# Electronic structure of correlated electron systems

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# First question 1 of the home work assignment

- 1a) Consider a H2 molecule described by the Hubbard Hamiltonian. Assume only 1s hydrogen like wave functions and inter atomic hoping t on site interaction U. Derive the energy and wave function for the ground state and the excited states of the N (i.e.2) electron system. Derive the Heisenberg exchange Hamiltonian for U>>t.
- b) What is the energy splitting between the spin singlet and triplet states for U>>t?
- c) Derive the eigenfunctions and eigenvalues for the N-1 and N+1 electron states. i.e. 1 electron and 3 electrons respectively
- d) What would the photoemission and inverse photoemission spectrum look like for U=0, U=t/2, U=t and U>>t. Note the difference when U=0 (molecular orbital limit) and U >> t Heitler London Limit)
- e) In the large U limit but for finite t why do we see two peaks in the photoemission spectrum?

#### PES and IPES for a hydrogen molecule

The ground state wave function of two electrons in a singlet state which we get by solving the Hubbard model is a combination of Slater determinants with various amplitudes of single and doubly occupied sites as shown in the previous lecture.

- Removing one electron in PES leaves one and the eigenstates are bonding and antibonding separated by 2t. If we add an electron in IPES we have one hole left. So also two peaks separated by 2t in principle but shifted up in energy by U from the PES spectrum.
- For U=0 electrons are in a bonding orbital spin antiparallel. If we remove one say spin up then the spin down one remains and its overlap integral squared with the eigenstate of the final state is 1. The anitbonding state has zero intensity.
- For U>>>t the two particle ground state is a singlet with one electron on each of the two H atoms. Removing one electron suddenly, leaves the other behind on the other atom and the overlap integral squared of this wave function with the eigenstates of the one electron problem is ½ for each of the bonding and antibonding states. Similarly for IPES
- For inbetween values of U there will be two peaks separated by 2t always and the weight will gradually shift from the high U values of equal weights towards all the weight being in the lowest energy peak i.e. the bonding state for the remaining electron in PES and the antibonding state for the remaining hole in IPES.

#### Back to screening and polarizability

#### Homogeneous Maxwell Equations $\epsilon(\mathbf{r},\mathbf{r'}) \longrightarrow \epsilon(\mathbf{r} - \mathbf{r'}) \longrightarrow \epsilon(\mathbf{q})$

Ok if polarizability is uniform Or for q close to zero corresponding to large distances

$$V(q) = \frac{V^{0}(q)}{\varepsilon(q)}$$

In most correlated electron systems and molecular solids the polarizability is actually Very NONUNIFORM

# In many solids the plarizability is very non uniform

- Short range interactions cannot be described in terms of E(r-r') but rather E(r,r') and so we cannot use E(q) to screen
- Rather than working with E go back to work in real space with polarizability
- Atomic plarizabilities are high frequency i.e. of order 5 or more eV. Most correlated systems involve narrow bands i.e. less than 2 eV and so the response of atomic polarizability to the motion of a charge in a narrow band is instantaneous.
- i.e Electrons are dressed by the polarizable medium and move like heavier electronic polarons

Screening or better reduction of the on site U simple model Recall U= EI - EA



Potential produced at the origin due to the polarization

$$\phi(0) = \int_{R}^{\infty} \frac{P}{r^2} dV = \frac{e}{R} (1 - \frac{1}{\varepsilon})$$

The energy involved in building up the charge to a value of e is given by

$$\int_{0}^{e} \frac{q}{R} (1 - \frac{1}{\varepsilon}) dq = \frac{1}{2} \frac{e^2}{R} (1 - \frac{1}{\varepsilon})$$

That is the energy cost to add a charge dq in the presence of a charge q and integrate this up to the total charge of e

Notice this goes like the charge squared so for two charges on the same site the net energy difference with that of two charges very widely separated in space is twice as large. i.e. charge of 2e versus two times the charge of e.

$$U = E_I - E_A$$
$$E_I = E_I^0 - \frac{e^2}{2R}(1 - \frac{1}{\varepsilon}) \qquad \qquad E_A = E_A^0 + \frac{e^2}{2R}(1 - \frac{1}{\varepsilon})$$
For  $\varepsilon$  large as in a metal  $U = U_0 - \frac{e^2}{R}$ 

NOTE we assume linear response theory which may not be correct!!

#### A Picture of Solvation of ions in a polarizable medium



Full polarization can develop provided that Dynamic Response Time of the polarizable medium is faster than hopping time of the charge

 $\Delta E$  (polarizability) > W ;  $\Delta E \approx MO$  energy splitting in molecules, plasma frequency in metals----

#### We are alive because of solvation!!

- Our body functions and signaling in the body depend on the transport of ions like Li+, Ca2+, K+ etc in and out of cells.
- Recall how dangerous an electrolyte imbalance can be
- Ions are produced by dissociation of salts like NaCl in a polar solvent like water

### For Ionic materials like TM oxides use polarizable atoms or ions

 The polarizability of an ion is roughly equal to to the volume. (See home work question ) The radius of anions like O2- is much larger than for cations like Cu2+. So to calculated the TM 3d U we need to determine the ionizatrion potential anelectron affinity in the presence of polarizable O2- ions. Consider the ionization potential of a central TM ion surrounded by Z nearest neighbour polarizable anions

 $E_{I} = E_{I}^{0} - \frac{1}{2} \sum_{j} \alpha_{j} E_{j}^{2}$  The factor of ½ because it is an induced effect and the sum is over the anion sites  $E_{j} = \frac{e}{R_{j}^{2}}$  Where Rj= the distance from the TM ion to the nn anions.  $U = U^{0} - \sum_{j} \frac{\alpha_{j} e^{2}}{R_{j}^{4}}$ 

For 6 nearest neighbor O2- ions and  $\alpha$ =1- 3Angstrom cubed And a nearest neighbor distance of 2 Angstroms we get a reduction of U by about 5-15eV. The bare U is around 26eV. In addition to ionic polarizability we also have bond polarizabilities For example If we remove a d electron from a TM ion there will Be a backflow of 4s and 4p electron density from the bonds to the Central ion reducing again the ionization potential for d electron Removal. In the end a complicated issue hard to really get good estimates but the effects are obviously huge.

#### Estimating U

- One often used method is to use DFT and calculated the total energy of a solid in the ground state.
- The remove a d electron from tm atoms on a super lattice preferably as big as possible so they don't interact and keep the d occupation fixed on these and again calculate the ground state energy.
- Repeat the above with one d electron added in the atoms in the super cell
- Since the other electrons will react to these charges we can then get an estimate of the total polarization energy including the above effects.

# Experimental determination of the ionic polarizability?

Remember it is the high frequency polarizability we need to describe the dressing of a moving charge. This can be obtained from the optical dielectric constant

# Use the optical dielectric constant and the Clausius Mosotti relation

 q=0 limit of ε(q) for a solid with polarizable atoms with polarizability α. At large distance from a charge the p is uniform

$$p = \frac{\varepsilon - 1}{4\pi} E_{applied} = \chi E_{applied}$$

$$p = N\alpha E_{local} \quad \text{N = the number density} \quad E_{loc} = E_{applied} + E_{induced}$$

$$E_{loc} = \frac{4\pi p}{\varepsilon - 1} + \sum_{i} \frac{3(p_i \bullet r_i)r_i - r_i^2 p_i}{r_i^5} = \frac{4\pi p}{\varepsilon - 1} + \frac{4\pi p}{3} = \frac{p}{n\alpha} \quad \text{Using a spherical average}$$

 $\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha \quad \text{Or} \qquad \frac{\varepsilon - 1}{4\pi} = \chi = \frac{N\alpha}{1 - \frac{4\pi}{3}N\alpha} \quad \mathcal{E} = \text{optical dielectric constant}$ 

# What about U etc for atoms or molecules close to a surface

- If the material the atom or molecule is close to has a very different dielectric constant than the material the atom or molecule is in then again we have a non uniform polarizable medium.
- Lets look at an example of C60 on a metallic surface

#### Recall U for C60



Compares well with our experiments !

U for C60 on a metal surface

#### Solvation by image charges



- Coulomb energy :
- Charge transfer energy :

:

Band gap

$$U = U_0 - \frac{e^2}{2D}$$
$$\Delta = \Delta_0 - \frac{e^2}{2D}$$
$$E_g = E_g^0 - \frac{e^2}{2D}$$



*Combined photoemission* (solid lines) and inverse photoemission (dots with solid lines as quide to the eye) spectra of the  $C_{60}$  monolayer on Ag(111) (upper panel) and the surface layer of solid  $C_{60}$ (lower panel). Also included are the photoemission spectra (dashed lines) of the fully doped  $C_{60}$  (" $K_6C_{60}$ ") monolayer on Ag(111) and the surface layer of solid  $K_{6}C_{60}$ .

Band gap is reduced !

Molecular Orbital Structure is conserved !

INTENSITY (arb. units)



Photoemission and inverse photoemission processes for a monolayer of  $C_{60}$  on metal (a) and for the surface of bulk  $C_{60}$  (b). In both cases, the final state charges and polarizations of the bucky-balls are indicated.



#### Potential of a point charge in the neighbourhood of a dielectric in general



Note that image charge screening goes as Q squared!!!

Cannot be treated as a change in single particle potential ELECTRONIC POLARONS

The energies of electrons (cond. Band ) and holes (valence band) are both lowered

Therefore conductivity gap is lowered

Both electrons and holes will want to move to the interface

Frenkel like exciton states are not affected to lowest order

# Dependence on the band width of propagating charges on a surface

- The above description is for the assumption that the charge particle near the interface is moving slowly as compared to the reponse time of the polarizable medium it is close to
- Therefore this is valid for narrow band width materials like many molecular solids and strongly correlated systems in close proximity to a metal.
- This is not valid for semiconductors like Si or Ge which have very large band widths so the electrons and holes move too fast for the image potential to build up.

### An artists concept of the difference in band widths for two classes



	Molecules	Si, Ge, GaAs
Band width	~ 0.5 eV	>10 eV
Exciton B.E.	~ 1 eV	~20 meV
Polarons	$\hbar \omega_0 \sim W \; (\alpha \sim >1)$	
Electr. – Electr.	U≥W	U< <w< td=""></w<>
Magnetism	Yes (T-S~0.5eV)	No
Cond. Gap	$E_{gap} \ge W$	$E_{gap} << W$

Conventional wide band semiconductor –metal interface Results in band bending at the interface



Narrow band semiconductor – metal interface results in band gap closing at the interface



polarizability in TM compounds is very non uniform

The dielectric constant is a function of r,r',w and not only r-r',w and so Is a function of q,q',w

### Strong local field corrections for short range interactions

Meinders et al PRB 52, 2484 (1995) Van den Brink et al PRL 75, 4658 (1995)

# Reduction of U due to polarizability of As 3- in the Fe Pnictides (SOLVATION)

$$U = E_I^{TM} - E_A^{TM} - 2Epol$$

 $E_{I} \quad \text{ionization energy} \\ E_{A} \quad \text{electron affinity energy} \\ E_{I} = E_{I}^{0} - \sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad E_{A} = E_{A}^{0} + \sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \\ E_{I} = E_{I}^{0} - \sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad E_{A} = E_{A}^{0} + \sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \\ E_{I} = 2\sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad For 4 \text{ nn As3- } \sim 17 \text{eV} \\ e_{I} = 2\sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad For 4 \text{ nn As3- } \sim 17 \text{eV} \\ e_{I} = E_{I} = 2\sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad For 4 \text{ nn As3- } \sim 17 \text{eV} \\ e_{I} = E_{I} = E_{I} = 2\sum_{i} \frac{1}{2} \alpha_{i} F_{i}^{2} \qquad For 4 \text{ nn As3- } \sim 17 \text{eV} \\ e_{I} = E_{$ 

Taking  $\alpha$ (As3-) to be 10  $A^3$ 

#### Whats the importance of As or P?

- Very large anions
- Electronic polarizabilities roughly equal to volume

$$\alpha(O^{2-}) \approx 1-3$$
  $\alpha(P^{3-}) \approx 8$ 

In units of Angstroms cubed

$$\alpha(Se^{2-}) \approx 8 \qquad \alpha(As^{3-}) \approx 10$$

- 4p orbitals have 2 radial nodes –very diffuse
- Weak hybridization with highly directed local Fe 3d orbitals (from band theory)
- Large polarizability strongly reduces U on Fe and the nearest neighbor interaction V between Fe 3d

#### What about intersite interaction V? $V = V_0 - \frac{1}{2} \sum_{common} \alpha [(\mathbf{E}_1 + \mathbf{E}_2)^2 - E_1^2 - E_2^2],$

which reduces to  $V = V_0 - 2\alpha \mathbf{E}_1 \cdot \mathbf{E}_2$ , where 2 ref.

For pnictides the Fe-As-Fe nn bond angle is ~70 degrees therefore V is strongly reduced for nearest neighbors and may even become attractive. The next next nearest neighbor interaction will be larger than the bare value because the bond angle is 120 degrees. This demonstrates a strange phenomena namely that the reduction of the coulomb interactions is not a monotonically varying function but can in fact oscillate wildly.

#### Polarization cloud For Two charges on Neighboring Fe



# Influence of polarizability on the crystal structure

- Ionic compunds are often cubic to maximize the Madelung energy i.e. negative charged ions surrounded by positive ones and visa versa
- Strongly polarizable ions could contribute with dipole –monopole interactions provided that they are asymmetrically coordinated as in layered compounds like TiS2 or MoS2
- They consist of a highly charged positive cation layer sandwiched between two polarizable anion layers.

	R <sub>M</sub> (A)	F	C1	Br	I
Ba2+	1.36	C1	C1,C23	C23	C23
Pb2+	1.18	C1	C23	C23	C6*
Sr2+	1.16	C1	C1	C53	-
	1.00	C1	C35	C35	C6*
	0.95	C1	C19*	C19*	C6*
	0.82	C4	C19*	C6*	C6*
2+	0.79	-	C6*	C6* 🥌	C6*
re2+	0.77	C4	C19*	C19*	C6*
$2n^{2+}$	0.75	C4	C19*	C19*	C6*
L02+	0.74	C4	C19*	C19*	C6*
<sup>Mg</sup> 2+	0.72	C4	C19*	C6*	C6*
N1 0.70 R <sub>M</sub> (A)	C4	C19*	C19*	C19*	
	R <sub>M</sub> (A)	0	S	Se	Te
$Th_{4+}^{4+}$	1.00	C1	C23	C23	-
Zr	0.72	C1	C6*	C6*	C6+
Hf₄+	0.71	C1	C6*	C6*	C6*
Sn <sub>4+</sub>	0.69	C5	C6*	📕 C6*	-
Pt <sub>4+</sub>	0.63	C6*	C6*	C6*	C6*
Ti	0.61	C4	C6*	C6*	C6*

These form layered Structures because of The large polarizability Of the anions

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> In the ionic model the lattice energy is given by  $E = -NAZ^2 e^{2} / R + NBR^{-n}$ .

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Reduction of onsite interactions and changing the nearest neighbor interactions with polarizable ions in a lattice. The picture Shows what happens to the nn atoms upon electron removal or Electron addition in a 1D Hubbarde chain with large U and polarizable atoms



We assume that the hole and electron move slowly compared to the response time of the polarizability of the atoms. Note the oppositely polarized atoms next to the hole and extra electron



This kind of polarization reduction of U will however bring with it a large repulsive interaction Between same charge particles on i and i+,-1 i.e. a second nearest neighbor interaction

$$H_{\text{int}} = (U - 2zP)\sum_{i} n_{i\uparrow}n_{i\downarrow} + 2P\sum_{l,i}n_{l}n_{l+2a_{i}}$$

So the reduction of the Hubbard U in a polarizable medium like this introduces a strong Next nn repulsive interaction. This changes our model!!

For a different geometry actually the intersite interaction can also be strongly reduced perhaps even Attractive (Fe Pnictides)

> Jeroen van den Brink Thesis U of Groningen 1997 Van den Brink et al PRL 75, 4658 (1995) J. van den Brink et al EPL 50, 447 (2000)



FIG. 5. The effective Coulomb interaction on different organic molecules. The carbon polarizability is 0.56 Å<sup>3</sup>. The full line represents the bare Coulomb repulsion. The dashed lines are guides for the eye.

Note short range interactions are reduced " screened " and intermediate range interactions are enhanced or antiscreened-quite opposite to conventional wisdom in solid state physics

Jeroen van den Brink Thesis U of Groningen 1997



FIG. 1. The polarization energy  $2E_p$  as a function of separation between the electrons in one dimension. The lattice spacing is taken to be unity. The dashed line represents  $2RE_p$  for  $\alpha = 0.15$ . Negative values of  $E_p$  represent screening and positive values anti-screening.

# Effective coulomb interaction in low dimensions

- In low dimensions the exact results for a lattice of polarizable atoms results in a flattening out of the R dependence of the coulomb interactions.
- Recall that if there was no R dependence then mean field theory is exact!!
- This type of screening results in a strong decrease of electron correlations and also a break down of the Hubbard model

A quantum mechanical model including non uniform polarizability

Meinders et al PRB 52, 2484 (1995) Van den Brink et al PRL 75, 4658 (1995)

### The New superconductors LaOFeAs as an example



Figure 1. Crystal structures of LaFeAsO (left) and BaFe<sub>2</sub>As<sub>2</sub> (right)

# The FeAs layer with Fe tetrahedrally coordinated by As



Both Fe and As layers are squares but relatively rotated by 45 degrees. i.e. the As are above and alternatively below the centers of the Fe squares

#### The model includes

- The nearest and next nearest neighbor hoping between the Fe centers in an assumed single band
- The on site coulomb repulsion of two electrons or holes on Fe
- The possible excitation of an As electron from occupied 4p to unoccupied 5s as a model for the polarizability
- An effective coupling of the As 4p and 5s due to a charge on Fe described by g

$$\mathcal{H}_{\rm Fe} = -\sum_{i,j,\sigma} \left( t_{ij} c_{i,\sigma}^{\dagger} c_{j,\sigma} + h.c. \right) + U_H \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$$\mathcal{H}_{As} = \Omega \sum_{i,\lambda,\sigma} p_{i,\lambda,\sigma}^{\dagger} p_{i,\lambda,\sigma}$$
, 5-10 eV i.e. high energy

$$\mathcal{H}_{\text{int}} = g \sum_{i,\sigma} \hat{n}_i \left[ s_{i,\sigma}^{\dagger} \left( -\sin\theta p_{i,2,\sigma} + \cos\theta p_{i,3,\sigma} \right) \right. \\ \left. + s_{i-y,\sigma}^{\dagger} \left( -\sin\theta p_{i-y,1,\sigma} + \cos\theta p_{i-y,3,\sigma} \right) \right. \\ \left. + s_{i-x-y,\sigma}^{\dagger} \left( \sin\theta p_{i-x-y,2,\sigma} + \cos\theta p_{i-x-y,3,\sigma} \right) \right. \\ \left. + s_{i-x,\sigma}^{\dagger} \left( \sin\theta p_{i-x,1,\sigma} + \cos\theta p_{i-x,3,\sigma} \right) + h.c. \right] (3)$$



Because Omega is a high energy we can use perturbation theory in t as the smallest We assume only one particle so that U is not active The electronic Polaron eigen energies are given by

$$E_P(\vec{k}) = 4(\Omega - \sqrt{\Omega^2 + 4g^2}) + \epsilon_{\text{eff}}(\vec{k}).$$

$$\epsilon_{\text{eff}}(\vec{k}) = -2t_{\text{eff}} \left[ \cos(k_x a) + \cos(k_y a) \right] - 4t'_{\text{eff}} \cos(k_x a) \cos(k_y a)$$

We use the know electronic polarizability of As to determine g For small g i.e. in the linear regime. g=2.5 eV for  $\alpha$ = 10 cubic A

#### The Motion of a single quasi particle These move like electronic polarons



#### i.e. the overlap integral of the polarization clouds



FIG. 3: (a)  $t_{\rm eff}/t$  and (b)  $t'_{\rm eff}/t'$  vs.  $\Omega$ , for a polarizability  $\alpha_p = 7,10$  and  $12\mathring{A}^3$ . The dots show the values used here.

The effective polaron mass is simply t/teff =2.2 this is light compared to conventional lattice polaron masses