The importance of inter-site coherences in the X-ray absorption spectra of mixed-valent systems

Subhra Sen Gupta\(^{(a)}\), Hiroki Wadati\(^{(b)}\) and G. A. Sawatzky

Department of Physics and Astronomy, University of British Columbia - Vancouver, BC V6T 1Z1, Canada

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Abstract – We study the importance of inter-site coherences and quantum interference effects in the X-ray absorption spectroscopy (XAS) of mixed-valent systems. We demonstrate its importance, first for a simple diatomic mixed-valent molecule to elucidate the physics involved, and finally for mixed-valent Ti oxides, using a model calculation including full spin and orbital multiplicities. Our calculations demonstrate the inefficacy of conventional approaches of describing the XAS from mixed-valent systems as incoherent combinations of XAS from the pure-valent end members, and that multiplets forbidden in the single-site approximation can be effectively reached within a multi-site description. These conclusions play an important role in the interpretation of XAS and resonant X-ray scattering (RXS) in terms of the electronic structure of strongly correlated systems.

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Introduction. – An important feature of transition metal (TM) compounds is the relatively small spatial extent of the TM valence 3d wave functions, which form narrow bands of widths often matched or overwhelmed by the electron-electron Coulomb interactions, leading to strong correlation effects. The physical properties of these systems are largely determined by rather local physics dictated by point group symmetries, Hund’s rule coupling of the d electrons and short-range superexchange interactions. XAS along with X-ray magnetic circular (XMCD) and linear (XMLD) dichroism, involving 2p \rightarrow 3d core-valence transitions on the TM site, has served as an important tool for investigating this local physics, viz. the oxidation states, the local orbital occupancies, spin-state, crystal field symmetry, metal-ligand hybridization, Coulomb correlation effects etc., in these systems\(^{[1,2]}\).

Furthermore, recently developed RXS methods where the cross section can be expressed in terms of simple first-order fundamental XAS spectra\(^{[3]}\), can, at least in principle, provide unique information concerning the ordering of spin, charge and orbitals in these systems. However, the information contained in the X-ray energy-dependent intensities at superlattice reflections often cannot be accessed, especially for doped systems, because of disagreement with conventionally used single-site cluster-like model calculations of the fundamental XAS spectra. In fact this disagreement may point to the importance of intersite coherences playing an important role.

Given the complexity of the problem due to several competing interactions, the inference of ground-state properties from the spectral lineshapes requires detailed many-body crystal or ligand field multiplet calculations within a configuration interaction (CI) approach\(^{[1]}\). The success of such local approaches, involving a single central correlated TM site coordinated by a shell of ligand atoms (e.g., oxygen, sulphur etc.), implicitly assumes a pure-valent system with an integral nominal filling per TM site (i.e., before hybridization with the ligands), which ensures that: (1) in the ground state, charge fluctuations involving neighboring TM sites are suppressed by the Hubbard U; and more importantly, (2) the locally photo-excited electron in the valence d orbital is strongly bound to the core-hole on the same atom in the final state, by an attractive 2p-3d Coulomb potential, \(Q \sim 1.2U\). This strongly suppresses charge fluctuations involving neighbouring TM sites, since the inter-TM-site effective hopping integrals, \(T\), are usually much smaller than \(Q\)\(^{[4,5]}\). See fig. 1 (configurations P1–P3) for a pictorial representation of the relevant physics. The net outcome is that the core-hole and extra valence electron form core-excitonic bound states, so that a single-site description suffices.

\(^{(a)}\)E-mail: subhra@phas.ubc.ca
\(^{(b)}\)Present address: Department of Applied Physics and QPEC, University of Tokyo-Hongo, Tokyo 113-8656, Japan.
Fig. 1: (Colour on-line) Schematic representing the various relevant final states and their energies, for the XAS of pure-valent [(P1)--(P3)] and mixed-valent [(M1)--(M3)] correlated systems, in a two-site picture.

However, things become more interesting for mixed-valent or valence fluctuating systems [6]. Many of the exotic manifestations of strong correlation e.g. various kinds of charge and spin density wave states, colossal magnetoresistance, high temperature superconductivity etc., arise when the parent compound is hole or electron doped, so that the average nominal number of electrons per TM site is no longer an integer. The interpretation of XAS in these systems is a very important problem, as it can yield important information concerning quantum fluctuations involving also neighboring TM sites. The general assumption, till now, has been that one can get away with incoherently averaging the spectra (weights determined by the doping) calculated on the basis of single-TM-site clusters with integral nominal fillings [7]. But this approach neglects crucial quantum interference effects arising out of coherent charge fluctuations between different TM sites and implies a phase-separated scenario instead of uniform mixed-valency.

To treat a doped system, the minimum extension should involve two TM sites with either an odd (mixed-valent) or an even (pure-valent) total number of d electrons, in the dimer, in the starting state. One can then compare the “exact” calculation for such a two-site cluster with the incoherent sum of the component spectra from single-site clusters, to verify the importance of coherence effects. Figure 1 compares the basic energetics of the various states involved, in the presence of a core-hole on one of the atoms and an additional valence electron, between mixed-valent and pure-valent systems. This demonstrates that while the energy difference between the two lowest energy final states, which are connected by a hopping integral $T$, is $Q$ for the pure-valent case, it is only $|U-Q|$ for the mixed-valent one. For $T$ much smaller than $U$ and $Q$, the mixing of (P1) and (P2) for the pure-valent case is small and can mostly be neglected. However, for $T \sim |U-Q|$, the mixing of (M1) and (M2) in the mixed-valent case can be very large indeed.

Fig. 2: (Colour on-line) Schematic representation of the various relevant initial ($|G_1\rangle$, $|G_2\rangle$) and final ($|F_1\rangle$--$|F_5\rangle$) configurations (basis states) for the Li$_2^+$ molecule, shown along with the initial ($H_{fin}$) and final ($H_{fin}$) state Hamiltonians. The final-state Hamiltonian is written in terms of a transformed basis which is defined below it. The action of the transition operator ($T$) on the initial basis states is also listed.

**A simple model.** -- To describe the physics involved we start with a simple model system, not complicated by a lot of multiplet structure viz., a fictitious diatomic Li$_2^+$ molecule with orbitally non-degenerate (but including spin degeneracies), core 1s and valence 2s levels at each Li site, as shown in fig. 2. This basic model was used previously to describe core-level photoemission from mixed-valent systems, illustrating there the importance of the broken symmetry ansatz [8]. The core 1s levels are filled with a total of 4 electrons, and the valence 2s levels share one electron in all, in the initial state, corresponding to 50% doping of the Li$_2$ molecule. We calculate the 1s $\rightarrow$ 2s excitation spectrum for this system, which contains the same basic physics as an allowed core-to-valence transition in XAS.

The Hamiltonian for this molecule is given by

$$H = \sum_{i, \sigma} \epsilon_{1s} c_{1s i}^{\dagger} c_{1s i} + \sum_{i, \sigma} \epsilon_{2s} c_{2s i}^{\dagger} c_{2s i} + \sum (T c_{2s i}^{A\uparrow} c_{2s i}^{B\downarrow} + h.c.) - J \sum_i \vec{\sigma}_i \cdot \vec{S}_i - Q \sum_{i, \sigma} (n_{h i}^{1s \uparrow} c_{2s i}^{\sigma\uparrow} c_{2s i}^{\sigma\downarrow} + \sum_i n_{2s i}^2 \cdot n_{2s i}^{\downarrow} + U \sum_i n_{2s i}^2),$$

where the sum over $i = A, B$ runs over the two Li sites, and $\sigma = \uparrow, \downarrow$ sums over the two spin projections. $c_{2s i}^{\sigma\uparrow}$ ($c_{1s i}^{\sigma\downarrow}$) creates (destroys) an electron at the site $i$ with spin $\sigma$, in the (1s, 2s) orbitals, respectively. Above, $n_{2s i}^2 = c_{2s i}^{\sigma\uparrow} c_{2s i}^{\sigma\downarrow}$ is the number operator for the 2s electrons, $(n_{1s i}^{1s \uparrow})^+ = (2 - \sum_{\sigma} c_{1s i}^{\sigma\uparrow} c_{1s i}^{\sigma\downarrow})$ counts the number of holes in the core 1s level, while $(\vec{S}_i)$ and $(\vec{\sigma}_i)$ denote the operators for the core and the valence spins, all at site $i$. In eq. (1) the first two terms refer to the on-site energies of the two orbitals ($\epsilon_{2s} > \epsilon_{1s}$), which merely shift the transition.
energy and which we take to be zero. The subsequent terms describe, respectively, the 2s electron inter-site hopping $T$, Hund’s rule like 1s–2s ferromagnetic exchange $J$, the 1s-hole, 2s-electron on-site attraction $Q$, and the 2s–2s on-site Coulomb repulsion $U$. In our convention while $T < 0$, $J$, $Q$ and $U$ are positive numbers.

In fig. 2 we show the basis configurations involved in the initial and final states, their diagonal energies and the off-diagonal matrix elements resulting from eq. (1), for the initial ($\mathcal{H}_{i\text{on}}$) and final ($\mathcal{H}_{f\text{on}}$) Hamiltonians. The initial Hilbert space involves two degenerate transition operators for the 1s–2s electron at the core-hole site $A$, and involves the only off-diagonal term. We take the 2s electron to be spin-up. The ground state for $T < 0$ is the bonding state, $|\psi_g\rangle = \frac{1}{\sqrt{2}}(|G_1⟩ + |G_2⟩)$. The final Hilbert space is more complex, consisting of five relevant configurations $|F_1⟩, |F_2⟩, |F_3⟩, |F_4⟩$, and $|F_5⟩$. It is instructive to talk in terms of spin states at the sites $A$ ($S_A$) and $B$ ($S_B$), as well as the total spin $S$. In this sense, $|F_1⟩$ and $|F_2⟩$ are $|S = 1/2, m = +1/2⟩$ states derived from the parents $|S_A = 1/2, m_A = +1⟩|S_B = 0, m_B = 0⟩$. These occur at the energies $(U - 2Q)$ and $U$. The state $|F_2⟩$, at energy $-(Q - \frac{J}{2})$, consists of the triplet state $|S_A = 1, m_A = +1⟩$ at site $A$ and the spectator doublet $|S_B = 1/2, m_B = -1/2⟩$ at site $B$. As demonstrated in fig. 2, we combine $|F_3⟩$ and $|F_5⟩$ to form singlet $|F_s⟩$ and triplet $|F_t⟩$ eigenstates of $S_A$. Both $|F_s⟩$ with $|S_A = 0, m_A = 0⟩$ at $-(Q + \frac{J}{2})$, and $|F_t⟩$ with $|S_A = 1, m_A = 0⟩$ at $-(Q - \frac{J}{2})$, can combine with the B-site spectator doublet $|F_2⟩$ for this model are

$$\text{Fig. 3: (Colour on-line)} (a) \text{Evolution of the scaled transition energies, } \omega/Q, \text{ to the final eigenstates with the magnitude of the scaled 2s-2s hybridization, } T/Q, \text{ for the } \text{Li}^+ \text{ model. The states at } T = 0 \text{ from which each eigenstate evolves are marked; (b)–(g) evolution of the 1s–2s excitation spectrum, with increasing } T/Q, \text{ within the same model. Numbers against peaks refer to the final eigenstate from which they originate.}$$

The importance of inter-site coherences in the X-ray absorption spectrum is given by the expression

$$I(\omega) = \sum_k |\langle \psi_f^k | T | \psi_g \rangle|^2 \delta(\omega - (E_f^k - E_g)). \quad (3)$$

The evolution of the transition energies, $\omega = (E_f^k - E_g) = (E_f^k - T)$, with $T$ is shown in fig. 3(a), for the values $U = 0.83Q$ (i.e., $Q = 1.2U$), $J = 0.2Q$. All numerical values for eigenenergies (E), hoppings (T) etc. for this model are henceforth quoted in units of $Q$. At $T = 0$ these correspond to the diagonal energies of $\mathcal{H}_{f\text{on}}$, as discussed above. From fig. 2 it is evident that the doublet $|\xi⟩$ hybridizes with $|F_1⟩, |F_4⟩$ with an amplitude $\sqrt{\frac{3}{2}}T$, the quartet state $|\chi⟩$ is completely non-bonding. This explains why the state $|\chi⟩$ does not disperse at all with $T$, which shows up as a linear movement of the transition energy, $\omega$, in fig. 3(a), due to the hybridization shift, $T$, of the ground state, while $|\xi⟩$ disperses only weakly, being repelled in opposite directions by $|F_1⟩$ and $|F_4⟩$.

Now turning to the trends in the intensities, we find that for $T = 0$, the spectra can be visualized as an incoherent combination of spectra from Li$,^0$, which involves a doublet to doublet transition $|G_1⟩ → |F_1⟩$ at $(U - 2Q)$, and from Li$^+$ which starts from a singlet at site $A$ $|G_2⟩$ and hence a transition to only the local singlet $|F_3⟩$, at $-(Q + \frac{J}{2})$ is possible for $T = 0$, the triplet $|F_5⟩$ being forbidden (fig. 3(b)). These peaks appear in the intensity ratio of $1:2$, corresponding to just one way of exciting the Li$^0$, compared to the two ways of exciting the Li$^+$. For small values of $T$, till about $T = 0.05$ as is evident from fig. 3(b), (c), the spectrum basically still has only two peaks with very little intensity in other regions. However,
as \( T \) increases, there is spectral weight transfer from higher to lower energy so that the two peaks tend towards equal intensities. We also see that the energy splitting between the \( \text{Li}^3 \) and \( \text{Li}^+ \) derived states shows very little change up to a critical value of \( |T_c| \sim |U - Q| \sim 0.17 \) or as long as \( |T| < |U - Q| \), and changes almost linearly for \( |T| > |U - Q| \). Thus, an analysis of these spectra in terms of an incoherent sum of the parent ion spectra would obviously lead to incorrect conclusions regarding both the composition of the material (level of doping) as well as the “chemical” shifts of the core-hole spectra.

Inspection of the unbrodened intensities for finite \( T \), especially for \( T = 0.1, 0.15 \) and 0.2 (fig. 3(d)–(f)), reveals the other crucial fact that for any realistic \( T \), transitions are now possible to previously forbidden (at \( T = 0 \)) multiplets in the \( \text{Li}^+ \)-like region, which now shows two peaks with finite intensities that change systematically. This is because at finite \( T \) only the total spin \( S \) is relevant. Thus starting from the ground-state doublet \( |S = 1/2, m_s = +1/2 \rangle \), we can only reach final-state doublets, which are the states derived from \( |F_1 \rangle, |F_2 \rangle, |F_3 \rangle \), and \( |\xi \rangle \), while the quartet \( |\chi \rangle \) which does not mix, is still forbidden. So \( |\xi \rangle \), which has 0.33 of the \( A \)-site forbidden triplet \( |F_2 \rangle \) mixed in at \( T = 0 \), always has a finite contribution from it for finite \( T \), demonstrating how forbidden multiplets in a single-site representation now appear as extra structures in the more correct multi-site approach.

### Realistic calculations for Ti oxides.

Although this simple model clarifies the basic physics, more realistic calculations including the full orbital and spin degeneracies of a TM ion, multiplet interactions and charge transfer from ligand atoms etc., are needed to approach real correlated systems. To this end we have calculated the isotropic XAS from a \textit{mixed-valent} \([\text{Ti-O-Ti}]\) cluster, mimicking the half-doped oxide \( \text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \). The pure-valent end members \( \text{SrTiO}_3 \) (STO) and \( \text{LaTiO}_3 \) (LTO) consist of \( \text{Ti}^{4+} \) (3\(d^0\)) and \( \text{Ti}^{3+} \) (3\(d^1\)) ions, respectively, so that the mixed-valent compound has one electron per two Ti atoms. Accordingly our cluster nominally has one electron shared between the two Ti atoms. Alternately, such a mixed-valent bond could also arise at a \( \text{STO}/\text{LTO} \) band-insulator/Mott insulator heterostructure interface, and calculations similar to the present one could help to understand the observed correlated metallic state [7,9] at the interface. Although the use of only a dimer of Ti atoms is a severe approximation to real systems in which there is no dimerization, a calculation with the full coordination of O and neighbouring Ti atoms is at the limits of feasibility even with modern computers. However, in many real systems in fact, dimer formation seems to occur in particular phases such as in the low temperature insulating phase of \( \text{VO}_2 \) [10], the \( \text{Zener} \) polaron-like scenarios proposed for some manganites [11], Peierls- or spin-Peierls-like ground states in quasi-one-dimensional systems, to name a few.

Our model calculations include the TM core 2\( p \) and valence 3\( d \) states as well as the O 2\( p \) valence states. Full multiplet Coulomb interactions and spin-orbit interaction within the Ti 3\( d \) manifold, the spin-orbit interaction within the Ti core 2\( p \), and final-state core-valence (2p-3d) multiplet interactions on the Ti were taken into account. The relevant spin-orbit parameters and the multipole Coulomb Slater-Condon parameters, \( F_{tt}, F_{dd} \) and \( F_{pd}, G_{pd}, G_{dd} \) were obtained from Cowan’s atomic Hartree-Fock code [12], and following the usual convention, were reduced to 80\% of their atomic values [13]. Based on reported values in the literature [5] the multiplet averaged 3\( d \)-3\( d \) and 2\( p \)-3\( d \) Coulomb interactions were set to \( U = 4.5 \) eV and \( Q = 1.2U = 5.4 \) eV, so that \( |U - Q| = 0.9 \) eV. The Ti(3\( d \))-O(2\( p \)) charge transfer energy (\( \Delta \)) was defined with respect to a 4\( d^0 \) system as in LTO, i.e., \( \Delta = E(d^2L) - E(d^4) \), where \( L \) denotes a ligand-hole state and set to \( \Delta = 6.0 \) eV [5]. An octahedral (\( O_h \)) crystal field of magnitude 10\( Dq = 1.5 \) eV was used on both the Ti sites to effectively account for their octahedral coordination, not included in this calculation. The metal-ligand hopping is given by the Slater-Koster parameters (\( pd \sigma, pd \pi \)), where \( pd\pi = -pd\sigma/2.2 \) was used in all cases [5]. Since our model includes only one ligand oxygen atom explicitly shared between the two Ti atoms, it is quite likely to find more than one hole on the oxygen atom. Thus the usual reasoning that the density of holes on the oxygen atoms is very low and hence the Hubbard \( U \) on the O 2\( p \) is ineffective, no longer holds. So we have also taken into account the full multiplet Coulomb interaction in the O 2\( p \) manifold with the multiplet averaged interaction \( U_{pp} = 4.0 \) eV [14]. Calculations were performed for various degrees of covalency, starting from a realistic value of \( pd\sigma = -2.5 \) eV and gradually reducing it through \( \{ -1.5, -0.5, -0.1 \} \) eV towards the free ion limit. For the purpose of truncation of the basis set, the convergence of the spectrum was checked as a function of the number of ligand-hole excitations for the largest value of hopping (\( pd\sigma = -2.5 \) eV), retaining up to 4 ligand-hole (\( L^1 \)) excitations. The spectrum was found to converge well at \( L^3 \). Hence the basis was truncated at \( L^3 \) for all the calculations, the ones for lower hopping being expected to converge even sooner.

These spectra are to be compared to an incoherent average of single-site pure-valent calculations, to bring out the differences. However an atomic \( O_h \) crystal field multiplet calculation for a \( \text{Ti}^{3+} \) and a \( \text{Ti}^{4+} \) ion does not suffice here, because in choosing a \( \text{Ti-O-Ti} \) cluster, we broke the \( O_h \) symmetry around the Ti ion via the Ti-O bond, and hence we can only compare to a single-site calculation that also breaks the symmetry in the same way. This is achieved by performing calculations for a \( [\text{Ti}^{3+}-\text{O}] \) and a \( [\text{Ti}^{4+}-\text{O}] \) cluster, retaining the 10\( Dq = 1.5 \) eV \( O_h \) crystal field, again for the various hoppings as mentioned above. All of the parameters, other than \( \Delta \), were kept the same as for the mixed-valent cluster. However, whereas \( \Delta = 6.0 \) eV was used for the \( [\text{Ti}^{3+}-\text{O}] \) cluster (3\( d^1 \)), an appropriately compensated value of
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Fig. 4: (Colour on-line) Calculated XAS from a mixed-valent [Ti–O–Ti] cluster (thick solid line) (mimicking La$_{0.5}$Sr$_{0.5}$TiO$_3$), compared with the incoherently averaged XAS (thin solid line) from pure-valent Ti$^{4+}$ ($d^0$) (mimicking SrTiO$_3$) and Ti$^{3+}$ ($d^1$) (mimicking LaTiO$_3$) [Ti–O] clusters, as a function of the Ti–O hopping: (a) $p_{\sigma} = -0.1\,\text{eV}$, (b) $p_{\sigma} = -0.5\,\text{eV}$, (c) $p_{\sigma} = -1.5\,\text{eV}$, (d) $p_{\sigma} = -2.5\,\text{eV}$ (realistic). In each case the component single-impurity spectra are also shown.

$\Delta' = \Delta - U = 1.5\,\text{eV}$ ($\Delta' = E(d^1_{L}) - E(d^0)$) was used for the [Ti$^{4+}$–O] cluster ($3d^0$), which is the effective charge transfer energy to the $d^0$ site within the coherent two-site mixed-valent calculation. For these calculations the full basis set was used without any truncation. A small Gaussian broadening of FWHM = 0.3 eV was used in all cases.

In fig. 4(a)–(d) we show the XAS spectra for the mixed-valent cluster (thick black line), starting with the smallest hopping ($p_{\sigma} = -0.1\,\text{eV}$, atomic-like situation) in panel (a) and then gradually increasing it to the realistic value of $p_{\sigma} = -2.5\,\text{eV}$ in panel (d). In each case we compare it with the spectrum obtained by averaging (thin red line) the XAS from the pure-valent [Ti$^{4+}$–O] (blue dashed line) and [Ti$^{3+}$–O] (green dash-dotted line) clusters. The shift between the center of gravities of the components is dictated by $|U - Q|$ and not set by hand. Just as in our Li$^2_2$ calculation, we find that the case for the smallest hopping (a) has almost no coherence between the Ti sites and is formally equivalent to the incoherent average of the XAS from the single-site clusters representing the pure-valent end members. However, as we increase the hopping, coherence begins to develop between the two Ti sites and the genuinely mixed-valent XAS begins to depart from the corresponding incoherent average. While for $p_{\sigma} = -1.5\,\text{eV}$ the differences are quite noticeable, for the realistic $p_{\sigma} = -2.5\,\text{eV}$, they become truly pronounced. So the single-site approximation completely breaks down for realistic hoppings in a mixed-valent system.

Finally, we demonstrate that this problem is much more pronounced in mixed-valent systems compared to pure-valent ones. For the latter, the differences between the two approaches is relatively small, so that one can get away with a single-site approximation. To this end we have calculated also the XAS from the two-site pure-valent clusters [Ti$^{4+}$–O–Ti$^{4+}$] and [Ti$^{3+}$–O–Ti$^{3+}$] which are meant to represent the stoichiometric compounds STO and LTO. In accordance with reported values for STO

Fig. 5: (Colour on-line) Calculated XAS from a pure-valent ($d^0$) [Ti$^{4+}$–O–Ti$^{4+}$] cluster (thick line) (mimicking LaTiO$_3$) compared with that from a pure-valent [Ti$^{3+}$–O] cluster (thin line), as a function of the Ti–O hopping: (a) $p_{\sigma} = -0.1\,\text{eV}$, (b) $p_{\sigma} = -0.5\,\text{eV}$, (c) $p_{\sigma} = -1.5\,\text{eV}$, (d) $p_{\sigma} = -2.5\,\text{eV}$ (realistic).

Fig. 6: (Colour on-line) Calculated XAS from a pure-valent ($d^0$) [Ti$^{4+}$–O–Ti$^{4+}$] cluster (thick line) (mimicking SrTiO$_3$ [15]) compared with that from a pure-valent [Ti$^{4+}$–O] cluster (thin line), as a function of the Ti–O hopping: (a) $p_{\sigma} = -0.1\,\text{eV}$, (b) $p_{\sigma} = -0.5\,\text{eV}$, (c) $p_{\sigma} = -1.5\,\text{eV}$, (d) $p_{\sigma} = -2.5\,\text{eV}$ (realistic).
and LTO [5], $\Delta = 6.0 \text{ eV}$ was used for both calculations. While $\Delta = 6.0 \text{ eV}$ is a bit on the higher side for STO, the exact value is unimportant and this serves well to bring out the physics involved [15]. All other parameters were exactly the same as used for the mixed-valent cluster. These were compared to the XAS from the pure-valent single-site clusters calculated for the same parameter values. The results are shown, for the Ti$^{3+}$ ($d^3$) and Ti$^{4+}$ ($d^0$) calculations, in fig. 5(a)–(d), and fig. 6(a)–(d), respectively, for the same values of hopping, and shown in the same order as in fig. 4. In each panel the XAS from the two-site pure-valent (thick black line) and single-site pure-valent (thin red line) clusters are compared. We find that the spectral shapes are very similar and the only noticeable differences exist for the largest hopping of $p_{da} = -2.5 \text{ eV}$ (panel (d) in each case), which are much smaller than in the mixed-valent case (fig. 4(d)).

**Conclusion.** – Our calculations demonstrate the importance of inter-TM-site coherences in the XAS of mixed-valent (doped) strongly correlated systems. These effects cause non-trivial differences between the XAS from a truly mixed-valent system and that obtained by incoherently averaging XAS from the corresponding pure-valent end members, whenever the hybridization is comparable to the difference between the valence band Coulomb repulsion ($U$) and the core-hole potential ($Q$). This results in strong changes in energy shifts, and a dramatic redistribution of spectral weight away from the statistical limit, between the so-called pure-valent components. It also shows that multiplets forbidden in the single-site approximation can effectively be reached within a multi-site description, for realistic hoppings. For pure-valent systems, this problem is much less severe and the single impurity approximation works reasonably well. This physics has important consequences for doped correlated systems, in general, and TM oxide heterostructures (like LTO/STO) having interfaces across which a change of nominal valency of the TM ion occurs [7,9]. This can also play an important role in distinguishing between charge disproportionation and Zener polaron- or dimeron-like scenarios [11].

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[15] The ionic-like spectrum for small $p_{da}$ (fig. 6(a)) differs from the experimental $L_{2,3}$ XAS spectrum for STO, since we have not included the large and very disparate broadening from the two peaks ($t_{2g}$- and $e_{g}$-like) in each of the $L_{2,3}$ regions, arising from lifetime, solid-state dispersive and vibrational effects. See: de Groot F. M. F., Fuggle J. C., Thole B. T. and Sawatzky G. A., *Phys. Rev. B*, 41 (1990) 928.