High Energy Photoionization Beyond Independent Particle Approximation

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Abstract

Using perturbative approach to IPA breaking effects we find analytical equations which enable to obtain the high energy behavior beyond IPA. The IPA breaking contributions to the cross sections are expressed as the IPA matrix elements of relatively simple operators. The equations for the cross sections ratios are shown to be valid in a broad energy interval. We obtain also the quantitative criteria, which enables to predict which of the couplings are significant for the fixed values of the photon energy. We compare our perturbative results to our numerical calculations. Account of IPA breaking effects is shown either to eliminate or to diminish strongly the discrepancy between the experimental data and the results of IPA calculations.

1 Introduction

The nonrelativistic high energy asymptotic behavior of photoionization cross section differs from that, predicted by independent particle approximation (IPA) for the values of the orbital momenta $\ell \geq 2$. At $\ell = 1$ the energy dependence is not altered beyond IPA, but the value of the coefficient changes (Drukarev *et al* 1999). In this paper we obtain the expressions describing the high energy behavior of cross sections for single photoionization beyond the independent particle approximation (IPA). We limit ourselves to nonrelativistic outgoing electron energies, and thus to photon energies $\omega \ll m$, with the electron mass $m \approx 511\,\mathrm{keV}$. The relativistic system of units with $\hbar = c = 1$ is used, and the electron mass is kept as m. We consider the states, for which the spin-orbit interaction is small enough, and thus space and spin variables can be separated.

The experiments of Dias *et al* (1997) and of Hansen *et al* (1999) for ionization of s and of p states of neon and of argon by the photons with the energies of about 1 keV attracted attention

to the high energy photoionization and stimulated the present analysis. The IPA cross-sections have been well studied. The values of the cross sections were computed and tabulated in various approximations for the wave functions of both initial and final states. In an IPA approach the nonrelativistic high energy asymptotic behavior is known to be (see, e.g. Amusia (1990))

$$\sigma^I_{n\ell}(\omega) \;=\; \frac{a_{n\ell}}{\omega^{7/2+\ell}}\;\left(1+O(\omega^{-1/2})\right)\;, \tag{1}$$

with n the principal quantum number of the electron which is photoionized. The coefficient $a_{n\ell}$ is independent of ω. The superscript I indicates the IPA value. The leading term of the expansion in powers of ω^{-1} is called the asymptotics.

In the preliminary report (Drukarev *et al* 1999) we suggested the mechanism of how IPA breaking interactions change the asymptotic behavior given by Eq.(1). The main idea is that the factor $\omega^{-\ell}$ comes because the photoionization takes place at the small distances of the order p^{-1} with p being the momentum of the outgoing electron. Once the nonrelativistic bound state wave function is proportional to r^ℓ, we obtain the factor $p^{-\ell}$ in the amplitude and the factor $\omega^{-\ell}$ in the cross-section. However the quenching can be avoided. The photon can interact directly with s-electron, which can knockout the electron with orbital momentum ℓ by electron impact. If the latter interaction takes place at the distances of the order of the size of the subshell with quantum number ℓ, there is no $p^{-\ell}$ quenching. However, since the time which the ionized electron needs to pass the distance is proportional to p^{-1} , we obtain this small factor in the amplitude. Thus, high energy behavior for $\ell \geq 1$ becomes

$$\sigma_{n\ell}(\omega) \;=\; \frac{A_{n\ell}}{\omega^{9/2}}\;\left(1+O(\omega^{-1/2})\right) \tag{2}$$

with $A_{n\ell} \neq a_{n\ell}$. Hence, for $\ell \geq 2$ the functional dependence on ω is altered. For $\ell = 1$ the functional dependence is not changed, but the value of the coefficient is modified. For $\ell = 0$ the IPA breaking effects provide the contributions beyond the asymptotics and

$$\sigma_{n0}(\omega) \;=\; \frac{A_{n0}}{\omega^{7/2}}\;\left(1+O(\omega^{-1/2})\right) \tag{3}$$

with $A_{n0} = a_{n0}$.

We noted also (Drukarev *et al* 1999) that for $\ell = 1$ the contribution of IPA breaking effects in the ground state provides a contribution with the same energy behavior. We gave the expression for this term through the total set of eigen-functions of the spectrum.

The investigation was continued by publication of Amusia *et al* (2000) were the general equations for the IPA breaking contribution have been obtained. It was shown that these expressions just correspond to the lowest order random phase approximation with exchange (RPAE) diagrams. Thus, the RPAE computations should reproduce the effect automatically.

In the paper of Avdonina *et al* (2002) the validity of nonrelativistic high energy description of photoionization processes was investigated. The analysis was based on asymptotic perturbation theory (APT) of Pratt and Tseng (1972), which enables to describe the photoionization in terms of the hydrogenlike functions. The leading corrections to the asymptotic behavior, i.e. the terms

$O(\omega^{-1/2})$ were found to depend on the specific parameter $\pi\xi_Z$ with

$$\xi_Z \;=\; \frac{m\alpha Z}{p}\;, \tag{4}$$

being Sommerfeld parameter of the interaction between the outgoing electron and the nucleus. Here Z denotes the charge of the nucleus while $\alpha = 1/137$ is the fine structure constant. The leading corrections to the asymptotic behavior depend linearly on $\pi\xi_Z$, i.e. they contain the minimal power of the parameter ξ_Z multiplied by relatively large coefficient. Hence, the photoionization cross-sections converge to the asymptotic limit very slowly. It was noticed by Avdonina *et al* (2002) that however, at least for the lowest bound states, the terms which depend on the parameter $\pi\xi_Z$ most rapidly compose a factor which was calculated explicitly. This factor, which we called a Stobbe factor, is common for the bound states and thus cancels in the ratios of the cross sections. There are still more cancellations for the cross section ratios of the ionization of the states with the same principle quantum numbers. This explains the much better convergence of the cross sections ratios, both in framework of IPA and beyond, e.g.

$$R_{n\ell}(\omega) \;=\; \frac{\sigma_{n0}(\omega)}{\sigma_{n\ell}(\omega)}\;. \tag{5}$$

This was supported by the IPA Hartree-Fock and IPA breaking RPAE computations for several specific cases, e.g. for those, for which the experimental data was provided by Dias *et al* (1997) and by Hansen *et al* (1999).

In the present paper we obtain analytical expressions for the asymptotics of cross sections of photoionization beyond the IPA in the lowest order of IPA breaking interaction. This was done by using the perturbative approach to the final state (FSI) interactions of the outgoing electrons, developed earlier for the FSI in the beta decay by Drukarev and Strikman (1986, 1987).

The calculations are based on the expansion in power series of Sommerfeld parameter of interaction between the outgoing and the bound electrons

$$\xi \;=\; \alpha/v_e\;, \tag{6}$$

(v_e is the velocity of the outgoing electron in units of c). This parameter is assumed to be small. The IPA breaking amplitude of a specific state is expressed linearly through the IPA amplitudes of ionization of the s states. The cross sections are presented through IPA ionization cross sections of the other states and the matrix elements of relatively simple operators, between the single-particle functions.

It was shown that for $\ell \geq 2$ only the IPA breaking effects in the final state are important in the asymptotics. However, for $\ell = 1$ the IPA breaking effects in initial state can be as important as in the final one. The IPA breaking effects in the initial state can be expressed through a single parameter of the single-particle wave function, i.e. through the first derivative at the origin which is the renormalization of the initial state by means of asymptotic Fourier theory (AFT), as shown by Suric *et al* (2003). However, there is no strict argument for possibility of calculation of this parameter in the lowest order of perturbative theory. Only in the

hydrogenlike approximation, i.e. for internal electrons of the relatively heavy atoms we can estimate parameter of the expansion as $1/Z$, as well as IPA breaking effects in the final state. Anyway, the importance of higher order IPA breaking terms in the ground state would mean, that single-particle presentation is not a good approximation for the initial state.

Similar expressions were obtained beyond the asymptotics for the photon energies large enough for the parameter ξ^2 to be small. This means that the photon energy being expressed in Rydbergs should be much larger that unity. In this case the IPA breaking amplitude of ionization of any state is expressed through the linear combination of the IPA ionization amplitudes of the other states of the spectrum. Also the ionization cross section is expressed through the combination of IPA cross sections.

In the asymptotic limit one should include the coupling of s electrons only (but these should be s electrons from all shells). However, in the applications we deal with specific finite values of energies and beyond the asymptotics the couplings between all the states do contribute. However, we can estimate some of them to be negligibly small if the split between the corresponding levels is not small enough. We obtain a quantitative criteria, which enables to predict which of the states contribute significantly to modify the IPA amplitude.

As an important special case we consider the atom with s and p electrons only. This is important for the applications. The lowest contribution beyond the asymptotics should include the influence of the states with higher ℓ on the cross section of ionization of s states. Such terms may appear to be numerically important at finite energies. Also, for the higher states they may appear to be the largest corrections to the asymptotics of the ratios $R_{n\ell}$, defined by Eq.(5). For $\ell = 1$ we have a very explicit picture. The high energy IPA asymptotics of $R_{n1}(\omega)$ is $R_{n1}(\omega) = \frac{a_{no}}{a_{n1}}\omega$. Account of coupling of s states to the ionization of p states changes the slope. Account of coupling of p states to the ionization of s states shifts the line $R_{n1}(\omega)$. The signs of the two effects are shown to be correlated: if the slope diminishes, the line is shifted down, and vice versa.

We show that the IPA and IPA breaking amplitudes, of ionization of all the bound states calculated with the accuracy $\xi_Z\tau/p$ with τ standing for the average momentum of the bound state obtain the common factor, containing all the dependence on the parameter $\pi\xi_Z$. We provide also a prove that the Stobbe factor. can be singled out for ionization of any state indeed. This supports the faster convergence of the cross section ratios defined by Eq.(5) comparing with the cross section themselves.

We apply our results for the specific case of ionization of external electrons in Ne and Ar, studied experimentally in by Dias *et al* (1997) and by Hansen *et al* (1999). Earlier Avdonina *et al*(2002) found that starting from the photon energies of about 0.7 keV the cross section ratios R_{21} in Ne, being calculated in the Hartree-Fock (HF) approximation indeed demonstrate the asymptotic behavior, while the cross sections do not. We show also that the RPAE calculations lead to similar behavior, with the split between RPAE and HF results being about 1/3–1/4 of the latter. Our perturbative method provides the close results, in agreement with the experimental data.

For the case of Ar our earlier calculations (Avdonina *et al* 2002) show the asymptotic

behavior of R_{21} calculated in RPAE in the same region. The HF results provide larger deviations from the asymptotical law. The split between RPAE and HF results is, as in Ne case about 1/3–1/4 of the latter. The results of our present approach are again close to those of RPAE. The HF calculations for Ar provide the results which overshoot the experimental data by a factor of about two. The IPA breaking interactions in the final state explain only 60% of the discrepancy. One of the possible reasons of the remaining discrepancy was mentioned by Amusia (2000). He reminded that the calculations carried out by Amusia *et al* (1982) demonstrated $3s$ state of Ar not to be well defined as a single-particle state. Thus, strong IPA breaking effects are present in the initial state. This leaves a room for further investigation of the case.

We present the main qualitative results in Sec.II and obtain our asymptotic equations in Sections III and IV. In SecV we present equations for account of all the couplings in the lowest order beyond the asymptotics. In Sec. VI we calculate the common energy dependent factor. In Sections VII and VIII we apply our results to investigation of ionization of external electrons of Ne and Ar at the photon energies of the order of 1 keV. The results are summarized in Sec.IX.

2 Main qualitative results

In the IPA framework the photoionization amplitude for the state with quantum numbers n, ℓ, ℓ_z is

$$\phi_{n\ell m} \;=\; \langle \psi_p | \gamma | \psi_{n\ell\ell_z} \rangle \;, \tag{7}$$

with ψ_p and $\psi_{n\ell\ell_z}$ the single-particle wave functions of the outgoing and the initial bound electron. The operator γ describes the electron–photon interaction. We assume the velocity form of electron-photon interaction operator. (We do not discuss the dependence of different contributions on the form of γ in this paper).

We investigate the high energy limit of this amplitude, when

$$\omega \;\gg\; I_{n\ell} \tag{8}$$

with $I_{n\ell}$ the binding energy of the ionized $n\ell$ subshell. Eq.(8) means that the momentum of the outgoing electron

$$p \;= [2m(\omega - I_{n\ell})]^{1/2} \;\gg\; \tau_{n\ell} \;. \tag{9}$$

Note, that one can present $\xi^2 = (m\alpha)^2/p^2 = I_0/E \simeq I_0/\omega$ with E standing for the energy of the outgoing electron, while $I_0 = m\alpha^2/2 = 13.6\,\mathrm{eV}$. (This makes just one Rydberg.) For most of atomic levels the binding energy is larger than that. Thus, condition (8) insures that

$$\xi^2 \;\ll\; 1 \;; \quad E \;\gg\; I_0 \tag{10}$$

required for perturbative treatment of FSI to be valid. We shall assume Eq. (10) to be true anyway.

Thus, Eq. (9) provides two scales for the momenta which are τ_{nl} and p. It is known that asymptotics of the amplitude $\varphi_{n\ell\ell_z}$, presented by Eq.(7), is determined by behavior of the wave

function $\psi_{n\ell\ell_z}$ at small values $r \sim p^{-1} \ll \tau_{n\ell}^{-1}$, i.e. at the distances, which are much smaller than the size of the atomic shell with quantum number "n". Since $\psi_{n\ell m}(r) \sim r^\ell$ at small ℓ, we find for the case, when $\tau_{n\ell} \simeq \tau_{n0} = \tau_n$

$$\varphi^{(0)}_{n\ell\ell_z} \;\sim\; \varphi^{(0)}_{n00} \left(\frac{\tau_n}{p}\right)^\ell \tag{11}$$

with upper index (0) denoting the asymptotics of the amplitudes. The value τ_n in nominator is dictated by dimension. In the hydrogenlike approximation this can be obtained explicitly with $\tau_n = m\alpha Z/n$.

However, there is an alternative mechanism. Instead of interacting with an $n\ell$ state, the photon can interact with a n's state, creating a hole. Then the knocked-out electron pushes the $n\ell$ electron into the n's hole by electron impact. This second step takes place at the distances of the order of the size of Bohr orbits (rather than the small distances at which the photoabsorption occurs), and thus we avoid suppression by powers of momentum. However interaction of the outgoing electron with the bound electron is proportional to the Sommerfeld parameter, defined by Eq. (6). Thus, asymptotics of the IPA breaking amplitude $\Phi_{n\ell}$ is $\Phi^{(0)}_{n\ell} \sim \xi\varphi_{n'0}$.

Hence, for $\ell \geq 2$ the asymptotics of the amplitude which is the sum of IPA and IPA breaking terms is totally determined by IPA breaking effects. The parameter estimation gives

$$\sigma^{(0)}_{n\ell}(\omega) \;\simeq\; \xi^2 \sigma^{I(0)}_{n0}(\omega)\;. \tag{12}$$

For $\ell = 0$ the IPA breaking terms contribute beyond the asymptotics only. For $\ell = 1$ interference of IPA and IPA breaking effects contributes to the cross section as

$$\frac{\sigma^I_{n1}(\omega) - \sigma_{n1}(\omega)}{\sigma^I_{n1}(\omega)} \;\simeq\; \kappa \tag{13}$$

with

$$\kappa = \left(\frac{a_{n0}}{a_{n\ell}} \cdot I_0\right)^{1/2}\;, \tag{14}$$

while the square of IPA breaking terms contribute κ^2 terms. In the case $\ell = 1$ there are IPA breaking effects in the initial state interaction as well. This is the admixture of higher lying states to the single-particle $n\ell$ state by electron-electron interaction. Parameter κ introduced above by Eq. (14) plays the role of Sommerfeld parameter of this interaction. Hence, such terms do not contribute to asymptotics in the case $\ell \geq 2$. However, for $\ell = 1$ they provide parametrically the same contribution as the FSI IPA breaking terms. One can see, that for the internal electrons of a heavy atom $\kappa \sim Z^{-1}$, and thus perturbative approach to IPA breaking in the initial state is approved. However, in the general case the higher order terms may appear to be important.

Now we come to quantitative description.

3 Main equations

To obtain the mathematical description of the IPA breaking mechanism, consider the two-electron states $|i,j\rangle$ with i denoting the set of quantum numbers $n\ell\ell_z$. In IPA the amplitude (7) is

$$\varphi_{n\ell\ell_z} \;=\; \langle p,j|\gamma|i,j\rangle \tag{15}$$

with p denoting state of the outgoing electron. In IPA the "j" electron is just a spectator.

Consider now admixture of other two-electron states by ee interaction V in the final state

$$\begin{aligned}\Phi_i \;&=\; \varphi_i + \sum_{k,j} \frac{\langle p,j|V|k,j\rangle\langle k,j|\gamma|i,j\rangle}{\varepsilon_i+\omega-\varepsilon_k} \;- \\ &- \;\sum_{k,j} \frac{\langle p,j|V|k,i\rangle\langle k,i|\gamma|j,i\rangle}{\varepsilon_j+\omega-\varepsilon_k}\end{aligned} \tag{16}$$

with "k" standing for the vacancies in both continuum and discrete spectra. In the second term of Eq.(16) the photon still interacts directly with the bound electron "i", while the third term describes the IPA breaking mechanism.

In the nonrelativistic approximation the interaction V does not depend on the spin variables. Thus, the spin projection in the states $|j\rangle$ and $|i\rangle$ should be the same. Hence, the space part of the wave function describing this two-electron state should be asymmetric.

The main contribution to the sum over "k" in the third term of Eq.(16) comes from continuum states with momentum $\bar{k}$ close to $\bar{p}$, i.e.

$$\bar{k} \;=\; \bar{p}+\bar{f} \tag{17}$$

with $|f|$ being of the order τ_i (see assume for simplicity, that $\tau_i \approx \tau_j$). To prove the statement, present

$$\langle p,j|V|k,i\rangle \;=\; \langle j|u|i\rangle \tag{18}$$

with

$$u(r) \;= \int \psi_p^*(r_1) v(r_1-r)\psi_k(r_1) d^3r_1 \tag{19}$$

$$\langle j|u|i\rangle \;= \int \psi_j^*(r) u(r)\psi_i(r) d^3r \;, \tag{20}$$

while v stands for ee interaction. The main oscillating terms in Eq.(19) are $e^{-i(pr_1)}$ and $e^{i(kr_1)}$ coming from the continuum wave functions ψ_p^* and ψ_k and the integral in Eq.(20) drops quickly if $|p-k| \gg \tau_i$. Thus, we can replace $\langle k,i|\gamma|j,i\rangle$ by $\langle p,i|\gamma|j,i\rangle \;= \phi_j$ in the last term of rhs of Eq (16) (this leads to the error of the order p^{-4}). Thus, we can write for the amplitude which accounts IPA breaking effects through the lowest order of the final state interactions

$$\Phi_i \;=\; \phi_i - \Lambda_{i,j}\phi_j \tag{21}$$

with

$$\Lambda_{i,j} \;=\; \int \frac{d^3f}{(2\pi)^3} \;\frac{\langle p,j|V|p+f,i\rangle}{\omega+\varepsilon_j-\varepsilon_{p+f}} \;. \tag{22}$$

Here we replaced integration over k by that over f. The matrix element in the rhs thus describes the transition between the two two-electron state. One of them consists of the bound electron in the state i and the continuum electron with momentum $\bar{p}+\bar{f}$. The second one consists of the bound electron in the state j and the continuum electron with momentum $\bar{p}$. All the electrons are moving in a certain effective field. Following previous discussion, we include the states $|j\rangle$ with zero value of angular momentum only.

Equation (21) expresses the IPA breaking amplitude through the IPA amplitudes in the lowest order of the final state $e-e$ interactions.

Now we shall see, how the asymptotics of the amplitudes (denoted by the upper index "(0)") are related. This means, that we must calculate the leading term of the expansion of Λ in powers of p^{-1}.

The leading term of the expansion in powers of p^{-1} comes from replacing of the continuum states in the matrix element in Eq.(18) by the plane waves. The interactions with the field of the residual ion takes place at the distances of the order of the size of the atom, providing the corrections of the order $\xi_Z \tau_{i(j)}/p$ (Drukarev and Strikman, 1986). Thus

$$\Lambda^{(0)}_{i,j} \;=\; \langle i|B|j\rangle \tag{23}$$

with

$$B(\bar{r}) \;=\; -\int \frac{d^3f}{(2\pi)^3}\;\frac{2m}{f^2+2(\bar{p}\bar{f})+2m\delta}\;v(f)e^{i(fr)}\;. \tag{24}$$

Here δ is the difference of binding energies, i.e. $\delta = I_{n'0}-I_{n\ell}$, and $v(f)$ is the Fourier transform of the interaction between two atomic electrons. Taking the direction of outgoing electron momentum as the axis of quantization of angular momentum, we find that the second term on the r.h.s. of Eq. (21) vanishes except for $\ell_z = 0$. Hence,

$$\Lambda_{n\ell\ell_z,n'00} \;=\; \delta_{\ell_z 0}\Lambda_{n\ell,n'0}\;. \tag{25}$$

(Here and below we omit the upper index for Λ, having in mind that Λ is described by Eq (23)). Thus, only the amplitudes of ionization of the states with $\ell_z = 0$ obtain IPA breaking admixture of the second term of Eq.(21).

As we discussed above, Λ contains the factor ξ. Recalling estimation of Eq.(12) we find that asymptotics of the cross section $\sigma_{n\ell}$ is determined by the second term of Eq.(21) for all $\ell \geq 2$:

$$\sigma^{(0)}_{n\ell}(\omega) \;=\; \sum_{n'} |\Lambda_{n\ell,n'0}(\omega)|^2\;\sigma^{I(0)}_{n'0}(\omega)\;. \tag{26}$$

The situation for $\ell = 1$ is more complicated, since, following previous discussion, we find both terms in r.h.s. to be of the same order. There is also a contribution of the IPA breaking effects in the ground state interaction. The IPA breaking interactions between the atomic electrons can provide admixture of the states j with the same angular momentum $\ell = 1$ to the ionized state. Such amplitude will have the same energy dependence as the IPA one, contributing to the asymptotics only in the case $\ell = 1$. Following AFT (Suric *et al* 2003) the high energy limit of amplitude of ionization of $\ell = 1$ state can be expressed through a single

parameter which is the derivative of the wave function of this state at the origin. Hence, the IPA breaking effect in initial state can be treated as certain renormalization of the single-particle wave function.

Thus, for $\ell = 1$ it is more convenient to present the results for the square of the amplitude $\Phi^{(0)}_{n1}$, since we must take care about the interference and watch the i factors. We find for the state $n10$

$$|\Phi^{(0)}_{n1}|^2 = |\varphi^{(0)}_{n1}|^2 + 2\mathrm{Re}\sum_{n'}\varphi^{(0)}_{n1}\Lambda_{n1,n'0}\varphi^{(0)}_{n'0} + \sum_{n'}|\Lambda_{n1n'0}|^2|\varphi^{(0)}_{n'0}|^2 + 2\mathrm{Re}\sum_{j}\varphi^{(0)}_{j}G_j \qquad (27)$$

with the last term in rhs describing the IPA breaking effects in the initial state,

$$G_j = \sum_r \frac{\langle j,r|V|r,i\rangle}{\varepsilon_i - \varepsilon_j}$$

and the sum is taken over all the atomic electron states r and over all possible admixed (both discrete and continuum) states j. If the latter belongs to continuum, $\varphi^{(0)}_j$ is the amplitude of the absorption of the photon by the electron moving in the field of the atom.

The higher order FSI terms provide contributions beyond the asymptotics of the cross-sections σ_{nl}.

4 Lowest order IPA breaking contribution

In this approximation we can assume the interaction between the atomic and ionized electrons not to be altered by the other bound electrons. Hence, we put

$$v(f) = \frac{4\pi\alpha}{f^2}\ . \qquad (28)$$

This enables us to obtain

$$B(\bar{r}) = i\xi(\ln r(1-t) + c) + O(\xi^2) \qquad (29)$$

with $B(\bar{r})$ given by Eq.(24). Here $t = (\bar{p}\bar{r})/pr$, c is a constant. This enables us to find for the function $\Lambda_{i,j}$, determined by Eq.(22)

$$\Lambda_{n\ell,n'0} = -i\xi(S_{n\ell,n'0} + O(\xi^2)) \qquad (30)$$

with the contributions $O(\xi)$ containing real terms, and

$$S_{n\ell,n'0} = \langle\psi_{n\ell0}|\ln(1-t)|\psi_{n'00}\rangle\ . \qquad (31)$$

The wave functions $\psi_{n\ell0}$ and $\psi_{n'00}$ describe the electron states in the atom and in the ion with the hole in $(n\ell0)$ state. The terms, containing the constant c and $ln\ r$ vanish due to orthogonality of the angular parts of the wave functions. Note, that Eq.(31) can be obtained

also by using the general approach to the final state interactions, developed by Drukarev and Strikman (1986, 1987).

The matrix element in the rhs of Eq. (31) can be presented as the product of the angular and radial matrix elements

$$S_{n\ell,n'0} \;=\; b_\ell d_{n\ell,n'0} \; . \tag{32}$$

Here

$$b_\ell \;=\; \frac{(2\ell+1)^{1/2}}{2} \int\limits_{-1}^{1} dt P_\ell(t) \cdot \ln(1-t) \tag{33}$$

is the angular matrix element with P_ℓ standing for Legendre polynomial, while the radial matrix element is

$$d_{n\ell,n'0} \;=\; \langle \psi^{(r)}_{n\ell} | \psi^{(r)}_{n'0} \rangle \; . \tag{34}$$

In Eq.(34) index (r) denotes the radial part of the wave functions. Recall, that the radial parts of the wave functions, describing the states with the different angular momenta are not orthogonal even for the same Hamiltonian.

Note that the function Λ expressed by Eq. (22) is imaginary in the leading order of expansion in powers of ξ. This reflects the two-step character of the process. After interaction with the photon, the quasi-real electron is created, which passes the distances of the order of the size of the atom before interacting with the electron with orbital momentum ℓ. The amplitudes $\varphi_{n\ell 0}$ have the form of real magnitudes, multiplied by the factor i^ℓ. Hence, for odd ℓ there is interference between IPA and IPA breaking terms, while for even ℓ they result in additive terms.

For the asymptotics at $\ell \geq 2$ we obtain

$$\sigma^{(0)}_{n\ell}(\omega) \;=\; \xi^2 b^2_\ell \sum_{n'} d^2_{n\ell,n'0} \sigma^{I(0)}_{n'0}(\omega) \tag{35}$$

and the coefficient $A_{n\ell}$, introduced in Eq(2) is

$$A_{n\ell} \;=\; I_0 b^2_\ell \sum_{n'} d^2_{n\ell,n'0} \frac{a_{n0}}{a_{n'o}} \; , \tag{36}$$

The ratios, defined by Eq(5) are

$$R^{(0)}_{n\ell}(\omega) \;=\; \frac{I_0}{\omega} b^2_\ell \cdot \sum_{n'} d^2_{n\ell,n'0} \frac{a_{n0}}{a_{n'o}} \tag{37}$$

For $\ell = 1$ the asymptotics is

$$\sigma^{(0)}_{n1}(\omega) = \sigma^{I(0)}_{n1}(\omega) + 2\xi b_1 \sum_{n'} d_{n1,n'0} \left(\sigma^{I(0)}_{n1}(\omega) \sigma^{I(0)}_{n'0}(\omega) \frac{N_0}{N_1} \right)^{\frac{1}{2}} \; +$$

$$+ \qquad \xi^2 b^2_1 \sum_{n'} d^2_{n1,n'0} \sigma^{I(0)}_{n'0}(\omega) + 2\mathrm{Re} \sum_k G_k \left(\sigma^{I(0)}_{n1}(\omega) \sigma^{I(0)}_{k}(\omega) \right)^{\frac{1}{2}} . \tag{38}$$

Here the last term stands for the interference between IPA contribution to the amplitude and IPA breaking terms in the ground state. The sum over "k" includes both discrete and continuum states. In the latter case σ_k stands for the cross section of the photon absorption by the electron moving in the atomic field.

The leading correction to Eqs. (35) and (38) coming from higher order of FSI is the interference of the second order FSI amplitude with the IPA amplitude. It contributes beyond the asymptotics containing the factor $\xi^2(\tau/p)^\ell$.

The coefficients A_{n1}, introduced in Eq.(2) are

$$A_{n1} = a_{n1} + b_1 \sum_{n'} d_{n\ell,n'0} \left(I_0 \frac{a_{n1} a_{n'0} N_0}{N_1} \right)^{1/2} + I_0 b_1^2 \sum_{n'} d^2_{n1,n'0} a_{n'0} + 2\mathrm{Re} \sum_k G_k (a_{n1} a_k)^{1/2}. \quad (39)$$

For the asymptotics of the ratio $R^{(0)}_{n\ell}$, defined by Eq(5) we find for $\ell = 1$

$$R^{(0)}_{n1}(\omega) \;=\; r_n \cdot \omega \; . \quad (40)$$

The IPA breaking effects thus change the IPA value $r^I_n = a_{n0}/a_{n1}$ to

$$r_n \;=\; r^I_n / K \quad (41)$$

with

$$K = 1 + b_\ell^2 \sum_{n'} d_{n\ell,n'0} \left(\frac{I_0 a_{n'0} N_0}{a_{n1} N_1} \right)^{1/2} + I_0 b_1^2 \sum_{n'} d^2_{n1,n'0} \frac{a_{n'0}}{a_{n1}} + 2\mathrm{Re} \sum_k G_k \left(\frac{a_k}{a_{n1}} \right)^{1/2} . \quad (42)$$

5 IPA breaking contributions beyond the asymptotics

The IPA breaking correlations in the final state can be treated perturbatively for all energies which satisfy the condition expressed by Eq. (10). It is not necessary for the cross sections or for their ratios follow the asymptotic behavior. Beyond the asymptotics we must include IPA breaking admixture of the states with all the orbital momenta (not only the s states, as it was in the asymptotics) to the ionized states.

Assume the ionized state i to have the angular momentum ℓ while the admixed states j have the orbital momentum ℓ'. Now let us see, how the states with different ℓ' contribute. Note, that the photoionization amplitude for the state with orbital momentum ℓ is proportional to the factor i^ℓ. We use also the fact that the lowest order mixing matrix $\Lambda_{i,j}$ is mostly imaginary, with the imaginary part being proportional to ξ and the real part being proportional to ξ^2 (Drukarev and Strikman 1986, 1987). Also the mixing matrix $\Theta_{i,j}$ which describes the final state interactions of the second order is proportional to ξ^2 with dominative real part. Thus, IPA breaking effects caused by mixing of the states with odd values of $\ell - \ell'$ are proportional to ξ, being determined by interference of IPA and lowest order IPA breaking terms. The terms of the order ξ^2 are determined by the square of the imaginary part of Λ in this case. For the even

values of $\ell - \ell'$ the effect is determined by interference of IPA amplitude with the real parts of Θ and Λ and by the square of the real part of Λ, being proportional to ξ^2.

In the general case we must include the final state IPA breaking interaction up to the second order. Following Drukarev and Strikman (1986, 1987) we present a general equation for the amplitude of ionization of a the state i with quantum numbers n, ℓ, ℓ_z with the couplings to the states j with quantum numbers $n', \ell', \ell'_z = \ell_z$ there is no coupling if the values of ℓ_z differ)

$$\Phi_i \;=\; \phi_i - \Lambda_{i,j}\phi_j - \Theta_{i,j}\phi_j \;. \tag{43}$$

Here $\Lambda_{i,j}$ and $\Theta_{i,j}$ describe the final state interactions in the first and second order of expansion in ξ. Using the approximations which have been used for the derivation of Eq.(29) we obtain

$$\Lambda_{i,j} \;=\; -i\xi S_{i,j} + \xi^2 T_{i,j} \tag{44}$$

with

$$S_{i,j} \;=\; \langle i|\ln r(1-t)|j\rangle, \tag{45}$$

corresponding to Eq.(31), while

$$T_{i,j} \;=\; \frac{r_0}{2}\langle i|\partial/\partial r|j\rangle \tag{46}$$

is the real part of $\Lambda_{i,j}$.

The second order amplitude in the same approximation is

$$\Theta_{i,j} \;=\; \xi^2 Q_{i,j} \tag{47}$$

with

$$Q_{i,j} \;=\; -\frac{1}{2}\langle i|\ln^2 r(1-t)|j\rangle \;. \tag{48}$$

The terms, containing $\ln\, r$ survive only if the states i and j have equal angular momenta. Otherwise, only $\ln(1-t)$ term of the sum $\ln r + \ln(1-t)$ contributes due to orthogonality of the angular wave functions. Also, the terms, containing the real part of Λ vanish if the two angular momenta differ.

Of course, one can not discriminate the terms of the order ξ^2 against those of the order ξ without additional information about the amplitudes involved. We saw earlier, what happens in the asymptotics. Here we present the formula for the cross-section accounting for the IPA breaking terms of the order ξ^2 in the final state and lowest order perturbative contribution of IPA breaking interactions in the initial state.

$$\begin{aligned}\sigma_i(\omega) \;&=\; \sigma_i^I(\omega) + 2\xi\sum_j S_{i,j}\left(\sigma_i^I(\omega)\sigma_j^I(\omega)\frac{N_j}{N_i}\right)^{\frac{1}{2}} + \xi^2\sum_j S_{ij}^2\sigma_j^I(\omega) \;+ \\ &+ \qquad 2\xi^2\sum_k (T_{ik}+Q_{ik})\left(\sigma_i^I(\omega)\sigma_k^I(\omega)\frac{N_k}{N_i}\right)^{\frac{1}{2}} + 2\mathrm{Re}\sum_p G_p\left(\sigma_i^I(\omega)\sigma_p^I(\omega)\right)^{\frac{1}{2}}.\end{aligned} \tag{49}$$

Here we labelled the states for which $\ell - \ell'$ is odd by j, and those for which it is even by k. In the last term, presenting the IPA breaking effects in initial state p denotes the states with the same orbital momentum as in the state i.

While considering the high energy limit one should include the s-electrons only, but from all the shells. Some of the contributions may appear to be small due to the small values of the mixing matrix elements $d_{n\ell,n'o}$. However, for the finite energies there is also a criterion, connected with the photon energy. Beyond the asymptotics it should be tried for the states with other orbital momenta as well. One can see Eq. (32) for $S_{i,j}$ to be true only if the energy difference $\delta = I_i - I_j$ is small enough

$$m|\delta| \ \leq \ p \cdot \tau \ ; \quad \tau \ = \ \min\{\tau_i \ , \tau_j\} \ . \tag{50}$$

Otherwise the value of Λ is much smaller. Indeed, the denominator of the integrand of the integral in the rhs of Eq. (24) is approximately $2m\delta$ and one must go to higher order terms of expansion in powers of small parameter $(pf)/m\delta \simeq p\tau/m\delta$ to obtain the contribution, that would lead to finite value of the matrix element, presented by Eq.(23). Say, for j being an s-state, we must go up to $\frac{1}{\delta}(\frac{(pf)}{m\delta})^\ell$ terms. Additional selection will be provided by the values of the mixing matrix elements $S_{i,j}$, $T_{i,k}$ and $Q_{i,k}$.

Consider as an example the case of mutual influence of s and p electrons of the same subshell. It is important for the nowadays applications. The influence of s electrons on the ionization of p ones is expressed by Eq.(38) with the upper indexes "(0)" being removed:

$$\sigma^I_{n1}(\omega) = \sigma^I_{n1}(\omega) + 2\xi b_1 \sum_{n'} d_{n1,n'0} \left(\sigma^I_{n1}(\omega)\sigma^I_{n'0}(\omega)\frac{N_0}{N_1}\right)^{\frac{1}{2}} \ +$$

$$+ \qquad \xi^2 b_1^2 \sum_{n'} d^2_{n1,n'0}\sigma^I_{n'0}(\omega) + 2\mathrm{Re}\sum_k G_k \left(\sigma^I_{n1}(\omega)\sigma^I_k(\omega)\right)^{\frac{1}{2}} . \tag{51}$$

For the influence of p states on the cross-section of ionization of s states we obtain

$$\sigma_{n0}(\omega) = \sigma^I_{n0}(\omega) - 2\xi b_1 \sum_{n'} d_{n0,n'1} \left(\sigma^I_{n0}(\omega)\sigma^I_{n'1}(\omega)\frac{N_0}{N_1}\right)^{\frac{1}{2}} + \xi^2 b_1^2 \sum_{n'} d^2_{n0,n'1}\sigma^I_{n'1}(\omega). \tag{52}$$

The minus sign of the second term is determined by interplay of i factors of the amplitude of ionization of p state and of the function $\Lambda_{i,j}$. We find an explicit picture for the case when the IPA ratio R^I_{n1} is determined by the asymptotic expansion — see Eq. (40), thus changing to

$$R_{n1}(\omega) \ = \ r^I_n \cdot \omega/K + c_n + g_n/\omega \tag{53}$$

with K being defined by Eq. (41), while,

$$c_n \ = \ -2b_1 \sum_{n'} d_{n0,n'1} \left(I_0 \frac{a_{n0}N_0}{a_{n'1}N_1}\right)^{1/2} \ , \tag{54}$$

and

$$g_n = I_0 b_1^2 \sum_{n'} d^2_{n0,n'1}\sigma^{I(0)}_{n'1}/\sigma^{I(0)}_{n1} \ . \tag{55}$$

All the terms in the rhs of Eq.(38) change the value of K. The largest change is caused by the second term which is proportional to the first power of small parameter ξ. The rhs of

Eq. (51) is also dominated by the second term which provides the finite value of c_n. The third term of rhs of (51) provides a small nonlinear contribution expressed by the last term rhs of Eq. (53).

Hence, the IPA breaking effects manifested themselves mostly in finite values of $K-1$ and of c_n. The first effect is thus the change of the slope of the line $R^I_{n1} = r^I_n \omega$. The second one is the shift of the line up or down. Note, that the signs of the effects are correlated. The decrease of the slope takes place together with the shift down, while the increase of the slope is accompanied by the shift up.

If the electrons from the same shell are included only, i.e. only the terms with $n = n'$ contribute to the sums in the second terms of rhs of Eqs (38) and (51) we find an interesting feature. If the IPA ratio $R^{(0)}_{n1} > 1$, the relative influence of s electrons on the cross section of ionization of p electrons appears to be larger than the influence of p electrons on ionization of s electrons. If $R^{(0)}_{n1} < 1$ we face the opposite situation.

6 Common energy-dependent factor beyond the IPA

Being treated in a straightforward way, i.e. as the lowest terms of p^{-1} expansion, the nonrelativistic asymptotic cross sections are rather of purely theoretical interest: the asymptotical regime is not reached in the nonrelativistic domain. However, one can separate two sources of the p^{-1} contributions and single-out those, which contain the parameter $\pi\xi_Z$.

Here we analyze the leading corrections to IPA and IPA breaking cross sections beyond the asymptotics, i.e. the terms, containing extra powers of p^{-1} in the amplitude. The asymptotics is provided by the lowest order terms of interaction of the outgoing electron with nucleus. In the case of ionization of s-electron this is a plane wave, for $\ell \geq 1$ the next term should be included.

Consider now next to leading terms of interaction of the outgoing electron with the residual ion. Start with the interaction between the electron and the nucleus, calculating the correction perturbatively. One can see, that the correction is caused by the small distances of the order p^{-1}, i.e. the same scale of distances, as the main process. Thus, the outgoing electron exchanges momentum of the order of p with the nucleus. The bound state wave function enters through the same normalization parameter as in the asymptotics. The direct calculation of the perturbative correction shows, that the correction manifests itself by the factor $(1 - \pi\xi_Z)$. Thus, the lowest powers of p^{-1} appear with the large numerical coefficient. Interaction of the outgoing electron with the residual ion includes the interaction with its electrons as well. In framework of IPA it can be included by a screening potential. This was done in analytical perturbation theory (APT) developed by Pratt and Tseng (1972). The interaction of the outgoing electrons with the electronic shell of the ion takes place at the distances of the order of the size of the shell, i.e. much larger than p^{-1}. In such interaction momentum q transferred to the nucleus is of the order of that of the bound electron τ. It is exchanged between the outgoing electron and the atomic shell. This interaction provides the higher order correction, found in framework of APT to be of the order $\xi\xi_Z/Z^{1/3}$ (Pratt and Tseng 1972, Oh *et al* 1976).

Thus, the terms of the order $\pi\xi_Z$ come from the interaction of the outgoing electron with the nucleus and do not come from the interactions with the atomic shell, irregardless of the approximation, used for the description of the outgoing electron.

Due to APT we can study the photoionization in terms of the hydrogenlike wave functions. Analytical formula have been obtained for the cross sections of photoionization of the lowest levels of the hydrogenlike atoms. Stobbe (1930) derived the equations for K and L-shells and Harriman (1956) — for M and N shells. Basing on these results we found (Avdonina *et al* 2002) that the most rapidly energy dependent terms compose the Stobbe factor

$$S(\pi\xi_Z) \;=\; \exp(-\pi\xi_Z)\;, \tag{56}$$

which does not depend on the quantum numbers of the ionized state. However, the values of ξ_Z at fixed value of the photon energy do. With p^{-2} accuracy we must neglect the terms $I_{n\ell}$ in expression (9), replacing ξ_Z by

$$\hat{\xi}_Z \;=\; \frac{m\alpha Z}{(2m\omega)^{1/2}}\;, \tag{57}$$

and the values of $S(\hat{\pi}\xi_Z)$ do not depend on the quantum numbers of the ionized state. The total factor which has the common functional dependence for the considered states was the "generalized Stobbe factor"

$$S_n(\pi\xi_Z) \;=\; \frac{2\pi\xi_Z}{e^{\pi\xi_Z}-e^{-\pi\xi_Z}}S(\pi\xi_Z)\exp\left(\frac{4\pi\xi_Z\arctan\xi_Z}{n}\right) \tag{58}$$

with n standing for the principle quantum number of the ionized state.

Now we show that the common factor is indeed described by Eq.(52) for any ionized state. Following Gorshkov *et al.* (1964) the amplitude of photoionization from the state $n\ell\ell_z$ can be presented as

$$\varphi_{n\ell\ell_z} = \;(4\pi\alpha)^{\frac{1}{2}}N_{n\ell\ell_z}N(\pi\xi_Z)\Gamma_{n\ell\ell_z}(\bar{e}\bar{\nabla}_k)X(\bar{k},\bar{p},\tau_{n\ell},\xi_Z) \tag{59}$$

with $N_{n\ell m}$ being a constant factor, depending on the quantum numbers of the bound states,

$$N(\pi\xi_Z) \;=\left[\frac{2\pi\xi_Z}{1-\exp(-2\pi\xi_Z)}\right]^{1/2} \tag{60}$$

is the normalization factor of the Coulomb wave function of the outgoing electron, i.e. it is the value of the nonrelativistic Coulomb function at the origin. Operator $\Gamma_{n\ell\ell_z}$ contains derivative over $\tau_{n\ell}$ and (for $\ell\neq 0$) gradients over photon momentum k. The function

$$X(\bar{k},\bar{p},\tau_{n\ell},\xi_Z)=\frac{1}{(\bar{p}-\bar{k})^2+\tau_{n\ell}^2}\left\{\frac{(p-k)^2+\tau_{n\ell}^2}{k^2-(p+i\tau_{n\ell})^2}\right\}^{i\xi_Z} \tag{61}$$

has the same form for any bound state. After all the derivatives are calculated, one should put $k=0$, neglecting the terms of the order $k/p\sim(\omega/m)^{1/2}$. Thus, the amplitudes contain the common factor

$$Q_n \;=\; N(\pi\xi_Z)\exp(-\pi\xi_Z)exp(2\xi_Z\arctan\xi_Z/n)\;. \tag{62}$$

Here we used that in the hydrogenlike approximation $\tau_{n\ell} = \xi_Z/n$ Note that the factor $(-1)^{i\xi_Z} = e^{-\pi\xi_Z}$ emerged just because in the photoionization $p \gg k$. This stresses the "model-independent" nature of this term.

Hence, the cross sections calculated in hydrogenlike approximation, contain the common factor Q_n^2. Comparing this formula to Eq. (52) we find immediately $Q_n^2 = S_n$ for all the bound states. Thus, equations (56) and (58) for the Stobbe factors are valid for all the bound states indeed.

Note that the Stobbe factor $S(\pi\xi_Z)$ contains the most sharp dependence on the parameter $\pi\xi_Z$ but does not pick all the terms which contain $\pi\xi_Z$. Treating $\pi\xi_Z$ as the separate parameter we find that all the dependence is reproduced by the factor

$$D(\pi\xi_Z) \;=\; H^2(\pi\xi_Z)\;, \tag{63}$$

while

$$H(\pi\xi_Z) \;=\; N(\pi\xi_Z)\exp(-\pi\xi_Z) \tag{64}$$

contains all such dependence in the amplitudes.

Thus, for IPA amplitudes we find

$$\varphi_{n\ell\ell_z} \;=\; H(\pi\xi_Z)\varphi^{(0)}_{n\ell\ell_z}(1+O(p^{-2}))\;, \tag{65}$$

while the amplitudes $\varphi^{(0)}_{n\ell\ell_z}$ describe photoionization with the terms of the order p^{-1} being neglected.

Now the IPA cross sections take the form

$$\sigma^I_{n\ell}(\omega) \;=\; \frac{a_{n\ell}D(\pi\xi_Z)}{\omega^{7/2+\ell}}\;\left(1+O(\omega^{-1})\right)\;. \tag{66}$$

Note that in contrast to Eq.(1) the next to leading terms are of the order $O(\omega^{-1})$ but not $O(\omega^{-1/2})$. In the hydrogenlike equations they are of the order $\xi_Z\tau/p$

We turn now to IPA breaking contributions, provided by the second term of the amplitude Eq.(21). As we saw earlier, the IPA amplitude ϕ_j, which contributes to amplitude of ionization of the state i, is determined by small distances of the order p^{-1} , and thus obtain the factor $H(\pi\hat{\xi}_Z)$. The matrix element $\Lambda^{(0)}$ describes the interactions on the distances of the order of the size of the atomic shell, and thus next to leading order corrections to $\Lambda^{(0)}$ are of the order p^{-2}.

Hence, for the amplitudes beyond IPA we have also

$$\Phi_{n\ell\ell_z} \;=\; H(\pi\xi_Z)\Phi^{(0)}_{n\ell\ell_z}(1+O(p^{-2}))\;, \tag{67}$$

while the amplitudes $\Phi^{(0)}_{n\ell\ell_z}$ describe photoionization with the terms of the order p^{-1} being neglected. Note, that for the analysis, and computations carried out by Avdonina *et al* (2002), as well as by Suric *et al* (2003) it was convenient to single out Stobbe factor depending on $\pi\xi_Z$, which does not contain all the dependence on this parameter.

And thus for the cross sections beyond the IPA for $\ell \geq 1$

$$\sigma_{n\ell}(\omega) \;=\; \frac{A_{n\ell} D(\pi\hat{\xi}_Z)}{\omega^{9/2}} \;\Big(1 + O(\omega^{-1})\Big) \tag{68}$$

and for $\ell = 0$

$$\sigma_{n0}(\omega) \;=\; \frac{A_{n0} D(\pi\hat{\xi}_Z)}{\omega^{7/2}} \;\Big(1 + O(\omega^{-1})\Big) \tag{69}$$

with $D(\pi\xi_Z)$ defined by Eq.(53). As well as in the IPA equation (66), the next to leading terms are of the order $O(\omega^{-1})$ but not $O(\omega^{-1/2})$. In the hydrogen-like equations they are of the order $\xi_Z\tau/p$. Due to the common factor $D(\pi\hat{\xi}_Z)$ Eqs.(37), (40)–(42) for the cross section ratios are true in much broader region of energies than Eqs.(35) and (38) for the cross sections. With the accuracy $\xi_Z\tau/p$ the parameter ξ_Z which values depend on the binding energy of the ionized state can be replaced by $\hat{\xi}_Z$, defined by Eq.(57), with the values common for all the bound states.

7 Ionization of L shell of neon

Let us see now, how this technique works for the description of ionization of L-shell of neon by the photon with the energy of 0.7–1 keV. This case is well studied experimentally by Dias *et al* (1997).

Here we analyze the case by using Hartree-Fock (HF) interaction as IPA approximation and by employing the equations describing the IPA breaking effects, obtained in the present paper. We use the results of our HF calculations and apply the general Eq.(53) for calculation of IPA breaking effects.

The analysis, carried out in the present paper enables to figure out the IPA breaking contributions to the ratio $R_{21}(\omega)$. Consider for example the point $\omega = 0.977\,\mathrm{keV}$ with the HF value of the ratio $R^I_{21} = 2.16$.

Since the condition expressed by Eq.(50) is not true for $1s$ electrons, they can be excluded immediately. We must include the couplings between $2s$ and $2p$ states only. The straightforward calculation provides $b_1 = -\sqrt{3}/2$. The HF value of the matrix element is $d_{21,20} = -0.95$

The terms, proportional to ξ in Eqs.(31) and (52) add -0.306 from the influence of $2s$ electrons on $2p$ electrons and -0.141 from the influence of $2p$ electrons on $2s$ electrons. The ξ^2 terms contribute -0.034. Summing these values the total shift caused by FSI IPA breaking effects is provided to be -0.481. Thus, the perturbative account of FSI IPA breaking effects leads to the value $R^{(0)}_{21} = 1.68$. The RPAE value is 1.82. With the realistic view on the accuracy we can say that the HF and RPAE values of the ratio are 2.2 and 1.8, while the perturbative approach provides the value 1.7. Calculations of the IPA breaking effects by the technique developed in this paper with HF IPA wave functions provide the results shown in Fig. 1. One can see the results to be close to those obtained in framework of RPAE. The splits between IPA and IPA breaking results obtained by the two methods differ by about 25%, reproducing the experimental data.

The calculated ratio $R_{21}(\omega)$ satisfies the asymptotic formula expressed by Eq.(40) with the accuracy of 10% for the photon energies between 0.7 and 1.0 keV. Thus, for illustrative purpose we can also use the asymptotical analysis. The ratio $R_{21}(\omega)$ is described by Eq.(40) with $r_2^I = 2.19\,\mathrm{keV}^{-1}$.

The contribution of $2s$ state on ionization of $2p$ state can be expressed by the parameter K defined by Eq. (41). Using Eq. (51) we find

$$K = 1 + \frac{2\sqrt{3}}{3} b_1 d_{2120} \left(r_2^I \cdot I_0\right)^{1/2} + (b_1 \cdot d_{21,20})^2 r_2^I \cdot I_0 + \delta K \ . \tag{70}$$

The four terms in the rhs correspond to the four terms in rhs of Eq.(42). Recall, that $I_0 = m\alpha^2/2 = 13.6\,\mathrm{eV}$. We find the numerical values 0.17 and 0.02 for the second and the third terms in rhs of Eq.(70). The last term presenting contribution of IPA breaking in initial state can be written, following Eq.(42) as

$$\delta K \ = \ 2\frac{\sqrt{3}}{2} \sum_k \mathrm{Re}\ G_k \left(\frac{d_{k1}}{d_{21}}\right)^{1/2} = \sum_k p_k + \int_0^\infty f(\varepsilon) d\varepsilon \tag{71}$$

with p_k standing for contribution of discrete spectrum states (recall that only states with $\ell = 1$ contribute). At $k \gg 1$ the excited states wave functions are hydrogenlike and one expects $p_k = C/k^3$. Our calculations show that such behavior becomes true, indeed at $k \geq 6$ with the accuracy of about 10%. This enables to obtain $f(0) = C/2$. One can estimate contribution of continuum, assuming that $f(\varepsilon)$ varies slowly at the energies of the order $I_p \approx 20\,\mathrm{eV}$, dropping fast at larger values. This provides the values $1.3 \cdot 10^{-2}$ and $4 \cdot 10^{-3}$ for the two terms in r.h.s. of Eq.(71).

Hence, the IPA breaking effects in the initial state contribute about 10% to the total difference $K - 1$. One could not predict this *a priori* since Eq.(14) gives $\kappa = 0.16$, and thus FSI and initial state IPA breaking effects could be expected to be of the same order. The much smaller magnitude can be understood as due to small value of ionization amplitude from the excited states.

Thus we come to the value $K = 1.17$, the difference $K - 1$ is determined mostly by IPA breaking in FSI.

While the influence of $2s$ channel on $2p$ changes the slope of the line, determined by Eq. (40), the influence of $2p$ channel on $2s$ channel shifts the line by the value of $c_2 = -0.16$ — see Eq.(53). Since the accuracy of the asymptotical analysis is about 10% in this case, we can neglect a small nonlinear contribution expressed by the last term of the rhs of Eq. (53). Thus, with the account of IPA breaking effects the cross section is described by Eq. (53) with

$$a \ = \ 1.87\ \mathrm{keV}^{-1}; \quad c_2 = \ -0.16\ ; \quad g_2 \ = \ 0\ . \tag{72}$$

8 Ionization of M shell of argon

Now we analyze ionization of M shell of argon in the same way, i.e. we calculate the ratio of ionization cross sections of $3s$ and $3p$ states the region of the photon energies 0.7–1.0 keV. The

experimental data is provided by Hansen *et al* (1999).

First we find out which of the couplings are important. Condition (50) excludes the influence of $1s$ electrons. Thus, we must investigate the couplings between M-shell electrons and the influence of L-shell.

The contributions, proportional to ξ come from sp couplings. The couplings between M electrons most important due to the large matrix element $d_{31,30} = -0.97$. The couplings between $2p$ and $3s$ and between $2s$ and $3p$ electrons are much smaller due to the small values of the matrix elements $d_{20,31} = 0.037$ and $d_{21,30} = 0.0032$. Thus, although the ionization cross sections of L electrons are about 10 times larger than the cross sections of M electrons, the couplings of M-shell electrons to the L-shell electrons yields only a small correction to the effects inside M-shell. However, this correction can be included. The other couplings provide much smaller values.

The correlations between the electrons with the same angular momenta contribute to the terms of the order ξ^2. They change the ratio R_{31} by about 0.2% and thus can be neglected.

Consider as an example the IPA breaking effects at $\omega = 1\,\mathrm{keV}$. The HF value of the cross-sections ratio $R^I_{31} = 0.78$ (Avdonina *et al* 2002) modified mostly by $3s3p$ coupling. The changes in the values of IPA cross sections of ionization of $3s$ and $3p$ states contribute -0.090 and -0.077 to the modification of the value of the ratio. As we noted at the end of Sec. V, the influence of p electrons on ionization of s electrons is stronger than the opposite one since $R^I_{31} < 1$. The perturbative account of IPA breaking effects yields thus $R^I_{31} = 0.61$, while the RPAE value is 0.58. Account of IPA breaking effects by pertrubative approach and in framework of IPA provides very close results — see Fig. 2.

One can see from Fig.2 that the HF results are about twice larger than the experimental ones. The account of IPA breaking effects diminishes the discrepancy between the theoretical and experimental results, making it about 3 times smaller, but does not eliminate it. As it was recently mentioned by Amusia (2000), the IPA breaking effects in the ground state may provide large contribution, quenching the ratio. Hence, there is hope, that account of both FSI and initial state IPA breaking effects will describe the data.

Our HF calculations show that this is not the asymptotical region for the cross-section ratio, i.e. the function $R_{31}(\omega)/\omega$ depends on ω. On the other hand, the RPAE results are much more alike to be the asymptotical ones. To understand this, note that deviations of HF results from the asymptotics are not large. The HF results can be approximated by inclusion of the lowest term beyond the asymptotics, i.e.

$$R^I_{31}(\omega) \;=\; a\omega + b \tag{73}$$

with $a = 0.65\,\mathrm{keV}^{-1}$, $b = 0.13$. As we saw in the end of Sec. V, the value of b is modified by the influence of ionization of $3s$ states by $3p$ states. Using Eq. (52) we find that the value of b changes to $b' = b + \delta b$ with $\delta b = -0.12$. Thus the IPA breaking effects diminish the value of b to large extent.

9 Summary

In this paper we presented our investigation of photoionization beyond IPA, started by a short report (Drukarev *et al* 1999), where we found, that the asymptotic behavior of the IPA cross sections is determined by Eq. (2) instead of IPA behavior given by Eq. (1). Thus, for $\ell \geq 2$ the form of the energy dependence changes. For $\ell = 1$ the form of the energy dependence does not change, but the value of the asymptotic coefficient does. The asymptotics does not change for $\ell = 0$,(Amusia *et al* 2000) It was obtained also, that the ratios of the cross sections, defined by Eq. (5) reach the asymptotics behavior at much smaller energies than the cross sections themselves. This is because the leading terms beyond the asymptotics form the factor, which is common for the cross sections of ionization of all the shells, thus canceling in the ratios determined by Eq.(5) (Avdonina *et al* 2002).

In the present paper we found the analytical expressions for the asymptotical coefficients of the photoionization cross sections beyond the IPA, by treating the final state correlations perturbatively, using the technique developed by Drukarev and Strikman (1986, 1987). They are given by Eqs. (37) and (39). These equations express the asymptotics through the matrix elements of relatively simple operators between the IPA wave functions. We show, that at $\ell \geq 2$ the IPA breaking effects in the final state determine the asymptotics, while for $\ell = 1$ the IPA breaking effects in the ground state should be included. The contribution of the latter is expressed through the complete set of IPA functions — Eq. (39).

We found the general expression for the ionization cross section of any state through the IPA cross sections in the lowest order of expansion in powers of ξ^2, defined by Eq. (6). This formula, presented by Eq.(49) is true for the photon energies exceeding strongly the value $I_0 = 13.6\,\mathrm{eV}$. In other words, the energy expressed in Rydbergs should exceed unity strongly.

We obtain also the quantitative criteria which enables to predict, which of the couplings are expected to be significant at the fixed value of the photon energy — Eq. (50). Additional selection is provided, of course, by the values of the matrix elements.

For the important special case of ionization of the atom with s- and p-electrons only, the asymptotics of the IPA ratio is described by Eq. (40). For this case we find a very explicit picture of manifestation of IPA breaking effects. They change the slope and shift the line described by Eq. (40). The change of the slope comes from the change in the value of the cross section of ionization of np state, while the change of the shift comes due to the change of cross section of the ionization of ns state — see Eqs. (51) and (52). The signs of the effects are shown to be correlated: the diminishing of the slope corresponds to the shift of the line below and vice versa.

We calculate also the common energy dependent factor, which is contained in the cross section of ionization of any state and contains the leading terms beyond the asymptotics. By using the results of asymptotic perturbation theory developed by Pratt and Tseng (1972) we show, that this factor, depending on parameter $\pi\xi_Z$ is caused by interactions of the outgoing electron with unscreened nucleus only and thus can be calculated by using the Coulomb wave function for the description of the outgoing electron. This enables us to present the analytical expression for this factor — Eqs. (63) and (64).

Our analysis is completely nonrelativistic, i.e. we neglected both relativistic kinematics and spin-orbit interactions. Thus, we limit ourselves to the values of the photon energies, which are much smaller than the electron rest energy (which is 511 keV). In the present form our approach also does not work for the internal electrons of the heavy atoms.

We apply our results for investigation of previously experimentally (Dias *et al* 1997, Hansen *et al* 1999) and theoretically (Avdonina *et al* 2002) studied cases of ionization of external electrons of Ne and Ar by the photons with the energies of about 1 keV. Note that the calculations have been carried out in the papers of Dias *et al* (1997) and Hansen *et al* (1999). However, the choise of IPA potentials was not clearified in these works. Thus, we can not compare our results with the results of these calculations. For the case of Ne we calculated IPA breaking effects both in the final and initial states by using Eqs. (51) and (52). The FSI determine about 90% of the total value. The splits between IPA and IPA breaking results obtained in frameworks of pertrubative approach and RPAE differ by less than 20%. Both results are consistent with the experimental data.

For the case of Ar the IPA breaking effects are mostly due to $3s - 3p$ coupling. The results of our perturbative calculations practically coincide with our RPAE results. By using the high energy formula we show how the account of IPA breaking effects diminishes the shift of the line determined by Eq. (73), i.e. how the account of IPA breaking effects brings us closer to the asymptotics. The influence of $3p$ electrons on the ionization of $3s$ state compensates to large extent the second (preasymptotic) term of rhs of Eq. (73). While the results of HF computations are about twice as large as the experimental values the IPA breaking effects in the final state diminish the discrepancy by about 60%. As it was reminded by Amusia (2000), there can be also strong IPA breaking interactions in initial $3s$ state of Ar (Amusia *et al* 1982). In the case of Ar our treatment of IPA breaking effects still diminishes strongly the discrepancy between the experimental and theoretical results.

Thus we conclude our approach to be a good tool for investigation of IPA breaking effects at the high energies.

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10 FIGURE CAPTIONS

Fig.1 — Ratio of the $2s$ to$2p$ ionization cross sections for Ne. The dots show the expetrimental points of Dias *et al* (1997). The dashed and dashed -dotted lines show our HF and RPAE results. The solid line shows our results with the perturbative treatment of IPA breaking effects.

Fig.2 — Ratio of the $3s$ to $3p$ ionization cross sections for Ar. The experimental points are those of Hansen *et al* (1999). The meaning of the three lines is the same as in Fig. 1.