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Two-photon ionization of the *K*-shell of a heavy beryllium-like atomic ion

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Within the framework of the second order of the non-relativistic quantum perturbation theory, the analytical structure and absolute values of the generalized cross-sections of the two-photon resonant single ionization of the *K*-shell of heavy beryllium-like ions of titanium (Ti^{18+}), chromium (Cr^{20+}), iron (Fe^{22+}) and zinc (Zn^{26+}) atoms were predicted. The complete wave functions of the ground state of the ion and the states of its ionization are obtained in the single-configuration Hartree-Fock approximation. The effects of (a) the occurrence of giant resonances in the subthreshold region of the generalized ionization cross-sections, (b) destructive quantum interference of the probability amplitudes of radiation transitions to intermediate states of *p*-symmetry, and (c) the leading role of the *d*-symmetry of the final ionization state in determining the values of the total generalized cross-section in the region of energies of absorbed photons of the hard X-ray range were established. A scheme of the proposed experiment with linearly polarized X-ray photons is presented to verify the theoretical results obtained

Keywords: beryllium-like atomic ion, two-photon ionization, probability amplitude, generalized cross-section.

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Introduction

Two-photon (nonlinear) ionization of deep shells of atoms, atomic ions, molecules, and solids is one of the fundamental processes in the microcosm. With the creation of the X-ray free-electron laser (XFEL) [1] as a source of hard multiphoton radiation, it has become possible to conduct high-precision experimental and theoretical studies of this process [2,3]. The completed theoretical studies of this process have revealed, in particular, the important roles of relativistic effects, screening effects and nondipole (quadrupole) effects in (a) defintion of the nonresonant structure of the generalized cross sections of two-photon ionization of the K-shell of an atom and atom ion [4–7] and (b) angular distribution of photoelectrons generated by above-threshold two-photon ionization of the *K*-shell of an atom [8,9]. The cited articles lack studies of the resonant subthreshold structure of the generalized cross section of two-photon ionization. Such structure within the second order of the nonrelativistic quantum perturbation theory was for the first time studied in [10,11] on the example of light neon atom (Ne), beryllium-like (Ne^{6+}) and helium-like (Ne^{8+}) atom ions. In this case, the main (leading in the infinite complete set) parts of the subthreshold resonant structure of the cross-section, the effects of radial relaxation of transition states in the field of a $1s$-vacancy, and only the projection $M = 0$ of the total angular moment $J = 2$ of the wave function of the final ionization state of d-symmetry were taken into account. In [12,13], the theory of papers [10,11] was modified to account for (a) the completeness of the set of intermediate $1s \to np$ photoexcitation states, (b) destructive quantum interference of partial probability amplitudes of the radiative transition, and (c) the nontrivial full ($J = 2$; $M = 0, \pm 1, \pm 2$)angular structure of the probability amplitude of the radiative transition to the final ionization states of$d$-symmetry. In this case, the results of [10,11] were generalized for a heavy neon-like ion of the iron atom Fe^{16+}) [12] and ions of the isonuclear sequence of the heavy nickel atom ($^{29}Ni \to Ni^{18+} \to Ni^{24+} \to Ni^{26+}$) [13]. In this article the theory [12,13] is modified (the dependence of radiation decay widths of $1s$-vacancy in intermediate photoexcitation states on the principal quantum number is take into account), and is generalized on the isoelectronic sequence of heavy beryllium-like atom ions. The study objects are beryllium-like ions of titanium atoms (Ti^{18+}, $Z = 22$ ion nucleus charge, configuration and term of the ground state $[0] = 1s^2 2s^2 [^1S_0]$), of chromium (Cr^{20+}, $Z = 24$), iron (Fe^{22+}, $Z = 26$) and zinc (Zn^{26+}, $Z = 30$). The isoelectronic sequence is selected for spherical symmetry of the ground state of ions, their availability in gas phase [14,15] when the experiment is conducted to absorb two XFEL-photons with energy $\hbar\omega$ ($\hbar$ — Planck constant, ω — circular frequency of photon) with ion captured in „trap“ [16,17], and for demand for their spectral characteristics, in particular, in X-ray diagnostics of hot laboratory [18,19] and astrophysical [20–22] plasma, and also structural materials in the units of controlled nuclear fusion [23–25].

1. Theory

Consider the following channel of two-photon resonant single ionization of the *K*-shell of a beryllium-like atomic ion:

$$2\hbar\omega + [0] \to 1s(n, x)p + \hbar\omega \to 1s\varepsilon l. \tag{1}$$

In (1) n — principal quantum number of excited states of discrete spectrum, $x(\varepsilon)$ — continuous spectrum electron energy, $l = s, d$ and filled $2s^2$-shell is not specified. The channel (1) structure corresponds to the following approximations.

Strong spatial and energy isolation of $2s^2$-shell from $1s^2$-shell of ion makes it possible to neglect the creation of terminal $1s^2 2s\varepsilon(s, d)$-states of two-photon ionization. For example, for Ti^{18+} ion the following inequalities are satisfied: $r_{1s} = 0.0367\,Å \ll r_{2s} = 0.1552\,Å$ (r_{ns} — average radius of ns-shell of ion), $I_{1s} = 6019.25\,eV$ (calculation of this paper) $\gg I_{2s} = 1346.89\,eV$ [26] (I_{ns} — energy of ionization threshold of ns-shell of ion).

The amplitude of two-photon ionization probability via the $2\hbar\omega + [0] \to 1s\varepsilon l$ channel is determined by the contact interaction operator

$$\hat{C} \sim \sum_{n=1}^{N} (\hat{A}_n \cdot \hat{A}_n)$$

(N — number of electrons in ion) and is proportional to the matrix element $\langle 1s|j_l|\varepsilon l\rangle$ [27]. Here j_l — spherical Bessel function that arises in expansion into the double functional row of the resulting exponent in operator $\hat{C}$. For the electromagnetic field $\hat{A}_n$ operator (in the second quantization representation), the dipole approximation is adopted:

$$\hat{A}_n \to \sum_{\mathbf{k}} \sum_{\rho=1,2} \mathbf{e}_{\mathbf{k}\rho} (\hat{a}^{+}_{\mathbf{k}\rho} + \hat{a}^{-}_{\mathbf{k}\rho}), \quad (2)$$

$$(\mathbf{k} \cdot \mathbf{r}_n) \ll 1 \Rightarrow \exp[\pm i(\mathbf{k} \cdot \mathbf{r}_n)] \cong 1, \quad (3)$$

$$r_{1s}/\lambda_\omega \ll 1. \quad (4)$$

In (2)−(4) $\mathbf{e}_{\mathbf{k}\rho}(\mathbf{k})$ — polarization vector (wave vector) of photon, $\hat{a}^{+}_{\mathbf{k}\rho}(\hat{a}^{-}_{\mathbf{k}\rho})$ — operator of photon creation (annihilation), $\mathbf{r}_n$ — radius-vector of n-electron and λ_ω — wavelength of absorbed photon. For example, for ion Ti^{18+} we have: $r_{1s} = 0.0367\,Å$, $\lambda_\omega = 2.0330\,Å$ ($\hbar\omega = 6.10\,keV$) and $r_{1s}/\lambda_\omega = 0.018 \ll 1$. Then $j_0 \to 1$, $j_2 \to 0$ and $\langle 1s|j_1|\varepsilon l\rangle \to 0$. Note here that in [28] the concept of „dipole approximation applicability criterion" is modified. As a result it is shown that the short-wavelength area of dipole approximation applicability by energy of the absorbed photon is much wider than the area determined by inequality (4).

1.1. Ionization probability amplitude

The probability amplitude of two-photon ionization via channel (1) is physically interpreted in Fig. 1 in the formalism of Feynman diagrams within the framework of the second (in the number of interaction vertices) order of nonrelativistic quantum perturbation theory. Let us establish its analytical structure. The formulae below in this section of the article are given in atomic units (a.u.; $e = \hbar = m_e = 1$). In subsequent sections of the article, ordinary units are restored. According to Fig. 1, for the desired amplitude we

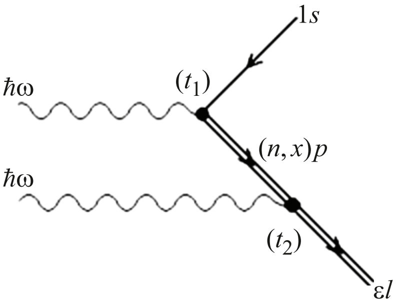

Figure 1. Probability amplitude of two-photon resonant single ionization of the K-shell of a beryllium-like atomic ion in Feynman diagram representation ($l = s, d$). Time direction is left to right ($t_1 < t_2$). Right arrow — electron, left arrow — vacancy. Double line indicates state obtained in Hartree-Fock field of $1s$-vacancy. The black dot represents the vertex of the radiative transition, $\hbar\omega$ is the absorbed photon.

have quantum interference of partial probability amplitudes of photoabsorption via intermediate states of the discrete and continuous spectra of p-symmetry:

$$A_l = A_l^{(1)} + A_l^{(2)}, \quad (5)$$

$$A_l^{(1)} = \sum_{M'} \sum_{N=2}^{\infty} \frac{\langle 0|\hat{R}|\Phi_n\rangle\langle\Phi_n|\hat{R}|\Psi_{\varepsilon l}\rangle}{\omega - I_{1snp} + i\gamma_{1s,n}}, \quad (6)$$

$$A_l^{(2)} = \sum_{M'} \int_0^\infty dx \frac{\langle 0|\hat{R}|\Phi_x\rangle\langle\Phi_x|\hat{R}|\Psi_{\varepsilon l}\rangle}{\omega - I_{1s} - x + i\gamma_{1s}}, \quad (7)$$

$$|0\rangle = [0] \otimes (a^{+}_{\omega})^2 |0_{ph}\rangle, \quad (8)$$

$$|\Phi_{n,s}\rangle = |1s(n,x)p(^1P_1), M'\rangle \otimes \hat{a}^{+}_{\omega}|0_{ph}\rangle, \quad (9)$$

$$|\Psi_{\varepsilon l}\rangle = |1s\varepsilon l(^1 l_{J=l}), M\rangle \otimes |0_{ph}\rangle, \quad (10)$$

$$\hat{R} = -\frac{1}{c} \sum_{n=1}^{N} (\hat{p}_n \cdot \hat{A}_n). \quad (11)$$

In (6)−(11) the following are defined: full wave functions of initial ($|0\rangle$), intermediate ($|\Phi\rangle$) and final ($|\Psi\rangle$) states of two-photon ionization , $\hat{R}$ — operator of radiation transition, c — light velocity in vacuum, $\hat{P}_n$ — operator of pulse of n-electron, projections of full angular moments of „ion residue $\otimes$ electron" system $M' = 0, \pm 1$, $M = 0$ for $l = s$, $M = 0, \pm 1, \pm 2$ for $l = d$, $|0_{ph}\rangle$ — wave function of photon vacuum of quantum electrodynamics, I_{1snp} — energy of photoexcitation $1s \to np$, $\gamma_{1s,n} = \Gamma_{1s,n}/2$ and $\gamma_{1s} = \Gamma_{1s}/2$, where $\Gamma_{1s,n}(\Gamma_{1s})$ — width of decay of $1s$-vacancy of $1snp$ ($1sxp$)-state. Note that the structure of the $^1 l_{J=l}$-terms of the final states of two-photon ionization ($J = 0 \Rightarrow {}^1S_0$; $J = 2 \Rightarrow {}^1D_2$) in (10) reproduces the Landau−Yang theorem [29,30] for the total angular moment of the system of two absorbed photons $J_\omega = 0, 2$.

Let us adopt the approximation of plane waves,

$$|x(r)\rangle \sim \sin(r\sqrt{2x}),$$

for the one-electron probability amplitude of the radiative transition between continuous spectrum states in (7):

$$(x-\varepsilon)\langle xp_+|\hat{r}|\varepsilon l_+\rangle \cong i\sqrt{2x}\cdot\delta(x-\varepsilon). \qquad (12)$$

The appearance of the imaginary unit in (12) is due to the implementation of the Sokhotski–Plemelj formula for the denominator $(x-\varepsilon-i0)^{-1}$ in the approximation of discarding the principal value (integral) according to Cauchy. Then, using the methods of the photon creation (annihilation) operator algebra [31], irreducible tensor operator theory [32] and non-orthogonal orbital theory [33], for amplitude (5) we obtain:

$$A_s = \xi\left(\mu + \sum_{n=2}^{\infty}\beta_n\langle np_+|\hat{r}|\bar{\varepsilon}s_+\rangle\right), \qquad (13)$$

$$A_d = \sqrt{6}\,\xi\left(\mu + \sum_{n=2}^{\infty}\beta_n\langle np_+|\hat{r}|\bar{\varepsilon}d_+\rangle\right)\cdot Q_M, \qquad (14)$$

$$\mu = i\cdot 2\sqrt{2\bar{\varepsilon}}\,\langle 1s_0\|\hat{r}\|\bar{\varepsilon}p_+\rangle, \qquad (15)$$

$$\beta_n = \frac{I_{1snp}(2\omega - I_{1snp})}{\omega - I_{1snp} + i\gamma_{1s,n}}\langle 1s_0\|\hat{r}\|np_+\rangle, \qquad (16)$$

$$Q_M = -\frac{4\pi}{3}\sum_{M'}\sum_{p}(-1)^{M'}Y_{1,M'}(\mathbf{e}_\omega)Y^*_{1,p}(\mathbf{e}_\omega)\begin{pmatrix}1 & 1 & 2\\ -M' & p & M\end{pmatrix}. \qquad (17)$$

Here $\xi = 4\pi/(3V\omega)$, $V(\text{cm}^3) = c$ — volume of quantization of the electromagnetic field (numerically equal to the light velocity in vacuum) [34], $\bar{\varepsilon} = 2\omega - I_{1s}$, $Y_{\alpha,\beta}(\mathbf{e}_\omega)$ — spherical function, index of summation in (17) $p = 0, \pm 1$, «*» — symbol of complex conjugation, defined $3j$-symbol of Wigner and single electron amplitude of photoexcitation probability $1s \to np$ is

$$\langle 1s_0\|\hat{r}\|np_+\rangle = \langle 1s_0|1s_+\rangle\langle 2s_0|2s_+\rangle^2\langle 1s_0|\hat{r}|np_+\rangle, \qquad (18)$$

$$\langle 1s_0|\hat{r}|np_+\rangle = \int_0^\infty P_{1s_0}(r)r\,P_{np_+}(r)dr. \qquad (19)$$

Indices «0» and «+» comply with $P(r)$-radial parts of wave functions of electrons obtained by solving single configuration Hartree–Fock equations for configurations of ion [0], $1s_+(n,x)p_+$ and $1s_+\varepsilon l_+$.

1.2. Generalized cross section of ionization

Let us establish the analytical structure of generalized cross section of two-photon single ionization of atomic ion. According to the definition of the concept of such cross section [35],

$$d\sigma_g^{(l)} = (V/2c)d\sigma_l, \qquad (20)$$

taking into account the „golden Fermi" rule [36],

$$d\sigma_l = (\pi V/c)|A_l|^2\cdot\delta(\varepsilon - \bar{\varepsilon})d\varepsilon, \qquad (21)$$

integrating in (21) by energy of photoelectron and summing by $l = s, d$, for the full generalized cross section we get the following:

$$\sigma_g(\text{cm}^4\cdot\text{s}) = (\eta/\omega)^2\sum_{l=s,d}\sum_{i=1.2}a_l\cdot L_{il}^2, \qquad (22)$$

$$L_{1l} = \sum_{n=2}^{\infty}(\omega - I_{1snp})B_{ln}. \qquad (23)$$

$$L_{2l} = D - \sum_{n=2}^{\infty}\gamma_{1s,np}B_{ln}, \qquad (24)$$

$$D = 2\sqrt{2\bar{\varepsilon}}\cdot\langle 1s_0\|\hat{r}\|np_+\rangle, \qquad (25)$$

$$B_{ln} = \frac{\beta_n}{\omega - I_{1snp} - i\gamma_{1s,n}}\langle np_+|\hat{r}|\bar{\varepsilon}l_+\rangle. \qquad (26)$$

Here it is accounted for that for xp-states of continuous spectrum the energy denominator of photoionization probability amplitude $1s \to xp$ in the point of pole $\bar{\varepsilon} = 2\omega - I_{1s}$ is

$$\omega - i\gamma_{1s} = \omega\cdot(1 - i\gamma_{1s}/\omega) \cong \omega$$

at $\omega \sim I_{1s} \gg \gamma_{1s}$. Here the values $\eta(\text{cm}^4\cdot\text{s}) = 0.278\cdot 10^{-52}$, $a_s = 1$,

$$a_d = \frac{3}{2}a_d^{(0)}\left(1 - \frac{1}{4\pi}\right)$$

and $a_d^{(0)} = 4/5$ [10,11] are also defined (only the projection $M = 0$ of full angular moment $J = 2$ is taken into account). The value of coefficient a_d is obtained using formula

$$a_d = 6\cdot\sum_{M=-2}^{2}|Q_M|^2 \qquad (27)$$

with account of the analytical result of paper [37] for the sum of products of two $3j$-symbols of Wigner. Besides, the implementation of the XFEL-experiment scheme is proposed for linearly polarized absorbed photons: $\mathbf{k} \in OZ$, $\mathbf{e}_\omega \in OX$ (OX, OZ — axes of the rectangular system of coordinates),

$$Y_{1,0}(\mathbf{e}_\omega) = 0, \quad Y_{1,\pm 1}(\mathbf{e}_\omega) = \mp 3/(4\pi\sqrt{2}). \qquad (28)$$

Note that $(a_d^{(0)}/a_d)\cdot 100\,(\%) \cong 72\,(\%)$. Therefore, the additional accounting of projections $M = \pm 1, \pm 2$ of the full angular moment $J = 2$ significantly (by $\sim 30\,\%$) increases the contribution of the component of generalized cross section (22) for $l = d$.

In (6) the following approximation of full width of decay of $1s$-vacancies is adopted:

$$\Gamma_{1s,n} = \Gamma_A + \Gamma_{R,n}, \qquad (29)$$

$$\Gamma_{R,n} = \alpha n^{-(\beta + \gamma/n)}. \qquad (30)$$

$$\lim_{n\to\infty}\Gamma_{1s,n} = \Gamma_A. \qquad (31)$$

Table 1. Parameters of the total decay widths of the $1s$-vacancy of intermediate $1snp$-states of photoexcitation (obtained from the theoretical data of paper [38]) from formula (29) and the ionization threshold energies (calculation of this paper) of the $1s^2$-shells (I_{1s}) of the ions under study

Ion	Γ_A, eV	α, eV	β	γ	I_{1s}, keV
Ti^{18+}	0.085	2.568	3.282	1.831	6.019
Cr^{20+}	0.087	3.474	3.279	1.679	7.230
Fe^{22+}	0.091	5.062	3.271	1.686	8.553
Zn^{26+}	0.097	13.051	3.264	1.589	11.544

In (29) Γ_A — width of auger–decay in channel $1s2s^2 \to 1s^2\varepsilon s$ in the approximation of independence of Γ_A on the principal quantum number (np-electron plays a role of „observer") and $\Gamma_{R,n}$ — width of radiation decay in channel $1snp \to 1s^2$. Parameters Γ_A, α, β, γ are defined by interpolation (for Ti^{18+} and Cr^{20+}) and extrapolation (for Zn^{26+}) of the theoretical data of paper [38] for $n = 2$ in ions of Mg^{8+}, Ar^{14+} and Fe^{22+} with account of the recurrent formula [39]:

$$\frac{\Gamma_{R,n}}{\Gamma_{R,n+1}} = \left(\frac{I_{1snp}}{I_{1s(n+1)p}}\right)^3 \left(\frac{\langle 1s|\hat{r}|np\rangle}{\langle 1s|\hat{r}|(n+1)p\rangle}\right)^2, \quad n \geq 2. \quad (32)$$

At high values of n from (30) we have the following:

$$\Gamma_{R,n} \sim n^{-\beta}. \quad (33)$$

Formula (33) qualitatively reproduces (see $\beta \cong 3$ in Table 1 of the article) the result of the quantum defect theory $\Gamma \sim n^{-3}$ [40], with the difference that in [40] the widths of autoionization resonances of photoabsorption cross-sections were studied.

Formally, mathematically infinite rows in (23), (24) correspond to taking into account the completeness of the set of intermediate photoexcitation states $1s \to np$. As far as we know, the problem of analytical accounting for the completeness of the set for the atom (atomic ion) with nonzero widths of decay, first of all, internal vacancies, remains open. In this article the numerical method of summation from paper [41] is implemented. Values I_{1snp} and $J_n = \langle 1s_0\|r\|np_+\rangle$ for $n \in [2;10]$ are obtained in the single configuration Hartree–Fock approximation. For $n \in [11;\infty)$ energy of photoexcitation $1s \to np$ are obtained by approximation of the following type:

$$I_{1snp} = I_{1s} - \frac{1}{n^2}\left(a - \frac{b}{n}\right), \quad \lim_{n\to\infty} I_{1snp} = I_{1s}, \quad (34)$$

where parameters a and b are defined by values I_{1smp} for $m = 9, 10$. For $n \in [11;\infty)$ probability amplitudes of $1s \to np$-photoexcitation are obtained by the following approximation:

$$J_n = \frac{1}{n^2}\left(c + \frac{d}{n} + \frac{f}{n^2}\right), \quad \lim_{n\to\infty} J_n = 0, \quad (35)$$

where parameters c, d and f are defined by values J_m for $m = 8, 9, 10$. For the integral $\langle np_+|\hat{r}|\bar{\varepsilon}l_+\rangle$ in (26), formula (35) is implemented, taking into account that the parameters c, d and f become functions of the energy of the absorbed photon ($\bar{\varepsilon} = 2\omega - I_{1s}$). In this case, it is necessary to take into account that, as a rule, numerical solutions of the Hartree–Fock equations do not satisfy the physical requirement of orthogonality of the wave functions of the ground states $|1s_+\rangle$ and $|2s_+\rangle$ to the excited state $|\bar{\varepsilon}s_+\rangle$ of the continuous spectrum of the same symmetry:

$$\alpha = \langle 1s_+|\bar{\varepsilon}s_+\rangle \neq 0, \quad \beta = \langle 2s_+|\bar{\varepsilon}s_+\rangle \neq 0. \quad (36)$$

To restore orthogonality, the Gram–Schmidt orthogonalization procedure was used [42]:

$$|\bar{\varepsilon}s_+\rangle \to |\tilde{\varepsilon}s_+\rangle = |\bar{\varepsilon}s_+\rangle - \alpha|1s_+\rangle - \beta|2s_+\rangle, \quad (37)$$

$$\langle 1s_+|\tilde{\varepsilon}s_+\rangle = \langle 2s_+|\tilde{\varepsilon}s_+\rangle = 0. \quad (38)$$

As a result, the wanted integral in (26) is:

$$\langle np_+|\hat{r}|\tilde{\varepsilon}s_+\rangle = \langle np_+|\hat{r}|\bar{\varepsilon}s_+\rangle - \alpha\langle np_+|\hat{r}|1s_+\rangle - \beta\langle np_+|\hat{r}|2s_+\rangle. \quad (39)$$

Results of Fig. 2 demonstrate the significant role of orthogonalization „effect" when building probability amplitudes of radiation transition $np_+ \to \tilde{\varepsilon}s_+$. A mathematically stricter approach (the concept of extended Hilbert space) to building the probability amplitudes of radiative transitions using the Gram–Schmidt orthogonalization procedure is presented in paper [43].

2. Results and discussion

The calculation results are given in Fig. 3–7 and in Table 1–3. Values of generalized cross section parameters (22) adopted in calculations are provided in Table 1 and in Fig. 3. For energies of XFEL-photons, the range $\hbar\omega \in (3;13)$ keV ([44] XFELO, USA; [45,46] European XFEL, Germany; [47] PAL–XFEL, Republic of Korea) is adopted.

Results in Fig. 4–7 and in Table 2 demonstrate clearly pronounced subthreshold resonant structure of generalized cross sections of two-photon ionization of the studied ions caused by occurrence of intermediate states of transition (the values of the principal quantum number $n \in [2;500]$ are taken into account). Decrease in the absolute values of resonances of the generalized cross section for some studied ions is caused by the decrease in the probability amplitudes of transitions $\langle 1s_0|\hat{r}|np_+\rangle$, $\langle np_+|\hat{r}|\tilde{\varepsilon}(s,d)_+\rangle$ in (26) and increase of full $\Gamma_{1s,n}$-widths of decay of $1s$-vacancy of $1snp$-states (Fig. 3). For example, for the leading resonance of photoexcitation $1s \to 2p$ we have the following: $\langle 1s_0|\hat{r}|2np_+\rangle \cdot 10^2 = 5.8$ (Ti^{18+}), 4.3 (Zn^{26+});

$$\langle 2p_+|\hat{r}|\varepsilon d_+\rangle \cdot 10^3\left(\frac{1}{\sqrt{\text{a.u.}}}\right) = 1.5 \ (Ti^{18+}),$$

0.8 (Zn^{26+}); $\Gamma_{1s,2}$ (eV) $= 0.225$ (Ti^{18+}), 0.879 (Zn^{26+}).

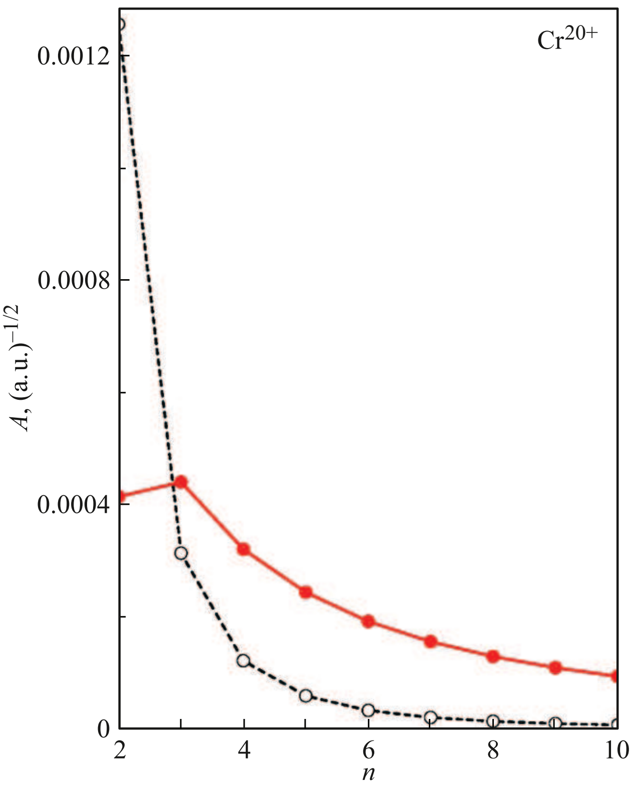

Figure 2. „Effect" of orthogonalization when building probability amplitude A of radiative transition from (39) using the example of ion Cr^{20+} for electron energy of continuous spectrum $\tilde{\varepsilon} = 2I_{1snp} - I_{1s}$. Dashed curve — prior to orthogonalization procedure, solid curve — after orthogonalization.

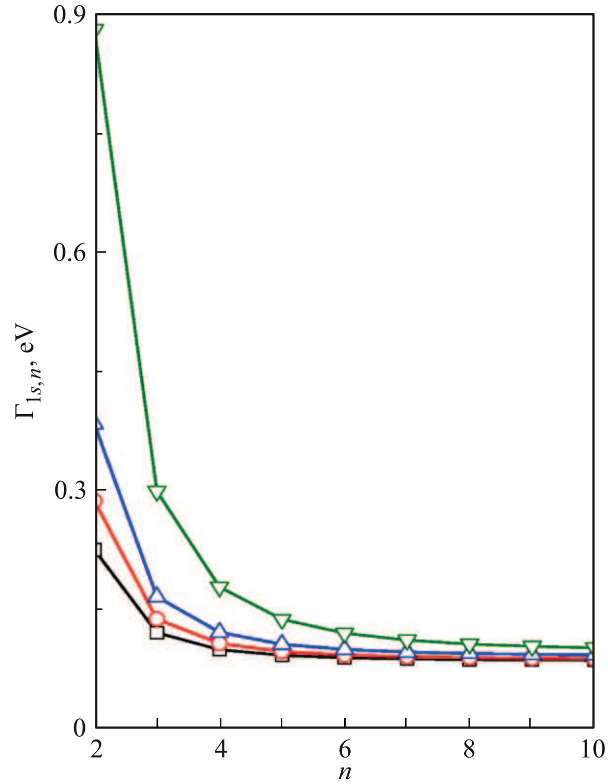

Figure 3. Full widths of ($\Gamma_{1s,n}$) decay of $1s$-vacancy of intermediate states of photoexcitation of $1s \to np$ ions Zn^{26+} — open triangles „down", Fe^{22+} — open triangles „up", Cr^{20+} — open circles and Ti^{18+} — open squares calculated using formula (29).

Results in Fig. 4–7 also demonstrate the effect of destructive (canceling) quantum interference of probability amplitudes of transitions $1s \to np$. This effect is caused by the alternating sign of the factor $\hbar\omega - I_{1snp}$ in (23) and the „immersion" of these states in the continuum (see D in (24)). Besides, for some studied ions between resonance maxima of the generalized cross section, energy gaps increase, and „transparency windows" arise in the form of sharp drop in the probability of two-photon ionization.

For one-electron probability amplitudes of transitions in (26) the following inequality is satisfied:

$$\langle np_+|\hat{r}|\bar{\varepsilon}d_+\rangle > \langle np_+|\hat{r}|\bar{\varepsilon}s_+\rangle. \quad (40)$$

For example, for the leading resonance of photoexcitation $1s \to 2p$ we have the following in Ti^{18+} ion:

$$\langle 2p_+|\hat{r}|\bar{\varepsilon}d_+\rangle \cdot 10^3 \left(\frac{1}{\sqrt{\text{a.u.}}}\right)$$

$$= 1.5 > \langle 2p_+|\hat{r}|\bar{\varepsilon}s_+\rangle \cdot 10^3 \left(\frac{1}{\sqrt{\text{a.u.}}}\right) = 0.5.$$

As a result, the data of Table 3 (see also Fig. 4–7 for partial and full generalized cross sections) show the leading role of

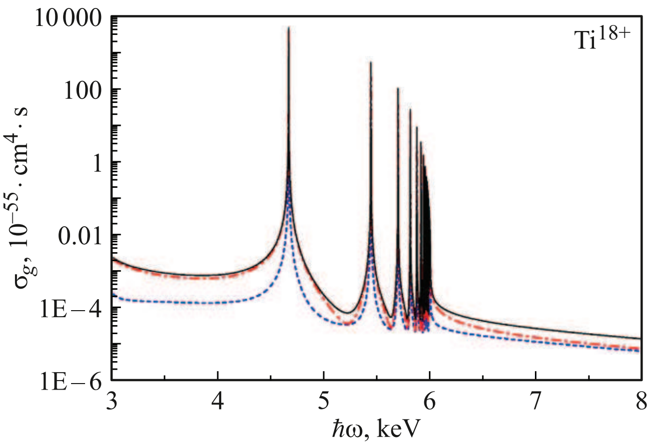

Figure 4. Generalized cross section of two-photon resonant single ionization of the K-shell of Ti^{18+} ion. $\hbar\omega$ — energy of absorbed photon. Dashed dotted curve — $\sigma_g^{(d)}$ (partial cross section of d-symmetry of final ionization state), dashed curve — $\sigma_g^{(s)}$ (partial cross section of s-symmetry of final ionization state), solid curve — $\sigma_g = \sigma_g^{(d)} + \sigma_g^{(s)}$ (full generalized cross section).

d-symmetry of the final state of ionization in the definition of absolute values, first of all, resonances of full generalized cross section at $\hbar\omega \in (3; 13)$ keV.

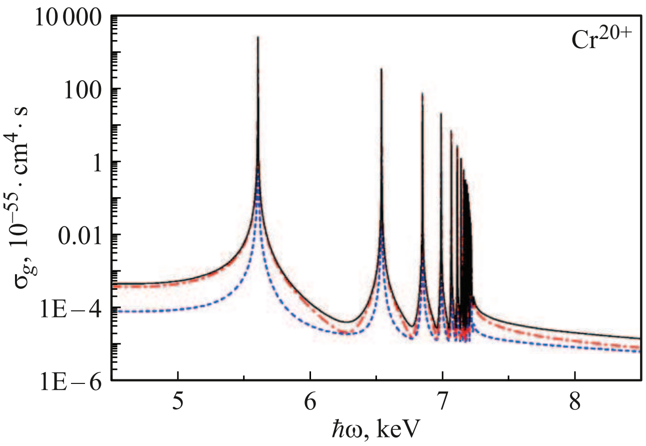

Figure 5. Same as in Fig. 4, but for ion Cr^{20+}.

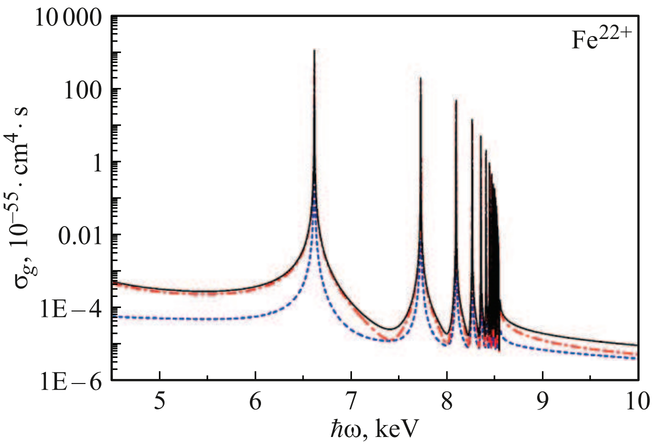

Figure 6. Same as in Fig. 4, but for ion Fe^{22+}.

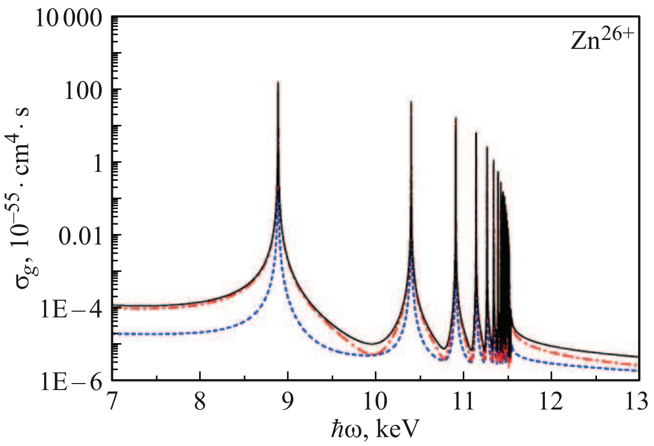

Figure 7. Same as in Fig. 4, but for ion Zn^{26+}.

3. Conclusion

A nonrelativistic version of the quantum theory of the process of two-photon resonant single ionization of the Kshell of a heavy beryllium-like atomic ion is constructed. The isoelectronic sequence of $Ti^{18+} \to Cr^{20+} \to Fe^{22+} \to Zn^{26+}$ ions is studied. The pronounced resonance subthreshold structures of the generalized cross sections and the effect of destructive quantum interference of probability amplitudes of radiative transitions into intermediate states of p-symmetry are established. Besides, the leading role of d-symmetry of the final state of

Table 2. Spectral characteristics of leading resonances of photoexcitation of $1s \to np$-generalized cross sections of two-photon single ionization of K-shell of the studied ions in the region of energies of absorbed photons $\hbar\omega \in (3; 13)$ keV

Ion	np	I_{1snp}, keV	σ_g, 10^{-52} cm$^4 \cdot$ s
Ti^{18+}	$2p$	4.6752	4.5445
	$3p$	5.4481	0.5120
	$4p$	5.7020	0.0979
Cr^{20+}	$2p$	5.5998 5.6160[a]	2.3279
	$3p$	6.5341	0.3405
	$4p$	6.8430	0.0723
Fe^{22+}	$2p$	6.6099 6.6287[b]	1.1402
	$3p$	7.7212	0.1967
	$4p$	8.0904	0.0479
Zn^{26+}	$2p$	8.8897	0.2868
	$3p$	10.4015	0.0798
	$4p$	10.9078	0.0294

Note. [a] Experiment [48]. [b] Relativistic calculation [49].

Table 3. Relative contribution of s- and d-symmetries of final state of ionization $\Lambda = \sigma_g^{(d)}/\sigma_g^{(s)}$ (cm (22) for summands $l = d$, $l = s$) to full generalized cross section of two-photon resonant single ionization of K-shell of studied ions. Energies of absorbed photons are taken $\hbar\omega = I_{1s2p}$ (upper line), $I_{1s} + 1$ (keV) (ower line)

Ion	$\hbar\omega$, keV	Λ
Ti^{18+}	4.6752	8.4972
	7.0200	1.3041
Cr^{20+}	5.5998	10.3713
	8.2300	1.3753
Fe^{22+}	6.6099	8.5061
	9.5530	1.4242
Zn^{26+}	8.8897	9.9992
	12.5440	1.5705

ionization is established in the definition of absolute values of full generalized cross section in the field of energies of XFEL-photons $\hbar\omega \in (3; 13)$ keV. Accounting for correlation and relativistic effects and going beyond the dipole approximation for the $\hat{R}(\hat{C})$radiation (contact) transition operator are the subjects of future theoretical development. The results of successful experiments observing two-photon ionization of atoms, molecules, and solids [50] allow us to believe that absolute values of the generalized cross section in Fig. 4−7 are quite accessible for measurement in the modern XFEL experiment.

Conflict of interest

The authors declare that they have no conflict of interest.

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