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Auger spectra of transition metals: a solution for the multi-band model

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Abstract. A solution for two-body Green function relevant to the calculation of Auger spectra in the case of systems described by a multi-band Hubbard Hamiltonian with partially filled bands is presented. In order to obtain the correct atomic limit the formalism of atomic operators is employed. Equations of motion for double-time Green functions are solved using a two-step decoupling scheme. First, we restrict ourselves to contributions from hopping processes in two bands containing the two studied particles. Second, to cut the hierarchy of equations we replace the local number operators by their average values. The obtained solution has the character of an effective-medium theory for the scattering of a pair of particles. Interpolating between the band and atomic limit yields exact results. It is also correct in the limit of completely filled bands. As an example, the case of five degenerate bands is studied numerically.

1. Introduction

There is an increasing interest in applications of Auger electron spectroscopy to the study of solids (Fuggle 1981, Weightman 1982). A possibility that it could yield information on the band structure was realized quite early (Lander 1953), but real progress was made following the development of high-resolution Auger spectroscopy at the end of 1960s. CVV Auger spectra can provide useful information on electron–electron correlations, because they are influenced by the correlation energy between two holes in a final state.

The correlation effects are particularly important in transition metals and their compounds. The Auger spectra of these materials are quite different from those of normal metals in that they are quasi-atomic (Antonides *et al* 1977, Bennett *et al* 1983, Gallon 1978, Madden *et al* 1978, Parry-Jones *et al* 1979).

To account for this difference Hubbard-type Hamiltonians have been employed. In the case of one completely filled band, which is an exactly soluble case, it has been shown (Cini 1977, Sawatzky 1977, Sawatzky and Lenselink 1980), that atomic-like behaviour appears for a sufficiently large ratio U/W (where U is the Coulomb integral, W is the band width). A band-like behaviour of Auger spectra (i.e., Auger intensity is proportional to a self-convolution of the single-particle density of states) dominates for small values of U/W. Also some extension to the multi-band case was considered (Cini 1978). This simple theory has been used to determine the value of an effective Coulomb interaction U_{eff} (Antonides *et al* 1977, Bennett *et al* 1983, Parry-Jones *et al* 1979, Sawatzky and Lenselink 1980).

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However, for the partially filled d-bands typical of transition metals like Ni, Co, Fe and Pd the situation is more complex. Cini (1979) first applied the low-density approximation, but this fails to explain the Auger spectra of Ni. It has been argued by Tréglia *et al* (1980), that this approach is unsuitable for materials like Ni because they have relatively large hole concentrations. These authors have developed the perturbation theory to second order in U/W for a degenerate Hubbard model applicable to any number of electrons in the d-band (Tréglia *et al* 1981b).

These two approaches have been compared in the case of a finite-cluster calculation (Cini and Verdozzi 1986, 1987) and in the case of one-dimensional chain (Oleś *et al* 1986). Cini's original theory was extended to a self-consistent version by Drchal and Kudrnovský (1984), which can be applied to a broader range of electron concentrations.

All these theories are limited either to low particle concentrations or to weak interactions. They have been used only in the case of single-band or degenerate multi-band models. Further development in two directions is desirable: (i) to develop an interpolating theory applicable to any hole concentration and to any strength of interactions, and (ii) to use non-degenerate multi-band Hamiltonians (Jennison 1978, Presilla and Sacchetti 1987).

Recently Presilla and Sacchetti (1987) derived an RPA-like solution, which is the extension of the previous work of Sawatzky (1977) to the non-degenerate multi-band Hamiltonian. Except for the single-band case, however, it fails in an atomic limit ($W = 0$). For the single-band Hubbard Hamiltonian another interpolating solution has been obtained by Drchal (1989). In contrast with the RPA-like solution, it has the correct transformation properties under electron–hole transformation.

In this work we derive a new solution for the multi-band Hubbard-type Hamiltonian, which interpolates between the band and atomic limit. We use the formalism of Hubbard atomic operators (Hubbard 1965) and the equation-of-motion method for double-time Zubarev Green functions (GF) (Zubarev 1960).

2. Preliminaries

In first-order perturbation theory the Auger rate is given by the Fermi golden rule. After some currently used approximations (neglecting the finite lifetime of the core hole, sudden approximation, neglecting interatomic processes and the $\boldsymbol{k}$-dependence of matrix elements) the intensity of CVV Auger spectra can be expressed via a two-particle GF K in the following form:

$$\frac{\mathrm{d}N}{\mathrm{d}E_k} \alpha -\frac{1}{\pi}\sum_{\hat{\mu}\hat{\nu}\hat{\rho}\hat{\tau}} \mathbf{M}^{*\hat{\mu}\hat{\nu}}\mathbf{M}^{\hat{\rho}\hat{\tau}}\ \mathrm{Im}\ K_{ii}^{\hat{\mu}\hat{\nu}\hat{\rho}\hat{\tau}}(\omega + \mathrm{i}\eta) \tag{1}$$

where $\omega = E_c - E_k$, E_k is an Auger electron energy, E_c is an energy of the core hole, $\mathbf{M}^{\hat{\mu}\hat{\nu}}$ are matrix elements, $\hat{\mu} = (\mu, \sigma)$, $\hat{\nu} = (\nu, \sigma')$, $\hat{\rho} = (\rho, \sigma'')$, $\hat{\tau} = (\tau, \sigma''')$, $\mu, \nu, \rho, \tau = 1, \ldots, L$ label the bands (L is the number of bands), σ's are the spin indices with values $+, -$, and

$$K_{ij}^{\hat{\mu}\hat{\nu}\hat{\rho}\hat{\tau}}(\omega) = \langle\langle c_{i\hat{\mu}}^{+} c_{i\hat{\nu}}^{+} | c_{j\hat{\rho}} c_{j\hat{\tau}} \rangle\rangle_{\omega} \qquad \hat{\mu} \neq \hat{\nu}, \hat{\rho} \neq \hat{\tau} \tag{2}$$

are Fourier components of the double-time GF (Zubarev 1960) and i, j are site indices.

To describe valence electrons in transition metals we consider the multi-band Hubbard-type Hamiltonian

$$H = \sum_i \Big[\sum_{\mu\sigma} \Big(T_0^\mu n_{i\mu\sigma} + \frac{I^\mu}{2} n_{i\mu\sigma} n_{i\mu-\sigma} \Big) + \tfrac{1}{2} \sum_{\hat{\mu}\hat{\nu}}{}' \sum_\sigma [U^{\mu\nu} n_{i\mu\sigma} n_{i\nu-\sigma} + (U^{\mu\nu} - J^{\mu\nu}) n_{i\mu\sigma} n_{i\nu\sigma}] \Big] + \sum_{ij} \sum_{\mu\sigma} t_{ij}^\mu c_{i\mu\sigma}^+ c_{j\mu\sigma} \qquad t_{ii}^\mu = 0, \; n_{i_{\mu\sigma}} = c_{i\mu\sigma}^+ c_{i\mu\sigma}. \tag{3}$$

Since

$$[H, N_{\mu\sigma}] = 0 \qquad N_{\mu\sigma} = \sum_i n_{i\mu\sigma} \tag{4}$$

we can confine ourselves to the GFs (2) with band indices $\rho = \nu$, $\tau = \mu$ or $\rho = \mu$, $\tau = \nu$ and with two possibilities for spin indices $\sigma'' = \sigma'$, $\sigma''' = \sigma$ and $\sigma'' = \sigma$, $\sigma''' = \sigma'$. From (4) it follows that $K^{\mu\sigma\nu-\sigma\nu\sigma\mu-\sigma} = K^{\mu\sigma\nu-\sigma\mu-\sigma\nu\sigma} = 0$. Then, because there holds $K^{\hat{\mu}\hat{\nu}\hat{\rho}\hat{\tau}} = -K^{\hat{\mu}\hat{\nu}\hat{\tau}\hat{\rho}}$ $(\hat{\rho} \neq \hat{\tau})$, it is sufficient to calculate only one set of GFs with indices $\hat{\mu}$, $\hat{\nu}$:

$$K_{ij}^{\hat{\mu}\hat{\nu}}(\omega) = \langle\langle c_{i\hat{\mu}}^+ c_{i\hat{\nu}}^+ | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle_\omega \tag{5}$$

where we have denoted

$$R_j^{\hat{\mu}\hat{\nu}} = c_{j\hat{\nu}} c_{j\hat{\mu}} \tag{6}$$

and all the remaining GFs can be expressed through them, for example $K^{\mu\sigma\nu\sigma'\nu\sigma\mu\sigma'} = (\delta_{\sigma\sigma'} - \delta_{\mu\nu}) K^{\mu\sigma\nu\sigma'}$. In order to obtain the correct atomic limit ($t_{ij} = 0$) we shall employ Hubbard's atomic operators (Hubbard 1965), i.e., we express the operator $c_{i\hat{\mu}}^+ c_{i\hat{\nu}}^+$ via the atomic operators X_i. For Hamiltonian (3) we find the decomposition

$$c_{i\hat{\mu}}^+ c_{i\hat{\nu}}^+ = \sum_{A_{\hat{\mu}\hat{\nu}}} X_i^{A_{\hat{\mu}\hat{\nu}}} \qquad X_i^{A_{\hat{\mu}\hat{\nu}}} = c_{i\hat{\mu}}^+ c_{i\hat{\nu}}^+ N_i^{A_{\hat{\mu}\hat{\nu}}} \qquad N_i^{A\beta\hat{\nu}} = \prod_{\rho \neq \hat{\mu}, \hat{\nu}} n_{i\rho}^{\alpha_\rho h}$$

$$n_{i\hat{\rho}}^+ = n_{i\hat{\rho}} \qquad n_{i\hat{\rho}}^- = 1 - n_{i\hat{\rho}} \tag{7}$$

where $A_{\hat{\mu}\hat{\nu}}$ is a multi-index derived from the $2L$-component multi-index $A = (\alpha_{1+}, \alpha_{1-}, \ldots, \alpha_{\lambda+}, \alpha_{\lambda-}, \ldots, \alpha_{L+}, \alpha_{L-})$, $\alpha_\lambda \varepsilon \{+, -\}$ by omitting $\alpha_{\hat{\mu}}$ and $\alpha_{\hat{\nu}}$. Then for the GFs we have the relations

$$K_{ij}^{\hat{\mu}\hat{\nu}}(\omega) = \sum_{A_{\hat{\mu}\hat{\nu}}} \langle\langle X_i^{A_{\hat{\mu}\hat{\nu}}} | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle_\omega. \tag{8}$$

In the following we calculate GFs for atomic operators.

3. Equations of motion

The GFs $\langle\langle X_i^{A_{\hat{\mu}\hat{\nu}}} | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle$ obey the equations of motion

$$(\omega - E^{A_{\hat{\mu}\hat{\nu}}}) \langle\langle X_i^{A_{\hat{\mu}\hat{\nu}}} | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle = \delta_{ij} \kappa_i^{A_{\hat{\mu}\hat{\nu}}} + \sum_l \sum_{\hat{\rho}} (t_{il}^\rho \langle\langle [X_i^{A_{\hat{\mu}\hat{\nu}}}, c_{i\hat{\rho}}^+] c_{l\hat{\rho}} | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle + t_{il}^\rho \langle\langle c_{i\hat{\rho}}^+ [X_i^{A_{\hat{\mu}\hat{\nu}}}, c_{i\hat{\rho}}] | R_j^{\hat{\mu}\hat{\nu}} \rangle\rangle) \tag{9}$$

where

$$E^{A_{\hat{\mu}\hat{\nu}}} = -T_0^\mu - T_0^\nu - \delta_{\hat{\mu}\hat{\nu}} \Big(I^\mu + \sum_{\rho \neq \mu} (2U^{\mu\rho} - J^{\mu\rho}) [\delta(\rho, \sigma) + \delta(\rho, -\sigma)] \Big) - (1 - \delta_{\mu\nu}) \langle I^\mu \delta(\mu, -\sigma) + I^\nu \delta(\nu, -\sigma') + U^{\mu\nu} [\delta(\mu, -\sigma)$$

$$+\delta(\nu,-\sigma')+1]+\sum_{\rho\neq\mu,\nu}[U^{\mu\rho}\delta(\rho,-\sigma)+(U^{\mu\rho}-J^{\mu\rho})\delta(\rho,\sigma)$$
$$+U^{\nu\rho}\delta(\rho,-\sigma')+(U^{\nu\rho}-J^{\nu\rho})\delta(\rho,\sigma')]$$
$$-J^{\mu\nu}\{\delta_{\sigma,\sigma'}+\delta_{\sigma,-\sigma'}[\delta(\mu,\sigma')+\delta(\nu,\sigma)]\}\rangle\qquad \delta(\rho,\sigma)=\delta_{\alpha_{\rho\sigma},+} \tag{10}$$

$$\kappa_i^{A\hat{\mu}\hat{\nu}}=\langle N_i^{A\hat{\mu}\hat{\nu}}(n_{i\hat{\mu}}+n_{i\hat{\nu}}-1)\rangle. \tag{11}$$

We also need the three-site GFs:

$$K_{ilj}^{\hat{\mu}\hat{\nu}}(\omega)=\langle\langle c_{i\hat{\mu}}^{+}c_{l\hat{\nu}}^{+}|R_j^{\hat{\mu}\hat{\nu}}\rangle\rangle_\omega\qquad i\neq l \tag{12}$$

which obey the equations of motion

$$(\omega+T_0^\mu+T_0^\nu)K_{ilj}^{\hat{\mu}\hat{\nu}}=\kappa_{ilj}^{\hat{\mu}\hat{\nu}}-\sum_m(t_{mi}^\mu K_{mlj}^{\hat{\mu}\hat{\nu}}+t_{ml}^\nu K_{imj}^{\hat{\mu}\hat{\nu}})$$
$$-\left\langle\!\!\left\langle\left(I^\mu n_{i\mu-\sigma}+I^\nu n_{l\nu-\sigma'}+\sum_{\rho\neq\mu}[U^{\rho\mu}n_{i\rho-\sigma}+(U^{\rho\mu}-J^{\rho\mu})n_{i\rho\sigma}]\right.\right.$$
$$\left.\left.+\sum_{\rho\neq\nu}[U^{\rho\nu}n_{l\rho-\sigma'}+(U^{\rho\nu}-J^{\rho\nu})n_{l\rho\sigma'}]\right)c_{i\hat{\mu}}^{+}c_{l\nu}^{+}|R_j^{\hat{\mu}\hat{\nu}}\right\rangle\!\!\right\rangle \tag{13}$$

where

$$\kappa_{ilj}^{\hat{\mu}\hat{\nu}}=\delta_{lj}\langle c_{i\hat{\mu}}^{+}c_{j\mu}\rangle+\delta_{ij}\langle c_{l\nu}^{+}c_{j\nu}\rangle. \tag{14}$$

4. Decoupling procedure

Equations (8), (9) and (13) form the basic set of equations that will be used to determine the GFs $K_{ij}^{\hat{\mu}\hat{\nu}}(\omega)$. To obtain a closed set of equations we employ the decoupling procedure for higher-order GFs on the right-hand side of (9) and (13).

First, for the three-site GFs in (9) ($i\neq l$ because $t_{ii}=0$) we use the approximation

$$\langle\langle[X_i^{A\hat{\mu}\hat{\nu}},c_{i\hat{\rho}}^{+}]c_{l\hat{\rho}}|R_j^{\hat{\mu}\hat{\nu}}\rangle\rangle\simeq 0$$
$$\langle\langle c_{l\hat{\rho}}^{+}[X_i^{A\hat{\mu}\hat{\nu}},c_{i\hat{\rho}}]|R_j^{\hat{\mu}\hat{\nu}}\rangle\rangle\simeq-\langle N_i^{A\hat{\mu}\hat{\nu}}\rangle(\delta_{\hat{\rho}\hat{\mu}}K_{lij}^{\hat{\mu}\hat{\nu}}+\delta_{\hat{\rho}\hat{\nu}}K_{ilj}^{\hat{\mu}\hat{\nu}}). \tag{15}$$

Using this decoupling we restrict ourselves only to the hopping processes in the investigated bands $\hat{\mu}$, $\hat{\nu}$. This is similar to the derivation of the alloy analogy solution for one-particle GFs (Kotrla and Drchal 1987). However, the remaining relevant processes are treated here in a simplified approximation.

Dividing now the approximated equation by $\omega-E^{A\hat{\mu}\hat{\nu}}$ and substituting the result into (8) we find equations for $K_{ij}^{\hat{\mu}\hat{\nu}}(\omega)$ with the correct atomic limit

$$\varphi_i^{\hat{\mu}\hat{\nu}}(\omega)K_{ij}^{\hat{\mu}\hat{\nu}}(\omega)=\delta_{ij}\chi_i^{\hat{\mu}\hat{\nu}}(\omega)-\sum_l(t_{li}^\mu K_{lij}^{\hat{\mu}\hat{\nu}}+t_{li}^\nu K_{ilj}^{\hat{\mu}\hat{\nu}}) \tag{16}$$

where

$$\frac{1}{\varphi_i^{\hat{\mu}\hat{\nu}}(\omega)}=\sum_{A\hat{\mu}\hat{\nu}}\frac{\langle N_i^{A\hat{\mu}\hat{\nu}}\rangle}{\omega-E^{A\hat{\mu}\hat{\nu}}}\qquad \chi_i^{\hat{\mu}\hat{\nu}}(\omega)=\varphi_i^{\hat{\mu}\hat{\nu}}(\omega)\sum_{A\hat{\mu}\hat{\nu}}\frac{\kappa_i^{A\hat{\mu}\hat{\nu}}}{\omega-E^{A\hat{\mu}\hat{\nu}}}. \tag{17}$$

Second, to calculate the three-site GFs appearing in (16) we use the following decoupling in equations (13)

$$\langle\langle n_{k\hat{\rho}}c_{i\hat{\mu}}^{+}c_{l\hat{\nu}}^{+}|R_j^{\hat{\mu}\hat{\nu}}\rangle\rangle\simeq\langle n_{k\hat{\rho}}\rangle\langle\langle c_{i\hat{\mu}}^{+}c_{l\hat{\nu}}^{+}|R_j^{\hat{\mu}\hat{\nu}}\rangle\rangle. \tag{18}$$

This has the character of an effective-medium approximation in the space of two-particle states. So we get the equation ($i\neq l$)

$$\Omega_{il}^{\hat{\mu}\hat{\nu}} K_{ilj}^{\hat{\mu}\hat{\nu}} = \kappa_{ilj}^{\hat{\mu}\hat{\nu}} - \sum_m (t_{mi}^{\mu} K_{mlj}^{\hat{\mu}\hat{\nu}} + t_{ml}^{\nu} K_{imj}^{\hat{\mu}\hat{\nu}}) \tag{19}$$

where

$$\Omega_{il}^{\hat{\mu}\hat{\nu}} = \omega + T_0^{\mu} + T_0^{\nu} + I^{\mu}\langle n_{i\mu-\sigma}\rangle + I^{\nu}\langle n_{l\nu-\sigma'}\rangle + \sum_{\rho\neq\mu} [U^{\rho\mu}\langle n_{i\rho-\sigma}\rangle + (U^{\rho\mu} - J^{\rho\mu})\langle n_{i\rho\sigma}\rangle] + \sum_{\rho\neq\nu} [U^{\rho\nu}\langle n_{l\rho-\sigma}\rangle + (U^{\rho\nu} - J^{\rho\nu})\langle n_{l\rho\sigma'}\rangle]. \tag{20}$$

5. Solution

A solution of a closed set of equations (16) and (19) can be found by expressing them in a matrix form in a linear space of the two-hole states spanned by a basis $\{|i\hat{\mu}l\hat{\nu}\rangle = c_{i\hat{\mu}}c_{l\hat{\nu}}|\text{vac.}\rangle\ |\forall i, l, \hat{\mu}, \hat{\nu}, \hat{\mu} \neq \hat{\nu}\}$; $|\text{vac.}\rangle$ is a ground state of the system. Then GFs $K_{ilj}^{\hat{\mu}\hat{\nu}}(\omega)$ are elements of matrix operator $\mathbf{K}(\omega)$ acting in this space and equations (16) and (19) can be rewritten in the form

$$(\mathbb{1}\boldsymbol{\Omega} - \mathbf{Pv} + \mathbf{W})\mathbf{K} = \mathbf{C}. \tag{21}$$

Here $\boldsymbol{\Omega}$ and $\mathbf{v}$ are diagonal operators,

$$v_{il}^{\hat{\mu}\hat{\nu}}(\omega) = \Omega_{il}^{\hat{\mu}\hat{\nu}} - \varphi_i^{\hat{\mu}\hat{\nu}}(\omega) \tag{22}$$

and

$$\mathbf{W} = \sum_{ilmn} \sum_{\hat{\mu}\hat{\nu}}{}' |i\hat{\mu}l\hat{\nu}\rangle(\delta_{ln}\, t_{mi}^{\mu} + \delta_{im} t_{nl}^{\nu})\langle m\hat{\mu}n\hat{\nu}| \tag{23}$$

$\mathbf{P}$ is a projector

$$\mathbf{P} = \sum_i \sum_{\hat{\mu}\hat{\nu}}{}' |i\hat{\mu}i\hat{\nu}\rangle\langle i\hat{\mu}i\hat{\nu}| \tag{24}$$

and

$$\langle i\hat{\mu}l\hat{\nu}|\mathbf{C}|j\hat{\nu}j\hat{\mu}\rangle = \delta_{il}\delta_{ij}\chi_i^{\hat{\mu}\hat{\nu}}(\omega) + (1-\delta_{il})\kappa_{ilj}^{\hat{\mu}\hat{\nu}}. \tag{25}$$

With the help of a resolvent $\mathbf{g}$ the solution of (21) is

$$\mathbf{K} = \mathbf{gC} \qquad \mathbf{g} = (\mathbb{1}\boldsymbol{\Omega} + \mathbf{W} - \mathbf{Pv})^{-1}. \tag{26}$$

If we define an unperturbed resolvent $\mathbf{g}_0$ and a T-matrix $\mathbf{T}$

$$\mathbf{g}_0 = [\mathbb{1}\boldsymbol{\Omega} + \mathbf{W}]^{-1} \qquad \mathbf{T} = \mathbf{Pv}/(1 - \Psi_0\mathbf{v}) \qquad \Psi_0 = \mathbf{Pg}_0\mathbf{P} \tag{27}$$

(here $\mathbf{P}/\mathbf{A}$ means the inverse in a subspace $\{\mathbf{P}\}$ and it holds that $\mathbf{PTP} = \mathbf{T}$) we get

$$\mathbf{Pg} = [\mathbf{P}/(1 - \Psi_0\mathbf{v})]\mathbf{g}_0. \tag{28}$$

This is sufficient for the determination of the elements K_{iij}. In the following we confine

ourselves to a homogeneous ground state $\langle n_{i\hat{\mu}}\rangle = n_{\hat{\mu}}$ and then we find the solution for the diagonal elements of GFs using a momentum representation in the form

$$K_{ii}^{\hat{\mu}\hat{\nu}}(\omega) = \frac{1}{N^2}\sum_{kl}\frac{g_0^{\hat{\mu}\hat{\nu}}(l, k-l, \omega)}{1-\psi_0^{\hat{\mu}\hat{\nu}}(k\omega)v^{\hat{\mu}\hat{\nu}}(\omega)}[\chi_i^{\hat{\mu}\hat{\nu}}(\omega)+n_{l\hat{\mu}}+n_{k-l\hat{\nu}}-n_{\hat{\mu}}-n_{\hat{\nu}}] \tag{29}$$

where

$$g_0^{\hat{\mu}\hat{\nu}}(k, l, \omega) = [\Omega^{\hat{\mu}\hat{\nu}}(\omega)+\varepsilon^{\mu}(-k)+\varepsilon^{\nu}(-l)]^{-1}$$

$$\psi_0^{\hat{\mu}\hat{\nu}}(k, \omega) = \frac{1}{N}\sum_{p} g^{\hat{\mu}\hat{\nu}}{}_0\ (p, k-p, \omega) \tag{30}$$

$$n_{k\hat{\mu}} = \sum_i \exp[-ik\cdot(R_i-R_j)]\langle c_{i\hat{\mu}}^{+}c_{j\hat{\mu}}\rangle \qquad \varepsilon^{\mu}(k) = \sum_i \exp[-ik\cdot(R_i-R_j)]t_{ij}^{\mu}.$$

To complete the solution we have to know the correlation functions $\mathcal{H}_i^{A\,\hat{\mu}\hat{\nu}}$, $\varphi_i^{\hat{\mu}\hat{\nu}}$ and the correlation functions $n_{k\hat{\mu}}$. The latter can be determined with the help of spectral relations (Zubarev 1960) from some approximate solution for one-particle GFs $\langle\langle c_{i\hat{\mu}}|c_{j\mu}^{+}\rangle\rangle$. For the former we could either try to use some further approximation of the type

$$\langle N_i^{A\,\hat{\mu}\hat{\nu}}\rangle \simeq \bigcap_{\hat{\rho}\neq\hat{\mu},\hat{\nu}}\langle n_{i\hat{\rho}}^{\alpha\hat{\rho}}\rangle \tag{31}$$

which is valid for weak correlations and then again to employ only the one-particle GFs, or we could employ the higher-order GFs, like $\langle\langle N_i^{A\,\hat{\mu}}c_{i\hat{\mu}}|c_{j\hat{\mu}}^{+}\rangle\rangle$ (Kotrla and Drchal 1987) to determine the correlation functions needed.

6. Limiting cases

Here we first consider three limiting cases in which it is possible to obtain an exact solution for the GFs K.

(*a*) Band limit ($I^{\mu}=U^{\mu\nu}=J^{\mu\nu}=0$). The equations for $K_{ij}^{\hat{\mu}\hat{\nu}}$ (including $i=l$) are now closed and with the help of the momentum representation we get

$$K_{ii}^{\hat{\mu}\hat{\nu}}(\omega) = \frac{1}{N^2}\sum_{kl}\frac{n_{l,\hat{\mu}}+n_{k-l,\hat{\nu}}-1}{\omega+E^{\mu}(-l)+E^{\nu}(l-k)} \qquad E^{\mu}(k) = T_0^{\mu}+\varepsilon^{\mu}(k). \tag{32}$$

(*b*) Atomic limit ($t_{ij}=0$). From (8) and (9) we have

$$K_{ii}^{\hat{\mu}\hat{\nu}}(\omega) = \sum_{A\,\hat{\mu}\hat{\nu}}\frac{K_i^{A\,\hat{\mu}\hat{\nu}}}{\omega-E^{A\,\hat{\mu}\hat{\nu}}}. \tag{33}$$

(*c*) Completely filled bands ($c_{j\hat{\rho}}^{+}|\text{vac.}\rangle = 0$). In this case the problem reduces to the two-particle problem (generalisation of the work of Sawatzky 1977) and the solution is

$$K_{ii}^{\hat{\mu}\hat{\nu}}(\omega) = \frac{1}{N}\sum_{k}\frac{\xi^{\hat{\mu}\hat{\nu}}(k)}{1-[\delta_{\mu\nu}I^{\mu}+(1-\delta_{\mu\nu})(U^{\mu\nu}-\delta_{\sigma,\sigma'}J^{\mu\nu})]\xi^{\hat{\mu}\hat{\nu}}(k)}$$

$$\xi^{\hat{\mu}\hat{\nu}}(k) = \frac{1}{N}\sum_{p}\Bigg(\omega+I^{\mu}+I^{\nu}+\sum_{\rho\neq\mu,\nu}(2U^{\mu\rho}+2U^{\nu\rho}-J^{\mu\rho}-J^{\nu\rho}) \tag{34}$$

$$+(1-\delta_{\mu\nu})(4U^{\mu\nu}-2J^{\mu\nu})+E^{\mu}(-p)+E^{\nu}(p-k)\Bigg)^{-1}.$$

It can be easily seen that our solution (29) is correct in all these three limits. It also has the correct first moment in energy ω.

The fourth special case is that of the single-band Hamiltonian, i.e., the usual Hubbard Hamiltonian.

(*d*) One band ($L = 1$). In this case the solution (29) is substantially simplified. The functions v and χ do not depend on ω and we obtain the solution (cf. Drchal 1989)

$$K_{ii}^{\sigma-\sigma}(\omega) = \frac{1}{N^2}\sum_{kl}\frac{n_{l,\sigma}+n_{k-l,-\sigma}-1}{\omega+E(-l)+E(l-k)+\mathrm{In}}\frac{1}{1-\mathrm{I}(n-1)\psi_0(\boldsymbol{k},\omega)}$$
$$\psi_0(\boldsymbol{k},\omega) = \frac{1}{N}\sum_{p}[\omega+E(-p)+E(p-k)+\mathrm{In}]^{-1} \qquad n = \langle n_{i+}+n_{i-}\rangle. \tag{35}$$

7. Case of degenerate bands

The solution is much more simple for degenerate bands $t_{ij}^{\mu} = t_{ij}$, $T_0^{\mu} = T_0$, $I^{\mu} = I$, $U^{\mu\nu} = U$, $J^{\mu\nu} = J$, and we shall confine ourselves to the paramagnetic case $n_{\hat{\rho}} = \tilde{n} = n/2L$; n is the total number of electrons. We have three different possibilities for the GFs K: (*a*) $\mu = \nu, \sigma' = -\sigma$; (*b*) $\mu \neq \nu, \sigma' = -\sigma$ and (*c*) $\mu \neq \nu, \sigma' = \sigma$. The situation simplifies even further, if we put $I = U, J = 0$. Let us consider here as an example this particular choice. Then the three above cases are equivalent and the solution (29) takes the form

$$K_{ii}(\omega) = \frac{1}{N^2}\sum_{kl}\frac{g_0(l,k-l,\omega)}{1-\psi_0(\boldsymbol{k},\omega)\nu(\omega)}[\chi(\omega)+n_l+n_{k-l}-2\tilde{n}] \tag{36}$$

where

$$g_0(\boldsymbol{k},\boldsymbol{l},\omega) = [\Omega+\varepsilon(-\boldsymbol{k})+\varepsilon(-\boldsymbol{l})]^{-1}$$
$$\Omega = \omega + 2T_0 + 2(2L-1)\tilde{n}U \qquad v(\omega) = \Omega - \varphi(\omega). \tag{37}$$

Here $\psi_0(\boldsymbol{k},\omega)$, n_l, $\varepsilon(\boldsymbol{k})$ are the same quantities as in (30), but now they are identical for all values of $\hat{\mu}$, $\hat{\nu}$. The functions $\chi(\omega)$ and $\varphi(\omega)$ are given in terms of the two types of correlation functions N_p and M_p in the following way

$$\frac{1}{\varphi(\omega)} = \sum_{p=0}^{2L-2}\frac{N_p C^{2L-2}}{\omega - E_p} \tag{38}$$

$$\chi(\omega) = \varphi(\omega)\sum_{p=0}^{2L-2}\frac{(2M_{p+1}-N_p)C_p^{2L-2}}{\omega-E_p} \tag{39}$$

where

$$E_p = -2T_0 - U(1+2p) \qquad C_p^q = \binom{q}{p}. \tag{40}$$

The correlation functions N_p and M_p are

$$N_p = \langle n_1 \ldots n_p(1-n_{p+1})\ldots(1-n_{2L-2})\rangle, \qquad p = 0,\ldots,2L-2 \tag{41}$$

$$M_p = \langle n_1 \ldots n_p(1-n_{p+1})\ldots(1-n_{2L-1})\rangle, \qquad p = 0,\ldots,2L-1 \tag{42}$$

where $a = 1,\ldots,2L$ in n_a labels combined band and spin indices (μ, σ) and all operators are taken at the same site.

To determine the Auger spectra from solution (36) we have overcome two difficulties. The first is technical in character. In the evaluation of formula (36) we have to carry out the $2d$-dimensional integration in the momentum space (d is the dimension of the space). In order to reduce the amount of the computational work we introduce some additional approximations, namely a scaling-factor approximation, an interpolating approximation and the semi-elliptical one-particle DOS (Drchal 1989).

The second complication is the determination of higher-order correlation functions M_p, N_p. The functions M_p can be calculated, for example, using the alloy analogy solution for one-particle GFs (Kotrla and Drchal 1987, Tréglia *et al* 1981a) in a self-consistent way, and the functions N_p are then easily obtained with the help of relations

$$N_p = M_p + M_{p+1}. \tag{43}$$

This work is still in progress, but here we employ as a first step a cruder approximation for correlation functions.

It turns out that the Hartree–Fock approximation (31) is inappropriate even for weak interactions, because it produces the unphysical zeros in the density of two-particle states. Instead, we start from the atomic limit, in which the correlation functions can be calculated exactly.

In the atomic limit the Hamiltonian reduces to

$$H = \sum_i h_i, \qquad h_i = \sum_{\hat{\mu}} T_0 n_{i\hat{\mu}} + (U/2) \sum_{\hat{\mu}\hat{\nu}}{}' n_{i\hat{\mu}}\, n_{i\hat{\nu}}. \tag{44}$$

h_i describes an atom with energy levels

$$e_q = qT_0 + (U/2)q(q-1), \tag{45}$$

where $q = 0, \ldots, 2L$ is the number of electrons in the corresponding eigenstate. The level e_q has a degeneracy $\binom{2L}{q}$. Here, in our simple example, atomic terms d^n and their corresponding energies have a simple form. However, a more realistic case can be described using the general Hamiltonian (3). Hence we could get a model for accounting of the quasi-atomic spectra using the atomic Hamiltonian. Here we take this limit as a starting point for the calculation of the correlation functions.

The Auger process corresponds to the transition from the state with $q+2$ electrons to the state with q electrons, with the change of energy

$$e_q - e_{q+2} = -2T_0 - U(1+2q) = E_q. \tag{46}$$

However, not all these peaks appear in the spectra. In the atomic limit only four of them may have a non-zero probability. In addition to the functions M_p, N_p we define the functions L_p

$$L_p = \langle n_1 \ldots n_p (1-n_{p+1}) \ldots (1-n_{2L}) \rangle \qquad p = 0, \ldots, 2L. \tag{47}$$

In the atomic limit there are only two non-zero L_p (cf. Tréglia *et al* 1981a)

$$L_{p_0} = (p_0 + 1 - n)/C_{p_0}^{2L} \qquad L_{p_0+1} = (n - p_0)/C_{p_0+1}^{2L} \tag{48}$$

where p_0 is the integer part of n. Then the M_p are obtained using the relations

$$M_p = L_p + L_{p+1}. \tag{49}$$

Therefore, the Auger spectrum exhibits at most four peaks in the atomic limit.

With this crude approximation for the correlation functions M_p, N_p and with the previously mentioned additional approximations we have calculated the spectra in the

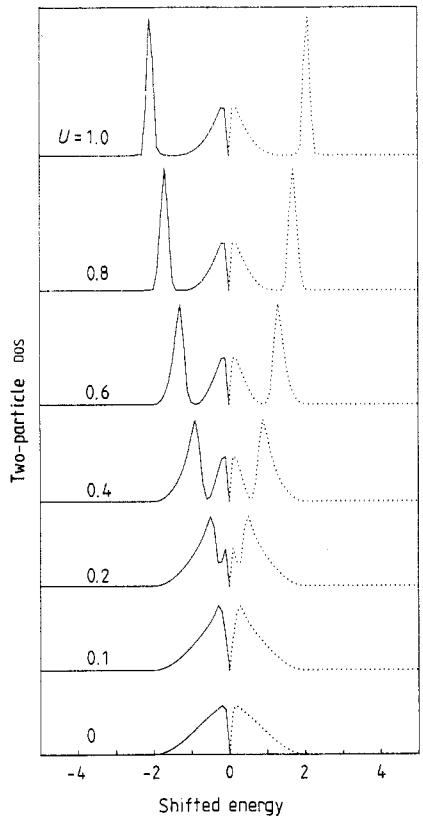

Figure 1. Numerical illustration of the two-hole, i.e., Auger (full curves) and the two-electron (dotted curves) spectra for the occupation $n = 5.0$ and different strengths of the interaction U.

case of five bands ($L = 5$). They are plotted for selected values of the occupation number n and for increasing values of the interaction U in figures 1–3 against the shifted energy variable $\Omega = \omega + 2(2L - 1)\tilde{n}U$ ($T_0 = 0$). The unperturbed band width is constant $W = 2$.

The energy $2E_F$ divides the two-hole and two-electron spectra (the small peaks which appear in the neighbourhood of the energy $2E_F$ in figure 2 are an artifact of the additional approximations used in the numerical calculation).

In figure 1, for the half-filled case ($n = 5$), the electron–hole symmetry of our solution is visible. With the increasing occupancy n, the number of the two-hole excitations increases and the number of the two-electron excitations decreases.

Numerical results clearly demonstrate the change from the band-like behaviour to the quasi-atomic spectra, with the increasing strength of the interaction U. For $U = 0$ we have the self-convolution of one-particle density of states. The spectra for $U = 1$ are already quite similar to the Lorentzian broadened spectra calculated in the atomic limit. In addition to large atomic peaks, however, our solution also contains smaller peaks of band origin situated in the neighbourhood of energy $2E_F$. With increasing U outer and inner peaks develop. While the outer peaks have large shift in energy the inner ones have almost no shift. The transition to quasi-atomic behaviour is also evident for $n = 5$, in contrast with the single-band case, in which the Auger spectra for the half-filled case remain band-like even for large U. As expected in the multi-band case, quasi-atomic behaviour appears for substantially weaker interactions than in the single-band model.

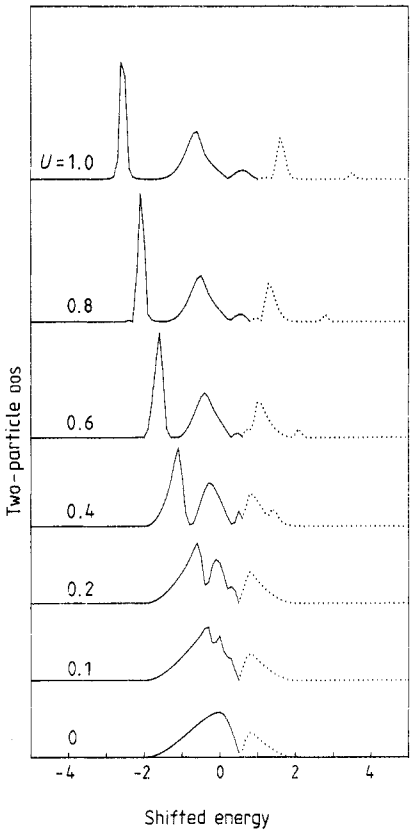

Figure 2. As figure 1, but for $n = 7.5$.

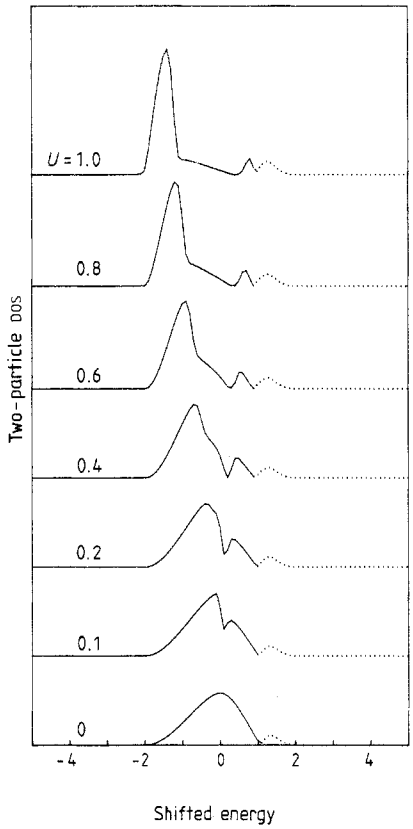

Figure 3. As figure 1, but for $n = 9.0$.

8. Conclusion

Using the formalism of atomic operators and the method of decoupling for Zubarev GFs we have derived new solutions for GFs, relevant for the calculation of Auger spectra in the case of multi-band Hubbard Hamiltonian. It can be applied to arbitrary hole concentration and to any strength of interactions and also to the non-degenerate bands. Our solution is exact in the band limit, in the atomic limit, and also in the limit of completely filled bands.

As an example we considered the special case of degenerate bands and, as an illustration, we calculated Auger spectra for a model with five bands using some additional approximations. The numerical results demonstrate the transition from band-like spectra to quasi-atomic spectra with the characteristic term structure.

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