Effective one–band electron–phonon Hamiltonian for nickel perovskites

J. Loos\textsuperscript{1} and H. Fehske\textsuperscript{2}

\textsuperscript{1}Institute of Physics, Czech Academy of Sciences, 16200 Prague, Czech Republic
\textsuperscript{2}Physikalisches Institut, Universität Bayreuth, D–95440 Bayreuth, Germany

(Bayreuth, 1 February 1997)

Abstract

Inspired by recent experiments on the Sr–doped nickelates, La\textsubscript{2–x}Sr\textsubscript{x}NiO\textsubscript{4}, we propose a minimal microscopic model capable to describe the variety of the observed quasi–static charge/lattice modulations and the resulting magnetic and electronic–transport anomalies. Analyzing the motion of low–spin (\(s = 1/2\)) holes in a high–spin (\(S = 1\)) background as well as their coupling to the in–plane oxygen phonon modes, we construct a sort of generalized Holstein t–J Hamiltonian for the NiO\textsubscript{2} planes, which contains besides the rather complex “composite–hole” hopping part non–local spin–spin and hole–phonon interaction terms.

PACS number(s): 71.27.+a, 71.38.+i, 75.10.Lp
Charge carrier doping of transition metal oxides with perovskite related structure induces remarkable phenomena, such as high-temperature superconductivity in cuprates (e.g., \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \)), intrinsic incommensurate charge and spin ordering in non-metallic nickelates \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) \( \text{[LSNO(x)]} \), metal-insulator transition and colossal magneto-resistance in Mn-oxides (e.g., \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \)). All these phenomena are strongly concentration dependent and the experiments suggest the decisive role of interconnection between the spin- and charge correlations and the lattice and transport properties for their emergence \( \text{[1,2]} \).

In this paper we derive an effective Hamiltonian describing the interplay of charge-, spin- and lattice degrees of freedom in doped Ni-oxides. As revealed by recent neutron scattering of LSNO(x) \( \text{[3]} \), the stripe order of both charge and spin densities in general is found to be incommensurate in the low-density region \( x \lesssim 0.3 \); commensurability is restricted to very special values of \( x \), such as 1/3 and 1/2 \( \text{[4]} \). The rich variety of charge and spin ordering accompanied by the transport anomalies in nickelates \( \text{[4,5]} \) deserves the attention not only by itself, but also with respect to understanding the superconducting state in isostructural cuprates. In fact, the incommensurate (stripe-like) spin-, charge-correlations and lattice structure modulations are observed also in the metallic cuprates but there they are of dynamical and very short-range character \( \text{[6]} \).

The parent compound of the LSNO(x) system is the antiferromagnetic (AF) insulator \( \text{La}_2\text{NiO}_4 \) with a Néel temperature \( T_N \approx 330 \text{ K} \) and an in-plane exchange constant \( J \approx 30 \text{ meV} \). The magnetic 3d\(^8\) \( \text{Ni}^{2+} \) ions, having holes in \( 3d_{x^2-y^2} \), \( 3d_{3z^2-1} \) orbitals, are in the high-spin state (HSS) with \( S = 1 \) according to Hund’s rule. Doping this parent compound induces additional holes in the \( \text{NiO}_2 \) plane, but, in contrast to the superconducting cuprates, the layered nickel oxides LSNO(x) become metallic only near \( x \approx 1 \).

An additional hole in the \( \text{NiO}_2 \) plane quasi-localized at some \( \text{Ni}^{2+} \) ion aligns its spin antiparallel to the \( S = 1 \) spin of the ion due to the strong effective on-site interaction originated by the crystal field effect (overcoming the Hund’s rule coupling) \( \text{[7]} \). The resulting low-spin state (LSS) with total spin 1/2 is tightly bound to the moving charge carrier forming a so-called “Zhang–Rice doublet” \( \text{[6]} \), which is the counterpart to the usual Zhang–
Rice singlet \[\uparrow\downarrow\] in the cuprates. Aiming at the construction of an one–band model, i.e., a sort of generalization of the t–J model for the NiO\(_2\) plane, we have to take into account the constraints put on the motion of the composite–hole LSS by the background of correlated HSS of Ni\(^{2+}\) ions.

The two configurations, corresponding to an extra hole trapped at one of the two nearest neighbor (NN) Ni\(^{2+}\) ions of the bond \(\langle ij\rangle\) (\(i, j\) label the sites of the square lattice built up by the Ni ions in the a–b plane), are connected by an effective transition constant determined by the second order effect of the intermediate configuration with the hole in the p–orbital of the central oxygen ion \[\uparrow\downarrow\]. Assuming the orbital \(d_{jx}^h\) of the hole localized at the site \(j\) to be nearly the same as the orbital \(d_{x^2−y^2}\) of the Ni–ion coupled to this extra hole (see Table I; in the following the indices \(x, z\) stand for the orbitals \(d_{x^2−y^2}, d_{3z^2−1}\), respectively), we shall take orbitals \(d_{jx}^h, d_{jx}\) to play equivalent roles in the hopping process (and likewise for analogical orbitals related to the site \(i\)). This assumption leads to two possible ways in which the two configurations (differing by the localization of the extra hole in the bond \(\langle ij\rangle\)) are connected (cf. Table I).

Moreover, the hopping rate of the hole from \(j\) to \(i\) also depends on the spin states of both configurations leading to different prefactors in front of the effective transfer constant \(t\) (which is determined by the overlap of the d– and p–orbital functions \(\propto t_{pd}\)). According to Serber’s method \[\uparrow\downarrow\] (generalizing the Dirac’s spin Hamiltonian), the transition matrix elements implying the effect of spin states associated with the initial and final configurations, are given by the matrix elements of the sum of the following operators

\[
\mathcal{H}^{(d)}_i = t Q_{j}^{\text{HSS}} Q_{i}^{\text{LSS}} P_1^s Q_j^{\text{LSS}} Q_i^{\text{HSS}},
\]

\[
\mathcal{H}^{(e)}_i = -t Q_{j}^{\text{HSS}} Q_{i}^{\text{LSS}} P_{12}^s Q_j^{\text{LSS}} Q_i^{\text{HSS}},
\]

acting in the spin function space of two NN Ni ions and one extra hole. The identical permutation operator \(P_1^s\) and the transposition operator \(P_{12}^s\), both acting on the spin variables with indices 1, 2, correspond to the direct–type and exchange–type hole transfers, respectively, distinguished in Table I. The operators \(Q_k^{\text{HSS}}\) (\(Q_k^{\text{HSS}}\)) project the spin functions pertaining
to site \( k \) on the subspace of LSS (HSS). Consequently, the projection operators restrict the motion of the composite hole to the subspace of LSS (for the hole occupied sites) and HSS (for the hole unoccupied ones).

The matrix elements of the transitions between configurations having the total spin projections \( M_T = 1/2 \) and \( M_T = 3/2 \) are given by the sum of matrices \([\mathcal{H}_t] = [\mathcal{H}_t^{(d)}] + [\mathcal{H}_t^{(e)}]\) as follows

\[
[\mathcal{H}_t^{(d)}] = \begin{pmatrix}
\langle i+ ,j0| & \langle i+ ,j1| & \langle i+ ,j1|
\end{pmatrix}
\begin{pmatrix}
\frac{1}{3}t & \frac{\sqrt{2}}{3}t & 0 \\
\frac{\sqrt{2}}{3}t & 0 & 0 \\
0 & 0 & \frac{2}{3}t
\end{pmatrix}
\]

(3)

\[
[\mathcal{H}_t^{(e)}] = \frac{1}{2}[\mathcal{H}_t^{(d)}].
\]

(4)

Here the whole numbers in the bra– and ket–vectors label the spin projection belonging to HSS, whereas spin–up and spin–down LSS are denoted by + and −, respectively. The remaining non–zero matrix elements corresponding to the transitions with the \( M_T = -1/2 \) and \( M_T = -3/2 \) conservation are connected with the previous ones by the time–reversal operation which leaves the matrices (3), (4) unchanged. Therefore, adding (3) and (4) three types of hopping processes with effective transition constants \( t/2 \) and \( t/\sqrt{2} \), and \( t \) are obtained.

Having determined the transition matrix elements of the hopping processes, the effective transport Hamiltonian in the space of LSS and HSS of Ni–ions may be written down. To this end we introduce the tensor product space \( \mathcal{H}^S \otimes \mathcal{H}^h \)

\[
\mathcal{H}^S = \prod_i \otimes \{|i0\} \quad m = \pm 1, 0,
\]

(5)

\[
\mathcal{H}^h = \prod_i \otimes \{|i\sigma\}, |i0\} \quad \sigma = \uparrow, \downarrow,
\]

(6)

where \( |i,m\rangle \) are the eigenfunctions of spin \( S = 1 \) operators \( \vec{S}_i^2, S_i^z \) at site \( i \) with spin projection \( m \). On the other hand, \( |i\sigma\rangle \) means an eigenfunction of of the spin \( s = 1/2 \)
operators \( \vec{s}_i^2, s_i^z \) of an additional hole at site \( i \) with spin projection up or down. The hole state \( |i0\rangle \) corresponds to no extra hole at \( i \).

The HSS creation and annihilation in the hopping process will be described by means of the operators \( \mathbf{7} \)

\[
B_{i,1}^\dagger = b_{ix,\uparrow}^\dagger b_{iz,\uparrow}^\dagger, \quad B_{i,-1}^\dagger = b_{ix,\downarrow}^\dagger b_{iz,\downarrow}^\dagger
\]

\[
B_{i,0}^\dagger = (b_{ix,\downarrow}^\dagger b_{ix,\downarrow}^\dagger + b_{ix,\uparrow}^\dagger b_{ix,\uparrow}^\dagger)/\sqrt{2}
\]

defined by the Schwinger boson creation operators \( b_{ix,\sigma}^\dagger, b_{iz,\sigma}^\dagger \). Denoting by \( |0\rangle_B \) the boson vacuum (with respect to the closed d–shells Ni configuration), the vectors

\[
|i, m\rangle = B_{i,m}^\dagger |0\rangle_B,
\]

and operators

\[
S_i^+ = \sqrt{2} (B_{i,1}^\dagger B_{i,0} + B_{i,0}^\dagger B_{i,-1})
\]

\[
S_i^z = B_{i,1}^\dagger B_{i,1} - B_{i,-1}^\dagger B_{i,-1}
\]

constitute a representation of spin \( S = 1 \) operators and states. With the above definitions of \( B \)–operators, the following relations become evident:

\[
B_{i,m}|0\rangle_B = 0, \quad B_{i,m}|jm\rangle = \delta_{ij}\delta_{mm'}|0\rangle_B.
\]

Accordingly, the HSS related to site \( i \) can be represented by the vectors

\[
|i m\rangle|i0\rangle = B_{i,m}^\dagger |0\rangle_B |i0\rangle.
\]

Now let us consider the LSS of composite holes formed by an extra hole antiferromagnetically tightly bound to the spin \( S = 1 \) of the Ni\(^{2+}\) ion. Defining the Hubbard operators

\[
X_i^{\sigma 0} = |i\sigma\rangle\langle i0|
\]

in the single–occupation space \( \mathcal{H}_h \) and taking into account the interior structure of the composite holes (which was neglected in the work of Zaanen and Oleś \( \mathbf{4} \)), the LSS will be expressed by means of the Clebsch–Gordon coefficients as follows:
\[ |i+\rangle = \frac{1}{\sqrt{3}} (-B_{i,0}^\dagger X_{i,0}^{0\uparrow} + \sqrt{2} B_{i,1}^\dagger X_{i,1}^{0\uparrow}) |0\rangle_B |i0\rangle \]  
\[ |i-\rangle = \frac{1}{\sqrt{3}} (-\sqrt{2} B_{i,-1}^\dagger X_{i,0}^{0\uparrow} + B_{i,0}^\dagger X_{i,0}^{0\downarrow}) |0\rangle_B |i0\rangle . \]  

Then, using the transition matrix elements given by (1)–(4) as well as the representation of HSS and LSS by (13), (15), (16), the effective transport Hamiltonian \( H_t \) may be rewritten as

\[ H_t = t \sum_{\langle i,j \rangle} (C_{i,\frac{1}{2}}^\dagger C_{j,\frac{1}{2}}^\downarrow + C_{i,-\frac{1}{2}}^\dagger C_{j,-\frac{1}{2}}^\uparrow) , \]  

with

\[ C_{j,\frac{1}{2}} = B_{j,0}^\dagger \left[ -\frac{1}{\sqrt{3}} B_{j,0} X_{j,0}^{0\uparrow} + \sqrt{\frac{2}{3}} B_{j,1} X_{j,1}^{0\uparrow} \right] + B_{j,-1}^\dagger \left[ -\sqrt{\frac{2}{3}} B_{j,-1} X_{j,1}^{0\uparrow} + \frac{1}{\sqrt{2}} B_{j,0} X_{j,0}^{0\downarrow} \right] , \]

where \( B_{j,0}^\dagger = \frac{1}{\sqrt{2}} B_{j,0}^\dagger \). The first term on the right hand side of (17) describes the four hole transport processes which are connected with the transfer of the spin projection equal to 1/2. The second term in (17), comprising the remaining four hopping processes obtained from the previous ones by the time reversal operation, corresponds to the transfer of spin projection equal to (−1/2).

Obviously, in \( H_t \) the Hubbard operators of holes are coupled to the Schwinger boson operators, showing thus a rather complicated dependence of the hole transport on the spin background. We can even go a step further by expressing the hole Hubbard operators in terms of decoupled charge (holon) and spin variables. Using a slightly modified treatment proposed recently for the mapping of the t–J model onto the tensor product space of holon and spin–1/2 states, the Hubbard operators (14) are obtained in terms of independent holon (\( h_i \)) and pseudo-spin–1/2 (\( \tilde{s}_i \)) operators as

\[ X_{i}^{0\uparrow} = h_i (\tilde{s}_i^+ \tilde{s}_i^- + e^{i\varphi} \tilde{s}_i^- \tilde{s}_i^+) / \sqrt{2} , \]

\[ X_{i}^{0\downarrow} = h_i (\tilde{s}_i^+ + e^{i\varphi} \tilde{s}_i^- \tilde{s}_i^+) / \sqrt{2} , \]

where the arbitrary phase factor \( \varphi \) has no effect on the matrix elements of physical variables.

The local number operator of spinless fermionic holons,
\[ h_i^\dagger h_i = \sum_\sigma X_i^{\sigma0} X_i^{0\sigma}, \] (21)

has eigenvalues \( n_i^h = 0, 1 \), and the spin operators of the physical hole–spins are connected with the pseudo-spin operators by

\[ s^\pm_i = h_i^\dagger \sigma_{3i} \sigma_{3i}^\dagger, \quad s^z_i = h_i^\dagger_\sigma \tilde{s}^z_i. \] (22)

The corresponding representation of the operators \( C_{j,\pm \frac{1}{2}} \) defined by (18) is given by

\[ C_{j,\frac{1}{2}} = \frac{1}{\sqrt{6}} h_j \left[ (\sqrt{2}B_{j,0}^0 B_{j,1}^1 + B_{j,-1}^1 B_{j,0}^0) \left( \tilde{s}^+_j + e^{i\phi} \tilde{s}^-_j \tilde{s}^+_j \right) \\
- \left( \tilde{B}_{j,0}^1 B_{j,-1}^1 B_{j,0}^0 + \sqrt{2} B_{j,-1}^1 B_{j,1}^0 \right) \left( \tilde{s}^+_j \tilde{s}^-_j + e^{i\phi} \tilde{s}^-_j \right) \right], \] (23)

and the effective transport Hamiltonian (17) becomes

\[ \mathcal{H}_t = \sum_{\langle i,j \rangle} \hat{t}_{ij} h_i^\dagger h_j. \] (24)

The latter expression (24) of \( \mathcal{H}_t \) has the form of a holon hopping Hamiltonian with the hopping constant \( t \) replaced by the transfer operator \( \hat{t}_{ij} \) which depends on the degrees of freedom of the spin–1 background, as well as on the spin variables of the charge carriers.

To demonstrate more explicitly the dependence of the charge transport on the spin background we shall consider the strong AF correlations of the Ni\(^{2+} \) spins at low hole concentrations, what enables us to use the spin wave approximation (SWA). In the spirit of SWA the states with double local spin deviations from the Néel ordering will be disregarded. Accordingly, separating the lattice sites into two AF sublattices \( \{k\}, \{l\} \) characterized by \( S^z_k = S, S^z_l = -S \), respectively, the states \( |k, -1\rangle, |l, 1\rangle \) of Ni\(^{2+} \) ions will be excluded. Then the representation of spin operators (10), (11) may be approximated by

\[ S_k^+ \simeq \sqrt{2} B_{k,1}^1 B_{k,0}^0, \quad S_k^- \simeq B_{k,1}^1 B_{k,-1}^1, \] (25)

\[ S_l^+ \simeq \sqrt{2} B_{l,0}^1 B_{l,-1}^1, \quad S_l^- \simeq B_{l,-1}^1 B_{l,1}^1, \] (26)

what makes possible to express the transport Hamiltonian given by (17), (18) by means of \( S^\pm \) (spin wave) operators, up to quadratic terms, as follows:
\[ H_{SW}^{t} = \frac{t}{6} \sum_{\langle kl \rangle} \left[ (S_k^- S_k^+ + S_l^- S_l^+) X_l^{10} X_k^{0\dagger} + (S_l^+ S_l^- + S_k^+ S_k^-) X_l^{10} X_k^{0\dagger} - 2 \left( S_k^- + S_l^- \right) X_l^{10} X_k^{0\dagger} + H.c. \right]. \]  

(27)

The difference of (27) with respect to the transport term of the standard t–J model consists in the spin dependence of the hole transport, as well as in the existence of hopping accompanied by hole–spin flipping. A closer resemblance of the t–J model is obtained if the transport Hamiltonian (27) is averaged with respect to the ground state of AF magnons. Following the procedure outlined for the t–J model in Ref. [11], we get the mean field Hamiltonian

\[ \overline{H}_{SW}^{t} = t_{eff} \sum_{\langle i,j \rangle} h_i^\dagger h_j (g_{ij} + \vec{s}_i \vec{s}_j + \frac{r}{4}) \]  

(28)

with

\[ t_{eff} = \frac{t}{3} \left( \langle \delta S_k^z \rangle + \frac{1}{2} \langle S_k^+ S_k^- \rangle \right), \]  

(29)

\[ g_{ij} = \left\{ e^{i\varphi} \left[ \left( \frac{1}{2} - \vec{s}_j^\dagger \vec{s}_j \right) \vec{s}_i^+ + \vec{s}_j^\dagger \left( \frac{1}{2} + \vec{s}_i^\dagger \right) \right] + e^{-i\varphi} \left[ \left( \frac{1}{2} + \vec{s}_j^\dagger \vec{s}_j \right) \vec{s}_i^+ + \vec{s}_j^\dagger \left( \frac{1}{2} - \vec{s}_i^\dagger \right) \right] \right\} / 2. \]  

(30)

Here \( \langle \delta S_k^z \rangle \) is the reduction of the local \( |S_i^z| \) from the classical value \( S \) in the ground state of AF magnons. The expectation values in (29) vanish in the classical AF Néel ground state. Supposing the quantum antiferromagnet, \( t_{eff} \) is non–zero owing to the zero–point fluctuations, but it is considerably reduced compared with the bare transfer integral. In this way, the spin correlations lead to strong magnetic confinement effects and therefore suppress the charge transport.

In a next step we consider the spin interactions. Here we have to take into account the strong effective on–site interaction, leading to the formation of LSS at the hole occupied sites and the (much weaker) superexchange interaction of the NN spins. Thus we get

\[ H_J = J_0 \sum_i h_i^\dagger h_i \vec{s}_i \vec{S}_i + \sum_{\langle i,j \rangle} J_{ij} \vec{J}_i \vec{J}_j, \]  

(31)

where

\[ \vec{J}_i = (1 - h_i^\dagger h_i) \vec{S}_i + h_i^\dagger h_i (\vec{S}_i + \vec{s}_i). \]  

(32)
The effective on-site coupling constant $J_0$ is given by the energy difference between the $J = 1/2$ (LSS) and $J = 3/2$ states of the Ni$^{2+}$ ion occupied by an additional hole. Dagotto’s estimate $[12]$ of the latter difference is $\sim 1.3$ eV, so that the on-site interaction is much stronger than than all the inter-site ones. Note that the superexchange interaction $\mathcal{J}(n^h_i, n^h_j)$ between the total spins $\vec{J}$ of the NN cations, represented by the second term in (31), depends strongly on the electronic configuration of the bond $\langle ij \rangle$ $[13]$. For pairs of Ni$^{2+}$ ions, $\mathcal{J}(0, 0)$ is the superexchange coupling constant in the parent compounds. Most notably, recent experiments $[3]$ show that the intersite spin interactions play a secondary role in formation the charge–spin stripe structure as the charge ordering occurs always at higher temperatures as the ordering of spins.

On the other hand, in the nickelates there is both experimental $[4, 5]$ and theoretical $[16, 17]$ evidence for a strong coupling of the doped holes to the in–plane oxygen phonon modes. It is believed that the observed charge and spin modulations are driven by a charge segregation in stripe–like structures, i.e. by phase separation on a mesoscopic length scale, connected with breathing–mode polaron formation. The mechanism for such polaron ordering is expected to be based on: (i) the non–local character of the electron–phonon interaction determining the energy gain caused by the bond deformation to be proportional to the hole population difference of the NN Ni–sites, and (ii) on the Coulomb polaron polaron interaction. Once the ordering of polarons is established, the distribution of LSS and HSS in the lattice is fixed and at sufficiently low temperature the stripe spin–ordering arises.

To include the in–plane electron–phonon coupling effects in our model Hamiltonian, we assume a Holstein–type interaction which takes the form

$$
\mathcal{H}_{h-p} = -A \sum_{\langle ij \rangle} \hat{u}_{ij} (\hat{h}_i^\dagger \hat{h}_i - \hat{h}_j^\dagger \hat{h}_j)
$$

for the case considered. Here $A$ denotes the local hole–lattice coupling constant and $\hat{u}_{ij}$ is the displacement operator of the oxygen in the bond $\langle ij \rangle$. That is, in our effective single–band description the formation of polarons is related to a quasi–static (oxygen–nickel) bond deformation given by $\langle \hat{u}_{ij} \rangle \neq 0$. As a second order effect the overlap integrals $t_{pd}$ and
thus the superexchange interactions are affected by a finite $\langle \hat{u}_{ij} \rangle$ as well, i.e. we have $J_{ij} = J(n_i^h, n_j^h, \langle \hat{u}_{ij} \rangle)$.

To this end, as an effective Hamiltonian for the theoretical description of the layered nickel perovskites we propose the following generalized Holstein t–J model

$$H = H_t + H_J + H_{h-p} + H_p,$$ (34)

where $H_p$ refers to the bare phonon part given in harmonic approximation.

In summary, we have derived the effective hopping transport Hamiltonian of spin–1/2 composite holes in the background of spin–1 Ni$^{2+}$ ions using Serber’s results for the transition matrix elements between different electron configurations. The suppression of the spin–dependent transport was explicitly demonstrated for the case that the Ni$^{2+}$–spins are strongly AF correlated. The experimentally observed stripe–structures appear to be comprehensible on the basis of the strong coupling of doped holes to the in–plane oxygen lattice modes, incorporated in the proposed effective Hamiltonian by a non–local Holstein–type interaction.

Finally, we would like to emphasize that applying the approach described above to the electronic transport in the ferromagnetic manganese compounds, e.g. La$_{1-x}$Ca$_x$MnO$_3$ [18], shows the two essential differences between the doped Ni– and Mn–oxides. First, the itinerant electron of Mn$^{3+}$ couples to the three $t_{2g}$ electrons according to Hund’s rule forming a high–spin state with total $S = 2$. In contrast the crystal field splitting is dominant for Ni$^{3+}$ ions leading to a low–spin state with total spin 1/2. Secondly, whereas the $e_g$ electrons of Mn–ions are separated from the spin background, determined by the localized $t_{2g}$ electrons, the holes in the $d_{x^2-y^2}$ orbitals of Ni–ions take part in the hopping, as well as in the formation of spin background.

This work was in part supported by the Grant Agency of
## TABLE I. Hole transfer processes.

| configuration | \(d_{jx}^h\) | \(d_{jx}\) | \(d_{jz}\) | \(p\) | \(d_{ix}^h\) | \(d_{ix}\) | \(d_{iz}\) |
|---------------|-------------|-------------|-------------|------|-------------|-------------|-------------|
| initial       | 1           | 2           | 3           |      | 4           | 5           |             |
| intermediate  | 2           | 3           | 1           |      | 4           | 5           |             |
| final         | 2           | 3           | 1           |      | 4           | 5           |             |

**direct–type transfer (d)**

| configuration | \(d_{jx}^h\) | \(d_{jx}\) | \(d_{jz}\) | \(p\) | \(d_{ix}^h\) | \(d_{ix}\) | \(d_{iz}\) |
|---------------|-------------|-------------|-------------|------|-------------|-------------|-------------|
| intermediate  | 1           | 3           | 2           |      | 4           | 5           |             |
| final         | 1           | 3           | 2           |      | 4           | 5           |             |

**exchange–type transfer (e)**
REFERENCES

[1] J. M. Tranquada et al., Nature 375, 561 (1995).
[2] S. Jin et al., Science 264, 413 (1994).
[3] J. M. Tranquada, D. J. Buttrey, and V. Sachan, Phys. Rev. B 54, 12318 (1996).
[4] S.-W. Cheong et al., Phys. Rev. B 49, 7088 (1994).
[5] S. M. Hayden et al., Phys. Rev. Lett. 68, 1061 (1992).
[6] A. P. Ramirez et al., Phys. Rev. Lett. 76, 447 (1996).
[7] J. Zaanen and A. M. Oles, Phys. Rev. B 48, 7197 (1993).
[8] F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
[9] Z. Tan et al., Phys. Rev. B 47, 12365 (1993).
[10] R. Serber, Phys. Rev. 45, 461 (1934).
[11] J. Loos, Phys. Rev. B 53, 12556 (1996).
[12] E. Dagotto, J. Riera, A. Sandvik, and A. Moreo, Phys. Rev. Lett. 76, 1731 (1996).
[13] P. W. Anderson, Phys. Rev. 79, 350 (1950).
[14] C. H. Chen, S.-W. Cheong, and A. S. Cooper, Phys. Rev. Lett. 71, 2461 (1993).
[15] X.-X. Bi and P. C. Eklund, Phys. Rev. Lett. 70, 2625 (1993).
[16] L. Pintschovious et al., EuroPhys. Lett. 5, 247 (1988).
[17] J. Zaanen and P. B. Littlewood, Phys. Rev. B 50, 7222 (1994).
[18] P. W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955).