

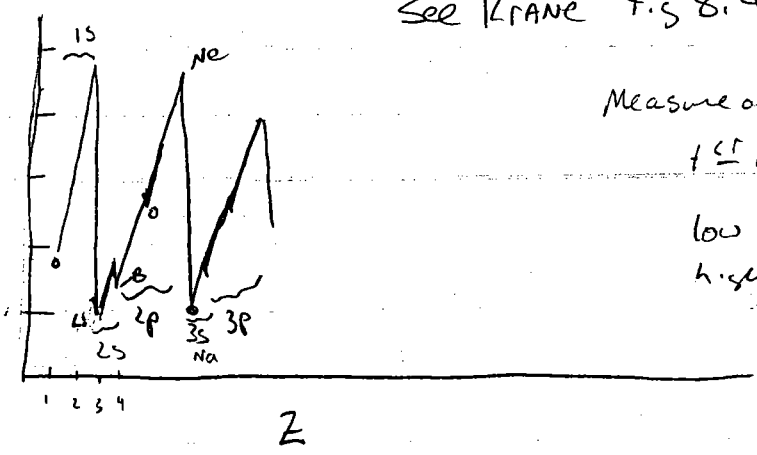
Periodic Chart reflects This structure:

Show chart from KRANE

Properties of chemical elements can be understood in terms of the Atomic level structure we are discussing

- Filled subshells, very stable configurations  
Normally do not contribute to "chemistry"
- Atoms having 1 e<sup>-</sup> over a filled shell will readily give that e<sup>-</sup> up in a chemical reaction (lowers overall energy)  
Atoms lacking 1 e<sup>-</sup> from a filled shell will react to gain that e<sup>-</sup> to form a filled shell (more stable)

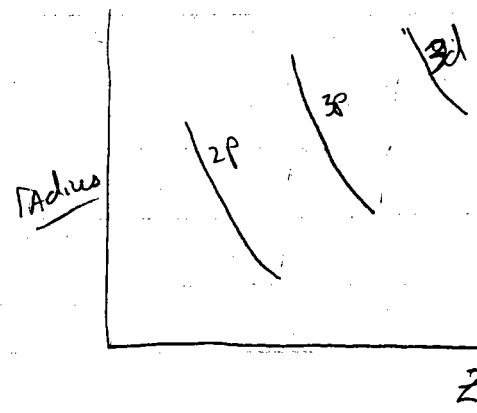
Ionization energy  
(eV)



See KRANE Fig 8.4 p210

Measure of ease w/ which  
1 e<sup>-</sup> given up  
low ≡ easy  
high ≡ hard

Atomic Radius



KRANE 8.3 p209

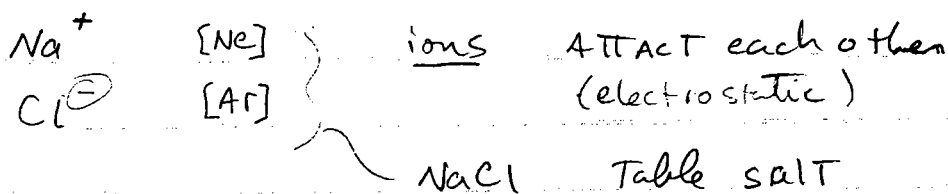
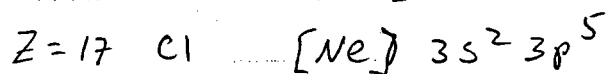
as Z increases within a shell  
Atomic radius decreases  
as new shell is added  
Atomic radius increases

Bohr Atom  $R \sim \frac{n^2}{Z}$

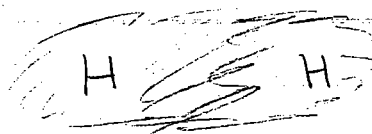
- H, Na are very reactive
- Noble gases He, Ne, Ar ... have filled levels  
are very inert chemically

## Chemical bonds

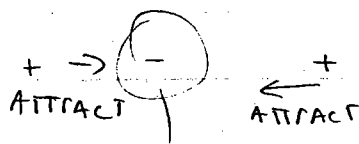
ionic bond - one ATOM takes  $e^-$  from another  
 $\Rightarrow$  both have filled shells (more stable)  
 and are charged (attract each other)



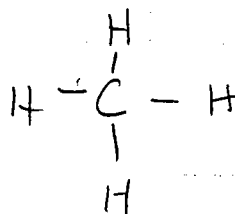
## Covalent bond



each H shares 2 electrons  
 $\Rightarrow$  molecular orbital



High  $\ominus$  charge density in the middle



Methane (C needs  $4e^-$  to get to [Ne])

(H needs  $2e^-$  to get to [He])

# Spectroscopy

Discrete energy levels

Key to understanding Atomic Structure



Transitions occur between allowed STATES

Permits a detailed Study of atomic Model, environment of Atom, Sample composition

(NMR)

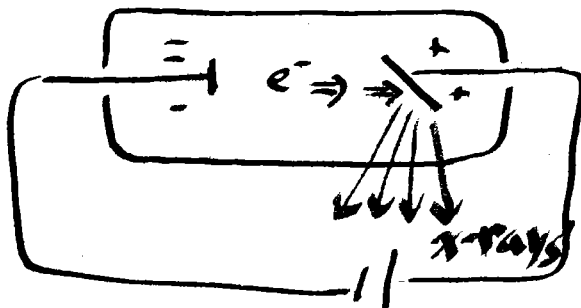
(Emission, Absorption spectra)

(ESR)

Many Applications: X rays, NMR, lasers ...

## X-rays

1895 discovery Roontgen



Cathode tube

Cathode rays

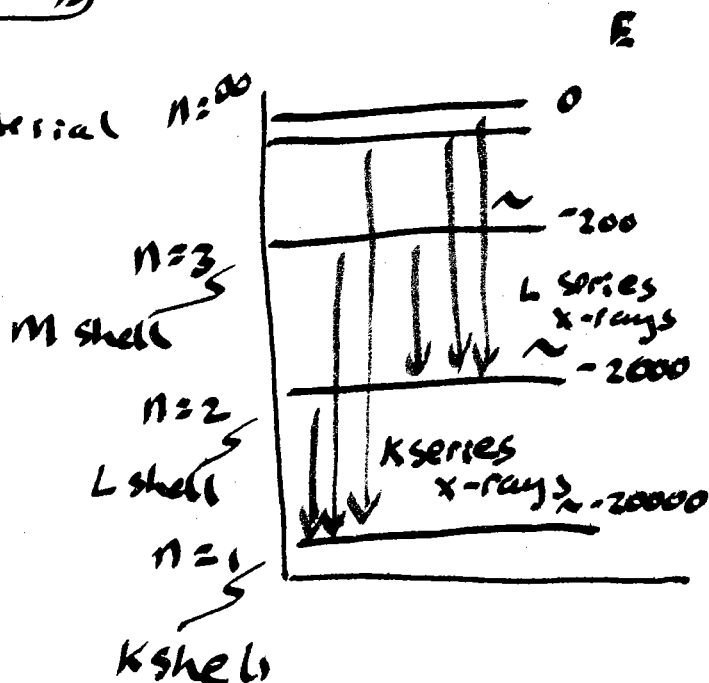
$e^-$  incident on a high  $Z$  material

X-rays

$$100 \sim 100,000 \text{ eV} = h\nu$$

overlaps w/ ultraviolet on the soft end

and gamma rays on the hard end



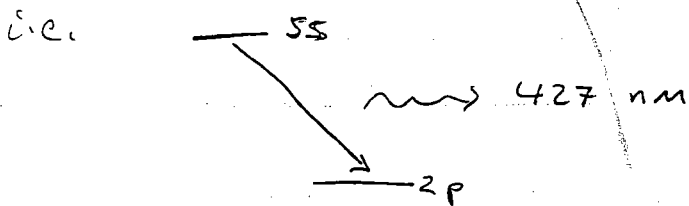
Principle - Chemistry, Biochemistry  
 explained by quantum mechanics  
 - Forces at work basically understood

- ⇒ Chemists, Biologists not out of business
- Cannot solve QM of complex systems like medium sized molecules or dogs.
  - New and unexpected phenomena come about with added complexity ⇒ Life

Key to understanding Atomic structure experimentally is spectroscopy

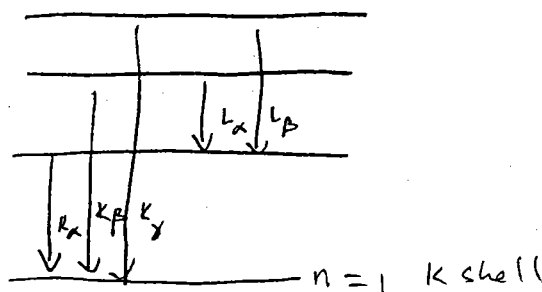
Many different kinds

optical transitions occur in relatively loosely held outer shells



(must obey selection rules)  
 conserve angular momentum and spin.

X-rays occur when tightly bound inner electron in high  $Z$  ~~electron~~ <sup>Atom</sup> is ejected and one of the outer electrons makes a transition down to the lower shell

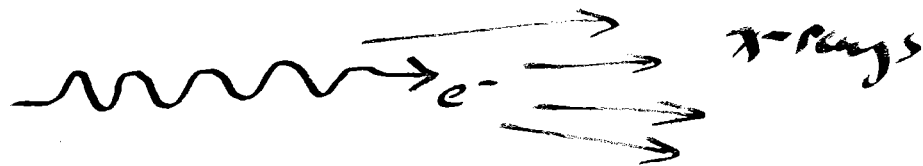
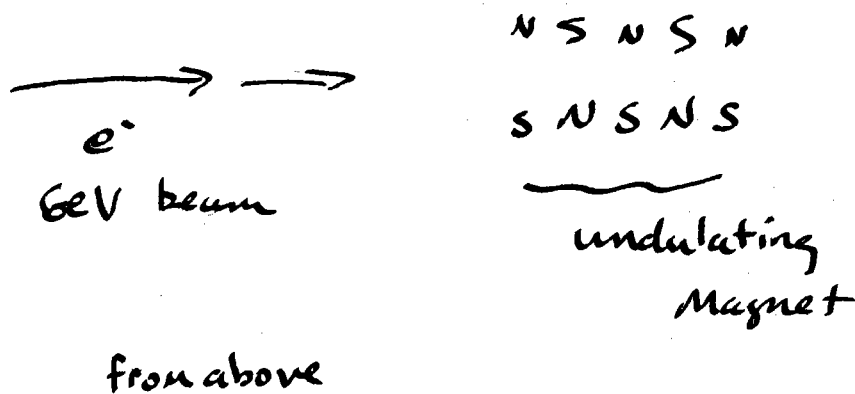


Calculate the energy necessary to "ionize" heavy element with  $Z = 40$  by removing  $e^-$  from  $n=1$  shell

$$E_n \sim -\frac{Z^2}{n^2} E_0 \sim -40^2 (13.6 \text{ eV}) \approx 22000 \text{ eV}$$

$\Rightarrow$  This is the order of magnitude for  $E_{\text{X-ray}}$  emitted as electrons from outer shells cascade down to fill the hole

X-rays also from high intensity light sources



frequency determined by  $P_{e^-}$  and spacing of Magnets

Very important source for of high intensity, high frequency electron ~~beam~~ X-ray beams for research

We will discuss absorption when we do Nuclear Physics.

# Election Spin Resonance (ESR)

# Nuclear Magnetic Resonance (NMR)

Recall



Particles can be thought of as "spinning" charge distributions w/ quantized

"allowed" values of Angular frequency

$\Rightarrow e^-$  point like as far as we know

$\Rightarrow$  Nuclei have structure

This is intrinsic spin  $\Rightarrow$  leads to a small magnetic moment  
Acts like a small Dipole

~~Spin~~

intrinsic Angular momentum  $I$

Total spin  $\frac{1}{2}$  for  $e^-$

integer or  $\frac{1}{2}$  integer for Nuclei

$1\frac{1}{2}, 1, \dots$  etc.

Spin  $Z$  component

$m = I, I-1, \dots, -I$

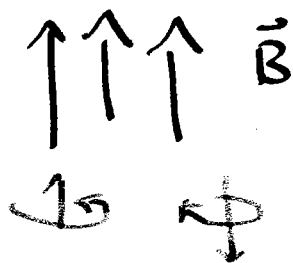
$e^- \pm \frac{1}{2} = m_s$

Nuclei also  $\pm$  value

Determining Spin structure is important in Nuclear structure expts

Spin can also be used as a diagnostic or tool for probing particle environment

# Dipole in Magnetic Field



Potential Energy in system  
Depends on the orientation of  
Dipole in B field

Let z direction be along  $\vec{B}$

$$E_{\text{mag}} = -g \mu B m_z$$

$g$ : constant (NOT g-factor)  
 $\mu$ : magnetic moment of particle  
 $B$ : magnitude  
 $m_z$ : z component of spin

For  $B=0$

atoms/nuclei w/ all  $m$  in a given energy level  
are degenerate in energy

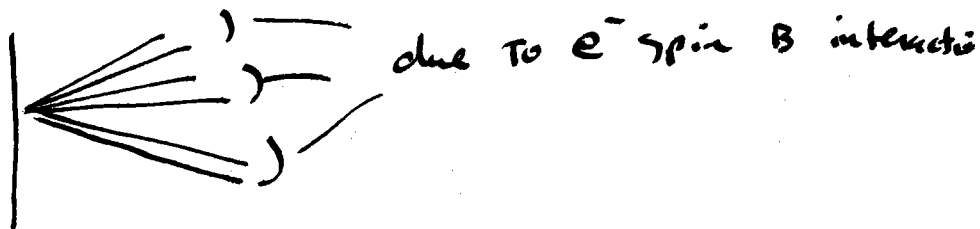
Atom  $n=3, l=1, m_l = \begin{matrix} 1 \\ 0 \\ -1 \end{matrix}$  } all have same energy  
 $m_s = \pm 1/2$

Turn on B



Split due to  
 $B m_l$   
Zeeman  
Splitting

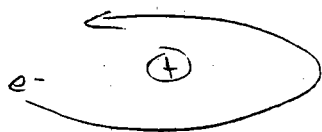
If an unpaired electron present  
get additional split



Spectroscopy in Magnetic fields / electric fields  
important tools!

ex Zeeman Splitting

recall



little magnetic dipole created  
by  $e^-$  orbiting around nucleus

$$\vec{\mu}_l = \frac{\mu_b}{\hbar} \vec{L} = \left(\frac{e}{2m}\right) \vec{L}$$

Suppose we have an atom w/  $e^-$  in 2p state (ignore  $e^-$  spin)

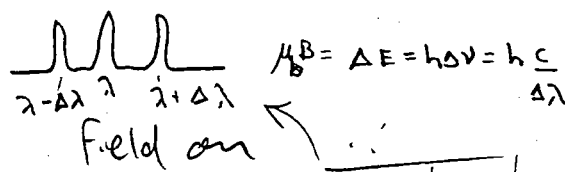
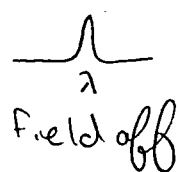
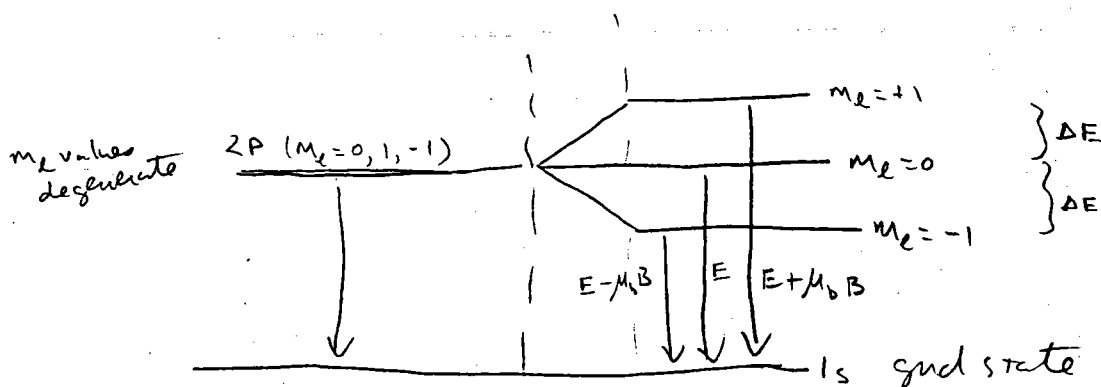
energy of interaction of  $\mu$  with  $B = V = -\vec{\mu} \cdot \vec{B}$

Let direction of  $B$  determine  $z$  axis

then

$$V = \left(\frac{e}{2m}\right) \vec{L} \cdot \vec{B} = \frac{e}{2m} L_z B = \frac{e\hbar}{2m} m_l B = \mu_b m_l B$$

2p state  $m_l = 1, 0, -1$

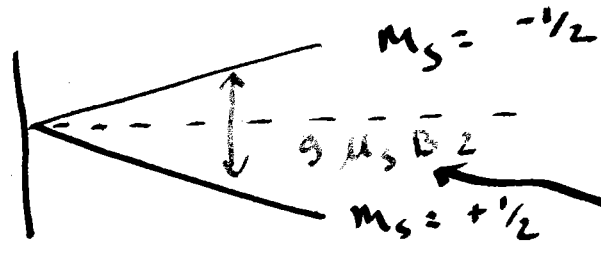


$$\mu_b B = \Delta E = h\nu = \frac{hc}{\Delta\lambda}$$

$$\Delta\lambda = \frac{hc}{\mu_b B}$$

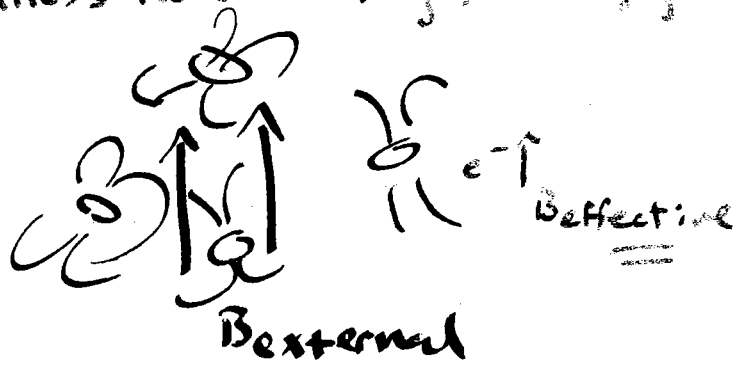


Transitions between  
 energy levels would be  
 at a diff frequency!

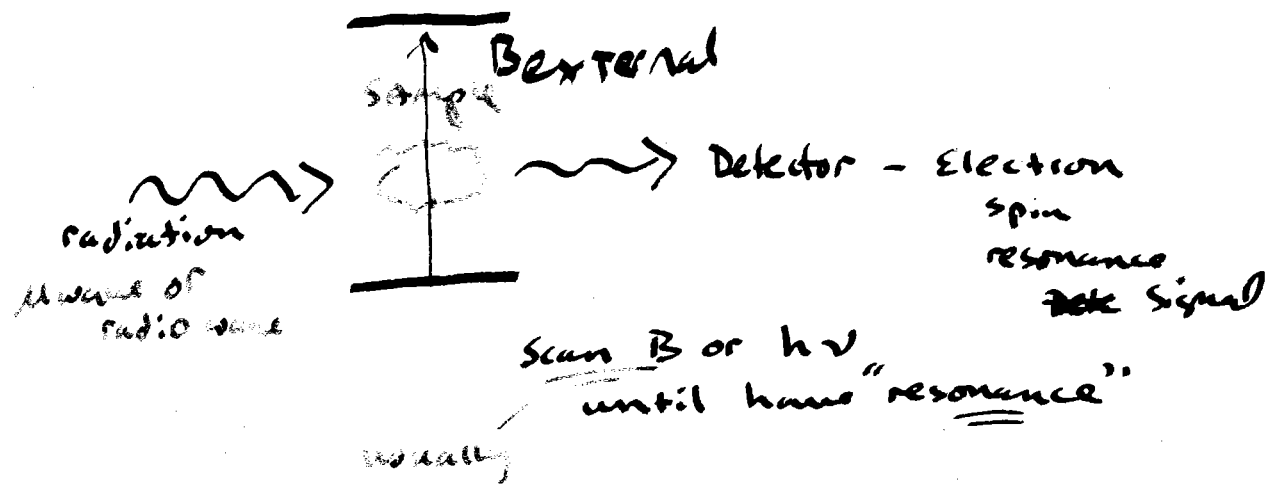
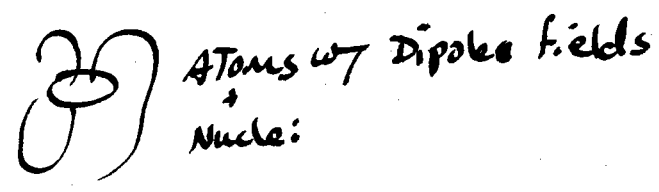


actual B at  $e^-$   
 NOT necessarily  
 applied B

Usefulness in chemistry, biology



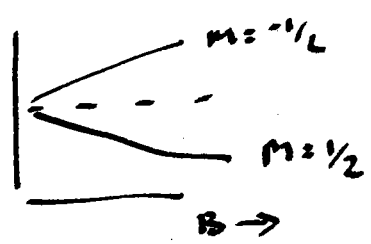
Effective depends  
 on the environment



Typical NMR

Put sample in B field

E state of depends on orientation of spin = 1/2 protons  
 w/ respect to B



apply  $h\nu$  to cause transitions  
 between two relative spin levels  
 exact  $h\nu$  depends on  
 $B_{eff}$  ... depends on  
 " Nuclear Environment "