Microscopic Hamiltonian for Zn or Ni substituted high temperature cuprate superconductors

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We have derived the effective low energy Hamiltonian for Zn or Ni substituted high-$T_c$ cuprates from microscopic three-band models consisting of the most relevant Cu or impurity 3d and O 2p orbitals. We find that both scattering potential and hopping integral induced by impurities have a finite range but decay very fast with distance from the impurity. The Zn scattering potential is very strong and attractive for electrons. The Ni scattering potential is much weaker than the Zn case, resulting from the hybridization between Ni ions and O holes. This profound difference is due to neither the electric charge nor d-level location, but rather because of the interplay between the valence state of the impurity and the strong correlation background. It gives a natural account for the unusual effect of Ni and Zn on the reduction of superconducting transition temperature.

Substitution of divalent transition metal Zn or Ni for Cu in Cu-O plane has offered a fruitful and challenging direction in exploring the nature of correlated electrons in high-$T_c$ cuprates. The effects of these impurities on superconducting properties are unusual and in many ways opposite to those observed in conventional superconductors. In particular, the $T_c$ reduction induced by non-magnetic Zn ions is almost three times larger than that by magnetic Ni ions. Also, the temperature dependence of the penetration depth shows a much stronger pair-breaking effect of Zn compared with Ni. The actual situation is more complicated than it appears: the NMR and susceptibility measurements do not show the existence of an induced local moment around Zn impurities. However, there exists a vast literature devoted to explore the impurity effects on d-wave superconductors, particularly to interpret the scanning tunneling microscopy (STM) experiments. However, the key issue, namely why Zn impurity is a very strong scatterer (close to the unitary limit), while Ni is a relatively weaker scatterer, is not well understood. The earlier efforts to address this issue using exact diagonalization of the $t-J$ model on finite clusters and the slave-particle treatments of the resonance valence bond (RVB) state show the importance of the strong correlation background, but are unable to elucidate the physics involved to the full extent.

In this paper, we present a theoretical derivation for the effective low-energy Hamiltonians for both Zn and Ni impurity systems. The aim is to find an accurate description for the impurity scattering potential and to clarify a number of important issues associated with the scattering phase shifts. We also present a detailed analysis for the anisotropic interlayer hopping process and discuss its impact on the scanning tunneling spectra of high-$T_c$ superconductors. We start from the three-band Hubbard model for the Cu-O plane, and study systematically the influence of the impurity on the Zhang-Rice singlet formation. In this work, only a single Zn or Ni impurity system is studied. However, it is straightforward to extend the derivation to a system of many Zn or Ni impurities, provided the direct interaction among them is negligible.

Let us first consider the case of Zn impurity. Zn$^{2+}$ has a 3d$^{10}$ configuration and no spin. Since the valence fluctuation of Zn$^{2+}$ is small, we can model Zn as an inert non-magnetic impurity with no coupling with surrounding O or Cu states. In high-$T_c$ oxides, the low energy physics is governed by one Cu 3d$_{x^2-y^2}$ and two O (2p$_x$, 2p$_y$) bands and the doped holes are predominantly on O (2p$_x$, 2p$_y$) states. Thus to study the physical effect of Zn, we should start from the following three-band Hamiltonian

$$
H = H_0 + H_1,
$$

$$
H_0 = \varepsilon_p \sum_{i} p^\dagger_i p_i + \sum_{i \neq i_0} \left( \varepsilon_d d^\dagger_i d_i + U_d d^\dagger_{i\uparrow} d_{i\uparrow} d^\dagger_{i\downarrow} d_{i\downarrow} \right),
$$

$$
H_1 = - \sum_{\langle ij \rangle \neq i_0} t_{pd} \left( p^\dagger_i d_j + d^\dagger_j p_i \right),
$$

where $d_i = \left( d^\dagger_{i\uparrow}, d^\dagger_{i\downarrow} \right)$ creates a Cu 3d$_{x^2-y^2}$ hole, and $p_i = \left( p^\dagger_{i\uparrow}, p^\dagger_{i\downarrow} \right)$ creates an O 2p$_l$ hole if $l = i \pm \frac{\tilde{z}}{2}$ or an O 2p$_g$ hole if $l = i \pm \frac{\tilde{y}}{2}$. (See Fig. 1 of Ref. [23] for the definition of relative phases of 3d$_{x^2-y^2}$ and O 2p orbitals.) $i_0$ is the impurity position. Without loss of generality, we set $\varepsilon_d = 0$ and $\varepsilon_p > 0$. The real system is in the limit $U_d \gg \varepsilon_p \gg t_{pd}$. An on-site Coulomb repulsion term for O holes is neglected since we are only interested in low doping cases and the probability for two holes to occupy one O site is very small.
The O 2p holes can be classified according to their hybridization with Cu 3d_{x^2-y^2} states as bonding and nonbonding Wannier orbitals. These orbitals are defined on the Cu lattice. The bonding orbital is defined by

\[ a_i = \frac{1}{\sqrt{N}} \sum_k e^{ikR_i} \beta_k^{-1} \cos(kx/2)p_{x,k} + \cos(ky/2)p_{y,k}, \]

where \( \beta_k = \sqrt{\cos^2(kx/2) + \cos^2(ky/2)} \) and \( N \) is the number of Cu sites. \( p_{x,k} \) and \( p_{y,k} \) are the Fourier transformation of \( p_{i+\hat{x}/2} \) and \( p_{i+\hat{y}/2} \), respectively. The nonbonding orbital is orthogonal to \( a_i \) and defined by \( b_i = \frac{1}{\sqrt{N}} \sum_k e^{ikR_i} \beta_k^{-1} [\cos(ky/2)p_{x,k} - \cos(kx/2)p_{y,k}] \). With these Wannier orbitals, the Hamiltonian (1) can be expressed as

\[
H_0 = \varepsilon_p \sum_i \left( a_i^\dagger a_i + b_i^\dagger b_i \right) + \sum_{i \neq \text{f}o} U_d d_{i \sigma}^\dagger d_{i \sigma} d_{\text{f}o \sigma}^\dagger a_{\text{f}o \sigma} ,
\]

\[
H_1 = -t_{pd} \sum_{i \neq j, i \neq \text{f}o} u(i-j) \left( a_i^\dagger d_i + d_{i \sigma}^\dagger a_{i \sigma} \right),
\]

where \( u(i) = \frac{2}{N} \sum_k \beta_k e^{ikR_i} \). The nonbonding orbitals do not couple to the other states and may be neglected.

In the limit \( U_d \gg \varepsilon_p \gg t_{pd} \), we can treat \( H_1 \) as a perturbation and use degenerate perturbation theory to project the Hamiltonian onto the Hilbert space spanned by the low-energy states of \( H_0 \). Up to the second order of perturbation, we find that an effective Hamiltonian for the system is given by

\[
H'_{Zn} = -\sum_{ij} t_{ij} a_i^\dagger a_j + t_{12} \sum_{i \neq \text{f}o} d_{i \sigma}^\dagger d_{i \sigma} a_{\text{f}o \sigma}^\dagger a_{\text{f}o \sigma},
\]

where \( t_{12} = t_1 + t_2 = t_{pd}^2/\varepsilon_p \), and \( t_{ij} = t_2 [4\delta_{i,j} + \delta_{(i,j)} - u(i_0 - i)u(i_0 - j)] \) (the second Kronecker symbol means \( i, j \) must be the nearest neighbours) and \( a_i = \sum_j u(i-j) a_j \). The coupling between \( d \) and \( a \) at different sites is much smaller than the on-site one. Thus, we can take the approximation \( a_i \approx u(0) a_0 \). This is also an approximation implicitly assumed in the work of Zhang and Rice [20].

In \( H' \), the coupling constant between O 2p and Cu 3d_{x^2-y^2} states is of the order \( (t_2 + t_1) u^2(0) \). This is a large energy scale compared with the hopping integral for the bonding O holes. An important consequence of this strong coupling between O 2p and Cu 3d_{x^2-y^2} holes, as first pointed out by Zhang and Rice [20], is that an O hole will form a local spin singlet with a Cu spin. The binding energy of the Zhang-Rice singlet is \( (t_2 + t_1) u^2(0) \). The energy difference between the Zhang-Rice singlet and the corresponding triplet is \( 2(t_2 + t_1) u^2(0) \). Since this difference is much larger than the bandwidth of the O holes, the triplet hole band can be neglected in the study of low energy excitations. Thus we can further project the Hamiltonian onto the subspace spanned by the Zhang-Rice singlets with unpaired Cu spins. The resulting effective Hamiltonian is then given by

\[
H''_{Zn} = \sum_i V_{Zn}(i) d_i^\dagger d_i - \sum_{i \neq j} t_{ij}^* Z_{ij} d_i^\dagger d_j \]

subjected to the constraint \( d_i^\dagger d_i \leq 1 \) when \( i \neq i_0 \). At the impurity site, \( d_{i_0} = (d_{i_0 \uparrow}, d_{i_0 \downarrow}) \) is defined from the creation operator of the bonding O hole: \( d_{i_0 \sigma} = -\sigma a_{i_0 \sigma}^\dagger \). We should emphasize that \( d_{i_0} \) is not an annihilation operator for the Zn 3d_{x^2-y^2} state. At the Zn site, there is no constraint imposed on \( d_{i_0} \). Thus two electrons with opposite spins can occupy this site simultaneously. This is consistent with the fact that there are two electrons in the 3d_{x^2-y^2} state of the Zn^{2+} ion, although our starting Hamiltonian (\( H \)) does not contain that state at all. Moreover, if the total number of doped holes in the system is \( N_h \), then it can be shown that \( \sum_i d_i^\dagger d_i = (N - N_h) + 1 \). Thus the total number of conducting electrons is more than the nominal charge of the system by one. This implies that Zn^{2+} can be effectively taken as an ion with one more charge than Cu^{2+}, although both are divalent. It further suggests that we only need to count the difference between the number of 3d electrons in Zn^{2+} and Cu^{2+} when the Friedel sum rule of phase shifts is used.

In (3), the hopping integral is defined by

\[
t_{ij} = \frac{\bar{t}_{ij}}{2} \delta_{i \neq \text{f}o, j \neq i_0} + \frac{t_{i0}}{\sqrt{2}} \delta_{i, i_0} + \frac{\bar{t}_{i0}}{\sqrt{2}} \delta_{j, i_0},
\]

where \( \bar{t}_{ij} = t_2 \delta_{(i,j)} - t_2 u(i_0 - i)u(i_0 - j) \). The first term in \( \bar{t}_{ij} \) is the usual hopping integral in a homogeneous system, and the second term is a small correction to the hopping integral by the Zn impurity. This impurity induced hopping integral is non-local but decays very fast with distance from the impurity.

The impurity potential \( V_{Zn}(i) \) is given by

\[
V_{Zn}(i) = -t_2 u^2(0) \delta_{i \neq i_0} - (2t_2 + t_1) u^2(0) \delta_{i, i_0}.
\]

This is an attractive potential. It is certainly not of a \( \delta \)-function form, but away from the Zn impurity, \( V_{Zn}(i) \) decays very fast, roughly as \( |i - i_0|^{-4} \). At the impurity site, \( |V_{Zn}(i_0)| \approx 3.67(t_2 + t_1) \) is about two orders of magnitude larger than the potential at the four nearest neighboring sites of Zn, \( |V_{Zn}(i)| \approx 0.0785 t_2 \). It is also more than one order of magnitude larger than the hopping constant \( t_2/2 \), in consistent with the STM measurement data [11]. This shows clearly that Zn impurity is indeed a strong potential scatterer.

The strong attractive potential induced by Zn is in fact due to a strong repulsion of Zn^{2+} to the bonding O holes at the impurity site. This strong repulsion of Zn^{2+} to O holes results from two distinguished physical effects. First, since Zn^{2+} has no spin, O holes cannot gain energy by forming a Zhang-Rice singlet with a 3d_{x^2-y^2} spin at the Zn site, this costs the O hole an energy of \( (t_2 + t_1) u^2(0) \). Second, since there is no hopping between O 2p and Zn 3d states, the O hole also suffers from a kinetic energy loss of \( t_2 u^2(0) \). The total energy loss of an O hole at the impurity site is thus \( (2t_2 + t_1) u^2(0) \). This
serves effectively as a repulsive potential to the O holes, or equivalently an attractive potential to the \( d_{3\pm} \) electrons, at the Zn site. This picture is completely different from the naive interpretation for the origin of the attractive potential of Zn in literature, which claims that the potential is attractive because Zn\(^{2+} \) has one more electron in its 3\( d_{z^2-r^2} \) orbital than Cu\(^{2+} \) and the 3\( d \) energy levels of Zn\(^{2+} \) are lower than those of Cu\(^{2+} \). We would like to particularly point out an intriguing connection between the scattering potential of Zn and the physics underlying the Zhang-Rice singlet. It suggests that through the measurement of the Zn scattering potential, we can even gain direct information on the binding energy of the Zhang-Rice singlet.

The Hamiltonian contains the most important information about the Zn scattering potential. However, to obtain the full effective Hamiltonian, we should include the fourth order of perturbation as in the derivation of the standard \( t-J \) model. In particular, two terms which are absent in the second order of perturbation should be included. One is the exchange energy between two Cu\(^{2+} \) spins on nearest neighboring sites. The other is the hopping of electrons between next or next-next nearest neighboring sites. This term has strong effect on the structure of Fermi surface. There is also a three-site hopping term, which is generally ignored for simplicity. The other terms generated from the fourth order of perturbation are small corrections to the terms in \( \mathbf{3} \) and can be omitted. Thus the full effective Hamiltonian for the Zn-substituted system is

\[
H_{Zn} = H''_{Zn} - \sum_{i \neq \bar{i} \neq i_0} t'_{ij} d_i^\dagger d_j + \sum_{\langle i,j \rangle \neq i_0} JS_i \cdot S_j, \tag{6}
\]

where \( S_i \) is the Cu spin operator, and \( t'_{ij} = t' \) if \( (i, j) \) are next neighbors, or \( t'' \) if \( (i, j) \) are next-next neighbors, or zero otherwise. \( t' \) and \( t'' \) always have opposite signs. They are of the same order as the exchange energy \( J \).

Now let us turn to the Ni case. As for Zn\(^{2+} \), Ni\(^{2+} \) is also in a divalent state. It has 8 electrons in its 3\( d \) states. In particular, it has one electron in the 3\( d_{3z^2-r^2} \) state and one in the 3\( d_{3z^2-r^2} \) state. These two electrons form a spin triplet via a strong Hund’s rule coupling. Like Zn\(^{2+} \), Ni\(^{2+} \) is also very stable. However, unlike Zn\(^{2+} \), the hybridization between the Ni (3\( d_{3z^2-r^2}, 3d_{3z^2-r^2} \)) and O (2\( p_x, 2p_y \)) states is strong since there is only one electron in each of these 3\( d \) states.

The appropriate three-band model for the Ni system is defined by the Hamiltonian

\[
H_{Ni} = H + \sum_\alpha \varepsilon_{\alpha} c_\alpha^\dagger c_\alpha - \sum_{\langle i,j \rangle \alpha} t_{ij}^{\alpha} \left( p_i^\dagger c_\alpha + h.c. \right) - JH c_\alpha^\dagger c_\alpha c_\alpha^\dagger c_\alpha + \sum_{\alpha} U_{\alpha}^{Ni} c_\alpha^\dagger c_\alpha c_\alpha^\dagger c_\alpha, \tag{7}
\]

where \( H \) is the same as defined in \( \mathbf{3} \). \( \alpha = 1 \) or \( 2 \) denotes the Ni\(^{2+} \) 3\( d_{3z^2-r^2} \) or 3\( d_{3z^2-r^2} \) state. \( c_\alpha = \left( c_{\alpha \uparrow}, c_{\alpha \downarrow} \right) \) is the electron operator for these Ni\(^{2+} \) states. \( \varepsilon_{\alpha}^{Ni}, U_{\alpha}^{Ni}, \) and \( t_{ij}^{\alpha} \) are the energy level, the on-site Coulomb repulsion, and the hopping integral of the corresponding 3\( d \) state of Ni\(^{2+} \), respectively. \( J_H \) is the Hund’s rule coupling constant.

In \( \mathbf{3} \), \( t_{ij}^{\alpha} \) is much smaller than \( J_H \). Thus this \( t_{ij}^{\alpha} \) term can be also treated as a perturbation. The effective one-band Hamiltonian for the Ni impurity can be derived following the same procedure as for the Zn impurity. The difference is that an O hole can now form a local spin doublet (an analogue to the Zhang-Rice singlet) with the Ni\(^{2+} \) spin at the impurity site. This difference is quite important, and it leads to a relatively weaker scattering potential for Ni. The effective one-band Hamiltonian we obtained for the Ni impurity is given by

\[
H_{Ni} = \sum_{i \neq \bar{i} \neq i_0} \frac{t_{ij}^{Ni}}{2} d_i^\dagger d_j - \sum_{i \neq \bar{i} \neq i_0} \frac{t_{ij}^{Ni}}{\sqrt{3}} \left( T_i^+ T + h.c. \right) + \sum_{i} V_{Ni}(i) d_i^\dagger d_i + \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j \tag{8}
\]

where \( T = (T_1, T_0, T_{-1}) \) is the annihilation operator for the three spin triplet states of Ni\(^{2+} \), and \( d_{i\alpha} = (d_{i\alpha \uparrow}, d_{i\alpha \downarrow}) \) is the annihilation operator of the local spin doublet formed by the Ni\(^{2+} \) spin and the bonding O hole at the impurity site. As for the Zn case, \( t_{ij} \) is not an electron operator for the 3\( d \) state of Ni\(^{2+} \). \( T_i^+ \equiv (d_{i\alpha \uparrow}^\dagger d_{i\alpha \downarrow}^\dagger, (d_{i\alpha \uparrow}^\dagger d_{i\alpha \downarrow}^\dagger) + \sqrt{2} d_{i\alpha \downarrow}^\dagger d_{i\alpha \uparrow}^\dagger). \) When \( i \neq i_0 \), the constraint \( d_i^\dagger d_i \leq 1 \) is imposed. At the impurity site, the constraint becomes \( d_{i_0}^\dagger d_{i_0} + T_0^+ T = 1 \), namely the impurity site must be either in a spin triplet state of pure Ni\(^{2+} \) or in a Zhang-Rice-type spin doublet state. The second term in \( H_{Ni} \) describes a swap process between the spin triplet and the spin doublet at the Ni site by absorbing or releasing an electron at the other site. The exchange constant \( J_{ij} = J \) if both \( i \) and \( j \) are not equal to \( i_0 \). For the bonds connecting the Ni site \( J_{ij} \) is different from but of the same energy scale as \( J \).

The hopping integral \( t_{ij}^{Ni} \) is

\[
t_{ij}^{Ni} = t_{ij}^{0} + (t_4 - t_2) u(i_0 - i) u(i_0 - j), \tag{9}
\]

where \( t_{ij}^{0} \) is the hopping integral as in the standard \( t-J \) model without impurities, including the hopping between nearest, next nearest and next-next nearest neighbors. The second term in \( t_{ij}^{Ni} \) is the hopping integral induced by the Ni impurity. This term is smaller than the corresponding term in the Zn case.

The scattering potential of Ni reads

\[
V_{Ni}(i) = \left( 2t_2 + t_1 - \frac{1}{2} t_3 - \frac{3}{2} t_4 \right) u(0) \delta_{i,i_0} - (t_2 - t_4) u^2(i_0 - i) \delta_{i \neq i_0}, \tag{10}
\]

where \( t_3 = \sum_\alpha \left( t_{ij}^{Ni} \right)^2 / \left( \varepsilon_\alpha - \varepsilon_\alpha^{Ni} + J_H / 2 \right) \) and \( t_4 = \sum_\alpha \left( t_{ij}^{Ni} \right)^2 / \left( U_\alpha^{Ni} - \varepsilon_\alpha + \varepsilon_\alpha^{Ni} + J_H / 2 \right) \). The \( t_3 \) term originates from the hopping between Ni\(^{2+} \) 3\( d \) and O 2\( p \) states.
The $t_4$ term comes from the energy gain by the formation of the local spin doublet at the impurity site. These terms compensate or even overcome the energy loss resulted from the $t_1$ and $t_2$ terms. Thus the scattering potential of Ni is much weaker than Zn.

The total number of unpaired electrons is now determined by the formula $N - N_{\text{hole}} = N - T T$. If the scattering potential is strong and repulsive to the spin doublet at the Ni site, then this site is essentially in the spin triplet state, i.e. $T T = 1$, and the conducting electron number is one less than the total number of charge. In this case the Friedel sum rule should be used as if one charge is absorbed by the Ni $^{2+}$. If, on the other hand, scattering potential is strong but attractive to the spin doublet at the Ni site, then this site is predominantly in the spin doublet state and the total number of conducting electrons is equal to the total number of charge. In this case, the scattering phase shifts of high angular momentum channels become important and the commonly adopted T-matrix approximation is no longer applicable. In real systems, the Ni site might be in a mixed valence state, with finite probabilities in both spin triplet and doublet states. In this case, a thorough analysis of the Ni scattering becomes very complicated, even without considering its magnetic coupling with Cu spins.

By comparing the results for Zn and Ni cases we clearly see the difference: Zn is a very strong scatterer, while Ni is a weak one. This profound difference is due to neither the electric charge nor $d$-level location, but rather because of the interplay between the valence state of the impurity and the strong correlation background. The underlying physics is best revealed using the three band model and the concept of Zhang-Rice singlet. The penetration depth measurements give us strong hints that Zn materializes a unitary scattering, whereas Ni is a scatterer close to the Born scattering limit. The present microscopic derivation provides a very good justification for this scenario. We did not calculate explicitly the magnetic moment distribution and the contribution of spin-flip scattering around a Zn or Ni impurity. However, we believe that these problems can be addressed by self-consistently solving the effective Hamiltonians for Zn or Ni impurities. The fact that the suppression of $T_c$ scales universally with the increase of the residual resistance, and the rough estimate of the dominance of the potential scattering over magnetic scattering, do support that the spin-flip scattering induced by Zn or Ni impurities is a secondary effect compared with the potential scattering, especially for the Zn case.

Finally, let us discuss the problem about the interlayer hopping of electron around an impurity. This problem is of great importance for the understanding of various experimental results related to impurities, especially the scanning tunneling data in the superconducting state around Zn or Ni. In high-$T_c$ materials, the interlayer hopping is fulfilled through a virtual hopping process assisted by Cu 4s orbitals. That is an O hole first hops to a Cu 4s orbital and then hops to other orbitals out of the CuO$_2$ plane. At the impurity site, the interlayer hopping is assisted by the Zn 4s or Ni 4s state. Since the 4s orbital is orthogonal to the $3d_{x^2-y^2}$ orbital at the same site, there is no hopping between these two orbitals. This 4s-orbital assisted hopping has profound consequences on c-axis dynamic properties.

The 4s-orbital assisted hopping in each CuO$_2$ layer is described by the following Hamiltonian:

$$H_c = \sum_{<il>} (-\alpha_i) t^{4s}_i \left( s_i^\dagger p_i + p_i^\dagger s_i \right)$$

(11)

where $(-\alpha_i) = 1$ if $l = i \pm \hat{x}/2$ and $(-\alpha_i) = -1$ if $l = i \pm \hat{y}/2$. $s_i = (s_{i\uparrow}, s_{i\downarrow})$ creates a hole in the local 4s state. $t^{4s}_i$ is the hopping integral between a 4s and its neighboring O 2p orbitals. By projecting this Hamiltonian onto the low energy subspace containing Zhang-Rice singlets, we find that $H_c$ can be expressed as

$$H_c = \sum_i t^{4s}_i s_i^\dagger D_i + h.c.$$  

(12)

where $s_i^\dagger = (s_{i\uparrow}, s_{i\downarrow})$ is the electron creation operator for the 4s state at site $i$.

$$D_i = \sum_j F_{i,j} \left( \delta_{j,i_0} + \frac{1}{\sqrt{2}} \delta_{j\neq i_0} \right) d_j$$

(13)

for the Zn impurity model, and

$$D_i = \sum_{j\neq i_0} \frac{F_{i,j}}{\sqrt{2}} d_j - \frac{F_{i,i_0}}{\sqrt{3}} d_{i_0}^\dagger \left( \sqrt{2} T_1, \frac{T_0}{\sqrt{2} T_{-1}} \right)$$

(14)

for the Ni impurity model. In Eqs. (13) and (14),

$$F_{i,j} = \frac{1}{N} \sum_k \beta_k^{-1} (\cos k x - \cos k y) e^{i(k(-j))}.$$  

(15)

It is straightforward to show that $F_{i,j} = 0$ when $i = j$ or when $i - j$ is along two diagonal directions. Thus in the effective one-band model, an electron in the CuO$_2$ plane cannot hop to a 4s orbital at the same site. This is a peculiar but important feature of the c-axis hopping integral.

The local tunneling current perpendicular to CuO$_2$ planes as measured by the STM is proportional to the probability of electrons in the CuO$_2$ plane hopping to the local 4s orbital from the low energy conducting band. From Eq. (12) one can show that the tunneling conductance at site $i$ is determined by the following non-local matrix element

$$g_i(V) \propto \left( D_i \delta(eV - H_{imp})D_i^\dagger \right)$$

(16)

where $V$ is the applied bias voltage and $H_{imp}$ is the system Hamiltonian as given in Eqs. (8) or (8). This formula
shows clearly that the scanning tunneling conductance is not simply a measure of the local density of states in high-Tc superconductors. In particular, as $F_{i,j} = 0$ when $i = j$, there is no contribution to $g_i(V)$ from the low-energy excitations at site $i$. This is a peculiar but intrinsic property of the in-plane electronic structure. It is not due to the blocking effect as suggested in Ref. 10. In Eq. (13) or (14), if $j$ in the summation only takes the four nearest neighboring sites of $i$, we then obtain the result given by Martin et al 15. Their result is a good approximation to Eq. (16) since $F_{i,j}$ decays very fast with the distance $|j-i|$. Eq. (16) is valid independent on the structure of the insulating layers between the top CuO$_2$ plane and the STM tip. Thus the normalized STM spectrum should be the same no matter whether the tip is above an insulating layer or directly above a CuO$_2$ layer.

In conclusion, we have derived the effective low energy Hamiltonian with the impurity scattering potential for Zn or Ni substituted high-Tc cuprates. Our results reveal an intrinsic connection of the impurity scattering potential with the correlation effect of electrons and set a solid microscopic starting point towards thorough understanding of the impurity effects in these materials. A number of observable physical quantities can be calculated explicitly based on this microscopic model. The STM spectrum perpendicular to CuO$_2$ is not simply a probe of the local density of states since the interlayer hopping is intrinsically anisotropic and non-local.

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