PHYSICAL REVIEW A VOLUME 59, NUMBER 4 APRIL 1999

Large nondipole correlation effects near atomic photoionization thresholds

M. Ya Amusia,[1,2,3] A. S. Baltenkov,[4] Z. Felfli,[1] and A. Z. Msezane[1]
[1]*Department of Physics and Center for Theoretical Studies of Physical Systems, Clark Atlanta University, Atlanta, Georgia 30314*
[2]*The Racah Institute of Physics, Hebrew University, Jerusalem 91904, Israel*
[3]*A. F. Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia*
[4]*Arifov Institute of Electronics, Akademgorodok, 700143 Tashkent, Republic of Uzbekistan*
(Received 2 June 1998; revised manuscript received 14 December 1998)

The parameter that determines the nondipole correction to the angular distribution is calculated for Ar $1s$ and $3s$ subshells in the Hartree-Fock (HF) approximation and taking account of the multielectron correlations, using the random-phase approximation with exchange. In the photoelectron energy range 0–100 eV the parameter, which for s subshells is nonzero at threshold, is found for Ar $3s$ to be strongly affected by multielectron correlations. Results are also presented for He and Be in the HF approximation.
[S1050-2947(99)50804-4]

PACS number(s): 31.25.−v, 32.80.Dz, 32.80.Fb

The motivation for this Rapid Communication is to carefully investigate the behavior of the nondipole photoelectron anisotropy parameter γ in the vicinity of photoionization thresholds of such outer subshells as the $3s$ in Ar. The use of correlated wave functions is fundamental to the proper study and understanding of the photoionization process in this energy region, which is generally characterized by a richer structure. For this reason, multielectron correlations were included in our calculation of Ar $1s$ and $3s$ subshells via the random-phase approximation with exchange (RPAE), while Hartree-Fock (HF) wave functions proved adequate for the study of the simpler systems such as He and Be.

Our investigation and presentation of the results for He, Be, and Ar s subshells are also very timely (and are further justified) in view of the the recent measurement of nondipole photoelectron angular distributions of Ar $1s$, Kr $2s$, and Kr $2p$ [1]. The experiment compared data with those from the most recent calculations [2,3], and stressed the need for careful studies of ''... less straightforward situations, for example the nondipolar asymmetries in the threshold region, in the region of resonances and of Cooper minima, which represent interesting subjects for future experimental and theoretical investigations.'' Therefore, the HF results for He and Be near threshold also constitute the necessary data acquisition and analysis required for the interpretation of the photoionization process.

Sommerfeld derived the photoelectron angular distribution with the lowest relativistic correction, which includes retardation [4]. For $1s$ electrons ionized by unpolarized light the photoelectron angular distribution is given by

$$\frac{d\sigma_{1s}(\omega)}{d\Omega}=\frac{3}{8\pi}\sigma_{1s}(\omega)\left(1+4\frac{v}{c}\cos\theta\right)\sin^2\theta, \qquad (1)$$

where $\sigma_{1s}(\omega)$ is the photon absorption cross section, ω the photon frequency, and θ the angle between the directions of the light and the photoelectron, with c and v being the corresponding speeds, respectively. Recently, Eq. (1) has been generalized to any hydrogenic level [5]. To investigate atoms other than hydrogen, a more general expression for $d\sigma_{nl}(\omega)/d\Omega$ is required, viz.,

$$\frac{d\sigma_{nl}(\omega)}{d\Omega}=\frac{\sigma_{nl}(\omega)}{4\pi}\left(1+\beta_{nl}(\omega)P_2(\cos\theta)+\frac{\omega}{c}[\gamma_{nl}(\omega)P_1(\cos\theta)+\eta_{nl}(\omega)P_3(\cos\theta)]\right). \qquad (2)$$

The leading terms in Eq. (2) were suggested by Yang [6], while the terms containing ω/c were introduced later [7]. To calculate the ω dependence of β, γ and explicit expressions are required for these coefficients via atomic matrix elements. An expression for $\beta_{nl}(\omega)$ has been derived in the one-electron approximation [8] and taking into account multielectron correlations [9,10]. Similarly, explicit expressions for γ and η have been given in the one-electron approximation [2,3], taking the multielectron correlations into account [9,10]. Numerical results have been obtained for the noble gases within the one-electron approximation [2,3]. In this Rapid Communication, we concentrate on the energy regime near thresholds. One-electron HF wave functions are used as an initial approximation and then multielectron correlations are taken into account.

In general, the expressions for $\gamma_{nl}(\omega)$ and $\eta_{nl}(\omega)$ are rather complicated [9]. But, to illustrate some qualitative features of the ω dependence of the nondipole corrections, we concentrate on s subshells for which the general expressions [9] simplify considerably, yielding in the one-electron approximation

$$\gamma_{ns}(\omega)=\frac{6}{5}\frac{q_2}{d_1}\cos(\delta_d-\delta_p), \qquad (3)$$

with $\gamma_{ns}(\omega)=-\eta_{ns}(\omega)$. Here q_2 and d_1 are the quadrupole and dipole radial matrix elements, respectively, between the one-electron initial state ns and the continuous spectrum ϵl

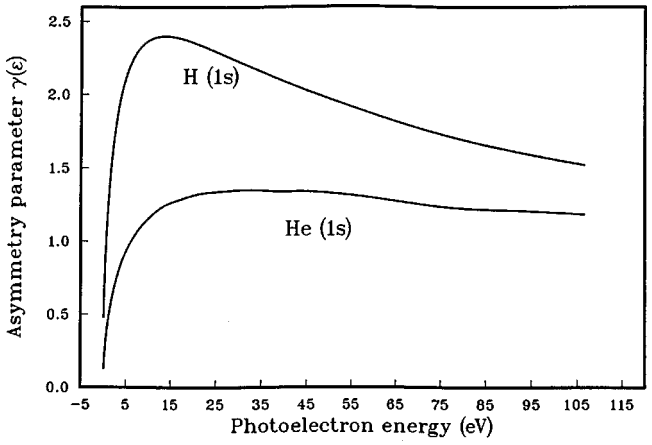

FIG. 1. Nondipole asymmetry parameter γ for the $1s$ photoionization of H and He as a function of photoelectron energy. Results for He were obtained in the HF approximation.

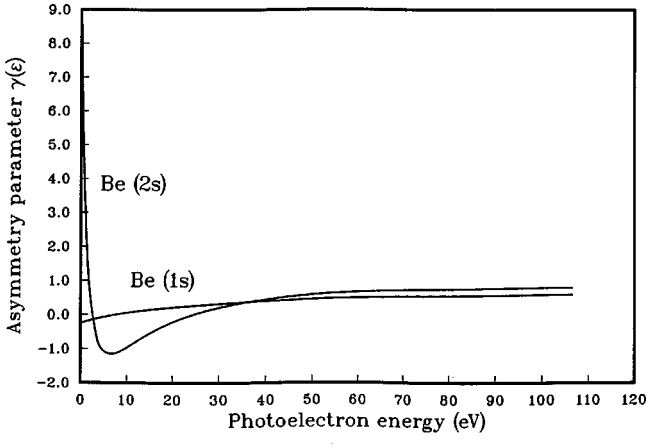

FIG. 2. Nondipole asymmetry parameter γ for photoionization out of the $1s$ and $2s$ subshells of Be as a function of photoelectron energy, calculated within the HF approximation.

($l=2$, or 1), where ϵ is the photoelectron energy; δ_d and δ_p are the d and p elastic scattering phases, respectively, with energy ϵ. Near threshold the ratio q_2/d_1 can be estimated as $q_2/d_1 \approx a_{ns}$ (a_{ns} is the ionizing shell radius), so that at threshold

$$\frac{\omega}{c}\gamma_{ns}(\omega) \sim \frac{\omega}{c} a_{ns} = k a_{ns}, \tag{4}$$

where k is the photon momentum consistent with [2]. For outer-shell thresholds (using atomic units) ($e=\hbar=m=1$), $\omega \approx 1$ and $\gamma_{ns} \approx 1/137$. The simplest possible one-electron Coulomb approximation gives a much smaller value. Indeed, for the hydrogenlike case, one obtains

$$\frac{q_2^c}{d_1^c} = \frac{2\sqrt{Z^2+4v^2}}{Z^2+v^2} \tag{5a}$$

and

$$\cos(\delta_d^c - \delta_p^c) = \frac{2v}{\sqrt{Z^2+4v^2}}, \tag{5b}$$

where Z is the nuclear charge. From Eqs. (5) and (2) we have

$$k\gamma_{1s}^c = \frac{12}{5}\frac{v}{c}, \tag{6}$$

in accord with Eq. (1), when expressed in terms of Legendre polynomials, as in Eq. (2).

Thus, consistent with the results of [2] the smallness of $k\gamma_{1s}$ results from a very delicate balance between the photoelectron p and d phases in the Coulomb field,

$$\delta_d^c - \delta_p^c = \frac{\pi}{2} - \arcsin\left[\frac{2v}{\sqrt{Z^2+4v^2}}\right]. \tag{7}$$

The presence of any short-range force along with the Coulomb one can destroy this balance, leading to much larger values of γ_{ns} than γ_{1s}^c close to threshold. To check this point, we performed calculations for He and Be using one-electron HF wave functions. The field acting upon the outgoing photoelectron in He is very close to the pure Coulombic one. Therefore $\gamma_{1s}^{\mathrm{He}}$ is positive. But even this small additional field altered the near-threshold value of $\gamma_{1s}^{\mathrm{He}}$ considerably leading to a nonzero value at threshold. Figure 1 compares the results for H and He. For Be, the coefficients $\gamma_{2s}^{\mathrm{Be}}$ and $\gamma_{1s}^{\mathrm{Be}}$ as functions of ϵ behave differently. Starting from a negative value at threshold, $\gamma_{1s}^{\mathrm{Be}}$ increases monotonically, while $\gamma_{2s}^{\mathrm{Be}}$ is a rather complicated sign-changing function (see Fig. 2). In He the γ parameter is a monotonical function of ϵ. However, this behavior, as in the case of Be, does not follow directly from Eq. (3) for any atom and any s subshell. Indeed, calculations have already revealed [2,3], in accord with recent experiment [11], that γ and η are nonmonotonical functions of ω and can even change sign, but at considerably higher energies than in Fig. 2.

In order to investigate the combined effects of a non-Coulombic central field and multielectron correlations, we consider the $3s$ and the $1s$ subshells in Ar. To account for electron correlations, Eq. (3) must be generalized [9]. The nondipole parameter is described by an expression similar to that in Eq. (3), but with the matrix elements q_2 and d_1 replaced by complex ones, Q_2 and D_1, which include the effects of electron correlations

$$\gamma_{ns}(\omega) = \frac{6}{5}\frac{(Q_2'D_1' + Q_2''D_1'')\cos(\delta_d-\delta_p) + (Q_2'D_1'' - Q_2''D_1')\sin(\delta_d-\delta_p)}{D_1'^2 + D_1''^2}, \tag{8}$$

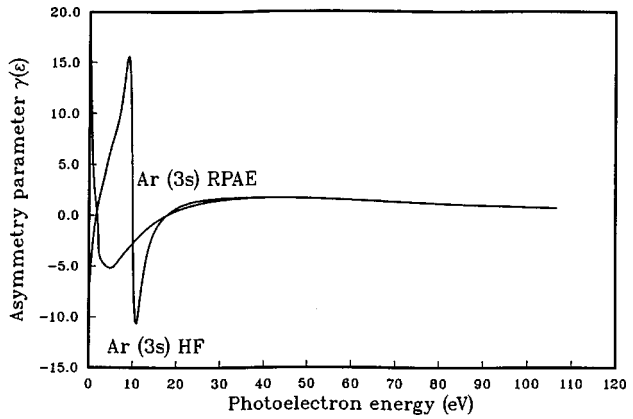

FIG. 3. Nondipole asymmetry parameter γ for photoionization out of the $3s$ subshell of Ar as a function of photoelectron energy, calculated in the HF approximation and the RPAE.

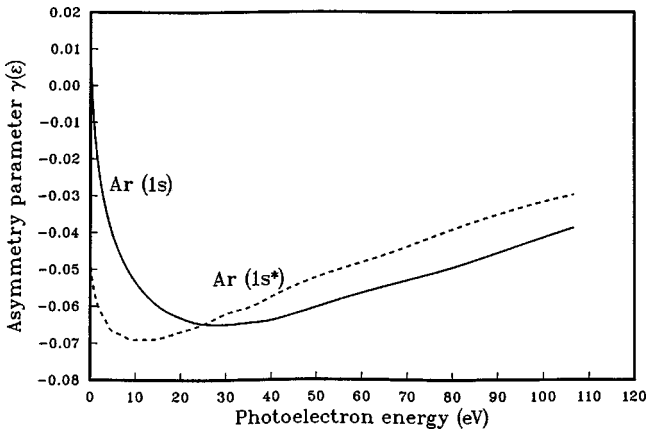

FIG. 4. Nondipole asymmetry parameter γ, as a function of photoelectron energy, for photoionization out of the $1s$ subshell of Ar. The calculation was performed within the RPAE (——), labeled Ar($1s$), and taking into account the rearrangement (− − −), labeled Ar($1s$*).

where Q_2' (D_1') and Q_2'' (D_1'') are the real and imaginary parts of the quadrupole (dipole) radial matrix elements, respectively. If Q and D are real, Eq. (8) reduces to Eq. (3). To calculate Q and D, we have selected the RPAE [12]. The RPAE has been successful in calculating the dipole photoionization cross sections and the angular anisotropy parameters in outer and intermediate subshells of numerous atoms. The $\gamma_{3s}(\omega)$ in Ar was obtained in the RPAE framework [12].

The procedure of solving the RPAE equations for the dipole channel is discussed in the recent book [13], and for the quadrupole matrix elements is similar to that for the dipole one. Symbolically, they can be expressed as

$$\hat{D}=\hat{d}+\hat{U}_1\hat{\chi}_1 D, \tag{9a}$$

$$\hat{Q}=\hat{q}+\hat{U}_2\hat{\chi}_2 Q, \tag{9b}$$

where $\hat{d}$ ($\hat{q}$) are the dipole (quadrupole) photon absorption operators in the one-electron approximation, and $\hat{U}_1$ ($\hat{U}_2$) are the dipole (quadrupole) components of a combination of the direct and exchange Coulomb interelectron interaction. The operators $\hat{D}(\hat{Q})$ and $\hat{d}(\hat{q})$ describe the elimination of an electron off the atom, i.e., creation of an electron-hole pair. The operators $\hat{\chi}_1(\hat{\chi}_2)$ describe the propagation of the initially created (or any other connected to it by the Coulomb interelectron interaction) electron-hole pair. Again, symbolically, $\hat{\chi}_1(\hat{\chi}_2)$ can be expressed as

$$\hat{\chi}_{1(2)}=\frac{\hat{1}}{\omega-\epsilon_{1(2)}-i\delta}-\frac{\hat{1}}{\omega+\epsilon_{1(2)}}. \tag{10}$$

Here $\epsilon_{1(2)}>0$ is the energy of an intermediate electron-hole state excited through a dipole (quadrupole) over which the summation for discrete states and integration for continuum states are performed. The imaginary parts of the D and the Q matrix elements come from the fact that the energy denominator of the first term in Eq. (10) can approach zero. The behavior near this singularity is defined by introducing the infinitesimal imaginary term $i\delta$. The first term in Eq. (10) can be expressed as

$$(\omega-\epsilon_{1(2)}-i\delta)^{-1}=\mathrm{P}(\omega-\epsilon_{1(2)})+i\pi\delta(\omega-\epsilon_{1(2)}), \tag{11}$$

where P denotes the principal value of the integration. Numerical calculations have been performed for the $3s$ subshell in Ar, which is under the very strong action of the $3p$ virtual excitations [12]. Our results are given in Fig. 3, where $k\gamma_{3s}(\epsilon)$ is seen to be represented by a nonmonotonic sign-changing function even in the HF one-electron approximation. The γ_{3s} parameter is not only nonzero at threshold but is also very large, at least 20 times larger than the expected order of $ka\approx 1/137$. The electron correlations in the RPAE, mainly the effects of $3p$ electrons, alter γ_{3s} dramatically; they change its sign near threshold and add an extra zero and an extra maximum. The large value of $k\gamma_{3s}$ at threshold results mainly from D_1 being small and Q_2 being large for the $3s$ subshell. For example, at threshold the HF values of q_2 and d_1 are 2.37 and 0.12, respectively.

The first zero in $\gamma_{3s}(\epsilon)$ at $\epsilon\cong 1.5$ eV is located where $\cos(\delta_2-\delta_1)$ goes through zero. At this same energy, $\epsilon Q_2''$ is close to zero as well. The last zero is due to the sign variation of the quadrupole matrix element at $\epsilon=18$ eV. Again, the imaginary part of the quadrupole term Q_2'' at this energy is almost zero. The large maximum and sign variation of γ_{3s} at $\epsilon=10$ eV is due to the sign variation of D_1', while D_1'' is very close to zero [12]. Thus, it is clear that $\gamma_{3s}(\epsilon)$ under the action of RPAE electron correlations becomes a complicated function of ϵ.

Consider now the $1s$ subshell of Ar. It is known that the RPAE correlations for the inner shells of intermediate and heavy atoms are rather unimportant [12]. However, the photoionization cross section, at least close to threshold, is far from being hydrogenic; it is strongly affected by the non-Coulomb nature of the field acting upon the photoelectron and by dynamical rearrangement effects [12]. The latter are a consequence of the comparatively fast inner vacancy decay in outer and intermediate shells and the formation of satellites with high probability. These effects also alter the field acting upon the photoelectron. The calculations of $\gamma_{1s}(\epsilon)$ were performed in the RPAE, HF approximation, and taking

account of rearrangement [12]. As in the case of the photoionization cross section, the difference between the RPAE and HF approximation is insignificant for the $1s$ subshell. Our results for $\gamma_{1s}(\epsilon)$ are given in Fig. 4. Clearly, in the Hartree-Fock approximation, $\gamma_{1s}(\epsilon)$ is nonhydrogenic, has a different sign, and has a nonzero value at threshold. Our calculations show that $\gamma_{1s}(\epsilon)$ changes its sign at about $\epsilon \approx 220$ eV and, starting from almost 30 eV, coincides with the results of Ref. [3].

In conclusion, our investigation finds that multielectron correlations are significant for γ for the Ar $3s$ subshell, leading to its rich structure. Although the recent experiment [1] agrees very well with the theoretical calculations [2,3] on γ for Ar $1s$ and Kr $2s$ beyond 30 eV, between threshold and 30 eV, the experiment does not appear to reveal the minimum in γ_{1s} predicted by our calculation. Consequently, further theoretical and experimental investigations are recommended for elucidation, particularly very close to threshold.

The work was supported by the NSF, the U.S. DOE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, and the AFOSR.

[1] B. Krassig, M. Jung, D. S. Gemmell, E. P. Kanter, T. Le Brun, S. H. Southworth, and L. Young, in *X-ray and Inner-Shell Processes*, Proceedings of the 17th International Conference, Hamburg, Germany, edited by R. L. Johnson, H. Schmidt-Bocking, and B. F. Sonntag, AIP Conf. Proc. No. 389 (AIP, Woodbury, NY, 1997), p. 659.

[2] A. Bechler and R. H. Pratt, Phys. Rev. A **39**, 1774 (1989); **42**, 6400 (1990).

[3] J. W. Cooper, Phys. Rev. A **42**, 6942 (1990); **47**, 1841 (1993).

[4] A. Sommerfeld, *Wave Mechanics* (Matheun, London, 1930).

[5] M. J. Seaton, J. Phys. B **28**, 3185 (1995).

[6] C. N. Yang, Phys. Rev. **74**, 764 (1948).

[7] M. Peshkin, Adv. Chem. Phys. **18**, 1 (1970).

[8] J. Cooper and R. N. Zare, J. Chem. Phys. **48**, 942 (1968).

[9] M. Ya Amusia *et al.*, Phys. Lett. **47A**, 66 (1974) (for more details see M. Ya Amusia, A. S. Baltenkov, A. A. Grinberg, and S. G. Shapiro, Zh. Eksp. Teor. Fiz. **68**, 28 (1975) [Sov. Phys. JETP **41**, 14 (1975)].

[10] M. Ya Amusia and N. A. Cherepkov, *Case Studies in Atomic Physics* (North-Holland, Amsterdam, 1975), Vol. 5, pp. 154–157.

[11] B. Krassig *et al.*, Phys. Rev. Lett. **75**, 4736 (1995); Phys. Rev. A **54**, 2127 (1996).

[12] M. Ya Amusia, *Atomic Photoeffect* (Plenum Press, New York, 1990).

[13] M. Ya Amusia and L. V. Chernysheva, *Computation of Atomic Processes, A Handbook for the Atom Programs* (Institute of Physics Publishing, Bristol, 1997).