Lecture 18

Wednesday, November 15, 2023 15:54

Hydrogen Atom Continued

$$R'' + \frac{2}{r}R' + \left[\frac{8\pi\varepsilon_0 E}{ae^2} + \frac{2Z}{ar} - \frac{\ell(\ell+1)}{r^2}\right]R = 0$$

$$\boxed{a \equiv \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}}$$

Solve using power-series method

Case 1 : r large

$$R'' + \frac{8\pi\varepsilon_0 E}{ae^2}R = 0$$

going back to the particle in a box,

$$\psi'' + c\psi = 0$$

$$R = c_1 e^{-(\overbrace{-8\pi\varepsilon_0 E/ae^2}^{\text{E is posive, this factor is imaginary}})^{\frac{1}{2}} r} + c_2 e^{+(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}} r}$$

If E is positive

$$R(r) \sim e^{\pm i\sqrt{2\mu E}\, r/\hbar}$$

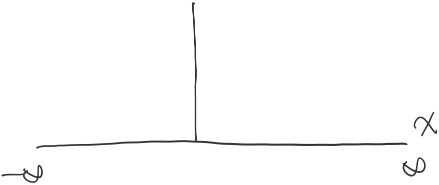
this is similar to the free-particle wavefunction

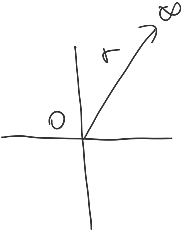
$E \geq 0$: all energies are allowed, not quantized

unbound states for the H-atom, corresponds to the ionized state

bound states: $E < 0$

$$R = c_1 e^{+\overset{\text{positive}}{(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}}} r} + \underbrace{c_2 e^{-(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}} r}}_{\text{finite as } r \to \infty}$$





goal: obtain a two-term recursion

relation

$$R(r) = e^{-Cr} K(r)$$

$$\boxed{C \equiv \left(-\frac{8\pi\varepsilon_0 E}{a e^2}\right)^{\frac{1}{2}}}$$

(a bunch of math here)

set to 0 when $j=k$

$$\boxed{b_{j+1} = \boxed{\frac{2C + 2C\ell + 2Cj - 2Za^{-1}}{j(j+1) + 2(\ell+1)(j+1)}} b_j}$$

examine the behaviour of this series at large r to determine the function it resembles

(previously for the harmonic osillator, compare the ratio of coefficients for two successive terms)

$$R(r) \sim e^{-Cr} r^{\ell} e^{2Cr} = \boxed{r^{\ell} e^{Cr}}$$

need to cut off series after a certain number of terms

$$2C + 2C\ell + 2Ck - 2Za^{-1} = 0$$

$$2C(\overset{\swarrow\ \text{integer}}{\underbrace{1+\ell+k}_{n}}) = 2Za^{-1},\ k=0,1,2,\ldots$$

$$n \equiv k+\ell+1,\quad n = 1,2,3$$

$$\ell \leq n-1$$

ℓ ranges from 0 to $n-1$

$$Cn = \frac{Z}{a}$$

$$\left(-\frac{8\pi\varepsilon_0 E}{ae^2}\right)^{\frac{1}{2}} n = \frac{Z}{a}$$

$$-\frac{8\pi\varepsilon_0 E}{ae^2} = \frac{Z^2}{a^2n^2}$$

$$E = -\frac{Z^2 \cancel{a} e^2}{8\pi\varepsilon_0 a^{\cancel{2}} n^2}$$

$$E = -\frac{Z^2 e^2 \cdot \mu e^2}{8\pi\varepsilon_0 n^2 \cdot 4\pi\varepsilon_0 \hbar^2} \qquad \hbar^2 = \frac{h^2}{4\pi^2}$$

$$E = -\frac{Z^2 \mu e^4}{8\varepsilon_0 n^2 \cdot 4\pi^2 \varepsilon_0 \hbar^2}$$

$$\boxed{E = -\frac{Z^2 \mu e^4}{8\varepsilon_0^2 n^2 h^2}}$$

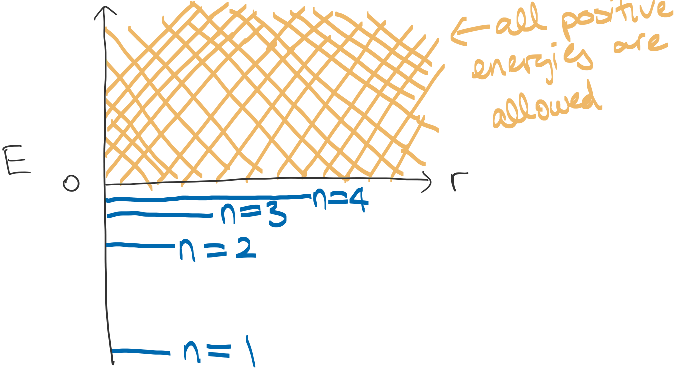
$Z=1$, H

$Z=2$, He^+

$Z=3$, Li^{2+}

⋮

bound-state energy levels for the hydrogen atom; quantized



transitions to/from any n are allowed

$$\tilde{\nu} \equiv \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_2 - E_1}{hc}$$

$$= \overset{R_H}{\boxed{\frac{e^2}{8\pi\varepsilon_0 a hc}}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\boxed{\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

$$R_H = \underline{13.6\ \text{eV}} = \frac{1}{2}\,\text{Ha}$$

$$\tilde{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$$

$\tilde{\nu} = 13.6\,\text{eV}$ ← first ionization energy of H

$n = 1, 2, 3, \ldots$ ← additional constraint

$$\left[\begin{array}{l} \ell = 0, 1, 2, \dots, n-1 \\ \\ m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell \end{array}\right.$$

$n = 1$

$\ell = 0$

$m = 0$

1s

1

$n = 2$

$\ell = 0$, $\ell = 1$

2s

$\searrow$

$m = -1, 0, 1$

$2p_x, 2p_y, 2p_z$

4

$n = 3$

$\ell = 0$

$m = 0$

3s

$n = 3$

$\ell = 1$

$m = -1, 0, 1$

$3p_x, 3p_y, 3p_z$

$n = 3$

$\ell = 2$

$m = -2, -1, 0, 1, 2$

$3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{x^2-y^2}, 3d_{z^2}$

9

degeneracy is n^2

$$\sum_{\ell=0}^{n-1}(2\ell+1) = \sum_{\ell=0}^{n-1} 2\ell + \underbrace{\sum_{\ell=0}^{n-1} 1}_{n}$$

101

101

$$1 + 2 + 3 + \cdots + 98 + 99 + 100$$

101

$$\boxed{\frac{(n+1)n}{2}} = 5050$$

each pair sums to 101

50 pairs total $\frac{n}{2}$

$$\sum_{\ell=0}^{n-1}(2\ell+1) + n$$

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

$$= n^2 - n + n$$

$$= n^2$$

Wave functions

$$\psi_{n\ell m} = R_{n\ell}(r)\,Y_{\ell}^{m}(\theta, \phi)$$

$$\boxed{\psi_{n\ell m} = R_{n\ell}(r)\,S_{\ell m}(\theta)\,\frac{1}{\sqrt{2\pi}}\,e^{im\phi}}$$

$$\psi_{100} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \qquad 1s$$

$$\psi_{200} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a} \qquad 2s$$

$$\psi_{21-1} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a} \sin\theta\, e^{-i\phi} \qquad 2p_x,\ 2p_y$$

$$\psi_{210} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{5/2} r e^{-Zr/2a} \cos\theta \qquad 2p_z$$

$$\psi_{211} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a} \sin\theta\, e^{i\phi} \qquad 2p_x,\ 2p_y$$