

Advances in
**Electronics and
Electron Physics**

EDITED BY
L. MARTON

VOLUME 44

73.6
M387
V 44.1

Advances in Electronics and Electron Physics

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ACADEMIC PRESS New York San Francisco London

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**ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003**

United Kingdom Edition published by
**ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1**

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 49-7504

ISBN 0-12-014644-4

PRINTED IN THE UNITED STATES OF AMERICA

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FOREWORD

The second part of S. T. Manson's review on "Atomic Photoelectron Spectroscopy" (the first part appeared in Volume 41 of these Advances) introduces our present volume. While the first part concentrated on the theoretical treatment of photoionization and of photoelectron angular distributions, in this second part the emphasis is on a comparison of theory with experiment, on the predictive power of theory, and on areas in which work is called for.

G. M. R. Winkler discusses the very important and interesting subject of "Timekeeping and Its Applications." Present-day physics and technology require an increasingly precise knowledge of time, both elapsed and "absolute." The philosophical and historical discussion of the subject in the introductory part of the review puts the whole problem in its proper perspective, so that the actual methods used can be succinctly presented. The review closes with a short survey of the principal applications of modern time-keeping methods.

In his review of "Electrodynamic Concepts of Wave Interactions in Thin Film Semiconductor Structures" A. A. Barybin shows how investigations of wave propagation and instabilities in solid state plasmas led to the conception of solid state traveling-wave amplifiers. After a discussion of methods of design and analysis, he investigates in this first part of the review the general theory of normal mode excitation of such waveguides by external sources.

In our Volume 39 (1975) we published the first part of a review on "Microwave Power Semiconductor Devices" by S. Teszner and J. L. Teszner. Whereas the first part was devoted to a discussion of two-terminal devices, the second part considers in detail two three-terminal devices: the bipolar transistor and the field⁴ effect transistor. For both classes of devices the general theory is followed by an examination of the technologies necessary for the production of these devices, as well as a discussion of their electrical characteristics. The review ends with an extrapolation to future development prospects for microwave power semiconductor devices.

D. J. Bates, R. I. Knight, S. Spinella, and A. Silzars present a review of "Electron Bombarded Semiconductor Devices." The development of these devices went through a long period of neglect, and it is only recently that their usefulness has been recognized. As the authors point out, the EBS is a hybrid vacuum tube-semiconductor device, in which both technologies are of essentially equal importance. A short survey of the principle of operation is followed by a discussion of the general characteristics and an analysis of

the relevant devices. An examination of the physical limitations to EBS capabilities is followed by a review of the technologies required for the production of the devices, as well as a survey of some device configurations and their performance.

The last review in this volume, by L. Kusak, is on "Basic Concepts of Minicomputers." A historical survey is followed by a description of the characteristics of the central processing unit of the minicomputer, of its memory, of the instruction repertoire, of the data checking facilities, of the protection against power failures, and of memory interactions. After a discussion of memory access, the author examines in detail many of the related technologies and applications.

The following is a list of reviews we expect to publish in forthcoming volumes:

In Situ Electron Microscopy of Thin Films

High Injection in a Two-Dimensional Transistor
 Physics of Ion Beams from a Discharge Source
 Physics of Ion Source Discharges
 Termination and Classification of Particle Beams
 On Teaching of Electronics
 Wave Propagation and Instability in Thin Film
 Semiconductor Structures. II
 The Gunn-Hilson Effect
 A Review of Applications of Superconductivity
 Minicomputer Technology
 Digital Filters
 Physical Electronics and Modeling of MOS Devices

Thin Film Electronics Technology
 Characterization of MOSFETs Operating in Weak
 Inversion
 Electron Impact Processes
 Sonar
 Microchannel Electron Multipliers
 Electron Attachment and Detachment
 Noise in Solid State Devices

Radar Signal Processing
 Electron Beam Controlled Lasers
 Amorphous Semiconductors
 Electron Beams in Microfabrication. I and II
 Photoacoustic Spectroscopy
 Design Automation of Digital Systems. I and II

Wire Antennas

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Image Transmission Systems	W. K. Pratt
Computer Techniques for Image Processing in Electron Microscopy	W. G. Saxton
High-Voltage and High-Power Applications of Thyristors	G. Karady

Our thanks go again to the many friends who helped us organize this and all other volumes of *Advances in Electronics and Electron Physics*. We are also grateful for the suggestions which have reached us and hope that many more will follow in the future.

L. MARTON
C. MARTON

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LLOYD KUSAK

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Atomic Photoelectron Spectroscopy. II*

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I. Photoionization Cross Sections	1
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I. PHOTOIONIZATION CROSS SECTIONS

In this section, the subject of partial photoionization cross sections, i.e., subshell photoelectron cross sections, will be discussed. The discussion will focus on three aspects of photoelectron cross sections: the variety of phenomena that are observed, the physical explanation of these phenomena, and the comparison of experimental results with the predictions of the various theoretical formulations described in Section II,A in Part I of this review (Manson, 1976), hereafter referred to as I.

In connection with the comparison of theory and experiment, note that in an energy region where the cross section for a particular subshell dominates the total photoionization cross section, measurements of photoabsorption will provide substantially the same information as photoelectron spectroscopy of that subshell. Thus, in these cases, we shall compare theory with the results of photoabsorption experiments when no photoelectron results are available.

Figure 1 shows the photoionization cross section of free atoms of sodium in the threshold region. The 3s is the only energetically accessible subshell in this energy range, so the cross section is entirely due to the 3s and is thus entirely equivalent to photoelectron spectroscopy results. The experimental cross section (Hudson and Carter, 1967a,b) shows a zero minimum just above threshold, and this behavior is reproduced quite well by the simple central field HS calculation (Manson and Cooper, 1968). This minimum,

* This work was supported by the National Science Foundation and the U.S. Army Research Office.

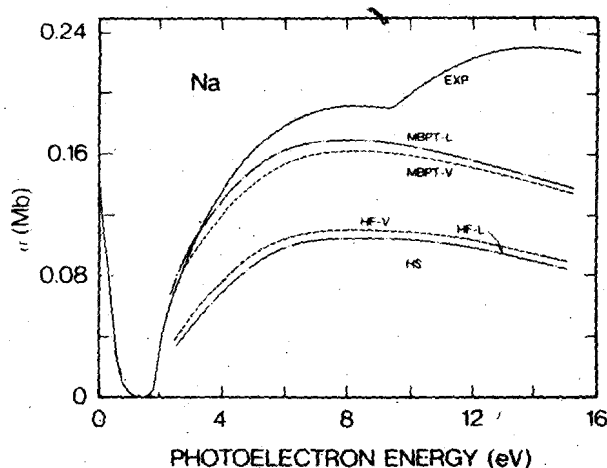


FIG. 1. Photoionization cross section of sodium. The experimental results are from Hudson and Carter (1967a,b), the HS results from Manson and Cooper (1968), and the HF and MBPT results from Chang (1975).

which is quite pronounced in sodium, is known as a Cooper (1964) minimum and was first explained by Seaton (1951). It is due to the $3s \rightarrow \epsilon p$ dipole matrix element going through a zero because of the positive and negative contributions just cancelling. If we use the convention that all wave functions have positive slope at the origin, the dipole matrix element is negative at threshold and becomes positive above the Cooper (1964) minimum. Using this convention, it can be shown that all $\langle nl|r|el \rangle$ dipole matrix elements are positive at high enough energy (Fano and Cooper, 1968). Thus, if the dipole matrix element for a photoionization process is negative at threshold, it is certain that a Cooper minimum will appear at some energy.

Also shown in Fig. 1 are the theoretical HF and MBPT results (Chang, 1975), but only above the minimum since at lower energies they are significantly the same as the HS cross section. At the higher energies, it is seen that the HS and HF results are significantly the same; the MBPT results are much closer to the experimental values but still fail to reproduce the "structure" seen just above 9 eV. Since the MBPT calculation includes the effects of ground state correlation, final state correlation, and interchannel coupling, it is difficult to see what could be omitted that would cause the structure seen. Thus, as pointed out by Chang (1975), "a review of the experimental situation would be desirable."

Cooper minima are found quite often in the photoionization of atoms in the *ground state* and some general rules about their behavior over the periodic system can be enunciated owing to extensive calculations (Cooper, 1962, 1964; Manson and Cooper, 1968; Fano and Cooper, 1968; Combet

Farnoux, 1969, 1971, 1972; Kennedy and Manson, 1972; Manson, 1973). First it is found that they appear only in $l \rightarrow l + 1$ transitions, although one case of a minimum appearing in an $l \rightarrow l - 1$ photoionizing transition has been found through photoelectron polarization measurements (Heinzmann *et al.*, 1976). Cooper minima appear only for outer and near outer subshells and only for subshells whose wave functions have nodes, i.e., they do not appear for photoionization of 1s, 2p, 3d, or 4f electrons. In addition, the Cooper minimum appears for a given (noded) subshell as soon as it becomes bound in the ground state and, with increasing Z , moves toward threshold and into the discrete spectrum, although not necessarily monotonically. Finally, the Cooper minima are generally not zero minima because for np , nd , and nf subshells, even though the $l \rightarrow l + 1$ dipole matrix element vanishes, the $l \rightarrow l - 1$ does not; in fact, the minimum can be overwhelmed entirely by the $l \rightarrow l - 1$ channel and not show up experimentally as a minimum at all.

Some examples of calculated Cooper minima (Manson and Cooper, 1968) are shown in Fig. 2 for the $3p \rightarrow \epsilon d$ photoionizing transition. From these central field HS results it is seen that the Cooper minimum for argon ($Z = 18$) has moved in slightly by copper ($Z = 29$) and is just below threshold for germanium ($Z = 32$).

Note that the above discussion refers to ground state atoms. Some very interesting effects have recently been uncovered in theoretical calculations of photoionization excited atomic states (Msezane and Manson, 1975). In particular, for the 5d excited state of cesium, shown in Fig. 3, the photoionization cross section has two minima. One, at higher energies (shown in the insert), is the ordinary Cooper minimum. Just above threshold, however, a very dramatic minimum in the cross section is found. This minimum is also due to the vanishing of the $5d \rightarrow \epsilon f$ dipole matrix element and this channel has a double minimum, a phenomenon not found for ground states. In addition, a minimum is found in the $5d \rightarrow \epsilon p$ channel and this minimum is quite close to the first $5d \rightarrow \epsilon f$ minimum, thus giving rise to the dramatic situation shown. The calculations show that this is not an isolated case (Msezane and Manson, 1977). The $5d \rightarrow \epsilon f$ double minimum is found to appear for $Z = 34-55$, and the $5d \rightarrow \epsilon p$ minimum for $Z = 9-55$. In addition, the calculations show minima in the $4d \rightarrow \epsilon p$ channel (when 4d is an excited state) over a wide range of Z 's, and even for excited 3d states a $3d \rightarrow \epsilon p$ minimum is found in a number of elements, despite the fact that the 3d wave function is nodeless. These minima are also found for higher excited d states and, although no experimental confirmation of these effects has yet been reported, they are expected soon.

The detailed reasons for these excited d state effects are presently under scrutiny. They illustrate, however, a fundamental physical difference between ground and excited atomic states. Ground states have a spatial extent

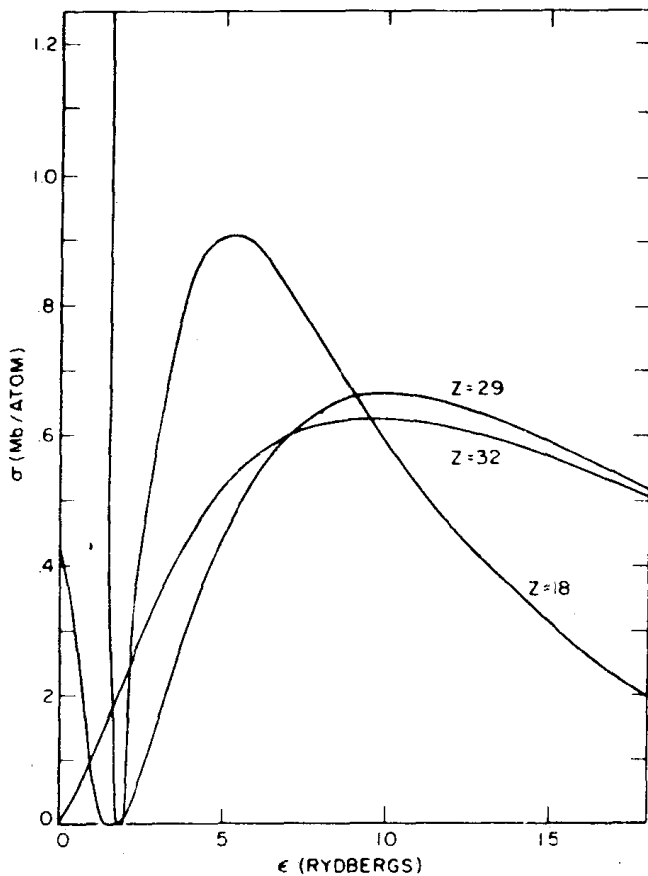


FIG. 2. Theoretical HS $3p \rightarrow ed$ photoionization cross sections for $Z = 18, 29,$ and 32 (Manson and Cooper, 1968).

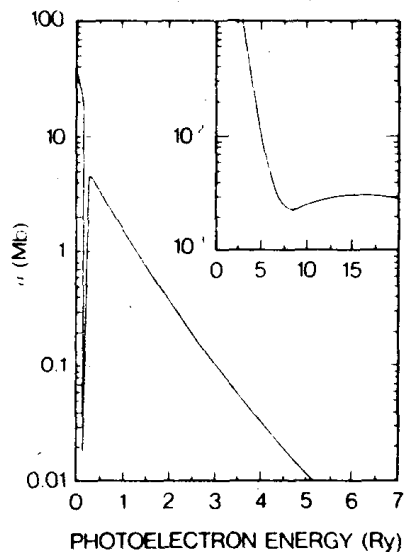


FIG. 3. Theoretical HS cross section for photoionization of cesium in the excited $5d$ state (Msezane and Manson, 1975).

of $\sim a_0$ from the atomic nucleus, while excited states are much larger. Thus the ground state wave function interacts with the continuum wave function over just a small region of space, while the excited state interaction extends over a much larger region where the character of the continuum wave function can be considerably different from its character near the nucleus. From another point of view, it seems that photoelectron spectroscopy of excited atomic states can provide valuable and basic information on continuum wave functions in regions of space inaccessible from the ground state.

Another phenomenon that is found throughout the periodic system is illustrated in Fig. 4. Here the $3d \rightarrow \epsilon f$ photoionization cross section, cal-

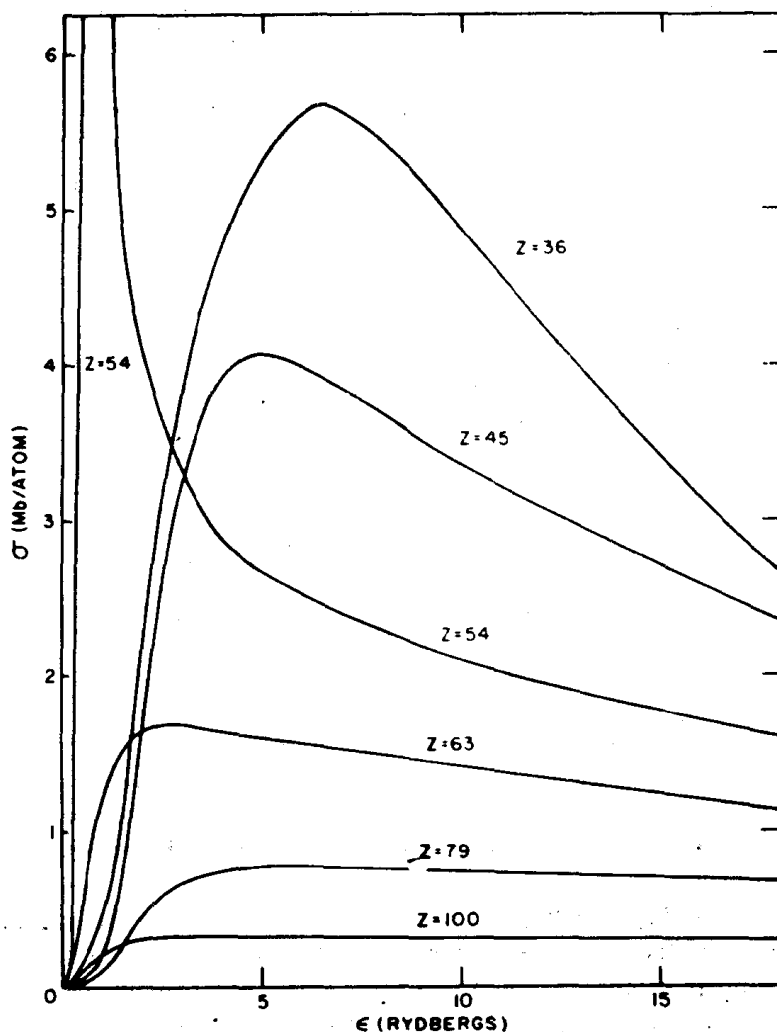


FIG. 4. Theoretical HS $3d \rightarrow \epsilon f$ photoionization cross sections for $Z = 36, 45, 54, 63, 79,$ and 100 (Manson and Cooper, 1968). The maximum for $Z = 54$ is 13.6 Mb at $\epsilon = 0.6$ Ry.

culated using HS wave functions (Manson and Cooper, 1968), is shown over a wide range of Z . Note that each cross section is very small at threshold and rises to a "delayed maximum" well above threshold. This is in contrast to the monotone decrease of the cross section from threshold that is characteristic of hydrogenic results (Hall, 1936). Physically this occurs because the effective potential, as "seen" by an f wave electron, contains a large centrifugal (angular momentum) repulsion, which keeps the ϵf wave function from penetrating into the atom (where the $3d$ wave function has appreciable amplitude) at threshold. At threshold therefore, the $3d \rightarrow \epsilon f$ dipole matrix element is quite small and thus the photoionization cross section is small. At higher energy, the ϵf continuum function can penetrate the atomic core more effectively, and the matrix element and cross section thus increases. This is illustrated in Fig. 5 for the $3d \rightarrow \epsilon f$ photoionization in krypton. Here it is

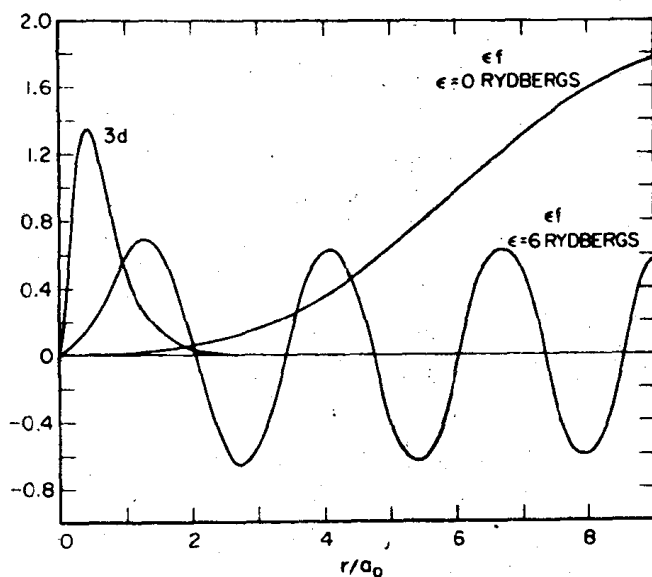


FIG. 5. The normalized $3d$ and ϵf wave functions in Kr ($Z = 36$).

seen that the overlap increases markedly in going from $\epsilon = 0$ to $\epsilon = 6$ Ry. For higher energies, the ϵf wave function continues to move in toward the nucleus and cancellation starts to occur owing to its oscillatory nature. This cancellation leads to a decrease in the cross section, with increasing energy, as shown in Fig. 4.

Thus, the delayed maximum phenomenon is related to the final angular momentum of the photoelectron and will be seen even more strongly for higher angular momenta, e.g., $f \rightarrow g$ transitions, but somewhat weaker for $p \rightarrow d$ photoionization channels, and almost nonexistent for $s \rightarrow p$. The effective potentials over the periodic system have been studied by Rau and Fano

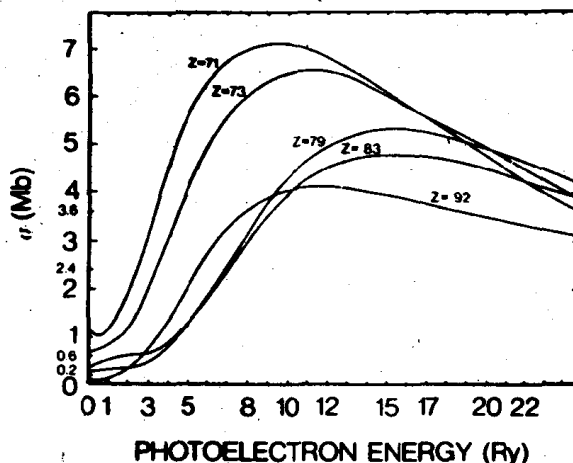


FIG. 6. Theoretical HS 4f photoionization cross sections for $Z = 71, 73, 79, 83,$ and 92 (Combet Farnoux, 1971).

(1968), where the details of the angular momentum barriers are discussed.

The photoionization cross sections for a number of 4f subshells, including both $f \rightarrow g$ and $f \rightarrow d$ contributions, calculated using HS wave functions (Combet Farnoux, 1971), are shown in Fig. 6. The cross section is not vanishingly small at threshold due to the $f \rightarrow d$ channel, but in each case a very strong delayed maximum is in evidence 100–200 eV above threshold. The maximum is so far above threshold owing to the strength of the centrifugal barrier for g waves.

For the case of gold ($Z = 79$), the region of the photoionization cross section dominated by the 4f has been measured (Jaeglé and Missoni, 1966; Haensel *et al.*, 1968, 1969; Jaeglé *et al.*, 1969) and the results are compared with the HS central field calculations (Combet Farnoux and Heno, 1967; Manson and Cooper, 1968) in Fig. 7. From this comparison it is seen that theory agrees quite well with experiment *qualitatively*, despite the fact that the experiment was performed on the solid. The 4f \rightarrow ϵg delayed maximum is too high and sharp, due to the only approximate inclusion of exchange in the HS calculation (Manson and Kennedy, 1970).

To include exchange more correctly, within the single-particle approximation, requires the use of HF theory, as discussed in I. Although no HF results have been published for the 4f subshell of gold, HF results for mercury ($Z = 80$) have been obtained (Shyu and Manson, 1975) and are shown in Fig. 8. From this result it is seen that the correct inclusion of exchange interactions (particularly the 4f \rightarrow ϵg terms) causes the delayed maximum to be lower and broader. This is precisely what was needed to bring theory and experiment together in the case of gold, as discussed above.

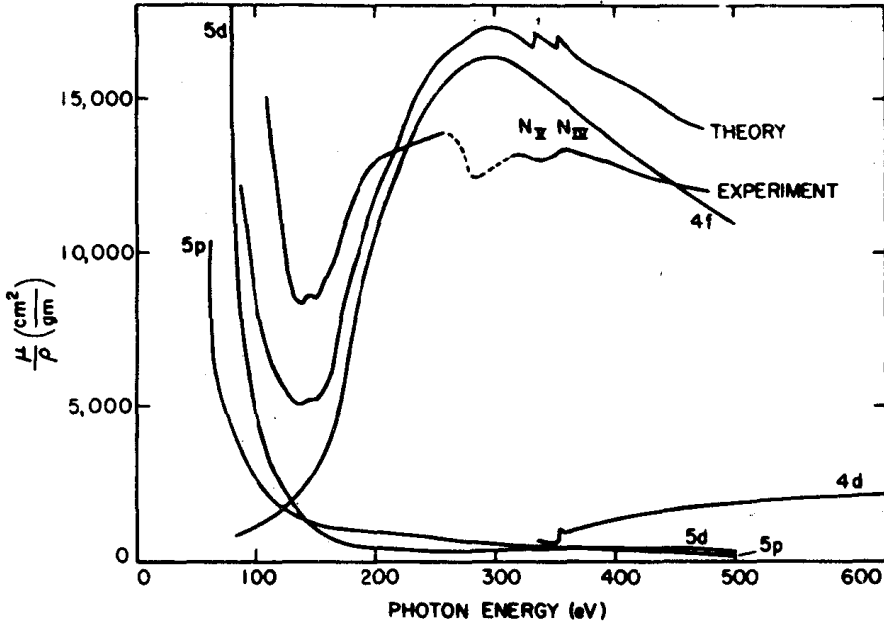


FIG. 7. Mass absorption coefficient of gold showing the theoretical HS subshell and total results (Manson and Cooper, 1968) and the experimental results (Jaeglé and Missoni, 1966). Note that the mass absorption coefficient is proportional to the photoionization cross section.

It turns out that the inclusion of exchange correctly, which can be done via HF or the intrachannel coupling formalism (Fano, 1961) as shown in I, generally has the effect of lowering and broadening the delayed maxima predicted by central field approximations (Starace, 1970; Combet Farnoux, 1970, 1972; Kennedy and Manson, 1972). This is illustrated in Fig. 9 for photoionization of 5d electrons in a number of cases (Combet Farnoux, 1972) where the lowering and broadening of the 5d \rightarrow ϵf delayed maximum in HF as compared to HS is seen for $Z = 79, 83,$ and 86 . For $Z = 88$ a rather different effect, almost the opposite, is seen. Note that for both HS and HF results in Fig. 9, the maximum gets narrower and higher and closer to threshold, with increasing Z from 79 to 86. This behavior continues to $Z = 88$ for the HF calculation, but for the HS the maximum has moved below threshold (into the discrete range) at $Z = 88$. Thus the effect of including exchange correctly is to make the effective potential for f waves somewhat less attractive near the outer edge of the atom; in the HS calculation the field is strong enough to depress the delayed maximum into the discrete, while for the HF calculation, the field is weaker and the $d \rightarrow f$ maximum remains above threshold.

From the above examples, it is seen that HF (*intrachannel coupling*) theory gives significant corrections to HS results in the energy region near