Applicability of a nonrelativistic asymptotic description of high-energy photoionization

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We show that while high-energy photoionization cross sections converge to their asymptotic forms only at relativistic energies, the leading deviation from the asymptotic energy dependence of nonrelativistic photoionization cross sections at high energy is the same for all cross sections. This factor can be obtained explicitly, and only asymptotic forms are needed for the remainder at high nonrelativistic energies. Since the factor is common, ratios of photoionization cross sections reach their asymptotic values at much lower energies than the cross sections themselves. Results are presented both in independent-particle approximation as well as including correlation effects, which modify the asymptotic behavior, especially for light elements or outer shells.

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I. INTRODUCTION

In this paper we investigate the high-energy behavior of cross sections for single photoionization of atomic systems. We find that a nonrelativistic asymptotic approach is not in itself adequate for calculation of high-energy photoionization cross sections, which converge to their asymptotic forms only at relativistic energies ω. However, in contrast to cross sections, the ratios of cross sections reach their asymptotic forms, except for the lightest elements, such as hydrogen and helium, at much lower energies. This is because a common explicit Coulombic-like factor (Stobbe factor) characterizes the leading deviations from asymptotic nonrelativistic energy dependence of all photoionization cross sections at high energies. This fact allows us to explain recent experimental measurements [1,2] of photoionization cross-section ratios utilizing asymptotic nonrelativistic results. Utilizing these asymptotic ratios together with the Stobbe factor, the cross sections may be predicted with good accuracy. In our discussion of this behavior, we may go beyond independent-particle approximation (IPA) and also include the consequences of electron-electron correlations, which modify the asymptotic behavior of the ratios.

There had been a general belief [3] that for large ω photoionization can be described within the framework of IPA. However, recent experiments of Dias *et al.* for the L shell of neon [1] and the M shell of argon [2] gave results in disagreement with IPA predictions. Examining the results, it was found that correlation effects persist for transitions from subshells with orbital quantum numbers $l=1$. These results were obtained in considering the asymptotic nonrelativistic behavior of the cross sections [4–6]. It may, however, be objected that the nonrelativistic asymptotic behavior is in fact not reached in the nonrelativistic regime, so that it is irrelevant and only of academic interest (see contrary arguments in [6]). Indeed, comparing results [7] obtained in the IPA with the corresponding nonrelativistic asymptotic predictions, we confirm that for the energies of the experiments (and well beyond), these cross sections are far from asymptotic. But in this paper we wish to point out that, in fact, the slowly convergent behavior can be identified and explicitly factored out. The remaining high-energy behavior indeed reaches an asymptotic form in the nonrelativistic regime (which will afterwards change, at relativistic energies).

We begin in Sec. II by reviewing the results for the asymptotic behavior of nonrelativistic high-energy photoionization cross sections. We also note the slow convergence of photoionization cross sections to their asymptotic forms. In Sec. III we analyze at the IPA level the approach to asymptotic behavior. The leading correction to the asymptotic amplitude, which is exponentiated, is of the order $\pi Z/p$ [8] (we use atomic units, Z is the nuclear charge and p is the momentum of the photoelectron). The Stobbe factor [9], common for all subshells, cancels in the ratio of photoionization cross sections, explaining why ratios converge to asymptotic behavior much faster than the cross sections themselves. In Sec. IV we go beyond independent-particle approximation, confirming that correlations change the asymptotic behavior of all cross sections with nonzero angular momentum quantum number l. However, we show that the leading correction to the asymptotic behavior of the cross sections is still determined by the Stobbe factor Eq. (7). Consequently the asymptotic ratio of our subshell photoionization cross sections calculated in the nonrelativistic approximation is in good agreement with the experimental results [1,2].

II. ASYMPTOTIC BEHAVIOR OF THE PHOTOIONIZATION CROSS SECTION

The nonrelativistic dipole IPA photoionization amplitude Φ^I_{nl} for a state with quantum numbers (nlm) is

$$\Phi^I_{nl}=\langle\Psi_p|g(\vec{r})|\Psi_{nl}\rangle \tag{1}$$

with single-particle wave functions (outgoing electron) Ψ_p and (initial bound electron) Ψ_{nl}. The index I denotes the IPA case. The operator $g(\vec{r})$ describes the dipole electron-photon interaction. The amplitude Φ^I_{nl} depends on the form (length, velocity, or acceleration) chosen for $g(\vec{r})$ if the wave functions Ψ_p and Ψ_{nl} are approximate, not exact eigenfunctions. In this section we consider the nonrelativistic range of photon energies $c^2\gg\omega\gg I_{nl}$, where I_{nl} is the photoionization energy ($c=137$ in atomic units, which we use in this paper).

Within the IPA framework each electron can be considered as moving in a common effective self-consistent field. Since near the origin this field has a nuclear point Coulombic behavior, the asymptotic behavior (i.e., the lowest-order term in an expansion in powers of ω^{-1}) of the partial photoionization cross section is known to be [9]

$$\sigma^I_{nl}(\omega)=\alpha_{nl}\omega^{-(\ell+7/2)}[1+O(\omega^{-1/2})], \tag{2}$$

where the coefficient α_{nl} is independent of ω.

In IPA the photon interacts with and is directly absorbed by an atomic electron, which is ejected in a continuum state, while the other atomic electrons do not change their states. However, going beyond IPA, one can see another mechanism for photoionization. Instead of interacting with a (nl) state, the photon can interact with a $(n'l')$ state, being absorbed and creating a hole in that state. Then the knocked-out electron can push an (nl) electron into the $(n'l')$ hole by electron impact, again leaving a (nl) hole and a continuum state. [Note that this second step takes place at distances of the order of the size of the Bohr $(n'l')$ orbit, rather than at the small distances at which the high-energy photoabsorption process occurs.]

Recently it was realized [1,2] that, for $l=1$, at high energies the second mechanism changes the behavior of the photoionization cross section from that given by Eq. (2). This can be understood by considering the asymptotic behavior of the amplitudes [5,6]. The full photoionization amplitude Φ_{nl} (beyond IPA) can be described as a sum of the amplitudes for the two mechanisms. In the first-order random-phase approximation with exchange (RPAE) [3] for the Coulomb interaction between atomic electrons, $V(r)=1/|\vec{r}_1-\vec{r}_2|$, the full amplitude Φ_{nl} is

$$\Phi_{nl}=\Phi^I_{nl}+\sum_{k,j}\frac{(\langle p,j|V|k,i\rangle-\langle p,j|V|i,k\rangle)\langle k|g(\overline{r})|j\rangle}{E_k-E_j-\omega+i\delta} \tag{3}$$

with summation over all intermediate single-particle states k and over bound states j with quantum numbers $(n'l'm')$, with i the single-particle bound state with quantum numbers (nlm), which is photoionized. If k belongs to the continuum the summation should be replaced by integration (the infinitesimal parameter δ shifts the singularity into the complex plane and in this way defines the contour of integration). The second term of this equation gives the IPA breaking contribution to the amplitude. We suppress here all many-electron indices in the full many-electron wave functions except for those that involve the active electrons.

In the high-energy limit, the denominator in Eq. (3) is small only for high-energy intermediate k states for which momentum $\vec{k}\approx\vec{p}$ ($|\vec{p}|=\sqrt{2\omega-(Z/n)^2}$). This means that the exchange matrix elements $\langle p,j|V|i,k\rangle$ are at least of order $1/p$ smaller than the direct matrix element $\langle p,j|V|k,i\rangle$ [10]. The denominator associated to the leading electron-electron Coulombic matrix element $\langle p,j|V|k,i\rangle$ contributes a factor $1/p$ to the asymptotic behavior of the second term of Eq. (3) for any intermediate state [5,6]. Since the IPA matrix element factor $\langle j|g(\vec{r})|k\rangle\sim p^{-(7/2+l)}$ [Eq. (2)], which is $\sim p^{-7/2}$ whenever j is an s state, the second term in Eq. (3) has $p^{-9/2}$ asymptotic behavior for any atom with at least a partially filled s subshell in the initial state. Thus, while for $l=0$ the IPA asymptotic result (2) is correct, for $l>0$ Eq. (2) should be changed to [5,6]

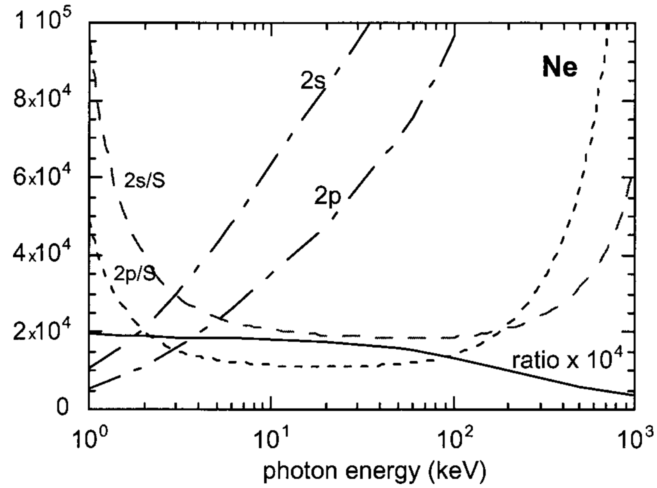

FIG. 1. Cross sections for transitions from $2s$ ($2s$ curves) and $2p$ ($2p$ curves) subshells of Ne obtained in the relativistic IPA [7] (in barn multiplied by powers of keV). Dashed-dotted lines are used for cross sections multiplied by the factor $\omega^{7/2}$ for photoionization of the $2s$ subshell, and by the factor $\omega^{9/2}$ for photoionization of the $2p$ subshell (ω in keV). Dashed lines are used for the cross sections $\omega^{7/2}\sigma^I_{2s}(\omega)$ and $\omega^{9/2}\sigma^I_{2p}(\omega)$ divided by the Stobbe factor $S(\xi)$ ($2s/S$ and $2p/S$ curves) [Eq. (7)] (and divided by a factor of 10 for convenience in presentation). The ratio $\sigma^I_{2s}(\omega)/\omega\sigma^I_{2p}(\omega)$ (in keV^{-1} multiplied by 10^4) is shown with a solid line.

$$\sigma_{nl}(\omega)=\beta_{nl}\omega^{-9/2}[1+O(\omega^{-1/2})]. \tag{4}$$

Note that for $l=1$ the functional dependence is not changed, but the value of the coefficient is modified: the IPA breaking effects result in the difference $(\beta_{nl}-\alpha_{nl})$ between the coefficients of Eqs. (2) and (4). For $l>1$ the functional dependence on ω is altered. The ratios of cross sections of angular momenta $l>0$ are independent of ω, unlike for the IPA result Eq. (3). The ratio $R_{s1}=[\sigma_{ns}(\omega)/\sigma_{n1}(\omega)]\sim\omega$, as in the IPA case, but the coefficient of ω is different. This explains the results presented in [1], where the slopes of the curves calculated in IPA and RPAE are different.

The first corrections to the asymptotic behaviors of the matrix elements (1) and (3) are smaller than the leading terms by only factors of order π/p. This implies a slow convergence of the cross sections to their asymptotic values. In Fig. 1 we show (dashed-dotted lines) results for the cross sections for neon obtained in the relativistic IPA approximation [7], multiplied by the factor $\omega^{7/2}$ for photoionization of the $2s$ subshell and by the factor $\omega^{9/2}$ for photoionization of the $2p$ subshell. Note that for low Z elements relativistic and retardation effects are small at low energies, so that one might have expected an initially flat behavior of the curves, corresponding to Eqs. (2) and (4). In both cases, however, we see that this does not occur. The actual energy dependence is due to the slow convergence of cross sections to their nonrelativistic asymptotic forms at lower energies and due to relativistic and retardation effects at higher energies; no regime exhibits nonrelativistic asymptotic behavior.

In the following section we discuss this slow convergence of the IPA photoionization cross sections to their asymptotic behavior at high photon energies, obtaining explicit expressions for the slowly convergent factors. We also show that the ratios of cross sections reach their asymptotic values at much lower energies than the cross sections. In the final section we extend this discussion to the non-IPA case, when correlations are included.

III. THE STOBBE FACTOR

We use the result of the analytic screening theory [11,12] that in the limit of high energies IPA photoionization is determined at small distances, i.e., by the Coulombic behavior of the wave functions near the nucleus. In the asymptotic nonrelativistic case, screening enters only in the change in the normalization N_i^I of the bound-state wave function

$$\sigma_{nl}^I(\omega)\sim(N_i^I)^2/(N_i^C)^2\sigma_{nl}^C(\omega), \tag{5}$$

where N_i^C is the normalization of the bound state of the hydrogenlike atom. The screening corrections due to wave-function shapes (and normalization of the continuum wave-function shapes) are, however, important at lower ω.

For the point-Coulomb case the full nonrelativistic dipole photoionization cross sections $\sigma_{nl}^C(\omega)$ were initially obtained for the K, L shells [9] and then for the M, N shells [13]. In general they can be written in the form

$$\sigma_{nl}^C(\omega)=\text{const}\times N^2(\xi)P_{nl}(\xi^2/n^2)\times\exp[-2\pi\xi+4\xi\arctan(\xi/n)]\omega^{-(7/2+l)}, \tag{6}$$

where $\xi=Z/p$ and $N(\xi)$ is the normalization of the Coulombic continuum wave function, i.e., $N^2(\xi)=|\Gamma(1-i\xi)|^2e^{\pi\xi}$. The polynomial ratio $P_{nl}(\xi^2/n^2)$ depends weakly (through the coefficients of the powers of ξ) on the orbital quantum number l of the initial state.

Note that the slow convergence of the cross sections to the exact asymptotic result Eq. (2) is primarily due to the product of $\exp(\pi\xi)$ and $\exp[-2\pi\xi+4\xi\arctan(\xi/n)]$ for small $\xi=Z/p$, where $\exp(\pi\xi)$ comes from the continuum state normalization factor $N^2(\xi)$. All other factors in Eq. (6) have faster convergence $O(\xi^2)$. This leading term in the departure of the Coulombic cross section $\sigma_{nl}^C(\omega)$ from its asymptotic value

$$S(\xi)=\exp(-\pi\xi) \tag{7}$$

we will call the Stobbe factor, recognizing the original Coulombic calculation of Stobbe [9] in which it was obtained; it is independent of n, l. Thus the leading correction to the asymptotic behavior of the cross sections $\sigma_{nl}^I(\omega)$ is determined by a factor of order $\pi\xi$, which is common for all transitions from all atomic subshells.

In Fig. 1 we show the scaled cross sections $\omega^{7/2}\sigma_{2s}^I(\omega)/S(\xi)$ and $\omega^{9/2}\sigma_{2p}^I(\omega)/S(\xi)$ for Ne, which reach their asymptotic behavior at high, but still nonrelativistic, energies (above 10 keV). However the remaining energy dependence $O(\xi^2)$ is still important at most nonrelativistic energies. The cancellation of the Stobbe factor $S(\xi)$ in ratios leads to a faster convergence of the ratios of the photoionization cross sections to their asymptotic form. We see in Fig. 1 that the ratio of these cross sections in fact converges much more rapidly (divided by ω to remove the asymptotic energy dependence, it is flat already below 10 keV), indicating additional cancellation of common factors.

The Stobbe factor $S(\xi)$ determines the behavior of cross sections only at very high energies $p\gg\pi Z$ ($\pi\xi\ll1$). For lower energies, larger n, or for heavier atoms the terms of order ξ^2 play an important role in the behavior of the photoionization cross section $\sigma_{nl}^I(\omega)$. The preasymptotic energy dependence of the cross section $\sigma_{nl}^I(\omega)$ is primarily determined by the generalized Stobbe factor

$$S_n(\xi)=|\Gamma(1-i\xi)|^2\exp[-\pi\xi+4\xi\arctan(\xi/n)] \tag{8}$$

of Eq. (6), which includes the normalization factor $N(\xi)$, i.e., one is still neglecting the energy dependence in the polynomial $P_{nl}(\xi^2/n^2)$ and that due to screening. The factor $|\Gamma(1-i\xi)|^2=2\pi\xi/(e^{\pi\xi}-e^{-\pi\xi})$ differs from 1 by terms of order $\pi^2\xi^2/6$; these start being important already for $p\leqslant\pi Z/\sqrt{6}$ ($\pi^2\xi^2/6\geqslant1$). The arctangent term $4\xi\arctan(\xi/n)$ in the exponential is of order $4\xi^2/n$, and for small $n<3$ it can play an even more important role than the corrections in $|\Gamma(1-i\xi)|^2$. Note that $S_n(\xi)$ is common for all transitions from the same atomic shell, since it does not depend on l. Divided by this factor, $\omega^{7/2}\sigma_{2s}^I(\omega)$ and $\omega^{9/2}\sigma_{2p}^I(\omega)$ converge to their asymptotic forms much faster than the cross sections themselves or the cross sections only divided by $S(\xi)$ of Eq. (7) [Fig. 2(a)].

The remaining second-order corrections are smaller in their effect than those that are included in the expression for $S_n(\xi)$ [Eq. (8)]. For light atoms (or inner shells of heavier atoms), these remaining effects are important only at energies lower than a few keV (but note, this is the region of energies for which experiments are now available). These remaining corrections are of two types. First of all, there are the polynomial ratios $P_{nl}(\xi^2/n^2)$ in the Coulombic cross section (5). Being of order ξ^2/n^2 their influence on the cross sections is less than the effect of $\exp[4\xi\arctan(\xi/n)]$ and the corrections in $|\Gamma(1-i\xi)|^2$ in Eq. (8). In Fig. 2(b) we show that the influence of the polynomial ratio $P_{2s}(\xi^2/2^2)=1+3(\xi/2)^2/[1+(\xi/2)^2]$ for $2s$ and $P_{2p}(\xi^2/2^2)=1+8(\xi/2)^2/3[1+(\xi/2)^2]$ for $2p$ on the cross sections in Ne is weaker and only affects convergence below a few keV.

When screening in the potential at small distances r is characterized by an expansion in powers of r, the remaining second-order corrections will be characterized by the coefficients of this expansion, which depend on the screening. Accordingly [11,12] screening contributes to the photoionization cross section through the normalization of the initial bound and continuum state wave functions, as well as in corrections to the reduced matrix element, which vanish asymptotically. One part of these screening corrections, already present asymptotically, comes from the screening effects on the bound-state normalization factor $(N_i^I)^2$ in Eq. (5). One can show that the screening effect due to the change in the normalization of the initial bound and continuum state wave functions can largely be taken into account by shifting the Coulombic ξ values in N_i^I to their physical values ξ_{nl}

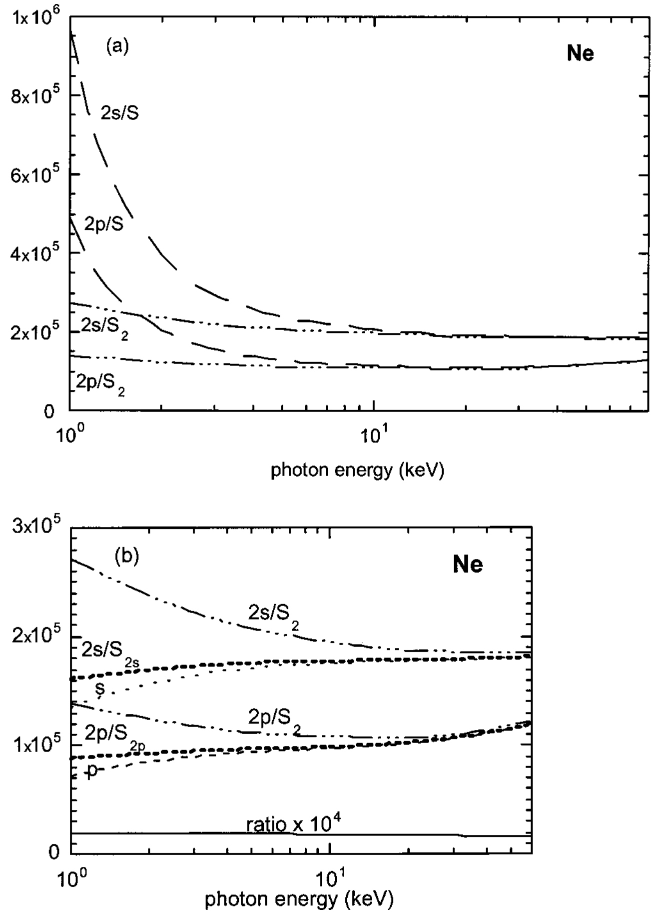

FIG. 2. (a) Cross sections $\omega^{7/2}\sigma^I_{2s}(\omega)$ and $\omega^{9/2}\sigma^I_{2p}(\omega)$ of Ne obtained as in Fig. 1, divided by $S(\xi)$ [dashed $2s/S$ and $2p/S$ lines, Eq. (7)], and by generalized factor $S_2(\xi)$ [dashed-triple-dotted $2s/S_2$ and $2p/S_2$ lines, Eq. (8)]; (b) $\omega^{7/2}\sigma^I_{2s}(\omega)$ and $\omega^{9/2}\sigma^I_{2p}(\omega)$ (in barn multiplied by powers of keV) divided by the adjusted generalized Stobbe factor $S_{2l}(\xi_{2l})$ of Eq. (9) (thick dotted $2s/S_{2s}$ and $2p/S_{2p}$ lines) as well, as divided by $S_2(\xi)$ [dashed-triple-dotted $2s/S_2$ and $2p/S_2$ lines, Eq. (8)]. The cross sections divided by both $S_2(\xi)$ and the polynomial ratio $P_{2s}(\xi^2/2^2)$ are also shown with thin dotted s and p lines for comparison. The ratio $\sigma^I_{2s}(\omega)/\omega\sigma^I_{2p}(\omega)$ (in keV^{-1} and multiplied by 10^4) is shown with a solid line.

$=Z/\sqrt{2(\omega-I_{nl})}$, with I_{nl} the physical ionization energy. This means that for given photon energy we should write the continuum normalization in terms of ξ_{nl} as $N_n^2(\xi_{n\ell}) =|\Gamma(1-i\xi_{n\ell})|^2 e^{\pi\xi_{n\ell}}$. Division of the cross sections $\omega^{7/2}\sigma^I_{2s}(\omega)$ and $\omega^{9/2}\sigma^I_{2p}(\omega)$ of Ne by such an adjusted generalized Stobbe factor

$$S_{nl}(\xi_{nl})=P_{nl}(\xi)|\Gamma(1-i\xi_{nl})|^2 \exp[-\pi(2\xi-\xi_{nl}) + 4\xi \arctan(\xi/n)] \tag{9}$$

[which includes also the polynomial ratios coming from the Coulombic cross section of Eq. (6)] makes them flatter even at low energies. In Fig. 2(b) we show this for the cross sections for neon obtained in the relativistic IPA [7]. Note also that the ratio $\sigma^I_{2s}(\omega)/\omega\sigma^I_{2p}(\omega)$ is approximately flat already by an energy of about a few keV.

In Fig. 3(a) the results of division by the generalized Stobbe factors $S_n(\xi)$ of Eq. (8) and adjusted generalized Stobbe factors $S_{nl}(\xi_{nl})$ of Eq. (9) are shown for the $2s$ and $2p$ photoionization cross sections of Ne calculated in the single-particle nonrelativistic Hartree-Fock approximation for energies lower than 1 keV. We can see that $\omega^{7/2}\sigma^I_{2s}(\omega)$ and $\omega^{9/2}\sigma^I_{2p}(\omega)$ divided by the Stobbe factors are only approximately flat at $\omega=700$ eV, because of further screening effects that are not yet taken into account, but are important for outer subshells at low energies.

We see similar behavior in the case of photoionization from Ar, where photoionization from $3s$ and $3p$ subshells was measured [2]. With increasing Z the cancellation effect of the common energy dependent factors in the ratio of the cross sections manifests itself at higher energies. Since Ar is a much heavier atom than Ne, its asymptotic behavior begins at much higher energies, where nonrelativistic considerations are not valid. Our calculations, however, show that the IPA ratios $\sigma^I_{2s}(\omega)/\omega\sigma^I_{2p}$ and $\sigma^I_{3s}(\omega)/\omega\sigma^I_{3p}$ are still approximately flat at the nonrelativistic energies of the experiment (about 1 keV), in accord with Eq. (2) (Fig. 3b).

Thus we can conclude that due to the common Stobbe factor $S_n(\xi)$ of Eq. (8) in cross sections for photoionization from subshells of given n with orbital quantum numbers l' and l, the IPA ratio of these cross sections converges rapidly to the asymptotic value $R_{ll'}\sim\omega^{l-l'}$. For different shells the ratio $\sigma^I_{n'l'}(\omega)/\sigma^I_{nl}(\omega)$ also converges to asymptotic values faster than the cross sections [due to the common Stobbe factor $S(\xi)$ from Eq. (7)], although in this case it can occur at energies so high that nonrelativistic considerations are not valid.

In this section we have demonstrated within IPA the applicability of asymptotic nonrelativistic ratios of cross sections. However, as we saw in Sec. II, the independent-particle approximation is not sufficient. Going beyond IPA, we have already considered the case of the Hartree-Fock approximation, finding similar behaviors for ratios of cross sections. In the following section we will extend our demonstration of the fast convergence of ratios, showing that it remains valid even when correlation effects are included.

IV. BEYOND IPA CORRELATION EFFECTS

We will now discuss how electron correlations change the results. We begin by showing that at high photon energy the leading correlation contributions to the RPAE amplitude, given by the second term of Eq. (3), can be written as a linear combination of IPA terms, with coefficients of order p^{-1} in the photoelectron momentum.

To obtain these leading terms at high energy, we neglect the exchange matrix element $\langle p,j|V|i,k\rangle$ in Eq. (3) and write

$$\Phi_{nl}=\Phi^I_{nl}+\sum_{k,j}\frac{\langle p,j|V|k,i\rangle\langle k|g(\vec{r})|j\rangle}{E_k-E_j-\omega+i\delta}, \tag{10}$$

where j is the single-particle bound state with quantum numbers $(n'l'm')$, and i is the bound state with quantum numbers (nlm).

The main contribution to the sum over k comes from continuum states with high momenta $\vec{k}$. Since the final electron momentum $\vec{p}$ is also large, the wave functions Ψ_k and Ψ_p in

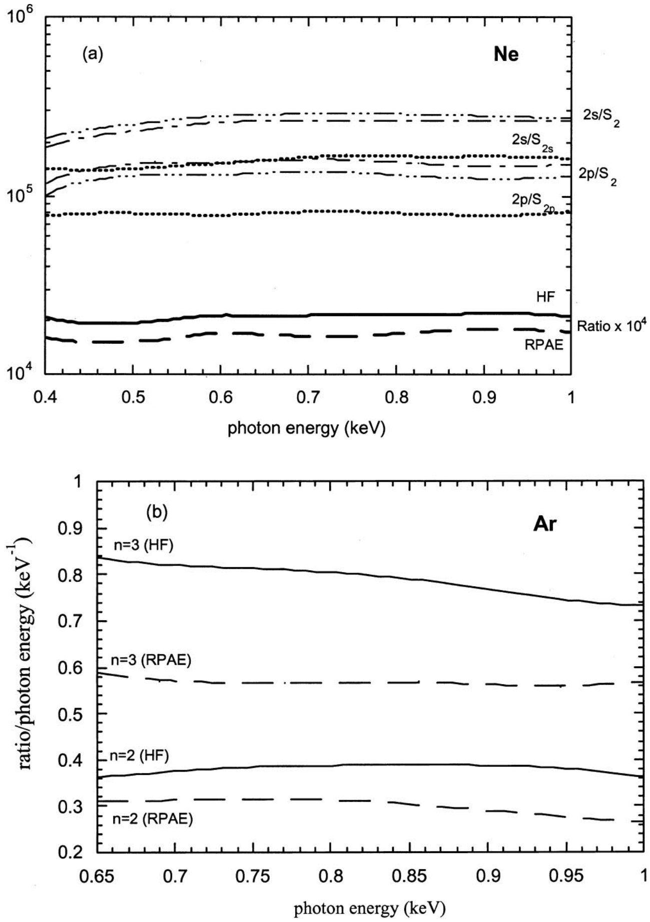

FIG. 3. (a) The cross sections for Ne in the Hartree-Fock approximation, divided by generalized factor $S_2(\xi)$ of Eq. (8) (dashed-triple-dotted $2s/S_2$ and $2p/S_2$ lines) and the adjusted generalized Stobbe factor $S_{2l}(\xi_{2l})$ of Eq. (9) (thick dotted $2s/S_{2s}$ and $2p/S_{2p}$ lines). The cross sections for Ne obtained in the same way but in RPAE are shown with long-dashed s and p lines (in barn multiplied by powers of keV). The ratios $R_{sp}(\omega)/\omega$ (in keV^{-1}) are obtained in the Hartree-Fock approximation (solid lines) and in RPAE (dashed lines). (b) The ratios $R_{2sp}(\omega)/\omega$ and $R_{3sp}(\omega)/\omega$ (in keV^{-1}) for Ar in the Hartree-Fock approximation (solid lines) and in RPAE (dashed lines).

the electron-electron interaction matrix element (though usually not in the radiation interaction matrix element) can be approximated as plane waves, giving

$$\langle p,j|V|k,i\rangle = \frac{1}{(2\pi)^3 f^2}\int \Psi^*_{n'l'}(\vec{r})e^{i\vec{f}\cdot\vec{r}}\Psi_{nl}(\vec{r})d\vec{r}. \quad (11)$$

Note that for a small momentum transfer $\vec{f}=\vec{p}-\vec{k}$ the only large matrix element in Eq. (10) is $\langle p,j|V|k,i\rangle$. Equation (10) can be then rewritten as a linear combination of the IPA amplitudes $\Phi^I_{n'l}$

$$\Phi_{nl}=\Phi^I_{nl}+\sum_{n'l'}\Lambda_{nl,n'l'}\Phi^I_{n'l}, \quad (12)$$

where $n'l'$ are the quantum numbers of the j state. The coefficients $\Lambda_{nl,n'l'}$ can be expressed in terms of the matrix elements of simple operators

$$\Lambda_{nl,n'l'}=\frac{1}{(2\pi)^3}\int \langle nl|e^{i\vec{f}\cdot\vec{r}}|n'I'\rangle \frac{d^3f}{f^2[E_f-(\vec{p}\cdot\vec{f})+i\delta]}. \quad (13)$$

For large p the coefficients are of order $1/p$. An explicit expression for $\Lambda_{nl,n'l'}$ was obtained in [14]. Since for the transitions from s states the first IPA matrix element in Eq. (12), $\Phi^I_{nl}\sim p^{-7/2}$, and the second term has at least $p^{-9/2}$ asymptotic behavior, for $l=0$ the asymptotic result for the photoionization amplitude is the same as the IPA result of Eq. (2). For any atom with at least a partially filled s subshell in the initial state, for transitions from states with $l>0$, the asymptotic behavior of the cross sections $\sigma_{nl}(\omega)$ are determined by the part of the second term of the amplitude (12) in which $l'=0$. If only correlations with the s-state $l'=0$ are significant $\sigma_{nl}(\omega)\sim\sigma^I_{ns}(\omega)/p$ and we get the asymptotic behavior of Eq. (4).

For our purpose, however, what is important is that, according to Eq. (12), the asymptotic behavior of the photoionization amplitude is determined by the common Stobbe factor $S(\xi)$ of Eq. (7). Thus, as in the IPA case, these cross sections, which have the same common factor as for $\sigma^I_{n's}(\omega)$, are only slowly convergent to asymptotic values. In the case of $l=1$ both terms in the amplitude (12) are of the same order, and both involve the same common Stobbe factor in their amplitudes. For $l=0$ the IPA term is dominant, again with the same Stobbe factor.

Since correlations are bigger for electrons of the same shell we can assume that the interaction between the atomic electron and the ionized electron is not altered by the bound electrons of another shell, and in Eq. (12) can include only terms with $n'=n$. In Fig. 3(a) we present results for RPAE photoionization cross sections from $2s$ and $2p$ subshells of Ne divided by the generalized Stobbe factor $S_n(\xi)$ of Eq. (8). This Stobbe factor, which includes terms of order ξ^2, and which plays an important role at lower p, will be the same for $\sigma_{nl}(\omega)$ and $\sigma^I_{nl}(\omega)$. In Fig. 3(a) we can see that RPAE results are quite different from the IPA cross sections. However, for photoionization from the $2s$ state the difference becomes smaller with increasing energy. This reflects the fact that the asymptotic leading term of $\sigma_{2s}(\omega)$ [Eq. (2)] is the same in both the RPAE and IPA cases. However, in the case of photoionization from the $2p$ state, the IPA breaking effect results in the difference $(\beta_{2p}-\alpha_{2p})$ between the coefficients of Eqs. (2) and (4), and therefore we do not see a decreasing difference between IPA and RPAE results.

Despite the slow convergence of the photoionization cross sections themselves, we can expect a fast convergence of their ratios, so that nonrelativistic values of the ratios will be achieved within the nonrelativistic range of photon energies. We demonstrate this in Fig. 3(a) for photoionization of neon. Since $R_{sp}(\omega)=[\sigma_{2s}(\omega)/\sigma_{2p}(\omega)]\sim\omega$, as in the IPA case (but with a different coefficient of ω), the $R_{sp}(\omega)/\omega$ curve in Fig. 3(a) calculated in RPAE is approximately flat. The ratio follows the asymptotic law with an accuracy of better than 10% for photon energies exceeding 700 eV.

In Fig. 3(b) we present results for the ratios R_{sp} for $n=2$ $[R_{2sp}(\omega)/\omega]$ and $n=3$ $[R_{3sp}(\omega)/\omega]$ subshells of Ar

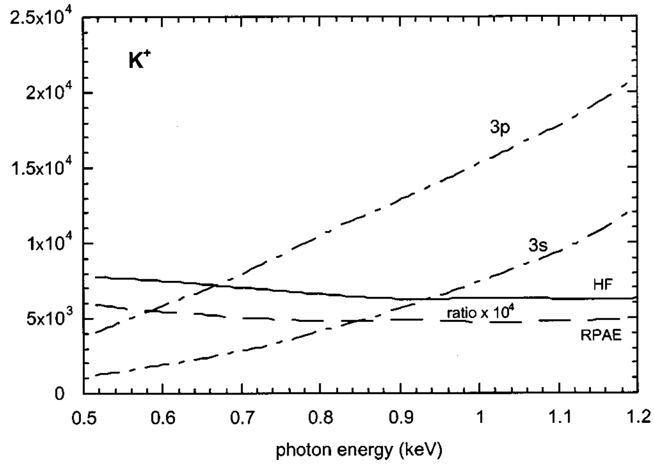

FIG. 4. The cross sections $\omega^{7/2}\sigma^{I}_{3s}(\omega)$ and $\omega^{9/2}\sigma^{I}_{3p}(\omega)$ in RPAE (in barn multiplied by powers of keV are shown with dashed-dotted lines), and the ratios $R_{3sp}(\omega)/\omega$ (in keV^{-1} and multiplied by 10^4) for K^+ in the Hartree-Fock approximation (solid lines) and in RPAE (dashed lines).

calculated in the Hartree-Fock and RPAE approximations. The ratios, which are divided by ω, are already close to constant (not the same constant) at energies of about 1 keV but the cross sections themselves are far from asymptotic, as had been noted in [5,6]. Our RPAE calculations involve couplings between M and L shell electrons. It is known [3] that near the ionization threshold the correlations are much more important for the outer shells. We can see the same effect at high energies as well—our Hartree-Fock and RPAE $R_{2sp}(\omega)/\omega$ curves for $n=2$ in Fig. 3(b) are only slightly different, while correlations enhance the Hartree-Fock $R_{3sp}(\omega)/\omega$ in the transitions from $3p$ subshell by about 25%.

Correlations in outer shells at high energies are also important for positive ions. We show their effect for K^+ ions in Fig. 4. The difference between Hartree-Fock and RPAE $R_{2sp}(\omega)/\omega$ values is as big as for neutral Ar, i.e., about 25%.

V. CONCLUSIONS

In summary, we have shown that despite the fact that high-energy photoionization cross sections do not converge to their nonrelativistic asymptotic behavior (except maybe in the lightest elements, such as hydrogen and helium) in the nonrelativistic photon energy region, a nonrelativistic asymptotic approach is still applicable for calculation of their ratios. The reason is the cancellation of explicitly known common Coulombic-like Stobbe factors Eq. (7), which characterize the primary deviations from the asymptotic nonrelativistic energy dependence. Utilizing the asymptotic ratios together with the Stobbe factor, the cross sections may be predicted with good accuracy. This supports our nonrelativistic consideration of the asymptotic behavior of the ratios of the photoionization cross sections in paper [6].

At lower energies we still can find a common factor, which now depends on the principal quantum number n, but is independent of the orbital quantum numbers [Eq. (8)]. Cancellation still occurs for photoionization cross sections from the same atomic shell. This explains the behavior of the ratios of the photoionization cross sections from s and p subshells in Ne and Ar [1,2]. Even at very low energies (below 1000 eV for the atoms we consider in this paper) cancellation of the generalized Stobbe factors [Eq. (9)] makes the ratios of the cross sections close to asymptotic.

Going beyond independent-particle approximation, we confirm that correlations change the asymptotic behavior of all cross sections with nonzero angular momentum quantum number l. However, we show that the leading correction to the asymptotic behavior of the cross sections is still determined by the Stobbe factor. Consequently the asymptotic ratio of our subshell photoionization cross sections, calculated in the nonrelativistic approximation with correlations, is in good agreement with the experimental results [1,2].

Here we have considered nonrelativistic photoionization. The Stobbe factor can be also identified within a relativistic approach, but in this case it is independent of the total energy E, since now at high energy $\xi = EZ/p$ does not depend on $E \sim p$. However, it is known that in the relativistic case there is also slow convergence with the energy of the photoionization cross sections in the parameter $1/p$.

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