Auger Transition from Orbitally Degenerate Systems: Effects of Screening and Multielectron Excitations

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We calculate Auger spectra given by the two-hole Green's function from orbitally degenerate Hubbard-like models as a function of correlation strength and band filling. The resulting spectra are *qualitatively* different from those obtained from fully filled singly degenerate models due to the presence of screening dynamics and multielectron excitations. Application to a real system shows remarkable agreement with experimental results leading to reinterpretation of spectral features. [S0031-9007(98)06904-X]

More than seventy years after its discovery [1], the Auger process continues to evoke strong research interest in the general community [2], since it is potentially a very powerful probe to investigate the electronic structure of any solid. Briefly, the Auger process involves the decay of a core hole by a nonradiative transition involving two electrons, one filling the core hole and one picking up the excess energy and making a transition into the continuum. The initial state of the normal Auger transition can be considered to be a singly ionized core-hole state and the final state is a doubly ionized state together with an electron in the continuum. When a core hole (C) decays via the Auger process involving two valence (V) electrons, it is usually termed a C-VV process. One can anticipate [3] the C-VV Auger spectral shape considering two limiting scenarios. The two final-state holes may be found on different atomic sites due to the presence of finite hopping interactions. In such a case they will be screened from each other and the Auger process can be described essentially by the self-convolution of the occupied part of the valence band density of states (DOS). In the opposite scenario, strong correlation effects may localize the holes at the same atomic site, shifting the corresponding energy higher than the screened two-hole case by approximately the Coulomb interaction strength, U. These expectations found a theoretical basis in the work of Cini [4] and Sawatzky [5] who calculated the two-hole Green's function for fully filled singly degenerate Hubbard-like models. The results indeed showed these two spectral signatures, often termed the correlated (or the satellite) and the uncorrelated (or the main) features. According to such analysis, Auger spectroscopy has the unique advantage of providing a direct experimental estimate of U and such an approach has often been adopted for the very same purpose [6].

The assumptions in the Cini-Sawatzky (CS) theory, however, may limit its applicability to real systems. The model assumes one orbital per atomic site, whereas most real systems invariably involve orbital degeneracies. The other assumption of a fully filled band limits the use of the model to few real systems such as Cu and Zn. It is not *a priori* evident what the consequences of relaxing these limitations would be on the Auger spectra compared to those inferred from the CS theory. Therefore, we theoretically investigate the Auger spectra from a multiband model as a function of band filling and Coulomb interaction strength in order to understand real systems better and to extend the usefulness of this very powerful spectroscopic technique. We find that the results are *qualitatively* different for partially filled bands compared to the fully filled case. These strong changes occur primarily due to the screening response to the core hole in the initial state and multielectron excitations in both initial and final states. While these processes are not possible for a fully filled case, our results clearly show that such processes are in fact the dominant ones in determining the Auger spectral shapes in the most often encountered partially filled systems.

The specific multiband model that we consider is based on a regular tetrahedron with four atomic sites each containing triply degenerate p-orbitals, allowing us to treat the full multiplet (orbital dependent) electron-electron interactions. However, the qualitative features presented here are independent of this specific choice, as we have explicitly checked by calculating the corresponding spectra with three degenerate s orbitals at each site, instead of the p-orbitals, as well as with five degenerate d-orbitals. The hopping interactions between different orbitals are given in terms of Slater-Koster parametrization [7]. In order to understand the influence of the core hole and the consequent screening dynamics, we have performed two sets of calculations, one with the core-hole potential and the other without. The core-hole potential is included in the Hamiltonian in the usual way [8], by including the term, $-U_c n_c n_d$, which effectively lowers the diagonal electronic energy by U_c at the core-hole site in the initial state of the Auger process. This assumes that the initial state is a completely screened core-hole state. This is reasonable for the transition elements, where the lifetime of the core hole is longer than the screening time scale, but may limit the applicability to other systems, such as the lanthanides, where these two time scales may compete with each other. We take U_c to be 1.2 times the effective U within the valence

band following the usual practice. We present here the results for the number (n) of electrons per atomic site being 1, 2, 3, 4, 5, and 6, with the last one ($n = 6$) being the fully filled case. We obtain the ground state and the corresponding two-hole Green's function by the Lanczos and the modified Lanczos methods [9].

In Fig. 1 we show some selected two-hole spectra for $n = 6$ with a few values of U/W. The Auger spectrum for the noninteracting limit ($U = 0$) is the self-convolution of the occupied DOS with a width equal to twice the occupied part of the single-particle bandwidth, W. With increasing U, the intensity within the uncorrelated energy region (~ 0–2.2) rapidly decreases, with increasing spectral weight thrown out in a narrow feature. This narrow feature with its characteristic dependence on U has primarily two holes at the same site and is easily identified with the strongly correlated Auger feature of the CS theory. To underline this similarity further, we plot the average energy separation (ΔE) and the intensity ratio (I_c/I_m) between the correlated (satellite) and the uncorrelated (main) Auger spectral features as functions of U/W and U^2/W^2, respectively, in the insets (solid circles) along with the results (open circles) from the CS theory. Clearly, both of these show linear dependences for larger U. Between the two models we find that ΔE are similar even quantitatively. I_c/I_m, though qualitatively similar in both models, is larger in the multiband model.

The spectra from partially filled bands (Fig. 2), however, show *qualitatively* different behavior compared to the fully
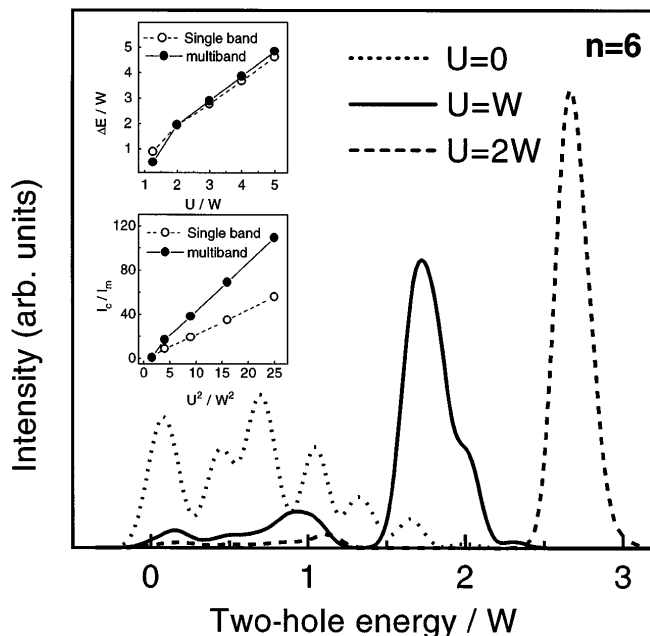
filled limit. For brevity, we show the results only for some selected n and U/W values; we find that the results for other values of n and U/W are qualitatively similar. Figures 2(a) and 2(b) show the results for $U/W = 0$, 1, and 2 in the absence of any core-hole potential ($U_c = 0$), while, in Figs. 2(c) and 2(d), we compare the results with and without U_c for the $U/W = 1$ case. In every case, the spectra appear a lot more complex than the simple and intuitive expectation of two groups of features arising from uncorrelated and correlated final states in the Auger spectrum. Evidently, the spectra exhibit multiple groups of distinct and intense spectral features (marked 1–5 in the figures for the $U/W = 1$ case) with as many as four spectral groups (2–5) appearing outside the energy region of the uncorrelated ($U/W = 0$) spectrum (marked 1). For example, the $U/W = 1$ case for $n = 3$ [Fig. 2(b)] has features at about 1.5, 2.8, 4, and 5.3. Such results cannot be understood within the CS theory or in terms of the qualitative arguments presented in the introduction. Additionally, ΔE and I_c/I_m exhibit no obvious dependence on U/W and U^2/W^2 in contrast to the fully filled case (Fig. 1). This is most apparent in Fig. 2(a), where the spectral feature 2 at about 1.3 moves to a *lower* energy with an *increase* of U/W from 1 to 2. In order to understand the origin of such complex

FIG. 1. Calculated Auger spectra for $U/W = 0$, 1, and 2 for the fully filled case. Insets show the variations in the relative energy position (ΔE) and the intensity (I_c/I_m) of the correlated feature compared to the uncorrelated ones as a function of U and U^2, respectively, for the multiband (solid circles) and the single band (open circles) models. All energies are in the units of the bandwidth, W.
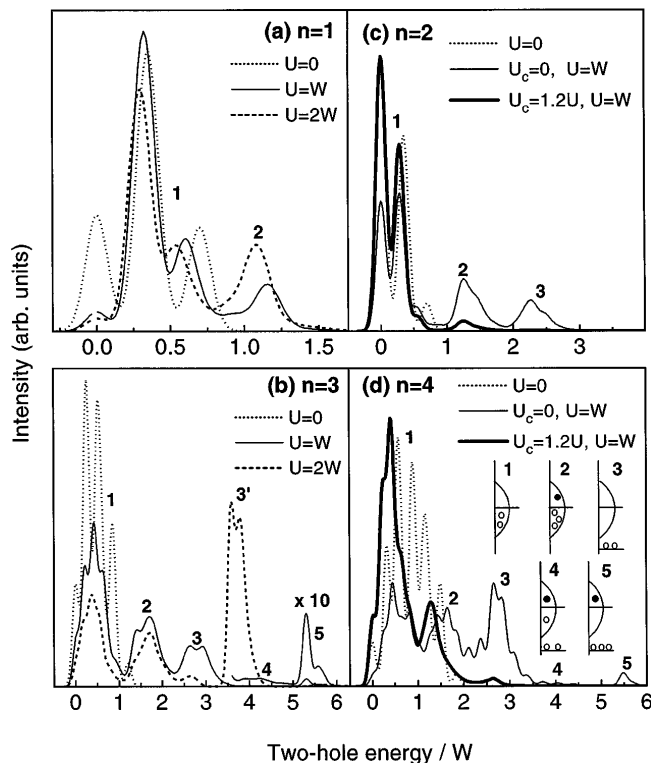

FIG. 2. Calculated Auger spectra for (a) $n = 1$, $U/W = 0$, 1, 2, and $U_c = 0$; (b) $n = 3$, $U/W = 0$, 1, 2, and $U_c = 0$; (c) $n = 2$, $U/W = 0$, and $U/W = 1$ with and without $U_c = 1.2U$; and (d) $n = 4$, $U/W = 0$, and $U/W = 1$ with and without $U_c = 1.2U$. Various groups of spectral features are marked as 1–5 and dominant contributions to the corresponding wave function are shown in panel (d) schematically. In panel (b), high-energy features for $U/W = 1$ are multiplied by 10 for clarity. All energies are in W.

behaviors, we have analyzed the character of the final-state two-hole wave functions responsible for these various features. We illustrate schematically the dominant contributions to the wave functions corresponding to each spectral group 1–5 in Fig. 2(d) in terms of electron and hole excitations with respect to the initial state. The screened, delocalized particles (open and closed circles representing holes and electrons, respectively) are shown within the semielliptical bandwidth which is arbitrarily chosen to be half filled for the purpose of clarity in the presentation. The localized hole states are shown in an atomiclike level. Thus, the spectral group marked 1 which corresponds to Auger transitions appearing within the energy interval of the uncorrelated ($U/W = 0$) case corresponds to two screened holes in the band [schematic 1 in Fig. 2(d)]. In each case, the large intensity spectral group marked 2 was found to arise from an extra electron-hole excitation accompanying the generation of two screened holes [see schematics in Fig. 2(d)]. The movement of the feature 2 to slightly lower energy with increasing U in Fig. 2(a) is due to the band-narrowing effects at larger U, as the process involves an excitation of an electron from the occupied to the unoccupied part. While the energy position of 2 is relatively insensitive to U [e.g., compare $U/W = 1$ and 2 in Fig. 2(b)], the existence of this feature is entirely dependent on the presence of correlation in the initial and final states and, consequently, this feature is completely absent for $U/W = 0$. Feature 3 corresponds closely to the correlated feature discussed within the CS theory with two holes localized at the same atomic site, as shown by the schematic process 3 in Fig. 2(d). Thus, this feature moves to higher energy and rapidly gains intensity with increasing U [compare features 3 and 3′ for $U/W = 1$ and 2, respectively, in Fig. 2(b)]. The very weak intensity feature 4 corresponds to an electron-hole excitation accompanying the generation of the two localized holes, whereas feature 5 at still higher energy arises from three holes localized at a site with an electron excited to a higher energy state. Although, in these finite size calculations, the features 2 and 4 appear as distinct peaks, in an extended metal such processes will have continuous energy spectra, thus substantially overlapping the corresponding main peaks, 1 and 3, respectively. These processes, however, will appear as distinct peaks in the case of insulators with finite band gaps. Obviously all of these processes (2–5 with the exception of 3) are not describable within any theory for a fully filled band, as it depends on multiparticle excitations possible only in partially filled bands.

The distinction between the partially filled and fully filled bands becomes all the more striking when the influence of the core hole is included. It is evident that the core hole, existing only in the initial state, does not have any effect in the fully filled limit irrespective of the strength of the core-hole potential (U_c), since there cannot be any screening dynamics here. On the other hand, any reasonable value of U_c completely alters the Auger spectrum for any configuration away from the fully filled limit, as we

show in Figs. 2(c) and 2(d), illustrating typical results for $n = 2$ and 4 with and without the core-hole potential. In both of these cases, correlation-induced features 2 and 3 can be seen with substantial intensity for $U/W = 1$ in the calculated spectra in the absence of a core-hole potential ($U_c = 0$; thin solid line) with weaker features 4 and 5 only for the $n = 4$ case. For $U_c \neq 0$ (thick solid line), however, the intensities in these features all but vanish completely, transferring almost all of the spectral weight to the uncorrelated spectral range, 1. This observation of disappearance of the correlation-induced features in the presence of U_c is found to be robust for all reasonable values of U and U_c, as explicitly checked with extensive calculations. Thus, one obtains here the paradoxical situation, where the pronounced manifestation of correlation effects within the valence band in terms of satellite features (2–5) is virtually wiped out *due to the presence of another correlation effect*, namely, that between the core hole and the valence electrons. In order to understand these changes, we note that the spectra of the final state energy eigenvalues are identical for the $U_c = 0$ and $\neq 0$ cases, since the core hole exists only in the initial state. Therefore, the drastic modifications in the spectral features arise only from changes in the transition probabilities via the modification of the initial state wave function due to the screening response to the core-hole potential. The effect of the core-hole potential in the initial state is primarily to increase the local site occupancy by nearly one electron to $(n + 1)$ as a screening response; analysis of the wave function character supports this view. Then, the subsequent Auger transition creates two holes which generate primarily a $(n - 1)$ configuration at the local site and, therefore, suppress the correlation-induced feature arising from $(n - 2)$ local occupancy. It is to be noticed that there are some important changes in the line shape of the spectral region 1 with correlation effects. In the absence of the core hole, there is a slight narrowing of this spectral region arising from band-narrowing effects in the presence of a finite U; with $U_c \neq 0$, there is a more significant narrowing in this spectral region [see Fig. 2(d)]. This arises from the above-mentioned changes in the transition probabilities transferring weights preferentially to lower energies within the uncorrelated region.

In order to ascertain the relevance of these results obtained from small, finite systems to strongly correlated extended solids, we have applied this method of calculation to a representative case, namely, the Auger spectrum of a typical correlated oxide system, $LaCoO_3$. The electronic structure of $LaCoO_3$ has been discussed extensively in past literature and there are reliable estimates of the various interaction strengths already obtained from the analysis of several spectroscopic results [10] within finite cluster many-body calculations involving one Co and six oxygen atoms in an octahedral geometry. In agreement with these estimates, we also use the same cluster with the charge-transfer energy $\Delta = 2.0$, $pd\sigma = -1.8$, $A = 4.21$, $B = 0.13$, and $C = 0.64$, amounting to a multiplet
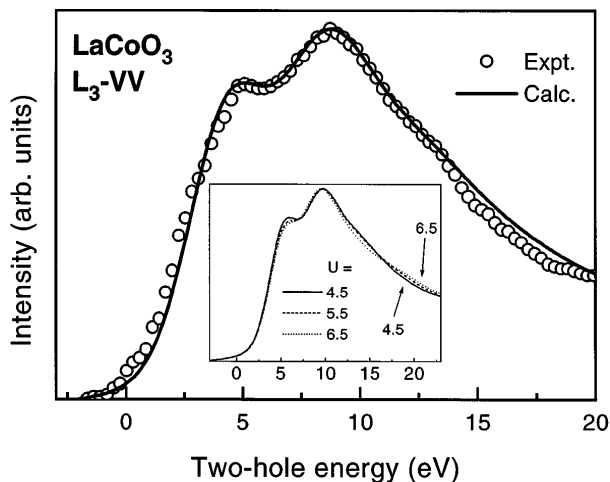
FIG. 3. Comparison of experimental and calculated Co L_3-VV Auger spectra from LaCoO$_3$. The inset illustrates the changes in the calculated spectra with changing U, showing the existence of weak and broad correlation-induced features at energies above $\sim$17 eV.

averaged U_{eff} of 4.5 eV. The calculated Auger spectrum which is the first of its kind is compared with the experiment [11] in Fig. 3, indicating a remarkable agreement. Such an agreement between the calculated and experimental spectra without the need to readjust parameter values firmly establishes the relevance of the results presented here. More importantly, it leads to a drastic reinterpretation of the experimental result. It has been believed that the most intense peak in the Auger spectrum in Fig. 3 at 8.8 eV for LaCoO$_3$ [11] arises from a Coulomb interaction driven localized two-hole final state, while the prominent shoulder at the lower energy (5 eV) arises from the screened and delocalized two-hole final states. An analysis of the wave functions clearly shows that all of the prominent features (i.e., at 5 and 8.8 eV) as well as the weak shoulder at about 13.3 eV arise from delocalized final states. We show calculated Auger spectra for LaCoO$_3$ with $U_{\text{eff}} = 4.5$, 5.5, and 6.5 eV. Besides minor changes, the results are essentially identical in spite of the strong variation in U establishing our conclusions. Additionally, one can see the emergence of a broad and weak feature beyond 17 eV that moves to higher energy with increasing U_{eff}; only such weak correlation-induced satellite features survive in the final spectrum. In order to understand the origin of these spectral features, we first note that the Co d related single-particle density of states is distributed basically in two groups, arising from the bonding-antibonding splitting of Co d–O p hybridized states [12]. Thus, the self-convolution of the single-particle density of states has three features corresponding to two holes occupying antibonding-antibonding (AA), antibonding-bonding (AB), and bonding-bonding (BB) combinations at 4.7, 8.8, and 13.5 eV, establishing the origin of the experimental features at the same energies arising from AA, AB and BB occupancies of the delocalized states. While the energetics can be explained by this procedure, interestingly the

spectral shape cannot be described by a self-convolution of the DOS, due to the influence of the valence-valence and valence-core interaction effects modifying the transition probabilities. It is found that these correlation effects enhance the relative intensity of the peak at 8.8 eV.

In conclusion, we have shown that the Auger spectra from strongly correlated, partially filled systems are profoundly influenced by the presence of screening dynamics and multielectron processes. Satellites in Auger spectra arising from correlation effects within the valence electrons are strongly suppressed by the presence of core-valence correlation effects leading to the surprising result of Auger spectra being dominated by uncorrelated spectral features in spite of the presence of strong interactions. This calculational method applied for the first time to a real system, LaCoO$_3$, shows remarkable agreement with the experimental results, leading to a reinterpretation of Auger spectra from such strongly correlated systems.

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