PHYS 3803: Quantum Mechanics I, Spring 2021 Lecture 25, April 29, 2021 (Thursday)

- Reading: Hydrogen Atom—Griffiths 4.2
- Assignments: Problem Set 10 due May 03 (Monday). Submit your homework assignments to Canvas.

Topics for Today: Hydrogen Atom [Griffiths 4.2]
6.2 Introduction to the Hydrogen Atom
6.3 Fundamental Quantities Associated with Hydrogen Atom
Next Lecture: Hydrogen Atom [Griffiths 4.2]
6.3 Fundamental Quantities Associated with Hydrogen Atom
6.4 Numerical Estimates

6.2 Hydrogen Atom

Defining $R_{E,\ell} \equiv u_{E,\ell}(r)/r$, we can write the equation for $u_{E,\ell}$ as

$$\frac{d^2 u_{E,\ell}}{dr^2} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] u_{E,\ell} = 0.$$

Let us introduce a dimensionless parameter

$$y = 2\left(\frac{2\mu|E|}{\hbar^2}\right)^{1/2}r$$
 and $\frac{d}{dr} = 2\left(\frac{2\mu|E|}{\hbar^2}\right)^{1/2}\frac{d}{dy}$.

In terms of the y variables, the equation now becomes

$$\frac{d^2 u_{E,\ell}}{dy^2} + \left[-\frac{1}{4} + \frac{\lambda}{y} - \frac{\ell(\ell+1)}{y^2} \right] u_{E,\ell} = 0 \,,$$

where

$$\lambda = \left(\frac{\mu}{2\hbar^2 |E|}\right)^{1/2} e^2 = \left(\frac{\mu e^4}{2\hbar^2 |E|}\right)^{1/2} \,.$$

This suggests a general solution of the form

$$u_{E,\ell}(y) = e^{-\frac{1}{2}y}v(y) = e^{-\frac{1}{2}y}y^{\ell+1}\sum_{k=0}^{\infty}a_ky^k.$$

Thus the equation for v becomes

$$\frac{d^2v}{dy^2} - \frac{dv}{dy} + \left[\frac{\lambda}{y} - \frac{\ell(\ell+1)}{y^2}\right]v = 0.$$

Applying the power series expansion of v(y)

$$v(y) = \sum_{k=0}^{\infty} a_k y^{k+\ell+1}$$

we obtain

$$\sum_{k=0}^{\infty} \left[\left((k+\ell+1)(k+\ell) - \ell(\ell+1) \right) a_k y^{k+\ell-1} - (k+\ell+1-\lambda) a_k y^{k+\ell} \right] = 0$$

In general the recursion relation would connect a_{k+1} to a_k . Thus looking at the coefficient of $y^{k+\ell}$ we have

$$[(k+1+\ell+1)(k+1+\ell) - \ell(\ell+1)]a_{k+1} = (k+\ell+1-\lambda)a_k \quad \text{or}$$
$$a_{k+1} = \frac{(k+\ell+1-\lambda)}{(k+1)(k+2\ell+2)}a_k.$$

Thus for large k

$$\frac{a_{k+1}}{a_k} \to \frac{1}{k} \,.$$

Unless the series terminates this would lead to an unphysical solution. The series terminates if

$$k+\ell+1-\lambda=0.$$

That leads to

$$\lambda = \left(\frac{\mu e^4}{2\hbar |E|}\right)^{1/2} = k + \ell + 1 = n \text{ and } E_n = -\frac{\mu e^4}{2n^2\hbar^2}.$$

Since both k and ℓ take positive integer values, n also take positive integer values. Even when ℓ and k are both equal to zero, n = 1. Thus the allowed values for n are

 $n = 1, 2, 3, \cdots, \infty$

In addition,

$$\ell = n - k - 1 = n - 1, n - 2, \cdots, 0$$

These are the allowed values of the orbital angular momentum for a given value of n.

Thus the solution of the differential equation is

$$u_{n,\ell}(y) = e^{-\frac{1}{2}y} \sum_{k=0}^{n-\ell-1} a_k y^{k+\ell+1}$$
$$= e^{-\frac{1}{2}y} y^{\ell+1} w(y)$$

The differential equation that w(y) satisfies is

$$y\frac{d^2w}{dy^2} + (2\ell + 2 - y)\frac{dw}{dy} + (n - \ell - 1)w(y) = 0$$

An equation of the form

$$y\frac{d^{2}L_{q}}{dy^{2}} + (1-y)\frac{dL_{q}}{dy} + qL_{q} = 0$$

is called the Laguerre equation and $L'_q s$ are called Laguerre polynomials of order q. The functions $L^p_q(y)$ are related to the L_q 's by the relation

$$L^p_q(y) = rac{d^p}{dy^p} L_q(y) \,, \quad q \ge p \,,$$

and they are known as the associated Laguerre polynomials. They are polynomials of order q - p and satisfy the differential equation

$$y\frac{d^{2}L_{q}^{p}}{dy^{2}} + (p+1-y)\frac{dL_{q}^{p}}{dy} + (q-p)L_{q}^{p} = 0$$

Comparing this equation with the one satisfied by the w's, we see that

$$w(y) = L_{n+\ell}^{2\ell+1}(y)$$
.

The radial wave function for the Hydrogen atom is

$$R_{n,\ell} = N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L_{n+\ell}^{2\ell+1}(y) \text{ where}$$
$$y = 2 \left(\frac{2\mu |E_n|}{\hbar^2}\right)^{1/2} r = \left(\frac{2\mu e^2}{\hbar^2 n}\right) r.$$

And the total wave function is

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

 $\mathbf{N.B}$ Griffiths chooses the radial wave function as

$$R_{n,\ell} = N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L_{n-\ell-1}^{2\ell+1}(y) \,.$$

Laguerre polynomials

It is convenient to evaluate the Laguerre polynomials with

$$L_p(y) = e^y \frac{d^p}{dy^p} \left(y^p e^{-y} \right) \,.$$

Exercise: Find L_0, L_1, L_2 and L_3 .

Associated Laguerre polynomials

The associated Laguerre polynomials are defined as

$$L_p^q(y) = \frac{d^q}{dy^q} L_p(y) \,.$$

Exercise: Find L_1^1, L_2^1 , and L_3^3 .

Laguerre polynomials

It is convenient to evaluate the Laguerre polynomials with

$$L_p(y) = e^y \frac{d^p}{dy^p} \left(y^p e^{-y} \right) \,.$$

For example,

$$L_{0}(y) = e^{y} \frac{d^{0}}{dy^{0}} (y^{0}e^{-y}) = 1,$$

$$L_{1}(y) = e^{y} \frac{d}{dy} (ye^{-y}) = -y + 1,$$

$$L_{2}(y) = e^{y} \frac{d^{2}}{dy^{2}} (y^{2}e^{-y}) = y^{2} - 4y + 2,$$

$$L_{3}(y) = e^{y} \frac{d^{3}}{dy^{3}} (y^{3}e^{-y}) = -y^{3} + 9y^{2} - 18y + 6.$$

Associated Laguerre polynomials

The radial wave function for the Hydrogen atom is

$$R_{n,\ell} = N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L_{n+\ell}^{2\ell+1}(y) \,.$$

The associated Laguerre polynomials are defined as

$$L_p^q(y) = \frac{d^q}{dy^q} L_p(y) \quad \text{with} \quad L_p(y) = e^y \frac{d^p}{dy^p} \left(y^p e^{-y} \right) \,.$$

For example,

$$L_1^1(y) = \frac{d}{dy}L_1(y) = -1, \quad n = 1, \ell = 0$$

$$L_2^1(y) = \frac{d}{dy}L_2(y) = 2y - 4, \quad n = 2, \ell = 0$$

$$L_3^3(y) = \frac{d^3}{dy^3}L_3(y) = -6, \quad n = 2, \ell = 1.$$

Generating function for the Laguerre polynomials

The generating function for the Laguerre polynomials is given by

$$G(y,t) = \frac{e^{-yt/(1-t)}}{1-t} = \sum_{n=0}^{\infty} \frac{L_n(y)}{n!} t^n \quad \text{with} \quad t < 1.$$

We often apply generating functions

- to derive the special functions, such as
 - (i) Hermite polynomials for harmonic oscillator,
 - (ii) Legendre polynomials for angular momentum eigenfunctions,
- (iii) Laguerre polynomials for Hydrogen atom,
- to derive the differential equations for special functions, and
- to find the orthonormal relations.

To see that this actually generates Laguerre polynomials we note that

$$\frac{\partial G}{\partial y} = -\frac{t}{1-t}G$$
 or $(1-t)\frac{\partial G}{\partial y} = -tG$.

Let us consider each side separately:

LHS =
$$(1-t)\frac{\partial G}{\partial y} = (1-t)\sum_{n=0}^{\infty} \frac{L'_n}{n!}t^n$$

= $\sum_{n=0}^{\infty} \frac{L'_n}{n!}t^n - \sum_{n=0}^{\infty} \frac{L'_n}{n!}t^{n+1}$
= $\sum_{n=0}^{\infty} \frac{L'_n}{n!}t^n - \sum_{n=1}^{\infty} \frac{L'_{n-1}}{n-1!}t^n = \sum_{n=0}^{\infty} \frac{L'_n}{n!}t^n - \sum_{n=0}^{\infty} \frac{nL'_{n-1}}{n!}t^n$, and
RHS = $-tG = -t\sum_{n=0}^{\infty} \frac{L_n}{n!}t^n = -\sum_{n=0}^{\infty} \frac{L_n}{n!}t^{n+1}$
= $-\sum_{n=1}^{\infty} \frac{L_{n-1}}{(n-1)!}t^n$
= $-\sum_{n=0}^{\infty} \frac{nL_n}{n!}t^n$.

That leads to

$$\sum_{n=0}^{\infty} \frac{L'_n}{n!} t^n - \sum_{n=0}^{\infty} \frac{nL'_{n-1}}{n!} t^n = -\sum_{n=0}^{\infty} \frac{nL_n}{n!} t^n$$

or

$$L'_{n} - nL'_{n-1} = -nL_{n-1}$$
(I),
$$L'_{n+1} - (n+1)L'_{n} = -(n+1)L_{n}$$
(II).

Furthermore,

$$\begin{aligned} \frac{\partial G}{\partial t} &= -y \left[\frac{1}{1-t} + \frac{t}{(1-t)^2} \right] G + \frac{1}{1-t} G \\ &= \left[-\frac{y}{(1-t)^2} + \frac{1}{(1-t)} \right] G \\ &= \left[\frac{(1-y-t)}{(1-t)^2} \right] G \,. \end{aligned}$$

That leads to

$$(1 - 2t + t^2)\frac{\partial G}{\partial t} = (1 - y - t)G.$$

Let us consider each side separately

LHS =
$$(1 - 2t + t^2) \sum_{n=1}^{\infty} \frac{L_n}{(n-1)!} t^{n-1}$$

= $\sum_{n=1}^{\infty} \left[\frac{L_n}{(n-1)!} t^{n-1} - \frac{2L_n}{(n-1)!} t^n + \frac{L_n}{(n-1)!} t^{n+1} \right]$
= $\sum_{n=0}^{\infty} \left[\frac{L_{n+1}}{n!} t^n - \frac{2nL_n}{n!} t^n + \frac{nL_n}{n!} t^{n+1} \right]$ and
RHS = $(1 - y - t)G = (1 - y - t) \sum_{n=0}^{\infty} \frac{L_n}{n!} t^n$
= $(1 - y) \sum_{n=0}^{\infty} \frac{L_n}{n!} t^n - \sum_{n=0}^{\infty} \frac{L_n}{n!} t^{n+1}$.

That leads to $\sum_{n=0}^{\infty} \left[\frac{L_{n+1}}{n!} t^n - \frac{2nL_n}{n!} t^n + \frac{nL_n}{n!} t^{n+1} \right] = (1-y) \sum_{n=0}^{\infty} \frac{L_n}{n!} t^n - \sum_{n=0}^{\infty} \frac{L_n}{n!} t^{n+1}$ or

$$\sum_{n=0}^{\infty} [L_{n+1} - 2nL_n - (1-y)L_n] \frac{t^n}{n!}$$

=
$$\sum_{n=0}^{\infty} -\frac{(n+1)L_n}{n!} t^{n+1} = -\sum_{n=1}^{\infty} \frac{nL_{n-1}}{(n-1)!} t^n = -\sum_{n=0}^{\infty} \frac{n^2L_{n-1}}{n!} t^n.$$

Comparing coefficients, we have

$$L_{n+1} = (2n+1-y)L_n - n^2 L_{n-1} \quad \text{(III)}$$

Differentiating (III) with respect to y we obtain

$$L'_{n+1} = (2n+1-y)L'_n - L_n - n^2 L'_{n-1} \text{ or}$$

$$n^2 L'_{n-1} = (2n+1-y)L'_n - L'_{n+1} - L_n . \quad (IV)$$

Multiplying (I) throughout by n and eliminating $n^2 L'_{n-1}$, we have $nL'_n + L'_{n+1} - (2n+1-y)L'_n + L_n = -n^2 L'_{n-1}$

or

$$L'_{n+1} - (n+1-y)L'_n + L_n = -n^2 L'_{n-1}$$

Applying equation (II), we obtain

$$-(n+1)L_n + yL'_n + L_n = -n^2L_{n-1}$$

or

$$yL_n' - nL_n = -n^2 L_{n-1} \; .$$

Differentiating this with respect to y, we have

$$yL''_{n} + L'_{n} - nL'_{n} = -n^{2}L'_{n-1} \text{ or}$$

$$yL''_{n} + (1-n)L'_{n} = -n^{2}L'_{n-1}$$

We can eliminate $n^2 L'_{n-1}$ by (IV)

$$yL_n'' + (1-n)L_n' + (2n+1-y)L_n' - L_{n+1}' - L_n = 0$$

Eliminating L'_{n+1} by (II), we obtain

$$yL_n'' + (1-n)L_n' + (n-y)L_n' + (n+1)L_n - L_n = 0$$

or

$$y\frac{d^2L_n}{dy^2} + (1-y)\frac{dL_n}{dy} + nL_n = 0.$$

Thus we see that the L_n 's satisfy the Laguerre equations.

Generating function for the Associated Laguerre polynomials The generating function for the associated Laguerre polynomials is

$$G_p(y,t) = \frac{d^p}{dy^p}G(y,t) = (-1)^p \frac{t^p e^{-yt/(1-t)}}{(1-t)^{p+1}} = \sum_{n=p}^{\infty} \frac{L_n^p(y)}{n!} t^n \,.$$

Thus the radial wave function for the Hydrogen atom is

$$R_{n,\ell} = N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L_{n+\ell}^{2\ell+1}(y)$$

where

$$y = 2\left(\frac{2\mu|E_n|}{\hbar^2}\right)^{1/2} r = \left(\frac{2\mu e^2}{n\hbar^2}\right) r \text{ and}$$
$$E_n = -\frac{\mu e^4}{2n^2\hbar^2}.$$

And the total wave function is

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

The normalization constant $N_{n,\ell}$ can be obtained from the generating function for the associated Laguerre polynomials.

Recall that the total wave function is

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

There are orthonormal relations for (a) the total wave function (ψ) , (b) the spherical harmonics, and (c) the radial wave function. The orthonormal relations of the spherical harmonics $(Y_{\ell,m})$ demand that a nonzero contribution comes only if $\ell' = \ell$ and m' = m

$$\int Y^*_{\ell',m'}(\theta,\phi)Y_{\ell,m}(\theta,\phi)\,d\Omega = \delta_{\ell'\ell}\delta_{m'm} \quad \text{with} \quad d\Omega = \sin\theta\,d\theta\,d\phi$$

In addition, we have orthonormal relations for the total wave function

$$\int \psi_{n',\ell',m'}^* \psi_{n,\ell,m} \, d^3r = \int \psi_{n',\ell',m'}^* \psi_{n,\ell,m} \, r^2 \, dr \, d\Omega = \delta_{n'n} \delta_{\ell'\ell} \delta_{m'm}$$

and the radial wave function

$$\int R_{n'\ell'}^*(r) R_{n\ell}(r) r^2 dr = \delta_{n'n} \delta_{\ell'\ell}$$

Let us look at

$$\int R_{n,\ell}^* R_{n,\ell} r^2 dr = \left(\frac{n\hbar^2}{2\mu e^2}\right)^3 |N_{n,\ell}|^2 \int y^2 e^{-y} y^{2\ell} L_{n+\ell}^{2\ell+1}(y) L_{n+\ell}^{2\ell+1}(y) dy$$
$$= \left(\frac{n\hbar^2}{2\mu e^2}\right)^3 |N_{n,\ell}|^2 \int y^{2\ell+2} e^{-y} L_{n+\ell}^{2\ell+1}(y) L_{n+\ell}^{2\ell+1}(y) dy.$$

We now write the associated Laguerre polynomials in terms of their generating functions

$$L_{n+\ell}^{2\ell+1}(y) = \frac{\partial^{n+\ell}}{\partial t^{n+\ell}} \left[(-1)^{2\ell+1} \frac{t^{2\ell+1}}{(1-t)^{2\ell+2}} e^{-yt/(1-t)} \right]_{t=0} \,.$$

The normalization constant of the radial wave function can be determined with

$$\begin{split} & \int y^{2\ell+2} e^{-y} L_{n+\ell}^{2\ell+1}(y) L_{n+\ell}^{2\ell+1}(y) dy \\ = & \frac{\partial^{n+\ell}}{\partial t^{n+\ell}} \frac{\partial^{n+\ell}}{\partial x^{n+\ell}} \left[\frac{(tx)^{2\ell+1}}{(1-t)^{2\ell+2}(1-x)^{2\ell+2}} \\ & \quad \times \int y^{2\ell+2} e^{-y} e^{-yt/(1-t)} e^{-yx/(1-x)} dy \right]_{t=x=0} \\ = & \frac{\partial^{n+\ell}}{\partial t^{n+\ell}} \frac{\partial^{n+\ell}}{\partial x^{n+\ell}} \left[\frac{(tx)^{2\ell+1}}{(1-t)^{2\ell+2}(1-x)^{2\ell+2}} \\ & \quad \times \int y^{2\ell+2} e^{-y(1-tx)/((1-t)(1-x))} dy \right]_{t=x=0}. \end{split}$$

Changing

$$y \to \left[\frac{(1-xt)}{(1-t)(1-x)}\right]^{-1} z$$

we obtain

$$\begin{aligned} &\frac{\partial^{n+\ell}}{\partial t^{n+\ell}} \frac{\partial^{n+\ell}}{\partial x^{n+\ell}} \left[\frac{(tx)^{2\ell+1}}{(1-t)^{2\ell+2}(1-x)^{2\ell+2}} \\ &\times \frac{(1-t)^{2\ell+3}(1-x)^{2\ell+3}}{(1-xt)^{2\ell+3}} \int z^{2\ell+2} e^{-z} dz \right]_{t=x=0} \\ &= \frac{\partial^{n+\ell}}{\partial t^{n+\ell}} \frac{\partial^{n+\ell}}{\partial x^{n+\ell}} \left[\frac{(tx)^{2\ell+1}(1-t)(1-x)}{(1-xt)^{2\ell+3}} \Gamma(2\ell+3) \right]_{t=x=0} \\ &= (2n) \frac{[(n+\ell)!]^3}{(n-\ell-1)!} \end{aligned}$$

The normalization becomes

$$\int R_{n,\ell}^* R_{n,\ell} r^2 dr = \left(\frac{n\hbar^2}{2\mu e^2}\right)^3 |N_{n,\ell}|^2 \int y^2 e^{-y} y^{2\ell} L_{n+\ell}^{2\ell+1}(y) L_{n+\ell}^{2\ell+1}(y) dy$$

$$= \left(\frac{n\hbar^2}{2\mu e^2}\right)^3 |N_{n,\ell}|^2 \int y^{2\ell+2} e^{-y} L_{n+\ell}^{2\ell+1}(y) L_{n+\ell}^{2\ell+1}(y) dy$$

$$= 1,$$

or

$$\left(\frac{n\hbar^2}{2\mu e^2}\right)^3 |N_{n,\ell}|^2 (2n) \frac{[(n+\ell)!]^3}{(n-\ell-1)!} = 1.$$

Choosing $N_{\ell,m}$ to be real and negative, we obtain

$$N_{\ell,m} = N_{\ell,m}^* = -\left[\left(\frac{2\mu e^2}{n\hbar^2}\right)^3 \frac{(n-\ell-1)!}{(2n)[(n+\ell)!]^3}\right]^{1/2}$$

Thus the normalized radial wave functions are

$$R_{n,\ell} = -\left[\left(\frac{2m_e e^2}{n\hbar^2}\right)^3 \frac{(n-\ell-1)!}{(2n)[(n+\ell)!]^3}\right]^{1/2} \times e^{-\frac{1}{2}y} y^\ell L_{n+\ell}^{2\ell+1}(y) \text{ with}$$
$$y = 2\left(\frac{2m_e |E|}{\hbar^2}\right)^{1/2} r = \left(\frac{2m_e e^2}{n^2\hbar^2}\right) r \text{ and } E_n = -\frac{m_e e^4}{2n^2\hbar^2}.$$

The first three radial functions are

$$R_{10} = 2\left(\frac{m_e e^2}{\hbar^2}\right)^{3/2} e^{-(m_e e^2/\hbar^2)r} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0},$$

$$R_{20} = \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/(2a_0)},$$

$$R_{21} = \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{\sqrt{3}a_0}\right) e^{-r/(2a_0)} \text{ with }$$

$$a_0 = \frac{\hbar^2}{m_e e^2} \text{ (Bohr radius).}$$

Radial wave function of the Hydrogen Atom

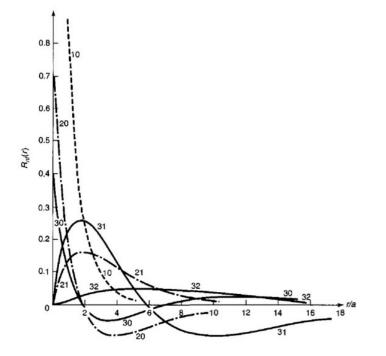


Figure 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

Figure 1: Hydrogen radial wave function.

6.3 Fundamental Quantities Associated with Hydrogen Atom

Looking at the wave functions for the Hydrogen atom, we notice that there is a fundamental length scale that enters the solutions:

$$a_0 = \frac{\hbar^2}{m_e e^2}$$

that is the Bohr radius.

In terms of this quantity, we can write down the radial solutions as

$$R_{n,\ell}(r) \sim e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1} \left(\frac{2r}{na_0}\right)$$

Remembering that $L_{n+\ell}^{2\ell+1}$ is a polynomial of order $n-\ell-1$, the most dominant behavior for large r $(r \gg a_0)$ would be

$$R_{n,\ell}(r) \sim (r)^{n-1} e^{-r/na_0}$$
.

Then the probability for finding the electron in a special shell of radius r and thickness dr

$$\begin{split} \int_{\Omega} \psi^* \psi r^2 dr d\Omega &\sim R_{n,\ell}^2(r) r^2 dr \\ &= (r)^{2n} e^{-2r/na_0} dr \end{split}$$

We can thus determine the radius of maximum probability as

$$\frac{d}{dr}\left((r)^{2n}e^{-2r/na_0}\right) = 2nr^{2n-1}e^{-2r/na_0} - \frac{2}{na_0}(r)^{2n}e^{-2r/na_0}$$
$$= \left(\frac{1}{na_0}\right)(r-n^2a_0)(r)^{2n-1}e^{-2r/na_0}$$
$$= 0$$

or

$$r_* = n^2 a_0 \; .$$

Thus we see that the Bohr radius a_0 is the most probable value of r in the ground state and thus defines the natural size of the Hydrogen atom. We also see that $\langle r \rangle$ grows as n^2 .

This theory also possesses a natural energy scale. Thus we define

$$R_y = \frac{m_e e^4}{2\hbar^2} = \text{Rydberg.}$$

The the energy levels for the Hydrogen atom become

$$E_n = -\frac{R_y}{n^2} \; .$$