MICROSCOPIC BASIS OF MAGNETISM

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Subhead:

MAGNETISM OF INSULATORS, METALS AND THINGS-IN-BETWEEN
Insulators

- Hydrogenic Atoms
- Review of 3d - transition metal atoms
  - Hund's Rule, Spin orbit X

- Hydrogen molecule $H_2$: Heitler-London vs. Muffin-Bands
  - onsite $U$, exchange $J$
  - overlap $\equiv$ bonding $\equiv$ AFM.

- Array of H atoms or Si P - Mott's problem
  - Long Ranged Coulomb - Mott's original problem
  - Short Ranged - Mott - Hubbard problem
  - $t/U$ expansion in insulators - Mott vs Halpern view

- Crystal Field splittings - overlap - Superexchange & Direct Exchange
  - Examples of C-F splittings
  - Anderson's superexchange vs. Charge Transfer Insulator
  - Goodenough - Kanamori - Anderson rules and their origin

- Double exchange: Manganese, Zener - Anderson - Heeger

- Small thing: Spin orbit X$^2$on and its consequences
  - Single Conformes, Dzyaloshinsky-Moriya $g$-factor
Hydrogenic atoms: quick review:

\[ H = \sum \frac{p_i^2}{2m} + \sum V(x_i) + e^2 \sum \frac{1}{r_{ij}} - g\mu_B \sum \vec{L} \cdot \vec{H} \]

\[ - g\mu_B \sum \vec{S} \cdot \vec{H} - \mu_B \sum \vec{S} \cdot \vec{H} \]

\[ + \frac{\hbar^2}{2m^*c^2} \sum \vec{S}_i \cdot \left\{ \vec{\nabla} V(x_i) \times \vec{P}_i \right\} + \frac{\hbar^2}{2m^*c^2} \sum \frac{\vec{S}_i \times \vec{P}_i}{2} \]

\[ \frac{\vec{S}_i \cdot \vec{S}_j}{\sqrt{\gamma_i \gamma_j}} \]

Here \( V(x_i) = -\frac{Ze^2}{r_i} \) is a Coulomb potential.

This is a formal \( \frac{1}{e} \) expansion since \( \mu_B = \frac{e\hbar}{2mc} \).

\[ \vec{\nabla} V(x_i) = \frac{\vec{v}_i}{r_i} \] \( b_i \) in Bohr units,

\[ \frac{\hbar^2}{2m^*c^2} \sum \frac{1}{r_i} \frac{\vec{S}_i \cdot \vec{P}_i}{2} \]

\[ \gamma_i = \frac{\vec{S}_i \times \vec{P}_i}{2} \]

\[ \sum \frac{\vec{S}_i \cdot \vec{S}_j}{\sqrt{\gamma_i \gamma_j}} \]

\[ \gamma(x_i) \geq 0 \]

This is too hard a many-body problem. We use Hartree-Fock orbitals to define effective one-body problem:

\[ V_{HF}(\gamma_i) = V(\gamma_i) + V_{Hartree} - V_{Fock} \]

Classical Bohr radius \( \gamma_{Bohr} = a_0 n^2/2 \) ; \( a_0 = \frac{\hbar^2}{me^2} = 52.9 \) Å

\[ \langle \gamma_{ne} \rangle = \frac{(3n-1)(3n-1+1)}{3} \gamma_{Bohr} \]

\( \gamma_{Cu} \) \( n=3 \) \( l=2 \) to 4
$Z ightarrow Z - \sigma \rightarrow Z_{\text{eff}} \quad \sigma = \text{screwing.}$

### Spin-orbit parameter

$$
\bar{f}(\nu) = \frac{\hbar^2 e^2}{2m_e c^2} \left( \frac{1}{\nu_c \nu} \right) \approx \frac{\nu^2}{c^2}
$$

$$
\lambda_{so} \approx \lambda \Sigma \bar{f}_{\nu_c \nu}
$$

$\lambda > 0 \sim \frac{\nu}{c^2}$ is quite appreciable for large $Z$.

In layer $s-o$ among metals

$\lambda \sim 10^8 \text{N} \text{m} \text{ to} \ 10^9 \text{N} \text{m}$

Trans metals $\sim$ Rare earths

### Magnetism mostly about unfilled shells

- $3-d \ T-M$
- $4-d \ T-M$
- $4-f \ \text{Lanthanides}$
- $5-f \ \text{Actinides}$

### Unfilled shells

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</table>

### Unfilled shells and Hund's rule:

1. $S_{\text{tot}}$ maximized
   - "J effect"
   - $S = \frac{3}{2}, L = \frac{1}{2}$

2. $L$ maximized
   - "U effect"
   - $S = \frac{1}{2}, L = \frac{3}{2}$
\[ (n) \quad \lambda > 0 \quad \text{for } n < \text{half} \quad : \quad |n - \frac{1}{2}| = \frac{1}{2} \]

\[ \lambda < 0 \quad \text{for } n > \text{half} \quad : \quad \frac{1}{n + \frac{1}{2}} = \frac{1}{2} \]

\[ V = \lambda \sum_{i} \bar{E}_i \bar{S}_i \]

\[ \mathcal{A} \geq 0 \quad \text{originally} \]

\[ \text{By } n > 0 \quad \text{half filling} \quad \text{add one subtract } \bar{E}_i \bar{S}_i \]

\[ \text{Filling shell} = \lambda \sum \bar{E}_i \bar{S}_i \]

But filling shell adds \[ \begin{align*}
\bar{V}_\gamma &= -A \sum \bar{E}_i \bar{S}_i \quad \text{(hole)} \\
\bar{V}_e &= A \sum \bar{E}_i \bar{S}_i \quad \text{(+)}
\end{align*} \]

\[ \bar{S}_i = \frac{\bar{S}}{n} \quad \text{(Wigner-Eckart Th.)} \]

\[ \bar{V}_\gamma = -2 \bar{E} \bar{S} \quad & \quad \bar{V}_e = 3 \bar{E} \bar{S} \]

3rd rule of Hund's

Degeneracy lifting by external fields \quad \text{e.g.} \quad \text{electric fields}

This is the basis of Crystal Field Effects - later.

\[ \psi_{n, l, m, o} = R_{nl}(I) \ Y_{lm}(S) \ \chi_o \]

\[ \mathcal{E} = E_n \quad \text{Bohr Atom} = -\frac{\mathcal{E}_0^2}{\mathcal{E}_0} \]

In reality due to \[ \chi_{\alpha} \quad \text{dependence} \quad \text{on} \]

\[ \psi_{n, l, m, o} \]
Origin of exchange: The \( \text{H}_2 \) molecule:

\[
\hat{H} = \frac{p_1^2 + p_2^2}{2m} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_2|}
\]

\[
\Psi(\mathbf{r}_1, \mathbf{r}_2) = - \Psi(\mathbf{r}_2, \mathbf{r}_1)
\]

\[
\chi_\uparrow(\mathbf{r}) = \chi \text{ or } \beta \text{ (spin-part)}.
\]

\( \mathbb{N} = 2 \) very special \( \Psi \) factors into spin \& space

\[
\Psi = \phi(\mathbf{r}_1, \mathbf{r}_2) \chi(\mathbf{r}_1, \mathbf{r}_2)
\]

\[
\begin{align*}
\text{sym} & \quad \rightarrow \text{a-sym} \\
\text{a-sym} & \quad \rightarrow \text{sym}
\end{align*}
\]

Spin: Triplet = symmetric \( \alpha_1, \beta_1, \alpha_2, \beta_2, \alpha_1\beta_2 + \beta_1\alpha_2 \)

Singlet = a-symmetric \( \alpha_1\beta_1 - \beta_1\alpha_1 \)

It does not explicitly depend on spin-variables and yet we claim:

\[
\mathcal{H}_{\text{eff}} = c + J \bar{S}_z \bar{S}_z \\
|\varepsilon_\uparrow - \varepsilon_\downarrow| = J
\]

Space part insoluble - Variational

Heitler London - vs - Mulliken molecular orbitals

Non-polar states —— Polar states
\[ \phi_t = \text{anti-sym (sp. part)} \quad \phi_s = \text{symm.-space part} \]

\[ \text{H-L choose two intuitively "good" states} \]

\[ \phi_{15} (r_1-R_1) \quad \text{and} \quad \phi_{15} (r_1-R_2) \quad \text{1-5 Hydrogenic states} \]

\[ \phi_s (r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \frac{\phi_{15} (r_1-R_1) \phi_{15} (r_1-R_2) + \phi_{15} (r_1-R_2) \phi_{15} (r_1-R_1)}{(1 + \Delta^2)^{1/2}} \right\} \]

\[ \Delta = \text{overlap} = \int \phi_{15} (r_1-R_1) \phi_{15} (r_1-R_2) \, dr_1 \]

\[ \sim \frac{e^{-|r_1-R_2|/a_0}}{\sqrt{2}} \]

\[ \varepsilon^t_s = 2 \varepsilon_0 + \frac{1}{\frac{1}{4} \alpha^2} \{ A + B \} \]

\[ \varepsilon_s - \varepsilon_k = \frac{2}{(1-\Delta^2)} \{ B - \Delta^2 A \} \]

\[ B = \int \phi (r_1-R_1) \phi (r_1-R_2) \phi (r_2-R_1) \phi (r_2-R_2) \left\{ \frac{e^2}{|r_1-r_2|} - \frac{e^2}{|r_1-R_2|} - \frac{e^2}{|r_2-R_1|} \right\} \]

\[ A = \int \phi^2 (r_1-R_1) \phi^2 (r_2-R_2) \left\{ \frac{e^2}{|r_1-r_2|} - \frac{e^2}{|r_1-R_2|} - \frac{e^2}{|r_2-R_1|} \right\} \]
The energy difference is determined largely by the B term. $E_s < E_t$ if $B < 0$

$$B = \int \mu(r_i) \mu(r_v) \, K(r_i-r_v) \quad \mu \text{ is a non-positive }$$

$$\phi_{\mu}(r_i-r_v) \, \phi_{\nu}(r_i-r_v)$$

If $K = \frac{e^2}{r_i-r_v}$ only, i.e., pure Coulomb, it is

true definite: $B > 0 \quad \{ \quad B = \langle \mu(r_i) \mu(r_v) \rangle = \frac{\sum K(r_i-r_v)^2}{2} \quad \}$

For $B$ to become negative, need overlap!

$$B = \int \mu(r_i) \mu(r_v) \, \frac{e^2}{(r_i-r_v)} - 2A \int \frac{e^2}{|r_i-r_v|} \, \phi_{\mu}(r_i-r_v) \, \phi_{\nu}(r_i-r_v)$$

**Adage:**

| no overlap (orthogonal orbitals) | F.M. $E_t < E_s$ |
| overlap | $\Rightarrow$ A.F.M. $E_s < E_t$ |

$J \simeq 0.1 \text{ eV (High Tc)} \left(1000^\circ k\right)$

$\sim 0.1 \text{ eV (100^\circ k)}$

$\sim 0.1 \text{ eV (10^\circ k)}$

}
Mulliken - M-O Theory

\[ \phi_\pm (r) = \left\{ \phi_{1s} (r-R_1) \pm \phi_{1s} (r-R_2) \right\} \frac{1}{2\sqrt{1+\Delta}} \]

\[ \phi_{\text{sym}} (\gamma, \nu) = \phi_+ (\gamma) \phi_+ (\nu) \quad \text{or} \quad \phi_- (\gamma) \phi_- (\nu) \]

\[ \phi_{\text{asym}} (\gamma, \nu) = \left[ \phi_+ (\gamma) \phi_- (\nu) - \phi_- (\gamma) \phi_+ (\nu) \right] \frac{1}{\sqrt{2}} \]

Here we find no binding!

Essential Difference:

\[ \text{M-O theory contains polar states} \]

\[ \text{e.g.} \quad \phi_{1s} (r_1-R_1) \phi_{1s} (r_2-R_2) \rightarrow \text{very costly} \]

\[ \text{due to Coulomb rep.} \]

\[ \text{H-L never has polar states.} \]

\[ \text{But H-L cannot carry a current} \quad \left\{ \begin{array}{l} \text{Insulator} \\text{Metal} \end{array} \right\} \]

M-O can!
§ Array of H atoms, Mott's problem:

Mott 1947

when a >> r_a expect isolated atom behaviour - insulator essentially distinguishable is s

For a << r_a orbitals "crunch" into each other - expect metallic behaviour: expect transition as a varies.

Shallow Donor states in Si: P: very popular 60's pic

Many complications in real systems
- multi valley
- Anderson Disorder
- M-A Traumkin

Perhaps Quantum dot arrays can be designed to realize Mott's

we can again approach problem from K-L or Band point of view. Need suitable l-e- functions.
\( \phi_{i\sigma}(r-R_k) \) is highly inconvenient, so we can
from Wannier fits from these in two steps:

**Step(i):**
\[
\phi_{\mathbf{k}\sigma}(r) = \delta \sum_n \phi_{\mathbf{k}\sigma}(r-R_n) e^{i \mathbf{k} \cdot (r-R_n)}
\]

\( k = \frac{2 \pi}{L} \{ m, m, m \} \) \hspace{1cm} \( \phi \) - normal

\( \phi_{\mathbf{k}\sigma} \) is a semiclass "natural" atomic state

\[
\left( \phi_{\mathbf{k}\sigma}, \phi_{\mathbf{k}\sigma} \right) = \delta_{\mathbf{k}\mathbf{k}'} \hspace{1cm} \phi_{\mathbf{k}\sigma}(r+R_j) = e^{i \mathbf{k} \cdot R_j} \phi_{\mathbf{k}\sigma}(r)
\]

**Step(ii):**
\[
W(r-R_k) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\sigma} e^{-i \mathbf{k} \cdot R_j} \phi_{\mathbf{k}\sigma}(r)
\]

we'll call these as \( W_n(r) \) and express \( \Psi \) in the
basis of \( W_n(r) \):

\[
\Psi(r) \approx \sum_n W_n(r) C_n \quad \{ \text{Strictly,} \quad W_n(r) C_n \}
\]

\( n \rightarrow \) Band index

\[
\left\{ \text{Projection to a} \quad \begin{array}{c}
\text{1 Band model!}
\end{array} \right\}
\]

Example of:

Program: search for (low energy) effective Hamiltonian!
\[ KE = \int \Psi^\dagger_\sigma(\mathbf{r}) \left[ \frac{p^2}{2m} + V(\mathbf{r}) \right] \Psi_\sigma(\mathbf{r}) \]

\[ - \sum_{i,j} \mathcal{T}_{ij} C^+_i \epsilon_{\sigma} \epsilon_{\sigma} C_i^+ \]

\[ \mathcal{T}_{ij} = \int W(\mathbf{r} - \mathbf{r}_i) \left\{ \rho^{\dagger}_{\text{total}} + U(\mathbf{r}) \right\} W(\mathbf{r} - \mathbf{r}_j) \]

\[ \epsilon_{\sigma} = t_{ii} \]

\[ P_{\text{KE}} = \frac{1}{2} \int \Psi^\dagger_\sigma(\mathbf{r}_1) \Psi^\dagger_\sigma(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \Psi_\sigma(\mathbf{r}_2) \Psi_\sigma(\mathbf{r}_1) \]

\[ = \frac{1}{2} \sum V_{ij,k \ell} C^+_i \epsilon_{\sigma} \epsilon_{\sigma} C_{k \ell} \]

\[ V_{ij,k \ell} = \int W(\mathbf{r}_1 - \mathbf{r}_i) W(\mathbf{r}_2 - \mathbf{r}_j) W(\mathbf{r}_1 - \mathbf{r}_k) W(\mathbf{r}_2 - \mathbf{r}_\ell) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \]

This is still too much detail (irrelevant?)

\[ \text{Mott: } \sim \frac{1}{2} \sum V_{ij,ij} C^+_i \epsilon_{\sigma} \epsilon_{\sigma} C_i \]

\[ V_{ij,ij} = U[\delta_{ij}] \sim \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \kappa \]

\[ \kappa = \text{dielectric constant} \]

{interband effects}

\[ \text{Anderson 1950,57} \}

\[ \text{Hubbard:1961} \]

\[ \approx \frac{1}{2} \sum V_{ij,ij} C^+_i \epsilon_{\sigma} \epsilon_{\sigma} C_i \]

\[ = \left\{ \begin{array}{l} U \sum n_{\epsilon_{\sigma} \mathbf{r}_i} n_{\epsilon_{\sigma} \mathbf{r}_j} \end{array} \right\} \]
\[ V = \begin{cases} \frac{2}{W(y_i - z_i)} \frac{2}{W(y_i - z_i)} \frac{e^2}{|y_i - z_i|} \\ \sim 5 \text{ eV} \\ 1 \text{ eV} \end{cases} \]

Using \( (\eta \sigma)^2 = \eta \sigma \), rewrite

\[ V_{int} = U \sum n_{i+y} n_{i-y} + \text{constant!} \]

Mott: \[ C_{eo} = \frac{1}{\sqrt{N}} \sum e^{-i k \cdot r_i} C_{i \sigma} \]

\[ H = \sum E_i C_i^+ e_o \sigma_0 + \frac{1}{2} \sum U_{ij} C_i^+ e_i \sigma_0 \sigma_0 \sigma_0 C_j^+ e_j \]

\[ U_{ij} = \frac{4 \pi e^2}{\kappa q^2} \]

\{correct for small q\}

Metals state for high enough density or small enough \( \kappa \).

Metals state characterized by screening

\[ \kappa \to \kappa = \left(1 + \frac{q^2 \tau F}{q^2} \right)^{1/2} \]

\[ q \tau F = \frac{4m e^2}{\kappa^2 \hbar} \]

\[ U_{ef}^{\text{eff}} = \frac{4 \pi e^2}{\kappa_0 (q^2 + q_{FP}^2)} \]
In absence of screening, e Coulomb has no bound state.
Hole & electron will form a bound molecule -

\[ \text{(Mott Exciton)} \]

Self-consistent insulating state.

If screening is nonzero and big enough, (i.e. \( g_{TF} > g^* \))
Yukawa potential has no bound state. (3-d)

\[ q^* = \frac{1}{\xi_0 a_0} \]

Metallic state is consistent for \( a < a^* \).
For \( a > a^* \) instability - (Mott Excitonic Instability)

\[ \Delta \]
Hubbard-Anderson limit.

Examine insulating state stability

\[ H = U \sum n_i^+ n_i^- - \sum t_{ij} \, c_i^+ c_j \]

\[ H_0 \quad H_1 = V \quad 1 \text{ e/atom} \]

\[ E = 0 \quad g^N \text{ fold deg.} \]

\[ E = 2U \]

\[ \begin{array}{c}
E_0 \\
V \quad 2N \quad 1^N \text{ HO} \\
0 \quad 2N \quad \text{ LHB}
\end{array} \]

qualitative lifting of degeneracy

In pictures

\[ \rightarrow \quad \rightarrow \quad \rightarrow \]

LHB \quad UHB \quad LHB

\[ \Psi_n = \text{ state in LHB} \]

\[ \chi_n = \ldots \text{ in } \text{ UHB} \]

**LHB**

**Lexical order and spin order.**

\[ \begin{aligned}
C_a^+ & C_b^+ C_d \downarrow \rightarrow \rightarrow \rightarrow \text{ ok} \\
C_a^+ & C_b^+ C_d \uparrow \rightarrow -C_a^+ C_b^+ C_d \uparrow
\end{aligned} \]
\( |\psi_0\rangle \) \text{ is } \epsilon, \epsilon_1, \epsilon_2 \text{ are the eigenvalues of } \mathcal{H} \text{ and } \langle \varphi | = c_1^+ c_2^+ c_3^+ c_4^+ \langle \psi_0 | \text{, where} \ \langle \psi_0 | \text{ is the ground state.}

Since \( 1, 2, 3, 4 \) are numbers, it can be specified by \( \alpha_1 = \cdots = \alpha_N \), \( \beta_j = \gamma \) \( \hat{V} = \hat{V} \text{ is first order in } t \)

\( |\psi(t)\rangle = \sum \langle \varphi_n | + \sum \alpha_n | \chi_n \rangle + \sum f_n | \varphi_n \rangle \)

\( (\mathcal{H}_0 + \hat{V}) |\psi(t)\rangle = (\epsilon + \hat{t}) |\psi(t)\rangle \quad \hat{t} = \epsilon \tau_i \)

\[ \sum \langle \chi_n | \mathcal{H}_0 - \epsilon_i | \varphi_n \rangle = 0 \quad \epsilon_i = \epsilon_j + \epsilon_k \]

\[ \sum \langle \chi_n | \mathcal{H}_0 - \epsilon_i | \varphi_n \rangle + \sum \alpha_n | \chi_n \rangle = \epsilon_i \sum \alpha_n | \varphi_n \rangle \]

\[ B_m = \langle \varphi_m | \hat{V} | \varphi_n \rangle = 0 \quad \epsilon_i = 0 \]

\[ d_n = - \sum \frac{\alpha_n | \chi_n \rangle}{n} \]

\[ (\epsilon^2) \]

\[ \epsilon_2 \sum \alpha_n | \varphi_n \rangle = \sum f_n (\mathcal{H}_0 - \epsilon_i) | \varphi_n \rangle + \sum d_n | \chi_n \rangle \]

\[ \langle \varphi_n | B_m = \langle \psi_n | \rho | \varphi_m \rangle = 0 \]

\[ \epsilon_2 \sum \alpha_n = \sum d_n \langle \chi_n | \hat{V} | \chi_m \rangle = - \frac{1}{n} \sum \epsilon_i \langle \chi_n | \hat{V} | \chi_m \rangle \]
\( \text{Effective Low-energy Hamiltonian} \)

\[ H_{\text{eff}} = - \frac{\sum_{ij} t_{ij} c_{i}^{\dagger} c_{j}}{\sqrt{N}} \]

\[ V = - \sum_{i} E_{i} g_{i} c_{i}^{\dagger} c_{i} \]

\[ V_{\text{eff}} = - \sum_{i} (t_{i} g_{i}) c_{i}^{\dagger} c_{i} \]

\[ V_{\text{eff}} = (1 - \frac{3}{\sqrt{5}})(\sum_{i} t_{i} g_{i}) \]

\[ \text{Exercise:} \]

\[ \text{Note:} \quad V \text{ cannot change } \vec{L}^{2} \text{ can - need to push more level.} \]
Note: In case you connect an extra site itself -
(less than \(\lambda\) filling)

\[ H = \Delta \mathbf{S} + U \sum \epsilon_{ij} \mathbf{C}_i^+ \mathbf{C}_j \]

Almost correct - 2nd order term picks up a correction
also

\[ H = \sum_i \epsilon_i \mathbf{S}_i + U \sum_i \mathbf{C}_i^+ \mathbf{C}_i \mathbf{C}_i^+ \mathbf{C}_i \]

\[ \mathbf{S}_i = \sum_{ij} \sum_{\alpha} \left( \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} n_i n_j \right) \mathbf{c}_i^\alpha \mathbf{c}_i^\alpha \mathbf{c}_j^\alpha \mathbf{c}_j^\alpha \]

\[ \mathbf{S}_i = \mathbf{t} \mathbf{C}_i^+ \mathbf{C}_i \]

Slater's split band AF state

\[ \{ SDW \text{ or commensurate} \} \]

At \( \lambda \) filling an insulating state emerges if we break translation invariance

\[ H = - \sum \epsilon_{ij} \mathbf{C}_i^+ \mathbf{C}_j + U \sum n_i \mathbf{c}_i \mathbf{c}_i^\dagger \mathbf{c}_i^\dagger \mathbf{c}_i \]

\[ n_i \mathbf{c}_i^\dagger \mathbf{c}_i = \frac{\sigma}{2} + (-1)^i \frac{m}{2} \]

Gap vanishes as \( m \to 0 \)

\[ \text{Above } T_N \text{ is again a metal} \]

The insulating state fundamentally differs from Mott's.
Mott's insulator need not have LRO -

However, \( \text{split-band AFM has magnon of scale that} \)

\[ \text{if } \lambda \to \lambda \frac{\mathbf{t}^2}{\mathbf{U}} \text{ for } \mathbf{v} >> \mathbf{t} \]
f Superexchange - CF splitting - Transition Metal Oxides
- Direct Exchange (M-M)

H.A. Kramers, P.W. Anderson, Corinna, Kanamori -

NaCl structure & Rocksalt

\[ M^{+}O^{-} \]

<table>
<thead>
<tr>
<th>Metal/ ion</th>
<th>Metal</th>
<th>Metal/Met/ins</th>
<th>AFM/F</th>
<th>Pauli</th>
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<tr>
<td>d^2 d^3 d^4</td>
<td>d^5</td>
<td>d^6 d^7 d^8</td>
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\[ T_n \]

120° 148° 293° 524° K

M - O - M structure

\[ La_2CuO_4 \]

\[ J_n 1000K \]

AFM
Crystal field splitting:

\[ d^1 \quad \{ Ti^{3+} \text{ or } Cu^{2+} \} \text{ in Octahedral Environment} \]

5 fold degeneracy lifted in intuitively clear way

Free space \( SU(2) \)

Octahedral \( a=b=c \)

Tetragonal distortion \( c < a=b \quad c > a \)

Crudely speaking \( V_{CF}(y) = \sum_{\text{near shell}} V(y-R_n) \)

In metals it is less meaningful - these orbitals overlap from bands - often broader than \( V_{CF} \)!
Tetrahedral env: inversion

Here the dry dry dry
orbits extend more towards $O^-$ are higher in energy.

\[
d_{xy} = \left( Y_a + Y_\perp \right) \frac{1}{\sqrt{2}} \\
d_{xz} = Y_0 \\
d_{yz} = \left( Y_a - Y_\perp \right) \frac{1}{\sqrt{2}} \\
d_{xz} = Y_0 + Y_\perp \\
d_{yz} = Y_0 - Y_\perp 
\]

$J \approx \text{Thoms}, U, V_{CF}$ are all 3 operative in a solid.

$d^5, d^6, d^7, d^8$ are more involved

- Querying $J$
- Wide variety of behaviours seen

Some simple: $M_{n^2}$: $d^5$: $S = \frac{5}{2}$ $J = 0$

Some Complex: $Na_xCoO_2$, $Co^{4+} - Co^{2+}$ \(\Delta V \text{ (eff)}\)

Co has low spin behavior:

Clearly $J_{H} < V_{CF}$

J. Karanomi, Pro. Theor. Phys. 17, 172 (57)
J. Chem. Solids 10, 87 (59)
$\delta \text{d}_{2, \alpha} \text{CuO}_4$ 
Superexchange vs. charge transfer $p+q$ view

$\text{Cu}^{2+}$ d$^9$ in tetragonal environment

$U > U_d$

\[ d_{x^2-y^2}, d_{x}^{\dagger}, d_{y}^{\dagger} \]

\[ E_p \quad P_x \quad \sigma \]

\[ \text{Cu} \quad \sigma \quad \text{O}_x \]

Convert to hole picture:

$E_p > E_d$ in the

$V_{dd} = \infty$

\[ E_d \quad \omega \quad \text{O}_y \quad \text{Cu} \]

\[ H = -V_{pd} \sum C_{d_{x}}^{+} p_{d_{x}^{\sigma}} + U_{pp} \sum n_{p_{x}} n_{p_{y}} + V_{dd} \sum n_{d_{x}} n_{d_{y}} \]

\[ + E_p \sum \left( p_{d_{x}^{z}}^{\sigma} p_{d_{x}^{z}}^{\sigma} + p_{d_{y}^{z}}^{\sigma} p_{d_{y}^{z}}^{\sigma} \right) + E_d \sum C_{d_{x}^{\sigma}}^{+} f_{d_{x}^{\sigma}}^{-} \]
Anderson's superexchange viewpoint

First forget U's & form bands

\[ \text{nonbonding} \]

\[ \text{band} \]

\[ \text{1 hole/Cu} \]

\[ V_{pd} = 0 \text{ levels} \]

\[ \text{band} \]

\[ \text{band} \]

5. Effectively 1 band model at \( \frac{1}{2} \) filling. Reunite in Wannier basis - back to Hubbard model \( t-J \)

Wannier states are "sophisticated"

Charge transfer point of view

 Charge transfer pt of view  G. Sawatzky  J. Allen

\[ \text{BDS spectroscopy gives locations of core levels} \]

\[ \text{XPS} \]

\[ \text{Bremsstrahlung, isochromat spectroscopy} \]

\[ \text{Knockout by X-rays} \]

\[ \text{two photon energy} \]

\[ \text{Gap is not U but } (\varepsilon_p - \varepsilon_d) \]

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\[ \text{Start} \rightarrow V_{pd} \rightarrow \text{Finish} \]

- It is a distinction without an essential difference at \% filling.

Does make a difference on Doping - not simple t-J model.

S.S. PRL 63 1288 (1989)

Goodenough-Kanamori-Anderson rules on strength & sign of J

1. 180° Bonds - Strong AFM

\[
\begin{align*}
\text{d}^2_s &- \text{p} - \text{d}_{2z} \\
\text{c}_{3z} &- \text{bonds}
\end{align*}
\]

\[
\text{C}_\text{111}^+ \quad \text{Cu} \quad \text{O}
\]

2. 90° Bonds \text{FeO}_\text{111} \rightarrow \text{AFM}

3. Orthogonal orbitals - FM

\[ \text{La}_2\text{FeCoO}_6 \quad \text{Terakura, PRL 66 104402 (2001)} \]
Double exchange:

Zener, Anderson-Hasegawa

\[ \text{La Mn}_3 \text{O}_3 \rightarrow \text{La}_{1-x} \text{Ca}_x \text{Mn}_{1-x} \text{Mn}_x \text{O}_3 \]

Peroxide

\[ \text{Mn}^{3+} \quad \text{Mn}^{4+} \]

Core forms \( s = \frac{3}{2} \) in both.

\( \text{Mn}^{3+} \) has extra e that can hop.

Consider 2 site problem

\[ H_{2s} = - \sum_{\alpha} \left( c_{\alpha A}^+ c_{\alpha A} + c_{\alpha B}^+ c_{\alpha B} \right) - J(\vec{s}_A \cdot \vec{s}_B + \vec{s}_A \cdot \vec{s}_B) \]

\( J \) in from Hund's rule and is \( > 0 \). If \( J \rightarrow 0 \) the argument still works provided it is so on both sites.

Main point: \( \vec{s}_A \approx \vec{s}_B \) are fairly large: semiclassical.

That hops does so conserving spin it prefers \( s_A \parallel s_B \)
It cannot hop if $\vec{s}_a$ anti parallel to $\vec{s}_b$.

F-M good, AFM bad.

We need to construct $\pm$ spins for local $\pm$ axial along some $\hat{z} = (0, 0, 1)$.

$$\chi^{\pm}_{x, \hat{z}} = \begin{bmatrix} \cos \theta \phi e^{i \phi z} \\ \sin \theta \phi e^{i \phi z} \end{bmatrix} \quad \text{and} \quad \chi^{-}_{x, \hat{z}} = \begin{bmatrix} -\sin \theta \phi e^{i \phi z} \\ \cos \theta \phi e^{i \phi z} \end{bmatrix}$$

$$\chi^+_{x, \hat{z}} \cdot \chi^{-}_{x, \hat{z}} = \delta_{\theta, \phi}$$

$$\langle \frac{\vec{s}}{2} \rangle = \pm \frac{1}{2} \hat{z} \quad \text{can be checked}$$

The hopping $\sum \gamma_{\vec{s}, \vec{s}_o}^{\pm} \vec{c}^\dagger_{\vec{s}, \sigma} \vec{c}_{\vec{s}_o, \sigma}$ is a spin scalar.

$$\text{can also be written as} \quad \sum \gamma_{\vec{s}, \vec{s}_o}^{\pm} \vec{c}^\dagger_{\vec{s}} \cdot \vec{c}_{\vec{s}_o}$$

where $\gamma_{\vec{s}, \vec{s}_o}^{\pm} = \sum_{\sigma} \chi^+_{\sigma, \vec{s}} \cdot \chi^{-}_{\sigma, \vec{s}_o}$

We need to do a simple semiclassical calculation for $\vec{s}_a$ and $\vec{s}_b$ along two directions. Think of $S \gg t$.

$$\langle \uparrow \downarrow \uparrow \downarrow \rangle = t \chi^+_{\uparrow, \vec{h}_b} \cdot \chi^{-}_{\downarrow, \vec{h}_a} = t \left\{ \cos \frac{\theta_1}{2} \cos \frac{\theta_2}{2} \right\}$$

$$= |b_{+4}|^2 \quad \text{Effective Perturbative phase factor!}$$

$$\psi_{\vec{h}} = 2 \tan^{-1} \left\{ \frac{\tan \frac{\theta_2 - \theta_1}{2} \cos (\theta_1 - \theta_2)}{\cos (\theta_1 + \theta_2)} \right\}$$
\[ \langle 1 | T_{12} | 7 \rangle = W_{n1} = W_{12} \cos \left( \frac{\theta_{12}}{2} \right) \]

- Energy of hopping prefers \( \theta_{12} \sim 0 \)

\[ E = - z t \sum \cos \theta_k + N J \sum \frac{z^2}{2} \cos \theta_k \]

- \# neighbors in interlayer terms

\[ x \approx 6, \quad \# = 45 \]

- Minimize

\[ \cos \frac{\theta}{2} = \frac{t x}{4 J z} \]

- Changes with \( x \)

\[ \text{C-M-R - an industrial scale effort - other lectures} \]

\[ \text{small things matter:} \]

- A typical Hamiltonian looks like

\[ H = \frac{1}{2} \sum \langle \downarrow \rangle J_{g} \vec{S}_{x} \cdot \vec{S}_{y} \]

- \[ - \frac{\mu B}{2} \sum \vec{S}_{x} \cdot \mathbf{B} \]

- \[ - \frac{1}{2} \sum \langle \downarrow \rangle \]

- \[ \frac{1}{2} \sum \left\{ \frac{\vec{S}_{x} \cdot \vec{S}_{y}}{\langle \uparrow \rangle} - \frac{3 (\vec{S}_{x} \cdot \vec{r}_{y}) (\vec{S}_{y} \cdot \vec{r}_{y})}{\langle \uparrow \rangle} \right\} \]

- \[ \mu_B = e h \]
Two "culprits" - dipole - dipole
spin-orbit coupling

6 Dipole - D. pole x ion

In purely cubic systems, if $J$ is very small - interesting
and novel physics - Gd$_2$Ti$_2$O$_7$ on pyrochlore as an example.
Usually $J$ is very big or lattice distort.

$< > \rightarrow - D s^2$ type for MnF$_2$ from intersite x

$< > - \frac{1}{2} (\bar{E}, \bar{s})^2$ on one site

+ $0 (s^2)$

6 spin-orbit coupling

4 Influence on g factor - uniaxial systems C > a > b

Again Cu$^{2+}$

$H = d_x^2 - d_y^2$  $\varepsilon_1$  $\delta_1$

$\# 1.  \varepsilon_1 \rightarrow \varepsilon_2$

Single site

$H = \mu_0 \bar{H} \bar{S} - \mu_0 \bar{H} \bar{L}$
In absence of $\lambda$ we have a state $\phi_i \chi_{\sigma, 0}$ $i = \pm 1$.

Perturbation in $\lambda$ yields a spin-orbit doublet (Kramers' theorem)

$$\Psi_{\pm} = \phi_{\pm} \chi_{\pm} + \sum_{\nu \neq \pm} \frac{1}{\varepsilon_{\nu} - \varepsilon_{\pm}} \phi_{\nu} \chi_{\nu}, \langle \phi_{\nu} \chi_{\nu} | \frac{\lambda}{\varepsilon_{\nu} - \varepsilon_{\pm}} | \phi_{\pm} \chi_{\pm} \rangle$$

Depending on $\sigma$, we can find non-vanishing matrix elements.

$\Psi_{\pm}$ are not "pure spin projection".

$$\widetilde{H} = H (\cos \theta, 0, \sin \theta)$$

$$\langle \Psi_{\pm} | \widetilde{H} \text{Kramers} | \Psi_{\pm} \rangle \in 2 \times 2 \text{ matrix}$$

$$\varepsilon = \pm \frac{\mu B H}{2} \sqrt{g_{1z}^2 \omega^2 + g_{1z}^2 \omega^2}$$

$$g_{1z} = 2 \left\{ 1 + \frac{2}{\varepsilon_{\nu} - \varepsilon_{\pm}} \right\} \quad g_{11} = 2 \left\{ 1 + \frac{4 \lambda}{\varepsilon_{3} - \varepsilon_{1}} \right\}$$

$$\Delta^2 \sim \lambda$$
\[ H' = + \lambda (\bar{L}_a \cdot \bar{S}_a + \bar{L}_b \cdot \bar{S}_b) - \tau_{ab} (c_{ao}^+ c_{ao} + c_{bo}^+ c_{bo}) \]
\[ + U \sum \int \nu \psi \left( \psi \mid \sum \lambda \nu \right) I \]
we transform to Kramers doubling at \( a \) and \( b \)

\[ \psi' = \bar{\phi} \chi' + \lambda \bar{\phi} \chi' + \mu \phi \chi' \]

\[ T = - \left( \tau_{oo} \chi' \chi' + \tau_{bb} \chi' \chi' + \tau_{aa} \chi' \chi' + \tau_{ab} \chi' \chi' \right) + h.c. + U \sum (n_{ao} n_{bo} + n_{ao} n_{bo}) \]

\[ \psi_{ab} = \int \psi' \left[ \int \chi' \left( \nu_0 + g \nu \right) \chi' \right] \psi_{bo} \]

\[ \tau_{oa} = \frac{1}{2} (\tau_{oo} + \tau_{bb}) \quad C_{ab} = \frac{1}{2} (\tau_{oo} - \tau_{bb}) \]

\[ C_{ao}^+ = k_{ao}^+ \quad C_{bo}^+ = k_{bo}^+ \]

\[ C_{ab}^+ = k_{ab}^+ \quad C_{ba}^+ = k_{ba}^+ \]

\( C_a^+ \) and \( C_b^+ \) are pure imaginary
(\( L \) is imaginary operator of Brillouin zone)

\[ \mathbf{T}_0 = - \tau_{oa} \Sigma C_{ao}^+ C_{bo}^+ + \tau_{ab} \Sigma C_{ao}^+ C_{bo} \rightarrow \mathbf{T}_1 \]
\[ H_{\text{eff}} = -\frac{1}{U} \cdot (T_0 + T_1) \cdot \langle T_0 + T_1 \rangle \]

\[ = H_{\text{Heff}} - \frac{1}{U} \left\{ T_0 \cdot \langle T_1 \rangle + T_1 \cdot \langle T_0 \rangle \right\} + O(\lambda^3) \]

\[ = H_{\text{Heff}} + H_{\text{OM}} \]

\[ H_{\text{OM}} = \frac{4i}{U} \sum \left( \mathbf{t}_{ab} \mathbf{C}_{ab} - \mathbf{t}_{ba} \mathbf{C}_{ba} \right) \cdot \mathbf{s}_a \times \mathbf{s}_b \]

\[ = \sum_{\langle \delta \rangle} D_{ab} \cdot \mathbf{s}_a \times \mathbf{s}_b \]

- \[ D_{ab} \neq 0 \text{ if } \exists \text{ inversion point between } A \& B \]

\[ D \rightarrow \text{ high } T_c \]

\[ \frac{D}{T} \sim \left( \frac{\Delta g}{g} \right) \]

This is experimentally a good rule of thumb.

- D direction \[ \begin{array}{ccc} a & b & D \text{ lies in mirror plane} \\ \text{16 on } a \end{array} \]