Electronic structure of correlated electron systems

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Classification scheme according to ZSA



Some systematic in the nature and size of band gaps

- As we go from left to right in the 3d series we expect gaps to go from MH like to CT like with an anomaly for d5 systems
- As we increase the oxidation state i.e. go from 2+ to 3+ to 4+ cations we expect the electron affinity to strongly increase and the ionization potential to also strongly increase so U at least the F0 integral stays more or less constant but the charge transfer energy strongly decreases although this decrease is largely compensated by the increase in Madelung potential contributions for strongly ionic materials. (can be complicated)
- For the anions as we down the periodic table from O ,S,Se,Te we decrease the electron negativity and so decrease the charge transfer energy going towards the CT gap region. At the same time we also decrease F0 because of the increased polarizability of the anions. I expect the net result to be going towards a CT gap system and perhaps even a negative CT gap which would result in a strange metal.

Systematics continued

- Cu in most sulfides, selenides like CuCr2X4 etc is d10 (1+) with holes in the anion bands. In the pyrites like FeS2 or fools gold the anions for pairs as (S2)2- with low lying empty antibonding S 2p states . i.e. holes in anion p bands.
- Holes in anion p bands may also be introduced by doping the material as in La2-xSrxCuO4 leading to a high temperature superconductor.
- As we go from 3d to 4d to 5d we expect U to decrease because of radial nodes and large extensions of wave functions. We also expect hybridization with anions to increase and ligand fields to increase. We also expect the Slater intergrals to decrease. All of the above move us first towards MH systems and then on towrads weak correlations.

Optical spectrum of cuprates

 Single particle electron removal spectrum from a d10 O2p6 vacuum state would yield all the crystal field states of Cu d9.



Energy level diagram for a single d hole in free space on the left and in D4h symmetry on the right calculated using the single hole greens function method. The splittings have been measured both with optical spectroscopy and resonant inelastic x ray scattering Cu2+ (d9) Impurity in CuO2 lattice The one electron removal spectrum in the 2D CuO2 laers of the high Tc's



FIG. 1. The *d*-electron-removal spectral weight calculated for A = 7.6 eV, $\Delta = 2.75 \text{ eV}$, $T(b_{1g}) = 2.35 \text{ eV}$, and W = 4.4 eV. Also shown are the contributions from the various irreducible representations.

Undoped La2CuO4 is an antiferromagnet with a conductivity gap of 2 eV



Shows the Cu O2 plane and the spin arrangement . The Superexchange interaction is J=130meV

With the phases shown in the figure for the O 2p orbital's, the Lowest energy electron removal state would involve the linear combination p1p2-p3+p4 which has the same symmetry as x2-y2 centered on the central Cu ion.



Note the factor of 4 in the Exchange stabilizing the Lowest energy singlet state!!

Importance of the ZR singlet

- In the hole doped materials the holes go on O suggesting at least a multiband system. However if they form very strong local singlets this looks like a simple Hubbard model in which the spin on the central Cu site has been removed because of the singlet formation
- This provides a path back to a simple single band Hubbard model.

Is single band Hubbard justified for Cuprates?

I ne localized states of (5) are, nowever, not ortnogonal because the neighboring squares share a common O site. Thus,

$$\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)\dagger} \rangle = \delta_{\sigma\sigma'} (\delta_{i,j} - \frac{1}{4} \delta_{\langle ij \rangle,0}) , \qquad (6)$$

where $\delta_{(ij),0} = 1$ if *i*, *j* are nearest neighbors. In analogy to the treatment of Anderson for the isolated spin quasiparticle,⁶ we construct a set of Wannier functions $(N_S = num)$



FIG. 1. Schematic diagram of the hybridization of the O hole $(2p^5)$ and Cu hole $(3d^9)$. The signs + and - represent the phase of the wave functions.

Zhang Rice PRB 1988 37,3759

Problem with ZR singlets

- The combination of O 2p states is not compatible with a band structure state
- The wave functions are non orthogonal

$$\phi_{i\sigma} = N_S^{-1/2} \sum_{\mathbf{k}} P_{\mathbf{k}\sigma} \exp(i\mathbf{k} \cdot \mathbf{R}_i) , \qquad (7)$$

$$P_{\mathbf{k}\sigma} = N_S^{-1/2} \beta_{\mathbf{k}} \sum_{i} P_{i\sigma}^{(S)} \exp(-i\mathbf{k} \cdot \mathbf{R}_i) , \qquad (8)$$

where $\beta_{\mathbf{k}}$ is a normalization factor

From ZR PRL 37,3759

$$\beta_{\mathbf{k}} = \left[1 - \frac{1}{2} \left(\cos k_x + \cos k_y\right)\right]^{-1/2} . \tag{9}$$

Note it goes to infinity at k=0, should we see it at Gamma in ARPES? Luckly it goes to 1 for K= Pi/2,Pi/2 and along the antiferromagnetic zone boundary where the doped holes go at low doping

P23 logether Sine LeT. PAY [-Pix + Pay + Pax - Pay] Try (b,) = 2 Try (single bond) Singlet stabalized by J~4[2Trd]²

This ZR like wave function is not orthogonal to the ZR state centered around a neighboring Cu. The intervening O 2p orbital has the opposite phase there and so for k=0 this Bloch state will be =zero

J is strongly enhanced by the coherent sum of O 2p orbitals

Problems with ZR singlets

- As we dope the system the integrety of the ZR states disappears
- As we dope the system the ZR states strongly overlap forbidden by Pauli so they must change.

High oxidation states

- In general we expect the charge transfer energy to strongly decrease for higher oxidation states!!!
- Be careful with "Co4+" CoO2 or Mn4+ SrMnO2 etc Delta could be negative!
- This would mean a different starting point i.e.
 Co4+→Co3+L and the charge degrees of freedom are on Oxygen. Some call these self doped systems

What about negative charge transfer energy

- We Know this happens in CuS (superconductor with holes in the S p band) i.e. Cu d9----Cu d10 L (Ligand hole)
- This also happens in CuCr2S4 (Cu1+) and CuCr2Se4
- Delta decreases as we go from O –S-Se-Te and F-Cl-Br-I Because of electron negativity
- Delta decreases as we go from Co 2+ to 3+ to 4+

²⁴F. Jellinek, *Inorganic Sulphur Chemistry* (Elsevier, Amsterdam, 1968), p. 669; *MTP International Review of Science, Inorganic Chemistry Series I* (Butterworths, London, 1972), Vol. 5, p. 339.

Wu et al PRL 94, 146402 (2005) O Kedge XAS Na.5CoO2



FIG. 2. O 1s XAS spectrum of $Na_{0.5}CoO_2$ measured in the total electron yield mode. The unoccupied bands with which O 2p states hybridize are denoted in the plot.

On ionizing Co3+ are the holes mostly on O?? i.e Delta negative in ZSA diagram?

In SrCoO3 we would have Co3+ and 1/3 hole per O Or 2 holes per octahedron!!!! These could be associated With alternating Co3+ removing the orbital degeneracy And resulting in what would look like charge disproportionation Without actually moving the charge around. I.e It would look Like Co5+ and Co3+

This is what happens in SrFeO3!!!

It is unlikely to happen in Co oxides because here open t2g orbitals Are involved but it is something to keep in mind

Charge disproportionation without moving charge

Consider SrFeO3 Fe4+ on average but label it as Fe3+L Then each Fe is surrounded by 2 L holes in SrFeO3(1 hole per 3 O) $2Fe4+ \longrightarrow Fe3+ + Fe5+$



Each second Fe3+ has an octahedron of O with two holes Of Eg symmetry in bonding orbital's I.e. d5 L

No Jahn Teller problem anymore



FIG. 2. Insulator-metal-antiferromagnetic phase diagram for $RNiO_3$ as a function of the tolerance factor and (equivalently) the ionic radius of the rare earth (R).

Mixed valent Manganites Where is the charge?

Zener polarons



Ionic picture (Mn³⁺/Mn⁴⁺) is not correct!

 \rightarrow Supported also by band-structure calculations.

A. Daoud-Aladine et al,, PRL 89, 097205 (2002).

Rather than one electon coupling two S=3/2 Mn4+ perhaps we should think of one hole Also largely on O 2p coupling two Mn3+ each of spin two

The nickaltes i.e. RENiO3 have a similar issue

Perovskite structures A(TM)O₃



Lets start with all Ni being d8 i.e. 2+ Then we have 1/3 hole per O or or 2 holes per O octahedron. Lets associate the two holes with one Ni which will then be a Spin zero cluster because of Jpd. The octahedron will contract leaving the other Ni neighbors in a d8 S=1 state. This gives the correct structure at low T and in fact also gives the correct spin structure . Again effective disproportionation without moving charge.

These are really subttle issues regarding how we should associate states in a correlated muiltiband system. Of course if we had an exact solution it all would not matter but we don't and so we resort to models. In the ZR case we "associated " the O 2p hole with a particular Cu by distributing it with suitable phases within a square around the Cu. This enhances Jpd and lowers the energy . Cluster model For 2 O 2p holes in an Octahedron

Definition of hopping parameters

 $t_{pp} = 1/2(t_{pp\sigma} - t_{pp\pi})$

t ' _{pp}=
$$1/2(t_{pp\sigma}+t_{pp\pi})$$

Elfimov et al PRL 89, 216403



FIG. 1: An artists concept of the oxygen σ (a) and π (b,c) bonding orbitals relative to the O-vacancy bond direction surrounding a Ca vacancy. Also shown are the definitions of the hopping integrals (b) t_{pp} , (c) $t_{pp\pi}$, and (d) t'_{pp} given in terms of electrons.

Exact diagonalization results



Three lowest states for two particl



- (a) HOLES in anion orbitals and
- (b) ELECTRONS in cation orbitals.

- (a) ELECTRONS in cation orbitals and
- (b) HOLES in anion orbitals. Solid symbols are for triplet state

This can lead to magnetism for cation vacancies in simple Oxides like MgO or CaO etc.

Back to the cuprates and the Zhang Rice singlet issue

Do they really exist? Or are there alternatives? What is the dispersion relation for the first electron removal states? This cannot be obtained from an impurity calculation of course

The dispersion relation for a single ZR singlet

 If we forget about the orthogonality issues we basically have the motion of a single hole in a s=1/2 2D antiferromagnet with an exchange coupling J and a hoping integral t determined by the motion of a ZR single. Actual calculations show that 3 hoping integrals t,t',t" corresponding to nn, nnn, and nnnn hopings



Sushkov et al PRB 56, 11769 (1997)

The t,t',t'' J model for the CuO2 plane in cuprates

$$\begin{split} H &= -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} - t' \sum_{\langle ij_1 \rangle \sigma} c^{\dagger}_{i\sigma} c_{j_1\sigma} - t'' \sum_{\langle ij_2 \rangle \sigma} c^{\dagger}_{i\sigma} c_{j_2\sigma} + J \sum_{\langle ij \rangle \sigma} \mathbf{S}_i \mathbf{S}_j \,. \\ \\ \sqrt{\frac{2}{N}} \sum_{i \in \uparrow} S^+_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \approx u_{\mathbf{q}} \alpha_{\mathbf{q}} + v_{\mathbf{q}} \beta^{\dagger}_{-\mathbf{q}} \,, \\ \sqrt{\frac{2}{N}} \sum_{j \in \downarrow} S^-_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \approx v_{\mathbf{q}} \alpha^{\dagger}_{\mathbf{q}} + u_{\mathbf{q}} \beta_{-\mathbf{q}} \,. \\ \\ \sqrt{\frac{2}{N}} \sum_{j \in \downarrow} S^-_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \approx v_{\mathbf{q}} \alpha^{\dagger}_{\mathbf{q}} + u_{\mathbf{q}} \beta_{-\mathbf{q}} \,. \\ v_{\mathbf{q}} = -\operatorname{sgn}(\gamma_{\mathbf{q}}) \sqrt{\frac{1}{\omega_{\mathbf{q}}} - \frac{1}{2}} \,. \end{split}$$



We treat the hole –spin interaction in the self consistent Born approximation. i.e. only Non crossing diagrams Sinlge electron removal spectrum i.e. ARPES Not the quasi particle and incoherent satellite Parts of the spectral function



FIG. 8. Plots of $-(1/\pi) \text{Im } G_c(\epsilon, \mathbf{k})$ for different values of \mathbf{k} . The Green's function is found from Dyson equation (21) relating G_c with that in self-consistent Born approximation.

Quasi particle weight Z



FIG. 9. Dependence of quasiparticle residues on \mathbf{k} along the (1,1) direction.



A new exact diagonalization study with large systems by Bayo Lau

Cluster of 64 Cu and 128 O sites used for the pure antiferromagnet ground state Calculation taking quantum fluctuations full into account.

PHYSICAL REVIEW B 81, 172401 (2010)



FIG. 1. (Color online) Square lattice divided in octads (shaded areas). Sites positioned similarly inside octads have the same label. Each is surrounded by neighbors with different labels.

For the single hole lowest energy state calc use 32 Cu and 64 O site clusters . This involves a basis ov more than 10**9 states

Bayo Lau et al PRL in press

FIG. 1. (a) Two adjacent unit cells of the CuO₂ plane. The orbitals kept in the 3-band model of Eq. (1) are shown, with white/shaded for positive/negative signs. The two ϵ vectors (solid arrow) and the four δ vectors (dashed arrow) are also shown. (b) Sketch of a virtual process of $T_{\rm swap}$.

Do we get Zhang Ruce singlets? Not really, Does this agree with t,t',t'',J? yes for the dispersion but not for the spectral weight

We find low energy spin 3/2 states!!!! (neutron resonance? At some k points these are in fact the ground states and so unreachable with ARPES 2



FIG. 2. a) Energy and b) quasiparticle weight (bottom) for the lowest eigenstates with $S_T = \frac{1}{2}$ and $\frac{3}{2}$ vs. momentum. Different sets are shifted so as to have the same GS energy.

Note a quantum spin ½ antiferromagnet has a nn spin correlation of -.33 A Neel antiferromagnet =- .25, and a ferromagnet =+.25

> **Shows strong ferro like correlations close to the doped hole**. i.e. a "3 spin polaron" suggested first by Emery et al 1989



FIG. 3. $\langle C_x(\delta, a) \rangle$ for the lowest energy state at (a) $(\frac{\pi}{2}, \frac{\pi}{2})$ with $S_T = \frac{1}{2}$, and (b) at (π, π) with $S_T = \frac{3}{2}$. The darklyshaded bullet denotes the oxygen position at $l + e_x$. Each bullet shows the correlation value between the two sandwiching Cu sites. The central 12 Cu sites are shown; the correlations between the other 20 Cu spins converge fast towards the AFM value of ~-0.33. $\langle C_y(\delta, a) \rangle$ is the $\hat{P}_{x \leftrightarrow y}$ reflection. The spin correlations are very different for k=0,pi



FIG. 4. $\langle C_{x/y}(\delta, a) \rangle$ for lowest state at $k=(0,\pi)$ with $S_T=1/2$.

a triplet of two d^9 Cu spin neighbors. This is the 3spin polaron (3SP) $|3SP\rangle = \sqrt{1/6} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) |\sigma\rangle_h - \sqrt{2/3} |\sigma\sigma\rangle| - \sigma\rangle_h$, first studied by Emery and Reiter [2].



phase coherence [4]. The 3SP can also be written as a superposition of two Cu-O singlets: $|3SP\rangle \sim (|\uparrow, \sigma\rangle| \downarrow$ $\rangle_h - |\downarrow, \sigma\rangle|\uparrow\rangle_h) + (|\sigma, \uparrow\rangle|\downarrow\rangle_h - |\sigma, \downarrow\rangle|\uparrow\rangle_h)$. Thus, the 3SP already stabilized by J_{pd} and J_{dd} is also expected to have an increased bandwidth because of $T_{pp} + T_{swap}$.

Conclusions

- The role of the anions is extremely important in many regards
- If we take them into account explicitly we can understand;
- the reduction of U from 20eV to several eV,
- The charge disproportionation without a large non uniform charge
- New magnetic materials based on defect structures
- Perhaps even high Tc cuprates as being 3 spin polaron like objects rather than ZR singlets