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Effect of spin fluctuations on T_c from density-functional theory for superconductors

M. Wierzbowska[a]

INFM DEMOCRITOS National Simulation Center, via Beirut 2–4, 34014 Trieste, Italy

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Abstract. The transverse spin fluctuations are introduced to the density functional theory for superconductors (SCDFT). Paramagnons are treated within the random phase approximation and assumed to be the same for the normal and superconducting state. The effect of spin fluctuations on T_c is studied for a few simple metals at ambient pressure and niobium at several pressures up to 80 GPa.

PACS. 74.40.+k Fluctuations (noise, chaos, nonequilibrium superconductivity, localization, etc.) – 74.62.-c Transition temperature variations – 74.70.Ad Metals; alloys and binary compounds (including A15, MgB2, etc.) – 71.70.Gm Exchange interactions

1 Introduction

Since the discovery of superconductivity many theories have been born to explain this phenomenon and calculate observables. First papers about the role of the spin fluctuations by Doniach and Engelsberg [1] and Izuyama et al. [2] were published in sixties. Till today, fluctuations have been introduced to the many-body and phenomenological models and a very popular semiempirical theory proposed by Eliashberg [3].

The goal of this work is to include the spin fluctuations into the density functional theory for superconductors which, in principle, enables to calculate all material properties, also in the superconducting state, from first principles. The framework of the SCDFT was set up by Oliveira, Gross and Kohn [4] in 1988. Recently, the SCDFT gap equation has been solved numerically for simple metals [5,6] and MgB_2 [7].

As for the critical temperatures, it is known for a long time, that the spin fluctuations decrease considerably T_c of some superconductors [8,9]. In our previous work for niobium under pressure [10], we solved the gap equation of the Eliashberg theory [3] with and without the spin fluctuations and the SCDFT gap equation only with the Coulomb and phonon interactions. We found that the effect of paramagnons decreased T_c obtained from the Eliashberg theory by 3–4 K, however, an approximate treatment of the Coulomb interactions by a simple constant, μ^*, led to a large disagreement of the theoretical results with the experimental data [11]. In contrast to the Eliashberg theory, the SCDFT scheme is parameter free, but the critical temperature calculated without the spin fluctuations for Nb at ambient pressure [10] was about 3.7 K higher than the experimental T_c.

In this work, we follow the derivations of the SCDFT gap equation given in a number of Ph.D. theses[1] [12–14], and we include the spin fluctuations. The paramagnon spectral function is calculated within the random phase approximation (RPA) with the assumption of the homogeneous electron gas, similarly to the work by Berk and Schrieffer [8]. We solve the obtained gap equation for a few simple metals and update our previous results for niobium under pressure. The estimate of the paramagnon spectral function from the homogeneous gas approximation, made in this paper, is very crude especially for materials with the Fermi nesting. Netherveless, in the literature, it is very common to correct in the same way the Eliashberg equation for the effect of the spin fluctuations. Fully ab initio calculation of this quantity runs out of the scope of this work, but should be performed in the future.

In the following sections, we introduce the SCDFT gap equation and the construction of the exchange-correlation functional, F_{xc}, by collecting the most important building blocks of the theory given by its authors [4] and first developers [12–16]. These sections are: 2 "SCDFT gap equation", 3 "Exchange-correlation functional", and 4 "Coulomb interaction and phonons in F_{xc}". Above sections are written using the notation according to Parks [17,18] and Vonsovsky [19]. This notation is at some points, such as Nambu Green's function and the selfenergy, different than the notation previously used for the SCDFT [12–14]. We introduce the spin fluctuations in Sections: 5 "Paramagnons in F_{xc}" and 6 "Gap equation with paramagnons and implementation details". We report ob-

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[a] e-mail: `wierzbom@ts.infn.it`

[1] Available at URL: `www.physik.fu-berlin.de/∼ag-gross`

tained critical temperatures in Section 7, and we summarize in Section 8.

2 SCDFT gap equation

In this section, we wish to guide the reader, step by step, to the gap equation which will be solved at the end of this work to calculate the critical temperatures. We start by bringing the foundations of the SCDFT [4] and the main approximations, such as a decoupling of the band energies and the superconducting gap and a linearization of the gap equation close to T_c, which were assumed for the numerical convenience [12–15]. We believe that these approximations do not cause any significant difference in the calculated critical temperatures.

Turning to the details of the SCDFT, in order to obtain the gap equation one needs to follow the steps below:

1. *The grand-canonical Hamiltonian* for a superconductor reads

$$\begin{aligned}\hat{H}_{v,\Delta} =& \sum_\sigma \int d^3r\ \hat{\psi}^\dagger_\sigma(\mathbf{r}) \left[-\frac{\nabla^2}{2} + v(\mathbf{r}) - \mu\right] \hat{\psi}_\sigma(\mathbf{r})\\ &+ \frac{1}{2}\int d^3r\ d^3r'\ \hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}^\dagger_\sigma(\mathbf{r}')\ \frac{1}{|\mathbf{r}-\mathbf{r}'|}\ \hat{\psi}_\sigma(\mathbf{r}')\hat{\psi}_\sigma(\mathbf{r})\\ &- \int d^3r_1\ d^3r'_1\ d^3r_2\ d^3r'_2\ \hat{\psi}^\dagger_\downarrow(\mathbf{r}'_1)\hat{\psi}^\dagger_\uparrow(\mathbf{r}_1)\\ &\times w(\mathbf{r}'_1,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}'_2)\ \hat{\psi}_\uparrow(\mathbf{r}_2)\hat{\psi}_\downarrow(\mathbf{r}'_2)\\ &- \left[\int d^3r\ d^3r'\ \Delta^*(\mathbf{r},\mathbf{r}')\ \hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}') + \text{h.c.}\right], \qquad (1)\end{aligned}$$

   where $v(\mathbf{r})$ and $\Delta(\mathbf{r},\mathbf{r}')$ are the external potential and the anomalous pair potential respectively. The pairing interaction w in the particular BCS case satisfies $w(\mathbf{r}'_1,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}'_2) = w(\mathbf{r}'_1-\mathbf{r}_1,\mathbf{r}_2-\mathbf{r}'_2)$. The normal and anomalous densities, $n(\mathbf{r})$ and $\chi(\mathbf{r},\mathbf{r}')$, are defined as

$$n(\mathbf{r}) = \sum_\sigma \langle\hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r})\rangle, \qquad (2)$$

$$\chi(\mathbf{r},\mathbf{r}') = \langle\hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}')\rangle. \qquad (3)$$

2. *The Hohenberg-Kohn theorem for superconductors* says that, at each temperature $\theta = 1/\beta$, the normal and anomalous densities, $n(\mathbf{r})$ and $\chi(\mathbf{r},\mathbf{r}')$, determine uniquely the density operator $\hat{\rho} = e^{-\beta\hat{H}_{v,\Delta}}/\text{Tr}e^{-\beta\hat{H}_{v,\Delta}}$ which minimizes the thermodynamic potential, $\Omega_{v,\Delta}[\hat{\rho}]$, given by

$$\Omega_{v,\Delta}[\hat{\rho}] = \text{Tr}\{\hat{\rho}\ \hat{H}_{v,\Delta} + \theta\ \hat{\rho}\ \ln\hat{\rho}\}. \qquad (4)$$

3. Furthermore, *the thermodynamic potential* can be expressed in terms of the densities and the potentials by involving *an universal functional* of the densities, $F[n,\chi]$, as follows

$$\begin{aligned}\Omega_{v,\Delta}[n,\chi] =& F[n,\chi] + \int d^3r\ v(\mathbf{r})n(\mathbf{r})\\ &- \int d^3r d^3r' [\Delta^*(\mathbf{r},\mathbf{r}')\chi(\mathbf{r},\mathbf{r}') + \text{h.c.}]. \qquad (5)\end{aligned}$$

4. The universal functional contains *the exchange-correlation (xc) free-energy functional,* $F_{xc}[n,\chi]$, as below

$$\begin{aligned}F[n,\chi] =& T_s[n,\chi] - \theta\ S_s[n,\chi] - \mu\ N\\ &+ \frac{1}{2}\int d^3r\ d^3r'\ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &- \int d^3r_1\ d^3r'_1\ d^3r_2\ d^3r'_2\ \chi^*(\mathbf{r}_1,\mathbf{r}'_1)\\ &\times w(\mathbf{r}'_1,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}'_2)\chi^*(\mathbf{r}_2,\mathbf{r}'_2) + F_{xc}[n,\chi], \qquad (6)\end{aligned}$$

   where $T_s[n,\chi]$ and $S_s[n,\chi]$ are the kinetic energy and the entropy of a noninteracting system with the noninteracting potentials, v_s and Δ_s, such that the densities n and χ are equal to those of the noninteracting system. In the above formula, μ is the chemical potential.

5. *The noninteracting grand-canonical Hamiltonian* can be written in terms of the noninteracting densities and potentials as

$$\begin{aligned}\hat{H}_s =& \sum_\sigma \int d^3r\ \hat{\psi}^\dagger_\sigma(\mathbf{r}) \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu\right] \hat{\psi}_\sigma(\mathbf{r})\\ &- \left[\int d^3r\ d^3r'\ \Delta^*_s(\mathbf{r},\mathbf{r}')\hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}') + \text{h.c.}\right]. \qquad (7)\end{aligned}$$

6. The diagonalization of the noninteracting Hamiltonian, $\hat{H}_s$, using the Bogoliubov transformation leads to the *Kohn-Sham-Bogoliubov-de Gennes (KS-BdG) equations*

$$\begin{aligned}\left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu\right] u_i(\mathbf{r}) &+ \int d^3r'\ \Delta_s(\mathbf{r},\mathbf{r}')v_i(\mathbf{r}')\\ &= E_i\ u_i(\mathbf{r}), \qquad (8)\\ -\left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu\right] v_i(\mathbf{r}) &+ \int d^3r'\ \Delta^*_s(\mathbf{r},\mathbf{r}')u_i(\mathbf{r}')\\ &= E_i\ v_i(\mathbf{r}), \qquad (9)\end{aligned}$$

   with $v_i(\mathbf{r})$ and $u_i(\mathbf{r})$ being the pair creation and anihilation amplitudes respectively.

7. *The noninteracting potentials,* v_s *and* Δ_s*,* consist of the external potentials, v_0 and Δ_0, and Hartree potentials, and the exchange-correlation potentials, v_{xc} and Δ_{xc}, as follows

$$\begin{aligned}v_s[n,\chi](\mathbf{r}) =&\ v_0(\mathbf{r}) + \int d^3r'\ \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &+v_{xc}[n,\chi](\mathbf{r}), \qquad (10)\\ \Delta_s[n,\chi](\mathbf{r},\mathbf{r}') =&\ \Delta_0(\mathbf{r},\mathbf{r}') + \int d^3r'\ \frac{\chi(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &+\Delta_{xc}[n,\chi](\mathbf{r},\mathbf{r}'). \qquad (11)\end{aligned}$$

   The external pairing potential, Δ_0, has been introduced in order to break the symmetry. Thus, in the calculations, we have $\Delta_0(\mathbf{r},\mathbf{r}') \longrightarrow 0$ in equation (11).

8. *The exchange-correlation potentials,* v_{xc} *and* Δ_{xc}*,* are defined as the derivatives of the *xc* functional,

$F_{xc}[n,\chi]$, with respect to the densities, n and χ, correspondingly as below

$$v_{xc}[n,\chi](\mathbf{r}) = \frac{\delta F_{xc}[n,\chi]}{\delta n(\mathbf{r})}, \tag{12}$$

$$\Delta_{xc}[n,\chi](\mathbf{r},\mathbf{r}') = -\frac{\delta F_{xc}[n,\chi]}{\delta \chi^*(\mathbf{r},\mathbf{r}')}. \tag{13}$$

9. The densities, n and χ, are defined as functions of the amplitudes $u_i(\mathbf{r})$ and $v_i(\mathbf{r})$ as:

$$n(\mathbf{r}) = 2\sum_i \left[\, |u_i(\mathbf{r})|^2 f_{\beta,i} + |v_i(\mathbf{r})|^2 (1 - f_{\beta,i})\,\right], \tag{14}$$

$$\chi(\mathbf{r},\mathbf{r}') = \sum_i \left[\, v_i^*(\mathbf{r}') u_i(\mathbf{r})(1 - f_{\beta,i}) - v_i^*(\mathbf{r}) u_i(\mathbf{r}') f_{\beta,i}\,\right], \tag{15}$$

with the Fermi distribution function $f_{\beta,i} = 1 + \exp(\beta E_i)$.

At this point, one could guess the densities, n and χ, and find the potentials, v_{xc} and Δ_{xc}, and solve the KS-BdG equations, and find new densities etc. Further for the practical reasons as we already mentioned at the begin of this section, one can make two approximations which we will discuss now.

10. The energy scales for the electronic energies and the superconducting energy gap differ by orders of magnitude. Therefore, the KS-BdG equations (8, 9), can be *decoupled* into the Kohn-Sham equation and the gap equation. This approximation was introduced to the SCDFT in reference [15].

    It holds within *the decoupling approximation* that:

    (a) the amplitudes $u_i(\mathbf{r})$ and $v_i(\mathbf{r})$ can be written in a form

$$u_i(\mathbf{r}) \approx u_i\ \varphi_i(\mathbf{r}) \quad ; \qquad v_i(\mathbf{r}) \approx v_i\ \varphi_i(\mathbf{r}), \tag{16}$$

    (b) the eigenvalues in equations (8) and (9) are defined by

$$E_i = \pm\sqrt{\xi_i^2 + |\Delta_i} \tag{17}$$

    where $\xi_i = \varepsilon_i - \mu$

    (c) the coefficients u_i and v_i are given by

$$u_i = \frac{1}{\sqrt{2}}\ sgn(E_i)\ e^{i\phi_i}\ \sqrt{1 + \frac{\xi_i}{E_i}}, \tag{18}$$

$$v_i = \frac{1}{\sqrt{2}}\ \sqrt{1 - \frac{\xi_i}{E_i}}, \tag{19}$$

    and the phase factor ϕ_i is defined by

$$e^{i\phi_i} = \frac{\Delta_i}{|\Delta_i|}, \tag{20}$$

    (d) the matrix elements Δ_i are defined as

$$\Delta_i = \int d^3r \int d^3r'\ \varphi_i^*(\mathbf{r}) \Delta_s(\mathbf{r},\mathbf{r}') \varphi_i(\mathbf{r}'), \tag{21}$$

    (e) and the normal and anomalous densities read respectively

$$n(\mathbf{r}) = \sum_i \left(1 - \frac{\xi_i}{E_i}\right) \tanh\left(\frac{\beta E_i}{2}\right) |\varphi_i(\mathbf{r})|^2, \tag{22}$$

$$\chi(\mathbf{r},\mathbf{r}') = \frac{1}{2}\sum_i \frac{\Delta_i}{E_i} \tanh\left(\frac{\beta E_i}{2}\right) \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}'). \tag{23}$$

11. The decoupling of the two energy scales yields a transformation of the KS-BdG equations into *the ordinary Kohn-Sham equation*

$$-\left[\frac{\nabla^2}{2} + v_s[n,\chi](\mathbf{r}) - \mu\right] \varphi_i(\mathbf{r}) = \epsilon_i\ \varphi_i(\mathbf{r}), \tag{24}$$

    and *the gap equation*

$$\Delta_i = \Delta_{Hxc,i}[\mu, \Delta_i]. \tag{25}$$

    The equation (25) stems from including equations (22) and (23) into equation (11), and using in equation (21) the potential given by formula (11).

12. *In vicinity of* T_c, the gap function is vanishing, therefore, it can be *linearized* in Δ_i.

The above twelve steps lead to the gap equation which can be expressed in the form

$$\Delta_i = -\frac{1}{2}\sum_j M_{Hxc,ij}[\mu]\ \frac{\tanh(\frac{\beta}{2}\xi_j)}{\xi_j} \Delta_j, \tag{26}$$

$$M_{Hxc,ij}[\mu] = -\frac{\delta \Delta_{Hxc,i}}{\delta \chi_j}, \tag{27}$$

where $\Delta_{Hxc,i}$ is defined by equation (13).
In other way, equation (27) can be written as

$$\Delta_i = -Z_i[\mu]\Delta_i - \frac{1}{2}\sum_j K_{ij}[\mu] \frac{\tanh(\frac{\beta}{2}\xi_j)}{\xi_j} \Delta_j. \tag{28}$$

K_{ij} and Z_i are the functionals only of the chemical potential in the case when the gap equation is linearized. The above gap equation will be solved later in this work. The explicit form of the kernel K_{ij} and the norm Z_i will be given in Section 6.

Since the gap function (25) contains the exchange-correlation part defined by equation (13), we will focus on the construction of the exchange-correlation free-energy functional, F_{xc}, in the following section.

3 Exchange-correlation functional, $F_{xc}[n,\chi]$

The derivation of the exchange-correlation energy, F_{xc}, by making use of *the perturbative expansion of the thermodynamic potential*, was given in reference [12]. For the purpose of inclusion the spin interactions, we will briefly draw a skeleton of this derivation here.

First, one can notice from equations (5) and (6) that

$$F_{xc} = \Omega - \Omega_s + \int d^3r\ [v_H(\mathbf{r}) + v_{xc}(\mathbf{r})]n(\mathbf{r}) - \int d^3r\ d^3r'\ [\Delta^*_{xc}(\mathbf{r},\mathbf{r}')\chi(\mathbf{r},\mathbf{r}') + \Delta_{xc}(\mathbf{r},\mathbf{r}')\chi^*(\mathbf{r},\mathbf{r}')] - \frac{1}{2}\int d^3r\ d^3r'\ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \qquad (29)$$

Then, one takes *the coupling constant integration formula* which reads

$$\Omega - \Omega_s = \int_0^1 \frac{d\lambda}{\lambda}\langle\lambda\hat{H}_1\rangle, \qquad (30)$$

where λ is the coupling constant, and the perturbation Hamiltonian $\hat{H}_1$ satisfies $\hat{H} = \hat{H}_s + \lambda\hat{H}_1$ with the interacting and noninteracting Hamiltonians, $\hat{H}$ and $\hat{H}_s$, respectively. The Hamiltonian $\hat{H}_1$ contains the difference between the exact Coulomb interaction and the exchange-correlation potentials, the electron-phonon interaction, the electron-paramagnon interaction, etc.
The average in equation (30) has to be taken with the density operator $\hat{\rho}_\lambda = e^{-\beta\hat{H}_\lambda}/Z_\lambda$.

Before an explicit evaluation of the coupling constant integration formula (30), we write here a definition of the Nambu Green's function

$$\bar{G}_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') = \begin{pmatrix} G_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') & F_{\sigma-\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') \\ F^\dagger_{-\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') & -G_{-\sigma'-\sigma}(\mathbf{r}'\tau',\mathbf{r}\tau) \end{pmatrix}, \qquad (31)$$

which is a 2×2-matrix of the normal and anomalous *single particle Green's functions*, $G_{\sigma\sigma'}$ and $F_{\sigma\sigma'}$, given respectively by

$$G_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') = -\langle\hat{T}\hat{\psi}_\sigma(\mathbf{r}\tau)\hat{\psi}^\dagger_{\sigma'}(\mathbf{r}'\tau')\rangle, \qquad (32)$$

$$F_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') = -\langle\hat{T}\hat{\psi}_\sigma(\mathbf{r}\tau)\hat{\psi}_{\sigma'}(\mathbf{r}'\tau')\rangle, \qquad (33)$$

$$F^\dagger_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') = -\langle\hat{T}\hat{\psi}^\dagger_\sigma(\mathbf{r}\tau)\hat{\psi}^\dagger_{\sigma'}(\mathbf{r}'\tau')\rangle. \qquad (34)$$

The detailed derivation of $\langle\hat{H}_1\rangle$ is given in references [12–14]. This derivation starts from *the equations of motion* for the field operator, $\hat{\psi}_\sigma$, and for the noninteracting Green's function, $\bar{G}^s_{\sigma\sigma'}$, which are as follows

$$\frac{\partial}{\partial\tau}\ \hat{\psi}_\sigma(\mathbf{r}\tau) = e^{\hat{H}\tau}\ [\hat{H},\hat{\psi}_\sigma(\mathbf{r})]\ e^{-\hat{H}\tau}, \qquad (35)$$

$$\hat{\mathcal{L}}\ \bar{G}^s_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau') = -\delta_{\sigma\sigma'}\ \delta(\mathbf{r}-\mathbf{r}')\ \delta(\tau-\tau'), \qquad (36)$$

with the Kohn-Sham Hamiltonian for the normal state, $\hat{h}_s$, and the operator $\hat{\mathcal{L}}$ given respectively by

$$\hat{h}_s(\mathbf{r}) = -\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu, \qquad (37)$$

$$\hat{\mathcal{L}} = \begin{pmatrix} \frac{\partial}{\partial\tau} + \hat{h}_s(\mathbf{r}) & \hat{\Delta}_s(\mathbf{r}) \\ \hat{\Delta}^*_s(\mathbf{r}) & \frac{\partial}{\partial\tau} - \hat{h}_s(\mathbf{r}) \end{pmatrix}. \qquad (38)$$

The operator $\hat{\Delta}_s(\mathbf{r})$ is defined as

$$\hat{\Delta}_s(\mathbf{r})\ f(\mathbf{r}) = \int d^3r'\ \hat{\Delta}_s(\mathbf{r},\mathbf{r}')f(\mathbf{r}'). \qquad (39)$$

In order to complete the derivation, one also needs to make use of *the Dyson's equation*

$$\bar{G}_{\sigma'\sigma}(\mathbf{r}\tau,\mathbf{r}'\tau') = \bar{G}^s_{\sigma'\sigma}(\mathbf{r}\tau,\mathbf{r}'\tau') + \sum_{\sigma\sigma'}\int d^3r_1\ d^3r_2 \int d\tau_1\ d\tau_2\ \bar{G}^s_{\sigma\sigma_1}(\mathbf{r}\tau,\mathbf{r}_1\tau_1) \times \bar{\Sigma}(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2)\ \bar{G}_{\sigma_2\sigma'}(\mathbf{r}_2\tau_2,\mathbf{r}'\tau'), \qquad (40)$$

with $\bar{\Sigma}$ being the selfenergy.

The above building blocks make us to arrive, after some algebra, at the relation

$$\Omega - \Omega_s = \frac{1}{2}\int_0^1 \frac{d\lambda}{\lambda}\Bigg\{\sum_{\sigma\sigma'}\int d^3r\ d^3r' \times \int d\tau'\ [\bar{\Sigma}^\lambda_{\sigma\sigma'}(\mathbf{r}\tau,\mathbf{r}'\tau')\bar{G}^\lambda_{\sigma'\sigma}(\mathbf{r}'\tau',\mathbf{r}\tau^+)]_{11} - \lambda\int d^3r\ [v_H(\mathbf{r}) + v_{xc}(\mathbf{r})]\ n^\lambda(\mathbf{r}) + 2\lambda\int d^3r\ d^3r'\ \Delta^*_{xc}(\mathbf{r},\mathbf{r}')\chi^\lambda(\mathbf{r},\mathbf{r}')\Bigg\}, \qquad (41)$$

which we can plug into the equation (29) for the exchange-correlation functional, $F_{xc}[n,\chi]$.

As for *the first-order selfenergy*, $\bar{\Sigma}_{\sigma\sigma'}$, for the nonmagnetic systems with the potential $v(\mathbf{r}\tau,\mathbf{r}'\tau')$, this energy is defined as

$$\bar{\Sigma}(\mathbf{r}\tau,\mathbf{r}'\tau') = -v(\mathbf{r}\tau,\mathbf{r}'\tau')\ \tau_3\bar{G}(\mathbf{r}\tau,\mathbf{r}'\tau')\tau_3, \qquad (42)$$

and τ_3 is one of the Pauli matrices:

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \tau_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix},$$

$$\tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},\ \tau_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

For the magnetic systems, the matrix τ_3 in the each vertex of Feynman diagrams for the selfenergy with the Coulomb and phonon interactions has to be replaced with the matrix $\tau_0\tau_3$.

In this section, we sketched main steps to be done for finding a general form of the $F_{xc}[n,\chi]$ functional for a superconductor. The final formula involves the selfenergy which will be evaluated in detail for the Coulomb and electron-phonon interactions in the next section and for the paramagnons in Section 5.

4 Coulomb and electron-phonon interactions in $\mathbf{F_{xc}[n,\chi]}$

The derivation of F_{xc} for the Coulomb and phonon interactions is given in detail in references [5,13]. Here, we report this derivation starting with the interactions in the selfenergy (in Eq. (42)) defined by

$$v^{el}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}, \tag{43}$$

$$v^{ph}(\mathbf{r}\tau,\mathbf{r}'\tau') = V_{\lambda\mathbf{q}}(\mathbf{r})D_{\lambda\mathbf{q}}(\tau-\tau')V_{\lambda\mathbf{q}}(\mathbf{r}'), \tag{44}$$

where $V_{\lambda\mathbf{q}}$ is the electron-phonon interaction vertex and $D_{\lambda\mathbf{q}}$ is the phonon Green's function defined as

$$D_{\lambda\mathbf{q}}(\tau,\tau') = \langle \hat{T}\hat{\Phi}_{\lambda\mathbf{q}}(\tau)\hat{\Phi}^{\dagger}_{\lambda\mathbf{q}}(\tau')\rangle, \tag{45}$$

with $\hat{\Phi}_{\lambda\mathbf{q}} = b_{\lambda,\mathbf{q}} + b^{\dagger}_{\lambda,-\mathbf{q}}$, and $b^{\dagger}_{\lambda,\mathbf{q}}$ ($b_{\lambda,\mathbf{q}}$) being the phonon creation (anihilation) operators.

Let us have a look now at the expression (29) for F_{xc} and the definitions of the Nambu Green's function and the selfenergy given by equations (31) and (42) respectively. The (1,1)-element of the $(\bar{\Sigma}\bar{G})$-matrix, present in the formula (41) and entering equation (29), is proportional to

$$G_{\uparrow\uparrow}G_{\uparrow\uparrow} - F_{\uparrow\downarrow}F^{\dagger}_{\uparrow\downarrow} = G_{\uparrow\uparrow}G_{\uparrow\uparrow} + F_{\uparrow\downarrow}F^{\dagger}_{\downarrow\uparrow} \tag{46}$$

and the corresponding terms with the opposite spins. The above terms appear in both the Coulomb and electron-phonon interactions, and later will lead to the opposite signums in the kernel K_{ij} and the norm Z_i in the gap equation. Just mentioned difference in signum, in the first order terms of the total energy with the normal and anomalous Green's functions, stems from the factor of (-1) which one has to associate with the each loop of anomalous Green's functions.

In order to evaluate further F_{xc}, we bring here the explicit expressions for the noninteracting propagators. The formulas given below were derived from the definitions (32–34) assuming the decoupling approximation, i.e. equations (16); the Kohn-Sham orbitals $\varphi_{\mathbf{k}}(\mathbf{r})$ were chosen to those of a homogeneous gas (w_n are the odd Matsubara frequencies)

$$\begin{aligned} G^{s}_{\sigma\sigma'}(\mathbf{k},w_n) &= \delta_{\sigma,\sigma'} \\ &\times \left[\frac{|u_{\mathbf{k}}|^2}{i\omega_n - E_{\mathbf{k}}} + \frac{|v_{\mathbf{k}}|^2}{i\omega_n + E_{\mathbf{k}}}\right], \end{aligned} \tag{47}$$

$$\begin{aligned} F^{s}_{\sigma\sigma'}(\mathbf{k};w_n) &= \delta_{\sigma,-\sigma'}\ \mathrm{sgn}(\sigma') \\ &\times u_{\mathbf{k}}v^{*}_{\mathbf{k}}\left(\frac{1}{i\omega_n + E_{\mathbf{k}}} - \frac{1}{i\omega_n - E_{\mathbf{k}}}\right), \end{aligned} \tag{48}$$

$$\begin{aligned} F^{s\dagger}_{\sigma\sigma'}(\mathbf{k};w_n) &= \delta_{\sigma,-\sigma'}\ \mathrm{sgn}(\sigma) \\ &\times u^{*}_{\mathbf{k}}v_{\mathbf{k}}\left(\frac{1}{i\omega_n + E_{\mathbf{k}}} - \frac{1}{i\omega_n - E_{\mathbf{k}}}\right). \end{aligned} \tag{49}$$

Now, we will combine equations (29) and (41), for the F_{xc} and $\Omega - \Omega_s$ respectively, with the definition of the Nambu Green's function, equation (31), and the expression for the selfenergy, equation (42). As for the noninteracting Green's functions, we use those obtained within the decoupling approximation, i.e. (47–49). This way, one arrives to the formulas for the xc energy, stemming from the normal and anomalous loops. The "normal" and "anomalous" terms of F_{xc} for the electronic contributions, $F^{el,1}_{xc}$ and $F^{el,2}_{xc}$, are as follows

$$\begin{aligned} F^{el,1}_{xc} &= -\frac{1}{4}\sum_{\mathbf{k}\mathbf{k}'}\left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}}\right)v(\mathbf{k},\mathbf{k}')\left(1 - \frac{\xi_{\mathbf{k}'}}{E_{\mathbf{k}'}}\right) \\ &\quad\times \tanh\left(\frac{\beta}{2}E_{\mathbf{k}}\right)\tanh\left(\frac{\beta}{2}E_{\mathbf{k}'}\right), \end{aligned} \tag{50}$$

$$\begin{aligned} F^{el,2}_{xc} &= \frac{1}{4}\sum_{\mathbf{k}\mathbf{k}'}v(\mathbf{k},\mathbf{k}')\frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}}\frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}} \\ &\quad\times \tanh\left(\frac{\beta}{2}E_{\mathbf{k}}\right)\tanh\left(\frac{\beta}{2}E_{\mathbf{k}'}\right). \end{aligned} \tag{51}$$

The electron-phonon terms, with the normal and anomalous loops, $F^{ph,1}_{xc}$ and $F^{ph,2}_{xc}$, respectively are given below

$$\begin{aligned} F^{ph,1}_{xc} &= -\frac{1}{2}\sum_{\mathbf{k}\mathbf{k}'}\int d\Omega\ \alpha^2F(\Omega) \\ &\quad\times \left[\left(1 + \frac{\xi_{\mathbf{k}}\xi_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}}\right)I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega)\right. \\ &\quad\left. + \left(1 - \frac{\xi_{\mathbf{k}}\xi_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}}\right)I(E_{\mathbf{k}},-E_{\mathbf{k}'},\Omega)\right], \end{aligned} \tag{52}$$

$$\begin{aligned} F^{ph,2}_{xc} &= \frac{1}{2}\sum_{\mathbf{k}\mathbf{k}'}\int d\Omega\ \alpha^2F(\Omega)\ \frac{\Delta_{\mathbf{k}}\Delta^{*}_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}} \\ &\quad\times [I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega) - I(E_{\mathbf{k}},-E_{\mathbf{k}'},\Omega)]. \end{aligned} \tag{53}$$

The function $I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega)$ is defined as

$$\begin{aligned} I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega) &= \frac{1}{\beta^2}\sum_{\omega_1\omega_2}\frac{1}{i\omega_1 - E_{\mathbf{k}}}\frac{1}{i\omega_2 - E_{\mathbf{k}'}} \\ &\quad\times \frac{-2\Omega}{(\omega_1-\omega_2)^2 + \Omega^2}. \end{aligned} \tag{54}$$

For the completeness, we give the definitions:

$$\begin{aligned} v(\mathbf{k},\mathbf{k}') &= \int d^3r\ d^3r'\ \varphi^{*}_{\mathbf{k}}(\mathbf{r})\varphi_{\mathbf{k}}(\mathbf{r}') \\ &\quad\times \frac{1}{|\mathbf{r}-\mathbf{r}'|}\ \varphi^{*}_{\mathbf{k}'}(\mathbf{r})\varphi_{\mathbf{k}'}(\mathbf{r}'), \end{aligned} \tag{55}$$

$$g^{\lambda\mathbf{q}}_{\mathbf{k},\mathbf{k}+\mathbf{q}} = \int d^3r\ \varphi^{*}_{\mathbf{k}}(\mathbf{r})\ V_{\lambda\mathbf{q}}\ \varphi_{\mathbf{k}+\mathbf{q}}(\mathbf{r}), \tag{56}$$

$$\begin{aligned} \alpha^2F(\Omega) &= \frac{1}{N(\varepsilon_F)}\sum_{\lambda\mathbf{q}}\sum_{\mathbf{k}}|g^{\lambda\mathbf{q}}_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2\ \delta(\Omega - \omega_{\lambda\mathbf{q}}) \\ &\quad\times \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F)\ \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_F), \end{aligned} \tag{57}$$

where $\omega_{\lambda\mathbf{q}}$ is the phonon frequency and $N(\varepsilon_F)$ is the density of states.

Using the formulas (50–54), one is ready to derive the exchange-correlation potential defined by equation (13). This derivation can be performed with the help of *the* *chain rule* as follows

$$\varDelta_{xc,i} = -\frac{\delta F_{xc}}{\delta\mu}\frac{\delta\mu}{\delta\chi_i^*} - \sum_j \left[\frac{\delta F_{xc}}{\delta|\varDelta_j|^2}\frac{\delta|\varDelta_j|^2}{\delta\chi_i^*} + \frac{\delta F_{xc}}{\delta(\phi_j)}\frac{\delta(\phi_j)}{\delta\chi_i^*}\right]. \tag{58}$$

Further evaluation of the above expression is given in detail in references [5,12]. In this work, we give the final formula for $\varDelta_{xc,i}$ which involves the phonon and paramagnon spectral functions and can be implemented in a straightforward way. We will give the details of implementation in Section 6.

At this point, we arrived to the explicit expressions for F_{xc} with the electronic and phononic parameters such as: the chemical potential μ, the density of states $N(\varepsilon_F)$, the single particle energies $\varepsilon_{\mathbf{k}}$, and the Eliashberg function $\alpha^2F(\varOmega)$. Now, we are ready to introduce the spin fluctuations into the discussed formalism, and we will do this in the following section.

5 Paramagnons in $\mathbf{F_{xc}[n,\chi]}$

We will introduce the transverse spin-fluctuations to the total energy within the SCDFT. For the simplicity, we will assume the singlet pairing and the *s*-wave symmetry of the gap function. An extension to the triplet superconductors could be done following the work by Capelle et al. [16,20]. In the case of magnetic superconductors, one should take also into account a correction for the Zeeman effect, i.e. the spin gap. As for the pairing potentials with the higher angular-momentum, one cannot average spherically the angular part of the interaction in the RPA formula for the paramagnon susceptibility. The aforementioned formula will be used later in this section.

Here, we start with the Nambu Green's function for the superconductors with magnetic interactions included into the description. This matrix is now 4×4 dimensional and reads

$$\bar{G}(\mathbf{r}\tau,\mathbf{r}'\tau') = -\langle \hat{T}\hat{\varPsi}^\dagger(\mathbf{r},\tau)\otimes\hat{\varPsi}(\mathbf{r}',\tau')\rangle, \tag{59}$$

with the 4-component field operators (the notation has been chosen according to Maki in Ref. [18] and x denotes the vector $(\mathbf{r},\tau)$)

$$\hat{\varPsi}(x) = \begin{pmatrix} \hat{\psi}_\uparrow(x) \\ \hat{\psi}_\downarrow(x) \\ \hat{\psi}_\uparrow^\dagger(x) \\ \hat{\psi}_\downarrow^\dagger(x) \end{pmatrix}, \quad \hat{\varPsi}^\dagger(x) = \left(\hat{\psi}_\uparrow^\dagger(x)\hat{\psi}_\downarrow^\dagger(x)\hat{\psi}_\uparrow(x)\hat{\psi}_\downarrow(x)\right). \tag{60}$$

The first-order selfenergy with the spin dependent interaction $v^{\mu\nu}$, where μ and ν denote the Cartesian components of the spin orientations of two interacting electrons, is given by

$$\bar{\varSigma}(\mathbf{r}\tau,\mathbf{r}'\tau') = -v^{\mu\nu}(\mathbf{r}\tau,\mathbf{r}'\tau')\,\hat{\alpha}_\mu\bar{G}(\mathbf{r}\tau,\mathbf{r}'\tau')\hat{\alpha}_\nu, \tag{61}$$

$$v^{\mu\nu}(\mathbf{r}\tau,\mathbf{r}'\tau') = I_{ex}(\mathbf{r})D^{\mu\nu}(\tau-\tau')I_{ex}(\mathbf{r}'). \tag{62}$$

The quantity I_{ex} is *the spin exchange interaction*, and $D^{\mu\nu}$ is *the spin Green's function*. The matrix $\hat{\alpha}_\mu$ is defined as

$$\hat{\alpha}_\mu = \begin{pmatrix} \sigma_\mu & 0 \\ 0 & -\sigma_\mu^{tr} \end{pmatrix}, \tag{63}$$

where σ_μ^{tr} denotes the matrix transposed to the Pauli matrix σ_μ (see Ref. [19]).

For the transverse spin fluctuations, the α-matrix, given by formula (63), involves the Pauli matrices σ^+ and σ^- defined as $\sigma^\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y)$; explicitly

$$\sigma^+ = \begin{pmatrix} 0\,1 \\ 0\,0 \end{pmatrix}, \quad \sigma^- = \begin{pmatrix} 0\,0 \\ 1\,0 \end{pmatrix}.$$

Evaluation of the selfenergy with paramagnons, according to equations (61–63), yields a very sparse 4×4-matrix which reads

$$\bar{\varSigma}(\mathbf{r}\tau,\mathbf{r}'\tau') = -v^{+-}(\mathbf{r}\tau,\mathbf{r}'\tau') \times \begin{pmatrix} G_{\downarrow\downarrow}(\mathbf{r}\tau,\mathbf{r}'\tau') & 0 & 0 & -F_{\downarrow\uparrow}(\mathbf{r}\tau,\mathbf{r}'\tau') \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -F_{\uparrow\downarrow}^\dagger(\mathbf{r}\tau,\mathbf{r}'\tau') & 0 & 0 & G_{\uparrow\uparrow}^\dagger(\mathbf{r}\tau,\mathbf{r}'\tau') \end{pmatrix}, \tag{64}$$

where $G_{\uparrow\uparrow}^\dagger = -G_{\uparrow\uparrow}$.

Now, let us go back to the previous section and look again at the (1,1)-element of the $(\bar{\varSigma}\bar{G})$-matrix. We see that for the Coulomb and electron-phonon interactions, the total energy is proportional to the expression (46). For the magnetic interactions, however, the Nambu Green's function is defined by equation (59) and the selfenergy is given by equation (64), therefore, the total energy is proportional to

$$G_{\downarrow\downarrow}G_{\uparrow\uparrow} - F_{\downarrow\uparrow}F_{\uparrow\downarrow}^\dagger = G_{\downarrow\downarrow}G_{\uparrow\uparrow} - F_{\uparrow\downarrow}F_{\downarrow\uparrow}^\dagger. \tag{65}$$

The above expression differs from relation (46) by signum in front of the anomalous Green's functions. This difference will show up in the kernel K_{ij} and the norm Z_i. The phonon and paramagnon spectral functions enter the kernel with different signum (originating from the anomalous loop of Green's functions) and the norm with the same signum (originating from the normal loop).

To proceed further with the evaluation of the *xc*-free energy, F_{xc}, we write explicitly the spin-fluctuation Green's function, $D^{\mu\nu}(\tau-\tau')$, used in equation (62). In the case of paramagnons, $D^{\mu\nu}(\tau-\tau')$ is the transverse spin susceptibility, χ^{+-}, defined as

$$\chi^{+-}(\mathbf{r}-\mathbf{r}',\tau-\tau') = \langle \hat{T}\hat{S}^-(\mathbf{r},\tau)\hat{S}^+(\mathbf{r}',\tau')\rangle, \tag{66}$$

with the operators increasing and lowering spin which are defined respectively as

$$\hat{S}^+(\mathbf{r},\tau) = \hat{\psi}_\uparrow^\dagger(\mathbf{r},\tau)\hat{\psi}_\downarrow(\mathbf{r},\tau), \tag{67}$$

$$\hat{S}^-(\mathbf{r},\tau) = \hat{\psi}_\downarrow^\dagger(\mathbf{r},\tau)\hat{\psi}_\uparrow(\mathbf{r},\tau). \tag{68}$$

For the conduction band, we can use a model of the homogeneous electron gas with the fluctuations treated on the level of the random phase approximation. The Fourier transform of the RPA-"dressed" paramagnon propagator is

$$\chi^{+-}(\mathbf{q},\nu_n) = \frac{\chi^0(\mathbf{q},\nu_n)}{1 - I_{ex}\chi^0(\mathbf{q},\nu_n)}, \tag{69}$$

with the Pauli susceptibility χ^0 and the even Matsubara frequencies ν_n.

It is convenient to introduce the spectral representation

$$\chi^{+-}(\mathbf{q},\nu_n) = -\int_0^\infty \frac{d\Omega}{\pi}\, D^0(\Omega,\nu_n)\, \Im m\, \chi^{+-}(\mathbf{q},\Omega), \tag{70}$$

$$D^0(\Omega,\nu_n) = \frac{-2\Omega}{\nu_n^2 + \Omega^2}, \tag{71}$$

and the momentum averaged paramagnon spectral function

$$P(\Omega) = N(\varepsilon_F) \int_0^{2k_F} dq\, \frac{q}{2{k_F}^2} \times |I(q)|^2 \left[-\frac{1}{\pi}\,\Im m\, \chi^{+-}(q,\Omega)\right]. \tag{72}$$

We assume that the interaction function, $I(q)$, is the momentum independent quantity, I_{ex}, which can be calculated in a way given for instance in reference [10].

Therefore, for the systems with the electron-paramagnon interactions, the exchange-correlation free energy is given by

$$F_{xc}^{sf,1} = -\frac{1}{2}\sum_{\mathbf{k}\mathbf{k}'} \int d\Omega\, P(\Omega) \times \left[\left(1 + \frac{\xi_{\mathbf{k}}\xi_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}}\right) I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega) + \left(1 - \frac{\xi_{\mathbf{k}}\xi_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}}\right) I(E_{\mathbf{k}},-E_{\mathbf{k}'},\Omega)\right], \tag{73}$$

$$F_{xc}^{sf,2} = -\frac{1}{2}\sum_{\mathbf{k}\mathbf{k}'} \int d\Omega\, P(\Omega)\, \frac{\Delta_{\mathbf{k}}\Delta^*_{\mathbf{k}'}}{E_{\mathbf{k}}E_{\mathbf{k}'}} \times [I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega) - I(E_{\mathbf{k}},-E_{\mathbf{k}'},\Omega)], \tag{74}$$

where the function $I(E_{\mathbf{k}},E_{\mathbf{k}'},\Omega)$ is defined by equation (54). The explicit formula for the paramagnon spectral function, $P(\Omega)$, within the RPA is given for instance in references [8,10,19].

6 Gap equation with paramagnons and implementation details

At this point, we have completed the derivation of all components of the exchange-correlation free energy: the Coulomb part — equations (50, 51), the phonon part — equations (52, 53), and the spin-fluctuation part — equations (73, 74). Now, we can write explicitly the gap equation given by equations (26–28).

The M_{ij}-matrix of the linearized equation (26) is the following function of the kernel K_{ij} and the norm Z_i

$$M_{ij} = -\frac{1}{2}\frac{K_{ij}\,[\Delta=0]}{1 - Z_i\,[\Delta=0]}. \tag{75}$$

The nondiagonal part of the M_{ij}-matrix is given by

$$K_{ij} = K_{ij}^{el} + K_{ij}^{ph+sf}, \tag{76}$$

where the electronic part is defined by

$$K_{ij}^{el} = w_{ij}, \tag{77}$$

$$w_{ij} = \frac{2\pi}{k_i k_j}\log\left(\frac{(k_i+k_j)^2 + k_{TF}^2}{(k_i-k_j)^2 + k_{TF}^2}\right). \tag{78}$$

The Coulomb interaction w_{ij} has been spherically averaged over the angular coordinates since, as we said before, we assumed the *s*-wave pairing. The electron correlations are taken into account by the Thomas-Fermi screening constant, k_{TF}, and k_i is an absolute value of the reciprocal vector.

The electron-phonon and electron-paramagnon interaction nondiagonal part of the M_{ij}-matrix is given by

$$K_{ij}^{ph+sf} = \frac{2}{\tanh(\beta\xi_i/2)\tanh(\beta\xi_j/2)} \times \int d\Omega\, \left[\alpha^2F(\Omega) - P(\Omega)\right] \times \left[I(\xi_i,\xi_j,\Omega) - I(\xi_i,-\xi_j,\Omega)\right]. \tag{79}$$

The diagonal part of the M_{ij}-matrix is

$$Z_i = Z_i^{el} + Z_i^{ph+sf}, \tag{80}$$

where the purely electronic part is

$$Z_i^{el} = -\frac{1}{2\xi_i}\left\{\sum_j w_{ij}\,[1 - \tanh(\beta\xi_j/2)] - \frac{\sum_{jk}\frac{\beta w_{jk}/2}{\cosh^2(\beta\xi_j/2)}\,[1 - \tanh(\beta\xi_k/2)]}{\sum_k \frac{\beta/2}{\cosh^2(\beta\xi_k/2)}}\right\}, \tag{81}$$

and the phononic and paramagnon part is

$$Z_i^{ph+sf} = \frac{-4\pi}{\tanh(\beta\xi_i/2)}\frac{1}{\beta}\int d\Omega\, \left[\alpha^2F(\Omega) + P(\Omega)\right] \times \sum_{\omega_2} \omega_2\, \mathrm{sgn}(\omega_2)\left[Z_{i,sym}^{ph+sf} + Z_{i,asym}^{ph+sf}\right], \tag{82}$$

$$Z_{i,sym}^{ph+sf} = [n_\beta(\Omega) + f_\beta(-\xi_i)]\,\frac{2(\xi_i+\Omega)}{\left[\omega_2^2 + (\xi_i+\Omega)^2\right]^2} + [n_\beta(\Omega) + f_\beta(\xi_i)]\,\frac{2(\xi_i-\Omega)}{\left[\omega_2^2 + (\xi_i-\Omega)^2\right]^2}. \tag{83}$$

Functions f_β and n_β are the Fermi-Dirac and Bose-Einstein distribution functions respectively.

For the electronic part of the norm, i.e. Z_i^{el}, we used the zero temperature approximation given in references [10,14]. This approximation can be justified by the fact that the critical temperatures of simple metals, which we calculate in this work, are very low. The above simplification is done for a sake of the numerical convenience since there are many singularities in the formula (81).

The subscripts "sym" and "asym" mean the symmetric and antisymmetric part of Z_i with respect to the electron-phonon coupling elements $g_{\mathbf{k},\mathbf{k}+\mathbf{q}}$. The electron-paramagnon interaction constant, $I(\mathbf{q})$, has been also averaged in $\mathbf{q}$ leading to I_{ex}. The antisymmetric part $Z_{i,asym}^{ph+sf}$ is omitted in our calculations according to the reasons discussed in references [5,14] and in our previous work [10]. Therefore, we do not give the expression for $Z_{i,asym}^{ph+sf}$ in this work.

7 Critical temperatures of simple metals

In the following two subsections, we report the critical temperatures obtained by solving the SCDFT gap equation with the spin fluctuations included. We compare these results with the results without the spin fluctuations and results from the Eliashberg theory. First, we calculate parameters of the gap equation for several simple metals: V, Mo, Ta, and Pd (fcc and bcc) at ambient pressure. At the end, we complete our previous results for Nb under pressure [10] reporting T_c obtained within the SCDFT with the paramagnons included.

The electronic structures, the densities of states (DOS) and the electron-phonon coupling constants and the phonon and magnon spectral functions for studied metals were calculated within the local density approximation (LDA). We used the pseudopotential plane wave codes PWSCF [21] and ESPRESSO [22]. The phonons and electron-phonon couplings were obtained from the density functional perturbation theory (DFPT) [23]. Since the calculation of the spectral function α^2F is very time consuming, we used the ultrasoft pseudopotentials (US PPs) [24]. The kinetic energy cut-offs for the wavefunctions and densities were 45 Ry and 270 Ry respectively in order to reproduce well all features of the phonon dispersions especially for the low frequency phonons (see Ref. [10]). The metallic broadening at the Fermi energy [25] was assumed at 0.03 Ry. We used the Monkhorst-Pack mesh [26] of (64,64,64)-points for the DOS calculations. The mesh of (16,16,16)-points was used for the self-consistent calculation of the electron-phonon-coupling matrix elements for the each phonon, the mesh of (8,8,8)-points was assumed to fit the phonon dispersions. We fit from (16,16,16) into (64,64,64) mesh-points to perform the integrands with the double-delta function present in the definition of the electron-phonon coupling constant, λ^{ph}, and the spectral function, $\alpha^2F(\omega)$.

The spin-exchange interaction constants, I_{ex}, for metals at ambient pressure were taken from the work by Singalas et al. [27]. Further, we used the aforementioned parameters for the calculation of the spectral function, $P(\omega)$, and the electron-paramagnon coupling constant, λ^{sf}. For niobium under pressure, we used I_{ex} and $P(\omega)$ calculated in our previous work [10].

All electronic parameters and the phonon and magnon spectral functions were assumed to be the same for the normal and superconducting state. The accuracy of functions $\alpha^2F(\omega)$ and $P(\omega)$ is very important for an exact estimation of the critical temperature. The electron-phonon spectral function is very time consuming for the calculations. The function α^2F contains all the specific information about the studied system. In contrast, the approximation which we used for the paramagnon spectral function, $P(\omega)$, to avoid calculation of this quantity from the time-dependent density functional theory, is insufficient. We made the assumption of the homogeneous electron gas for the spin susceptibility. The only spin-dependent quantity which we calculated specifically for a given metal was the exchange constant. The calculation of this constant, i.e. I_{ex}, is very difficult. Obtained results have a large error due to their very small values and necessity to calculate the response function to very small magnetizations applied to the system. Therefore, as we will see below, the obtained critical temperatures are not always very close to the experimental ones. Further development should be directed into more accurate calculation of the spectral functions, especially $P(\omega)$.

7.1 Transition metals at ambient pressure

In Table 1, we report the critical temperatures and parameters which enter the gap equation calculated by means of the Eliashberg theory and the SCDFT for a few simple metals: vanadium, molybdenum and tantalum in bcc lattice structure and palladium in fcc and bcc structures. Our calculated densities of states, $N(\varepsilon_F)$, and the electron-phonon coupling constants, λ^{ph}, are in a good agreement with the previous calculations by Savrasov et al. [28]. The Eliashberg functions calculated within the DFPT are presented in Figure 1. The Coulomb parameter, μ^*, was obtained from the Benneman-Garland formula [10,29], which employs the density of states. The spin exchange constant, I_{ex}, taken from reference [27], has been used to obtain the paramagnon spectral function, $P(\omega)$, which we draw in Figure 2.

As for the critical temperatures, for tantalum, the SCDFT result is in a very small relative error, defined in Table 1, of 3% with respect to the experimental data [30]. While, the Eliashberg result with the spin fluctuations included is in the error of 81%. For molybdenum, T_c from the Eliashberg gap equation is smaller than the experimental one, even without the paramagnon effect. But the absolute error of all calculated temperatures for Mo is smaller than 1 K. Palladium in both structures fcc and bcc is nonsuperconducting and the SCDFT reproduces well this result. In contrast to the SCDFT result, from the Eliashberg theory we obtained superconductivity with a very small T_c for Pd in the bcc structure.

Table 1. Various parameters such as: crystal symmetry, density of states $N(\varepsilon_F)$ per Ry and per both spins, coupling constants I_{ex} [Ry/both spins], electron-phonon λ^{ph}, electron-paramagnon λ^{sf}, and T_c [K] calculated from the Eliashberg theory and the SCDFT with the Coulomb and phonon interactions only (ep) and with spin fluctuations (epsf), the experimental T_c^{exp} (from Ref. [30]), and the "error" defined as $(T_c^{epsf} - T_c^{exp})/T_c^{exp}$ [%] with T_c^{epsf} calculated within the SCDFT.

						Eliashberg		SCDFT			
system	$N(\varepsilon_F)$	I_{ex}	λ^{ph}	λ^{sf}	μ^*	T_c^{ep}	T_c^{epsf}	T_c^{ep}	T_c^{epsf}	$\sim T_c^{exp}$	"error"
V bcc	24.98 (26.14^a)	0.0218^b	0.91 (1.19^a)	0.430^c	0.212	9.0	5.9	16.1	7.4	5.38	38
Mo bcc	8.81 (8.34^a)	0.0184^b	0.47 (0.42^a)	0.024^c	0.198	0.8	0.7	1.5	1.4	0.92	52
Ta bcc	18.60 (18.38^a)	0.0162^b	0.97 (0.86^a)	0.096^c	0.209	8.7	8.1	5.9	4.6	4.48	3
Pd fcc	30.68 (34.14^a)	0.0230^b	0.35 (0.35^a)	0.972^c	0.213	0.01	-	–	–	-	-
Pd bcc	16.60 (18.49^b)	0.0229^b	0.68 (--)	0.167^c	0.208	1.3	0.8	–	–	-	-

^{a} Values from reference [28].
^{b} Values from reference [27].
^{c} Calculated with I_{ex} from reference [27].

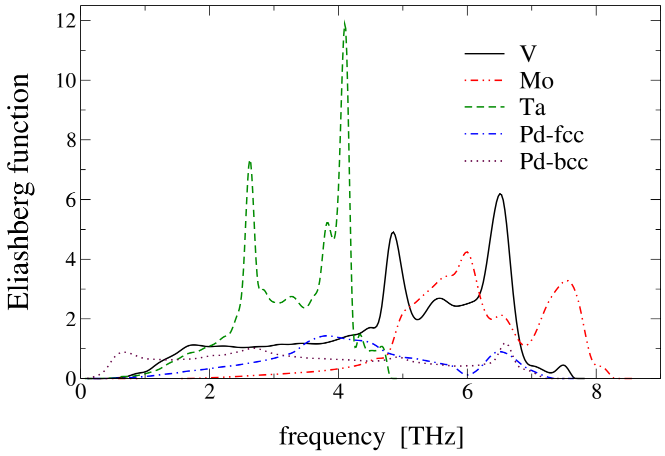

Fig. 1. The Eliashberg functions of V, Mo, Ta in bcc structure and Pd in both bcc and fcc structures.

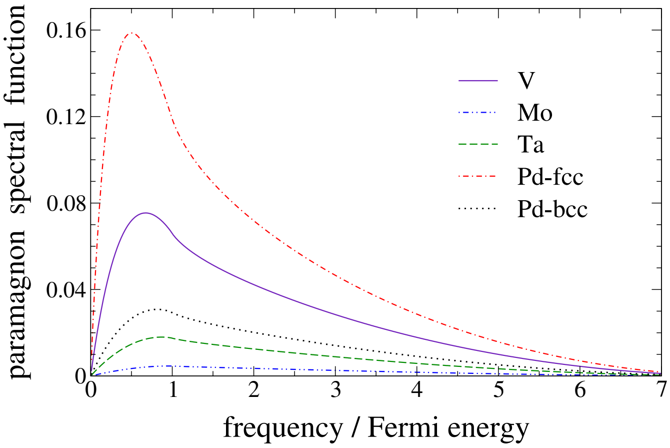

Fig. 2. The paramagnon spectral functions of V, Mo, Ta in bcc structure and Pd in both bcc and fcc structures.

Usually, the critical temperatures from the SCDFT are lower than temperatures from the Eliashberg theory. In some cases, however, the SCDFT temperatures are higher. This situation is for vanadium and molybdenum. Especially for vanadium, T_c from the SCDFT gap equation is about 2 K higher than the experimental data [30], even after inclusion of the spin fluctuations. This fact may indicate that, either the spin exchange constant, I_{ex}, was underestimated, or a contribution of the asymmetric part of the phononic term in the SCDFT gap equation is quite large. As we know from results reported in references [5,10], if we neglect the asymmetric part in the electron-phonon-coupling matrix elements by taking the $\alpha^2F(\omega)$ averaged at the Fermi level, the critical temperatures are higher (see the discussion in Sect. 6). The last approximation, however, must be done if we do not evaluate formulas with the $g_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ elements explicitly.

In general, the critical temperatures obtained from the SCDFT are in a good agreement with the measured temperatures [30], and the effect of paramagnons improves the result considerable for many simple metals.

7.2 Niobium under pressure

In Table 2, we present the critical temperatures and the parameters of the gap equation for niobium at eight pressures in the range from −17 GPa up to 80 GPa. The spin exchange constants, I_{ex}, have been calculated from first principles in reference [10], and the electron-phonon and electron-magnon spectral functions for Nb have been presented also in that work.

Here, we complete our previous results by reporting the effect of paramagnons on T_c calculated from the SCDFT. After the inclusion of the spin fluctuations, the critical temperatures obtained from the SCDFT are closer to the experimental T_c's for pressures in the range of 0–40 GPa, i.e. pressures between the two anomalies measured by Struzhkin et al. [11]. The dependence of the

Table 2. Results for Nb; applied pressure p [GPa], density of states $N(\varepsilon_F)$ per Ry and per both spins, spin exchange integral I_{ex} [Ry/both spins] (from Ref. [10]), coupling constants: electron-phonon λ^{ph}, electron-paramagnon λ^{sf}, and T_c [K] calculated from the Eliashberg theory (with μ^*=0.21) and SCDFT with Coulomb and phonon interactions only (ep) and with spin fluctuations (epsf). The experimental T_c^{exp} has been estimated from the picture given in reference [11]. Last column shows the "error" of the SCDFT calculations for T_c^{epsf} defined in Table 1.

					Eliashberg		SCDFT			
p	$N(\varepsilon_F)$	I_{ex}	λ^{ph}	λ^{sf}	T_c^{ep}	T_c^{epsf}	T_c^{ep}	T_c^{epsf}	$\sim T_c^{exp}$	"error"
–16.59	22.82	0.0211	1.91	0.28	20.3	16.7	14.4	6.2	-	-
–9.45	21.60	0.0213	1.60	0.25	19.5	15.5	13.2	6.4	-	-
–0.63	20.24	0.0217	1.41	0.22	18.8	14.7	12.9	7.2	9.2	-22
9.98	19.38	0.0204	1.65	0.17	19.6	15.8	13.4	9.8	10.0	-2
22.89	18.32	0.0189	1.47	0.13	19.4	16.0	13.2	11.3	9.8	15
38.79	17.10	0.0228	1.29	0.16	18.4	14.1	12.0	10.1	9.7	4
56.73	15.42	0.0292	1.10	0.23	16.1	10.7	10.1	8.4	9.5	–12
78.37	13.10	0.0347	0.86	0.24	13.7	7.3	8.2	7.9	8.8	–10

measured critical temperature as a function of pressure is no longer reproduced by our calculations when we take into account paramagnons. At ambient pressure and for higher pressures, paramagnons seem to make the theoretical result worse. The above effect, could be explained by making the observation that, in every case where the exchange constant I_{ex} is large, the theoretical temperature underestimates the measured temperature, and vice versa, for the smallest I_{ex} the critical temperature obtained from the SCDFT is the highest and the error is positive.

Concluding this section, the implementation of paramagnons to the SCDFT generally makes the calculated critical temperatures closer to the experimental ones. But our calculated exchange constants, I_{ex}, are not sufficiently accurate. This fact gives a direction for the future development.

8 Summary

In the present work, we included the transverse spin fluctuations to the density functional theory for superconductors. The SCDFT is presented from its foundations, through the decoupling approximation, the gap equation and the details of the implementation. We assumed the singlet and the s-wave pairing potential; The extension to the triplet superconductors could be done following the work by Capelle et al. [16,20]. The electron-phonon couplings and the electron-paramagnon couplings were averaged at the Fermi energy, therefore the asymmetric part of the functional with respect to the electron-phonon matrix elements and to the spin-exchange interaction constants were omitted. Through the whole work, we kept the notation to be consistent with Parks [17,18] and Vonsovsky [19].

Paramagnons and phonons in the superconducting state were assumed to be the same like in the normal state. The Eliashberg spectral function has been calculated within the density functional perturbation theory and it is fully material specific. Paramagnons, in contrast, have been obtained from the random phase approximation for the homogeneous electron gas and only the spin exchange constants were calculated from the electronic structure.

We reported the critical temperatures obtained from the SCDFT and the Eliashberg linearized gap equation with and without spin fluctuations for a few simple metals: V, Mo, Ta, Pd at ambient pressure and Nb at several pressures up to 80 GPa. Some discrepancies between the temperatures calculated from the SCDFT and the measured temperatures are due to the fact that it is quite difficult to obtain the accurate spin-exchange constants and/or to the fact that the spectral functions have been averaged at the Fermi level. Netherveless, the results show that the inclusion of paramagnons improves the critical temperatures obtained from both methods, the SCDFT and the Eliashberg theory. The critical temperatures obtained from the parameter-free SCDFT are in most cases closer to the experimental data than the results obtained from the Eliashberg theory.

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