Hydrogen Atom

Reading course MAT394 "Partial Differential Equations", Fall 2013

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Schrödinger Equation

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi(\vec{r},t) + V(\vec{r})\Psi(\vec{r},t) \quad (1)$$

where $\vec{r} = (\rho, \varphi, \Theta)$ is the positional vector, and t is time,

$$V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\rho} \quad (2)$$

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Then LHS and RHS are constants. Let $\mathrm{E} = i\hbar\frac{T'(t)}{T(t)}$

$$T(t) = ce^{-\frac{iE}{\hbar}t} \tag{3}$$

Separation of Variables 2

(1) becomes Time Independent Schrödinger Equation:

$$-\frac{\hbar^2}{2m}\Delta\Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{4}$$

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$$\Delta = \frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\Lambda,$$

$$\Lambda = \frac{1}{\sin(\phi)}\frac{\partial}{\partial\phi}(\sin(\phi)\frac{\partial}{\partial\phi}) + \frac{1}{\sin^2(\phi)}\frac{\partial^2}{\partial\theta^2},$$

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$$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial\rho^2}P(\rho)Y(\phi,\theta) + \frac{2}{\rho}\frac{\partial}{\partial\rho}P(\rho)Y(\phi,\theta) + \frac{1}{\rho^2}\Lambda Y(\phi,\theta)P(\rho))+$$
$$V(\vec{r})P(\rho)Y(\phi,\theta) = EP(\rho)Y(\phi,\theta)$$

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$$-\frac{\hbar^2}{2m}\left(\frac{P''(\rho)}{P(\rho)}+\frac{2}{\rho}\frac{P'(\rho)}{P(\rho)}+\frac{1}{\rho^2}\frac{\Lambda Y(\phi,\theta)}{Y(\phi,\theta)}\right)+V(\vec{r})-E=0,$$

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Let $\lambda_1=-\frac{\Lambda Y(\phi,\theta)}{Y(\phi,\theta)}$

$$\Lambda Y(\phi,\theta)=-Y(\phi,\theta)\lambda_1$$

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Separate Variables once again. Let $(\phi, \theta) = \Phi(\phi)\Theta(\theta)$

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Once again, both sides are constants. Let $-\frac{\Theta''(\theta)}{\Theta(\theta)} = \lambda_2$

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ϕ Equation

From (5), plug in m

$$\frac{\sin(\phi)}{\Phi(\phi)}\frac{d}{d\phi}(\sin(\phi)\Phi'(\phi)) + \lambda_1 \sin^2(\phi) = m^2, m\epsilon\mathbb{Z}$$

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$$\frac{d}{dx}((1-x^2)\frac{d\Phi}{dx}) + (\lambda_1 - \frac{m^2}{1-x^2})\Phi = 0 \qquad (7)$$

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$$f'(x) = \sum_{j=0}^{\infty} j a_j x^{j-1}$$

$$f''(x) = \sum_{j=0}^{\infty} j(j-1) a_j x^{j-2}$$

Legendre Polynomials

$$\sum_{j=0}^{\infty} j(j-1)a_j x^{j-2} - \sum_{j=0}^{\infty} j(j-1)a_j x^j - 2\sum_{j=0}^{\infty} j a_j x^j + \lambda_1 \sum_{j=0}^{\infty} a_j x^j = 0$$

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$$(j+2)(j+1)a_{j+2} - (-j(j+1)+\lambda_1)a_j = 0$$

$$a_{j+2} = \frac{j(j+1)-\lambda_1}{(j+2)(j+1)}a_j \tag{8}$$

Legendre Polynomials

Since, we want it to be analytic, we need $\lim_{k\to\infty} a_j = 0$. For that, we need to have the series terminate at some j_{max} such that $a_{j_{max}+1} = 0$. Let $j_{max} = k$

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Rodrigues' Formula

If we take $a_0 = 1$, then solution to $f_k(x)$ is:

$$f_k(x) = \frac{1}{2^k k!} \frac{d^k}{dx^k} (x^2 - 1)^k \tag{9}$$

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$$g'(x) = 2nx(x^2 - 1)^{n-1} = 2nx \frac{g(x)}{x^2 - 1}$$
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$$2ng(x) + 2(n-1)xg'(x) - (x^2 - 1)g''(x) = 0$$

Rodrigue's Formula

Proof(continued).

Using Leibniz Formula and applying derivative n times:

$$\frac{d^n}{dx^n}A(x)B(x) = \sum_{k=0}^{n} \frac{n!}{k!(n-k)!} \frac{d^k A}{dx^k} \frac{d^{n-k} B}{dx^{n-k}}.$$

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First term becomes: $2ng^{(n)}$

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First term becomes: $2ng^{(n)}$
Second term becomes: $2(n-1)xg^{(n+1)} + 2n(n-1)g^{(n)}$

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Proof(continued).

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Third term becomes: $-(x^2-1)g^{(n+2)}(x) - n2xg^{(n+1)} - \frac{n(n-1)}{2}2g^{(n)}(x)$

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Third term becomes: $-(x^2-1)g^{(n+2)}(x) - n2xg^{(n+1)} - \frac{n(n-1)}{2}2g^{(n)}(x)$
Hence, we get:

$$(1-x^2)g^{(n+2)}(x) + -2xg^{(n+1)} + n(n+1)g^{(n)} = 0$$

Hence $g^{(n)}$ satisfies Legendre's Equation □

Associated Legendre Equation

Going back to hydrogen atom, from (7):

$$\frac{d}{dx}((1-x^2)\frac{d\Phi}{dx}) + (\lambda_1 - \frac{m^2}{1-x^2})\Phi = 0$$

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Let $\Phi = (1-x^2)^{\frac{|m|}{2}} f(x)$

$$\frac{d\Phi}{dx} = |m|\,x(1-x^2)^{\frac{|m|}{2}-1} f(x) + (1-x^2)^{\frac{|m|}{2}} f'(x)$$

$$\frac{d^2\Phi}{dx^2} = (1-x^2)^{\frac{|m|}{2}} f''(x) - 2\,|m|\,|x(1-x^2)^{\frac{|m|}{2}-1} f(x)$$
$$+ (-\,|m|\,(1-x^2)^{\frac{|m|}{2}-1} + |m|\,(|m|-2)(1-x^2)^{\frac{|m|}{2}-2}) f(x)$$

Associated Legendre Equation

Plugging it into the equation:

$$(1 - x^2)f'' + 2(|m| + 1)xf'(x) + (\lambda_1 - |m|(|m| + 1)) = 0 \qquad (10)$$

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Do power series expansion. Let $f(x) = \sum_{j=0}^{\infty} a_j x^j$

Associated Legendre Equation

Plugging it into the equation:

$$(1 - x^2)f'' + 2(|m| + 1)xf'(x) + (\lambda_1 - |m|(|m| + 1)) = 0 \qquad (10)$$

Do power series expansion. Let $f(x) = \sum_{j=0}^{\infty} a_j x^j$

$$\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}x^j - \sum_{j=0}^{\infty}[j(j - 1 + 2|m| + 2) \\ - (\lambda_1 - |m|(|m| + 1))]a_j x^j = 0$$

Associated Lagguere Equation

$$a_{j+2} = \frac{j(j + 2|m| + 1) - (\lambda_1 - |m|(|m| + 1))}{(j + 2)(j + 1)} a_j \tag{11}$$

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Since $k \geq 0 \Rightarrow |m| \leq \ell$ and $\ell \epsilon \mathbb{Z}^+$

Rodrigues' Formula for ALE

$\Psi(\phi) = P_\ell^m(x)$ where $x = \cos(\phi)$

$$P_\ell^m(x) = (1 - x^2)^{\frac{|m|}{2}} \frac{1}{2^\ell \ell!} \frac{d^{\ell+|m|}}{dx^{\ell+|m|}} (x^2 - 1)^\ell \tag{12}$$

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From Rodrigues' Formula, $g(x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2 - 1)^\ell$ satisfies $(1 - x^2) g''(x) - 2x g'(x) + \ell(\ell + 1) g(x)$

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$(1-x^2)g''(x) - 2xg'(x) + \ell(\ell+1)g(x)$
Taking $|m|$ derivatives of it

$$(1-x^2)g^{(|m+2|)}(x) - 2(|m|+1)xg^{(|m+1|)}(x) + (\ell(\ell+1) - |m|(|m|+1))g^{(|m|)}(x) = 0$$

Hence, $g^{(|m|)}(x)$ satisfies (10) □

ϕ solution

Solution to Φ eigenfunction is

$$\Phi_{\ell,m}(\phi) = P_\ell^m(cos\phi) \tag{13}$$

where $m \epsilon \mathbb{Z}$, $\ell \epsilon \mathbb{Z}^+$ and $|m| \leq \ell$
And $P_\ell^m(\cos\phi)$ is given by (12)

Radial Equation

Going back to Radial Equation and plugging in values for eigenvalues:

$$\rho^2 P''(\rho) + 2\rho P'(\rho) + (E - V)\frac{2m\rho^2}{\hbar^2} P(\rho) = \ell(\ell + 1)P(\rho) \qquad (14)$$

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$$\frac{\hbar^2}{2m}u''(\rho) + \left(\frac{\hbar^2\ell(\ell+1)}{2m\rho^2} + V(\rho)\right)u(\rho) = Eu(\rho)$$

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We are looking for bound states so $E < 0$

let $k = \frac{\sqrt{-2mE}}{\hbar}$

Plug in k and potential equation from (2)

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$$w'(r) = ku'(\rho) \Rightarrow w''(r) = k^2u''(\rho)$$

$$w''(r) = \left(1 - \frac{\rho_0}{r} + \frac{\ell(\ell+1)}{r^2}\right)w(r) \tag{15}$$

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This is a Euler Equation, so let $w(r) = r^j$

$$j(j-1) = \ell(\ell+1)$$

$$j = -\ell \text{ or } j = \ell + 1$$

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$$w''(r) = r^{\ell} e^{-r} \left[\left(-2\ell - 2 + r\frac{\ell(\ell+1)}{r} \right) v(r) + 2(\ell + 1 - r) v'(r) + r v''(r) \right]$$

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$$r^{\ell}e^{-r}\left[\left(-2\ell - 2 + r\frac{\ell(\ell+1)}{r}\right)v(r) + 2(\ell+1-r)v'(r) + rv''(r)\right] = \left(1 - \frac{\rho_0}{r} + \frac{\ell(\ell+1)}{r^2}\right)r^{\ell+1}e^{-r}v(r)$$

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$$rv''(r)+2(\ell+1-r)v'(r)+(\rho_0-2(\ell+1))v(r)=0 \qquad (16)$$

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Expand v(r) as power series: $v(r) = \sum_{j=0}^{\infty} c_j r^j$

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and $w(r) = r^{l+1} e^{r}$ which we don't want

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Hence, series has to terminate. $\exists j_{max} > 0, c_{j_{max}+1} = 0$
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$$\rho_0 = 2n = \frac{me^2}{2\pi\epsilon_0\hbar^2}\frac{1}{k} \tag{18}$$

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$$0 = (j_{max} - q) a_{j_{max}}$$

$$j_{max} = q$$

Associated Lagguere Polynomials

Claim: $a_j = \dfrac{(-1)^j (p+q)!}{(q-j)!(p+j)!j!} = \dbinom{q+p}{q-j}\dfrac{1}{j!}$

Proof.

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Hence, $y(x) = \sum_{j=0}^{q} \binom{q+p}{q-j} \frac{x^j}{j!}$

Radial Solution

Combining (16) and (18) we get:

$$rv''(r) + 2(\ell + 1 - r)v'(r) + 2(n - (\ell + 1))v(r) = 0$$

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$$L^{2\ell+1}_{n-\ell-1}(2r) = \sum_{j=0}^{n-\ell-1} \binom{\ell + n}{j - 2\ell - 1} \frac{(-1)^j}{j!} 2^j r^j \tag{22}$$

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Using (19) for k

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with n $\epsilon\mathbb{N}$, ℓ $\epsilon\mathbb{Z}^+$, m $\epsilon\mathbb{Z}$ and n-1 $\geq \ell \geq |m|$ and c is normalization constant

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Note: Not considering spin, ℓ has $2\ell + 1$ degrees of freedom or degeneracy and n has $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$ degrees of freedom

Example

$n = 1 \Rightarrow \ell = 0$ and $m = 0$

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$$P_{n=1,\ell=0}(\rho) = \frac{e^{-\frac{\rho}{a_1}}}{a_1}$$

$$\Phi(\phi) = 1$$

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General Solution

$$\Psi_{\ell,m,n} = \sum_{|m|\leq\ell<n=1}^{\infty} c_{n,\ell,m}\frac{1}{\rho}\left(\frac{\rho}{na_1}\right)^{\ell+1} e^{-\frac{\rho}{na_1}} L_{n-\ell-1}^{2\ell+1}\left(\frac{2\rho}{na_1}\right) P_\ell^m(\cos\theta) e^{im\phi} e^{\frac{-iE_1}{n^2\hbar}t} \tag{25}$$

where $\ell\epsilon\mathbb{Z}^+$ and $m\epsilon Z$

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