PH102, 2012W, Lecture Notes: January 23, Mon, Class 6

Hydrogen Atom: Degeneracies, Normalization, Probability Densities, & Hydrogenlike atoms

Objectives:

- List degeneracies for each n state.
- Come up with the normalization condition for a spherically symmetric potential in (r, θ, ϕ).
- Recognize characteristics of radial and angular probability densities using n, l, m_l.
- Extend the Schrodinger Equation solutions of the hydrogen atom to the hydrogenlike atoms.

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In the last class, we learned that the time independent Schrodinger Equation can be turned into three equations after the separation of variable method as follows:

$$\begin{cases} \dfrac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi \\ sin\theta \dfrac{\partial}{\partial \theta}\left(sin\theta \dfrac{\partial \Theta}{\partial \theta}\right) + [l(l+1)sin^2\theta - m_l^2]\Theta = 0 \\ \dfrac{\partial}{\partial r}\left(r^2 \dfrac{\partial R}{\partial r}\right) + \dfrac{2mr^2}{\hbar^2}\left(E - U(r)\right)R - l(l+1)R = 0 \end{cases}$$

Three quantum numbers are defined so that the resulting wave functions can satisfy the Schrodinger Equation:

- Principal quantum number, *n*
- Orbital quantum number, *l*,
- Magnetic quantum number, m_l

where

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\,\hbar^2}\right)\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$L^2 = l(l+1)\hbar^2$$

$$L_z = m_l\hbar$$

where Bohr radius $a_0 = \frac{4\pi\varepsilon_0\,\hbar^2}{me^2}$= 0.053 nm or 0.53 A; and

Hydrogen atom's ground state energy, $E_1 = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right) = -13.6\ eV$

Wave function = $\psi(r,\theta,\phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}\mathbf{Y}_l^{m_l}$

where $\Theta_{l,m_l}\Phi_{m_l}$= $\mathbf{Y}_l^{m_l}$ (Spherical harmonics)

These relationships can be simply written using operator notations:

$$\mathbf{H}\psi_{n,l,m_l} = \boldsymbol{E_n}\psi_{n,l,m_l}$$
$$\mathbf{L^2}\psi_{n,l,m_l} = \boldsymbol{l(l+1)}\hbar^2\psi_{n,l,m_l}$$
$$\mathbf{L_z}\psi_{n,l,m_l} = \boldsymbol{m_l}\hbar\psi_{n,l,m_l}$$

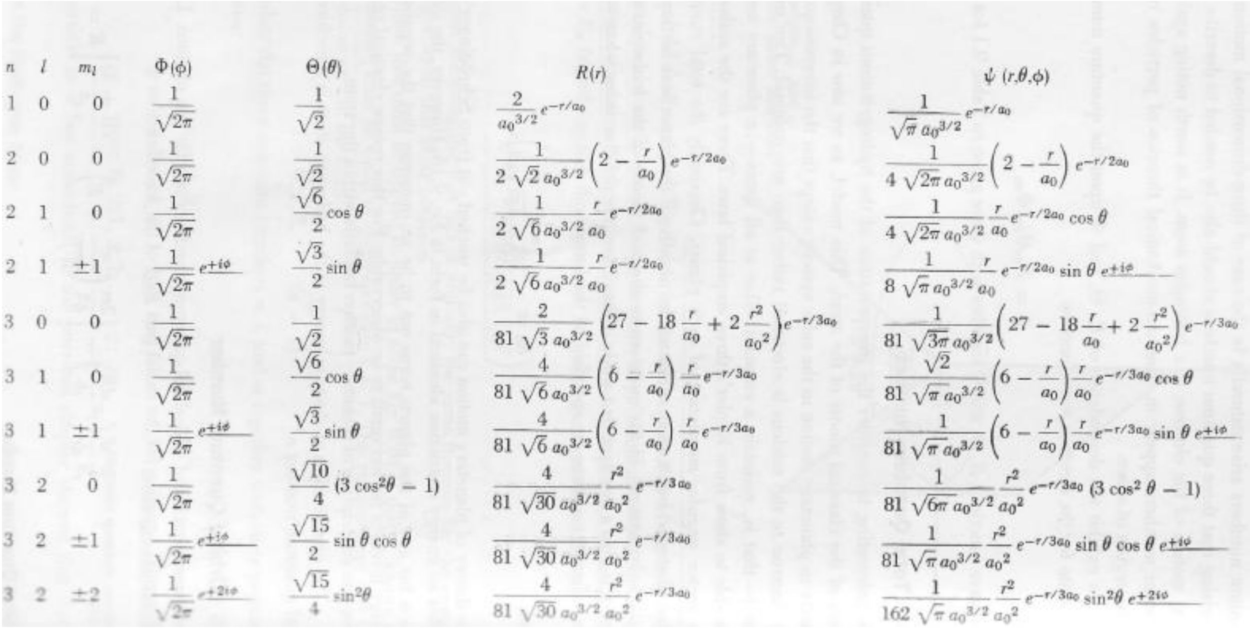
Note. These equations can be applied to all systems where the Hamiltonian (H = T+V) has a spherical symmetry (remember that the hydrogen atom's potential energy has a spherical symmetry). In such a case, the wave function, ψ_{n,l,m_l}, is an eigenfunction of **H,** $\mathbf{L^2}, \mathbf{L_z}$ **and** $\boldsymbol{E_n, L^2, and\ L_z}$ **are all quantized.**

Degeneracies in the Hydrogen Atom

According to the rules related to the three quantum numbers above, the following states (wave functions) are possible in each energy level:

n	l	m_l	E_n(eV)	$\|L\|$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2^2)	2s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		
3	0	0	-1.51	0	0	ψ_{300}	$R_{30}\mathbf{Y}_0^0$	9 (=3^2)	3s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{31-1}	$R_{31}\mathbf{Y}_1^{-1}$		3p
		0			0	ψ_{310}	$R_{31}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{311}	$R_{31}\mathbf{Y}_1^1$		
	2	-2		$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}	$R_{32}\mathbf{Y}_2^{-2}$		3d
		--1			$-\hbar$	ψ_{32-1}	$R_{32}\mathbf{Y}_2^{-1}$		
		0			0	ψ_{320}	$R_{32}\mathbf{Y}_2^0$		
		1			$+\hbar$	ψ_{321}	$R_{32}\mathbf{Y}_2^1$		
		2			$+2\hbar$	ψ_{322}	$R_{32}\mathbf{Y}_2^2$		

Therefore, in the hydrogen atom, there are n^2degenerate wave functions associated with each E_n.



n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$
2	1	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\cos\theta$
3	1	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta-1)$
3	2	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	±2	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

Normalization

The probability density of the hydrogen atom can be written as:

$$|\psi_{n,l,m_l}|^2 = R(r)^2\Theta(\theta)^2\Phi(\phi)^2$$

Normalization condition: $|\psi_{n,m,m_l}|^2$ $over\ all\ space\ (dV = r^2 sin\theta\ drd\theta d\phi)$

$$\int |\psi_{n,l,m_l}|^2\, dV = \int |\psi_{n,l,m_l}|^2\, r^2 sin\theta\ drd\theta d\phi$$

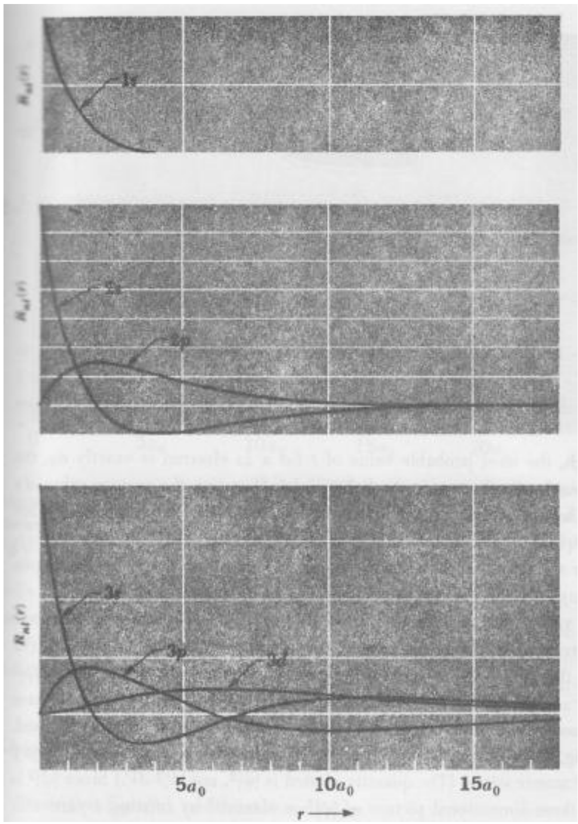
$$= \int_0^\infty R(r)^2 r^2\, dr \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi$$

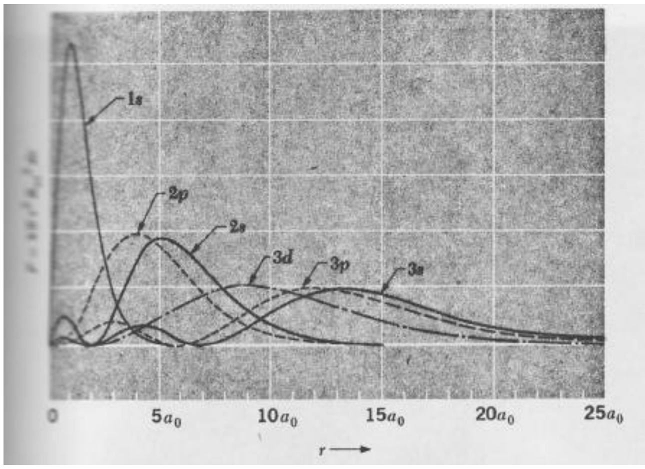
$$\begin{cases} \int_0^\infty R(r)^2 r^2\, dr = 1 \\ \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi = 2\pi \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta = 1 \end{cases}$$

Electron’s Whereabouts

Radial Probability Density

$$P(r)dr = R(r)^2 r^2 dr$$



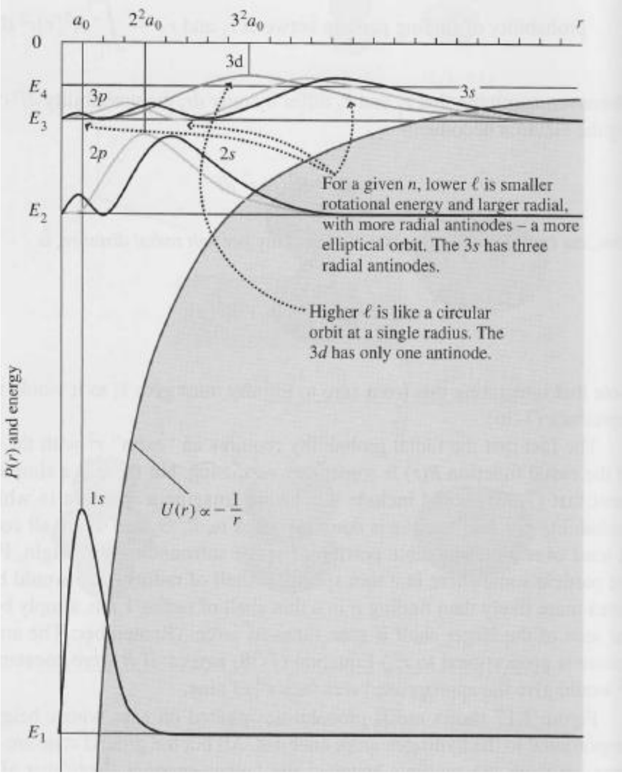


$R_{n,l}(r)$ $r^2R_{n,l}(r)^2$

- According to $R_{n,l}(r)$, there is a finite probability at the center for all *s* orbitals (*l*=0).
- Radial probabilities, $4\pi r^2 R_{n,l}(r)^2$, and energies are drawn in the hydrogen atom's Coulomb potential on the right.
- As n increases, the orbital radius increases.
- As n increases, the number of nodes in the same *l* orbital increases.
- When l = n-1, the most probable radius can be shown to have

  $r_{n,\, l=n-1}$ $(_{\text{most probable})} = n^2a_0$

  That is,
  r_{10} (1s, $_{\text{most probable}}$) = a_0
  r_{21} (2p, $_{\text{most probable}}$) = $4a_0$
  r_{32} (3d, $_{\text{most probable}}$) = $9a_0$



For a given *n*, lower ℓ is smaller rotational energy and larger radial, with more radial antinodes – a more elliptical orbit. The 3*s* has three radial antinodes.

Higher ℓ is like a circular orbit at a single radius. The 3*d* has only one antinode.

The most probable r value is different from the expected r value since

The most probable r value is obtained when $\frac{dP(r)}{dr} = \frac{dr^2 R_{n,l}(r)^2}{dr} = 0$

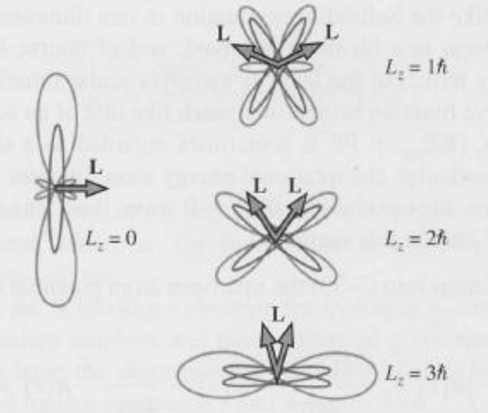
And the expected r value is obtained when <r> = $\int_0^\infty r \cdot r^2 R_{n,l}(r)^2 dr$

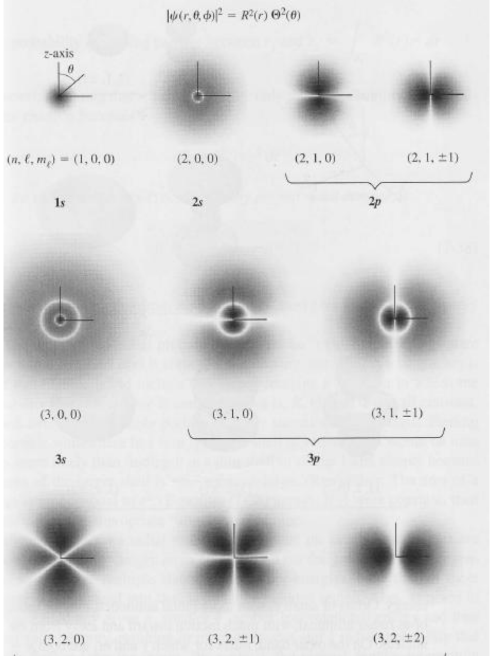
- According to the radial probability distribution, the expected r value is larger than the most probable r value for a given orbital.

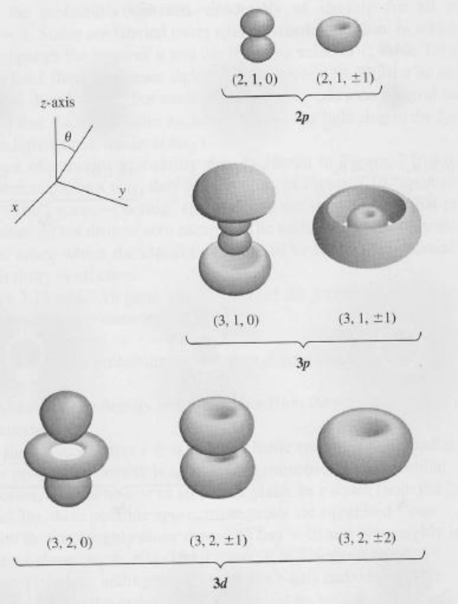
Angular Probability Density

- The probability density is a diffuse cloud spread over space.
- The probability density extends farther from the origin (where the proton is) as n increases.
- The probability density should be symmetric along the ϕ axis.
- In s states where l = 0, the kinetic energy is solely radial, so the probability density is spherically symmetric. No orbital motion.
- Note that the electron is orbiting the place perpendicular to the direction of $L_z. See\ Figure\ on\ the\ right.$
- In p states where (l=1), three possible probability distributions: $L_z = 1, 0, -1$. See Figure below.
- In d states where (l=2), five possible probability distributions $L_z = 2, 1, 0, -1, -2$.

Figure 7.14 A crude correspondence to orbital motion.







- There is no probability at the center when $l \neq 0$. Take a look at the p, d, f orbitals as compared to s orbitals.
- At fixed *l*, the number of radial anti-nodes increases as *n* increase because of increasing radial energy without increasing rotational energy
    - 1s vs. 2s vs. 3s
    - 2p vs. 3p vs. 4p
- At fixed *n*, the number of radial anti-nodes decreases as *l* increases because of increasing rotational energy while the total energy is fixed.
    - 2s vs. 2p
    - 3s vs. 3p vs. 3d

Hydrogenlike Atom

Hydrogen like atoms are atoms containing one electron but with a nucleus more than a single proton (Z*e*). The potential becomes

$$U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e \cdot Ze}{= \ r} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

Example: ionized Helium where the nucleus has a charge of +2*e* and the orbiting electron has a charge of –*e*.

In that case,

$$E_{n\ hydrogen} = -\frac{m(e^2)e^2}{32\pi^2\varepsilon_0^2\hbar^2}(\frac{1}{n^2}) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\ \hbar^2}\right)(\frac{1}{n^2}) = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\ (\frac{1}{n^2})$$

$$E_{n\ hydrogenlike} = -\frac{m(Z^2e^2)e^2}{32\pi^2\varepsilon_0^2\hbar^2}(\frac{1}{n^2}) = -\left(\frac{Z^2e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\ \hbar^2}\right)(\frac{1}{n^2}) = -\left(\frac{Z^2e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\ (\frac{Z^2}{n^2})$$

The most probable r vale for the orbital *l* = *n* – 1

$$r_{n,\ l=n-1\ (most\ probable)\ hydrogen} = n^2 a_0$$

$$r_{n,\ l=n-1\ (most\ probable)\ hydrogenlike} = \frac{1}{Z}n^2 a_0$$

Bound energies are deeper by Z^2, the orbital most probably radii smaller by $\frac{1}{Z}$