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A GENERAL FORMULA FOR THE CALCULATION OF ATOMIC PHOTO-IONIZATION CROSS SECTIONS

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Summary

The general formula is derived by considering the model of a single electron moving in a central field. Approximate bound–state radial functions, accurate for large radial distances, may be obtained once the effective quantum numbers $\nu(=n^*)$ are known. Bates and Damgaard have shown that such functions may be used to obtain good estimates for bound–bound transition integrals. For bound–free transitions use is made of approximate free-state radial functions having exact asymptotic forms, their phases being given by $\delta=\pi\mu$ where μ is the extrapolated quantum defect ($\mu=n-\nu$).

The results of extensive numerical calculations are summarized in tables which permit the rapid calculation of transition integrals once the energy levels are known. Both bound–free and bound–bound transition integrals may be obtained. For bound–bound transitions $\nu\to\nu'$ good agreement is obtained with the Bates and Damgaard tables for $|\nu-\nu'|\geq 1\cdot 5$.

Comparisons are made with other results for bound–free transitions, as obtained both from theory and from experiment. In nearly all cases the general formula gives results at least as accurate as those obtained in the best alternative methods of calculation.

Introduction.—In order to calculate the intensities to be expected in a recombination spectrum one requires many radiative transition probabilities and recombination coefficients. Most of the bound–bound transition probabilities required may be calculated using the tables of Bates and Damgaard (**1**). In order to calculate the recombination coefficients as functions of electron temperature one requires the corresponding photo-ionization cross sections as functions of the kinetic energy of the ejected electron.

Bates (2) has given formulae which may be used for the calculation of photo-ionization cross sections when the bound–state wave functions are known and when regular Coulomb functions may be used for the state of the ejected electron. Although these formulae are very useful for certain special problems they cannot be used for many cases of practical importance. Vainshtein and Yavorsky (3) have attempted to allow for distortion of the continuum wave function by using an effective charge Z_{eff} but they give no general rule which may be used to determine the value of this effective charge. Their method may be criticized on the grounds that their continuum functions will have incorrect asymptotic form.

Our method of calculation is similar to that used by Bates and Damgaard for bound–bound transitions. The asymptotic forms of the wave functions, for both the bound and the continuum states, are determined from the known energy levels of the initial atomic system. We use the theory of the Quantum Defect Method described in a previous paper (4), which will be referred to as QDM.

Our results may be used to calculate probabilities for both bound–free and bound–bound transitions. They are found to be consistent with the Bates and Damgaard tables and enable similar tables to be obtained for larger values of the effective quantum numbers.

In later papers we shall apply the results of our calculations to the problems of interpreting recombination spectra in gaseous nebulae and of developing a quantitative theory of ionization equilibria in nebulae. Our results should also prove to be useful in stellar opacity calculations.

2. *The quantum theory of atomic photo-ionization.*—We consider ionization of an N-electron atom* by light quanta of energy $h\tilde{\nu}$. The quantal formula for the cross section is

$$a_{\tilde{\nu}} = \frac{8\pi^3 e^2 \tilde{\nu}}{3c\omega} \sum{}' \left| \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | a) \boldsymbol{R} \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | i, E)\, d\tau \right|^2 \tag{1}$$

where $\tilde{\nu}$ is the frequency and

$$\boldsymbol{R} = \sum_{j=1}^{N} \boldsymbol{r}_j. \tag{2}$$

The initial atom wave function is $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | a)$ where $\mathbf{x}_j = (\boldsymbol{r}_j, \sigma_j)$ is the space and spin co-ordinate of electron j. The final wave function for the system of ion plus ejected electron is $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | i, E)$, E being the electron kinetic energy. The energy conservation condition is $h\tilde{\nu} = I + E$ where I is the threshold ionization energy. The initial wave function is normalized to unity and the final wave function to

$$\int \Psi^*(i, E') \Psi(i, E)\, d\tau = \delta(E - E'), \tag{3}$$

$\delta(E-E')$ being a Dirac delta-function. The summation Σ' in (1) is over all initial and final states of fixed energy and ω is the statistical weight of the initial energy level of the atom.

Equation (1) may be re-written

$$a_{\tilde{\nu}} = \frac{4\pi\alpha a_0^2}{3} (I + k^2) \frac{1}{\omega} \mathbf{S} \tag{4}$$

where

$$\mathbf{S} = \sum{}' \left| \int \Psi^*(a) \boldsymbol{R} \Psi(i, k^2)\, d\tau \right|^2 \tag{5}$$

and where α is the fine-structure constant and a_0 is the Bohr radius. In (4), k^2 is the electron kinetic energy and both I and k^2 are in Rydberg units (13·60 eV or 109 737 cm^{-1}). The quantity $\mathbf{S}$ is in atomic units and the normalization condition for $\Psi(i, k^2)$ is

$$\int \Psi^*(i, k'^2) \Psi(i, k^2)\, d\tau = \pi\delta(k^2 - k'^2). \tag{6}$$

The atom wave function $\Psi(a)$ is anti-symmetric in the co-ordinates $\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N$ and the ion wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_{N-1} | i)$ is anti-symmetric in the co-ordinates $\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_{N-1}$. For $\Psi(i, k^2)$ one should use anti-symmetric functions of the type

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | i, k^2) = N^{-1/2} \sum_{j=1}^{N} (-1)^{N-j} \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_{j-1}, \mathbf{x}_{j+1}, \ldots \mathbf{x}_N | i) \psi_k(\mathbf{x}_j). \tag{7}$$

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* The initial system is referred to as the atom. It may, of course, be an ionized atom.

If ψ_k is of the form

$$\psi_k(\boldsymbol{x}) = Y_{l'm_l'}(\hat{\boldsymbol{r}})\delta(\sigma|m_s')\frac{1}{r}G_{kl'}(r), \tag{8}$$

where $Y_{l'm_l'}$ is a normalized spherical harmonic and $\delta(\sigma|m_s')$ a normalized spin function, the normalization condition (6) requires that $G_{kl'}$ should have asymptotic amplitude $k^{-1/2}$ (5). In (5), Σ' includes a summation over $l'm_l'm_s'$.

Assuming LS coupling one may take the atom quantum numbers to be αSLM_SM_L and the ion quantum numbers to be $\alpha''S''L''M_S''M_L''$. For the final state it is convenient to use functions $\Psi(\alpha''S''L''kl'S'L'M_S'M_L')$ where $S'L'M_S'M_L'$ refer to the complete system; such functions may be obtained from (7) and (8) using vector-coupling formulae. The radial functions $G_{kl'}$ will then depend on $\alpha''S''L''kl'S'L'$ but will not depend on $M_S'M_L'$. The usual selection rules apply: $S=S'$, $M_S=M_S'$, $L=L'$, $L'\pm 1$, $M_L=M_L'$, $M_L'\pm 1$. For $\mathbf{S}/\omega$ we obtain

$$\frac{\mathbf{S}}{\omega} = \frac{1}{(2S+1)(2L+1)}\sum_{M_SM_Ll'L'M_L'}\left|\int \Psi^*(\alpha SLM_SM_L)\boldsymbol{R}\Psi(\alpha''S''L''kl'SL'M_SM_L')\,d\tau\right|^2. \tag{9}$$

We consider the usual approximation in which the atom and ion wave functions are built up from one-electron orbitals and we assume ψ_k to be orthogonal to all the orbitals for the atom. We then obtain the selection rule that only one-electron jumps occur*. Let the nl electron be ejected and let the threshold ionization energy be I_{nl}. The angular momentum quantum number of the ejected electron is then $l'=l\pm 1$. From (9) one obtains

$$\frac{\mathbf{S}}{\omega} = \sum_{l'=l\pm 1} C_{l'}\left|\int_0^\infty P_{nl}(r)rG_{kl'}(r)\,dr\right|^2 \tag{10}$$

where $P_{nl}(r)$ is the radial function for the nl electron. If more than one value of L' is allowed by the selection rules the right hand side of (10) should include a summation over L'. Let $n''l''$ be an electron which is not ejected. We assume the radial functions $P_{n''l''}$ to be the same for the atom and for the ion; this will introduce only a small error in the calculated cross section (**6**, **7**). With this approximation the $C_{l'}$ in (10) are algebraic factors obtained from the integrations over spin and angular co-ordinates. These may be evaluated using standard atomic structure methods (**8**, **9**, **10**). We consider the three cases of greatest practical importance.

Firstly we consider an initial configuration consisting of closed shells together with an electron nl. For ejection of nl one obtains for $C_{l\pm 1}$:

$$\begin{aligned} C(l\to l+1) &= (l+1)/(2l+1) \\ C(l\to l-1) &= l/(2l+1). \end{aligned} \tag{11}$$

Secondly we consider an initial state $\alpha S''L''nlSL$ where $\alpha S''L''$ specifies a parent term. One obtains the selection rule that transitions do not occur to states $\alpha S'''L'''$ of the ion with $(S''', L''')\neq(S'', L'')$. For transitions to states $\alpha S''L''$ of the ion one obtains for $C_{l'}$:

$$C(S''L''lSL\to S''L''l'SL') = (2l+1)(2L'+1)W^2(ll'LL';\ 1L'')C(l\to l') \tag{12}$$

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* One may obtain finite probabilities for transitions violating this rule if one allows for differences between the orbitals for the atom and the orbitals for the ion.

1960MNRAS.120..121B

where $C(l\rightarrow l')$ is given by (11) and where W is a Racah coefficient. Expressions for W^2 are given in Table I. Using a sum rule for W^2 one obtains

$$\sum_{L'} C(S''L''lSL\rightarrow S''L''l'SL') = C(l\rightarrow l'). \qquad (13)$$

In (10) one may therefore use $C_{l'} = C(l\rightarrow l')$ if the radial integral is effectively independent of L' or if only one value of L' is allowed by the selection rules.

Table I

L'	$W^2(ll+1LL';\ 1L'')$
$L-1$	$\dfrac{(L''+L-l)(L''+L-l-1)(L''-L+l+2)(L''-L+l+1)}{4(2L+1)(2L-1)L(l+1)(2l+1)(2l+3)}$
L	$\dfrac{(L''+L+l+2)(-L''+L+l+1)(L''-L+l+1)(L''+L-l)}{4L(2L+1)(L+1)(2l+1)(l+1)(2l+3)}$
$L+1$	$\dfrac{(L''+L+l+3)(L''+L+l+2)(-L''+L+l+2)(-L''+L+l+1)}{4(2L+3)(L+1)(2L+1)(2l+3)(l+1)(2l+1)}$

Note that $W^2(ll'LL';\ 1L'') = W^2(l'lL'L;\ 1L'')$.

Thirdly we consider ionization from a configuration nl^q of equivalent electrons With initial state nl^qSL and final state $nl^{q-1}S''L''kl'SL'$ one obtains

$$C(l^qSL\rightarrow l^{q-1}S''L''l'SL')$$
$$= q|(l^qSL\{|l^{q-1}(S''L'')lSL)|^2 C(S''L''lSL\rightarrow S''L''l'SL') \qquad (14)$$

where $(l^qSL\{|l^{q-1}(S''L'')lSL)$ is a fractional parentage coefficient. This coefficient is unity for $q=2$. Defining

$$C(l^qSL\rightarrow l^{q-1}S''L''l') = \sum_{L'} C(l^qSL\rightarrow l^{q-1}S''L''l'SL') \qquad (15)$$

one obtains, using (13),

$$C(l^qSL\rightarrow l^{q-1}S''L''l') = q|(l^qSL\{|l^{q-1}(S''L'')lSL)|^2 C(l\rightarrow l'). \qquad (16)$$

Therefore

$$C(l^qSL\rightarrow l^{q-1}S''L''l'SL')$$
$$= (2l+1)(2L'+1)W^2(ll'LL';\ 1L'')C(l^qSL\rightarrow l^{q-1}S''L''l'). \qquad (17)$$

Values (6, **11**) of the coefficients $C(p^qSL\rightarrow p^{q-1}S''L''l')$ are given in Table II.

Table II

The coefficients $C(p^qSL\rightarrow p^{q-1}S''L''s)$

q	SL	$S''L''$	C	q	SL	$S''L''$	C
1	^{2}P	^{1}S	1/3	4	^{3}P	^{4}S	4/9
2	^{3}P	^{2}P	2/3	4	^{3}P	^{2}D	5/9
2	^{1}D	^{2}P	2/3	4	^{3}P	^{2}P	1/3
2	^{1}S	^{2}P	2/3	4	^{1}D	^{4}S	0
3	^{4}S	^{3}P	1	4	^{1}D	^{2}D	1
3	^{4}S	^{1}D	0	4	^{1}D	^{2}P	1/3
3	^{4}S	^{1}S	0	4	^{1}S	^{4}S	0
3	^{2}D	^{3}P	1/2	4	^{1}S	^{2}D	0
3	^{2}D	^{1}D	1/2	4	^{1}S	^{2}P	4/3
3	^{2}D	^{1}S	0	5	^{2}P	^{3}P	1
3	^{2}P	^{3}P	1/2	5	^{2}P	^{1}D	5/9
3	^{2}P	^{1}D	5/18	5	^{2}P	^{1}S	1/9
3	^{2}P	^{1}S	2/9	6	^{1}S	^{2}P	2

Note that $C(p^qSL\rightarrow p^{q-1}S''L''d) = 2C(p^qSL\rightarrow p^{q-1}S''L''s)$.

3. *Use of the Quantum Defect Method.*—We consider the radial equation

$$\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-V(r)+E\right]y=0 \tag{18}$$

where E and V are in Rydbergs and where $V(r)=-2z/r$ for r large. We put

$$E=\epsilon z^2 \quad \text{and} \quad \rho=rz. \tag{19}$$

For $E<0$ solutions of (18) satisfying

$$\int_0^\infty P_{nl}{}^2(r)\,dr=1 \tag{20}$$

exist only for the eigenvalues ϵ_{nl} of ϵ. We put $\epsilon_{nl}=-1/\nu^2$ where ν is the effective quantum number*. The quantum defect is defined at the eigenvalues by $\mu(\epsilon_n)=n-\nu$ where n is the usual principal quantum number. A generalized quantum defect $\mu(\epsilon)$ is obtained on interpolation or extrapolation from the values of $\mu(\epsilon_n)$.

For $\epsilon>0$ we put $\epsilon=k^2/z^2$ and define $G_{kl}(r)$ to be the solution of (18) satisfying $G_{kl}(0)=0$ and

$$G_{kl}(r) \underset{r\to\infty}{\sim} k^{-1/2}\sin[x+\delta(\epsilon)] \tag{21}$$

where

$$x=kr-\tfrac{1}{2}l\pi+\frac{z}{k}\ln(2kr)+\arg\Gamma(l+1-iz/k). \tag{22}$$

We wish to calculate

$$g(\nu l;\ \epsilon' l')=I_{nl}\int_0^\infty P_{nl}(r)rG_{k'l'}(r)\,dr \tag{23}$$

where $l'=l\pm1$ and where $I_{nl}=z^2/\nu^2$, $\epsilon'=(k'/z)^2$. We assume that the eigenvalue spectrum is known but that the form of $V(r)$ may not be known for small r. The Quantum Defect Method enables us to obtain the form of the radial functions for large r. Our method of calculation depends on the fact that, for typical atomic potentials, $g(\nu l;\ \epsilon' l')$ is usually insensitive to the exact form of the radial functions for small values of r. Approximate values of g may therefore be obtained if we make certain reasonable assumptions concerning the radial functions for small r.

It is shown in QDM that

$$P_{nl}(r)=z^{1/2}\mathrm{K}(\nu,l)W_{\nu,\,l+\frac{1}{2}}(2\rho/\nu) \quad (r \text{ large}) \tag{24}$$

where W is the Whittaker function. The normalizing factor is

$$\mathrm{K}(\nu,l)=[\zeta(\nu)\nu^2\Gamma(\nu+l+1)\Gamma(\nu-l)]^{-1/2} \tag{25}$$

where

$$\zeta(\nu)=1+\frac{2}{\nu^3}\frac{\partial\mu(\epsilon)}{\partial\epsilon}.$$

When ν is not small one may usually put $\zeta(\nu)=1$. The asymptotic form of the Whittaker function is

$$W_{\nu,l+\frac{1}{2}}(2\rho/\nu)=\left(\frac{2\rho}{\nu}\right)^{\nu}e^{-\rho/\nu}\sum_{t=0}^{t_0}b_t(\nu,l)\rho^{-t}+O(\rho^{-t_0-1}) \tag{26}$$

where $b_0=1$ and

$$b_t=\frac{\nu}{2t}[l(l+1)-(\nu-t)(\nu-t+1)]b_{t-1}, \quad (t\geqslant1). \tag{27}$$

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*The symbol n_{nl}^* is often used for the effective quantum number. In QDM we used ν_{nl} or ν_n.

An approximate bound–state radial function is defined for all r by

$$P_{\nu l}(r)=z^{1/2}\mathrm{K}(\nu,l)\left(\frac{2\rho}{\nu}\right)^{\nu}\mathrm{e}^{-\rho/\nu}\sum_{t=0}^{t_0}b_t(\nu,l)\rho^{-t}. \tag{28}$$

For $\nu=n=(l+1)$, $(l+2)\ldots$ the expansion terminates at $t=n-l-1$ and is then equal to the exact hydrogenic eigenfunction. Bates and Damgaard (1) have shown that, with suitable choice of t_0, (28) may be used to obtain good estimates of the bound–bound transition integrals,

$$\int_0^\infty P_{nl}(r)rP_{n'l'}(r)\,dr.$$

We shall consider positive energies E' such that

$$\exp[-2\pi/\epsilon'^{1/2}]\ll 1. \tag{29}$$

The phase δ' in $G_{k'l'}$ is then given by

$$\delta'(\epsilon')=\pi\mu'(\epsilon') \tag{30}$$

where μ' is the extrapolated quantum defect for the $n'l'$ series. The Coulomb functions $y_1'=y_1(i\epsilon'^{-1/2},l';\rho)$ and $y_3'=y_3(i\epsilon'^{-1/2},l';\rho)$ defined in QDM are solutions of (18) in the limit of large r. Using (29) we obtain the asymptotic forms

$$y_1'\underset{\rho\to\infty}{\sim}\left(\frac{2}{\pi\epsilon'^{1/2}A'}\right)^{1/2}\sin(x') \tag{31}$$

$$y_3'\underset{\rho\to\infty}{\sim}-\left(\frac{2A'}{\pi\epsilon'^{1/2}}\right)^{1/2}\cos(x') \tag{32}$$

where

$$A'=[1+\epsilon'l'^2][1+\epsilon'(l'-1)^2]\ldots[1+\epsilon']. \tag{33}$$

At the origin y_1' behaves as $\rho^{l'+1}$ and y_3' as $\rho^{-l'}$ together with logarithmic terms. We define

$$F(\epsilon',l';\rho)=\left(\frac{\pi A'}{2}\right)^{1/2}y_1' \tag{34}$$

and

$$H(\epsilon',l';\rho)=[1-\exp(-\tau_{l'}\rho)]^{2l'+1}\left(\frac{\pi}{2A'}\right)^{1/2}y_3', \tag{35}$$

where $\tau_{l'}$ is real and positive. The functions F and H behave as $\rho^{l'+1}$ at the origin and have asymptotic forms $F\sim\epsilon'^{-1/4}\sin(x')$ and $H\sim-\epsilon'^{-1/4}\cos(x')$. As an approximate positive energy function we use

$$G_{k'l'}(r)=z^{-1/2}\{F(\epsilon',l';\rho)\cos\pi\mu'(\epsilon')-H(\epsilon',l';\rho)\sin\pi\mu'(\epsilon')\} \tag{36}$$

which behaves as $\rho^{l'+1}$ at the origin and has asymptotic form

$$G_{k'l'}\sim k^{-1/2}\sin(x'+\pi\mu').$$

Using (28) and (36) the integral (23) is given by

$$g(\nu l;\,\epsilon'l')=f(\nu l;\,\epsilon'l')\cos\pi\mu'(\epsilon')-h(\nu l;\,\epsilon'l')\sin\pi\mu'(\epsilon'), \tag{37}$$

where

$$f(\nu l;\,\epsilon'l')=\frac{\mathrm{K}(\nu,l)}{\nu^2}\left(\frac{2}{\nu}\right)^{\nu}\sum_{t=0}^{t_0}b_t(\nu,l)\int_0^\infty\rho^{\nu+1-t}\mathrm{e}^{-\rho/\nu}F(\epsilon',l';\rho)\,d\rho \tag{38}$$

and

$$h(\nu l;\,\epsilon'l')=\frac{\mathrm{K}(\nu,l)}{\nu^2}\left(\frac{2}{\nu}\right)^{\nu}\sum_{t=0}^{t_0}b_t(\nu,l)\int_0^\infty\rho^{\nu+1-t}\mathrm{e}^{-\rho/\nu}H(\epsilon',l';\rho)\,d\rho. \tag{39}$$

It is seen that g, f and h do not depend explicitly on z.

1960MNRAS.120..121B

Choice of $\tau_{l'}$ *and of* t_0. For small r the radial functions we have adopted depend on the choice of t_0 and of $\tau_{l'}$. The method of calculation depends on the fact that, once reasonable values of these parameters have been chosen, the integrals are insensitive to small changes in the parameters*.

The Coulomb functions y_1' and y_3' are solutions of

$$\left[\frac{d^2}{d\rho^2}-\frac{l'(l'+1)}{\rho^2}+\frac{2}{\rho}+\epsilon'\right]y'=0. \tag{40}$$

With increasing ρ the first point of inflection of y' occurs at $\rho=\rho_{l'}$ where

$$-\frac{l'(l'+1)}{\rho_{l'}{}^2}+\frac{2}{\rho_{l'}}+\epsilon'=0.$$

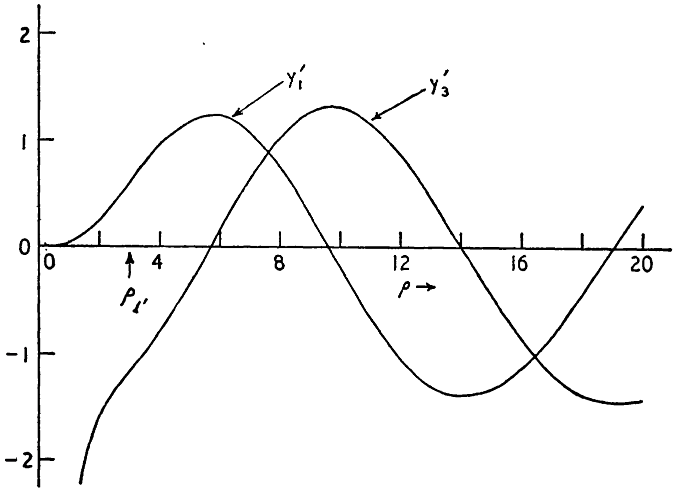

FIG. 1.—*The regular Coulomb function,* y_1' *and the irregular function* y_3' *for* $\epsilon'=0$, $l'=2$.

For the values of ϵ' of interest $\rho_{l'}$ differs little from the value $\rho_{l'}=l'(l'+1)/2$ for $\epsilon'=0$. For $\rho>\rho_{l'}$ the functions y_1' and y_3' are both oscillatory, but for $\rho<\rho_l'$, y_1' is small and y_3' starts to diverge (see Fig. 1). The cut-off factor

$$[1-\exp(-\tau_{l'}\rho)]^{2l'+1}$$

multiplying y_3' in the function H is therefore chosen to be close to unity for $\rho>\rho_{l'}$ and to be small for $\rho\ll\rho_{l'}$. The condition we adopt is $\tau_{l'}\rho_{l'}\simeq 5$ giving $\tau_{l'}\simeq 10/l'(l'+1)$. This condition suggests an infinite value for τ_0, corresponding to omission of the factor $[1-\exp(-\tau_0\rho)]$ in the s-wave function $H(\epsilon', 0;\ \rho)$. This is in fact quite satisfactory since $H(\epsilon', 0;\ \rho)$ has only a weak logarithmic divergence at the origin. Functions $G_{k'l'}(r)$ calculated with $\tau_{l'}=10/l'(l'+1)$ have been compared with radial functions calculated by numerical integration for various atomic potentials. For the values of ρ of importance satisfactory agreement was obtained. Final calculations of the integrals were made for $\tau_0=\infty$, $\tau_1=5$, $\tau_2=1{\cdot}5$ and $2{\cdot}0$.

The choice of t_0 has been discussed by Bates and Damgaard. They consider two possible criteria. Criterion (a), which is similar to that used for an asymptotic expansion, is that the series should be terminated at the minimum term. Criterion

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* One could obviously consider various alternative definitions of the radial functions for small r. Instead of using the asymptotic expansion of the Whittaker function, Hylleraas (**12**) has represented this function by a contour integral and has then deformed the path of integration so as to obtain convergent bound–bound transition integrals. This method gives results very similar to those obtained by Bates and Damgaard.

(*b*) is to neglect in the integral powers of ρ less than 2; t_0 is then the integer satisfying

$$\nu + l' - 1 < t_0 < \nu + l'.$$

Bates and Damgaard found these two criteria to give practically identical results. This was also found to be the case in most of our calculations but (*a*) and (*b*) were found to give significantly different results for $(l, l') = (2, 1)$ and $(3, 2)$. In these cases criterion (*a*) was adopted. With exact wave functions the integrand would behave as $\rho^{l+l'+3}$ for ρ small and it is therefore evident that criterion (*b*) will become unsatisfactory for large l, l'.

4. *Evaluation of the integrals.*—The integrals f and h may be expressed as power series in ϵ':

$$f(\nu l;\ \epsilon' l') = f_0(\nu l;\ l') + \epsilon' f_1(\nu l;\ l') + \ldots \tag{41}$$

$$h(\nu l;\ \epsilon' l') = h_0(\nu l;\ l') + \epsilon' h_1(\nu l;\ l') + \ldots. \tag{42}$$

Using

$$A' = 1 + \tfrac{1}{6} l'(l'+1)(2l'+1)\epsilon' + \ldots \tag{43}$$

together with formulae given in Appendix I of QDM we obtain for the leading terms in the expansions of F and H:

$$\begin{aligned} F(\epsilon, l;\ \rho) = (\pi\rho)^{1/2} \Big\{ & J_{2l+1}(\sqrt{8\rho}) \\ & + \frac{\epsilon}{12}[l(l+1)(2l+1)J_{2l+1}(\sqrt{8\rho}) - 3(l+1)(2\rho)J_{2l+3}(\sqrt{8\rho}) \\ & + (2\rho)^{3/2} J_{2l+4}(\sqrt{8\rho})] \Big\} + O(\epsilon^2) \end{aligned} \tag{44}$$

and

$$\begin{aligned} H(\epsilon, l;\ \rho) = [1 - \mathrm{e}^{-\tau_l \rho}]^{2l+1} (\pi\rho)^{1/2} \Big\{ & Y_{2l+1}(\sqrt{8\rho}) \\ & + \frac{\epsilon}{12}[l(l+1)(2l+1)Y_{2l+1}(\sqrt{8\rho}) - 3(l+1)(2\rho)Y_{2l+3}(\sqrt{8\rho}) \\ & + (2\rho)^{3/2} Y_{2l+4}(\sqrt{8\rho})] \Big\} + O(\epsilon^2). \end{aligned} \tag{45}$$

The integrals for f_0 and f_1 may be evaluated using

$$\begin{aligned} & \int \mathrm{e}^{-\rho/\nu} \rho^{q+1/2} J_{2m+1}(\sqrt{8\rho})\, dp \\ & \qquad = \frac{\Gamma(m+q+2) 2^{m+1/2} \nu^{m+q+2}}{\Gamma(2m+2)} \Phi(m+q+2, 2m+2;\ -2\nu) \end{aligned} \tag{46}$$

(**13**) where Φ is the confluent hypergeometric function defined by

$$\Phi(a, c;\ x) = 1 + \frac{a}{c}\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \ldots. \tag{47}$$

Using Kummer's transformation,

$$\Phi(m+q+2, 2m+2;\ -2\nu) = \mathrm{e}^{-2\nu}\Phi(m-q, 2m+2;\ 2\nu), \tag{48}$$

and recurrence relations satisfied by the confluent hypergeometric functions (**14**, **15**) one obtains

$$f_0(\nu l, l') = \frac{R(\nu l, l')}{\zeta^{1/2}(\nu, l)} S(\nu l, l')$$

and

$$f_1(\nu l, l') = \frac{R(\nu l, l')}{\zeta^{1/2}(\nu, l)} \left[\frac{l'(l'+1)(2l'+1)}{12} S(\nu l, l') - \frac{\nu^2 Q(\nu l, l')}{6(l'+1)} \right]$$

where

$$R(\nu l, l')=\left[\frac{2\pi}{\Gamma(\nu+l+1)\Gamma(\nu-l)}\right]^{1/2}\frac{2^{\nu+l'}\nu^{l'}}{(2l'+1)!}\,\Gamma(\nu+l'+3)\,\mathrm{e}^{-2\nu},$$

$$S(\nu l, l')=\sum_{t=0}^{t_0} q_t(\nu l, l')\phi_t(\nu, l'),$$

$$Q(\nu l, l')=\sum_{t=0}^{t_0} p_t(\nu l, l')\theta_t(\nu l, l'),$$

$$q_0=1,\quad q_t=\frac{[l(l+1)-(\nu-t)(\nu-t+1)]}{2t(l'+\nu-t+3)}\,q_{t-1}\quad (t\geqslant 1),$$

$$p_t=(l'+\nu-t+4)(l'+\nu-t+3)q_t,$$

$$\phi_t(\nu, l')=\Phi(l'-\nu+t-1,\ 2l'+2;\ 2\nu),$$

$$\theta_t(\nu l, l')=\phi_{t-1}(\nu, l')+\frac{[l'(l'+1)-\nu(l'-\nu+t-2)]}{(l'+1)(2l'+3)}\,\phi_{t-1}(\nu, l'+1).$$

The functions $\phi_t(\nu, l')$ may be evaluated using the series expansion (47). For given ν, l' it suffices to calculate ϕ_t for two values of t; to obtain ϕ_t for other values of t one may then use the recurrence relation

$$(l'+\nu-t+3)\phi_{t-1}(\nu, l')+2(t-2)\phi_t(\nu, l')-(l'-\nu+t-1)\phi_{t+1}(\nu, l')=0.$$

Calculations of f_0 and f_1 were made for the following values of the arguments:

l	l'	ν
0	1	0·2(0·2)5·0,* 1·0(1·0)12·0
1	0	1·0(0·2)5·0, 6·0(1·0)12·0
1	2	1·0(0·2)5·2, 6·0(1·0)12·0
2	1	2·0(0·2)5·0, 6·0(1·0)12·0
2	3	2·0(0·2)5·0, 6·0(1·0)12·0
3	2	3·0(0·2)5·0, 6·0(1·0)12·0

Analytic expressions were obtained for h_0 and h_1 but were found to be so complicated that it was decided to evaluate these functions by direct numerical integration. Whenever numerical integration was used for h_0, h_1, the functions f_0 and f_1 were calculated both by numerical integration and from the analytic expressions. Numerical integration was used to calculate h_0 and h_1 for the following values of the arguments

l	l'	ν
1	0	1·0(0·2)3·0
1	2	1·2(0·2)3·0

For $(l, l')=(0, 1)$ the functions f and h were calculated by numerical integration for $\epsilon'=0·00, 0·05, 0·10$. The continuum Coulomb functions given by Bates and Massey (**16**) were used, the range of ρ being extended by numerical solution of the Coulomb equation. The ranges of ν were

ϵ'	ν
0	1·0(0·2)3·8
0·05	1·0(0·2)3·0
0·10	1·0(0·2)3·0

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* In this range we calculated f_0 but not f_1.

5. *Behaviour of the integrals.*—The functions $f(\nu l;\ \epsilon' l')$ and $h(\nu l;\ \epsilon' l')$ were found to be oscillatory functions of ν with period tending to 2 for large ν. Furthermore, f and h were found to have phase differences of approximately $\pi/2$. This behaviour is illustrated in Fig. 2. We therefore put

$$f(\nu l;\ \epsilon' l') = \frac{G(\nu l;\ \epsilon' l')}{\zeta^{1/2}(\nu, l)} \cos \pi[\nu + \chi(\nu l;\ \epsilon' l')] \tag{49}$$

and

$$h(\nu l;\ \epsilon' l') = \frac{G(\nu l;\ \epsilon' l')}{\zeta^{1/2}(\nu, l)} \sin \pi[\nu + \chi(\nu l;\ \epsilon' l')] \tag{50}$$

giving

$$g(\nu l;\ \epsilon' l') = \frac{G(\nu l;\ \epsilon' l')}{\zeta^{1/2}(\nu, l)} \cos \pi[\nu + \mu'(\epsilon') + \chi(\nu l;\ \epsilon' l')]. \tag{51}$$

The functions G and χ, calculated from

$$G = \zeta^{1/2}(f^2 + h^2)^{1/2}, \quad \pi(\nu + \chi) = \arctan(h/f), \tag{52}$$

were found to vary smoothly with ν. For ν not small it was found that χ could be represented by two or three terms of an expansion in powers of $1/\nu$ and it was therefore decided that χ must tend to a finite limit for large ν.

The behaviour of the integrals may be understood by considering the limit of large ν. For ρ not too large the radial functions for small negative energies are similar to those for small positive energies. Let ν vary from ν_a to $(\nu_a + 2)$ where ν_a is large. There is then only a small change in the energy parameter $\epsilon = -1/\nu^2$. The main change in the radial function is a change in the positions of the nodes, this change being similar to that for a positive energy function when μ changes from μ_a to $\mu_a - 2$. From the fact that the radial functions are similar for $\nu = \nu_a$ and $\nu = \nu_a + 2$ one may understand why χ depends little on ν for large ν. In a similar way one may understand why f and h are $\pi/2$ out of phase in the limit of large ν.

If f is known as a function of ν the equation $f = G \cos \pi(\nu + \chi)$ does not, in general, suffice to determine both G and χ. However, if one assumes G to be non-zero, χ is determined at the values of ν for which $f = 0$. There is generally one such zero between each integer value of ν. If one further asumes that χ varies smoothly between the values determined at the zeros of f one may determine χ for intermediate values of ν by interpolation and for larger values of ν by extrapolation. Having calculated χ from the zeros of f one may calculate h from $h = f \tan \pi(\nu + \chi)$. The values of h obtained in this way may then be compared with those obtained by direct numerical integration. Such comparisons have been made for $(l, l') = (0, 1)$, $(1, 0)$ and $(1, 2)$. The comparison for $(l, l') = (1, 2)$ is shown in Fig. 2. The two methods of calculation are found to give good agreement for $\nu \geqslant (l + 1)$. For $l = 2$ and 3, h was not calculated by numerical integration.

For $\nu > 5$, f_0 and f_1 were calculated only for integer values of ν, and G was then calculated using extrapolated values of χ. Since G varies slowly with ν, values for non-integral ν greater than 5 may be obtained by interpolation.

Energy variations. Values of $f(nl;\ \epsilon' l')$ may be calculated exactly for all ϵ'. Such calculations for* $n = 1$, 2, 3, and 4 show that the linear approximation, $f = f_0 + \epsilon' f_1$, is valid only for very small values of ϵ'. We therefore sought to

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* These calculations were made by Dr A. Dalgarno.

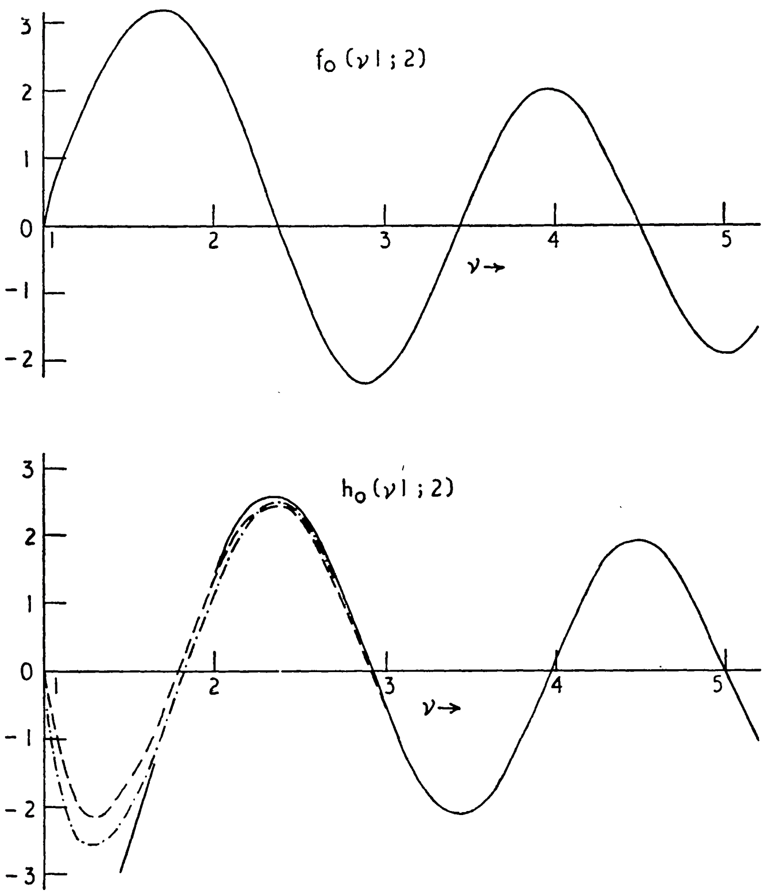

FIG. 2.—*The functions* $f_0(\nu 1; 2)$ *and* $h_0(\nu 1; 2)$. *The full line curve for* h_0 *is obtained from* $h_0 = f_0 \tan \pi(\nu + \chi_{1,2})$ *where* $\chi_{1,2}$ *is obtained from the zeros of* f_0. *The curve* – – – *for* h_0 *is obtained from numerical integration using* $\tau_2 = 1\cdot5$ *and the curve* – · – · – · – *using* $\tau_2 = 2\cdot0$. *Comparison of radial functions suggests that* $\tau_2 = 1\cdot5$ *will usually give the most accurate results.*

express our results in a form which would be valid for larger values of ϵ'. We first considered negative values of ϵ'.

The positive energy functions $F(\epsilon', l'; \rho)$ and the bound-state functions $P_{\nu' l'}(r)$ are both proportional to the function $\mathscr{F}$ defined in QDM, this function being an entire analytic function of the energy. Comparison of the proportionality factors (QDM, Section 4), shows that the integral

$$(\nu l|r|\nu' l') = \int_0^\infty P_{\nu l}(r) r P_{\nu' l'}(r)\, dr \tag{53}$$

is given by

$$(\nu l|r|\nu' l') = \frac{\nu^2}{z}\left[\frac{2}{\pi\zeta(\nu', l')\nu'^3}\right]^{1/2}(-1)^{n'+l'+1} g\left(\nu l;\ \frac{-1}{\nu'^2}, l'\right) \tag{54}$$

or, using (51),

$$(\nu l|r|\nu' l') = \frac{\nu^2}{z}\left[\frac{2}{\pi\zeta(\nu, l)\zeta(\nu', l')\nu'^3}\right]^{1/2}(-1)^{l'+1} \times G\left(\nu l;\ \frac{-1}{\nu'^2}, l'\right)\cos\pi\left[\nu - \nu' + \chi\left(\nu l;\ \frac{-1}{\nu'^2}, l'\right)\right]. \tag{55}$$

The Bates and Damgaard calculations show that $\chi\left(\nu l;\ \frac{-1}{\nu'^2}, l'\right)$ and $G\left(\nu l;\ \frac{-1}{\nu'^2}, l'\right)$

vary smoothly but increase rapidly as ν tends to ν' and have large but finite values for $\nu=\nu'$. Since we are not concerned with the immediate neighbourhood of $\nu=\nu'$ we considered functional forms which are singular for $\nu=\nu'$. The following were finally adopted:

$$G(\nu l;\ \epsilon' l')=(-1)^{l'+1}G_{ll'}(\nu)[1+\epsilon'\nu^2]^{-\gamma_{ll'}(\nu)} \tag{56}$$

$$\chi(\nu l;\ \epsilon' l')=\chi_{ll'}(\nu)+\frac{\epsilon'\nu}{1+\epsilon'\nu}\alpha_{ll'}(\nu)+\frac{\epsilon'\nu^2}{1+\epsilon'\nu^2}\beta_{ll'}(\nu). \tag{57}$$

The functions $G_{ll'}$, $\gamma_{ll'}$, $\chi_{ll'}$, $\alpha_{ll'}$ and $\beta_{ll'}$ were determined from the results of our calculations. In all cases it was found that $\alpha_{ll'}$ could be taken to be independent of ν and in nearly all cases that $\beta_{ll'}$ could also be taken to be independent of ν. The energy variations obtained give close agreement with: (i) the Bates and Damgaard tables for $(\nu'-\nu)\geqslant 1{\cdot}5$; (ii) values of $g(\nu\,0;\ \epsilon' 1)$ for $\nu=1{\cdot}0(0{\cdot}2)3{\cdot}0$ and $\epsilon'=0{\cdot}00$, $0{\cdot}05$ and $0{\cdot}10$; (iii) values of $f(nl;\ \epsilon' l')$ calculated exactly for $n=1, 2, 3$ and 4 and $0\leqslant\epsilon'\leqslant 1{\cdot}0$ (iv) values of $f(nl;\ \epsilon' l')$ calculated from asymptotic expansions (**17**), for the ranges of n, l, ϵ' and l' over which the asymptotic expansions are valid. Further checks are provided by the comparisons with other calculations (Section 7).

6. *Summary of results.*—Let I_{nl} be the threshold ionization energy and k^2 the energy of the ejected electron, both measured in Rydberg units, and let z be the charge on the final ion. Put $I_{nl}=z^2/\nu^2$ and $k^2=z^2\epsilon'$. The photoionization cross section is

$$a_{\bar\nu}(nl)=8{\cdot}559\times 10^{-19}\left(\frac{I_{nl}+k^2}{I_{nl}^{\,2}}\right)\sum_{l'=l\pm1}C_{l'}|g(\nu l;\ \epsilon' l')|^2\,\mathrm{cm}^2 \tag{58}$$

where

$$g(\nu l;\ \epsilon' l')=\frac{G(\nu l;\ \epsilon' l')}{\zeta^{1/2}(\nu,l)}\cos\pi[\nu+\mu'(\epsilon')+\chi(\nu l;\ \epsilon' l')], \tag{59}$$

$$G(\nu l;\ \epsilon' l')=(-1)^{l'+1}G_{ll'}(\nu)[1+\epsilon'\nu^2]^{-\gamma_{ll'}(\nu)}, \tag{60}$$

$$\chi(\nu l;\ \epsilon' l')=\chi_{ll'}(\nu)+\frac{\epsilon'\nu}{1+\epsilon'\nu}\alpha_{ll'}+\frac{\epsilon'\nu^2}{1+\epsilon'\nu^2}\beta_{ll'}(\nu) \tag{61}$$

and where $\mu'(\epsilon')$ is the extrapolated quantum defect for the $n'l'$ series. Expressions for the algebraic factors $C_{l'}$ are given in Section 2. The quantity

$$\zeta(\nu,l)=1+\frac{2}{\nu^3}\frac{\partial\mu(\epsilon)}{\partial\epsilon}, \tag{62}$$

where $\mu(\epsilon)$ is the quantum defect for the nl series and $\epsilon=-1/\nu^2$, is usually close to unity when ν is not small. For $\nu\to l$, $G_{ll'}(\nu)$ behaves as $(\nu-l)^{1/2}$ and $\zeta(\nu,l)$ behaves as $(\nu-l)$; therefore $\zeta^{-1/2}G_{ll'}$ tends to a constant.

Results for $\nu\geqslant(l+2)$. One may take $\beta_{ll'}$ to be independent of ν and one may represent $\chi_{ll'}(\nu)$ by

$$\chi_{ll'}(\nu)=a_{ll'}+b_{ll'}/\nu+c_{ll'}/\nu^2. \tag{63}$$

The coefficients $a_{ll'}$, $b_{ll'}$, $c_{ll'}$, $\alpha_{ll'}$ and $\beta_{ll'}$ are given in Table III, and the functions $G_{ll'}(\nu)$ and $\gamma_{ll'}(\nu)$ are given in Tables IV and V. These tables give values of $G_{ll'}$ and $\gamma_{ll'}$ for $\nu\geqslant l+1$; they may be used for ν between $(l+1)$ and $(l+2)$ but will give results slightly less accurate than those obtained from Tables VI to VIII. Whenever Tables IV and V are used $\chi_{ll'}$ should be calculated from (63) and Table III.

Tables III, IV and V have been published previously in a short report on the present work (**18**).

TABLE III

l	l'	$a_{ll'}$	$b_{ll'}$	$c_{ll'}$	$\alpha_{ll'}$	$\beta_{ll'}$
0	1	−0·147	+0·2515	−0·078	+0·310	0·000
1	0	−0·216	−0·171	0·000	0·000	0·000
1	2	−0·120	+0·600	0·000	+0·362	+0·0535
2	1	−0·247	−0·272	0·000	−0·010	−0·019
2	3	−0·117	+1·170	0·000	+0·321	+0·106
3	2	−0·362	+0·599	−2·432	−0·390	+0·050

TABLE IV

$G_{ll'}(\nu)$

ν	$(l, l')=(0, 1)$	$(1, 0)$	$(1, 2)$	$(2, 1)$	$(2, 3)$	$(3, 2)$
1	2·723	...	...	...	...	...
2	2·095	1·028	2·840	...	...	...
3	1·856	1·117	2·264	0·669	3·000	...
4	1·718	1·152	2·010	0·818	2·413	0·468
5	1·623	1·168	1·856	0·899	2·139	0·599
6	1·553	1·175	1·749	0·952	1·971	0·704
7	1·498	1·177	1·666	0·988	1·854	0·793
8	1·452	1·176	1·601	1·014	1·765	0·868
9	1·414	1·173	1·546	1·033	1·694	0·933
10	1·381	1·170	1·501	1·047	1·635	0·991
11	1·352	1·165	1·461	1·058	1·585	1·041
12	1·327	1·161	1·427	1·065	1·543	1·085

TABLE V

$\gamma_{ll'}(\nu)$

ν	$(l, l')=(0, 1)$	$(1, 0)$	$(1, 2)$	$(2, 1)$	$(2, 3)$	$(3, 2)$
1	1·754	...	...	...	...	...
2	1·605	1·667	1·574	...	...	...
3	1·591	1·667	1·582	1·819	1·447	...
4	1·590	1·667	1·579	1·771	1·535	1·850
5	1·591	1·667	1·582	1·741	1·544	1·908
6	1·594	1·667	1·587	1·722	1·549	1·918
7	1·596	1·667	1·593	1·707	1·556	1·920
8	1·599	1·667	1·598	1·697	1·564	1·921
9	1·601	1·667	1·603	1·688	1·573	1·922
10	1·603	1·667	1·608	1·682	1·581	1·924
11	1·605	1·667	1·614	1·676	1·589	1·926
12	1·607	1·667	1·618	1·672	1·596	1·928

Results for ν *small.* The various (l, l') cases are considered separately.

$ns \to k^2p$

$$\chi(\nu 0;\ \epsilon' 1) = \chi_{01}(\nu) + \frac{\epsilon'\nu}{1+\epsilon'\nu} \times 0{\cdot}310. \tag{64}$$

G_{01}, γ_{01} and χ_{01} are given in Table VI for $\nu = 1{\cdot}0(0{\cdot}2)2{\cdot}0$.

Table VI

ν	$G_{01}(\nu)$	$\gamma_{01}(\nu)$	$\chi_{01}(\nu)$
0·6	3·259	1·85	+0·143
0·8	2·976	1·77	+0·085
1·0	2·739	1·701	+0·043
1·2	2·527	1·655	+0·011
1·4	2·360	1·632	−0·008
1·6	2·244	1·620	−0·020
1·8	2·162	1·612	−0·031
2·0	2·095	1·604	−0·041

$np \to k^2s$ $\chi(\nu 1;\ \epsilon' 0)$ is independent* of ϵ' for all ϵ' and $\gamma_{10}(\nu)$ is independent of ν for $\nu \geqslant 2$. Table VII gives $G_{10}(\nu)/(\nu-1)^{1/2}$ for $\nu = 1\cdot0(0\cdot2)1\cdot6$, and $G_{10}(\nu)$, $\gamma_{10}(\nu)$ and $\chi_{10}(\nu) = \chi(\nu 1;\ \epsilon' 0)$ for $\nu = 1\cdot0(0\cdot2)3\cdot0$.

Table VII

ν	$\dfrac{G_{10}(\nu)}{(\nu-1)^{1/2}}$	$G_{10}(\nu)$	$\gamma_{10}(\nu)$	$\chi_{10}(\nu)$
1·0	1·88	0·000	1·333	−0·330
1·2	1·50	0·670	1·515	−0·321
1·4	1·31	0·826	1·585	−0·313
1·6	1·18	0·911	1·630	−0·306
1·8	...	0·962	1·655	−0·300
2·0	...	0·999	1·667	−0·295
2·2	...	1·029	1·667	−0·290
2·4	...	1·058	1·667	−0·286
2·6	...	1·080	1·667	−0·281
2·8	...	1·100	1·667	−0·277
3·0	...	1·117	1·667	−0·273

$np \to k^2d$

$$\chi(\nu 1;\ \epsilon' 2) = \chi_{12}(\nu) + \frac{\epsilon'\nu}{1+\epsilon'\nu} \times 0\cdot362 + \frac{\epsilon'\nu^2}{1+\epsilon'\nu^2}\beta_{12}(\nu). \tag{65}$$

Table VIII gives $G_{12}(\nu)/(\nu-1)^{1/2}$ for $\nu = 1\cdot0(0\cdot2)1\cdot6$ and $G_{12}(\nu)$, $\gamma_{12}(\nu)$, $\chi_{12}(\nu)$, $\beta_{12}(\nu)$ for $\nu = 1\cdot0(0\cdot2)3\cdot0$.

Table VIII

ν	$\dfrac{G_{12}(\nu)}{(\nu-1)^{1/2}}$	$G_{12}(\nu)$	$\gamma_{12}(\nu)$	$\chi_{12}(\nu)$	$\beta_{12}(\nu)$
1·0	5·69	0·000	2·340	0·650	0·079
1·2	5·57	2·489	1·911	·511	·069
1·4	5·02	3·174	1·703	·389	·054
1·6	4·25	3·291	1·625	·287	·038
1·8	...	3·075	1·624	·210	·029
2·0	...	2·757	1·658	·164	·035
2·2	...	2·512	1·675	$\cdot142_5$	·053
2·4	...	2·415	1·635	·131	·068
2·6	...	2·386	1·593	·115	·068
2·8	...	2·340	1·576	$\cdot094_5$	·060
3·0	...	2·251	1·597	0·073	0·050

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* α_{10} and β_{10} being both zero.

7. *Comparison with results derived by other methods.*—For bound–bound transitions Bates and Damgaard have compared the results of their calculations with many other results, obtained both from theory and from experiment. They conclude that their method gives remarkably accurate results for simpler systems and, for complex systems, results which are useful and in some cases precise. Our calculations are based on a further development of the Bates and Damgaard method and enable the Bates and Damgaard tables to be reproduced for $|\nu-\nu'|$ not too small. Our results for bound–bound and bound–free transitions should be of an accuracy not inferior to that of the Bates and Damgaard results.

In assessing the accuracy of calculated transition probabilities it is necessary to consider whether the radial integral is sensitive to small changes in the wave functions. When such sensitivity occurs our results will be sensitive to small changes in the effective quantum numbers. The sensitivity is usually determined by the degree of cancellation which occurs between positive and negative contributions to the radial integral (23). A further cause of sensitivity may also be noted. In transitions $\nu l \rightarrow \epsilon' l+1$ with ν small (for example, in certain $2p \rightarrow \epsilon' d$ transitions) the radial integral will be sensitive to $P_{\nu l}$ for large values of ρ. For such values of ρ the sensitivity of $P_{\nu l}$ to ν will be determined mainly by the exponential factor $e^{-\rho/\nu}$ in (28). To obtain a measure of the sensitivity we write equation (59) as

$$g(\nu l;\ \epsilon' l') = \frac{G(\nu l;\ \epsilon' l')}{\zeta^{1/2}(\nu, l)} \cos\phi(\epsilon') \tag{66}$$

where

$$\phi(\epsilon') = \pi[\nu + \mu'(\epsilon') + \chi(\nu l;\ \epsilon' l')]. \tag{67}$$

We may then say that sensitivity will be great when $\cos\phi$ is small.

Radiative transition probabilities may be expressed in terms of the matrix elements of the dipole length, of the dipole velocity or of the dipole acceleration. All three give identical results when exact wave functions are employed but may give significantly different results when approximate wave functions are used. The dipole length expression gives the greatest weight to large radial distances and is therefore to be preferred in our method of calculation. In the following discussion we do not consider the relative merits of the alternative expressions when other methods of calculation are employed and when quoting results obtained by other methods we consider only the use of the dipole length formulae.

In certain previous calculations accurate bound-state wave functions have been employed together with undistorted regular Coulomb functions for the continuum states. In such cases the accuracy of our calculations may be tested by putting $\mu' = 0$ in our formulae.

We consider separately transitions of the following types: (i) $ns \rightarrow \epsilon' p$, (ii) $np \rightarrow \epsilon' s$, (iii) $np \rightarrow \epsilon' d$, (iv) $nd \rightarrow \epsilon' f$, (v) $nd \rightarrow \epsilon' p$ and $nf \rightarrow \epsilon' d$ and (vi) initial nl^q states with $q > 1$.

(i) $ns \rightarrow \epsilon' p$ *transitions*

He 2 ^{1}S. Both Huang (**19**) and Goldberg (**20**) have used 9-parameter bound-state functions together with undistorted Coulomb functions for the ejected electron. Their results are in close agreement and, as shown in Fig. 3(*a*), are in good agreement with our results calculated with $\mu' = 0$. For this case the sensitivity is small ($\cos\phi(0) = 0{\cdot}82$). In Fig. 3(*a*) we also give results calculated with values of μ' determined from extrapolated quantum defects of the $n\,^1$P series. The correction for distortion is seen to be quite small.

He 2 ^{3}S. The sensitivity is not large ($\cos\phi(0)=0{\cdot}67$). Fig. 3(*b*) shows that our results with $\mu'=0$ are in good agreement with results obtained by Huang (**19**) using a 9-parameter bound–state function together with undistorted Coulomb functions for the ejected electron. Goldberg (**20**) has used a less accurate 3-parameter bound-state function and, for the ejected electron, has used regular Coulomb functions calculated with an effective value of z suggested by $n\,^3$P energy level data. Although this procedure makes some allowance for distortion it may be criticized on the grounds that the continuum functions will have incorrect asymptotic forms. In Fig. 3(*b*) Goldberg's results are compared with our results calculated with μ' determined from $n\,^3$P energy levels. It is seen that the effect of distortion is similar in the two cases and it is a good deal greater than that for 2 ^{1}S. Dalgarno and Kingston (**21**) have shown that our results, with allowance for distortion, are consistent with the requirement of continuity between bound–bound and bound–free matrix elments, the bound–bound matrix elements being calculated by the Hartree–Fock method. The results of Huang are not consistent with this requirement.

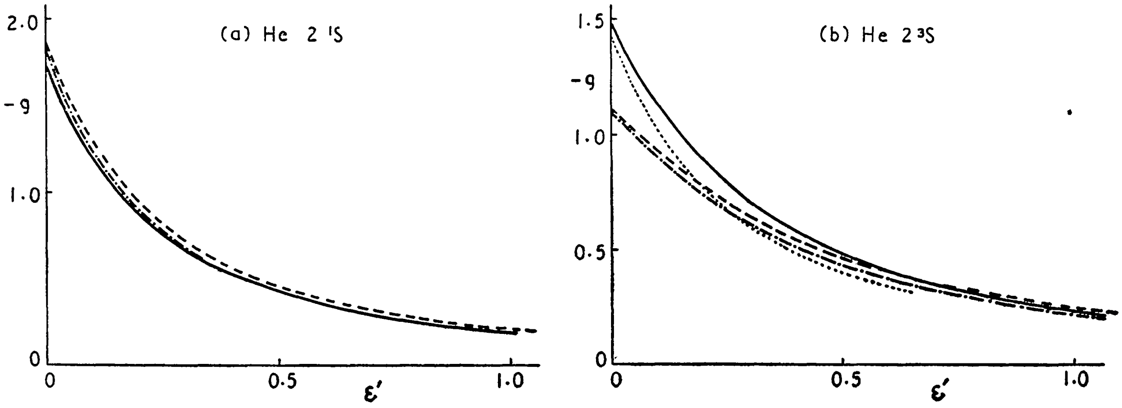

FIG. 3.—(*a*) *He* 2 ^{1}S

- – – – *Calculations of Huang* (**19**) *with* $\mu'=0$ *for the* $\epsilon'\,^1$P *continuum.*
- – · – · – *General formula with* $\mu'=0$.
- ——— *General formula with* μ' *obtained from the* $n'\,^1$P *series.*

(*b*) *He* 2 ^{3}S

- – – – *Calculations of Huang* (**19**) *with* $\mu'=0$ *for the* $\epsilon'\,^3$P *continuum.*
- – · – · – *General formula with* $\mu'=0$.
- .... *Calculations of Goldberg* (**20**) *with some allowance for distortion in the* $\epsilon'\,^3$P *continuum.*
- ——— *General formula with* μ' *obtained from the* $n'\,^3$P *series.*

Li 2*s*. In view of surprisingly large differences between experimental and theoretical results we consider both the 2*s*-*np* series and the $2s\to\epsilon'p$ ionization continuum. For the bound–bound transition $a\to b$ the oscillator strength is defined by

$$f(b,a)=\tfrac{1}{3}(E_b-E_a)\frac{1}{\omega_a}\,\mathbf{S}(b,a) \tag{68}$$

where the energies E_b, E_a are in Rydberg units and where the line-strength **S** is in atomic units. For ionizing transitions we define

$$\frac{df(\epsilon',a)}{d\epsilon'}=\tfrac{1}{3}z^2(I_a+z^2\epsilon')\frac{1}{\pi\omega_a}\,\mathbf{S}(\epsilon',a) \tag{69}$$

where $S(\epsilon', a)$ is defined by (5) and (6). In Fig. 4 we plot $\frac{1}{2}\nu'^3 f(np, 2s)$ against $-1/\nu'$ and $df(\epsilon', 2s)/d\epsilon'$ against $\sqrt{\epsilon'}$. All points should lie on a single smooth curve (as may be shown by the argument leading to equation (54)). We give the experimental results of Fillipov (**22**) for $\frac{1}{2}\nu'^3 f$ and the experimental results of Tunstead (**23**) for $df/d\epsilon'$. These independent experimental results are seen to be reasonably consistent one with the other. We also give the results of Hartree–Fock calculations for $\frac{1}{2}\nu'^3 f$ (Fock and Petrashen, **24**) and for $df/d\epsilon'$ (Stewart, **25**). Finally we give the results of Bates and Damgaard for transitions to $3p$, $4p$, and $5p$ together with our results for transitions to higher excited states and to the continuum.

Since the sensitivity is only moderate ($\cos\phi(0) = 0{\cdot}36$) the difference between the experimental and the theoretical results are larger than would have been expected.

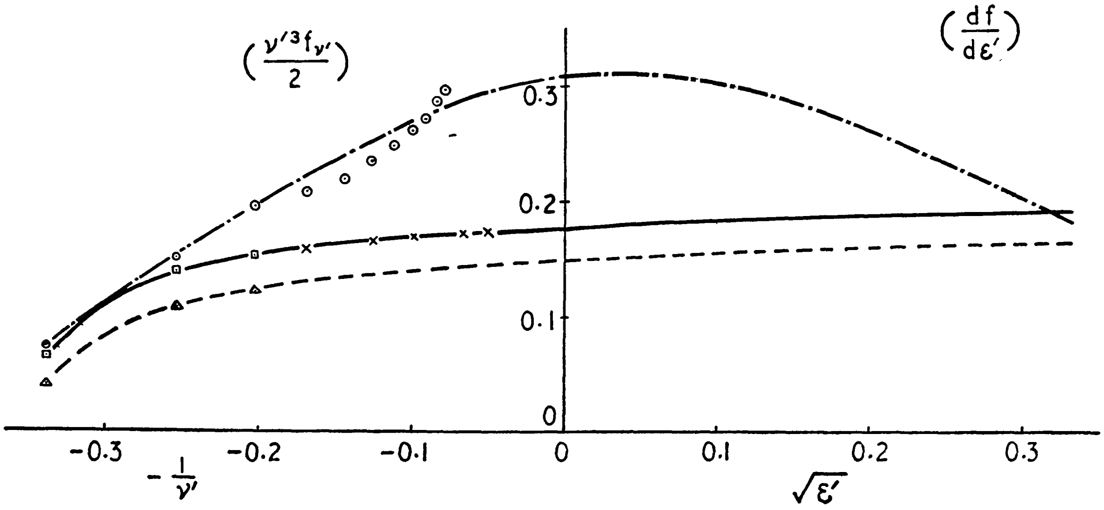

FIG. 4.—*Oscillator strengths for* Li $2s \rightarrow n'p$ *and* $2s \rightarrow \epsilon' p$.

— · — · — *Experimental results of Tunstead* (**23**) *for* $(df/d\epsilon')$ *and curve through experimental points* (○) *of Fillipov* (**22**) *for* $(\nu'^3 f_{\nu'}/2)$.

— — — — *Results of Hartree–Fock calculations made by Stewart* (**25**) *for* $(df/d\epsilon')$ *and by Fock and Petrashen* (**24**) *for* $(\nu'^3 f_{\nu'}/2)$.

——— *General formula. For* $(\nu'^3 f_{\nu'}/2)$ *the points* ⊡ *are obtained from the Bates and Damgaard tables and the points* × *from our calculations.*

If the experimental results are correct there must be comparatively large errors in the separable wave functions used in the Hartree–Fock calculations and in our method of calculation.

Although it would be of interest to make further calculations using non-separable variational functions for the Li ground state it is by no means evident that any substantial modification of the calculated cross section would be obtained. The Hartree–Fock term value, $\epsilon_{2s} = -0{\cdot}393$, is in very good agreement with the experimental value, $\epsilon_{2s} = -0{\cdot}396$. The Hartree–Fock np term values are also in good agreement with experiment. Our calculations, based on experimental energies, would not be in such close agreement with the Hartree–Fock calculations if there were substantial errors in the Hartree–Fock energies and phases.

Na 3s. In Fig. 5 our results for the photo-ionization cross section are compared with results of Hartree–Fock calculations (Seaton, **26**) and of an experimental determination (Ditchburn, Jutsum and Marr, **27**). Since the sensitivity is considerable ($\cos\phi(0) = 0{\cdot}12$) and since the error in the experimental results may be as great as ±20 per cent, the general agreement between theory and experiment may be considered to be satisfactory. There is as yet no satisfactory explanation of the non-zero minimum in the measured cross section, the calculated cross sections having zero minima corresponding to a change in the sign of the matrix elements.

In Fig. 5 we have also plotted some results obtained by Rudkjøbing (**28**). These are discussed further in the next paragraph.

Na 4s. Agreement with calculations by Rudkjøbing (Fig. 6) must be regarded as poor even when allowance is made for fairly great sensitivity ($\cos\phi(0) = 0{\cdot}20$). Rudkjøbing used a Hartree–Fock 4*s* function and calculated a continuum function $G_{\epsilon' p}$ using a central field adjusted to give approximate agreement with experimental energies for 3*s*, 3*p* and 3*d*. To these functions $G_{\epsilon' p}$ he then added linear combinations of Hartree–Fock radial functions P_{3p} and P_{4p} in such a way as to obtain $\epsilon' p$ radial functions orthogonal to P_{3p} and P_{4p}. This addition of combinations of P_{3p} and P_{4p} produces an undesirable distortion of the $\epsilon' p$ radial functions at fairly large radial distances. No such distortion appears in the Hartree–Fock radial functions (Seaton, **26**). Since the dipole matrix elements are large for 4*s*–3*p* and particularly for 4*s*–4*p* the admixture of even small amounts of 3*p* and 4*p* functions has a considerable influence on the calculated 4*s*–$\epsilon' p$ matrix elements. Similar considerations apply to the 3*s*–$\epsilon' p$ transitions and for this case the moderately good agreement between our results and those of Rudkjøbing appears to be largely fortuitous.

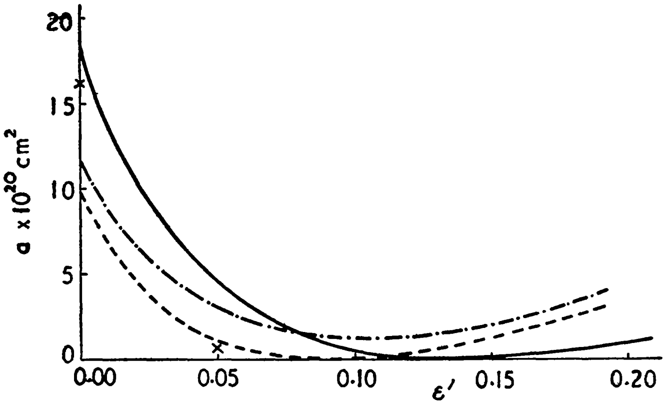

FIG. 5.—*The photo-ionization cross section for Na 3s.*

— · — · — *Experimental results of Ditchburn and Marr* (**27**).

— — — — *Hartree–Fock calculations* (*Seaton*, **26**).

× *Values calculated by Rudkjøbing* (**28**).

——— *General formula.*

Mg⁺ 3s and **Si⁺ 4s.** Biermann and Lübeck (**29**) have calculated cross sections for ionization from several states of Mg^+ and of Si^+. To the central potentials obtained from non-exchange self-consistent field calculations they add polarization potentials behaving asymptotically as α/r^4 where the polarizability α is estimated from quantum defects for the *f* series. The potentials are further modified by including a function intended to make approximate allowance for exchange interactions. This function contains an adjustable parameter $\Delta\beta$ which is assumed to be constant for the bound and continuum states of each *l* series,

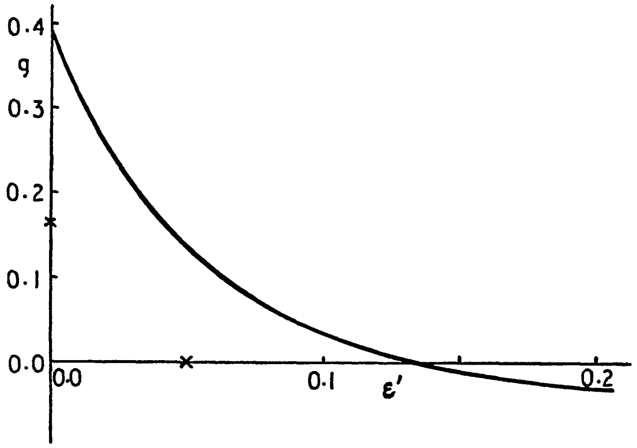

Fig. 6.—*Na* 4*s*.

× *Values calculated by Rudjøbing* (28).

——— *General formula.*

the value of $\Delta\beta$ being chosen so as to give the correct energy for one of the bound-states of the series. This method should give good wave functions for the state used for the determination of $\Delta\beta$ but may give less accurate functions for the remaining bound-states and for the continuum. For the p-wave potentials the values of $\Delta\beta$ are determined from the $3p$ state of Mg^+ and from the $4p$ state of Si^+. In Fig. 7 our results are compared with those of Biermann and Lübeck.

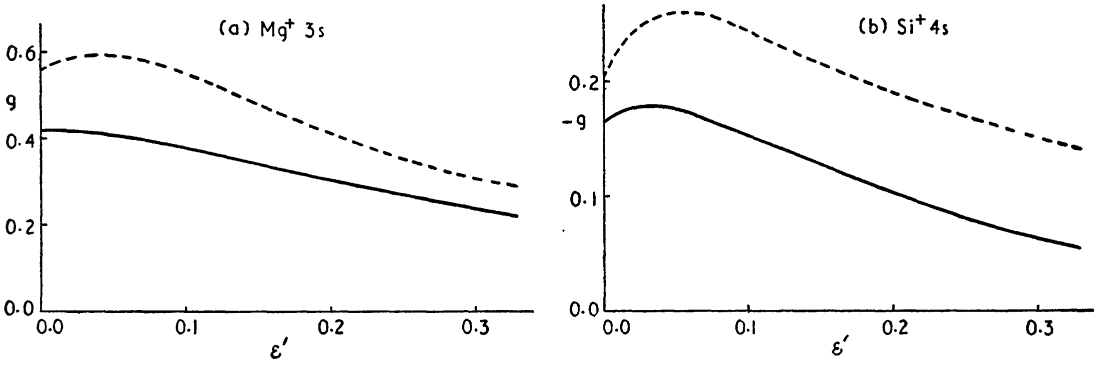

Fig. 7.

(*a*) *Mg*$^+$ 3*s*, (*b*) *Si*$^+$ 4*s*

– – – – *Biermann and Lübeck* (29)

——— *General formula*

The sensitivity is considerable ($\cos\phi(0) = 0{\cdot}19$ for Mg^+ $3s$ and $\cos\phi(0) = 0{\cdot}08$ for Si^+4s) and the differences between the results obtained are therefore no greater than would be expected.

K 4s. For this case the sensitivity is so great that accurate calculation of the cross section is scarcely possible. Bates (30) has shown that approximate agreement with the measured cross section (27) may be obtained using a Hartree–Fock $4s$ function and $\epsilon' p$ continuum functions calculated with a suitably modified central field. It is of interest to see if the continuum functions which give approximate agreement with the experimental cross section have phases consistent with extrapolated quantum defects. We have therefore made calculations using a Hartree–Fock 4*s* function together with continuum functions of the form (36). From *np* energy levels we obtain $\mu'(\epsilon')=\mu'(0)-0{\cdot}261\epsilon'$ with $\mu'(0)=1{\cdot}711$. We have made calculations for various values of $\mu'(0)$. It is seen (Fig. 8(*a*)) that the best agreement with the experimental cross section is obtained with a value of $\mu'(0)$ not far different from the experimental value ($\mu'(0)=1{\cdot}690$ in place of $1{\cdot}711$).

In the general formula we consider the effect of using the extrapolated experimental quantum defect, $\mu'=1{\cdot}711-0{\cdot}261\epsilon'$, and of varying the effective quantum number ν for 4*s*. With the experimental value, $\nu=1{\cdot}770$, we obtain $\cos\phi(0)=-0{\cdot}15$ and with the Hartree–Fock value, $\nu=1{\cdot}852$, we obtain $\cos\phi(0)=+0{\cdot}09$. Fig. 8(*b*) shows that the best agreement with the experimental cross section is obtained with values of ν intermediate between the experimental and Hartree–Fock values.

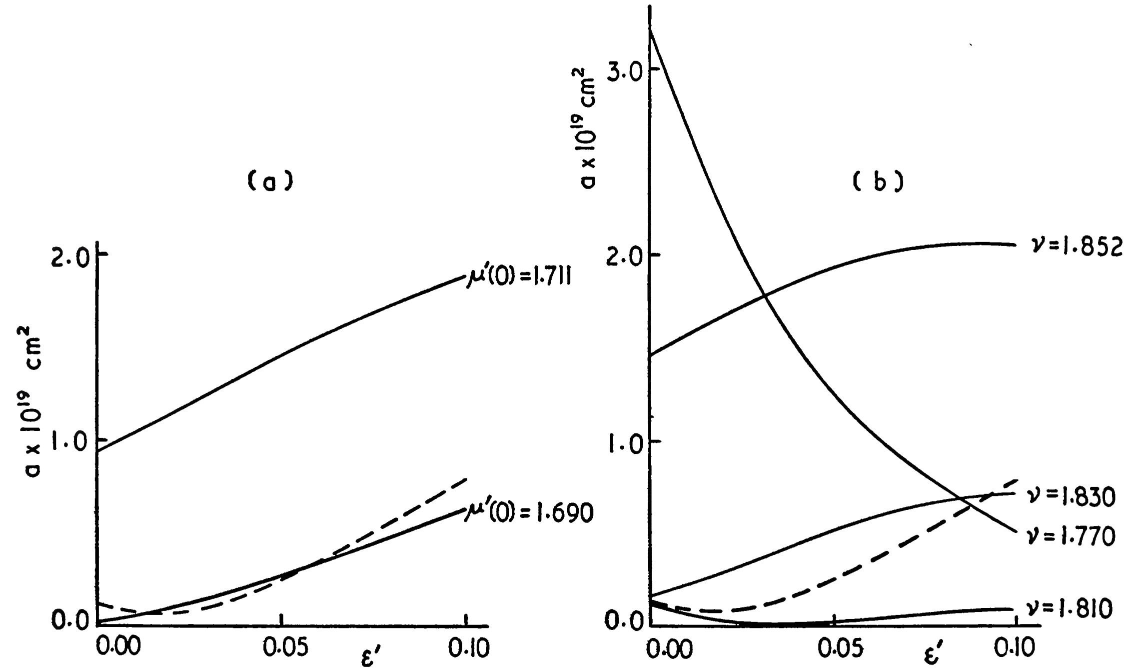

FIG. 8.—*Cross sections for photo-ionization of K 4s*

(*a*) *The experimental cross section* (– – –) (27) *and cross-sections* (———) *calculated using a Hartree–Fock 4s function and continuum functions* (36) *with two different values of* $\mu'(0)$; $\mu'(0)=1{\cdot}711$ *is the experimental value.*

(*b*) *The experimental cross section* (– – –) *and cross sections* (———) *calculated using the general formula with the extrapolated empirical quantum defect and various values of the effective quantum number* ν *for 4s. The experimental value is* $\nu=1{\cdot}770$ *and the Hartree–Fock value is* $\nu=1{\cdot}852$.

Comparison of the curve $\mu'(0)=1{\cdot}711$ of Fig. 8(*a*) with the curve $\nu=1{\cdot}852$ of Fig. 8(*b*) shows, for a sensitive case, the differences in the calculated cross section due to differences between the Hartree–Fock bound-state function and the function (28) calculated with the Hartree–Fock effective quantum number.

Ca^+ 4s. Although this is also a sensitive case the sensitivity is less than for K 4*s*. From *np* energies we obtain $\mu'=1{\cdot}435-0{\cdot}407\epsilon'$. With the experimental 4*s* effective quantum number, $\nu=2{\cdot}141$, we obtain $\cos\phi(0)=+0{\cdot}094$ and with the Hartree–Fock value, $\nu=2{\cdot}196$, we obtain $\cos\phi(0)=+0{\cdot}255$. The corresponding threshold cross sections are $0{\cdot}4\times10^{-19}\,cm^2$ (experimental ν) and $2{\cdot}8\times10^{-19}\,cm^2$

(Hartree–Fock ν). A full Hartree–Fock calculation (**16, 31**) gives a threshold cross-section of $1\cdot2\times10^{-19}\,\mathrm{cm}^2$.

The Ca$^+$ 4*s* cross section is required for the study of the interstellar ionization equilibrium. For the iso-electronic case of K 4*s*, and also for Na 3*s*, the best estimate of the cross section is obtained with a value $\bar{\nu}$ of ν intermediate between the experimental and Hartree–Fock values. We may expect that this will also be the case for Ca$^+$4*s*. We put

$$\bar{\nu}=c\nu(\text{experimental})+(1-c)\nu(\text{Hartree–Fock}).$$

For K 4*s* we obtain the best results with $c\simeq0\cdot39$. For Ca$^+$ 4*s* we adapt $c=0\cdot39$ to obtain $\bar{\nu}=2\cdot175$. Fig. 9 shows the cross section calculated with this value of $\bar{\nu}$ and, for comparison, the cross section calculated by the Hartree–Fock method.

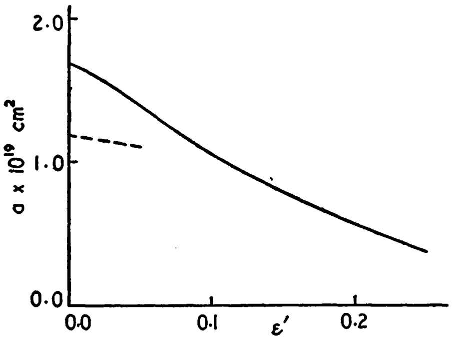

FIG. 9.—*Cross sections for photo-ionization of Ca$^+$ 4s.*

- - - - *Hartree–Fock calculation* (**16, 31**).

——— *General formula with effective quantum number $\bar{\nu}=2\cdot175$ for 4s (see text).*

The full line curve is probably the most accurate estimate of the cross section. Note that the kinetic energy of the ejected electron, in units of 13·60 eV, is $k'^2=4\epsilon'$.

(ii) *np→ε′s transitions*

Na 3*p*→ε′*s* and 4*p*→ε′*s*. For these two cases there is no great sensitivity ($\cos\phi(0)\simeq0\cdot8$). Fig. 10 shows our results to be in good agreement with the results of Rudkjøbing (**28**). For the *s*-continuum Rudkjøbing used wave functions more satisfactory than those employed for the *p*-continuum (see discussion of Na 4*s* above).

Mg$^+$ 3*p*→ε′*s* and Si$^+$ 3*p*→ε′*s* and 4*p*→ε*s*′. For these cases sensitivity is slight, $\cos\phi(0)$ being almost unity. Our results are in satisfactory agreement with those of Biermann and Lübeck (**29**) (Fig. 10).

Ca$^+$ 4*p*→ε′*s*. The good agreement with calculations by Green (**31**) (Fig. 10) may be largely fortuitous since Green neglected exchange in the calculation of continuum wave functions. For this case the sensitivity is very slight, ($\cos\phi(0)=0\cdot999$).

(iii) *np→ε′d transitions*

Na 3*p*→ε′*d* and 4*p*→ε′*d*. There is no great sensitivity ($\cos\phi(0)\simeq0\cdot7$). Fig. 11 shows our results to be in good agreement with those of Rudkjøbing (28).

Mg$^+$ 3*p*→ε′*d* and Si$^+$ 3*p*→ε′*d* and 4*p*→ε′*d*. In Fig. 11 our results are compared with those of Biermann and Lübeck (**29**).

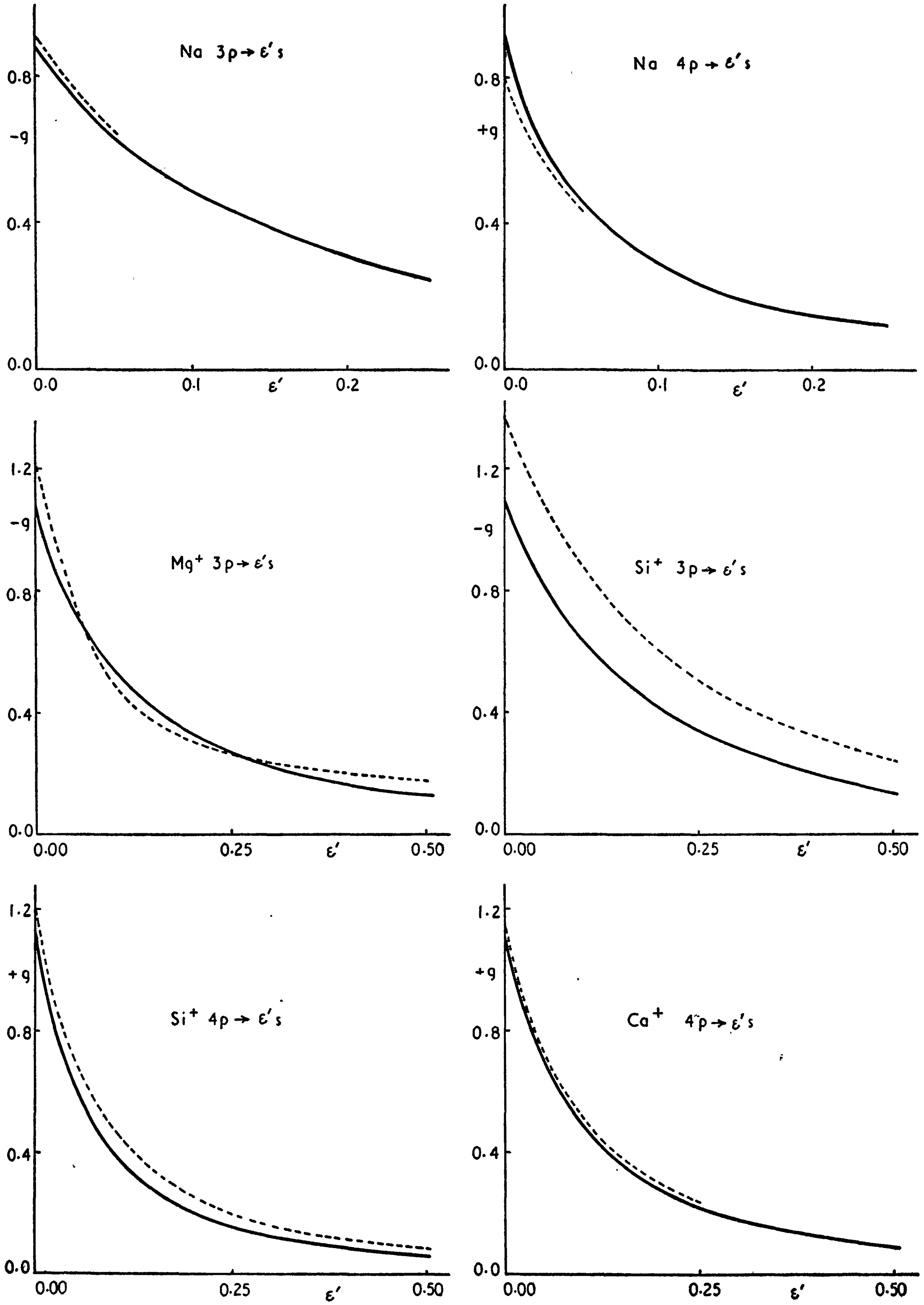

FIG. 10.—*np→ ε′s transitions.*

- - - - *Calculations of Rudjøbing* (**28**) *for Na, of Biermann, and Lübeck* (**29**) *for* Mg^+ *and* Si^+ *and of Green* (**31**) *for* Ca^+.

——— *General formula.*

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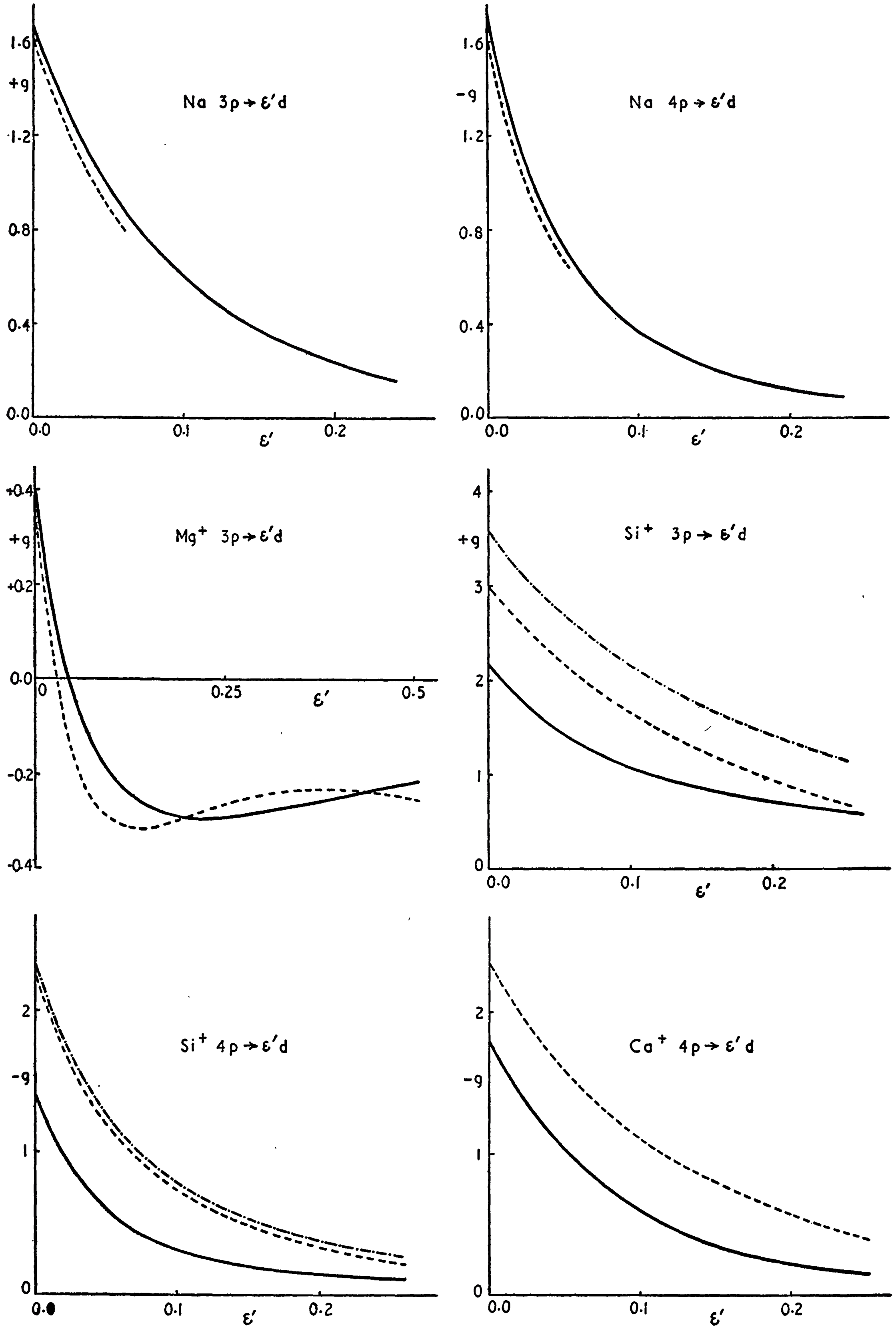

FIG. 11.—*$np \rightarrow \epsilon' d$ transitions.*

– – – – *Calculations of Rudjøbing* (**28**) *for Na, of Biermann and Lübeck* (**29**) *for Mg^+ and Si^+ and of Green* (**31**) *for Ca^+.*

——— *General formula.*

– · – · – · *General formula with $\mu' = 0$.*

The agreement for Mg^+ $3p \rightarrow \epsilon' d$ is especially satisfactory in view of the fact that $\cos\phi(0) = 0{\cdot}16$ and $\cos\phi(\epsilon')$ goes through zero as ϵ' increases.

The agreement for Si^+ $3p \rightarrow \epsilon' d$ and $4p \rightarrow \epsilon' d$ is poor despite the fact that sensitivity is only moderate ($\cos\phi(0) \simeq 0{\cdot}6$ in both cases). This may be explained as follows. For the *d*-continuum Biermann and Lübeck used a central potential adjusted so as to give a correct energy for Si^+ $3d$ (see discussion of Si^+ $4s$ above) which is a perturbed member of the *nd* series. Fig. 12 shows quantum defects and η-defects (see QDM, Section 3) for Si^+ *nd*. This should be compared with Fig. 1 of QDM which shows quantum-defects and η-defects for unperturbed *d*-series. It would appear that Si^+ $3s^2 3d\ ^2D$ is perturbed upwards by Si^+ $3s\ 3p^2\ ^2D$. The effect of the perturbation will be to give values of μ' in the *d*-continuum functions of Biermann and Lübeck which will be too small. In Fig. 11 we give results calculated by our method with $\mu' = 0$. It is seen that the results of Biermann and Lübeck lie between our results with $\mu' = 0$ and with $\mu' \neq 0$.

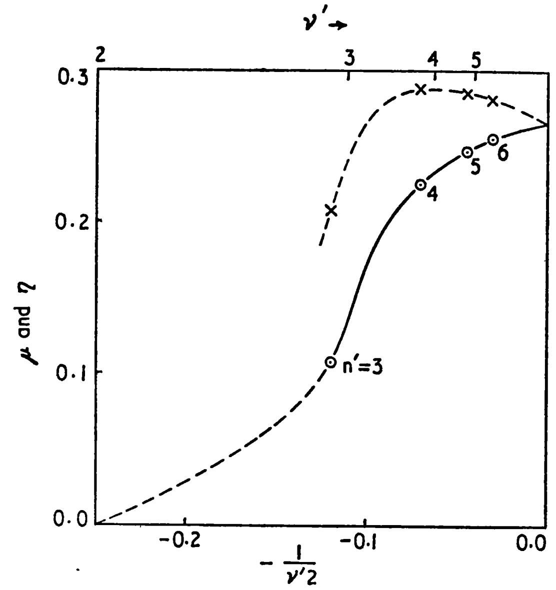

FIG. 12.—*Quantum defects* (⊙) *and* η*-defects* (×) *for* Si^+ *n'd. This figure should be compared with Fig.* 1 *of QDM, which shows quantum defects and* η*-defects for unperturbed d-series.*

Ca^+ $4p \rightarrow \epsilon' d$. The poor agreement between our results and those of Green (**31**) (Fig. 11) is probably due to neglect of exchange in the calculation of the continuum functions used by Green. It should be noted that the sensitivity ($\cos\phi(0) = 0{\cdot}72$) is greater than for the Ca^+ $4p \rightarrow \epsilon' s$ case above.

(iv) *nd→ε'f transitions*

Mg^+ $3d \rightarrow \epsilon' f$ and **Si^+ $3d \rightarrow \epsilon' f$.** For these two cases the sensitivity is not great ($\cos\phi(0) \simeq 0{\cdot}7$), and Fig. 13 shows our results to be in good agreement with those of Biermann and Lübeck (**29**).

(v) *nd→ε'p* and *nf→ε'd transitions*

Mg^+ $3d \rightarrow \epsilon' p$ and **$4f \rightarrow \epsilon' d$.** For $3d \rightarrow \epsilon' p$ the sensitivity is not great ($\cos\phi(0) = 0{\cdot}52$), but Biermann and Lübeck (**29**) give values for $df/d\epsilon'$ which are ten times greater than those obtained from the general formula. It does not appear that the values

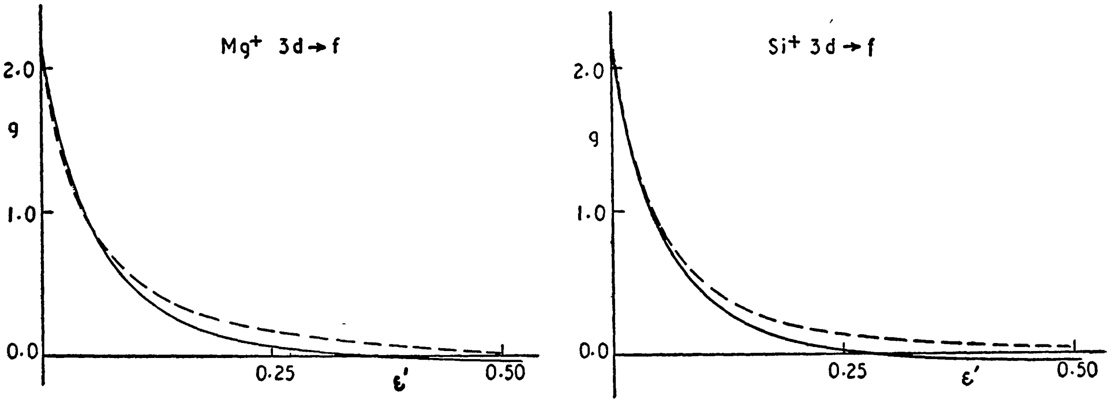

Fig. 13.

(*a*) Mg^+ $3d \to \epsilon' f$, (*b*) Si^+ $3d \to \epsilon' f$.
– – – – *Biermann and Lübeck* (**29**).
———— *General formula.*

given by Biermann and Lübeck can be correct, as it would require a value of $\cos \phi(0) \simeq 1{\cdot}4$ in the general formula to reproduce their threshold result.

For $4f \to nd$, an accurate comparison cannot be made as Biermann and Lübecks' results are given to only one significant figure; however their results agree with ours to within this accuracy.

$Si^+ 3d \to \epsilon' p$ and $4f \to \epsilon' d$. Again Biermann and Lübeck give results to only one significant figure. For $3d \to \epsilon' p$ their results and ours agree to within this accuracy. It is interesting to note however that the Biermann and Lübeck results for $4f \to \epsilon' d$ lie between those obtained from the general formula with $\mu'(\epsilon' d) = 0$ and with $\mu'(\epsilon' d)$ obtained by extrapolation of the *nd* series (see discussion of $Si^+ 3p \to \epsilon' d$ and $4p \to \epsilon' d$ above).

(vi) *Initial nl^q states with $q > 1$*

In the derivation of our formulae we considered radial equations of the type (18) and later identified the energy parameter E with the energy required to remove an electron. Although it is not easy to give a theoretical justification for this procedure for the case of initial states consisting of groups of equivalent electrons, the work of Bates and Damgaard suggests that useful results may nevertheless be obtained. For such cases $(\partial\mu/\partial\nu)$ may be quite large and careful consideration must be given to the factor $\zeta = (1 + \partial\mu/\partial\nu)$ required for the normalization of the bound-state wave functions.

He $1s^2$. In Fig. 14 we plot quantum defects μ against effective quantum numbers ν for He $1s^2\ {}^1S$, $1s2s\ {}^1S$ and $1s3s\ {}^1S$. For $\nu = 0$ the extrapolated quantum defect must have an integer value (Section 3 of QDM) and from the trend of the curve in Fig. 14, it would appear that this value should be unity. From the experimental data it is not easy to obtain a precise value of $\partial\mu/\partial\nu$ for $1s^2$. From the normalization of Hartree wave functions (Wilson and Lindsay, **32**) we obtain

$$(\partial\mu/\partial\nu) = -0{\cdot}167$$

for $1s^2$. This gives the dashed tangent of Fig. 14 which is seen to be consistent with the other data. We adopt $(\partial\mu/\partial\nu) = -0{\cdot}167$ for $1s^2$.

Huang (**19**) has calculated $(df/d\epsilon')$ using a six-parameter function for $1s^2$ and undistorted Coulomb functions for the ejected electron. The sensitivity

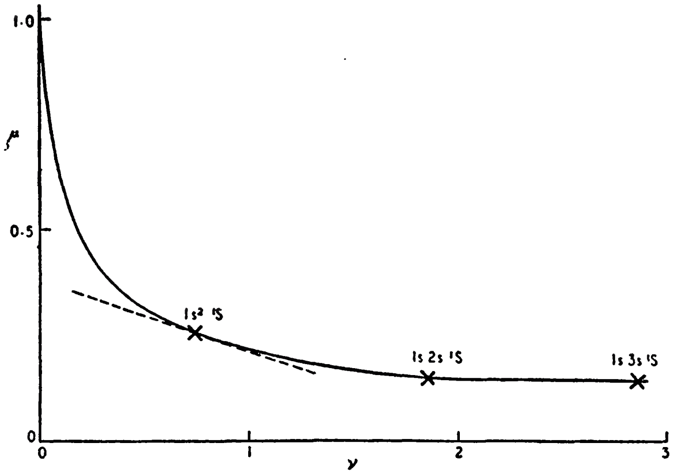

FIG. 14.—*Quantum defects for He* $1s^2\ {}^1S$ *and* $1s\ ns\ {}^1S$ *against effective quantum numbers* ν. *The tangent* – – – *is obtained from the normalization factor of Hartree wave functions. Note that the extrapolated quantum defect equals* 1 *for* $\nu = 0$.

is slight ($\cos\phi(0) \simeq 0{\cdot}86$), and Fig. 15 shows that the results are in good agreement with our results calculated with $\mu' = 0$. Improved calculations have recently been made by Stewart and Wilkinson (**33**). For $1s^2$ they use the 6-parameter function employed by Huang and for the ejected electron they use Hartree–Fock functions. Let $\Delta(\epsilon')$ be the correction to be added to $(df/d\epsilon')$ calculated with neglect of distortion. In Table IX values of Δ obtained by Stewart and Wilkinson are compared with those obtained by our method. It is seen that the corrections are small in both cases and that the agreement for small ϵ' is better than that for larger ϵ'.

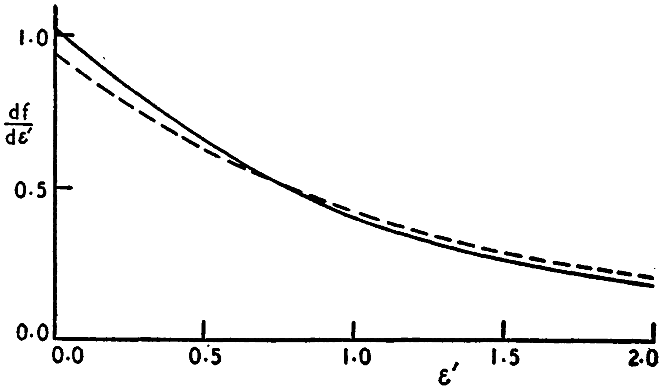

FIG. 15.—*He* $1s^2$ *values of* $df/d\epsilon'$.

– – – – – *Calculated by Huang* (**19**) *with undistorted Coulomb functions for the ejected electron.*
———— *General formula with* $\mu' = 0$.

TABLE IX

ϵ'	$\left(\frac{df}{d\epsilon'}\right)_{\mu=0}$	$\Delta(\epsilon')$	
	General formula	General formula	Stewart and Wilkinson
0·0	1·016	−0·043	−0·032
0·5	0·652	−0·018	+0·010
1·0	0·407	−0·006	+0·028

Lassetre and Silverman (34) deduce oscillator strengths from experimental data on the scattering of high energy (~ 500 eV) electrons. When the energy is great enough for the Born approximation to be employed the scattering data may be used to obtain the generalized oscillator strengths defined by

$$f(b, a|K) = \frac{(E_b - E_a)}{K^2} \left|(b|\sum_j e^{i\boldsymbol{K}.\boldsymbol{r}_j}|a)\right|^2 \qquad (70)$$

where $\boldsymbol{K} = \boldsymbol{k}_a - \boldsymbol{k}_b$ and where $\boldsymbol{k}_a$, $\boldsymbol{k}_b$ are the initial and final propagation vectors. In the limit of $K \to 0$, $f(b, a|0) = f(b, a)$, where $f(b, a)$ is the optical oscillator strength. The absolute values obtained by Lassetre and Silverman are obtained by calibrating against $f(2\,{}^1\text{P}, 1s^2|K)$ calculated accurately over a wide range of K values. Fig. 16 gives a comparison of optical oscillator strengths for transitions from

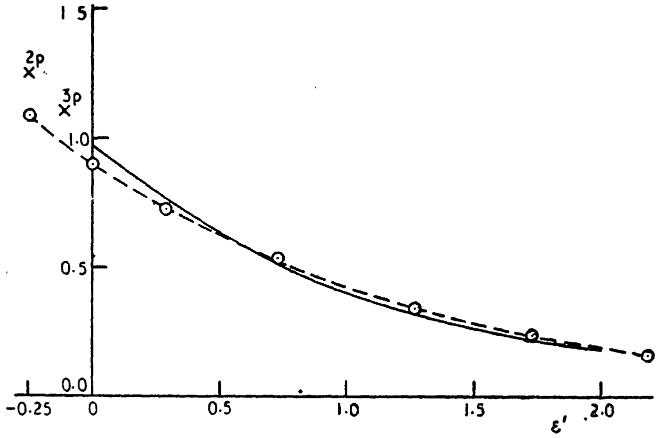

FIG. 16.—*He* $1s^2$: *values of* $\frac{1}{2}\nu'^3 f_{\nu'}$ *and* $df/d\epsilon'$.

– – – – *Curve through experimental points* (⊙) *of Silverman and Lassetre* (34).

———— *General formula* ($\mu' \neq 0$).

× *Calculations using tables of Bates and Damgaard* (1) *and* $(\partial\mu/\partial\nu) = -0{\cdot}167$ *for* $1s^2$.

He $1s^2$ (values of $\frac{1}{2}\nu'^3 f_{\nu'}$ and of $df/d\epsilon'$). In addition to the results of Lassetre and Silverman we give points for $1s^2 \to 2\,{}^1\text{P}$ and $3\,{}^1\text{P}$ calculated from the Bates and Damgaard tables with $(\partial\mu/\partial\nu) = -0{\cdot}167$ for $1s^2$ and our values of $(df/d\epsilon')$ calculated with allowance for distortion. In the range $0 \leqslant \epsilon' \leqslant 2{\cdot}0$ our results are in good agreement with the experimental results. At higher energies ($\epsilon' = 2{\cdot}60$ and $2{\cdot}86$) the experimental results show peaks in oscillator strengths which are due to doubly-excited states of auto-ionization type. Such effects, which in other systems may occur at lower energies, are not properly taken into account in our method of calculation.

Mg $3s^2$. For this case a plot of the $3sns\ {}^1\text{S}$ series quantum defects against ν indicates that $\mu_{ns} \to 2$ as $\nu \to 0$, and the graph enables a fairly reliable estimate of $\zeta = (1 + \partial\mu/\partial\nu)$ to be made since μ_{ns} does not vary as rapidly with ν as in the previous case of the He $n\,{}^1\text{S}$ series (Fig. 14). In Fig. 17 our results for the cross section are compared with the experimental results of Ditchburn and Marr (35). Also shown are values of the cross section calculated using the Hartree–Fock $3s^2$ function given by Biermann and Trefftz (36) and the continuum function $G_{k'p}(r)$ (equation (36)), with $\mu'(\epsilon' p)$ extrapolated from observed $3s\,np\ {}^1\text{P}$ quantum defects. The agreement obtained is probably as good as may be expected in view of the moderate sensitivity ($\cos\phi(0) = 0{\cdot}356$) and the possible error of

± 20 per cent in the observed threshold cross section. The relative accuracy of the general formula results does not appear to be greatly inferior to that obtained using a Hartree–Fock bound function.

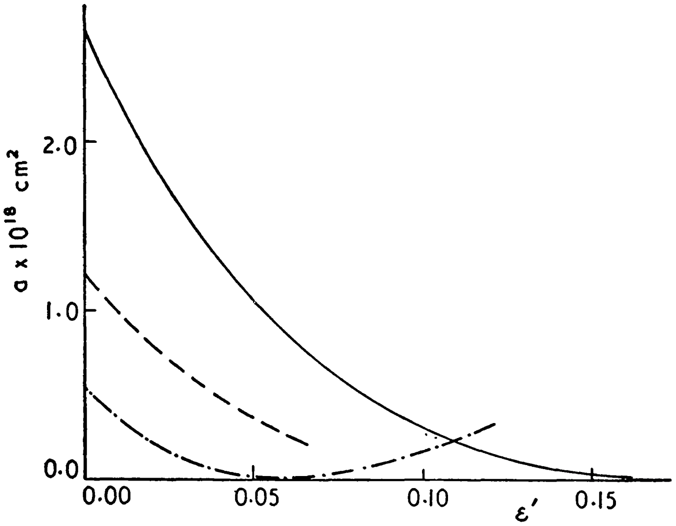

FIG. 17.—*Cross section for photo-ionization of Mg* $3s^2$

- - - - *Experimental results of Ditchburn and Marr* (35).
———— *General formula.*
–·–·–· *Calculations with Hartree–Fock* $3s^2$ *function.*

Ions with outer $2p^q$ configurations. In QDM (Section 4) it was shown that, for the $2p$ radial functions of atomic oxygen ions, a good approximation to the factor ζ is given by

$$\zeta = \frac{(\nu-1)(\nu+2)}{\nu(\nu+1)}. \tag{71}$$

TABLE X

	ν	$p \to d$			$p \to s$		
		cos ϕ(o)	g_0		cos ϕ(o)	g_0	
			General formula	Hartree–Fock		General formula	Hartree–Fock
O $2p^4\,{}^3$P	1·000	0·45	2·11	1·57	−0·51	−0·78	−0·62
N $2p^3\,{}^4$S	0·967	0·43	1·90	2·32	−0·41	−0·65	−1·07
C $2p^2\,{}^3$P	1·099	0·54	2·63	2·82	−0·76	−1·10	−1·41
Na$^+$ $2p^6\,{}^1$S	1·072	0·51	2·47	2·54	−0·70	−1·03	−1·24
O$^+$ $2p^3\,{}^4$S	1·244	0·65	3·35	3·35	−0·97	−1·31	−1·47
Mg^{+2} $2p^6\,{}^1$S	1·235	0·64	3·30	3·21	−0·97	−1·30	−1·45
Ne^{+2} $2p^4\,{}^3$P	1·387	0·77	3·77	3·39	−0·97	−1·26	−1·40
O^{+2} $2p^2\,{}^3$P	1·493	0·86	4·16	3·78	−0·84	−1·08	−1·05
Ne^{+3} $2p^3\,{}^4$S	1·496	0·86	4·16	3·83	−0·83	−1·08	−1·00
O^{+3} $2p$ ^{2}P	1·677	0·97	4·22	3·60	−0·39	−0·49	−0·37
Ne^{+4} $2p^2\,{}^3$P	1·640	0·96	4·25	3·70	−0·50	−0·62	−0·48

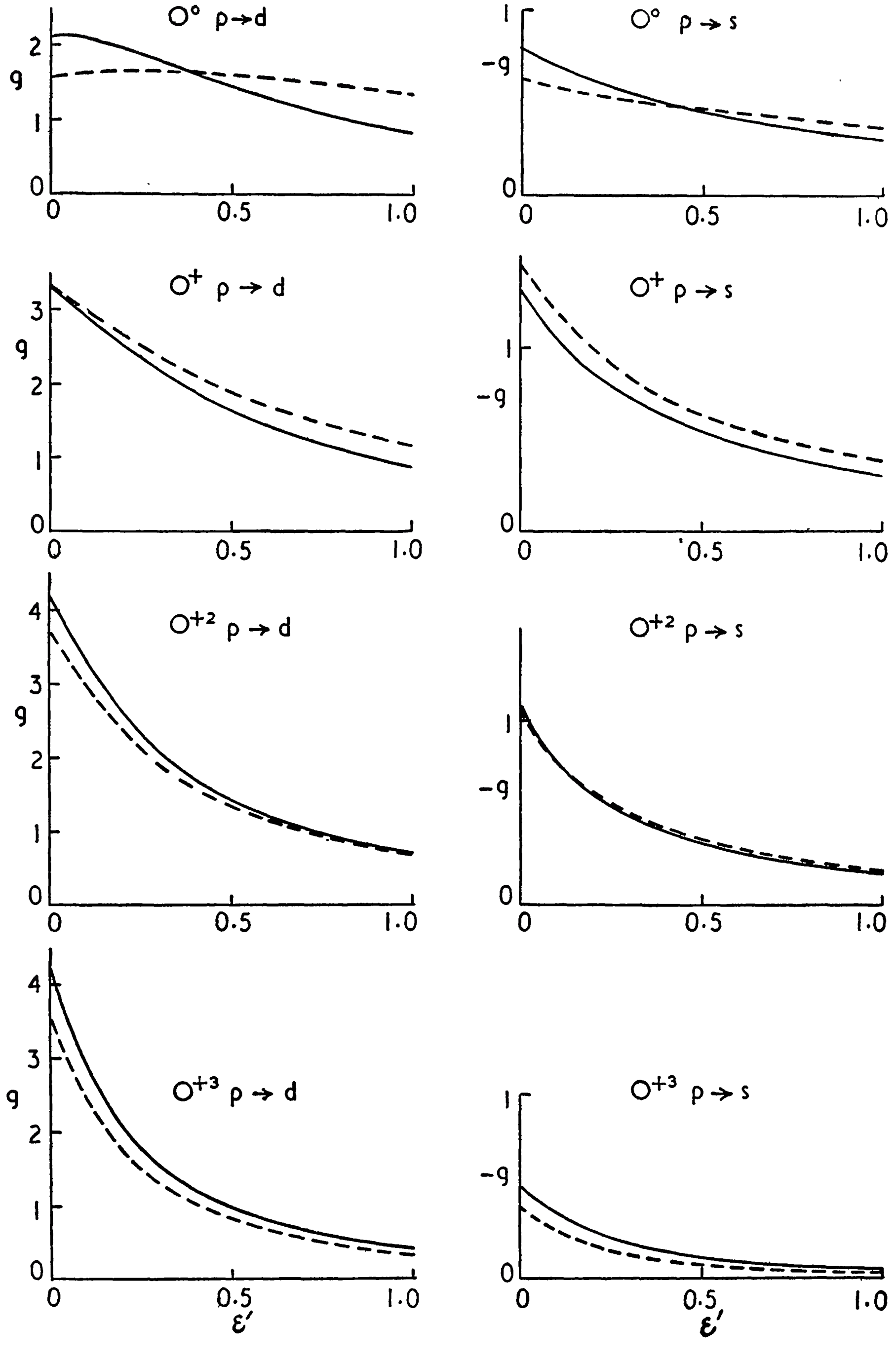

FIG. 18.—*$2p\to\epsilon'd$ and $2p\to\epsilon's$ transitions in atomic oxygen ions. All calculations with $\mu'=0$.*

– – – – *Hartree–Fock calculations.*

——— *General formula.*

This factor is adopted for all ions with outer $2p^q$ configurations. From previous calculations (Bates and Seaton, (7); Seaton (37)) it is known that $2p \rightarrow \epsilon' d$ transitions are more important than $2p \rightarrow \epsilon' s$ transitions and that effects arising from distortion of the $\epsilon' d$ continuum are fairly small. In order to assess the accuracy of the general formula for transitions from $2p^q$ configurations we compare our results with those obtained using Hartree–Fock $2p$ radial functions. In all cases we consider undistorted continuum functions for both $\epsilon' s$ and $\epsilon' d$. Table X gives the results of threshold calculations for eleven different ions and Fig 18 gives energy variations for atomic oxygen ions. The calculations with Hartree–Fock wave functions were made using formulae given by Bates (2). It should be emphasized that Table X and Fig. 15 are intended only to give comparison with Hartree–Fock calculations and that improved results, particularly for $2p \rightarrow \epsilon' s$, would be obtained by allowing for distortion in the general formula.

It is seen that the overall agreement is good, but that our results are less satisfactory for systems, such as neutral atomic oxygen, for which the effective quantum number for $2p$ is particularly small. We may conclude that satisfactory results should be obtained on using the general formula for photo-ionization from $2p^q$ configurations and on using the Bates and Damgaard tables, with inclusion of the factor (71), for transitions $2p^q \rightarrow 2p^{q-1}n's$ and $n'd$.

8. *Conclusions.*—From the comparisons with results derived by other methods it may be concluded that our method will give good results whenever there is no great sensitivity to details of the atomic wave functions.

Our main interest is in the application of our calculations to the calculation of recombination spectra and of total radiative recombination rates. For these problems one requires sums over large numbers of recombination rates to individual states. Whenever the calculations for any given states are sensitive to the wave functions the calculated rates will be small and will contribute little to the sums. Since there is no reason to suspect systematic errors in our method we should obtain particularly good accuracy in results involving sums over many states.

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