On the Electronic Structure of Transition Metal Carbonitrides, Carboxides, and Oxinitrides. I. Theoretical Approach

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On the Electronic Structure
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I. Theoretical Approach

By

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In Part I of the paper the theoretical approach as used for a study of the electronic structure of TiC_xN_{1-x}, TiC_xO_{1-x}, and TiN_xO_{1-x} (Part II) and for the calculation of the "4f"-binding energies in HfC_xN_{1-x} (Part III) is summarized. In particular Part I consists of a collection of formulas comprising the main aspects of the relativistic KKR-coherent potential approximation (KKR-CPA) especially with respect to its real space single site scattering (averaged t-matrix, ATA) or multiple-scattering (Cluster CPA) approximations as well as with respect to the angular momentum dependent local density of states and intensities for X-ray emission.

Im ersten Teil dieser Arbeit wird der theoretische Ansatz zusammengefaßt, der den beiden folgenden Teilen, nämlich der Beschreibung der elektronischen Struktur von TiC_xN_{1-x}, TiC_xO_{1-x} und TiN_xO_{1-x}, sowie der Berechnung der "4f"-Bindungsenergien in HfC_xN_{1-x}, zu Grunde liegt. In diesem Teil wird die relativistische KKR-coherent-potential-Approximation (KKR-CPA) beschrieben, vor allem in Hinblick auf Einzentrenstreuungs- (averaged t-Matrix, ATA) und Mehrzentrenstreuungs- (Cluster-CPA)-Näherungen im reellen Raum, sowie in Hinblick auf drehmomentabhängige lokale Zustandsdichten und Röntgenemissionsintensitäten.

1. Introduction

Because of their unusual macroscopic physical properties, refractory phases became a rather well studied class of compounds (for a review see [1]). Though still some aspects deserve further considerations, it seems that by now for a wide range of carbides, nitrides, and oxides the problem of the electronic structure is fairly settled. The theoretical methods used were either within a band model (APW, KKR, etc.) or based on cluster approaches (SW-method, Lloyds density of states formulation). A good deal of these calculations were performed self-consistently in order to account for charge transfer effects. For quite a number of compounds, theoretical results were compared with soft X-ray emission spectra and/or XP (X-ray photoemission) spectra and found to be in reasonably good agreement with the experimental data. However, most of these calculations described the electronic structure of the ideal stoichiometric binary phases, only in very few cases the virtual crystal approximation was employed to discuss effects of non-stoichiometry.

Concomitantly for the electronic structure of substitutional alloys theoretical considerations were presented both within a tight-binding description and a multiple-scattering approach and used successfully to calculate the density of states and related quantities for metallic alloys (for a review see [2, 3]).

The aim of the present paper is to combine methods usually used for the description of alloy systems with the experience gained by means of ordinary band structure calculations for the binary phases MeX, Me being the transition metal and X the non-metal constituent. However, in order to proceed it seems necessary to partition the

paper into a theoretical part (Part I), where the theoretical basis is summarized and into parts connected with applications to different systems and different aspects of information on the electronic structure of these systems.

2. Theoretical Approach: the Relativistic KKR Coherent Potential Approximation

Since the KKR-CPA method [2 to 5], especially its relativistic version [6] has not yet become a standard theory, the following sections summarize briefly its main aspects. Although the main outline will rely on the relativistic description, for matters of completeness the main quantities are defined also in the non-relativistic limit. Section 2.1 presents relativistic multiple scattering in real space, Section 2.2 in reciprocal space. Sections 2.3 and 2.4 summarize the CPA, the Cluster CPA, and the ATA (averaged t-matrix approximation), whereas in Sections 2.5 and 2.6 "physical observables" such as the DOS (density of states) and the intensity of soft X-ray emission are formulated.

2.1 Relativistic multiple scattering and the scattering path operator

Let H be the Dirac Hamiltonian in the following eigenvalue problem:

$$H \left| \Psi \right\rangle = W \left| \Psi \right\rangle , \qquad H = \boldsymbol{\alpha} \cdot \boldsymbol{p} + (\beta + V) I_4 , \tag{1}$$

where W is the total energy of the relativistic electron, $\boldsymbol{p}$ the momentum operator

$$W = p_0 , \qquad W^2 = p^2 + 1 , \tag{2}$$

and where $\boldsymbol{\alpha}$ and β are defined as follows:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} , \qquad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix} , \tag{3}$$

σ being a vector consisting of the Pauli spin matrices and I_n being an n-dimensional unit matrix.

The solutions $\left| \Psi \right\rangle$ are given in terms of the Lippmann-Schwinger equation as

$$\left| \Psi \right\rangle = \left| \Phi_0 \right\rangle + G_0^+ T \left| \Phi_0 \right\rangle , \tag{4}$$

where G_0^+ is the resolvent of the unperturbed Dirac Hamiltonian H_0

$$H_0 = \boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta , \tag{5}$$

$$G_0^+ = \lim_{\varepsilon \to 0} (p_0 - H_0 + i\varepsilon)^{-1} , \tag{6}$$

and $\left| \Phi_0 \right\rangle$ is an eigenfunction of H_0. The transition operator T is itself given by the following Lippmann-Schwinger equation of 4×4 matrix operators:

$$T = V I_4 + T G_0^+ V . \tag{7}$$

By assuming V to be a superposition of individual local, spin-independent potential operators V_i at positions $\boldsymbol{R}_i$

$$\left\langle \boldsymbol{r} \right| V = \sum_i \left\langle \boldsymbol{r} - \boldsymbol{R}_i \right| V_i , \tag{8}$$

such that the domains of any pair of such operators V_i are disjoint in the tensorial space of spin and configuration, T can be written as a sum of scattering path operators τ^{ij}

$$T = \sum_{i,j} \tau^{ij} , \tag{9}$$

$$\tau^{ij} = t_i \delta_{ij} + \sum_{k \neq i} t_i G^{ik} \tau^{kj} , \tag{10}$$

$$t_i = V_i I_4 + V_i G_0^+ t_i , \tag{11}$$

where G^{ik} is the spin and configuration representative of the incomplete structural Green's function [7].

Let the set of operators V_i be represented by a system of non-overlapping central field potentials, i.e. let V be a potential of muffin-tin type

$$V_i(\boldsymbol{r}_i) = \begin{cases} V_i(r_i); & r_i = |\boldsymbol{r}_i| \leqq R_S^i , \\ 0; & \text{otherwise,} \end{cases} \tag{12}$$

$$\boldsymbol{r}_i = \boldsymbol{r} - \boldsymbol{R}_i ,$$

then the corresponding individual Dirac Hamiltonians H_i satisfy the following commutation rules:

$$\left. \begin{aligned} &[H_i, J^2]_- = [H_i, J_z]_- = [H_i, S^2]_- = [H_i, K]_- = 0 , \\ &K = \beta(1 + \boldsymbol{\sigma} \cdot \boldsymbol{L}) , \end{aligned} \right\} \tag{13}$$

$\boldsymbol{L}$ being the angular momentum operator. Because of the matrix structure of β solutions to a particular H_i will be block-diagonal fourfold spinors and an angular momentum representation of the scattering path operator can be given in terms of spin-spherical harmonics

$$\langle \boldsymbol{r} \mid Q \rangle = \langle \boldsymbol{r} \mid \chi_\varkappa^\mu \rangle = \sum_{s=\pm 1/2} C(l\,\tfrac{1}{2}\,j; \mu - s, s) \langle \boldsymbol{r} \mid l, \mu - s \rangle \, \Phi(s) , \tag{14}$$

where the coefficients $C(l\,\tfrac{1}{2}\,j; \mu - s, s)$ are Clebsch-Gordan coefficients [8] and $\langle \boldsymbol{r} \mid L \rangle = \langle \boldsymbol{r} \mid lm \rangle$ is a spherical harmonic.

By taking the "on the energy shell" momentum representation of (10) and using the following angular momentum representations for the structural Green's function and the individual single-site t-operators:

$$G^{ik} = \sum_{Q, Q'} G_{QQ'}^{ik}(p) \, |\Psi_Q\rangle \langle \Psi_{Q'}| , \tag{15}$$

$$t^i = \sum_{Q, Q'} t_{QQ'}^i(p) \, |\Psi_Q\rangle \langle \Psi_{Q'}| , \tag{16}$$

$$|\Psi_Q\rangle = \begin{pmatrix} |l\varkappa\mu\rangle \\ \dfrac{ipS_\varkappa}{p_0 + 1} |\bar{l} - \varkappa\mu\rangle \end{pmatrix} , \tag{17}$$

where

$$\left. \begin{aligned} &\langle \boldsymbol{r} \mid l\varkappa\mu\rangle = \langle pr \mid \mathrm{j}_l \rangle \langle \boldsymbol{r} \mid Q \rangle = \mathrm{j}_l(pr) \langle \boldsymbol{r} \mid Q \rangle , \\ &l = \begin{cases} \varkappa; & \varkappa > 0 \\ -(\varkappa + 1); & \varkappa < 0 , \end{cases} \qquad \bar{l} = \begin{cases} \varkappa - 1; & \varkappa > 0 \\ -\varkappa; & \varkappa < 0 , \end{cases} \end{aligned} \right\} \tag{18}$$

$$S_\varkappa = \varkappa \, |\varkappa|^{-1} , \tag{19}$$

and $\mathrm{j}_l(x)$ is a spherical Bessel function, the following set of equations for the scattering path operator $\tau^{ij}(p)$ is obtained:

$$\tau_{Q_1 Q_2}^{ij}(p) = t_{Q_1 Q_2}^i(p) \, \delta_{ij} + \sum_{k \neq i} \sum_{Q_3, Q_4} t_{Q_1 Q_3}^i(p) \, G_{Q_3 Q_4}^{ik}(p) \, \tau_{Q_4 Q_2}^{kj}(p) . \tag{20}$$

For a spherically symmetric potential $V_i(r_i)$ $t_{QQ'}^i(p)$ is diagonal in Q and is determined by the $\varkappa$-like phase shift $\delta_\varkappa^i(p)$

$$\left. \begin{aligned} &t_{QQ'}^i(p) = \delta_{QQ'} t_Q^i(p) , \\ &t_Q^i(p) = -[p(p_0 + 1)]^{-1} \sin \delta_\varkappa^i(p) \, \mathrm{e}^{i\delta_\varkappa^i(p)} , \end{aligned} \right\} \tag{21}$$

which is given by the following relation:

$$\tan \delta_\varkappa^i(p) = \left(\frac{f_\varkappa^i(r) \langle pr \mid \mathrm{j}_l \rangle - \dfrac{S_\varkappa p}{p_0 + 1} g_\varkappa^i(r) \langle pr \mid \mathrm{j}_{\bar{l}} \rangle}{f_\varkappa^i(r) \langle pr \mid \mathrm{n}_l \rangle - \dfrac{S_\varkappa p}{p_0 + 1} g_\varkappa^i(r) \langle pr \mid \mathrm{n}_{\bar{l}} \rangle} \right)_{r = R_S^i} , \tag{22}$$

$f_\varkappa^i(r)$ and $g_\varkappa^i(r)$ being the solutions of the radial part of the Dirac equation

$$\left. \begin{aligned} \frac{\mathrm{d}g_\varkappa^i(r)}{\mathrm{d}r} - (1 - \varkappa) \frac{g_\varkappa^i(r)}{r} - (p_0 + 1 - V_i) f_\varkappa^i(r) = 0 , \\[2mm] \frac{\mathrm{d}f_\varkappa^i(r)}{\mathrm{d}r} + (1 - \varkappa) \frac{f_\varkappa^i(r)}{r} + (p_0 - 1 - V_i) g_\varkappa^i(r) = 0 , \end{aligned} \right\} \tag{23}$$

and $\langle pr \mid \mathrm{n}_l \rangle$ being a spherical Neumann function.

The matrix $G_{QQ'}^{ik}(p)$ in (15) is given by

$$G_{QQ'}^{ik}(p) = (B_{QQ'}^{ik}(p) + ip\delta_{QQ'}\delta_{ik}) (p_0 + 1) . \tag{24}$$

By neglecting terms of the order c^{-2} (c speed of light) in comparison with unity, i.e. by approximating $p(p_0 + 1)$ by p, the matrix $B_{QQ'}^{ik}(p)$ can be obtained from its non-relativistic counterpart $A_{LL'}^{ik}(p)$, $L = (lm)$ by means of the following transformation [9]:

$$B_{QQ'}^{ik}(p) = \sum_{s = \pm 1/2} C(l j \tfrac{1}{2}; \mu - s, s) A_{LL'}^{ik}(p) C(l' j' \tfrac{1}{2}; \mu' - s, s) , \tag{25}$$

where $A_{LL'}^{ik}(p)$ is the usual matrix of structural constants [10] in the non-relativistic multiple-scattering approach.

Applying (21) and having in mind (25), equation (20) can be written as follows:

$$\sum_k \sum_{Q''} \{ t_Q^i(p)^{-1} \delta_{QQ''}\delta_{ik} - G_{QQ''}^{ik}(p) \} \tau_{Q''Q'}^{kj}(p) = \delta_{ij}\delta_{QQ'} , \tag{26}$$

whereby the non-relativistic limit of (26) is given by the usual set of equations for the scattering path operator [3]

$$\sum_k \sum_{L''} \{ t_L^i(p)^{-1} \delta_{ik}\delta_{LL''} - G_{LL''}^{ik}(p) \} \tau_{L''L'}^{kj}(p) = \delta_{ij}\delta_{LL'} . \tag{27}$$

In this case $t_L^i(p)$ and $G_{LL'}^{ik}(p)$ are given by

$$t_l^i(p) = -(p)^{-1} \sin \delta_l^i(p) \, \mathrm{e}^{i\delta_l^i(p)} , \tag{28}$$

$$G_{LL'}^{ik}(p) = A_{LL'}^{ik}(p) + ip\delta_{ik}\delta_{LL'} \tag{29}$$

with $p = W^{1/2}$ and $\delta_l^i(p)$ being the l-like non-relativistic phase shift for the i-th scatterer.

2.2 Multiple scattering in reciprocal space

For ideal crystals the scattering path operator is invariant under transformations $[\varepsilon \mid \boldsymbol{R}_i]$ of the translational group, where ε denotes a unit rotational operation and $\boldsymbol{R}_i$ an operator corresponding to a vector of the real lattice.

Let P_k be a projection operator for the k-th irreducible ray representation $D^k(\varepsilon \mid \boldsymbol{R}_i)$ of the translational group of the order $|T|$

$$P_k = |T|^{-1} \sum_{(\varepsilon \mid \boldsymbol{R}_i)} D^k(\varepsilon \mid \boldsymbol{R}_i)^* [\varepsilon \mid \boldsymbol{R}_i] , \tag{30}$$

$$\sum_k P_k = 1 , \tag{31}$$

then the following operation corresponds precisely to a lattice Fourier transform, if $D^k(\varepsilon \mid \boldsymbol{R}_i)$ is an irreducible vector representation of the translational group

$$
\begin{aligned}
\tau^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j; p) = \tau^{ij}(p) &= \sum_{k,k'} P_k \tau^{ij}(p)\, P_{k'} \\
&= \sum_k P_k \tau^{ij}(p)\, P_k = \sum_k |T|^{-2} \sum_{\boldsymbol{R}_i, \boldsymbol{R}_j} \mathrm{e}^{-ik(\boldsymbol{R}_i - \boldsymbol{R}_j)}\, \tau^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j; p) \\
&= |T|^{-1} \sum_k \tau^{ij}(\boldsymbol{k}, p)\,,
\end{aligned}
\tag{32}
$$

where for $\tau^{ij}(\boldsymbol{k}, p)$ i and j refer to the positions $\boldsymbol{a}_i$ of the scatterers in the unit cell.

For a particular (wave) vector $\boldsymbol{k}$, the corresponding equations for $\tau^{ij}(\boldsymbol{k}, p)$ follow from (26):

$$
\sum_{k,Q''} \{ t_Q^i(p)^{-1}\, \delta_{ik}\delta_{QQ''} - G_{QQ''}^{ik}(\boldsymbol{k}, p) \}\, \tau_{Q''Q'}^{kj}(\boldsymbol{k}, p) = \delta_{ij}\delta_{QQ'}\,,
\tag{33}
$$

whereby $G_{QQ'}^{ik}(\boldsymbol{k}, p)$ are the relativistic structure constants as given by Onodera and Okazaki [9]. The poles of the $\boldsymbol{k}$-th component of the scattering path operator correspond to the zeros of the relativistic KKR determinant [6, 9]

$$
|| t_\varkappa^i(p)^{-1}\, \delta_{ij}\delta_{\varkappa\varkappa'} - G_{QQ'}^{ij}(\boldsymbol{k}, p) || = 0\,,
\tag{34}
$$

the non-relativistic limit of which is defined in terms of equations (27) to (29):

$$
|| t_L^i(p)^{-1}\, \delta_{ij}\delta_{LL'} - G_{LL'}^{ij}(\boldsymbol{k}, p) || = 0\,.
\tag{35}
$$

From (33) one can see that the $\boldsymbol{k}$-th component of the scattering path operator $\tau_{QQ'}^{ij}(\boldsymbol{k}, p)$ is given by the inverse of the KKR matrix

$$
\tau_{QQ'}^{ij}(\boldsymbol{k}, p) = \{ [t(p)^{-1} - G(\boldsymbol{k}, p)]^{-1} \}_{QQ'}^{ij}
\tag{36}
$$

which then resolves $\tau_{QQ'}^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j; p)$ in terms of (32) or in terms of a Brillouin zone integral

$$
\tau_{QQ'}^{ij}(p) = \frac{1}{\Omega_{\mathrm{BZ}}} \int \mathrm{d}^3\boldsymbol{k}\, \{ [t(p)^{-1} - G(p, \boldsymbol{k})]^{-1} \}_{QQ'}^{ij}\,.
\tag{37}
$$

Since the single-site scattering amplitudes $f_\varkappa^i(p)$ are defined as

$$
f_\varkappa^i(p) = -p t_\varkappa^i(p)
\tag{38}
$$

in the following both quantities $f_\varkappa^i(p)$ and $t_\varkappa^i(p)$ will be referred to as "scattering amplitudes".

2.3 The coherent potential approximation

The aim of the CPA is to find an ordered lattice of effective scatterers such that the motion of an electron through the effective lattice resembles the averaged motion of an electron in the random lattice. The effective scatterers are described by single-site t-matrices $t_{C,QQ'}(p)$, which are no longer diagonal in Q and which have to be determined by the scattering amplitudes $t_{A,QQ'}^{-1}(p)$ and $t_{B,QQ'}^{-1}(p)$ of the components A and B forming the random lattice.

In order to find the unknown $t_{C,QQ'}(p)$ one considers an $A(B)$ impurity at $\boldsymbol{R}_0$ (origin) of the coherent potential lattice. In this case the scattering is described by the $i = 0$ site diagonal element of the scattering path operator $\tau_{QQ'}^{A(B),ii}(p)$, which is given by [2, 3, 6]

$$
\tau_{QQ'}^{A(B),00}(p) = \{ [1 - (t_{A(B)}^{-1} - t_C^{-1})\, \tau^{C,00}]^{-1}\, \tau^{C,00} \}_{QQ'}\,,
\tag{39}
$$

where $\tau_{QQ'}^{C,00}(p)$ is defined in terms of equations (32) or (37) as the following Brillouin zone integral:

$$\tau_{QQ'}^{C,00}(p) = \frac{1}{\Omega_{BZ}} \int d^3\boldsymbol{k} \; \{[t_C^{-1}(p) - G(p, \boldsymbol{k})]^{-1}\}_{QQ'}^{00} . \tag{40}$$

Demanding that on the average such impurities do not scatter, i.e.

$$c\tau_{QQ'}^{A,00}(p) + (1 - c)\,\tau_{QQ'}^{B,00}(p) = \tau_{QQ'}^{C,00}(p) , \tag{41}$$

where c is the concentration of species A in the effective lattice, the unknown scattering amplitudes $t_{C,QQ'}^{-1}(p)$ are given by [6]

$$t_{C,QQ'}^{-1}(p) = ct_{A,QQ'}^{-1}(p) + (1 - c)\,t_{B,QQ'}^{-1}(p) +$$
$$+ \sum_{Q_1, Q_2} [t_{C,QQ_1}^{-1}(p) - t_{A,QQ_1}^{-1}(p)]\,\tau_{Q_1 Q_2}^{C,00}(p)\,[t_{C,Q_2 Q'}^{-1}(p) - t_{B,Q_2 Q'}^{-1}(p)] . \tag{42}$$

Equations (42) are the relativistic analogues to the non-relativistic CPA equations as given by Gyorffy and Stocks [3]. These equations have to be solved iteratively, whereby the Brillouin zone integral (40) must be calculated several times. Since the t-matrix has poles of the type $1/x$, this is no easy task. It should be noted that in the non-relativistic case this self-consistent procedure has been applied successfully to random metallic alloys [11].

In the case of random alloys of d-band metals, the above procedure (42) can be simplified substantially by restricting the angular momentum expansions to a maximum quantum number corresponding to $l \leq 2$ [6].

In order to avoid the Brillouin zone integral several approximate methods can be applied, namely (1) a single-site description, usually referred to as averaged t-matrix approximation (ATA), (2) a cluster-type multiple-scattering approach in the real lattice of effective scatterers, (3) the use of a sufficiently small order of the translational group.

2.4 The cluster CPA and the ATA method

Suppose the effective lattice can be represented by a cluster of effective scatterers. Let N be the total number of scatterers in the cluster and let $t_{C,QQ'}^i(p)^{-1}$ be the effective scattering amplitude at the site i, then the scattering path operator $\tau_{QQ'}^{C,ij}(p)$, where i and j refer to particular sites $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ with respect to the origin of the cluster, is given by

$$\sum_{k=1}^{N} \sum_{Q''} \{t_{C,QQ''}^i(p)^{-1} \delta_{ik} - G_{QQ''}^{ik}(p)\}\,\tau_{Q''Q'}^{C,kj}(p) = \delta_{ij}\delta_{QQ'} . \tag{43}$$

Let $\tau_{QQ'}^{C,00}(p)$ be the site-diagonal element of the scattering path operator referring to the origin $\boldsymbol{R}_0$ of the cluster, then the unknown scattering amplitudes $t_{C,QQ}^{-1}(p)$ can be obtained in terms of the CPA condition (42)

$$t_{C,QQ'}^{-1}(p) = \left(ct_{A,QQ'}^{-1}(p) + (1 - c)\,t_{B,QQ'}^{-1}\right) \delta_{QQ'} +$$
$$+ \sum_{Q_1, Q_2} [t_{C,QQ_1}^{-1}(p) - t_{A,QQ_1}^{-1}(p)\,\delta_{QQ_1}]\,\tau_{Q_1 Q_2}^{C,00}(p)\,[t_{C,Q_2 Q_1}^{-1}(p) - t_{B,Q_2 Q'}^{-1}(p)\,\delta_{Q_2 Q'}] . \tag{44}$$

In (44) explicit reference is given to the fact that the single-site t-matrices for the components are diagonal in Q.

Having solved (43) and (44) iteratively, the self-consistent cluster scattering amplitudes $t_{C,QQ'}^{-1}(p)$ can then be used as a very appropriate starting point for solving equations (40) to (42) or to calculate directly the density of states and related quantities (Section 2.5).

However, if even this approximate method to calculate the CPA equations is out of the range, then the number of scatterers N can be reduced to one, i.e. a single site description for the effective scattering amplitude can be applied:

$$t_{C,QQ'}(p) = \{ct_{A,QQ'}(p) + (1-c)\,t_{B,QQ'}(p)\}\,\delta_{QQ'}\,. \tag{45}$$

This approximation is usually called the averaged t-matrix approximation (ATA).

Within the ATA the effective scattering amplitudes are therefore simply given by

$$f_{C,\varkappa}(p) = \sum_i x_i \sin \delta_\varkappa^i(p)\, e^{i\delta_\varkappa^i(p)} = \frac{1}{2i} \sum_i x_i(e^{2i\delta_\varkappa^i(p)} - 1)\,, \tag{46}$$

where x_i is the molar fraction of the i-th component, $\sum x_i = 1$, and $\delta_\varkappa^i(p)$ is the corresponding phase shift (22). In terms of the optical theorem the inelasticity $\alpha_\varkappa^2(p)$ of the scattering process is related to the effective amplitude by

$$\alpha_\varkappa^2(p) = 1 + 4\{|f_{C,\varkappa}(p)|^2 - \operatorname{Im} f_{C,\varkappa}(p)\}\,. \tag{47}$$

Both, the effective scattering amplitude (46) and the inelasticity (47) are very useful quantities in a qualitative description of the electronic structure of effective lattices.

2.5 The integrated DOS, Bloch-like spectral functions, and ray-like spectral functions

Having solved the CPA equations (42) in one or the other way, the integrated DOS and related quantities can be calculated. In terms of the quantities discussed, the integrated DOS is given by [3, 6]

$$N(\varepsilon) = N_1(\varepsilon) - (\pi\Omega_{\mathrm{BZ}})^{-1} \int \mathrm{d}^3 k\, \operatorname{Im} \ln ||t_{C,QQ'}^i(\varepsilon)^{-1}\,\delta_{ij} - G_{QQ'}^{ik}(\mathbf{k}, \varepsilon)||\,, \tag{48}$$

where the more commonly used parameter $\varepsilon = p^2$ has replaced p and

$$N_1(\varepsilon) = N_0(\varepsilon) + \pi^{-1} \left\{ (1-c) \operatorname{Im} \ln \left\| \frac{t_{A,QQ'}^{-1}(\varepsilon) - \langle t_{QQ'}^{-1}(\varepsilon)\rangle}{t_{A,QQ'}^{-1}(\varepsilon) - t_{C,QQ'}^{-1}(\varepsilon)} \right\| + \right.$$
$$\left. + c \operatorname{Im} \ln \left\| \frac{t_{B,QQ'}^{-1}(\varepsilon) - \langle t_{QQ'}^{-1}(\varepsilon)\rangle}{t_{B,QQ'}^{-1}(\varepsilon) - t_{C,QQ'}^{-1}(\varepsilon)} \right\| \right\}, \tag{49}$$

$$\langle t_{QQ'}^{-1}(\varepsilon)\rangle = ct_{A,QQ'}^{-1}(\varepsilon) + (1-c)\,t_{B,QQ'}^{-1}(\varepsilon)\,, \tag{50}$$

and $N_0(\varepsilon)$ is the contribution of the free electrons. The second term in (48) refers to the KKR determinant as calculated with the obtained self-consistent or approximated effective scattering amplitude.

Referring to the following quantity:

$$N(\mathbf{k}, \varepsilon) = N_1(\varepsilon) - \pi^{-1} \operatorname{Im} \ln ||t_{C,QQ'}^i(\varepsilon)\,\delta_{ij} - G_{QQ'}^{ij}(\mathbf{k}, \varepsilon)|| \tag{51}$$

as integrated Bloch-like spectral function, then the DOS can be given most appropriately in terms of the energy derivatives of $N(\mathbf{k}, \varepsilon)$

$$n(\varepsilon) = \frac{\mathrm{d}N(\varepsilon)}{\mathrm{d}\varepsilon} = \Omega_{\mathrm{BZ}}^{-1} \int \mathrm{d}^3 k\, \frac{\mathrm{d}}{\mathrm{d}\varepsilon}\, N(\mathbf{k}, \varepsilon)$$
$$= \Omega_{\mathrm{BZ}}^{-1} \int \mathbf{k}\mathrm{d}^3\, n(\mathbf{k}, \varepsilon)\,. \tag{52}$$

For a finite translational group $n(\varepsilon)$ will be simply given by

$$n(\varepsilon) = |T|^{-1} \sum_{\boldsymbol{k}} n(\boldsymbol{k}, \varepsilon) .$$

Similarly a ray-like spectral function can be defined, which represents the DOS along a particular direction of the reciprocal space

$$\bar{n}(\hat{\boldsymbol{k}}, \varepsilon) = |T(\boldsymbol{k})|^{-1} \sum_{\boldsymbol{k}'} n(\boldsymbol{k}', \varepsilon)\, \delta(\hat{\boldsymbol{k}}', \boldsymbol{k}) \qquad (53)$$

where $\boldsymbol{k}''$ is an element of a particular ray k and $T(k)$ refers to the order of the translational group used to sample this ray.

2.6 Local $\varkappa$-like DOS and soft-X-ray emission

Considering only elastic scattering the site diagonal elements of the scattering path operator are related to the imaginary part of the Green's function (spin and configuration space representative of the resolvent of the Dirac Hamiltonian (1)) as follows:

$$\operatorname{Im} \langle \boldsymbol{r} \mid G^+(\varepsilon) \mid \boldsymbol{r}' \rangle = \sum_{Q, Q'} \varDelta_Q(\boldsymbol{r})\, \operatorname{Im} \tau_{QQ'}^{ii}(\varepsilon)\, \varDelta_{Q'}(\boldsymbol{r}_i') , \qquad (54)$$

where $\boldsymbol{r} = \boldsymbol{r}_i + \boldsymbol{R}_i$, $\boldsymbol{r}' = \boldsymbol{r}_i' + \boldsymbol{R}_i$ and $\varDelta_Q(\boldsymbol{r}_i)$ is given by

$$\varDelta_Q(\boldsymbol{r}_i) = -p[\sin \delta_\varkappa^i(\varepsilon)]^{-1} \langle \boldsymbol{r}_i \mid \varrho_Q(\varepsilon) \rangle . \qquad (55)$$

In (55) $|\varrho_Q(\varepsilon)\rangle$ is given in terms of a solution of (23)

$$\varrho_Q(\varepsilon) = \begin{Bmatrix} g_\varkappa(\varepsilon) \, |\varkappa\mu\rangle \\ if_\varkappa(\varepsilon) \, |-\varkappa\mu\rangle \end{Bmatrix} \qquad (56)$$

and is normalized according to single-site scattering [7]. The local DOS ($\boldsymbol{r}$ and $\boldsymbol{r}'$ refer to the same muffin-tin sphere) is then defined as

$$n^i(\varepsilon) = -\pi^{-1} \int_0^{R_S^i} r_i^2\, dr_i\, \langle \boldsymbol{r}_i| \operatorname{Im} G^+(\varepsilon) \, |\boldsymbol{r}_i'\rangle = \sum_\varkappa n_\varkappa^i(\varepsilon) , \qquad (57)$$

where $n_\varkappa^i(\varepsilon)$ is given by

$$n_\varkappa^i(\varepsilon) = -\pi^{-1} \varepsilon \big(\sin \delta_\varkappa^i(\varepsilon)\big)^{-2}\, N_\varkappa^i(\varepsilon) \sum_\mu \operatorname{Im} \tau_{\varkappa\mu, \varkappa\mu}^{ii}(\varepsilon) \qquad (58)$$

and $N_\varkappa^i(\varepsilon)$ is a radial normalization integral

$$N_\varkappa^i(\varepsilon) = \int_0^{R_S^i} [f_\varkappa^i(r_i, \varepsilon)^2 + g_\varkappa^i(r_i, \varepsilon)]^2\, r_i^2\, dr_i . \qquad (59)$$

These $\varkappa$-like local DOS $n_\varkappa^i(\varepsilon)$ are of some importance for a theoretical calculation of soft-X-ray emission spectra [12]. If the final state (core state) of the emission process is an eigenstate of the Dirac Hamiltonian (1) with energy ε_f and an eigenstate of J^2 with the eigenvalue $j(j + 1)$ (with respect to a particular central field region), then the matrix elements in (60) derived in terms of first order time dependent perturbation theory can be restricted to this particular scattering region

$$I_0(\omega) \approx \Delta\varepsilon\, S \sum_i |\langle i| \, H' \, |f\rangle|^2\, \delta(\varepsilon_\mathrm{f} - \varepsilon_\mathrm{i} + \hbar\omega) . \qquad (60)$$

In (60) $\Delta\varepsilon = \varepsilon_\mathrm{f} - \varepsilon_\mathrm{i}$, S denotes an average and summation over all unobservables and H' is the interaction Hamiltonian

$$H' = \boldsymbol{\alpha} \cdot \boldsymbol{A} , \qquad (61)$$

A being the vector potential of the radiation field. Considering only electric dipole transitions it can be shown [6, 12] that the intensity $I_0(\omega)$ is given by the following expression:

$$I_0(\omega) \sim \frac{4\pi}{3}(\Delta\varepsilon)^3 \sum_{j'} (2j+1) \begin{pmatrix} j & 1 & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2 R^i_{\varkappa\varkappa'}(\varepsilon_f,\varepsilon)^2 \times$$

$$\times N^i_{\varkappa'}(\varepsilon)^{-1} n^i_{\varkappa}(\varepsilon) \, \delta(\varepsilon_f + \hbar\omega - \varepsilon) , \tag{62}$$

where j refers to the core state, j' to the partial waves of the initial state, $\begin{pmatrix} j & 1 & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}$ are Wigner $3j$ symbols and

$$R^i_{\varkappa\varkappa'}(\varepsilon_f,\varepsilon) = \int_0^{R^i_S} [f^i_{\varkappa}(r_i, \varepsilon_f) f^i_{\varkappa'}(r_i, \varepsilon) + g^i_{\varkappa}(r_i, \varepsilon_f) g^i_{\varkappa'}(r_i, \varepsilon)] \, r^3_i \, dr_i . \tag{63}$$

If in terms of the transition energy $(\Delta\varepsilon)$ in the effective lattice at a site $\boldsymbol{R}_i$ a constituent of type α (A or B) is depicted, then $\tau^{ii}_{QQ'}(\varepsilon)$ in (58) has to be replaced by $\tau^{\alpha,ii}_{QQ'}(\varepsilon)$ as given by (39) [6].

With respect to soft X-ray emission the $\varkappa$-like DOS (58) are therefore of physical importance. The non-relativistic analogue of (62) is simply given [3, 13, 14] by the following set of formulas:

$$I_0(\omega) \sim \frac{4\pi}{3}(\Delta\varepsilon)^3 \sum_{l'} (2l+1) \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^i_{ll'}(\varepsilon_f, \varepsilon)^2 \, N^{-1}_{l'}(\varepsilon) \, n^i_{l'}(\varepsilon) \, \delta(\varepsilon_f + \hbar\omega - \varepsilon) ,$$

$$\tag{64}$$

$$R^i_{ll'}(\varepsilon_f, \varepsilon) = \int_0^{R^i_S} r^3_i [R^i_l(\varepsilon_f, r_i) \, R^i_{l'}(\varepsilon, r_i)] \, dr_i , \tag{65}$$

$$N^i_l(\varepsilon) = \int_0^{R^i_S} r^2_i [R^i_l(\varepsilon, r_i)]^2 \, dr_i , \tag{66}$$

$$n^i_l(\varepsilon) = -\pi^{-1}\varepsilon [\sin \delta^i_l(\varepsilon)]^{-2} \, N^i_l(\varepsilon) \sum_m \mathrm{Im} \, \tau^{ii}_{lm,lm}(\varepsilon) , \tag{67}$$

where $\delta^i_l(\varepsilon)$ are the non-relativistic phase shifts for the i-th scatterer.

The equations for the $\varkappa$- or l-like local DOS and for the soft X-ray intensity apply of course to both, to pure and effective lattices.

2.7 Discussion with respect to application

The relativistic KKR-CPA is of course not a very easy scheme to apply, since even for cubic lattices the use of cubic harmonics [15] does not yield diagonal or block-diagonal matrices for $t_{C,QQ'}(\varepsilon)$. Only in the case of alloys of d-band metals a more tractable scheme can be given [6]. Even then one would like to stick to only one composition of the effective lattice.

If a larger number of concentrations is of interest, it seems that approximate methods (Cluster CPA, ATA) are useful schemes to apply, although the information obtained will have inherent sources of errors. Depending therefore on the type of description one likes to give, the calculations have to be performed on a more or less advanced level.

From experience with cluster calculations for pure systems and cluster CPA calculations [16 to 18] it seems that in all cases, where either alloys of two strong scatterers (e.g. Cu and Ni) or one strong and one weak scatterer (e.g. Ni and Al) or relatively ionic compounds (e.g. oxides) are investigated, a first- or second-neighbour

cluster is sufficient to get fairly accurate effective scattering amplitudes. In cases of predominantly covalent compounds a cluster approach will be less satisfying.

If one is only interested in an overall description of a system, then the ATA method will give the quickest answers.

Disregardingly whether one uses a more or less advanced scheme, the problem of the construction of the muffin-tin potentials will remain. Since the presented theory is not self-consistent with respect to the applied potential field, the choice of the muffin-tin potential will be essential. It seems, therefore that in all cases, where the ordered or pure phases have been studied already in terms of some self-consistent band theory approach, the corresponding self-consistent potentials are the most appropriate basis for KKR-CPA investigations.

Whenever one of the components of the effective lattice shows considerable relativistic effects already within a single-site scattering description (phase shifts etc.) the application of the relativistic KKR-CPA scheme is of crucial importance [6]. For all other cases the simpler non-relativistic approach is sufficient. In the case of the ATA approach the actual effort for a relativistic calculation is roughly the same as in the non-relativistic case.

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