Hydrogen Radial Wavefunctions

The Hydrogen atom is special because it has electronic states and properties that scale with n and ℓ 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 ℓ, 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

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

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

$\psi(r,\theta,\phi) = R(r) Y_\ell^m(\theta,\phi)$

trial form for separation of ψ

$$\hat{H}\psi = \left(\frac{\hat{p}_r^2}{2\mu} + \frac{\boldsymbol{\ell}^2}{2\mu r^2} + V(r)\right) Y_\ell^m(\theta,\phi) R(r) = E\psi$$

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

$$\hat{H}\psi = Y_\ell^m(\theta,\phi)\left(\frac{\hat{p}_r^2}{2\mu} + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)}_{V_\ell(r)}\right) R(r) = E\psi$$

so we can take $Y_\ell^m(\theta,\phi)$ 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 ℓ-dependence of $V_\ell(r)$, the effective potential energy function.

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

Usually n specifies the number of radial nodes and ℓ 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 $\mathbf{P}_r^2$ is derived and inserted, has the form

$$\left\{ \underbrace{\left[-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{d^2}{dr^2} r \right]}_{\mathbf{T}_r} + \underbrace{\left[\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) \right]}_{V_\ell} \right\} R_{n\ell}(r) = E_{n\ell} R_{n\ell}(r)$$

It is customary to simplify this equation by replacing $R_{n\ell}(r)$ by $\frac{1}{r} u_{n\ell}(r)$

$$R_{n\ell}(r) = \frac{1}{r} u_{n\ell}(r)$$

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

insert $\frac{1}{r} u_{n\ell}(r)$ in place of $R_{n\ell}(r)$ and then multiply through <u>on left</u> by r

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) - E_{n\ell} \right] u_{n\ell}(r) = 0$$

looks like ordinary 1-D Schrödinger Equation.
Boundary condition:

$u_{n\ell}(r) \to 0$ as $r \to 0$

$\boxed{\text{WHY? Because for all } \ell > 0,\ V_\ell(0) \to \infty.}$

exactly <u>as if</u> $V(r) = \infty \quad r \le 0$, but of course $r < 0$ is impossible, so we had better be careful about behavior of $u_{n\ell}(r)$ and $R_{n\ell}(r)$ as $r \to 0$

Note also that $d^3r = r^2 \sin\theta dr d\theta d\phi$

$$R^*_{n'\ell'} R_{n\ell} \; r^2 dr = u^*_{n'\ell'}(r) u_{n\ell}(r) dr$$

r^2 cancelled. 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

$$\frac{d^2}{dr^2} rR_{n\ell}(r) = \frac{d^2}{dr^2} Cr^{s+1} = (s+1)(s)Cr^{s-1}$$

$$\mathbf{T}_r = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}$$

$$\mathbf{H}R_{n\ell}(r) = -\frac{\hbar^2}{2\mu}C(s+1)(s)r^{s-2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu}Cr^{s-2} + V(r)Cr^s - E_{n\ell}Cr^s = 0$$

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

$\left[\begin{array}{c}\text{As } r \to 0 \;\; V(r) \text{ rarely diverges} \\ \text{more rapidly than } 1/r, \text{ thus} \\ V(r)C\, r^s \text{ gives } r^{s-1}.\end{array}\right]^*$

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 $V_\ell(r)$.

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 $R_{n\ell}(r) \to \underbrace{r^{\ell}}_{\substack{\text{well behaved}\\ \text{at } r \to 0}}$ OR (if $s = \pm(\ell+1)$) $\dfrac{1}{\underbrace{r^{\ell+1}}_{\substack{\text{disaster even if}\\ \ell = 0}}}$ as $r \to 0$

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

$$R_{n\ell}(r) \to r^{\ell} \quad \text{as} \quad r \to 0$$

$R_{ns}(0) \neq 0$ special situation for $R_{ns}(r)$

$R_{n\ell>0}(0) = 0$

$u_{n\ell}(0) = 0$ for all ℓ

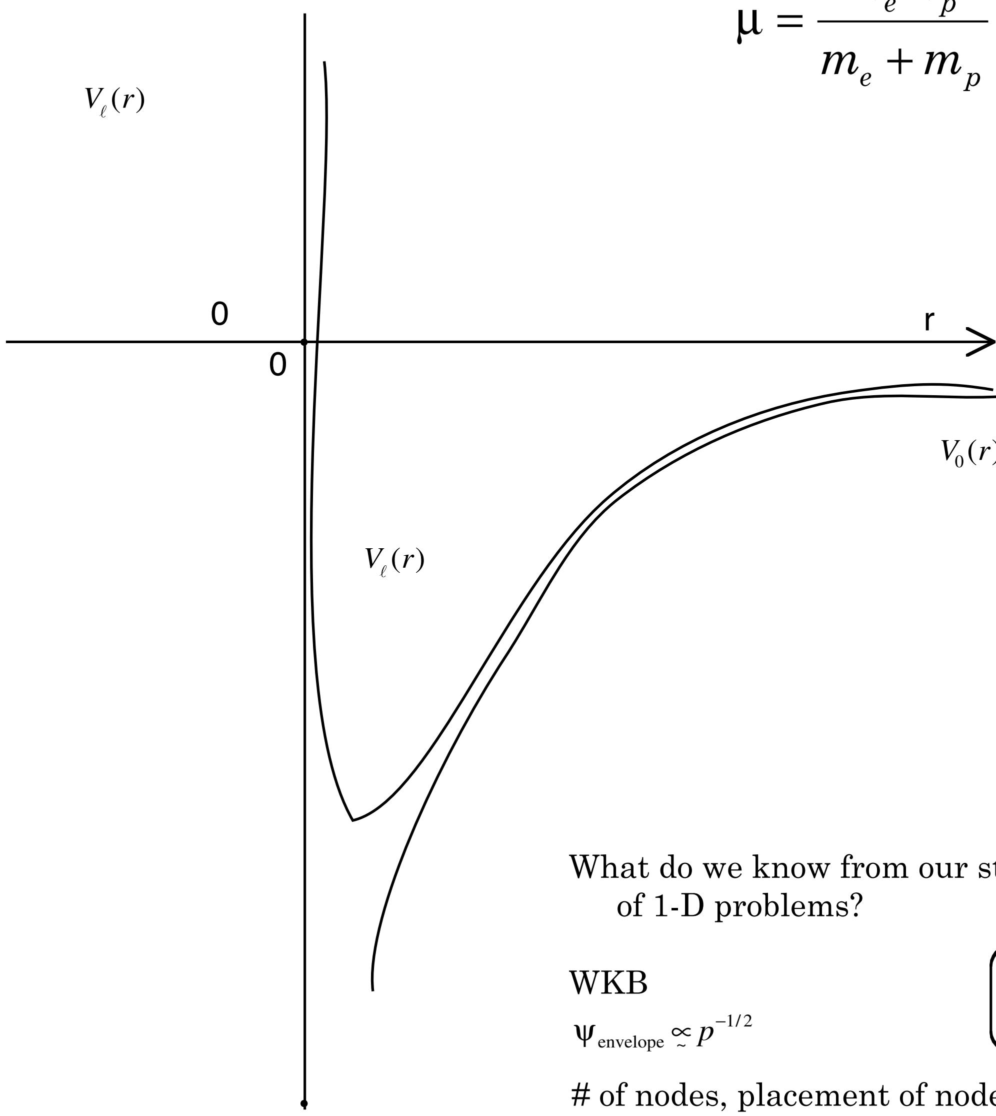
(no special case for $u_{ns}(r)$)

For Hydrogen

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

$$e^2 \equiv \frac{q^2}{4\pi\varepsilon_\circ}$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e$$



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

WKB

$\psi_{\text{envelope}} \underset{\sim}{\propto} p^{-1/2}$

$$\frac{\lambda}{2} = \frac{h}{2p(r)}$$

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

ASK QUESTIONS
shape of $u_{n\ell}(r)$
1st lobe, last lobe

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

$$\left[\text{recall} \int_{r_<(E)}^{r_>(E)} p(r)dr = \tfrac{h}{2}(n+1/2)\right]$$

Find that $\quad E_{n\ell} = -\dfrac{\Re}{n^2} \qquad \Re = \dfrac{e^4 m_e}{2\hbar^2}$

At turning point $\quad V_\ell(r) = E_{n\ell}$

$$-\frac{\Re}{n^2} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r_\pm^2} - \frac{e^2}{r_\pm}$$

$$-\frac{\Re}{n^2} = \frac{\hbar^2\ell(\ell+1) - r_\pm e^2 2\mu}{2\mu r_\pm^2}$$

$$-\frac{2\mu \Re r_\pm^2}{n^2} = \hbar^2 \ell(\ell+1) - r_\pm e^2 2\mu$$

solve for $r_\pm$ as function of n and ℓ

Use Quadratic formula to find $r_\pm(n)$

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

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

$a_0 = \dfrac{\hbar^2}{e^2 m_e}$ Bohr radius

when $\ell << n$, where are r_+ and r_- ?

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

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surprising systematic degeneracy

etc.

3s ——— 3p ——— 3d ———

2s ——— 2p ———

$E_{n\ell}$

1s ———

Because of pattern, we use n to label degenerate groups

$$E_{n\ell} = -\frac{\Re}{n^2}$$

hence n is <u>not</u> # 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 ℓ

total # nodes $n-1$

n	degeneracy
1	1
2	$1 + (2\ell + 1) = 4$
3	$1 + 3 + 5 = 9$
…	
n	n^2

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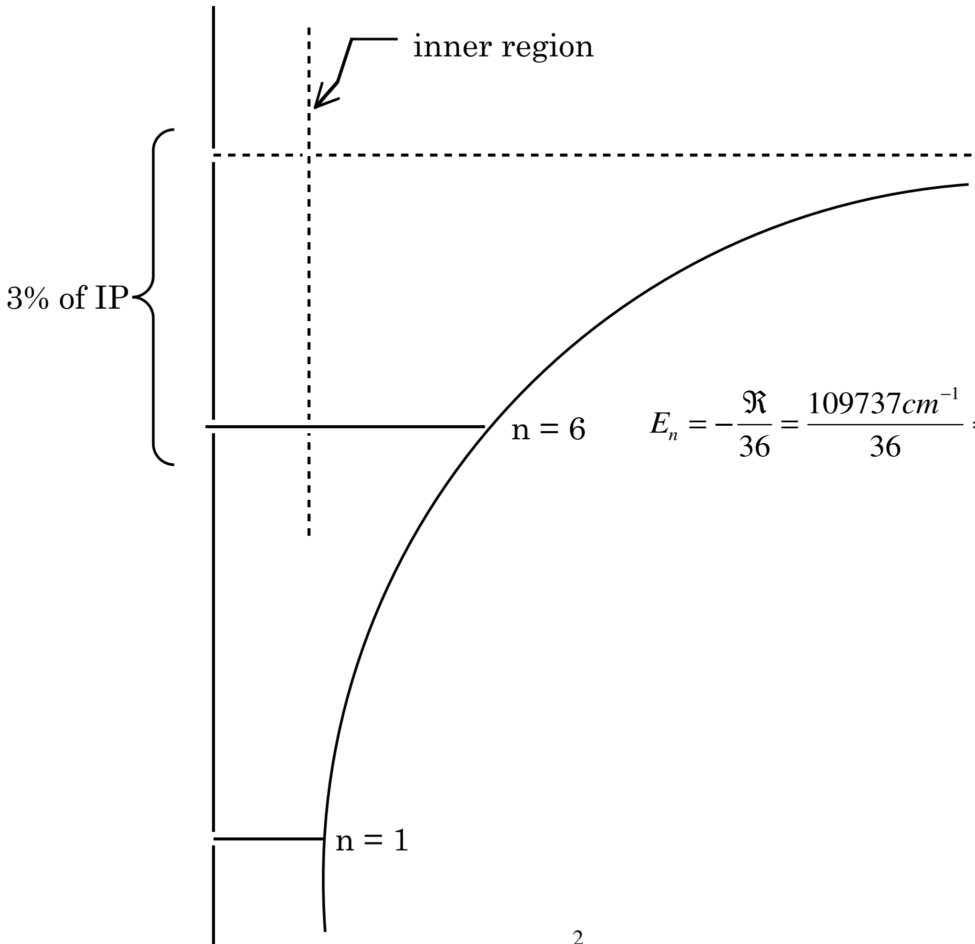
n - scaling of $\langle r^{\sigma} \rangle$

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

Expectation values of r^{σ} vs. transition moments and off--diagonal matrix elements of r^{σ}. Stationary phase.



$$E_n = -\frac{\Re}{36} = \frac{109737 cm^{-1}}{36} \approx 3000 cm^{-1}$$

$$T = \frac{p^2}{2\mu} > \text{IP in the “inner region.”}$$

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

variation of p < 1.5%

$\left.\begin{array}{l} \text{deBroglie } \lambda \sim \frac{h}{p} \\ \text{location of innermost node} \end{array}\right\}$ independent of n ! Because p is large and fractional change of p vs. n is negligible.

e^- comes into core region fast and leaves fast — Δt same for all n

fraction of time inside core? $\dfrac{\text{time inside}}{\text{one period}} = \dfrac{2(v/\lambda)^{-1}}{\dfrac{h}{E_n - E_{n+1}}}$

$$= \frac{2\left[\dfrac{\frac{h}{p}}{p/m}\right]}{\dfrac{h}{2\Re/n^3}} \approx \frac{4m\Re}{p^2 n^3}$$

$\boxed{\lambda/v}$

$E_n = -\Re/n^2$

$E_{n+\delta/2} - E_{n-\delta/2} = \dfrac{2\delta\Re}{n^3}$

n-independent

probability of finding e^- inside core $\propto n^{-3}$!

fraction of time inside $\underset{\sim}{\propto}$ n^{-3}

$$\boxed{\text{amplitude of } \psi_{n\ell} \propto \; n^{-3/2} \text{ inside core region}}$$

Basis of all Rydberg scaling

$$\text{inner lobe}\left\{\begin{array}{l}\text{1st node does not shift with n}\\ \text{amplitude in first lobe scales as } n^{-3/2}\end{array}\right\}\text{Astonishingly important!}$$

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

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

McQuarrie, page 223

$$R_{n\ell}(r) = -\underbrace{\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2}}_{\text{normalization}} r^{\ell} \underbrace{e^{-r/na_0}}_{\substack{\text{exponential}\\ \to 0 \text{ as } r \to \infty}} \underbrace{L_{n+1}^{2\ell+1}\left(\frac{2r}{na_0}\right)}_{\substack{\text{associated}\\ \text{Laguerre functions}\\ \text{(polynominals)}}}$$

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

	$u_{n\ell}(r) \equiv rR(r)$		$r \to 0$	$r \to \infty$
regular	$f(E,\ell,r)$	$\propto$	$r^{\ell+1}$	$u(\nu,\ell,r)\sin \pi\nu - v(\nu,\ell,r)e^{i\pi\nu}$, which is an increasing exponential *except* when ν is a positive integer. Need some other way to satisfy $r \to \infty$ boundary condition when ν is not an integer
irregular	$g(E,\ell,r)$	$\propto$	$r^{-(\ell)}$	$-u(\nu,\ell,r)\cos \pi\nu + v(\nu,\ell,r)e^{i\pi(\nu+1/2)}$, which blows up. * $u(\nu,\ell,r)$ is an increasing exponential as $r \to \infty$ * $v(\nu,\ell,r)$ is a decreasing exponential as $r \to \infty$ (see Gallagher, page 16)

T.F. Gallagher, Rydberg Atoms, page 25

$\langle r \rangle$	$\frac{1}{2}\left[3n^2 - \ell(\ell+1)\right]$
$\langle r^2 \rangle$	$\frac{n^2}{2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]$
$\langle 1/r \rangle$	$1/n^2$
$\langle 1/r^2 \rangle$	$\frac{1}{n^3(\ell+1/2)}$
$\langle 1/r^3 \rangle$	$\frac{1}{n^3(\ell+1)(\ell+1/2)\ell}$
$\langle 1/r^4 \rangle$	$\frac{3n^2 - \ell(\ell+1)}{2n^5(\ell+3/2)(\ell+1)(\ell+1/2)\ell(\ell-1/2)}$
$\langle 1/r^6 \rangle$	$\frac{35n^4 - 5n^2\left[6\ell(\ell+1) - 5\right] + 3(\ell+2)(\ell+1)\ell(\ell-1)}{8n^7(\ell+5/2)(\ell+2)(\ell+3/2)(\ell+1)(\ell+1/2)\ell(\ell-1/2)(\ell-1)(\ell-3/2)}$

Note!

all $\langle r^{\sigma} \rangle$	$\sigma < -1$	scale as n^{-3}!
	$\sigma > 0$	scale as $n^{2\sigma}$!