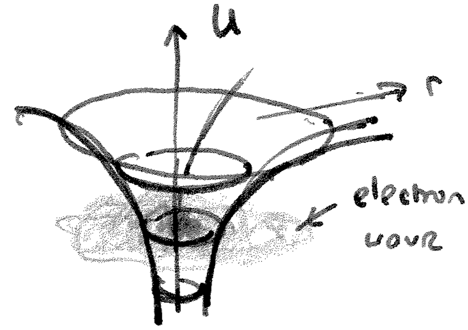
L14. ATOMIC STRUCTURE

In the late 19th century, a Russian chemist, Dmitri Mendeleev discovered that when the elements are ordered according to their atomic weight, they organize themselves so that their chemical properties "repeat" in periods. This led to his famous "Periodic Table of the Elements". Some 50 years later, the explanation of these mysterious periods began to come clear with the application of Schrödinger's wave equation to atomic structure.

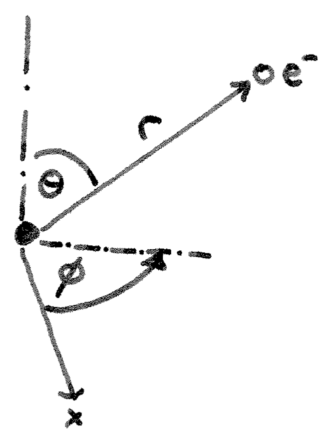
The key to the periodic table lies in the way electron waves can fit into the "box" defined by the attractive Coulomb potential of the nucleus. For a hydrogen atom, this potential is

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$



The specific form of the electron waves that form in an atom can be parameterized by a set of "QUANTUM NUMBERS". In the case of a particle in a box, there was just one quantum number "n" (=1, 2, 3 etc).

For the Hydrogen atom, the wavefunction depends both on the radius, and on the two "polar angles" that determine the location of the electron



and surprisingly, the wavefunction can be written as a product of a radial & two angular wavefunctions

$$\Psi(r,\theta,\phi) = R_n(r)\,\Theta(\theta)\,\Phi(\phi)$$

Loosely speaking there is one quantum number for each of these functions

$n = 1, 2 \ldots$ Principal Quantum # $\nearrow$ radial motion, $\searrow$ energy

$\ell \, (< n) = 0, 1 \ldots n-1$ Orbital angular momentum quantum #
(Angular motion)

m_ℓ magnetic quantum number
$m_\ell = -\ell, -\ell+1 \ldots \ell-1, \ell$
(z-component of angular momentum)

To these we will later add the spin angular momentum quantum number $S_z = \pm 1/2$. Remarkably – these quantum numbers are closely linked with Mendeleev's table. In other words – the shape & "wiggles" of the electron wave about an atom are intimately linked with CHEMISTRY!

41.1 H- ATOM

- Principal quantum number determines Energy

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2} \times \left(\frac{1}{n^2}\right) = -\frac{13.60}{n^2}\,eV$$

Quantization of Angular Velocity

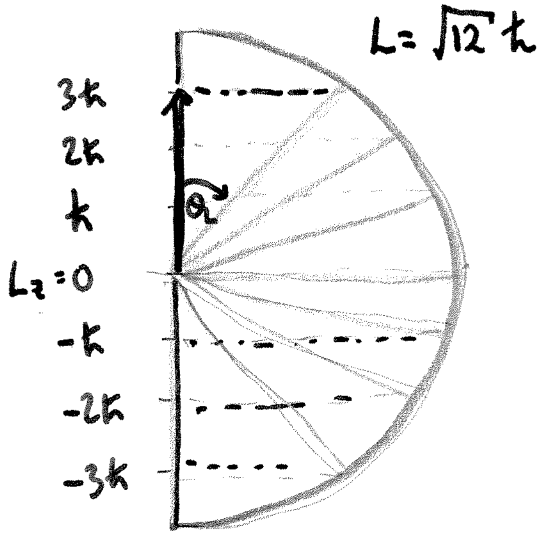
Requirement that Θ be finite at $\theta = 0$ & π quantizes the angular momentum. Possible values of L are

$$L = \hbar\sqrt{\ell(\ell+1)} \qquad (\ell = 0, 1, 2 \ldots n-1)$$

and the allowed values of the z-component of angular momentum are

$$L_z = m_\ell \hbar \qquad (m_\ell = 0, \pm 1, \pm 2 \ldots, \pm \ell)$$

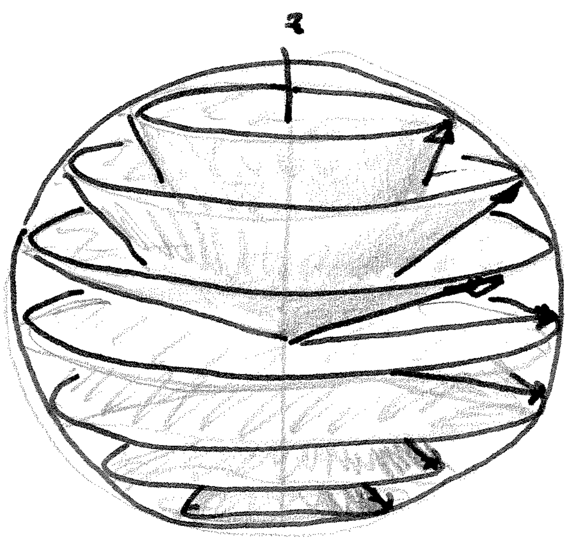
e.g. $\ell = 3$



$\ell = 3$

$$\theta_L = \cos^{-1} \frac{3\hbar}{\hbar\sqrt{12}} = 30^\circ$$

$|L_z|$ always $< L$: Uncertainty in angle and angular momentum are related by uncertainty principal.



Cone's of allowed directions of $\vec{L}$

SELECTION RULES

$$\boxed{n > \ell \geq |m_\ell|}$$

NOTATION

ORBITAL

$\ell = 0$	s
$= 1$	p
$= 2$	d
$= 3$	f

SHELL STRUCTURE

$n = 1$	K
2	L
3	M
4	N

n	ℓ	m_ℓ	Spectroscopic Notation	SHELL
1	0	0	1s	K
2	0	0	2s	L
2	1	-1, 0, 1	2p	
3	0	0	3s	M
3	1	-1, 0, 1	3p	
3	2	-2, -1, 0, 1, 2	3d	

e.g. How many states (n, ℓ, m_ℓ) with $n = 3$

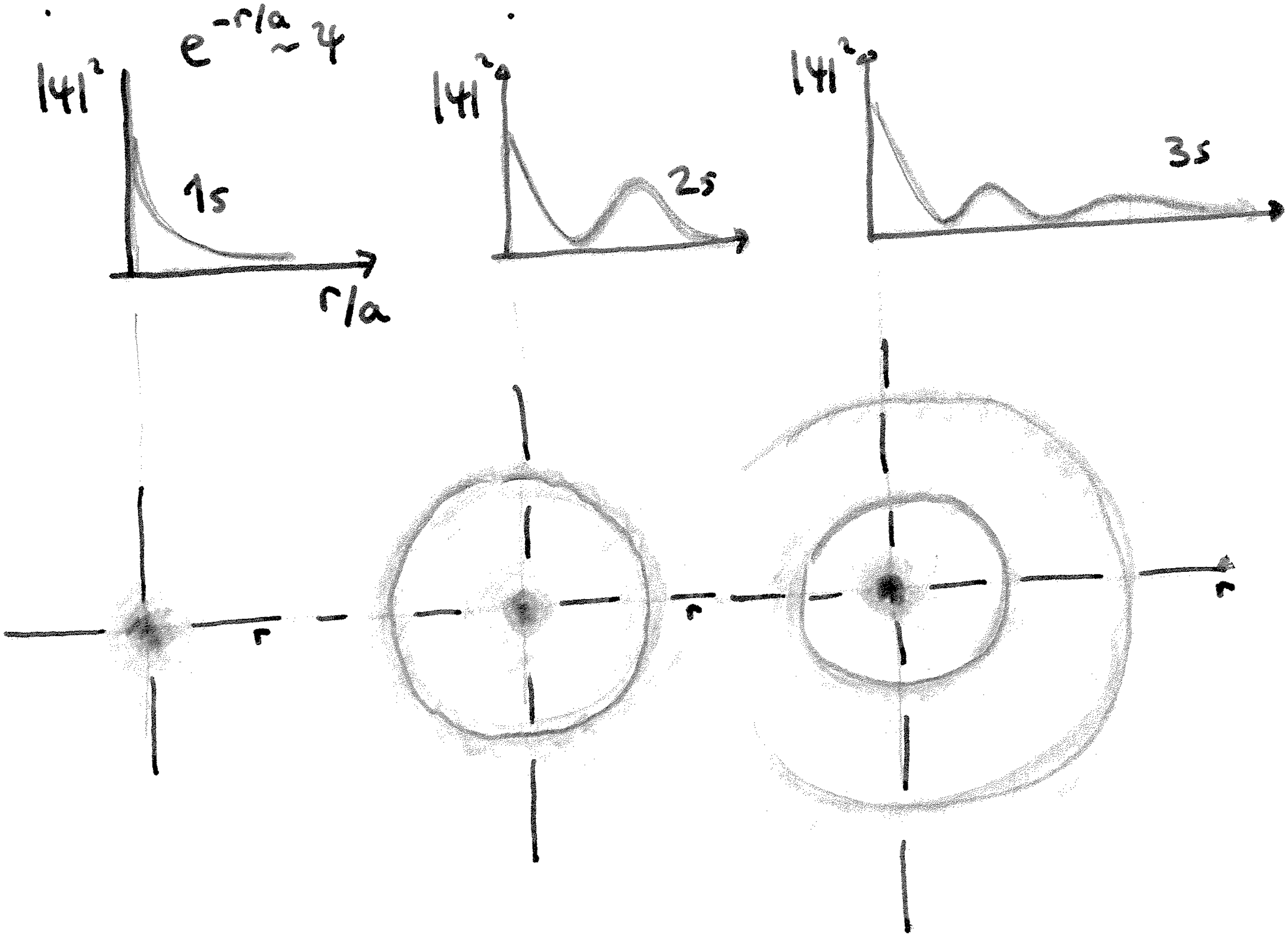
				m_ℓ
$n=3 \Rightarrow$	$\ell =$	2	3d	$-2, -1, 0, 1, 2$
		1	3p	$-1, 0, -1$
		0	3s	0

9 different orbitals. In H, each has energy

$$E_3 = -\frac{13.60\,eV}{3^2} = \underline{\underline{-1.51\,eV}}$$

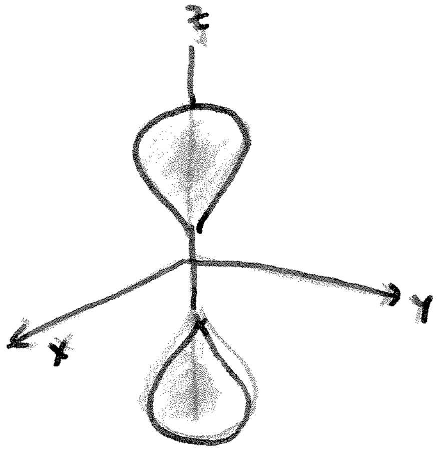
ELECTRON PROBABILITY DISTRIBUTIONS

$$\boxed{P(r)\,dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr}$$



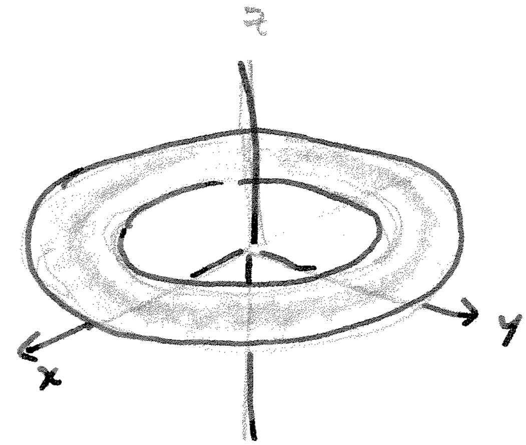
$$a = \text{Bohr radius} = \frac{\epsilon_0 h^2}{\pi m e^2} = 5.29 \times 10^{-11}\ \text{m}.$$

When $\ell > 0$, charge distribution becomes asymmetric



2p $m_\ell = 0$

"DUMBELL"



2p $m_\ell = \pm 1$

"DONUT"

The shapes of these orbitals are of great importance to the chemistry & physics of molecules & materials