ELECTRONIC STRUCTURE OF STRONGLY CORRELATED SYSTEMS

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- SOME HISTORICAL NOTES
- WHY ARE 3D TRANSITION METALS AND RARE EARTHS SPECIAL
- ONE ELECTRON THEORY DENSITY FUNCTIONAL THEORY, LOCAL DENISTY APROXIMATION (+U)
- WHY MODELS TO DESCRIBE CORRELATION
- POLARITY FLUCTUATIONS COMPETING WITH THE MINIMIZATION OF THE KINETIC ENERGY
- SPECTROSCOPIC METHODS FOR ELECTRONIC STRUCTURE AND MODEL HAMILTONIAN PARAMETERS-

- •THE ONE ELECTRON GREENS FUNCTION AND THE TWO PARTICLE SPECTRAL FUNCTION (HOPEFULLY A LECTURE BY DAMASCELLI ON ANGULAR RESOLVED PHOTO ELECTRON SPECTROSCOPY)
- •SIMPLE MODELS CHARGE VS. SPIN FLUCTUATIONS-INTERATOMIC EXCHANGE INTERACTIONS
- •HUBBARD MODEL –1D
- •1D- SPIN CHARGE SEPARATION, RESONANT VALENCE BOND VS NEEL ORDER, SPINON'S VS SPIN WAVES,
- NEUTRON SCATTERING (HOPEFULLY A LECTURE BY VLADIMIR HINKOV ON NEUTRON SCATTERING)

- T J MODEL- SPINLESS FERMION
- SPECTRAL WEIGHT TRANSFER VS. MEAN FIELD
- EXTENDED HUBBARD EXCITONIC STATES
- SPIN DENSITY AND CHARGE DENSITY WAVES
- DRESSING THE ELECTRON –QUASI PARTICLE-SPECTRAL FUNCTION
- H2 MOLECULAR LATTICE AS AN EXAMPLE (POLARON)
- SPIN POLARON SINGLE ELECTRON (HOLE) IN A HEISENBERG FERROMAGNET – EXACT SOLUTION

- SCREENING : RANDOM PHASE APPROXIMATION (LINDHARD), 1,2,3,D; PEIERLS TRANSITION, GIANT KOHN ANOMALIE,
- NON UNIFORM POLARIZABILITY; THE IMPORTANCE OF LOCAL FIELD CORRECTIONS— SCREENING OF THE ON SITE COULOMB INTERACTION IN A POLARIZABLE MEDIUM
- SCREENING IN LOW DIMENSIONS
- EXAMPLE SOLID C60 AND TRANSITION METAL COMPOUNDS - STRANGE SCREENING BEHAVIOUR
- ELECTRON -PHONON AND ELECTRON -EXCITON INTERACTION ---POLARONS (HOPEFULLY A LECTURE BY MONA BERCIU)

- TRANSITION METAL AND RARE EARTH COMP. ; HIGH TC, MAGNETISM, COLOSSAL MAGNETO RESISTANCE, ACTINIDES
- ATOMIC MULTIPLETS, HUNDS' RULES
- TRANSITION METAL OXIDES -CHARGE TRANSFER VS MOTT HUBBARD, A CLASSIFICATION SCHEME
- CRYSTAL FIELD SPLITTINGS AND IMPORTANCE OF LOCAL POINT GROUP SYMMETRY
- HIGH SPIN VS LOW SPIN
- SUPEREXCHANGE
- PARAMETERS FOR HIGH TC'S, ZHANG RICE SINGLETSvs 3 SPIN POLARON --TOWARDS AN EFFECTIVE HAMILTONIAN (HOPEFULLY Doug Bonn WILL GIVE A LECTURE ON QUANTUM OASCILLATIONS IN TRANSPORT I.E. POCKETS VS ARCS IN HIGH Tc's)

- COLOSSAL MAGNETO RESISTANCE MATERIALS DOUBLE EXCHANGE
- IMPORTANCE OF ORBITAL DEGREES OF FREEDOM – ORBITAL ORDERING (ORBITONS), SPIN – CHARGE AND ORBITAL DEGREES OF FREEDOM)
- WAYS OF BREAKING ORBITAL DEGENERACIES I.E. JAHN TELLER THEOREM
- CHARGE DISPROPORTIONATION WITHOUT MOVING CHARGE

- SURFACE AND INTERFACE OF CORRELATED ELECTRON SYSTEMS (HOPEFULLY A LECTURE BY(ELFIMOV ON THIN FILMS SURFACES AND POLAR CATASTROPHIES)
- INTERFACE ENGINEERING OF NEW MATERIALS
 AND DEVICES
- HETEROSTRUCTURES OF TRANSITION METAL COMPOUNDS
- EXPERIMENTAL METHODES TO STUDY BURRIED INTERFACES
- RESONANT (SOFT) X RAY SCATTERING

Some Historical Landmarks

- 1929-1931 Bloch Wilson theory of solids
- 1937 De Boer and Verwey (NiO-CoO breakdown of band theory
- 1937 Peierls 3d electrons avoid each other (basically the Hubbard model)
- 1949 Mott Metal insulator transition
- 1950 Jonker, van Zanten, Zener Pervoskites double exchange
- 1957 BCS theory of superconductivity
- 1958 Friedel Magnetic impurities in metals
- 1959 Anderson superexchange (U>>W)
- 1962 Anderson model for magnetic impurities in metals
- 1964 Kondo theory of Kondo effect
- 1964 Hubbard model- Hohenberg Kohn DFT- Goodenough Transition metal compounds

Some historical notes

- 1964 Hohenberg Kohn density functional theory and Kohn Sham application to band theory
- 1964 John Goodenough basic principles of transition metal compounds
- 1965 Goodenough Kanamori Anderson rules for superexchange interactions
- 1968 Lieb and Wu exact solution of 1D Hubbard model

Some historical notes

- 1972 Kugel Khomskii theory of orbital ordering and superexchange
- 1985 Van Klitzing quantum Hall effect
- 1985 ZSA classification scheme of transition metal compounds
- 1986 Bednorz and Muller High Tc superconductors
- 1988 Grunberg and Fert giant magneto resistance

Some historical notes

 of course there are many other new developments both experimentally like Scanning Tunnelling microscopy (Binnig and Rohrer 1986), new materials like C60 (Kroto and Smalley 1985-1996), Colossal (Cheong et al mid 90's), Topological insulators (Kane 2005 Mollenkamp, 2007), Graphene (Geim and Novosolov 2009), MgB2, FePnictides,---- as well as in theory.

Everybody in condensed matter should be familiar with the periodic table of elements

- Alkali metals Li,Na,K,Rb,Cs one outer valence electron loosely bound- strongly electro positive- i.e. NaCl- low work function- photoelectric effect- night vision- and of course the Li ion battery ~5000 of which power the electric Tesla sports car.
- Alkaline earth metals with 2 valence electrons also electro positive divalent cations Be, Mg,Ca,Sr,Ba --- MgO transparent insulator,
- Transition metals 3d Sc,Ti,V.Cr,Mn,Fe,Co,Ni, can have various valencies or oxidation states i.e. 2+ TiO, 3+ Ti2O3, 4+ TiO2 or SrTiO3, 5+ V2O5, 1+ Cu2O, The 3d wave functions are very atomic like, the 4d and 5d are more and more diffuse. These form many of the correlated electron systems with a large variety of properties, including magnetic electrical etc.

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- The rare earths and actinides also electro positive forming positive ions. Localized valence orbitals are 4f and 5f with 4f very strongly bound and small spatial extend wave functions. Usually 2+ or 3+ ions in compounds for the rare earths. Many applications phosphors, permanent magnets (fridge door SmCo5, -----,
- Noble metals Cu,Ag,Au also for compounds like Cu2O or La2CuO4 (superconductor)
- Poor metals and non metals i.e. B,C,Mg,Al,Si Ge -----

- Pnictides N,P,As,Sb can be either electro positive or negative but generally thought of as trivalent anions i.e. 3- charge.
- Chalcogenides O,S,Se,Te which generally form divlanet anions with a strong electron affinity i.e. 2- as in MnO with Mn2+ ,O2-, etc
- Halides F,Cl,Br,I which are mostly monovalent anions i.e. 1- as in NaCl or in CuCl.
- And then of course the inert gases.

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Strongly correlated materials

- Often 3d transition metal compounds
- Often Rare earth metals and compounds
- Some 4d and some actinides
- Some organic molecular systems C60, TCNQ salts
- Low density 2D electron gases Quantum and fractional quantum Hall effect
- Magnetic materials and impurities

Wide diversity of properties

Take for example only the transition metal oxides

- Metals: CrO2, Fe3O4 T>120K
- Insulators: Cr2O3, SrTiO3,CoO
- Semiconductors: Cu2O
- Semiconductor metal: VO2,V2O3, Ti4O7
- Superconductors: La(Sr)2CuO4, LiTiO4, LaFeAsO
- Piezo and Ferroelectric: BaTiO3
- Multiferroics
- Catalysts: Fe,Co,Ni Oxides
- Ferro and Ferri magnets: CrO2, gammaFe2O3
- Antiferromagnets: alfa Fe2O3, MnO, NiO ---

Properties depend on composition and structure in great detail

Phase Diagram of La_{1-x}Ca_xMnO₃ Uehara, Kím and Cheong

R: Rombohedral

O: Orthorhombic (Jahn-Teller distorted)

O*: Orthorhombic (Octahedron rotated)

CAP = canted antiferromagnet

FI = Ferromagnetic Insulator

CO = charge ordered insulator

FM= Ferromagnetic metal

AF= Antiferromagnet



THE SUPERCONDUCTING TO BEFORE 1986



Thought to be BCS electron phonon driven Tc Max ~35K

Theory in 1957 -1961 led us To believe to avoid magnetism avoid oxides, start with reasonable conductors



Contrary to conventional wisdom Bednorz and Muller in 1986 discovered much higher Tc's in MAGNETIC OXIDES OF Cu.



The many-body quantum state underpinning these phenomena (equivalent of Fermi Liquid for BCS) has not been identified.

Ordering in strongly correlated systems



Model for Charge, Spin and Orbital Correlations in Manganites

Mn4+, d3, S=3/2, No quadrupole; Mn3+, S=2, orbital degeneracy



Mízokawa et al (2001)

Extra d electron In Mn3+

Why are the 3d transition metals and rare earths so special?

The small spatial extend of the open shell wave functions i.e. 3d and 4f compared to the interatomic distances.

Why Models ?

- After all we know all the interactions
- Unsolvable many body problem. Some models may be solvable!
- We need to understand the low energy scale ~kT excursions from the ground state resulting from external stimuli like T, light, pressure, fields in order to understand the properties , predict new properties , and optimize them.
- The response of the lowest binding energy electrons, i.e. valence electrons
- Obviously our success at prediction of the most spectacular properties is very limited as evidenced by continual surprises.

Two extremes for atomic valence states in solids

Valence extreme Two Types of states Large overlap R~d - Large dispersion E(A) - t eiter (free electr.) 5, p valence. \oplus \oplus \oplus \oplus \oplus \oplus \oplus \oplus \oplus \oplus Little overlap · R << d - Little dispersion Alomic Like (~ 1 fe^{ik-R}: W(r-R:) (Eight binding) = Correlated.

Coexistance-----Hybridization

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

Extreme valence orbitals

- Recall that the effective periodic corrugation of the potential due to the nuclei screened by the "core" electrons is very small for R>>D leading to free electron like or nearly free electron like behavior.
- For R<<D the wave functions are atomic like and feel the full corrugation of the screened nuclear potentials leading to quantum tunneling describing the motion of tight binding like models.

Characteristics of solids with extreme valence orbitals

R>> D

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

R<<D

- Valence Electrons remain atomic
- Narrow bands
- Large electron electron interactions (on site)
- Low energy scale-spin fluctuations
- Magnetic (Hunds' rule)
- Gd, CuO, SmCo3

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

Special place for transition metal and rare earths

Atoms in a periodic array in solids One electron approximation

Fig. 5-1. The electrostatic potential through a line of atoms in a crystal and parallel to such a line

We are interested in the potential Produced by the nuclei and the inner electrons on the outermost "Valence" electrons

K=2pi/wave length

Ef is the Fermi level up to which Each k state is filled with 2 electrons

ONLY METALS (or semiconductors for nearly free Approximation electron) !!

More atomic like states for atoms in solids with large inter-atomic spacing compared to orbital radius

Electrons can quantum mechanically Tunnel from atom to atom forming again Waves and bands of states but now the Bands are finite in width. If such a band is full (2 electrons per atom for S orbitals the material will be an insulator Because of a forbidden gap to the next band of states INSULATOR OR SEMICONDUCTOR

Still rather boring since we have no magnetism With an odd number of electrons per atom would all be metallic i.e. CuO,La2CuO4, CoO, MnO (all insulators)

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

What have we forgotten ? The electron electron repulsive interaction Why are 3d and 4f orbitals special

- Lowest principle q.n. for that I value
- Large centrifugal barrier l=2,3
- Small radial extent, no radial nodes orthogonal to all other core orbitals via angular nodes
- High kinetic energy (angular nodes)
- Relativistic effects
- Look like core orb. But have high energy and form open shells like valence orb.

A bit more about why 3d and 4f are special as valence orbitals

Hydrogenic orbital energy non relativistic

$$E_n^0 = \frac{mz^2 e^4}{2h^2 n^2}$$
 Hydrogenic orbital energy non relativistic

$$\varepsilon = \sqrt{p^2 c^2 + m^2 c^4} \approx mc^2 + \frac{p^2}{2m} - \frac{1}{8} \frac{p}{m^2 c^2}^4$$
 Relativistic contribution

$$\Delta E = -\frac{1}{2me^2} \left(\left(E_n^0 \right)^2 + eE_n^0 z e^2 \left\langle 1/r \right\rangle_{nl} + z^2 e^4 \left\langle 1/r^2 \right\rangle_{nl} \right) \quad \left\langle 1/r \right\rangle = \frac{z}{a_0 n^2} \quad \left\langle 1/r^2 \right\rangle = \frac{z^2}{a_0 n^2 (l+1/2)}$$
$$\Delta E_{nl} = \left(\frac{z^2 \alpha^2}{n^2} \right) \left(\frac{n}{l+1/2} - 3/4 \right) E_n^0 \qquad \alpha = \frac{e^2}{hc}$$

3d of Cu; binding energy of 3s=120 eV, 3p=70 eV, 3d=10 eV.

Strong energy dependence on I due to relativistic effects.

Charge density of outer orbitals of the **Rare earths**

Atomic radius in solids

Elemental electronic configuration of rare earths

$$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{N}5s^{2}5p^{6}6s^{2}$$

The earth metal For N<14 open shell

A rare earth metal

Hubbard for 4f

Hubbard U

5d6s form a broad conduction Band

4f is not full and not empty

Plot of the orbital volume /Wigner sites volume of the elemental solid for rare Earth 4f's, actinide 5f's, transition metal 3d's,4d'sand 5d's

In compounds the ratio will be strongly reduced because the Element is "diluted" by other components

Van der Marel et al PRB 37, (1988)

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