A representability problem in density functional theory for superconductors

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Aiming at a unified treatment of correlation and inhomogeneity effects in superconductors, Oliveira, Gross and Kohn proposed in 1988 a density functional theory for the superconducting state. This theory relies on the existence of a Kohn–Sham scheme, i.e., an auxiliary noninteracting system with the same electron and anomalous densities of the original superconducting system. However, the question of noninteracting ψ-representability has never been properly addressed and the existence of the Kohn-Sham system has always been assumed without proof. Here, we show that indeed such a noninteracting system does not exist at zero temperature. In spite of this result, we also show that the theory is still able to yield good results, although in the limit of weakly correlated systems only.

The correct description of superconductors continues to be one of the great questions of modern condensed matter theory. We still have a poor understanding of the superconducting features of high-Tc cuprates [1] or layered organic materials [2]. Moreover, recent exciting discoveries of superconductivity in two layers of graphene rotated by a small angle [3, 4], or in hydrides at high pressure [5, 6] (whose transition temperatures are quickly approaching room temperature) continue to challenge our understanding of superconducting systems.

Until the discovery of unconventional superconductivity by Bednorz and Müller [7], Bardeen-Cooper-Schrieffer (BCS) theory [8] as well as its theoretical extensions [9, 10] were the main framework for understanding superconductivity. While the electron-phonon interaction is well accounted for in BCS and Eliashberg’s theories, correlation effects due to the electron-electron Coulomb repulsion are extraordinarily difficult to handle. Since those effects are usually condensed in a single parameter (namely, µ∗), which is almost always treated as an adjustable quantity, the predictive capability of the theory is quite limited.

Aiming for a unified treatment of electronic correlation and inhomogeneity effects in superconductors, in 1988 Oliveira, Gross and Kohn proposed a density functional theory (DFT) for the superconducting state (SCDFT) [11]. Normal DFT is based on the famous Hohenberg-Kohn theorems [12], whose main statement is the observation that for non-degenerate systems there is a one-to-one correspondence between the external potential, the (non-degenerate) many-body ground state and the associated ground-state electronic density. The DFT formalism for superconductivity is based on a similar theorem, the Oliveira-Gross-Kohn theorem [11], which guarantees a one-to-one mapping between the equilibrium statistical density operator and the electronic n(r) ≡ ⟨ψ†(r)ψ(r)⟩ and the anomalous χ(r, r′) ≡ ⟨ψ↑(r)ψ↓(r′)⟩ densities:

\[
(n, \chi) \xleftrightarrow{1-1} \hat{\rho},
\]

where \( \hat{\rho} \) is the equilibrium statistical operator, and \( \hat{H}_{\psi}\Delta \) is the grand-canonical Hamiltonian for a superconductor in an external potential \( v(r) \) and a non-local pair potential \( \Delta(r, r') \). The field operator \( \hat{\psi}_\sigma(r) (\hat{\psi}^\dagger_\sigma(r)) \) destroys (creates) an electron with spin \( \sigma \) at position \( r \).

Although SCDFT was later extended to consider the nuclear density [13, 14], the electronic problem is still treated at the level of a two-component DFT. This version of SCDFT has been extremely successful in predicting superconductivity in a wide variety of materials [15–17] and proved especially useful for the investigation of superconductivity in high-pressure environments [18–20]. This success of SCDFT stems mainly from two facts: First, the gap equation is a single 3-dimensional integral equation, while Eliashberg equations form a system of 4-dimensional integral equations in momentum and frequency space; Second, it is much simpler to approximate and evaluate the electron-electron interaction term in SCDFT. This allows us not to use a semi-empirical \( \mu^* \), rendering therefore SCDFT a truly ab initio, predictive theory.

In principle, the formalism is able to describe superconductivity in all systems, for all complexities of the many-electron problem are cast into a universal exchange-correlation functional whose existence is ensured by the Oliveira-Gross-Kohn theorem. Yet, the practical applicability of SCDFT rests (as in the standard DFT) on a Kohn-Sham scheme, which maps the real interacting system of interest to an auxiliary noninteracting one with the same equilibrium electronic and anomalous densities. The Kohn-Sham system of SCDFT is described in second quantization by the following Hamiltonian:

\[
H_\kappa = -\sum_\sigma \int \hat{\psi}_\sigma^\dagger(r) \left[ \nabla^2 \frac{1}{2} + \mu - v_\kappa(r) \right] \hat{\psi}_\sigma(r) dr 
- \int \left[ \Delta_\kappa^*(r, r') \hat{\psi}_\uparrow(r) \hat{\psi}_\downarrow(r') + h.c. \right] dr dr',
\]

where \( \mu \) is the chemical potential and \( v_\kappa(r) \) and \( \Delta_\kappa(r, r') \) are the normal and anomalous Kohn-Sham potentials, computed by means of functional derivatives of the uni-
versal SCDFT functional.

In standard DFT, the question whether one can always find a noninteracting system with external potential \( v \) for which the ground-state electron density is the same of the full interacting system, is known as the noninteracting \( \nu \)-representability problem [21–23]. In SCF the system is noninteracting \( (\nu, \Delta) \)-representable if a noninteracting system defined through the potentials \( v(r) \) and \( \Delta(r, r') \) can be found such that the equilibrium densities of the system are respectively equal to \( n(r) \) and \( \chi(r, r') \). Unlike zero-temperature DFT [24], in SCF this question has never been properly addressed and the existence of the Kohn-Sham system has always been assumed without proof. In this letter we prove that indeed such a noninteracting system does not exist, at least at zero temperature!

By and large, this is a difficult problem in the light of the well-known fact that the set of interacting pure-state \( \nu \)-representable electronic densities

\[
\mathcal{B} = \{ n = \langle \Psi | n | \Psi \rangle | | \Psi \rangle \in \mathcal{G} \},
\]

where \( \mathcal{G} \) is the set of ground states for some external potential \( v \), is not identical to the set of noninteracting pure-state \( \nu \)-representable electronic densities [25]. As such, representability questions are well-known problems in many-body physics with no general answers. For instance, for spin-polarized systems two different non-degenerate ground states always lead to two different sets of electronic and magnetization densities. Yet two different sets of external potentials \( (v, B) \) can lead to the same ground state, and therefore —unlike standard DFT— the potentials of spin-polarized systems are not unique functionals of the spin densities [26].

A second example, that will turn out to be essential for our purposes, is reduced density matrix functional theory (RDMFT). Instead of the density, in RDMFT the main object is \( \rho_1 \), the one-particle reduced density matrix, whose diagonal is the electronic density \( n(r) \). Similarly to DFT, RDMFT is based on a variational principle stating that the ground-state energy of a fermionic system can be obtained by minimizing some energy functional on the set of \( N \)-representable one-body reduced density matrices [27]. The condition that \( \rho_1 \) satisfy in order to ensure its \( N \)-representability (i.e. that there is a fermionic statistical operator whose contraction leads to \( \rho_1 \) ) reads simply [28]: \( 0 \leq \rho_1 \leq 1 \), provided that \( \text{Tr}[\rho_1] = N \). For pure systems these representability conditions are known to be more stringent [29, 30]. Yet, when the fermionic density operator corresponds to a noninteracting system at zero temperature (and the many-body state reduces to a single Slater determinant) the one-body reduced density matrix is in addition idempotent, namely,

\[
\rho_1^2 = \rho_1.
\]

Zero-temperature noninteracting one-body reduced densities are on the boundary of the set of all fermionic one-body reduced densities. Since for interacting systems \( \rho_1 \) is not idempotent (in fact, \( \rho_1^2 < \rho_1 \) [31]) it is known that there is no Kohn-Sham system for RDMFT at zero temperature. In other words, interacting one-body reduced density matrices are non-noninteracting \( \nu \)-representable at zero temperature.

Now, returning to the problem of noninteracting representability in SCF, we notice that the Hamiltonian (2) can be diagonalized by a Bogoliubov transformation of the field operators \( \psi_\sigma \):

\[
\hat{\psi}_\sigma(r) = \sum_k u_k(x) \hat{\gamma}_{k,\sigma} - \text{sign}(\sigma) v_k(x) \hat{\gamma}_{k,-\sigma}^\dagger.
\]

Here \( \hat{\gamma}_{k,\sigma} \) and \( \hat{\gamma}_{k,-\sigma} \) are creation and annihilation operators of fermionic quasiparticles. The transformation (5) leads to a set of Bogoliubov-de Gennes equations for the coefficient functions \( u_k(r) \) and \( v_k(r) \) as well as the excitation energies of the quasiparticles \( E_k \). These equations are the counterpart to the Kohn-Sham orbital equations in normal DFT. Moreover, we arrive at a set of self-consistent equations for the ground-state densities, which take the following form at zero temperature:

\[
\rho_1(r, r') = \sum_k u_k(r) u_k^*(r') \theta(-E_k) + v_k(r) v_k^*(r') \theta(E_k),
\]

\[
\chi(r, r') = \sum_k u_k(r) v_k^*(r') \theta(E_k) - u_k(r') v_k^*(x) \theta(-E_k),
\]

with \( \theta(x) \) being the step function. Clearly, the ground-state density is equal to \( n(r) = \rho_1(r, r) \). In order to treat the problem of the existence of the Kohn-Sham system in the zero-temperature case, we will make use of the Nambu-Gorkov formalism. In Nambu-Gorkov space the field operators are defined as the following spinors:

\[
\tilde{\psi}_\downarrow(r) = \begin{pmatrix} \psi_{1,\downarrow}^\dagger(r) \\ \psi_{1,\uparrow}^\dagger(r) \end{pmatrix} \quad \text{and} \quad \tilde{\psi}_\uparrow(r) = \begin{pmatrix} \psi_{1,\downarrow}^\dagger(r) \\ \psi_{1,\uparrow}^\dagger(r) \end{pmatrix}.
\]

We can write the generalized one-body reduced density matrix as a tensor-product of Nambu-Gorkov field-operators:

\[
\Gamma(r, r') = \langle \tilde{\psi}_\downarrow(r) \otimes \tilde{\psi}_\uparrow^\dagger(r') \rangle.
\]

Obviously, \( \Gamma(r, r') \) can be expressed in terms of the normal one-body reduced density matrix \( \rho_1(r, r') \) and the anomalous density \( \chi(r, r') \).

To answer the question of noninteracting \( (\nu, \Delta) \)-representability of the superconducting densities it is worth studying the structure of the ground states of the Hamiltonian (2). In the case of the normal noninteracting electronic system (i.e. \( \Delta = 0 \)) the ground-state one-body reduced density matrix is idempotent (4). Surprisingly, the
same is true for the Nambu-Gorkov generalized one-body reduced density matrix for the noninteracting Hamiltonian \( (2) \), namely, \( \tilde{\Gamma}^2 = \tilde{\Gamma} \). It is simple to show that idempotency of \( \tilde{\Gamma} \) reduces to the equation:

\[
\rho_1 = \tilde{\rho}_1^2 + \chi^\dagger \chi.
\]  

(9)

This is a particular case of a general result in mathematical physics, especially generalized Hartree-Fock-Bogoliubov theory \cite{32}. Indeed, by a generalization of the Lieb’s variational principle, for systems with semi-bounded Hamiltonians, the infimum of the energy over quasifree states (the ones satisfying Wick’s theorem) is reached by a pure state \cite{33, 32}. A quasifree state is pure if and only if \( \tilde{\Gamma} \) is idempotent \cite{32, 33}.

Yet in SCDFT we are not interested in \( \rho_1(r, r') \) but in the electronic density \( n(r) \). From Eq. (9), for a superconducting noninteracting system, \( n(r) \) can be written in terms of \( \tilde{\rho}_1 \) and \( \chi \). It reads:

\[
n(r) = \text{Tr} \left[ \tilde{\rho}_1^2(r, r') + |\chi(r, r')|^2 \right].
\]  

(10)

By construction, in SCDFT no prior relation exists between \( n(r) \) and \( \chi(r, r') \) and they are assumed to be independent variables.

We will now demonstrate that in the Kohn-Sham system these two quantities are not independent for translation-invariant systems, for which the one-body reduced density matrix \( \rho_1(r, r') = \rho_1(r-r', 0) \) only depends on the differences \( r-r' \). In reciprocal space such density depends on one variable:

\[
\rho_1(k) = \int \rho_1(r-r', 0) e^{-i k (r-r')} d(r-r').
\]  

(11)

Analogously we can write \( \chi(r, r') \) as \( \chi(k) \) \cite{34}. For the Kohn-Sham noninteracting system \( \Gamma^2 = \Gamma \), and therefore \( \rho_1(k) = \tilde{\rho}_1^2(k) + |\chi(k)|^2 \). It yields:

\[
\rho_1(k) = \frac{1 + \text{sign}(E_k) \sqrt{1 - 4|\chi(k)|^2}}{2}.
\]  

(12)

We already noted that Eq. (10) is valid in the noninteracting system case. For translation-invariant systems this results in:

\[
n(r) = \int \frac{1}{2} \left( 1 + \text{sign}(E_k) \sqrt{1 - 4|\chi(k)|^2} \right) dk
\]  

(13)

In other words, we have an explicit equation for the electron density in terms of \( \chi(r, r') \) and we can write:

\[
\frac{\delta n(r)}{\delta \chi(k)} = -\frac{2 \text{sign}(E_k)}{\sqrt{1 - 4|\chi(k)|^2}} \chi^*(k),
\]  

(14)

As expected, \( n \) and \( \chi(r, r') \) are not independent and one is unequivocally determined by each other. Now, it is evident that the set of noninteracting \((v, \Delta)\)-representable densities and the set of interacting \((v, \Delta)\)-representable densities cannot coincide. Hence, no Kohn-Sham system can in general exist at zero temperature in the formalism of SCDFT.

It is possible to gain further insight into this problem at least for weakly correlated systems. Indeed, it is quite remarkable that for the homogeneous electron gas including electron-electron interactions to the Hamiltonian \( (2) \) maintains the idempotency of \( \tilde{\Gamma} \) in first-order perturbation theory. To see that let us perturb \( H_0 \) with the Coulomb interaction, namely, \( \tilde{H} = H_0 + \lambda W_{ee} \). In first-order perturbation theory the perturbed wave function includes only double and quadruple excitations of the quasiparticle vacuum (the superconducting ground state) \( |0\rangle \) (see Supplemental Material). It reads:

\[
|0\chi\rangle = |0\rangle + \lambda \sum_k b_k \hat{\gamma}_{k0}^\dagger \hat{\gamma}_{k1}^\dagger |0\rangle
\]  

\[
+ \lambda \sum_{qkk'} d_{qkk'} \hat{\gamma}_{(k+q)0}^\dagger \hat{\gamma}_{(k'-q)1}^\dagger \hat{\gamma}_{-k'0}^\dagger \hat{\gamma}_{k1}^\dagger |0\rangle + O(\lambda^2),
\]  

(15)

where the amplitudes are given as the expected value of the interelectronic interaction between the quasiparticle vacuum and the excited state \( \hat{\gamma}_{k0}^\dagger \hat{\gamma}_{k1}^\dagger |0\rangle \) (with energy \( E_k \)):

\[
b_k = \frac{\langle 0 | \hat{\gamma}_{k0}^\dagger \hat{\gamma}_{k1}^\dagger W_{ee} | 0 \rangle}{E_0 - E_k},
\]  

(16)

where \( E_0 \) is the vacuum’s energy, as well as with the state \( \hat{\gamma}_{(k+q)0}^\dagger \hat{\gamma}_{(k'-q)1}^\dagger \hat{\gamma}_{-k'0}^\dagger \hat{\gamma}_{k1}^\dagger |0\rangle \) (with energy \( E_{qkk'} \)),

\[
d_{qkk'} = \frac{\langle 0 | \hat{\gamma}_{k1}^\dagger \hat{\gamma}_{-k'0}^\dagger \hat{\gamma}_{-(k'-q)1}^\dagger \hat{\gamma}_{(k+q)0}^\dagger W_{ee} | 0 \rangle}{E_0 - E_{qkk'}},
\]  

(17)

Notice that in Eq. (15) \( \langle 0 | \chi \rangle \) = \( 1 + O(\lambda^2) \), so that in leading order the wave function is fairly normalized. It is easy to see that the perturbed diagonal densities read

\[
\rho'_k = \rho_k + \lambda \rho^{(1)}_k + O(\lambda^2), \quad \chi'_k = \chi_k + \lambda \chi^{(1)}_k + O(\lambda^2),
\]

where \( \rho^{(1)}_k = b_k v_k^* v_k + b_k^* u_k v_k \) and \( \chi^{(1)}_k = -b_k u_k^2 + b_k^* v_k^2 \).

Since \( 2\rho_k \rho^{(1)}_k + (\chi^*_k \chi^{(1)}_k + \text{c.c.}) = \rho^{(1)}_k \), \( \tilde{\Gamma} \) is idempotent in first order perturbation theory.

This result indicates that, for weakly correlated systems, in principle it is still possible to find a noninteracting system that reproduces the corresponding densities in first order of the perturbation. This result also explains why despite the fact that a Kohn-Sham system does not exist in general in SCDFT, the theory is still able to give good results for weakly correlated systems. A different conclusion arises from second-order perturbation theory, since the idempotency is, indeed, broken at such order (see Supplemental Material).

In layman’s terms, at zero temperature the existence of a Kohn-Sham system is equivalent to the fact that for every interacting pair \((n, \chi)\) there is a noninteracting system that has the same noninteracting \((n, \chi)\). However,
our result implies that there is a class of systems where all noninteracting densities are of the form \((n, \chi[n])\). This immediately proves that there are an infinite set of interacting \((n, \chi)\) that are not noninteracting \((v, \Delta)\)-representable, for which therefore no Kohn-Sham system exists.

We note that this problem of non-interacting \((v, \Delta)\)-representability is to some extent caused by the use of both a local density \(n\) and a component of the density matrix \(\chi\). As such, DFT for superconductors is somewhat a hybrid theory, inheriting the problems of both DFT and RDMFT. A possible workaround is to simply use the density matrix in Nambu-Gorkov space as a fundamental variable. This would lead to a more symmetric and elegant theory, namely a reduced-density matrix theory for superconductors, that would circumvent many of the problems of the current approach. Work along this lines is already in progress.

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[1] Patrick A. Lee, Naoto Nagaosa, and Xiao-Gang Wen, “Doping a mott insulator: Physics of high-temperature superconductivity,” Rev. Mod. Phys. 78, 17-85 (2006).

[2] B. J. Powell and R. H. McKenzie, “Quantum frustration in organic mott insulators: from spin liquids to unconventional superconductors,” Rep. Prog. Phys. 74, 056501 (2011).

[3] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, “Unconventional superconductivity in magic-angle graphene superlattices,” Nature 556, 43 (2018).

[4] C. Xu and L. Balents, “Topological superconductivity in twisted multilayer graphene,” Phys. Rev. Lett. 121, 087001 (2018).

[5] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, “Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system,” Nature (London) 525, 73 (2015).

[6] I. Errea, M. Calandra, C. Pickard, J. Nelson, R. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, “High-pressure hydrogen sulfide from first principles: A strongly anharmonic phonon-mediated superconductor,” Phys. Rev. Lett. 114, 157004 (2015).

[7] J. G. Bednorz and K. A. Müller, “Possible highTc superconductivity in the Ba-La-Cu-O system,” Z. Phys. B 64, 189 (1986).

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, “Theory of superconductivity,” Phys. Rev. 108, 775–1204 (1957).

[9] G. M. Eliashberg, “Interactions between electrons and lattice vibrations in a superconductor,” Sov. Phys. JETP 11, 696 (1960).

[10] L. P. Gor’kov, “On the energy spectrum of superconductors,” Sov. Phys. JETP 34, 505 (1958).

[11] L. N. Oliveira, E. K. U. Gross, and W. Kohn, “Density-functional theory for superconductors,” Phys. Rev. Lett. 60, 2430 (1988).

[12] P. Hohenberg and W. Kohn, “Inhomogeneous electron gas,” Phys. Rev. 136, B864 (1964).

[13] M. Lüders, M. A. L. Marques, N. N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda, and E. K. U. Gross, “Ab initio theory of superconductivity. I. Density functional formalism and approximate functionals,” Phys. Rev. B 72, 024545 (2005).

[14] M. A. L. Marques, M. Lüders, N. N. Lathiotakis, G. Profeta, A. Floris, L. Fast, A. Continenza, E. K. U. Gross, and S. Massidda, “Ab initio theory of superconductivity. II. Application to elemental metals,” Phys. Rev. B 72, 024546 (2005).

[15] A. Sanna, G. Profeta, A. Floris, A. Marini, E. K. U. Gross, and S. Massidda, “Anisotropic gap of superconducting CaC6: A first-principles density functional calculation,” Phys. Rev. B 75, 020511 (2007).

[16] J. A. Flores-Livas, M. Amsler, T. J. Lenosky, L. Lehtovaara, S. Botti, M. A. L. Marques, and S. Goedecker, “High-pressure structures of disilane and their superconducting properties,” Phys. Rev. Lett. 108, 117004 (2012).

[17] A. Floris, A. Sanna, S. Massidda, and E. K. U. Gross, “Two-band superconductivity in pb from ab initio calculations,” Phys. Rev. B 75, 054508 (2007).

[18] G. Profeta, C. Franchini, N. N. Lathiotakis, A. Floris, A. Sanna, M. A. L. Marques, M. Lüders, S. Massidda, E. K. U. Gross, and A. Continenza, “Superconductivity in lithium, potassium, and aluminum under extreme pressure: A first-principles study,” Phys. Rev. Lett. 96, 047003 (2006).

[19] R. Akashi, M. Kawamura, S. Tsuneyuki, Y. Nomura, and R. Arita, “First-principles study of the pressure and crystal-structure dependences of the superconducting transition temperature in compressed sulfur hydrides,” Phys. Rev. B 91, 224513 (2015).

[20] J. A. Flores-Livas, A. Sanna, and E. K.U. Gross, “High temperature superconductivity in sulfur and selenium hydrides at high pressure,” Eur. Phys. J. B 89, 63 (2016).

[21] E. Engel and R. Dreizler, Density Functional Theory: An Advance Course (Springer, Heidelberg, 2011).

[22] Robert van Leeuwen, “Density functional approach to the many-body problem: Key concepts and exact functionals,” Adv. Quantum Chem. 43, 25 (2003).

[23] A. Pribram-Jones, S. Pittalis, E. K. U. Gross, and K. Burke, “Thermal density functional theory in context,” Lecture Notes in Comput. Sci. 124, 25 (2014).

[24] M. Levy, “Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem,” Proc. Natl. Acad. Sci. 76, 6062 (1979).

[25] E. H. Lieb, “Density functionals for coulomb systems,” Int. J. Quantum Chem. 24, 243 (1983).

[26] K. Capelle and G. Vignale, “Nonuniqueness of the potentials of spin-density-functional theory,” Phys. Rev. Lett. 86, 5546–5549 (2001).

[27] T. L. Gilbert, “Hohenberg-Kohn theorem for nonlocal external potentials,” Phys. Rev. B 12, 2111 (1975).

[28] A. J. Coleman, “Structure of fermion density matrices,” Rev. Mod. Phys. 35, 668–686 (1963).

[29] A. Klyachko, “Quantum marginal problem and N-representability,” J. Phys. 36, 72 (2006).

[30] C. Schilling, C. L. Benavides-Riveros, and P. Vrana, “Re-
constructing quantum states from single-party information,” *Phys. Rev. A* **96**, 052312 (2017).

[31] E. Lieb and R. Seiringer, *Stability of Matter in Quantum Mechanics* (Cambridge University Press, 2010).

[32] V. Bach, E. H. Lieb, and J. P. Solovej, “Generalized Hartree-Fock theory and the Hubbard model,” *J. Stat. Phys.* **76**, 3–89 (1994).

[33] V. Bach, S. Breteaux, H. K. Knörr, and E. Menge, “Generalization of Lieb’s variational principle to Bogoliubov–Hartree–Fock theory,” *J. Math. Phys.* **55**, 012101 (2014).

[34] C. Hainzl, E. Hamza, R. Seiringer, and J. P. Solovej, “The BCS Functional for General Pair Interactions,” *Commun. Math. Phys.* **281**, 349 (2008).
**SUPPLEMENTAL MATERIAL**

In this Supplemental Material we provide the proof of two statements made in the main text. First, that for the homogeneous electron gas the generalized one-particle reduced density operator $\Gamma(\lambda)$ is idempotent in first order perturbation theory. Since the infimum of the energy for the Bogoliubov-de Gennes Hamiltonian is reached by a pure state, with an idempotent generalized one-particle reduced density matrix, this can explain why SCDFT yields good results for many superconductors. Second, that $\Gamma(\lambda)$ is not idempotent in second order.

The Hamiltonian we consider here is $\hat{H} = \hat{H}_0 + \lambda \hat{W}_{e-e}$, where $\hat{H}_0$ is the noninteracting Bogoliubov-de Gennes Hamiltonian introduced in Eq. (2) and $\hat{W}_{e-e}$ is the electronic repulsion operator. Let us use the well-known Bogoliubov transformations for the electron creation and annihilation operators $(\hat{c}_{k\sigma}, \hat{c}^\dagger_{k\sigma})$, namely,

\[
\hat{c}_{k\uparrow} = u_k^\alpha \gamma_{k0} + v_k^\alpha \gamma_{k1}, \tag{18}
\]

\[
\hat{c}^\dagger_{k\downarrow} = -v_k^\gamma \gamma_{k0} + u_k^\gamma \gamma_{k1}. \tag{19}
\]

The multiplication of creation and annihilation electron operators reads in the quasiparticle operators:

\[
\hat{c}^\dagger_{k\uparrow} \hat{c}_{k\uparrow} = |u_k |^2 \gamma_{k0}\gamma_{k0} + u_k^2 \gamma_{k0}\gamma_{k1} + u_k v_k \gamma_{k0}\gamma_{k1} + |v_k |^2 \gamma_{k1}\gamma_{k1}, \tag{20}
\]

\[
\hat{c}_{k\downarrow} \hat{c}_{k\downarrow} = -u_k^2 \gamma_{k0}\gamma_{k0} + u_k^2 \gamma_{k0}\gamma_{k1} - u_k v_k \gamma_{k0}\gamma_{k1} + v_k^2 \gamma_{k1}\gamma_{k1}. \tag{21}
\]

At zero order (i.e., $\lambda = 0$) the ground state is $|\text{BCS}\rangle$, the quasiparticle vacuum or more commonly the BCS state. The densities at zero order are given by

\[
\rho^{(0)}_{kk} = \langle \text{BCS}|\hat{c}^\dagger_{k\uparrow} \hat{c}_{k\uparrow}|\text{BCS}\rangle = |v_k|^2 \tag{22}
\]

\[
\chi^{(0)}_{kk} = \langle \text{BCS}|\hat{c}_{k\downarrow} \hat{c}_{k\downarrow}|\text{BCS}\rangle = -u_k^2 v_k \tag{23}
\]

Notice that

\[
(\rho^{(0)}_{kk})^2 + |\chi^{(0)}_{kk}|^2 = |v_k|^4 + |v_k|^2 |u_k|^2 = \rho^{(0)}_{kk} \tag{24}
\]

and trivially $\rho^{(0)}_{kk} \chi^{(0)}_{kk} + (1 - \rho^{(0)}_{kk}) \chi^{(0)}_{kk} = \chi^{(0)}_{kk}$. These are nothing more than the conditions for the idempotency at zero order, a quite well known result in superconductivity.

The particular combination of field-operators that enter the Coulomb interaction terms and produce relevant terms for the 1RDM/anomalous density is

\[
\hat{c}^\dagger_{(k+q)\uparrow} \hat{c}^\dagger_{(k' - q)\downarrow} \hat{c}_{k'\downarrow} \hat{c}_{k\uparrow} = \tag{25}
\]

\[
(u_{k+q} \gamma_{(k+q)0})^\dagger (u^*_{k' - q} \gamma_{(k' - q)0}^\dagger - v^*_{k' - q} \gamma_{(k' - q)0} - u_{k' - q} \gamma_{(k' - q)1}) \hat{c}_{k\uparrow} \hat{c}_{k\uparrow} + \text{h.c.},
\]

and expanding the products yields

\[
\hat{c}^\dagger_{(k+q)\uparrow} \hat{c}^\dagger_{(k' - q)\downarrow} \hat{c}_{k'\downarrow} \hat{c}_{k\uparrow} = \tag{26}
\]

\[
+ u_{k+q} v^*_{(k' - q)} v_{k'} v_{k} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} v^*_{(k' - q)} u_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} u^*_{(k' - q)} v_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} u^*_{(k' - q)} u_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - \gamma_{(k' - q)1}^\dagger \gamma_{k1}^\dagger
\]

\[
- u_{k+q} u^*_{(k' - q)} v_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} \gamma_{(k' - q)0}^\dagger - u_{k+q} v^*_{(k' - q)} v_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} v_{k'} \gamma_{(k' - q)0}^\dagger
\]

\[
- u_{k+q} u^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} u^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger
\]

\[
- u_{k+q} u^*_{(k' - q)} v_{k'} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger
\]

\[
- u_{k+q} u^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} v^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger
\]

\[
- v^*_{k+q} u_{(k' - q)} v_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u^*_{(k' - q)} v_{k'} \hat{c}_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger - u_{k+q} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u_{k+q} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger
\]

\[
- v^{*}_{k+q} u_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger + u^*_{(k' - q)} \gamma_{(k+q)0}^\dagger \gamma_{(k' - q)0}^\dagger.
\]
We are interested in the expectation value between the BCS state and the excited states of the Bogoliubov-de Gennes Hamiltonian (say, $\ket{s}$). We have therefore

\[
\langle s|c_{(k+q)\uparrow}^\dagger c_{k\downarrow}^\dagger \hat{c}_{k'\downarrow} \hat{c}_{k1}\rangle_{\text{BCS}} = \]
\[
u_{k+q} u_{(k'-q)}^* v_{k} \langle s|\gamma_{(k+q)0}^\dagger \gamma_{(k'-q)0} \gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}} - \nu_{k+q} u_{(k'-q)}^* v_{k} \langle s|\gamma_{(k+q)0}^\dagger \gamma_{(k'-q)1} \gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}}
\]
\[
+ \nu_{k-1} u_{(k'-q)}^* v_{k} \langle s|\gamma_{(k+q)0} \gamma_{(k'-q)1} \gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}} - \nu_{k-1} u_{(k'-q)}^* v_{k} \langle s|\gamma_{(k+q)0} \gamma_{(k'-q)0} \gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}}
\]
\[
(27)
\]
that reduces to

\[
\langle s|c_{(k+q)\uparrow}^\dagger c_{k\downarrow}^\dagger \hat{c}_{k'\downarrow} \hat{c}_{k1}\rangle_{\text{BCS}} = \delta^{0}_{q} u_{k} |v_{-k'}|^2 v_{k} \langle s|\gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}} + \delta^{0}_{k'} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{(k+q)0} \gamma_{(k'-q)1}\rangle_{\text{BCS}}
\]
\[
- \delta^{0}_{k'} \nu_{k} u_{k+q} u_{k-q} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}} + \delta^{0}_{q} |v_{-k'}|^2 \nu_{k} \langle s|\gamma_{(k+q)1} \gamma_{(k'-q)0}\rangle_{\text{BCS}}
\]
\[
- \nu_{k+q} u_{(k'-q)}^* v_{k} \langle s|\gamma_{(k+q)1} \gamma_{(k'-q)0} \gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}}.
\]
\[
(28)
\]
For the homogeneous electron gas we only have to consider $q \neq 0$ which reduces the contributions to solely:

\[
\langle s|c_{(k+q)\uparrow}^\dagger c_{k\downarrow}^\dagger \hat{c}_{k'\downarrow} \hat{c}_{k1}\rangle_{\text{BCS}}
\]
\[
= \delta^{0}_{k'} \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}} - \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}}
\]
\[
- \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}} - \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}}
\]
\[
= \delta^{0}_{k'} \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0}^\dagger \gamma_{k1}\rangle_{\text{BCS}} - \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}}
\]
\[
- \nu_{k} u_{k+q} u_{k-q} \nu_{k} v_{k} \langle s|\gamma_{k0} \gamma_{k1}\rangle_{\text{BCS}}.
\]
\[
(29)
\]
Notice that in Eq. (29) only double and quadruple excitations of the vacuum show up in that expression. Single excitations of the vacuum, for instance, contribute nothing in first-order perturbation theory. With this result we can prove that

**Theorem 1.** $\Gamma(\lambda)$ is idempotent at first order.

**Proof.** Let us take the first-order correction to the quasiparticle vacuum:

\[
|\Psi_1(\lambda)\rangle = |\text{BCS}\rangle + \lambda \sum_{k} b_{k} \gamma_{k0}^\dagger \gamma_{k1} |\text{BCS}\rangle + \lambda \sum_{qkk'} d_{qkk'} \gamma_{(k+q)0}^\dagger \gamma_{(k'-q)1} \gamma_{k0}^\dagger \gamma_{k1} |\text{BCS}\rangle + O(\lambda^2)
\]
\[
(30)
\]
That this is the correct wave function in first order can be seen from Eq. (29). Notice also that in first order the wave function (30) is correctly normalized. The parameters $d_{qkk'}$ and $b_{k}$ stem from perturbation theory. Writing the (diagonal) densities as

\[
\rho_{kk}(\lambda) \equiv \rho_{kk}^{(0)} + \lambda \rho_{kk}^{(1)} + O(\lambda^2) \quad \text{and} \quad \chi_{kk}(\lambda) \equiv \chi_{kk}^{(0)} + \lambda \chi_{kk}^{(1)} + O(\lambda^2),
\]
\[
(31)
\]
we have for $|\Psi_1(\lambda)\rangle$

\[
\rho_{kk}^{(1)} = b_{k} \langle \text{BCS}|c_{k\uparrow}^\dagger \gamma_{k0}^\dagger \gamma_{k1} |\text{BCS}\rangle + c.c. = b_{k} u_{k}^* v_{k} + b_{k}^* u_{k} v_{k},
\]
\[
(32)
\]
\[
\chi_{kk}^{(1)} = b_{k} \langle \text{BCS}|c_{k\uparrow}^\dagger \gamma_{k0}^\dagger \gamma_{k1} |\text{BCS}\rangle + b_{k}^* \langle \text{BCS}|\gamma_{k0} \gamma_{k1} c_{k\uparrow}^\dagger \gamma_{k1} |\text{BCS}\rangle = -b_{k} u_{k}^* v_{k}^2 + b_{k}^* v_{k}^2.
\]
\[
(33)
\]
Notice that to compute the first-order contribution to the densities only double excitations are included. This comes from the fact that the expressions (20) and (21) only contains pairs of creation/annihilation operators. We also have

\[
2\rho_{kk}^{(0)} \rho_{kk}^{(1)} + (\chi_{kk}^{(1)} - \chi_{kk}^{(0)} \chi_{kk}^{(1)} + c.c.) = 2|v_{k}|^2 (b_{k} u_{k}^* v_{k} + b_{k}^* u_{k} v_{k}) + [-v_{k}^* u_{k} (-b_{k} u_{k}^2 + b_{k}^* v_{k}^2) + c.c.]
\]
\[
= b_{k} (|v_{k}|^2 u_{k}^* v_{k} + v_{k}^* u_{k}^2 |u_{k}|^2) + c.c.
\]
\[
= b_{k} u_{k}^* v_{k}^2 + c.c. = \rho_{kk}^{(1)}.
\]
\[
(34)
\]
This proves that the idempotency holds in first order. \qed

Theorem 2. $\Gamma(\lambda)$ is not idempotent at second order.

Proof. Consider the wave function:

$$|\Psi_2(\lambda)\rangle = |\Psi_1(\lambda)\rangle + \lambda^2 \alpha |\text{BCS}\rangle + \cdots,$$

where $\alpha$ is, once again, a parameter stemming from perturbation theory. Notice that

$$\langle\Psi_2(\lambda)|c_k^\dagger c_k|\Psi_2(\lambda)\rangle = \rho_{kk}^{(0)} + \lambda^2 \rho_{kk}^{(1)} + \lambda^2 \rho_{kk}^{(2)} + \lambda^2 \rho_{kk}^{(3)} + \cdots$$

$$+ \lambda^2 \left[ |u_k|^2 f_k^{(1)} + |v_k|^2 f_k^{(2)} + u_k^* v_k^* f_k^{(3)} + |v_k|^2 f_k^{(4)} \right].$$

To alleviate the notation we define the following expectation values:

$$f_k^{(1)} = \langle \Phi | \gamma_{k\alpha k}^\dagger \gamma_{k\alpha k} | \Phi \rangle, \quad f_k^{(2)} = \langle \Phi | \gamma_{k\alpha k}^\dagger \gamma_{k\alpha k}^\dagger | \Phi \rangle, \quad f_k^{(3)} = \langle \Phi | \gamma_{k\alpha k}^\dagger \gamma_{k\alpha k}^\dagger | \Phi \rangle \quad \text{and} \quad f_k^{(4)} = \langle \Phi | \gamma_{k\alpha k}^\dagger \gamma_{k\alpha k} | \Phi \rangle,$$

with $|\Phi\rangle = \sum_{qkk'} d_{qkk'} \gamma_{k+q}^\dagger \gamma_{k}^\dagger |\Phi\rangle$. In the same vein we arrive at

$$\langle\Psi_2(\lambda)|c_k^\dagger c_{-k}|\Psi_2(\lambda)\rangle = \chi_{kk}^{(0)} + \lambda \chi_{kk}^{(1)} + \lambda^2 \chi_{kk}^{(2)} + \lambda^2 \chi_{kk}^{(3)} + \cdots$$

$$+ \lambda^2 \left[ u_k^* v_k f_k^{(1)} - u_k^* f_k^{(3)} + u_k^* f_k^{(2)} - v_k^* u_k f_k^{(4)} \right].$$

Since the wave function (34) is this time non-normalized, normalization has to be imposed. Therefore, to second order we can write the (diagonal) densities as:

$$\rho_{kk}(\lambda) = \rho_{kk}^{(0)} + \lambda \rho_{kk}^{(1)} + \lambda^2 \rho_{kk}^{(2)} + \cdots$$

$$\chi_{kk}(\lambda) = \chi_{kk}^{(0)} + \lambda \chi_{kk}^{(1)} + \lambda^2 \chi_{kk}^{(2)} + \cdots$$

where $A$ is the normalization factor, such that $\langle \Psi_2(\lambda)|\Psi_2(\lambda)\rangle = 1 + \lambda^2 A + O(\lambda^3)$. Thus, $A = \sum_k |b_k|^2 + \sum_{qkk'} |d_{qkk'}|^2 + \alpha + \alpha^*$. Notice now that second-order idempotency would imply:

$$2\rho_{kk}^{(0)} \rho_{kk}^{(2)} + (\rho_{kk}^{(1)})^2 + (\chi_{kk}^{(0)})^2 + (\chi_{kk}^{(1)})^2 + (\chi_{kk}^{(2)})^2 + (\chi_{kk}^{(3)})^2 = 0.$$

Carrying out this calculation leads to the following contradiction:

$$2\rho_{kk}^{(0)} \rho_{kk}^{(2)} + (\rho_{kk}^{(1)})^2 + (\chi_{kk}^{(0)})^2 + (\chi_{kk}^{(1)})^2 + (\chi_{kk}^{(2)})^2 + (\chi_{kk}^{(3)})^2 = 0.$$
In the above discussion we have only computed the effect of one part of the electronic interaction. Indeed, we are
still the repulsion of two electrons with parallel spin in Eq. (25). Yet including such a term does not change our
conclusions. It can be easily seen from the expression for parallel-spin electronic interaction which is given by
\[
\hat{c}^\dagger_{(k+q)\uparrow} \hat{c}^\dagger_{(k'-q)\uparrow} \hat{c}_{k'\uparrow} \hat{c}_{k\uparrow}
\]
\[
(u_{k+q} \hat{\gamma}_{(k+q)0} + v_{k+q} \hat{\gamma}_{(k+q)1})(u_{k'-q} \hat{\gamma}_{(k'-q)0} + v_{k'-q} \hat{\gamma}_{(k'-q)1})(u_k \hat{\gamma}_{k\uparrow} + v_k \hat{\gamma}_{k\uparrow}^\dagger).
\]
For the homogeneous electron gas we have \(q \neq 0\). Therefore,
\[
\langle s | c^\dagger_{(k+q)\uparrow} c^\dagger_{(k'-q)\uparrow} c_{k'\uparrow} c_{k\uparrow} | \text{BCS} \rangle = u_{k+q} u_{k'-q} v_{k'} v_k \langle s | \gamma_{(k+q)0} \gamma_{(k'-q)0} \gamma_{k'\uparrow} \gamma_{k\uparrow}^\dagger | \text{BCS} \rangle.
\]
Hence, this term only contributes to the quadruple excitations in first-order perturbation theory.