

Ab initio theory of superconductivity. I. Density functional formalism and approximate functionals

M. Lüders,^{1,2} M. A. L. Marques,^{2,3} N. N. Lathiotakis,^{2,3} A. Floris,^{3,4} G. Profeta,⁵ L. Fast,^{2,6} A. Continenza,⁵ S. Massidda,^{4,*} and E. K. U. Gross^{2,3}

¹Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

²Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

³Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

⁴INFM SLACS, Sardinian Laboratory for Computational Materials Science and Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari, S. P. Monserrato-Sestu km 0.700, I-09124 Monserrato (Cagliari), Italy

⁵CASTI—Istituto Nazionale Fisica della Materia (INFM) and Dipartimento di Fisica, Università degli studi dell'Aquila, I-67010 Coppito (L'Aquila) Italy

⁶SP Swedish National Testing and Research Institute, P. O. Box 857, S-501 15 Borås, Sweden

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An approach to the description of superconductors in thermal equilibrium is developed within a formally exact density functional framework. The theory is formulated in terms of three “densities:” the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N -body density matrix. The electron density and the order parameter are determined by Kohn-Sham equations that resemble the Bogoliubov–de Gennes equations. The nuclear density matrix follows from a Schrödinger equation with an effective N -body interaction. These equations are coupled to each other via exchange-correlation potentials which are universal functionals of the three densities. Approximations of these exchange-correlation functionals are derived using the diagrammatic techniques of many-body perturbation theory. The bare Coulomb repulsion between the electrons and the electron-phonon interaction enter this perturbative treatment on the same footing. In this way, a truly *ab initio* description is achieved which does not contain any empirical parameters.

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I. INTRODUCTION

One of the great challenges of modern condensed-matter theory is the prediction of material specific properties of superconductors, such as the critical temperature T_c or the gap at zero temperature Δ_0 . The model of Bardeen, Cooper, and Schrieffer¹ (BCS) successfully describes the universal features of superconductors, i.e., those features that all (conventional, weak-coupling) superconductors have in common, like the universal value of the ratio $2\Delta_0/k_B T_c$. The great achievement of BCS theory was the microscopic identification of the superconducting order parameter which led, after more than 50 years of struggling, to a microscopic understanding of the phenomenon of superconductivity.

BCS theory, however, cannot be considered a predictive theory in the sense that it would allow the computation of material-specific properties. Moreover, materials with strong electron-phonon coupling, such as niobium or lead, are poorly described by BCS theory. In these strong-coupling materials, phonon retardation effects play a very important role. A proper treatment of those effects was developed by Eliashberg.^{2,3} His theory can be viewed as a GW approximation⁴ in terms of the Nambu-Gorkov⁵ Green's functions. Eliashberg's theory not only achieves a successful description of the strong-coupling simple metals like Nb and Pb, it also provides a convincing explanation of the superconducting features of more complex materials such as MgB_2 .⁶

In spite of its tremendous success, Eliashberg theory, in its practical implementation, has to be considered a semiphe-

nomenological theory. While the electron-phonon interaction is perfectly accounted for, correlation effects due to the electron-electron Coulomb repulsion are difficult to handle in this theory. Those effects are condensed in a single parameter μ^* , which represents a measure of the effective electronic repulsion. Although μ^* could, in principle, be calculated by diagrammatic techniques,³ first-principles estimates of μ^* are extremely hard to make, and in practice, μ^* is treated as an adjustable parameter, usually chosen such that the experimental T_c is reproduced.

The goal of this work is to develop a true *ab initio* theory for superconductivity which does not contain any adjustable parameters. The crucial point is to treat the electron-phonon interaction and the Coulombic electron-electron repulsion on the same footing. This is achieved within a density functional framework.

Density functional theory⁷⁻⁹ (DFT) enjoys enormous popularity as an electronic-structure method in solid-state physics, quantum chemistry, and materials science. DFT combines good accuracy with moderate numerical effort and is often the method of choice especially for large molecules and solids with a big unit cell. DFT is based on the Hohenberg-Kohn⁷ theorem which ensures a rigorous 1:1 correspondence between the ground-state density and the external potential. At finite temperature, the correspondence holds¹⁰ between the density in thermal equilibrium and the external potential. As a consequence, all physical observables of an interacting electron system become functionals of the density. The practical implementation of DFT rests on the

Kohn-Sham⁸ scheme which maps the interacting system of interest on an auxiliary noninteracting system with the same ground-state thermal density.

Traditional DFT, by its very nature, inevitably involves the Born-Oppenheimer approximation: One is supposed to calculate the electronic ground-state thermal density that corresponds 1:1 to the electrostatic potential of clamped nuclei. To overcome this limitation Kreibich and Gross¹¹ (KG) recently presented a multicomponent DFT which treats both electrons and nuclei quantum mechanically on the same footing. The KG theory involves two “densities:” the electronic density $n(\mathbf{r})$ referring to a body-fixed coordinate frame, and the diagonal $\Gamma(\mathbf{R})$ of the nuclear N -body density matrix. The exchange-correlation functional appearing in the resulting Kohn-Sham equations depends on both “densities” and contains, formally, all nonadiabatic couplings between the electrons and the nuclei.

Hence, in principle, the KG framework should be able to describe (conventional) superconductivity. In practice, however, it is not advisable to attempt such a description. The situation is quite similar to the DFT treatment of magnetic effects: By virtue of the Hohenberg-Kohn theorem, magnetic effects can be described on the basis of the density alone. In particular, the order parameter of spin magnetism, the spin magnetization $\mathbf{m}(\mathbf{r})$, is a functional of the density $m = m[n]$. However, this functional has to be highly non-local and its explicit form is unknown. Therefore, it is advisable to include the order parameter $\mathbf{m}(\mathbf{r})$ as an additional density in the DFT formulation.¹² This version of DFT is known as spin DFT. It is the standard form of DFT that is employed in all practical applications.

A similar idea was suggested in 1988 by Oliveira, Gross, and Kohn¹³ (OGK) to treat superconductors in a DFT framework. OGK proposed the inclusion of the order parameter $\chi(\mathbf{r}, \mathbf{r}')$ that characterizes the superconducting phase as a basic density in the DFT formulation. OGK dealt with singlet order parameters. A generalization to triplet order parameters was given later.¹⁴

The complexities of the many-body problem were cast into an exchange and correlation term, but in contrast to ordinary density functional theory where a variety of functionals has appeared over the past 30 years, very few exchange-correlation functionals have been proposed for the superconducting state. To our knowledge, only a local density approximation describing the purely electronic interactions has been presented.¹⁵ However, the usefulness of the OGK approach was demonstrated by Györfy and co-workers in their study of niobium and $\text{YBa}_2\text{Cu}_3\text{O}_7$ using a semiphenomenological parametrization of the exchange-correlation functional.^{17,18}

The OGK formulation was triggered by the discovery of high- T_c superconductors¹⁹ where an electronic pairing mechanism was believed to be dominant. Hence, the OGK description treats the Coulomb repulsion between electrons formally exactly while the electron-phonon coupling only enters through a given, nonretarded BCS-type electron-electron interaction, i.e., strong electron-phonon coupling cannot be dealt with.

In this work we develop a DFT for superconductors based on the three densities $n(\mathbf{r})$, $\chi(\mathbf{r}, \mathbf{r}')$ and $\Gamma(\mathbf{R})$. The formalism

can thus be viewed as a superconducting generalization of KG theory or as a strong-coupling generalization of OGK formalism. It leads to a set of—formally exact—Kohn-Sham equations for electrons and nuclei. These equations contain exchange-correlation potentials which are universal functionals of the three densities n , χ , and Γ . For the time being, we do not study effects found in the presence of magnetic fields. Those can be accommodated by generalizing the framework to include the current density as an additional variable.^{20,21}

The success of any density functional theory crucially depends on the availability of accurate approximations for the exchange-correlation functionals. The main body of this paper is devoted to the construction of such approximate exchange-correlation functionals. Diagrammatic many-body perturbation theory is used for this purpose. In a second paper (henceforth referred to as II), these approximate functionals are employed to calculate superconducting properties of elemental metals.

The present paper is organized as follows. In Sec. II we derive a multicomponent DFT for the superconducting state. This theory leads to a set of Kohn-Sham equations that are described in the following section. Section IV is devoted to the development of Kohn-Sham perturbation theory. The resulting exchange-correlation potentials are discussed in Sec. V. A simple BCS-like model is described in Sec. VI. This model is used, in Sec. VII, to analyze the approximate exchange-correlation kernels entering the linearized DFT gap equation. Finally, in Sec. VIII, the exchange-correlation contributions to the nonlinear gap equation are discussed.

II. MULTICOMPONENT DFT FOR SUPERCONDUCTORS

It is clear that a balanced treatment of the electron-phonon and Coulomb interactions has to start from the many-body electron-nuclear Hamiltonian (atomic units are used throughout this paper)

$$\hat{H} = \hat{T}^e + \hat{U}^{ee} + \hat{T}^n + \hat{U}^{nn} + \hat{U}^{en}, \quad (1)$$

where \hat{T}^e represents the electronic kinetic energy, \hat{U}^{ee} the electron-electron interaction, \hat{T}^n the nuclear kinetic energy, and \hat{U}^{nn} the Coulomb repulsion between the nuclei. The interaction between the electrons and the nuclei is described by the term

$$\hat{U}^{en} = - \sum_{\sigma} \int d^3r \int d^3R \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Phi}^{\dagger}(\mathbf{R}) \frac{Z}{|\mathbf{r} - \mathbf{R}|} \hat{\Phi}(\mathbf{R}) \hat{\Psi}_{\sigma}(\mathbf{r}), \quad (2)$$

where $\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r})$ and $\hat{\Phi}^{\dagger}(\mathbf{R})$ are, respectively, electron and nuclear creation operators. (For simplicity we assume the nuclei to be identical, and we neglect the nuclear spin degrees of freedom. The extension of this framework to a more general case is straightforward.) Note that there is no external potential in the Hamiltonian.

To develop a multicomponent DFT for the electron-nuclear system we have to proceed with care. The Hamiltonian (1) describes a translationally invariant and isotropic system. Thus, both the electronic and nuclear one-particle

densities are constant and therefore not useful to characterize the system. This problem can be solved by adopting a body-fixed reference frame.^{11,22} In this paper we are interested in infinite solids where the nuclei perform small oscillations around the equilibrium positions. Furthermore, we assume that the solid is not rotating as a whole. Fortunately, in this case, the body-fixed reference frame coincides with the normal Cartesian system commonly used to describe solids. The situation is very different for finite systems, which have to be handled by using appropriate internal coordinates.

In order to formulate a Hohenberg-Kohn type statement, the Hamiltonian (1) is generalized to

$$\hat{H} = \hat{T}^e + \hat{T}^n + \hat{U}^{\text{en}} + \hat{U}^{\text{ee}} + \hat{V}_{\text{ext}}^e + \hat{V}_{\text{ext}}^n + \hat{\Delta}_{\text{ext}} - \mu \hat{N}. \quad (3)$$

The external potential for the electrons is defined as

$$\hat{V}_{\text{ext}}^e = \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) v_{\text{ext}}^e(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}). \quad (4)$$

Since, at this level, the nuclei are taken into account explicitly, the lattice potential is not treated as an external field, but is included via the interaction term \hat{U}^{en} . The term \hat{V}_{ext}^e is introduced as a mathematical trick to prove the Hohenberg-Kohn theorem, and will be taken to zero at the end of the derivation. \hat{V}_{ext}^n is a multiplicative N -body operator with respect to the nuclear coordinates

$$\hat{V}_{\text{ext}}^n = \int d^3\mathbf{R} v_{\text{ext}}^n(\mathbf{R}) \hat{\Gamma}(\mathbf{R}), \quad (5)$$

where we have defined $\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$, $d^3\mathbf{R} = d^3R_1 d^3R_2 \dots d^3R_N$, and

$$\hat{\Gamma}(\mathbf{R}) = \hat{\Phi}^{\dagger}(\mathbf{R}_1) \dots \hat{\Phi}^{\dagger}(\mathbf{R}_N) \hat{\Phi}(\mathbf{R}_N) \dots \hat{\Phi}(\mathbf{R}_1) \quad (6)$$

is the diagonal part of the nuclear N -particle density matrix operator. Note that the term \hat{V}_{ext}^n includes the interaction between the nuclei \hat{U}^{nn} (to which it reduces if no other external nuclear potentials are present). The term

$$\hat{\Delta}_{\text{ext}} = - \int d^3r \int d^3r' \left[\Delta_{\text{ext}}^*(\mathbf{r}, \mathbf{r}') \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') + \text{H.c.} \right] \quad (7)$$

describes an external pairing field, and usually vanishes unless our system is in the proximity of an adjacent superconductor. However, this term is required to break the gauge invariance of the Hamiltonian, and the limit $\Delta_{\text{ext}} \rightarrow 0$ can only be taken at the end of the derivation. Note that the term (7) describes a singlet pairing field. The extension to triplet superconductors is straightforward.¹⁴ Finally, μ stands for the chemical potential, and \hat{N} is the number operator for the electrons (we treat the electronic degrees of freedom in a grand-canonical ensemble).

Our multicomponent formulation is based on three densities.

(i) The electronic density

$$n(\mathbf{r}) = \sum_{\sigma} \langle \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \rangle \quad (8)$$

is defined in the usual way. The bracket $\langle \dots \rangle$ denotes the thermal average $\langle \hat{A} \rangle = \text{Tr}\{\hat{\rho}_0 \hat{A}\}$, with the grand canonical statistical density operator $\hat{\rho}_0 = e^{-\beta \hat{H}} / \text{Tr}\{e^{-\beta \hat{H}}\}$ in the superconducting state. We furthermore define the inverse temperature $\beta = 1/T$.

(ii) The anomalous density

$$\chi(\mathbf{r}, \mathbf{r}') = \langle \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') \rangle \quad (9)$$

is the order parameter characterizing the singlet superconducting state. This quantity is finite for superconductors below the transition temperature and zero above this temperature.

(iii) To describe the nuclear degrees of freedom, we use the diagonal part of the nuclear N -particle density matrix $\Gamma(\mathbf{R}) = \langle \hat{\Gamma}(\mathbf{R}) \rangle$. Alternatively, one could define a multicomponent DFT using the one-particle density for the nuclei $n_n(\mathbf{R}) = \langle \hat{\Phi}^{\dagger}(\mathbf{R}) \hat{\Phi}(\mathbf{R}) \rangle$. However, in the following it will be convenient to transform the nuclear degrees of freedom to collective (phonon) coordinates. Using $n_n(\mathbf{R})$ would lead to a *one-body* equation for noninteracting nuclei. Thus, the nuclear Kohn-Sham equation would not lead to realistic phonons with a proper dispersion relation. Only Einstein phonons could be present in this system. This is also clear from the fact that a system of noninteracting particles does not exhibit collective modes. With our choice of $\Gamma(\mathbf{R})$, the nuclei obey an N -particle equation, very similar to the Born-Oppenheimer equation, and where phonon coordinates can be easily introduced.

As usual, the Hohenberg-Kohn theorem guarantees a one-to-one mapping between the set of the densities $\{n(\mathbf{r}), \chi(\mathbf{r}, \mathbf{r}'), \Gamma(\mathbf{R})\}$ in thermal equilibrium and the set of their conjugate potentials $\{v_{\text{ext}}^e(\mathbf{r}), \Delta_{\text{ext}}(\mathbf{r}, \mathbf{r}'), v_{\text{ext}}^n(\mathbf{R})\}$. As a consequence all observables are functionals of the set of densities. Finally it assures that the grand-canonical potential

$$\begin{aligned} \Omega[n, \chi, \Gamma] = & F[n, \chi, \Gamma] + \int d^3r n(\mathbf{r}) [v_{\text{ext}}^e(\mathbf{r}) - \mu] \\ & - \int d^3r \int d^3r' [\chi(\mathbf{r}, \mathbf{r}') \Delta_{\text{ext}}^*(\mathbf{r}, \mathbf{r}') + \text{H.c.}] \\ & + \int d^3\mathbf{R} \Gamma(\mathbf{R}) v_{\text{ext}}^n(\mathbf{R}) \end{aligned} \quad (10)$$

is minimized by the equilibrium densities. We use the notation $A[f]$ to denote that A is a functional of f . The functional $F[n, \chi, \Gamma]$ is universal, in the sense that it does not depend on the external potentials, and is defined by

$$\begin{aligned} F[n, \chi, \Gamma] = & T^e[n, \chi, \Gamma] + T^n[n, \chi, \Gamma] + U^{\text{en}}[n, \chi, \Gamma] \\ & + U^{\text{ee}}[n, \chi, \Gamma] - \frac{1}{\beta} S[n, \chi, \Gamma], \end{aligned} \quad (11)$$

where S stands for the entropy of the system

$$S[n, \chi, \Gamma] = -\text{Tr}\{\hat{\rho}_0[n, \chi, \Gamma] \ln(\hat{\rho}_0[n, \chi, \Gamma])\}. \quad (12)$$

The proof of the theorem follows closely the proof of the Hohenberg-Kohn theorem at finite temperatures¹⁰ and will not be presented here.

In standard DFT one normally defines a Kohn Sham system, i.e., a noninteracting system chosen such that it has the same ground-state density as the interacting one. In our formulation, the Kohn-Sham system consists of noninteracting (superconducting) electrons, and *interacting* nuclei. It is described by the thermodynamic potential [cf. Eq. (10)]

$$\begin{aligned} \Omega_s[n, \chi, \Gamma] = & F_s[n, \chi, \Gamma] + \int d^3r n(\mathbf{r})[v_s^e(\mathbf{r}) - \mu_s] \\ & - \int d^3r \int d^3r' [\chi(\mathbf{r}, \mathbf{r}') \Delta_s^*(\mathbf{r}, \mathbf{r}') + \text{H.c.}] \\ & + \int d^3R \Gamma(\mathbf{R}) v_s^n(\mathbf{R}), \end{aligned} \quad (13)$$

where F_s is the counterpart of Eq. (11) for the Kohn-Sham system, i.e.,

$$F_s[n, \chi, \Gamma] = T_s^e[n, \chi, \Gamma] + T_s^n[n, \chi, \Gamma] - \frac{1}{\beta} S_s[n, \chi, \Gamma]. \quad (14)$$

Here $T_s^e[n, \chi, \Gamma]$, $T_s^n[n, \chi, \Gamma]$, and $S_s[n, \chi, \Gamma]$ are the electronic and nuclear kinetic energies and the entropy of the Kohn-Sham system, respectively.

From Eq. (13) it is clear that the Kohn-Sham nuclei interact with each other through the N -body potential $v_s^n(\mathbf{R})$ while they do not interact with the electrons.

By applying the Hohenberg-Kohn theorem to both the interacting and the noninteracting systems, and requiring the densities of the Kohn-Sham system to reproduce the densities of the fully interacting one, we can identify the expressions for the effective Kohn-Sham potentials. As usual, these include contributions from external fields, Hartree, and exchange-correlation terms. The latter account for all the many-body effects stemming from the electron-electron and electron-nuclear interactions. To simplify the expressions, we now set the auxiliary external potentials to zero.

The Kohn-Sham potential for the electrons $v_s^e(\mathbf{r})$ reads as

$$\begin{aligned} v_s^e[n, \chi, \Gamma](\mathbf{r}) = & -Z \sum_{\alpha} \int d^3R \frac{\Gamma(\mathbf{R})}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & + v_{xc}^e[n, \chi, \Gamma](\mathbf{r}). \end{aligned} \quad (15)$$

The first term, the electron-nuclear Hartree potential, reduces to the usual nuclear attraction potential if we assume that the nuclei are classical and perfectly localized at their equilibrium positions. This term is usually treated as the external potential in standard DFT. The last two contributions to $v_s^e(\mathbf{r})$ are, respectively, the Hartree potential, which accounts for the classical repulsion between the electrons, and the exchange-correlation term.

The anomalous Kohn-Sham potential Δ_s is given by

$$\Delta_s[n, \chi, \Gamma](\mathbf{r}, \mathbf{r}') = -\frac{\chi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \Delta_{xc}[n, \chi, \Gamma](\mathbf{r}, \mathbf{r}'). \quad (16)$$

Note that the first term, the so-called anomalous Hartree potential, gives rise to a positive contribution to the energy.

Finally, the nuclear potential is

$$\begin{aligned} v_s^n[n, \chi, \Gamma](\mathbf{R}) = & \sum_{\alpha \neq \beta} \frac{Z^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} - Z \sum_{\alpha} \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \\ & + v_{xc}^n[n, \chi, \Gamma](\mathbf{R}). \end{aligned} \quad (17)$$

The first term stems from \hat{U}^{nn} , and describes the bare nuclear-nuclear repulsion. The second is the nuclear-electron Hartree term and is the counterpart of the first term in Eq. (15).

As in standard DFT, the exchange-correlation potentials are defined as functional derivatives,

$$v_{xc}^e[n, \chi, \Gamma](\mathbf{r}) = \frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta n(\mathbf{r})}, \quad (18a)$$

$$\Delta_{xc}[n, \chi, \Gamma](\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta \chi^*(\mathbf{r}, \mathbf{r}')}, \quad (18b)$$

$$v_{xc}^n[n, \chi, \Gamma](\mathbf{R}) = \frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta \Gamma(\mathbf{R})}. \quad (18c)$$

The exchange-correlation free energy is defined through the equation

$$\begin{aligned} F[n, \chi, \Gamma] = & F_s[n, \chi, \Gamma] + F_{xc}[n, \chi, \Gamma] + U^{nn}[\Gamma] \\ & + E_H^{ee}[n, \chi] + E_H^{en}[n, \Gamma]. \end{aligned} \quad (19)$$

There are two contributions to E_H^{ee} , one stemming from the electronic Hartree potential, and the other from the anomalous Hartree potential,

$$\begin{aligned} E_H^{ee}[n, \chi] = & \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & + \int d^3r \int d^3r' \frac{|\chi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (20)$$

Finally, E_H^{en} denotes the electron-nuclear Hartree energy

$$E_H^{en}[n, \Gamma] = -Z \sum_{\alpha} \int d^3r \int d^3R \frac{n(\mathbf{r})\Gamma(\mathbf{R})}{|\mathbf{r} - \mathbf{R}_{\alpha}|}. \quad (21)$$

III. THE KOHN-SHAM EQUATIONS

The problem of minimizing the Kohn-Sham grand canonical potential (13) can be transformed into a set of three differential equations that have to be solved self-consistently. Two of them are coupled and describe the electronic degrees of freedom. Their algebraic structure is similar to the Bogoliubov–de Gennes equations. The third is an equation for the nuclei resembling the familiar nuclear Born-Oppenheimer equation.

A. Electronic equations

The Kohn-Sham Bogoliubov–de Gennes (KS-BdG) equations¹⁶ read

$$\left[-\frac{\nabla^2}{2} + v_s^e(\mathbf{r}) - \mu \right] u_i(\mathbf{r}) + \int d^3r' \Delta_s(\mathbf{r}, \mathbf{r}') v_i(\mathbf{r}') = \tilde{E}_i u_i(\mathbf{r}), \quad (22a)$$

$$-\left[-\frac{\nabla^2}{2} + v_s^e(\mathbf{r}) - \mu \right] v_i(\mathbf{r}) + \int d^3r' \Delta_s^*(\mathbf{r}, \mathbf{r}') u_i(\mathbf{r}') = \tilde{E}_i v_i(\mathbf{r}), \quad (22b)$$

where $u_i(\mathbf{r})$ and $v_i(\mathbf{r})$ are the particle and hole amplitudes. This equation is very similar to the Kohn-Sham equations in the OGK formalism.¹³ However, in our formulation the lattice potential is not considered as an external potential but enters via the electron-ion Hartree term. Furthermore, our exchange-correlation potentials depend parametrically on the nuclear density matrix, and therefore on the phonons.

Although these equations have the structure of static equations, they contain, in principle, all retardation effects through the exchange-correlation potentials.

A direct solution of the Kohn-Sham Bogoliubov–de Gennes equations¹⁷ is faced with the problem that one needs extremely high accuracy to resolve the superconducting energy gap, which is about three orders of magnitude smaller than typical electronic energies. At the same time, one has to cover the whole energy range of the electronic band structure. The so-called decoupling approximation^{23–25} relieves the problem by separating these two energy scales.

The particle and hole amplitudes can be expanded in the complete set of wave functions $\{\varphi_i\}$ of the normal-state Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2} + v_s^e[n, \chi, \Gamma](\mathbf{r}) - \mu \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad (23)$$

which can be solved by standard band-structure methods. The decoupling approximation then implies the following form for the particle and hole amplitudes, where only one term of the expansion is retained:

$$u_i(\mathbf{r}) \approx u_i \varphi_i(\mathbf{r}), \quad v_i(\mathbf{r}) \approx v_i \varphi_i(\mathbf{r}). \quad (24)$$

In this way the eigenvalues in Eq. (22) become $\tilde{E}_i = \pm E_i$, where

$$E_i = \sqrt{\xi_i^2 + |\Delta_i|^2}, \quad (25)$$

and $\xi_i = \epsilon_i - \mu$. This form of the eigenenergies allows the interpretation of the matrix elements of the pair potential as the gap function of the superconductor. The coefficients u_i and v_i also have simple expressions within this approximation,

$$u_i = \frac{1}{\sqrt{2}} \text{sgn}(\tilde{E}_i) e^{i\phi_i} \sqrt{1 + \frac{\xi_i}{\tilde{E}_i}}, \quad (26a)$$

$$v_i = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{\xi_i}{\tilde{E}_i}}. \quad (26b)$$

Finally, the matrix elements Δ_i are defined as

$$\Delta_i = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \Delta_s(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}'), \quad (27)$$

and ϕ_i is the phase $e^{i\phi_i} = \Delta_i / |\Delta_i|$. Within the decoupling approximation, the normal and the anomalous densities can be easily obtained from the particle and hole amplitudes,

$$n(\mathbf{r}) = \sum_i \left[1 - \frac{\xi_i}{E_i} \tanh\left(\frac{\beta E_i}{2}\right) \right] |\varphi_i(\mathbf{r})|^2, \quad (28a)$$

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_i \frac{\Delta_i}{E_i} \tanh\left(\frac{\beta E_i}{2}\right) \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}'). \quad (28b)$$

The validity and limitations of the decoupling approximation will be discussed in detail in II.

B. Nuclear equation

The Kohn-Sham equation for the nuclei has the form

$$\left[-\sum_{\alpha} \frac{\nabla_{\alpha}^2}{2M} + v_s^n(\mathbf{R}) \right] \Phi_I(\mathbf{R}) = \mathcal{E}_I \Phi_I(\mathbf{R}). \quad (29)$$

This equation has the same structure as the usual nuclear Born-Oppenheimer equation. We emphasize that the Kohn-Sham equation (29) does not rely on any approximation and is, in principle, exact. As already mentioned, we are interested in solids at relatively low temperature, where the nuclei perform small-amplitude oscillations around their equilibrium positions. In this case, we can expand the $v_s^n[n, \chi, \Gamma]$ in a Taylor series around the equilibrium positions, and transform the nuclear degrees of freedom into collective (phonon) coordinates. In harmonic order, the nuclear Kohn-Sham Hamiltonian then reads

$$\hat{H}_s^{\text{ph}} = \sum_{\lambda, \mathbf{q}} \Omega_{\lambda, \mathbf{q}} \left[\hat{b}_{\lambda, \mathbf{q}}^{\dagger} \hat{b}_{\lambda, \mathbf{q}} + \frac{1}{2} \right], \quad (30)$$

where $\Omega_{\lambda, \mathbf{q}}$ are the phonon eigenfrequencies, and $\hat{b}_{\lambda, \mathbf{q}}$ destroys a phonon from the branch λ and wave vector \mathbf{q} . Note that the phonon eigenfrequencies are functionals of the set of densities $\{n, \chi, \Gamma\}$, and can therefore be affected by the superconducting order parameter. Within the harmonic approximation, the nuclear density matrix $\Gamma(\mathbf{R})$ is given by

$$\Gamma(\mathbf{R}) = \sum_{\lambda, \mathbf{q}} n_{\beta}(\Omega_{\lambda, \mathbf{q}}) |h_{\lambda, \mathbf{q}}(\mathbf{Q})|^2, \quad (31)$$

where $n_{\beta}(\Omega)$ denote the Bose occupation numbers and $h_{\lambda, \mathbf{q}}(\mathbf{Q})$ are harmonic oscillator wave functions referring to the collective coordinates \mathbf{Q} .

C. Gap equation

In Fig. 1 we sketch the Kohn-Sham self-consistent procedure within the decoupling approximation. We start by find-

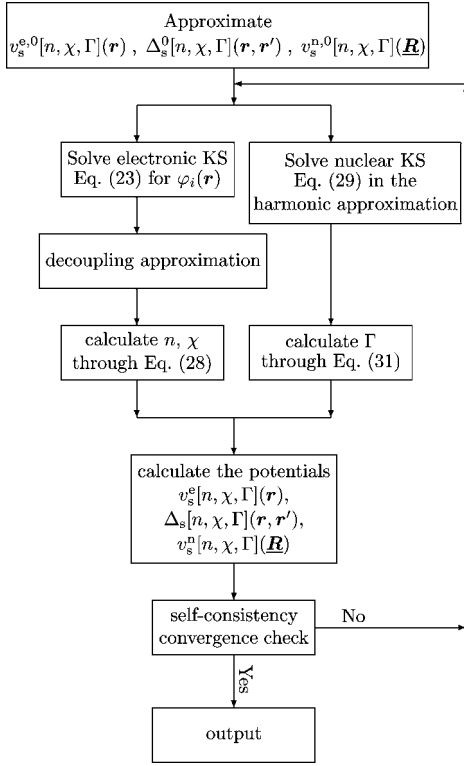


FIG. 1. Schematic flow chart for the iterative Kohn-Sham scheme within the decoupling approximation.

ing suitable approximations for the Kohn-Sham potentials to start the cycle: for $v_s^{e,0}[n, \chi, \Gamma]$ we can use the Kohn-Sham potential stemming from a standard DFT calculation for the nonsuperconducting ground state, i.e., $v_s^{\text{GS}}[n]$. This is a very good approximation as the dependence of $v_s^e[n, \chi, \Gamma]$ on χ and Γ is certainly very weak for the usual superconductors at low temperature; the starting pair potential $\Delta_s^0[n, \chi, \Gamma]$ can be approximated by a square well centered at the Fermi energy with width of the order of the Debye frequency and height computed from a BCS model; finally, for $v_s^{n,0}[n, \chi, \Gamma]$ we can use the ground-state Born-Oppenheimer potential. The next two steps of the self-consistent cycle can be performed in parallel.

(1) Equation (23) is solved to obtain the wave functions φ_i 's and the eigenenergies ϵ_i 's. These can then be used within the decoupling approximation, Eq. (24), to calculate the normal and anomalous densities through Eqs. (28). We note that the chemical potential μ entering Eq. (23) has to be adjusted at every iteration, such that the density $n(\mathbf{r})$ integrates to the correct particle number N .

(2) With $v_s^n[n, \chi, \Gamma]$ we solve the nuclear equation (29) by expanding the nuclear potential to harmonic order to obtain the phonon eigenfrequencies and eigenmodes. The nuclear density matrix Γ then follows from Eq. (31).

Finally, the set of densities $\{n, \chi, \Gamma\}$ is used to evaluate the new Kohn-Sham potentials $\{v_s^e, \Delta_s, v_s^n\}$ from the definitions (15),(16),(17). At this point, if self-consistency is reached, the cycle is stopped. Otherwise, the new potentials are used to restart the cycle.

It is clear that, even within the decoupling approximation, the task of solving the self-consistent cycle depicted in Fig. 1

is rather demanding. Furthermore, we are required to provide (good) approximations for the three functionals $v_s^e[n, \chi, \Gamma]$, $\Delta_s[n, \chi, \Gamma]$, and $v_s^n[n, \chi, \Gamma]$. As our objective is to study superconductivity, we will make two simplifying assumptions. (i) $v_s^e[n, \chi, \Gamma]$ can be well approximated by the ground-state functional used in standard density functional theory $v_s^{\text{GS}}[n]$. As the energy scale of the phonons and of the superconducting gap is three orders of magnitude smaller than electronic energy scales (like the Fermi energy) this is a very reasonable assumption. (ii) The nuclear functional $v_s^n[n, \chi, \Gamma]$ is approximated by the ground-state Born-Oppenheimer energy surface. It is well known that calculations performed within the Born-Oppenheimer approximation yield phonon frequencies that are in excellent agreement with experimental dispersions.²⁶ We therefore expect this to be an excellent approximation to the Kohn-Sham phonons. However, we are neglecting the effect of the superconducting pair potential on the phonon dispersion. This effect has been measured experimentally,²⁷ and it turns out to be quite small. Note that these two approximations are equivalent to fixing $v_s^e[n, \chi, \Gamma]$ and $v_s^n[n, \chi, \Gamma]$ to $v_s^{e,0}[n, \chi, \Gamma]$ and $v_s^{n,0}[n, \chi, \Gamma]$.

By inserting Eqs. (28) in Eq. (16) and by subsequently inserting Eq. (16) on the right-hand side of Eq. (27), we obtain the DFT gap equation

$$\Delta_i = \Delta_{\text{Hxc } i}[\mu, \Delta_i], \quad (32)$$

where Δ_{Hxc} stands for the sum of the Hartree and exchange-correlation contributions to the functional. Note that through the exchange-correlation functional the right-hand side of Eq. (32) becomes a highly complicated functional of μ and Δ_i . The dependence on the gap function is totally different from the usual mean-field gap equation (cf. Sec. VIII).

After these simplifying approximations, a Kohn-Sham calculation proceeds as follows. (i) Using a standard band-structure code, the ground-state wave functions and band structure are obtained. (ii) The Born-Oppenheimer phonon frequencies and eigenmodes are obtained from linear-response²⁶ calculations, again using standard tools widely available to the community. (iii) The gap equation (32) is iterated until self-consistency is achieved. We can now see how the different energy scales are separated: The normal density, the anomalous density, and the phonon properties are obtained from three separate equations.

In the vicinity of the transition temperature, the anomalous density will be vanishingly small. In this regime, the gap equation can be linearized in χ , leading to

$$\check{\Delta}_i = -\frac{1}{2} \sum_j \mathcal{F}_{\text{Hxc } i,j}[\mu] \frac{\tanh[(\beta/2)\xi_j]}{\xi_j} \check{\Delta}_j, \quad (33)$$

where the anomalous Hartree exchange-correlation kernel of the homogeneous integral equation reads

$$\mathcal{F}_{\text{Hxc } i,j}[\mu] = - \left. \frac{\delta \Delta_{\text{Hxc } i}}{\delta \chi_j} \right|_{\chi=0} = \left. \frac{\delta^2 (E_{\text{H}}^{\text{cc}} + F_{\text{xc}})}{\delta \chi_i^* \delta \chi_j} \right|_{\chi=0}. \quad (34)$$

We emphasize that the linearized gap equation can only be used to calculate the superconducting transition temperature.

In particular, the function $\check{\Delta}_i$ that stems from the solution of this equation does not have any physical interpretation.

We can gain further insight into Eq. (33) if we separate the kernel $\mathcal{F}_{\text{Hxc } i,j}$ into a purely diagonal term \mathcal{Z}_i and a non-diagonal part $\mathcal{K}_{i,j}$

$$\check{\Delta}_i = -\mathcal{Z}_i[\mu]\check{\Delta}_i - \frac{1}{2} \sum_j \mathcal{K}_{i,j}[\mu] \frac{\tanh[(\beta/2)\xi_j]}{\xi_j} \check{\Delta}_j. \quad (35)$$

This equation has the same structure as the BCS gap equation with the kernel $\mathcal{K}_{i,j}$ replacing the model interaction of BCS theory. On the other hand, \mathcal{Z}_i plays a similar role as the renormalization term in the Eliashberg equations. This similarity allows one to interpret the kernel $\mathcal{K}_{i,j}$ as an effective interaction responsible for the binding of the Cooper pairs. The function $\mathcal{K}_{i,j}$ is a quantity of central importance in the density functional theory for superconductors. By studying $\mathcal{K}_{i,j}$ for a specific material as a function of i and j one can learn which orbitals are responsible for superconductivity and, ultimately, by identifying those parts of the exchange-correlation functional (phononic and/or Coulombic) that lead to an effective attraction, one can trace the mechanism responsible for the superconducting state.

Note that Eq. (35) is considerably simpler than the Eliashberg equations as it does not depend explicitly on the frequency. However, phonon retardation effects are included through the exchange-correlation terms. Furthermore, Eq. (35) is not a mean-field equation as in BCS theory but contains correlation effects. A linearized gap equation can also be derived without the decoupling approximation,^{25,28} leading to a similar equation, but with a four-point kernel. From this point of view, the decoupling approximation can be viewed as a diagonal approximation to this four-point kernel, neglecting the corresponding off-diagonal elements.

IV. KOHN-SHAM PERTURBATION THEORY

In the previous sections we showed how to develop a density functional theory for the superconducting state. The main equation of this theory, the gap equation (32), allows, in principle, the calculation of the superconducting gap for any system. However, to solve this equation one needs approximations for Δ_{xc} , the exchange-correlation contribution to the Kohn-Sham pair potential. In the following, we will develop such approximations by applying Kohn-Sham perturbation theory, as described by Görling and Levy,²⁹ to superconducting systems.^{25,30} This perturbation theory, that will treat both the electron-electron and electron-phonon interactions on the same footing, is a generalization of the method used by Kurth *et al.* to calculate the exchange-correlation energy of the uniform superconducting electron gas.¹⁵

Our starting point is the Hamiltonian of the electron-nuclear system as defined in Eq. (3). This Hamiltonian is then split into a suitably chosen reference Hamiltonian \hat{H}_0 and the remainder, which is treated as a perturbation. The most appropriate reference system for this formalism is as follows. (i) The nuclear Kohn-Sham Hamiltonian (29) rigorously defines the nuclear equilibrium positions \mathbf{R}_0 . When

expanded to harmonic order around these positions it can be written as the phonon Hamiltonian \hat{H}^{ph} (30). (ii) Next we define a Born-Oppenheimer Kohn-Sham Hamiltonian via a rigid-lattice potential given by the equilibrium coordinates \mathbf{R}_0 ,

$$\hat{H}_{\text{BO}}^e = \hat{T}^e + \hat{V}_{\text{latt},\mathbf{R}_0}^e + \hat{V}_{\text{Hxc}}^e + \hat{\Delta}_{\text{Hxc}}, \quad (36)$$

where

$$\hat{V}_{\text{Hxc}}^e = \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \left[\int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}^e(\mathbf{r}) \right], \quad (37)$$

while $\hat{\Delta}_{\text{Hxc}}$ includes the anomalous Hartree and exchange-correlation contributions

$$\hat{\Delta}_{\text{Hxc}} = - \int d^3r \int d^3r' \left\{ \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') \times \left[\frac{\chi^*(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \Delta_{\text{xc}}^*(\mathbf{r},\mathbf{r}') \right] + \text{H.c.} \right\}. \quad (38)$$

With the choice $\hat{H}_0 = \hat{H}^{\text{ph}} + \hat{H}_{\text{BO}}^e$, the interaction Hamiltonian reads

$$\hat{H}_1 = \hat{U}^{\text{ee}} + \hat{U}_{\text{BO}}^{\text{e-ph}} - \hat{V}_{\text{Hxc}}^{\text{n}} - \hat{V}_{\text{Hxc}}^e - \hat{\Delta}_{\text{Hxc}}. \quad (39)$$

The Born-Oppenheimer electron-phonon coupling operator $\hat{U}_{\text{BO}}^{\text{e-ph}}$ is given by

$$\hat{U}_{\text{BO}}^{\text{e-ph}} = \sum_{\sigma} \sum_{\lambda,q} \int d^3r V_{\lambda,q}^{\text{BO}}(\mathbf{r}) \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \hat{\Phi}_{\lambda,q}, \quad (40)$$

where $V_{\lambda,q}^{\text{BO}}(\mathbf{r})$ is basically the gradient of the electronic Kohn-Sham potential with respect to the nuclear coordinates and the phononic field operator is $\hat{\Phi}_{\lambda,q} = \hat{b}_{\lambda,q} + \hat{b}_{\lambda,-q}^{\dagger}$. Note that now we have set the auxiliary external potentials \hat{V}_{ext}^e and $\hat{\Delta}_{\text{ext}}$ to zero, and $\hat{V}_{\text{ext}}^{\text{n}}$ to the bare internuclear interaction.

We believe that this is the most physical way to split the Hamiltonian, since the electronic-structure calculation for $n(\mathbf{r})$, in practice, is usually performed for fixed nuclear positions; the nuclear dynamics is absorbed in the exchange correlation functionals. Furthermore, standard calculations for the electron-phonon coupling, which are based on linear response theory, involve the above coupling potentials $V_{\lambda,q}^{\text{BO}}(\mathbf{r})$. Note that, besides the interaction terms \hat{U}^{ee} and $\hat{U}_{\text{BO}}^{\text{e-ph}}$, the perturbation includes the Hartree and exchange-correlation potentials. In the Appendix we give some more details of this construction.

We now develop a many-body perturbational approach, which will ultimately lead to explicit expressions for the exchange-correlation functionals. The construction of this approach follows closely the standard many-body perturbation theory described in many textbooks.³¹ Our objective is to expand the difference $\Delta\Omega = \Omega - \Omega_s$ in a power series. From this difference and with the definitions (10) and (13) it is straightforward to derive an expression for the functional F_{xc} .

In standard perturbation theory $\Delta\Omega$ is written as an expansion in powers of e^2 and g^2 , where e (the electron charge) and g (the electron-phonon coupling constant) measure, respectively, the strength of the Coulomb and of the electron-phonon interactions. In our approach, however, every order in perturbation theory contains *all* orders in e^2 and g^2 . This is due to the special form of the perturbation \hat{H}_1 that involves the exchange-correlation potentials which contain implicitly all orders in the interactions. Therefore, for book-keeping purposes, we multiply the perturbation \hat{H}_1 by a dimensionless parameter Λ . In this way, the terms appearing in the perturbative expansion can be labeled by powers of Λ .

The grand-canonical potential Ω can be written as

$$\Omega = -\frac{1}{\beta} \ln(Z), \quad (41)$$

where the partition function has the definition $Z = \text{Tr}\{\exp(-\beta\hat{H})\}$. From this expression it follows directly that

$$\Omega - \Omega_s = -\frac{1}{\beta} \ln\left(\frac{Z}{Z_s}\right), \quad (42)$$

where Z_s is the partition function of the Kohn-Sham system. It is then straightforward, using the standard machinery of many-body perturbation theory, to write the ratio Z/Z_s as a series expansion in Λ which can be evaluated with the help of Wick's theorem. Moreover, the number of terms in the series can be reduced by using a generalization of the linked-cluster theorem.³² The final result reads

$$\Omega - \Omega_s = -\frac{1}{\beta} \sum (\text{all connected diagrams}). \quad (43)$$

In this expression the sum runs over all connected Feynman diagrams that are topologically distinct. (Alternatively, one can expand diagrammatically the propagators and use the Galitskii-Migdal formula to evaluate the energy.³³ The two approaches are equivalent.)

There are several Kohn-Sham propagators that enter the Feynman diagrams. First we have the contraction that reduces to the usual Green's function for systems that are not superconducting

$$G_{\sigma\sigma'}^s(\mathbf{r}\tau, \mathbf{r}'\tau') = -\langle \hat{T} \hat{\psi}_\sigma(\mathbf{r}\tau) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}'\tau') \rangle_s, \quad (44)$$

where \hat{T} is the time-ordering operator, which orders the operators from right to left in ascending imaginary time order, and the average $\langle \cdots \rangle_s$ is done with respect to the Kohn-Sham statistical density operator $\hat{\rho}_s$. This Green's function is represented in the Feynman diagrams by a line with two arrows pointing in the same direction. Furthermore, due to the presence of pairing fields in the Kohn-Sham system (13), the following (anomalous) averages are nonvanishing for superconducting systems:

$$F_{\sigma\sigma'}^s(\mathbf{r}\tau, \mathbf{r}'\tau') = -\langle \hat{T} \hat{\psi}_\sigma(\mathbf{r}\tau) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}'\tau') \rangle_s, \quad (45a)$$

$$F_{\sigma\sigma'}^{s\dagger}(\mathbf{r}\tau, \mathbf{r}'\tau') = -\langle \hat{T} \hat{\psi}_\sigma^\dagger(\mathbf{r}\tau) \hat{\psi}_{\sigma'}(\mathbf{r}'\tau') \rangle_s. \quad (45b)$$

In Feynman diagrams these propagators appear as lines with two arrows pointing outward (for F^s) and as lines with two arrows pointing inward (for $F^{s\dagger}$). [The Green's function (44) and the anomalous averages (45) can be conveniently assembled into a matrix Green's function in Nambu-Gorkov space.⁵] Finally, as the perturbation includes the electron-phonon interaction term $\hat{H}_{\text{e-ph}}$, some diagrams contain the phonon propagator (represented as a curly line)

$$D_{\lambda,q}^s(\tau, \tau') = \langle \hat{T} \hat{\Phi}_{\lambda,q}(\tau) \hat{\Phi}_{\lambda,q}^\dagger(\tau') \rangle_s. \quad (46)$$

As usual in finite-temperature many-body theory, it is convenient to work in imaginary frequency space. The time Fourier transform of the Green's function (45) is defined as

$$G_{\sigma\sigma'}^s(\mathbf{r}\tau, \mathbf{r}'\tau') = \frac{1}{\beta} \sum_{\omega_n} e^{-i\omega_n(\tau-\tau')} G_{\sigma\sigma'}^s(\mathbf{r}, \mathbf{r}'; \omega_n), \quad (47)$$

where $\omega_n = (2n+1)\pi/\beta$ are the odd Matsubara frequencies. The frequency-dependent anomalous propagators have a similar definition. In Matsubara space the Kohn-Sham propagators read, in terms of the Kohn-Sham particle and hole amplitudes and of the Kohn-Sham eigenenergies,

$$G_{\sigma,\sigma'}^s(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma,\sigma'} \sum_i \left[\frac{u_i(\mathbf{r})u_i^*(\mathbf{r}')}{i\omega_n - E_i} + \frac{v_i(\mathbf{r})v_i^*(\mathbf{r}')}{i\omega_n + E_i} \right], \quad (48a)$$

$$F_{\sigma,\sigma'}^s(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma,-\sigma'} \text{sgn}(\sigma') \times \sum_i \left[\frac{v_i^*(\mathbf{r})u_i(\mathbf{r}')}{i\omega_n + E_i} - \frac{u_i(\mathbf{r})v_i^*(\mathbf{r}')}{i\omega_n - E_i} \right], \quad (48b)$$

$$F_{\sigma,\sigma'}^{s\dagger}(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma,-\sigma'} \text{sgn}(\sigma) \times \sum_i \left[\frac{u_i^*(\mathbf{r})v_i(\mathbf{r}')}{i\omega_n + E_i} - \frac{v_i(\mathbf{r})u_i^*(\mathbf{r}')}{i\omega_n - E_i} \right]. \quad (48c)$$

On the other hand, the phonon propagator depends on the even Matsubara frequencies $\nu_n = 2n\pi/\beta$,

$$D_{\lambda,q}^s(\nu_n) = -\frac{2\Omega_{\lambda,q}}{\nu_n^2 + \Omega_{\lambda,q}^2}. \quad (49)$$

In first order in Λ there is only one diagram contributing to F_{xc} . This diagram, depicted in Fig. 2(a), is of purely electronic origin and has the same form as the standard exchange diagram. [The wavy line in Fig. 2(a) represents the Coulomb interaction.] This term can be written as (for simplicity we write all contributions to F_{xc} within the decoupling approximation)

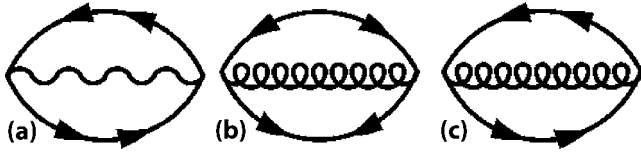


FIG. 2. Lowest-order electronic (a) and phononic (b), (c) contributions to F_{xc} .

$$F_{xc}^{(a)} = -\frac{1}{4} \sum_{ij} v_{ij} \left[1 - \frac{\xi_i}{E_i} \tanh\left(\frac{\beta}{2} E_i\right) \right] \left[1 - \frac{\xi_j}{E_j} \tanh\left(\frac{\beta}{2} E_j\right) \right], \quad (50)$$

where the matrix elements of the Coulomb interaction are defined as

$$v_{ij} = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}'). \quad (51)$$

As the expectation value $\langle \Phi_{\lambda,q} \rangle = 0$, the electron-phonon interaction does not contribute to F_{xc} in first-order perturbation theory in Λ . The first nonvanishing terms appear in second order in Λ (first order in g^2) and are depicted in Figs. 2(b) and 2(c). The first of these terms [Fig. 2(b)] is the counterpart of the anomalous term that contributes to the electronic Hartree energy (20). Its analytic form can be written as

$$F_{xc}^{(b)} = \frac{1}{2} \sum_{\lambda,q} \sum_{ij} |g_{\lambda,q}^{ij}|^2 \frac{\Delta_i \Delta_j^*}{E_i E_j} \left[I(E_i, E_j, \Omega_{\lambda,q}) - I(E_i, -E_j, \Omega_{\lambda,q}) \right], \quad (52)$$

where we defined the matrix elements of the electron-phonon coupling constant

$$g_{\lambda,q}^{ij} = \int d^3r \varphi_i^*(\mathbf{r}) V_{\lambda,q}^{\text{BO}}(\mathbf{r}) \varphi_j(\mathbf{r}), \quad (53)$$

while the function I is

$$I(E, E', \Omega) = \frac{1}{\beta^2} \sum_{\omega_1 \omega_2} \frac{1}{i\omega_1 - E} \frac{1}{i\omega_2 - E'} \frac{-2\Omega}{(\omega_1 - \omega_2)^2 + \Omega^2}. \quad (54)$$

The three fractions in the sum come from the denominators of the two Green's functions G^S and from the phonon propagator D^S . It is possible to perform the frequency sums using standard complex contour integration methods. The final result is

$$I(E_i, E_j, \Omega) = f_\beta(E_i) f_\beta(E_j) n_\beta(\Omega) \times \left[\frac{e^{\beta E_i} - e^{\beta(E_j + \Omega)}}{E_i - E_j - \Omega} - \frac{e^{\beta E_j} - e^{\beta(E_i + \Omega)}}{E_i - E_j + \Omega} \right]. \quad (55)$$

A diagram analogous to the one depicted in Fig. 2(b) but with the phonon propagator replaced by the bare Coulomb interaction exists as well. This diagram is the anomalous Hartree term which appears as the second term on the right-hand side of Eq. (20). Since this term is treated explicitly in the electronic Kohn-Sham equations it is not part of the exchange-correlation functional.

Note that expression (52) is so much more complicated than the anomalous Hartree term simply because the phonon propagator describes a *retarded* interaction. If we assumed a retarded electronic interaction instead of the instantaneous Coulomb potential $1/|\mathbf{r} - \mathbf{r}'|$ the anomalous Hartree contribution would look very similar to (52).

The second phononic term that contributes to F_{xc} is depicted in Fig. 2(c). This Feynman diagram has the same structure as the electronic exchange term [Fig. 2(a)]. However, and again due to retardation effects, its analytic structure is more complicated than Eq. (50), namely,

$$F_{xc}^{(c)} = -\frac{1}{2} \sum_{\lambda,q} \sum_{ij} |g_{\lambda,q}^{ij}|^2 \left[\left(1 + \frac{\xi_i \xi_j}{E_i E_j} \right) I(E_i, E_j, \Omega_{\lambda,q}) + \left(1 - \frac{\xi_i \xi_j}{E_i E_j} \right) I(E_i, -E_j, \Omega_{\lambda,q}) \right]. \quad (56)$$

The self-energy diagrams contributing to $F_{xc}^{(b)}$ and $F_{xc}^{(c)}$ resemble the self-energy diagrams that appear in Eliashberg theory.^{2,3} By virtue of Migdal's theorem,³⁴ vertex corrections should be small and are therefore neglected, both in Eliashberg theory and in our treatment. There is, however, an important difference: in Eliashberg theory the propagators that enter the self-energy diagrams are *dressed* propagators, while in our case we have *bare* (Kohn-Sham) propagators. By using the bare propagators we neglect more diagrams than those containing vertex corrections. We postpone a more detailed discussion of this problem to the section on the exchange-correlation kernels.

V. FUNCTIONAL DERIVATIVES AND THE CHAIN RULE

We have seen in Eq. (18b) how the anomalous exchange-correlation potential is defined as the functional derivative of the exchange-correlation free-energy functional with respect to the anomalous density χ . However, the contributions to the exchange-correlation free-energy functional that stem from Kohn-Sham perturbation theory are only known as explicit functionals of the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$, the Kohn-Sham single-particle energies $(\epsilon_i - \mu)$, and the pair potential Δ_i . Of course, the Hohenberg-Kohn theorem tells us that these quantities are themselves functionals of the densities, so the free energy is an *implicit* functional of the densities. Furthermore, if one makes the additional approximation that v_{xc}^e does not depend on χ then the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ and the eigenenergies ϵ_i are also independent of the anomalous density. F_{xc} is then a function of the chemical potential μ and a functional of the (complex) pair potential Δ_i

$$F_{xc} = F_{xc}[\mu, |\Delta_i|^2, \phi_i]. \quad (57)$$

For convenience, instead of working with Δ_i and Δ_i^* , we prefer using the modulus squared of the pair potential and its phase as independent variables. The anomalous exchange-correlation potential can thus be evaluated using the chain rule for functional derivatives

$$\Delta_{xc} = - \frac{\delta F_{xc}}{\delta \mu} \frac{\delta \mu}{\delta \chi_i^*} - \sum_j \left[\frac{\delta F_{xc}}{\delta |\Delta_j|^2} \frac{\delta |\Delta_j|^2}{\delta \chi_i^*} + \frac{\delta F_{xc}}{\delta (\phi_j)} \frac{\delta (\phi_j)}{\delta \chi_i^*} \right]. \quad (58)$$

The partial derivatives of F_{xc} can now be calculated directly. The remaining functional derivatives are somehow harder to obtain, but can be derived from the definitions of the densities, Eqs. (28), and from the fact that the particle density and the anomalous density are independent variables. This latter condition can be expressed through the relation

$$\frac{\delta n(\mathbf{x})}{\delta \chi^*(\mathbf{r}, \mathbf{r}')} = 0. \quad (59)$$

Moreover, we make use of the two trivial conditions

$$\frac{\delta \chi_i^*}{\delta \chi_j} = \delta_{i,j}, \quad \frac{\delta \chi_i}{\delta \chi_j^*} = 0. \quad (60)$$

From the above conditions, and after some algebra, we arrive at the expressions for the remaining functional derivatives,

$$\frac{\delta |\Delta_j|^2}{\delta \chi_i^*} = \frac{2}{Y_j^0} \left[E_j^2 \Delta_j \delta_{i,j} - Y_j^1 |\Delta_j|^2 \frac{\delta \mu}{\delta \chi_i^*} \right], \quad (61a)$$

$$\frac{\delta (\phi_j)}{\delta \chi_i^*} = i \delta_{i,j} \frac{E_i}{\Delta_i \tanh[(\beta/2)E_i]}, \quad (61b)$$

$$\frac{\delta \mu}{\delta \chi_i^*} = - Z_i^1 / \sum_j Z_j^0. \quad (61c)$$

The functions Z_i^0 and Z_i^1 have the definitions

$$Z_i^0 = \frac{E_i (\beta/2) \tanh[(\beta/2)E_i]}{Y_i^0 \cosh^2[(\beta/2)E_i]}, \quad Z_i^1 = \frac{Y_i^1}{Y_i^0} \Delta_i, \quad (62)$$

and, finally, the two functions Y_i^0 and Y_i^1 read

$$Y_i^0 = \frac{\xi_i^2}{E_i} \tanh\left(\frac{\beta}{2} E_i\right) + \frac{(\beta/2) |\Delta_i|^2}{\cosh^2[(\beta/2)E_i]}, \quad (63a)$$

$$Y_i^1 = \frac{\xi_i}{E_i} \tanh\left(\frac{\beta}{2} E_i\right) - \frac{(\beta/2) \xi_i}{\cosh^2[(\beta/2)E_i]}. \quad (63b)$$

There exists another method to obtain exchange-correlation functionals using Kohn-Sham perturbation theory *without* resorting to functional derivatives. This method follows the ideas of Sham and Schlüter,³⁵ and provides a very direct connection between many-body perturbation theory and the normal and anomalous exchange-correlation functionals. In the following we will give a brief account of the Sham-Schlüter method for superconductors.

There is a simple connection between the electron density $n(\mathbf{r})$ and the interacting many-body Green's function

$$n(\mathbf{r}) = \lim_{\eta \rightarrow 0^+} \frac{1}{\beta} \sum_{\omega_n} \sum_{\sigma} e^{i\eta\omega_n} G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}; \omega_n). \quad (64)$$

The definition of the interacting Green's function is similar to Eq. (44), but with the thermal average weighted by the

interacting statistical operator $\hat{\rho}_0$. The infinitesimal η is used to ensure the correct ordering of the field operators in Eq. (44) so that Eq. (64) is satisfied. In the same way it is simple to prove that the anomalous density obeys the relation

$$\chi(\mathbf{r}, \mathbf{r}') = - \lim_{\eta \rightarrow 0^+} \frac{1}{\beta} \sum_{\omega_n} e^{i\eta\omega_n} F_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}'; -\omega_n), \quad (65)$$

where F is the interacting anomalous propagator. On the other hand, we defined the Kohn-Sham system as the *noninteracting* system whose both normal and anomalous densities are equal to the densities of the *interacting* system. Therefore, one can equally calculate the interacting densities from the Kohn-Sham Green's functions

$$n(\mathbf{r}) = \lim_{\eta \rightarrow 0^+} \frac{1}{\beta} \sum_{\omega_n} \sum_{\sigma} e^{i\eta\omega_n} G_{\sigma\sigma}^s(\mathbf{r}, \mathbf{r}; \omega_n), \quad (66)$$

with an equation similar to Eq. (65) relating χ and F^s . We then expand perturbatively the interacting Green's functions in Eqs. (64) and (65), and equate the two equations for $n(\mathbf{r})$, and the two equations for $\chi(\mathbf{r}, \mathbf{r}')$. As the perturbation (39) includes the terms \hat{V}_{xc}^e and $\hat{\Delta}_{xc}$, the resulting equations form a system of two coupled integral equations that allow the determination of v_{xc}^e and Δ_{xc} . Those integral equations are the so-called Sham-Schlüter equations.

The two methods to obtain the exchange-correlation potentials are conceptually quite different. The first uses the definitions (18) to derive the exchange-correlation potentials using a series of chain rules. The Sham-Schlüter approach is closer to many-body perturbation theory, and provides a natural relationship between the Green's function and the exchange-correlation potentials of DFT. However, both approaches lead to the same result if the free energy in the first method is expanded up to the same order in perturbation theory as the Green's functions in the second method.

VI. A SIMPLE BCS-LIKE MODEL

We now introduce a simple model that will allow us to study in detail the functionals developed in this article. For simplicity, we assume that the pair potential has *s*-wave symmetry and behaves approximately like $\Delta_i = \Delta(\xi_i)$. This assumption is satisfied by all traditional superconductors. In this model, we can transform the gap equation into a one-dimensional equation in energy space

$$\Delta(\xi) = - \mathcal{Z}(\xi) \Delta(\xi) - \frac{1}{2} \int_{-\mu}^{\infty} d\xi' N(\xi') \mathcal{K}(\xi, \xi') \times \frac{\tanh[(\beta/2)\xi']}{\xi'} \Delta(\xi'), \quad (67)$$

where $N(\xi)$ is the density of states at the energy ξ . It is possible to further simplify this equation by assuming a BCS-like model for both \mathcal{K} and \mathcal{Z} . If we assume that the kernel \mathcal{K} and the renormalization term \mathcal{Z} are constant in a shell of width ω_c around the Fermi energy and zero outside this region, Eq. (67) can be solved analytically for the transition temperature T_c .

$$T_c \propto \exp\left[\frac{1 + \mathcal{Z}(0)}{N(0)\mathcal{K}(0)}\right], \quad (68)$$

where $\mathcal{K}(0)$ and $\mathcal{Z}(0)$ are the values of $\mathcal{K}(\xi, \xi')$ and $\mathcal{Z}(\xi)$ at the Fermi surface. Equation (68) has exactly the same structure as McMillan's formula,^{36,37} which is an approximate solution of the Eliashberg equations. This latter formula reads

$$T_c = \frac{\Omega_{\text{in}}}{1.20} \exp\left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right]. \quad (69)$$

The number μ^* , the Coulomb pseudopotential of Eliashberg theory, measures the strength of the electron-electron interaction. This parameter is quite hard to calculate and is often fitted to experimental data. As μ^* is normally positive, it tends to decrease the superconducting transition temperature. On the other hand, λ is a measure of the electron-phonon coupling strength

$$\lambda = 2 \int d\Omega \frac{\alpha^2 F(\Omega)}{\Omega}. \quad (70)$$

The behavior of T_c with λ is very nonlinear. For small values of λ , T_c grows exponentially; However, as λ increases, the superconducting transition temperature saturates. The parameter Ω_{in} is a weighted average of the phonon frequencies

$$\Omega_{\text{in}} = \exp\left[\frac{2}{\lambda} \int d\Omega \ln(\Omega) \frac{\alpha^2 F(\Omega)}{\Omega}\right] \quad (71)$$

and is of the order of the Debye frequency of the material. Finally, the Eliashberg spectral function is the electron-phonon coupling constant averaged on the Fermi surface,

$$\alpha^2 F(\Omega) = \frac{1}{N(0)} \sum_{ij} \sum_{\lambda, q} |g_{\lambda, q}^{ij}| \delta(\xi_i) \delta(\xi_j) \delta(\Omega - \Omega_{\lambda, q}). \quad (72)$$

It is widely accepted that McMillan's formula gives a quite accurate description of the transition temperature for simple, BCS-like, superconductors. Therefore, by comparing expressions (68) and (69) for the phonon-only case, i.e., $\mu^* = 0$, we obtain that for BCS-like superconductors

$$N(0)\mathcal{K}(0) \approx -\lambda, \quad \mathcal{Z}(0) \approx \lambda. \quad (73)$$

This is an extremely important property of the exchange-correlation kernel, which should be satisfied by any approximate functional.

VII. APPROXIMATIONS TO THE ANOMALOUS HARTREE EXCHANGE-CORRELATION KERNEL

From the perturbative expansion of the exchange-correlation free energy it is clear that we can split the free energy into three parts. The first contains the purely electronic terms, i.e., the terms that do not contain explicitly the electron-phonon coupling constant; the second, terms only involving the electron-phonon coupling constant; and the last, which we define as the total free energy minus the two first parts, will have mixed contributions from the Coulomb and electron-phonon interactions. The exchange-correlation

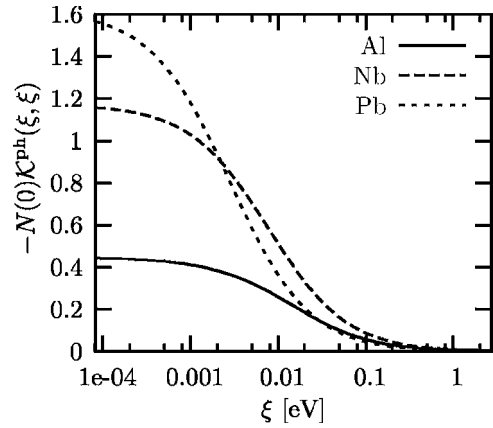


FIG. 3. The function $-N(0)\mathcal{K}^{\text{ph}}(\xi, \xi)$ for Al, Nb, and Pb, calculated at $T=0$ K.

potentials and the exchange-correlation kernels can be split in the same way.

In this section we develop exchange-correlation kernels to be used in the linearized gap equation (35). Functionals that can be used in the nonlinear gap equation (32) are discussed later. This section is divided into two parts. First we look at the purely electron-phonon contributions to the exchange-correlation kernel. Such functionals are developed using the machinery of Kohn-Sham perturbation theory together with the chain rule introduced earlier. In the second part, we turn our attention to the purely electronic part of the kernel. Two functionals will be presented: the first has the form of a local density approximation (LDA), while the second is a functional that avoids the direct computation of the screened Coulomb matrix elements. The mixed contributions appearing in the perturbational expansion of the free energy are neglected in the current treatment.

A. Electron-phonon contributions

In first order in g^2 there are two terms stemming from the electron-phonon interaction that contribute to the exchange-correlation free energy: $F_{\text{xc}}^{(b)}$ given by Eq. (52), and $F_{\text{xc}}^{(c)}$ given by Eq. (56). The exchange-correlation kernel derived from $F_{\text{xc}}^{(b)}$ is nondiagonal and has the form

$$\mathcal{K}_{ij}^{\text{ph}} = \frac{2}{\tanh[(\beta/2)\xi_i]\tanh[(\beta/2)\xi_j]} \sum_{\lambda, q} |g_{\lambda, q}^{ij}|^2 \times [I(\xi_i, \xi_j, \Omega_{\lambda, q}) - I(\xi_i - \xi_j, \Omega_{\lambda, q})]. \quad (74)$$

To gain further insight into this term, we use a simplified model: we approximate the electron-phonon coupling constants by their average value at the Fermi surface and the electronic energy dispersion is replaced by the free-electron model. In Fig. 3 we depict the diagonal $\mathcal{K}^{\text{ph}}(\xi, \xi)$ for aluminum, niobium, and lead at zero temperature for this simplified model. As this contribution to the exchange-correlation kernel exhibits particle-hole symmetry we only plot the region $\xi > 0$. This term is sharply peaked at the Fermi energy (note the logarithmic scale on the ξ axis). Furthermore, the width of the curves for each material is of the order of the

corresponding Debye frequency. The value of the kernel at the Fermi energy can be calculated analytically,

$$N(0)\mathcal{K}^{\text{ph}}(0,0) = - \int d\Omega \alpha^2 F(\Omega) \times \frac{2}{\Omega} \left[1 - \frac{4}{\beta\Omega} \coth\left(\frac{\beta\Omega}{2}\right) + \frac{8}{(\beta\Omega)^2} \right]. \quad (75)$$

At zero temperature, the value of $N(0)\mathcal{K}^{\text{ph}}(0,0)$ reduces to $-\lambda$, which is the value expected from the comparison to McMillan's formula [cf. Eq. (73)]. However, at higher temperature $N(0)\mathcal{K}^{\text{ph}}(0,0)$ decreases monotonically.

The second phononic contribution to the exchange-correlation kernel coming from the Kohn-Sham perturbation theory (PT) originates from the diagram $F_{xc}^{(c)}$. It is a diagonal term, which reads

$$\begin{aligned} \mathcal{Z}_i^{\text{ph,PT}} = & - \frac{2}{\sum_j (\beta/2) / \cosh^2[(\beta/2)\xi_j]} \\ & \times \left[\frac{1}{\xi_i} - \frac{\beta/2}{\sinh[(\beta/2)\xi_i] \cosh[(\beta/2)\xi_i]} \right] \\ & \times \sum_{jl} \sum_{\lambda,q} |g_{\lambda,q}^{jl}|^2 I'(\xi_j, \xi_i, \Omega_{\lambda,q}) \\ & + \frac{1}{\tanh[(\beta/2)\xi_i]} \sum_j \sum_{\lambda,q} |g_{\lambda,q}^{ij}|^2 \left\{ \frac{1}{\xi_i} [I(\xi_i, \xi_j, \Omega_{\lambda,q}) \right. \\ & \left. - I(\xi_i, -\xi_j, \Omega_{\lambda,q})] - 2I'(\xi_i, \xi_j, \Omega_{\lambda,q}) \right\}, \quad (76) \end{aligned}$$

where the function I' is defined as

$$I'(\xi_i, \xi_j, \Omega_{\lambda,q}) = \frac{\partial}{\partial \xi_i} I(\xi_i, \xi_j, \Omega_{\lambda,q}). \quad (77)$$

If we try to apply the simplified model presented earlier we find that $\mathcal{Z}_i^{\text{ph,PT}}$ diverges logarithmically. This divergence can be traced back to the substitution of $g_{\lambda,q}^{ij}$ by its value at the Fermi surface. This problem can be solved by retaining the full dependence of the electron-phonon coupling constant on the indices i and j : $g_{\lambda,q}^{ij}$ then decays as a function of energy thereby making the integrals present in Eq. (76) convergent. A closer analysis of the expressions also reveals that the divergent part of the integrands is antisymmetric around the Fermi surface. Therefore, the divergent integrals would vanish in the case of particle-hole symmetry. It seems then reasonable to neglect the antisymmetric part of the integrands, retaining only the symmetric part. The new functional reads

$$\begin{aligned} \mathcal{Z}_i^{\text{ph,sym}} = & \frac{1}{\tanh[(\beta/2)\xi_i]} \sum_j \sum_{\lambda,q} |g_{\lambda,q}^{ij}|^2 \\ & \times [I'(\xi_i, \xi_j, \Omega) + I'(\xi_i, -\xi_j, \Omega)]. \quad (78) \end{aligned}$$

In Fig. 4 this term is plotted for niobium for several temperatures. It turns out that the function $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ is a smooth function of the energy, and its value at the Fermi surface

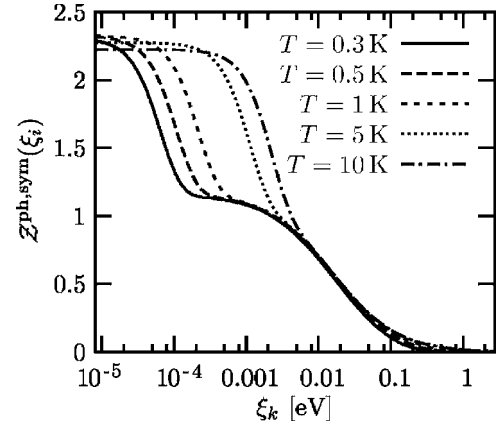


FIG. 4. The dependence of $\mathcal{Z}_i^{\text{ph,sym}}$ on temperature for niobium.

($\xi_k=0$) is approximately 2λ . This is twice the value expected from the comparison to McMillan's formula [cf. Eq. (73)]. Furthermore, a careful analysis of Fig. 4 suggests that $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ can be written as the sum of two terms: (i) one broader and very weakly temperature dependent; (ii) a second contribution whose width decreases significantly with the temperature. Both terms contribute with approximately λ to the value of $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ at the Fermi surface. As the renormalization term $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ appears to be too large, one can expect that transition temperatures calculated with this functional will be too small. The situation should be worst for the strong-coupling superconductors like niobium or lead, where the renormalization is large. This is confirmed by Table I where we list the transition temperatures obtained with the phononic part of the functional. These numbers are compared to solutions of Eliashberg's equation where we neglected the electron-electron repulsion.

We believe that the shortcomings of this functional can be traced back to the following: Migdal's theorem tells us that, to a very good approximation, we can neglect in the perturbative expansion diagrams including vertex corrections due to the electron-phonon interaction. However, diagrams including self-energy insertions of phononic origin should be included to have a consistent description of the electron-phonon interaction. Therefore the bare Green's functions entering in the diagrams depicted in Figs. 2(b) and 2(c) should be replaced by dressed propagators. In a first step to improve our functionals we dressed the propagators with a subset of phonon self-energy insertions. We found that the nondiagonal term \mathcal{K}^{ph} is basically insensitive, while the term $\mathcal{Z}_i^{\text{ph,sym}}$ is reduced by roughly 20%. This is almost half the correction necessary to satisfy Eq. (73). We expect that the other 30% is accounted for by the remaining self-energy insertions. However, this approach is quite involved numerically, so we choose a different path to improve our functional.

We know that the phonon renormalization term should have the value λ at the Fermi surface. Furthermore, this term should have a width comparable to the Debye frequency. It is clear that the broader contribution to $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ obeys these requirements. We therefore propose to separate the two parts of $\mathcal{Z}_i^{\text{ph,sym}}(\xi_i)$ and use the part (i) as our renormalization term.

TABLE I. Transition temperatures from numerical solutions of the phonon-only DFT and Eliashberg equations. All temperatures are in kelvin.

	Al	Nb	Mo	Ta	V	Pb
$\mathcal{K}^{\text{ph}} + \mathcal{Z}^{\text{ph,sym}}$	5.59	15.7	4.14	8.48	23.2	8.12
$\mathcal{K}^{\text{ph}} + \mathcal{Z}^{\text{ph}}$	7.10	23.0	5.23	11.7	34.2	12.8
Eliashberg	9.75	24.7	7.31	14.0	36.4	12.2

We believe that this procedure is at least partially justified by the results obtained by dressing the Green's functions. The functional corrected in this way reads

$$\mathcal{Z}_i^{\text{ph}} = \frac{1}{\tanh[(\beta/2)\xi_i]} \sum_j \sum_{\lambda,q} |g_{\lambda,q}^{ij}|^2 [J(\xi_i, \xi_j, \Omega_{\lambda,q}) + J(\xi_i, -\xi_j, \Omega_{\lambda,q})], \quad (79)$$

where the function J is defined by

$$J(\xi, \xi', \Omega) = \tilde{J}(\xi, \xi', \Omega) - \tilde{J}(\xi, \xi', -\Omega). \quad (80)$$

Finally we have

$$\tilde{J}(\xi, \xi', \Omega) = -\frac{f_{\beta}(\xi) + n_{\beta}(\Omega)}{\xi - \xi' - \Omega} \left[\frac{f_{\beta}(\xi') - f_{\beta}(\xi - \Omega)}{\xi - \xi' - \Omega} - \beta f_{\beta}(\xi - \Omega) f_{\beta}(-\xi' + \Omega) \right]. \quad (81)$$

The functional \mathcal{Z}^{ph} is smooth both as a function of the energy and as a function of the temperature. Furthermore, it has approximately the value λ at the Fermi surface. The functional (79), together with the phononic kernel (74), is a central result of our work. It is the functional that will be used in the calculations of II. In Table I, we present the phonon-only transition temperatures calculated with this functional. All T_c 's are in quite good agreement with transition temperatures calculated from Eliashberg's equation. We emphasize that the transition temperatures in Table I are given exclusively for the purpose of testing and/or calibrating the approximations made for the phononic part of the exchange-correlation functional. T_c 's resulting from setting $\mu^* = 0$ in the Eliashberg equations and setting the Coulomb terms to zero in the DFT context have, of course, nothing to do with the T_c 's observed in nature. For results including the Coulomb terms, we refer the reader to II.

B. Electron-electron contributions

We now develop functionals that take into account the Coulombic part of the interaction. There are two terms in the energy functional that give contributions to the linearized gap equation (35). The first is the anomalous contribution to the Hartree energy, given by Eq. (20), and the second is the

exchange term F_{xc}^a depicted in Fig. 2(a). The interaction that enters these expressions is the bare Coulomb interaction $1/|\mathbf{r}-\mathbf{r}'|$. However, electrons in a metal do not feel the bare Coulomb interaction, but a much weaker interaction, screened by the sea of electrons. To take this into account, we take a step back, and propose an alternative form to the energy functional based on the superconducting version of the local density approximation.¹⁵ In this approach the exchange-correlation energy of the inhomogeneous system is written in terms of the exchange-correlation energy density of the homogeneous superconducting electron gas,

$$F_{xc}^{\text{SCLDA}}[n(\mathbf{R}), \chi(\mathbf{R}, \mathbf{k})] = \int d^3R f_{xc}^{\text{hom}}[n, \chi(\mathbf{k})] \Big|_{\chi=\chi_W(\mathbf{R}, \mathbf{k})}^{n=n(\mathbf{R})}, \quad (82)$$

where $\chi_W(\mathbf{R}, \mathbf{k})$ is the Wigner transform of the anomalous density of the inhomogeneous system, given by

$$\chi_W(\mathbf{R}, \mathbf{k}) = \int d^3s e^{i\mathbf{k}\cdot\mathbf{s}} \chi\left(\mathbf{R} + \frac{\mathbf{s}}{2}, \mathbf{R} - \frac{\mathbf{s}}{2}\right). \quad (83)$$

It is easy to see that this definition reduces to the usual LDA for nonsuperconducting systems in the limit $\chi \rightarrow 0$. Moreover, it is possible to prove that this is the only consistent definition of a LDA for the superconducting state.³⁸ As an approximation to the exchange-correlation energy of the electron-gas one could take the random-phase approximation functional proposed in Ref. 15. However, this functional has only been evaluated for a very simple class of pair potentials, namely, Gaussians centered at the Fermi surface. We therefore propose an alternative and simpler form to the Coulombic contribution to F_{xc} . For convenience, we approximate *together* the anomalous Hartree and the exchange-correlation contributions. Our approximation reads

$$f_{\text{Hxc}}^{\text{hom}}[\chi](n) - f_{xc}^{\text{hom,NS}}(n) = \int d^3(r-r') |\chi(\mathbf{r}-\mathbf{r}')|^2 v^{\text{TF}}(\mathbf{r}-\mathbf{r}'), \quad (84)$$

where $v^{\text{TF}}(\mathbf{r}-\mathbf{r}')$ is the Coulomb interaction screened by a Thomas-Fermi model. In coordinate space the Thomas-Fermi interaction reads

$$v^{\text{TF}}(\mathbf{r}-\mathbf{r}') = \frac{e^{-k_{\text{TF}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}, \quad (85)$$

with the Thomas-Fermi screening length k_{TF} given by

$$k_{\text{TF}}^2 = 4\pi N(0). \quad (86)$$

By inserting expression (84) in the definition of the LDA, Eq. (82), we can identify this approximation as a *Thomas-Fermi screened anomalous Hartree* contribution to the free energy.

The anomalous Hartree exchange-correlation kernel stemming from this term is simply

$$\mathcal{K}_{ij}^{\text{TF}} = v_{ij}^{\text{TF}}, \quad (87)$$

where the matrix elements of the Thomas-Fermi interaction are defined by

$$v_{ij}^{\text{TF}} = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}') v^{\text{TF}}(\mathbf{r} - \mathbf{r}') \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \quad (88)$$

where the φ_i 's are the Kohn-Sham orbitals of the inhomogeneous system at hand.

In II we will compare the results obtained with the above approximation with further simplified expressions. In the simplest model, the Kohn-Sham orbitals are taken to be plane waves with a parabolic dispersion. In this case, the kernel can be written in energy space (after averaging over the angles) as

$$\mathcal{K}_{\text{TF}}(\xi, \xi') = \frac{\pi}{kk'} \ln \left[\frac{(k+k')^2 + k_{\text{TF}}^2}{(k-k')^2 + k_{\text{TF}}^2} \right], \quad (89)$$

with $k = \sqrt{2(\xi - \mu)}$ and $k' = \sqrt{2(\xi' - \mu)}$. Using the BCS-like two-well model one can extract the counterpart of the Coulomb pseudopotential μ^* from Eliashberg theory. A crude estimate for $r_s=2$ gives a value around 0.1, which compares well with the typical values of μ^* for simple metals ($\mu^* = 0.10-0.15$).³⁷ It should be stressed again at this point that the present method does not require μ^* . The estimates given here are used to demonstrate to which values of μ^* our *ab initio* Coulomb terms correspond.

While the replacement of the Kohn-Sham orbitals in Eq. (88) by plane waves may be acceptable for simple metals, it will be too crude for more complex materials. In those cases it is still possible to avoid the direct computation of the screened Coulomb matrix elements (88), by going along the lines described by Sham and Kohn.³⁹ We briefly outline here the main points of this classical paper, which deals with an approximate way of getting an electron self-energy for the normal state. We assume, as usual within the LDA, that our system can be described around the point \mathbf{r} by a homogeneous electron gas of density $n(\mathbf{r})$. The wave functions of this electron gas can be locally expressed as plane waves of momentum $\mathbf{p}(\mathbf{r})$ whose value is determined, in a semiclassi-

cal way, from the electron energy of the real system. In the simplest form, the mapping can be obtained from Eqs. (4.5) and (4.13) of Ref. 39 as

$$\frac{p^2}{2} = \xi_i + \mu_h(n(\mathbf{r})), \quad (90)$$

where $\mu_h(n)$ is the chemical potential of a noninteracting homogeneous electron gas with density n . Furthermore, we approximate $\mu_h(n(\mathbf{r}))$ by the constant $\mu_h(n)$, where n is the average density of the material. We suggest here to approximate the Coulomb interaction kernel between electrons at energies $\varepsilon_{\mathbf{k}}$ and $\varepsilon_{\mathbf{k}'}$ by the corresponding quantities in the free-electron gas. We then replace $p^2/2 \rightarrow \xi_i + \mu_h = \eta_i$, and rewrite the interaction (89) as

$$\mathcal{K}_{ij}^{\text{SK}} = \frac{\pi}{2\sqrt{\eta_i \eta_j}} \ln \left(\frac{\eta_i + \eta_j + 2\sqrt{\eta_i \eta_j + k_{\text{TF}}^2/2}}{\eta_i + \eta_j - 2\sqrt{\eta_i \eta_j + k_{\text{TF}}^2/2}} \right). \quad (91)$$

In principle, one could consider not only p but also k_{TF} as locally dependent on the density $n(\mathbf{r})$. In our simplified approach, however, we fix the Thomas-Fermi screening length to a constant value.

Equation (90) is conceived in terms of wave packets, and is valid if $n(\mathbf{r})$ does not vary too much on the scale of the Fermi length, exactly as in the normal state LDA. One can speculate, however, that when applied to the superconducting state the relevant length scale becomes the coherence length, normally much larger than the atomic scale. Therefore, we may assume that local variations of the density on the atomic scale will not affect the final superconducting properties.

It should be noted that this approximation, although derived in the spirit of a LDA, is not a local density approximation, since it does not depend explicitly on the densities, but *implicitly* via the single-particle energies ξ_i .

VIII. FUNCTIONALS FOR THE NONLINEAR GAP EQUATION

In this section we provide approximations to the exchange-correlation kernel that can be used in the nonlinear gap equation (32). These functionals will obey one constraint, namely, that upon linearization they will reduce to the functionals presented in the previous section. This assures that the gap functions obtained from Eq. (32) and the transition temperatures calculated from Eq. (32) are consistent. Furthermore, we require these functionals to be “well behaved,” i.e., without discontinuities or any other kind of pathological behaviors.

The simplest way to derive an exchange-correlation functional is to use the expressions derived through Kohn-Sham perturbation theory in the definition (18b). For example, the first phononic contribution $F_{\text{xc}}^{(b)}$ [Fig. 2(b)] yields the contribution

$$\begin{aligned} \Delta_{xc\ i}^{\text{ph.(b)}} = & \frac{1}{2} \sum_j \frac{Z_j^1}{Z_j^0} \sum_{jl} \sum_{\lambda,q} |g_{\lambda,q}^{jl}|^2 \frac{\Delta_j \Delta_l^* + \Delta_j^* \Delta_l}{E_j^2 E_l} \left\{ \frac{\xi_j}{E_j} \left[1 - \frac{Y_j^1}{Y_j^0} \xi_j \right] [I(E_j, E_l, \Omega_{\lambda,q}) - I(E_j, -E_l, \Omega_{\lambda,q})] \right. \\ & - \left. \left[\xi_j + \frac{Y_j^1}{Y_j^0} |\Delta_j|^2 \right] [I'(E_j, E_l, \Omega_{\lambda,q}) - I'(E_j, -E_l, \Omega_{\lambda,q})] \right\} \\ & - \frac{1}{2} \sum_j \sum_{\lambda,q} \frac{\Delta_j}{Y_j^0 E_j} |g_{\lambda,q}^{jj}|^2 \left\{ \left[\frac{(\beta/2)(\Delta_j \Delta_j^* - \Delta_j^* \Delta_j)}{\tanh[(\beta/2)E_j] \cosh^2[(\beta/2)E_j]} + 2 \frac{\Delta_j \xi_j^2}{\Delta_j E_j} \right] [I(E_j, E_j, \Omega_{\lambda,q}) - I(E_j, -E_j, \Omega_{\lambda,q})] \right. \\ & \left. + (\Delta_j \Delta_j^* + \Delta_j^* \Delta_j) [I'(E_j, E_j, \Omega_{\lambda,q}) - I'(E_j, -E_j, \Omega_{\lambda,q})] \right\}. \end{aligned} \quad (92)$$

It can be seen here that the nonlinear gap equation (32), in general, does not have the simple structure of a BCS-like gap equation and thus goes beyond the simple picture of an effective interaction mediating the pairing. However, this approach encompasses several problems. First, the resulting functionals have extremely complicated analytical structures and are very hard to interpret in simple physical terms. Furthermore, these functionals contain several divergences and pathological behaviors that have to be taken care of. For the time being, we restrict ourselves to using the *partially linearized* exchange-correlation potential, leading to the BCS-type gap equation

$$\Delta_i = - \frac{1}{2} \sum_j \mathcal{F}_{\text{Hxc } i,j} \frac{\tanh[(\beta/2)E_j]}{E_j} \Delta_j, \quad (93)$$

where $\mathcal{F}_{\text{Hxc } i,j}$ are the linearized functionals defined in Eq. (34) and derived in detail in the previous section. It turns out that superconducting gap functions obtained with these functionals are in rather good agreement with experimental results (see II).

IX. CONCLUSIONS

In this work we have developed a truly *ab initio* approach to superconductivity. No adjustable parameters appear in the theory. The key feature is that the electron-phonon interaction and the Coulombic electron-electron repulsion are treated on the same footing. This is achieved within a density-functional-type framework. Three densities, the ordinary electronic density, the superconducting order parameter, and the diagonal of the nuclear N -body density matrix, were identified as suitable quantities to formulate the density functional framework. The formalism leads to a set of Kohn-Sham equations for the electrons and the nuclei. The electronic Kohn-Sham equations have the structure of Bogoliubov–de Gennes equations but, in contrast to the latter, they incorporate normal and anomalous xc potentials. Likewise, the Kohn-Sham equation describing the nuclear motion contains, besides the bare nuclear Coulomb repulsion, an exchange-correlation interaction. The latter is an N -body interaction, i.e., the nuclear Kohn-Sham equation is an N -body Schrödinger equation. The exchange-correlation

potentials are functional derivatives of a universal functional $F_{\text{xc}}[n, \chi, \Gamma]$ which represents the exchange-correlation part of the free energy. Approximations for this functional were then derived by many-body perturbation theory. To this end, the effective nuclear interaction was expanded to second order in the displacements from the nuclear equilibrium positions. By introducing the usual collective (phonon) coordinates, the nuclear Kohn-Sham equation is then transformed into a set of harmonic oscillator equations describing independent phonons. These noninteracting phonons, together with noninteracting but superconducting (Kohn-Sham) electrons, serve as the unperturbed system for a Görling-Levy-type perturbative expansion of F_{xc} . The electron-phonon interaction and the bare electronic Coulomb repulsion, as well as some residual exchange-correlation potentials, are treated as the perturbation. In this way, both Coulombic and electron-phonon couplings are fully incorporated. The solution of the KS Bogoliubov–de Gennes equation (or the KS gap equation together with the normal-state Schrödinger equation) fully determines the Kohn-Sham system. Therefore, within the usual approximation to calculate observables from the Kohn-Sham system, one can apply the full variety of expressions for physical quantities, known from phenomenological Bogoliubov–de Gennes theory, also in the present framework. This approach was already successfully applied within a semiphenomenological parametrization of the exchange-correlation functional, e.g., to the specific heat¹⁸ and to the penetration depth⁴⁰ of the cuprates. It should further be emphasized that the formalism, developed in this paper, is not restricted to perfect periodic systems. It was for this purpose that we presented all formulas in terms of general quantum numbers. The formalism can, in principle, be applied as well to inhomogeneous systems, containing, e.g., impurities or surfaces, as to perfect periodic crystals.

In the succeeding paper (II) we will detail the numerical implementation of this theory and present the first full-scale applications to simple metals.

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APPENDIX: ON THE ELECTRON-PHONON COUPLING

In this appendix we discuss the electron-phonon coupling potential which appears in the phononic exchange-correlation terms. If we decomposed the Hamiltonian into the ionic Kohn-Sham Hamiltonian and the electronic Kohn-Sham Hamiltonian as the reference system and the rest as perturbation, this perturbation would include the bare electron-ion interaction. Clearly, the use of the bare vertex, i.e., the gradient of the bare nuclear potential with respect to the nuclear positions, would yield an unphysical electron-phonon interaction. This bare vertex will be screened by the conduction electrons. This screening could be taken care of by a diagrammatical resummation.²²

Here we will sketch a different approach which directly generates the screened coupling potential. A natural coupling potential in the context of DFT is the gradient with respect to the nuclear positions of the effective Kohn-Sham potential within the Born-Oppenheimer approximation. This is also exactly the quantity that is obtained from the standard DFT electron-phonon calculations based on linear response theory with respect to small lattice distortions.

$$\begin{aligned} \nabla_{\mathbf{R}} v_{s,\mathbf{R}}(\mathbf{r}) &= \nabla_{\mathbf{R}} v_{\mathbf{R}}^{\text{latt}}(\mathbf{r}) \\ &+ \int d^3 r' \int d^3 r'' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \mathcal{X}(\mathbf{r}', \mathbf{r}'') [\nabla_{\mathbf{R}} v_{\mathbf{R}}^{\text{latt}}(\mathbf{r}'')]. \end{aligned} \quad (\text{A1})$$

$\mathcal{X}(\mathbf{r}, \mathbf{r}')$ denotes the linear density-density response function and

$$f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta}{\delta n(\mathbf{r}')} \{v_{\text{H}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r})\}. \quad (\text{A2})$$

We are going to outline an approach that generates exactly this gradient of the effective Kohn-Sham potential as the coupling potential. The effective Kohn-Sham Hamiltonian (29) for the nuclei gives rise to a set of equilibrium coordinates and phonon eigenstates. It can then (up to harmonic order) be written as Eq. (30). The equilibrium positions \mathbf{R}_0

can be employed to define an electronic Born-Oppenheimer (BO) Hamiltonian with a lattice potential referring to these coordinates

$$\hat{H}^{\text{BO}} = \hat{T}^e + \hat{U}^{\text{ee}} + \hat{V}_{\mathbf{R}_0}^{\text{latt}}. \quad (\text{A3})$$

This BO Hamiltonian, without the electron-phonon coupling, gives rise to the electronic density $n_{\mathbf{R}_0}$. We now add and subtract all Hartree and exchange-correlation terms as well as the BO lattice potential to the full Hamiltonian,

$$\begin{aligned} \hat{H} &= (\hat{T}^n + \hat{U}^{\text{mn}} + \hat{V}_{\text{Hxc}}^n) + (\hat{T}^e + \hat{V}_{\mathbf{R}_0}^{\text{latt}} + \hat{V}_{\text{Hxc}}^e + \hat{\Delta}_{\text{Hxc}}^e) + \hat{U}^{\text{ee}} \\ &+ (\hat{U}^{\text{en}} - \hat{V}_{\mathbf{R}_0}^{\text{latt}}) - \hat{V}_{\text{Hxc}}^n - \hat{V}_{\text{Hxc}}^e - \hat{\Delta}_{\text{Hxc}}^e. \end{aligned} \quad (\text{A4})$$

The first three terms of this operator represent the nuclear Kohn-Sham Hamiltonian. Assuming that the equilibrium density $n(\mathbf{r})$ entering the functional $v_{\text{Hxc}}^e[n](\mathbf{r})$ will be close to the equilibrium density $n_{\mathbf{R}_0}(\mathbf{r})$ resulting from the BO Hamiltonian (A3) we can expand the Hartree exchange-correlation potential around the BO density,

$$v_{\text{Hxc}}^e[n](\mathbf{r}) = v_{\text{Hxc}}^e[n_{\mathbf{R}_0}](\mathbf{r}) + \int d^3 r' f_{\text{Hxc}}[n_{\mathbf{R}_0}](\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}'), \quad (\text{A5})$$

where the small density change $\delta n(\mathbf{r})$ is induced by the difference of the full electron-ion interaction and the BO potential. The density change can, in principle, be calculated via linear response to that perturbation. We expect this density change to be close to

$$\delta n(\mathbf{r}') = \int d^3 r'' \chi(\mathbf{r}', \mathbf{r}'') [\nabla_{\mathbf{R}} v_{\mathbf{R}}^{\text{latt}}(\mathbf{r}'')]. \quad (\text{A6})$$

If we keep only the BO part of the electronic Hartree exchange-correlation potential, i.e., the term stemming from $n_{\mathbf{R}_0}(\mathbf{r})$, in the electronic Kohn-Sham Hamiltonian, we can combine the remainder with the electron-ion interaction, and can identify (up to first order)

$$\begin{aligned} \sum_i \frac{Z}{|\mathbf{r} - \mathbf{R}_i|} - \sum_i \frac{Z}{|\mathbf{r} - \mathbf{R}_{0,i}|} + \int d^3 r' f_{\text{Hxc}}[n_{\mathbf{R}_0}](\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') \\ \approx \nabla_{\mathbf{R}} v_{s,\text{BO}}(\mathbf{r}). \end{aligned} \quad (\text{A7})$$

This is the desired result, which allowed us to use the electron-phonon couplings, determined by linear response calculations, as the coupling potentials in our Kohn-Sham perturbation theory.

*Also at LAMIA-INFM, Genova, Italy.

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