

very noticeable continuous spectrum were present. Using a moderately narrow slit, the secondary spectrum could be found visually only by those who knew just where to look for it.

<sup>3</sup> K. F. Bonhoeffer, *Zeit. Physik. Chem.*, 113, 199 (1924).

<sup>4</sup> M. Born and J. Franck, *Ann. Physik*, 76, 225 (1925) and *Zeit. Physik*, 31, 411 (1925).

## THE DISPERSION OF ATOMIC HYDROGEN II—A CALCULATION

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In the preceding paper experimental evidence is brought forward to show that at a wave-length  $\lambda = 6000 \text{ \AA}$  the index of refraction of atomic hydrogen is  $\mu_H = 1.000068$ . Expressions for this quantity derived by Sommerfeld and Epstein\* check this value but cannot be taken as correct because they all require anomalous dispersion at frequencies corresponding to the mechanical frequencies of the model and nothing in particular at the spectral frequencies. It is significant that these classical computations using atomic models given by the quantum theory should give a correct result for long wave-lengths. On the other hand—as shown in this paper—attempts to adjust the dispersion formulae to give the proper frequencies for anomalous dispersion lead to a numerical value for  $\mu_H$  which is decidedly too large.

The author has calculated and will publish elsewhere the perturbations of a known system by a force of the form  $E_0 F(t)$ . As a special case we have the problem of dispersion—namely, an atomic system acted on by a plane wave. In this case we have an electric field  $E_0 \cos 2\pi\nu t$ . If general cylindrical coordinates are chosen with the  $z$  direction parallel to the electric field, the expression for an element of the first order perturbation of the  $2f$  dimensional matrix  $q_s$  is given by<sup>1</sup>

$$q_s^1(n_1 \dots n_f, m_1 \dots m_f) = \frac{eE_0 \cos 2\pi\nu t}{2\pi i h m} \sum_{k_1 \dots k_f} \frac{q_s^0(n_1 \dots n_f, k_1 \dots k_f) p_s^0(k_1 \dots k_f, m_1 \dots m_f) - p_s^0(n_1 \dots n_f, k_1 \dots k_f) q_s^0(k_1 \dots k_f, m_1 \dots m_f)}{(\nu_0(n_1 \dots n_f, k_1 \dots k_f) + \nu)(\nu_0(k_1 \dots k_f, m_1 \dots m_f) + \nu)} \quad (1)$$

where  $f$  is the number of degrees of freedom of the system,  $m$  the mass of the electron and  $q_s^0, p_s^0$  are the unperturbed canonical matrices corre-

sponding to the cylinder coördinate  $z$ . The summation extends over all combinations of the  $k$ 's excepting that which makes  $\nu_0(n_1 \dots n_f, k_1 \dots k_f) = 0$ . The quantities  $\nu_0(n_1 \dots n_f, k_1 \dots k_f)$ ,  $\nu_0(k_1 \dots k_f, n_1 \dots n_f)$  are the frequencies characteristic of changes to or from the state  $(n_1 \dots n_f)$ . If  $n_i$  is the main quantum number then for  $n_i > k_i$  we have an emission and for  $n_i < k_i$  an absorption. The elements of the matrix  $q_z^1$  which are interesting for dispersion are those with the same frequency as that of the incident light so that  $\nu_0(n_1 \dots n_f, m_1 \dots m_f) = 0$ , viz., the diagonal terms

$$q_z^1(n_1 \dots n_f, n_1 \dots n_f) = - \frac{eE_0 \cos 2\pi\nu t}{2\pi i h m} \sum_{k_1 \dots k_f} \frac{q_z^0(n_1 \dots n_f, k_1 \dots k_f) p_z^0(k_1 \dots k_f, n_1 \dots n_f) - p_z^0(n_1 \dots n_f, k_1 \dots k_f) q_z^0(k_1 \dots k_f, n_1 \dots n_f)}{\nu_0(n_1 \dots n_f, k_1 \dots k_f)^2 - \nu^2} \tag{2}$$

If we separate the emission from the absorption terms and note that the product

$$p_z^0(n_1 \dots n_f, k_1 \dots k_f) q_z^0(k_1 \dots k_f, n_1 \dots n_f)$$

has numerically opposite signs in the two cases we have

$$q_z^1(n_1 \dots n_f, n_1 \dots n_f) = - \frac{eE_0 \cos 2\pi\nu t}{2\pi i h m} \left\{ \sum_{n_i < k_i} \frac{p_z^0(n_1 \dots n_f, k_1 \dots k_f) q_z^0(k_1 \dots k_f, n_1 \dots n_f) - q_z^0(n_1 \dots n_f, k_1 \dots k_f) p_z^0(k_1 \dots k_f, n_1 \dots n_f)}{\nu_0(n_1 \dots n_f, k_1 \dots k_f)^2 - \nu^2} - \sum_{n_i > k_i} \frac{p_z^0(n_1 \dots n_f, k_1 \dots k_f) q_z^0(k_1 \dots k_f, n_1 \dots n_f) - q_z^0(n_1 \dots n_f, k_1 \dots k_f) p_z^0(k_1 \dots k_f, n_1 \dots n_f)}{\nu_0(n_1 \dots n_f, k_1 \dots k_f)^2 - \nu^2} \right\} \tag{3}$$

where only absolute magnitudes of the two summations are to be taken into account.

To arrive at an expression for the index of refraction of all the atoms in the state  $(n_1 n_2 \dots n_f)$  we use the relation

$$\mu^2 - 1 = \frac{4\pi P N}{E_0 \cos 2\pi\nu t} = \frac{4\pi N e}{E_0 \cos 2\pi\nu t} q_z^1(n_1 \dots n_f, n_1 \dots n_f).$$

Where  $P$  is the polarization due to the electric field and  $N$  is the number of atoms per cc. in the state  $(n_1 \dots n_f)$ . Remembering that  $z$  being a cylinder coördinate  $p_z = m \dot{q}$  and referring to the work of Kramers and Heisenberg<sup>2</sup> and also that of Born and Jordan<sup>3</sup> it is seen that the matrix mechanics expression as derived from (3) namely

$$\begin{aligned}
 (\mu^2 - 1)_M &= -\frac{2e^2N}{ihm} \\
 &\left\{ \sum_{n_i < k_i} \frac{p_s^0(n_1..n_f, k_1..k_f)q_s^0(k_1..k_f, n_1..n_f) - q_s^0(n_1..n_f, k_1..k_f)p_s^0(k_1..k_f, n_1..n_f)}{v_0(n_1..n_f, k_1..k_f)^2 - v^2} \right. \\
 &\quad \left. - \sum_{n_i > k_i} \frac{p_s^0(n_1..n_f, k_1..k_f)q_s^0(k_1..k_f, n_1..n_f) - q_s^0(n_1..n_f, k_1..k_f)p_s^0(k_1..k_f, n_1..n_f)}{v_0(n_1..n_f, k_1..k_f)^2 - v^2} \right\} \quad (4)
 \end{aligned}$$

has the same satisfactory form as that given by Kramers<sup>4</sup>

$$(\mu^2 - 1)_K = \frac{e^2N}{\pi m} \left\{ \sum_a \frac{f_a}{v_a^2 - v^2} - \sum_e \frac{f_e}{v_e^2 - v^2} \right\}. \quad (5)$$

To those who had been following the work of Kuhn, Thomas, Reiche and Heisenberg<sup>5</sup> leading to the matrix mechanics it was not surprising that the condition

$$p q - q p = \frac{h}{2\pi i} 1$$

should give a result quite analogous to that of Kramers, but it is not obvious that the two theories should give identical numerical values for the index of refraction.

Using the results in a very interesting paper of Reiche and Thomas<sup>6</sup> we can write for the case of atomic hydrogen in the normal state

$$\sum_a f_a - \sum_e f_e = 1. \quad (6)$$

For the corresponding part of (4) we have

$$\begin{aligned}
 &\sum_{n_i < k_i} p_s^0(n_1..n_f, k_1..k_f)q_s^0(k_1..k_f, n_1..n_f) - q_s^0(n_1..n_f, k_1..k_f)p_s^0(k_1..k_f, n_1..n_f) \\
 &- \sum_{n_i > k_i} p_s^0(n_1..n_f, k_1..k_f)q_s^0(k_1..k_f, n_1..n_f) - q_s^0(n_1..n_f, k_1..k_f)p_s^0(k_1..k_f, n_1..n_f) \\
 &= \sum_{k_1..k_f} p_s^0(n_1..n_f, k_1..k_f)q_s^0(k_1..k_f, n_1..n_f) - q_s^0(n_1..n_f, k_1..k_f)p_s^0(k_1..k_f, n_1..n_f) = \frac{h}{2\pi i}, \quad (6')
 \end{aligned}$$

showing that in this case at least the numerical values of  $\mu$  calculated from (4) and (5) are equal.

With the possibility of an experimental verification at hand it becomes interesting to make this calculation. And here we appreciate the strength of Kramers' dispersion formula—for not only is it difficult to check experimentally but the numerical computation is none too simple. For the sums (6) and (6') and not the same as those appearing in (4) and (5).

In fact until reliable "transition-probability coefficients" are obtained the theory is almost safe. Not quite, however, for we can find a lower bound for  $\mu_{\text{H}}$  by noticing that since for the normal state the series is the Lyman series

$$\nu_a = R \left( 1 - \frac{1}{a^2} \right) < R,$$

so that

$$\frac{1}{\nu_a^2 - \nu^2} > \frac{1}{\nu_a^2} > \frac{1}{R^2},$$

and

$$\sum_e f_e = 0$$

it follows from (4) or (5) using (6) or (6')

$$(\mu_{\text{H}}^2 - 1) = \frac{e^2 N}{\pi m} \sum_a \frac{f_a}{\nu_a^2 - \nu^2} > \frac{e^2 N}{\pi m R^2} \sum_a f_a. \quad (7)$$

This gives for both theories for atomic hydrogen at 1 atmosphere and 0°C.

$$\mu_{\text{H}}^2 - 1 > 2.03 \times 10^{-4}, \quad (8)$$

whereas experiments by the author done at the California Institute of Technology and discussed in the preceding paper of these PROCEEDINGS show (taking the extreme estimate of the error),

$$(\mu_{\text{H}}^2 - 1)_{\text{exp.}} \doteq [1.36 \pm 0.34] \times 10^{-4}. \quad (9)$$

The discrepancy is really much more serious. For Schrödinger<sup>7</sup> has recently calculated the values of  $f_a$  for the Balmer series on the basis of his formulation of the quantum theory and obtained in agreement with the empirical results due to Ladenburg<sup>8</sup> the relative values

$$f_{\text{H}_\alpha} : f_{\text{H}_\beta} : f_{\text{H}_\gamma} : f_{\text{H}_\delta} = 1.281 : 0.2386 : 0.08975 : 0.04418.$$

If it is assumed that the same proportions hold for the Lyman series we get instead of (7) for visible light where we can take  $\nu \doteq 0$

$$(\mu_{\text{H}}^2 - 1) \doteq \frac{e^2 N}{\pi m R^2} \cdot \frac{1}{165} \left[ \frac{128}{(3/4)^2} + \frac{24}{(3/9)^2} + \frac{9}{(15/16)^2} + \frac{4}{(24/25)^2} \right], \quad (10)$$

giving to compare with (9)

$$(\mu_{\text{H}}^2 - 1) \doteq 3.38 \times 10^{-4}. \quad (11)$$

On the other hand, if we allow that the compatibility between theory and experiment in the case of the Balmer series establishes Pauli's direct calculation on the Lyman series mentioned at the end of Schrödinger's paper we have instead of (10)

$$(\mu_{\text{H}}^2 - 1) \doteq \frac{e^2 N}{\pi m R^2} \frac{1}{801} \left[ \frac{625}{(3/4)^2} + \frac{119}{(8/9)^2} + \frac{42}{(15/16)^2} + \frac{21}{(24/25)^2} \right] \quad (10')$$

giving to compare with (9)

$$(\mu^2 - 1) = 3.34 \times 10^{-4}. \quad (11')$$

If the improved experiments now in progress verify the violent disagreement between (8), (11) or (11') and (9) it will not be sufficient to search for a modification of the perturbation theory of the matrix calculus. The difficulty apparently strikes through the Kramers' dispersion theory at the very foundation of the matrix mechanics, viz., the Correspondence Principle. Or else, since in this simple case the original work of Ladenburg<sup>9</sup> leads to the very expression derived by Kramers in his development of that work, we begin to suspect that there may be something wrong with our notion as to the nature of the phenomena of dispersion.

\* A. Sommerfeld—Elster and Geitel—"Festschrift," p. 575 (1916), and P. S. Epstein, *Zeit. Physik*, 9, 93 (1922).

<sup>1</sup> The equivalent expression for the case of systems of one degree of freedom and using cartesian coördinates was given by M. Born, W. Heisenberg and P. Jordan, *Zeit. Physik*, 35, 572 (1926), and by Born in his *Problems of Atomic Dynamics*, page 90. The factor 2 by which the latter differs is apparently a typographical error.

<sup>2</sup> H. A. Kramers and Heisenberg, *Zeit. Physik*, 31, 693 (1925).

<sup>3</sup> M. Born and P. Jordan, *Zeit. Physik*, 34, 887 (1925).

<sup>4</sup> H. A. Kramers, loc. cit., also *Nature*, 113, 673 (1924) and 114, 310 (1924).

<sup>5</sup> W. Kuhn, *Zeit. Physik*, 33, 408 (1925). W. Thomas, *Naturwissenschaften*, 13, 627 (1925). F. Reiche and W. Thomas, *Zeit. Physik*, 34, 510 (1925). W. Heisenberg, *Zeit. Physik*, 33, 879 (1925).

<sup>6</sup> F. Reiche and W. Thomas, loc. cit.

<sup>7</sup> E. Schrödinger, *Ann. Physik* (4), 80, 477 (1926).

<sup>8</sup> R. Ladenburg, *Ann. Physik* (4), 38, 249 (1912).

<sup>9</sup> R. Ladenburg, *Zeit. Physik*, 4, 451 (1921); also R. Ladenburg and F. Reiche, *Naturwissenschaften*, 1923, p. 584.