

Electronic structure of correlated electron systems 2011

George Sawatzky

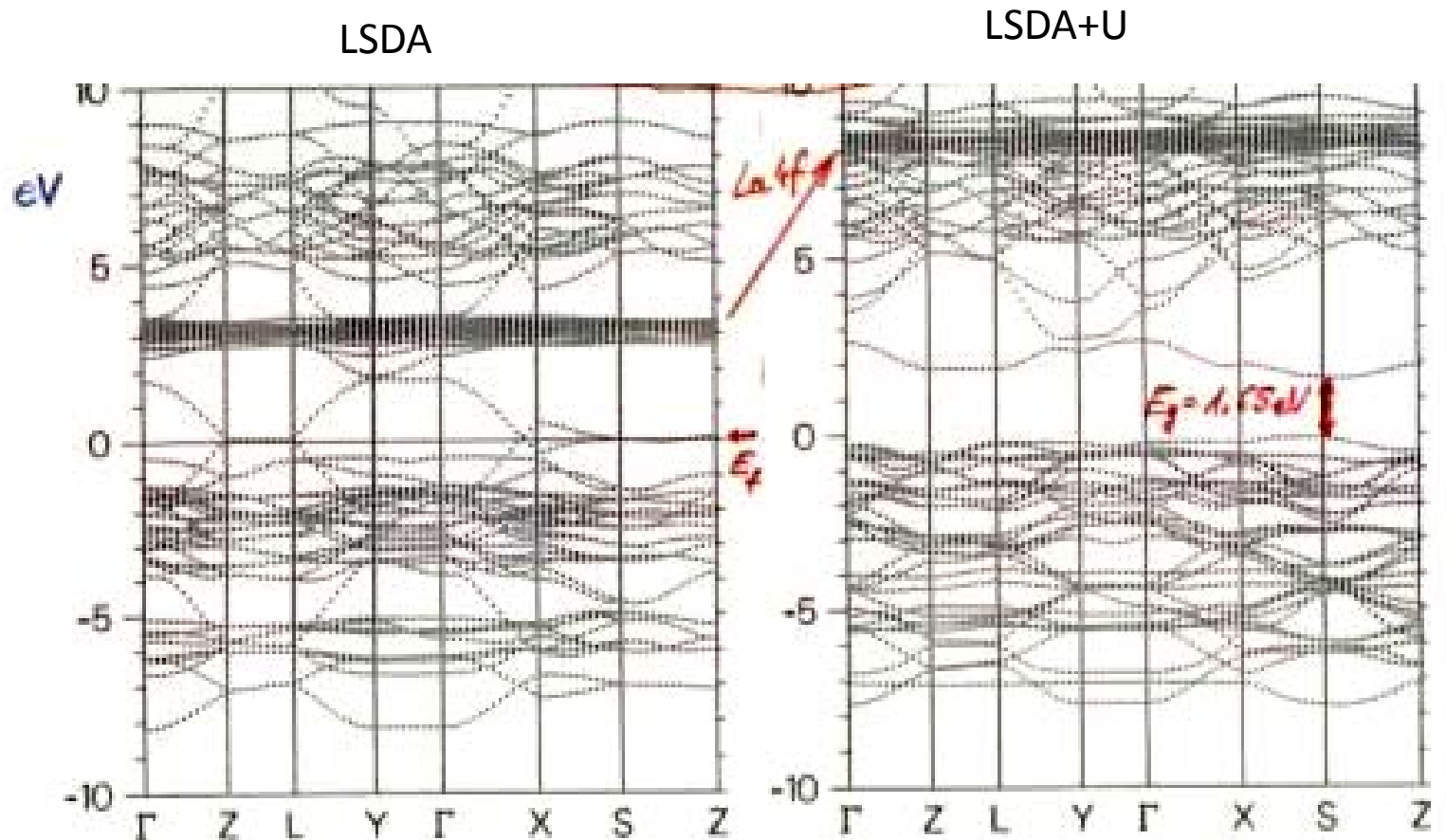
Lecture 3

Problems with band gaps or conductivity gaps

- One particle theory like DFT predicts La_2CuO_4 to be a non magnetic metal while experiment shows it is a strongly antiferromagnetic insulator with a ~ 2 eV conductivity gap
- This is the case for many transition metal and rare earth compounds and a general problem for correlated electron systems
- Also excitonic states in semiconductors and insulators are not described with conventional DFT methods

La₂CuO₄

LSDA+U antiferromagnetic $S=.8$ Bohr magnetons, $E_{\text{gap}} = 1.65$ eV



LSDA+U also has no electron correlation in the wave Function (Single Slater det. of Bloch states). No multiplets.

What is LSAD+U?

- Consider again a lattice of H atoms at relatively large spacing.
- We introduce an extra potential for an electron in a 1s spin up atomic state equal to U times the probability that the spin down state is also occupied.
- So adding an electron to H costs U but removing one from H does not save U if it was singly occupied in the first place.
- In actual practice we use $U/2$ in both cases to take care of another problem in DFT namely the self interaction

LDA Problems

- Self-interaction : Since Coulomb energy in LDA is expressed in terms of electron density and because the exact form of exchange correlation functional is unknown, the electron-electron interaction has artificial contribution from an electron interacting with itself.

$$E_{ee}[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

- We see that this provides for an energy difference between the electron removal energy i.e. the final state is the $N-1$ electron state and the electron addition state or the $N+1$ electron state.
- For the ionization potential i.e. $E(N-1)-E(N)$ in our example the H 1s state is empty in the final state.
- For the electron affinity state there are two electrons in the 1s in the final state and so the potential energy is higher by U when we add an electron.
- We see that now we get a gap between the occupied and unoccupied states i.e. a correlation gap of U
- Formally things are more difficult since we have to take care of double counting interactions etc.
- Note also that polarity fluctuations are now reduced.

LSDA+U (SIC)

Treat atomic like orbitals (3d, 4f ...) in non LDA manner:
orbital dependent potential with on-site Coulomb and
exchange interactions (U and J_H)

$$E^{LDA+U}[\rho^\sigma(\vec{r}), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(\vec{r})] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}]$$

$$E_{dc}[\{n^\sigma\}] = \frac{1}{2}U n_d(n_d - 1) - \frac{1}{2}J[n_d^\uparrow(n_d^\uparrow - 1) + n_d^\downarrow(n_d^\downarrow - 1)]$$

$$E^U[\{n\}] = \frac{1}{2} \sum_{\{m\}, \sigma} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{mm'}^\sigma n_{m''m'''}^{-\sigma} + \\ + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{mm'}^\sigma n_{m''m'''}^\sigma \}$$

LSDA+U (SIC) potential

$$E = E_{LDA} - UN(N-1)/2 + \frac{1}{2}U \sum_{i \neq j} n_i n_j$$

$$\epsilon_i = \partial E / \partial n_i = \epsilon_{LDA} + U \left(\frac{1}{2} - n_i \right)$$

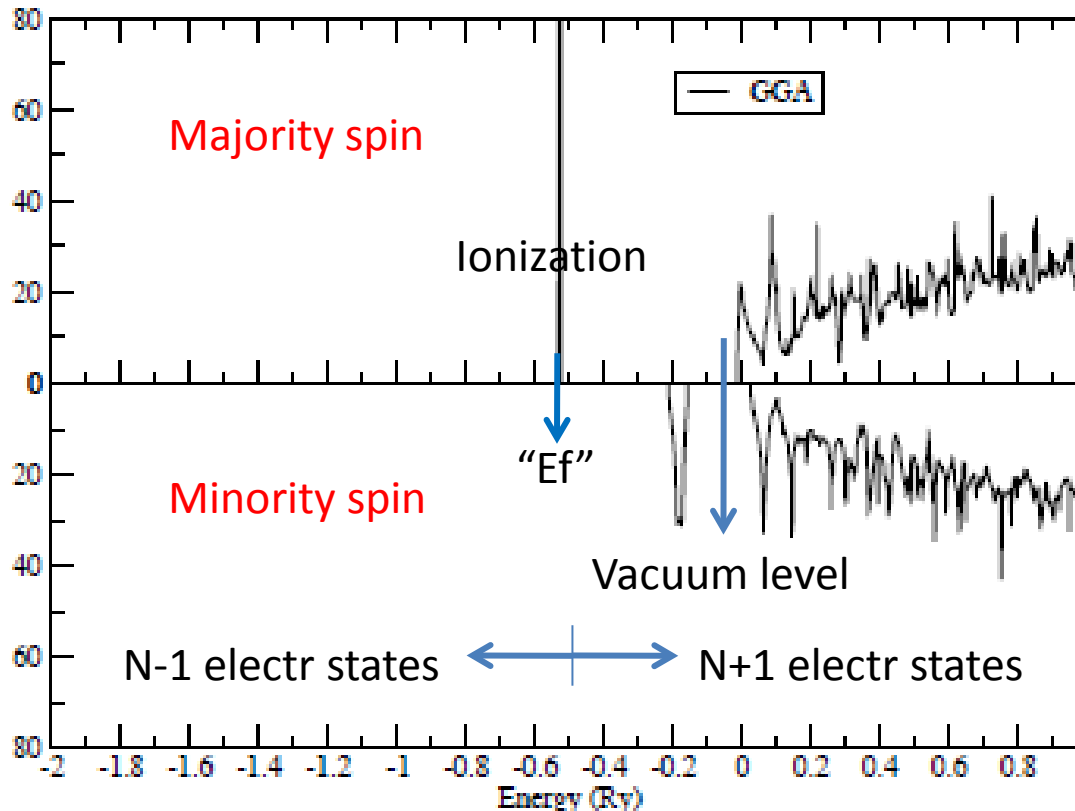
$$V_i(\mathbf{r}) = V_{LDA}(\mathbf{r}) + U \left(\frac{1}{2} - n_i \right)$$

LSDA+U (AMF)

$$\begin{aligned} E^{\text{LSDA+AMF}} = E^{\text{LSDA}} &+ \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} (n_{m\sigma} - n_{\sigma}^0) \\ &\times (n_{m'-\sigma} - n_{-\sigma}^0) \\ &+ \frac{1}{2} \sum_{m,m',m \neq m',\sigma} (U_{mm'} - J_{mm'}) (n_{m\sigma} - n_{\sigma}^0) \\ &\times (n_{m'\sigma} - n_{\sigma}^0) . \end{aligned} \quad (3)$$

Hydrogen lattice, simple cubic, large interatomic spacing in LSDA ($W \sim 0$) with ferromag. order

We need the order so that the occupation numbers per spin will not all be 1/2



$$E_{\text{tot}} = -0.958 \text{ Ry}$$

$$\epsilon_{1s} = -0.534 \text{ Ry}$$

Electron addition yields H-
i.e. 2 1s electrons

Should be:

$$E_{\text{tot}} = -1 \text{ Ry}$$

$$\epsilon_{1s} = -1 \text{ Ry}$$

Several points about the H lattice

- Note the 1s electron binding energy relative to the vacuum level is much too low (due to the self interaction in DFT)
- Note the 1s electron affinity is about 3eV which is much too high. It should be 0.7eV
- Note the electron addition state i.e. 1s² state is rather broad even for a large lattice constant while the electron removal width is very small. This is a result of the 1s wave function radial extent being strongly dependent on its occupation because the second electron is screened from the nuclear potential by the first.

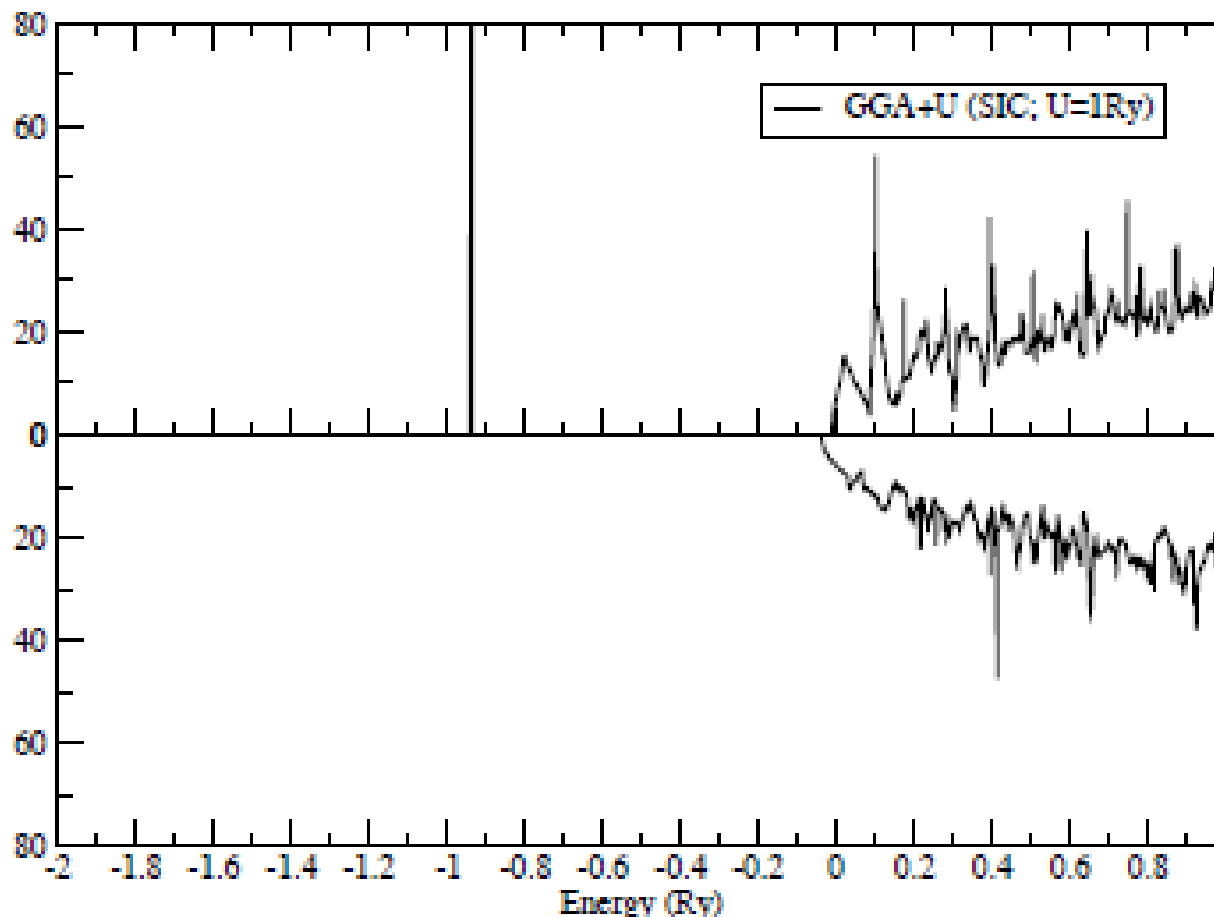
$$\sqrt{\langle r^2 \rangle} = 0.8A - \text{for}(H) - \text{and} = 1.72A - \text{for} - H^-$$

- This also means that our second quantization H is not correct since the atomic wave function depends on its occupation. This strongly increases the hopping integral for the motion of the second 1s electron. This is the so called occupation dependent hopping proposed by Hirsch as important for the cuprates.
- Eder et al PRB 56, 10115 (1997) , Hirsch et al PRB 48, 3327 (1993)

Hydrogen ionization potential in LSDA + U +SIC

Ferromagnetic large lattice spacing simple cubic

Uses $U/2$ for each Occupied / unoccupied state to take care of self interaction



$$E_{\text{tot}} = -0.927\text{Ry}$$
$$\epsilon_{1s} = -0.938\text{Ry}$$

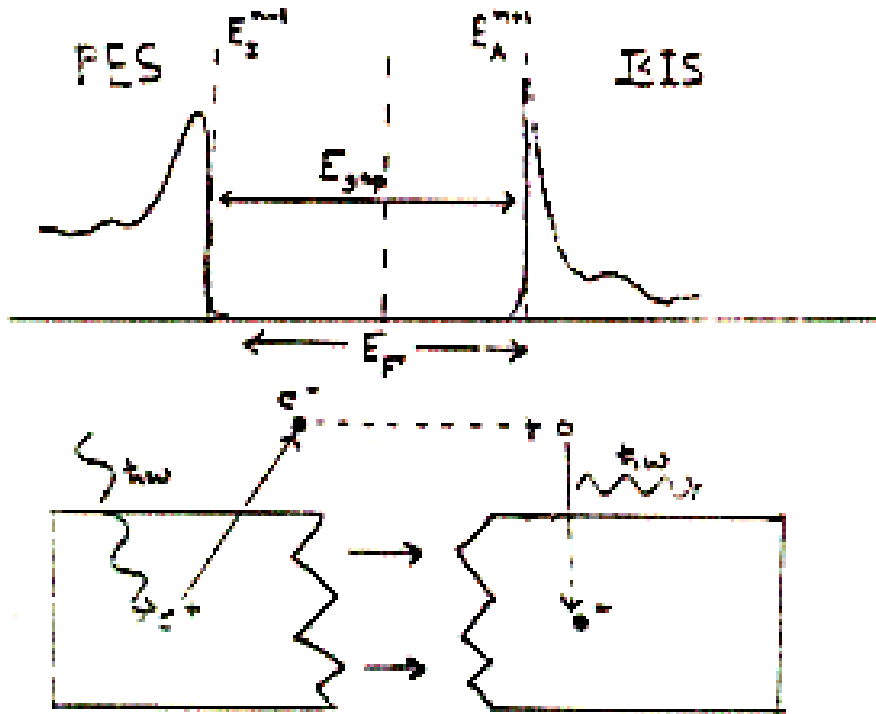
Now the 1s binding
Energy is close to exp
i.e 13.6eV or 1 Ryd but
The electron affinity
Now is negative.

LDA+U

- Has no correlation in the wave functions
- Single Slater determinants
- Spin is not a good quantum number only the z component
- Either magnetic order and mag moment per atom or no order and also no magnetic moment. I.e. no paramagnets with local Spins
- It can get the gap right and the right spin structure for many insulators
- As we will see below it does not get spectral weights right

What do we mean by the conductivity gap in a material

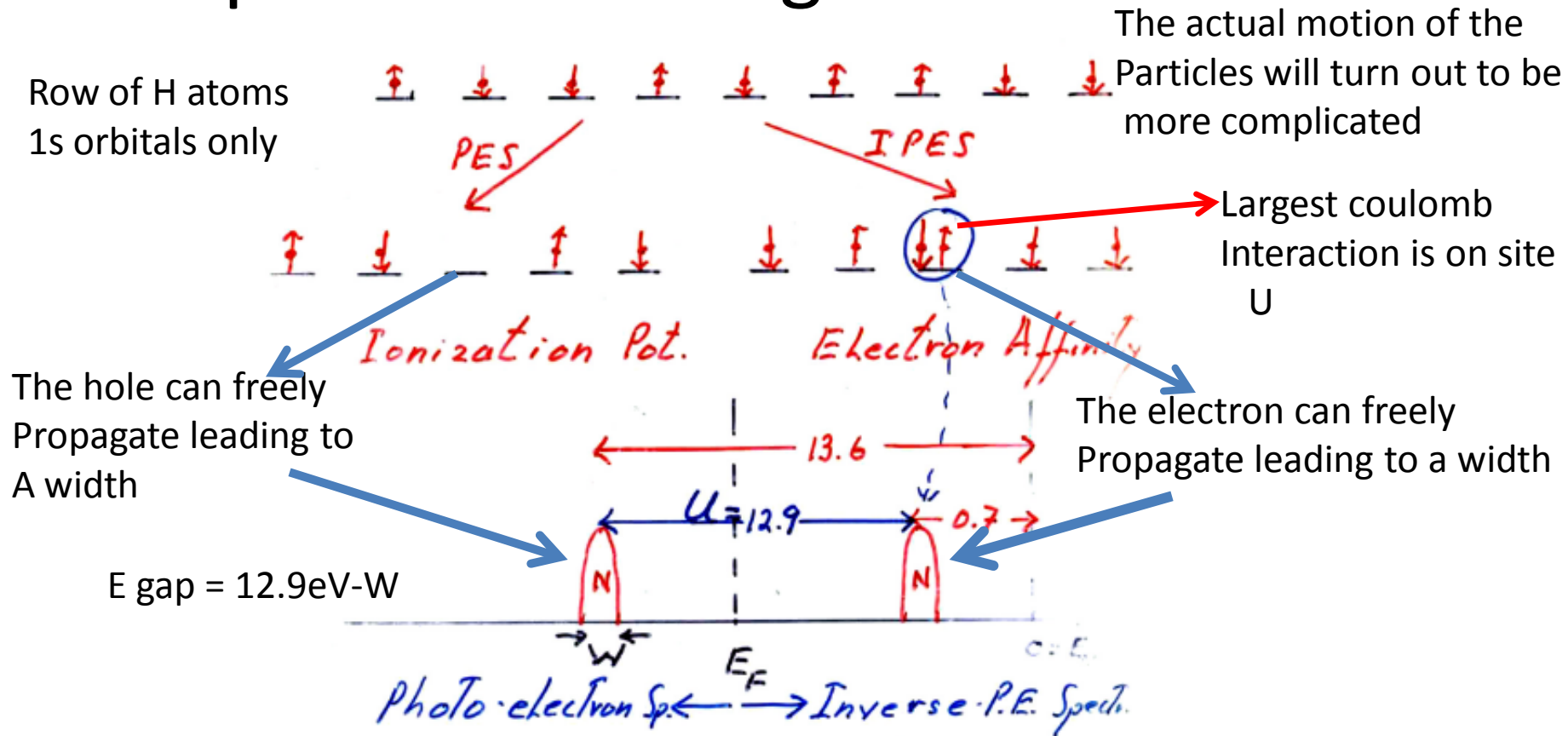
The minimum energy cost to remove an electron minus the maximum energy gain to add one to the ground state



$$E_{\text{gap}} = E_0(N-1) + E_0(N+1) - 2E_0(N)$$

N is the number of electrons in the ground state. E_0 here stands for the lowest energy state in each case.

Simplest model single band Hubbard



The simplest Hamiltonian to describe this involves nearest hopping and on site U

Hubbard

$$H = t \sum_{i,j(i \neq j)} c_{i\sigma}^+ c_{j\sigma} + U \sum_i n_{i\sigma} n_{i,-\sigma}$$

$$n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$$

H in terms of Hamiltonian matrix elements

- First note that we have neglected the dependence of the atomic wave function on its occupation number. i.e. occupation dependent hopping.
- The hopping term $\langle \varphi_i | H | \varphi_{i+1} \rangle = t$
- The interaction term $\langle \Psi_{i\uparrow, i\downarrow} | H | \Psi_{i\downarrow, i\uparrow} \rangle = U$

What happens for $U \gg W$

- The charge excitations as pictured are high energy scale
- The low energy scale is dominated by spin excitations since each atom has an unpaired electron with spin $=1/2$
- Virtual charge fluctuations involving U will generate a nearest neighbor antiferromagnetic exchange interaction $J = \frac{4t^2}{U}$
- We come back to this later

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?

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

Heisenberg Spin Hamiltonian

Concept of spectral weight transfer

- What happens in a strongly correlated system i.e. $U \gg W$ If we change the electron concentration i.e. as in doping a high T_c materials?
- Do we simply move the chemical potential into the lower Hubbard band and have one empty state per removed electron as we would in a simple semiconductor?
- Indeed this is what would happen in LDA+U

What would a mean field theory give you?

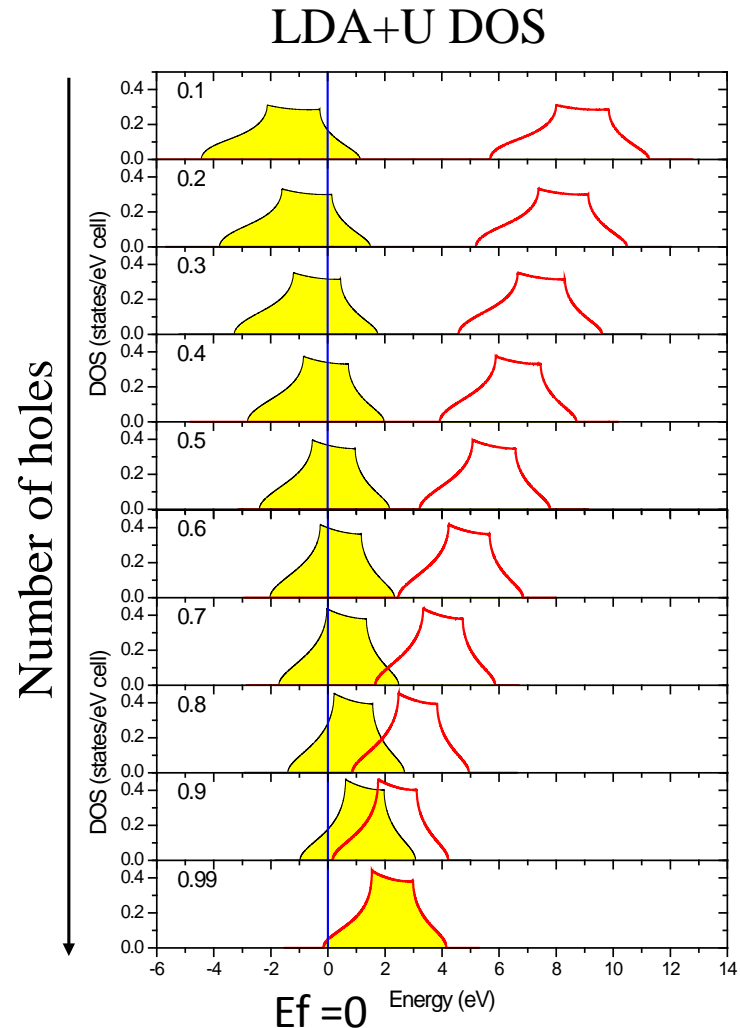
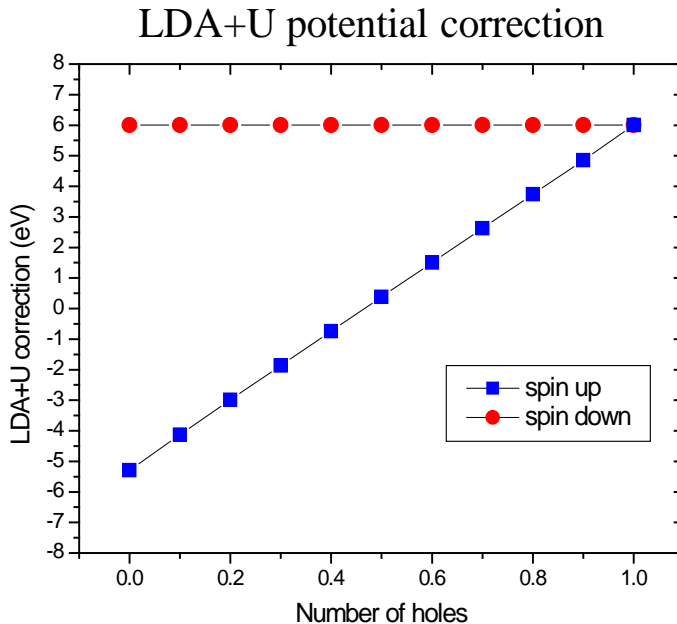
Elfimov unpublished

SC Hydrogen

ferromagnetic

$$a = 2.7 \text{ \AA}$$

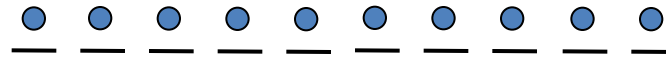
$$U = 12 \text{ eV}$$



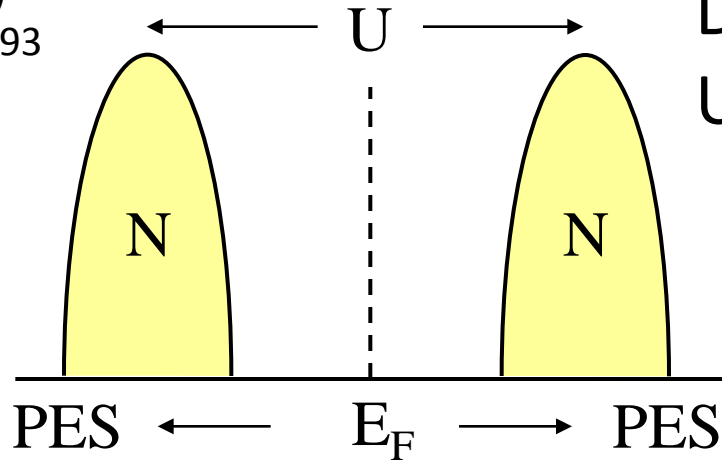
Note that there is no spectral weight transfer and a gap closing with doping From half filled. Both opposite to the real situation. The gap Closing is due to the mean field nature.

Spectral weight transfer

Mott – Hubbard

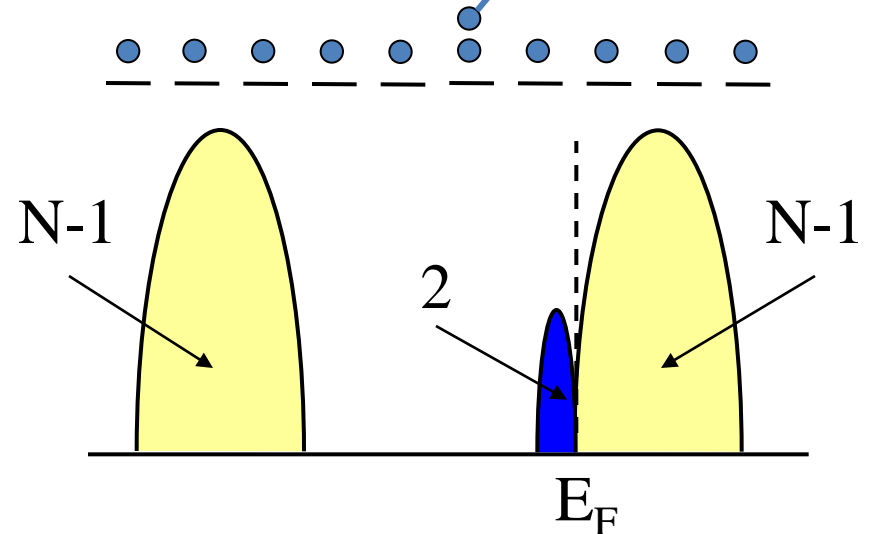
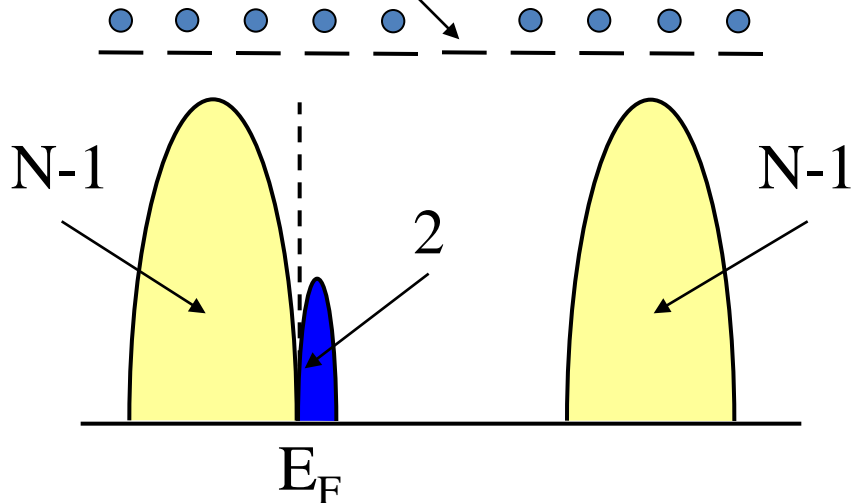


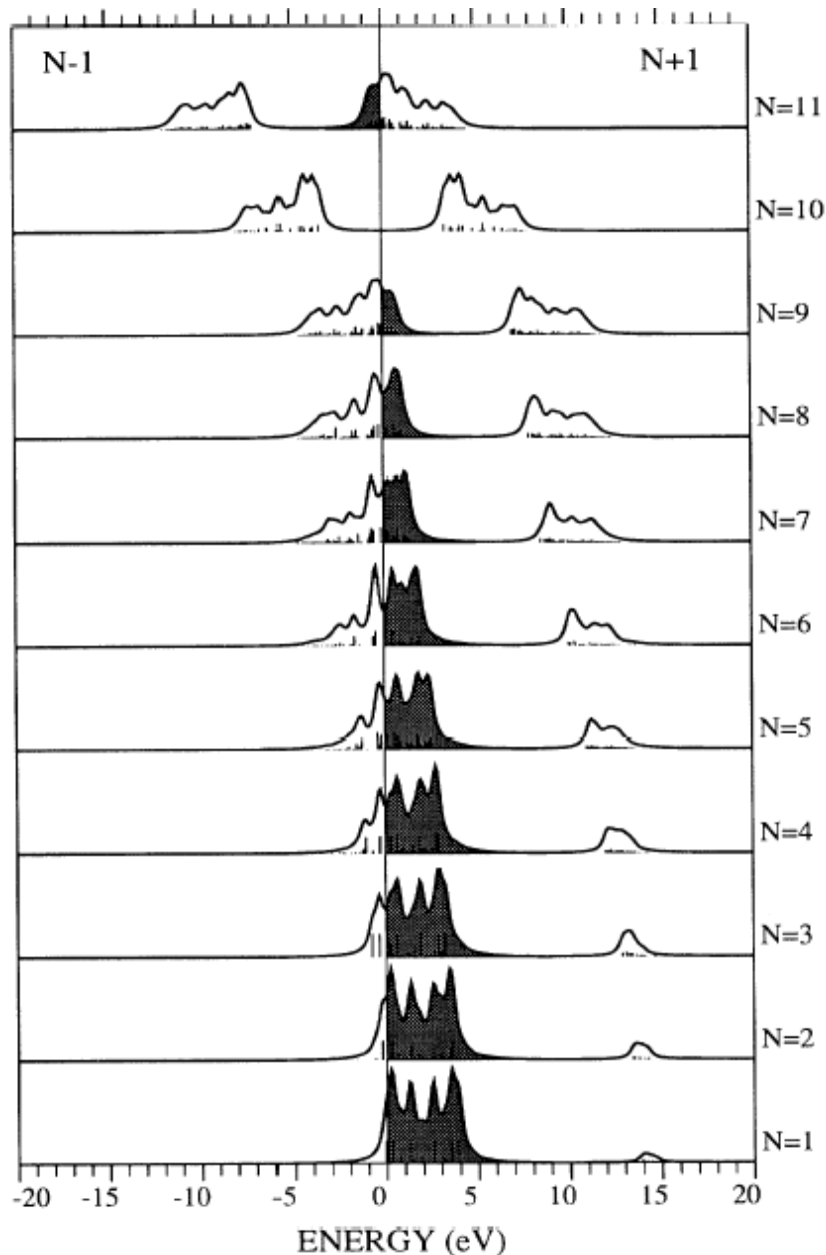
Dots indicate spin
Up Or spin down!!



Remove one electron
Create two addition
states At low energy

Adding one electron
Creates two addition
states At low energy





Exact diagonalization in 1D
Hubbard 10 sites $U=10t$

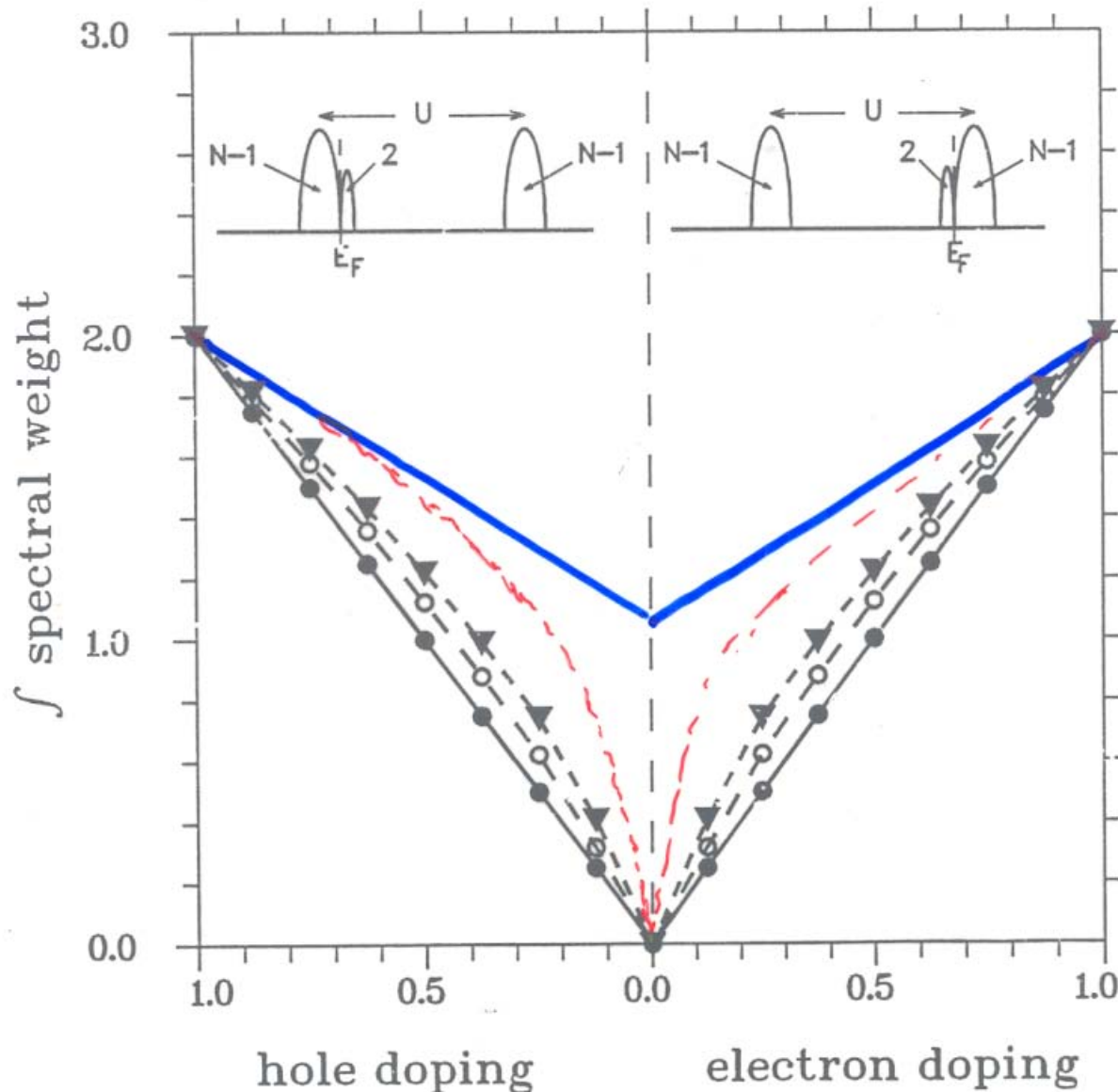
- U Gap increases with doping
- Spectral weight is transferred from the upper Hubbard band to the lower Hubbard band
- In a mean field theory the gap would close i.e.

$$U_{eff} = \langle n_i \rangle U$$

Dynamic spectral weight transfer

- For finite hopping i.e. $U > W$ but t finite even more weight is transferred from the upper to the lower Hubbard band. This is rather counter intuitive since for increasing t we would have expected to go towards the independent particle limit. However this seems to happen in a rather strange way .

These particles block 2 or more states



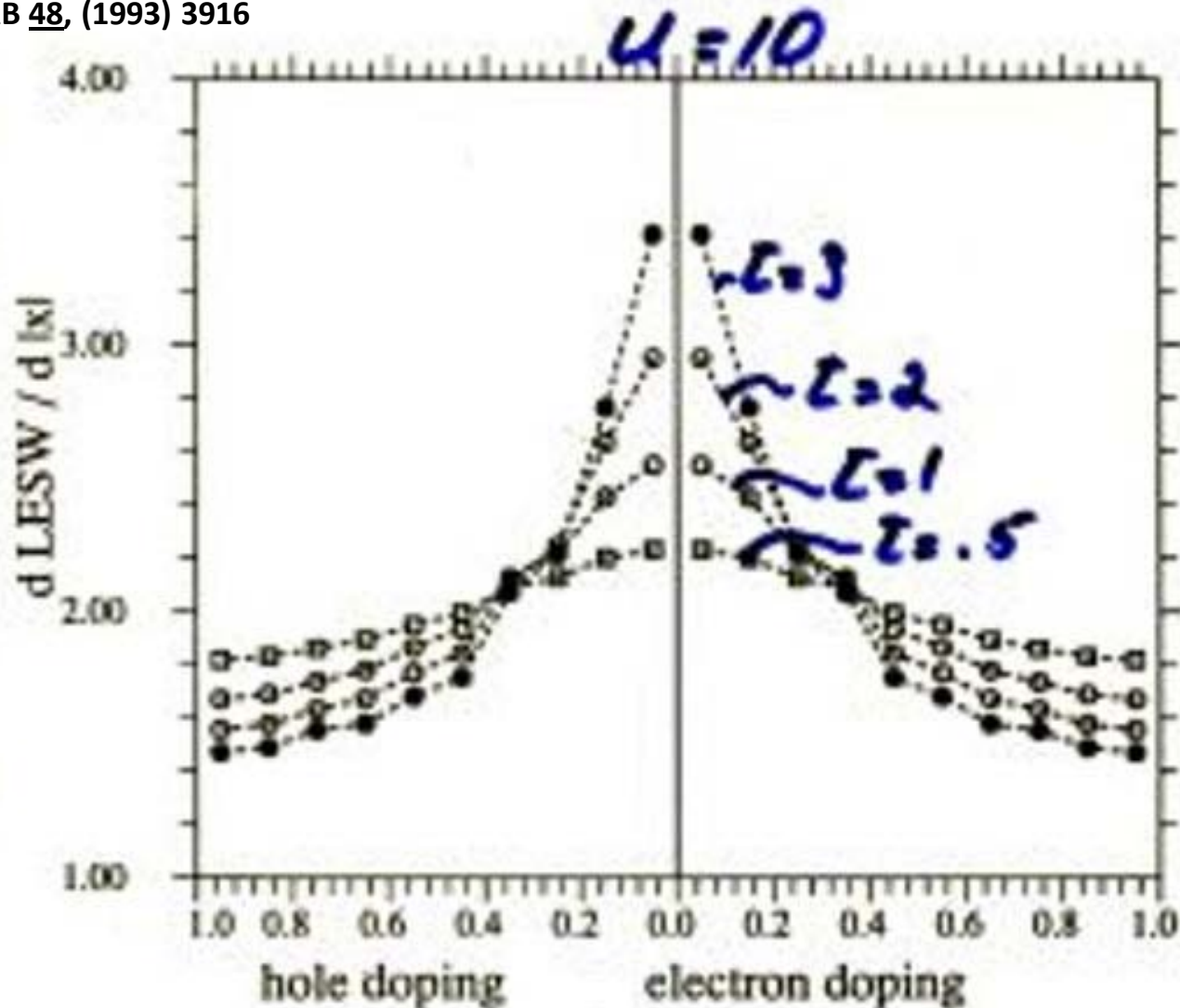
Bosons – block 0 states
Fermions – block 1 state

Integral of the low Energy spectral weight For electron addition if Hole doped (left) and Electron removal for e Doped (right side). The blue Lines indicate what would be Expected for $U=0$. i.e. slope of 1. The initial slope increases with The hopping integral t

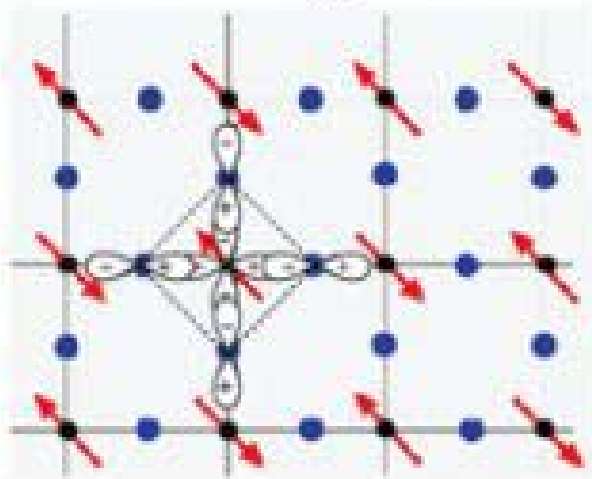
The derivative of the low energy spectral weight
As a function of doping and the hopping integral t
Showing the divergent behavior with t close to zero doping

Eskes et al PRL 67, (1991) 1035

Meinders et al PRB 48, (1993) 3916



Doped holes in cuprate



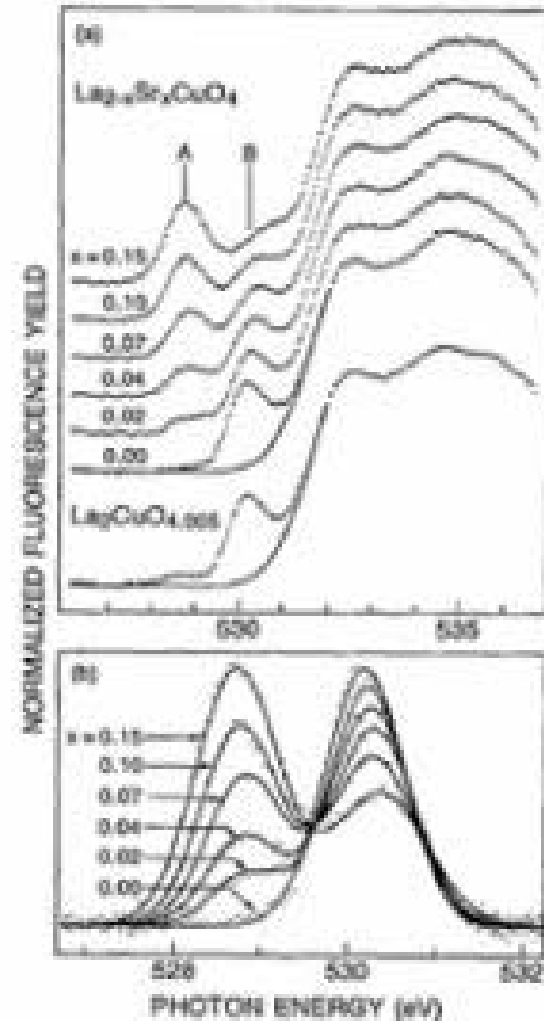
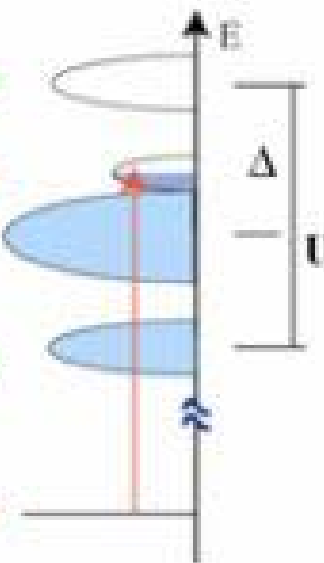
Upper Hubbard band $d^9 \rightarrow d^{10}$

Zhang-Rice singlet band

Charge transfer band $d^9 \rightarrow d^9 1^{-1}$

Lower Hubbard band $d^9 \rightarrow d^8$

Oxygen 1s



C. T. Chen et al. PRL 66, 194 (1991)

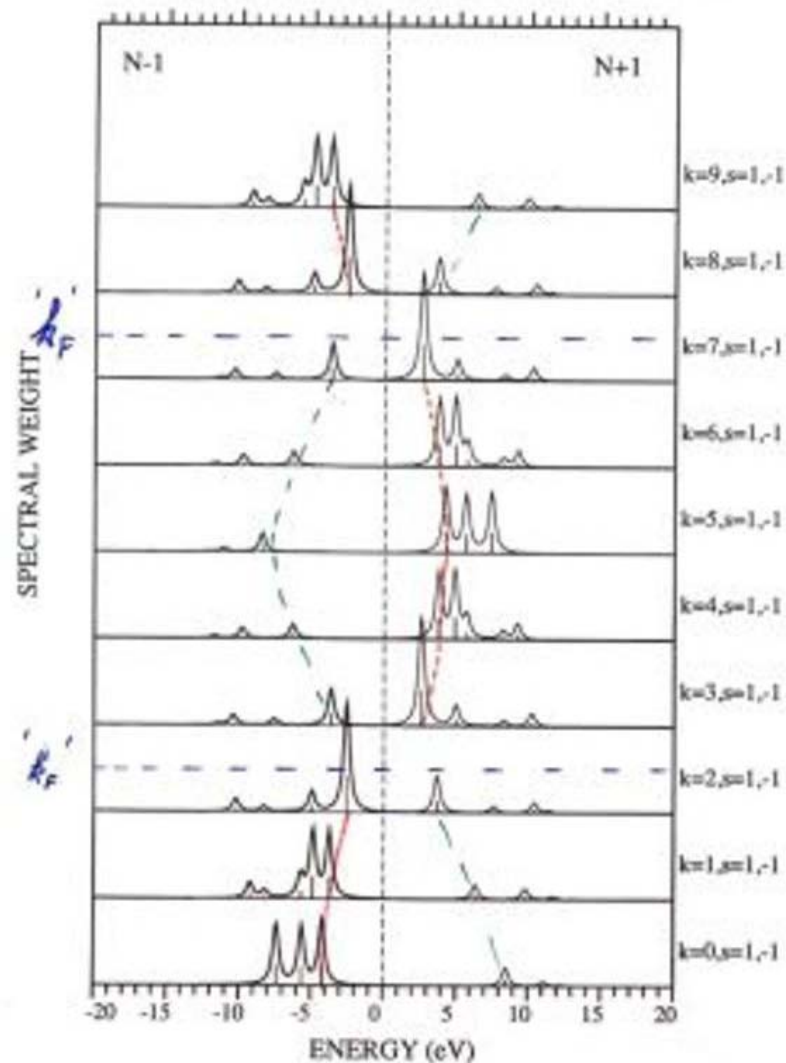
Spectral function for electron removal

- One particle theory would give a sharp peak in energy for each momentum and band index and no spectral weight transfer from high to low energy scales
- Strongly correlated systems have strong spectral weight transfer
- Strongly correlated systems exhibit strong energy dependent structure in the spectral function for each momentum
- This brings us directly to the concept of dressing of the particles
- When you suddenly remove an n electron the dressing stays behind and this evolves into the eigenstates of the $N-1$ - electron system. This may be very k dependent.

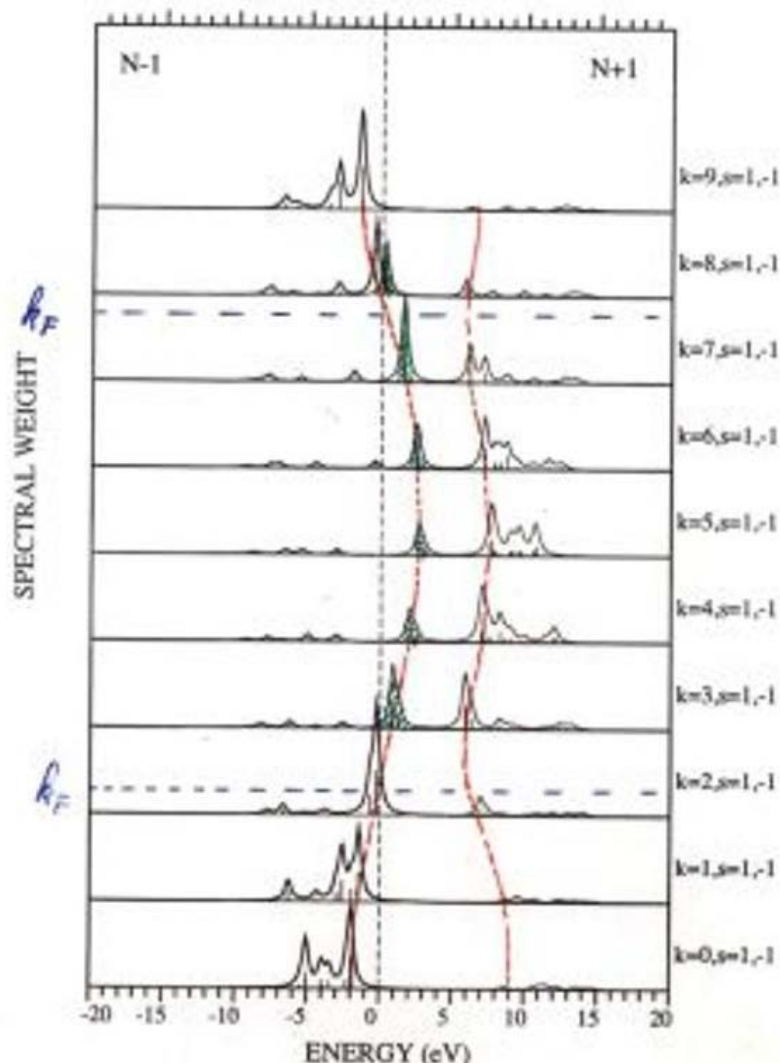
Exact diagonalization 1D Hubbard

Meinders et al,
PRB 48, 3916 (1993)

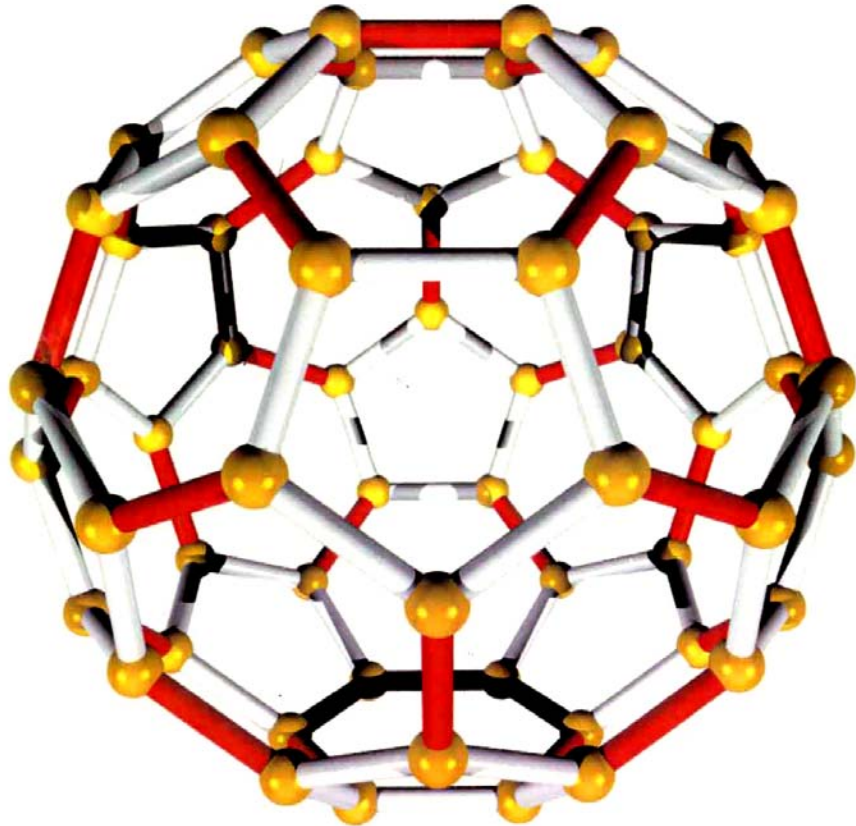
the Spectral function is very different from single part. Theory
 1D Hubbard (10 uc), $U = 10.0$, $t = -2.0$ eV
 10 electron Ground-State ($K=0$, $S=0$)
i.e. $E_k = 2t \cos k$



1D Hubbard (10 uc), $U = 10.0$, $t = -2.0$ eV
 9 electron Ground-State ($K=2$, $S=1$)



Correlation is also very important in molecular solids. Usually here The band widths are very small i..of order 1 eV or less so even a small U can yield strong correlations. U in these systems is usually defined not as an atomic U but a molecular one. That is the ionization potential minus the electron affinity of the molecule corrected for the molecular orbital energy splitting.



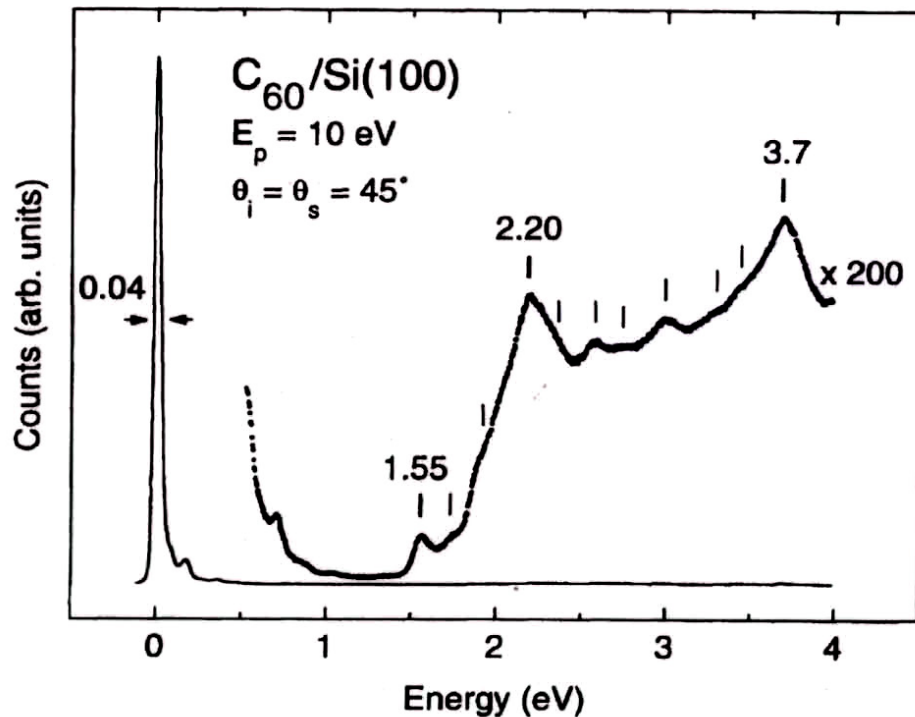
C60 or the Bucky ball or Fullerene named after Buckminster Fuller an architect , crystalizes in a face centered cubic structure of C60 molecules at 300K. The compound K3C60 is a superconductor at 20K and others of this family up to 63 K.

Can we get an experimental value for
U in solid C60?

- Use photo and inverse photoemission and gas phase optics.

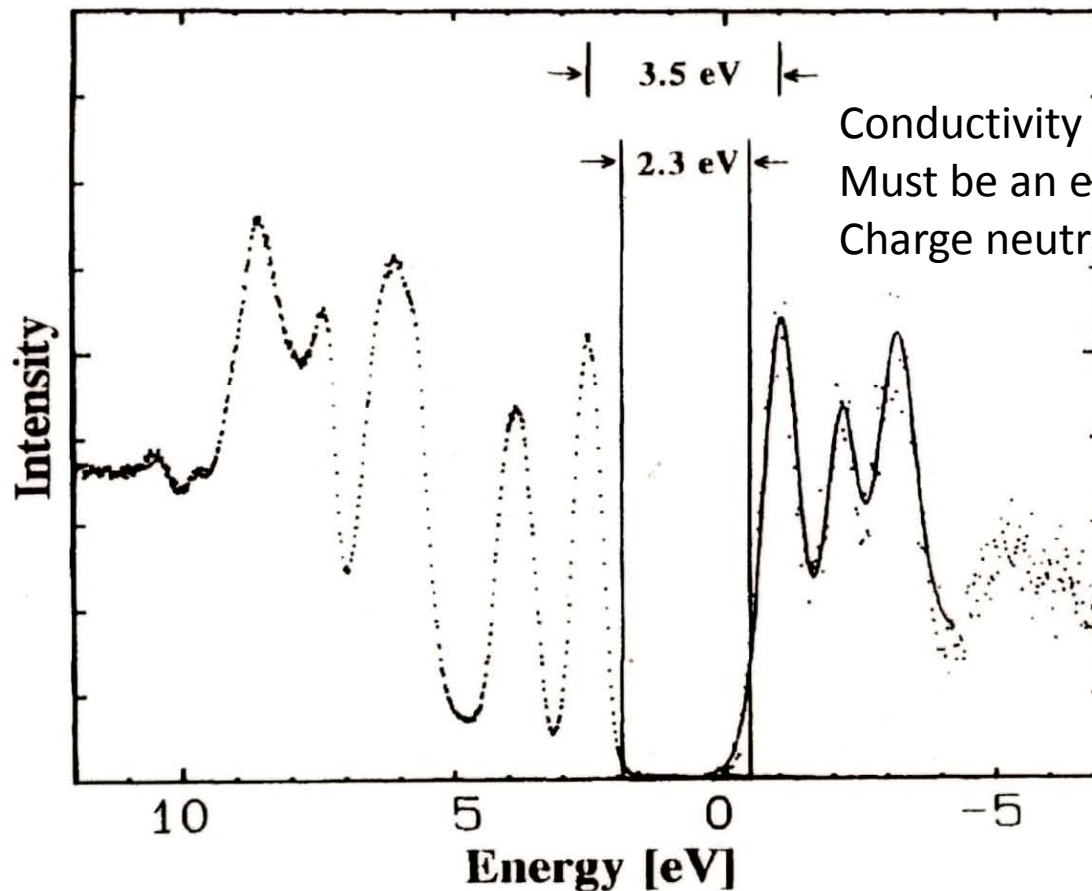
Electron energy loss spectroscopy indicates a gap of 1.55 eV. Is this really the conductivity gap?

The 1.55 eV excitation which agrees with the DFT band gap was thought to be the conductivity gap.



Using photo and inverse photoelectron spectroscopy we see only Charged states and not the charge neutral excitations also present In optics or electron energy loss.

R.W. Loft *et al*, PRL **68**, 3924 (1992)



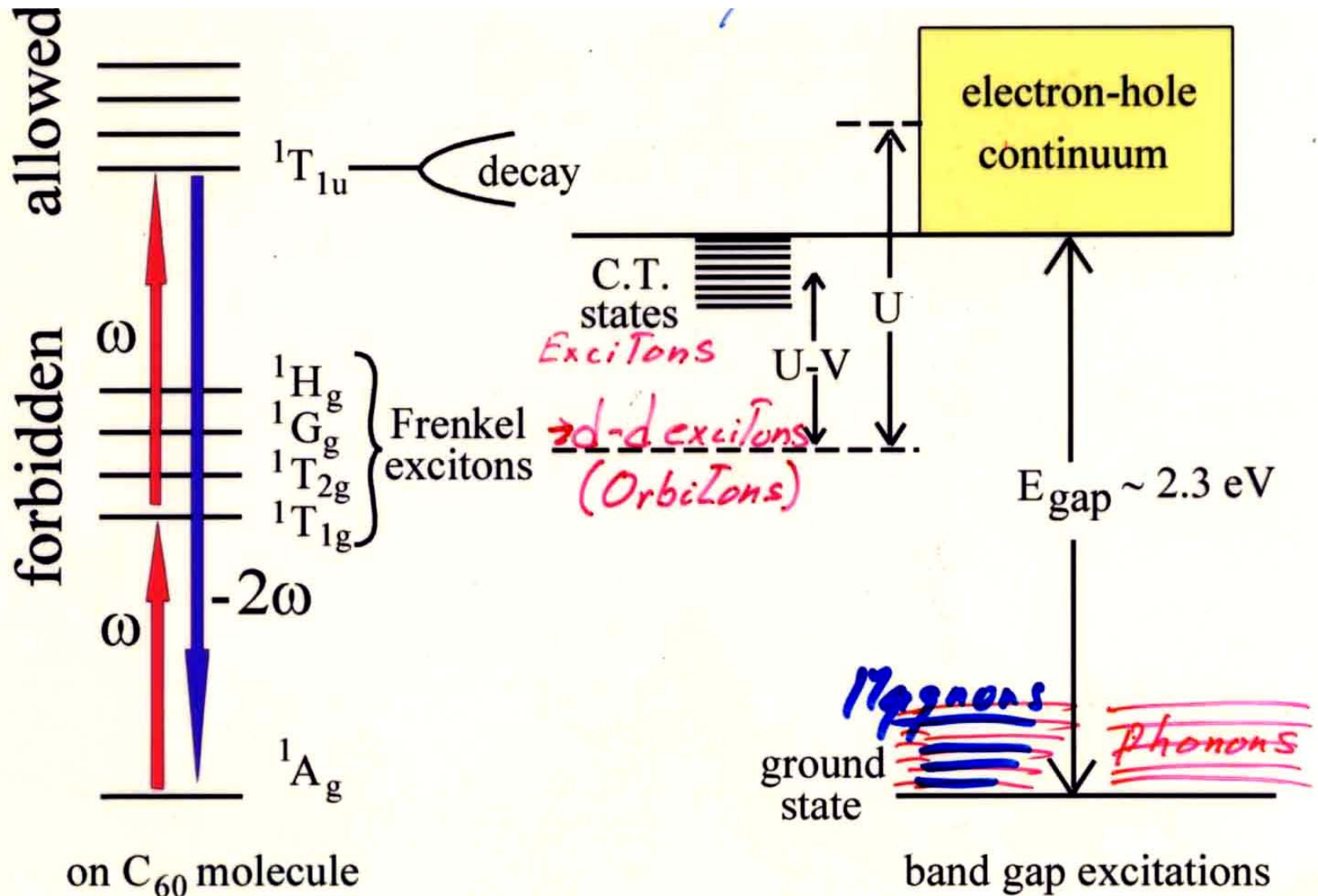
Conductivity gap is 2.3 eV the 1.55 eV
Must be an excitonic excitation i.e.
Charge neutral.

Definition of Conductivity Gap

$$\begin{aligned} E_{\text{gap}} &= (E_{\text{gr}}^{N-1} - E_{\text{gr}}^N) + (E_{\text{gr}}^{N+1} - E_{\text{gr}}^N) \\ &= E_{\text{gr}}^{N-1} + E_{\text{gr}}^{N+1} - 2 E_{\text{gr}}^N \end{aligned}$$

E_{gr} \longrightarrow Ground state

General elementary excitations



How to get U from the electron spectroscopy experiment.

$$E_{\text{gap}} = 2.3 \text{ eV} \quad [\text{Conductivity}]$$

$$E_{\text{opt}} = 1.5 \text{ eV} \quad [\text{Must be Locally Charge conserving}]$$

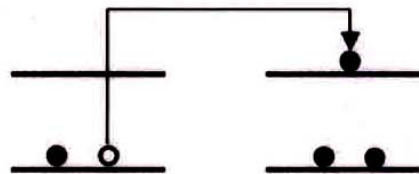
$$W \approx 0.5 \text{ eV}$$



Excitons

Exciton binding energy $\sim 0.8 \text{ eV}$ i.e. $2.3 - 1.5$

Requires electron—hole attraction $\sim 1.6 \text{ eV}$



PES + IPES

$$E_{\text{gap}} = E_I - E_A = U + \Delta E$$



Total Coulomb for ground state = $2U$

Total Coulomb for excited state = $3U$



Optical

$$E_{\text{ex}} = \Delta E$$

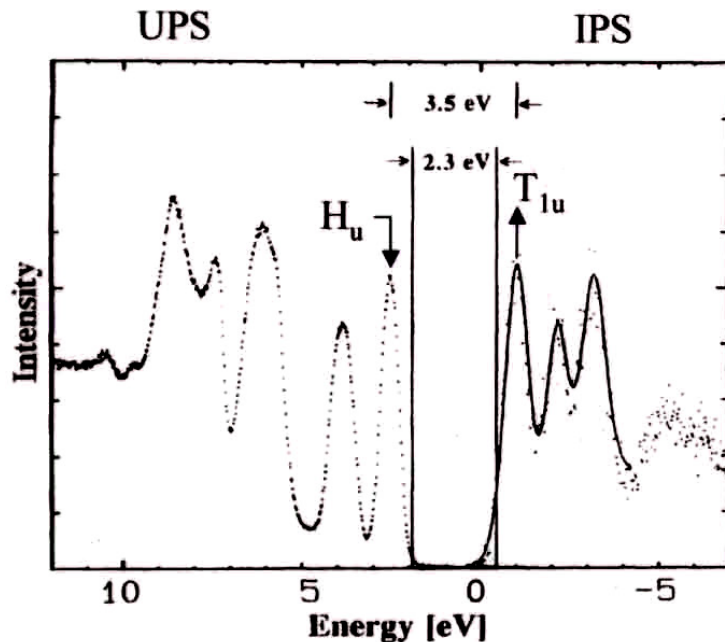
Total Coulomb for ground state = $2U$

Total Coulomb for excited state = $2U$

U for C₆₀ solid from Auger spectroscopy

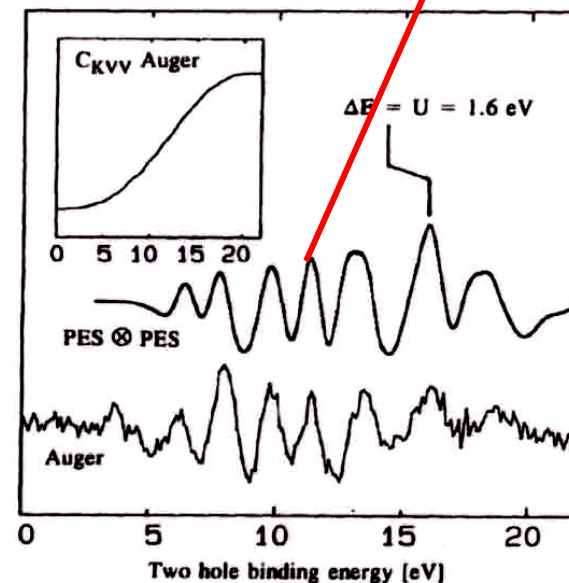
A shift of 1.6 eV is needed to match the self convolution with Auger

Photo-electron Spectroscopy



$$E_{\text{gap}} = 2.3 \text{ eV}$$

Auger C_{KVV}



$$U = 1.6 \text{ eV}$$

Is this U reasonable ?

Gas phase :

$$I = 7.6 \text{ eV}$$

$$A = 2.65 \text{ eV}$$

$$E_{T_{1u}-H_u} = 1.6 \text{ eV}$$

} Smalley

$$U = I - A - E = 3.4 \text{ eV}$$

$$U [\text{'atomic'}] = 3.4 \text{ eV}$$

Solid \Rightarrow Screening *[We return to a description later]*

$$E_p = \frac{ze^2\alpha}{R^4}$$

Z=12 [FCC] but smaller at surface

$$E_I = E_I^0 - E_p$$

$$E_A = E_A^0 + E_p$$

effect: $\begin{cases} \text{reduction} & I \\ \text{increase} & A \end{cases}$

α = Polarizability

$$\alpha(C60) = 8nm^3$$

Now:

$$U [\text{'solid'}] = 1.6 \text{ eV}$$

Compares well with our experiments !

Two particles in a periodic solid as a function of U/t

- The Hubbard Hamiltonian for only one particle i.e. 1 electron or one hole in an empty/full respectively band does not contain the U term. i. Photoemission spectrum of the d band in Cu metal.
- Two electron or holes in a otherwise empty/full band respectively can also be solved for a Hubbard Hamiltonian.

Two particles in a Hubbard model

$$H = t \sum_{R,s,\sigma} c_{R+s,\sigma}^+ c_{R,\sigma} + U \sum_R c_{R,\uparrow}^+ c_{R,\uparrow} c_{R,\downarrow}^+ c_{R,\downarrow}$$

R=lattice position
s=nearest neighbor vector

$$H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^+ c_{k,\sigma} + \frac{U}{N} \sum_{k,l,q} c_{l+q,\uparrow}^+ c_{l\uparrow} c_{k-q}^+ c_k$$

$$c_k = \frac{1}{\sqrt{N}} \sum_R c_R e^{ik \cdot R}$$

Total Momentum and total spin 0,1 conservation $[H, K] = 0, \dots [H, S] = 0$

$$G_{q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow} = \langle 0 | c_{K-k\downarrow} c_{k\uparrow} G(z) c_{q\uparrow}^+ c_{K-q\downarrow}^+ | 0 \rangle$$

$$G(z) = \frac{1}{z - H}$$

For triplet solutions the U term is not active

$$G_{q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow} = \left(\delta_{kq} - \delta_{k, K-q} \right) \frac{1}{z - \varepsilon_k - \varepsilon_{K-k}}$$

The two particle density of states =
Im (sum over K and k of G) = self
convolution of the one particle density
of states

The singlet $S=0$ two particle greens function in Hubbard

Use the Dyson equation : $G = G_0 + G_0 H_1 G$

With $H = H_0 + H_1$ single particle + U respectively

$$G_{0q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow}(z) = \delta_{k,q} \frac{1}{z - \varepsilon_k - \varepsilon_{K-k}} = \delta_{k,q} G_0(k, K-k; z)$$

$$G_{q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow} = \delta_{k,q} G_0(k, K-k) + G_0(k, K-k) \frac{U}{N} \sum_{\kappa} G_{q\uparrow, K-q\downarrow}^{\kappa\uparrow, K-\kappa\downarrow}$$

Now sum the left and right hand sides of k

$$\sum_k G_{q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow} = G_0(q, K-q) + \sum_k G_0(k, K-k) \frac{U}{N} \sum_{\kappa} G_{q\uparrow, K-q\downarrow}^{\kappa\uparrow, K-\kappa\downarrow}$$

$$\sum_k G_{q\uparrow, K-q\downarrow}^{k\uparrow, K-k\downarrow}(z) = \frac{G_0(q, K-q; z)}{1 - \frac{U}{N} \sum_k G_0(k, K-k; z)}$$

Two particle eigenenergies

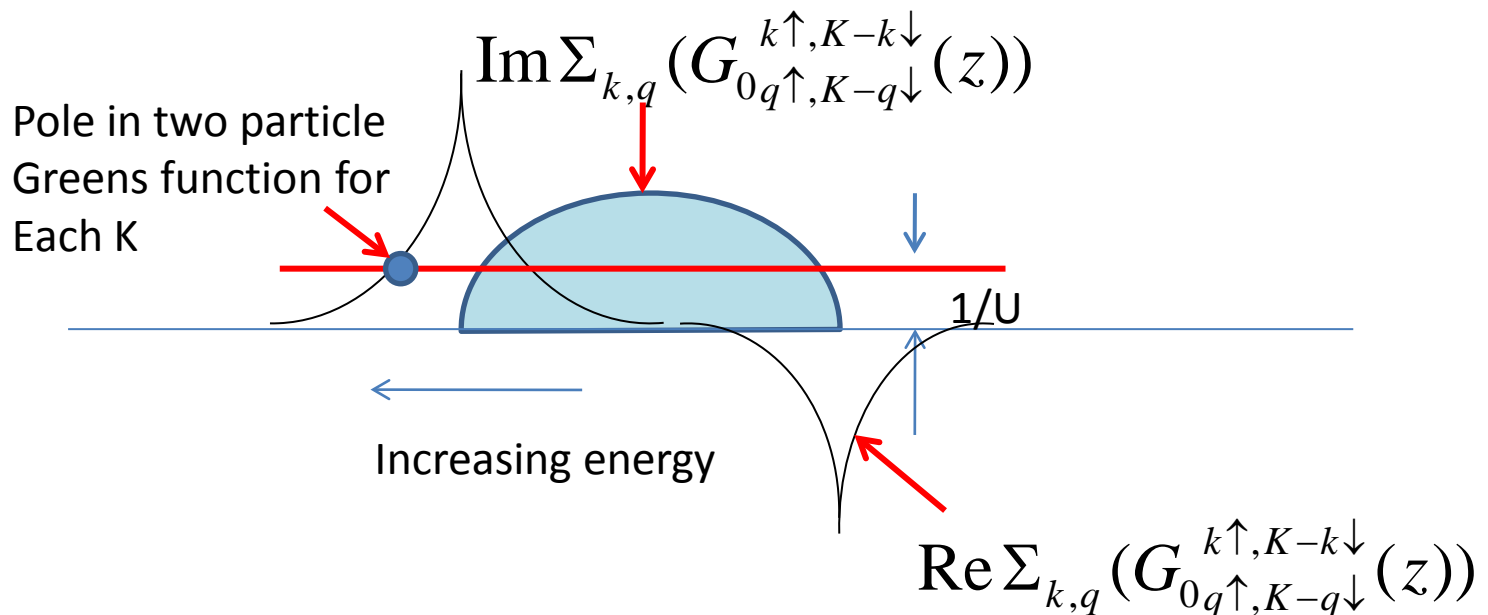
- There are two kinds of states 1. appearing inside the convolution of the single particle density of states governed by the imaginary part of the numerator. And 2 the two particle bound states which appear outside this region at energies where the real part of the denominator goes to zero.

$$\text{Re} \left(\sum_k G_0(k, K-k; E_n) \right) = \frac{N}{U} \text{ --- where } E_n \text{ Are the singlet eigenenergies}$$

Discussion of two particle states

- The imaginary part of G_d is the two particle non interacting density of states and forms a bounded continuum of states.
- The real part for two holes for example looks like goes to is peaked at the band edges positive at high energies (and negative at low energies) and then goes to zero as $1/E^2$ as we move to even higher energies. Remember we are talking about holes as in Auger spectroscopy

The two particle states outside of the convolution of the single particle density of states will occur at the poles for each K as in the figure below. Since these poles depend on K we will get a two particle bound state dispersion



Local Two particle density of states

one particle $\eta_1(\epsilon)$

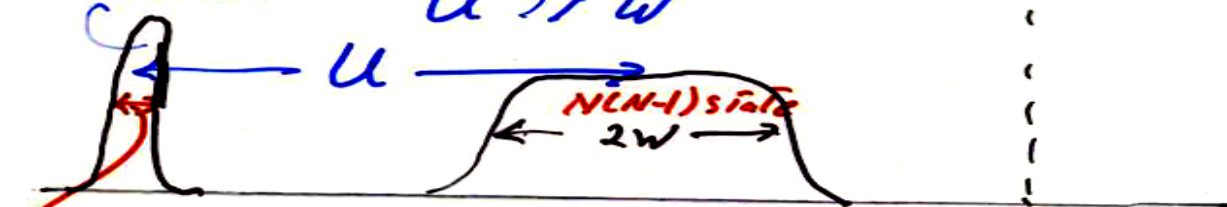


Two particle $\eta_2(\epsilon) = \text{self convolution of } \eta_1(\epsilon)$
For $U=0$



N states

$U \gg W$



$\approx \frac{2Z^2}{U} \times \text{No of nearest neighbours}$

Auger spectrum

