Hydrogen Radial Wavefunctions

The Hydrogen atom is special because it has electronic states and properties that scale with $n$ and $\ell$ in a simple and global way. This is “structure” that is more than a collection of unrelated facts. H serves as our model for “electronic structure” of many-electron atoms, molecules, and possibly solids.

By showing how $E$, $\langle r^\sigma \rangle$ (size and shapes), $\langle n\ell | r | n'\ell' \rangle$ (general matrix element) scale with $n$ and $\ell$, it tells us the kind of behavior to look for in more complex systems.

* as a perturbation on H (quantum defects)
* as a hint of relationships useful for extrapolation, assignment, for recognizing when something behaves differently from naive expectations.

TODAY

1. Simplified Radial Equation
2. Boundary conditions at $r \to 0$ and $r \to \infty$
3. qualitative features of $R_{n\ell}(r)$
4. n-scaling of $\langle r^\sigma \rangle$
5. mathematical form of $R_{n\ell}(r)$
6. regular and irregular Coulomb functions
For any central force problem

\[ H = \left[ \frac{\hat{p}_r^2}{2\mu} + \frac{\ell^2}{2\mu r^2} \right] + V(r) \]

We know that \( \hat{H}, \ell^2, \ell_z \) commute, so spherical harmonics, \( Y_{\ell m}^\theta(\theta, \phi) \), are eigenfunctions of \( \hat{H} \) with eigenvalues \( \hbar^2 \ell(\ell + 1) \).

\[ \psi(r, \theta, \phi) = R(r)Y_{\ell m}^\theta(\theta, \phi) \]

trial form for separation of \( \psi \)

\[ \hat{H}\psi = \left( \frac{\hbar^2 \ell^2}{2\mu r^2} + V(r) \right) Y_{\ell m}^\theta(\theta, \phi) R(r) = E\psi \]

Operate on the \( Y_{\ell m}^\theta(\theta, \phi) \) angular wavefunction and move it through to left.

\[ \hat{H}\psi = Y_{\ell m}^\theta(\theta, \phi) \left( \frac{\hbar^2 \ell^2}{2\mu r^2} + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} + V(r) \right) R(r) = E\psi \]

so we can take \( Y_{\ell m}^\theta(\theta, \phi) \) out of the Schrödinger Equation and we are left with a 1-D radial equation where the only trace of the angular part is the \( \ell \)-dependence of \( V_{\ell}(r) \), the effective potential energy function.

Since the differential equation depends on \( \ell \), \( R(r) \) must also depend on \( \ell \), thus \( R_{n\ell}(r) \) is the radial part of \( \psi \), and it will generally be an explicit function of two quantum numbers, \( n \) and \( \ell \).

Usually \( n \) specifies the number of radial nodes and \( \ell \) the number of angular nodes, but a special numbering convention for Hydrogen (and hydrogenic ions) causes a slight distortion of this rule.
The radial equation, when the explicit differential operator form of $P_r^2$ is derived and inserted, has the form
\[
\left\{ \left[ -\frac{\hbar^2}{2\mu} \frac{d}{dr} \frac{1}{r} \right] + \left[ \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} + V(r) \right] \right\} R_{nl}(r) = E_{nl} R_{nl}(r)
\]

It is customary to simplify this equation by replacing $R_{nl}(r)$ by $\frac{1}{r} u_{nl}(r)$
\[ R_{nl}(r) = \frac{1}{r} u_{nl}(r) \]

* equation looks simpler
* volume element looks simpler
* behavior as $r \to 0$ seems more familiar

insert $\frac{1}{r} u_{nl}(r)$ in place of $R_{nl}(r)$ and then multiply through on left by $r$
\[
\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} + V(r) - E_{nl} \right] u_{nl}(r) = 0
\]

looks like ordinary 1-D Schrödinger Equation.
Boundary condition:
\[ u_{nl}(r) \to 0 \quad \text{as} \quad r \to 0 \quad \text{WHY? Because for all } \ell > 0, V(0) \to \infty. \]

exactly as if $V(r) = \infty$ $r \leq 0$, but of course $r < 0$ is impossible, so we had better be careful about behavior of $u_{nl}(r)$ and $R_{nl}(r)$ as $r \to 0$
Note also that \( d^3 r = r^2 \sin \theta \, drd\theta d\phi \)

\[
R^*_{n'\ell}, R_{n\ell} \quad r^2 \, dr = u^*_{n'\ell}(r)u_{n\ell}(r) \, dr
\]

So volume element looks just as in 1-D problem

Return to special situation as \( r \to 0 \).

Why do we care? It turns out that s-orbitals have \( R_{ns}(0) \neq 0 \) and that in ESR one measures “Fermi-contact” hyperfine structure which is the spin-density at specific nuclei. It is a direct measure of the ns atomic orbital character in each molecular orbital!

CTDL, p. 781

What is the worst possible divergence of \( R_{n\ell}(r) \) as \( r \to 0 \)?

For \( r \to 0 \), \( R_{n\ell}(r) \) will be dominated by \( r^s \) where \(|s|\) is as small as possible. This is the most strongly divergent part of \( R_{n\ell}(r) \), which is all we need to be concerned with as \( r \to 0 \).

Let \( R_{n\ell} \sim Cr^s \), where this is a good approximation at \( r \to 0 \).

Plug this definition into Schrödinger Equation

\[
\frac{d^2}{dr^2} r R_{n\ell}(r) = \frac{d^2}{dr^2} C r^{s+1} = (s+1)(s)C r^{s-1}
\]

\[
T_r = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{d^2}{dr^2}
\]

\[
HR_{n\ell}(r) = -\frac{\hbar^2}{2\mu} C(s+1)(s)r^{s-2} + \frac{\hbar^2}{2\mu} C r^{s-2} + V(r)C r^{s} - E_{n\ell}C r^{s} = 0
\]

if \( V(r) \propto \frac{1}{r} \)

As \( r \to 0 \) \( V(r) \) rarely diverges more rapidly than \( 1/r \), thus \( V(r)C r^s \) gives \( r^{-1} \).

Then, in the limit \( r \to 0 \), the coefficients of the \( r^{s-2} \) term (i.e. the most rapidly divergent term) must be \( = 0 \)

\[
-(s+1)s + \ell(\ell+1) = 0
\]

*This excludes the stronger divergence of the centrifugal barrier term in \( V_r(r) \).
satisfied if \( s = \ell \) or \( s = - (\ell + 1) \)

verify second possibility:
\[
s(s + 1) = (-\ell - 1)(-\ell - 1 + 1) = - (\ell + 1)(-\ell) = \ell(\ell + 1)
\]

In other words \( R_{n\ell}(r) \to r^\ell \) OR (if \( s = \pm (\ell + 1) \)) \( \frac{1}{r^{\ell + 1}} \) as \( r \to 0 \)

well behaved at \( r \to 0 \)

disaster even if \( \ell = 0 \)

Actually both of these possibilities satisfy the differential equation for
\( V(r) = \frac{1}{r} \) (known as the Coulomb – or H atom Hamiltonian), but the one that diverges as \( r \to 0 \) cannot satisfy the \( r \to 0 \) boundary condition for the H atom.

** Regular and Irregular Coulomb wavefunctions – we will return to these later in the context of Quantum Defect Theory.

So for now we insist that
\[
R_{n\ell}(0) \neq 0 \quad \text{special situation for } R_{ns}(r)
\]

\[
R_{n\ell > 0}(0) = 0
\]

\[
u_{n\ell}(0) = 0 \quad \text{for all } \ell
\]

(no special case for \( u_{ns}(r) \))
For Hydrogen

\[ V_\ell(r) = + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} - \frac{e^2}{r} \]

\[ e^2 \equiv \frac{q^2}{4\pi\varepsilon_0} \]

\[ \mu = \frac{m_e m_p}{m_e + m_p} \approx m_e \]

What do we know from our study of 1-D problems?

WKB

\[ \psi_{\text{envelope}} \propto p^{-1/2} \]

# of nodes, placement of nodes, degeneracy, behavior at inner and outer turning points, location of inner and outer turning points

inner vs. outer part of \( u_{nl}(r) \) – where is the extra \( \frac{h}{2} \) of action acquired (associated with tunneling into nonclassical region)?

\[ \text{recall } \int_{r_c(E)}^{r_s(E)} p(r)dr = \frac{h}{2}(n + 1/2) \]
5.73 Lecture #28

Find that \[ E_{n\ell} = -\frac{\mathcal{R}}{n^2} \]

At turning point \[ V_{\ell}(r) = E_{n\ell} \]

\[ -\frac{\mathcal{R}}{n^2} = \frac{\hbar^2 \ell (\ell + 1)}{2\mu r_{\pm}^2} - \frac{\epsilon^2}{r_{\pm}} \]

solve for \( r_{\pm} \) as function of \( n \) and \( \ell \)

\[ r_{\pm} = a_0 \left[n^2 \pm n(n^2 - \ell(\ell + 1))^{1/2}\right] \]

\[ = a_0 n^2 \left[1 \pm \left(1 - \frac{\ell(\ell + 1)}{n^2}\right)^{1/2}\right] \]

Use this equation for the turning points to construct qualitatively correct cartoons of \( R_{n\ell}(r) \) in crucial regions.

Use Quadratic formula to find \( r_{\pm}(n) \)

\[ a_0 = \frac{\hbar^2}{2\mu e^2} \quad \text{Bohr radius} \]

when \( \ell \ll n \), where are \( r_{r} \) and \( r_{\pm} \)?

surprising systematic degeneracy

\[ \begin{align*}
3s & \quad 3p & \quad 3d \\
2s & \quad 2p \\
1s & \quad & \quad\text{etc.}
\end{align*} \]

\[ E_{n\ell} \]

Because of pattern, we use \( n \) to label degenerate groups

\[ E_{n\ell} = -\frac{\mathcal{R}}{n^2} \]

hence \( n \) is not # of radial nodes.
orbital # of radial nodes
1s 0
2s 1
2p 0 (because it is lowest solution to $\ell = 1$ equation)
3s 2
3p 1
3d 0

# radial nodes = $(n - 1) - \ell$
# angular nodal surfaces $\ell$
total # nodes $n - 1$

\begin{align*}
 n & \quad \text{degeneracy} \\
 1 & \quad 1 \\
 2 & \quad 1 + (2\ell + 1) = 4 \\
 3 & \quad 1 + 3 + 5 = 9 \\
 \vdots & \\
 n & \quad n^2
\end{align*}

\text{n - scaling of $\langle r^\sigma \rangle$}

two limits: $\sigma < 0$ vs. $\sigma > 0$
determined near inner turning point $\sim n^{-3}$
Bohr model $r_{\text{nd}} = a_0 n^2$
(seen argument on next page)$\langle r^\sigma \rangle \sim a_0^\sigma n^{2\sigma}$

Expectation values of $r^\sigma$ vs. transition moments and off--diagonal matrix elements of $r^\sigma$. Stationary phase.
$T = \frac{p^2}{2\mu} > \text{IP in the “inner region.”}$

Variation of $T$ from $n = 6$ to $n = \infty < 3\%$

Variation of $p < 1.5\%$

DeBroglie $\lambda \sim \frac{\hbar}{p}$

Location of innermost node is $n$-independent. Because $p$ is large and fractional change of $p$ vs. $n$ is negligible.

$e^-$ comes into core region fast and leaves fast — $\Delta t$ same for all $n$

Fraction of time inside core?

Time inside one period

$$= \frac{2(v/\lambda)^{-1}}{h} \frac{E_n - E_{n+1}}{E_n}$$

$$= \left[ \frac{2h}{p} \right] \left[ \frac{p}{m} \right] \approx \frac{4m\hbar}{\hbar \frac{2\delta R}{n^3}} \approx \frac{4m\hbar}{\hbar^2} \frac{p^2}{n^3}$$

Probability of finding $e^-$ inside core $\propto n^{-3}$!
fraction of time inside $\sim n^{-3}$

**amplitude of** $\psi_{n\ell} \sim n^{-3/2}$ **inside core region**

Basis of all Rydberg scaling

inner lobe

\[
1\text{st node does not shift with } n \\
\text{amplitude in first lobe scales as } n^{-3/2}
\]

Astonishingly important!

all $n, n'$ matrix elements of $r^\sigma$ where $\sigma < 0$ scale as $(nn')^{-3/2}$!

Some matrix elements scale this way even when $\sigma > 0$.

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**McQuarrie, page 223**

\[
R_{n\ell}(r) = -\left[\frac{(n - \ell - 1)!}{2n[(n + \ell)!]^3}\right]^{1/2} \left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+1}^{2\ell+1}\left(\frac{2r}{na_0}\right) \text{ exponential (polynomials)}
\]

\[
\text{normalization} \rightarrow 0 \text{ as } r \rightarrow \infty
\]

Regular and Irregular Coulomb functions ($E \leq 0$)

- **regular** $f(E, \ell, r) \propto r^\ell$ 
  - $u(v, \ell, r) \sin \pi v - v(v, \ell, r)e^{i\pi v}$, which is an increasing exponential *except* when $v$ is a positive integer. Need some other way to satisfy $r \rightarrow \infty$ boundary condition when $v$ is not an integer.

- **irregular** $g(E, \ell, r) \propto r^{-i\ell}$
  - $-u(v, \ell, r) \cos \pi v + v(v, \ell, r)e^{i\pi(v+1/2)}$, which blows up.
  - $u(v, \ell, r)$ is an increasing exponential as $r \rightarrow \infty$
  - $v(v, \ell, r)$ is a decreasing exponential as $r \rightarrow \infty$

(see Gallagher, page 16)
\begin{align*}
\langle r \rangle &= \frac{1}{2} \left[ 3n^2 - \ell(\ell + 1) \right] \\
\langle r^2 \rangle &= \frac{n^2}{2} \left[ 5n^2 + 1 - 3\ell(\ell + 1) \right] \\
\langle 1/r \rangle &= \frac{1}{n^2} \\
\langle 1/r^2 \rangle &= \frac{1}{n^3(\ell + 1/2)} \\
\langle 1/r^3 \rangle &= \frac{1}{n^3(\ell + 1)(\ell + 1/2)\ell} \\
\langle 1/r^4 \rangle &= \frac{3n^2 - \ell(\ell + 1)}{2n^3(\ell + 3/2)(\ell + 1)(\ell + 1/2)\ell(\ell - 1/2)} \\
\langle 1/r^6 \rangle &= \frac{35n^4 - 5n^2\left[ 6\ell(\ell + 1) - 5 \right] + 3(\ell + 2)(\ell + 1)\ell(\ell - 1)}{8n^7(\ell + 5/2)(\ell + 2)(\ell + 3/2)(\ell + 1)(\ell + 1/2)\ell(\ell - 1/2)(\ell - 1/2)(\ell - 3/2)}
\end{align*}

Note! \begin{align*}
\langle r^\sigma \rangle &\quad \sigma < -1 \quad \text{scale as } n^{-3}! \\
\sigma &\quad \sigma > 0 \quad \text{scale as } n^{2\sigma}!
\end{align*}