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2008 J. Phys.: Condens. Matter 20 474209

(http://iopscience.iop.org/0953-8984/20/47/474209)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 474209 (5pp) doi:10.1088/0953-8984/20/47/474209

On Coster–Kronig line shapes of solids

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Received 21 April 2008
Published 6 November 2008
Online at stacks.iop.org/JPhysCM/20/474209

Abstract

In this work we set up a model aimed at the calculation of three-hole features like the ones due to core–valence–valence Auger decays following Coster–Kronig transitions. While several experiments made in the 1970s and in the 1990s on the Auger core–valence–valence spectra of transition metals showed the existence of these structures, a theory able to explain and predict them is still missing today. Our model is grounded on the one-step approach, but the use of a valence band fully below the Fermi level allows us to treat our calculations in a three-step approach, so keeping complications to a minimum in this exploratory work. The Hamiltonian of the system is placed in an Anderson-like picture and the spectra are computed by evaluating a three-body Green function. Within our model we arrive at a simple and closed formula covering the whole range between weak and strong correlations. We find that, in general, the satellites cover separated spectral regions with three-hole multiplets, shifted and broadened two-hole features and distorted band-like continua.

1. Introduction

Coster–Kronig satellites leading to three-hole final states have so far been considered as a mere background in the measured photoemission and Auger spectra. This is due mainly to both experimental and theoretical difficulties. Among the former a dominant role has been played by problems in isolating the signal coming from this kind of transition from that of the other superimposing parent Auger decay. Another source of difficulties was the theoretical hardship in finding a recipe for calculating an interacting three-particle Green function. Notwithstanding the fact that the study of such satellites is very interesting because they are due to strongly correlated effects in highly excited states, they also represent a real mine of information about strongly correlated materials.

In this work we address in particular the L_2–$L_2L_3M_{4,5}$–$M_{4,5}M_{4,5}(M_{4,5})$ processes from transition metals or else a transition started with a $2p_{1/2}$ core hole which decays through a first Coster–Kronig (CK) transition, L_2–$L_3M_{4,5}$, and then through a core–valence–valence (CVV) Auger process, $L_3(M_{4,5})$–$M_{4,5}M_{4,5}(M_{4,5})$, in the presence of a spectator hole in the 3d valence band, $(M_{4,5})$. The theory here presented, however, holds general for M–MMN–NNN and many other kinds of CK preceded Auger decay.

Such satellites were isolated for the first time in the 1980s [1] thanks to the use of the Auger-photoelectron coincidence spectroscopy (APECS), then in later experiments they were more extensively measured in several first-row transition elements [2–5]. In the 1990s Thurgate and co-workers [4, 5] measured the APECS spectra of Ni, Fe, Co and Ga, where they isolated and observed intense L_2–$L_2L_3M_{4,5}$–$M_{4,5}M_{4,5}(M_{4,5})$ satellites in all cases except Ga and their line shapes were found to show a sort of atomic-like or band-like shape phenomenology recalling to the mind that of the two-hole Auger line shapes of the Cini–Sawatzky theory [6–8]. The model we set up is able to explain this different kind of behavior, predicting also some features that are completely new. The mechanism at the heart of our method is tightly related to the breaking of the independent particle picture for the description of the sample valence hole. We suspect in fact that to observe the three-hole peak phenomenology, typical of that kind of CK transition we are interested in, a key role must be played by an interplay between kinetic and potential energy or else by the competition between valence hole delocalization and the $L_3M_{4,5}$–$M_{4,5}M_{4,5}(M_{4,5})$ decay. Its result, in the case of any narrowing of the line shape, will be a fingerprint of correlation effects. As will be described in full detail in the following sections, the origin of

this behavior must come in fact from processes started with a local M spectator hole due to the early decay of the L_3 hole before M escapes and probably the localization of the spectator hole is due to the fact that it is bound in a two-hole resonance.

This paper is organized as follows: in section 2 our model will be presented, while in section 3 an application of this approach to the rectangular band case for an initial monodeterminantal state, $|^4F\rangle$, will be shown. Finally, some conclusions will be drawn in section 4.

2. The model

The presence of any narrowing in the final three-hole line shape of CK preceded Auger satellites reveals, as we said before, a clear footmark of the breaking of the independent particle picture of M holes. If an independent particle picture of valence states were valid, in fact one should predict that there is ample time for the M spectator hole to delocalize before the L_3 hole decays, since the valence bandwidth is expected to be much larger than the L_3 core-level width[3]. In this case, the influence of a far-away spectator should be negligible and one should observe a normal L_3VV decay initiated by the L_2 hole. There should be no reason to expect any narrowing of the satellite line shape, but on the contrary one would predict a broadening due to a convolution with the L_2 photoemission peak. Any deviation from this result as observed in Co and Ni [4, 5] must come from processes starting with a local $M_{4,5}$ spectator hole during the Auger decay of the L_3 hole, before the $M_{4,5}$ hole escapes and/or binds to a resonance. For the reasons above, we expect that two-hole resonances must be involved in keeping the spectator hole on-site. The intensity of this three-hole satellite should be computed in terms of the probability of decay in the presence of a localized spectator. Then, the probability that the ($M_{4,5}$) hole sticks on-site may be estimated as the intensity of the split-off peak of the $L_3M_{4,5}$ resonance. Probably because this intensity vanishes or is small unless the hole–hole interaction U is comparable with the bandwidth, one should see no change at all compared to the $L_3M_{4,5}M_{4,5}$ line shape unless we are quite close to the atomic-like limit. In the light of the above discussion, we argue that not only the ($M_{4,5}$) hole is unscreened but it is localized in a two-hole resonance with high probability, a property which requires strong correlation. Besides this the same spectral region should also contain intensity arising from the band-like part of the $L_3M_{4,5}$ resonance and contributing with a normal L_3MM feature that will exhibit no narrowing and will tend to broaden the sharp features.

The total Hamiltonian of our problem can be decomposed as:

$$H = \widetilde{H} + H_A + T_A + T_p \tag{1}$$

where the Coulomb interaction operator responsible for the Auger transitions, H_A, can be written also singling out CK and CVV contributions and disregarding all the possible contributions of other decay channels: $H_A = H_A^{(CK)} + H_A^{(CVV)}$. In this picture $H_A^{(CK)}$ produces the CK precursor decay, and $H_A^{(CVV)}$ represents the following CVV Auger decays leading us to our three-hole final state. T_A and T_p are instead, respectively, the Auger electron and the photoelectron kinetic energies. The dynamics of the system with no Auger transitions are included in all the remaining terms making up the rest of H, $\widetilde{H}$.

For the sake of simplicity we develop our model in what we call a 'three-step approach' [9]. Its physical meaning can be easily understood by writing down its expression for the Auger current, which can be obtained by extending the one-step approach given by Gunnarsson and Schönhammer [10] to the case with two emitted Auger electrons, where the first Auger electron is not detected. The expression corresponding to the three-step approach is obtained this way but neglecting virtual transitions, the mixing with other channels and all the possible intermediate excited states of L_3M. This tells us that by using this approximation we are treating the initial photoemission and the two following Auger decays as three-distinct processes not interfering one with the other. In this picture we can restrict ourselves to consider only the three holes that effectively take part in the process analyzed, discarding all the other target passive holes.

The Auger spectrum up to a constant is given by:

$$S(\omega) = -\mathrm{Im}\,\mathrm{Tr}[M^\dagger(\omega)\Phi(\omega)M(\omega)] \tag{2}$$

where M is the Auger matrix and Φ is the interacting three-hole Green function which can be written within the three-step approach as:

$$\Phi_{\alpha_1,\alpha_2,\alpha_3;\beta_1,\beta_2,\beta_3}(z) = \langle 0|c_{\alpha_3}c_{\alpha_2}c_{\alpha_1}\frac{1}{z-H}c^\dagger_{\beta_1}c^\dagger_{\beta_2}c^\dagger_{\beta_3}|0\rangle \tag{3}$$

where the α and the β represent single-particle spin–orbital states on the valence shell of the Auger site (local atom), the average is over the vacuum state and H is the total Hamiltonian.

To evaluate (3) we assume an Anderson-like approach, so our Hamiltonian is reduced to:

$$H = H_{at} + H_S + V \tag{4}$$

where H_{at} and H_S are, respectively, the terms describing the target atom and the remaining solid, while V accounts for one-body hopping between the atom and the solid. The Hamiltonian representing the solid is modeled as: $H_S = \sum_\alpha \sum_k \varepsilon_{k\alpha}c^\dagger_{k\alpha}c_{k\alpha}$, while to calculate V we assume that a hole in the atomic state α can only hop into the corresponding continuum of states $\{k\alpha\}$. This means that: $V = \sum_\alpha \sum_k V_{k\alpha}(c^\dagger_{k\alpha}c_\alpha + c^\dagger_\alpha c_{k\alpha})$. The atomic Hamiltonian is given instead by the sum: $H_{at} = H^{(0)}_{at} + H_C$, in which $H^{(0)}_{at} = \sum_\alpha \varepsilon_\alpha c^\dagger_\alpha c_\alpha$ is the one-body term, and $H_C = \sum_{\alpha_1\alpha_2\alpha_3\alpha_4} U_{\alpha_1\alpha_2\alpha_3\alpha_4}c^\dagger_{\alpha_1}c^\dagger_{\alpha_2}c_{\alpha_4}c_{\alpha_3}$ is the screened Coulomb repulsion.

The Hilbert space of our system is made up of four different kind of states which are: our final three-hole state, all the two-hole states that can be reached from this last one emitting one hole in the continuum, all the single-hole states that can be reached from the initial three-hole one setting free this time two electrons and, finally, a state in which all the holes present in the final state of the considered process are free. So once we have identified the final three-hole states of

[3] Data on core-level widths are not available, but they would be useful.

our system, we can build the Hilbert space of our problem. Then projecting a Dyson-like equation on this space we can get the following system of coupled equations, which are closed thanks to the hypothesis of closed bands and represent the exact solution of our problem:

$$\begin{aligned}\underline{\Phi} &= \underline{\Phi}^{(0)} + \underline{\Phi}^{(0)}\underline{U}\ \underline{\Phi} + \sum_k \underline{\Phi}^0_k \underline{U}\ \underline{\Phi}_k \\ \underline{\Phi}_k &= \underline{\Phi}^{(0)}_k + \underline{\Phi}^{(0)}_k \underline{U}\ \underline{\Phi} + \sum_{\mathrm{p}} \underline{\Phi}^{(0)}_{k,p}\underline{U}\ \underline{\Phi}_{\mathrm{p}}\end{aligned} \tag{5}$$

where the underlined quantities are matrices or else they are the corresponding operators, $\widehat{\Phi}(\omega) = \frac{1}{\omega - H + \mathrm{i}\delta}$, $\widehat{\Phi}_0(\omega) = \frac{1}{\omega - H_0 + \mathrm{i}\delta}$ (with $H_0 = H - H_C$) and H_C, projected on the Hilbert space of the treated transition. In particular $\underline{\Phi}$ and $\underline{\Phi}^{(0)}$ are, respectively, the interacting and non-interacting three-hole Green function projected on localized on-site three-hole final states. $\underline{\Phi}_k$ and $\underline{\Phi}^{(0)}_k$ are respectively the operators $\widehat{\Phi}$ and $\widehat{\Phi}_0$ closed between a localized three-hole state and a localized two-hole one with a free hole characterized by a momentum k. $\underline{\Phi}^{(0)}_{k,p}$ is again $\widehat{\Phi}^{(0)}$ but closed this time between two localized two-hole states.

3. The ^{4}F and the rectangular band case

As a first simple application of this model we restrict our analysis to consider the case of a single monodeterminantal three-hole final state, the ^{4}F, which can be written in the three-step approach as $c^+_{m_l=0}c^+_{m_l=1}c^+_{m_l=2}|0\rangle$. The atomic Hamiltonian is the sum of:

$$\begin{aligned}H^{(0)}_{\mathrm{at}} &= \sum_{m_{l_i}=-2}^{2} \varepsilon_{m_{l_i}} c^\dagger_{m_{l_i}} c_{m_{l_i}}; \\ H_C &= \sum_{m_{l_1}+m_{l_2}=m_{l_3}+m_{l_4}} U_{m_{l_1}m_{l_2}m_{l_3}m_{l_4}} c^\dagger_{m_{l_1}} c^\dagger_{m_{l_2}} c_{m_{l_4}} c_{m_{l_3}}.\end{aligned} \tag{6}$$

To further simplify our analysis we restrict ourselves to degenerate atomic levels, $\varepsilon_{m_{l_i}} = \varepsilon_0$ for all i, and to hopping integrals independent of the magnetic quantum number m_{l_i}, $V_{km_{l_i}} = V_k$. In this case the two-hole states of the Hilbert space of the system are given not only by all the possible four states obtained setting free one electron from the $|^4F\rangle$, $\{|i,k\rangle\} = \{|m_{l_\mathrm{p}}\uparrow, m_{l_q}\uparrow, m_{l_r}k\uparrow\}$ ($m_{l_{p,q,r}} = 0,1,2$), but also by $c^+_{m_l=2,k}c^+_{m_l=-1}c^+_{m_l=2}|0\rangle$. This state cannot be reached by hopping from $|^4F\rangle$ but only by the Coulomb interaction, $\tilde{U}$, with $c^+_{m_l=2,k}c^+_{m_l=0}c^+_{m_l=1}|0\rangle$, so H_C in (6) can be re-written as:

$$\begin{aligned}H_C &= U_0 c^\dagger_1 c^\dagger_2 c_2 c_1 + U_1 c^\dagger_0 c^\dagger_2 c_2 c_1 + U_2 c^\dagger_0 c^\dagger_1 c_1 c_0 \\ &\quad + \tilde{U}(c^\dagger_0 c^\dagger_1 c_2 c_{-1} + c^\dagger_{-1} c^\dagger_2 c_1 c_0) + \cdots\end{aligned} \tag{7}$$

where the remaining terms can be neglected as they do not contribute.

As we said before, to gain a prediction for the CK three-hole line shape the quantity we are interested in is the interacting three-hole Green function which is in this case:

$$\Phi(z) = \langle {}^4F | \frac{1}{z - H} | {}^4F \rangle. \tag{8}$$

For $\tilde{U} = 0$ we found an approximate solution of (5) which is valid for all cases where the final three-hole state is a monodeterminantal one:

$$\Phi(z) = \frac{1}{z - 3\varepsilon_0 - W - \sum_{i,k} \frac{V_k^2}{z - 2\varepsilon_0 - \varepsilon_k - U_i - 4\sum_{\mathrm{p}} \times X_{\mathrm{p}}}} \tag{9}$$

where $X = \frac{V_{\mathrm{p}}^2}{z - \varepsilon_0 - \varepsilon_k - \varepsilon_p - 3\Sigma(z - \varepsilon_k - \varepsilon_{\mathrm{p}})}$. In this expression $W = \sum_{i=0}^{2} U_i$ and the U_i ($i = 0,1,2$) are respectively the three- and two-hole Coulomb interaction, i.e. $H_C|^4F\rangle = W|^4F\rangle$ and $H_C|i,k\rangle = U_i|i,k\rangle$. $\Sigma(z) = \sum_k V_k^2/(z - \varepsilon_k)$ is the self-energy, V_k and V_{p} are the hopping terms and ε_0 is the band center. In the narrow-band limit involving a single k-state, (9) is equal to the exact solution of the problem.

As a test-bed we consider an application to a rectangular valence band case: the Anderson model parameters ε_0, ε_k and V_k are chosen in such a way that $-(1/\pi)\,\mathrm{Im}[G(z)] = \theta(a - |z|)/2a$ with $2a$ the bandwidth. The results of this calculations for different U_i are shown in figure 1 together with a comparison with the exact numerical solution of the integral equation obtained by taking a finite number N of k-states. In particular figure 1 has been obtained with $N = 24$.

As one can see, the approximate solution cannot be distinguished from the exact one. As expected, we found many analogies with the two-hole resonances. From figure 1 it is evident that increasing the two-hole Coulomb interactions, or else going from panels (a) to (f), we recollect all the shape phenomenology of the basic form of the Cini–Sawatzky theory. The spectra in fact remain band-like when $U/a \ll 1$ but the line shape is progressively distorted with increasing U/a (panel (b)) and for $U/a \gg 1$ (panel (e) and (f)) split-off two-hole resonances develop. The intermediate cases (panels (c) and (d)) instead show new features and, besides the distorted continuum, one can have a non-split-off two-hole resonance around $\omega \sim U$. The two-hole resonances are not sharp but rather smeared out and their width is of the order of $2a$. This is due to the bound hole that makes virtual trips in the valence band. All spectra are dominated by a quasi-atomic three-hole resonance, while the two-hole features show rather small and unequal intensity in comparison.

For $\tilde{U} \neq 0$ instead $\Phi(z)$ is obtained as $[G \otimes P](z)$ where $\otimes$ stems from a convolution product, G is the single-particle Green function and P is the interacting two-hole Green function:

$$P(z) = \frac{1}{P_0^{-1}(z) - \tilde{U}^2 P_0(z)} \tag{10}$$

while $P_0(z) = [G \otimes G](z)$ is the non-interacting one. Figure 2 shows the interacting three-hole Green function calculated for different values of U_i.

As for the $\tilde{U} = 0$ case, also this time we found in the calculated spectra many analogies with the two-hole phenomenology of the Cini–Sawatzky theory, but for $\tilde{U} \neq 0$ also new interesting features arise. It is found in fact that the presence of a non-vanishing $\tilde{U}$ acts only on one of the three U_i, U_2 and this effect is equivalent to a sort of dynamical renormalization of U_2. Physically this was due to the possibility of multiple scattering of the two holes with $m_l = 0,1$ between the states $c^+_{m_l=2,k}c^+_{m_l=-1}c^+_{m_l=2}|0\rangle$ and $c^+_{m_l=2,k}c^+_{m_l=0}c^+_{m_l=1}|0\rangle$, which makes U_2 behave as $\tilde{U}^2/z$ for

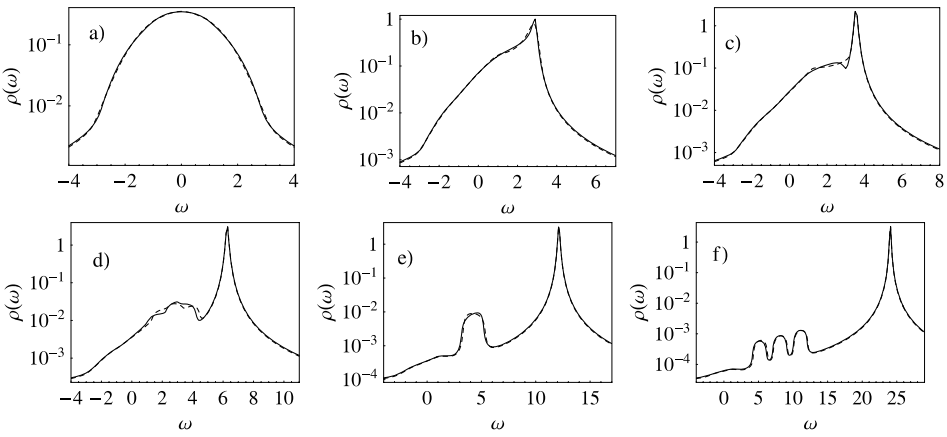

Figure 1. Each panel displays the comparison between the exact (solid line) and the approximate (dashed line) $\rho(\omega) = -(1/\pi)\mathrm{Im}[\Phi(\omega + \mathrm{i}0^+)]$. The first one is obtained solving numerically the equation (5) for a number of k-states $N = 24$. The latter instead has been reached by evaluating equation (9). All reported patterns have been evaluated in the case of a rectangular band for different values of the Coulomb parameters U_i: (a) $U_0 = U_1 = U_2 = 0$; (b) $U_0 = 0.4$, $U_1 = U_2 = 0.8$; (c) $U_0 = U_1 = U_2 = 1$; (d) $U_0 = U_1 = 1.5$, $U_2 = 3$; (e) $U_0 = U_1 = U_2 = 4$; (f) $U_0 = 5$, $U_1 = 8$, $U_2 = 11$. The values of U and ω are in units of a.

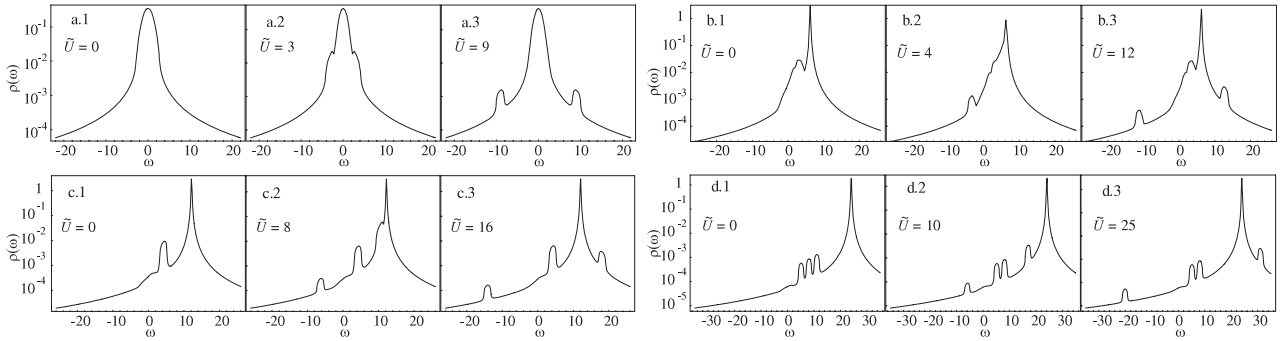

Figure 2. Each panel displays the plot of $\rho(\omega) = -(1/\pi)\,\mathrm{Im}[\Phi(\omega + \mathrm{i}0^+)]$ as obtained from the numerical solution of equation (5) in the case of a rectangular band. All the showed pattern are calculated for different values of the Coulomb parameters U_i and increasing $\tilde{U}$. (a) $U_0 = U_1 = U_2 = 0$; (b) $U_0 = U_1 = 1.5$, $U_2 = 3$; (c) $U_0 = U_1 = U_2 = 4$; (d) $U_0 = 5$, $U_1 = 8$, $U_2 = 11$. The values of U and ω are in units of a.

large z. This explains the splitting of the resonance at about U_2 in two peaks centered at energies $\sim U_2 \pm |\tilde{U}|$.

The results for the exactly solvable model $U_0 = U_1 = U_2 = 0$ and $\tilde{U} \neq 0$ are shown in panel (a). Panel (b.1) ($\tilde{U} = 0$) exhibits a spectrum with a split-off three-hole peak at energy $\sim W$ and a distorted continuum, but with increasing $\tilde{U}$ well defined two-hole structures start to develop. They eventually split off from the top and the bottom of the continuum as in panels (b.2) and (b.3). The same behavior is observed for $U_0 = U_1 = U_2 = 4$ (panel (c)), where the only difference is the fact that the continuum is completely dominated by the degenerate two-hole resonance. The effect of the dynamical renormalization of U_2 is evident in the strong coupling limit which is shown in panel (d). Indeed, the two-hole resonances at U_0 and U_1 are not affected by $\tilde{U}$ while the one at U_2 splits into a double resonance at energies $\sim U_2 \pm |\tilde{U}|$, see panels (d.2) and (d.3).

A direct consequence of the Pauli exclusion principle is the complete lack of sensitivity of the three-hole resonance to the strength of $\tilde{U}$. This is due to the fact that the scattering $(m_{l_i}, m_{l_j}) = (0, 1) \leftrightarrow (2, -1)$ is forbidden in the presence of a hole with $m_l = 2$ on the local site.

4. Results and conclusions

Until today the field of CK preceded Auger satellites was theoretically quite undiscovered and experimentally neglected because of the reputation of this kind of transition being a mere background. This work clearly shows that CK preceded Auger satellites are instead a real mine of information about strongly correlated materials because they give us the unique opportunity to characterize the system by measuring what happens when a strongly correlated system responds to a strong local perturbation. The line shape of these processes in fact contains information on three-hole multiplet states of the atom and on the two-hole multiplets that result when one of the holes explores the surroundings. The two-hole multiplet structures differ widely in shape, intensities and position from those of the Auger transitions leading to two valence holes. For instance peaks corresponding to forbidden Auger transitions can be prominent in CK satellites. Moreover, the two-hole states displayed in figures 1 and 2 have a broadening of the order of the bandwidth.

To compare the above results with experiment, more modeling and computational work is needed and it is still

under way. Here we have tried to address some simpler aspects of the theoretical problems that CK transitions pose, in order to prepare the ground for a future extended theory. In particular, the extension to open bands along the lines of [11] and [12] is a challenging task for future research.

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