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Partial cancellation of correlations in the nonrelativistic high-energy asymptotics of the photoeffect

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We investigate the total effect of correlations on photoionization of atomic states with nonzero orbital momentum in the nonrelativistic high-energy asymptotic limit, considering the exclusive case of the dominant final state of an initial neutral atom. We find that the substantial cancellation of the dominant intrashell correlations, which had been reported earlier, can be understood utilizing the closure properties satisfied by the eigenfunctions of the nonrelativistic Hamiltonian. Considering the sum of correlations with all states, occupied or not, we show that complete sum is equal to the contribution of the high-energy part of the continuum. Consequently there is a total cancellation between the contributions of the bound states (occupied and unoccupied) and the low-energy part of the continuum states. This means that the real correlations in the physical atom due to the sum rule over the occupied states can be also obtained as the negative of the sum of contributions of low-energy bound and continuum unoccupied states. We calculate this in the framework of the quantum-defect model. As we would expect, the results are close to those obtained earlier in particular cases by direct summation over the occupied states. However this approach also allows us to see that the sum of correlations over the occupied states is smaller than the dominant intrashell correlation. Hence, there is a partial cancellation between correlations with the occupied states. We can also obtain some limits on the correlation effects by considering calculations with the screened Coulomb functions. The role of correlations in the exclusive photoionization processes, also the modification of correlations in the case of atomic ions, is discussed.

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I. INTRODUCTION

For many years there was a general belief that, at photon energies far above the thresholds, the photoionization can be described in framework of the independent particle approximation (IPA). However, the experimental data for photoionization of p states of external shells of neon by photons of the energies of about 1 keV [1] could not be interpreted in the framework of IPA. Later the breakdown of IPA in the high-energy photoionization was found in experiments [2,3] and was also looked for in [4]. This was followed by a number of theoretical studies of the subject [1,4–9]. Thus during the last decade the IPA breaking effects were in line with such major items as nondipole effects in photoionization and electron correlations in double photoionization, see, e.g., [10].

In IPA the p electron is ionized by direct interaction with the photon. Dias *et al.* [1] suggested a mechanism of IPA breaking by the final-state electron interactions. The photon ionizes rather the s electron of the same subshell. In a next step the outgoing electron moves the p electron to fill the hole in the s state created by the photon. The final-state correlations have been studied later in [5–8], with the initial-state IPA breaking effects being included in [6], where they were shown to be small except some special cases. It was demonstrated for several cases that at still larger energies, much greater than all the binding energies of the atom, there is a large cancellation between correlations with various shells. Such cancellations were first found in the angular distributions of photoionization [5] and later at the amplitude level [8].

In this paper we study the effect of the final-state correlations on the amplitudes and cross sections of photoionization of atomic states with nonzero values of orbital momenta in the nonrelativistic high-energy asymptotic limit. We demonstrate that the tendency of the sum of such correlations to cancel, demonstrated in [5,8], for several particular cases is quite a general feature based on the propertied of the eigenfunctions of the nonrelativistic Hamiltonian. As it stands now, there is no experimental data on IPA breaking effects for this energy region. Our results are in agreement with previous theoretical results [5,8].

As a practical outcome of our analysis we can recommend an energy region, which is most appropriate for observation of the IPA breaking effects. The photon energies should not exceed strongly the binding energies in the K shell. Also, the correlations manifest themselves stronger in positive ions, where some of participants of cancellations are removed.

Calculations involving cancellations require very accurate wave functions since subtraction of close values is involved. That is why we try to demonstrate the cancellations in another way. We consider *asymptotic energies* of the outgoing electron,

$$E \gg I,$$

where I is the ionization energy of the single-particle ground state, and we seek to obtain the asymptotic amplitude. Thus we assume E to be much larger then all single-particle bound state energies. Our analysis is completely nonrelativistic, i.e., we assume $E \ll m$, with m as the electron mass (we employ the system of units with $\hbar = c = 1$). We consider only relatively light atoms, with not very large values of the nuclear charge Z, describing the bound electrons by nonrelativistic functions, with corrections of the order of $(\alpha Z)^2$ being neglected. We focus on the case of p electron photoionization.

Assuming that all initial electrons are moving in the same self-consistent field, we show that these cancellations can be understood, utilizing the closure properties satisfied by the eigenfunctions of the nonrelativistic Hamiltonian. Considering the sum of correlations with all states, occupied or not, we demonstrate that complete sum is equal to the contribution of the high-energy part of the continuum. Thus there is total cancellation between the contributions of the bound states (both occupied and unoccupied) and the low-energy part of the continuum states, for which we will give a precise definition. However, this sum contains the contribution of the unoccupied states. Hence the sum of the physical correlations, which includes only the correlations with the occupied states, can be expressed as the negative of the sum over low-energy unoccupied states.

We perform some explicit calculations for real atoms by calculating the contribution of low-energy unoccupied states, using the quantum-defect model combined with the Fermi-Segre theorem and making a rough estimate of the contribution of the low-energy part of the continuum. In our approach all such terms are positive. Our results are close to those obtained by direct summation over the occupied shells.

These direct terms occur with both signs, in the cases where such summations were carried out [5,8]. Hence, there is a partial cancellation between the correlations with the occupied states in a real atom.

For example, in ionization of the $2p$ electrons in neon the correlations with $1s$ electrons are -1.11 times correlations with the $2s$ electrons [5,8], with the sum being -0.11 times of the latter. In our approach the small number -0.11 is obtained as a sum of two terms of the same sign $-(0.04+0.07)$ coming from discrete and continuum states. For ionization of $3p$ states in argon correlations with $1s$ and $2s$ states make -1.12 and -0.03 of correlations with $2s$ state correspondingly. Thus "shell by shell" summation of correlations provides $1-1.12-0.03=-0.15$ times correlation with the $3s$ electrons. In our approach this will be again a sum of two numbers with the same signs, i.e., $-(0.05+0.10)=-0.15$.

We have carried out direct calculations also for the Coulomb case, and we find certain limits on the correlation effects in this case. Using perturbative treatment of the screening we show that the magnitude of cancellations in the real atom is greater.

In our analysis we have used the perturbative approach to the final-state interactions of the electrons developed in [11]. This approach was employed earlier for investigation of the IPA breaking in photoionization [6]. Inclusion of these effects removed or strongly diminished the discrepancy between experimental data and the IPA calculations. We shall use the expressions obtained in [6] throughout the paper.

In particular calculations we use the simplifying assumption that the overlap matrix elements between the orbitals of different subshells in the initial-state atom and the final-state ion are small and can be neglected. In this approximation the spectator electrons (i.e., those that do not interact with the photon directly) do not change their states, and the inclusive cross section (i.e., summed over the final states of the spectator electrons) coincides with a particular case of the exclusive one (by exclusive process we mean the one with a fixed final state of the spectator electrons) in which the state of the spectator electrons does not change. The latter cross sections correspond to the experiments [1,12]. We show that the correlations considered in the paper can also manifest themselves stronger in exclusive processes of photoionization accompanied by excitation of external electrons. In the case of atomic ions there will be less cancellation among the correlations.

The paper is organized as follows. In Sec. II we recall the main equations for the perturbative treatment of the IPA breaking effects in photoionization. In Sec. III we write the sum rules provided by closure and show that they have the consequence that there is total cancellation between the sum over all bound states (occupied and unoccupied) and the low-energy continuum states. In Sec. IV we obtain the correlations of the occupied states, both directly (from previous work [8]), and as the negative of the sum over unoccupied low-energy states. In Sec. V we make explicit calculations using some simplified models. We show the results of these approaches in Table II, including also the cases of large Z for illustrative purpose. For the direct calculations we investigate the Coulomb case in Sec. VI, with the results given in Table III, and give some discussion of screening in an effective charge approach. In Sec. VII we consider the role of correlation in exclusive processes and for atomic ions. We summarize in Sec. VIII. Some details of computations are presented in Appendixes A and C.

II. PERTURBATIVE TREATMENT OF IPA BREAKING EFFECTS

We recall the general points of our perturbative approach [11], restricting ourselves here to asymptotic analysis. We shall use a simplifying assumption that the bound electrons are described by single-particle wave functions. This is not a necessary assumption, and the approach has been employed for the case of correlated functions as well [13,14]. Consider the asymptotic amplitudes F_i for ionization of initial state i with quantum numbers $i=n,\ell,\ell_z$. The final-state interactions between the outgoing electron and the residual ion in their lowest order in the amplitude beyond the IPA can be expressed in terms of a linear combination of the IPA asymptotic amplitudes F_j^0 for ionization of all the other occupied atomic states j:

$$F_i = F_i^0 + \sum_j F_j^0 \Lambda_{j,i}, \tag{1}$$

with $\Lambda_{j,i}$ as the matrix element for a transition from the state i to the state $j=n',\ell',\ell'_z$ caused by the outgoing electron following photoionization of the state j. In the asymptotics $F_j^0 \sim \omega^{-(3+\ell')/2}$ [15,16], and thus only correlations with $n's$ states contribute to asymptotics of the amplitude F_i. Hence we must include only

$$F_j^0=\langle\psi_f^0|\hat{\gamma}|\psi_j\rangle=\frac{(4\pi)^{1/2}}{m}\frac{\tau(\boldsymbol{e}\cdot\boldsymbol{P})}{P^4}N^r_{n's},\quad j=n',0,0, \tag{2}$$

with ψ_f^0 as the plane-wave approximation for the wave function of the outgoing ejected electron, $N^r_{n's}$ as the normalization factor of the radial function of the $n's$ electron $\psi_{n's}(\boldsymbol{r})=\psi^r_{n's}(r)/\sqrt{4\pi}$; $N^r_{n's}=\psi^r_{n's}(0)$, $\tau=m\alpha Z$, and $\hat{\gamma}=-i(\boldsymbol{e}\cdot\boldsymbol{\nabla})/m$ is the interaction operator between the photon with polarization vector $\boldsymbol{e}$ and the electron.

The plane-wave approximation

$$\psi_f^{(0)}(\boldsymbol{r})=\exp[i(\boldsymbol{P}\cdot\boldsymbol{r})] \tag{3}$$

with momentum of the outgoing electron $P\gg\tau$ is appropriate for Eq. (2) in velocity form. This corresponds to normalization of the continuum wave functions by the condition [17]

$$\int d^3r\psi^*_{\boldsymbol{P}}(\boldsymbol{r})\psi_{\boldsymbol{P}'}(\boldsymbol{r})=(2\pi)^3\delta(\boldsymbol{P}-\boldsymbol{P}').$$

The amplitude F_j^0 is evaluated in Appendix A.

If the photon energy well exceeds the binding energies of the bound states i and j, the matrix elements $\Lambda_{j,i}$ can be represented as

$$\Lambda_{j,i}=i\xi S_{j,i}, \tag{4}$$

with $\xi=m\alpha/P$ (P as the momentum of the outgoing electron) as the Sommerfeld parameter of the final-state interaction of the outgoing electron with the residual ion. The matrix elements

$$S_{ji}=\langle j|\ln(r-z)|i\rangle \tag{5}$$

(with z as the projection of the coordinate vector $\boldsymbol{r}$ on the direction of the momentum of the outgoing electron) obtained in [11] describe the transfer of an electron from the states i to fill the hole in the state j of the positive ion with the hole in i state. The operator $\ln(r-z)$ comes from integration over the distances between the photoelectron and the bound i electron. One can write $\ln(r-z)=\ln r+\ln(1-t)$, with $t=(\boldsymbol{P}\cdot\boldsymbol{r})/Pr$ and $\boldsymbol{P}$ as the momentum of the outgoing electron. For states i and j with different angular momenta the matrix element [Eq. (5)] with $\ln r$ vanishes due to orthogonality of the angular parts of the wave functions of the states i and j. Thus when the states i and j have different angular momenta we can write

$$S_{j,i}=\langle j|\ln(1-t)|i\rangle. \tag{6}$$

Only such states contribute to the asymptotic amplitude when i is not a s state (which we will assume) since the dominant asymptotic amplitudes F_j^0 require j to be a s state. Thus, we shall consider only the states j with quantum numbers $\ell=\ell_z=0$, i.e., $j=n',0,0$. Taking the direction of the outgoing electron momentum as the axis of quantization of angular momentum, we find that correlations occur only for i states with $\ell_z=0$ since only these states are coupled by Eq. (6).

We may therefore write

$$F_i=F_i^0+i\xi\Sigma_jA_{j,i}, \tag{7}$$

where

$$A_{j,i}=F_j^0S_{ji}, \tag{8}$$

with $S_{j,i}$ given by Eq. (6) as the photon energies, well exceeding the binding energies of i and j states (being suppressed otherwise [1,11]). For example, as shown in [1], in ionization of the $2p$ electrons of neon by photons with energies of about 1 keV correlations with $2s$ electrons are important, while those with $1s$ electrons are not but by 10 keV correlations with $1s$ electrons become important. We will write $A_{j,i}$ as A_j omitting the index i.

Note that we did not use the partial wave expansion. Since F_i^0 are the asymptotics of the IPA amplitudes, they should be considered in the dipole approximation since the higher angular momenta terms drop faster with the increasing photon energy. However, for example, amplitude F^0_{np} for ionizations of np state actually contains the contributions, corresponding to s and d waves of the photoelectron.

Now we restrict ourselves to the case of ionization of p states only, i.e., we consider the case $i=n,1,0$. We use the standard spectroscopic notation, e.g., the state with quantum numbers $n,0,0$ is a ns state. Then Eq. (6) can be evaluated as

$$S_{ji}=-\frac{\sqrt{3}}{2}\langle\phi^r_{n's}|\psi^r_{np}\rangle, \tag{9}$$

with the first factor coming from the angular integration, ψ^r_{np} and $\phi^r_{n's}$ are, respectively, the radial wave functions in the field of the atom and of the ion with the hole in np state, and

$$\langle\phi^r_{n's}|\psi^r_{np}\rangle=\int drr^2\phi^r_{n's}(r)\psi^r_{np}(r).$$

Note that since all the other electrons in initial and final states belong to different Hamiltonians, there are nonzero overlap integrals between orbitals of different subshells. This makes the whole picture more complicated, see [18]. For example, in our case there are other channels for ionization of $2p$ state. In one of them the photon interacts directly with $2s$ electron, while the $1s$ electron suffers shakeup into the hole in the $2s$ state of the ion. The photoelectron pushes the $2p$ electron into $1s$ hole of the final-state ion at the end of the story. The contribution of this channel to the total amplitude of ionization from the $2p$ state is thus $F^0_{2s}\Lambda_{1s,2p}\langle\phi^r_{2s}|\psi^r_{1s}\rangle$. If $|\langle\phi^r_{2s}|\psi^r_{1s}\rangle|\ll1$ we can neglect this contribution with respect to the other terms on the right-hand side (rhs) of Eq. (1).

We shall consider this very case, thus assuming that $|\langle\phi^r_{n's}|\psi^r_{ns}\rangle|\ll1$ for all $n\neq n'$. Hence we find $1-|\langle\phi^r_{ns}|\psi^r_{ns}\rangle|^2\ll1$ for all n, and the inclusive cross section with the sum over all possible states of the final ion coincides with the exclusive cross section in which the spectator electrons do not suffer transitions. In this approximation we must replace Eq. (9) by

$$S_{ji}=-\frac{\sqrt{3}}{2}\langle\psi^r_{n's}|\psi^r_{np}\rangle. \tag{10}$$

Hence,

$$A_{n's}=-\frac{\sqrt{3}}{2}F^0_{n's}\langle\psi^r_{n's}|\psi^r_{np}\rangle. \tag{11}$$

Recall that $F^0_{n's}$ the asymptotic IPA amplitude for ionization of a $n's$ bound state. We shall omit the upper index IPA further. For correlations inside the same shell

$$A_{ns} = -\frac{\sqrt{3}}{2} F^0_{ns} \langle \psi^r_{ns} | \psi^r_{np} \rangle .$$

For ionization of $2p$ states, i.e., $n=2$,

$$\langle \psi^r_{2s} | \psi^r_{2p} \rangle \approx -1 \tag{12}$$

for all atoms. This matrix element calculated with Hartree-Fock wave functions is -0.91 for $Z=5$ with the value becoming closer to -1 for larger Z. The Coulomb value is $-\sqrt{3}/2$. Thus we can estimate that

$$A_{2s} = \frac{\sqrt{3}}{2} F^0_{2s} . \tag{13}$$

For photon energies well exceeding the bounding energy of L shell but not of the K shell, the correlation with the $2s$ electron dominates. Correlations with $1s$ electrons are small at these energies [1,6]. Correlations with other s electrons, if there are any, are small. This happens for two reasons. The overlap matrix elements $|\langle \psi^r_{n's} | \psi^r_{2p} \rangle| \ll |\langle \psi^r_{2s} | \psi^r_{2p} \rangle|$ for $n' \neq 2$ due to Eq. (12) and to the closure relation $\Sigma_{xs} |\langle \psi^r_{xs} | \psi^r_{2p} \rangle|^2 = 1$ (with summation over the states of both discrete and continuum spectra). Also the asymptotic IPA amplitudes $F^0_{n's}$ drop with n'. Hence at such energies the value [Eq. (13)] determines the scale of IPA breaking effects.

However, at larger energies, greatly exceeding the binding energy of the $1s$ electrons, A_{1s} becomes comparable to A_{2s}, and there is a large cancellation between contributions of the K shell and the other shells. Such cancellations were first found in the angular distributions of photoionization [5] and then observed at the amplitude level [8]. The calculations require knowledge of rather precise wave functions for the description of the bound electrons.

For photon energies much greater than all the binding energies the asymptotic contribution of correlations to the amplitude is

$$\tilde{T}_d = \Sigma_{\tilde{j}} A_{\tilde{j}} = \Sigma_{\tilde{n}s} A_{\tilde{n}s} , \tag{14}$$

with the sum over all occupied $\tilde{n}s$ states, where $A_{\tilde{n}s}$ is given by Eq. (11) for all occupied states $\tilde{j}$ and A_j is given by Eq. (8), namely,

$$A_{\tilde{j}} = \langle \psi^0_f | \hat{\gamma} | \psi_{\tilde{j}} \rangle \langle \phi_{\tilde{j}} | \ln r(1-t) | \psi_i \rangle \approx \langle \psi^0_f | \hat{\gamma} | \psi_{\tilde{j}} \rangle \langle \psi_{\tilde{j}} | \ln r(1-t) | \psi_i \rangle . \tag{15}$$

There are only two active electrons in our analysis, while the others are just ignored. This corresponds to calculation of the amplitude for an inclusive process since the sum over all possible final states Φ_f of the spectator electrons in the final-state ion described in the initial-state atom by the function Ψ,

$$\sum_f \langle \Phi_f | \Psi \rangle^2 = 1 .$$

III. CLOSURE CONDITION AND SUM RULES

Using closure we can write simple relations for amplitudes such as $\tilde{T}_d$ in Eq. (14), but now summed over various states j. We will do it in a $3d$ formalism. We will sketch these relations here and complete their proof subsequently. The closure condition for the wave functions of the initial-state nonrelativistic Hamiltonian can be written as

$$\sum_j |\psi_j\rangle\langle\psi_j| = 1 = \sum_{\tilde{j}} |\psi_{\tilde{j}}\rangle\langle\psi_{\tilde{j}}| + \sum_{j^*} |\psi_{j^*}\rangle\langle\psi_{j^*}| + \sum_{j_c} |\psi_{j_c}\rangle\langle\psi_{j_c}| , \tag{16}$$

with $\tilde{j}$ and j^* labeling the occupied and unoccupied states of discrete spectrum correspondingly, while j_c are suitably normalized continuum states. The closure condition can be represented as

$$\int \frac{d^3Q}{(2\pi)^3} \psi^*_Q(\boldsymbol{r}) \psi_Q(\boldsymbol{r}') + \sum_{n',\ell',m'} \psi^*_{n',\ell',m'}(\boldsymbol{r}) \psi_{n',\ell',m'}(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') ,$$

for Ψ_Q which are asymptotically plane waves as in Eq. (3). For any state j, occupied or not, we can write, generalizing Eq. (15),

$$\langle \psi^0_f | \hat{\gamma} | \psi_j \rangle = \frac{(\boldsymbol{e} \cdot \boldsymbol{P})}{m} \langle \psi^0_f | \psi_j \rangle , \tag{17}$$

$$A_j = \frac{(\boldsymbol{e} \cdot \boldsymbol{P})}{m} \langle \psi^0_f | \psi_j \rangle \langle \psi_j | \ln r(1-t) | \psi_i \rangle .$$

We may write using Eq. (16)

$$T = T_d + T_c , \tag{18}$$

with

$$T \equiv \Sigma_j A_j = \langle \psi^0_f | \hat{\gamma} \ln r(1-t) | \psi_i \rangle = \frac{(\boldsymbol{e} \cdot \boldsymbol{P})}{m} \langle \psi^0_f | \ln r(1-t) | \psi_i \rangle \tag{19}$$

as the sum over the complete set of states j, T_d is the sum over occupied and unoccupied states j of the discrete spectrum, while T_c is the sum over the continuum states.

We may now separate the continuum amplitude T_c for which the continuum states j_c may be labeled by asymptotic momentum Q, in two parts

$$T_c = T_{c1} + T_{c2} . \tag{20}$$

Here, T_{c1} will sum states for which $q \ll P$ and T_{c2} states with $Q \sim P$. More precisely, we pick a Q_0 for which $p \gg Q_0 \gg \tau_c$, with τ_c as the characteristic momentum of the bound state (one can assume $\tau_c \approx m\alpha Z$), and define T_{c1} as the sum over states $Q < Q_0$ and T_{c2} as the sum over $Q > Q_0$.

We may show (see Appendix B) that for states in T_{c2} the wave function ψ_Q may be replaced by a plane wave: $\psi^0_Q = \exp[i(\boldsymbol{Q} \cdot \boldsymbol{r})]$. We may also show (see Sec. IV) that the sum over plane-wave states $\Sigma_{Q>Q_0} |\psi^0_Q\rangle\langle\psi^0_Q|$ in T_{c2} may be extended to a sum over all plane-wave states Σ_Q, that is, the sum over plane-wave states, $Q<Q_0$ makes no contribution in T_{c2}. But $\Sigma_Q|\psi_Q^0\rangle\langle\psi_Q^0|$ over plane-wave states is a sum over a complete set of states (=1), and therefore for T_{c2} one again obtains Eq. (19), i.e., in the asymptotics

$$T=T_{c2}. \tag{21}$$

In Appendix C we show that the amplitude T_{c2} has the same asymptotics as T_d. Hence, presenting

$$T_d=\tilde{T}_d+T_d^*, \tag{22}$$

with $\tilde{T}_d$ and T_d^* as the sums over occupied and unoccupied states of the discrete spectrum correspondingly, we can write

$$0=\tilde{T}_d+T_d^*+T_{c1};\quad \tilde{T}_d=-T_d^*-T_{c1}. \tag{23}$$

This gives an alternative way to calculate $\tilde{T}_d$ which, as we shall see, has some advantages. [In fact all these are asymptotic amplitudes, and so for Eq. (23) to follow from Eq. (21) we must show that these are all amplitudes of the same order. We shall do this in Sec. IV.] In Sec. IV we shall make explicit calculations of the amplitudes, determining $\tilde{T}_d$ from T_d^* and T_{c1}, as well as further discussing its direct calculations in Sec. V.

IV. FORMALISM FOR PARTICULAR AMPLITUDES

In $3d$ formalism all of the particular amplitudes of the previous section are of the form of Eq. (14), except that the summation $\Sigma_{\tilde{j}}$ in $\tilde{T}_d$ is replaced by summation Σ_{j^*} in T_d^* for unoccupied bound states and by integration $\int\frac{d^3Q}{(2\pi)^3}$ in T_c for continuum states with $Q<Q_0$ and $Q>Q_0$ for T_{c1} and T_{c2} correspondingly. Also, T, corresponding to summing over the complete set of states, was given explicitly in Eq. (19).

We can also represent the amplitudes in terms of radial functions. Using Eqs. (2) and (10) we can write

$$T_d=-\frac{2\sqrt{3}\pi^{1/2}\tau}{m}\frac{(\boldsymbol{e}\cdot\boldsymbol{P})}{P^4}\sum_{n'}N_{n's}^r\langle\psi_{n's}^r|\psi_{np}^r\rangle \tag{24}$$

and correspondingly for partitions $\tilde{T}_d$ and T_d^* summing over occupied or unoccupied bound states $n's$.

Continuum radial wave functions for s states (as well as those for a nonzero value of ℓ) are normalized by condition

$$\int dr\,\psi_{\varepsilon,s}^{r*}(r)\psi_{\varepsilon',s}^r(r)=\delta(\varepsilon-\varepsilon'),$$

with $\psi_{\varepsilon',s}^r(r)=\psi_{P,s}^r(r)/(2\pi P)^{1/2}$, $\psi_{\boldsymbol{P}}^r(\boldsymbol{r})=\psi_{P,s}^r(r)/2P+$terms with nonzero values of ℓ. The closure relation is

$$\int d\varepsilon\,\psi_{\varepsilon,s}^{r*}(r)\psi_{\varepsilon,s}^r(r')+\sum_{n',s}\psi_{n',s}^{r*}(r)\psi_{n',s}(r')=\delta(r-r').$$

Thus the calculation of T_{c1} proceeds in the same way again (see Appendix A) and yields Eq. (24), except that for the radial functions we write $\int_0^\infty d\varepsilon$ instead of $\Sigma_{n'}$ and replace $N_{n's}^r$ by $N_{\varepsilon s}^r$. (The integration over energies has been extended to infinity, with the energies exceeding strongly the binding energy of the ionized state, including those for which $\varepsilon>Q_0^2/2m$, providing a negligible contribution.)

For T_{c2}, where $Q>Q_0$, we may argue (Appendix B) that in F_Q^0, corresponding to Eq. (2), ψ_Q^0 is to be replaced by a plane wave. Thus $F_Q^0=\frac{(\boldsymbol{e}\cdot\boldsymbol{P})}{m}\delta(\boldsymbol{P}-\boldsymbol{Q})$. Hence, with plane wave for ψ_Q we may extend the integration over Q to include $Q<Q_0\ll P$, since there is no contribution from this region. On the other hand, we can evaluate explicitly (see Appendix C)

$$T_{c2}=\frac{(\boldsymbol{e}\cdot\boldsymbol{P})}{m}\frac{6\sqrt{3}\pi N_{np}^r\tau}{P^4}. \tag{25}$$

As we have already seen, $T=T_{c2}$. Note that we have also now shown that all these terms are of the same asymptotic order, which we had needed to prove Eq. (23).

Note that we can write Eq. (23) in the form

$$\sum_{n'}F_{n's}^{(0)}S_{n's,np}+\int\frac{d^3Q}{(2\pi)^3}F_Q^{(0)}S_{Q,np}=0, \tag{26}$$

with $S_{j,i}$ defined by Eq. (5), $F_{n's}^{(0)}$ are the high-energy IPA photoionization amplitudes [19] while $F_Q^{(0)}$ is the bremsstrahlung amplitude in the tip region [20]. Following the previous analysis, the integral in the second term involves all values of Q. However it is determined by $Q\sim\tau=m\alpha Z$.

We can now write expand the radial function $\psi_{np}^r(r)$ in terms of the functions $\psi_{xs}^r(r)(x=n',\varepsilon)$:

$$\psi_{np}^r(r)=\sum\psi_{n's}^r(r)a_{n's,np}+\int_0^\infty d\varepsilon\,\psi_{\varepsilon s}^r(r)a_{\varepsilon s,np}, \tag{27}$$

with

$$a_{n's,np}=\langle\psi_{n's}^r|\psi_{np}^r\rangle,\quad a_{\varepsilon s,np}=\langle\psi_{n's}^r|\psi_{np}^r\rangle, \tag{28}$$

while the closure can be written as

$$\sum_{n'}a_{n's,np}^2+\int_0^\infty d\varepsilon\,a_{\varepsilon ns,np}^2=1. \tag{29}$$

[Note that $a_{xs,np}=-2/\sqrt{3}S_{xs,np}$, with $S_{xs,np}$ given by Eqs. (6) and (9)]. Note that integrals on the rhs of Eqs. (27) and (29) are determined by energies of the order of the np electron binding energy.

The ratio of correlations of the np state with $n's$ and εs to correlation with the ns state may be described by the factors

$$x_{n's,np}=\frac{N_{n's}^r a_{n's,np}}{N_{ns}^r a_{ns,np}},\quad x_{\varepsilon s,np}=\frac{N_{\varepsilon s}^r a_{\varepsilon,n}}{N_{ns}^r a_{n,n}}. \tag{30}$$

We can write Eq. (23) in the form

$$\sum_{n'}x_{n's,np}+\int_0^\infty d\varepsilon\,x_{\varepsilon s,np}=0. \tag{31}$$

The value

$$x_{ph}=\sum_{\tilde{n}}x_{\tilde{n}s,np}, \tag{32}$$

with $\tilde{n}$ as the occupied states measures the total amount of correlation relative to the intrashell ns,np correlation. It will be the subject of our calculations in the next section.

V. CALCULATION OF THE PHYSICAL VALUE x_{ph}

Using Eq. (30) for $x_{n's,np}$ one can see that there is a tendency of cancellation of correlation effects for the $2p$ electrons. Employing Eqs. (12) and using Eq. (39) we find $|a_{n's2p}| \ll 1$ for $n' \neq 2$. Since the normalization factors $N^r_{n's}$ drop when n' increases, the contribution of these states to the rhs of Eq. (32) can be neglected for $n' > 2$. The case of $n' = 1$ requires additional analysis since $N_{1s} > N_{2s}$. One can see that the contributions of $n' = 1$ and $n' = 2$ to x_{ph} have different signs; from Eq. (12) $a_{2s,2p} < 0$, while $a_{1s,2p} > 0$ since the function ψ^r_{1s} has no nodes, while the function ψ^r_{2p} is nonnegative. Hence, there is a partial cancellation between the terms corresponding to correlations with the $1s$ and $2s$ states, i.e., the sum of these correlations is smaller than each of them taken separately.

Now we try to calculate x_{ph} in another way, i.e., as the negative of the sum of contributions of low-energy unoccupied states, bound (x_d) and continuum (x_c):

$$x_{ph} = \sum_{\tilde n} x_{\tilde n,n} = -x_d - x_c, \quad x_d = \sum_{n^*} x_{n^*s,np}, \quad x_c = \int d\varepsilon x_{\varepsilon s,np}, \tag{33}$$

with n^* labeling the unoccupied states of the discrete spectrum.

A. Discrete states

It is known that for $n' \gg n$ the dominant region of coordinate space in the integral $\langle \psi^r_{n's} | \psi^r_{np} \rangle$ is determined by the characteristic size of the np state. These values of r are much smaller than the characteristic size of the $n's$ state. The dependence on the energy of the n'th state in the Schrödinger equation for $\psi^r_{n's}$ can be dropped [15], and the only n' dependence of this matrix element is contained in the normalization factors $N_{n's}$. Thus, from Eq. (30), the ratio

$$x_{n's,np} = \frac{N^2_{n's}}{N^2_{ns}}. \tag{34}$$

To estimate $N^2_{n^*s}$ for the unoccupied states with principal quantum numbers n^*, we use the quantum-defect approach, in which the binding energy $E_{n'}$ of the $n's$ state is

$$E_{n'} = -\frac{\nu}{2(n' - \Delta_{n'})^2}, \tag{35}$$

with $\nu = m\alpha^2$ and

$$\Delta_{n'} \to \Delta \quad \text{as} \quad n' \to \infty. \tag{36}$$

Here the quantum defect Δ does not depend on n'.

Combining Eq. (35) with the Fermi-Segre formula [21],

$$N^2_{n's} = 4Z\frac{dE_{n'}}{dn'}, \tag{37}$$

we obtain

$$x_{n's,np} = \left(\frac{n - \Delta_n}{n' - \Delta_{n'}}\right)^3 \kappa_{n',n}, \tag{38}$$

with

$$\kappa_{n',n} = \frac{1 - \Delta'_{n'}}{1 - \Delta'_n}. \tag{39}$$

We neglect the derivatives $\Delta'_{n'}$, as justified below. Applying Eq. (39) to the highest occupied state $\tilde n_h$ of known binding energy, we find its quantum defect Δ_h. Alternatively, for the lowest unoccupied level of s electrons, $n^* = \tilde n_h + 1$, we identify the quantum defect Δ_n with the limiting value Δ, defined by Eq. (36). The latter can be extracted from the results of [22], on the phase shifts with respect to Coulomb values $\delta(E)$ since $\Delta = \delta(0)/\pi$. The values of Δ_h, calculated by using the normalization factors $N^2_{n's}$ given in [23], and Δ, are shown in Table I. We will assume that Δ_n for all unoccupied states is independent of n, $\Delta_n = \Delta$. The comparison of Δ_h and Δ indicates the type of error that is being made. Relatively small value of the difference $\Delta_h - \Delta$ justifies neglect of the derivatives $\Delta'_{n'}$.

The contribution of unoccupied discrete levels can be written as

$$x_d = \sum_{n_h+1} x_{n^*s,np}, \tag{40}$$

with n_h as the principal quantum number of the highest occupied state. The summation over unoccupied states in Eq. (40) can be carried out by using the formula [24]

$$\sum_{\tilde n_h+1}^{\infty} \frac{1}{(k+a)^3} = -\frac{1}{2}\psi''(a) - \sum_{0}^{\tilde n_h} \frac{1}{(k+a)^3}, \tag{41}$$

with $\psi(a) = \Gamma'(a)/\Gamma(a)$, where $\Gamma(a)$ is the Euler gamma function and $\tilde n_h + 1$ is the principle quantum number of the lowest unoccupied state.

B. Continuum states

Equations (35) and (37) reflect the Coulomb-like behavior of the excited states of the discrete spectrum at $n' \to \infty$. Thus for the continuum states with $\varepsilon = 0$ we can write

$$x_{0s,np} = \frac{1}{2I_0} \lim_{n' \to \infty} (n'^3 x_{n's,np}), \tag{42}$$

with $I_0 = m\alpha^2/2 = 13.6$ eV, or

$$x_{0s,np} = \frac{4ZI_0}{N^2_{ns}}. \tag{43}$$

Since the only characteristic energy is the binding energy $E_{np} < 0$ of the ionized state, we may suppose that the integral in the last equality of Eq. (33) is determined by $\varepsilon \sim |E_{np}|$. If we suppose that $x_{\varepsilon s,np} = x_{0s,np}$ for $\varepsilon < |E_{np}|$ $x_{\varepsilon s,np} = 0$ for $\varepsilon > |E_{np}|$ we find

TABLE I. The quantum defects of the highest occupied bound states Δ_h and the asymptotic values Δ as defined by Eq. (36) obtained from [22]; Z is the nuclear charge.

Z	Δ_h	Δ
5	0.96	0.76
7	1.23	0.95
10	1.44	1.27
14	2.00	1.69
18	2.31	2.04
32	3.04	2.74
36	3.28	3.06
50	3.96	3.37

$$x_c \approx \frac{4ZI_0|E_{np}|}{N_{ns}^2}. \tag{44}$$

This is clearly a fairly crude estimate, but we will see that it is consistent with results from direct calculations of x_{ph}.

C. Results for x_{ph}

Note that in the quantum-defect approach $x_d > 0$. Assumption (44) provides also $x_c > 0$. Hence the values x_{ph} are negative. This means that the total correlation effect in the amplitude has a sign, which is opposite to that of correlation inside the same shell. Employing Eqs. (40), (41), and (44) we find the values of x_{ph} shown in Table II.

Our results are in good agreement with the results x^{dir} obtained by direct summation of the correlations with occupied shells in the photoionization amplitude [8]. Results of [8] obtained by inclusion of correlations with 2*s* and 1*s* shells in nitrogen and neon are $x_{ph}=-0.18$ and $x_{ph}=-0.11$, respectively. Since the results of [8] are in good agreement with those of [6] for angular distributions, our results agree with those of [6] as well. For ionization of the 3*p* state in argon, shell by shell calculation [8] gives $x_{ph}=-0.14$, also in agreement with the result of the present work.

Now we estimate the total contribution of correlations to the amplitudes and cross sections of photoionization of *p* states. We use the estimate $\langle \psi_{np} | \psi_{ns} \rangle \approx -1$ for all n [see Eq. (12)]. Presenting the ratio of IPA amplitudes in terms of normalization factors $F_{n,0,0}/F_{n,1,0}=N_s^r/\sqrt{3}N_p^r$, we find

$$F_{n,1,0} = F^0_{n,1,0}\left(1+\frac{N^r_{ns}}{2N^r_{np}}x_{ph}\right), \tag{45}$$

and thus the cross section for ionization of *np* state beyond IPA is

$$\sigma_{np} = \sigma^0_{np}\left(1+\frac{N^r_{ns}}{3N^r_{np}}x_{ph}\right), \tag{46}$$

with σ^0_{np} standing for the IPA values.

Using the numerical values of the normalization factors [23] we find that the total correlations diminish the values of cross sections of photoionization of 2*p* states in nitrogen and neon only by about 2.5%. In contrast, inclusion of correlations only with the 2*s* shell would increase the cross sections by 18% and 22% correspondingly. The full cross section for ionization of 3*p* states in argon becomes smaller by 1.8%, while it becomes larger by 12% if only correlation with the 3*s* shell is considered.

TABLE II. The values of x_d, x_c and x_{ph} as defined by Eq. (33), where n is the principal quantum number of the ionized *np* state and Z stands for nuclear charge. The values x^{dir} presented in the last column are the results of direct summation over occupied states [Eq. (32)].

Z	n	x_d	x_c	x_{ph}	x^{dir}
5	2	0.08	0.12	−0.20	
7	2	0.05	0.09	−0.14	−0.18
10	2	0.04	0.07	−0.11	−0.11
14	2	0.06	0.16	−0.22	
14	3	0.08	0.12	−0.20	
18	2	0.06	0.20	−0.26	
18	3	0.05	0.10	−0.15	−0.14
32	3	0.01	0.18	−0.19	
32	4	0.13	0.11	−0.24	
36	3	0.01	0.19	−0.20	
36	4	0.08	0.11	−0.19	
50	5	0.06	0.13	−0.19	

VI. CALCULATION FOR HYDROGENLIKE FUNCTIONS AND LIMITATIONS FOR THE MANY-ELECTRON ATOMS

We can also make explicit calculations of correlations in the case of Coulomb wave functions and also in using an effective charge approximation for screening. All results for Coulomb functions can be obtained analytically. The results for $x_{n's,np}$ do not depend on the values of nuclear charge Z.

Starting with ionization of 2*p* electrons we obtain the values of the parameters that are presented in Table III (upper indices C indicate that the quantities are calculated in the Coulomb field of the nucleus).

One can see that in this case the correlation with the 1*s* state is about 50% larger than that with the 2*s* state. For the contribution of the continuum with $\varepsilon \ll E$ one can obtain by direct calculation

$$x_{\varepsilon 2p} = \frac{C\Phi(\varepsilon)}{(\varepsilon + I_Z/4)^2},$$

TABLE III. Parameters for ionization of 2*p* and 3*p* states obtained by using Coulomb functions.

n'	$x^C_{n's,2p}$	$x^C_{n's,3p}$
1	−1.58	−1.26
2	1.00	−0.02
3	0.041	1.00
4	0.015	0.04

$$\Phi(\varepsilon) = \exp\{-2\xi_1[\arctan(2/\xi_1)] - 2/\xi_1\}),$$

$$\xi_1 = \tau/\varepsilon = \sqrt{I_Z/\varepsilon}, \quad \Phi(0) = 1, \tag{47}$$

where

$$C = 2 \lim_{n'\to\infty} n'^3 x^C_{n's,2p} = 0.78 \tag{48}$$

is obtained by using the well-known Coulomb wave function for the bound $n's$ state for $n' \gg 1$ [15]. This gives $x_c = 0.52$, in agreement with Eq. (31).

Consider now ionization of $3p$ electrons, see again Table III. The correlation with $1s$ and $3s$ states cancel to a larger extent than in the case of the $2s$ state. The contribution of the continuum is now $x_c = 0.22$.

Now we analyze the situation for more realistic atomic models. We shall compare the values x_{ph} calculated is the unscreened and screened Coulomb fields. Here we obtain x_{ph} as the sum over occupied states, taking into account that, as we showed above, for ionization of a np state only correlations with ns and $1s$ states are important. Using Eq. (30) we can write in this approximation

$$x_{ph} = 1 + x_{1s,np}, \tag{49}$$

with $x_{1s,np} < 0$, as shown above. As one can see from Table III, the Coulomb values $|x^C_{1s,np}| > 1$. Now we show that for the screened Coulomb values $|x_{1s,np}| < |x^C_{1s,np}|$, and thus the Coulomb values x^C can be used as the lower limits for the physical values x_{ph}.

We can calculate the screening effects, assuming that the initial electrons are described by the Coulomb functions with effective values of the nuclear charge $Z_{n\ell} = Z - \delta_{n\ell}$ [15,25]. In this approach we find for ionization of $2p$ electrons

$$x_{1s,np} = x^C_{1s,np}\eta;$$

$$\eta = \left(\frac{Z_{1s}}{Z_{2s}}\right)^3 \left(\frac{3Z}{2Z_{1s} + Z_{2p}}\right)^4 \left(\frac{Z_{2s} + Z_{2p}}{2Z}\right)^5 \frac{2Z}{3Z_{2s} - Z_{2p}}, \tag{50}$$

with $\eta = 1$ if screening is neglected and thus $Z_{1s} = Z_{2s} = Z_{2p} = Z$. In the lowest order of expansion in powers of $\delta_{n\ell}$ Eq. (50) provides $\eta = 1 + \delta/Z$, with $\delta = -\delta_{1s}/3 - 5\delta_{2p}/3 + 2\delta_{2s}$. If a small influence of the electrons in the higher states on the values of $\delta_{n\ell}$ is neglected, δ is the same for all atoms with the totally occupied K and L shells. Using the values $\delta_{1s} = 0.35$, $\delta_{2s} = 3.25$, and $\delta_{2p} = 4.75$ [25], we find $\delta < 0$. Thus $\eta < 1$, and indeed

$$x_{phys} > x^C, \tag{51}$$

while $x^C < 0$. Using Eq. (50) for neon with these values of $\delta_{n\ell}$ we find $\eta = 0.676$, providing $x_{1s,2p} = -1.068$ and thus $x_{phys} = -0.068$, with $|x_{phys}|$ smaller then that shown in Table II. Note however that this value is a result of subtraction of two much larger values. Putting $\eta = 0.702$, i.e., increasing it by 4% we would find $x_{phys} = -0.11$, in agreement with the data in Table II.

VII. EXCLUSIVE AND INCLUSIVE PROCESSES IN NEUTRAL ATOMS AND IONS

Instead of photoionization of neutral atoms we can consider photoionization of ions. Since the cancellation of correlations is due mainly to cancellation between correlations with $1s$ and with ns electrons, a hole in either the $1s$ or ns shell breaks this balance, and the net correlations will greatly increase. This was observed earlier [5] for the cases of nitrogen and neon. A hole in other shells will not influence strongly the total correlation.

One is often interested in exclusive photoionization, as in ionization of a $2p$ state but perhaps also exciting other electrons. The theory of such processes was much studied [26–28] in the case of shake off and shake up.

As already noted, our discussion considering only two active electrons was inclusive in its treatment of the spectator electrons; it could be exclusive if overlap integrals between initial and final spectator states were considered. Note that in principle one should have also, in the presence of correlations, include other electrons as active, capable to undergo further excitation or ionization beyond the shake-off or shake-up mechanism. We can try to estimate the magnitude of these various mechanisms.

Assume that the bound electrons, moving in a certain self-consistent field, find themselves in another field after the electron is ejected. Photoionization of an n,ℓ state can be followed by a transition of an electron n',ℓ' to the state n^*,ℓ^*. One should consider the process simultaneously with ionization of n',ℓ' state followed by a transition of an electron n,ℓ to the state n^*,ℓ^*. The asymptotic IPA amplitude of the process, without correlations, is

$$\mathcal{F}^0 = F^0_{n\ell}\langle\phi_{n^*\ell^*}|\psi_{n'\ell'}\rangle - F^0_{n'\ell'}\langle\phi_{n^*,\ell^*}|\psi_{n\ell}\rangle, \tag{52}$$

with ψ and ϕ as the functions in the fields of the atom and of the ion with a hole in n,ℓ and n',ℓ' states for the two terms in the right-hand sides (rhs) of Eq. (52) correspondingly, $F^0_{n\ell}$ is the asymptotic IPA amplitude for ionization of $n\ell$ state. One needs $\ell^* = \ell'$ or $\ell^* = \ell$ otherwise the matrix element vanishes due to orthogonality of the angular parts of the wave functions.

Correlations provide another mechanism of the process in which n,ℓ electron is ionized by direct interaction with the photon, and in the next step the photoelectron excites the $n'\ell'$ electron to $n^*\ell^*$ state. One should include possible permutation of the $n\ell$ and $n'\ell'$ states. The amplitude, which includes the correlations can be written as

$$\mathcal{F} = \mathcal{F}^0 + F^0_{n\ell}\Lambda_{n^*\ell^*,n'\ell'} - F^0_{n'\ell'}\Lambda_{n^*\ell^*,n\ell}, \tag{53}$$

with $\mathcal{F}^0$ given by Eq. (52). The correlations can cause these transitions even if ℓ^* coincides neither with ℓ nor with ℓ', and the shakeup mechanism can not contribute.

Note that the contribution of correlations on the rhs of Eq. (53) is written omitting the terms containing as additional factors the overlap matrix elements of the type $\langle\phi_{n'\ell}|\psi_{n'\ell}\rangle$. We neglected such terms in particular calculations through the paper, see Sec. III. Inclusion of such terms would not alter the asymptotic energy dependence of the amplitude. Hence we shall use Eq. (53).

Consider, for example, photoionization of Be with the final-state ion containing electron excited into $2p$ state. In this case $n=1, n'=n^*=2, \ell=\ell'=0, \ell^*=1$. Both terms on the rhs of Eq. (53) turn to zero, providing $\mathcal{F}^0=0$, and thus

$$\mathcal{F}=F^0_{1s}\Lambda_{2p,2s}-F^0_{2s}\Lambda_{2p,1s}. \tag{54}$$

Now we study the relative role of the shakeup and correlation mechanisms of the process for various relations between ℓ, ℓ', and ℓ^*. To obtain the energy dependence of the contributions on the rhs of Eq. (53) one can employ that in the asymptotics

$$F^0_{n\ell}\sim\omega^{-(3+\ell)/2},\quad \Lambda_{n*\ell*,n\ell}\sim\omega^{-1/2}. \tag{55}$$

The estimation for $F^0_{n\ell}$ is well known [15]. The estimation for $\Lambda_{n*\ell*,n\ell}$ is the consequence of Eq. (4), in which the matrix element of Λ between the bound states is proportional to the factor $\xi\sim\omega^{-1/2}$.

As we have seen for $\ell\neq\ell'\neq\ell^*$ only correlations contribute. Turn now to other cases. If $\ell\neq\ell'=\ell^*$ the second term on the rhs of Eq. (52) vanishes and the IPA amplitude is

$$\mathcal{F}^0=F^0_{n\ell}\langle\phi_{n^*\ell'}|\psi_{n'\ell'}\rangle.$$

Using Eq. (55) we find that the second term on the rhs of Eq. (53) drops faster than $\mathcal{F}^0$, and hence the asymptotics is

$$\mathcal{F}=F^0_{n\ell}\langle\phi_{n^*\ell'}|\psi_{n'\ell'}\rangle-F^0_{n'\ell'}\Lambda_{n*\ell',n\ell}. \tag{56}$$

Further analysis depends on relation between ℓ and ℓ'.

For $\ell'=\ell^*<\ell-1$(for example, $n's\to n^*s$ and $n'p\to n^*p$ transitions in ionization of d states), the correlations determine the asymptotics of the process since the first term on the rhs of Eq. (56) drops with energy faster then the second term. For $\ell'=\ell^*=\ell-1$ (for example, $n's\to n^*s$ transitions in ionization of p states) states the two terms on the rhs of Eq. (56) behave with energy in the same way. However the first term is proportional to the overlap matrix element, which is usually small. If it is the case, the correlations dominate the process.

Similar analysis shows that for $\ell'=\ell^*>\ell-1$, including the case $\ell=\ell'=\ell^*$ (for example, $n's\to n^*s$ transitions in ionization of s states), asymptotic is determined by the shake-up mechanism, described by the first term on the rhs of Eq. (56). However, at finite energies, where the experimental data are available, interplay of the shakeup and correlation terms appears to be important [14,29].

To obtain the cross section for the inclusive process one should sum the squared amplitude given by Eq. (53) over n' and n^*, depending on the conditions of experiment.

VIII. SUMMARY

We have calculated the IPA breaking correlation corrections to the high-energy photoionization amplitude, focusing on ionization of p states. Instead of carrying out summation over occupied states, we employed the closure results for summation over all states of the spectrum. We showed that the sum over all states of the spectrum is equal to the contribution of its high-energy part. Therefore there is total cancellation between contributions of discrete and low-energy part of continuum spectra. This provided identities involving the asymptotics of the amplitudes of photoionization and of bremsstrahlung amplitudes at the tip region [Eqs. (26) and (31)].

We calculated the sum of correlations with the occupied bound states as the negative of the sum over the unoccupied bound states and the low-energy continuum states. We made conclusions in a simple model based on the general features of the bound states with large principal quantum numbers n. In this approach the sum of the occupied state correlations has a sign, which is opposite to that of the correlation inside the same shell. In spite of a crude model for the continuum, the results are in good agreement with those obtained earlier in direct calculation (Table II).

The sum of correlations with the occupied states calculated in such a way appeared to be smaller than the correlation with each of the occupied state considered separately. Hence, there is a partial cancellation between the terms corresponding to correlations with the occupied states. Thus we have shown that there is a general tendency of cancellation for the correlation effects. We demonstrated also that calculations with Coulomb functions give limits for the correlation effects in screened atoms [Eq. (51)].

We showed also that the correlations beyond shake-off and shake-up effects are important in inclusive processes, where photoionization is accompanied by excitation of other electrons. The relative role of the shake-up and correlation mechanisms was found to depend on relations between orbital momenta ℓ and ℓ' of the removed electrons and orbital momentum ℓ^* of the excited electron. In some of the cases the correlations dominate in the process. In the particular cases, for which experimental data are available, interplay of the two mechanisms is important.

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APPENDIX A

We calculate the asymptotic amplitude [Eq. (2)] for the bound $n's$ states, following the approach of [19]. Note that it is determined at small $r\sim 1/P$. Thus we can use expansion of the function $\psi_{ns}(r)$ at $r\to 0$,

$$\psi_{ns}(r)=\frac{N^r_{ns}}{\sqrt{4\pi}}(1+a_s r)\exp(-\lambda r),\quad \lambda>0,\quad \lambda\to 0. \tag{A1}$$

Here the last factor has been introduced to insure the convergence of the integral in the intermediate steps. We have kept two terms of expansion in powers of r in brackets since the lowest one, as we shall see below, vanishes at $\lambda=0$. (Higher terms in r would contribute in higher terms in $1/P$.) The parameter a_s on the rhs of Eq. (A1) should is equal to the first derivative of the function $\psi_{ns}(r)$ as determined by the first Kato cusp condition [30], being $a_s = -m\alpha Z = -\tau$. Since

$$\int d^3 r e^{i(\boldsymbol{P}\cdot\boldsymbol{r})-\lambda r} = \left(-\frac{\partial}{\partial\lambda}\right)\int d^3 r e^{i(\boldsymbol{P}\cdot\boldsymbol{r})}\frac{e^{-\lambda r}}{r} = \frac{8\pi\lambda}{(P^2+\lambda^2)^2} \tag{A2}$$

and $re^{-\lambda r} = (-\frac{\partial}{\partial\lambda})e^{-\lambda r}$, we obtain Eq. (2).

Evaluation of the matrix element in Eq. (2) corresponding to a continuum state j with asymptotic momentum $Q \ll P$ can be done in the same way, with the same form of expansion of ψ_{Qs}. Since only s waves contribute, we can write

$$\langle \psi_f^{(0)}|\hat{\gamma}|\psi_{Qs}\rangle = F^0_{Qs} = \frac{(\boldsymbol{e}\cdot\boldsymbol{P})}{m}X_{\varepsilon s}, \tag{A3}$$

where ε is the energy of the continuum electron,

$$X_{\varepsilon s} = \frac{4\pi^{1/2}N^r_{\varepsilon s}\tau}{P^4}, \tag{A4}$$

with $N^r_{\varepsilon s} = \psi^r_{\varepsilon s}(0)$, where the upper index r again denotes the radial part of the function, yielding Eq. (2).

APPENDIX B

Now we evaluate the amplitude T_{c2} defined, following Eq. (17), as

$$T_{c2} = \frac{(\boldsymbol{eP})}{m}\int\frac{d^3Q}{(2\pi)^3}\langle\psi^0_f|\psi_Q\rangle X(Q), \tag{B1}$$

with integration over $Q \gg \tau$ and with

$$X(Q) = \langle\psi_Q|\ln r(1-t)|\psi_i\rangle. \tag{B2}$$

Using Eq. (9.6) of [15] and taking the first iteration, we obtain

$$\langle\psi^0_f|\psi_Q\rangle = (2\pi)^3\delta(\boldsymbol{P}-\boldsymbol{Q}) + h(Q), \tag{B3}$$

with

$$h(Q) = 2m\frac{V(\boldsymbol{P}-\boldsymbol{Q})}{(Q+P)(Q-P+i\nu)}, \qquad \nu > 0, \qquad \nu \to 0. \tag{B4}$$

The first term on the right hand side of Eq. (B3) immediately gives

$$T_{c2} = \frac{(\boldsymbol{eP})}{m}X(P), \tag{B5}$$

leading to Eq. (21) due to Eq. (19).

Now we show that the second term on the right-hand side of Eq. (B3) provides higher-order terms of expansion in powers of P^{-1}.

We put $2mV(q) = \tau_c v(q^2)$, with τ_c being of the order $\tau \ll P$. One can see immediately that the regions $|\boldsymbol{Q}-\boldsymbol{P}| \sim P$ lead to corrections of the order $1/P$. The vicinity of the point $\boldsymbol{Q}=\boldsymbol{P}$ requires special analysis. Near this point we use the well-known relation

$$\frac{1}{x+i\nu} = \mathrm{P}\frac{1}{x} - i\pi\delta(0). \tag{B6}$$

For the first term on the right-hand side of Eq. (B6) the result of integration over the angles leads to a function of $(P-Q)^2$, i.e., to an even function of $P-Q$. Together with the denominator $P-Q$ this leads to an odd function of $P-Q$ in the integrand of the integral over Q, providing contribution of the order of $\sim\tau_c X(p)/P$. Contribution of the same order comes from the whole interval $Q \sim P$. In a similar way one can see that the second term on the right-hand side of Eq. (B6) also contributes only beyond the asymptotics. Thus, indeed we can neglect the second term on the right-hand side of Eq. (B3).

APPENDIX C

In order to calculate T_{c2} we must evaluate the matrix element defined by Eq. (B2) of Appendix B. Since $Q \gg \tau$ we first describe ψ_Q by a plane wave [Eq. (3)]. Then

$$X(Q) = \int dVe^{-iQz}\ln(r-z)\psi_i(r). \tag{C1}$$

For p states we can write

$$\psi_i(r) = \sqrt{\frac{3}{4\pi}}t\psi^r_i(r) \tag{C2}$$

(recall that we need only the states with $\ell_z=0$). Since we shall need $\psi_i(r)$ at $r \sim 1/Q$, we can put $\psi^r_i(r) = N^r_i re^{-\lambda r}$ ($\lambda \to 0$) in Eq. (A4), and thus $\psi_i(r) = \sqrt{3/4\pi}N^r_i re^{-\lambda r}$. We use $ze^{-iQz} = iD_Q e^{-iQz}$ (with $D_p = \partial/\partial p$) and use the parabolic coordinates

$$\xi = r+z, \qquad \eta = r-z, \qquad \phi = \arctan(x/y)$$

so that

$$r = \frac{\xi+\eta}{2}, \qquad z = \frac{\xi-\eta}{2},$$

and

$$dV = \frac{\xi+\eta}{4}d\xi d\eta d\phi.$$

Thus we find

$$X(Q) = \frac{-i\sqrt{3}\pi^{1/2}N_{np}}{2}D_Q D_\lambda J_Q, \tag{C3}$$

with

$$J_Q = \int d\xi\exp\left(-\frac{\lambda+iQ}{2}\right)\int d\eta\exp\left(-\eta\frac{\lambda-iQ}{2}\right)\ln\eta = \frac{-4}{\lambda^2+Q^2}\left(\gamma_E + \ln\frac{\lambda-iQ}{2}\right), \tag{C4}$$

with $\gamma_E \approx 0.578$ as the Euler constant, leading to asymptotics $1/Q^4$.

Note that the asymptotics Q^{-4} of the function $X(Q)$ is due to the logarithmic term in the integrand. Replacing it by a constant, we would obtain the asymptotics Q^{-5}. Indeed, replacing $\ln \eta$ by a constant, we would immediately find $X(Q)=0$ due to the operator D_λ. Thus we must include the next term of expansion of the function $\psi_i(r)$ in powers of r in a way similar to Appendix A. This gives $X(Q) \sim D_Q D_\lambda^2[1/(\lambda^2+Q^2)]=4/Q^5$. It can be shown that the higher-order corrections to the function ψ_Q contribute only to higher orders of expansion in powers of $1/Q$.

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