

HYDROGEN ORBITALS

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0.1 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

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

Our problem is to solve this equation for $u(r)$, and determine the allowed energies, E .The coulomb potential admit continuum states($E \geq 0$). describing electron-proton scattering,as well as discrete bound states,representing th hydrogen atom.

0.2 The Radial Wave function

Let $\kappa \equiv \frac{-2mE}{\hbar^2}$ [for bound states E is -ve, is real]

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

This suggests that we introduce

$$\rho \equiv \kappa r, \text{ and } \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

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

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

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

The general solution is

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

but e^ρ blows up (as $\rho \rightarrow \infty$), so $B=0$. Evidently
 $u(\rho) \approx Ae^{-\rho}$

for large ρ . On the other hand as $\rho \rightarrow 0$ 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 $\rho \rightarrow 0$), 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 determine 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;

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

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

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

$$\text{then, } 2(j_{max} + l + 1) - \rho_0 = 0$$

defining

$$n \equiv j_{max} + l + 1$$

n:principal quantum no.

$$\rho_0 = 2n$$

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 $a \equiv \frac{4\pi\epsilon_0 h^2}{me^2} = 0.529 \times 10^{-10}$ a is called the bohr radius
it follows

$$\rho = \frac{r}{an}$$

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 coefficients 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 $E_1 = -13.6 \text{ eV}$.

Evidently the binding energy is 13.6 eV.

For hydrogen after limitations $l=0, m=0$, 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

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

normalizing it we get $c_0 = 2/\sqrt{4\pi} a$.

Meanwhile $Y_0^0 = 1/\sqrt{4\pi}$

and hence the ground state of hydrogen is

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

For arbitrary n, the possible values of l are

$l=0, 1, 2, \dots, n-1$.

and for each l there are (2l+1) possible values of m, so the total degener-

acy 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

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

is an associated Laguerre polynomial, and

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

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

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

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