Hydrogen Radial Wavefunctions

The Hydrogen atom is special because it has electronic states and properties that scale with the principal, n, and orbital angular momentum, ℓ quantum numbers, in a simple and global way. This is "structure" that is more than a collection of unrelated facts. The H atom 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), $\langle n\lambda|r|\nu'\ell'\rangle$ (general matrix elements) scale with the n and ℓ quantum numbers, it tells us the kind of behavior to look for and how to understand it in more complex systems.

- * as a perturbation on the Hydrogen atom (quantum defects)
- * as a hint of relationships that are useful for extrapolation, assignment, and for recognizing when something behaves differently from naive expectations.

<u>TODAY</u>

0. A warning.
1. Simplified Radial Equation − a trick to make it look exactly like the 1D problems we have already solved.
2. Boundary conditions as $r \to 0$ and $r \to \infty$
3. qualitative features of $R_{n\ell}(r)$
4. n-scaling of $\langle r^{\sigma}\rangle$, where σ is an integer
5. mathematical form of $R_{n\ell}(r)$
6. regular and irregular Coulomb functions

Warning: This first lecture on the Hydrogen atom is not what you expect. Most textbooks treat the H atom as an exactly solved problem. The solution is based on standard techniques for solving differential equations and the solutions are expressed in terms of named and tabulated special function. The exact and analytic solution for the H atom is presented as a unique, beautiful gem to be admired and stored in a safe place, out of view and out of use. What I present here is based on techniques and approximations discussed in previous lectures. My goal is to arm you with methods to answer questions that apply to many-electron atoms, molecules, and to quantum number "scaling-rules" that provide a framework for describing intra-species and inter-quantum-state patterns of observable properties. These quantum number scaling ideas are mostly based on the stationary phase approximation (in what local region of space does an integral accumulate to its final value, what does the WKB approximation tell you about wavefunction amplitudes and node-spacing in this special region) and perturbation theory. These are techniques and ideas that you will use throughout your career to build insights that will amaze your colleagues.

For *every* central force problem

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

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

$*\psi(\mathrm{r},\theta,\phi) = R(r)Y_\ell^m(\theta,\phi)$

$*$trial form for separation of variables in ψ

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

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

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

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 remaining hint 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 two (not 3) 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

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

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

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

- * the resulting equation looks simpler
- * the resulting volume element looks simpler
- * the 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, we get

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

This 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 as if $V(r) = \infty$ for $r \le 0$, 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 the volume element is $dV = r^2 \sin\theta dr d\theta d\phi$

and the r-dependence of the integrand is $R^*_{n'\ell'} R_{n\ell}\, r^2 dr = u^*_{n'\ell'}(r) u_{n\ell}(r) dr$

↑

the r^2 factor is cancelled. So the volume element looks just as in 1-D problems

Return to special situation as r → 0.

Why do we care? It turns out that only s-orbitals have $R_{ns}(0) \neq 0$ and that in ESR one measures "Fermi-contact" hyperfine structure which is related to 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 → 0?

For r → 0, $R_{n\ell}(r)$ will be dominated by r^s where the exponent $|s|$ 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 → 0.

Let $R_{n\ell} \sim Cr^s$, where this is a good approximation as r → 0.

Plug this definition into the Schrödinger Equation

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

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

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

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

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

$$-(s+1)s + \ell(\ell+1) = 0$$

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*This excludes the stronger divergence of the centrifugal barrier term in $V_\ell(r)$, which is included separately.

Satisfied if $s = \ell$ or $s = -(\ell + 1)$

explore the second possibility:

$$s(s+1) = (-\ell - 1)(-\ell - 1 + 1) = -(\ell + 1)(-\ell) = \ell(\ell + 1)$$

If $s = \ell$, the $r \to 0$ form of $R_{n\ell}(r) = cr^{\ell}$ which is OK for all ℓ.
If $s = -(\ell + 1)$, the $r \to 0$ form of $R_{n\ell}(r) = cr^{-(\ell+1)}$ diverges for all r.

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

Actually, both of these possibilities satisfy the differential equation in the limit $r \to 0$ 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, but it turns out we will need both types of solution.

** "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 $u_{ns}(r)$!)

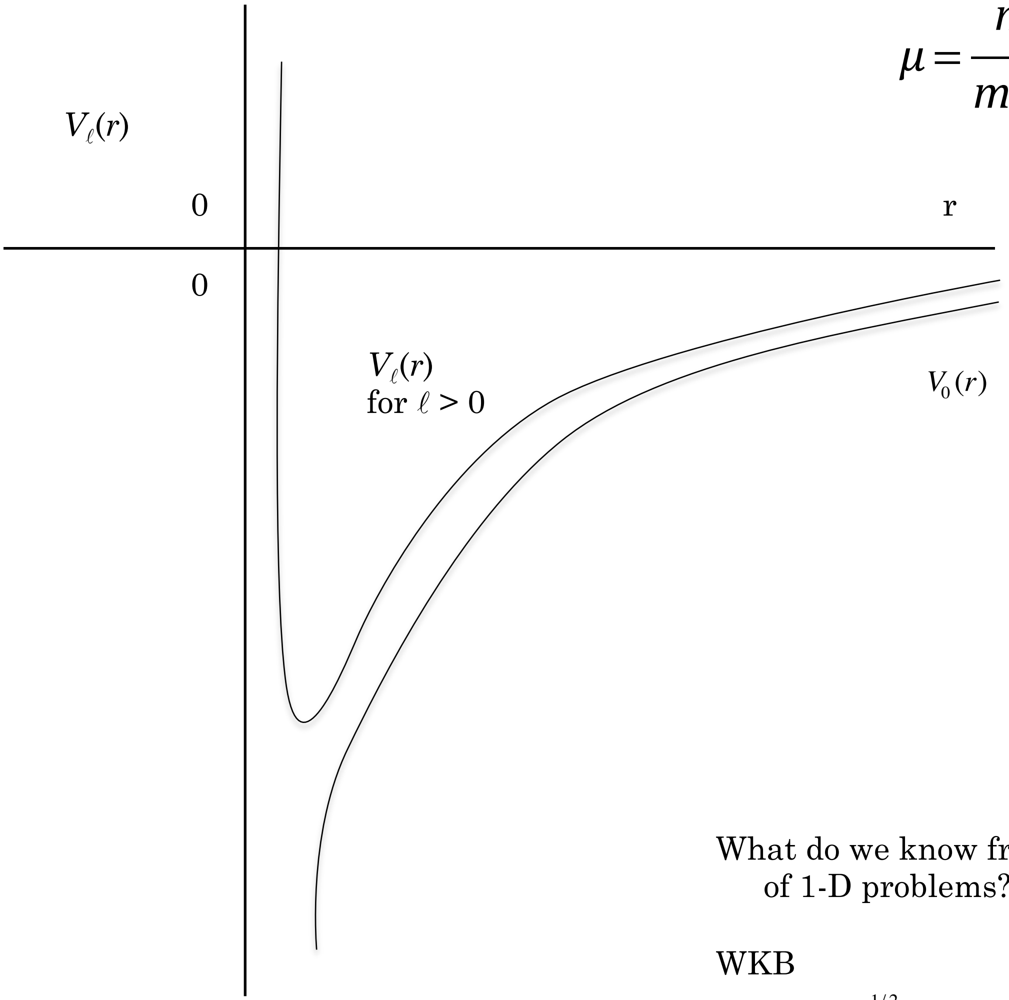
updated August 17, 2020 9:08 AM

For Hydrogen

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

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

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



ASK QUESTIONS:
What are the qualitative shapes of $u_{n\ell}(r)$ in innermost and outermost lobes?

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

inner vs. outer part of $u_{n\ell}(r)$ — where is the extra $\frac{h}{2}$ of action $\left(J = \oint p(r)\,dr = h\left(n+\frac{1}{2}\right)\right)$ acquired

(associated with tunneling into nonclassical region)?

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

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

$$\mu_H = \frac{(m_{e^-})(m_{p^+})}{m_{e^-} + m_{p^+}} \simeq m_e$$

At turning point $V_\ell(r_\pm) = E_{n\ell}$

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

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

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

Use Quadratic formula to find r$_\pm$(n)

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

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

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

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

when $\ell \ll n$, where are r_+ and r_-? (see table on page 28-12)

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

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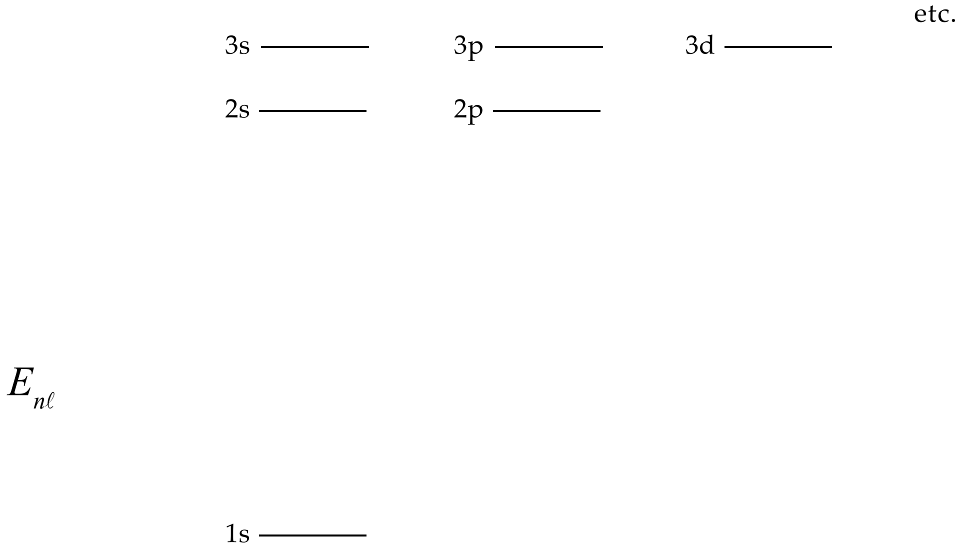
surprising systematic degeneracy



Because of the pattern of degeneracies, we use n to label degenerate groups rather than number of radial nodes

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

hence n is <u>not</u> # of radial nodes.

orbital	# of radial nodes	
1s	0	
2s	1	
2p	0	(because it is the lowest energy solution to the $\ell = 1$ equation)
3s	2	
3p	1	
3d	0	

$$\text{\# radial nodes } = (n-\ell)-1$$

$$\text{\# angular nodal surfaces} = \ell$$

total # nodes is $n-1$. What is the degeneracy?

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

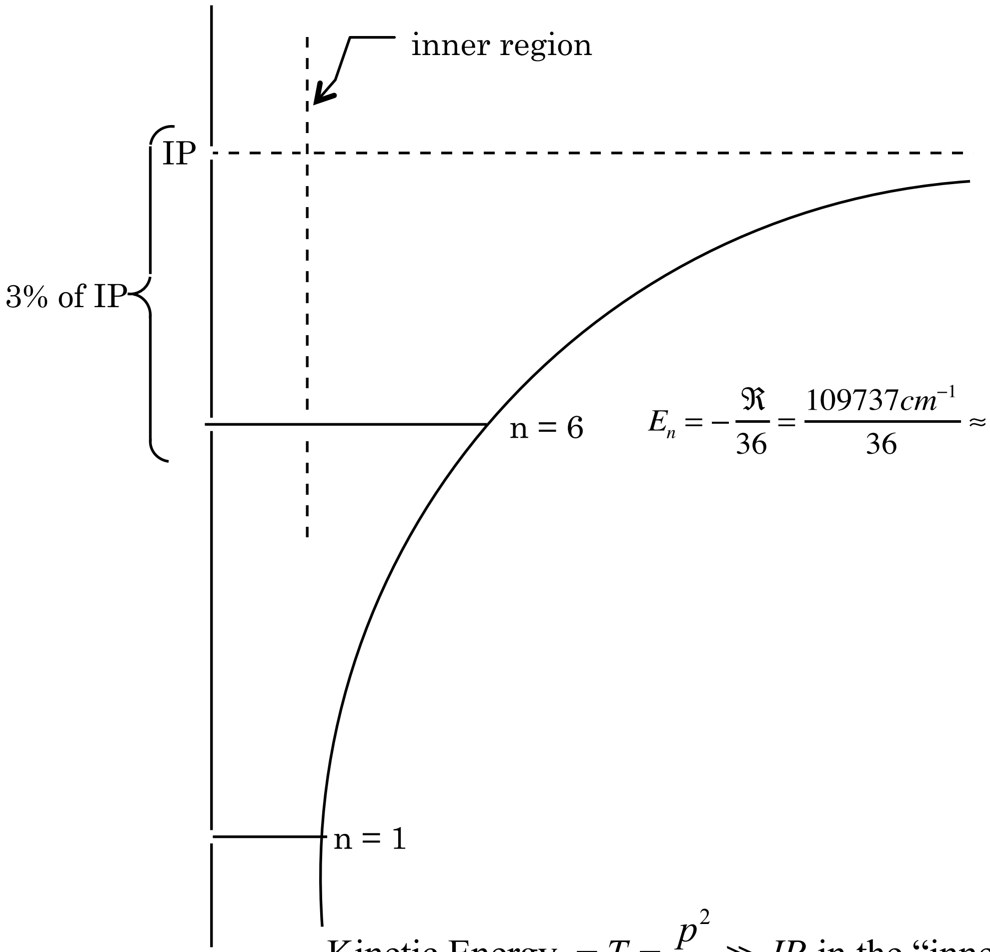
n-scaling of $\langle r^{\sigma} \rangle$

two limits	$\sigma < -1$	vs.	$\sigma > 0$
determined near:	inner turning point		outer turning point
scaling:	$\sim n^{-3}$		Bohr model $r_{n\ell} = a_0 n^2$
	(see argument for inner lobe on next page)		$\langle r^{\sigma} \rangle \propto a_0^{\sigma} n^{2\sigma}$ see table on page 11

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

↓

usually occurs in first (inner-most) lobe



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

Kinetic Energy $= T = \frac{p^2}{2\mu} \gg IP$ in the "inner region."

variation of T from $n = 6$ to $n = \infty < 3\%$
variation of p $< 1.5\%$

deBroglie $\lambda \sim \frac{h}{p}$

$r = \frac{\lambda}{2}$ is the location of innermost node

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?
Same as probability inside core.

$$\frac{\text{time inside}}{\text{one period}} = \frac{2(v/\lambda)^{-1}}{\left(\frac{h}{E_n - E_{n+1}}\right)} \quad v \text{ is velocity}$$

$$E_n = -\Re/n^2$$

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

$$\text{probability in inner lobe} = \frac{2\left[\frac{\frac{h}{p}}{v = p/m}\right] \leftarrow \boxed{\lambda}}{\frac{h}{2\Re/n^3}} \approx \frac{4m\Re}{p^2 n^3}$$

n-independent (approximately for $n = 6$ to $n = \infty$)

probability of finding e⁻ inside core μ n^{-3} !

updated August 17, 2020 9:08 AM

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

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

This is the basis of all Rydberg scaling

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

All n,n' matrix elements of r^{σ}, where $\sigma < -1$ scale as $\left(nn'\right)^{-3/2}$! what happens at $\sigma = -1$?

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

McQuarrie, page 223

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

exponential → 0 as r → ∞

associated Laguerre functions (polynominals)

Regular and Irregular Coulomb functions (E ≤ 0)

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

to behave properly as $r \to \infty$ we need to take linear combination of the f and g functions. Possible only at certain values of ν (we sometimes call this n*)

T.F. Gallagher, Rydberg Atoms, page 25

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

Note!

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

$\sigma>0$ scale as $n^{2\sigma}$!

Outer and Inner Turning Points

Orbital	$r_+(n,\ell)$/Å	$r_-(n,\ell)$/Å
1s	1.058	0.00
2p	3.612	0.624
3d	7.508	2.012
4f	12.696	4.232
5g	19.137	7.313
10s	105.8	0.00
10p	105.3	0.529
10d	104.2	1.587
10f	102.5	3.280

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

in atomic units:

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

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Fall 2018