Exchange Mechanisms

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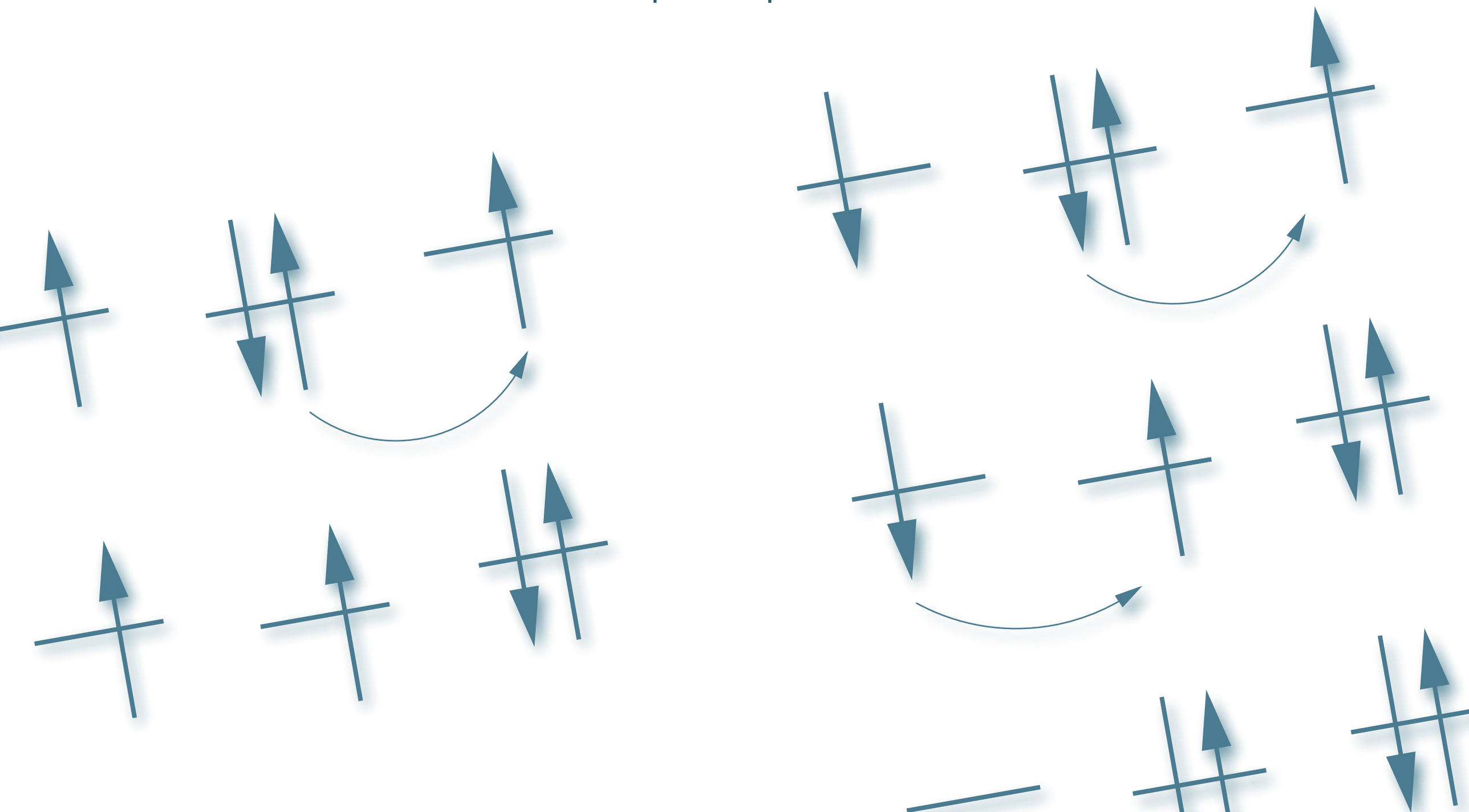


Magnetism is Quantum Mechanical

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 ⇒ does not change kinetic energy

Boltzmann statistics occupies states according to energy

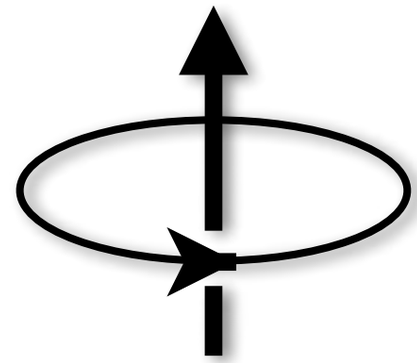
magnetic moments

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

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



electron spin

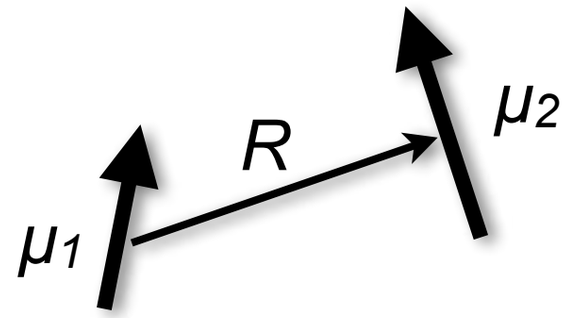
$$\vec{\mu}_S = -g_e\mu_B\langle\vec{S}/\hbar\rangle\,, \quad g_e \approx 2.0023\ldots$$

atomic moments of the order of μ_B

magnetic interaction

dipole-dipole interaction

$$\Delta E = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\hat{R} \cdot \vec{\mu}_1)(\hat{R} \cdot \vec{\mu}_2)}{4\pi\varepsilon_0 c^2 \, R^3}$$



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

$$\Delta E = -\frac{2\mu_B^2}{4\pi\varepsilon_0 c^2 (2a_0)^3} = -\frac{1/2}{137^2\, 8} \text{ Hartree} \approx 0.09\,\text{meV}$$

expect magnetic ordering below temperatures of about 1 K

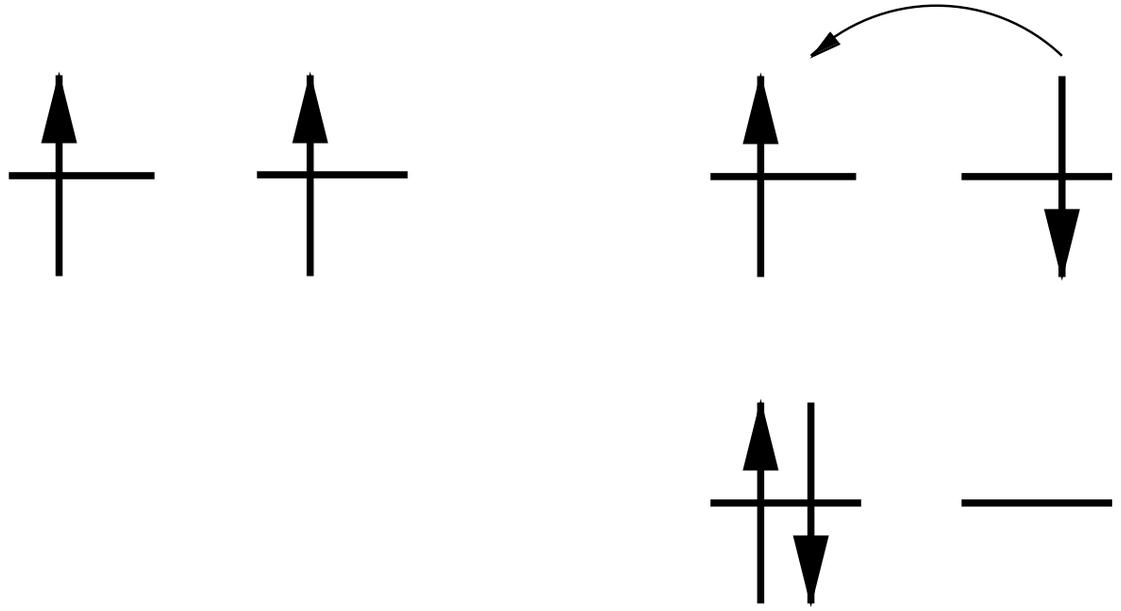
what about magnetite (Fe_3O_4)
with $T_c \approx 840$ K ?

Weiss Bezirke (magnetic domains)

dipole-dipole interaction

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.

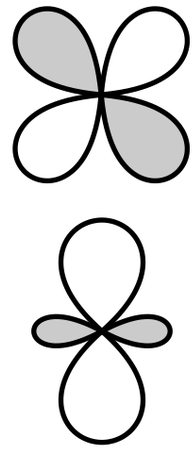
P.W. Anderson
Local Moments and Localized States
Nobel Lecture 1977

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:

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

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

Coulomb exchange: same spin

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

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

Coulomb matrix-element

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

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

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

Coulomb exchange: opposite spin

when electrons have opposite spin: σ = -σ'

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

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

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

off-diagonal matrix-elements $\left\langle \psi_{a\uparrow;\, b\downarrow} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \psi_{a\downarrow;\, b\uparrow} \right\rangle \quad = -J_{ab}$

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

Coulomb exchange

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

eigenstates

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

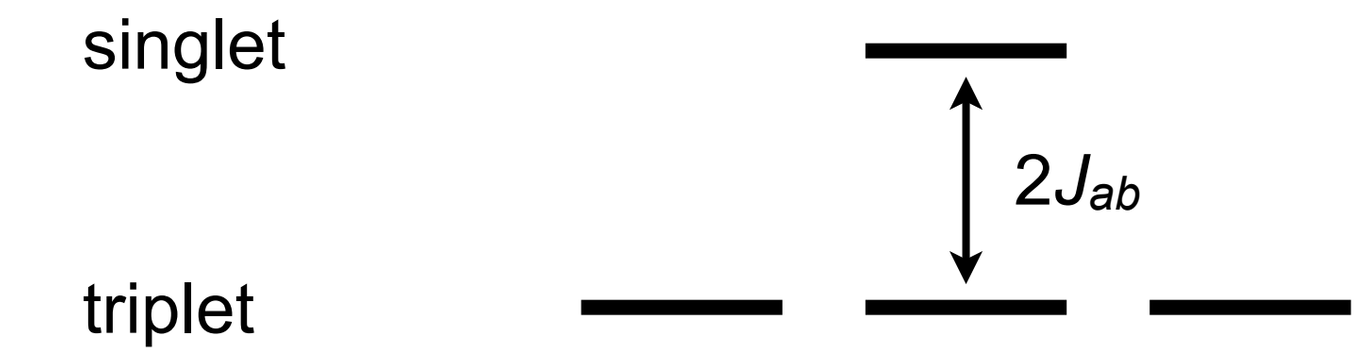
$$\begin{aligned} \psi_{\uparrow\uparrow} &= \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)\Big) && |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}\Big(\psi_{\uparrow\downarrow} + \psi_{\downarrow\uparrow}\Big) &= \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)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

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

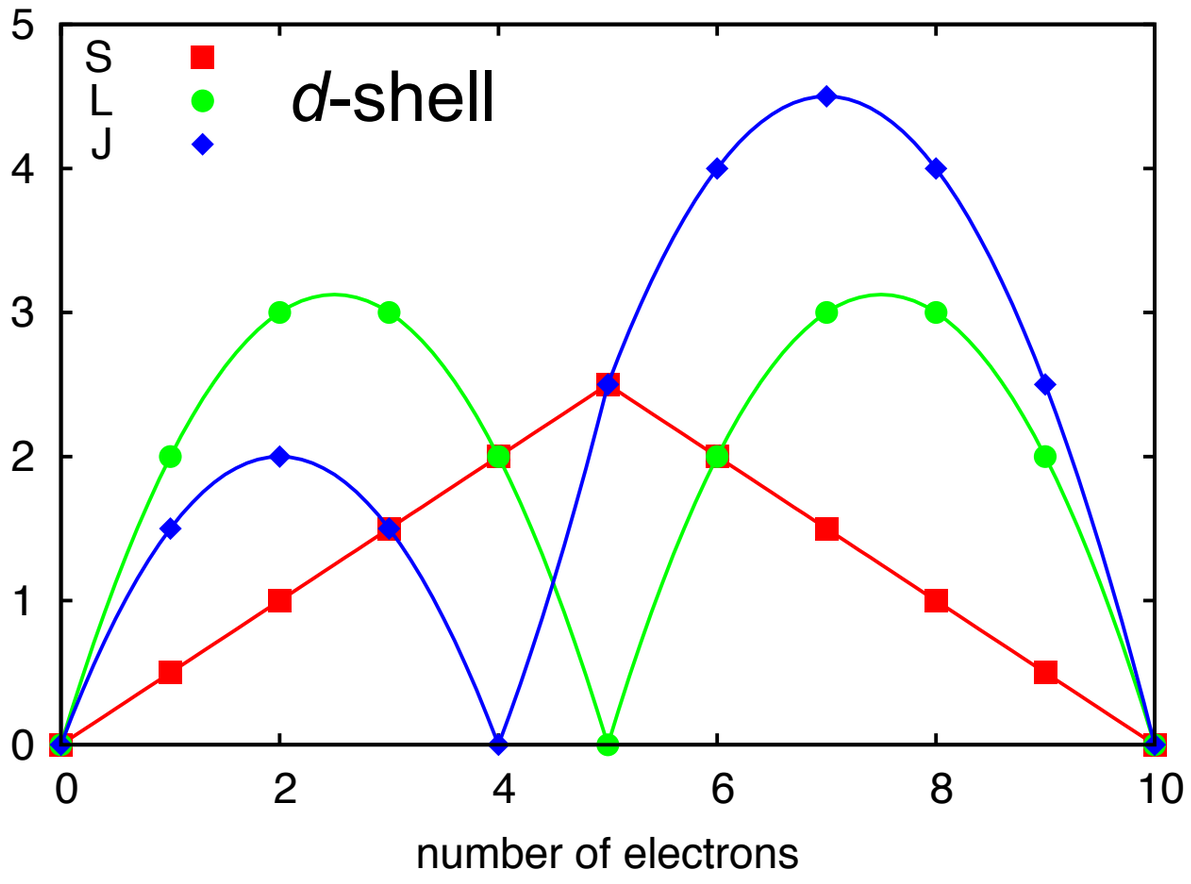
$$\frac{1}{\sqrt{2}}\Big(\psi_{\uparrow\downarrow} - \psi_{\downarrow\uparrow}\Big) = \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)\Big) \frac{1}{\sqrt{2}}\Big(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\Big)$$

Coulomb exchange

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



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

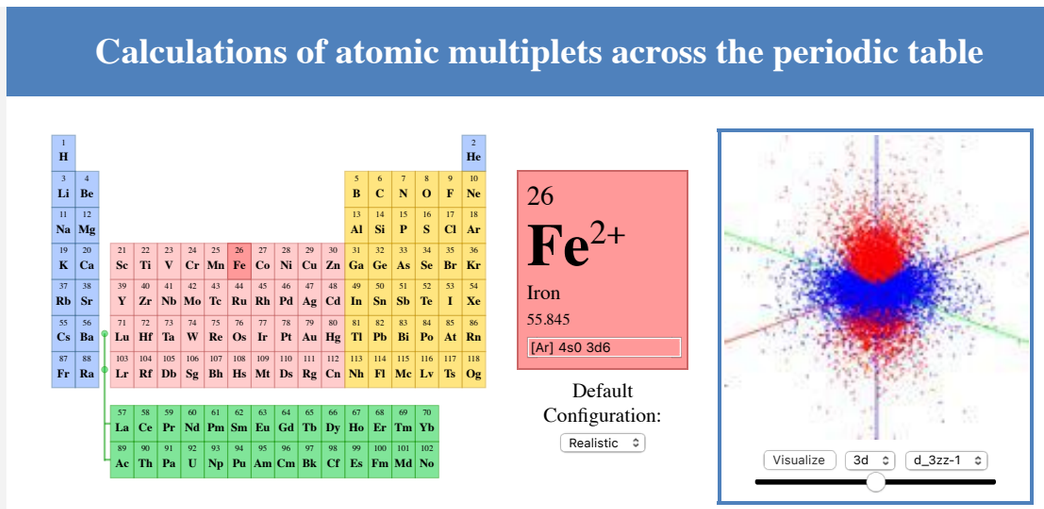


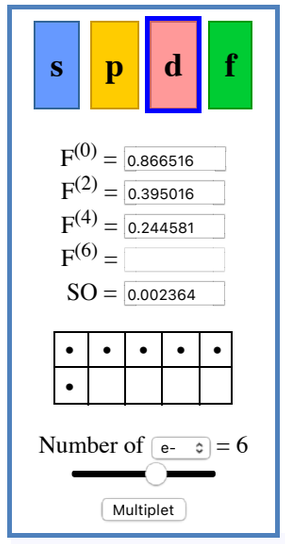
more electrons
more complicated
Coulomb matrix

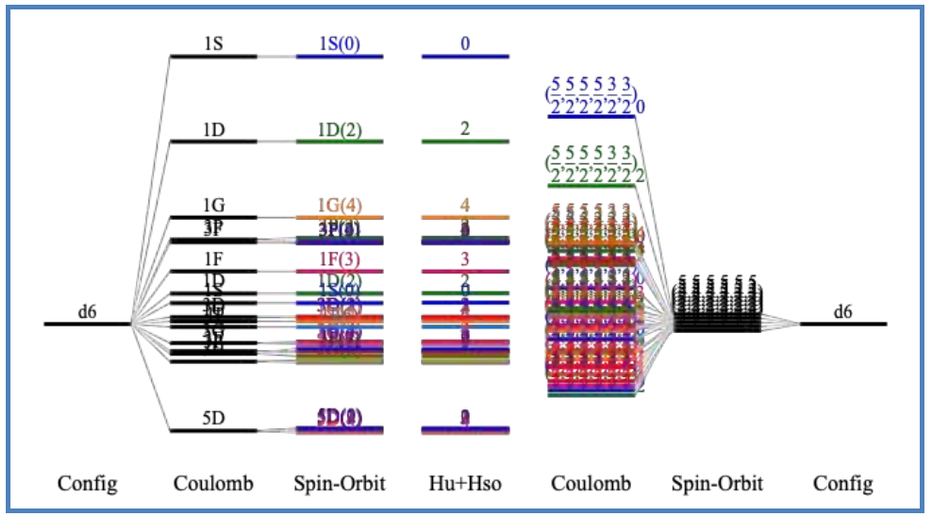
Multiplets in Transition Metal Ions

atomic multiplets

Q. Zhang:
Calculations of Atomic Multiplets
across the Periodic Table
MSc thesis, RWTH Aachen 2014
www.cond-mat.de/sims/multiplet







^5D

$$E = F^{(0)}\left[15\right] + F^{(2)}\left[-\tfrac{5}{7}\right] + F^{(4)}\left[-\tfrac{5}{7}\right]$$

$$|2,\ 2,2,\ 2\rangle = c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle$$

$$|2,\ 2,2,\ 1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle$$

$$|2,\ 2,2,\ 0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\downarrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-}\right.$$

$$|2,\ 2,2,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\uparrow}\right)|0\rangle$$

$$|2,\ 2,2,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle$$

$$|2,\ 1,2,\ 2\rangle = c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle$$

$$|2,\ 1,2,\ 1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle$$

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$$|2,-1,2,\ 2\rangle = c^\dagger_{-1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle$$

kinetic exchange

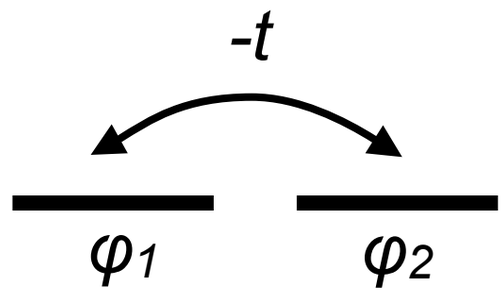
Coulomb exchange: Coulomb **matrix** for anti-symmetric wave functions

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)

$$H = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} \qquad \begin{matrix} |\uparrow, \cdot\rangle \\ |\cdot, \uparrow\rangle \end{matrix}$$

eigenstates

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

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)

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

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

direct exchange: opposite spin

two electrons of opposite spin: basis states

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

Hamiltonian

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

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

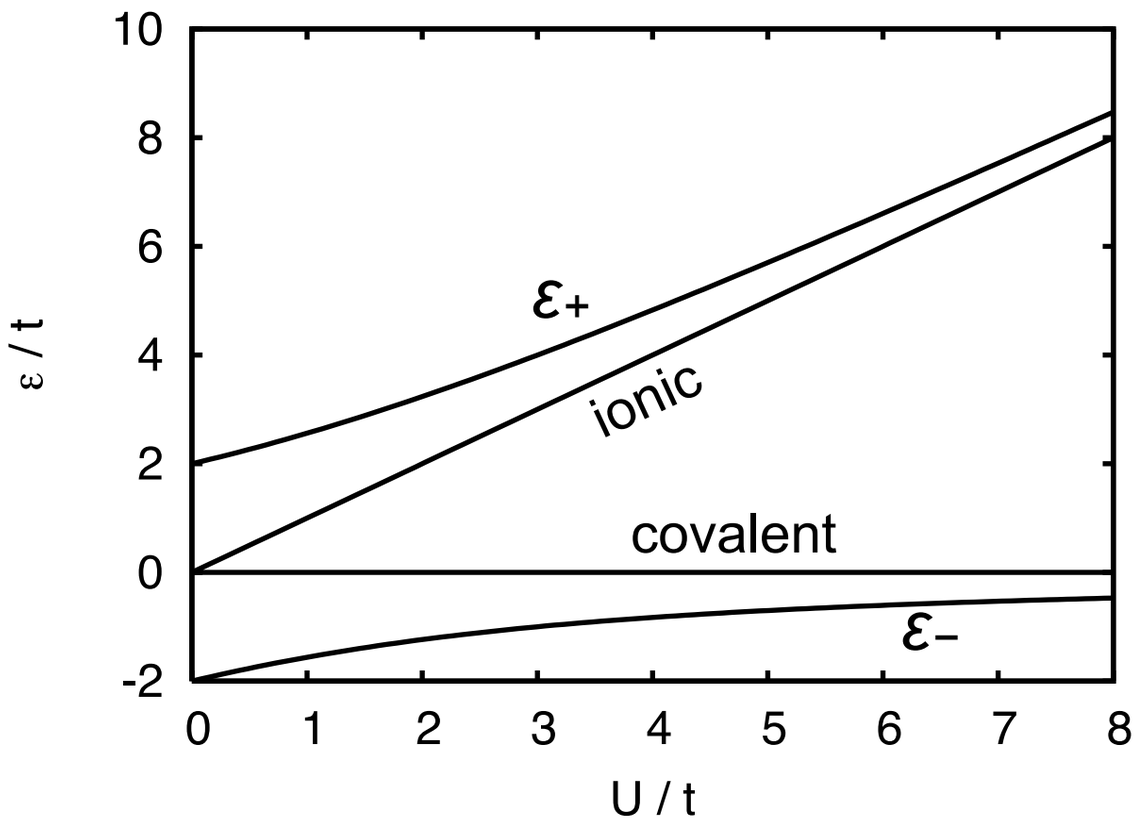
direct exchange: opposite spin

eigenstates

$$\varepsilon_\pm = \frac{U}{2} \pm \frac{\sqrt{U^2 + 16\,t^2}}{2} \quad , \quad \psi_\pm = \frac{\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle - \frac{\varepsilon_\pm}{2t}\left[|\!\uparrow\downarrow, \cdot\rangle + |\cdot, \uparrow\!\downarrow\rangle \right] \right)}{\sqrt{2 + \varepsilon_\pm^2/(2t^2)}}$$

$$\varepsilon_{\mathrm{cov}} = 0 \quad , \quad \psi_{\mathrm{cov}} = \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle \right) \qquad (\varepsilon_{\mathrm{triplet}})$$

$$\varepsilon_{\mathrm{ion}} = U \quad , \quad \psi_{\mathrm{ion}} = \frac{1}{\sqrt{2}}\left(|\uparrow\!\downarrow, \cdot\rangle - |\cdot, \uparrow\!\downarrow\rangle \right)$$



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

$$\varepsilon_+ \quad \to \quad U + 4t^2/U$$

$$\varepsilon_- \quad \to \quad -4t^2/U$$

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

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

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

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

invert block-2×2 matrix

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

solve

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

$$\begin{aligned} A\tilde{A} + B\tilde{C} &= 1 && = (A - BD^{-1}C)\tilde{A} \\ C\tilde{A} + D\tilde{C} &= 0 \quad \rightsquigarrow \quad \tilde{C} = -D^{-1}C\tilde{A} \end{aligned}$$

$$\rightsquigarrow \tilde{A} = \left(A - BD^{-1}C\right)^{-1}$$

direct exchange: effective Hamiltonian

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

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

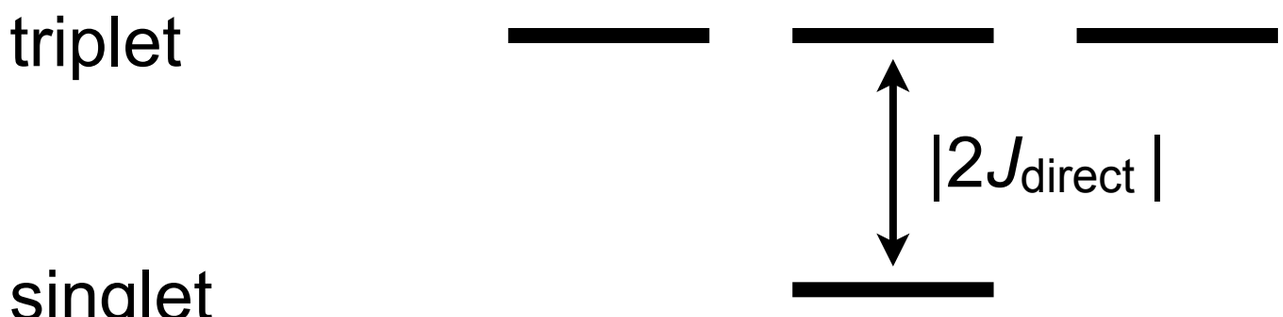
diagonalize H_{eff}

$$\varepsilon_t = 0 \qquad \psi_t = \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\Big) \qquad \text{triplet}$$

$$\varepsilon_s = -\frac{4t^2}{U} \qquad \psi_s = \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\Big) \qquad \text{singlet}$$

direct exchange: effective spin-coupling

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



effective spin-Hamiltonian

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

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

Heisenberg J

second quantization: formalism

vacuum state $|0\rangle$

and

set of operators c_α related to single-electron states $\varphi_\alpha(x)$

defined by:

$$c_\alpha|0\rangle = 0 \qquad \left\{c_\alpha, c_\beta\right\} = 0 = \left\{c_\alpha^\dagger, c_\beta^\dagger\right\}$$

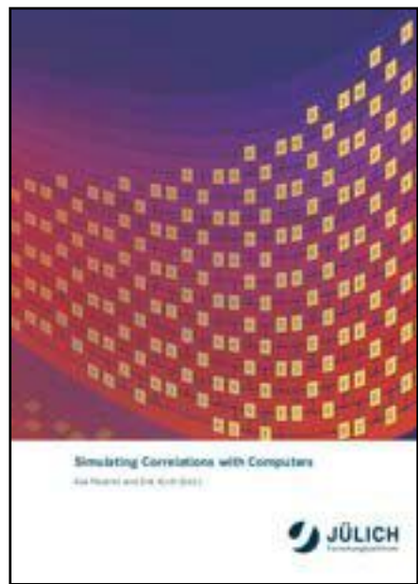
$$\langle 0|0\rangle = 1 \qquad \left\{c_\alpha, c_\beta^\dagger\right\} = \langle\alpha|\beta\rangle$$

creators/annihilators operate in Fock space
transform like orbitals!

field operators $\hat{\psi}(x) = \sum_n \varphi_{\alpha_n}(x)\, c_{\alpha_n}$

Slater determinant $\frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1)\hat{\psi}(x_2)\ldots\hat{\psi}(x_N)\, c_{\alpha_N}^\dagger \ldots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \right| 0 \right\rangle$

www.cond.mat.de/events/correl21/manuscripts/koch.pdf



Hartree-Fock

ansatz: Slater determinant

$$|\psi(\theta_\uparrow, \theta_\downarrow)\rangle = \left(\sin(\theta_\downarrow)\, c^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\, c^\dagger_{2\downarrow}\right)\left(\sin(\theta_\uparrow)\, c^\dagger_{1\uparrow} + \cos(\theta_\uparrow)\, c^\dagger_{2\uparrow}\right)\Big|0\Big\rangle$$

energy expectation value

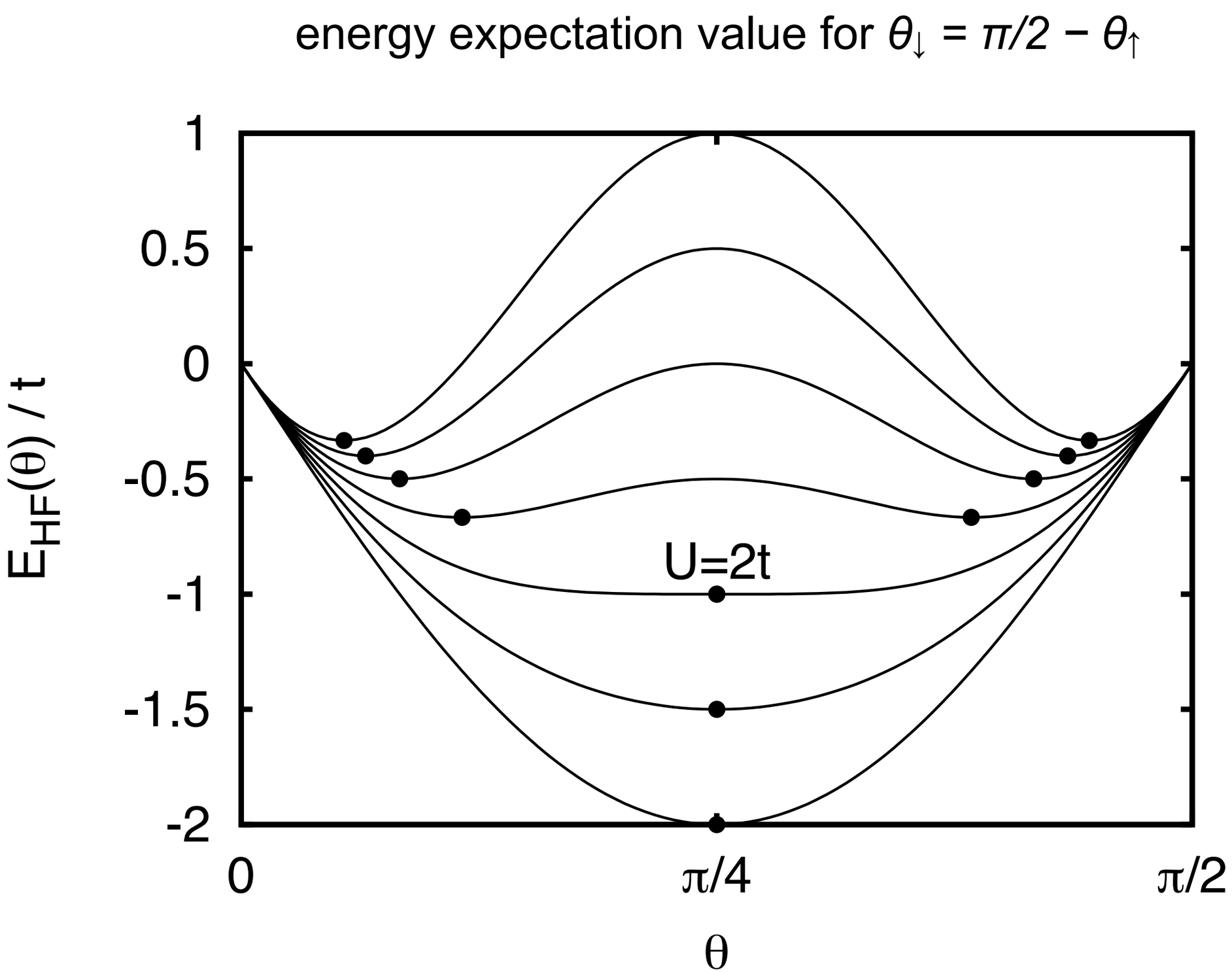
$$E(\theta_\uparrow, \theta_\downarrow) = -2t\,(\sin\theta_\uparrow \sin\theta_\downarrow + \cos\theta_\uparrow \cos\theta_\downarrow)(\cos\theta_\uparrow \sin\theta_\downarrow + \sin\theta_\uparrow \cos\theta_\downarrow)$$
$$+U\left(\sin^2\theta_\uparrow \sin^2\theta_\downarrow + \cos^2\theta_\uparrow \cos^2\theta_\downarrow\right)$$

minimize wrt $\theta_\uparrow$ and $\theta_\downarrow$

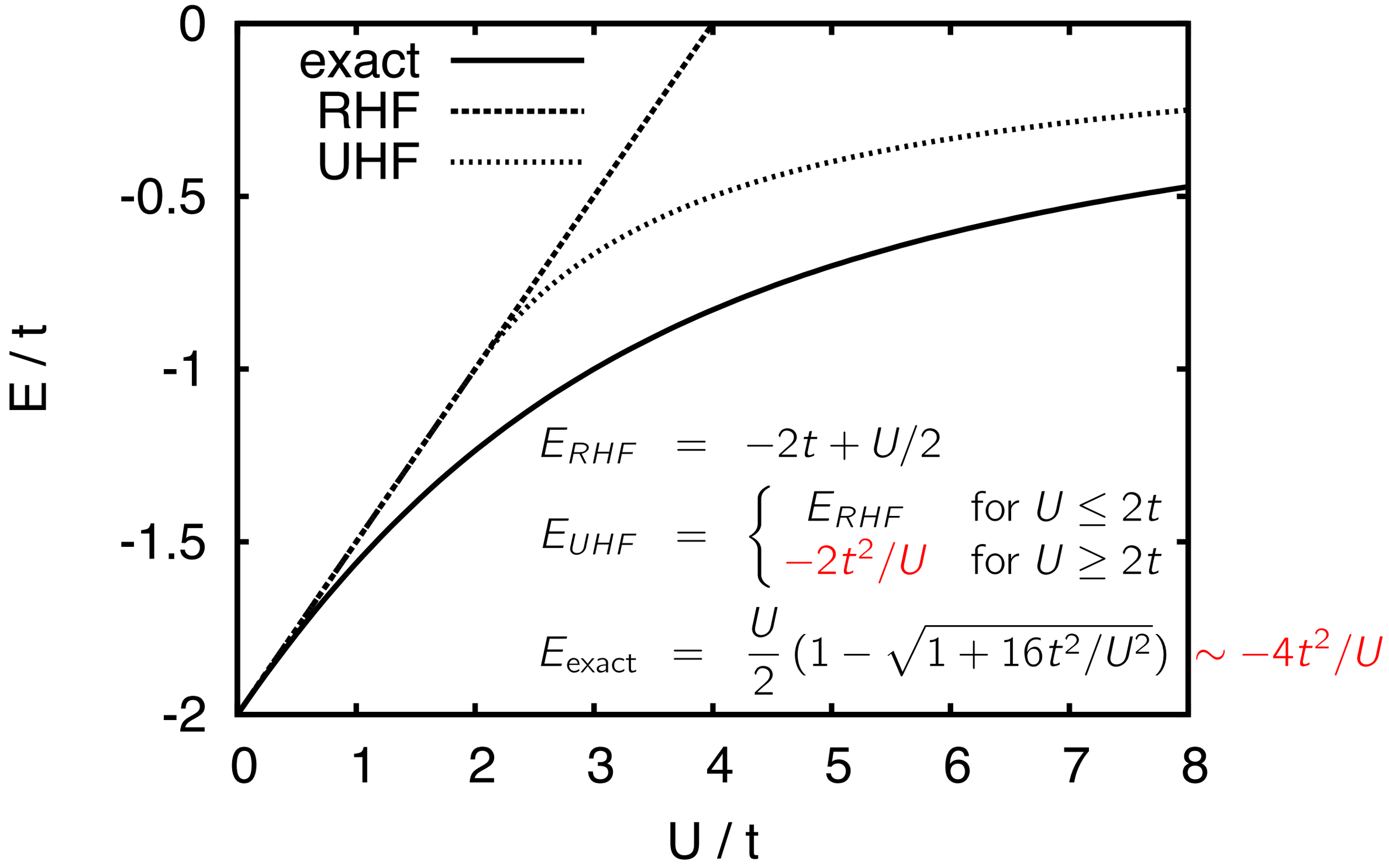
HF orbitals respect symmetry of model: restricted Hartree-Fock (RHF)
here: $\theta_\uparrow = \theta_\downarrow = \pi/4$

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

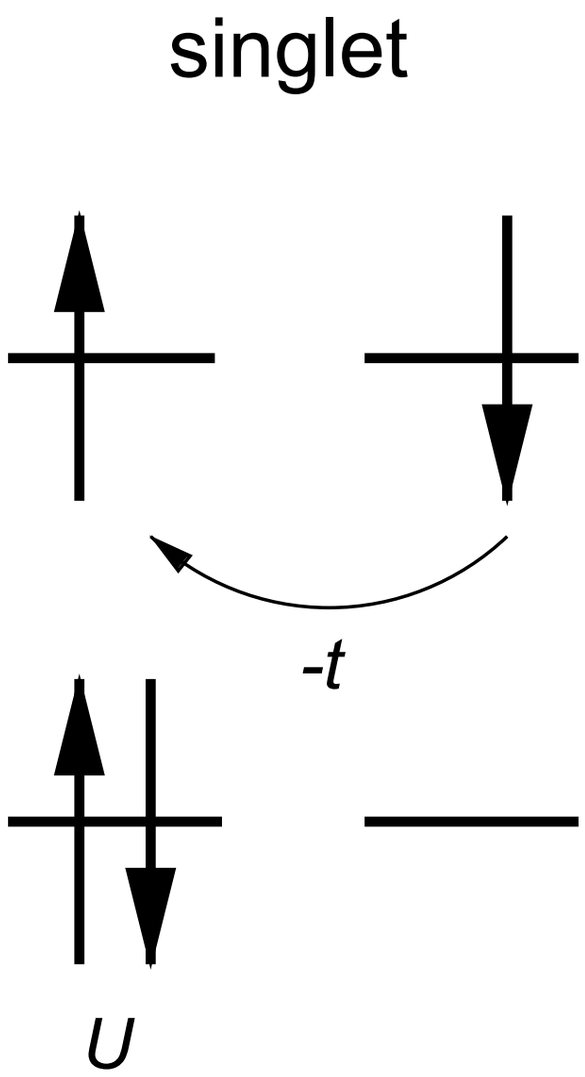
Hartree-Fock



Hartree-Fock



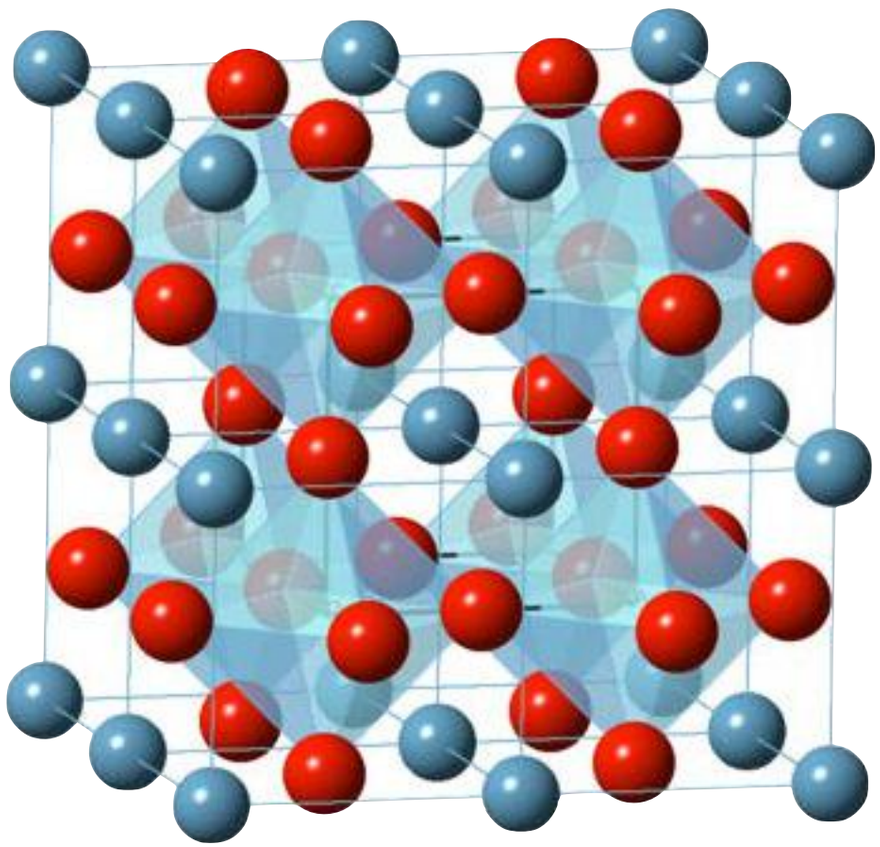
direct kinetic exchange



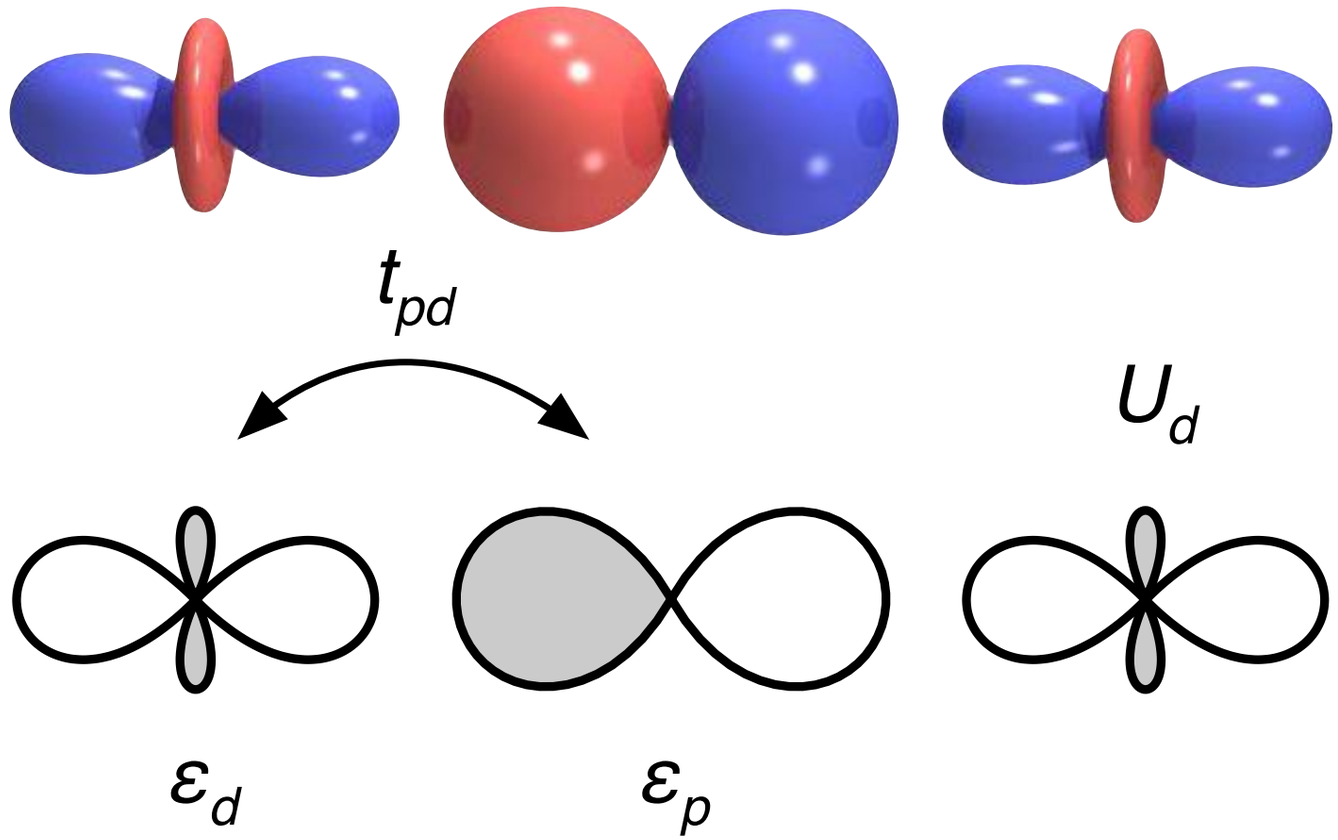
direct exchange

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

superexchange



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



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

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

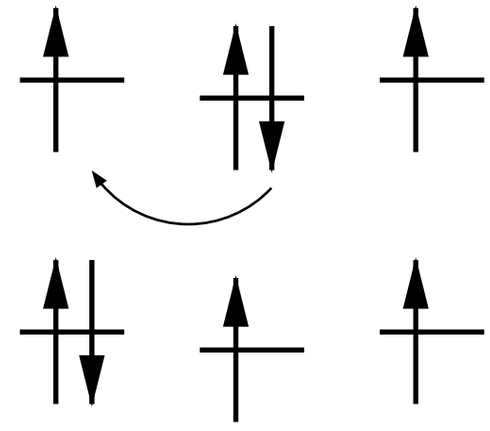
superexchange: same spin

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

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

$$H = \left(\begin{array}{c|cc} 0 & t_{pd} & t_{pd} \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 \\ t_{pd} & 0 & U_d + \Delta_{pd} \end{array} \right)$$

$$c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\uparrow} |0\rangle$$
$$c^\dagger_{2\uparrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle$$
$$c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{p\uparrow} c^\dagger_{1\uparrow} |0\rangle$$

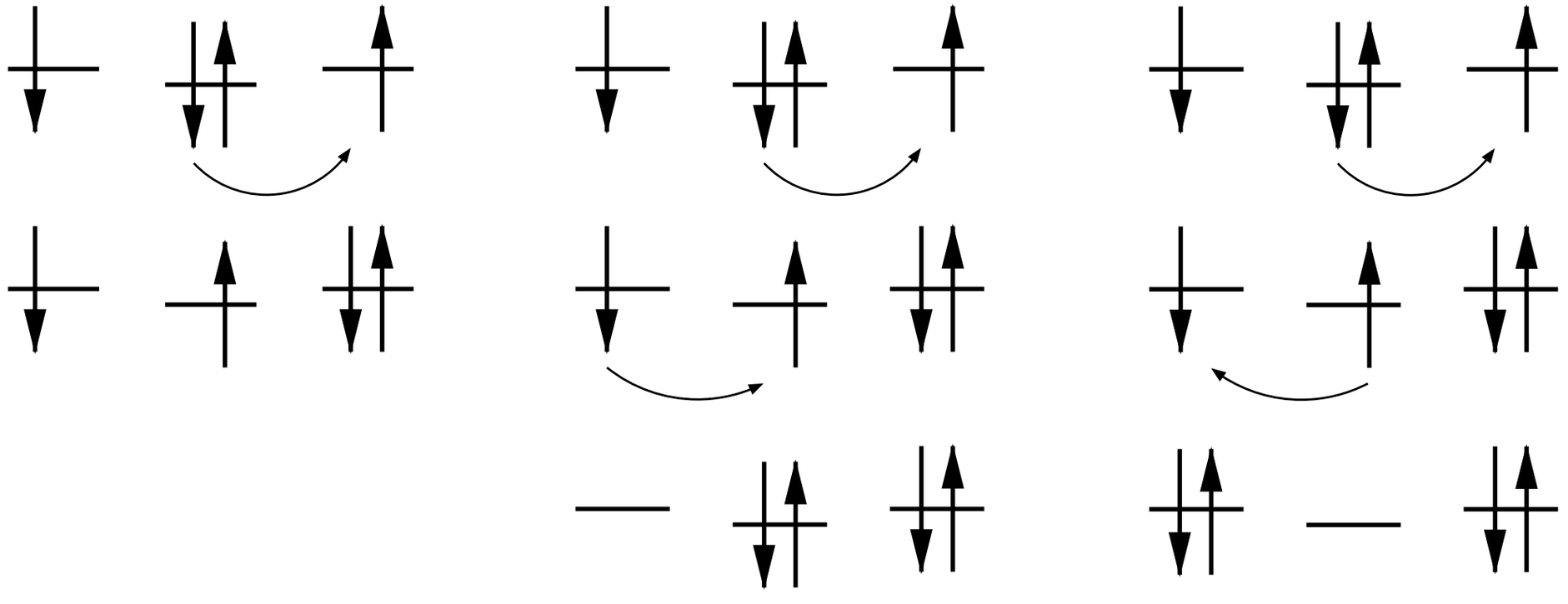


$$H_{\text{eff}} = (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix}^{-1} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \approx -\frac{2 t_{pd}^2}{U_d + \Delta_{pd}}$$

superexchange: opposite spin

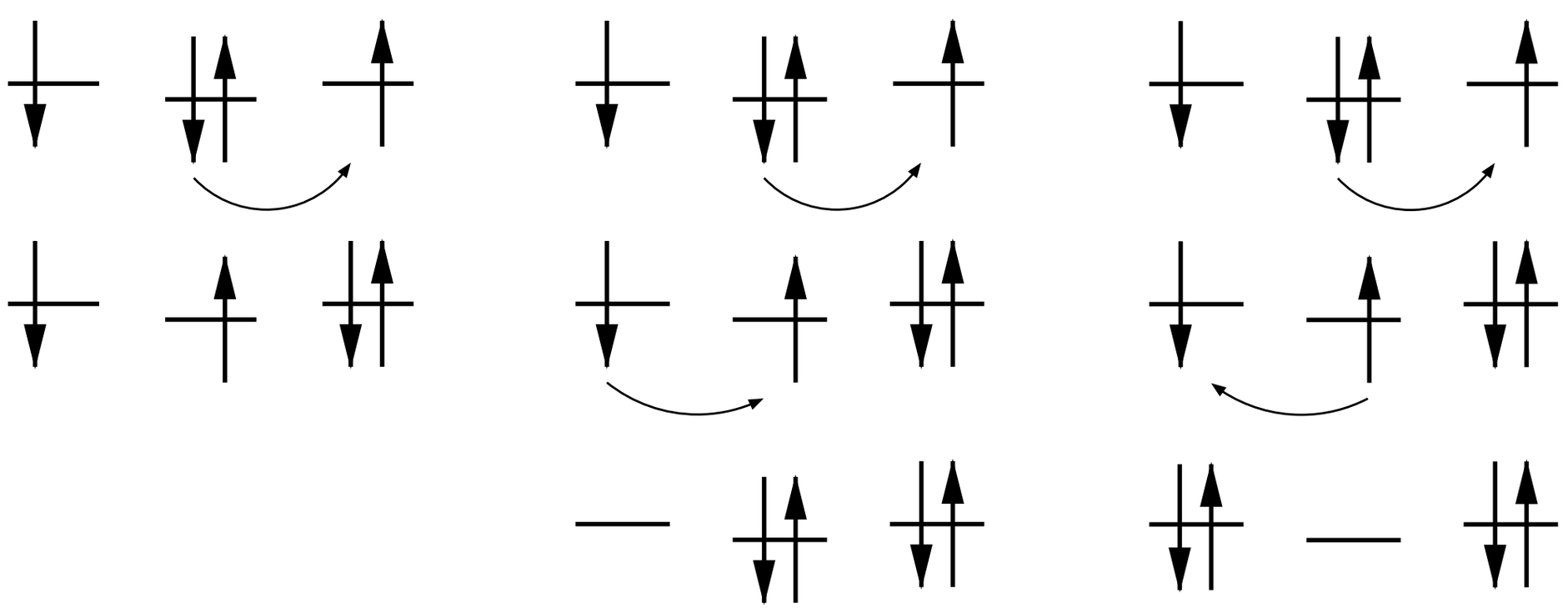
$$
\left(\begin{array}{cc|cccc|ccc}
0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 \\
\hline
+t_{pd} & 0 & U_d+\Delta_{pd} & 0 & 0 & 0 & -t_{pd} & 0 & -t_{pd} \\
+t_{pd} & 0 & 0 & U_d+\Delta_{pd} & 0 & 0 & 0 & -t_{pd} & -t_{pd} \\
0 & +t_{pd} & 0 & 0 &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

$$
\begin{array}{l}
c^\dagger_{2\downarrow}c^\dagger_{p\downarrow}c^\dagger_{p\uparrow}c^\dagger_{1\uparrow}|0\rangle \\
c^\dagger_{2\uparrow}c^\dagger_{p\downarrow}c^\dagger_{p\uparrow}c^\dagger_{1\downarrow}|0\rangle \\
c^\dagger_{2\downarrow}c^\dagger_{p\uparrow}c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle \\
c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}c^\dagger_{p\downarrow}c^\dagger_{1\uparrow}|0\rangle \\
c^\dagger_{2\uparrow}c^\dagger_{p\downarrow}c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle \\
c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}c^\dagger_{p\uparrow}c^\dagger_{1\downarrow}|0\rangle \\
c^\dagger_{p\downarrow}c^\dagger_{p\uparrow}c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle \\
c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}c^\dagger_{p\downarrow}c^\dagger_{p\uparrow}|0\rangle \\
c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle
\end{array}
$$



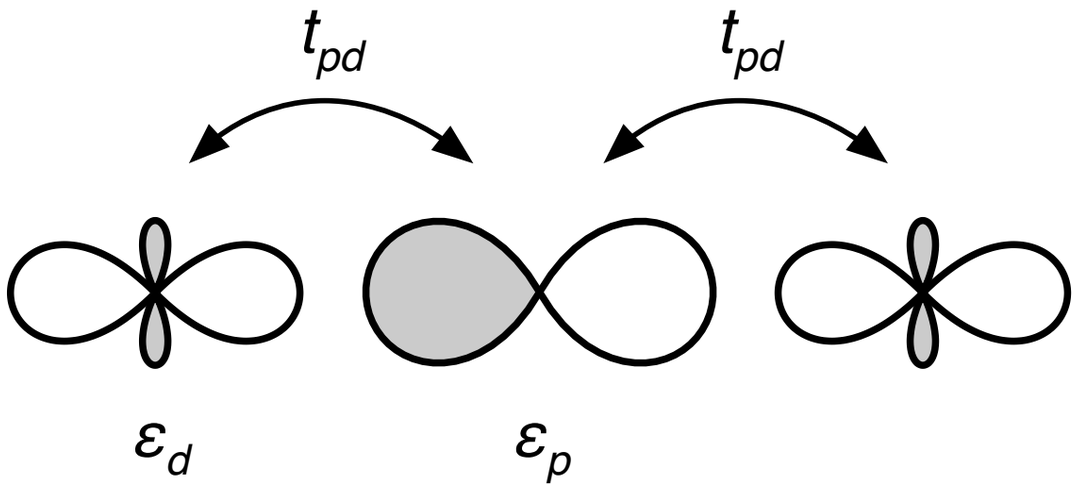
superexchange: opposite spin

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



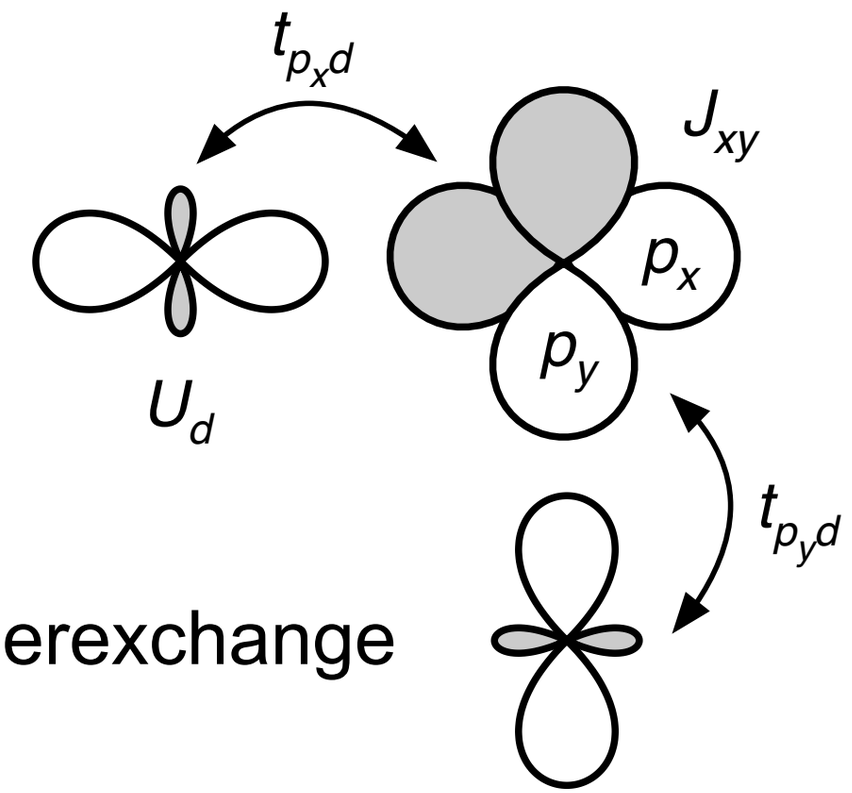
singlet-triplet splitting: $$J = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2}\left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}}\right)$$

ferromagnetic superexchange



180˚ superexchange

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



90˚ superexchange

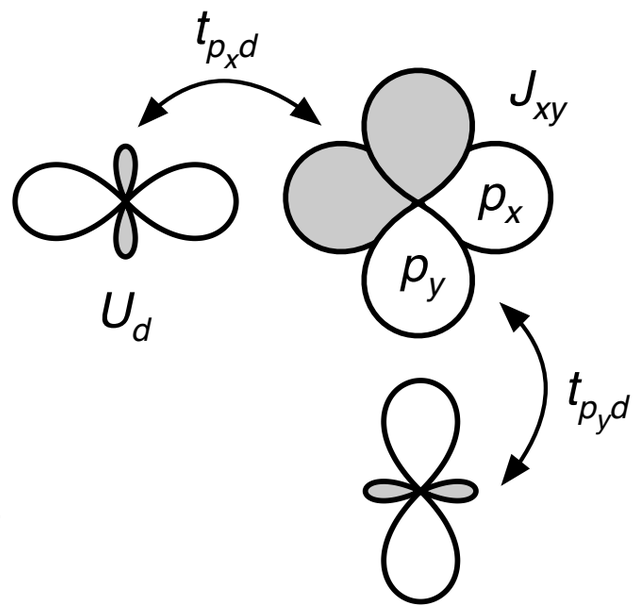
no hopping connecting *d*-orbitals but Coulomb exchange on oxygen

double exchange

ferro superexchange: same spin

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

$$\begin{array}{l} c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\uparrow}|0\rangle \\ c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\uparrow}|0\rangle \\ c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \\ c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\uparrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}c^\dagger_{2\downarrow}|0\rangle \end{array}$$



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

hopping *p*-electrons have same spin
Hund's rule coupling J_{xy} on *p*

ferro superexchange: opposite spin

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

$$
\begin{array}{l}
c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{y\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{x\downarrow}c^\dagger_{x\uparrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\uparrow}c^\dagger_{y\downarrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \\
c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{x\downarrow}c^\dagger_{y\uparrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle
\end{array}
$$

$$
\begin{aligned}
H_{\text{eff}} &= -\frac{2t_{pd}^2}{U_d+\Delta_{pd}}\begin{pmatrix}1&0\\0&1\end{pmatrix} - \frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{1}{4(U_d+\Delta_{pd})^2-J_{xy}^2}\begin{pmatrix}2(U_d+\Delta_{pd}) & +J_{xy}\\ +J_{xy} & 2(U_d+\Delta_{pd})\end{pmatrix} \\
&= -\left(\frac{2t_{pd}^2}{U_d+\Delta_{pd}} + \frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{1}{2(U_d+\Delta_{pd})-J_{xy}}\right) \quad \text{(as for same spin)} \\
&\quad + \frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{J_{xy}}{4(U_d+\Delta_{pd})^2-J_{xy}^2}\begin{pmatrix}1&-1\\-1&1\end{pmatrix}
\end{aligned}
$$

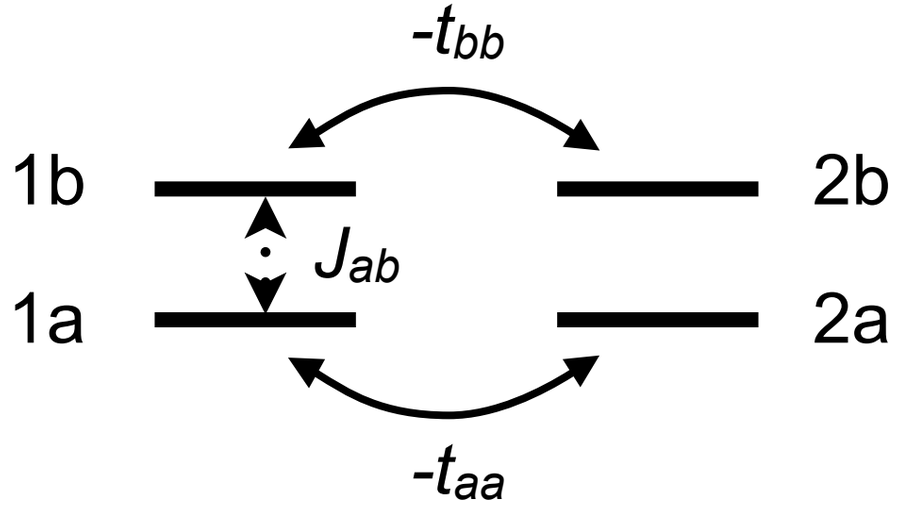
singlet-triplet splitting $\qquad J = -\dfrac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\dfrac{2J_{xy}}{4(U_d+\Delta_{pd})^2-J_{xy}^2}$

double exchange

double exchange involves both, full Coulomb matrix and hopping

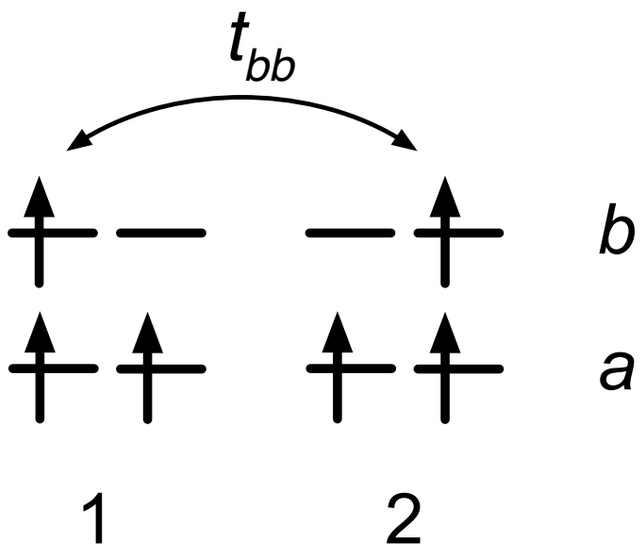
mixed-valence compound: non-integer filling of *d*-orbital
d-electrons can hop even when *U* is large

simple model: two sites with two orbitals each



double exchange

S_z=3/2



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

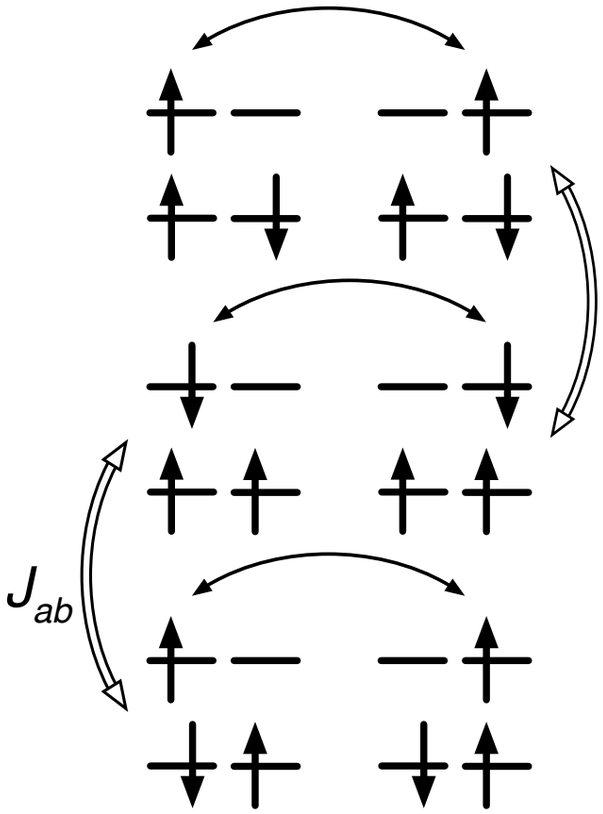
$$\varepsilon_{\pm} = -J_{ab} \pm t_{bb}$$

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

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

double exchange

S_z=1/2



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

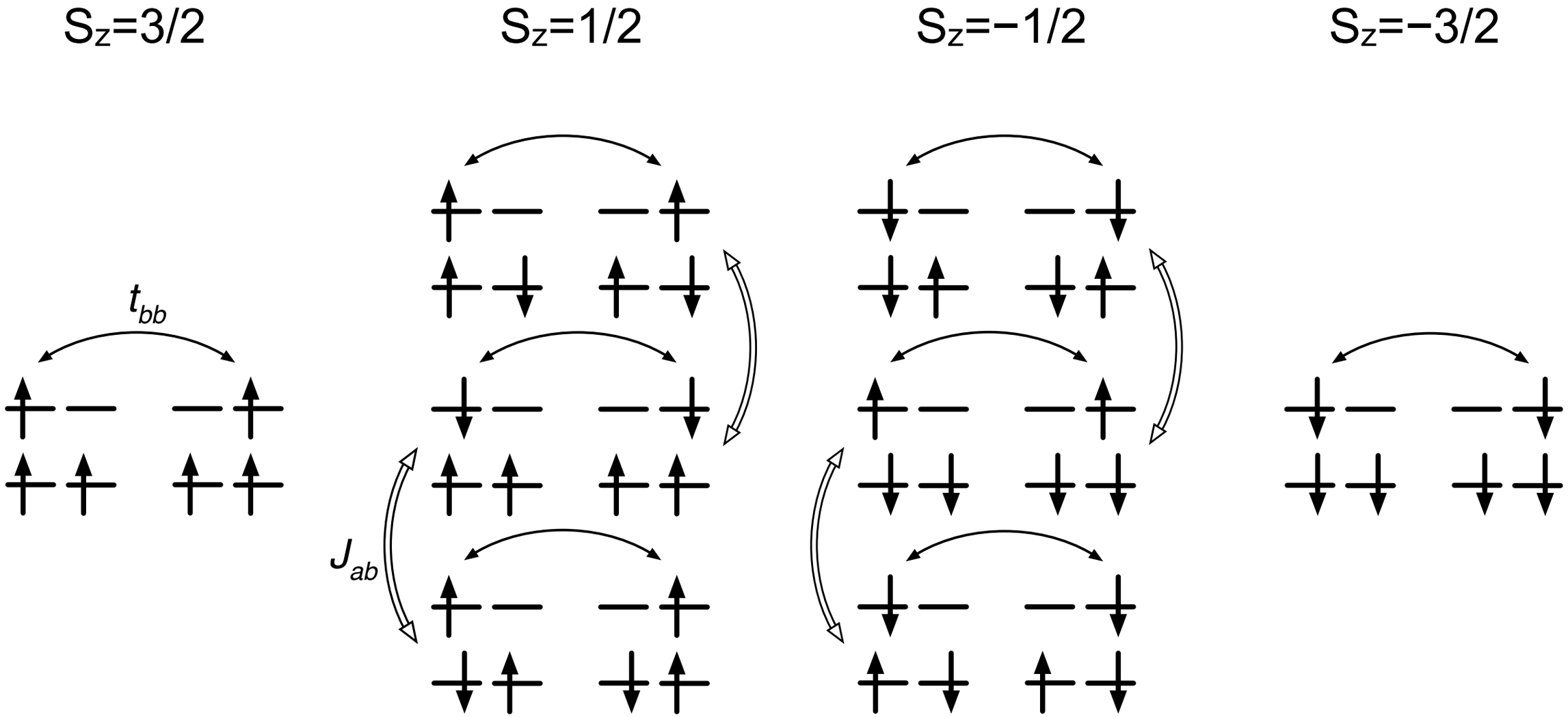
ground state $\quad \varepsilon_0 = -J_{ab} - t_{bb}$

$$\frac{1}{\sqrt{6}}\Big(|\uparrow,\uparrow\rangle_1|\cdot,\downarrow\rangle_2+|\cdot,\uparrow\rangle_1|\uparrow,\downarrow\rangle_2+|\cdot,\uparrow\rangle_1|\downarrow,\uparrow\rangle_2+|\downarrow,\uparrow\rangle_1|\cdot,\uparrow\rangle_2+|\uparrow,\downarrow\rangle_1|\cdot,\uparrow\rangle_2+|\cdot,\downarrow\rangle_1|\uparrow,\uparrow\rangle_2\Big)$$

$$= \frac{1}{\sqrt{2}}\Big(|\uparrow,\cdot\rangle_b + |\cdot,\uparrow\rangle_b\Big)\,\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle_a + |\downarrow,\uparrow\rangle_a\Big) + \frac{1}{\sqrt{2}}\Big(|\downarrow,\cdot\rangle_b + |\cdot,\downarrow\rangle_b\Big)\,|\uparrow,\uparrow\rangle_a$$

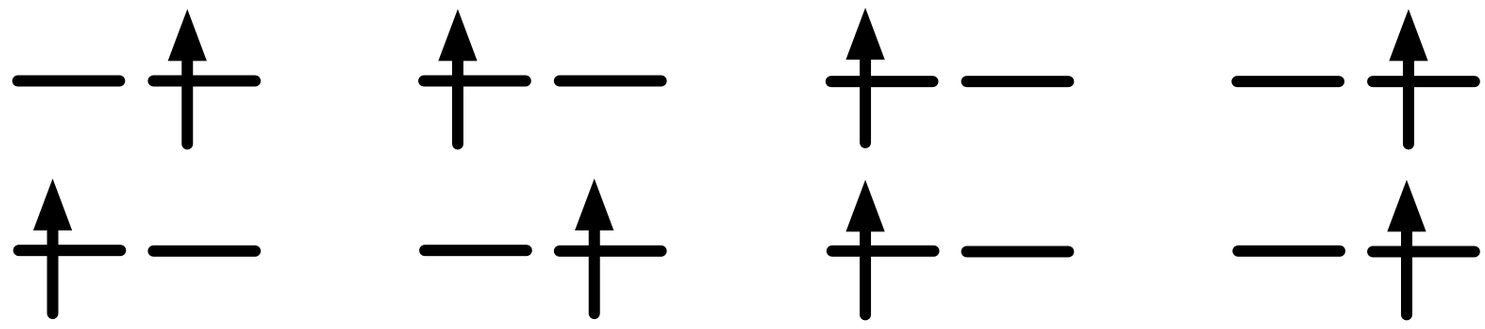
hopping electron aligns *a*-electrons ferromagnetically
(teleports local triplet into triplet of *a*-electrons)

double exchange



orbital ordering

same model, but now one electron per orbital

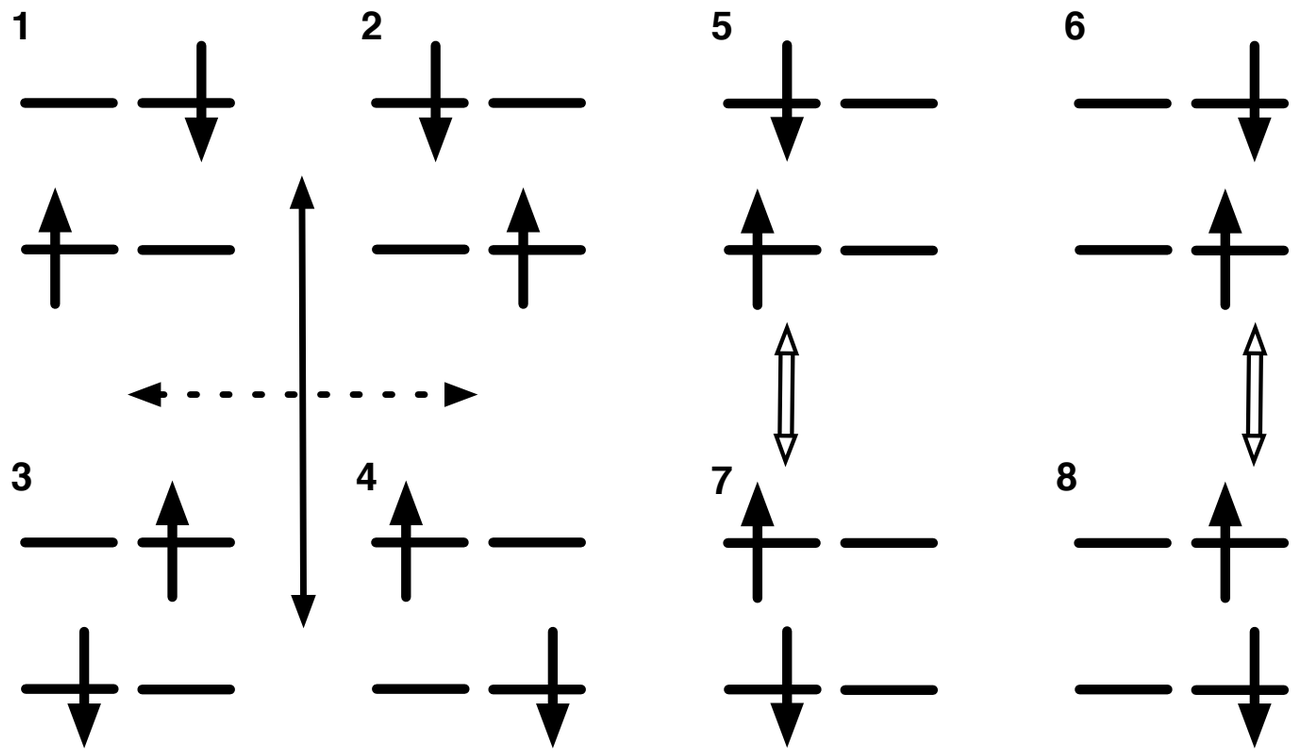


$$H = \left(\begin{array}{cc|cc} 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & U_{ab}-J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & U_{ab}-J_{ab} \end{array}\right)$$

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

effective interaction between orbitals: orbital singlet/triplet

orbital ordering: opposite spins



$$H = \left(\begin{array}{cccc|cccc} 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & 0 & 0 & U_{ab} & 0 & -J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & 0 & 0 & U_{ab} & 0 & -J_{ab} \\ 0 & 0 & -t_{bb} & +t_{aa} & -J_{ab} & 0 & U_{ab} & 0 \\ 0 & 0 & -t_{aa} & +t_{bb} & 0 & -J_{ab} & 0 & U_{ab} \end{array}\right)$$

orbital-ordering: opposite spin

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

$$= -\frac{1}{U_{ab}^2 - J_{ab}^2} \begin{pmatrix} U_{ab} & J_{ab} \\ J_{ab} & U_{ab} \end{pmatrix} \otimes \begin{pmatrix} t_{aa}^2 + t_{bb}^2 & -2t_{aa}t_{bb} \\ -2t_{aa}t_{bb} & t_{aa}^2 + t_{bb}^2 \end{pmatrix}$$

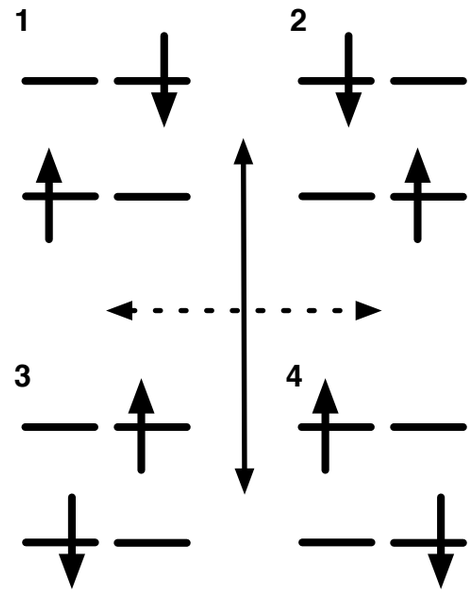
$$= -\frac{1}{U_{ab}^2 - J_{ab}^2} \left[U_{ab} + J_{ab} - J_{ab} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right] \otimes \left[(t_{aa} - t_{bb})^2 + 2t_{aa}t_{bb} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right]$$

spin-exchange

orbital-exchange

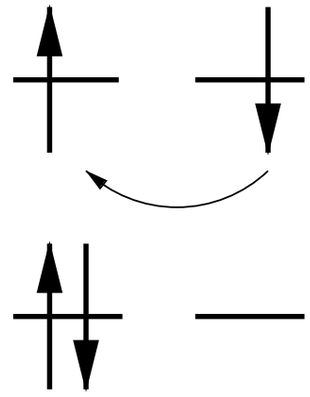
simultaneous coupling of spins and orbital occupations

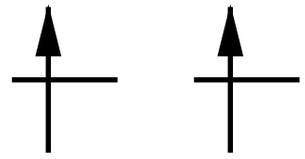
spin- and orbital-exchange tend to have opposite sign



summary

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

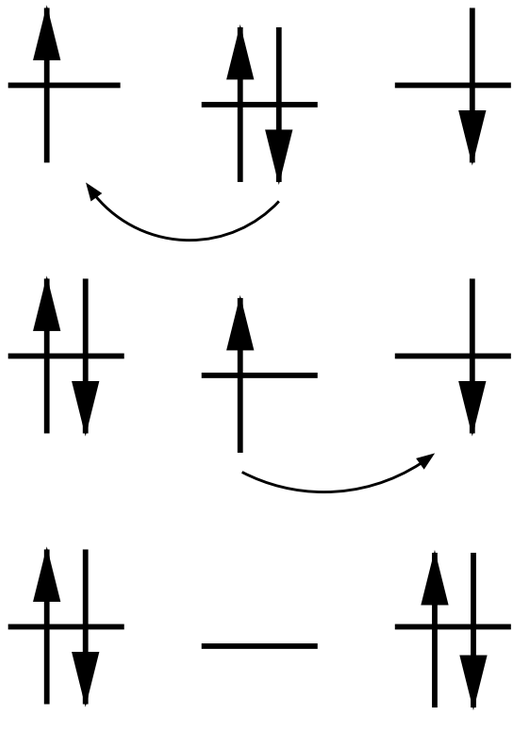


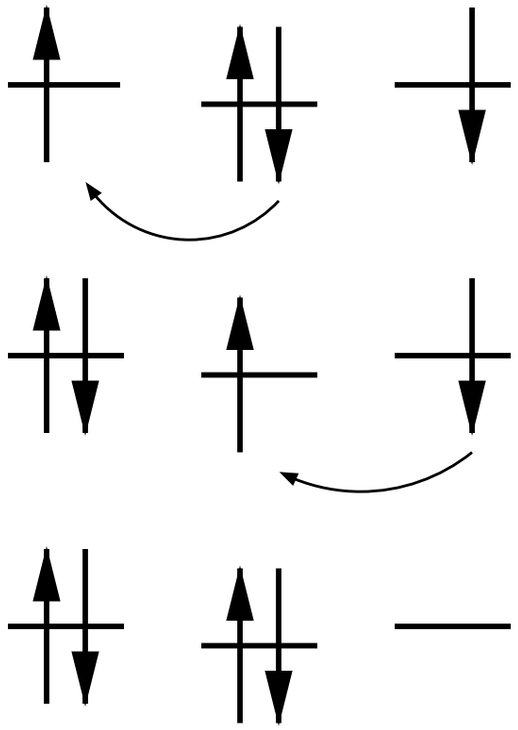


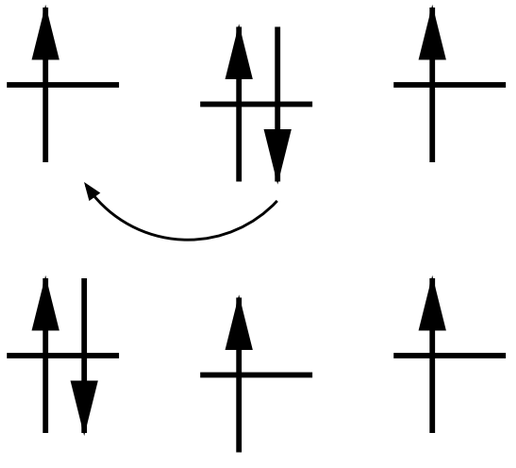
direct exchange

Coulomb exchange:
ferro (Hund's rule)

kinetic exchange:
anti-ferro



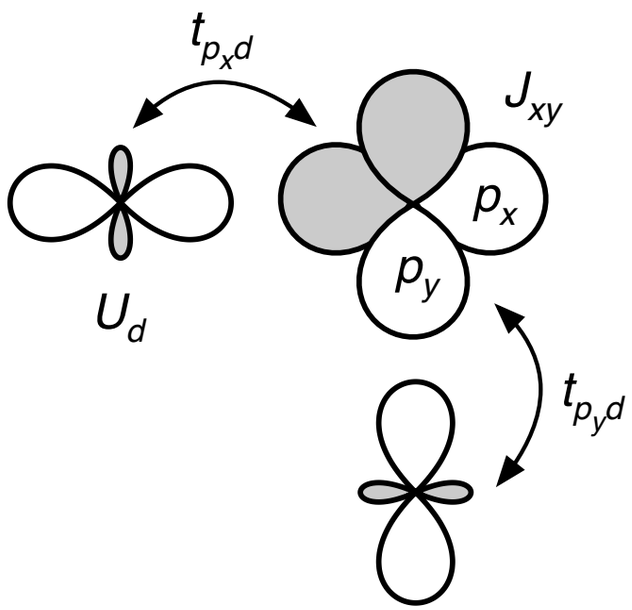


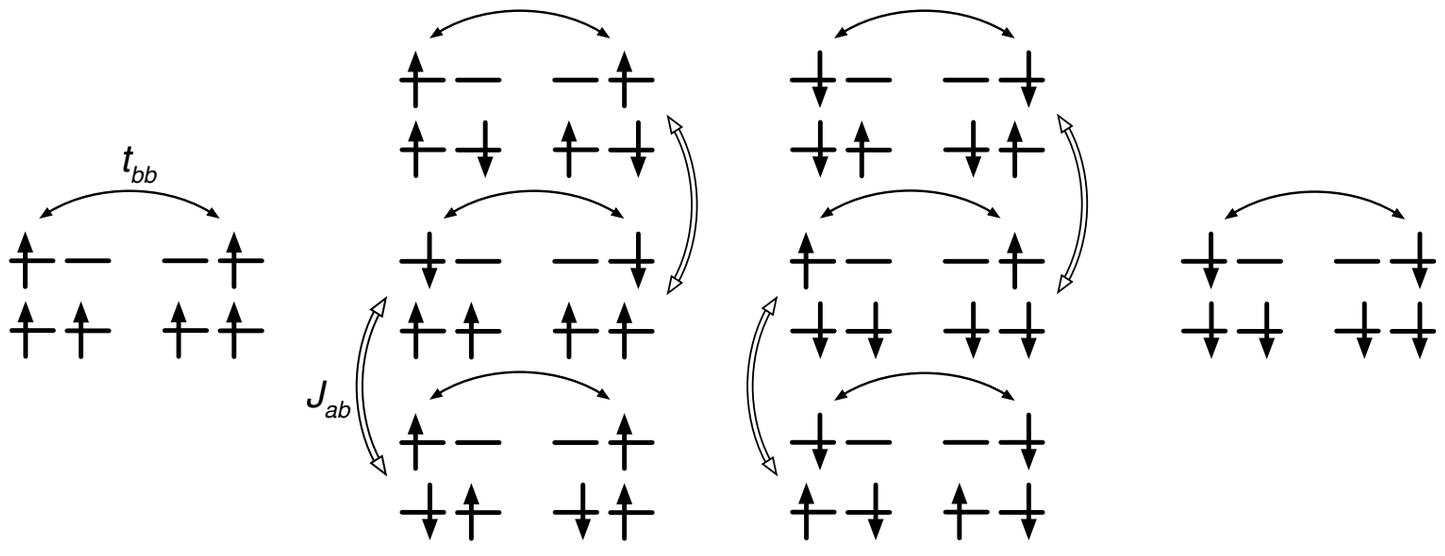


superexchange

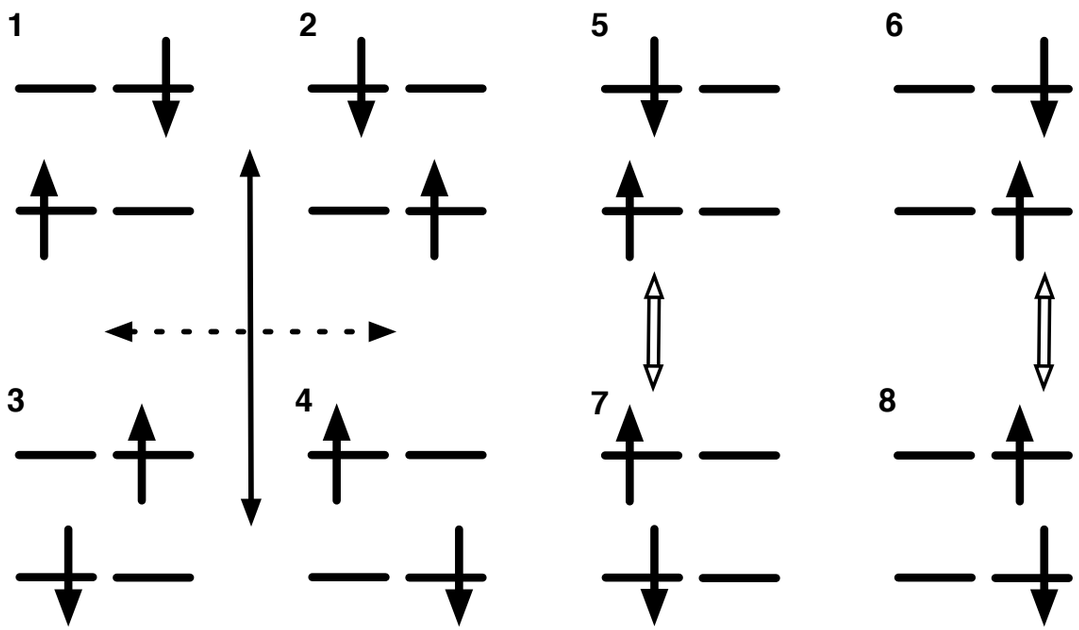
summary

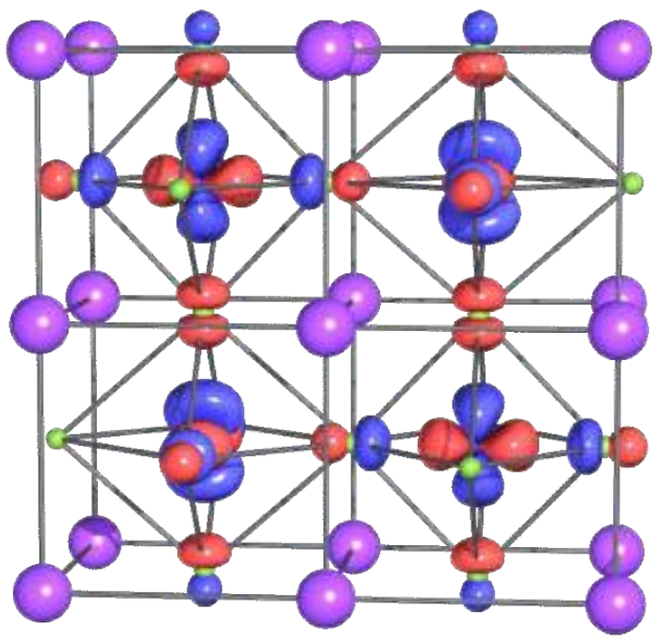
double exchange: often ferro





orbital-ordering





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