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TOPICAL REVIEW — Unconventional superconductivity

Relevance of 3d multiplet structure in nickelate and cuprate superconductors*

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The recent discovery of superconductivity in doped rare-earth infinite-layer nickelates RNiO$_2$, R = Nd, Pr as a new family of unconventional superconductors has inspired extensive research on their intriguing properties. One of the major motivation to explore the nickelate superconductors originated from their similarities with and differences from the cuprate superconductors, which have been extensively studied over the last decades but are still lack of the thorough understanding. In this short review, we summarized our recent investigation of the relevance of Ni/Cu-3d multiplet structure on the hole doped spin states in cuprate and recently discovered nickelate superconductors via an impurity model incorporating all the 3d orbitals. Further plausible explorations to be conducted are outlined as well. Our presented work provides an insightful framework for the investigation of the strongly correlated electronic systems in terms of the multiplet structure of transition metal compounds.

Keywords: strongly correlated systems, cuprate superconductors, infinite-layer nickelates, multi-orbital Hubbard model

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1. Introduction

1.1. Cuprate superconductors

There is no doubt that the cuprate superconductors are among the most extensively studied materials in condensed matter physics. Unfortunately, however, they are among the most complicated materials so that are still lack of thorough understanding despite of the intense effort that produced numerous proposals over the past decades. In particular, understanding the mechanism responsible for the appearance of high temperature superconductivity[1,2] remains one of the top challenges.

Theoretically, one central issue in debate is the proper minimal model to capture the essential low-energy properties. Anderson once proposed that the single-band Hubbard model can be employed to understand all the essential physics of cuprates.[3,4] Later on the even simpler t–J model describing a square lattice with the charge carriers moving in a spin background was believed to provide a good description of the Hubbard model in the strong coupling limit by discarding all doubly occupied states. Both the Hubbard and t–J models have been extensively investigated. However, their common intrinsic assumption is that the cuprate parent compounds, which are charge transfer insulators,[5] can be instead modeled as effective Mott–Hubbard insulators. Therefore, the importance of explicitly including the O ions hosting the doped holes motivated the proposal of the three-band Emery model[6] with additional two ligand O-2p$_\sigma$ orbitals apart from the Cu $d_{x^2-y^2}$ orbital. The dichotomy between the one- and three-orbital scenarios was resolved by the idea of Zhang–Rice singlet (ZRS) with one hole (spin) residing on the central Cu site locked with the doped holes occupying the $^1A_1$ linear combination of O orbitals.[7]

In the past decades, various analytical approximations and numerical studies of these model Hamiltonians have revealed many insights on the cuprate superconductors including the antiferromagnetism of parent compounds, d-wave pairing, pseudogap phenomena and so on. Nonetheless, the validity of the ZRS concept[8,9] and more generally the equivalence between one- and three-orbital models to explain the low-energy properties remain open questions. On the one hand, the existence and stability of ZRS-like states have been confirmed in photoemission experiments;[10–12] on the other hand, recent calculations contrasting the dynamics of a single doped hole in the one-band vs. the three-band model revealed qualitative differences.[13–15] In particular, the background spin fluctuation was found to play an essential role in the one-band model while only minor role in the three-band model. Furthermore, recent high-energy optical conductivity study questioned the ZRS argument by revealing a strong mixture of singlet and triplet configurations in the lightly hole-doped Zn-LSCO single crystal,[8] which also exhibits strong ferromagnetic correlations between Cu spins near the doped holes, as predicted by

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the three-orbital model.[13] In a word, cuprate superconductors are still the most fascinating research areas full of open questions to explore.

1.2. New Ni-based superconductors

Given that the understanding of cuprates encountered much difficulty, one promising strategy of breaking this deadlock is "reasoning-by-analogy", which is widely adopted in the investigation of quantum materials. It is believed that some other families of quantum materials, e.g., twisted bilayer graphene,[16,17] Fe-based superconductors,[18,19] and spin–orbit coupled Sr_2IrO_4,[20,21] host similar properties to the cuprates.

One of the routes, which has been debated for decades, being pursued is to replace Cu^{2+} with Ni^{1+} in compounds such as $LaNiO_2$ and $NdNiO_2$.[22–24] Both Cu^{2+} and Ni^{1+} are in the $3d^9$, $S = 1/2$ configuration in the parent compound, so the infinite NiO_2 planes appear to be direct counterparts of the CuO_2 planes. After several failed attempts,[25–27] the superconductivity in doped $Nd_{0.8}Sr_{0.2}NiO_2$ thin films with $T_c \sim 9$–15 K was recently reported.[28] Right after its discovery, this fascinating new system has been investigated by various research groups around the world using a wide range of experimental and theoretical methods. Furthermore, it strongly implies the existence of a Ni-based family of high-T_c superconductors[29] that is reminiscent of the cuprate and the Fe-based families. Although the initial excitation of drawing a similar picture between cuprate and nickelate superconductors has been largely surpassed, there are still much debating issues on this new family of materials including the similarities with the cuprate superconductors.

Experimentally, the temperature dependence of the resistivity has an upturn at low temperatures,[28,29] which indicates the involvement of Kondo physics[30] and the normal state can be treated as a bad metal or weak insulator.[31] Besides, there is no clear evidence of the existence of long-range magnetic order,[32,33] although the recent NMR study revealed the presence of antiferromagnetic fluctuations and quasi-static antiferromagnetic order.[34] The measured Hall coefficient illustrated some intriguing behavior of its sign change as a function of both temperature and doping. Specifically, at low temperatures, the charge carriers change from electrons in the parent compounds to holes in the superconducting and over-doped systems.[29,35,36] This was once believed to originate from the multiband character in infinite-layer nickelates,[37] although there have been proposals supporting the single-band picture on its understanding.[38] Regarding the superconducting pairing symmetry, the recent single particle tunneling spectrum revealed the spatial coexistence of d-wave and s-wave,[39] whose clarification is still on its way. Due to the difficulty of the synthesis and characterization of these new nickelate superconductors composed of the unusual Ni^+ ions, the superconducting T_c is strongly sample dependent,[28,35,36,40] whose exact reasons remain unclear. In a word, these various experiments have uncovered some important difference from the traditional cuprate superconductors.[31]

Immediately after the discovery of the superconducting rare-earth infinite-layer nickelates, a range of theoretical methodologies have been adopted to explore this new system. Most studies focused on the electronic structure calculations with DFT[23,41–52] and/or DFT+DMFT[53–68] and so on, which can be seen as the starting point to understand the contributions from different orbitals involved. These studies confirmed that the nickelate superconductors host a distinct multiband interplay, which manifests already within the Ni ions. Precisely, not only the Ni-$3d_{x^2-y^2}$ but also the Ni-$3d_{z^2}$ orbitals are found to cross the Fermi level. Besides, Nd-5d orbitals also play a significant role in the band structure, which is believed to be essential to explain the self-doping effect in the parent compound.[30] Moreover, the multi-orbital nature including the involvement of Nd-5d orbitals has been argued to be closely related to the potential existence or suppression of the magnetic order.[23,37,41,49,52,60,62,68] There is a general consensus that the bad metallic or weakly insulating behavior of the normal states can be understood as a manifestation of the correlation effects. However, the dichotomy between Hubbard vs. Hund mechanism has emerged as a conflicting issue.[56,64,67] Regarding the origin of superconductivity in these materials, it has been proposed that the spin fluctuations play a central role so that the d-wave pairing is desired,[42,43,53,54,69,70] similar to the cuprates, although our early work showed that the relatively large charge transfer energy would decrease the superexchange interaction by one order of magnitude.[71]

In general, the experimental studies lag behind the theoretical investigation in some sense with many theoretical proposals awaiting for their anticipated experimental verifications.

1.3. Picture from charge transfer energy difference

With the advent of the newly discovered Ni-based superconductors, for which there are accumulated studies confirming that these systems should be regarded as a new class of unconventional superconductors, it is attractive to gauge how similar and/or different this new system is compared to the traditional cuprates. Before detailed calculations presented later, it is worthwhile remarking on the difference between cuprate and nickelate compounds from the point of view of their distinct charge transfer energy scales.

If we focus on the NiO_2 layer, regardless of the role played by Nd orbitals, the major feature is immediately apparent: NiO_2 resides in the Mott insulator[38,44,52,72–74] regime of

the Zaanen–Sawatzky–Allen (ZSA) scheme,[75] which is distinct from the nature of the cuprates as charge-transfer insulators. In the schematic shown in Fig. 1, the narrow (blue) bands denote the Hubbard 3d bands while the broader (red) band is the O-2p band before switching on p–d hybridization. Below (above) the chemical potential μ are the electron removal (addition) states, if the starting configuration is Ni/Cu-3d^9 plus a full O-2p band. This sketch assumes some basic arguments: because the smaller nuclear charge of Ni causes a 5–6 eV upward shift of the d^{10} state in NiO_2, the charge transfer energy is estimated to be $\Delta \approx 9$ eV in NiO_2 compared to $\Delta \approx 3$ eV in CuO_2; nevertheless, other energy scales, in particular $U_{dd} \approx 6$–7 eV, are similar in both NiO_2 and CuO_2.[76]

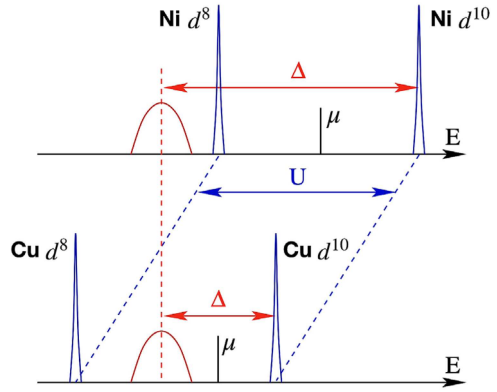


Fig. 1. Sketch of a Mott insulator (top) vs. a charge transfer insulator (bottom) adapted from Ref. [71]. The narrow (blue) bands are the Hubbard 3d bands while the broader (red) band is the O-2p band before the p–d hybridization has been switched on. The sketch assumes a similar U but a significantly larger Δ, like for $NdNiO_2$ as compared to $LaCuO_4$. Below (above) the chemical potential μ are the electron removal (addition) states, if the starting configuration is Ni/Cu 3d^9 plus a full O 2p band.

The most important consequence of the larger Δ in NiO_2 is that the superexchange interaction[77]

$$J_{dd} = \frac{4t_{pd}^4}{\Delta^2 U_{dd}} + \frac{8t_{pd}^4}{\Delta^2(U_{pp}+2\Delta)}$$

must be around one order of magnitude smaller than that in cuprates.[52] This observation is consistent with the absence of antiferromagnetic (AFM) order in the parent compound.[26,27] It also poses strong constraints on the spin fluctuation mediation as the primary mechanism for the Cooper pairing, which is insofar the leading scenario for cuprate superconductors.

Now that the NiO_2 layer is more likely within the Mott-Hubbard regime of ZSA classification, distinct from cuprates, the doped holes would preferably reside on Ni instead of the O-2p band. Because Ni^{2+} (3d^8) is predominantly $S = 1$ state in other known Ni^{2+} oxides, this triplet state would lead to some puzzling controversy with the appearance of rather high-T_c superconductivity in accordance with the absence of determined triplet superconductors. One interesting question is whether there are still some possible mechanisms to have a ZRS-like hole-doped state that makes NiO_2 more similar to CuO_2. To deal with this puzzling problem, it is requisite to consider the multiplets of 3d orbital in all transition metal oxides.

1.4. Importance of multiplet structure

Considering that there have been strong evidence that the newly discovered Ni-based superconductors (Nd,Sr)NiO_2 and (Pr,Sr)NiO_2 require the multi-orbital description, we remark on the significance of the multiplet structure of 3d transition metal elements in understanding the Cu-, Fe-, and Ni-based superconductors.

Take cuprates as the example, although the significance of Cu-3d$_{x^2-y^2}$ is well established and associated single- and/or three-band Hubbard/Emery models have been extensively explored aiming to understand the physical properties, there are both theoretical and experimental results pointing out the importance of non-planar orbitals like Cu-3d$_{z^2}$.[78–89] Specifically, the importance of Cu-3d$_{z^2}$ is manifested by the recent discovery[90] of the cuprate superconductor $Ba_2CuO_{4-\delta}$ with $T_c \sim 70$ K, which was claimed that some doped holes probably reside in the 3d$_{z^2}$ orbital because of the compressed c-axis bond length. Besides, early Auger spectroscopy[78] demonstrated strong multiplet effects ranging over a large energy scale in Cu compounds such as CuO and Cu_2O. For instance, in Cu_2O the lowest energy Cu-3d^8 state is likely a triplet state consistent with the expectation from Hund's rule.

More evidence for the significance of the multiplet structure came from the x-ray absorption (XAS) experiments displaying a strong change from purely x, y polarized absorption to the one including a large contribution of z polarized intensity for the O and Cu core-to-valence transition upon increased doping.[78] These early reports implied that the wavefunction of the doped holes has a considerable character of Cu-3d$_{z^2}$ or O-2p$_z$ orbitals, which points to the possible breakdown of the single-band or even three-band (based on Cu-3d$_{x^2-y^2}$ orbital) description of the cuprate superconductors.

In fact, during the early days when the ZRS was proposed, Eskes *et al.* carried out a generic study considering Cu-3d multiplet structure, i.e., all singlet and triplet irreducible representations in the D_{4h} point group spanned by two 3d holes (3d^8 electronic configuration) and their corresponding Coulomb and exchange interactions.[91–93] This early work revealed that the first ionization state starting from a Cu-3d^9 state and a full O-2p band, which results in the two hole eigenstates involving 3d^8 multiplets, is indeed in the $^1A_1$ symmetry channel, which is consistent with the proposal of the ZRS state. Another observation was that the energy difference between the lowest ionization states for various symmetry channels is rather small. This implies the potential impact of other symmetry channels on the lowest $^1A_1$ states. Moreover, these differences may strongly depend on the doping dependent electronic structure.

Hence, these results in the early stage of the investigation on cuprates had casted doubt on whether the effective minimal model suffices to consider only the $d_{x^2-y^2}$ orbital instead of the full Cu-3d multiplet structure.

Regarding the newly discovered Ni-based superconductors, the strong evidence of their multi-orbital nature, especially the role of Ni-e_g orbitals, motivated us to systematically explore the importance of the full Ni-3d multiplet structure on their low-energy properties and further compare with the case of Cu-3d. In this short review, we will summarize our recent investigation of these intriguing issues.

2. Model and methodology

Owing to the unusual valence of Ni^+ and the uncertainty of the synthesized sample quality, the nature of the parent compound $NdNiO_2$ is still unclear. The thin film in Ref. [28] is metallic, but recent reports found both thin films and bulk crystals that are insulators.[94,95] As mentioned above, although *ab-initio* studies confirmed a metallic band mainly from the Nd orbitals, the consensus is that the correlation effects originate from the Ni-3d orbitals. Besides, the metallicity of the Nd layers is undoubtedly connected to the physics in NiO_2 layers, specifically to where the bands with strong Ni-3d character are located. This close relation originates from the charge neutrality: in the stoichiometric compound, any density of electrons in the Nd layers must be compensated by the same density of holes in the NiO_2 layers. This is possible only if some NiO_2 bands (together with a Nd band) cross the Fermi energy, as indeed predicted by the *ab-initio* calculations. The inclusion of correlation effects on Ni would further push the Ni-3d occupied bands to lower energy and raises the empty 3d bands to higher energy (mimicking the Mott physics). In other words, the NiO_2 layers are strongly involved with and control the low-energy physics. Similarly, whether or not the Nd layer is metallic, the NiO_2 layers become doped upon doping the whole system.

All these reasons point to the necessity to understand the physics of the holes residing in the NiO_2 layers first. Following these arguments and given the fact that the CuO_2 and NiO_2 planes have the same lattice geometries, to make a direct comparison between them, we would focus on the role of Ni-3d and O-2p states in determining the low-energy physics of stochiometric NiO_2 layer and neglect the Nd orbitals for simplicity throughout this review. The role of other orbitals will be investigated in the next stage, which will be discussed later.

2.1. Multi-orbital impurity model

To further simplify the realistic calculation, our description of the Ni(Cu)O_2 lattice will be replaced by a single Ni^{1+}/Cu^{2+}-$3d^9$ impurity properly embedded in a square lattice of O-$2p^6$ ions so that the resulting $3d^8$ two-hole problem can be solved exactly. The complete treatment of the whole Ni/Cu lattice will be discussed later. The schematic geometry consisting of the Ni/Cu impurity and its four nearest neighbor (NN) O ions (our calculations are conducted on the full O lattice) is depicted in Fig. 2. The Hamiltonian reads

$$\begin{aligned} H &= E_{\rm s} + K_{\rm pd} + K_{\rm pp} + V_{\rm dd}, \\ E_{\rm s} &= \sum_{m\sigma} \varepsilon_{\rm d}(m) d^{\dagger}_{m\sigma} d_{m\sigma} + \sum_{jn\sigma} \varepsilon_{\rm p} p^{\dagger}_{jn\sigma} p_{jn\sigma}, \\ K_{\rm pd} &= \sum_{\langle .j\rangle mn\sigma} (T^{\rm pd}_{mn} d^{\dagger}_{m\sigma} p_{jn\sigma} + {\rm h.c.}), \\ K_{\rm pp} &= \sum_{\langle jj'\rangle nn'\sigma} (T^{\rm pp}_{nn'} p^{\dagger}_{jn\sigma} p_{j'n'\sigma} + {\rm h.c.}), \\ V_{\rm dd} &= \sum_{\bar{m}_1\bar{m}_2\bar{m}_3\bar{m}_4} U(\bar{m}_1\bar{m}_2\bar{m}_3\bar{m}_4) d^{\dagger}_{\bar{m}_1} d_{\bar{m}_2} d^{\dagger}_{\bar{m}_3} d_{\bar{m}_4}. \end{aligned} \tag{1}$$

Note that the model adopts the hole language. Here $\varepsilon_{\rm d/p}(m)$ are onsite energies with m denoting Ni/Cu-3d orbital b_1 ($d_{x^2-y^2}$), a_1 ($d_{3z^2-r^2}$), b_2 (d_{xy}), e_x (d_{xz}), e_y (d_{yz}) and n the O-2p orbitals p_x, p_y, p_z or a subset of them. $\varepsilon_{\rm d}(m) = 0$ are assumed to be independent of m to omit the point-charge crystal splitting, whose validity is by virtue of the fact that the Ni/Cu-O hybridization results in the difference between the effective on-site energies of different 3d orbitals. The charge transfer energy $\Delta = \varepsilon_{\rm p} - \varepsilon_{\rm d}$ measures the on-site energy difference between 3d and 2p orbitals, as measured from the full O-2p band to the Ni/Cu-d^{10} state. As a result, $\Delta = \varepsilon_{\rm p}$ is assumed in our calculations. We remark that $\varepsilon_{\rm d}(m) = 0$ might not necessarily appropriate for NiO_2 as indicated by recent experiment[38] and we will discuss this issue later.

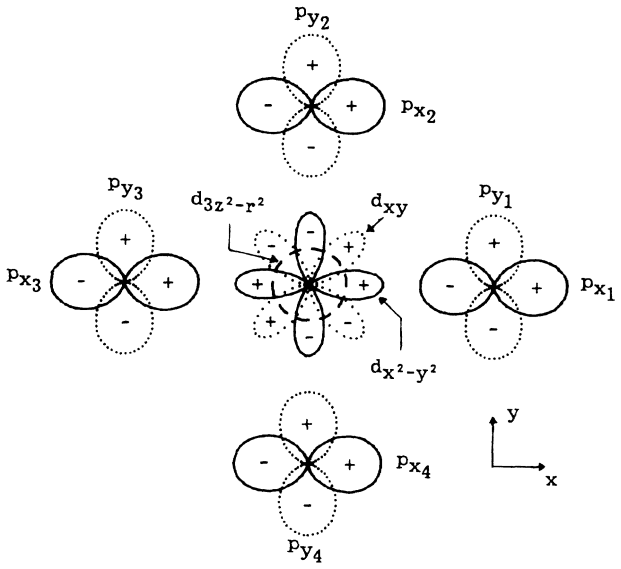


Fig. 2. Schematic view of the orbitals involved in our model calculations, adapted from Eskes's previous related work.[92] The Ni/Cu-d_{xz}, d_{yz} and the O-p_z orbitals are not shown. Only the four O adjacent to the Ni/Cu impurity are depicted despite that we consider the full O square lattice.

Different numbers of O-2p orbitals included lead to a few possible models: (i) N7, where $m \in \{a_1, b_1, b_2, e_x, e_y\}$ and $n \in \{p_{x_1}, p_{y_2}\}$, i.e., multiplet physics is added to the Emery model of cuprates; and (ii) N9, where $m \in \{a_1, b_1, b_2, e_x, e_y\}$ and $n \in \{p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}\}$, i.e., keep both in-plane O-2p orbitals; and (iii) N11, where $m \in \{a_1, b_1, b_2, e_x, e_y\}$ and $n \in \{p_{x_1}, p_{y_1}, p_{z_1}, p_{x_2}, p_{y_2}, p_{z_2}\}$, i.e., keep all three O-2p orbitals.

The K_{pd} and K_{pp} describe the Ni/Cu–O and O–O hoppings, respectively. The labels j, j' run over the positions of the O atoms, $\langle . j\rangle$ is a sum over the four O adjacent to the j-th Ni/Cu site, and only NN pp hopping is included. The Ni/Cu–O and O–O hopping integrals T^{pd}_{mn} and $T^{pp}_{nn'}$ are determined following Slater and Koster.[96]

The V_{dd} denotes the two-hole Coulomb and exchange interactions for all singlet/triplet irreducible representations of the D_{4h} point group spanned by two d holes, in terms of the Racah parameters A, B, and C, where the shorthand notation $\bar{m}_x \equiv m_x\sigma_x$, with $x = 1, \ldots, 4$ denote spin-orbitals. Without loss of generality, the free-ion values $B = 0.15$ eV and $C = 0.58$ eV are adopted and A is treated as a variable. Regarding U_{pp}, we have confirmed that it plays little role in the results discussed here (similar results were obtained for $U_{pp} = 3$ eV for instance) so that we set $U_{pp} = 0$ for simplicity.

Our aim is to explore the ground state of this impurity model with either one hole (undoped) or two holes (doped) using variational exact diagonalization. More details of this model and method were discussed in our recent work of the Cu^{2+} impurity.[97]

2.2. Two-hole spectra

Before proceeding to illustrate our results, we elaborate on the key physical quantities we are interested. Starting from the Ni/Cu-d^{10}+O-$2p^6$ system, the single electron removal eigenstates, namely, the single hole problem, can be solved trivially. As expected, if the bottom of the oxygen band locates at $\Delta - 4t_{pp} > \varepsilon_d$, then the lowest energy electron removal state is dominated by an (antibonding) orbital of b_1 symmetry, which has predominantly Ni/Cu-d^9 character mixed with the ligand hole $d^{10}L$ states with smaller amplitude of probability. Photoemission or doping of the system leads to a two-hole problem that is exactly solvable as well using the Cini–Sawatzky method.[97–99]

To comply with the $3d^9$ character of the single hole system, we will concentrate on the $3d^8$ partial density of states $A^{\Gamma}(\omega)$ assuming that one hole has already occupied the b_1 orbital (remember that $d^{\dagger}_{b_1}|0\rangle$ is the dominant contribution to $|\psi_{g.s.}\rangle$):

$$A^{\Gamma}(\omega) = -\frac{1}{\pi}\sum_m \lim_{\delta\to 0} \mathrm{Im}\, G_d(m, b_1, \omega + i\delta; \Gamma),$$

$$G_d(m, z; \Gamma) = \langle 0|d_{b_1} d_m \hat{G}(z) d^{\dagger}_m d^{\dagger}_{b_1}|0\rangle,$$
$$\hat{G}(z) = (z - \hat{H})^{-1}, \quad z = \omega + i\delta. \tag{2}$$

Here, $|0\rangle$ is the Ni/Cu-$3d^{10}$+O-$2p^6$ state, i.e., the state with no holes, while $|\psi_{g.s.}\rangle$ is the one-hole ground-state.

For an isolated Ni/Cu-$3d^8$ ion, we have ^{1}S, ^{3}P, ^{1}D, ^{3}F, ^{1}G configurations with energies listed in Ballhausen[100] so that $A^{\Gamma}_{d^8}(\omega)$ consists of one or more discrete peaks located at these five energies. Besides, the number of peaks and their corresponding spectral weights are dependent on the irreducible representation Γ.

We remark that we adopt the usual convention of photoemission spectroscopies that the electron removal (addition) energy, namely, the hole (electron) energy, increases to the left (right).

3. Results

We recently investigated the single Ni/Cu impurity with their 3d multiplet structure and explored the impact on the doped hole ground states. Here we briefly discuss the essential results and we refer the readers for more details in our earlier work.[71,97]

3.1. CuO_2

In Ref. [97], we followed Eskes *et al.*[91,92] to study a single Cu impurity using Eq. (1) and focused on the impact of the Cu-3d multiplet structure on relevant cuprate properties. Distinct from the previous work, we used a proper realistic band-structure of O-2p, which is essential due to the fact that the O-2p bandwidth can be as large as $8t_{pp} = 4.4$ eV for a typical O–O hybridization $t_{pp} = 0.55$ eV. By solving the two-hole problem discussed above, we identified the symmetry, spin, and orbital composition of the first ionization state, and to further gauge its similarity to a Zhang–Rice singlet.

Figure 3(a) illustrates the characteristic spectra corresponding to the ground state of cuprates. The most important feature is that, at moderate $\Delta = 2.75$ eV, the lowest energy state (blue peak) is a singlet state with $^1A_1$ symmetry as the ZRS state instead of the naively expected triplet according to the Hund's rule. Precisely, the ground state is

$$|\psi\rangle = \sqrt{0.072}|b_1 b_1\rangle + \sqrt{0.549}|b_1 L_{b_1}\rangle + \sqrt{0.054}|b_1 L'_{b_1}\rangle + \sqrt{0.275}|d^{10}L^2\rangle + \cdots, \tag{3}$$

where $\cdots$ are contributions with a_1a_1, b_2b_2, ee, etc. characters. Here L_{b_1} denotes a hole in the linear combination of b_1 symmetry of the four O orbitals nearest to the Cu impurity and L'_{b_1} denotes the configurations where the hole is further away from the Cu impurity, which are discarded in the original definition of ZRS. Equation (3) indicates that the ground-state has

only about 55% ZRS-like components, i.e., $|b_1 L_{b_1}\rangle$, although a recent work criticized our definition of ZRS.[101] The appearance of different spectral peaks together with their broadening for various symmetries is induced by the t_{pd} hybridization, which also introduces the ligand field like splittings to mix various atomic multiplets.

Another important feature uncovered, which is reminiscent of the observation of ARPES experiments in cuprates, is that the lowest bound state of $^1A_1$ symmetry is away from its spectral continuum corresponding to the states with doped hole in the O-2p band by about 1 eV. The two-hole continuum with both holes in the O-2p band and the Cu in a d^{10} state lies at even higher energies. Therefore, a broad spectral structure with mixed character forms and can be potentially associated with the origin of the so called "waterfall" feature.[102] Our results[97] indicated that to describe spectroscopies like ARPES up to one or more eV below the Fermi energy, it is essential to include the multiplet structure since all the symmetries have considerable spectral weights extending to energies well above 1 eV.

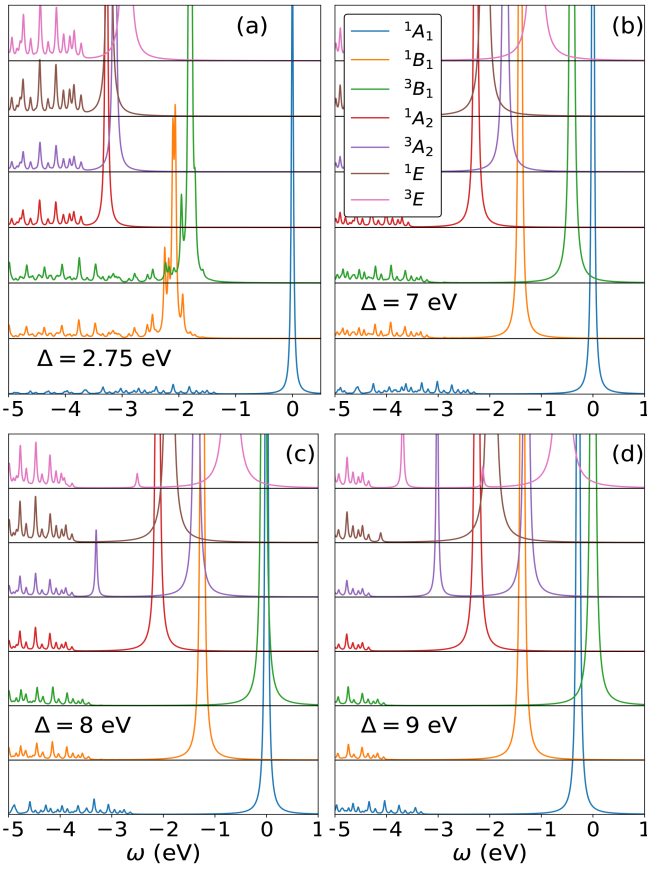


Fig. 3. The two-hole spectra $A^{\Gamma}(\omega)$ calculated for various irreducible representations Γ in N7 model for (a) Cu and (b)–(d) Ni impurity that hybridizes with the O lattice. Two characteristic cases of two-hole ground state of $^1A_1$ (a)–(c) and $^3B_1$ (d) symmetry are shown. The spectra are shifted such that the ground state is located at zero energy. The parameters are (a) $\Delta = 2.75$ eV, $A = 6.5$ eV and (b)–(d) $\Delta = 7, 8, 9$ eV, $A = 6.0$ eV with $t_{pd} = 1.5$ eV, $t_{pp} = 0.55$ eV. Adapted from Refs. [71,97].

3.2. NiO_2

In the case of NiO_2 plane, we estimated the Ni–O and O–O hybridizations to be $t_{pd} \approx 1.3$–1.5 eV and $t_{pp} \approx 0.55$ eV from the *ab-initio* results,[59,103,104] which are similar to the values believed to be relevant in cuprates. The similar scale of t_{pd} comes from a partial cancellation between the larger lattice constant of the nickelates and the larger orbital radius of the Ni-3d orbital due to Ni^+'s smaller nuclear charge. Besides, t_{pp} does not differ much from the cuprates under our assumption that the increase of the lattice constant in the nickelates is not significant. Meanwhile, the Racah parameters B, C are set by atomic physics and not much influenced by the screening effects, as verified experimentally in other systems with Ni^{2+} ions[76] so that we keep the same values $B = 0.15$ and $C = 0.58$ eV as in cuprates.

As mentioned before, the on-site Coulomb repulsion on the Ni^{1+} is expected to be comparable to that of Cu^{2+}, namely, $U_{dd} = A + 4B + 3C \approx 6$–$7$ eV, while the charge transfer $\Delta \approx 7$–9 eV as opposed to $\Delta \approx 3$ eV in cuprates,[105] which locates the system within the Mott–Hubbard rather than the charge-transfer regime in the ZSA classification scheme. We should emphasize that there is no consensus on the exact values of U_{dd} and Δ in both nickelate and cuprate superconductors, whose precise determination is indeed quite challenging both theoretically and experimentally.

With the inadequate information of these energy scales, our aim is to investigate whether it is possible for the doped states of a Mott insulator to behave more like those of a charge-transfer insulator. Figures 3(b)–3(d) illustrate the two-hole spectra resolved by different symmetries, where the three panels correspond to $\Delta = 7$ eV, 8 eV ,9 eV. With increasing Δ, the two-hole ground state transits from $^1A_1$ symmetry (blue peak) to $^3B_1$ symmetry (green peak) in accordance with the Hund's rule in the large Δ limit.

Moreover, increasing Δ leads to the incremental separation between the discrete peaks and their corresponding continuum describing the excited states with the doped hole moving in the O band. Physically, when this separation is smaller or comparable with t_{pd}, their hybridization induces the low-energy bound states of various symmetries, for instance, the one with $^1A_1$ or $^3B_1$ symmetry as the ground-state. As Δ increases and the distance between the two features dominates over t_{pd}, the ground state switches to $^3B_1$ character for a Mott insulator as expected from the conventional Hund's rule.

3.3. Effects of the number of orbitals

Figure 3 indicates that the conventional three-orbital (N3) model cannot capture the full spectra due to the lack of the involvement of the a_1 $(d_{3z^2-r^2})$ orbital. To investigate the effects of including more Cu-3d and/or O-2p orbitals in the model Hamiltonians, we further explored the impact of the

number of orbitals, for instance, the inclusion of additional π-bonding oxygen orbitals, considered in our model Eq. (1) for cuprates.[97]

We found that the ground state weight of $^1A_1$ symmetry shown in Eq. (3) is almost independent of the number of orbitals included, namely, independent of N3, N7, N9, or N11 models. Although this appears to confirm the validity of the conventional three-orbital Emery model for describing the low energy physics of cuprates, the additional hybridization of O-2p orbitals with Cu-t_{2g} orbitals extends the spectra to lower energies for all the symmetries, which in turn causes a much smaller difference between the continuum bottom of various A and B types of symmetries. This implies the importance of the order of various continuum in determining the low-energy states. For example, if the $^1A_1$ continuum would also be involved in the hybridization with the $^3B_1$ or $^1B_1$ state, these states would be appreciably closer to the lowest energy state of $^1A_1$ symmetry and even cross it. This could in principle occur if we take into account the full lattice of Ni/Cu-3d^9.[13]

3.4. Phase diagram: CuO_2 vs. NiO_2

To have an overall picture of the comparison between CuO_2 and NiO_2, Fig. 4 shows the two-hole A–Δ phase diagram consisting of two regions with distinct ground states (GS) of $^1A_1$ and $^3B_1$ symmetry,[91,97,100] respectively. In the $^3B_1$ region, the doped hole primarily sits on the Ni/Cu and forms a triplet state with the other 3d^9 hole by Hund's exchange. Specifically, as shown in the schematic insets, one hole occupies a wavefunction with dominant 3d$_{x^2-y^2}$ character plus a minor contribution from the linear combination of adjacent O-2p orbitals of x^2-y^2 symmetry; while the second hole occupies the $3z^2-r^2$ counterpart. In contrast, in the $^1A_1$ region, the doped hole primarily occupies the "molecular"-like O-2p orbital of x^2-y^2 symmetry plus a small admixture of the 3d$_{x^2-y^2}$ orbital, and forms a singlet state with the other hole which has primarily 3d$_{x^2-y^2}$ character.

The phase boundary shifts with varying t_{pd}. From the estimated parameters for CuO_2 and NiO_2, we locate their corresponding phases in Fig. 4. In particular, the shaded ellipse can be possibly relevant for the NiO_2; while the red star denotes the expected region relevant for CuO_2. Figure 4 appears to show that NiO_2 lies in the critical region of the ZSA diagram, where the two-hole ground states with singlet and triplet nature cross. Therefore, it is possible that the holes doped in NiO_2 have a considerable O-2p component with the same $^1A_1$ symmetry like the Zhang–Rice singlet (ZRS) of cuprates.[7] This may be consistent with how the superconductivity could emerge upon doping of NiO_2 despite of its likely Mottness. In fact, our recent preliminary extensive study showed that the consideration of additional crystal field splitting motivated by the experiments further stabilizes the $^1A_1$ regime, which provides more evidence on the similarity of the doped hole character with the cuprates. Furthermore, Fig. 4 suggests that small changes in the parameters, which may come from the variations in lattice parameters through chemical composition or applied pressure, could also stabilize the $^3B_1$ state. This may be relevant to the reported sensitivity of the properties of thin films and bulk crystals with applied pressure.

Regarding the minimal model, Fig. 4 hints that one only needs to include the e_g orbitals instead of all five Ni 3d orbitals. Even simpler minimal models may describe each phase effectively. On the $^1A_1$ side, one can project down to a single band Hubbard-like or t–J-like model[7] after the careful consideration of whether the O orbitals should be integrated out.[13–15] On the $^3B_1$ side, a so-called type-II t–J model has been recently proposed to describe the motion of a hole with spin $S=1$ in a background of spin-1/2;[106] older work along similar lines was reported in Ref. [107].

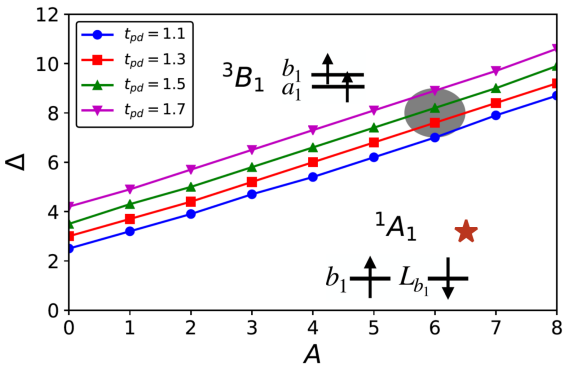


Fig. 4. Two-hole phase diagram for the stability of $^3B_1$ triplet ground state expected for a doped Mott insulator, vs. $^1A_1$ singlet ground state. Other parameters are $t_{pp}=0.55$ eV, $B=0.15$ eV, $C=0.58$ eV. The four lines correspond to $t_{pd}=1.1, 1.3, 1.5$ and 1.7 eV. We expect NiO_2 to lie in the shaded region and CuO_2 in the red star regime. Adapted from Ref. [71].

4. Summary and outlook

In summary, we used variational exact diagonalization to investigate the spectra of two holes doped into an otherwise full Ni/CuO_2 layer, modeled as a Ni/Cu-d^{10} impurity properly embedded into a square lattice of O-2p^6, to examine the relevance of multiplet structure on their properties.

For the CuO_2 layer, we proved that using a realistic O-2p band structure has non-trivial quantitative consequences, which is significant to the detailed modelling and comparison to the experiments. We also provided the evidence that although the three-band Emery model can essentially reproduce the low-energy properties of the cuprates, it is necessary to include the multiplet effects when discussing energy scales larger than about 1 eV, which might be closely related to, for example, the "waterfall" feature.[102]

For the NiO_2 layer, we pointed out that this system has larger charge transfer energies Δ so that the superexchange interaction reduces by around an order of magnitude compared

to cuprates. This observation puts forward strong constraints on the scenario of spin fluctuation mediated superconductivity for infinite-layer nickelates. Despite nominally being in the Mott–Hubbard regime of the ZSA scheme, our impurity calculation demonstrated that the NiO_2 layer can possibly reside at a critical region where the singlet hole doped state is formed similar to the cuprates. This criticality also points to the sensitivity of NiO_2 to various changes in the parameters resulting from the lattice structure with chemical substitution, epitaxial strain, and/or pressure. While our results suggest that in this sense this new nickelate material may mimic the cuprates, we point out that the superexchange is much smaller, so magnons are not likely to be the pairing "glue". As mentioned before, to go any further, one would need to know the impact of other bands associated with the Nd layers, which is still an open question.

Given that the rapid development in the understanding of the rare-earth infinite-layer nickelates RNiO$_2$, R = Nd, Pr as a new family of unconventional superconductors which has challenged various theoretical proposals, we have to continuously modify our model Hamiltonians according to the new experimental findings. Hence, before closing, we have a few remarks on our earlier investigation summarized above, specifically the inadequacy of our earlier results in terms of the absence of the inclusion of Nd orbitals and O vacancies and our strategy to refine our minimal models.

4.1. Inclusion of crystal fields and more orbitals

The recent x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) experiments[38] criticized our earlier results since it demonstrated that the energies of a hole in d_{xy}, $d_{xz/yz}$, and d_{z^2} are at 1.4 eV, 2.0 eV, and 2.7 eV, respectively, which is quite different from what we obtained by only taking into account the in-plane hybridization. In particular, the experimental indication lies in the larger splitting between $d_{x^2-y^2}$ and d_{z^2} than we obtained. Therefore, we need an additional strong spectral shift of the d_{z^2} peak.

One way to rectify the inadequacy is to examine the one hole spectra and readjust them by adding a crystal field term to self-consistently obtain its reasonable value to be compatible with the experimental results. With this additional crystal field term, we could perform the two-hole calculations to obtain the spectra for various symmetries. The expected result is that the singlet state will again be more stabilized than the triplet state bringing the material much closer to the cuprate limit. In other words, the phase boundary shown in Fig. 4 will probably shift upwards to leave the estimated ellipse within the region with $^1A_1$ symmetry steadily.

Compared to adding the additional crystal field term, the more physical way may be via the additional hybridization with the empty states left by the missing O above and below the NiO_2 planes. These additional hybridizations can largely modify the hole energies. The *ab-initio* calculations of our collaborators indicated that there is a so-called "Zeronium" band centered at the O vacancy crossing the Fermi energy.[104] Although the band structure revealed that there is also a p orbital involved in the creation of this vacancy, it would only hybridize with π type with $d_{xz/yz}$ but not much. Consequently, the O vacancy can be reasonably approximated as an s-like orbital with a relatively strong dispersion only in the Nd layer. Moreover, only Ni-d_{z^2} orbital has appreciable hopping to these s-like orbitals so that it is reasonable to explore the impact of this additional orbital.

In addition, there have been strong experimental and theoretical evidences that Nd's 5d and even 4f orbitals play the important role in determining the properties of infinite-layer nickelates RNiO$_2$, R = Nd, Pr. Undoubtedly, it is requisite to explicitly consider the effects of Nd in the model Hamiltonians appropriately. For example, it is worthwhile starting the investigation from the Ni impurity hybridizing with eight neighboring Nd ions above and below the NiO_2 plane. Because the Nd band is believed to be responsible for the self-doping effect on NiO_2, in the framework of our impurity calculation, we could take into account its impact via its possible occupation with electrons instead of holes as in NiO_2 plane. This mixed electron vs. hole treatment is currently being investigated.

4.2. Ni/Cu impurity vs. lattice

Our impurity studies have clear implications on the celebrated dynamical mean field approach (DMFT). Insofar as one can think of DMFT as being an impurity calculation embedded within a self-consistency loop, it is fair to remark that our results suggest that the bath to which the impurity is coupled, should be described as accurately as possible. Despite of the advent of more and more LDA+DMFT studies, there are still plenty of DMFT-based studies (for all sorts of models, not CuO_2 specific) where the baths are featureless, based on the idea that if the lattice becomes infinitely dimensional (with a semi-elliptical DOS), then DMFT becomes exact. Our investigation on CuO_2, which was based on the realistic O-2p band structure instead of the earlier featureless consideration of O band, pointed out that such studies are likely to be quantitatively inaccurate so that more cautious examination needs to be performed.

We remark that the projection onto different $3d^8$ irreducible representations is only possible when we treat a single Ni/Cu impurity as shown here. In the broader sense, one needs to be careful in drawing conclusion about the nature of the actual material simply based on the results from impurity calculations. In fact, there are many caveats in the single impurity approximation, for instance, how different might be the results for two coupled impurities. After all, ultimately we

have to resolve the outstanding issues of cuprate and nickelate superconductors based on the whole lattice calculations.

In the treatment of the full lattice, the various irreducible representation of D_{4h} symmetry group will mix everywhere in the Brillouin zone except at those high symmetry points. Thus it is requisite to examine whether the states with other symmetries are truly irrelevant to the lowest ground states as in impurity calculations. In fact, the early study by Lau[13] clearly demonstrated a strong ferromagnetic ordering of the two Cu spins sandwiching an oxygen hole, which indicated that extended lattice models are necessary to uncover the potential impact of the long range magnetic order and the doping on the stability of the ZRS in single-band Hubbard model scenario.

Compared to an impurity calculation, another feature of the lattice one is its lower symmetry, which may help explain how the z-axis polarization in XAS experiments emerges. Although the $d_{3z^2-r^2}$, d_{xz} and d_{yz} orbitals have little contribution to the $^1A_1$ ground state, they play the vital role in the low-energy peaks of other symmetry channels. Hence, a lattice calculation breaking the D_{4h} symmetry can boost their significance to the ground state and the hybridization with O-$2p_z$ orbitals. To tackle with these issues, the thorough lattice calculations of the N7, N9, N11 models using variational approximations similar to the approaches used here are our plan.

In fact, the treatment of Ni/CuO_2 full lattice is also reminiscent of the "Kondo"-like screening between localized Ni/Cu orbitals and itinerant O orbitals, which is essentially similar to the heavy fermion physics. Owing to the discovery of the resistivity's upturn[28,29] at low enough temperature, the intrinsic heavy fermion physics have attracted much attention.[30,31,108] One of the key questions concerns whether the conventional or modified Kondo/Anderson lattice models serve as the natural platform to describe the heavy fermion properties in infinite-layer nickelate superconductors. It is anticipated that the consideration of the multiplet effects of Ni-3d orbitals will largely modify the physics associated with the standard Kondo/Anderson lattice models, which deserves future investigation.

4.3. Superconductivity

The recent investigations have implications that the superconductivity in the new nickelate compounds may differ from that of cuprates, which suggests the fascinating possibility of alternative mechanism to induce and stabilize the unconventional superconductivity in doped $NdNiO_2$. Although various theoretical works have already emerged,[30,37,43,47,48,51,53,54,106,108–111] its nature is still largely unknown. We believe that it is imperative to understand the interplay between Nd, O vacancy and the NiO_2 layers before realistic proposals for the mechanism of superconductivity can be offered. Specifically, one must first know the precise nature of its metallicity. For example, is the interesting physics purely located inside the NiO_2 layers (in analogy with the cuprates) or not? Can the Nd–Ni hybridization fully explain the resistivity's upturn at low temperature?

Our investigation summarized here was to answer questions that can be addressed well at this point. One valuable insight from our work is that these materials can be very sensitive to the system parameters as any of them could move the system back into the canonical Mott insulator regime, with triplets instead of singlets forming upon doping.

Despite that our current investigation only focused on the NiO_2 layer, its demonstration that it should neither be treated like simple Mott insulators nor charge transfer insulators largely stimulated extensive studies afterwards. The more involved investigations along those thoughts outlined in our discussion above are ongoing.

Finally, one important issue we want to emphasize is whether the multi-orbital physics demonstrated so far in the nickelate superconductors can be mimicked appropriately by a renormalized single-orbital model, especially for the description of the unconventional superconductivity, similar to the role of the single-band Hubbard model claimed to be descriptive for the cuprate superconductors. There have been some proposals along this line of thoughts.[38,51] Naturally, the debate between the desirable simplicity of single-orbital description and complicated accuracy of multi-orbital treatment may arise similar to the investigation on the cuprate superconductors.

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