HYDROGEN ORBITALS

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1 Introduction

The Hydrogen Atom consists of a heavy ,essentially motionless proton,of charge e,together with a much lighter charged elecron From Coulomb's law potential enrgy is

$$V(r) = \frac{-e^2}{4\pi\epsilon r}$$

The radial equation is

$$\frac{-h^2 d^2 u}{2m dr^2} + \left[\frac{-e^2}{4\pi\epsilon r} + \frac{h^2 l(l+1)}{2mr^2}\right] u = Eu$$

Our problem is to solve this equation for $u(r)$, and determine the allowed energies,E.The coulomb potential admit continuum states(E0). describing electron-proton scattering,as well as discrete bound states, representing the hydrogen atom.

2 The Radial Wave function

Let $\kappa \equiv \frac{-2mE}{h}$ for bound states E is negative and real

$$\frac{d^2 u}{\kappa^2 dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon h^2 \kappa(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right] u$$

This suggests that we introduce

$\rho \equiv \kappa r$, and $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 h^2 \kappa}$ so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u$$

Next we examine the asymptotic form of th solutions as $\rho \to \infty$, the constnants term in the bracket dominates,so(approx.)

$$\frac{d^2u}{d\rho^2} = u$$

The general solution is

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

but e^{ρ} blows up (as $\rho \to \infty$), so $B = 0$. Evidently

$$u(\rho) \approx Ae^{-\rho}$$

for large ρ. On the other hand as $\rho \to 0$ the centrifugal term dominates approximately then:

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

The general solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

but ρ^{-l} blows up (as $\rho \to 0$), so $D = 0$. Thus

$$u(\rho) = C\rho^{l+1}$$

for small ρ. The next step is to peel off the asymptotic behaviour introducing the new function $v(\rho)$:

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho),$$

Differentiating:

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l + 1 - \rho)v + \rho\frac{dv}{d\rho}\right]$$

and

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho} \left[[-2l - 2 + \rho + \frac{l(l+1)}{\rho}]v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2} \right]$$

In terms of $v(\rho)$, then the radial equation reads

$$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$$

Finally, we assume the solution$v(\rho)$can be expressed as a power series in ρ :

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

Differentiating term by term to detemine the coefficients:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

Differentiating again and adjusting the dummy index j;

$$\frac{d^2u}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

Solving;

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

Equating the coefficients of like power yields

$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right] c_j$$

This recursion formula determines the coefficients and hence the function.

For large j the recursion formula can be approximated to

$$c_{j+1} \cong \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j$$

Suppose for a moment that this were exact.Then

$$c_j = \frac{2^j}{j!}c_0$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!}\rho^j = c_0 e^{2\rho}$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

which blows up at large ρ because of exponential factor
For finding solution that we are interested in the series must terminate such that

$$c_{(j_{max}+1)} = 0$$

then, $2(j_m ax + l + 1) - \rho_0 = 0$ defining

$$n \equiv j_m ax + l + 1$$

n = principal quantum number
$\rho_0 = 2n$

so the allowed energies

$$E = \frac{-h^2\kappa^2}{2m} = \frac{me^4}{8\pi^4\epsilon_0^4 h^2 \rho_0^4}$$

this is the bohr formula.

Above equations give

$$\kappa = \left[\frac{me^2}{4\pi\epsilon_0 h^2}\right]\frac{1}{an} = \frac{1}{an}$$

where

$$\text{Bohor's Radius} = a \equiv \frac{4\pi\epsilon_0 h^2}{me^2} = 0.529 \times 10^{-10}$$

It follows that $\rho = \frac{r}{an}$ and the spatial wave function for hydrogen are labelled by three quantum numbers (n,l,m)

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

where

$$R_{nl}(r) = \frac{\rho^{l+1}e^{-\rho}v(\rho)}{r}$$

and $v(\rho)$ is a polynomial of degree $j_{max} = n - l - 1$ whose coefficeints are determined by the recursion formula.

$$c_{j+1} = \left[\frac{2(j+l+1-n)}{(j+1)(j+2l+2)}\right]c_j$$

The ground state (n=1) is $E_1 = -13.6eV$. Evidently the binding energy is 13.6 eV.

For hydrogen, after limitaions l=0,m=0 ,so, $\psi_{100}(r,\theta,\phi) = R_{10}(r)Y_0^0(\theta,\phi)$
The recursion formula truncates after the first term so $v(\rho)$is a constant(c_0), and

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a}$$

After normalizing it we get $c_0 = 2 \times \sqrt{a}$ and $Y_0^0 = 1/\sqrt{4\pi}$
Therefore, the ground state of hydrogen is

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}e^{-r/a}$$

For arbitray n, the possible values of l are $l = 0, 1, 2, \ldots, n-1$ and for each l there are $(2l+1)$ possible values of m,so the total degeneracy of the energy level E_n is $d(n) = \sum_{l=0} n - 1 = n^2$. The formula for $v(\rho)$ is a function well known to applied mathematician; apart from normalization ,it can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \frac{d}{dx}^P L_q(x)$$

is an associated Laguerre polynomial, and

$$L_q(x) = e^x \frac{d}{dx}^q (e^{-x} x^q)$$

is the q^{th} Laguerre Polynomial.The normalized hydrogen wavefunctions are

$$\psi = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n((n+1)!)^3}} \times e^{-r/na} \times \frac{2r}{na}^l \times \left(L_{n-l-1}^{2l+1} \times \frac{2r}{na}\right) \times Y_l^m(\theta, \phi)$$

This is one of the very few realistic systems that can be solved at all in exact closed form.The wave function de[end on all three quantum numbers whereas the energies are determined by n alone.