PHYS 460 - LECTURE 21

MAGNETISM IN REAL MATERIALS

NOW THAT WE HAVE CONSIDERED A SERIES OF IDEALIZED MODELS, IT IS TIME TO TALK ABOUT HOW IT APPLIES TO REAL MATERIALS.

AS WITH TRANSPORT, MAGNETIC RESPONSE DEPENDS ALMOST ENTIRELY ON ELECTRONS. WE CAN BROADLY SEPARATE ELECTRONS BY THEIR BEHAVIOR:

(I) DELOCALIZED ELECTRONS - THIS IS THE FOUNDATION OF BAND THEORY, AND WE ALREADY WORKED OUT THE LOW-FIELD MAGNETIC RESPONSE THAT COMES FROM ENERGY SHIFTS IN SPIN UP AND DOWN BANDS

$$\chi_{PAULI} = \mu_0 \mu_B^2 g(\varepsilon_F)$$

THIS FORMULA WAS DERIVED FOR THE FREE ELECTRON MODEL, BUT SINCE THE RESPONSE RELIES ONLY ON THE ELECTRON ENERGY DENSITY AT THE FERMI SURFACE AND NOT ITS SHAPE, IT IS ACTUALLY QUITE GENERAL.

WHAT WE NEGLECTED TO CONSIDER WAS THE MODIFICATION OF THE FREE ELECTRON ORBITALS WHICH GIVES A DIAMAGNETIC CONTRIBUTION (I PRESENT WITHOUT PROOF): $\chi_{LANDAU} = -\frac{1}{3}\chi_{PAULI}$

NOT FULL SHELL →

$$\Rightarrow \chi_{ITINERANT} = \frac{2}{3} \mu_0 \mu_B^2 g(\varepsilon_F)$$

Ⅱ LOCALIZED ELECTRONS WITH $J=0$ (OR ORBITALS LEADING TO COMPLETELY FILLED BAND)

THIS LEADS TO A LARMOR DIAMAGNETIC TERM, AND IS PRESENT FOR ALMOST EVERY MATERIAL DUE TO CORE ELECTRONS IN FULL SHELLS

FOR NOBLE GASES, IT ALMOST ENTIRELY CAPTURES THE MAGNETIC RESPONSE

$$\chi_{LARMOR} = -\frac{Z n e^2 \mu_0 \langle r^2 \rangle}{6 m_e}$$

FOR COMPLETION, I SHOULD NOTE THAT THERE IS ALSO A SMALL PARAMAGNETIC CORRECTION TO THIS FORMULA DUE TO QUANTUM FLUCTUATIONS OUT OF THE $J=0$ STATE TO OTHER STATES $|n\rangle$

$$\chi_{VAN\ VLECK} = 2 n \mu_B^2 \sum_n \frac{|\langle J=0|(L_z + g S_z)|n\rangle|^2}{E_n - E_0}$$

BY 2nd ORDER PERTURBATION THEORY

THUS, ACCORDING TO BAND THEORY, MAGNETIC SUSCEPTIBILITY IS LARGELY TEMPERATURE INDEPENDENT AND GIVEN BY

$$\chi = \chi_{PAULI} + \chi_{LANDAU} + \chi_{LARMOR} + \chi_{V.V.}$$

NOTE THAT $|\chi_{VV}| \ll |\chi_{LAR}|$ TYPICALLY, BUT $\chi_{PAULI} \sim |\chi_{LAR}$
AS A RESULT METALS CAN BE DRIVEN DIAMAGNETIC, DEPENDING ON THE DETAILS (e.g Cu OR Ag)

Ⅲ LOCALIZED ELECTRONS WITH $J \neq 0$

THIS SCENARIO ONLY OCCURS WHEN BAND THEORY BREAKS DOWN (e.g. MOTT INSULATORS), BUT ARGUABLY LEADS TO THE MOST INTERESTING BEHAVIOR. WE CONSIDERED THE MOST IDEAL CASE, WITH PERFECTLY ISOLATED MOMENTS. FOR THAT CASE SUSCEPTIBILITY WAS GIVEN BY

$$\chi_{\text{CURIE}} = \frac{n\, J(J+1)\, \tilde{g}\, \mu_0 \mu_B^2}{3 k_B T} \equiv \frac{C}{T}$$

WE FOUND THAT χ WAS PARAMAGNETIC AND WAY LARGER THAN ANY TERM FROM BAND THEORY PREDICTIONS. TEMP DEPENDENCE WENT LIKE $\frac{1}{T}$, WITH A COEFFICIENT THAT WENT LIKE μ_J^2 (WHICH COULD ALSO BE EXTRACTED FROM SATURATION M AT HIGH FIELDS)

IDEALLY, THIS $\mu_J = \tilde{g} \mu_B \sqrt{J(J+1)}$ WHERE J IS DETERMINED BY HUND'S RULES, BUT IN REAL MATERIAL, SEVERAL IMPORTANT FACTORS NEED TO BE CONSIDER:

- DIAMAGNETISM FROM CORE e^- – χ_{LARMOR}, AGAIN
- DISORDER
- PARTIAL DELOCALIZATION
- MODIFIED VALENCE
- CRYSTAL FIELDS *
- INTERACTIONS BETWEEN SPINS *

(DISORDER, PARTIAL DELOCALIZATION, MODIFIED VALENCE:) CHANGES J

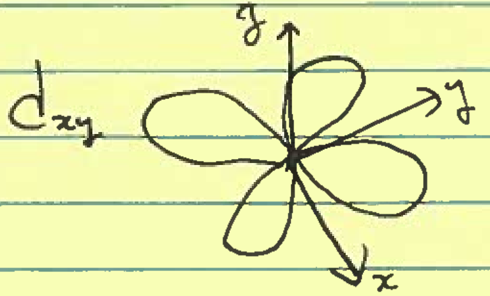
LET'S CONSIDER THESE LAST TWO POINTS IN DETAIL

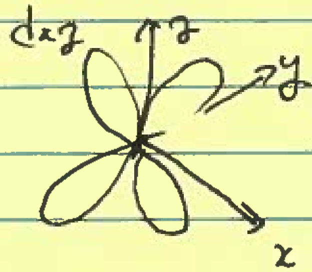
CRYSTAL FIELDS

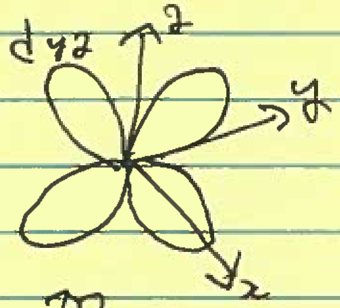
HUND'S RULES ASSUME AN ISOTROPIC ELECTRIC POTENTIAL (e.g ELECTRONS ORBITING A POSITIVELY CHARGED NUCLEUS). IN THIS CASE, ALL L_z ORBITALS ARE DEGENERATE.

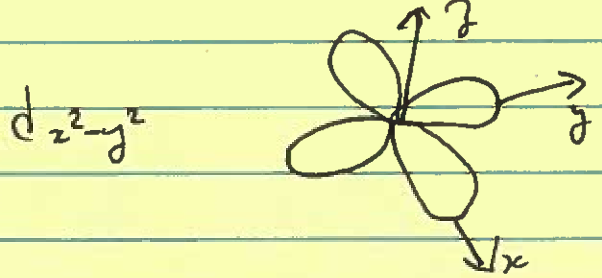
SO, FOR EXAMPLE, FOR $L=2$ (d-ORBITALS)

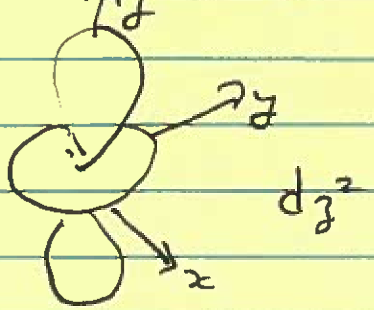
ORBITALS



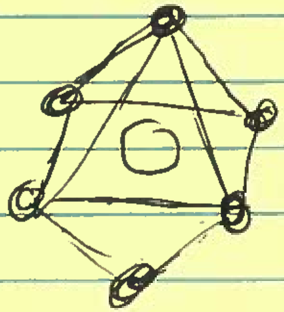




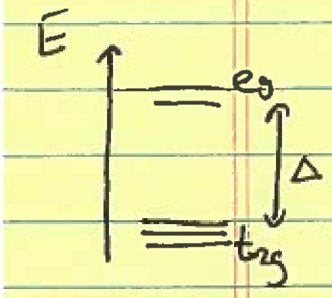


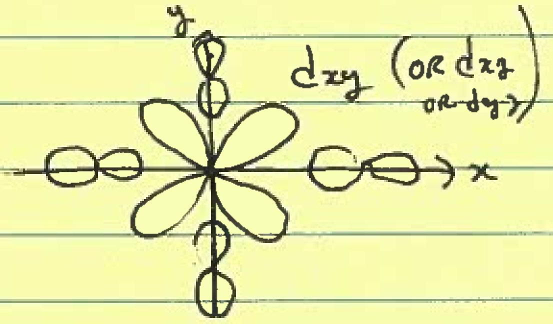


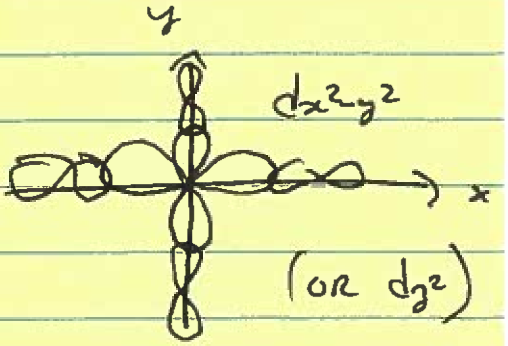
IN REAL MATERIALS, THIS DEGENERACY IS BROKEN BY THE PRESENCE OF OTHER ATOMS. FOR EXAMPLE, A COMMON SCENARIO IS WHEN A MAGNETIC CATION IS IN THE CENTER OF AN OCTAHEDRA OF OXYGEN ANIONS



THESE ANIONS HAVE A NET NEGATIVE CHARGE DENSITY, WHICH LOWERS THE ENERGY OF ORBITALS THAT PLACE ELECTRON DENSITY BETWEEN NEIGHBORING OXYGENS AND RAISE ENERGIES OF ORBITALS THAT MAXIMIZES OVERLAP



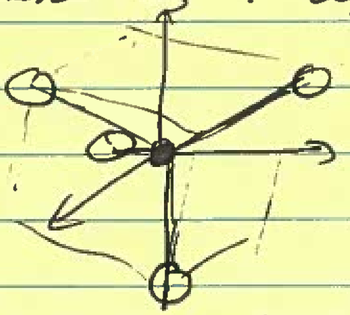


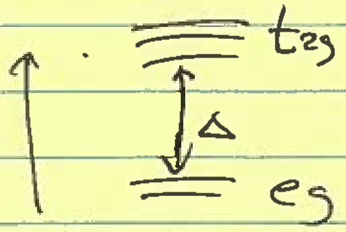


~~THERE~~ THERE ARE THREE LOWER ENERGY ORBITALS (KNOWN AS t_{2g} ORBITALS) AND TWO HIGHER ENERGY ORBITALS (KNOWN AS e_g ORBITALS)

ANOTHER COMMON SCENARIO HAS A CATION IN A SO-CALLED OXYGEN TETRAHEDRA

THIS REVERSES e_g & t_{2g}





THIS MODIFIES HUND'S RULES AND CAN LEAD TO VIOLATIONS OF THE THIRD LAW

i.e. What is larger, crystal field energy or spin-orbit coupling?

e.g.

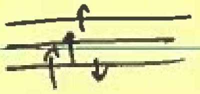
Fe^{2+}

$3d^6$

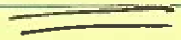
$\Delta \ll E_{so}$

$S=2$

"WEAK FIELD"

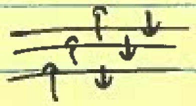


$\Delta \gg E_{so}$



$S=0$

"STRONG FIELD"



ORBITAL QUENCHING

IN THE STRONG FIELD LIMIT, THE SITUATION DIFFERS EVEN MORE GREATLY THAN IT FIRST APPEARS. CONSIDER THE CRYSTAL FIELD HAMILTONIAN, WHICH ONE CAN SHOW CAN BE APPROXIMATED BY

(Taylor expansion of coloumb potential due to octahedral cage)

$$V = \text{Const} + A\left(x^4+y^4+z^4-\frac{3}{5}r^4\right)+\mathcal{O}(r^6)$$

Important thing to note is that V is REAL.

FOR $A \gg \underset{\text{S-O COUPLING CONSTANT}}{\lambda}$, THIS IMPLIES THAT $\hat{H}$ IS <u>REAL</u>.

$\Rightarrow$ ALL EIGENFUNCTIONS OF THE HAMILTONIAN (i.e. ALL ELECTRON WAVEFUNCTIONS) ARE <u>REAL</u>

BUT THE ANGULAR MOMENTUM OPERATOR IS PURE IMAGINARY

$$\hat{L} = \hat{r}\times\hat{p} = -i\,\hat{r}\times\vec{\nabla}$$

$$\Rightarrow \langle \hat{L} \rangle = \langle \psi | \hat{L} | \psi \rangle = \underline{\text{IMAGINARY}}$$

BUT ANGULAR MOMENTUM IS AN OBSERVABLE

$$\Rightarrow \langle \hat{L} \rangle = \underline{\text{REAL}}$$

THE ONLY WAY BOTH CONDITIONS CAN BE SATISFIED IS IF $L = 0$ ALWAYS

(Thus, when degeneracy of Lz is broken, new orbitals are formed that are linear combinations with Lz=0.)

<u>NOTES</u>: ① CRYSTAL FIELDS ARE MOST IMPORTANT FOR 3d ORBITALS, SINCE $H_{SO} \propto Z^4$ AND d ORBITALS ARE MOST EXTENDED

② IN REAL SITUATIONS, $\mathcal{H}_{S\text{-}O}$ IS LARGE ENOUGH BE IMPORTANT → L IS GREATLY REDUCED BUT NOT IDENTICALLY ZERO

→ IN PRACTICE, LOCAL MOMENTS ARE DIFFICULT TO CALCULATE AND HAVE TO BE MEASURED

WHEN $L=0$ (USUALLY IN 3d MAGNETS), TOTAL MOMENTS REALLY ARE JUST SPIN. IN THAT CASE, WE SAY ORBITAL ANGULAR MOMENTUM IS "QUENCHED"

SPIN ANISOTROPY

MORE GENERALLY, THE DISTRIBUTION OF ATOMS IN A MATERIAL WILL PREFER SOME ORBITALS WITH RESPECT TO OTHERS. THROUGH SPIN-ORBIT COUPLING THEN, CERTAIN SPIN DIRECTIONS ARE PREFERRED TO OTHERS. THIS "SINGLE ION ANISOTROPY" IS OFTEN TAKEN INTO ACCOUNT BY ADDING A (PHENOMENOLOGICAL) TERM TO THE SPIN HAMILTONIAN

$$\mathcal{H}_{\text{anisotropy}} = -K \sum_i (S_i^z)^2$$

INTERACTIONS

PERHAPS THE BIGGEST DEVIATION FROM THE LONE ATOM PICTURE IS THAT THE ATOMS (AND THUS SPINS) ARE NOT ALONE. THERE ARE MULTIPLE SPINS IN THE MATERIAL AND THEY DO NOT ACT INDEPENDENTLY. IN FACT THE DIRECTION OF ONE SPIN DEPENDS ON THE DIRECTION OF SPINS ON NEIGHBORING SITES.

THE MECHANISM IS THE "EXCHANGE INTERACTION" WHICH WE HAVE SEEN MANY TIMES BEFORE. FOR TWO SPINS, THE EFFECTIVE HAMILTONIAN IS GIVEN BY

$$\mathcal{H} = -J\vec{S}_1 \cdot \vec{S}_2$$

WHERE $J = E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$

$= \text{EXCHANGE ENERGY}$

FOR TWO ELECTRONS ON THE SAME ATOM, WE HAVE ARGUED $J > 0$ AND SPINS ALIGN.

WE ALSO SAW WHEN WE WERE CONSIDERING COVALENT BONDING THAT THE SYMMETRIC "BONDING" ORBITAL HAD LOWER ENERGY BECAUSE DELOCALIZING ELECTRONS LOWERS GROUND STATE ENERGY (DOUBLING SIZE OF "BOX" IN WHICH TWO PARTICLES ARE CONFINED)

→ EXCHANGE FAVOR ANTIALIGNED SPINS ON NEIGHBORS

GENERALIZING THIS 2-PARTICLE HAMILTONIAN TO A LATTICE, WE GET THE "HEISENBERG HAMILTONIAN":

$$\mathcal{H} = -\frac{1}{2}\sum_{i,j} J_{ij}\,\vec{S}_i \cdot \vec{S}_j + \sum_i g\mu_B\,\vec{B}\cdot\vec{S}_i$$

SO WE DON'T DOUBLE COUNT

WHERE SUM IS OVER ALL LATTICE SITES, AND THE SECOND TERM ALLOWS FOR THE APPLICATION OF AN EXTERNAL MAGNETIC FIELD.

SINCE EXCHANGE IS DUE TO HOPPING, IT IS USUALLY SUFFICIENT TO CONSIDER ONLY NEAREST NEIGHBORS ON THE SPIN LATTICE. IF EXCHANGE BETWEEN NEIGHBORS ARE THE SAME $J_{ij} \equiv J \;\; \forall \langle i,j \rangle$

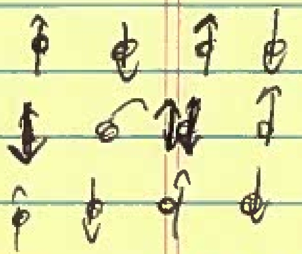
$$\Rightarrow \mathcal{H} = -\frac{1}{2}\sum_{\langle i,j\rangle} J\,\vec{S}_i \cdot \vec{S}_j + \sum_i g\mu_B\,\vec{B}\cdot\vec{S}_i$$

neighbors

THIS IS A GENERAL HAMILTONIAN, WHERE J CAN REFLECT SEVERAL DIFFERENT SPECIFIC MECHANISMS.

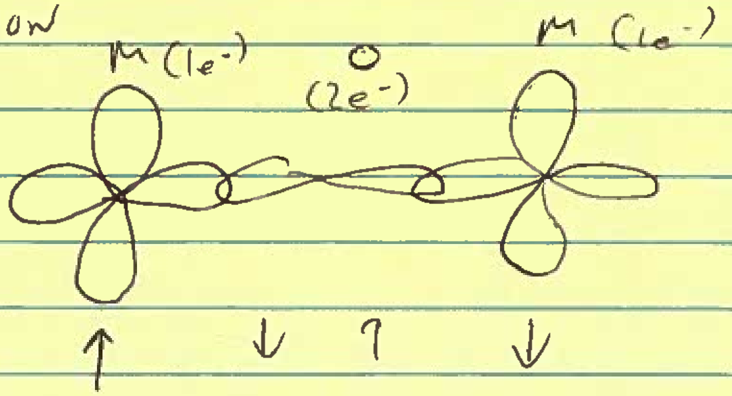
QUICK RUNDOWN:

(I) DIRECT EXCHANGE : EXACTLY WHAT WE HAVE BEEN TALKING ABOUT.



NEIGHBOR SPINS PREFER TO BE ANTI-PARALLEL BECAUSE IT ALLOWS FOR ELECTRONS TO HOP TO NEIGHBORS AND BACK, INCREASING DELOCALIZATION

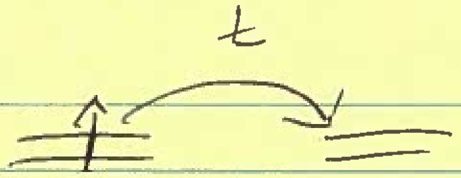
(II) SUPEREXCHANGE : SIMILAR, BUT ELECTRONS HOP THROUGH INTERMEDIARY LIGAND ANION

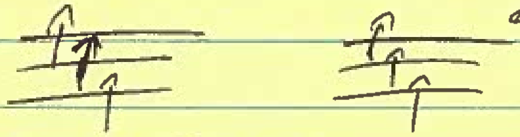


IF NEIGHBOR M's HAVE ↑↓, THEN ELECTRONS CAN BE DELOCALIZED ACROSS M-O-M MOLECULE

(III) DOUBLE EXCHANGE : IF AN ELECTRON HOPS INTO AN EMPTY ORBITAL, HUND'S FIRST RULE FORCES SPIN TO ALIGN TO OTHER SPINS (HUND'S COUPLING)

→ DELOCALIZATION POSSIBLE ONLY FOR ALIGNED NEIGHBORS e.g



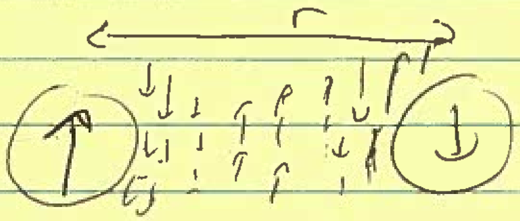


IF THESE SPINS WERE ↓↓↓, $t \to 0$

DEVIATIONS FROM HEISENBERG MODEL

(IV) **RKKY**: SPIN EMBEDDED IN A METAL

IT WILL POLARIZE ITINERANT ELECTRONS, WHICH CARRIES INFO TO NEIGHBOR



$$J \propto \frac{\cos(2k_F r)}{r^3}$$

(V) DZYALOSHINSKY - MURIYA

SECOND ORDER EFFECT MEDIATED BY SPIN-ORBIT COUPLING

$$\hat{H}_{DM} = \vec{D} \cdot (\vec{S}_1 \times \vec{S}_2)$$