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Resonant-electron-transfer model for the electronic structure of high-T_c superconductors

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Abstract. A model for the structure of doped $Cu^{(II)}$ oxides is proposed. To perform accurate *ab initio* Green function calculations, a small cluster is introduced and found to mimic the metallic doped oxides consistently. The results obtained are consistent with the experimental observations. In particular, the calculations predict, in agreement with photoemission experiments, the appearance of two weak bands close to the Fermi level and identify them as *non*-quasi-particle excitations originating from metal-to-metal resonant electron transfer. Some implications for superconductivity are briefly discussed.

The origin of the perplexing normal-state electronic structure and properties of $Cu^{(II)}$ oxide-based high-T_c superconductors has been a central and controversial issue of the high-T_c superconductivity problem [1-3]. In particular, much attention has been paid to the microscopic nature of the insulator–metal and antiferromagnet–superconductor transitions caused by hole doping. For the experimental findings resulting from the hole doping of the parent antiferromagnetic insulating $Cu^{(II)}$ oxides see, for instance, [4] and references therein. In spite of the observed drastic changes in many physical properties, the angle-integrated photoemission spectra of the doped and undoped materials show, at first sight, only minor changes. The major difference is the appearance of two weak bands in the vicinity of the Fermi level of $Bi_2Sr_2CaCu_2O_8$ [5, 6] (see bands A and B in the experimental data [6] collected in table 1). These bands are not observed in the insulating oxides. It has been argued that the corresponding electronic excitations are related to the superconducting electron pairs [5, 6]. The origin of these two bands and the nature of the corresponding excitations at the very top of the valence band are therefore currently of great interest [7].

This work aims at understanding the origin of these bands by means of *ab initio* computational quantum physics methods, i.e. without using any adjustable parameters in the Hamiltonian. We shall show that all the experimental observations mentioned above follow from a single hypothesis. Not only does hole doping produce holes on O atoms, but a doped primary hole on an O atom of the parent insulator also induces electron transfer from another O^{2-} to a neighbouring Cu^{2+}, thus creating a Cu^+ and O^- ion pair. In other words, we assume that the doped O 2p hole induces $p^6d^9p^5$–$p^5d^{10}p^5$ excitations, generating local diamagnetic order (instead of the local ferromagnetic order as proposed in [8]) in the region close to the doped hole. At rather strong doping levels a new metallic non-magnetic phase arises. The insulating CuO_2^{2-} sheet of the parent insulator has the formal valence formula $Cu^{(II)}O_2^{(II)}$. According to the above assumption, doping leads to a metallic $Cu_2O_4^{3-}$

sheet of the superconductor with the formal valence formula $Cu^{(II)}O_2^{(I)}Cu^{(I)}O_2^{(II)}$. Each Cu is surrounded by two $O^{(I)}$ and two $O^{(II)}$ atoms in the plane.

To be able to perform sufficiently precise *ab initio* calculations on the photoemission spectrum, we have to restrict ourselves to a rather small number of atoms. The smallest cluster needed to describe the local electronic structure should consist of two Cu and two O atoms. For obvious symmetry reasons we have chosen a linear CuOCuO cluster with interatomic distances taken from the solid [9]. The Madelung field of the crystal remnant has been conveyed by two point charges, 2− on the left- and 2+ on the right-hand side of the cluster. Equal distances of 2.67 au between a point charge and its neighbouring terminal atom were chosen to create on these atomic sites total Madelung potentials equalling the corresponding values computed by means of Ewald's method for the CuO crystal.

As a first step we have carried out *ab initio* self-consistent field calculations on the above cluster (the calculations are analogous to those carried out in [10] on undoped $Cu^{(II)}$ oxides, where technical details are given). The following charges on the atoms have been obtained: $Cu^{2.2+}O^{1.0-}Cu^{1.2+}O^{2.4-}$, i.e. the formal valence formula $Cu^{II}O^{I}Cu^{I}O^{II}$ is applicable. This result is fully consistent with our basic assumption concerning the charges in the metallic sheet and, in fact, supports its validity.

The computed electronic structure of the cluster can, roughly speaking, be imagined to originate from a simple superposition of the one-particle states (orbitals) of a $Cu^{(II)}$ oxide and those of a $Cu^{(I)}$ oxide. The strongly localized $Cu^{(II)}$ 3d states are at the bottom (about 25 eV) and the delocalized $Cu^{(I)}$ 3d states are at the top (about 12 eV) of the valence band. The ground-state electronic configuration of the cluster is evident from table 1 where the orbitals and their characterization are shown. In all orbitals the first of the indicated leading atomic contributions is by far the dominating contribution. The closed-shell structure [11] of the cluster and delocalized nature of the highest occupied 5σ and 4π states are consistent also with non-magnetic behaviour (e.g. the Meissner effect) and metallic conductivity (see also the following discussion) of the doped oxides.

The photoemission spectrum is computed via the one-particle Green function (GF) [12]. Several interesting GF calculations on cuprate superconductors which are based on model Hamiltonians have been reported in the literature (see [13, 14] and references therein). Here, we evaluate the GF using the *ab initio* algebraic diagrammatic construction approach in third order [15] which has been successful in many applications to molecules. The basis set used in the computations is the same as that in [10]. The pole positions of the GF constitute the ionization potentials I_n, i.e. the positions of the bands in the photoemission spectrum, and the residues are the spectroscopic factors (SFs) $|Z_k^n|^2 = |\langle \Psi_n^{N-1}|c_k|\Psi_0^N\rangle|^2$, where Ψ_n^M is the mth state of the M-electron system and c_k is an annihilation operator for an electron in the kth orbital. On the relation between the SF and relative intensities in the photoemission spectrum see [16].

Let us briefly discuss our GF approach. For details we refer to [15]. In the algebraic diagrammatic construction approach of nth order the Dyson equation is solved using a self-energy part which consists of all Feynman diagrams up to and including nth-order perturbation theory. In addition, higher-order terms are taken into account by partial summation of all diagrams which arise from those up to nth order. For instance, in the third-order approach used in the present computations the ring-and-ladder diagrams (including all possible exchange terms) and all their combinations are included up to infinite order. Using a finite basis set the Dyson equation can be formulated as a secular equation. The eigenvalues are the ionization potentials and electron affinities, and the eigenvectors provide the spectroscopic factors.

The results of our GF calculations on the Cu_2O_2 cluster hole spectrum are given in

Table 1. The theoretical photoemission spectrum of the Cu_2O_2 cluster calculated by the *ab initio* GF method in comparison with the experimental photoemission spectrum of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_8$. The orbital energies ϵ_k, ionization potentials I_n, relative ionization potentials ΔI_n and SF $|Z_k^n|^2$ are shown. The electron affinity of Cu_2O_2 has also been computed.[a]

Experiment[b]			Theory, GF method			
Band	ΔI_n (ev)	State characterization[c,d]	$-\epsilon_k$ (eV)	I_n (eV)	ΔI_n (eV)	$|Z_k^n|^2$
A	−1.2	$1\pi^{-1}5\sigma^{-1}6\sigma^1$, $1\pi^{-1}5\sigma^{-1}8\sigma^1$		9.18	−0.88	0.03(1π), 0.02(4π)
B	−0.8	$1\delta^{-1}5\sigma^{-1}6\sigma^1$, $1\delta^{-1}5\sigma^{-1}8\sigma^1$		9.32	−0.74	0.03(1δ)
C	0.0	$5\sigma(Cu^{(I)}3d + O^{(I)}2p)^{-1}$	10.58	10.06	0.00	0.81(5σ)
		$4\pi(O^{(I)}2p + Cu^{(I)}3d)^{-1}$	10.56	10.06	0.00	0.79(4π), 0.04(3π)
D	2.0	$2\delta(Cu^{(I)}3d)^{-1}$	12.64	11.64	1.58	0.90(2δ)
		$3\pi(Cu^{(I)}3d + O^{(II)}2p + O^{(I)}2p)^{-1}$	12.58	11.67	1.61	0.82(3π), 0.04(4π), 0.01(2π)
E	3.0	$2\pi(O^{(II)}2p + Cu^{(I)}3d)^{-1}$	14.23	13.02	2.96	0.88(2π), 0.01(3π)
F	4.5	$4\sigma(O^{(I)}2p + Cu^{(I)}3d)^{-1}$	13.69	14.10	4.04	0.73(4σ), 0.04(5σ)
		$3\sigma(O^{(II)}2p)^{-1}$	17.80	17.55	7.49	0.83(3σ)
G	10.5	$1\delta(Cu^{(III)}3d)^{-1}$, $1\delta^{-1}5\sigma^{-1}6\sigma^1$	23.89	20.53	10.46	0.57(1δ)
		$1\pi(Cu^{(III)}3d)^{-1}$+mixture	25.45	21.29	11.23	0.34(1π)

[a] The calculated electron affinity A_n of the orbital $6\sigma(Cu^{(III)}3d + Cu^{(III)}4s)$ is equal to 3.01 eV; the respective SF is 0.70(6σ). The orbital energy $\epsilon_{6\sigma} = -0.90$ eV.
[b] Photoemission spectrum from [6]. The peak energies are approximately estimated from the figures given there.
[c] For the main lines the compositions of the cluster orbitals are shown schematically in parentheses. The compositions of the first three unoccupied orbitals read: $6\sigma \simeq$ $Cu^{(III)}3d + Cu^{(III)}4s$; $7\sigma \simeq Cu^{(I)}4s$ and $8\sigma \simeq Cu^{(I)}4s + O^{(I)}2p$.
[d] x^{-1} denotes a single hole in the orbital x. $x^{-1}y^{-1}x^1$ denotes a two-hole one-particle excitation.

table 1 with the respective experimental photoemission spectrum data for the superconductor $Bi_2Sr_2CaCu_2O_8$. There is good agreement between theory and experiment with respect to the energies of the basic spectral features which enables us to give an assignment of the experimental bands. The theory shows that many excitations have a large SF close to unity and can therefore be without doubt regarded as well defined quasi-particles. It is important to note that they have the same quantum numbers as those of the corresponding ionized cluster orbitals, i.e. 5σ, 4π, etc. Such quasi-particles give rise to the main bands of a photoemission spectrum. Normally, only quasi-particles appear close to the Fermi energy. The situation is, however, different in the present case. As can be seen from table 1, the first two features A and B in the photoemission spectrum are weak satellites which correspond to many-electron excitations. That these bands have low intensity is evident from their small SF. These many-electron bands are followed by the two intense main features C and D which correspond to overlapping pairs of quasi-particles, $5\sigma + 4\pi$ and $2\delta + 3\pi$, respectively.

Towards the bottom of the valence band, the quasi-particle picture gradually deteriorates as expected and indicated by the decreasing values of the corresponding SF. The SF of the 1π quasi-particle, for instance, is as low as 0.34, implying that 66% of the intensity carried by the 1π orbital has been 'borrowed' by many-electron satellite states. This is a phenomenon common to most molecules where the quasi-particle picture has been found to break down for inner valence electrons [16]. In the present case the physical reason for this phenomenon can be easily revealed from the calculations as due to strong oxygen-to-metal charge-transfer screening of the $Cu^{(II)}$ 3d hole. A similar situation has been found also in the case of the undoped $Cu^{(II)}$ oxides [10].

We mention that many additional many-electron satellite states have been calculated but are not shown in the table because they are not of relevance to the central issue of this work. These satellites are located energetically on and between the quasi-particle bands, the first being of a somewhat similar nature to band A and lies on the high-energy wing of the quasi-particle band C. Most of the satellites emerge from oxygen-to-metal charge transfer. The computed data on the satellites are available from the authors.

Let us return to the major point of this paper. The first two excitations of the cluster hole spectrum are evidently not quasi-particles at all; they are many-electron excitations connected mainly with the creation of the $Cu^{(II)}$ 3d hole and the simultaneous additional electron excitations from the occupied 5σ orbital to the empty 6σ and 8σ orbitals, thereby screening the primary $Cu^{(II)}$ 3d hole. In other words, the creation of a $Cu^{(II)}$ 3d hole induces a transfer of a Cu 3d electron from a $Cu^{(I)}$ to a $Cu^{(II)}$ atom. To some extent the corresponding many-electron excitations are fermionic excitations which can be thought of as a strongly interacting superposition of a $Cu^{(II)}$ 3d fermionic quasi-particle and a bosonic $Cu^{(I)}3d \rightarrow Cu^{(II)}$ 3d excitation.

To our knowledge this metal-to-metal resonant-electron-transfer (RET) screening mechanism has not yet been described in the literature. Evidently, it cannot take place in undoped $Cu^{(II)}$ oxides. The emerging satellite bands deserve some discussion. The energy splitting ΔT_h between the quasi-particle line and the accompanying $5\sigma \rightarrow 6\sigma$ RET satellite is given in first-order perturbation theory by the following expression:

$$\Delta T_h = (\epsilon_{6\sigma} - \epsilon_{5\sigma}) - J_{h6\sigma} - J_{5\sigma6\sigma} + J_{h5\sigma} \tag{1}$$

where h denotes the orbital corresponding to the quasi-particle state. The J stand for the usual Coulomb integrals and ϵ are the orbital energies. For simplicity of discussion we have omitted all the small exchange integrals appearing in the full expression [17]. According to our computation, $J_{1\pi6\sigma} = 20.8$ eV, $J_{1\pi5\sigma} = 5.5$ eV, $J_{5\sigma6\sigma} = 5.2$ eV, $J_{1\delta6\sigma} = 20.1$ eV,

$J_{1\delta 5\sigma} = 5.4$ eV and $\epsilon_{6\sigma} - \epsilon_{5\sigma} = 9.7$ eV. Using these values in equation (1) results in the large negative splittings, -10.8 eV and -10.2 eV for the primary hole being on 1π and 1δ orbitals, respectively. The RET results in a substantial energy gain compared with the respective quasi-particle Cu$^{(II)}$ 3d excitation and the many-electron excitations show up in the photoemission spectrum as shake-down satellites. Upon creation of a Cu$^{(II)}$ 3d hole, the strong intra-atomic Coulomb Cu$^{(II)}$ interactions $J_{1\pi 6\sigma}$ and $J_{1\delta 6\sigma}$ pull down the empty localized Cu$^{(II)}$6σ level below the filled delocalized Cu$^{(I)}$5σ level.

However, since the Cu$^{(II)}$ 3d orbitals 1π and 1δ are low lying, even this large energy gain is not yet able to place these RET satellites at the very beginning if the spectrum. The electron–electron interactions beyond first order accomplish this phenomenon. As can be easily seen from table 1 the main many-electron effect arises here from an interaction of the $h^{-1}5\sigma^{-1}6\sigma^1$ and $h^{-1}5\sigma^{-1}8\sigma^1$ configurations. Interestingly, this interaction leads to two delocalized natural orbitals, each carrying one electron, which are approximately the *gerade* and *ungerade* superpositions of the Cu$^{(II)}$ and Cu$^{(I)}$ 3d orbitals. This result sheds light on the electron transfer mechanism; two electrons have been half-transferred, resulting in the total net transfer of one charge. This may lead to interesting pair formation possibilities.

In the photoemission spectrum the satellites have aquired their intensity by borrowing it from quasi-particles. The SFs of the corresponding many-electron states determine this borrowing, e.g. band A borrowed its intensity from the 1π and 4π quasi-particles (see table 1).

It should be noted that band A shows strong enhancement at 18 eV radiation corresponding to the O 2s→O 2p resonance. On these grounds a dominant O 2p nature has been attributed to this band [6]. According to our results, this finding is partially true in the sense that the intensity of the respective RET satellite is substantially borrowed from the main line of the 4π orbital consisting to a large extent of O$^{(I)}$ 2p orbitals. Consequently, all the energy dependences and angle-resolved and dispersive behaviours of this satellite have to mimic partially those for the 4π main line when using exciting vacuum ultraviolet radiation [18]. However, the structure of the respective many-electron state has almost nothing to do with the $4\pi^{-1}$ state. According to our data, $4\pi^{-1}$ has only a 2% share in the structure of the satellite and this is also the reason why its intensity in the spectrum is very small.

The data obtained calls for revising the conventional ideas on electrical and other properties of the doped metallic Cu oxides because most of the respective ideas are based on the canonical Fermi-liquid theory. The first postulate of this theory is that the excitations at least at the very top of the valence band have to be quasi-particles with the same quantum numbers as the orbitals of the ground state. Our results clearly show a breakdown of this behaviour at the very top of the valence band where two many-electron excitations and not quasi-particles are the closest excitations to the Fermi level. Consequently, most of the physical properties of the respective solid state oxides have to be controlled by these many-electron excitations. We think therefore that the normal state of the superconductors cannot be described by the Fermi-liquid theory. In this respect our results are consistent with the viewpoint of [1] and the phenomenological marginal Fermi-liquid theory [2].

According to our GF results the interatomic RET Cu$^{(I)}$3d →Cu$^{(II)}$ 3d excitations are the closest excitations to the Fermi level and may even overlap it; they are hence the most probable candidates for revealing the nature of superconducting electron pair formation provided that this formation is purely electronic. This conclusion is supported by our CI calculations on the Cu$_2$O$_2$ cluster ground state. They show that the largest many-electron contributions to this state include the $5\sigma \rightarrow 6\sigma$ single hole-particle excitation which can be roughly regarded as a theoretical evidence for the existence of singlet bosonic RET

$Cu^{(I)}$ 3d $\rightarrow$ $Cu^{(II)}$ 3d excitations in the ground normal state. Provided that pair formation is of a pure electronic nature, we could use the antigerromagnetic exchange constant J as an approximate estimation for the $Cu^{(I)}$ 3d $\rightarrow$ $Cu^{(II)}$ 3d pair binding energy (and consequently for T_c).

In summary, we have proposed a new RET model for the electronic structure of the $Cu^{(II)}$-oxide-based high-T_c superconductors that is consistent with a variety of experimental results. In particular, the model is able to predict and identify *ab initio* the first two weak bands A and B in the photoemission spectrum of the conducting oxides and their absence in the parent insulating oxides. We believe that the structure of the respective many-electron excitations may provide us with a strong hint about the superconducting electron pair formation mechanism [19]. The single hypothesis made here is that doping of the insulating CuO_2^{2-} sheet leads to a metallic sheet of the superconductor with alternating $Cu^{(I)}$ and $Cu^{(II)}$ atoms. This basic assumption is supported by the calculations on our cluster. As long as this assumption is valid, the qualitative conclusions drawn here on the elementary excitations and photoemission spectrum are largely independent of the size of the cluster. From the discussion about equation (1) it becomes evident that the charge-transfer mechanism depends mainly on the fact that the 3d orbitals on $Cu^{(II)}$ are much more localized than those on $Cu^{(I)}$.

Acknowledgments

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[19] The $Cu^{(I)}$ 3d–$Cu^{(II)}$ 3d electron pairs can either be directly related to the superconducting pairs or mediate the formation of the latter via the exchange of the bosonic $Cu^{(I)}$ 3d $\rightarrow$ $Cu^{(II)}$ 3d excitations in a similar way as in the scenario of the well known exciton mechanism of superconductivity of [20].

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