Properties of Bound Electron Pairs

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Abstract
The energies of spin singlet and triplet bound electron pairs are reckoned for electrons interacting through the Coulomb interaction, while sitting on neighboring lattice sites. It is concluded that triplet pairs are unlikely to be observed due to screening. The interplay of inter-electron couplings of different spatial range is investigated. High-pressure induced superconductivity is analysed and qualitative agreement is achieved with observed results by working out the dependence of the critical temperature on the microscopic parameters, characterising the electron motion. This approach can be applied to other kinds of inter-electron interactions.

Keywords Cooper pair · BCS theory · Pairing symmetries

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1 Introduction
The paramount role of bound electron pairs in superconductivity [1, 2] has ever been known since Cooper’s seminal work [3], even though assuming an attractive interaction between electrons, as done by Cooper and furthermore by BCS [4], has been shown to be inconsistent with persistent currents [5], thermal equilibrium [6], occurrence of a second order transition [7, 8] at the critical temperature $T_c$ and the Josephson effect [9]. Nevertheless it has been established [6] that the bound electron pair of energy $\epsilon_B$ turns continuously into a many bound electron (MBE) state, carrying persistent currents, at finite electron concentration $c_s$. In particular, there is [5, 6]

$$\mu(c_s = 0) = \frac{\epsilon_B}{2},$$

with $\mu(c_s)$ being the chemical potential of superconducting electrons, making up the MBE state. Besides describing the inter-electron coupling by means of the Hubbard Hamiltonian [3, 4, 6, 8] entails, as a consequence of Pauli’s principle, that the spin of any bound pair can be but equal to 0 and the ensuing MBE state has thence vanishing spin too, which has been confirmed experimentally [1, 2]. However this broaches the issue of why it is so, because, as shown below, triplet pairs do indeed arise, if electrons, sitting on neighboring sites, are allowed to interact.

Yet, opposing the hereabove statement, experimental evidence of spin triplet pairs was reported [10, 11] in superconducting materials of type II, subjected to a magnetic field $H$, giving rise to a vortex lattice. Actually, it was inferred from the magnetisation $M$ being temperature independent, while crossing $T_c$. However, due to the Meissner effect, $H$ and thence $M$ are bound to vanish in bulk superconducting matter. Furthermore, the macroscopic susceptibility should be diamagnetic, as resulting from Lenz’s law [12–14], and weak with respect to the paramagnetic (Pauli-like) one, associated with the spin of normal electrons [15], and it ought to have thence the opposite sign. Therefore, the most likely conclusion is that the measurements [10, 11] have actually probed but the magnetisation of normal electrons inside the vortices.

Another topic of significance is pressure proving instrumental on $T_c$, particularly after the recent discovery of high-pressure induced superconductivity at room-temperature [16–18]. It has been known [19] for long that pressure gives rise to opposite trends in low- and high-$T_c$ superconductors, respectively. Regarding these materials, exhibiting no isotope effect, no cogent explanation has been offered so far, whereas a theory, based on Eliashberg’s work [20], has been
widely used for those which do so. Unfortunately it relies heavily on the BCS theory [4], which has been proved to be marred [5–9] by major inconsistencies, recalled above. Likewise a cornerstone assumption of the BCS scheme [4] requires that the electron-phonon interaction reverse the sign of the Coulomb repulsive force and thus give rise eventually to an effective, attractive coupling between two electrons, located on the same atomic site. However a more accurate treatment [7] has disproved such a statement. Therefore this work is also intended at investigating how pressure alters the microscopic parameters [8], governing the motion of electrons coupled through the Coulomb interaction, and assigns thereby $T_c$.

The outline is as follows: Sect. 2 deals with the properties of bound pairs, resulting from first neighbour electrons, coupled through the Coulomb repulsion; the role of the interaction range is elucidated in Sect. 3, while high-pressure induced superconductivity is addressed in Sect. 4; the physical significance of this work is stressed in Sect. 5.

2 Bound Electron Pairs

For simplicity, a one-dimensional ($d = 1$) lattice, containing $N >> 1$ of atomic sites labelled by index $i = 1, .., N$, is considered. The lattice parameter is taken equal to unity and each site can accommodate at most two electrons of opposite spin $\sigma = \pm 1/2$. The Hamiltonian $H_1$ then reads

$$H_1 = \sum_{i,j,\sigma} \left( \frac{\hbar^2}{2m} c^+_i c_{i,\sigma} + c^+_i c_{j,\sigma} \right) + (U_1 - J) c^+_i c_{i,\sigma} c_{j,\sigma} + U_1 c^+_i c^+_j c_{i,\sigma} c_{j,\sigma} - J c^+_i c^+_j c_{i,\sigma} c_{j,\sigma}$$

wherein the sum is carried out over $\sigma = \pm 1, i = 1, .., N - 1$ with $j = i + 1$ and $c^+_i, c_{i,\sigma}$ are one-electron creation and annihilation operators on the Wannier [15] state $|i, \sigma\rangle$

$$|i, \sigma\rangle = c^+_i |0\rangle, \quad |0\rangle = c_{i,\sigma} |i, \sigma\rangle,$$

with $|0\rangle$ being the no electron state. Then $\hbar^2, U_1, J$ designate the hopping, Coulomb and exchange integrals, respectively

$$t = 2 \langle c_{i,\sigma} V_e c_{i,\sigma} \rangle, \quad U_1 = \langle c_{i,\sigma} c_{i,\sigma} V_e c_{i,\sigma} \rangle, \quad J = \langle c_{i,\sigma} c_{i,\sigma} V_e c_{i,\sigma} \rangle$$

with $V_e$, $V_e$, referring to the electron-nucleus and electron-electron Coulomb potentials, respectively. Note that there is in general $|J| << U_1$ due to the Wannier wave-functions decaying exponentially [15] with growing inter-atomic distance.

It is convenient to recast $H_1$ into momentum space. To that end, let us first recall the definitions of the one-electron creation and annihilation operators on the Bloch [15] state $|k, \sigma\rangle$

$$\langle k, \sigma | c^+_k \rangle = \delta_{k,0} |0\rangle, \quad \langle 0 | c_{k,\sigma} \rangle = \langle k, \sigma | 0 \rangle,$$

with $k$ being any vector of the Brillouin zone, fulfilling periodic boundary conditions. They enable us to introduce the pair creation and annihilation operators [6, 21]

$$b^+_i \cdot \vec{K} \cdot \vec{k} = c^+_k c^+_k, \quad b^+_i \cdot \vec{K} \cdot \vec{k} = c^+_k c^+_k, \quad b^+_i \cdot \vec{K} \cdot \vec{k} = c^+_k c^+_k,$$

with $\vec{K}$ being any vector of the Brillouin zone and the subscripts $s, t$ referring to singlet and triplet, because the spin $\zeta$ of the corresponding electron pair, projected onto any axis, is equal to 0, ±1, respectively. The hereabove definitions deserve some further comments:

- those pair operators are neither bosons, nor fermions, but the operational rules, governing their algebraic properties, will be given below in section IV;
- the notation $s, t$, albeit convenient, is not exact, because the true singlet and triplet pair states with $\zeta = 0$, read actually $\left( b^+_i \cdot \vec{K} \cdot \vec{k} \pm b^+_i \cdot \vec{K} \cdot \vec{k} \right) |0\rangle$.

Then $H_1$ reads in momentum space

$$H_1 = H_d + \sum_k (H_k^e + H_k^s)

$$

$$H_d = \sum_{k,\sigma} \epsilon(k) c^+_k c_{k,\sigma}, \quad \epsilon(k) = t \cos(k)

$$

$$H_k^e = \frac{1}{N} \sum_{k,k'} V_k V_k^t b^+_k b_{k',k'}

$$

$$V_k = (U_1 - J) \cos(k - k'),

$$

$$H_k^s = \frac{1}{N} \sum_{k,k'} V_k V_k^s b^+_k b_{k',k'}

$$

$$V_k = 2(U_1 \cos(k - k') + J \cos(K - k' - k'))

$$

where the sums over $K, k, k'$ are to be carried out over the whole Brillouin zone. The Hamiltonian $H_d$ describes the motion of independent electrons of one-electron energy $\epsilon(k)$, whereas $H_k^e, H_k^s$ account for two-electron scattering of triplet and singlet pairs, respectively. Due to Pauli’s principle, there is $V_k V_k^t \neq V_k V_k^s$, so that the outcome of two-electron scattering differs [21] according to whether the incoming electrons have same or opposite spin direction, although the Coulomb interaction is spin-independent.

Because of $H_k^e, b^+_k b_{k'} |0\rangle = 0$ if $K \neq K'$ or $\alpha \neq \alpha'$, each solution $\psi, \epsilon$ of the Schrödinger equation, written for a single pair,
\( (H_d + H^{s=\pm}_K - \varepsilon) \psi = 0 \)

is also a solution \([21]\) of
\( (H_1 - \varepsilon) \psi = 0 \).

Besides, triplet pairs are such that \( b_{t,k} = -b_{t,K,k}^{+} \), which entails \( \sum_k = \frac{1}{2} \), by contrast with singlet pairs for which there is \( b_{s,k} = b_{s,K,k}^{+} \Rightarrow \sum_k = N \). Two consequences can be deduced from this property

- the Schrödinger equation for one singlet pair has twice more solutions than for one triplet pair;
- the following identity ensues for any function \( f(k) \) in case of \( N \rightarrow \infty \)

\[
\sum_k \frac{f(k)}{N} = \int_{-\pi}^\pi f(k) \rho(k) dk ,
\]

with \( \rho(k) = \frac{1}{4\pi} \) and \( \rho(k) = \frac{1}{2\pi} \) for triplet and singlet pairs, respectively.

Let us begin with solving the Schrödinger equation for one triplet pair

\[
(H_d + H_K - \varepsilon(K)) \psi = 0, \psi = \sum_k a(k) b_{t,K,k}^{+}|0\rangle
\]

\[
\alpha(k) = \sum_{k'} \alpha(k') \frac{V_{k,k'}}{N(\varepsilon(k')-\varepsilon(k))} \}
\]

\[
\frac{U_{1/2}}{U_{1/2}} \Delta_S = \sum_k \frac{\varepsilon(k)-\varepsilon(K)}{\sin(k) N} , \quad \Delta_S = \sum_k \frac{a(k)\sin(k)}{N}
\]

Equation (2) can then be recast as a homogeneous system of two linear equations in terms of two unknowns \( \Delta_s, \Delta_j \)

\[
\Delta_j \left( \frac{1}{U_{1/2}} - S_{cc} \right) - \Delta_s S_{cc} = 0
\]

\[
\Delta_s S_{cc} + \Delta_j (S_{cc} - \frac{1}{U_{1/2}}) = 0
\]

with \( S_{cc}, S_{ct}, S_{st} \) defined as follows in case of \( N \rightarrow \infty \)

\[
S_{cc} = \int_{-\pi}^\pi \frac{\cos^2(k) - \varepsilon(K)}{4\pi} \frac{dk}{\sin(2k)} \quad S_{ct} = \int_{-\pi}^\pi \frac{\sin(k) - \varepsilon(K)}{4\pi} \frac{dk}{\sin(2k)} \quad S_{st} = \int_{-\pi}^\pi \frac{\cos^2(k) - \varepsilon(K)}{4\pi} \frac{dk}{\sin(2k)}
\]

Finally, \( \varepsilon(K) \) is found by equating to 0 the determinant of the system in Eq. (3).

\[
(\varepsilon_1, \varepsilon_2, \Delta_s, \Delta_j) = \Delta_s \frac{U_{1/2}}{U_{1/2}} \Delta_j \] \[ \Delta_j \left( U_{1/2} \cos^2(k) + J \cos^2(k) \right) + \Delta_s \left( U_{1/2} \sin(k) + J \sin^2(k) \right) = 0
\]

Equation (5) is recast into a homogeneous system of two linear equations in terms of the same unknowns \( \Delta_s, \Delta_j \)

\[
\Delta_s \left( U_{1/2} \cos^2(k) + J \cos^2(k) \right) + \Delta_j \left( U_{1/2} \sin(k) + J \sin^2(k) \right) = 0
\]

marked contrast with the Hubbard Hamiltonian, for which there is a bound electron pair in one and two dimensions, even though the on-site Coulomb integral

\[
U_0 = \langle 0| c_{i,-} c_{i,+} V_{i,i+} c_{i+,-} c_{i+,-}|0\rangle
\]

go \([3, 6, 8]\) down to 0. Due to screening, there is \( U_1 < U_0/5 \), so that \( U_1 > 5t \) is unlikely to occur in metals because of \( U_0 \approx t \). Finally it is impossible to have \( U_1 > J \), which accounts for no triplet bound pair being indeed observed \([1, 2]\) in any superconductor.

The singlet pair eigenvalues will be calculated too, because they are needed for the next section. The Schrödinger equation reads then

\[
(H_d + H_K - \varepsilon(K)) \psi = 0, \psi = \sum_k a(k) b_{s,K,k}^{+}|0\rangle
\]

\[
\alpha(k) = \sum_{k'} \alpha(k') \frac{V_{k,k'}}{N(\varepsilon(k')-\varepsilon(k))} \}
\]

\[
\frac{U_{1/2}}{U_{1/2}} \Delta_S = \sum_k \frac{\varepsilon(k)-\varepsilon(K)}{\sin(k) N} , \quad \Delta_S = \sum_k \frac{a(k)\sin(k)}{N}
\]
with $S_{cc}, S_{ct}, S_{ss}$ defined this time as follows for $N \to \infty$

\[
S_{cc} = \int_{-\pi}^{\pi} \frac{\cos^2(k)}{\epsilon(k) - \epsilon(K, k)} \frac{dk}{2\pi}, \\
S_{ct} = \int_{-\pi}^{\pi} \frac{\sin^2(k)}{\epsilon(k) - \epsilon(K, k)} \frac{dk}{4\pi}, \\
S_{ss} = \int_{-\pi}^{\pi} \frac{\sin(k)}{\epsilon(k) - \epsilon(K, k) - \epsilon(\bar{K}, \bar{k})} \frac{dk}{2\pi}. 
\]

(6)

The resulting eigenvalues have been plotted in Fig. 2. Similarly to Eq. (3), Eq. (5) has at most two solutions $\epsilon_1(K) < \epsilon_2(K)$, associated with a *bound* pair but, in contrast with triplet pairs, they are not degenerate at $K = \pi$, that is $\epsilon_1(\pi) = U_1 - J \neq \epsilon_2(\pi) = U_1 + J$. Likewise $\epsilon_1(K), \epsilon_2(K)$ vanish quickly for $U_1/t$ decreasing under 1.2. Even though this threshold value, for a singlet pair to arise, is less demanding than for a triplet pair, a singlet pair, made up of electrons interacting on first neighbouring sites, is unlikely to be observed because of screening, too. However, it is of interest to study to which extent such a weak inter-electron coupling, embodied by $U_1 < U_0, J << U_0$, might modify the energy of a bound pair, stemming from the much stronger Hubbard interaction. This is the purview of the next section.

### 3 Role of the Interaction Range

Let us consider the Hamiltonian $H_2$, defined as

\[
H_2 = H_0 + H_1 - H_d, 
\]

where $H_1, H_d$ are defined in Eq. (1) and $H_0$ refers to the one-dimensional Hubbard Hamiltonian, recalled below [6, 21].

\[
H_0 = H_d + \sum_k H_k, \quad V^s_{K,k,k'} = U_0, \quad \forall K, k, k'. 
\]

Thus $H_2$ reads as expressed in Eq. (1), but with $U_0$ being added to every $V^s_{K,k,k'}$. Conversely, $H_d$ remains unaltered, because of $V^t_{K,k,k'} = 0, \quad \forall K, k, k'$ for $H_0$.

The Hubbard Hamiltonian has long been known to sustain one singlet bound pair [3, 6] of energy $\epsilon_0(K)$, obtained by solving the following equation [6, 8]

\[
\frac{2\pi}{U_0} = \int_{-\pi}^{\pi} \frac{dk}{\epsilon_0(K) - \epsilon(K, k)}. 
\]

(7)

The dispersion of $\epsilon_0(K)$ has been calculated for $U_0 = t$ and plotted in Fig. 3. There is $\epsilon_0(\pi) = \epsilon_0$. Though $H_0$ sustains a bound pair even for $U_0 \to 0$ in one and two dimensions [3, 6, 8], the prerequisite $\Delta s < .5$ must still be fulfilled [6, 8] for a bound pair to arise in three dimensions.

Combining $H_0$ and $H_1$ will cause $\epsilon_0(K)$ to shift to the singlet bound pair energy $\eta(K)$ of $H_2$, to be reckoned as follows

\[
(H_2 - \eta(K))\psi = 0, \quad \psi = \sum_k a(k)\phi^*_K |0\rangle \\
\eta(K) = U_0\Delta_0 + 2\Delta_s (U_1 \cos(k) + J \cos(K - k)) + \Delta_s (U_1 \sin(k) + J \sin(K - k)) 
\]

(8)

with $\epsilon(K, k), \Delta_s$ defined as in Eq. (2) and $\Delta_0$ reading

$\Delta_0 = \sum_k a(k)/N$.
Equation (8) can be recast as a homogeneous system of linear equations in terms of three unknowns $\Delta_0, \Delta_c, \Delta_s$

\[
\begin{bmatrix}
\Delta_0 \\
\Delta_c \\
\Delta_s
\end{bmatrix} = 0
\]

The $3 \times 3$ matrix $A$ reads then

\[
\begin{align*}
A_{1,1} &= U_0 S_c - 1, \quad A_{2,1} = U_0 S_s, \quad A_{3,1} = U_0 S_s \\
A_{1,2} &= 2(U_1 S_c + J \sin(K) S_s) \\
A_{1,3} &= 2(U_1 S_c + J \sin(K) S_c) \\
A_{2,2} &= 2(U_1 S_c + J \sin(K) S_s) - 1 \\
A_{2,3} &= 2(U_1 S_s + J \sin(K) S_s) - 1 \\
A_{3,2} &= 2(U_1 S_s + J \sin(K) S_c) \\
A_{3,3} &= 2(U_1 S_s + J \sin(K) S_s) - 1
\end{align*}
\]

with $S_0, S_c, S_s$ reading for $N \to \infty$

\[
S_c = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \frac{\sin(k)}{\eta(K) - \epsilon(K) - \Delta} \\
S_s = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \frac{\sin(k)}{\eta(K) + \epsilon(K) + \Delta}
\]

$S_{cc}, S_{cs}, S_{ss}$ are defined as in Eq. (6), but with $\eta(K)$ showing up instead of $\epsilon(K)$. Finally the dispersion curve $\eta(K)$ is obtained by equating the determinant of $A$ to 0. We have chosen to plot rather $\epsilon_0(K) = \frac{\eta(K)}{\epsilon_0(K)} - 1$ in Fig. 3, because the small, upward shift of $\epsilon_0$ toward $\eta$, observed for the highest $U_1$ value, illustrates how barely the long range Coulomb coupling affects the pair energy obtained for the Hubbard model. Hence any interaction beyond first neighbours can be neglected because of screening. Besides, note that the curves $\epsilon_{i=1,2}(K)$ of $H_2$ have merged into the continuum $[-t_K, t_K]$ because the chosen $U_1$ values are below the threshold $U_{c1} \approx 1.2$.

### 4 Role of Pressure

Pressure is expected to cause the lattice parameter to decrease and hence $t$ to increase due to increasing overlap of Wannier wave-functions $c_{i\sigma}^+|0\rangle$, $c_{i+1\sigma}^+|0\rangle$, whereas $U_0$ is likely to be hardly altered, because it is almost independent from the lattice parameter. Thus let us begin with analysing the dependence of $T_c$ upon decreasing $U_0/t$ for the Hubbard Hamiltonian $H_0$. Hence, as done elsewhere [5–8], the conduction electrons are taken to compose bound and independent electrons, in respective temperature dependent concentration $c_1(T), c_2(T)$, such that

\[
c_0 = c_1(T) + c_2(T)
\]

with $c_0$ being the total concentration. The conduction electrons are organised as a many bound electron [6, 8] (MBE)

state and a Fermi gas [15], characterised, respectively, by the chemical potential $\mu(c_s)$ and the Fermi energy $E_F(T, c_n)$. Then the necessary conditions for a second order transition to occur at $T_c$ read [7, 8]

\[
E_F(T_c, c_0) = \mu(0), \quad \rho'(E_F(T_c, c_0)) > 0
\]

\[
\frac{dE_F}{dc_n}(T_c, c_0) = -\frac{d\mu}{dc_s}(0), \quad \frac{dE_F}{dc_n} > 0, \quad \frac{d\mu}{dc_s} < 0,
\]

for which $\rho(e)$, $e$ refers to the one-electron density of states and energy [15] and $\rho'(e) = \frac{d\rho}{de}$. Equation (9) expresses the property that the set of conduction electrons is at stable, thermal equilibrium [5] at $T_c$, whereas Eq. (10) ensures that the superconducting phase is stable [7, 8] with respect to the normal one for $T < T_c$.

Since the normal electrons make up a degenerate Fermi gas (\( \Rightarrow T_c << EF/k_B \) with $k_B$ being Boltzmann’s constant), the Sommerfeld expansion [15] can be used up to $T^2$ and yields

\[
E_F(T_c, c_0) = E_F(0, c_0) - \frac{\rho'(\frac{\pi}{6} k_B T_c^2)^2}{\rho} \frac{\dot{\epsilon}_0(K)}{6}
\]

\[
\frac{dE_F}{dc_n}(T_c, c_0) = \left( \rho + \rho'' \frac{\pi}{6} k_B T_c^2 \right)^2
\]

with $\rho = \rho(E_F(0, c_0), \rho' = \frac{d\rho}{dE_F}(E_F(0, c_0)), \rho'' = \frac{d^2\rho}{dE_F^2}(E_F(0, c_0))$. Likewise, the following results have been worked out [5, 6]

\[
\frac{d\mu}{dc_s}(K, c_s = 0) = -\frac{\epsilon_0(K)}{2} \int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0} = -\int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0} \int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0}
\]

\[
\mu(K, c_s = 0) = \epsilon_0(K) \int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0} = \frac{\epsilon_0(K)}{2} \int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0} = \frac{\epsilon_0(K)}{2} \int_{-\Delta}^{\Delta} \frac{d\epsilon}{\pi t_0}
\]

The $T_c$ dependence on $U_0/t$ will be discussed by assuming the following one-electron density of states

\[
\rho(e) = \frac{2}{\pi t_0} \sqrt{1 - \left( \frac{e}{t_0} \right)^2}
\]

with $e \in [-t_0, t_0]$ (\( \Rightarrow \int_{-\Delta}^{\Delta} \rho(e)de = 2 \) electrons per atomic site). Remarkably, the condition $\rho'(E_F(T_c, c_0)) > 0$ in Eq. (9) requires $c_0 > 1$, whereas the opposite condition $c_0 < 1$ must be fulfilled in the three-dimensional case [8].

Combining Eqs. (9, 10, 11, 12) yields [8] finally a system of two equations

\[
E_F - \frac{\rho'(\frac{\pi}{6} k_B T_c^2)^2}{\rho} = \epsilon_0(K)
\]

\[
\left( \rho + \rho'' \frac{\pi}{6} k_B T_c^2 \right)^2 + \frac{d\mu}{dc_s}(K, c_s = 0) = 0
\]

to be solved for the unknowns $K(E_F, T_c), U_0(E_F, T_c)$ with
Table 1 Solutions

| $K$ | $c_0$ | $U_0(T_1)$ | $u_0(T_1)$ | $E_0(T_1)$ | $K(T_2)$ | $u_0(T_2)$ | $E_0(T_2)$ |
|-----|-------|------------|------------|------------|------------|------------|------------|
| 1.64 | .977 | .33 | .169 | .914 | .174 | .16 |
| 1.66 | .932 | .27 | .172 | .908 | .151 | .162 |
| 1.68 | .919 | .242 | .175 | .904 | .128 | .164 |
| 1.7  | .91  | .219 | .178 | .9    | .106 | .165 |
| 1.72 | .903 | .198 | .181 | .897 | .083 | .161 |
| 1.74 | .897 | .177 | .184 | .896 | .062 | .166 |

$E_F = E_F(T = 0, c_0) , \quad c_0 = \int_0^{E_F} \rho(\epsilon) d\epsilon , \quad \text{while } T_c \text{ will be dealt with as a disposable parameter.}$

To begin with, starting values are needed for $K, U_0$ in order to launch Newton's procedure. To that end, let us choose $K = \pi, T_c = 0$, which implies $6$, with help of Eqs. (7, 10, 11), $\epsilon_0 = U_0 \Rightarrow E_F = \int_0^{U_0} \frac{\mu}{\pi} d\epsilon \Rightarrow K = \pi, c_s = 0 = \frac{\mu}{\pi} U_0$ and $\rho(E_F) = \frac{2}{U_0}$ and yields finally $U_0 = \frac{2}{\sqrt{\pi U_0}}$ and $c_0 = 1.64$ electrons per site.

Then $K$ can be assigned thanks to Eqs. (12, 13). At last this $K$ value is fed into Eq. (7) to determine $U_0$. The results are presented in Table 1.

Equation (13) are seen to have no solution $K \in [0, \pi]$ for $c_0 < 1.64$ and there is no $U_0 > 0$ for $c_0 > 1.74$, whereas $U_0 > 0$ has been known as a prerequisite for persistent currents $5$, thermal equilibrium $6$, occurrence of a second order transition $7, 8$ at the critical temperature $T_c$ and the Josephson effect $9$. Likewise there is no solution for $T_c > 220K$. The main conclusion, drawn from Table 1, is that the inequality $U_0(T_2) < U_0(T_1)$ is indeed seen to hold for every $c_0$ value, in qualitative agreement with the observed, pressure induced $[16-18]$ rise of $T_c$. A similar trend had been already noticed in the $d = 3$ case $8$, for which $\frac{U_0(T_1=1K)}{U_0(T=300K)} > 1$ was yet found smaller than in the $d = 1$ case. This is likely to stem from the $d$-dependent behaviour of $\rho(\epsilon) \propto \epsilon - \epsilon_{\text{VH}}^{d-1} (d = 1, 2, 3)$ for $\epsilon$ close to a Van Hove singularity, located at $\epsilon_{\text{VH}}$.

A similar analysis will now be applied to $H_2$. Each bound electron pair of energy $\eta(K)$, as plotted in Fig. 3, turns $6$ continuously into a MBE state $\Phi$ at finite concentration $c_s$. As recalled above for a single pair, the corresponding Schrödinger equation

$$(H_2 - NE) \Phi = 0$$

can be recast $21$, but only for $N \to \infty$, into

$$(H_d + H'_K - NE) \psi' = 0 .$$

There is $\psi'_K \in S'_K$ and the Hilbert space $S'_K$ is subtended $21$ by a basis of many-pair states, such as $\prod_{i=1...n} b^+_{s,K,i} |0\rangle$, with $n = \frac{N}{2}$ being the number of electron pairs.

Then, taking $\langle \psi'_K | \psi'_K \rangle = \langle \Phi | \Phi \rangle = 1$ yields $E(c_s) = \langle \psi'_K | H_2 + H'_K + \psi'_K \rangle = \langle \Phi | H_2 + \psi'_K \rangle$, which can be reckoned by implementing a variational procedure, developed elsewhere $6$ for $H_0$. It is based on the following assumptions

$$n_k = \langle \Phi | b^+_{s,K,k} | \Phi \rangle = n = \sum \mu n_k$$

$$f(k) = \sqrt{n_k (1 - n_k)} , \quad \langle \Phi | b^+_{s,K,k} b_{s,K,k'} | \Phi \rangle = f(k)f(k')$$

Then $E$ reads

$$E = \sum_k \epsilon(K, k) \frac{n_k}{N} + U_0 \Delta^2 c + 2(U_1 (\Delta^2 c + 2 \Delta^2 )$$

Then $E$ reads

$$\Delta = \sum_k \cos(k) f(k) , \quad \Delta_s = \sum_k \sin(k) f(k) .$$

Fig. 4 Plots of $\mu(c_s)$, calculated for $H_2$ at $K = 0$ (solid and dotted line) and $K = \pi/2$ (dashed line and white circle) for $U_i = 1.2$ and $U_i = 2U_0 , J = 1U_0$, respectively; $c_s$ is the concentration of bound electrons, expressed as the number of electrons per site.
Furthermore minimising $\mathcal{E}$ ($\Rightarrow d\mathcal{E} = 0$), under the constraint of $c_\ell$ kept constant ($\Rightarrow dc_\ell = 0$), while taking [2] $n_k = \sin^2(\theta_k)$ with $\theta_k \in [0, \frac{\pi}{2}]$, yields

$$\tan(2\theta_k)\left(\mu - \frac{\epsilon(K)}{2}\right) = U_0\Delta_0$$

$$+ 2\left(\frac{U_1\cos(k) + J\cos(K - k)}{2}\right)\Delta_c$$

$$+ \left(\frac{U_1\sin(k) + J\sin(K - k)}{2}\right)\Delta_s$$

Due to $\mu = \frac{\partial \mathcal{E}}{\partial n_k}, \forall k$, the chemical potential $\mu$, associated with the electrons making up the MBE state, plays also the role of a Lagrange multiplier [6]. Note that, in case of $U_1 = J = 0$, Eq. (14) gives indeed for $\theta_k$ the expression [6] worked out for $H_0$. At last $\Delta_0, \Delta_c, \Delta_s$ can be recast as

$$\Delta_0 = \int_0^\pi \frac{2}{\pi} \sin(2\theta_k)\frac{dk}{\sin(k)}$$

$$\Delta_c = \int_0^\pi \frac{2}{\pi} \sin(2\theta_k)\cos(k)\frac{dk}{\sin(k)}$$

$$\Delta_s = \int_0^\pi \frac{2}{\pi} \sin(2\theta_k)\sin(k)\frac{dk}{\sin(k)}$$

The system of Eq. (15), comprising three transcendental equations in terms of three unknowns $\Delta_0(\mu), \Delta_c(\mu), \Delta_s(\mu)$ with $\theta_k(\mu)$ defined by Eq. (14), has been solved thanks to Newton’s method. This has enabled us to calculate $c_k(\mu)$ without having to calculate $\Delta_0, \Delta_c, \Delta_s$. The resulting $\mu(c_k)$ data have been plotted in Fig. 4. They share several common properties with similar data obtained [6] for $H_0$

- there is $\mu(c_k \to 0) \to \frac{\eta(K)}{\pi}$,
- $U_0 > 0$ implies $\frac{\partial \mu}{\partial c_k} < 0$, which has been recognised as the prerequisite, conditioning all aspects of superconductivity [5–9];
- $\frac{\partial \mu}{\partial c_k}$ depends weakly on $c_k$.

Equations (13) can now be solved for $H_2$, with $\eta(K)$ showing up instead of $\epsilon_0(K)$, and the resulting data are available in Table 2. Note that there is no solution for $T_c > 160K$. Meanwhile they are close to those of Table 1, which concurs with the weak dependence of $\eta(K)$ on $U_1, J$, illustrated by Fig. 3. In particular, the inequality $U_0(T_2) < U_0(T_1)$ is seen to hold again, in qualitative agreement with the measurements, carried out under high pressure [16–18]. They hint also at a practical route to achieve higher $T_c$ values at ambient pressure. Accordingly, there, in most superconducting materials, several one-electron bands, crossing $E_F(c_k, T_c)$ and pertaining to different symmetry classes of the crystal point group [8]. Hence, was it possible to sort out that one, contributing at most to $\rho(E_F)$ and the corresponding atoms, associated with the hopping integral $t$, it would be tempting to substitute them for isovalent atoms, so as to cause the lattice parameter to shrink, in order to see whether this might give rise to increasing $T_c$.

### 5 Conclusion

It has been concluded that triplet bound electron pairs are unlikely to arise in three-dimensional metals, unlike singlet pairs, the properties of which are conditioned primarily by the on-site Coulomb integral $U_0 > 0$. The prominent role of the repulsive Hubbard Hamiltonian in the whole realm of superconductivity is thereby ascertained.

Nevertheless, the weaker Coulomb repulsion between electrons, located at neighbouring sites, has proven instrumental in shifting $T_c$ upward with decreasing $U_0/t$, which agrees qualitatively with observed pressure induced effect. Likewise, indirect two-electron couplings, such as mediated by electron-phonon (known [1, 2] to be influential on the isotope effect) or electron-spin interaction [22–24], may also alter $T_c$ and the corresponding $T_c$ behaviour could be assessed by working out the effective two-electron potential, as done elsewhere [7], and then solving the relevant Eq. (13), as done above for $H_0, H_2$.

At last, since the Coulomb repulsion governs the electron motion in metals, one might wonder why not every metallic compound is superconducting. It is not so,
because solutions of Eq. (10) can be found, but inside a narrow range of $c_0, U_0$ values, as illustrated by the data in Tables 1 and 2. Remarkably, $T_c$ has a Hamiltonian dependent, upper bound.

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