

# Electronic structure of correlated electron systems : theory and experiment Lecture 1,2

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# Rough content of 5 lectures

- Lecture 1 and 2: Electronic structure of correlated and narrow band systems.
- Lecture 2 and 3: Electronic structure and theory of transition metal oxides (orbital, charge, spin and lattice degrees of freedom)
- Importance of non uniform polarizabilities  
Surfaces, interfaces of strongly correlated Oxides.
- Basic electronic structure and theoretical models of Fe Pnictides

# Content Lecture 1,2

- Electronic structure of correlated electron systems
  - Why are TM compounds and rare earths special
  - Quasi atomic vs band structure approaches
  - A bit about DFT, LDA+U, DMFT, Model H exact diagonalization
  - A bit about Auger and ARPES
  - Spectral weight transfer arguably the most direct evidence for strong correlation
  - Models and curiosity's

# Some Old Historical milestones

- 1929-1931 Bloch Wilson theory of solids
- 1937 De Boer and Verwey ( NiO-CoO breakdown of band theory)
- 1937 Peierls 3d electrons avoid each other ( basically the Hubbard model)
- 1950 Jonker van Zanten - Zener Pervoskites double exchange
- 1959 Anderson superexchange ( $U \gg W$ )
- 1964 Hubbard model-, Hohenberg Kohn DFT-Kohn Sham, Goodenough Transition metal compounds

Everyone claiming to work on real materials  
should be familiar with this

# Periodic Table of the Elements 2005

1 H 1.01																	18 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 25.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)							



58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

# Wide diversity of properties

- Metals:  $\text{CrO}_2$ ,  $\text{Fe}_3\text{O}_4$   $T > 120\text{K}$
- Insulators:  $\text{Cr}_2\text{O}_3$ ,  $\text{SrTiO}_3$ ,  $\text{CoO}$
- Semiconductors:  $\text{Cu}_2\text{O}$
- Semiconductor –metal:  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Ti}_4\text{O}_7$
- Superconductors:  $\text{La}(\text{Sr})_2\text{CuO}_4$ ,  $\text{LiTiO}_4$ , YBCO
- Piezo and Ferroelectric:  $\text{BaTiO}_3$
- Catalysts: Fe, Co, Ni Oxides
- Ferro and Ferri magnets:  $\text{CrO}_2$ ,  $\gamma\text{Fe}_2\text{O}_3$
- Antiferromagnets:  $\alpha\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{NiO}$  ---
- Ionic conductors (batteries)  $\text{Li}_x\text{Ni}_{1-x}\text{O}$
- Oxide fuel cells use Manganites and cobaltates

**Properties depend in detail on composition and structure**

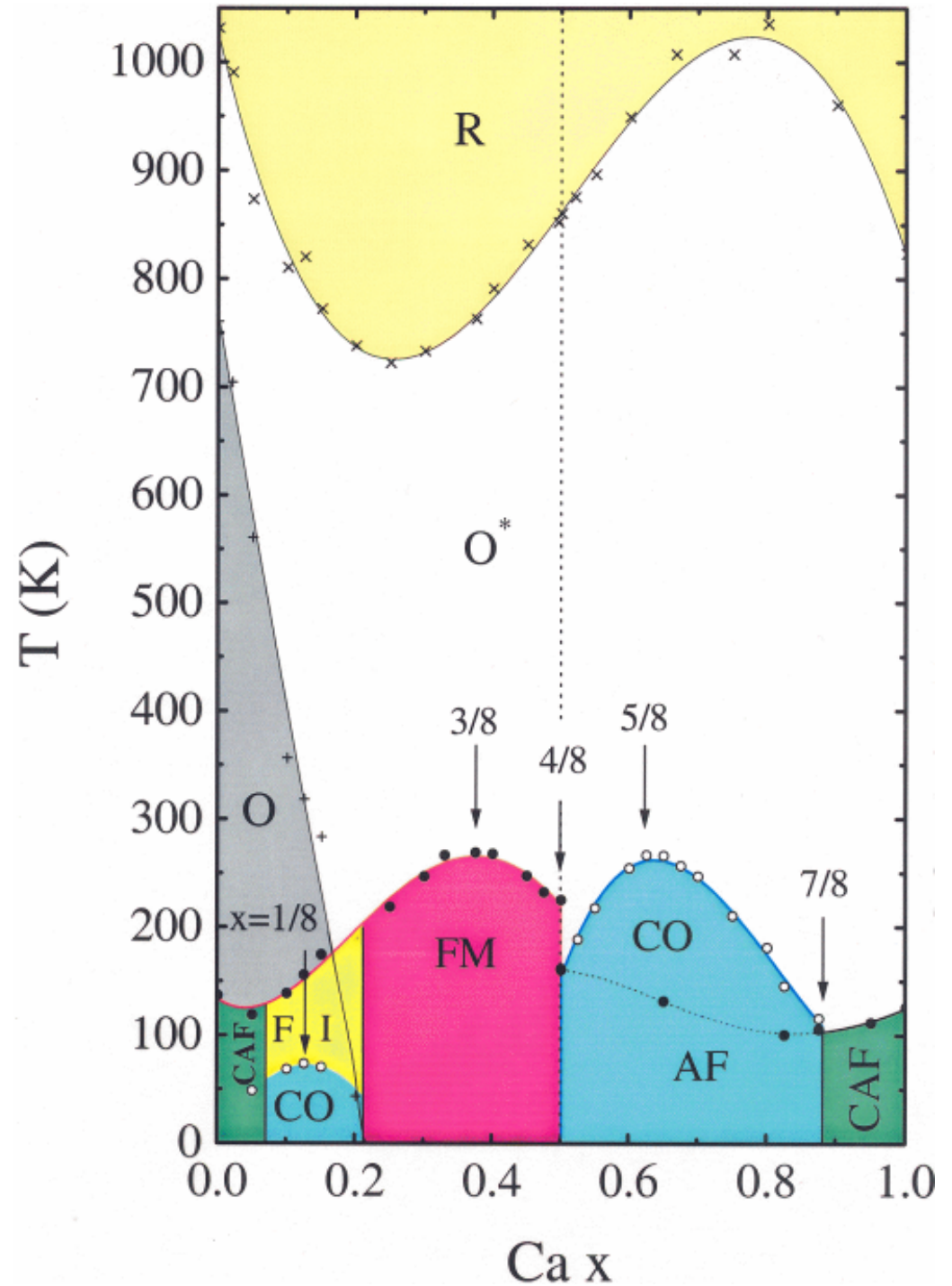
# Phase Diagram of $La_{1-x}Ca_xMnO_3$

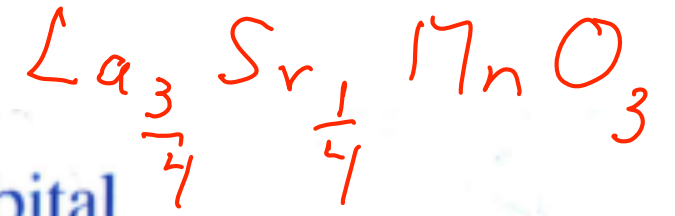
*Uehara, Kim and Cheong*

R: Rhombohedral

O: Orthorhombic  
(Jahn-Teller distorted)

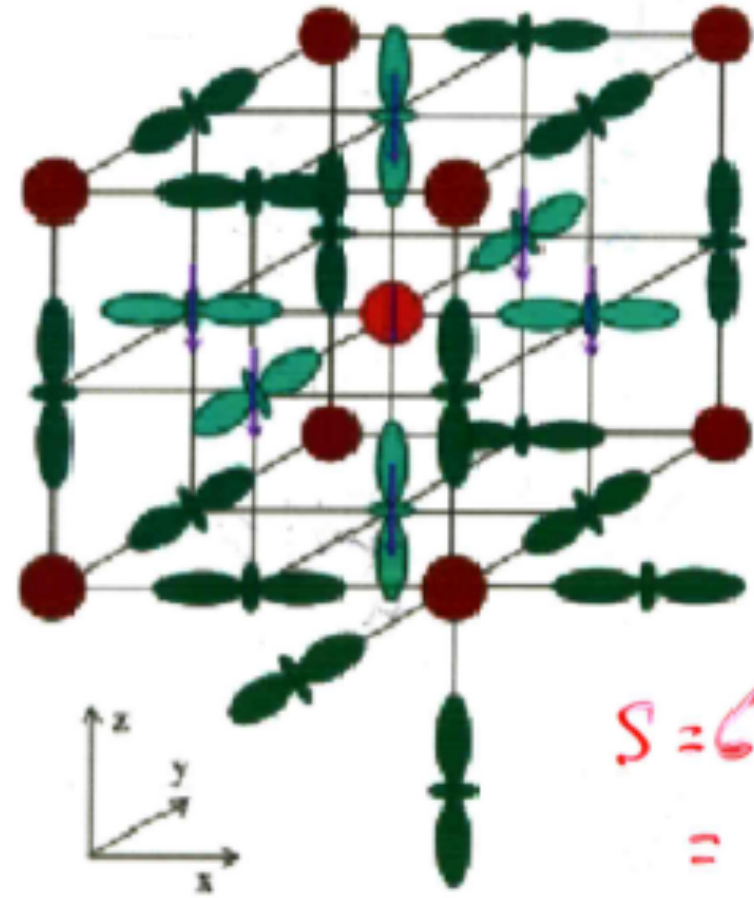
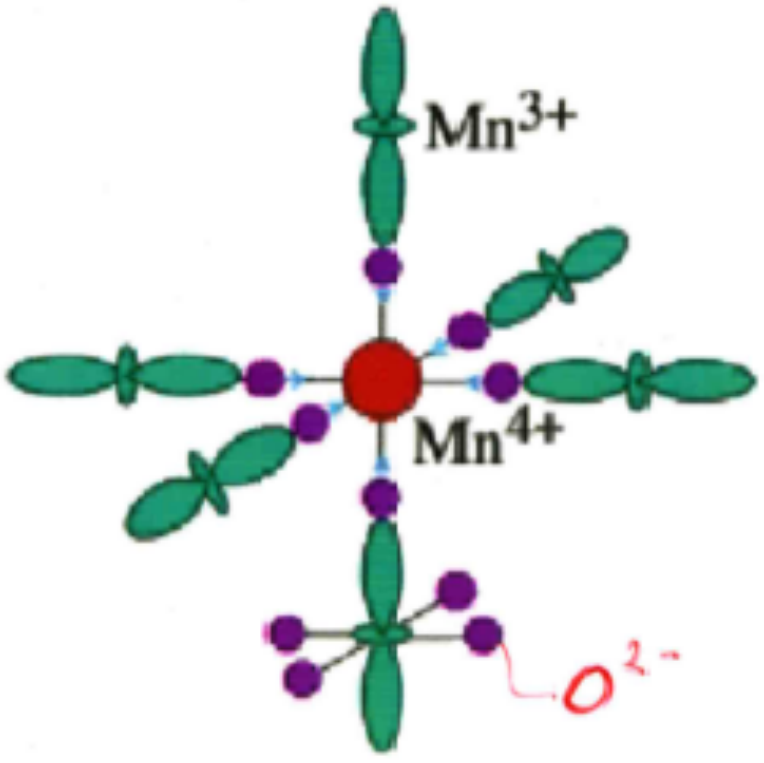
O\*: Orthorhombic  
(Octahedron rotated)





# Model for Charge, Spin and Orbital Correlations in Manganites

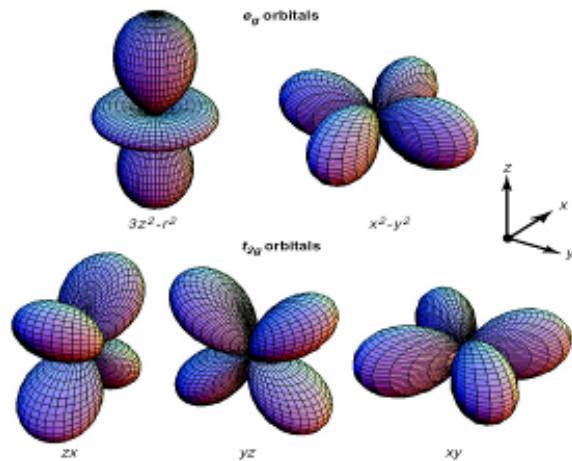
Mn<sup>4+</sup>, d<sup>3</sup>, S=3/2, No quadrupole; Mn<sup>3+</sup>, S=2, orbital degeneracy



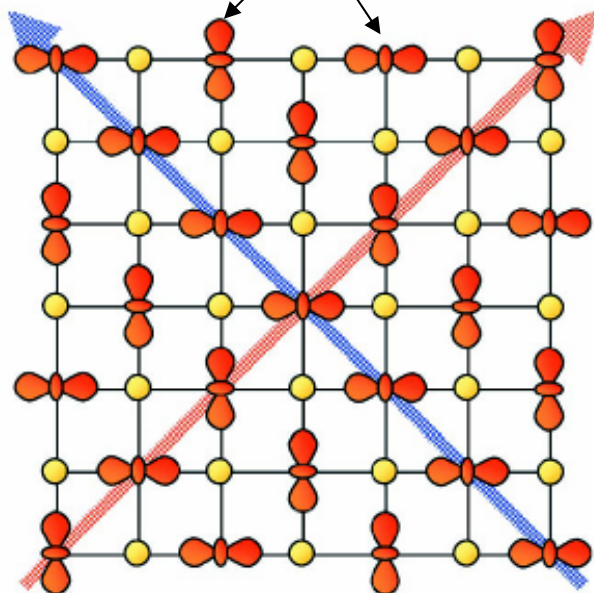
$S = 6 \times 2 + \frac{3}{2}$   
 $= \frac{27}{2}$



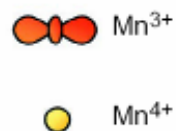
# Ordering in strongly correlated systems



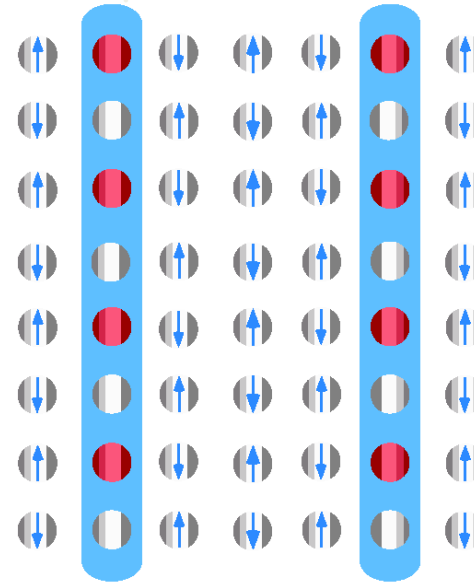
Quadrupole moment ordering



$DQ_c \sim 1 e$   
 $DQ_o \sim 0$



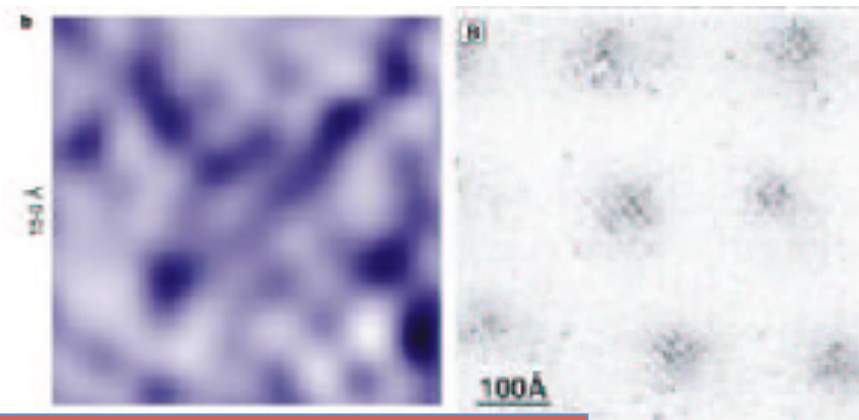
Stripes in Nd-LSCO



rivers of  
 Charge—  
 Antiferro/  
 Antiphase

$DQ < 0.5 e$

Charge inhomogeneity in Bi2212



Pan, *Nature*, **413**, 282 (2001);  
 Hoffman, *Science*, **295**, 466 (2002)

$DQ \sim 0.1 e$

It's the outermost valence electron states that determine the properties ; Both the occupied and unoccupied ones

# Two extremes for atomic valence states in solids

extreme Valence  
Two Types of states

Large overlap  $R \sim d$  - Large dispersion  $E(k)$   
 $\psi_A \sim \frac{1}{\sqrt{N}} e^{ik \cdot r}$  (free electr.)  $\rightarrow$  s, p valence.

Little overlap -  $R \ll d$  - Little dispersion  
 $\psi_A \sim \frac{1}{\sqrt{N}} \sum_i e^{ik \cdot R_i} \psi_d(r - R_i)$   
 (tight binding)  $\Rightarrow$  Correlated.  
 $\rightarrow$  Atomic like 3d, 4f states

## Where is the interesting physics?

### Coexistence-----Hybridization

Kondo, Mixed valent, Valence fluctuation, local moments, Semicond.-metal transitions, Heavy Fermions, High Tc's, Colossal magneto resistance, Spin trionics, orbitronics

# Characteristics of solids with 2 extreme valence orbitals

## $R \gg D$

- electrons lose atomic identity
- Form broad bands
- Small electron electron interactions
- Low energy scale –charge fluctuations
- Non or weakly magnetic
- Examples Al, Mg, Zn, Si

## $R \ll D$

- Valence Electrons remain atomic
- Narrow bands
- Large electron electron interactions (on site)
- Low energy scale-spin fluctuations
- Magnetic (Hunds' rule)
- Gd, CuO, SmCo<sub>3</sub>

Many solids have coexisting  $R \gg D$  and  $R \ll D$  valence orbitals i.e. rare earth 4f and 5d, CuO Cu 3d and O 2p, Heavy Fermions, Kondo, High T<sub>c,s</sub>, met-insul. transitions

## Why are the valence 3d and 4f orbitals in transition metal and rare earth compounds special

- Lowest principle q.n. for that  $l$  value
- Large centrifugal barrier  $l=2,3$
- Small radial extent, no radial nodes, orthogonal to all other core orbital's via angular nodes (snuggle up to the nucleus)
- High kinetic energy ( angular nodes) compensates for the strong potential energy
- Relativistic effects
- Look like core orb. But have high energy and form open shells like valence orb.

Why does  $E_{nl}$  depend on  $l$ ?

Atomic - hydrogenic

$$E_n^0 = \frac{mZ^2e^4}{2\hbar^2 n^2}$$

$n$  = principle q. n

$l$  comes in relativistic effects

$$E = \sqrt{p^2c^2 + m^2c^4} \approx mc^2 + \frac{p^2}{2m} + \frac{1}{8} \frac{(p^2)^2}{m^3c^2}$$

From  $\langle p^2 \rangle \propto (E_n^0 + Ze^2 \langle \frac{1}{r} \rangle)$  mass velocity

$$\Delta E = -\frac{1}{2mc^2} \left( (E_n^0)^2 + 2E_n^0 Ze^2 \langle \frac{1}{r} \rangle + Ze^4 \langle \frac{1}{r^2} \rangle \right)$$

$\langle \frac{1}{r} \rangle$  independent of  $l = \frac{Z}{a_0 n^2}$

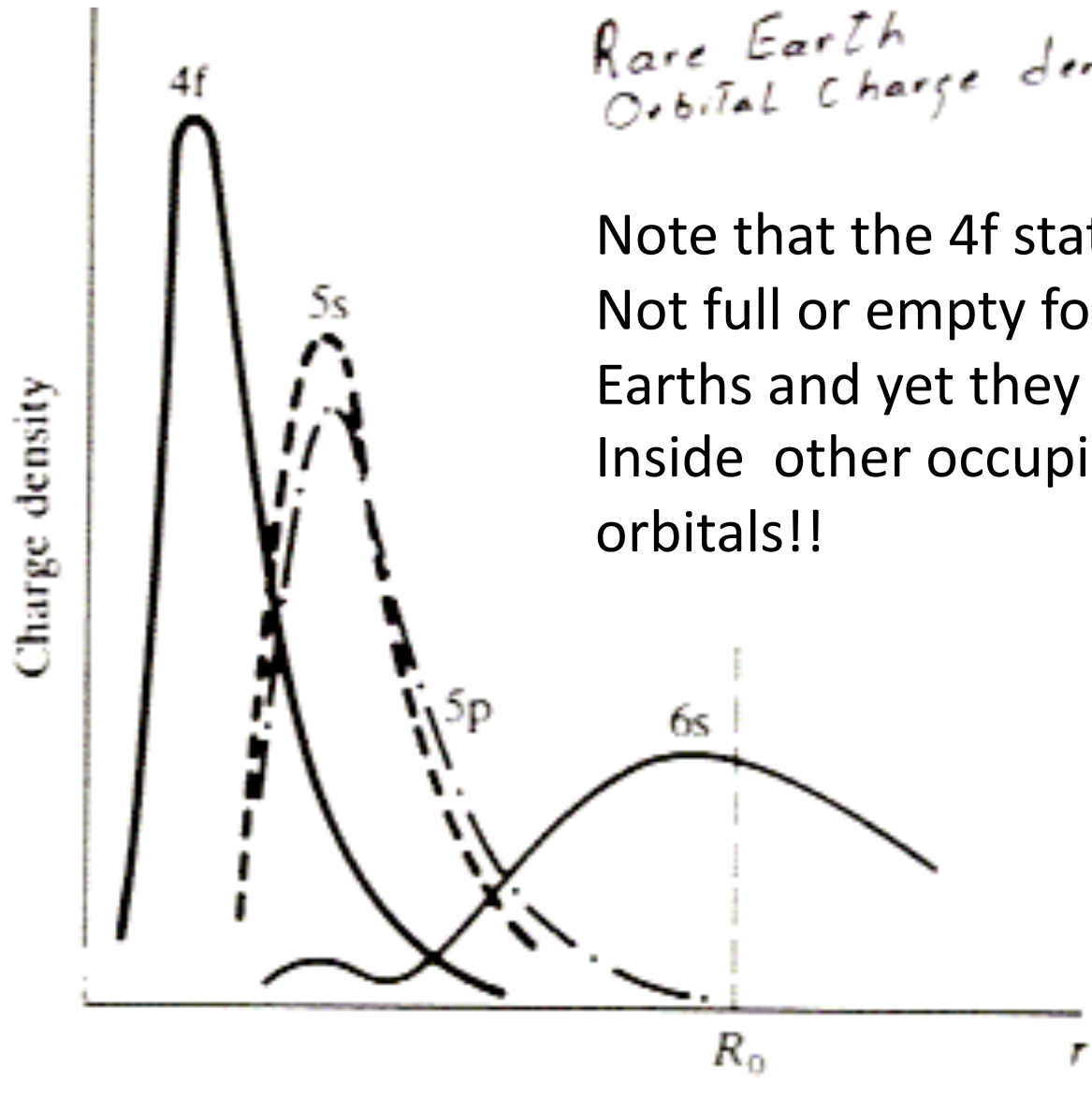
$\langle \frac{1}{r^2} \rangle_{nl} = \frac{Z^2}{a_0^2 n^3 (l+1/2)}$   $a_0$  = Bohr radius

$$\Delta E_{nlm} = \frac{(Za_0)^2}{n^2} \left( \frac{n}{l+1/2} - \frac{3}{4} \right) E_n^0 \left[ \left( \alpha Z \frac{e^2}{\hbar c} \right) \right]$$

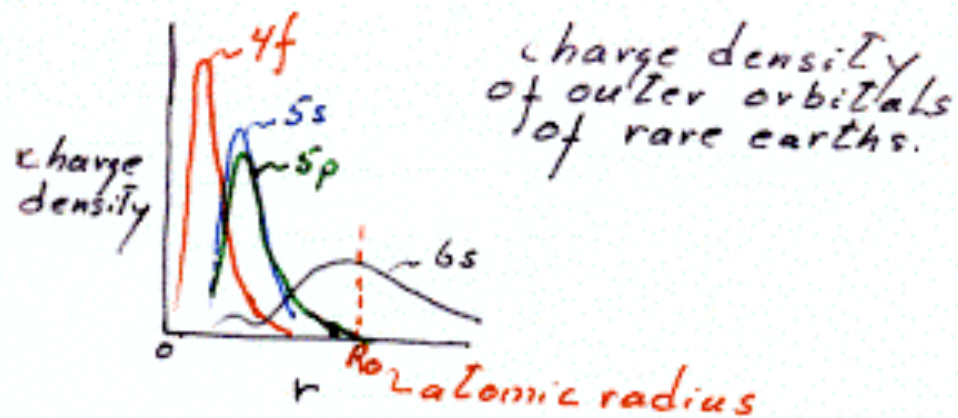
For 3d (Cu) 3s energy  $\sim 120$  eV  
                   3p           "        $\sim 70$  eV  
                   3d           "        $\sim 10$  eV

$E_{nl}$  can be larger than  $E_{n+1,0}$   
 if we include larger Coulomb repulsion

## Special place for transition metal and rare earths



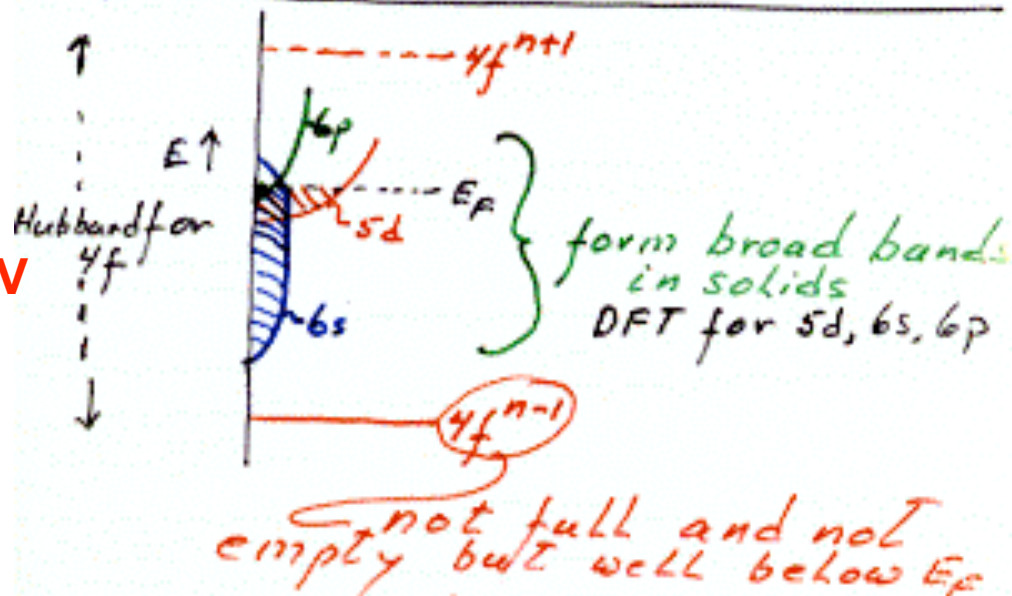
Note that the 4f states are  
Not full or empty for the rare  
Earths and yet they are well  
Inside other occupied  
orbitals!!



Elemental configuration  
 $4f^{(n)} 5s^2 5p^6 6s^2 5d^1$   
 <14 (open) but atomic

We will see later how to model this

Hubbard  
 For 4f U as  
 large as 12eV





# Band Structure approach vs atomic

## Band structure

- Delocalized Bloch states
- Fill up states with electrons starting from the lowest energy
- No correlation in the wave function describing the system of many electrons
- Atomic physics is there only on a mean field like level
- Single Slater determinant states

## Atomic

- Local atomic coulomb and exchange integrals are central
- Hund's rules for the Ground state -Maximize total spin-  
Maximize total angular momentum-total angular momentum  $J = L - S$  for  $< 1/2$  filled shell ,  $J = L + S$  for  $> 1/2$  filled shell
- Mostly magnetic ground states

# Band theory - DF

$$\Psi = \frac{1}{\sqrt{n!}} |\phi_{k_1} \dots \phi_{k_n}| \quad (\text{Slater det.})$$

$\phi_{k_i}$  are one electron Bloch states

No correlation in  $\Psi$  but in  $\mathcal{H}_{\text{eff}}$

$$\left[ -\frac{1}{2} \nabla^2 + W(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

2 one particle problem

$$V_{\text{H}} = \int d^3r' V(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}')$$

$$V_{\text{xc}} = f(\rho(\mathbf{r})) \quad \rho(\mathbf{r}) = \sum_{i=1}^n |\phi_i(\mathbf{r})|^2$$

$$\mathcal{E}_{\text{xc}} = \frac{\delta E_{\text{xc}}(\rho)}{\delta \rho} \quad \text{exchange-correlation potential}$$

Hohenberg Kohn exact for  $E_0 \rightarrow \rho$  (ground state)

$\phi_i$  &  $\epsilon_i$  have no physical meaning!!  
math. functions to get  $\bar{E}$  &  $\rho$ .

Single Slater det. Of One electron Bloch States. No correlation In the wave function

Recall that the ground State has few properties It is the excited states that Determine the response to External perturbations such as fields.

$\bar{\Psi}^{DF}$  also has no physical significance

$E_g$  is exact  $\phi_g(r)$  is exact but

$$\mathcal{H}_{\text{exact}} \bar{\Psi}^{DF} \neq E_g \bar{\Psi}^{DF}$$

$$\mathcal{H}_{\text{exact}} = \sum_{i=1}^n \left[ -\frac{1}{2} \nabla_i^2 + W(r_i) + \frac{1}{2} \sum_{\substack{j \\ j \neq i}} \frac{e^2}{|r_i - r_j|} \right]$$

→ nuclear electronic

in  $\bar{\Psi}_g$   $\phi_i$  have  $\hbar$  as good g.m.

( $\mathcal{H}_{\text{eff}}^{DF}$  has transl. symm.)

$$\mathcal{H}_{\text{eff}}^{DF} \bar{\Psi}_g = E_g \bar{\Psi}_g$$

The terms  $\frac{e^2}{|r_i - r_j|}$  will always have  
matrix elements scattering

$k_L, k'_L \rightarrow k'_R, k''_R$  i.e. from below to above  $k_F$

e.g.  $\phi_k = \frac{1}{\sqrt{N}} \sum_i \phi(r - R_i) e^{ik \cdot R_i}$  [tight binding]

For  ~~$A \ll d$~~   $A \ll d$   $\langle \frac{e^2}{|r_i - r_j|} \rangle$  will

dominate for two electrons on one  
site.  $\langle \frac{e^2}{|r_i - r_j|} \rangle = U$

Interaction between two Bloch wave electrons =  $U/N \sim 0$   
So is correlation negligible?

$$\langle \bar{\Psi} | \mathcal{H}_{int} | \bar{\Psi}_{\substack{A \rightarrow A_i \\ k_1 \rightarrow k_i}} \rangle = \frac{1}{N} U \delta(k_1 + k_2 - k_i - A_i)$$

$\rightarrow 0$  for  $N \rightarrow \infty$

Small if  $U \ll W$  or  $E_F$  so only few electrons are involved

For  $U \gg W$  must sum over all other electrons  $\rightarrow \frac{n}{N} U$  or for  $n \sim N \rightarrow U$

$\therefore$  off diagonal matrix elements

are large  $\bar{\Psi}^{DF}$  is not an eig. fund.

For  $R \ll d$   $1/2$  filled s band  
if we neglect  $W$  (Transl. symm.)

$$\bar{\Psi}_A = \frac{1}{\sqrt{N}} | \phi_1 \phi_2 \dots \phi_n |$$

one electr./atom

Surely a lattice of H atoms separated by say 1 cm would not behave like a metal

What have we forgotten ?

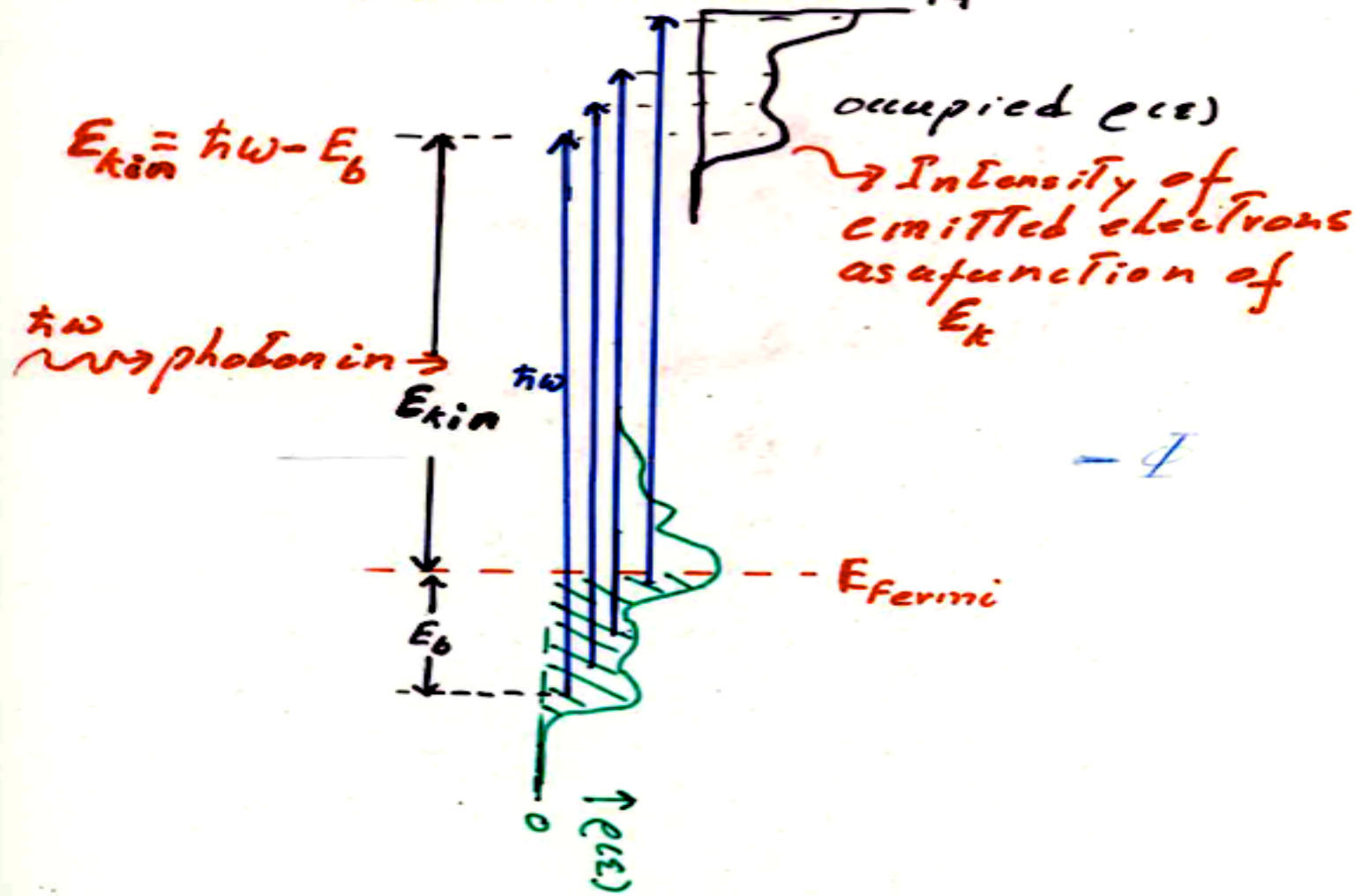
The electron electron repulsive  
interaction

Experimental evidence for atomic  
like behaviour in transition metal  
compounds and rare earths  
Photoemission/inverse  
photoemission and Auger  
spectroscopy

# PES (Photoelectron Spectr.)

involves low  $\hbar\omega \rightarrow$  valence electrons

consider a metal  $\Psi$



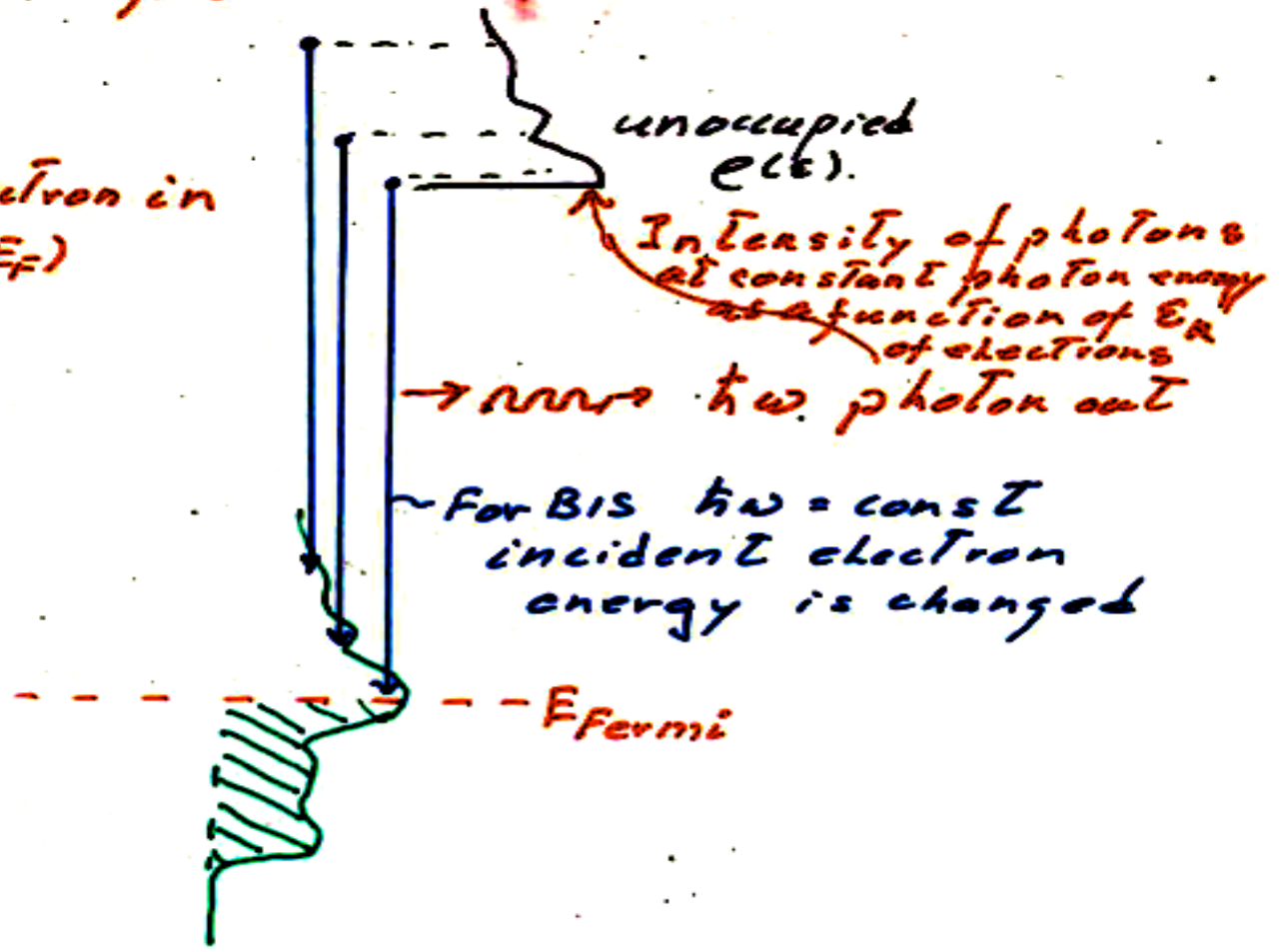
Measure density of states for electron removal  $\times$  Matrix element



(Inverse PES) IPES / BIS (Bremsstrahlung isochromat Spectr.)  
 involves conduction band states

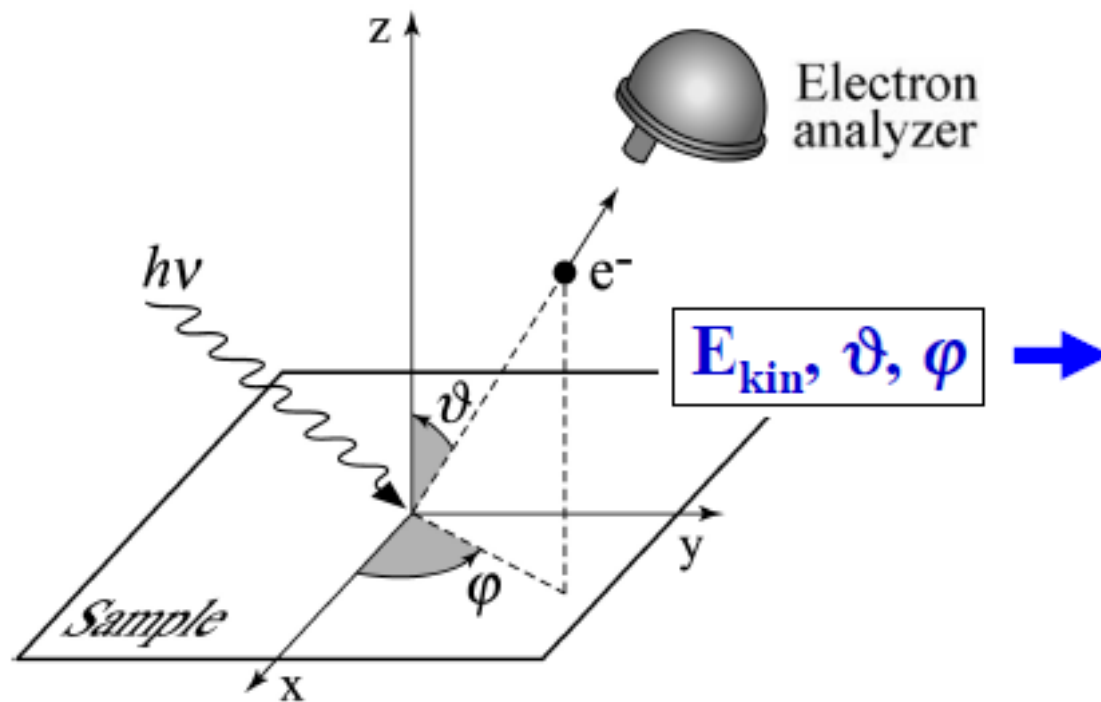
Measure  $I(\hbar\omega)$  as a function of  $E_R$   
 fixed

$E_R \rightarrow$  electron in  
 (relative to  $E_F$ )



Measures  $\rho(e)$  for electron addition

# High resolution angular resolved photoelectron spectroscopy



$$\mathbf{K} = \mathbf{p} / \hbar = \sqrt{2mE_{kin}} / \hbar$$

$$K_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \cos \varphi$$

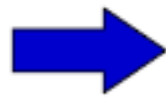
$$K_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \sin \varphi$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \vartheta$$

Vacuum

$$E_{kin}$$

$$\mathbf{K}$$



Conservation laws

$$E_f - E_i = h\nu$$

$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$



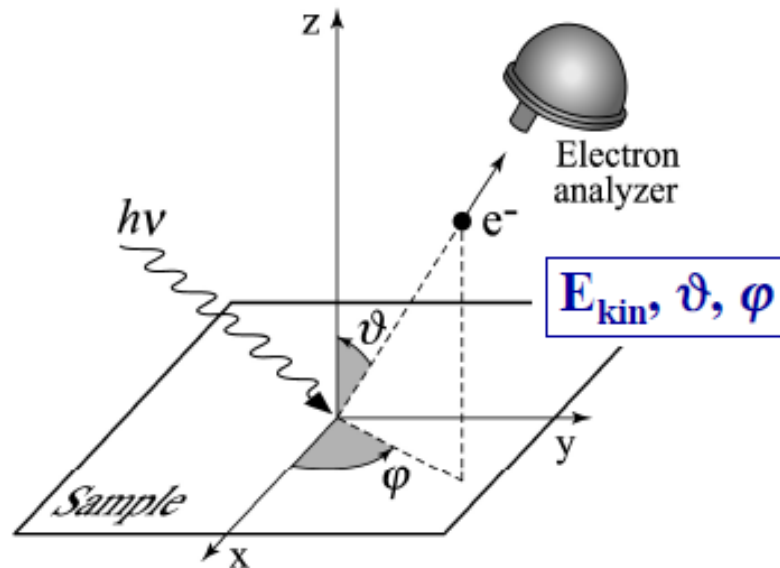
Solid

$$E_B$$

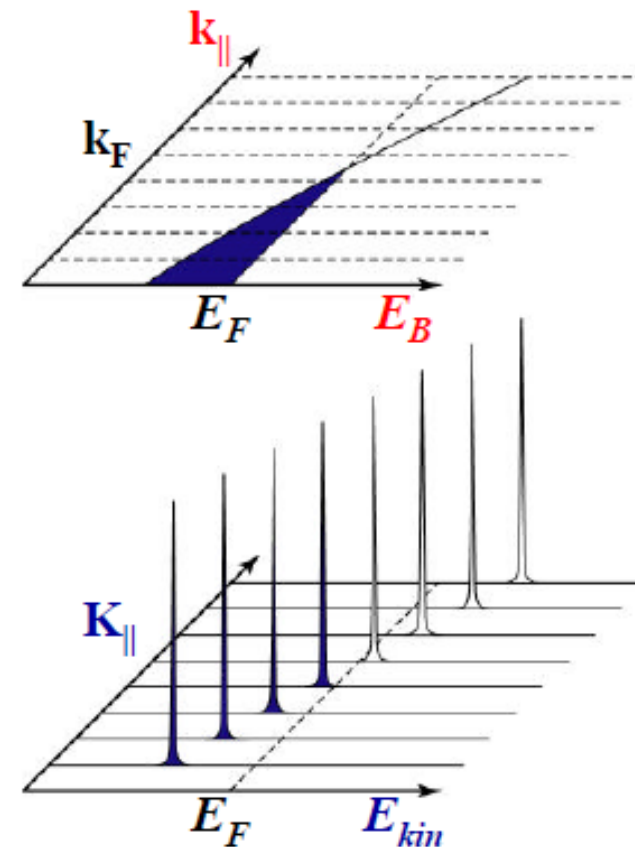
$$\mathbf{k}$$

## Example of a simple metal in one electron theory

### ARPES: Energetics and Kinematics



### Electrons in Reciprocal Space



Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

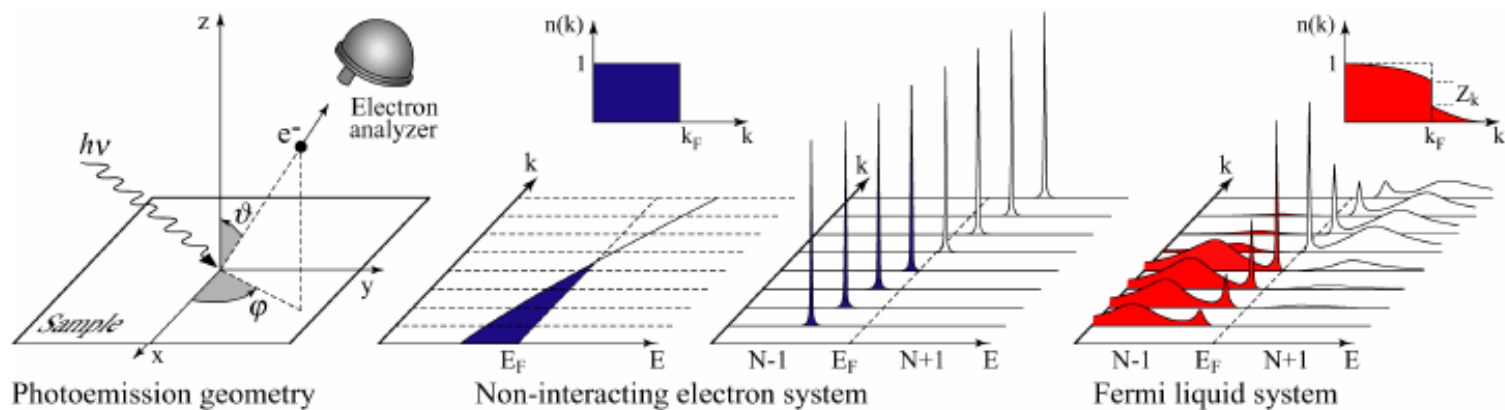
Momentum Conservation

$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2m E_{kin}} \cdot \sin \vartheta$$

# Example of a metal in which electrons are dressed

## ARPES: The One-Particle Spectral Function

A. Damascelli, Z. Hussain, Z.-X Shen, Rev. Mod. Phys. 75, 473 (2003)



**Photoemission intensity:**  $I(k, \omega) = I_0 |M(k, \omega)|^2 f(\omega) A(k, \omega)$

### Single-particle spectral function

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \frac{\Sigma''(\mathbf{k}, \omega)}{[\omega - \epsilon_{\mathbf{k}} - \Sigma'(\mathbf{k}, \omega)]^2 + [\Sigma''(\mathbf{k}, \omega)]^2}$$

$\Sigma(\mathbf{k}, \omega)$  : the “self-energy” captures the effects of interactions

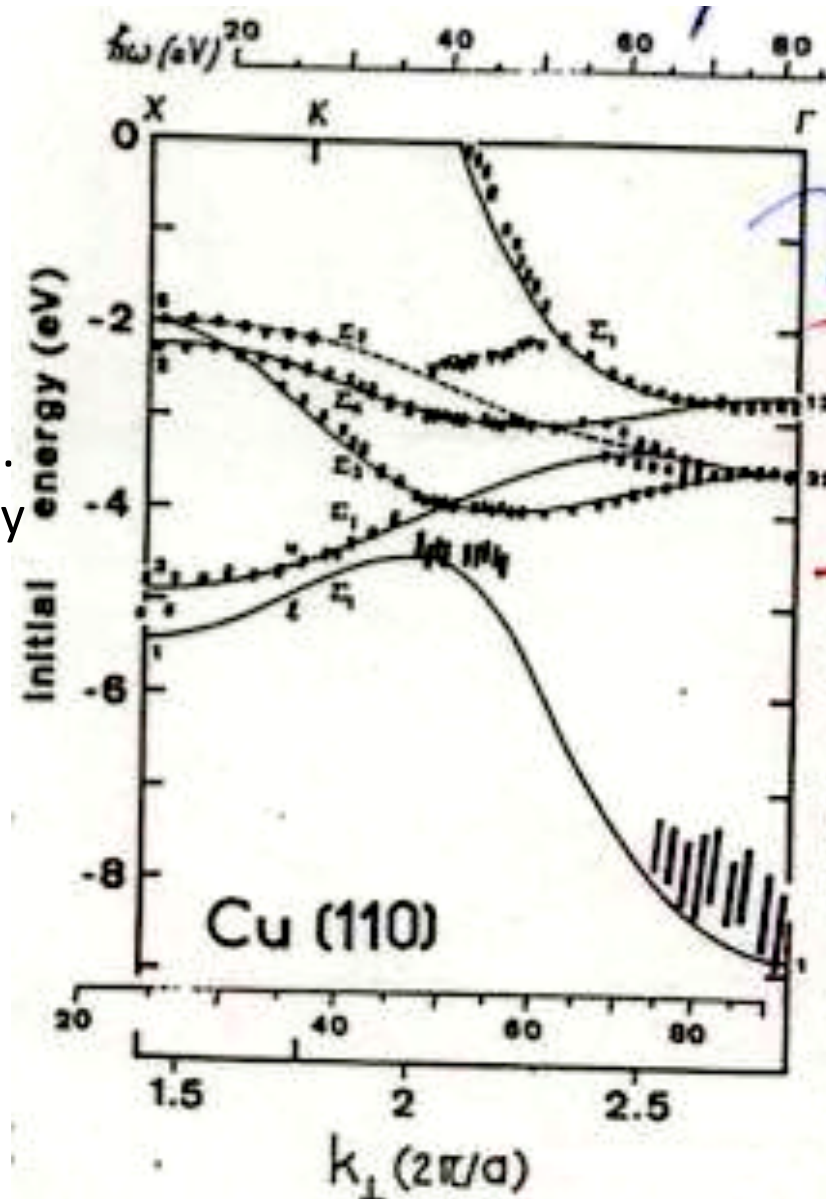
# Angular resolved photoelectron spectroscopy (ARPES) of Cu metal

Thiry et al 1979

## ARPES Cu

Cu is d10 so one d hole  
Has no other d holes to  
Correlate with so 1 part.  
Theory works if the only  
Important interaction is  
The d-d interaction.

Great agreement with  
DFT



Points - exp.  
Lines - DFT

3d bands

4s,4p,band

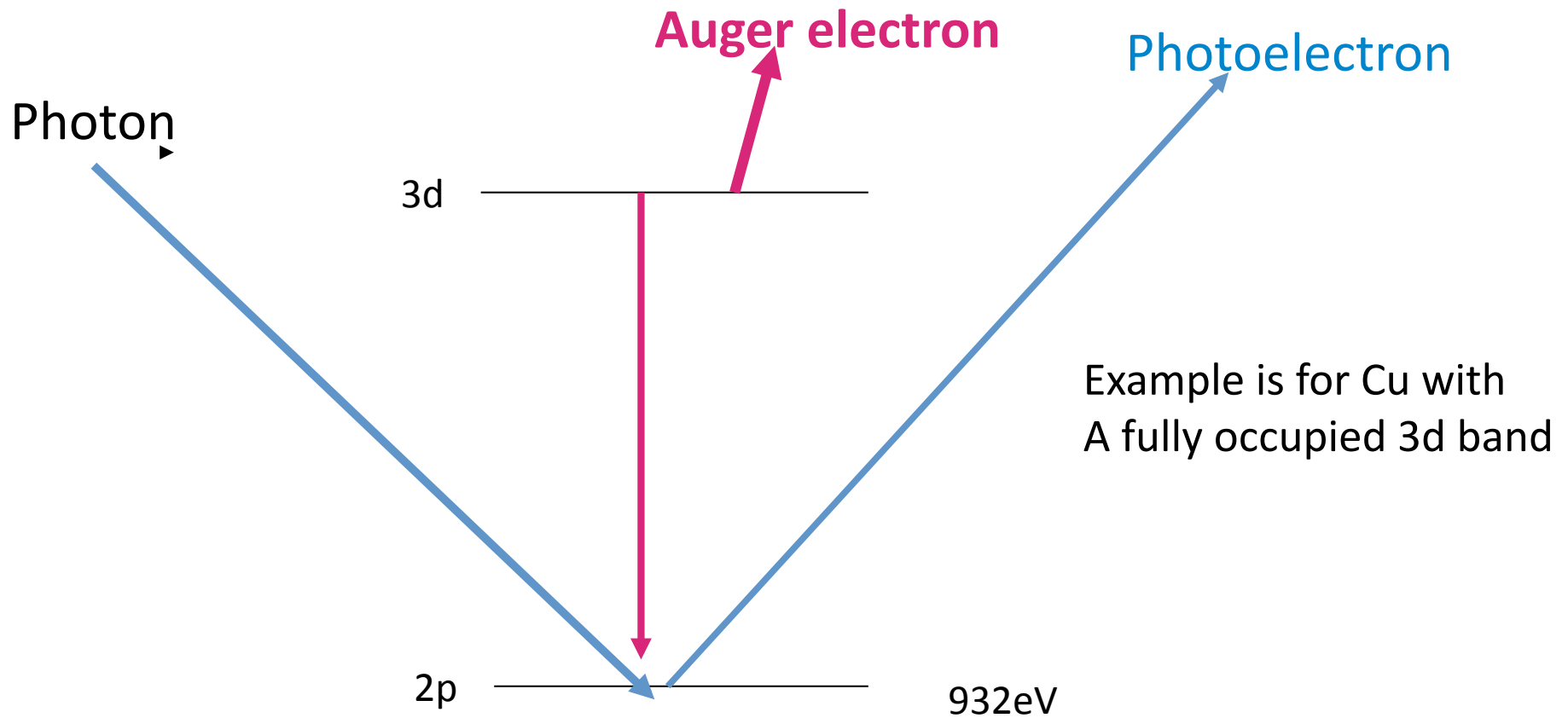
We note that for Cu metal with a full 3d band in the ground state one particle theory works well to describe the one electron removal spectrum as in photoelectron spectroscopy this is because a single d hole has no other d holes to correlated with. So even if the on site d-d coulomb repulsion is very large there is no phase space for correlation.

The strength of the d-d coulomb interaction is evident if we look at the Auger spectrum which probes the states of the system if two electrons are removed from the same atom

If the d band had not been full as in Ni metal we would have noticed the effect of d-d coulomb interaction already in the photoemission spectrum as we will see.

# What if we remove 2- d electrons ?

## Two hole state with Auger spectroscopy

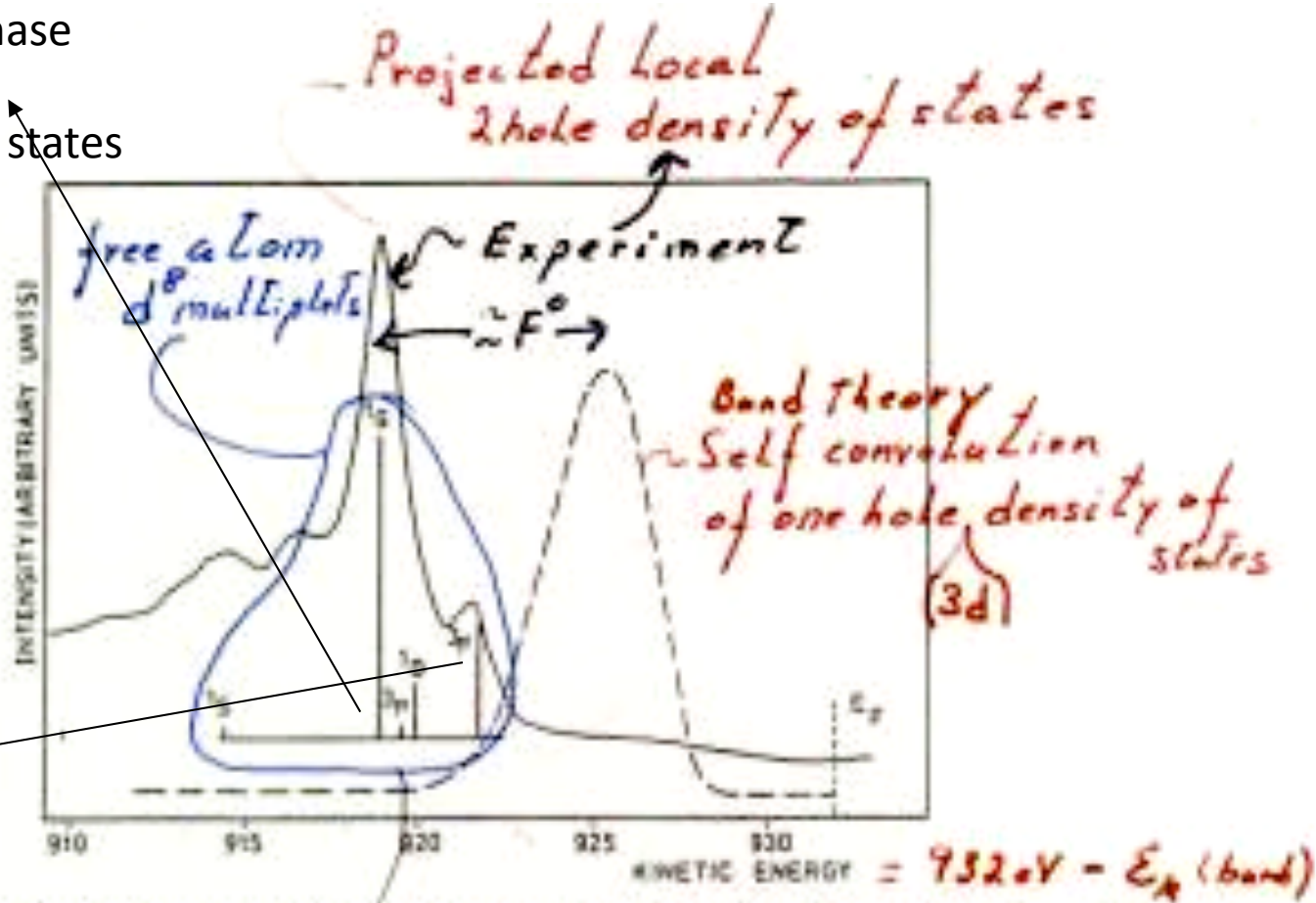


$$E(\text{photon}) - E(\text{photoelectr}) = E(2p) , \quad E(2\text{-d holes}) = E(2p) - E(3d) - E(\text{Auger})$$

$$U = E(2\text{-d holes}) - 2 \times E(1\text{-d hole})$$

# Auger spectroscopy of Cu metal

Atomic multiplets  
 Looks like gas phase  
 $U > W$   
 Two hole bound states



Hund's rule  
 Triplet F is  
 Lowest

The L3M45M45 Auger spectrum of Cu metal i.e final state has 2 -3d holes on the Atom that started with a 2p hole. Solid line is the experiment. Dashed line is one Electron DFT theory, vertical bars and lables are the free atom multiplets for 8- 3d electrons on a Cu atom . E<sub>f</sub> designates the postion of the Fermi level in the DFT .



## Two particles in Hubbard (s band)

$$\begin{aligned} \mathcal{H} &= t \sum_{R,S,\sigma} C_{R+S,\sigma}^\dagger C_{R,\sigma} + U \sum_R C_{R\uparrow}^\dagger C_{R\uparrow} C_{R\downarrow}^\dagger C_{R\downarrow} \\ &= \sum_{k\sigma} \epsilon_k C_{k\sigma}^\dagger C_{k\sigma} + \frac{U}{N} \sum_{k\uparrow\downarrow} C_{k\uparrow}^\dagger C_{k\uparrow} C_{k\downarrow}^\dagger C_{k\downarrow} \end{aligned}$$

Momentum + Spin conservation

$$[H, K] = 0 \quad [H, S] = 0$$

$K$  = Total momentum       $S = 0$  or  $1$

For  $G_{\gamma+\kappa, \gamma\downarrow}^{\uparrow\kappa, \downarrow\downarrow} = \langle 0 | C_{\kappa, \uparrow} C_{\kappa, \uparrow}^\dagger G(\omega) C_{\gamma, \uparrow}^\dagger C_{\kappa+\gamma, \downarrow} | 0 \rangle$

contains both singlet + Triplet

Triplet - soln. - self convolution of 1 part.  
density of states  
 $\hookrightarrow U$  is not active

$$G = (\delta_{k\gamma} - \delta_{\kappa, \gamma}) \frac{1}{z - \epsilon_k - \epsilon_{\kappa-k}}$$

Dyson  $G = G_0 + G_0 M_1 G$ ;  $G = \frac{1}{z - M}$

$$G_0 = \frac{1}{z - M_0}$$

$$G_{g \uparrow k \uparrow g \downarrow}^{k \uparrow k \downarrow} = \int_{k_1} \frac{1}{z - \epsilon_{k_1} - \epsilon_{k-k_1}} = \int_{k_1} G_0(k, k-k; z)$$

$$G_{g \uparrow k \uparrow g \downarrow}^{k \uparrow k \downarrow} = \int_{k_1} G_0(k, k-g) + G_0(k, k-A) \frac{U}{N} \sum_{g'} G_{g \uparrow k \uparrow g \downarrow}^{k \uparrow k \downarrow}$$

$$\sum_k = G_0(g, k-g) + \sum_k G_0(k, k-A) \frac{U}{N} \sum_k$$

$$\sum_k G_{g \uparrow k \uparrow g \downarrow}^{k \uparrow k \downarrow} = \frac{G_0(g, k-g)}{1 - \frac{U}{N} \sum_k G_0(k, k-A)}$$

Ladder approximation  
Is exact for only two particles

Zero's on real axis provide singlet energies

$$\text{Re} \sum_k G_0(k, k-A; \omega_s) = \frac{N}{U}$$

For  $U \gg W$  (band width)

Two sets of poles

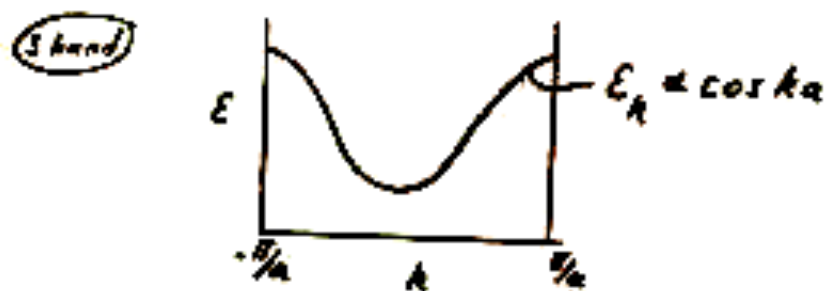
- Centered around self convolution of one particle energy's  $\rightarrow N(N-1)$  states
- Centered close to  $U$  with little dispersion  $\rightarrow N$  states

for  $W \gg U$  one electron theory

for  $W \ll U$  strong correlation

For strong correlation energy levels depend on the number of electrons

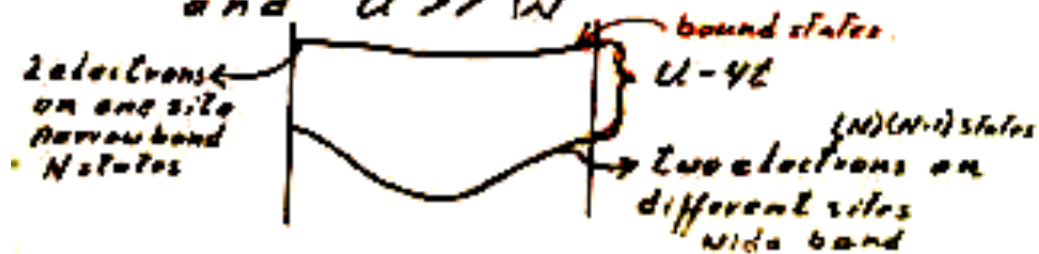
For 1 electron  $M_s = 0$



For 2 spin parallel electrons same as for 1 electron

For 2 spin antiparallel electrons

and  $U \gg W$

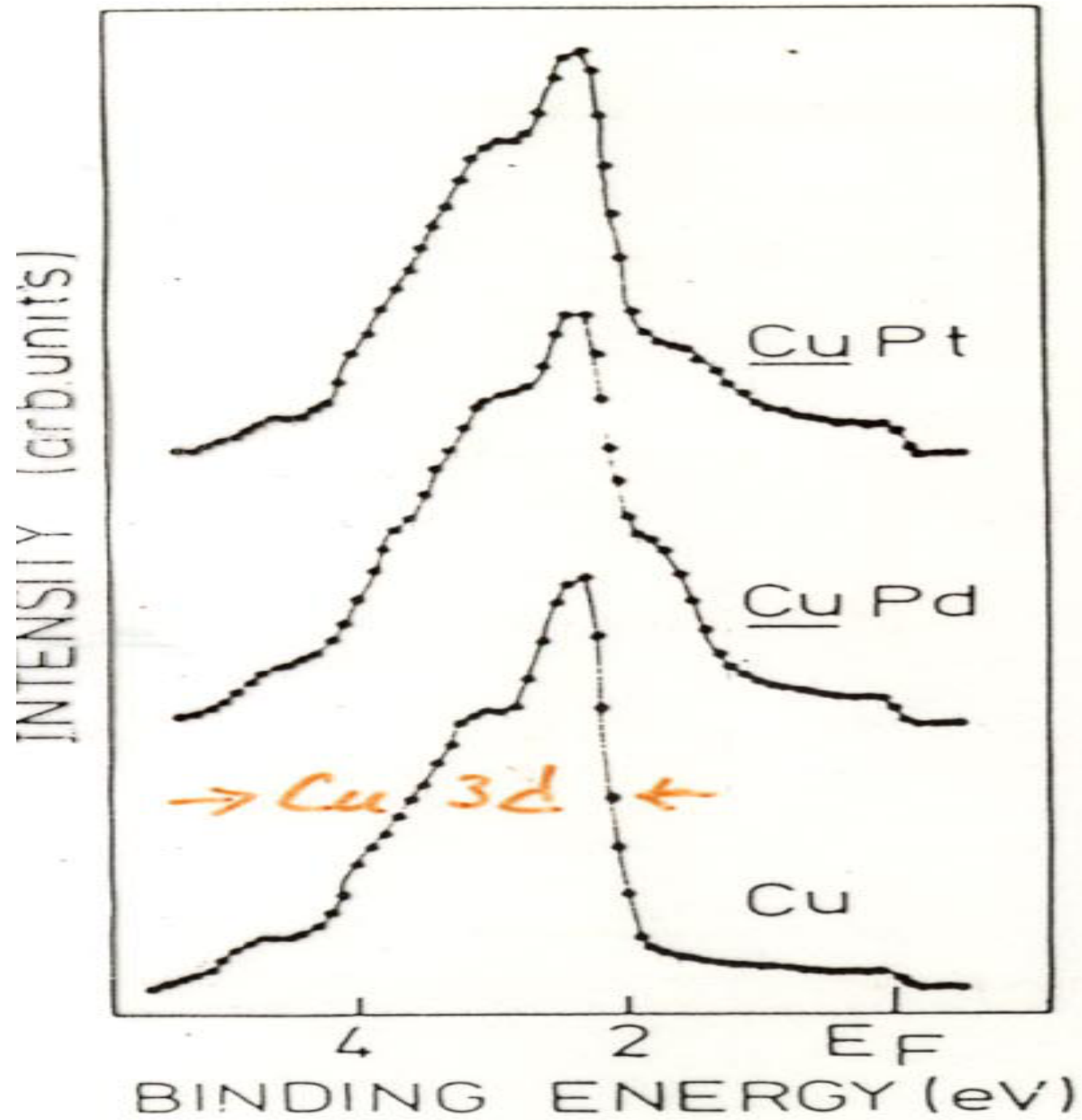


# D shells are complicated by multiplet structure

- Atomic physics – d orbital is 5 fold degenerate not including the spin and neglecting the spin orbit coupling .
- Two d electrons or holes with orbital angular momentum =2 and spin of  $\frac{1}{2}$  can couple into total angular momentum states L with total spin 1 or 0 as follows ; singlet S, singlet G, singlet D and triplet P and triplet F
- The energy separations in the Cu Auger spectrum are from atomic coulomb integrals with triplet F as the lowest energy state for 8 d electrons as given by Hunds' rule

For  $U \gg W$  and in the presence of unfilled bands the one particle removal spectrum will be very different from that of a filled band

Compare the PES of Cu metal with a full d band to that of Ni with on the average 0.6 holes in the 3d band

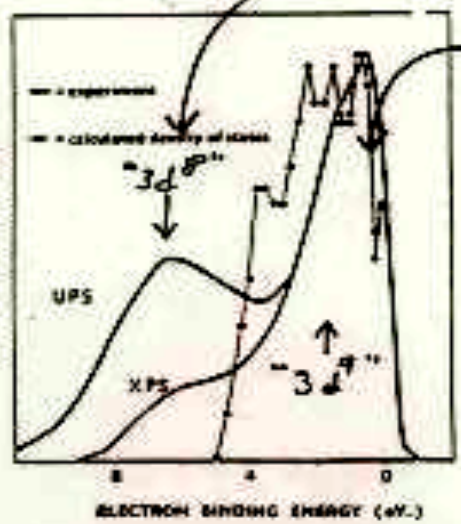


Cu ( $\sim 3d^{10}$ ) closed band  $\therefore$  no problem in ARPES - one particle Green's fun.

For Ni Open d band  $\therefore$  problem occurs for one electron removal

Take a snapshot  $\rightarrow d^8 \quad d^9 \quad d^{10} \quad d^9 \quad d^{10} \quad d^9$   
For minimum polarity fluct.  
Ni -  $3d^{9.4} 4s^{0.6}$   
UPS  $\rightarrow 3d^8$  or  $3d^9$  Like

Ni metal is like a hole doped insulator with a 4s band charge reservoir. with strong hybridization



$U \approx 3$   
 $W \approx 7.5$

Figure 4.- Comparison between the calculated density of one-electron states (DOS) for nickel [21] and the valence-band photoemission spectra in the ultraviolet (UPS) and the X-ray (XPS) regions [31].

The relative weights Of the  $d^9$  and  $d^8$  (satellite) configurations depend on Initial  $d$  occupation and i.e. mixing i.e. band width Both in the initial and final states

For a LDA/DMFT try see Lichtenstein et al PRL 067205 (2001)

In one electron theory

$$P(n) = \frac{m!}{(m-n)! n!} (1-c)^{m-n} c^n$$

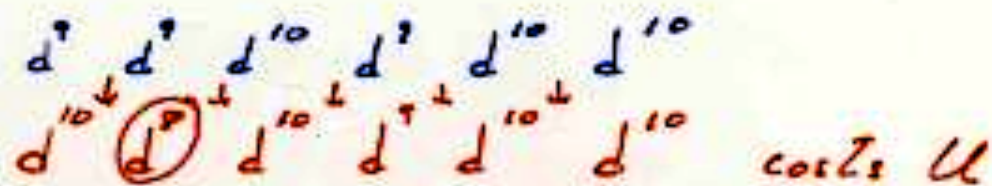
= Probability that a site has  $n$  electrons  
 $m$  = degeneracy       $c$  = concentration  
of electr. =  $\frac{\langle n \rangle}{m}$

So for Ni  $c = 0.94$  all conf.

$d^0 \rightarrow d^{10}$  occur without  
energetic considerations

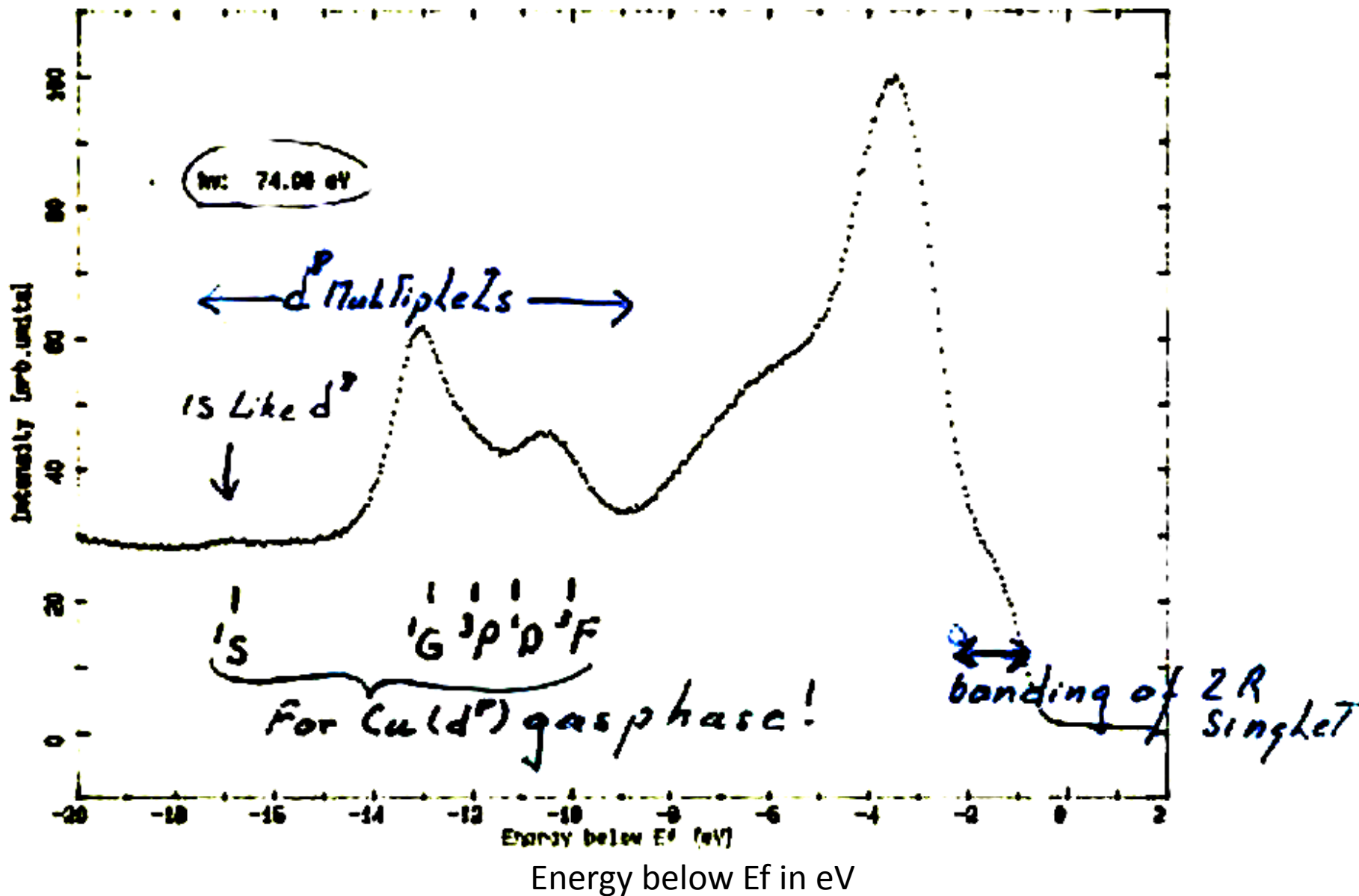
In atom starting point

Ni fluctuates between  $d^9$  &  $d^{10}$



Atomic theory minimizes  
polarity fluctuations





**Note the atomic like multiplet structure as for the rare earths**

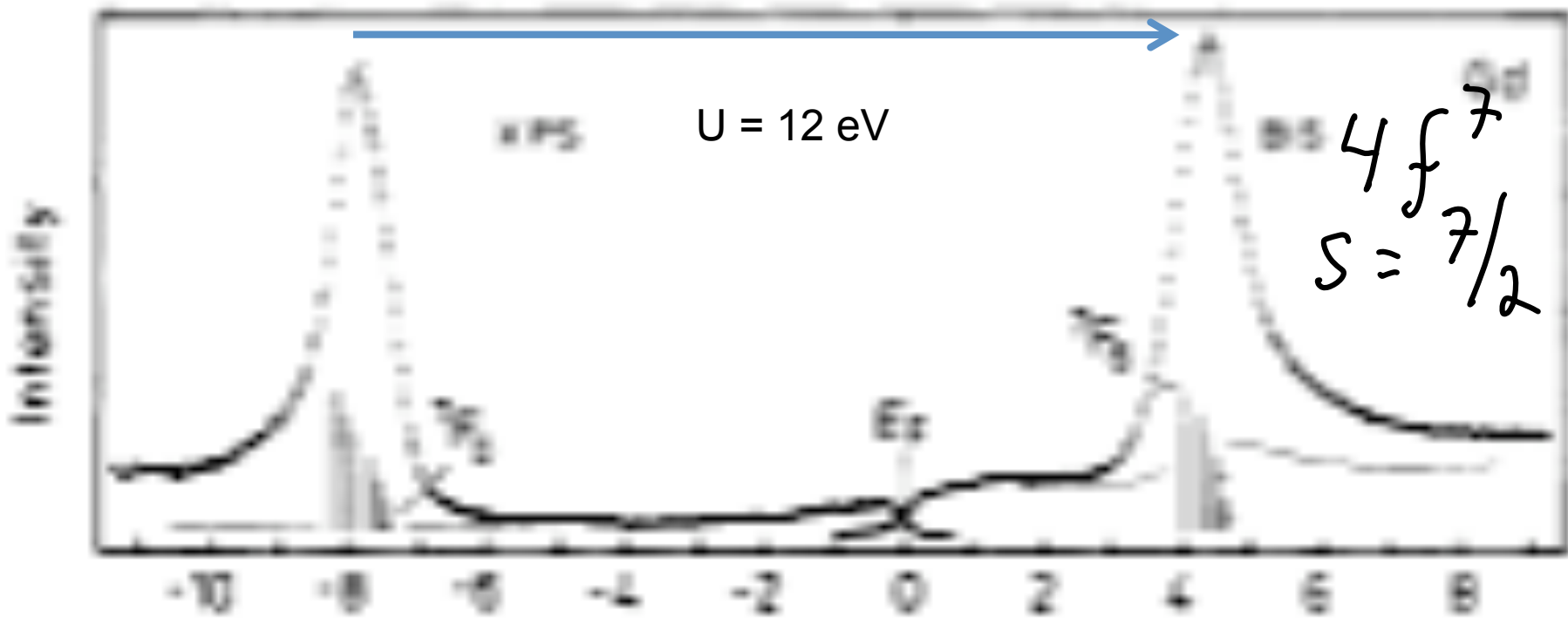
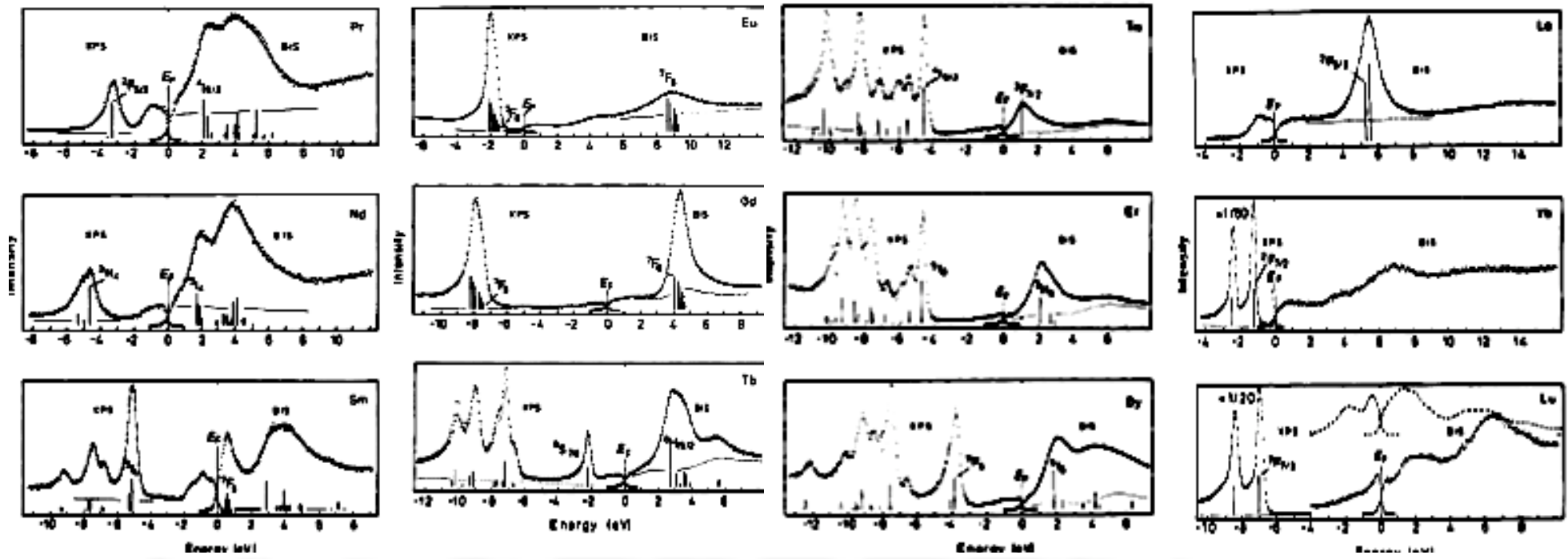
We will come back to the  
Photoemission and Zhang Rice  
singlets later.

# Transition metal d-d interactions

- The satellite position gives an estimate of the F0 Slater integral or U. More details below
- Important is that the multiplet spread is given by only slightly decreased gas phase atomic values i.e. F2 and F4 Slater integrals or J hund =  $(1/14)(F2 + F4)$  is reduced by at most 20% from the atomic values.
- F0 on the other hand is reduced from the atomic  $>20\text{eV}$  to about 7 eV!!!!

# Lang Baer and Cox J Phys F 11, 121 (1981)

- Photoemission and inverse photoemission of all the rare earth metals
- Demonstrates the atomic multiplets of the 4f electron removal and addition states
- Intensities given by atomic coefficients of fractional parentage starting from the Hund's rule ground state



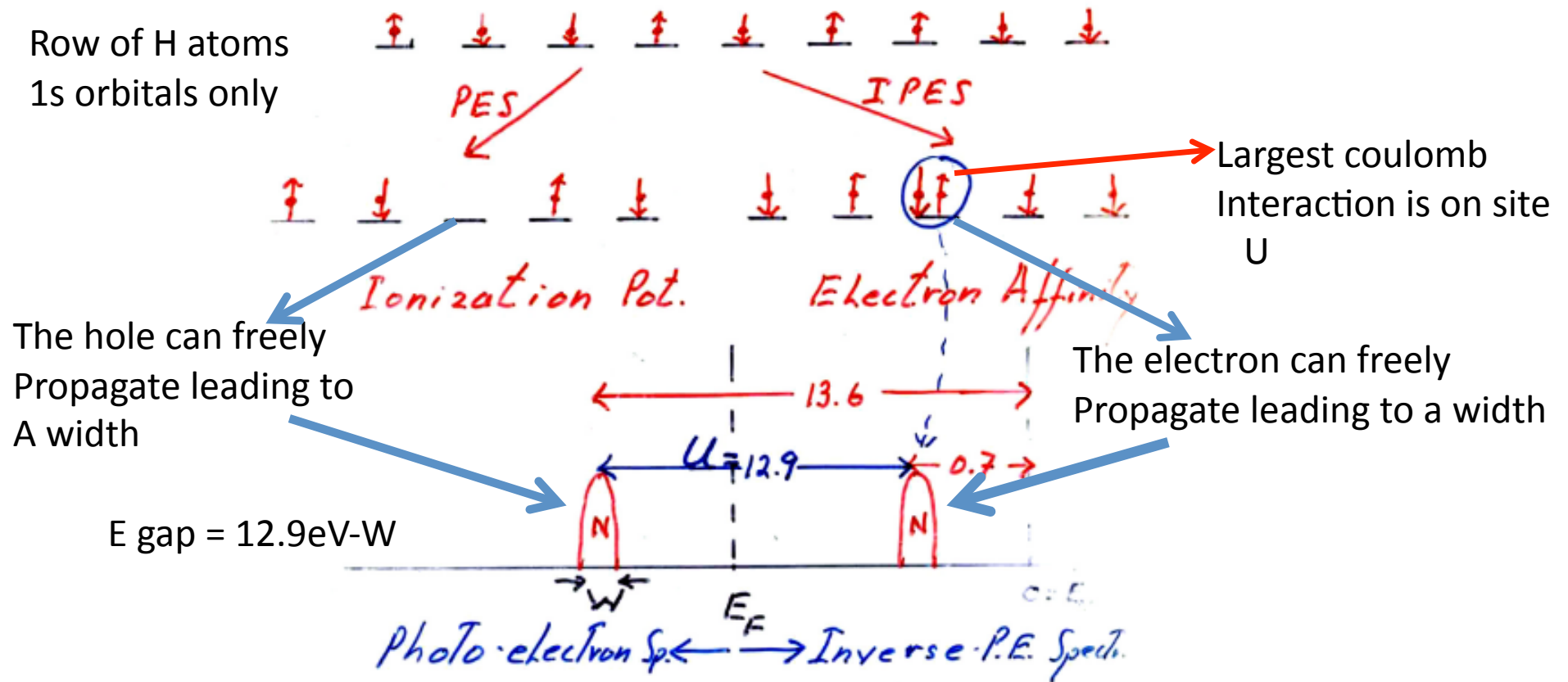
# MORE ON RARE EARTHS

- The Hubbard  $U$ ; as clearly demonstrated, its definition depends on which multiplets you take and depends strongly on the element. Convention is to either take the multiplet average or the Slater  $F_0$  integral.
- The multiplet splitting is very close to the atomic value little SCREENING OF THE HUNDS RULES INTERACTIONS I.E. SLATER  $F_2, F_4, F_6$  INTERACTIONS

Note the atomic physics needed to describe the rare earth 4f electron removal and addition spectrum

For the 3d transition metal compounds things are a lot more subtle. In some cases we need the atomic approaches and in others one particle theory seems to work very well

# Simplest model single band Hubbard



Simplest  $\mathcal{H}$

$$\mathcal{H} = \mathcal{H}_{\text{one elect.}} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Insulator for  $U > W$ .

The actual motion of the Particles will turn out to be more complicated



# For large $U \gg W$ and 1 electron per site

- ----Insulator
- Low energy scale physics contains no charge fluctuations
- Spin fluctuations determine the low energy scale properties
- Can we project out the high energy scale?

$$H = \sum_{i,j} J S_i S_j \quad J = 4t^2 / U$$

Heisenberg Spin Hamiltonian

We should be a bit careful  
about decoupling spin and  
charge degrees of freedom  
even in this case

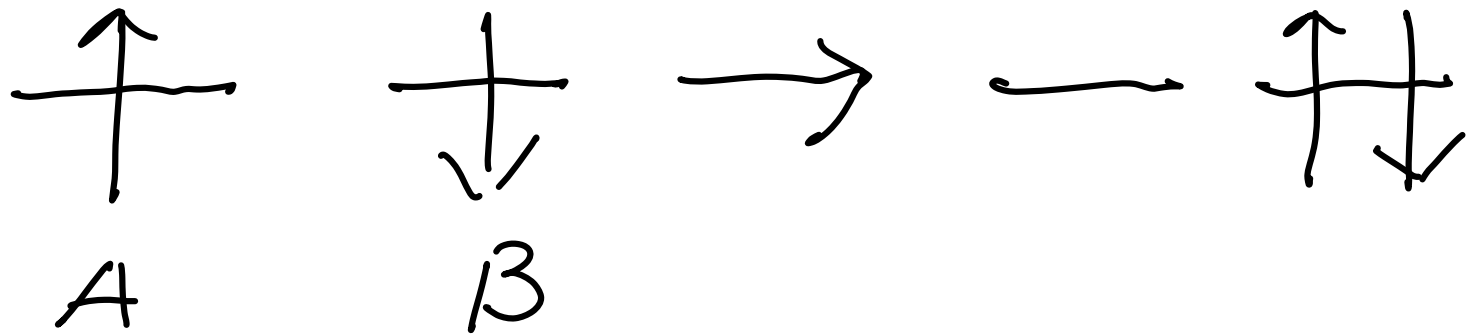
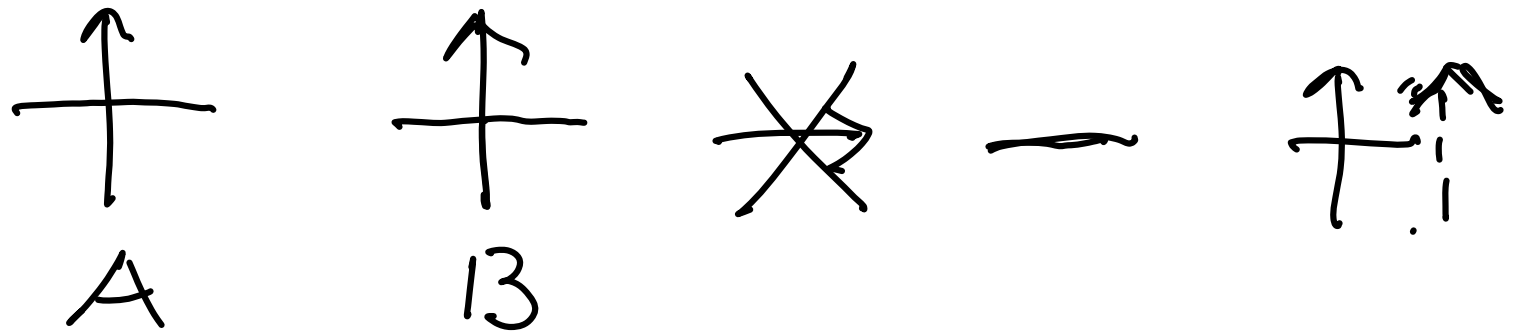
The charge distribution for the antiparrallel and parallel nn spin states are different! For the singlet there is admixture of doubly occupied sites. For triplets there is not!

Has strong consequences!

Temperature dependent Optical conductivity

Tsvetkov et al PRB 69, 075110 (2004)

# Spin order dependent Optical transitions



Before we go on lets look at a specific property of the Hubbard model which is measurable for a “doped” MH system

Seamus Davis the STS asymmetry  
CT Shen X ray absorption in doped  
Cuprates

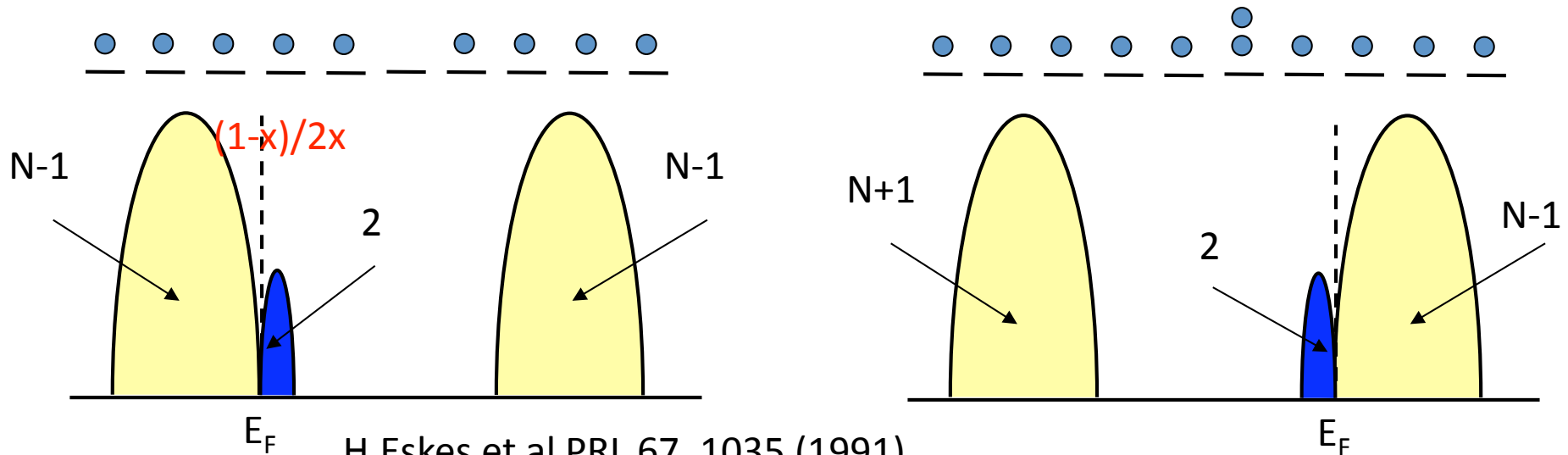
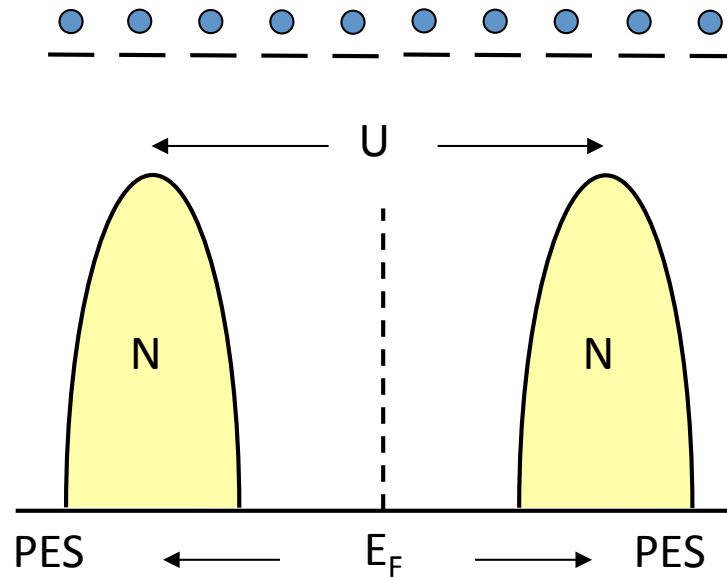
# Spectral weight transfer

The real signature of strong  
correlation effects

H.Eskes et al PRL 67, 1035 (1991)

Meinders et al, PRB 48, 3916 (1993)

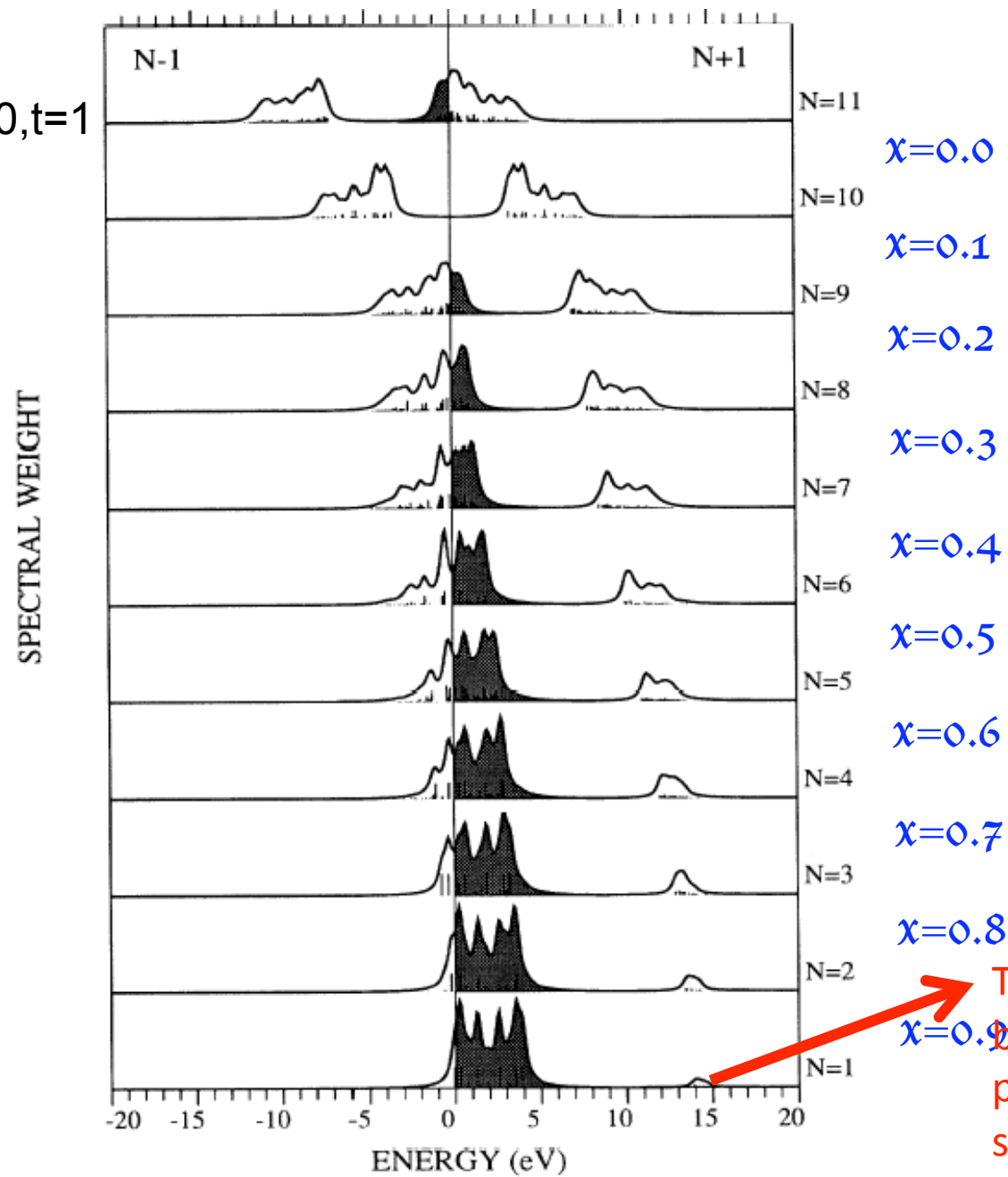
# Doping a Mott – Hubbard system



H.Eskes et al PRL 67, 1035 (1991)

Meinders et al, PRB 48, 3916 (1993)

10 site Hubbard  
1 D periodic  $U=10, t=1$



$\chi=0.0$

$\chi=0.1$

$\chi=0.2$

$\chi=0.3$

$\chi=0.4$

$\chi=0.5$

$\chi=0.6$

$\chi=0.7$

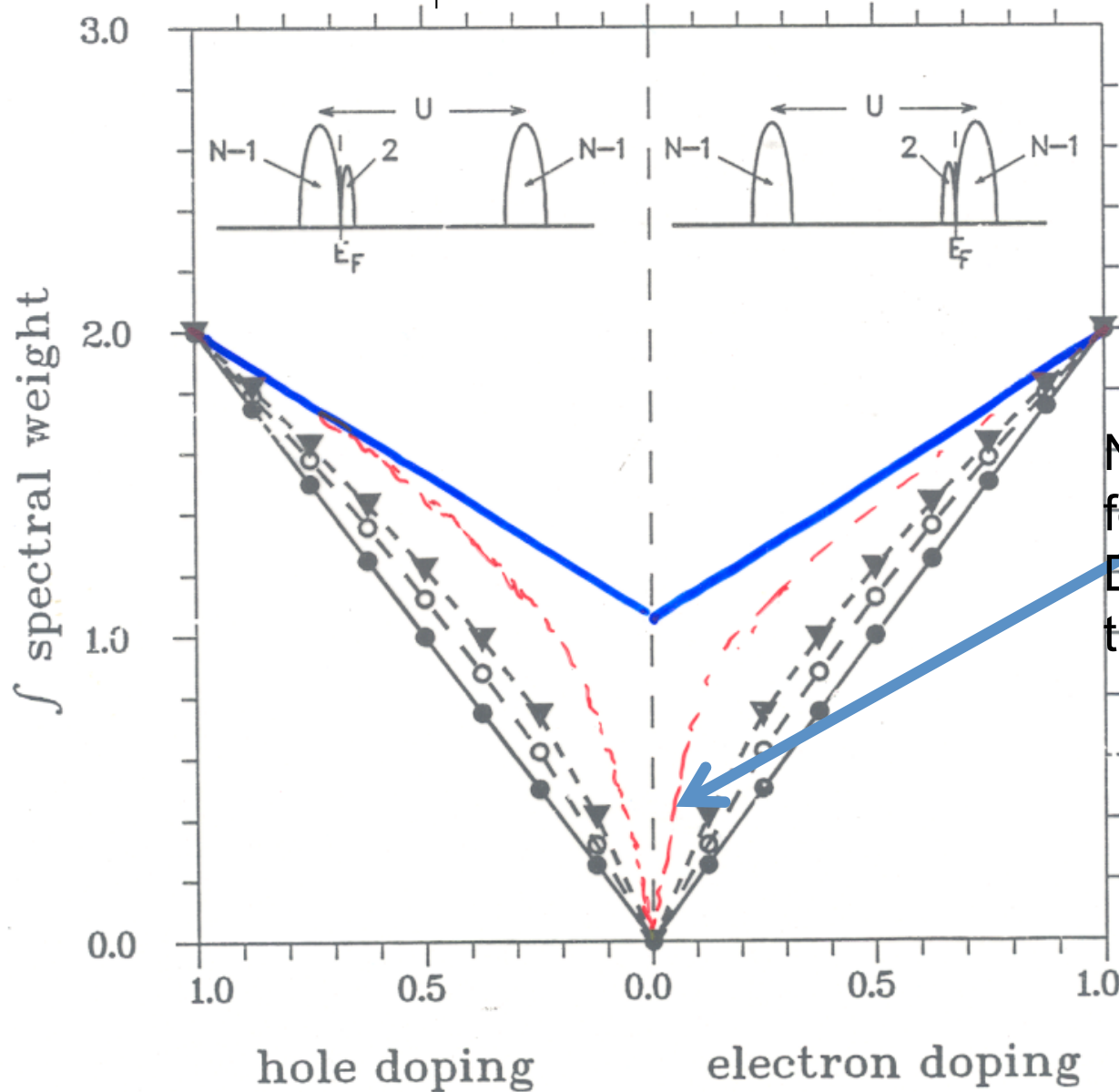
$\chi=0.8$

$\chi=0.9$

These states would be visible in a two particle addition spectral function



These particles block 2 or more states



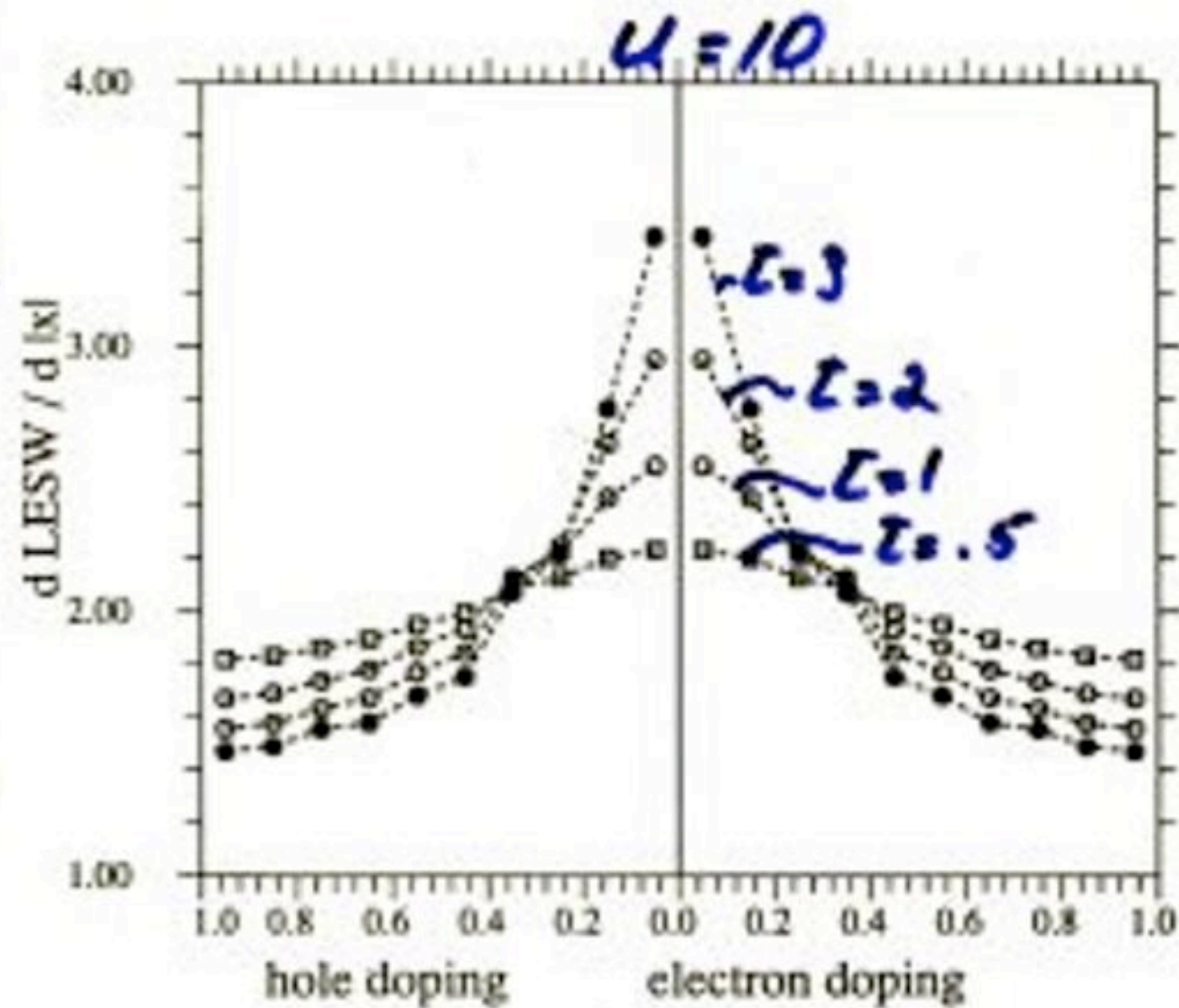
Bosons – block 0 states  
Fermions – block 1 state

These –block 2 states on  
The low energy scale

Note the even larger slop  
for finite hopping integrals  
Dynamic spectral weight  
transfer

Phillip Phillips uses this to  
Define “Mottness”  
Stanescu ,phillips PRB 69  
245104 (2004)

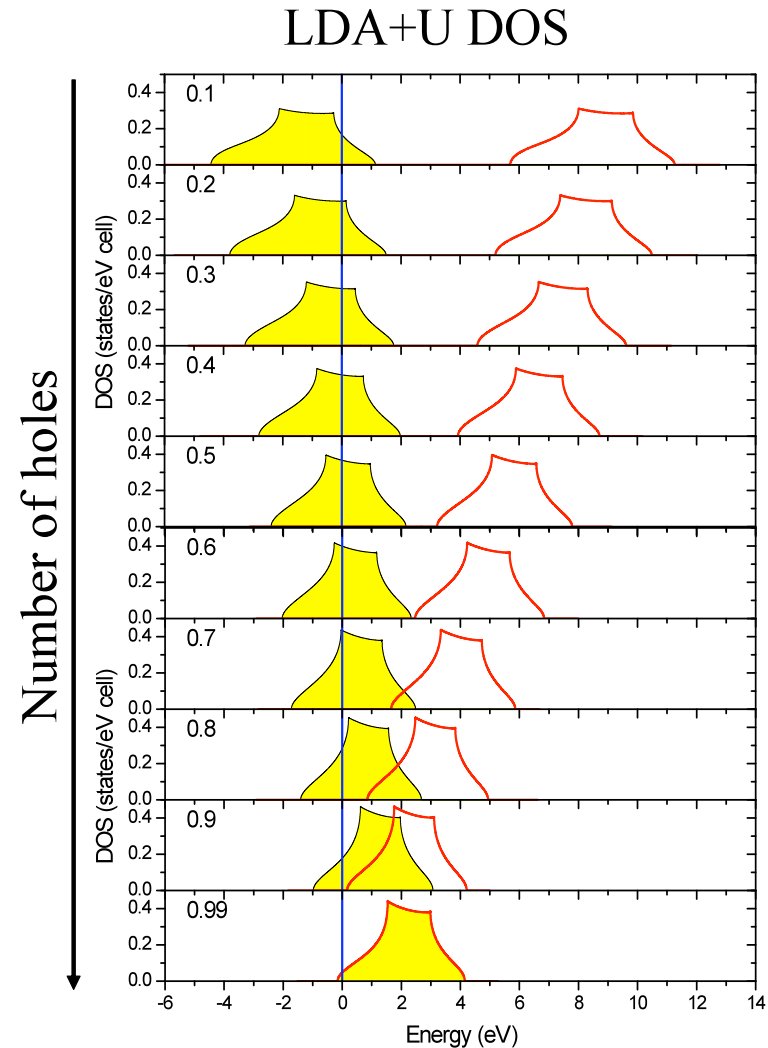
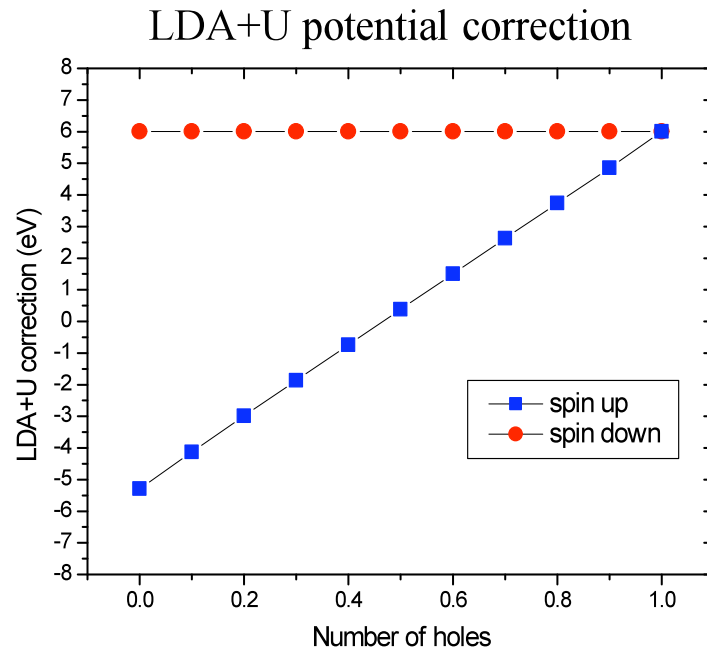
Eskes et al PRL 67, (1991) 1035  
Meinders et al PRB 48, (1993) 3916



# SC Hydrogen

$a = 2.7 \text{ \AA}$

$U = 12 \text{ eV}$



Note that there is no spectral weight transfer and a gap closing with doping From half filled . Both opposite to the real situation

We come back to spectral weight  
transfer later for the transition  
metal compounds

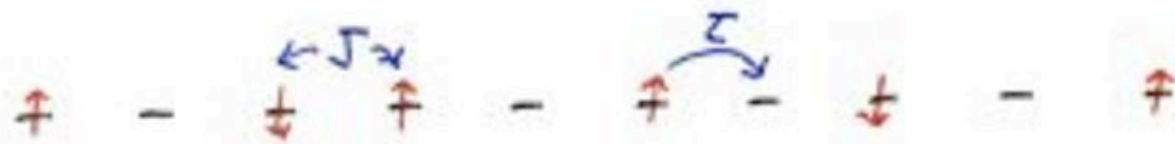
Hubbard model is not exactly solvable except in 1 D but even then the spectral functions are difficult to extract

Lieb and Wu PRL 20, 1445, (1968)

A bit more about simple models  
and some peculiar properties in 1  
and 2 dimensions of the simple  
models

Less than 1/2 filled Hubbard

First  $U \gg t$



$t, J$  Model

$$\mathcal{H} = t \sum_{\langle ij \rangle} \{ (1-n_{i\uparrow}) c_{i\uparrow}^\dagger c_{j\uparrow} (1-n_{j\downarrow}) \} + H.c. + J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$$

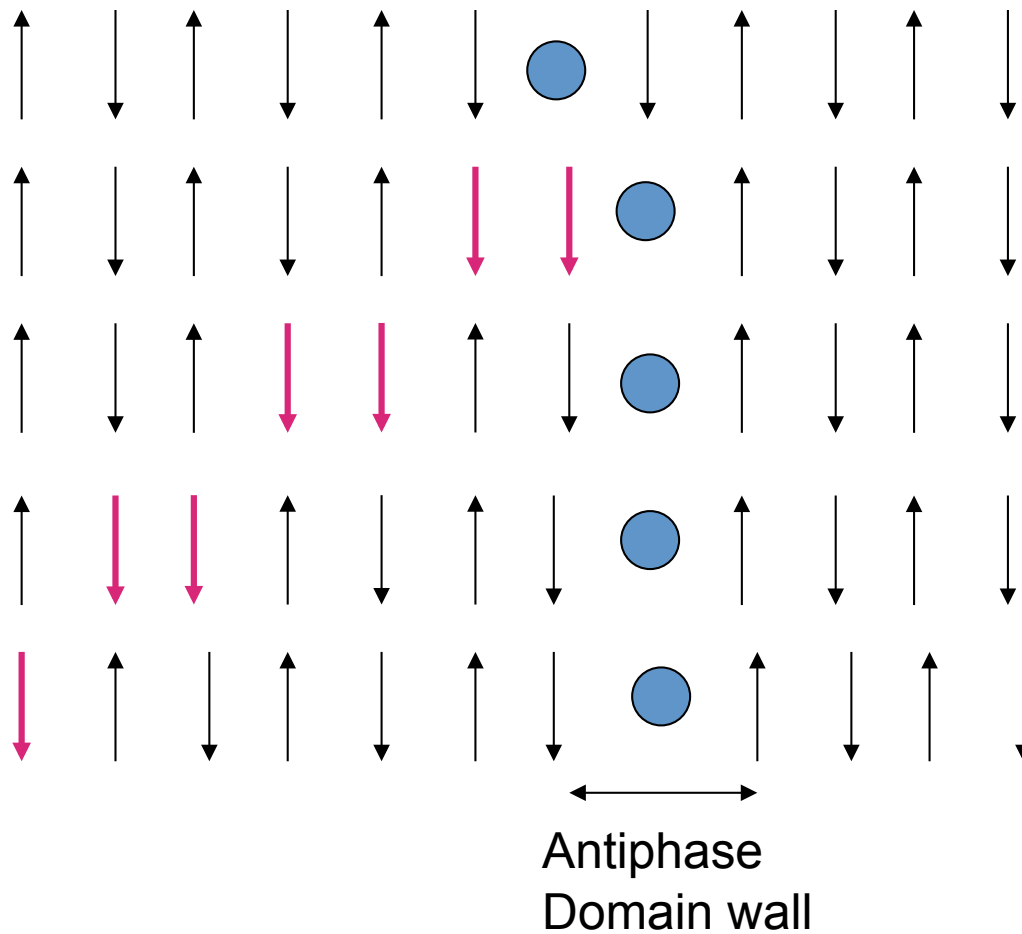
avoids double occ.

goes to Heisenberg for 1/2 filled.

Also this is not solvable

Don't know of a rigorous  
Proof of Hubb---t,J ( $U \gg w$ )

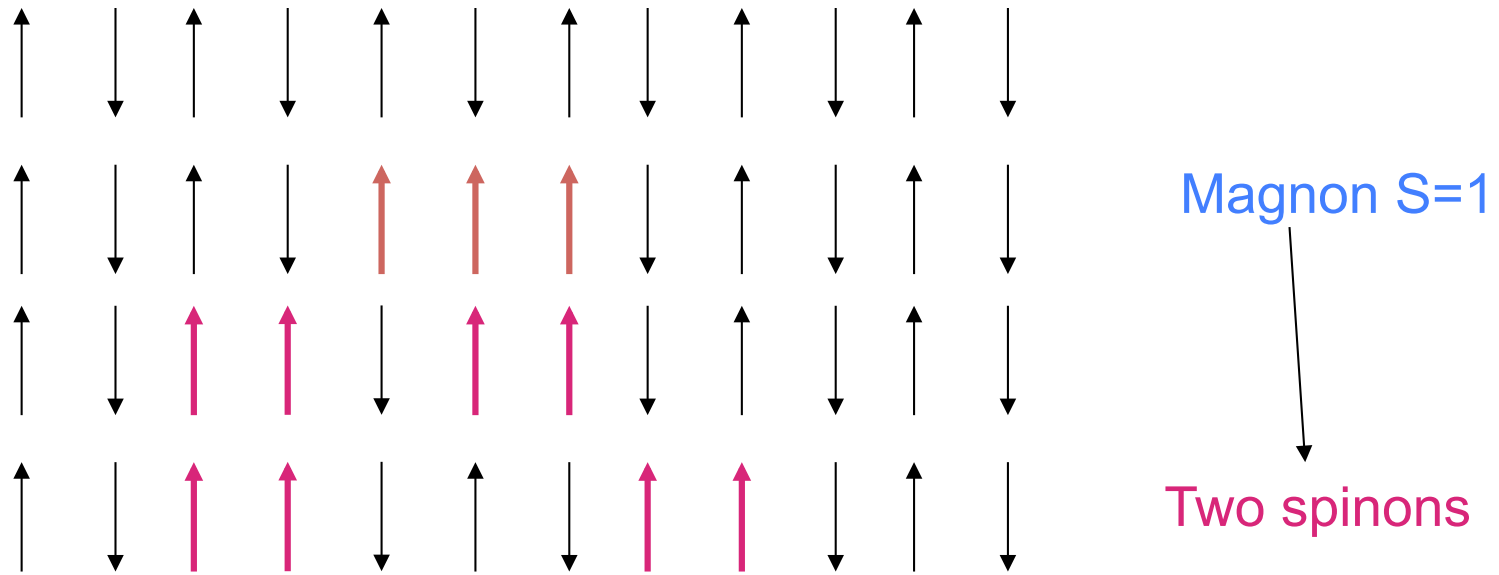
# Spin charge separation in 1D



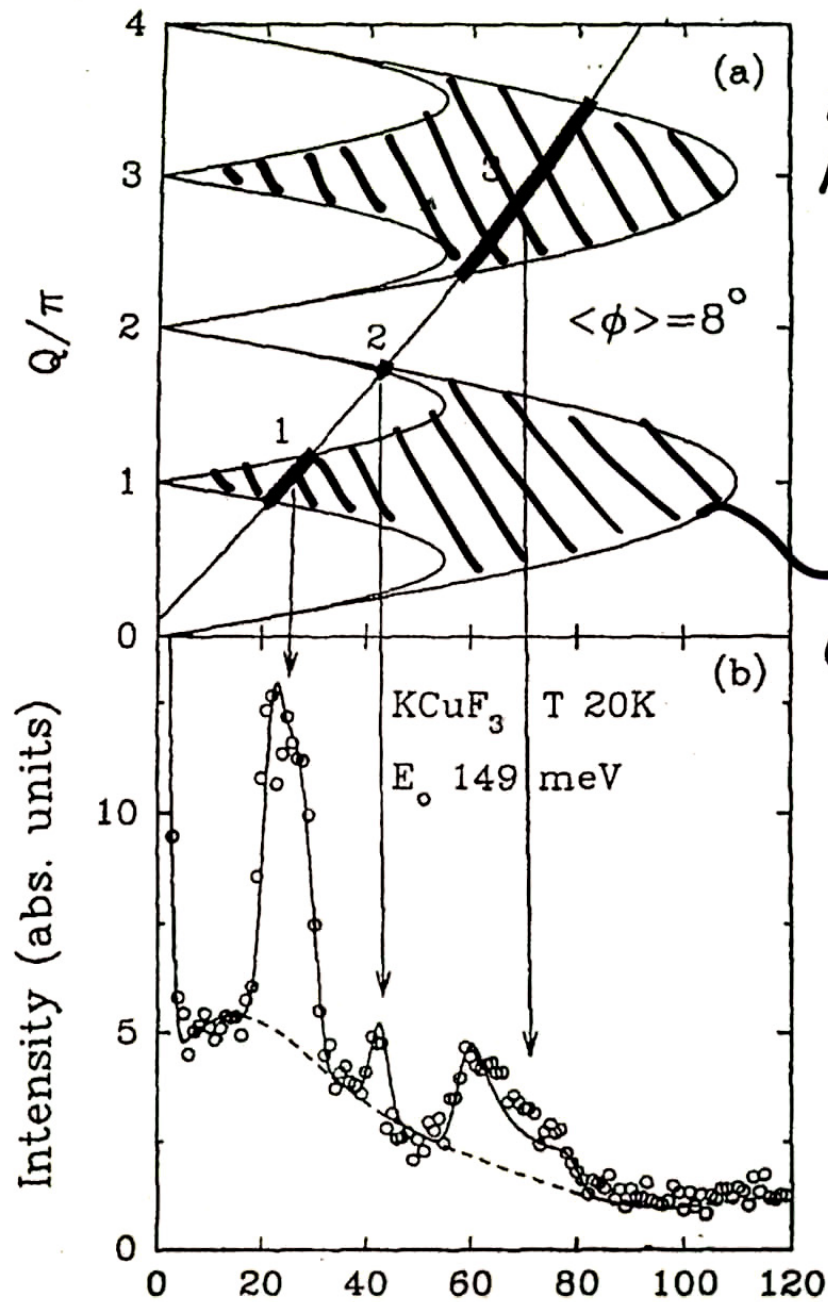
Now the charge is free to move



# Magnons and spinons in 1D



Spinons propagate via  $J S_i^+ S_{i+1}^-$



Tennant et al  
 Phys. Rev. B 52  
 13368 (1995)

Two Spinon  
 Continuum.

Inelastic Neutron scattering

Figure 2.14: Neut  
 continuum in 1D.  
 [182] The largest

**Quantum Spin Excitations in the Spin-Peierls System CuGeO<sub>3</sub>**

**M. Arai, M. Fujita, M. Motokawa, J. Akimitsu, and S. M. Bennington**

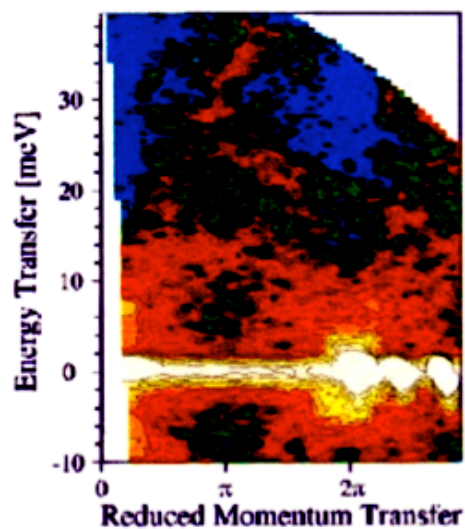


FIG. 4(color). The dynamical structure factor at 300 K. The spin continuum persists, but with the maximum reduced from 37 to 30 meV. The lower boundary has changed completely

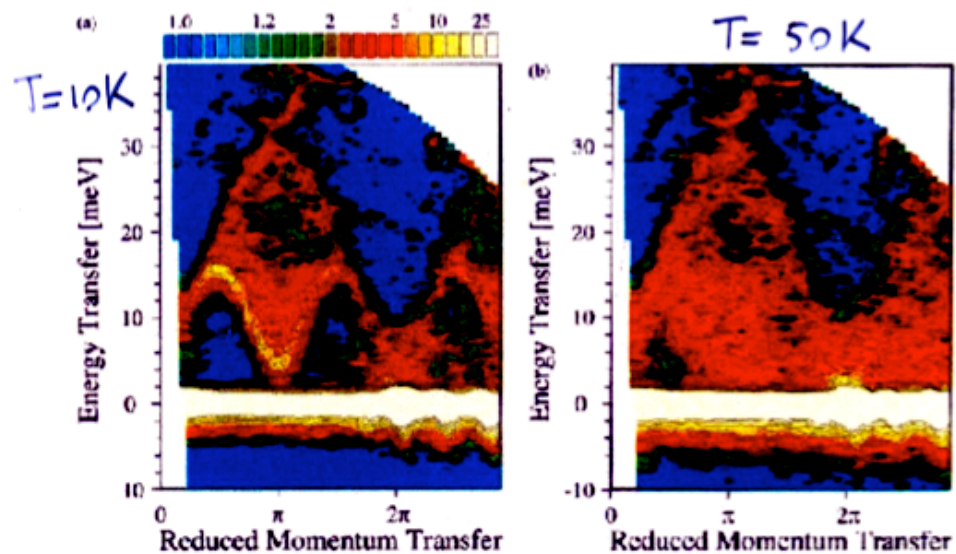


FIG. 1(color). A color contour map of the dynamical structure factor at 10 K (a) and 50 K (b).

in 2D things are much  
less clear!!

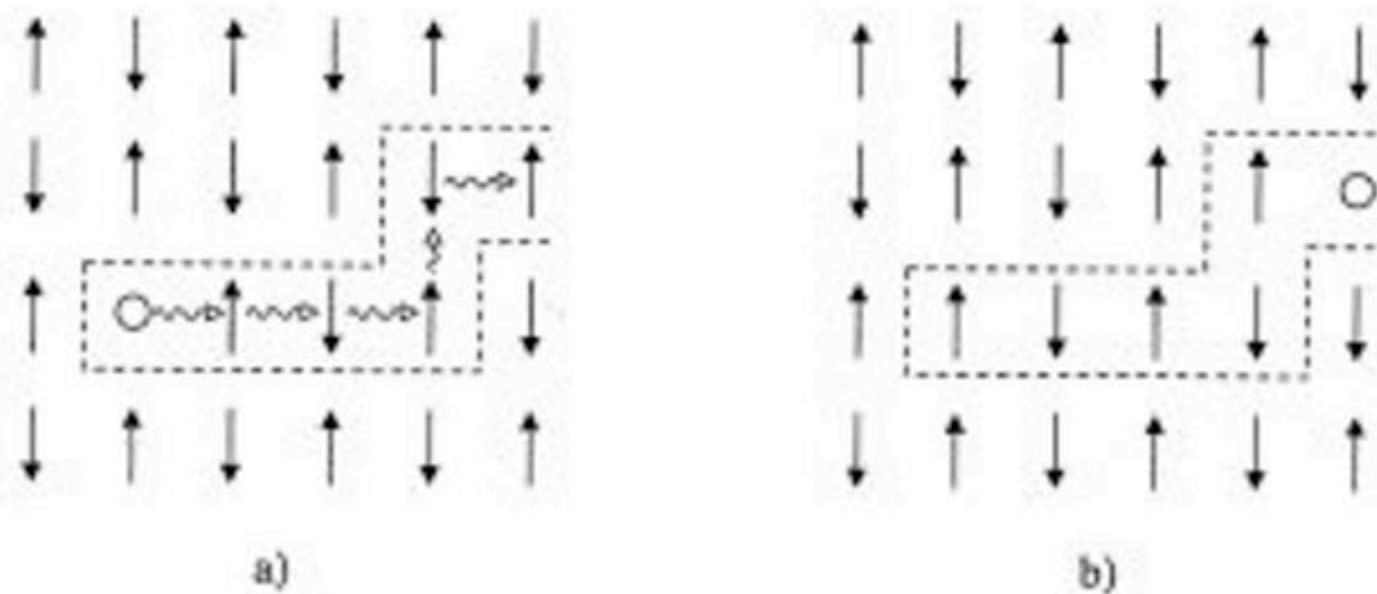
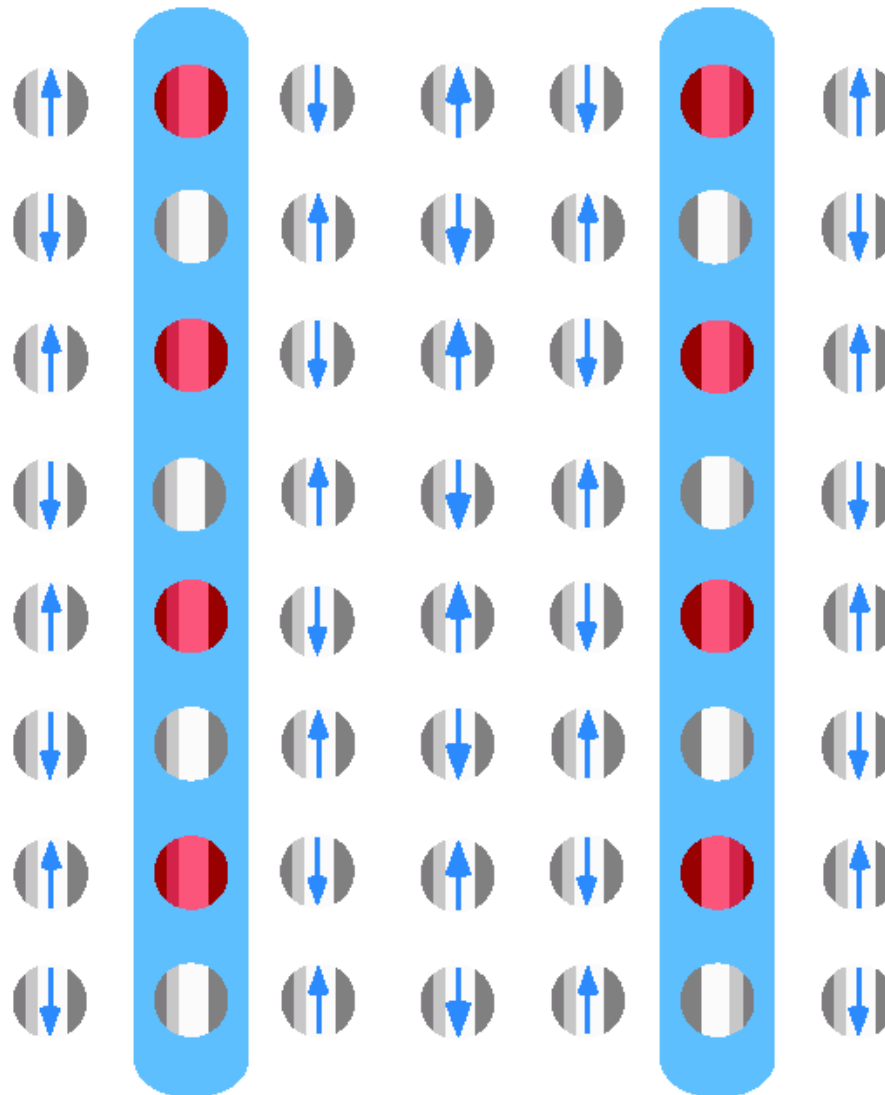


fig. 5

Self Confinement?

Similar in some sense to the 1D case it is proposed that one has 2D rivers of charge separating anti-phase domain walls. Charges can now fluctuate from left to right without costing  $J$

Anisimov, Zaanen, Andersen, Kivelson, Emery-----



# Please cite as:

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*Italy, October 5 – 16, 2009.*