MAGNETISM IN MATERIALS

Lecture 4: Interactions

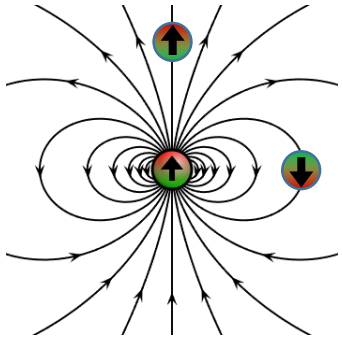
Ivica Zivkovic

11.03.2025

EPFL

- dipole-dipole
- (direct) exchange
- GKA rules
- double exchange
- Dzyaloshinskii-Moriya interaction

- long-range
- it can act both FM and AFM



$$E = \frac{\mu_0}{4\pi}\left[\frac{\vec{\mu}_1\vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1\vec{r})(\vec{\mu}_2\vec{r})}{r^5}\right] \approx \frac{\mu_0}{4\pi}\frac{\mu^2}{r^3} \xrightarrow{\mu=\mu_B, r=1\text{Å}} 10^{-23}J \approx 1K$$

- typical distances in materials are 2-3 Å
- at those distances exchange interactions are (usually) significantly stronger

image source: wikimedia.org

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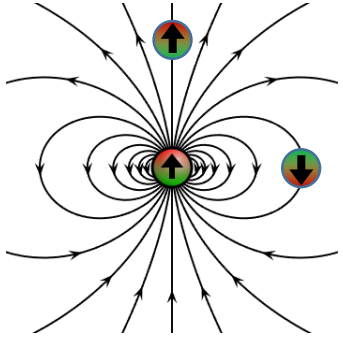
- it can act both FM and AFM



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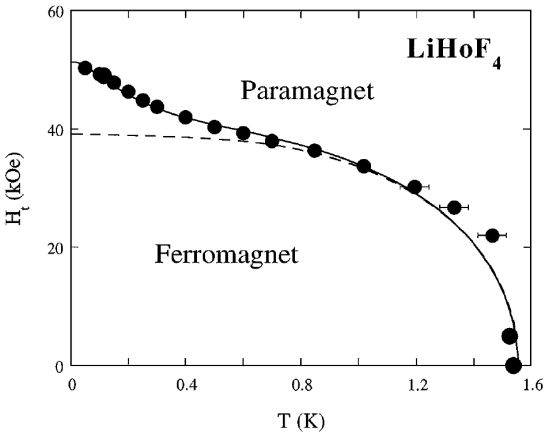
PRL 77, 940 (1996)

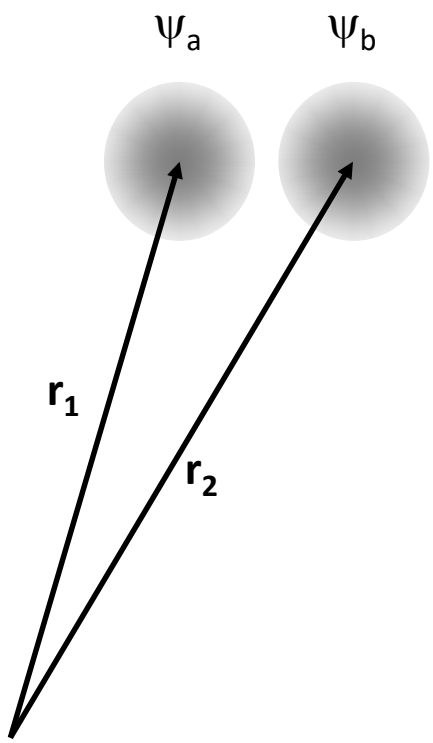


$$H = \sum_{i,j}^{N} J_{ij}\sigma_i^z\sigma_j^z - \Gamma\sum_{i}^{N}\sigma_i^x$$

- *RE* = Ho (*c*-axis anisotropy) a ferromagnet with Tc=1.5K
- *RE* = Er (*ab*-plane anisotropy) an antiferromagnet with Tc=0.38K
- transverse field induced QPT

image source: wikimedia.org

- (very) short-range
- 'side-effect' of electro-static interactions



$$\Psi_e = \Psi_{spatial}\Psi_{spin}$$

spatial part	spin part	
$\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\,\psi_b(\vec{r}_1)$	singlet (antisymmetric)	$\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle$
$\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\,\psi_b(\vec{r}_1)$	triplet (symmetric)	$\lvert\uparrow\downarrow\rangle + \lvert\downarrow\uparrow\rangle, \lvert\uparrow\uparrow\rangle, \lvert\downarrow\downarrow\rangle$

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\,\psi_b(\vec{r}_1)]\psi_{singlet} \qquad E_1 = \int \Psi_1^* \hat{\mathcal{H}} \Psi_1 d\vec{r}_1 d\vec{r}_2$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\,\psi_b(\vec{r}_1)]\psi_{triplet} \qquad E_2 = \int \Psi_2^* \hat{\mathcal{H}} \Psi_2 d\vec{r}_1 d\vec{r}_2$$

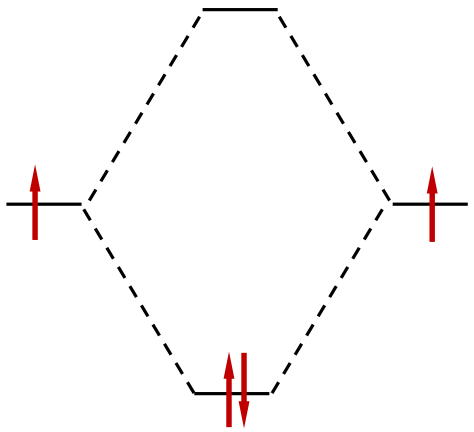
- without knowing E_1 and E_2, rewrite the Hamiltonian

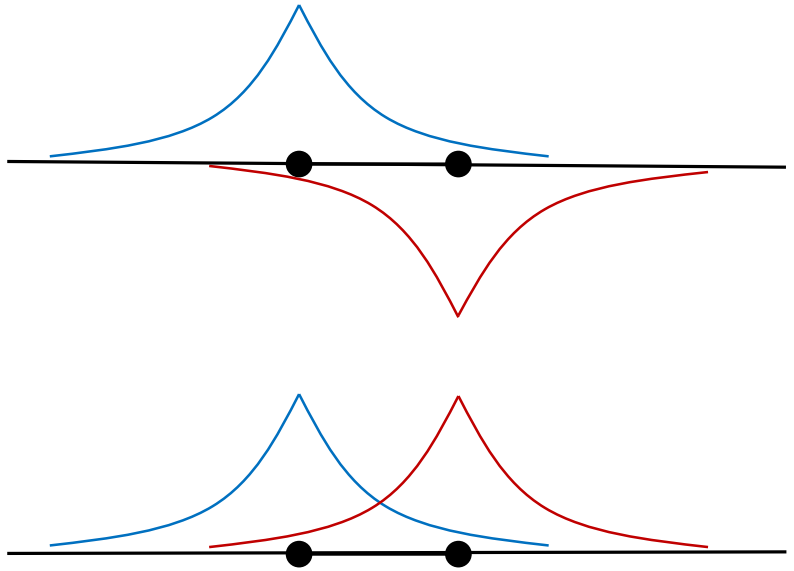
$$\hat{\mathcal{H}} = \frac{1}{4}(E_1 + 3E_2) - (E_1 - E_2)\boldsymbol{S^a S^b} \longrightarrow \hat{\mathcal{H}} = -J\boldsymbol{S^a S^b} \longrightarrow \hat{\mathcal{H}} = -\sum_{i,j} J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j$$

	s^{tot}	$s^{tot}(s^{tot}+1)$	E	m_s
(↑)(↓)	0	0	-3J/4	0
(↑)(↑)	1	2	J/4	-1,0,1

$$J = \int \psi_a^*(\vec{r}_1)\psi_b^*(\vec{r}_2)\hat{\mathcal{H}}\,\psi_a(\vec{r}_2)\psi_b(\vec{r}_1)d\vec{r}_1 d\vec{r}_2$$

❖ two atoms (H_2) → 'bounding box', kinetic energy ~ L^{-2}

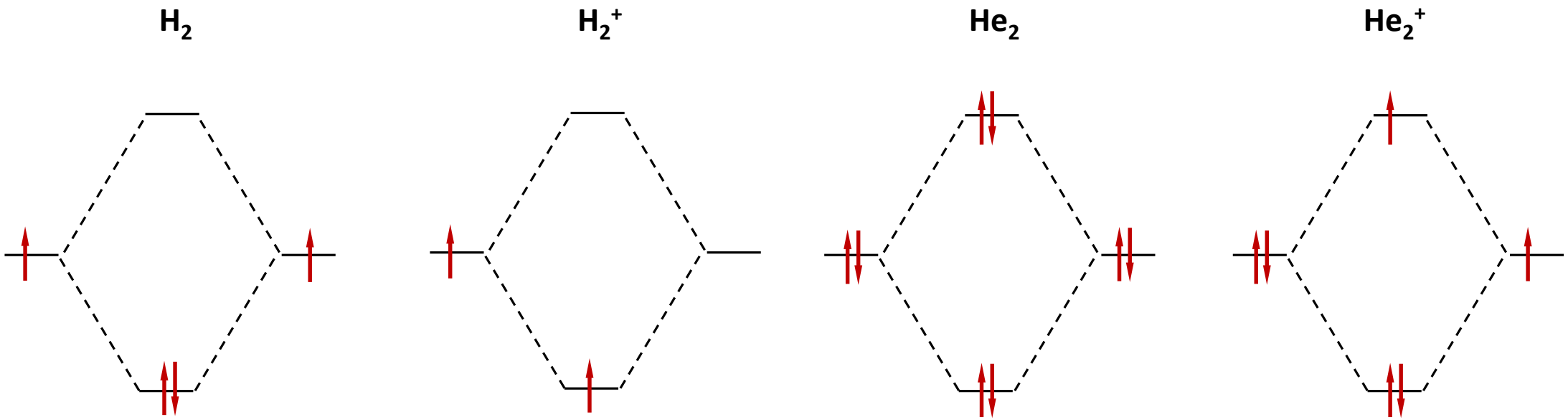




antibonding

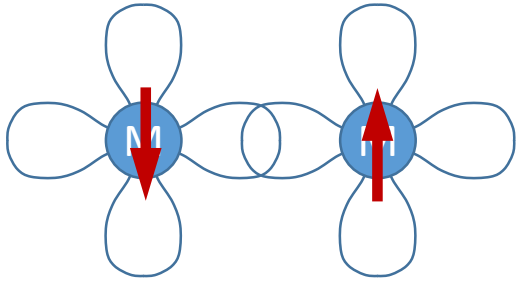
bonding

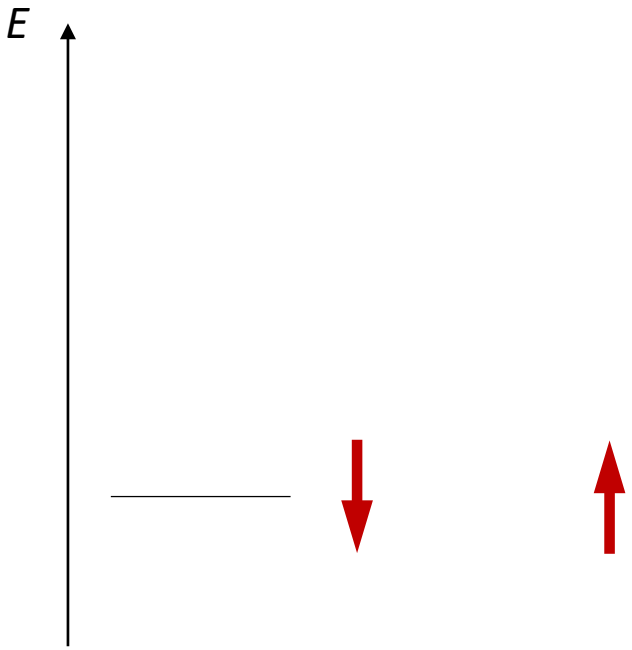
❖ two atoms (H_2) → 'bounding box', kinetic energy ~ L^{-2}



- the number of interacting atoms = 10^{23} → valence and conduction bands!
- predictions for metallic hydrogen (p > 400 GPa), no magnetism
- some 3*d* transition metal elements do show magnetic phases in elemental form (band structure!)

1. GKA rule (AFM, equivalent orbitals, half full)





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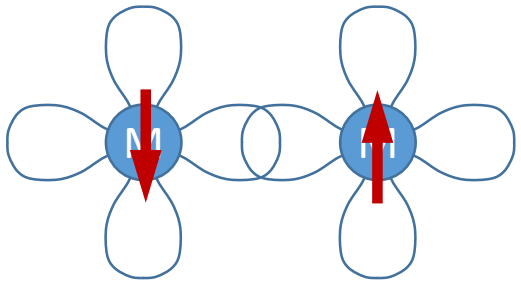

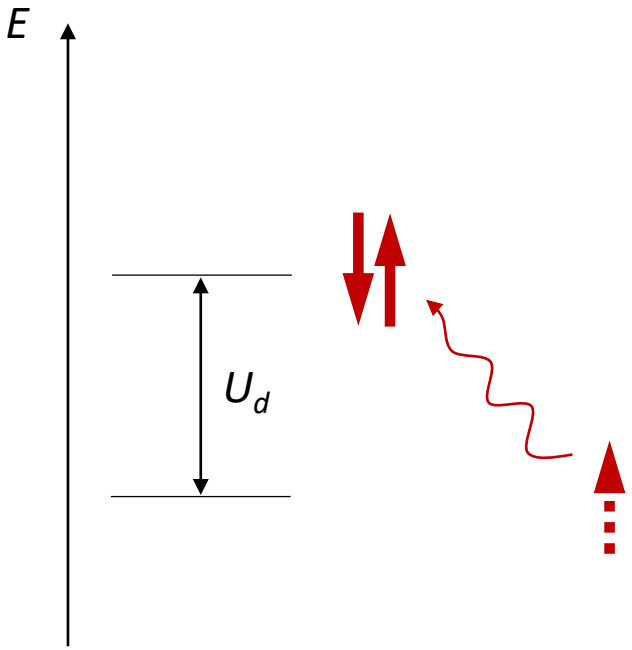

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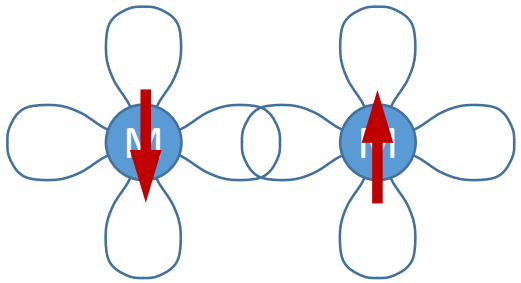

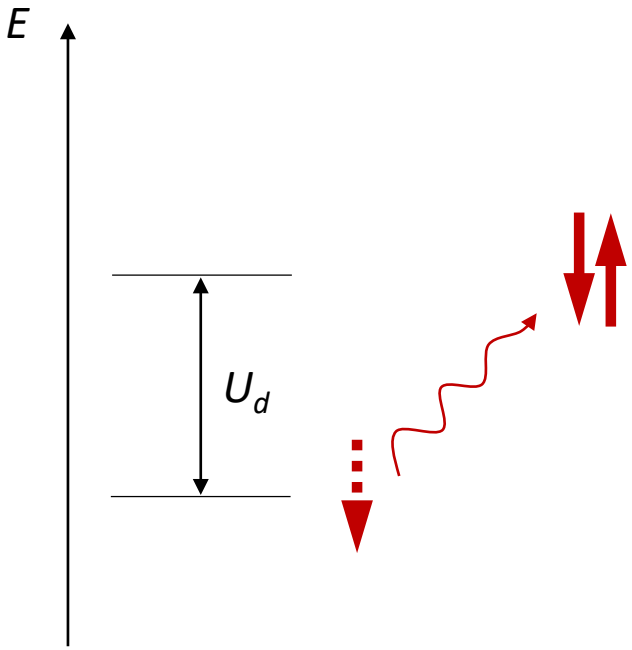

$$E^{(2)} = \frac{\left|\left\langle \psi_{GS}^{(0)} | H' | \psi_{exc}^{(0)} \right\rangle\right|^2}{E_{exc}^{(0)} - E_{GS}^{(0)}} = \frac{t^2}{U} = J_{AFM}$$

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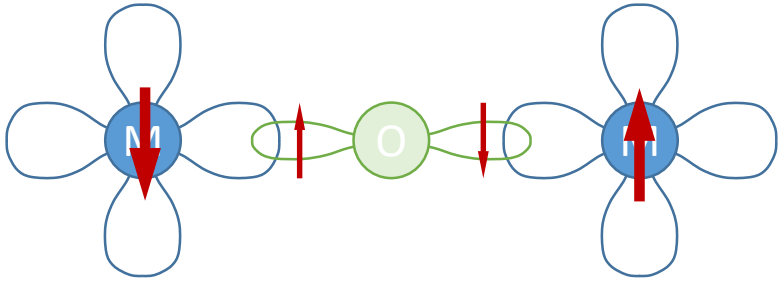

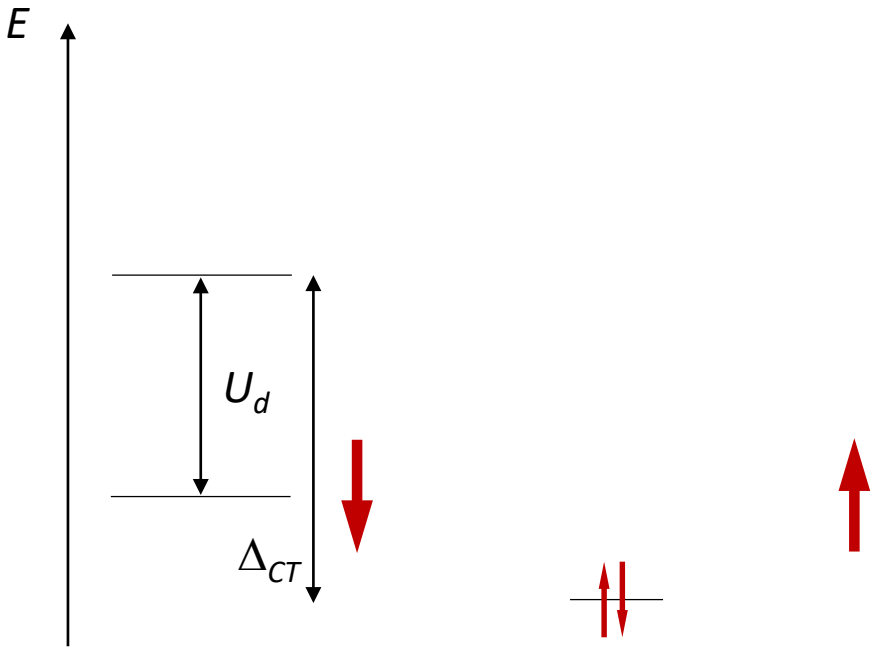

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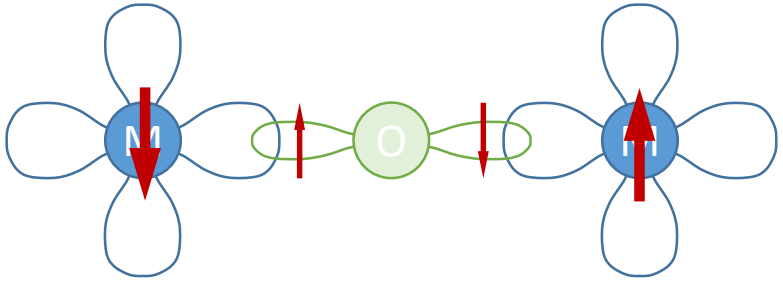

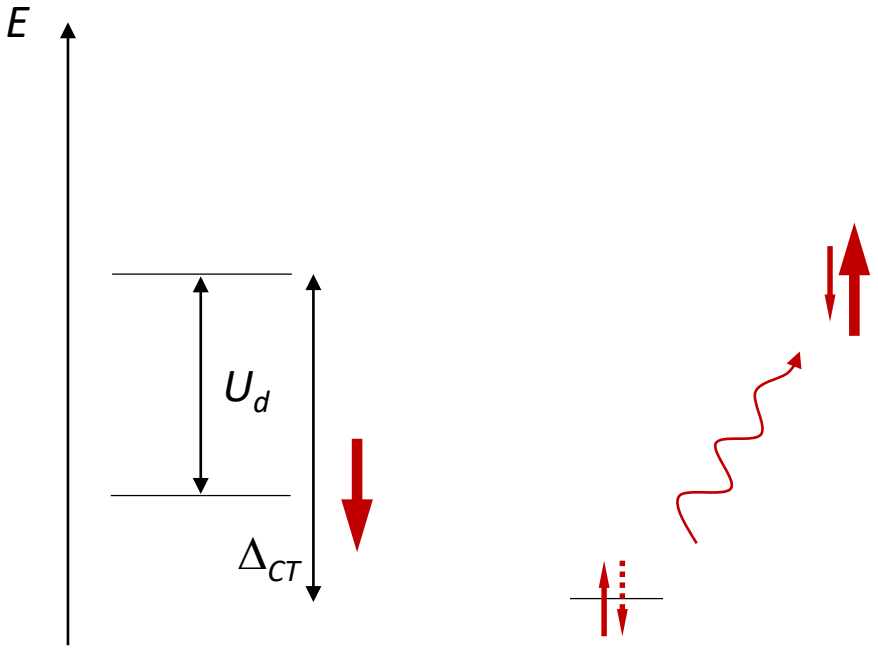

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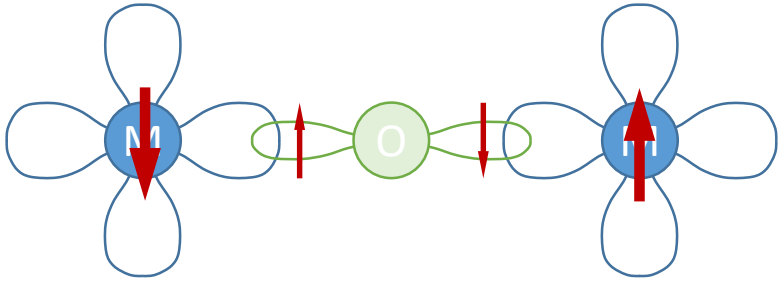

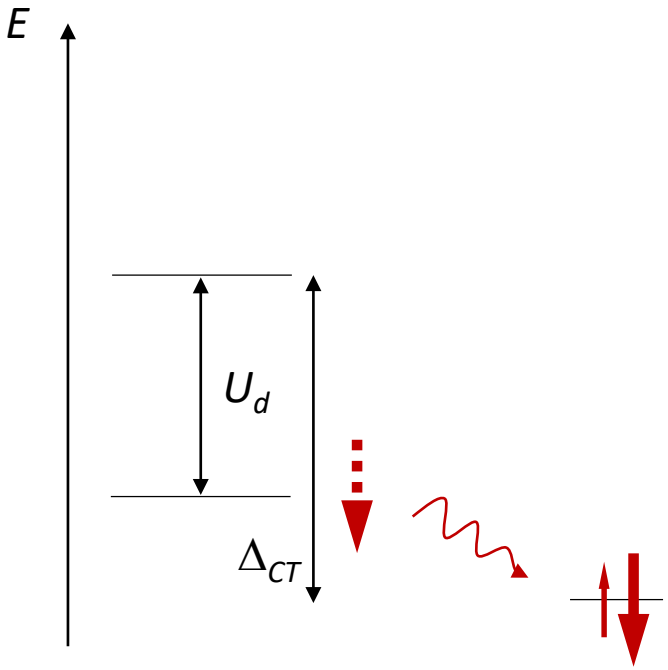

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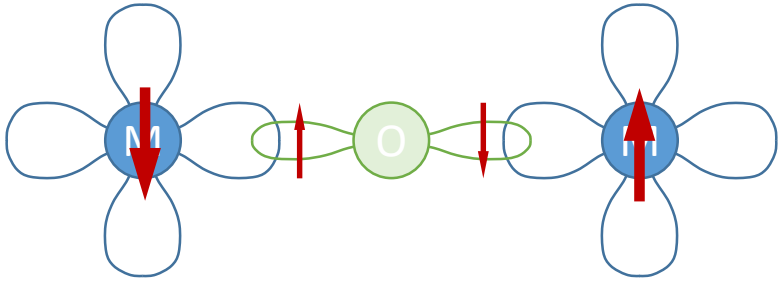

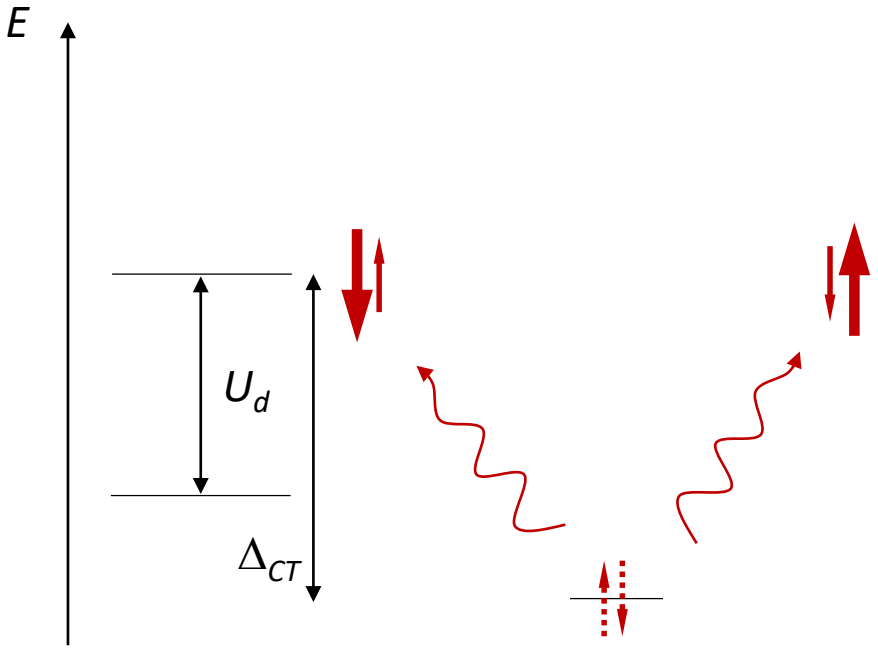

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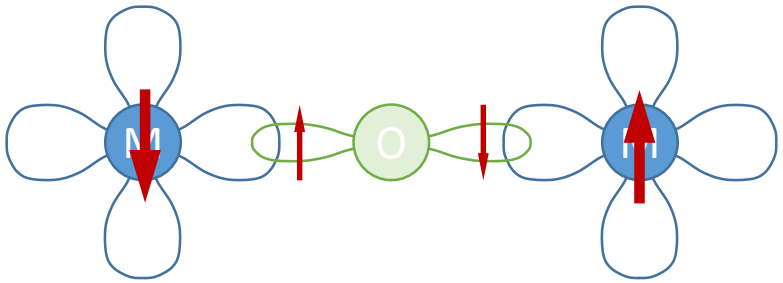
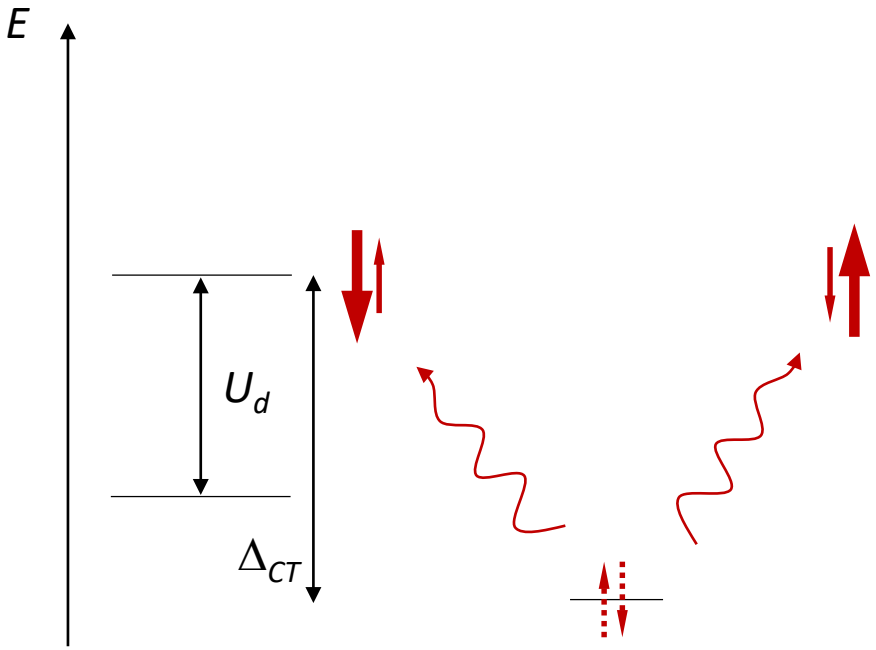




semi-covalent exchange

$$J_{AFM} = \frac{2t_{pd}^4}{\Delta_{CT}^2}\left(\frac{1}{U_d} + \frac{1}{\Delta_{CT} + \frac{1}{2}U_p}\right)$$

Mott-Hubbard regime

$U_d \ll \Delta_{CT}$

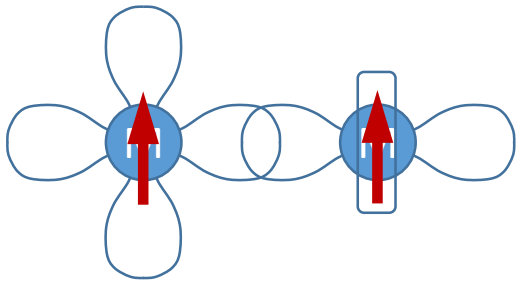
$$J_{AFM} = \frac{2t_{dd}^2}{U_d} \qquad t_{dd} = \frac{t_{pd}^2}{\Delta_{CT}}$$

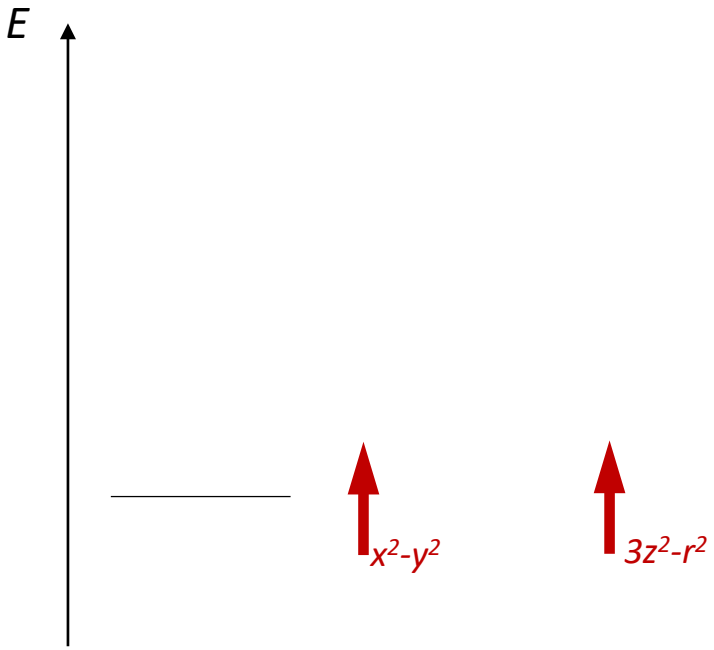
super-exchange

$t_{pd} \ll \Delta_{CT}$

insulators

2. GKA rule (FM, orthogonal orbitals, half full)





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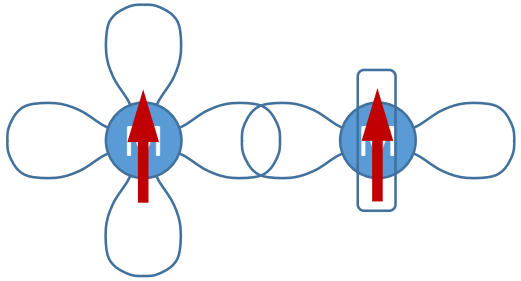

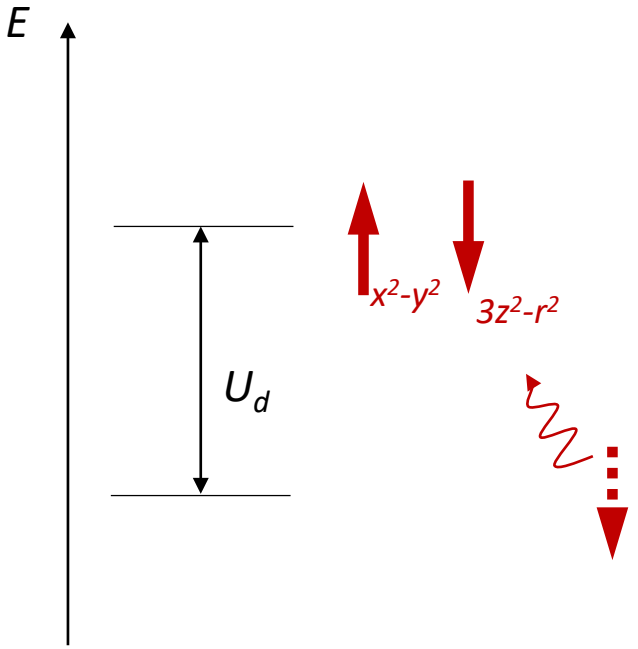

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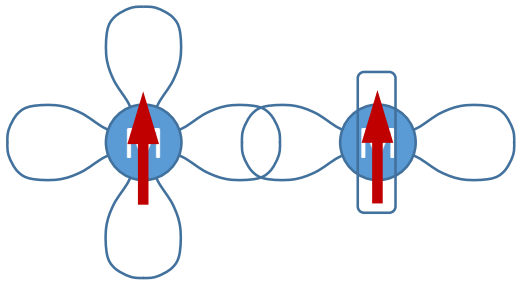
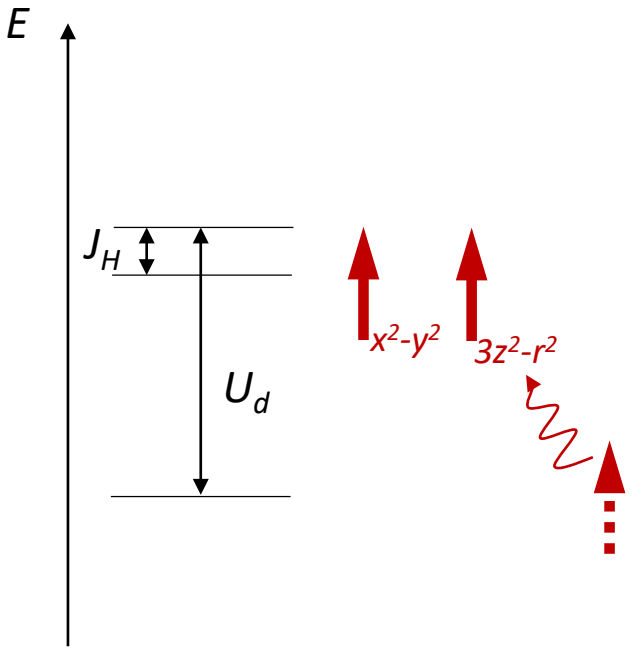


$$J_{FM} = -t_{dd}^2 \left(\frac{1}{U_d - J_H} - \frac{1}{U_d} \right) \xrightarrow{J_H < U_d} - \frac{t_{dd}^2}{U_d} \frac{J_H}{U_d}$$



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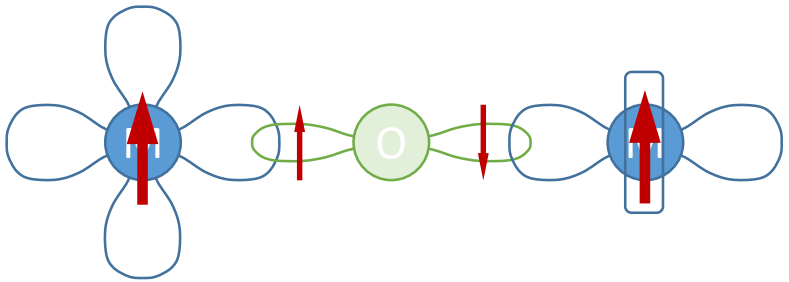

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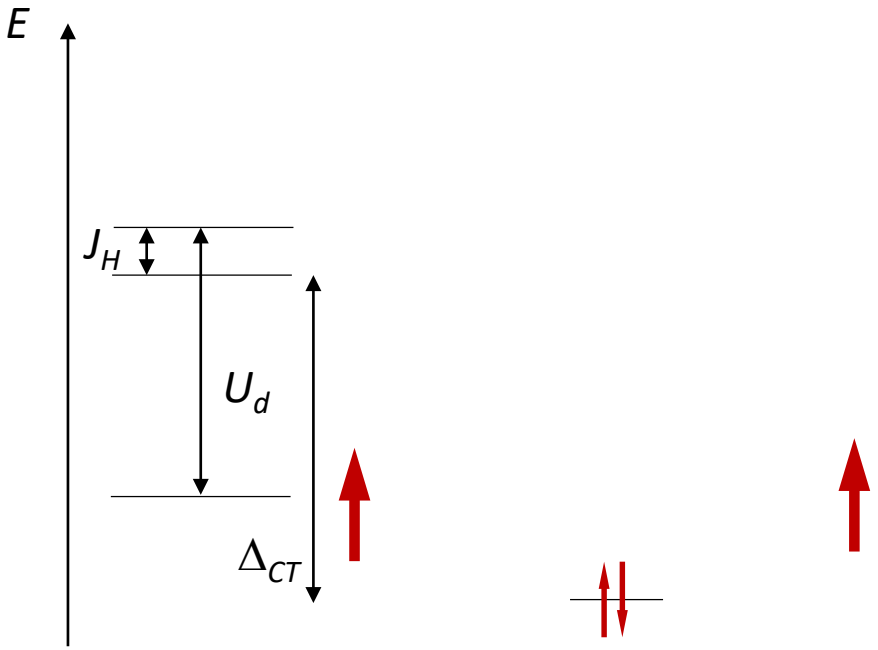
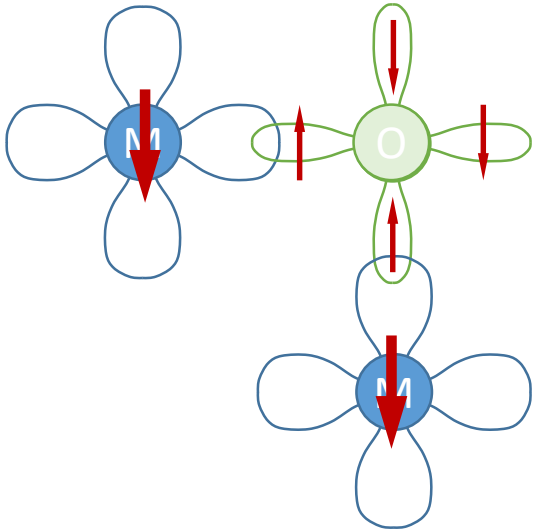
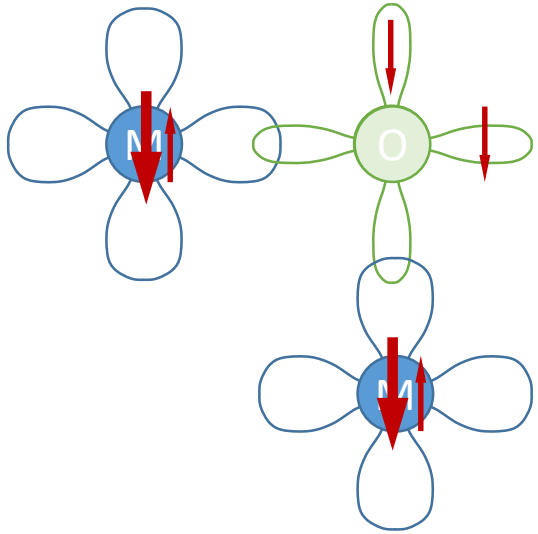
$$\Downarrow$$

$$t_{dd} = \frac{t_{pd}^2}{\Delta_{CT}}$$



3. GKA rule (FM, orthogonal *p*-orbitals, half full)

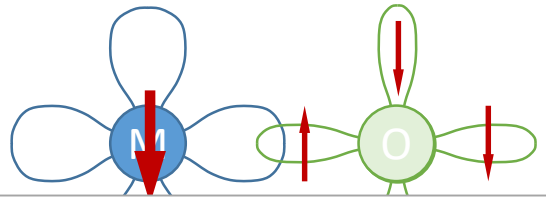


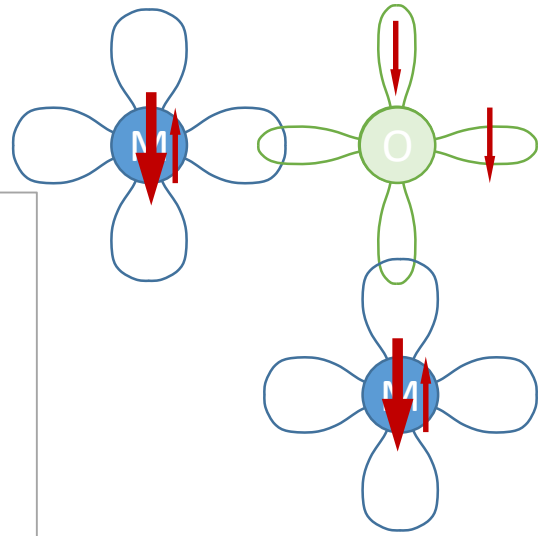


$$J_{FM} = -\frac{t_{dd}^2}{\Delta_{CT} + \frac{1}{2}U_p}\frac{J_H^p}{\Delta_{CT}}$$

❖ a crossover from FM to AFM for angles 95-100deg

3. GKA rule (FM, orthogonal *p*-orbitals, half full)





Inorganic Chemistry

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Antiferromagnetic to Ferromagnetic Coupling Crossover in Hybrid Nickel Chain Perovskites

Teresa Lee, Daniel B. Straus, Kasey P. Devlin, Xin Gui, Pria Louka, Weiwei Xie, and Robert J. Cava*

Cite This: *Inorg. Chem.* 2022, 61, 10486–10492 Read Online

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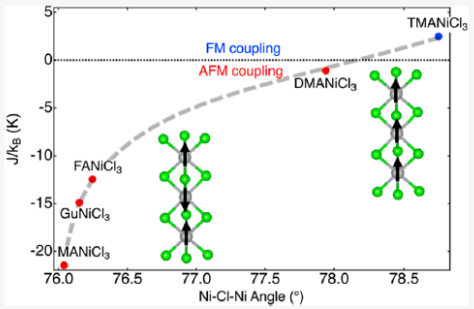
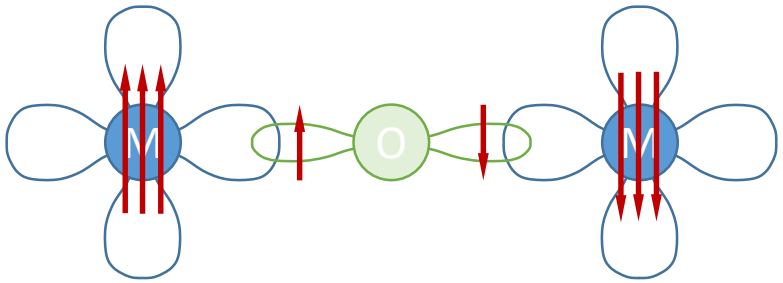
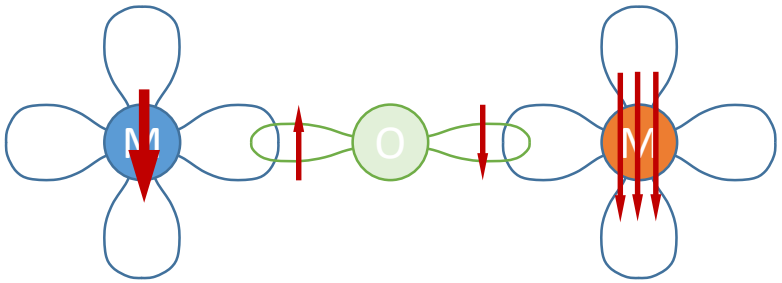
ABSTRACT: We synthesize and characterize the magnetic and thermodynamic properties of the quasi one-dimensional organic–inorganic hybrid $ANiCl_3$ compounds [A = $N(CH_3)_4^+$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $C(NH_2)_3^+$, and $CH(NH_2)_2^+$]. Additionally, the crystal structure of $(CH_3)_2NH_2NiCl_3$ is reported. These materials possess chains of face-sharing $NiCl_6$ octahedra in a triangular array. The chains run in one direction and are separated from one another by organic cations of different sizes and geometries. In accordance with the 90° superexchange model, we find that the nature of the magnetic coupling within chains can be predicted by the value of the Ni–Cl–Ni angle. As the Ni–Cl–Ni angle decreases from 90°, the magnetic interactions become increasingly antiferromagnetic. These findings provide a foundation for predicting the magnetic properties of quasi one-dimensional organic–inorganic hybrid $ANiCl_3$ compounds.



$$J_{FM} = -\frac{t_{dd}^2}{\Delta_{CT} + \frac{1}{2}U_p}\frac{J_H^p}{\Delta_{CT}}$$

❖ a crossover from FM to AFM for angles 95-100deg


M
O
M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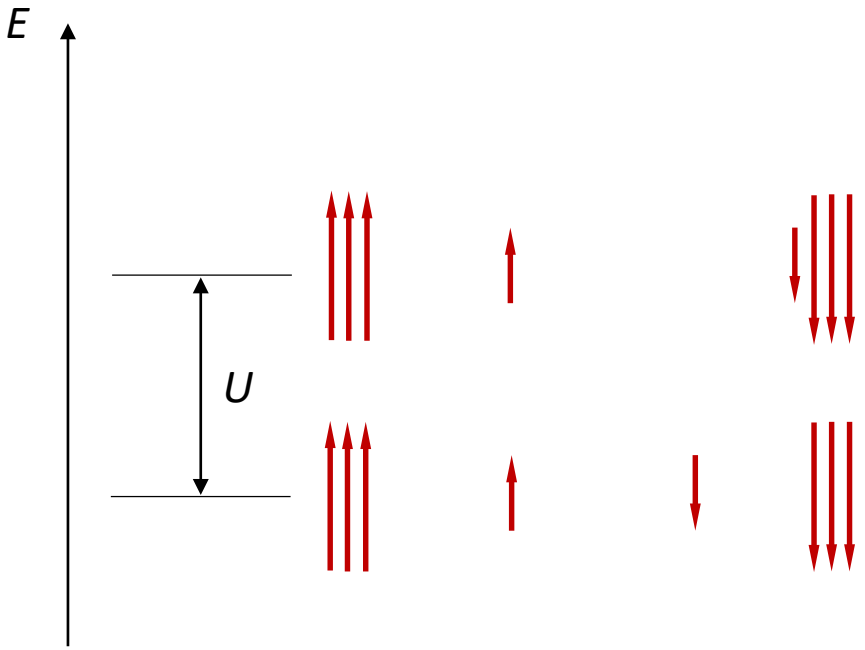
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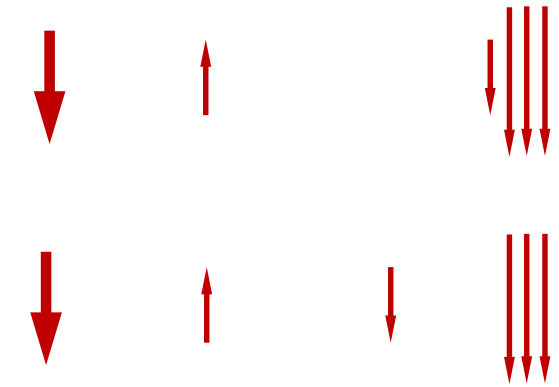
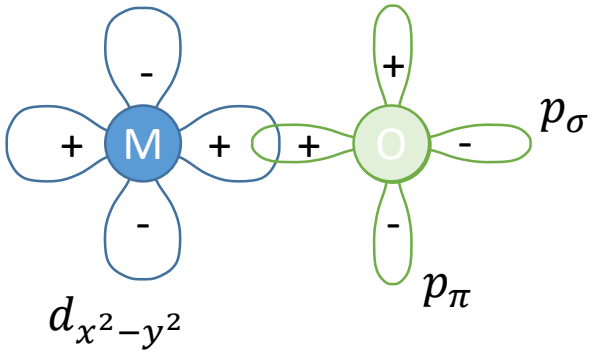
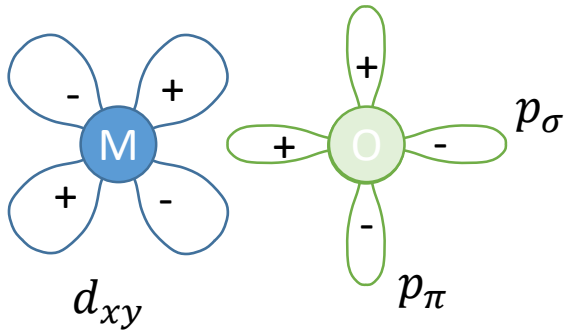


❖ symmetries of respective orbitals



$$\int \Psi^*_{d_{x^2-y^2}} \Psi_{p_\sigma} dV \neq 0$$

$$\int \Psi^*_{d_{x^2-y^2}} \Psi_{p_\pi} dV = 0$$



$$\int \Psi^*_{d_{xy}} \Psi_{p_\sigma} dV = 0$$

$$\int \Psi^*_{d_{xy}} \Psi_{p_\pi} dV \neq 0$$

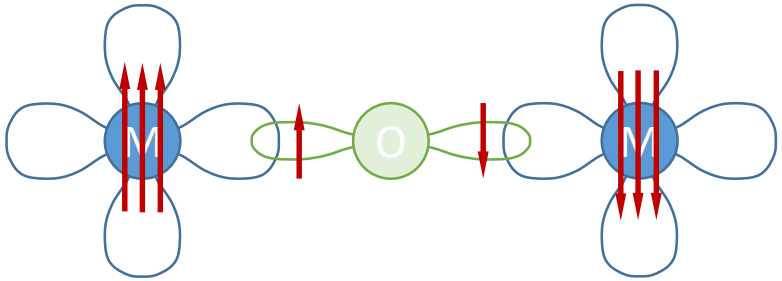
❖ *s-p* hybridization

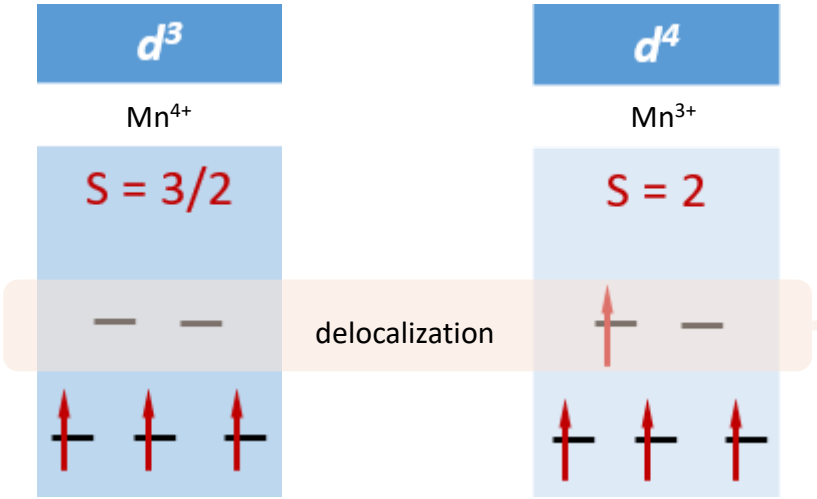
❖ JT effect

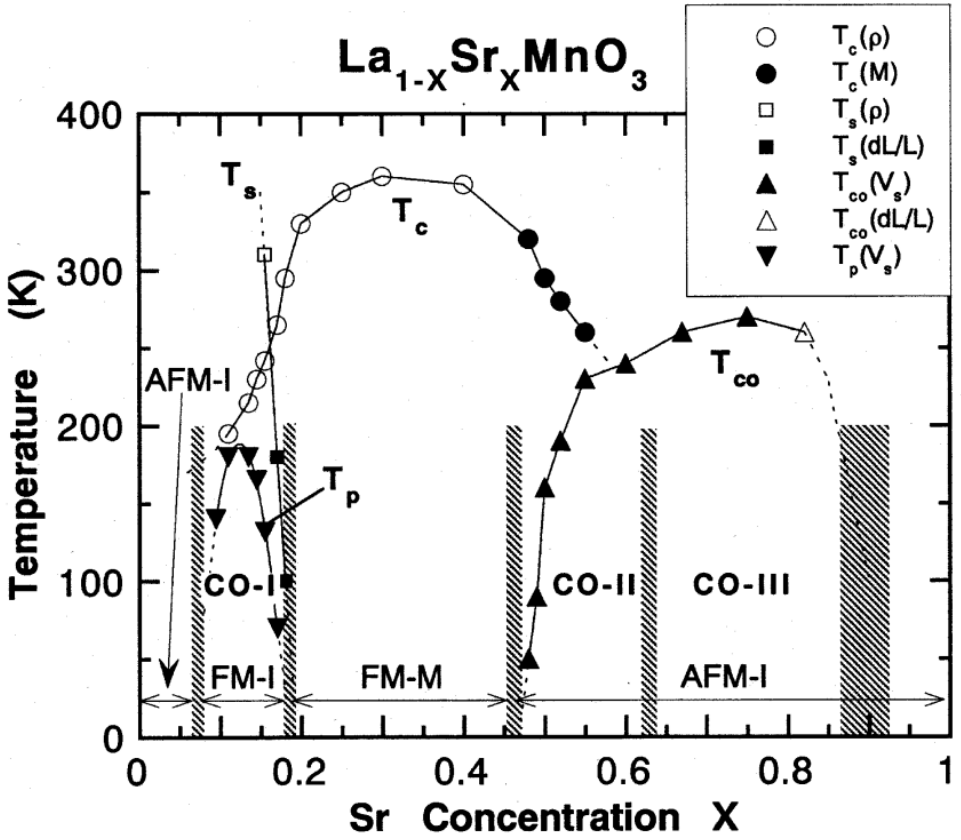
❖ 180deg is always AFM

❖ for smaller angles every path/integral contributes individually → DFT

❖ FM coupling due to mixed valences







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not just the nearest neighbor → metallicity

$$\mathcal{H}_{ij} = \boldsymbol{S}_i \cdot \bar{\bar{J}} \cdot \boldsymbol{S}_j = \sum_{\alpha\beta} S_{i\alpha} J_{\alpha\beta} S_{j\beta}$$

$$\mathcal{H} = \sum_{ij} J_{\parallel} S_i^z S_j^z + J_{\perp}(S_i^x S_j^x + S_i^y S_j^y)$$

$$J_{\parallel} \neq J_{\perp}$$

anisotropic

$$\mathcal{H}_{ij} = \boldsymbol{S}_i \cdot \bar{\bar{J}} \cdot \boldsymbol{S}_j = \sum_{\alpha\beta} S_{i\alpha} J_{\alpha\beta} S_{j\beta}$$

off-diagonal

$$D_\alpha = \sum_{\beta\gamma} \varepsilon_{\alpha\beta\gamma} J_{\beta\gamma}$$

$$\mathcal{H}_{ij}^{DM} = \boldsymbol{D}_{ij} \cdot (\boldsymbol{S}_i \times \boldsymbol{S_j})$$

antisymmetric

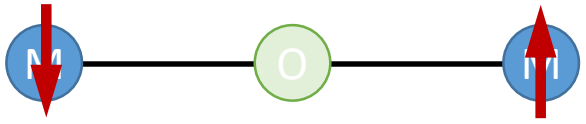
symmetric

$$\mathcal{H} = \sum_{ij} J_\parallel S_i^z S_j^z + J_\perp (S_i^x S_j^x + S_i^y S_j^y)$$

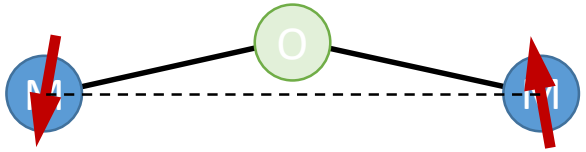
$$J_\parallel \neq J_\perp$$

anisotropic

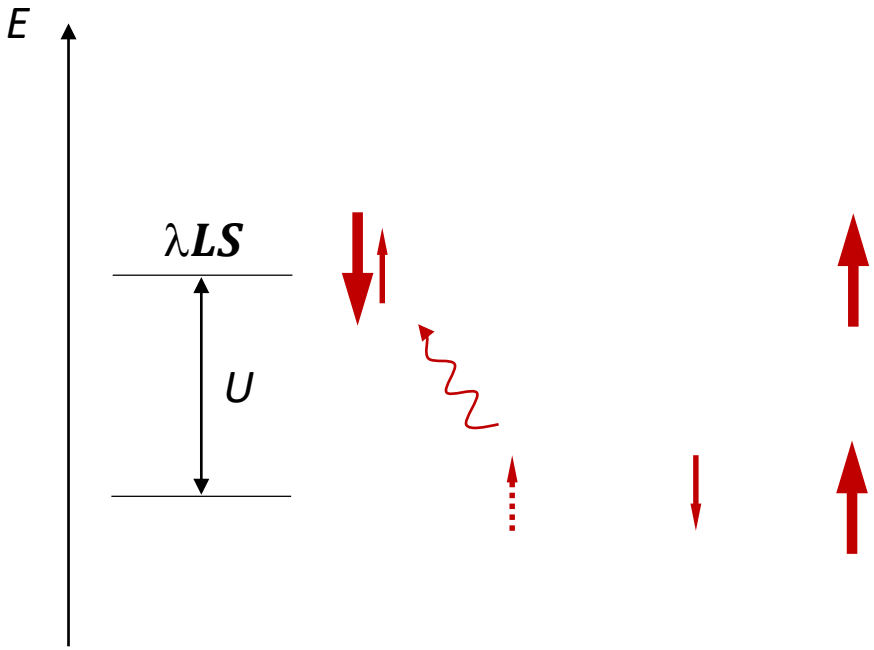
- often called Dzyaloshinskii-Moriya interaction (DMI)



$$\hat{\mathrm{H}} = -J\boldsymbol{S^a S^b}$$



$$\hat{\mathrm{H}} = -J\boldsymbol{S^a S^b} + \underbrace{\boldsymbol{D}(\boldsymbol{S^a} \times \boldsymbol{S^b})}$$

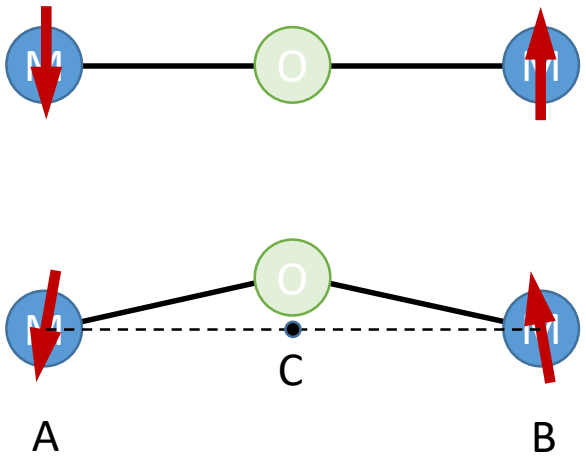


$$E^{(2)} = \frac{\left\langle \psi^{(0)}_{GS|a} | \lambda \boldsymbol{L^a S^a} | \psi^{(0)}_{exc|a} \right\rangle J_{(GS|a)(exc|a)(GS|b)(GS|b)} \boldsymbol{S^a S^b}}{E^{(0)}_{exc} - E^{(0)}_{GS}} +$$

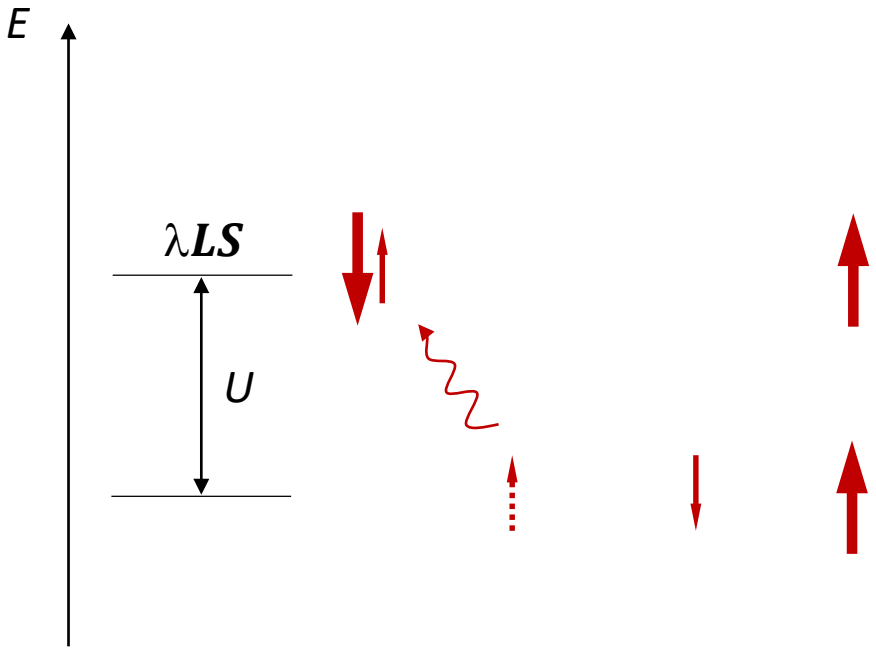
$$+ \frac{J_{(GS|a)(exc|a)(GS|b)(GS|b)} \boldsymbol{S^a S^b} \left\langle \psi^{(0)}_{exc|a} | \lambda \boldsymbol{L^a S^a} | \psi^{(0)}_{GS|a} \right\rangle}{E^{(0)}_{exc} - E^{(0)}_{GS}} + \cdots$$

non-degenerate ground state & $\boldsymbol{L}$ is purely imaginary

- often called Dzyaloshinskii-Moriya interaction (DMI)



$$\boldsymbol{D}_{ij} = 2i\lambda \sum_{m,m'} \left[\frac{J(nn'mn')}{E_n - E_m} \langle n|\mathbf{L_i}|m\rangle - \frac{J(nn'nm')}{E_{n'} - E_{m'}} \langle n'|\mathbf{L_j}|m'\rangle \right]$$



1) When a center of inversion exists, $\boldsymbol{D} = 0$
2) When a mirror plane perpendicular to *AB* passes through *C*, *D* || mirror plane or $D \perp AB$
3) When there is a mirror plane including *A* and *B*, $D \perp$ mirror plane
4) When a 2-fold rotation axis perpendicular to *AB* passes through *C*, $D \perp$ 2-fold axis
5) When there is an *n*-fold axis ($n \geq 2$) along *AB*, $D \parallel AB$