

High Temperature Superconductivity in Strongly Correlated Electronic Systems

Lawrence J. Dunne^{a, b, c, *}, Erkki J. Brändas^d, Hazel Cox^c

^a School of Engineering , London South Bank University, London SE1 0AA, UK,

^b Department of Materials, Imperial College London, London SW7 2AZ, UK,

^c Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, UK

^d Institute of Theoretical Chemistry, Ångström Laboratory, University of Uppsala, Box 518, Uppsala, S-75120, Sweden

*corresponding author. email: Dunnel@lsbu.ac.uk tel:+44(0)207 815 7944

Abstract

In this paper we give a selective review of our work on the role of electron correlation in the theory of high temperature superconductivity. The question of how electronic repulsions might give rise to off-diagonal long range order (ODLRO) in high temperature superconductors is currently one of the key questions in the theory of condensed matter. This paper argues that the key to understanding the occurrence of high temperature superconductivity (HTSC) in cuprates is to be found in the Bohm-Pines Hamiltonian modified to include a polarisable dielectric background. The approach uses reduced electronic density matrices and discusses how these can be used to understand whether ODLRO giving rise to superconductivity might arise from a Bohm-Pines type potential which is comprised of a weak long-range attractive tail and a much stronger short-range repulsive Coulomb interaction. This allows time-reversed electron pairs to undergo a superconducting condensation on alternant Cuprate lattices. Thus, a detailed summary is given of the arguments that such interacting electrons can cooperate to produce a superconducting state in which time-reversed pairs of electrons effectively avoid the repulsive hard-core of the inter-electronic Coulomb interaction but reside on average in

the attractive well of the effective potential. In a superconductor the plasma wave function becomes the longitudinal component of a massive photon by the Anderson-Higgs mechanism. The alternant cuprate lattice structure is the key to achieving HTSC in cuprates with $d_{x^2-y^2}$ symmetry condensate symmetry.

Keywords

Off-diagonal Long-Range Order (ODLRO), cuprate superconductivity, strongly correlated electronic systems, Bohm-Pines, Plasmon, Anderson-Higgs mechanism, condensate wave function.

Contents

- 1. Per Olov Löwdin**
- 2. Introduction to superconductivity**
- 3. The Pairing instability in Classical and High Temperature Superconductors**
- 4. Off- diagonal long-range order (ODLRO) in Superconductors and relation to Bardeen –Cooper-Schrieffer Theory.**
- 5. The Bohm-Pines Hamiltonian**
 - 5.1 The Short-Range Hamiltonian H_{sr}**
 - 5.2 Long-Range Hamiltonian and Plasma Oscillations**
- 6. Total Hamiltonian**
- 7. Choice of localized Basis Functions and Summary of Group Theoretical Analysis of Cuprate Superconductor real space condensate wave function.**
- 8. The superconducting Ground State**
- 9. Condensate Wave functions**
- 10. Role of Electron Correlation**
- 11. References**

1. Per Olov Löwdin

In celebrating the centenary of Per Olov Löwdin's birth and reflecting upon his contributions to science we cannot help being in awe at the breadth and depth of his insights. The review we present here is in a real sense a small tribute to Per Olov Löwdin's enormous contribution to theoretical chemistry and physics. Configuration interaction, electron correlation, density matrices, eigenvalues of density matrices, natural orbitals and geminals, variational problems, effective Hamiltonians all have a prominent part and Per Olov played a key role in their development. In a series of seminars on correlation and density matrix theory given by Per Olov in Uppsala, during the very cold Swedish winter of 1978/1979 he reviewed the conditions for superconductivity stressing the necessity of a macroscopically large eigenvalue of the second order reduced electronic density matrix analogous to Bose-Einstein condensation. It is not widely known that complementing the famous work of Chen Ning Yang such a condition was also discovered at about the same time by Sasaki working in Per Olov's group in Uppsala as discussed here. It was during these seminars in 1978/1979 and inspired by Per Olov that the ideas discussed in this paper were born.

2. Introduction to superconductivity

Superconductors are materials which transport electric charge without resistance¹ and with the display of associated macroscopic quantum phenomena such as persistent electrical currents and magnetic flux quantization. These quantum phenomena are associated with macroscopic wave functions characteristic of off-diagonal long-range order (ODLRO), a name first introduced by Chen Ning Yang². This order is characterised by a long-range coherence of the quantum mechanical phase which demonstrates itself as macroscopic quantum phenomena. The focus of this paper is to give a very selective review of the role of electron correlation in HTSC where we put forward the view that this is very largely an electron correlation effect due to electronic repulsions but with a prominent role played by the plasma modes in the energetics and electrodynamics of superconductors. This review follows earlier work on aspects of these topics^{3,4,5,6,7}.

Bednorz and Müller⁸ first made the discovery of HTSC in the cuprates which set off a very well-known avalanche of theoretical and experimental activity resulting in the discovery of many hole and electron-doped superconducting cuprates and their related properties. Sometime after the discovery of the cuprates (see Fig. 1 for chemical structures), iron based high temperature superconducting compounds^{9,10} were discovered in Japan. These two types of chemical structure highlighted the role of alternant lattices which exist in these materials and shown specifically for the cuprates below in Fig. 1 and discussed in refs [^{1,2,3,4,5,6,7}]. For structures of the iron-based compounds see eg ref¹¹

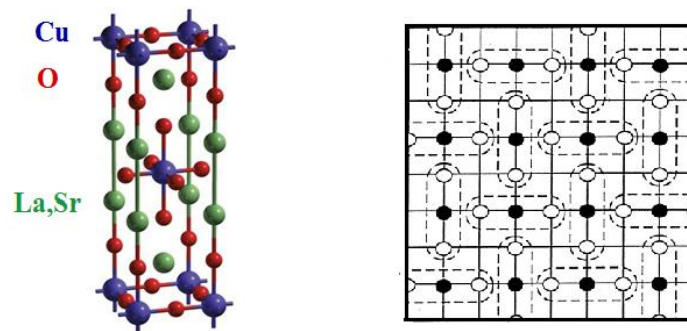


Fig.1 Left side: Structure of Lanthanum Strontium Cuprate. Reproduced from ref¹² with the permission of the National Academy of Sciences of the US. Right side-Alternant Cuprate layer ● - Copper ○ -Oxygen (Reproduced from ref⁶ with permission from Elsevier)

The microscopic origin driving the superconducting condensation in these solids is the focus of very many theories and speculations which are too numerous to review here. However, there is a widely held view that HTSC materials are ‘electronic superconductors’ in which the participation of phonons is at best secondary. No theory has yet been widely accepted despite numerous studies and many notable and highly interesting proposals^{13,14,15}. There are many aspects and properties of HTSC materials which we do not consider here such as charge density waves and the origin of the pseudogap which have both attracted wide attention. Hence here we will focus in a limited way on our view of the role of Coulomb repulsions in high temperature cuprate superconductivity.

3. The Pairing instability in Classical and High Temperature Superconductors

The theory of conventional low temperature metallic superconductors is due to Bardeen - Cooper-Schrieffer theory (BCS)¹⁶ where there is an attractive phonon-induced electron-electron attraction which causes a Cooper pair instability¹³. In a conventional metallic superconductor¹³ the effective electron-electron interaction V_{eff} is made up of the contributing interactions $V_{eff} = V_{sc} + V_{el-ph-el}$. Here V_{sc} is the screened Coulomb repulsion and $V_{el-ph-el}$ is the phonon induced electron-electron interaction^{13,14,16}. The BCS Hamiltonian or variants of it have been widely discussed but some original points will be revisited below. It does not seem likely that the BCS Hamiltonian applies to the cuprates but the study of this points to the features which will give rise to superconductivity in the cuprates.

There is a well-known symmetry in the doping phase diagram for HTSC cuprates where electron doping or hole doping of the cuprate layer both lead to similar magnetic and superconducting features⁵. To give our point of view, in alternant lattices (see Figs. 1) unit cells may be given a sign with opposite signs for nearest neighbours. Electron pairs in time-reversed states on alternant Cuprate lattices interact with a short range Coulomb repulsion and longer range attraction. Electrons in the coherent ground state can avoid each other at short-range. It is suggested here that the cause of the long-range attractive part of the effective interaction is to be found in the short range part of the Bohm-Pines^{17,18,19,20,21} potential to be discussed below and shown in Fig. 2.

The symmetry of the condensate wave function has been experimentally established in hole doped cuprates and there is a broadly held opinion that the condensate wave function has $d_{x^2-y^2}$ symmetry in superconducting hole doped cuprates^{13,14,22,23} and this seems probable too in electron doped cuprates²⁴

The model describes in detail a mechanism in which the Coulombic interactions allow a superconducting state on a cuprate layer to appear. Pairs of electrons in the superconducting condensate correlate over longer distances in the attractive well in the Bohm-Pines potential^{5,18,19} and avoid each other at very short separations. This gives a lower Coulomb repulsion than in the uncorrelated normal state with which it competes. It is a mechanism for electrons to stay out of the hard Coulombic core but reside in the attractive region of the potential at longer range. A conventional BCS singlet type s-wave condensate wave function does not have such

embedded correlations. Yet, a d-wave or sign alternating s-wave does have such in built electronic correlations.

BCS used an independent particle model whose success was a surprise. In an important paper which is seldom referred to in recent discussions of superconductivity Bardeen and Pines¹⁷ give a careful justification for such a theoretical line of attack on the problem of superconductivity. As is well-known the long-range Coulomb interaction between electrons in a good metal are screened out. The basis for the success of the apparent neglect of the long-range Coulomb interaction arises from the role of the zero-point energies of the Plasmon modes in a metal. This is intimately tied up with currently hotly discussed questions about the massive longitudinal photons and the Anderson-Higgs mode in superconductors. Historically, the idea of the Higgs particle and mass acquisition by elementary particles finds its origin in Anderson's famous paper²⁵ written following an idea put forward by Schwinger²⁶. Anderson's idea was taken up by Peter Higgs²⁷ [see ref [28] for a more complete historical perspective].and others and the rest, including the Large Hadron Collider at CERN, as they say - is history.

In a superconductor the system undergoes a spontaneously broken symmetry and chooses a phase. The low lying phase excitations or Goldstone mode becomes the longitudinal degree of freedom of a massive vector Boson via the Anderson-Higgs mechanism^{29,30}. Much more work remains to be done to clarify the interconnection between the Thomas-Fermi screening and the role of the Anderson-Higgs mechanism.

The plasma modes are comprised of the long-wavelength Fourier components of the Coulomb interaction leaving behind a residual screened electron-electron interaction. The plasmon energies are high enough that they are not thermally populated at room temperature and therefore they do in a sense drop out of the problem. So the BCS wave function is actually a wave function for the quasiparticles.

In conventional superconductors exchange of virtual phonons induces an attractive effective interaction between electrons of opposite spin and momentum whereby the Fermi Sea becomes unstable to electron pair formation. This is the so-called Cooper pair instability^{5,14,16} which is widely discussed as an n-fold stabilization effect. Consider n-degenerate states which are Slater determinants in a basis of pair-wise occupied states required to obtain a coherence of the sign of the matrix elements. The diagonal elements are at an energy U above some reference energy with off-diagonal elements matrix element $-V$ due to the attractive phonon induced electron-

electron coupling. One of the eigenvalues at energy $U-nV$ splits off from the rest giving the well known Cooper pair instability. (see refs [3-7,13,14] for discussion).

However as has been discussed in detail elsewhere beginning in 1979^{3-7, 31,4,5,6,7} (see section 1 for the historical context.) other scenarios with repulsive matrix elements are possible which give a similar type of n-fold stabilization effect. We consider a real symmetric $2k$ -dimensional configurational interaction Hamiltonian matrix composed of two blocks. The first block is a k -dimensional diagonal sub-matrix with diagonal elements equal to U . The second is a k -dimensional full off-diagonal block with a repulsive matrix element, $V > 0$ in all sub-block elements as indicated below³⁻⁷.

The following eigenvalue/eigenvector relationships given below are easily verified.

$$\left(\begin{array}{ccc|ccc} U & 0 & V & \dots & & \\ 0 & \ddots & V & V & & \\ \hline V & V & U & 0 & & \\ \dots & V & 0 & \ddots & & \end{array} \right) \begin{pmatrix} 1 \\ \dots \\ -1 \\ \dots \end{pmatrix} = (U-kV) \begin{pmatrix} 1 \\ \dots \\ -1 \\ \dots \end{pmatrix} \quad \left(\begin{array}{ccc|ccc} U & 0 & V & \dots & & \\ 0 & \ddots & V & V & & \\ \hline V & V & U & 0 & & \\ \dots & V & 0 & \ddots & & \end{array} \right) \begin{pmatrix} 1 \\ \dots \\ 1 \\ \dots \end{pmatrix} = (U+kV) \begin{pmatrix} 1 \\ \dots \\ 1 \\ \dots \end{pmatrix} \quad (3.1)$$

The lowest energy ($U-kV$) eigenvector is a $2k$ -dimensional vector with elements ± 1 . Real-space pairwise occupation of the single particle localized states making up the Slater determinant basis functions is essential to obtain the coherence of the matrix element signs and give the block structure to the Hamiltonian matrix shown above.

Subject to the magnitudes of U and kV the lowest eigenvalue at $U-kV$ can thus cross over into a new low energy ground state just as in Cooper's problem.

In the condensed matter literature there has been extensive discussion^{13,32} of the BCS gap equation given by

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{k}'} V_{\mathbf{k},\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} \quad (3.2)$$

for the zero temperature case where $E_{\mathbf{k}}$ and $\Delta_{\mathbf{k}}$ are respectively the BCS excitation energy and gap parameter. Superconducting low energy solutions exist for repulsive matrix elements $V_{\mathbf{k},\mathbf{k}'}$ if the variational coefficients $\Delta_{\mathbf{k}}$ change sign coherently across the Fermi surface. Although expressed somewhat differently such a result is a special case of the more general situation discussed for the first time in ref [31] and discussed in section. 1 and followed up in other

publications^{3-7,33}. We will return to this question where Eqn(3.2) is derived by the assumption of an extreme state and the existence of Yang's off-diagonal long-range order to be discussed below.

4. Off-diagonal long-range order (ODLRO) in Superconductors

A key insight into the ordered nature of the superconducting state was suggested by London³⁴ who proposed the centrally important idea of momentum space ordering of the electrons in superconductors and the rigidity or stiffness of the superconducting wave function. It has taken a very long time since this and other early early insights³⁵ to understand even conventional superconductivity. It was some while after BCS theory¹⁶ appeared that the nature of the ordering in superconductivity became clearer. Ginzburg and Landau³⁶ had created a very successful model of a superconductor near to the transition temperature by invoking a superconducting order parameter with an associated wave function. Following earlier work of Onsager and Penrose³⁷ on the condensate in liquid ⁴He, and other important work by Gorkov on a non-diagonal order parameter³⁸, Chen Ning Yang² introduced the concept of off-diagonal long range order (ODLRO). Yang's analysis gives a method for deciding whether a many electron wave function has the ODLRO property which characterizes the superconducting state whereby an electron pair population analysis is undertaken using the second order reduced electronic density matrix $\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$ ^{3-7,39,40} (See also Sasaki⁴¹ referred to in section 1.) Evaluation of the eigenvalues of a pair-space sub-block P of $\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$ can demonstrate the existence of Off-diagonal Long-range Order (ODLRO) in an electronic wave function. The second order reduced electronic density matrix for a many-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{2M})$ is defined in the Yang normalization as

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = 2M(2M-1) \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \dots \mathbf{x}_{2M}) \Psi^*(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3 \dots \mathbf{x}_{2M}) d\mathbf{x}_3 \dots d\mathbf{x}_{2M} \quad (4.1)$$

In order to undertake a pair –population analysis $\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$ may be expressed as

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \sum_{ij,kl} g_{ij}(\mathbf{x}_1, \mathbf{x}_2) g_{kl}^*(\mathbf{x}'_1, \mathbf{x}'_2) P_{ij,kl} = \mathbf{gPg}^\dagger \quad (4.2)$$

$P_{ij,kl}$ is an element of the pair sub-space population coefficient matrix \mathbf{P} . In Eqn(4.2) $g_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ is a two-electron Slater determinant and $\mathbf{x}_1, \mathbf{x}_2, \dots$ are spin-space variables. The normalization of $g_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ is such that the density matrix eigenvalues correspond to populations of electron pairs in a particular germinal state. ODLRO is present and characterizes a superconducting condensate for a many-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{2M})$ when one of the eigenvalues λ_L of the matrix \mathbf{P} is macroscopically large. This macroscopically large number of electron pairs populating the same pair state is analogous to Bose-Einstein condensation^{2,5,6}. Leggett¹³ has given an extensive discussion of the eigenvector of the density matrix associated with the large eigenvalue is superconducting condensate wave function $\psi(\mathbf{x}_1, \mathbf{x}_2)$ and the relation to superconductivity.

Diagonalization of \mathbf{P} in \mathbf{gPg}^\dagger gives

$$\mathbf{gPg}^\dagger = \mathbf{gSS}^\dagger \mathbf{PSS}^\dagger \mathbf{g}^\dagger = (g'_{11}, g'_{22}, \dots) \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_N \end{pmatrix} \begin{pmatrix} g'_{11} \\ g'_{22} \\ \vdots \\ g'_{NN} \end{pmatrix} \quad (4.3)$$

The unitary transformation \mathbf{S} which is the matrix of orthonormal eigenvectors of the matrix \mathbf{P} relates the bases \mathbf{g} and \mathbf{g}' .

Hence in diagonal form

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \sum_i^n g'_{ii}(\mathbf{x}_1, \mathbf{x}_2) g'^*_{ii}(\mathbf{x}'_1, \mathbf{x}'_2) \lambda_i \quad (4.4)$$

The mean of the eigenvectors associated with the small eigenvalues are assumed to be negligible in the limit when the couple at $(\mathbf{x}_1 \square \mathbf{x}_2)$ is well separated from $(\mathbf{x}'_1 \square \mathbf{x}'_2)$. The electron pair density matrix then factorizes to give a Ginsburg-Landau type macroscopic wave function³⁶ of the form $\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sqrt{\lambda_L} g'_L(\mathbf{x}_1, \mathbf{x}_2)$. To connect with the n-fold stabilization problems above

consider the simplest Coleman^{42,43} extreme state where we have M electron pairs distributed in a pairwise fashion over possible permutations of pair states occupying N time-reversed pair states. We will consider both attractive and repulsive cases where each Slater determinant basis function has the same absolute weight and so this extreme state is close in form to a projected BCS wave function . For both attractive and repulsive cases the matrix \mathbf{P} has a macroscopically large eigenvalue. Firstly as shown below for Cooper's problem with attractive matrix elements we have

$$\begin{pmatrix} \frac{M}{N} & M \frac{(N-M)}{N(N-1)} & M \frac{(N-M)}{N(N-1)} & \dots \\ M \frac{(N-M)}{N(N-1)} & \ddots & \vdots & \vdots \\ M \frac{(N-M)}{N(N-1)} & \vdots & \frac{M}{N} & \vdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \\ \vdots \\ 1 \end{pmatrix} = (M(1 - \frac{M}{N}) + \frac{M}{N}) \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \\ \vdots \\ 1 \end{pmatrix} \quad (4.5)$$

and in Eqn(9.1) for repulsive matrix elements. The details of how these matrix elements are obtained are given in full in refs [3,7]. It can be seen that both scenarios for attractive and repulsive matrix elements in these degenerate systems can produce low energy states exhibiting ODLRO with superconducting properties. The point of view presented here is that the cuprates and possibly the iron –based superconductors^{9,10,11} are examples of the latter scenario. The reader is referred to recent developments⁴⁴ relating to the large eigenvalue of the cumulant part of the two-electron reduced density matrix as a measure of off-diagonal long-range order relevant to HTSC. In this paper we will consider the reduced electronic density matrix of the quasiparticle wave function which comes from the Bohm-Pines method¹⁸⁻²⁰.

Before moving on we will make a connection between BCS theory¹⁶ and Yang's Concept of ODLRO² and Coleman's extreme state given in ref [33]. We consider a many-electron Hamiltonian for n electrons given by

$$H = \sum_{i=1}^n h_i + \sum_{i < j}^n h_{ij} \quad (4.6)$$

where the terms on the right are the sums of one –body and two-body interactions.

We focus only on that part of the energy (the pairing energy) which changes in a BCS condensation. Eqn (4.6) can be decomposed into a sum of electron pair Hamiltonians using centre-of-mass (R) and internal coordinates (r).

$$H_2 = \left(\frac{P_r^2}{2\mu_r} + \frac{P_R^2}{2M_R} \right) + V(r) \quad (4.7)$$

where $\mu_r = m_e / 2$ and $M_R = 2m_e$. In an extreme state the total pairing energy $\langle E \rangle$ can be expressed as

$$\langle E \rangle = \lambda_L \langle g_L | H_2 | g_L \rangle + \lambda_s \sum_{k=2}^N \langle g_k | H_2 | g_k \rangle \quad (4.8)$$

where λ_L and λ_s are the large and small eigenvalues of the box P defined above.

$$\text{Expanding } \sqrt{\lambda_L} |g_L\rangle = \sum_k F_k^L \exp(i\mathbf{k}\cdot\mathbf{r}) \quad \text{and} \quad \sqrt{\lambda_s} |g_s\rangle = \sum_k F_k^s \exp(i\mathbf{k}\cdot\mathbf{r})$$

Following refs [^{13,33}] the BCS pairing energy is

$$\langle E \rangle = \sum_k |F_k^L|^2 \frac{\hbar k^2}{m} + \sum_{s=2}^N \sum_k |F_k^s|^2 \frac{\hbar k^2}{m} + \sum_{k,k'} F_k^* F_{k'} V_{k,k'} \quad (4.9)$$

If we now assume that the magnitude of the Fourier coefficients is essentially constant over the Fermi surface we obtain

$$\langle E \rangle = \frac{1}{N} (\lambda_L + (N-1)\lambda_s) \sum_k \left(\frac{\hbar k^2}{m} \right) + \sum_{k,k'} F_k^* F_{k'} V_{k,k'} \quad (4.10)$$

which for an extreme state can be written

$$\langle E \rangle = \frac{M}{N} \sum_k \left(\frac{\hbar k^2}{m} \right) + \sum_{k,k'} F_k^* F_{k'} V_{k,k'} \quad (4.11)$$

Following ref [³³] we also have

$$|F_k^L|^2 = \lambda_L / N = \frac{M}{N} - \left(\frac{M}{N} \right)^2 \quad (4.12)$$

which can be solved to give

$$2\frac{M}{N} = 1 - \sqrt{1 - 4|F_k|^2}. \quad (4.13)$$

Insertion into Eqn (4.12) gives

$$\langle E \rangle = \sum_k (1 - \sqrt{1 - 4|F_k|^2}) \left(\frac{\hbar k^2}{2m} \right) + \sum_{k,k'} F_k^* F_{k'} V_{k,k'} \quad (4.14)$$

Minimisation of $\langle E \rangle$ with respect to F_k^* and appropriate identification of F_k^* with $E_{\mathbf{k}}$ and $\Delta_{\mathbf{k}}$ which are respectively the BCS excitation energy and gap parameter gives the BCS gap equation given by Eqn (3.2) above and in detail in refs [13,33], for example. It is appropriate to remark that Eqn(4.13) has another roots which may be appropriate to hole-doping of a nearly full band.

5. The Bohm-Pines Hamiltonian

The existence of plasma oscillations in metals was suggested many years ago yet the understanding of this continues to develop. A plasmon^{45,46} may be described as a quantised excitation of a neutral system made up of positive and negative charges. The longitudinal oscillations of such a system (like sound waves) give rise to unique behaviour and here it is argued that it is intimately related to the occurrence of high temperature superconductivity in cuprates and iron-based materials.

The importance of plasma oscillations in metals was not appreciated until the work of David Bohm and David Pines in a series of ground breaking papers¹⁸⁻²⁰ published during the early 1950's. Although initially controversial, the physical picture which has emerged has been very significant in theoretical condensed matter physics. At that time the theory of metals was still in an unsatisfactory state [(for an early review see ref [46] and for a more recent review by David Pines see [14] p85)

Bohm and Pines [17] demonstrated that the Coulomb interaction in a metal can be split into two regions. These are a long -range (*lr*) part due to the collective plasmon modes and a short-range (*sr*) part which is the screened Coulomb interaction. It is this 'screened' interaction which will interest us here. Plasmons have been described as 'longitudinal

photons¹⁸. In a superconductor following the Anderson-Higgs mechanism a Plasmon is a longitudinal component of a massive vector Boson which also gives mass to the transverse photons^{25,28-30}.

We consider a collection of charges $\{\mu\}$ with masses m_μ , charges Z_μ and coordinates \mathbf{r}_μ in a cuprate superconductor. The system has an overall electrical neutrality so that $\sum_\mu Z_\mu = 0$.

The system of charges interact in the presence of polarisable atomic cores which give rise to a high frequency background dielectric constant ϵ into which the set of charges $\{Z_\mu\}$ are introduced. The charge carriers associated with the cuprate layers give rise to screening of the type appropriate to an electron gas yet the polarisable atomic cores give rise to the screening associated with a classical dielectric medium which we represent by the high frequency dielectric constant ϵ . The standard Hamiltonian for all the particles is given by

$$H = \sum_\mu \frac{1}{2m_\mu} \left(\mathbf{p}_\mu - \frac{Z_\mu}{c} \mathbf{A}(\mathbf{r}_\mu) \right)^2 + \frac{1}{2\epsilon} \sum_{\mu, \nu} \frac{Z_\mu Z_\nu}{r_{\mu\nu}} \quad (5.1)$$

\mathbf{A} is an irrotational magnetic vector potential. The electric scalar potential is zero and does not appear in the Hamiltonian in the temporal gauge.

We will split the total Hamiltonian into $H = H_{sr} + H_{lr}$ with $\mathbf{A} \cdot \mathbf{p}$, $\mathbf{p} \cdot \mathbf{A}$ type coupling terms neglected. Thus, H is split into 2 decoupled Hamiltonians given by

$$H = H_{sr} + H_{lr} \quad (5.2)$$

which corresponds to decomposition into short-range H_{sr} and long-range H_{lr} Hamiltonians.

Henceforth in the short-range Hamiltonian H_{sr} the nuclei will be regarded as infinitely heavy so that the Born-Oppenheimer approximation is effectively made so that only electronic motions will be considered.

5.1 The Short-Range Hamiltonian H_{sr}

The short range Hamiltonian is given by

$$H_{sr} = \sum_\mu \frac{\mathbf{p}_\mu^2}{2m_\mu} + \frac{2\pi}{\epsilon\Omega} \sum_{\mu, \nu} Z_\mu Z_\nu \sum_{k > k_c} \frac{1}{k^2} \exp(i\mathbf{k} \cdot \mathbf{r}_{\mu\nu}) \quad (5.3)$$

The last term will now be evaluated by replacing the sum by integration over k-space. Hence the short-range Hamiltonian is given by

$$H_{sr} = \sum_{\mu} \frac{\mathbf{p}_{\mu}^2}{2m_{\mu}} + \frac{1}{2} \sum_{\mu, \nu} \frac{Z_{\mu} Z_{\nu}}{\epsilon r_{\mu\nu}} \left(1 - \frac{2}{\pi} \int_0^{k_c r_{\mu\nu}} \frac{\sin(kr)}{kr} d(kr) \right) \quad (5.4)$$

The short-range potential itself, $v_{sr}(r) = \frac{Z_{\mu} Z_{\nu}}{\epsilon r} \left(1 - \frac{2}{\pi} \int_0^{k_c r} \frac{\sin(kr)}{kr} d(kr) \right)$ between two charges Z_{μ} , Z_{ν} at separation r is the second term in Eqn(5.4). This is easily evaluated numerically and is extremely interesting and will be discussed in detail next.

k_c is the inverse screening length. We will estimate k_c using the inverse Thomas-Fermi screening length given by $k_c^2 = 16 \pi^2 m e^2 (3 \eta_c / \pi)^{1/3} / \epsilon \hbar^2$ where η_c is the carrier density and ϵ the high frequency dielectric constant of the polarizable background taken to be about 5 as used in refs^[3-7]. We are forced by the difficulty of the problem to use the Thomas-Fermi approximation⁴⁷ to estimate screening lengths. For a hole doped valence band or an electron doped conduction band as in cuprate superconductors the screening length is readily related to the carrier concentration η_c by $k_c^2 = 16 \pi^2 m e^2 (3 \eta_c / \pi)^{1/3} / \epsilon \hbar^2$. If the bands are anisotropic the details change but the qualitative picture remains.

In Fig.2 the potential $v_{sr}(r)$ calculated from Eqn (5.4) for two electrons is plotted. The potential has a long-range oscillatory tail.

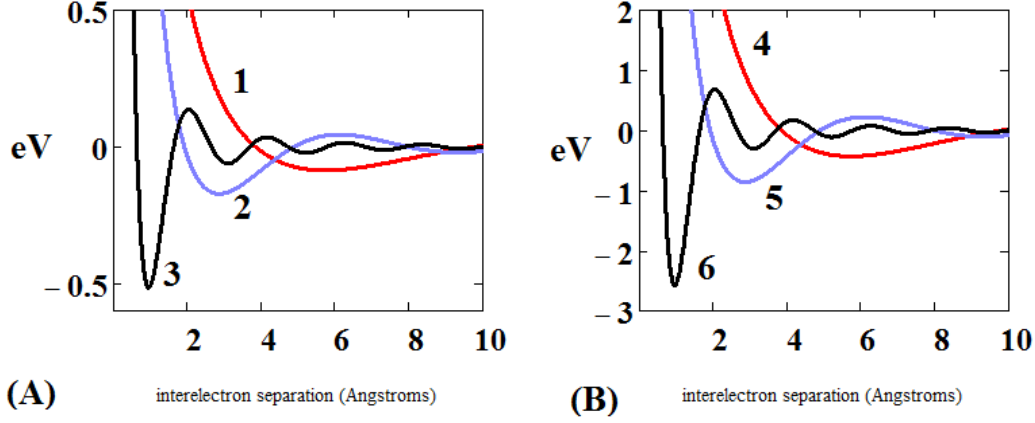


Fig.2 Bohm-Pines effective electron-electron potential, $v_{sr}(r)$ calculated from Eqn(5.4) for

(A) 1, $k_c=0.5 \text{ \AA}^{-1}$. 2, $k_c=1.0 \text{ \AA}^{-1}$. 3, $k_c=3 \text{ \AA}^{-1}$. each with $\epsilon=5$

(B) 4, $k_c=0.5 \text{ \AA}^{-1}$. 5, $k_c=1.0 \text{ \AA}^{-1}$. 6, $k_c=3 \text{ \AA}^{-1}$. each with $\epsilon=1$

Note that for the same k_c value the potential is inversely proportional to ϵ .

At short range the Bohm-Pines effective potential is very close numerically with the

Thomas-Fermi potential $v(r)_{\text{TF}} = \frac{1}{\epsilon r} \exp(-k_c r)$.

It is the long-range oscillations in such a potential which will be the focus for the occurrence of HTSC. These are also well-known as Friedel oscillations⁴⁸ and discussed by March and Murray⁴⁹ and Langer and Vosko⁵⁰.

5.2 Long-Range Hamiltonian and Plasma Oscillations

The long-range Hamiltonian is given by

$$H_{lr} = \frac{1}{2\epsilon} \sum_{k < k_c} P_k^* P_k + \frac{\omega^2}{2} \sum_{k < k_c} Q_k^* Q_k - \left(\sum_{\mu} \frac{2\pi Z_{\mu}^2}{\epsilon \Omega} \right) \sum_{k < k_c} \frac{1}{k^2} \quad (5.5)$$

where

$$\omega^2 = \frac{4\pi}{\Omega} \sum_{\mu} \frac{Z_{\mu}^2}{m_{\mu}}$$

The last term in H_{lr} is a constant self-energy term.

The above readily gives the energies of the Plasmons as

$$E_k = (n_k + \frac{1}{2})\hbar\omega_p \quad \text{where} \quad \omega_p^2 = \frac{4\pi}{\epsilon\Omega} \sum_{\mu} \frac{Z_{\mu}^2}{m_{\mu}}. \quad (5.6)$$

where $n_k = 0, 1, 2, \dots$. The coefficients $\{Q_k\}$ are the Fourier components of the longitudinal magnetic vector potential discussed in detail in ref [19]. The plasmon energies are large compared to thermal energies. Hence a large part of the correlation energy is accounted for by the plasmon zero point energies namely $\frac{1}{2}\hbar\omega_p$ for each mode k .

The eigenfunctions of H_{lr} are the plasmon wave functions. The plasmons are sometimes regarded as longitudinal photons. A longitudinal electromagnetic wave can propagate in the electron gas at ω_p . The plasmon energies are usually regarded as too high to be easily excited and thus may be regarded as remaining in their ground states. Thus the ground state Plasmon wave function is simply the product of the ground state wave functions of all the plasmonic oscillators which we will denote by $X_{plasmon}$.

6. Total Hamiltonian

We study an effective short-range Bohm-Pines Hamiltonian H_{sr} (the random phase approximation) for the electrons on the cells of a square alternant arrangement of unit cells with local C_{4v} point group symmetry.

$$H_{sr} = \sum_i h(i) + \frac{1}{2} \sum_{i,j} v_{sr}(r_{ij}) \quad (6.1)$$

The many electron wave function may be expanded in a basis of Slater determinants $\{\Phi_k\}$ where $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots) = \sum c_k \Phi_k$ where $\{c_k\}$ are the set of expansion coefficients obtained as an eigenvector of the Hamiltonian matrix. The total wave function will be a product of the form

$$X_{plasmon} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots) = X_{plasmon} \sum_k c_k \phi_k \quad (6.2)$$

The total energy is then

$$\langle E \rangle = \langle H_{sr} \rangle + \sum_{k < k_c} \frac{1}{2} \hbar \omega_p - \frac{2\pi}{\epsilon \Omega} \left(\sum_{\mu} Z_{\mu}^2 \sum_{k < k_c} \frac{1}{k^2} \right) \quad (6.3)$$

7. Choice of localized Basis Functions and Summary of Group Theoretical Analysis of Cuprate Superconductor real space condensate wave function.

The cuprate lattice is an alternant layer structure with local C_{4v} local point group symmetry as shown Figs. 1. The lattice may be partitioned into + or - sub-lattices where each unit cell has nearest neighbors with opposite signs. It is established experimentally that the superconducting condensate pair function in the hole doped cuprates has singlet 1B_1 symmetry under the operations of the C_{4v} point group⁵¹. This information about the symmetry of the cuprate two-point function condensate wave function permits some very fundamental deductions to be made about the localized electronic orbitals which can be used to construct the condensate wave function. The distance over which the condensate wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ stays finite as $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$ is a measure of the superconducting coherence length ξ_0 or the pair size. Experiments point to a very short ξ_0 of only a few Ångstroms in cuprate superconductors¹³ and this characteristic is commonly believed to indicate real space pairing occurs in cuprate superconductors. Hence we have chosen to work in a localized basis. A widely held view is that the active electronic orbitals are derived from oxygen (2p) or copper (3d) bands or some hybrid of these. We are seeking to identify a single or group of localized orbitals which allows pairs of electrons to evade the short range Coulomb repulsion and yet to exploit any longer range attractive region of the effective electron-electron interaction. Early on after the discovery of superconducting cuprates Sawatzky et al⁵² made a group theoretical analysis of the charge transfer in CuO but which was before the discovery of the d-wave condensate in superconducting cuprates. Following this, some years ago⁵¹ we identified a pair of localized

Wannier-type orbitals which we labeled as (px, py) with e-symmetry in the C_{4v} point group, which seem on balance likely to play a significant role in cuprate superconductivity. In the cuprate layers oxygen $2p_x, 2p_y, 2p_z$ orbitals hybridize with the Cu d-orbitals to form a set of symmetry adapted orthogonalised localized basis functions $\{\phi_i(\mathbf{r})\}$ which make up the condensate wave function. The shapes of these is given in Figs. 4a and 4b.

Decomposing $\psi(\mathbf{x}_1, \mathbf{x}_2)$ leads to

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi(\Gamma) + \sum_k \varphi_k \quad (7.1)$$

The first term on the right-hand side $\chi(\Gamma)$ indicates the sum of the pair functions centered on the principal axis at the centre of the unit cell transforming as the irreducible representation Γ in the C_{4v} point group. The second term on the right represents a linear combination of all the terms which transform collectively as the irreducible representation Γ and most significantly these are derived from the surrounding crystal. If the condensate wave function $\psi(\mathbf{x}_1, \mathbf{x}_2)$ has 1B_1 symmetry under the operations of the C_{4v} group then all the terms in Eqn(7.1) are required to individually have 1B_1 symmetry.

If the Wannier functions are assumed real the $(px(1)px(2) - py(1)py(2))$ pairing is composed of electrons in time-reversed states where such a choice of pairing is considered the best candidate for producing robust HTSC. We disregard other pairing candidates as unlikely for reasons given elsewhere³⁻⁵¹. These are shown on a cuprate lattice below and we will now discuss how we can obtain a low energy superconducting state from electronic correlations where the (px, py) choice of active localized basis functions leads straightforwardly to low energy ground state exhibiting ODLRO.

8. The superconducting Ground State

We consider a square cuprate lattice composed of $N/2$ cells as shown in Fig.1 (right). A pair $\{\phi_{l,px}(\mathbf{x})\}, \{\phi_{l,py}(\mathbf{x})\}$ of Wannier type functions are localized at the centre of each cell with index l .

Each member of the pair $(l, px\uparrow, l, px\downarrow)$ of Wannier orbitals is assigned a signature $(-1)^l$ and each pair $(l, py\uparrow, l, py\downarrow)$ a signature $(-1)^{l+1}$ as shown in the Fig.3. The layer is decorated with Wannier pair functions which show an alternant pattern. Most importantly, each Wannier function has nearest and next-nearest neighbors with opposite signs as shown in the blue/red crosses in Fig 3.

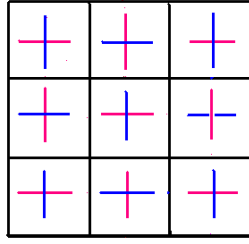


Fig. 3. Signatures of Wannier pair functions a cuprate layer showing nine unit cells. The Wannier pair functions are labeled with a positive (dark-greyscale, red-color online) or negative sign (light -greyscale, blue-color online). Reproduced with the permission of J.Wiley (taken from Dunne and Brändas [3])

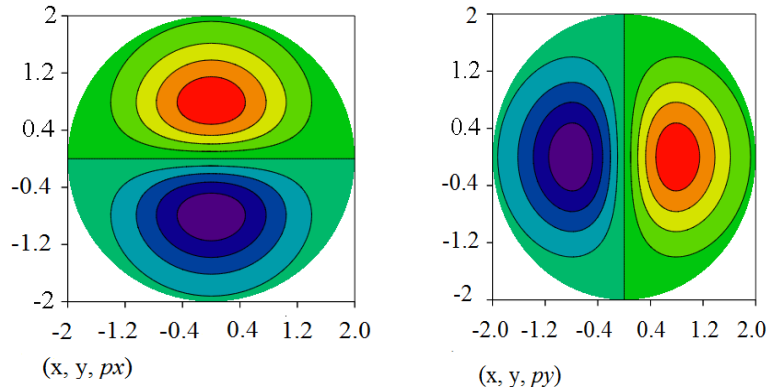


Fig. 4 (a), (b) Shape of px - py pair of Wannier functions (or e-representation in square symmetry) for Cuprate superconductors. These orbitals are expected to be largely out-of-phase combinations of ligand O(2p) orbitals as discussed in the text. The lobes with red and blue (dark and light in greyscale) centers have opposite signs. Reproduced with the permission of J.Wiley (taken from Dunne and Brändas [3])

We consider a basis of Slater determinants generated by populating M singlet coupled electron pairs randomly over the N Wannier orbitals so that each pair is either occupied by 2 electrons or vacant as depicted in Fig. 5 . with a filling fraction $\rho = M/N$. The number of ways of arranging M electron singlet coupled pairs randomly over N occupied orbitals is $\frac{N!}{M!(N-M)!}$.Each

configuration is given an overall signature given by the product of the signs of the occupied pairs of orbitals such that each Slater determinant basis function may be grouped into one of 2 classes according to the overall signature.

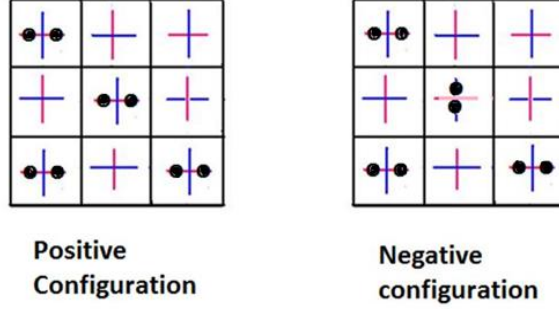


Fig. 5. Two typical configurations of singlet coupled time-reversed electron pairs (black balls referred to as a ‘dimer’ in the text) on the lattice with opposite signatures. Reproduced with the permission of J.Wiley (Modified from Dunne and Brändas [3])

Expansion in a basis of Slater determinants $\{\phi_k\}$ gives the many electron wave function as $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots) = \sum_k c_k \phi_k$. The set of variationally determined coefficients $\{c_k\}$ for a given state is obtained by calculation of the associated eigenvector of the Hamiltonian matrix where for the ground state $\{c_k\}$ is determined remarkably simply from the product $c_k = \prod_{i \in k} \sigma_i$ which runs over all occupied pairs of orbitals in the configuration k . In second quantized form the ground state wave function is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots) = \left(\sum_l (-1)^l (a^\dagger_{lp_x \uparrow} a^\dagger_{lp_x \downarrow} - a^\dagger_{lp_y \uparrow} a^\dagger_{lp_y \downarrow}) \right)^M |0\rangle \quad (8.1)$$

On average each configuration has $5M(I-\rho)$ nearest or next-nearest neighbor interactions with basis functions of opposite sign where there is one Wannier pair difference in the occupation numbers. The matrix elements between these states populate off-diagonal blocks of the Hamiltonian matrix.

The matrix element intracell two-electron integrals for px - py pair transfers inside cell is given by

$$v = \langle \phi_{i,px}(\mathbf{r}_1) \phi_{i,px}(\mathbf{r}_2) | v_{sr}(r_{12}) | \phi_{i,py}(\mathbf{r}_1) \phi_{i,py}(\mathbf{r}_2) \rangle \quad (8.2)$$

whereas next nearest neighbor pair transfer matrix elements between px - px (or py - py) orbitals, between cells i and are given by

$$V = \langle \phi_{i,px}(\mathbf{r}_1) \phi_{i,px}(\mathbf{r}_2) | v_{sr}(r_{12}) | \phi_{j,px}(\mathbf{r}_1) \phi_{j,px}(\mathbf{r}_2) \rangle \quad (8.3)$$

The Coulomb repulsion between a pair of electrons in the same pair of px - px (or py - py) Wannier orbitals is

$$u = \langle \phi_{i,px}(\mathbf{r}_1) \phi_{i,px}(\mathbf{r}_2) | v_{sr}(r_{12}) | \phi_{i,px}(\mathbf{r}_1) \phi_{i,px}(\mathbf{r}_2) \rangle \quad (8.4)$$

Significant values for V and v demand significant localized orbital overlap. Only nearest and next nearest neighbor interactions are important and can be neglected unless there is significant overlap. This happens most readily for Slater determinants with opposite signature and this feature renders the Hamiltonian matrix with block structure shown in Eqn(3.4) and discussed earlier.

If the minimum in $v_{sr}(r)$ falls outside the overlap region of two Wannier orbitals then the contribution of the attractive parts of $v_{sr}(r)$ to the matrix elements v and V will be small. At very short range screening is not really effective and so we may use the approximation

$$v \approx \langle \phi_{i,px}(\mathbf{r}_1) \phi_{i,px}(\mathbf{r}_2) | \frac{e^2}{\epsilon r_{12}} | \phi_{i,py}(\mathbf{r}_1) \phi_{i,py}(\mathbf{r}_2) \rangle \quad (8.5)$$

and similarly for V . Yet u defined in Eqn (8.4) can be effectively screened where the minimum in $v_{sr}(r)$ can make a significant contribution to lowering u so that it becomes less energetically demanding to bring a pair of electrons into the same Wannier orbital.

Let us assume for a very simple model in which the superconducting ground state energetically competes with a normal ground state whose wave function is a single Slater determinant Ψ_{normal} . In a localized basis with screened but locally strong Coulomb repulsions interactions and maximally unpaired electrons in the normal phase the energy is given by the expectation value of

$$\langle E \rangle = \langle H_{sr} \rangle + \sum_{k < k_c} \frac{1}{2} \hbar \omega_p - \frac{2\pi}{\epsilon \Omega} \left(\sum_{\mu} Z_{\mu}^2 \sum_{k < k_c} \frac{1}{k^2} \right) \quad (8.6)$$

But the last two terms do not contribute to the energy difference between states as long as the use of the same screening constant k_c is a reasonable approximation so that only $\langle H_{sr} \rangle$ is

important. An *estimate* of the energy of the short range Hamiltonian $\langle H_{sr} \rangle$ for such a normal state with the long-range part removed is

$$\langle H_{sr} \rangle = 2M \langle h \rangle + M_D u \quad (8.7)$$

M_D is the number of paired electrons in the configuration. $2M \langle h \rangle$ represents the one body terms. These energy differences between the superconducting state and such a normal state cancel. Thus assuming that the sum of the Plasmon zero point energies which describe long-range energy differences are the same in both the normal and superconducting state then we estimate of the energy difference/orbital between the energetically competing normal and superconducting phases as

$$\begin{aligned} (1-\rho)u - (4V+v)\rho(1-\rho) & \quad \text{if } \rho > 1/2 \\ \rho u - (4V+v)\rho(1-\rho) & \quad \text{if } \rho < 1/2 \end{aligned} \quad (8.8)$$

The energy expression given in (8.8) can become negative as the screening increases with doping and this allows the superconducting state to become the ground state, as depicted in Fig. 6.

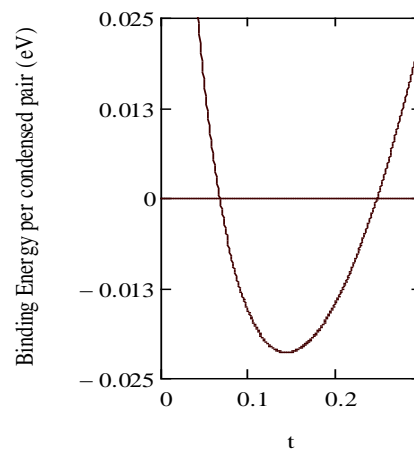


Fig 6. Binding energy /condensed pair against dopant concentration for the parameters discussed in the text. For electron doping $t=p$ and for hole doping $t=(1-p)$. The parameterization $u \approx \frac{e^2}{\epsilon L/2} \exp(-k_c L/2)$, $(4V+v)=0.64\text{eV}$ has been used. L is the unit cell length ($\approx 4\text{\AA}$). Reproduced from [5]. Copyright J. Wiley

The behavior of the appearance/ disappearance of superconductivity observed on doping is reproduced along with the well-known electron/hole doping symmetry.

9. Condensate Wave functions

For the wave function given in Eqn(9.1) the pair population density coefficient pair sub-matrix \mathbf{P} is given by

$$\begin{pmatrix} \frac{M}{N} & -M \frac{(N-M)}{N(N-1)} & M \frac{(N-M)}{N(N-1)} & \dots \\ -M \frac{(N-M)}{N(N-1)} & \ddots & \vdots & \vdots \\ M \frac{(N-M)}{N(N-1)} & \vdots & \frac{M}{N} & \vdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 1 \\ -1 \\ 1 \\ \vdots \\ \vdots \\ 1 \end{pmatrix} = \left(M \left(1 - \frac{M}{N} \right) + \frac{M}{N} \right) \begin{pmatrix} 1 \\ -1 \\ 1 \\ \vdots \\ \vdots \\ 1 \end{pmatrix} \quad (9.1)$$

Such a macroscopically large eigenvalue shown above which indicates a superconducting condensation also occurs for the ground state wave function given in Eqn (3.4). Hence, n-fold stabilization with ODLRO can occur with both the attractive and repulsive matrix elements in the Hamiltonian matrix of the type discussed above.

The matrix \mathbf{P} has a macroscopically large eigenvalue λ_L given by

$$\lambda_L = M \left(1 - \frac{M}{N} \right) + \frac{M}{N} \quad (9.2)$$

The associated eigenvector as given in Eqn(4.7) or in normalized form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \left(\rho - \rho^2 \right)^{1/2} \sum_l (-1)^l \left(a_{lpx\uparrow}^\dagger a_{lpx\downarrow}^\dagger - a_{lpy\uparrow}^\dagger a_{lpy\downarrow}^\dagger \right) |0\rangle \quad (9.3)$$

The macroscopically large eigenvalue represents a condensate of electron pairs and numerically equals Yang's upper bound [2] which was also derived by Sasaki⁴¹ in Uppsala at about the same time as Yang did his work but Sasaki's work is rarely discussed.

The superconducting condensate density n_s is proportional to $\lambda_L/N = \rho(1-\rho)$ and is an example Coleman's extreme case⁴² discussed by Weiner and Ortiz⁴³.

For hole doping when $\rho \rightarrow 1$ and electron doping when $\rho \rightarrow 0$ and then n_s is practically linear in the dopant density. This prediction has been discussed by Dunne⁵ who re-worked the analysis made by Dunne and Spiller⁵³ for 2 bands relevant to the case here and to which the reader is referred. Valence counting was used to calculate the hole densities used in ref[⁵³]. The result given in ref [⁵] is that the broad features of the experimental observations⁵⁴ are satisfactorily described by the theory. A model of thermal properties of the model is also given in ref[⁵]. The singlet condensate wave function has d-wave symmetry in \mathbf{k} -space and in real space and as shown below in Fig. 7(a),(b).

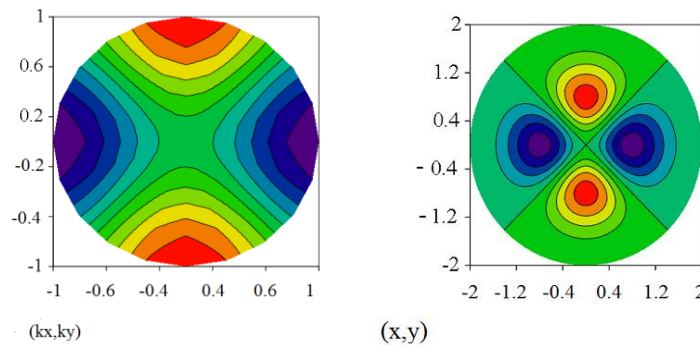


Fig. 7(a), (b) Shape of Cuprate condensate wave function in k-space(F_k) and real-space ($\psi(r)$). The relative coordinate is $r = r_1 - r_2$. The range over which $\psi(r)$ is significant measures the pair size or coherence length. In the above figures the range shown is 4\AA but the condensate wavefunction remains significant out to about 10\AA . The lobes with red and blue (dark and light in greyscale) centers have opposite signs. The green areas (grey in greyscale) are close to zero. Reproduced with the permission of J.Wiley (taken from Dunne and Brändas [³])

10. Role of Electron Correlation

An examination of the energy difference between the normal state and the superconducting state shows that there is a coherent lowering of the electronic energy on the cuprate lattice.

Let us focus simply on the electron doped case where we have the energy difference as

$\rho u - (4V + v)\rho(1 - \rho)$ from Eqn(8.8). The first term is the increase in Coulomb repulsion between the paired electrons. There is a long-range contribution to the integral u which is due to the minimum in v_{sr} . The latter term is a correlation term which arises from keeping pairs of electrons apart at very short range. It is of the utmost importance to appreciate that the last term is made up from contributions which act collectively to lower the energy. In Fig 3, for any unit cell the region in between red/blue lines for nearest and next nearest neighbours are regions of space with a reduced probability of finding a pair of electrons with opposite spin close together. This collective reduction in the Coulomb repulsion allows the attractive part of the long-range Bohm-Pines potential to play a significant role in the energetics.

The sign alternation in the condensate wave function indicates that a ‘hole’ develops in regions of space around each electron keeping pairs of electrons out of the hard-core Coulombic repulsion. This allows them to reside with higher probability at the minimum of $v_{sr}(\mathbf{r})$.

A weakness in the current approach is the use of a uniform high-frequency dielectric constant ϵ . It has been shown recently^{55,56} that a two-electron system can hold a bound state with a mean nuclear-electron distance $\langle r \rangle = 3.5\text{\AA}$ for the outer electron at the critical nuclear charge for binding. It would be highly interesting to study a 2 electron atomic problem with the nucleus replaced by a polarizable body to mimic the Cu atom in the situation shown in Fig.7.

Finally we remark that electron correlation was central to Per Olov’s work and in refs [40,57,58] the ground work for key aspects of the discussion in this contribution was laid. Also, in his book⁵⁹ on linear algebra he discusses the ‘mirror theorem’. In principle, it goes beyond the Born–Oppenheimer (BO) approximation. A superconductor would be divided into two parts: (a) the light fermions and (b) the heavy nuclear framework which are linked through the ‘mirror theorem’. Investigating the consequences of this linkage for superconductors possibly by tracing over the nuclear coordinates might be of interest.

11. References

- ¹ J.F Annett. “ Superconductivity, Superfluidity and Condensates” Oxford University Press. Oxford 2004
- ² Yang, C. N. Concept of Off-Diagonal Long-Range Order and the Quantum Phases of Liquid He and of Superconductors; *Rev. Mod. Phys.* **1962**, 34, 694–704.
- ³ Dunne, L. J.; Brändas. E. J. Superconductivity from Repulsive Electronic Correlations on Alternant Cuprate And Iron-Based Lattice; *Int. J. Quantum Chem.* **2013**, 113, 2053-2059
- ⁴ L. J. Dunne and E. J. Brändas. Review of Off-Diagonal Long-Range Order and High-Temperature Superconductivity from Repulsive Electronic Correlations. *Adv. Quant. Chem.* **2013**, 66, 1-30
- ⁵ Dunne, L J. High-temperature superconductivity and long-range order in strongly correlated electronic systems *Int. J. Quant. Chem.* **2015**, 115, 1443-1458
- ⁶ Dunne, L.J., Murrell, J.N., Brändas, E.J. Off-Diagonal Long Range Order from Repulsive Electronic Correlations in a Localised Model of a High Tc Cuprate Superconductor; *Physica* **1990**, C 169, 501-507
- ⁷ L. J Dunne. Off-Diagonal Long-Range Order and Essential Phenomenological Description of some Properties of High Tc Cuprate Superconductors

Physica **1994**, C 223, 291-312

⁸ Bednorz, J. G.; Müller, K. A. Possible High T_c Superconductivity in the Ba-La-Cu-O System; *Z. Phys. B* **1986**, 64, 189–193.

⁹ Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs (x=0.05–0.12) with T_c=26 K; *J. Am. Chem. Soc.* **2008**, 130, 3296–3297.

¹⁰ Takahashi, H.; Igawa, K.; Arii, K.; Kamihara, Y.; Hirano, M.; Hosono, H. Superconductivity at 43 K in an Iron-Based Layered Compound LaO_{1-x}F_xFeAs; *Nature* **2008**, 453, 376–378.

¹¹ Andersen, O. K.; Boeri, L. On the Multi-Orbital Band Structure and Itinerant magnetism of Iron-Based Superconductors; *Ann. Phys.* **2011**, 523, 8–50.

¹² Neven Barišić, Mun K. Chan, Yuan Li, Guichuan Yu, Xudong Zhao, Martin Dressel, Ana Smontara, Martin Greven, Universal sheet resistance and revised phase diagram of the cuprate high-temperature superconductors
Proc. Natl. Acad. Sci. USA **2013**, 110 30, 12235-12240
doi:10.1073/pnas.1301989110

¹³ For a good review of early work see Leggett, A. J. *Quantum Liquids*; Oxford University Press: New York, 2006.

¹⁴ see eg *BCS: 50 Years*, World Scientific Publishing Co. Pte. Ltd 2011 Edited by Leon N Cooper and Dmitri Feldman

¹⁵ Sumitendra Mazumdar ; Rudolf Torsten Clay. The Chemical Physics of Unconventional Superconductivity *International Journal of Quantum Chemistry*, **2014** 114(16), 1053-1059

¹⁶ Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. Theory of Superconductivity; *Phys. Rev.*

1957, 108, 1175–1204.

¹⁷ Bardeen J and Pines D. Electron-Phonon Interaction in Metals, *Phys. Rev.* **1955**, 99, 1140-1150

¹⁸ Bohm, D.; Pines, D. A Collective Description of Electron Interactions: III. Coulomb Interactions in a Degenerate Electron Gas, *Phys. Rev.* **1953**, 92, 609–625.

¹⁹ Dunne, L J; Order in superconductors and the repulsive electronic correlation model of high Tc cuprate superconductivity *Theochem-journal of Molecular Structure* **1995**, 341, 101-114

²⁰ A. Huang, Theoretical Solid State Physics, Pergamon Press, Oxford, 1972

²¹ B. Donovan, Elementary Theory of Metals, Pergamon Press, Oxford 1967

²² Wollman, D. A.; Van Harlingen, D. J.; Lee, W. C.; Ginsberg, D. M.; Leggett, A. J. Experimental-Determination of the Superconducting Pairing State in YBCO from the Phase Coherence of YBCO-Pb DC Squids. *Phys. Rev. Lett.* **1993**, 71, 2134–2137.

²³ Tsuei, C. C.; Kirtley, J. R. Phase-Sensitive Tests of Pairing Symmetry in Cuprate Superconductors; *Physica*. **1997**, 282–287 C, 4–11.

²⁴ Tsuei, C. C.; Kirtley, J. R. Pairing Symmetry in Cuprate Superconductors; *Rev. Mod. Phys.* **2000**, 72, 969–1016.

²⁵ P.W Anderson, Plasmons, Gauge Invariance, and Mass; *Phys. Rev.* **1962**, 130, 439-442

- ²⁶ J. Schwinger, Gauge Invariance, and Mass, *Phys.Rev* ,**1962**, 125, 397-398
- ²⁷ P. Higgs , Broken Symmetries and the Masses of Gauge Bosons
Phys. Rev.Lett; **1964** 13, 508-509
- ²⁸ R.E Allen, The London–Anderson–Englert–Brout–Higgs–Guralnik–Hagen–Kibble–Weinberg mechanism and Higgs boson reveal the unity and future excitement of physics *J. Modern Optics* **2013** DOI: 10.1080/09500340.2013.818170
- ²⁹ Greiter M, Is Electromagnetic Gauge Invariance Spontaneously Violated in Superconductors?
Annals of Physics **2005**, 319 , 217-219
- ³⁰Negele J.W and Orland H, Quantum Many-Particle Systems Frontiers in Physics, Addison-Wesley 1988
- ³¹ . Dunne, L. J.; Brändas, E. J. Possible New Coherence Effects in Condensed Systems with Repulsive Interactions; *Phys. Lett.* **1979**, A 71, 377–381. See also misprint correction *Phys. Lett.* **1990**, A149, 488, 377–381.
- ³² Scalapino, D. J. The case for $d_{x^2-y^2}$ pairing in the cuprate superconductors; *Phys. Rep.* **1995**, 250, 329–365.
- ³³ Brändas, Erkki; Dunne, Lawrence J. Bardeen-Cooper- Schrieffer BCS theory and Yang's concept of off- diagonal long- range order ODLRO *Molecular Physics*, **2014**, 112 Issue: 5-6 Special Issue: SI 694-699
- ³⁴ London, F. Superfluids; Wiley: New York, 1950
- ³⁵ Gorter, C. J.; Casimir, H. B. G. On supraconductivity I; *Physica* **1934**, 1, 306–320.

- ³⁶ Ginsburg, V. L.; Landau, L. D. On theory of superconductivity; *Zh. Eksperim. I. Teor. Fiz.* **1950**, 20, 1064–1082.
- ³⁷ Penrose, O.; Onsager, L. Bose-Einstein Condensation and Liquid Helium; *Phys. Rev.* **1956**, 104, 576–584.
- ³⁸ L. P Gorkov – see *Methods of Quantum Field Theory in Statistical Physics* A.A Abrikosov, L.P Gorkov and I.E Dzyaloshinski , Dover Publications New York 1963, Translated and edited by R A Silverman.
- ³⁹ R Mc Weeney and B. T.Sutcliffe *Methods of Molecular Quantum Mechanics* Academic Press, New York 1969
- ⁴⁰ Löwdin, P. O. Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction; *Phys. Rev.* **1955**, 97, 1474–1489.
- .
- ⁴¹ Fukashi Sasaki, Eigenvalues of Fermion Density Matrices. *Phys Rev.* **1965** 138B ,1338 - 1342,
Technical Note Quantum Chemistry Group, University of Uppsala, Sweden, **1962** no 77
- ⁴² Coleman, A. J. Structure of Fermion Density Matrices; *Rev.Mod. Phys.* **1963**, 35, 668–689.
- ⁴³ Weiner, B.; Ortiz, J. V. Construction of Unique Canonical Coefficients for Antisymmetrized Geminal Power States; *Int. J. Quant. Chem.* **2004**, 97, 896–907.
- ⁴⁴ Alexandra Raeber, David A. Mazziotti, Large eigenvalue of the cumulant part of the two-electron reduced density matrix as a measure of off-diagonal long-range order, *Physical Review* **2015** DOI: 10.1103/PhysRevA.92.052502

⁴⁵ Theory of Quantum Liquids Vol. I David Pines and Philippe Nozières, W.A. Benjamin, Inc. New York, 1966

⁴⁶ S. Raimès, Theory of Plasma Oscillations in Metals . *Rep. Prog. Phys.* **1957** ,vol 20 ,1-37

⁴⁷ Mott, N. F.; Davis, E. A. Electronic Processes in Non-crystalline Materials; Clarendon Press: Oxford, UK, 1971.

⁴⁸ Blandin, A.; Daniel, E.; Friedel, J. On the Knight Shift of Alloys; *Philos. Mag.* **1959**, 4, 180–182.

⁴⁹ N. H. March and A. M. Murray, Electronic Wave Functions Round a Vacancy in a Metal *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **1960**, 256, No. 1286 pp. 400-415

⁵⁰ S. Langer, S.H. Vosko , The shielding of a fixed charge in a high-density electron gas , *Journal of Physics and Chemistry of Solids* 1960, 12, Issue 2, 196-205

⁵¹ Dunne, L. J.; Brändas, E. J.; Murrell, J. N.; Coropceanu, V. Group Theoretical Identification of Active Localised Orbital Space in High Tc Cuprate Superconductors; *Solid State Commun.* **1998**, 108, 619–623

⁵² H. Eskes, L.H Tjeng and G.A Sawatzky, Cluster-model calculation of the electronic structure of CuO: A model material for the high-Tc superconductors *Phys.Rev.* **1990**, 41B 288-299

⁵³ Dunne, L. J.; Spiller, T. P. Condensate Fraction in High Tc Cuprate Superconductors; *J. Phys. Condens. Matter* **1993**, 4, L563.

⁵⁴ Y.J. Uemura. and Luke, G. M. and Sternlieb, B. J. and Brewer, J. H. and Carolan, J. F. and Hardy, W. N. and Kadono, R. and Kempton, J. R. and Kiefl, R. F. and Kretzmann, S. R. and Mulhern, P. and Riseman, T. M. and Williams, D. Ll. and Yang, B. X. and Uchida, S. and

Takagi, H. and Gopalakrishnan, J. and Sleight, A. W. and Subramanian, M. A. and Chien, C. L. and Cieplak, M. Z. and Xiao, Gang and Lee, V. Y. and Statt, B. W. and Stronach, C. E. and Kossler, W. J. and Yu, X. H

Universal Correlations between T_c and n_s/m^* (Carrier Density over Effective Mass) in High- T_c Cuprate Superconductors *Phys. Rev. Lett.* **1989**, 62, 2317-2320

⁵⁵ A.W King, L.C Rhodes and Hazel Cox , Inner and Outer radial Density Functions in Correlated two-electron Systems, *Phys. Rev A* **2016**, 93 , 022509

⁵⁶ A.W King, L.C Rhodes, C.A Readman and Hazel Cox, Effect of Nuclear Motion on the Critical Nuclear Charge for two-electron systems *Phys. Rev A* **2015**, 91 , 042512

⁵⁷ Löwdin, P.-O. Some Aspects of the Correlation Problem and Possible Extensions of the Independent-Particle Model; *Adv. Chem. Phys.* **1969**, 14, 283–340

⁵⁸ Löwdin, P.-O Band Theory, Valence Band Tight-Binding Calculations. *J. Appl. Phys.* **1962**, 33, 251-280,

⁵⁹ P.-O. Löwdin, *Linear Algebra for Quantum Theory* (Wiley-Interscience, New York, 1998).