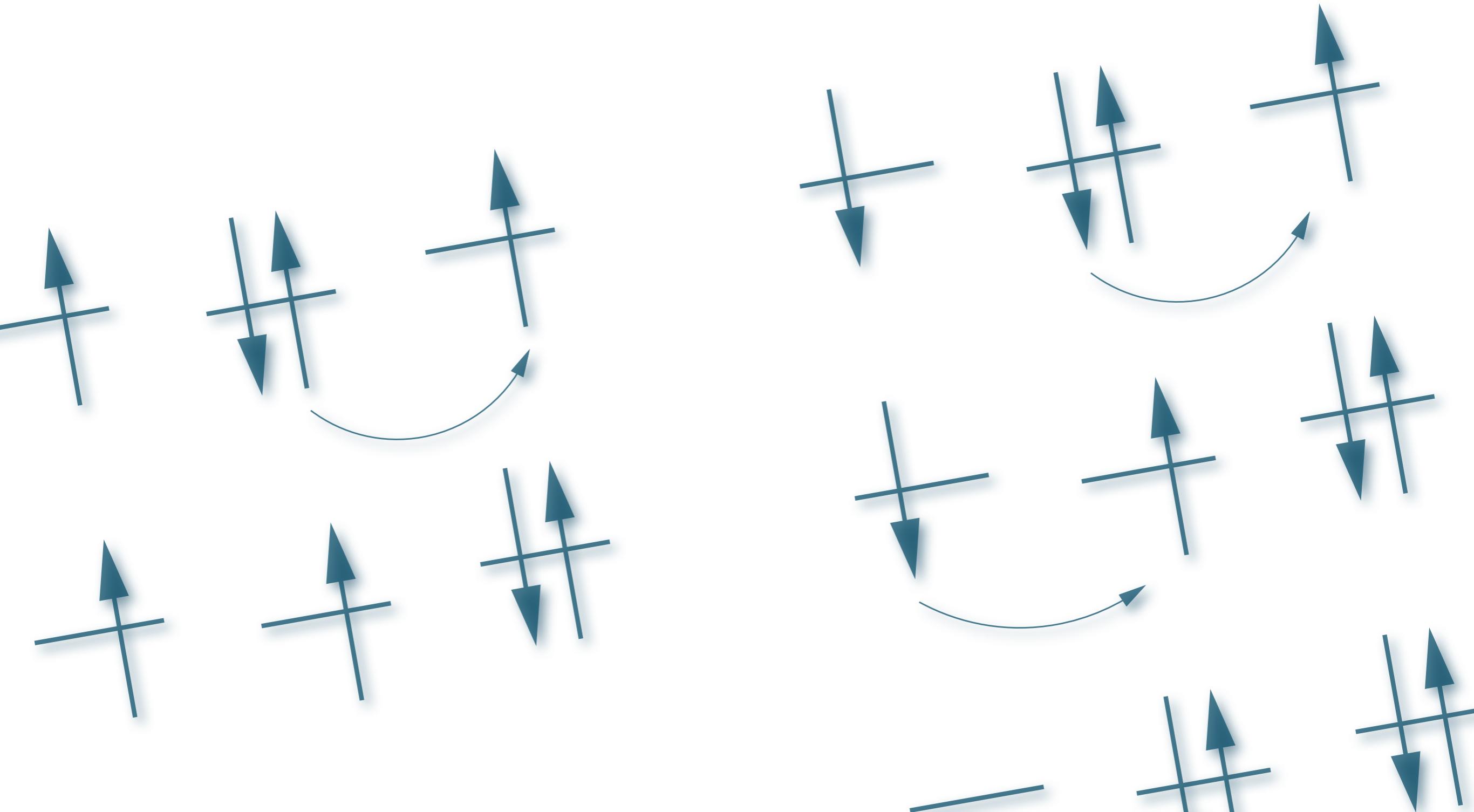


Exchange Mechanisms

Erik Koch

German Research School for Simulation Sciences, Jülich



Magnetism is Quantum Mechanical

QUANTUM MECHANICS THE KEY TO UNDERSTANDING MAGNETISM

Nobel Lecture, 8 December, 1977

J.H. VAN VLECK

Harvard University, Cambridge, Massachusetts, USA

Bohr – van Leeuwen theorem
in a classical system in thermal equilibrium
a magnetic field will not induce a magnetic moment

Lorentz force perpendicular to velocity \Rightarrow does not change kinetic energy
Boltzmann statistics occupies states according to energy

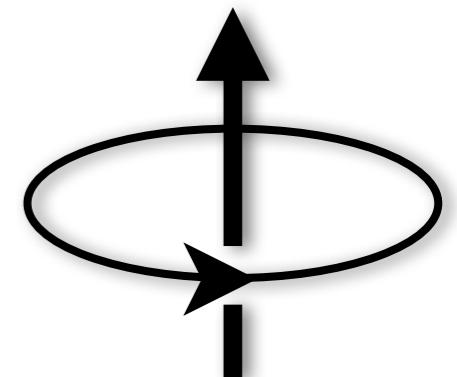
magnetic moments

complex wave function: current density

$$\vec{j}(\vec{r}) = -\frac{e\hbar}{2im_e} \left(\overline{\psi(\vec{r})} \nabla \psi(\vec{r}) - \psi(\vec{r}) \nabla \overline{\psi(\vec{r})} \right)$$

orbital magnetic moment

$$\vec{\mu} = \frac{1}{2} \int \vec{r} \times \vec{j} d^3 = -\frac{e\hbar}{2m_e} \langle \vec{L} \rangle = -\mu_B \langle \vec{L} \rangle$$



electron spin

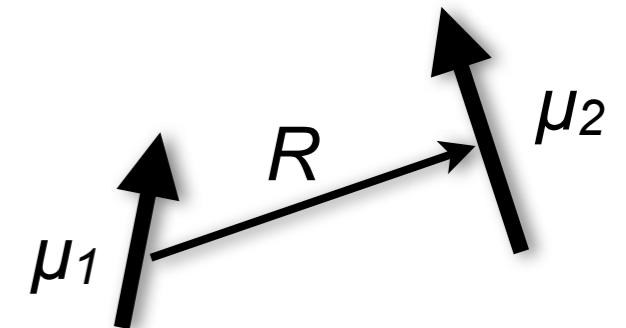
$$\vec{\mu}_S = -g_e \mu_B \langle \vec{S} \rangle, \quad g_e \approx 2.0023\dots$$

atomic moments of the order of μ_B

magnetic interaction

dipole-dipole interaction

$$\Delta E = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\hat{R} \cdot \vec{\mu}_1)(\hat{R} \cdot \vec{\mu}_2)}{4\pi\epsilon_0 c^2 R^3}$$



interaction energy of two dipoles μ_B two Bohr radii a_0 apart:

$$\Delta E = -\frac{2\mu_B^2}{4\pi\epsilon_0 c^2 (2a_0)^3} = -\frac{1/2}{137^2 8} \text{ Hartree} \approx 0.09 \text{ meV}$$



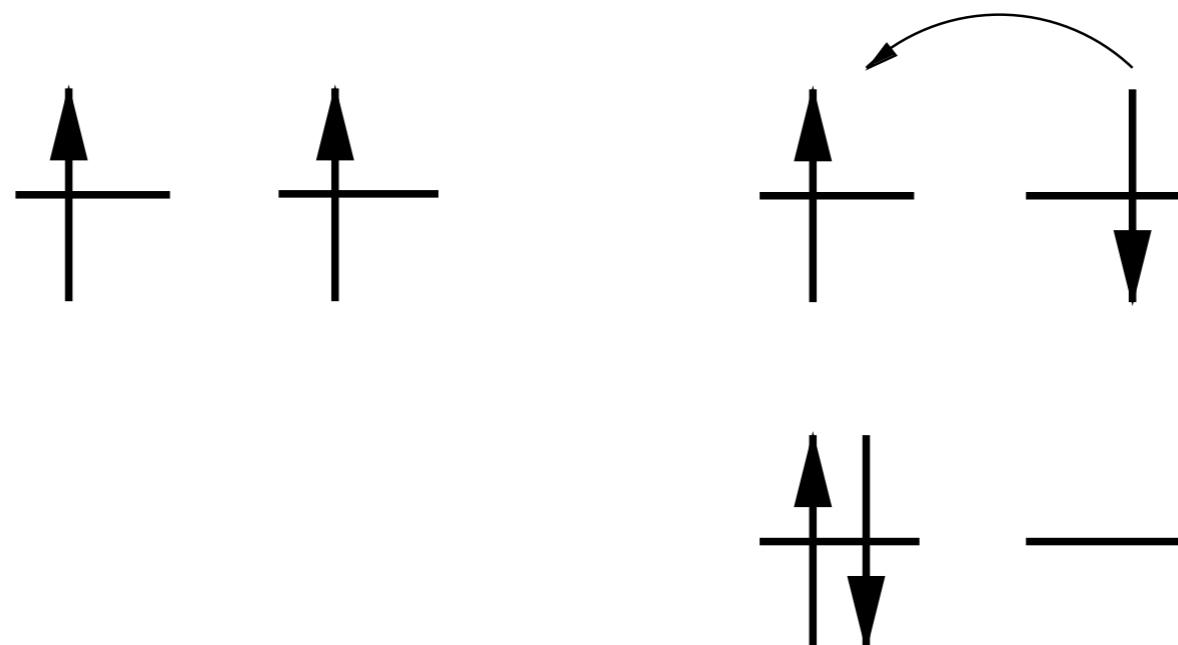
expect magnetic ordering below temperatures of about 1 K

what about magnetite (Fe_3O_4)
with $T_c \approx 840 \text{ K}$?



exchange mechanisms

coupling of magnetic moments
results from the interplay of
the Pauli principle
with Coulomb repulsion
and electron hopping



not a fundamental but an **effective interaction**: model/mechanism

Models and Mechanisms

The art of model-building is the exclusion of real but irrelevant parts of the problem, and entails hazards for the builder and the reader. The builder may leave out something genuinely relevant; the reader, armed with too sophisticated an experimental probe or too accurate a computation, may take literally a schematized model whose main aim is to be a demonstration of possibility.



P.W. Anderson
Local Moments and Localized States
Nobel Lecture 1977

Coulomb Exchange

Coulomb repulsion between electrons

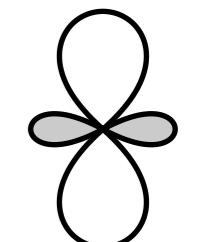
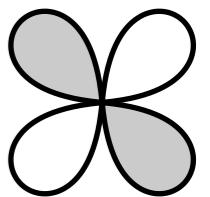
$$H_U = \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

consider two electrons in orthogonal orbitals φ_a and φ_b

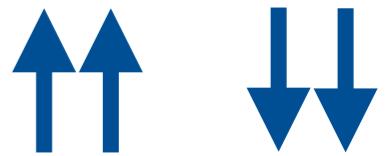
Slater determinant of spin-orbitals:

$$\psi_{a,\sigma; b\sigma'}(\vec{r}_1, s_1; \vec{r}_2, s_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\vec{r}_1) \sigma(s_1) & \phi_a(\vec{r}_2) \sigma(s_2) \\ \phi_b(\vec{r}_1) \sigma'(s_1) & \phi_b(\vec{r}_2) \sigma'(s_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left(\phi_a(\vec{r}_1) \phi_a(\vec{r}_2) \sigma(s_1) \sigma'(s_2) - \phi_b(\vec{r}_1) \phi_a(\vec{r}_2) \sigma'(s_1) \sigma(s_2) \right)$$



Coulomb exchange: same spin



when electrons have same spin: $\sigma = \sigma'$

$$\psi_{a,\sigma; b\sigma} = \frac{1}{\sqrt{2}} \left(\phi_a(\vec{r}_1) \phi_b(\vec{r}_2) - \phi_b(\vec{r}_1) \phi_a(\vec{r}_2) \right) \sigma(s_1) \sigma(s_2)$$

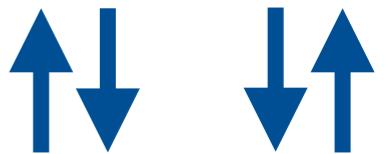
Coulomb matrix-element

$$\left\langle \psi_{a,\sigma; b,\sigma} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \psi_{a,\sigma; b,\sigma} \right\rangle = \frac{1}{2} (U_{ab} - J_{ab} - J_{ba} + U_{ba}) = U_{ab} - J_{ab}$$

Coulomb integral $U_{ab} = \int d^3 r_1 \int d^3 r_2 \frac{|\phi_a(\vec{r}_1)|^2 |\phi_b(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$

exchange integral $J_{ab} = \int d^3 r_1 \int d^3 r_2 \frac{\overline{\phi_a(\vec{r}_1)} \phi_b(\vec{r}_1) \overline{\phi_b(\vec{r}_2)} \phi_a(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$

Coulomb exchange: opposite spin



when electrons have opposite spin: $\sigma = -\sigma'$

$$\Psi_{a,\uparrow;b\downarrow}(\vec{r}_1, s_1; \vec{r}_2, s_2) = \frac{1}{\sqrt{2}} \left(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) \uparrow(s_1)\downarrow(s_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2) \downarrow(s_1)\uparrow(s_2) \right)$$

$$\Psi_{a,\downarrow;b\uparrow}(\vec{r}_1, s_1; \vec{r}_2, s_2) = \frac{1}{\sqrt{2}} \left(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) \downarrow(s_1)\uparrow(s_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2) \uparrow(s_1)\downarrow(s_2) \right)$$

diagonal matrix-elements

$$\left\langle \Psi_{a,\sigma; b,-\sigma} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a,\sigma; b,-\sigma} \right\rangle = U_{ab}$$

off-diagonal matrix-elements

$$\left\langle \Psi_{a\uparrow; b\downarrow} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a\downarrow; b\uparrow} \right\rangle = -J_{ab}$$

Coulomb matrix

$$\begin{pmatrix} U_{ab} & -J_{ab} \\ -J_{ab} & U_{ab} \end{pmatrix}$$

Coulomb exchange

$$H_U = \begin{pmatrix} U_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & U_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & U_{ab} & 0 \\ 0 & 0 & 0 & U_{ab} - J_{ab} \end{pmatrix}$$

eigenstates

triplet: $\Delta\epsilon_{triplet} = U_{ab} - J_{ab}$

$$\psi_{\uparrow\uparrow} = \frac{1}{\sqrt{2}} (\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)) \quad |\uparrow\uparrow\rangle$$

$$\frac{1}{\sqrt{2}} (\psi_{\uparrow\downarrow} + \psi_{\downarrow\uparrow}) = \frac{1}{\sqrt{2}} (\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)) \frac{1}{\sqrt{2}} (|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

$$\psi_{\downarrow\downarrow} = \frac{1}{\sqrt{2}} (\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)) \quad |\downarrow\downarrow\rangle$$

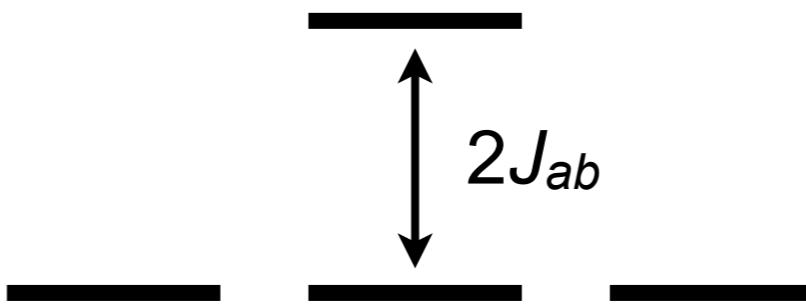
singlet: $\Delta\epsilon_{singlet} = U_{ab} + J_{ab}$

$$\frac{1}{\sqrt{2}} (\psi_{\uparrow\downarrow} - \psi_{\downarrow\uparrow}) = \frac{1}{\sqrt{2}} (\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)) \frac{1}{\sqrt{2}} (|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$$

Coulomb exchange

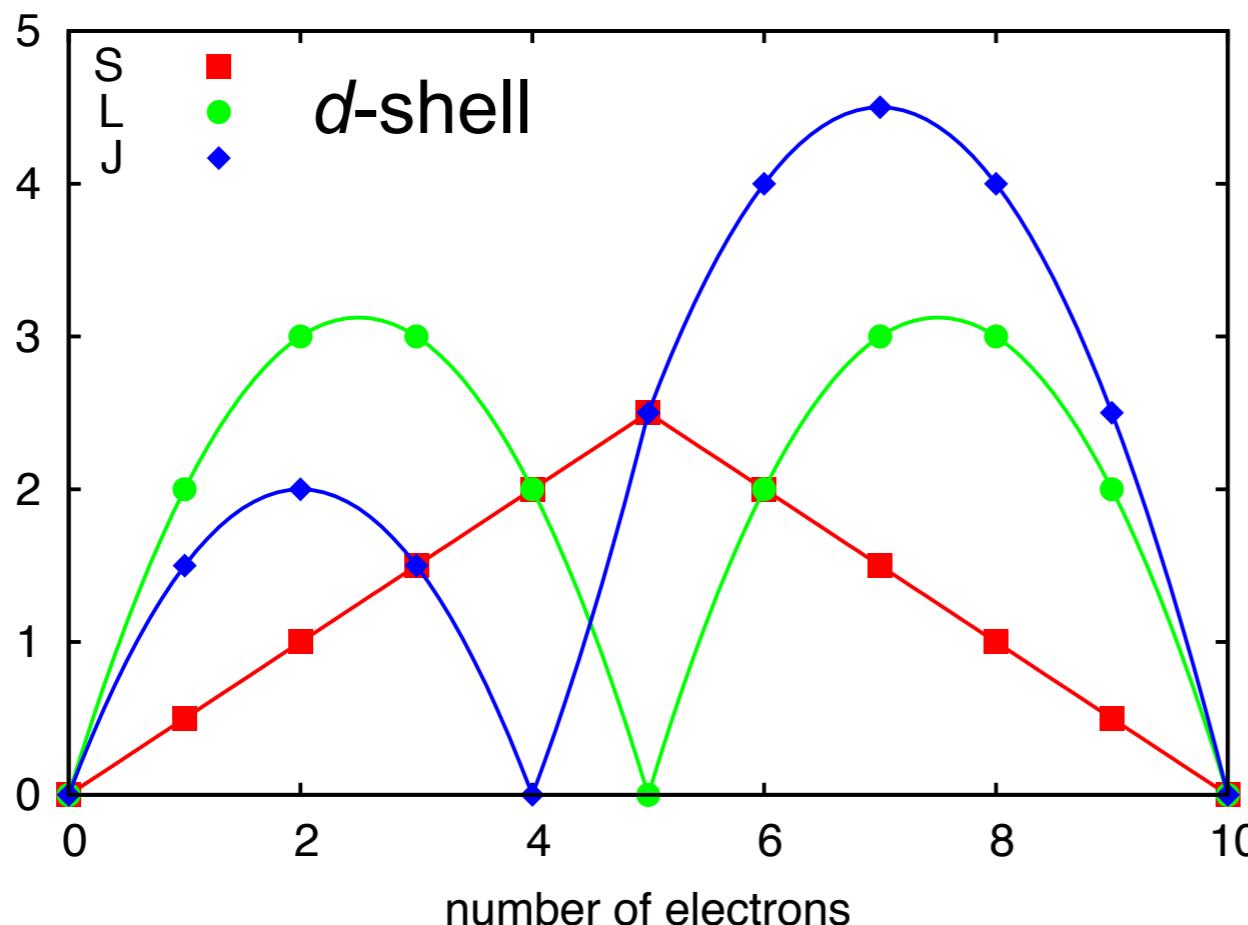
orthogonal orbitals φ_a and φ_b : $J_{ab} > 0$

singlet



triplet

first of Hund's rules: ground-state has maximum spin



more electrons
more complicated
Coulomb matrix

Robert Eder:
Multiplets in
Transition Metal Ions

kinetic exchange

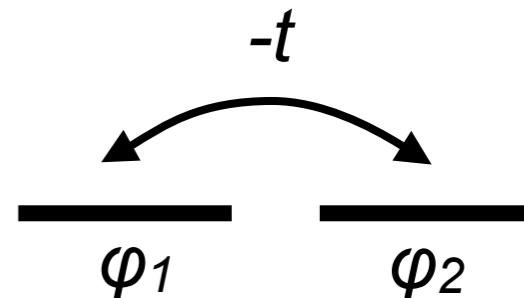
Coulomb exchange: Coulomb **matrix** for anti-symmetric wave functions

kinetic exchange: only diagonal U , interplay of Pauli principle and **hopping**

toy model — two sites with a single orbital

hopping between orbitals: t

two electrons in same orbital: U



one electron Hamiltonian (tight-binding)

$$H = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} \quad \begin{array}{l} |\uparrow, \cdot\rangle \\ |\cdot, \uparrow\rangle \end{array}$$

eigenstates

$$\phi_{\pm} = \frac{1}{\sqrt{2}} (\phi_1 \pm \phi_2) \quad \varepsilon_{\pm} = \mp t$$

direct exchange: same spin



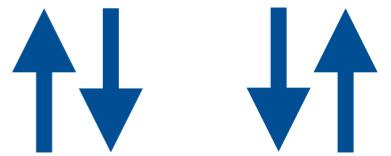
two electrons of same spin: basis states $|\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle$

Hamiltonian: no hopping, no Coulomb matrix element (Pauli principle)

$$H = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad |\uparrow, \uparrow\rangle \\ |\downarrow, \downarrow\rangle$$

$$\epsilon_{\text{triplet}} = 0$$

direct exchange: opposite spin



two electrons of opposite spin: basis states

$|\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle$ (covalent states) $|\uparrow\downarrow, \cdot\rangle, |\cdot, \uparrow\downarrow\rangle$ (ionic states)

Hamiltonian

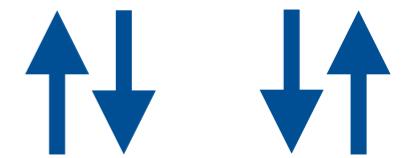
$$H = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ -t & +t & 0 & U \end{pmatrix} \quad \begin{array}{l} |\uparrow, \downarrow\rangle \\ |\downarrow, \uparrow\rangle \\ |\uparrow\downarrow, \cdot\rangle \\ |\cdot, \uparrow\downarrow\rangle \end{array}$$

hopping $-t$: keep track of **Fermi sign!**

$$|\uparrow, \downarrow\rangle \xrightarrow{-t} |\uparrow\downarrow, \cdot\rangle$$

$$|\downarrow, \uparrow\rangle \xrightarrow{-(-t)} |\uparrow\downarrow, \cdot\rangle$$

direct exchange: opposite spin



eigenstates

$$\varepsilon_{\pm} = \frac{U}{2} \pm \frac{\sqrt{U^2 + 16t^2}}{2}$$

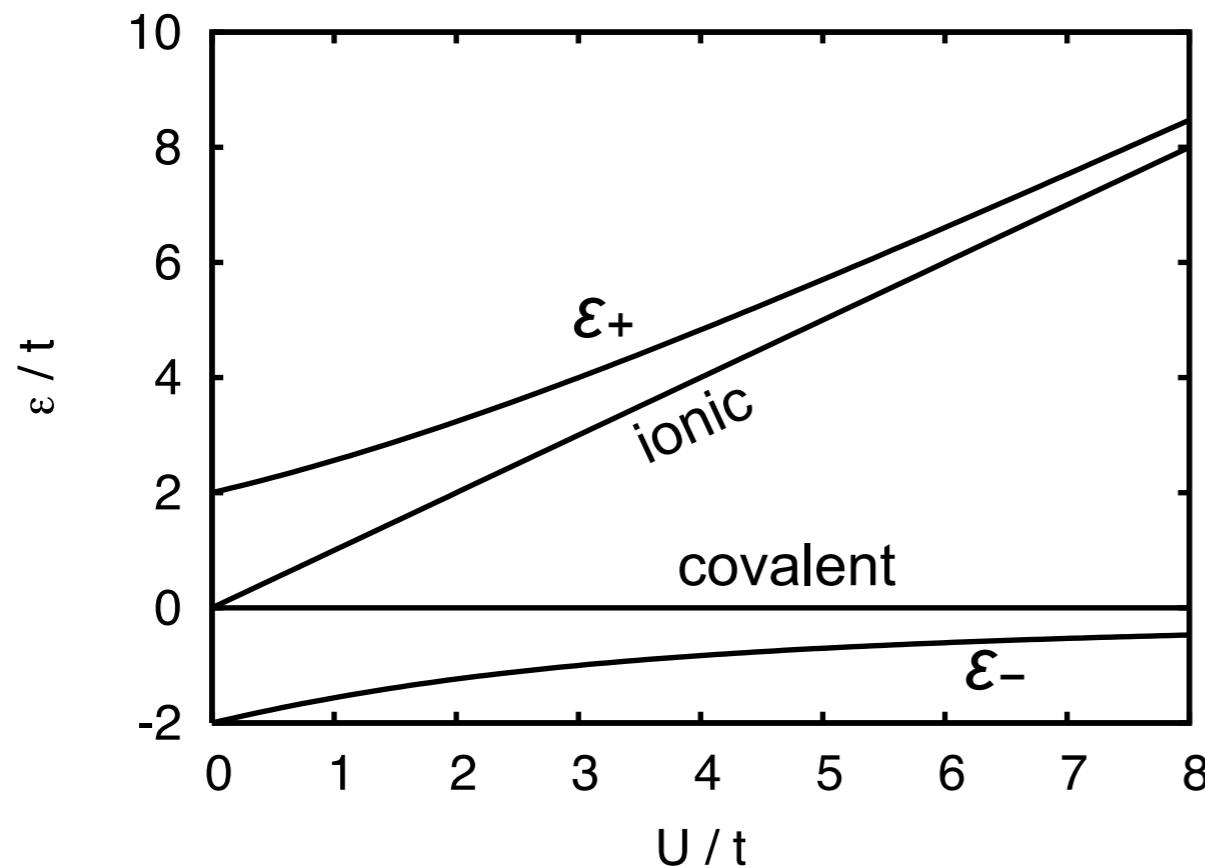
$$\psi_{\pm} = \frac{(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle - \frac{\varepsilon_{\pm}}{2t} [|\uparrow\downarrow, \cdot\rangle + |\cdot, \uparrow\downarrow\rangle])}{\sqrt{2 + \varepsilon_{\pm}^2/(2t^2)}}$$

$$\varepsilon_{\text{cov}} = 0$$

$$\psi_{\text{cov}} = \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) \quad (\varepsilon_{\text{triplet}})$$

$$\varepsilon_{\text{ion}} = U$$

$$\psi_{\text{ion}} = \frac{1}{\sqrt{2}} (|\uparrow\downarrow, \cdot\rangle - |\cdot, \uparrow\downarrow\rangle)$$



limit $U \rightarrow \infty$ (or $t \rightarrow 0$):

$$\varepsilon_- \rightarrow U + 4t^2/U$$

$$\varepsilon_+ \rightarrow -4t^2/U$$

downfolding

partition Hilbert space

$$H = \begin{pmatrix} H_{00} & T_{01} \\ T_{10} & H_{11} \end{pmatrix}$$



resolvent

$$G(\varepsilon) = (\varepsilon - H)^{-1} = \begin{pmatrix} \varepsilon - H_{00} & -T_{01} \\ -T_{10} & \varepsilon - H_{11} \end{pmatrix}^{-1}$$



inverse of 2×2 block-matrix

$$G_{00}(\varepsilon) = \left(\varepsilon - [H_{00} + T_{01}(\varepsilon - H_{11})^{-1}T_{10}] \right)^{-1}$$



downfolded Hamiltonian

$$H_{\text{eff}} \approx H_{00} + T_{01}(\varepsilon_0 - H_{11})^{-1}T_{10}$$

good approximation: narrow energy range and/or small coupling

inversion by partitioning

2×2 matrix

$$M = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad M^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$$

invert block-2×2 matrix

solve

$$M = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \quad M^{-1} = \begin{pmatrix} \tilde{A} & \tilde{B} \\ \tilde{C} & \tilde{D} \end{pmatrix} \quad \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} \tilde{A} & \tilde{B} \\ \tilde{C} & \tilde{D} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$A\tilde{A} + B\tilde{C} = 1 \quad = (A - BD^{-1}C)\tilde{A}$$

$$C\tilde{A} + D\tilde{C} = 0 \rightsquigarrow \tilde{C} = -D^{-1}C\tilde{A}$$

direct exchange: effective Hamiltonian

systematic treatment of limit $U \rightarrow \infty$ (or $t \rightarrow 0$): downfolding

$$H = \left(\begin{array}{cc|cc} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ \hline -t & +t & U & 0 \\ -t & +t & 0 & U \end{array} \right)$$

downfolding eliminates ionic states (actually change of basis)

$$H_{\text{eff}}(\varepsilon) = \begin{pmatrix} -t & -t \\ +t & +t \end{pmatrix} \begin{pmatrix} \varepsilon - U & 0 \\ 0 & \varepsilon - U \end{pmatrix}^{-1} \begin{pmatrix} -t & +t \\ -t & +t \end{pmatrix} \approx -\frac{2t^2}{U} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

diagonalize H_{eff}

$$\varepsilon_t = 0$$

$$\Psi_t = \frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)$$

triplet

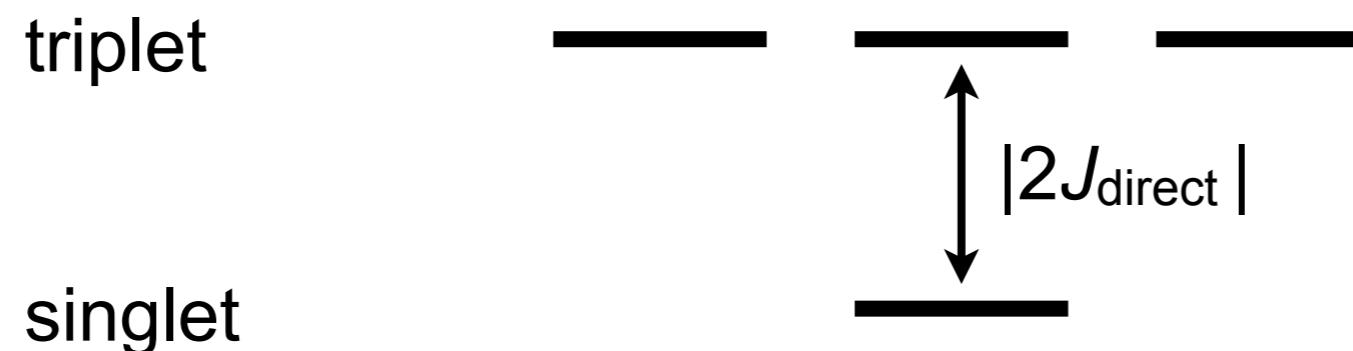
$$\varepsilon_s = -\frac{4t^2}{U}$$

$$\Psi_s = \frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)$$

singlet

direct exchange: effective spin-coupling

$$J_{\text{direct}} = \varepsilon_{\text{triplet}} - \varepsilon_{\text{singlet}} = 4t^2/U \quad J > 0 \quad \text{AF coupling}$$



effective spin-Hamiltonian

$$H_{\text{eff}} = -\frac{2t^2}{U} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad |\uparrow, \downarrow\rangle \quad |\downarrow, \uparrow\rangle$$

$$= +\frac{2t^2}{U} \left(2S_1^z S_2^z - \frac{1}{2} + (S_1^+ S_2^- + S_1^- S_2^+) \right) = \frac{4t^2}{U} \left(\vec{S}_1 \cdot \vec{S}_2 - \frac{1}{4} \right)$$



Heisenberg J

book-keeping: second quantization

introduce operators $c_{i\sigma}^\dagger$ that put electron of spin σ in orbital φ_i :

no electron:

$$|\cdot, \cdot\rangle = |0\rangle$$

electrons anti-commute:

$$c_{i\sigma}^\dagger c_{j\sigma'}^\dagger = -c_{j\sigma'}^\dagger c_{i\sigma}^\dagger$$

single electron:

$$|\uparrow, \cdot\rangle = c_{1\uparrow}^\dagger |0\rangle$$

$$\{c_{i\sigma}^\dagger, c_{j\sigma'}^\dagger\} = c_{i\sigma}^\dagger c_{j\sigma'}^\dagger + c_{j\sigma'}^\dagger c_{i\sigma}^\dagger = 0$$

$$|\cdot, \uparrow\rangle = c_{2\uparrow}^\dagger |0\rangle$$

anticommutator

two electrons:

$$|\uparrow, \downarrow\rangle = c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$$

$$|\downarrow, \uparrow\rangle = c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle$$

$$|\uparrow\downarrow, \cdot\rangle = c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$$

$$|\cdot, \uparrow\downarrow\rangle = c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$$

second quantization: operators

adjoin: $(c_{i\sigma}^\dagger |0\rangle)^\dagger = \langle 0| c_{i\sigma}$ $\{c_{i\sigma}, c_{j\sigma'}\} = 0 = \{c_{i\sigma}^\dagger, c_{j\sigma'}^\dagger\}$

annihilation operator:

removes electron
of spin σ from orbital φ_i

in particular $c_{i\sigma}|0\rangle = 0$

$$\begin{aligned} c_{i\sigma} c_{j\sigma'}^\dagger |0\rangle &= \delta_{i,j} \delta_{\sigma,\sigma'} |0\rangle \\ c_{i\sigma}^\dagger c_{j\sigma'} |0\rangle &= 0 \end{aligned} \quad \{c_{i\sigma}, c_{j\sigma'}^\dagger\} = \delta_{i,j} \delta_{\sigma,\sigma'}$$

$$n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$$

second quantization: examples

two-site model with one electron

$$H = -t \left(c_{1\uparrow}^\dagger c_{2\uparrow} + c_{2\uparrow}^\dagger c_{1\uparrow} + c_{1\downarrow}^\dagger c_{2\downarrow} + c_{2\downarrow}^\dagger c_{1\downarrow} \right) = -t \sum_{i,j,\sigma} c_{j\sigma}^\dagger c_{i\sigma}$$

two-site model with two electrons

$$\begin{aligned} H &= -t \left(c_{1\uparrow}^\dagger c_{2\uparrow} + c_{2\uparrow}^\dagger c_{1\uparrow} + c_{1\downarrow}^\dagger c_{2\downarrow} + c_{2\downarrow}^\dagger c_{1\downarrow} \right) + U \left(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow} \right) \\ &= -t \sum_{i,j,\sigma} c_{j\sigma}^\dagger c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \end{aligned}$$

also works for single electron

- easy to write down many-body Hamiltonian
- easy to handle Slater determinants

Hartree-Fock

ansatz: Slater determinant

$$|\psi(\theta_{\uparrow}, \theta_{\downarrow})\rangle = (\sin(\theta_{\downarrow}) c_{1\downarrow}^{\dagger} + \cos(\theta_{\downarrow}) c_{2\downarrow}^{\dagger}) (\sin(\theta_{\uparrow}) c_{1\uparrow}^{\dagger} + \cos(\theta_{\uparrow}) c_{2\uparrow}^{\dagger}) |0\rangle$$

energy expectation value

$$\begin{aligned} E(\theta_{\uparrow}, \theta_{\downarrow}) = & -2t (\sin \theta_{\uparrow} \sin \theta_{\downarrow} + \cos \theta_{\uparrow} \cos \theta_{\downarrow}) (\cos \theta_{\uparrow} \sin \theta_{\downarrow} + \sin \theta_{\uparrow} \cos \theta_{\downarrow}) \\ & + U (\sin^2 \theta_{\uparrow} \sin^2 \theta_{\downarrow} + \cos^2 \theta_{\uparrow} \cos^2 \theta_{\downarrow}) \end{aligned}$$

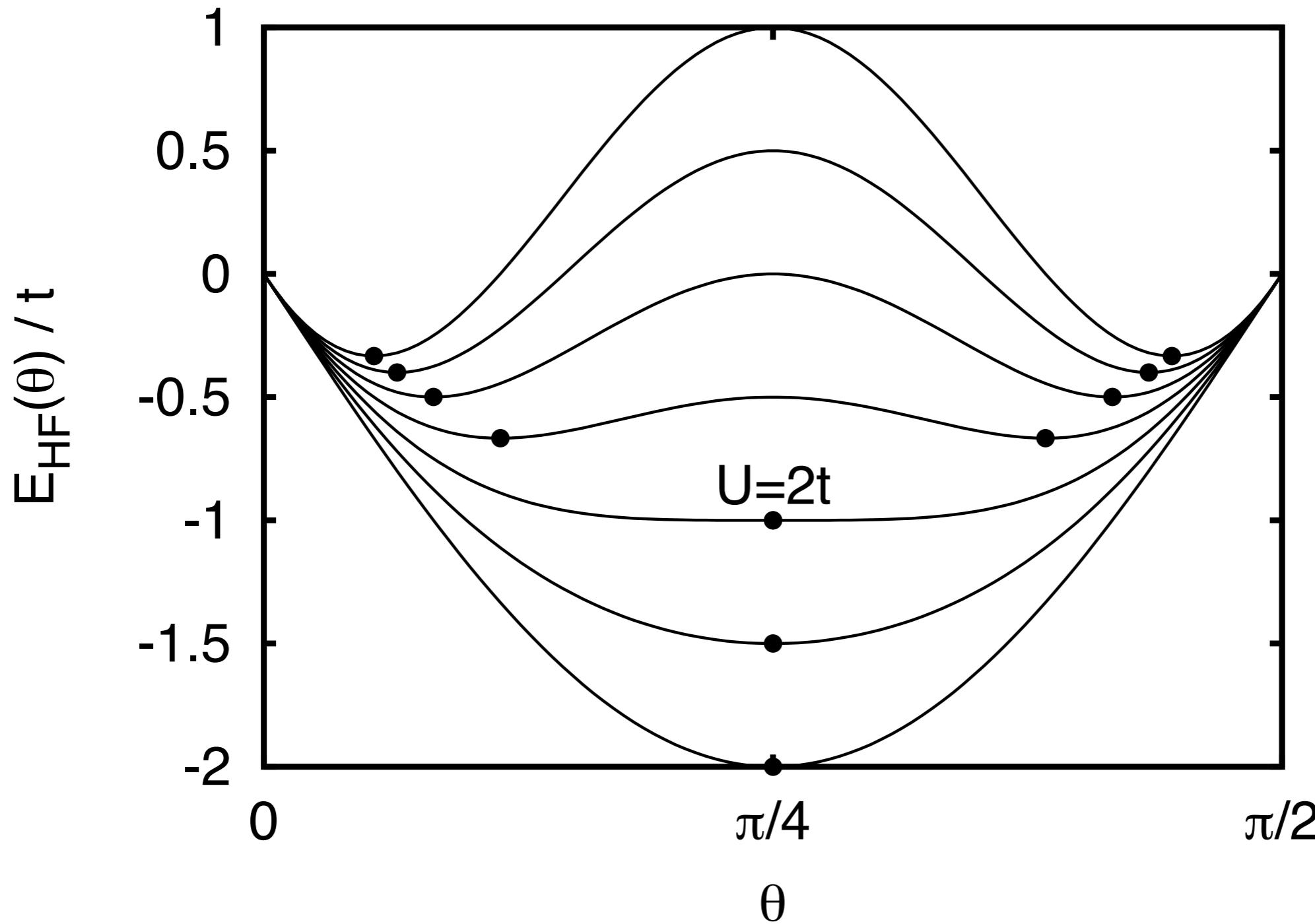
minimize wrt θ_{\uparrow} and θ_{\downarrow}

HF orbitals respect symmetry of model: restricted Hartree-Fock (RHF)
here: $\theta_{\uparrow} = \theta_{\downarrow} = \pi/4$

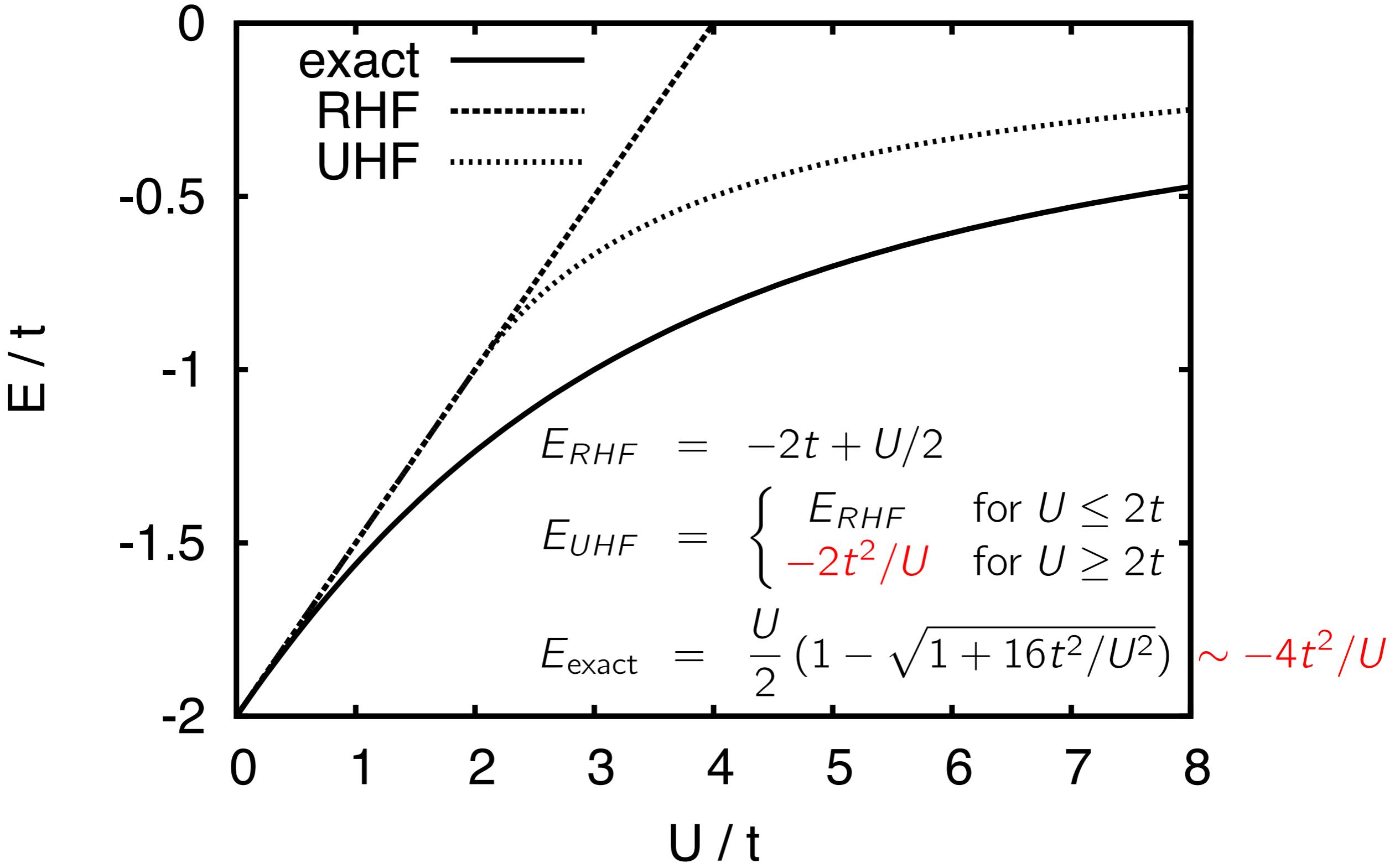
HF allowed to break symmetry: unrestricted Hartree-Fock (UHF)
here: $\theta_{\downarrow} = \pi/2 - \theta_{\uparrow}$

Hartree-Fock

energy expectation value for $\theta_{\downarrow} = \pi/2 - \theta_{\uparrow}$

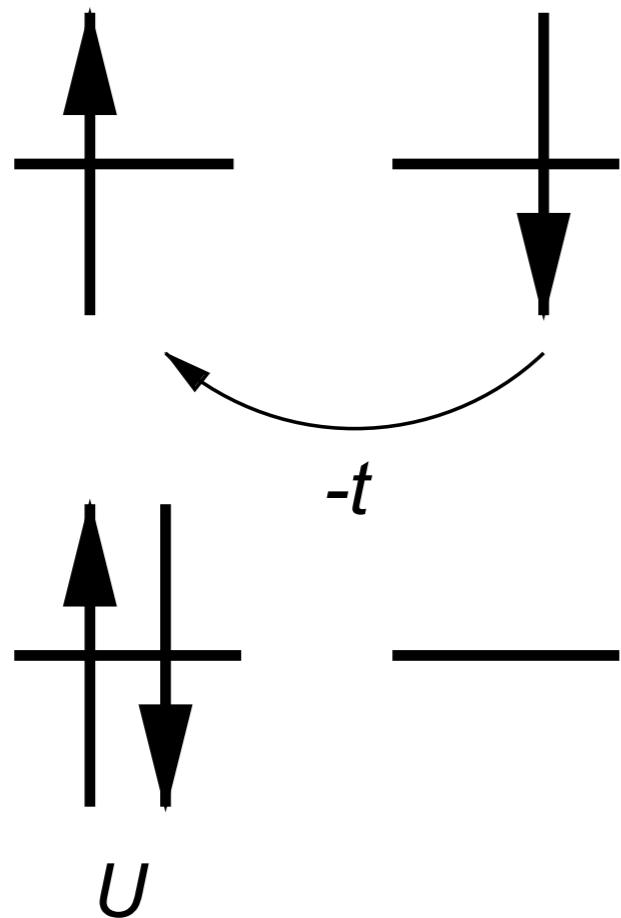


Hartree-Fock

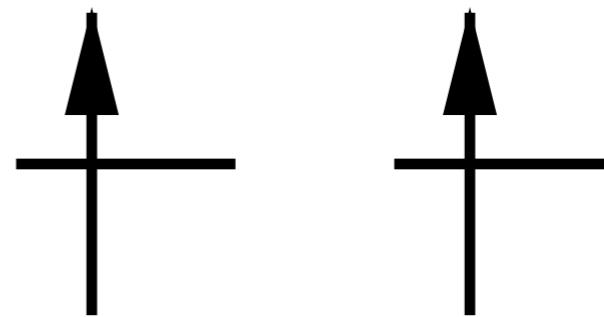


direct kinetic exchange

singlet



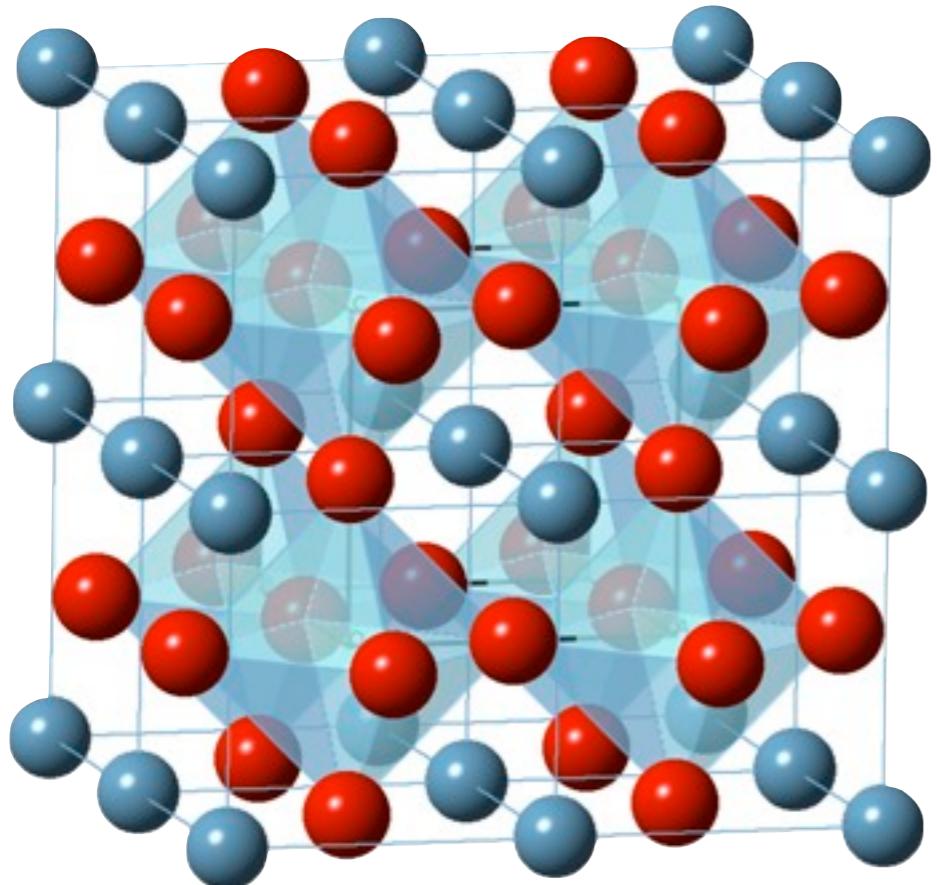
triplet



direct exchange

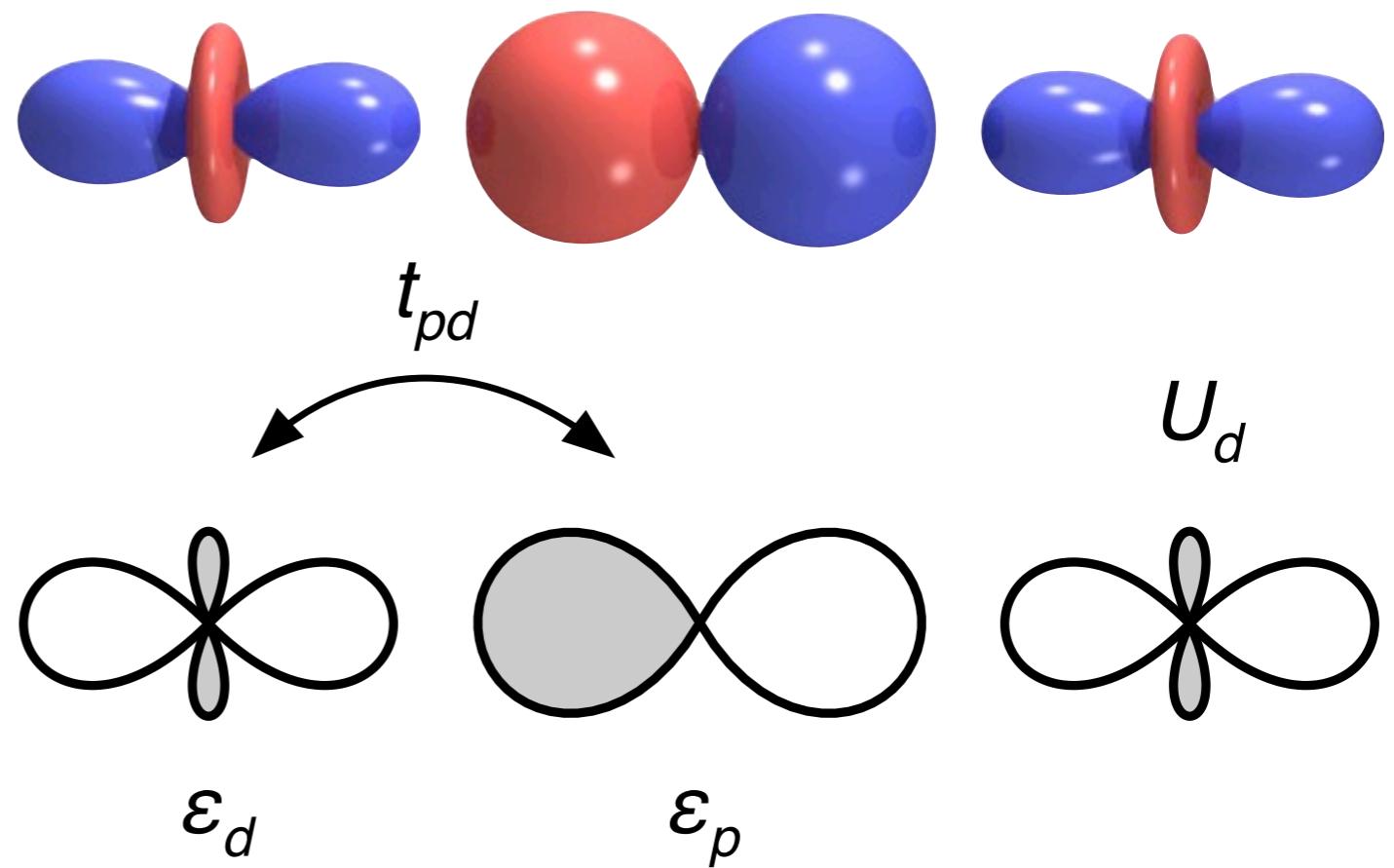
virtual hopping $-t^2/U \times 2$

superexchange



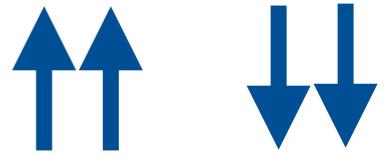
symmetry:
only one oxygen-*p*
involved in hopping

TMOs: negligible direct hopping
between *d*-orbitals
instead hopping via oxygen



$$H = \sum_{\sigma} \left(\varepsilon_d \sum_i n_{i\sigma} + \varepsilon_p n_{p\sigma} - t_{pd} \sum_i \left(c_{i\sigma}^{\dagger} c_{p\sigma} + c_{p\sigma}^{\dagger} c_{i\sigma} \right) \right) + U_d \sum_i n_{i\uparrow} n_{i\downarrow}$$

superexchange: same spin

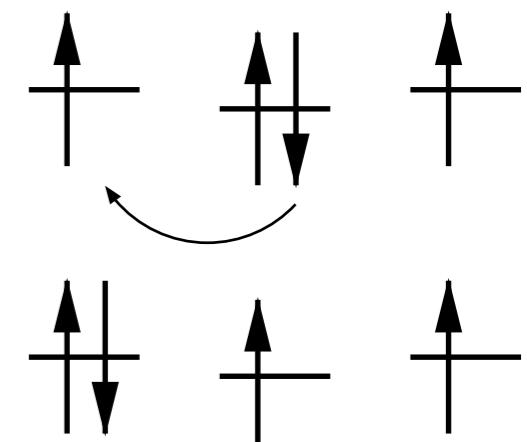


$$H = \sum_{\sigma} \left(\varepsilon_d \sum_i n_{i\sigma} + \varepsilon_p n_{p\sigma} - t_{pd} \sum_i (c_{i\sigma}^\dagger c_{p\sigma} + c_{p\sigma}^\dagger c_{i\sigma}) \right) + U_d \sum_i n_{i\uparrow} n_{i\downarrow}$$

oxygen-*p* full, two *d*-electrons of same spin

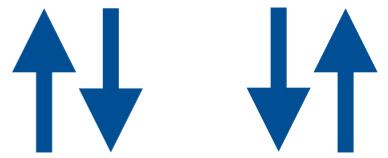
$$H = \begin{pmatrix} 0 & t_{pd} & t_{pd} \\ t_{pd} & U_d + \Delta_{pd} & 0 \\ t_{pd} & 0 & U_d + \Delta_{pd} \end{pmatrix}$$

$$\begin{aligned} &c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ &c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ &c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \end{aligned}$$



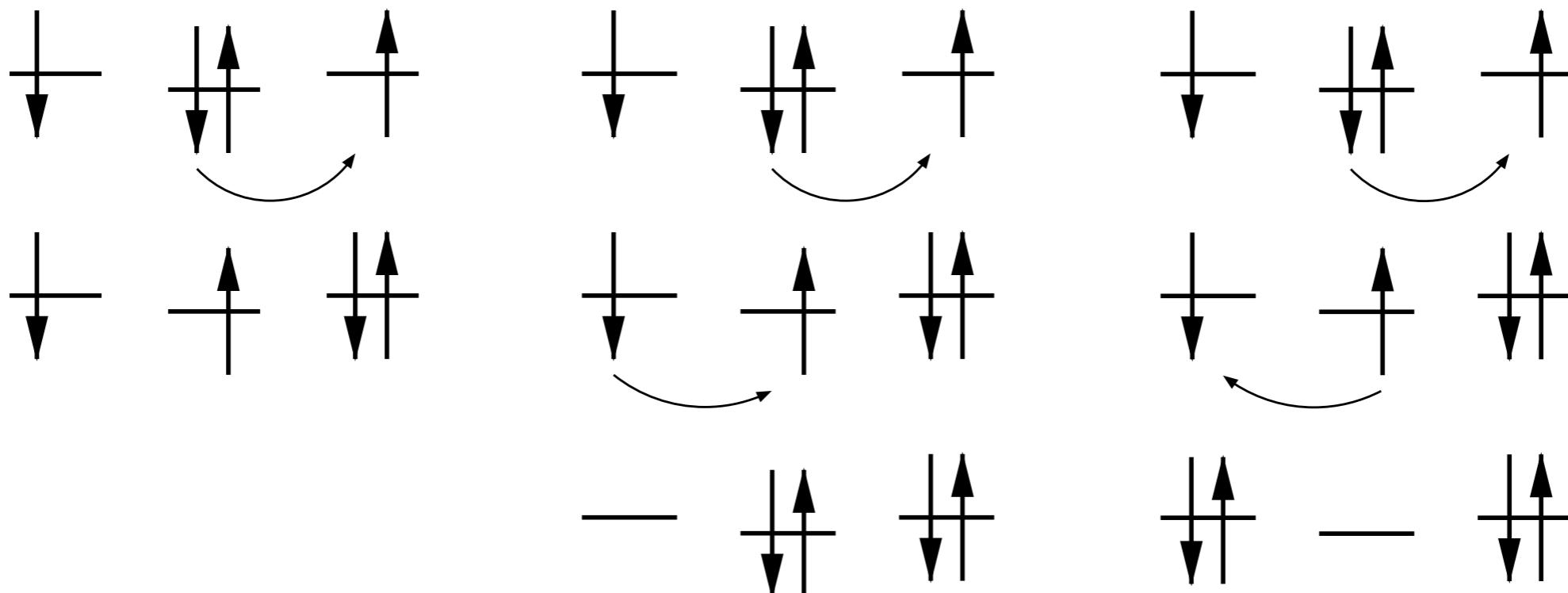
$$H_{\text{eff}} = (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \approx -\frac{2t_{pd}^2}{U_d + \Delta_{pd}}$$

superexchange: opposite spin



$$\left(\begin{array}{cc|ccccc|ccc} 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 \\ \hline +t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & 0 & -t_{pd} \\ +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & -t_{pd} \\ 0 & +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & 0 & +t_{pd} \\ 0 & +t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & +t_{pd} \\ \hline 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 & 0 \\ 0 & 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 \\ 0 & 0 & -t_{pd} & -t_{pd} & +t_{pd} & +t_{pd} & 0 & 0 & 2(U_d + \Delta_{pd}) \end{array} \right)$$

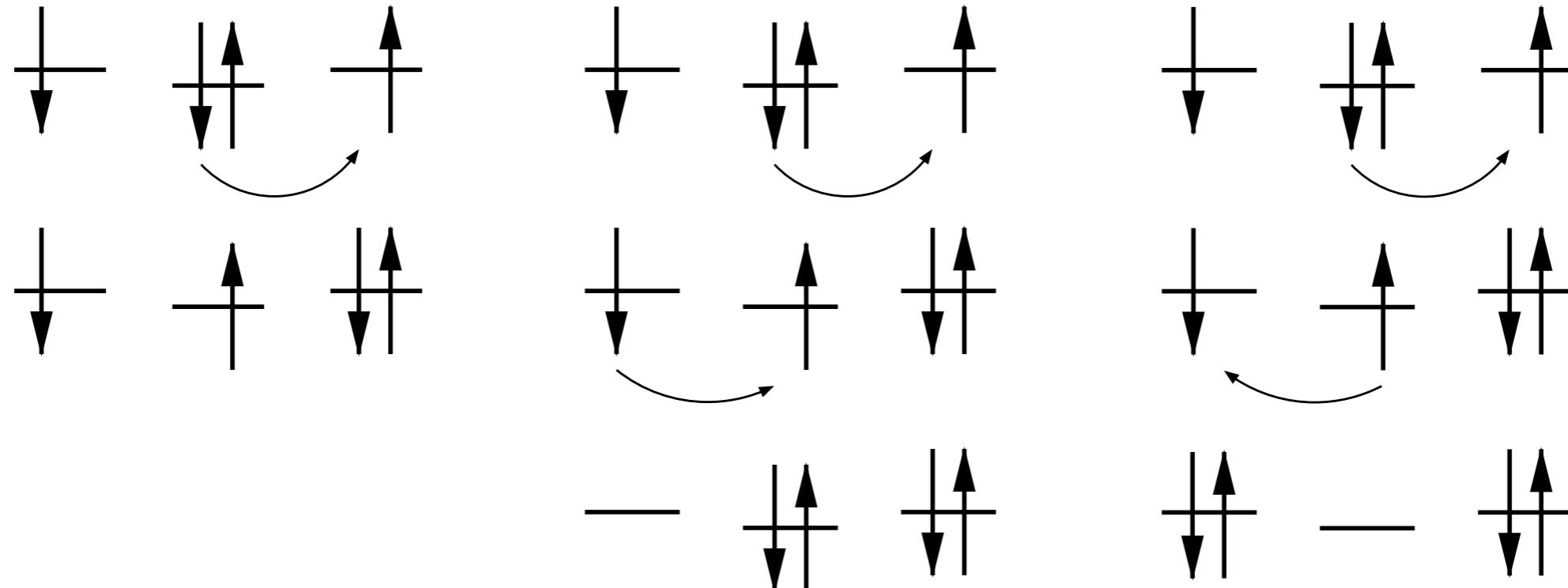
$C_{2\downarrow}^{\dagger}$	$C_{p\downarrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\uparrow}^{\dagger}$	$C_{p\downarrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$ 0\rangle$
$C_{2\downarrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\downarrow}^{\dagger}$	$C_{2\uparrow}^{\dagger}$	$C_{p\downarrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\uparrow}^{\dagger}$	$C_{p\downarrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\downarrow}^{\dagger}$	$C_{2\uparrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$ 0\rangle$
$C_{p\downarrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\downarrow}^{\dagger}$	$C_{2\uparrow}^{\dagger}$	$C_{p\downarrow}^{\dagger}$	$C_{p\uparrow}^{\dagger}$	$ 0\rangle$
$C_{2\downarrow}^{\dagger}$	$C_{2\uparrow}^{\dagger}$	$C_{1\downarrow}^{\dagger}$	$C_{1\uparrow}^{\dagger}$	$ 0\rangle$



superexchange: opposite spin



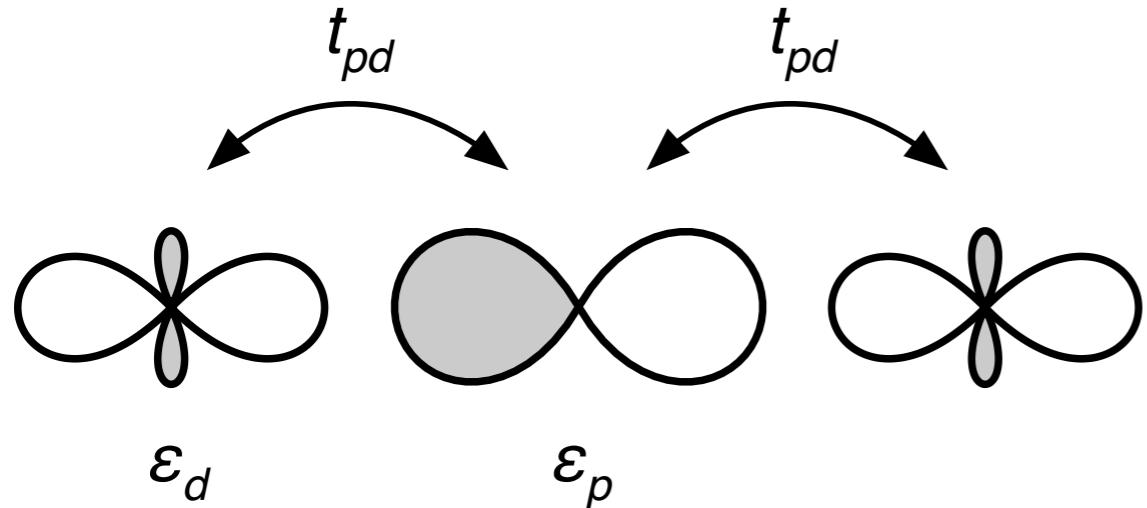
$$\begin{aligned}
 H_{\text{eff}} &= H_{00} + T_{01} \left(\varepsilon - \left(H_{11} + T_{12} (\varepsilon - H_{22})^{-1} T_{21} \right) \right)^{-1} T_{10} \\
 &\approx H_{00} - T_{01} H_{11}^{-1} T_{10} - T_{01} H_{11}^{-1} T_{12} H_{22}^{-1} T_{21} H_{11}^{-1} T_{10} \quad \text{expand in } 1/U_d \\
 &= -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{2t_{pd}^4}{(U_d + \Delta_{pd})^2} \left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}
 \end{aligned}$$



singlet-triplet splitting:

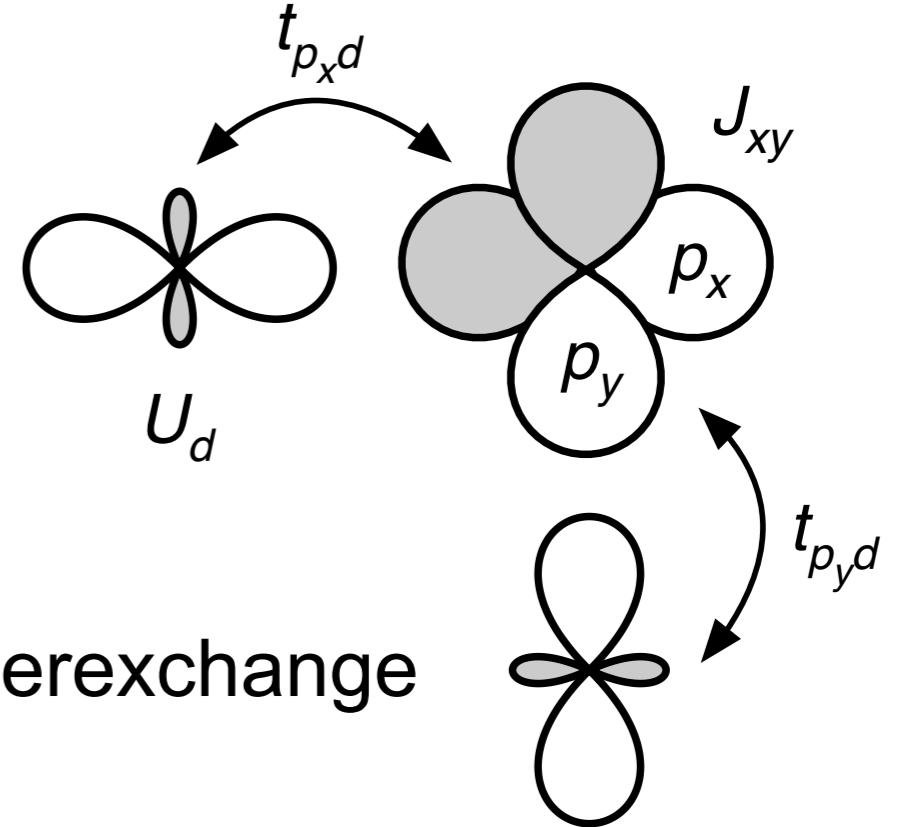
$$J = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right)$$

ferromagnetic superexchange



180° superexchange

hopping only via oxygen-*p* pointing
in direction connecting *d*-orbitals

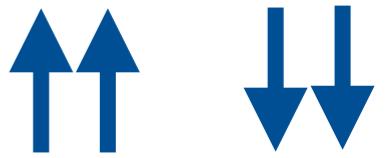


90° superexchange

no hopping connecting *d*-orbitals
but Coulomb exchange on oxygen

double exchange

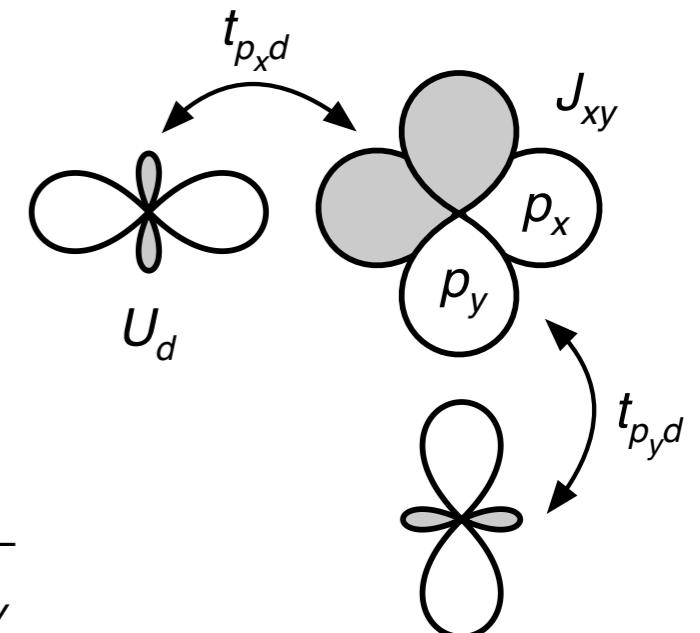
ferro superexchange: same spin



$$\begin{pmatrix} 0 & t_{pd} & t_{pd} & 0 \\ t_{pd} & U_d + \Delta_{pd} & 0 & t_{pd} \\ t_{pd} & 0 & U_d + \Delta_{pd} & t_{pd} \\ 0 & t_{pd} & t_{pd} & 2(U_d + \Delta_{pd}) - J_{xy} \end{pmatrix}$$

$$\begin{aligned} c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\downarrow}^\dagger |0\rangle \end{aligned}$$

$$H_{\text{eff}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{2(U_d + \Delta_{pd}) - J_{xy}}$$



ferro superexchange: opposite spin

0	0	t_{pd}	0	t_{pd}	0	0	0
0	0	0	t_{pd}	0	t_{pd}	0	0
t_{pd}	0	$U_d + \Delta_{pd}$	0	0	0	t_{pd}	0
0	t_{pd}	0	$U_d + \Delta_{pd}$	0	0	0	t_{pd}
t_{pd}	0	0	0	$U_d + \Delta_{pd}$	0	t_{pd}	0
0	t_{pd}	0	0	0	$U_d + \Delta_{pd}$	0	t_{pd}
0	0	t_{pd}	0	t_{pd}	0	$2(U_d + \Delta_{pd}) - J_{xy}$	$-J_{xy}$
0	0	0	t_{pd}	0	t_{pd}	$-J_{xy}$	$2(U_d + \Delta_{pd})$

$c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{x\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\uparrow}^\dagger c_{y\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$
 $c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{x\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$
 $c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle$

$$H_{\text{eff}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \begin{pmatrix} 2(U_d + \Delta_{pd}) & +J_{xy} \\ +J_{xy} & 2(U_d + \Delta_{pd}) \end{pmatrix}$$

$$= -\left(\frac{2t_{pd}^2}{U_d + \Delta_{pd}} + \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{2(U_d + \Delta_{pd}) - J_{xy}} \right) \quad (\text{as for same spin})$$

$$+ \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{J_{xy}}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

singlet-triplet splitting

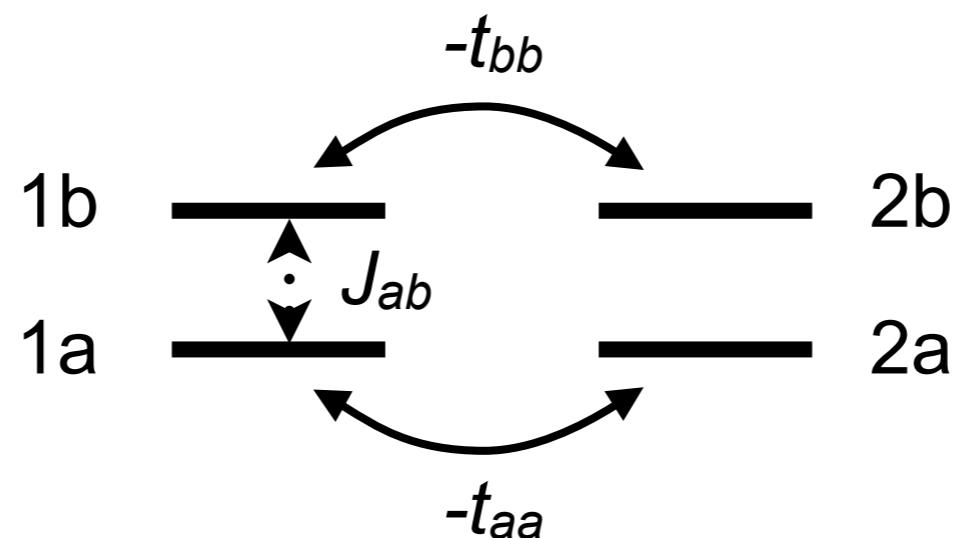
$$J = -\frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{2J_{xy}}{4(U_d + \Delta_{pd})^2 - J_{xy}^2}$$

double exchange

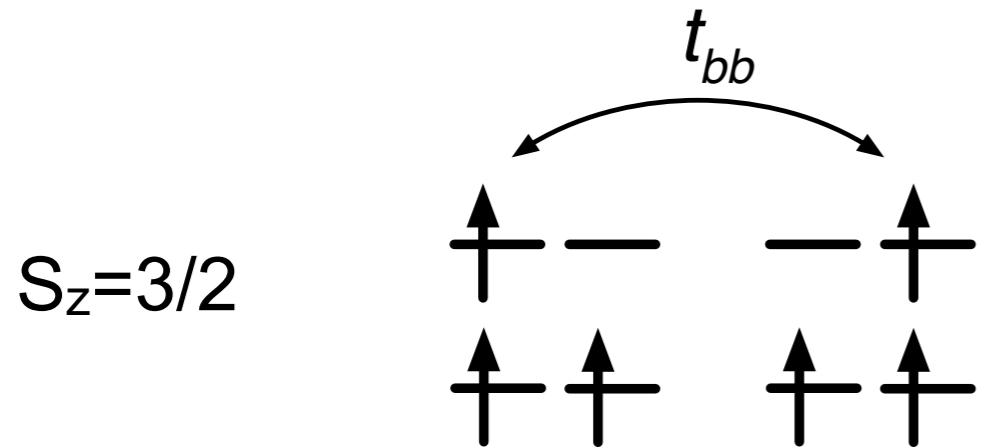
double exchange involves both, full Coulomb matrix and hopping

mixed-valence compound: non-integer filling of d -orbital
 d -electrons can hop even when U is large

simple model: two sites with two orbitals each



double exchange



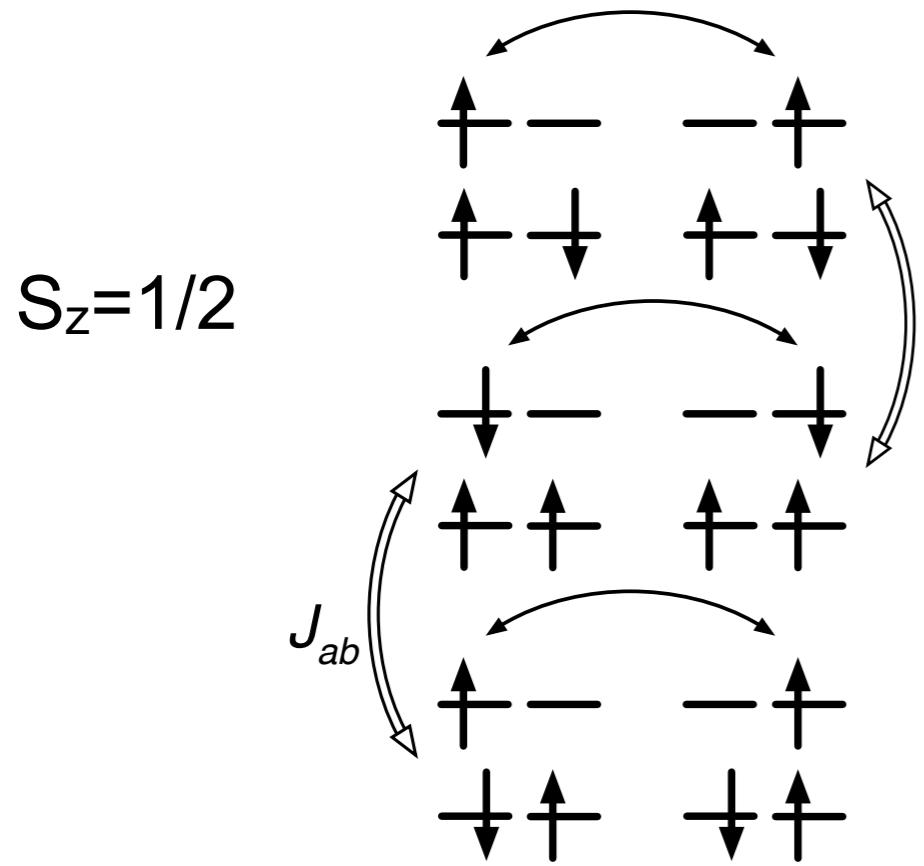
$$H = \begin{pmatrix} -J_{ab} & -t_{bb} \\ -t_{bb} & -J_{ab} \end{pmatrix}$$

$$\varepsilon_{\pm} = -J_{ab} \pm t_{bb}$$

$$\psi_{\pm} = \frac{1}{\sqrt{2}} \left(| \uparrow, \uparrow \rangle_1 | \cdot, \uparrow \rangle_2 \pm | \cdot, \uparrow \rangle_1 | \uparrow, \uparrow \rangle_2 \right) = \frac{1}{\sqrt{2}} \left(| \uparrow, \cdot \rangle_b \pm | \cdot, \uparrow \rangle_b \right) | \uparrow, \uparrow \rangle_a$$

b-electron hops against background of half-filled *a*-orbitals

double exchange



$$H = \begin{pmatrix} -J_{ab} & -t_{bb} & 0 & 0 & 0 & 0 \\ -t_{bb} & 0 & -J_{ab} & 0 & 0 & 0 \\ 0 & -J_{ab} & 0 & -t_{bb} & 0 & 0 \\ 0 & 0 & -t_{bb} & 0 & -J_{ab} & 0 \\ 0 & 0 & 0 & -J_{ab} & 0 & -t_{bb} \\ 0 & 0 & 0 & 0 & -t_{bb} & -J_{ab} \end{pmatrix}$$

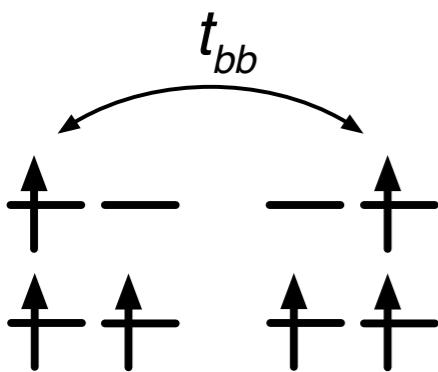
ground state $\varepsilon_0 = -J_{ab} - t_{bb}$

$$\begin{aligned} & \frac{1}{\sqrt{6}} (| \uparrow, \uparrow \rangle_1 | \cdot, \downarrow \rangle_2 + | \cdot, \uparrow \rangle_1 | \uparrow, \downarrow \rangle_2 + | \cdot, \uparrow \rangle_1 | \downarrow, \uparrow \rangle_2 + | \downarrow, \uparrow \rangle_1 | \cdot, \uparrow \rangle_2 + | \uparrow, \downarrow \rangle_1 | \cdot, \uparrow \rangle_2 + | \uparrow, \downarrow \rangle_1 | \cdot, \downarrow \rangle_2 + | \cdot, \downarrow \rangle_1 | \uparrow, \uparrow \rangle_2) \\ &= \frac{1}{\sqrt{2}} (| \uparrow, \cdot \rangle_b + | \cdot, \uparrow \rangle_b) \frac{1}{\sqrt{2}} (| \uparrow, \downarrow \rangle_a + | \downarrow, \uparrow \rangle_a) + \frac{1}{\sqrt{2}} (| \downarrow, \cdot \rangle_b + | \cdot, \downarrow \rangle_b) | \uparrow, \uparrow \rangle_a \end{aligned}$$

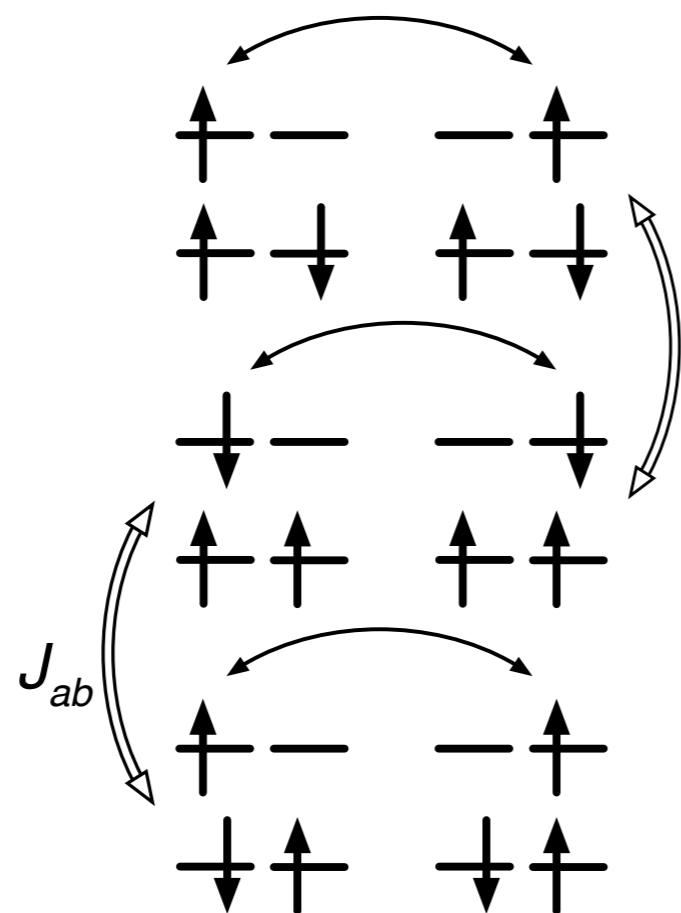
hopping electron aligns a -electrons ferromagnetically
(teleports local triplet into triplet of a -electrons)

double exchange

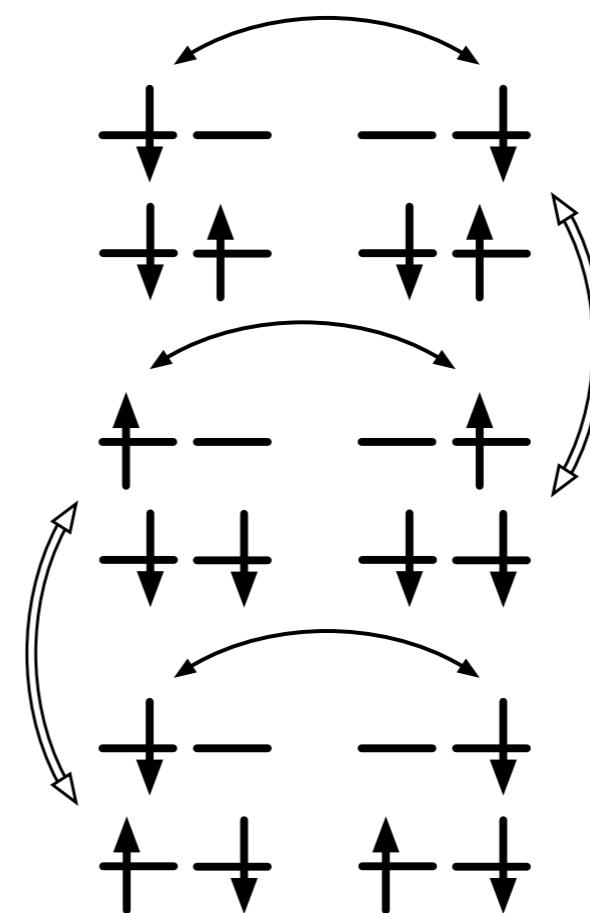
$S_z=3/2$



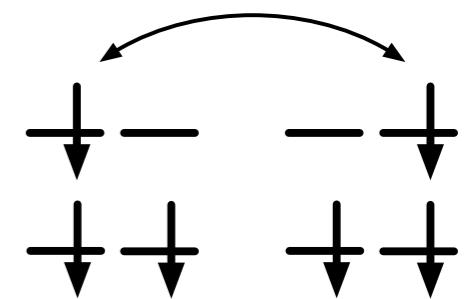
$S_z=1/2$



$S_z=-1/2$



$S_z=-3/2$



double exchange

alternative model:

assume passive orbitals with many electrons (large Hund's rule spin)

example: e_g electrons hopping against t_{2g} background

consider these spins fixed with quantization axis tilted by ϑ relative to each other



rotation of quantization axis

$$d_{2b\uparrow} = \cos(\vartheta/2) c_{2b\uparrow} - \sin(\vartheta/2) c_{2b\downarrow}$$

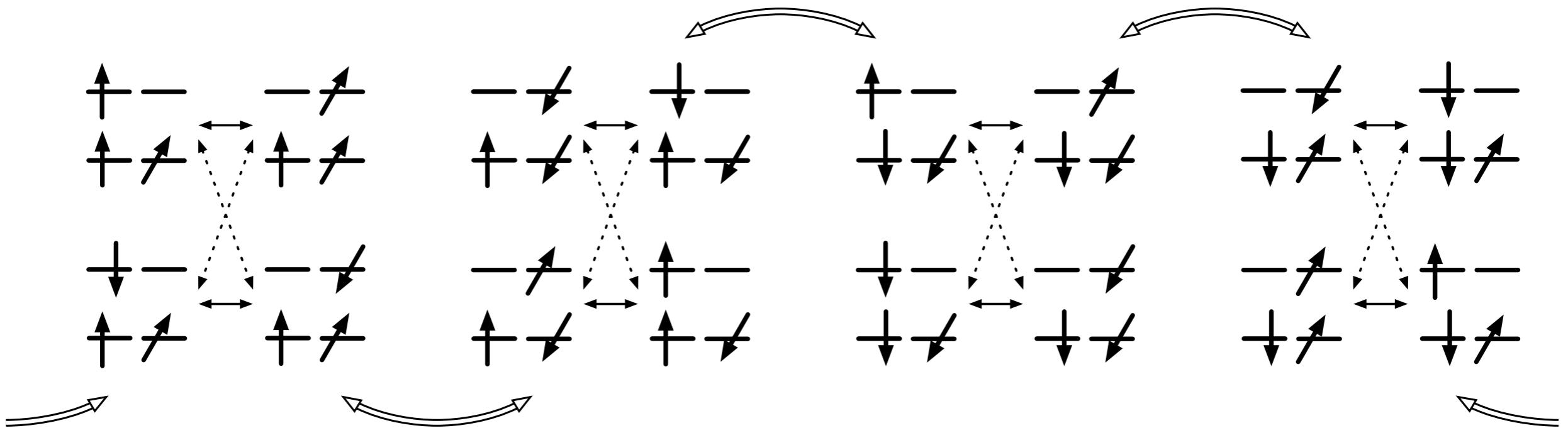
$$d_{2b\downarrow} = \sin(\vartheta/2) c_{2b\uparrow} + \cos(\vartheta/2) c_{2b\downarrow}$$

hopping mixes spins

$$-t_{bb} c_{2b\uparrow}^\dagger c_{1b\uparrow} = -t_{bb} \left(+ \cos(\vartheta/2) d_{2b\uparrow}^\dagger + \sin(\vartheta/2) d_{2b\downarrow}^\dagger \right) c_{1b\uparrow}$$

$$-t_{bb} c_{2b\downarrow}^\dagger c_{1b\downarrow} = -t_{bb} \left(- \sin(\vartheta/2) d_{2b\uparrow}^\dagger + \cos(\vartheta/2) d_{2b\downarrow}^\dagger \right) c_{1b\downarrow}$$

double exchange



assume a -spins cannot be flipped \Rightarrow no J terms

4 independent 2×2 Hamiltonians

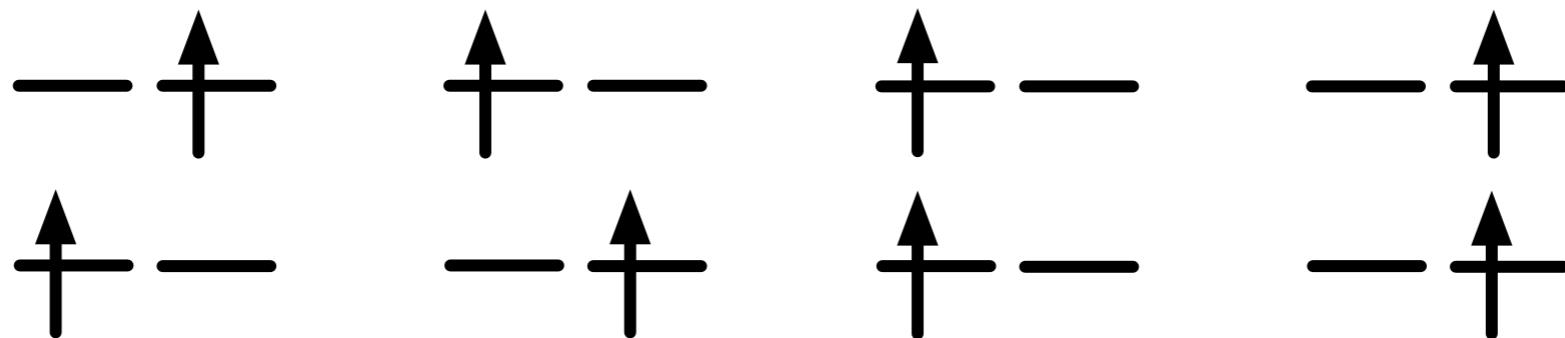
for $t_{bb} \ll J_{ab}$ tilt merely reduces width of b -band

$$\varepsilon_{\pm} = -J_{ab} \pm t_{bb} \cos(\vartheta/2)$$

again, hopping of b -electron prefers ferro aligned a -electrons

orbital ordering

same model, but now one electron per orbital

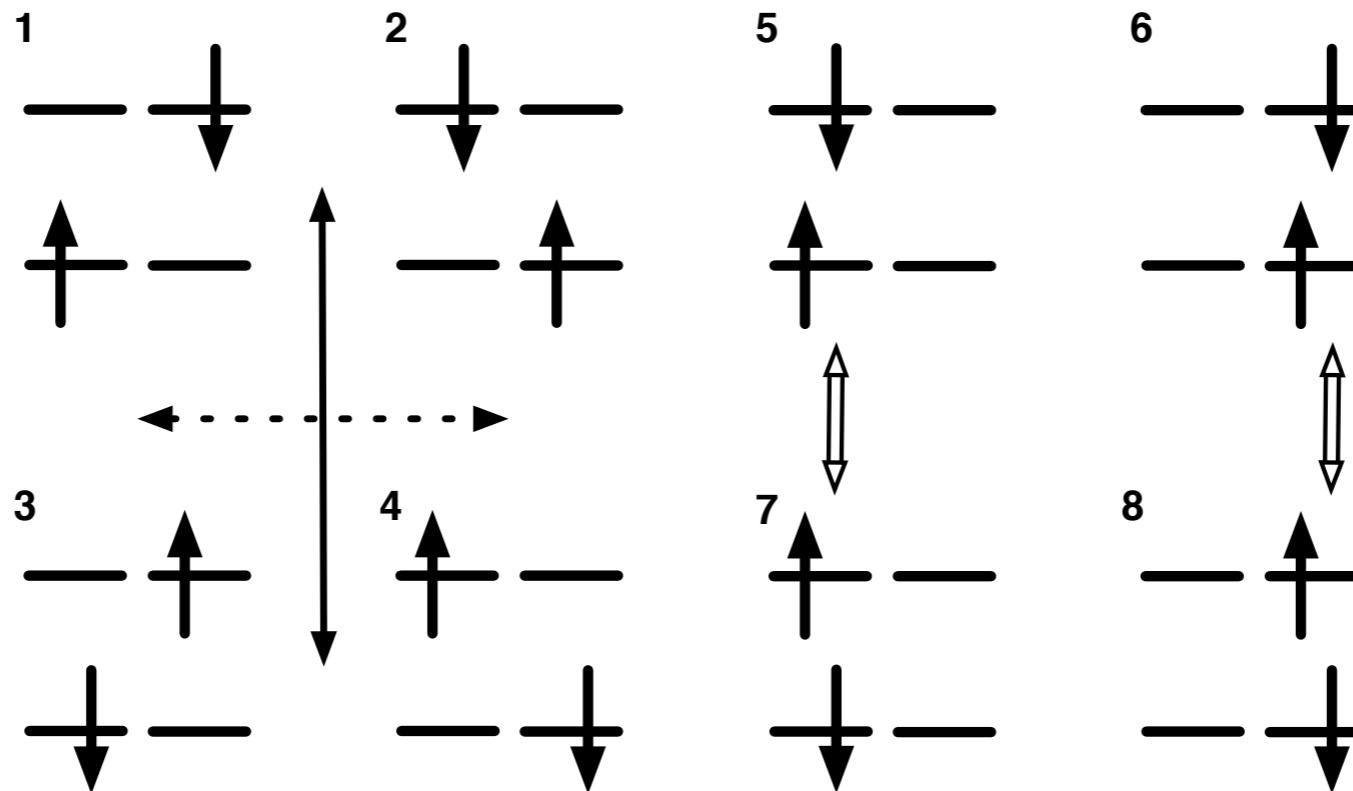


$$H = \begin{pmatrix} 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & +t_{aa} & +t_{bb} \\ -t_{bb} & +t_{aa} & U_{ab} - J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & U_{ab} - J_{ab} \end{pmatrix}$$

$$H_{\text{eff}} \approx -\frac{1}{U_{ab} - J_{ab}} \begin{pmatrix} t_{aa}^2 + t_{bb}^2 & -2t_{aa}t_{bb} \\ -2t_{aa}t_{bb} & t_{aa}^2 + t_{bb}^2 \end{pmatrix} = -\frac{(t_{aa} - t_{bb})^2}{U_{ab} - J_{ab}} - \frac{2t_{aa}t_{bb}}{U_{ab} - J_{ab}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

effective interaction between orbitals: orbital singlet/triplet

orbital ordering: opposite spins

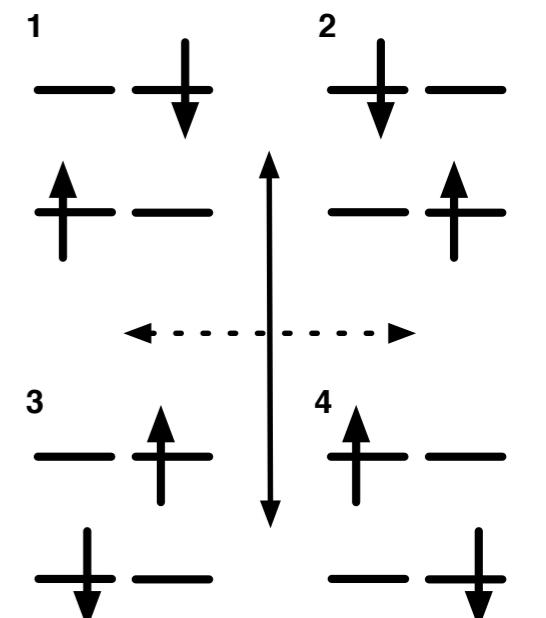


$$H = \begin{pmatrix} 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & 0 & 0 & U_{ab} & 0 & -J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & 0 & 0 & U_{ab} & 0 & -J_{ab} \\ 0 & 0 & -t_{bb} & +t_{aa} & -J_{ab} & 0 & U_{ab} & 0 \\ 0 & 0 & -t_{aa} & +t_{bb} & 0 & -J_{ab} & 0 & U_{ab} \end{pmatrix}$$

orbital-ordering: opposite spin

$$\begin{aligned}
H_{\text{eff}} &\approx \frac{1}{U_{ab}^2 - J_{ab}^2} \begin{pmatrix} (t_{aa}^2 + t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}U_{ab} & (t_{aa}^2 + t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}J_{ab} \\ -2t_{aa}t_{bb}U_{ab} & (t_{aa}^2 + t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}J_{ab} & (t_{aa}^2 + t_{bb}^2)J_{ab} \\ (t_{aa}^2 + t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}J_{ab} & (t_{aa}^2 + t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}U_{ab} \\ -2t_{aa}t_{bb}J_{ab} & (t_{aa}^2 + t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}U_{ab} & (t_{aa}^2 + t_{bb}^2)J_{ab} \end{pmatrix} \\
&= \frac{1}{U_{ab}^2 - J_{ab}^2} \begin{pmatrix} U_{ab} & J_{ab} \\ J_{ab} & U_{ab} \end{pmatrix} \otimes \begin{pmatrix} t_{aa}^2 + t_{bb}^2 & -2t_{aa}t_{bb} \\ -2t_{aa}t_{bb} & t_{aa}^2 + t_{bb}^2 \end{pmatrix} \\
&= \frac{1}{U_{ab}^2 - J_{ab}^2} \left[U_{ab} + J_{ab} - J_{ab} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right] \otimes \left[(t_{aa} - t_{bb})^2 + 2t_{aa}t_{bb} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right]
\end{aligned}$$

simultaneous coupling of spins and orbital occupations
spin- and orbital-exchange tend to have opposite sign



summary

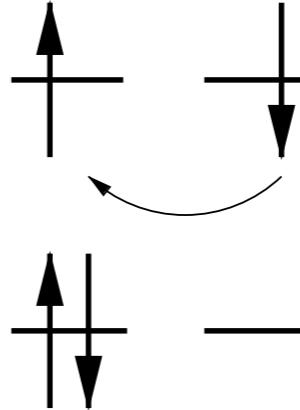
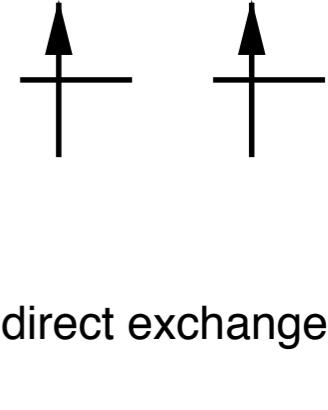
exchange mechanisms

dominant magnetic interaction in materials

not a fundamental but an **effective interaction**: model/mechanism

- ▶ Coulomb exchange: off-diagonal Coulomb matrix-elements;
ferromagnetic coupling (Hund's rule)
- ▶ kinetic exchange: only diagonal Coulomb matrix-elements & hopping
- ▶ direct exchange: anti-ferromagnetic spins: virtual hopping $-4t^2/U$
- ▶ superexchange: hopping via O-*p* orbitals
 - tends to be anti-ferromagnetic (180° superexchange)
 - but 90° superexchange is ferromagnetic
- ▶ double exchange: hopping electrons align spins ferromagnetically
- ▶ orbital ordering: exchange interaction between orbital occupations

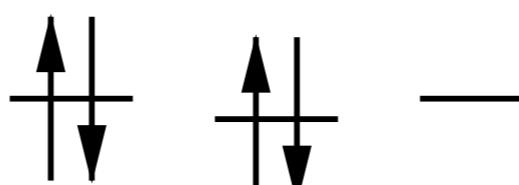
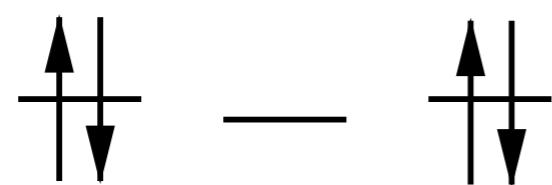
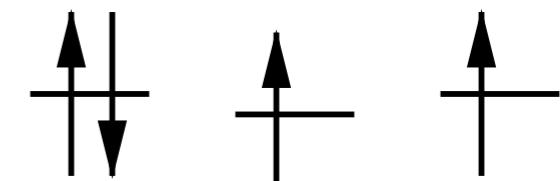
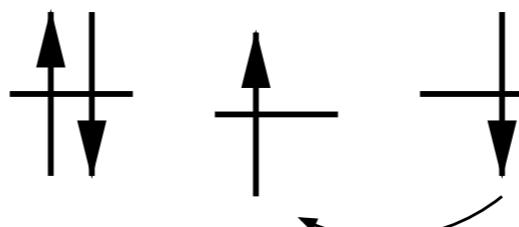
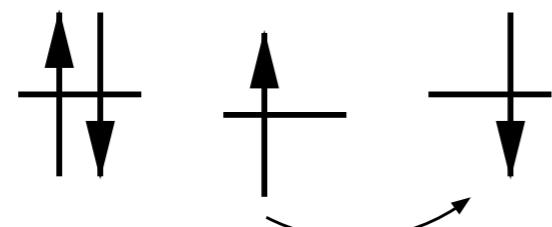
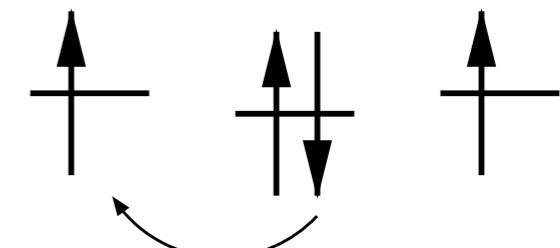
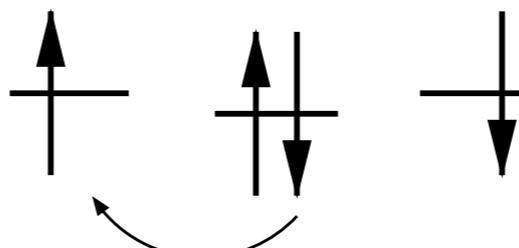
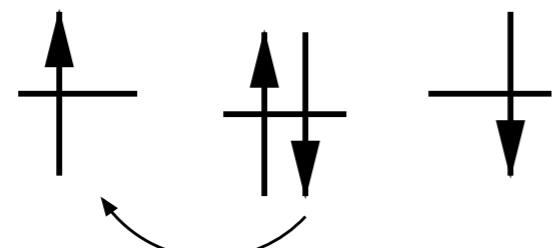
summary

$$H_U = \begin{pmatrix} U_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & U_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & U_{ab} & 0 \\ 0 & 0 & 0 & U_{ab} - J_{ab} \end{pmatrix}$$



direct exchange

Coulomb exchange:
ferro (Hund's rule)

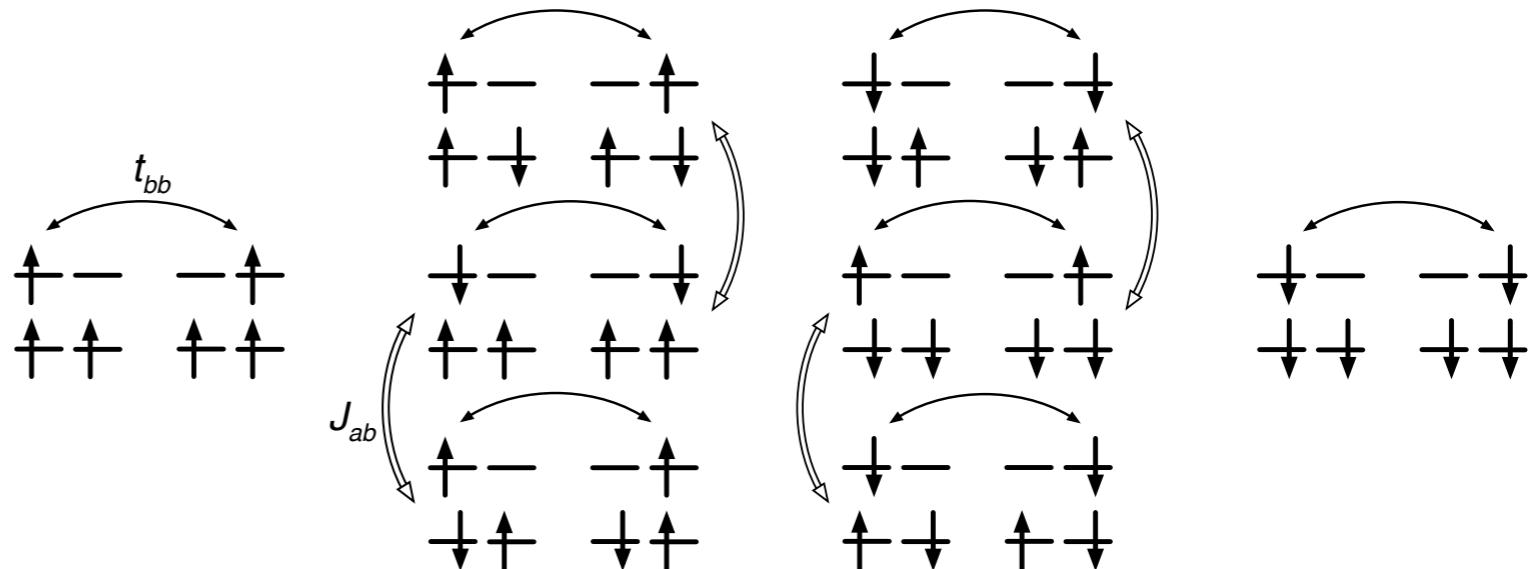
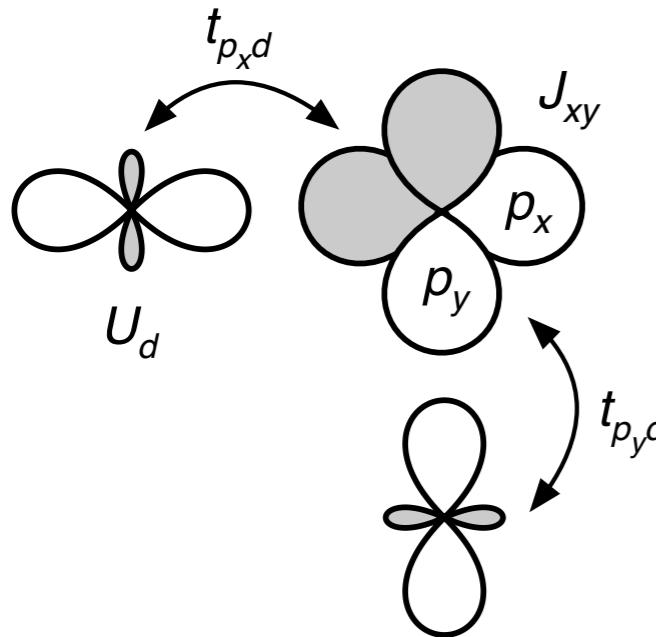
kinetic exchange:
anti-ferro



superexchange

summary

double exchange: often ferro



orbital-ordering

