Electronic structure of correlated electron systems

Lecture 2

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
- Hunds rules for the Ground state -Maximize total spin-Maximize total angular momentum-total angular momentum J =L-S<1/2 filled shell , J=L+S for >1/2 filled shell
- Mostly magnetic ground states

Taken from the lecture notes of Ilya Elfimov UBC which will also be put on a web site.

Problem at hands

Solve Schrödinger equation for any system (atom, molecule, solid)

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$$

$$\hat{H} = -\frac{1}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha}{r_{i\alpha}} + \underline{\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}}$$

Problem: no analytical solution for more than one electron due to el-el interaction

Density functional theory

Hohenberg and Kohn 1964 (proof of existence):
"the external potential $V_{ext}(\vec{r})$ is (to within a costant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$ "

$$\rho(\vec{r}) = N \int ... \int \mid \Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) \mid^2 d\vec{x}_2 ... d\vec{x}_N$$

$$E[\rho] = \underbrace{T[\rho] + E_{ee}[\rho]}_{\text{Universally valid}} + \underbrace{E_{en}[\rho]}_{\text{System dependent}}$$

P. Hohenberg and W. Kohn Phys. Rev. 136, B864 (1964)

$$V_{ext} \Rightarrow \hat{H} \Rightarrow \Psi \Rightarrow \rho(\vec{r}) \Leftarrow \Psi' \Leftarrow \hat{H}' \Leftarrow V'_{ext}$$

1) use Ψ' as a trial wave function for $\hat{H}$

$$E_0 < \left\langle \Psi' \mid \hat{H} \mid \Psi' \right\rangle = \left\langle \Psi' \mid \hat{H}' \mid \Psi' \right\rangle + \left\langle \Psi' \mid \hat{H} - \hat{H}' \mid \Psi' \right\rangle$$

which yield

$$E_0 < E'_0 + \int \rho(\vec{r})[V_{ext} - V'_{ext}]d\vec{r} \qquad (1)$$

2) repeat the same steps for Ψ and $\hat{H}'$

$$E'_0 < E_0 - \int \rho(\vec{r})[V_{ext} - V'_{ext}]d\vec{r} \qquad (2)$$

Adding (1) and (2) gives contradiction

$$E_0 + E'_0 < E'_0 + E_0 \quad \text{or} \quad 0 < 0$$

Therefore, there can not be two different V_{ext} that yield the same ground state electron density.

Second HK theorem

The functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the ground state density.

$$\left\langle \widetilde{\Psi} \mid \hat{H} \mid \widetilde{\Psi} \right\rangle = T[\widetilde{\rho}] + V_{ee}[\widetilde{\rho}] + \int \widetilde{\rho}(\vec{r}) V_{ext} d\vec{r} = E[\widetilde{\rho}]$$

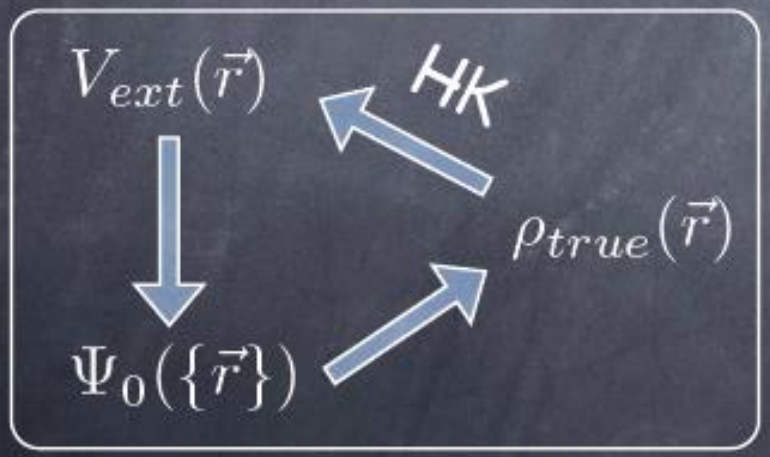
$$E[\widetilde{\rho}] \geq E_0[\rho_0] = \left\langle \Psi_0 \mid \hat{H} \mid \Psi_0 \right\rangle$$

Problem: Hohenberg-Kohn theorems give us no clue about neither the nature of the density functional nor how to find it.

Kohn-Sham ansatz

The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles.

Interacting system



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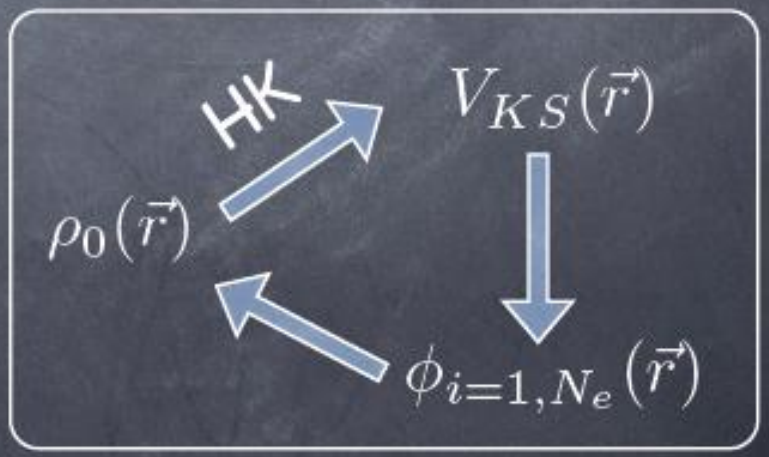
Non-interacting system



W. Kohn and L.J. Sham Phys. Rev. 140, A1133 (1965)

XC functional

This functional contains everything that is unknown

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho])$$

True kinetic energy of the **interacting** system

None-interacting

True el-el interaction

Hartree term

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}d\vec{r}'$$

Kohn-Sham one-electron equation

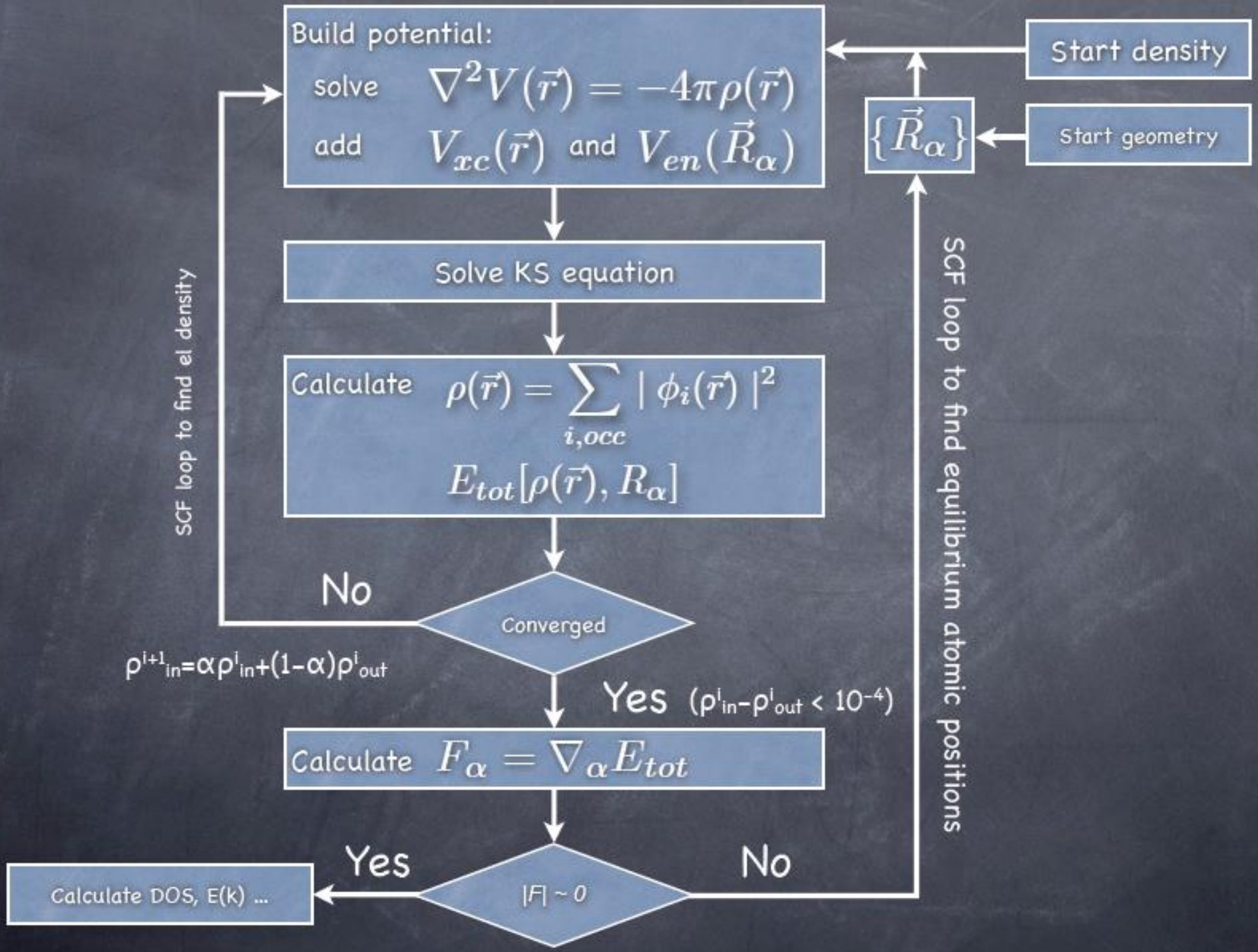
$$\rho(\vec{r}) = \sum_{i}^{N} \mid \phi_i(\vec{r}) \mid^2 = \rho_{true}(\vec{r})$$

$$(-\frac{1}{2}\vec{\nabla}^2 + \int \frac{\rho(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}' + V_{xc} + V_{ext})\phi^n(\vec{r}) = \epsilon^n \phi^n(\vec{r})$$

V_{eff} = Hartree + exchange-correlation + electron-nuclear

Note, this is self consistent operator i.e. the operator depends on its own solution! Therefore, one needs an iterative method to solve this problem.

W. Kohn and L.J. Sham Phys. Rev. 140, A1133 (1965)


Build potential:
solve $\nabla^2 V(\vec{r}) = -4\pi\rho(\vec{r})$
add $V_{xc}(\vec{r})$ and $V_{en}(\vec{R}_\alpha)$
Start density
$\{\vec{R}_\alpha\}$
Start geometry
Solve KS equation
Calculate $\rho(\vec{r}) = \sum_{i,occ} |\phi_i(\vec{r})|^2$
$E_{tot}[\rho(\vec{r}), R_\alpha]$
SCF loop to find el density
SCF loop to find equilibrium atomic positions
No
Converged
$\rho^{i+1}_{in} = \alpha\rho^i_{in} + (1-\alpha)\rho^i_{out}$
Yes ($\rho^i_{in} - \rho^i_{out} < 10^{-4}$)
Calculate $F_\alpha = \nabla_\alpha E_{tot}$
Yes
No
Calculate DOS, E(k) ...
|F| ~ 0

Local density approximation

LDA assumes that XC energy for an inhomogeneous electron gas can be partitioned into smaller regions that are locally homogeneous and that total XC energy is just a sum of these smaller regions:

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r})\epsilon_{xc}(\rho(\vec{r}))d\vec{r}$$

from inhomogeneous system

from homogeneous electron gas

Exchange correlation energy

$$\epsilon_{xc}(\rho(\vec{r})) = \epsilon_x(\rho(\vec{r})) + \epsilon_c(\rho(\vec{r}))$$

$$\epsilon_x(\rho(\vec{r})) = -\frac{3}{4}\left(\frac{6\rho(\vec{r})}{\pi}\right)^{1/3}$$

This is simply the exchange energy per electron of the homogeneous gas

??

There is no such explicit expression for the correlation energy

Example: correlation energy of uniform electron gas which satisfies strong and weak coupling limits

$$e_c(n) = -2c_0(1+\alpha_1 r_s)\ln\left[1+\frac{1}{2c_0(\beta_1 r_s^{1/2}+\beta_2 r_s+\beta_3 r_s^{3/2}+\beta_4 r_s^2)}\right] ,$$

where

$$\beta_1 = \frac{1}{2c_0}\exp\left(-\frac{c_1}{2c_0}\right) , \tag{144}$$

$$\beta_2 = 2c_0\beta_1^2 . \tag{145}$$

The coefficients $\alpha_1 = 0.21370$, $\beta_3 = 1.6382$, and $\beta_4 = 0.49294$ are found by fitting to accurate Quantum Monte Carlo correlation energies [57] for r_s =2, 5, 10, 20, 50, and 100.

57. D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

DFT and band theory of solids

The many electron wave function is assumed to be a single Slater determinant of one electron Bloch states commensurate with the periodic symmetry of the atoms in the lattice and so has no correlation in it

$$\Psi = \sqrt{\frac{1}{N!}} \left| \varphi_{k1} \varphi_{2k} \varphi_{3k} ------ \varphi_{kN} \right|$$

The single particle wave functions ϕ contain the other quantum numbers like atomic nlm and spin. k represents the momentum vector

The effects of correlation are only in the effective one particle Hamiltonian

$$v_{eff} = v_{nuclear} + \int \frac{n(r')}{r - r'} d^3 r' + v_{xc}$$

Using such a single Slater determinant means that there is no correlation in this many electron wave function. The effects of correlation are in H only in the form of effective single particle potentials. In a simple physical picture of this we imagine that each electron repels other electrons and produces a suppression of density around it. This is referred to as an " exchange correlation hole". In this form of DFT the effect of this is in the potential but cannot be included in the many electron wave function

Abinito approach to DFT as applied to band theory of solids

- We can get the “exact” ground state energy and ground state density (crystal structure) provided the exchange correlation potential is known
- Recall that the ground state has few properties i.e.energy and density, It is the excited states that determine the response to External perturbations such as fields
- If we had the ground state wave function on the other hand we could at least guess at some of the properties such as metallic or insulating, magnetic or not etc.

DFT band theory in LDA

Remember that the one electron wavefunctions φ in the above have no physical meaning in fact and neither do the one electron energies . They are merely a tool to calculate the total ground state energy and density.

Note also that the total many body wave function also has no meaning physically and actually is not an eigenfunction of the original Hamiltonian.

Non the less in band theory these are taken to be the “quasi” particle energies and wave functions in comparisons with experiment.

The DFT wave function is not an eigen function of the exact Hamiltonian

$$\mathrm{H}_{dft}\Psi^{dft} = E_G\Psi^{dft}$$ However $$\mathrm{H}_{exact}\Psi^{dft} \neq E_G\Psi^{dft}$$

$$H_{exact} = \sum_{i=1}^{n}\left[-1/2\nabla_i^2 + W(r_i) + 1/2\Sigma_{j,i\neq j}\frac{e^2}{|r_i - r_j|}\right]$$

The single particle wave functions have k as a good quantum number in DFT. The electron -electron term in H exact will always have scattering matrix elements

$$\varphi_k\varphi_{k'} \longrightarrow \varphi_{k''}\varphi_{k'''}$$

i.e. 2 electrons k,k' scatter from below to above k'',k''' the Fermi Energy.

. Consider tight binding one electron Wave functions

$$\varphi_k = 1/\sqrt{N}\sum_i \phi(r - R_i)e^{ik\bullet R_i}$$

$$\left\langle \left|\frac{e^2}{r_i - r_j}\right| \right\rangle$$

These matrix elements will be largest if the two electrons are on the same atomic site in which case = U i.e. Hubbard.

Now look at the electron electron scattering due to a Hubbard like U

$$\left\langle \Psi_{gdft} \middle| H_{\text{int}} \middle| \Psi_{\frac{k\to k'}{k''\to k'''}} \right\rangle = \frac{U}{N}$$

With k+k' -k''-k''' = 0 for momentum conservation Where k and k' are occupied states and k' and k''' are unoccupied.

GOES TO ZERO FOR N INFINITE. However we have to sum over all these scattering events and if U is comparable to the band width W or the Fermi energy as measured from the bottom of the band then basically all electrons are involved and in the total we have to sum over these resulting in an effective a scattering matrix element of one electron due to interaction with all the others of U. This demonstrates how one can be misled by looking at a single off diagonal matrix element and that for U comparable to W the effective scattering is actually U. IN OTHER WORDS ψdft is far from being an eigenfunction of the exact Hamiltonian if U is comparable to W.

For systems with R<<D

For R<<D and Large U we get a qualitatively different ansatz wave function. Consider a half filled s like band i.e. 1 electron per atom on average. For a zero band width W the ground state wave function might look more like .

$$\Psi_A = \sqrt{\frac{1}{N!}}\left|\varphi_1\varphi_2\varphi_3 - - - - - - \varphi_N\right|$$

Where the integers now label sites
And the one electron wave functions
Are atomic orbitals center at cite i

The off diagonal matrix elements now involve W i.e. hoping so this is better for U>>W. Note that also here we have on the Average one electron per atom as in the DFT wave function

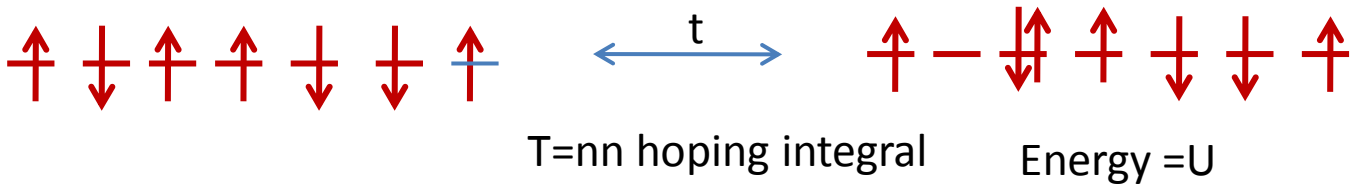
In the zero band width limit and again a single s like band the electron charge density in DFT would also correspond to exactly one electron per atom but the wave function would be a single Slater determinant of one electron Bloch waves and not a single Slater determinant of atomic site localized s orbitals with one electron at each site. In the DFT case there would be two electrons with opposite spin in each k state while in the atomic case each atom would have one unpaired electron and S=1/2. This would yield a paramagnetic susceptibility i.e. 1/Temp as expected for a collection of independent atoms with one electron per atom. In the DFT approach the material would be expected to be metallic since the band is half full and the band is centered at Ef . The atomic like approach would obviously yield an insulator since to move an electron we reguire an excitation to an doubly occupied cite resulting in an excitation Energy of U>>W.

Including the exchange correlation hole in DFT wave function

In our simple example of a lattice of H atoms with one electron per atom we could conceptually include an exchange correlation hole in the wave function. Basically it would correspond to every occupied by one electron is also forced to have an unoccupied opposite spin orbital on that atom. This if we could impliment it would result in qualitatively the same properties as the atomic limit. However we don’t really know how to impliment this.

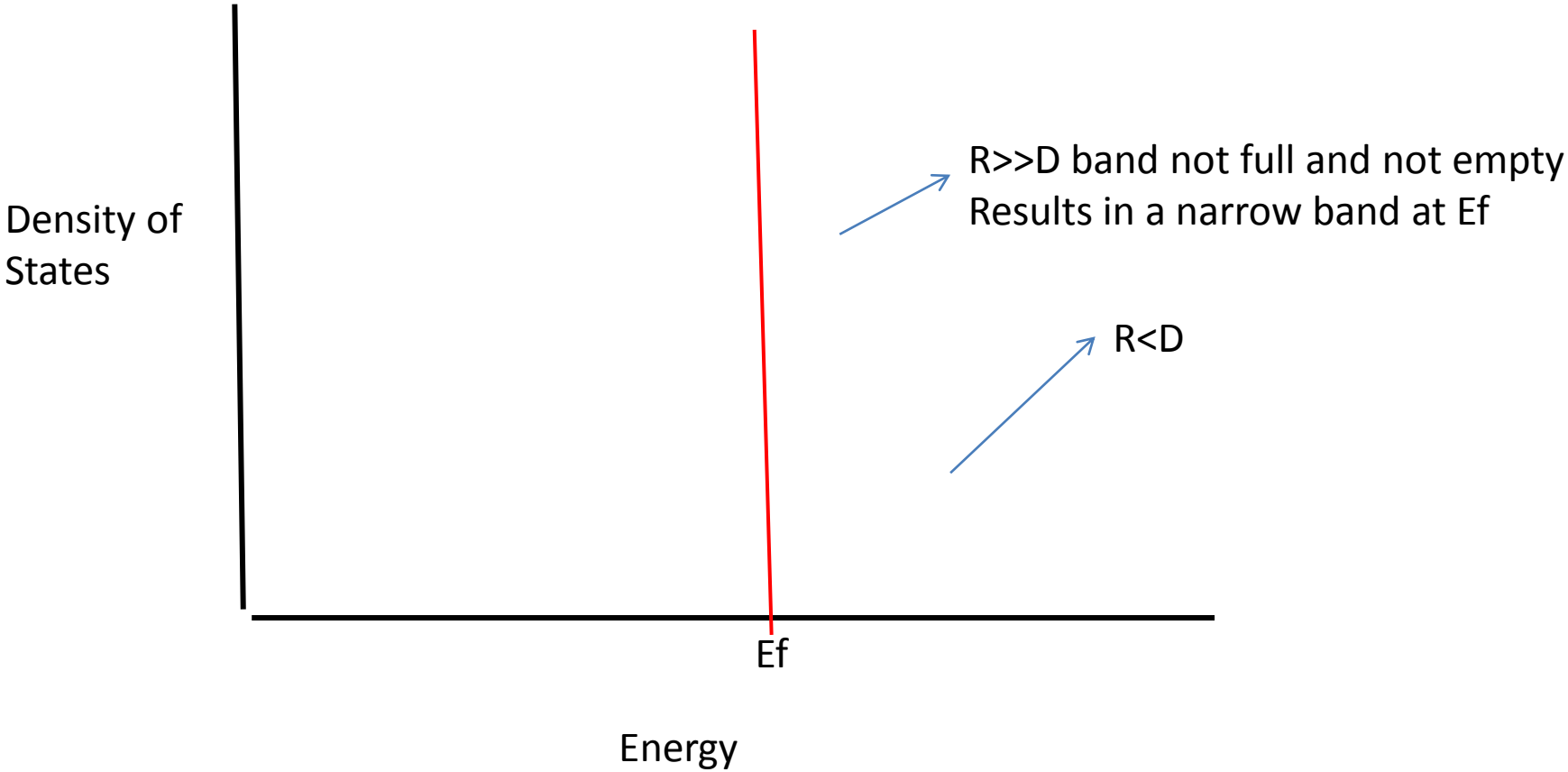
Configuration interaction approach

The one electron wave functions in ψ atomic do not possess the symmetry of the lattice which in chemistry is called a broken symmetry ansatz. To include intersite hoping perturbatively we consider mixing in electron configurations with now empty sites and others with two electrons on a site.



Mixing in of this excited state wave function amplitude = t/U But there are an infinite Number of these virtual excitations in a configuration interaction approach.

Band theory result for a coexistence of extreme states



Huge successes of DFT

- Obtain the correct ground state crystal structure and quite accurate lattice parameters for a large diversity of systems
- Obtain the correct magnetic structure for a large diversity of materials
- First principles method to calculate electron phonon coupling by introducing lattice distortions and obtaining the new ground state energy
- Extremely important role in also correlated electron systems for the determination of parameters to be used in many body Hamiltonian approaches.

What do we really mean by states above and below Ef?

- E<Ef eigenstates of the N-1 electron system i.e. ionization states of the N electron system i.e. Reachable by photoemission
- E>Ef eigenstates of the N+1 electron system i.e. electron affinity states of N particle system i.e. reachable by inverse photo electron spectroscopy states
- These two differ by two electrons

Experimental measurement

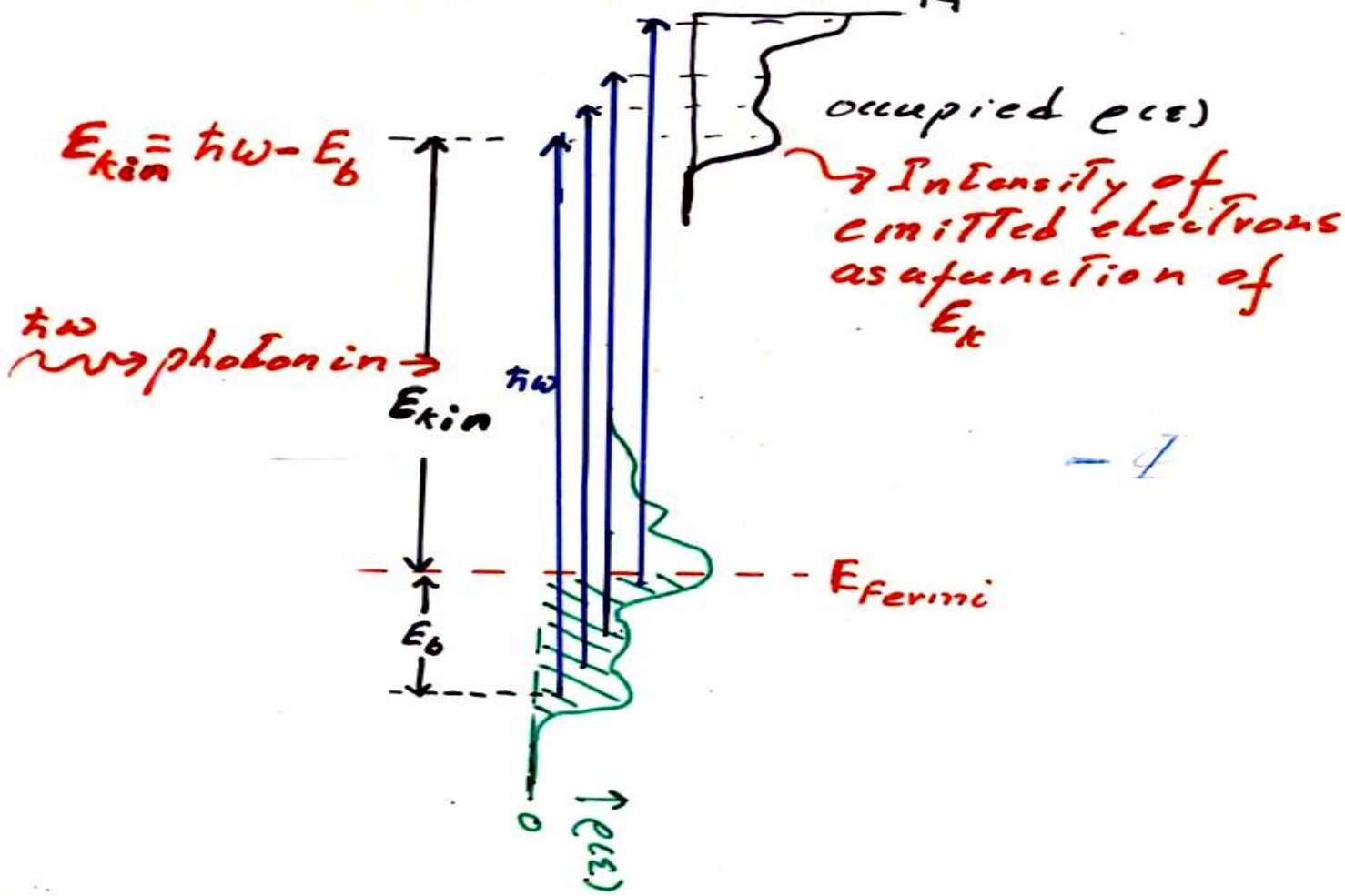
- States below Ef ----Photoelectron spectroscopy PES or ARPES. Removes one electron

- States above Ef ---Inverse photoelectron spectroscopy IPES. Adds one electron

PES (Photo electron Spectr.)

involves low $\hbar\omega$ → valence electrons

Consider a metal

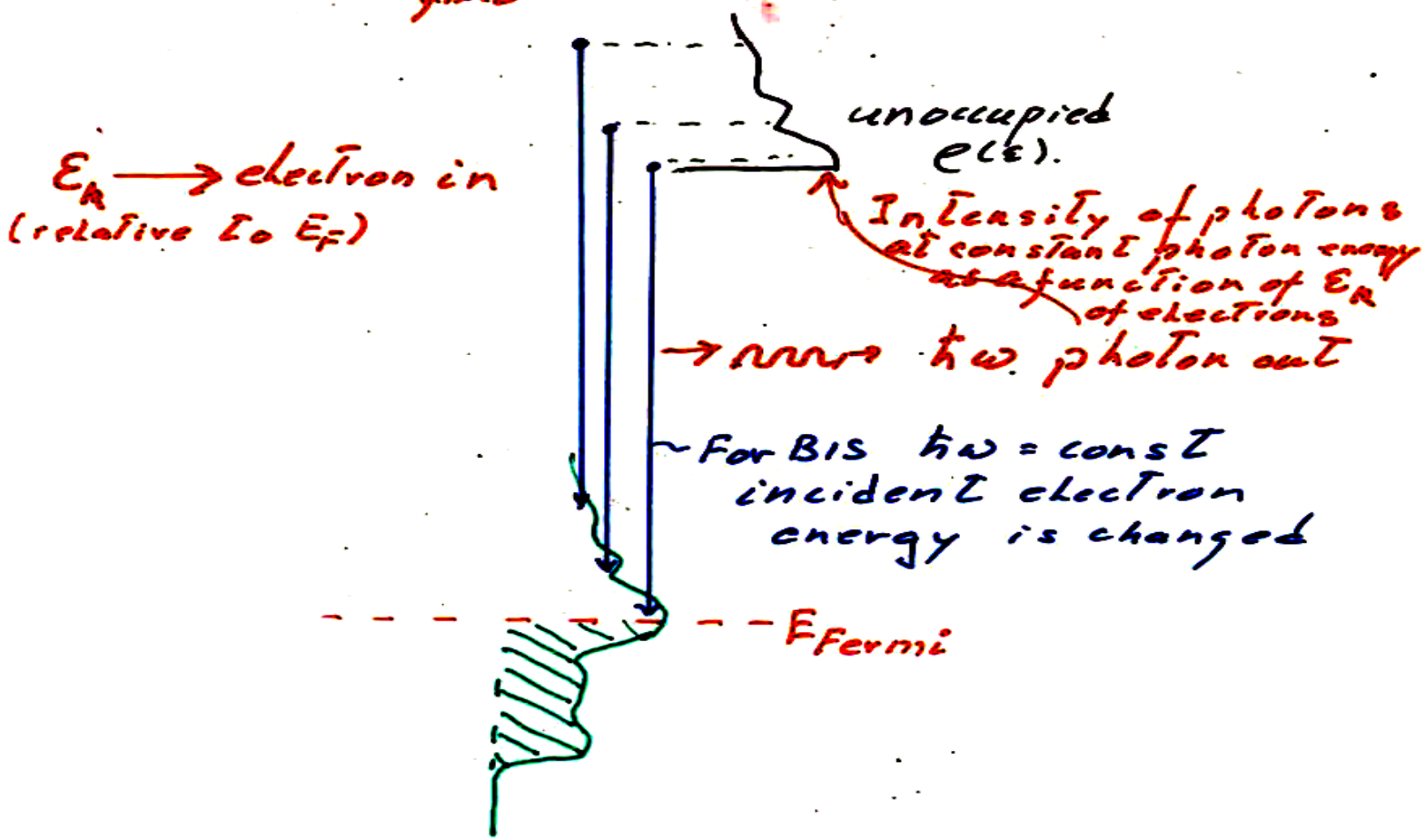


Measure density of states for electron removal × Matrix element

(Inverse PES) IPES / BIS (Bremsstrahlung isochromat Spectr.)

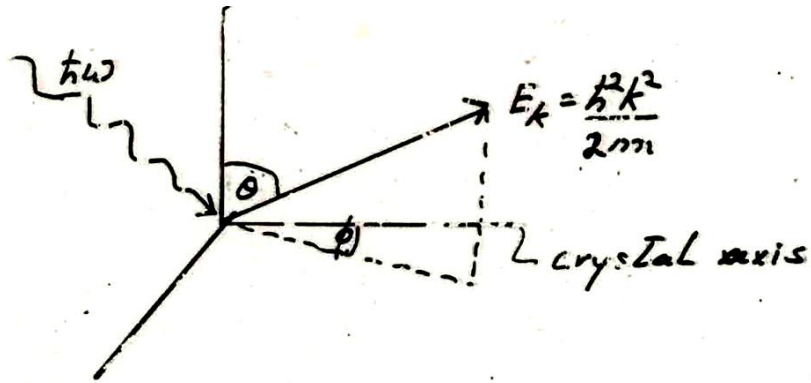
involves conduction band states

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



Measures $\rho(\varepsilon)$ for electron addition

Angular resolved photo and inverse photo electron spectroscopy

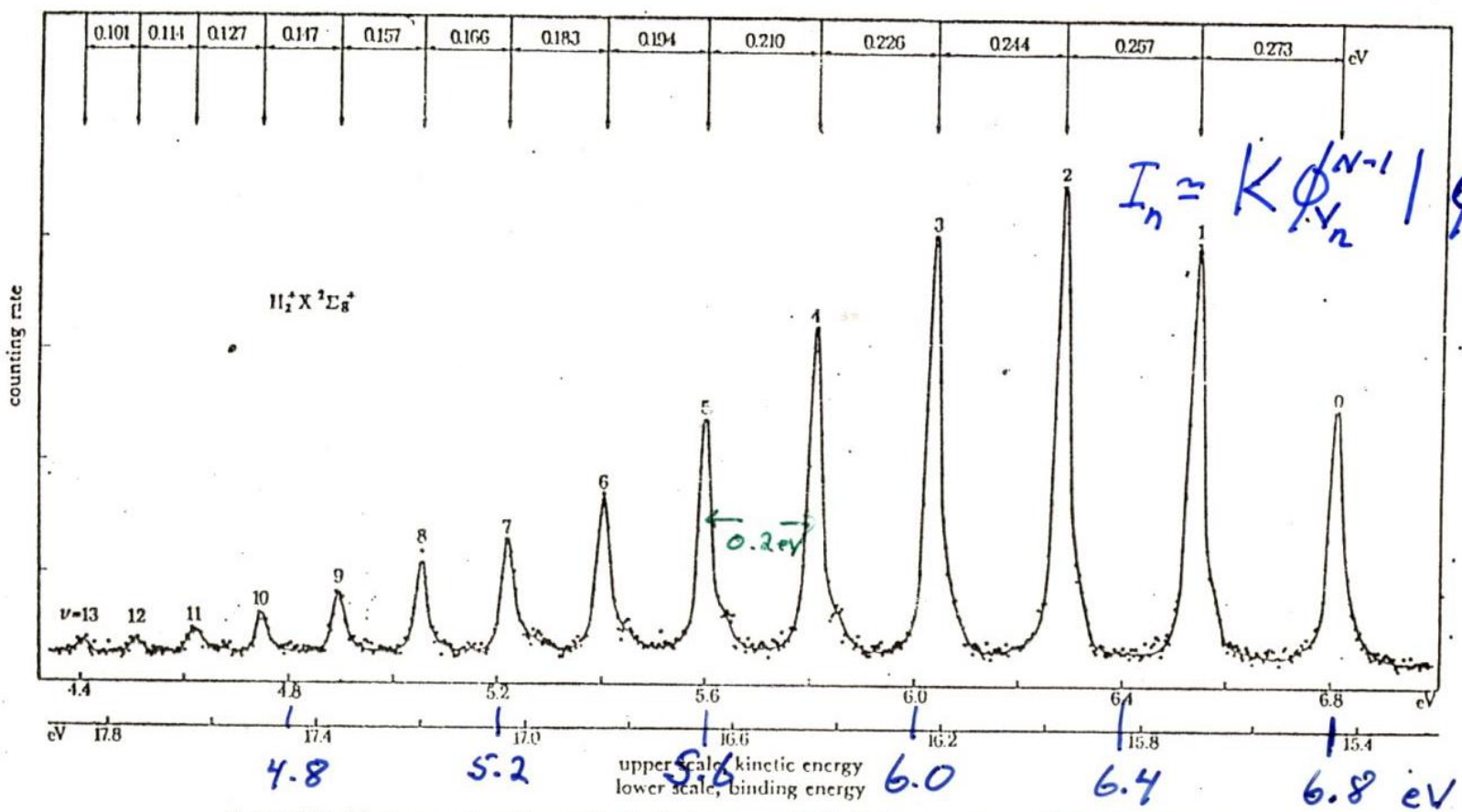


- Consider a single cryst
- Eigenstates have periodicity of the crystal
- Momentum (k) is a good quantum number
- Photon energy is low, long wave length, zero momentum change
- Energy conservation E(K)=e(k) +e(photon) , e(k) = band dispersion
- Momentum conservation K = k + G

One example of the many N-1 electron eigenstates which in this case result in Various numbers of vibrational excitations

The electrons in H2 are " dressed" with lattice molecular vibrations-phonons in solids

PES of H_2



$$I_n \simeq K \langle \phi_{v_n}^{N-1} | \phi_{v_g}^{N} \rangle^2$$

Fig 1.3

FIGURE 27a. Electron spectrum from molecular hydrogen, excited by helium resonance radiation. Fourteen peaks are seen which correspond to vibrational levels of the molecule ion.

K. SIEGBAHN

54

Electron removal spectral function for H2 molecular solid with large lattice spacing

- For large lattice spacing band width is zero.
- Sudden removal of an electron decreases the binding between the H atoms in a molecule causing an increase in the equilibrium bond length for He+ molecule.
- The N-1 electron eigenstates will involve the vibrational excitations of the H2+ molecule
- Energy conservation will result in the photoelectron exhibiting peaks including the possible vibrational excitations of H2+
- The intensity of each peak will be given by the overlap integral of the ground state H2 vibrational wave function with that of the vibrational eigenstates of the H2+ molecule.
- The lowest energy N-1 electron state will have a spectral weight of about 10% of the total which in a solid would mean a quasi particle weight of 10 reducing the band width by 10.
- The electron in the solid is dressed by Phonons resulting in a polaronic like state

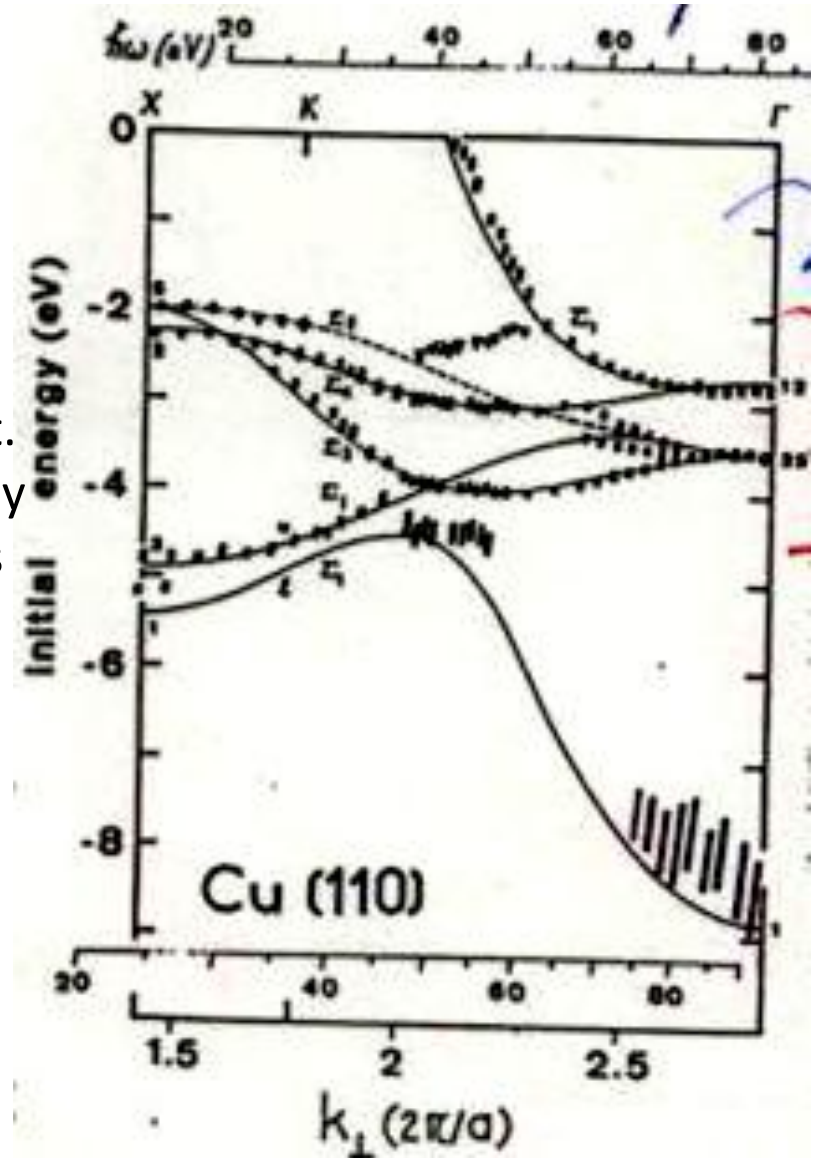
Andrea Damascelli will give a lecture in beginning of March I hope about angular resolved photoelectron.

Mona Berciu has agreed to give a lecture in the beginning of March as an introduction to electron phonon coupling in solids.

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

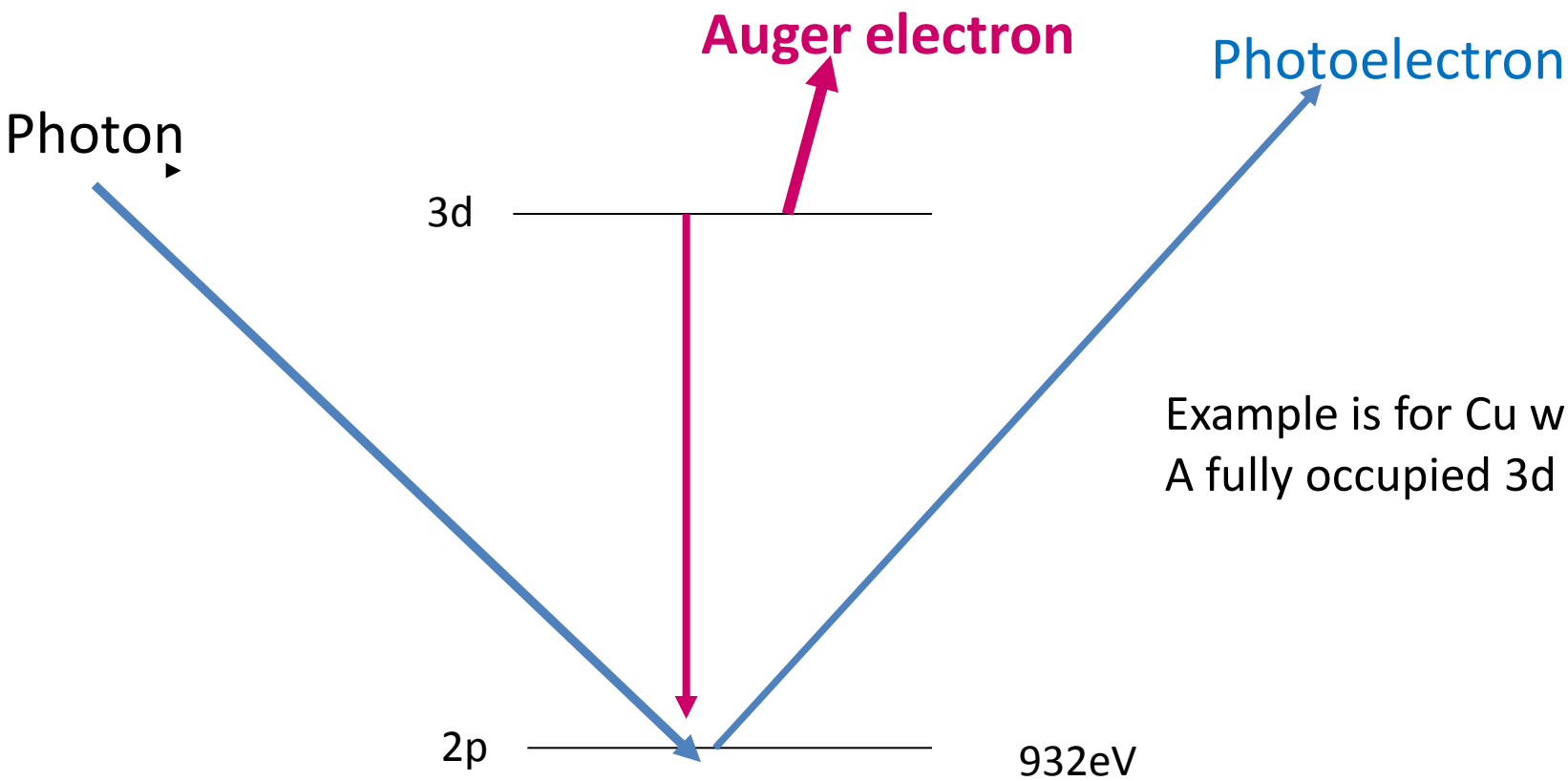


Points –exp.
Lines - DFT

3d bands

4s,4p,band

What if we remove 2- d electrons ?
Two hole state with Auger spectroscopy



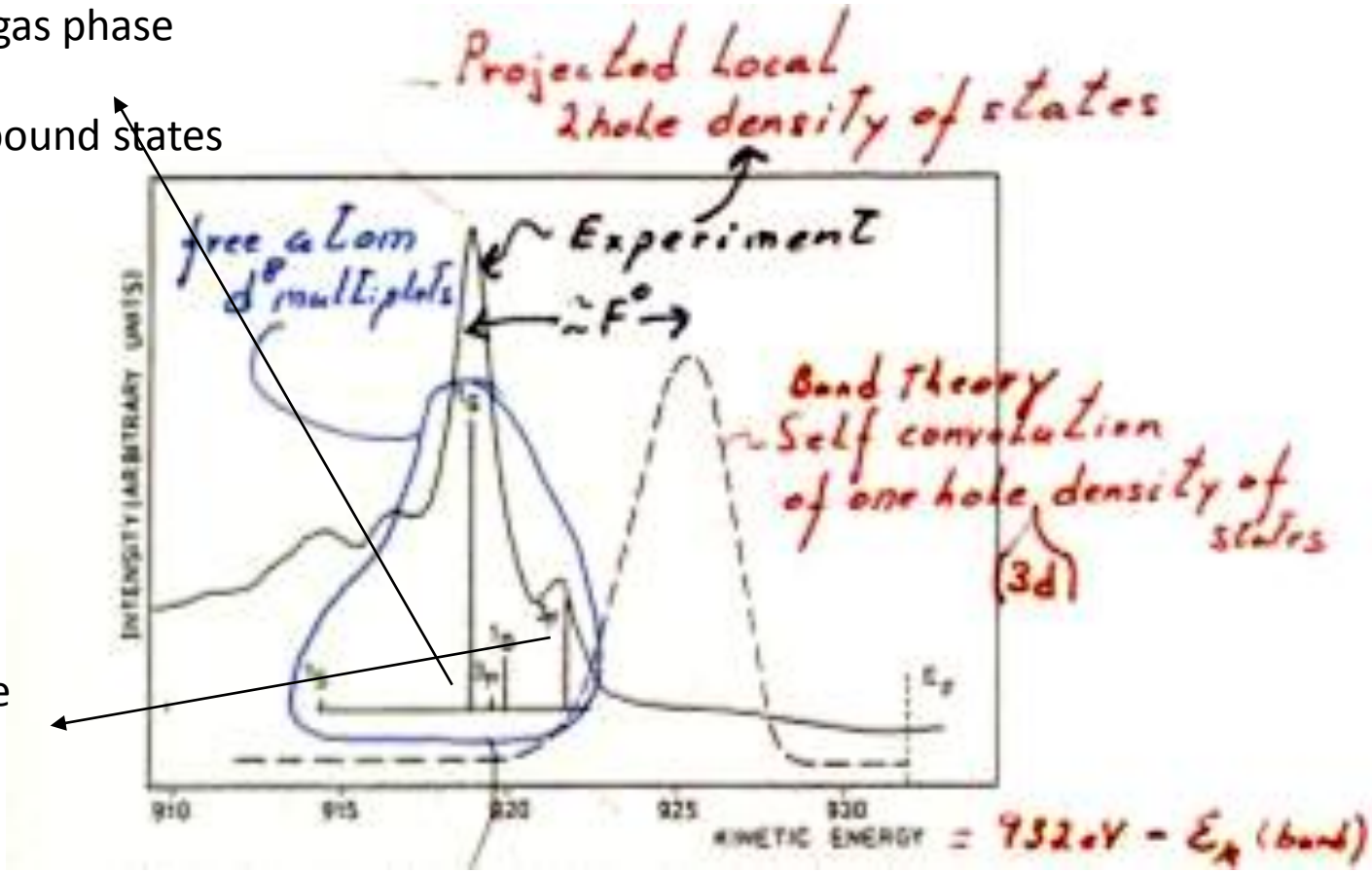
Example is for Cu with
A fully occupied 3d band

E(photon)-E(photoelectr) = E(2p) , E (2-d holes)= E(2p)-E(3d)-E(Auger)

U = E(2-d holes) -2xE(1-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 . Ef designates the postion of the Fermi level in the DFT .

Antonides et al 1977

Sawatzky **theory 1977**

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.

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 ½ 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>>W and in the presence of unfilled bands the one particle removal spectrum will be very different from that of a filled band

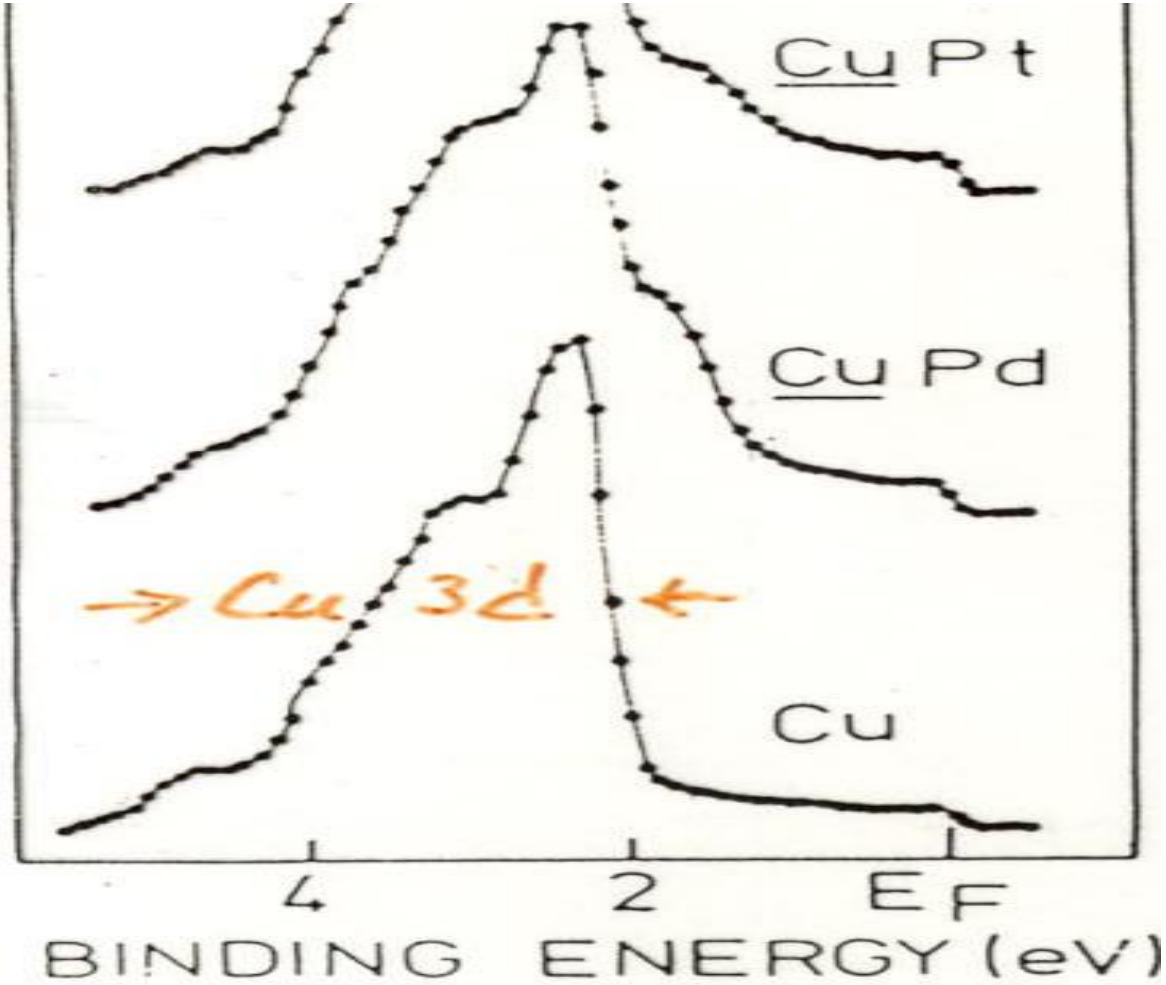
Compare the PES of Cu metal with a full d band to that of Ni with on the average 0.6 holes in the 3d band

Phtoemission from Full versus partly full 3d bands

- If the band is full as in Cu the removal spectrum of one electron leaves only one hole and one particle theory will work. This is why DFT band theory works so well for Cu.
- In Ni metal the 3d band is partly full as seen below. In this case things are more difficult since the atomic 3d occupation number fluctuates (quantum fluctuations) resulting from the band structure.

Lower fig shows the Cu Density of states as measured in angular Integrated photoemission spectroscopy

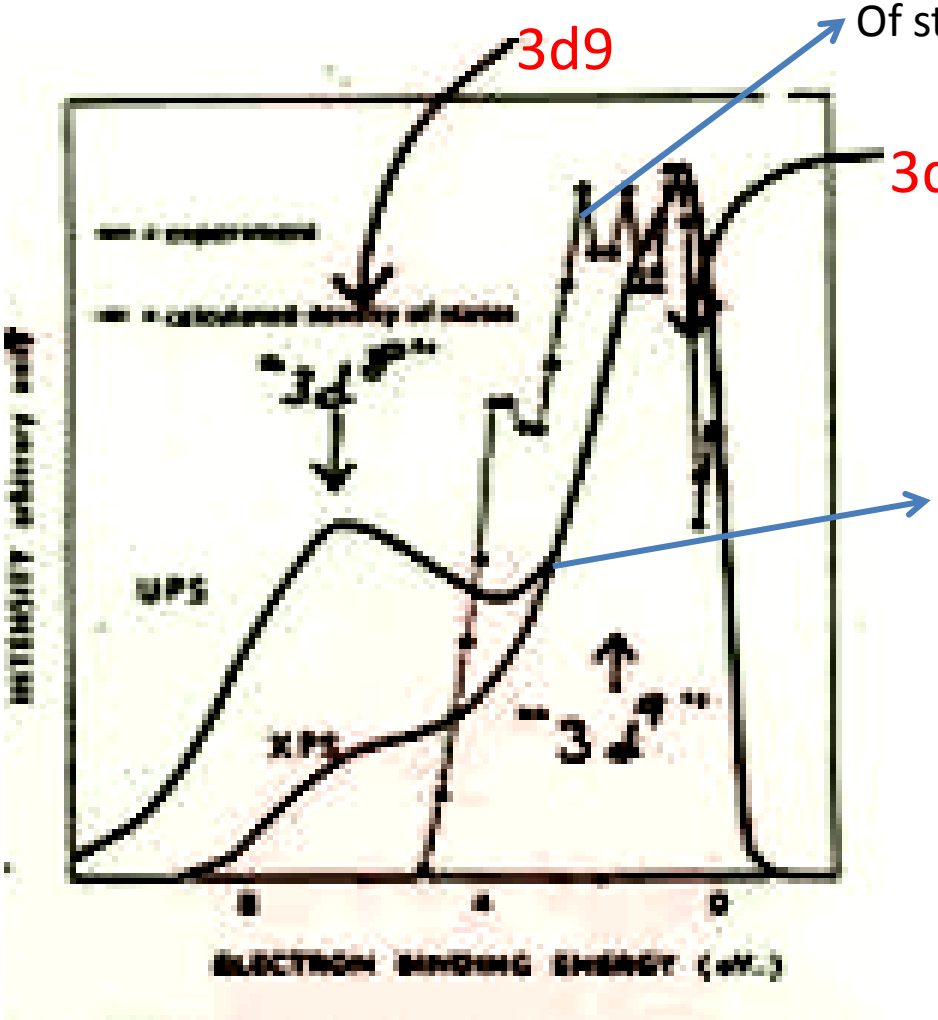
Density ofStates or Photoemission Intensity. The broad Band crossing Ef Is the Cu 4s " free Electron like band



Contrast Cu with Ni

- For Ni the 3d band crosses Ef. 3d states are in the limit R<D i.e. correlation if bands are not full or empty on average about 9.4 per atom.
- Snapshot picture of the local atomic d occupation
- d9 d10 d9 d9 d10 d10 d9 --------
- Removing a d electron yields states like d8 which involves U and d9 which does not
- We can expect two energy regions for d electron removal from Ni separated by about U in energy

Ni metal 3d density of states and phtoemission spectrum



DFT band theory density
Of states

Photoemission
spectrum of Ni metal
Depends on phtoton
energy

A Slater determinant of one electron Bloch states involves huge polarity fluctuations

- In band theory the probability that an atom has n d electrons (d states are 10 fold degenerate) is purely statistical i.e. not taking into account the huge energy differences with n due to the interactions.

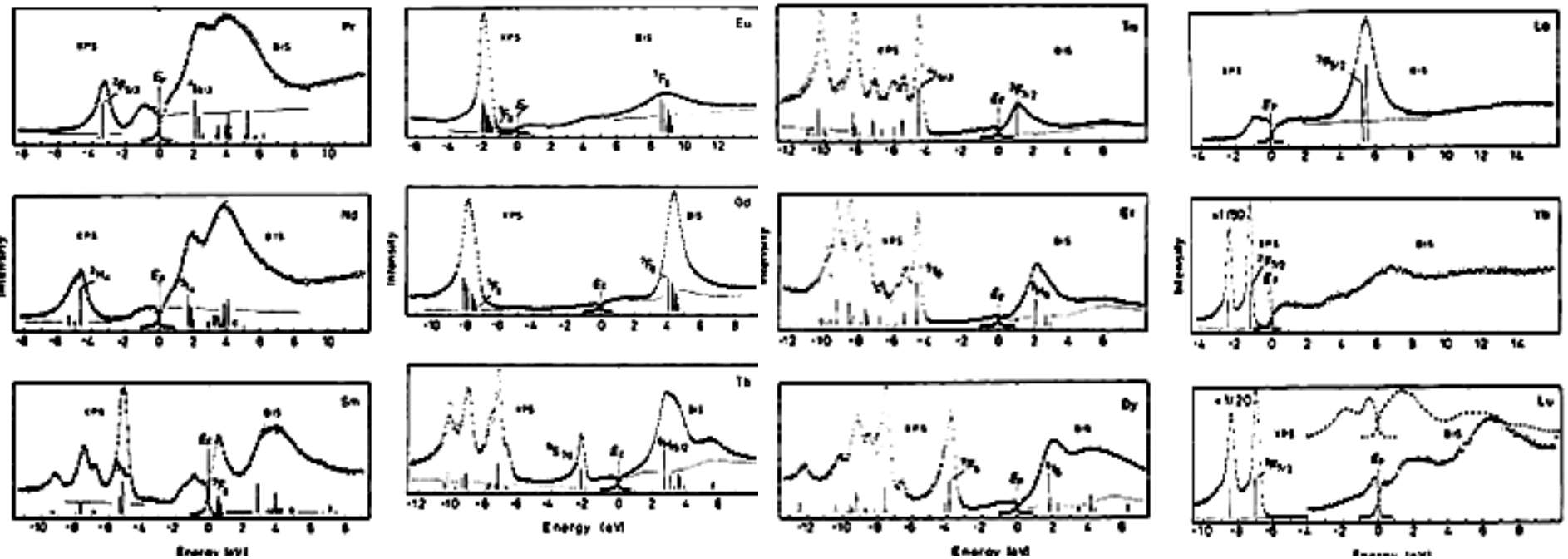
$$P(n) = \frac{m!}{(m-n)!\,n!} c^m (1-c)^{m-n}$$

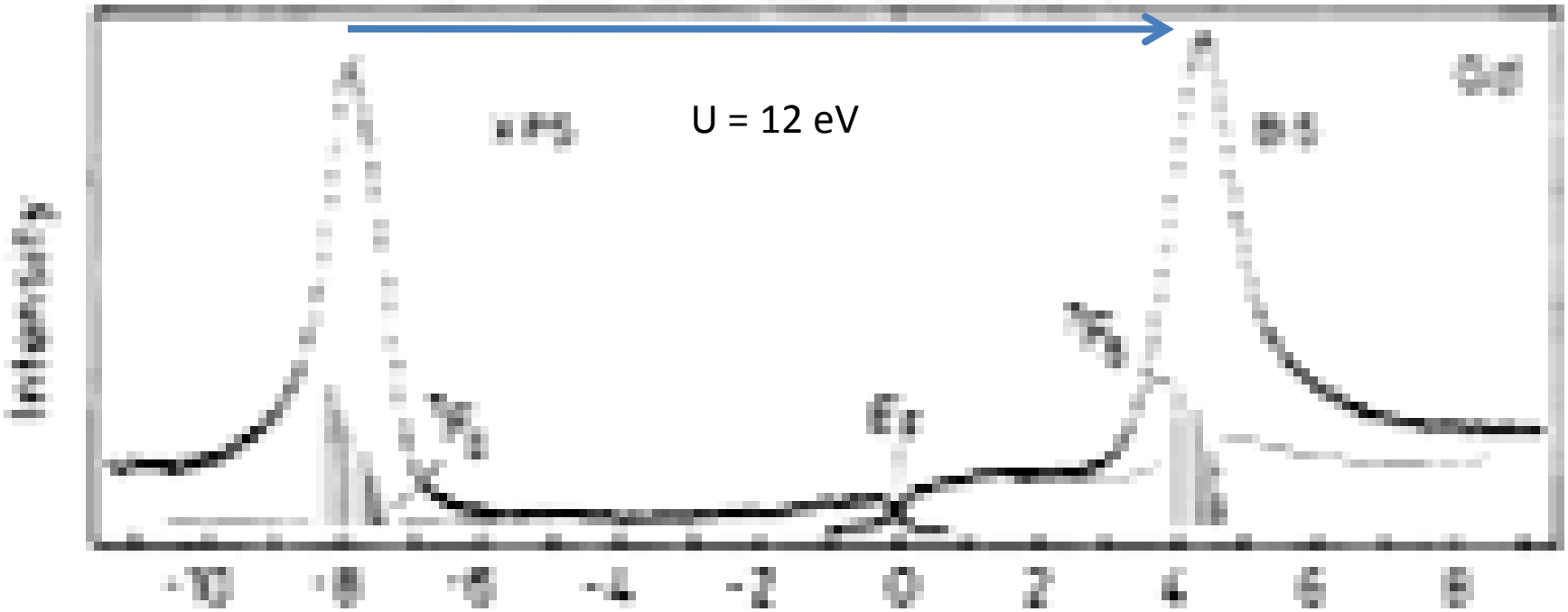
Where m=degeneracy, c is the Electron concentration =9.4 for Ni

- In real life of course fluctuations from the average cost coulomb energy so in actual fact the d occupation will be much more peaked about the average. This is why we consider Ni to have either d10 or d9 and not higher deviations from the average occupation i.e. U is large

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 Hunds' rule ground state


Pr
Eu
Tm
Lu
Nd
Gd
Er
Yb
Sm
Tb
Dy
Lu
Energy (eV)


U = 12 eV
Intensity
Gd

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 F0 integral.
- The multiplet splitting is very close to the atomic value little SCREENING OF THE HUNDS RULES INTERACTIONS I.E. SLATER F2,F4,F6 INTERACTIONS

. We will come back to this later.

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