

## § 6. Quantum magnetism

### \* Super-exchange and Heisenberg models

Single-band Hubbard model:

$$H = -t \sum_{\langle i,j \rangle} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$\downarrow$

$U \gg t$ , half filling  
( $N_e = N$ )

$$H_{\text{eff}} = J \sum_{\langle i,j \rangle} \vec{s}_i \cdot \vec{s}_j$$

single site:  $S=1/2$        $\uparrow$        $\downarrow$

Antiferromagnetic super-exchange interaction:  $J = \frac{4t^2}{U} > 0$

- Heisenberg interaction for two sites with  $S=1/2$ :

$$H = J \vec{s}_1 \cdot \vec{s}_2$$

$$= \frac{J}{2} \left[ (\vec{s}_1 + \vec{s}_2)^2 - \vec{s}_1^2 - \vec{s}_2^2 \right]$$

$$\vec{s}^2 = (\vec{s}_1 + \vec{s}_2)^2$$

$$\vec{s}_1^2 = \vec{s}_2^2 = S(S+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$$

total spin:  $1/2 \times 1/2 \rightarrow 0 + 1$

$$= \frac{J}{2} \left( \vec{s}^2 - \frac{3}{2} \right)$$

$$\hookrightarrow S_{\text{tot}}(S_{\text{tot}}+1), S_{\text{tot}} = 0 \text{ or } 1$$

$$\Rightarrow E = \begin{cases} -\frac{3}{4}J, & S_{\text{tot}}=0 \\ \frac{1}{4}J, & S_{\text{tot}}=1 \end{cases}$$

Energy splitting:  $J$

Ground state for  $J > 0$ :  $S_{\text{tot}} = 0$  (antiferromagnetic)

$$|S\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)$$

AFM

singlet

$$H|S\rangle = -\frac{3}{4}J|S\rangle$$

Ground state for  $J < 0$ :  $S_{\text{tot}} = 1$  (ferromagnetic)

$$|t_+\rangle = |\uparrow\rangle_1|\uparrow\rangle_2$$

FM

$$|t_0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2)$$

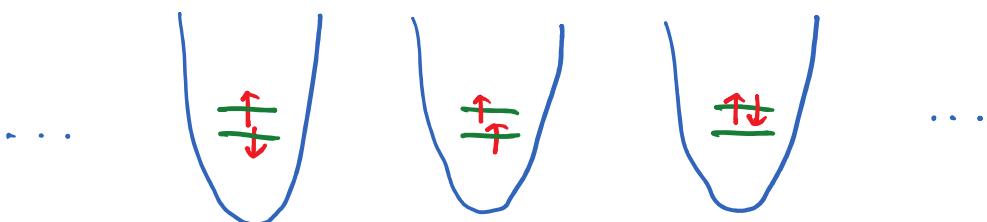
$$|t_-\rangle = |\downarrow\rangle_1|\downarrow\rangle_2$$

$$H|t_\alpha\rangle = \frac{1}{4}J|t_\alpha\rangle \quad (\alpha = \pm 1, 0)$$

## \* ) Direct exchange & large spin formation

In solid-state materials local magnetic moments with  $S > 1/2$  are quite common. Why?

Let's consider two nearly degenerate orbitals:



$$\begin{aligned}
 H = & \int d\vec{r} \psi_{\sigma}^{+}(\vec{r}) \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r}) \right] \psi_{\sigma}^{+}(\vec{r}) \\
 & + \frac{1}{2} \int d\vec{r} d\vec{r}' V(|\vec{r} - \vec{r}'|) \psi_{\sigma}^{+}(\vec{r}) \psi_{\sigma}^{+}(\vec{r}') \psi_{\sigma}^{-}(\vec{r}') \psi_{\sigma}^{-}(\vec{r})
 \end{aligned}$$

( c.f. electron-3.pdf )

Tight-binding approximation with **two** localized Wannier/atomic orbitals: (c.f. band-4.pdf)

$$\psi_{\sigma}^{+}(\vec{r}) \simeq \sum_j \sum_{a=1}^2 \phi_a^{*}(\vec{r} - \vec{R}_j) c_{j,a,\sigma}^{+} + \dots$$

↑      ↑      ↑      ↑  
 site orbital    Wannier/atomic wave function    other orbitals

$$H = H_0 + H_I$$

$$\begin{aligned}
 H_0 &\simeq \int d\vec{r} \sum_{i,j} \sum_{a,a'} \phi_a^*(\vec{r} - \vec{R}_i) \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r}) \right] \phi_{a'}(\vec{r} - \vec{R}_j) \\
 &\quad \times C_{i,a,\sigma}^+ C_{j,a',\sigma} \\
 &= \sum_{i,j} \sum_{a,a'} \underbrace{t_{(i,a);(j,a')}}_{\text{hopping integral}} C_{i,a,\sigma}^+ C_{j,a',\sigma} + \sum_{i,a} \underbrace{\epsilon_a}_{\text{atomic energy levels}} C_{i,a,\sigma}^+ C_{i,a,\sigma}
 \end{aligned}$$

$$\begin{aligned}
 H_I &\simeq \frac{1}{2} \int d\vec{r} d\vec{r}' V(|\vec{r} - \vec{r}'|) \sum_{i,j,k,l} \underbrace{\sum_{a,a',b,b'}}_{\text{}} \\
 &\quad \times \phi_a^*(\vec{r} - \vec{R}_i) \phi_{a'}^*(\vec{r}' - \vec{R}_j) \phi_b(\vec{r}' - \vec{R}_k) \phi_{b'}(\vec{r} - \vec{R}_l) \\
 &\quad \times C_{i,a,\sigma}^+ C_{j,a',\sigma'}^+ C_{k,b,\sigma'} C_{l,b',\sigma}
 \end{aligned}$$

dominant term: onsite interactions ( $i=j=k=l$ )

reason: large overlaps of atomic orbitals

$$\Rightarrow H_I \simeq \sum_i \sum_{a,a',b,b'} \frac{U_{a,a',b,b'}}{Z} C_{i,a,\sigma}^+ C_{i,a',\sigma'}^+ C_{i,b,\sigma'} C_{i,b',\sigma}$$

Warm-up exercise:

If only one band is considered ( $a = a' = b = b' = 1$ ), we would obtain the one-band Hubbard model.

$$\begin{aligned}
 H_I &\simeq \sum_i \frac{U}{2} C_{i,\sigma}^+ C_{i,\sigma'}^+ \underbrace{C_{i,\sigma'} C_{i,\sigma}}_{\text{}} \\
 &= - \sum_i \frac{U}{2} C_{i,\sigma}^+ \underbrace{C_{i,\sigma'}^+}_{\parallel} C_{i,\sigma} C_{i,\sigma'} \\
 &\quad \{ C_{i,\sigma'}^+, C_{i,\sigma} \} - C_{i,\sigma} C_{i,\sigma'}^+ \\
 &\quad \parallel \\
 &\quad \delta_{\sigma\sigma'} - C_{i,\sigma} C_{i,\sigma'}^+ \\
 &= \sum_i \frac{U}{2} \left( \underbrace{C_{i,\sigma}^+ C_{i,\sigma}}_{\parallel} \underbrace{C_{i,\sigma'}^+ C_{i,\sigma'}}_{\parallel} - \underbrace{C_{i,\sigma}^+ C_{i,\sigma}}_{\parallel} \right) \\
 &\quad n_{i\uparrow}^2 = n_{i\uparrow} \\
 &\quad n_{i\downarrow}^2 = n_{i\downarrow} \\
 &= U \sum_i n_{i\uparrow} n_{i\downarrow} \quad \checkmark \quad \text{Hubbard } U\text{-term!}
 \end{aligned}$$

$$\begin{aligned}
 U &= \int d\vec{r} d\vec{r}' V(|\vec{r}-\vec{r}'|) \phi^*(\vec{r}-\vec{R}_i) \phi^*(\vec{r}'-\vec{R}_i) \\
 &\quad \vec{r}-\vec{R}_i \rightarrow \vec{r} \quad \vec{r}'-\vec{R}_i \rightarrow \vec{r}' \\
 &\quad \times \phi(\vec{r}'-\vec{R}_i) \phi(\vec{r}-\vec{R}_i) \\
 &= \int d\vec{r} d\vec{r}' \underbrace{V(|\vec{r}-\vec{r}'|)}_0 |\phi(\vec{r})|^2 |\phi(\vec{r}')|^2 > 0
 \end{aligned}$$

Now let's go back to the two-band case.

$$H_I = \sum_i \sum_{a,a',b,b'=1}^2 \frac{U_{a,a',b,b'}}{2} C_{i,a,\sigma}^+ C_{i,a',\sigma'}^+ C_{i,b,\sigma'} C_{i,b',\sigma}$$

$$\begin{aligned} U_{a,a',b,b'} &= \int d\vec{r} d\vec{r}' V(|\vec{r}-\vec{r}'|) \phi_a^*(\vec{r}-\vec{R}_i) \phi_{a'}^*(\vec{r}'-\vec{R}_i) \\ &\quad \times \phi_b(\vec{r}-\vec{R}_i) \phi_{b'}(\vec{r}-\vec{R}_i) \\ &= \int d\vec{r} d\vec{r}' V(|\vec{r}-\vec{r}'|) \phi_a^*(\vec{r}) \phi_{a'}^*(\vec{r}') \phi_b(\vec{r}') \phi_{b'}(\vec{r}) \end{aligned}$$

Case 1:  $a=b'$  &  $a'=b$

$$\begin{aligned} &C_{i,a,\sigma}^+ C_{i,b,\sigma'}^+ C_{i,b,\sigma'} C_{i,a,\sigma} \\ &= -C_{i,a,\sigma}^+ (\underbrace{\delta_{ab} \delta_{\sigma\sigma'}}_{\parallel} - C_{i,a,\sigma}^+ C_{i,b,\sigma'}) C_{i,b,\sigma'} \\ &= \underbrace{n_{i,a} n_{i,b}}_{\parallel} - n_{i,a} \delta_{ab} \\ &\quad \left\{ \begin{array}{l} n_{i,a} n_{i,b} \text{ for } a \neq b \\ (n_{i,a,\uparrow} + n_{i,a,\downarrow})^2 = 2n_{i,a,\uparrow} n_{i,a,\downarrow} + n_{i,a}^2 \end{array} \right. \\ &\quad \text{for } a=b \end{aligned}$$

Case 2:  $a=b \neq a' \neq b'$  ( $a \neq a'$ , otherwise included in case 1)

$$C_{i,a,\sigma}^+ C_{i,a',\sigma'}^+ C_{i,a,\sigma'} C_{i,a',\sigma} \quad (a \neq a')$$

$$= -2 \left( \vec{S}_{i,a} \cdot \vec{S}_{i,a'} + \frac{1}{4} n_{i,a} n_{i,a'} \right),$$

where

$$\vec{S}_{i,a} = \frac{1}{2} \sum_{\sigma, \sigma'} C_{i,a,\sigma}^+ \vec{\tau}_{\sigma\sigma'} C_{i,a,\sigma'} \quad \begin{matrix} \uparrow \\ \text{Pauli matrices} \end{matrix}$$

Proof:

$$\begin{aligned} \vec{S}_{i,a} \cdot \vec{S}_{i,a'} &= \frac{1}{4} \sum_{\sigma, \sigma', \sigma'', \sigma'''} C_{i,a,\sigma}^+ C_{i,a',\sigma'}^+ C_{i,a',\sigma''}^+ C_{i,a'',\sigma'''}^+ \\ &\quad \times \underbrace{\sum_{\alpha=x,y,z} \tau_{\sigma\sigma'}^\alpha \tau_{\sigma'',\sigma'''}^\alpha}_{= 2 \delta_{\sigma\sigma''} \delta_{\sigma'\sigma''} - \delta_{\sigma\sigma'} \delta_{\sigma''\sigma'''}} \quad (a \neq a') \\ &= - \frac{1}{2} C_{i,a,\sigma}^+ C_{i,a',\sigma'}^+ C_{i,a,\sigma'} C_{i,a',\sigma} \\ &\quad - \frac{1}{4} n_{i,a} n_{i,a'} \quad \checkmark \end{aligned}$$

Other cases (e.g.  $a=a'=b \neq a'$ ) are possible,

but we will ignore them.

(In some cases, these terms vanish due to the symmetry of the orbital wave functions.)

$$H_I = \sum_i \left[ \sum_{a \neq b} U_{ab} n_{i,a} n_{i,b} + \sum_a 2U_{a,a} n_{i,a,\uparrow} n_{i,a,\downarrow} \right]$$

$$+ \sum_{a \neq b} J_F \underbrace{C_{i,a,\sigma}^+ C_{i,b,\sigma'}^+ C_{i,a,\sigma'}^- C_{i,b,\sigma}^-}_{\parallel}$$

$$-2 \vec{S}_{i,a} \cdot \vec{S}_{i,b} - \frac{1}{2} n_{i,a} n_{i,b}$$

absorb into  $U_{ab}$ -term

$$U'_{ab} = U_{ab} - \frac{1}{2} J_F$$

$$U_{ab} = \frac{1}{2} \int d\vec{r} d\vec{r}' V(|\vec{r} - \vec{r}'|) |\phi_a(\vec{r})|^2 |\phi_b(\vec{r}')|^2 > 0$$

$$J_F = \frac{1}{2} \int d\vec{r} d\vec{r}' V(|\vec{r} - \vec{r}'|) \phi_a^*(\vec{r}) \phi_b^*(\vec{r}') \phi_a(\vec{r}') \phi_b(\vec{r})$$

The sign of  $J_F$  is important!

Short-range potential  $V(|\vec{r} - \vec{r}'|) = g \delta(\vec{r} - \vec{r}')$

$$\Rightarrow J_F = \frac{g}{2} \int d\vec{r} |\phi_a(\vec{r})|^2 |\phi_b(\vec{r})|^2 > 0$$

Long-range Coulomb potential  $V(|\vec{r} - \vec{r}'|) = \frac{1}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{r}'|}$

$V_{\vec{r}, \vec{r}'}$  is viewed as a matrix, which is positive

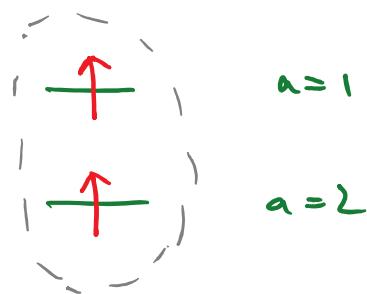
$$\int d\vec{r} e^{i\vec{k} \cdot \vec{r}} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r} - \vec{r}'|} = \frac{1}{\epsilon_0} \frac{e^2}{|\vec{k}|^2} e^{i\vec{k} \cdot \vec{r}'}$$

Plane waves are eigenvectors of  $V_{\vec{r}, \vec{r}'}$  with eigenvalues  $\frac{1}{\epsilon_0} \frac{e^2}{|\vec{k}|^2} > 0$  !

$$\begin{aligned} J_F &= \frac{1}{2} \int d\vec{r} d\vec{r}' V(|\vec{r} - \vec{r}'|) [\underbrace{\phi_a^*(\vec{r}) \phi_b(\vec{r})}_{\Phi^*(\vec{r})}] [\underbrace{\phi_b^*(\vec{r}') \phi_a(\vec{r}')}_{\Phi(\vec{r}')} ] \\ &= \langle \Phi | V | \Phi \rangle > 0 \end{aligned}$$

We expect that  $J_F > 0$  for more general potentials.

Important consequence:



Two electrons per site, one occupying each orbital:

Because of  $\underbrace{-J_F \vec{S}_{i,a} \cdot \vec{S}_{i,b}}$  with  $J_F > 0$ ,

two electrons tend to form a **triplet** with  
**parallel spins**!

Low energy subspace :  $S = 1$

This is the microscopic origin of the first  
Hund's rule and also explains the tendency  
to form large-spin magnetic moments in  
a number of solid-state materials.