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³ Orndorff, Gibbs and co-workers, *J. Amer. Chem. Soc.*, (a) **47**, 2767 (1925); (b) **48**, 1327 (1926); (c) **48**, 1994 (1926); (d) **49**, 1541, 1545 (1927); (e) unpublished data.

⁴ Gomberg, J., *J. Amer. Chem. Soc.*, **35**, 1035 (1913).

⁵ Orndorff and McNulty, *Ibid.*, **49**, 1588 (1927).

THE DISPERSION BY HYDROGEN-LIKE ATOMS IN UNDULATORY MECHANICS

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1. In view of the recent experimental determination of the dispersion by atomic hydrogen¹ it seems interesting to apply the theory of dispersion developed by Schrödinger² to this case. In this paper we restrict ourselves to an approximation in which terms of the order of relativistic correction are neglected. For this purpose it is simpler to obtain our wave equation by the operational method of Schrödinger³ and Eckart,⁴ as extended by Epstein,⁵ for in this way we immediately obtain an equation free of relativistic terms.

2. We assume the incident light to be a plane polarized wave of frequency ν propagated along the Y axis, with the electric vector along Z , the nucleus being situated at the origin. The field of the wave and of the nucleus can be represented by a vector potential \bar{A} and a scalar potential ϕ . We take $A_x = A_y = 0$, $A_z = -c^2 F \sin \omega(t - y/c)/\omega$, and $\phi = \kappa e/r$, where $\omega = 2\pi\nu$, κe the charge of the nucleus, c the velocity of light and F a constant, all quantities being in electrostatic units.

The corresponding Hamiltonian function is

$$\frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + \frac{eF}{\mu\omega} p_z \sin \omega(t - y/c) + \frac{e^2 F^2}{2\mu\omega^2} \sin^2 \omega(t - y/c) - \kappa e^2/r$$

where $\mu =$ mass of the electron and $\bar{p} = (p_x, p_y, p_z)$ its momentum. From this we obtain by the method indicated⁵ the following equation for ψ

$$\nabla^2 \psi - \frac{2ieF}{h\nu} \frac{\partial \psi}{\partial z} \sin \omega(t - y/c) + \frac{8\pi^2 \mu e^2}{h^2} \left[\frac{\kappa}{r} - \frac{F^2}{2\mu\omega^2} \sin^2 \omega(t - y/c) \right] \psi - \frac{4\pi i \mu}{h} \frac{\partial \psi}{\partial t} = 0$$

which, to the desired degree of approximation, reduces to

$$\nabla^2 \psi + \frac{8\pi^2 \mu e^2 \kappa}{h^2 r} \psi - \frac{4\pi i \mu}{h} \frac{\partial \psi}{\partial t} = \frac{2ieF}{h\nu} \frac{\partial \psi}{\partial z} \sin \omega t \quad (1)$$

where on the right we omitted terms in F^2 and a factor $e^{\pm i\omega y/c}$ since $\omega y/c$ is very small for light of visible frequencies and lower.

To solve equation (1) we let

$$\psi = \psi(l, m, n) = A(l, m, n) e^{2\pi i E_l t/h} [\psi_0(l, m, n) + \psi_1(l, m, n)] \quad (2)$$

where $A(l, m, n)$ is a normalizing factor, and $\psi_0(l, m, n)$ satisfies the equation

$$\nabla^2 \psi_0(l, m, n) + \frac{8\pi^2 \mu}{h^2} \left(\frac{\kappa e^2}{r} + E_l \right) \psi_0(l, m, n) = 0. \quad (3)$$

Then, to the desired order of approximation, equation (1) reduces to

$$\nabla^2 \psi_1(l, m, n) + \frac{8\pi^2 \mu}{h^2} \left(\frac{\kappa e^2}{r} + E_l \right) \psi_1(l, m, n) - \frac{4\pi i \mu}{h} \frac{\partial \psi_1(l, m, n)}{\partial t} = \frac{2ieF}{h\nu} \frac{\partial \psi_0}{\partial z} \sin \omega t. \quad (4)$$

We now express $2i \sin \omega t$ as the difference of two exponentials; then, letting

$$\psi_1(l, m, n) = e^{i\omega t} u_1(l, m, n) - e^{-i\omega t} u_2(l, m, n) \quad (5)$$

equating separately the coefficients of the two exponentials, and combining the two resulting equations into one, we obtain

$$\nabla^2 u(l, m, n) + \frac{8\pi^2 \mu}{h^2} \left(\frac{\kappa e^2}{r} + E_l \pm h\nu \right) u(l, m, n) = \frac{eF}{h\nu} \frac{\partial \psi_0(l, m, n)}{\partial z} \quad (6)$$

where, as in the following, the upper sign goes with the subscript 1, the lower with the subscript 2.

3. The next step in our process is to expand $\partial \psi_0 / \partial z$ and u each into a series of suitable functions. For this purpose it seems natural to use the set of solutions of the equation of the unperturbed atom, i.e., the set $\psi_0(l, m, n)$, as was done by Schrödinger.² Unfortunately, this set is not a *complete* orthogonal set unless a continuous range of complicated functions corresponding to imaginary values of l are included. To avoid this complication we follow a procedure analogous to that used by Epstein for a similar purpose, i.e., we use for our expansion another set of functions, $T(l', m', n')$, defined as follows

$$T(l', m', n') = e^{im'\phi} P_{n'}^{m'}(\cos \theta) Z(l', n', \alpha) \quad (7)$$

where $Z(l', n', \alpha)$ satisfies Schrödinger's conditions of finiteness and the differential equation

$$\frac{d^2 Z(l', n', \alpha)}{dr^2} + \frac{2}{r} \frac{dZ(l', n', \alpha)}{dr} - \left(\frac{n'(n' + 1)}{r^2} + \frac{2\alpha l'}{r} + \alpha^2 \right) Z(l', n', \alpha) = 0. \tag{8}$$

We have, therefore,

$$\nabla^2 T(l', m', n') - (\alpha^2 + 2\alpha l'/r) T(l', m', n') = 0. \tag{9}$$

It can be shown⁶ that $T(l', m', n', \alpha)$ thus defined, for any constant real value of α , form a complete orthogonal set with respect to a function decreasing rapidly with increasing r , such as $r\partial\psi_0/\partial z$. We shall assume α to be negative. We may, therefore, write

$$r\partial\psi_0/\partial z = \sum a(l', m', n') T(l', m', n') \tag{10}$$

and

$$u = \sum b(l', m', n') T(l', m', n'). \tag{11}$$

It may be objected that since we do not know the properties of the function u we may not write (11), as the set $T(l', m', n')$ may not be complete for this function. However, if to complete the expansion of u we would add to the right member of (11) a sum of terms each of the type cS , where the S 's are functions different from the T 's, we would find that on account of inhomogeneity of equation (6) all c 's must be zeros. Thus the set of T 's is sufficient.

Substituting (10), (11) and then (9) into (6) and equating the coefficients of corresponding T 's, we obtain

$$b(l', m', n') \left[\alpha^2 + \frac{2\alpha l'}{r} + \frac{8\pi^2 \mu}{h^2} \left(\frac{\kappa e^2}{r} + E_l \mp h\nu \right) \right] = eFa(l', m', n')/h\nu r. \tag{12}$$

If we let

$$\alpha^2 = -8\pi^2 \mu (E_l \mp h\nu)/h^2 \tag{13}$$

we find that (12) will be satisfied provided

$$b(l', m', n') = \eta eFa(l', m', n')/2h\nu(1 + l'\eta\alpha) \tag{14}$$

where $\eta = h^2/4\pi^2 \mu e^2 \kappa$.

4. We normalize the solution of (8) in such a way that

$$Z(l', n', \alpha) = \sum_{j=0}^{l'-n'-1} \frac{r^{n'} e^{\alpha r} (2\alpha r)^j}{j!(l' - n' - 1 - j)!(2n' + 1 + j)!}; \quad l' > n'. \tag{15}$$

Except for a numerical coefficient and notation these functions are the same as the $\chi(s, \alpha)$ functions used by Epstein,⁷ so that we may use the relations obtained by him.

The usual solution of (3) may be put in the form

$$\psi_0(l, m, n) = e^{im\varphi} P_n^m(\cos \theta) \chi(l, n) \tag{16}$$

where

$$\chi(l, n) = \sum_{j=0}^{l-n-1} \frac{r^n e^{-r/\eta} (-2r/\eta)^j}{j!(l-n-1-j)!(2n+1+j)!} \tag{17}$$

and

$$E_l = -2\pi^2 \mu e^4 \kappa^2 / h^2 l^2.$$

5. We are interested in the case of atoms in the normal state, i.e., the case when $l = 1, m = n = 0$. In this case

$$\partial \psi_0(1, 0, 0) / \partial z = -e^{-r/\eta} \cos \theta / \eta$$

so that we can put $m' = 0, n' = 1$ and (10) reduces to

$$r \partial \psi_0(1, 0, 0) / \partial z = \cos \theta \sum_{s=2}^{\infty} a(s, \alpha) Z(s, 1, \alpha) \tag{18}$$

where

$$a(s, \alpha) = -\eta^3 (1 + \alpha \eta)^{s-2} (s+1)! (2\alpha)^4 / (1 - \alpha \eta)^{s+2}. \tag{19}$$

We can now obtain the expression for $\psi_1(1, 0, 0)$ if we note that now, by (7), (11) and (14)

$$u_1 = \cos \theta \sum_{s=2}^{\infty} b(s, \alpha_1) Z(s, 1, \alpha_1) = \frac{\eta e F}{2h\nu} \cos \theta \sum_{s=2}^{\infty} \frac{a(s, \alpha_1) Z(s, 1, \alpha_1)}{(1 + s\eta\alpha_1)} \tag{20}$$

with a similar expression for u_2 . In equation (13) we are to take + for α_1 and - for α_2 .

If we impose the normalizing condition that $\int \psi(l, m, n) \bar{\psi}(l, m, n) d\tau = 1$ when integrated over the whole space, we obtain for $A(l, m, n)$ of the equation (2) an expression which gives $A^2(1, 0, 0) = 1/\pi\eta^3$.

6. We can now compute the electric moments. We obtain $M_x = M_y = 0$, and

$$\begin{aligned} M_z &= \int z \psi(1, 0, 0) \bar{\psi}(1, 0, 0) d\tau \\ &= -\frac{128e^2\eta^6}{3h\nu} F \cos \omega t \left[\alpha_1^4 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2+s\eta\alpha_1)(1+\alpha_1\eta)^{2s-5}}{(1+s\eta\alpha_1)(1-\alpha_1\eta)^{2s+5}} \right. \\ &\quad \left. - \alpha_2^4 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2+s\eta\alpha_2)(1+\alpha_2\eta)^{2s-5}}{(1+s\eta\alpha_2)(1-\alpha_2\eta)^{2s+5}} \right]. \tag{21} \end{aligned}$$

Since this quantity M is also the leading term of the matrix $M(l, m, n)$, i.e., $M(1, 0, 0)$, we have for the index of refraction n , the relation $n^2 - 1 = 4\pi MN/F \cos \omega t$, where N is the number of atoms per unit volume.

Thus, we finally have

$$n^2 - 1 = \frac{16Nh^6}{3\pi^5 e^6 \mu^3 \kappa^4 \beta^6} \left[(1 - \beta)^2 \sum_{s=2}^{\infty} \frac{s(s^2 - 1)(2 - sq_1)}{(sq_1 - 1)} \left(\frac{1 - q_1}{1 + q_1}\right)^{2s} + (1 + \beta)^2 \sum_{s=2}^{\infty} \frac{s(s^2 - 1)(2 - sq_2)}{(sq_2 - 1)} \left(\frac{1 - q_2}{1 + q_2}\right)^{2s} \right] \quad (22)$$

where $\beta = -h\nu/E_1 = \nu/\nu_1 = h^3\nu/2\pi^2\kappa^2\mu e^4$, $q_1 = \sqrt{1 - \beta}$, $q_2 = \sqrt{1 + \beta}$, ν_1 the ionization frequency of the atom.

We may first note that $n^2 - 1$ becomes infinite when $sq_1 - 1 = 0$, or $h\nu = -E_1(1 - 1/s^2)$, i.e., when ν corresponds to one of the absorption frequencies of the atom in the normal state. Since q_2 and s are each greater than 1, $sq_2 - 1$ is never zero. Expanding in powers of β and of the wavelength λ we may write

$$\begin{aligned} n^2 - 1 &= \frac{9Nh^6}{32\pi^5 e^6 \mu^3 \kappa^4} (1 + 1.477\beta^2 + 2.39\beta^4 + \dots) \\ &= \frac{9Nh^6}{32\pi^5 e^6 \mu^3 \kappa^4} (1 + 1.477c^2/\nu_1^2\lambda^2 + \dots). \end{aligned}$$

When $\nu = 0$, these formulæ give $n^2 - 1 = 9Nh^6/32\pi^5 e^6 \mu^3 \kappa^4$, which is in exact agreement with the result obtained for the dielectric constant by Van Vleck,⁸ Epstein⁹ and Pauling.¹⁰

7. For hydrogen we put $\kappa = 1$, and obtain

$$n^2 - 1 = 2.24 \times 10^{-4}(1 + 1.228 \times 10^{-10}/\lambda^2).$$

Substitution of numerical values into (22) gives the following

$h\nu/E_1$	λ IN Å	$(n^2 - 1) \times 10^4$
0.30	3039	2.59
0.25	3647	2.47
0.20	4559	2.38
0.15	6079	2.31
0.10	9118	2.27
0.00	∞	2.24

These results are not in a very good agreement with Langer's determination,¹ but the great experimental difficulties connected with this measurement could account for the disagreement.

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¹ Langer, R. M., *Proc. Nat. Acad. Sci.*, **12**, 639 (1926).

² Schrödinger, E., *Ann. Physik*, **81**, 112 (1926), §2.

³ Schrödinger, E., *Ibid.*, **79**, 745 (1926).

⁴ Eckart, C., *Physic. Rev.*, **28**, 711 (1926).

- ⁵ Epstein, P. S., *Proc. Nat. Acad. Sci.*, **12**, 637 (1926), §5.
⁶ Courant-Hilbert, *Mathem. Physik*, **V**, §5, p. 239.
⁷ Epstein, P. S., *Proc. Nat. Acad. Sci.*, **12**, 630 (1926).
⁸ Van Vleck, J. H., *Ibid.*, **12**, 662 (1926).
⁹ Epstein, P. S., *Ibid.*, **13**, 432 (1927).
¹⁰ Pauling, L., *Proc. Royal Soc.*, **114**, 198 (1927).

THE PRODUCTION OF ACTIVE NITROGEN

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Strutt² found that the presence of two per cent of oxygen in nitrogen was sufficient to practically destroy the active nitrogen afterglow. Recently, Constantinides³ studied the changes produced in the afterglow when foreign gases were introduced into the discharge itself and also when gases were introduced into the afterglow. Among the gas studied was oxygen and the results showed that oxygen caused changes in both the color and in the duration of the active nitrogen afterglow. Both Strutt and Constantinides found that, when the amount of oxygen present was in proportion to the amount present in air, the afterglow produced was a yellow-green afterglow whose spectrum was found to be continuous. Strutt attributed this yellow-green afterglow to the reaction between ozone and nitric oxide. Long exposures on this glow by the author gave only the previously observed continuous spectrum and the OH band at 3064 Å. The absence of band emission indicates that there is no active nitrogen present in this yellow-green glow. As far as the writer is aware no experiments have been reported in which the active nitrogen afterglow has been observed in discharge tubes containing air, and the purpose of this note is to describe briefly some experiments in which active nitrogen has been obtained in air discharge tubes.

The discharge tube was a bulb of about 12 cm. diameter having tungsten electrodes. Air at 5 mm. pressure was pumped through the tube continuously through a capillary open to the atmosphere. No effort was made to exclude either water or mercury vapors from the tube. The discharge was excited by means of an induction coil giving a six-inch spark that corresponds roughly to a voltage of 120,000. The discharge was condensed and a spark gap was connected in series with the tube and the condenser.

The glow was blue in color and changed to the ordinary yellow-green glow with continuous spectrum if the spark gap was excluded. The spectrum of the glow was photographed with a small Hilger quartz spectro-