The *Schrödinger* equation in the motion of electrons

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Abstract

In the present work the solution of the *Schrödinger* equation for the Hydrogen atom in spherical coordinates is exposed in development. This equation is separated into a polar, azimuthal and radial equation by means of the method of separation of variables, the solutions of these equations allow to obtain the 3 quantum numbers: principal quantum number, orbital quantum number and magnetic quantum number.

1 Introduction

The *Schrödinger* equation for the time-independent hydrogen atom consists of a differential equation whose solution gives the probability of finding the electron in a certain region of space. Given the geometry of the hydrogen atom, it is convenient to approach this equation in spherical coordinates and arrive at its solution by means of the method of separation of variables, which consists of separating the wave function (solution of the equation) as the multiplication of three functions, a that depends on the radius, another that depends on the polar angle and a last one that depends on the azimuth angle.[1].

2 Methods

To arrive at the solution of the polar, azimuthal, and radial equations, it was necessary to learn topics such as:

- **Method of separating variables:**
  Let $T = T(x, y)$ perform the substitution $T(x, y) = X(x)Y(y)$ Thus, for

  $$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0$$

  We perform the replacement and obtain:

  $$\frac{\partial^2 XY}{\partial x^2} + \frac{\partial^2 XY}{\partial y^2} = 0$$

  Since Y does not depend on x, nor does X depend on y, we obtain

  $$Y\frac{\partial^2 X}{\partial x^2} + X\frac{\partial^2 Y}{\partial y^2} = 0$$

  Dividing by XY we get

  $$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = 0$$

The term on the left depends on x and the term on the right depends on y, but they must add to zero for any combination, so they must be constant or equal with opposite signs. Let $-k^2$ be the separation constant, then:

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{1}{Y}\frac{d^2Y}{dy^2} = -k^2$$

So

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k^2$$
$$\frac{1}{Y}\frac{d^2Y}{dy^2} = k^2$$

EDO

Requirements to apply the method of separation of variables

- Any function defined such that when looking for solutions in the form of the product of functions of a variable, they give rise to differentiable equations for each of the variables.

  Example

  $$U_{tt} = U_{xx} + Ax$$

  Let's consider $U(x,t) = X(x)T(t)$.
  Replacing we get

  $$XT'' = X''T + Ax$$

  Divide by XT.

  $$\frac{T''}{T} = \frac{X''}{X} + \frac{Ax}{XT}$$

  Variables cannot be separated

- All second order PDEs with constant coefficients, except those with cross derivatives.

- **Legendre differential equation** Legendre's differential equation is of the form

$$(1-x^2)y'' - 2xy' + n(n+1)y = 0 \tag{1}$$

Whose solution can be obtained by means of series of powers, of the form

$$y = \sum_{m=0}^{\infty} C_m x^m$$

After replacing in the equation, it is possible to find a relationship between the coefficients, described as:

$$C_{m+2} = -\frac{(n-m)(n+m+1)}{(m+2)(m+1)}C_m$$

So

$$y = C_0\left(1 - \frac{n(n+1)}{2}x^2 + \frac{(n-2)(n+3)n(n+1)}{4!}x^4 + ...\right)$$
$$+C_1\left(x - \frac{(n-1)(n+2)}{3!}x^3 + \frac{(n-3)(n+4)/n-1)(n+2)}{5!}x^5\right)$$

If n is not an integer, these series converge for $-1 < x < 1$ but diverge if $x = \pm 1$. If n is a positive integer or zero, one of the series ends up becoming a polynomial, while the other converges for $-1 < x < 1$ but diverges for $x = \pm 1$.

When finding the Legendre polynomials, it is necessary to multiply by a chosen constant so that the polynomial has the value of 1 if x = 1.

Let's see some examples:

- $P_0(x) = 1$
- $P_1(x) = x$
- $P_2(x)$

$$1 - 3x^2$$
$$(1 - 3x^2)\frac{1}{2}$$
$$(3x^2 - 1)\frac{1}{2}$$

- $P_3(x)$

$$x - \frac{10}{6}x^3$$
$$x - \frac{5}{3}x^3$$
$$3x - 5x^3$$
$$(5x^3 - 3x)\frac{1}{2}$$

3 Results

3.1 Equation of *Schrödinger* in spherical coordinates

Let's remember:
In the hydrogen atom:

$$H = \frac{-h^2}{2m} \bigtriangledown^2 - K\frac{q_e^2}{r}$$

Where:

- h = Planck's constant.
- m = mass of the particle.
- $bigtriangledown^2$ = Laplacian.
- K is the Coulomb constants
- r is the distance between the particles

So the equation for *Schr ddotodinger* is of the form:

$$H\varphi = E\varphi \tag{2}$$

Laplacian in spherical coordinates We know that, in rectangular coordinates

$$\bigtriangledown^2\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2}$$

Transformation of rectangular coordinates to spherical coordinates:

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$$

$$\phi = tan^{-1}\left(\frac{y}{x}\right)$$

Making use of the chain rule. For $\varphi(r,\theta,\phi)$

$$\frac{\partial\varphi}{\partial x} = \frac{\partial\varphi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\varphi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\varphi}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$\frac{\partial\varphi}{\partial y} = \frac{\partial\varphi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial\varphi}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial\varphi}{\partial\phi}\frac{\partial\phi}{\partial y}$$

$$\frac{\partial\varphi}{\partial z} = \frac{\partial\varphi}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial\varphi}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial\varphi}{\partial\phi}\frac{\partial\phi}{\partial z}$$

Taking into account that:

$$x = rsen(\theta)cos(\phi)$$

$$y = rsen(\theta)sen(\phi)$$

$$x = rcos(\theta)$$

We obtain

$$\frac{\partial r}{\partial x} = \frac{\partial}{\partial x}\left(\sqrt{x^2+y^2+z^2}\right) = \frac{2x}{2\sqrt{x^2+y^2+z^2}} = \frac{x}{r}$$

$$\frac{\partial r}{\partial y} = \frac{\partial}{\partial y}\left(\sqrt{x^2+y^2+z^2}\right) = \frac{2y}{2\sqrt{x^2+y^2+z^2}} = \frac{y}{r}$$

$$\frac{\partial r}{\partial z} = \frac{\partial}{\partial z}\left(\sqrt{x^2+y^2+z^2}\right) = \frac{2z}{2\sqrt{x^2+y^2+z^2}} = \frac{z}{r}$$

$$\frac{\partial\theta}{\partial z} = \frac{-(z/r)'}{\sqrt{1-(z/r)^2}} = \frac{-1}{sen(\theta)}\frac{\partial}{\partial z}\left(\frac{z}{r}\right) = \frac{-1}{sen(\theta)}\frac{r - z(\partial r/\partial z)}{r^2}$$

$$= \frac{-1}{sen(\theta)}\frac{r-(r^2cos^2(\theta)/r)}{r^2} = \frac{-1}{sen(\theta)}\frac{sen^2(\theta)}{r} = \frac{-sen(\theta)}{r}$$

$$\frac{\partial\theta}{\partial x} = \frac{cos(\theta)cos(\phi)}{r}$$

$$\frac{\partial\theta}{\partial y} = \frac{cos(\theta)cos(\phi)}{r}$$

Thus:

$$\frac{\partial\varphi}{\partial x} = sen(\theta)cos(\phi)\frac{\partial\varphi}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial\varphi}{\partial\theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial\varphi}{\partial\phi}$$

We define $\frac{\partial}{\partial x}$ as an operator that acts on φ. Then

$$\frac{\partial}{\partial x} = sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial\phi}$$

So

$$\frac{\partial^2}{\partial x^2} = \left(sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial\phi}\right)$$
$$\left(sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial\phi}\right)$$

Using the product rule

$$\frac{\partial^2}{\partial x^2} = sen^2(\theta)cos^2(\phi)\frac{\partial}{\partial r^2} + sen(\theta)cos(\phi)\left(\frac{-1}{r^2}cos(\theta)cos(\phi)\frac{\partial}{\partial\theta} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial^2}{\partial r\partial\theta}\right)$$

$$-cos(\phi)sen(\phi)\left(-r^2\frac{\partial}{\partial\phi}+\frac{1}{r}\frac{\partial^2}{\partial r\partial\theta}\right)+\frac{1}{r}cos(\theta)cos^2(\phi)\left(cos(\theta)\frac{\partial}{\partial r}+sen(\theta)\frac{\partial^2}{\partial r\partial\theta}\right)$$

$$+\frac{1}{r^2}cos(\theta)cos^2(\phi)\left(-sen(\theta)\frac{\partial}{\partial\theta}+cos(\theta)\frac{\partial^2}{\partial\theta^2}\right)-\frac{1}{r^2}cos(\theta)cos(\phi)sen(\phi)\left(-sen^2(\theta)cos(\theta)\frac{\partial}{\partial\phi}\right)$$

$$-\frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\left(-sen(\phi)\frac{\partial}{\partial r}\Delta + cos(\theta)\frac{\partial^2}{\partial\phi\partial\theta}\right)$$

Thus

$$\bigtriangledown^2\varphi(r,\theta,\phi)=\frac{\partial^2\varphi}{\partial r^2}+\frac{2}{r}\frac{\partial\varphi}{\partial r}+\frac{cos(\theta)}{r^2sen(\theta)}\frac{\partial\varphi}{\partial\theta}+\frac{1}{r^2}\frac{\partial^2\varphi}{\partial\theta^2}+\frac{1}{r^2sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}$$

This is

$$\bigtriangledown^2\varphi(r,\theta,\phi)=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right)+\frac{1}{r^2sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta}\right)+\frac{1}{r^2sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}$$

Rewriting equation (2) we obtain

$$\frac{-h^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right)+\frac{1}{r^2sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta}\right)+\frac{1}{r^2sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}\right)-\frac{kq_e^2}{r}\varphi=E\varphi$$

This is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right)+\frac{1}{r^2sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta}\right)+\frac{1}{r^2sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)\varphi=0 \quad (3)$$

3.2 Variable separation method for the *Schrödinger* equation

Now, using the variable separation method:

$$\varphi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

Since Y does not depend on r and R does not depend on θ or phi, we get

$$\frac{\partial\varphi}{\partial r}=\frac{\partial}{\partial r}RY=Y\frac{dR}{dr}$$

$$\frac{\partial\varphi}{\partial\theta}=\frac{\partial}{\partial\theta}RY=R\frac{\partial Y}{\partial\theta}$$

$$\frac{\partial\varphi}{\partial\phi}=\frac{\partial}{\partial\phi}RY=R\frac{\partial Y}{\partial\phi}$$

Replacing in (3)

$$\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2sen^2(\theta)}\frac{\partial^2Y}{\partial\phi^2}+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)RY=0$$

Multiplying by r^2 and dividing by RY, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{Ysen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Ysen^2(\theta)}\frac{\partial^2Y}{\partial\phi^2}+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)=0$$

Separating the radial part and the angular part of the equations and taking into account that a separation constant must be used (see methods section - separation of variables), we obtain the following radial and angular equations

Radial equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)R-AR=0 \tag{4}$$

Angular equation

$$\frac{1}{sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sen^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}+AY=0$$

Where A is the separation constant.
Note that Y still depends on two variables, so for this function we will also proceed to perform the method of separation of variables.
Suppose that

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

So

$$\frac{\partial Y}{\partial\theta}=\frac{\partial}{\partial\theta}\Theta\Phi=\Phi\frac{d\Theta}{d\theta}$$
$$\frac{\partial Y}{\partial\phi}=\frac{\partial}{\partial\phi}\Theta\Phi=\Theta\frac{d\Phi}{d\phi}$$

Replacing in the angular equation we obtain:

$$\frac{\Phi}{sen(\theta)}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+\frac{\Theta}{sen^2(\theta)}\frac{d^2\Phi}{d\phi^2}+A\Phi\Theta=0$$

Multiplying by $sin^2(\theta)$ and dividing by $\Phi\Theta$

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+Asen^2(\theta)=0$$

We separate the polar part (θ) and the azimuthal part (ϕ), obtaining

Polar part

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+Asen^2(\theta)-B=0 \tag{5}$$

Azimuth part

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+B=0 \tag{6}$$

Now we will proceed with the solution of equations (4), (5) and (6), taking into account the following restrictions for the wave function

- The squared wave function is absolutely integrable.
- φ must take a single value at each point in space.
- φ must be continuous.

In addition to this, as previously mentioned, each of the equations to solve provides a quantum number, as we will see below:

- The solution of the radial equation is restricted to integer values. This gives the **principal quantum number** n.
- The solution of the polar equation gives the **orbital quantum number** l
- The solution of the azimuthal equation gives the **magnetic quantum number** m. This given that m represents the dependence with the azimuth angle.

3.3 Solution of the azimuthal equation

$$\frac{d^2\Phi}{d\phi^2} + B\Phi = 0$$

$$\phi(0) = 0\phi(2\pi) = 0$$

ODE of constant coefficients.

Auxiliary equation

$$r^2 + B = 0$$

- if $B < 0$, then $B = -\alpha$, with $\alpha > 0$ then

  $$r^2 - \alpha = 0$$

  $$r = \pm\sqrt{\alpha}$$

  So

  $$\Phi(\phi) = C_1 e^{-\sqrt{\alpha}\phi} + C_2 e^{\sqrt{\alpha}\phi}$$

  Since $\phi(0) = 0$, $C_1 = -C_2$. Later

  $$\Phi = C_2\left(-e^{-\sqrt{\alpha}\phi} + e^{\sqrt{\alpha}\phi}\right)$$

  Since $\phi(2\pi) = 0$. $C_2 = 0$ (trivial solution) or $-e^{-\sqrt{\alpha}2\pi} + e^{\sqrt{\alpha}2\pi} = 0$
  So

  $$2\sqrt{\alpha}2\pi = 0$$

  $$\alpha = 0$$

- If B = 0, then

  $$\Phi'' = 0$$

  $$\Phi' = C$$

  $$\Phi = C\phi + D$$

  Since $\phi(0) = 0$, D = 0 and since $\phi(2\pi) = 0$, then $C2\pi = 0$, then C = 0. Trivial solution

It must happen that $B > 0$, like this

$$r^2 + B = 0$$

$$r = \pm\sqrt{B}i$$

Let $m^2 = B$, we have

$$\Phi(\phi) = C_1 e^{im\phi} + C_2 e^{-im\pi}$$

Since the angle ϕ is the azimuth, we are going to define this angle by measuring itself in the opposite direction to the hands of the clock, from a given angle, thus doing $C_2 = 0$. Then

$$\Phi(\phi) = C_1 e^{im\phi}$$

Note that since the wave function must have a single value at each point in space, then the value of ϕ must be equal to the value of $\phi + 2\pi$ Let's see that it is only fulfilled when m is integer.

m	Φ=C₁(cos(mϕ) +isen (mϕ))	Φ=C₁(cos(m(ϕ+2π) +isen(m(ϕ+2π))
0	C_1(cos (0) +isen (0)) = C_1	C_1(cos(2π) +isen(2π)) = C_1
1	C_1(cos(ϕ)+isen(ϕ))	C_1(cos(m(2π) +isen(m(2π))
2	C_1(cos(2ϕ) +isen(2ϕ))	C_1(cos(2ϕ+4π) +isen(2ϕ+4π))
1/2	C_1(cos(ϕ/2) +isen(ϕ/2))	C_1(cos(ϕ/2+π) +isen(ϕ/2+π))

Thus, m must be an integer and defines the magnetic quantum number, furthermore as:

$$m = -l, -(l+1), ..., 0, 1, ..., l$$

It must happen that l can only take natural values.

3.4 Solution of the polar equation

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + Asen^2(\theta) - B = 0$$

Since $B = m^2$, we have

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + Asen^2(\theta) - m^2 = 0$$

Dividing by $sin^2(\theta)$ and multiplying by Θ

$$\frac{1}{sen(\theta)}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)\Theta = 0 \tag{7}$$

We carry out the replacement

$$P(cos(\theta)) = \Theta(\theta); x = cos(\theta)$$

$$\frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -sen(\theta)\frac{d}{dx}; \frac{d\Theta}{d\theta} = \frac{dP}{dx}\frac{dx}{d\theta} = -sen(\theta)\frac{dP}{dx}$$

Replacing in (7)

$$\frac{1}{sen(\theta)}\frac{d}{dx}\left(sen(\theta)(-sen(\theta))\frac{dP}{dx}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)P = 0$$

$$\frac{d}{dx}\left(1 - x^2\frac{dP}{dx}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)P = 0$$

Applying the product rule for the first term

$$(1-x^2)\frac{d^2P}{dx} - 2x\frac{dP}{dx} + + \left(A - \frac{m^2}{1-x^2}\right)P = 0$$

Similar to **Legendre equation**
Power series solution
Let's suppose

$$P = \sum_{n=0}^{\infty} a_n x^n$$

$$P' = \sum_{n=1}^{\infty} n a_n x^{n-1}$$

$$P'' = \sum_{n=2}^{\infty} n(n-1)a_n x^{n-2}$$

Note that these derivatives are well defined, by the linearity of the derivative.
Replacing

$$(1-x^2)\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} - 2x\sum_{n=1}^{\infty} n a_n x^{n-1} + (A-m^2)\sum_{n=0}^{\infty} a_n x^n = 0$$

Applying the distributive law

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} - \sum_{n=2}^{\infty} n(n-1)a_n x^n - 2\sum_{n=1}^{\infty} n a_n x^n + A\sum_{n=0}^{\infty} a_n x^n - m^2\sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=0}^{\infty}(n+2)(n+1)a_{n+2}x^n - \sum_{n=2}^{\infty} n(n-1)a_n x^n - 2\sum_{n=1}^{\infty} n a_n x^n + A\sum_{n=0}^{\infty} a_n x^n - m^2\sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=2}^{\infty}[(n+2)(n+1)a_{n+2} + ((-n(n-1) - 2n + A - m^2)a_n]x^n = 0$$

We add the terms

$$2a_2 + 6a_3x - 2a_1x + Aa_0 + Aa_1x - m^2a_0 - m^2a_1x = 0$$

Given the linearity of each x^n, we have that these values must be different from zero, then, it must happen that

$$2a_2 + Aa_0 - m^2a_0 = 0$$

$$6a_3 - 2a_1 + Aa_1 - m^2a_1 = 0$$

$$(n+2)(n+1)a_{n+2} + ((-n(n-1) - 2n + A - m^2)a_n = 0 \tag{8}$$

Based on (8) we obtain

$$a_{n+2} = \frac{(n+m)(n+m+1-A)}{(n+2)(n+1)}a_n$$

So

$$P = a_0 + a_1x + \frac{m(m+1)-A}{2}a_0x^2 + \frac{(m+1)(m+3)}{3!}a_1x^3$$
$$+\frac{[((2+m)(3+m)-A)(m(m+1)-A}{4!}a_0x^4 + ...$$

Thus

$$P = a_0(1 + \frac{m(m+1)-A}{2}x^2 + \frac{[((2+m)(3+m)-A)(m(m+1)-A}{4!}x^4 + ...)$$
$$+a_1\left(x + \frac{(m+1)(m+3)}{3!}a_1x^3 + ...\right)$$

Taking this into account, we have that the solution of the equation is of the form

$$P_l^m = (1-x^2)^{m/2}\left(a_0\sum_{n=0}^{\infty}\frac{a_{2n}}{a_0}x^{2n} + a_1\sum_{n=1}^{\infty}\frac{a_{2n+1}}{a_1}x^{2n+1}\right)$$

With coefficients

$$a_{n+2} = \frac{(n+m)(n+m+1-A)}{(n+2)(n+1)}a_n$$

A series solution is useful if the series converges so that from a certain value it can be truncated.This particular series converges if $A = l(l+1)$.
The values of the coefficients a_0 and a_1 are chosen depending on the values of l, to ensure that only the convergent series survives.

3.5 Radial equation solution

Before proceeding with the solution of the equation, it is necessary to emphasize the concepts of particle in bound and unbound state.

- **Particle in a bound state**
  Given a small particle, whose presence is confined to a fairly localized region, such as an atom, its quantum state can be adequately represented by a wave function. The function will only take on significantly nonzero values in a region roughly the size of the atom.

$$Pr(V) = \int_V |\phi(x)|^2 dx$$

- **Particle in an unbound state**
  Their collision states represent particles that can move through an infinite region of space and whose wave function does not decay exponentially toward zero. A particle without spin with a completely defined moment $p = (p_x, p_y, p_z)$ has a state that can be represented by the function:

$$\phi(x, y, z) = e^{i(p_x x + p_y y, p_z z)/h}$$

  Non-normalizable function

Remembering the radial equation

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{h^2}\left(E + \frac{KZq_e^2}{r}\right) R - AR = 0$$

Since $A = l(l+1)$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{h^2}\left(E + \frac{KZq_e^2}{r}\right) R - l(l+1)R = 0$$

Terms

- $R \to 0$ if $r \to \infty$ for all l
- $R \to 0$ if $r \to 0$ for $l \neq 0$

For the chain rule

$$\left[r^2 \frac{d^2}{dr^2} + 2r\frac{d}{dr} + \frac{2mr^2 E}{h^2} + \frac{2mr^2 KZq_e^2}{h^2} - l(l+1)\right] R(r) = 0 \tag{9}$$

It makes sense to use the energy of the free electron as the zero point of the potential energy, that is, in the case $E \to 0$ for the electron away from the nucleus, since it is practically free. Since the presence of positive charge stabilizes the atom. We must consider solutions in which E becomes negative as it approaches the nucleus.
What's more

- If $E > 0$, unbound state, ϕ not normalizable.
- If $E < 0$, bound state, region confined particle, ϕ normalizable.

Let $\alpha^2 = \frac{-2mE}{h^2}$;$\rho = 2\alpha r$. We have

$$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = 2\alpha\frac{d}{d\rho}$$

$$\frac{d^2}{dr^2} = 4\alpha^2\frac{d^2}{d\rho^2}$$

substituting in (9) we obtain

$$\left[\rho^2\frac{d^2}{d\rho^2} + 2\rho\frac{d}{d\rho} - \frac{\rho^2}{4} + \frac{2mKq_e^2\rho}{2\alpha h^2} - l(l+1)\right]R(\rho) = 0$$

If we denote $\beta = \frac{mKZq_e^2}{\alpha h^2}$ and divide by ρ^2 we obtain

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{1}{4} + \frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \tag{10}$$

When $\rho \to \infty$ we obtain:

$$\frac{d^2R}{d\rho^2} - \frac{R}{4} = 0$$

ODE of constant coefficients.

Auxiliary equation

$$r^2 - \frac{1}{4} = 0$$

$$r^2 = \frac{1}{4}$$

$$r = \pm\frac{1}{2}$$

$$R(\rho)_{\rho\to\infty} = e^{\pm\frac{\rho}{2}}$$

Taking into account the conditions previously established for the radial equation, we will only consider the solution with a negative exponent. This is:

$$R(\rho) = e^{-\rho/2}$$

We propose solutions of the form

$$R(\rho) = G(\rho)e^{-\rho/2}$$

So

$$\frac{dR}{d\rho} = \frac{d}{d\rho}e^{-\rho/2} = e^{-\rho/2}\left[\frac{dG}{d\rho} - \frac{G}{2}\right]$$

$$\frac{d^2R}{d\rho^2} = \frac{d^2}{d\rho^2}Ge^{-\rho/2} = \frac{d}{d\rho}e^{-\rho/2}\left[\frac{dG}{d\rho} - \frac{G}{2}\right] = e^{-\rho/2}\left[\frac{d^2G}{d\rho^2} - \frac{dG}{d\rho} + \frac{G}{4}\right]$$

Substituting in (10) we obtain

$$\left[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} + \frac{1}{4} + \frac{2}{\rho}\left(\frac{d}{d\rho} - \frac{1}{2}\right) - \frac{1}{4} + \frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]G = 0$$

Reordering and multiplying by ρ^2

$$\left[\rho^2\frac{d^2}{d\rho^2} + \rho(2-\rho)\frac{d}{d\rho} + \rho(\beta-1) - l(l+1)\right]G = 0 \tag{11}$$

Power series solution

$$G(\rho) = \rho^s \sum_{j=0}^{\infty} b_j \rho^j$$

Thus

$$\rho(2-\rho)\frac{dG}{d\rho} = \rho(2-\rho)\frac{d}{d\rho}\sum_{j=0}^{\infty} b_j \rho^{j+s} = \rho(2-\rho)\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1} = 2\rho\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1} - \rho^2\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1}$$

$$= 2\rho^s \sum_{j=0}^{\infty} b_j(j-s)\rho^j - \rho^{s+1}\sum_{j=0}^{\infty} b_j(j-s)\rho^j$$

$$\rho^2\frac{d^2G}{d\rho^2} = \rho^2\frac{d^2}{d\rho^2}\sum_{j=0}^{\infty} b_j\rho^{j+s} = \rho^2\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^{j+s-2} = \rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j$$

Substituting in (11)

$$\rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j + 2\rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j - \rho^{s+1}\sum_{j=0}^{\infty}(j+s)b_j\rho^j$$

$$+(\beta-1)\rho^{s+1}\sum_{j=0}^{\infty}b_j\rho^j - l(l+1)\rho^s\sum_{j=0}^{\infty}b_j\rho^j = 0$$

Dividing by ρ^s

$$\sum_{j=0}^{\infty} b_j\rho^j[(j+s)(j+s-1)+2(j+s)-l(l+1)] = \sum_{j=0}^{\infty} b_j\rho^j[j+1-\beta+1] \tag{12}$$

The summation on the left can be written as

$$\sum_{j=0}^{\infty} b_j\rho^j[(j+s)(j+s-1)+2(j+s)-l(l+1)] = b_0[s(s-1)+2s-l(l+1)]$$

$$+\sum_{j=0}^{\infty} b_{j+1}\rho^{j+1}[(j+1+s)(j+s)+2(j+s+1)-l(l+1)]$$

We can rewrite (12) as

$$b_0[s(s-1)+2s-l(l+1)] + \sum_{j=0}^{\infty}\rho^{j+1}\{b_{j+1}((j+1+s)(j+1)+2(j+s+1)-l(l+1))$$

$$-b_j(j+s-\beta+1)\} = 0$$

Then since ρ^j are linearly independent, it happens that

$$b_0[s(s-1)+2s-l(l+1)] = 0$$

So $s = l$ y for all j

$$b_{j+1} = \frac{j+l+1-\beta}{(j+1)(j+2l+2}b_j$$

For R not to be divergent, it must truncate at some point, that is, from a certain value it must be zero, there exists j = k such that

$$b_{k+1} = \frac{k+l+1-\beta}{(k+1)(k+2l+2}b_k = 0$$

So

$$k+l+1-\beta = 0$$

This is

$$\beta = k+l+1$$

We going to call $n = k+l+1$ **principal quantum number** which is an integer and $n = 1, 2, 3, ...$
Remembering the definition of β and α

$$\beta^2 = n^2 = \frac{m^2Z^2q_e^4}{\alpha^2h^4} = \frac{-h^2}{2mE}\frac{m^2Z^2q_e^4}{h^4} = \frac{-mZ^2q_e^4}{2Eh^4}$$

So

$$E_n = \frac{-Z^2q_e^2}{2n^2a_0}$$

Where $a_0 = \frac{h^2}{mq_e^2}$ is called the Bohr radius

4 Scope

No updates of the objectives are presented for the second installment, the next step consists of establishing the relationships between the solutions of the equations and corroborating these solutions by means of the finite difference method.

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