

PROBABILITIES OF IONIZATION AND EXCITATION OF CLOSED SHELL ELECTRON OF LI BY ELECTRON IMPACT

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ABSTRACT

With the aid of analytic wave functions determined by the variational method, the quantum mechanical cross-sections for the excitation of the valence electron, an electron in an inner closed shell, and of the simultaneous excitation and ionization have been calculated analytically for the lithium atom. It is found that the probability of excitation of an electron in a closed shell is in general very small compared with those for the excitation of the valence electron, but is of the same order of magnitude as those for the simultaneous excitation and ionization. The experiments of Lee on electron collision and the observation of Edlén and Tyren on the satellite lines in atomic spectra are briefly discussed on the basis of these calculations.

INTRODUCTION

The recent experiments of Lee on the energy loss of electrons on inelastic collisions with the atoms of Hg, Cd and Zn on the one hand¹, and the observations of Edlén and Tyren on the appearance of satellite lines on the long wave length side of the lines $1s\ ^2S-2p\ ^2P$, $1s\ ^2S-1s2p\ ^1P$ in the spectra of the ions of the light atoms on the other² call for the excitation of electrons in an inner closed shell for their explanation. While their explanations are most probably correct, it is nevertheless desirable to have some theoretical estimates of the

(1) Lee, *Proc. Roy. Soc. A* 173, 569, (1939)

(2) B. Edlén and F. Tyren, *Nature* 134, 940, (1939)

probabilities of some typical processes involving the excitation of an electron from a closed shell and the simultaneous ionization and excitation of an electron from a closed shell. It appears that in the literature calculations have been made only for the lightest of atoms, namely, H and He. This is obviously due to the lack of accurate wave functions for the other atoms. With the wave functions for the 2- and 3-electron spectra of the atoms from Li to F now available from the variational method³, it should be possible to calculate the quantum mechanical cross-sections of such processes analytically without undue labor. For simplicity in the calculations we shall choose the Li atom which is the simplest atom having a valence electron outside a closed shell. It is believed that these calculations will indicate the order of magnitude of the probabilities for the various processes in heavier atoms for which accurate calculations cannot be easily carried out, at least analytically.

CALCULATIONS

We shall employ Born's approximation in which the wave functions for the incident, scattered and the ejected electrons are represented by plane waves. For fast electrons this approximation will be valid. A comparison of the calculated cross-sections for the ionization of He obtained by Wetzel⁴ by this method with those obtained by the use of a better wave function⁵ shows that Born's approximation is justified in the following calculations when the energies of the electrons are not too low.

The total cross-section for the excitation of an atom from the state i to the state f by an electron is given by

(3) T. Y. Wu and S. T. Shen, the preceding paper.

(4) W. W. Wetzel, *Phys. Rev.* 44 25, (1933)

(5) Mott and Massey, *Theory of Atomic Collisions*, P. 180, (1933)

$$Q(k) = \frac{4\pi^2 m^2}{h^4} \frac{k'}{k} \int |U|^2 d\Omega'$$

where

$$U = \int \psi_i e^{i\vec{k} \cdot \vec{r}} V \psi_f^* e^{-i\vec{k}' \cdot \vec{r}} d\tau. \quad (1)$$

Here V is the interaction potential between the incident electron and the atomic electrons, ψ_i, ψ_f are the wave functions of the initial and the final states of the atom, $\vec{k} (h/2\pi)$ and $\vec{k}' (h/2\pi)$ are the momentum vectors of the incident and the scattered electron respectively. The integration in U is taken over the coordinates of all the electrons while the integration over Ω' is taken over all directions for the scattered electron.

For the simultaneous ionization and excitation of the atom, the total cross-section is given by

$$Q(k) = \frac{m^2}{2\pi h} \frac{k'}{k} \int |U|^2 dk'' d\Omega' d\Omega'',$$

where

$$U = \int \psi_i e^{i\vec{k} \cdot \vec{r}_1} V \psi_f^* e^{-i\vec{k}' \cdot \vec{r}_1} e^{-i\vec{k}'' \cdot \vec{r}_2} d\tau. \quad (2)$$

Here $\vec{k}'' (h/2\pi)$ is the momentum vector of the ejected electron. The integration in U is again taken over the coordinates of all the electrons, $d\Omega', d\Omega''$ are the elements of the solid angles into which the scattered and the ejected electron, respectively, are directed. By properly choosing the polar axes, the integration over the azimuths φ', φ'' about them can be immediately carried out, giving a factor of 2π each.

We define the momentum vectors

$$\vec{q} = \vec{k} - \vec{k}', \quad \vec{l} = \vec{q} - \vec{k}'' \quad (3)$$

so that

$$q^2 = k^2 + k'^2 - 2kk' \cos \theta, \quad l^2 = q^2 + k''^2 - 2qk'' \cos \theta''$$

where θ' is the angle of scattering, and θ'' is the angle between \vec{q} and \vec{k}' . From the energy principle, we have, corresponding to (1),

$$\frac{h^2}{8\pi^2 m} (k^2 - k'^2) = E_f - E_i$$

and to (2),

$$\frac{h^2}{8\pi^2 m} (k^2 - k'^2 - k''^2) = E_f - E_i, \quad (4)$$

where E_i and E_f are the energies of the initial and the final state of the atom or ion.

In the following calculations, the atomic wave functions are antisymmetric combinations of single electron wave functions which are orthogonal among themselves. The normalized single electron wave functions are the following:

$$\begin{aligned} 1s: \psi_1 &= \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r} \\ 2s: \psi_2 &= \left(\frac{3\beta^5}{\pi(\alpha^2 - \alpha\beta + \beta^2)}\right)^{\frac{1}{2}} \left(1 - \frac{\alpha + \beta}{3} r\right) e^{-\beta r} \\ 2p: \psi_3 &= \left(\frac{\gamma^5}{\pi}\right)^{\frac{1}{2}} r e^{-\gamma r} P_1^0(\cos \theta), \\ 3p: \psi_4 &= \left(\frac{10\epsilon^7}{\pi(3\epsilon^2 - 4\epsilon\gamma + 3\gamma^2)}\right)^{\frac{1}{2}} \left(1 + \frac{\epsilon + \gamma}{5} r\right) e^{-\epsilon r} P_1^0(\cos \theta), \\ 3d: \psi_5 &= \left(\frac{\delta^7}{18\pi}\right)^{\frac{1}{2}} r^2 e^{-\delta r} P_2^0(\cos \theta), \end{aligned} \quad (5)$$

where the parameters $\alpha, \beta, \gamma, \delta, \epsilon$ are determined for each state by the variational method. It is convenient in the following to express the cross-sections $Q(V)$ as functions of the energy of the incident electron expressed in volts. Accordingly we make the substitution

$$k^2 = CV, \quad k'^2 = CV', \quad k''^2 = CV'', \quad \alpha^2 = Ca^2, \quad \beta^2 = Cb^2, \quad \gamma^2 = Cc^2, \quad \delta^2 = Cd^2, \quad \epsilon^2 = Ce^2, \quad C = 8\pi^2 me/300h^2 = 0.265 \times 10^{16}. \quad (6)$$

All quantities referring to the final state have the subscripts 1.

(1) The excitation $1s^2 2s^2 {}^2S-1s^2 2p {}^2P$.

The $1s$ wave functions in the states $1s^2 2s {}^2S$ and $1s^2 2p {}^2P$ are practically identical. On introducing the momentum variable q in (3), setting $q^2 = x$, and making use of (6), we obtain from (1).

$$Q(V) = \frac{16^4 \pi^5 m^2 e^4 b^5 c_1^5}{3 \hbar^4 (a^2 - ab + b^2) C^2} \cdot \frac{1}{V} \int_{\lambda - \mu}^{\lambda + \mu} \frac{[(b+c)^2(5a+2b-3c_1) - (a+4b+3c_1)x]}{x[(b+c_1)^2 + x]^3} dx, \quad (7)$$

where

$$\lambda = V + V', \quad \mu = 2(VV')^{\frac{1}{2}}. \quad (8)$$

(7) can be integrated analytically.

For Li, the constants are as follows:

$$1s^2 2s {}^2S: \quad \alpha = 2.694/r_0, \quad \beta = 0.764/r_0, \quad E_i = -14.956 R\hbar c$$

$$1s^2 2p {}^2P: \quad \alpha_1 = 2.694/r_0, \quad \gamma_1 = 0.525/r_0, \quad E_f = -14.829 R\hbar c$$

where r_0 is the first Bohr radius of hydrogen. The total cross-sections are given in Table 1 and Fig. 1.

(2) The excitation $1s^2 2s {}^2S-1s^2 3p {}^2P$

For this process, one obtains

$$Q(V) = \frac{30.16^4 \pi^5 m^2 e^4 b^5 c_1^7}{\hbar^4 c^2 (a^2 - ab - b^2) (3\epsilon_1^2 - 4\epsilon_1 c_1 + 3c_1^2)} \cdot \frac{1}{V} \int_{\lambda - \mu}^{\lambda + \mu} \frac{[\xi + \eta x + \zeta x^2]^2}{x[(b+\epsilon_1)^2 + x]^{10}} dx, \quad (9)$$

where

$$\xi = (b+\epsilon_1)^3 \left[(b+\epsilon_1)^2 - 5 \left(\frac{a+b}{3} + \frac{c_1+\epsilon_1}{5} \right) (b+\epsilon_1) - 2(a+b)(c_1+\epsilon_1) \right],$$

$$\eta = 2(b+\epsilon_1) \left[(b+\epsilon_1)^2 - 2(b+\epsilon_1) \left(\frac{a+b}{3} + \frac{c_1+\epsilon_1}{5} \right) - \frac{3}{5}(a+b)(c_1+\epsilon_1) \right],$$

$$\zeta = b+\epsilon_1 + (a+b)/3 + (c_1+\epsilon_1)/5.$$

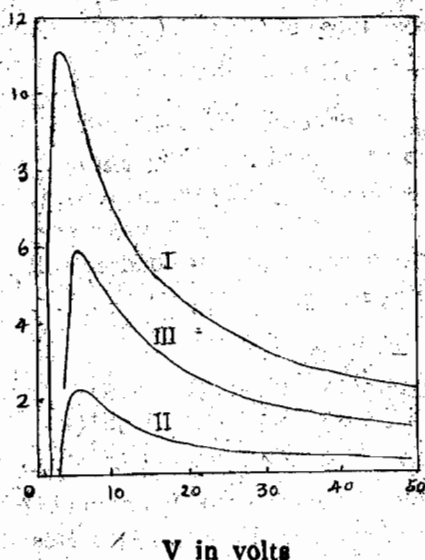


Fig. 1. (I) $Q(V)$ for $1s^2 2s^2 S-1s^2 2p^2 P$ in 10^{-15} cm^2
 (II) $Q(V)$ for $1s^2 2s^2 S-1s^2 3p^2 P$ in 10^{-16} cm^2
 (III) $Q(V)$ for $1s^2 2s^2 S-1s^2 3d^2 D$ in 10^{-17} cm^2

For Li, $\alpha_1 = 2.69/r_0$ for $1s^2 3p^2 P$. The integration can be carried out analytically and the total cross-sections are given in Table 1 and Fig. 1. They are approximately 50 times smaller than those for the excitation to $1s^2 2p^2 P$.

(3) The excitation $1s^2 2s^2 S-1s^2 3d^2 D$.

For this process one obtains

$$Q(V) = \frac{16^5 \pi^5 m^2 e^4 b^5 d_1^7}{6 h^4 (a^2 - ab + b^2) C^2 V} \int_{\lambda - \mu}^{\lambda + \mu} \frac{[(b + d_1)^2 (3d - 4b - 7a) + (a + 4b + 3d_1)^2 x]^2}{[(b + d_1)^2 + x]^8} dx. \quad (10)$$

For $1s^2 3d^2 D$ of Li, $\delta = 0.3359/r_0$. This integral can also be evalu-

ated analytically. The result is given in Table 1 and Fig. 1. The integral in (10) differs from those in (7) and (9) chiefly in the absence of the main logarithmic term of the type $\ln \left(\frac{\lambda + \mu}{\lambda - \mu} \frac{b + c_1 + \lambda - \mu}{b + c_1 + \lambda + \mu} \right)$ which is present in the latter two. This is quite a general result that the probability of excitation of optically forbidden transitions decreases more rapidly with increasing exciting energy than that for the excitation of allowed transitions. This difference will manifest itself for electron energies exceeding a few hundred volts.

(4) The excitation $1s^2 2s^2 S - 1s2s2p^2 P, ^2P$.

The wave function Ψ_i for $1s^2 2s^2 S$ is

$$\Psi_i = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_1 S^+(1) & \psi_1 S^-(1) & \psi_2 S^+(1) \\ \psi_1 S^+(2) & \psi_1 S^-(2) & \psi_2 S^+(2) \\ \psi_1 S^+(3) & \psi_1 S^-(3) & \psi_2 S^+(3) \end{vmatrix}$$

where the $S^+(1)$ denotes the spin wave function of electron 1 with $m_s = +\frac{1}{2}$, etc. The wave functions of the two 2P states of $1s2s2p$ are given by

$$\Psi_+ = \frac{1}{\sqrt{1+f^2+g^2}} (\Psi_1 + f\Psi_2 + g\Psi_3)$$

$$\Psi_- = \frac{1}{\sqrt{1+s^2+t^2}} (\Psi_1 + s\Psi_2 + t\Psi_3)$$

where Ψ_1, Ψ_2, Ψ_3 are antisymmetric wave functions built up of the single electron wave functions, similar to Ψ_i above, and f, g, s, t are functions of the exchange integrals for the $1s, 2s, 2p$ electrons. It can be shown that the integral U for the excitation to the 2P with the wave function Ψ_+ is given by

$$|U| = \frac{4\pi e^2 (g-1) N}{q^2 \sqrt{1+f^2+g^2}} \int \Psi_1 \phi_1 d\tau_1 \int \Psi_2 \phi_2 d\tau_2 \int e^{iq \cdot r} d\tau \quad (11)$$

where $N = \int \psi_1 \phi_1 d\tau_1 \int \psi_2 \phi_2 d\tau_2$. ψ_1, ϕ_1 are the normalized wave

functions for the 1s electron in $1s^2 2s^2 S$ and $1s2s2p^2 P$ respectively, and ψ_2, ϕ_2 , are their respective 2s wave functions. The cross-section $Q(V)$ is given by

$$Q(V) = \frac{N^2 \cdot 16^4 \pi^5 m^2 e^4 a^3 c_1^5 (a+c_1)^2 (g-1)^2}{h^4 c^2 (1+f^2+g^2)} \cdot \frac{1}{V} \int_{\lambda-\mu}^{\lambda+\mu} \frac{dx}{x[(a+c_1)^2+x]^5} \quad (11a)$$

The last integral can be evaluated analytically. On writing $p=(a+c_1)^2$, and $p\omega=(p+\lambda)^2-\mu^2$, we have

$$Q(V) = \frac{N^2 16^4 \pi^5 m^2 e^4 a^3 c_1^5 (g-1)^2}{h^4 c^2 (1+f^2+g^2)^2 p^5} \cdot \frac{1}{V} \left\{ \ln \left(\frac{\lambda+\mu}{\lambda-\mu} \frac{p+\lambda-\mu}{p+\lambda+\mu} \right) - \frac{2\mu}{\omega} \left[1 + \frac{p+\lambda}{\omega} + \frac{3(p+\lambda)^2 + \mu^2}{3\omega^2} + \frac{(p+\lambda)((p+\lambda)^2 + \mu^2)}{\omega^3} \right] + \frac{5(p+\lambda)^4 + 10(p+\lambda)^2 \mu^2 + \mu^4}{5\omega^4} \right\} \quad (11b)$$

The expression for the cross-section for the excitation to the other 2P state with the wave function ψ_2 is entirely similar, and is obtained by replacing the factor $(g-1)^2/(1+f^2+g^2)$ in (11b) by $(t-1)^2/(1+s^2+t^2)$ and employing the appropriate constants for this 2P states. The presence of the logarithmic term is again characteristic of excitations of optically allowed transitions.

The constants for the $1s2s2p^2 P, ^2P$ states of Li are as follows:

$$E(^2P) = -10.3785 Rhc, \quad f = -1.61, \quad g = 0.122,$$

$$E(^2P) = -10.5397 Rhc, \quad s = 0.721, \quad t = -1.72,$$

$$\alpha_1 = 3.00/r_0, \quad \beta_1 = 1.11/r_0, \quad \gamma_1 = 0.877/r_0.$$

The total cross-sections are given in Table 2 and Fig. 2. It is seen that these cross sections are approximately 1000 times smaller than those for the excitation of the valence electron $1s^2 2s^2 S - 1s^2 2p^2 P$ for exciting electrons of 800 volts.

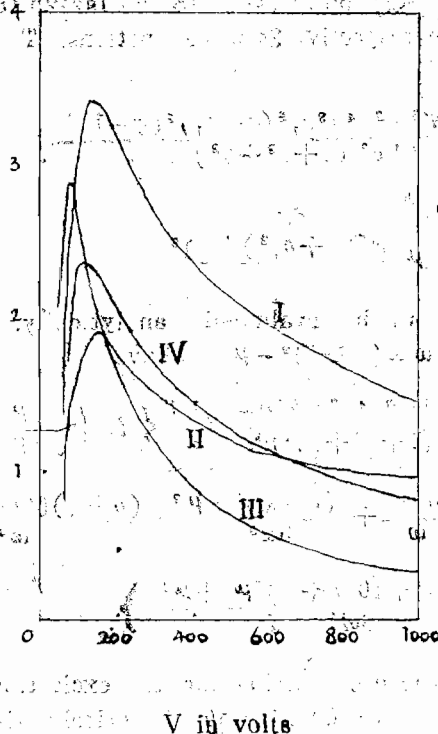


Fig. 2 (I) $Q(V)$ for $1s^2 2s^2 2S-1s 2s^2 p^2 P$ in 10^{-16} cm^2
 (II) $Q(V)$ for $1s^2 2s^2 2S-1s 2s^2 p^2 P$ in 10^{-18} cm^2
 (III) $Q(V)$ for $1s^2 2s^2 2S-1s 2s^2 2S$ in 10^{-19} cm^2
 (IV) $Q(V)$ for $1s^2 2s^2 2S-1s 2p^2 3D$ in 10^{-20} cm^2

(5) The excitation $1s^2 2s^2 2S-1s 2s^2 2S$.

The cross-section for the excitation of the $1s$ electron in the closed shell to the $2s$ shell is given approximately by (1) (2) (3)

$$Q(k) \sim 2 \frac{16\pi^2 m^2 e^4 \alpha^2 B_1^2 (\alpha + \beta_1)^2 K'}{5 \hbar^2 (\alpha^2 + \beta_1^2 + 4\beta_1^2) K} \int_0^\pi \frac{1}{((\alpha + \beta_1)^2 + q^2)^6} \sin^2 \theta' d\theta',$$

$$\text{or } Q(V) = N \frac{E}{v} \int_{\lambda - \mu}^{\lambda + \mu} \frac{1}{[p + x]^6} = \frac{N}{5V} \left[\frac{1}{(p + \lambda - \mu)^5} - \frac{1}{(p + \lambda + \mu)^5} \right] \quad (12)$$

where

$$N = \int \psi_{1s} \phi_{1s} d\tau \int \psi_{2s} \phi_{2s} d\tau = \frac{16^4 \pi^5 m^2 e^4 a^3 b_1^5 (a_1 + b_1)^2}{3 h^4 (a_1^2 - a_1 b_1 + b_1^2) c^2}, \quad p = (a_1 + b_1)^2$$

when we assume orthogonality between the $1s$ wave function of $1s^2 2s$ and the $2s$ wave function of $1s 2s^2$, i. e., $\alpha = \alpha_1$.

The constants for $1s 2s^2 \ ^3S$ of Li are the following:

$$E = -10.685 \text{ Rhc}, \quad \alpha_1 = 3.0268/r_0, \quad \beta_1 = 1.074/r_0.$$

The cross-sections calculated are given in Table 2 and Fig. 2. For high energies, the $Q(V)$ decreases as V , the energy of the exciting electron.

(6) The excitation $1s^2 2p \ ^3P - 1s 2p^2 \ ^3D, \ ^3P, \ ^3S$.

The probabilities of the excitations from $1s^2 2p \ ^3P$ to $1s 2p^2 \ ^3D, \ ^3P, \ ^3S$ can be immediately obtained from (11). The cross-section for the excitation to the 3D state is given by

$$Q(V) = \frac{N^2 16^4 \pi^5 m^2 e^4 a^3 c_1^5}{h^4 c^2 p^5} \frac{1}{v} \{ \ln \dots \} \quad (13)$$

where

$$N = \int \psi_1 \phi_1 d\tau \int \psi_2 \phi_2 d\tau = \frac{4 \cdot 8^2 (\alpha^2 \alpha_1^3 \gamma^5 \gamma_1^5)^2}{(\alpha_1 + \alpha_1)^3 (\gamma_1 + \gamma_1)^5},$$

α_1, γ_1 referring to the $1s 2p^2 \ ^3D$ state and the expression in the brackets being identical with that in (11b). The values of $Q(V)$ in (13) calculate with the constants for $1s 2p^2 \ ^3D$ of Li

$$E(1s 2p^2 \ ^3D) = -10.350 \text{ Rhc}, \quad \alpha_1 = 2.975/r_0, \quad \gamma_1 = 0.892/r_0.$$

are given in Table 2 and Fig. 2. These are about 10 times smaller than those for the excitation $1s^2 2s \ ^3S - 1s 2s 2p \ ^3P$. The cross-sections for excitation to the 3S states differ from (13) by numerical factors whose order of magnitude is not very different from one.

(7) The excitation $1s^2 2s \ ^3S - 1s 2s 3p \ ^3P, \ ^3P$.

The calculation of the cross-sections for these processes is parallel to that for the excitation to $1s 2s 2p \ ^3P$, except that now the integral

in U is replaced by $\int \psi_{1s} \phi_{2p} e^{iq \cdot r} d\tau$. Without going through the calculations, one can roughly estimate the probabilities to be smaller than those for $1s2s2p \rightarrow 1s2s3d$ by a factor of 20 or so. The excitation to such states as $1s2s3s$, $1s2s3d$ will have even smaller probabilities.

(8) The double excitation $1s^2 2s^2 S \rightarrow 1s2p^2 \rightarrow D, {}^3P, {}^1S$.

The probabilities of this and other double excitation processes can be shown to be zero in the first approximation, since the integral $U = 0$ on account of the orthogonality of the single electron wave functions in the initial approximation. To obtain the cross-sections it is necessary to go to the next approximation in which the perturbations of the atomic electron wave functions by their interactions with the incident electron are taken into account. In general one may expect these cross-sections to be small compared with those for the single excitation processes. An example in point is furnished by the calculations of Massey and Mohr on the double excitations of helium⁶. The probabilities are in general of the order of one hundredth those for the single excitations.

(9) The simultaneous ionization and excitation $1s^2 2s^2 S \rightarrow 1s2p \rightarrow P, {}^1P$.

We may consider two distinct processes which can take place under the condition that the spins of the atomic electrons remain unchanged by the excitation: (a) one of the $1s$ electrons is excited to $2p$ and the $2s$ electron is ejected, and (b) one of the $1s$ electrons is ejected and the $2s$ electron is excited to $2p$. The process (a) gives only the 1P of $1s2p$, while (b) gives either 1P or 3P .

The integration over the directions of the scattered and the ejected electrons in equation (2) can be performed by choosing the direction of k as the polar axis for θ' and the direction of q as that for θ'' . The integrations over φ' and φ'' of the scattered and the

(6) Massey and Mohr, *Proc. Camb. Soc.* 31, 694, (1935).

ejected electrons then give simply a factor of 2π each. On introducing the momentum variables q and l in (3), the integration over θ'' may be replaced by an integration over l from $q-k''$ to $q+k''$. The result is, for (a),

$$Q(V) = \frac{4 \cdot 16^5 \pi^4 m^2 e^4 a^6 a_1^3 b^5 c_1^5 (a+c_1)^2}{3h^4 c^2 (a+a_1)^6 (a^2-ab+b^2)} \cdot \frac{1}{V} \int_0^{V''_{max}} \frac{(3ab^2 - (a+4b)V'')^2 \sqrt{V''} dV''}{[b^2 + V'']^3 b} \int_{\lambda-\mu}^{\lambda+\mu} \frac{dx}{x[(a+c_1)^2+x]^6} \quad (14a)$$

and for (b),

$$Q(V) = \frac{4 \cdot 16^4 \pi^4 m^2 e^4 a^5 a_1^3 b^5 c_1^6}{3h^4 c^2 (a+a_1)^6 (a^2-ab+b^2)} \cdot \frac{1}{V} \int_0^{V''_{max}} \frac{\sqrt{V''} dV''}{(a^2+V'')^4} \int_{\lambda-\mu}^{\lambda+\mu} \frac{[(b+c_1)^2(5a+2b-3c_1) - (a+4b+c_1)x]^2}{x[(b+c_1)^2+x]^8} dx \quad (14b)$$

where $\lambda = V_i + V_f = 2V - (V_f - V_i) - V''$; $\mu = 3V^{\frac{1}{2}} [V - (V_f - V_i) - V'']^{\frac{1}{2}}$; $V''_{max} = V - (V_f - V_i)$; V_i, V_f, V'' being the energy of the incident, the scattered, and the ejected electron respectively; V_i, V_f being the energy of the atomic system in the initial and the final state, respectively, in volts. The integrations over x can again be carried out analytically, but the integrations over the energy V'' of the ejected electron are more conveniently performed graphically. The total cross-sections obtained with the following constants for Li

$$\begin{aligned} 1s2p \ ^3P: & \quad E = -10.055 Rhc; \quad \alpha_1 = 2.98/r_0; \quad \gamma_1 = 1.075/r_0; \\ 1s2p \ ^1P: & \quad E = -9.987 Rhc; \quad \alpha_1 = 3.00/r_0; \quad \gamma_1 = 0.98/r_0. \end{aligned}$$

are given in Table 2 and Fig. 3.

The differential cross-sections $Q(V, V'')$ defined by the equation

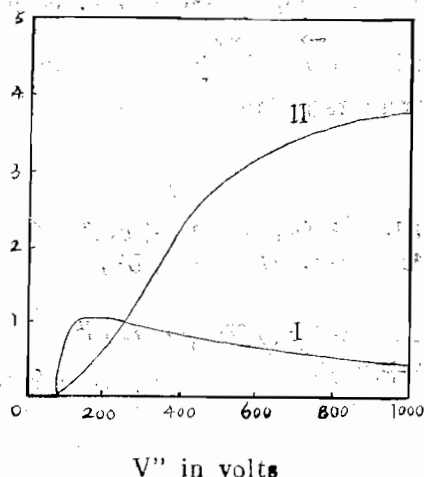


Fig. 3. (I) $Q(V)$ for $1s^2 2s^2 2s-1s2p$ 1P in 10^{-18} cm^2
 (II) $Q(V)$ for $1s^2 2s^2 2s-1s2p$ 3P in 10^{-18} cm^2

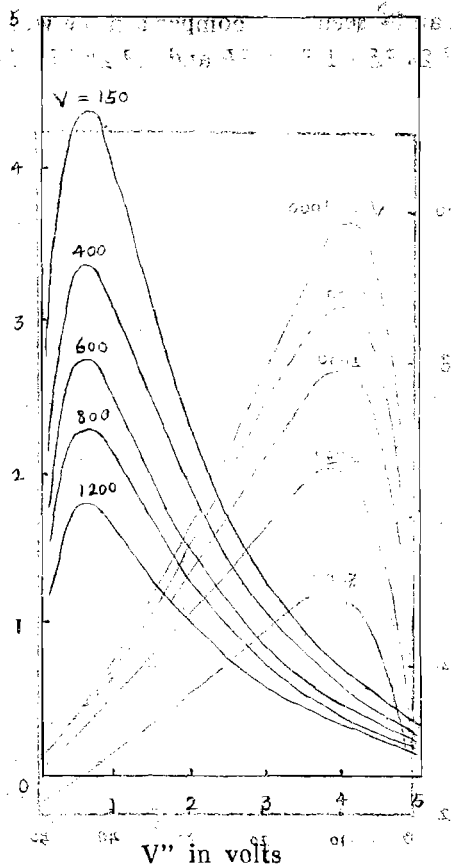
$$Q(V) = \int_0^{V''_{\max}} Q(V, V'') dV''$$

are given in Figs. 4 and 5. It is seen that $Q(V, V'')$ is large only for small energies of the ejected electron V'' , that is, the contribution to $Q(V)$ comes mostly from collisions in which the scattered electron retains practically all of the energy balance $V - (V_f - I_i)$. This is particularly so for the process (a).

(10) The simultaneous ionization and excitation $1s^2 2s^2 S-1s3p^3P$, 1P .

The probabilities for these processes can be obtained in an entirely similar manner. Corresponding to (14a) and (14b) respectively for the excitation to $1s2p$, one replaces the integrals in x in (14a) and (14b), respectively by

$$\int_{\lambda-\mu}^{\lambda+\mu} \frac{[5(a+\varepsilon_1)^2(a+2\varepsilon_1+c_1)-(5a+4\varepsilon_1+c_1)x]^2}{x[(a+\varepsilon_1)^2+x]^8} dx, \quad (15a)$$


 Fig. 4 $1s^2 2s^2 S-1s 2p^1 P$

$$\int_{\lambda-\mu}^{\lambda+\mu} \frac{[\xi + \eta x + \zeta x^2]^2}{x[(b + \epsilon_1)^2 + x^2]^2} dx \quad (15b)$$

where ξ , η , ζ are given in (9); and makes the appropriate changes in the constant factors. The values of these cross-sections can be estimated to be approximately 1/50 of those in (14a) and (14b); on a consideration of the results in (7) and (9). For excitation to such

states as $1s3d\ ^3D$, 1D , the cross-sections are again smaller by another factor of 10, as can be seen on a comparison between the values for the processes $1s^2\ 2s\ ^2S-1s^2\ 2p\ ^2P$ and $1s^2\ 2s\ ^2S-1s^2\ 3d\ ^2D$.

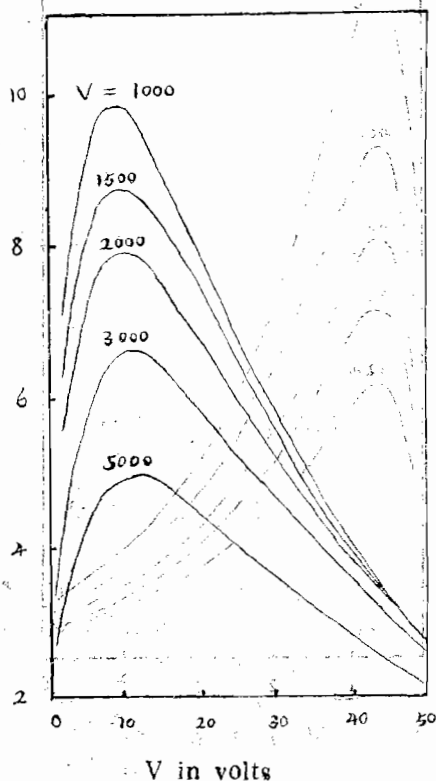


Fig. 5 $1s^2\ 2s\ ^2S-1s\ 2p\ ^2P$

(11) The double ionization $1s^2\ 2s\ ^2S-1s\ ^2S$:

The cross-sections for the double ionization process can be calculated in a similar manner, but on account of the extra degree of freedom for the distribution of the energy among the scattered and the two ejected electrons, the actual computation will be extremely lengthy. Perhaps the cross sections can be estimated to be slightly

Table 1.

V in volts	2.5	3.6	4.0	5.0	10	15	20	30	40	50	75	100	300	800
$1s^2 2s^2 S - 1s^2 2p^2 P$	10.2	11.1	10.9	10.2	7.1	5.36	4.40	3.19	2.58	2.15	1.67	1.16	0.36	$0.14 \cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 3p^2 P$			1.84	2.25	1.58	0.99	0.74	0.51	0.44	0.37				$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 3d^2 D$			4.01	5.79	4.51	3.20	2.57	1.79	1.44	1.10				$\cdot 10^{-18}$

Table 2.

V in volts	70	80	100	150	200	300	400	600	800	1000	1500	3000
$1s^2 2s^2 S - 1s^2 2s^2 p^2 P$	1.35	2.30	2.98	3.40	3.15	2.72	2.37	1.95	1.61		1.01	$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 2s^2 p^2 P$	7.50	13.3	16.5	18.9	17.5	15.1	13.2	10.8	8.94		5.60	$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 2s^2 \ ^2S$	2.62	2.36	2.70	2.03	1.62	1.13	0.85	0.57	0.43		0.21	$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 2p^2 \ ^2D$		2.33	2.25	2.03	1.72	1.38	1.10	0.90	0.76			$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 2p \ (a)$	0.60	0.92	1.07	1.06	0.95	0.85	0.68	0.59	0.50	0.33		$\cdot 10^{-18}$
$1s^2 2s^2 S - 1s^2 2p \ (b)$			0.62	1.40	2.30	3.20	3.60	3.72	3.70	3.23		$\cdot 10^{-18}$

greater than, but of the same general order of magnitude as, those for the simultaneous ionization and excitation $1s^2 2s^2 S - 1s 2p^2 P, ^1P$ by analogy with the relative values for the excitation and ionization in the cases of H and He .

DISCUSSIONS

From these calculations, it is seen that the probabilities of excitation of an electron in an inner closed shell of an atom are in general very small compared with those for the excitation of a valence electron. The calculated cross-sections for the processes $1s^2 2s^2 S - 1s^2 2p^2 P, 1s^2 2s^2 S - 1s^2 3p^2 P, 1s^2 2s^2 S - 1s^2 3d^2 D$ are probably too large for the low energy range on account of the failure of Born's approximation employed, and the error introduced by this approximation is most serious for the two optically allowed transitions⁷. For the other processes here calculated, Born's approximation is presumably valid for the energy range $E > 200$ volts. An interesting result is that the probabilities of simultaneous excitation of an electron from a closed shell and ionization by electrons of a few hundred volts are somewhat greater than, but of the same general order of magnitude as, those for the excitation of a closed shell electron alone.

In a note⁸ it was shown that Edlen and Tyren's explanation of the satellite lines on the long wave length side of the lines $1s^2 ^1S - 1s 2p ^1P$ of CV as due to such transitions in CIV as $1s^2 2s^2 S - 1s 2s 2p^2 P, 1s^2 2p^2 P - 1s 2p^2 ^2S, ^2P, ^2D$, etc., is compatible with the theoretical positions of these latter transitions calculated by means of the variational method, and with their expected intensities on consideration of (i) the relative probabilities of the production of the initial states involved in these transitions, and (ii) the relative values of the transition probabilities. For Li , the production of the state $1s 2p ^1P$ is the

(7) Mott and Massey *loc. cit.* pp. 197-8.

(8) T. Y. Wu, *Phys. Rev.* 58, 1114; (1940). The cross-sections given for the excitation of a closed shell electron and the simultaneous excitation and ionization are too large by a numerical factor.

process of simultaneous ionization and excitation of a closed shell electron, the contribution from the two-stage process $1s^2 2s^2 S - 1s^2 1S$ followed by $1s^2 1S - 1s 2p^1 P$ being neglected, while for the emission of the satellite line $1s^2 2s^2 S - 1s 2s 2p^2 P$, the process is the excitation of an $1s$ electron from the closed shell. For electron of 1500 volts, the ratio of the cross-sections of these processes is of the order 6-7, and this value increases for higher electron energies. From the variational wave functions, the ratio of the square of the electric moment for the transitions $1s^2 1S - 1s 2p^1 P$ and $1s^2 2s^2 S - 1s 2s 2p^2 P$ in LiII and LiI can be calculated to be 1.6. Thus on considerations of these two factors alone, one would expect the relative intensities of the main line $1s^2 1S - 1s 2p^1 P$ and the satellite line $1s^2 2s^2 S - 1s 2s 2p^2 P$ to be of the order 10 (and greater for higher energy electrons). For the satellite lines $1s^2 2p^2 P - 1s 2p^2 D, ^2P, ^2S$, the relative intensities would be of the order of 100 since the excitation cross-sections for the $1s 2p^2 D, ^2P, ^2S$ states are 10 times smaller than those for the excitation to $1s 2s 2p$. For other satellite lines, their intensities relative to the main line would be even smaller. These considerations are quite compatible with the observed low intensities of the satellite lines by Edlen and Tyren, although for CV and CIV, both the excitation cross-sections and the transition probabilities have different absolute values.

The relative cross-sections for the excitation of the valence and a closed shell electron here calculated also furnish corroborative evidence for the explanation of Lee¹. One would expect that in the magnetic spectrum of electrons scattered by an atom, one would find electrons whose energy losses correspond to the excitation of a closed-shell electron with a very much smaller intensity than those corresponding to the excitation of a valence electron. Similar calculation for such atoms as Hg, Cd, and Zn would be exceedingly lengthy and uncertain on account of the lack of accurate simple wave functions. On the other hand, a measurement of the relative intensities of the various lines in the magnetic spectrum of the scattered electrons under suitable conditions would furnish one with the experimental values of the cross-sections for the various processes of excitation.