Difference between the atomic ionization spectra in (γ, e) and $(e, 2e)$ reactions

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It is shown that the relative intensity of the principal and satellite lines in the atomic ionization spectrum depends significantly on the mechanism responsible for the formation of the ion. This dependence is explained by the influence of many-electron correlations in the initial state of the atom to be ionized, which is considerable in the case of photoionization [(γ, e) reaction] but, under certain definite conditions the effect is small for ionization by electron impact [symmetric, noncoplanar $(e, 2e)$ reaction]. Consequently, the spectroscopic factor for the different final states of the ion, as defined in the usual way, can be measured only for the symmetric, noncoplanar $(e, 2e)$ reaction, but a more involved interpretation is necessary for the (γ, e) reaction. Comparison of the calculated spectroscopic factors of the eigenstates of the ArII^2S ion with the corresponding experimental data on the (γ, e) and $(e, 2e)$ reactions has confirmed these conclusions.

1. INTRODUCTION

It will be shown in this paper that the relative line intensity in the atomic ionization spectrum, which determines the spectroscopic factors of the different final states of the ion, depends on the mechanism responsible for the ionization process and may be different for photoionization [(γ, e) reaction] and ionization by electron impact [symmetric noncoplanar $(e, 2e)$ reaction]. This difference is explained by the influence of many-electron correlations in the initial state of the atom to be ionized, which means that the concept of the spectroscopic factor assumes a more complicated physical meaning.

The problem of the difference between the ionization spectra of the same atomic shell in the (γ, e) and $(e, 2e)$ reactions arises in connection with measurements of the spectroscopic factor of the outermost shell of inert-gas atoms.[1] Photoelectron spectroscopy and inelastic scattering of fast electrons yield very different values of the spectroscopic factor of the same final state of the ion.

On the other hand theoretical analysis of ionization spectra has shown that the spectroscopic factors of the two reactions should be equal. This analysis[1] is based on the assumption of the Hartree-Fock character of the initial state of the target atom. Under this condition, the spectroscopic factor of an arbitrary final state of the ion is defined as the contribution to the state of the Hartree-Fock configuration in the form of a vacancy (hole) in the "frozen" atomic core. The spectroscopic factor defined in this way is a purely structural characteristic of the final state of the ion, and should not depend on the ionization mechanism.

In a preliminary communication,[2] we have demonstrated that there is a definite type of many-electron correlation in the initial state of the atom that has an appreciable effect on the relative line intensity in the energy spectrum of the final states of the ion, and that this effect is different for photoionization and for ionization by electron impact. We shall show in this paper that this property of correlations in the initial state of the atom can be used to explain the difference between ionization spectra in the (γ, e) and $(e, 2e)$ reactions. We shall also show that the spectroscopic factors measured in the two reactions have a different physical meaning.

We shall take many-electron correlations into account by a perturbation theory in the direct electron interaction, constructed on the basis of the Hartree-Fock many-particle wave functions. If we know the exact wave functions of the initial and final states of the system, we can calculate the amplitude and cross section for the ionization process. In Section 2, we give for the (γ, e) and $(e, 2e)$ cross sections expressions obtained on the usual assumption of the Hartree-Fock nature of the ground state of the ionized atom, which are then improved by taking into account many-electron correlations in this state. It will be shown in Section 3 that the relative line intensity in the ionization spectrum is then determined not only by the contribution of the pure one-hole component of the wave function in the final state of the ion, but also by the contributions of the more complicated component consisting of two holes and an excited electron. The relative magnitude of these contributions and, consequently, the line intensity is a complicated function of the method of ionization [(γ, e) or $(e, 2e)$] and of the reaction kinematics.

The ionization spectra of the outermost shells of inert-gas atoms are analyzed in Sections 4 and 5. By using the explicit form of the expansion of the wave function of the final state of the ion in the Hartree-Fock basis, we have been able to perform a complete analysis of the ionization spectra produced in (γ, e) and $(e, 2e)$ reactions, and to deduce simple expressions for the spectroscopic factor. The results of this analysis can be summarized as fallows. For ionization by photons with arbitrarily high energy, the contributions of the pure single-hole and of the more complicated components of the ion wave function to the relative intensity of the lines are of the same order of magnitude. As a result, the spectroscopic factor of the (γ, e) reaction does not have the simple physical meaning assumed previously, and the existing interpretation of photoionization spectra turns out to be

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invalid.

For the $(e, 2e)$ reaction, the relative intensity of the lines in the ionization spectrum is strongly dependent on the momentum transferred to the ions in the course of the reaction. When the transferred momentum is large, the relative line intensities are given by an expression analogous to that in the case of photoionization, i.e., the spectroscopic factors of the (γ, e) and $(e, 2e)$ reactions are equal. In the other limiting case of very low transferred momenta, we can neglect the correction in the expression for the relative line intensity that represents the contribution of the ion state in the form of two holes and an excited electron. As a result, the spectroscopic factor is found to be equal to the contribution of the simple one-hole final state of the ion.

It was previously considered that it was precisely this quantity that was measured in both (γ, e) and $(e, 2e)$ reactions.

The origin of the discrepancy between the spectroscopic factors obtained in (γ, e) and $(e, 2e)$ experiments is now clear. As a rule, the spectroscopic factor has been measured in the symmetric, noncoplanar $(e, 2e)$ reaction in which the momentum transferred to the ion is small. This means that physically very different quantities were measured in the (γ, e) and $(e, 2e)$ reactions.

These conclusions are in agreement with calculations of the spectroscopic factor of the ground and several excited states of the ion ArII^2S, which are listed in Section 6. Two sets of values of the spectroscopic factor corresponding to the limiting cases of large and small transverse momenta have been calculated. As expected, the first set is in agreement with photoionization data, whereas the second is in agreement with inelastic scattering of fast electrons.

2. IONIZATION CROSS SECTION OF AN ATOM WITH ALLOWANCE FOR CORRELATIONS IN THE FINAL STATE OF THE ION

We shall assume a Hartree-Fock type ground state of the target atom, and will describe it by the wave function $|N, 0\rangle$, which is the antisymmetrized product on N one-electron wave functions. The final state of the ion will be described by the function $|N-1, \alpha\rangle$, where α is the quantum number or a set of quantum numbers defining the state of the ion. Let us expand this function over the Hartree-Fock basis:

$$|N-1, \alpha\rangle = t_i^{\alpha}\hat{a}_i|N, 0\rangle + \sum_{jlk} t_{jlk}^{\alpha}\hat{a}_j\hat{a}_l\hat{a}_k^{+}|N, 0\rangle + \ldots, \tag{1}$$

where a_i and a_k^{+} are the second quantization operators corresponding, respectively, to the annihilation and creation of an electron in a definite Hartree-Fock state. The first term on the right-hand side of (1) is therefore a hole in the frozen atomic core, the second consists of two holes and an excited electron, and so on. The quantum numbers $i, j, l, k, \ldots$ in (1) are such that all the states in the expansion have the orbital angular momentum and the spin of the exact state α of the ion.

The quantity

$$S_{\alpha} = |t_i^{\alpha}|^2 = |\langle N-1, \alpha|\hat{a}_i|N, 0\rangle|^2 \tag{2}$$

defines the contribution of the pure one-hole state $\hat{a}_i|N, 0\rangle$ to the exact state $|N-1, \alpha\rangle$. It is precisely this quantity that is usually referred to as the spectroscopic factor because, in the absence of correlations in the initial state of the atom, it determines the intensity of the corresponding lines in the ionization spectra.

Let us therefore now consider the ionization of an atom by electron impact. Suppose that a fast electron with momentum $\mathbf{K}_0$ collides with an atom in the state $|N, 0\rangle$. Ionization results in the appearance of an ion in the state $|N-1, \alpha\rangle$ and two electrons with momenta $\mathbf{K}_1$, $\mathbf{K}_2$. When the two secondary electrons are also fast, the reaction is an elastic collision between two free electrons, one of which is the atomic electron with momentum $\mathbf{q}_1$ before collision, which is given by the conservation law $\mathbf{K}_0 + \mathbf{q}_1 = \mathbf{K}_1 + \mathbf{K}_2$. Under these conditions the reaction amplitude can be shown[3] to split into two parts. One of them describes the elastic collision between two free electrons which, in the center-of-mass system, looks like scattering by a Coulomb center. The other is the Fourier component of the overlap integral of the wave functions of the initial state of the atom and the final state of the ion:

$$F_{0\alpha}(\mathbf{q}) = \int d^3r \exp(-i\mathbf{qr})\langle N-1, \alpha|N, 0\rangle, \tag{3}$$

where $\mathbf{q} = -\mathbf{q}_1$ is the momentum transferred to the ion.

Let us now substitute the expansion (1) in (3), and use the obvious relationship

$$\langle N, 0|\hat{a}_i|N, 0\rangle = \varphi_i(\mathbf{r}), \qquad \langle N, 0|\hat{a}_j\hat{a}_l\hat{a}_k^{+}|N, 0\rangle = 0.$$

None of the other terms in (1) will contribute to the overlap integral either, since the corresponding combination of the creation and annihilation operators averaged over the ground state of the atom will yield zero. The final result is

$$F_{0\alpha}(\mathbf{q}) = t_i^{\alpha}\varphi_i(\mathbf{q}),$$

where $\varphi_i(\mathbf{q})$ is the Fourier component of the one-electron wave function corresponding to the ith Hartree-Fock orbital.

The ionization cross section for the process in which secondary electrons with particular energy and angle of emission are recorded in coincidence is determined by the square of the amplitude, summed over all the final states of the ion. Apart from a constant kinematic factor, we have

$$\frac{d\sigma}{d\mathbf{k}_1\, d\mathbf{k}_2} \backsim \sum_{\alpha} S_{\alpha}|\varphi_i(\mathbf{q})|^2 \delta(E_0 - E_1 - E_2 + \varepsilon_{\alpha}), \tag{4}$$

where E_0, E_1, and E_2 are the energies of the incident and emitted electrons, respectively, and $\varepsilon_{\alpha} = E(N, 0) - E(N-1, \alpha)$ is the energy of the ion in the state α, measured from the ground-state energy of the atom. It follows from (4) that a δ-shaped line in the energy spectrum of the final states of the ion corresponds to each final state of the ion, and the relative intensity of the line is S_{α}. The quantity S_{α} is therefore the spectroscopic factor of the ion state α.

An analogous result is valid for photoionization. The photoionization amplitude is determined by the matrix element of the electron interaction operator:

$$\langle f, N-1, \alpha| \sum_{a=1}^{N} \hat{z}_a|N, 0\rangle = t_i^{\alpha}\langle f|\hat{z}|i\rangle,$$

where $|f\rangle$ is the photoelectron wave function. In deriving this expression, we have used the expansion (1). Apart from an unimportant constant factor, the photoionization cross section is given by

$$\frac{d\sigma}{dE_f}\infty\sum_{\alpha}S_\alpha|\langle f|\hat{z}|i\rangle|^2\delta(\omega-E_f+\varepsilon_\alpha),\qquad(5)$$

where ω is the photon energy and E_f the energy of the photoelectron.

Comparison of (4) and (5) will show that the relative line intensities in the photoionization spectrum and the spectrum produced by electron impact are equal, as are the spectroscopic factors defined by (2), which gives the spectroscopic factor as the fraction of the pure one-hole component in the ion wave function.

3. ALLOWANCE FOR CORRELATIONS IN THE INITIAL STATE OF THE ATOM

When many-electron correlations are taken into account, the wave function of the initial state of the atom can be written in the form

$$|N\rangle=t_0|N,0\rangle+\sum_{jlpk}t_{jlpk}\hat{a}_j\hat{a}_l\hat{a}_p^+\hat{a}_k^+|N,0\rangle+\dots.$$

The terms omitted from this expansion correspond to the simultaneous creation of two or more electron-hole pairs. The term corresponding to the creation of one pair does not appear because correlations of this type have already been taken into account in the Hartree-Fock approximation (by definition). We shall confine our attention to first-order perturbation theory in the direct electron interactions. In this approximation, the initial-state wave function of the atom is given by

$$|N\rangle=t_0\left\{|N,0\rangle+\sum_{jlpk}\frac{\langle pk|\hat{V}|jl\rangle}{\varepsilon_p+\varepsilon_k-\varepsilon_j-\varepsilon_l}\hat{a}_j\hat{a}_l\hat{a}_p^+\hat{a}_k^+|N,0\rangle\right\},\qquad(6)$$

where we have used the expression for the coefficient t_{jlpk}, given in Ref. 4, in which ε_n, $n=j, l, p, k$ are the energies of the corresponding one-particle Hartree-Fock states and $\langle pk|\hat{V}|jl\rangle$ is the matrix element of the Coulomb interaction between electrons.

The final-state wave function of the ion is given by the following expression in first-order perturbation theory:

$$|N-1,\alpha\rangle=t_i^\alpha\left\{\hat{a}_i|N,0\rangle+\sum_{jlk}\frac{\langle ik|\hat{V}|jl\rangle}{\varepsilon_\alpha-\varepsilon_j-\varepsilon_l+\varepsilon_k}\hat{a}_j\hat{a}_l\hat{a}_k^+|N,0\rangle\right\}.\qquad(7)$$

The normalization condition for the wave function (7) yields

$$|t_i^\alpha|^2=S_\alpha=\left\{1+\sum_{jlk}|\langle ik|\hat{V}|jl|^2(\varepsilon_\alpha-\varepsilon_j-\varepsilon_l+\varepsilon_k)^{-2}\right\}^{-1}.\qquad(8)$$

In first-order perturbation theory, we also have the following expression for the final-state energy of the ion[4]

$$\varepsilon_\alpha=\varepsilon_i+\sum_{jlk}|\langle ik|\hat{V}|jl\rangle|^2(\varepsilon_\alpha-\varepsilon_j-\varepsilon_l+\varepsilon_k)^{-1},\qquad(9)$$

where $\varepsilon_\alpha=E(N)-E(N-1,\alpha)$.

We now substitute the expressions for the wave functions (6) and (7) into the formulas for the ionization amplitudes in the (γ, e) and $(e, 2e)$ reactions. For ionization by electron impact, we obtain

$$F_{0\alpha}(\mathbf{q})$$
$$=t_0t_i^\alpha\left\{\varphi_i(\mathbf{q})-\sum_{jlpk}\frac{\langle ik|\hat{V}|jl\rangle\langle pk|\hat{V}|jl\rangle^*}{(\varepsilon_\alpha-\varepsilon_l-\varepsilon_j+\varepsilon_k)(\varepsilon_p+\varepsilon_k-\varepsilon_j-\varepsilon_l)}\varphi_p(\mathbf{q})\right\},\qquad(10)$$

and, for photoionization, we have

$$\langle fN-1,\alpha|\sum_{a=1}^{N}\hat{z}_a|N\rangle$$
$$=t_0t_i^\alpha\left\{\langle f|\hat{z}|i\rangle-\sum_{jlpk}\frac{\langle ik|\hat{V}|jl\rangle\langle pk|\hat{V}|jl\rangle^*}{(\varepsilon_\alpha-\varepsilon_l-\varepsilon_j+\varepsilon_k)(\varepsilon_p+\varepsilon_k-\varepsilon_j-\varepsilon_l)}\times\langle f|\hat{z}|p\rangle\right\}.\qquad(11)$$

The squares of the matrix elements (10) and (11) give the relative line intensities in the corresponding ionization spectra. Let us compare them with the corresponding expressions given in the last section, in which correlations in the initial state of the atom were not taken into account. Apart from the constant factor t_0, which is the same for all the final states α of the ion, the inclusion of correlations produces an additional term which contains the final-state energy ε_α of the ion. If this term is not small, it may influence the relative line intensity.

The ionization spectra assume fundamentally new properties as a result of this effect. The relative contribution of the two terms on the right-hand sides of (10) and (11) is determined by different factors. For photoionization, they are the matrix elements $\langle f|\hat{z}|i\rangle$ and $\langle f|\hat{z}|p\rangle$, whereas for ionization by electron impact they are the Fourier components $\varphi_i(\mathbf{q})$ and $\varphi_p(\mathbf{q})$. It is therefore clear that the relative line intensities in the (γ, e) and $(e, 2e)$ spectra should not, in general, be equal. Moreover, the line intensity in the $(e, 2e)$ reaction can, in principle, depend on the transverse momentum, and is therefore determined by the reaction kinematics.

4. SPECTROSCOPIC FACTOR CORRECTED FOR CORRELATIONS IN THE INITIAL STATE OF THE ATOM. PHOTOIONIZATION

The complexity of expressions (10) and (11) for the relative line intensities in the ionization spectra prevents us from using them directly to analyze experimental spectra. Let us consider these expressions in the special case of the outermost shells of inert-gas atoms, for which we have an explicit expression for the final-state wave function of the ion.

The outermost shell is completely filled and has the electron configuration ns^2np^6, where the principal quantum number is $n=3$ for Ar, $n=4$ for Kr, and $n=5$ for Xe. The fact that the outermost shell is completely filled produces a substantial simplification of the expansion of the ion wave function over the Hartree-Fock basis. It has been shown[5] that the state of the ion with orbital angular momentum $L=0$ and spin $S=\frac{1}{2}$ contains only two principal Hartree-Fock components, namely, the simple pure one-hole ns^1np^6 and the more complicated ns^2np^4md, $m=n, n+1, \dots$. Expressions (10) and (11) thus contain the following one-electron states: $i=ns$; $j=l=np$; $k=md, \varepsilon d$; $p=ms, \varepsilon s$. The angular momentum and spin components are omitted for simplicity, The states k, p of the excited electron include the continuum.

Using the explicit form of the one-electron states, we can transform (10) and (11) to obtain simpler formulas for the relative line intensity, i.e., expressions for the corresponding spectroscopic factors. In this section, we shall consider photoionization. Ionization by electron impact will be examined in the next section.

We first perform the following transformations. In (11), we sum over the components of the angular momenta of the one-electron states. For this, we isolate the radial parts of the photoionization matrix elements and the Coulomb matrix elements of the electron interaction. The remaining angular factors, which are combinations of 3*j*–symbols containing the components of angular momenta, will be summed with the aid of the well-known formula given in Ref. 6. The original expression (11) then assumes the form

$$t_{ns}{}^{\alpha}\Big\{\langle\varepsilon p\|r\|ns\rangle-\sum_{m}\frac{1}{3}\,\frac{\langle ns\,md\|V_1\|np\,np\rangle}{\varepsilon_\alpha-2\varepsilon_{np}+\varepsilon_{md}}\times\sum_{m'}\frac{\langle m's\,md\|V_1\|np\,np\rangle}{\varepsilon_{md}+\varepsilon_{m's}-2\varepsilon_{np}}\langle np\|r\|m's\rangle\Big\},\qquad(12)$$

where we have omitted unimportant angular factors which are the same for all the states of the ion α. The summation over the excited-electron states *md*, *m's* includes integration over the continuum. According to Ref. 7, the matrix elements of the operators r and V_1 take the form of the reduced photoionization matrix elements and the Coulomb matrix elements of the electron interaction, respectively.

We now take outside the sum over m' the mean value of the energy denominator

$$\Delta_m=\varepsilon_{md}+\bar{\varepsilon}_{m's}-2\varepsilon_{np}.$$

The remaining expression will be transformed using the completeness of the set of radial wave functions with the same angular momentum:

$$\sum_{n'\leqslant n}R_{n's}(r)R_{n's}(r')+\sum_{m'>n}R_{m's}(r)R_{m's}(r')=\delta(r-r')/r^2.\qquad(13)$$

The result of these transformations is

$$\sum_{m'}\frac{\langle m's\,md\|V_1\|np\,np\rangle\langle\varepsilon p\|r\|m's\rangle}{\varepsilon_{md}+\varepsilon_{m's}-2\varepsilon_{np}}=\frac{1}{\Delta_m}\{\langle\varepsilon pmd\|rV_1\|np\,np\rangle-\langle nsmd\|V_1\|np\,np\rangle\langle\varepsilon p\|r\|ns\rangle\}.\qquad(14)$$

In this equation, we have restricted our attention to a single-hole state $n's = ns$ in the shell to be ionized. This is valid because the Coulomb electron interaction within the confines of one shell is much stronger than the intershell interaction, but the photoionization matrix elements $\langle\varepsilon p\|r\|n's\rangle$ of different states are of the same order of magnitude. Actually, when the photoelectron energy ε is high, these matrix elements contain the small parameter $1/K$, where $K = (2\varepsilon)^{1/2}$ is the photoelectron momentum in atomic units. This parameter is small because the matrix element includes an integral of the rapidly oscillating radial function of the photoelectron:

$$R_{\varepsilon p}(r)=j_1(Kr)=\sin Kr/(Kr)^2-\cos Kr/(Kr),$$

which is the spherical Bessel function. It has been shown[8] that such integrals, which appear in the valuation of high-order Fourier components of wave functions, are of the order of $(1/K)^\beta$ because of the singularity of the wave functions at the origin. The exponent β depends only on the behavior of these functions near the nucleus, and it is well-known that this is determined by the angular momentum. It may be shown that the photoionization matrix elements of the *s*-subshell have the order of magnitude $\langle\varepsilon p\|r\|n's\rangle\sim(1/K)^5$, which is the same for all n'. Analogous estimates can be used to show that $\langle\varepsilon pmd\|rV_1\|npnp\rangle\sim(1/K)^7$, i.e., the first term on the right-hand side of (14) is of a higher order of small quantities, and can therefore be neglected when the photoelectron energy is high. The result of this is that the original expression (12) can now be written in the form

$$t_{ns}{}^{\alpha}\langle\varepsilon p\|r\|ns\rangle\Big\{1+\frac{1}{3}\sum_{m}\frac{|\langle nsmd\|V_1\|np\,np\rangle|^2}{\varepsilon_\alpha-2\varepsilon_{np}+\varepsilon_{md}}\,\frac{1}{\Delta_m}\Big\}.\qquad(15)$$

We now take outside the sum over m the average value of the energy denominator

$$\Delta=\bar{\Delta}_m=\bar{\varepsilon}_{md}+\bar{\varepsilon}_{m's}-2\varepsilon_{np}$$

and use (9) which, in this case, can be written in the form

$$\varepsilon_\alpha=\varepsilon_{ns}+\frac{1}{3}\sum_{m}|\langle nsmd\|V_1\|np\,np\rangle|^2(\varepsilon_\alpha-2\varepsilon_{np}+\varepsilon_{md})^{-1}.\qquad(16)$$

The relative line intensity in the photoelectron spectrum is then given by the square of (15). The spectroscopic factor for photoionization is therefore given by

$$\tilde{S}_\alpha=S_\alpha[1+(\varepsilon_\alpha-\varepsilon_{ns})/\Delta]^2.\qquad(17)$$

It is precisely this quantity and not S_α, as assumed earlier, that is the spectroscopic factor measured in photoelectron spectroscopy.

We note that the difference between S_α and $\tilde{S}_\alpha$ remains as the photon energy increase, i.e., the spectroscopic factor in the photoelectron spectrum always has a more complicated physical meaning than simply the probability of detecting the ion in the pure one-hole state. Actually, the mean energy denominator is practically independent of the photoelectron energy ε. This can be estimated as follows. Suppose that we take the plane wave $|p\rangle = \exp(i\mathbf{K}_p\cdot\mathbf{r})$ as the complete set of wave functions $|p\rangle$. The completeness condition (13) will then involve only the integral over the continuous spectrum $\varepsilon's$ and the sum over the filled states $n's$ will not be involved. The right-hand side of (14) will therefore contain only the first term, which is parametrically small in comparison with the second. Hence, it follows that the principal contribution to the sum over the states $m's$, $\varepsilon's$ on the left-hand side of (14) will indeed be due to states that cannot be replaced with plane waves. These are discrete states and low-energy states in the continuum. In approximate estimates, we can therefore put $\bar{\varepsilon}_{m's} = 0$. Next, we must allow for the fact that the reduced matrix element $\langle nsmd\|V_1\|npnp\rangle$ of the interelectron Coulomb interaction with $m = n$ (i.e., all the states refer to the same shell) is much greater than all the other matrix elements. Hence, the principal contribution to the sum over m in (15) is provided by the single term $m = n$. Consequently, we may put

$$\Delta=\tilde{\Delta}_m=\varepsilon_{nd}-2\varepsilon_{np}.$$

The average value of the energy denominator and, together with it, the expression for the photoelectron spectroscopic factor (17) do not, therefore, contain the photoelectron energy. This enables us to look upon $\tilde{S}_\alpha$ as a structural characteristic of the ion, although it is more complicated than S_α.

5. SPECTROSCOPIC FACTOR WITH ALLOWANCE FOR CORRELATIONS IN THE INITIAL STATE OF THE ATOM. IONIZATION BY ELECTRON IMPACT

We must now transform (10) in precisely the same way as was done in connection with (11). We first sum over the components of the angular momentum of the one-electron states. The result is

$$F_{0\alpha}(q)\propto t_{ns}{}^{\alpha}\Big\{\langle q\|ns\rangle-\frac{1}{3}\sum_m\frac{\langle nsmd\|V_1\|np\,np\rangle}{\varepsilon_\alpha-2\varepsilon_{np}+\varepsilon_{md}}$$

$$\times\sum_{m'}\frac{\langle m'smd\|V_1\|np\,np\rangle}{\varepsilon_{md}+\varepsilon_{m's}-2\varepsilon_{np}}\langle q\|m's\rangle\Big\},\qquad(18)$$

where

$$\langle q\|ns\rangle=\int_0^\infty r^2\,drR_{ns}(r)j_0(qr),\quad j_0(qr)=\sin qr/(qr)$$

is the radial overlap integral which involves the zero-order spherical Bessel function. We now extract from the sum over m' the average value of the energy denominator and use the completeness condition. Instead of (14), we then obtain the following expression:

$$\Delta_m{}^{-1}\{\langle qmd\|V_1\|npnp\rangle-\langle nsmd\|V_1\|npnp\rangle\langle q\|ns\rangle\}.\quad(19)$$

Let us now examine this expression for different values of the momentum transferred to the ion. When the momentum transfer is large, $q\gg1$, we can use, as before, the parametric smallness of the matrix elements:

$$\langle qmd\|V_1\|npnp\rangle\propto(1/q)^6,\qquad\langle q\|ns\rangle\propto(1/q)^4.$$

This enables us to discard the first term in (19), and the result of this is that the relative line intensity is given by an expression that is identical with (17). The spectroscopic factor for ionization by electron impact with high momentum transfer is thus seen to be equal to the "photoelectron" spectroscopic factor.

Let us now consider the other limiting case of low transferred momenta. Direct evaluation of the matrix elements that appear in (19) show that, as $q\to0$, the two terms cancel out exactly. This result can be explained in the following qualitative way. By definition, the matrix element of the Coulomb electron interaction $\langle nsmd\|V_1\|npnp\rangle$ contains the following radial integral:

$$\int_0^\infty dr\,r^2\int_0^\infty dr_1\,r_1{}^2R_{ns}(r)R_{np}(r)\frac{r_<}{r_>^2}R_{md}(r_1)R_{np}(r_1),\qquad(20)$$

where the symbol $r_>$ ($r_>$) represent the greater (smaller) of the two variable r and r_1. Since the states ns and np refer to the same shell to be ionized, the principal contribution to the integral with respect to the two variables r and r_1 is provided by the same range of values of distance, which is of the order of the radius of the shell. This means that we can put $r/r_1\simeq1$ in (20). Integration with respect to r and r_1 then becomes independent, and the entire integral splits into two parts, one of which is the overlap integral

$$\langle ns\|np\rangle=\int_0^\infty dr\,r^2R_{ns}(r)R_{np}(r).$$

We can therefore write

$$\langle nsmd\|V_1\|npnp\rangle=b\langle ns\|np\rangle,$$

where b is a constant. When q is small, the function $j_0(qr)$ is a slowly-varying function of distance. We therefore have another equation:

$$\langle qmd\|V_1\|npnp\rangle=b\langle q\|np\rangle.$$

As a result, expression (19) can be written in the form

$$\Delta_m{}^{-1}b\{\langle ns\|np\rangle\langle q\|ns\rangle-\langle q\|np\rangle\}.\qquad(21)$$

We shall now show that, when q is small, the expression in braces will tend to zero. Actually, as $q\to0$, we have $j_0(qr)\to1$ and the overlap integrals of $\langle q\|ns\rangle$ and $\langle q\|np\rangle$ reduce simply to the integrals of the radial function $R_{ns}(r)$ and $R_{np}(r)$. The number of zeros of these functions differs by unity and the functions have different signs at distances of the order of the radius of the shell. Since it is precisely a distance of this order that provides the main contribution to the integrals containing these functions, and they are both normalized to unity, the functions $R_{ns}(r)$ and $R_{np}(r)$ turn out to be equal in the "integral sense." Each can be replaced with the other under the integral sign if the entire expression is, at the same time, multiplied by ~1. In particular, the following equation should be valid:

$$\langle ns\|np\rangle\approx-\langle ns\|ns\rangle=-1,\qquad\langle1\|ns\rangle/\langle1\|np\rangle\approx-1.$$

The precise values of these expressions with Coulomb functions are equal and given by

$$-[(n+1)(n-1)/n^2]^{1/2}=-1+1/2n^2+o(1/n^2).$$

The numerical values with the Hartree-Fock radial functions are equal to -1 with approximately the same precision. If we substitute these relations in (21), we see that the two terms in braces cancel out exactly. Thus, only the first term remains in (18), and this means that the line intensity in the atomic ionization spectrum produced by electron impact with low transferred momentum is determined exclusively by the contribution of the pure single-hole component of the wave function of the ion, and the spectroscopic factor is equal to S_α.

We thus see that the spectroscopic factor of the $(e, 2e)$ reaction is not, strictly speaking, a purely structural characteristic, since it is determined by the reaction kinematics. Its value varies from S_α to $\tilde{S}_\alpha$, depending on the momentum transferred to the ion.

6. CALCULATION OF THE RELATIVE LINE INTENSITY IN (γ, *e*) AND (*e*, 2*e*) SPECTRA OF THE OUTERMOST SHELL OR ARGON

We have established that the difference between the relative line intensities in the ionization spectra of the outer-

TABLE I. Energies and spectroscopic factors of the eigenstates of the ion ArII^2S

State of ion	Energy, eV			Spectroscopic factor			
	Experiment		Calculation	(γ, e)		$(e, 2e)$	
	(γ, e)	$(e, 2e)$		Experiment	Calculation	Experiment	Calculation
$3s^13p^6$	29,3±0,1	29,3±0,1	29,3	0,80±0,03	0,79	0,58±0,06	0,55
$3s^23p^43d$	38,7±0,1	38,6±0,1	38,6	0,15±0,01	0,15	0,23±0,02	0,20
$3s^23p^44d$	41,2±0,2	41,2±0,2	41,1	0,05±0,02	0,07	0,13±0,02	0,11
$3s^23p^45d$	–	43,4±0,1	42,6	–	0,02	0,06±0,02	0,04

most shells of inert-gas atoms is due to the difference between the spectroscopic factors S_α and $\widetilde{S}_\alpha$ of the (γ, e) and $(e, 2e)$ reactions, respectively. To confirm this, we have calculated the spectroscopic factor of the ArII^2S ion. The results of these calculations are listed in this section.

We first calculated the one-electron wave functions of filled states that form the Hartree-Fock atomic core. This involved the numerical solution of the set of equations for the self-consistent field of the neutral argon atom. The wave functions were calculated for excited electrons in the field of the frozen atomic core. The matrix elements of the Coulomb electron interaction were then evaluated in the basis of one-electron functions. The algorithms and programs for these calculations are described in Ref. 9.

Next, (16) was solved numerically, and the exact final-state energies ε_α were found. It has been shown[10] that these states can be placed in correspondence with the Hartree-Fock states in terms of which the final-state wave function of the ion is expanded. The meaning of this correspondence is that, as the direct electron interaction is gradually "turned on," the energies of the exact state of the ion will tend to the energies of the corresponding Hartree-Fock states.

Having determined the ion energy ε_α from (8), we can calculate S_α. By using (17), we can determine $\widetilde{S}_\alpha$ as well. The average value of the energy denominator was estimated from the expression $\Delta = -2\varepsilon_{sp} + \varepsilon_{3d}$, and the values of ε_α, S_α, and $\widetilde{S}_\alpha$, calculated in this way, are listed in the table.

The table also lists photoelectron data on the (γ, e) reaction,[11] which correspond to the limit of high transferred momenta. The photon energy in this experiment was $\omega = 1487$ eV and the photoelectron momentum was $K \simeq 10$. The spectroscopic factors S_α are listed in the table together with the experimental data on the inelastic scattering of fast electrons [symmetric noncoplanar $(e, 2e)$ reaction].[1] These data correspond to the limit of low transferred momenta. The incident-electron energy in this experiment is $E_0 = 800$–1000 eV and the momentum transferred to the ion is $q = 0.1$–0.5.

7. DISCUSSION

Despite the fact that qualitative estimates were used in our calculations, the results of these calculations are in reasonable agreement with experiment. The leading features of the ionization spectrum are correctly reproduced. The relative intensity of the principal line in the (γ, e) reaction turns out to be greater, whilst the satellite line intensity turns out to be lower than the intensity of the corresponding lines in the $(e, 2e)$ reaction. This feature of the spectra follows directly from (17). It has been shown[10] that the energy of the ground state of the ion is greater than the Hartree-Fock energy of the shell to be ionized, but the energy of the excited states is lower. We recall that the energy of the ion is measured from the ground state of the atom and is therefore negative. This behavior of the relative line intensities in the (γ, e) and $(e, 2e)$ spectra is characteristic not only for argon but also for other inert gases such as krypton and xenon.[1]

The analysis given above exploits the explicit form of the expansion of the wave function of the final state of the ion over the Hartree-Fock basis, and is valid only for inert-gas atoms. It is very likely, however, that the results obtained in this way are a consequence of some more general principles and are valid for arbitrary atoms. The main conclusion of our work, namely, the dependence of the ionization spectra on the transferred momentum, can be checked by direct experiment. It will be sufficient to examine the $(e, 2e)$ reaction for low and high momentum transfers. The intensity of the principal line in the spectrum will then increase, whereas the intensity of the satellite lines will fall. Finally, for high momentum transfers $q \gg 1$, the ionization spectrum in the $(e, 2e)$ reaction should be identical with the (γ, e) spectrum. It is quite possible that this property will also be observed in nuclear reactions, for example, (γ, p) and $(p, 2p)$, and in other reactions.

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