## The Dispersion and Absorption of Helium

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An investigation is made of the relative importance of singly-excited, doublyexcited, and continuous states in the dispersion and absorption spectrum of helium. The *f*-values of the lines due to singly-excited and doubly-excited states are calculated by using wave functions of a screening-constant type, the most important of them having been obtained by variational methods. The *f*-sum of the continuous spectrum is then obtained by difference, from the Kuhn-Reiche sum rule. It is shown that the role of the singly-excited states is moderate, of the doubly-excited states small, and of the continuous spectrum very large. A table is given of relative intensities in the principal series absorption spectrum. Incidentally, a variational calculation of a wave function for the doubly-excited state  $(2s)(2p)^1P$  places this level  $302,000 \text{ cm}^{-1}$  above the limit of single ionization. The corresponding absorption line comes out about one-thirtieth as strong as the first absorption line of the principal series or about as strong as the fifth line of this series.

T IS our purpose to investigate the relative importance of the discrete and continuous energy states of atomic helium in dispersion and absorption.

The refractive index of a gas is given by  $\mu^2 = 1 + 4\pi L\alpha$ , where  $\mu$  is the refractive index, L the number of atoms per unit volume, and  $\alpha$  the polarizability of the atom. The polarizability of an *N*-electron atom is given by an expression of the form:

$$\alpha = \frac{2}{3} \frac{e^2}{h} \sum_{k \neq 0} \frac{\nu_{k0}(|x_{0k}|^2 + |y_{0k}|^2 + |z_{0k}|^2)}{\nu_{k0}^2 - \nu^2}.$$

Here e and h have their usual meanings,  $\nu_{k0}$  is the frequency difference between the excited state k and the normal state 0,  $\nu$  is the frequency of the incident radiation, and  $ez_{0k}$ , e.g., is the matrix element between the states 0 and k of the z-component of electric moment, so that:

$$z_{0k} = \int \overline{\psi}_0 \left( \sum_{\mu=1}^N z_\mu \right) \psi_k d\tau_1 \cdots d\tau_N,$$

where  $\psi_0$  and  $\psi_k$  are the wave functions of the state 0 and k. The summation is to be extended over all the excited states of the atom, continuous included, which have dipole combinations with the normal state.

We can most easily investigate the role of the various parts of the energy spectrum by writing the above formula for  $\alpha$  in atomic units, expressing lengths in terms of  $a_0$  (Bohr radius) as unit, and energies in terms of  $e^2/(2a_0)$ :

$$\alpha = 4a_0^3 \sum_{k \neq 0} \frac{(\frac{1}{3})(W_k - W_0)(|x_{0k}|^2 + |y_{0k}|^2 + |z_{0k}|^2)}{(W_k - W_0)^2 - W_{\nu}^2} .$$

Here  $W_{\nu}$  is the energy in atomic units of a quantum of the incident radiation. If the applied frequency  $\nu$  is not too large (not greater than that corresponding to 600A), we have  $W_{\nu} \leq 1.5$ . For any state beyond the limit of single ionization (i.e., any doubly-excited or continuous state),  $W_k \geq -4$ . Then, since  $W_0 = -5.81$ , we have  $W_k - W_0 \geq 1.81$ , and  $(W_k - W_0)^2 - W_{\nu}^2 \geq 1$ . Thus the numerator for such a state gives an upper limit to its contribution to the dispersion formula; this numerator is called an *f*-value. The sum of the *f*-values of all the doubly-excited and continuous states thus gives an upper limit to their dispersion contribution.

The only singly-excited states which have dipole combinations with the normal state are the "principal series"  $(1s) (np)^{1}P$ . One can show that their *f*-sum gives a lower limit to their dispersion contribution, since for most of them (the lower and thus more important ones) the denominator is less than unity.

These *f*-values satisfy a simple sum rule by means of which we can estimate the role of the continuous spectrum without handling any continuous spectrum wave functions. Using atomic units, let

$$z = \sum_{\mu=1}^{N} z_{\mu}, \ z_{0k} = \int \overline{\psi}_0 z \psi_k d\tau_1 \cdots d\tau_N, \text{ etc.},$$

and

$$f_{k0} = (\frac{1}{3})(W_k - W_0)(|x_{0k}|^2 + |y_{0k}|^2 + |z_{0k}|^2).$$

Then

$$\sum_k f_{k0} = N.$$

For atomic helium, N=2, so that

$$\sum_{k} f_{k0} = 2. \tag{1}$$

(The summation sign is used for all the states, but is understood to include an integral over the continuous spectrum.) We obtain the form pertinent to our problem by splitting the sum into the parts: f', referring to the states  $(1s) (np)^1P; f''$ , referring to doubly excited states arising from the configurations sp, pd, df, etc.;<sup>1</sup> and  $f_c$ , referring to the mixed and purely continuous states lumped together.

Then

$$f' + f'' + f_c = 2. (2)$$

We proceed to calculate f'. Now

$$z_{n0} = \int \overline{\psi}_n(r_1 \cos \theta_1 + r_2 \cos \theta_2) \psi_0 d\tau_1 d\tau_2,$$

where  $\psi_0$  refers to the normal state,  $\psi_n$  to the state (1s)  $(np)^1P$ , and the in-

 $^1\ \mathrm{By}$  the Laporte rule no other configurations have dipole combinations with the normal state.

tegration is extended over the coordinates of both electrons. For  $\psi_0$  we use a function due to Eckart:<sup>2</sup>

$$\psi_0 = \left[ u(\gamma 1) u(\delta 2) + u(\gamma 2) u(\delta 1) \right] / \left[ 2(1+c^2) \right]^{1/2} \tag{3}$$

where the *u*'s are hydrogenic functions for 1s, with parameters  $\gamma = 2.14$  and  $\delta = 1.19$  in place of Z = 2.

This function has the property of giving slightly too large a value for the diamagnetic susceptibility  $|\chi|$ ; the calculation of  $|\chi|$ , involving as it does  $(\sum_i r_i^2)_{00}$ , weights comparatively heavily the values of the wave function for large values of r. This means that  $\psi_0$  is likely to be too large rather than too small at large distances; any error in  $|z_{n0}|^2$  due to  $\psi_0$  is thus likely to be positive (since  $z_{n0}$  contains  $r_1$ ,  $r_2$  in the integrand). The error in  $\psi_0$  is thus such as to make the calculated f' slightly too large, so that if in spite of this, we find a large value for  $f_c$  from the sum rule, we know that such a result is not due to error in  $\psi_0$ .

Letting  $\psi_2$  refer to (1s)  $(2p)^1P$ , we use the function of Eckart:<sup>3</sup>

$$\psi_2 = \left[ u(\alpha 1) v(\beta 2) + u(\alpha 2) v(\beta 1) \right] / 2^{1/2}, \tag{4}$$

where u and v are hydrogenic functions of 1s and 2p, and  $\alpha = 2.003$ ,  $\beta = 0.965$ , are parameters replacing Z = 2. For  $\psi_n$  we take the hint from  $\psi_2$  and use a function with zero screening for 1s, and unit screening for np, since the p electron is now at least two shells farther out than the s-electron:

$$\psi_n = \left[ u(Z1)v_n(\beta 2) + u(Z2)v_n(\beta 1) \right] / 2^{1/2}, \tag{5}$$

where u and  $v_n$  refer to the hydrogenic functions for 1s and np, Z now replacing  $\alpha$ , which in  $\psi_2$  differed negligibly from Z, and  $\beta = Z - 1 = 1$ . Because of this slight difference we treat  $z_{20}$  and  $z_{n0}$  separately. By integration,

$$|z_{20}|^2 = [A(\delta)B(\gamma) + A(\gamma)B(\delta)]^2/(1+c^2),$$

where

$$\begin{aligned} c^2 &= 64(\gamma\delta)^3(\gamma+\delta)^{-6} = 0.775\\ A(\epsilon) &= 4(2\beta^5\epsilon^3)^{1/2}(\epsilon+\beta/2)^{-5}\\ B(\epsilon) &= 8(\alpha\epsilon)^{3/2}(\alpha+\epsilon)^{-3}. \end{aligned}$$

Inserting the values of  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ,  $|z_{20}|^2 = 0.224$ . Similarly, for n > 2:

$$|z_{n0}|^{2} = [E(\delta)F(\gamma) + E(\gamma)F(\delta)]^{2}/1.775$$
(6)

where

$$E(\epsilon) = \int u(Z1)u(\epsilon 1)d\tau_1 = 8(Z\epsilon)^{3/2}(Z+\epsilon)^{-3}$$
$$F(\epsilon) = \int r_1 \cos \theta_1 u(\epsilon 1)\bar{v}(\beta 1)d\tau_1$$

<sup>2</sup> C. Eckart, Phys. Rev. 36, 883, Eq. (17) (1930).

<sup>3</sup> C. Eckart, Phys. Rev. 36, 883, Eq. (18) (1930).

$$= 16\beta^{-4} (\epsilon^{3}\beta^{3}/3)^{1/2} (2\epsilon/\beta - 1)n^{3} [(n+1)n(n-1)]^{1/2} (\epsilon n/\beta - 1)^{n-3} (\epsilon n/\beta + 1)^{-(n+3)}.$$
(7)

By using  $E(\gamma) = 0.998$ ,  $E(\delta) = 0.905$ , we get the Table I:

TABLE I. (Energies and lengths are in atomic units.)

$ z_{n0} ^2$	$(W_n - W_0)$ obs.	$f_{n0} = (W_n - W_0)  z_{n0} ^2$
0.224	1.5593	0.349
0.0547	1.6966	0.0928
0.0204	1.7448	0.0357
0.0100	1.7671	0.0177
0.00588	1.7792	0.0105
0.00351	1.7866	0.0063
	$\begin{array}{c c} &   \ z_{n0}  ^2 \\ \hline \\ 0.0547 \\ 0.0204 \\ 0.0100 \\ 0.00588 \\ 0.00351 \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

We find  $\sum_{n=2}^{7} f_{n0} = 0.512$ , and we get an upper limit to  $f_{8,0} + f_{9,0} + f_{10,0}$  by taking  $3f_{7,0} = 3 \times 0.0063 = 0.0189$ . Thus  $\sum_{2}^{10} f_{n0} = 0.53$ , and by using asymptotic symptotic symptot totic values of  $W_n - W_0$  and  $F(\epsilon, n)$  for large n, we find that the sum from 11 to  $\infty$  is of the order 0.0095. Thus essentially,

$$f' \equiv \sum_{n=2}^{\infty} f_{n0} = 0.54.$$
 (8)

3.01

1.80

Since  $h\nu_{0n}B_{0n}$  (where  $B_{0n}$  is the usual probability of induced transition) is proportional to  $f_{0n}$ , the relative intensities of the lines of the absorption spectrum are given by the last column of Table I. Taking the intensity of the first absorption line  $(1s)^{2} {}^{1}S \rightarrow (1s) (2p)^{1}P$  arbitrarily as 100, the relative intensities of absorption are given by Table II.

TABLE II. Relative intensities of absorption per unit intensity of incident radiation.  $2^{1}P$ 31P  $4^{1}P$  $5^{1}P$ 5.07  $6^{1}P$  $7^1 P$ 10.2

100

26.6

Table II can be continued by means of formulas (6) and (7). For n > 10, the asymptotic calculations previously referred to show that  $|z_{0n}|^2$  and thus  $f_{0n}$  and the entries in Table II fall off inversely as  $n^3$ .

We now consider the doubly-excited states. From the Laporte rule,<sup>4</sup> or directly from the angular parts of the wave functions, we see that such states as  $(2s)^{2}$  <sup>1</sup>S, etc., do not combine with the normal state, and that the only doubly-excited states which do so are the singlet states arising from the configurations (ms) (np), (mp) (nd), (md) (nf), etc. In order to obtain an idea of the order of magnitude of the transition probabilities involved, we next investigate in detail that state from this group which is expected to be the most important, namely (2s)  $(2p)^{1}P$ .

If  $u_2$  and v are hydrogenic functions of 2s and 2p, respectively, the "unperturbed" wave function of (2s)  $(2p)^{1}P$  is:

$$\left[u_2(Z1)v(Z2) + u_2(Z2)v(Z1)\right]/2^{1/2}$$

<sup>4</sup> L. Pauling and S. Goudsmit, Structure of Line Spectra, McGraw-Hill, 1930, p. 94.

Suppose we should introduce a parameter  $\beta$  in place of Z in the function v, leaving  $u_2$  unchanged. Then

$$\phi = \left[ u_2(Z1)v(\beta 2) + u_2(Z2)v(\beta 1) \right] / 2^{1/2}.$$
(9)

Now Eckart's function for  $(1s) (2p)^1P$ , which is presumably good because of the close check which it gives for the energy, has the form (4), where  $\alpha$  is very closely equal to Z, and  $\beta = 0.965$ . For  $(1s) (np)^1P$ , where n > 2, we have used (5). We see then that the above trial function  $\phi$  for  $(2s) (2p)^1P$  is orthogonal to the wave functions of all the states  $(1s) (np)^1P$ ; this statement follows from the presence of the function  $u_2(Z)$  without parameters. Because of the angle functions it is orthogonal to the wave functions of all singlyexcited singlet states not included in  $(1s) (np)^1P$ , and to the wave function of  $(2s)^{2} {}^1S$ . Finally, because of its symmetry in electrons 1 and 2, it is orthogonal to the functions of all the triplet states. It is thus a function with the proper symmetry to represent  $(2s) (2p)^1P$ , possessing the property of orthogonality to the wave functions of all lower states. The minimum of the integral  $E \equiv \int \overline{\phi} H \phi d\tau$  with respect to the parameter  $\beta$  is thus expected to furnish a value of the energy better than the usual first approximation, and higher than the true energy.<sup>5</sup>

This trial function leads to the variational integral:  $-E = Z^2/4 + [2(Z-\sigma)-\beta]\beta/4$ , where  $\sigma = 1+J$ , and  $I = (4/\beta) \int (u^2(Z1)|v(\beta 2)|^2/r_{12})d\tau_1 d\tau_2$ 

or 
$$I = \frac{x}{(1+x)^5} \left[ 1 + \frac{5x}{1+x} - \frac{15x^2}{(1+x)^2} + \frac{105x^3}{(1+x)^3} \right]$$
  
 $\left[ + \frac{x^3}{(1+x)^3} \left[ 1 + \frac{3(1-x)}{1+x} + \frac{3(x^2 - 4x + 2)}{(1+x)^2} + \frac{5(3x^2 - 6x + 2)}{(1+x)^3} + \frac{15x(3x - 4)}{(1+x)^4} + \frac{105x^2}{(1+x)^5} \right]$   
 $J = (4/\beta) \int u(Z1)u(Z2)v(\beta 1)\overline{v}(\beta 2)/r_{12}d\tau_1d\tau_2$   
 $= \frac{4x^3}{3(1+x)^7} \left[ 14 - \frac{98x}{1+x} + \frac{185x^2}{(1+x)^2} \right], \ x = Z/\beta.$ 

The minimum of E occurs at  $\beta = 1.58$  and has the value -1.25 atomic units, thus placing the level  $3.02 \times 10^5$  cm<sup>-1</sup> above the limit of single ionization. This value can be checked against the value of  $2^1P$  extrapolated from BII. The nucleus of boron plus its K shell we take as equivalent to a nucleus of charge  $Z^*$ , and treat BII as a helium-like atom of nuclear charge  $Z^*$ . Expressing the term value in atomic units as  $(Z^* - s)^2/2^2$ , the assumption of perfect shielding by the K shell leads to  $Z^* = 3$  and s = 0.90; the assumption of 85 percent shielding by each K electron (from Slater's rules) leads to  $Z^* = 3.30$  and s = 1.20. These values of s applied to  $(2s) (2p)^1P$  of helium lead

<sup>5</sup> C. Eckart, Phys. Rev. 36, 880, 881 (1930).

636

to -1.30 and -1.16, respectively, for the total energy, so that our value -1.25 lies in the correct range.

A direct application of Slater's<sup>6</sup> shielding rules to (2s) (2p) of helium gives the value -1.36. Majorana<sup>7</sup> also has computed this energy, using a variational method due to Fock,<sup>8</sup> and obtains the value -1.31; this value, however, is apt to be lower than the correct value, because the variational method of Fock does not make the trial function orthogonal to the wave functions of the lower states.

With our wave function for  $j \equiv (2s) \ (2p)^1 P$  and Eq. (1) for the normal state 0, we find:

$$|z_{0j}|^2 = [M(\delta)N(\gamma) + M(\gamma)N(\delta)]^2/1.775,$$

where

$$\begin{split} M(\epsilon) &= 4(2\beta^{5}\epsilon^{3})^{1/2}(\epsilon + \beta/2)^{-5} \\ N(\epsilon) &= 2(2Z^{3}\epsilon^{3})^{1/2}(\epsilon - Z)(\epsilon + Z/2)^{-4}. \end{split}$$

By inserting  $\gamma = 2.14$ ,  $\delta = 1.19$ ,  $\beta = 1.58$ , Z = 2, we find that  $|z_{0j}|^2 = 0.00251$ . Since  $W_i - W_0 = 4.56$ , we obtain  $f_{0j} = 4.56 \times 0.00251 = 0.0114$ . By comparing with Table I, we see that the absorption line due to (2s)  $(2p)^1P$  comes out about one-thirtieth as strong as the first absorption line of the principal series, or about as strong as the fifth line of the principal series.

We have now the problem of finding a wave function valid in the general case (ms)  $(np)^{1}P$ , where  $m \ge 2$ ,  $n \ge 2$ , computing the matrix elements, and summing  $f_{0i}$  over the whole square array of such states. We picture the array as follows:

(	2	s)	(2)	Þ)		(2	2 <i>s</i>	)(	3	p)	)	·	•	·	(	2	s)	)(	10	p	)	•	•	·	(	2	s)	(1	n1	Þ)	•	•	•
(	3	s)	(2)	Þ)		(3	3 <i>s</i>	)(	3	p)	)	•	•	•	(	3	s)	)(:	10	p.	)	•	•	•	(	3	s)	(1	n1	<i>b</i> )	:	•	•
; (:	10	s)	(2)	 p)	•					•					(1	10	s)	)(	10	P	)				(1	0	s)	(1	n1	<i>b</i> )			• •
(	m	s)	(2)	р)						•					(	m	s)	)(	10	· P	)	•			; (	m	s)	(1	n <sub>1</sub>	( )	•		
	•	•		• •	•	•	•	•	•	•	•	•	•	•					·	•	•	•	•	•	•	•	•				•	•	•

We must consider separately the upper right half, the lower left half, and the main diagonal of this array. To treat the upper right half, we can write the unperturbed wave function for  $(ms) (np)^{1}P$ :

$$[u_{ms}(Z1)v_{np}(\beta 2) + u_{ms}(Z2)v_{np}(\beta 1)]/2^{1/2}$$
(10)

replacing in  $v_{np}$ , however, Z by the parameter  $\beta = Z - 1 = 1$ . That is, we consider the *ms* electron to be a perfect shield when n > m; this procedure is suggested by the similar one for (1s)  $(np)^{1}P$ .

- <sup>6</sup> J. C. Slater, Phys. Rev. 36, 57 (1930).
- <sup>7</sup> E. Majorana, Nuovo Cimento VIII, (2) 78 (1931).
- <sup>8</sup> V. Fock, Zeits. f. Physik 63, 855 (1930).

## J. P. VINTI

To treat the main diagonal (ns)  $(np)^{1}P$ , we use the same form of wave function, taking for  $\beta$  the value 1.58 found by actual calculation in the case (2s)  $(2p)^{1}P$  (justification later).

The lower left half is not amenable to treatment in this way, since we cannot expect a p electron to be as complete a shield as an s electron, because of the non-spherical symmetry. Since, however, we have no reason to believe that its f-sum would be greater than that of the upper right half, we take its f-sum equal to that of the upper right half. This procedure gives us an upper limit, which is all that we need.

The total f-sum of all the doubly-excited sp states can then be expressed as 2R+D, where R is the f-sum of the upper right half and D that of the main diagonal.

To obtain R, we first calculate  $|z_{0j}|^2$  between the normal state 0 and the excited state j, using Eq. (1) for  $\psi_0$  and Eq. (9) for  $\psi_j$ . We find:

$$|z_{0j}|^2 = [F(\delta)G(\gamma) + F(\gamma)G(\delta)]^2/1.775,$$
(11)

where  $F(\epsilon)$  is given by Eq. (7) with  $\beta = 1$ , and

$$G(\epsilon) = 8(m/Z)^{3}(Z\epsilon)^{3/2}m^{-1/2}[(\epsilon m/Z - 1)/(\epsilon m/Z + 1)]^{m-2}(\epsilon/Z - 1)(1 + \epsilon m/Z)^{-4}.$$
(12)

By using the asymptotic values of  $F(\epsilon)$  and  $G(\epsilon)$  for large *m* and *n*, and replacing the double summation by a double integral which can be shown to be larger, one can show that  $\sum_{n>m>10} f_{0j}$  is of the order  $10^{-7}$ , so that the infinite "tail" of *R* is negligible.

R thus consists essentially of the sum of the f-values of the finite half-array:

Using formulas (11) and (12), we obtain for the sum of  $|z_{0j}|^2$  for the first row the value 0.000568/1.775, and since  $W_j - W_0$  is of the order  $5.807 - 1 - 1/n^2$ , we have  $W_j - W_0 < 4.807$ ; thus the *f*-sum of the first row is less than  $4.807 \times 0.000568/1.775$  or 0.00154. There are eight rows in all, each row containing one less member than the preceding, and each member lies higher in the diagram of energy levels than the one immediately above, so that its *f*-value must be less. We thus arrive at an upper limit for *R* by multiplying 0.00154 by the factor 8, so that R < 0.0123, and 2R < 0.0246. That is, 0.0246 is an upper limit to the *f*-sum of all the doubly-excited *sp* states in which the two electrons have different principal quantum numbers.

We now turn to D, the diagonal *f*-sum. We must obtain a wave function for  $(ns) (np)^{1}P$ . We have already found a function for  $(2s) (2p)^{1}P$  of the form (9), where  $\beta = 1.58$ . As the best improvement that we can make over the

638

unperturbed zeroth approximation (without encountering prohibitive labor), we can write down such a function for (ns)  $(np)^{1}P$ , where u and v now refer to the states ns and np; we take  $\beta = 1.58$ . The argument for such a procedure is this: Such a function with  $\beta = 2$  is the zeroth approximation, in which the interaction of the electrons is entirely neglected; we know, however, that the deviation from "hydrogenness" can be expressed in most cases sufficiently well by considering that the interaction of the electrons results in a screening effect. If the screening were perfect, we should have  $\beta = 1$ ; no screening means  $\beta = 2$ .  $\beta$  thus lies between 1 and 2, and since it equals 1.58 for n=2, 1.58 is our only possible estimate for the general case (ns)  $(np)^{1}P$ .

With this function, the squared matrix element  $|z_{n0}|^2$  is given by Eq. (11), where now  $G(\epsilon)$  is given by Eq. (12) with *m* replaced by *n*, and  $F(\epsilon)$  is given by Eq. (7) with  $\beta = 1.58$ .

By using the asymptotic values of  $F(\epsilon)$  and  $G(\epsilon)$  for large *n*, we can then show that the diagonal *f*-sum from n = 11 to  $n = \infty$  is less than an integral of the order  $2 \times 10^{-7}$ , so that it is negligible.

To obtain the diagonal *f*-sum from n = 3 to n = 10, we use the formula just found for  $|z_{n0}|^2$  and estimate  $W_n$  by means of Slater's shielding rules, obtaining  $W_n \sim -2(Z-0.35)^2/n^2 = -5.44/n^2$ . Thus  $W_n - W_0 \sim 5.807 - 5.44/n^2$ . The *f*-value of (3s)  $(3p)^1P$  turns out to be  $7.55 \times 10^{-4}$ , and we can obtain an upper limit to the *f*-sum from n = 3 to n = 10 by applying to this the factor 8; this limit is 0.006. On adding 0.0114, the *f*-value of  $(2s) (2p)^1P$ , the diagonal *f*-sum *D* becomes  $\leq 0.017$ . Since

 $2R \leq 0.0025$ , and  $D \leq 0.017$ , we have  $f'' \equiv 2R + D \leq 0.042$ . (13)

Using Eqs. (2), (8) and (13), we have:

$$f_c = 2 - 0.54 - 0.04 = 1.42. \tag{14}$$

We wish now to investigate the question as to whether allowance for all the other doubly-excited states which combine with the normal state would affect appreciably the value of f''. We have to consider the states  $(ml_1)$  $(nl_2)^1P$ , where  $1_1+1_2$  is odd (by the Laporte rule). In our screening constant functions, the function of  $(ml_1)$   $(nl_2)$  differs from that of (ms)  $(np)^1P$  only in the angle functions. Since the latter contribute a factor to  $|z_{n0}|^2$  which is less than unity, we can obtain an upper limit for each  $(ml_1)$   $(nl_2)$  by taking it to be equal to that of (ms) (np).  $W_n - W_0$  for a state  $(ml_1)$   $(nl_2)$  is of the same order as for the state (ms) (np), since the principal quantum numbers play the principal role in the determination of the energy. We can thus obtain an upper limit to the f-contribution of a given part of the array which gives f'', when all these other states are included, by applying to the *f*-value of each (ms) (np) a factor  $g_{mn}$  denoting the number of configurations which have values of *m* and *n* in common. Neglect of the Laporte rule leads to  $g_{mn} \leq mn$ ; recognition of the rule leads to a smaller value. If, accordingly, a portion of f which was negligible before is found still to be so when the factor mn is applied to each part, we know that it will still be negligible when the Laporte rule is used. In this way it is found that the infinite tails that we met before

J. P. VINTI

are still negligible. On applying the factor mn to the other parts, we find that  $f'' \leq 0.043$ . Thus Eqs. (13) and (14) remain essentially unchanged by this correction.

It is interesting to compare these figures with some obtained by Margenau.<sup>9</sup> He finds by a semi-empirical method f'=0.18, and  $f''+f_e=1.82$ . From the large value of the latter he concludes that the neglect of "double jumps" is responsible for the inaccurate value found in the simple theory of London for van der Waals forces in helium. The present work makes it appear very probable that the inclusion of states beyond the ordinary series limit is essential, but it indicates that of these states, the continuous ones are by far the most important; namely, that part of the continuous spectrum which lies at the limit of the principal series. Stated in another way, the principal series lines in the absorption spectrum of helium are of moderate intensity, the lines due to jumps from the normal state to doubly-excited states are very weak, and the continuous absorption spectrum is very strong. These results are certainly in qualitative agreement with experiment, as evidenced by the measurements of Herzfeld and Wolf on the dispersion of helium.<sup>10</sup> Quantitative comparison can be made only after the absorption spectrum, which lies in the far ultraviolet (around 700A) has been photographed and measured.

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<sup>9</sup> H. Margenau, Phys. Rev. 37, 1425 (1931).

<sup>10</sup> K, F. Herzfeld and K. L. Wolf, Ann. d. Physik 76, 71 (1925); 76, 567 (1925).