Note on Super-Exchange Interaction

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See also "The Quantum Theory of Magnetism" by Norberto Maklis, World Scientific, Sigapore (2000).

Levels of details for magnetism

- Atomic level:
 - Exchange interaction that aligns atomic moments $J_{ij}\vec{S_i}\cdot\vec{S_j}$
- Micromagnetic level
 - Smear the individual atoms into continuum, see magnetization as a function of position (domain wall)
- Domain level
 - Domains are separated by walls of zero thickness
- Nonlinear level
 - Average magnetization of the entire magnet



Super-exchange interaction (simplified model)



The energy difference can be represented by the expression:

 $J\vec{S}_{1} \cdot \vec{S}_{2}$ J > 0, antiparallel - alignmentJ < 0, parallel alignment



How to calculate **J**?

Fundamental interactions: 1. Hopping (bonding)



$$\begin{array}{c}
 M\\
\vec{S}_1\\
\vec{S}_1\\
\vec{S}_2\\
\vec{O}\\
\vec{V}\\
\vec{S}_2
\end{array}$$

$$E_{a} = \epsilon_{a} + \frac{4t^{2}}{2(\epsilon_{a} - \epsilon_{b})}$$

$$E_{b} = \epsilon_{b} - \frac{4t^{2}}{2(\epsilon_{a} - \epsilon_{b})}$$

$$t \equiv \langle \phi_{a} | V_{a} | \phi_{b} \rangle$$

$$\approx \langle \phi_{a} | V_{b} | \phi_{b} \rangle$$

$$\psi_{a} = \phi_{a} + \frac{t}{2(\epsilon_{a} - \epsilon_{b})} \phi_{b}$$

$$\psi_{b} = \phi_{b} - \frac{t}{2(\epsilon_{a} - \epsilon_{b})} \phi_{a}$$

Fundamental interactions:

2. on site repulsion



Two electrons on metal orbital (localized), generating a coulomb repulsion energy **U**.

3. Orbital energy



Typically, metal orbital has lower energy (this is why there is chemical bonding). Define: $D \equiv \epsilon_d - \epsilon_0$

Possible states:



Three groups:

- Total spin $S_z = 1$ $|\uparrow 2\uparrow\rangle, |2\uparrow\uparrow\rangle, |\uparrow\uparrow 2\rangle$
- Total spin $S_z = 1$ $|\downarrow 2 \downarrow\rangle|2 \downarrow\downarrow\rangle|\downarrow\downarrow 2\rangle$
- Total spin $S_z = 0$ $|\downarrow 2 \uparrow\rangle|2 \downarrow\uparrow\rangle|\downarrow\uparrow 2\rangle$ $|\uparrow 2 \downarrow\rangle|2 \uparrow\downarrow\rangle|\uparrow\downarrow 2\rangle$ $|022\rangle|202\rangle|220\rangle$

All the interactions we considered are S_z conserving, so when we solve their energy by looking at the groups separately.

Hamiltonian for $S_z = 1$



The energy of the lowest energy state: $E'_{|\uparrow 2\uparrow\rangle} = 2D - \frac{t^2}{U+D} + \frac{2t^4}{(D+U)^3}$

2nd order perturbation:
$$E_g^{(2)} = \frac{t_{ga}^2}{E_g - E_a}$$
, $t_{ga} = \langle \phi_g | H_1 | \phi_a \rangle$
4th order perturbation: $E_g^{(4)} = \frac{t_{ga}t_{ab}t_{bc}t_{cg}}{E_{ga}E_{gb}E_{gc}} - \begin{pmatrix} t_{ga}^2t_{gc}^2\\ E_{ga}E_{gc}^2 \end{pmatrix}$
 $t_{ga} = t_{ab} = t_{bc} = t_{cg} = t$
 $E_{ga} = -D - U$, $E_{gc} = -D - U$

Hamiltonian for $S_{Z_{|c|}} = 0$

		↓2↑⟩	2 ↓↑>	↓↑ 2>	$ \uparrow 2\downarrow\rangle$	2 ↑↓>	↑↓ 2>	022>	202>	220>
$ g\rangle$	↓2↑>	2 <i>D</i>		t						
	2 ↓↑⟩	t	3D + U						t	t
	↓↑ 2>	t		3D + U				t	t	
	↑2↓⟩				2 <i>D</i>	t	t			
	2 ↑↓⟩				t	3D + U			t	t
	↑↓ 2>				t		3D + U	t	t	
	022>			t			t	2D + U		
<i>b</i> >	202>		t	t		t	t		4D + 2U	
	220>		t			t				2D + U

The energy of the lowest energy state:

$$E'_{|\downarrow 2\uparrow\rangle} = 2D - \frac{t^2}{U+D} - \frac{t^4}{(D+U)^3} + \frac{2t^4}{(D+U)^3}$$

2nd order perturbation:
$$E_g^{(2)} = \frac{t_{ga}}{E_g - E_a}$$
, $t_{ga} = \langle \phi_g | H_1 | \phi_a \rangle$
4th order perturbation: $E_a^{(4)} = \frac{t_{ga}t_{ab}t_{bc}t_{cg}}{E_g - E_a} - \frac{t_{ga}^2 t_{gc}^2}{E_g - E_a}$

The order perturbation:
$$E_g^{c} = \frac{1}{E_{ga}E_{gb}E_{gc}} - \frac{1}{E_{ga}E_{gc}^2}$$

 $t_{ga} = t_{ab} = t_{bc} = t_{cg} = t$
 $E_{ga} = -D - U, E_{gb} = -2D - 2U, E_{gc} = -D - U$

Compare the energy

$$E'_{|\uparrow 2\uparrow\rangle} = 2D - \frac{t^2}{U+D} + \frac{2t^4}{(D+U)^3}$$

$$E'_{|\downarrow 2\uparrow\rangle} = 2D - \frac{t^2}{U+D} - \frac{t^4}{(D+U)^3} + \frac{2t^4}{(D+U)^3}$$

Exchange energy:
$$J\vec{S}_1 \cdot \vec{S}_2$$

$$J = \frac{2t^4}{(D+U)^3}$$



Conclusion

- Simple model to illustrate the super-exchange interaction
- The difference comes from the 4th order perturbation
- The energy reduction comes from the hopping of the electron between the oxygen and metal states. More hopping, more energy reduction, lower energy.

Note that in Anderson's original paper "New Approach to the Theory of Superexchange Interactions" Physical Review 115, 2 (1959), he started with the wavefunction of the 1st order correction. His results show $J = \frac{b^2}{U}$, where $b = \frac{t^2}{U}$ in this presentation.