PHYSICAL REVIEW A VOLUME 40, NUMBER 8 OCTOBER 15, 1989

Theoretical multiconfiguration Dirac-Fock method study on the x-ray spectra of multiply ionized heavy atoms: The structure of the $K\alpha L^0M^r$ lines

Marek Polasik
Institute of Physics, Nicholas Copernicus University, 87-100 Toruń, ul. Grudziądzka 5, Poland

(Received 5 April 1989)

Detailed multiconfiguration Dirac-Fock calculations through the proposed alternative special average-level version with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections have been carried out on molybdenum, palladium, and holmium to elucidate the structure of the $K\alpha L^0M^r$ lines in their x-ray spectra and to explain reliably the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^0$ bands. The structure of $K\alpha L^0M^r$ lines has been shown to be very complex. Because the distances between the neighboring $K\alpha L^0M^r$ lines are very small, the effects of multiple M-shell ionization are manifested in the spectra as an asymmetric broadening and net shift of $K\alpha_1L^0$ and $K\alpha_2L^0$ bands. The results obtained in the present work corroborate some of my previous conclusions [Polasik, Phys. Rev. A **39**, 616 (1989)]: that removing a $3p$ electron is more effective than a $3s$ or $3d$ electron in producing a $K\alpha L^0$ energy shift and that the shift effects remarkably increase with atomic number and are strongly nonadditive. The results of this work can be used to construct different shapes of theoretical $K\alpha L^0$ bands for molybdenum, palladium, and holmium, satisfactorily reproducing the shapes and positions of various experimental $K\alpha L^0$ bands generated by different inducing projectiles.

I. INTRODUCTION

The x-ray spectra of multiply ionized atoms have recently become the subject of intensive studies, both experimental and theoretical. A detailed knowledge of the shapes and parameters of these spectra is essential in the nuclear fusion reactions investigations[1] and in the calculations of primary vacancies distribution.[2]

It is well known that in the case of the heavy-ion-induced $K\alpha$ x-ray spectra multiple ionization of the N, M, and L shells is extremely likely to occur. Generally, the shape of a $K\alpha$ x-ray spectrum depends both on the kind of the inducing particles and the Z value of the element under study.[3] The shapes and positions of the $K\alpha L^n$ bands (corresponding transitions from initial states which have n holes in the L shell) are influenced mainly by the multiple M-shell ionization (the influence of ionization of N shell is much smaller[4]). However, in contrast with the L-shell ionization, it is not possible to deduce the degree of M-shell ionization from the energy shifts alone.[4] It was therefore thought worthwhile to examine the influence of additional holes in the M shell on the $K\alpha L^0$ bands in the x-ray spectra.

In the first paper of this series,[3] hereafter referred to as I, relativistic multiconfiguration Dirac-Fock (MCDF) calculations done through the standard average-level (MCDF-AL) version with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections have been carried out on palladium to elucidate the structure of the $K\alpha L^n$ satellite lines in its x-ray spectra, which was the first systematic theoretical study on the structure of these lines for a heavy atom. The availability of recently measured[4] high-resolution x-ray spectra of molybdenum was the inspiration to perform a theoretical simulation of these spectra in which a model which assumes only the transitions of $K\alpha L^n$ type was applied.[5] The effect of M-shell holes has been taken into account in a crude way by simply shifting the spectrum towards higher energies and applying larger Gaussian linewidths. Although this procedure has succeeded in general, it turned out that calculations including the M-shell holes explicitly are necessary to reproduce such effects as the asymmetry of the bands which is particularly evident for the $K\alpha_2L^0$ band.

The effect of removing M-shell electrons on the principal $K\alpha$ ($K\alpha L^0$) bands for molybdenum, palladium, lanthanum, and holmium was also analyzed in I. The examination of the effect of removing the whole subshells of the M shell on the $K\alpha L^0$ lines indicates that except for the case of holmium the effect of removing a particular subshell increases in the order going from $3d$ to $3s$ to $3p$ (see I). In the case of $3d$ this effect is relatively small and the lines can be shifted either to higher or to lower energies, while in the remaining cases the shift is large and towards higher energies. It has also been observed that the energy shifts remarkably increase with the atomic number and are strongly nonadditive. Therefore, to better explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^0$ bands, it is necessary to perform a detailed investigation in which all the possible combinations of M-shell holes are to be considered.

Generally, the groups of lines labeled by $K\alpha_1L^0M^r$ and $K\alpha_2L^0M^r$ correspond to transitions from initial states which have one hole in the K shell, no hole in the L shell, and r holes in the M shell.

Preliminary calculations for the simplest case of the $K\alpha L^0M^r$ lines have been already performed on palladium and have also been presented in I. The results of those pilot calculations confirm my previous conclusions (see I) that removing a $3p$ electron is more effective than removing a $3s$ or a $3d$ electron in producing $K\alpha L^0$ energy shift and that the energy shifts are strongly nonadditive.

To reliably explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^0$ bands, the present extensive MCDF studies on the structures of $K\alpha L^0 M^r$ lines have been performed for molybdenum, palladium, and holmium in the proposed special average-level (MCDF-SAL) version (see Sec. II) with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections. The present studies are based on the MCDF package developed by Grant and co-workers.[6,7]

II. THEORETICAL BACKGROUND

The MCDF method which is used in the present study has been described in detail in many papers.[6–11] Moreover, some basic ideas have been presented in I. However, for the sake of clarity, some essential details are very briefly recapitulated here.

Within the MCDF scheme the effective Hamiltonian for an N-electron system is to be expressed by

$$H=\sum_{i=1}^{N} h_D(i)+\sum_{i<j}^{N} C_{ij} , \tag{1}$$

where $h_D(i)$ is the Dirac operator for ith electron (see I) and the terms C_{ij} account for electron-electron interactions and come from a one-photon exchange process. Each C_{ij} can be expressed by[9]

$$C_{ij}=1/r_{ij}+T(r_{ij}) , \tag{2}$$

where $1/r_{ij}$ is the Coulomb interaction operator (due to longitudinally polarized photons) and $T(r_{ij})$ is the transverse Breit operator (due to transversely polarized photons):

$$T(r_{ij})=-\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{r_{ij}}+(\boldsymbol{\alpha}_i\cdot\nabla_i)(\boldsymbol{\alpha}_j\cdot\nabla_j)\frac{\cos(\omega r_{ij})-1}{\omega^2 r_{ij}} . \tag{3}$$

In the MCDF method an atomic state function (ASF) with the total angular momentum J and parity p is assumed in the multiconfigurational form[6,10]

$$\Psi_s(J^p)=\sum_m c_m(s)\Phi(\gamma_m J^p) , \tag{4}$$

where $\Phi(\gamma_m J^p)$ are configuration state functions (CSF), $c_m(s)$ are the configuration mixing coefficients for state s, γ_m represents all information required to uniquely define a certain CSF.

Actually, in solving the eigenproblem for such a Hamiltonian the transverse (Breit) interaction (3) is neglected. The corresponding contribution to energy is added as a first-order perturbation correction after self-consistence is achieved.[7]

Applying the variational principle to the energy functional with such a defined Hamiltonian yields integrodifferential equations for the orbitals; these equations contain also the mixing coefficients $c_m(s)$ as parameters. In practice, a trial set of orbitals is chosen to form the Hamiltonian matrix which, after diagonalization, gives the set of coefficients, which in turn can be inserted into the integrodifferential equations mentioned above to give "improved" orbitals. The cycle is repeated until convergence is achieved. Such a scheme is called the optimal-level version of MCDF calculation[6,10] (MCDF-OL).

However, in the theoretical studies on the x-ray spectra of multiply ionized heavy atoms, we must not forget that they occur between hundreds of states. The application of the standard MCDF-OL method would thus imply a separate MCDF-OL calculation for each state, which is very time consuming. Another difficulty is connected with the fact that although the transition energies can be directly calculated, the calculation of the transition probabilities should take into account the fact of nonorthogonality of the orbitals corresponding to the pairs of initial and final states. This is a very difficult problem, which is, in practice, solved only approximately.[12] In order to cope with the above difficulties, some other methods (different from MCDF-OL) are used to study the transition probabilities. The main feature of those methods is the fact that they are using the common set of the orbitals for all the initial and final states. This removes the problem of nonorthogonality of the orbitals and, moreover, greatly reduces the computational effort, as only the coefficients $c_m(s)$ have to be determined for each state by diagonalizing the matrix of the Hamiltonian in the space of relevant CSF's. It is evident that for each particular state such orbitals yield higher energy than those obtained from MCDF-OL calculations for each state (the effect of relaxation). However, usually all energy levels are shifted by approximately the same extent (see Sec. III). Two standard schemes have been elaborated up to the present, which are based on this idea, namely the average-level version of MCDF (MCDF-AL) and extended average-level version of MCDF (MCDF-EAL).

In both MCDF-AL and MCDF-EAL schemes the energy functional is averaged over all the initial and final states and can be expressed by

$$E=E_{\mathrm{opt}}+\sum_a \bar{q}_a\varepsilon_a\mathcal{N}(a,a)+\sum_{\substack{a,b\\ a\neq b}}\varepsilon_{ab}\mathcal{N}(a,b) , \tag{5}$$

where $\bar{q}_a$ is the generalized occupation number for orbital a, ε_a and ε_{ab} are the Lagrange multipliers, $\mathcal{N}(a,b)$ is the overlap integral. In the MCDF-AL scheme E_{opt} is taken in the form

$$E_{\mathrm{opt}}=\frac{1}{n}\sum_{l=1}^{n} H_{ll} , \tag{6}$$

where n is the number of CSF's defining the initial and final states of the transitions considered, and H_{ll} are the diagonal contributions to the Hamiltonian matrix, while the MCDF-EAL scheme is based on E_{opt} representing a weighted sum of the diagonal Hamiltonian matrix elements:

$$E_{\mathrm{opt}}=\left[\sum_{i=1}^{n} w_i\right]^{-1}\sum_{l=1}^{n} w_l H_{ll} , \tag{7}$$

where the weights are chosen as $w_l=2J_l+1$, with J_l denoting the total angular momentum of the relevant

TABLE I. Comparison of the $K\alpha L^0 M^0$ and $K\beta L^0 M^0$ transition energies (in eV) calculated in the MCDF-SAL scheme for palladium with their experimental counterparts and with the values obtained in the standard MCDF-OL (DF), MCDF-EAL, and MCDF-AL schemes (see Sec. II). The uncertainties of experimental results are marked in parentheses.

	Transition energies (eV)				
Method	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$K\beta_3$	$K\beta_2$
MCDF-OL	21 177.365	21 020.229	23 817.469	23 789.419	24 296.145
MCDF-EAL	21 179.867	21 022.978	23 829.528	23 801.632	24 317.306
MCDF-AL	21 178.144	21 021.395	23 824.093	23 796.315	24 308.717
MCDF-SAL	21 176.603	21 019.925	23 818.960	23 791.254	24 300.493
Expt.[a]	21 177.1(1)	21 020.1(1)	23 818.7(2)	23 791.1(2)	24 299.1(2)

[a] Bearden (Ref. 14).

CSF.

From my numerical experience it is evident that the MCDF-AL scheme gives the results which are in a much better agreement with experiment (see also Table I) than the results obtained in the MCDF-EAL scheme. Therefore, in my previous works[3,5] I successfully applied the MCDF-AL scheme to elucidate the structure of the $K\alpha L^n$ satellite lines in x-ray spectra of palladium and to perform a theoretical simulation of the $K\alpha L^n$ spectra for molybdenum.

However, in theoretical studies, which concerns the effect of the multiple M-shell ionization, the energy shifts to the reflected are very small when compared with the shifts due to L-shell ionization studied in the previous works (see I). Preliminary test calculations have shown that MCDF-AL is indeed not accurate enough in such cases. The reason of an insufficient accuracy of the MCDF-AL approach seems to be the fact that the definition of E_{opt} in Eq. (6) does not consider the different number of the initial and final states. Therefore the orbitals obtained in this scheme in a sense favor those states (initial or final) which are more numerous. Because the essence of the present investigations are the reliable calculations of the transition energies and transition probabilities between the initial and final states, it is appropriate to formulate such a functional which enables to some extent the compensation of this imbalance.

In the novel special average-level version of the MCDF calculations, (MCDF-SAL) which is proposed in this work, E_{opt} is to be expressed in the form

$$E_{\text{opt}}=\frac{1}{\sqrt{n_i}+\sqrt{n_f}}\left[\frac{1}{\sqrt{n_i}}\sum_{i=1}^{n_i}H_{ii}+\frac{1}{\sqrt{n_f}}\sum_{f=1}^{n_f}H_{ff}\right], \tag{8}$$

where H_{ii} and H_{ff} are the diagonal contributions to the Hamiltonian matrix, the first sum runs over all the initial CSF's (n_i), and the second sum runs over all the final CSF's (n_f).

It seems that the orbitals determined in the MCDF-SAL version are better suited for calculations of the transition probabilities than those determined in the standard MCDF-AL version. This is due to the fact that, unlike the MCDF-AL version, where all states are uniformly represented in the energy functional, in the MCDF-SAL version the weights of the contributions corresponding to the more numerous configurations are reduced in the energy functional. This is a remedy against exaggerating the contribution of the more numerous configurations to the energy functional. Very recently, it has been concluded[13] that a scheme based on this idea and designed for a particular case of the investigations in $I(K\beta)/I(K\alpha)$ intensity ratios gives results in a better agreement with experiment than the standard MCDF-EAL and MCDF-AL versions.

Apart from the transverse (Breit) interaction two types of energy corrections are included, namely the self-energy and vacuum polarization corrections (see Ref. 3). The formulas for the transition matrix elements and spontaneous emission probabilities can be found in the work of Grant.[11]

III. RESULTS AND DISCUSSION

As pointed out in the Introduction, the shapes and positions of $K\alpha L^0$ bands are influenced mainly by the multiple M-shell ionization. To examine the influence of various types of additional M-shell holes on the structures and positions of the $K\alpha L^0 M^r$ lines, an extensive study has been carried out on molybdenum, palladium, and holmium.

As has been shown in I, the MCDF-AL scheme is relevant to describe the $K\alpha L^n$ x-ray transitions. To test the quality of the MCDF-SAL scheme used in further calculations, I first performed a comparative study on the $K\alpha L^0 M^0$ and $K\beta L^0 M^0$ transition energies of palladium, using the MCDF-OL, MCDF-EAL, MCDF-AL, and MCDF-SAL schemes. Because, in the present study, the electron correlation has not been taken into account, the MCDF-OL calculations are in fact separate one-configuration Dirac-Fock (DF) ones for each initial and final state. The results are compared with their experimental counterparts[14] in Table I. As shown, the MCDF-SAL scheme generally gives the results of the same quality as those of the MCDF-OL method (the effect of relaxation on the $K\alpha L^0 M^0$ transition energies is very small). Moreover, for each $K\alpha L^0 M^0$ and $K\beta L^0 M^0$ transitions the MCDF-SAL results are in an excellent agreement with the experiment. This means that the MCDF-SAL scheme is adequate to reliably describe the relevant states and correctly reproduce the effect of removing M-shell electrons on the $K\alpha L^0$ bands.

TABLE II. CSF sets used in the calculations of the structures of the particular transition types of the $K\alpha L^0M^r$ lines. The numbers of CSF's in the j-j coupling scheme are also given.

		CSF sets		
Transition type	Initial	Number of CSF's	Final	Number of CSF's
		$K\alpha L^0M^0$		
$1s^{-1} \to 2p^{-1}$	$1s^1 2p^6 3s^2 3p^6 3d^{10}$	1	$1s^2 2p^5 3s^2 3p^6 3d^{10}$	2
		$K\alpha L^0M^1$		
$(1s3s)^{-1} \to (2p3s)^{-1}$	$1s^1 2p^6 3s^1 3p^6 3d^{10}$	2	$1s^2 2p^5 3s^1 3p^6 3d^{10}$	4
$(1s3p)^{-1} \to (2p3p)^{-1}$	$1s^1 2p^6 3s^2 3p^5 3d^{10}$	4	$1s^2 2p^5 3s^2 3p^5 3d^{10}$	10
$(1s3d)^{-1} \to (2p3d)^{-1}$	$1s^1 2p^6 3s^2 3p^6 3d^9$	4	$1s^2 2p^5 3s^2 3p^6 3d^9$	12
		$K\alpha L^0M^2$		
$1s^{-1}3s^{-2} \to 2p^{-1}3s^{-2}$	$1s^1 2p^6 3s^0 3p^6 3d^{10}$	1	$1s^2 2p^5 3s^0 3p^6 3d^{10}$	2
$1s^{-1}3p^{-2} \to 2p^{-1}3p^{-2}$	$1s^1 2p^6 3s^2 3p^4 3d^{10}$	8	$1s^2 2p^5 3s^2 3p^4 3d^{10}$	21
$1s^{-1}3d^{-2} \to 2p^{-1}3d^{-2}$	$1s^1 2p^6 3s^2 3p^6 3d^8$	16	$1s^2 2p^5 3s^2 3p^6 3d^8$	45
$(1s3s3p)^{-1} \to (2p3s3p)^{-1}$	$1s^1 2p^6 3s^1 3p^5 3d^{10}$	7	$1s^2 2p^5 3s^1 3p^5 3d^{10}$	18
$(1s3s3d)^{-1} \to (2p3s3d)^{-1}$	$1s^1 2p^6 3s^1 3p^6 3d^9$	8	$1s^2 2p^5 3s^1 3p^6 3d^9$	23
$(1s3p3d)^{-1} \to (2p3p3d)^{-1}$	$1s^1 2p^6 3s^2 3p^5 3d^9$	23	$1s^2 2p^5 3s^2 3p^5 3d^9$	65

Let us consider the "pure" $K\alpha L^0M^r$ transitions, i.e., those in which there are no holes in shells higher than M. All the types of transitions considered here can be classified into three groups, depending on the number of holes in the M shell in the initial and final states. These are $K\alpha L^0M^0$ (reference lines), $K\alpha L^0M^1$ (preliminary calculations have been presented in I), and $K\alpha L^0M^2$. All possible CSF's in the j-j coupling scheme due to the nonrelativistic configurations listed in Table II were used in the present study. It can be seen from Table II that, in most cases, removing even one or two electrons from the M shell causes a strong increase of the number of states possible for the given initial and final configurations.

In Figs. 1–6 both stick and synthesized spectra for all types of the $K\alpha L^0M^r$ transitions ($r=0,1,2$) for molybdenum, palladium, and holmium are presented together with the summary spectra for each $K\alpha L^0M^r$. Two synthesized spectra for all cases have been constructed: one is the sum of the Lorentzian natural line shapes with the width[15] of 6.82 eV for Mo, 9.00 eV for Pd, and 35.0 eV for Ho, respectively (dotted lines), and, to simulate better the experimental spectra, the other one (solid lines) is a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having the width of 10.5 eV for Mo,[4] 10.0 eV for Pd,[2] and 45.0 eV for Ho,[16] respectively.

For the simplest case of the $K\alpha L^0M^r$ lines ($K\alpha L^0M^0$ reference lines) only two lines are present, namely $K\alpha_1L^0M^0$ and $K\alpha_2L^0M^0$. In the case of $K\alpha L^0M^1$ lines, we have three possible types of transitions: $(1s3s)^{-1} \to (2p3s)^{-1}$, $(1s3p)^{-1} \to (2p3p)^{-1}$, and $(1s3d)^{-1} \to (2p3d)^{-1}$. For each type of transition (see Figs. 1–3 for molybdenum, palladium, and holmium, respectively) two clearly separated groups of lines ($K\alpha_1L^0M^1$ and $K\alpha_2L^0M^1$) are observed. In the first case there are six states and six possible transitions, while in the second case there are 14 states and 30 transitions, of which 25 are of a remarkable intensity. In the last transition type there are 16 states and 36 transitions of which 34 are of a remarkable intensity. In this case the distances between the neighboring lines are very small. As shown, for all types of $K\alpha L^0M^1$ transitions, very weakly structured bands ($K\alpha_2L^0M^1$ and $K\alpha_1L^0M^1$) are observed only in

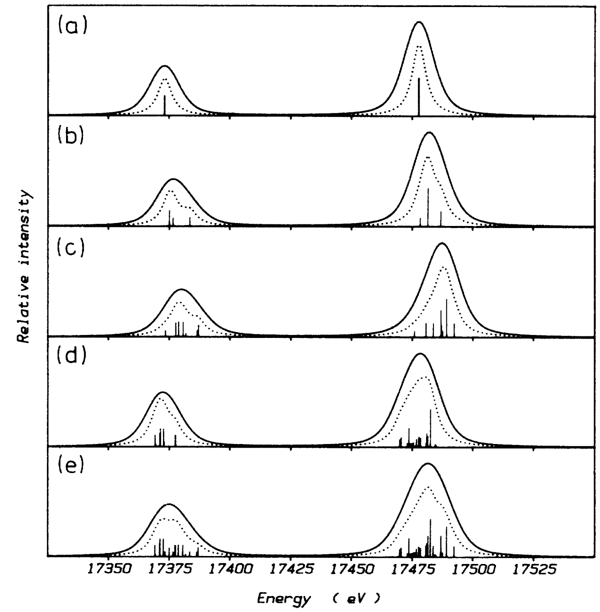

FIG. 1. Calculated stick spectra (line positions with their relative intensities, to the same scale) and synthesized spectra [one being the sum of the Lorentzian natural line shapes (dotted lines) and the other one obtained by the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response (solid lines)] for $K\alpha L^0M^0$ and $K\alpha L^0M^1$ transitions in molybdenum of the following types: (a) $1s^{-1} \to 2p^{-1}$ ($K\alpha L^0M^0$ reference lines), (b) $(1s3s)^{-1} \to (2p3s)^{-1}$, (c) $(1s3p)^{-1} \to (2p3p)^{-1}$, (d) $(1s3d)^{-1} \to (2p3d)^{-1}$, and (e) $K\alpha L^0M^1$, summary spectrum [(b), (c), (d)].

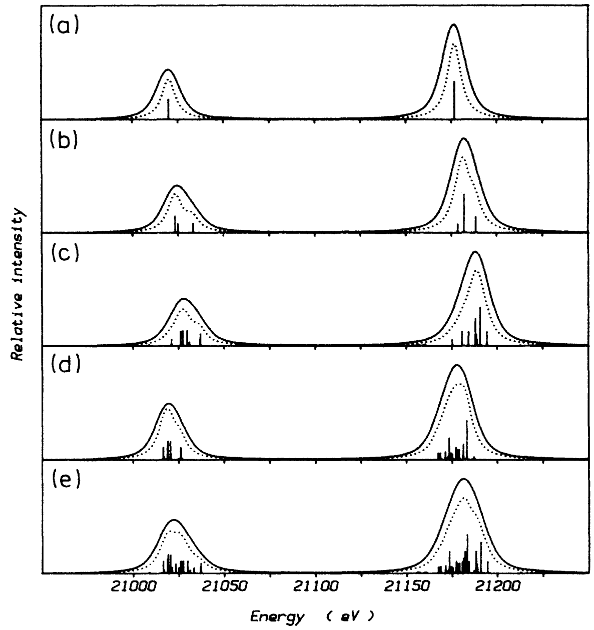

FIG. 2. Same as Fig. 1, but for $K\alpha L^0M^0$ and $K\alpha L^0M^1$ transitions in palladium.

the case of a sum of Lorentzian line shapes, while the convolution of Lorentzian line shapes with Gaussian instrumental response smooths very much the resultant spectra. Moreover, the structures of the appropriate groups of $K\alpha L^0M^1$ lines of molybdenum, palladium, and holmium are very similar (see stick spectra in Figs. 1–3) while the relevant $K\alpha L^0M^1$ bands, which are the sum of the Lorentzian natural line shapes, are much smoother for holmium than for molybdenum and palladium.

In the case of $K\alpha L^0M^2$ we have six possible types of transitions: $1s^{-1}3s^{-2}\rightarrow 2p^{-1}3s^{-2}$, $1s^{-1}3p^{-2}\rightarrow 2p^{-1}3p^{-2}$, $1s^{-1}3d^{-2}\rightarrow 2p^{-1}3d^{-2}$, $(1s3s3p)^{-1}\rightarrow(2p3s3p)^{-1}$, $(1s3s3d)^{-1}\rightarrow(2p3s3d)^{-1}$, and $(1s3p3d)^{-1}\rightarrow(2p3p3d)^{-1}$. Both stick and synthesized theoretical spectra are displayed in Figs. 4–6 for molybdenum, palladium, and holmium, respectively. The first one is the simplest case as far as the $K\alpha L^0M^r$ lines are concerned as its structure is identical with the structure of the $K\alpha L^0M^0$ transitions. In the remaining cases the number of transitions is very great and in the last case it can be observed that the structure of the spectra is the most complex (88 states and 939 transitions of which 605 are of a remarkable intensity) and the distances between the neighboring lines become extremely small.

Generally, it can be found that for all types of the $K\alpha L^0M^r$ transitions [with the exception of $1s^{-1}3s^{-2}\rightarrow 2p^{-1}3s^{-2}$ and $(1s3s)^{-1}\rightarrow(2p3s)^{-1}$ cases]

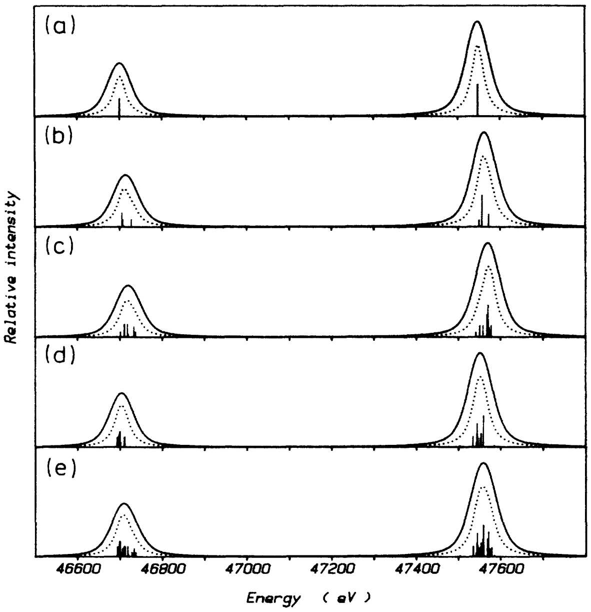

FIG. 3. Same as Fig. 1, but for $K\alpha L^0M^0$ and $K\alpha L^0M^1$ transitions in holmium.

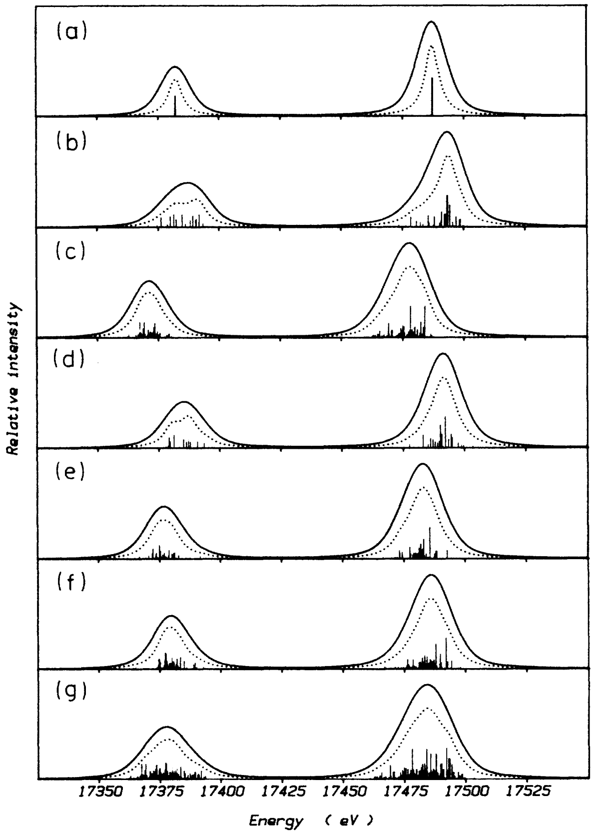

FIG. 4. Calculated stick spectra and synthesized spectra [the sum of the Lorentzian components (dotted lines) and the convolution of the Lorentzian natural line shapes with the Gaussian instrumental response (solid lines)] for $K\alpha L^0M^2$ transitions in molybdenum of the following types: (a) $1s^{-1}3s^{-2}\rightarrow 2p^{-1}3s^{-2}$, (b) $1s^{-1}3p^{-2}\rightarrow 2p^{-1}3p^{-2}$, (c) $1s^{-1}3d^{-2}\rightarrow 2p^{-1}3d^{-2}$, (d) $(1s3s3p)^{-1}\rightarrow(2p3s3p)^{-1}$, (e) $(1s3s3d)^{-1}\rightarrow(2p3s3d)^{-1}$, (f) $(1s3p3d)^{-1}\rightarrow(2p3p3d)^{-1}$, and (g) $K\alpha L^0M^2$, summary spectrum [(a)–(f)].

the distances between the neighboring lines are very small, i.e., of the order of 0.1–1.0 eV for palladium. As is displayed in the theoretical spectra, only for a sum of the Lorentzian line shapes are very weakly structured bands ($K\alpha_2L^0M^r$ and $K\alpha_1L^0M^r$) observed, while for the convolution of a sum of the Lorentzian line shapes with the Gaussian instrumental response the shapes of both bands are very smooth. A comparison of Figs. 1—3 and 4–6 indicates that the structures of the appropriate groups of $K\alpha L^0M^r$ lines of molybdenum, palladium, and holmium are very similar (see the stick spectra in the figures) while the relevant bands (the sum of the Lorentzian natural line shapes) are much smoother for holmium than for molybdenum and palladium. Moreover, for $K\alpha_2L^0M^r$ bands a sum of the Lorentzian line shapes is a little more structured than for $K\alpha_1L^0M^r$. It can be seen that for all cases (with the exception of the $1s^{-1}3s^{-2}\rightarrow 2p^{-1}3s^{-2}$ case) the widths of the $K\alpha L^0M^r$ bands obtained by the convolution of a sum of the Lorentzian line shapes with the Gaussian instrumental response are greater than the widths of reference $K\alpha L^0M^0$ bands. Moreover, it can also be noted that the $K\alpha_2L^0M^r$ bands are somewhat more asymmetric than the $K\alpha_1L^0M^r$ bands. It can also be found that because the positions of various types of the $K\alpha L^0M^r$ bands are shifted by a different extent (with respect to $K\alpha L^0M^0$), the summary $K\alpha L^0M^r$ spectra for certain r are much broader (and smoother) than the particular components.

A detailed comparison of the experimentally observed shifts of the positions of the "$K\alpha_1L^0$" and "$K\alpha_2L^0$" bands in ^{16}O-induced x-ray spectra of molybdenum,[4] palladium,[2] and holmium[16] (with respect to the $K\alpha_1L^0M^0$ and $K\alpha_2L^0M^0$ lines[14]) with the theoretical relative "average" positions of each group of lines $K\alpha_1L^0M^r$ (with respect to $K\alpha_1L^0M^0$) and $K\alpha_2L^0M^r$ (with respect to $K\alpha_2L^0M^0$) have been given in Table III. The theoretical positions of the respective groups of lines have been calculated by taking the weighted averages of all the transitions energies corresponding to a given transition type, the weights being the transition probabilities multiplied by the degeneracies of the initial states, which are $2J+1$. The results presented in Table III corroborate my previous conclusion (see paper I) that removing a $3p$ electron is more effective in producing the $K\alpha L^0$ energy shift than removing a $3s$ or a $3d$ electron. In the case of $3d$ this effect is relatively small and a transition can be shifted either towards higher or lower energies, while in the remaining cases the shift is large and towards higher energies. It can also be observed that the shift effects are strongly nonadditive and remarkably increase with the atomic number.

Only the structures of the particular types of the groups of $K\alpha L^0M^r$ lines and the summary spectra of all the types (for certain r) have been presented above. In

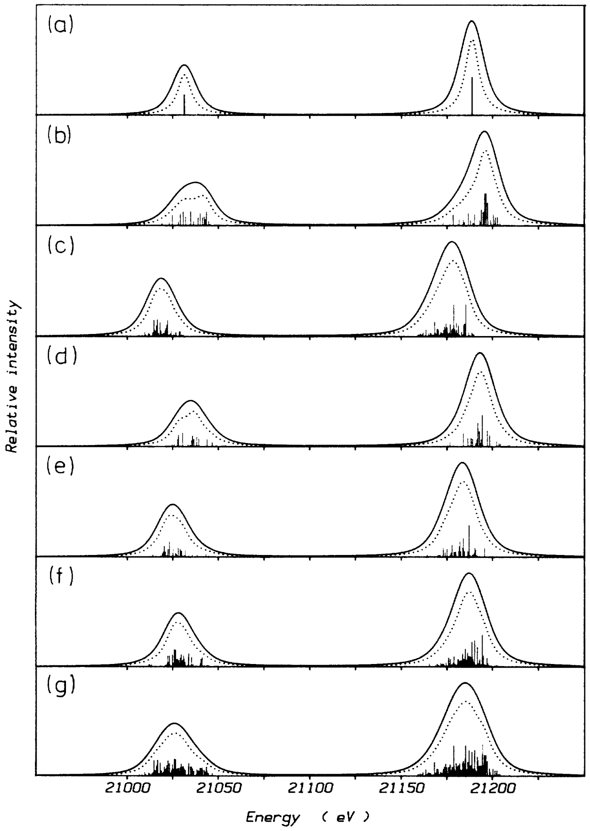

FIG. 5. Same as Fig. 4, but for $K\alpha L^0M^2$ transitions in palladium.

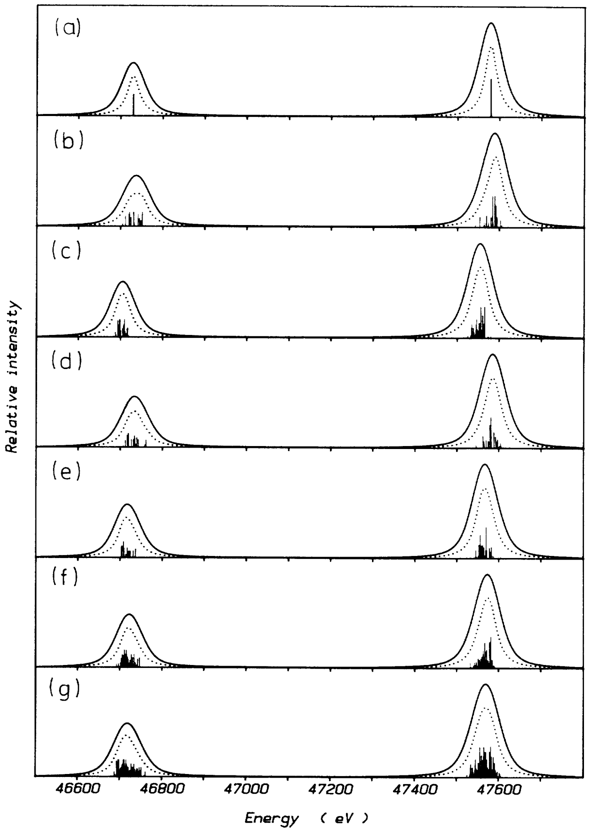

FIG. 6. Same as Fig. 4, but for $K\alpha L^0M^2$ transitions in holmium.

TABLE III. Comparison of the theoretical relative "average" positions of $K\alpha L^0M^r$ lines (with respect to $K\alpha L^0M^0$) with the experimentally observed shifts of $K\alpha L^0$ lines (in eV) in ^{16}O-induced x-ray spectra of Mo ($Z=42$), Pd ($Z=46$), and Ho ($Z=67$). The uncertainties of experimental results are marked in parentheses.

Types of $K\alpha L^0M^r$ lines	$K\alpha_1L^0M^r$			$K\alpha_2L^0M^r$		
	Mo	Pd	Ho	Mo	Pd	Ho
	Theoretical $K\alpha L^0M^1$ [a]					
$(1s3s)^{-1}$	4.455	5.709	15.200	4.457	5.639	13.944
$(1s3p)^{-1}$	8.777	10.429	21.911	7.565	9.137	19.546
$(1s3d)^{-1}$	0.032	0.455	3.965	−0.387	0.033	2.859
$K\alpha L^0M^1$ [b]	3.492	4.420	11.270	2.842	3.732	9.708
	Theoretical $K\alpha L^0M^2$ [a]					
$1s^{-1}3s^{-2}$	9.428	11.882	31.115	9.141	11.472	28.383
$1s^{-1}3p^{-2}$	13.717	16.743	38.854	13.051	15.966	35.766
$1s^{-1}3d^{-2}$	−0.952	−0.208	6.499	−1.662	−0.918	4.503
$(1s3s3p)^{-1}$	13.172	15.981	37.020	12.453	15.133	33.959
$(1s3s3d)^{-1}$	4.630	6.249	19.358	4.210	5.755	16.992
$(1s3p3d)^{-1}$	7.703	9.650	24.338	7.030	8.937	22.055
$K\alpha L^0M^2$ [b]	5.833	7.563	20.970	5.178	6.861	18.610
Expt. $K\alpha L^0$ [c]	6(1)[d]	6.3(5)[e]	13(2)[f]	5(1)[d]	5.5(8)[e]	

[a] The theoretical results for particular types of transitions of each $K\alpha L^0M^r$ lines (only the initial configurations of the corresponding types of transitions are indicated in the table).

[b] The global theoretical results for $K\alpha L^0M^r$ lines.

[c] Experimentally measured effect of removing electrons from the M shell.

[d] Perny *et al.* (Ref. 4).

[e] Rymuza *et al.* (Ref. 2).

[f] Rymuza *et al.* (Ref. 16).

fact, the situation is much more complex, because the real $K\alpha L^0$ bands consist, in general, of all the groups of lines (corresponding to all the possible $K\alpha L^0M^r$ transitions) which also strongly overlap. Therefore, to theoretically simulate the bands which are experimentally observed as the "$K\alpha_1L^0$" and "$K\alpha_2L^0$" bands one should combine linearly all the contributions to the spectrum of $K\alpha L^0M^r$ type. The coefficients of this combination are, however, strongly dependent on the type of the assumed distribution of the population of M-shell holes. However, based on the experimentally observed (in O-induced x-ray spectra) shifts of the $K\alpha L^0$ bands with respect to the bands corresponding to the "pure" $K\alpha L^0$ transitions (see Table III), it can be concluded that although the shift increases with increasing the atomic number, the heavier the element, the less average number of M-shell electrons can be removed by a certain projectile. In the case of molybdenum this number is probably very close to 2, in the case of palladium it is remarkably lower, and in the case of holmium is about 1.

IV. CONCLUSIONS

The test studies have shown that the proposed MCDF-SAL version of the MCDF method with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections is accurate enough to reproduce very well the experimental positions of the $K\alpha L^0M^0$ and $K\beta L^0M^0$ lines.

To reliably explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^0$ bands, considerable attention has been paid to the analysis of the structure of the groups of $K\alpha L^0M^r$ lines corresponding to various types of transitions. On the basis of the calculations for molybdenum, palladium, and holmium some general conclusions can be drawn.

First, in the case of each type of transition two clearly separated groups of lines are observed, from which, those of lower energies can be attributed to $K\alpha_2L^0M^r$ and those of higher energies to $K\alpha_1L^0M^r$. Second, in most cases, removing even a small number of electrons from the M shell causes a strong increase of the number of states possible for the given initial and final configurations and a dramatic increase of the number of possible transitions. Third, it can be observed that in all cases [with the exception of those of $1s^{-1}3s^{-2}\rightarrow 2p^{-1}3s^{-2}$ and $(1s3s)^{-1}\rightarrow(2p3s)^{-1}$], the structures of the $K\alpha L^0M^r$ lines are very complex and the distances between the neighboring lines are very small, i.e., of the order of 0.1–1.0 eV for palladium. Fourth, only for a sum of the Lorentzian natural line shapes are very weakly structured $K\alpha L^0M^r$ bands observed, while for the convolution of a sum of the Lorentzian line shapes with the Gaussian instrumental response the shapes of both bands are very smooth. Fifth, the structures of the appropriate groups of $K\alpha L^0M^r$ lines of molybdenum, palladium, and holmium are very similar (see the stick spectra) while the relevant bands, the sum of the Lorentzian natural line shapes, are much smoother for holmium than for molybdenum and palladium. Sixth, for all cases (with the exception of the $1s^{-1}3s^{-2} \rightarrow 2p^{-1}3s^{-2}$ case) the widths of the $K\alpha L^0 M^r$ bands are significantly greater than the widths of reference $K\alpha L^0 M^0$ bands. Seventh, because the positions of various types of the $K\alpha L^0 M^r$ bands are shifted by a different extent, the summary $K\alpha L^0 M^r$ spectra for certain r are much broader (and smoother) than the particular components. Eighth, because the $K\alpha L^0 M^r$ bands corresponding to various r are also overlapped, the effects of multiple M-shell ionization are manifested in the spectra merely as an asymmetric broadening and net shift of $K\alpha_1 L^0$ and $K\alpha_2 L^0$ bands. Ninth, removing a $3p$ electron is more effective than a $3s$ or $3d$ electron in producing the $K\alpha L^0$ energy shift. Tenth, the shift effects are strongly nonadditive and increase remarkably with the atomic number.

The comparison of the theoretical and experimental (in ^{16}O-induced x-ray spectra) shifts of the positions of the $K\alpha L^0 M^r$ bands with respect to the "pure" $K\alpha L^0$ lines reveals that although the experimental shift increases with increasing the atomic number, for the elements of greater Z it is less probable to ionize multiply the M shell, which is consistent with the well-known relation $P_i \sim Z_p^2 / Z_t^2$, where P_i is the ionization probability and Z_p and Z_t are the atomic numbers of the projectile and target, respectively. In the case of molybdenum and palladium the effect of shifting measured experimentally can be attributed to the presence of approximately two M-shell holes, while in the case of holmium to the presence of approximately one hole.

The author believes that the results of his analysis will be helpful in a better understanding of the structure of the $K\alpha L^0 M^r$ lines in x-ray spectra of multiply ionized heavy atoms. Moreover, the results of this work can be used to construct different shapes of theoretical $K\alpha L^0$ bands for molybdenum, palladium, and holmium, satisfactorily reproducing the shapes of various experimental $K\alpha L^0$ bands generated by different inducing projectiles.

Obviously, the present study concerns the effect of M-shell holes on the principal $K\alpha L^0$ bands only. Undoubtedly, for a complete description of the heavy-particle-induced x-ray spectra, it is necessary to perform calculations on all the possible $K\alpha L^n M^r$ transitions and to examine the effect of N-shell holes. The investigations are already in progress and the results will be published in forthcoming papers.

ACKNOWLEDGMENTS

This work has been supported by the Polish Central Project for Fundamental Research CPBP-01.06.

---

[1] Z. Sujkowski, D. Chmielewska, P. Rymuza, G. J. Balster, B. Kotliński, R. H. Siemssen, and H. W. Wilschut, Phys. Lett. B **196**, 122 (1987).

[2] P. Rymuza, Z. Sujkowski, M. Carlen, J.-Cl. Dousse, M. Gasser, J. Kern, B. Perny, and Ch. Rhême, Z. Phys. D (to be published).

[3] M. Polasik, Phys. Rev. A **39**, 616 (1989).

[4] B. Perny, J.-Cl. Dousse, M. Gasser, J. Kern, Ch. Rhême, P. Rymuza, and Z. Sujkowski, Phys. Rev. A **36**, 2120 (1987).

[5] M. Polasik, Phys. Rev. A **39**, 5092 (1989).

[6] I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[7] B. J. McKenzie, I. P. Grant, and P. H. Norrington, Comput. Phys. Commun. **21**, 233 (1980).

[8] I. P. Grant and B. J. McKenzie, J. Phys. B **13**, 2671 (1980).

[9] J. Hata and I. P. Grant, J. Phys. B **16**, 3713 (1983).

[10] I. P. Grant, Int. J. Quantum Chem. **25**, 23 (1984).

[11] I. P. Grant, J. Phys. B **7**, 1458 (1974).

[12] J. H. Scofield, Phys. Rev. A **9**, 1041 (1974).

[13] K. Jankowski and M. Polasik, J. Phys. B (to be published).

[14] J. A. Bearden, Rev. Mod. Phys. **39**, 78 (1967).

[15] S. I. Salem and P. L. Lee, At. Data Nucl. Data Tables **18**, 233 (1976).

[16] P. Rymuza, Z. Sujkowski, M. Carlen, J.-Cl. Dousse, M. Gasser, J. Kern, B. Perny, and Ch. Rhême (unpublished).