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Spintronics Basic II

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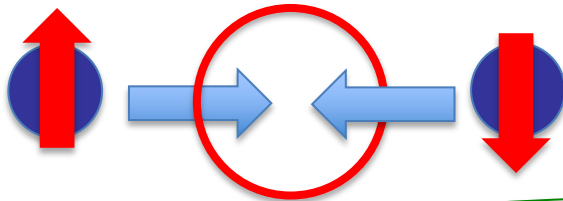
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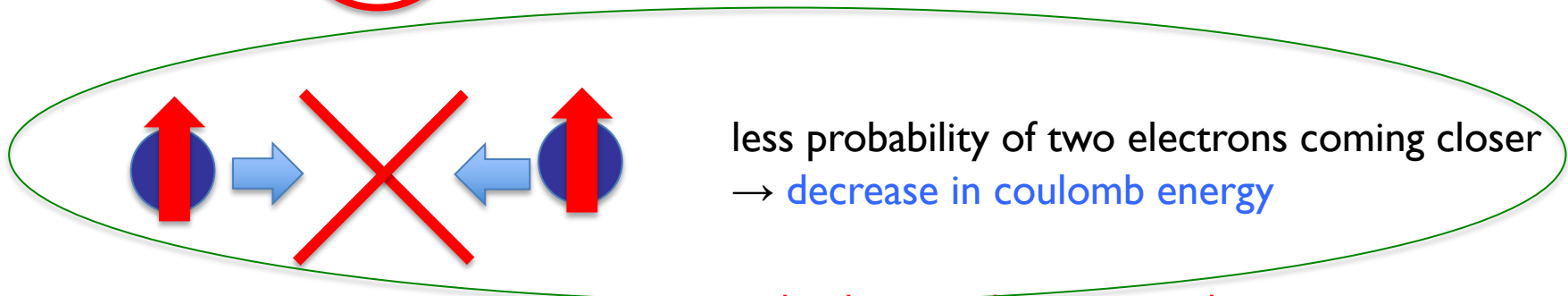
- Origin of magnetism and magnetic structures
 - Exchange interaction
 - Exchange interaction between two atoms
 - Heitler–London limit and molecular orbital limit
 - Direct exchange and kinetic exchange
 - Atoms in a crystal
- A bit more details
 - Kanamori–Goodenough rule
 - Double-exchange
 - Magnetic anisotropy
 - Anisotropic exchange
 - Dzialshinsky-Moriya interaction
 - Heisenberg model

Interaction between electrons

■ two electrons—Pauli's exclusion principle



possibility of two electrons coming closer
→ increase in coulomb energy



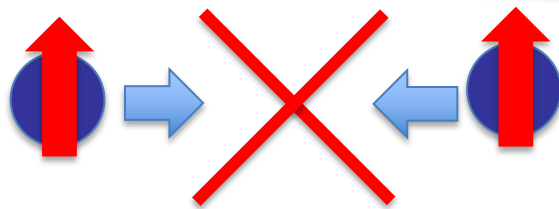
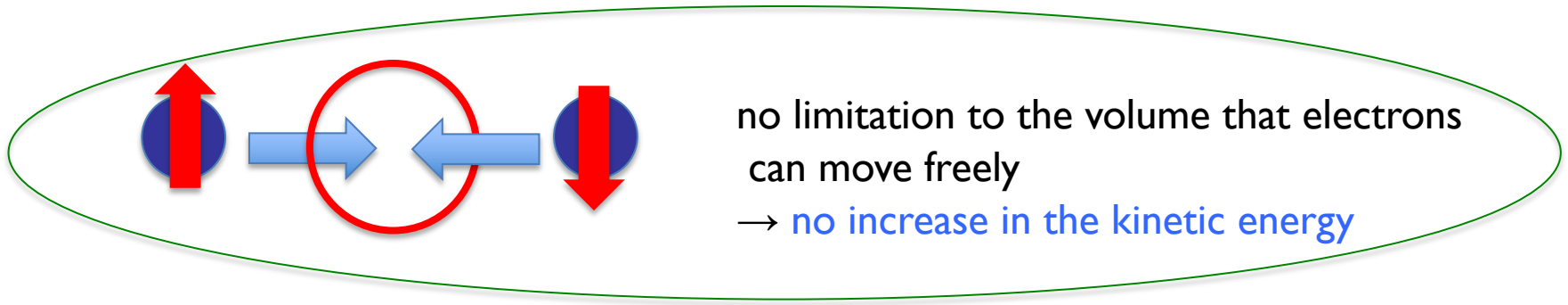
less probability of two electrons coming closer
→ decrease in coulomb energy

reason why electrons do not come closer is not
coulomb repulsion but Pauli's exclusion principle

parallel spin is preferable

Kinetic energy of electrons

■ two electrons –Pauli's exclusion principle



the volume that electrons can move is halved
→ increase in zero-point energy

$$\Delta r \Delta p \sim \hbar$$

antiparallel spin is preferable

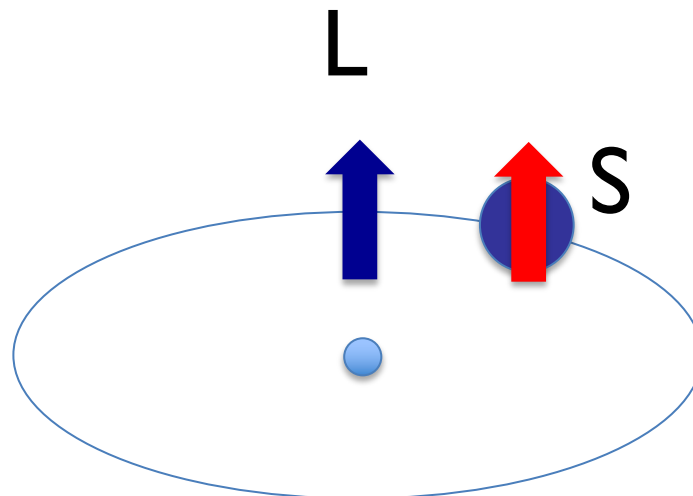
Exchange interaction between electrons

- energy difference between parallel and antiparallel coupled electrons, positive or negative?

$$E_x = E \begin{array}{c} \uparrow \\ \bullet \\ \downarrow \end{array} \begin{array}{c} \bullet \\ \downarrow \end{array} - E \begin{array}{c} \uparrow \\ \bullet \\ \uparrow \end{array} \begin{array}{c} \bullet \\ \uparrow \end{array} \cong 0 ?$$

Single atom

- electrons are bound in a potential
- a neutral atom with an odd number of electrons
 - nonzero total electron spin
 - nonzero angular momentum in general
 - shows magnetism (paramagnetic)



Tow atoms

- interaction between atomic magnetic moments
 - parallel or antiparallel coupling
 - exchange interaction **between atoms**

$$E_x = E \begin{array}{c} \uparrow \downarrow \\ \bullet \bullet \end{array} - E \begin{array}{c} \uparrow \uparrow \\ \bullet \bullet \end{array}$$

parallel if $E_x > 0$, antiparallel otherwise

Parallel or antiparallel?

■ Simple model I: Heitler–London limit

- two hydrogen atoms (hydrogen atom1 and hydrogen atom2)
- potential of each atom $v(r - R)$

atomic hamiltonian

atomic orbital

hydrogen atom1 $H_1 = -\nabla_1^2 + v(r_1 - R_1)$

$$H_1\phi_1 = \epsilon\phi_1$$

hydrogen atom2 $H_2 = -\nabla_2^2 + v(r_2 - R_2)$

$$H_2\phi_2 = \epsilon\phi_2$$

(we use Slater's atomic unit: $\hbar = 1$, $m = 1/2$, $e^2 = 2$)

Parallel or antiparallel?

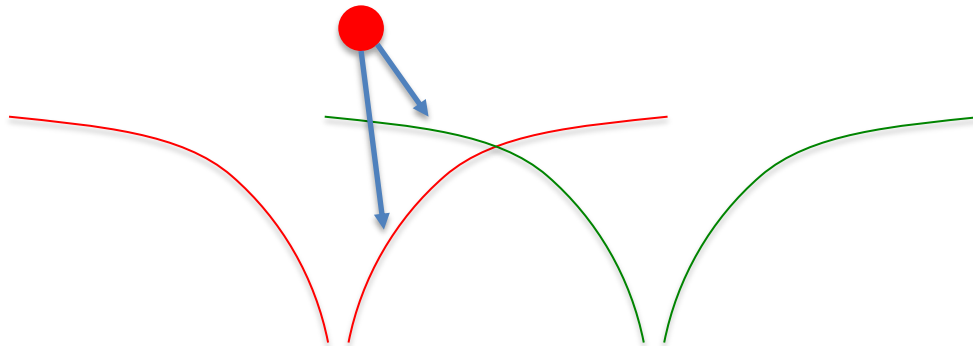
■ Simple model I: Heitler–London limit

- two hydrogen atoms (hydrogen atom1 and hydrogen atom2)
- potential of each atom

hamiltonian of hydrogen molecule coulombic interaction

$$H = H_1 + H_2 + H_{12} + V(r_1 - r_2)$$

$$H_{12} = v(r_1 - R_2) + v(r_2 - R_1) \quad \text{attractive potential due to the other atom}$$



Parallel or antiparallel?

■ Simple model I: Heitler–London limit

- assume that each atom keeps charge neutrality
- assume that the wave function of hydrogen molecule is a product of 1s wave functions ϕ 's of two hydrogen atoms

hamiltonian of hydrogen molecule coulombic interaction

$$H = H_1 + H_2 + H_{12} + V(r_1 - r_2)$$

$$H_{12} = v(r_1 - R_2) + v(r_2 - R_1) \quad \text{attractive potential due to the other atom}$$

molecular wavefunction $\Psi(r_1, r_2) \sim \phi_1(r_1)\phi_2(r_2)$

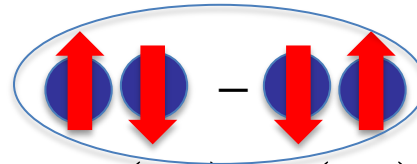
molecular energy $E \simeq \int \Psi^* H \Psi d^3r$

Parallel or antiparallel?

■ Simple model I: Heitler–London limit

- antisymmetrization (sign change accompanied by exchange of two electrons)
- two cases depending on spin configuration

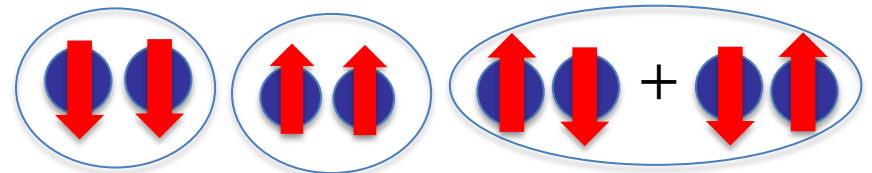
$s=0$ state (spin singlet)



$$\Psi_0(r_1, r_2) = A_0 \{ \phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1) \}$$

(symmetric orbital, antisymmetric spin)

$s=1$ state (spin triplet)



$$\Psi_1(r_1, r_2) = A_1 \{ \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1) \}$$

(antisymmetric orbital, symmetric spin)

Parallel or antiparallel?

■ Simple model I: Heitler–London limit

expectation value of energy

spin singlet

$$\int \Psi_0(r_1, r_2)(H_1 + H_2 + H_{12} + V)\Psi_0(r_1, r_2)dr_1dr_2 = E_0$$

spin triplet

$$\int \Psi_1(r_1, r_2)(H_1 + H_2 + H_{12} + V)\Psi_1(r_1, r_2)dr_1dr_2 = E_1$$

$$E_x = E_0 - E_1$$

Parallel or antiparallel?

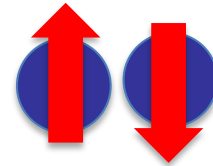
■ Simple model I: Heitler–London limit

s=0 state (spin singlet)

$$\Psi_0(r_1, r_2) = A_0 \{ \phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1) \}$$

$$\Psi_0(r_1, r_2) \neq 0 \quad \text{even if } r_1 = r_2$$

large interaction V



s=1 state (spin triplet)

$$\Psi_1(r_1, r_2) = A_1 \{ \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1) \}$$

$$\Psi_1(r_1, r_2) = 0 \quad \text{if } r_1 = r_2$$

small interaction V



$$\int \Psi_0(r_1, r_2) V \Psi_0(r_1, r_2) dr_1 dr_2 > \int \Psi_1(r_1, r_2) V \Psi_1(r_1, r_2) dr_1 dr_2$$

Parallel or antiparallel?

■ Simple model I: Heitler–London limit

s=0 state (spin singlet)

$$\Psi_0(r_1, r_2) = A_0 \{ \phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1) \}$$

$$\int \Psi_0(r_1, r_2)(H_1 + H_2 + H_{12})\Psi_0(r_1, r_2)dr_1dr_2 = 2\epsilon'$$

s=1 state (spin triplet)

$$\Psi_1(r_1, r_2) = A_1 \{ \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1) \}$$

$$\int \Psi_1(r_1, r_2)(H_1 + H_2 + H_{12})\Psi_1(r_1, r_2)dr_1dr_2 = 2\epsilon'$$

the same energy except coulomb interaction energy

$$\left(\epsilon' = \epsilon + \int \phi_1(r)v(r - R_2)\phi_1(r)dr < \epsilon \right)$$

Heitler–London limit

therefore

$$\int \Psi_0(r_1, r_2) H \Psi_0(r_1, r_2) dr_1 dr_2 > \int \Psi_1(r_1, r_2) H \Psi_1(r_1, r_2) dr_1 dr_2$$

$$E_x = E_0 - E_1 > 0$$

- triplet state realized in Heitler-London limit
- not corresponding to most two-atom molecules
 - two-atom molecules are mostly spin singlet
- molecular bonding is caused by H_{12}
 - $\varepsilon' < \varepsilon$: effect of attractive potential of a neighbor

Parallel or antiparallel?

■ Simple model 2: molecular orbital limit

- two hydrogen atoms (hydrogen atom1 and hydrogen atom2)
- wavefunctions are molecular orbitals constructed from two atomic orbitals
- two molecular orbitals: bonding and antibonding states
- how to place two electrons in these molecular orbitals?

bonding state

$$\Psi_b(r) = A\{\phi_1(r) + \phi_2(r)\}$$

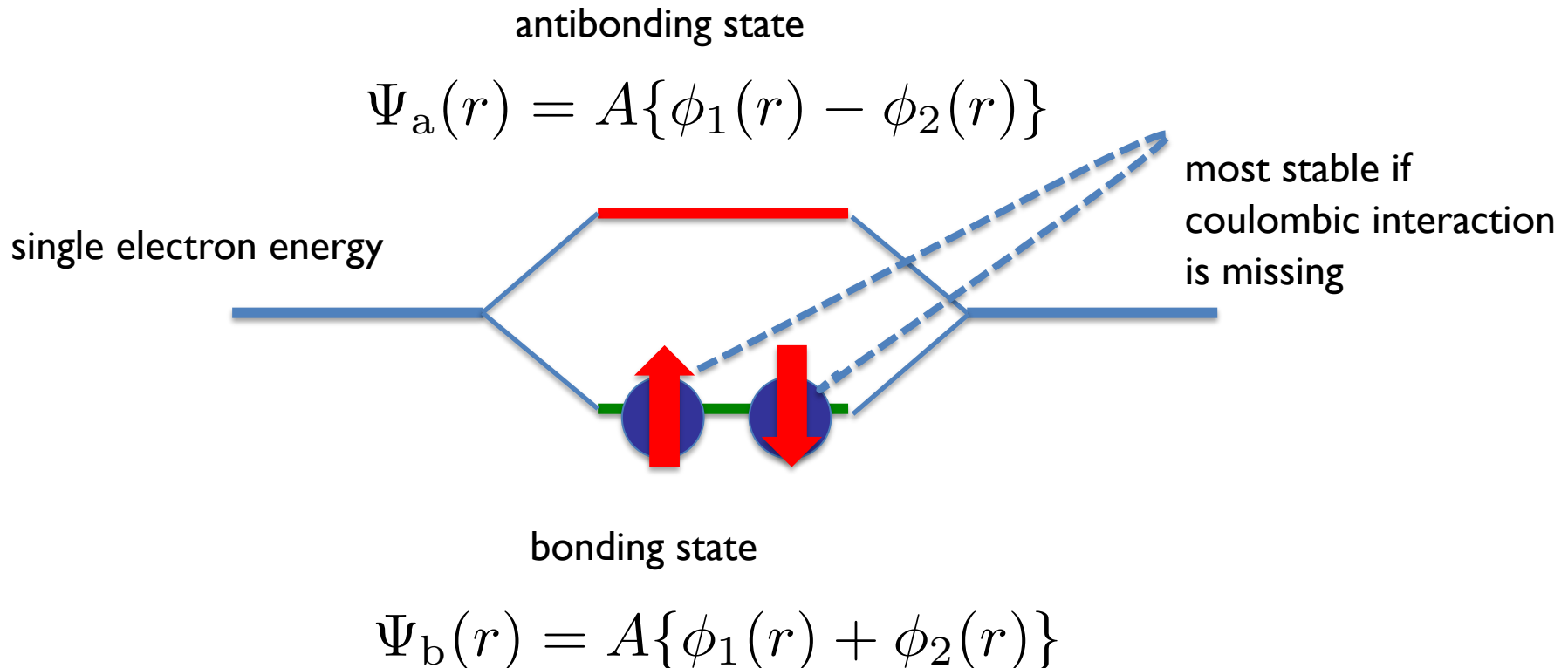
antibonding state

$$\Psi_a(r) = A\{\phi_1(r) - \phi_2(r)\}$$

$$\left(\phi_i(r) \equiv \phi(r - R_i) \right)$$

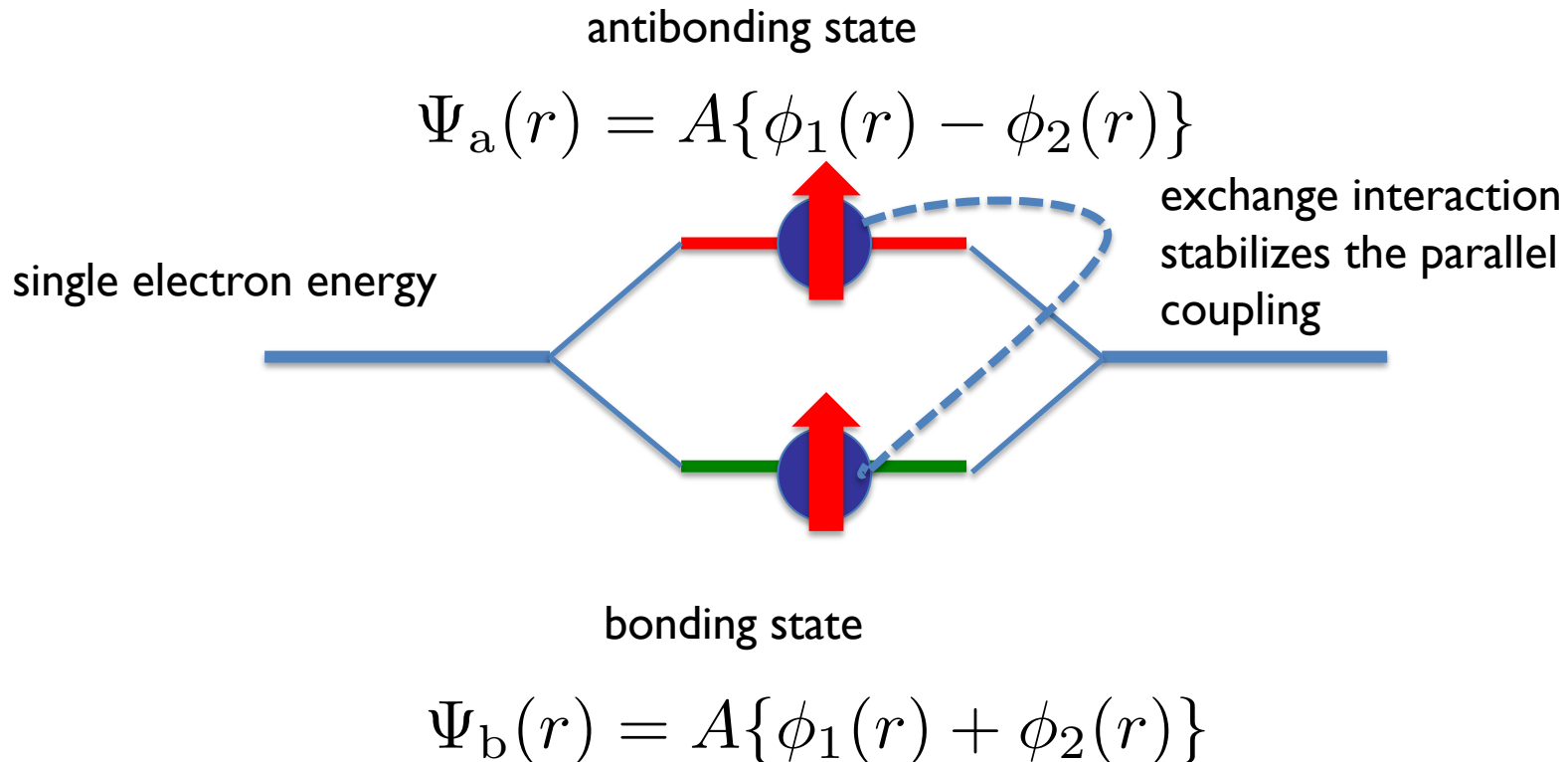
Parallel or antiparallel?

■ Simple model 2: molecular orbital limit



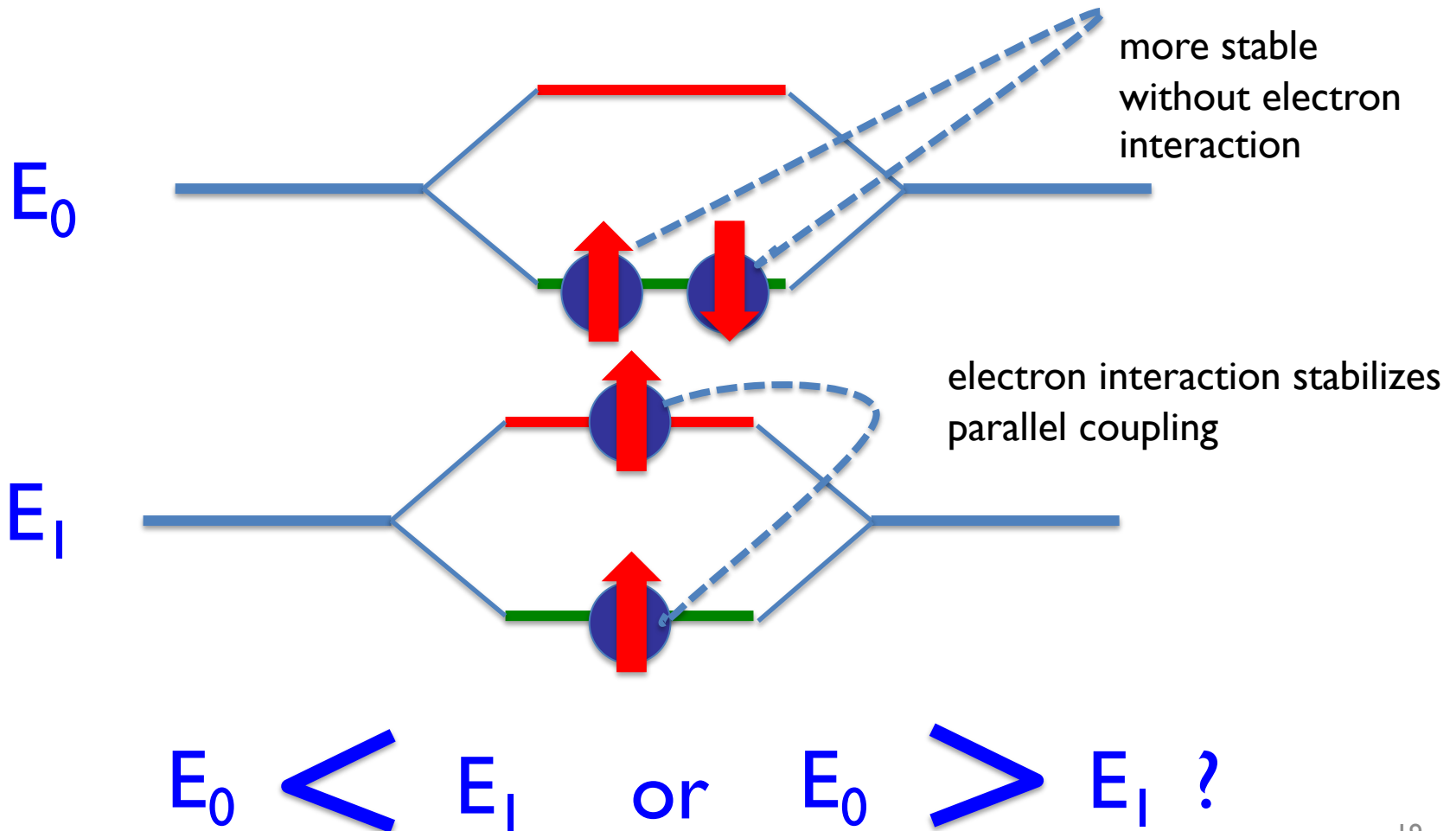
Parallel or antiparallel?

■ Simple model 2: molecular orbital limit



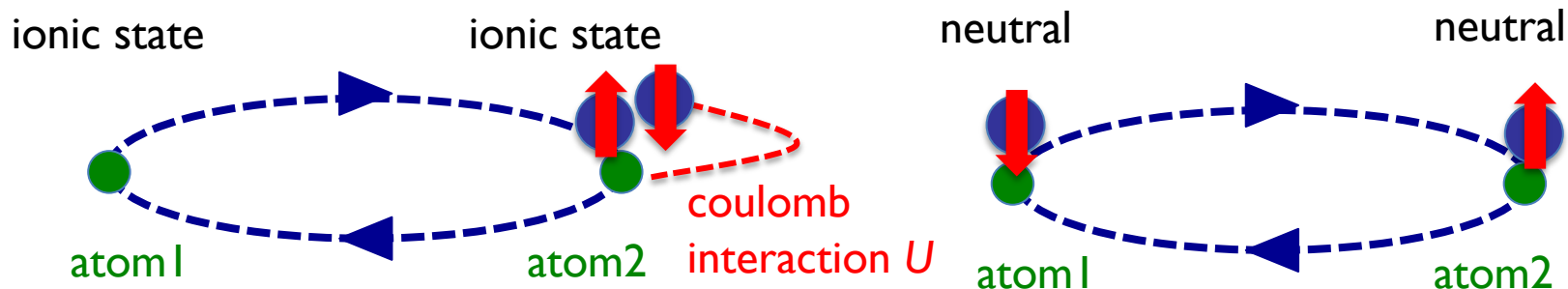
Parallel or antiparallel?

■ Simple model 2: molecular orbital limit



Hitler–London vs. molecular orbital limits

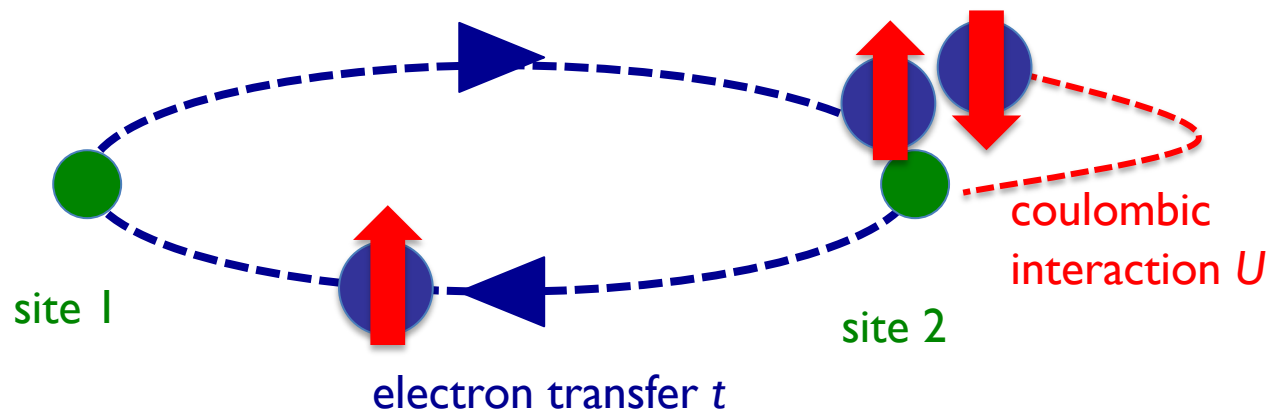
- Heitler–London limit excludes ionic states
 - strong correlation limit
 - electron interaction energy \gg kinetic energy
- equal probability of ionic and neutral states in molecular orbital limit
 - weak correlation limit
 - electron interaction energy \ll kinetic energy



Analysis using simple model

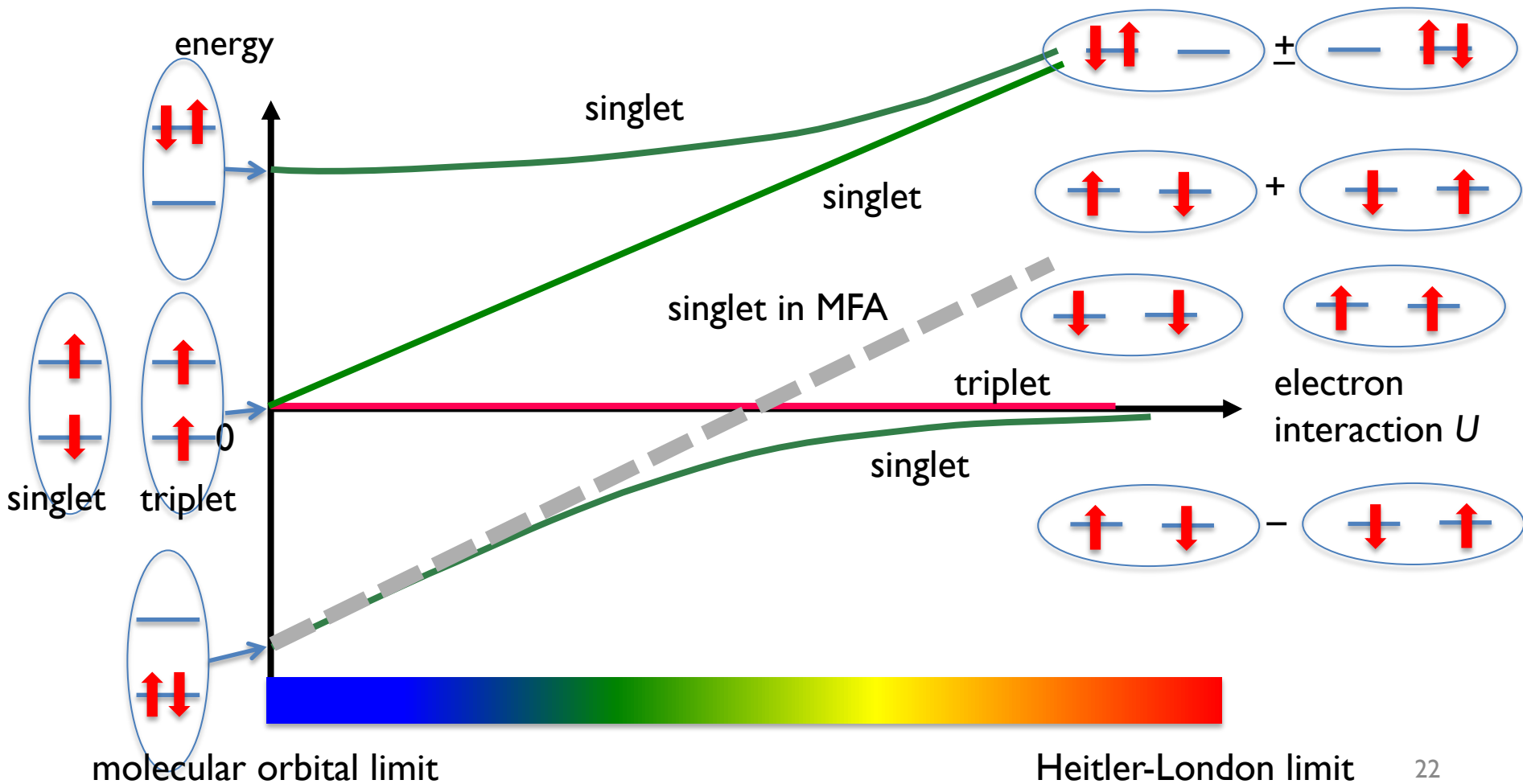
■ 2-site Hubbard model

$$H = t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}$$



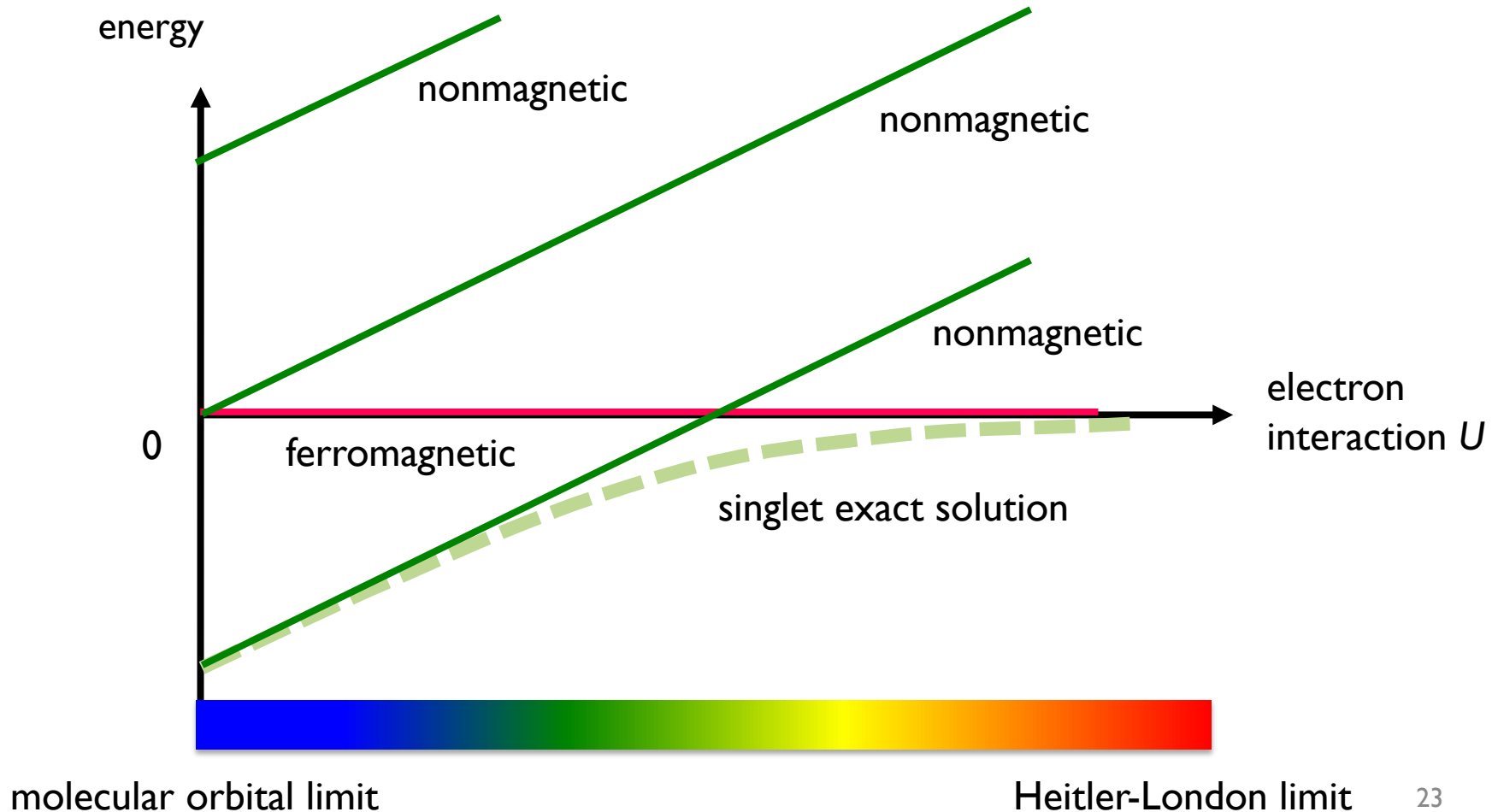
Exact solution

■ ground state at $U=0$ and ∞



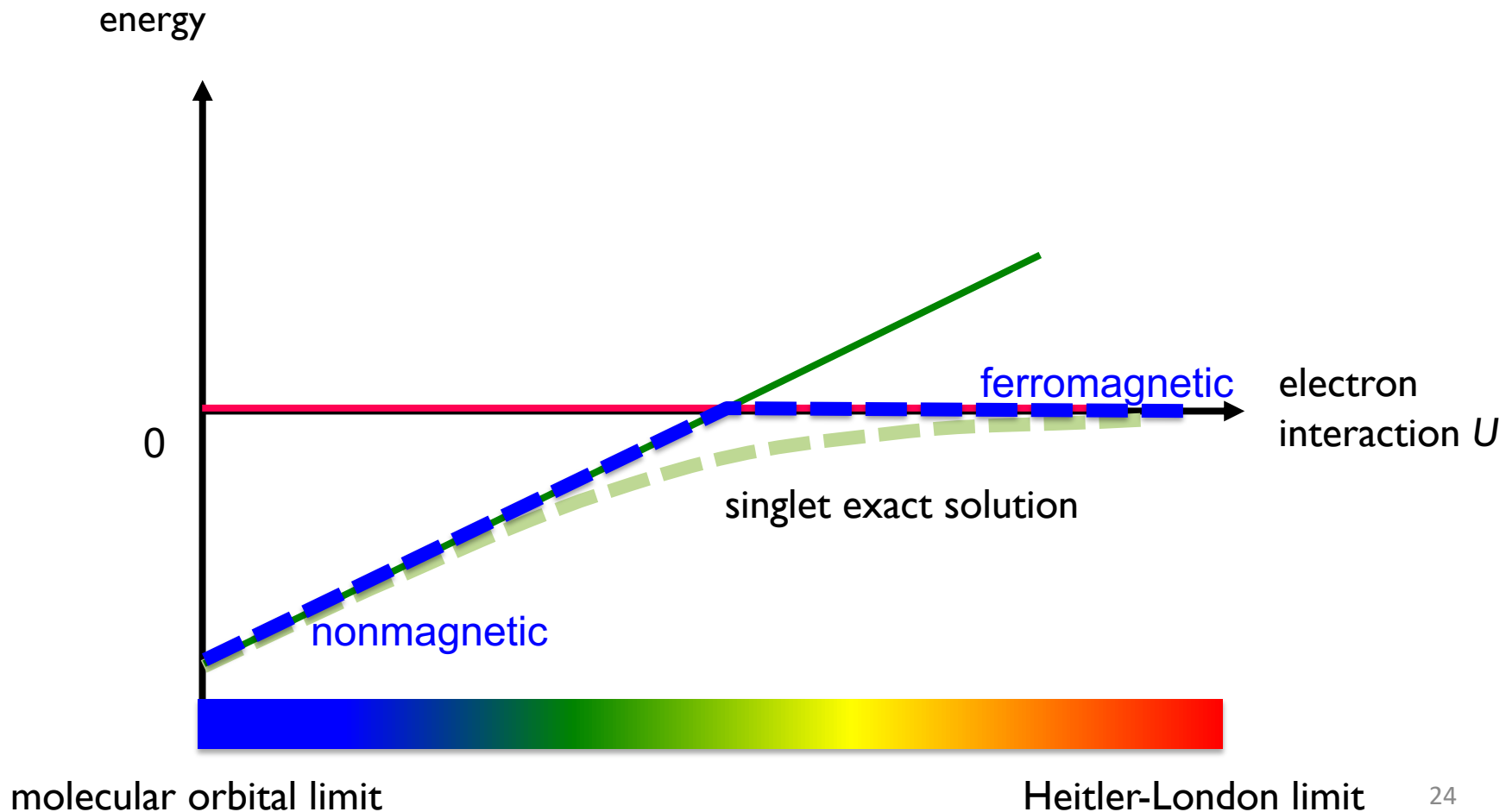
Mean field approximation (MFA)

- nonmagnetic to ferromagnetic transition occurs



Mean field approximation (MFA)

- nonmagnetic to ferromagnetic transition occurs



In reality

- somewhere in between Heitler-London and molecular orbital
 - starting from Heitler-London
 - ionic states gradually mixed into neutral states
 - although ionic states have higher energies, energy gain due to electron transfer is expected
 - starting from molecular orbital limit
 - ionic states are suppressed owing to their higher energy
 - bonding–antibonding splitting decreases, which reduces energy gain due to electron transfer

Real atomic exchange couplings

- between two atomic spins \mathcal{S}_1 and \mathcal{S}_2 of atom 1 and atom 2, there exists an interaction of the form

$$E_x = E_0 - E_1 = -2(J_{12} + W_{12})\mathcal{S}_1 \cdot \mathcal{S}_2$$

where

$$J_{12} > 0, \quad W_{12} < 0$$

is always satisfied and in many cases

$$J_{12} + W_{12} < 0$$

Direct and kinetic exchanges

- J: direct exchange
- W: kinetic exchange
- in many cases, W determines magnetic structures

Hereafter, we use J to indicate a sum of J and W

$$J_{12} + W_{12} \Rightarrow J_{12}$$

Therefore J_{12} can be either positive or negative.
A positive J is ferromagnetic and vice versa.

If many atoms exist

- when interaction is strong enough, spontaneous symmetry breaking occurs
 - magnetic moment arises at each site
 - stable magnetic structure realized
 - in this situation MFA gives reasonable descriptions
 - energy of systems depends on magnetic structures
 - lowest energy structure is realized at ground states

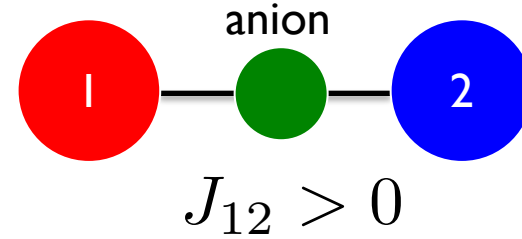
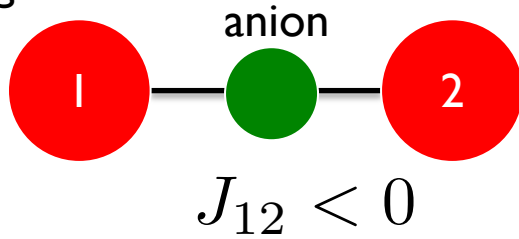
Magnetic ions in solids

- consider a situation where interactions are large enough to realize a magnetic state
 - each atom carries a magnetic moment
- consider at $T=0$
 - which magnetic structure is most stable?
 - what determines the magnetic structure?

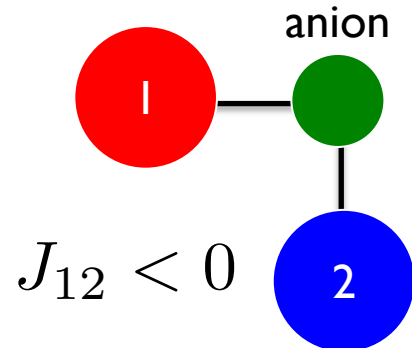
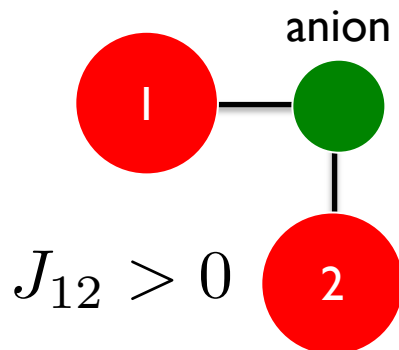
Kanamori–Goodenough rule

■ exchange interactions of oxides and halides

180° configuration



90° configuration



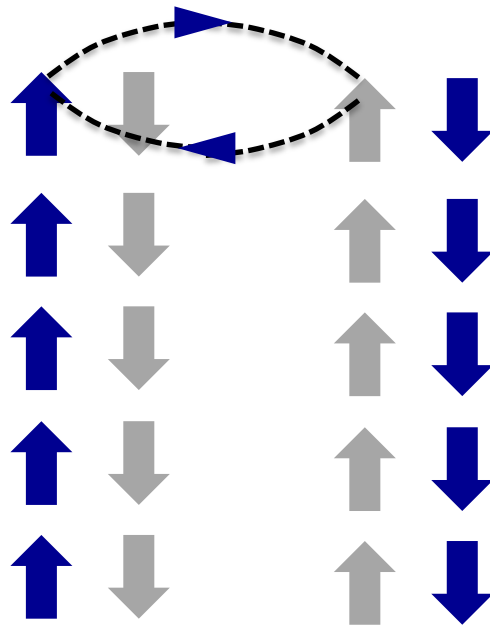
Analysis using Hubbard model

- simple but qualitatively correct

$$H = t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}$$

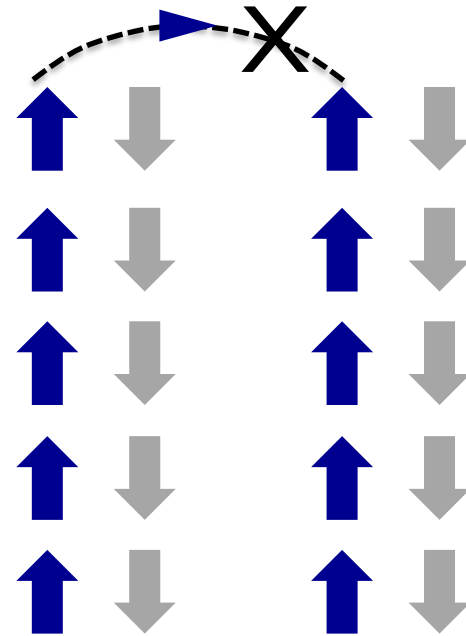
superexchange

energy gain due to electron transfer $-\frac{t^2}{U}$



antiferromagnetic
atom 1 atom 2

no energy gain because electron transfer is prohibited



ferromagnetic
atom 1 atom 2

Analysis using Hubbard model

- simple but qualitatively correct

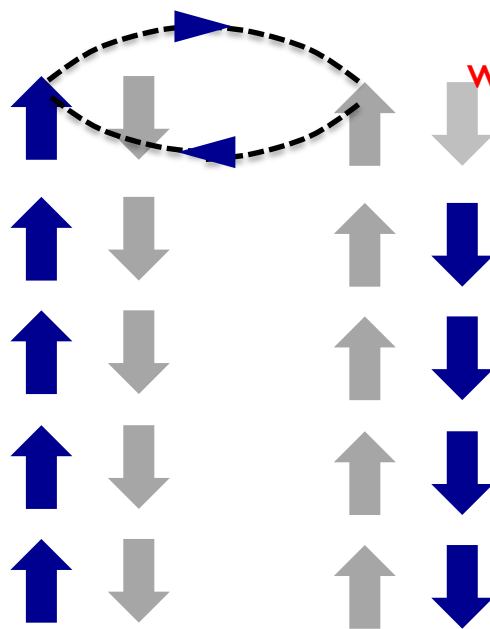
$$H = t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}$$

superexchange

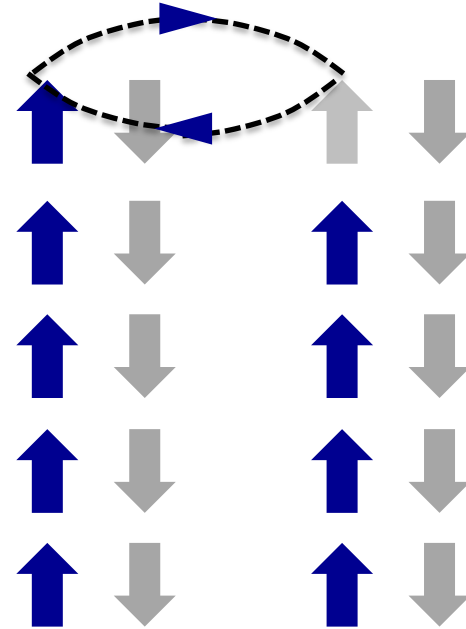
double-exchange

energy gain due to electron transfer $-\frac{t^2}{U}$

energy gain due to electron transfer $-nt$



when holes exist



antiferromagnetic

ferromagnetic

atom 1

atom 2

atom 1

atom 2

Ferromagnetism appears if carriers exist

- at half-filled cases only superexchange works
 - antiferromagnetic (effects in second order of t)
- if carriers exist, double-exchange works in proportion to carrier concentration (effects in first order in t)
 - when n exceeds some value, ferromagnetism appears
- for small t 's, even a small n realizes ferromagnetism

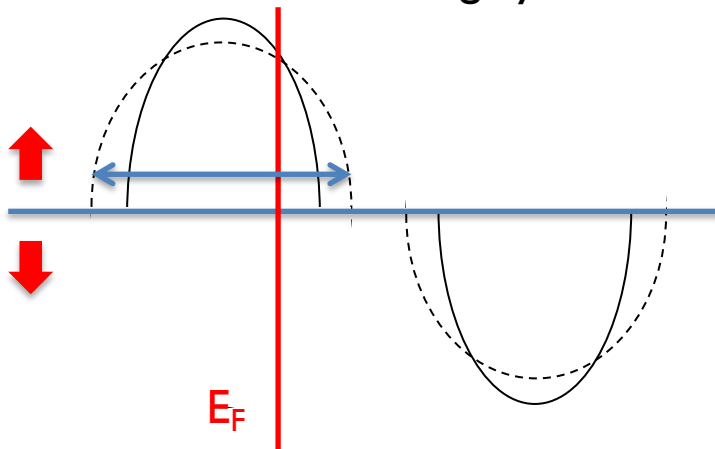
$$\frac{t^2}{U} < nt \quad \text{for small } t$$

In terms of band electron

■ two mechanisms in band picture

ferromagnetism stabilized

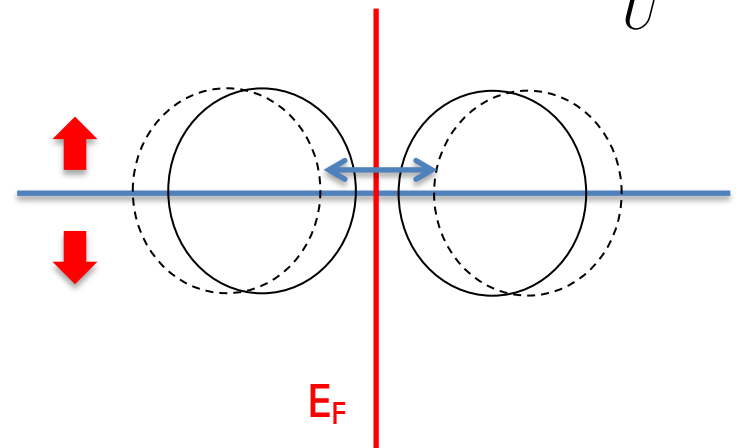
band broadening by $2t$



double-exchange

antiferromagnetism stabilized

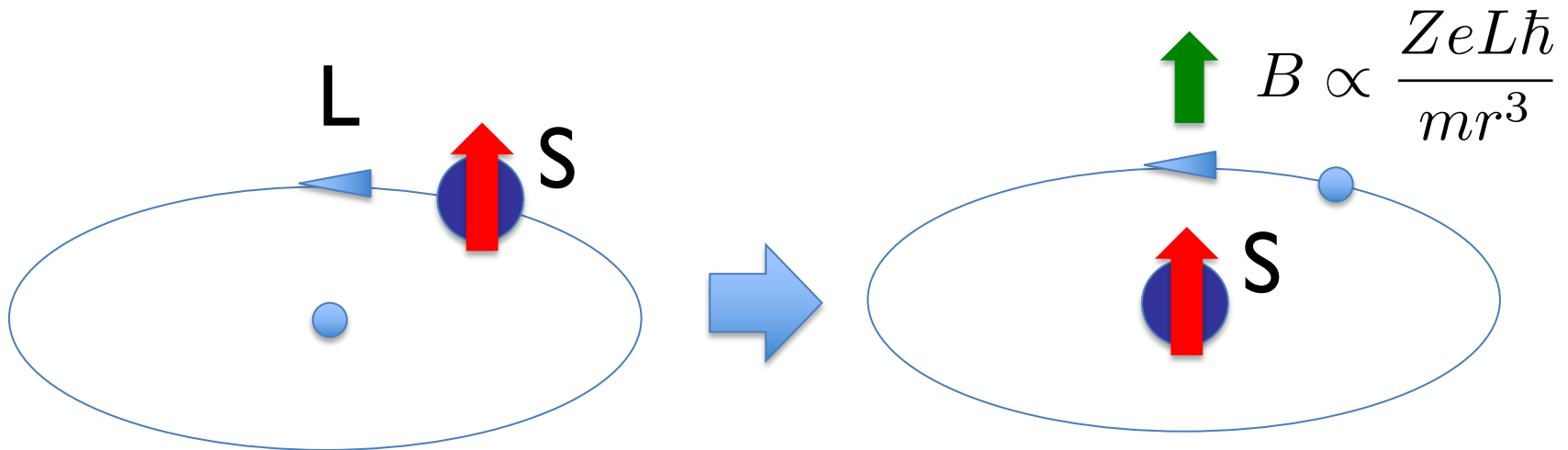
widening of split by $2\frac{t^2}{U}$



superexchange

Spin-orbit interaction

- a relativistic effect
- in view of electrons turning around a nucleus, the nucleus is turning around the electrons
- turning nucleus thus produces electric current



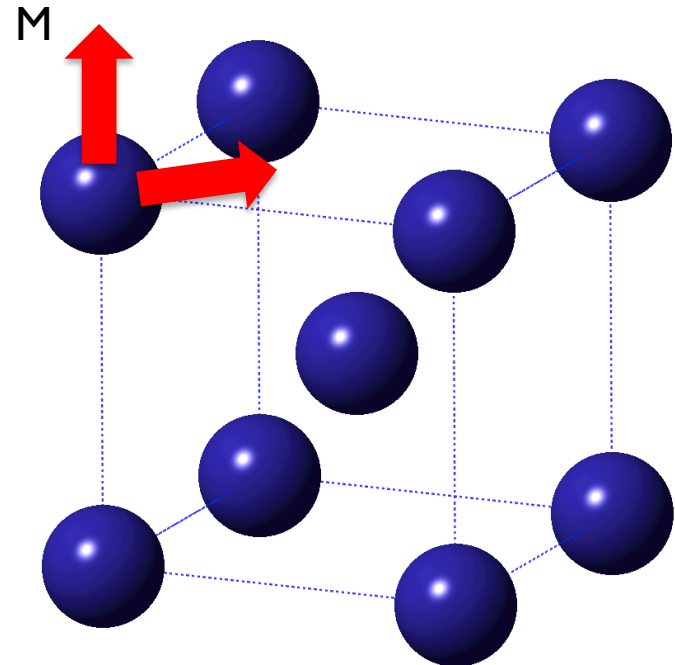
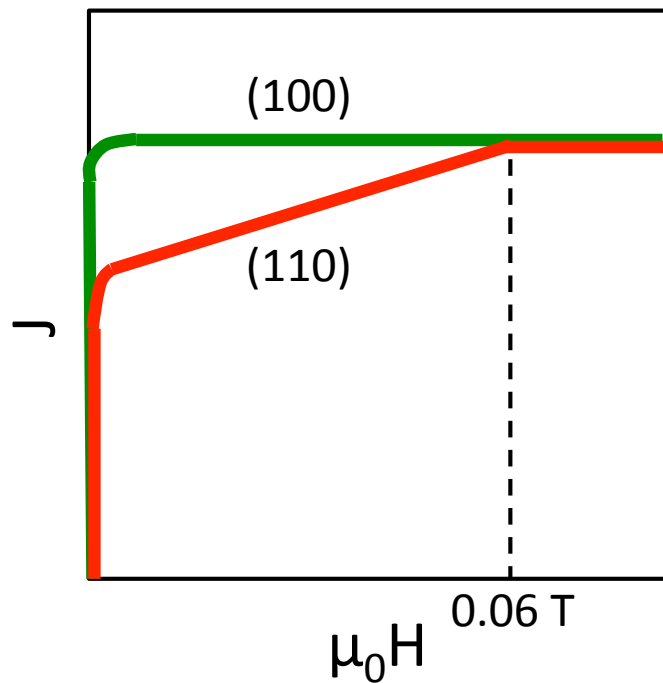
$$H_{\text{so}} = \lambda \mathbf{L} \cdot \mathbf{S}$$

Effects of spin-orbit interaction

- magnetic anisotropy
 - without spin-orbit interaction, spins do not see lattices
 - because of spin-orbit interactions, correlation between directions of spins and lattice orientations arises
 - spins prefer special direction relative to a lattice
- anisotropic exchange interaction
- anti-symmetric exchange interaction
(Dzyaloshinsky–Moriya interaction: DMI)
- orbital magnetic moment in crystals

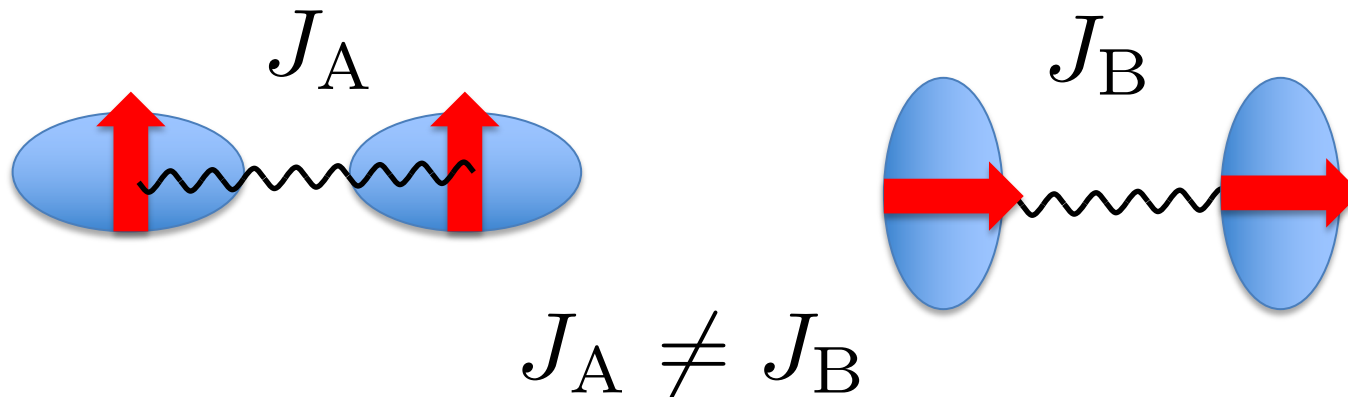
Magnetic anisotropy

- there exists a special direction to which magnetization is apt to align



Anisotropic exchange

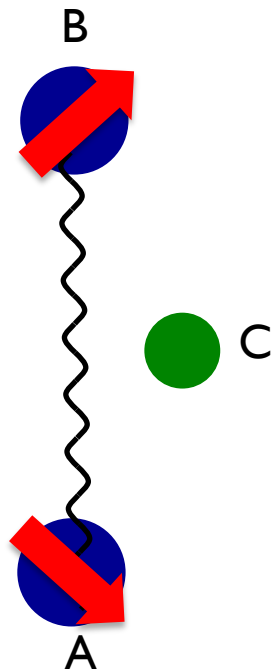
- orbitals are distorted as a result of spin-orbit interaction
- exchange interaction thus depends on the direction of spins



This interaction can be expressed as $\mathbf{S}_A \mathbf{J} \mathbf{S}_B$ using symmetric tensor \mathbf{J}

Dzyaloshinsky–Moriya interaction

- because of spin-orbit interaction, J depends on direction (along or opposite way)



Due to $\sin \theta$ dependence, the two spins cant

- from A to B, there is C to the **right** of interaction line

- from B to A, there is C to the **left** of interaction line

As a result $J_{AB} \neq J_{BA}$

In general J is expressed as

$$J = J_s \pm J_a$$

This can either be expressed using spin as

$$-2J\mathbf{S}_A \cdot \mathbf{S}_B + \mathbf{D} \cdot (\mathbf{S}_A \times \mathbf{S}_B)$$

The second terms is called anti-symmetric exchange interaction (Dzyalonsinsky–Moriya interaction: DMI). The interaction depends on the angle between direction of two spins θ as $\sin \theta$.

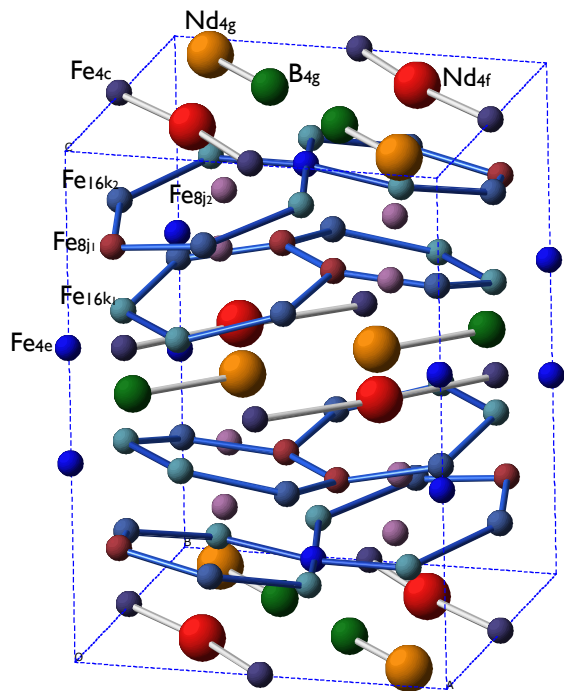
Heisenberg model

- phenomenological model describing magnetism of materials
- describes magnetic behavior of magnetic insulators rather well
- sometimes can be used for phenomenological description of metallic magnetism as well (there also are many cases where this does not work at all)

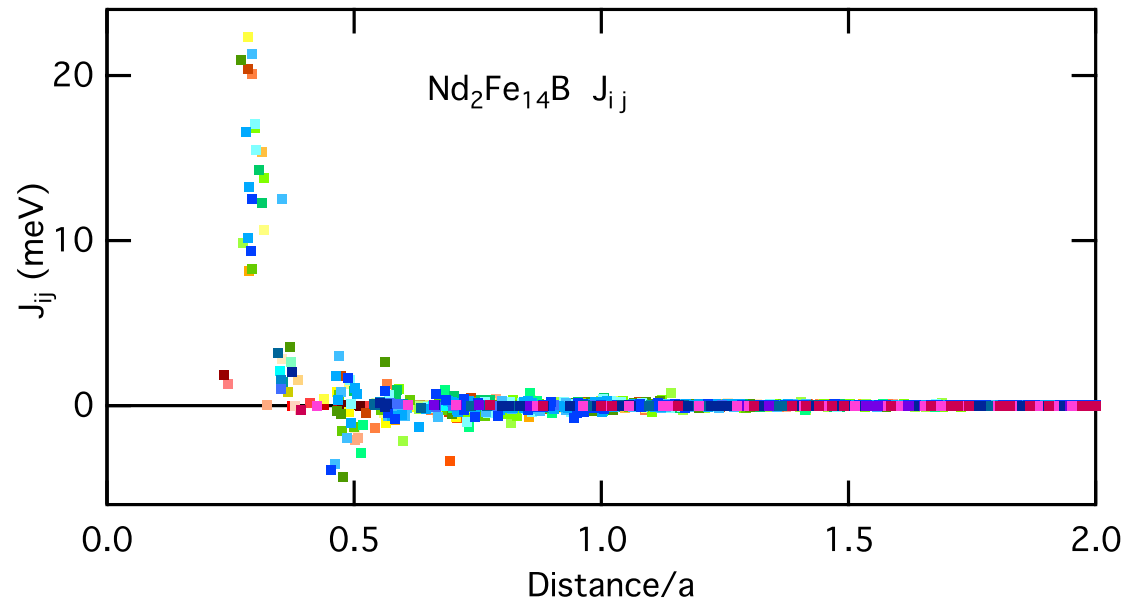
$$H = - \sum_{\langle ij \rangle} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

J_{ij} obtained from electronic structure calculation

■ example of calculated exchange coupling constants



Nd₂Fe₁₄B 68 atoms/u.c. P4₂/mnm



Heisenberg model

- magnetic anisotropy, anisotropic exchange, antisymmetric exchange, etc. can be also treated in the framework
- variations such as Ising model, XY model
- typical playground for statistical physics is used to discuss finite temperature properties and phase transitions of magnetic materials.

$$H = - \sum_{\langle ij \rangle} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Summary

- magnetism of insulators in mind, we discussed
 - atomic magnetism
 - molecular magnetism and exchange interactions
 - mechanisms of exchange interactions
 - exchange interactions between magnetic ions in crystals
 - effects of spin-orbit interactions
 - Heisenberg model
- for further study:
 - J. Kanamori, “Magnetism” (Japanese) (Baifukan, Physics Series 7)