A

THESIS

ENTITLED

THE DISPERSION BY HYDROGEN-LIKE ATOMS IN WAVE MECHANICS

Presented by

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INTRODUCTION

1. In view of the recent experimental determination of the dispersion by atomic hydrogen[1] it seems interesting to apply the theory of dispersion developed by Schrodinger[2] 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 Schrodinger[3] and Eckart[4], as extended by Epstein[5], for in this way we immediately obtain an equation free of relativistic terms.

In what follows, in order to preserve a continuity of the discussion, details of calculations are omitted from the main text and are given as Supplementary Notes at the end of the paper. References will be found immediately preceding the Supplementary Notes.

THE WAVE EQUATION

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 nucleous being situated at the origin. The field of the wave and of the nucleous can be represented by a vector potential $\overline{A}$ and a scalar potential ϕ. We may take $A_x = A_y = 0$, $A_z = -c^2F \sin\omega(t-y/c)/\omega$, and $\phi = \kappa e/r$, where $\omega = 2\pi\nu$,

κe the charge of the nucleous, c the velocity of light, and F a constant, all quantities being in electrostatic units. In fact, using these potentials in $\bar{B} = \frac{1}{c^2} \nabla \times \bar{A}$ we obtain

$$B_x = \frac{F}{c} \cos \omega (t - y/c), \quad B_y = B_z = 0,$$

$$H_x = F c \cos \omega (t - y/c), \quad H_y = H_z = 0.$$

Similarly, substituting $\bar{A}$ and ϕ into $\bar{E} = -\nabla\phi - \frac{1}{c^2}\frac{\partial \bar{A}}{\partial t}$, there results

$$E_x = \frac{ex}{r^3}, \quad E_y = \frac{ey}{r^3}, \quad E_z = \frac{ez}{r^3} + F \cos \omega (t - y/c).$$

These quantities satisfy Maxwell's equations and represent the desired fields.

The corresponding Hamilton-Jacobi partial differential equation is

$$\frac{1}{2\mu}\left[\left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2\right] + \frac{eF}{\mu\omega}\frac{\partial S}{\partial z} \sin \omega (t - y/c) + \frac{e^2F^2}{2\mu\omega^2} \sin^2 \omega (t - y/c)$$
$$- \frac{\kappa e^2}{r} + \frac{\partial S}{\partial t} = 0$$

where μ = mass of the electron and $\bar{p} = (p_x, p_y, p_z)$ its momentum (see Note A). Putting $\frac{\partial S}{\partial x} = \frac{hi}{2\pi}\frac{\partial}{\partial x}$,

$$\frac{\partial S}{\partial y} = \frac{hi}{2\pi}\frac{\partial}{\partial y}, \quad \frac{\partial S}{\partial z} = \frac{hi}{2\pi}\frac{\partial}{\partial z}, \quad \frac{\partial S}{\partial t} = \frac{hi}{2\pi}\frac{\partial}{\partial t}$$

and considering the resulting expression as operating on ψ, we obtain, upon slight simplification

$$\nabla^2\psi - \frac{2ieF}{h\nu}\frac{\partial \psi}{\partial z} \sin \omega (t - y/c) + \frac{8\pi^2\mu e^2}{h^2}\left[\frac{\kappa}{r} - \frac{F^2 \sin^2 \omega (t - y/c)}{2\mu\omega^2}\right]\psi$$
$$- \frac{4\pi i \mu}{h}\frac{\partial \psi}{\partial t} = 0 \qquad (1)$$

which, to the desired degree of approximation, reduces to

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

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 (2) we let

$$\psi = \psi(l,m,n) = A(l,m,n)e^{\frac{2\pi i E_l t}{h}}\left[\psi_0(l,m,n) + \psi_1(l,m,n)\right] \qquad (3)$$

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

$$\nabla^2\psi_0(l,m,n) + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_l\right)\psi_0(l,m,n) = 0. \qquad (4)$$

Then, to the desired order of approximation, equation (2) reduces to

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

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

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

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

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

where, as in the following, the upper sign goes with the subscript 1, the lower with the subscript 2. (For reduction of (1) to (6) see Note B).

SOLUTION OF THE WAVE EQUATION

3. The usual method of solving an equation such as (6) is to expand $\partial\psi_0(\ell,m,n)/\partial z$ and $u(\ell,m,n)$, 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 $\psi_0(\ell,m,n)$, as was done by Schrodinger[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, $T(\ell',m',n')$, defined as follows

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

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

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

We have therefore, (see Note C)

$$\nabla^2 T(l',m',n') - \left(\alpha^2 + \frac{2\alpha l'}{r}\right) T(l',m',n') = 0 \qquad (9)$$

It can be shown[6] (see Note D) 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

$$r\partial\psi_0(l,m,n)/\partial z = \sum a(l,m,n;l',m',n')\, T(l',m',n') \qquad (10)$$

and

$$u(l,m,n) = \sum b(l,m,n;l',m',n')\, T(l',m',n') \qquad (11)$$

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 inhomogeniety of equation (6) all c's must be zeros. Thus, the set of T's is sufficient.

Substituting (10) and (11) into (6)

$$\sum b(l,m,n;l',m',n')\nabla^2 T(l',m',n')$$

$$+\ \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r}+E_l\pm h\nu\right)\sum b(l,m,n;l',m',n')T(l',m',n')$$

$$=\frac{eF'}{h\nu}\cdot\frac{1}{r}\sum a(l,m,n;l',m',n')\,T(l',m',n'),$$

or using (9) and equating coefficients of corresponding T's, we obtain

$$b(l,m,n;l',m',n')\left[\alpha^2+\frac{2\alpha l'}{r}+\frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r}+E_l\pm h\nu\right)\right]$$

$$=\frac{eF'}{h\nu r}a(l,m,n;l',m',n') \qquad (12)$$

If we let

$$\alpha^2=-8\pi^2\mu(E_l\pm h\nu)/h^2, \qquad (13)$$

equation (12) reduces to

$$2b(l,m,n;l',m',n')\left[\alpha l'+\frac{8\pi^2\mu\kappa e^2}{h^2}\right]=\frac{eF'a(l,m,n;l',m',n')}{h\nu}$$

which is satisfied provided

$$b(l,m,n;l',m',n')=eF'a(l,m,n;l',m',n')/2h\nu(\eta+l'\alpha) \qquad (14)$$

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

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

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

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

The usual solution of (4) may be put in the form

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

where

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

and

$$E_\ell = -2\pi^2 \kappa^2 \mu e^4 / h^2 \ell^2.$$

APPLICATION TO THE NORMAL STATE

5. We are interested in the case of atoms in the normal state, i.e. the case when $\ell = 1$, $m = n = 0$. In this case, by (16) and (17)

$$\psi_0(1,0,0) = \chi(1,0) = e^{-r\eta}$$

$$\partial\psi_0(1,0,0)/\partial z = (\partial r/\partial z)\, \partial\psi_0(1,0,0)/\partial r = -\eta e^{-r\eta} \cos\theta \qquad (18)$$

Comparing (18) with (10) and (7) we see that since $\frac{\partial\psi_0(1,0,0)}{\partial z}$ does not contain φ, $a(1,0,0; \ell', m', n') = 0$, unless $m' = 0$. Then, since θ enters (18) only as $\cos\theta$,

$a(1, 0, 0; \ell', 0, n') = 0$, unless $n' = 1$.

Putting $n' = 1$, and remembering that $\ell' > n'$, equation (10) reduces to

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

Since a's may depend upon α, we put $a(1,0,0;\ell',0,1) = a(\ell';\alpha)$, so that, changing the summation index, (10) reduces to

$$r\partial\psi_0(1,0,0)/\partial z = \cos\theta \sum_{s=2}^{\infty} a(s,\alpha)\, Z(s,1,\alpha) \qquad (19)$$

The coefficents $a(s,\alpha)$ are found to be (see Note E)

$$a(s,\alpha) = -\eta(\eta+\alpha)^{s-2}(s+1)!\,(2\alpha)^4/(\eta-\alpha)^{s+2}. \qquad (20)$$

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

$$u_1 = \cos\theta \sum_{s=2}^{\infty} b(s,\alpha_1)\, Z(s,1,\alpha_1) = \frac{eF}{2h\nu}\cos\theta \sum_{s=2}^{\infty} \frac{a(s,\alpha_1)\, Z(s,1,\alpha_1)}{\eta + s\alpha_1} \qquad (21)$$

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

ELECTRICAL MOMENTS AND DISPERSION

6. We can now compute the electric moments. We obtain (see Note G) $M_x = M_y = 0$, and

$$M_z = e\int z\,\psi(l,m,n)\,\overline{\psi}(l,m,n)\,d\tau$$

$$= \frac{-128e^2\eta^4}{3h\nu} F\cos\omega t \left[\alpha_1^4 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2\eta+s\alpha_1)(\eta+\alpha_1)^{2s-5}}{(\eta+s\alpha_1)(\eta-\alpha_1)^{2s+5}}\right.$$

$$\left. - \alpha_2^4 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2\eta+s\alpha_2)(\eta+\alpha_2)^{2s-5}}{(\eta+s\alpha_2)(\eta-\alpha_2)^{2s+5}}\right] \qquad (22)$$

Since this quantity M is also the leading term of the matrix $M(l,m,n)$, i.e. $M(1,0,0;1,0,0)$ 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 (see Note G)

$$n^2-1 = \frac{16\,N\,h^6}{3\pi^5 e^6 \mu^3 \kappa^4 \beta^6}\left[(1-\beta)^2 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2-sq_1)}{(sq_1-1)}\left(\frac{1-q_1}{1+q_1}\right)^{2s}\right.$$

$$\left. + (1+\beta)^2 \sum_{s=2}^{\infty} \frac{s(s^2-1)(2-sq_2)}{(sq_2-1)}\left(\frac{1-q_2}{1+q_2}\right)^{2s}\right] \qquad (23)$$

where $\beta = -h\nu/E_1 = \nu/\nu_1 = h^3\nu/2\pi^2\kappa^2\mu e^4$, $q_1 = \sqrt{(1-\beta)}$, $q_2 = \sqrt{(1+\beta)}$, and 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 wave length λ we may write

$$n^2-1=\frac{9Nh^6}{32\pi^5e^6\mu^3\kappa^4}\left(1+1.477\beta^2+2.39\beta^4+\dots\right)$$

$$=\frac{9Nh^6}{32\pi^5e^6\mu^3\kappa^4}\left(1+1.477\,c^2/\nu_1^2\lambda^2+\dots\right)$$

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

APPLICATION TO THE HYDROGEN ATOM

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

$$n^2-1=2.24\times10^{-4}(1+1.228\times10^{-10}/\lambda^2).$$

Substitution of numerical values into (22) gives the following

$-h\nu/E_1$	λ in Å.	$(n^2-1)\times10^4$
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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SUPPLEMENTARY NOTES

Note A. The Lagrangian function in this case is

$$L = T_\mu + T_e - U, \quad \text{where}$$

T_μ = kinetic energy of the electron mass

$$= \tfrac{1}{2}\mu\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$$

T_e = kinetic energy of the electro-magnetic field of the electron

$$= e\bar{v}\cdot\bar{A}/c^2 = e v_z A_z/c^2 = -e\dot{z}F\sin\omega(t-y/c)/\omega$$

U = potential energy of the electron

$$= -e\phi = -\kappa e^2/r$$

Now

$$p_x = \frac{\partial L}{\partial \dot{x}} = \mu\dot{x}, \quad p_y = \frac{\partial L}{\partial \dot{y}} = \mu\dot{y}, \quad p_z = \frac{\partial L}{\partial \dot{z}} = \mu\dot{z} - eF\sin\omega(t-y/c)/\omega$$

and therefore

$$\dot{x} = p_x/\mu, \quad \dot{y} = p_y/\mu, \quad \dot{z} = p_z/\mu + eF\sin\omega(t-y/c)/\mu\omega$$

Therefore the Hamiltonian function is

$$H = -L + \sum p\dot{q} = -L + p_x\dot{x} + p_y\dot{y} + p_z\dot{z}$$

$$= -\tfrac{1}{2}\mu\left(\dot{x}^2+\dot{y}^2+\dot{z}^2\right) + e\dot{z}F\sin\omega(t-y/c)/\omega - \kappa e^2 r$$

$$+\mu\dot{x}^2 + \mu\dot{y}^2 + \mu\dot{z}^2 - eF\dot{z}\sin\omega(t-y/c)/\omega$$

$$= \frac{1}{2}\mu(\dot{x}^2+\dot{y}^2+\dot{z}^2) - \kappa e^2/r$$

$$= \frac{1}{2}\mu\Big[p_x^2/\mu^2 + p_y^2/\mu^2 + p_z^2/\mu^2 + e^2F'^2\sin^2\omega(t-y/c)/\mu^2\omega^2$$

$$+ 2p_z eF'\sin\omega(t-y/c)/\mu^2\omega\Big] - \kappa e^2/r$$

$$= \frac{1}{2\mu}(p_x^2+p_y^2+p_z^2) + p_z eF'\sin\omega(t-y/c)/\mu\omega$$

$$+ e^2F'^2\sin^2\omega(t-y/c)/2\mu\omega^2 - \kappa e^2/r.$$

Therefore the Hamilton-Jacobi equation is

$$H\left(x,y,z;\ \frac{\partial S}{\partial x},\ \frac{\partial S}{\partial y},\ \frac{\partial S}{\partial z};\ t\right) + \frac{\partial S}{\partial t} = 0$$

or $$\frac{1}{2\mu}\left\{\left(\frac{\partial S}{\partial x}\right)^2+\left(\frac{\partial S}{\partial y}\right)^2+\left(\frac{\partial S}{\partial z}\right)^2\right\} + \frac{eF'}{\mu\omega}\left(\frac{\partial S}{\partial z}\right)\sin\omega(t-y/c)$$

$$+ \frac{e^2F'^2}{2\mu\omega^2}\sin^2\omega(t-y/c) - \kappa e^2/r + \frac{\partial S}{\partial t} = 0$$

<u>Note B.</u> Taking F as large as .04E.S.U. we have

$$\frac{F'^2}{2\mu\omega^2}\sin^2\omega(t-y/c)\ (=)\ F'^2/2\mu\omega^2$$

$$\frac{F'^2}{2\mu\omega^2}\Big/\frac{\kappa}{r}\ (=)\ \frac{F'^2 r}{2\mu\omega^2} = \frac{F'^2 r}{8\pi^2\mu\nu^2}$$

$$(=)\ \frac{.0016\times 0.5\times 10^{-8}}{8\pi^2\times 9\times 10^{-28}\nu^2}\ (=)\ 10^{14}/\nu^2$$

Thus the term in F^2 of equation (1) can certainly be neglected if $10^{14}/\nu^2 < 10^{-4}$, or $\nu > 10^9$.

Since

$$\sin\omega(t-y/c) = \frac{1}{2i}\left(e^{i\omega t}e^{-i\omega y/c} - e^{-i\omega t}e^{i\omega y/c}\right)$$

and

$$e^{\pm i\omega y/c} = \cos(\omega y/c) \pm i\sin(\omega y/c)$$
$$= 1 \pm i\omega y/c - (\omega y/c)^2 \pm \ldots\ldots$$

the factor $e^{\pm i\omega y/c}$ will be negligible whenever $\omega y/c \ll 1$.

But $\omega y/c \ (=)\ 2\pi\nu\cdot 5\cdot 10^{-9}/3\cdot 10^{10} \ (=)\ 10^{-18}\nu$

and since for visible $\nu < 10^{15}$, $\omega y/c < 10^{-3} \ll 1$,

we are justified in writing $\sin\omega t$ instead of $\sin\omega(t-y/c)$.

Equation (1) then takes the form of (2).

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

Using substitution

$$\psi = A(l,m,n)\, e^{2\pi i E_l t/h}\left[\psi_0(l,m,n) + \psi_1(l,m,n)\right] \qquad (3)$$

we reduce (2) to the form

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

By the condition (4), since ψ_0 is not a function of t, this becomes on division by $A(l,m,n)e^{2\pi i E_l t/h}$

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

Since, as we will see, ψ_1 is small compared to ψ_0, the second term on the right side is a small correction to a small quantity, and hence can be neglected. We then obtain

$$\nabla^2\psi_1 + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_\ell\right)\psi_1 - \frac{4\pi i\mu}{h}\frac{\partial\psi_1}{\partial t} = \frac{2ieF}{h\nu}\frac{\partial\psi_0}{\partial z}\sin\omega t$$

Putting $\psi_1 = e^{i\omega t}u_1 - e^{-i\omega t}u_2$, and $\sin\omega t = \frac{1}{2i}\left(e^{i\omega t} - e^{-i\omega t}\right)$

we have, assuming u_1 and u_2 independent of t,

$$e^{i\omega t}\left[\nabla^2 u_1 + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_\ell\right)u_1 + \frac{4\pi\mu\omega}{h}u_1\right]$$

$$- e^{-i\omega t}\left[\nabla^2 u_2 + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_\ell\right)u_2 - \frac{4\pi\mu\omega}{h}u_2\right]$$

$$= \frac{eF}{h\nu}\frac{\partial\psi_0}{\partial z}\left(e^{i\omega t} - e^{-i\omega t}\right)$$

Equating coefficients of the two exponentials

$$\nabla^2 u_1 + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_\ell + h\nu\right)u_1 = \frac{eF}{h\nu}\frac{\partial\psi_0}{\partial z}, \text{ and}$$

$$\nabla^2 u_2 + \frac{8\pi^2\mu}{h^2}\left(\frac{\kappa e^2}{r} + E_\ell - h\nu\right)u_2 = \frac{eF}{h\nu}\frac{\partial\psi_0}{\partial z},$$

which can be written as (6).

<u>Note C.</u> Equation (7) may be written

$T = S_n Z/r^n$, where S_n is a spherical harmonic.

$$S_{n'} = r^{n'} e^{im'\varphi} P_{n'}^{m'}(\cos\theta).$$

Then

$$\nabla^2 T = \frac{Z}{r^{n'}} \nabla^2 S_{n'} + 2\nabla S_{n'} \cdot \nabla \frac{Z}{r^{n'}} + S_{n'} \nabla^2 \frac{Z}{r^{n'}}.$$

Now $\nabla^2 S_{n'} = 0$, and $\nabla \frac{Z}{r^{n'}}$ is in the direction of the radius vector so that we only need $\nabla_r S_{n'}$ which is equal to $n' S_{n'}/r$. Therefore

$$\nabla^2 T = \frac{2n' S_{n'}}{r} \frac{d}{dr}\left(\frac{Z}{r^{n'}}\right) + S_{n'} \frac{1}{r^2} \frac{d}{dr}\left[r^2 \frac{d}{dr}\left(\frac{Z}{r^{n'}}\right)\right]$$

$$= S_{n'} r^{-n'} \left[\frac{d^2 Z}{dr^2} + \frac{2}{r}\frac{dZ}{dr} - \frac{n'(n'+1)}{r^2} Z\right],$$

or by equation (8)

$$= S_{n'} \frac{Z}{r^{n'}} \left(\frac{2\alpha l'}{r} + \alpha^2\right),$$

$$= T\left(\frac{2\alpha l'}{r} + \alpha^2\right),$$

which is the equation (9).

If in the equation (8) we put $\alpha^2 = -2\mu E/\mathcal{K}^2$; $2\alpha l' = -2\mu e^2/\mathcal{K}^2$, and $n' = k-1$, we obtain Epstein's equation for $X(s, \alpha)$. See reference 7, equation (2).

<u>Note D.</u> Since $e^{im'\varphi} P_{n'}^{m'}(\cos\theta)$ of T is the usual surface spherical harmonic we need to prove only the completeness of the function $Z(l', n', \alpha; r)$ as defined in equation (15).

Equation (8) can be put in the usual Sturm-Liouville's form[6] by multiplying by r^2

$$pZ'' + p'Z' - [n'(n'+1) + \alpha^2]Z + \lambda\rho Z = 0$$

where $p = r^2$, $\rho = r$, $\lambda = -2\alpha l'$. Thus the set of all solutions satisfying the Sturm-Liouville's boundary conditions form a complete orthogonal set.

In the first place λ must be real. For, suppose that corresponding to a complex λ there is a complex solution $Z(\lambda)$, then obviously the conjugate of Z will be a solution for the conjugate value of λ.

Thus, if $Z(\lambda) = X + iY$ is a solution, $X - iY$ will be the solution $Z(\lambda^*)$. Then

$$\int_0^\infty Z(\lambda)\, Z(\lambda^*)\,\rho\, dr = \int_0^\infty (X^2 + Y^2)\,\rho\, dr$$

which is a positive quantity, contrary to the orthogonality conditions.

We may therefore assume l' to be real.

The solution of (8) is easily put in the form $Z = r^{n'}U$, where U satisfies the equation

$$U'' + \frac{2(n'+1)}{r}U' - \left(\alpha^2 + \frac{2\alpha l'}{r}\right)U = 0$$

so that

$$Z = r^{n'} \int_C e^{rz} (z-\alpha)^{n'-l'} (z+\alpha)^{n'+l'} dz$$

where C is chosen so that

$$\int_C \frac{d}{dz}\left[e^{rz}(z-\alpha)^{n'-l'+1}(z+\alpha)^{n'+l'+1}\right] dz = 0.$$

From (9) it is evident that the only singularities to be considered are at $r = 0$, and $r = \infty$. The first has as exponents n' and $-n'-1$. Of these the second leads to a solution infinite at the origin. Thus, our solution must behave as $r^{n'}$ at the origin. Then, by investigation completely analogous to that used by Schrodinger[11], we can easily establish that Z can be finite everywhere only if l' is an integer greater than n'. Then $Z = -\alpha$ is an ordinary point, and $Z = \alpha$ is a pole. This leads immediately to (15).

<u>Note E.</u> Using formula (21) of reference 7, our orthogonality relations for $Z(s,n,\alpha)$ become

$$\int_0^\infty Z(s,n,\alpha)\,Z(s',n,\alpha)\,r\,dr = 0, \quad \text{if } s \neq s',$$

$$\int_0^\infty Z(s,n,\alpha)\,Z(s,n,\alpha)\,r\,dr = \frac{1}{(s+n)!\,(s-n-1)!\,(2\alpha)^{2n+2}}$$

We can also derive the relation

$$\int_0^\infty r^m e^{\beta r} Z(s,n,\alpha)\,dr = \frac{(-1)^{m+n}}{(\alpha+\beta)^{m-n}(2\alpha)^{2n+1}(s-2)!}\,\frac{d^{m-n-1}}{dx^{m-n-1}}\left\{x^{m+n}(1+x)^{s-n-1}\right\}$$

where $x = -2\alpha/(\alpha+\beta)$.

Equations (18) and (19) give

$$-\eta r e^{-r\eta} = \sum_{s=2}^{\infty} a(s,\alpha)\,Z(s,1,\alpha)$$

therefore

$$-\eta\int_0^\infty r^2 e^{-r\eta} Z(s,1,\alpha)\,dr = a(s,\alpha)\int_0^\infty Z(s,1,\alpha)Z(s,1,\alpha)\,r\,dr$$

or, by the above formulae

$$\frac{-\eta(\eta+\alpha)^{s-2}}{(s-2)!\,(\eta-\alpha)^{s+2}} = \frac{a(s,\alpha)}{(s+1)!\,(s-2)!\,(2\alpha)^4}$$

which gives equation (20).

<u>Note F.</u> We must normalize ψ so that $\int \psi\overline{\psi}\,d\tau = 1.$ By (3) this condition becomes

$$A^2(l,m,n)\int \left|\psi_0(l,m,n)+\psi_1(l,m,n)\right|^2 d\tau = 1.$$

Neglecting $\psi_1\overline{\psi}_1$ the left member becomes

$$A^2(l,m,n)\int(\psi_0\overline{\psi}_0 + \psi_0\overline{\psi}_1 + \overline{\psi}_0\psi_1)\,d\tau.$$

Now

$$\psi_0\overline{\psi}_1+\overline{\psi}_0\psi_1 = e^{im\varphi}P_n^m(\cos\theta)\chi(l,n)\left[e^{-i\omega t}\overline{u}_1 - e^{i\omega t}\overline{u}_2\right]$$
$$+ e^{-im\varphi}P_n^m(\cos\theta)\chi(l,n)\left[e^{i\omega t}u_1 - e^{-i\omega t}u_2\right],$$

so that in the $\int(\psi_0\overline{\psi}_1+\overline{\psi}_0\psi_1)\,d\tau$ integration, with respect to φ, will introduce a factor

$$\int_0^{2\pi} e^{\pm im\varphi}\,d\varphi = \frac{1}{\pm im}\left[e^{\pm im\varphi}\right]_0^{2\pi} = 0.$$

Our normalizing condition therefore becomes

$$A^2(l,m,n)\int\psi_0(l,m,n)\,\overline{\psi}_0(l,m,n) = 1.$$

Now

$$\int \psi_0 \bar{\psi}_0 \, d\tau = \int_0^\infty r^2 [\chi(l,n)]^2 dr \int_0^\pi [P_n^m(\cos\theta)]^2 \sin\theta \, d\theta \int_0^{2\pi} d\varphi$$

$$= 2\pi \int_0^\infty r^2 [\chi(l,n)]^2 dr \int_{-1}^{1} [P_n^m(\xi)]^2 d\xi$$

$$= \frac{4\pi (n+m)!}{(2n+1)(n-m)!} \int_0^\infty r^2 [\chi(l,n)]^2 dr$$

Using equation (22) of reference 7, we easily obtain

$$\int_0^\infty r^2 [\chi(l,m,n)]^2 dr = \frac{2\, l^{2n+4}}{(2\eta)^{2n+3}(l+n)!\,(l-n-1)!},$$

so that

$$A^2(l,m,n) = \frac{(2n+1)(2\eta)^{2n+3}(n-m)!\,(l+n)!\,(l-n-1)!}{8\pi (n+m)!\, l^{2n+4}}$$

When $l=1$, $m=n=0$, this becomes $A^2(1,0,0) = \eta^3/\pi$

Note G.

$$M_x = e\int x \psi \bar{\psi}\, d\tau = e A^2(1,0,0) \int x [\psi_0 \bar{\psi}_0 + \psi_0 \bar{\psi}_1 + \bar{\psi}_0 \psi_1] d\tau$$

as in Note F. Since the expression in brackets now does not contain φ and $x = r \sin\theta \cos\varphi$, integration with respect to φ will introduce a factor $\int_0^{2\pi} \cos\varphi \, d\varphi \equiv 0$. Thus $M_x = 0$. Precisely similar argument holds for M_y. For M_z the calculations are as follows:

$$M_z = e\int z \psi \bar{\psi}\, d\tau = e A^2(1,0,0) \int z [\psi_0 \bar{\psi}_0 + \psi_0 \bar{\psi}_1 + \bar{\psi}_0 \psi_1] d\tau.$$

Integration of the first term with respect to θ will contain a factor $\int_0^{\pi} \cos\theta \sin\theta \, d\theta \equiv 0$. Therefore

$$M_z = e A^2(1,0,0) \int z (\psi_0 \overline{\psi}_1 + \overline{\psi}_0 \psi_1) d\tau$$

$$= e A^2(1,0,0) \int z \psi_0 (\psi_1 + \overline{\psi}_1) d\tau, \text{ since } \psi_0 = \overline{\psi}_0 .$$

Now $\psi_1 + \overline{\psi}_1 = [e^{i\omega t} u_1 - e^{-i\omega t} u_2] + [e^{-i\omega t} \overline{u}_1 - e^{i\omega t} \overline{u}_2]$.

Further , by (11), (14)

$$u(1,0,0) = \sum b(1,0,0; l', m', n') T(l', m', n')$$

$$= \frac{eF}{2h\nu} \sum \frac{a(1,0,0; l', m', n')}{(\eta + l'\alpha)} T(l', m', n')$$

which, since m'= 0 and n'= 1, becomes on using (7)

$$u(1,0,0) = \frac{eF}{2h\nu} \sum_{l'=2}^{\infty} \frac{a(1,0,0; l', 0, 1)}{(\eta + l'\alpha)} T(l', 0, 1)$$

$$= \frac{eF}{2h\nu} \cos\theta \sum_{s=2}^{\infty} \frac{a(s,\alpha)}{(\eta + s\alpha)} Z(s, 1, \alpha),$$

with notation as in (19) and (20). Thus u is real, and therefore

$$\psi_1 + \overline{\psi}_1 = 2(u_1 - u_2) \cos \omega t$$

$$M_z = 2e A^2(1,0,0) \cos \omega t \int z \psi_0 (u_1 - u_2) d\tau$$

Now

$$\int z\,\psi_0\,u\,d\tau = \int r\cos\theta\,\chi(1,0)\,u\,d\tau$$

$$= \frac{eF'}{2h\nu}\sum_{s=2}^{\infty}\frac{a(s,\alpha)}{(\eta+s\alpha)}\int r\cos^2\theta . e^{-\eta r}Z(s,1,\alpha)\,d\tau$$

$$= \frac{eF'}{2h\nu}\sum_{s=2}^{\infty}\frac{a(s,\alpha)}{(\eta+s\alpha)}\int_0^{\infty} r^3 e^{-\eta r}Z(s,1,\alpha)\,dr\int_0^{\pi}\cos^2\theta\,\sin\theta\,d\theta\int_0^{2\pi}d\varphi$$

$$= \frac{\pi eF'}{h\nu}\sum_{s=2}^{\infty}\frac{a(s,\alpha)}{(\eta+s\alpha)}\int_0^{\infty} r^3 e^{-\eta r}Z(s,1,\alpha)\,dr\int_0^{\pi}\cos^2\theta\,\sin\theta\,d\theta$$

$$= \frac{2\pi eF'}{3h\nu}\sum_{s=2}^{\infty}\frac{a(s,\alpha)}{(\eta+s\alpha)}\int_0^{\infty} r^3 e^{-\eta r}Z(s,1,\alpha)\,dr.$$

Using the formula of Note E, this becomes

$$= \frac{4\pi eF'}{3h\nu}\sum_{s=2}^{\infty}\frac{a(s,\alpha)(2\eta+\alpha s)\,(\eta+\alpha)^{s-3}}{(s-2)!\,(\eta+s\alpha)\,(\eta-\alpha)^{s+3}}$$

or, substituting from (20)

$$\int z\,\psi_0\,u\,d\tau = -\frac{64\pi\eta eF'}{3h\nu}\alpha^4\sum_{s=2}^{\infty}\frac{s(s^2-1)(2\eta+\alpha s)\,(\eta+\alpha)^{2s-5}}{(\eta+s\alpha)\,(\eta-\alpha)^{2s+5}}$$

Thus

$$M_z = 2eA^2(1,0,0)\cos\omega t\int z\,\psi_0\,(u_1-u_2)\,d\tau$$

$$= \frac{2e\eta^3}{\pi}\cos\omega t\int z\,\psi_0\,(u_1-u_2)\,d\tau$$

$$= -\frac{128e^2\eta^4}{3h\nu}F'\cos\omega t\Bigg[\alpha_1^4\sum_{s=2}^{\infty}\frac{s(s^2-1)(2\eta+\alpha_1 s)\,(\eta+\alpha_1)^{2s-5}}{(\eta+s\alpha_1)(\eta-\alpha_1)^{2s+5}}$$

$$-\alpha_2^4\sum_{s=2}^{\infty}\frac{s(s^2-1)(2\eta+\alpha_2 s)(\eta+\alpha_2)^{2s-5}}{(\eta+s\alpha_2)(\eta-\alpha_2)^{2s+5}}\Bigg] \qquad (22)$$

Since by (13) and (14)

$$\alpha^2/\eta^2 = \frac{-h^2(E_1 \pm h\nu)}{2\pi^2\mu e^4 \kappa^2} = \frac{-h^2E_1(1 \pm h\nu/E_1)}{2\pi^2\mu e^4 \kappa^2} = 1 \pm h\nu/E_1$$

$= 1 \mp \beta$, where $\beta = -h\nu/E_1$. Putting $q_1 = \sqrt{1-\beta}$, $q_2 = \sqrt{1+\beta}$, and substituting these relations into (22) we obtain (23).