Spintronics Basic II

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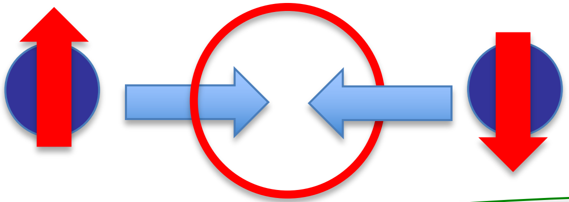
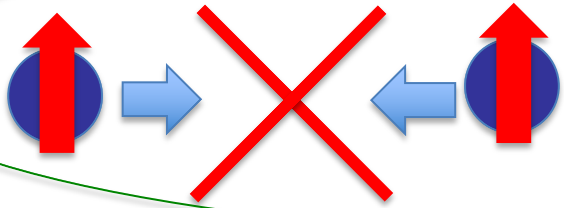
Contents

Interaction between electrons

🟩 two electrons–Pauli's exclusion principle works



possibility of two electrons coming closer
→ increase in coulombic energy



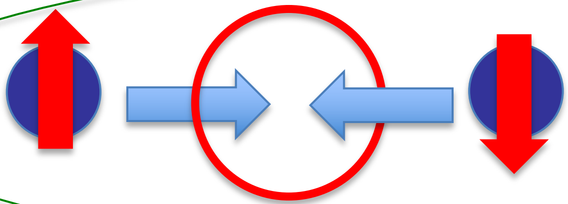
less probable that two electrons come closer
→ decrease in coulombic energy

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

parallel spins preferable in view of interaction

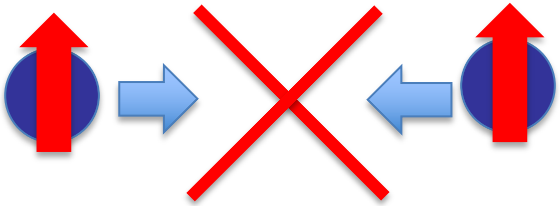
Kinetic energy of electrons

🟩 two electrons–Pauli's exclusion principle works



no limitation to the volume that electrons can move freely

→ no increase in kinetic energy



the volume that electrons can move is halved

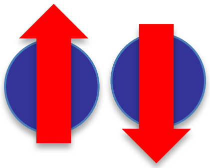
→ increase in zero-point energy

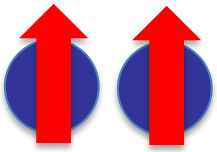
$$\Delta r \Delta p \sim \hbar$$

antiparallel spins preferable in view of kinetic energy

Exchange interaction between electrons

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

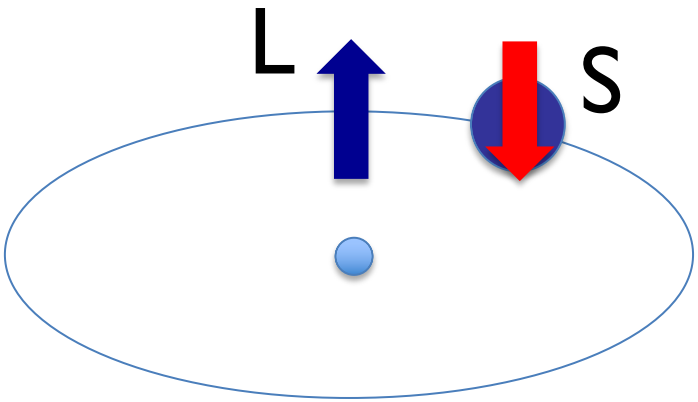




$$E_X = E_{\uparrow\downarrow} - E_{\uparrow\uparrow} \gtrless 0\ ?$$

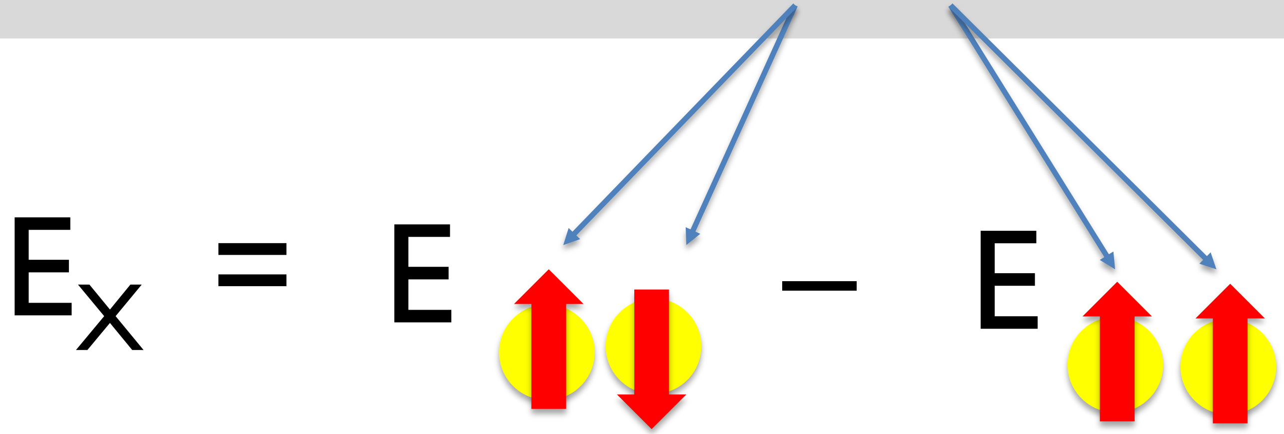
A single atom

- electrons are bound in a potential
- a neutral atom with an odd number of electrons
  - total electron spin: half integer
  - total orbital momentum: integer
  - non-zero total angular momentum
  - shows magnetism in general (paramagnetic)



Two atoms

- interaction between atomic magnetic moments
  - parallel or antiparallel coupling?
  - exchange interaction between atoms (not electrons)



$$E_X = E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$$

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 $v(r-R)$ R: center of the atom

	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 exists

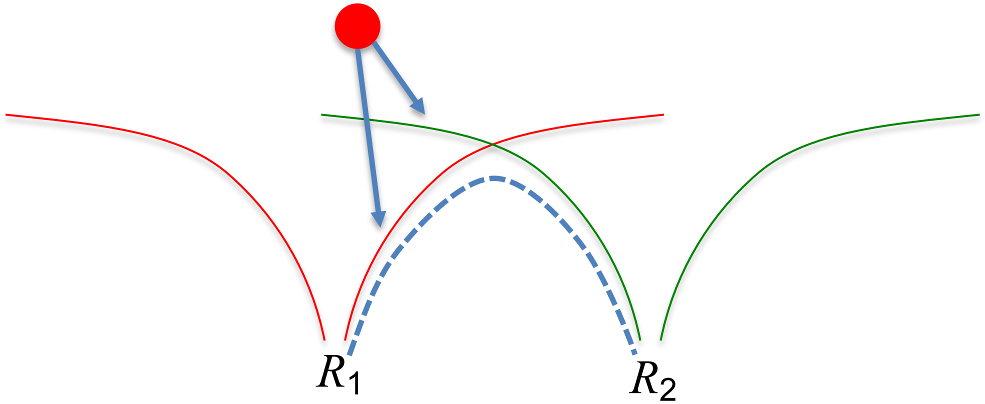
Hamiltonian of a hydrogen molecule

coulombic interaction

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

$$H_{12} = v(r_1 - R_2) + v(r_2 - R_1)$$

atractive potential due to the other atom



Parallel or antiparallel?

- Simple model I: Heitler–London limit
  - assume that no charge fluctuation occurs in each atom
  - 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

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

$$H_{12} = v(r_1 - R_2) + v(r_2 - R_1)$$

atractive potential due to the other atom

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

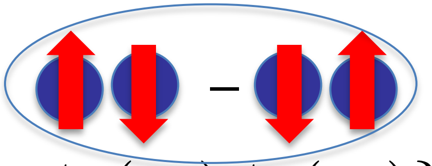
molecular energy $E \simeq \int \Psi^* H \Psi \, d^3 r$

Parallel or antiparallel?

Simple model I: Heitler–London limit

- antisymmetrization (sign change associated with exchange of two electrons)
- two cases occur depending on spin configuration

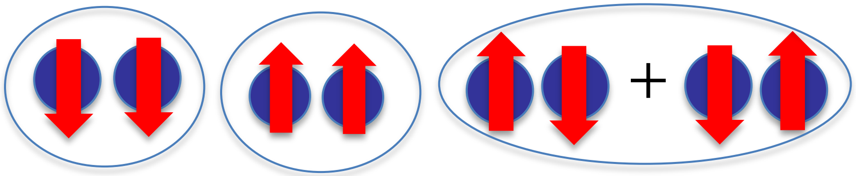
s=0 state (spin singlet)



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

(orbital symmetric, spin antisymmetric)

s=1 state (spin triplet)



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

(orbital antisymmetric, spin symmetric)

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

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

$$E_{\mathrm{x}}=E_0-E_1$$

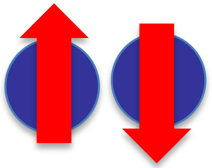
Parallel or antiparallel?

Simple model 1: Heitler–London limit

s=0 state（spin singlet）

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

strong interaction V



$$\Psi_0(r_1,r_2)\neq 0$$ even if $r_1=r_2$

s=1 state（spin triplet）

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

weak interaction V

$$\Psi_1(r_1,r_2)=0$$ if $r_1=r_2$

$$\boxed{\int\Psi_0(r_1,r_2)V\Psi_0(r_1,r_2)dr_1dr_2>\int\Psi_1(r_1,r_2)V\Psi_1(r_1,r_2)dr_1dr_2}$$

Parallel or antiparallel?

Simple model I: Heitler–London limit

s=0 state（spin singlet）

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

$$\int \Psi_0(r_1, r_2)(H_1 + H_2 + H_{12})\Psi_0(r_1, r_2)dr_1 dr_2 = 2\epsilon'$$

s=1 state（spin triplet）

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

$$\int \Psi_1(r_1, r_2)(H_1 + H_2 + H_{12})\Psi_1(r_1, r_2)dr_1 dr_2 = 2\epsilon'$$

the same energy except coulombic interaction energy

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

Heitler–London limit

therefore

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

$$E_{\mathrm{x}} = E_0 - E_1 > 0$$

- 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}
  - ε’ < ε : 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

$$\Psi_{\mathrm{b}}(r) = A\{\phi_1(r) + \phi_2(r)\}$$

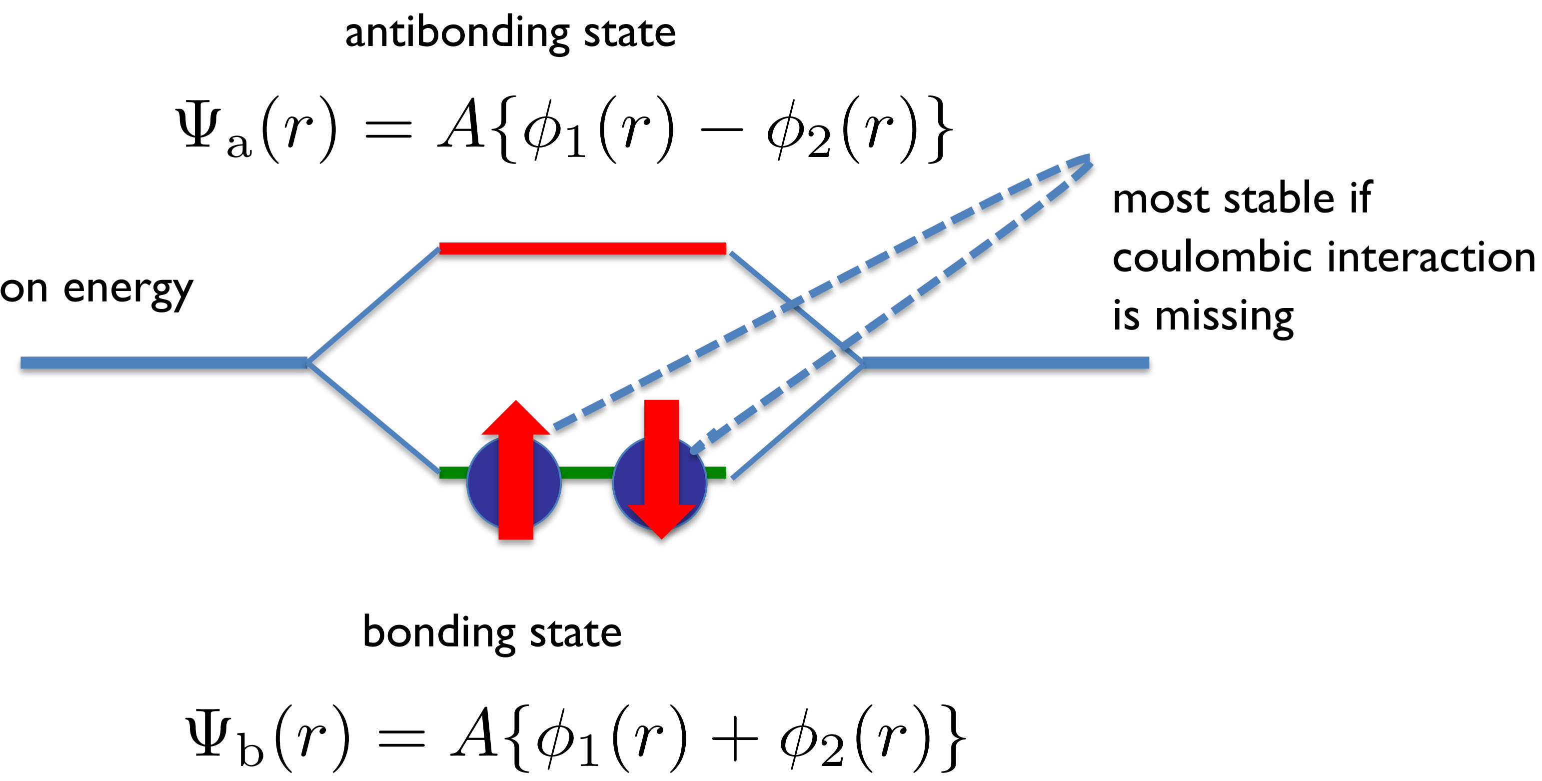
antibonding state

$$\Psi_{\mathrm{a}}(r) = A\{\phi_1(r) - \phi_2(r)\}$$

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

Parallel or antiparallel?

Simple model 2: molecular orbital limit



antibonding state

$$\Psi_\mathrm{a}(r) = A\{\phi_1(r) - \phi_2(r)\}$$

most stable if coulombic interaction is missing

single electron energy

bonding state

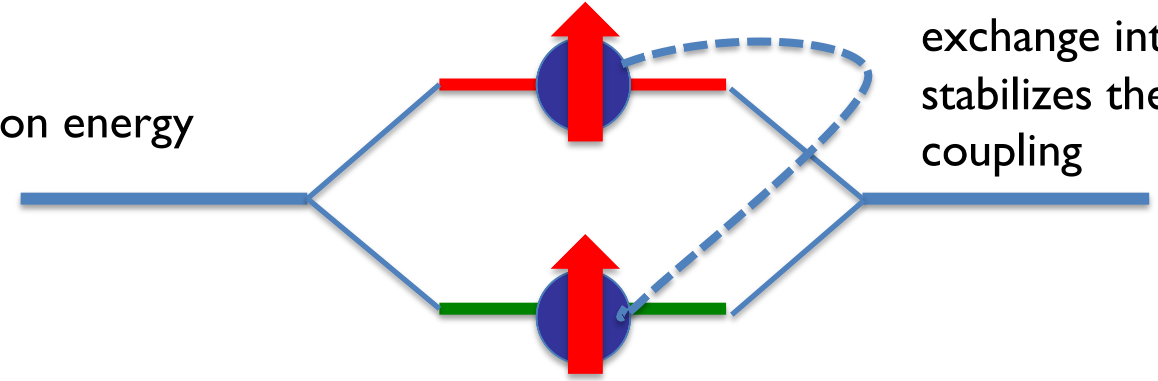
$$\Psi_\mathrm{b}(r) = A\{\phi_1(r) + \phi_2(r)\}$$

Parallel or antiparallel?

■ Simple model 2: molecular orbital limit

antibonding state

$$\Psi_{\mathrm{a}}(r) = A\{\phi_1(r) - \phi_2(r)\}$$



single electron energy

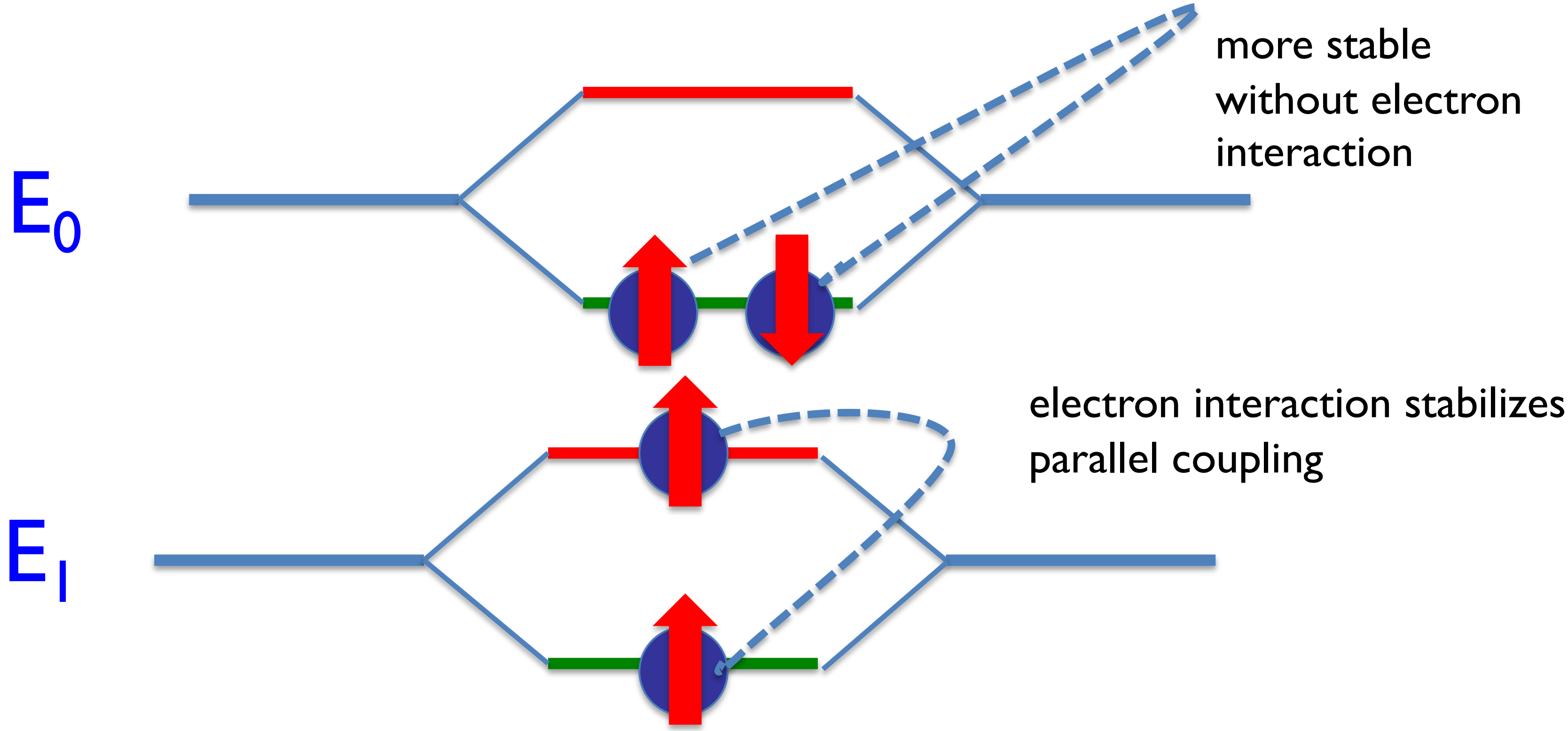
exchange interaction
stabilizes the parallel
coupling

bonding state

$$\Psi_{\mathrm{b}}(r) = A\{\phi_1(r) + \phi_2(r)\}$$

Parallel or antiparallel?

- Simple model 2: molecular orbital limit



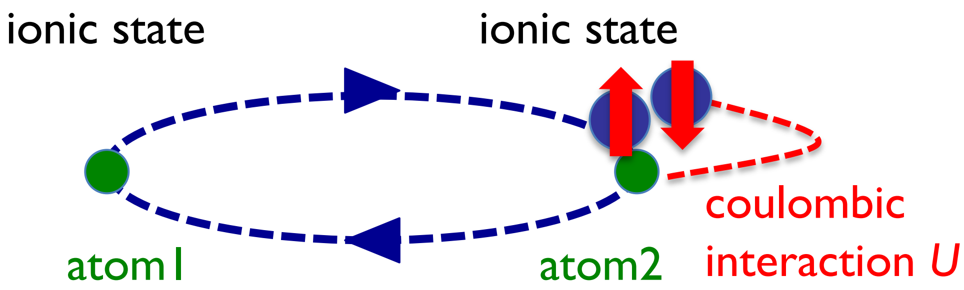
more stable without electron interaction

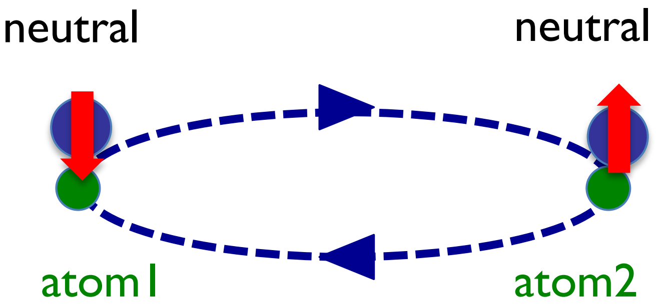
electron interaction stabilizes parallel coupling

$$E_0 < E_1 \quad \text{or} \quad E_0 > E_1 \ ?$$

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

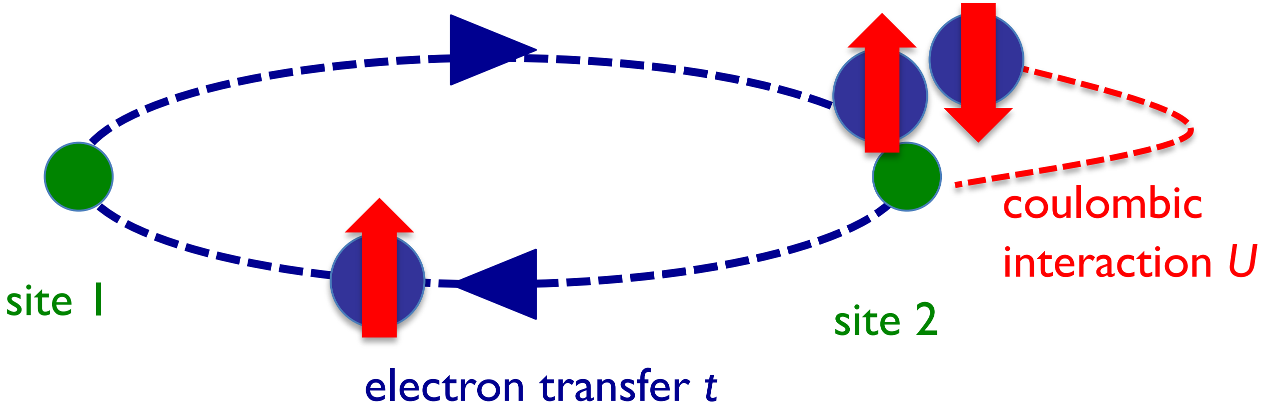




Analysis using simple model

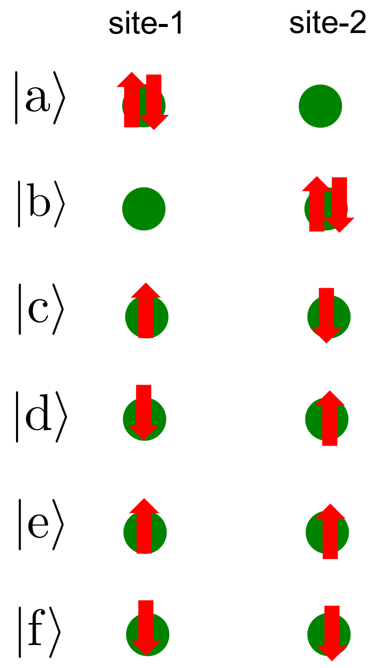
2-site Hubbard model

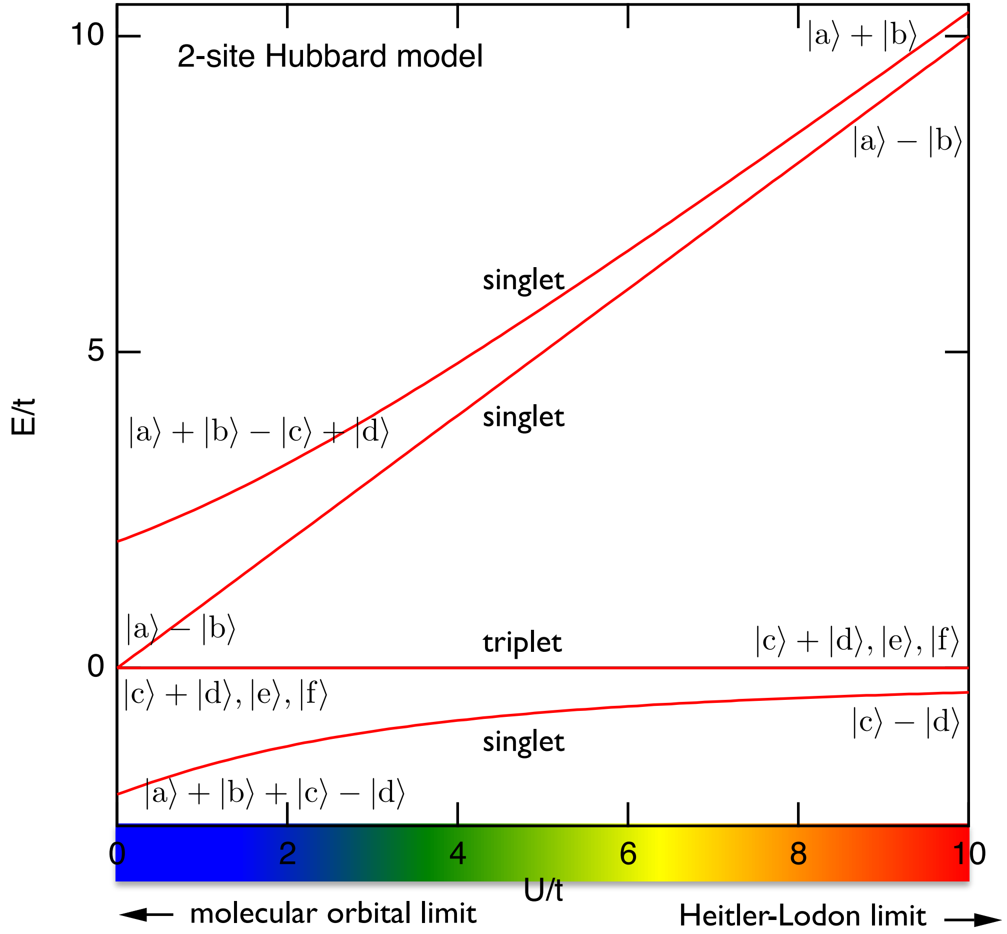
$$H = t \sum_{\sigma} (a^{\dagger}_{1\sigma} a_{2\sigma} + a^{\dagger}_{2\sigma} a_{1\sigma}) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}$$



Exact solution

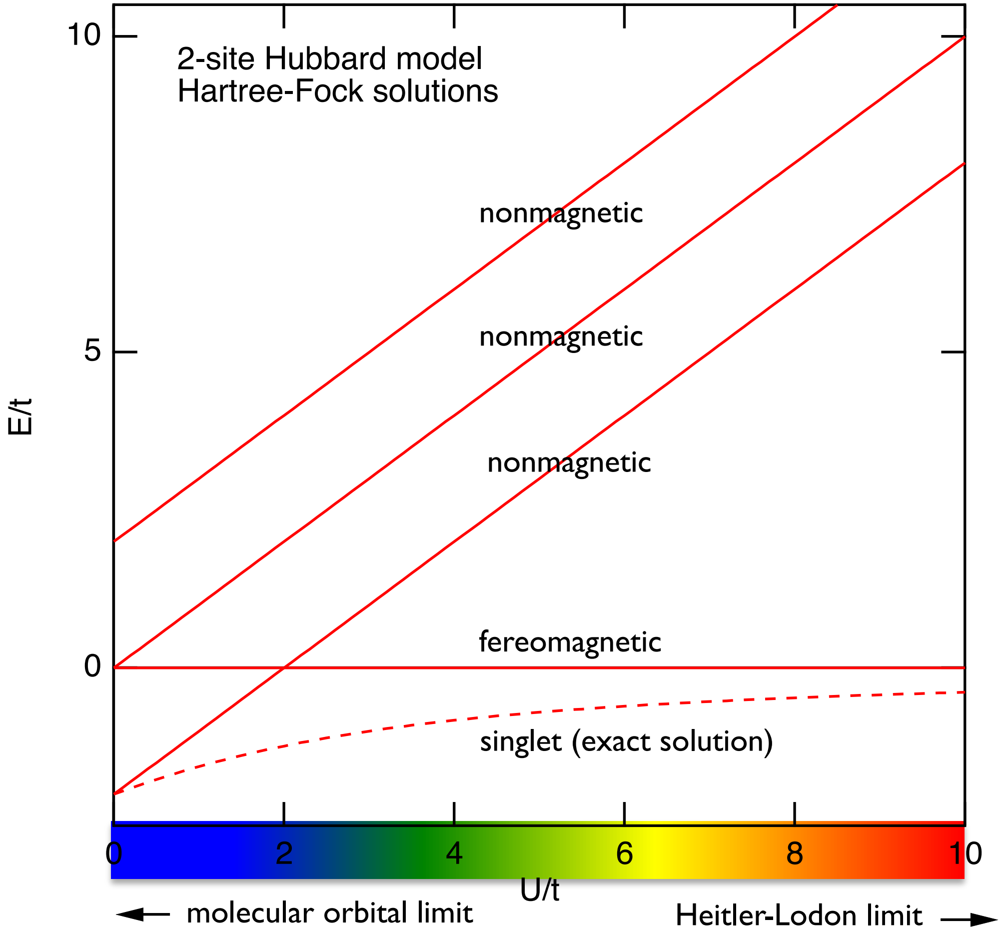
- eigen states of arbitrary *U*/*t*





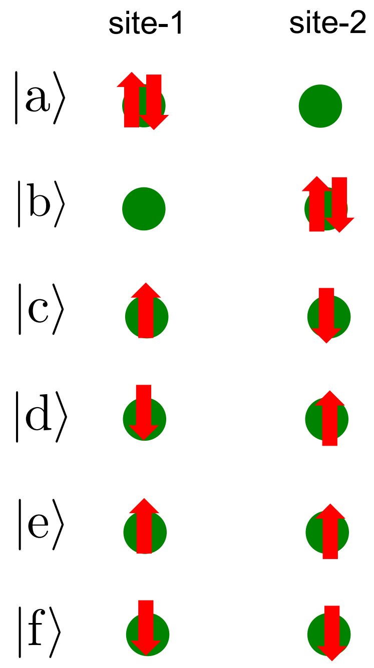
Mean field approximation (MFA)

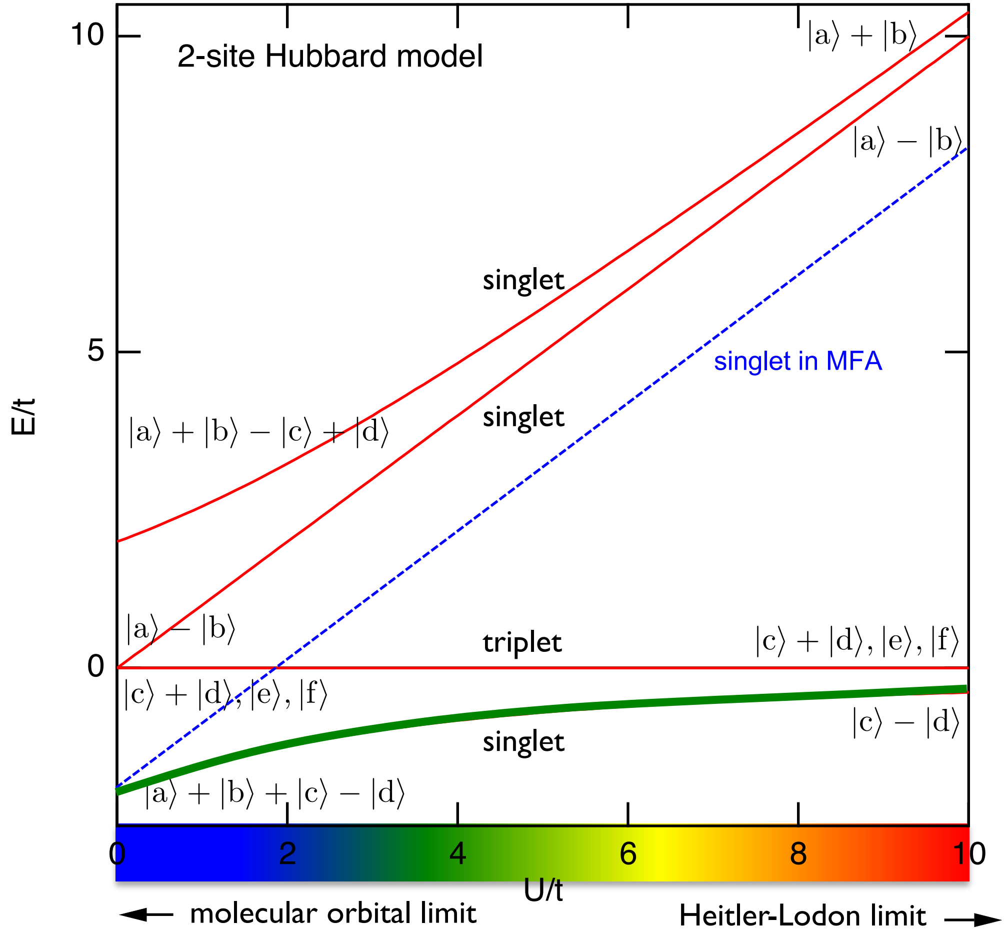
- nonmagnetic to ferromagnetic transition occurs



Exact solution

- ground state is spin singlet state for any *U*





Mean field approximation (MFA)

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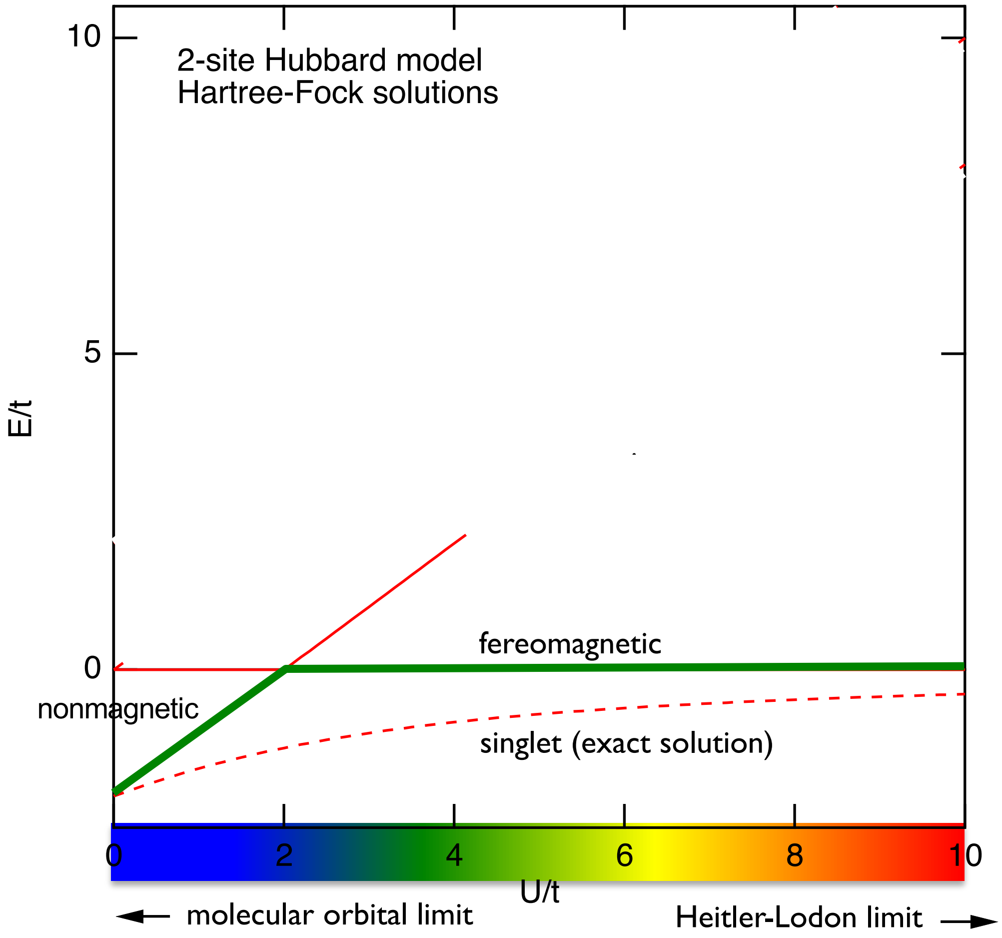


In reality

- 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 $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ of atom 1 and atom 2, there exists an interaction of a form

$$E_{\mathrm{x}} = E_0 - E_1 = -2(J_{12} + W_{12})\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$$

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 either be 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 strong 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 haleids

180° configuration

90° configuration

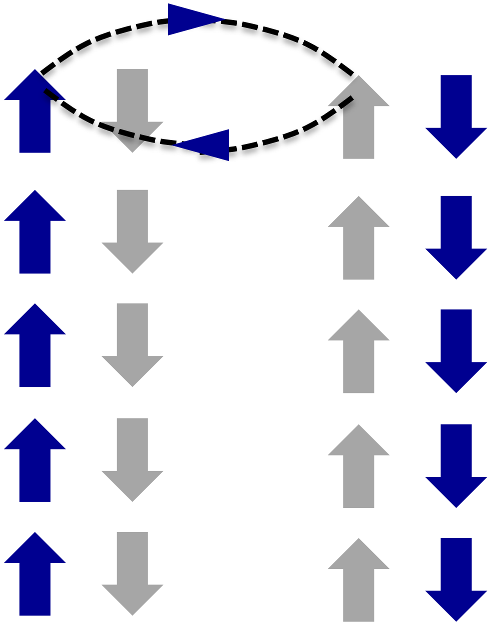
Analysis using Hubbard model

- simple but qualitatively correct

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

superexchange

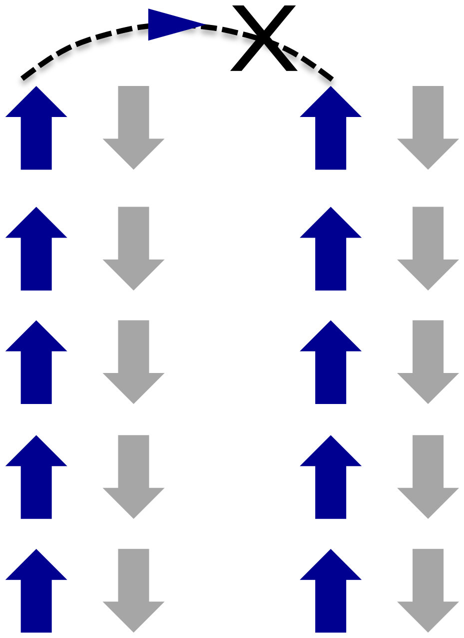
energy gain due to electron transfer $-\frac{t^2}{U}$



antiferromagnetic

atom1 atom2

no energy gain because electron transfer is prohibited



ferromagnetic

atom1 atom2

Analysis using Hubbard model

- simple but qualitatively correct

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

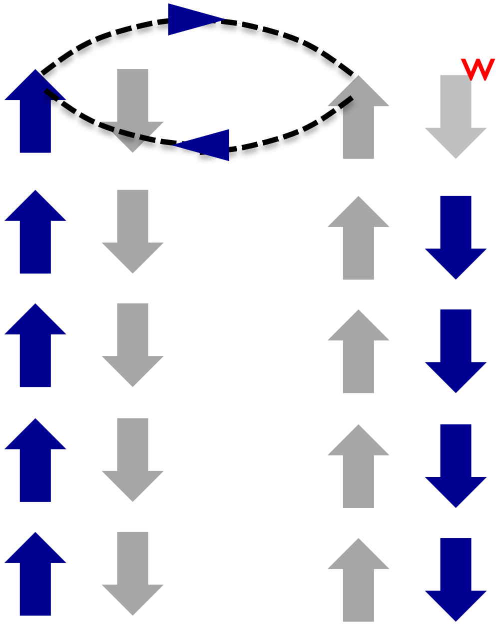
superexchange

double-exchange

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

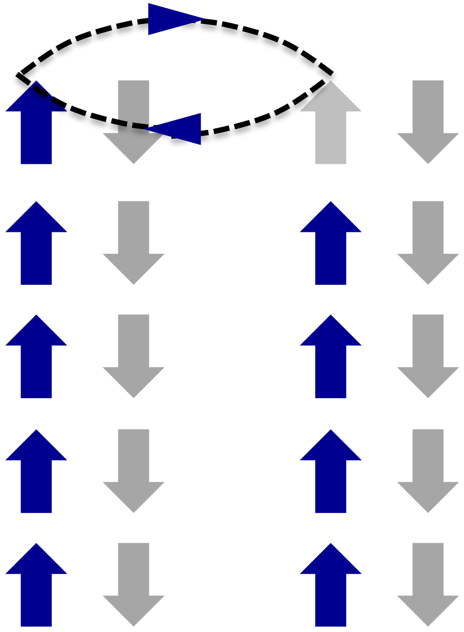
energy gain due to electron transfer $-nt$

when holes exist



antiferromagnetic

atom1 atom2



ferromagnetic

atom1 atom2

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

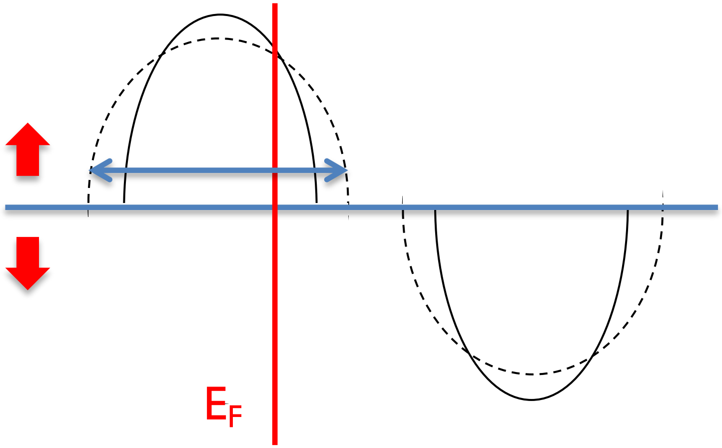
$$\frac{t^2}{U} < nt \quad \text{for small} \quad t$$

In terms of band electron

- two mechanisms in band picture

ferromagnetism stabilized

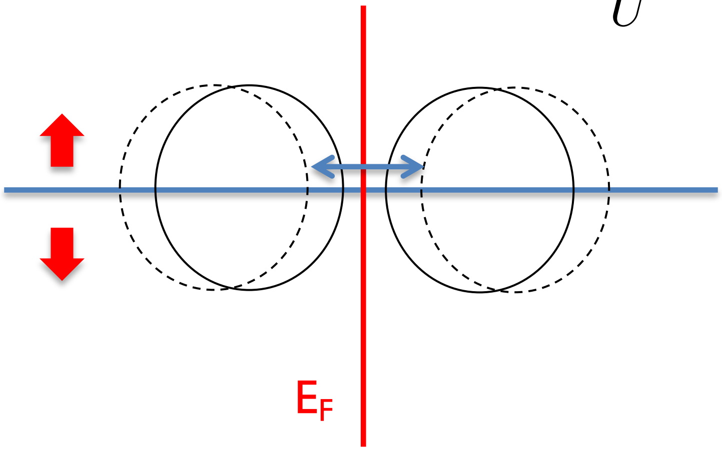
band broadening by $2t$



double-exchange

antiferromagnetism stabilized

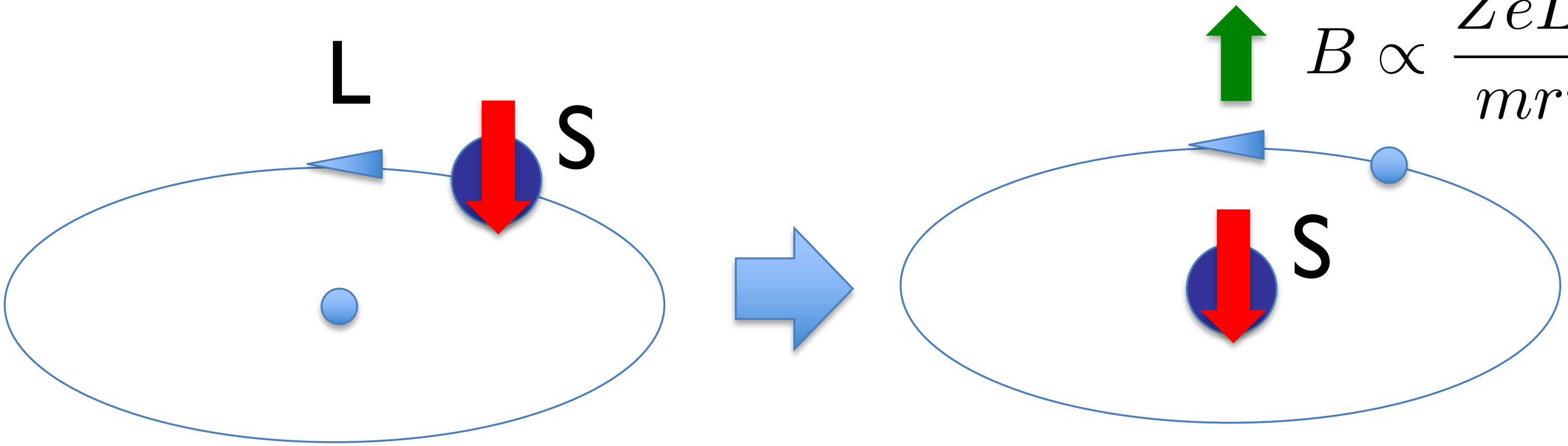
widening of split by $2\frac{t^2}{U}$



spuperexchange

Spin-orbit interaction

- a relativistic effect
- in view of an electron that turns around a nucleus, the nucleus is turning around that electron
- turning nucleus thus produces electric current



$$B \propto \frac{ZeL\hbar}{mr^3}$$

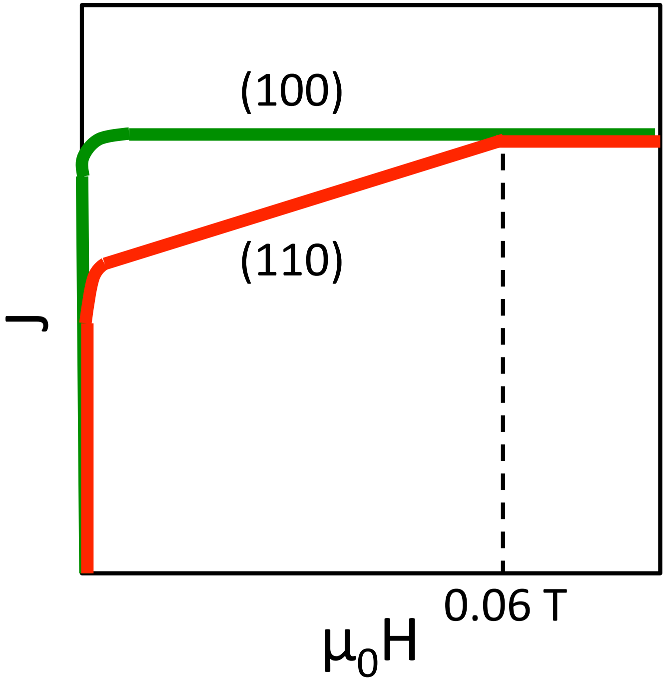
$$H_{\mathrm{so}} = \lambda \boldsymbol{L} \cdot \boldsymbol{S}$$

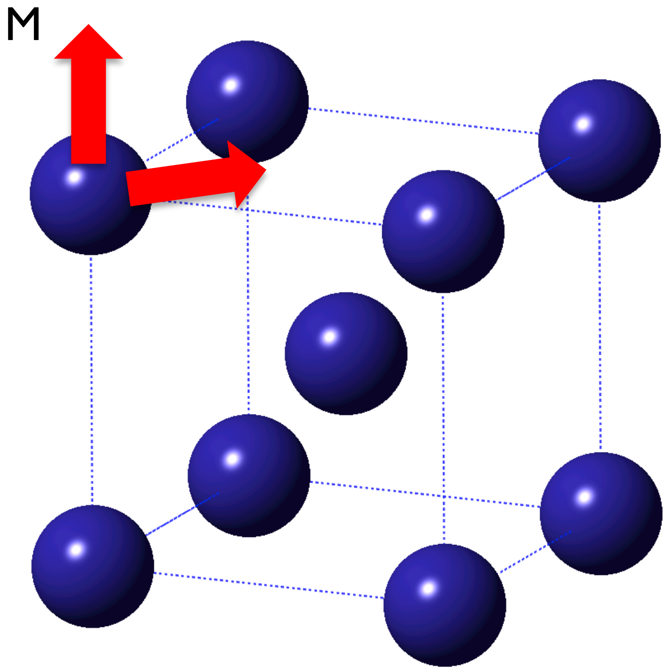
Effects of spin-orbit interaction

- 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 in a lattice
- anisotropic exchange interaction
- anti-symmetric exchange interaction (Dzyaloshinskii–Moriya interaction: DMI)
- orbital magnetic moment in crystals

Magnetic anisotropy

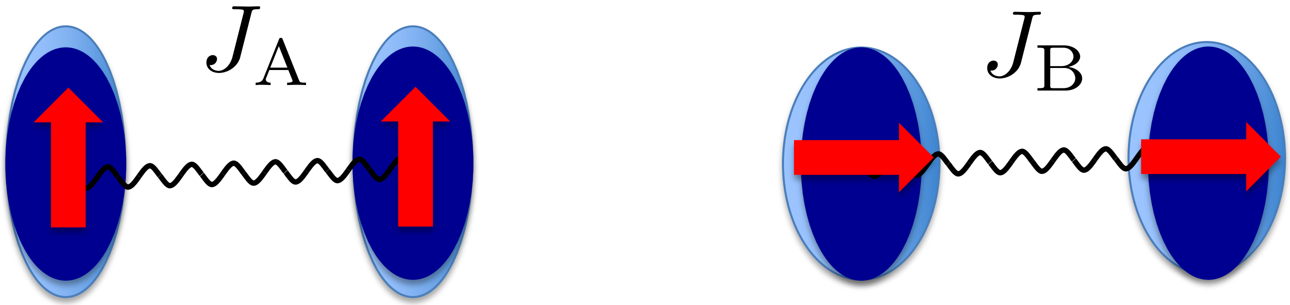
- there exists a special direction to which magnetization is apt to aligns





Anisotropic exchange

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

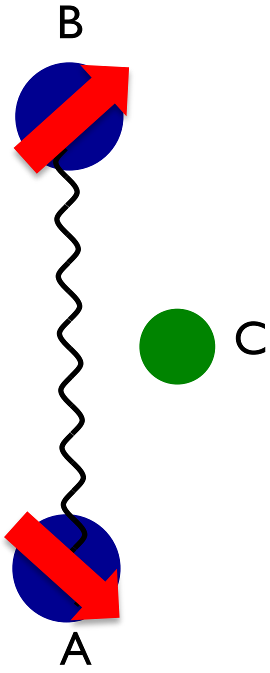


$$J_\mathrm{A} \neq J_\mathrm{B}$$

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

Dzyaloshinskii–Moriya interaction

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



Due to sin θdependence, 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 $J_{\mathrm{AB}} \neq J_{\mathrm{BA}}$

In general J is expressed as

$$J = J_{\mathrm{s}} \pm J_{\mathrm{a}}$$

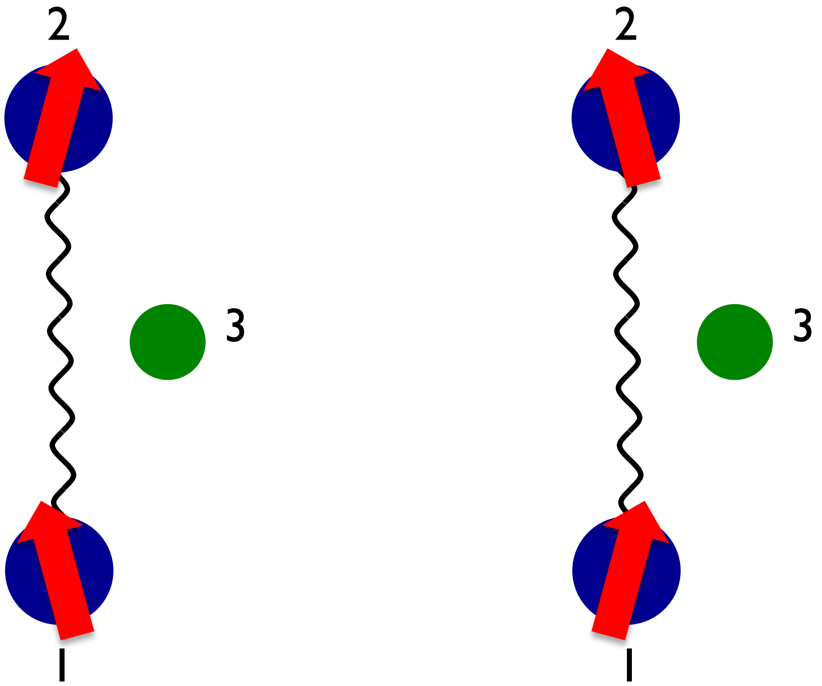
This can either be expressed using spin as

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

The second terms is called anti-symmetric exchange interaction (Dzyalonshinsky–Moriya interaction: DMI). The interaction depends on the angleθ between direction of two spins as sinθ.

Dzyaloshinskii–Moriya interaction

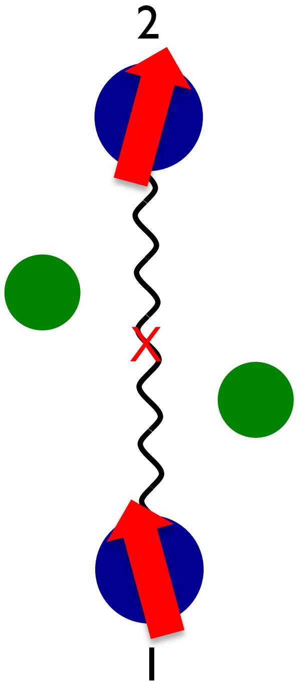
When no inversion symmetry exits.



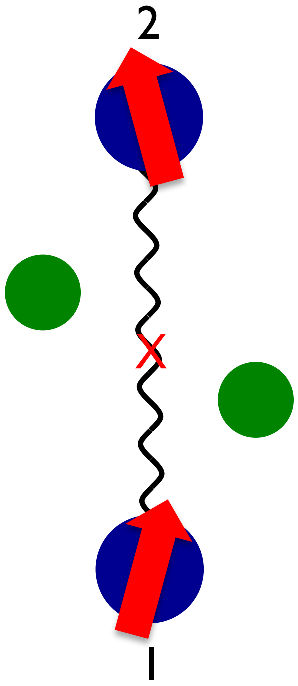
(A) (B)

Dzyaloshinskii–Moriya interaction

When a inversion center exits at the center of the interaction line.



(A)



(B)

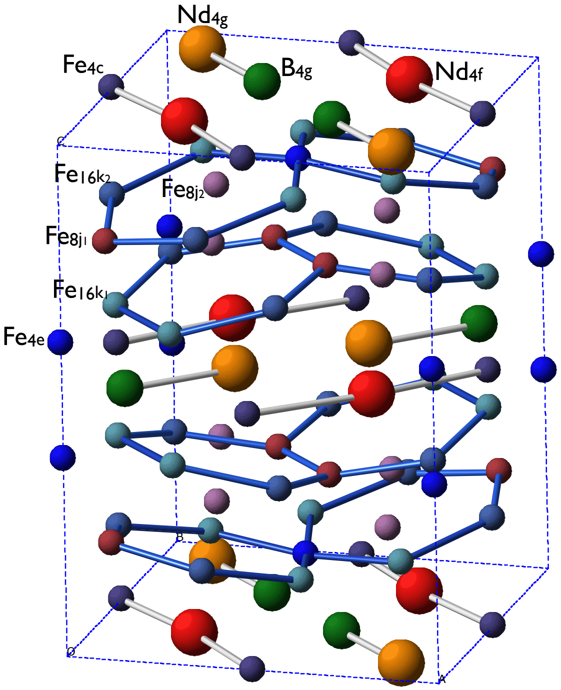
Heisenberg model

- 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) ⇒low energy effective hamiltonian

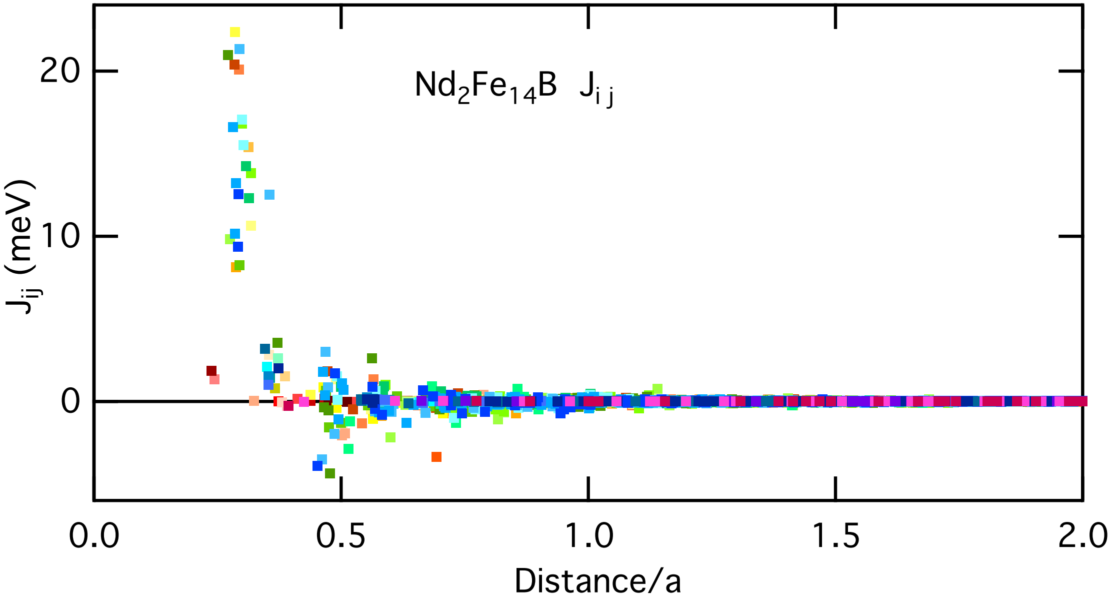
$$H = -\sum_{<ij>} 2J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

J_{ij} obtained from electronic structure calculation

- example of calculated exchange coupling constants



$Nd_2Fe_{14}B$ 68 atoms/u.c. $P4_2/mnm$



Heisenberg model

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

$$H = -\sum_{<ij>} 2J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

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)