

It is intended to apply these equations to obtain the correction to the binding energy of the Thomas-Fermi atom due to relativistic effects. At present, the relativistic effect is known only on the basis of rough numerical estimates,⁸ although it represents a significant correction to the binding energy of the heavier elements. Rudkjøbing's results can be used also to obtain a relativistic analog of Hellmann's equation,⁹ in which the angular momenta of the electrons enter explicitly into the electron density.

⁸ J. M. C. Scott, *Phil. Mag.* **43**, 859 (1952).

⁹ H. Hellmann, *Acta Physicochim. (U.R.S.S.)* **4**, 225 (1936).

The expression for the density of states corresponding to (4), suitably modified to apply to nucleons, may have application in the statistical theory¹⁰ of the nucleus. The analog of Hellmann's equation noted above, suitably modified to apply to nucleons, may be of help in clarifying aspects of the spin-orbit coupling in the shell model of the nucleus.

The author wishes to thank Dr. A. L. Latter and Dr. R. Latter of the Rand Corporation for helpful discussions.

¹⁰ P. Gombas, *Ann. Physik* **10**, 253 (1952); **12**, 155 (1953); W. G. McMillan, *Phys. Rev.* **92**, 210 (1953).

Approximate Hartree-Type Wave Functions and Matrix Elements for the *K* and *L* Shells of Atoms and Ions

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Perturbation effects of electron screening on wave functions and dipole matrix elements of *K* and *L* electrons of ions or inner shells of atoms have been computed to order Z^{-1} . Some screening effects of this order have also been computed for the *M* shell. Some of the terms of order Z^{-2} have also been evaluated and found to be small compared with those neglected in this paper. The dipole matrix elements have been used to compute x-ray mass absorption coefficients and the comparison with the experimental values is discussed.

INTRODUCTION

FOR many problems, such as the determination of the photoelectric absorption, ionization by electron impact, stopping power for fast particles, etc., one needs to know atomic wave functions and dipole matrix elements for atoms and ions. In the case of highly ionized atoms such as found in stellar interiors, or for atoms of atomic number of 20 or greater, the wave functions of *K* and *L* shells are sufficiently "hydrogen-like" so that the effects of screening can be roughly estimated.¹ These estimates serve to give the order of magnitude of screening effects but in many cases may be off by large factors. In some problems such as that of determining the Rosseland mean opacity of matter under conditions of high temperature and pressure, one needs to be able to calculate the photoelectric cross sections for a large variety of atoms in all stages of ionization. The straightforward procedure of obtaining, say, Hartree wave functions for a sample of states of each atom for each stage of ionization, is a prohibitively long program even for high-speed computers. Since the quantities involved are nearly hydrogen-like, it is probable that such a program would be greatly overdoing the problem and that the same amount of information can be obtained with considerably less work.

A possible analytical approach to this problem might

be to employ the set of approximate variational functions of Morse, Young, and Hawrwtiz² for the bound states and Coulomb free functions using an atomic number equal to that of the nucleus, minus the number of screening electrons in the shell of the initial state and those lying inside that shell.³ This procedure suffers from two difficulties: first, in not correctly representing the actual potential in which the optical electron moves, and second, in not obtaining the correct wave functions for even the assumed potential. Since the dipole moment is the expansion coefficient of r times the bound wave functions in terms of the wave functions of the upper state, this moment may be very sensitive to small changes in the form of the function assumed. The correction thus obtained to the hydrogen-like values may merely represent the error in the assumed solution.

In order to eliminate part of the uncertainty in the calculation, we have employed a method in which the potential is assumed but the radial wave equation and the dipole moment are solved for directly. This enables one to investigate, without ambiguity, the dependence of the dipole moment on the form of the potential assumed. The results of these computations can also be used as a basis for testing the validity of variational wave functions since they are solutions of a definite non-Coulombic problem.

The method of the present paper is to extend the

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¹ H. Hall, *Revs. Modern Phys.* **8**, 358 (1936).

² Morse, Young, and Hawrwtiz, *Phys. Rev.* **48**, 948 (1935); also, L. Goldberg and A. M. Clogston, *Phys. Rev.* **56**, 696 (1939).

³ J. A. Wheeler, *Phys. Rev.* **43**, 258 (1933).

computations by developing the wave functions and dipole matrix elements in power series in the number of screening electrons divided by the atomic number. The validity of this expansion is investigated and an experimental verification is made using the observed x-ray mass absorption coefficient.

THE CALCULATIONAL PROCEDURE

A. Bound Wave Functions

Hartree wave functions are solutions of the central field problem. The radial wave functions R_{nl} of type nl are solutions of Schrödinger's radial equation

$$\frac{d^2 R_{nl}}{dr^2} + \left[\epsilon_{nl} + \frac{2}{r} - \frac{1}{Z} \sum' N_{ij} V_{ij} - \frac{l(l+1)}{r^2} \right] R_{nl} = 0, \quad (1)$$

where Z is the atomic number, ϵ_{nl} is the energy parameter in units $Z^2 e^2 / 2a_0$, and r is in units a_0 / Z , where a_0 is the Bohr radius. N_{ij} is the number of screening electrons of type ij (the prime on the summation indicates that the nl term whose wave function is being computed is omitted from the summation). V_{ij} is the screening potential of a radial charge distribution of type R_{ij} .

$$V_{ij} = - \frac{2}{r} \int_0^r [R_{ij}]^2 dr + 2 \int_r^\infty [R_{ij}]^2 dr / r. \quad (2)$$

The Hartree method consists of making an initial guess of the radial wave functions R_{ij}^0 , using these to compute the potential V_{ij}^0 , and then solving the differential equation (1) for the resulting set of functions, say R_{nl}^1 . These functions are then used in Eq. (2) to compute a new potential V_{ij}^1 which is again used in Eq. (1) to determine a new set of solutions R_{nl}^2 etc., until there is no change in the resulting wave functions. Since we are dealing with high stages of ionization and inner shells of atoms, we take hydrogenic functions as our initial guess, i.e., $R_{ij}^0 = R_{ij}^H$.

Each solution of Eq. (1) will be a function of Z , the number of screening electrons in the configuration, and the particular stage of the iteration process. We express this dependence in the following example. The $2s$ radial wave function for $Z=26$, which is a solution of the differential equation (1) in the configuration $(1s)^x (2s)^y (2p)^z$ in which hydrogen-like screening functions were used in Eq. (2) for the potential, will be written as $R_{2s}^1 [Z; (1s^0)^x (2s^0)^{y-1} (2p^0)^z]$. In the next iteration the screening functions would be $(1s^1)^x (2s^1)^{y-1} \times (2p^1)^z$ so that the function would be written $R_{2s}^2 \times [Z; (1s^1)^x (2s^1)^{y-1} (2p^1)^z]$.

The method of the present paper is based on the assumption that the effect of the screening potential on any solution of Eq. (1) is given sufficiently well by a first order perturbation of the corresponding hydrogen-like wave function. Taking hydrogen-like zero-order functions, the r th iterative solution of Eq. (1) can be written as

$$R_{nl}^r = R_{nl}^H + \frac{1}{Z} \sum' N_{ij} \sum' \frac{[V_{ij}^{r-1}]_{pl, nl} R_{pl}^H}{\epsilon_n^H - \epsilon_p^H}, \quad (3)$$

where as before the indices i, j run over all the screening electrons, and $[V_{ij}^{r-1}]_{pl, nl}$ is the matrix element of V_{ij}^{r-1} calculated with the hydrogen-like radial functions R_{nl}^H and R_{pl}^H . The quantity

$$\sum' \frac{[V_{ij}^{r-1}]_{pl, nl} R_{pl}^H}{\epsilon_n^H - \epsilon_p^H} \equiv \Delta R_{nl}(ij^{r-1}), \quad (4)$$

which we will call the change in the radial wave function of type nl introduced by the radial wave functions of type (ij^{r-1}) , is independent of the atomic number Z and of the number of screening electrons present when hydrogen-like functions are used in Eq. (2). Equation (3) can then be written

$$R_{nl}^r = R_{nl}^H + \frac{1}{Z} \sum' N_{ij} \Delta R_{nl}(ij^{r-1}). \quad (5)$$

The $2s$ radial wave functions for an ion of nuclear charge Z having a full K and L shell screened by hydrogen-like screening functions would be written

$$R_{2s}^1 [Z; (1s^0)^2 (2s^0) (2p^0)^6] = R_{2s}^H + (2/Z) \Delta R_{2s}(1s^0) + (1/Z) \Delta R_{2s}(2s^0) + (6/Z) \Delta R_{2s}(2p^0). \quad (6)$$

Since the ΔR 's are orthogonal to R^H to the approximation used here, the functions on the left-hand side of the Eqs. (5) and (6) are normalized as they stand to terms of order $(1/Z^2) \int_0^\infty (\Delta R_{2s})^2 dr$.

In the second approximation when one inserts R_{nl}^1 from Eq. (5) into Eq. (2) for the potential, V_{ij}^1 can be written in a manner analogous to Eq. (5) as

$$V_{ij}^1 = V_{ij}^0 + \frac{1}{Z} \sum' N_{nl} \Delta V_{ij}(nl^0), \quad (7)$$

if we neglect the term involving the square of ΔR . If we neglect the terms $\Delta R_{1s}(2s^0)$ and $\Delta R_{1s}(2p^0)$ as is the usual practice in the Hartree method, the $2s$ and the $2p$ radial solutions of Eq. (1) for a configuration $(1s)^x \times (2s)^y (2p)^z$ can be written

$$R_{2s}^2 [Z; (1s^1)^x (2s^1)^{y-1} (2p^1)^z] = (2s^0) + \frac{x}{Z} \Delta_{2s}(1s^0) + \frac{x(x-1)}{Z^2} \Delta_{2s}[\Delta_{1s}(1s^0)] + \frac{(y-1)}{Z} \Delta_{2s}(2s^0) + \frac{x(y-1)}{Z^2} \Delta_{2s}[\Delta_{2s}(1s^0)] + \frac{(y-1)(y-1)}{Z^2} \Delta_{2s}[\Delta_{2s}(2s^0)] + \frac{(y-1)z}{Z^2} \Delta_{2s}[\Delta_{2s}(2p^0)] + \frac{z}{Z} \Delta_{2s}(2p^0) + \frac{zx}{Z^2} \Delta_{2s}[\Delta_{2p}(1s^0)] + \frac{zy}{Z^2} \Delta_{2s}[\Delta_{2p}(2s^0)] + \frac{z(z-1)}{Z^2} \Delta_{2s}[\Delta_{2p}(2p^0)]; \quad (8)$$

$$\begin{aligned}
R_{2p}^2[Z; (1s)^x(2s^1)^y(2p^1)^{z-1}] &= (2p^0) + \frac{x}{Z}\Delta_{2p}(1s^0) \\
&+ \frac{x(x-1)}{Z^2}\Delta_{2p}[\Delta_{1s}(1s^0)] + \frac{y}{Z}\Delta_{2p}(2s^0) + \frac{xy}{Z^2}\Delta_{2p}[\Delta_{2s}(1s^0)] \\
&+ \frac{y(y-1)}{Z^2}\Delta_{2p}[\Delta_{2s}(2s^0)] + \frac{yz}{Z^2}\Delta_{2p}[\Delta_{2s}(2p^0)] \\
&+ \frac{(z-1)}{Z}\Delta_{2p}(2p^0) + \frac{(z-1)x}{Z^2}\Delta_{2p}[\Delta_{2p}(1s^0)] \\
&+ \frac{(z-1)y}{Z^2}\Delta_{2p}[\Delta_{2p}(2s^0)] + \frac{(z-1)(z-1)}{Z^2} \\
&\quad \times \Delta_{2p}[\Delta_{2p}(2p^0)], \quad (9)
\end{aligned}$$

where the expression $\Delta_{2s}[\Delta_{1s}(1s^0)]$ etc., the change in a $2s$ due to the change in a $1s$ by a $1s^0$, etc., are merely an extension of the notation $\Delta_{2s}(1s^0)$, etc. For simplicity in the above and following equations, the R will be suppressed whenever no confusion from this results. It is at once apparent from the point of view of perturbation theory, that the Hartree procedure is a power series expansion of the radial wave functions in essentially the number of screening electrons divided by the atomic number Z . If this expansion parameter is small, convergence is, of course, rapid. The rapid increase in the number of terms in the expression with each stage of the iteration process, as well as the fact that we have neglected terms of order $1/Z^2$ in the first iteration, make the extension of the present method past R_{nl}^2 unprofitable.

B. Free Wave Functions

The free radial wave functions result from a solution of Eq. (1) for positive values of the energy parameter $\epsilon_{nl} = \eta$. In the one-electron problem, η is, of course, the kinetic energy of the escaping electron. The expression analogous to Eq. (5) for the free function is

$$R_{\eta l}^1 = R_{\eta l}^0 + \frac{1}{Z} \sum'_{ij} N_{ij} \Delta R_{\eta l}(ij), \quad (10)$$

where we have replaced n by η as a subscript of R . Since second-order effects are likely to be unimportant for the free functions, no second-order terms are considered. We should point out that $R_{\eta l}^1$ in Eq. (10) is the wave function for the *same energy* ϵ_{nl} as $R_{\eta l}^0$.

C. Matrix Elements

Consider the matrix element $I_{nl}^{n'l'}$ defined as

$$I_{nl}^{n'l'} = \int_0^\infty R_{nl} r R_{n'l'} dr, \quad (11)$$

with R_{nl} and $R_{n'l'}$ defined as in Eq. (5):

$$I_{nl}^{n'l'} = H I_{nl}^{n'l'} + \frac{1}{Z} \sum'_{ij} N_{ij} \Delta I_{nl}^{n'l'}(ij), \quad (12)$$

where we neglect terms in $Z^{-2} \int_0^\infty R_{nl} r \Delta R_{n'l'} dr$. Matrix elements involving R_{2s}^2 and R_{2p}^2 can be obtained from Eqs. (8) and (9) on replacing $\Delta_{2s}(1s^0)$, $\Delta_{2s}[\Delta_{2s}(2s^0)]$, etc., by $\Delta I_{2s}^{n'l'}(1s^0)$ and $\Delta I_{2s}^{n'l'}[\Delta_{2s}(2s^0)]$, etc., respectively.

Care must be exercised in the use of Eq. (12) in computing $[I_{nl}^{n'l'}]^2$ as $(1/Z)\Delta I$ is not necessarily small compared to I , so that terms in $(1/Z^2)[\Delta I]^2$ must be retained.

COMPUTATIONAL DETAILS

A. First-Order Terms

In order to evaluate the first-order terms in Eqs. (8) and (9) the following computations were made:

$$\begin{aligned}
&R_{1s}^1[6; (1s^0)], \quad R_{2s}^1[6; (1s^0)], \quad R_{2p}^1[6; (1s^0)], \\
&R_{3s}^1[6; (1s^0)], \quad R_{3p}^1[6; (1s^0)], \quad R_{3d}^1[6; (1s^0)], \\
&\quad R_{2s}^1[26; (1s^0)(2s^0)], \\
&R_{2p}^1[26; (1s^0)^2(2s^0)], \quad R_{3s}^1[26; (1s^0)^2(2s^0)], \\
&\quad R_{3p}^1[26; (1s^0)^2(2s^0)], \\
&R_{3d}^1[26; (1s^0)^2(2s^0)], \quad R_{2s}^1[26; (1s^0)^2(2p^0)], \\
&\quad R_{2p}^1[26; (1s^0)^2(2p^0)], \\
&R_{3s}^1[26; (1s^0)^2(2p^0)], \quad R_{3p}^1[26; (1s^0)^2(2p^0)], \\
&\quad R_{3d}^1[26; (1s^0)^2(2p^0)], \\
&R_{\eta s}^1[6; (1s^0)], \quad R_{\eta p}^1[6; (1s^0)], \quad R_{\eta d}^1[6; (1s^0)], \\
&\quad R_{\eta f}^1[6; (1s^0)], \\
&R_{\eta s}^1[26; (1s^0)^2(2s^0)], \quad R_{\eta p}^1[26; (1s^0)^2(2s^0)], \\
&\quad R_{\eta d}^1[26; (1s^0)^2(2s^0)], \\
&R_{\eta f}^1[26; (1s^0)^2(2s^0)], \quad R_{\eta p}^1[26; (1s^0)^2(2p^0)], \\
&R_{\eta f}^1[26; (1s^0)^2(2p^0)], \quad R_{\eta d}^1[26; (1s^0)(2p^0)], \\
&R_{\eta f}^1[26; (1s^0)^2(2p^0)].
\end{aligned}$$

The free functions were computed for $\eta = 0.00, 0.25, 0.50, 1.00$. The International Business Machines Card Programmed Calculator was used for this computation using the Noumerov method. A description of this method has already been given by Pratt.⁴

The free functions were computed numerically out to distances required to evaluate the matrix elements. At that point they were joined to a WKB-Jeffreys solution for purposes of normalization.

Since the method involves taking of differences, considerable accuracy was maintained throughout the

⁴ G. W. Pratt, Jr., Phys. Rev. 88, 1217 (1952).

calculation. In all the work 10 decimal places were carried in the computation, and the wave functions are expected to be good to five or six places. In this approximation, the radial functions for the same Z and screening are strictly orthogonal. Our numerical functions turned to be orthogonal to about 1 part in 10^6 .

In Table I are listed the energy parameters obtained in the calculation of the bound functions. A plot of the various ΔR 's can be found in ANL-5008.⁵ The plotting accuracy is sufficient so that if one desires first-order wave functions, they are obtainable from these graphs and a good table of hydrogen-like wave functions. In Table II are listed the intensity integrals, I , computed with these functions, and the ΔI 's. For reference, a list of hydrogen-like integrals are also given. The functions $R_{\eta s}[26; (1s^0)^2(2p^0)]$ were not computed because they should be very similar to $R_{\eta s}[26; (1s^0)^2(2s^0)]$. The latter function was used to compute the intensity integral $I_{2p}^{\eta s}[26; (1s^0)^2(2p^0)]$. This should be permissible since these transitions are not very important in most applications. As a matter of fact, most of the free functions might have been taken as Coulomb functions for $Z = Z - N_b$ where N_b is the number of bound screening electrons. A check of this was made in one case by setting $V_{ij} = 2$ in Eq. (1) for $Z = 6$ and $l = 1$ and computing the free wave function for $\eta = \frac{1}{4}$. The corresponding intensity integral $I_{1s}^{\eta p}$ was 1.26017 as compared with 1.24435 for the correct wave function, while that of $I_{2s}^{\eta p}$ was 1.65975 as compared with 1.65106 for the correct wave functions.

Since the first-order functions R_{nl}^1 , have all been computed in the same potential, the sum rule,

$$\sum_n [I_{nl}^{\eta' \nu}]^2 = \int_0^\infty R_{n\nu} r^2 R_{nl} dr,$$

should hold exactly. For completeness, we have also computed $\int_0^\infty R_{nl} r^2 R_{nl} dr$ for the bound states, and have included this in Table II.

A check of the over-all numerical procedure, as well as the method of normalization of the free functions, was made by computing the hydrogen-like intensity integral $I_{1s}^{\eta p}$ for $\eta = 0.7949720$. The numerical result was 0.5120256 as compared with the result of 0.5120225 obtained on evaluating the usual formula.

B. Second-Order Terms

Second-order terms have been computed for the L shell only. The following computations were made:

$$\begin{aligned} &R_{2s}^2[6; (1s^1)], R_{2p}^2[6; (1s^1)], R_{1s}^2[6; (1s^1)], \\ &R_{2s}^2[26; (1s^1)^2], R_{2p}^2[26; (1s^1)^2], R_{2s}^2[26; (1s^1)^2(2s^1)], \\ &R_{2p}^2[26; (1s^1)^2(2s^1)], R_{2s}^2[26; (1s^1)^2(2p^1)], \\ &R_{2p}^2[26; (1s^1)^2(2p^1)], \end{aligned}$$

⁵ R. E. Meyerott, Argonne National Laboratory Report ANL-5008, 1953 (unpublished).

TABLE I. Energy parameters.*

$\epsilon_{1s}[6; (1s^0)]$	-0.7949720
$\epsilon_{2s}[6; (1s^0)]$	-0.1838118
$\epsilon_{2p}[6; (1s^0)]$	-0.1749160
$\epsilon_{3s}[6; (1s^0)]$	-0.080076815
$\epsilon_{3p}[6; (1s^0)]$	-0.077584471
$\epsilon_{3d}[6; (1s^0)]$	-0.077171480
$\epsilon_{2s}[26; (1s^0)^2(2s^0)]$	-0.207294688
$\epsilon_{2p}[26; (1s^0)^2(2s^0)]$	-0.201800451
$\epsilon_{3s}[26; (1s^0)^2(2s^0)]$	-0.090172552
$\epsilon_{3p}[26; (1s^0)^2(2s^0)]$	-0.088502789
$\epsilon_{3d}[26; (1s^0)^2(2s^0)]$	-0.087328213
$\epsilon_{2s}[26; (1s^0)^2(2p^0)]$	-0.206515011
$\epsilon_{2p}[26; (1s^0)^2(2p^0)]$	-0.200498725
$\epsilon_{3s}[26; (1s^0)^2(2p^0)]$	-0.089998252
$\epsilon_{3p}[26; (1s^0)^2(2p^0)]$	-0.088238438
$\epsilon_{3d}[26; (1s^0)^2(2p^0)]$	-0.087186374
$\epsilon_{1s}[6; (1s^1)]$	-0.801402423
$\epsilon_{2s}[6; (1s^1)]$	-0.184327493
$\epsilon_{2p}[6; (1s^1)]$	-0.175211915
$\epsilon_{2s}[26; (1s^1)^2]$	-0.218559937
$\epsilon_{2p}[26; (1s^1)^2]$	-0.213908925
$\epsilon_{2s}[26; (1s^1)^2(2s^1)]$	-0.207711391
$\epsilon_{2s}[26; (1s^1)^2(2s^1)]^*$	-0.206912949
$\epsilon_{2p}[26; (1s^1)^2(2s^1)]^*$	-0.201314780
$\epsilon_{2s}[26; (1s^1)^2(2p^1)]^*$	-0.206124176
$\epsilon_{2p}[26; (1s^1)^2(2p^1)]^*$	-0.199982918

* See footnote to Table III.

where

$$\begin{aligned} 1s^1 &= 1s^0 + (1/6)\Delta_{1s}(1s^0) \quad \text{for } Z=6, \\ 1s^1 &= 1s^0 + (1/26)\Delta_{1s}(1s^0) \quad \text{for } Z=26. \end{aligned} \quad (13)$$

For the R_{2s} function the $2s^1$ and $2p^1$ screening functions were taken to be, respectively,

$$\begin{aligned} 2s^1 &= 2s^0 + (2/26)\Delta_{2s}(1s^0) + (1/26)\Delta_{2s}(2s^0), \\ 2p^1 &= 2p^0 + (2/26)\Delta_{2p}(1s^0) + (1/26)\Delta_{2p}(2s^0). \end{aligned} \quad (14)$$

For the R_{2p}^2 function the $2s^1$ and $2p^1$ screening functions were taken to be, respectively,

$$\begin{aligned} 2s^1 &= 2s^0 + (2/26)\Delta_{2s}(1s^0) + (1/26)\Delta_{2s}(2p^0), \\ 2p^1 &= 2p^0 + (2/26)\Delta_{2p}(1s^0) + (1/26)\Delta_{2p}(2p^0). \end{aligned} \quad (15)$$

The functions $1s^1$, $2s^1$, and $2p^1$ used in computing the potential were normalized even though this is not assumed according to our procedure. As stated before, this is a small correction.

By mistake, the sign of the correcting terms in Eqs. (13), (14), and (15) was reversed in computing the functions used for $R_{2s}^2[26; (1s^1)^2(2s^1)]$, $R_{2p}^2[26; (1s^1)^2(2p^1)]$, $R_{2p}^2[26; (1s^1)^2(2s^1)]$, and $R_{2s}^2[26; (1s^1)^2 \times (2p^1)]$. This should not cause any trouble but merely change the sign of some of the differences. To check the consistency of the result, $R_{2s}^2[26; (1s^1)^2(2s^1)]$ was computed with the correct signs of the correcting terms. Any differences between the two functions are due to higher-order terms appearing in Eq. (3).

The functions computed are insufficient to evaluate all the quantities needed in Eqs. (8) and (9). We can

only evaluate

$$\begin{aligned} &\Delta_{2s}[\Delta_{1s}(1s^0)], \quad \Delta_{2p}[\Delta_{1s}(1s^0)], \quad \Delta_{2s}[\Delta_{2s}(1s^0)^2(2s^0)], \\ &\Delta_{2s}[\Delta_{2p}(1s^0)^2(2s^0)], \quad \Delta_{2p}[\Delta_{2s}(1s^0)^2(2p^0)], \\ &\quad \Delta_{2p}[\Delta_{2p}(1s^0)^2(2p^0)]. \end{aligned}$$

Since these second-order terms are small, we have resorted to an approximation in order to reduce the amount of computing necessary.

Inspection of Figs. 2 and 3 in ANL-5008 shows that $\Delta_{2s}(1s^0)$, $\Delta_{2s}(2s^0)$, and $\Delta_{2s}(2p^0)$ are approximately proportional, as are $\Delta_{2p}(1s^0)$, $\Delta_{2p}(2s^0)$, and $\Delta_{2p}(2p^0)$. Also, since the changes due to the $1s^0$ are considerably larger, not much error will be made if we assume those due to the $2s^0$ and $2p^0$ are strictly proportional to that of $1s^0$ for the purpose of computing the second-order terms. The proportionality constant has been chosen at the first maxima for the $2p$ function and second maxima for the $2s$ function. This is on the assumption that this region is the most important for the L -shell functions.

We then have

$$\begin{aligned} \Delta_{2p}(2p^0) &= 0.369\Delta_{2p}(1s^0), \\ \Delta_{2s}(2p^0) &= 0.325\Delta_{2s}(1s^0), \\ \Delta_{2s}(2s^0) &= 0.236\Delta_{2s}(1s^0), \\ \Delta_{2p}(2s^0) &= 0.223\Delta_{2p}(1s^0). \end{aligned} \quad (16)$$

The various Δ 's are given by

$$\begin{aligned} \Delta_{2p}[\Delta_{2p}(1s^0)] &= 0.4221\Delta_{2p}[\Delta_{2p}(1s^0)^2(2p^0)], \\ \Delta_{2p}[\Delta_{2p}(2s^0)] &= 0.0942\Delta_{2p}[\Delta_{2p}(1s^0)^2(2p^0)], \\ \Delta_{2p}[\Delta_{2p}(2p^0)] &= 0.1558\Delta_{2p}[\Delta_{2p}(1s^0)^2(2p^0)], \\ \Delta_{2p}[\Delta_{2s}(1s^0)] &= 0.4301\Delta_{2p}[\Delta_{2s}(1s^0)^2(2p^0)], \\ \Delta_{2p}[\Delta_{2s}(2s^0)] &= 0.1012\Delta_{2p}[\Delta_{2s}(1s^0)^2(2p^0)], \\ \Delta_{2p}[\Delta_{2s}(2p^0)] &= 0.1398\Delta_{2p}[\Delta_{2s}(1s^0)^2(2p^0)], \\ \Delta_{2s}[\Delta_{2s}(1s^0)] &= 0.4472\Delta_{2s}[\Delta_{2s}(1s^0)^2(2s^0)], \\ \Delta_{2s}[\Delta_{2s}(2s^0)] &= 0.1055\Delta_{2s}[\Delta_{2s}(1s^0)^2(2s^0)], \\ \Delta_{2s}[\Delta_{2s}(2p^0)] &= 0.1455\Delta_{2s}[\Delta_{2s}(1s^0)^2(2s^0)], \\ \Delta_{2s}[\Delta_{2p}(1s^0)] &= 0.4498\Delta_{2s}[\Delta_{2p}(1s^0)^2(2s^0)], \\ \Delta_{2s}[\Delta_{2p}(2s^0)] &= 0.1003\Delta_{2s}[\Delta_{2p}(1s^0)^2(2s^0)], \\ \Delta_{2s}[\Delta_{2p}(2p^0)] &= 0.1659\Delta_{2s}[\Delta_{2p}(1s^0)^2(2s^0)]. \end{aligned} \quad (17)$$

For a full K and L shell, substitution in Eqs. (8) and (9) gives

TABLE III. Second-order integrals.*

η	$Z=6(1s^1)$ screening			
	$I_{1s}^{\eta p}$	$I_{2s}^{\eta p}$	$I_{2p}^{\eta s}$	$I_{2p}^{\eta d}$
0.00	2.00996	6.22435	2.27097	7.84849
0.25	1.24534	1.65412	0.469878	1.23067
0.50	0.846387	0.776522	0.190117	0.448074
1.00	0.463290	0.298905	0.0596231	0.129059
η	$Z=26(1s^1)^2(2s^1)$ screening			
	$I_{2s}^{\eta p}$	$I_{2p}^{\eta s*}$	$I_{2p}^{\eta d*}$	
0.00	5.64154	1.86353	6.9001	
0.25	1.64003	0.448450	1.29724	
0.50	0.791521	0.191707	0.495553	
1.00	0.310500	0.0633291	0.147244	
η	$Z=26(1s^1)^2(2p^1)$ screening			
	$I_{2s}^{\eta p*}$	$I_{2p}^{\eta s*}$	$I_{2p}^{\eta d*}$	
0.00	5.65849	1.91256	6.90200	
0.25	1.62687	0.455107	1.28726	
0.50	0.778468	0.193193	0.490782	
1.00	0.306751	0.0631279	0.145772	

* The I 's in this table marked with *, and also the E_{nl} of Table I marked with *, refer to those functions mentioned in part B of the section on Computational Details, computed using the wrong sign of the second-order potential correction.

$$\begin{aligned} R_{2s}^2[Z; (1s^1)^2(2s^1)^1(2p^1)^6] &= (2s^0) + \frac{2}{Z}\Delta_{2s}(1s^0) \\ &+ \frac{2}{Z^2}\Delta_{2s}[\Delta_{1s}(1s^0)] + \frac{1}{Z}\Delta_{2s}(2s^0) \\ &+ \frac{1.8729}{Z^2}\Delta_{2s}[\Delta_{2s}(1s^0)^2(2s^0)] + \frac{6}{Z}\Delta_{2s}(2p^0) \\ &+ \frac{9.7782}{Z^2}\Delta_{2s}[\Delta_{2p}(1s^0)^2(2s^0)], \end{aligned} \quad (18)$$

and

$$\begin{aligned} R_{2p}^2[Z; (1s^1)^2(2s^1)^2(2p^1)^5] &= (2p^0) + \frac{2}{Z}\Delta_{2p}(1s^0) \\ &+ \frac{2}{Z^2}\Delta_{2p}[\Delta_{1s}(1s^0)] + \frac{2}{Z}\Delta_{2p}(2s^0) \\ &+ \frac{3.6004}{Z^2}\Delta_{2p}[\Delta_{2s}(1s^0)^2(2p^0)] + \frac{5}{Z}\Delta_{2p}(2p^0) \\ &+ \frac{9.058}{Z^2}\Delta_{2p}[\Delta_{2p}(1s^0)^2(2p^0)]. \end{aligned} \quad (19)$$

The second-order L -shell functions were used with the corresponding first-order free functions to evaluate the intensity integrals. These are listed in Table III. As before in $Z=26$, we have insufficient functions to evaluate all the ΔI 's needed. We can evaluate

$$\begin{aligned} &\Delta I_{2p}^{\eta d}[\Delta_{2p}(1s^0)^2(2p^0)], \quad \Delta I_{2p}^{\eta d}[\Delta_{2s}(1s^0)^2(2p^0)], \\ &\Delta I_{2s}^{\eta p}[\Delta_{2s}(1s^0)^2(2s^0)], \quad \Delta I_{2s}^{\eta p}[\Delta_{2p}(1s^0)^2(2s^0)], \\ &\Delta I_{2p}^{\eta s}[\Delta_{2p}(1s^0)^2(2p^0)], \quad \Delta I_{2p}^{\eta s}[\Delta_{2s}(1s^0)^2(2p^0)]. \end{aligned}$$

TABLE IV. Second-order ΔI 's.

η	$\Delta I_{1s}{}^{\eta p}[\Delta_{1s}(1s^0)]$	$\Delta I_{2s}{}^{\eta p}[\Delta_{1s}(1s^0)]$	$\Delta I_{2p}{}^{\eta s}[\Delta_{1s}(1s^0)]$	$\Delta I_{2p}{}^{\eta d}[\Delta_{1s}(1s^0)]$
0.00	-0.301896	-1.00654	-0.60932	+0.3978
0.25	+0.035808	+0.110054	-0.09714	+0.3534
0.50	+0.121108	+0.141244	-0.06068	+0.2171
1.00	+0.129326	+0.0951983	-0.02715	+0.09886
η	$\Delta I_{2s}{}^{\eta p}[\Delta_{2s}(1s^0)^2(2s^0)]$	$\Delta I_{2p}{}^{\eta s}[\Delta_{2s}(1s^0)^2(2p^0)]$	$\Delta I_{2p}{}^{\eta d}[\Delta_{2s}(1s^0)^2(2p^0)]$	
0.00	-1.00976	-8.6206	+10.6743	
0.25	+3.11999	-0.6028	+5.3768	
0.50	+1.82818	+0.1281	+2.0019	
1.00	+0.68336	+0.1551	+0.3990	
η	$\Delta I_{2s}{}^{\eta p}[\Delta_{2p}(1s^0)^2(2s^0)]$	$\Delta I_{2p}{}^{\eta s}[\Delta_{2p}(1s^0)^2(2p^0)]$	$\Delta I_{2p}{}^{\eta d}[\Delta_{2p}(1s^0)^2(2p^0)]$	
0.00	-3.27519	-10.9453	+11.711	
0.25	-2.68340	-1.2717	+6.869	
0.50	+1.93914	-0.2796	+2.938	
1.00	+0.80006	+0.0695	+0.7803	

The ΔI 's corresponding to the ΔR 's can be found from Eq. (17). The corresponding Δ 's are given in Table IV. For atoms or ions having full K and L shells, the substitution of I for R in Eqs. (18) and (19) lead to expressions for I of the form

$$I_{nl}{}^{\eta l'} = {}^H I_{nl}{}^{\eta l'} + a_{nl}{}^{\eta l'}/Z + b_{nl}{}^{\eta l'}/Z^2. \quad (20)$$

In Table V are listed the a 's and b 's for the case of atoms or ions having initially full K and L shells.

For ions having electrons in K and L shells only, the $I_{nl}{}^{\eta l'}$ are those which correspond to electrons leaving the system with kinetic energy η . It is shown in Appendix I for atoms or ions which have electrons in M or higher shells, that the intensity integral is the one for an electron leaving the system with kinetic energy $\eta + \epsilon_0$, where ϵ_0 is the change in the ionization energy due to external screening.

ACCURACY OF THE PERTURBATION APPROXIMATION

The difference between first- and second-order radial functions for the same Z and screening is due to the change in the potential. This has been computed and

TABLE V. Values of a and b for Eq. (20) for atoms and ions with full K and L shells.

η	${}^H I_{1s}{}^{\eta p}$	$a_{1s}{}^{\eta p}$	${}^H I_{2s}{}^{\eta p}$	$a_{2s}{}^{\eta p}$	$b_{2s}{}^{\eta p}$
0.00	1.5311	2.923	4.6888	62.37	-35.93
0.25	1.0137	1.384	1.5463	6.769	-20.18
0.50	0.7201	0.7374	0.77891	1.145	+22.67
1.00	0.4162	0.2611	0.31669	-0.04312	9.29
η	${}^H I_{2p}{}^{\eta s}$	$a_{2p}{}^{\eta s}$	$b_{2p}{}^{\eta s}$		
0.00	1.3535	28.82	-131.4		
0.25	0.39925	4.198	-13.884		
0.50	0.18359	1.0022	-2.193		
1.00	0.08268	-1.932	+1.1336		
η	${}^H I_{2p}{}^{\eta d}$	$a_{2p}{}^{\eta d}$	$b_{2p}{}^{\eta d}$		
0.00	5.4142	99.50	145.0		
0.25	1.2629	9.902	82.3		
0.50	0.51928	1.459	34.3		
1.00	0.16354	-0.2427	8.70		

found to be small, as is indicated by the small change in the intensity integrals. Since this change is so small, we can compare $\Delta_{2s}(1s^1)$ or $\Delta_{2p}(1s^1)$ computed for $Z=6$, with the same quantities computed for $Z=26$ as a measure of error introduced due to neglect of further terms in Eq. (5). In Fig. 1, $\Delta_{2s}(1s^1)$ and $\Delta_{2p}(1s^1)$ are plotted for $Z=6$ and $Z=26$. To the accuracy of this graph, $\Delta_{2s}(1s^0)$ and $\Delta_{2p}(1s^0)$ computed for $Z=6$ would be coincident with $\Delta_{2s}(1s^1)$ and $\Delta_{2p}(1s^1)$ respectively computed for $Z=6$. It can be seen that the Δ 's computed for $Z=6$ and $Z=26$ agree to about 10 percent, so that, since the Δ 's themselves do not contribute more than about 10 percent to the total wave function, the use of either Δ would give errors of the order of 1 percent. The difference between the Δ 's for $Z=6$ and $Z=26$ which is due to neglect of further terms in Eq. (5) is several times larger than the change in the Δ 's because of the change in the screening potential from its hydrogen-like value.⁶ Repeating the calculation for one more Z value would enable one to evaluate terms of order Z^{-2} . In that event, the Z^{-2} terms computed here due to the change in screening from its hydrogen-like value can be used and need not be recomputed.

THE ENERGY PARAMETER

Some problem exists regarding the interpolation of the energy parameter, ϵ_{nl} . In the first-order solutions, R_{nl}^1 contains terms of order $1/Z$, and hence the corresponding energy parameter ϵ_{nl}^1 ⁷ can, in principle, be determined to terms of order $1/Z^2$. To do this, we can

⁶ The quantities A , B , C , D , $(1/26)\Delta_{2s}[\Delta_{1s}(1s^0)]$, and $(1/26)\Delta_{2p}[\Delta_{1s}(1s^0)]$ shown in ANL-5008, were computed using $\Delta_{2s}(1s^1)$ and $\Delta_{2p}(1s^1)$ from $Z=26$, and $\Delta_{2s}(1s^0)$ and $\Delta_{2p}(1s^0)$ from $Z=6$. It is evident that the functions plotted there are essentially due to the higher terms in Eq. (5) and not to the change in the potential.

⁷ According to this notation, ϵ_{nl}^0 is the hydrogen-like energy parameter. ϵ_{nl}^1 is the first-order energy parameter computed with hydrogen-like functions and then ϵ_{nl}^2 would be that computed with the function R_{nl}^1 .

make use of $F_0(nl, n'l')$ ⁸ integrals computed analytically with hydrogen-like wave functions. The first-order energy parameter for say the 2s function in the configuration $(1s)^x(2s)^y(2p)^z$ would be

$$\epsilon_{2s}^1 = \epsilon_{2s}^0 + (x/Z)F_0(1s, 2s) + [(y-1)/Z]F_0(2s, 2s) + (z/Z)F_0(2p, 2s). \quad (21)$$

The energy parameters ϵ_{nl}^2 given in Table I found in the first-order computation can then be used to determine the terms of order $1/Z^2$. However, when we use R_{nl}^2 , this contains terms of order $1/Z^2$ so that the energy parameter should contain terms of order $1/Z^4$. We have no method for using the computed parameters ϵ_{nl}^3 to determine the coefficients of these terms.

Fortunately, we can make use of screening constants, as was suggested by Slater. In Eq. (21), $\epsilon_{2s}^0 = -\frac{1}{4}$, if we write Eq. (21) as

$$\epsilon_{2s}^1 = -\frac{1}{4} \left[1 - \frac{x4F_0(1s, 2s)}{2Z} - \frac{(y-1)4F_0(2s, 2s)}{2Z} - \frac{z4F_0(2p, 2s)}{2Z} \right], \quad (22)$$

we have an expression which is identical with Eq. (21) to first-order terms but includes terms of higher order. The energy parameter given by Eq. (22) compares favorably with that obtained in the second-order computations so that we have used this approximation to obtain our energy parameters. The quantities

$$\sigma_{n'l', nl} = \frac{1}{2}n^2F_0(n'l', nl) \quad (23)$$

are screening constants and turn out to be practically the same as those derived by Slater.⁹ For reference, Table VI is a list of these constants taken from Harris Mayer.¹⁰

THE MASS ABSORPTION COEFFICIENT

If the linear absorption coefficient is denoted by μ , for matter of density ρ , then the contribution to the mass absorption coefficient μ/ρ , by transitions $nl \rightarrow n'l'$

TABLE VI. Screening constants.

	1s	$\sigma(n'l', nl)$ 2s	2p
1s	0.6250	0.8395	0.9712
2s		0.6016	0.6484
2p			0.7266

⁸ See E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1950), p. 177.

⁹ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

¹⁰ H. Mayer, Los Alamos Report LADC-464 (unpublished).

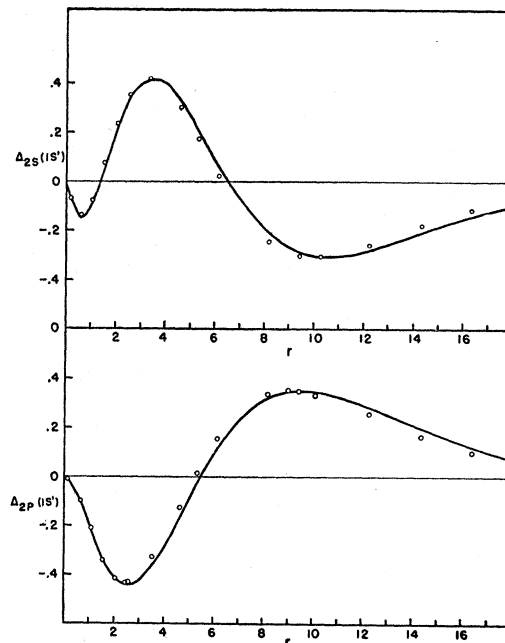


FIG. 1. $\Delta_{2s}(1s^1)$ and $\Delta_{2p}(1s^1)$ plotted as a function of r . The solid curves computed from $Z=6$, while the points indicate the same quantities for $Z=26$.

is given by

$$\begin{aligned} \mu/\rho &= N_{nl} \cdot \frac{4\pi^2\alpha a_0^2 A}{MZ^2} \cdot N_{n'l'} \frac{1 \text{ Max}(l, l')}{3(2l+1)} \nu [I_{nl} n'l']^2 \\ &= \frac{4.8596 \times 10^6}{MZ^2} \cdot N_{n'l'} \frac{1 \text{ Max}(l, l')}{3(2l+1)} \nu [I_{nl} n'l']^2, \end{aligned} \quad (24)$$

where N_{nl} = number of electrons per atom in the state specified by nl , a_0 = radius of the first Bohr orbit, α = fine structure const., A = Avogadro's Number, M = molecular weight of the substance, and ν = frequency of radiation absorbed expressed in Rydberg units.

Equation (24) assumes product-type wave functions and neglects exchange effects as well as lack of orthogonality of the initial and final state wave functions of electrons not making the transition.

The methods discussed in the previous sections can be used with Tables II to IV to calculate the I 's in Eq. (24). However, since the mass absorption coefficient varies approximately as ν^{-3} , it is important to know the value of ν with some precision. Strictly speaking, when we use the first-order wave functions and compute the I 's to order $1/Z$, the energy parameter, which is taken to be the same as the ionization energy, should be taken to order $1/Z^2$. Second-order corrections in the I 's are not as important as the effect of change in the frequency, ν .

For purposes of experimental comparison, the mass absorption coefficients have been computed for aluminum and copper for frequencies beyond the K absorp-

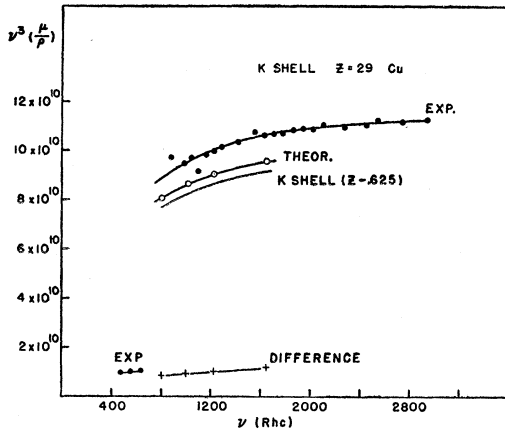


FIG. 2. $\nu^3(\mu/\rho)$ for the K shell of copper. Experimental data by Schulz.

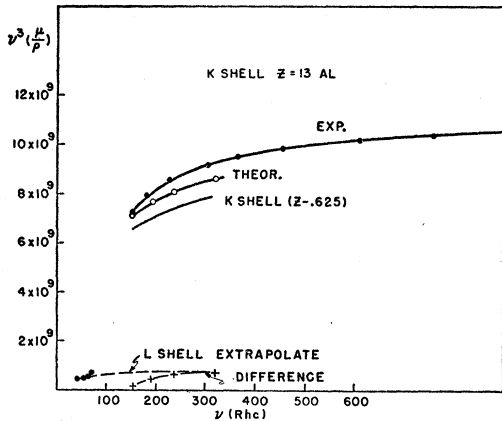


FIG. 3. $\nu^3(\mu/\rho)$ for the K shell of aluminum. The points below K edge are taken from Hill. The points above K edge are taken from Victoreen.

tion edge, and for aluminum, copper, and silver for frequencies between the L absorption edge and the K absorption edge. Since the mass absorption coefficients for the photoelectric effect vary approximately as ν^{-3} , $\nu^3(\mu/\rho)$ was plotted instead of μ/ρ . The results are shown in Figs. 2 to 6. For comparison the experimental values of the same quantities are shown. These data were taken from Landolt-Börnstein (data by Schulz, Jönsson, Andrews), Victoreen, Hill, Biermann, and Tomboulian and Pell,¹¹ as indicated in the figures, and have been corrected for scattering by the tables given by White.¹²

Unfortunately only the total absorption is measured and not the contribution due to the various electron shells. It is only at the absorption edges that one

¹¹ H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie* (Springer Verlag, Berlin, 1950), sixth edition, Vol. I, pp. 314-316; J. A. Victoreen, *J. Appl. Phys.* **20**, 1141 (1949); R. D. Hill, *Proc. Roy. Soc. (London)* **A161**, 284 (1937); H. H. Biermann, *Ann. Physik* **26**, 740 (1936); D. H. Tomboulian and E. M. Pell, *Phys. Rev.* **83**, 1196 (1951).

¹² Gladys R. White, National Bureau of Standards Report NBSR-1003 (unpublished).

knows that the increase in absorption is due to a new shell. Here also, there is uncertainty since the effects of the lattice structure gives the experimental points considerable scatter.

The results of the present calculation and the magnitude of the absorption from the M and higher-lying shells can be somewhat better understood by making a comparison with the Coulomb result for some effective Z . Since $\nu^3(\mu/\rho)$ varies like Z^4 for the Coulomb problem, it seems likely that the maximum value for this quantity should be that computed for the effective $Z^*=Z$, the nuclear charge of the atom in question. For the K shell, where screening is relatively unimportant, we have shown for comparison, the Coulomb result for $Z^*=Z-0.625$ the screening constant result. It can be seen that our theoretical curve lies somewhat above this curve. The difference between the theoretical curve and the experimental curve in copper is a reasonable extrapolation of the L -shell absorption below the K edge. In the case of aluminum, the experimental data has considerable scatter so that we have used Victoreen's curve for the K absorption and Hill's experimental points for the L absorption. In this case, the difference is small but is in reasonable agreement with experiment, considering the experimental difficulties in the longer-wavelength regions.

In the region of the L shell the Coulomb result for the L shell is shown for $Z^*=Z-2$ and $Z^*=Z-6.522$, the latter being the energy screening constant result. It can be seen that in the frequency range considered, our theoretical curve starts in the neighborhood of the $Z-6.522$ curve and becomes asymptotic to the $Z-2$ curve, indicating the more or less complete screening of the two K electrons on the L shell.

It is not possible to use the mass absorption coefficient for the M shell for neutral atoms computed from Table II since the M -shell screening has not been taken into account. However, we have plotted in Figs. 7 and 8, $\nu^4 I^2$ averaged over the M shell for $Z=6$ and $Z=26$

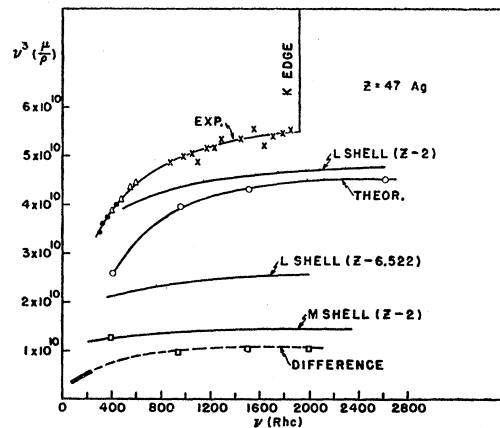


FIG. 4. $\nu^3(\mu/\rho)$ for the L shell of silver... and the data represented by the solid curve below the L edge are from Biermann. Δ data are from Andrews. $\times\times$ data are from Schulz.

from the values given in Table II. Since in $Z=6$, there was screening by a $1s^0$ charge distribution, and in $Z=26$ screening by a $(1s^0)^2(2s^0)$ charge distribution, the Coulomb values of $\nu^4 I^2$ for $Z^*=6$ and $Z^*=5$, and $Z^*=24$ and $Z^*=23$, respectively, for $Z=6$ and $Z=26$, are also shown. In the case of $Z=6$, it can be seen that the $Z^*=5$ fits the calculations reasonably well. In $Z=26$, however, the calculation behaves at high frequency, more like $Z-2$ than $Z-3$. The L -shell screening in this limit has little effect on the M shell.

For $Z=47$ and 29 the Coulomb result of $\nu^3(\mu/\rho)$ for the M shell computed with $Z^*=Z-2$ is also shown in Figs. 4 and 5. In $Z=47$ the difference between the experimental curve and the theoretical curve extrapolate reasonably well from the experimental points below the L edge. This difference curve lies somewhat below the M shell $Z-2$ curve and the remainder of the absorption is of the correct order of magnitude for the remaining 19 electrons in the N and higher shells. In the case of copper, the difference curve lies somewhat below the M shell $Z-2$ limit, indicating that the M shell $Z-2$ limit may not apply for that low a nuclear charge.

The first point on the difference curve seems to be too high for silver and perhaps for copper depending on how one wishes to draw the curve. This "bump" does not appear in the curves for tin as published in ANL-5008, but an error was found in the Landolt-Börnstein Tables¹³ from which the data was obtained, and when one uses the original data of Biermann this "bump" also appears in tin. While there is no other data for the M shell below the L edge for elements in the neighborhood of $Z=25$, the difference curve shows the same behavior for nickel in the region of the L absorption as it does for copper.

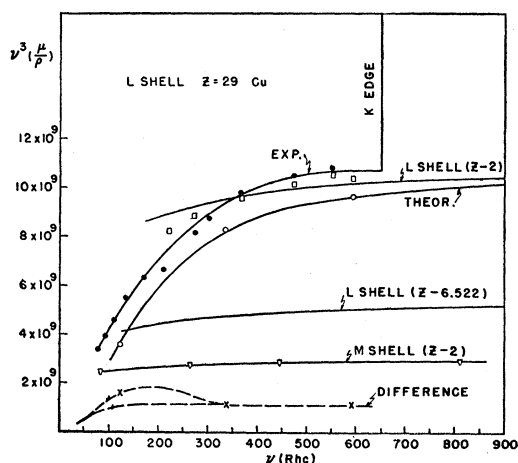


FIG. 5. $\nu^3(\mu/\rho)$ for the L shell of copper. ●● data by Jönsson. □□ data by Andrews. Solid curve below L edge represents 3 points taken from Hill.

¹³ Apparently the measurements given by Landolt-Börnstein, page 316, from $\lambda 2.0988 \rightarrow \lambda 9.8678$ for Sn and Ta should be for Ag and Sn, respectively.

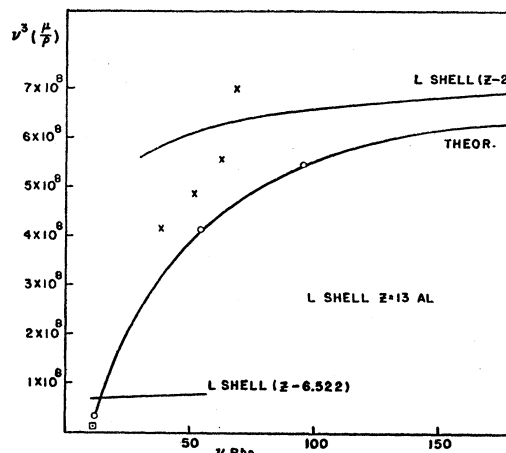


FIG. 6. $\nu^3(\mu/\rho)$ for the L shell of aluminum. ×× data by Hill. □□ data by Tomboulian and Pell.

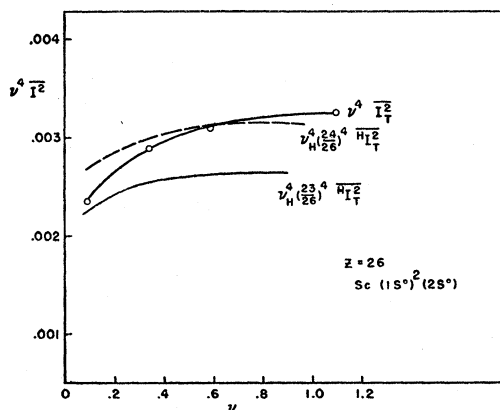


FIG. 7. $\nu^4(I^2)_{AV}$ for the M shell for $Z=6$, with $1s^0$ screening. The curve labeled $\nu^4(I^2)_{AV}$ was computed from the integrals in Table II.

The origin of this apparent irregularity is, of course, not known. It may be due to effects not considered in this paper, such as the neglect of the penetration of the M -shell charge distribution into the L shell, exchange effects or two-electron transitions. An estimate of the latter effect appears to amount to a correction at the edge of less than one percent. It is very likely that fault lies with the present scaling procedures and that the terms of order $1/Z^2$ in Eq. (5) contribute errors at this point where first-order corrections themselves are large.

In the case of the absorption due to the L shell of aluminum, there are very few data in this long-wavelength region, and the effects of screening are large. The ratio of the number of bound electrons to Z is $10/13$ which is not a small quantity. Nevertheless, the qualitative agreement between the theoretical curve and the data is surprisingly good. The fact that the one experimental point due to Tomboulian and Pell falls on the theoretical curve is not to be taken too seriously,

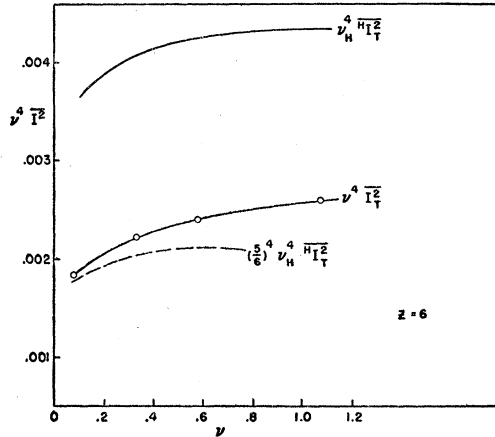


FIG. 8. $\nu^4 \langle I^2 \rangle_{Av}$ for the M shell for $Z=26$ screened by $(1s^0)^2(2s^0)$. The curve labeled $\nu^4 \langle I^2 \rangle_{Av}$ was computed from the integrals in Table II.

since this point was obtained from a small logarithmic plot in the published paper.

CONCLUSIONS

The scaling procedures used in this paper which properly take into account the first-order corrections to Coulomb wave functions and dipole moments, give corrections to the theoretical mass absorption by factors of two over the screening constant approximation. The comparison with experiments, while it is apparently better than the screening approximation, is not conclusive. Further experiments designed to measure the absorption due to each shell separately are highly desirable. Such information might be obtained by a study of the velocity distribution of the ejected photoelectrons.

The separation of the absorption by each shell might be handled theoretically by computing the dipole moments for a complete atom in the neighborhood of atomic number 30. A comparison of the K - and L -shell absorption with our scaled values would provide a further check on these numbers. The M -shell computation could be used to check the difference curve between the theory and experiment. One could then see whether the Hartree functions are good enough to explain the observed absorption or whether other effects must be taken into consideration.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of Donald A. Flanders who set up the numerical procedures used in this work, and that of Janet Sukup for programming and supervising the machine calculations. Thanks are also due to Lucille Renick for assistance in the latter parts of the work.

APPENDIX I

If there are screening electrons whose charge distribution is external to that of the optical electron, then in carrying out the integration of Eq. (1) for the charge distribution of the optical electron, $\sum_{\text{ext.}} V_{ij}$ for these external electrons according to Eq. (2) will be just

$$V_e = \sum_{\text{ext.}} V_{ij} = +2 \sum_{ij} \int_0^\infty \frac{[R_{ij}]^2}{r} dr = -\epsilon_e \text{ a constant.}$$

Thus the energy parameter for these cases ϵ_{nl}^1 , plus this interaction term, $-\epsilon_0$, will have to be the same as the energy parameter without external screening, ϵ_{nl} . Hence,

$$\epsilon_{nl} = \epsilon_{nl}^1 - \epsilon_0, \quad (1A)$$

or

$$\epsilon_{nl}^1 = \epsilon_{nl} + \epsilon_0.$$

The energy differences are the same as before, except that the free function having energy parameter η that corresponded to an electron leaving the system with kinetic energy η , now corresponds to an electron leaving the system with energy $\eta + \epsilon_0$.

The free wave functions are still correctly normalized. For the free function, the numerical solution to Eq. (1) is continued by means of the WKB-Jeffreys solution. This solution has an amplitude factor of the form $(\epsilon_{nl}^1 + V)^{-1/2}$. If we write V as $V = V_i + V_e$, where V_i is the potential due to the nuclear charge plus the internal screening electrons and, V_e is as before the potential due to the external electrons, for small r , the amplitude becomes $(\epsilon_{nl} + \epsilon_0 + V_e + V_i)^{-1/2}$. Using Eq. (1A) this is just $(\epsilon_{nl} + V_i)^{-1/2}$, the amplitude in absence of external screening. For large r , $V \rightarrow 0$ and the amplitude becomes $(\epsilon_{nl}^1)^{-1/2}$ as it should.

Hence, the external screening integrals correspond to transitions to free functions of kinetic energy $\eta + \epsilon_0$ rather than of kinetic energy η .