On the Satellite Lines in Atomic Spectra and the Excitation of Electrons from Closed Shells

TA-YOU WU
Department of Physics, National University of Peking, Kun-ming, China
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RECENTLY Edlén and Tyrén have reported the observation of groups of weak lines on the long wave-length sides of the lines $1s^2\,{}^1S-1snp\,{}^1P$, $1s\,{}^2S-2p\,{}^2P$ in the spectra C V and C VI, respectively.[1] These "satellite" lines they ascribed to transitions in the preceding spectra with an additional external electron whose effect of screening on the energy of the transition giving rise to the main line is small. Thus the transition $1s^2\,{}^1S-1s2p\,{}^1P$ may have as satellites $1s^22s\,{}^2S-1s2s2p\,{}^2P$, ${}^2P$, $1s^22p\,{}^2P-1s2p^2\,{}^2P$, ${}^2D$, ${}^2S$, $1s^23s\,{}^2S-1s2p3s\,{}^2P$, ${}^2P$, etc. Dr. Edlén kindly sent to the writer a microphotometer tracing of the group of lines at 40.27A of C V $1s^2\,{}^1S-1s2p\,{}^1P$, together with their wave-lengths. The purpose of this note is to discuss these lines in greater detail.

With a view to examining the above explanation of the satellite lines, the writer has undertaken some calculations of the energy states involved in these transitions by the variational method of wave mechanics. The radial parts of the single electron wave functions employed for the $1s$, $2s$, $2p$ electrons are $\psi_{1s}=(4\alpha^3)^{\frac{1}{2}}e^{-\alpha r}$, $\psi_{2s}=(12\beta^5/\alpha^2-\alpha\beta+\beta^2)^{\frac{1}{2}}\cdot[1-\frac{1}{3}(\alpha+\beta)r]e^{-\beta r}$, $\psi_{2p}=(4\gamma^5/3)^{\frac{1}{2}}re^{-\gamma r}$, where α, β, γ are parameters to be determined by the variational process. The energy states calculated include the following: $2s2p\,{}^1P,{}^3P$; $2p^2\,{}^3P,{}^1D,{}^1S$; $1s2s^2\,{}^2S$; $1s2s2p\,{}^4P,{}^2P$, ${}^2P$; $1s2p^2\,{}^4P$, ${}^2P$, ${}^2D$, ${}^2S$; $2s^22p\,{}^2P$; $2s2p^2\,{}^4P$, ${}^2P$, ${}^2D$, ${}^2S$; $2p^3\,{}^4S$, ${}^2D$, ${}^2P$ in the 2 and 3 electron spectra of the atoms from Li to F. The accuracy of the calculated energies increases with the atomic number Z, and for carbon the error varies from $\frac{1}{2}$ to $\frac{1}{10}$ of a percent for the different configurations. The accuracy of the calculated positions of the various expected transitions is, however, somewhat better since the calculated energies always lie above the true values and in forming their differences the errors are partially compensated. Table I gives a comparison between the observed satellite lines and their tentative identifications based on the calculated energies. There are 5 very weak lines between 40.35 and 40.47A. They can be ascribed to such transitions as $1s^23s\,{}^2S-1s2p3s\,{}^2P$, $1s^23p\,{}^2P-1s2p3p\,{}^2P$, etc., which can be expected to lie closer to the main line since the interactions between a $3s$, $3p$, $3d$, etc., electron and the $1s$, $2p$ electrons are smaller.

Concerning the relative intensities of the main $1s^2\,{}^1S-1s2p\,{}^1P$ line and the transitions shown in Table I, one must consider the following factors: (1) the relative probabilities for the production of the initial states involved in these transitions, and (2) the relative values of the transition probabilities. In carbon, one needs for (1) to know the cross sections of the ionization and excitation processes $1s^22s^22p^2\rightarrow 1s2p$ and $1s^22s^22p^2\rightarrow 1s2s2p\,{}^2P$ by electron impact. Such calculations will be exceedingly lengthy on account of the large number of electrons ejected; and to obtain an estimate of their relative probabilities, the writer has made the calculations for Li, namely, for the process of simultaneous ionization and the excitation of an electron from a closed shell $1s^22s\,{}^2S\rightarrow 1s2p\,{}^1P$, and the process of excitation from a closed shell $1s^22s\,{}^2S\rightarrow 1s2s2p\,{}^2P$, ${}^2P$. The cross sections are obtained as functions of the energy of the colliding electron by using Born's approximation in which the ejected electron is represented by a plane wave. That this is justified is seen from the good agreement between the cross section for the ionization of helium calculated by this method and that calculated by a better approximation for the wave function of

TABLE I. *Suggested transitions and calculated wave-lengths for the satellite lines observed by Edlén on the long wave-length side $1s^2\,{}^1S-1s2p\,{}^1P$.*

OBS. λ (EDLÉN)	TRANSITION	CALC. λ
40.27A very strong		
40.73 weak	$1s^22s\,{}^2S-1s2s2p\,{}^2P$	40.7A
	$1s^22p\,{}^2P-1s2p^2\,{}^2S$	40.7
41.33 weak	$1s^22p\,{}^2P-1s2p^2\,{}^2D$	41.3
41.36 very weak	$1s^22p\,{}^2P-1s2p^2\,{}^2P$	41.4
41.54 weak	$1s^22s\,{}^2S-1s2s2p\,{}^2P$	41.5

[1] B. Edlén and F. Tyrén, Nature **143**, 940 (1939).

TABLE II. *Total cross sections for* Li *in* cm^2.

ELECTRON ENERGY (EV) →	5	10	30	50	70	100	200	400	800	
$1s^22s\ ^2S \rightarrow 1s^22p\ ^2P$	10.2	7.1	3.2	2.2	1.7	1.2	0.5	0.28	0.14	$\times 10^{-15}$
$1s^22s\ ^2S \rightarrow 1s^23p\ ^2P$	2.3	1.6	0.5	0.3						$\times 10^{-16}$
$1s^22s\ ^2S \rightarrow 1s^23d\ ^2D$	5.8	4.5	1.8	1.1						$\times 10^{-17}$
$1s^22s\ ^2S \rightarrow 1s2p\ ^1P$	—	—	—	—		3.1	3.8	3.1	2.5	$\times 10^{-17}$
$1s^22s\ ^2S \rightarrow 1s2s2p\ ^2P$	—	—	—	—	2.4	4.0	4.0	2.9	1.9	$\times 10^{-18}$
$1s^22s\ ^2S \rightarrow 1s2s2p\ ^2P$	—	—	—	—	1.9	3.1	3.1	2.3	1.5	$\times 10^{-18}$

the ejected electron.[2] Table II gives these cross sections together with those for the excitation of the valence electron for comparison.[3] An interesting result is that the cross section for the simultaneous ionization and excitation is roughly 10 times greater than that for excitation alone, for electron energy of about 400 volts. The ratio increases slowly with increasing energy of the electron.

The ratio of the transition probabilities of $1s^2\ ^1S-1s2p\ ^1P$ and $1s^22s\ ^2S-1s2s2p\ ^2P$ can be readily calculated with the variational wave functions for these states to be approximately 2.0. Thus in Li one would expect the ratio of the intensities of these two lines to be about 20 and 30 (for transitions from the $2\ ^2P$ states of $1s2s2p$) for excitation by electrons of a few hundred volts. These values would certainly be different for carbon; but their order of magnitude would perhaps be about the same.

[2] Compare W. W. Wetzel, Phys. Rev. **44**, 25 (1933) and N. E. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, 1934), p. 180.

[3] The relative probabilities for the excitation of the valence electron and for the excitation of an electron in an inner closed shell are important in connection with the experiments of Lee and Whiddington, Proc. Roy. Soc. **A173**, 569 (1939) in which are observed energy losses of electrons during inelastic collisions with Zn, Cd and Hg atoms, which correspond to the excitation of a d electron in the closed shell, on comparison with the results of H. Beutler on their absorption spectra.

In his private communication, Dr. Edlén tentatively assigned the 40.73A line to the forbidden transition $1s^2\ ^1S_0-1s2p\ ^3P_1$. Now the intensity of this transition in C V can be readily calculated with the variational wave functions already obtained. The integral of the spin-orbit interaction

$$\xi=\frac{R\alpha^2}{4}\int \psi_{2p}^*\frac{1}{r}\frac{dV}{dr}\psi_{2p}dr,$$

where α is the fine structure constant, R the Rydberg constant, and

$$V=-\frac{2Z}{r}+\frac{2}{r}\int_0^r|\psi_{1s}|^2r^2dr+2\int_r^\infty|\psi_{1s}|^2rdr,$$

is found to be 120 cm^{-1}, and the ratio of the f values for the allowed $1s^2\ ^1S_0-1s2p\ ^1P_1$ and the forbidden $1s^2\ ^1S_0-1s2p\ ^3P_1$ transitions comes out to be of the order 10^5.[4] While it is not possible to determine the relative intensities of the 40.27A and 40.73A lines from his microphotometer tracing because the former was greatly overexposed, it is certain that the 40.73A line is more intense than the other satellite lines and is hence too intense to be the singlet-triplet transition, although its position agrees with the theoretically calculated value. For this reason, the suggested assignment in Table I is given.

Details concerning the variational wave functions and energies and the quantum-mechanical cross sections of these and other processes will be given in a forthcoming paper in the *Chinese Journal of Physics*.

[4] G. W. King and J. H. Van Vleck, Phys. Rev. **56**, 464 (1939). For C V, it is immaterial whether the same or different $2p$ wave functions are employed for $1s2p\ ^1P$ and $1s2p\ ^3P$, since the spin-orbit interaction is very small, of the order of 1/100, compared with the singlet-triplet separation.