New Minima in Photoionization Cross Section*

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It has been found that for certain excited atomic states, the dipole matrix element for the $l \rightarrow l+1$ photoionization channel has *two* minima and the $l \rightarrow l-1$ channel has a minimum as well. Results for Cs $5d$ photoionization showing these phenomena are presented.

The existence of Cooper minima[1,2] in photoionization cross sections has been known for some time. They can occur in the photoionization of outer (and near-outer) nl electrons, provided the discrete nl wave function has at least one node, i.e., $n > l+1$. Minima arise when the matrix element in the $l \rightarrow l+1$ photoionization channel vanishes as a result of the equality of the positive and negative contributions to the dipole matrix element caused by the details of the overlap between the discrete nl and continuum $\epsilon, l+1$ wave functions. Quite a number of these minima have been found, both theoretically and experimentally in ground states of atoms.[1-5] It is found that with increasing atomic number, the wave function becomes more compact for a given nl wave function and the Cooper minimum moves in toward threshold, i.e., occurs at lower and lower photoelectron energy, until it moves into the discrete.[2,3] In this paper, we investigate what can occur when a wave function becomes very diffuse. To this end excited atomic states were studied. In particular, we chose the $5d$ state of cesium ($Z = 55$) to illustrate the results that two minima other than the usual Cooper minimum can occur, as well as to point out some of the implications of these minima.

Within the framework of a single-particle central-field approximation, the photoionization cross section of an nl subshell is given by[2,3]

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

Here ϵ_{nl} and ϵ (both in rydbergs) are the binding energy of an electron in the nl subshell and the photoelectron energy, respectively ($h\nu = \epsilon - \epsilon_{nl}$), α is the fine-structure constant, a_0 is the Bohr radius, and N_{nl} is the number of electrons in the subshell. The radial dipole matrix elements are

$$R_{l\pm1}(\epsilon) = \int_0^\infty u_{nl}(r)\, r\, u_{\epsilon,l\pm1}(r)\, dr, \quad (2)$$

where u_{nl}/r and $u_{\epsilon,l\pm1}/r$ are the radial parts of the wave functions of the active electron before and after photoionization. We have used the same Hartree-Slater potential,[6] appropriate to the $5d$ state of cesium, to generate the discrete $5d$ and continuum ϵp and ϵf wave functions by using methods discussed in detail previously.[3]

In our convention of all wave functions having positive slope at the origin, the usual Cooper minimum occurs when the $l \rightarrow l+1$ matrix element, $R_{l+1}(\epsilon)$, is negative at threshold. At large energies it must, however, be positive.[2] Thus, it must vanish at some energy leading to the minimum. Our calculated results for $R_{l\pm1}(\epsilon)$ for Cs $5d$ are shown in Fig. 1. Here it is seen that $R_f(\epsilon)$ starts out positive and rapidly drops to a zero at $\epsilon = 0.164$ Ry. Above this energy, $R_f(\epsilon)$ goes negative and continues to increase (in absolute value) until about $\epsilon = 0.25$ Ry where it reaches its maximum negative value. At higher energy, $R_f(\epsilon)$ increases (becomes less negative) slowly and it has another zero at $\epsilon = 7.4$ Ry above which $R_f(\epsilon)$ becomes positive. This higher-energy zero is the conventional Cooper minimum, while the lower-energy zero is a new minimum; this is the first incidence of a single photoionization channel hav-

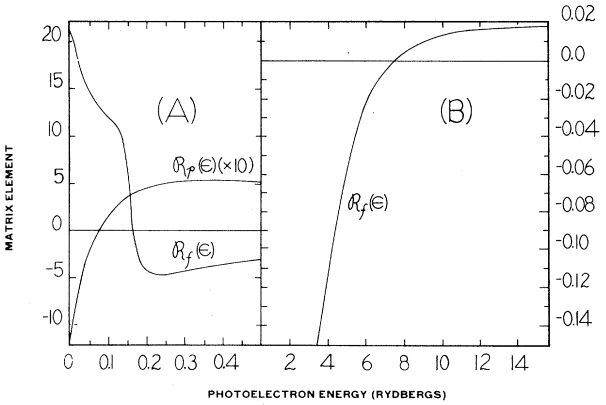

FIG. 1. Dipole matrix elements for Cs $5d$ photoionization; $R_f(\epsilon)$ and $R_p(\epsilon)$ refer to transitions to ϵf and ϵp continua, respectively.

ing more than one zero. In addition, Fig. 1(a) also shows $R_p(\epsilon)$ which has a zero at = 0.074 Ry. No previous case has been reported of a zero in an $l \rightarrow l-1$ channel and up to now, it was thought never to exist.

The double minimum in $R_f(\epsilon)$ comes about because the nodes of the $5d$ wave function are displaced significantly toward the nucleus as compared to the ϵf at threshold; i.e., $\delta_f(0) \simeq 0$ while the quantum defect of the $5d$ is about $2.5\,[\delta_d(0) \simeq 2.5\pi]$.[7] Thus, at threshold, the first node in the ϵf occurs at a large value of r where the $5d$ has almost gone to zero. The major contribution to the dipole matrix element, at threshold, therefore, comes from the overlap of the first loop of the ϵf (which is positive) with the third (outer) loop of the $5d$ (also positive) so that the dipole matrix element is positive. $\delta_f(0) \simeq 0$ because the effective potential (electrostatic plus centrifugal) for f waves has an inner well *and* an outer well separated by a barrier about 0.2 Ry high.[8] For $Z = 55$ the inner well is not deep enough to support a bound f state and the ϵf function has no appreciable amplitude inside the barrier. As the energy increases, however, the ϵf function begins to penetrate the barrier and as the energy approaches the barrier height, ϵf moves swiftly into the inner well and δ_f increases to $\sim\pi$, i.e., a shape resonance.[7] When this occurs the principal overlap is between the *second* loop of the ϵf (which is negative) and the outer loop of the $5d$ and the dipole matrix element is thus negative. Since it is a continuous function of energy, at some intermediate value the dipole matrix element, $R_f(\epsilon)$, vanishes, as shown in Fig. 1(a). As the energy increases further, the ϵf continues to contract and eventually the diple matrix element becomes positive again and, thus, goes through another zero as shown in Fig. 1(b). This leads to the well-known Cooper minimum.

The overlap of the ϵp continuum function with the $5d$ is quite complex since the inner *six* loops of the ϵp contribute substantially. It is found, however, that $R_p(\epsilon)$ is negative at threshold and as the energy increases and the ϵp function moves in toward the nucleus, a change in sign of $R_p(\epsilon)$ occurs; i.e., $R_p(\epsilon)$ goes through a zero. It is not surprising that so complicated an overlap can be positive or negative. What is surprising, however, is that a zero in the $l \rightarrow l-1$ dipole matrix element has never been seen in photoionization from ground states. This point is being pursued further.

The cross section for photoionization of the Cs $5d$ is shown in Fig. 2 where the effects of the zeros in $R_p(\epsilon)$ and $R_f(\epsilon)$ are seen. The cross section drops more than three orders of magnitude just above threshold [reflecting the first zero in $R_f(\epsilon)$] and then rises more than two orders of magnitude. This is seen more clearly in Fig. 3 which shows a close-up of this region. The drop is so dramatic because when $R_f(\epsilon)$ has a zero the

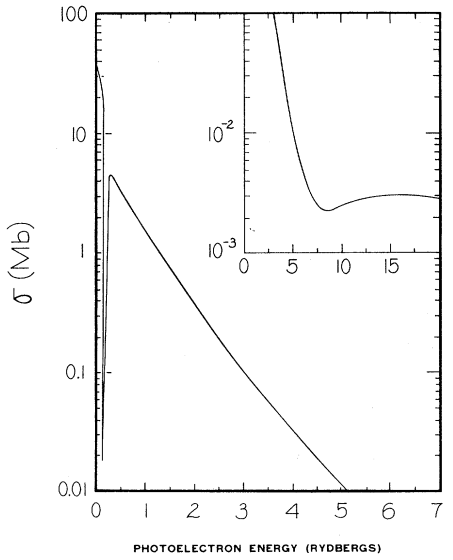

FIG. 2. Photoionization cross section for photoionization of Cs $5d$.

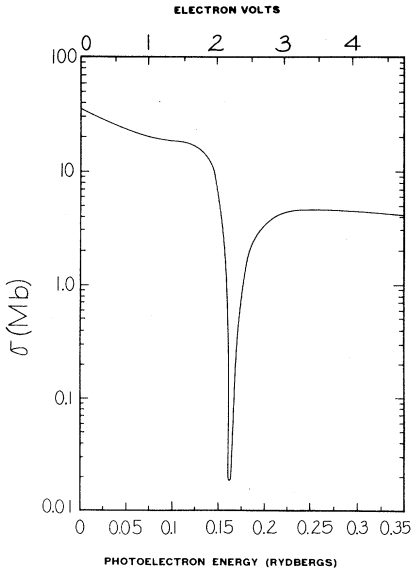

FIG. 3. Photoionization cross section for photoionization of Cs $5d$.

cross section is entirely due to the $5d \rightarrow \epsilon p$ channel which is quite small since it is just above the zero in $R_p(\epsilon)$ as seen in Fig. 1(a). The "window" is so narrow because of the rapidity of the contraction of the ϵf wave function (increase in δ_f) in the energy range around the potential barrier height. This minimum is in contrast to the relatively smooth effects of the second zero in $R_f(\epsilon)$ which gives rise to the usual Cooper minimum as shown in the inset in Fig. 2. The "window" in the cross section looks very much like autoionizing window resonances[9,10] but is really from the effect of a shape resonance.

The first minimum arises if $\delta_d(0)$ is sufficiently larger than $\delta_f(0)$ (by $\sim 2\pi$ at least). By using quantum-defect theory[11] we get these phase shifts from experimental energy-level data and we find that our calculated values are substantially correct. Thus, despite the simple Hartree-Slater potential used in the calculation, we feel that our results are at least qualitatively correct. A more exact calculation (Hartree-Fock, close-coupling, or many-body-perturbation theory) would modify the position and shape of the minimum somewhat, but would not alter the basic structure. In addition, a fine-structure effect on the ϵf wave function (the Fano effect[12]) would tend to obliterate the first minimum somewhat. It is nevertheless felt that it will be quite observable and one reason cesium was picked for calculation was that the energies involved are accessible with lasers so that the experiment is possible despite the fact that the $5d$ in Cs is not metastable as it is in Ba.

From the above discussion, it is clear that the double minima will occur over a broad range of excited atoms. We have already determined that it occurs for $5d$ from $Z = 37$ to 55 and for $6d$ over an even wider range of Z's. Work is in progress to determine the details of where and under what conditions these new minima appear.

Finally we note that this effect has been seen[13,14] in discrete photoexcitation of Ba^+. It was this that called our attention to the new minima and we gratefully thank Professor Ugo Fano and Dr. C. D. Lin for bringing it to our attention.

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Stark Ionization of High-Lying States of Sodium*†

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By using stepwise excitation in an atomic beam, we have excited slow-moving atoms to pure high-lying quantum states at densities low enough to avoid loss by collision. The atoms were detected with high efficiency by Stark ionization. Results are presented of a study of the threshold field for ionization for s states of sodium with principal quantum number n from 26 to 37.

We report the production of highly excited sodium atoms in pure quantum states, and observations on their ionization threshold in an electric field. There has recently been a growing interest in the properties of high-lying states of atoms near the ionization limit. These states, which are essentially hydrogenic, are characterized by very long lifetimes, large polarizabilities and