

CALCULATION OF THE PHOTO-IONIZATION CROSS SECTION FOR ARGON  
IN THE HARTREE-FOCK APPROXIMATION

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The cross sections for photo-ionization of the L and M shells of Ar are obtained in the Hartree-Fock approximation with three different wave functions of the expelled electron being used: that for the field of a neutral atom, for the field of the ion, and for a Herman-Skillman potential. The cross sections are determined for photon energies between 15 and 1000 eV. In all three cases the calculated cross sections differ from the experimental values. This indicates that multi-electron correlations play an important role in the atom.

1. THE question of the role played by multielectron correlations in atoms has been under extensive discussion recently.<sup>[1-6]</sup> However, owing to the large computational difficulties, no clear-cut answer to this question has been obtained so far. It is therefore of interest to calculate in the single-particle approximation the cross sections of the processes in which the expected role of multielectron correlations is large, and to obtain information concerning the role of correlations in atoms by comparing the experimental and calculated results.<sup>[2]</sup> One of the processes to be considered is photoionization. In this paper we calculate the photoionization cross sections of the L and M shells of argon in the Hartree-Fock approximation. It is assumed here that only one electron, the one leaving the atom, takes part in the photon-absorption process. When account is taken of the multi-electron effects, the mechanism of this process is much more complicated. A comparison of the results of the calculation with the experimental data indicates that they differ noticeably from each other near the ionization threshold.

A study of the photoionization cross section in the Hartree-Fock approximation is also of independent interest. Until relatively recently, photoionization cross section calculations were available only in the hydrogen-like approximation,<sup>[7]</sup> and the results deviated greatly from the experimental data. The first calculation in the Hartree-Fock approximation for the M-shell of argon was made by Cooper.<sup>[8]</sup> The results obtained by him do not agree with the results obtained in the present paper. This difference is apparently due to the procedure used by him to localize the exchange part of the potential. Manson and Cooper<sup>[9]</sup> repeated the calculations with functions in the Herman-Skillman potential.<sup>[10]</sup> It will be shown below, however, that the results obtained with the single-electron Herman-Skillman wave functions cannot be used for the study of multielectron correlations. The reason is that the Herman-Skillman potential is chosen empirically, and the wave functions in this potential take into account a certain inaccurately-determined part of the multi-electron effects.

2. If the wave function of the atom can be represented in the form of a determinant made up of single-particle wave functions, then the photoionization cross

section of the  $nl$ -th subshell is determined by the formula<sup>[9]</sup>

$$\sigma_{nl}(\epsilon) = \frac{4\pi^2 a_0^2 N_{nl}(\epsilon - \epsilon_{nl})}{3} \frac{1}{2l+1} [lR_{\epsilon, l-1}^2 + (l+1)R_{\epsilon, l+1}^2]. \quad (1)$$

Here  $N_{nl}$  and  $\epsilon_{nl}$  are respectively the number of electrons in the subshell and the binding energy of the electron (in Rydberg units),  $\alpha = 1/137$ ,  $a_0$  is the radius of the first Bohr orbit,  $\omega = \epsilon - \epsilon_{nl}$  is the energy of the incident photon, and  $R_{\epsilon, l \pm 1}$  are dipole matrix elements:

$$R_{\epsilon, l \pm 1} = \int_0^\infty P_{nl}(r) P_{\epsilon, l \pm 1}(r) r dr, \quad (2)$$

where  $P_{nl}$  and  $P_{\epsilon l}$  are the radial parts of the single-particle wave functions. The wave functions of the continuous spectrum are normalized to a  $\delta$  function of the energy and have the following asymptotic form at infinity:

$$P_{\epsilon l}(r) \sim \pi^{-1/2} e^{-i/4} \sin \left[ \sqrt{\epsilon} r - \frac{\pi l}{2} - \sqrt{\epsilon} \ln 2\sqrt{\epsilon} r + \delta_l(\epsilon) \right]; \quad (3)$$

$\delta_l(\epsilon)$  is the phase shift.

The wave functions of the occupied states  $P_{nl}$  are chosen in the Hartree-Fock approximation. The wave functions of the outgoing electron  $P_{\epsilon l}$  can be defined here in various ways. Strictly speaking, the set of functions  $P_{nl}$  and  $P_{\epsilon l}$  should form a complete set of the eigenfunctions of one operator. In this case, the functions  $P_{\epsilon l}$  will correspond to an electron moving in the field of a neutral atom. We shall henceforth denote such a solution of the Hartree-Fock equation by the symbol  $P_{\epsilon l}^{N+1}$ , since it corresponds to the  $N+1$ -st electron ( $N$ -number of electrons in the atom). On the other hand, in the photoionization process, the number of electrons in the system remains equal to  $N$ . We can therefore seek the functions  $P_{\epsilon l}$  in the field of a singly-charged ion. These functions are determined in the following manner: we substitute in the Hartree-Fock equation for  $P_{\epsilon l}$  the functions  $P_{nl}$  corresponding to the ground state of the atom. The function  $P_{\epsilon l}$  is sought in the field of an atom that lacks one electron, and the equation is solved without self consistency. The solution of this equation will be denoted by  $P_{\epsilon l}^N$ . The func-

tions defined in this manner were used by Kelly.<sup>[5]</sup>

3. We shall show that the use of the functions  $P_{\epsilon l}^N$  in place of  $P_{\epsilon l}^{N+1}$  to determine the photoionization cross section is equivalent to inclusion in the self-consistent field of a part of the multiparticle correlations which are usually taken into account in the random-phase approximation<sup>[11]</sup> (Fig. 1).

The first diagram in Fig. 1 is the simplest one, corresponding to the photoionization process. The solid line corresponds here to the propagation of a particle or a hole, and the dashed line to the propagation of an incident photon;  $\epsilon_j < 0$  is the hole energy,  $\epsilon_j + \omega$  is the energy of the outgoing electron. As is well known,<sup>[11]</sup> the zeroth-approximation wave functions should form a complete orthonormal basis, and therefore it is necessary to choose as the wave function of the particle the previously defined functions  $P_{\epsilon l}^{N+1}$ .

The photoionization cross section obtained from formula (1) with the functions  $P_{\epsilon l}^{N+1}$  corresponds thus to the process represented by the first diagram of Fig. 1.

We now sum an infinite sequence of the diagrams shown in Fig. 1, where the wavy line represents the Coulomb interaction between the electrons of the atom. It is important that the hole  $j$  is always the same in all the diagrams, and has the same set of quantum numbers  $n/l/m$  ( $s$ -spin projection). This sequence in the atom is the most important one and, as will be shown, the summation of diagrams in Fig. 1 is equivalent to a redefinition of the potential in which the outgoing particle moves.

In order to verify this, let us examine the diagrams of Fig. 2a. The first of them is the direct interaction between the outgoing particle and one of the background particles, and the second belongs to the summed sequence. Using the rules for setting up the analytic expressions corresponding to the diagrams,<sup>[11]</sup> we can readily verify that the expressions corresponding to these diagrams differ only in sign, and yield 0 when summed. The same holds for the diagrams of Fig. 2b. It can be verified that the summation of the entire sequence leads to compensation of the interaction of the knocked-out electron by the background electron in the state  $j$ . This can be taken into account by a simple redefinition of the potential in which the outgoing electron moves: the contribution of the entire sequence of diagrams of Fig. 1 is equal to the contribution of only the first diagram of Fig. 1, in which the wave function of the particle  $P_{\epsilon l}^{N+1}$  should be replaced by another wave function, defined in the field of the atom without one electron in the state  $j$ , i.e., we must take  $P_{\epsilon l}^N$  in place of  $P_{\epsilon l}^{N+1}$ . To emphasize the importance of summing the aforementioned sequence, we note that the functions  $P_{\epsilon l}^{N+1}$  either have no discrete spectrum, or have only one or several levels (they correspond to a negative ion), whereas the functions  $P_{\epsilon l}^N$  have a discrete spectrum with a condensation point.

In atomic calculations, frequent use is made of single-particle wave functions obtained in the Herman-Skillman potential.<sup>[10]</sup> This potential coincides at small distances from the nucleus with the Hartree-Fock-Slater potential  $V_{\text{HFS}}$ , and at large distances it equals

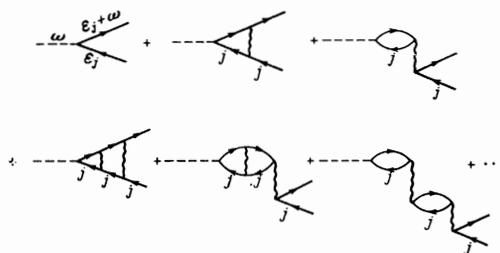


FIG. 1.

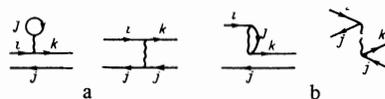


FIG. 2.

$V_1 = 1/r$ . The mixing takes place at the point where  $V_{\text{HFS}} = V_1$ . Since this potential decreases at infinity like  $1/r$ , the wave function in this potential,  $P_{\epsilon l}^{\text{HS}}$ , should be close to the function  $P_{\epsilon l}^N$ . However, whereas the substitution of the function  $P_{\epsilon l}^N$  in place of  $P_{\epsilon l}^{N+1}$  in the formula for the photoionization of distinctly defined diagrams shown in Fig. 1, the use of the function  $P_{\epsilon l}^{\text{HS}}$ , which is a solution of the Schrödinger equation with a certain empirically chosen potential, does not correspond to the summation of any definite diagrams.

Figure 3 shows all the wave functions of the continuous spectrum, obtained in the present study<sup>1)</sup> at an energy  $\epsilon = 0.368$  Ry (5 eV) and  $l = 2$ . The function  $P_{\epsilon d}^N$  depends on the shell in which the hole is located, and therefore the figure shows two functions, one of which is determined in the field of an atom without one  $2p$ -electron ( $P_{(2p)\epsilon d}^N$ ), and the other in the field of an atom without one  $3p$ -electron ( $P_{(3p)\epsilon d}^N$ ).

4. The total photoionization cross section of the  $L$  and  $M$  shells of argon for all three cases is shown in Figs. 4 and 5. These figures show also the experimental cross section taken from the papers of Samson<sup>[12]</sup> and Lukirskii and Zimkina.<sup>[13]</sup> The greatest deviation from the experiment is observed near the ionization thresholds, where multiparticle effects should appear.

The cross section obtained with the functions  $P_{\epsilon l}^N$  beyond the ionization threshold of the  $M$  shell has a small but broad maximum, which is more clearly pronounced than on the experimental curve, and which is shifted towards higher energies. The character of the behavior beyond the ionization threshold of the  $L$  shell is the same in both cross sections, but the calculated curve always lies higher than the experimental one. The jump at the ionization threshold of the  $L$  shell is larger by 1.7 times than the experimental value, and that at the threshold of the  $L_I$  subshell is larger than the experimental value by a factor of 2.

The cross section obtained with the wave functions in the Herman-Skillman potential has, for both shells, rel-

<sup>1)</sup>All the functions used in this paper were calculated with the BESM-3 computer. The equations were solved by successive refinements.

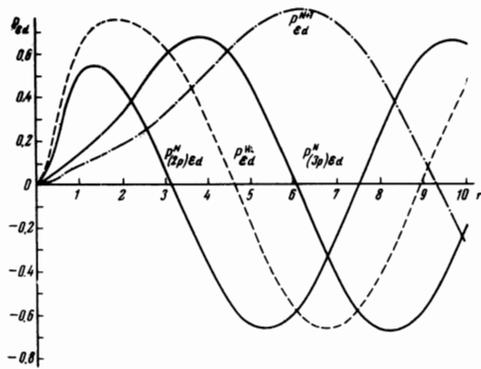


FIG. 3. Wave functions of continuous spectrum at  $\epsilon = 0.368$  Ry and  $l = 2$ .

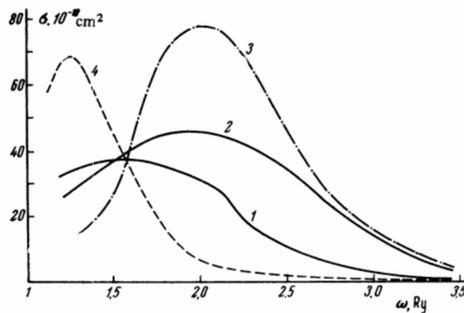


FIG. 4. Photoionization cross section of M shell of argon: 1—experiment [12], 2—calculated cross section with functions  $P_{\epsilon l}^N$ , 3—with functions  $P_{\epsilon l}^{N+1}$ , 4—with functions  $P_{\epsilon l}^{HS}$ .

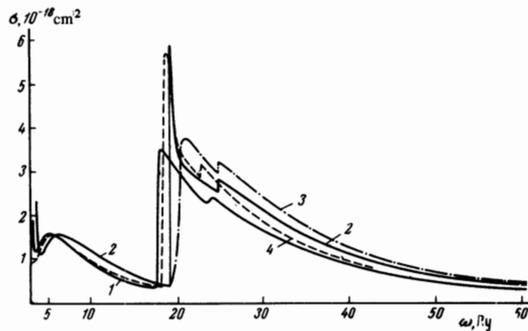


FIG. 5. Photoionization cross section of M and L shells of argon: 1—experiment [13], 2—calculated cross section with functions  $P_{\epsilon l}^N$ , 3—with functions  $P_{\epsilon l}^{N+1}$ , 4—with functions  $P_{\epsilon l}^{HS}$ .

actively sharp maxima beyond the ionization thresholds. It differs greatly from the cross section obtained with the functions  $P_{\epsilon l}^N$ . Thus, the simplifications made in the determination of the Herman-Skillman potential lead to a very noticeable change of both the wave functions (Fig. 3) and the cross sections obtained in this potential, compared with the corresponding Hartree-Fock quantities. The results of the present paper for the M shell in the Herman-Skillman potential coincide fully with the results obtained earlier by Manson and Cooper.<sup>[9]</sup> To simplify the calculation, the nonlocal exchange potential was replaced approximately in [8] by a local potential, and therefore the results obtained

there differ from the corresponding results obtained in the present paper with the functions  $P_{\epsilon l}^N$ .

The difference in the behavior of the cross sections obtained with different wave functions can be readily understood by analyzing the behavior of these functions at the same energy. Since the main contribution of the cross section is made by the transition  $np \rightarrow \epsilon d$ , it suffices to consider functions with  $l = 2$ . The magnitude of the matrix element (2) is determined by the amplitude of the wave function  $P_{\epsilon d}$  at the place where  $P_{np}$  differs from 0, i.e., at distances on the order of  $a_0$  from the nucleus. The probability that the  $N+1$ -st electron will stay inside the neutral atom at low energies is quite small, owing to the repulsion of the electron cloud.

Therefore the first maximum of the function  $P_{\epsilon l}^{N+1}$  is located at a large distance from the nucleus (Fig. 3). On the other hand, if the outgoing electron moves in the field of an ion with a positive net charge, the probability of its staying inside the atom at the same energy is much higher, and the deeper the hole the larger this probability. Therefore the first maximum of the function  $P_{(sp)\epsilon d}^N$  is close to the nucleus than that of  $P_{(sp)\epsilon d}^{N+1}$ . In the Herman-Skillman potential, the function  $P_{\epsilon d}^{HS}$  does not depend on the position of the hole, and as can be seen from Fig. 3, its first maximum lies precisely between the maxima of the functions  $P_{(sp)\epsilon d}^N$  and  $P_{(sp)\epsilon d}^{N+1}$ . Accordingly, the matrix element (2), meaning also the photoionization cross section at the M-shell threshold, should be largest for the function  $P_{\epsilon d}^{HS}$  and smallest for  $P_{\epsilon d}^{N+1}$  whereas at the L-shell threshold they should be largest for the function  $P_{(sp)\epsilon d}^N$  and smallest again for  $P_{\epsilon d}^{N+1}$ .

For certain transitions to discrete excited states, we determined the oscillator strengths  $f_{nl \rightarrow n'l'}$ , which are defined in the following manner:<sup>[7]</sup>

$$f_{nl \rightarrow n'l'} = \frac{2l+1 \pm 1}{6(2l+1)} (\epsilon_{n'l'} - \epsilon_{nl}) R_{nl \rightarrow n'l'}^2, \quad (4)$$

where

$$R_{nl \rightarrow n'l'} = \int_0^\infty P_{nl}(r) P_{n'l'}(r) r dr. \quad (5)$$

The calculation was performed with functions  $P_{n'l}^N$ . The results are as follows:

Transition: $3p \rightarrow 4s$	$3p \rightarrow 3d$	$3s \rightarrow 4p$	$2p \rightarrow 4s$	$2p \rightarrow 3d$
$f$ : 0.055	0.027	0.00196	0.00092	0.0358

The results obtained by Cooper<sup>[8]</sup> in a Herman-Skillman potential are as follows:

Transition: $3p \rightarrow 4s$	$3p \rightarrow 3d$
$f$ : 0.055	0.196

As is well known, the photoionization cross section satisfies the sum rule:<sup>[7]</sup>

$$\frac{1}{4\pi^2 a_0^2} \sum_{nl} \int \sigma_{nl}(\epsilon) d\epsilon = N, \quad (6)$$

where  $N$  is the number of electrons in the atom. The sign of the integral in this formula denotes also summa-

tion over the discrete spectrum. The sum rule is satisfied approximately separately for each shell. In the derivation of this formula, we used the well known relation between the matrix elements of the coordinate and momentum operators:

$$\langle k|\hat{p}|l\rangle = i(E_k - E_l)\langle k|\hat{r}|l\rangle. \quad (7)$$

Relation (7) is satisfied only if the potential of the system commutes with the operator of the coordinate. In the Hartree-Fock equation, the potential contains a nonlocal term corresponding to exchange interaction, which does not commute with the coordinate operator. In this case we obtain in place of (7) the following relation for the matrix elements:

$$(E_k - E_l)\langle k|\hat{r}|l\rangle = -i\langle k|\hat{p}|l\rangle + \sum_i \int \psi_i^*(r')\psi_i(r')\frac{r-r'}{|r-r'|}\psi_i(r)\psi_k^*(r)dr dr'. \quad (8)$$

Therefore, the sum rule (6) should not be satisfied in the Hartree-Fock approximation.<sup>[14]</sup> Indeed, substitution of the cross section obtained with the functions  $P_{\epsilon l}^N$  into formula (6) yields (without a discrete spectrum) a value 18.4 in place of 16, and with the functions  $P_{\epsilon l}^{N+1}$ , a value 22. In the Herman-Skillman potential, the nonlocal exchange term is replaced by a local one, and therefore the sum rule should hold for the cross section obtained with the wave functions  $P_{\epsilon l}^{HS}$ . The integration of the cross section obtained in this paper (without the discrete spectrum) makes a contribution equal to 14.7 to the sum rule. When the discrete spectrum is taken into account, a quantity sufficiently close to 16 is obtained.

The foregoing comparison of the theoretical curves shows that the photoionization cross section depends strongly on the choice of the single-particle wave functions. But for any choice of the single-particle functions, the calculated cross section differs strongly from the experimental one in the vicinity of the thresholds.

This difference can be due only to multielectron correlations.

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<sup>1</sup>W. Brandt and S. Lundqvist, Phys. Lett. 4, 47 (1963); Phys. Rev. 132, 2135 (1963).

<sup>2</sup>M. Ya. Amusia, V. V. Afrosimov, Yu. S. Gordeev, N. A. Cherepkov, and S. I. Sheftel, Phys. Lett. 24A, 394 (1967).

<sup>3</sup>W. Brandt, L. Eder, and S. Lundqvist, J. Quant. Spectrosc. Radiat. Transfer 7, 185 (1967).

<sup>4</sup>M. Ya. Amusia, N. A. Cherepkov, and S. I. Sheftel, Phys. Lett. 24A, 541 (1967).

<sup>5</sup>H. P. Kelly, Phys. Rev. 136, B896 (1964); 144, 39 (1966).

<sup>6</sup>P. L. Altick and A. E. Glassgold, Phys. Rev. 133, A632 (1964).

<sup>7</sup>H. A. Bethe and E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press, 1957).

<sup>8</sup>J. W. Cooper, Phys. Rev. 128, 681 (1962).

<sup>9</sup>S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968).

<sup>10</sup>F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., 1963).

<sup>11</sup>D. J. Thouless, Quantum Mechanics of Many-body Systems (Academic Press, 1961), Ch. 4.

<sup>12</sup>J. A. R. Samson, Advan. Atomic Mol. Phys. 2, 178 (1966).

<sup>13</sup>A. P. Lukirskii and T. M. Zimkina, Izv. AN SSSR, ser. fiz. 27, 817 (1963).

<sup>14</sup>V. A. Fock, Z. Phys. 89, 744 (1934).