Exchange Mechanisms

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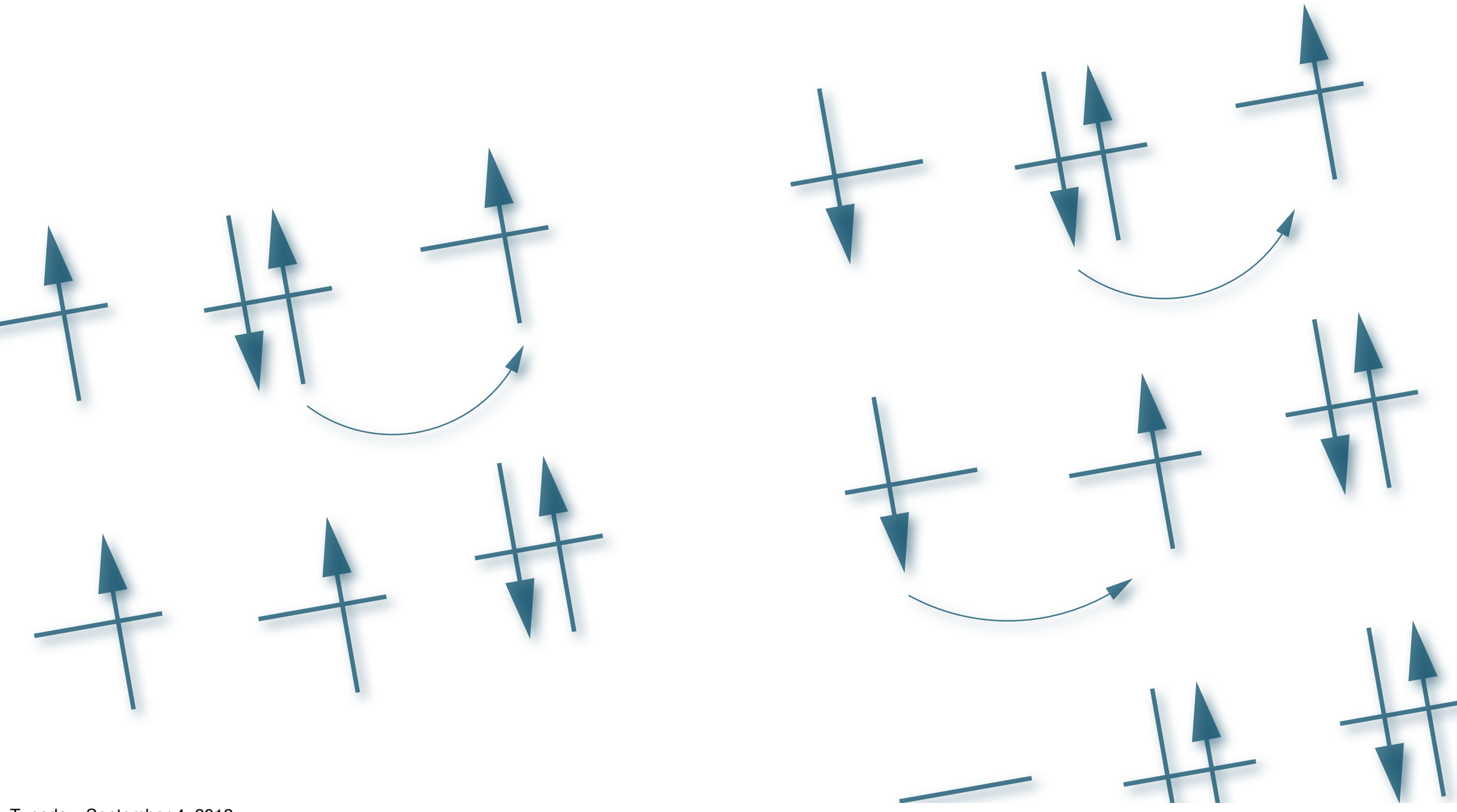


Magnetism is Quantum Mechanical

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

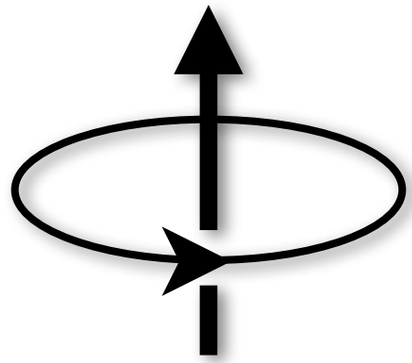
magnetic moments

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

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



electron spin

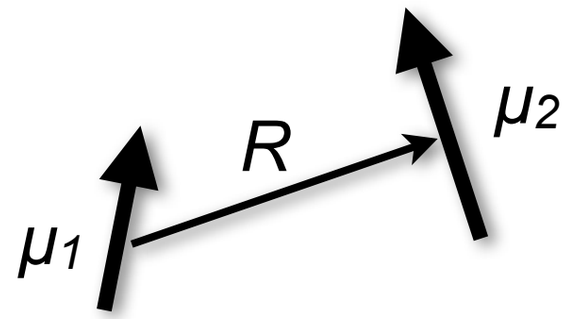
$$\vec{\mu}_S = -g_e\mu_B\langle\vec{S}\rangle\,, \quad g_e \approx 2.0023\ldots$$

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:

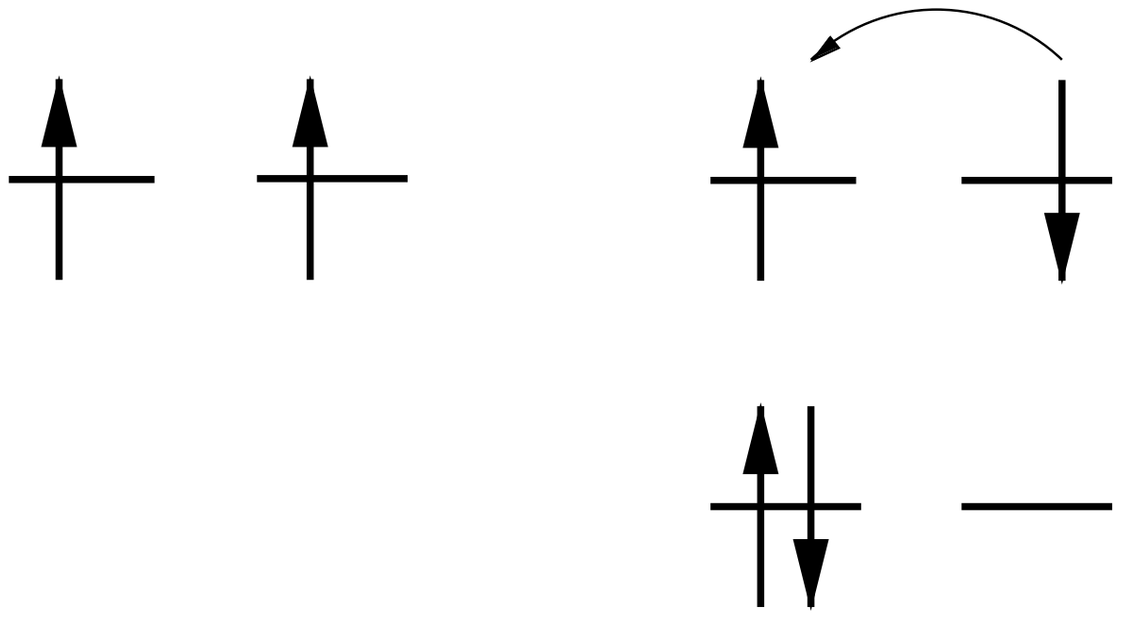
$$\Delta E = -\frac{2\mu_B^2}{4\pi\varepsilon_0 c^2 (2a_0)^3} = -\frac{1/2}{137^2\, 8}\ \text{Hartree} \approx 0.09\,\text{meV}$$

expect magnetic ordering below temperatures of about 1 K

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

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

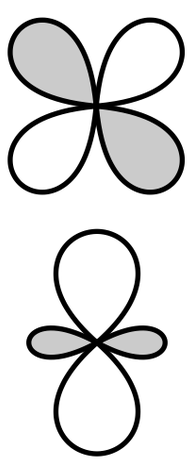
Coulomb Exchange

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

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

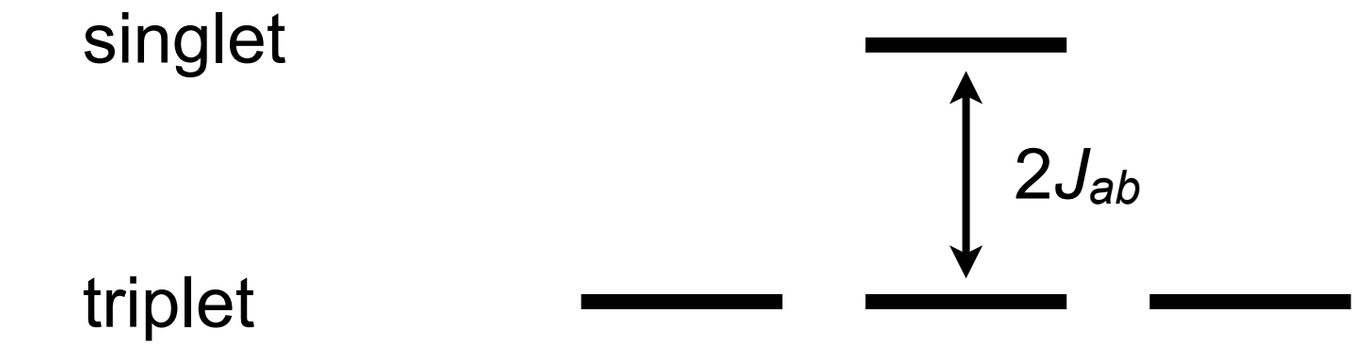
$$\begin{aligned} \psi_{\uparrow\uparrow} &= \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)\Big) && |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}\Big(\psi_{\uparrow\downarrow} + \psi_{\downarrow\uparrow}\Big) &= \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)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

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

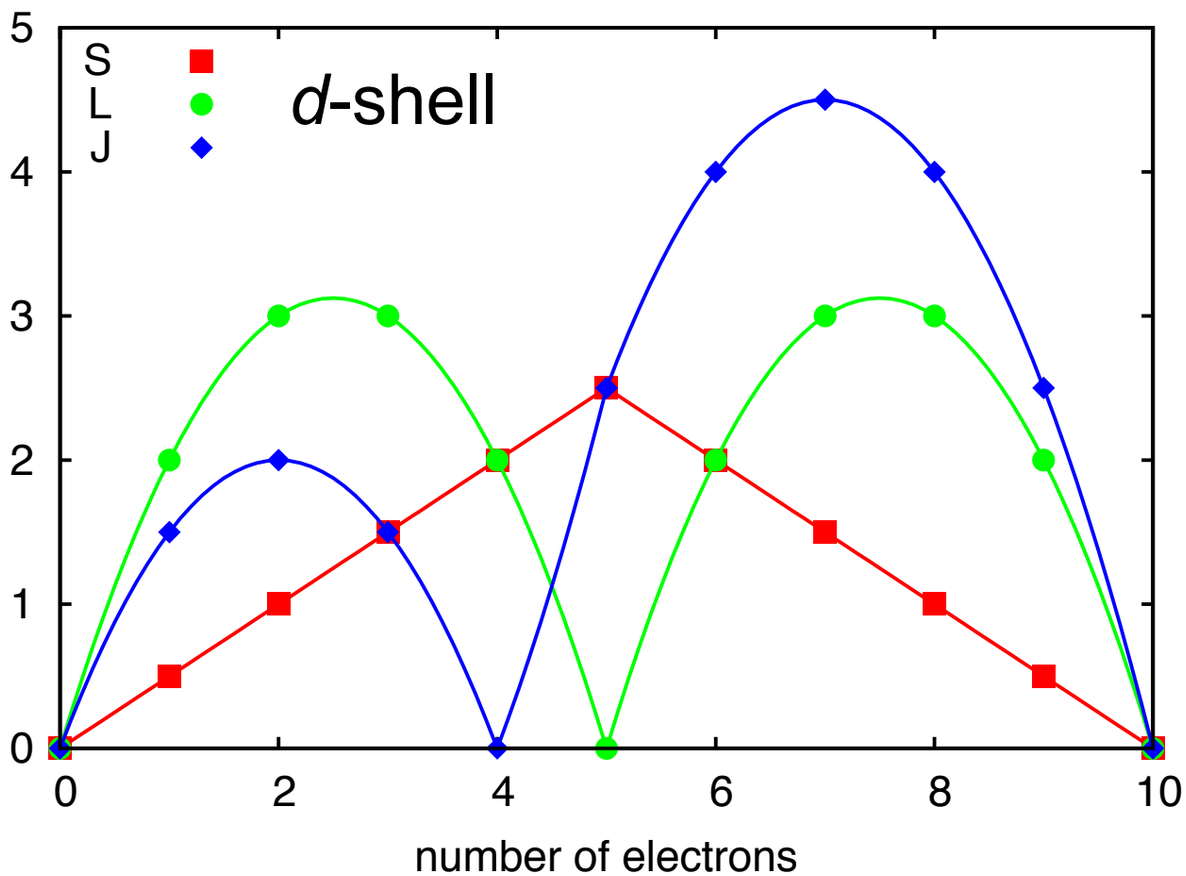
$$\frac{1}{\sqrt{2}}\Big(\psi_{\uparrow\downarrow} - \psi_{\downarrow\uparrow}\Big) = \frac{1}{\sqrt{2}}\Big(\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_b(\vec{r}_1)\phi_a(\vec{r}_2)\Big) \frac{1}{\sqrt{2}}\Big(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\Big)$$

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

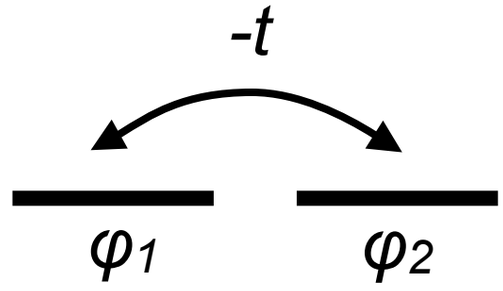
Robert Eder: Multiplets in Transition Metal Ions

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)

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

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) $\qquad$ $|\uparrow\downarrow,\ \cdot\rangle,\ |\ \cdot,\uparrow\downarrow\rangle$ (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**!

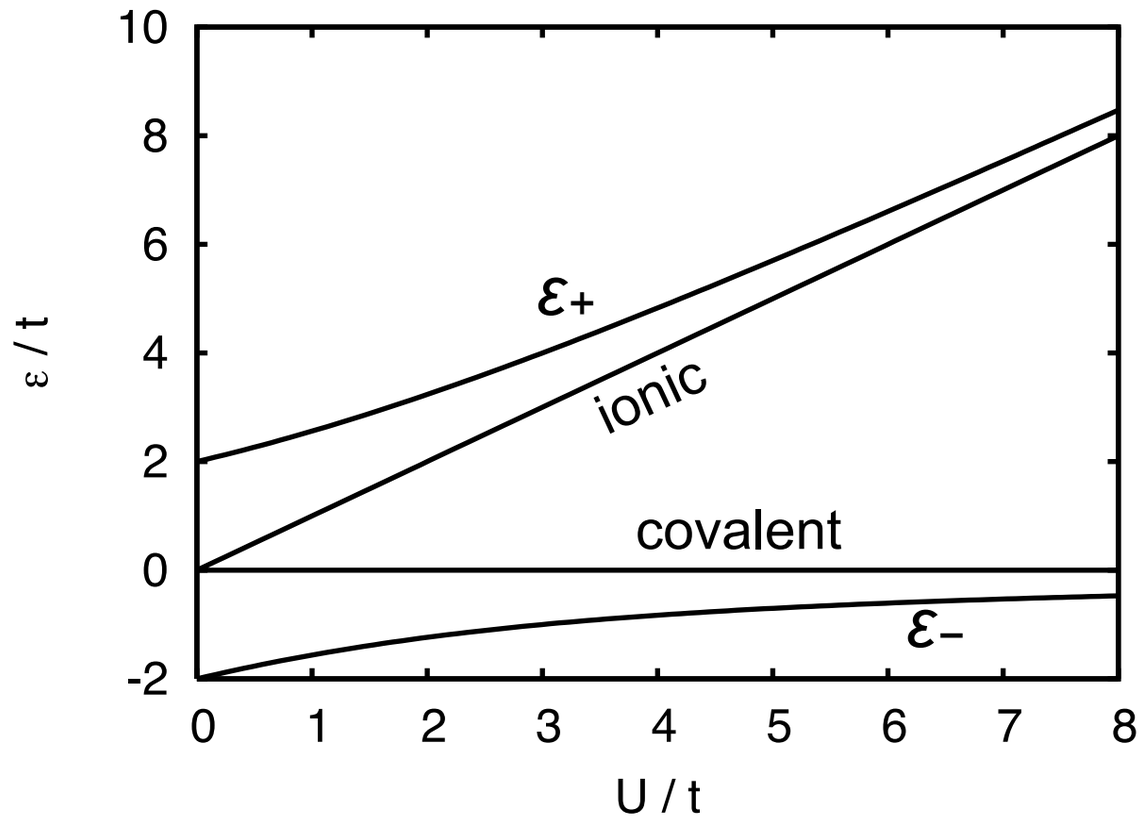
direct exchange: opposite spin

eigenstates

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

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

$$\varepsilon_{\mathrm{ion}} = U \quad , \quad \psi_{\mathrm{ion}} = \frac{1}{\sqrt{2}}\Big(|\!\updownarrow,\cdot\,\rangle - |\,\cdot,\!\updownarrow\rangle \Big)$$



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

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

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

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)

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

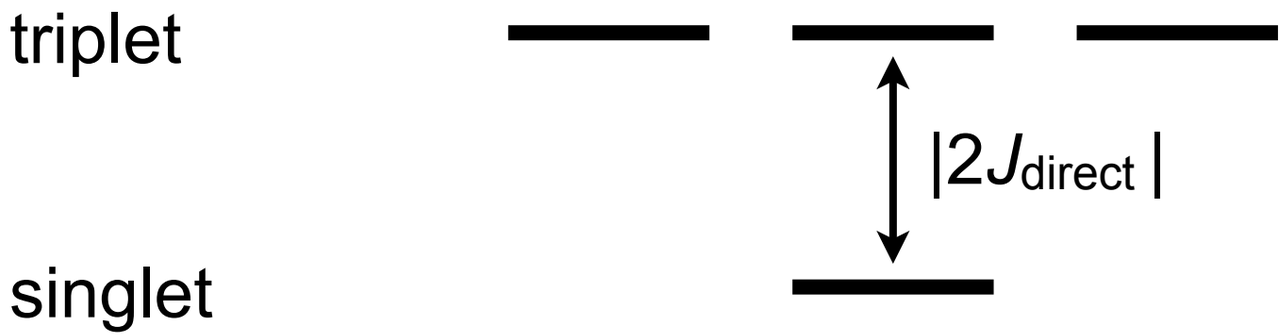
diagonalize H_{eff}

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

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

direct exchange: effective spin-coupling

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



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

book-keeping: second quantization

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

no electron:

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

single electron:

$$|\uparrow\,,\,\cdot\rangle \;=\; c^\dagger_{1\uparrow}|0\rangle$$

$$|\cdot\,,\uparrow\rangle \;=\; c^\dagger_{2\uparrow}|0\rangle$$

two electrons:

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

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

$$|\updownarrow\,,\,\cdot\rangle \;=\; c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle$$

$$|\cdot\,,\updownarrow\rangle \;=\; c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle$$

electrons anti-commute:

$$c^\dagger_{i\sigma}c^\dagger_{j\sigma'} = -c^\dagger_{j\sigma'}c^\dagger_{i\sigma}$$

anticommutator

$$\{c^\dagger_{i\sigma},\, c^\dagger_{j\sigma'}\} = c^\dagger_{i\sigma}c^\dagger_{j\sigma'} + c^\dagger_{j\sigma'}c^\dagger_{i\sigma} = 0$$

second quantization: operators

adjoin: $\left(c_{i\sigma}^{\dagger}|0\rangle\right)^{\dagger} = \langle 0|c_{i\sigma}$

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

annihilation operator:
removes electron
of spin σ from orbital φ_i

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

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

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

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

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

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

energy expectation value

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

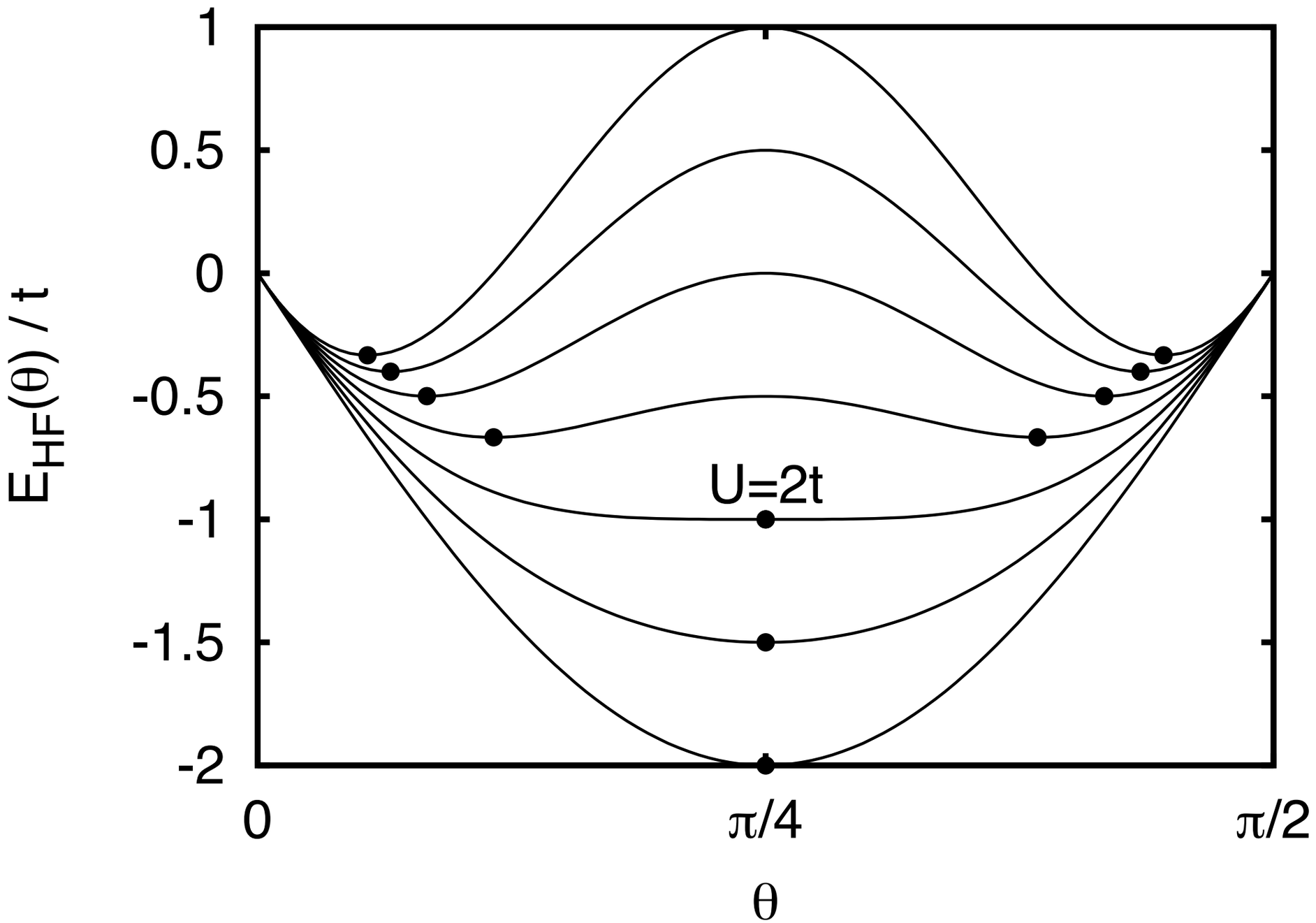
minimize wrt $\theta_\uparrow$ and $\theta_\downarrow$

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

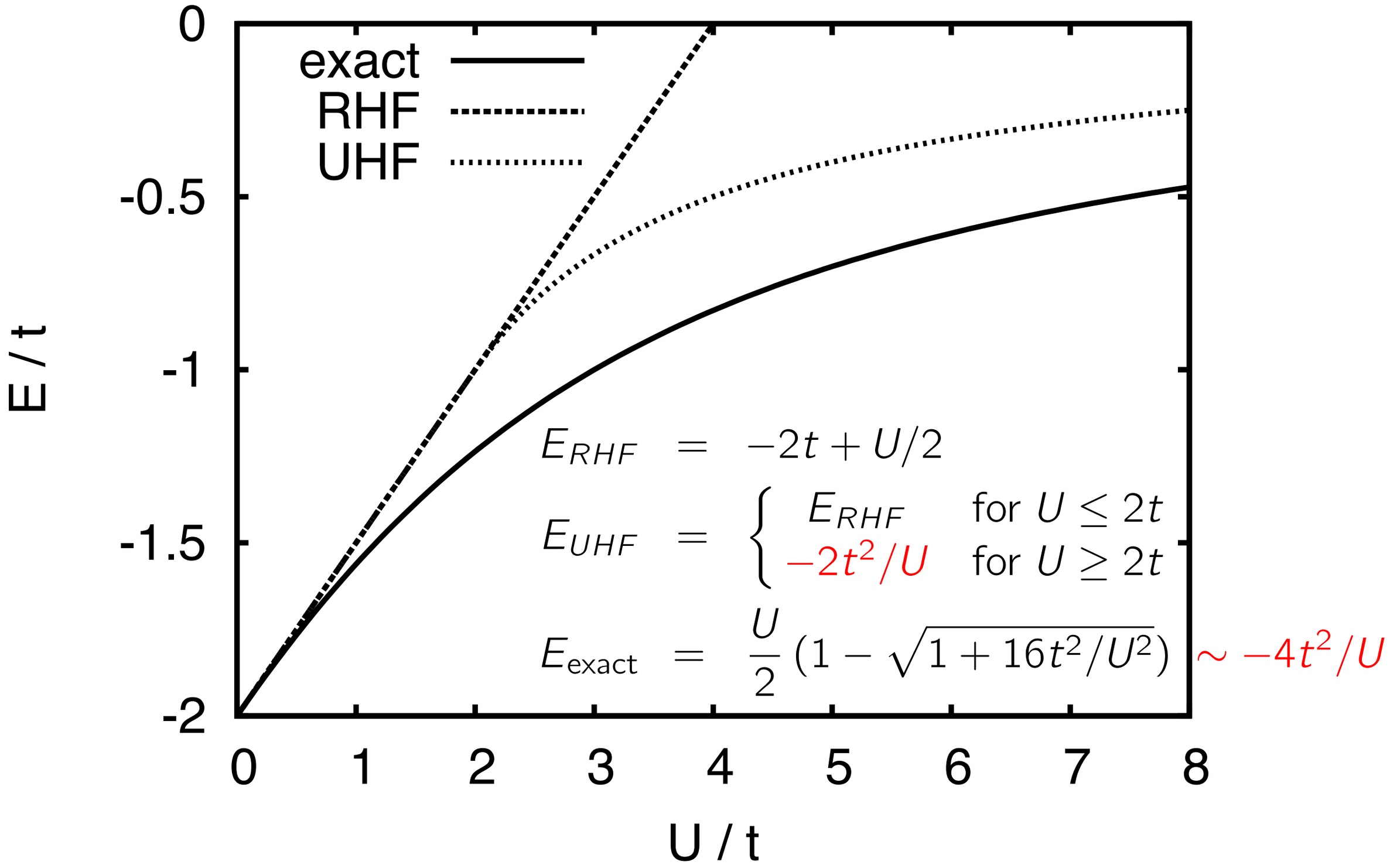
HF allowed to break symmetry: unrestricted Hartree-Fock (UHF)
here: $\theta_\downarrow = \pi/2 - \theta_\uparrow$

Hartree-Fock

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

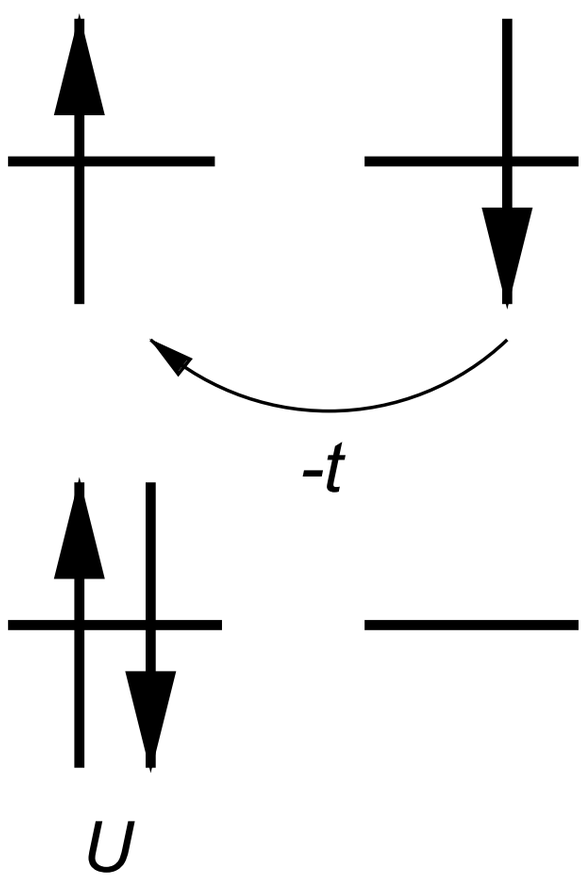


Hartree-Fock

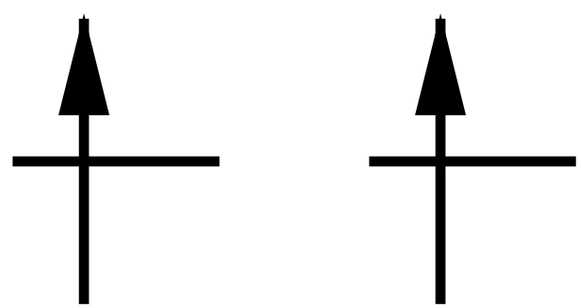


direct kinetic exchange

singlet



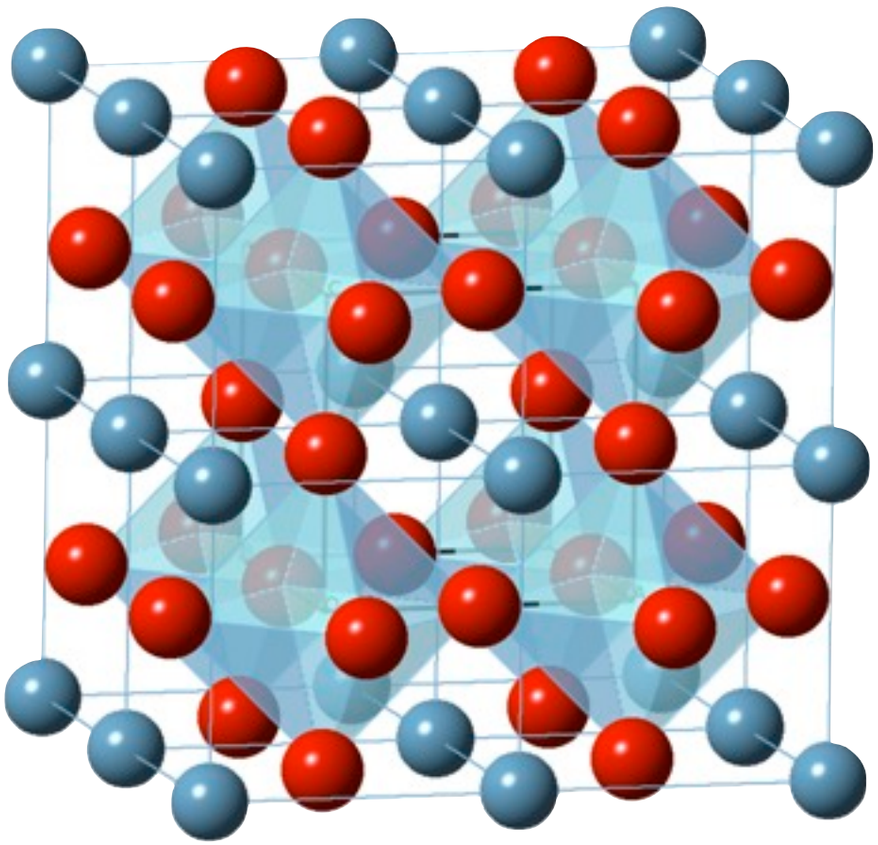
triplet



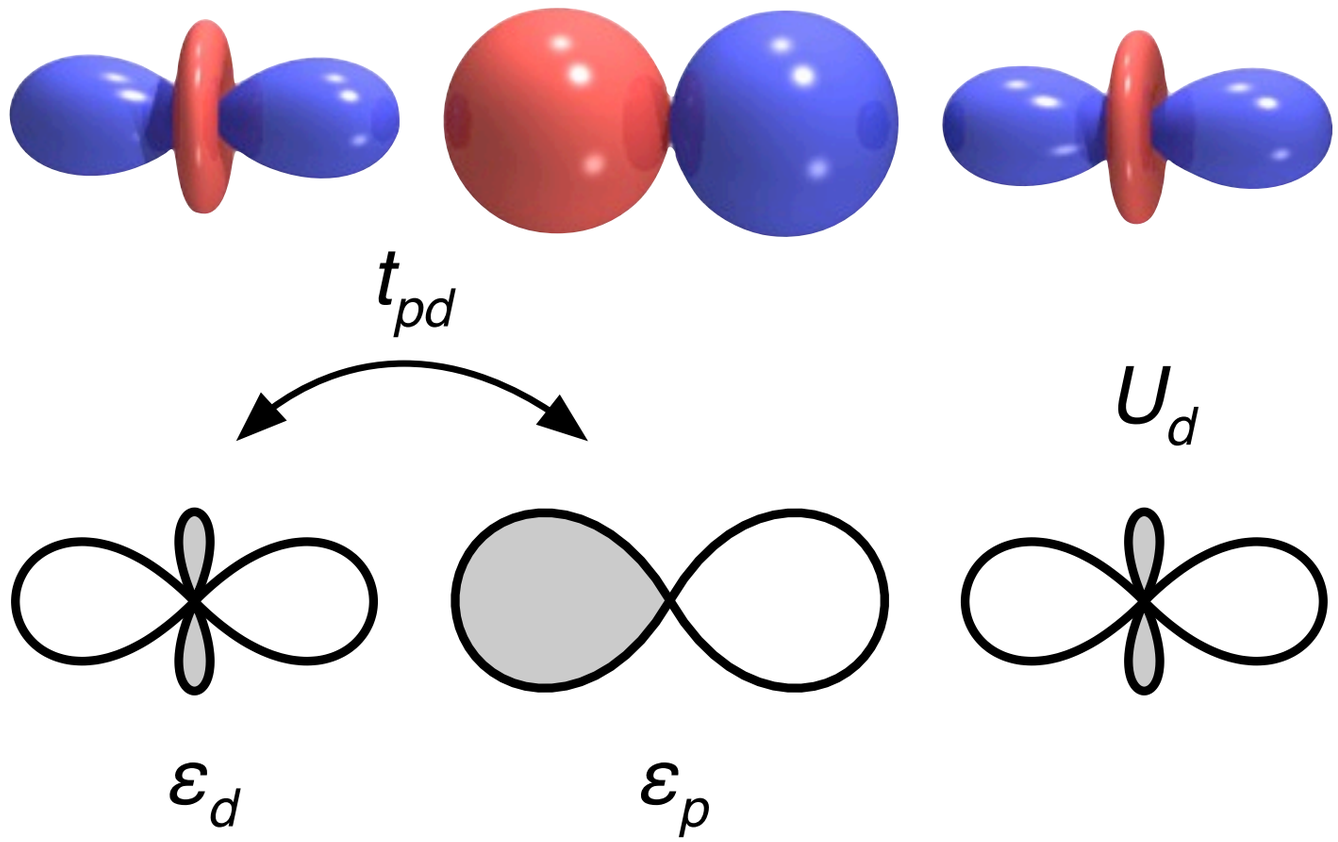
direct exchange

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

superexchange



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



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

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

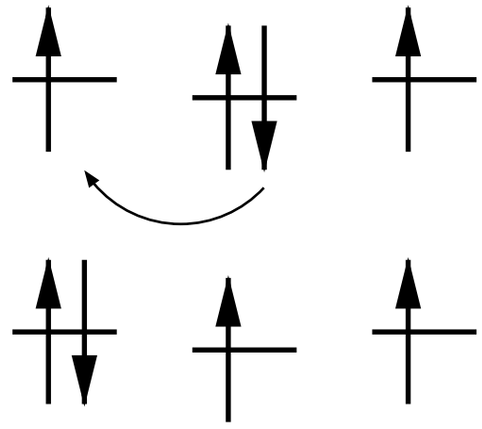
superexchange: same spin

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

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

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

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

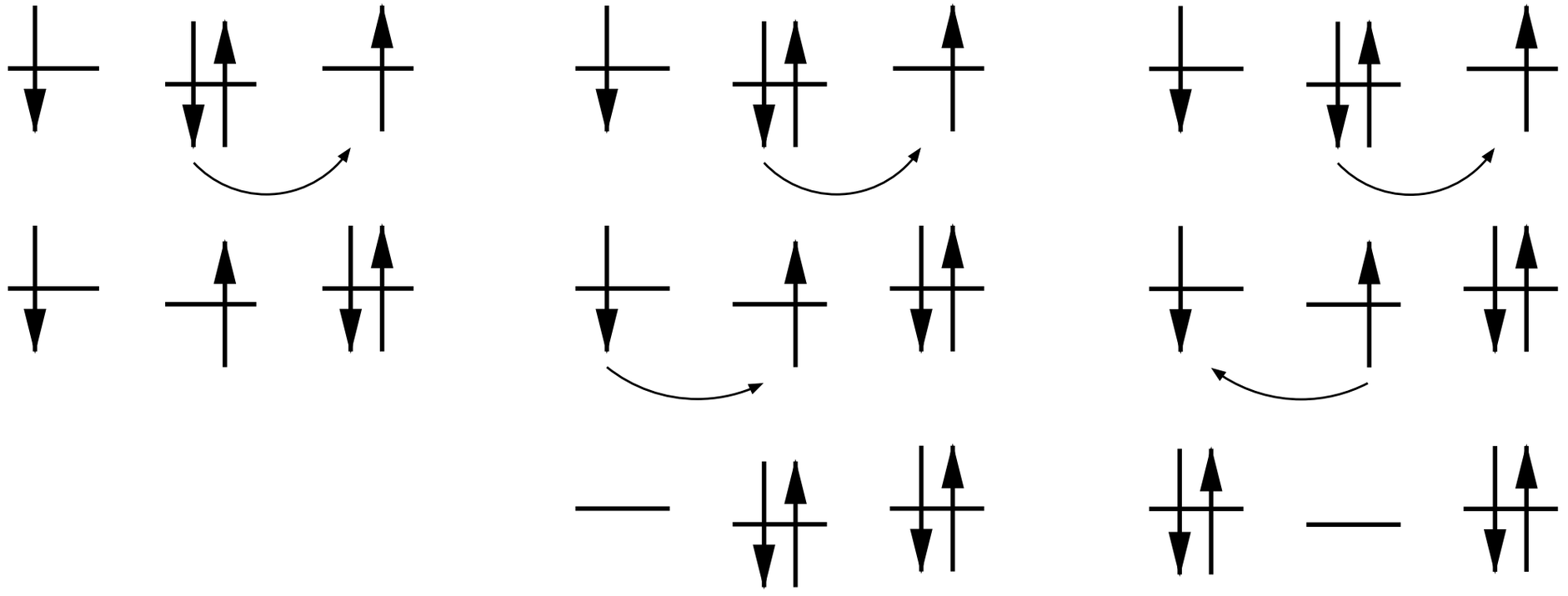


$$H_{\text{eff}} = (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \approx -\frac{2 t_{pd}^2}{U_d + \Delta_{pd}}$$

superexchange: opposite spin

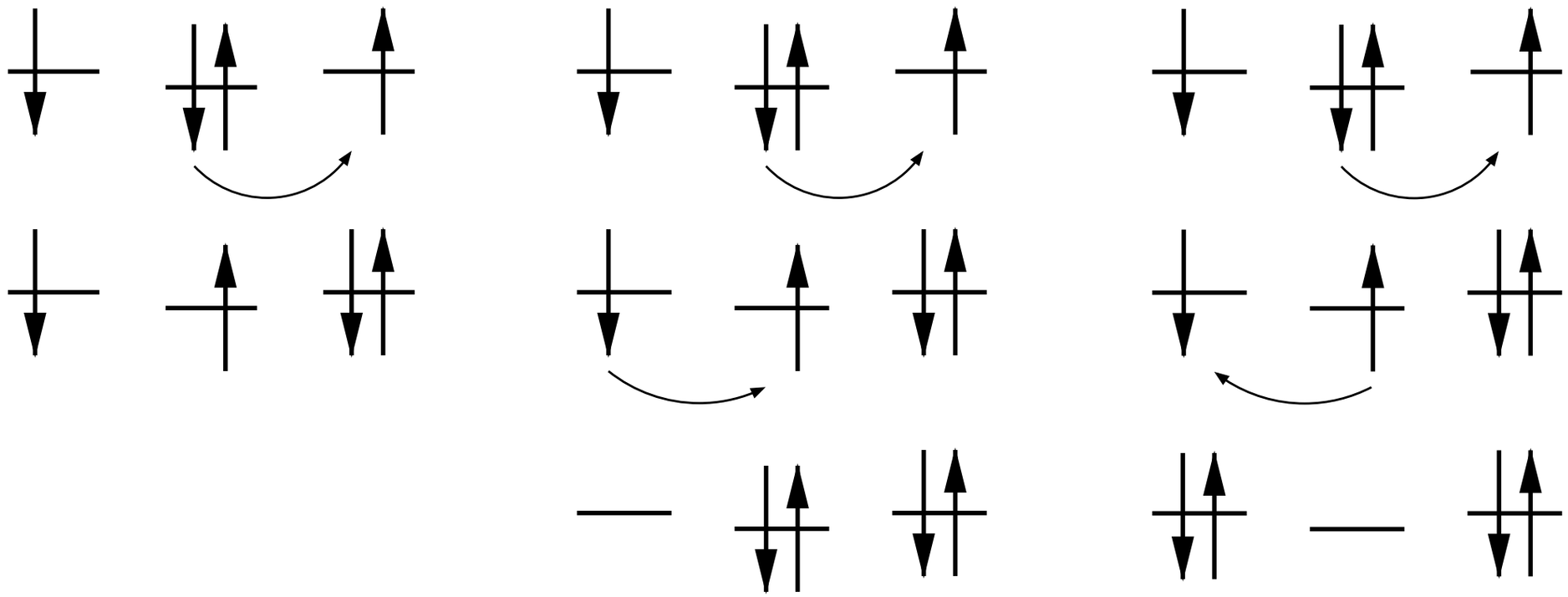
$$
\left(\begin{array}{cc|cccc|ccc}
0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 \\
\hline
+t_{pd} & 0 & U_d+\Delta_{pd} & 0 & 0 & 0 & -t_{pd} & 0 & -t_{pd} \\
+t_{pd} & 0 & 0 & U_d+\Delta_{pd} & 0 & 0 & 0 & -t_{pd} & -t_{pd} \\
0 & +t_{pd} & 0 & 0 &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

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



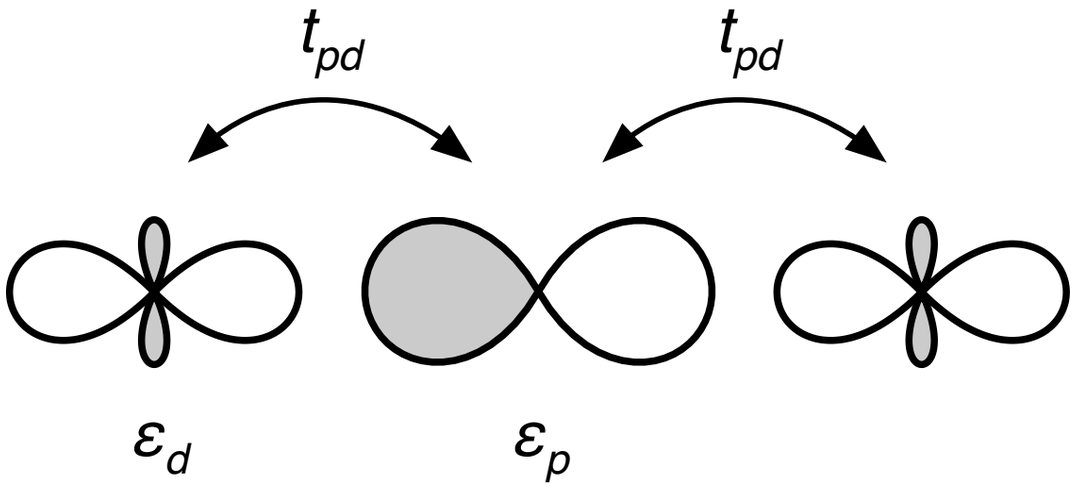
superexchange: opposite spin

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



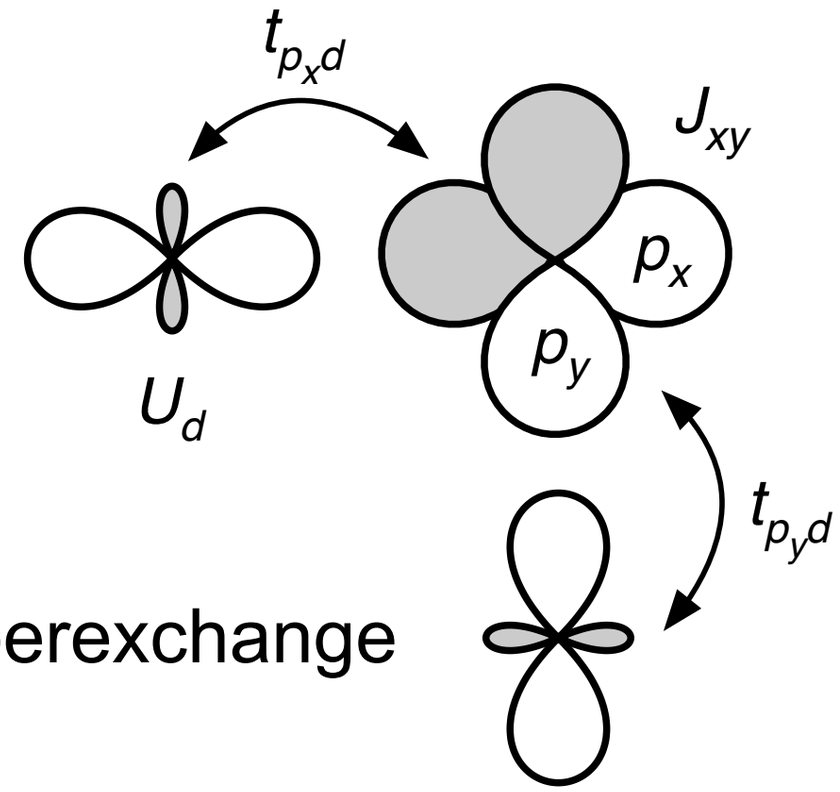
singlet-triplet splitting: $\quad J = \dfrac{4t_{pd}^4}{(U_d + \Delta_{pd})^2}\left(\dfrac{1}{U_d} + \dfrac{1}{U_d + \Delta_{pd}}\right)$

ferromagnetic superexchange



180° superexchange

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



90° superexchange

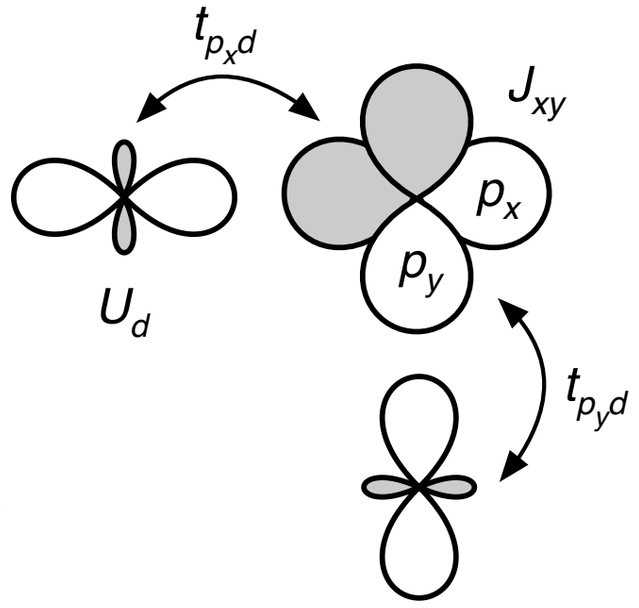
no hopping connecting *d*-orbitals but Coulomb exchange on oxygen

double exchange

ferro superexchange: same spin

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

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



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

ferro superexchange: opposite spin

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

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

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

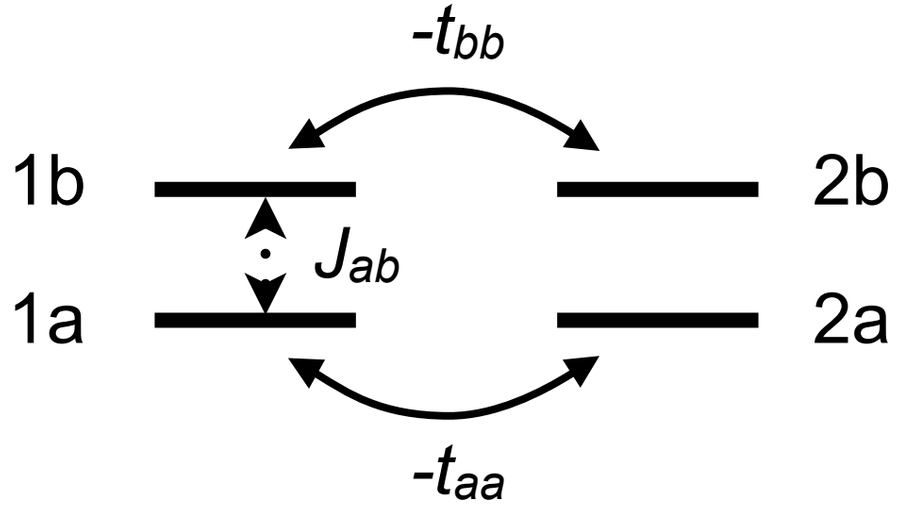
singlet-triplet splitting $\qquad J = -\dfrac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\dfrac{2J_{xy}}{4(U_d+\Delta_{pd})^2-J_{xy}^2}$

double exchange

double exchange involves both, full Coulomb matrix and hopping

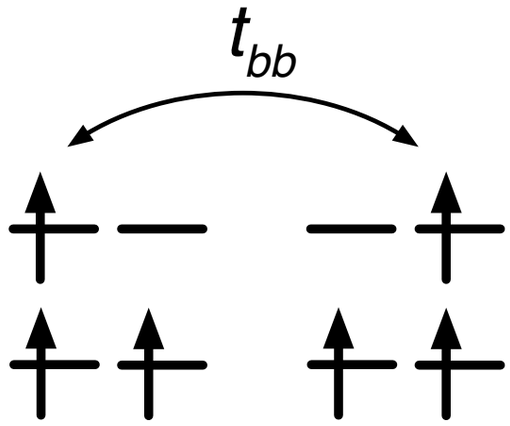
mixed-valence compound: non-integer filling of *d*-orbital
d-electrons can hop even when *U* is large

simple model: two sites with two orbitals each



double exchange

S_z=3/2



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

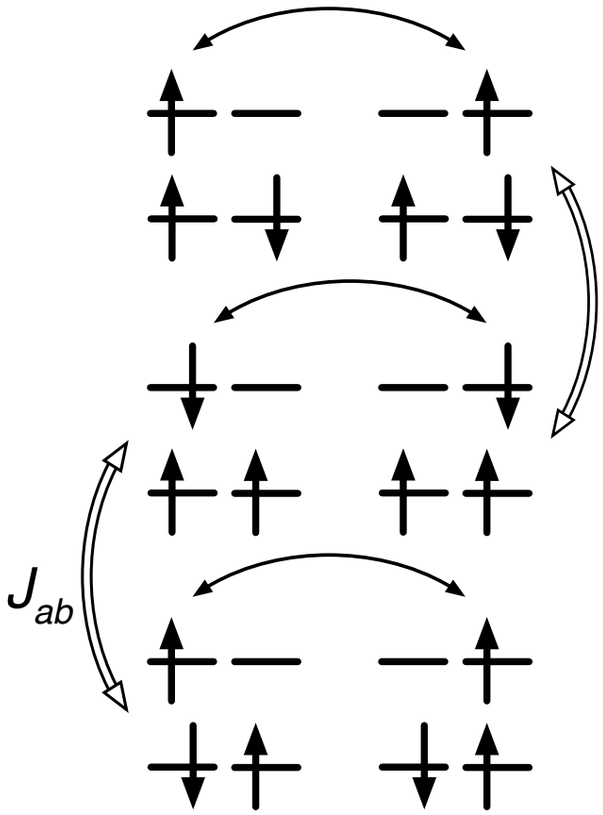
$$\varepsilon_{\pm} = -J_{ab} \pm t_{bb}$$

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

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

double exchange

S_z=1/2



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

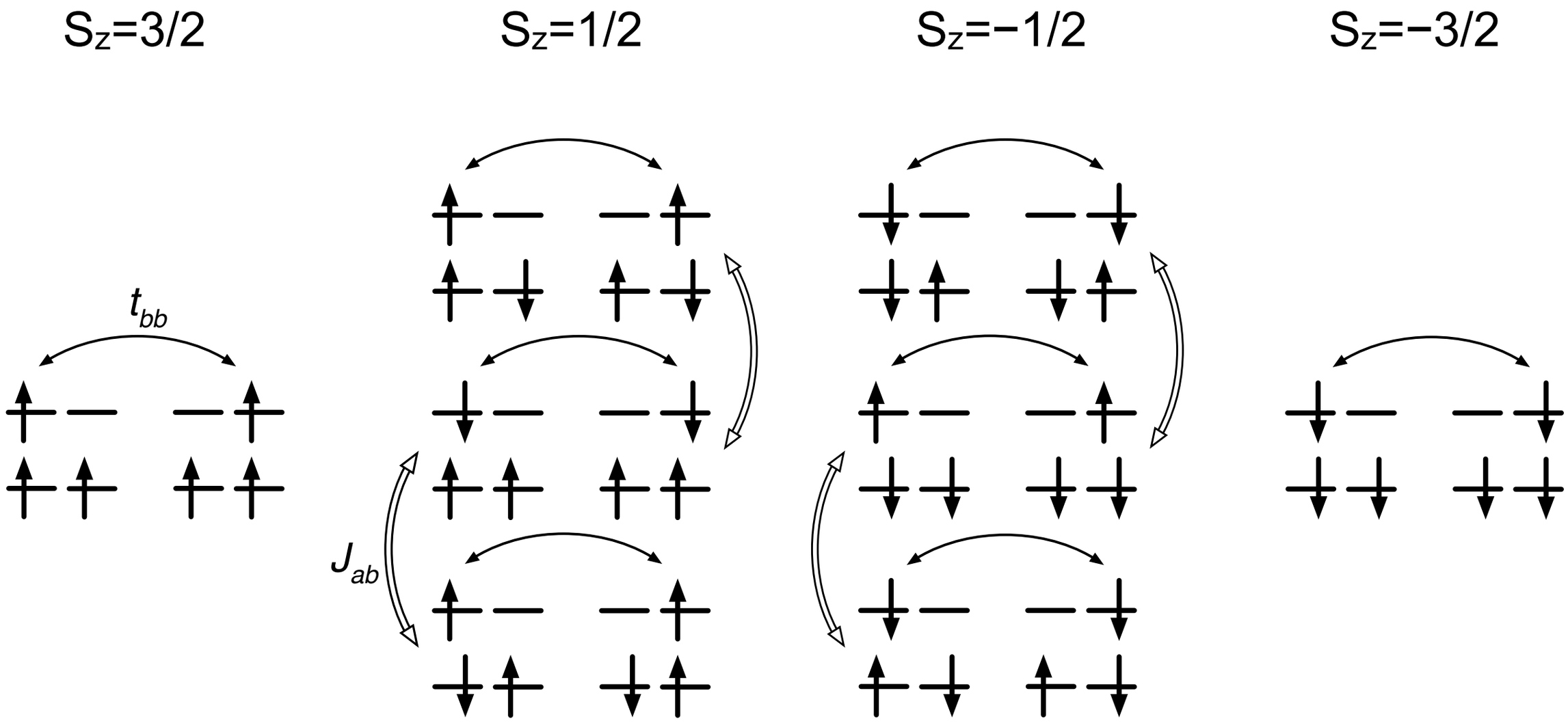
ground state $\quad \varepsilon_0 = -J_{ab} - t_{bb}$

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

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

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

double exchange



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

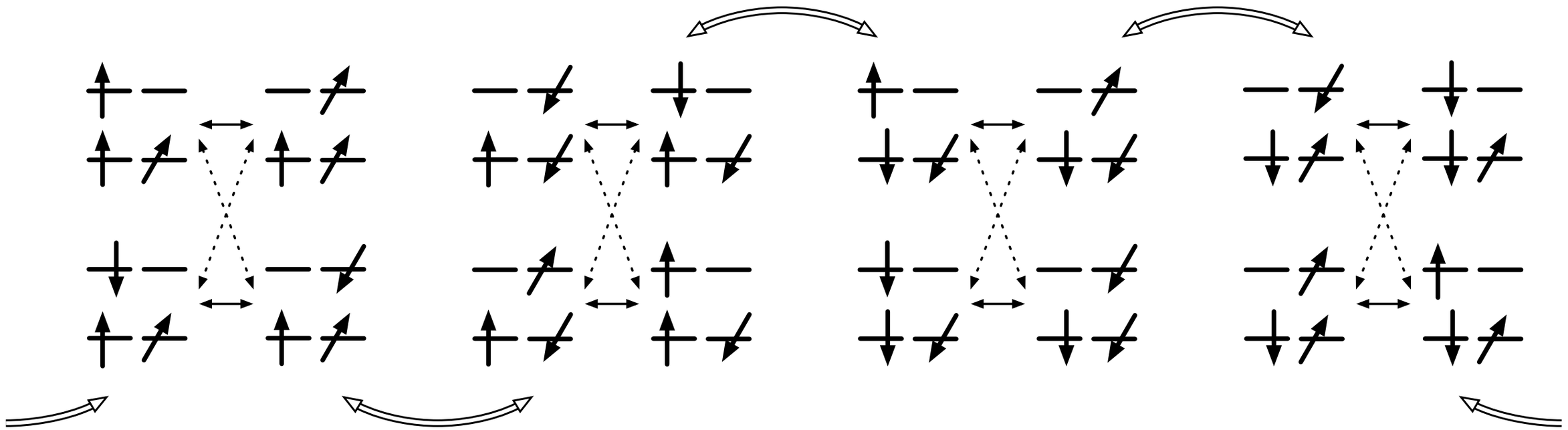
rotation of quantization axis

$$
\begin{aligned}
d_{2b\uparrow} &= \cos(\vartheta/2)\, c_{2b\uparrow} - \sin(\vartheta/2)\, c_{2b\downarrow} \\
d_{2b\downarrow} &= \sin(\vartheta/2)\, c_{2b\uparrow} + \cos(\vartheta/2)\, c_{2b\downarrow}
\end{aligned}
$$

hopping mixes spins

$$
\begin{aligned}
-t_{bb}\, c^\dagger_{2b\uparrow} c_{1b\uparrow} &= -t_{bb} \left(+\cos(\vartheta/2)\, d^\dagger_{2b\uparrow} + \sin(\vartheta/2)\, d^\dagger_{2b\downarrow} \right) c_{1b\uparrow} \\
-t_{bb}\, c^\dagger_{2b\downarrow} c_{1b\downarrow} &= -t_{bb} \left(-\sin(\vartheta/2)\, d^\dagger_{2b\uparrow} + \cos(\vartheta/2)\, d^\dagger_{2b\downarrow} \right) c_{1b\downarrow}
\end{aligned}
$$

double exchange



assume *a*-spins cannot be flipped ⇒ no *J* terms

4 independent 2×2 Hamiltonians

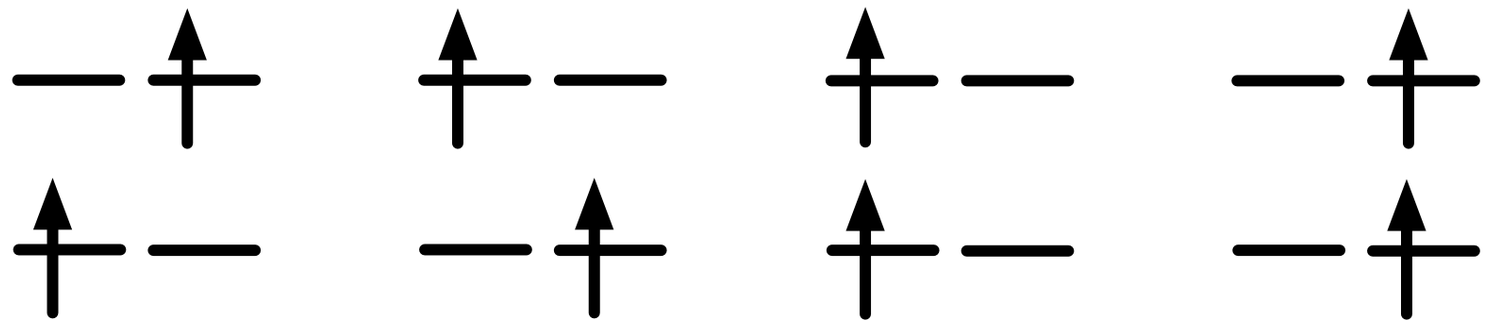
for $t_{bb} \ll J_{ab}$ tilt merely reduces width of *b*-band

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

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

orbital ordering

same model, but now one electron per orbital

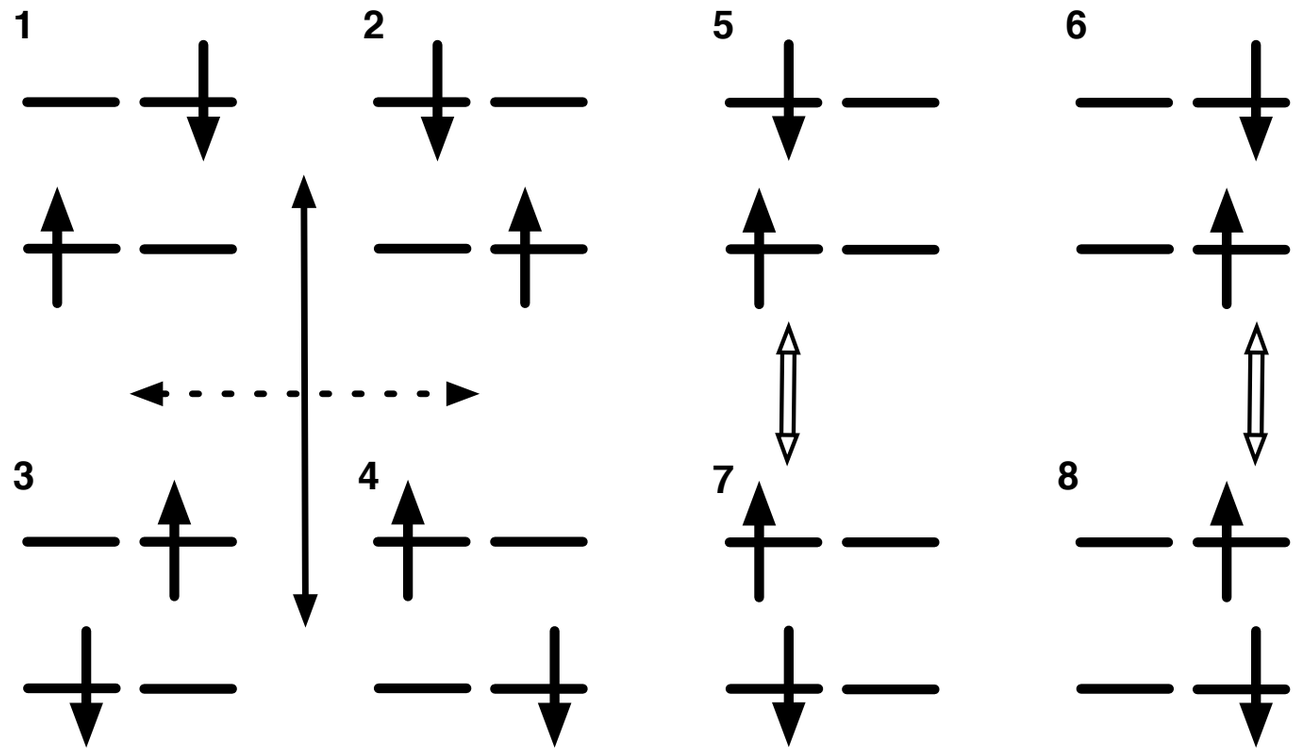


$$H = \left(\begin{array}{cc|cc} 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & U_{ab} - J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & U_{ab} - J_{ab} \end{array}\right)$$

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

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

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

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

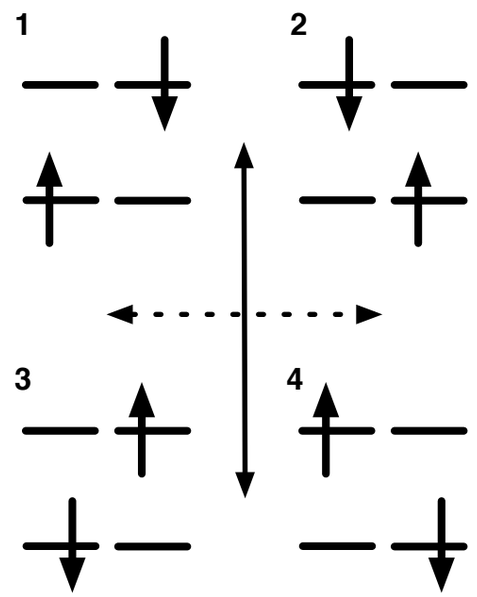
$$= \frac{1}{U_{ab}^2 - J_{ab}^2} \left[U_{ab} + J_{ab} - J_{ab} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right] \otimes \left[(t_{aa} - t_{bb})^2 + 2t_{aa}t_{bb} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right]$$

spin-exchange

orbital-exchange

simultaneous coupling of spins and orbital occupations

spin- and orbital-exchange tend to have opposite sign



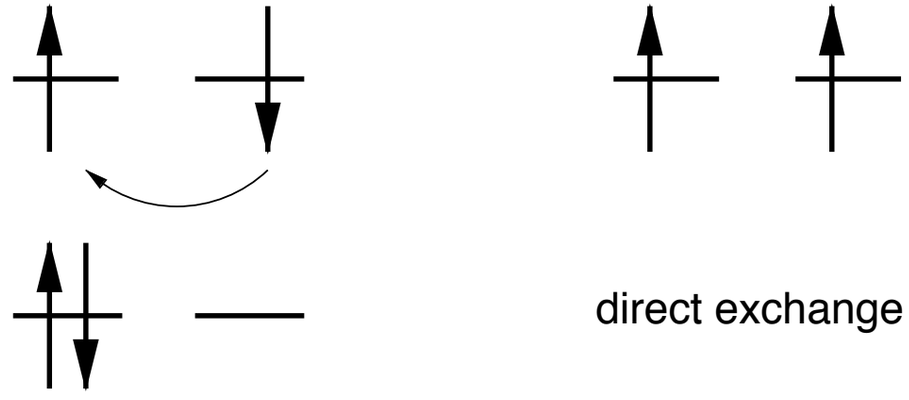
summary

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^o superexchange)
    but 90^o superexchange is ferromagnetic
- double exchange: hopping electrons align spins ferromagnetically
- orbital ordering: exchange interaction between orbital occupations

summary

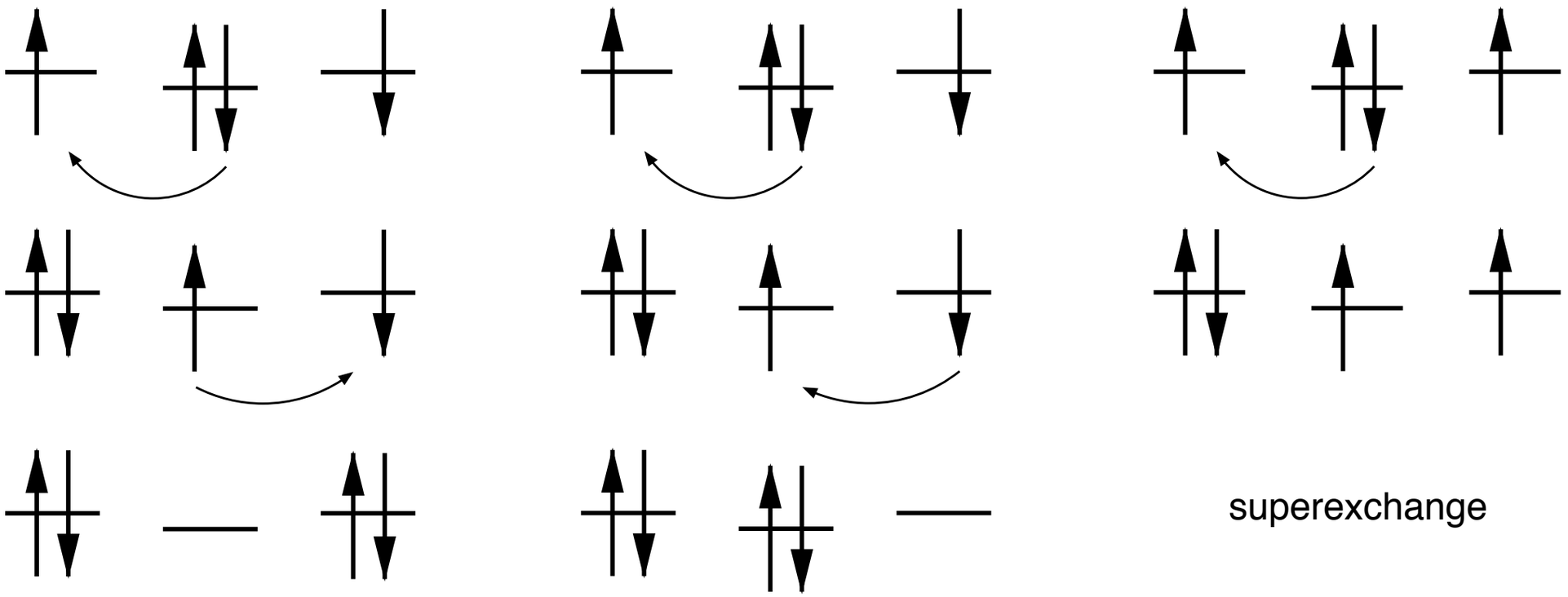
$$H_U = \begin{pmatrix} U_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & U_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & U_{ab} & 0 \\ 0 & 0 & 0 & U_{ab} - J_{ab} \end{pmatrix}$$



direct exchange

Coulomb exchange:
ferro (Hund's rule)

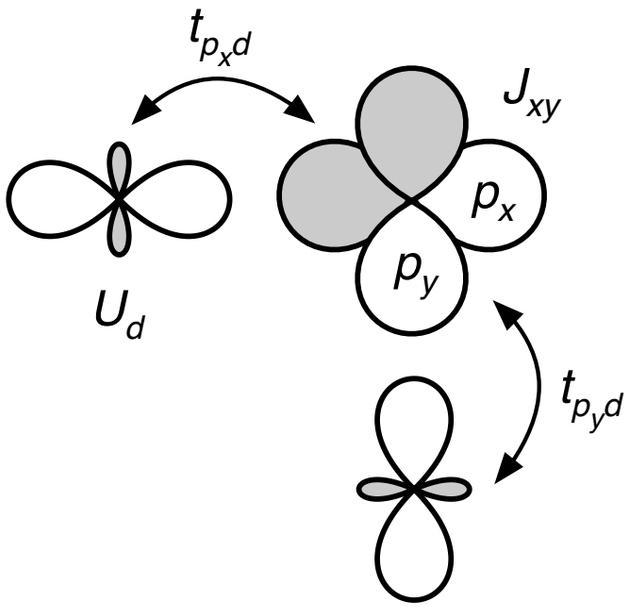
kinetic exchange:
anti-ferro

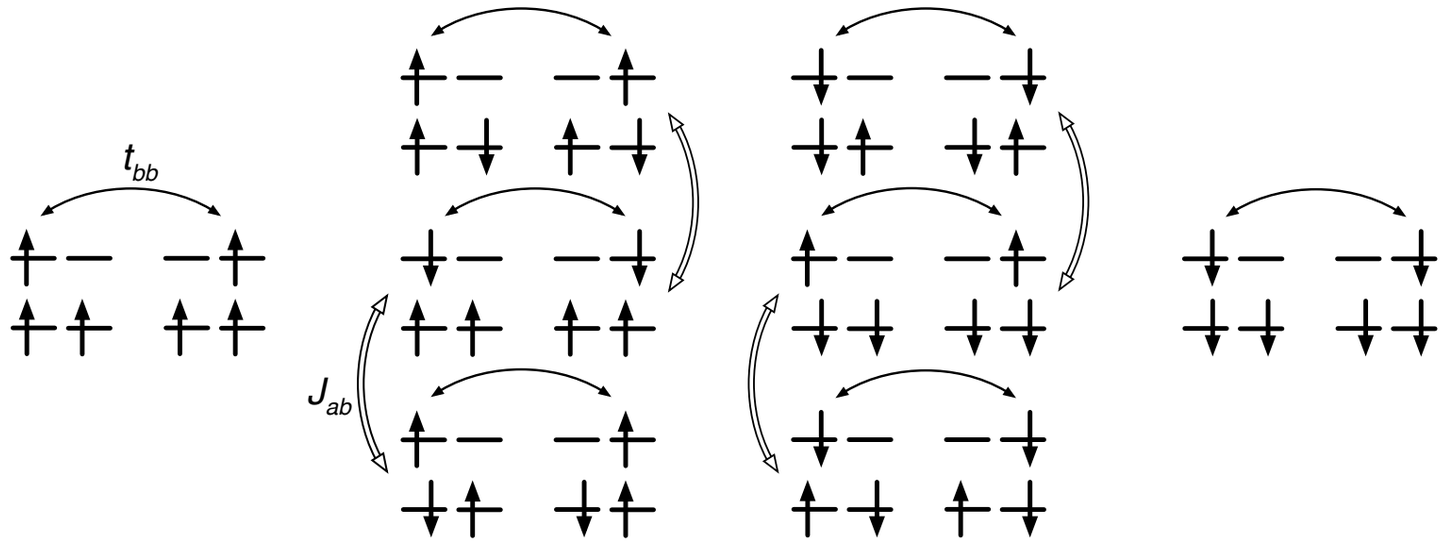


superexchange

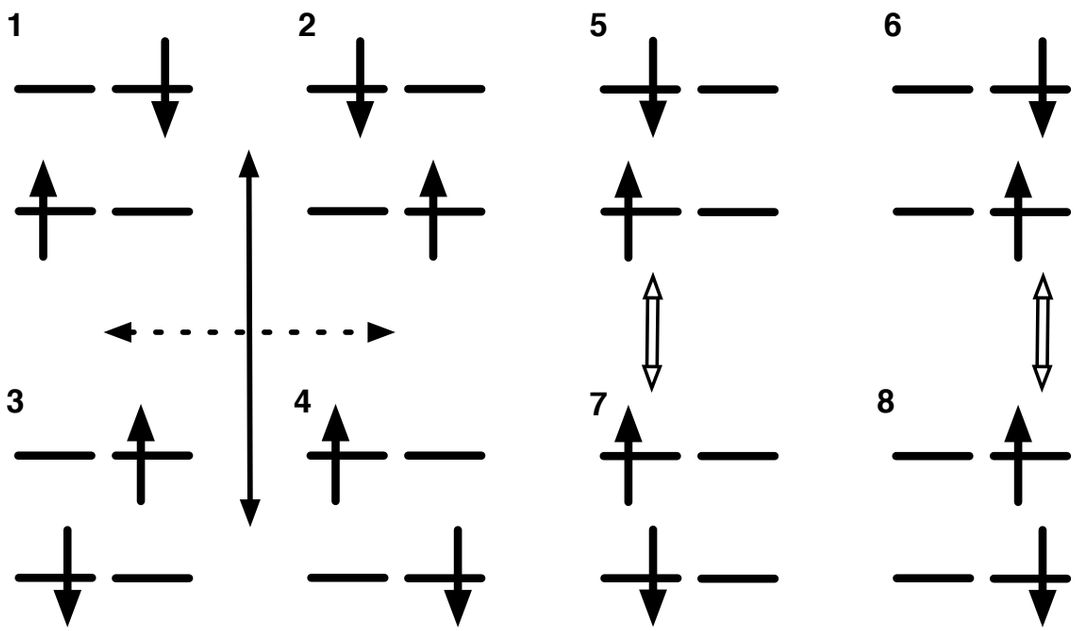
summary

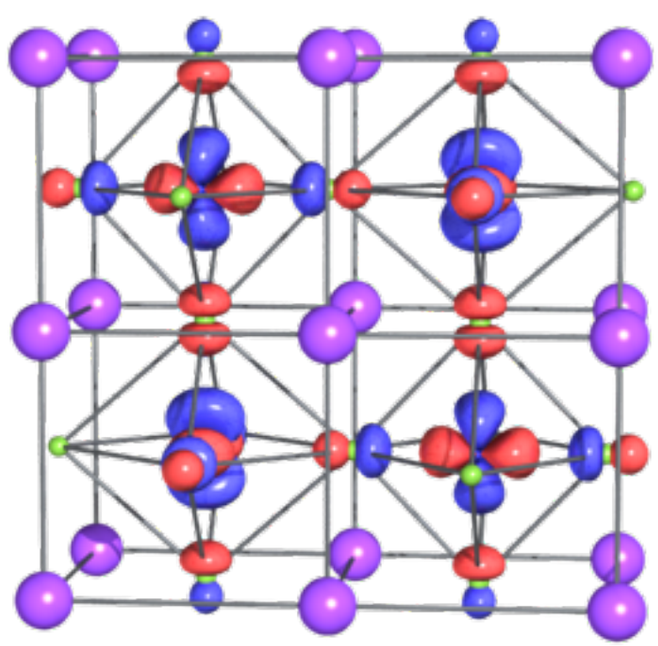
double exchange: often ferro





orbital-ordering





Computer Center, around 1890

OPINION BIG DATA NATURE|Vol 455|4 September 2008

ESSAY

The Harvard computers

Observatories hired ***computers*** — a term used for human processors since the early 1700s

The first mass data crunchers were people, not machines. **Sue Nelson** looks at the discoveries and legacy of the remarkable women of Harvard's Observatory.

BIG DATA

A photograph taken at the Harvard Observatory in Cambridge, Massachusetts, *circa* 1890, features eight women in what looks like a Victorian-style sitting room. They wear long skirts, have upswept hair and are surrounded by flowered wallpaper and mahogany tables. At first glance they seem to be sampler stitching or reading. In fact these 'human computers' are analysing photographs of the heavens, cataloguing stars.

When cameras were first attached to telescopes, with the ability to capture the image of thousands of stars on a single photographic plate, people were needed to trawl through these new data. Observatories hired 'computers' — a term used for human processors since the early 1700s — to do the painstakingly repetitive work of measuring the brightness, position and colours of these stars.

From the 1880s until the 1940s, the Harvard College Observatory amassed half a million photographic glass plates, weighing around 300 tonnes and holding images of tens of millions of stars. A team of women trawled through these photos with nothing more than magnifying glasses — often for little pay and with no scientific training.

HARVARD COLL. OBSERV.

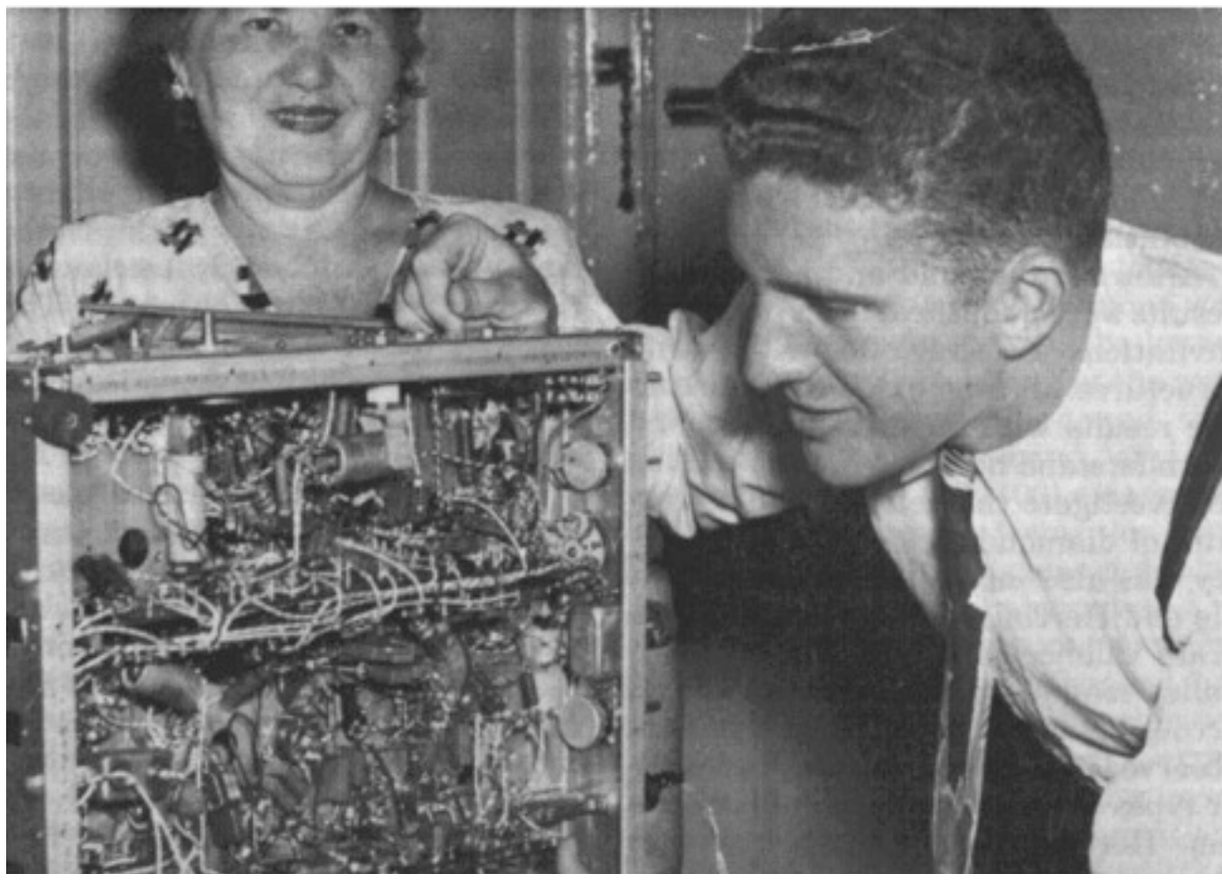
Williamina Fleming stands in the centre of the Harvard computers as Edward Pickering looks on.

Homecomputer, about 1951

[…] all went smoothly until I had to face up to **the problem of factoring high-order secular equations**. I knew how to do this by hand, but the task was time-consuming, and it was necessary to check and recheck the factoring to make sure no errors were made. **It then occurred to me that my mother could help me** with some of this work. I had read about the Hartrees how the younger Hartree (Douglas R.) had been aided by his father (William), who was a retired railroad engineer and enjoyed doing sums on a desk calculator. I showed my mother how to set up the OPW secular equations and how to factor them, and she agreed to do some of this in her spare time […]

Frank Herman: *Elephants and mahouts — early days in semiconductor physics*

Physics Today, June 1984, p.56



Wachstum der Rechenleistung