Exactly Soluble System (II)
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LEGENDRE POLYNOMIALS AND ASSOCIATED LEGENDER FUNCTIONS AND SOLLUTION

The first result in the search for separated solution e.g $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\frac{1}{r^2\sin\phi}\left(\sin\phi\frac{\partial\phi}{\partial\phi^2}\right)=0$ which ultimately leads to the formulas pair $r^n p_n \cos\phi$ and $r^{-(n+1)} P_n \cos\phi$, is the pair of differential equations

$$\frac{d}{dz}\left[(1-z^2)\frac{dP_l(z)}{dz}\right]+l(l+1)P_l(z)=0$$

where $P_l z$ is the Legendre Polynomial of degree l. The properties of polynomial restric l in such a way that is must be zero or an integer.

$$P_l(z)=\frac{1}{2^l \lfloor l}\frac{d^l(z^2-1)}{dz^l}$$

[The r-equation is equidimensional and thus has solution, easily found, which are powers of r. The ϕ-equation is legendre's equation. We begin by transforming it to a somewhat simpler form by a change of independent variable

$$r^2\frac{d^2f}{dr^2}+2r\frac{df}{dr}-\lambda f=0 \text{ and}$$

$$\frac{d}{d\phi}\left(\sin\phi\frac{dP}{d\phi}\right)+\lambda\sin\phi P=0\,]$$

$$z=\cos\phi\,]$$

When we know two adjacent polynomials, one can calculate others from the recursion formula.

$$(l+1)P_{l+1}(z)-(2l+1)zP_l(z)+lP_{l-1}(z)=0$$

The associated functions of degree l and $|m|$, where $l=0,1,2\cdots$ and $|m|=0,1,2\cdots l$

are defined in terms of the legendre Polynomials by

$$P_l^{|m|}(z) = (1-z^2)^{|m|/2} \frac{d^{|m|}}{dz^{|m|}} P_l(z)$$

This Satisfies the differential equation

$$(1-z^2)\frac{d^2 P_l^{|m|} z}{dz^2} - 2z\frac{dP_l^{|m|}}{dz} + \left[l(l+1) - \frac{m^2}{1-z^2}\right] P_l^{|m|}(z) = 0 \quad -(1)$$

Solution of $T(\theta)$ dependent-equation

Comparing equation (1), the differential equation which is satisfied by the associated legendre function, with equation -

$$(1-z^2)\frac{d^2 P}{dz^2} - 2z\frac{dP}{dz} + \left[\beta - \frac{m^2}{1-z^2}\right] P = 0$$

(from transformed $T(\theta)$ equation), we see that they are of the same form, we need only to identify $P(z)$ with $P_l^{|m|}(z)$ and β with $l(l+1)$. we need now have

$$T(\theta) = N\theta\, P_l^{|m|}(z) \quad -(2)$$

$$\beta = l(l+1) \quad -(3)$$

Where l is known as the azimuthal quantum number. Here $l \geq m, (m+1)(m+2)(m+3)---$

One should now normalize $T(\theta)$. One knows that since the variable is $z = \cos\theta$, the electron is confined between $z=-1$ and $z=+1$

The value of the integral is

$$\int_{-1}^{+1} P_l^{|m|}(z) P_{l'}^{|m|}(z)\, dz = \frac{2}{(2l+1)} \frac{l+|m|!}{l-|m|!} \delta_{ll'} \quad -(4)$$

has been determined. The symbol $\delta_{ll'}$ the Kronecker delta.

has the value zero when $l \neq l'$ and unity when $l = l'$.

variation form $z = -1$ to $z = +1$, corresponds to variation of θ from zero to π. The normalisation integral.

$$\int_0^{\pi} T^*_{(\theta) mL} \, T_{(\theta) mL} \sin\theta \, d\theta = 1$$

becomes.

$$N_\theta^2 \int_{-1}^{+1} P_L^{(M)} z \, P_L^{|M|} z \, dz = 1 \quad -(5)$$

in terms of the associated legendre functions. Substituting for the integral its value in terms of L and m from equation (4). in 3(5) we find

$$N_\theta^2 = \frac{(2L+L)\,(L-|m|)!}{2(L+|m|)!}$$

substituting above equation in (2), we get

$$T_\theta = \frac{(2L+1)\,(l-|m|)!}{2(L+|m|)!} \, P_L^{|m|} \cos\theta \quad - (6)$$

The Solution of r dependent equation:-

$$\text{Equation} - \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR(r)}{dr}\right) - \frac{\beta}{r^2} R(r) + \frac{8\pi^2 \mu}{h^2}\left[E-V\right] R(r) = 0 \quad -(7)$$

Here we know that $\beta = L(l+1)$ and E is negative and

$$V = -\frac{ze^2}{r}$$

Suppose we make the following substitutions

$$\alpha^2 = -\frac{8\pi^2 \mu E}{h^2} \quad \text{and} \quad \lambda = \frac{4\pi^2 \mu z e^2}{h^2 \alpha} \quad -(8)$$

and $\rho = 2\alpha r$, where ρ is a new independent variable lying between 0 and ∞

$$S(\rho) = R(r) \text{ then}$$

$$\frac{dS}{d\rho} = \frac{dS}{dr} \cdot \frac{dr}{d\rho} \text{ and } \frac{d\rho}{dr} = 2\alpha$$

Putting $\beta = l(l+1)$ and, making the appropriate substitutions, the r dependent equation (7) modifies

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2 \frac{dS}{d\rho}\right) + \left[-\frac{l(l+1)}{\rho^2} \frac{1}{4} + \frac{\lambda}{\rho}\right]S = 0 \quad (9)$$

For large values of ρ, equation (9) becomes approximately as

$$\frac{d^2S}{d\rho^2} = \frac{S}{4} \quad \text{— (10)}$$

Solution of this equation are $S = e^{\rho/2}$ and $S = e^{-\rho/2}$; Only the Second is suitable for wave functions. Assume that the Solution of the complete equation is in the following form

$$S(\rho) = e^{-\rho/2} F ; \; 0 \leq \rho \leq \infty \quad \text{— (11)}$$

Then $\dfrac{dS}{d\rho} = e^{-\rho/2}\dfrac{dF}{d\rho} - \dfrac{1}{2} e^{-\rho/2} F$ — (12)

On making the appropriate substitutions in equation (9)

$$\frac{d^2f}{d\rho^2} + \frac{df}{d\rho}\left(\frac{2}{\rho} - 1\right) + \left(\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} - \frac{1}{\rho}\right)f = 0 \quad -(13)$$

Coefficients of $\frac{df}{d\rho}$ and f posses singularities at the origin, which is a regular point. Therefore a power series can be substituted for f begining with a non-vanishing constant term.

let $f = \rho^s L$ where $L = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots$ $-(14)$

Then $\frac{df}{d\rho} = \rho^s \frac{dL}{d\rho} + s\rho^{s-1}L$ $-(15)$

and $\frac{d^2f}{d\rho^2} = \rho^s \frac{d^2L}{d\rho^2} + 2s\rho^{s-1}\frac{dL}{d\rho} + s(s-1)\rho^{s-2}L$ $-(16)$

Multiplying equation (13) by ρ^2

$$\rho^2 \frac{d^2f}{d\rho^2} + (2\rho - \rho^2)\frac{df}{d\rho} + (\lambda-1)\rho f - l(l+1)f = 0 \quad -(17)$$

Substituting for $\frac{d^2f}{d\rho^2}$ and $\frac{df}{d\rho}$

$$\rho^{s+2}\frac{d^2L}{d\rho^2} + 2s\rho^{s+1}\frac{dL}{d\rho} + s(s-1)\rho^s L + 2\rho^{s+1}\frac{dL}{d\rho} + 2s\rho^s L$$
$$- \rho^{s+2}\frac{dL}{d\rho} - s\rho^{s+1}L + (\lambda-1)\rho^{s+1}L - l(l+1)\rho^s L = 0 \quad -(18)$$

The equation is an identity in ρ, and therefore coefficient of individual powers of ρ get vanished.

Taking the coefficient of ρ^s

$$[s(s-1) + 2s - l(l+1)]a_0 = 0$$

Since $a_0 \neq 0$ therefore $[s(s-1) + 2s - l(l+1)] = 0$ $-(19)$

Therefore either $s = l$ or $s = -(l+1)$ but the second value does not lead to an acceptable wave funtion.

taking $s = l$

$f(\rho) = \rho^l L$. use equ (14)

Substituting l for s and dividing by ρ^{l+1} in equa (18)

(6)

$$\rho \frac{d^2L}{d\rho^2} + \{2(l+1) - \rho\} \frac{dL}{d\rho} + (\lambda - 1 - l)L = 0 \quad — (20)$$

Suppose $L = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots$ (21)

$$\frac{dL}{d\rho} = a_1 + 2a_2\rho + 3a_3\rho^2 \quad — (22)$$

and $\frac{d^2L}{d\rho^2} = 2a_2 + 6a_3\rho + \cdots$ (23)

Substituting equation (21), (22) and (23) in (20), we get

$$2a_2\rho + 6a_3\rho^2 + 12a_4\rho^3 + \cdots \cdot 2(l+1)(a_1 + 2a_2\rho + 3a_3\rho^2$$
$$- a_1\rho - 2a_2\rho^2 - 3a_3\rho^3 - \cdots) + (\lambda - l - 1)(a_0 + a_1\rho + a_2\rho^2 + \cdots) = 0$$

The equation is an identity in ρ, and therefore, co-efficient of powers of ρ must be vanish individually.

Thus $(\lambda - l - 1)a_0 + 1 \times 2(l+1)a_1 = 0$

and $(\lambda - l - 1)a_1 + \{2 \times 2(l+1) + 1 \times 2\}a_2 = 0$

and $(\lambda - l - 1)a_2 + \{3 \times 2(l+1) + 2 \times 3\}a_3 = 0$

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$$(\lambda - l - 1 - \nu)a_\nu + 2(\nu+1)(l+1) + \nu(\nu+1)a_{\nu+1} = 0$$

if the solution of the main equation is acceptable as a wave function, the series should break off after a finite number of terms (So that ψ approaches zero at infinity). If it break off after the term $\nu = \rho^{n'}$, then we get $(\lambda - l - 1 - n') = 0$ — (24)

where n' has an integral value, 0, 1, 2

Suppose $\lambda = n$, then

$$n \geq l+1 \quad - - (25)$$

As l is an integer, n should be an integer of series 1, 2, 3 . . . n is known as the Principal quantum number. Thus the three quantum numbers defining the State of hydrogen atom are as follows:

Magnetic quantum number $m = 0, \pm 1, \pm 2, \pm 3 \ldots$

Azimuthal quantum number $l \geq m, (m+1), (m+2) (m+3) \ldots$

Principal quantum number $n \geq l \pm 1$

It becomes more convenient for the interpretation of spectra to rewrite these number as:

$$n = 1, 2, 3 \ldots$$
$$l = 0, 1, 2 \ldots (n-1)$$
$$m = -l, -l+1 \ldots -1, 0, +1 \ldots +l-1, l$$

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