

# Modern Atomic Theory

<u>Reading:</u> Ch. 9, sections 1-4 Ch. 7, sections 5-6 (lec) Ch. 7, sections 1-3 (lab)	<u>Homework:</u> Chapter 9: 37*, 39*, 41 Chapter 7: 59, 61*, 63, 65 (lec.) Chapter 7: 39, 41, 43, 47 (lab)
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\* = 'important' homework question

Note: Much of the early reading from Ch9. pertains to material covered in the next 'applications' packet.

## The Electronic Structure of Atoms – Empirical 'Particle' Models

Recall: What called Mendeleev to stack certain elements in 'Family' groups within the periodic table?

**Periodic Table**

Periods →      ↓ Groups

Alkali metals												Nonmetals						Noble Gases	
Alkaline Earth metals												Metalloids						Halogens	
												Main group metals							
1	2											13	14	15	16	17	18		
H	He											B	C	N	O	F	Ne		
1	2											5	6	7	8	9	10		
Li	Be											Al	Si	P	S	Cl	Ar		
3	4											13	14	15	16	17	18		
Na	Mg	Transition metals										Ga	Ge	As	Se	Br	Kr		
11	12	3	4	5	6	7	8	9	10	11	12	31	32	33	34	35	36		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te	I	Xe		
19	20	21	22	23	24	25	26	27	28	29	30	49	50	51	52	53	54		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb	Bi	Po	At	Rn		
37	38	39	40	41	42	43	44	45	46	47	48	81	82	83	84	85	86		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Une											
87	88	89	104	105	106	107	108	109											
Lanthanide series		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
		58	59	60	61	62	63	64	65	66	67	68	69	70	71				
Actinide series		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				
		90	91	92	93	94	95	96	97	98	99	100	101	102	103				

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Macroscopic properties: Elements in the same group (column) of the periodic table have similar chemical and physical properties.

e.g. All the group II elements (the alkali earths) are all metallic, form alkali solutions when mixed with water and form +2 charge cations when ionized.

Why is this? What is the underlying microscopic ‘answer’ that explains these facts?

**Microscopic properties: Elements in the same group (column) of the periodic table have similar outer (valence) electronic configurations.**



**The loss /gain (ionic bonding), or the sharing (covalent bonding), of an atom’s outer most electrons IS chemistry.**

Chemistry is ‘all about’ making new materials (as described by a chemical reaction’s equation) – to do this *new bonds are made* (in the products) and *old bonds are broken* (in the reactants). Bond making and breaking **ONLY** involves the outer valence electrons of atoms.

Empirical Electronic (‘Dot’) configurations of the first 12 elements (leave space for more or write on the rear of this sheet!)

## Seven Key facts



1.



2.



3.



4.



5.



6.



7.



Important definitions:

Electron 'dot' symbol: Includes BOTH outer (valence) AND inner (core) electrons

Lewis symbol: Includes outer (valence) electrons ONLY

Task: Draw electron 'dot' *and* Lewis symbols for:


**Si**

**Cl**

**P**

Add these Dot diagrams to your periodic table of electronic structure.  
**Complete the table for all atom types up to and including Ca**

Task: Complete the following table:

<u>Atom</u>	<u>Group number</u>	<u>Number of valence electrons</u>	<u>Lewis Symbol</u>
N			
P			
O			
S			
C			
Si 			



**Recall that the number of valence electrons an atom has is equal to its group number – this is why elements in the same group have similar chemical properties (similar valence configurations)**

## The Octet Rule (Full Valence Shell rule – more detail later!)



**ATOMS WITH FULL OUTER (VALENCE) SHELLS ARE STABLE**  $\Rightarrow$  Atoms will lose, gain or share electrons to have an inert gas (full valence shell) configuration.

**THIS IS THE 'DRIVING' FORCE BEHIND ALL CHEMICAL PROCESSES** (see slide).

### Examples:

#### 1. Ionic bonding – the formation of LiF

Recall: Ionic bonds form between atoms (metal and non-metal, which then become ions) with a large difference in electronegativity

Task: Write a similar reaction for the formation of MgO.

#### 2. Covalent bonding – the formation of F<sub>2</sub> (g)

Recall: Covalent bonds form between atoms (two non-metals) with little or no difference in electronegativity

Note: We will return to constructing molecular models from Lewis symbols later in the course.

## The Electronic Structure of Atoms – True ‘Wave’ Models

Background: The turn of the 20th century was a golden era for the physical sciences. Einstein was working towards the theory of special relativity (and was receiving *all* the attention), while Erwin Schrödinger was quietly ‘turning the science on its head’ by redefining how scientists fundamentally think about matter, particularly ‘small’ particles, such as electrons.



Erwin Schrödinger, as seen on a one thousand schilling Austrian bank note in the late 1930's. Note the ‘ $\Psi$ ’ symbol.



“So, you are telling me electrons aren’t particles anymore?”

Schrödinger’s great genius was devising a form of math that explained the behavior of electrons (or any other ‘small particle’) in terms of WAVE, rather than PARTICLE, math. This new math is called *quantum mechanics*, with the main equation used to solve such problems called the *Schrödinger equation*. The affects of this ‘quiet revolution’ totally changed how we now view the structure of the atom.

**Instead of electrons ‘orbiting’ a nucleus (PARTICLE MODEL), they are now known to exist as waves in diffuse clouds around the nucleus (WAVE MODEL).**

*Got proof? Yes!*

## The Schrödinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V^2 \psi = E \psi$$



The Schrödinger equation, as seen on his and hers 'nerd' T shirts at Star Trek Conventions, Physics conferences etc.(left and above). Hard core 'Trekies' (right)

## The Power of the Schrödinger Equation

The Schrödinger equation supplies information pertinent to an electron(s)' energy (E, V) and location ( $\nabla$ ) within ANY atom or molecule in terms of the behavior of electron 'clouds' or waves ( $\Psi$ ).



**Solving the Schrödinger equation for valence electrons tells you everything about their interactions with one another**

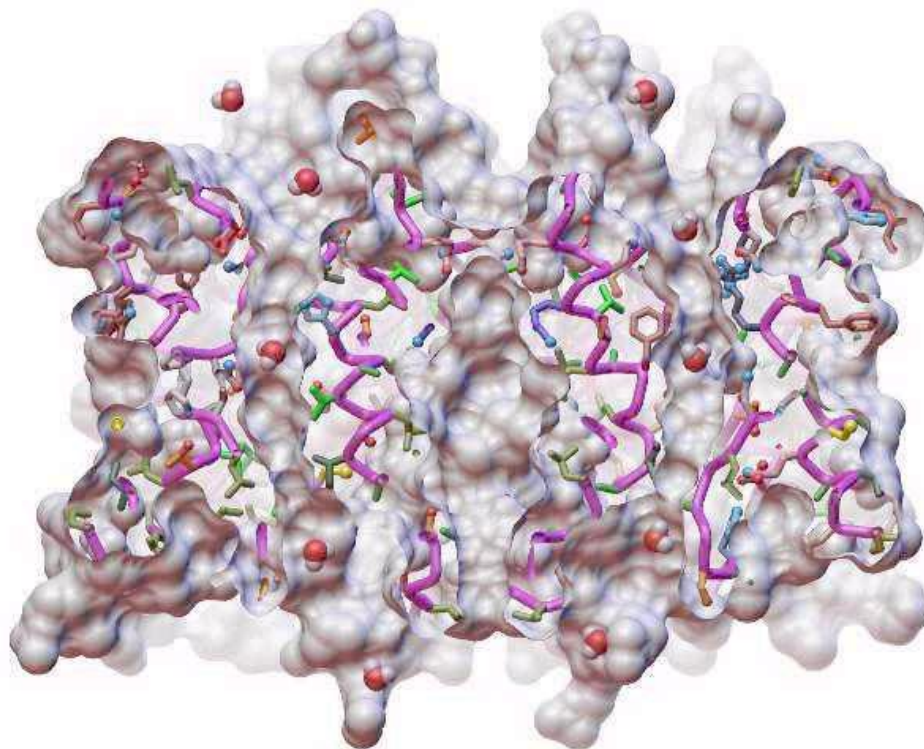
**\*\*THIS IS CHEMISTRY\*\***

**We will use the RESULTS\* from such calculations in order to better understand atomic structure (i.e. where electrons are located in atoms)**

\*ask me to tell you a scary story from grad. school!



Current Applications: The mathematical resources required to solve the Schrödinger equation are immense – until several years ago entire main frame computers were required to run for several days in order to ‘map’ a simple molecule. With the advent of modern high powered computers, such calculations can now be conducted much more quickly – **chemical processes (such as drug synthesis) are now most often modeled using a computer *before* performing an experiment!**



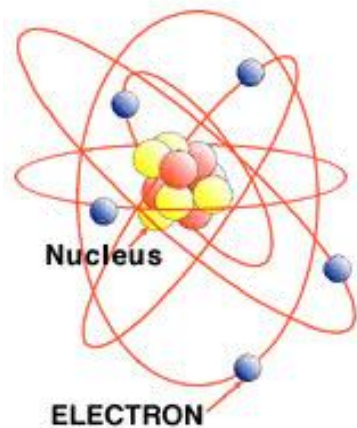
An electron density map of a complex organic molecule – created on a computer by solving Schrödinger’s equation

### **An overview comparison of ‘wave’ and ‘particle’ models**

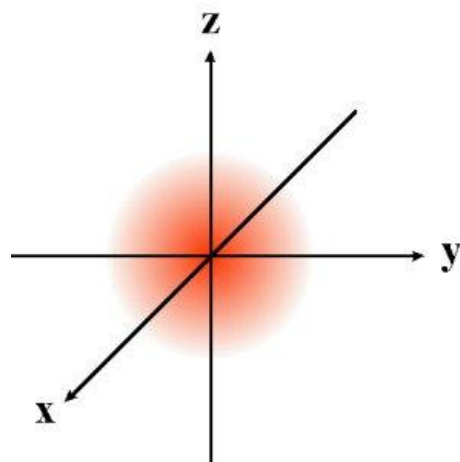
Background: the empirical Lewis and ‘dot’ models work (*to a point*) because they in many ways mimic ‘how it really is’ in terms of the electronic structure of the atom.

Objective: We will develop an understanding of the ‘true’ (wave) models of the atom by building on our knowledge of the more ‘common sense’ empirical (Lewis and ‘dot’) models.

Task: In your own words, compare and contrast the generic ‘particle’ and ‘wave’ models of an atom’s electrons, as shown below (see slide also)



Classical (particle) model of a Boron atom



Electron density map (wave) model of a Hydrogen atom

We will return to comparisons like this periodically through the handout

Notes:

## Quantum Numbers and Atomic Orbitals



The results of the Schrödinger equation (info. regarding electron position and energy in an atom) are expressed in terms of *quantum numbers*.

Each electron in an atom has a unique set of quantum numbers – they may be considered its '*atomic address*' (the orbital it resides in)

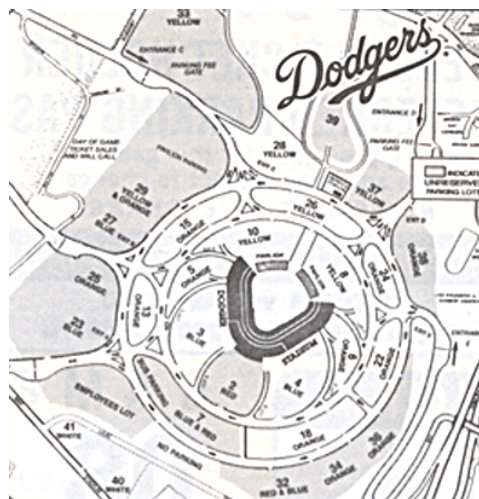
There are five quantum numbers:  $n$ ,  $l$ ,  $m_l$  and  $m_s$

Definition: An *orbital* is a region of space around the nucleus (with specific shape and direction) where (up to two) electrons can exist. When occupied by electron(s), orbitals become 'electron clouds'. In the above example (H), the orbital is spherical in shape and contains 1 electron.

Analogy: Think of the nucleus as a sports stadium surrounded by numerous empty parking spaces (orbitals). Cars (electrons) fill some of these spaces (make electron clouds). The number of electrons attracted (cars in the lot) depends on the atom ( ${}_1\text{H}$ ,  ${}_2\text{He}$  etc.) *The address of each 'space' (orbital), and therefore the car (electron) parked within it, is defined by a unique set of quantum numbers – discussed below.*



Dodger Stadium and its parking lot



The Dodger Stadium parking lot

Note: Every atom is assumed to have the same 'infinitely' large parking lot (number of available orbitals). 'How many electrons' and 'where they go' are what we really need to know for each atom – this is next!

Overview of an Orbital's Quantum Numbers and their Meaning:

<u>Quantum number</u>	<u>Atomic Description</u>
n	Average <b>distance</b> of orbital from nucleus
l	<b>Shape</b> of orbital (spherical or 'dumbbell', see below)
$m_l$	<b>Direction</b> of orbital in space (oriented in x, y or z direction)
$m_s$	' <b>Spin</b> ' of electron(s) ( $\downarrow$ or $\uparrow$ ) residing within the orbital

Details regarding Orbitals and the Quantum numbers that describe them

Simple ideas (same as for the empirical models):

1. Electrons (-ve) are attracted to the nucleus (+ve).
2. The number of electrons attracted  $\equiv$  number of protons in the nucleus (atomic number,  $Z$ )
3. As with Dodger stadium, there is more space (available parking) further from the nucleus (stadium). Diagram:

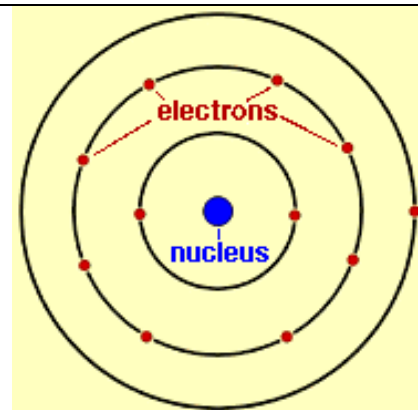
Specific details (some analogies with classic ‘particle’ models)

<u>Quantity</u>	<u>Associated Quantum number</u>	<u>Range of allowed values</u>	<u>Details</u>
‘Distance’	“Principle quantum number” <b>n</b>	<b>n = 1, 2, 3....</b>	<b>n ∝ distance orbital is from the nucleus</b> <b>n = 1 is the closest energy level</b> <b>Analogous to the empirical ‘dot’ model.</b> <b>Highest n = element’s row in p. table</b>

Example (recall your Atomic Fingerprint lab):

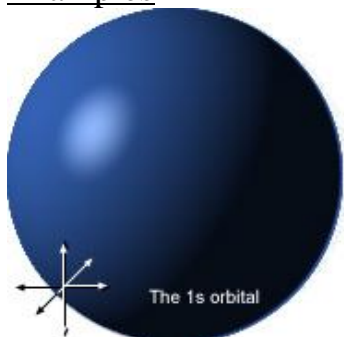
As with the empirical ‘dot’ models, an electron’s distance from the nucleus relates to which ‘orbit’ (particle model) or energy level (wave model) it is in.

⇒ The valence ‘orbit’ of Na (row 3 p. table) has n = 3. The core (full) levels are n=2 and n = 1.

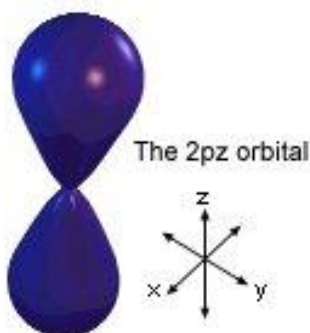


‘Shape’	“Angular momentum quantum number” <b>l</b>	<b>l = 0 → (n-1)</b>	<b>l defines the shape of an orbital</b> when <b>l = 0</b> , orbital is a spherical ‘s’ orbital when <b>l = 1</b> , orbital is a dumbbell ‘p’ orbital when <b>l = 2</b> , orbital is a fan/donut ‘d’ orbital <b>key:</b> the value of n determines the range of l
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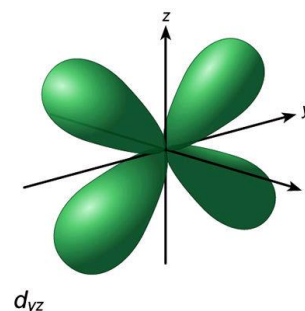
Examples



A 1s (spherical) orbital



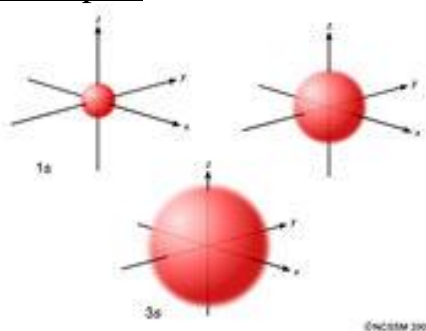
A 2p (‘dumbbell’) orbital



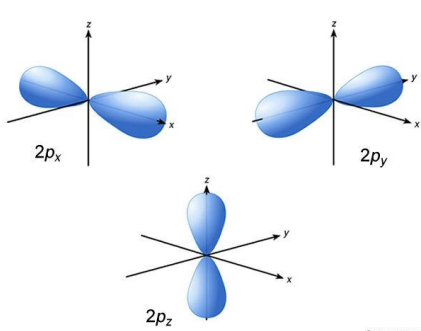
A 3d (‘fan’) orbital

‘Direction’	“magnetic quantum number” $m_l$	$m_l = 0 \rightarrow \pm 1$	<b><math>m_l</math> defines the direction of an orbital when <math>l=0, m_l=0</math></b> (only one possible direction for ‘s’ orbitals) <b>when <math>l=1, m_l=-1, 0</math> or <math>+1</math></b> (3 possible directions for ‘p’ orbitals) <b>when <math>l=2, m_l=-2, -1, 0, +1</math> or <math>+2</math></b> (5 possible directions for ‘d’ orbitals) <b>key: the value of <math>n</math> determines the range of <math>l</math>, which then determines the range of <math>m_l</math></b>
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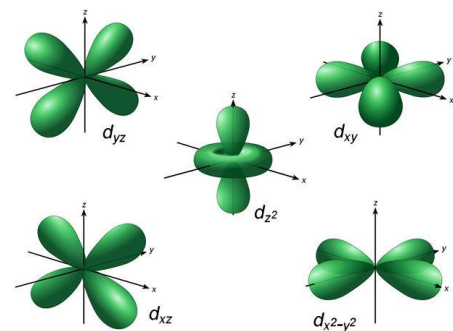
Examples:



Only one possible direction for a spherical ‘s’ orbital, regardless of the value of n.



Three possible directions for ‘p’ orbitals ( $p_x, p_y, p_z$ ) when  $n=2$  or greater

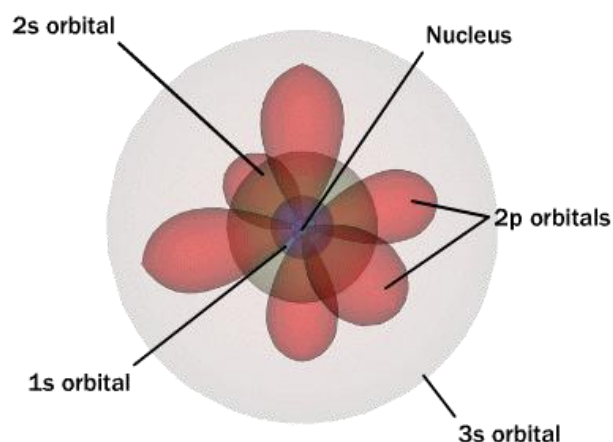


Five possible directions for ‘d’ orbitals ( $d_{xy}, d_{yz}, d_{xz}, d_{xy}, d_{x^2-y^2}$ ) when  $n=3$  or greater

Pictorial review of the parking lot analogy



Dodger Stadium (park your car at...)



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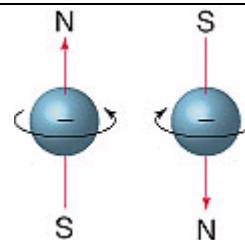
The Atom (park your electron at...)

For the electrons themselves (the ‘cars’ that park in the ‘spaces’ detailed above)

<p><b>‘Orientation’</b></p>	<p>“magnetic spin quantum number” <math>m_s</math></p>	<p><math>m_s = -1/2</math> or <math>+1/2</math></p>	<p><b><math>m_s</math> is an intrinsic property of the electron. Electrons are either ‘spin up’ (<math>\uparrow</math>), <math>m_s = +1/2</math> or spin down (<math>\downarrow</math>), <math>m_s = -1/2</math></b>  <u>Analogy:</u> It’s a bit like being either male (<math>\♂</math>) or female (<math>\♀</math>)!  <b>key: ANY orbital can contain a MAX of 2 electrons – one ‘spin up’ (<math>\uparrow</math>), <math>m_s = +1/2</math> and one ‘spin down’ (<math>\downarrow</math>), <math>m_s = -1/2</math></b>  <u>Analogy:</u> It’s a bit like having to get married before you move in together!</p>
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Example: Electrons either align *with* or *against* an external magnetic field, depending on whether they are respectively either ‘spin up’ ( $\uparrow$ ),  $m_s = +1/2$ ) or spin down ( $\downarrow$ ),  $m_s = -1/2$ ).

There are essentially equal numbers of each type of electron, which under certain circumstances can change from ‘spin up’ to ‘spin down’ (just like people!). However, there is no ‘gay marriage’ for electrons!



Typical ‘starter’ question: Sketch the shape and orientation of the following types of orbitals. See the appendix for more details.

$s$

$p_z$

$d_{xy}$

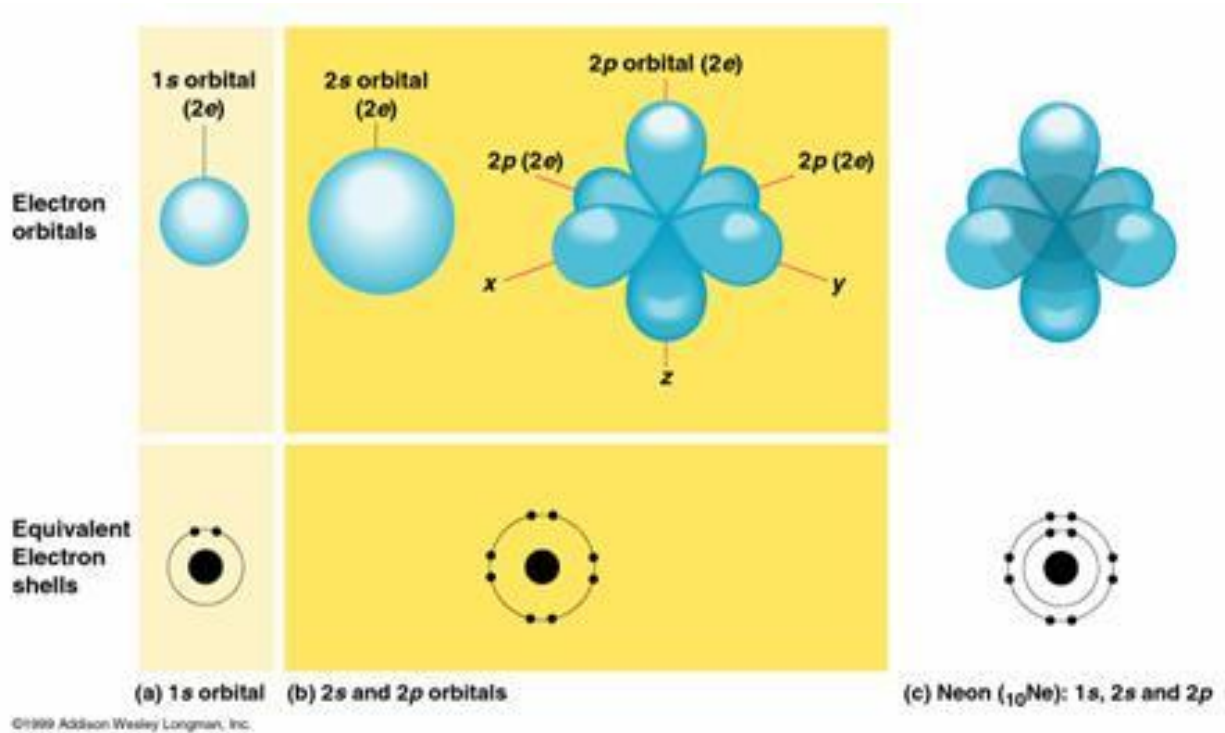


America’s next top model is.....

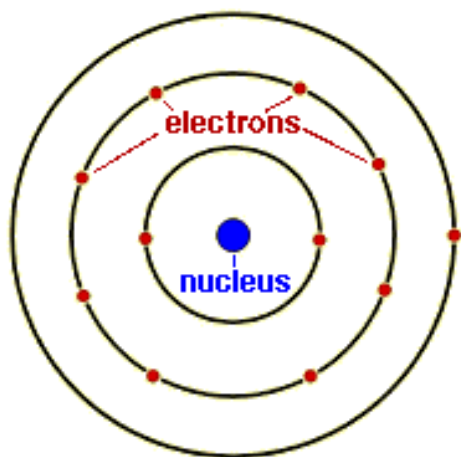
Schrödinger’s wave model is a more sophisticated version of the analogous Lewis style particle description.

**In other words, both models work, but the wave model is a better description of how things really are in nature.**

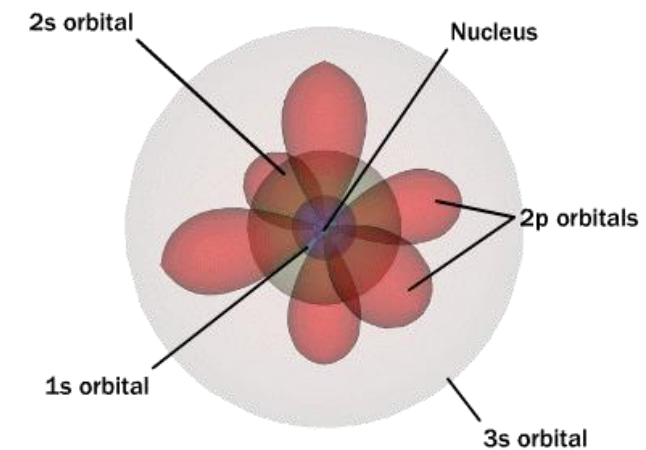
Putting it all together: a comparison of particle and wave models



Side by Side Comparison of the Two Types of Model



Particle model



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Wave Model





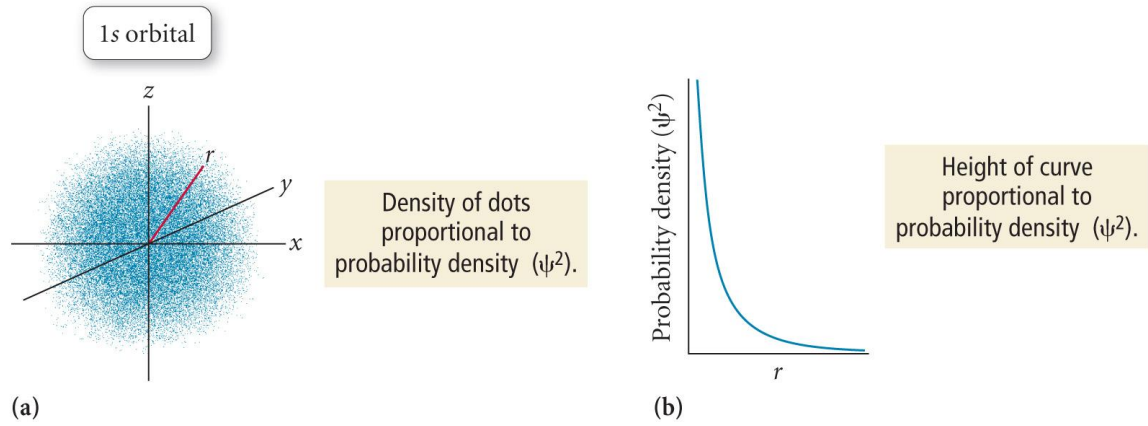
*"Lewis symbols and Dot structures"*

The following question was taken from your 2nd practice midterm:

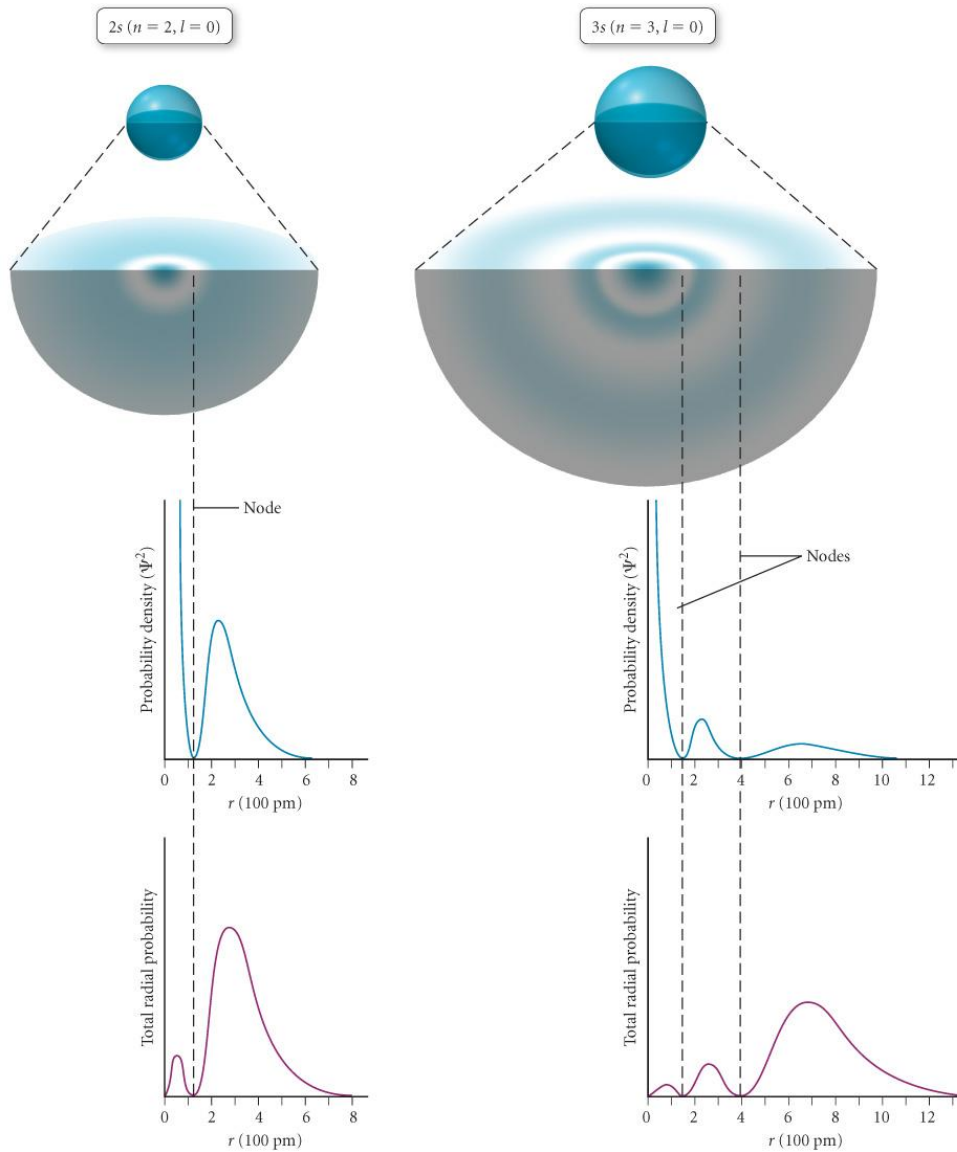
Draw Lewis symbols and 'dot' structures and for the following:

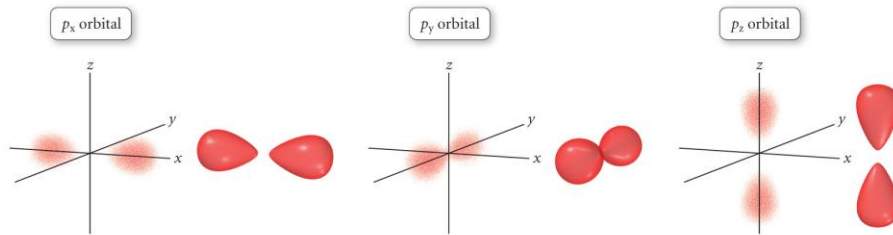
	<b>Lewis symbol</b>	<b>Dot structure</b>
Carbon atom		
Oxide anion		
Sodium atom		
Hydrogen atom		
Magnesium ion		

## Appendix: s, p and d Orbital Plots

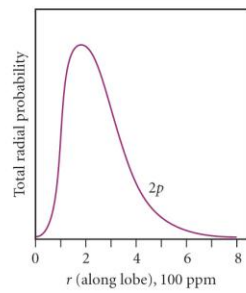


### The 2s and 3s Orbitals



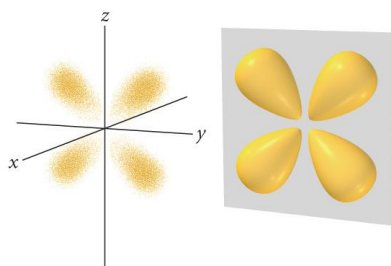


Radial Distribution Function

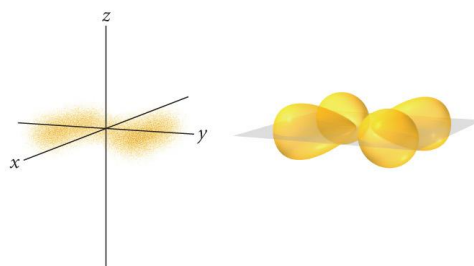


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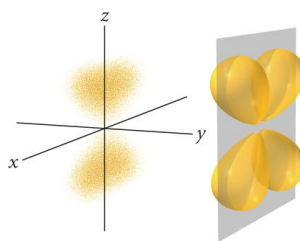
$d_{yz}$  orbital



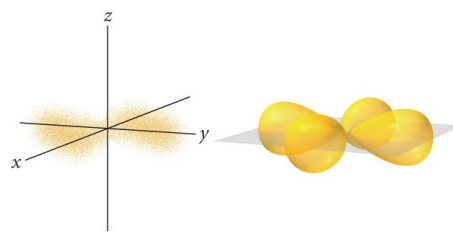
$d_{xy}$  orbital



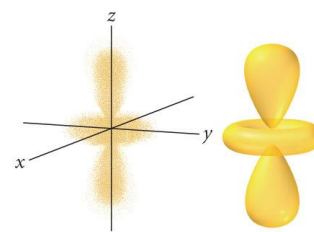
$d_{xz}$  orbital



$d_{x^2 - y^2}$  orbital



$d_{z^2}$  orbital



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