

Challenges from experiment: Correlation effects and electronic dimer formation in Ti_2O_3



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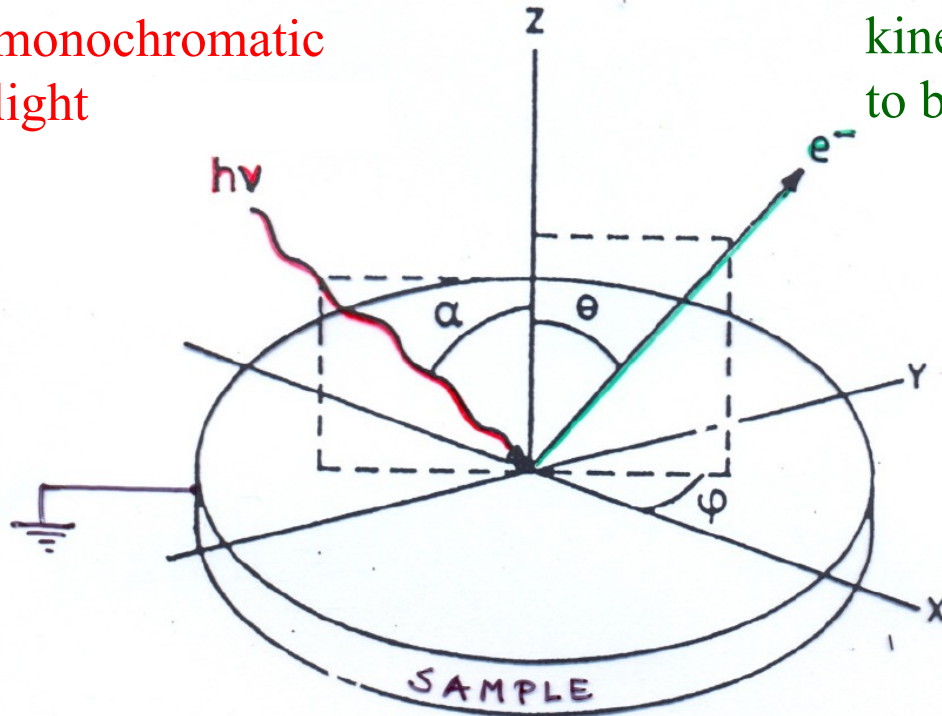
II. Physics Institute
University of Cologne
Cologne

Max-Planck-Institute
Chemical Physics of Solids
Dresden

Photoelectric effect:

monochromatic
light

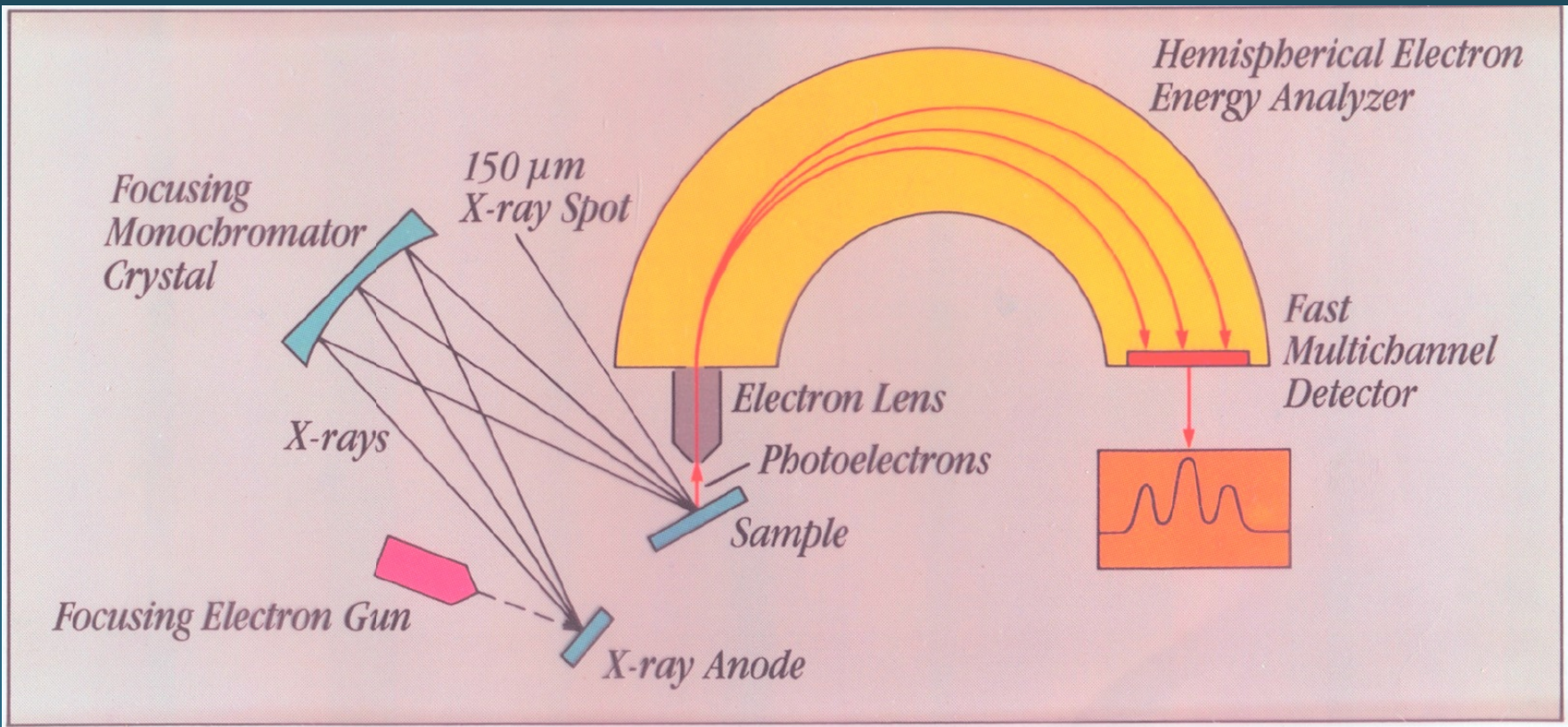
kinetic energy
to be analyzed



Conservation of energy:

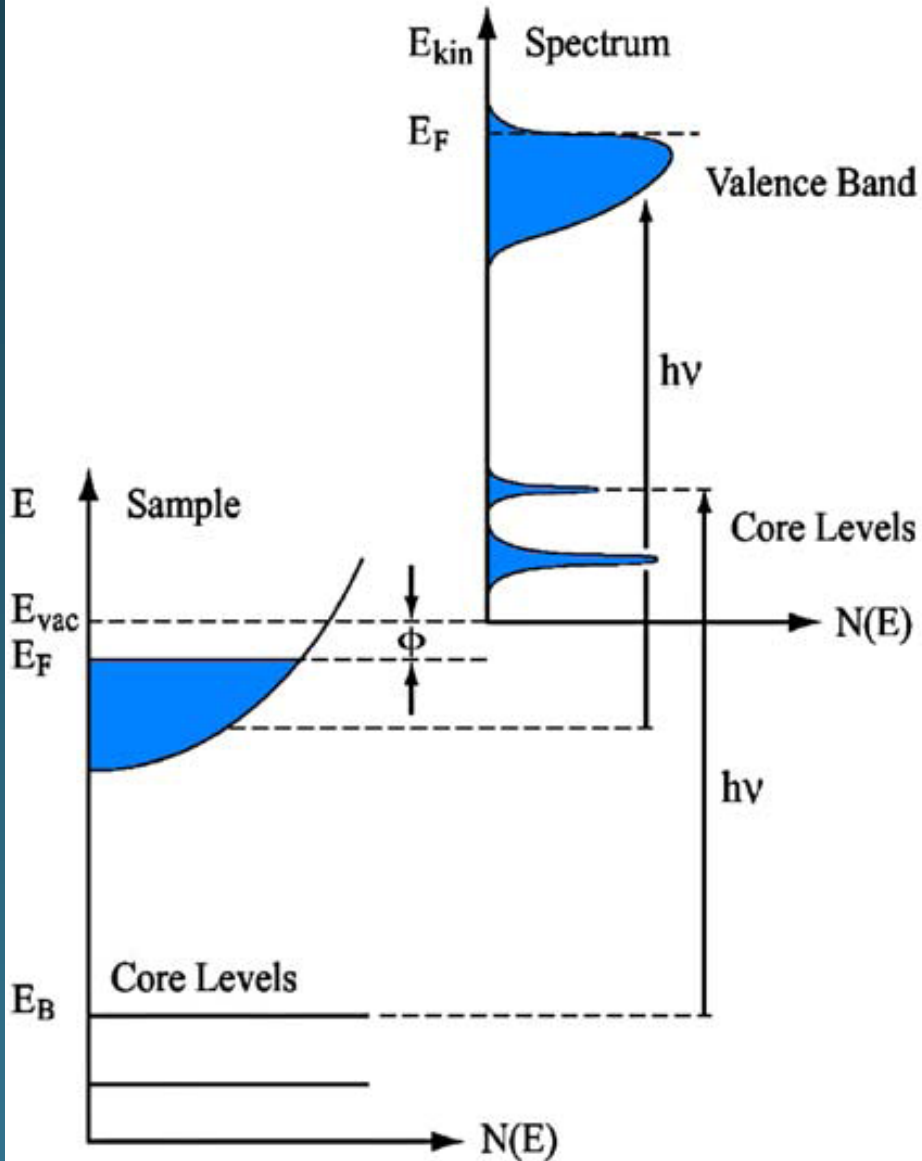
- near sample : $E_{\text{kinetic}} = h\nu - E_{\text{binding}} - \Phi_{\text{sample}}$

- near analyzer: $E_{\text{kinetic}} = h\nu - E_{\text{binding}} - \Phi_{\text{analyzer}}$

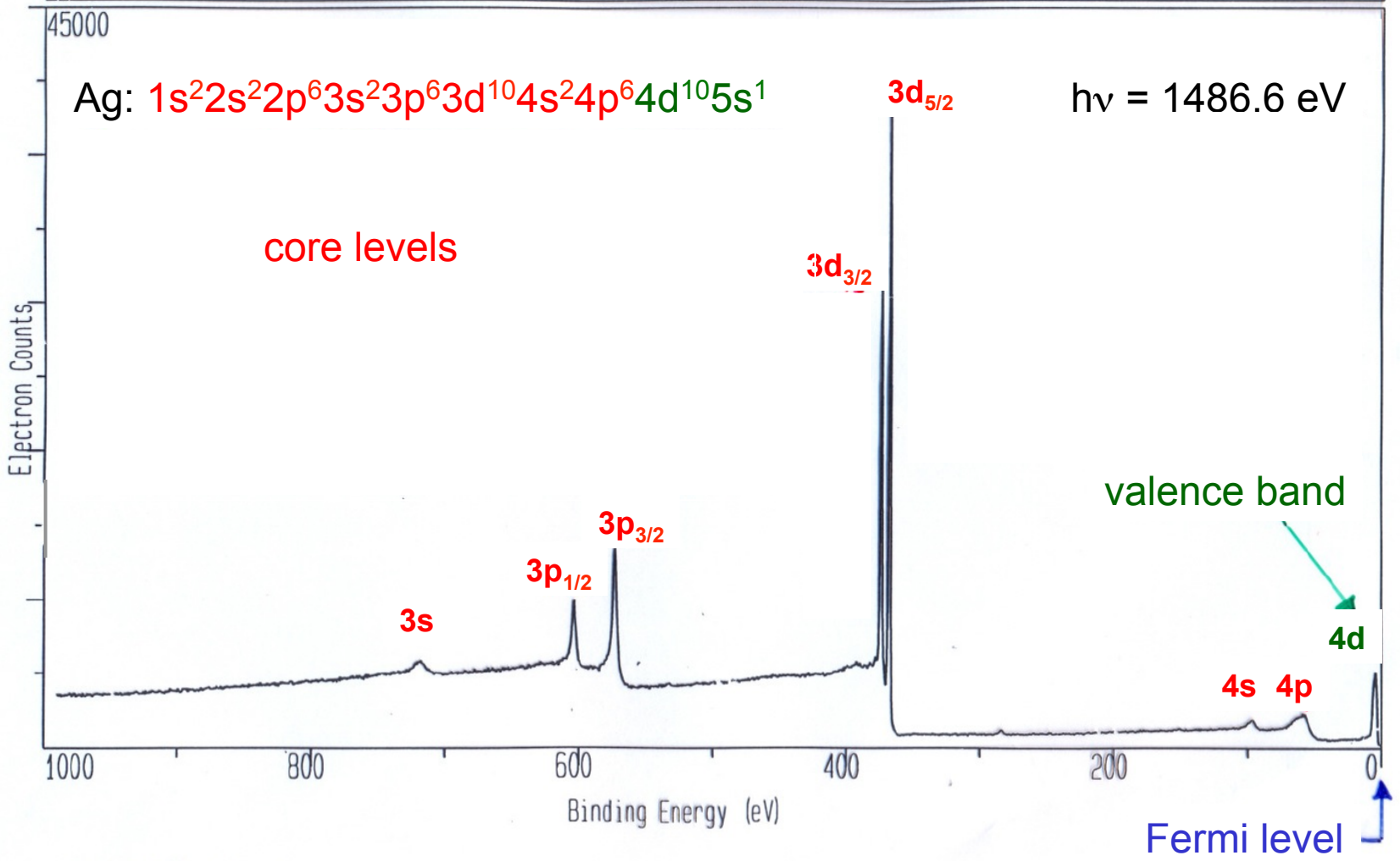


One-particle approximation

- Photoelectron Spectroscopy
 - “occupied” density of states
- Inverse Photoelectron Spectroscopy
 - “unoccupied” density of states

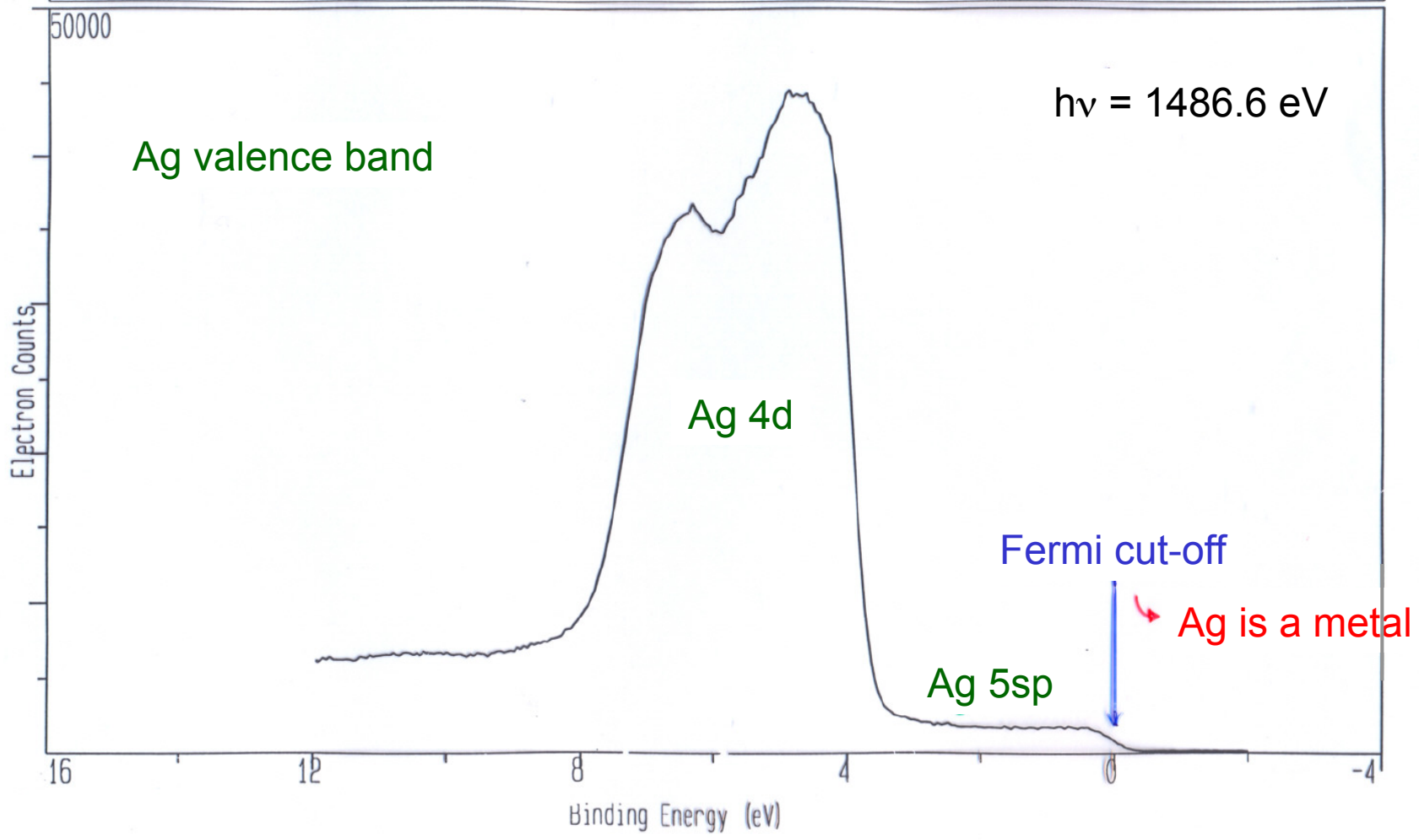


File: SX99Q279	Spot: 600	Flood Gun: Off	Data Points: 2001	Date: Nov 15 1999
Region: 1	Resolution: 4	Scans, Time: 1	Time/Point: 200	Operator: OR
Description: sputtered poly Ag Clean polycrystalline silver				

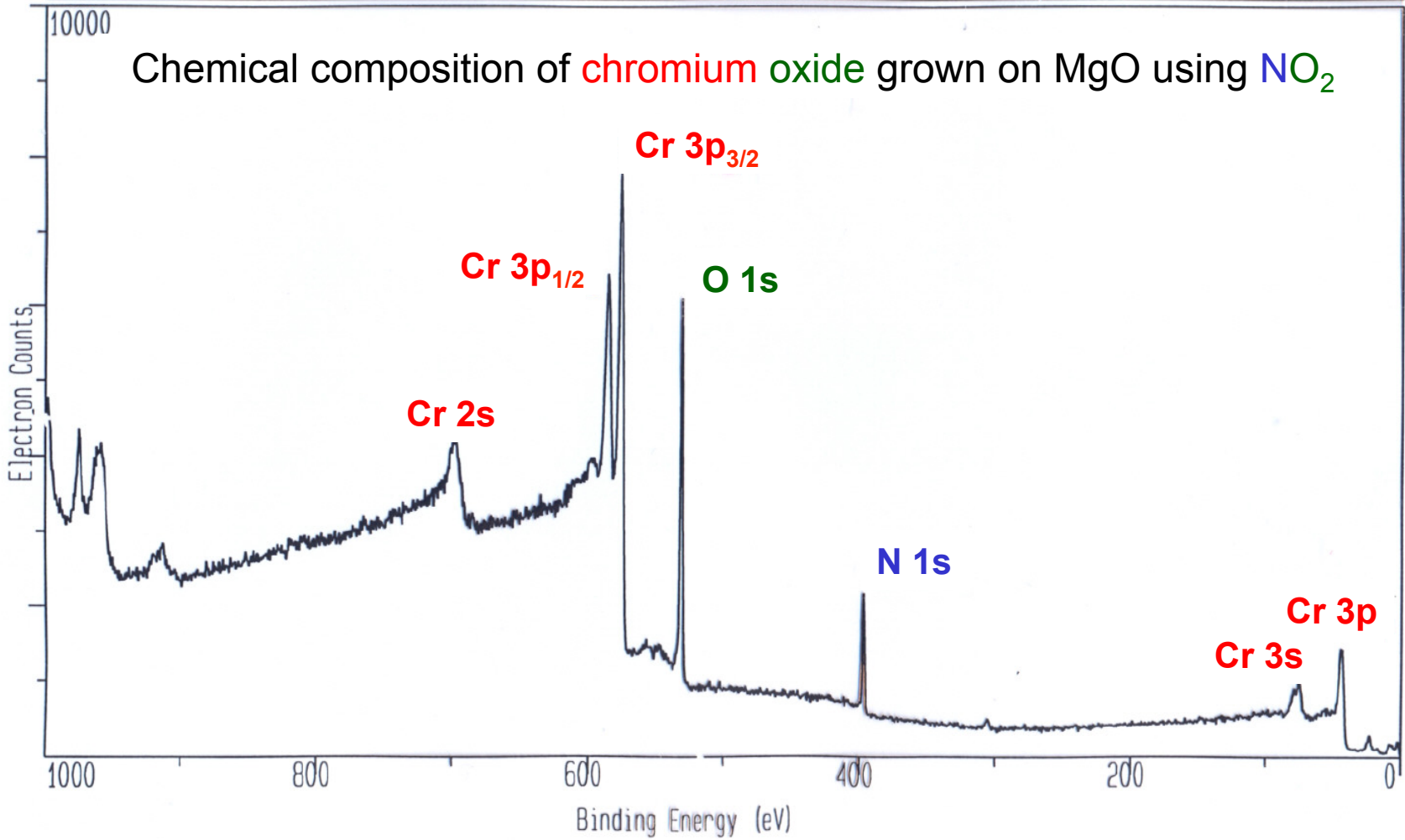


File: SX99Q281	Spot: 600	Flood Gun: Off	Data Points: 281	Date: Nov 15 1999
Region: 1	Resolution: 2	Scans, Time: 50	Time/Point: 200	Operator: OR

Description: poly Ag sputtered **Clean polycrystalline silver**



File: SX99Q330	Spot: 600	Flood Gun: 0.1	Data Points: 2801	Date: Dec 13 1999
Region: 1	Resolution: 4	Scans, Time: 1	Time/Point: 200	Operator: OR
Description: #24 CrO on MgO				



Chemical Environment

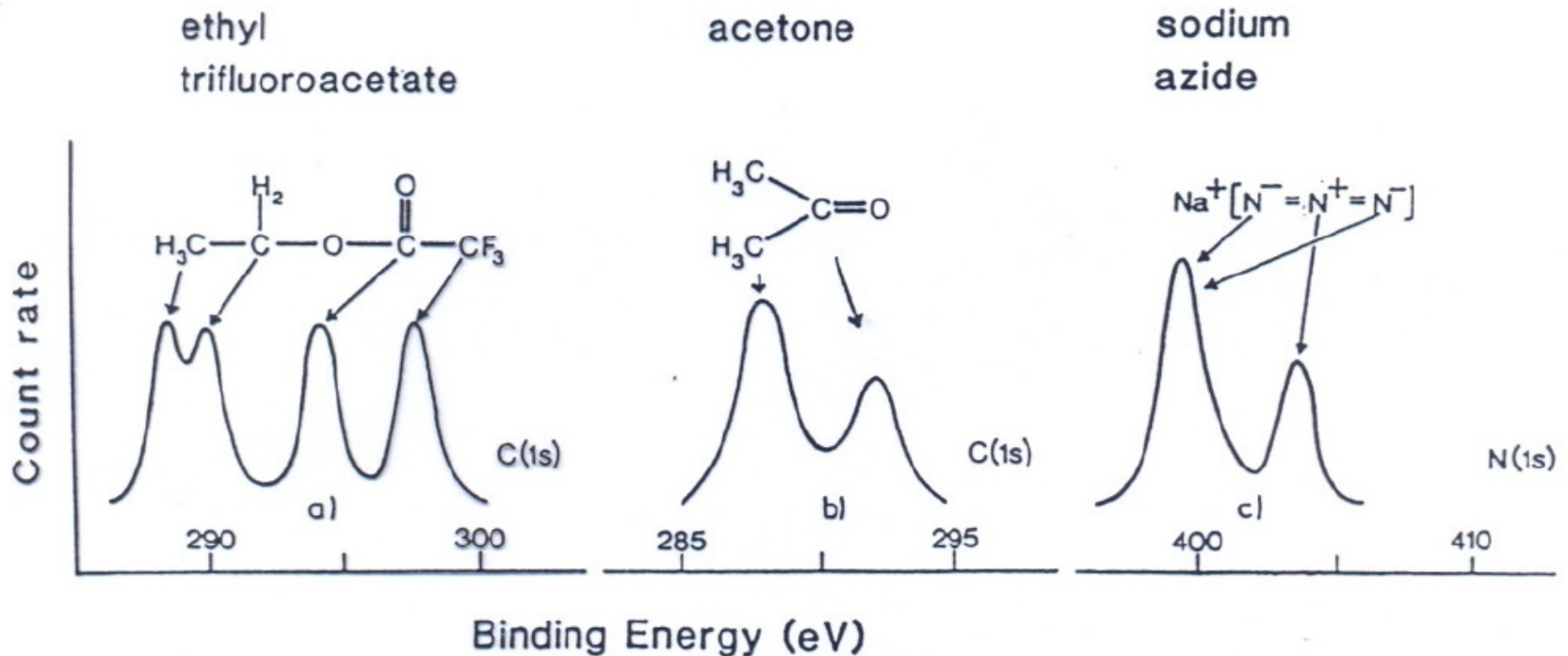


Fig.2.5. Chemical shifts for the C 1s levels in ethyl trifluoroacetate (a), and acetone (b), and the N 1s levels in sodium azide (c). Chemical shifts can be crudely related to electronegativity differences: The known [2.8] electronegativity differences (Δx) are C-H: $\Delta x = 0.4$, C-O: $\Delta x = 1.0$; C-F: $\Delta x = 1.5$, which rationalize the chemical shifts in ethyl trifluoroacetate [2.3]

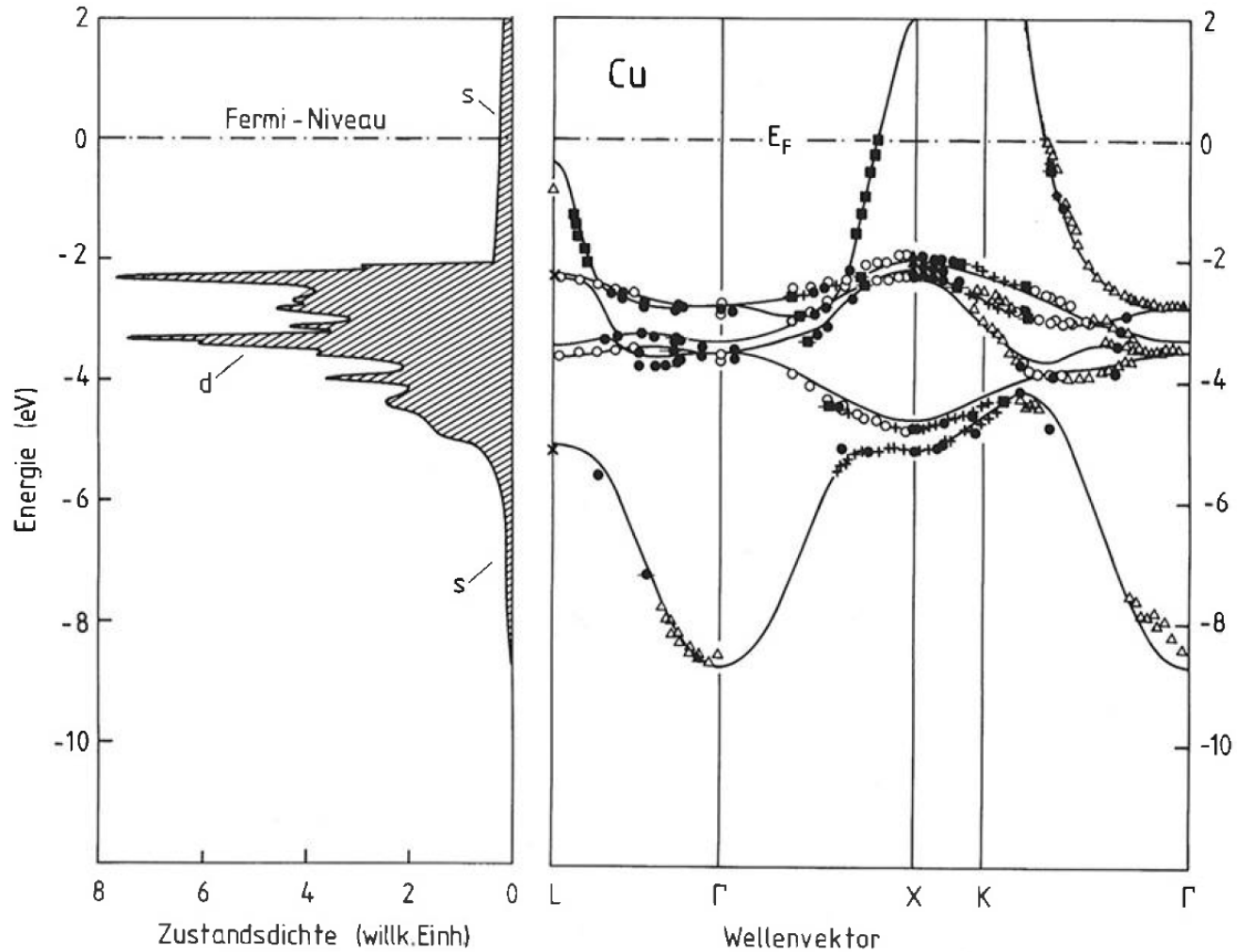
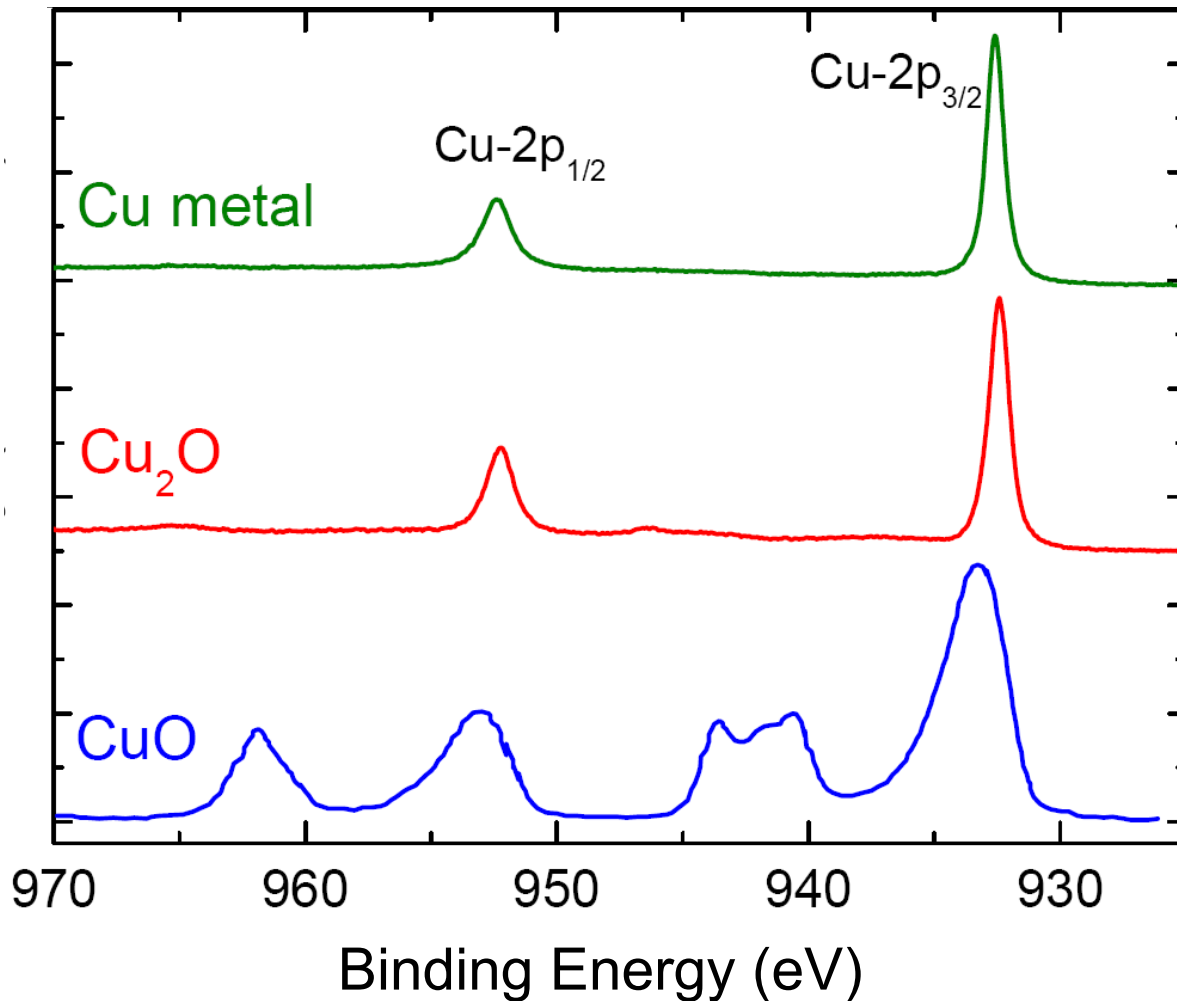


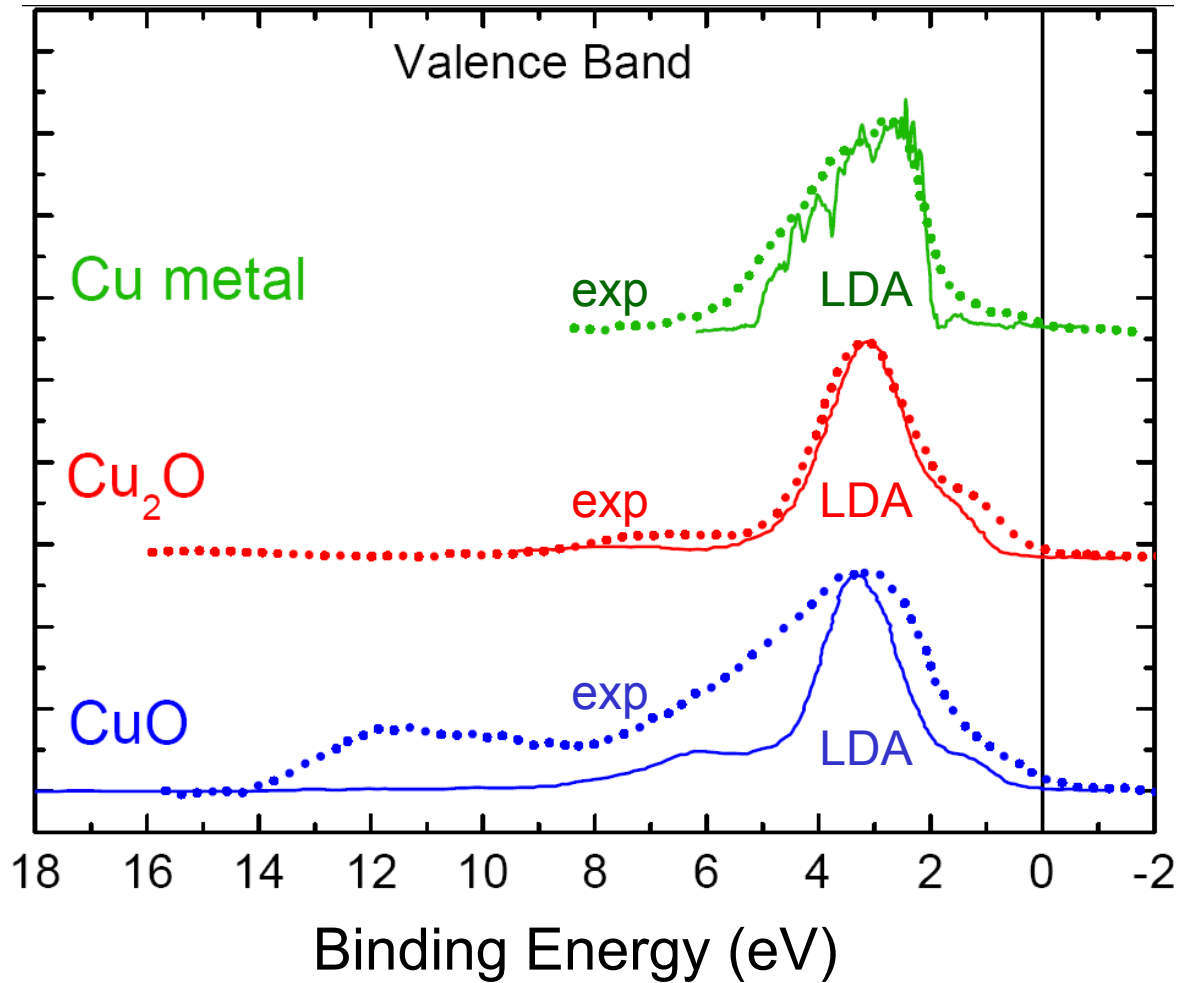
Abb. 7.12. Bandstruktur $E(k)$ längs Richtungen hoher Kristallsymmetrie für Kupfer (rechts). Die experimentellen Daten stammen von verschiedenen Autoren und wurden von Courths und Hüfner [7.4] zusammengestellt. Die ausgezogenen Linien des $E(k)$ -Verlaufes und die Zustandsdichte (links) wurden von Eckhardt et al. [7.5] berechnet. Bemerkenswert ist die gute Übereinstimmung sowohl der experimentellen Daten untereinander als auch die Übereinstimmung mit der Theorie

Can we understand the spectral lineshape ?



Why extra peaks in Cu 2p core level of CuO ?

Can we understand the spectral lineshape ?



Why extra high energy peaks in VB of CuO ?

The oxygen bands in a transition metal compound like NiO show in an actual experiment the expected dispersion, and the data reproduce very well the predictions of local density theory. However, the 3d experimental structure is a final state which is distinctly different from that calculated in local density theory for the Ni 3d-bands. It is a structure which is excitonic-like and has to be described by a molecular orbital theory in first approximation where the dispersion can be put on as a small perturbation. Therefore the interpretation of the spectra of a system like NiO has to follow the lines which have been found for the rare earths materials [9]. There also one has 5d bands of considerable widths which are described well by local density theory, whereas the 4f excitations are better described by a local approach.

This does not mean a break down of local density theory. It rather signals that photoemission produces for the excitation out of the 3d band, final states, which still are highly excited and therefore are so distinctly different from the ground state 3d bands that it is inadequate to compare the measured dispersion curves with those calculated in a local density approach. Rather it looks that one has to start out from a local model like the cluster approach and then add on the dispersions which probably will only amount to a few tenths of an eV at best. In this sense for the interpretation of the photoemission spectra of NiO a hybrid model [21] has to be applied in the same way as it was used so successfully for rare earth systems.

We note that similar observations can be made for CoO [17, 35] and NiI₂ [18]. Again the 02p and 14p derived bands show large dispersions and are favourably compared with the results of band structure calculations. In contrast the 3d derived photoemission features, which should not be confused with the initial state d-bands, have little dispersion and are shifted closer to the p-bands as expected for these excitonic states.

True !

These are incorrect statements:
“ground state d-bands“
is an invalid concept !!

This is an incorrect statement:
“initial state d-bands“
is an invalid concept !!

The discussion about the cause of the insulating nature of NiO (and related compounds) has unfortunately been obscured by argument about terminology [17]. Therefore a few very simple statements seem to be appropriate. Because of the translational symmetry of a crystal, and the very nature of the wavefunctions of the ions from which they are made up the electronic states in a crystal are bands with a nonzero dispersion [38]. It is a different question whether a particular experimental technique like photoemission spectroscopy is able to measure these bands. Applied to NiO this means that it is established from very simple principles [38], that the electronic states of these materials are bands and it is known that the broad *p*-bands exhibit their dispersion in photoemission experiments while the more narrow *d*-bands cannot be mapped by this technique.

One may argue that a band structure that cannot be measured by photoemission spectroscopy is not meaningful and that the *d*-bands as measured by this technique (Fig. 8, and [17, 18, 34, 35]) are the real ones and that the discrepancy evident in Fig. 8 is due to a failure of local density theory. While we can not dismiss this argument in total, we think that the evidence is more against than for it. The measurement of the ground state band structure of a localized system (like *d*-electrons in NiO or *4f* electrons in rare earth compounds) is hampered by the fact, that within the time scale of the experiment not enough charge can be provided by the crystal in order to screen out the hole to a degree, that makes it look similar to the initial state. However, thermodynamic experiments sample this band structure (although in a more indirect way) and the activation measurements seem to be in agreement with the energy level diagram in Fig. 2 substantiating the reasoning behind it [21-25]. Also the data in Figs. 1 and 4, which show the d^8L^{-1} state at 2 eV below E_p , indicate the excitonic nature of the excited state and the thermodynamics that pin the Fermi energy to the ground state band structure at the top of the valence band.

This is an incorrect statement:
“ground state d-bands“
do not exist and
can therefore not be measured

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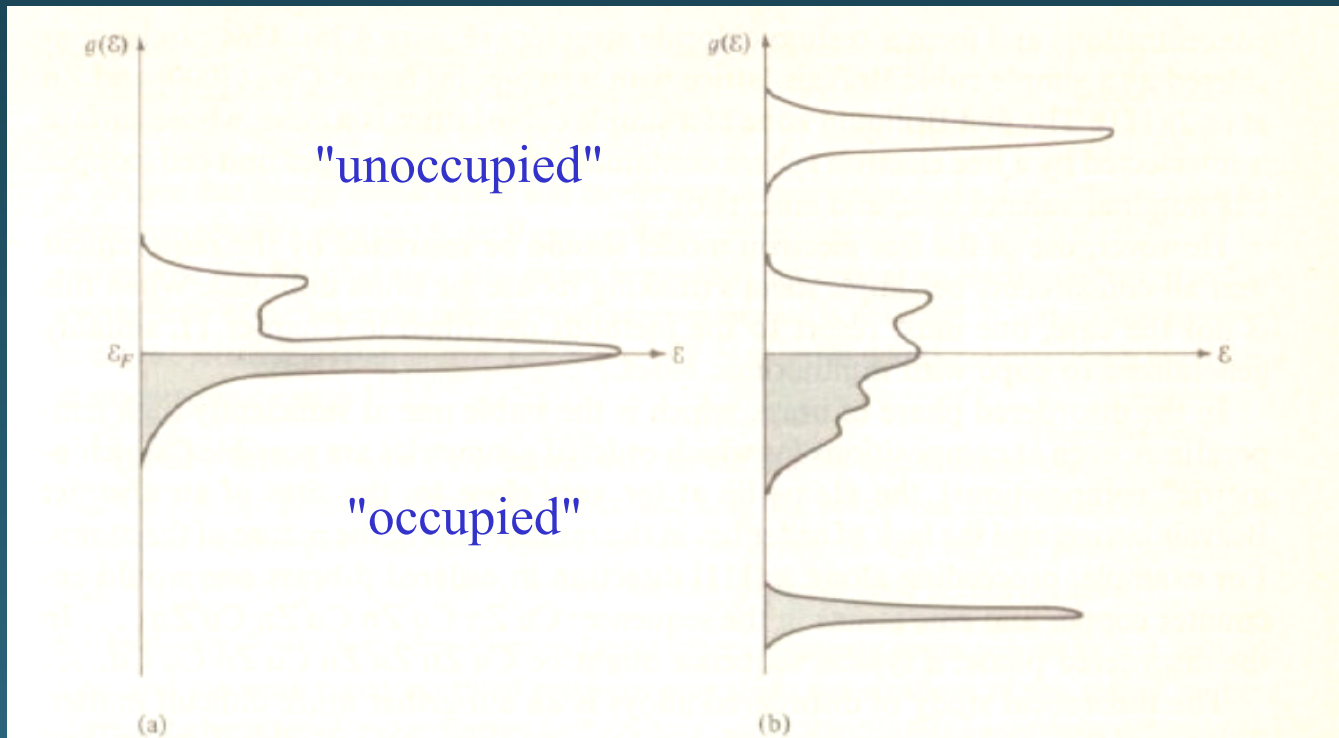


Figure 15.20

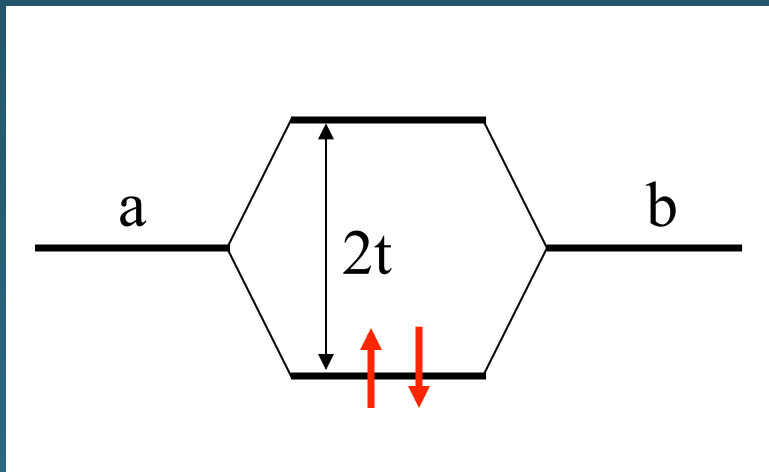
Two hypothetical level density curves for a rare earth metal. (a) The incorrect form, which naively superposes on a fairly broad s - p - d band a sharp f -band peak, at the Fermi energy. (b) The partially correct form, which has a fairly broad s - p - d form in the neighborhood of the Fermi energy, and two f -band peaks, one well below and one well above the Fermi energy. The most realistic point of view probably abandons the independent electron approximation (and hence the possibility of drawing simple one-electron densities of levels) for the $4f$ electrons.

Photoelectron spectroscopy and correlated systems

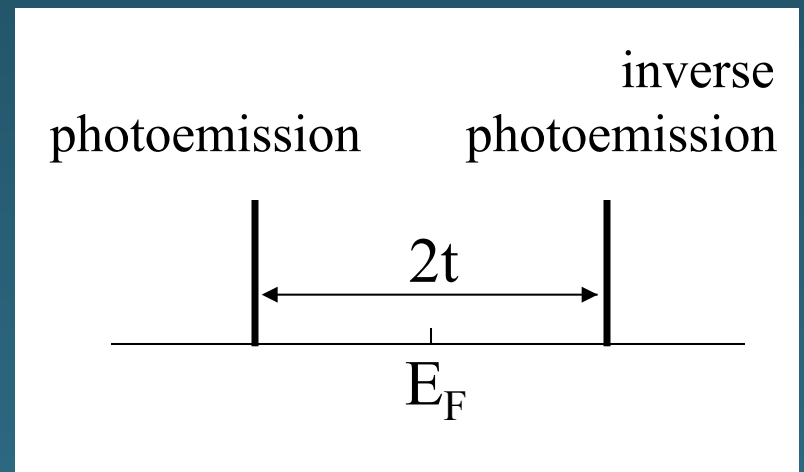
H₂ molecule model

one-electron approximation

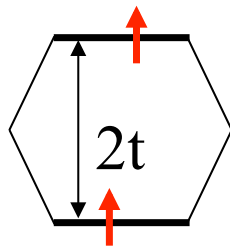
energy level diagram



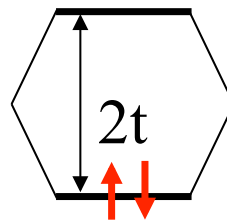
spectrum



triplet



singlet



$$E_t - E_s = 2t$$

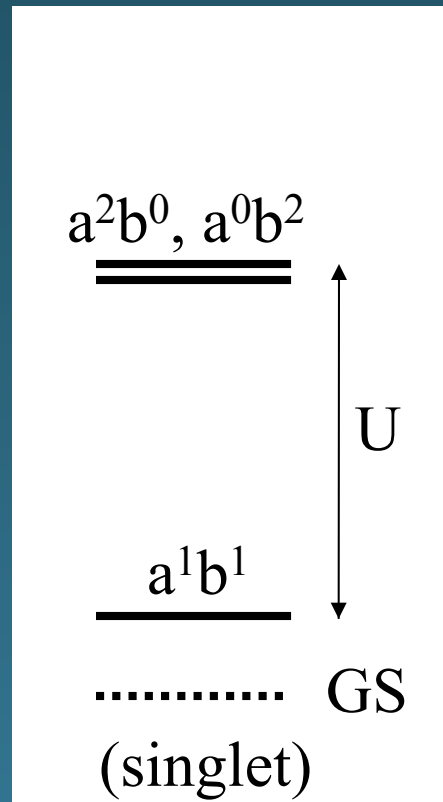
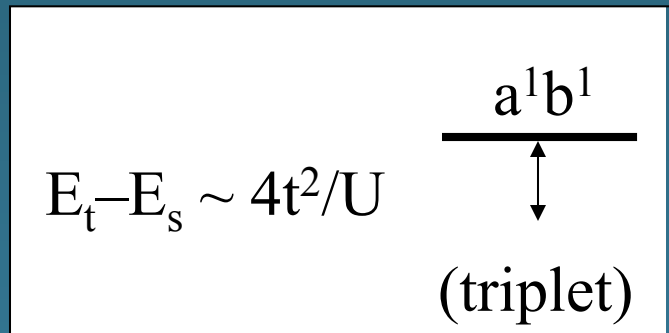
too large !!

H₂ molecule model

Hubbard model

total energy level diagram

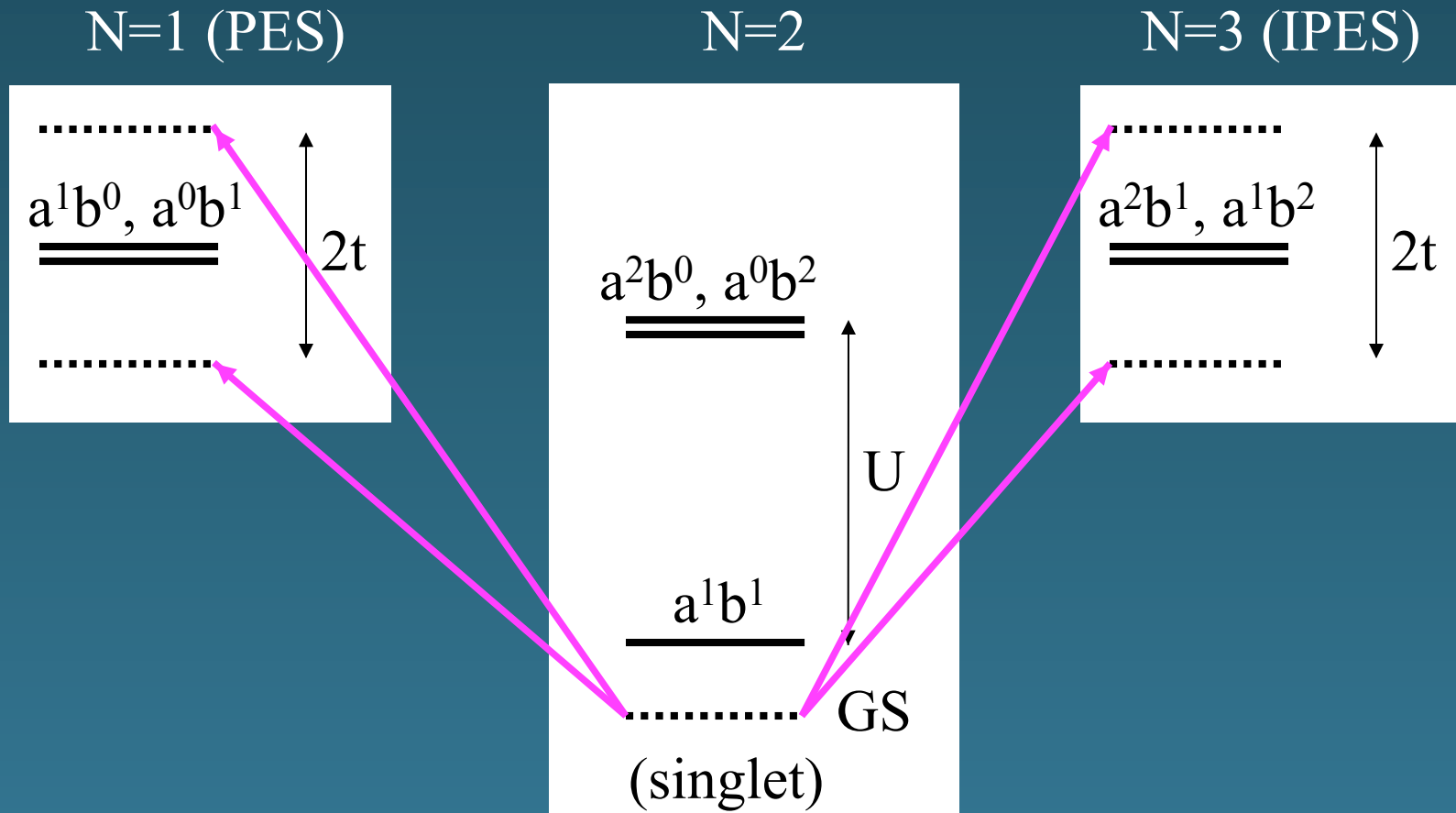
N=2



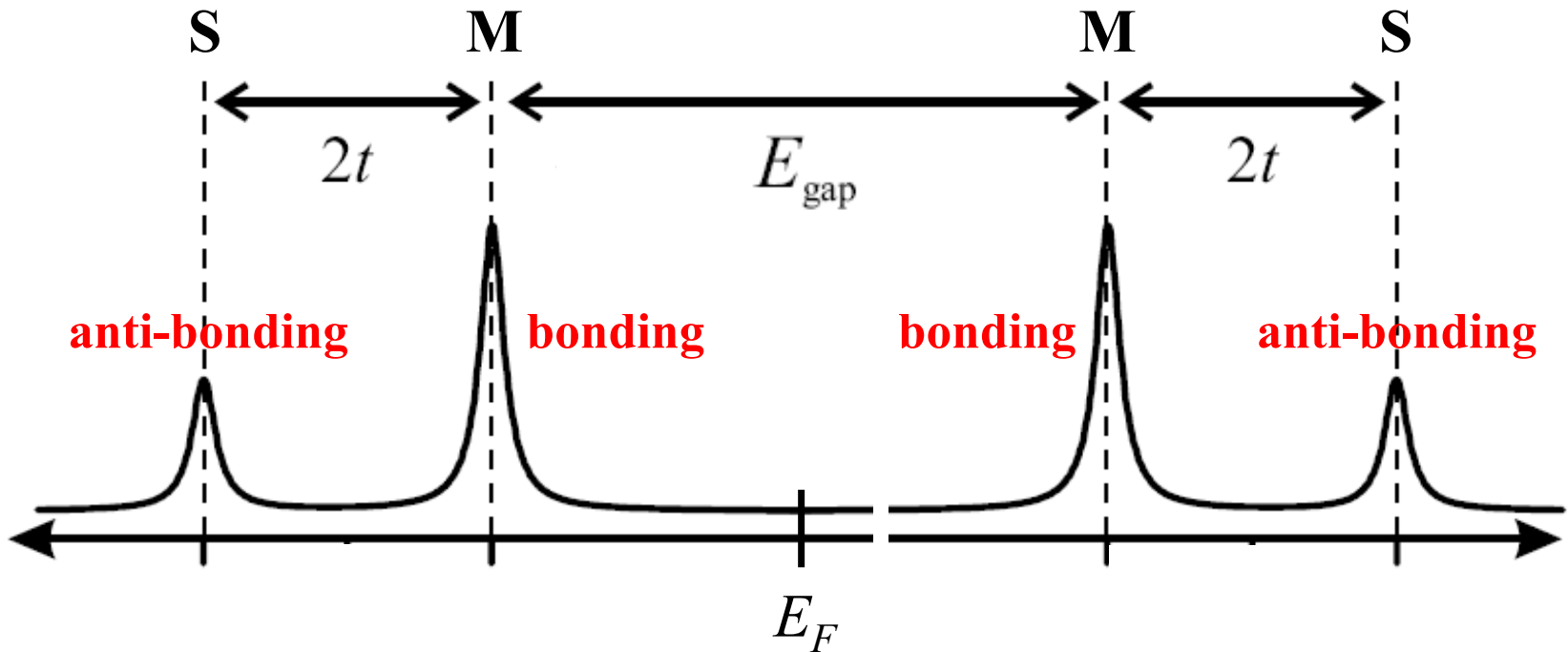
H₂ molecule model

Hubbard model

total energy level diagram

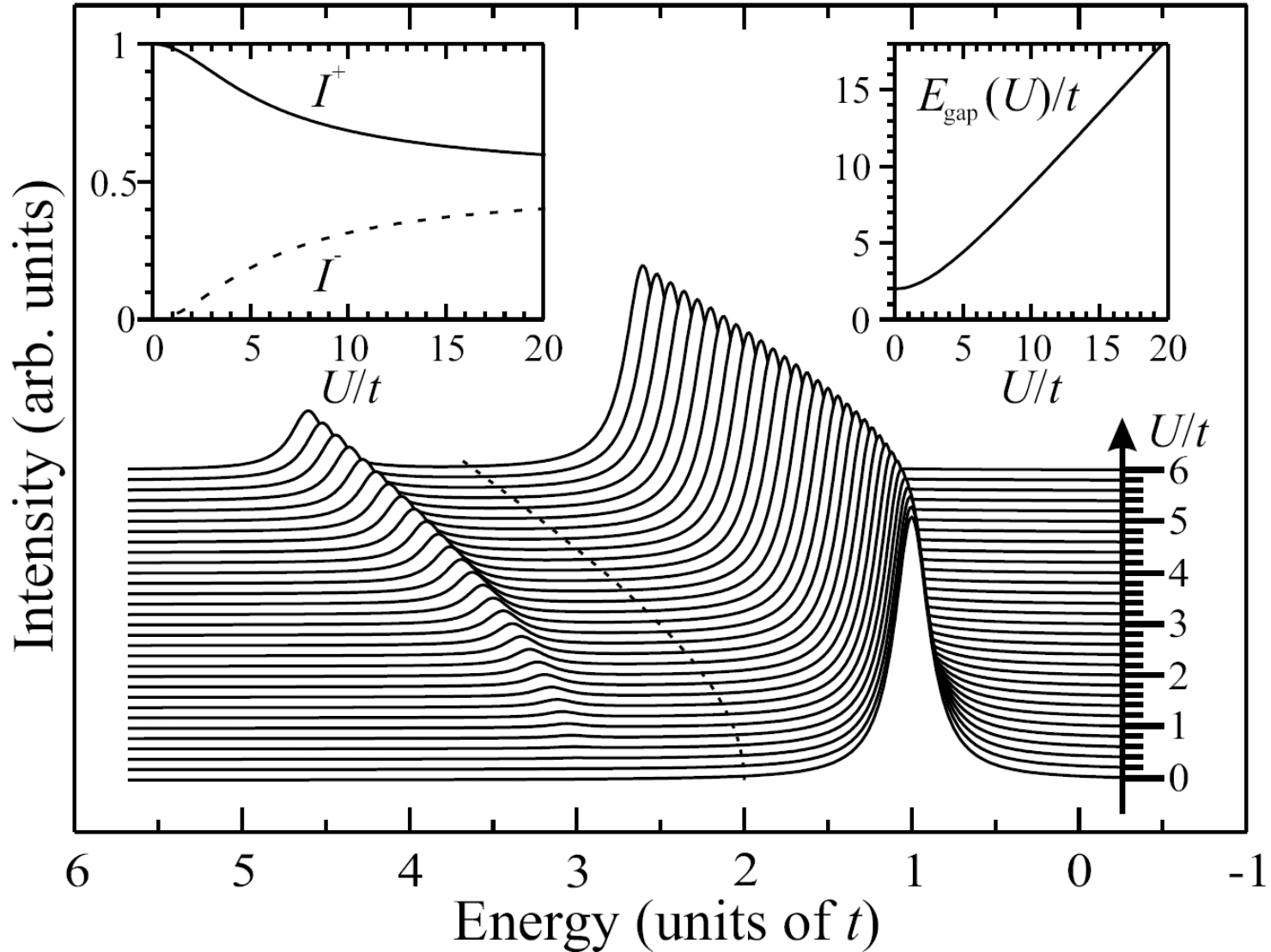


H₂ molecule model : *Hubbard model*



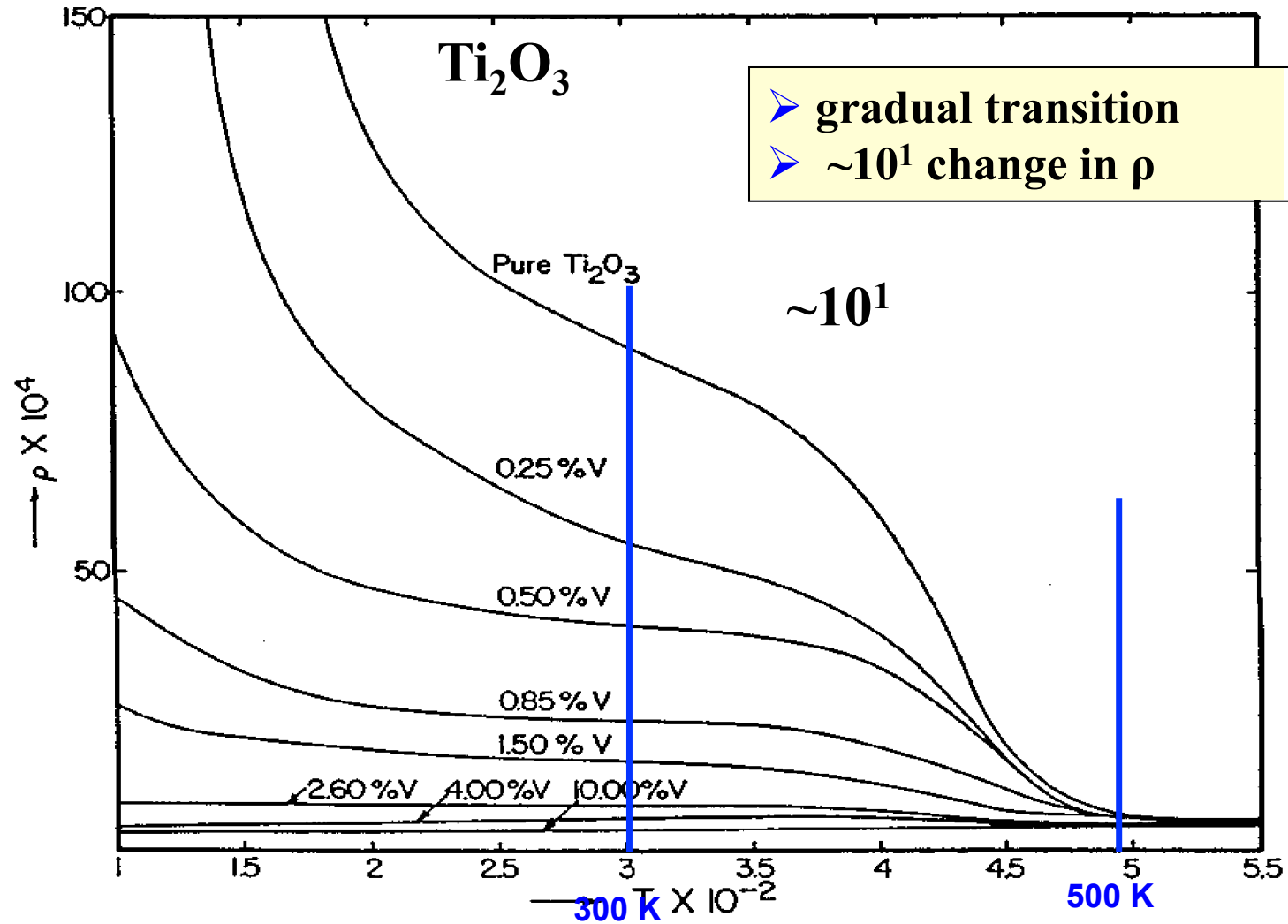
$$E_{\text{gap}} = \sqrt{U^2 + 16t^2} - 2t$$

H₂ molecule model : *Hubbard model*



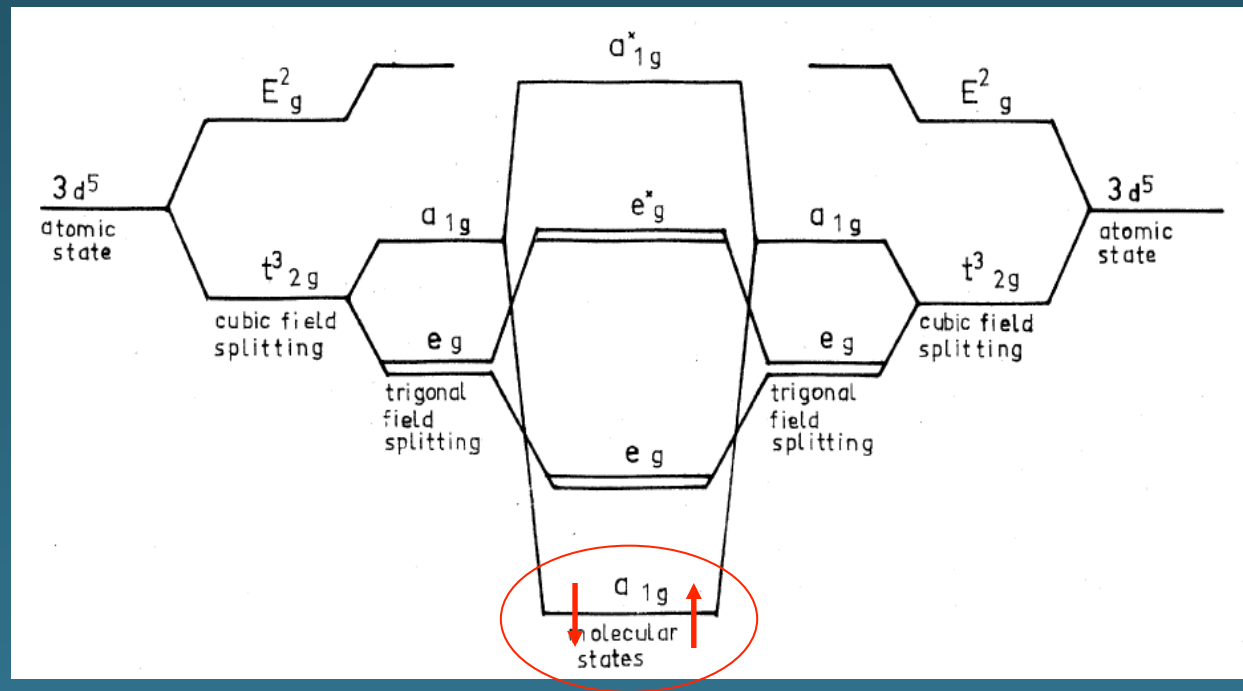
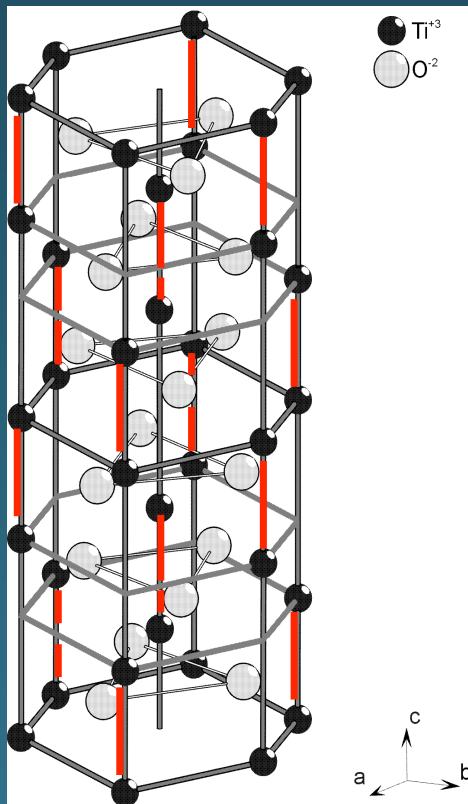
Example: Ti_2O_3
electronic structure and dimer formation

Metal-Insulator-Transition in Ti_2O_3



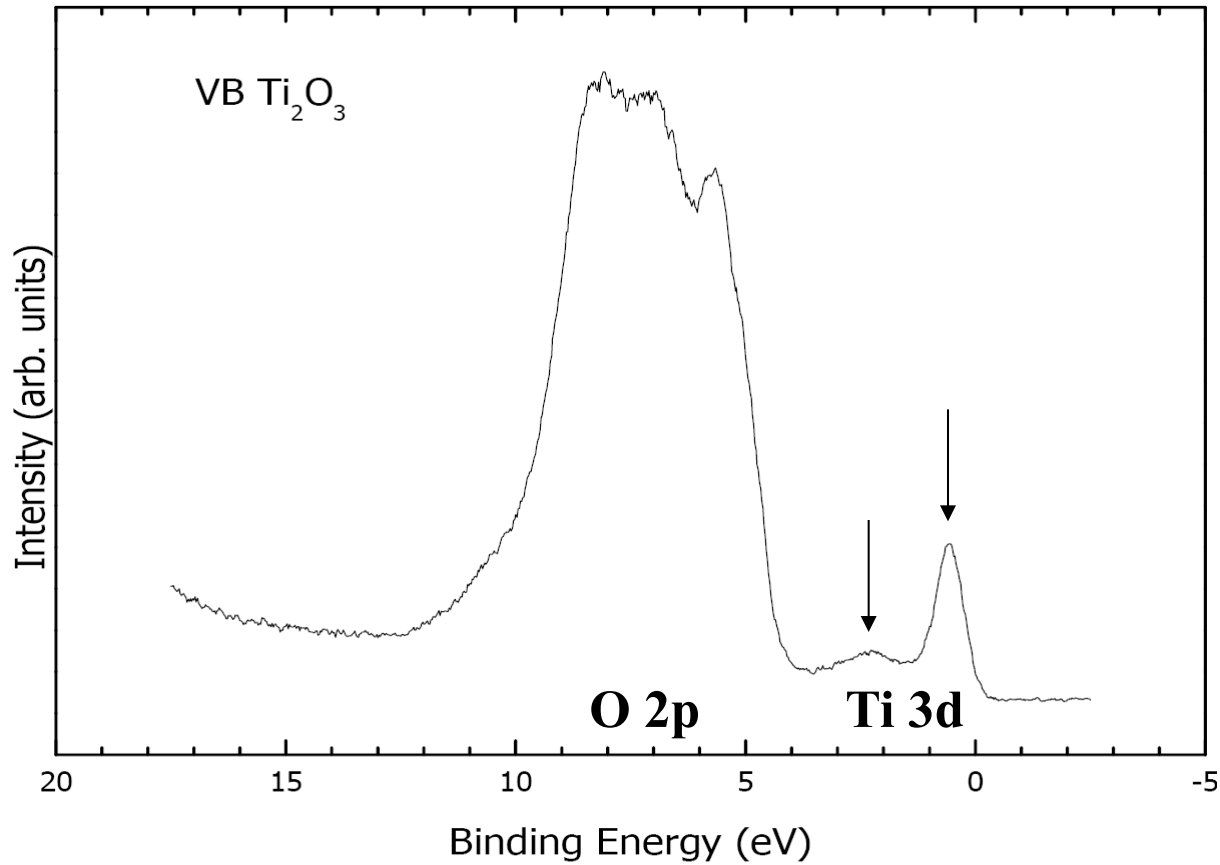
c-axis dimer Ansatz for Ti_2O_3

- Ti^{3+} : $3d^1$, $S=1/2$
- Ti^{3+} - Ti^{3+} pairs : a_{1g} molecular singlet formation \rightarrow effectively $S=0$



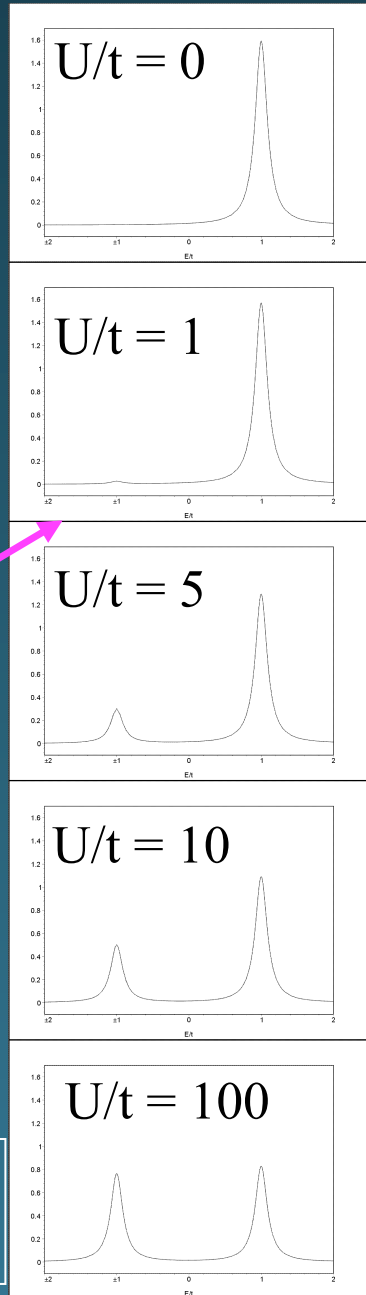
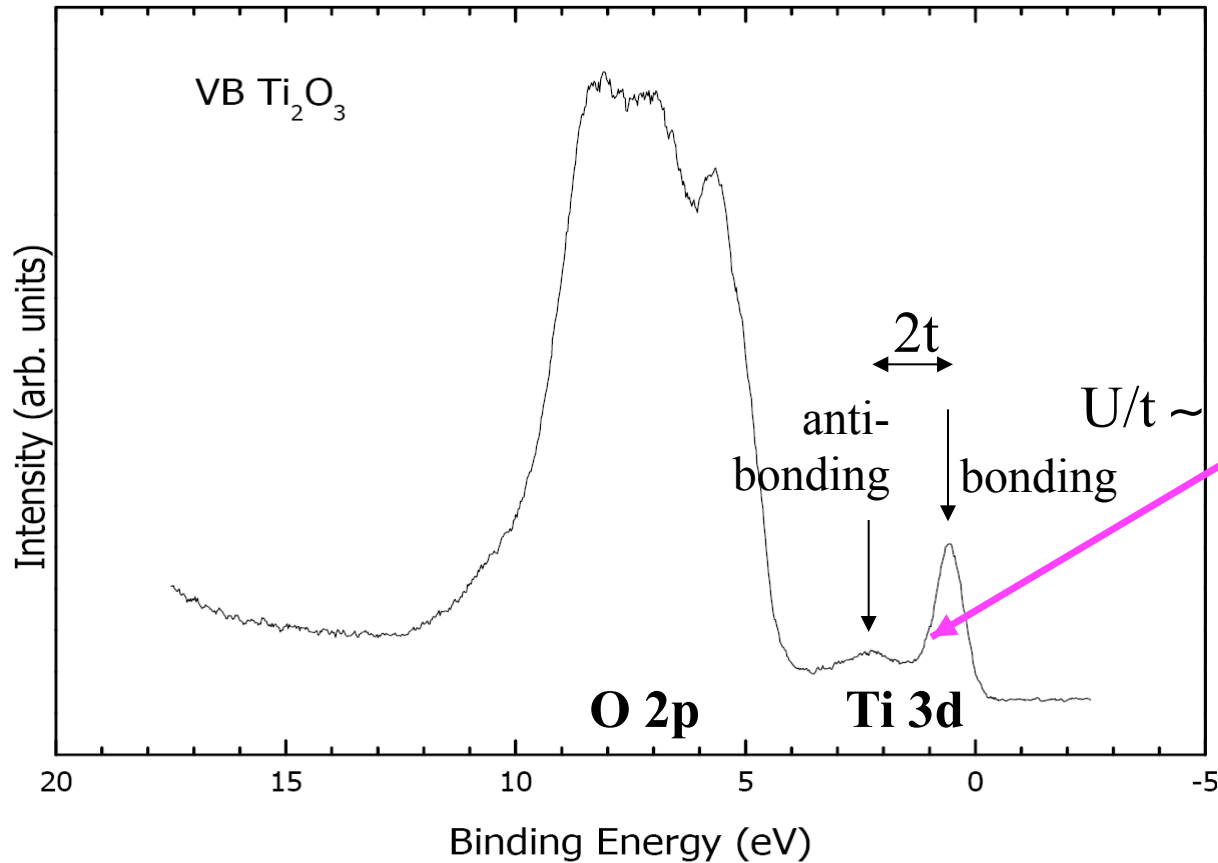
valence band photoemission on Ti_2O_3 single crystals

room temperature : insulating phase



valence band photoemission on Ti_2O_3 single crystals

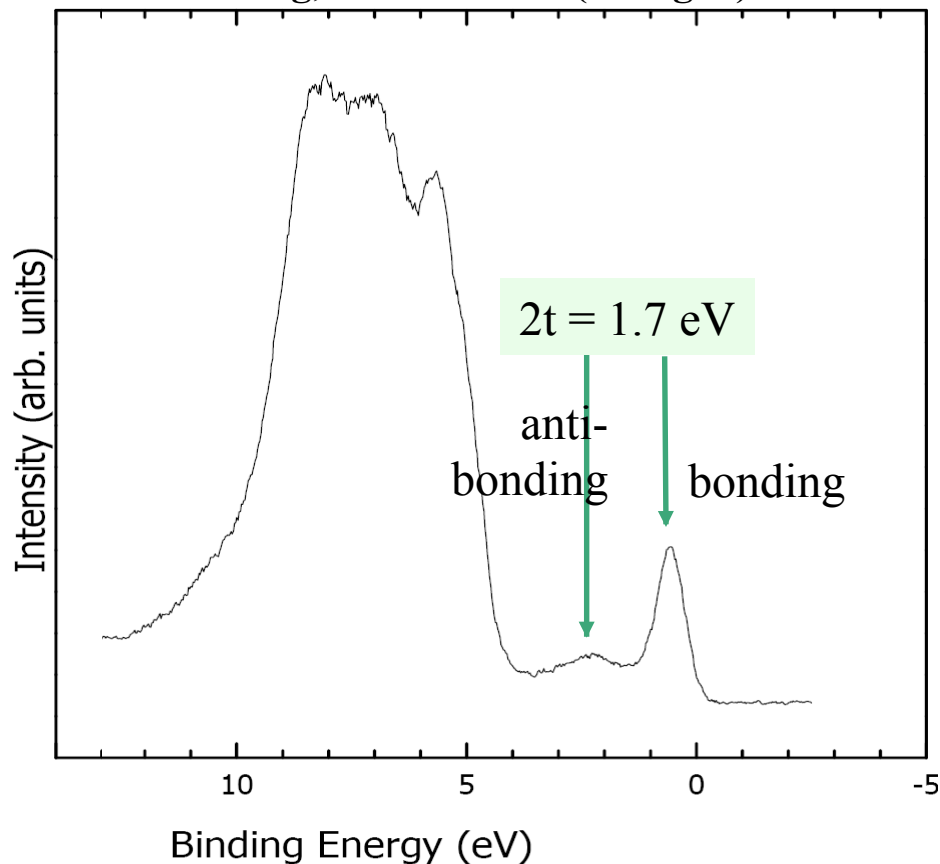
room temperature : insulating phase



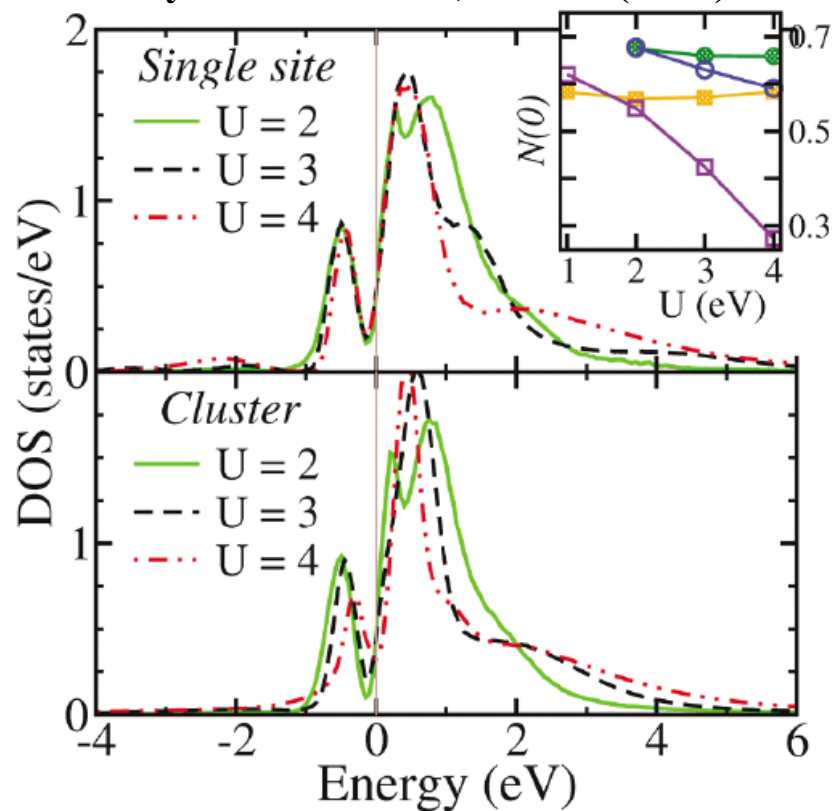
Two-peak structure like in a H_2 molecule model \rightarrow
(relative weights according to quantum mechanical interference effect)

Comparison experiment vs. C-DMFT

Chang, Koethe et al. (Cologne)

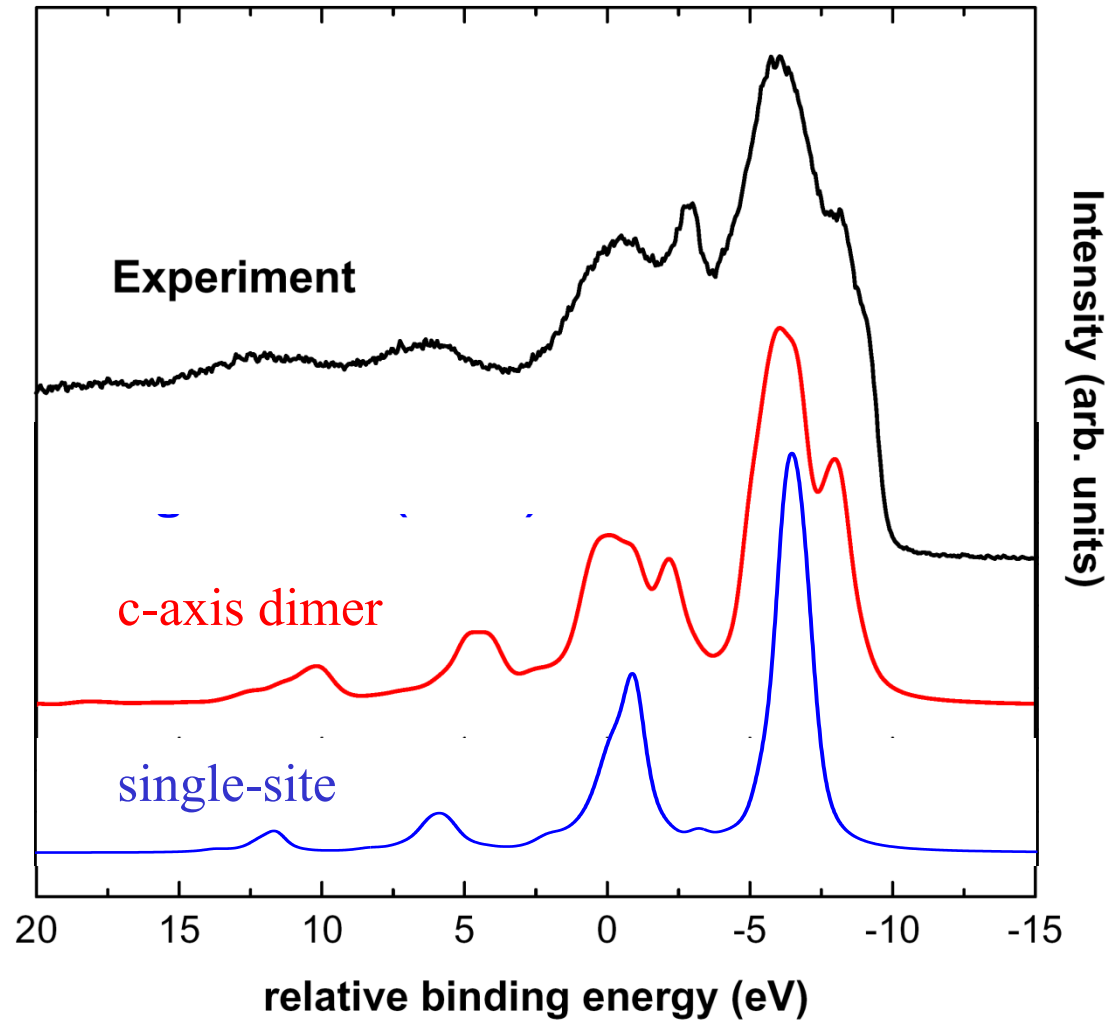


Poteryaev, Lichtenstein, Kotliar.,
Phys. Rev. Lett. 93, 086401 (2004).

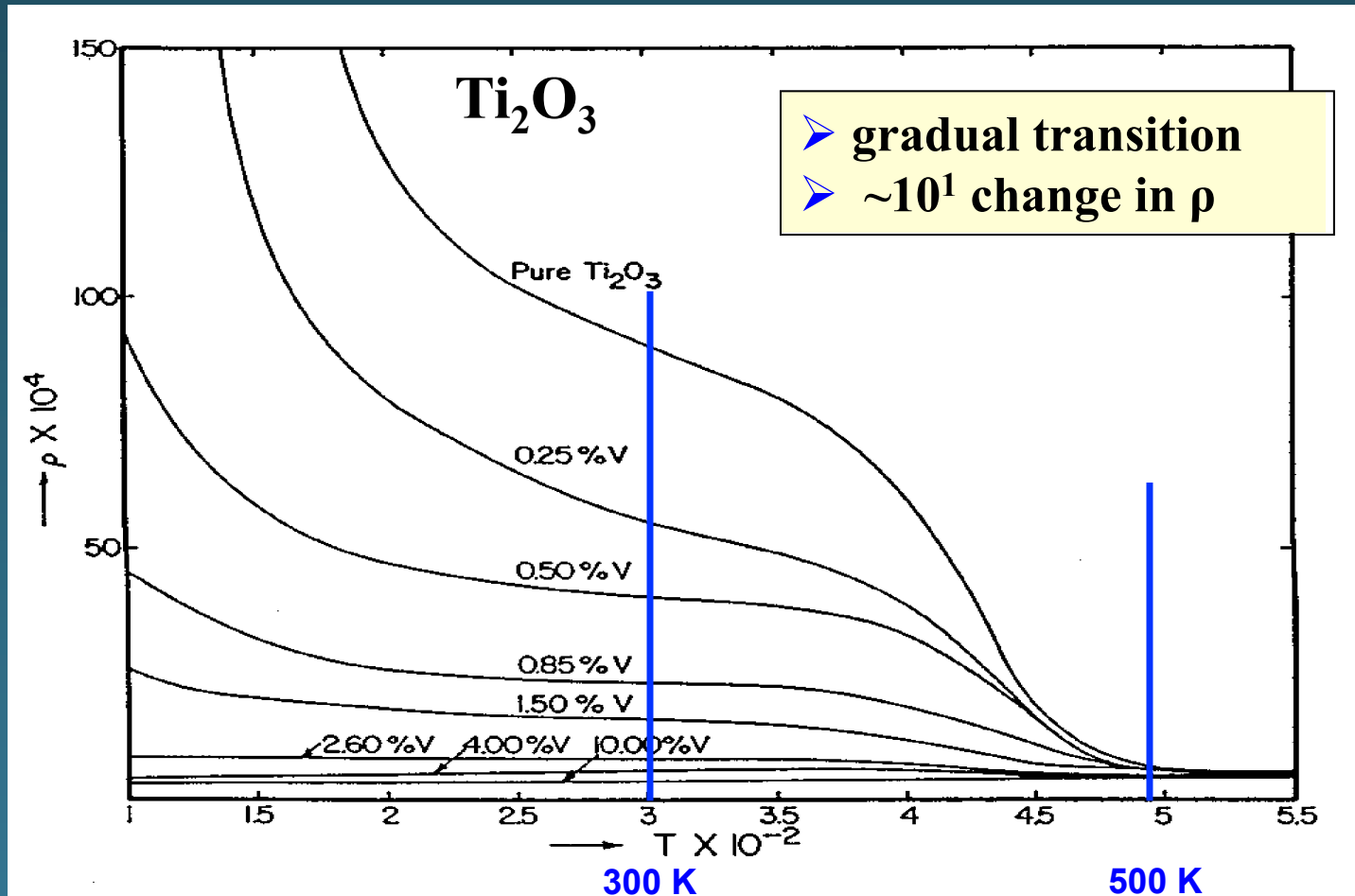


too low intensity of anti-bonding peak ?!

Ti 2p core level XPS: experiment vs. multiplet theory



What happens across the Metal Insulator Transition ?



Orbital occupation in Ti_2O_3 from XAS: across MIT

“dimer”

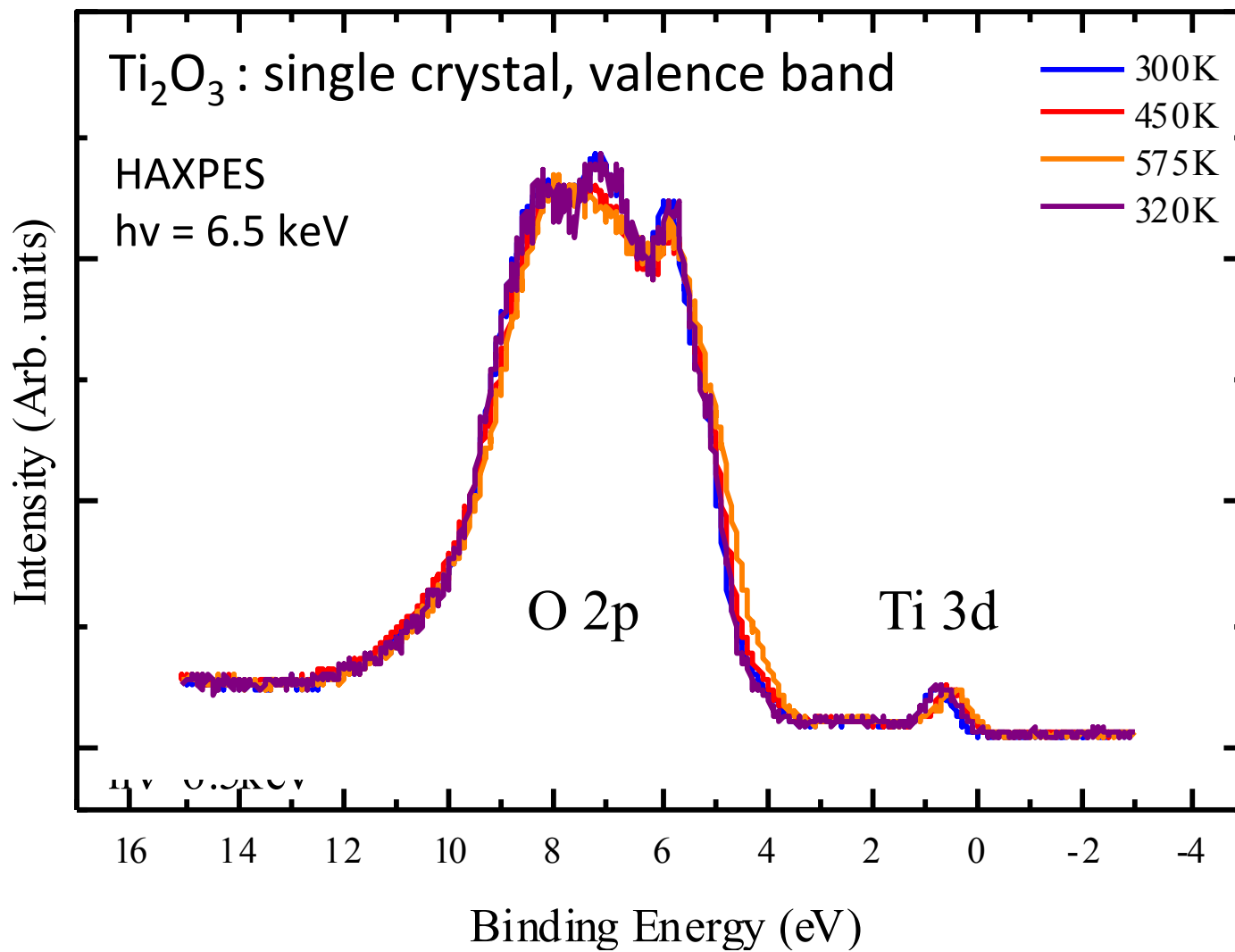
“isotropic”

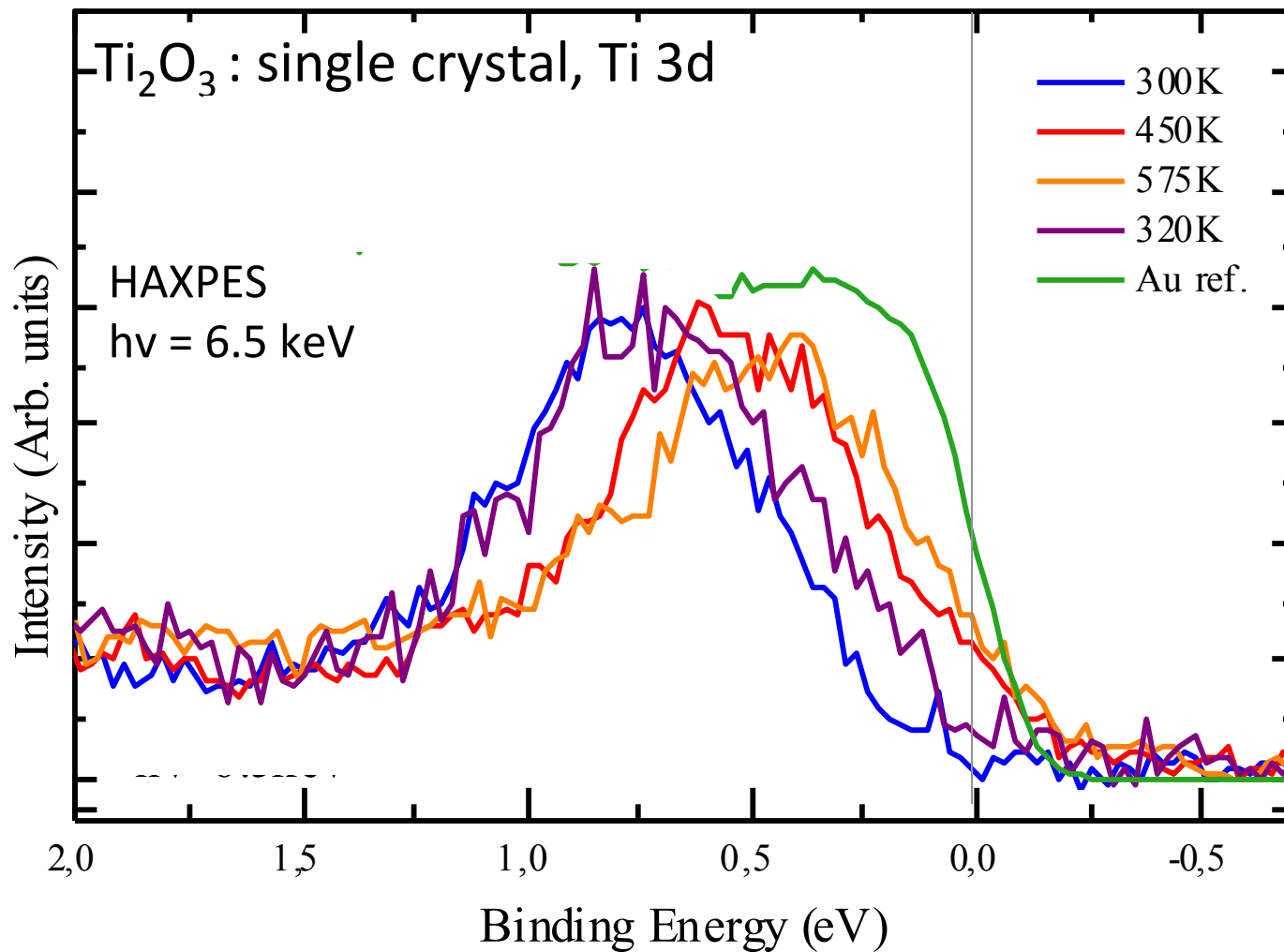
	<i>T= 300 K</i>		<i>T= 458 K</i>		<i>T= 500 K</i>		<i>T=575 K</i>	
	sym.	3d occ.	sym.	3d occ.	sym.	3d occ.	sym.	3d occ.
$\mathbf{a_{1g}a_{1g}}$	1.00	0.997	0.78	0.888	0.72	0.857	0.49	0.745
$\mathbf{a_{1g}e_g^\pi}$	0.00	0.178	0.22	0.231	0.28	0.246	0.51	0.300
$\mathbf{e_g^\sigma}$	0.00	0.198	0.00	0.255	0.00	0.271	0.00	0.328
tot.	1.00	1.373	1.00	1.374	1.00	1.374	1.00	1.373

Break-up of “dimers”

MIT = going from a collection of “dimers” into a 3-dimensional solid

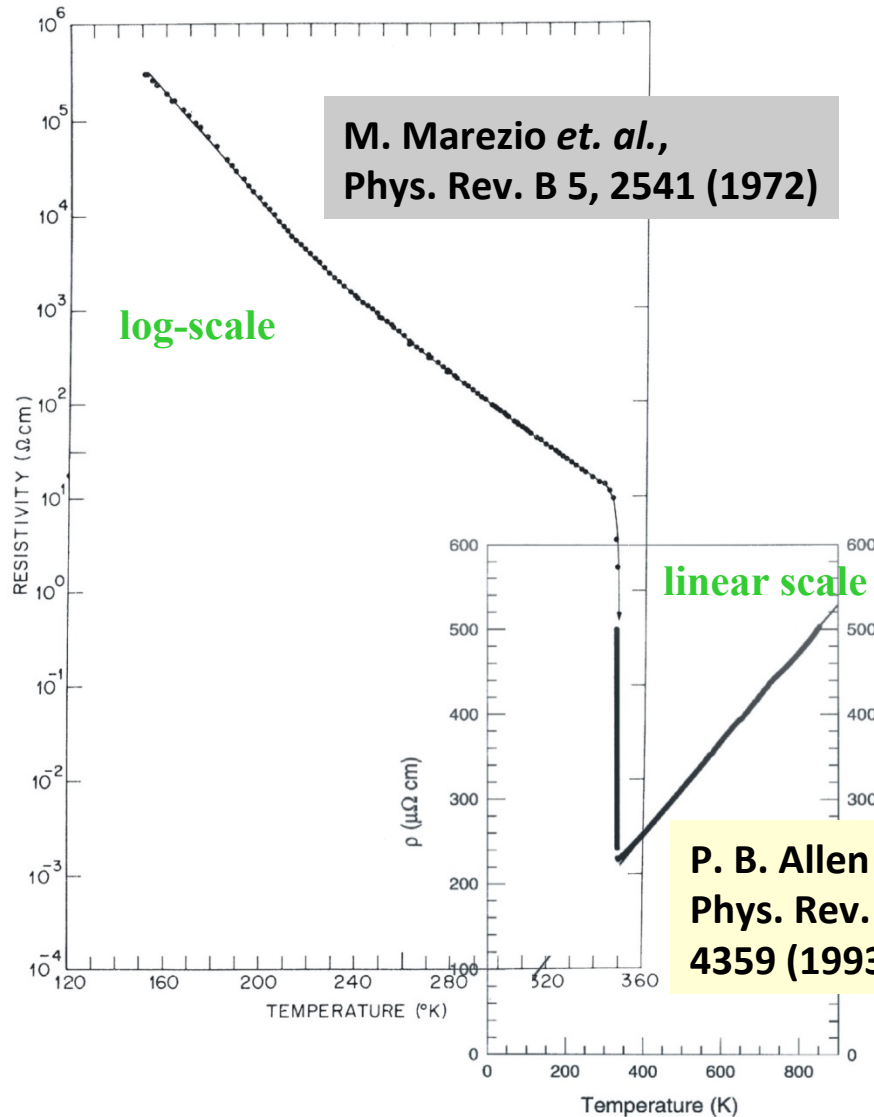
“Making hydrogen metallic”





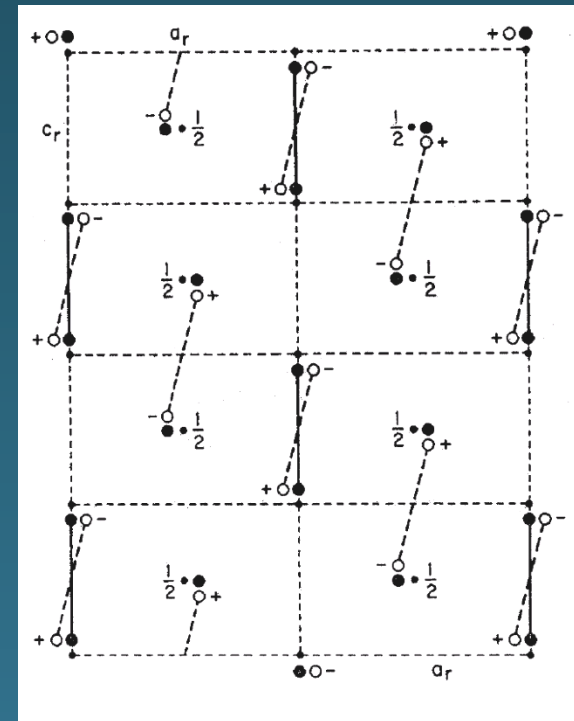
Gradual MIT – bad metal in metallic phase

1st order Metal Insulator Transition in VO_2

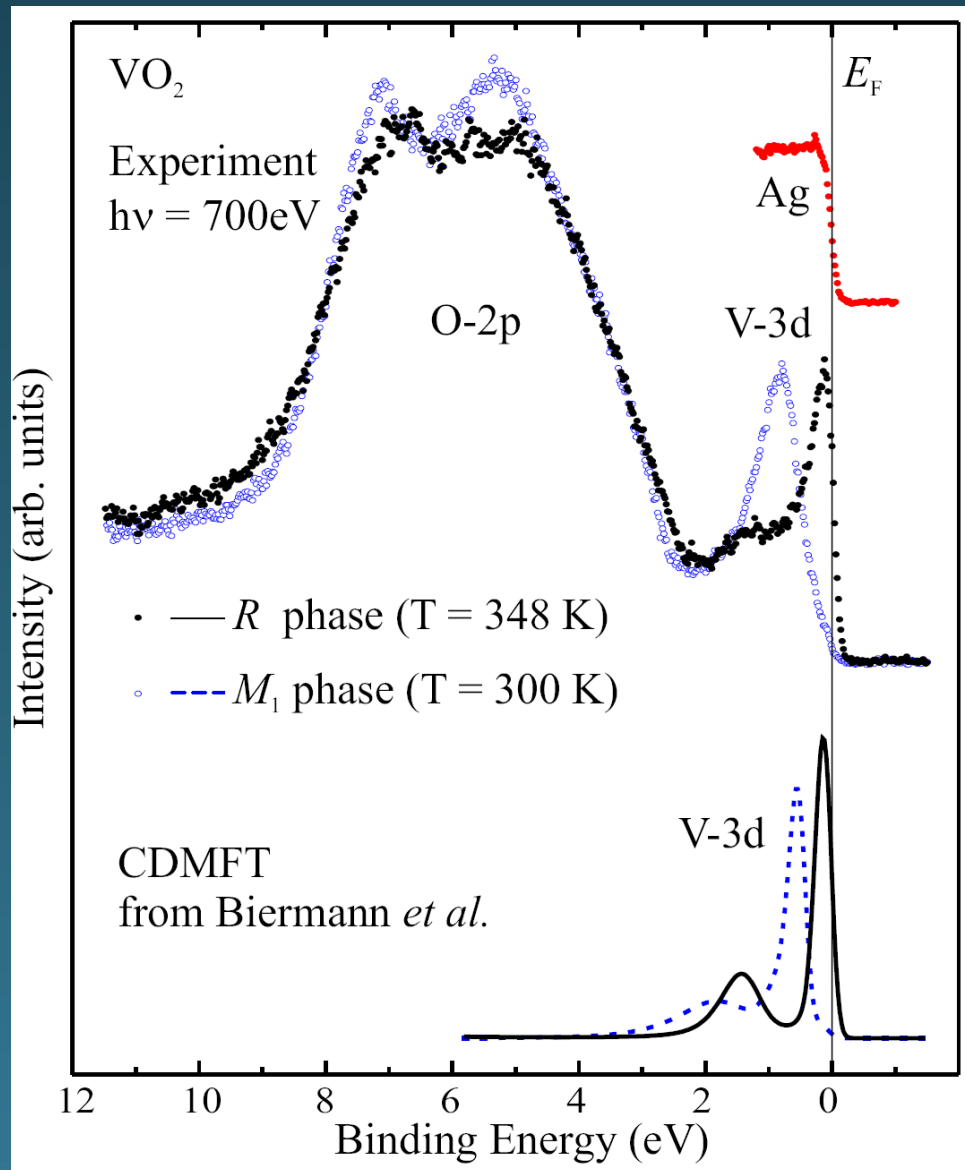


$T > 340\text{K}$: metal, rutile

**$T < 340\text{K}$: insulator, monoclinic,
dimerized zig-zag chain**



1st order Metal Insulator Transition in VO₂



Koethe et al., PRL (2006)

Let us go back to the black board

Hydrogen-molecule : 1-electron theory

Direct Exchange [see also Ashcroft & Mermin ch.32]

* 2 sites : a and b

* basis functions : s-like orbitals $|a\rangle, |b\rangle$

* $\langle a|a\rangle = 1, \langle b|b\rangle = 1, \langle a|b\rangle = 0, \langle b|a\rangle = 0$

* $\langle a|H|a\rangle = E_0, \langle b|H|b\rangle = E_0$: on-site energy.

* $\langle a|H|b\rangle = t, \langle b|H|a\rangle = t$: hopping integral ($t < 0$)

$$H\psi = E\psi \quad : \quad H = \begin{bmatrix} E_0 & t \\ t & E_0 \end{bmatrix}, \quad \psi = \alpha a + \beta b, \quad \alpha^2 + \beta^2 = 1$$

$$\psi_+ = \frac{a+b}{\sqrt{2}} \quad E_+ = t \quad (t < 0) : \text{lowest state}$$

$$\psi_- = \frac{a-b}{\sqrt{2}} \quad E_- = -t$$

The hydrogen molecule contains 2 electrons.

In the 1-electron theory, one takes the calculated 1-electron orbitals and fill these with 2 electrons.

The ground state will then be 2 electrons residing both in the φ_+ orbitals, one with spin up (\uparrow) and one with spin-down (\downarrow). The ground state will be a singlet:

$$\begin{aligned}\psi_s &= A \{ \varphi_+ \uparrow \varphi_+ \downarrow \} = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)+b(1)}{\sqrt{2}} \uparrow(1) & \frac{a(2)+b(2)}{\sqrt{2}} \uparrow(2) \\ \frac{a(1)+b(1)}{\sqrt{2}} \downarrow(1) & \frac{a(2)+b(2)}{\sqrt{2}} \downarrow(2) \end{vmatrix} \\ &= \frac{a(1)+b(1)}{\sqrt{2}} \cdot \frac{a(2)+b(2)}{\sqrt{2}} \cdot \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}} \\ &= \left\{ \frac{a(1)a(2)}{2} + \frac{a(1)b(2)}{2} + \frac{b(1)a(2)}{2} + \frac{b(1)b(2)}{2} \right\} \cdot \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}}\end{aligned}$$

$$\begin{aligned}
 \psi_s &= A \{ \varphi_{+ \uparrow} \varphi_{+ \downarrow} \} = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)+b(1)}{\sqrt{2}} \uparrow(1) & \frac{a(2)+b(2)}{\sqrt{2}} \uparrow(2) \\ \frac{a(1)+b(1)}{\sqrt{2}} \downarrow(1) & \frac{a(2)+b(2)}{\sqrt{2}} \downarrow(2) \end{vmatrix} \\
 &= \frac{a(1)+b(1)}{\sqrt{2}} \cdot \frac{a(2)+b(2)}{\sqrt{2}} \cdot \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}} \\
 &= \left\{ \frac{a(1)a(2)}{2} + \frac{a(1)b(2)}{2} + \frac{b(1)a(2)}{2} + \frac{b(1)b(2)}{2} \right\} \cdot \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}}
 \end{aligned}$$

The probability to find 2 electrons on site a is:

$$|\langle a(1)a(2) | \psi_s \rangle|^2 = \left| \frac{1}{2} \right|^2 = \frac{1}{4}$$

The probability to find 2 electrons on site b is:

$$|\langle b(1)b(2) | \psi_s \rangle|^2 = \left| \frac{1}{2} \right|^2 = \frac{1}{4}$$

The probability to find 1 electron on a and 1 on b is:

$$|\langle a(1)b(2) | \psi_s \rangle|^2 + |\langle b(1)a(2) | \psi_s \rangle|^2 = \left| \frac{1}{2} \right|^2 + \left| \frac{1}{2} \right|^2 = \frac{1}{2}$$

The first excited state will have one electron in the φ_+ orbital and one in the φ_- orbital. This can be a triplet or a singlet. Let us consider the triplet: $\uparrow\uparrow$ (or $\downarrow\downarrow$).

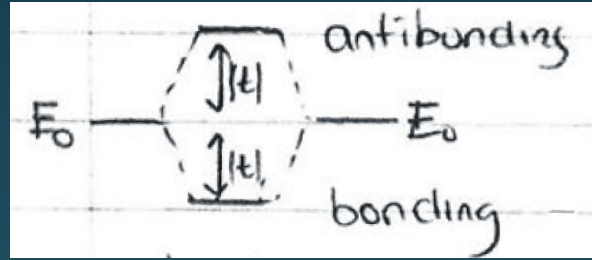
$$\begin{aligned}
 \Psi_{\pm} &= A \{ \varphi_+ \uparrow \varphi_- \uparrow \} = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)+b(1)}{\sqrt{2}} \uparrow(1) & \frac{a(2)+b(2)}{\sqrt{2}} \uparrow(2) \\ \frac{a(1)-b(1)}{\sqrt{2}} \uparrow(1) & \frac{a(2)-b(2)}{\sqrt{2}} \uparrow(2) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} \left\{ \frac{a(1)+b(1)}{\sqrt{2}} \cdot \frac{a(2)-b(2)}{\sqrt{2}} - \frac{a(1)-b(1)}{\sqrt{2}} \cdot \frac{a(2)+b(2)}{\sqrt{2}} \right\} \uparrow(1)\uparrow(2) \\
 &= \frac{1}{\sqrt{2}} \left\{ \frac{-a(1)b(2) + b(1)a(2) - a(1)b(2) + b(1)a(2)}{\sqrt{2} \cdot \sqrt{2}} \right\} \uparrow(1)\uparrow(2) \\
 &= \frac{b(1)a(2) - a(1)b(2)}{\sqrt{2}} \cdot \uparrow(1)\uparrow(2) \quad (\text{and } \downarrow\downarrow \text{ equivalently})
 \end{aligned}$$

The probability to find 2 electrons on site a is zero

The probability to find 2 electrons on site b is zero

The probability to find 1 electron on a and 1 on b is 100%

How about the energies?



→ from the one-electron wavefunctions φ_+ and φ_- with eigen energies $E_+ = E_0 - |t|$ and $E_- = E_0 + |t|$, respectively,

$$\text{we get: } E(\psi_s) = E(\varphi_+ \varphi_+) = 2E_+ = 2E_0 + 2t \quad (t < 0)$$

$$E(\psi_t) = E(\varphi_+ \varphi_-) = E_+ + E_- = 2E_0$$

$$E(\psi_s^*) = E(\varphi_- \varphi_-) = 2E_- = 2E_0 - 2t \quad (t < 0)$$

The singlet-triplet splitting is: $E(\psi_t) - E(\psi_s) = -2t$

This is a useful quantity to describe the low energy excitations of the system:

$$H^{\text{spin}} = -J \cdot s_1 \cdot s_2 \quad \text{with } J = 2t \quad (t < 0 \rightarrow -J > 0)$$

→ "anti-parallel" spin alignment (singlet) is favoured.

Hydrogen-molecule: Hubbard Model

Direct Exchange [see also Ashcroft & Mermin, ch. 32, 33]

* 2 sites; s-like orbitals a, b ; spin \uparrow, \downarrow ; 2 electrons.

* hopping integral $t \equiv \langle a | H | b \rangle$ $\langle a | b \rangle = \langle b | a \rangle = 0$

* on-site energy $E_0 \equiv \langle a | H | a \rangle = \langle b | H | b \rangle$ $\langle a | a \rangle = \langle b | b \rangle = 1$

* Coulomb energy U for doubly occupied site:

$$U = \langle a \uparrow a \downarrow | H | a \uparrow a \downarrow \rangle = \langle b \uparrow b \downarrow | H | b \uparrow b \downarrow \rangle \quad ; \quad 2 \text{ electron operator}$$

Basis set:

$$\uparrow \uparrow : a \uparrow b \uparrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) \uparrow(1) & a(2) \uparrow(2) \\ b(1) \uparrow(1) & b(2) \uparrow(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \{ a(1)b(2) - a(2)b(1) \} \uparrow(1) \uparrow(2)$$

$$\downarrow \downarrow : a \downarrow b \downarrow = \frac{1}{\sqrt{2}} \{ a(1)b(2) - a(2)b(1) \} \downarrow(1) \downarrow(2)$$

$$\uparrow \downarrow : a \uparrow b \downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) \uparrow(1) & a(2) \uparrow(2) \\ b(1) \downarrow(1) & b(2) \downarrow(2) \end{vmatrix} = \frac{a(1)b(2) \uparrow(1) \downarrow(2) - a(2)b(1) \downarrow(1) \uparrow(2)}{\sqrt{2}}$$

$$\downarrow \uparrow : a \downarrow b \uparrow = \frac{1}{\sqrt{2}} \{ a(1)b(2) \downarrow(1) \uparrow(2) - a(2)b(1) \uparrow(1) \downarrow(2) \}$$

$$\uparrow \downarrow - : a \uparrow a \downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) \uparrow(1) & a(2) \uparrow(2) \\ a(1) \downarrow(1) & a(2) \downarrow(2) \end{vmatrix} = a(1)a(2) \left\{ \frac{\uparrow(1) \downarrow(2) - \downarrow(1) \uparrow(2)}{\sqrt{2}} \right\}$$

$$\downarrow \uparrow - : b \uparrow b \downarrow = \frac{1}{\sqrt{2}} \{ b(1)b(2) \left[\frac{\uparrow(1) \downarrow(2) - \downarrow(1) \uparrow(2)}{\sqrt{2}} \right] \}$$

Hamiltonian:

$a^\uparrow b^\uparrow$	$2E_0$								$\bullet = 0$ (no spin-flip in Hamiltonian)
$a^\downarrow b^\downarrow$	\bullet	$2E_0$							
$a^\uparrow b^\downarrow$	\bullet	\bullet	$2E_0$						$- = 0$ (no hopping for <u>2</u> electrons at the same time)
$a^\downarrow b^\uparrow$	\bullet	\bullet	\bullet	$2E_0$					
$a^\uparrow a^\downarrow$	\bullet	\bullet	t	t	$2E_0 + U$				
$b^\uparrow b^\downarrow$	\bullet	\bullet	t	t	$- 2E_0 + U$				

$a^\uparrow b^\uparrow, a^\downarrow b^\downarrow$: triplet : antisymmetric in orbital and symmetric in spin upon interchange of particle coordinates

$a^\uparrow a^\downarrow, b^\uparrow b^\downarrow$: singlet : symmetric in orbital and antisymmetric in spin.
How about $a^\uparrow b^\downarrow$ and $a^\downarrow b^\uparrow$?

Let us make the following linear combinations:

$$\begin{aligned}\frac{a\uparrow b\downarrow + a\downarrow b\uparrow}{\sqrt{2}} &= \frac{a(1)b(2)\uparrow(1)\downarrow(2) - a(2)b(1)\downarrow(1)\uparrow(2) + a(1)b(2)\downarrow(1)\uparrow(2) - a(2)b(1)\uparrow(1)\downarrow(2)}{\sqrt{2} \cdot \sqrt{2}} \\ &= \frac{\{a(1)b(2) - a(2)b(1)\} \uparrow(1)\downarrow(2) + \{a(1)b(2) - a(2)b(1)\} \downarrow(1)\uparrow(2)}{\sqrt{2} \cdot \sqrt{2}} \\ &= \left\{ \frac{a(1)b(2) - a(2)b(1)}{\sqrt{2}} \right\} \left\{ \frac{\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)}{\sqrt{2}} \right\} \\ &= \text{"ab-triplet"}\end{aligned}$$

$$\begin{aligned}\frac{a\uparrow b\downarrow - a\downarrow b\uparrow}{\sqrt{2}} &= \left\{ \frac{a(1)b(2) + a(2)b(1)}{\sqrt{2}} \right\} \left\{ \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}} \right\} \\ &= \text{"ab-singlet"}\end{aligned}$$

The Hamiltonian is then:

$a^\uparrow b^\uparrow$	$2E_0$				
$a^\downarrow b^\uparrow$	\cdot	$2E_0$			
ab -triplet	\cdot	\cdot	$2E_0$		
ab -singlet	\cdot	\cdot	\cdot	$2E_0$	
$a^\uparrow a^\downarrow$	\cdot	\cdot	0	$\sqrt{2}t$	$2E_0 + U$
$b^\uparrow b^\downarrow$	\cdot	\cdot	0	$\sqrt{2}t$	$-2E_0 + U$

The 6×6 Hamiltonian falls apart into three 1×1 Hamiltonians and one 3×3 Hamiltonian.

The three 1×1 Hamiltonians are all triplet in character and have the same energy E_0 . This 3-fold degeneracy is after all the reason to call these states triplets.

The 3×3 Hamiltonian belongs to the singlet Hilbert space.

Remark: The factor $\sqrt{2}$ in the hopping matrix element basically indicates that there are two ways to let an electron hop from a doubly occupied site to a neighbor while being in the singlet state: namely with spin \uparrow or \downarrow .

For the 3×3 Hamiltonian can be simplified further by taking the following linear combination of the singlet states $a^\uparrow a^\downarrow$ and $b^\uparrow b^\downarrow$, namely $\frac{a^\uparrow a^\downarrow + b^\uparrow b^\downarrow}{\sqrt{2}}$ and $\frac{a^\uparrow a^\downarrow - b^\uparrow b^\downarrow}{\sqrt{2}}$ (these are still singlets):

$$\begin{array}{l} \text{ab-singlet} \\ \frac{a^\uparrow a^\downarrow + b^\uparrow b^\downarrow}{\sqrt{2}} \\ \frac{a^\uparrow a^\downarrow - b^\uparrow b^\downarrow}{\sqrt{2}} \end{array} \left[\begin{array}{ccc} 2E_0 & & \\ 2t & 2E_0 + U & \\ 0 & 0 & 2E_0 + U \end{array} \right]$$

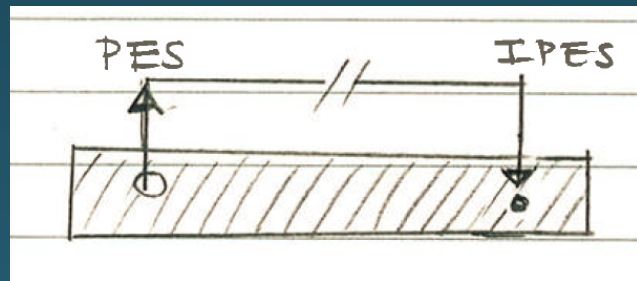
The 2×2 submatrix will have $2E_0 - \frac{(2t)^2}{U}$ as the lowest energy (for $t \ll U$), and $2E_0 + \frac{(2t)^2}{U}$ as the highest.

The 1×1 submatrix keeps $2E_0 + U$ as energy eigenvalue

Conclusion:

The spins on the two sites will form a singlet state, since the lowest singlet state has an energy which is lower by $\frac{4t^2}{U}$ as compared to the triplets.

PES/IPES - Bandgaps - energy reference - chemical potential μ



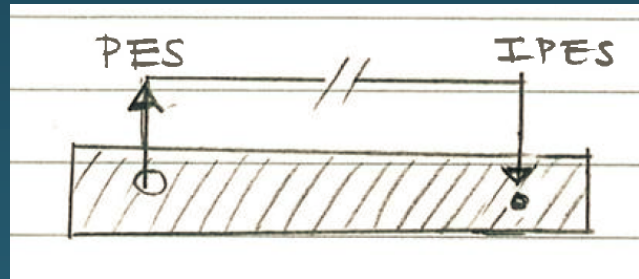
system with N -electrons:

$$\begin{array}{l} \text{PES: } N \rightarrow N-1 \\ \text{initial: } E_N^{\text{GS}} \\ \text{final: } E_{N-1}^i + E_{\text{ref}} \end{array} \left. \vphantom{\begin{array}{l} \text{PES: } N \rightarrow N-1 \\ \text{initial: } E_N^{\text{GS}} \\ \text{final: } E_{N-1}^i + E_{\text{ref}} \end{array}} \right\} E_{\text{PES}}^i = E_{N-1}^i - E_N^{\text{GS}} + E_{\text{ref}}$$

$$\begin{array}{l} \text{IPES: } N \rightarrow N+1 \\ \text{initial: } E_N^{\text{GS}} \\ \text{final: } E_{N+1}^i - E_{\text{ref}} \end{array} \left. \vphantom{\begin{array}{l} \text{IPES: } N \rightarrow N+1 \\ \text{initial: } E_N^{\text{GS}} \\ \text{final: } E_{N+1}^i - E_{\text{ref}} \end{array}} \right\} E_{\text{IPES}}^i = E_{N+1}^i - E_N^{\text{GS}} - E_{\text{ref}}$$

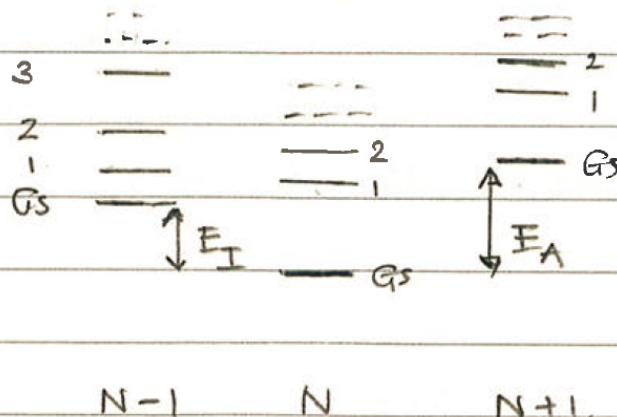
[GS = Ground state, $i = \text{GS}, 1, 2, 3, \dots$ (excited states)]

PES/IPES - Bandgaps - energy reference - chemical potential μ



$$E_{\text{gap}} = E_{\text{PES}}^{\text{GS}} + E_{\text{IPES}}^{\text{GS}} = E_{N-1}^{\text{GS}} - E_N^{\text{GS}} + E_{N+1}^{\text{GS}} - E_N^{\text{GS}}$$

$$= E_{N-1}^{\text{GS}} + E_{N+1}^{\text{GS}} - 2E_N^{\text{GS}}$$



$$E_{\text{gap}} = E_{\text{I}} + E_{\text{A}}$$

($E_{\text{I}} \equiv E_{\text{PES}}^{\text{GS}}$, $E_{\text{A}} \equiv E_{\text{IPES}}^{\text{GS}}$)

E_{I} = ionization energy
 E_{A} = affinity energy

H₂ molecule, Hubbard Model, PES/IPES spectral weights

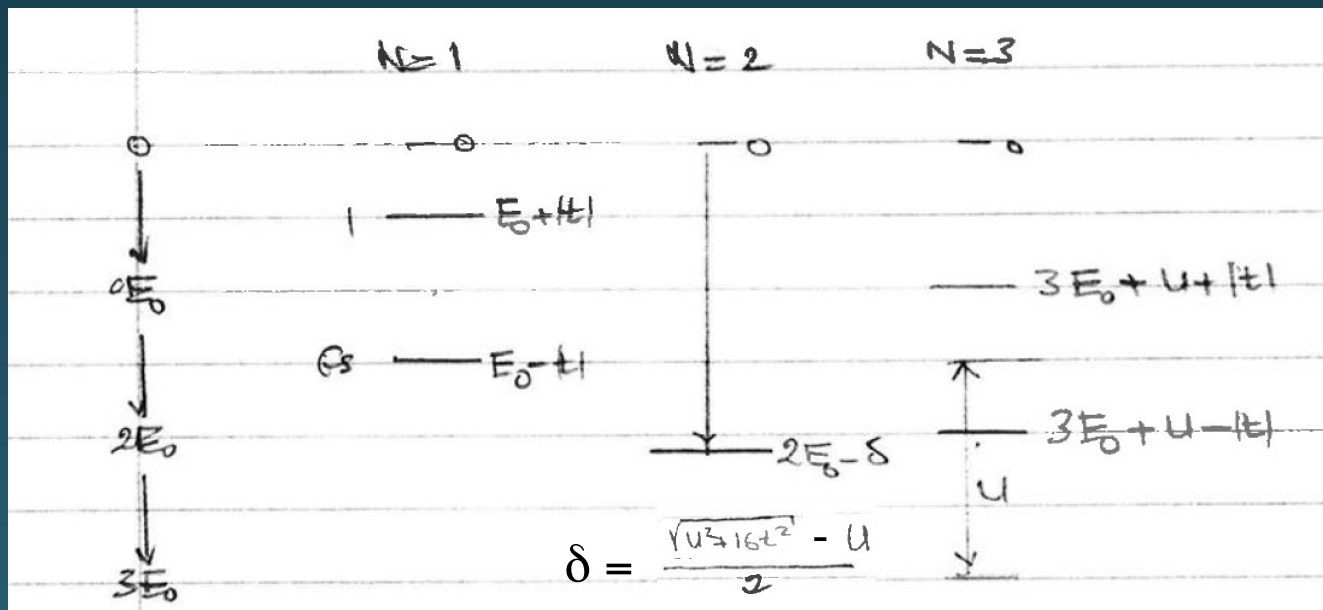
* description in terms of total energy diagram:

$$N=2 \quad \begin{array}{l} \frac{1}{\sqrt{2}}(a\uparrow b\downarrow - a\downarrow b\uparrow) \\ \frac{1}{\sqrt{2}}(a\uparrow a\downarrow + b\uparrow b\downarrow) \end{array} \quad \begin{bmatrix} 2E_0 & 2t \\ 2t & 2E_0 + U \end{bmatrix} \quad \begin{bmatrix} \Delta & t \\ t & \Delta \end{bmatrix} \rightarrow E_{\pm} = \frac{\Delta \pm \sqrt{\Delta^2 + 4t^2}}{2}$$

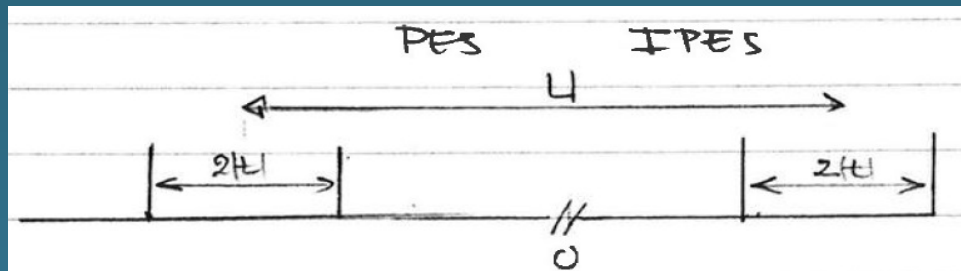
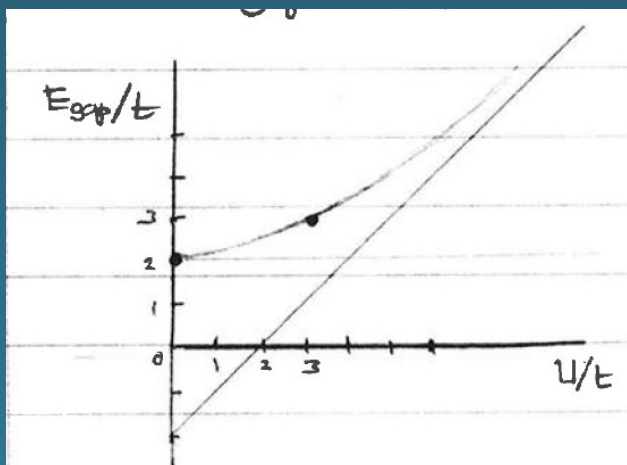
$$E_{N=2}^{\text{GS}} = 2E_0 + \frac{U - \sqrt{U^2 + 16t^2}}{2}$$

$$N=1 \quad \begin{array}{l} a\uparrow \\ b\uparrow \end{array} \quad \begin{bmatrix} E_0 & t \\ t & E_0 \end{bmatrix} \quad E_{N=1}^{\text{GS}} = E_0 - |t|, \quad E'_{N=1} = E_0 + |t|$$

$$N=3 \quad \begin{array}{l} \underline{a}\uparrow \\ \underline{b}\uparrow \end{array} \quad \begin{bmatrix} 3E_0 + U & t \\ t & 3E_0 + U \end{bmatrix} \quad E_{N=3}^{\text{GS}} = 3E_0 + U - |t|, \quad E'_{N=3} = 3E_0 + U + |t|$$



$$E_{\text{gap}} = E_0 - |t| + 3E_0 + U - |t| - 2 \left\{ 2E_0 + \frac{U - \sqrt{U^2 + 16t^2}}{2} \right\} = \sqrt{U^2 + 16t^2} - 2|t|$$



$$\Psi_{N=2}^{\text{GS}} = \alpha \left| \frac{1}{\sqrt{2}} (a^\uparrow b^\downarrow - a^\downarrow b^\uparrow) \right\rangle + \beta \left| \frac{1}{\sqrt{2}} (a^\uparrow a^\downarrow + b^\uparrow b^\downarrow) \right\rangle.$$

$$\Psi_{N=1}^{\text{GS}} = \frac{1}{\sqrt{2}} |a^\uparrow\rangle + \frac{1}{\sqrt{2}} |b^\uparrow\rangle \quad (\text{bonding}) \quad (\text{also for } \downarrow)$$

$$\Psi_{N=1}^{\uparrow} = \frac{1}{\sqrt{2}} |a^\uparrow\rangle - \frac{1}{\sqrt{2}} |b^\uparrow\rangle \quad (\text{anti-bonding}) \quad (\text{also for } \downarrow)$$

Spectral weight \rightarrow PES at site @, e.g. remove a^\downarrow electron.

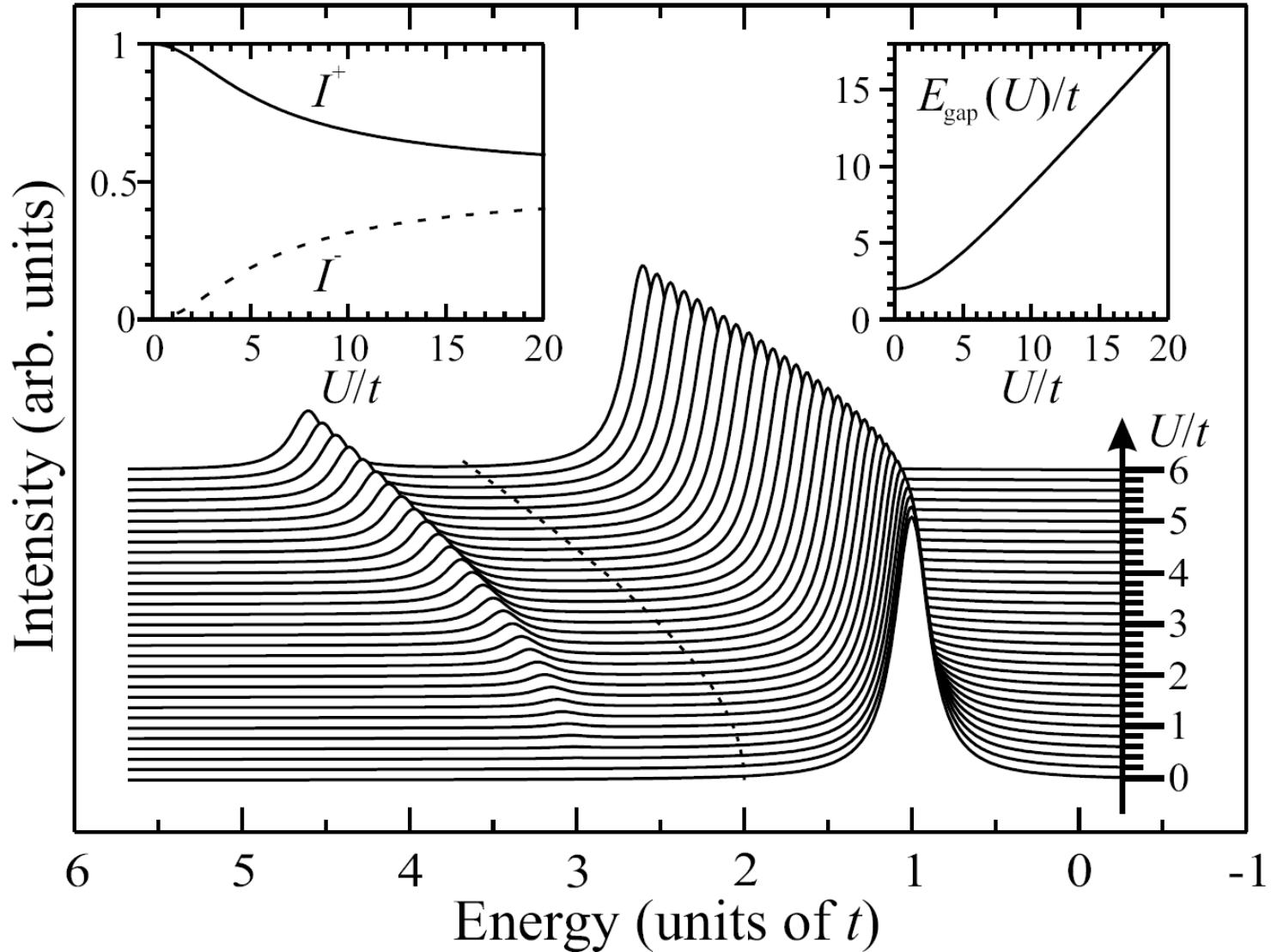
$$\begin{aligned} I_{\text{PES}}^{\text{GS}} &= \left| \left\langle \frac{1}{\sqrt{2}} \langle a^\uparrow | + \frac{1}{\sqrt{2}} \langle b^\uparrow | \right| a^\downarrow \left| \alpha \left| \frac{a^\uparrow b^\downarrow - a^\downarrow b^\uparrow}{\sqrt{2}} \right\rangle + \beta \left| \frac{a^\uparrow a^\downarrow + b^\uparrow b^\downarrow}{\sqrt{2}} \right\rangle \right|^2 \\ &= \frac{1}{4} \left| \langle a^\uparrow | a^\downarrow | \beta | a^\uparrow a^\downarrow \rangle + \langle b^\uparrow | a^\downarrow | -\alpha | a^\downarrow b^\uparrow \rangle \right|^2 = \frac{1}{4} |\beta + \alpha|^2 \end{aligned}$$

$$I_{\text{PES}}^{\uparrow} = \left| \left\langle \frac{1}{\sqrt{2}} \langle a^\uparrow | - \frac{1}{\sqrt{2}} \langle b^\uparrow | \right| \dots \right|^2 = \frac{1}{4} |\beta - \alpha|^2$$

$$\ast U=0 \rightarrow \alpha=\beta=\frac{1}{\sqrt{2}} \rightarrow I_{\text{PES}}^{\text{GS}} = \frac{1}{4} \left| \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2}, \quad I_{\text{PES}}^{\uparrow} = 0.$$

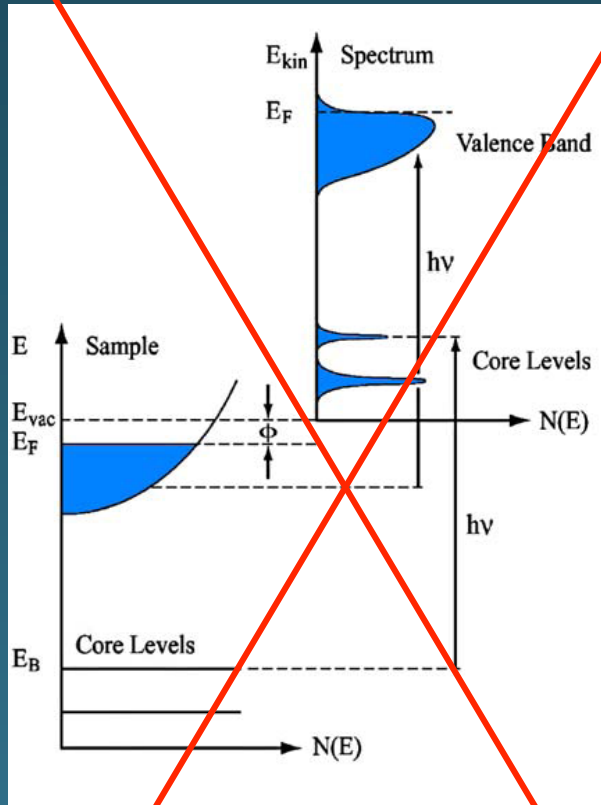
$$\ast U \rightarrow \infty \rightarrow \alpha=1, \beta=0 \rightarrow I_{\text{PES}}^{\text{GS}} = \frac{1}{4} |0+1|^2 = \frac{1}{4}, \quad I_{\text{PES}}^{\uparrow} = \frac{1}{4} |0-1|^2 = \frac{1}{4}.$$

H₂ molecule model : *Hubbard model*



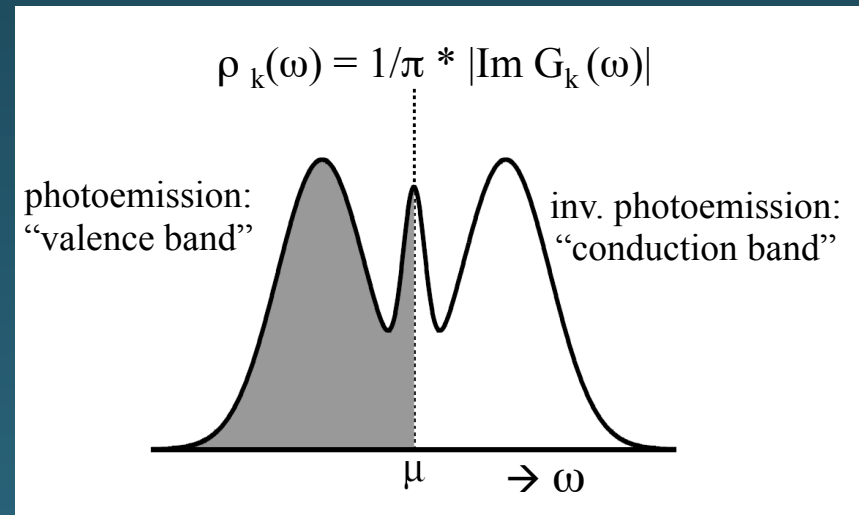
Concluding remarks : Photoelectron Spectroscopy: ideal to study electron correlations

One-particle approximation

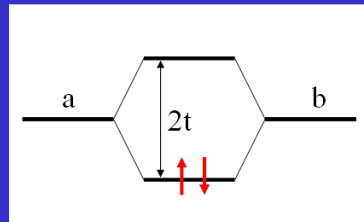


- photoemission:
--- “occupied” density of states
- inverse photoemission:
--- “unoccupied” density of states

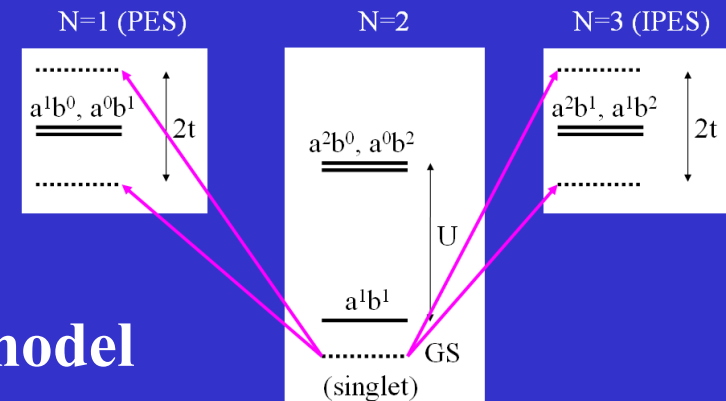
Many-body framework



energy level diagram



total energy level diagram



H₂ Hubbard model