

Many-electron effects in the absorption of a photon by an argon atom near the ionization threshold of the 1s shell

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The influence of monopolar restructuring of electron shells, of correlation “shake” of the electron density, of vacuum correlations, and of virtual Auger decay of a 1s vacancy on the cross section for absorption of a photon by an argon atom near the ionization threshold of the 1s shell is investigated in the multiconfigurational Hartree–Fock approximation. The theoretical cross section agrees well with the experimental cross section for absorption of synchrotron x rays by an argon atom. © 1995 American Institute of Physics.

1. INTRODUCTION

Many-electron effects in the absorption of an x-ray photon by inner shells of free atoms have been the subject of intensive experimental and theoretical investigations in recent years.¹ In this paper the problem of the theoretical description of the types and influence of many-electron effects in the absorption of a photon near the ionization threshold of the 1s shell of a free atom is investigated for the example of the argon atom—a simple many-electron system with filled shells in the ground state.

By theoretical investigations of the cross section for absorption of a photon near the ionization threshold of the 1s shell of the Ar atom, both in the framework of the relativistic² and nonrelativistic³ one-configuration Hartree–Fock approximations and also by the methods of many-body theory,⁴ the following has been established. To obtain 75–80% agreement of the theory with experiment^{5,6} it is necessary to take into account the effect of monopolar restructuring (i.e., restructuring without change of the symmetry of the state) of the electron shells of the atomic residue in the field of the 1s vacancy. The appearance of the 1s vacancy results in the electron shells reducing their mean radius in the atomic residue. The displacement of the electron density of the shells of the atomic residue toward the nucleus is accompanied by delocalization of the photoelectron and, as a consequence, by decrease in the photon-absorption amplitude. A calculation of the cross section near the ionization threshold of the 1s shell without allowance for the restructuring of the electron shells gives results approximately twice as large as the experimental results.

To establish the reasons for the remaining 20–25% discrepancies between the theory and experiment, in Refs. 7 and 8, together with the influence of the restructuring of the electron shells, the influence of nonpolar channels (i.e., channels preserving the 1s vacancy) of one-photon multiple virtual excitation/ionization on the theoretical cross section of the absorption of a photon by the 1s shell of the Ar atom was investigated. To be precise, the process considered was virtual $3p^{-2} - n_1(p,d)n_2(p,d)$ excitation/ionization of the 3p shell in the final photoabsorption state $1s^1 2s^2 2p^6 3s^2 3p^6 np$ (np is the photoelectron; henceforth, in writing out the configuration we omit the filled shells). The photoabsorption

amplitude was constructed by the methods of the theory of nonorthogonal orbitals⁹ in the framework of the nonrelativistic multiconfigurational Hartree–Fock approximation. Here, it was shown that the “shake” of the 3p shell in the $1s^1 np(^1P_1)$ state as a result of virtual excitations and ionization is equivalent to the appearance for the photoelectron of a correlation potential supplementing the Hartree–Fock potential. The corresponding variations in the theoretical photoabsorption cross section can be interpreted as the effect of the correlation shake of the density of the 3p valence shell in the $1s^1 np(^1P_1)$ state. For example, correlation shake leads to a ~5% increase in the Hartree–Fock cross section for the absorption of a photon by an Ar atom near the ionization threshold of the 1s shell.⁷ For comparison, we note that in the absorption of a photon by the 2p shell of the Ar atom, by virtue of the strong sensitivity of a photoelectron of collapsing *d*-symmetry to small variations in the self-consistent potential of the atomic residue,¹⁰ the phenomenon of correlation shake increases by ~20% the Hartree–Fock cross section for absorption of a photon near the ionization thresholds of the $2p_{1/2}$ and $2p_{3/2}$ shells.⁷ The absorption of a photon by the $3p^{-2} - n_1(p,d)n_2(p,d)$ excitation/ionization states of the $1s^2(^1S_0)$ Fermi vacuum leads to a change in the structure and magnitude of the Hartree–Fock photoabsorption amplitude. The corresponding changes in the theoretical photoabsorption cross section can be interpreted as a vacuum correlation effect. Thus, the vacuum correlation effect leads to a ~10–15% increase in the Hartree–Fock cross section for absorption of a photon by an Ar atom near the ionization threshold of the 1s shell.⁸

We note that both in Refs. 7 and 8 and in the present paper, the relativistic spin-orbit splitting of the 3p shell of Ar in the $3p^{-2} - n_1(p,d)n_2(p,d)$ states has not been taken into account because of its smallness:¹¹ $I_{1/2} - I_{3/2} = 0.1790$ eV (I is the ionization potential of the 3p shell), whereas the FWHM of the profile of the brightest 1s–4p photoexcitation line was measured in Ref. 5 to be 1.20 eV. Relativistic effects associated with the spinor structure of the wave functions of the atomic electrons were also not taken into account, since the difference between the results of the relativistic² and nonrelativistic³ calculations of the photoabsorption cross section near the 1s ionization threshold of Ar did not exceed ~2%.

Allowance for polar (not containing a $1s$ vacancy) radiative and Auger decay channels of the $1s$ vacancy, and for channels the RPAE type (random-phase approximation with exchange¹²) cannot explain the order of magnitude of the above-indicated discrepancies between theory²⁻⁴ and experiment.⁵ The strong spatial and energy separation of the $1s$ shell from the other shells of the atomic residue leads to the result that the contributions of these channels to the total photoabsorption amplitude and the corresponding correlation potentials supplementing the Hartree–Fock correlation potential for the photoelectron can change the Hartree–Fock cross section near the $1s$ shell ionization threshold by not more than 5%. For example, in Ref. 2 it was found that the difference of the cross sections for absorption of a photon by the $1s$ shell of the Ar atom when calculated as a form of the radius and as a form of the velocity does not exceed 1–2%. This implies that the contribution of the RPAE channels to the total photoabsorption amplitude does not exceed 2% of the magnitude of the partial amplitude for $1s$ – np photoabsorption. In Refs. 13 and 14 the effect of Auger and RPAE channels on the Hartree–Fock potential for the photoelectron was investigated. The appearance of the Auger-correlation potential leads to the autoionization redistribution of the electron density of the atomic residue. The effect is due to the response of the photoelectron to the Hartree–Fock potential (which changes as a result of the virtual Auger decay of the vacancy) and to the electrostatic interaction of the photoelectron with the Auger electron. Allowance for this effect in the calculation of the photoexcitation cross section of a $2p$ electron of the Ar atom into a collapsing $3d$ state increases the Hartree–Fock cross section by not more than $\sim 3\%$. The appearance of the RPAE-correlation potential¹⁴ leads principally to a change in the Hartree–Fock exchange interaction, and hence to a change in the corresponding magnitude of the quantum attraction of the photoelectron by the vacancy. When the contribution of virtual RPAE channels to the total photoabsorption amplitude (i.e., absorption of a photon by the $3s$ and $3p$ shells of the Ar atom) is substantial, allowance for the RPAE-correlation potential changes the corresponding Hartree–Fock cross sections by not more than $\sim 10\%$.

However, Auger channels play the leading role in the formation of the total width Γ_{1s} of the decay of the $1s$ vacancy in atoms with atomic number $Z \leq 20$ (Ref. 15). In Refs. 7 and 8 the fact of the finite lifetime of a $1s$ vacancy was taken into account only by “smearing out” the theoretical spectrum into Lorentzian dispersion curves with FWHM Γ_{1s} . The theoretical spectrum itself was obtained without taking into account the requirement that the pole Auger channels be included in the procedure for normalization of the total wave function of the final photoabsorption state.

The neglect in Refs. 7 and 8 of channels of Auger decay of the $1s$ vacancy in the normalization of the total wave function of the final photoabsorption state lowered the quality of the theoretical description of the effects of correlation shake and vacuum correlations. On the other hand, when theoretical results from recent papers^{13,16} are taken into account, it is possible to construct a mathematical model for the photoabsorption process in which the procedure for obtaining a Lorentzian spectral function for the differential

photoabsorption cross section and the procedure involving the generalized Hartree–Fock equation for the photoelectron with allowance for the correlation potentials can be made consistent.

Thus, the problem arises of the theoretical description of how the photoabsorption cross section near the ionization threshold of the $1s$ shell of the Ar atom is jointly influenced by many-electron effects of monopole restructuring of the electron shells, correlation shake, vacuum correlations, and virtual Auger decay of the $1s$ vacancy, in the framework of a mathematical model of the photoabsorption process in which:

1) in the normalization of the total wave function of the final photoabsorption state the pole nature of the Auger channels is taken into account;

2) for the photoelectron a generalized Hartree–Fock equation is specified that contains a) a correlation potential due to virtual $3p^2 - n_1(p,d)n_2(p,d)$ excitations/ionization of the $1s^1 np(^1P_1)$ state, and b) effective occupation numbers of the electron shells of the atomic residue, expressed in terms of the spectroscopic factor of the state $1s^1 np(^1P_1)$.

This paper is devoted to solving this problem.

2. THEORY OF THE METHOD

2.1. The energy and wave function of the final state: photoexcitation

We consider a stationary state of the Schrödinger equation for the atom:

$$\hat{H}|E\rangle = E|E\rangle, \quad (1)$$

with the nonrelativistic Hamiltonian

$$\hat{H} = \sum_i \left(-\frac{\Delta_i}{2} - \frac{z}{r_i} \right) + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

and with a total wave function of the final photoexcitation state in the form of a superposition of the state $|E_0\rangle = |n_0 l_0^{4l_0+1} n l\rangle$; nl is the photoelectron), N_1 channels of the nonpole type, and N_2 pole Auger channels of decay of the vacancy ($N = N_1 + N_2$):

$$|E\rangle = \alpha_E \left(|E_0\rangle + \sum_{i=1}^N \sum_{m>F} S \beta_{im}^E |m, i\rangle \right), \quad \langle E|E'\rangle = \delta(E - E'). \quad (3)$$

In (2), Z is the atomic number of the nucleus, \mathbf{r}_i is the position vector of the i th electron of the atom, and the summation is performed over all the electrons of the atom. In (3) α_E is a normalization factor, β_{im}^E are the configuration-interaction coefficients, S denotes summation (integration) over the virtual states of the discrete (continuous) spectrum, F denotes the Fermi level (the set of principal quantum numbers of the valence shell of the atomic residue), and

$$\hat{H}|E_0\rangle = E_0|E_0\rangle, \quad \hat{H}|m, i\rangle = E_{im}|m, i\rangle,$$

$$\langle E_0|E_0\rangle = 1, \quad \langle m, i|m', j\rangle = \delta_{ij}\delta(m - m').$$

Taking into account that

$$\langle m, i | \hat{H} | m', j \rangle = E_{im} \delta_{ij} \delta(m - m'), \quad (4)$$

and neglecting matrix elements of interchannel mixing as quantities of a higher order of smallness in comparison with (4), from (1), (2), and (3) we obtain

$$\beta_{im}^E = V_{im} (E - E_{im})^{-1}, \quad V_{im} \equiv \langle E_0 | \hat{H} | m, i \rangle \quad (5)$$

for channels of the nonpole type, and

$$\beta_{im}^E = V_{im} \{ \mathcal{P}(E - E_{im})^{-1} + z_E \delta(E - E_{im}) \} \quad (6)$$

for Auger channels, where \mathcal{P} signifies the Cauchy principal value.¹⁷ The expression (6) is the equivalent of the general solution in generalized functions,

$$f(x) = \mathcal{P}(1/x) + z \delta(x),$$

of the equation $xf(x) = 1$, with z an arbitrary function that does not depend on x . In contrast to the choice $z = \pm i\pi$ when using the Sokhotskiĭ–Plemel' formula¹⁷

$$\lim_{\varepsilon \rightarrow 0} (x \mp i\varepsilon)^{-1} = \mathcal{P}(1/x) \pm 1\pi \delta(x),$$

in the present paper (taking account of Ref. 18) the function z_E is real, and will be defined below.

Using (5) and (6), after substitution of (3) into (1), for the energy of the final photoexcitation state we obtain

$$E = E_0 + W + F + z_E (\Gamma/2\pi). \quad (7)$$

In (7) we have defined the quantities

$$W = \sum_{i=1}^{N_1} \sum_{m>F} S a_{im} (E - E_{im})^{-1}, \quad a_{im} = |V_{im}|^2, \\ F = \sum_{j=1}^{N_2} f_j, \quad f_j = \mathcal{P} \sum_{m>F} S a_{jm} (E - E_{jm})^{-1}, \quad (8) \\ \Gamma = 2\pi \sum_{j=1}^{N_2} a_{jE},$$

which describe the $W + F$ shift of the resonance photoexcitation energy relative to E_0 , and Γ is the width of this resonance.

The normalization factor α_E in (3) can be obtained from the normalization of the final photoexcitation state:

$$\langle E | E' \rangle = \delta(E - E') = \alpha_E \alpha_{E'} \left(1 + \sum_{i=1}^N \sum_{m>F} S \beta_{im}^E \beta_{im}^{E'} \right). \quad (9)$$

Using the Fano identity¹⁸ for the product of the singular factors

$$\frac{1}{(E - E_{im})(E' - E_{im})} = \frac{1}{E' - E} \left(\frac{1}{E - E_{im}} - \frac{1}{E' - E_{im}} \right) \\ + \pi^2 \delta(E - E') \delta \left(E_{im} - \frac{1}{2} [E + E'] \right),$$

after substitution of (4), (5), and (6) into (9) we obtain

$$|\alpha_E|^2 = \frac{\Gamma}{2\pi} \left\{ (E - E_0 - W - F)^2 + \frac{\Gamma^2}{4} \right\}^{-1}. \quad (10)$$

The function (10) determines a Lorentzian lineshape for the photoexcitation resonance.

2.2 Generalized Hartree–Fock equation for the photoelectron

We carry out subsequent development of the method for an atom with filled shells in the ground state.

The traditional choice for the energy functional for variation of the quantity E from (1) and the subsequent construction of a system of multiconfigurational Hartree–Fock–Jucys equations^{19,20} assumes a lack of pole states in (3). Allowance for pole states, however, means that the expression (7) becomes a definition for the real function z_E , and cannot be used directly for the variation.

With the aim of obtaining a generalized Hartree–Fock equation for the photoelectron from the variational principle, we consider the functional E in (10) for which the factor $|\alpha_E|^2$ in the photoexcitation cross section reaches a maximum, i.e., we consider the solution of the integral equation

$$E - E_0 - W - F = 0. \quad (11)$$

The Hartree–Fock equation can be obtained²¹ from the condition

$$\delta_{nl} \left(E - \sum_{n'} \lambda_{nn'} \langle nl | n' l \rangle \right) = 0, \quad (12)$$

where $\delta_{nl} \equiv \delta / \delta P_{nl}$ is the variational derivative with respect to the radial function $|nl\rangle = P_{nl}(r)$ of the photoelectron, $\lambda_{nn'}$ are Lagrange multipliers that ensure that the photoelectron function is orthogonal to the electron functions (of the atomic residue) of the same symmetry and that the sum contains $n = n'$, and we have used the notation

$$\langle nl | n' l \rangle = \int_0^\infty P_{nl}(r) P_{n'l}(r) dr.$$

We now find $\delta_{nl} E$. We represent each term of the functional (8) by a Taylor series up to and including the first derivative,

$$f_j \approx \bar{f}_j + \zeta_j (E - \bar{E}_j), \\ \zeta_j = \left\{ \frac{\partial}{\partial E} \mathcal{P} \sum_{m>F} S a_{jm} (E - E_{jm})^{-1} \right\}_{E = \bar{E}_j},$$

where, in the Koopmans approximation,²¹ $\bar{E}_j = E_{nl}^j + \varepsilon_j$, where E_{nl}^j is the Hartree–Fock energy of the Auger state j without the Auger electron and ε_j is the energy of the real Auger electron of channel j . Then, taking into account that for atoms with filled shells in the ground state, $\delta_{nl} \bar{f}_j = 0$ and $\delta_{nl} \zeta_j = 0$, from (11) we obtain

$$\delta_{nl} E = s \left(\delta_{nl} E_0 + \sum_{i=1}^{N_1} \sum_{m>F} S \eta_{im} \delta_{nl} E_{im} - \sum_{j=1}^{N_2} \zeta_j \delta_{nl} \bar{E}_j \right). \quad (13)$$

In (13) we put $\eta_{im} = a_{im} / (E - E_{im})^2$ and define the spectroscopic factor^{12,13} of the state $|E_0\rangle$

$$s = \left(1 + \sum_{i=1}^{N_1} \sum_{m>F} S \eta_{im} - \sum_{j=1}^{N_2} \zeta_j \right)^{-1}, \quad (14)$$

which characterizes the "weight" with which this state is represented in the final photoabsorption state.

In the general case, some of the states $|m, i\rangle$ in (3) contain virtual electrons from the continuum. For the energy of such states, we have from (4)

$$E_{im} = \int dm' \langle m, i | \hat{H} | m', i \rangle,$$

and substitution of the variational derivative of this into (13) leads to the cumbersome general structure of the generalized Hartree–Fock equation from (12). Therefore, we shall specialize (12) to the case considered in the present paper (the absorption of a photon by the $1s$ shell of the Ar atom), whereupon $\zeta_j \approx 0$ for each j and the principal contribution to (3) is given by the virtual states

$$|m, i\rangle = |n_0 l_0^{A l_0 + 1} m l^A m_1 l_1 m_2 l_2 n l\rangle$$

with excited $m_{1,2} l_{1,2}$ electrons of the discrete spectrum. Taking (13) and (14) into account, from (12) we obtain the desired generalization of the Hartree–Fock equation for the photoelectron:

$$\left\{ \hat{h}_l + \sum_{n' \leq F} \left(N_{n'l'}^{\bar{s}} Y_{n'n'}^0 + \sum_{k > 0} \alpha_k^{\bar{s}} Y_{n'n'}^k \right) + A^{\bar{s}} - \varepsilon_{nl} \right\} |nl\rangle = \sum_{k \geq 0} \left(\sum_{n' \leq F} \beta_k^{\bar{s}} Y_{nn'}^k |n'l'\rangle + B_n^{\bar{s}k} \right) + \sum_{n' \neq n} \lambda_{nn'} |n'l\rangle. \quad (15)$$

In (15) we have defined the following quantities:

$$\hat{h}_l = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}, \quad (16)$$

$$N_{n'l'}^{\bar{s}} = \bar{s} \left(N_{n'l'}^{(0)} + \sum_{i,m} \eta_{im} N_{n'l'}^i \right), \quad \bar{s} = \left(1 + \sum_{i,m} \eta_{im} \right)^{-1},$$

$$\alpha_k^{\bar{s}} = \bar{s} \left(\alpha_k^{(0)} + \sum_{i,m} \eta_{im} \alpha_k^i \right), \quad \beta_k^{\bar{s}} = \bar{s} \left(\beta_k^{(0)} + \sum_{i,m} \eta_{im} \beta_k^i \right), \quad (17)$$

$$A^{\bar{s}} = \bar{s} \sum_{i,m} \eta_{im} \left(Y_{m_1 m_1}^0 + \sum_{k > 0} \alpha_k^i Y_{m_1 m_1}^k + m_1 \rightarrow m_2 \right),$$

$$B_n^{\bar{s}k} = \bar{s} \sum_{i,m} \eta_{im} \left(\beta_k^i Y_{nm_1}^k |m_1 l_1\rangle + m_1 \rightarrow m_2 \right), \quad (18)$$

$$Y_{nn'}^k = \frac{1}{r} \left\{ \int_0^r dr' P_{n'l'}(r') \left(\frac{r'}{r} \right)^k P_{nl}(r') + \int_r^\infty dr' P_{n'l'}(r') \left(\frac{r}{r'} \right)^{k+1} P_{nl}(r') \right\},$$

where $\sum_{i,m}$ denotes summation over $i=1,2,\dots,N_1$, and $m_{1,2} > F$; $N_{n'l'}^{(0)}$ and $N_{n'l'}^i$ (the occupation numbers of the $n'l'$ shell of the atomic residue) and $\alpha^{(0)}$, $\beta^{(0)}$, α^i , β^i (the angular coefficients in the Slater integrals) are defined for the configurations $|E_0\rangle$ and $|m, i\rangle$, respectively; $\varepsilon_{nl} = \lambda_{nn}$ is the photoelectron energy.

When $V_{im} = 0$ for all i , Eq. (15) goes over into the equation of the one-configuration Hartree–Fock approximation used in Ref. 3.

According to (15), the photoelectron moves in the field of the atomic residue with effective electron-shell occupation numbers $N_{n'l'}^{\bar{s}} \leq N_{n'l'}^{(0)}$. Thus, in the case of absorption of a photon by the $1s$ shell of the Ar atom with the total wave function (3) of the final photoabsorption state, constructed from the wave functions of the states $|E_0\rangle = |1s' np\rangle$ and $|m, i\rangle = |1s' 3p^4 m_1(p, d) m_2(p, d) n p\rangle$, it follows from (16) that

$$N_{1s}^{\bar{s}} = 1, \quad N_{2s}^{\bar{s}} = N_{3s}^{\bar{s}} = 2, \quad N_{2p}^{\bar{s}} = 6, \quad (19)$$

$$N_{3p}^{\bar{s}} = 6 - 2(1 - \bar{s}), \quad \bar{s} < 1.$$

According to (17), the "missing" $2(1 - \bar{s})$ part of the electron density of the $3p$ shell of the atomic residue is distributed over the virtual $m_{1,2}(p, d)$ states. The appearance of the direct (17) and exchange (18) correlation potentials of the electrostatic interaction of the photoelectron with the virtual $m_{1,2}(p, d)$ electrons does not cancel the enhancement of the attraction of the photoelectron by the nucleus as a result of shake of the $3p$ shell of the atomic residue. As a consequence, the mean radius of the wave function and the binding energy of the photoelectron are decreased in comparison with those calculated in the one-configuration Hartree–Fock approximation. The corresponding changes in the theoretical photoabsorption cross section can be interpreted as correlation shake⁷ of the electron density of the $3p$ shell in the final state of the absorption of a photon by the $1s$ shell of the Ar atom.

2.3 Photoexcitation cross section

We shall assume that the total wave function of the initial state of the photoabsorption should be determined as a superposition of the ground state $|0\rangle$ of the atom and its virtual, nonpole states $|m\rangle$ of excitations/ionization:

$$|\bar{0}\rangle = \alpha_0 |0\rangle + \sum_{m > F} \beta_{m,0} |m\rangle, \quad \langle \bar{0} | \bar{0} \rangle = 1, \quad (20)$$

$$|\alpha_0|^2 = \left(1 + \sum_{m > F} |\beta_{m,0}|^2 \right)^{-1}.$$

Then, following Ref. 21 and using (3) and (20), we obtain an expression for the cross section and oscillator strengths of the $n_0 l_0 - n l$ transitions in natural units ($\hbar = m = e = 1$)

$$\sigma_{n_0 l_0}^{nl}(\omega) = \frac{8}{3} \alpha (\pi a_0)^2 l_m \omega_{nl} |\alpha_0 \alpha_\omega (M + \Phi)|^2, \quad (21)$$

$$f_{nl} = \sigma_{n_0 l_0}^{nl}(\omega_{nl}) / 2\alpha (\pi a_0)^2, \quad (22)$$

where

$$\omega = E - E(\bar{0}), \quad \omega_{nl} = E_0 + W + F - E(\bar{0}),$$

α is the fine-structure constant, a_0 is the Bohr radius, $l_m = \max(l_0, l)$; $E(\bar{0})$ is the energy of the state described by the wave function (20), ω is the energy of the absorbed photon, and ω_{nl} is the energy of the $n_0 l_0 - n l$ transition. In (21), M is the radial part of the matrix element $\langle 0 | \hat{D} | E_0 \rangle$ of the transition operator. The correction of this is

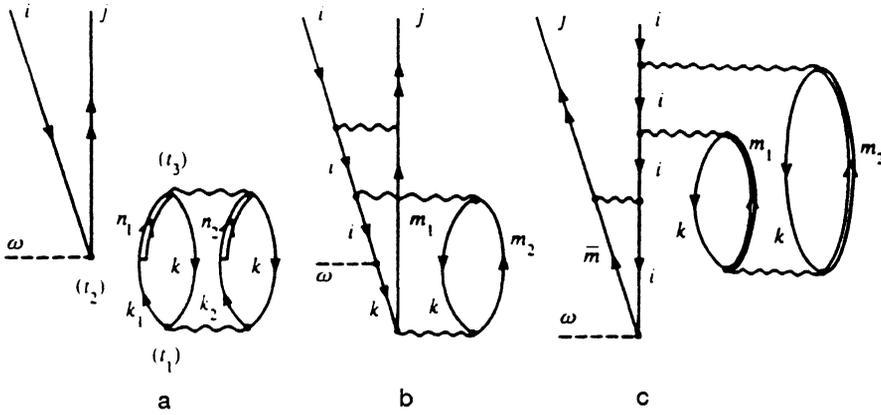


FIG. 1. First leading terms in the infinite series of Goldstone-Feynman diagrams for the partial amplitudes C (a), A (b), and B (c) in the case of absorption of a photon by the $1s$ shell of the Ar atom.

$$\Phi = \frac{1}{\sqrt{2}l_m} (A + B + C) \quad (23)$$

and is due to the structure of the states $|E\rangle$ and $|\bar{0}\rangle$:

$$A = \langle 00 | \hat{D} | E_0 \rangle, \quad B = \langle 0 | \hat{D} | ++ \rangle, \quad C = \langle 00 | \hat{D} | ++ \rangle,$$

$$|00\rangle = \sum_{m>F} S \beta_{m,0} |m\rangle, \quad |++\rangle = \sum_{i=1}^N \sum_{m>F} S \beta_{im}^\omega |m, i\rangle.$$

The quantity M describes the Hartree-Fock photoexcitation amplitude with allowance for the restructuring of the shells of the atomic residue in the field of the vacancy. For example, in the case of absorption of a photon by the $1s$ shell of the Ar atom, by the methods of the theory of nonorthogonal orbitals,⁹ to within terms of first order of smallness and with allowance for the requirement that the $1s^1 np$ state be orthogonal to the energetically lower-lying $ms^1 np$ states ($m=2,3$) of the same symmetry, in the dipole approximation for the transition operator we obtain

$$M = N_{1s} \left(\langle 1s_0 | \hat{r} | np \rangle - \sum_{m=2,3} \langle 1s_0 | \hat{r} | mp \rangle \frac{\langle mp_0 | np \rangle}{\langle mp_0 | mp \rangle} \right). \quad (24)$$

In (24) N_{1s} is the product of overlap integrals of the wave functions of the electrons of the atomic residue that do not take part in the transition; the states $|l_0\rangle$ and $|l\rangle$ are obtained by solving the Hartree-Fock equations for the configurations $1s_0^2(^1S_0)$ and $1s^1 np(^1P_1)$, and

$$\langle n1 | \hat{r} | n'l' \rangle = \int_0^\infty P_{nl}(r) P_{n'l'}(r) r dr.$$

A nonzero value of the amplitude Φ leads to corresponding changes in the Hartree-Fock cross section, which in Ref. 8 were interpreted as a vacuum correlation effect. The partial photoabsorption amplitudes in (23) describe A) virtual excitation/ionization of the vacuum up to the moment of absorption of the photon by the atom; B) virtual excitation/ionization of the atomic residue; C) interference of virtual excitations/ionizations of the vacuum and the atomic residue.

A physical interpretation of the vacuum correlations is conveniently given in the representation of Goldstone-Feynman diagrams in many-body theory.¹² In Fig. 1, in the case of absorption of a photon by the $1s$ shell of the Ar atom

the first (principal) terms of the infinite diagrammatic series for the amplitudes A , B , and C are given. The following notation is introduced: ω is the absorbed photon, i is the $1s$ vacancy, j is the np photoelectron, an arrow above (below) means that the state lies above (below) the Fermi level; a line with one arrow means that the state is obtained in the Hartree-Fock field of the configuration $1s_0^2(^1S_0)$; a line with two arrows means that the state is obtained with allowance for correlation shake; a double line means that the state is obtained in the Hartree-Fock field of the $1s^1(^2S_{1/2})$ configuration; the combination of a line with a double line corresponds to an overlap integral; a wavy line corresponds to the Coulomb interaction; the direction of time is from bottom to top ($t_1 < t_2 < t_3$). As follows from Fig. 1, in order of magnitude the inequality $C > A > B$ has been determined.

2.4 Photoionization

For an nl photoelectron in the continuum, the total wave function of the final photoionization state is obtained in the same way as (3):

$$|E_n\rangle = \alpha_{En} \left(|E_0^n\rangle + \sum_{i=1}^N \sum_{m,n'>F} S \beta_{im}^{nn'}(E) |mn'; i\rangle \right). \quad (25)$$

The subsequent analysis and results are analogous to those in the case of photoexcitation. However, the description of the photoionization amplitude and cross section has its distinctive features.

The amplitudes A and C in (23) contain divergent overlap integrals $\langle ml_0 | nl_+ \rangle$ of radial continuum functions from different basis sets: the states $|ml_0\rangle$ are obtained in the atomic-residue Hartree-Fock field formed upon virtual excitations/ionization of the state $|0\rangle$; the states $|nl_+\rangle$ are obtained in the atomic-residue Hartree-Fock field formed upon virtual excitations/ionization of the state $|E_0\rangle$. Since the numerical calculation of such integrals is impossible, it is necessary to establish the analytic form of their singular and regular parts. The solution of this problem is given in the Appendix.

According to (25), the differential photoionization cross section is proportional not to a Dirac δ -function but to a

Lorentzian spectral function (10). Integrating it over the photoelectron energy, we obtain for the photoionization cross section

$$\sigma_{n_0 l_0}(\omega) = \int_0^\infty \sigma_{n_0 l_0}^{n l}(\omega) d\varepsilon_{n l}. \quad (26)$$

3. RESULTS OF THE CALCULATION

The method detailed above was applied to the calculation of the cross section for absorption of a photon by an Ar atom near the threshold of ionization of the 1s shell.

In the construction of the complete final-state wave functions (3) and (25), we took into account virtual discrete excitations $A_{12} = 3p^{-2} - m_1 d m_2 d$ of the outer 3p shell, which give an ~85% contribution to the spectroscopic factor \bar{s} . In the construction of the total initial-state wave function (20), we took into account the virtual double-excitation channels $A_{12} = 3p_0^{-2} - \varepsilon_1(p, d)_0 \varepsilon_2(p, d)_0$ of the outer 3p shell, which give an ~80% contribution to the normalization factor α_0 . The wave functions of the virtual $m_{1,2}d$ and $\varepsilon_{1,2}(p, d)_0$ electrons are obtained in the term-averaged Hartree-Fock fields of the configurations $1s^1 3p^5$ and $3p_0^5$, respectively. Here, the wave functions of the electrons of the atomic residues are obtained by solving the Hartree-Fock equations for the configurations $1s^1(^2S_{1/2})$ and $1s_0^2(^1S_0)$, respectively. The virtual channels $B_{12} = 3s^{-2} - n_1 l_1 n_2 l_2$ and $C_{12} = 3s^{-1} 3p^{-1} - n_1 l_1 n_2 l_2$, which give only an ~15% contribution to \bar{s} and α_0 , were not taken into account. However, in the calculation of the effective occupation numbers in (15) and the photoabsorption cross sections (21) and (26) we used the values $\bar{s} = 0.9042$ and $\alpha_0 = 0.9400$ determined by the A_{12} , B_{12} , and C_{12} channels.

The contribution of the virtual channels of Auger decay of the 1s vacancy to the spectroscopic factor (14) did not exceed 1%. For example, when we restrict attention to just the fundamental $2p^4 \varepsilon d n p(^1P_1)$ Auger channel, which gives an ~65% contribution to the theoretical width $\Gamma_{1s} = 0.69$ eV (Ref. 15), for the quantity ζ in (14) we obtain 0.0000224. Therefore, in the construction of the total final-state wave function the Auger channels were taken into account only in terms of the 1s-vacancy decay width formed by them, which appears in the normalization factor (10). As Γ_{1s} in this work we took the FWHM of the line profile of the 1s-4p photoexcitation in the experimental spectrum of the absorption of a photon by the 1s shell of the Ar atom,⁵ which is equal to 1.20 eV.

The photoelectron wave function, the oscillator strengths of the transitions (22), and the photoabsorption cross sections (21) and (26) were calculated with allowance for the monopole restructuring of the electron shells in the following approximations.

1) Approximation I: The photoelectron states were obtained by solving the Hartree-Fock equation for the configuration $1s^1 n p(^1P_1)$; the wave functions of the electrons of the atomic residue were obtained by solving the Hartree-Fock equations for the configuration $1s^1(^2S_{1/2})$. In the construction of the Hartree-Fock photoabsorption amplitude (24), the requirement that the state $1s^1 n p$ be orthogonal to

TABLE I. Intensities I_{np} and oscillator strengths f_{np} of the principal $1s-np$ transitions for the argon atom in approximations I and II.

n	I_{np} , Mb*		$f_{np} \cdot 10^3$	
	I	II	I	II
4	0.0940	0.1130	1.6142	1.9405
5	0.0309	0.0340	0.5306	0.5839
6	0.0146	0.0150	0.2507	0.2576

*The intensity of the transition is determined by the resonance value of the photoexcitation cross section (21): $I_{np} = 2\sigma_{1s}^{np}(\omega_{np})/\pi\Gamma_{1s}$.

the states $m s^1 n p$ ($m = 2, 3$) of the same symmetry is realized using the Gram-Schmidt orthogonalization procedure.²²

2) Approximation II: The photoelectron states for the calculation of the partial photoabsorption amplitude M in (21) were obtained by solving the generalized Hartree-Fock equation (15) for the photoelectron in the configuration $1s^1 3p^{n-1} 3d^{n-1} n p(^1P_1)$, in which the effective occupation number $n_1 = 5.8083$ of the 3p shell was calculated using Eq. (19) and the nonzero population of the virtual $m_{1,2}d$ orbitals was represented by the electron density of the 3d shell with occupation number $n_2 = 6 - n_1$. The wave function of the 3d electron was obtained by solving the Hartree-Fock equation for the configuration $1s^1 3p^4 3d^2(^2S_{1/2})$. This model for the description of the correlation-shake effect was adopted because the virtual $3p^{-2} - 3d^2$ excitation gives the principal (~65%) contribution to the spectroscopic factor \bar{s} . The calculation showed that near the ionization threshold of the 1s shell, the correlation-shake effect increases the Hartree-Fock values of the amplitude M by not more than ~2.5%. This made it possible in the calculation of the partial photoabsorption amplitudes A , B , and C in (23) to obtain the photoelectron state in the approximation I. In the calculation of the amplitude A containing the overlap integral $\langle \varepsilon p | \varepsilon_{1,2} p_0 \rangle$, results from the Appendix were used.

The results of the calculation of the characteristics of the discrete spectrum and the cross section for absorption of a photon by the 1s shell of the Ar atom in the approximations described above are given in Table I and in Fig. 2.

In Table I we give the data of the calculation only for transitions with principal quantum number $n = 4, 5, 6$. Lines with $n \geq 7$ were not calculated, and, in particular, the magnitude of the dip in the photoabsorption intensity in the region $\omega \approx 3203$ eV in the theoretical cross section is connected with this. For the threshold energy for ionization of the 1s shell in the one-configuration Hartree-Fock approximation with allowance for the relativistic correction $\Delta\omega_K = 10.0$ eV (Ref. 23) the value $\omega_K = 3204.30$ eV was obtained; $\omega_K - \omega_{np} = 2.56, 1.20, 0.34$ eV for $n = 4, 5, 6$, respectively. The magnitudes of the correlation corrections W and F in (10) to the Hartree-Fock values of the transition energies and ionization threshold were not calculated, since they were estimated not to exceed 1-2 eV.

We now analyze the changes in the characteristics of the 1s-4p transition, which describes the brightest line in the spectrum. Allowance for correlation shake leads to only a ~5% increase in the intensity for the 1s-4p photoexcitation. This is explained by the fact that the p symmetry of the

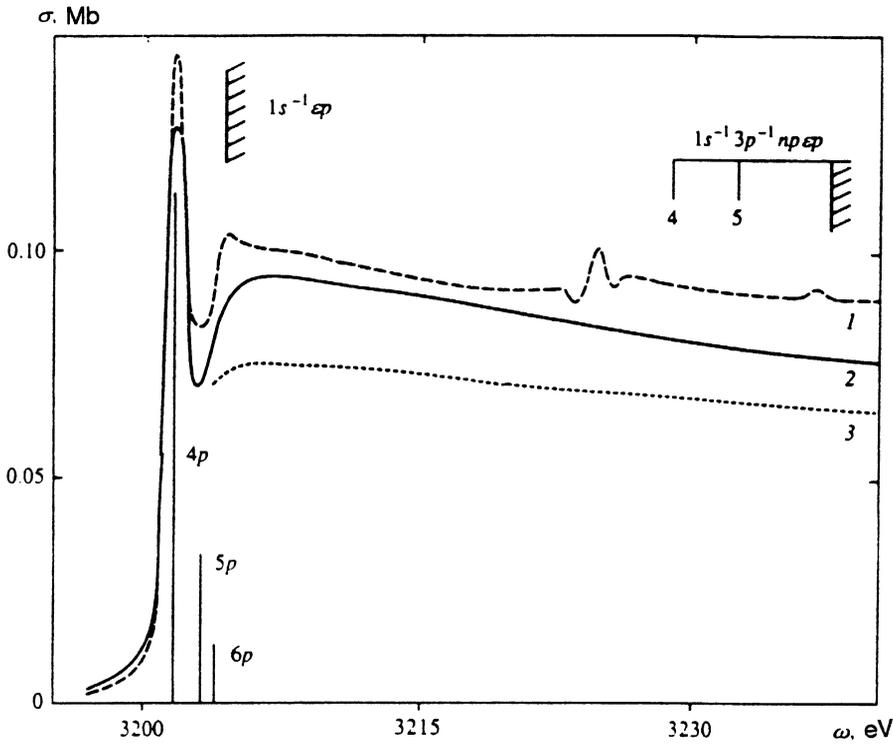


FIG. 2. Cross section for absorption of a photon by the $1s$ shell of the argon atom (theory from this paper): 1) experiment⁵; 2) approximation II; 3) approximation I. The height of the vertical straight line is equal to the photoexcitation intensity I_{np} from Table I; ω is the energy of the absorbed photon.

excited states in the absorption of a photon by the $1s$ shell of the Ar atom is not a collapsing symmetry, and, thus, responds only weakly to the appearance of a correlation potential supplementing the Hartree–Fock potential in the generalized Hartree–Fock equation (15) for the photoelectron. The principal influence on the characteristics of the discrete spectrum as calculated in approximation I comes from vacuum correlations. According to the data in Table I, it increases the intensity and oscillator strength of the $1s$ – $4p$ transition by $\sim 12\%$.

When we go from the discrete spectrum to the continuum, the role of the correlation-shake effects and vacuum correlations does not change qualitatively: the correlation-shake effect increases the Hartree–Fock values of the cross section near the ionization threshold of the $1s$ shell by $\sim 5\%$, while vacuum correlations increase them by $\sim 15\%$. This result qualitatively confirms the result of Ref. 8, although it does not make it quantitatively more accurate.

According to the results of Fig. 2, allowance for vacuum correlations leads to a redistribution of the photoabsorption intensity calculated in approximation I near the ionization threshold of the $1s$ shell, thereby establishing $\sim 90\%$ agreement between the theory of this paper and experiment.⁵

The nearby fine structure in the spectrum of the absorption of a photon by the $1s$ shell of the Ar atom, observed⁵ in the region $\omega \geq 3223$ eV (Fig. 2) is due to one-photon double excitation/ionization $1s^{-1}3p^{-1} - n_1l_1n_2l_2$ of the ground state of the argon atom. A calculation and interpretation of this structure in the framework of the nonrelativistic multi-configurational Hartree–Fock approximation with allowance for multiplet effects and monopole restructuring of the electron shells in the field of the $1s$ and $3p$ vacancies are given in Ref. 24.

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APPENDIX

We now establish the analytic structure of the overlap integral of the radial functions of the continuum that satisfy the Hartree–Fock self-consistent field equations:

$$\begin{aligned} (\hat{h}_l + V^+ - \varepsilon_n^+) |nl_+\rangle &= |\Psi_n^+\rangle, \\ (\hat{h}_l + V^0 - \varepsilon_m^0) |ml_0\rangle &= |\Psi_m^0\rangle, \end{aligned} \quad (\text{A1})$$

where

$$\begin{aligned} V &= \sum_{n' \leq F} \left(N_{n'l'} Y_{n'n'}^0 + \sum_{k>0} \alpha_k Y_{n'n'}^k \right), \\ |\Psi_n\rangle &= \sum_{k \geq 0} \sum_{n' \leq F} \beta_k Y_{nn'}^k |n'l'\rangle + \sum_{m' \leq F} \lambda_{nm'} |m'l\rangle. \end{aligned}$$

We require that the overlap integrals be real:

$$\langle ml_0 | nl_+\rangle = \langle nl_+ | ml_0\rangle.$$

Then, from (A1) for $r < \infty$, it follows that

$$X_{mn}(r) \Delta_{nm} = Q_{mn}(r) + L_{mn}(r), \quad (\text{A2})$$

where

$$X_{mn}(r) = \int_0^r P_n^+(z) P_m^0(z) dz = \langle ml_0 | nl_+\rangle_r,$$

$$\Delta_{nm} = \varepsilon_n^+ - \varepsilon_m^0,$$

$$Q_{mn}(r) = \frac{1}{2} \left(P_n^+ \frac{dP_m^0}{dr} - P_m^0 \frac{dP_n^+}{dr} \right),$$

$$L_{mn}(r) = \langle ml_0 | V^+ - V^0 | nl_+ \rangle_r + \langle nl_+ | \Psi_m^0 \rangle_r - \langle ml_0 | \Psi_n^+ \rangle_r.$$

The expression (A2) was obtained under the condition that the functions $P_n^+(0)=0$ and $P_m^0(0)=0$ and that their first derivatives be bounded as $r \rightarrow 0$.

We consider $X_{mn}(r)$ to be the kernel of the integral operator that acts on a certain function φ in accordance with the rule

$$\mathcal{P} \int_0^\infty [Q_{mn}(r) + L_{mn}(r)] \Delta_{nm}^{-1} \varphi(\varepsilon_m^0) d\varepsilon_m^0. \quad (\text{A3})$$

The function $\varphi(x)$ is assumed to be defined and continuous for all x in the range $[0, \infty)$.

We assume that the physically observable asymptotic form of the Hartree–Fock potential of the atomic residue corresponds to the screened Coulomb potential $V \propto q r^{-(1+\rho)}$, where q is the multiplicity of the ion and ρ can be an arbitrarily small but nonzero positive quantity.²⁵ In this case the exact asymptotic solution of the Hartree–Fock equation (A1) for the radial wave function in the continuous spectrum has the form

$$P_{nl}(r) \sim \sqrt{\frac{2}{\pi k_n}} \sin \left(k_n r - \frac{\pi l}{2} + \gamma_{nl} \right),$$

where $k_n^2 = 2\varepsilon_{nl}$ (ε_{nl} is the energy of the nl electron) and γ_{nl} is the phase shift (dependent on ε_{nl}) of the electron wave in the given Hartree–Fock potential.

Then, using the following representations for the Dirac δ -function:¹⁷

$$\lim_{r \rightarrow \infty} \frac{\sin(xr)}{\pi x} = \delta(x),$$

$$\lim_{r \rightarrow \infty} \frac{1 - e^{-ixr}}{ix} = \pi \delta(x) - i \mathcal{P} \left(\frac{1}{x} \right),$$

$$\delta(x-a) + \delta(x+a) = 2|a| \delta(x^2 - a^2),$$

and

$$\int_0^a \varphi(x) \delta(x-a) dx = \frac{1}{2} \varphi(a),$$

$$\int_0^\infty \varphi(x) \delta(x) dx = \frac{1}{2} \varphi(0)$$

we obtain from (A3) the desired expression for the overlap integral as a real generalized function of the form

$$\langle ml_0 | nl_+ \rangle = \cos(\gamma_{nl}^+ - \gamma_{nl}^0) \delta(\Delta_{nm}) + \mathcal{A} L_{mn} \Delta_{nm}^{-1}, \quad (\text{A4})$$

where $L_{mn} \equiv L_{mn}(\infty)$.

The singular part of the integral (A4) corresponds to the normalization condition for continuum functions from the same basis set. In fact, since

$$\lim_{+ \rightarrow 0} L_{mn} = 0, \quad \lim_{+ \rightarrow 0} (\gamma_{nl}^+ - \gamma_{nl}^0) = 0,$$

we have, according to (A4),

$$\lim_{+ \rightarrow 0} \langle ml_0 | nl_+ \rangle = \delta(\Delta_{nm}).$$

The regular part of the integral (A4) and the difference of the phase shifts is due the difference of the Hartree–Fock potentials in Eqs. (A1) for the states $|ml_0\rangle$ and $|nl_+\rangle$.

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