Hydrogen Atom

Hydrogen Atom – two particles with an attractive force F = $\frac{f V}{f R}$ only dep on dist R

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$V = {-e^2}/{R}$ or $\frac{-2e}{R}$ nucleus: Z at #

$F = \frac{-f V}{f R} = -(-)\frac{-e^2}{R^2} = \frac{-e^2}{R^2}$

[Note: Review 1,8, p, 18 – units F = Q_1Q_2/r^2 – coulomb law in Gaussian units

F-dynes, Q-stat coul, r-cm

Units SI: same eigen but F = $Q_1{}^1Q_2{}^2/r^2$

F = neutron, $Q^1 = Q/(4\pi\varepsilon_0)^{1/2}$, Q in coul, r – m

most QM texts drop $(4\pi\varepsilon_0)^{1/2}$ for simplicity]

Now what do you expect _ symmetrical potential so have same energy either "side" – only dist not dimen

– imagine a virtual other side or rotate the V(r) around r = 0 axis to get surface

See have a well – finite since V(∞) = 0 so what do we expect for solution

ψ(∞) _ 0 must be bound ~e^{Kr} depend

ψ(0) _ ? but must have curvature

$2\hat{T} = s\hat{V}$ V = ( )/r = ( )r^{-1} s = -1 $\hat{T} = -\hat{V}/2$

since $\hat{V}$? 0 except at r = ∞, $\hat{T}$? 0 must curve

As increase $\hat{V}$ expect $\hat{T}$ increase _ oscillate to get more curvature

At high V expect energy _ polynomial solu again

levels to become closer together ~finite V

At E > 0 expect continuum of states

_ plane wave solution _ dissociation

E = 0 _ separate particles at r = ∞

Now let's look at the Hamiltonian:

$$H\Psi = ¾\frac{-\hbar^2}{2m_e} \quad e^2 - \frac{\hbar^2}{2m_N} \quad N^2 - \frac{Z_n e^2}{r_{eN}}\surd\Psi = E\Psi$$

Note: This is a two particle problem and separable as before into center of Mass and relative coordinate dependent prob: $H = h_{CoM} + h_{reN}$

C of M: $H_{CoM} = \frac{-\hbar^2}{2M} \quad R^2$ _ translation of atom get continuous E's _ plane wave

transform relative coordinates to spherical $r_{eN} = r$

$H_{rel} = \frac{-\hbar^2}{2\mu} \quad r^2 - \frac{Ze^2}{r} \qquad \mu = \frac{M_e M_N}{M_e + M_N} \sim M_e$

$\left(\frac{1}{r}\right)\frac{f^2}{fr^2}(r\Psi) + \frac{1}{r^2}\Lambda^2\Psi + \frac{2\pi Ze^2}{\hbar^2 r}\Psi = -\frac{¾2\mu E}{\hbar^2}\surd\Psi$

Now recall how we separated particle on a sphere
there r const so first ten _ 0
here r a real variable but only in potential and angular terms only in second term
-- expect to separate: (mult by r^2)
$\Lambda^2\Psi = -\ell(\ell+1)\Psi$
$\Psi = \Psi_{lm}(\theta,\varphi)$ -- spherical harmonics
but can insert this into H:
let $\Psi = Ry_{lm}$

$\left(\frac{1}{r}\right)\frac{f^2}{fr^2}(rRY) + \frac{2\pi e^2}{\hbar^2 r} - \frac{1}{r^2}\ell(\ell+1)?? \; RY_{\ell m} = -\frac{¾2\pi E}{\hbar^2}\surd \; RY_{\ell m}$

see Y_{lm} can cancel out as expected,
and let P = rR (by mult through by r)

$\frac{f^2}{fr^2}P(r) + \frac{2\pi}{\hbar^2} \; \frac{e^2}{r} - \frac{\hbar^2}{2\pi r^2}\ell(\ell+1)?? \; P(r) = -\frac{¾2\pi E}{\hbar^2}\surd \; P$

(Atkins 4.3)
Now this has an interesting form –
1st term is typical K.E.
so 2nd is a P.E. _ note 2 effects
1st _ attractive electrostat ~ 1/r
2nd _ form dep on ang. mom.
$F_{centrif}$ = (ang mom)$^2/\pi r^3$ _ V ~ $L^2/2\mu r^2 \sim 1/r_2$
Repulsive force _ repulsive pt. (decays thru attract pot)

INSERT GRAPH

– V_{eff} is some sort of effective pot balancing centrif repuls _ attract electrostatic
[Note: ℓ = 0 _ no ang mom _ no centrif]
for ℓ 0 _ bit force keeping away from molecules _ really huge K.E. close in

Can look at this at extremes

L = 0 r _ 0 $-e^2/r$ dominate E: $\frac{f^2 p}{f r^2} + \frac{2\pi e^2}{\hbar^2 r} p \sim 0$

so here $P \sim Ar + 1/2r^2$ from P = rR

and R ~ A as r _ 0 on a const

so l = 0 has non zero prob at nucleus

(Note: no violation of continuity since no neg r)

l = 0 r _ 0 centrif dom E: $\frac{f^2 p}{f r^2} - \ell(\ell+1)\frac{\hbar^2}{r^2} p \sim 0$

so solu $P \sim Ar^{l+1} + Br^{-l}$ P = 0 at r _ B = 0

and $R = p/r \sim Ar^l$ r _ 0

R(0) = 0 for all l = 0 _ always a node

_ Clearly radial solu will depend on l and shape will change from **INSERT GRAPH** to **INSERT GRAPH**

Solu Levine p. 121 ff

Solving the radial equations:

same strong find solved

by power series _ Laguerre polynomials

quantized to get oscill in pot _ n = 1,2, . . .

but as above also depend on _ ℓ = 0,1,(n-1)

and must decay exponentially: $e^{-\gamma/2}$

n	l	$R_{nl}(r)$ $\gamma = (2Z/na)r$; $a = h^2/\mu e^2$

1	0 (1s)	$\left(\frac{Z}{a}\right)^{3/2} 2e^{-\gamma/2}$
2	0 (2s)	$\left(\frac{Z}{a}\right)^{3/2} \left(\frac{1}{2\sqrt{2}}\right) (2-\gamma)\, e^{-\gamma/2}$
	1 (2p)	$\left(\frac{Z}{a}\right)^{3/2} \left(\frac{1}{2\sqrt{6}}\right) (\gamma)\, e^{-\gamma/2}$
3	0 (3s)	$\left(\frac{Z}{a}\right)^{3/2} \left(\frac{1}{9\sqrt{3}}\right) (6 - 6\gamma + \gamma^2)\, e^{-\gamma/2}$
	1 (3p)	$\left(\frac{Z}{a}\right)^{3/2} \left(\frac{1}{9\sqrt{6}}\right) (4 - \gamma)\, e^{-\rho/2}$
	2 (3d)	$\left(\frac{Z}{a}\right)^{3/2} \left(\frac{1}{2\sqrt{2}}\right) \gamma^2\, e^{-\rho/2}$

handout on overhead figures p. 73 – Atkins

Note: s – zone zero at nucleus
– # nodes = (n-1)
– radial extent increases fast
p, d, etc.: – all zero at nucleus
– # nodes = $(n - 1 - \ell)$
– radial extent inc with ℓ but slowly

Now along with wave fct – insert into Sch. Eqn and get <u>energies</u>

$$E_n = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2} = \frac{-Z^2}{n^2}\left(\frac{e^2}{2a}\right) \quad n = 1, 2, \ldots$$

$E_n \sim 1/n^2$ fit Bohr model
Balm/Rodberg series etc.
levels collapse as nine and E _ 0
degenerate: ℓ _ (n-1)
m _ $(2\ell+1)$
Levine 127: result = n^2 degen
no spin (only H-atom ???)

<u>H-atom energies/spectra</u>

$$E_n = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2} = \frac{-Z^2}{n^2}\left(\frac{e^2}{2a}\right) \qquad n = 1, 2, 3, \ldots$$

big behaviours: $E_n \sim 1/n^2$
so energy levels collapse as n inc.
a has units of length, if $\mu \sim m_e$ _ a_0 – Bohr radius
and a constant so only other variable Z
$E_n \sim Z^2$ expect much higher energies for other ions (correspond to smaller radii)

INSERT PICTURE

In terms of spectros copy all Δn allowed (if Δl = 1) gap is generally very large (E_1 ~ 13.6 eV for #) so all population is in ground state unless excite with light (or e) Fits the Bohr atom exactly because that works to explain H-atom spectra)

Spectra:
INSERT PICTURE from n = 0 _ n = 1, 2, 3, . . . -- Lyman
INSERT PICTURE n = 1 _ n = 2, 3, -- Balm
INSERT PICTURE n = 2 _ n = 3, 4 -- Pasch

These are the spectra that fir the Rydberg series

$$\hat{\nu} = R^{3/4}\ 1/n_2^2 - 1/n_1^2 \sqrt{} \qquad R \sim 10^5\ cm^{-1}$$

but that generally is done by emission (excite atom relax back to various n's)

<u>Orbitals</u> – combining the three dimensional solu
$\Psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\ \Psi_{lm}(\theta,\varphi)$
gives the solu but cannot plot well since would require some 4-D representative (to do take slices through 3D space and on each 2-D slice plot ψ or ψ*ψ value. Note – this is some technique used for making e-density maps in xtalography)

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see magnitude at nucleus drop with n – radical extent grow ~ n^2
1st look at parts
$R_{nl}(r)$ $\ell = 0$
Levine p 132-133 (overhead)
nodes = $n-1-\ell$

Since sampling (θ,φ) with this function, often re-rep as radial distribution fct

$R^2R_{nl}^1(r)$

Idea – integrate out (θ,φ) on prob of being in a sphere at r away from nucleus and dr thickness

$$\int_0^{\pi}\int_0^{2\pi} R_{n\ell}^2(r)\, Y_{\ell m}^* \, Y_{\ell m}\, r^2 \sin\theta d\theta d\varphi dr = r^2 R_{n\ell}^2(r) dr$$

now cannot mag at nucleus * zero volume

INSERT GRAPHS

outer lobes bigger (bigger vol)

see max prob move out fast

Angular part – know from before can plot length of (Y_{lm}) as vector at (θ,φ)

INSERT PICTURE $\ell = 0$, $m = 0$ sphere

INSERT PICTURE $\ell = 1$, $m = 0$ targential spheres

INSERT PICTURE $(Y_{11} - Y_{1-1})$ $(Y_{11} + Y_{1-1})$ but alone – complex

Levine p 138-139

Put together see as expand sphere of consideration going to get varying picture can take contours – like hiking map

1s: like onion layers further apart with r since $e^{-\gamma/2}$ dependence

INSERT PICTURE

2s: same but change sign – layers bunch than spread

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2po = 2pz: sort of squashed and opp sign on z

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3po: must have radial sign change plus opp. sign lobes

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$n-\ell-1 = 2$
nodes are model plane is a <u>sphere</u>
the other is a <u>plane</u>