Class 1.1

Introduction; Atomic Structure I

Monday, Aug. 30

CHEM 462

T. Hughbanks

About grades

- Grading criteria for this course are outlined in the syllabus and on the course web site.
- Aside from being ~25% of the total grade, homeworks should be of some use for studying for exams.
- I will try to place some past exam(s) on the web in the period preceding an exam.
- I'll try to answer just about any question [except maybe, "Is this going to be on an exam?" :)].

What's "hard" about this course?

- Success depends on recall and integration of material from previous courses; You will be expected to use things you learned in general, organic and some extent, physical chemistry.
- Success depends on ability to think about and apply previous material - not just memorization and regurgitation for exams.

Prerequisite material

- To remind you of some things that you should have seen in earlier courses, I have posted 6 files, prereq#.pdf (# - 1–6), in the 'Handouts' section of the course web site: http://www.chem.tamu.edu/rgroup/hughbanks/courses/462/chem462.html
- Download these now – and look them over before we get to the relevant sections in this course!

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Announcements, Reading

- Text: Shriver & Atkins, 3rd ed.: "Inorganic Chemistry"
- We're starting with Chapter 1 for two or three lectures
- We will review things you should have seen in Freshman Chem., and again (in more detail) in P. Chem.
- 1st homework set is posted: http://www.chem.tamu.edu/rgroup/hughbanks/courses/462/chem462.html
- Lecture notes, handouts, old exams, etc. posted in the same place.

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Inorganic vs. Organic Chem.

- 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 wrt air or water
- Widely ranging solubilities

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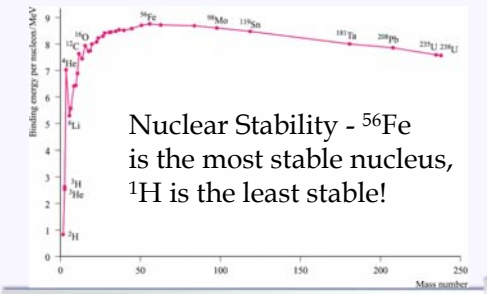
The Elements

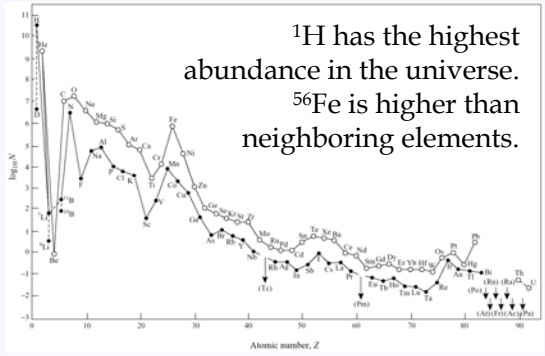
- ~ 107 of them ....
- Most are metals: solids, electrical conductors, good thermal conductors, sometimes with high mechanical strength and ductility. Structures: ccp, hcp, bcc, and other types
- ~ 22 nonmetals (As, Sb, Te, … ?)
- At ambient temp.: 11 gases, 2 liquids (Br, Hg), [+ Cs (m.p. 28.5 ˚C) &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

Nuclear Stability vs Cosmic Abundance



Nuclear Stability - ^{56}Fe is the most stable nucleus, ^{1}H is the least stable!

Nuclear Stability vs Cosmic Abundance



^{1}H has the highest abundance in the universe. ^{56}Fe is higher than neighboring elements.

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_2 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).

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

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

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

$$\mathbf{V} = -\frac{Ze^2}{r}\left[= -\frac{Ze^2}{4\pi\varepsilon_0 r} \text{ in SI units}\right] \qquad Z \text{ is the nuclear charge.}$$

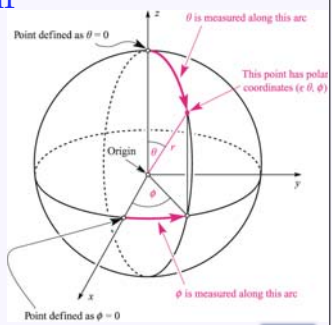
Spherical polar coordinates

x, y, z ↔ r, θ, ϕ

$\Psi(x,y,z) \rightarrow \Psi(r,\theta,\phi)$

Ψ can be written as a product of radial and angular parts:

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



Spherical polar coordinates for the atom

The potential energy depends only on r

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

So the differential operators (and, most important, Ψ) are expressed in terms of spherical polar coordinates:

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

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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.)

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Quantum Numbers

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

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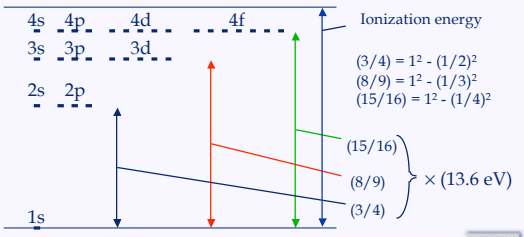
Allowed combinations

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*

Hydrogen atom Orbital Energies

$$E = \frac{-13.6\ \text{eV}}{n^2} = \frac{-2.18 \times 10^{-18}\ \text{J}}{n^2}$$

n - principal quantum no.



The meaning of Ψ

- 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

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

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

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

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

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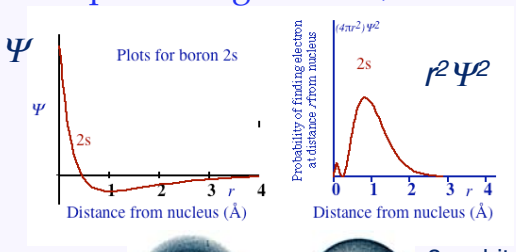
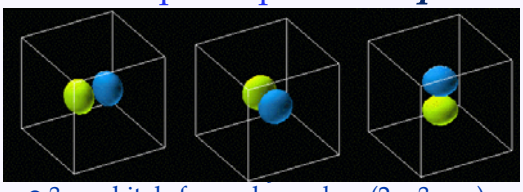
Representing Orbitals, Ψ & Ψ^2



2s orbital - cutaway Ψ^2

2s orbital - 90% enclosure surface

Shapes of p-orbitals Ψ



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

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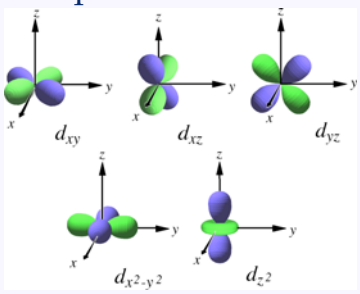
Shapes of 3d Orbitals



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Orbital Filling

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

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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"*

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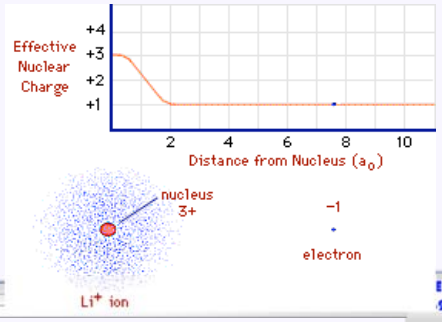
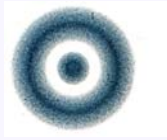
Screening (or "Shielding")

- 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.

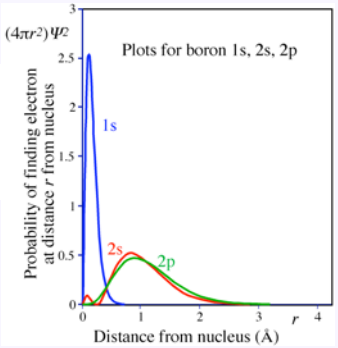
How Screening Works

Example
$Li^+ + e^-$

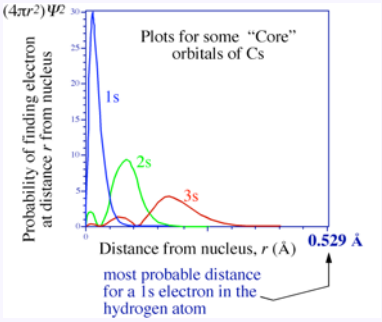




How Screening Works



Core Orbital Sizes



Screening - Explain the Data

Ionization Energies (eV)

	Hydrogen	He^+	He atom
$n = 1$	13.6	54.4	24.58($1s^2$)
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.