Electronic structure of correlated electron systems lecture 9

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Lecture 9 (7 is from Mona Berciu and 8 is from Andrea Damascelli)
Brief review of what we did in lecture 6
Two new complications

• d(n) multiplets determined by Slater atomic integrals or Racah parameters A,B,C for d electrons. These determine Hund’s rules and magnetic moments

• d-O(2p) hybridization (d-p hoping int.) and the O(2p)-O(2p) hoping (O 2p band width) determine crystal field splitting, superexchange, super transferred hyperfine fields etc.
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;

\[
A = F_0 - 49F_4; \quad B = F_2 - 5F_4; \quad C = 35F_4
\]

Where in another convention;

\[
F_2 = \frac{1}{49} F^2; \quad F_4 = \frac{1}{448} F^4; \quad F_0 = F^0
\]

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.
Reduction of coulomb integrals in the solid

- As we noted above the F0 integral or what we called U before is strongly reduced in the presence of a polarizable medium since it involves a change in the local charge i.e. ionization potential minus electron affinity.
- However the other higher order multipole integrals involve simply a dependence on the way the orbitals are occupied keeping the electron count fixed. The surroundings hardly notices such changes and so these integrals remain close to the atomic values.
Hunds’ rules
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

• 2nd 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

$$H_{so} = \sum_j \frac{1}{2mc^2}(\nabla V(r_j) \times p_j) \cdot s_j$$

- Spin orbit results in magnetic anisotropy, g factors different from 2, orbital contribution to the magnetic moment, ---
Multiplet structure for free TM atoms rare Earths can be found in the reference

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

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

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

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

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

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

Where Hund refers to the Hund’s rule ground state in each case. That is, the lowest energy state for the given number of d electrons

\[ \alpha_I(n) = n; \quad \alpha_{F^0}(n) = \frac{n!}{2}; \quad \alpha_J(n) = \text{No. of parallel spin pairs} \]
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>$\alpha_{F^0}$</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>$F^0-J-C$</td>
</tr>
<tr>
<td>$d^2(^3F)$</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$F^0-J+C$</td>
</tr>
<tr>
<td>$d^3(^4F)$</td>
<td>3</td>
<td>3</td>
<td>-3</td>
<td>-1</td>
<td>$F^0-J+C$</td>
</tr>
<tr>
<td>$d^4(^5D)$</td>
<td>4</td>
<td>6</td>
<td>-6</td>
<td>0</td>
<td>$F^0-J-C$</td>
</tr>
<tr>
<td>$d^5(^6S)$</td>
<td>5</td>
<td>10</td>
<td>-10</td>
<td>0</td>
<td>$F^0+4J$</td>
</tr>
<tr>
<td>$d^6(^5D)$</td>
<td>6</td>
<td>15</td>
<td>-10</td>
<td>0</td>
<td>$F^0-J-C$</td>
</tr>
<tr>
<td>$d^7(^4F)$</td>
<td>7</td>
<td>21</td>
<td>-11</td>
<td>-1</td>
<td>$F^0-J+C$</td>
</tr>
<tr>
<td>$d^8(^3F)$</td>
<td>8</td>
<td>28</td>
<td>-13</td>
<td>-1</td>
<td>$F^0-J+C$</td>
</tr>
<tr>
<td>$d^9(^2D)$</td>
<td>9</td>
<td>36</td>
<td>-16</td>
<td>0</td>
<td>$F^0-J-C$</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>
Note the strong difference in the effective U for a half filled d shell!!

- The half filled shell is special and has a very large contribution to “U” as we defined it compared to all the other fillings.

- Note that J Hund for the 3d transition metal atoms is about 0.7-0.8 eV and IT IS NOT OR HARDLY REDUCED IN THE SOLID.

- Using the expression for U effective we have

\[ U_{\text{eff}}(d^5) = E(\uparrow\uparrow\uparrow\uparrow\uparrow) + E(\uparrow\uparrow\uparrow\uparrow\downarrow) - 2E(\uparrow\uparrow\uparrow\uparrow\uparrow) = F^0 + 4J \]

i.e. it costs 4J to remove a parallel spin electron from d5 and you don’t gain this back when You add an electron to d5

\[ U_{\text{eff}}(d^4) = E(\uparrow\uparrow\uparrow\uparrow) + E(\uparrow\uparrow\uparrow\uparrow\uparrow) - 2E(\uparrow\uparrow\uparrow\uparrow\uparrow) = F^0 - J - C \]

costs 3J to remove from d4 but win back 4J when you add to d4
Nultiplet structure of 3d TM free atoms

Note the high energy scale
Note also the lowest energy state for each case i.e. Hunds’ Rule;

This diagram was made based on theory and experiment on TM impurities in Cu, Ag, Au from which \( I = -3.2, F_0 = 1.04 \text{eV}, F_2 = 8.94 \) and \( F_4 = 5.62 \) as in the relations for \( J \) and \( C \) used in the Hunds rule ground state energies. The excited states using relations from Slaters book. Note that \( F_0 \) is very strongly reduced in these noble metal hosts.
Combining crystal and ligand fields with the coulomb and exchange interactions in compounds
Use the crystal field and coulomb matrix elements for real orbitals in the tables from Ballhausen and the spin orbit couplling and diagonalize
Angular distribution of “real” d orbitals
In the next slide is an example of the multiplet structure for Ni 2+ in NiO. NiO has a rock salt structure i.e. NaCl in which Ni 2+ is surrounded by 6 O 2- ions in an octahedron. The crystal and ligand fields as described before split the 5 fold degenerate d levels into doubly degenerate eg and triply degenerate t2g levels. These are then occupied by 8 d electrons which according to Hund's rules will have a total spin of 1 and if the crystal field splitting is zero a total orbital angular momentum of 3 and with spin orbit coupling J = 4. The extreme left side gives the free ion results and the extreme right the very strong crystal field limit.
Interplay between crystal Fields and multiplet structure

Tanabe Sugano diagrams for Ni\(^{2+}\) in Octahedral coordination.

J phys soc Jap 9, 753 (1954)

Note the small spin orbit splitting For the free ion and the lack of any influence of the spin orbit coupling For the large crystal field limit.
Why is the spin orbit coupling not effective for Ni2+ with large crystal field

\[ d_{xy}, d_{xz}, d_{yz} \rightarrow t_{2g} \]

\[ d_{x^2-y^2}, d_{3z^2-r^2} \rightarrow e_g \]

\[ d_{xy} = \frac{1}{i\sqrt{2}} ([2,2] - [2,-2]) \]

\[ d_{3z^2-r^2} = [2,0] \]

\[ d_{x^2-y^2} = \frac{1}{\sqrt{2}} ([2,-2] + [2,2]) \]

\[ d_{xz} = \frac{1}{i\sqrt{2}} ([2,1] - [2,-1]) \quad d_{xz} = \frac{1}{\sqrt{2}} ([2,1] + [2,-1]) \]

Spin orbit coupling is of the form

\[ H_{so} = \sum \lambda \vec{U}_i \cdot \vec{s}_i \]

Where the sum is over the electrons. This couples only states which differ in the ml quantum numbers by 0 or ±1. So eg’s are not affected. And for large crystal fields the eg-t2g splitting is much larger than the spin orbit coupling and so this mixing is also suppressed. So SO coupling will have little effect in a perturbation description for large Crystal field splitting and a d8 configuration.
For partially filled t2g orbitals the orbital degeneracy is present as for Ti3+ in OH symmetry SO can at least partially lift this degeneracy and therefore is very important potentially
How can we experimentally observe the d-d multiplet splittings?

• Optical absorption (actually d-d transitions are forbidden but somewhat allowed via SO and electron phonon coupling)
• Optical Raman spectroscopy
• Electron Energy Loss spectroscopy
• Resonant soft x ray inelastic scattering which is actually x ray Raman spectroscopy
The d-d transitions are clearly visible inside the conductivity gap or charge transfer gap of about 4eV. The excitation below 1 eV is a phonon plus two magnons excitations which is sharp and weakly allowed.
How could we describe this theoretically

• Treat Ni\(^{2+}\) in NiO as an impurity in a lattice of O\(^{2-}\) ions. That is neglect the influence of other Ni ions in the lattice because of the very atomic character of the 3d states.

• Then we basically have a two particle problem. i.e. two holes in an otherwise full band system.

• The two holes could both be on Ni i.e. Ni\(^{2+}\) but could be in any of the d\(^8\) multiplet states or one hole could be on O and one on Ni or both holes on the same or different O ions.
Use our Auger theory for two particles

• If we take the vacuum as Ni d10 and all O 2p6 and we determine the two hole eigenstates as in Auger spectroscopy including the crystal fields and Ni3d-O2p hoping integrals plus the full d-d coulomb interactions we should generate the full spectrum of two hole states.

• We can use the two particle Greens function formalism
Model theory for d-d excitations in NiO

• Use the two hole (Auger) theory described before and a vacccum state of d10 for Ni and a full O 2p band

• Add a point charge crystal field and a Ni3d-O2p hybridization for eg and t2g orbitals and an O2p band structure of the form

\[ H(\text{hyp}) = \sum_{k,n,\sigma} V_{k,n} (c_{k,n,\sigma}^* d_{n,\sigma} + d_{n,\sigma}^* c_{k,n,\sigma}) \]  

(n lables t2g or eg)

• Add the d-d full coulomb interactions between two d holes

\[ H(\text{int}) = \sum_{i,j,l,m} U(i,j,l,m) d_i^* d_j d_l^* d_m \]

• Use the two particle Greens function to calculate the energies of all the states corresponding to two holes in Ni 3d
Ni 3d8 states in OH symmetry

- The irreducible representations spanned by 2 holes in a d level are $3A_1g^1E_g^1T_{2g}^3T_{1g}^3T_{2g}^3T_{1g}^1A_1g$.
- Corresponding to the arrangement of two holes in eg and t2g orbitals.
- Use the Dyson equation for the two particle Greens function:
  \[ G_{i,j}^{i,j'}(IR,z) = G_{0,i,j}^{i,j'}(IR,z)\delta_{i,i'}\delta_{j,j'} + \sum_{m,n} G_{0,i,j}^{i,j}(IR,z)U_{i,j}^{m,n}G_{m,n}^{i,j'}(IR,z) \]
- In which i,j refer to eg or t2g and spins IR are the various irreducible representations and
- $G_{0,i,j}^{i,j} = g_{eg} \otimes g_{eg}$ or involving two t2g state the small g’s are the single hole greens functions involving the hybridization with the O 2p band.
Unfortunately this cannot be used for more than two holes.
In order to get a picture of the basic physics for various d occupations covering basically the whole 3d series we resort to a simplified but very useful model
Simplified picture of Crystal fields and multiplets

• Determine $d^n$ energy levels assuming only crystal and ligand fields and Hund's' first rule i.e.

$$F^0, \text{and } J = \frac{1}{14} (F^2 + F^4)$$

• Neglect other contributions like C in our former slides and the SO coupling

• This is a good starting point to generate a basic understanding. For more exact treatments use Tanabe-Sugano diagrams
Crystal fields, multiplets, and Hunds rule for cubic (octahedral) point group

**Free ion**

- $d_5$; Mn$^{2+}$, Fe$^{3+}$
  - $4J$
  - $\uparrow\uparrow\uparrow\uparrow\uparrow$
  - $\downarrow\downarrow\downarrow\downarrow\downarrow$

**Cubic Oh**

- $\uparrow\uparrow\uparrow$
- $\downarrow\downarrow\downarrow$
- $10DQ$
- $S=5/2$
- No degeneracy

$\langle 4J \rangle$ is the energy to flip One of spins around $10DQ$= crystal field

$d_4$; Mn$^{3+}$, Cr$^{2+}$

- $3J$
- $\uparrow\uparrow\uparrow$
- $\downarrow\downarrow\downarrow$

- $\uparrow\uparrow\uparrow$
- $\downarrow\downarrow\downarrow$
- $S=2$ two fold degenerate
d6; Fe\(^{2+}\), Co\(^{3+}\)

S=2; 3 fold degenerate

d2; Ti\(^{2+}\), V\(^{3+}\)

S=1; 3 fold degenerate
Physical picture for high spin to low spin transition

$\begin{align*}
\text{d6; Fe}^{2+}, \text{Co}^{3+} & : 3J \\
10DQ & \\
\text{t2g} & \\
\text{eg} & \\
E(\text{HS}) = -10J - 4DQ & \\
E(\text{LS}) = -6J - 24DQ & \\
\text{HS to LS for } 10DQ > 2J & \\
\text{d5; Fe}^{3+}, \text{Co}^{4+} & : 4J \\
10DQ & \\
\text{t2g} & \\
\text{eg} & \\
E(\text{HS}) = -10J & \\
E(\text{LS}) = -4J - 20DQ & \\
\text{HS to LS for } 10DQ > 3J & 
\end{align*}$
What would happen if $2J < 10Dq < 3J$ and we are in a mixed Valen system? If we remove one electron from d6 we would go from $S=0$ in d6 to $S=5/2$ in d5. The “hole” would carry a spin of $5/2$ as it moves in the d6 lattice.

LaCoO3 is in a low spin Co3+ i.e. $S=0$ state for Temp$<100K$. The first ionization state would be Co4+ High Spin ($S=5/2$). This lowest energy state cannot be reached by removing 1 electron with Spin $\frac{1}{2}$ i.e. invisible to photoemission (from Damascelli notes Z=0). This would correspond to a very heavy quasi particle. In a mixed valent system like La1-$x$Sr$x$CoO3 the charge carriers would be very heavy. i.e. low electrical conductivity high thermal power.
TABLE 8.1. The possible lowest and highest spin states of an 3d ion with n d electrons in a local surrounding of octahedral (O_{6h}) or tetrahedral (D_{4h}) symmetry. The arrows indicate electron removal or electron addition transitions with \(|\Delta S| > \frac{1}{2}\).

<table>
<thead>
<tr>
<th></th>
<th>d^0</th>
<th>d^1</th>
<th>d^2</th>
<th>d^3</th>
<th>d^4</th>
<th>d^5</th>
<th>d^6</th>
<th>d^7</th>
<th>d^8</th>
<th>d^9</th>
<th>d^{10}</th>
</tr>
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<tbody>
<tr>
<td>O_{6h}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>3/2</td>
<td>2</td>
<td>5/2</td>
<td>2</td>
<td>3/2</td>
<td>1</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>Low</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>3/2</td>
<td>1</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>D_{4h}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>High</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>3/2</td>
<td>2</td>
<td>5/2</td>
<td>2</td>
<td>3/2</td>
<td>1</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>Low</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
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<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE 8.2. The combined crystal and ligand field splitting (10D_q) required for a transition from high spin to low spin.

<table>
<thead>
<tr>
<th></th>
<th>d^2</th>
<th>d^3</th>
<th>d^4</th>
<th>d^5</th>
<th>d^6</th>
<th>d^7</th>
<th>d^8</th>
<th>d^9</th>
</tr>
</thead>
<tbody>
<tr>
<td>10D_q (eV)</td>
<td>-</td>
<td>-</td>
<td>2.36</td>
<td>2.67</td>
<td>1.74</td>
<td>1.98</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A window of 1 eV!!
If the charge transfer energy $\Delta$ gets small we have to modify the superexchange theory. Anderson 1961

Goodenough-Kanamori-Anderson rules i.e. interatomic superexchange interactions

And magnetic structure

For example Cu$^{2+}$---O---Cu$^{2+}$ as in La$_2$CuO$_4$ and superconductors. Cu$^{2+}$ is d9 i.e. 1 eg hole (degenerate in OH) but split in D$_{4h}$ as in a Strong tetragonal distortion for La$_2$CuO$_4$ structure. The unpaired electron or hole is in a dx$^2$-y$^2$ orbital with lobes pointing to the 4 Nearest O neighbors.

The sum leads to a huge antiferro Interatomic $J^{\text{(sup)}}$ = 140 meV for the Cuprates
Superexchange for a 90 degree bond angle

The hoping as in the fig leaves two holes in the intervening O 2p states i.e. a p4 configuration. The lowest energy state according to Hund’s rule is Spin 1. So this process favours a ferromagnetic coupling between the Cu spins.

\[
J(90) = 2 \frac{t_{pd}^4}{\Delta^2} \left[ \frac{2}{2\Delta} - \frac{2}{2\Delta - J(\text{hundO}2-)} \right]
\]

So the net exchange as a function of the bond angle is:

\[J(\theta) = J(180) \cos^2(\theta) + J(90) \sin^2(\theta)\]
Superexchange between singly occupied t2g orbitals

\[
J_{anti} = \frac{2t_{pd\pi}^4}{\Delta^2} \left[ \frac{2}{2\Delta + U_{pp}} + \frac{1}{U_{dd}} \right]
\]

If we now rotate one of the bonds around the z axis the superexchange does not change, but for rotation around the y axis it changes as for eg orbitals. Since

\[
t_{pd\pi} \approx \frac{1}{2} t_{pd\sigma} \quad J_{pd\pi} \approx \frac{1}{16} J_{pd\sigma}
\]
If we have “spectator spins” as in Mn$^{3+}$ in OH

For ferro orbital ordering we will get a strong antiferromagnetic superexchange since the same intervening O 2p orbital is used in intermediate States as in the example above.

For antiferro orbital ordering

The factor of 3 in the Hunds’ Rule of Mn is from the “spectator” spins.
For example in LaMnO₃ and the “Colossal” magneto resistance materials La(1-x)CaxMnO₃ and now with “orbital ordering” the extra eg spin has a strong antiferro superexchange coupling for ferro orbital ordering i.e. as in the example above for 180 degree bond. But the superexchange is weakly ferromagnetic for antiferro orbital ordering since then both ferro and antiferro terms compete differing only by the Hund’s’ rule which now also involves the “spectator” spins in t₂g orbitals. We have neglect the wuperexchange involvong the t₂g orbitals here.
Zener Double exchange

- This is important in for example in La(1-x)CaxMnO3 which are colossal magneto resistance materials. Here the extra eg electron pictured in former slides is free to move even if U is large because of the mixed valent nature of the Mn. Some of the Mn3+ (d4) is now Mn3+(d3) which has empty eg orbitals. However the eg electron can only move freely if the spectator t2g spins are ferromagnetically aligned yield a large band width and so a lowering of the kinetic energy. The ferromagnetic exchange is proportional to the one electron band width