Condensation energy of the homogeneous electron gas from density-functional theory for superconductors

M. Wierzbowska[1,2,*] and J. W. Krogh[1]
[1]*Department of Theoretical Chemistry, University of Lund, Chemical Centre P.O.B 124, S-221 00 Lund, Sweden*
[2]*Institut fürn Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*
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The condensation energy of homogeneous electron gas is calculated within the density-functional theory for superconductors. Purely electronic considerations include the exchange energy exactly and the correlation energy on a level of the random phase approximation. Singlet superconductivity is assumed, and the Coulomb interaction is studied with a model pairing potential at angular momentum up to $l=9$ and densities $1 \leqslant r_s \leqslant 10$. The homogeneous gas remains nonsuperconducting up to $r_s \simeq 9$. A very weak negative value of the condensation energy has been found for f waves and higher-l pairing at $r_s=10$.

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I. INTRODUCTION

For superconductivity both the electronic and the electron-phonon interactions are important. While for the BCS (Ref. 1) superconductors the electron-phonon contributions dominate, for novel high-T_c materials the Coulomb interactions play a key role. Eliashberg theory,[2] being a generalization of Migdal's theorem,[3] is able to treat the electron-phonon interaction in both the weak- and strong-coupling regimes, but the electronic interactions are averaged to a single parameter μ^*. This might be insufficient even for strongly correlated systems.[4] In this work, we focus on purely electronic interactions in the superconducting homogeneous gas for which the results obtained in the last 40 years still remain controversial.

The existence of superconductivity at higher-angular-momentum pairing without phononic contributions was suggested by Kohn and Luttinger[5] in 1965. The mechanism proposed there was based on the presence of the long-range oscillatory potential in ordinary space due to the sharpness of the Fermi surface and the fact that Cooper pairs[6] could form taking advantage of the attractive regions. Interestingly, some features of the phonon spectra have been explained due to Friedel oscillations.[7]

More than 20 years ago, Takada[8] solved the Eliashberg equations and estimated the transition temperature T_c due to the plasmon exchange. His solution assumed weak electron-phonon coupling for which the Kirzhnits-Maksimov-Khomskii (KMK) approximation[9] can be justified. Other authors, Rietschel and Sham[10] and Shuh and Sham,[11] solved the strong-coupling Eliashberg equations linearized in the gap function. For the Coulomb interactions, they also assumed the random phase approximation[12] (RPA) and found unrealistically high critical temperatures. Later papers included vertex corrections yielding a counterpart for the plasmon exchange which overestimate the Coulomb attraction. Obtained this way, critical temperatures were much lower.[13–16]

Nowadays, we can use a standard solid state method, the density-functional theory[17] (DFT), generalized to the superconducting state (SCDFT) by Oliveira, Gross, and Kohn[18] in 1988. The formal framework, which we briefly describe in the next section, has been developed over more than ten years[19] and extended to relativistic superconductors.[20] The first solutions of the SCDFT scheme for simple metals predicted the critical temperatures[21] quite well, although the electronic correlations have been taken into account only by the Thomas-Fermi screening of the Coulomb interaction. Then, the semiphenomenological correlation functional was constructed and tested, first for Nb[22] and later for YBCO (Ref. 23) using the eight-band model.[24] The formulation of the local density approximation (LDA) for superconductors was given by Kurth *et al.*[25] in 1999. The attempt to construct the exchange-correlation functional from *first principles* was made[25] using as a starting point the RPA (Ref. 12) generalized to the superconducting state.[26] The condensation energy of the homogeneous gas has been calculated within that scheme for the model pairing potential of s type[25] and no superconductivity has been found up to $r_s=5$.

After the discovery of the anisotropic gaps in B2212 (Ref. 27) and YBCO (Ref. 28) by angular-resolved photoemission experiments, it is interesting to look closer at the higher-angular-momentum channels within the SCDFT method. This is a step toward DFT calculations for the superconducting state of high-T_c compounds. Recently, the condensation energy for systems with the anisotropic gaps has been studied by Haslinger and Chubukov within the Eliashberg theory adapted for the spin-fluctuation mediated pairing[29,30] (see also references therein).

The fact that the model calculations based on results obtained for a homogeneous gas have been performed for strongly correlated layered superconductors by Bill, Morawitz, and Kresin[31] and Seibold[32] shows that our studies can contribute to understanding physics of complicated systems. The data for a homogeneous gas obtained with our code[33] can also give a basis for the parametrization of an LDA functional for inhomogeneous superconductors in a similar philosophy as an ordinary LDA is a parametrization[34] of the quantum Monte Carlo data[35] calculated for a representative set of r_s (Wigner radius) values.

This paper is organized as follows: after a brief description of the theoretical background in the next section, we

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show the results of the condensation energy calculations in Sec. III and make a comparison with findings of other authors in Sec. IV.

II. THEORETICAL BACKGROUND

The framework of a DFT for superconductors was formulated by Oliveira, Gross, and Kohn.[18] It rests on 1-1 mapping between the density

$$n(\mathbf{r}) = \sum_{\sigma} \langle \hat{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \rangle \tag{1}$$

and the superconducting order parameter

$$\chi(\mathbf{r},\mathbf{r}') = \langle \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') \rangle, \tag{2}$$

on the one hand, and the electrostatic and pairing potentials $v_s(\mathbf{r})$ and $\Delta_s(\mathbf{r},\mathbf{r}')$, on the other hand. Here, we assumed singlet pairing; however, the triplet pairing can be treated analogously.[36] The noninteracting Kohn-Sham potentials are functionals of both the normal density and the order parameter:

$$v_s[n,\chi](\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n,\chi](\mathbf{r}), \tag{3}$$

$$\Delta_s[n,\chi](\mathbf{r},\mathbf{r}') = \Delta_0(\mathbf{r},\mathbf{r}') + \int d^3r' \frac{\chi(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \Delta_{xc}[n,\chi](\mathbf{r},\mathbf{r}'), \tag{4}$$

where $v_0(\mathbf{r})$ is the lattice potential and $\Delta_0(\mathbf{r},\mathbf{r}')$ is an external pairing potential of an adjacent superconductor. The second term in $\Delta_s(\mathbf{r},\mathbf{r}')$ is the anomalous Hartree potential. The exchange-correlation potentials are defined as functional derivatives of the exchange-correlation (xc) free energy functional $F_{xc}[n,\chi]$ over the normal and anomalous densities:

$$v_{xc}[n,\chi](\mathbf{r}) = \frac{\delta F_{xc}[n,\chi]}{\delta n(\mathbf{r})}, \tag{5}$$

$$\Delta_{xc}[n,\chi](\mathbf{r},\mathbf{r}') = -\frac{\delta F_{xc}[n,\chi]}{\delta \chi^{*}(\mathbf{r},\mathbf{r}')}. \tag{6}$$

The corresponding Kohn-Sham equations have the form of the Bogoliubov–de Gennes equations[18,37] (μ is a chemical potential of the superconductor):

$$u_k(\mathbf{r}) = \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right] u_k(\mathbf{r}) + \int d^3r' \Delta_s(\mathbf{r},\mathbf{r}') v_k(\mathbf{r}'), \tag{7}$$

$$v_k(\mathbf{r}) = -\left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right] v_k(\mathbf{r}) + \int d^3r' \Delta_s(\mathbf{r},\mathbf{r}') u_k(\mathbf{r}'), \tag{8}$$

and result from diagonalization of the noninteracting Hamiltonian

$$\hat{H}_s = \sum_{\sigma} \int d^3r \hat{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right] \hat{\Psi}_{\sigma}(\mathbf{r}) - \left[\int d^3r \int d^3r' \Delta^{*}_s(\mathbf{r},\mathbf{r}') \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') + \text{H.c.} \right]. \tag{9}$$

The exchange-correlation functional includes in general the electronic and phononic contributions.[19] Here, however, we are interested in the electronic part only, treated within the RPA (Ref. 12) for the superconducting state.[26] The LDA scheme for superconductors[25] has been constructed analogously to the local spin density approximation (LSDA). In superconductors, the order parameter plays a similar role to that of the spin magnetization in the LSDA. The electron gas is exposed to the external pairing potential of the superconductor, just as the LSDA gas is under the influence of a magnetic field.

The exchange energy of the superconducting gas is given by the expression

$$f_x[\mu_s,\Delta_s] = -\frac{1}{4} \int \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|^2} \times \left[1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} E_{\mathbf{k}} \right) \right] \times \left[1 - \frac{\xi_{\mathbf{k}'}}{E_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} E_{\mathbf{k}'} \right) \right], \tag{10}$$

where $E_{\mathbf{k}} = \sqrt{\xi^2_{\mathbf{k}} + |\Delta_s(\mathbf{k})|^2}$ is the quasiparticle spectrum and $[\xi_{\mathbf{k}} = (k-k_F)^2/2] - \mu$. The anomalous Hartree energy f_{AH} is a functional of the pairing potential only:

$$f_{AH}[\mu_s,\Delta_s] = \frac{1}{4} \int \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|^2} \frac{\Delta_s(\mathbf{k}) \Delta^{*}_s(\mathbf{k}')}{E_{\mathbf{k}} E_{\mathbf{k}'}} \times \tanh\left(\frac{\beta}{2} E_{\mathbf{k}} \right) \tanh\left(\frac{\beta}{2} E_{\mathbf{k}'} \right). \tag{11}$$

The RPA energy results from the summation of bubble diagrams with the normal and anomalous Green's functions[25,26] G and F (see Fig. 1) and can be written as

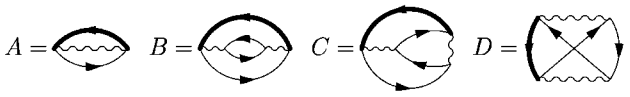
$$f_{RPA}[\mu_s,\Delta_s] = \frac{1}{2\beta} \int \frac{d^3q}{(2\pi)^3} \sum_{\nu_n} \times \left(\ln\left[1 - \Pi_s(\mathbf{q},\nu_n) \frac{4\pi}{q^2} \right] + \Pi_s(\mathbf{q},\nu_n) \frac{4\pi}{q^2} \right), \tag{12}$$

where the Matsubara frequencies, even $\nu_n = 2n\pi/\beta$ and odd $\omega_n = [(2n+1)\pi]/\beta$, enter the Fourier transform of the irreducible polarization propagator $\Pi_s(\mathbf{q},\nu_n)$, with $\mathbf{q}$ being the momentum exchange of the interacting electrons, as follows:

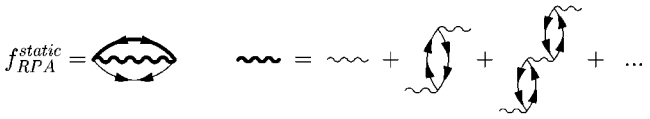
$$\Pi_s(\mathbf{q},\nu_n) = \frac{2}{\beta} \int \frac{d^3k}{(2\pi)^3} \sum_{\omega_n} [G(\mathbf{k},\omega_n) G(\mathbf{k}+\mathbf{q},\omega_n+\nu_n) + F(\mathbf{k},\omega_n) F^{\dagger}(\mathbf{k}+\mathbf{q},\omega_n+\nu_n)]. \tag{13}$$

Evaluation of Green's functions in the polarization propaga-

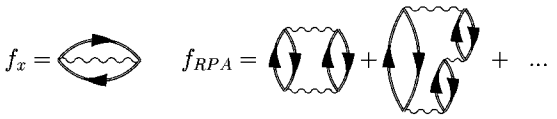
Kohn and Luttinger in 1965



Takada in 1978



Rietschel and Sham in 1983



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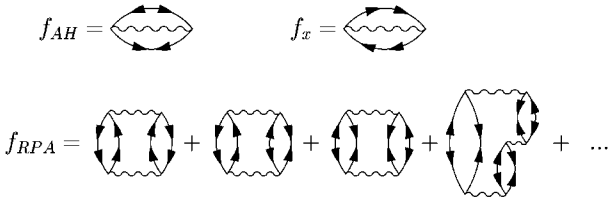

Legend

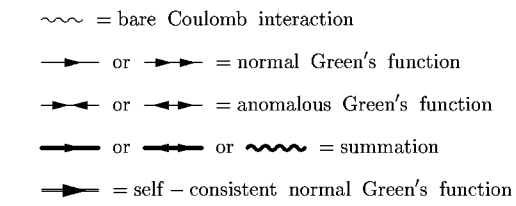

FIG. 1. Feynman diagrams for the total energy contributions considered by other authors (Refs. 5, 8, and 10) and in this work.

tor leads to the explicit functional of the Coulomb and pairing potentials:

$$\Pi_s(\mathbf{q},\nu_n) = \int \frac{d^3k}{(2\pi)^3}\left\{ \frac{E_{\mathbf{k}}+E_{\mathbf{k+q}}}{\nu_n^2+(E_{\mathbf{k}}+E_{\mathbf{k+q}})^2} \times\left[1-\frac{\xi_{\mathbf{k}}\xi_{\mathbf{k+q}}}{E_{\mathbf{k}}E_{\mathbf{k+q}}}+\frac{\Delta_s(\mathbf{k})\Delta_s^*(\mathbf{k}+\mathbf{q})}{E_{\mathbf{k}}E_{\mathbf{k+q}}}\right] \times\left[\frac{1}{2}\tanh\left(\frac{\beta}{2}E_{\mathbf{k}}\right)+\frac{1}{2}\tanh\left(\frac{\beta}{2}E_{\mathbf{k+q}}\right)\right] + \frac{E_{\mathbf{k}}-E_{\mathbf{k+q}}}{\nu_n^2+(E_{\mathbf{k}}-E_{\mathbf{k+q}})^2} \times\left[1+\frac{\xi_{\mathbf{k}}\xi_{\mathbf{k+q}}}{E_{\mathbf{k}}E_{\mathbf{k+q}}}-\frac{\Delta_s(\mathbf{k})\Delta_s^*(\mathbf{k}+\mathbf{q})}{E_{\mathbf{k}}E_{\mathbf{k+q}}}\right] \times\left[\frac{1}{2}\tanh\left(\frac{\beta}{2}E_{\mathbf{k}}\right)-\frac{1}{2}\tanh\left(\frac{\beta}{2}E_{\mathbf{k+q}}\right)\right]\right\}.$$

We assumed above that the Kohn-Sham orbitals are plane waves, because we are interested in the condensation energy of the homogeneous electron gas. The way to obtain the LDA functional for inhomogeneous superconducting system is given in Ref. 25. Feynman diagrams for the contributions to the total energy considered in this work are displayed in Fig. 1 and compared to those diagrams from earlier papers.

The condensation energy can be obtained from

$$E_{S-N} = T_{kin}[\mu_s,\Delta_s] - T_{kin}[\mu_s,0] + f_{ah}[\mu_s,\Delta_s] + f_x[\mu_s,\Delta_s] - f_x[\mu_s,0] + f_c^{RPA}[\mu_s,\Delta_s] - f_c^{RPA}[\mu_s,0], \quad (14)$$

where the kinetic energy difference of the superconducting and normal states in a homogeneous gas at zero temperature is

$$T_{kin}[\mu_s,\Delta_s] - T_{kin}[\mu_s,0] = \sum_{\mathbf{k}} \frac{k^2}{2}\left[\frac{1}{2}-\frac{1}{2}\frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}}\right]\mathrm{sgn}(\mathbf{k}-\mathbf{k}_F).$$

III. CONDENSATION ENERGY CALCULATIONS

The first calculations of the condensation energy within the LDA for superconductors with the RPA functional were performed for the *s*-wave pairing only and no superconductivity was found.[25] We calculate the condensation energy of the homogeneous electron gas at zero temperature, assuming a model nonspherical gap function of the form

$$\Delta_s^{lm}(\mathbf{k}) = \delta \exp\left(\frac{-(k-k_F)^2}{\sigma^2}\right) P_l^m(\mathbf{k}), \quad (15)$$

where δ and σ are parameters in units of μ and k_F, respectively, and $P_l^m(\mathbf{k})$ are associated Legendre polynomials. The above parametrization of the gap makes it possible to control the strength, range, and angular shape of the pairing. In this work, we are mainly interested in the angular part. It will be clear from the further discussion that variational determination of δ and σ in such a way that the condensation energy is maximally negative would lead to either zero values for these parameters if E_{S-N} is positive or to infinite values of these parameters if E_{S-N} is negative. As we will see later, the condensation energy is also monotonic with l, but we were not able to predict this result from the analytical form of expression (14).

The *s*-wave calculations appeared smooth in δ and μ parameters[25] in the ranges $0.01<\sigma<1$ and $0.01<\delta\cdot 100<1$ at $r_s=0.1$ and $1\leqslant r_s\leqslant 5$. Therefore, in this work, we fixed the strength of the potential at $\delta=0.01\mu$ and the range of the pairing interaction at $\sigma=0.1k_F$, and we present results for this choice of the parameters. Later, we will discuss changes in the condensation energy when it is calculated with two other sets of parameters δ and σ: namely, with $\delta=0.01\mu$ and $\sigma=0.05k_F$ and with $\delta=0.001\mu$ and $\sigma=0.1k_F$.

Turning to the details of the implementation, the eight-dimensional integrals of the energy functionals have been reduced by one dimension in electronic Matsubara frequency which can be evaluated analytically. Several singularities present in the formulas need special grids. For the calculation of f_{AH} and f_x and the radial part of f_{RPA}, we used a

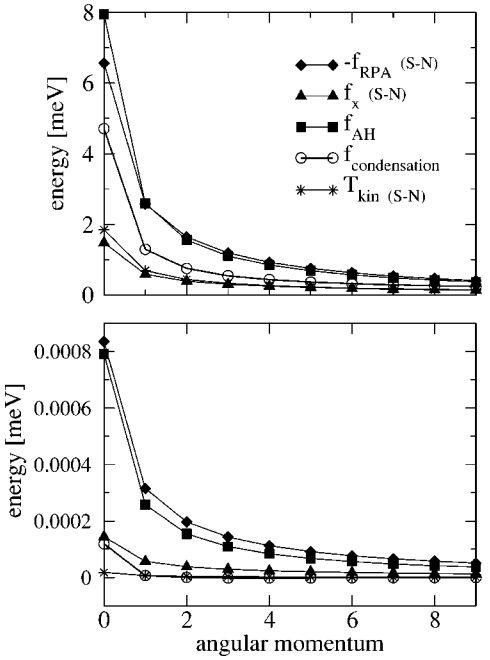

FIG. 2. The condensation energy $f_{condensation}$ and its components: the difference between the superconducting and the normal state of the RPA correlation energy f_{RPA} (S-N) and that of the exchange energy f_x (S-N) and of the kinetic energy T_{kin} (S-N) and the anomalous Hartree energy f_{AH} (this is nonzero only in the superconducting state). All energies are shown calculated at two densities: $r_s=1$ a.u. (upper panel) and $r_s=10$ a.u. (lower panel). The model parameters in the pairing potential were fixed at $\delta=0.01\mu$ and $\sigma=0.1k_F$. Zero temperature was assumed.

modified Gauss-Legendre quadrature. For the angular part of f_{RPA}, we combined the Lobatto grid[38] for the **q**-momentum integration and Sobolev's quasirandom method[39] to generate the mesh used by the Monte Carlo quadrature over the angular part of the **k** momentum. Details of the singularities and parallel code are given in Ref. 33.

We will focus now on the results obtained with $\delta=0.01\mu$ and $\sigma=0.1k_F$. We see in Fig. 2 the angular momentum dependence of the condensation energy and its components: the anomalous Hartree energy (f_{AH}) and the difference (S-N) of the exchange energy f_x between the superconducting and normal states and that difference (S-N) of the RPA correlation energy f_{RPA}, calculated at $r_s=1$ and at $r_s=10$. The condensation energy and all its components decrease monotonically with the angular momentum. The anomalous Hartree energy is the biggest positive component, almost completely balanced by the negative RPA energy which acts in favor of superconductivity. The exchange energy difference between the superconducting and the normal state is positive, and tends to destroy pairing. We show results for all momentum numbers l from 0 to 9. However, for the antisymmetric fermionic function only the even numbers make sense, because we assumed singlet spin pairing for the order parameter. The condensation energies at $r_s=1$ are positive for $0\leqslant l\leqslant 9$. At the density $r_s=10$, s-wave pairing also does not allow superconductivity.

In order to show the energetics as a function of the density of a homogeneous electron gas, we present, in Table I, the condensation energy and its components for the s-type and d-type as well as f-type pairing potentials and for the r_s parameter in the range of 1–10 a.u. Decreasing the density from $r_s=1$ to $r_s=3$, all energies decrease by two orders of magnitude, from a few meV to a few percent of meV. Further dilution of the electron gas to $r_s=10$ lowers the energies by another two orders of magnitude. This shows how delicate the balance is between the superconducting phase and the normal state.

Slightly negative values of the condensation energies at $r_s=10$ are obtained for f waves and higher-angular-momentum pairing, but all components are very small and the most negative value is of order $\sim 1.5\times 10^{-6}$ meV. Since the biggest contributions to this negative energy are f_{RPA} and f_{AH}, which are of order 1×10^{-4} meV while the condensation energy is of order 1×10^{-6} meV and since we trust to our numerical results up to the three leading digits, it is plausible that a change by 1 in the last position in the correlation and the anomalous Hartree energy may cause a change of sign in the condensation energy. Actually for the same reason, the condensation energy at $r_s=10$ for the d-wave pairing could be negative (because it is three orders of magnitude smaller than the leading contributions). But this uncertainty due to the numerical accuracy will happen neither for s-wave pairing nor for smaller r_s parameters, as one can see in Table I. Later, we will show calculations for $r_s=10$ with another choice of δ and σ.

Finally, we change the parameters in the model pairing potential. These results are presented in Table II for $r_s=1$ and for the angular momentum up to 3 (since before we found the possibility for a phase transition for f waves).

First, we change σ parameter for $0.05k_F$ (before it has been fixed at $0.1k_F$), and we keep the same δ as in Table I—i.e., 0.01μ. For this choice of δ and μ, all energies are smaller, and we do not find superconductivity at $r_s=1$ up to $l=3$. The typical bandwidths at the Fermi surface are much more narrow than $0.1k_F$. The results of calculations for s waves performed by previous authors[25] were smooth in σ, and our results with two values of σ appear smooth with respect to a variation of the angular momentum. Therefore, we do not expect any change in conclusions by changing the σ parameter.

Second, we change the δ parameter for 0.001μ (before it has been fixed at 0.001μ) and we keep the same σ as in Table I—i.e., $0.1k_F$. Now, all energies are smaller, and the decrease of the condensation energy is about one and half order of magnitude while the change of the pairing amplitude δ is by a factor of 0.1. The BCS behavior of the condensation energy is proportional to a square of the gap, $\sim\Delta^2$. We find in our calculations that the dependence of the condensation energy on the gap amplitude is a bit weaker than the BCS one. For the lower-momentum channels a power of that dependence is smaller than for the higher-angular-momentum channels. This seem to be in contrast with measurements for ordinary, BCS-like, superconductors which have a gap of the s type. On the other hand, measurements are not able to split the purely electronic and the phononic contributions, and we did not add phonons to our calculations.

TABLE I. The condensation energy f_{cond} and its components f_{RPA} (S-N), f_x (S-N), f_{AH}, and T_{kin} (S-N), calculated for s waves, d waves, and f waves for fixed $\delta=0.01\mu$ and $\sigma=0.1k_F$, and at zero temperature (T = 0 K) for different electronic densities r_s. Energies are given in meV, and parameters μ, k_F, and r_s are in atomic units.

r_s	f_{cond}	$-f_{RPA}$	f_x	f_{AH}	T_{kin}
			s waves		
1	4.71×10^{0}	6.56×10^{0}	1.48×10^{0}	7.95×10^{0}	1.84×10^{0}
3	2.30×10^{-2}	9.37×10^{-2}	1.81×10^{-2}	9.79×10^{-2}	7.59×10^{-2}
5	2.82×10^{-3}	1.28×10^{-2}	2.33×10^{-3}	1.27×10^{-2}	5.90×10^{-4}
7	6.81×10^{-4}	3.33×10^{-3}	6.05×10^{-4}	3.29×10^{-3}	1.10×10^{-4}
8.5	2.87×10^{-4}	1.55×10^{-3}	2.78×10^{-4}	1.52×10^{-3}	4.16×10^{-5}
10	1.19×10^{-4}	8.35×10^{-4}	1.45×10^{-4}	7.91×10^{-4}	1.84×10^{-5}
			d waves		
1	8.28×10^{-1}	1.64×10^{0}	3.93×10^{-1}	1.56×10^{0}	4.43×10^{-1}
3	2.04×10^{-3}	2.18×10^{-2}	4.80×10^{-3}	1.92×10^{-2}	1.82×10^{-3}
5	4.21×10^{-4}	2.82×10^{-3}	6.19×10^{-4}	2.48×10^{-3}	1.42×10^{-4}
7	8.40×10^{-5}	7.49×10^{-4}	1.61×10^{-4}	6.46×10^{-4}	2.64×10^{-5}
8.5	2.16×10^{-5}	3.59×10^{-4}	7.38×10^{-5}	2.97×10^{-4}	9.99×10^{-6}
10	7.80×10^{-7}	1.97×10^{-4}	3.85×10^{-5}	1.55×10^{-4}	4.43×10^{-6}
			f waves		
1	7.24×10^{-1}	1.10×10^{0}	3.02×10^{-1}	1.19×10^{0}	3.32×10^{-1}
3	3.07×10^{-3}	1.56×10^{-2}	3.69×10^{-3}	1.36×10^{-2}	1.37×10^{-3}
5	3.31×10^{-4}	2.01×10^{-3}	4.75×10^{-4}	1.76×10^{-3}	1.06×10^{-4}
7	5.87×10^{-5}	5.41×10^{-4}	1.23×10^{-4}	4.57×10^{-4}	1.97×10^{-5}
8.5	1.21×10^{-5}	2.62×10^{-4}	5.66×10^{-5}	2.10×10^{-4}	7.48×10^{-6}
10	-1.45×10^{-6}	1.44×10^{-4}	2.95×10^{-5}	1.10×10^{-4}	3.32×10^{-6}

TABLE II. The condensation energy and its components f_{RPA} (S-N), f_x (S-N), f_{AH}, and T_{kin} (S-N), calculated as functions of the angular momentum l for three sets of parameters: r_s, δ, and σ. Energies are given in meV.

l	f_{cond}	$-f_{RPA}$	f_x	f_{AH}	T_{kin}
$r_s=1,\ \delta=0.01k_F,\ \sigma=0.05\mu$					
0	3.22×10^{0}	4.91×10^{0}	1.09×10^{0}	5.65×10^{0}	1.39×10^{0}
1	9.18×10^{-1}	2.03×10^{0}	4.47×10^{-1}	1.97×10^{0}	5.37×10^{-1}
2	5.39×10^{-1}	1.34×10^{0}	3.05×10^{-1}	1.23×10^{0}	3.52×10^{-1}
3	3.94×10^{-1}	1.00×10^{0}	2.37×10^{-1}	8.90×10^{-1}	2.66×10^{-1}
$r_s=1,\ \delta=0.001k_F,\ \sigma=0.01\mu$					
0	1.07×10^{-1}	2.24×10^{-1}	3.90×10^{-2}	2.58×10^{-1}	3.39×10^{-2}
1	2.59×10^{-2}	8.12×10^{-2}	1.44×10^{-2}	8.06×10^{-2}	1.20×10^{-2}
2	1.43×10^{-2}	4.97×10^{-2}	9.23×10^{-3}	4.72×10^{-2}	7.53×10^{-3}
3	1.02×10^{-2}	3.53×10^{-2}	6.90×10^{-3}	3.31×10^{-2}	5.53×10^{-3}
$r_s=10,\ \delta=0.1k_F,\ \sigma=0.5\mu$					
0	7.85×10^{-3}	2.90×10^{-2}	5.05×10^{-3}	3.04×10^{-2}	1.40×10^{-3}
1	1.49×10^{-3}	1.03×10^{-2}	2.23×10^{-3}	9.02×10^{-3}	5.39×10^{-4}
2	1.13×10^{-3}	5.91×10^{-3}	1.58×10^{-3}	5.11×10^{-3}	3.53×10^{-4}
3	9.17×10^{-4}	4.05×10^{-3}	1.25×10^{-3}	3.45×10^{-3}	2.67×10^{-4}

Our result indicates that we should not expect superconductivity at small r_s. Since all the energy components grow with δ and σ, we can say that the maximally negative condensation energy would be for $\sigma = k_F$ (all states contribute to pairing) and that there is no upper limit for δ. This is due to the fact that our condensation energy is proportional to Δ^n with $1.5 < n < 2$. The value of δ, which we set to 0.01μ, is much bigger than typical gaps. For instance, for Nb, we have *s*-wave pairing, $r_s = 0.87$, $\mu = 33.13$ eV, while the experimental gap is 1.55 meV. We have chosen a large δ—i.e., $0.01\mu \sim 330$ meV—for most of our calculations for the sake of accuracy, since the conclusions about the angular dependence of the condensation energy do not change with this parameter.

For lower density—i.e., $r_s = 10$—we calculated again the condensation energy but for a new choice of the gap parameters: $\delta = 0.1\mu$ and $\sigma = 0.5k_F$, which are unrealistically high but the numerical accuracy is much better in this case. The result of above calculations is negative for superconductivity, which makes also a situation that the phase transition occurs for a small gap less probabilistic.

If we wanted to include the electron-phonon or electron-paramagnon interaction, the expression for the total energy would be frequency independent because the frequency is integrated out in the SCDFT scheme (see, for instance, Refs. 18 and 19). Similar to the total energy, also the gap function would be static, as it is now. This is in contrast to the Eliashberg formalism where inclusion of strong coupling changes the gap function to a dynamic parameter.[30] As for the feedback effect of phonons or spin fluctuations for the electronic energy and vice versa, this effect would exist if one solved the SCDFT equations in the Bogoliubov–de Gennes form (for this formulation of SCDFT see, for example, Ref. 23). In the way we calculate the condensation energy in this work, the aforementioned feedback would not exist since all energy components contribute to the total energy independently through a single equation. This is another difference from the Eliashberg scheme, where three coupled equations have to be solved for the self-energy Σ, pairing-vertex Φ, and polarization (Refs. 29 and 30).

Summarizing the results, the condensation energy is positive for all angular momentums, which indicates that we are unlikely to obtain superconductivity from the electronic correlations only. For the very dilute gas at $r_s = 10$, we obtained slightly negative values of the condensation energy when the gap is small. These results should be, however, viewed with care, because all the energy components are very small and at the limit of numerical accuracy for the multidimensional quadrature. We trust to three leading digits in Tables I and II, while the condensation energy at $r_s = 10$ is three orders of magnitude smaller than the biggest contributions. Also the random phase approximation[12] for the correlation energy is exact only in the limit of high density[40]—i.e., $r_s < 1$. This treatment of the Coulomb interaction might be insufficient for the density at $r_s = 10$. Whether it is an appropriate approach it depends also on the angular momentum of the pairing potential and on the physical property one is interested.[16,41]

IV. DISCUSSION AND CONCLUSIONS

Whether the superconductivity can exist without phonons or not is a very old problem. In 1965, Kohn and Luttinger[5] suggested a mechanism of the Cooper pair[6] formation in the homogeneous gas due to Friedel oscillations.[7] These authors did not assume any particular form of the interaction, which could even be purely repulsive, since the attractive regions could form in real space because of a sharpness of the Fermi surface in the reciprocal space. It has been discussed that, for the pairing potential at higher angular momentum, the superconducting state was more favorable than for *s* waves. The above conclusions were based on the mathematical analysis of irreducible vertexes with the particle-particle interaction up to the second order (see Fig. 1). The criterion used for the superconductivity was the occurrence of a pole at T_c in the scattering amplitude for pairs of quasiparticles of equal and opposite momenta and in the total energy corresponding to two particles on the Fermi surface.

Later work on the superconducting homogeneous gas within the Eliashberg theory, treating the Coulomb interactions on the RPA level and beyond, can be compared to the results presented in this paper.

Superconductivity obtained due to the plasmon exchange alone seemed to be overestimated. Several papers solving the Eliashberg equations with the RPA model for the Coulomb interaction predicted superconductivity for *s*-wave pairing at quite high densities. Within the weak-coupling limit of the electron-phonon interaction the Eliashberg equations could be considered as **k** dependent only due to the KMK approximation.[9] In the limit of strong coupling to phonons, the **k**- and ω-dependent equations have to be solved. While first approximation led to superconductivity[8] at a density lower than $r_s = 6$, solving the strong-coupling regime equations yields a change in a sign of the Coulomb parameter[10] ($\mu^* < 0$) at the density $r_s \sim 2.5$. The total energy diagrams included in both approaches are shown in Fig. 1. The common assumption in the aforementioned two approaches is that the polarization function, which enters the RPA screened interaction, contains only normal Green's function loops, neglecting the anomalous ones which are also included in our scheme. In addition, the normal Green's function used by Sham and co-workers was obtained self-consistently in contrast to all the other papers discussed here. The correctness of such an approach was discussed by several authors[16,42] also by occasion of the GW approximation.[43,44] The criterion for superconductivity used by Takada[8] was a nonzero critical temperature. Sham and co-workers[10,13,14,42] considered the electron gas to be superconducting when the Coulomb pseudopotential μ^* was positive.

A number of papers that included vertex corrections on different level approximations predicted decreased temperatures of phase transition. Grabowski and Sham[13] studied the ω-dependent-only Eliashberg equations with vertex corrections up to second order. Within that simplified model, the signum of μ^* changed at $r_s = 7$. More extensive studies of vertex corrections were done within the KMK, **k**-dependent scheme extended to the strongly correlated systems by

Takada,[15] who included more than 50 diagrams systematically using the effective-potential expansion. As a conclusion of that work the phase transition occurred at $r_s > 3.9$, the maximum of the critical temperature was obtained at $r_s = 7.2$, and T_c decreased for lower densities. Büche and Rietschel[14] added the vertex corrections, within the phenomenological model by Kukkonen and Overhauser[45] (KO), to the earlier work by Rietschel and Sham,[10] and did not obtain superconductivity up to $r_s = 5$. The parameter μ^* for gas in the range of $1 \leqslant r_s \leqslant 5$ was positive and varied between 0.05 and 0.1. Then, Takada[16] performed **k**- and ω-dependent calculations with the local-field correction of the KO model and showed a significant effect of corrections beyond RPA around $r_s = 5$. Another observation made in his work was that, although the compressibility κ and the spin susceptibility χ were strongly dependent on the vertex corrections, T_c of gas at the density $r_s > 20$ was similar to the temperature obtained from RPA. For $r_s > 40$ the critical temperature has been approximated by $T_c \approx 0.04 E_F$.

All the aforementioned papers on the superconducting homogeneous gas, within the RPA and beyond, dealt with the pairing potential of the *s* type. The *s*-, *p*-, and *d*-type pairing potentials examined in Ref. 41 led to the conclusion that the vertex corrections to *s* waves are much more important than to the higher-momentum channels.

In this work, we calculated the condensation energy at zero temperature, instead of solving the gap equation for finite temperatures. This way we are not able to determine the critical temperature for the densities at which we find superconductivity. On the other hand, negative values of the condensation energy are very small, of order $\sim 1.5 \times 10^{-6}$ meV, at the densities $r_s \geqslant 10$ for *f* waves and the higher-*l* channels. For *d* waves, the condensation energy is positive but very small.

We concluded that this effect might be due to an accuracy of the multidimensional numerical quadrature of objects with many singularities. On this point we want to comment that most of standard quantum chemistry programs which calculate two-electron integrals do not accede an accuracy higher than six important digits. Our task is even more difficult because in addition to calculating the **k**- and **q**-momentum vectors, we have to perform the quadrature over the bosonic Matsubara frequency, and singularities in the superconducting state have much more complicated shape[33] than those of the two-electron integrals calculated for the normal state.

The positive aspect of the method employed here is the absence of any approximation except the RPA. The DFT is exact for the ground state studied here. We do not make any assumption about phononic interactions, which we neglect. But if we wanted to include the electron-phonon interactions, then the way of treating the weak and the strong coupling would be the same.[21] We do not drop either the momentum dependence or the frequency dependence of the Coulomb interaction. The vertex corrections, especially important for the moderate densities for the properties like the critical temperature,[16] are not taken into account in this work. However, we believe that the inclusion of vertex corrections would not change the conclusions, because for *f* waves the strength of the Coulomb attraction is not as much overestimated by the polaron exchange as for *s* waves.[41]

Another interesting question would be whether it is possible that at some densities *s* waves are favorable for the superconducting state and at other densities the higher-*l* pairing would lead to lower energy. Such an *s*-wave to *p*-wave transition has been reported by Takada[41] at $r_s = 4.7$ while for higher densities the energy of *p* waves was lower. Küchenhoff and Wölfle,[46] by solving two coupled Bethe-Salpeter equations for the two-particle vertex functions in the particle-hole channels, found the *p*-wave superconductivity for $10 < r_s < 35$ and the *s*-wave superconductivity for $r_s > 35$. From our results, which are monotonic with the angular momentum number, such an *l*-wave–to–*l′*-wave transition seems not to be the case.[54]

We assumed singlet pairing. Thus, only the even numbers *l* (like *s* waves, *d* waves, etc.) are relevant, and it would be incorrect from the symmetry point of view to compare the total energy of *s* waves with the total energy of *p* waves. On the other hand, if there is not much energy gain by the Cooper pair formation, then the spin pairing in the superconducting phase probably is the same as the magnetic phase of the normal state. Within quantum Monte Carlo methods,[47] it has been widely examined theoretically that the ground state of the homogeneous electron gas is paramagnetic for high and intermediate densities and the transition to the ferromagnetic phase occurs at about $r_s \simeq 25$. There is experimental evidence[48] for the ferromagnetic phase in $Ca_{1-x}La_xB_6$ at the density $r_s = 28$ a.u., where the saturation moment of $0.07 \mu_B$ per electron resists below the temperature 600 K, which is of the order of the Fermi temperature of the electron gas. However, for this experiment the iron substrate was chosen. Another experimental group[49] could not find any evidence for the intrinsic ferromagnetism in any of $A_{1-x}La_xB_6$ ($A = Ca, Sr$) samples. As for the novel superconducting materials with triplet pairing, they cannot be described within a model based on the local spin density approximation, where the parametrization on a homogeneous gas results works well. In order to describe those superconductors, like Sr_2RuO_4 or $(TMTSF)_2X$, it has been shown by Shimahara in Ref. 50 that one should add strong short-range correlations to weaken the Coulomb interaction and then the electron-phonon mechanism could cause pairing. Moreover, the model assumed in our work is three dimensional (3D), while Sr_2RuO_4 should be described in 2D and $(TMTSF)_2X$ in 1D.

There is also a question about an effect of the fluctuations which could mediate the pairing interaction (for such a model see the work of Abanov and Chubukov in Ref. 51). Such calculations for the condensation energy in strongly correlated systems, where both effects of the electron-phonon and electron-paramagnon interactions are taken into account, have been performed by Haslinger and Chubukov in Ref. 30. The essential difference between those calculations and ours, if we included phonons and paramagnons, would be in the frequency dependence of the gap function, which in our case is static due to different formulation of the problem from the very beginning. For the inclusion of the dynamical effect to the gap, one needs to go beyond the Born-Oppenheimer approximation. In fact, such formulation exists within the multicomponent DFT scheme proposed by Kreibich and Gross[52] and developed by van Leeuwen.[53]

In conclusion we have calculated the condensation energy of the homogeneous electron gas at zero temperature within

the density-functional theory for superconductors. The random phase approximation was assumed for the Coulomb interaction and no phononic contributions have been added. We did not consider pairing mechanism mediated by fluctuations. Within this approach, there is no superconductivity for any momentum of the pairing potential for the densities up to $r_s \simeq 9$. We found very weak superconductivity for f waves and higher-l pairing at $r_s = 10$, but this effect is so small that could be due to the neglecting of the vertex correction or due to the accuracy of the numerical quadrature.

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*Present address: INFM DEMOCRITOS National Simulation Center, via Beirut 2-4, 34014 Trieste, Italy.

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