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Mixed-valence state treatment for x-ray emission spectra of cuprate superconductors

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Abstract. In the investigation reported here the system of all electrons in a solid is divided into two different subsystems. One of the subsystems consists of well localized electrons and the other of itinerant electrons, a division common for solids. Electron interchange between the subsystems is allowed. The expression for each matrix element of any operator acting upon electronic states can then be viewed as a sum of matrix elements corresponding to component subsystems and a hopping (hybridization) matrix element. It is clear that the basic representations for the subsystems can be freely and independently changed. After a general introduction the structure of an infinite matrix of the Hamiltonian is discussed and ways of simplifying it are mentioned. The theory is then applied after the conditions of a particular problem are detailed. The case is one of localized electrons described by only atomic-physics methods, but nevertheless elaborate ones. The algorithm and computer programs used in the calculations of matrix elements are specified. While dealing with the Cu 2p x-ray emission spectra (XES) intensity curves as an illustration, it is shown that such an ‘atom in an environment’ model comes close to the situation reported in experiment when the inner vacancy of an atom is filled up theoretically with electrons only from the ground state of a configuration with a vacancy.

1. Introduction

The individual properties of different atoms and ions are of varying importance in different models of solids. The interplay of intra- and interatomic interactions leads to a situation where electrons, once in a free atom bound to their own nucleus, either stay bound or become itinerant in a solid. The electrons closer to the nucleus more or less retain their localization, while the delocalization refers mainly to the outer shell electrons. Different energies are characteristic of those different groups of electrons, so different models and methods of investigation are applied for the localized and the itinerant electrons. This problem has been recently reviewed in a paper by Vonsovskiy and co-workers [1], where the physical basis is discussed in detail and a vast list of relevant literature is presented.

The formal subdivision of electrons in a many-particle quantum system into groups, each containing different kinds of electrons, leads one to the following expression for a wavefunction:

$$|A; N\rangle = \{A\} \sum_i \sum_{a_i, a'_i} |a_i; i\rangle |a'_i; N-i\rangle \langle a_i, a'_i | A \rangle \quad (1.1)$$

where the wavefunctions $|a_i; i\rangle$ and $|a'_i; N-i\rangle$ correspond to the entities of localized and delocalized states respectively, $\langle a_i, a'_i | A \rangle$ is the mixing and $\{A\}$ is a normalization factor. Hereafter, we use capital letters for general characteristics of the whole system,

while small letters mark the parameters of subsystems. The characteristics of delocalized electron subsystems are primed. While representing the wavefunctions by $|\psi\rangle$ we denote the additional parameters of a particular state with the first letter, and the letter after the semicolon means the number of particles.

The matrix elements of an operator acting upon electron states, in the basis of functions (1.1), are obviously expressed as a superposition of results for atomic (localized electrons) and environmental (delocalized electrons, at least with respect to the atom chosen) parts, with additional terms corresponding to the interchange of electrons between the subsystems. The analogous expressions, though differing sometimes in detail and level of simplification, are well known and widely used. From those general expressions the quantitative results are difficult to obtain, unless the conditions of a problem are detailed in such a way that the parametrization or the elimination of particular terms is plausible.

The idea of incorporating well developed methods of atomic structure calculations into descriptions of solid state properties seems promising and is welcomed [2, 3]. Both localized and delocalized electrons should be accounted for, as already pointed out by Slater [4]. In section 2, therefore, we concentrate on the atomic part of the problem, in an attempt to make a closer link between the methods used in atomic and condensed matter physics. The treatment presented there is close to the Anderson impurity Hamiltonian model [5–8], the essence of which is in the above-mentioned separation of states. There, a similar decomposition of the Hamiltonian is possible, in order to single out the atomic, valence and mixed parts [9], and the atomic part may be estimated by using existing computer programs [10, 11]. Despite that similarity, we wish to stress that the results are obtained by deforming in some way the solutions of two separate problems, the factor of this deformation being the off-diagonal matrix element that mixes two atomic subsystems of different valence.

In section 3, the case when the atomic part dominates is treated in detail. We describe our theoretical investigation of x-ray emission spectra (XES) for high- T_c cuprate superconductors. The results obtained by various authors in the past few years in superconductivity and copper oxide compounds fields [9, 12, 13] provide us with a good basis for reference and comparison. Of particular interest is the fundamental significance attributed to the existence of different configurations for an atomic Cu subsystem in high- T_c phenomena [9, 14, 15], and this very property is incorporated into our developments.

The results presented here are only qualitative. In an investigation of a specific compound, details of the method used and the values of parameters must be defined more exactly. Those, however, are the perspectives of future investigation, which are mentioned briefly in section 4, along with some conclusions based on our XES investigation.

Here we investigate a system consisting of electrons of two kinds, which is described by the Anderson model only under some limiting conditions. Therefore, in defining the parameters we tried to keep to the matrix representation inherent in the atomic *ab initio* methods, where the origin of those parameters is easily traced. In the appendix we discuss the explicit expressions for matrix elements of the energy operator.

2. Calculation algorithm

For the many-electron system under investigation, we decompose the matrix element of any operator into three parts: atomic, environment and mixed. The decomposition for a Hamiltonian operator is presented in detail in the appendix. We then pass over to the submatrix elements (i.e. the factors of matrix elements that are independent of angular momenta projections), in order to make effective use of an atomic Hartree–Fock computer program [11].

In the energy matrix, the atomic submatrix elements form a quasideagonal matrix, which we fill according to the following scheme. First, we define the blocks with fixed particle numbers i in the atomic subsystem. Then, inside these blocks, the sequences of atomic matrices with definite total angular momenta are placed on the diagonals. The sequences are repeated as many times as there are states in the complementary subsystem.

The matrix elements (A9) of a primed subsystem (the environment) are defined in the diagonal blocks with respect to the number of particles i , and generally are situated on the diagonals of blocks that connect the same atomic configurations. It is convenient to move to the eigenfunctions for this subsystem, such that

$$H_a |e'_i J'_i M'_i; N - i\rangle = E'(e'_i J'_i; N - i) |e'_i J'_i M'_i; N - i\rangle. \quad (2.1)$$

In this basis the matrix elements for the primed subsystem $E'(e'_i J'_i; N - i)$ depend only upon the properties of this subsystem, and they should be added to the corresponding atomic subsystem's diagonal elements. It is hard to calculate E' from first principles, but it may be estimated fairly well by investigating energy spectra of similar compounds.

The matrix elements of the operator $H_{aa'}$ (see (A1)) generally fill all the matrix. Approximately, they may be considered to be equal inside a block of the matrix that is associated with the subsystem having one more or one fewer particle, another block for two more or two fewer particles, and so on. This means that we consider this interaction only as an effective one, averaged over the influence of particular states.

The energy matrix obtained in this way should be infinite. In practice we can deal only with a finite energy matrix, and with discrete energies. Although the number of states of itinerant electrons is almost infinite, their energies change in a relatively narrow continuous interval. This infinity of continuum is replaced by a finite set. The energy interval is discretized by choosing several essential reference points. This choice depends on the model and the problem solved; we have to point out here, however, that the reference points generally do not represent real concrete states but only some effective averaged states. Also, the order of the matrix is reduced by imposing a physical limit on the number of particles hopping between the atom and the environment. The energy needed for such excitations may then be considered as well as the finite number of electrons in a shell. So only one, or just a few, atomic configurations remain, and both the calculations and interpretation may be simplified.

After such approximations are made, the expression for a wavefunction (see (A4)) contains several terms in a sum over i . In the case of copper compounds, the maximum rank of matrix that we had to deal with was 14.

The limitations imposed by us make this problem analogous to the Anderson impurity model. That allows us to make use of the numerous results by other authors, in comparing both the initial parameters (input) and the output.

The values of radial integrals calculated for free ions are diminishing and have been used in solid state models [16, 17]. The diminishing is due to the environment field. The exact solution of Hartree-Fock equations is not quite so straightforward here as for free atoms and ions, because other factors should also be taken into account (i.e. the existence of the environment and its point symmetry, as in cluster method calculations [9, 18]). Therefore we choose a simpler method, described below.

The multiplicity of states of the atomic subsystem arises from the electrons that are in the open shells. Usually these are the outer electron shells, and their contribution to the total energy of the subsystem is smaller than that of the inner ones, especially for the heavy elements. So

$$E_k = E_0 + e_k \quad E_0 \gg e_k \quad (2.2)$$

where E_0 is a reference point (an average, the lowest-lying state, etc.) from which the energy e_k of a particular state is measured. The e_k , after being exactly determined in the framework of the chosen atomic model, may be modified in some way. The energy of the state under investigation is therefore relatively near to the reference energy point and, depending on the external conditions (for example, after accounting for the dielectric screening of interaction in solids), may change slightly. We adopt that approximation and modify the expression (3.9) by introducing an additional screening factor c :

$$E_k = E_0 + ce_k \quad 0 \leq c \leq 1. \quad (2.3)$$

In practice, this is carried out by multiplying by c all the off-diagonal matrix elements of the atomic subsystem (after diagonalization they contribute to e_k), and by applying (3.10) for the diagonal ones. The matrix elements of the itinerant electron subsystem are adjusted parameters here, so their scaling makes no sense. The similar different scaling of radial integrals contributing to the diagonal and the off-diagonal matrix elements respectively, is used in [19], for example.

We notice that such scaling brings to a point the interval of states considered when c approaches zero. The multiplicity effects in the spectra investigated disappear, and one may get the results obtained with the corresponding traditional model Hamiltonians.

Further simplifications may occur as the conditions of a particular problem are specified. That is the case in x-ray transition investigations, when we choose the usual one-electron operator of the electric dipole transition approximation. The initial and final states in the process differ by a strong excitation (a vacancy in the inner shell) in the atomic part, i.e. the states of the atomic subsystem are different. The $\delta(b_j, a_i)$ appearing then eliminates the matrix elements (of (A9) type, see the appendix) of the itinerant electron subsystem. We express the remnant, which is an atomic part of the electric dipole transition operator $T^{(1)}$, as

$$\langle B; N \| T^{(1)} \| A; N \rangle = \sum_i \sum_{b_j, J_j, a_i, J_i} \langle b_j J_j; i \| T^{(1)} \| a_i J_i; i \rangle \sum_{e'_i} \langle B | b_j J_j, e'_i \rangle \langle a_i J_i, e'_i | A \rangle \quad (2.4)$$

In comparison with the expressions known in atomic theory, this formula has an additional summation over the number of electrons in the atomic subsystem i , and the single product of weight coefficients is replaced by a sum of their products.

The intensity $I(\omega)$ of multipole radiation is proportional to the second power of the matrix element of the transition operator, and the frequency ω corresponds to the difference in energies of initial $|i\rangle$ and final $|f\rangle$ states:

$$I(\omega) \sim |\langle f | p | i \rangle|^2 \delta(\omega - E_f + E_i). \quad (2.5)$$

This formula describes a linear spectrum. In solids, because of the uncertainties, the lines turn into contours, and that is represented by the replacement

$$\delta(\omega - E_f + E_i) \longrightarrow L(\omega - E_f + E_i) \quad (2.6)$$

where $L(x)$ stands for the contour of a line.

3. XES for Cu in an environment

We illustrate the proposed scheme with a rather simple example of the calculation of x-ray emission spectra for cuprate superconductors. As indicated by numerous investigations of those systems, and as mentioned at the beginning of this paper, the existence of different atomic configurations for Cu has great significance. One can hope that the method of essentially superposing these configurations should be effective for the superconducting compounds. On the other hand, in comparison with lanthanides where similar effects are reported [2, 6, 17, 20], the d -electron systems investigated here are much simpler, and that reduces the irrelevant difficulties, which are mostly technical.

First, we point out once more that the main role in superconductivity of such compounds is played by the CuO_2 planes rather than other chemical elements, as indicated by structural analysis (see, for example, [21]) and other investigations. The considerable anisotropy of conductivity leads us to the idea that the interchange of electrons between the planes and their surroundings is not big, and therefore we can treat the planes as closed systems with a fixed number of particles.

Second, a comparison of x-ray spectra of various compounds [9, 18, 22]) allows us to come to the conclusion that Cu in the investigated materials retains its individual properties and it may be plausible to treat it as a separate subsystem. The other itinerant electron subsystem consists of the delocalized O 2p electrons in the Cu environment.

In accordance with our approach the states of the compound are described by the products of wavefunctions for Cu and its environment. As indicated by other investigations [9, 15], the Cu atom here has lost two of its electrons, so its outer shell configuration is $3d^9$. The environment, in turn, has a filled valence band that consists of delocalized one-particle states for oxygen 2p electrons. This configuration of the CuO_2 plane is $3d^9\underline{1}^0$ ($\equiv 3d^9$), where the underline marks holes (in the valence band, in this case) and the upper index is the number of them. By taking into account only the interchange of Cu 3d and O 2p electrons, we can add to this configuration only one other, namely $3d^{10}\underline{1}$.

In the x-ray emission process the initial state has a vacancy in the inner shell (in our case it is Cu 2p), which is accessed by removing one electron from there. We describe this state by the following superposition:

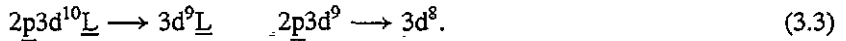
$$2p3d^{10}\underline{1} + 2p3d^9. \quad (3.1)$$

The inner vacancy is filled up with electrons in a relatively short time, and the excessive energy is emitted as an x-ray quantum. The final state for this process is

$$3d^9\underline{1} + 3d^{10}\underline{1}^2 + 3d^8. \quad (3.2)$$

The atomic part of the energy matrix for the system under investigation has been determined using the program by Froese Fischer [11] and by introducing the screening factor c (see (2.4)). The calculated average energy of the configuration has been used for the reference point E_0 . The initial numerical values of the itinerant electron subsystem and the hybridization matrix elements have been evaluated as given in [18, 22, 23] and adjusted in the course of later calculations, paying attention to the shape of the curves obtained as a result. The number of discretization points has been chosen to be unity. The matrix formed according to the scheme described earlier is diagonalized, and the eigenvalues are sorted into ascending order. This last point is of use when dealing with particular parts of the spectrum. The numerical values of the parameters used, and the results obtained, are presented in the corresponding tables and graphs.

By knowing the energy spectra and by accounting for only the selection rules defined by the atomic dipole transition, we obtain the following permitted transitions:



Their matrix elements are described by (A8) and calculated mainly by the Froese Fischer program [11] with some additional manipulations. Then, after using (2.5) and bearing in mind the considerations accompanying it, the intensity curves for Cu XES have been drawn. The curves have been obtained incorporating both the complete spectrum of the initial state (3.1) and only its lower-lying part.

Table 1. Some of the atomic parameters determined via *ab initio* calculations for different atomic configurations. E_a : average energy of the configuration, from $3d^{10}$; E_g : energy of the ground state, from $3d^{10}$; W_c : width of the configuration energy spectra; K_{\max} : total number of states in a configuration.

	$3d^{10}$	$3d^9$	$3d^8$	$2p3d^{10}$	$2p3d^9$
E_a (eV)	0.00	17.31	53.14	955.86	993.79
E_g (eV)	0.00	17.17	50.45	949.30	983.36
W_c (eV)	0.00	0.35	9.17	19.65	23.40
K_{\max}	1	2	9	2	12

Table 2. The values of adjusted parameters for the calculated spectral curves.

c (2.4)	t (A10)	Shape	Halfwidth
0.8	2.6 eV	Lorentzian	0.91 eV

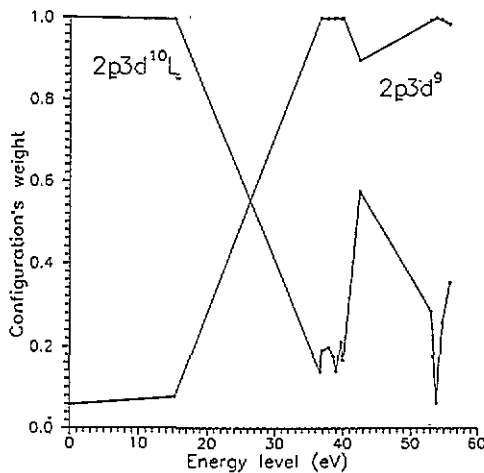


Figure 1. Initial-stage configuration weights as functions of the energy levels from the ground state. Calculations were performed under the conditions given in table 2.

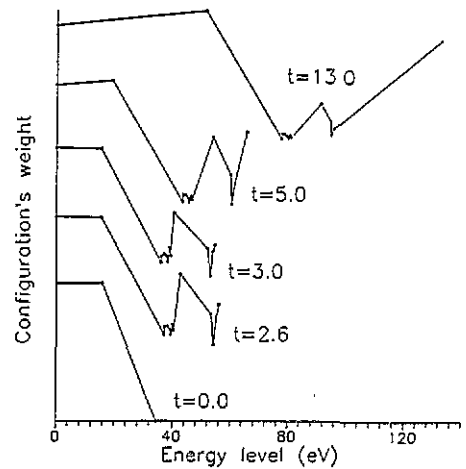


Figure 2. Initial-stage configuration $2p3d^{10}\underline{L}$ weight as a function of the energy levels for different t ; we shift the graphs upwards as t increases.

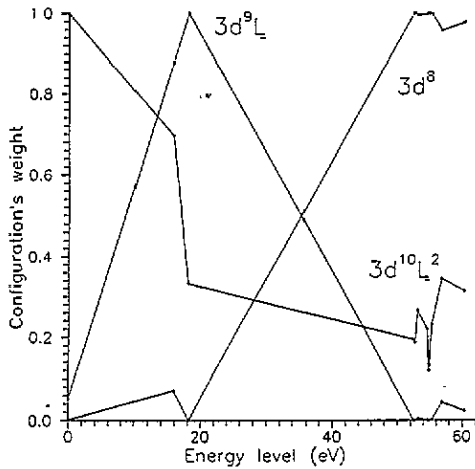


Figure 3. Final-stage configuration weights as functions of the energy levels from the ground state. Calculations were performed under the conditions given in table 2.

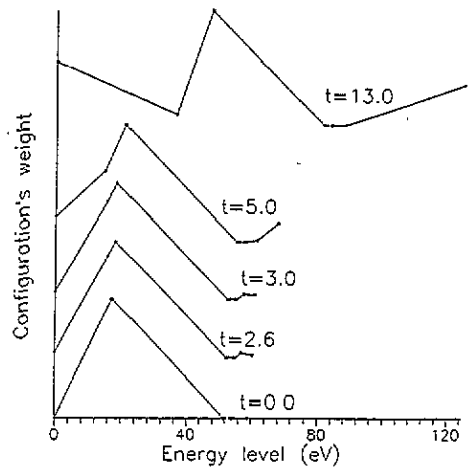


Figure 4. Final-stage configuration $3d^9 L$ weight as a function of energy levels for different t ; we shift the graphs upwards as t increases.

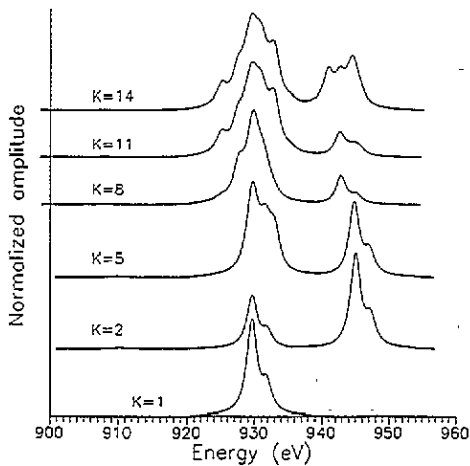


Figure 5. Cu $L\alpha$ emission spectra for the different number of levels K at the initial stage. The main peak is moved to 929.7 eV. The other conditions are as given in table 2.

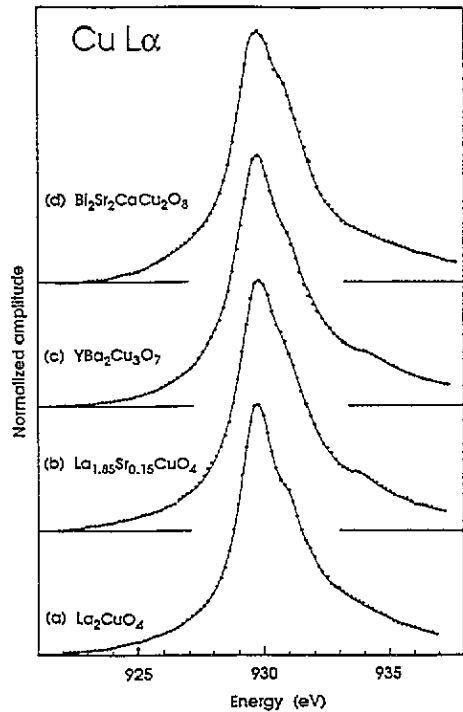


Figure 6. Cu $L\alpha$ XES for La_2CuO_4 and three superconducting cuprates from [22].

The energy spectra obtained are presented in table 1 (atomic configuration parameters), table 2 (values of adjusted parameters) and figures 1–4. In figure 1 the contribution of the initial-state configuration upon the system energy is shown, and in figure 2 the effect of different hybridization magnitudes V is shown. Figures 3 and 4 are the analogous curves for the final-state configurations. There the contribution of a configuration is measured by the probability of its appearance in the state under consideration, and is calculated by summing the squares of the corresponding weight factors:

$$\langle i, J|A \rangle = \sum_{a_i J_i e_i J_i'} |\langle a_i J_i, e_i J_i' J|A \rangle|^2. \quad (3.4)$$

The dependence of Cu 2p XES upon the number K of levels considered in the initial state of the radiation transition is presented in figure 5. The experimental data from [22] is reproduced in figure 6. The shape of the calculated spectra at different values of the hybridization matrix element is shown in figure 7.

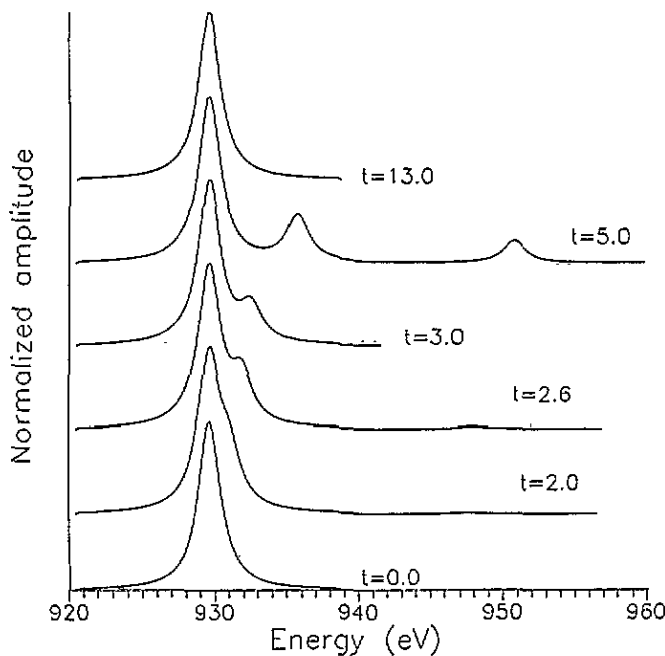


Figure 7. Cu $L\alpha$ emission spectra for the different t magnitudes. The number of levels at the initial stage $K = 1$. The other conditions are as in table 2.

The complex curve of XES intensity obtained in a standard way (figure 5, upper curve) only vaguely resemble the experimental data from [22, 24] (figure 6). The closest resemblance is achieved in the lowest curve of figure 5, where it is assumed that the system is already in the ground state (with a 2p vacancy) at the initial stage of the process. Physically, this could mean that the lifetimes of excited states are much shorter than that of the ground state, so they decay quickly and the x-ray emission is observed only from the lowest state. In comparing this result with the energy spectrum calculation (figure 1) we see that the first two atomic levels are considerably separated from the other ones, and they

are fairly well ascribed to the $2p3d^{10}\underline{L}$ configuration. The weight of the opposing $2p3d^9$ configuration is only 0.06. As for the remaining 12 levels, they cluster into two groups with the energy interval between them similar to that between the first two levels. Here the configuration mixing is stronger, and the $2p3d^9$ configuration dominates. The picture for the final stage of the process is even more complex (figure 3). Here, the lowest-lying state (in contrast to [9]) belongs to the $3d^{10}\underline{L}^2$ configuration, but it does not contribute to the results because according to (3.3) there are no dipole transitions to it. Again, because of the same reason, the further two levels may be treated as belonging to $3d^9\underline{L}$, despite the considerable admixture of $3d^{10}\underline{L}^2$. The remaining cluster of levels at a distance of some 34 eV from the former ones belong to the $3d^8$ configuration.

The electric dipole transition is thus identified as that from the ground state of $2p3d^{10}\underline{L}$ to the two already mentioned levels of $3d^9\underline{L}$, with the following characteristics:

(i) Main line $\omega_m = 929.7$ eV, $I(\omega_m) = 1.000$:

$$77\%(0.927, 2p3d^{10}\underline{L}, 1, 1.5) \longrightarrow (0.444, 3d^9\underline{L}, 3, 2.5)$$

$$35\%(0.927, 2p3d^{10}\underline{L}, 1, 1.5) \longrightarrow (0.556, 3d^9\underline{L}, 3, 1.5)$$

$$- 14\%(0.014, 2p3d^{10}\underline{L}, 1, 0.5) \longrightarrow (0.556, 3d^9\underline{L}, 3, 1.5).$$

(ii) Satellite line $\omega_s = 931.96$ eV, $I(\omega_s) = 0.298$:

$$150\%(0.927, 2p3d^{10}\underline{L}, 1, 1.5) \longrightarrow (0.494, 3d^9\underline{L}, 2, 2.5)$$

$$- 54\%(0.927, 2p3d^{10}\underline{L}, 1, 1.5) \longrightarrow (0.383, 3d^9\underline{L}, 2, 1.5)$$

$$21\%(0.014, 2p3d^{10}\underline{L}, 1, 0.5) \longrightarrow (0.383, 3d^9\underline{L}, 2, 1.5).$$

Here the intensities are expressed in relative units so that the main maximum is normalized to unity. The percentage is a contribution of an atomic component to the transition investigated, and it is obtained from the expansion coefficient matrix for the total wavefunction. Since in the algorithm used by us the matrix elements are summed before squaring them to obtain the intensities, the contribution of a particular component may appear to be negative. The sum of all the existing percentages for a single transition is 100%. The minor contributions of other components are not presented (the tolerance parameter, the ratio of a matrix element to the leading one, is less than 0.01 for them). The parameters of levels (in brackets) are the weight of a configuration in a level, the configuration itself, the sequence number of a level and the resulting J .

The account for the second energy level belonging to the configuration $2p3d^{10}\underline{L}$ (figure 1) in this investigation (figure 5, curve $K = 2$) leads us to an additional maximum belonging to the transitions between the same configurations, $2p3d^{10}\underline{L} \longrightarrow 3d^9\underline{L}$. The further levels are ascribed to the configuration $2p3d^9$, so they correspond to the transitions $2p3d^9 \longrightarrow 3d^8$. These transitions are observed in the same region as the previously mentioned ones, and so they only modify the existing form and intensity. That happens because the energy interval between the level clusters of $2p3d^9$ configuration is much the same as between the levels of the first, $2p3d^{10}\underline{L}$ configuration, which identify the separated maxima.

As one may notice in figures 2 and 4, the influence of the hybridization matrix element magnitude upon the energy spectra is predictable. Only the width of the spectrum increases with increasing the parameter V , while the relative positions and weights of the levels change only slightly. The changes in relative radiation intensities that occur (figure 7) suggest that there is an interval of V between 2–3 eV, where an experimental peculiarity, a satellite line present on the right-hand side of a maximum and close to it, is observed.

4. Conclusions

The simple model of accounting for both localized and delocalized electron states in solids is the Anderson impurity model, when both kinds of states are parametrized. The numerous practical applications of this model resulted in successful reproduction of experimental data. Furthermore, peculiarities that are observed may be obtained by increasing the number of parameters. We have started from a different point of view here: the atomic states are determined by the *ab initio* methods of contemporary atomic physics, and the qualitative influence of the environment (which is parametrized) upon those states is theoretically investigated. After a number of assumptions we have arrived at expressions that are analogous to those obtained from the Anderson model, but the atomic part is not concealed behind parameters and can be traced still further by investigating the physical phenomena, as has been illustrated here with an XES example.

Two opinions on the process of x-ray emission in solids may be found in the literature [25]. One side says that after an electron from an inner shell state is emptied, all the excited states that appear participate in the radiation. The other side tells us that it is a two-stage process, where the system in the first stage relaxes to the lowest-lying excited state, and only then does the emission from that state occur. By assuming the nature of that radiation to be purely atomic, and by knowing the positions of energy levels, we are able to check both pictures in the framework of our approach. Our results (figure 5) indicate that in the case of Cu compounds the two-stage hypothesis is more plausible. The final word belongs to the complex investigations involving several phenomena in the same compounds, in a similar fashion to [26].

The investigation presented here is a simplified case. In order to obtain more accurate results one should account for more factors. Here we wish to make a few comments regarding possible modifications to our approach.

First, by approximating the magnitude of the hybridization matrix element with a single parameter, we have actually investigated an average influence of different atomic configurations upon one another. There are serious reasons to believe the effect of mixing valences to be different for different states. These differences may decide a number of physical effects that are masked by the averaging. It may appear that a tensorial representation of the operator is of use here, which easily generates the selection rules. However, problems may occur with the discretized states of the itinerant electrons, which are described by some generalized characteristics.

Second, the reduction of the interaction realized by (2.3) is a crude way of modifying the states of atomic valence electrons. Another possible way is related to the location of states in the vicinity of a reference point. The practical application of the latter in the atomic calculation scheme proposed here means the modification or introduction of new angular coefficients for the radial integrals. The physical reason for this is the point symmetry of the lattice.

Third, in the x-ray spectra investigation we have eliminated the major part of the environmental influences, leaving only an averaged contribution. An opposite approach is also possible, where attention is paid to the properties of delocalized electrons, and the atom is evaluated in few parameters. Either approach is inevitable in an investigation of systems where the role of electrons of both kinds (bound and delocalized) is comparable.

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Appendix

In order to apply the traditional methods of precise atomic calculations (see, for example, [27]) and use existing computer programs [10, 11] to the scheme proposed in section 2, we base our approach upon the 'atom in the environment' picture. The wavefunction of the atomic bound electrons (non-primed subsystem) is an eigenfunction of angular momentum:

$$a_i J_i M_i \longrightarrow a_i. \quad (\text{A1})$$

The spherical symmetry is not characteristic of the itinerant electron (primed) subsystem wavefunction. However, due to the pre-determined procedure of computation, the momentum and its projection for that system must be well defined. We therefore choose the following representation:

$$|a'_i; N - i\rangle = \sum_{e'_i, J'_i, M'_i} |e'_i J'_i M'_i; N - i\rangle \langle e'_i J'_i M'_i | a'_i \rangle \quad (\text{A2})$$

where, unlike the atomic subsystem wavefunction, we must take a sum instead of a single term. By putting these two transformations into (1.1), after some steps we get

$$|A; N\rangle = \{A\} \sum_i \sum_{a_i, J_i, M_i, a'_i, e'_i, J'_i, M'_i} |a_i J_i M_i; i\rangle |e'_i J'_i M'_i; N - i\rangle \langle e'_i J'_i M'_i | a'_i \rangle \langle a_i J_i M_i, a'_i | A \rangle. \quad (\text{A3})$$

Here the wavefunctions of subsystems still depend on the projections of angular momenta. The formalism of atomic theory allows one to factorize out that dependence analytically (as done, for example, in [28]), so that it does enter the final expressions, namely

$$\begin{aligned} |A; N\rangle &= \{A\} \sum_i \sum_{a_i, J_i, M_i, e'_i, J'_i, M'_i} |a_i J_i M_i; i\rangle |e'_i J'_i M'_i; N - i\rangle \delta(M_i M'_i, M_j M'_j) \\ &\quad \times \sum_{a'_i, M'_i, M'_j} \langle e'_i J'_i M'_i | a'_i \rangle \langle a_i J_i M_i, a'_i | A \rangle \\ &= \{A\} \sum_{JM} \sum_i \sum_{a_i, J_i, e'_i, J'_i} \sum_{M_i M'_i} |a_i J_i M_i; i\rangle |e'_i J'_i M'_i; N - i\rangle \begin{bmatrix} J_i & J'_i & J \\ M_i & M'_i & M \end{bmatrix} \\ &\quad \times \sum_{a'_i, M'_i, M'_j} \langle e'_i J'_i M'_i | a'_i \rangle \langle a_i J_i M_i, a'_i | A \rangle \begin{bmatrix} J_i & J'_i & J \\ M_i & M'_i & M \end{bmatrix} \\ &= \sum_{JM} \sum_i \sum_{a_i, J_i, e'_i, J'_i} |a_i J_i e'_i J'_i JM; i, N\rangle \langle a_i J_i e'_i J'_i JM | A \rangle \end{aligned} \quad (\text{A4})$$

where

$$\langle a_i J_i e'_i J'_i J M | A \rangle = \{A\} \sum_{a'_i M'_i} \langle e'_i J'_i M'_i | a'_i \rangle \langle a_i J_i M_i, a'_i | A \rangle \begin{bmatrix} J_i & J'_i & J \\ M_i & M'_i & M \end{bmatrix} \quad (\text{A5})$$

$$|a_i J_i e'_i J'_i J M; i, N\rangle = \sum_{M_i M'_i} |a_i J_i M_i; i\rangle |e'_i J'_i M'_i; N - i\rangle \begin{bmatrix} J_i & J'_i & J \\ M_i & M'_i & M \end{bmatrix} \quad (\text{A6})$$

and $[\dots]$ is a Clebsch–Gordan coefficient.

The expression (A4) leads us to the functions (A6), which are similar to the functions of coupled momenta of two shells in the theory of an atom (see [28]); the expansion coefficients (A5) are commonly found by direct methods based upon the energy minimum principle, therefore the complexity of their expressions is only of minor importance.

When the Hamiltonian acts only upon separate electrons, we can always formally write

$$H = H_a + H_{a'} + H_{aa'}. \quad (\text{A7})$$

Here H_a is the part of the complete Hamiltonian that acts only upon the electrons of the subsystem with non-primed parameters (the atom). The $H_{a'}$ is an analogous term for the primed subsystem (environment), and the third term $H_{aa'}$ is the rest of Hamiltonian, where electrons of both primed and non-primed subsystems are acted upon. The last term corresponds to the matrix elements of hybridization (hopping, t).

The energy operator (A7) is scalar in angular momentum space (denoted later by the superscript (0)). Therefore an application of the Wigner–Eckart theorem in the basis of functions (A6) yields (see, for example, [28]) for the atomic part

$$\begin{aligned} \langle b_j J_j f'_j J'_j J' M'; j, N | H_a^{(0)} | a_i J_i e'_i J'_i J M; i, N \rangle \\ = \sum_{M_i M'_i M_j} \langle f'_j J'_j M'_j; N - j | e'_i J'_i M'_i; N - i \rangle \langle b_j J_j M_j; j | H_a^{(0)} | a_i J_i M_i; i \rangle \\ \times \begin{bmatrix} J_i & J'_i & J \\ M_i & M'_i & M \end{bmatrix} \begin{bmatrix} J_j & J'_j & J' \\ M_j & M'_j & M' \end{bmatrix} \\ = \delta(i, j) \delta(f'_j J'_j M'_j, e'_i J'_i M'_i) \delta(J M, J' M') \langle b_j J_j; i | H_a^{(0)} | a_i J_i; i \rangle \end{aligned} \quad (\text{A8})$$

i.e. the submatrix element $\langle \parallel \parallel \rangle$ common in atomic physics is obtained, with additional Kronecker symbols diagonalizing all the supplementary characteristics. A similar expression is also true for the environment part:

$$\begin{aligned} \langle b_j J_j f'_j J'_j J' M'; j, N | H_{a'}^{(0)} | a_i J_i e'_i J'_i J M; i, N \rangle = \delta(i, j) \delta(b_j J_j M_j, a_i J_i M_i) \\ \delta(J M, J' M') \langle f'_j J'_j; N - i | H_{a'}^{(0)} | e'_i J'_i; N - i \rangle. \end{aligned} \quad (\text{A9})$$

The expression for the hopping matrix element is more complex, although the Wigner–Eckart theorem yields here $\delta(J M, J' M')$, also. The approximation usually made here is based upon energy considerations. It is assumed that the hopping decreases rapidly when more than one electron participates in it. So for the hopping of a single-electron matrix element we get

$$\begin{aligned} \langle b_j J_j f'_j J'_j J' M'; j, N | H_{aa'}^{\text{single}} | a_i J_i e'_i J'_i J M; i, N \rangle = \delta(i, j \pm 1) \delta(J M, J' M') \\ \times \langle b_j J_j f'_j J'_j J; j, N | H_{aa'}^{\text{single}} | a_i J_i e'_i J; i, N \rangle. \end{aligned} \quad (\text{A10})$$

References

- [1] Vonsovskiy S V, Katsnelson M I and Trefilov A V 1993 *Fiz. Metall. Metall.* **76** 3 (in Russian)
- [2] Connerade J P and Karnatak R C 1990 *Comments Atom. Mol. Phys.* **24** 1
- [3] Matthew J A D 1993 *Contemp. Phys.* **B 4** 2
- [4] Slater J C 1968 *Methods in Computational Physics* vol 8 ed B Alder, S Fernbach and M Rotenberg (New York: Academic)
- [5] Anderson P W 1961 *Phys. Rev. A* **124** 41
- [6] Gunnarsson O and Schönhammer K 1983 *Phys. Rev. B* **28** 4315; 1985 *Phys. Rev. B* **31** 4813; 1987 *Phys. Scr.* **T19** 273
- [7] Gunnarsson O, Andersen O K, Jepsen O and Zaanen J 1989 *Phys. Rev. B* **39** 1708
- [8] Kotani A, Ogasawara H, Okada K, Thole B T and Sawatzky G A 1989 *Phys. Rev. B* **40** 65
- [9] Kotani A and Okada K 1990 *Prog. Theor. Phys. Suppl.* **101** 329
- [10] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press)
- [11] Froese Fischer Ch 1991 *Comput. Phys. Commun.* **64** 399
- [12] Pickett W E 1989 *Rev. Mod. Phys.* **61** 2
- [13] Hass K C 1989 *Solid State Phys.* **42** 213
Zaanen J and Sawatzky G A 1990 *Prog. Theor. Phys. Suppl.* **101** 231
Parlebas J C 1993 *Phys. Stat. Solidi B* **178** 9
- [14] Gupta R P and Gupta M 1989 *J. Phys.: Condens. Matter* **1** 1543
Krasnikova M V and Moyzhes B Ya 1989 *Fiz. Tverdogo Tela* **31** 270 (in Russian)
Eremin M and Anikeenok O 1991 *Physica* **185-9C** 1521
Makarov L L, Batrakov Yu F and Aksenov N D 1993 *Sverkhprovodimost: Fizika, Khimiya, Tekhnika* **6** 1247 (in Russian)
- [15] Hüfner S 1990 *Solid State Commun.* **74** 969
- [16] Okada K and Kotani A 1989 *J. Phys. Soc. Japan* **58** 2578
- [17] Band I M, Kikoin K A, Trzhaskovskaya M B and Khomskii D I 1988 *Sov. Phys.-JETP* **94** 79 (in Russian)
- [18] Okada K and Kotani A 1989 *J. Phys. Soc. Japan* **58** 1095
- [19] Lynch D W and Cowan R D 1987 *Phys. Rev. B* **36** 9228
- [20] Ramakrishnan T V 1981 *Valence Fluctuations in Solids* (Amsterdam: North-Holland)
- [21] Batlogg B 1991 *Physica B* **169** 7
- [22] Barnole V, Mariot J-M, Hague C F, Michel C and Raveau B 1990 *Phys. Rev. B* **41** 4262
- [23] Mila F 1988 *Phys. Rev. B* **38** 11538
- [24] Tanaka S, Okada K and Kotani A 1991 *Physica C* **185-9** 1489
- [25] van Veenendaal M A and Sawatzky G A 1994 *Phys. Rev. B* **49** 3473
- [26] Tanaka S, Okada K and Kotani A 1989 *J. Phys. Soc. Japan* **58** 813
Drager G, Werfel F and Leiro J A 1990 *Phys. Rev. B* **41** 4050
Tanaka S and Kotani A 1992 *J. Phys. Soc. Japan* **61** 4212
Tjeng L H, Chen C T and Cheong S-W 1992 *Phys. Rev. B* **45** 8205
- [27] Jucys A P and Savukynas A J 1972 *Mathematical Foundations of Atomic Theory* (Vilnius: Mintis) (in Russian)
Nikitin A A and Rudzikas Z B 1983 *Fundamentals of the Theory of Atom and Ion Spectra* (Moscow: Nauka) (in Russian)
- [28] Jucys A P and Bandzaitis A A 1977 *Theory of Angular Momentum in Quantum Mechanics* (Vilnius: Mokslas) (in Russian)