

Quantum Comeback

The Finale - 1

The Hydrogen Atom

Consists of heavy, motionless proton together with a much lighter electron.

From Coulomb's law, the potential energy of the electron

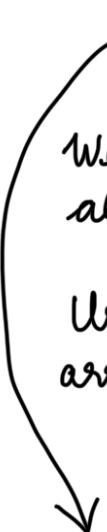
$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

and the radial equation:

$$-\frac{\hbar^2}{2m_e} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] u = Eu.$$

We will now solve this equation for $u(r)$ and determine the allowed energies.

Using the method of analytical solution in HO, we will arrive at the solution to this system. Let us dive right in:



$$k = \sqrt{-\frac{2m_e E}{\hbar^2}}. \quad (\text{For bound states, } E \text{ is -ve, so } k = \text{real})$$

$$\Rightarrow \frac{1}{k^2} \frac{d^2u}{dr^2} = \left[1 - \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k} \cdot \frac{1}{(kr)} + \frac{l(l+1)}{(kr)^2} \right] u.$$

Let $\rho = kr$ and $\rho_0 = \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k}$

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

Now let us examine the asymptotic form of solutions:

$$\text{As } p \rightarrow \infty \quad \frac{d^2u}{dp^2} = u \dots$$

$$\therefore \text{General soln: } u(p) = Ae^{-p} + Be^p$$

But as Be^p blows up at $p \rightarrow \infty$, $B=0$.

$$u(p) \sim Ae^{-p}$$

$$\text{If, if } p \rightarrow 0, \quad \frac{d^2u}{dp^2} = \frac{\ell(\ell+1)}{p^2} u$$

The general solution thus is $\underline{u(p) = Cp^{\ell+1} + Dp^{-\ell}}$. ??

But $p^{-\ell}$ blows up as $p \rightarrow 0$, so $D=0$.

$$\therefore u(p) \sim Cp^{\ell+1}. \quad (\text{small } p)$$

The next step is to peel off the asymptotic behaviour,

let us introduce $\gamma(p)$:

$$u(p) = p^{\ell+1} e^{-p} \gamma(p) \rightarrow \text{Why? Let's see:}$$

differentiating the eqn once:

$$\frac{du}{dp} = p^{\ell+1} e^{-p} \gamma + p^{\ell+1} e^{-p} \frac{d\gamma}{dp} - p^{\ell+1} e^{-p} \gamma$$

$$= p^{\ell} e^{-p} \left[(\ell+1-p)\gamma + p \frac{d\gamma}{dp} \right]$$

differentiating once more ...

$$\frac{d^2u}{dp^2} = \ell p^{\ell-1} e^{-p} \left[(\ell+1-p)\gamma + p \frac{d\gamma}{dp} \right] - p^{\ell} e^{-p} \left[(\ell+1-p)\gamma + p \frac{d\gamma}{dp} \right]$$

$$+ \hat{p} e^{-\rho} \left[-\gamma + (\ell+1-\rho) \frac{d\gamma}{dp} + \frac{d\gamma}{dp} + \rho \frac{d^2\gamma}{dp^2} \right] \quad \text{[Eq 1]}$$

$$= p^\ell e^{-\rho} \left\{ \left[-2\ell - 2 + \rho + \frac{\ell(\ell+1)}{p} \right] \gamma + 2(\ell+1-\rho) \frac{d\gamma}{dp} + \rho \frac{d^2\gamma}{dp^2} \right\}$$

In terms of $\gamma(p)$, radial eqⁿ reads:

$$\rho \frac{d^2\gamma}{dp^2} + 2(\ell+1-\rho) \frac{d\gamma}{dp} + [p_0 - 2(\ell+1)] \gamma = 0.$$

Finally we assume the solution $\gamma(p)$ can be expressed as a power series in p .

$$\gamma(p) = \sum_{j=0}^{\infty} c_j p^j$$

Now, we need to find the coefficients ... We do that by "term by term" differentiation.

$$\frac{d\gamma}{dp} = \sum_{j=0}^{\infty} j c_j p^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} p^j$$

$$\frac{d^2\gamma}{dp^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} p^{j-1}$$

Putting these in the radial eqⁿ of the form $\gamma(p)$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} p^{j-1} + 2(\ell+1) \sum_{j=0}^{\infty} j(j+1) c_{j+1} p^j$$

$$- 2 \sum_{j=0}^{\infty} j c_j p^j + [p_0 - 2(\ell+1)] \sum_{j=0}^{\infty} c_j p^j = 0$$

Equating the coefficients of like powers yields

$$j(j+1) c_{j+1} + 2(\ell+1)(j+1) c_{j+1} - 2j c_j + [p_0 - 2(\ell+1)] c_j = 0$$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - p_0}{(j+1)(j+2l+2)} \right\} c_j$$

The recursion formula for large j :

$$c_{j+1} = \frac{2j}{j(j+1)} = \frac{2}{j+1}; \quad c_j \approx \frac{2^j}{j!} c_0$$

From this recursion relation, we can get $\nu(p)$.

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

$$\therefore u(p) = c_0 p^{l+1} e^p \rightarrow \text{blows up at } p \rightarrow \infty.$$

There's only one escape to this problem: The series must
TERMINATE

$c_{N-1} \neq 0$ but $c_N = 0$. What is the 'N' that gives us this?

$$2(N+l+1) - p_0 = 0.$$

defining $N+l+1 \equiv n$,

$$p_0 = 2n.$$

But p_0 determines E .

$$\therefore E = \frac{-k^2 k^2}{2m} = \frac{-m_e e^4}{8\pi^2 G_0^2 k^2 p_0^2}$$

\therefore Allowed energies:

$$E_n = - \left[\frac{m_e}{2k^2} \left(\frac{e^2}{4\pi G_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n}, \quad n=1, 2, 3, \dots$$



The famous Bohr's formula!

$$\text{Now, we know } \rho_0 = 2n \text{ and } \rho_0 = \frac{m_e e^2}{2\pi\epsilon_0 h^2 k}$$

$$\therefore k = \frac{m_e e^2}{4\pi\epsilon_0 h^2 n} = \frac{1}{an} \quad \text{where } a = \frac{4\pi\epsilon_0 h^2}{m_e e^2}$$

$$a = 0.529 \times 10^{-10} \text{ m} \Rightarrow \text{so-called Bohr Radius.}$$

$$\text{Now } \rho = kr \quad \therefore \quad \rho = \frac{r}{an}$$

The spatial wave functions are labelled by three quantum numbers (n, l, m)

$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_l^m(\theta, \phi)$$

$$\text{where } R_{n,l}(r) = \frac{1}{r} r^{l+1} e^{-\rho} \varphi(r)$$

where $\varphi(r)$ — polynomial of degree $n-l-1$ in r .

whose coefficients are determined by the recursion formula

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

The ground state Energy ($n=1$):

$$E_1 = \left[\frac{m_e}{2h^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV.}$$

aka the Binding energy of hydrogen atom

At ground state, $l=m=0$

$$\therefore \Psi_{100}(r, \theta, \phi) = R_{1,0}(r) Y_0^0(\theta, \phi)$$

$$\text{and } R_{1,0}(r) = \underline{C_0} e^{-r/a}.$$

$$\text{Normalising: } \int_0^\infty |R_{10}|^2 r^2 dr = \frac{|C_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr$$

$$= |C_0|^2 \frac{a}{4} = 1. \quad \therefore C_0 = \sqrt{\frac{4}{a}} \text{ and } Y_0 = \frac{1}{\sqrt{4\pi}}.$$

$\therefore \psi_{100}(r, \theta, \phi) \rightarrow \text{the ground state of hydrogen}$

$$= \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

Now, the first excited state $\rightarrow n=2$, l can be 0, 1,
 $m = -1, 0, 1$. If $l=0$,

Recursion relation gives $C_1 = -C_0$ and $C_2 = 0$
 $(j=0)$ $(j=1)$

$$\therefore v(p) = C_0(1-p)$$

$$\therefore R_{20}(r) = \frac{C_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}.$$

If $l=1$, recursion formula terminates after the first term, i.e., $v(p) = \text{constant}$.

$$\therefore R_{21}(r) = \frac{C_0}{4a^2} r e^{-r/2a}.$$

Now, for arbitrary n , possible values of l are:

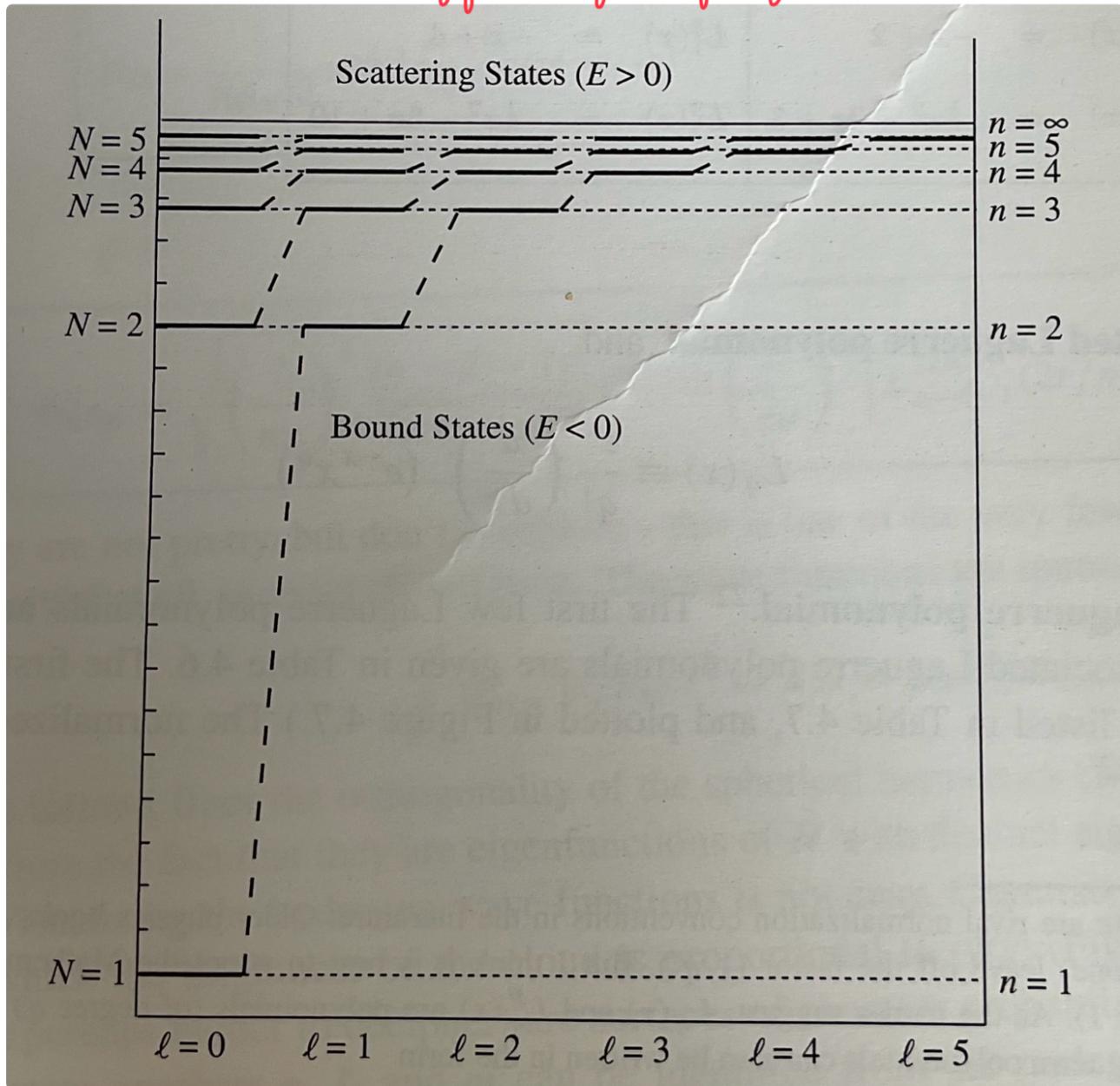
$$l = 1, 2, \dots, n-1.$$

and for each of those l , there are $2l+1$ possible values of m .

\therefore The total degeneracy of the energy level E_n :

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

Energy levels for Hydrogen.



The polynomial $v(p) \Rightarrow$ Well known polynomial actually

$$v(p) = L_{n-\ell-1}^{2\ell+1}(2p)$$

where $L_q^P(x) \equiv (-1)^P \left(\frac{d}{dx}\right)^P L_{P+q}(x)$

and $L_q(x) \equiv \frac{e^x}{x!} \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$

Associated
Laguerre
Polynomial

q^{th} Laguerre
polynomial

Table 4.5: *The first few Laguerre polynomials.*

$L_0(x) = 1$
$L_1(x) = -x + 1$
$L_2(x) = \frac{1}{2}x^2 - 2x + 1$
$L_3(x) = -\frac{1}{6}x^3 + \frac{3}{2}x^2 - 3x + 1$
$L_4(x) = \frac{1}{24}x^4 - \frac{2}{3}x^3 + 3x^2 - 4x + 1$
$L_5(x) = -\frac{1}{120}x^5 + \frac{5}{24}x^4 - \frac{5}{3}x^3 + 5x^2 - 5x + 1$
$L_6(x) = \frac{1}{720}x^6 - \frac{1}{20}x^5 + \frac{5}{8}x^4 - \frac{10}{3}x^3 + \frac{15}{2}x^2 - 6x + 1$

Table 4.6: *Some associated Laguerre polynomials.*

$L_0^0(x) = 1$	$L_0^2(x) = 1$
$L_1^0(x) = -x + 1$	$L_1^2(x) = -x + 3$
$L_2^0(x) = \frac{1}{2}x^2 - 2x + 1$	$L_2^2(x) = \frac{1}{2}x^2 - 4x + 6$
$L_0^1(x) = 1$	$L_0^3(x) = 1$
$L_1^1(x) = -x + 2$	$L_1^3(x) = -x + 4$
$L_2^1(x) = \frac{1}{2}x^2 - 3x + 3$	$L_2^3(x) = \frac{1}{2}x^2 - 5x + 10$

Let us now look at the Radial Wave functions of the Hydrogen Atom

Table 4.7: The first few radial wave functions for hydrogen,
 $R_{n\ell}(r)$.

$R_{10} = 2a^{-3/2} \exp(-r/a)$
$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) \exp(-r/2a)$
$R_{21} = \frac{1}{2\sqrt{6}} a^{-3/2} \left(\frac{r}{a}\right) \exp(-r/2a)$
$R_{30} = \frac{2}{3\sqrt{3}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$
$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$
$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$
$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$
$R_{41} = \frac{5}{16\sqrt{15}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \left(\frac{r}{a}\right) \exp(-r/4a)$
$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a}\right) \left(\frac{r}{a}\right)^2 \exp(-r/4a)$
$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$

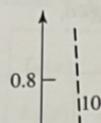
$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na)\right] Y_\ell^m(\theta, \phi). \quad (4.89)$$

They are not pretty, but don't complain—this is one of the very few realistic systems that can be solved at all, in exact closed form. The wave functions are mutually orthogonal:

$$\int \psi_{n\ell m}^* \psi_{n'\ell' m'} r^2 dr d\Omega = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}. \quad (4.90)$$

This follows from the orthogonality of the spherical harmonics (Equation 4.33) and (for $n \neq n'$) from the fact that they are eigenfunctions of \hat{H} with distinct eigenvalues.

Visualising the Hydrogen Wave functions



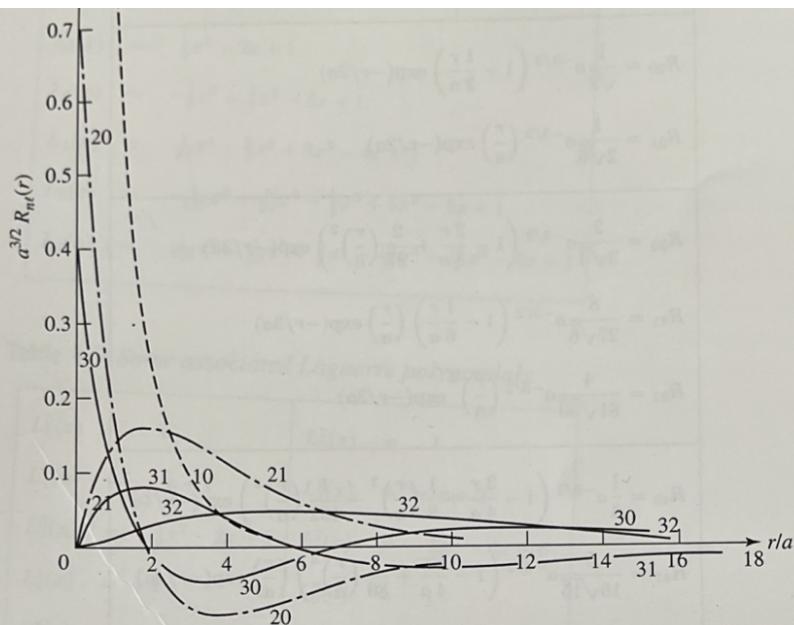


Figure 4.7: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

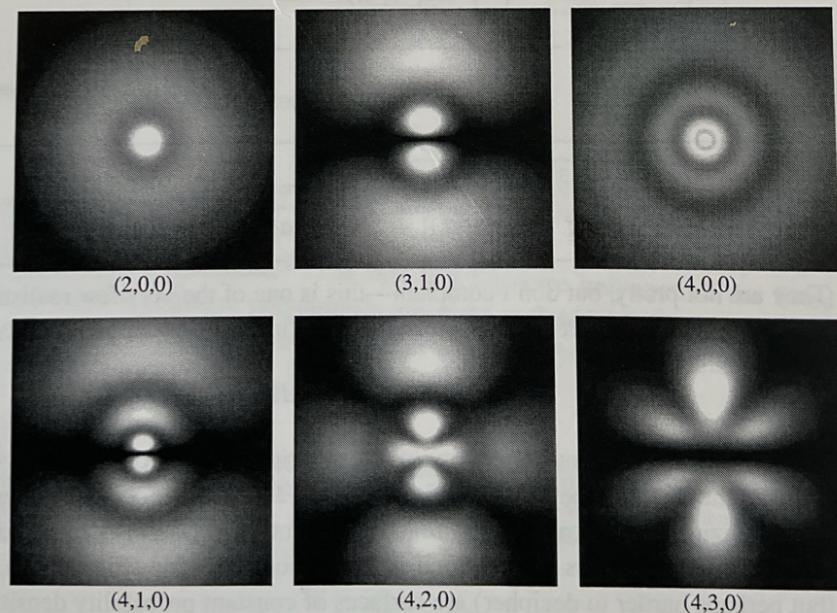
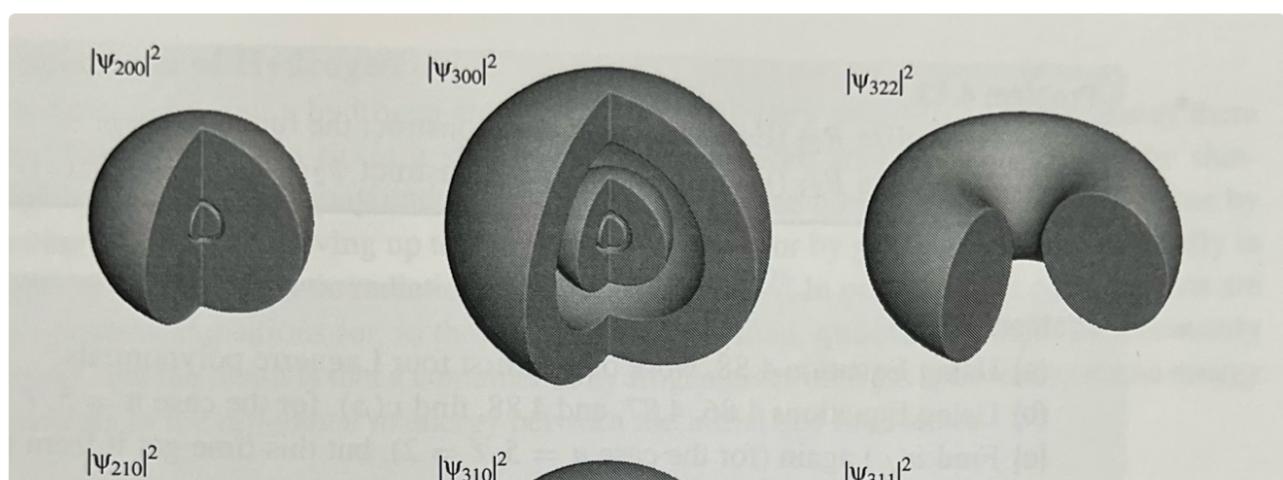
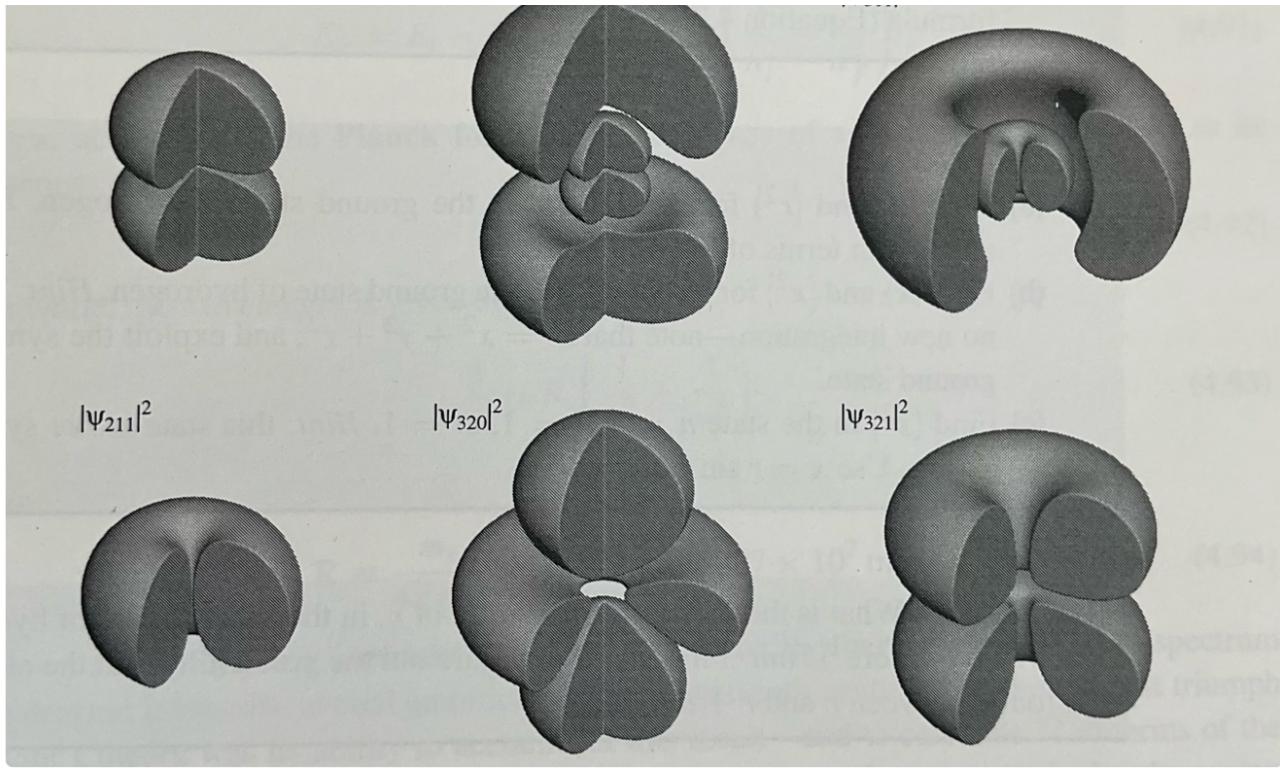


Figure 4.8: Density plots for the first few hydrogen wave functions, labeled by (n, ℓ, m) . Printed by permission using “Atom in a Box” by Dauger Research. You can make your own plots by going to: <http://dauger.com>.





The wave functions are mutually orthogonal :

$$\int \Psi_{n,l,m}^* \Psi_{n',l',m'} r^2 dr d\Omega = \delta_{ll'} \delta_{mm'} \delta_{nn'}$$

The number of radial nodes = $N - 1 = n - l - 1$. For each radial node, the wave function vanishes on a sphere.

The total number of nodes of the real part of the wave function in ϕ direction = m .

$l - m$ = number of modes in θ direction

The Spectrum of Hydrogen

Obtained due to transition of the atom from one stationary state to another [aka Quantum jumps] to give off photons that make this spectrum -

Energy difference in photons :

$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

According to Planck's formula,

$$E_{\text{rf}} = h\nu \text{ and } \lambda = c/\nu$$

$$\therefore \frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ and}$$

$$R = \frac{m_e}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}.$$

↑
Rydberg constant for Hydrogen spectrum.

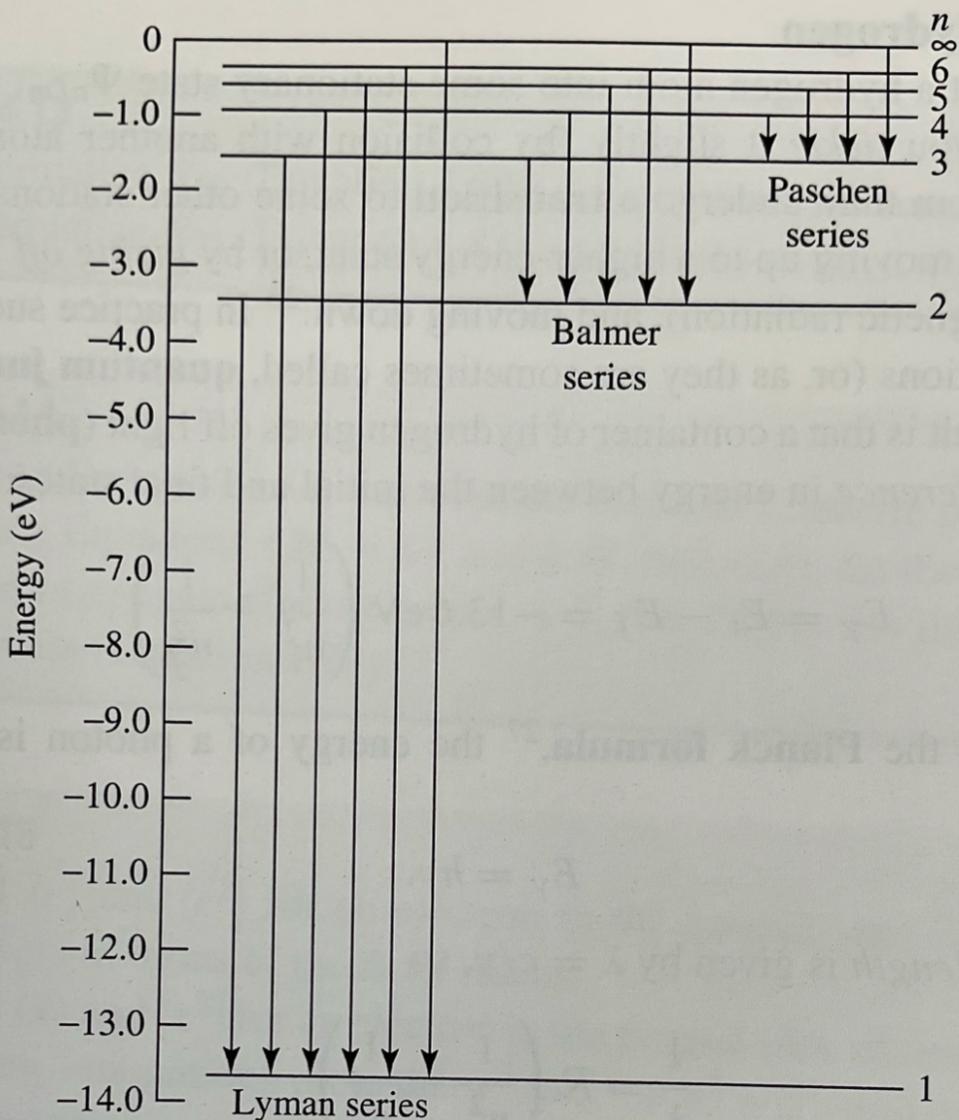


Figure 4.10: Energy levels and transitions in the spectrum of hydrogen.

The wavelength of the photon emitted in a transition from a highly excited state to the next lower state is equal to the distance light would travel in one orbital period.