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Auto-Ionization in Doubly Excited Helium and the λ320.4 and λ357.5 Lines

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The probabilities of auto-ionization of the $2s^2\,{}^1S$, $2s2p\,{}^3P$, $2p^2\,{}^1D$, $3d^2\,{}^1G$ states of He are calculated with continuous wave functions which are obtained by numerical integration of the wave equation including the effect of exchange. The probabilities are 4×10^{14}, 5×10^{13}, 1×10^{14}, 4.9×10^{13} per second, respectively, for these states. On the basis of these calculations and the theoretical energies of the doubly excited states, the identification of the two lines λ320.4 and λ357.5 observed by Compton and Boyce and by Kruger is discussed. The former has been reasonably definitely ascribed to the transition $1s2p\,{}^3P-2p^2\,{}^3P$, the state $2p^2\,{}^3P$ not being subject to auto-ionization. The latter line cannot be satisfactorily accounted for with respect to both the position and the width of the line.

THERE have been many investigations on different aspects of the problem of doubly excited helium. Compton and Boyce,[1(a)] and later Kruger,[1(b)] observed in the extreme ultraviolet region two lines λ320.4 ($\nu=312{,}117$ cm^{-1}) and λ357.5 ($\nu=279{,}715$ cm^{-1}) which they ascribed to transitions from the doubly excited to the ordinary singly excited states of helium. Considerable interest on the energy states of doubly excited helium has been aroused by the suggestion, now abandoned, that the corona lines may be due to transitions among the doubly excited states of helium.[2] This has led to the theoretical calculation of these energy states by many authors.[3] Many attempts[4] have been made to observe the spectrum of doubly excited helium under experimental conditions that would have been most favorable for their excitation according to the theoretical excitation probabilities of these states by electron impact.[5] All these attempts have failed. Approximate calculations of the natural lifetime of the $2s3s\,{}^3S$ state as the result of auto-ionization have been carried out by Kreisler[6] and by Kiang, Ma, and Wu.[4] They found a natural lifetime of the order 10^{-14}–10^{-15} second.

It was pointed out by Kiang, Ma, and Wu that the failure to observe the spectrum of doubly excited helium may be understood on the basis of the theoretical great natural width of these states, since the spreading of a "line" over a spectral region of the order 100–1000 angstroms renders its observation exceedingly difficult. It was pointed out, however, by these authors that on accepting this theoretical probability of auto-ionization and on assuming the probabilities for

[1] (a) K. T. Compton, and Boyce, J. Frank. Inst. **205**, 497 (1928); (b) P. Gerald Kruger, Phys. Rev. **36**, 855 (1930).
[2] Rosenthal, Zeits. f. Astrophys. **1**, 115 (1932); Goudsmit and Wu, Astrophys. J. **80**, 154 (1934).
[3] F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 77 (1934); T. Y. Wu, *ibid.* **46**, 239 (1934); T. Y. Wu and S. T. Ma, *ibid.* **48**, 917 (1935); Chin, J. Chem. Soc. **4**, 344 (1936); W. Wilson, Phys. Rev. **48**, 536 (1935).
[4] Kiang, Ma, and Wu, Phys. Rev. **50**, 673 (1936); Chin. J. Phys. **2**, 117, (1936); F. Bundy, Phys. Rev. **52**, 452 (1937).
[5] Massey and Mohr, Proc. Camb. Phil. Soc. **31**, 604 (1935).
[6] Kreisler, Acta Physica Polonica **4**, 15 (1935).

TABLE I. Probabilities of auto-ionization.

State i	State f	Atomic wave functions	E_i in Rh	P in sec.$^{-1}$
$2s^2\,{}^1S$	$1sks\,{}^1S$	$\psi_{2s}\sim(1-\beta r)e^{-\beta r}$, $\beta=0.8469$	-1.4440	4×10^{14}
$2s2p\,{}^3P$	$1skp\,{}^3P$	$\psi_{2s}\sim(1-\beta r)e^{-\beta r}$, $\psi_{2p}\sim re^{-\gamma}$, $\beta=0.874$, $\gamma=0.862$	-1.5043	5×10^{13}
$2p^2\,{}^1D$	$1skd\,{}^1D$	$\psi_{2p}\sim re^{-\gamma r}$, $\gamma=0.815$	-1.328	1×10^{14}
$3d^2\,{}^1G$	$1skg\,{}^1G$	$\psi_{3d}\sim r^2e^{-\delta r}$, $\delta=0.659$	-0.868	4.2×10^{11}
$3d^2\,{}^1G$	$2skg\,{}^1G$	$\psi_{3d}\sim r^2e^{-\delta r}$, $\delta=0.659$	-0.868	4.9×10^{13}

the other doubly excited states to be of the same order of magnitude, one would expect a width of the order 1 angstrom for the lines λ320.4 and λ357.5 whereas the observed lines appear to be as sharp as the ordinary lines of He II. The situation is hence an unsatisfactory one. Either the calculated probability of auto-ionization for $2s3s^3S$ is grossly in error and the assumption that all the doubly excited states have about the same lifetime is not justified, or an explanation of the λ320.4 and λ357.5 lines must be sought elsewhere. The purpose of the present study is to make more calculations for a few doubly excited states of helium and to discuss the possible identification of the λ320.4 and λ357.5 lines.

PROBABILITY OF AUTO-IONIZATION

The general theory of the process of auto-ionization is a well-known one.[7] Let Ψ_i, Ψ_f be the wave functions of the initial (a doubly excited atom, for example) and the final (an ion plus an ejected electron) state. The probability of auto-ionization is then

$$P=\frac{4\pi^2}{h}|V_{if}|^2=\frac{4\pi^2}{h}\left|\int\Psi_i^*\left(\sum\frac{e^2}{r_{kj}}\right)\Psi_f d\tau\right|^2, \quad (1)$$

where the integration is taken over the coordinates of all the electrons. For a triplet or a singlet state, we have, respectively,

$$\Psi_i=\frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2)\mp\psi_b(1)\psi_a(2)), \quad (2)$$

$$\Psi_f=\frac{1}{\sqrt{2}}(\psi_c(1)\psi_k(2)\mp\psi_k(1)\psi_c(2)), \quad (3)$$

where ψ_a, ψ_b, ψ_c are the discrete atomic wave functions and ψ_k is the continuous wave function of the ejected electron. Kreisler employed for ψ_k the continuous wave function of hydrogen, thereby approximating the atomic field due to the nucleus and an electron by that of a bare nucleus of charge 1; whereas Kiang, Ma, and Wu employed, for $2s3s^3S$,

$$\psi_k=\frac{1}{h}\left(\frac{8\pi m}{k}\right)^{\frac{1}{2}}\frac{1}{r}\cos(kr-\alpha). \quad (4)$$

This amounts to employing for ψ_k its asymptotic form for large r which does not hold for small r, and with a phase α so chosen that (4) is not valid for large r. Both calculations neglected the effect of exchange on the solution ψ_k of the wave equation. As the value of the matrix element V_{if} in (1) depends rather strongly on the overlap of the various wave functions, it is thought that the insufficiently accurate ψ_k of the earlier calculations may cause considerable error in the probability of auto-ionization. In the present calculation we shall seek a solution ψ_k, taking into account the effect of exchange and the actual atomic field.

The function Ψ_f is the solution of the Schrödinger equation

$$\left[\Delta_1+\Delta_2+E+\frac{2Z}{r_1}+\frac{2Z}{r_2}-\frac{2}{r_{12}}\right]\Psi_f=0, \quad (5)$$

and ψ_c is the solution of

$$\left[\Delta+E_c+\frac{2Z}{r}\right]\psi_c=0, \quad (6)$$

where energy is in units of the ionization energy of hydrogen and distance in units of the first Bohr radius of hydrogen. Substitution of (3) into (5) and making use of (6) give the integro-differential equation[8]

$$[\Delta+k^2-V(r)](r\psi_{kl})=\mp U(r)(r\psi_c)\begin{cases}\text{triplet}\\ \text{singlet}\end{cases} \quad (7)$$

[7] Condon and Shortley, *Theory of Atomic Spectra* (1935), p. 369.

[8] Cf. P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

in which

$$V(r_2)=2\int\left(\frac{1}{r_{12}}-\frac{Z}{r_2}\right)\psi_c^2(r_1)d\tau_1 \qquad (8)$$

and

$$U(r_2)=2\int\frac{1}{r_{12}}\psi_c(r_1)\psi_{kl}(r_1)d\tau_1 - (k^2-E_c)\int\psi_c(r)\psi_{kl}(r)d\tau. \qquad (9)$$

k^2 is the kinetic energy of the ejected electron so that $E=E_c+k^2$. V is the energy of the ejected electron in the atomic field and $U(r)$ represents the effect of exchange. The subscript l is the azimuthal quantum number of the ejected electron. For a given initial state $\Psi_i(n_a, l_a; n_b, l_b)$ and a given $\psi_c(n_c, l_c)$, the value of l is determined by the following rule for the non-vanishment of the matrix element V_{if} and hence for the presence of auto-ionization: The states i and f must (*i*) be of the same parity, (*ii*) have the same value of J, and in the case of L, S coupling, (*iii*) have the same values of L and S. To obtain the solution of (7), since the effect of exchange is expected to be small, we shall, as an initial approximation, obtain the solution of the homogeneous equation

$$[\Delta+k^2-V(r)](r\psi_{kl})=0 \qquad (10)$$

by numerical integration. The solution $\overset{0}{\psi}_{kl}$ so obtained is substituted into (9) and Eq. (7) is solved again by numerical integration. If the solution $\overset{(1)}{\psi}_{kl}$ so obtained differs considerably from the initial $\overset{0}{\psi}_{kl}$, Eq. (7) is solved again by using $\overset{(1)}{\psi}_{kl}$ in $U(r)$. The process is repeated until the ith solution $\overset{(i)}{\psi}_{kl}$ of (7) gives a value for V_{if} differing by less than 20 percent from the one obtained with the previous solution $\overset{(i-1)}{\psi}_{kl}$. It is found that the successive approximations oscillate about and converge upon the final solution very rapidly.

For the discrete wave functions, the simple variational wave functions of the earlier work[3] are employed. The continuous wave function is normalized according to (4) where $\cos(kr-\alpha)$ is the asymptotic form of $r\psi_{kl}$.

As an example, the equation for the radial part of the continuous wave function for the auto-ionization of $2s2p^3P$ is

$$\frac{d^2}{dr^2}(r\psi_{kl})+\left[2.4957+\frac{2}{r}+\left(4+\frac{2}{r}\right)e^{-4r}-\frac{2}{r^2}\right](r\psi_{kl}) = -\frac{64}{3}e^{-2r}r\left[\frac{1}{r^2}\int_0^r re^{-2r}(r\psi_{kl})rdr + r\int_r^\infty\frac{1}{r^2}e^{-2r}(r\psi_{kl})rdr\right].$$

The probabilities of auto-ionization of a few states of doubly excited helium calculated in this manner are given in Table I.

Concerning the magnitude of the probability of auto-ionization in general, very little can be said on the basis of these calculations. It appears, however, from the values of P for the auto-ionization of $3d^2\,{}^1G$ into $1s\times g\,{}^1G$ and $2s\times g\,{}^1G$ that P decreases very rapidly as the overlap of the atomic wave functions in the initial and the final states decreases.

THE λ320.4 AND λ357.5 LINES OF HELIUM

As the above calculations seem to indicate a probability of auto-ionization of the order 10^{13}–10^{14} per second for the doubly excited states of helium, and as the observed lines λ320.4 and λ357.5 do not seem to show any diffuseness, we would first try to identify them with transitions from such states as not being subject to auto-ionization. Of the configurations $2sns$, $2snd$, $2pnp$, $3dnd$, $2snp$, $2pnd$, only the states $2pnp\,{}^1P$, ${}^3P$; $2pnd\,{}^1D$, ${}^3D$; $3dnd\,{}^1D$, ${}^3D$ do not undergo auto-ionization. The energy of $2p^2\,{}^3P$ has been calculated by Wilson by the method of self-consistent field and is $E(2p^2\,{}^3P)=-1.4018$ Rh measured from the state of the naked nucleus.[3] This value is lower than that obtained by the use of simple variational wave functions, but a still better approximation to the true energy value of $2p^2\,{}^3P$ can be made by means of the method of Stevenson.[9] This method consists in using for the variational wave function the function $(1+c\cos\theta_{12})\Psi$ where Ψ is the correct combination of one-electron wave functions determined by the method of self-consistent field, and θ_{12} is the angle between r_1 and r_2 of the two electrons. Applica-

[9] A. F. Stevenson, Phys. Rev. **56**, 586 (1939).

tion of the variational principle to the determination of the parameter c leads to the secular equation for the energy of the system. For our purpose, we shall evaluate the integrals involved in the theory by means of the variational wave functions of Wu and Ma instead of Wilson's self-consistent field solutions. Since the energy correction given by Stevenson's method is small in any case, this procedure is completely justified.

Using the notation of Stevenson, and with $\psi_{2p}\sim re^{-\gamma r}$ where $\gamma=0.836$, we find

$$H_{01}=7\gamma/192,\quad H'_{11}=4\gamma^2/5,\quad \Delta E=-0.0091 \text{ Rh}.$$

Thus the corrected energy of $2p^2\,{}^3P$ is $-1.4018-0.0091=-1.4109$ Rh. With this value, the calculated frequency of the line $1s2p^3P-2p^2\,{}^3P$ is 313,348 cm^{-1} which differs by 0.4 percent from the observed 312,117 cm^{-1} for the line λ320.4. As the true value of $E(2p^2\,{}^3P)$ lies probably somewhat lower than -1.4109 Rh, one may feel reasonably sure of the identification of λ320.4 with the transition $1s2p^3P-2p^2\,{}^3P$.

With the other line λ357.5 ($\nu=179{,}715$ cm^{-1}), the situation is far less satisfactory. From the calculated energy states of doubly excited helium, it is found that only the lowest one, namely, $2s2p^3P$, lies within 280,000 cm^{-1} from the ionization limit of He I, the other states all being too high. On assuming the line λ357.5 to originate from $2s2s^3P$, it may then be compared with the following transitions

$$1s4s^3S-2s2p^3P=282{,}120 \text{ cm}^{-1};$$
$$1s4d^3D-2s2p^3P=280{,}968 \text{ cm}^{-1}.$$

But then the auto-ionization of $2s2p^3P$ would broaden the line to about 0.3A which is apparently too great compared with the observation. Also it is not clear why the transition $1s2s^3S-2s2p^3P$, which is expected to be stronger than the two above, did not appear on the same spectrogram. Hence it appears that, unless the calculated energies of the doubly excited states and the probabilities of auto-ionization are seriously in error, the line λ357.5 cannot be satisfactorily explained.

SATELLITE LINES IN C V AND C VI OBSERVED BY EDLÉN

Edlén and Tyrén observed groups of weak lines on the long wave-length side of the lines $1s^2\,{}^1S-1s2p^1P$, $1s^2S-2p^2P$ in C V and C VI, respectively.[10] These satellite lines they ascribed to $1s^22s^2S-1s2s2p^2P$, $1s^22p^2P-1s2p^2P$, ${}^2D$, ${}^2S$, etc., in C IV, and $1s2s^{1,3}S-2s2p^{1,3}P$, $1s2p^{1,3}P-2p2p^3P$, ${}^1D$, ${}^1S$ in C V, respectively. An attempt has been made by the writer to correlate the individual satellite lines with such transitions on the basis of energies of such doubly excited states calculated by the variational method.[11] Most of these doubly excited states are capable of auto-ionization and accordingly the satellite lines should show some broadening. If, however, the probabilities of auto-ionization of such states as $1s2p^2\,{}^2D$ are of the same general order of magnitude as in He, namely, 10^{13}–10^{14} per second, the width of these lines in the region of 40A would be 0.001–0.01A, which is not hopelessly inconsistent with observation, in distinction to the case of the λ357.5 line of He.

[10] Edlén and Tyrén, Nature **143**, 940 (1939).
[11] T. Y. Wu, Phys. Rev. **58**, 1114 (1940).