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Ab-initio Computation of Superconducting Properties of Elemental Superconductors and MgB_2

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We present *ab-initio* predictions of superconducting properties of some elemental superconductors and of MgB_2, based on the Super-Conducting Density Functional theory (SC-DFT). This formalism allows a description of superconducting properties at thermal equilibrium by means of three "densities": the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N-body density matrix. These quantities are determined through self-consistent solutions of Bogoliubov-de Gennes Kohn-Sham like equations, involving exchange-correlation potentials which are universal functionals of the three abovementioned quantities. By means of approximate expressions for the relevant functionals, we obtain an *ab-initio* description of the superconducting state, completely free of empirical parameters. The results of our present implementation of SC-DFT for selected materials are discussed in terms of superconducting energy gap, critical temperature and specific heat, and compared with experiments.

KEY WORDS: *Ab-initio* computation; superconducting density functional theory; magnesium diboride.

1. INTRODUCTION

While great success has been achieved, over the past decades, by computational condensed matter theory in predicting and determining the equilibrium normal state properties of materials, no similar breakthroughs have been obtained in the prediction of superconducting properties. Present theoretical methods, in fact, can not provide a quantitative, and at the same time *ab-initio*, prediction of superconducting properties even for weak coupling electron–phonon superconductors, well described by the microscopic theory of Bardeen, Cooper and Schrieffer (BCS) [1]. In these, let us say, "simple" systems, superconductivity is mainly determined by the interaction between electrons and phonons, the quantized lattice vibrations of a crystalline solid. The difficulties that every theoretical framework has to overcome, mainly stem from the different time (i.e., energy) scales dictated by the motion of the particles involved: namely, electrons and ions. Superconducting electron pairing can in fact only result from phonon-mediated electron–electron attraction overcoming the Coulomb electron repulsion, thanks to retardation effects.

This was shown by model calculations [2,3] which pointed out how the different time scales of the electronic and ionic motions are able to weaken the repulsive Coulomb interaction. In order to take into account this effect, a renormalized parameter was introduced that would measure the strength of the *weakened* Coulomb interaction. This parameter is the so-called μ^* which is usually treated as an adjustable parameter in Eliashberg equations [4]. As a result, and in spite of its tremendous success,

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Eliashberg theory (in its practical implementation), can be considered semi-phenomenological.

Recently, after the generalization of a density-functional framework to the superconducting state put forward by Oliveira, Gross, and Kohn [5,6], a full Superconducting Density Functional Theory (SCDFT) was developed that is able to describe the superconducting properties at thermal equilibrium by means of three densities: the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N-body density matrix [7,8]. Moreover, appropriate approximations for the exchange-correlation functionals required by the theory have been developed [7,8] and the validity of the proposed approach was demonstrated for various materials, ranging from weak to strong coupling.

In the present paper, after assessing the validity of this new approach in some simple cases, we apply it to MgB_2 and discuss the peculiarity of this material in terms of the superconducting gap and transition temperature.

2. SIMPLE METALS

As shown in Refs. [7,8], it is possible to obtain Kohn-Sham eigenvalues for the superconducting state through self-consistent solution of coupled Bogoliubov-de Gennes equations involving effective potentials which are functional of three densities: namely, the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N-body density matrix. The nuclear coordinates are treated in harmonic approximations and enter the formalism through an Eliashberg-type electron–phonon spectral function.

Therefore, starting from the *ab-initio* calculated normal state properties, it is possible to obtain the superconducting properties of a given material, using appropriate approximate functionals describing the exchange-correlation and the electron–phonon terms [7,8]. We will not go into the details of the theory nor of the implementation used; for this, we refer the interested reader to our previous work [7,8].

Normal state properties have been computed using the FLAPW [9] method while electron–phonon Eliashberg coupling functions have been taken from Ref. [10].

In order to assess the validity of the approach used, we show in the Table I a comparison between calculated and experimental [11] superconducting gap calculated at the Fermi energy and at $T = 0.01$ K as well as the critical temperature (T_c), for several different elemental materials ranging from weak (Al) to strong (Nb) electron–phonon coupling. The results reported are calculated using a simplified Coulomb repulsion term, that is a k-dependent Thomas-Fermi type screening, and a Fermi-surface averaged electron–phonon Eliashberg function, as described in Ref. [8].

Table I. Comparison between calculated and experimental [11] superconducting gap (Δ_0, meV) and critical temperature (T_c, K) for several different elemental superconductors

	Δ_0 (theory)	Δ_0 (exp)	T_c (theory)	T_c (exp)	λ
Al	0.15	0.179	1.0	1.18	0.44
Ta	0.76	0.694	4.8	4.48	0.84
Pb	1.31	1.33	6.8	7.2	1.62
Nb	1.79	1.55	9.4	9.3	1.18

Note. The electron–phonon coupling costant λ [10], is also reported.

The effect of different functionals describing the Coulomb repulsion among electrons on the calculated critical temperatures and superconducting gap is shown to be material dependent and is discussed at length on Ref. [8]. It is interesting to point out, that the largest deviations occur in materials with strongly localized electron states (such as Ta), where a free-electron-like description is less justified.

Solution of the coupled Boguliobov-de Gennes equations, allows us to calculate thermodynamic functions such as the electronic entropy and, from this, the specific heat. In order to show how well our calculations reproduce the intrinsic properties of the materials considered we report in Table II the electronic specific heat discontinuity at T_c ($C_e^S(T_c)/C_e^N(T_c)$) compared with the experimental counterpart.

Once again the results are in quite good agreement with experiments reproducing the BCS value for weak coupling elements (such as Al and Ta) as well as the values for strong-coupling materials.

Table II. Normalized electronic specific heat discontinuity at $T_c(C_e^S(T_c)/C_e^N(T_c))$

	Theory	Experiment [11]
Al	2.46	2.43
Ta	2.64	2.63
Nb	2.87	2.8–3.07
Pb	2.93	3.57–3.71

We stress that the agreement of our results with experiments, without making use of any adjustable parameter, is very promising and unprecedented in the field of superconductivity.

3. MgB_2

We turn now to MgB_2, a material which is superconductor below 39.5 K and hides very interesting fundamental properties behind a relative simple crystal structure. This compound is, in fact, characterized by a very strong coupling between a particular phonon mode and selected electronic states, resulting in the presence of two superconducting gaps at the Fermi level.

Two band superconductivity has been shown to favor a high T_c, and has been discussed [12,13] as resulting from a peculiarity of the symmetry of the electronic σ and π wave functions: it therefore represents a very important test case for our novel approach for superconductors.

The Fermi surface (FS) of MgB_2 has several sheets with different orbital character. In particular, the tubular structures with σ character are very strongly coupled to the E_{2g} phonon mode, corresponding to a B–B bond-stretching in the boron planes. In addition, in MgB_2 there are also three-dimensional π bands that give rise to a complicated FS. The π bands are coupled much less efficiently to phonons, but are nevertheless crucial to superconductivity. A remarkable feature of this compound is the presence of two gaps on the σ and π bands, as clearly demonstrated by, e.g., tunneling experiments and measurements of the specific heat. On the theoretical side, this system has been treated within Eliashberg theory [12,14,15], using two-bands with four electron–phonon spectral functions to represent the distinct couplings. However, there have also been reports of calculations averaging out the different electron–phonon coupling for σ and π bands [14].

In our present investigation we apply the SCDFT formalism to this compound neglecting anisotropy effects, therefore using a band-unresolved Eliashberg function [15] and a Coulomb repulsion described through a Thomas-Fermi like scheme which, however, takes into account the real bands of the material.

We find that the integral of the averaged Eliashberg electron–phonon coupling function gives $\lambda = 0.87$, a moderately large value (see Table I).

Table III. Calculated and experimental critical temperatures (T_c, K), superconducting gaps (Δ, meV), at E_F and $T = 0.01$ K, electron–phonon coupling λ, for MgB_2 and Pb, according to different approximations used (see text)

	Δ^{theory}	Δ^{expt}	T_c^{theory}	T_c^{expt}	λ
MgB_2	2.99	7.07,2.86	17.5	39	0.87
MgB_2^{ph}	3.56	–	53	–	0.87
Pb	1.31	1.33	6.8	7.2	1.62
Pb^{ph}	2.42	–	13	–	1.62

Solving the gap equation in analogy with what done previously for the elemental superconductors considered above, we find the superconducting value and the critical temperatures reported on Table III (Δ, T_c).

Both the values obtained for the gap and the critical temperature are much lower than those found in experiment thus confirming, in agreement with previous Eliashberg results [14, 15], the crucial role played by anisotropy in setting such an high T_c in MgB_2. Remarkably, we note that MgB_2 has a rather high predicted critical temperature ($T_c = 17.5$ K) when compared with a simpler elemental superconductor with much larger electron–phonon coupling parameter, such as Pb ($T_c = 7.2$ K). This indicates that even within the rather crude approximations taken (full isotropy in both electron–phonon and electron repulsion terms) the present theory accounts for the different Coulomb repulsion and electron–phonon interactions, peculiar of each individual material.

In order to investigate separately the role played by Coulomb repulsion and electron–phonon attraction, we perform self-consistent calculations neglecting completely the repulsive term (i.e., electron–electron interaction) in both materials taken as reference, namely MgB_2 and Pb: the quantities obtained in this approximation are reported on Table III (MgB_2^{ph}, Pb^{ph},respectively). It is interesting to note that in MgB_2 the critical temperature jumps at 53 K, while in Pb it roughly doubles. Therefore, the electron–phonon interaction in the diboride is much more effective than in Pb and, in addition, its interplay with the repulsive Coulomb term is far from trivial.

In order to obtain a full and complete description of superconductivity in MgB_2, which well reproduces the experimental findings, we need to fully take into account the anistropy of the compound in both the repulsive and attractive terms, as shown in a forthcoming publication [16]. We stress that the

approach presented is completly general and allows inclusion of k-dependent as well as k-independent functionals without relying on phenomenological parameters.

4. CONCLUSIONS

In this contribution we presented application of a recently developed *ab-initio* theory of superconductivity. In particular, we first showed results for selected elemental metals showing weak as well strong coupling and then discuss the more complicated case of MgB_2. For the elemental superconductors considered, we obtain values of T_c, superconducting gap as well as the specific heat as a function of temperature in very good agreement with experiment for all the materials considered. The results presented for MgB_2 highlight the shortcomings of the isotropic approximation for such a compound, thus calling for a full treatment of the relevant interactions [16].

We stress the predictive power of the approach presented: being, for its very nature, a fully *ab-initio* approach, it does not require semi-phenomenological parameters, such as μ^*. Nevertheless, it is able to reproduce with good accuracy superconducting properties, up to now out of reach of first principles calculations.

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