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Superconductivity of overdoped cuprates: the modern face of the ancestral two-electron exchange

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Abstract

The single-site two-electron exchange amplitude J_{sd} between the Cu 4s and Cu $3d_{x^2-y^2}$ states is found to be the pairing mechanism of high-T_c overdoped cuprates. The noninteracting part of the Hamiltonian spans the copper Cu 4s, Cu $3d_{x^2-y^2}$ and oxygen O $2p_x$ and O $2p_y$ states. Within the standard BCS treatment an explicit expression for the momentum dependence of the gap Δ_p is derived and shown to fit the angle-resolved photoemission spectroscopy data. The basic thermodynamic and electrodynamic properties of the model (specific heat $C(T)$ and London penetration depth $\lambda(T)$) are analytically derived. These are directly applicable to cuprates without complicating structural accessories (chains, double CuO_2 planes etc). We advocate that the pairing mechanism of overdoped and underdoped cuprates is the same, as T_c displays smooth doping dependence. Thus, a long-standing puzzle in physics is possibly solved.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of high-temperature superconductivity [1] in cuprates and the subsequent 'research rush' have led to the appearance of about 100 000 papers to date [2]. Virtually every fundamental process known in condensed matter physics was probed as a possible mechanism of this phenomenon. Nevertheless, none of the theoretical efforts resulted in a coherent picture [2]. For the conventional superconductors the mechanism was known to be the interaction between electrons and crystal-lattice vibrations, but the development of its theory lagged behind the experimental findings. The case of cuprate high-T_c superconductivity appears to be the opposite: we do not convincingly know which mechanism is to be incorporated

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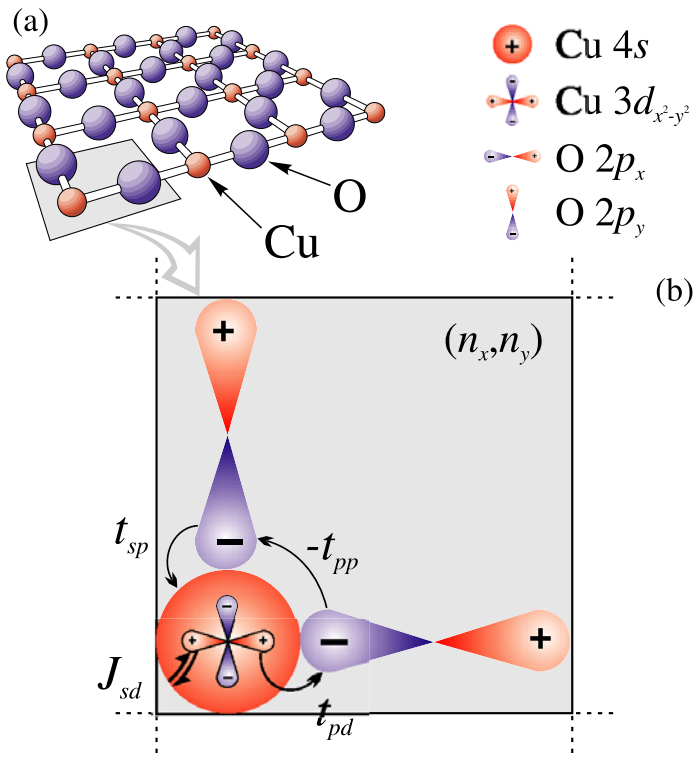

Figure 1. (a) Ball-and-stick model of the CuO_2 plane. The shaded square is the unit cell indexed by $\boldsymbol{n} = (n_x, n_y)$, $n_{x,y} = 0, \pm1, \pm2, \ldots$. (b) The LCAO basis set: a single electron hops from the 3d atomic orbital to $2p_x$ with amplitude t_{pd}, contained in $\hat{\mathcal{H}}_{BH}$. From $2p_x$ to $2p_y$ the hopping amplitude is t_{pp}, and from there to 4s the hopping amplitude is t_{sp}. Correlated hopping of two electrons in opposite directions between 3d and 4s with amplitude J_{sd} is depicted as a double arrow (see the discussion in sections 4 and 5).

in the traditional Bardeen–Cooper–Schrieffer (BCS) theory [3]. Thus the path to high-T_c superconductivity in cuprates, perhaps carefully hidden or well forgotten, has turned into one of the long-standing mysteries in physical science.

Features of the electronic spectrum of the CuO_2 plane, figure 1(a), the structural detail responsible for the superconductivity of the cuprates, have become accessible from the angle-resolved photoemission spectroscopy (ARPES) [4, 5]. Thus, any theory which pretends to explain the cuprate superconductivity is bound to include these features and account for them consistently. A number of extensive reviews over the past years have been devoted to that theoretical problem [6–15]. For further related discussion we also refer the reader to the review [16] on NMR–NQR spectroscopies in high-T_c superconductors.

In contrast with all previous proposals, we have advanced in [17] the *intra-atomic* exchange [18] of two electrons between the 4s and $3d_{x^2-y^2}$ states of the Cu atom as the origin of high-T_c superconductivity in the layered cuprates and have shown that the basic spectroscopic and thermodynamic experiments can be explained by it. Previously only *inter-atomic* Heitler–London (HL) type [19] two-electron exchange [20–22] has been discussed. Thus, the present work is the unabridged version of our theory announced in [17]. It builds upon the standard Bloch–Hückel (BH) [23–26] (tight-binding) approximation to the electronic band structure of the CuO_2 plane, developed in an earlier work [27]. We derive an analytical expression for the

BCS kernel, or pairing potential $V_{pp'}$. For the case of the s–d pairing the analytical solution is compared to the ARPES data. Extensive discussion is also provided to help the juxtaposition of our theory with other models. Finally, exact expressions within the s–d model are given for the specific heat, London penetration depth, Cooper-pair effective mass and Hall constant of the vortex-free Meissner–Ochsenfeld phase.

2. Lattice Hamiltonian

The electronic properties of materials are strongly influenced by the local environment and in this sense the electronic features are local physics. The simplest possible model for high-T_c superconductivity contains single-particle and correlated two-electron hoppings between nearest neighbours and next-nearest neighbours. Formally, this is an expansion of the many-particle Hamiltonian containing two- and four-fermion operators. The two-fermion Hamiltonian determines the band structure, briefly considered in section 2.1, while the four-fermion terms (section 2.2) determine the pairing interaction, and lead to the gap equations considered in section 3.

2.1. The four-band model in a nutshell

Every high-T_c superconductor has its specific properties. It is strongly believed, however, that the main features of the electronic band structure of the CuO_2 plane are adequately described by the four-band model spanning the Cu $3d_{x^2-y^2}$, Cu 4s, O $2p_x$ and O $2p_y$ orbitals, figure 1(b). In the spirit of the BH model, using Jordan's second quantization language, we introduce Fermi annihilation operators for an electron with spin projection α at a particular orbital, respectively, $\hat{D}_{n\alpha}$, $\hat{S}_{n\alpha}$, $\hat{X}_{n\alpha}$ and $\hat{Y}_{n\alpha}$ in the unit cell with index $\boldsymbol{n} = (n_x, n_y)$. It is convenient to introduce a multicomponent Fermi creation operator in momentum space, $\hat{\Psi}^\dagger_{p\alpha} = (\hat{D}^\dagger_{p\alpha}, \hat{S}^\dagger_{p\alpha}, \hat{X}^\dagger_{p\alpha}, \hat{Y}^\dagger_{p\alpha})$. In this notation the one-electron BH Hamiltonian reads

$$\hat{\mathcal{H}}'_{\mathrm{BH}} = \hat{\mathcal{H}}_{\mathrm{BH}} - \mu\hat{\mathcal{N}} = \sum_{p,\alpha} \hat{\Psi}^\dagger_{p\alpha}(H_{\mathrm{BH}} - \mu\,\mathbb{I}_{4\times4})\hat{\Psi}_{p\alpha}, \tag{2.1}$$

where μ is the chemical potential, and (cf [27])

$$H_{\mathrm{BH}} = \begin{pmatrix} \epsilon_{\mathrm{d}} & 0 & t_{\mathrm{pd}}s_x & -t_{\mathrm{pd}}s_y \\ 0 & \epsilon_{\mathrm{s}} & t_{\mathrm{sp}}s_x & t_{\mathrm{sp}}s_y \\ t_{\mathrm{pd}}s_x & t_{\mathrm{sp}}s_x & \epsilon_{\mathrm{p}} & -t_{\mathrm{pp}}s_xs_y \\ -t_{\mathrm{pd}}s_y & t_{\mathrm{sp}}s_y & -t_{\mathrm{pp}}s_xs_y & \epsilon_{\mathrm{p}} \end{pmatrix}; \tag{2.2}$$

ϵ_{d}, ϵ_{s} and ϵ_{p} are the single-site energies of the Cu $3d_{x^2-y^2}$, Cu 4s, O $2p_x$ and O $2p_y$ states, respectively. The hopping amplitudes between these states are t_{sp}, t_{pd} and t_{pp}, figure 1(b). Note that because of the orbital orthogonality $t_{\mathrm{sd}} = 0$. For brevity, we have also introduced the notation

$$\begin{aligned} &s_x = 2\sin(p_x/2), \qquad &&s_y = 2\sin(p_y/2), \qquad &&\boldsymbol{s} = (s_x, s_y), \\ &x = \sin^2(p_x/2), \qquad &&y = \sin^2(p_y/2). \end{aligned} \tag{2.3}$$

From a classical point of view, the Cu $3d_{x^2-y^2}$ state corresponds to a circular electron rotation in the CuO_2 plane while the Cu 4s state corresponds to a classical ensemble of electrons of zero angular momentum continuously falling to the nucleus. Pictorially, the s electrons fall to the nuclei like comets, but after the impact the turning point of their motion is very far from the nucleus. This is the reason why t_{sp} is considerably larger than t_{pd}. The transfer amplitude t_{pp} is the smallest one since the hopping to the next-nearest neighbour requires a tunnelling through free space. As a rule, the electron band calculations significantly overestimate t_{pp}, but

the latter can be reliably calculated using the surface integral method, cf [27]. Even for the largest transfer integrals t_{sp} and t_{pd}, which determine the bandwidth of the conduction band, the *ab initio* calculations give a factor of two or even three 'overbinding'. Nonetheless, the band calculations substantiate this choice for the LCAO (linear combination of atomic orbitals) basis set and provide an adequate language for interpretation. In the end, these parameters should be determined by fitting to the spectroscopy data and be treated in the model lattice Hamiltonian as phenomenological parameters of the microscopic many-body theory. We shall briefly recall some basic properties of the four-band model as derived in [27].

Let $\epsilon_{b,\boldsymbol{p}}$ and $\Psi_{b,\boldsymbol{p}}$ be the eigenvalues and the corresponding eigenvectors of the BH Hamiltonian, $H_{BH}\Psi_{b,\boldsymbol{p}} = \epsilon_{b,\boldsymbol{p}}\Psi_{b,\boldsymbol{p}}$, where $b = 1, \ldots, 4$ is the band index. For the 'standard model', $\epsilon_p < \epsilon_d < \epsilon_s$, the lowest energy band, $b = 1$, is an oxygen bonding band having a minimum at the (π, π) point. The next band, $b = 2$, is a narrow 'nonbonding' oxygen band with an exactly (within the framework of the model) zero dispersion along the $(0, 0)$–$(\pi, 0)$ direction, i.e., this band is characterized by an extended Van Hove singularity. The conduction band, $b = 3$, is a nearly half-filled Cu $3d_{x^2-y^2}$ band with the analytical eigenvector

$$\tilde{\Psi}_{3,\boldsymbol{p}} = \begin{pmatrix} D_{3,\boldsymbol{p}} \\ S_{3,\boldsymbol{p}} \\ X_{3,\boldsymbol{p}} \\ Y_{3,\boldsymbol{p}} \end{pmatrix} = \begin{pmatrix} -\varepsilon_s\varepsilon_p^2 + 4\varepsilon_p t_{sp}^2(x+y) - 32 t_{pp}\tau_{sp}^2 xy \\ -4\varepsilon_p t_{sp} t_{pd}(x-y) \\ -(\varepsilon_s\varepsilon_p - 8\tau_{sp}^2 y) t_{pd} s_x \\ (\varepsilon_s\varepsilon_p - 8\tau_{sp}^2 x) t_{pd} s_y \end{pmatrix}, \tag{2.4}$$

where the ε denote the energies measured relative to their respective atomic levels: $\varepsilon_s = \epsilon - \epsilon_s$, $\varepsilon_p = \epsilon - \epsilon_p$, $\varepsilon_d = \epsilon - \epsilon_d$ and $\tau_{sp}^2 = t_{sp}^2 - \varepsilon_s t_{pp}/2$. The topmost band, $b = 4$, is an empty Cu 4s band. In elementary metals like Cu and Fe, the 4s band is a wide conduction band, but for the CuO_2 plane it is completely 'oxidized'. Having the analytical eigenvector we can calculate the corresponding eigenvalue:

$$\epsilon_{3,\boldsymbol{p}} = \frac{\langle\tilde{\Psi}_{3,\boldsymbol{p}}|H_{BH}|\tilde{\Psi}_{3,\boldsymbol{p}}\rangle}{\langle\tilde{\Psi}_{3,\boldsymbol{p}}|\tilde{\Psi}_{3,\boldsymbol{p}}\rangle}. \tag{2.5}$$

If necessary, the nonorthogonality of the atomic orbitals at neighbouring atoms can be easily taken into account. In this case the normalizing denominator in the above equation reads (for arbitrary band index)

$$\begin{aligned}\langle\tilde{\Psi}_{\boldsymbol{p}}|\tilde{\Psi}_{\boldsymbol{p}}\rangle = {} & D_{\boldsymbol{p}}^2 + S_{\boldsymbol{p}}^2 + X_{\boldsymbol{p}}^2 + Y_{\boldsymbol{p}}^2 + 2g_{pd}s_x D_{\boldsymbol{p}}X_{\boldsymbol{p}} - 2g_{pd}s_y D_{\boldsymbol{p}}Y_{\boldsymbol{p}} \\ & + 2g_{sp}s_x S_{\boldsymbol{p}}X_{\boldsymbol{p}} + 2g_{sp}s_y S_{\boldsymbol{p}}Y_{\boldsymbol{p}} - 2g_{pp}s_x s_y X_{\boldsymbol{p}}Y_{\boldsymbol{p}},\end{aligned} \tag{2.6}$$

where the 'metric tensor' g_{ij} is given by the integral

$$g_{ij} = \int \psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r} - \boldsymbol{R})\,\mathrm{d}\boldsymbol{r}, \tag{2.7}$$

where $\psi_i^*(\boldsymbol{r})$ and $\psi_j(\boldsymbol{r} - \boldsymbol{R})$ are the atomic wavefunctions, and $\boldsymbol{R}$ is the inter-atomic distance. The phases are chosen such that all overlap integrals g_{pd}, g_{sp} and g_{pp} are positive parameters, like the hopping integrals t_{pd}, t_{sp} and t_{pp}. Note that these provisions apply only to the single-particle spectrum. As long as one deals with a single conduction band, all Bloch states are orthogonal and the further treatment of the second-quantized Hamiltonian proceeds in the standard way.

Thus, using the Rayleigh quotient iteration for equations (2.2)–(2.5) one can obtain numerically the eigenvalue and the eigenvector. The band energies $\epsilon \equiv \epsilon_{b,\boldsymbol{p}}$ satisfy the secular equation

$$\det(H_{BH} - \epsilon\,\mathbb{I}_{4\times4}) = \mathcal{A}xy + \mathcal{B}(x+y) + \mathcal{C} = 0, \tag{2.8}$$

where the energy-dependent coefficients read [27]

$$\begin{aligned}\mathcal{A}(\epsilon) &= 16(4t_{\rm pd}^2t_{\rm sp}^2 + 2t_{\rm sp}^2t_{\rm pp}\varepsilon_{\rm d} - 2t_{\rm pd}^2t_{\rm pp}\varepsilon_{\rm s} - t_{\rm pp}^2\varepsilon_{\rm d}\varepsilon_{\rm s}),\\ \mathcal{B}(\epsilon) &= -4\varepsilon_{\rm p}(t_{\rm sp}^2\varepsilon_{\rm d} + t_{\rm pd}^2\varepsilon_{\rm s}),\\ \mathcal{C}(\epsilon) &= \varepsilon_{\rm d}\varepsilon_{\rm s}\varepsilon_{\rm p}^2.\end{aligned} \tag{2.9}$$

Furthermore, we introduce the normalized eigenvector $\Psi_{b,\boldsymbol{p}} = \tilde{\Psi}_{b,\boldsymbol{p}}/\|\tilde{\Psi}_{b,\boldsymbol{p}}\|$ and write the noninteracting Hamiltonian in diagonal form,

$$\hat{\mathcal{H}}'_{\rm BH} = \sum_{b,\boldsymbol{p},\alpha}(\epsilon_{b,\boldsymbol{p}} - \mu)\hat{c}^\dagger_{b,\boldsymbol{p}\alpha}\hat{c}_{b,\boldsymbol{p}\alpha}. \tag{2.10}$$

The Fermi operators in real-space representation can be easily expressed using the band representation,

$$\hat{\Psi}_{\boldsymbol{n}\alpha} \equiv \begin{pmatrix}\hat{D}_{\boldsymbol{n}\alpha}\\ \hat{S}_{\boldsymbol{n}\alpha}\\ \hat{X}_{\boldsymbol{n}\alpha}\\ \hat{Y}_{\boldsymbol{n}\alpha}\end{pmatrix} = \frac{1}{\sqrt{N}}\sum_{b,\boldsymbol{p}}{\rm e}^{{\rm i}\boldsymbol{p}\cdot\boldsymbol{n}}\begin{pmatrix}D_{b,\boldsymbol{p}}\\ S_{b,\boldsymbol{p}}\\ {\rm e}^{{\rm i}\varphi_x}X_{b,\boldsymbol{p}}\\ {\rm e}^{{\rm i}\varphi_y}Y_{b,\boldsymbol{p}}\end{pmatrix}\hat{c}_{b,\boldsymbol{p}\alpha}, \tag{2.11}$$

where N is the number of unit cells, and the two phases in the right-hand side of the equation read $\varphi_x = \frac{1}{2}(p_x - \pi)$ and $\varphi_y = \frac{1}{2}(p_y - \pi)$. This transformation will be used in the next subsection for deriving the interaction Hamiltonian.

2.2. The Heitler–London and Schubin–Wonsowsky–Zener interaction

The HL interaction Hamiltonian describes the (intra- and inter-atomic) two-electron exchange. It comprises four parts [20, 21] corresponding to Cu 4s $\leftrightarrow$ O 2pσ, O 2pσ $\leftrightarrow$ Cu 3d$_{x^2-y^2}$, O 2p$_x$ $\leftrightarrow$ O 2p$_y$ and Cu 3d$_{x^2-y^2}$ $\leftrightarrow$ Cu 4s exchanges with transition amplitudes $J_{\rm sp}$, $J_{\rm pd}$, $J_{\rm pp}$ and $J_{\rm sd}$, respectively:

$$\begin{aligned}\hat{\mathcal{H}}_{\rm HL} = &-J_{\rm sd}\sum_{\boldsymbol{n},\alpha\beta}\hat{S}^\dagger_{\boldsymbol{n}\alpha}\hat{D}^\dagger_{\boldsymbol{n}\beta}\hat{S}_{\boldsymbol{n}\beta}\hat{D}_{\boldsymbol{n}\alpha} - J_{\rm sp}\sum_{\boldsymbol{n},\alpha\beta}[\hat{S}^\dagger_{\boldsymbol{n}\alpha}\hat{X}^\dagger_{\boldsymbol{n}\beta}\hat{S}_{\boldsymbol{n}\beta}\hat{X}_{\boldsymbol{n}\alpha} + \hat{S}^\dagger_{\boldsymbol{n}\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{S}_{\boldsymbol{n}\beta}\hat{Y}_{\boldsymbol{n}\alpha}\\ &+ \hat{S}^\dagger_{(n_x+1,n_y)\alpha}\hat{X}^\dagger_{\boldsymbol{n}\beta}\hat{S}_{(n_x+1,n_y)\beta}\hat{X}_{\boldsymbol{n}\alpha} + \hat{S}^\dagger_{(n_x,n_y+1)\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{S}_{(n_x,n_y+1)\beta}\hat{Y}_{\boldsymbol{n}\alpha}]\\ &- J_{\rm pd}\sum_{\boldsymbol{n},\alpha\beta}[\hat{D}^\dagger_{\boldsymbol{n}\alpha}\hat{X}^\dagger_{\boldsymbol{n}\beta}\hat{D}_{\boldsymbol{n}\beta}\hat{X}_{\boldsymbol{n}\alpha} + \hat{D}^\dagger_{\boldsymbol{n}\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{D}_{\boldsymbol{n}\beta}\hat{Y}_{\boldsymbol{n}\alpha}\\ &+ \hat{D}^\dagger_{(n_x+1,n_y)\alpha}\hat{X}^\dagger_{\boldsymbol{n}\beta}\hat{D}_{(n_x+1,n_y)\beta}\hat{X}_{\boldsymbol{n}\alpha} + \hat{D}^\dagger_{(n_x,n_y+1)\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{D}_{(n_x,n_y+1)\beta}\hat{Y}_{\boldsymbol{n}\alpha}]\\ &- J_{\rm pp}\sum_{\boldsymbol{n},\alpha\beta}[\hat{X}^\dagger_{\boldsymbol{n}\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{X}_{\boldsymbol{n}\beta}\hat{Y}_{\boldsymbol{n}\alpha} + \hat{X}^\dagger_{\boldsymbol{n}\alpha}\hat{Y}^\dagger_{(n_x+1,n_y)\beta}\hat{X}_{\boldsymbol{n}\beta}\hat{Y}_{(n_x+1,n_y)\alpha}\\ &+ \hat{X}^\dagger_{(n_x,n_y+1)\alpha}\hat{Y}^\dagger_{\boldsymbol{n}\beta}\hat{X}_{(n_x,n_y+1)\beta}\hat{Y}_{\boldsymbol{n}\alpha} + \hat{X}^\dagger_{(n_x,n_y+1)\alpha}\hat{Y}^\dagger_{(n_x+1,n_y)\beta}\hat{X}_{(n_x,n_y+1)\beta}\hat{Y}_{(n_x+1,n_y)\alpha}].\end{aligned} \tag{2.12}$$

Let us now analyse the structure of the total electron Hamiltonian $\hat{\mathcal{H}}' = \hat{\mathcal{H}}'_{\rm BH} + \hat{\mathcal{H}}_{\rm HL}$. In terms of the Fermi operators $\hat{\Psi}_{i\alpha}$, corresponding to the atomic orbitals, $\hat{\mathcal{H}}'$ reads

$$\hat{\mathcal{H}}' = \sum_{i,\alpha}(\epsilon_i - \mu)\hat{\Psi}^\dagger_{i\alpha}\hat{\Psi}_{i\alpha} - \sum_{i<j,\alpha}(\tilde{t}_{ji}\hat{\Psi}^\dagger_{j\alpha}\hat{\Psi}_{i\alpha} + \tilde{t}^*_{ji}\hat{\Psi}^\dagger_{i\alpha}\hat{\Psi}_{j\alpha}) - \sum_{i<j,\alpha\beta}J_{ij}\hat{\Psi}^\dagger_{i\beta}\hat{\Psi}^\dagger_{j\alpha}\hat{\Psi}_{i\alpha}\hat{\Psi}_{j\beta}, \tag{2.13}$$

where $\tilde{t}_{ji} = t_{ji}{\rm e}^{{\rm i}\phi_{ji}}$, $t_{ji} = t_{ij}$ and $\phi_{ji} = \phi_j - \phi_i$ is the phase difference between the ith and jth atomic orbitals in the overlapping domain. Roughly speaking, onto every single-electron hopping amplitude t_{ij} one can map a corresponding two-electron hopping amplitude J_{ij}. The

case of a strong electron correlation implies that J_{ij} could be of the order of t_{ij}. Thus, one can expect that the following inequalities hold true: $J_{\rm pp} < J_{\rm pd} < J_{\rm sp} < J_{\rm sd}$.

In fact, the s–d exchange is the basic process responsible for the magnetism of transition metals; see for example [18]. It has been understood since the dawn of quantum physics that the mechanism of ferromagnetism [28] is the two-electron exchange owing to the electron correlations [29].

Here we shall add a few words in retrospect concerning the two-electron correlation parametrized by J_{ij} in (2.13). Probably the first two-electron problem was Bohr's consideration of the He atom [30] (cf [31, 32]) in which two electrons have opposite coordinates $\boldsymbol{r}_2 = -\boldsymbol{r}_1$ and momenta $\boldsymbol{p}_2 = -\boldsymbol{p}_1$. For a purely radial motion, such a fall to the nucleus is stable and many years after Bohr's prediction double Rydberg states, with an effective $Ry_{\rm eff} = (2 - 1/4)Ry$, were discovered by electron energy loss spectroscopy [33]. These double Rydberg states with opposite electron momenta can be considered as proto-forms of the Cooper pairs. Interestingly, in 1914, Sir J J Thomson proposed [34] (cf also the textbook [35]) that electric charge can propagate as electron doublets—another proto-form of the local (Ogg–Schafroth) pairs [36, 37]. Before the appearance of quantum mechanics, Lewis [38] and Langmuir [39] introduced the idea of electron doublets in order to explain the nature of the chemical bond. At nearly the same time Parson [40] came to the conclusion that 'an electron is not merely an electron charge but a small magnet' or in his terminology 'a magneton', cf [38]. Later, in 1926, Lewis also introduced the notion of a photon [41], without any reliable theoretical background at the time.

In the era of new quantum mechanics Heitler and London [19] realized the idea of electron doublets [42] and convincingly demonstrated how the two-particle correlation owing to a strong Coulomb repulsion can lead to a decrease of the energy, and, by virtue of the Hellmann–Feynman theorem, to inter-atomic attraction for the singlet state of the electron doublet. The original HL calculation, which is nowadays interpreted in every textbook in quantum mechanics and/or quantum chemistry, indeed gives a wrong sign of the exchange energy for very large inter-atomic distances but, in principle, there are no conceptual difficulties in the HL theory. The exchange energy J was represented [43] as a surface integral in the two-electron six-dimensional space $(\boldsymbol{r}_1, \boldsymbol{r}_2)$ and this was shown to be an asymptotically exact result, cf also [44]. The surface integral method gives amazingly accurate results (cf the excellent monograph by Patil and Tang [45]) even if the exchange energy is of the order of the energies typical for solid state phenomena. Unfortunately, this method, that ought to be applied to *ab initio* calculated (e.g., from density functional theory (DFT) [46]) wavefunctions, is barely known in the solid state community (although a very recent work by Gor'kov and Krotkov [47] indicates that it is not completely forgotten).

This is one of the reasons why the t and J transfer integrals have been treated phenomenologically just as fitting parameters of the theory. A valuable discussion on a similar scope of ideas has recently been given by Brovetto *et al* [48] but it may well not be the only case. In order to ease comparison of the HL Hamiltonian with the other types discussed in the search for a theory of high-$T_{\rm c}$ superconductivity we shall rewrite it in terms of spin variables.

The grounds for our theory were first set by Schubin and Wonsowsky and later in clearer notions and notation by Zener [18]. The s–d two-electron exchange is the intra-atomic version of the HL interaction. Both of those four-fermion interactions due to HL and Schubin–Wonsowsky–Zener can in principle mediate superconductivity and magnetism.

2.2.1. Spin variables. Let us introduce the spin operator $\hat{\boldsymbol{S}}_i$ and particle number operator $\hat{n}_i$ for each atomic orbital,

$$\hat{\boldsymbol{S}}_i = \hat{\Psi}_i^\dagger \frac{\boldsymbol{\sigma}}{2} \hat{\Psi}_i, \qquad \hat{n}_i = \hat{\Psi}_i^\dagger \sigma_0 \hat{\Psi}_i, \qquad \hat{\Psi}_i^\dagger = (\hat{\Psi}_{i\uparrow}^\dagger, \hat{\Psi}_{i\downarrow}^\dagger), \tag{2.14}$$

where $\sigma_0 = \mathbb{1}_{2\times 2}$ and $\boldsymbol{\sigma}$ are the Pauli sigma matrices, and the first two formulae imply summation over the spin indices. Also introducing the spin exchange operator $\hat{P}_{ij}$,

$$P\hat{\Psi}_{i\alpha}\hat{\Psi}_{j\beta} = \hat{\Psi}_{i\beta}\hat{\Psi}_{j\alpha}, \qquad \hat{P}_{ij} = \sum_{\alpha\beta}(\hat{\Psi}_{i\alpha}\hat{\Psi}_{j\beta})^{\dagger} P \hat{\Psi}_{i\alpha}\hat{\Psi}_{j\beta}, \tag{2.15}$$

we can rewrite the HL Hamiltonian *per bond* as [49–51]

$$-J\sum_{\alpha\beta}\hat{\Psi}^{\dagger}_{i\beta}\hat{\Psi}^{\dagger}_{j\alpha}\hat{\Psi}_{i\alpha}\hat{\Psi}_{j\beta} = J\hat{P}_{ij} = 2J(\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j + \tfrac{1}{4}\hat{n}_i\hat{n}_j). \tag{2.16}$$

We should stress that in the t–J model the term $\propto \hat{n}_i\hat{n}_j$ enters with negative sign [52, 53]. Let us also provide the 'mixed' representation:

$$\begin{aligned} 2\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j &= \hat{S}_{i,x}(\hat{\Psi}^{\dagger}_{j\uparrow}\hat{\Psi}_{j\downarrow} + \hat{\Psi}^{\dagger}_{j\downarrow}\hat{\Psi}_{j\uparrow}) + \hat{S}_{i,y}(-\mathrm{i}\hat{\Psi}^{\dagger}_{j\uparrow}\hat{\Psi}_{j\downarrow} + \mathrm{i}\hat{\Psi}^{\dagger}_{j\downarrow}\hat{\Psi}_{j\uparrow}) + \hat{S}_{i,z}(\hat{n}_{j\uparrow} - \hat{n}_{j\downarrow}) \\ &= \hat{S}_{i,+}\hat{\Psi}^{\dagger}_{j\downarrow}\hat{\Psi}_{j\uparrow} + \hat{S}_{i,-}\hat{\Psi}^{\dagger}_{j\uparrow}\hat{\Psi}_{j\downarrow} + \hat{S}_{i,z}(\hat{n}_{j\uparrow} - \hat{n}_{j\downarrow}), \end{aligned} \tag{2.17}$$

where $\hat{n}_{j\uparrow} \equiv \hat{\Psi}^{\dagger}_{j\uparrow}\hat{\Psi}_{j\uparrow}$, and $\hat{S}_{i,+} = \hat{\Psi}^{\dagger}_{i\uparrow}\hat{\Psi}_{i\downarrow} = \hat{S}^{\dagger}_{i,-}$. Note that (2.16) implies a purely orbital motion without spin flip: two electrons exchange their orbitals and only the spin indices reflect this correlated hopping. For $J > 0$, the HL Hamiltonian has a singlet ground state

$$|\mathrm{S}\rangle = \frac{1}{\sqrt{2}}(\hat{\Psi}^{\dagger}_{i\uparrow}\hat{\Psi}^{\dagger}_{j\downarrow} - \hat{\Psi}^{\dagger}_{i\downarrow}\hat{\Psi}^{\dagger}_{j\uparrow})|\mathrm{vac}\rangle, \qquad \hat{\Psi}_{i\alpha}|\mathrm{vac}\rangle = 0, \qquad \langle\mathrm{vac}|\mathrm{vac}\rangle = 1, \tag{2.18}$$

with eigenvalue $-J$. The lowering in energy of the singlet state, having a symmetric orbital wavefunction, is of purely kinetic origin related to the delocalization of the particles at different orbitals. Symbolically, the 'location' of the (approximately) localized electron doublet(s) in the structure signature of a molecule is designated by a colon, e.g., H:H for the H_2 molecule. This Lewis notation for the valence bond with energy $-J$ (or four-fermion terms in the second-quantization language) is an important ingredient of the chemical intuition. In principle, such an exchange lowering is expected to exist for Bose particles as well. For electrons, however, we have triplet excited states

$$\begin{aligned} |\mathrm{T}+1\rangle &= \hat{\Psi}^{\dagger}_{i\uparrow}\hat{\Psi}^{\dagger}_{j\uparrow}|\mathrm{vac}\rangle, \\ |\mathrm{T}0\rangle &= \frac{1}{\sqrt{2}}(\hat{\Psi}^{\dagger}_{i\uparrow}\hat{\Psi}^{\dagger}_{j\downarrow} + \hat{\Psi}^{\dagger}_{i\downarrow}\hat{\Psi}^{\dagger}_{j\uparrow})|\mathrm{vac}\rangle, \\ |\mathrm{T}-1\rangle &= \hat{\Psi}^{\dagger}_{i\downarrow}\hat{\Psi}^{\dagger}_{j\downarrow}|\mathrm{vac}\rangle, \end{aligned} \tag{2.19}$$

with eigenvalue J. In the present work we consider the parameter J to be *positive if it corresponds to antiferromagnetism, or pairing in the singlet channel*. Thus the singlet–triplet splitting for the single-bond HL Hamiltonian (2.16) is $2J$. Similarly, the bonding–antibonding splitting for the single-particle hopping Hamiltonian $-t\sum_{\alpha}(\hat{\Psi}^{\dagger}_{j\alpha}\hat{\Psi}_{i\alpha} + \hat{\Psi}^{\dagger}_{i\alpha}\hat{\Psi}_{j\alpha})$ is $2t$, and the energy threshold for creation of a pair of normal carriers, considered in the next section, is 2Δ. Besides stemming from bare inter- and intra-atomic processes, two-electron hopping amplitudes J can be created by strong correlations within the Hubbard model. For a nice review on this subject the reader is referred to the article by Spalek and Honig [53].

3. Reduced Hamiltonian and the BCS gap equation

Substituting the Fermi operators $\hat{\Psi}_{n\alpha}$, equation (2.11), into (2.12) one obtains the HL interaction Hamiltonian in a diagonal band representation. For the case of zero electric current [54], solely the reduced Hamiltonian $\hat{\mathcal{H}}_{\mathrm{HL-R}}$, including only creation and annihilation operators with opposite momenta, has to be taken into account:

$$\hat{\mathcal{H}}_{\mathrm{HL-R}} = \frac{1}{2N}\sum_{b,\boldsymbol{p}}\sum_{b',\boldsymbol{p}'}\sum_{\alpha\beta}\hat{c}^{\dagger}_{b,\boldsymbol{p}\beta}\hat{c}^{\dagger}_{b,-\boldsymbol{p}\alpha}V_{b,\boldsymbol{p};b',\boldsymbol{p}'}\hat{c}_{b',-\boldsymbol{p}'\alpha}\hat{c}_{b',\boldsymbol{p}'\beta}. \tag{3.1}$$

For singlet superconductors it is necessary to take into account the pairing with opposite spins; thereby, the *total reduced* Hamiltonian reads

$$\hat{\mathcal{H}}'_{\mathrm{R}} = \sum_{b,\boldsymbol{p},\alpha} \eta_{b,\boldsymbol{p}} \hat{c}^{\dagger}_{b,\boldsymbol{p}\alpha} \hat{c}_{b,\boldsymbol{p}\alpha} + \frac{1}{N} \sum_{b,\boldsymbol{p}} \sum_{b',\boldsymbol{p}'} V_{b,\boldsymbol{p};b',\boldsymbol{p}'} \hat{c}^{\dagger}_{b,\boldsymbol{p}\uparrow} \hat{c}^{\dagger}_{b,-\boldsymbol{p}\downarrow} \hat{c}_{b',-\boldsymbol{p}'\downarrow} \hat{c}_{b',\boldsymbol{p}'\uparrow}, \tag{3.2}$$

where $\eta_{b,\boldsymbol{p}} \equiv \epsilon_{b,\boldsymbol{p}} - \mu$ are the band energies measured from the chemical potential [54]. Hence the BCS equation [3] for the superconducting gap takes the familiar form

$$\Delta_{b,\boldsymbol{p}} = \frac{1}{N} \sum_{b',\boldsymbol{p}'} (-V_{b,\boldsymbol{p};b',\boldsymbol{p}'}) \frac{1 - 2n_{b',\boldsymbol{p}'}}{2E_{b',\boldsymbol{p}'}} \Delta_{b',\boldsymbol{p}'}, \tag{3.3}$$

where $E_{b,\boldsymbol{p}} = (\eta^2_{b,\boldsymbol{p}} + |\Delta_{b,\boldsymbol{p}}|^2)^{1/2}$ are the quasiparticle energies and $n_{b,\boldsymbol{p}} = [\exp(E_{b,\boldsymbol{p}}/k_{\mathrm{B}}T) + 1]^{-1}$ are the Fermi filling factors with k_{B} the Boltzmann constant, and T the temperature. The summation over the band index b' should be restricted to the partially filled (metallic) bands, comprising sheets of the Fermi surface. Applying this standard procedure to the HL Hamiltonian (2.12), and after some algebra, we obtain the desired BCS pairing kernel,

$$\begin{aligned} V_{b,\boldsymbol{p};b',\boldsymbol{p}'} = {} & -2J_{\mathrm{sd}} S_{\boldsymbol{p}} S_{\boldsymbol{p}'} D_{\boldsymbol{p}} D_{\boldsymbol{p}'} - J_{\mathrm{pp}} \gamma_x X_{\boldsymbol{p}} X_{\boldsymbol{p}'} \gamma_y Y_{\boldsymbol{p}} Y_{\boldsymbol{p}'} \\ & + 2(J_{\mathrm{sp}} S_{\boldsymbol{p}} S_{\boldsymbol{p}'} + J_{\mathrm{pd}} D_{\boldsymbol{p}} D_{\boldsymbol{p}'})(\gamma_x X_{\boldsymbol{p}} X_{\boldsymbol{p}'} + \gamma_y Y_{\boldsymbol{p}} Y_{\boldsymbol{p}'}), \end{aligned} \tag{3.4}$$

where

$$\gamma_x = 4\cos\left(\frac{p_x + p'_x}{2}\right), \qquad \gamma_y = 4\cos\left(\frac{p_y + p'_y}{2}\right). \tag{3.5}$$

As the band indices b and b' enter implicitly in the band energies $\epsilon_{b,\boldsymbol{p}}$ in the equation for the eigenvectors $\Psi_{\boldsymbol{p}}(\epsilon_{b,\boldsymbol{p}})$, we will suppress them hereafter. The layered cuprates, admittedly, have a single conduction band and their Fermi surface has the shape of a rounded square. In this simplest case one has to solve numerically the nonlinear integral equation

$$\Delta_{\boldsymbol{p}} = \int_{-\pi}^{\pi} \frac{\mathrm{d}q_x}{2\pi} \int_{-\pi}^{\pi} \frac{\mathrm{d}q_y}{2\pi} (-V_{\boldsymbol{pq}}) \frac{\Delta_{\boldsymbol{q}}}{2E_{\boldsymbol{q}}} \tanh\left(\frac{E_{\boldsymbol{q}}}{2k_{\mathrm{B}}T}\right). \tag{3.6}$$

The solution to this general gap equation, depending on the J_{ij} values, can exhibit s-, p- or d-type symmetry. It has been shown previously that a purely p–p model [21, 55] ($J_{\mathrm{pp}} > 0$) results in a d_{xy} ($\mathrm{B}_{2\mathrm{g}}$) gap anisotropy. However, we found that an agreement with the experimentally observed $\mathrm{d}_{x^2-y^2}$ ($\mathrm{B}_{1\mathrm{g}}$) gap anisotropy (for a review see for example [56]) can be achieved only in the simplest possible case of a dominant s–d exchange. This separable Hamiltonian deserves special attention and we will analyse it in the next sections.

4. Separable s–d model

For the special case of a purely s–d model, $J_{\mathrm{sp}} = J_{\mathrm{pd}} = J_{\mathrm{pp}} = 0$, representing the spin exchange operator $\hat{P}$ as a (4×4) matrix, cf equations (2.15) and (2.16), the reduced pairing Hamiltonian takes the form

$$\hat{\mathcal{H}}_{\mathrm{HL-R}} = \frac{J_{\mathrm{sd}}}{N} \sum_{\boldsymbol{p},\boldsymbol{q}} \begin{pmatrix} \hat{S}_{-\boldsymbol{p}\uparrow} \hat{D}_{\boldsymbol{p}\uparrow} \\ \hat{S}_{-\boldsymbol{p}\uparrow} \hat{D}_{\boldsymbol{p}\downarrow} \\ \hat{S}_{-\boldsymbol{p}\downarrow} \hat{D}_{\boldsymbol{p}\uparrow} \\ \hat{S}_{-\boldsymbol{p}\downarrow} \hat{D}_{\boldsymbol{p}\downarrow} \end{pmatrix}^{\dagger} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{S}_{-\boldsymbol{q}\uparrow} \hat{D}_{\boldsymbol{q}\uparrow} \\ \hat{S}_{-\boldsymbol{q}\uparrow} \hat{D}_{\boldsymbol{q}\downarrow} \\ \hat{S}_{-\boldsymbol{q}\downarrow} \hat{D}_{\boldsymbol{q}\uparrow} \\ \hat{S}_{-\boldsymbol{q}\downarrow} \hat{D}_{\boldsymbol{q}\downarrow} \end{pmatrix}. \tag{4.1}$$

Carrying out an additional reduction for a spin-singlet pairing, the interaction Hamiltonian reads

$$\hat{\mathcal{H}}_{\mathrm{HL-R}} = -\frac{J_{\mathrm{sd}}}{N} \sum_{\boldsymbol{p},\boldsymbol{q},\alpha} \hat{S}^{\dagger}_{\boldsymbol{p},\alpha} \hat{D}^{\dagger}_{-\boldsymbol{p},-\alpha} \hat{D}_{-\boldsymbol{q},-\alpha} \hat{S}_{\boldsymbol{q},\alpha}, \tag{4.2}$$

where $-\alpha$ stands for the electron spin projection opposite to α. For comparison, we again provide the kinetic energy part of the Hamiltonian employing the same notation,

$$\hat{\mathcal{H}}'_{\mathrm{BH}} = \sum_{\boldsymbol{p},\alpha} \begin{pmatrix} \hat{D}_{\boldsymbol{p},\alpha} \\ \hat{S}_{\boldsymbol{p},\alpha} \\ \hat{X}_{\boldsymbol{p},\alpha} \\ \hat{Y}_{\boldsymbol{p},\alpha} \end{pmatrix}^{\dagger} \begin{pmatrix} \epsilon_{\mathrm{d}}-\mu & 0 & t_{\mathrm{pd}}s_x & -t_{\mathrm{pd}}s_y \\ 0 & \epsilon_{\mathrm{s}}-\mu & t_{\mathrm{sp}}s_x & t_{\mathrm{sp}}s_y \\ t_{\mathrm{pd}}s_x & t_{\mathrm{sp}}s_x & \epsilon_{\mathrm{p}}-\mu & -t_{\mathrm{pp}}s_xs_y \\ -t_{\mathrm{pd}}s_y & t_{\mathrm{sp}}s_y & -t_{\mathrm{pp}}s_xs_y & \epsilon_{\mathrm{p}}-\mu \end{pmatrix} \begin{pmatrix} \hat{D}_{\boldsymbol{p},\alpha} \\ \hat{S}_{\boldsymbol{p},\alpha} \\ \hat{X}_{\boldsymbol{p},\alpha} \\ \hat{Y}_{\boldsymbol{p},\alpha} \end{pmatrix}. \tag{4.3}$$

Within the s–d model considered, the pairing kernel (3.4) factors into functions depending only on $\boldsymbol{p}$ or $\boldsymbol{q}$,

$$(-V_{\boldsymbol{pq}}) = 2J_{\mathrm{sd}}S_{\boldsymbol{p}}D_{\boldsymbol{p}}S_{\boldsymbol{q}}D_{\boldsymbol{q}} \equiv 2J_{\mathrm{sd}}\chi_{\boldsymbol{p}}\chi_{\boldsymbol{q}}. \tag{4.4}$$

A schematic representation of the J_{sd} exchange amplitude is given in figure 2. This factorizable Markowitz–Kadanoff [57] form of the pairing kernel is a direct consequence of the local intra-atomic character of the s–d exchange in the transition ion. Substituting in equation (3.6)

$$\Delta_{\boldsymbol{p}}(T) = \Xi(T)S_{\boldsymbol{p}}D_{\boldsymbol{p}} = \Xi(T)\chi_{\boldsymbol{p}}, \tag{4.5}$$

one obtains in a closed form, cf [58], a simple BCS equation for the temperature dependence of the gap,

$$2J_{\mathrm{sd}}\left\langle \frac{\chi_{\boldsymbol{p}}^2}{2E_{\boldsymbol{p}}} \tanh\left(\frac{E_{\boldsymbol{p}}}{2k_{\mathrm{B}}T}\right)\right\rangle = 1, \tag{4.6}$$

where

$$E_{\boldsymbol{p}} \equiv (\eta_{\boldsymbol{p}}^2 + \Delta_{\boldsymbol{p}}^2)^{1/2} = [(\epsilon_{\boldsymbol{p}} - E_{\mathrm{F}})^2 + (\Xi(T)\chi_{\boldsymbol{p}})^2]^{1/2}, \tag{4.7}$$

$$\langle f_{\mathrm{p}}\rangle = \int_0^{2\pi}\int_0^{2\pi} \frac{\mathrm{d}p_x\,\mathrm{d}p_y}{(2\pi)^2} f(\boldsymbol{p}), \tag{4.8}$$

$E_{\mathrm{F}} \equiv \mu$. We wish to mention that separability of the order parameter (4.5) has been derived by Pokrovsky [59] in the general weak-coupling case and not only for factorizable pairing kernels.

According to (2.4) we have

$$\begin{aligned}\chi_{\boldsymbol{p}} \equiv S_{\boldsymbol{p}}D_{\boldsymbol{p}} = {} & 4\varepsilon_{\mathrm{p}}t_{\mathrm{sp}}t_{\mathrm{pd}}(x-y)[\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{p}}^2 - 4\varepsilon_{\mathrm{p}}t_{\mathrm{sp}}^2(x+y) + 32t_{\mathrm{pp}}\tau_{\mathrm{sp}}^2xy] \\ & \times \{[4\varepsilon_{\mathrm{p}}t_{\mathrm{sp}}t_{\mathrm{pd}}(x-y)]^2 + [\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{p}}^2 - 4\varepsilon_{\mathrm{p}}t_{\mathrm{sp}}^2(x+y) + 32t_{\mathrm{pp}}\tau_{\mathrm{sp}}^2xy]^2 \\ & + 4x[(\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{p}} - 8\tau_{\mathrm{sp}}^2y)t_{\mathrm{pd}}]^2 + 4y[(\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{p}} - 8\tau_{\mathrm{sp}}^2x)t_{\mathrm{pd}}]^2\}^{-1}.\end{aligned} \tag{4.9}$$

The gap symmetry is then easily made obvious in the narrow-band approximation. Formally, it is the asymptotic behaviour of the eigenvector (2.4) for vanishing hopping integrals $t \to 0$. In this limit case [27], we have $\epsilon_{3,\boldsymbol{p}} \approx \epsilon_{\mathrm{d}}$, and

$$\tilde{\Psi}_{3,\boldsymbol{p}} = \begin{pmatrix} D_{3,\boldsymbol{p}} \\ S_{3,\boldsymbol{p}} \\ X_{3,\boldsymbol{p}} \\ Y_{3,\boldsymbol{p}} \end{pmatrix} \approx \begin{pmatrix} 1 \\ -(t_{\mathrm{sp}}t_{\mathrm{pd}}/\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{p}})(s_x^2 - s_y^2) \\ (t_{\mathrm{pd}}/\varepsilon_{\mathrm{p}})s_x \\ (t_{\mathrm{pd}}/\varepsilon_{\mathrm{p}})s_y \end{pmatrix}. \tag{4.10}$$

Clearly, $D_{3,\boldsymbol{p}}$ exhibits $\mathrm{A}_{1\mathrm{g}}$ symmetry, while $S_{3,\boldsymbol{p}}$ has the $\mathrm{B}_{1\mathrm{g}}$ symmetry, whence the product $S_{3,\boldsymbol{p}}D_{3,\boldsymbol{p}} \propto \cos p_x - \cos p_y$ 'inherits' the $\mathrm{B}_{1\mathrm{g}}$ symmetry, figure 3(b), which is conserved even for realistic values of the hopping integrals, and from (4.5) it follows that

$$\Delta_{\boldsymbol{p}} \propto S_{3,\boldsymbol{p}}D_{3,\boldsymbol{p}} \approx \frac{2t_{\mathrm{sp}}t_{\mathrm{pd}}}{(E_{\mathrm{F}}-\epsilon_{\mathrm{s}})(E_{\mathrm{F}}-\epsilon_{\mathrm{p}})}(\cos p_x - \cos p_y). \tag{4.11}$$

As can be seen in figure 3(c) this small-t approximation fits the ARPES data for the gap anisotropy quite well. Similar experimental data have been previously reported, e.g., in [63].

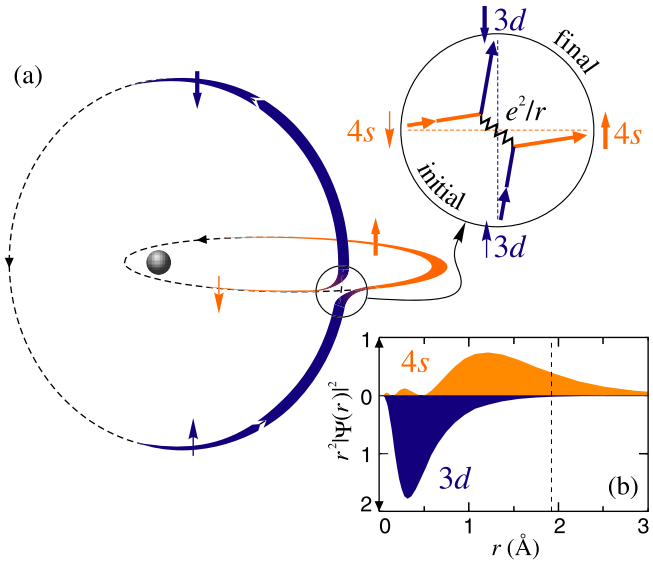

Figure 2. Pairing two-electron exchange amplitude J_{sd} 'hidden' in the Cu atom. (a) Classical Bohr–Sommerfeld representation of the s–d two-electron exchange process. The inset shows how the Coulomb scattering leads to an effective electron spin exchange. (b) Electron charge distribution for Cu 4s and Cu 3d orbitals: the dashed line marks the Cu–O distance in the CuO_2 plane.

Note, additionally, that close to the (π,π)-point, where $(p_x-\pi)^2+(p_y-\pi)^2 \ll 1$, the angular dependence of the gap can be written in the form

$$\Delta_{\boldsymbol{p}} \propto \cos p_x - \cos p_y \approx [(p_x-\pi)^2+(p_y-\pi)^2]\cos 2\phi, \qquad \tan\phi = \frac{p_y-\pi}{p_x-\pi}. \tag{4.12}$$

The d-type angular dependence of both the gap anisotropy and the separable pairing kernel is often postulated in phenomenological model Hamiltonians to describe high-T_c superconductivity. The previous discussion thus provides a microscopic justification based on the fundamental exchange amplitudes. For the oxygen scenario [27, 64], in which the Fermi level falls in a nonbonding oxygen band, $\epsilon_{2,\boldsymbol{p}} \approx \epsilon_p$ and $t \to 0$ [20], the gap function has different or additional nodes along the Fermi contour,

$$\begin{pmatrix} D_{2,\boldsymbol{p}} \\ S_{2,\boldsymbol{p}} \\ X_{2,\boldsymbol{p}} \\ Y_{2,\boldsymbol{p}} \end{pmatrix} \approx \frac{1}{\sqrt{s_x^2+s_y^2}} \begin{pmatrix} -2(t_{pd}/\varepsilon_d)s_x s_y \\ 2t_{sp}(t_{pp}\varepsilon_d+2t_{pd}^2)(\varepsilon_d t_{sp}^2+\varepsilon_s t_{pd}^2)^{-1}s_x s_y(s_x^2-s_y^2) \\ -s_y \\ s_x \end{pmatrix}. \tag{4.13}$$

Here $D_{2,\boldsymbol{p}}$ and $S_{2,\boldsymbol{p}}$ exhibit B_{2g} and A_{2g} symmetries, respectively. Let us also mention that the $\boldsymbol{s}$-vector components, equation (2.3), constitute the arguments of the basis functions of the symmetry representations.

Employing the analytical expression (2.8) for the constant-energy contours (CECs), one can implement an efficient numerical integration,

$$\int_0^{2\pi} \mathrm{d}p_x \int_0^{2\pi} \mathrm{d}p_y\, f(\epsilon_{\boldsymbol{p}}) = \int_{\epsilon_b}^{\epsilon_t} \mathrm{d}\epsilon \oint \frac{\mathrm{d}p_l}{v_{\boldsymbol{p}}} f(\epsilon), \tag{4.14}$$

where

$$v_{\boldsymbol{p}} = \left|\frac{\partial\epsilon_{\boldsymbol{p}}}{\partial \boldsymbol{p}}\right| = \frac{[(\mathcal{A}y+\mathcal{B})^2x(1-x)+(\mathcal{A}x+\mathcal{B})^2y(1-y)]^{1/2}}{|\mathcal{A}'xy+\mathcal{B}'(x+y)+\mathcal{C}'|}, \tag{4.15}$$

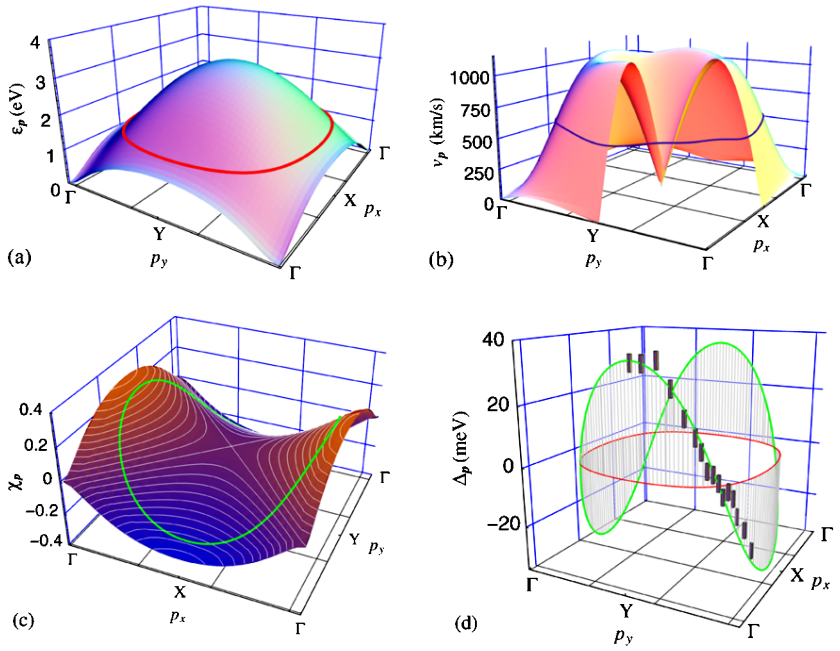

Figure 3. Electronic properties of the superconducting CuO_2 plane. (a) Conduction band energy ϵ_p as a function of the quasimomentum p. The red contour corresponding to the Fermi energy, $\epsilon_p = E_F$, is in excellent agreement with the ARPES data [60]. (b) Quasiparticle velocity v_p as a function of quasimomentum. The velocity variation along the Fermi contour is less than 10%. The energy parameters are fitted to be in agreement with the typical *ab initio* calculations [61]. The significant overestimate disappears if the bandwidth is fitted to the experimental data, but the shape is conserved. (c) Momentum dependence of the gap-anisotropy function χ_p within the s–d model. The functional values along the Fermi contour are indicated by a green line. (d) Superconducting gap at zero temperature Δ_p (green line) according to our analytical result (4.5), plotted along the Fermi contour (red line). The ARPES data [62] for BSCCO are given as prisms with sizes corresponding to the experimental error bars. The gap function along the Fermi contour has the same qualitative behaviour and symmetry as the Cu $3d_{x^2-y^2}$ electron wavefunction along the circular orbit sketched in figure 1(a).

with $\mathcal{A}'$, $\mathcal{B}'$ and $\mathcal{C}'$ being the energy derivatives of the polynomials (2.9),

$$\begin{aligned}\mathcal{A}'(\epsilon) &= 16[2t_{\rm sp}^2 t_{\rm pp} - 2t_{\rm pd}^2 t_{\rm pp} - t_{\rm pp}^2(\varepsilon_{\rm d} + \varepsilon_{\rm s})],\\ \mathcal{B}'(\epsilon) &= -4(t_{\rm sp}^2\varepsilon_{\rm d} + t_{\rm pd}^2\varepsilon_{\rm s}) - 4\varepsilon_{\rm p}(t_{\rm sp}^2 + t_{\rm pd}^2),\\ \mathcal{C}'(\epsilon) &= \varepsilon_{\rm s}\varepsilon_{\rm p}^2 + \varepsilon_{\rm d}\varepsilon_{\rm p}^2 + 2\varepsilon_{\rm d}\varepsilon_{\rm s}\varepsilon_{\rm p}.\end{aligned} \tag{4.16}$$

Using these functions, the band spectrum, see (2.8), can be obtained by Newton iterations

$$\epsilon_p^{[i]} = \epsilon_p^{[i-1]} - \frac{\mathcal{A}xy + \mathcal{B}(x+y) + \mathcal{C}}{\mathcal{A}'xy + \mathcal{B}'(x+y) + \mathcal{C}'} \tag{4.17}$$

with initial approximation for the conduction band $\epsilon_{3,p}^{[0]} = \epsilon_d$.

The charge carrier velocity is $v_p a_0/\hbar$, a_0 is the lattice constant, p_l the dimensionless momentum component along the CEC and $\epsilon_{\rm b}$ and $\epsilon_{\rm t}$ are the bottom and the top of the conduction band, respectively, $\epsilon_{\rm b} \leqslant \epsilon_p \leqslant \epsilon_{\rm t}$. The canonic equation for the CEC (2.8),

$$\mathcal{A}\cos p_x \cos p_y - (\mathcal{A} + 2\mathcal{B})(\cos p_x + \cos p_y) + \mathcal{A} + 4\mathcal{C} = 0, \tag{4.18}$$

can be cast in an explicit form

$$p_{y,1}(p_x) = 2\arcsin\sqrt{-\frac{\mathcal{B}x+\mathcal{C}}{\mathcal{A}x+\mathcal{B}}}, \qquad p_{y,2}(p_x) = 2\pi - p_{y,1}(p_x), \tag{4.19}$$

and for the length element $\mathrm{d}p_l$ we obtain

$$\mathrm{d}p_l = \sqrt{1+\left(\frac{\mathrm{d}p_y}{\mathrm{d}p_x}\right)^2}\,\mathrm{d}p_x, \qquad \left(\frac{\mathrm{d}p_y}{\mathrm{d}p_x}\right)^2 = \frac{x(1-x)}{y(1-y)}\left(\frac{\mathcal{A}y+\mathcal{B}}{\mathcal{A}x+\mathcal{B}}\right)^2. \tag{4.20}$$

The contour integration along the hole pocket $\varepsilon_{\boldsymbol{p}} = \text{const}$ centred at the (π,π) point only needs to be performed over one-eighth of the CEC

$$\oint \mathrm{d}p_l\, f(p_x, p_y) = 8\int_{p_d}^{\pi} f(p_x, p_y(p_x))\left(\frac{\mathrm{d}p_d(p_x)}{\mathrm{d}p_x}\right)\mathrm{d}p_x, \tag{4.21}$$

where

$$x_d = \sin^2\left(\frac{p_d}{2}\right), \qquad \mathcal{A}x_d^2 + 2\mathcal{B}x_d + \mathcal{C} = 0. \tag{4.22}$$

5. Antiferromagnetic character of J_{sd}

Let us address now the atomic physics underlying the s–d pairing mechanism. Within the framework of the Hartree–Fock (HF) theory the exchange energy is given [65] as an integral of the Cu 4s and Cu $3\mathrm{d}_{x^2-y^2}$ atomic wavefunctions,

$$-J_{\mathrm{sd}}^{(\mathrm{HF})} = \int\int \psi_{\mathrm{s}}^*(\boldsymbol{r}_1)\psi_{\mathrm{d}}^*(\boldsymbol{r}_2)\frac{e^2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\psi_{\mathrm{d}}(\boldsymbol{r}_1)\psi_{\mathrm{s}}(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2, \tag{5.1}$$

and its sign corresponds to repulsion and depairing for singlet Cooper pairs. Thus, one can formulate the following conceptual problem, emerging in fundamental physics:

(1) is it possible, as in the case of a covalent bond, for two-electron correlations to trigger a change of the sign of the exchange amplitude?
(2) how can one adapt the HL idea to a transition ion perturbed by ligands?

There is no doubt that the solution to this problem will illuminate other problems in the physics of magnetism as well. In brief, the enigma can be stated as to whether the HL approximation for the exchange energy may result in $J_{\mathrm{sd}} > 0$, cf [65]. Let us recall that as early as 1962 Herring [43] was advocating that 'antiferromagnetic J_{ij}'s should be the rule, ferromagnetic J_{ij}'s the exception'. For the present, we can adopt the s–d model as a convenient microscopic phenomenology of superconductivity in the CuO_2 plane. On the other hand, the exchange amplitude J_{sd} is an important ingredient in the physics of magnetism as well.

The physics of magnetism certainly displays lots of subtleties, but for a qualitative comparison let us trace the 'operation' of the s–d exchange amplitude J_{sd} in the case of the simplest model for a ferromagnetic metal. While for the CuO_2 plane the s band is empty, for transition metals it is the widest conduction band. The width of the d band is significantly smaller and thus, making a caricature of the ferromagnetic metals, we completely neglect the width of the d band. In this 'heavy-fermion' approximation the d electrons are considered as localized, and without significant energy loss they can be completely spin polarized, $\langle\hat{n}_{\mathrm{d}\uparrow}\rangle \approx 1$, $\langle\hat{S}_{\mathrm{d},z}\rangle \approx \frac{1}{2} > 0$. In this case the self-consistent approximation applied to (2.17) gives

$$2\hat{\boldsymbol{S}}_{\mathrm{d}}\cdot\hat{\boldsymbol{S}}_{\mathrm{s}} \approx \hat{S}_{\mathrm{d},z}(\hat{n}_{\mathrm{s}\uparrow}-\hat{n}_{\mathrm{s}\downarrow}) \approx \langle\hat{S}_{\mathrm{d},z}\rangle(n_{\mathrm{s}\uparrow}-n_{\mathrm{s}\downarrow}). \tag{5.2}$$

Here $n_{s\alpha} \equiv \langle \hat{n}_{s\alpha} \rangle$ denotes the average number of s electrons per atom with spin projection α. In order to calculate these variables one has to take into account the different filling of the s bands with different polarizations, and sum over the quasimomenta. Finally, the exchange energy per atom reads

$$E_X = -\tfrac{1}{2} J_{sd}(n_{s\downarrow} - n_{s\uparrow}) < 0. \tag{5.3}$$

In the CuO_2 plane, positive values of the J_{sd} parameter lead to singlet superconductivity. For ferromagnetic metals, positive values of J_{sd} correspond to polarization of the s band opposite to d-state polarization, $n_{s\downarrow} - n_{s\uparrow} > 0$. Thereby, ferromagnetism could be brought about by an exchange amplitude with a sign corresponding to antiparallel spin polarization of s and d orbitals, cf figure 4–15 of [50]. Thus the same sign of the s–d exchange amplitude J_{sd} can be at the origin of ferromagnetism, e.g., in Fe and Ni, and superconductivity in the CuO_2 plane. This is perhaps the simplest scenario for cuprate superconductivity based on the two-electron exchange processes.

According to a naive interpretation of Hund's rule the Kondo effect should not exist. In the epoch-making paper [66] on the resistance minimum in dilute magnetic alloys Kondo concluded that in the s–d exchange model, due to Zener [18], Kasuya and Yosida [67], the sign of the direct exchange amplitude J_{sd} must be antiferromagnetic. And vice versa, the minimum disappears if J_{sd} is ferromagnetic. Such minimum exists for many magnetic metals and alloys and is another hint in favour of Herring's argument [43] mentioned earlier. In his analysis Kondo speculates that J_{sd} is a parameter whose sign and magnitude have to be determined so as to fit the experiment, and concluded that antiferromagnetic values of the order of electron volts are quite reasonable. For a review on the Kondo problem we refer the reader to [68].

On the other hand, every textbook on atomic physics tells us that parallel electron spins and an antisymmetric wavefunction minimize the electrostatic energy. Put differently, the tendency toward ferromagnetism in Hund's rule is of electrostatic origin. As Kondo has pointed out [66], the problem is to find the origin of an antiferromagnetic J_{sd}, or how to overcome the strong electrostatic repulsion. It is very plausible that it is not a single driving force, but instead one has to take into account several interfering electron scattering amplitudes.

5.1. Intra-atomic correlations

The self-consistent approximation has been known in celestial mechanics for ages. Accordingly, the motion of a planet is averaged over its orbit. One then has to calculate the potential created by this orbital-averaged motion and perform a sum over all particles. Where does this scheme fail? It fails in the case of a resonance when the periods for some planets are commensurate or just equal. This is nothing but the case of a transition ion for which the energies and classical periods are very close. Then the resonant repetitive electron scattering, symbolically presented in figure 2, leads to strong electron correlations as in the double Rydberg states of atoms [33]. For double Rydberg states in He it is necessary to solve a two-electron quantum problem but for other atoms we have to take into account the influence of the other electrons in some self-consistent approximation, the local density approximation (LDA), for example. For two 4s electrons the two-electron correlations are so strong that they have to be taken into account from the very beginning [33]. There is no doubt that the two-electron correlations between 4s and 3d electrons having almost equal energies cannot be neglected. In other words, HF theory cannot be used directly. Hence, the Bohr picture is not merely a historical remark but rather an indispensable ingredient of the contemporary physics of magnetism: two-electron correlations can be important even in a *single* atom. We thus conclude that the two-electron correlations may overrule Hund's rule for the local s–d

exchange. Note also that the single-particle orbitals (accessible, e.g., from DFT [46], HF and X_α methods etc) only form an adequate basis for a subsequent account of electronic correlations. A first step in this direction will be *ab initio* calculation of the J_{sd}.

5.2. Indirect s–d exchange

The antiferromagnetism of the insulating phase of the undoped cuprates is mediated by the Bloch–Kramers–Anderson indirect exchange [69] between 3d electrons of nearest-neighbour Cu ions via O 2p electrons. It is unlikely that the numerical value of this J_{dd} exchange integral is dramatically changed in the metallic phase obtained by hole doping. In the metallic phase, however, the same indirect exchange mechanism will operate between 3d and 4s electrons at the same Cu atom via the 2p electrons of the O ligands. For illustration, let us compare the indirect s–d exchange amplitude $J_{sd}^{(ind)}$ with J_{dd}. There are three important factors: (i) Every Cu ion has four O ligands, figure 1(a). (ii) The hopping amplitude between 4s and 2p orbitals is bigger than the 3d–2p transfer. (iii) The Cu on-site Coulomb repulsion between 4s and 3d electrons U_{sd} is much smaller than the 3d–3d Hubbard repulsion U_{dd}. Taking these factors into account one can expect that $J_{sd}^{(ind)}$ is an order of magnitude bigger than J_{dd}:

$$J_{sd}^{(ind)} \simeq 4\left(\frac{t_{sp}}{t_{pd}}\right)^2 \frac{U_{dd}}{U_{sd}} J_{dd}. \tag{5.4}$$

The relatively small J_{dd} ensures Néel temperatures T_N of the order of room temperature. Hence, we can conclude that the indirect exchange can contribute significantly to the total J_{sd} amplitude responsible for the pairing. However, only very detailed first-principles calculations can clarify the relative contributions of the direct and the indirect s–d exchange.

5.3. Effect of mixing wavefunctions

In an early paper [70], by analysing the g-shift and the anomalous Hall effect in Gd metal, Kondo showed that an antiferromagnetic J_{sd} can result from the effect of mixing the wavefunctions of conduction and d electrons. We believe that this property is preserved if the d electrons also form a conduction band, or even in the case of a single s–p–d hybridized band. We should note that Kondo's argumentation for the need of a J_{sd} with an antiferromagnetic sign in the Kondo effect is related to Anderson's consideration of localized magnetic states in metals [71]. In the latter schematized model, based on the works of Friedel [72], Anderson shows that 'any g-shift caused by free-electron polarization will tend to have antiferromagnetic sign.'

As it was expected by various investigators the later numerical calculations confirmed that the striking features of negative hyperfine field with large amplitude comes mainly from the contact contribution of the core electrons [73–75]. The antipolarization between the s- and d electrons in transition metal compounds is also well observed by Mössbauer spectroscopy; however, the contribution of the core s electrons and conduction band cannot be experimentally resolved. For the pairing, the amplitude of the s–d Kondo scattering is essential because in some terminology the CuO_2 plane can be considered to be a single-band Kondo lattice, cf [76].

Given the above diversity of channels for s–d exchange it is not surprising that an adequate first-principles scheme to calculate J_{sd} is still sought. Furthermore, J_{sd} is involved in the theory of magnetism in an entangled way precluding so far a direct relation between *ab initio* calculations and formulae fitting the experiment [77].

6. Dogmatics, discussion, conclusions and perspectives

In a review on the history of studies of superconductivity and the prospects for further research in the field Ginzburg [2] conditionally divided the history into several periods.

(i) *The 'day before yesterday' (1911–1941).* This period starts with the discovery of superconductivity in Leiden by Gilles Holst and Heike Kamerlingh Onnes [2, 78].
(ii) *'Yesterday' (1942–1986).* This period embraces the appearance of the Ψ–Δ theories and the first significant technical applications.
(iii) *'Today' (1987–?).* This epoch emerged with the discovery of the high-T_c cuprates [1].
(iv) *'Tomorrow' (?).* The final landmark of 'today' must be some event.

Long ago, in the 'day before yesterday', high-T_c superconductivity was known as a 'blue dream' of physicists. Considerable theoretical efforts were applied 'yesterday', attempting to predict possible realizations of this phenomenon [79]. At that time the problem of high-T_c superconductivity was 'one of the most interesting and attractive problems from the purely scientific point of view' [79]. Intriguingly, the special role of *layered metallic systems* and *almost two-dimensional superconductivity* [80] was mentioned as early as this epoch, and a big variety of mechanisms of superconductivity were considered including s–d exchange [81, 82]. This exchange process has been well known in the physics of magnetism since the dawn of quantum mechanics. Thus it is not surprising that the first work on the s–d pairing mechanism, by Akhiezer and Pomeranchuk [81], was accomplished about a year after the celebrated BCS paper [3]. These pioneering works, however, 'have been ignored thus far' [83].

After the work of Bednorz and Müller [1] the problem of high-T_c superconductivity soon came into fashion. 'After experiencing the "smell of roast meat", yesterday skeptics or even critics can become zealous advocates of a new direction of endeavor. But this is another story—more in the realm of psychology and sociology than scientific and technical activity' [84]. All models of high-T_c superconductivity were revisited in great detail in the uncountable number of papers that have appeared in the epoch 'today'.

6.1. Aesthetics and frustrations of the central dogmas

The common trends of some new theoretical models for cuprate superconductivity were systematized by Anderson [85] in six dogmas. We find it very instructive to compare our theory of high-T_c superconductivity with these dogmas.

'Dogma I: All the relevant carriers of both spin and electricity reside in the CuO_2 plane and derive from the hybridized O 2p–Cu $3d_{x^2-y^2}$ orbital which dominates the binding in these compounds. . . . in summary look at the planes only (a great and welcome simplification)'.

The key ingredient of our pairing theory is the four-fermion s–d interaction between the Cu 4s and Cu $3d_{x^2-y^2}$ orbitals. If we cut the Cu 4s orbital off from the Hilbert space of the CuO_2 plane such a pairing interaction cannot exist. Although Cu 4s is an empty band, it is an important component of the theory of high-T_c superconductivity. The O 2p orbitals are the intermediaries between the Cu 4s and Cu $3d_{x^2-y^2}$ orbitals that create the necessary s–d hybridization of the conduction Cu $3d_{x^2-y^2}$ band.

'Dogma II: Magnetism and high-T_c superconductivity are closely related, in a very specific sense: i.e., the electrons which exhibit magnetism are the same as the charge carriers. . . . We must solve the old problem of doping of a single Mott–Hubbard band before we can begin the problem of high-T_c.'

The incommensurate spin-density waves (SDWs) observed in the superconducting phase of $La_2CuO_{4.11}$ and $La_{1.88}Sr_{0.12}O_4$ by neutron scattering [86] and muon spin

relaxation [87], respectively, demonstrated that antiferromagnetism of the Cu site is innocuous for superconductivity in the cuprates. These antiferromagnetic correlations are not depairing and do not significantly change T_c and the electronic structure of the CuO_2 plane. The observed correspondence between the magnetic and the superconducting order parameters is an additional hint that both phenomena have a common origin [88]; see also the detailed theoretical works [89]. Nevertheless the coexistence of SDW and superconductivity with a common critical temperature cannot be clearly observed in every high-T_c cuprate. As a result, superconductivity can be considered, at least in a first approximation, separately from a possible antiferromagnetism as is done in the present paper. In Cr metal the amplitude of the SDW shows also a BCS-like temperature dependence [90] and the SDW theory is based on the conventional theory of metals based in turn on the Landau Fermi-liquid theory. We consider the quasiparticle picture as a reliable starting point for the theory of high-T_c cuprates as well.

'Dogma III: The dominant interactions are repulsive and their energy scales are all large. . . . Restrict your attention to a single band, repulsive (not too big) U Hubbard model.'

Indeed, the dominant interactions are repulsive—'Nobody has abrogated the Coulomb law', as Landau used to emphasize [2]. However, something subtle occurs when the atomic orbitals are analysed. The strong electron repulsion leads to HL-type correlations: two electrons cannot simultaneously occupy the same orbital, even if they have opposite spins. The exchange of electrons between two orbitals decreases the electron kinetic energy and thereby the total energy of the whole system. In molecular physics, according to the Hellmann–Feynman theorem such a decrease in energy drives an inter-atomic attraction for large inter-atomic distances. Thus, the valence attraction is the final result of the dominant Coulomb repulsion between electrons. In this way the HL-type exchange between itinerant electrons gives rise to electron-electron attraction and conventional Cooper pairing. The s–d exchange, 'residing' in the Cu atom, can be considered as an 'intra-atomic-valence bond'—an attraction-sign scattering amplitude due to the Coulomb repulsion between the correlated electrons. The s–d exchange in the transition ions is one of the most intensive exchange processes in solid state physics. Such a high-frequency process is described by the exchange amplitude J_{sd} in the lattice models for the electronic structure and its sign is determined by the inter-electronic Coulomb repulsion. The HL interaction is a result of strong electron repulsion and survives even for infinite Hubbard U. This interaction is lost when starting with the infinite-U Hubbard model, however. Thus, not a single-band Hubbard model but a single-band s–d model with antiferromagnetic exchange amplitude is the adequate starting point for a realistic treatment of CuO_2 superconductivity.

'Dogma IV: The 'normal' metal above T_c . . . is not a Fermi liquid . . . but retains a Fermi surface satisfying Luttinger's theorem at least in the highest-T_c materials. We call this a Luttinger Liquid.'

Very recently, the crucial experiment was finally conducted. After 15 years of intensive investigations of the cuprates it is now experimentally established [91] that the overdoped cuprates obey the 150 year old Wiedemann–Franz law within a remarkable 1% accuracy. After this experimental clarification the theoretical comprehension will hardly keep us waiting long. This experiment has also solved the old problem of the nature of charge carriers created by doping of a single Mott–Hubbard band, cf *dogma II*. Now we know that charge carriers of the normal state are standard Landau quasiparticles [92] for which we have conventional Cooper pairing in the superconducting phase. 'Holons', 'spinons' and spin–charge separation are unlikely to occur and behave so as to emulate the properties of the ideal Fermi gas. As a function of the hole doping per Cu atom, $\tilde{p}$, the critical temperature is a smooth parabola,

$$T_c/T_c^{max} \approx 1 - 82.6(\tilde{p} - 0.16)^2. \tag{6.1}$$

Thus, it is improbable that the nature of the carriers and pairing mechanism can be dramatically changed in the optimal and underdoped regimes although a number of new and interesting phenomena complicate the physics of the underdoped cuprates.

In short, in our opinion the experimental validation of the Wiedemann–Franz law in overdoped cuprates [91] is a triumph of the Landau [92] and Migdal concept of Fermi quasiparticles (and Landau spirit of *trivialism* in general) and provides a refutation of the spin–charge separation in cuprates [93]. Hence, the problem of deriving the Wiedemann–Franz law for strongly correlated electrons in the CuO_2 plane has just been set in the agenda. According to the Fermi liquid theory [94] interactions between the particles create an effective self-consistent Hamiltonian. As Kadanoff [95] has pointed out, this idea was much developed by Landau [96] and Anderson [97]. Unfortunately, for high-T_c cuprates a link is still missing between the Landau quasiparticle concept and the one due to Slater that even scattering matrix elements can be calculated from first principles.

'Dogma V: Nonetheless, enough directions have been probed to indicate strongly that this odd–even splitting of CuO_2 planar states does not exist. ... The impact of Dogma V, then, is that the two-dimensional state has separation of charge and spin into excitations which are meaningful only within their two-dimensional substrate; to hop coherently as an electron to another plane is not possible, since the electron is a composite object, not an elementary excitation.'

Within the single-particle approximation (section 2) the bilayer band splitting is readily obtained from (2.8) and (4.19) by the replacements

$$\epsilon_i \to \epsilon_i \pm t_{\perp,ii}, \qquad i = \mathrm{s, p, d}, \tag{6.2}$$

where $t_{\perp,ii}$ is the hopping amplitude between the ith orbitals in the adjacent CuO_2 planes. In other words, the two constant energy curves due to the bilayer splitting are described by the same equation (2.8). Since it is plausible that $t_{\perp,\mathrm{ss}}$ dominates, from (4.10) one finds

$$\Delta E_{\mathrm{bilayer}} \approx 2t_{\perp,\mathrm{ss}}|S_{3,p}|^2 \approx 22\ \mathrm{meV}\ (\cos p_x - \cos p_y)^2, \tag{6.3}$$

in agreement with [61, 98]. The numerical value of 22 meV has been reported for heavily overdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) [98]. This experiment, crucial for *dogma V*, cf [99], is another piece of evidence in favour of the conventional behaviour of the electron excitations in the $(CuO_2)_2$ slab. Since $\Delta E_{\mathrm{bilayer}}$ is relatively small in comparison with the width of the conduction band, it is another hint that even for bilayer superconductors like BSCCO and $YBa_2Cu_3O_{7-\delta}$ (YBCO) the analysis of a single CuO_2 plane is an acceptable initial approximation.

'Dogma VI: Interlayer hopping together with the 'confinement' of Dogma V is either the mechanism of or at least a major contributor to superconducting condensation energy.'

The interlayer hopping which is understood as a single-electron process definitely cannot be considered as a two-electron pairing interaction creating the condensation energy. It is only one of the details when one concentrates on the material-specific effects in high-T_c superconductors. The inter-slab hopping between double $(CuO_2)_2$ layers is a coherent Josephson tunnelling responsible for the long-living plasma oscillations with frequency $\omega_{\mathrm{pl}} < \Delta$. These plasma oscillations along with far-infrared transparency of the superconducting phase were theoretically predicted [100] for BSCCO—one of the few predictions made for high-T_c cuprates, cf the postdiction [101]. After the experimental observation [102], the plasma resonances associated with the Cooper-pair motion soon turned into a broad research field [103]. Subgap plasmons were predicted [104] for conventional superconducting thin films as well, and shortly after experimentally confirmed [105] for thin Al films on $SrTiO_3$ substrate. The relatively lagged development of the physics of this effect was partially due to the false neglect of the longitudinal current response in the classical works on microscopic

theory. Concluding, let us note that the London penetration depth λ can be considered as the Compton wavelength of the Higgs boson of mass $m_{\mathrm{H}}c^2 = \hbar\omega_{\mathrm{pl}}$, but the overall contribution of the interlayer hopping to the condensation energy is negligible.

6.2. Discussion

The band structure of the CuO_2 plane is now believed to be understood. However, after 15 years of development a mismatch of a factor of two or three between the *ab initio* and the experimental spectroscopic estimates for the single-electron hopping amplitudes t, or the bandwidth, tends to be interpreted rather as a state-of-the-art 'coincidence'. The HL approach is well known in quantum chemistry [106, 107], and has been successfully used for a long time in the physics of magnetism [108]. We hope that realistic first-principles calculations aiming at the exchange integrals J of the CuO_2 plane can be easily carried out. Should they validate the correct (antiferromagnetic) sign and the correct order of magnitude of J_{sd}, we can consider the theory of high-T_{c} superconductivity established. We stress that the two-electron exchange, analysed here, is completely different from the double exchange considered in [109].

In order to compare the derived results with the experiment, it is necessary that the tight-binding conduction band energy be fitted to the available ARPES data. In doing so a few parameters have to be properly taken into account: the Fermi energy E_{F}, as determined from the total area of the hole Fermi contour, the difference between the Fermi energy and the Van Hove singularity, $E_{\mathrm{F}} - \epsilon(\pi, 0)$, and the difference between the Van Hove singular point and the bottom of the conduction band at the Γ point, $\epsilon(\pi, 0) - \epsilon(0, 0)$. The fit may further allow us to take into account a possible realization of the Abrikosov–Falkovsky scenario, cf [27]. According to the latter, for $\varepsilon_{\mathrm{d}} < \varepsilon_{\mathrm{p}} < \varepsilon_{\mathrm{s}}$ and sufficiently small t_{pd}, the conduction band can be the narrow (nonbonding) oxygen band having a perfect (within the framework of the four-band model) extended Van Hove singularity. If the superconducting gap has a B_{1g}-type symmetry, its maximum value along the Fermi contour, $\Delta_{\max} = \max|\Delta_p(T = 0)|$, determines the J_{sd} exchange integral in the s–d model. Thus, the temperature dependence of the gap, described by the function $\Xi(T)$, and the overall thermodynamic behaviour and low frequency electrodynamic response will be determined without free fitting parameters.

The derived gap anisotropy function (4.9) and its interpolation (4.11) compared to the ARPES experiment showed that the 'standard' four-band model, spanned on the Cu $3d_{x^2-y^2}$, Cu 4s, O $2p_x$ and O $2p_y$ orbitals, with an antiferromagnetic s–d pairing interaction, successfully describes the main features of the ARPES data: the rounded-square-shaped Fermi surface, small energy dispersion along the $(0, 0)$–$(2\pi, 0)$ line and d-type (B_{1g}) symmetry of the energy gap Δ_p along the Fermi contour. According to the pairing scenario proposed here, strong electron correlations 'drive' the electron exchange amplitudes. These inter- and intra-atomic processes occur on energy scales unusually large for solid state physics. However, the subsequent treatment of the lattice Hamiltonian can be performed completely within the framework of the traditional BCS theory. The criterion for applicability of the BCS scheme is not given by the J versus t, but rather by the T_{c} versus $E_F - \epsilon_{\mathrm{b}}$ relation. Taking into account the typical ARPES-derived bandwidths, which are much bigger than T_{c}, we come to the conclusion that the BCS trial wavefunction [110] is applicable for the description of superconductivity in the layered cuprates with an acceptable accuracy if T_{c} does not significantly exceed room temperature.

It is worth also adding a few remarks on the normal properties of the layered cuprates. All these compounds are strongly anisotropic and two-dimensional models give a reasonable starting point to analyse the related electronic processes. Most importantly, the picture of a layered metal brings in something qualitatively new which does not exist for a bulk metal—

the 'interstitial' electric field between the layers, like the one in any plane capacitor. The thermodynamic fluctuations of this electric field and related fluctuations of the electric potential and charge density constitute an intensive scattering mechanism analogous to the blue-sky mechanism of light scattering by density fluctuations. It has recently been demonstrated [111] that the experimentally observed linear resistance can be rationalized in terms of the plane capacitor scenario; density fluctuations in the layered conductors are more important than the nature of the interaction. In such a way the linear normal-state resistivity is an intrinsic property [111] of the 'layered' electron gas and cannot be used as an argument in favour of non-Fermi-liquid behaviour. The resistance of the normal phase may not be directly related to the pairing mechanism and these problems can be solved separately. Nevertheless it will be interesting to check whether the anisotropic scattering in cuprates [112, 113] can be explained within the framework of the s–d pairing Hamiltonian.

The proposed mechanism for pairing in the CuO_2 plane can be handled much like an 'Alice in Wonderland' toy model, but we find it fascinating that all ingredients of our theory are achievements of quantum mechanics dating back to the memorable 1920s, currently described in every physical textbook, and constituting the fundamentals of solid state physics [114, 115]. It would be worthwhile to attempt to apply the approach used in this paper for modelling triplet and heavy-fermion superconductivity as well.

6.3. Conclusions: the reason for the success of the CuO_2 plane

We find it very instructive to analyse qualitatively the reasons for the success of the realization of high-T_c superconductivity in the CuO_2 plane.

(i) Because of the relatively narrow quasi-two-dimensional conduction d band, due to p–d hybridization, the density of states is rather high. The wide s band resulting from s–p hybridization is completely empty, which is somewhat unusual for compounds containing transition ions.

(ii) The pairing s–d exchange process has been known since the first years of quantum physics. It is omnipresent in the physics of the transition ions but in order for it to become the pairing mechanism in perovskites it is necessary that the s and d levels be close. In other words, a virtual population of the s level is at least needed in order to make the J_{sd} amplitude operative. Indeed, the conduction d band is, actually, a result of the s–p–d hybridization in the two-dimensional CuO_2 plane.

With the above remarks, one can speculate that among the perovskites the layered ones are more favourable for achieving higher T_c. The transition ion series ends with Cu^{2+} and the Cu $3d_{x^2-y^2}$ and 4s levels are too close. One should keep in mind that the filling of the electron shells finishes with a 'robbery' in Cu [50]: $3d^{10}4s^1$ instead of $3d^94s^2$ as one could expect from the electron configuration of the Ni atom ($3d^84s^2$). However, the energy difference between these two Cu shell configurations is very small.

Another favourable factor is the proximity of the O 2p and Cu $3d_{x^2-y^2}$ levels. Thus, *post factum* the success of Cu and O looks quite deterministic: the CuO_2 plane is a tool to realize a narrow d band with a strong s–p–d hybridization. It was mentioned earlier that J_{sd} is one of the largest exchange amplitudes, but the 4s and 3d orbitals are orthogonal and necessarily require an intermediary whose role is played by the O 2p orbital. Hence this theory can be nicknamed '*the 3d-to-4s-by-2p highway to superconductivity*' [17].

How this qualitative picture can be employed to predict new superconducting compounds is difficult to assess immediately. We believe, however, that this picture, working well for the overdoped regime, is robust enough against the inclusion of all the accessories inherent to the

physics of optimally doped and underdoped cuprates: cohabitation of superconductivity and magnetism [88], stripes [116], pseudo-gap [117], interplay of magnetism and superconductivity at individual impurity atoms [118], apex oxygen, CuO_2 plane dimpling, doping in chains [119], the 41 meV resonance [120] etc. Perhaps some of these ingredients can be used in the analysis of triplet superconductivity in the copper-free layered perovskite Sr_2RuO_4 [121]. It is also likely that the superconductivity of the RuO_2 plane is a manifestation of a ferromagnetic exchange integral J. The two-electron exchange mediates superconductivity and magnetism in heavy-fermion compounds [122] as well. We suppose that lattice models similar to the approach here will be of use in revealing the electronic processes in these interesting materials. Two-electron exchange may even contribute to the 30 K T_c of the cubic perovskite $Ba_{0.6}K_{0.4}BiO_3$, but so far it is difficult to separate the exchange contribution from the phonon part of the pairing interaction. However, the strange doping behaviour of $Tl_2Ba_2CuO_{6\pm\delta}$ in comparison with YBCO requires more detailed investigation [10].

6.4. Perspectives: if 'tomorrow' comes . . .

The technological success in preparing the second generation of high-T_c superconducting cables by depositing thin-layer superconducting ceramics on a flexible low-cost metallic substrate is crucial for future energy applications. The USA Department of Energy suggests global superconducting energy products would command an annual market of 30 G$ by about 2020. High-T_c superconductor power cables, transformers, motors and generators could grab a 50% market share by 2013, 2015, 2016 and 2021, respectively [123]. On the other hand atomic-layer engineering of superconducting oxides will trigger progress in materials science and electronics. One can envision multi-functional all-oxide electronics, e.g., sensors, processing and memory devices, all monolithically integrated within a single chip [124]. In spite of the technological progress and tens of thousands of publications the theoretical '*picture in early 2000 remains fairly cloudy on the whole*' [2]. The landmark of 'today' must be some event. 'What event will it be? It is desirable that this landmark be the insight into the mechanism of superconductivity in high-T_c cuprates' [2].

In this paper we have presented a traditional theory for superconductivity in overdoped, and possibly also optimally doped, cuprates. All of its ingredients can be found in the textbooks and there is a considerable chance that we witness the victory of traditionalism, as it was in the history of quantum electrodynamics (QED) half a century ago, but it may well be just a personal viewpoint '*brainwashed by Feynman*' [125]. Nonetheless, let us use the example of QED to illustrate the essence of our contribution. QED appeared as a synthesis between perturbation theory and relativity. Both components had been known well before the QED conception. Similarly, both the BCS theory and the exchange interaction have been known for ages, so the point in the agenda was how to conceive out of them the theory of high-T_c cuprates. Such a theory contains necessarily a big number of energy parameters (E_F, ϵ_s, ϵ_p, ϵ_d, t_{sp}, t_{pp}, t_{pd}, J_{sd}, J_{pd}, J_{sp} and J_{pp}) which are difficult to determine simultaneously[4] (for the current status of the problem see for example [126]). The first step will definitely be to use ARPES data in which the spectrum is clearly seen and to neglect in a first approximation the 'irrelevant' inter-atomic exchange integrals J_{pd}, J_{sp} and J_{pp}. In this case, for a known normal spectrum one can determine J_{sd} from T_c or from the maximum gap at $T = 0$.

[4] The gap-anisotropy fit in figure 3(d) is quite robust against the choice of the parameters. To illustrate and emphasize the capability of the model we have used, for example, unrealistically big values of the hopping integrals: $\varepsilon_d = 0$, $\varepsilon_s = 5$, $\varepsilon_p = -0.9$, $t_{pd} = 1.13$, $t_{sp} = 1.63$ and $t_{pp} = 0.2$ eV. This set of parameters corresponds to band calculations but gives a two to three times wider conduction band. If the band is fitted to the ARPES data J_{sd} can be less than 1 eV. A realistic fit is deemed to be a subject of a collaboration with experimentalists.

A crucial 'meeting point' between theory and experiment is the Ginzburg–Landau (GL) theory. The general form of the GL coefficients for anisotropic-gap superconductors, including the effect of disorder, is given in [127] and is directly applicable to the present model. For the s–d separable kernel (4.4) the specific heat $C(T)$ in the clean limit can also be explicitly derived [128] and has the GL form $C(T) = C_{\rm N} + C_{\Delta}$, with

$$\begin{aligned} C_{\rm N}(T) &= \frac{\pi^2}{3}\langle q_c(\nu_{\boldsymbol{p}})\rangle, \\ C_{\Delta}(T) &= k_{\rm B}T\frac{\alpha^2}{b} = \frac{4\pi^2}{7\zeta(3)}\frac{\langle\chi_{\boldsymbol{p}}^2 q_a(\nu_{\boldsymbol{p}})\rangle^2}{\langle\chi_{\boldsymbol{p}}^4 q_b(\nu_{\boldsymbol{p}})\rangle}\theta(T_{\rm c}-T), \end{aligned} \tag{6.4}$$

where $\nu_{\boldsymbol{p}} = \frac{E_{\boldsymbol{p}}}{2k_{\rm B}T}$, and

$$\begin{aligned} &\alpha(T) = \frac{1}{2(k_{\rm B}T)^2}\langle\chi_{\boldsymbol{p}}^2 q_a(\nu_{\boldsymbol{p}})\rangle, \qquad b(T) = \frac{7\zeta(3)}{16\pi^2(k_{\rm B}T)^3}\langle\chi_{\boldsymbol{p}}^4 q_b(\nu_{\boldsymbol{p}})\rangle, \\ &q_a(\nu) = \frac{1}{2\cosh^2\nu}, \qquad q_b(\nu) = \frac{\pi^2}{14\zeta(3)}\frac{1}{\nu^2}\left(\frac{\tanh\nu}{\nu} - \frac{1}{\cosh^2\nu}\right), \\ &q_c(\nu) = \frac{6}{\pi^2}\frac{\nu^2}{\cosh^2\nu}. \end{aligned} \tag{6.5}$$

Accordingly, the jump of the specific heat at $T_{\rm c}$ is expressed by the GL coefficients α and b, $\Delta C = k_{\rm B}T_{\rm c}\alpha^2(T_{\rm c})/b(T_{\rm c})$. With the help of the general equations (6.5) one can further determine the influence of the Van Hove singularity on the thermodynamic and electrodynamic behaviour. For ΔC the effect of the Van Hove singularity is reported in [129], and for a general review on the Van Hove scenario of high-$T_{\rm c}$ superconductivity we refer the reader to [130]. When the Fermi level is not close to the Van Hove singularity the GL coefficients can be worked out as integrals over the Fermi surface; methodological details are given in [131]. Knowledge of the GL coefficients is also fundamental for the physics of fluctuation phenomena in superconductors [132].

Furthermore, a microscopic consideration of the London penetration depth λ for screening currents in the CuO_2 plane gives [133]

$$\begin{aligned} &\frac{1}{\lambda^2(T)} = \frac{e^2}{\varepsilon_0 c^2\hbar^2 d_{\rm eff}}\oint v_{\boldsymbol{p}} r_d(\nu_{\boldsymbol{p}})\frac{{\rm d}p_l}{(2\pi)^2}, \\ &r_d(\nu) = \nu^2\sum_{n=0}^{\infty}[\nu^2 + \pi^2(n+1/2)^2]^{-3/2}, \end{aligned} \tag{6.6}$$

where the integration is performed along the Fermi contour. The penetration depth (6.6) is involved in the Bernoulli effect in superconductors [134]:

$$\frac{\Delta\varphi}{\mathcal{R}_{\rm H}} = -\frac{e^2}{2\varepsilon_0 c^2}\lambda^2(T)j^2, \qquad \frac{1}{\mathcal{R}_{\rm H}} = \frac{2|e|}{a_0^2 d_{\rm eff}}\oint p_y(p_x)\frac{{\rm d}p_x}{(2\pi)^2}, \tag{6.7}$$

where $\Delta\varphi$ is the change of the electric potential induced by a current density $\boldsymbol{j}$ and $1/\mathcal{R}_{\rm H} = en_{\rm tot}$ is the volume charge density of the charge carriers, with $d_{\rm eff}$ the effective spacing between the CuO_2 planes.

For given penetration depth extrapolated to zero temperature, $\lambda(0)$, and Hall constant of the superconducting phase, one can easily determine the effective mass of the Cooper pairs

$$m^* = \frac{e^*\lambda^2(0)}{\varepsilon_0 c^2\mathcal{R}_{\rm H}}, \qquad |e^*| = 2|e|. \tag{6.8}$$

This important material parameter m^* is experimentally accessible from the electrostatic modulation of the kinetic inductance of thin superconducting films [135] as well as from the surface Hall effect [136].

Having a big variety of calculated variables, the parameters of the theory can be reliably fitted. Another research direction is the first-principles calculation of the transfer amplitudes and two-electron exchange integrals. The level of agreement with the fitted values will be indicative of the completeness of our understanding. In addressing more realistic problems, the properties of a single space-homogeneous CuO_2 plane will be a reasonable starting point. Concluding, we believe that there is a true perspective for the theoretical physics of cuprate superconductors to become an important ingredient of their materials science.

Magnetism and superconductivity are among the most important collective phenomena in condensed matter physics. And, remarkably, magnetism of transition metals and high-T_c superconductivity of cuprates seem to be two faces of the same ubiquitous two-electron exchange amplitude.

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Note added in proof. A short discussion on new works on the Kondo effect, Kadowaki-Woods ratio, three-dimensional Fermi surface and isotope effect in cuprates will be given in the cond-mat version of the present paper [137].

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