Cooper Pairs in Alternating Layers of Light and Heavy Atoms

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Abstract

The Hamiltonian and trial function in the BCS theory are improved to test the limit of this theory. The Cooper pairs arise from standing electron waves, ready to move with atoms, giving high $T_c$. The Hamiltonian is derived from alternating layers of light and heavy atoms, giving a forbidden zone hosting no standing wave pairs. The exchange term may force singlet pairs into this zone, leaving triplet pairs outside, giving magnetic excitations. If the Fermi energy is crossed only by the CuO$_2$ band, then the forbidden zone and triplet pairs will vanish, consistent with experimental evidence.

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Recently there has been considerable interest in the original theory of Bardeen, Cooper and Schriefer (BCS) [1]. It was used by Nunner, Schmalian and Bennemann to explain the isotopic effect of cuprates [2]. It was also used by Nozières and Pistolesi to study pseudogaps [3]. Following this line of thinking, we adopt the view that cuprates have a Fermi surface and electron-phonon interactions. We also adopt the BCS formalism, which is relatively simple, due to neglecting damping and retardation, with negligible effects [4].

The BCS theory is based on variational evaluation of the Fröhlich Hamiltonian, with the Cooper pairs as the trial function [1, 5]. With an improved Hamiltonian and trial function, we may explain further properties of cuprates. In order to improve the Hamiltonian, we use a simple model of alternating layers of light and heavy atoms (Fig. 1), because in cuprates the CuO$_2$ layers are always sandwiched by heavy atoms. For example, in La$_2$CuO$_4$ we have a ratio 96/310 when comparing the atomic wt. of the CuO$_2$ layer and the two LaO layers. In YBa$_2$Cu$_3$O$_7$ we have a ratio 281/386 when comparing the two CuO$_2$ layers (including the Y atom in between) with other atoms. In Tl$_2$Ba$_2$CuO$_6$ the ratio is 96/746, which becomes 256/746 and 416/746 when the number of CuO$_2$ layers are 2 and 3 (including Ca in between). In HgBa$_2$CuO$_4$ the ratios are 96/507, 232/507 and 368/507 when the number of CuO$_2$ planes are 1, 2 and 3 (including Ca in between) [6].

The classic Cooper pairs arise from traveling electron waves, which are mobile in all directions. However, the resistance of cuprates in the c axis is significantly larger than that in the a-b plane [6]: most electrons are mobile only in that plane. It is reasonable to assume that the atomic layers act as potential wells to retain electrons. Being reflected back and forth in potential wells, electrons must be in the form of standing waves. Indeed, according to energy band calculation, in cuprates the Fermi surfaces join together in the c direction [7], a familiar sign of electron standing waves in that direction. In the case of Bragg scattering only some electrons are reflected, giving narrow ‘necks’ to join Fermi surfaces. In cuprates virtually all electrons are reflected in the c direction, so that the Fermi surface becomes cylindric. In fact, many cuprate theories assume that carriers are somehow bound around the CuO$_2$ plane [8], i.e. they are standing waves across that plane. We add two Bloch functions together to model electrons in cuprates. The result is a traveling wave in the a-b plane but a standing wave in the c direction (Fig. 1). The Cooper pairs arise from such waves. These pairs concentrate in the layers of light atoms (CuO$_2$ planes) as a natural result of our theory.

First, we explore the prediction power of the BCS theory. The reduced Hamiltonian [1] involves a series of pair generation and destruction operators
with the $c$-number coefficient

$$V(\mathbf{k}, \mathbf{q}) = \sum_{l=1}^{3} \frac{2\hbar \omega_l(\mathbf{q}) \mathcal{M}_l^2(\mathbf{k}, \mathbf{q})}{[\hbar \omega_l(\mathbf{q})]^2 - [\epsilon(\mathbf{k} + \mathbf{q}) - \epsilon(\mathbf{k})]^2}$$  \hspace{1cm} (1)$$

where $\mathbf{k}$ and $\epsilon$ are electron vector and energy (measured from the Fermi surface), $\mathbf{q}$ and $\omega_l$ phonon vector and frequency, and $l$ identifies phonon branch (excluding transverse phonons, which do not interact with electrons in $N$-processes) \[4\]. The matrix element

$$\mathcal{M}_l(\mathbf{k}, \mathbf{q}) = \tilde{q}_l \left[ \frac{\hbar N}{2 M \omega_l(\mathbf{q})} \right]^{1/2} \int_{\Omega} \psi_{k+\mathbf{q},\sigma}(\mathbf{r}) \delta \mathcal{V}(\mathbf{r}) \psi_{k,\sigma}(\mathbf{r}) d\mathbf{r}$$  \hspace{1cm} (2)$$

measures the strength of electron-phonon interaction. Here $\psi$ is the electron wave function, $\sigma$ spin $\uparrow$ or $\downarrow$, $M$ the mass of an atom, $N$ the number of atoms in unit volume, $\mathbf{r}$ the coordinates in real space, $\Omega_0$ a volume surrounding the atom, $\Gamma_0$ its boundary, and $\delta \mathcal{V}(\mathbf{r}) = \mathcal{V}(\mathbf{r}) - \mathcal{V}(\Gamma_0)$, $\mathcal{V}$ being the potential field. We define $\tilde{q}_l$ as the $l$-th component of $\mathcal{U} \mathbf{q}$, $\mathcal{U}$ being the $3 \times 3$ unitary matrix found when solving the classical equation of motion for the atom. Mott and Jones found matrix elements when $\Omega_0$ is the Wigner-Seitz cell \[11\]. We find equation \[2\] when $\mathcal{V}(\Gamma_0)$ is constant (this defines $\Omega_0$ in a natural manner). The BCS self-consistent equation \[11\]

$$\Delta(\mathbf{k}) = \sum_{\mathbf{q}} \frac{\Delta(\mathbf{k} + \mathbf{q})}{\Delta^2(\mathbf{k} + \mathbf{q}) + \epsilon^2(\mathbf{k} + \mathbf{q})}$$  \hspace{1cm} (3)$$

is an integral equation of the Cauchy type: $V(\mathbf{k}, \mathbf{q})$ is singular \[11\]. We solve equation \[3\] through iteration \[11\]. With a proper first approximation, we may expect reasonable accuracy after just one iteration. We use free electron energy to evaluate equation \[4\], where the denominator turns out to be $4 \epsilon_F \epsilon_q \delta_t^2 - (\zeta + \cos \theta)^2$, $\epsilon_F = (\hbar^2/2m)|\mathbf{k}|^2$ is the Fermi energy (we study $|\mathbf{k}|$ near the Fermi surface), $\epsilon_q = (\hbar^2/2m)|\mathbf{q}|^2$, $\delta_t^2 = (m/2)v_t^2/\epsilon_F$, $v_t = \omega_l(\mathbf{q})/|\mathbf{q}|$ the sound velocity. In the Debye approximation $\delta_t = (Z/16)^{1/3} \Theta_D/\Theta_F \approx 10^{-3}$ in all superconducting metals, where $Z$ is the valency, $\Theta_D$ and $\Theta_F$ are the Debye and Fermi temperatures. Therefore $V(\mathbf{k}, \mathbf{q}) > 0$ (condition to have an energy gap) holds in equation \[4\] only when $\zeta + \cos \theta \approx 0$, $\zeta = |\mathbf{q}|/|2\mathbf{k}|$, $\theta$ being the angle between $\mathbf{k}$ and $\mathbf{q}$, so that $|\mathbf{k} + \mathbf{q}|^2 = |\mathbf{k}|^2 + |\mathbf{q}|^2 + 2|\mathbf{k}||\mathbf{q}| \cos \theta \approx |\mathbf{k}|^2$. Thus $\epsilon(\mathbf{k} + \mathbf{q}) \approx \epsilon(\mathbf{k})$, i.e. electrons changes direction but not energy in scattering, which is used as our first approximation (also used to study metal resistivity) \[10\]. The use of free electron energy implies a spherical Fermi surface and hence an isotropic
energy gap, so that $\Delta(k + q) = \Delta(|k + q|) \approx \Delta(|k|) = \Delta(k)$. These lead through equation 3 to:

$$E_{TRV} = \sum_q V(k, q) = \frac{\hbar e^2}{k_B T_P} \eta \rho \nu v^2$$

(4)

where $E_{TRV} = [\Delta^2(k) + \epsilon^2(k)]^{1/2}$ at $T = 0$, $TRV$ standing for travelling wave, $e$ and $n$ are electron charge and density, $k_B$ the Boltzmann constant, $\rho$ the resistivity at temperature $T_P$, $v = k_B \Theta_D / \hbar k_D$ the Debye sound velocity, $k_D$ being the phonon cut-off wavenumber, and

$$\eta = \frac{1}{\pi} \int_0^{(4Z)^{-1/3}} F^2(x) \frac{x^2 d\zeta}{1 - \zeta^2} / \int_0^{(4Z)^{-1/3}} F^2(x) \zeta^3 d\zeta \approx 1$$

(5)

Here $F(x) = 3(x \cos x - \sin x) / x^3$ is the overlap integral function, $x = 3.84\zeta^{1/3}Z^{1/3} \zeta$, $\alpha = N\Omega_0 / \Omega$ the fraction of $\Omega_0$ in a primitive cell, and $\Omega$ the unit volume. We assume $|q| / 2k < \zeta < (4Z)^{-1/3} < 1$, because equation 3 arises from a canonical transformation 4, where operator commutation requires $q \neq \pm 2k$. In first iteration, the pair occupancy varies linearly if $-E_{TRV} < \epsilon(k) < E_{TRV}$, otherwise equation 3 has improper solutions (occupancy $< 0$ or $> 1$). This justifies the BCS approach to integrate equation 3 only in a thin layer across the Fermi surface 4. This surface does not have to be spherical, so long as $k_D << |k|$ (integration area small).

In order to find $T_c$ we follow BCS 4 to minimize the free energy of the electron-phonon system. Evaluating the result via iteration, we find

$$E = E_{TRV} \tanh(E / 2k_B T)$$

(6)

where $E = [\Delta^2(k) + \epsilon^2(k)]^{1/2}$ at $T > 0$. Since $\tanh(E / 2k_B T) < E / 2k_B T$, we have $T \leq E_{TRV} / 2k_B$ and hence $2E_{TRV} / k_B T_c = 4$. It is easy to prove, by direct substitution, that $E$ from equation 3 is also the exact solution of equation 3.27 in 4 (BCS self-consistent equation for $T > 0$), provided that $\hbar \omega N(0)V = E_{TRV}$ in that equation. Clearly, $E$ is not a function of $k$, the so-called gap parameter $\Delta(k)$ is, contrary to general perception. This is justified: according to BCS it is $E$ that measures the energy gap, $\Delta$ is just an approximation, i.e. $\epsilon \approx 0$ near the Fermi surface giving $E = (\Delta^2 + \epsilon^2)^{1/2} \approx \Delta$ 4. What arises from experiment is actually $2E_{TRV} / k_B T_c$, whose value may deviate from 4 for reasons other than $\hbar \omega / k_B T_c >> 1$ (weak coupling).

Since $E$ is constant, any Cooper pairs are equally likely to be excited. This is also justified: $\mathcal{M}_I$ (measuring the strength of electron-phonon interaction) in equation 4 varies little across the Fermi surface.

According to equations 4 and 5 a good superconductor must have numerous free electrons (large $n$) scattered frequently by atoms (large $\rho$) moving
quickly to facilitate pairing (large $v$). The factor $\eta$ arises when the summation over $q$ in equation \(3\) is replaced by an integration over $(4\pi/3)k_D^3$ (volume of the first Brillouin zone), which exists in the sense of the Cauchy principal value (used by Kuper to verify the BCS theory) \[11, 12\], i.e. positive and negative contributions of $V(k, q)$, if finite, are cancelled on a series of spherical surface, the singular point ignored. We are entitled to do so, because equation 3 is defined on a grid of $k$ and $q$, which may not be in precise combinations to let $V(k, q) = \infty$. We can also avoid such combinations by suppressing a few phonons with little physical consequence. This principal value varies little among phonon branches, allowing us to use $\sum_l q_l^2 = |q|^2 (U$ unitary) to find the numerator in equation 5. We use the expression for metal resistivity to calibrate $\delta V$, and this leads to the denominator in equation 5. When $\alpha = 1$, equation 4 yields $2E_{TRV} = 2.2, 18$ and $27$ for Cd, Ta and Nb (1.5, 14 and 30.5 experimentally, in $10^{-4}$eV), which are of the right order, although over and under-estimations are possible. On average equation 4 yields $2E_{TRV} = 15.7$ for Zn, Cd, Hg, Al, Ga, Tl, Sn, Pb, V, Nb, Ta and Mo (11.3 experimentally).

Now consider a crystal of alternating layers of light and heavy atoms (Fig. 1). For Cooper pairs of traveling electron waves, equations \(3\) and \(6\) are still valid. The derivation is straightforward in principle but involved technically. In equation 6 the upper limit of integration is replaced by $(8Z)^{-1/3}$: the first Brillouin zone is smaller the larger the primitive cell. We also have $\alpha = 2N\Omega_0/\Omega$ (assuming $\Omega_0$ invariant in the cell) and $Z$ averaged over different atoms. In order to model electrons in cuprates, we notice that, in principle, electrons of any configuration can be expanded into Fourier series in terms of plane waves. These series can be shortened, when the plane waves are replaced by waves resembling more closely the actual configuration of the electrons in the crystal, as is done by various sophisticated methods to calculate the electron band structure \[7\]. For simplicity, we consider series of superpositions of just two Bloch functions:

\[
\psi_{k,\sigma}^{(1)}(r) \propto \exp[i(k_xx + k_yy)] \cos(\pi z/c) \tag{7}
\]

\[
\psi_{k,\sigma}^{(2)}(r) \propto \exp[i(k_xx + k_yy)] \sin(\pi z/c) \tag{8}
\]

where $k = xk_x + yk_y$ is a 2D wavevector. Both $\psi^{(1)}$ and $\psi^{(2)}$ are traveling waves in the $a$-$b$ plane. On the other hand, $\psi^{(1)}$ is confined in layer 1 (its anti-nodes are in that layer), whereas $\psi^{(2)}$ is confined in layer 2 (Fig. 1). Apparently, electrons overlap with those in the neighboring layer, but not with those in the next neighboring layer (there is a node in between, see Fig. 1). These appear to be reasonable as first order approximation. We assume that both $\psi^{(1)}$ and $\psi^{(2)}$ are close to the Fermi surface. This is true at least
in some cuprates: the chain band crosses $\epsilon_F$ in $\text{YBa}_2\text{Cu}_3\text{O}_7$, so does the TIO band in $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, the BiO band in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, etc. [7].

We use standing electron waves to build Cooper pairs. The formalism parallels that for the classic Cooper pairs: in second quantization the basis states do not have to be plane waves [1, 3]. This is necessary, because superconductivity is a second order process. Unless the configuration of (single) electrons is chosen properly (a first order process), the energy gap cannot be maximized. In equation 3, $V$ is replaced by $V_{ij}$ ($i, j = 1, 2$), $l$ runs from 1 to 6, and $\mathcal{M}_l$ is replaced by $\mathcal{M}_l^{(ij)}$ to link $\psi^{(i)}$ and $\psi^{(j)}$. Both intra ($i = j$) and inter-layer ($i \neq j$) couplings are possible, because electrons in neighboring layers overlap (Fig. 1). If we use $c/2$ to replace $c$ in equations 7 and 8, then we are out of the first Brillouin zone. As a result, $\psi^{(1)}$ and $\psi^{(2)}$ become identical, giving no inter-layer coupling and reduced energy gap, as will be shown. If we use $2c, 3c, ...$ to replace $c$, then $E_{12}$ in Appendix becomes smaller. This weakens the inter-layer coupling, a choice not preferred. Indeed, the classic Cooper pair (spin $\uparrow, \downarrow$ and wavevector $k, -k$) is also a choice (i.e. a trial function) to maximize the energy gap.

Letting $f_k^{(1)}$ and $f_k^{(2)}$ be the over-all probability of excitations in layer 1 and 2, we have $-4k_B \sum_k[(f_k^{(1)}/2 + f_k^{(2)}/2) + (1 - f_k^{(1)}/2 - f_k^{(2)}/2) \ln(1 - f_k^{(1)/2} - f_k^{(2)/2})]$ as the entropy of the pair ensemble, which is from the consideration that pairs in either layer may have the same energy, so that thermodynamically they fall into the same group of entities, i.e. there can be 4 electrons at the same energy level, giving the degeneracy factor 4. Note that in cuprates bands of both the light and heavy layers may cross $\epsilon_F$ [7], so that the above degeneracy is possible. Minimizing the free energy of the pair ensemble, we find through iteration two equations with the solution

\begin{align}
1 - 2f_k^{(1)} &= \frac{E_{12} - E_{22}}{E_{12}^2 - E_{11}E_{22}} k_B T \ln \frac{2 - f_k^{(1)} - f_k^{(2)}}{f_k^{(1)} + f_k^{(2)}} \\
1 - 2f_k^{(2)} &= \frac{E_{12} - E_{11}}{E_{12}^2 - E_{11}E_{22}} k_B T \ln \frac{2 - f_k^{(1)} - f_k^{(2)}}{f_k^{(1)} + f_k^{(2)}}
\end{align}

Here $E_{ij} = \sum_{\mathbf{q}} V_{ij}(\mathbf{k}, \mathbf{q})$ and the summation over $\mathbf{q} = xq_x + yq_y$ is in 2D, i.e. the standing electron waves emit and absorb phonons in 2D. Since $E_{ij} = N_{z}^{-1} \sum E_{ij}$ when the summation is over $q_z$ (not an argument of $E_{ij}$), $N_z$ being the number of $q_z$ in the first Brillouin zone, we integrate $E_{ij}$ in 3D (in the sense of the Cauchy principal value) for convenience. Equations 9 and 10 apply to pure intra-layer couplings when $E_{12} = 0$, and pure inter-layer couplings when $E_{11} = 0$ and $E_{22} = 0$. Both lead to an energy gap, because $E_{ij} > 0$ always holds (Appendix).
The inter and intra-layer couplings are in competition. If none dominates, then both are suppressed. Since $M_1 < M_2$, we have $E_{22} < E_{11}$ (Appendix). When $E_{22} < E_{12} < (E_{11}E_{12})^{1/2}$, the two sides of equations [9] have opposite signs: $f_k^{(1)} = 1/2$ and $T = 0$ must hold to give $f_k^{(2)} = 1/2$ via equation [10]. Similarly $T = 0$ when $(E_{11}E_{22})^{1/2} < E_{12} < E_{11}$. Clearly $E_{22} < E_{12} < E_{11}$ (inter-layer coupling weaker than the coupling in layer 1 but stronger than that in layer 2) is a forbidden zone hosting no standing wave pairs. Outside this zone, equations [9] and [10] can be added together to recover equation 6, with $E$ replaced by $1 - f_k^{(1)} - f_k^{(2)}$ and $E_{TRV}$ replaced by

$$E_{STD} = \frac{E_{12}^2 - E_{11}E_{22}}{E_{12} - (E_{11} + E_{22})/2}$$

(11)

$STD$ standing for standing wave. If all Cooper pairs are excited, then $f_k^{(1)}, f_k^{(2)} \rightarrow 1/2$ giving $2E_{STD}/k_BT_c = 4$ to estimate $T_c$.

In Fig. 1 $E_{STD}/E_{TRV} > 5.57$ when $E_{11} < E_{12}$. This large ratio arises from equation [11], where $E_{11} \rightarrow E_{12}$ leads to $E_{STD} \rightarrow 2E_{11}$: the energy gap is larger the stronger the inter-layer coupling. At this point, equation [9] yields $f_k^{(2)} = 1/2$: all the pairs in layer 2 are excited, apparently draining much of the excitation energy. Pairs in layer 1 (light atoms) are more or less left alone: superconducting carriers are in the CuO$_2$ layers. Furthermore, $E_{11} > E_{TRV}$ holds as a result of the symmetry of the standing waves (with respect to $a$-$b$ planes, rather to sites of atoms) reflecting the fact that bound electrons are readier to move with the atoms. In Fig. 1 $E_{11} < E_{12}$ for $Z < 0.1314$. This small valency arises, because on average phonons have smaller $|q|$ to pair electrons on a smaller Fermi sphere, so that $M_i^{(1)}(\propto |q|) < M_i^{(12)}(\propto 2\pi/c)$ holds to give $E_{11} < E_{12}$. Assuming $E_{STD}/E_{TRV} = 5.57$, we have $T_c \approx 130K$ when $E_{TRV} = 40.2 \times 10^{-4}$eV ($40 \times 10^{-4}$eV for Nb$_3$Ge). In Ba$_2$YC$_3$O$_7$ we have $k_D = (6\pi^2N/\Omega)^{1/3} = 6.99 \times 10^8$m$^{-1}$, $\Theta_D \approx 400K$, $v = k_B\Theta_D/hk_D \approx 7.49 \times 10^3$ms$^{-1}$, $\rho = 70 - 550 \times 10^{-8}$Ωm $(a$-$b$ plane) and $n \approx 6 \times 10^{27}$m$^{-3}$ from infrared reflectivity [6, 14]. Taking surface values, these lead through equation [11] to $E_{TRV} = 10 - 77 \times 10^{-4}$eV ($\eta = 1$). A point to notice: $\rho$ is for traveling waves in equation [11]. Although standing electron waves are easier to be scattered, giving larger $\rho$, this is more or less compensated by the weak coupling at their nodes. It is interesting that, in Ba$_2$YC$_3$O$_7$, $N = 5.76 \times 10^{27}$m$^{-3}$, so that $Z = (1/13)n/N \approx 0.08$ [6].

We may have spin singlet pairs in the forbidden zone, triplets outside. Specifically, while $E_{12} < E_{11}$ holds for singlet pairs, $E_{12} > E_{11}$ may hold for triplet pairs, i.e. $E_{11}$ declines faster when the pair symmetry changes, due to the stronger effect of the exchange term on $E_{11}$, which is related to intra-layer coupling, where electron waves overlap to a greater extent.
Outside the forbidden zone, $E_{STD}$ changes $\sim 10\%$ when $Z$ drops just 0.001 from 0.1314. Across the zone border, $Z_{STD}$ changes more dramatically (Fig. 1). In both cases doping may obscure the isotopic effect. The Fermi surface of cuprates is not strictly cylindric \cite{7}; classic Cooper pairs may arise to give superconductivity inside the forbidden zone. Since $E_{TRV}$ changes slowly with $Z$ (Fig. 1), the isotopic effect will be more apparent. Indeed, in cuprates the isotopic effect is minimum when $T_c$ peaks with proper doping \cite{15}. Although travelling electron wave pairs (giving $E_{TRV}$) cannot compete with standing wave pairs (giving $E_{STD} > E_{TRV}$) in the $a$-$b$ plane, they can move in the $c$ axis (standing waves cannot) to make the Knight shift complicated \cite{13, 17}, and give energy gap anisotropy and pair symmetry anisotropy (well documented for cuprates) \cite{18, 19, 20, 21, 22, 23}.

In conclusion, rather surprisingly and significantly, the BCS theory may play a major role to explain the properties of cuprates. We show that this theory can be used to calculate $T_c$ from first principles, the first time to our knowledge, giving $T_c \sim 130K$ for cuprates. The impression that $T_c$ is low in the BCS theory arises from McMillan’s calculation, where the $T_c$ of an alloy family is clamped to that of the parent metal, assumed to be a natural element of low $T_c$ \cite{24}. Another worry about the BCS theory is the Migdal instability which, according to Waldram, may not set in at 130K \cite{13, 25}.

We also show that in a complex system like cuprates the microscopic physics may manifest itself as a paradox: the exchange term may drive the singlet pairs into the forbidden zone, leaving the triplet pairs outside. Indeed neutron scattering does exhibit a magnetic peak below $T_c$ from YBa$_2$Cu$_3$O$_8$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$ \cite{26} and the references therein. In addition to adding another explanation to the already long list of explanations, our theory has a specific experimental basis. In the above cuprates $\epsilon_F$ is crossed by both the CuO$_2$ and heavy atom layer bands \cite{7}; our theory applicable. On the other hand, magnetic excitations are absent in La$_{2-x}$Sr$_x$CuO$_4$ \cite{27} where $\epsilon_F$ is crossed only by the CuO$_2$ band \cite{7}. Therefore we have to assume $M_1 = M_2$: heavy atom layers are not involved in the electron-phonon interaction near the Fermi surface. As a result, both the forbidden zone and triple pairs vanish. It appears worthwhile to search magnetic excitations from e.g. HgBa$_2$Ca$_2$Cu$_3$O$_8$ and Tl$_2$Ba$_2$CuO$_6$, as example and counter-example of cuprates, where $\epsilon_F$ is crossed only by the CuO$_2$ band \cite{7, 28}.

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Appendix

For a spherical Fermi surface

\[ E_{11} = C \int_0^{(8Z)^{-1/3}} \frac{1}{2} \left[ \frac{(A + B)^2}{M_1} + \frac{(A - B)^2}{M_2} \right] \frac{\zeta^2 d\zeta}{1 - \zeta^2} \]

\[ E_{12} = C \int_0^{(8Z)^{-1/3}} \frac{1}{2} \left[ \frac{B^2}{M_1} + \frac{B^2}{M_2} \right] \frac{0.65 a^3 c}{Z^{2/3} c^3} \frac{\zeta^2 d\zeta}{(1 - \zeta^2)^2} \]

where \( A \) and \( B \) are values of the overlap integral function \( F(x) \), with \( x = 3.84\alpha^{1/3} Z^{1/3} \zeta(1 - \zeta^2)^{1/2} \) and \( 3.84\alpha^{1/3}[Z^{2/3}\zeta^2(1 - \zeta^2) + 0.65(a/c)^{4/3}]^{1/2} \), respectively, and \( C = 6Zm\alpha^2(\delta V)^2/\epsilon_F \). If \( M_1 \) and \( M_2 \) are interchanged, then \( E_{11} \) is turned into \( E_{22} \). For Cooper pairs of traveling waves \( B = 0 \) and \( x = 3.84\alpha^{1/3} Z^{1/3} \zeta \), so that \( E_{11} \) is reduced to \( E_{TRV} \) in equation [4] (\( E \) expressed in n. \( \rho \) and \( v \)). The factor \( (1 - \zeta^2)^{-1} \) in \( E_{11} \) (or \( E_{TRV} \)) and \( E_{12} \) is related to the Cauchy principal value, which starts to fail when \( \zeta = |q|/2k \to 1 \), where the canonical transformation also fails. However, in Fig. 1 \( E_{TRV} \) shows little sign of divergence when \( Z > 0.13 \). Another factor \( (1 - \zeta^2)^{-1} \) in \( E_{12} \) is from the denominator \( (\propto |q|^2) \) in equation [4], which is cancelled in \( E_{11} \) (\( M_1^{11} \propto |q|) \) but not in \( E_{12} \) (\( \propto 2\pi/c) \), so that in Fig. 1 \( E_{STD} \) turns upwards when \( Z \to 0.13 \).

Figure legend

Fig. 1 Crystal of light (wt. \( M_1 \) in layer 1, open circles) and heavy atoms (wt. \( M_2 \) in layer 2), \( a, b \) and \( c \) are lattice constants, the anti-nodes of \( \psi^{(1)}_{K,\sigma} \) and \( \psi^{(2)}_{K,\sigma} \) are in layer 1 and 2, respectively; \( E_{STD} \) (solid line, a.u.) and \( E_{TRV} \) (broken line, a.u.) are found when \( M_1/M_2 = 0.7 \) and \( a = b = 0.5c; Z < 0.1314 \) \( (E_{11} < E_{12}) \) and \( Z > 0.1361 \) \( (E_{12} < E_{22}) \) border the forbidden zone.

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