$

To prove this equation, we use the (exact) representation (14) of $\Delta(\mathbf{r},\mathbf{r}')$, apply the identity

$$f_\beta(-E) = 1 - f_\beta(E) \tag{32}$$

and insert the completeness relation (27) .

Since the xc pair potential is a functional derivative with respect to $\Delta^*(\mathbf{r},\mathbf{r}')$ (cf. Eq.(19)), it must have the same symmetry property as Δ , i.e.,

$$D^\beta_{xc}(\mathbf{r},\mathbf{r}') = D^\beta_{xc}(\mathbf{r}',\mathbf{r}). \tag{33}$$

As a consequence of Eqs. (8) and (31), the second, i.e. the mean-field contribution to the effective pair-potential (17) is invariant under exchange of $\mathbf{r}$ and $\mathbf{r}'$ as well. The external part, on the other hand, can be viewed as the mean-field (plus possibly xc) pair field of an adjacent superconductor so that

$$D_{ext}(\mathbf{r},\mathbf{r}') = D_{ext}(\mathbf{r}',\mathbf{r}). \tag{34}$$

We conclude that

$$D_s(\mathbf{r},\mathbf{r}') = D_s(\mathbf{r}',\mathbf{r}). \tag{35}$$

Now we proceed to the decoupling of Eqs. (11) - (17) into a set of normal Kohn-Sham equations and a BCS-type gap equation. In order to obtain a good initial guess for the iteration, we first perform an ordinary Kohn-Sham calculation for the material in question, i.e. the equations

$$\left(-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d^3\mathbf{r}' + v_{xc}[\rho](\mathbf{r})\right)\varphi_{\alpha,\mathbf{k}}(\mathbf{r}) = \varepsilon_{\alpha,\mathbf{k}}\varphi_{\alpha,\mathbf{k}}(\mathbf{r}) \tag{36}$$

$$\rho(\mathbf{r}) = \sum_{\alpha,\mathbf{k}} f_\beta(\varepsilon_{\alpha,\mathbf{k}} - \mu)|\varphi_{\alpha,\mathbf{k}}(\mathbf{r})|^2 \tag{37}$$

are solved in self-consistent fashion. In a periodic crystal, the eigenfunctions $\varphi_{\alpha,\mathbf{k}}(\mathbf{r})$ are Bloch waves; α denotes the band index and $\mathbf{k}$ is the crystal momentum. As a consequence of time reversal symmetry, the energy eigenvalues satisfy the identity (Kramers' theorem) [13]

$$\varepsilon_{\alpha,\mathbf{k}} = \varepsilon_{\alpha,-\mathbf{k}}. \tag{38}$$

Following Wacker [7] , we then make an ansatz for the solutions of Eq. (20) of the following form :

$$\chi_{\alpha,\mathbf{k}}(\mathbf{r}) = \begin{pmatrix} u_{\alpha,\mathbf{k}}\varphi_{\alpha,\mathbf{k}}(\mathbf{r}) \\ v_{\alpha,\mathbf{k}}\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}) \end{pmatrix} \tag{39}$$

$u_{\alpha,\mathbf{k}}$ and $v_{\alpha,\mathbf{k}}$ are complex numbers to be determined in such a way that Eq. (20) is satisfied. Furthermore, the orthonormality condition (29) requires that

$$|u_{\alpha,\mathbf{k}}|^2 + |v_{\alpha,\mathbf{k}}|^2 = 1 \tag{40}$$

be satisfied. For the densities (13) and (14) , the ansatz leads to

$$\rho(\mathbf{r}) = \sum_{\alpha,\mathbf{k}} \left(|u_{\alpha,\mathbf{k}}|^2 f_\beta(E_{\alpha,\mathbf{k}}) + |v_{\alpha,\mathbf{k}}|^2 f_\beta(-E_{\alpha,\mathbf{k}})\right)\left(|\varphi_{\alpha,\mathbf{k}}(\mathbf{r})|^2 + |\varphi_{\alpha,-\mathbf{k}}(\mathbf{r})|^2\right) \tag{41}$$

and

$$\Delta(\mathbf{r},\mathbf{r}') = \frac{1}{2}\sum_{\alpha,\mathbf{k}} v^*_{\alpha,\mathbf{k}} u_{\alpha,\mathbf{k}} \left(f_\beta(-E_{\alpha,\mathbf{k}}) - f_\beta(E_{\alpha,\mathbf{k}})\right)\left(\varphi_{\alpha,\mathbf{k}}(\mathbf{r})\varphi_{\alpha,-\mathbf{k}}(\mathbf{r}') + \varphi_{\alpha,\mathbf{k}}(\mathbf{r}')\varphi_{\alpha,-\mathbf{k}}(\mathbf{r})\right) \tag{42}$$

where $E_{\alpha,\mathbf{k}}$ is the energy eigenvalue corresponding to $\chi_{\alpha,\mathbf{k}}$. Eq. (42) shows that the ansatz (39) also satisfies the symmetry condition (31) .

We now determine the amplitudes $u_{\alpha,\mathbf{k}}, v_{\alpha,\mathbf{k}}$. Insertion of the ansatz (39) in Eq. (20) leads to the 2×2 eigenvalue problem

$$\begin{pmatrix} (\varepsilon_{\alpha,\mathbf{k}} - \mu) & D_s(\alpha,\mathbf{k}) \\ D^*_s(\alpha,-\mathbf{k}) & -(\varepsilon_{\alpha,-\mathbf{k}} - \mu) \end{pmatrix} \begin{pmatrix} u_{\alpha,\mathbf{k}} \\ v_{\alpha,\mathbf{k}} \end{pmatrix} = E_{\alpha,\mathbf{k}} \begin{pmatrix} u_{\alpha,\mathbf{k}} \\ v_{\alpha,\mathbf{k}} \end{pmatrix} \tag{43}$$

where

$$D_s(\alpha,\mathbf{k}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}') D_s(\mathbf{r},\mathbf{r}'). \tag{44}$$

As a consequence of the symmetry relation (35) we find

$$D_s(\alpha,\mathbf{k}) = D_s(\alpha,-\mathbf{k}). \tag{45}$$

Using this result and Eq. (38), the solutions of Eq. (43) can be written as

$$E_{\alpha,\mathbf{k}} = \pm\sqrt{(\varepsilon_{\alpha,\mathbf{k}}-\mu)^2 + |D_s(\alpha,\mathbf{k})|^2} \tag{46}$$

$$u_{\alpha,\mathbf{k}} = \frac{1}{\sqrt{2}}(sign E_{\alpha,\mathbf{k}})e^{i\delta_{\alpha,\mathbf{k}}}\left[1+\frac{\varepsilon_{\alpha,\mathbf{k}}-\mu}{E_{\alpha,\mathbf{k}}}\right]^{\frac{1}{2}} \tag{47}$$

$$v_{\alpha,\mathbf{k}} = \frac{1}{\sqrt{2}}\left[1-\frac{\varepsilon_{\alpha,\mathbf{k}}-\mu}{E_{\alpha,\mathbf{k}}}\right]^{\frac{1}{2}} \tag{48}$$

with

$$e^{i\delta_{\alpha,\mathbf{k}}} = \frac{D_s(\alpha,\mathbf{k})}{|D_s(\alpha,\mathbf{k})|}. \tag{49}$$

Eq. (46) once again demonstrates the redundance of the eigenvalue spectrum of Eq. (20). Inserting the amplitudes (47), (48) in Eqs. (41) and (42), one obtains for the densities

$$\rho(\mathbf{r}) = \sum_{\alpha,\mathbf{k}}\left[1-\frac{(\varepsilon_{\alpha,\mathbf{k}}-\mu)}{R_{\alpha,\mathbf{k}}}tanh\left(\frac{\beta R_{\alpha,\mathbf{k}}}{2}\right)\right]|\varphi_{\alpha,\mathbf{k}}(\mathbf{r})|^2 \tag{50}$$

and

$$\Delta(\mathbf{r},\mathbf{r}') = \frac{1}{2}\sum_{\alpha,\mathbf{k}}\left[\frac{D_s(\alpha,\mathbf{k})}{R_{\alpha,\mathbf{k}}}tanh\left(\frac{\beta R_{\alpha,\mathbf{k}}}{2}\right)\right]\varphi_{\alpha,\mathbf{k}}(\mathbf{r})\varphi_{\alpha,-\mathbf{k}}(\mathbf{r}') \tag{51}$$

where $R_{\alpha,\mathbf{k}}$ represents the **positive** root

$$R_{\alpha,\mathbf{k}} \equiv +\sqrt{(\varepsilon_{\alpha,\mathbf{k}}-\mu)^2 + |D_s(\alpha,\mathbf{k})|^2}. \tag{52}$$

The densities, as given by (50) - (52), depend on $D_s(\alpha,\mathbf{k})$ which is yet to be determined. By Eqs. (17) and (44), $D_s(\alpha,\mathbf{k})$ can be written as

$$\begin{aligned}
&D_s(\alpha,\mathbf{k}) = \\
&= \int d^3\mathbf{r}\int d^3\mathbf{r}'\varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}')D_{ext}(\mathbf{r},\mathbf{r}') + \\
&+ \int d^3\mathbf{r}\int d^3\mathbf{r}'\int d^3\mathbf{x}\int d^3\mathbf{x}'\varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}')w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}')\Delta(\mathbf{x},\mathbf{x}') + \\
&+ \int d^3\mathbf{r}\int d^3\mathbf{r}'\varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}')D_{xc}[\rho,\Delta](\mathbf{r},\mathbf{r}').
\end{aligned} \tag{53}$$

Obviously, $D_s(\alpha,\mathbf{k})$ depends on the densities ρ , Δ . Thus, in order to determine $D_s(\alpha,\mathbf{k})$, Eqs. (50) - (52) and Eq. (53) have to be solved self-consistently. Since $\varphi_{\alpha,\mathbf{k}}$ and $\varepsilon_{\alpha,\mathbf{k}}$ are kept fixed during this iteration, $D_{xc}[\rho,\Delta]$ becomes a functional of $D_s(\alpha,\mathbf{k})$ alone. As a consequence of that, the self- consistency loop, i.e., insertion of Eqs. (50) - (52) in Eq. (53), leads to a single integral equation for $D_s(\alpha, \mathbf{k})$:

$$D_s(\alpha,\mathbf{k}) = D_{ext}(\alpha,\mathbf{k}) + \frac{1}{2}\sum_{\alpha',\mathbf{k}'} \frac{w(\alpha\mathbf{k},\alpha'\mathbf{k}')D_s(\alpha',\mathbf{k}')}{R_{\alpha',\mathbf{k}'}} tanh\left(\frac{\beta R_{\alpha',\mathbf{k}'}}{2}\right) + D_{xc}[D_s](\alpha,\mathbf{k}) \quad (54)$$

with

$$D_{ext}(\alpha,\mathbf{k}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}') D_{ext}(\mathbf{r},\mathbf{r}') \quad (55)$$

$$D_{xc}[D_s](\alpha,\mathbf{k}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}') D_{xc}[\rho,\Delta](\mathbf{r},\mathbf{r}') \quad (56)$$

and

$$w(\alpha\mathbf{k},\alpha'\mathbf{k}') =$$

$$= \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \varphi^*_{\alpha,\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha,-\mathbf{k}}(\mathbf{r}') w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}') \varphi_{\alpha',\mathbf{k}'}(\mathbf{x})\varphi_{\alpha',-\mathbf{k}'}(\mathbf{x}') \quad (57)$$

Once $D_s(\alpha, \mathbf{k})$ has been obtained from the integral equation (54), the densities $\rho(\mathbf{r})$,$\Delta(\mathbf{r},\mathbf{r}')$ are known by Eqs. (50) - (52). Using these densities, we then determine the single-particle potential [1]

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' + v_{xc}[\rho,\Delta](\mathbf{r}) \quad (58)$$

and solve with this (fixed) potential the single-particle equations

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right)\varphi_{\alpha,\mathbf{k}}(\mathbf{r}) = \varepsilon_{\alpha,\mathbf{k}}\varphi_{\alpha,\mathbf{k}}(\mathbf{r}). \quad (59)$$

This yields a new set of orbitals $\varphi_{\alpha,\mathbf{k}}$ and energies $\varepsilon_{\alpha,\mathbf{k}}$ which serve as input for the next iteration. The whole cycle of Eqs. (50) - (52), (54) - (59) is repeated until self-consistency is reached. One easily verifies that the self-consistent solutions satisfy the exact completeness and orthonormality relations (26), (27) and (29), (30).

The separation of the original single-particle equations (11) - (17) into a BCS-type gap equation, Eq. (54), and a normal Kohn-Sham equation, Eq. (59), is of tremendous practical importance because it achieves a separation of energy scales: the gap function $D_s(\alpha, \mathbf{k})$ (as determined by Eq. (54)) is typically three orders of magnitude smaller than the characteristic features, such as band gaps, of the normal band structure $\varepsilon_{\alpha,\mathbf{k}}$ (as

[1] In practice, the functional dependence of v_{xc} on the densities ρ , Δ is of course only approximately known

determined by Eq. (59)). Furthermore, the effect of Δ in the single-particle potential (58) is expected to be small, so that a fully converged **traditional** Kohn-Sham solution (as obtained from Eqs. (36),(37)) will be very close to the final result for $\varphi_{\alpha,\mathbf{k}}, \varepsilon_{\alpha,\mathbf{k}}$ of the full self-consistency cycle (50) - (52), (54) - (59).

In the homogeneous limit,

$$\varphi_{\alpha,\mathbf{k}} \equiv \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\mathbf{k}\mathbf{r}}, \quad \varepsilon_{\alpha,\mathbf{k}} = \frac{\mathbf{k}^2}{2}, \tag{60}$$

Eq. (54) reduces rigorously to the BCS gap equation if D_{xc} is neglected. Thus, the traditional BCS model can be viewed as the homogeneous Hartree limit of the density functional theory for superconductors presented here.

The fact that Eq. (54) involves a gap function $D_s(\alpha, \mathbf{k})$ for each band index α is a particularly welcome feature because it accomodates in a natural way the possible occurance of more than one gap indicated in recent experiments [14].

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