

Calculating the Critical Temperature of Superconductors from First Principles

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Abstract. We present a novel approach to the theory of superconductivity based on a formally exact density functional formulation. Within this framework, we perform first-principles calculations of the critical temperatures of conventional superconductors with strong and weak electron-phonon coupling.

Within the theory of Bardeen, Cooper and Schrieffer (BCS) [1], some quantities, such as the ratio $\Delta_0/2k_B T_c$ or the temperature dependence of the critical magnetic field, are remarkably well reproduced. However, the so-called strong-coupling superconductors like Nb or Pb are not properly described. In these systems retardation effects play a very important role, and must be included in any realistic description of the superconducting phase. This was achieved by Eliashberg in 1960 [2], using a generalization of Migdal's treatment of the electron-phonon interaction [3]. Eliashberg's theory allows accurate predictions of material dependent quantities of strong-coupling superconductors [4], but its formulation has a weakness: The Coulomb interaction between the electrons is effectively replaced by a single number, μ^* . This quantity is quite hard to calculate from first-principles, so it is usually treated as a material-dependent adjustable parameter chosen, for example, to reproduce the experimental transition temperatures. Even if other quantities can then be calculated without further approximations, and found to be close to their experimental values, the whole procedure is, in fact, semi-phenomenological. Furthermore, in other systems where a more detailed description of the Coulomb interaction is necessary, Eliashberg theory yields sometimes unphysical answers: For example, in the extreme case of the uniform electron-gas, treating the Coulomb interaction at the level of an RPA, the gas is predicted to be superconducting at unreasonable densities [5].

In 1986, Bednorz and Müller found superconductivity in an oxide material. Their discovery of the high- T_c compounds revitalised research in the field of superconductivity, and raised many fundamental (and yet unanswered) questions. Although a consensus has not been reached, it is reasonable to assume that, in these mate-

rials, both strong-coupling electron-phonon and electron-electron interactions play an important role. Other superconducting systems recently discovered, like the heavy-fermions and the organic superconductors, also exhibit a wealth of phenomena that cannot easily be accommodated within the standard theory. Therefore, a new treatment of the superconducting phase appears highly desirable.

Shortly after the discovery of the high- T_c materials, Oliveira, Gross and Kohn [6] proposed a density functional theory (DFT) for the superconducting state. Their theory was an extension of the very successful normal-state DFT [7], and aimed at a unified treatment of correlation and inhomogeneity effects in superconductors. In the original article, only the Coulomb part of the interaction was handled at an exact level, while the electron-phonon term was approximated by an effective electron-electron interaction, like the ones studied by BCS [1], or by Bardeen and Pines [8]. Such a description, although sufficient for weak-coupling or electronically driven superconductors, does not incorporate retardation effects, and is therefore inadequate to study strong-coupling systems. In this communication we present an approach that incorporates exactly both electronic and phononic correlations. It starts from the full Hamiltonian describing the complete system of electrons and ions.

Traditional DFT is based on two statements: The Hohenberg-Kohn theorem [9] establishes a one-to-one correspondence between the external potential and the electronic density; and the Kohn-Sham construction [10], which uses an auxiliary non-interacting system to obtain the density of the interacting system. In our treatment we use a set of three densities consisting of the usual electronic density $n(r)$, an anomalous electronic density (the superconducting order parameter), $\chi(r, r')$, and the diagonal part of the nuclear N -body density matrix, $\Gamma(R_1 \cdots R_{N_n})$. With this set of densities, it is easy to prove a Hohenberg-Kohn theorem, and to construct a Kohn-Sham system, which in this case comprises three coupled differential equations: A system of two electronic equations, with the same form as the Bogoliubov-de Gennes equations [11]; and a nuclear equation, featuring an N -body interaction, similar to the familiar Born-Oppenheimer equation for the nuclei [12]. One should stress that no approximation is involved in the derivation of these equations, and that all many-body and beyond-Born-Oppenheimer effects are included through the exchange and correlation (xc) potentials. As usual, these are functionals of all densities, implying that the Kohn-Sham equations have to be solved in a self-consistent way. Starting, for example, with an approximation to the densities, we first calculate the xc potentials; with these potentials we then solve our coupled set of equations and obtain the Kohn-Sham states; these, in turn, are used to recalculate the densities, *etc.*, until self-consistency is reached.

To perform the self-consistency cycle just described is a formidable task, even for present-day computers. We therefore make a number of approximations that reduce dramatically the complexity of the problem. First we note that, in a solid well below the melting point, the nuclei describe small amplitude oscillations around their equilibrium positions. It is then sufficient to make a harmonic expansion of the nuclear KS equation around those positions and diagonalise the nuclear Hamiltonian

by introducing collective (phonon) coordinates. We emphasize again that the nuclear Kohn-Sham equation is a Schrödinger equation with an N_n -body-interaction. This N_n -body potential is expected to be very close to the ground state Born-Oppenheimer surface. We therefore approximate the DFT phonon eigenspectrum and electron-phonon coupling constants by the Born-Oppenheimer ones, calculated within linear-response theory. Here we used results by Savrasov [13,14]. Of course, changes in the phonon-spectrum caused by superconductivity, which were recently observed near T_c [15–17] cannot be described within this approximation. To deal with such effects the functional dependence of the nuclear N_n -body Kohn-Sham potential on the superconducting order parameter $\chi(r, r')$ need to be taken into account.

Next, by applying the so-called decoupling approximation [18], we separate the problem of solving the electronic Kohn-Sham Bogoliubov-de Gennes equations into two independent parts: First, the solution of the ordinary Kohn-Sham equation, Eq.(1) (which can be achieved using standard band-structure methods)

$$\left(-\frac{\nabla^2}{2} + V_{KS}(r)\right)\varphi_k(r) = \epsilon_k\varphi_k(r), \quad (1)$$

and second, the solution of a gap equation. This approximation achieves a separation of the two energy scales present in the system: the one-particle energies, of the order of the Fermi energy, are determined by the normal-state Kohn-Sham equation, while the superconducting gap, usually two or three orders of magnitude smaller, is given by the gap equation. At temperatures close to the superconducting transition temperature, T_c , the order parameter (and the gap function) will be small. If we are only interested in calculating T_c , we are allowed to solve the much simpler linearised form of the gap equation:

$$\Delta(k) = -\frac{1}{2} \sum_{k'} \frac{\tanh\left(\frac{\beta}{2}(\epsilon_{k'} - \mu)\right)}{(\epsilon_{k'} - \mu)} \Delta(k') \times \\ \times (w_{Cib}(k, k') + w_{ee}(k, k') + w_{e-ph}(k, k')) \quad (2)$$

where

$$w_{ee/e-ph}(k, k') = \\ = \int d^3(rr'xx') \varphi_k^*(r) \varphi_k(r') \left(\frac{\delta^2 F_{xc}^{ee/e-ph}[\rho, \chi]}{\delta\chi^*(r, r') \delta\chi(x, x')} \right) \Big|_{\chi=0} \varphi_{k'}^*(x') \varphi_{k'}(x) \quad (3)$$

$$w_{Cib}(k, k') = \int d^3(rr') \varphi_k^*(r) \varphi_k(r') \frac{1}{|r - r'|} \varphi_{k'}^*(r') \varphi_{k'}(r). \quad (4)$$

The effective interaction appearing in the gap Eq.(2) consists of three contributions: an unscreened Coulomb part, w_{Cib} , given by Eq.(4), a purely electronic xc part, w_{ee} , and an xc contribution, w_{e-ph} , due to the electron-phonon interaction. Eq.(3) shows how these xc kernels are related to the purely electronic and

TABLE 1. Transition temperatures from numerical solutions of the linearised DFT gap equation and phonon-only Eliashberg calculations. The experimental T_c s are also shown. T_c s are in Kelvin.

	Al	Nb	Mo	Ta	Pb	Cu	Pd
DFT ph. only	9.47	27.3	6.97	14.4	14.9	0.055	2.64
Eliashberg	9.75	24.7	7.31	14.0	12.2	0.065	2.74
Rel. diff. (%)	-2.9	10.5	-4.6	2.8	22.1	-15.4	-3.6
DFT	1.31	12.3	0.64	5.35	8.26	-	0.12
Experimental	1.18	9.5	0.92	4.48	7.2	-	-
Error (%)	11.0	29.5	-30.4	19.4	14.7	-	-

the electron-phonon part of the xc free energy functional $F_{xc}^{ee/e-ph}$. We emphasize that the DFT gap equation is an integral equation in momentum space *only*. The frequency-dependence associated with the electron-phonon retardation effects is entirely contained in the xc potentials appearing in the DFT gap-equation.

Although the DFT presented above is an exact reformulation of the original many-body problem, practical applications of the theory depend on the availability of approximations for the exchange-correlation potentials. While a wealth of approximations exist for normal-state DFT, the situation is quite different for the case of superconductors. The first DFT calculations for superconductors were performed for Niobium [19] and YBCO [20,21]. These calculations used a *phenomenological* model for the xc potential. Only in 1999, the first universal xc functional was presented [22]: The superconducting counterpart of the successful normal-conducting local spin density approximation. This functional, however, is an approximation of F_{xc}^{ee} , *i.e.* it deals with electronic correlations only. To include the electron-phonon coupling we have developed a diagrammatic perturbation theory for the inhomogeneous system where the unperturbed Hamiltonian is given by the Kohn-Sham Hamiltonian discussed above. The diagrammatics involves the normal and the anomalous electron propagators as well as the phonon propagator corresponding to the Kohn-Sham phonons. In terms of these quantities, the exact functional F_{xc}^{e-ph} is given by the sum of all diagrams containing at least one phonon propagator while F_{xc}^{ee} consists of all other diagrams. In the present context we approximate F_{xc}^{e-ph} by the sum of the two 1st-order diagrams in the phonon propagator. From the xc energy functional calculated in this way, the xc kernels entering the linearised gap equation are obtained from Eq.(3).

The DFT transition temperatures were obtained by solving numerically the linearised DFT gap equation. In order to assess the quality of our approximation for F_{xc}^{e-ph} we first performed phonon-only calculations by setting $w_{Clb} = w_{ee} = 0$ in Eq.(2). The resulting values for the critical temperature are compared by numerically solving the linearised Eliashberg equations in imaginary frequency space with $\mu^* = 0$. As can be seen from Table(1), the DFT results agree rather closely with the Eliashberg results. The mean relative deviation of 8.8% demonstrates that the electron-phonon part of the xc energy functional, at the present level of

approximation, leads to results essentially equivalent to Eliashberg phonon-only calculations. To obtain critical temperatures that can be compared with experiment, purely electronic interactions have to be taken into account as well. As a first estimate, we have approximated $(w_{C1b} + w_{ee})$ in Eq.(2) by the simplest possible density functional, namely a Thomas-Fermi-screened Coulomb interaction, where the Thomas-Fermi screening length is obtained from the average density of the respective material. The resulting DFT transition temperatures are quite encouraging: Table(1) shows that the mean relative deviation from experimental T_c values is 23%. In view of these results we expect that the density functional theory presented here will become a useful tool to calculate properties of superconductors from first-principles.

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