On the microscopic theory for high temperature superconductors

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Abstract. The microscopic theory of superconductivity is expressed through a gap equation. The construction of such equations, and methods for solving them under different simplifying assumptions, are reviewed. The physical parameters in these equations have yet to be fully defined and to be determined by complete first principle calculations. The way to further progress requires not only better band calculation but also more rigorous theoretical determination of such physical qualities as elastic constants, and comparison with experimental evidence.

1. Introduction

The modern microscopic theory of superconductivity starts with the advent of the BCS model. The idea of a collective pairing state stabilized by electron-phonon interaction has since this time been at the basis of all attempts of rational prediction of T_c. The microscopic model has been so successful in explaining the thermodynamical electromagnetic acoustical and tunnelling properties, that its basic soundness was never in doubt. Nevertheless, as B. T. Matthias likes to point out, the model has so far made no direct contribution to the discovery of materials of high T_c. In order to understand this state of affairs, and perhaps to see the way to further progress, we want to review three aspects of superconductivity theory:

(i) nature of the model,
(ii) techniques for solving the gap equation,
(iii) origin of parameters in the gap equation.

2. Nature of the model

The microscopic theory of superconductivity is most frequently expressed in terms of a gap equation, giving the energy gap for pair breaking excitations. T_c is found from the condition that the gap is vanishingly small. In the original BCS theory the gap equation is based on an attractive interaction between the electrons via the phonons, which is assumed to be instantaneous and weak, justifying the neglect of self-consistency. When trying to understand high T_c, and therefore strong coupling

superconductivity, one has to take into account both self-consistency and the retarded nature of this interaction.

This has been done using Green's functions and the Nambu operators to couple time reversed states. Writing down the second order self-consistent self-energy expressions one gets the Eliashberg equations, having the following form in the Matsubara representation (using imaginary discrete frequencies $i\omega_n$) [1]

$$Z(\mathbf{k}, i\omega_n) = 1 + \frac{1}{\beta\omega_n} \sum_{\mathbf{k}'n'} \frac{\omega_{n'} Z(\mathbf{k}', i\omega_{n'}) D(\mathbf{k}, \mathbf{k}', i\omega_n - i\omega_{n'})}{[\omega_{n'} Z(\mathbf{k}', i\omega_{n'})]^2 + \varepsilon_{\mathbf{k}'}^2 + \phi(\mathbf{k}', i\omega_{n'})^2} \tag{1a}$$

$$\phi(\mathbf{k}, i\omega_n) = \frac{1}{\beta} \sum_{\mathbf{k}'n'} \frac{\phi(\mathbf{k}', i\omega_{n'})[D(\mathbf{k}, \mathbf{k}', i\omega_n - i\omega_{n'}) - V(\mathbf{k}, \mathbf{k}')]}{[\omega_{n'} Z(\mathbf{k}', i\omega_{n'})]^2 + \varepsilon_{\mathbf{k}'}^2 + \phi(\mathbf{k}', i\omega_{n'})^2} \tag{1b}$$

where $\varepsilon_{\mathbf{k}}$ are the band energies relative to the Fermi surface, V is the screened Coulomb interaction, D is the interaction between the electrons via the phonons, Z is the mass renormalization, and $\Delta = \phi/Z$ plays the role of the superconducting gap. These equations are largely valid for most superconductors. But when discussing extreme materials, one has to be aware of possible limitations of their validity.

They are based on the Migdal approximation, closely related to the adiabatic approximation, which relies on the fact that the ions move much slower than the electrons, and that corrections of order θ_D/E_F are negligible. This approximation becomes questionable when the Fermi level falls on a peak not much wider than θ_D/E_F. This might happen in the A15 compounds and in the Chevrel phases. The band energies $\varepsilon_{\mathbf{k}}$ and the screened Coulomb interaction V include correlation effects, and should in principle depend on frequency. Non-instantaneous Coulomb interaction will modify the equation for Z.

Apart from these special effects, the Eliashberg equations should allow a first principle calculation, within the adiabatic approximation. All screening and dressing effects will have to be included correctly, however. Some of these calculations might be avoided by determining parameters from experiment. This is done for the phonon frequencies in all present calculations. The electron-phonon spectral function $\alpha^2 F(\omega)$ (being a convolution of the electron-phonon coupling α^2, and the phonon density of states F) and Coulomb repulsion pseudo-potential μ^* can be determined from tunneling experiments [2]. However, difficulties have appeared for niobium where the fit seems to give negative repulsion [3]. Another way to determine $\alpha^2 F(\omega)$ is the study of phonon line widths [4] [5]. The mass renormalization parameter can be inferred from comparison of calculated bare masses with specific heat and de Haas van Alphen (dHvA) results [6].

3. Solving the gap equation

Let us now examine the simplifying assumptions made usually before solving the gap equation. Since the screened Coulomb interaction is assumed to be instantaneous compared to the phonon interaction, one applies a Morel-Anderson type transformation and obtains a pseudo retarded interaction which is about an order of magnitude smaller. This explains why the repulsive interaction does not destroy superconductivity.

The variation of electronic properties perpendicular to the Fermi surface is commonly neglected compared to the variation of the phonon properties. This assumption is again invalid if the Fermi level falls on a peak of width of order θ_D.

Preliminary calculations giving up this hypothesis have been done several times [7] and an increased T_c was found. However, as pointed out already, the Migdal approximation becomes questionable and a more complete formalism should be adopted. The **k** dependence of electrons, phonons, coupling and gap function are generally neglected. This isotropic approximation simplifies the problem considerably by avoiding the **k** summation in the gap equations with the help of spherical averaged quantities. But in the case of more anisotropic substances, and of more anisotropic properties such as critical fields, bigger effects occur [8].

A further assumption used in most calculations of T_c is the separation of the problem into a phonon part and an electron part. In this way, McMillan got his analytical solution of the gap equation, and his famous semiempirical formula for T_c [9]. There have since been many attempts for new versions of his formula, with the goal of finding better fits while preserving the same functional form. However it seems to us that more effort has to be put into developing algorithms for more exact solutions of the gap equations, particularly in view of the efforts for obtaining the complete parameters contained therein.

The use of imaginary frequencies (Matsubara representation) [10] [11] simplifies the solution of the gap equations by avoiding the poles along the real axis. In order to get the maximal physical information one needs of course to know the gap as function of real frequencies. But this problem can be solved starting from imaginary frequencies by means of Padé approximants [12]. By use of such algorithms, it is not hard to solve the gap equations without recourse to averaging approximations. Such approximations appear therefore no longer justified as soon as the full **k**-dependence of phonons, electrons and their interaction is known. Already the use of a two band model helps in understanding the problem of anisotropy. Butler and Allen [13] have treated this problem in the case of niobium by keeping separate phonon and electron parts and expanding the second in Fermi surface harmonics. Thomlinson and Carbotte [14] gave a complete treatment of the anisotropy problem for lead. But since they calculated the gap directly along the real axis, they could not make more than one iteration for computer time reasons. The authors have completed a calculation using the Matsubara representation for the case of niobium [1]. The Fermi surface was divided into 22 pieces, and all the interactions between them were calculated for up to 24 frequencies. It turned out that in this calculation the effect of anisotropy on T_c was an increase of 0.24 K versus 0.06 K obtained by Butler and Allen. The discrepancy is probably due to the different methods of calculating the electron-phonon coupling constants. We noted that 60 % of the anisotropy effect could be obtained already from a suitably chosen two band model. Markowitz and Kadanoff [15] have noted that observation of such anisotropy effects requires the scattering lengths to be at least of the order of the coherence length.

An important problem that can be examined by solving the gap equation is the effect of various factors on the increase of T_c. Bergmann and Rainer [10] calculated the functional dependence of T_c on $\alpha^2 F(\omega)$ and found a maximum for frequencies slightly above $2\pi T_c$, which are then often interpreted as the optimal frequencies for getting high T_c. However, such interpretations depend on the constraints imposed on the variations of parameters. Allen and Dynes [11] examine $T_c/\langle\omega\rangle$ as a function of the parameter λ defined by

$$\lambda = 2 \int_0^\infty d\omega \alpha^2 F(\omega)/\omega \simeq \frac{N(O)\langle I^2 \rangle}{M\langle\omega^2\rangle} \tag{2}$$

and find a monotonously increasing behaviour. Leavens and Carbotte [16] place their emphasis on the size of the spectral function A

$$A = \int_0^\infty d\omega \alpha^2 F(\omega) \simeq \frac{N(O)\langle I^2 \rangle \langle \omega \rangle}{2M \langle \omega^2 \rangle} \qquad (3)$$

Again their most favourable frequency is of order $2\pi T_c$, and $k_B T_c \leq 0.231$ A.

Rainer (private communication) proposes to analyse the problem in terms of the first moment of the spectral functions B

$$B = 2 \int_0^\infty d\omega \, \omega \alpha^2 F(\omega) \simeq \frac{N(O)\langle I^2 \rangle}{M} \qquad (4)$$

since this moment depends mainly on electronic contributions. He finds that T_c increases asymptotically as the root of this moment $k_B T_c \leq 0.1827\sqrt{B}$; the most important frequencies being the soft modes. These studies, while thought-provoking, merit to be continued with the precautions cited earlier.

Hanke et al. [17] and others have shown that the conditions for high T_c may also be the ones for lattice instabilities.

4. Calculation of the physical parameters

4.1. Electrons

Rigid lattice electron parameters enter the Eliashberg equations through the band energies and the Coulomb interaction. In principle, corrections due to lattice vibrations should also be included, but they are small in the domain of validity. The main theoretical problem in band calculations is the correct inclusion of exchange and correlation effects. The most favoured way to do this at present seems to be the self-consistent calculation in the local density approximation. In this approach, one approximates the effects of exchange and correlation by means of a density dependent potential $V[n(r)]$ which enters into a single particle Schroedinger or Dirac equation. Non self-consistent Slater local exchange approximation also gives accurate results.

There are three different types of approach for solving the effective single particle problem. First there is the OPW or Pseudopotential method which uses a basis of plane waves orthogonalized to the core orbitals. This method becomes complicated when treating transition metals and their compounds which generally are the high T_c superconductors. Second, there is the cellular type approach including methods such as the localized orbitals, the APW, the KKR and the LMTO. In these methods one starts from atomic type potentials and applies boundary conditions connecting the atoms to form the crystal. Third, there are the LCAO and the Tight Binding methods (Slater-Koster interpolation scheme). They are generally not useful in giving first principle results, but allow fits with few parameters to more complete calculations. As we will see, these fits are suitable for calculating derived physical quantities. Using this scheme, energies and matrix elements are calculated in points in the Brillouin zone (BZ), and a further interpolation is often made, by means of schemes by Raubenheimer-Gilat, Jepson-Andersen and others. The authors have adopted an interpolation scheme which is based directly on constant energy surfaces, which allows simple treatment of the fast variations occurring in a direction perpendicular to those surfaces in the BZ [18].

These schemes can be fitted to reliable band results which begin now to appear. For the A15 compounds there are the new results by Van Kessel *et al.* [19] which show impressive agreement with several experiments, including tentative positron results by Manuel and others; and also the calculations of Klein *et al.* [20] remarkable by their energy resolution. For the Chevrel phases there are the calculations of Andersen *et al.* [21], of Mattheiss and Fong [22], and of Bullet [23], for the $ErRh_4B_4$ the one by Jarlborg *et al.* [24].

Coulomb matrix elements have been approximated by one or several parameters. Trying to calculate them, all types of screening and dressing should be included. It might be possible to obtain, within the local density approximation, an algorithm to calculate these effects simply by studying changes in the effective potential $V[n(r)]$ due to virtual change of occupation of the electronic states and by calculating both the diagonal and nondiagonal changes in the matrix elements due to this change.

4.2. *Phonons and electron-phonon interaction*

The phonon frequencies and the electron-phonon interaction parameters enter into the retarded interaction D between pairing electrons (equation 1). Since no reliable first principle phonon calculations have been done up to now, parametrized neutron diffraction results had to be used in superconducting calculations. Recently, however, encouraging progress has been reported on the theory of the calculation of phonons in transition metals by several authors. Calculation of phonon energies are closely related to the calculation of electron-phonon coupling constants. In both cases, the main problem is the correct treatment of screening due to charge redistribution.

There are two different formulations of the electron-phonon coupling problem. In the Bloch formulation, the phonon induced lattice potential change is treated by orthodox perturbation theory. The second approach was started by Fröhlich and allows the localized parts of the wave-functions to follow the motion of the atomic cores when a phonon is excited. It has been used for numerous tight-binding calculations. It has been criticized since it is difficult to define the moving wavefunctions properly so as to obtain a complete orthogonal set and to define a consistent perturbation procedure. However, Van Hay has shown how to introduce orthogonalization corrections [25]. Alternatively, calculations can be carried out on a non-orthogonal basis, as done by Varma *et al.* [26]. The authors [27] have shown how both the Fröhlich and Bloch approach lead to the same physical results, if one stays within the adiabatic approximation, and considers both first and second order vertices. (The simple exercise of treating a particle displacement by perturbation expansion shows how different orders in perturbation contribute to the same order in the result.) For the superconducting problem, however, only the first order elements are relevant.

The most common approximation for the calculation of the electron-phonon coupling constants in transition metals is the rigid muffin tin approximation (RMTA) first used by Sinha [28]. In this case one uses the Bloch approach and assumes that the phonons rigidly shift the muffin tin potentials. Hopfield [29] used this approximation to derive a formula for the average electron-phonon interaction by means of an angular momentum decomposition, and claimed that $p \to d$ scattering dominates in transition metals. Gaspari and Gyorffy [30] followed Hopfield's idea and obtained by spherical averaging a simple formula for $\langle I^2 \rangle$ in terms of phase shifts. Butler *et al.* [31] generalized this work including non-spherical terms, and found as Klein and

Papaconstantopoulos [32] before that the $d \rightarrow f$ terms dominate, where the f components are due to the tails of the d functions from the neighbouring atoms.

Sinha and Harmon [33] have shown how to introduce screening corrections to the RMTA by means of linear response theory. They could explain phonon anomalies and instabilities in Nb, NbC and in many other systems. Their method is similar to the one of Hanke et al. [17] and based on the tendency of certain charge fluctuations to appear as resonance terms in the screened electron-phonon coupling constants.

The Fröhlich approach for electron-phonon coupling calculation has been applied in tight binding calculations. Birnboim and Gutfreund [34] calculated the averaged electron-phonon interaction for several transition metals. The authors [1] calculated by the same method non-averaged electron-phonon couplings for use in the gap equation for niobium. The mass enhancement anisotropy they obtained agrees with dHvA results [6], whereas the RMTA calculations [35] give the wrong sign. Using the same method, the authors [36] could explain anomalies in the temperature dependence of the elastic constants in Nb–Zr alloys.

Varma et al. [26] used the same approach and included orthogonalization corrections. This resulted in reduced electron-phonon coupling, allowing a good fit of T_c in niobium. They used this approach also to explain the anomalies in the phonon spectra of Nb, Mo, and the alloys between them. It may therefore be said that the distance dependent tight binding method allows successful calculations of properties involving first order electron-phonon coupling. The reason for these successes lies, in our opinion, in the description of the phonon induced potential variation δv. In the RMTA approximation, the muffin-tin potentials are shifted, but not deformed, whereas in the tight-binding approximation, there is deformation because of overlap between shifted atomic potentials. This results in a more realistic change of potential and screening. The fact that this deformation is non-spherical around the atoms might explain the remarkable difference in the predicted anisotropic properties between RMTA and tight binding, both for mass enhancement [1], [35] and for the effect on T_c [1], [13].

In future calculations one will have to concentrate on the screening problem. Frozen phonon calculations such as those by Gale and Pettifor [37] are a logical improvement of the Fröhlich approach. This approach seems particularly appropriate for quasi molecular crystals such as the Chevrel phases. Substances of this kind will facilitate the simultaneous application of theoretical analysis and physical synthesis. Alloys on the other hand are more difficult to treat because of deviations from rigid band behaviour. Corrections of the type proposed by Miedema [38] might be necessary, and complicate the problem. However, Papaconstantopoulos et al. [39] have done both CPA and rigid band calculations on the palladium hydrides, and got close results for states around E_F.

5. Conclusion

In conclusion, we would like to point out three points.

First, the present difficulty of obtaining proper phonon spectra shows that present schemes for band-structure calculations, developed to give plausible results within a given symmetry, have troubles coping with symmetry changes and need to be improved in this respect. The calculation of elastic constants should serve as a simple test of this property for any band scheme.

Second, in spite of fundamental difficulties, efforts should continue upon calculations not only of band structures, but also upon the derived physical quantities, including T_c. In this way, computing power and algorithms will develop in parallel, until they converge to calculations of T_c in agreement with experiment. During this process of computational improvement, progress should be judged by logical consistency and realistic error estimates, even more than by striking fits to experimental data obtained by judicious choice of adjustable parameters.

Third, we would like to point out that the choice of one-body potentials for band calculations involves an element of arbitrary choice. Maybe there exist criteria for 'best' one-body potentials. Or maybe the present emphasis on band calculations is not the best way to obtain other physical properties than Fermi surfaces. Definitive first principle theories for critical temperatures may have to await further progress in the understanding of these deeper questions.

Acknowledgement

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