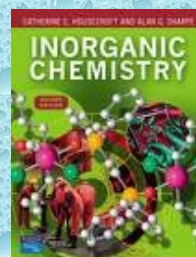




Fall 2006-2007

# Advanced Inorganic Chemistry

Michael Prushan, Ph.D.



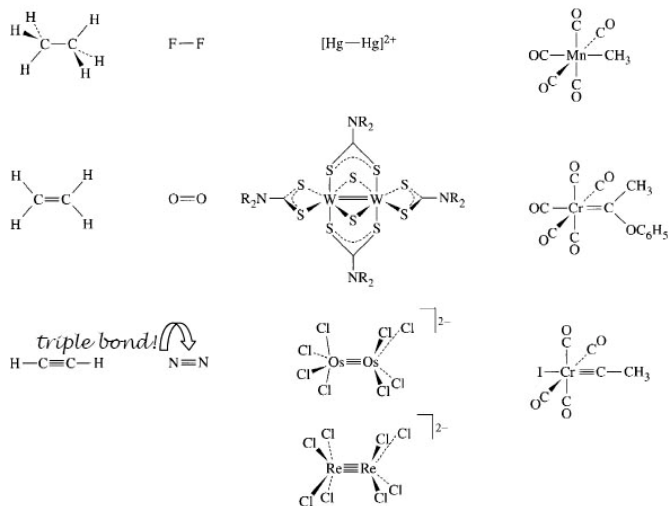
## What's Inorganic Chemistry??

- *Organic chemistry is defined as the chemistry*
- *of hydrocarbon compounds and their derivatives*
- *But how about CO, CO<sub>2</sub>, and HCN...for instance?*
- *Inorganic chemistry can be described broadly as the chemistry of “everything else”*

## Organic vs. Inorganic

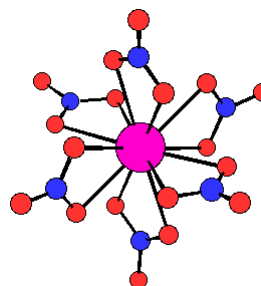
- Involves few elements
- forming mostly covalent or polar covalent bonds
- Mostly molecular solids (except polymers)
  - Usually air-stable
- Commonly soluble in nonpolar solvents
- Distillable, crystallizable
- Bonding involves s & p electrons
- **All** the elements, involving **all modes** of Bonding
  - Ionic, extended-network (metallic/covalent), & molecular solids
  - All possibilities concerning stability with air or water
  - Widely ranging solubilities

## Bonding in Organic and Inorganic



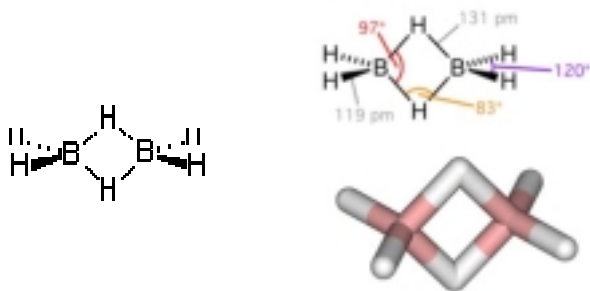
## The Weird and Wacky World of Inorganic Chemistry

Of course you can form **One, Two, Three and Four Bonds**, BUT that is only part of the story.... The most common number of bonds to a transition metal ion is SIX, but that does not mitigate against larger coordination numbers. There are many compounds which contain 7,8,9 bonds to a single atom.



Common conceptions of bonding are not enough.

As an example, understanding the bonding in  $\text{B}_2\text{H}_4$ .



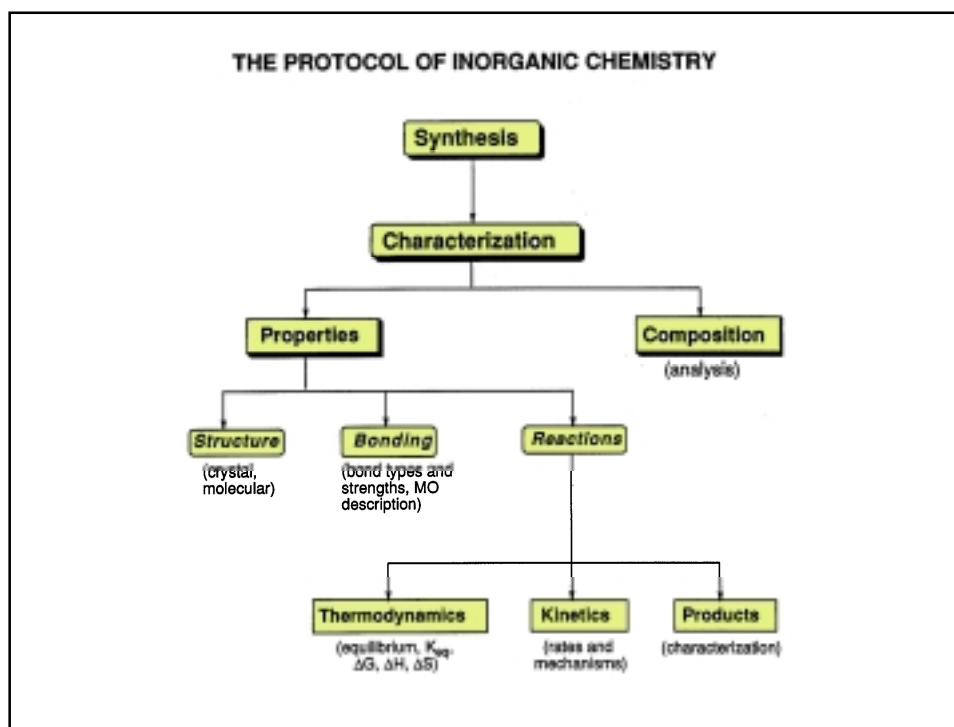
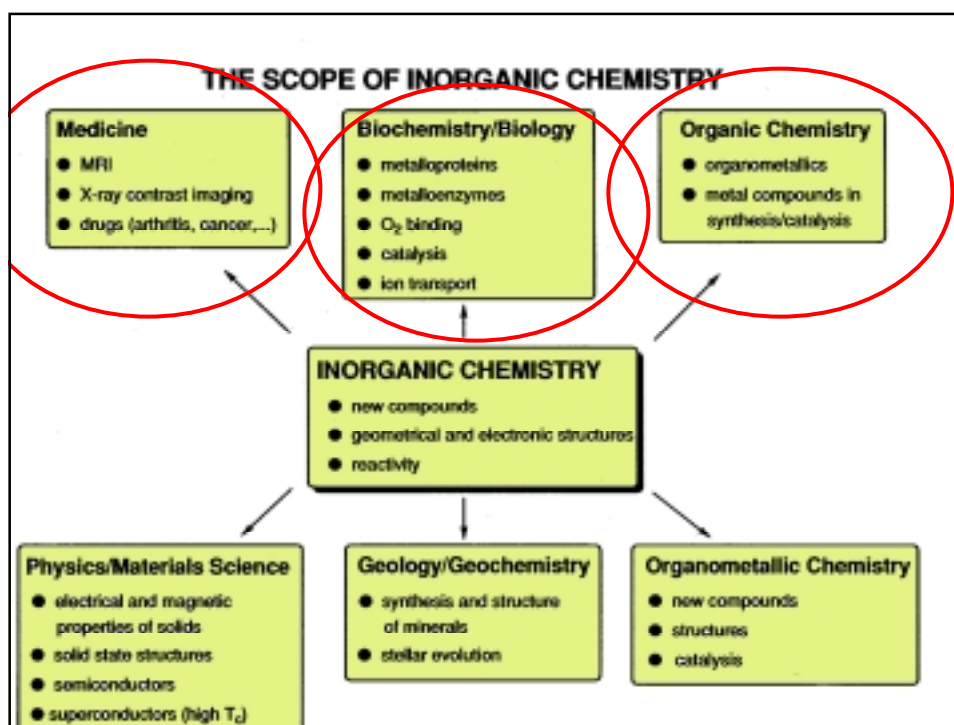
**HYDROGEN FORM HOW MANY BONDS???**

## The Elements

- ~ 107 of them ....
- Most are metals: solids, electrical conductors,
- good thermal conductors, sometimes with
- high mechanical strength and ductility.
- ~ 22 nonmetals (As, Sb, Te, ... ?)
- At ambient temp.: 11 gases, 2 liquids (Br,
- Hg), [+ Cs (m.p. 28.5 °C) & Ga (m.p. 29.8 °C)]

## Abundances in Earth's Crust

- Order of occurrence (weight % abundances):
- O(45.5) > Si(25.7) > Al(8.3) > Fe(6.2) >
- Ca(4.66) > Mg(2.76) > Na(2.27) > K(1.84)
- All others < 3% combined (**including beloved Carbon and Hydrogen!**)
- SiO<sub>2</sub> and silicates are constituents of most rocks
- and many “ores” of other metallic elements.
- All these elements are the principal constituents of
- most minerals (also important: P, S, Mn, Cr, Ti, Cu).

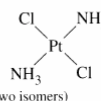
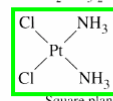
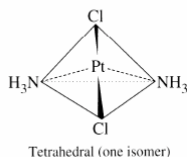


## Medicinal Inorganic Chemistry

### cis- and trans- Platinum Isomers: Serendipity in Chemistry



cis - and trans - Diamminedichloroplatinum (II),  $[\text{PtCl}_2(\text{NH}_3)_2]$



Prof. Barnett Rosenberg, MSU  
(Prof. S.J. Lippard, MIT)

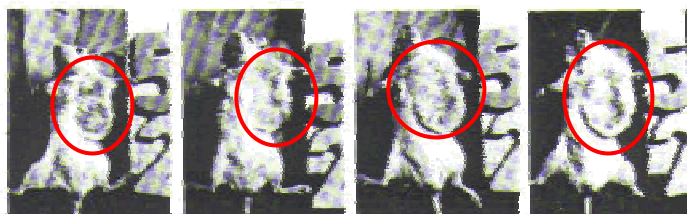
Cisplatin was approved by the FDA for the treatment of genitourinary tumors in 1978.

Since then, Michigan State has collected over \$160 million in royalties from cisplatin and a related drug, carboplatin, which was approved by the FDA in 1989 for the treatment of ovarian cancers.

"Testicular cancer went from a disease that normally killed about 80% of the patients, to one which is close to 95% curable. This is probably the most exciting development in the treatment of cancers that we have had in the past 20 years. It is now the treatment of first choice in ovarian, bladder, and osteogenic sarcoma [bone] cancers as well."

—Barnett Rosenberg, who led the research group that discovered cisplatin, commenting on the impact of cisplatin in cancer chemotherapy

CONTROL SARCOMA 180



DIED - day 21

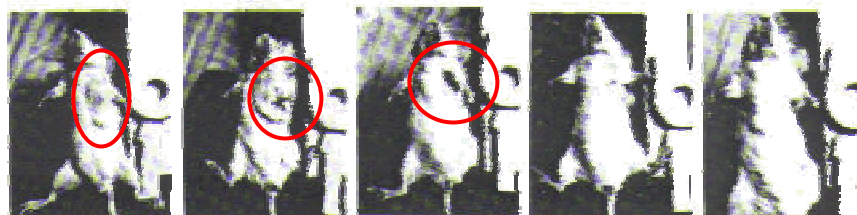
day 8

day 12

day 15

day 20

TREATED - SINGLE INJECTION CIS- $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$  - 8 mg/kg - DAY 8



day 8

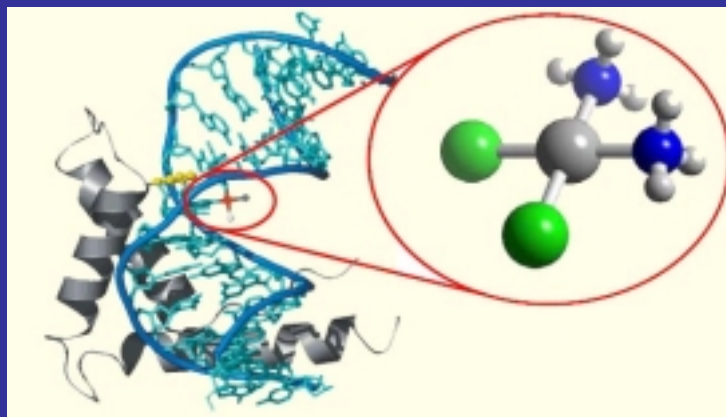
day 12

day 16

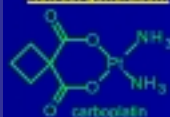
day 20

day 36

Cisplatin acts by cross-linking DNA in several different ways, making it impossible for rapidly dividing cells to duplicate their DNA for mitosis. The damaged DNA sets off DNA repair mechanisms, which activate apoptosis when repair proves impossible. The trans-isomer does not have this pharmacological effect.



Newest generation:



B. Rosenberg et al. in Nature 1965, 206, 688

Stephen J. Lippard et al. in Nature (1999), 399, 708 - 712

Basis for recognition of cisplatin-modified DNA by high-mobility-group proteins

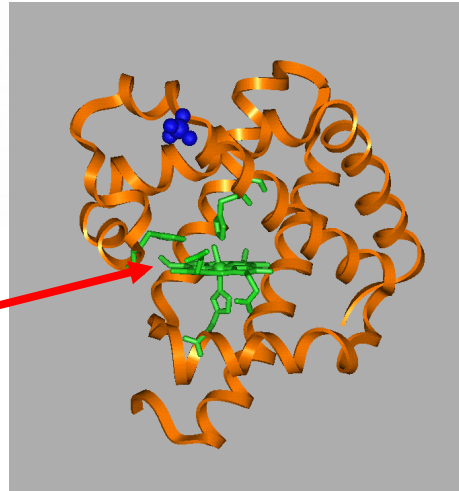
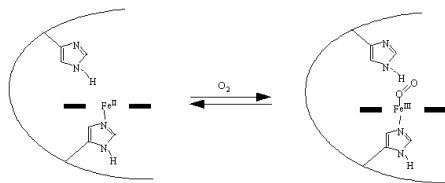
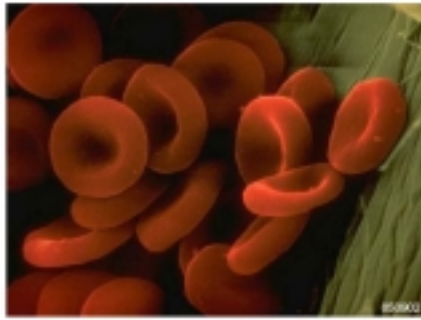
**SUMMARY:** The anticancer activity of cis -diamminedichloroplatinum(II) (cisplatin) arises from its ability to damage DNA, with the major adducts formed being intrastrand d(GpG) and d(ApG)

## Bioinorganic Chemistry

- Approximately 40 percent of all enzymes have metal ions in their active sites
- The presence of the metal is what governs the reactivity of the enzyme

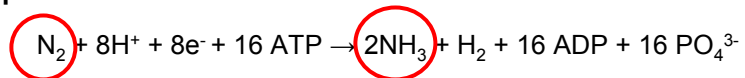


## Hemoglobin and Myoglobin



## • Nitrogenase

- Catalyzes the “nitrogen” fixation process in plants.





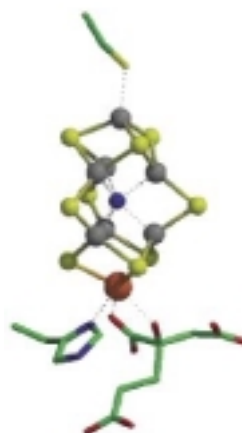
### Industrial

500 °C , 200 atm pressure



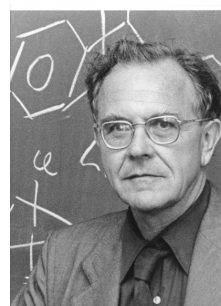
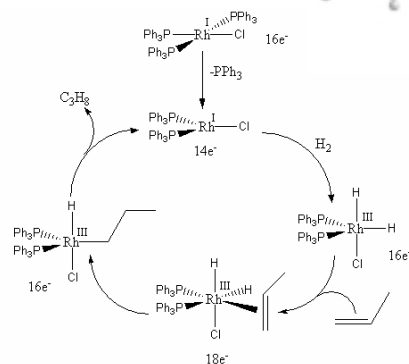
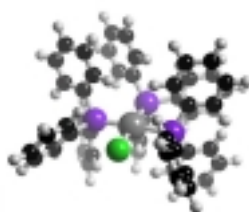
### Plants

20 °C, 1 atm pressure



## Organometallic Chemistry

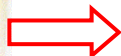
- catalysis



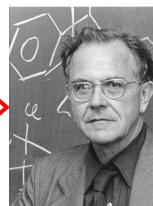
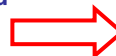
Sir Geoffrey Wilkinson  
Nobel Prize 1973

## Kevin Bacon and Inorganic Chemistry

Or something like that



Robert Gillard



## Atomic Structure - Begin with H-atom

In the beginning, comes the Schrödinger  
Eqn...

$$\mathcal{H}\Psi = E\Psi$$

The Hamiltonian,  $\mathcal{H}$ , is an operator with  
kinetic (T) and potential (V) energy parts

$$\mathcal{H} = \mathbf{T} + \mathbf{V}$$

$$\mathbf{T} = \frac{1}{2m}(\mathbf{p}_x^2 + \mathbf{p}_y^2 + \mathbf{p}_z^2) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\mathbf{V} = -\frac{Ze^2}{r} \left[ = -\frac{Ze^2}{4\pi\epsilon_0 r} \text{ in SI units} \right] \quad Z \text{ is the nuclear charge.}$$

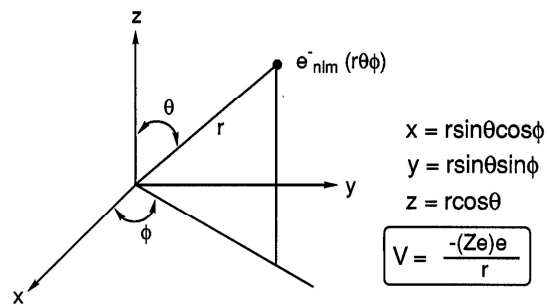
## Spherical polar coordinates for the atom

The potential energy depends only on  $r$

$$\mathcal{H} = \mathbf{T} + \mathbf{V} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} \quad \text{where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

So the differential operators (and, most important,  $\mathbf{Y}$ ) are expressed in terms of spherical polar coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$



## Orbitals

Each  $e^-_{nlm}$  in an atom is described by a wave function, or atomic orbital.

$$\psi_{nlm} = \underset{\substack{\uparrow \\ \text{radial}}}{R_{nl}(r)} \cdot \underset{\substack{\uparrow \\ \text{angular}}}{Y_{lm}(\theta\phi)}$$

This function is devoid of physical significance, but

$$\psi^2_{nlm}(r\theta\phi) \leftrightarrow \text{probability density of } e^-_{nlm} \text{ at } (r\theta\phi)$$

$$\int_{\text{all space}} \psi^2_{nlm}(r\theta\phi) d\tau = \int_0^\infty \underset{\substack{\uparrow \\ \text{probability of } e^-_{nl} \\ \text{at distance } r}}{R^2_{nl}(r)r^2 dr} \cdot \int_0^{2\pi} \int_0^\pi \underset{\substack{\uparrow \\ \text{probability of } e^-_{nl} \\ \text{at angles } (\theta\phi)}}{Y^2_{lm}(\theta\phi)\sin\theta d\theta d\phi} = 1$$

Wave function "normalized" to one; i.e., unit probability that  $e^-_{nlm}$  is in all space.

## Orbitals & Quantum Numbers

- Quantum numbers:  $n$ ,  $l$ , and  $m_l$ .
- "principal," "azimuthal," and "magnetic" quantum numbers.
- A set of these 3 defines an orbital.
- Recall that an orbital is a kind of standing wave that is the probability *amplitude* describing an electron's position. ( $|\Psi|^2$  gives the probability density.)

## Quantum Numbers

- $n$  - principal quantum number
  - influences energy and size of the orbital
  - $n = 1, 2, 3, \dots$
- $l$  - azimuthal quantum number
  - shape of orbital (mainly)
  - $l = 0, 1, 2, \dots, (n-1)$
- $m_l$  - magnetic quantum number
  - orientation of orbital (mainly)
  - $m_l = -l, \dots, 0, \dots, +l$

### Allowed combinations

$n$	$l$	$m_l$	# of orbitals	type of orbitals
1	0	0	1	1s
2	0	0	1	2s
	1	-1,0,+1	3	2p
3	0	0	1	3s
	1	-1,0,+1	3	3p
	2	-2,-1, 0,+1,+2	5	3d

## The meaning of $\Psi$

- Orbitals are wavefunctions, defined in mathematical terms.
- Physical interpretation?
  - ☛  $|\Psi|^2$  tells us the probability of finding the electron at some point in space.
- “Pictures” of orbital shapes (without “signs”) are actually graphs of  $|\Psi|^2$ .

## Some Orbital Wavefunctions

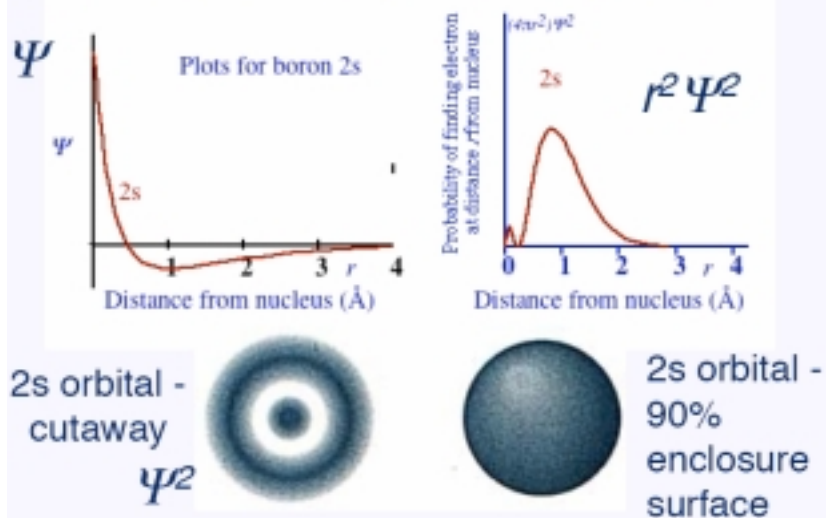
$$\Psi_{2s} = (2a)^{-3/2} \left(2 - \frac{r}{a}\right) \exp(-r/2a) \sqrt{\frac{1}{4\pi}}$$

$$\Psi_{2pz} = \frac{1}{\sqrt{3}} (2a)^{-3/2} \frac{r}{a} \exp(-r/2a) \sqrt{\frac{3}{4\pi}} \cos\theta$$

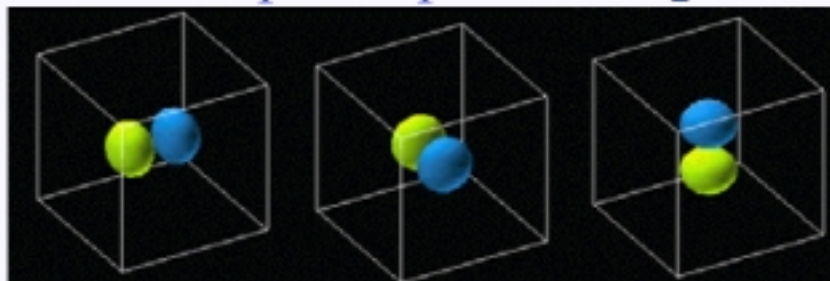
$$\Psi_{2px} = \frac{1}{\sqrt{3}} (2a)^{-3/2} \frac{r}{a} \exp(-r/2a) \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi$$

$$\Psi_{2py} = \frac{1}{\sqrt{3}} (2a)^{-3/2} \frac{r}{a} \exp(-r/2a) \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi$$

## Representing Orbitals, $\Psi$ & $\Psi^2$



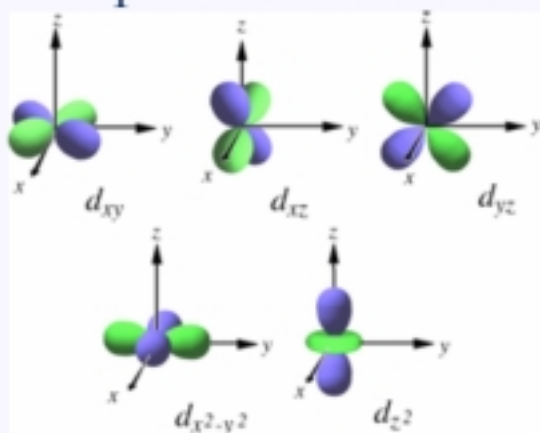
## Shapes of p-orbitals $\Psi$



- 3  $p$ -orbitals for each  $n$ -value (2p, 3p, ...)
- all same shape
- lobes point in perpendicular directions

## Shapes of 3d Orbitals

$\Psi$



## Orbital Filling

- Low energy orbitals fill first.
- Orbital energy increases
  - rapidly as  $n$  increases
  - more slowly as  $l$  increases



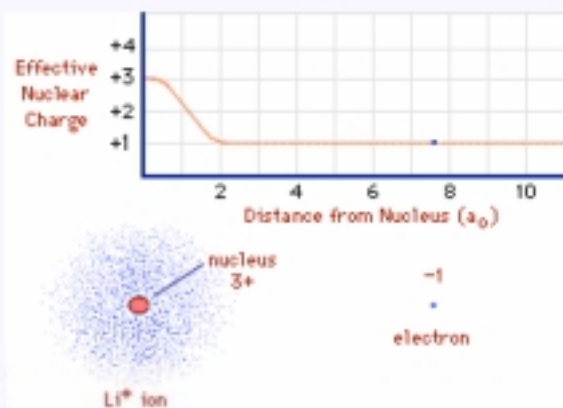
## From orbitals to atoms - configurations

- Each orbital can “hold” 2 electrons, provided they have opposite spins.
- Build up atoms by filling orbitals with appropriate # of electrons.
- Start at low energy, work toward high energy.
- *“Electron configurations”*

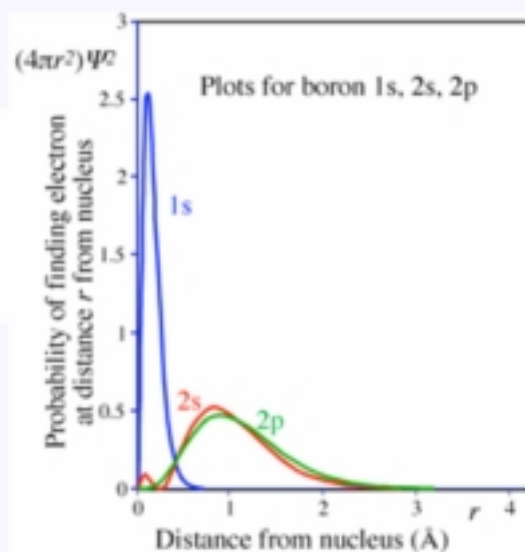
## Screening (or “Shielding”)

- Outer electrons “feel” a fairly small nuclear charge. (Why?)
- Electrons in orbitals with higher  $l$  values are screened somewhat more than those in orbitals with low  $l$  values.

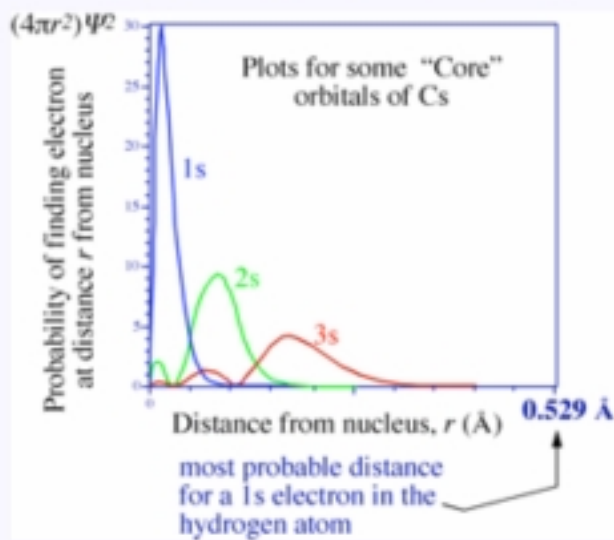
## How Screening Works Example $\text{Li}^+ + \text{e}^-$



## How Screening Works



## Core Orbital Sizes



## Screening - Explain the Data

### Ionization Energies (eV)

	<u>Hydrogen</u>	<u>He<sup>+</sup></u>	<u>He atom</u>
$n = 1$	13.6	54.4	24.58(1s <sup>2</sup> )
Excited atoms (electron comes from 2p):			
$n = 2$	3.40	13.6	3.65(1s2p)

H-atom formula

$$E = \frac{Z^2(-13.6 \text{ eV})}{n^2}$$

$Z$  - nuclear charge

$n$  - principal quantum no.

$$R_{nl}(r, Z_{\text{eff}})$$

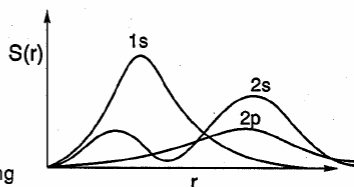
H atom

(1)  $Z = 1$ ,  $1 e^-$ , no screening

Polyelectronic atom,  $(y + 1) e^-$

(2)  $Z_{\text{eff}} = Z - y$ , **perfect** screening

(3)  $Z_{\text{eff}} = Z - y^*$  ( $y^* < y$ ), **imperfect** screening



orbital energy order:

