Many-electron effects in anomalous elastic x-ray scattering by an atom

A. N. Khoperskiĭ and V. A. Yavna

Rostov State University of Means of Communications, 344017 Rostov-on-Don, Russia

(Submitted 10 June 1994)
Zh. Eksp. Teor. Fiz. **107**, 328–336 (February 1995)

The Ne atom is used as an example to study the effect of a monopole restructuring of the electron shells in the field of a virtual vacancy and the effect of shake-up (or shake-off) processes on the differential cross section for anomalous elastic scattering of x radiation by an atom near the threshold of the atomic $1s$ shell. The theoretical results derived here for the region of scattering resonances are of a predictive nature. © *1995 American Institute of Physics.*

1. INTRODUCTION

Elastic scattering of x radiation by free atoms near the K-shell threshold has recently attracted increased experimental and theoretical interest.[1,2]

The existing theoretical methods (modifications of the form-factor approximation and the S-matrix formalism)[3] for calculating the differential cross section for anomalous elastic scattering give a good description at energies of the scattered x ray which are far from the K threshold (the discrepancies with experimental data are at most 2–5%). Near the K threshold, in contrast, the discrepancies with experiment rise to[4] 40–70%. In addition, right where the differential cross section is very nonlinear—in the region of the resonances—these methods give the energy positions of the resonances only within certain errors, while they predict infinite (nonphysical) amplitudes for these resonances.[3,5] This divergence of the amplitudes of the scattering resonances can be eliminated by existing methods for incorporating the finite lifetime of a virtual $1s$ vacancy. That correction, however, does not solve the problem of these discrepancies between theory and experiment.

In all the theoretical models used for the elastic scattering of a photon by an atom, the dispersive part of the amplitude for the process can be expressed in terms of the photoabsorption amplitudes of atomic shells. The implication here is that the primary cause of the discrepancies between theory and experiment is an inaccurate description of the photoabsorption amplitudes of the atom near the threshold of the $1s$ shell of the atom.

It has been established that the absorption of x radiation by an atom near the thresholds of the deep levels of the atom is definitely a many-electron process.[6] The following points have been established. The many-electron effect which has the greatest influence on the absolute value of the photoabsorption cross section is a monopole restructuring of the electron shells of the atomic core in the field of a deep vacancy which forms.[7,8] The generation of an nl vacancy has the consequence that it is primarily the outer shells of the atomic core which react to the "destruction" of the nl^{4l+2} screen between themselves and the nucleus, with the result that their average radius decreases significantly. The shift of electron density of the shells of the atomic core toward the nucleus is accompanied by an additional delocalization of a photoelectron from its periphery. This delocalization reduces the photoabsorption amplitude. In the case of the Ne atom, for example, incorporating the monopole restructuring of electron shells reduces the photoabsorption cross section by a factor ~2 from that calculated without consideration of the relaxation of the atomic core in the field of the $1s$ vacancy near the K threshold.[8]

In addition to the delocalization of a photoelectron, this radical restructuring of the core leads to nonzero probabilities for shake-up and shake-off processes: one-photon multiple excitation/ionization of an atom. For example, the K-XANES (x-ray absorption near edge structure) which has been observed experimentally[9] for the Ne atom is caused primarily by one-photon double KL_{23} excitation/ionization.[10,11]

In an experiment on photoabsorption, the total photoabsorption cross section which is observed is the sum of the cross sections of real, physically distinguishable processes of multiple excitation/ionization of the atom. The thresholds for the processes which lead to XANES in terms of the energy of the absorbed photon lie well above the K ionization threshold. As a result, the cross section near the K threshold can be described well by considering only one-photon single excitation/ionization.[8,12]

In the case of anomalous elastic scattering a) the processes of excitation/ionization of atomic shells of different multiplicities occur in a virtual level; b) the partial amplitude for the scattering of a photon by a fixed atomic shell is proportional to the sum of the squares of the amplitudes of the processes of different multiplicities for excitation/ionization of this shell; and c) the total scattering cross section is proportional to the square of the sum of the partial scattering amplitudes. Interference of scattering amplitudes rules out representing the scattering cross section as a sum of partial cross sections corresponding to channels of fixed multiplicity of the excitation/ionization of the atom. As a result, the limitation imposed by the incorporation of monopole restructuring of electron shells, without processes which lead to XANES, can substantially degrade a theoretical description of the scattering cross section near the threshold of a deep atom shell. In the present paper we demonstrate this assertion in the particular case of the Ne atom.

At the same time, theoretical results on atomic photoionization cross sections (Refs. 13 and 14, for example) which are used in calculating differential cross sections for anomalous elastic scattering have been derived without consider-

1063-7761/95/020174-05$10.00

ation of many-electron effects such as monopole restructuring of electron shells. Far above the threshold, the effect of this restructuring on the photoabsorption cross section becomes negligible. This circumstance explains the good agreement (mentioned above) between theory and experiment on elastic scattering above the threshold. However, it might be suggested that this restructuring and the accompanying shake-up and shake-off can no longer be ignored near the K threshold. As a result, the use of data like the results of Refs. 13 and 14 in the vicinity of the K threshold should lead to a substantial discrepancy with experiment, as was apparently seen in Ref. 4.

The present paper is devoted to an analysis of this suggestion.

Elastic scattering of a photon in the immediate vicinity of thresholds (within $\sim\pm 10$–100 eV of the thresholds, in either direction) of deep shells of many-electron systems has received essentially no study, either theoretical or experimental. Nevertheless, it is in this region of energies of the scattered photon that we would expect anomalous disruptions of the smoothness of the scattering cross sections because of many-electron effects. This circumstance in turn presents an opportunity to obtain a wealth of information on the structure and properties of the many-electron scattering system. The present paper is an attempt to take a step in this research direction.

2. THEORY OF THE METHOD

In the case of anomalous elastic scattering of unpolarized x radiation by an atom with a $^1S_0$ ground-state term, the existing expression[15] for the differential cross section for the process can be reduced to

$$d\sigma/d\Omega=(1/2)r_0^2(1+\cos^2\theta)\left|F+\sum_{nl} Q_{nl}\right|^2, \tag{1}$$

where r_0 is the classical radius of an electron, Ω is the solid angle, and θ is the scattering angle. In (1), the following have been defined in the atomic system of units ($\hbar=m=e=1$):

a) The atomic form factor in the nonrelativistic approximation,

$$F=\sum_{nl} N_{nl}\int_0^\infty P_{nl}^2(r)\,\frac{\sin(kr)}{kr}\,dr,\quad k=\frac{2\omega}{c}\sin\frac{\theta}{2}, \tag{2}$$

where $P_{nl}(r)$ is the radial part of the wave function of the atomic nl electron, N_{nl} is the occupation number of the nl atomic shell in the ground state, ω is the energy of the scattered x-ray, and c is the velocity of light.

b) The Kramers–Heisenberg dispersion terms of the amplitude for elastic scattering in second-order with respect to the operator representing the interaction of the atom with the electromagnetic field,

$$Q_{nl}=\frac{2}{3}\underset{m>F}{S}\frac{\bar{\omega}_m\omega_m^2}{\omega^2-\bar{\omega}_m^2}|D_{nl}^m|^2. \tag{3}$$

Here $\bar{\omega}_m=\omega_m\mp i\Delta_{nl}, \omega_m$ is the energy of the virtual transition from the $|0;^1S_0\rangle$ state of the atom to the intermediate $|nl^{-1}m;\ ^1P_1\rangle$ state of the system consisting of the atomic core and the virtual photoelectron, F is the Fermi level, $2\Delta_{nl}=\Gamma_{nl}$ is the total decay width of the virtual nl vacancy, S means a summation (integration) over all intermediate states of the discrete (continuous) spectrum, and the matrix element of the transition operator $\hat{D}$ is

$$D_{nl}^m=\langle 0;^1S_0|\hat{\mathbf{D}}|nl^{-1}m;^1P_1\rangle. \tag{4}$$

The summation in (1) and (2) is to be carried out over all atomic shells.

The monopole restructuring of electron shells can be incorporated by modifying the matrix element (4) using the methods of the theory of nonorthogonal orbitals.[16] In the case of $1s-np$ photoabsorption of the Ne atom, for example, the radial (R) part of the matrix element (4) takes the following form in the dipole approximation:[8,12]

$$D_{1s,\mathrm{R}}^{np}=A_{1s}\left(\langle 1s_0|r|np\rangle-\langle 1s_0|r|2p\rangle\,\frac{\langle 2p_0|np\rangle}{\langle 2p_0|2p\rangle}\right). \tag{5}$$

Here the $1s_0$, $2p_0$ and $2p$, np functions are found through a solution of the Hartree–Fock equations for the $1s_0^2 2s_0^2 2p_0^6(^1S_0)$ and $1s^1 2s^2 2p^6 np(^1P_1)$ configurations, respectively; A_{1s} is the product of the overlap integrals of the wave functions of the electrons which are not involved in the transition; and we are also using

$$\langle 2p_0|np\rangle=\int_0^\infty P_{2p_0}(r)P_{np}(r)dr,\quad \langle 1s_0|r|np\rangle$$

$$=\int_0^\infty P_{1s_0}(r)P_{np}(r)rdr.$$

The expression which we are using here for the differential cross section for the anomalous elastic scattering is derived from (1) by incorporating the relationship between the matrix element (4) and the photoabsorption cross section:[15]

$$\sigma_{nl}(\omega_m)=\frac{4}{3}\,\pi^2\,\frac{\omega_m}{c}\,|D_{nl}^m|^2. \tag{6}$$

To study the near fine structure in the scattering spectrum near the K threshold, we use the method of Refs. 10 and 11 to calculate the matrix elements in (4) and the corresponding cross sections for one-photon double excitation/ionization.

3. RESULTS OF THE CALCULATIONS

We selected the Ne atom for this study. This is a simple many-electron system with a $1S_0$ ground-state term and a clearly defined discrete structure in the K photoabsorption spectrum.[9]

The radial parts of the matrix elements in (4) and corresponding cross sections in (6) were derived in two approximations.

1. First, we ignored the many-electron restructuring of the electron shells. The wave function of the virtual np photoelectron was found by solving the Hartree–Fock equation for the $1s_0^1 2s_0^2 2p_0^6 np(^1P_1)$ configuration (in the field of a $1s_0$ vacancy with a "unrestructured" atomic core). The wave

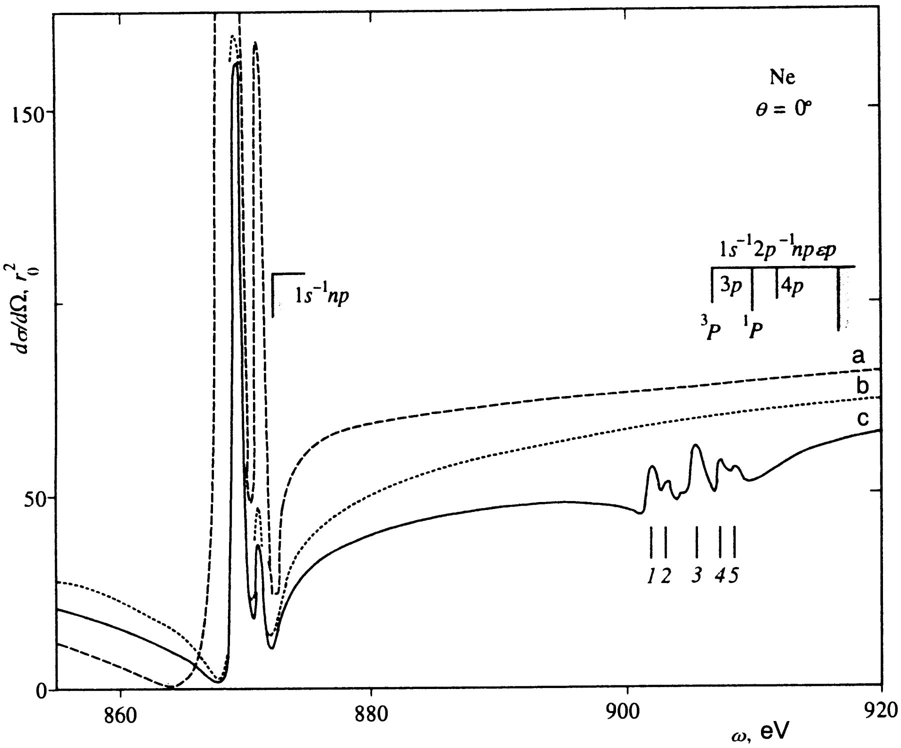

FIG. 1. Differential cross section for the elastic scattering of an unpolarized x ray by a Ne atom (in the region of scattering resonances). a—Without consideration of monopole restructuring of electron shells; b—with this restructuring, but without shake-up and -off processes; c—with monopole restructuring and shake-up and -off processes. The numbered resonances are identified in the text proper; ω is the energy of the scattered x ray.

functions of the $1s_0$, $2s_0$, and $2p_0$ electrons of the core were found by solving the Hartree–Fock equations for the $1s_0^2 2s_0^2 2p_0^6(^1S_0)$ configuration. In this case the radial parts of the matrix elements (4) contain only the first terms in parentheses in expressions like (5) with $A_{nl}=1$. The probabilities for shake-up and shake-off processes are zero.

2. In other calculations we took the monopole restructuring into account. The wave function of the virtual np photoelectron was found by solving the Hartree–Fock equation for the $1s^1 2s^2 2p^6 np(^1P_1)$ configuration. The wave functions of the $1s$, $2s$, and $2p$ electrons of the atomic core were found by solving the Hartree–Fock equations for the $1s^1 2s^2 2p^6(^2S_{1/2})$ configuration (relaxation of the core in the field of the $1s$ vacancy which forms was taken into account). In this case the radial parts of matrix elements (4) contain the additional terms in parentheses in expressions like (5) with $A_{nl}<1$.

Only the most intense transitions, to the $3p$ and $4p$ virtual states of the photoelectron, were taken into account in the calculation of the discrete part of the K photoabsorption spectrum. Transitions to these states give rise to the principal resonances in the elastic scattering in the energy region $\omega \simeq 870\pm3$ eV in Fig. 1. As the total decay width of the virtual $1s$ vacancy we used the value $\Gamma_{1s}=0.65$ eV, found from an experimental spectrum.[9]

In the second approximation, we took virtual *shake-up* (*off*) processes into account along with $1s-np$ excitation/ionization.

The amplitudes of the *shake-up* processes are described by matrix element (4) in the multiconfiguration Hartree–Fock approximation with intermediate states of the form

$$|i\rangle=\sum_{LS}\sum_{n_{1,2}l_{1,2}} a^i_{12(LS)}\psi^{LS}_{12}, \tag{7}$$

where $a^i_{12(LS)}$ are configurational-mixing coefficients. The states in (7) were found by diagonalizing the energy matrix constructed from configurations of KL_{23} photoexcitation:

$$\psi^{LS}_{12}=|1s^{-1}2p^{-1}(^{2S+1}P)n_1l_1n_2l_2(LS);^1P_1\rangle,$$

$$n_1l_1n_2l_2=\left\{\begin{matrix}3p3p\\4p\\5p\end{matrix}\right\},\left\{\begin{matrix}3d3d\\4d\end{matrix}\right\},\left\{\begin{matrix}3s3s\\4s\end{matrix}\right\},\left\{\begin{matrix}3s3d\\4d\end{matrix}\right\}. \tag{8}$$

The amplitudes of *shake-off* processes were described in the one-configuration Hartree–Fock approximation by means of transitions to states (8) with

$$n_1l_1n_2l_2=(np\varepsilon p),(\varepsilon p\varepsilon' p), \quad (n=3,4). \tag{9}$$

For the first channel we incorporated the electrostatic splitting of the ^1P and ^3P terms of the atomic core: $\gamma_{1,3}=1s^{-1}2p^{-1}(^{1,3}P)$. For the third channel in (3) we determined the double improper integral over ε and ε', the energies of electrons of the continuous spectrum. To transform it we used the representation

$$\int\int_0^\infty dxdy\Phi(x,y)=\int_a^\infty d\alpha\int_0^{\alpha-a}d\beta\Phi(\alpha,\beta). \tag{10}$$

Equation (10) corresponds to the coordinate transformation (a=const) $x=\alpha-\beta-a$, $y=\beta$, with a unit Jacobian. Expression (3) then reduces to the integral of a function proportional to the cross section for double photoionization over the variable $\alpha=\omega_{12}+\varepsilon+\varepsilon'$ ($\beta=\varepsilon'$; $a=\omega_{12}$ is the threshold energy for double photoionization) between ω_{12} and infinity. The latter arises in the course of the inner integration in (10) over the energy surface $\varepsilon+\varepsilon'=\alpha-\omega_{12}$. The channels in (9) open up at x-ray energies of 906.82 (^3P), 909.81 (^1P), 911.70 and 916.60 eV, respectively.

The wave functions of the n_1l_1 and n_2l_2 electrons were found by solving Hartree–Fock equations for the $1s^12s^22p^5n_1l_1n_2l_2$ configuration, averaged over the $^1P,^3P$, and LS terms. The wave functions of the $1s$, $2s$, and $2p$ core electrons were found by solving the Hartree–Fock equations for the $1s^12s^22p^5$ configuration averaged over the ^1P and ^3P terms (relaxation of the core in the field of the $1s$ and $2p$ vacancies was taken into account).

The most prominent resonances in the region of the near fine structure in the elastic-scattering spectrum (Fig. 1) correspond to transitions to virtual states of double photoexcitation:

$$|1\rangle=\gamma_3 3p^2[0.97(^3P)],$$

$$|2\rangle=\gamma_1[0.903s3d(^1D)-0.503p^2(^1D)],$$

$$|3\rangle=\gamma_1 3p^2[0.70(^1D)+0.60(^1S)],$$

$$|4\rangle=\gamma_1 3p4p[0.90(^1D)],$$

$$|5\rangle=\gamma_1 3p5p[0.80(^1D)],$$

where we have retained terms with $|a^i|\geqslant 0.50$. In the Ne atom, the d symmetry of the excited states is a collapsing symmetry. As a result, there is a pronounced interaction between the $\gamma_1 3p^2(^1D)$ and $\gamma_1 3s3d(^1D)$ configurations. As a further result, the intensity of the transition to the "pure" $\gamma_1 3p^2(^1D)$ state is distributed between the $|2\rangle$ and $|3\rangle$ channels. The leading component in the $|2\rangle$ channel, $\gamma_1 3s3d(^1D)$, is a "shadow" component, since the intensity of the transition to the $|2\rangle$ state is determined by the $\gamma_1 3p^2(^1D)$ component.

The radial parts of matrix elements (4) and the cross sections for L_1 and L_{23} photoabsorption [see (6)] were found in calculations incorporating both the monopole restructuring of electron shells and the correlations of the random-phase approximation with exchange (RPAE).[7] When virtual $2s$ and $2p$ vacancies form, the monopole restructuring is negligible. In contrast, RPAE correlations strongly influence the absolute values of the cross sections for L_1 and L_{23} photoabsorption near the threshold. In the case of the L_1 photoabsorption, for example, incorporating the mixing of the virtual $|2s^{-1}np(^1P_1)\rangle$ state of photoabsorption with the $|2p^{-1}md(^1P_1)\rangle$ RPAE channel leads to a RPAE cross section smaller by a factor of ~1.8 than the cross section for direct L_1 photoionization in the vicinity of the L_1 threshold.[17] Since the $1s$ shell is far from the $2s$ and $2p$ shells of the atomic core in terms of energy, the RPAE correlations have a negligible effect on the differential cross section for elastic scattering near the K threshold in the case of L_1 and L_{23} photoabsorption. We did not study discrete structure in the spectra for L_1 and L_{23} photoabsorption in these calculations, so they are not reflected in the calculations in (1).

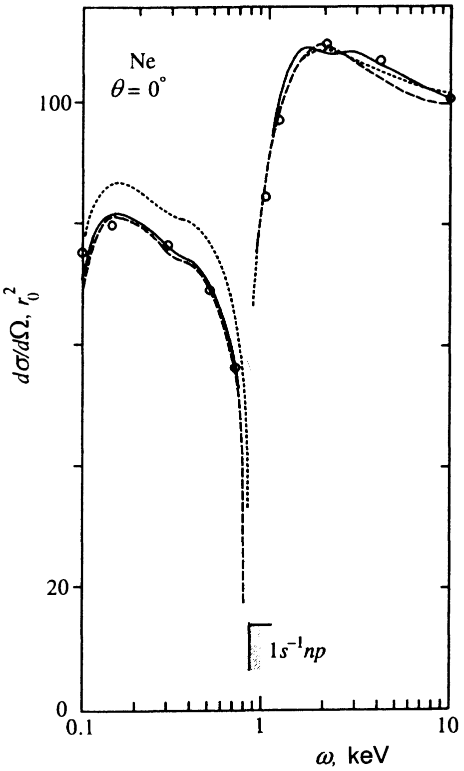

FIG. 2. Differential cross section for the elastic scattering of an unpolarized x-ray by a Ne atom (the near-threshold scattering region). The circles are the results of calculations in Ref. 5; the notation is otherwise the same as in Fig. 1. Some details of the region of scattering resonances have been omitted. The energy scale is logarithmic.

Figures 1 and 2 and Table I show results calculated for the case $\theta=0°$ (forward scattering). We can draw several conclusions from these results.

1. Near the principal scattering resonances, the monopole restructuring of the electron shells dramatically suppresses the amplitudes and shifts the energies of the resonances calculated without treating the relaxation of the atomic core in the field of a deep virtual $1s$ vacancy.

2. In the region of near-threshold scattering, the monopole restructuring of electron shells leads to a redistribution, between the short- and long-wave regions of the scattering spectrum, of the scattering intensity calculated without consideration of the relaxation of the atomic core in the field of a deep virtual $1s$ vacancy.

3. Incorporating *shake-up* and *shake-off* processing strongly influences the magnitude and direction of the redis-

TABLE I. Calculated characteristics of the principal resonances in the elastic scattering of an unpolarized x-ray by a Ne atom near the K threshold in approximations a, b, and c (Fig. 1).

nl	ω, eV		$d\sigma/d\Omega,\ r_0^2$		
	a	b,c	a	b	c
$3p$	868.64	869.40	1900.00	170.00	162.50
$4p$	870.96	871.10	167.60	47.26	37.53

tribution of the scattering intensity, both near the principal resonances of the scattering and in the region of near-threshold scattering.

4. Near the threshold for scattering, the results of the present study are essentially the same as those of Ref. 5, which were derived by quantum-electrodynamics methods (by the S-matrix formalism). The reason for this agreement is that, at these energies of the scattered x-ray, the incorporation of the monopole restructuring of electron shells and *shake-up* (*off*) processes in calculations of partial photoabsorption cross sections essentially reproduces the results of a one-electron approximation like that in Refs. 13 and 14.

Since no experimental data are available on the differential cross section for elastic x-ray scattering near the K threshold of the Ne atom, the results of this theoretical study of the region of scattering resonances are of a predictive nature.

It may be that this study could be extended to elastic and inelastic scattering of x-rays near the thresholds for deep shells of many-electron systems, not only atoms but also molecules and simple clusters.

The demonstration in this paper that the theoretical differential cross section for elastic scattering in the region of resonances is highly sensitive to the particular approximation used also suggests that an experimental study of primarily scattering resonances near the thresholds of deep atomic shells may prove to be an effective tool for studying the nature and role of many-electron correlations in the interaction of an atom with x radiation.

We wish to thank V. F. Demekhin, B. M. Lagutin, and A. G. Kochur for a useful discussion of this study.

[1] L. Kissel and R. H. Pratt, Acta Cryst. A **46**, 170 (1990).

[2] P. P. Kane, L. Kissel, R. H. Pratt, and S. C. Roy, Phys. Rep. **140**, 75 (1986).

[3] L. Kissel, R. H. Pratt, and S. C. Roy, Phys. Rev. A **22**, 1970 (1980).

[4] P. P. Kane, G. Basavaraju, S. M. Lad *et al.*, Phys. Rev. A **36**, 5626 (1987).

[5] G. Basavaraju, L. Kissel, J. C. Parker *et al.*, Phys. Rev. A **34**, 1905 (1986).

[6] M. Ya. Amus'ya, *The Atomic Photoelectric Effect* [in Russian] (Nauka, Moscow, 1987), p. 1.

[7] M. Ya. Amusia and N. A. Cherepkov, Case St. Atom. Phys. **5**, 47 (1975).

[8] V. L. Sukhorukov, V. F. Demekhin, V. V. Timoshevskaya, S. V. Laurent'ev, Opt. Spektrosk. **47**, 407 (1979) [Opt. Spectrosc. (USSR) **47**, 228 (1979)].

[9] J. M. Esteva, B. Gauthe, P. Dhez, and R. C. Karnatak, J. Phys. B **16**, L263 (1983).

[10] V. L. Sukhorukov, A. N. Hopersky, I. D. Petrov *et al.*, J. Phys. (Paris) **48**, 1677 (1987).

[11] A. N. Hopersky, I. D. Petrov, and V. L. Sukhorukov, in *Ninth Int. Conf. on Vacuum Ultrav. Radiat. Physics*, ed. by S. Fadley and D. A. Shirley (Honolulu, Hawaii, 1980), p. 282.

[12] A. N. Hopersky, V. A. Yavna, I. D. Petrov, Opt. Spektrosk. **63**, 204 (1987) [Opt. Spectrosc. (USSR) **63**, 119 (1987).

[13] B. L. Henke, P. Lee, T. J. Tanaka *et al.*, At. Data Nucl. Data Tables **27**, 1 (1982).

[14] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[15] R. Karaziya, *Introduction to the Theory of the x-Ray and Electron Spectra of Free Atoms* [in Russian] (Vil'nyus, Moscow, 1987), p. 1.

[16] A. P. Yutsis and V. I. Tutlis, Lit. Fiz. Sb. **11**, 927 (1971).

[17] M. Ya. Amusia, V. K. Ivanov, N. A. Cherepkov, and N. V. Chernysheva, Phys. Lett. A **40**, 361 (1972).

Translated by D. Parsons