

Electron spectroscopy, electronic structure and all that

D.D. Sarma

Solid State and Structural Chemistry Unit

Indian Institute of Science, Bangalore 560012

**Also at, CSIR-Network of Institutes for Solar Energy, India, and
Department of Physics and Astronomy, Uppsala University, Sweden**

email: sarma@sscu.iisc.ernet.in

<http://sscu.iisc.ernet.in/DDSarma>



A brief introduction to photoemission techniques:

In a translationally invariant system, the state of an electron is described by four quantum numbers:

- (i) ENERGY
- (ii) MOMENTUM
- (iii) SYMMETRY
- (iv) SPIN

Electron spectroscopy, in its various forms, can provide information on ALL these.

Disclaimer: It cannot, however, probe the electric polarization!



HIGH-ENERGY(ELECTRON) SPECTROSCOPIES:

P/E (i) Photoelectron Spectroscopies -X-RAY (XPS) - UV (UPS)

P,E/E (ii) Auger Electron Spectroscopy (AES)

E/P (iii) Bremsstrahlung Isochromat Spectroscopy (BIS)

E/E (iv) Electron Energy Loss Spectroscopy (EELS)

P/P (v) X-Ray Absorption Spectroscopy (XAS)

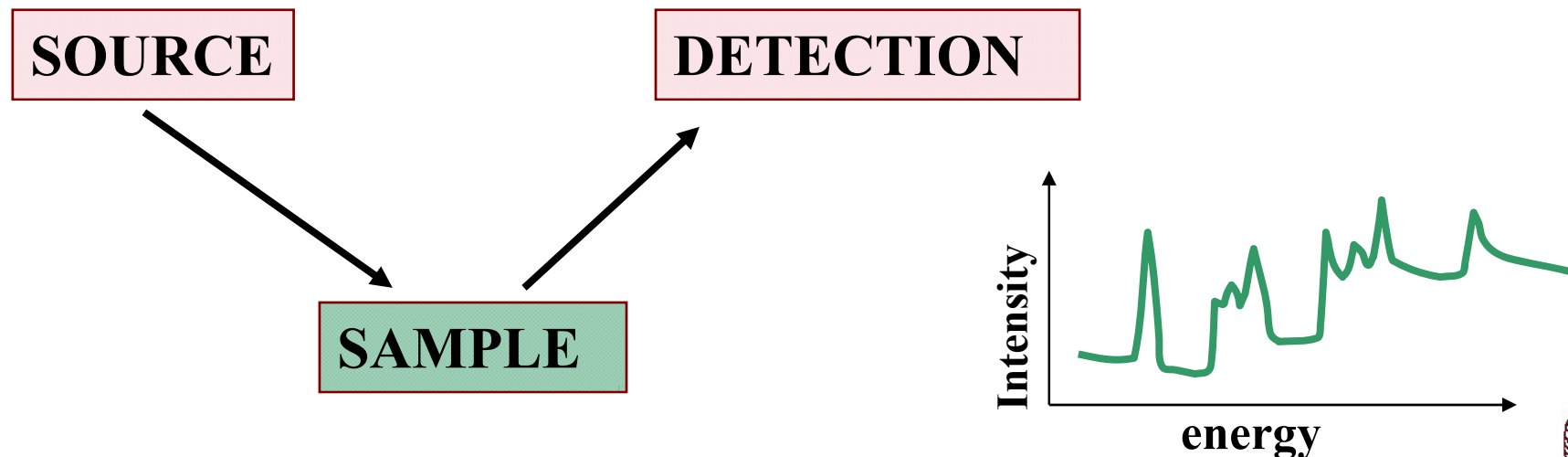
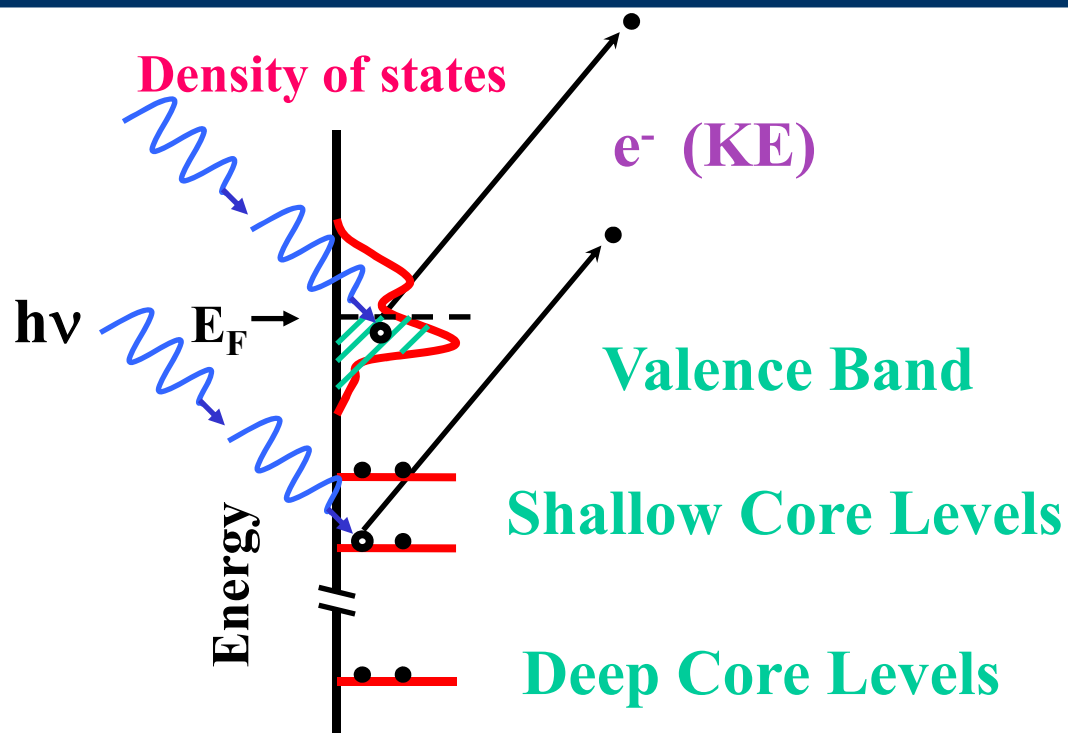


PHOTO ELECTRON SPECTROSCOPIES



Energy Conservation: $E_i(N) + hv = E_f(N-1) + KE$

$$hv - KE = [E_f(N-1) - E_i(N)]$$

known
measure

[As $KE \geq 0 \quad \therefore BE \leq hv$]

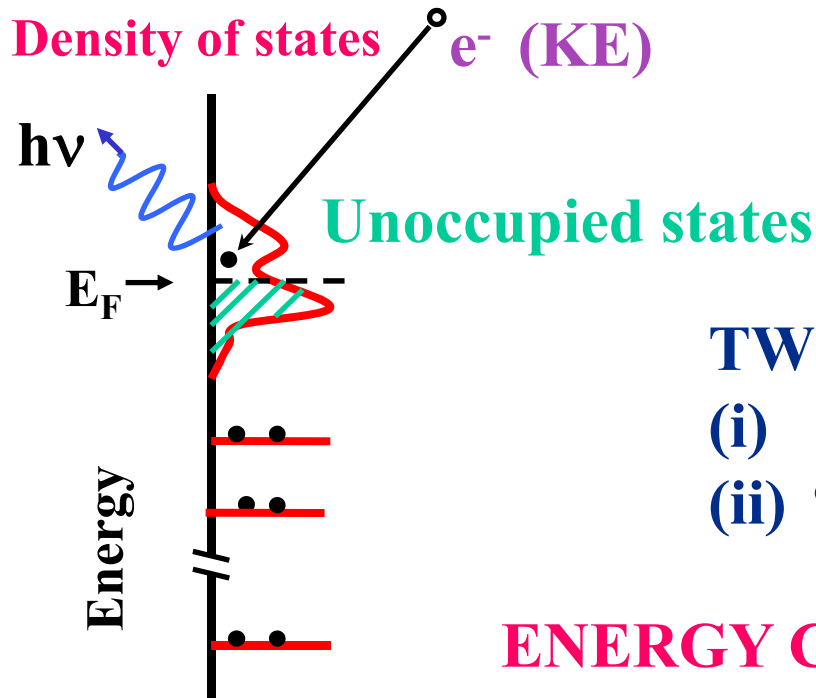
Also as $BE \geq 0 \quad \therefore KE \leq hv$

Evaluate

“BE”



BREMSSTRAHLUNG ISOCHROMAT SPECT:



INVERSE PHOTOEMISSION

TWO MODES OF OPERATION :

- (i) ISOCHROMAT (BIS)
- (ii) "ISO-KE"

ENERGY CONSERVATION:

$$E_i(N) + KE = E_f(N+1) + hv$$

$$KE - hv = E_f(N+1) + E_i(N)$$

↑

Sweep

↑

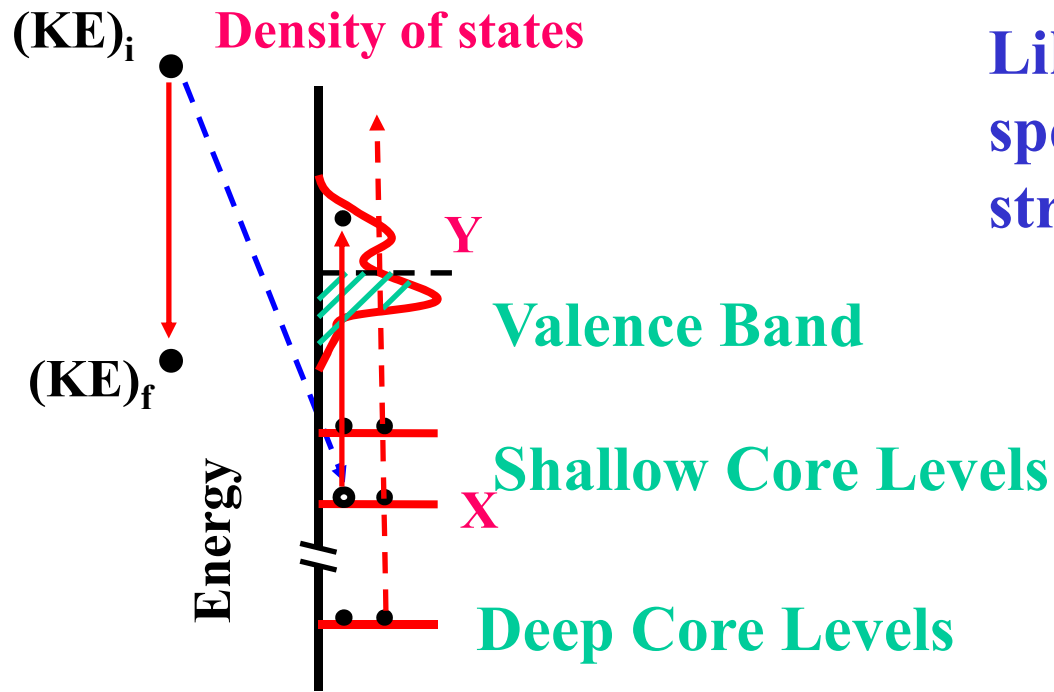
fixed



evaluate "BE" of the empty level



ELECTRON ENERGY LOSS SPECTROSCOPY:



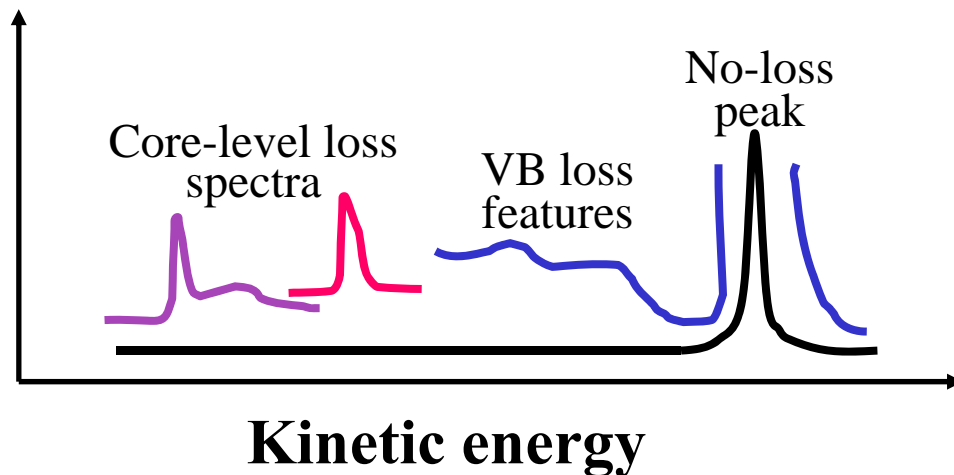
Like x-ray absorption spectroscopy, but without the stringent dipole selection rules

Energy conservation:

$$(KE)_i + E_i = (KE)_f + E_f$$

$$\Delta E_{\text{loss}} \stackrel{\Delta}{=} (KE)_i - (KE)_f = E_f(N) - E_i(N)$$

$$\text{“BE(X) – BE(Y)”}$$



Measures transitions between a localized and empty levels, thereby probing and providing information about the levels above E_F .



Typical laboratory photon sources:

X-RAY: $AlK\alpha$ $h\nu = 1486.6 \text{ eV}$

$MgK\alpha$ $h\nu = 1253.6 \text{ eV}$

$Z\gamma M\xi$

Ag/Y

UV : HeI $h\nu = 21.2 \text{ eV}$

$HeII$ $h\nu = 40.8 \text{ eV}$

Ar/Ne

Synchrotron sources:

**eV – several keV and
continuous tunable**

TYPICAL KINETIC ENERGY OF ELECTRONS: 10eV ----- 1.5KeV

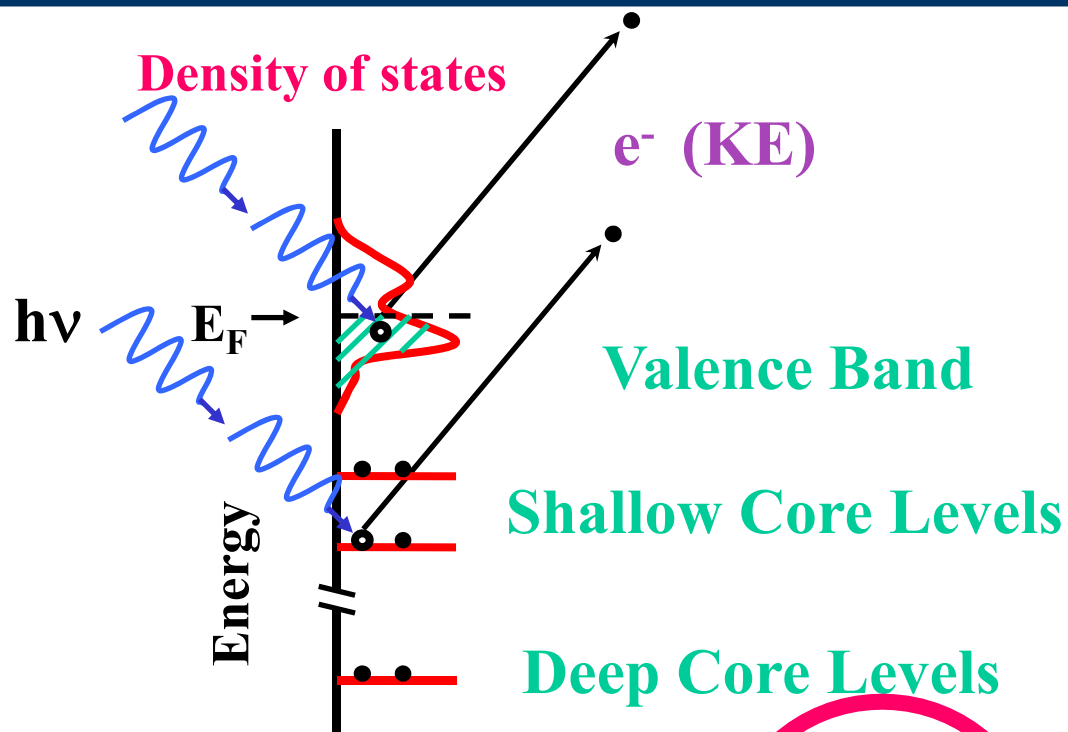
MEAN FREE PATH OF AN ELECTRON: $\leq 20 \text{ \AA}$ or so!!!

EXTREMELY SURFACE SENSITIVE.

∴ NEED UHV CONDITIONS AND IN-SITU SURFACE TREATMENT



PHOTO ELECTRON SPECTROSCOPY



Energy Conservation: $E_i(N) + h\nu = E_f(N-1) + KE$

$h\nu - KE = [E_f(N-1) - E_i(N)]$

known *measure* **“BE”**

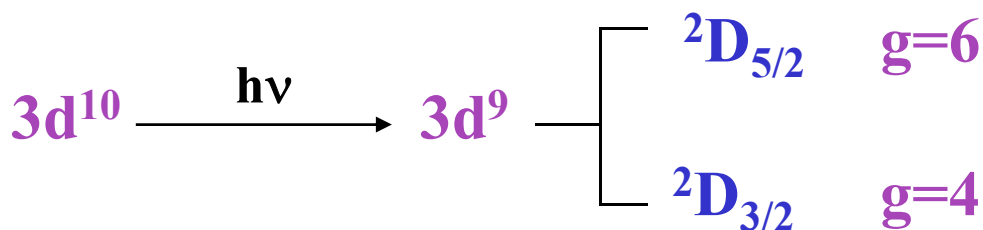
Evaluate



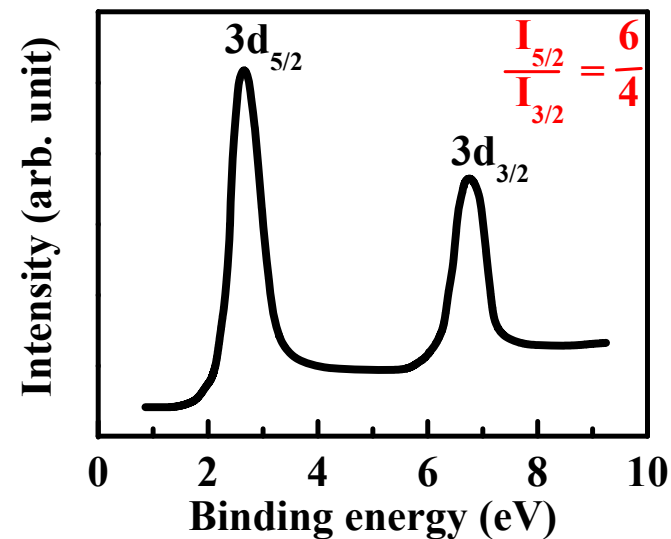
Case studies with a transition metal oxide (e.g. MnO) and a lanthanide metal (e.g. Tb):

Deep core levels:

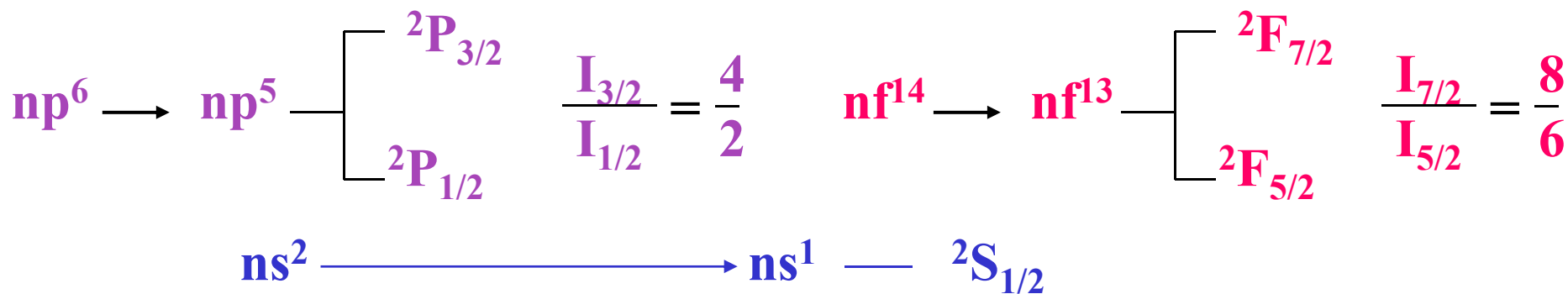
e.g. Tb 3d



$E_f(N-1)$



SPIN ORBIT SPLITTING:



No spin-orbit interaction (or splitting) for s-levels
[angular momentum = 0]

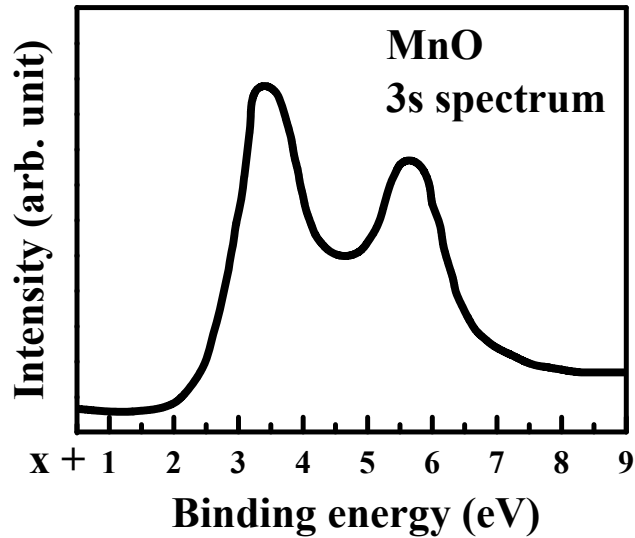


But s-level does show splitting!

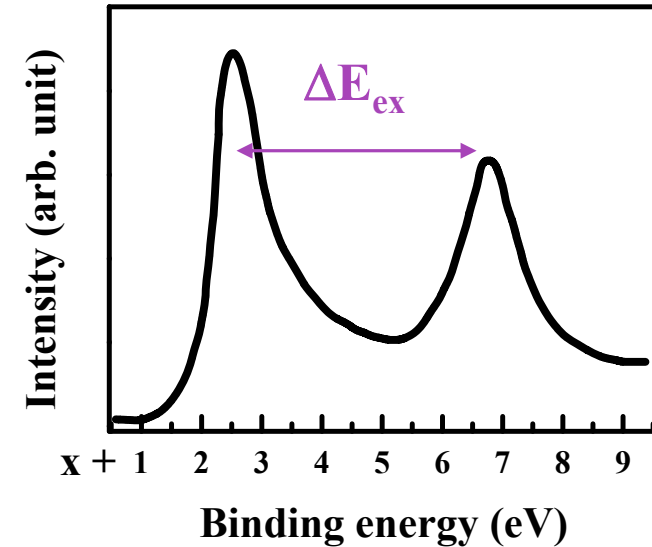
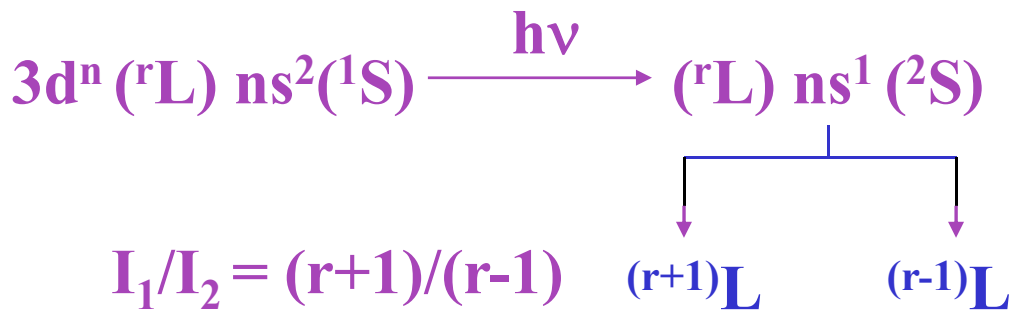
e.g. 3s in MnO or any other TM compound
or 5s or 4s in Tb or any other RE!!

MnO: ionic view : $Mn^{2+} 3d^5 6s$

in general : rL



Two different situations may occur:



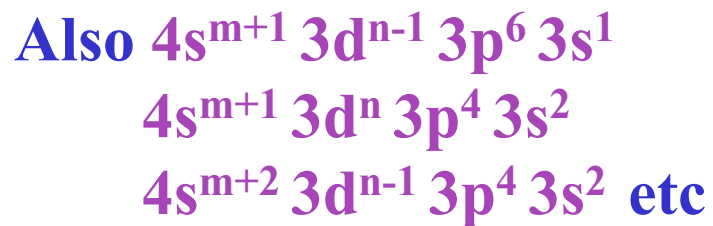
ΔE_{ex} can be evaluated within HF.

ΔE_{ex} as well as I_1/I_2 for 3s in TM and 4s in RE do not agree with the theoretical expectations/ calculations!!



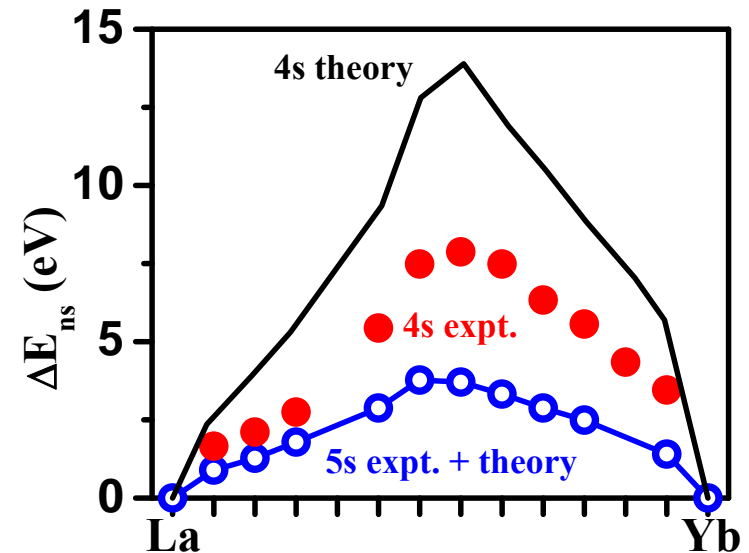
While 3s in TM and 4s in RE misbehave,
5s fulfils the expectations !!

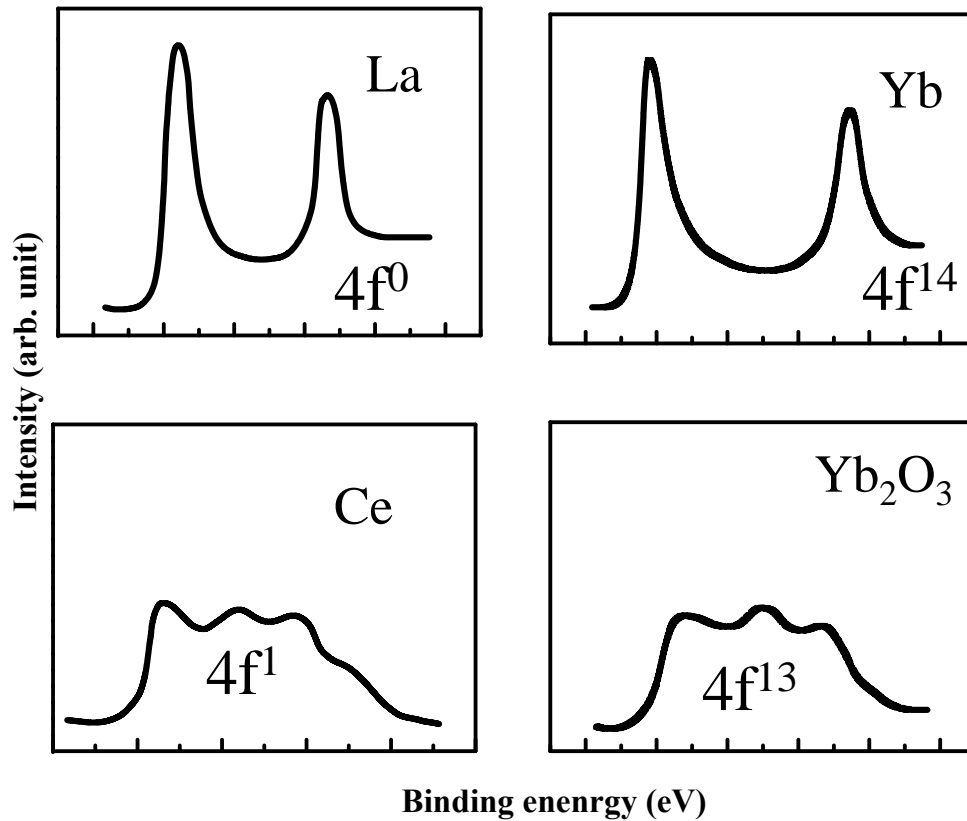
The discrepancy in 3s and 4s is mainly
due to CI effects



CI effects are mainly important when all
the orbitals involved are from the same
“n” quantum number.

[That explains 5s!]





Similar situation exists for the 3p of the Tm's , however both the interactions are weak here.

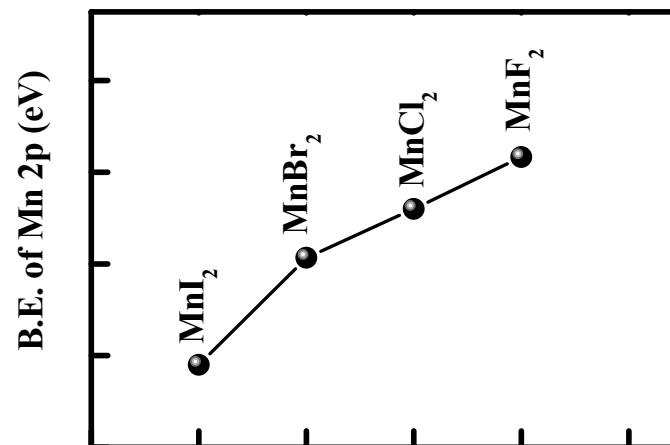
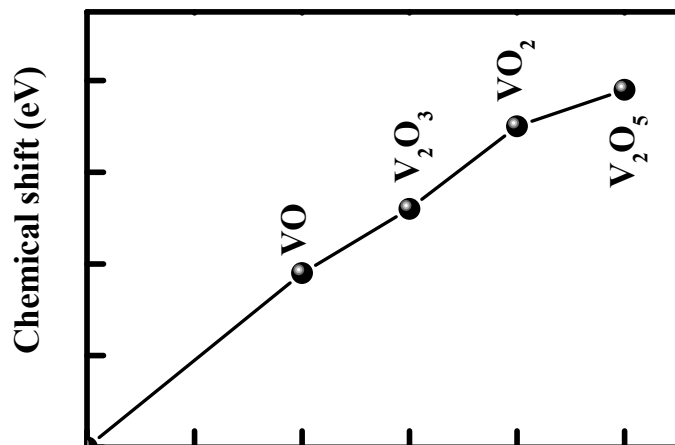
NOTE: “SPIN-ORBIT” discussion is valid, if “EXCHANGE” interaction is very weak *and vice versa*. It can very well happen that both these interactions are comparable. Then it is no more possible to discuss separately these two interactions. In such a case, one has to account for the complete multiplet interactions involving all terms. **Example: 4d level of the $4f^n$ RE's**



PHOTOELECTRON SPECTROSCOPY:

CHEMICAL SHIFT?

The measured binding energy of core levels normally increases with increasing oxidation state or with increasing electronegativity of the ligand.



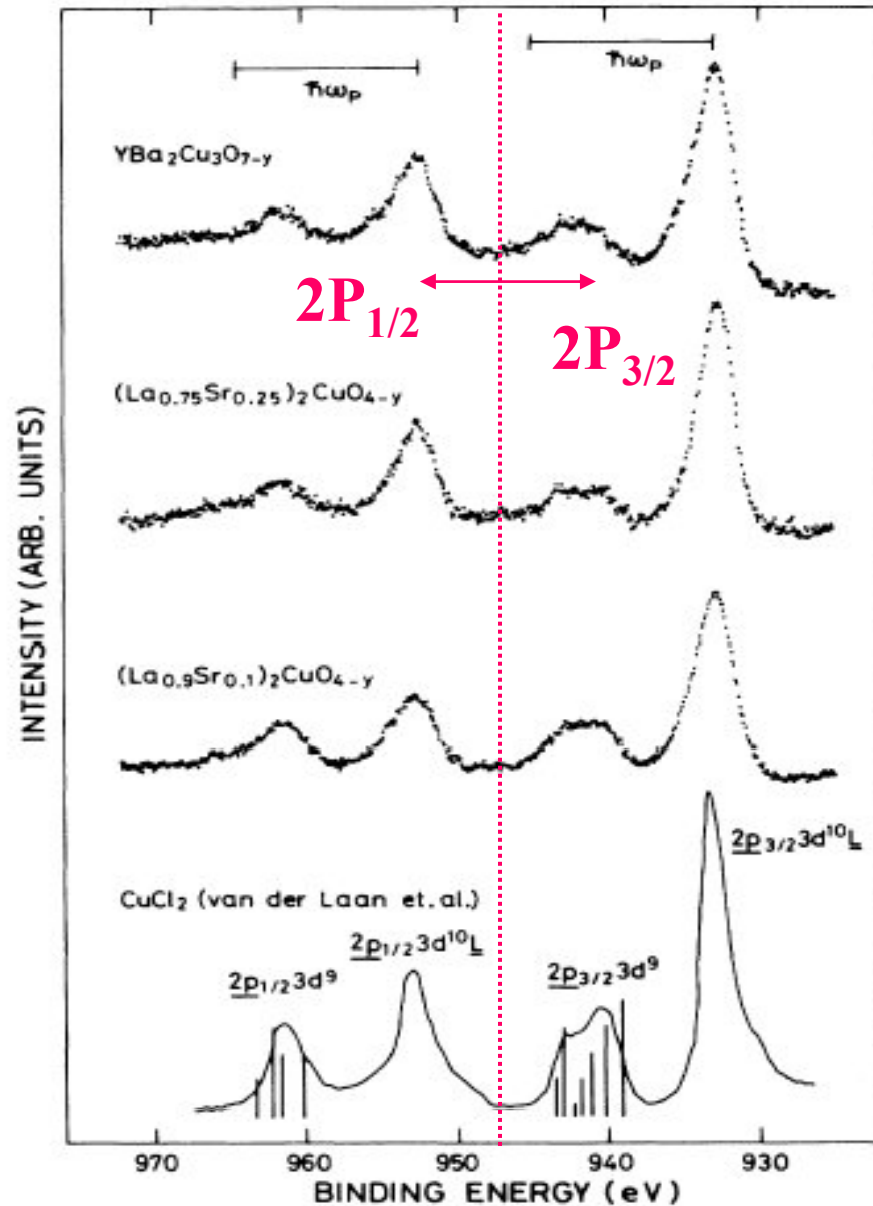
HOWEVER, THERE ARE MANY EXCEPTIONS.

e.g. Cu₂O/Cu, Ag₂O/Ag, La₂O₃/La, and the alkali metal oxides.

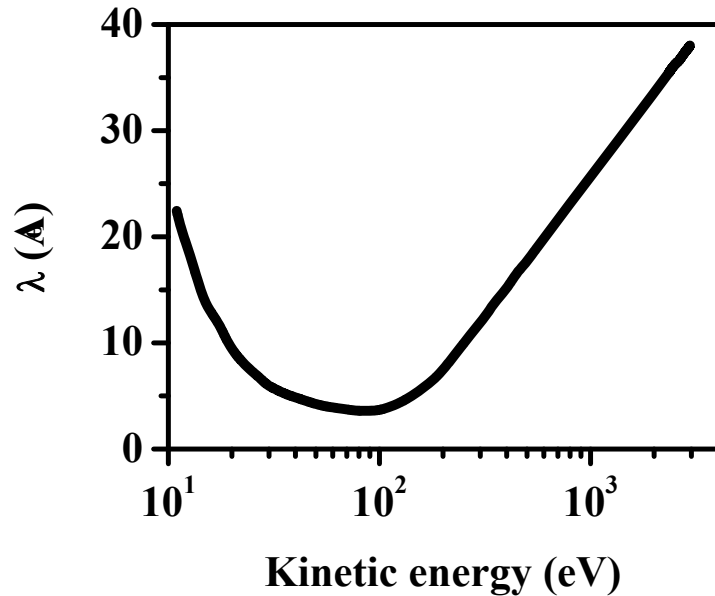
Electron Spectroscopy for Chemical Analysis (ESCA)



More complex structures in the core level spectra: Satellites



A. Fujimori et al. PRL, 35, 8814 (1987)



**Mean free path of an electron:
Extreme surface sensitivity!!**

ESSENTIALS OF SUDDEN APPROXIMATION:

[H for $t < t_1$ and H' for $t > t_2$ and $t_1 - t_2$ is small]

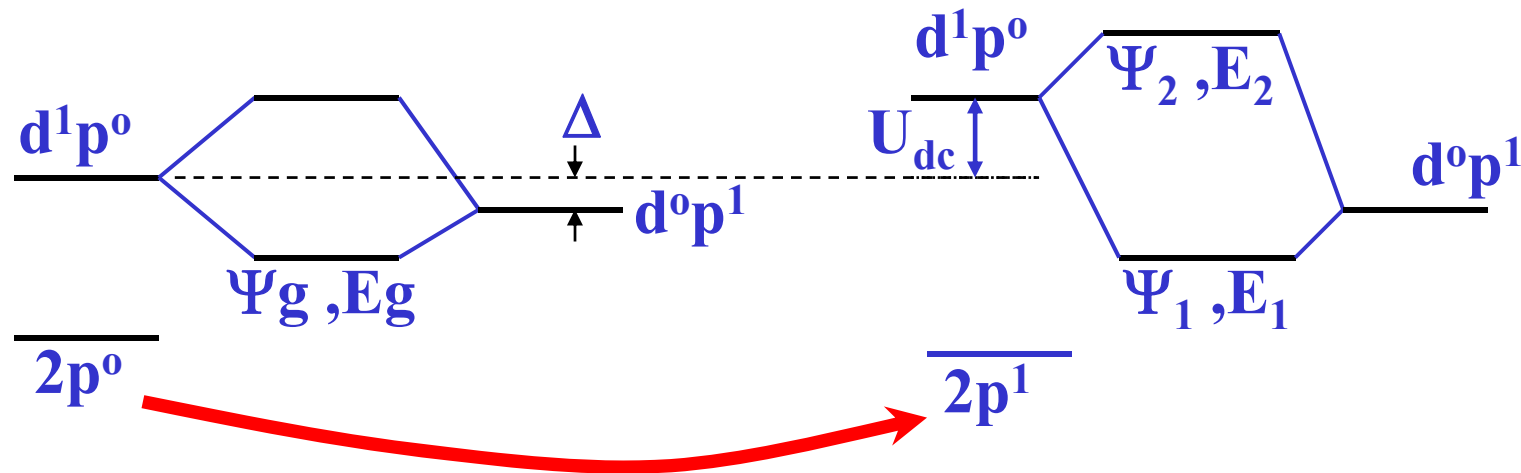
$H\Psi = E\Psi$ $t < 0$ and $H'\Psi = \epsilon\Psi$ $t > 0$

$\Psi_g(t=0^-) = \sum_i C_i \Psi_i(t=0^+)$

$|C_i|^2 = |\langle \Psi_i | \Psi_g \rangle|^2$ is the probability of finding the system in Ψ_i^{th} eigen state of the final Hamiltonian.



Before and after core photoionization:



Two peaks separated by $\Delta E = E_1 - E_2$ and intensities proportional to $|\langle \Psi_g | \Psi_i \rangle|^2$ where $i=1$ and 2 .

For CuO_4 with $d_{x^2-y^2}$ and p_σ :

$$\Delta E = [\Delta - U_{dc} + 2t_{pp}]^2 + 4t^2]^{1/2} \text{ and } I_{\text{sat}}/I_{\text{main}} = \tan^2(\theta - \phi)$$

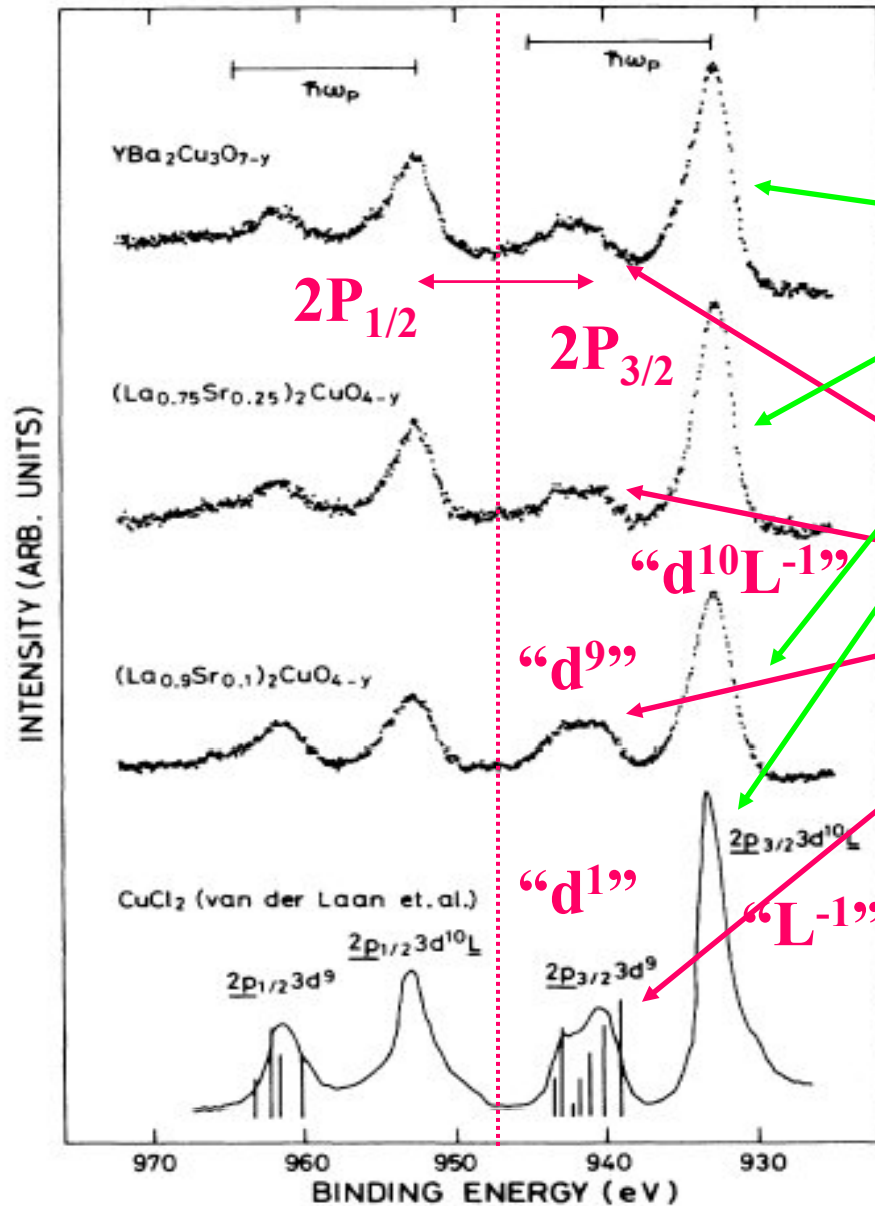
$$\sin^2 \theta = 1/2 [1 + (\Delta + 2t_{pp}) / \{[(\Delta + 2t_{pp})^2 + 4t^2]\}^{1/2}]$$

$$\sin^2 \phi = 1/2 [1 + (\Delta + 2t_{pp} - U_{dc}) / \Delta E]$$

Phys. Rev. B
42, 6817
(1990).



More complex structures in the core level spectra: Satellites

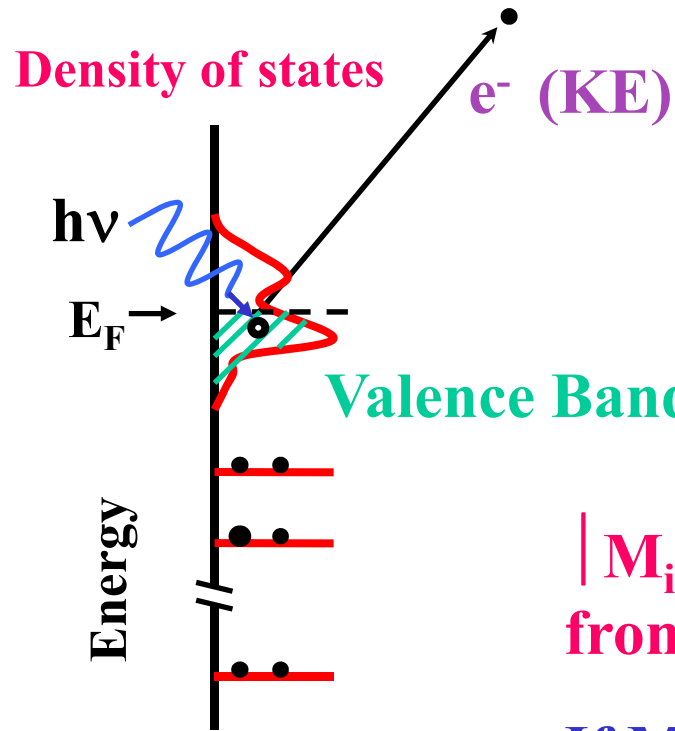


“Well-screened”
or transition to the
lower level.

“Poorly screened”
or transition to
the upper level.

A. Fujimori et al. PRL, 35, 8814 (1987)

PHOTOEMISSION SPECTROSCOPY



Intensity or number of electrons emitted with a given KE (which corresponds to a fixed BE)

$$\propto (\text{probability of emission from that BE}) \times (\text{Number of states at that BE})$$

$$\Rightarrow |M_{if}|^2 \cdot \text{DOS}$$

$|M_{if}|^2 =$ Transition probability of an electron from the initial state (i) to the final state (f).

If M_{if} is constant \Rightarrow Intensity \propto DOS



Playing around with transition probability: $|M_{if}|^2$

(1) Variation of $|M_{if}|^2$ with $h\nu$ for all levels.

$h\nu$	\longrightarrow	21	800eV
Cu 3d		7.5	0.03
O 2p		10.7	0.002
d/p	\sim	0.7	15.0

(2) Cooper Minimum

(3) Resonant photoemission



The spectral functions corresponding to photoemission and inverse photoemission and inverse photoemission are given by

$$I(\omega) = \sum_{i,j} \left| \langle \Psi_f^j(N-1) | a_i | \Psi_g(N) \rangle \right|^2 \delta(\omega - E_f^j(N-1) + E(N))$$

$$I(\omega) = \sum_{i,j} \left| \langle \Psi_f^j(N+1) | a_i | \Psi_g(N) \rangle \right|^2 \delta(\omega - E_f^j(N+1) + E(N))$$

Here $\Psi_g(N)$ corresponds to the ground state wavefunction of the N particle system, while Ψ_f^j correspond to the various (j) final state wavefunctions. The operators a_i (a_i) create (annihilate) an electron at the spin – orbital labelled i . If we have two different types of spin – orbitals, say d and p kinds as in TMO, we can construct I^{total}

$$I^d(\omega) = \sum_{i,j} \left| \langle \Psi_f^j(N-1_d) | a_i^d | \Psi_g(N) \rangle \right|^2 \delta(\omega - E_f^j(N-1) + E(N))$$

$$I^p(\omega) = \sum_{i,j} \left| \langle \Psi_f^j(N-1_p) | a_i^p | \Psi_g(N) \rangle \right|^2 \delta(\omega - E_f^j(N-1) + E(N))$$

With $I^{\text{total}}(\omega) = |M_d|^2 I^d(\omega) + |M_p|^2 I^p(\omega)$

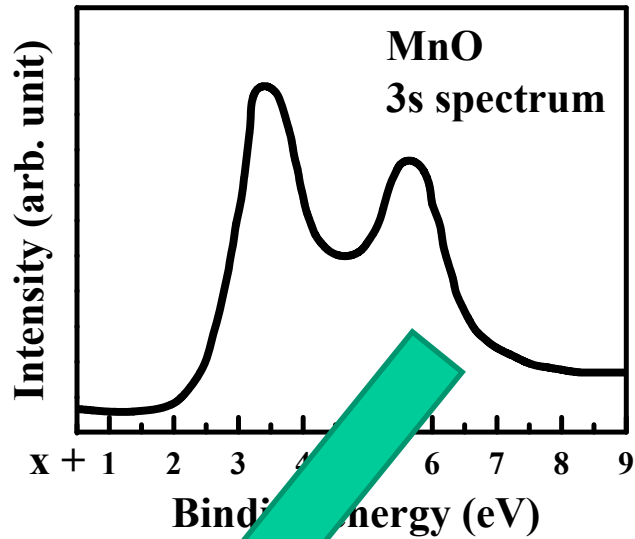


How do we probe magnetism?

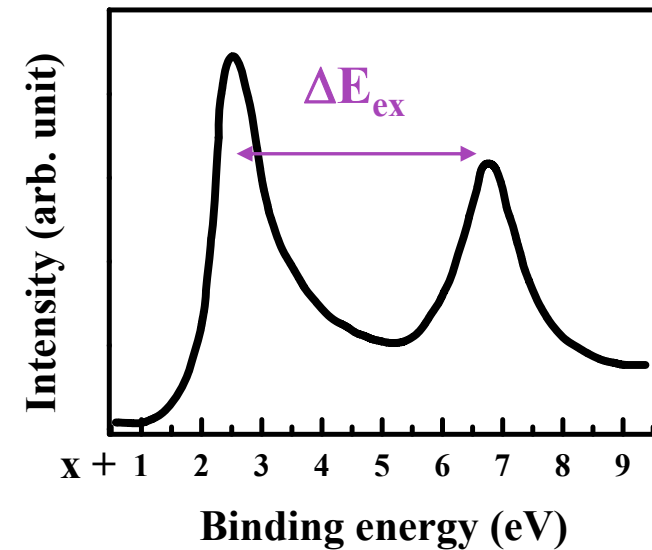
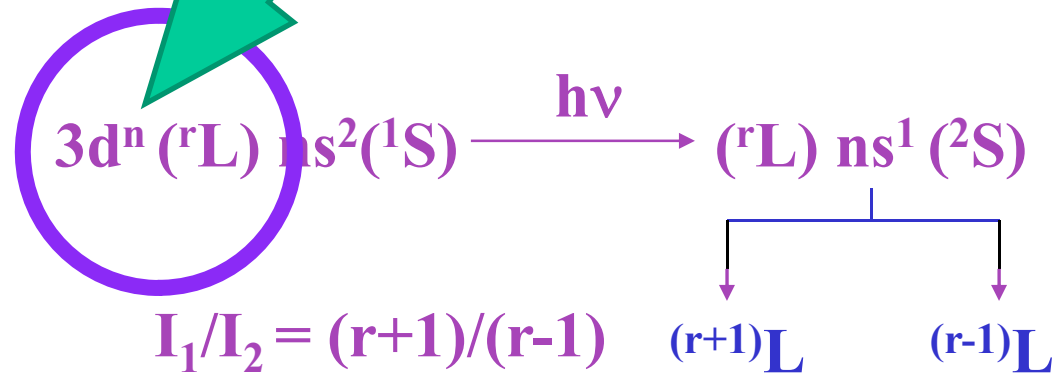
Two components to magnetism:

- **Moment formation** 
- **Long range ordering of moments**

But we already know:



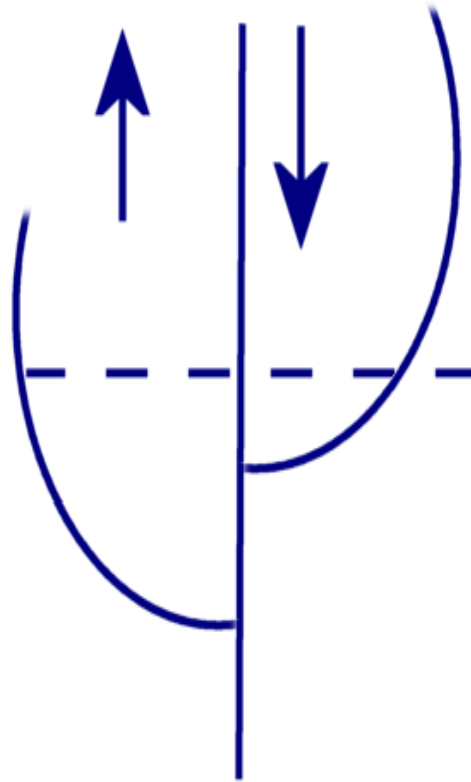
s-level shows splitting!



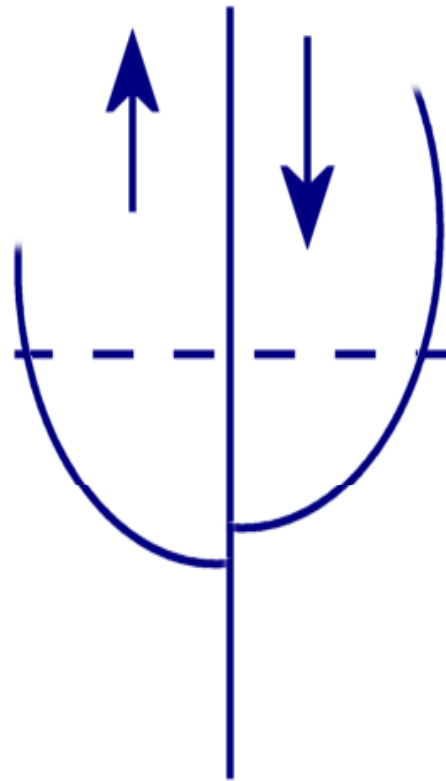
How do we probe magnetism?

Stoner Model

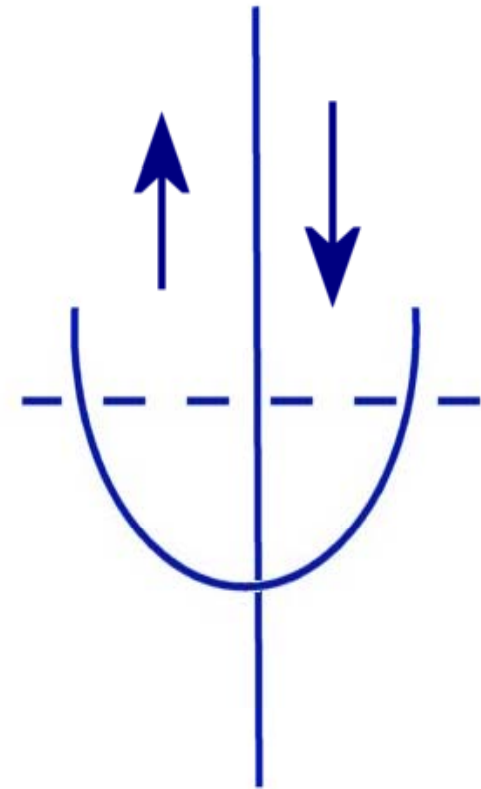
Ferromagnet



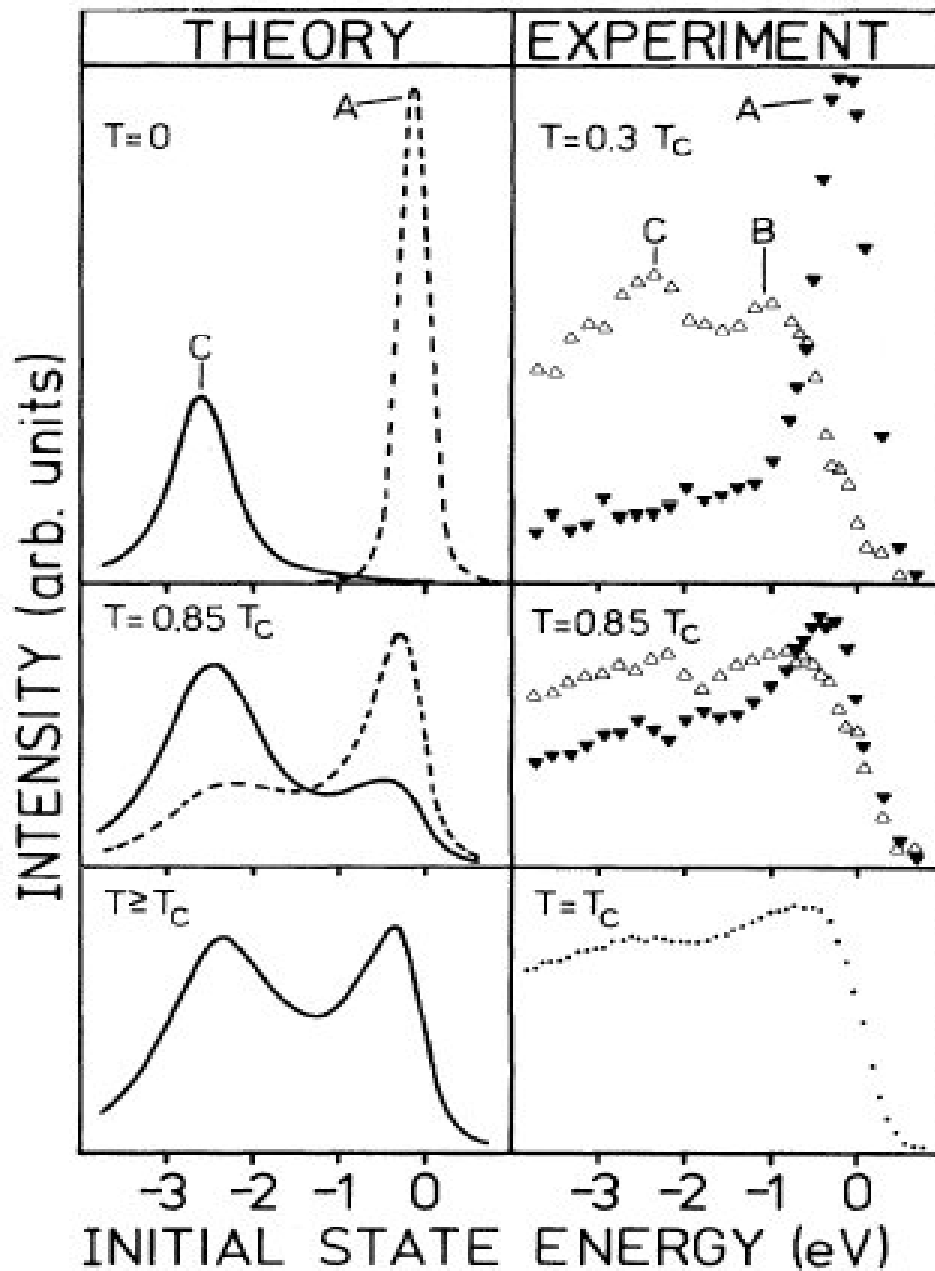
$$T \ll T_c$$



$$T < T_c$$



$$T \geq T_c$$



SPIN -POLARISED

$T/T_c =$

0.3

0.85

1.0

*E.M.Haines et.al, PRL,
54, 932 (1985)*



PROPERTIES OF SYNCHROTRON RADIATION:

- Continuously tunable energy
- High Intensities
- Highly collimated.
- Linearly polarised in plane.
- Elliptical /circular polarisation above and below.
- Small source size
- Well – defined time structure.

Each of these properties are useful to perform photoemission spectroscopy and to expect important information about electronic structure which otherwise would be impossible with conventional laboratory sources

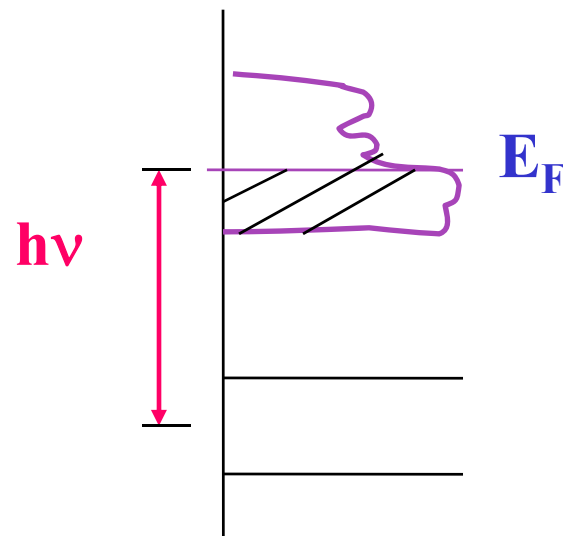


SYNCHROTRON LIGHT SOURCE:

- Tunability
- Polarisation
- High Intensity

Tunability: Gives Nature of the state.

- 1) Cross-section (σ) Dependence on Photon Energy ($h\nu$).
- 2) Selective Opening of Channels.



Polarization :

Gives symmetry information concerning a state

High Intensity:

**Allows for experiments otherwise difficult to perform.
(e.g. spin Resolved measurements).**

$h\nu$ Tunability + Angle –Resolved Technique:

Provides momentum information.



End of the first set

Thank you