Lecture 15

Thursday, November 7, 2024 11:30

Hydrogen Atom Continued

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

when r is large, these terms go to 0

If r is large,

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

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

$$x = \pm\left(-\frac{8\pi\varepsilon_0 E}{ae^2}\right)^{\frac{1}{2}}$$

$$R_1 = e^{-(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}}r}, \quad R_2 = e^{(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}}r}$$

If $E > 0$, then $\left(-\frac{8\pi\varepsilon_0 E}{ae^2}\right)^{\frac{1}{2}}$

is imagina

is imaginary

$$R(r) \sim e^{\pm(8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}} ir}$$

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

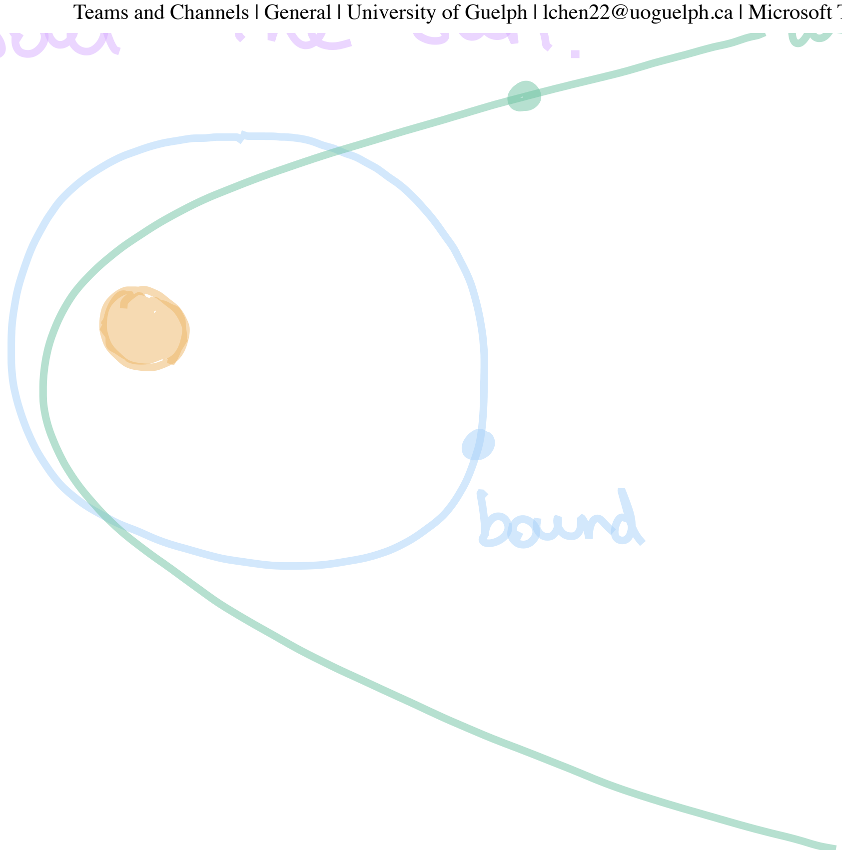
$$\frac{8\pi\varepsilon_0 E}{ae^2} = \frac{\overset{2}{\cancel{8}}\cancel{\pi}\cancel{\varepsilon_0} E \mu \cancel{e^2}}{\cancel{4}\cancel{\pi}\cancel{\varepsilon_0}\hbar^2 \cancel{e^2}} = \frac{2\mu E}{\hbar^2}$$

$$\boxed{R(r) \sim e^{\pm(2\mu E)^{\frac{1}{2}} ir/\hbar}, \quad E \geq 0}$$

asymptotic behaviour; resembles the free-particle wavefunction

These eigenfunctions correspond to states in which the electron is not bound to the nucleus; i.e. the atom is ionized.

Classical mechanical analogy: a comet moving in a hyperbolic orbit about the Sun ... unbound orbit about the sun.



How about bound states?

That is to say, states in which

$\psi = 0$ as $x \to \pm\infty$

$$e^{\pm(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}} r}$$

$$E < 0, \text{ so } -\frac{8\pi\varepsilon_0 E}{ae^2} > 0$$

To ensure ψ remains finite, take the negative sign in the exponent, so

$$-(-8\pi\varepsilon_0 E/ae^2)^{\frac{1}{2}} r$$

$$R(r) = e$$

Make substitution to set up the recursion relation:

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

where $C \equiv \left(-\frac{8\pi\varepsilon_0 E}{ae^2}\right)^{\frac{1}{2}}$

$$\boxed{R'(r) = -Ce^{-Cr}K(r) + e^{-Cr}K'(r)}$$

$$R''(r) = (-C)^2 e^{-Cr}K(r) - Ce^{-Cr}K'(r)$$

$$+ (-C)e^{-Cr}K'(r) + e^{-Cr}K''(r)$$

$$\boxed{R''(r) = C^2 e^{-Cr}K(r) - 2Ce^{-Cr}K'(r) + e^{-Cr}K''(r)}$$

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

$$\overbrace{C^2 \cancel{e^{-Cr}}K(r) - 2C\cancel{e^{-Cr}}K'(r) + \cancel{e^{-Cr}}K''(r)}^{R''}$$

$$+ \frac{2}{r}\Big[\overbrace{\cancel{e^{-Cr}}K'(r) - C\cancel{e^{-Cr}}K(r)}^{R'}\Big]$$

$$+\left[\frac{8\pi\varepsilon_0 E}{ae^2} + \frac{2Z}{ar} - \frac{l(l+1)}{r^2}\right]\cancel{e^{-cr}}K(r) = 0$$

$$c^2K(r) - 2cK'(r) + K''(r) + \frac{2}{r}K'(r)$$

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

$\cdot r^2$

$$\cancel{c^2r^2K(r)} - 2rcK(r) + \cancel{r^2\frac{8\pi\varepsilon_0 E}{ae^2}}K(r)$$

$$+2Za^{-1}rK(r) - l(l+1)K(r) - 2cr^2K'(r)$$

$$+2rK'(r) + r^2K''(r) = 0$$

$$c \equiv \left(-\frac{8\pi\varepsilon_0 E}{ae^2}\right)^{\frac{1}{2}} \qquad c^2 = -\frac{8\pi\varepsilon_0 E}{ae^2}$$

$$\left[2Za^{-1}r - l(l+1) - 2rc\right]K(r)$$

$$+(2r - 2cr^2)K'(r) + r^2K''(r) = 0$$

$$r^2K''(r) + (2r - 2cr^2)K'(r) + \left[(2Za^{-1} - 2c)r - l(\right.$$

Try power series: $K = \sum_{k=0} c_k$

First few coefficients end up being 0 (generally); set c_s to be the first nonzero coefficient.

$$K = \sum_{k=s}^{\infty} c_k r^k, \quad c_s \neq 0$$

$$j \equiv k - s, \quad a_j \equiv c_{j+s} \quad (j+s=k)$$

$$K = \sum_{j=0}^{\infty} c_{j+s} r^{j+s} = r^s \sum_{j=0}^{\infty} a_j r^j, \quad a_0 \neq 0$$

$$\boxed{K(r) = r^s M(r)}$$

$$M(r) = \sum_{j=0}^{\infty} a_j r^j, \quad a_0 \neq 0$$

$$\boxed{K'(r) = s r^{s-1} M(r) + r^s M'(r)}$$

$$\boxed{K''(r) = s(s-1) r^{s-2} M(r) + 2s r^{s-1} M'(r) + r^s M''(r)}$$

$r^2 s(s-1) r^{s-2} M(r) + r^2 2s r^{s-1} M'(r)$

$$+ r^2 r^s M''(r) + 2rsr^{s-1}M(r) + 2r\cdot r^s M'(r)$$

$$- 2Cr^2\cdot sr^{s-1}M(r) - 2Cr^2\cdot r^s M'(r)$$

$$+\left[(2Za^{-1}-2C)r - \ell(\ell+1)\right] r^s M(r) = 0$$

divide by r^s

$$r^2M'' + (2sr + 2r - 2Cr^2)M' + \left[s^2 + s - 2Crs\right.$$

$$\left. + (2Za^{-1} - 2C)r - \ell(\ell+1)\right] M(r) = 0$$

$$r^2M'' + \left[(2s-2)r - 2Cr^2\right]M' + \left[s^2 + s\right.$$

$$\left. + (2Za^{-1} - 2C - 2Cs)r - \ell(\ell+1)\right] M = 0$$

Consider when $r = 0$:

$$M(r) = \sum_{j=0}^{\infty} a_j r^j, \quad a_0 \neq 0$$

$$M(0) = a_0$$

$$M'(0) = a_1 \qquad M'(r) = \sum_{j=0}^{\infty} a_j \cdot j\, r^{j-1}, \quad a_0 \neq 0$$

$$M''(0) = 2a_2 \qquad M''(r) = \sum^{\infty} j(j-1)a_j r^{j-2}, \quad a_0 \neq 0$$

For $r=0$, $(s^2+s-\ell^2-\ell)a_0=0$

Since $a_0\neq 0$, $\boxed{s^2+s-(\ell^2+\ell)=0}$

roots: $s=\ell$ and $s=-\ell-1$

Two linearly independent solutions.

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

$$K(r)=r^{s}M(r)$$

$$M(r)=\sum_{j=0}^{\infty}a_j r^j,\quad a_0\neq 0$$

$$\boxed{R(r)=e^{-Cr}\,r^{s}\sum_{j=0}^{\infty}a_j r^j}$$

$$e^{-Cr}=1-Cr+\frac{(Cr)^2}{2!}-\frac{(Cr)^3}{3!}+\cdots$$

For small r, $R(r)$ behaves as a_0r^s.

For $s=\ell$, $R(r)$ behaves properly at the origin.

For $s=-\ell-1$, $R(r)\sim\frac{1}{r^{\ell+1}}$

Since $l = 0, 1, 2, \ldots$, the root $s = -l - 1$ makes the radial factor in the wavefunction infinite at the origin. Reject $s = -l - 1$.

(For more information, see textbook pages 132-133.)

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

$$r^2 M'' + \left[(2s+2)r - 2Cr^2\right] M' + \left[s^2 + s + (2Za^{-1} - 2C - 2Cs)r - l(l+1)\right] M = 0$$

$s = l$, so

$$r^{\cancel{2}} M'' + (2l\cancel{r} + 2\cancel{r} - 2Cr^{\cancel{2}}) M'$$
$$+ \left[\cancel{l^2 + l} + (2Za^{-1} - 2C)\cancel{r} - 2Cl\cancel{r}\right.$$
$$\left. - \cancel{l^2 - l}\right] M = 0$$

$$rM'' + (2l + 2 - 2Cr) M' + (2Za^{-1} - 2C - 2Cl) M =$$

$$M(r)=\sum_{j=0}^{\infty} a_j r^j$$

$$M'(r)=\sum_{j=0}^{\infty}(j+1)a_{j+1}r^j$$

$$M''(r)=\sum_{j=0}^{\infty}(j+1)j\,a_{j+1}r^{j-1}$$

$$\sum_{j=0}^{\infty}\left[j(j+1)a_{j+1}+2(\ell+1)(j+1)a_{j+1}+\left(\frac{2Z}{a}-2C-2C\ell-2Cj\right)a_j\right]r^j=0$$

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

recursion relation

How does $M(r)$ behave for large r?

$$\frac{a_{j+1}}{a_j}=\frac{\cancel{2C}+\cancel{2C\ell}+2Cj-\cancel{2Za^{-1}}}{j^2+j+2\ell j+\cancel{2\ell}+2j+\cancel{2}}$$

$$=\frac{2Cj}{\quad}$$

$$j^2 + j + 2\ell j + 2j$$

$$= \frac{2C}{j + 1 + \cancel{1} + \cancel{2\ell} + \cancel{2}}$$

$$\frac{a_{j+1}}{a_j} = \frac{2C}{j}$$

$$e^{2Cr} = 1 + 4C^2 r^2 + \cdots$$

$$+ \frac{(2Cr)^j}{j!} + \frac{(2Cr)^{j+1}}{(j+1)!} + \cdots$$

$$\frac{2^{\cancelto{1}{j+1}}\, C^{\cancelto{1}{j+1}}}{(j+1)\cancel{(j)}\cancel{(j-1)}\cdots} \cdot \frac{\cancel{j}\cancel{(j-1)}\cancel{(j-2)}\cdots}{\cancel{2^j}\,\cancel{C^j}} = \frac{r^{j+1}}{r^j}$$

$$\frac{r^{j+1}}{r^j} = \frac{2C}{j+1} \approx \frac{2C}{j}$$

For large r, R behaves as

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

terminate after a finite number of terms

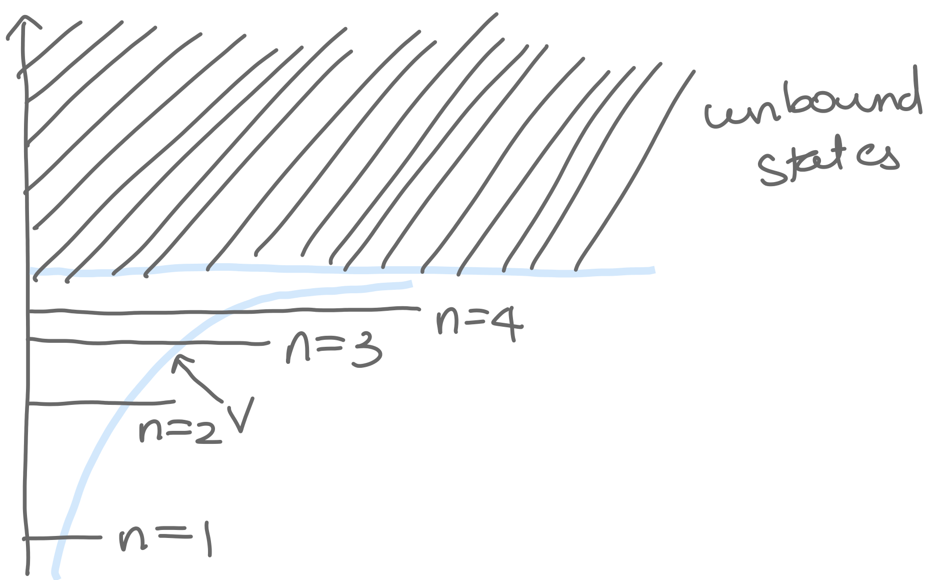
$$2c + 2cl + 2ck - 2Za^{-1} = 0$$

$$2c(k+l+1) = 2Za^{-1}, \quad k = 0, 1, 3, \ldots$$

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

$$l \leq n-1$$

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



all changes in n are allowed in light absorption and emission