Theoretical multiconfiguration Dirac-Fock method study on the x-ray spectra of multiply ionized heavy atoms: The structure of the $K\alpha L^1M^r$ satellite lines

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Very extensive multiconfiguration Dirac-Fock calculations done through the alternative special average-level version [Polasik, Phys. Rev. A **40**, 4361 (1989)] with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections have been performed on palladium to shed light on the structure of the $K\alpha L^1M^r$ satellite lines in its x-ray spectra and moreover, to explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^1$ satellite bands. For each type of $K\alpha L^1M^r$ line two theoretical spectra have been synthesized: one a sum of the Lorentzian natural line shapes and the other a convolution of the sum of the Lorentzian natural line shapes with a Gaussian instrumental response. It has been found that in some cases the structures of $K\alpha L^1M^r$ satellite lines are extremely complex and the distances between the neighboring lines are very small. It has been also observed that the effect of M-shell holes smooths the shapes of the $K\alpha L^1$ satellite bands. Moreover, the positions of the resultant bands are shifted and their shapes more closely resemble the Voigt profiles than the reference $K\alpha L^1M^0$ bands. It has been concluded that removing a $3p$ electron is more effective in producing a $K\alpha L^1$ energy shift than removing a $3s$ or $3d$ electron. The results of this and previous papers of this series can be used for theoretical simulations of various experimental $K\alpha L^n$ spectra of palladium generated by different inducing projectiles.

I. INTRODUCTION

The K x-ray spectra of multiply ionized heavy atoms have recently become the subject of intensive experimental and theoretical studies in atomic as well as nuclear physics. For example, it is well known that in the case of the heavy-ion-induced x-ray spectra the shapes and positions of the $K\alpha L^n$ bands are influenced mainly by the multiple M-shell ionization (the influence of N-shell ionization is much smaller).[1] Moreover, the analysis of $K\alpha$ and $K\beta$ bands of x-ray spectra accompanying a nuclear-fusion reaction, which provides a test of theoretical predictions for atomic collisions (half-trajectory collisions), also indicates the multiple ionization of the N, M, and L shells.[2] However, in contrast with the L-shell ionization, it is not possible to deduce the degree of M-shell ionization on the basis of experimental data only.[1] It was therefore thought worthwhile to examine theoretically the influence of various additional holes in the M shell on the shapes of the $K\alpha L^n$ x-ray spectra. Generally, the groups of lines labeled by $K\alpha_1L^nM^r$ and $K\alpha_2L^nM^r$ correspond to transitions from initial states that have one hole in the K shell, n holes in the L shell, and r holes in the M shell.

In the first paper of this series,[3] hereafter referred to as I, multiconfiguration Dirac-Fock (MCDF) calculations in the 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 shed light on the structure of the $K\alpha L^n$ satellite lines in its x-ray spectra (the first systematic theoretical study on the structure of these lines for a heavy atom). The availability of recently measured[1] high-resolution $K\alpha$ x-ray spectra of molybdenum was the inspiration to perform a theoretical simulation of these spectra applying a theoretical model in which a spectrum is represented as a sum of the bands (being the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) resulting from transitions of the $K\alpha L^n$ type only.[4] The effect of M-shell holes has been taken into account in a crude way by simply shifting a spectrum towards higher energies and applying larger Gaussian linewidths. Although this procedure has succeeded in general, it has turned out that to reproduce accurately both the positions of the bands and the shape of the experimental spectrum including $K\alpha L^n$ satellites it is necessary to perform a detailed investigation in which various M-shell holes will be taken into account together with L-shell holes (the $K\alpha L^nM^r$ lines). Therefore in the second paper of this series,[5] hereafter referred to as II, detailed MCDF calculations in the alternative special average-level (MCDF-SAL) version with the inclusion of the transverse (Breit) interaction, self-energy, and vacuum polarization corrections have been performed on molybdenum, palladium, and holmium to elucidate the structure of the $K\alpha L^0M^r$ lines in their x-ray spectra and to reliably explain the influence of additional holes in the M shell on the shapes and positions of the $K\alpha L^0$ bands. It has been shown that the structures of the $K\alpha L^0M^r$ lines are very complex. Moreover, it has been found that the structure of the appropriate groups of $K\alpha L^0M^r$ lines of molybdenum, palladium, and holmium is very similar while the relevant bands, being the sum of the Lorentzian natural line shapes, are much smoother for holmium than for molybdenum and palladi-

um. The convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response smooths the shapes of $K\alpha L^0M^r$ bands greatly. 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 $K\alpha_1 L^0$ and $K\alpha_2 L^0$ bands. The results obtained in II corroborate my previous conclusions (see I) that removing a $3p$ electron is more effective than removing a $3s$ or $3d$ electron in producing a $K\alpha L^0$ energy shift and that the shift effects remarkably increase with the atomic number and are strongly nonadditive. Moreover, it has also been found that for a complete description of the heavy-ion-induced $K\alpha$ x-ray spectra it is necessary to perform calculations on the $K\alpha L^nM^r$ lines. The comparison of the theoretical and experimental (in ^{16}O-induced x-ray spectra) shifts of the positions of the $K\alpha L^0M^r$ bands with respect to the reference $K\alpha L^0M^0$ bands reveals (see II) that in the case of palladium the effect of shifting measured experimentally can be attributed to the presence of no more than (in an average sense) two M-shell holes. Therefore, to explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^1$ satellite bands the present very extensive systematic study on the structure of the $K\alpha L^1M^r$ lines has been performed on palladium only for $r=0,1,2$. The study presented in this paper is the first theoretical study on the structure of the lines of the $K\alpha L^nM^r$ (for $n\neq 0$) type.

II. THEORETICAL BACKGROUND

The MCDF method employed in the present study has been described in detail in many papers.[6–9] Moreover, all basic ideas of the alternative special average-level version of the MCDF method which is used here have been presented in II. However, for the sake of clarity, some essential details are very briefly recapitulated below.

Within the MCDF scheme the effective Hamiltonian for an N-electron system is to be expressed by (atomic units are used)

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

where $h_D(i)$ is the Dirac operator for ith electron (see paper I) and the terms C_{ij} account for electron-electron interactions and come from the one-phonon exchange process. Each C_{ij} can be expressed[8] by

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

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):

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

In the MCDF method an atomic state function (ASF) with the total angular momentum J and parity p is assumed in the multiconfigurational form:[6,9]

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

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

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

In the alternative MCDF-SAL version of the calculations which was proposed in II the energy functional is specially averaged over all the initial and final states and can be expressed by

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

where $\bar{q}_a$ is the generalized occupation number for the orbital a, ε_a and ε_{ab} are the Lagrange multipliers, $S(a,b)$ is the overlap integral, and $E_{\rm opt}$ is taken in the form

$$E_{\rm opt}=\frac{1}{\sqrt{n_i}+\sqrt{n_f}}\left[\frac{1}{\sqrt{n_i}}\sum_{i=1}^{n_i} H_{ii}+\frac{1}{\sqrt{n_f}}\sum_{f=1}^{n_f} H_{ff}\right] , \tag{6}$$

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).

In this version of the calculations the common set of the orbitals (for all the initial and final states) is to be determined. This removes the problem of nonorthogonality of the orbitals[5] 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 the relevant CSF's. It is evident that for each particular state such orbitals yield a higher energy than those obtained from optimal level version of MCDF (MCDF-OL) calculations for each state (the effect of relaxation). However, usually all energy levels are shifted by approximately the same extent (see II). 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 average-level version (MCDF-AL).[5] 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 remedy against exaggerating the contribution of the more numerous configurations to the energy functional.

Apart from the transverse (Breit) interaction two types of energy corrections are included, namely the self-energy and vacuum polarization corrections (see I). The formulas for the transition matrix elements, spontaneous emission probabilities, and oscillator strengths can be found in the work of Grant.[10] The studies presented in this paper

are based on the MCDF package developed by Grant and co-workers.[6,7]

III. RESULTS AND DISCUSSION

It is well known that removing additional electrons from the L shell results in the appearance of the $K\alpha L^n$ satellite bands in the spectrum. As pointed out in the Introduction, in the case of the heavy-ion-induced x-ray spectra the shapes and positions of the $K\alpha L^n$ bands are influenced mainly by the multiple M-shell ionization. To elucidate for the first time the structure of the $K\alpha L^1M^r$ satellite lines and to examine the influence of various types of additional holes in the M shell on the shapes and positions of the $K\alpha L^1$ satellite bands in the x-ray spectra of a heavy atom very extensive MCDF-SAL calculations have been performed on palladium.

Let us consider the "pure" $K\alpha L^1M^r$ transitions, i.e., those which occur between the states in which there are no holes in shells higher than M. All possible CSF's in j-j coupling scheme due to the nonrelativistic configurations listed in Table I were used in the present study. It can be seen from Table I that in most cases removing even one or two electrons from the M shell causes a very strong increase of the number of states possible for the given initial and final configurations.

A detailed analysis of the structure of the groups of $K\alpha L^1M^r$ lines (r=0,1,2) corresponding to all possible types of transitions has been carried out as in II. In the stick spectra the initial states statistical populations, which are proportional to $2J+1$ have been taken into account (J being the total angular momentum of a state). To show better the influence of various types of additional holes in the M shell on the shapes and positions of the $K\alpha L^1$ satellite bands for each type of $K\alpha L^1M^r$ lines two theoretical spectra have been synthesized: one the sum of the Lorentzian natural line shapes with a width of 9.00 eV (Ref. 11) (dotted lines) and the other one (solid lines) the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having a width of 10.0 eV (Ref. 5), to better reflect the experimental spectra.

In Figs. 1–4 both stick and synthesized spectra for all types of the $K\alpha L^1M^r$ transitions (r=0,1,2) are presented together with the summary spectra for a certain r. At first it should be noted that the "reference" $K\alpha L^1M^0$ transitions (without M-shell ionization) can be either of the type $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ [see Fig. 1(a)] or $(1s2p)^{-1}\rightarrow 2p^{-2}$ [see Fig. 2(a)]. Generally it can be noted that in all cases of the $K\alpha L^1M^r$ transitions two separated groups of lines are observed, from which those of lower energies can be attributed to $K\alpha_2L^1M^r$ and those of higher energies to $K\alpha_1L^1M^r$. When analyzing the shapes of the synthesized $K\alpha L^1M^r$ bands (both those which are the sum of the Lorentzian natural line shapes and those which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) it can be observed in general that in the case of transitions from the initial states having one $2s$ hole [see Figs. 1 and 3; e.g., reference $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ bands in Fig. 1(a)] there are many more scattered bands than in the case of transitions from the initial

TABLE I. CSF sets used in the calculations of the structures of the particular transition types of the $K\alpha L^1M^r$ lines (r=0,1,2). The numbers of CSF's in the j-j coupling scheme are also given.

Transition type		CSF sets: Initial	No. of CSF's	Final	No. of CSF's
		$K\alpha L^1M^0$			
$(1s2s)^{-1}$	$\rightarrow(2s2p)^{-1}$	$1s^12s^12p^63s^23p^63d^{10}$	2	$1s^22s^12p^53s^23p^63d^{10}$	4
$(1s2p)^{-1}$	$\rightarrow 2p^{-2}$	$1s^12s^22p^53s^23p^63d^{10}$	4	$1s^22s^22p^43s^23p^63d^{10}$	5
		$K\alpha L^1M^1$			
$(1s2s3s)^{-1}$	$\rightarrow(2s2p3s)^{-1}$	$1s^12s^12p^63s^13p^63d^{10}$	3	$1s^22s^12p^53s^13p^63d^{10}$	7
$(1s2s3p)^{-1}$	$\rightarrow(2s2p3p)^{-1}$	$1s^12s^12p^63s^23p^53d^{10}$	7	$1s^22s^12p^53s^23p^53d^{10}$	18
$(1s2s3d)^{-1}$	$\rightarrow(2s2p3d)^{-1}$	$1s^12s^12p^63s^23p^63d^9$	8	$1s^22s^12p^53s^23p^63d^9$	23
$(1s2p3s)^{-1}$	$\rightarrow 2p^{-2}3s^{-1}$	$1s^12s^22p^53s^13p^63d^{10}$	7	$1s^22s^22p^43s^13p^63d^{10}$	8
$(1s2p3p)^{-1}$	$\rightarrow 2p^{-2}3p^{-1}$	$1s^12s^22p^53s^23p^53d^{10}$	18	$1s^22s^22p^43s^23p^53d^{10}$	21
$(1s2p3d)^{-1}$	$\rightarrow 2p^{-2}3d^{-1}$	$1s^12s^22p^53s^23p^63d^9$	23	$1s^22s^22p^43s^23p^63d^9$	28
		$K\alpha L^1M^2$			
$(1s2s)^{-1}3s^{-2}$	$\rightarrow(2s2p)^{-1}3s^{-2}$	$1s^12s^12p^63s^03p^63d^{10}$	2	$1s^22s^12p^53s^03p^63d^{10}$	4
$(1s2s)^{-1}3p^{-2}$	$\rightarrow(2s2p)^{-1}3p^{-2}$	$1s^12s^12p^63s^23p^43d^{10}$	16	$1s^22s^12p^53s^23p^43d^{10}$	42
$(1s2s)^{-1}3d^{-2}$	$\rightarrow(2s2p)^{-1}3d^{-2}$	$1s^12s^12p^63s^23p^63d^8$	32	$1s^22s^12p^53s^23p^63d^8$	90
$(1s2s3s3p)^{-1}$	$\rightarrow(2s2p3s3p)^{-1}$	$1s^12s^12p^63s^13p^53d^{10}$	14	$1s^22s^12p^53s^13p^53d^{10}$	36
$(1s2s3s3d)^{-1}$	$\rightarrow(2s2p3s3d)^{-1}$	$1s^12s^12p^63s^13p^63d^9$	16	$1s^22s^12p^53s^13p^63d^9$	46
$(1s2s3p3d)^{-1}$	$\rightarrow(2s2p3p3d)^{-1}$	$1s^12s^12p^63s^23p^53d^9$	46	$1s^22s^12p^53s^23p^53d^9$	130
$(1s2p)^{-1}3s^{-2}$	$\rightarrow(2p3s)^{-2}$	$1s^12s^22p^53s^03p^63d^{10}$	4	$1s^22s^22p^43s^03p^63d^{10}$	5
$(1s2p)^{-1}3p^{-2}$	$\rightarrow(2p3p)^{-2}$	$1s^12s^22p^53s^23p^43d^{10}$	42	$1s^22s^22p^43s^23p^43d^{10}$	51
$(1s2p)^{-1}3d^{-2}$	$\rightarrow(2p3d)^{-2}$	$1s^12s^22p^53s^23p^63d^8$	90	$1s^22s^22p^43s^23p^63d^8$	111
$(1s2p3s3p)^{-1}$	$\rightarrow 2p^{-2}(3s3p)^{-1}$	$1s^12s^22p^53s^13p^53d^{10}$	36	$1s^22s^22p^43s^13p^53d^{10}$	42
$(1s2p3s3d)^{-1}$	$\rightarrow 2p^{-2}(3s3d)^{-1}$	$1s^12s^22p^53s^13p^63d^9$	46	$1s^22s^22p^43s^13p^63d^9$	56
$(1s2p3p3d)^{-1}$	$\rightarrow 2p^{-2}(3p3d)^{-1}$	$1s^12s^22p^53s^23p^53d^9$	130	$1s^22s^22p^43s^23p^53d^9$	158

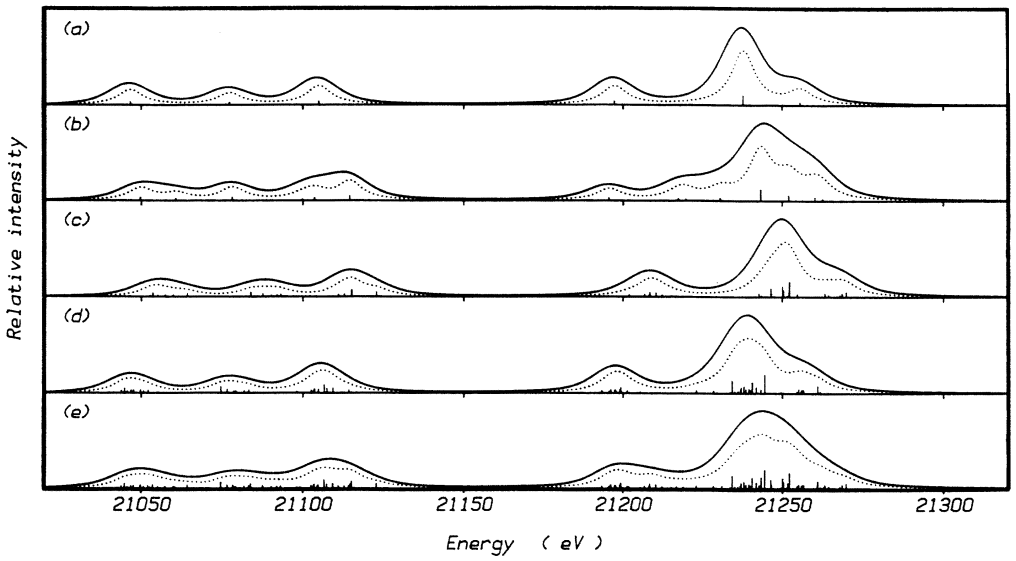

FIG. 1. Effect of one-electron ionization of the M shell on the shapes and positions of the $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ satellite bands. Calculated stick spectra (line positions with their relative intensities, to the same scale) and synthesized spectra (one being the sum of the Lorentzian natural 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 following transitions: (a) $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ (reference satellite lines, see text), (b) $(1s2s3s)^{-1}\rightarrow(2s2p3s)^{-1}$, (c) $(1s2s3p)^{-1}\rightarrow(2s2p3p)^{-1}$, (d) $(1s2s3d)^{-1}\rightarrow(2s2p3d)^{-1}$, and (e) summary spectrum [(b)+(c)+(d)].

states having one $2p$ hole [see Figs. 2 and 4; e.g., reference $(1s2p)^{-1}\rightarrow 2p^{-2}$ bands in Fig. 2(a)]. In all cases the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response greatly smooths the resultant spectrum. Moreover, it can be seen that in the case of transitions from the initial states having one $2p$ hole (see Figs. 2 and 4) the lines are grouped to give two $K\alpha L^1M^r$ bands which are only slightly structured (being the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response).

In the case of the $K\alpha L^1M^1$ lines we have six possible types of transitions: $(1s2s3s)^{-1}\rightarrow(2s2p3s)^{-1}$, $(1s2s3p)^{-1}\rightarrow(2s2p3p)^{-1}$, $(1s2s3d)^{-1}\rightarrow(2s2p3d)^{-1}$ [see Figs. 1(b)–1(d)], $(1s2p3s)^{-1}\rightarrow 2p^{-2}3s^{-1}$, $(1s2p3p)^{-1}\rightarrow 2p^{-2}3p^{-1}$, and $(1s2p3d)^{-1}\rightarrow 2p^{-2}3d^{-1}$ [see Figs. 2(b)–2(d)]. It should be noted that removing even one M-shell electron results in a considerable increase in the

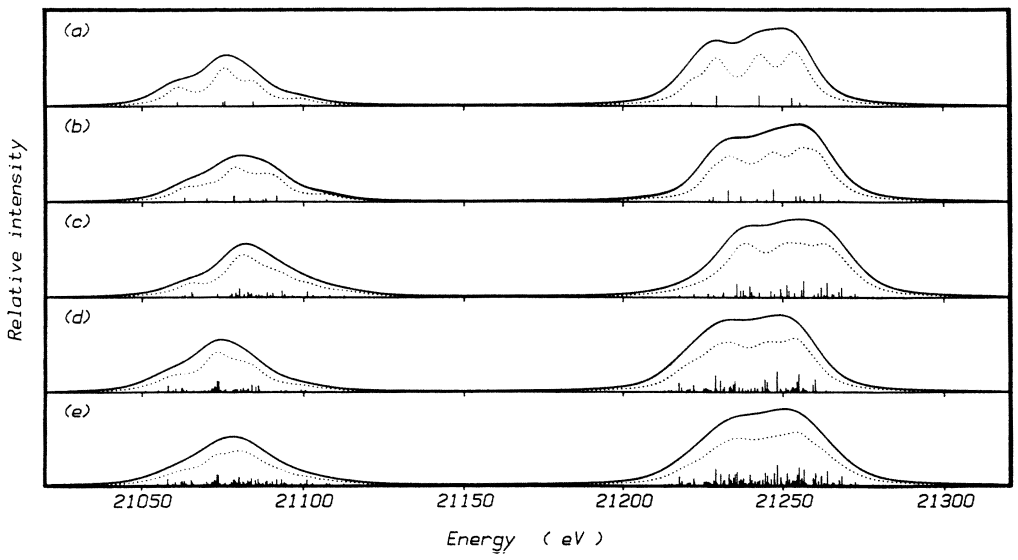

FIG. 2. Effect of one-electron ionization of the M shell on the shapes and positions of the $(1s2p)^{-1}\rightarrow 2p^{-2}$ satellite bands. Calculated stick and synthesized spectra (see Fig. 1) for the following transitions: (a) reference $(1s2p)^{-1}\rightarrow 2p^{-2}$ lines, (b) $(1s2p3s)^{-1}\rightarrow 2p^{-2}3s^{-1}$, (c) $(1s2p3p)^{-1}\rightarrow 2p^{-2}3p^{-1}$, (d) $(1s2p3d)^{-1}\rightarrow 2p^{-2}3d^{-1}$, and (e) summary spectrum [(b)+(c)+(d)].

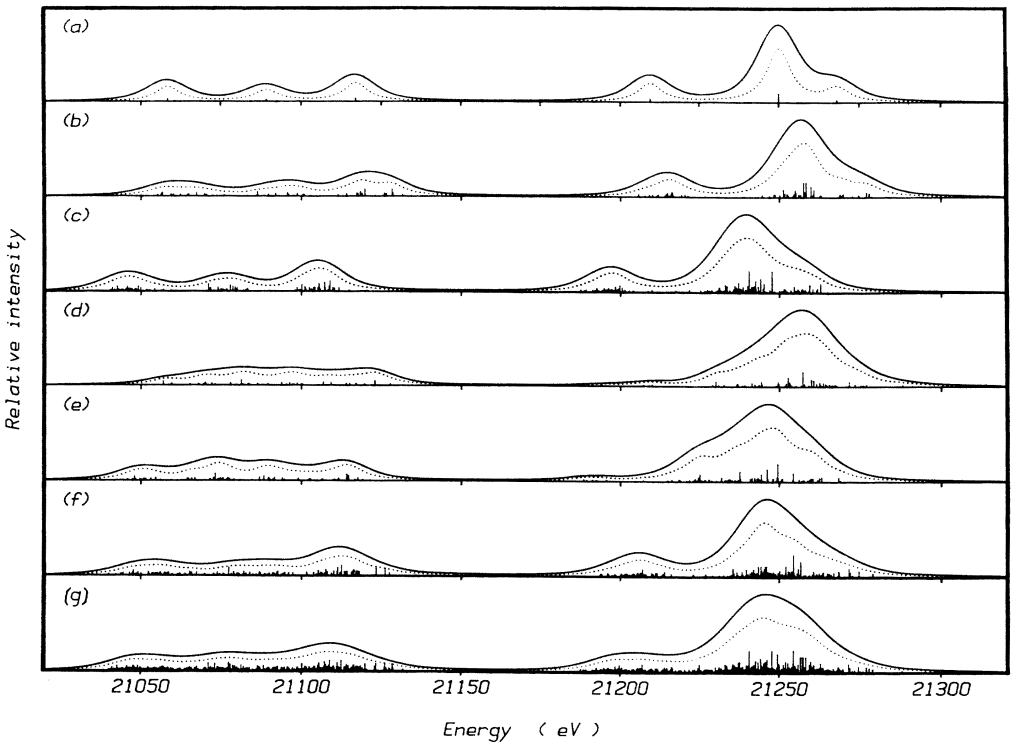

FIG. 3. Effect of two-electron ionization of the M shell on the shapes and positions of the $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ bands. Calculated stick and synthesized spectra for following transitions: (a) $(1s2s)^{-1}3s^{-2}\rightarrow(2s2p)^{-1}3s^{-2}$, (b) $(1s2s)^{-1}3p^{-2}\rightarrow(2s2p)^{-1}3p^{-2}$, (c) $(1s2s)^{-1}3d^{-2}\rightarrow(2s2p)^{-1}3d^{-2}$, (d) $(1s2s3s3p)^{-1}\rightarrow(2s2p3s3p)^{-1}$, (e) $(1s2s3s3d)^{-1}\rightarrow(2s2p3s3d)^{-1}$, (f) $(1s2s3p3d)^{-1}\rightarrow(2s2p3p3d)^{-1}$, and (g) summary spectrum [(a)+(b)+(c)+(d)+(e)+(f)].

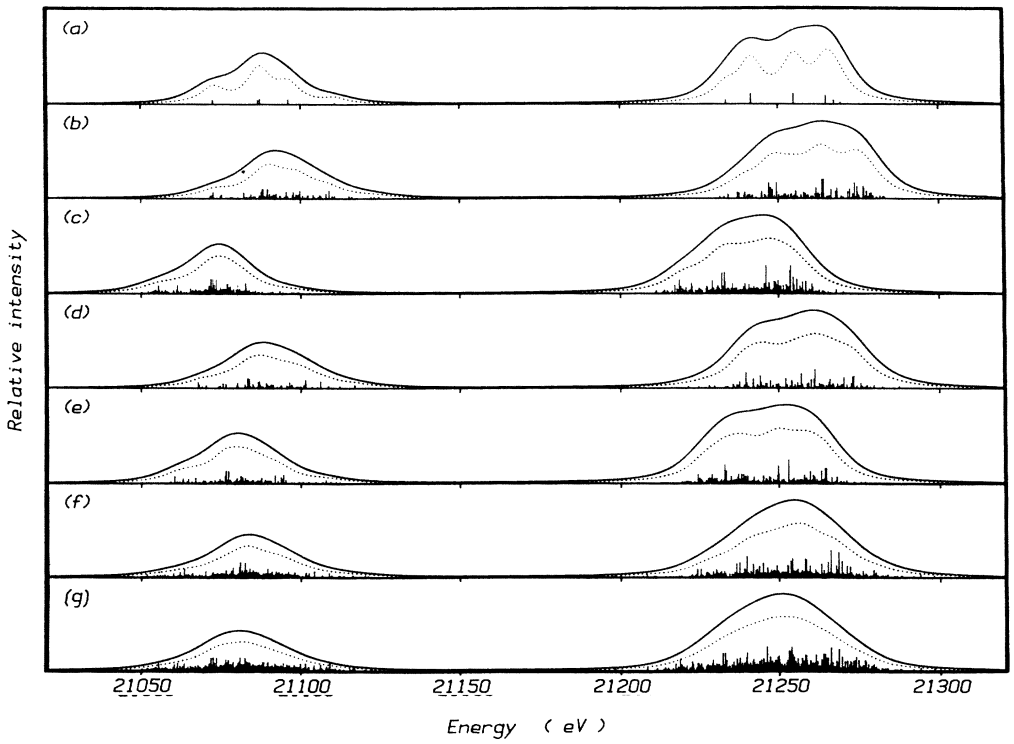

FIG. 4. Effect of two-electron ionization of the M shell on the shapes and positions of the $(1s2p)^{-1}\rightarrow2p^{-2}$ satellite bands. Calculated stick and synthesized spectra (see Fig. 1) for the following transitions: (a) $(1s2p)^{-1}3s^{-2}\rightarrow(2p3s)^{-2}$, (b) $(1s2p)^{-1}3p^{-2}\rightarrow(2p3p)^{-2}$, (c) $(1s2p)^{-1}3d^{-2}\rightarrow(2p3d)^{-2}$, (d) $(1s2p3s3p)^{-1}\rightarrow2p^{-2}(3s3p)^{-1}$, (e) $(1s2p3s3d)^{-1}\rightarrow2p^{-2}(3s3d)^{-1}$, (f) $(1s2p3p3d)^{-1}\rightarrow2p^{-2}(3p3d)^{-1}$, and (g) summary spectrum [(a)+(b)+(c)+(d)+(e)+(f)].

number of transitions allowed and thus in significantly more complex stick spectra. In the case of the transition of the type $(1s2s3s)^{-1}\rightarrow(2s2p3s)^{-1}$ also the theoretically synthesized spectrum being the sum of the Lorentzian natural line shapes (dotted lines) is slightly more structured than the reference spectrum in the case of transitions $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$. In the remaining cases the synthesized bands which are the sum of the Lorentzian natural line shapes are less structured than the appropriate reference bands. It can be seen that in all cases $K\alpha L^1M^1$ bands which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response (solid lines), which better reflect the experimental spectra, are less structured than the appropriate reference $K\alpha L^1M^0$ bands. In the case of each type of transitions the widths of the $K\alpha L^1M^1$ bands are only somewhat greater than the widths of the reference $K\alpha L^1M^0$ bands. It can be found that as positions of various types of the $K\alpha L^1M^1$ bands are shifted by a different extent, the widths of summary bands [Figs. 1(e) and 2(e)] are greater than the widths of the particular components.

In the case of $K\alpha L^1M^2$ the following types of transitions are possible:

$$(1s2s)^{-1}3s^{-2}\rightarrow(2s2p)^{-1}3s^{-2},$$

$$(1s2s)^{-1}3p^{-2}\rightarrow(2s2p)^{-1}3p^{-2},$$

$$(1s2s)^{-1}3d^{-2}\rightarrow(2s2p)^{-1}3d^{-2},$$

$$(1s2s3s3p)^{-1}\rightarrow(2s2p3s3p)^{-1},$$

$$(1s2s3s3d)^{-1}\rightarrow(2s2p3s3d)^{-1},$$

$$(1s2s3p3d)^{-1}\rightarrow(2s2p3p3d)^{-1}$$

[see Figs. 3(a)–3(f)],

$$(1s2p)^{-1}3s^{-2}\rightarrow(2p3s)^{-2},$$

$$(1s2p)^{-1}3p^{-2}\rightarrow(2p3p)^{-2},$$

$$(1s2p)^{-1}3d^{-2}\rightarrow(2p3d)^{-2},$$

$$(1s2p3s3p)^{-1}\rightarrow2p^{-2}(3s3p)^{-1},$$

$$(1s2p3s3d)^{-1}\rightarrow2p^{-2}(3s3d)^{-1},$$

and

$$(1s2p3p3d)^{-1}\rightarrow2p^{-2}(3p3d)^{-1}$$

[see Figs. 4(a)–4(f)]. The first and seventh ones are the simplest cases as far as the $K\alpha L^1M^r$ lines are concerned, as their structures are identical with the structures of the reference $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ and $(1s2p)^{-1}\rightarrow2p^{-2}$ lines, respectively. 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 stick spectrum is the most complex[12] (288 states and about 12 000 transitions, about 5000 of which are of a remarkable intensity) and the distances between the neighboring lines become extremely small, of the order of 0.01 eV. It can be noted that in all cases the $K\alpha L^1M^2$ bands (both those which are the sum of the Lorentzian natural line shapes and those which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) are less structured than the appropriate reference $K\alpha L^1M^0$ bands. Moreover, in the case of each type of transition the positions of the $K\alpha L^1M^2$ bands are shifted and their widths are only somewhat greater than the widths of the reference $K\alpha L^1M^0$ bands. Because the positions of various types of the $K\alpha L^1M^2$ bands are shifted by a different extent the summary spectra [Figs. 3(g) and 4(g)] are much smoother and broader than the particular components.

At this point one must bear in mind that in resolving the experimental spectra the contribution of a particular $K\alpha L^n$ satellite to the spectrum is approximated by two Voigt profiles (convolution of a single Lorentzian line shape with the Gaussian instrumental response), one for the $K\alpha_1L^n$ band and one for the $K\alpha_2L^n$ band. It has been found, very recently, for molybdenum (see Ref. 4) that the theoretically synthesized summary $K\alpha L^1M^0$ bands (without M-shell ionization), constructed under the assumption that the populations of the $2s$ and $2p$ holes depend only on the number of ways in which a particular initial-hole state can be formed, are evidently too narrow, have too many details not observed experimentally, and cannot be represented as two Voight functions, even in a very crude approximation. Therefore it is very interesting to examine the influence of ionization of the M shell on the shapes and positions of the summary $K\alpha L^1$ satellite bands.

In Figs. 5 and 6 the effects of various one- and two-electron ionizations of the M shell on the shapes and positions of the "reference" summary $K\alpha L^1M^0$ satellite bands have been shown. It should be noted that the reference summary $K\alpha L^1M^0$ satellite bands [Fig. 5(a)] are the superposition of bands of the types $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ [Fig. 1(a)] and $(1s2p)^{-1}\rightarrow2p^{-2}$ [Fig. 2(a)]. Also, all the summary $K\alpha L^1M^r$ spectra (for $r\neq0$) are the superpositions of the appropriate bands of both types $(1s2s)^{-1}\rightarrow(2s2p)^{-1}$ (Figs. 1 and 3) and $(1s2p)^{-1}\rightarrow2p^{-2}$ (Figs. 2 and 4), constructed under the assumption that the populations of the $2s$ and $2p$ holes depend only on the number of ways in which a particular initial-hole state can be formed.

The reference summary $K\alpha L^1M^0$ satellite bands (without M-shell ionization) have been shown in Fig. 5(a). It can be noted that the theoretically synthesized spectrum, being the sum of the Lorentzian natural line shapes (dotted lines), has a subtle structure which is lost in a large part after convoluting with the Gaussian instrumental response (solid lines). However, it can also be noted that the resultant $K\alpha_1L^1M^0$ (for higher energies) and $K\alpha_2L^1M^0$ (for lower energies) bands cannot be well represented as two Voigt functions.

It can be found that removing even one M-shell electron (see Fig. 5) results in a considerable increase in the number of transitions allowed (the number of transitions increases in the order going from $3s$ [Fig. 5(b)] to $3p$ [Fig. 5(c)] to $3d$ ionization [Fig. 5(d)]) and thus also in significantly more structured stick spectra. In all cases $K\alpha L^1M^1$ bands (both those which are the sum of the Lorentzian natural line shapes and those which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) are less

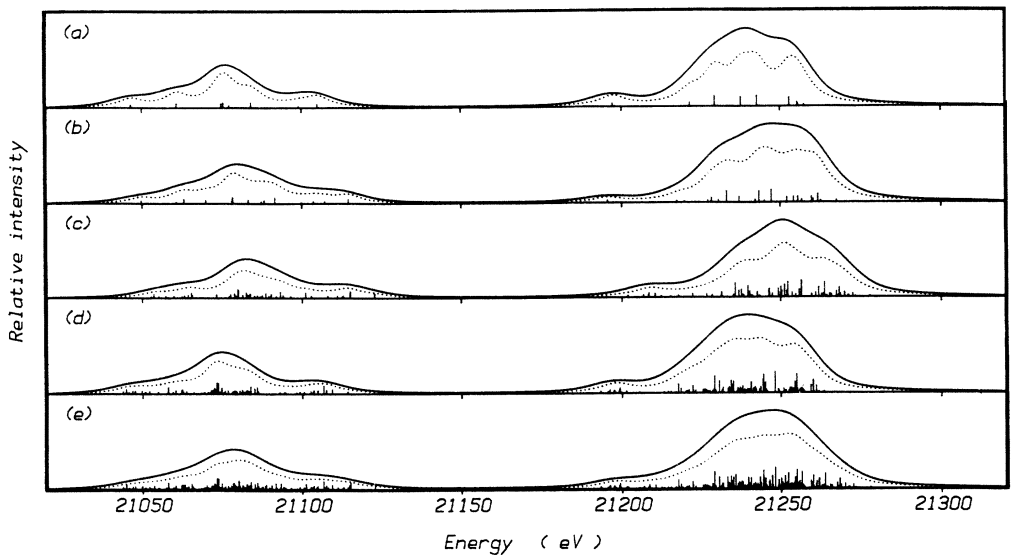

FIG. 5. Effect of various types of one-electron ionization of the M shell on the shapes and positions of the summary $K\alpha L^1$ satellite bands (see text). Calculated stick and synthesized spectra (see Fig. 1) for $K\alpha L^1 M^0$ and $K\alpha L^1 M^1$ transitions: (a) reference summary $K\alpha L^1 M^0$ satellite, (b) effect of $3s^{-1}$ on the $K\alpha L^1$ satellite, (c) effect of $3p^{-1}$ on the $K\alpha L^1$ satellite, (d) effect of $3d^{-1}$ on the $K\alpha L^1$ satellite, and (e) summary effect of M^{-1} on the $K\alpha L^1$ satellite.

structured than the appropriate reference $K\alpha L^1 M^0$ bands [Fig. 5(a)]. Moreover, the positions of the $K\alpha L^1 M^1$ bands are shifted towards higher energies and their shapes are somewhat broader and more close to the Voigt profiles than reference $K\alpha L^1 M^0$ bands. Because the positions of various types of the $K\alpha L^1 M^r$ bands are shifted by a different extent the summary bands [Fig. 5(e)] are much broader and more close to the Voigt profiles than the particular components. From Fig. 5 it results that, very similar to $K\alpha L^0$ energy shifts (see I and II), the

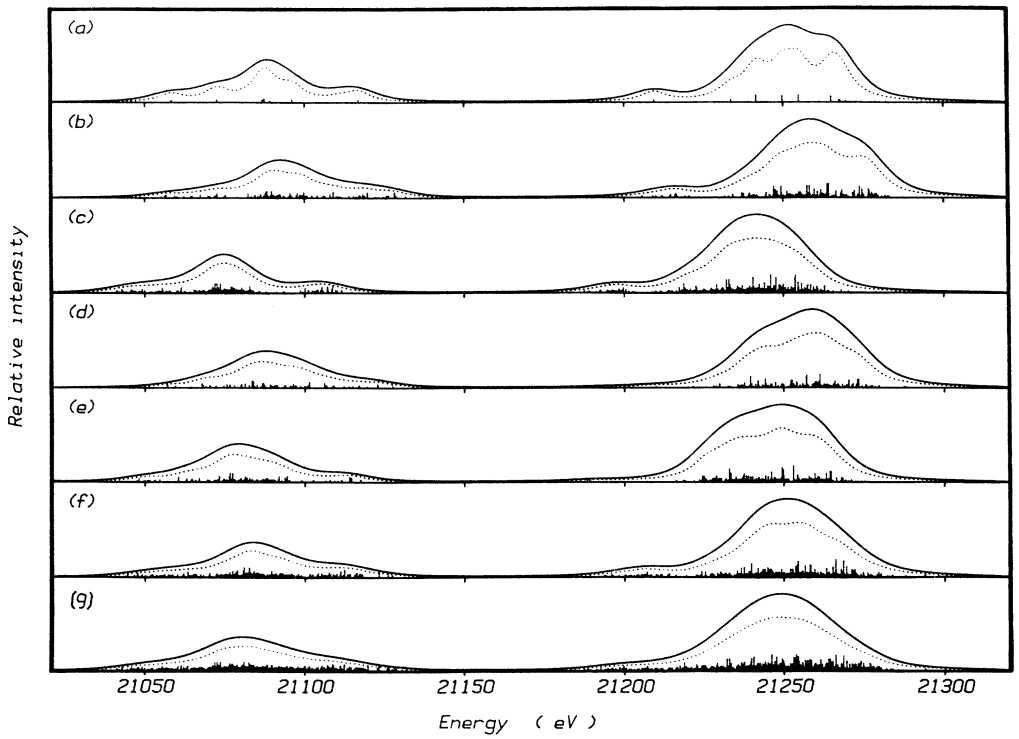

FIG. 6. Effect of various types of two-electron ionization of the M shell on the shapes and positions of the summary $K\alpha L^1$ satellite bands. Calculated stick and synthesized spectra (see Fig. 1) for $K\alpha L^1 M^2$ transitions: (a) effect of $3s^{-2}$ on the $K\alpha L^1$ satellite, (b) effect of $3p^{-2}$ on the $K\alpha L^1$ satellite, (c) effect of $3d^{-2}$ on the $K\alpha L^1$ satellite, (d) effect of $(3s3p)^{-1}$ on the $K\alpha L^1$ satellite, (e) effect of $(3s3d)^{-1}$ on the $K\alpha L^1$ satellite, (f) effect of $(3p3d)^{-1}$ on the $K\alpha L^1$ satellite, and (g) summary effect of M^{-2} on the $K\alpha L^1$ satellite.

most significant effect in producing $K\alpha L^1$ energy shifts is the effect of removing a $3p$ electron (about 10 eV) and next a $3s$ electron (about 6 eV), while in the case of a $3d$ electron this effect is relatively small (about 0.2 eV).

The influence of various types of two-electron ionization of the M shell on the shapes and positions of the summary $K\alpha L^1$ satellite bands has been shown in Fig. 6. It can be noted that in all cases (with the exception of the case [Fig. 6(a)] in which only the whole $3s$ subshell has been removed from the initial states) the number of transitions is very great and the $K\alpha L^1M^2$ bands (both those which are the sum of the Lorentzian natural line shapes and those which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) are less structured and closer to the Voigt profiles than the appropriate reference $K\alpha L^1M^0$ bands. In the last case [see Fig. 6(f)] it can be observed that the number of transitions is extremely great (about 15 000), the structure of the stick spectrum is the most complex, and the distances between the neighboring lines are of the order of 0.01 eV.

The summary effect of two-electron ionization of the M shell on the shapes and positions of the reference summary $K\alpha L^1M^0$ satellite bands has been shown in Fig. 6(g). It can be found that the resultant summary $K\alpha_1 L^1M^2$ and $K\alpha_2 L^1M^2$ bands are much smoother and broader than the particular components [Figs. 6(a)–6(f)] and, moreover, than the summary $K\alpha_1 L^1M^1$ and $K\alpha_2 L^1M^1$ bands [Fig. 5(e)], and can be well approximated by two Voigt functions.

IV. CONCLUSIONS

To reliably explain the influence of additional holes in the M shell on the shapes and positions of $K\alpha L^n$ satellite bands in the x-ray spectra of a heavy atom considerable attention has been paid for the first time to the detailed analysis of the structure of the groups of $K\alpha L^1M^r$ lines corresponding to various types of transitions. On the basis of the calculations for palladium some general conclusions can be drawn.

First, in the case of each type of transition two separated groups of lines are observed, from which those of lower energies can be attributed to $K\alpha_2 L^1M^r$ and those of higher energies to $K\alpha_1 L^1M^r$. Second, generally the synthesized $K\alpha L^1M^r$ bands (both those which are the sum of the Lorentzian natural line shapes and those which are the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) are much more scattered in the case of transitions from the initial states having one $2s$ hole than in the case of transitions from the initial states having one $2p$ hole. Third, in all cases the convolution of the sum of the Lorentzian natural line shapes with Gaussian instrumental response greatly smooths the resultant spectra. Fourth, in most cases removing even a small number of electrons from the M shell causes a very strong increase of the number of states possible for the given initial and final configurations and a very dramatic increase of the number of possible transitions. Fifth, in some cases the structures of $K\alpha L^1M^2$ satellite lines are extremely complex and the distances between the neighboring lines are very small, of order of 0.01–0.1 eV. Sixth, in all cases the $K\alpha L^1M^r$ bands (being the convolution of the sum of the Lorentzian natural line shapes with Gaussian instrumental response) are less structured than the appropriate reference $K\alpha L^1M^0$ bands. Seventh, generally, in contrast to the $K\alpha L^0M^r$ bands (see II), the widths of the $K\alpha L^1M^r$ bands ($r\neq 0$) for each type of transition are only somewhat greater than the widths of reference $K\alpha L^1M^0$ bands. Eighth, because the positions of various types of the $K\alpha L^1M^r$ bands are shifted by a different extent the summary $K\alpha L^1M^r$ spectra for certain r are much broader (and smoother) than the particular components. Ninth, because the $K\alpha L^1M^r$ bands corresponding to various r are also overlapped the effects of multiple M-shell ionization are manifested in the spectra as a broadening and a net shift of the $K\alpha_1 L^1$ and $K\alpha_2 L^1$ bands. The shapes of the resultant bands are closer to the Voigt profiles than the reference $K\alpha L^1M^0$ bands. Tenth, very similar to $K\alpha L^0$ energy shifts (see I and II), the most significant effect in producing $K\alpha L^1$ energy shifts is the effect of removing a $3p$ electron and next a $3s$ electron, while in the case of a $3d$ electron this effect is relatively small. The shift effects are strongly nonadditive.

A general conclusion which can be drawn is that any experimental technique will be powerless as far as the examination of the detailed structure of the groups of $K\alpha L^nM^r$ lines in x-ray spectra of heavy atoms is concerned. This is due simply to the nature of those groups of lines, each one of which, in reality, consists of thousands of very strongly overlapped components. However, though individual $K\alpha L^nM^r$ lines cannot be resolved experimentally it is necessary to very accurately evaluate the influence of various $K\alpha L^nM^r$ transitions on the shapes and positions of the resultant $K\alpha L^n$ bands in order to achieve the correct interpretation of the heavy-ion-induced x-ray spectra.

The author believes that the results of his analysis will be helpful in discovering and understanding of the structure of $K\alpha L^1M^r$ lines in x-ray spectra of multiply ionized heavy atoms. Moreover, the results of this and previous works (see I and II) can be used to construct different shapes of theoretical $K\alpha L^n$ spectrum for palladium, satisfactorily reproducing the shapes of various experimental $K\alpha L^n$ x-ray spectra generated by different inducing projectiles. Therefore, these results will also be very helpful in an achievement of the correct interpretation of the heavy-ion-induced $K\alpha$ x-ray spectra of palladium.

Obviously, the present study concerns the effect of M-shell holes on the $K\alpha L^1$ 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 $K\alpha L^nM^r$ 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.

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[1]B. Perny, J.-Cl. Dousse, M. Gasser, J. Kern, Ch. Rhême, P. Rymuza, and Z. Sujkowski, Phys. Rev. A **36**, 2120 (1987).
[2]Z. Sujkowski, D. Chmielewska, P. Rymuza, G. J. Balster, B. Kotliński, R. H. Siemssen, and H. W. Wilschut, Phys. Lett. B **196**, 122 (1987).
[3]M. Polasik, Phys. Rev. A **39**, 616 (1989).
[4]M. Polasik, Phys. Rev. A **39**, 5092 (1989).
[5]M. Polasik, Phys. Rev. A **40**, 4361 (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]J. Hata and I. P. Grant, J. Phys. B **16**, 3713 (1983).
[9]I. P. Grant, Int. J. Quantum Chem. **25**, 23 (1984).
[10]I. P. Grant, J. Phys. B **7**, 1458 (1974).
[11]S. I. Salem and P. L. Lee, At. Data Nucl. Data Tables **18**, 233 (1976).
[12]It should be interesting to compare the results of my detailed MCDF calculations with the results of unresolved transition array (UTA) method (Ref. 13). The UTA method may be very effective in treating these complex spectra, but so far there are no applications of this method to the $K\alpha L^n M^r$ x-ray transitions.
[13]M. Klapisch, E. Meroz, P. Mandelbaum, A. Zigler, C. Bauche-Arnoult, and J. Bauche, Phys. Rev. A **25**, 2391 (1982); M. Klapisch, J. Bauche, and C. Bauche-Arnoult, Phys. Scr. **T3**, 222 (1983); C. Bauche-Arnoult, J. Bauche, and M. Klapisch, Phys. Rev. A **20**, 2424 (1979); **25**, 2641 (1982); **31**, 2248 (1985), and references therein.