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Engineering room-temperature superconductors via ab-initio calculations

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Abstract

The BCS, or bosonic model of superconductivity, as Little and Ginzburg have first argued, can bring in superconductivity at room temperatures in the case of high-enough frequency of bosonic mode. It was further elucidated by Kirzhnits *et al*., that the condition for existence of high-temperature superconductivity is closely related to negative values of the real part of the dielectric function at finite values of the reciprocal lattice vectors. In view of these findings, the task is to calculate the dielectric function for real materials. Then the poles of this function will indicate the existence of bosonic excitations which can serve as a "glue" for Cooper pairing, and if the frequency is high enough, and the dielectric matrix is simultaneously negative, this material is a good candidate for very high-T_c superconductivity. Thus, our approach is to elaborate a methodology of *ab-initio* calculation of the dielectric function of various materials, and then point out appropriate candidates. We used the powerful codes (TDDF with the DP package in conjunction with ABINIT) for computing dielectric responses at finite values of the wave vectors in the reciprocal lattice space. Though our report is concerned with the particular problem of superconductivity, the application range of the data processing methodology is much wider. The ability to compute the dielectric function of existing and still non-existing (though being predicted!) materials will have many more repercussions not only in fundamental sciences but also in technology and industry.

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Keywords: superconductors; ab-initio calculations; dielectric function; transition temperature

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1. Introduction

Room-temperature superconductivity (RTS) is long considered a Holy Grail of contemporary science and technology because of enormous impact it may have on human life. It is therefore not surprising from how many different ways this problem is being attacked. To name a few: intercalated graphene layers, decorated nanotubes, oxides, pniktides, monolayers, interfaces, organic materials, metallic hydrogen, *etc*. Manifestos, articles, books and reports [Basov and Chubukov (2011), Mazin (2010), Mourachkine (2006), DoE Report (2006)] are being published, and special school and institute sessions are being held [IBM Almaden Institue, (2012)]. In principle, all these efforts are reasonable, and perhaps could be justified, even in case when the research is being done with cold atoms in quantum optics with a promise to contribute to still elusive mechanism of high-temperature superconductivity...

Actually, the work on RTS has been theoretically ignited by Little (1964), whose ideas resonated with Ginzburg's perception of superconductivity [Ginzburg (1964), Ginzburg *et al.* (1982)]. They both referred to the Bardeen, Cooper, Schrieffer (1957) model. According to the BCS model, which later was clarified by many others, the electrons are dynamically interacting with each other via crystalline field (phonons). Because of the involvement of this phonon field, the electron-electron interaction is attractive, thus reducing the energy of the ground state, and modifying the electronic system to become superfluid. Can this modification occur at room temperatures? The search for RTS was revolutionized by the discovery of high-temperature superconductivity by Bednorz and Mueller (1987). Almost immediately the field became populated by many researchers, with Sir Nevill Mott remarking that the number of theories suggested for its explanation had become close to the number of theorists involved. Sad to say, the theory is not yet constructed. However, the absence of theory is not a problem for searching for RTS, because the theory was never a direct instrument of discovery of novel materials. Historically, it was more fruitful for explaining various properties of novel materials and suggesting their applications, like the Josephson (1962) theory. Nevertheless, theory provided some advice in which direction to look for prospective materials. For example, Bednorz and Mueller (1986) were looking at materials with very strong electron-lattice interaction. Their belief was related to the BCS expression for critical temperature:

$$T_c \sim \omega_D \exp(-1/\lambda) \tag{1}$$

(here ω_D is the Debye frequency of phonons, and λ is the coupling constant of electrons with phonons),which indicates that T_c is bigger when λ is bigger. How high can Eq. (1) take the T_c? Unfortunately, at proper consideration of Coulomb interaction [Bogolyubov *et al.* (1958)], as well as strong electron-phonon interaction [Eliashberg (1960)], this equation should be renormalized and converted into

$$T_c \approx \omega_D \exp\{-[1.04(1+\lambda)]/[\lambda-\mu^*(1+0.62\lambda)]\} \tag{2}$$

[McMillan, 1968], so that when λ is big, T_c is limited. In this equation μ^* stands for the screened Coulomb repulsion between paired electrons: $\mu^* = \mu/[1+\mu\ln(\omega_c/\omega_D)]$, where μ is the unscreened Coulomb repulsion; ω_c is the plasma frequency. Since typically $\mu \sim 1$, and $\omega_c/\omega_D \gg 1$, resulting in a μ^* , almost independent on μ : $\mu^* \approx \ln^{-1}(\omega_c/\omega_D) \sim 0.15-0.2$. These renormalizations essentially reduce the values of T_c, so that even if $\omega_D \sim 1000K$, which is rare in solids, the T_c~*10K*. For the majority of solids $\omega_D \sim 100K$ is a better estimate, which moves the hopes for room temperature superconductivity away from the electron-phonon interaction.

However, the BCS formalism is applicable not only to phonon-mediated electron-electron interaction, but virtually to any other Bose-field serving as a Cooper pair-glue [see, *e.g.*, Carbotte, (1990)]. Thus one can expect high values of T_c if the pre-factor ω in Eq. (1) is on the electronic scale of energy: $\omega \sim \omega_c \cong E_F \sim 10^5 K$, yielding $T_c > 300K$ at moderate values of interaction constant λ . This idea [Little, (1964)] initiated an avalanche of responses. Leaving for a moment supportive ones aside, we will focus on the criticism by Cohen and Anderson (1972). It was noticed that raising the frequency of Bose-field cannot raise the T_c unrestrainedly. Indeed, subject to

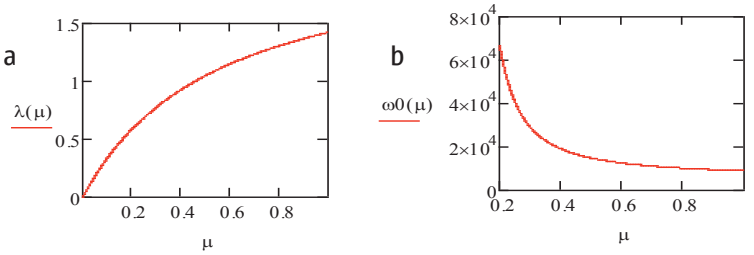


Fig. 1.(a) $\lambda(\mu)$ in the bosonic model with T_c^{max}=300 K; ω_c=10^5 K; (b)corresponding value of the Bose-field frequency.

ω-dependence of μ^* the value of T_c, at given λ and μ, has a maximum at $\omega=\omega_0$. Approximating T_c in Eq. (2) by $T_c \approx \omega\exp\{-(1+\lambda)/[\lambda-\mu^*(1+\lambda)]\}$ we find $\omega_0=\omega_c\exp[-(2/\lambda-1/\mu+2)]$ and consequently obtain $T_c^{\max}=\omega_c\exp[-(4/\lambda-1/\mu+4)]$. Physical reason of non-monotonic behaviour of $T_c(\omega)$ is the reduction of retardation effect at Cooper pairing: the screening of μ turns ineffective, and $\mu^*\to\mu$. Using obtained analytical expression for T_c and representing it in the form

$$\lambda(\mu)=4/\ln[(\omega_c/T_c^{\max})+1/\mu-4], \qquad (3)$$

one can make quantitative predictions by substituting $T_c^{\max}=300K$ in Eq. (3), Fig. 1. Obviously, *300 K*-superconductivity requires $\lambda>\mu$. Here is where the crucial point comes in: for λ to exceed μ, the negative values of the inverse total dielectric function $\varepsilon_{tot}^{-1}(q,\omega)$ at zero frequencies and finite wave vectors $\boldsymbol{q}$ are required in view of the relation $\mu-\lambda=\int dq\{4\pi e^2/[q^2\varepsilon_{tot}(q,0)]\}$. Achievability of this requirement was disputed in the literature [Cohen, Anderson (1972), Kirzhnitz (1976), Dolgov, Kirzhnitz, Maksimov (1981)]. The current understanding is that because of the local field effects it really may occur in condensed matter, and not only in superconductors [Dolgov, Maksimov (1978)], but also in other structures, like Wigner crystals [Bagchi (1969)].

In the rest of the article the sign of the dielectric function at different values of $\boldsymbol{q}$ and ω is the major concern.

2. "Frozen lattice" model

The considerations above allow us to ignore the phonon dynamics for now: the mechanism of the Cooper pairing would then be fully electronic. Indeed, in Fig. 1b, the values of μ should not exceed ½ because of Stoner's criterion of ferromagnetism. The frequency $\omega_0(\mu\le 1/2)$ is then too high for phonons though may be much lower than the Fermi-energy, and thus can exist in solids as a collective electronic mode. For the electron dynamics determined by this mode, one can safely drop the lattice degree of freedom, and consider it "frozen". In the rest of the article we will assume this assumption valid.

3. Codes and calculation procedures

We made use of the Density Functional Theory (DFT) code ABINIT [Gonze *et. al* (2005) and (2009)] and the add-on Time Dependent Density Functional Theory (TDDFT) code DP. ABINIT was used to compute the electronic density and band structure. The computed data were then fed into DP to calculate the dielectric function.

4. Models and results

Prior to considering materials where the purely electronic pairing could be expected, we tried materials (like *Al*) in which analytical considerations have revealed negative $\varepsilon_{tot}^{-1}(q,\omega=0)$, and also materials such as *Si*, where the computational scheme was already advanced by the originators of the code.

4.1. Silicon and germanium

Additional interest in this case arose also because of an opinion [Dolgov, Kirzhnitz, Maksimov (1982)] that $\varepsilon_{tot}^{-1}(q,\omega)$ can be negative in *Si* and/or *Ge*. We first reproduced the *ab-initio* results by Reining *et al*. (2002), which match well with the experimental data by Aspnes, Studna (1983), Fig. 2a. This requires the so-called long-range contribution (LRC) regime in DP. This approximation goes beyond the local density approximation (LDA) by using an exchange correlation kernel $f_{xc} = \alpha / q^2$; for *Si*, $\alpha = -0.2$ gives a good agreement with the experimental results. Also, a scissor shift must be applied to correct the band structure, as the LDA never gives the correct band gap in semiconductors.

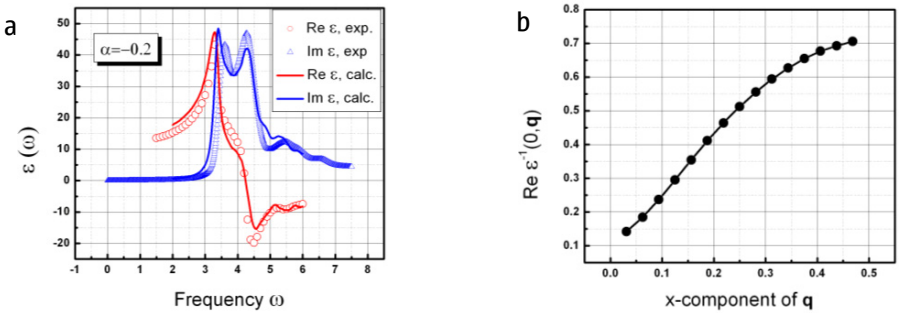


Fig. 2. (a) real and imaginary parts of $\varepsilon_{tot}(q=0,\ \omega)$ in *Si* ; (b) real part of $\varepsilon_{tot}^{-1}(q,\ \omega=0)$ in *Si*, $\boldsymbol{q}$ along the direction (1,0,0).

With the parameters from this computation, $\varepsilon_{tot}^{-1}(q,\omega=0)$ was computed with q in the direction (1,0,0), Fig 2b. It was found that $\varepsilon_{tot}^{-1}(q,\omega=0)$ does not possess a negative sign. Germanium provided a similar result.

4.2. Aluminum

First, to test the accuracy of the codes and parameters, we reproduced the experimental data of Ehrenreich *et. al*, (1918) of $\varepsilon(\omega)$ at $\boldsymbol{q}=0$. The results are show in Fig. X. The red curve represents the result of ABINIT/DP computations of the dielectric function, which takes into account only intraband transitions; by adding interband transitions (Given by the simple Drude formula; black curve), the experimental curve of (Ehrenrich et. al., 1968) is reproduced. We then proceeded to compute the dielectric function as a function of q, $\varepsilon(\boldsymbol{q},\ \omega = 0)$ using the parameters from this calculation. The results are shown in Fig. 3a. However, these results differ qualitatively from the graph computed by Dolgov & Maximov (1978). In particular, $\varepsilon_{tot}^{-1}(q,\omega=0)$ does not become negative at any value of $\boldsymbol{q}$. It can be concluded then that in *Al*, which is a classical superconductor, the negativity of the dielectric function is due also to phonon effects, and cannot be reproduced in "frozen lattice" approach, at least with ABINIT/DP.

Given these findings, the next question is: using the *ab-initio* method, can we explore for systems in which non-classical superconductivity arises from purely electronic mechanisms? Little's model provides one way, in theory. Thus, our next computations were of dielectric functions in carbon nanotubes (in rope configurations, and in single systems).

4.3. Carbon nanotubes

For a given CNT, the dielectric function may be computed with the nanotubes in an optimized array ("rope" configuration) with close intertube distance, or with enough vacuum padding between the nanotubes to simulate an individual nanotube. The dielectric function of roped configurations was studied by Reining *et al.* (2008).

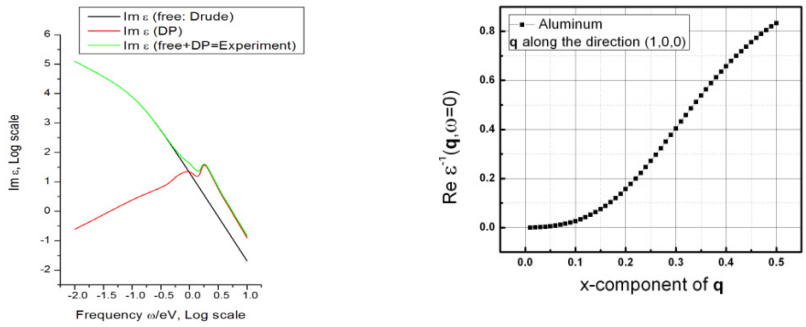


Fig. 3. (a) - the sum of the DP-computed intraband contribution to $\varepsilon_{tot}(q,\omega)$ plus the Drude formula gives agreement with experiment; (b) - $\varepsilon_{tot}^{-1}(q,\omega=0)$ for Al.

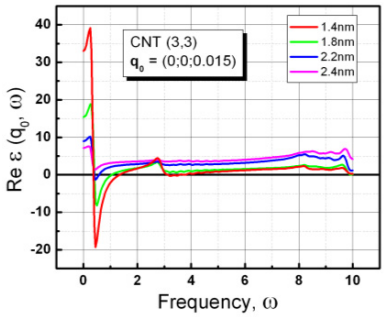
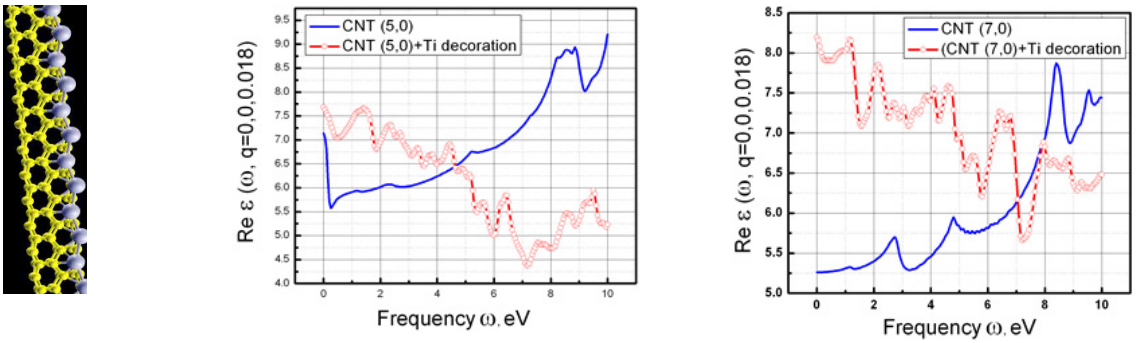


Fig. 4. $\varepsilon_{tot}^{-1}(q,\omega=0)$ in a (3,3) CNT with various intertube distances.



(a) (b) (c)

Fig. 5. (a) - The relaxed Ti-decoration of a CNT; (b) - comparison of the dielectric function of decorated and undecorated (5,0) CNT; (c) - the same for a (7,0) CNT.

As for *Al* and *Si*, our computations of $\varepsilon_{tot}^{-1}(q,\omega=0)$ in either systems did not yield negativity. Yet, carbon nanotube systems look promising: as Fig. 4 shows, for low intertube distance (*i.e.*, ropes) and for small ω, the dielectric function does becomes negative. Moreover, although for isolated nanotubes, for which the intertube distance is high, no sign change occurs (Fig. 4, curve 24 A), such systems can host a variety of decorations that may change the dielectric function. In Fig. 5, we show the effect of titanium decoration on the dielectric function of (5,5) and (7,0) nanotubes in vacuum. These systems (Fig 5a) were first explored by first principle computations by Yang *et al.* (2002); we decorated and relaxed the system using the commercial code QuantumWise ATK prior to applying the ABINIT/DP codes to obtain results in Figs. 5 b & c. Although a sign change is not observed, the dielectric function is decreased in certain frequency ranges.

5. Discussion and conclusion

Classical superconductivity does not require $\varepsilon_{tot}^{-1}(q,\omega=0)<0$. However, it does require negativity of $\varepsilon_{tot}^{-1}(q,\omega)$ at some values of ω and q, as one can notice in simplistic jellium model [De Gennes (1966)]:

$$V(q,\omega)=V_{Coulomb}+V_{el-ph}=4\pi e^2/[\varepsilon(q,\omega)q^2];\quad \varepsilon(q,\omega)=[q^2/(q^2+k_{TF}^2)][1+\omega_q{}^2/(\omega^2-\omega_q{}^2)]. \qquad (4)$$

That changes the repulsive static Coulomb interaction $4\pi e^2/q^2$ by a dynamic interaction with attraction: $4\pi e^2/[\varepsilon(\omega,q)q^2]$. This property is present in Fig. 4 when nanotubes are closer within the rope! One can expect superconductivity in these systems, and in similar cases which will be explored in the future. To examine the predictive power of the approach and the method itself, it is interesting to compute this function for 2-dimensional Cu-O layer(s) with oxygen vacancies, which may possess negativity of $\varepsilon_{tot}^{-1}(q,\omega)$ in the adopted electronic model.

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