ELECTRONIC STRUCTURE OF STRONGLY CORRELATED SYSTEMS

G.A.SAWATZKY
UBC PHYSICS & ASTRONOMY
AND CHEMISTRY
Max Planck/UBC center for Quantum Materials
Much of the material will be from thesis of some of my former student and old lecture notes

- Antonides, Tjeng, van Elp, Kuipers, van der Laan, Goedkoop. De Groot, Zaanen, Pothuizen, Eskes, van den Brink, Macridin, Lau,
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 landmarks

• 1964 Hohenberg Kohn density functional theory and Kohn Sham application to band theory
• 1964 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
• 1972 Kugel Khomskii theory of orbital ordering
• 1985 Van Klitzing quantum Hall effect
• 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, H2S at high pressure 190K superconductor, ---- as well as in theory.
It’s the outermost valence electron states (both the occupied and unoccupied ones) that determine the properties.
Two Extreme classes of valence orbitals

• For $R \gg D$ The effective corrugation of the periodic potential due to the nuclei screened by the “core” electrons is very small leading to free electron like or nearly free electron like behavior.

• For $R \ll D$ 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. ATOMIC PHYSICS BECOMES VERY IMPORTANT
Two extremes for atomic valence states in solids

Where is the interesting physics?

Coexistence-----Hybridization
Kondo, Mixed valent, Valence fluctuation, local moments, Semicond.-metal transitions, Heavy Fermions, High Tc's, Colossal magneto resistance, Spintronics, Orbitronics
Atoms in a periodic array in solids

single electron approximation

We are interested in the potential produced by the nuclei and the inner electrons on the outermost “Valence” electrons.

\[ \psi_k(r) = \frac{1}{\sqrt{\Omega}} e^{ik \cdot r} \]

\[ E_k = \frac{\hbar^2 k^2}{2m} \]

K = 2π/\text{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 electron approximation
More atomic like states for atoms in solids with large inter-atomic spacing compared to valence 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)
Characteristics of solids with 2 extreme valence orbitals

R>> D
• electrons lose 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 (on site) electron-electron interactions
• Low energy scale-spin fluctuations
• Magnetic (Hunds’ rule)
• EXAMPLES Gd, CuO, SmB6

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
Single electron 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 of one electron Bloch waves.

**Atomic**
- Local atomic coulomb and exchange integrals are central
- Hund's 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
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’s and 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)
The hole can freely propagate leading to a width.

The electron can freely propagate leading to a width.

The actual motion of the particles will turn out to be more complicated.

Largest coulomb interaction is on site $U$.

The simplest model single band Hubbard.

Row of H atoms
1s orbitals only

The hole can freely propagate leading to a width.

E gap = 12.9eV-W

The simplest Hamiltonian to describe this involves $n_n$ hopping and on site $U$.

Hubbard

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

$$n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$$
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 $J = \frac{4t^2}{U}$
- Atomic physics dominates
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?

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

Heisenberg Spin Hamiltonian
Example of two Fermions in U=∞ limit

\[ H = \begin{pmatrix} 0 & t & \pm t \\ t & 0 & t \\ \pm t & t & 0 \end{pmatrix} \]

\[ \Psi = \phi(x_1, x_2) \cdot \chi(m_{s1}, m_{s2}) \]

\[ \chi(m_{s1}, m_{s2}) = \begin{cases} \frac{1}{\sqrt{2}}(\chi_+ + \chi_-) & \text{Triplet} \\ \frac{1}{\sqrt{2}}(\chi_+ - \chi_-) & \text{Singlet} \end{cases} \]

Energy level diagram for holes (t>0)

This result is general for two holes in an odd membered ring of s state atom.
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?

**SC Hydrogen**

ferromagnetic

\( a = 2.7 \ \text{Å} \)

\( U = 12 \text{eV} \)

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

Meinders et al, PRB 48, 3916 (1993)

Remove one electron
Create two addition states At low energy

Dots indicate spin
Up Or spin down!!

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.

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

Meinders et al, PRB 48, 3916 (1993)
Dynamic spectral weight transfer

- For finite hoping 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 hoping integral t
The derivative of the low energy spectral weight as a function of doping and the hoping 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 $d^9 \rightarrow d^9 \Delta^{-1}$

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

Oxygen 1s

C. T. Chan et al. PRL 65, 184 (1991)
Strongly correlated materials

- Often 3d transition metal compounds
- Often Rare earth metals and compounds
- Some 4d, 5d and some actinides
- Some organic molecular systems $\text{C}_{60}$, TCNQ salts
- Low density 2D electron gases Quantum and fractional quantum Hall effect
- Strong magnetism is often a sign of correlation
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 $La_{1-x}Ca_xMnO_3$

Uehara, Kim 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
High Tc superconductor phase diagram

Schematic phase diagram of hole-doped cuprates

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

Stripes in Nd-LSCO

- Rivers of Charge—Antiferro/ Antiphase
- $\Delta Q < 0.5 \, \text{e}$

Charge inhomogeneity in Bi2212

- $\Delta Q \sim 0.1 \, \text{e}$
- $\Delta Q \sim 1 \, \text{e}$
- $\Delta Q_0 \sim 0$

Quadrupole moment ordering

Pan, Nature, 413, 282 (2001);
Model for Charge, Spin and Orbital Correlations in Manganites

Mn$^{4+}$, d3, $S=3/2$, No quadrupole; Mn$^{3+}$, S=2, orbital degeneracy

$S = 6 \times 2 + 3/2 = 2 \frac{2}{2}$
Why are 3d and 4f orbitals special

- Lowest principle q.n. for that l 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

\[ E_n^0 = \frac{mz^2 e^4}{2\hbar^2 n^2} \]

Hydrogenic orbital energy non relativistic

\[ \varepsilon = \sqrt{p^2 c^2 + m^2 c^4} \approx mc^2 + \frac{p^2}{2m} - \frac{p}{8 m^2 c^2} \]

Relativistic contribution

\[ \langle p^2 \rangle = 2m(E_n^0 + Ze^2 \langle \frac{1}{r} \rangle) \]

\[ \Delta E = -\frac{1}{2me^2} \left( (E_n^0)^2 + eE_n^0 Ze^2 \langle \frac{1}{r} \rangle_{nl} + z^2 e^4 \langle \frac{1}{r^2} \rangle_{nl} \right) \]

\[ \langle 1/r \rangle = \frac{Z}{a_0 n^2} \quad \langle 1/r^2 \rangle = \frac{Z^2}{a_0 n^2(l+1/2)} \]

\[ \Delta E_{nl} = \left( \frac{z^2 \alpha^2}{n^2} \right) \left( \frac{n}{l+1/2} - 3/4 \right) E_n^0 \quad \alpha = \frac{e^2}{\hbar c} \]

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

Strong energy dependence on l due to relativistic effects.
Highly confined orbitals will have a large $U$

Charge density of outer orbitals of the Rare earths

Atomic radius in solids

Elemental electronic configuration of rare earths

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

A rare earth metal

Hubbard for 4f

5d6s form a broad conduction Band

4f is not full and not empty

Hubbard U

For $N<14$ open shell
Band Structure approach vs atomic

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- Mostly magnetic ground states
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

\[ \Psi = \sqrt{\frac{1}{N!}} \left| \phi_{k1} \phi_{2k} \phi_{3k} \cdots \phi_{kN} \right| \]

The single particle wave functions \( \phi \) 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. NO CORRELATION IN THE WAVE FUNCTION

\[ v_{\text{eff}} = v_{\text{nuclear}} + \int \frac{n(r')}{r-r'} d^3 r' + v_{xc} \]
Configuration interaction approach

The one electron wave functions in $\psi$ 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.

\[
t = \text{nn hoping integral}
\]

\[
\text{Energy} = U
\]

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.
General band theory result for $R \ll d$ together with $R \gg d$ states

For open shell bands $R \ll d$ $R \ll d$ so bands are narrow open therefore must be at $E_f$
What do we mean by the states below and above the chemical potential

The eigenstates of the system with one electron removed or one electron added respectively i.e Photoelectron and inverse photoelectron spectroscopy

\[ \text{IPES} \]

\[ \text{E}_{\text{gap}} = E(N-1) + E(N+1) - 2E(N) \]
Photo and inverse Photo electron spectra of the rare earth Metals (Lang and Baer (1984)). $0$ is $E_{\text{Fermi}}$

Solid vertical lines are atomic multiplet theory
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 FOR N-1
if the only Important
interaction isthe d-d
interaction.
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.
What if we remove 2- d electrons locally? Two hole state with Auger spectroscopy

Example is for Cu with A fully occupied 3d band

\[ E(\text{photon}) - E(\text{photoelectr}) = E(2p), \quad E (2-d \text{ holes}) = E(2p) - E(3d) - E(\text{Auger}) \]

\[ U = E(2-d \text{ holes}) - 2xE(1-d \text{ hole}) \]
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
In Fig. 5.5 is shown the gas phase L$_3$ M$_{4,5}$ M$_{4,5}$ spectrum of Zinc collected using electron excitation with a primary beam energy of 2.5 KeV.

FIG. 5.5. The separation of the experimental L$_3$ M$_{4,5}$ M$_{4,5}$ spectrum into its different components. The experimental results are described by the points and the sum components by the solid lines. (ref: Aksela et. al., Phys. Rev. Lett. 33, 999, (1974)).
$U_{\text{eff}} \sim 9\,\text{eV}$

Fig. 5.12 (Ref: E. Antonides et al. Phys. Rev. B, 15, 1669 (1977))

NOTE MULTIPLET STRUCTURE IS THE SAME AS IN THE GAS PHASE
Unfortunately the extraction of \( U \) from the experiment is only rigorously possible for the case of full d bands i.e. Cu, Zn etc. In which case it corresponds to a two particle Greens function calculation.

So the cases for partly filled bands cannot really be trusted.

Fig. 5.14. $U_{\text{eff}}$ (squares on dashed line) and $2\Gamma_{M45}$ (circle on solid lines) vs atomic number for Fe, Co, Ni, Cu, Zn, Ga and Ge in eV. The closed circles were obtained from ref. E. Antonides et. al, Phys. Rev. B, 15, 1669 (1977).
For $U \gg W$ 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.
ARPES of Cu is not a problem since there are no d holes to correlate with Ni however has a partly filled 3d band i.e. about 9.4 3d electrons on average

Think of Ni as a mixed valent /valence fluctuating system

\[ \text{d}_{9} \quad \text{d}_{9} \quad \text{d}_{10} \quad \text{d}_{9} \quad \text{d}_{10} \quad \text{d}_{9} \quad \text{d}_{9} \quad \text{d}_{9} \quad \text{d}_{10} \quad \text{d}_{9} \quad \text{d}_{10} \quad \text{d}_{9} \]

Removal from d9 states
Will be U higher in energy

Taken from Falicov 1987
Some properties of DFT theory

- single Slater determinant of one electron Bloch waves
- Each k state can accommodate n electrons
- Average d electrons on an atom for Ni 9.4
- Concentration per state is c = 0.94
- The expectation value for n electrons on a site
  \[ P(n) = \frac{m!}{(m-n)!n!} (1 - c)^{m-n} c^n \] purely statistical
- No on site coulomb distinction
- DFT = Strong POLARITY fluctuations in ground state
- Large U \sim W reduces polarity fluctuations to at most 2 occupations i.e Ni d9 or d10 no d8 or d7 etc
For U large $U \gg W$

- Atomic physics is very important
- We have atomic multiplets with potentially large splittings (>10eV) because of small radial of atomic wave functions especially 3d and 4f
- On to atomic physics with open d and f shells
- AFTER THIS WE NEED TO UNDERSTAND WHY $U(\text{effective})$ is strongly reduced in the solid while the multiplet splitting is not
Hunds’ rules – atomic ground state
First the Physics

• Maximize the total spin—spin parallel electrons must be in different spatial orbitals i.e. m values (Pauli) which reduces the Coulomb repulsion

• 2\textsuperscript{nd} Rule then maximize the total orbital angular momentum L. This involves large m quantum numbers and lots of angular lobes and therefore electrons can avoid each other and lower Coulomb repulsion
Hunds’ third rule

• < half filled shell J=L-S > half filled shell J=L+S

• Result of spin orbit coupling

\[ H_{so} = \sum_{j} \frac{1}{2mc^2} \left( \nabla V(r_j) \times p_j \right) \cdot s_j \]

• Spin orbit results in magnetic anisotropy, g factors different from 2, orbital contribution to the magnetic moment, ---
More formal from Slater “Quantum theory of Atomic structure chapter 13 and appendix 20

One electron wave function

\[ U_{nle_2} (r, \theta, \phi) = (-1)^{(m_2 + |m_2|)/2} \frac{\sqrt{(2l+1)(2l-1|m_2|)!}}{(l+|m_2|)!} \]
\[ \times R_{n}^{l_1 m_1} (r) \vec{P}^{l_2 m_2} (\cos \theta) e^{im_2 \phi} \]

\[ \rho_{ij} = \sum_i \rho_i + \sum_i (\text{pairs } \vec{r}_i) g_{ij} \]

one electron = \[ -\vec{V}^2 - \frac{2}{\vec{r}^2} \]

\[ g_{ij} = \frac{2}{r_{ij}} \rightarrow \text{Multiplets} \rightarrow \text{Hund's rule} \]

We need to calculate \[ \langle ij | g | rt \rangle \]

Where \( i, j, r, t \) label the quantum Numbers of the occupied states and we sum over all the occupied states in the total wave function
Two Types of Integrals \[ \langle ij|ql|ij \rangle \] and \[ \langle ij|ql|ij \rangle \]

For 2 electrons in same shell
\[ \langle ij|ql|ij \rangle = \sum_{k=0}^{\infty} \alpha^k(l_i m_i; l_j m_j) F^k(n_i l_i; n_j l_j) \]

\[ F^k = R^k(lij; ij) \rightarrow \text{product of } C's \]

Direct Coulomb
\[ \langle ij|ql|ij \rangle = S(l_i m_i; l_j m_j) \sum_{k=0}^{\infty} b^k(l_i m_i; l_j m_j) G^k(n_i l_i; n_j l_j) \]

\[ b^k(l_i m_i; l_j m_j) = \left[ C^k(l_i m_i; l_j m_j) \right]^2 \]

\[ G^k(n_i l_i; n_j l_j) = \int R^*(r_i) R^k(r_j) R(r_i) R(r_j) \frac{2}{r_i r_j} \, dr_i \, dr_j \]
\[ \frac{1}{v_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-1+m_1)!}{(k+m_1)!} \frac{v_k^k}{v_r^{k+1}} P_{k+m_1}^{1+m_1} P_{k}^{m_1} P_{k}^{m_2} P_{k}^{m_1} \times \cos \theta_1 \cos \theta_2 \]

\[ \lim_{\phi \to \phi_2} \frac{\phi_1 - \phi_2}{1} \times e^{-i \iota \phi_1 \phi_2} \]

\[ \left< \iota \phi_1 \phi_2 \right> = \int \int \psi_1^*(\iota \phi_1) \psi_2^*(\iota \phi_2) \frac{1}{v_{12} v_{12}} \frac{\phi_1}{\phi_2} d\phi_1 d\phi_2 \]

\[ \therefore \quad \sqrt{\frac{Q_{e_1} + 1}{Q_{e_1} - 1}} = \frac{2}{\sqrt{Q_{e_1} + 1}} \times \frac{z}{r^2} \times \frac{z}{r^2} \times \frac{z}{r^2} \times \frac{z}{r^2} \times \]

\[ x \int \int R_{v_1}^*(\iota \phi_1) R_{v_2}^*(\iota \phi_2) R_{v_1}^*(\iota \phi_2) R_{v_2}^*(\iota \phi_2) \frac{2 \sqrt{2 \pi} v_k}{\sqrt{v_r^{k+1}}} r_1 r_2 d\phi_1 d\phi_2 \]

\[ \times \int \int \frac{P_{k+m_1}^{1+m_1}}{P_{k}^{m_1} P_{k}^{m_2} P_{k}^{m_1}} \times \frac{\sin \theta_1}{2} \]

\[ \left( e^{-i \iota \phi_1 \phi_2} \right) d\phi_1 \times \int \left( e^{-i \iota \phi_1 \phi_2} \right) d\phi_2 \]
From orthogonality $S \neq$

\[ m = m_x^2 - m_y^2 = -m_x^2 + 2m_z \]

\[ m_x^2 + m_y^2 = m_x^2 + m_z^2 \quad \text{(conserv. 17)} \]

So we use

\[ C^k (l_1 m_1; l_2 m_2) = (-1)^k \frac{(m + 1m_1 + m + 1m_2 + (m - 1m_1 + 1m - 1m_2))}{2} \]

\[ \times \sqrt{\frac{(k - 1m - 1m_2)!}{(k + 1m_1 - 1m_2)!}} \sqrt{\frac{(2k + 1)(l_1 m_1)!}{(l_1 + m_1)!}} \sqrt{\frac{(2k + 1)(l_1 m_2)!}{(l_1 + m_2)!}} \]

\[ \times \frac{1}{2} \int \frac{P^{1m_1}_{l_1+1}(u) P^{1m_2}_{l_2}(u) P^{1m_2}_{l_2}(u)}{u} \sin \theta \sin \phi \sin \phi \text{ d}u \text{ d}\phi \]

Tabulated $\rightarrow$ Appendix 20

\[ \langle i \mid g_1 \mid v_2 \rangle = S(m_1, m_2) S(m_3, m_4) S(m_x + m_y, m_x + m_z) \]

\[ \times \sum_{k=0}^{2} C^k (l_1 m_2; l_2 m_2) C^k (l_1 m_4; l_2 m_2) R^{k+\ell}_{\ell}(\theta, \phi) \]

Highest possible value of $k = \ell + \ell'$

i.e. $l_x + l_y$ or $l_x + l_y'$
The d-d coulomb interaction terms contain density-density like integrals, spin dependent exchange integrals and off diagonal coulomb integrals i.e. where \( n,n' m,m' \) are all different. The monopole like coulomb integrals determine the average coulomb interaction between d electrons and basically are what we often call the Hubbard U. This monopole integral is strongly reduced in polarizable surroundings as we discussed above. Other integrals contribute to the multiplet structure dependent on exactly which orbitals and spin states are occupied. There are three relevant coulomb integrals called the Slater integrals:

\[
F^0 = \text{monopole integral} \\
F^2 = \text{dipole like integral} \\
F^4 = \text{quadrupole integral}
\]

For TM compounds one often uses Racah Parameters A, B, C with:

\[
A = F^0 - 49F^4; B = F^2 - 5F_4; C = 35F^4
\]

Where in another convention:

\[
F^2 = \frac{1}{49}F^2; F^4 = \frac{1}{441}F^4; F^0 = F^0
\]

The B and C Racah parameters are close to the free ion values and can be carried over from tabulated gas phase spectroscopy data. "Moores tables" They are hardly reduced in a polarizable medium since they do not involve changing the number of electrons on an ion.
Multiplet structure for free TM atoms rare Earths can be found in the reference

\[ E(n, L, S, \lambda) = nI \frac{1}{2} n(n-1)U_{\text{ave}} + U(n, L, S, \lambda) \]

For Hund’s Rule ground state

\[ U_{\text{ave}} = F^0 + 2 \frac{2}{63} (F^2 + F^4) = F^0 - \frac{2l}{4l+1} J(d, d) \]

\[ J(d, d) = \frac{1}{14} (F^2 + F^4) \]

\[ C(d, d) = \frac{1}{14} \left( \frac{9}{7} F^2 - \frac{5}{7} F^4 \right) \]

\[ E(n, \text{Hund}) = \alpha_I(n)I + \alpha_{F^0}(n)F^0 + \alpha_J(n)J + \alpha_C(n)C \]

\[ U^{\text{eff}} = E(n+1, \text{Hund}) + E(n-1, \text{Hund}) - 2E(n, \text{Hund}) \]

\[ \alpha_I(n) = n; \alpha_{F^0}(n) = \frac{n!}{2}; \alpha_J(n) = \text{No. of parallel spin pairs} \]

VanderMarel et al PRB 37, 10674 (1988) and thesis also Haverkort thesis for more detail and Kanamori parameters.
Table 2.1. Parameters determining the energies of the Hund’s Rule ground states in LS coupling for all d occupations and the expression for the d-d gap for those occupations.

<table>
<thead>
<tr>
<th>state</th>
<th>$\alpha_I$</th>
<th>$\alpha_{F0}$</th>
<th>$\alpha_J$</th>
<th>$\alpha_{C}$</th>
<th>$U^{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0(^1S)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$d^1(^2D)$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$d^2(^3F)$</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$F^0_0-J-C$</td>
</tr>
<tr>
<td>$d^3(^4F)$</td>
<td>3</td>
<td>3</td>
<td>-3</td>
<td>-1</td>
<td>$F^0_0-J+C$</td>
</tr>
<tr>
<td>$d^4(^5D)$</td>
<td>4</td>
<td>6</td>
<td>-6</td>
<td>0</td>
<td>$F^0_0-J-C$</td>
</tr>
<tr>
<td>$d^5(^6S)$</td>
<td>5</td>
<td>10</td>
<td>-10</td>
<td>0</td>
<td>$F^0_0+4J$</td>
</tr>
<tr>
<td>$d^6(^5D)$</td>
<td>6</td>
<td>15</td>
<td>-10</td>
<td>0</td>
<td>$F^0_0-J-C$</td>
</tr>
<tr>
<td>$d^7(^4F)$</td>
<td>7</td>
<td>21</td>
<td>-11</td>
<td>-1</td>
<td>$F^0_0-J+C$</td>
</tr>
<tr>
<td>$d^8(^3F)$</td>
<td>8</td>
<td>28</td>
<td>-13</td>
<td>-1</td>
<td>$F^0_0-J+C$</td>
</tr>
<tr>
<td>$d^9(^2D)$</td>
<td>9</td>
<td>36</td>
<td>-16</td>
<td>0</td>
<td>$F^0_0-J-C$</td>
</tr>
<tr>
<td>$d^{10}(^1S)$</td>
<td>10</td>
<td>45</td>
<td>-20</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Multiplet structure of 3d TM free atoms

Note the high energy scale
Note also the lowest energy state for each case i.e. Hund's Rule;
Reduction of coulomb and exchange in solids

- Recall that U or F₀ is strongly reduced in the solid. This is the monopole coulomb integral describing the reduction of interaction of two charges on the same atom.

- However the other integrals F₂ and F₄ and G’s do not involve changes of charge but simply changes of the orbital occupations of the electrons so these are not or hardly reduced in solids. The surroundings does not care much if locally the spin is 1 or zero.

- This makes the multiplet structure all the more important!!!!!! It can in fact exceed U itself.
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.e. 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

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

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

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

Total Momentum and total spin 0,1 conservation

\[ [H,K] = 0, \cdots [H,S] = 0 \]

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

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 = \[ \text{Im} \left( \text{sum over K and k of G} \right) = \text{self convolution of the one particle density of states} \]
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

\[
G_{0q \uparrow, K-q \downarrow}^{k \uparrow, K-k \downarrow}(z) = \delta_{k,q} \frac{1}{z - \epsilon_k - \epsilon_{K-k}} = \delta_{k,q} G_0(k, K-k; z)
\]

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

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.

\[
\text{Re}\left(\sum_k G_0(k, K-k; E_n)\right) = \frac{N}{U} \quad \text{where } E_n
\]

Are the singlet eigenenergies
Discussion of two particle states

• The imaginary part of $G$ 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 it 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.

\[
\text{Pole in two particle Greens function for Each } K
\]

\[
\text{Increasing energy}
\]

\[
\text{Re} \Sigma_{k,q} (G_{0q}^{k,\uparrow,K-k,\downarrow}(z))
\]

\[
\text{Im} \Sigma_{k,q} (G_{0q}^{k,\uparrow,K-k,\downarrow}(z))
\]
Local Two particle density of states

One particle $\eta(E)$

Two particle $\eta_2(E) = \text{self convolution of } \eta_1(E)$

For $U = 0$

$E_F$

$N_{\text{States}}$

$2W$

$N^2_{\text{States}}$

$W = 2E \times \text{No of nearest neighbors}$

$E_F$

$U > 2W$

$U$

$N(2W)$

$\approx \frac{2E^2}{U} \times \text{No of nearest neighbors}$

Auger spectrum

$E_F$