

Advanced Materials Modeling

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Magnetism

□ Applications of magnetic materials

Data storage

Electric motors, generators, speakers

Spectroscopy (NMR, EPR)

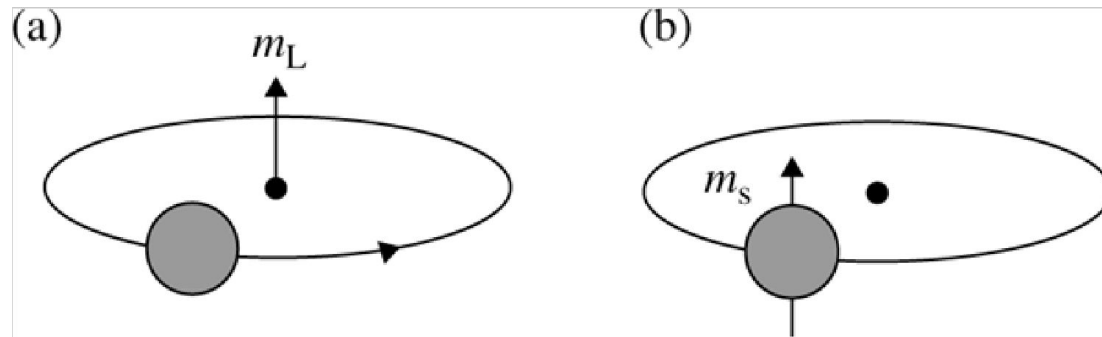
Magnetic resonance tomography (imaging)

Spintronics (?)

Magnetism

□ Basic concepts

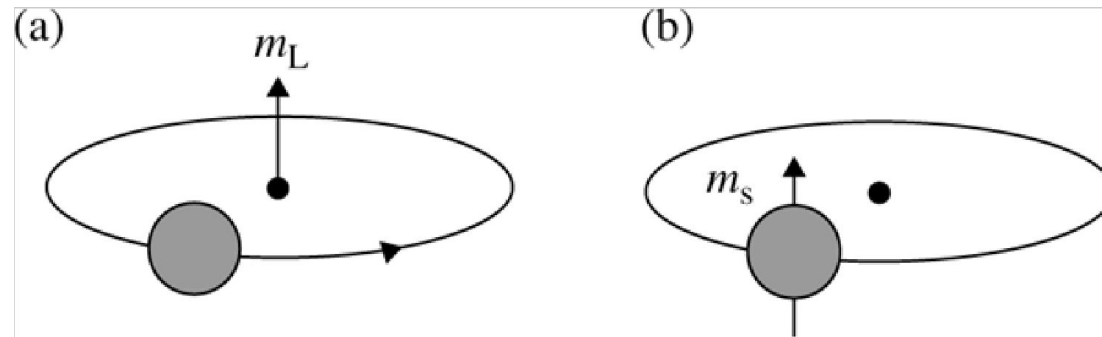
Magnetic moment: $d\vec{m} = \vec{M}dV$, \vec{M} -- magnetization



Magnetism

□ Basic concepts

Magnetic moment: $d\vec{m} = \vec{M}dV$, \vec{M} -- magnetization



For an atom with spin \vec{S} and orbital momentum \vec{L} :

$$\vec{m} = -g \frac{\mu_B}{\hbar} \vec{J}, \quad \vec{J} = \vec{L} + \vec{S}, \quad \mu_B = \frac{e\hbar}{2m_e} \text{ -- Bohr magneton,}$$
$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \text{ -- total Landé factor (spin } g\text{-}$$

factor approximated by 2 ($g_S = 2.002319304 \dots$)

Magnetism

□ Basic concepts

The orbital moment is quenched by the crystal field (the interaction with neighboring atoms destroys the current loops) $\rightarrow m_S \gg m_L$. For example, in Fe 95% of magnetic moment is due to spin

Magnetic susceptibility χ : $\vec{M} = \chi \vec{H}$

Magnetic field (induction) \vec{B} and magnetizing field (magnetic field strength, “free” magnetic field) \vec{H} :

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0(1 + \chi)\vec{H}$$

In general χ is a tensor and non-linear: $\chi_{\alpha\beta} = \frac{\partial M_\alpha}{\partial H_\beta}$

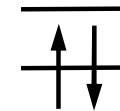
Moreover, \vec{M} may not be a unique function of \vec{H} (hysteresis)

Magnetism

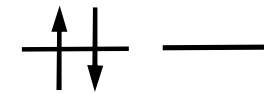
□ Magnetic properties of materials

$$\vec{M} = \chi \vec{H}$$

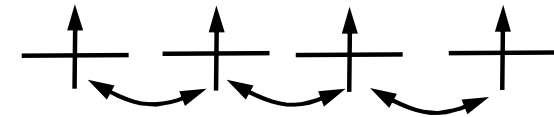
Diamagnetic: $\chi \sim -10^{-5}$, $\chi(T) \approx \text{const}$



Paramagnetic: $\chi \sim 10^{-3}$ (300 K), $\chi(T) \approx \frac{C}{T}$

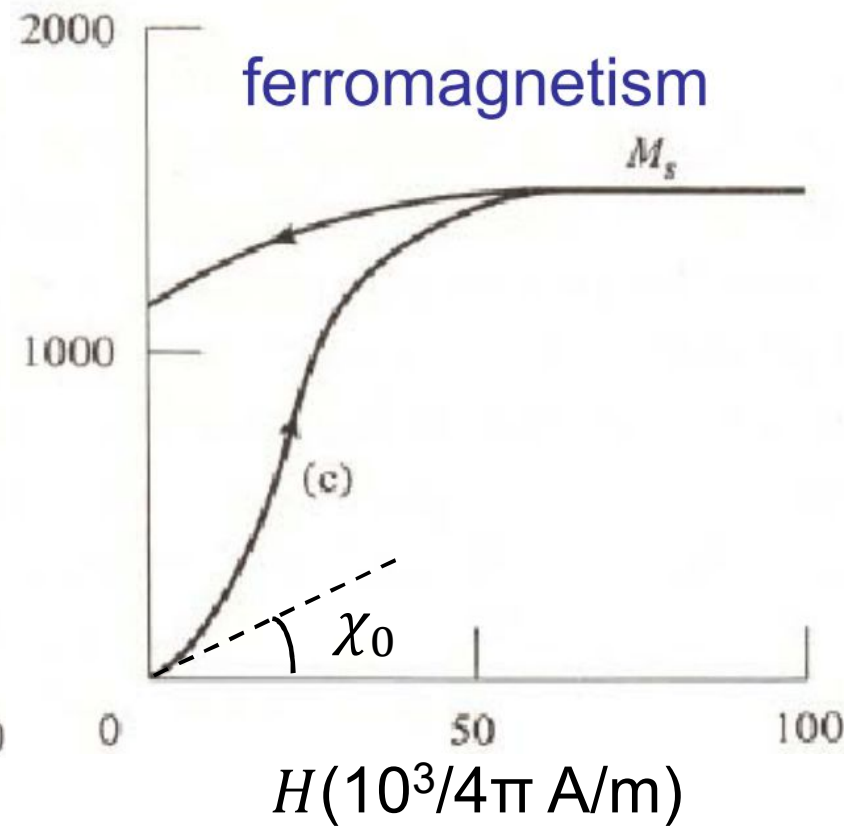
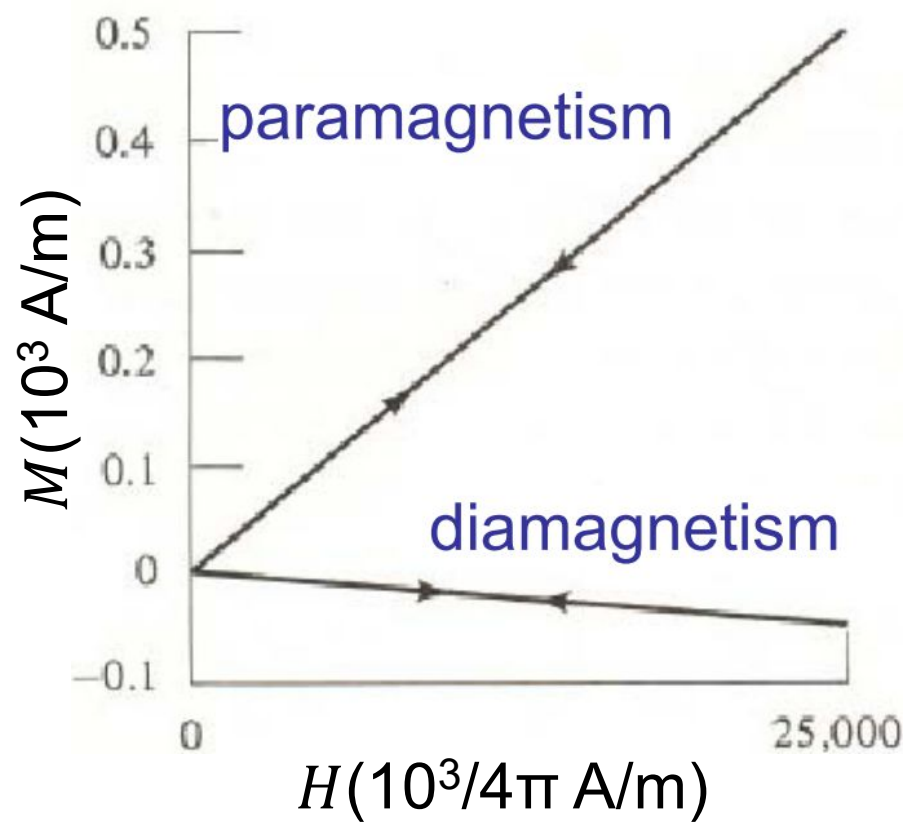


Ferromagnetic: $\chi > 0.01 - 0.1$, $\chi(T) - ?$



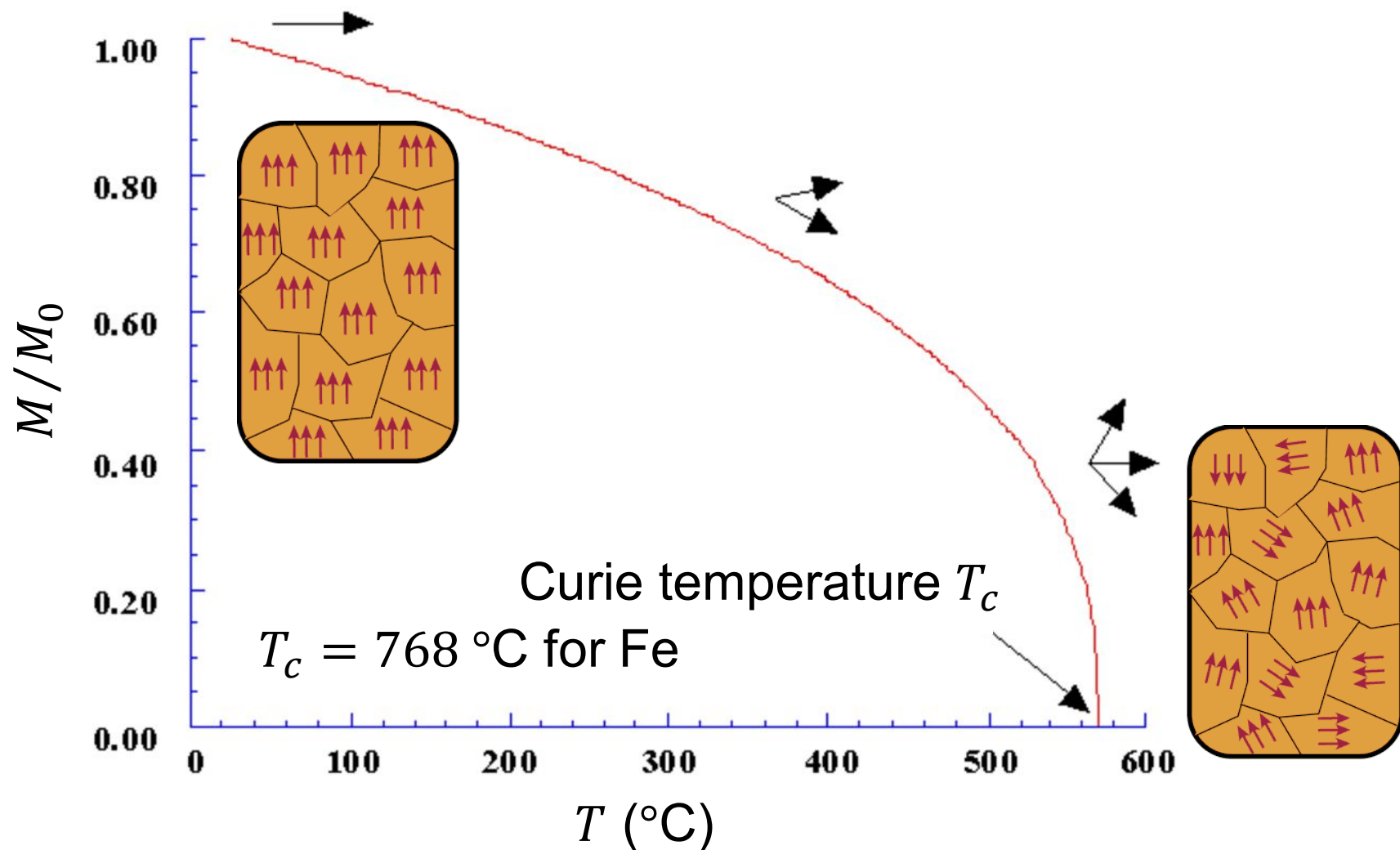
Magnetism

□ Magnetic properties of materials



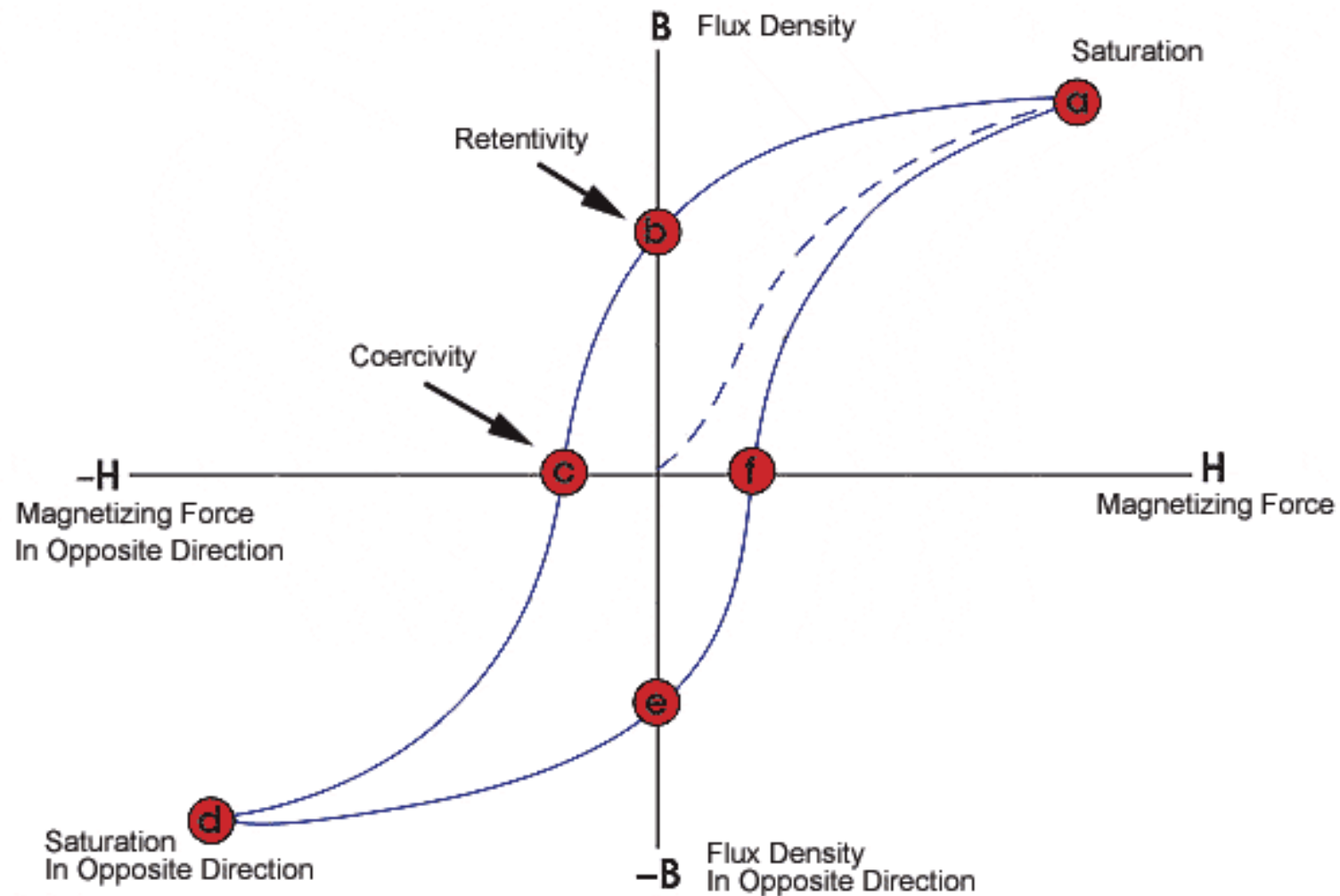
Magnetism

□ Magnetic properties of materials



Magnetism

□ Magnetic properties of materials

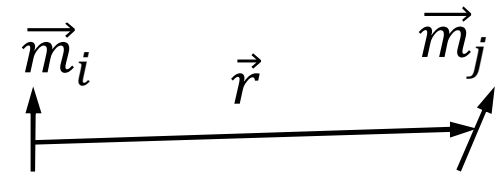


Magnetism

□ Magnetic interactions

What is the reason for magnetization?

1) Dipole-dipole interaction:



$$E_{ij}^{dip} = \frac{\mu_0}{4\pi} \frac{r^2(\vec{m}_i \cdot \vec{m}_j) - 3(\vec{m}_i \cdot \vec{r})(\vec{m}_j \cdot \vec{r})}{r^5} \text{ -- interaction energy}$$

For a crystal of moments $E = \frac{1}{2} \sum_{ij} E_{ij}^{dip} \sim z E_{ij}^{dip}$, z -- number of nearest neighbours

Magnetization is destroyed when $kT \sim z |E_{ij}^{dip}| \rightarrow$ for electron spins separated by distance a : $kT_c \sim z \frac{\mu_0}{4\pi} \frac{2e^2 \hbar^2}{4m_e^2 a^3}$

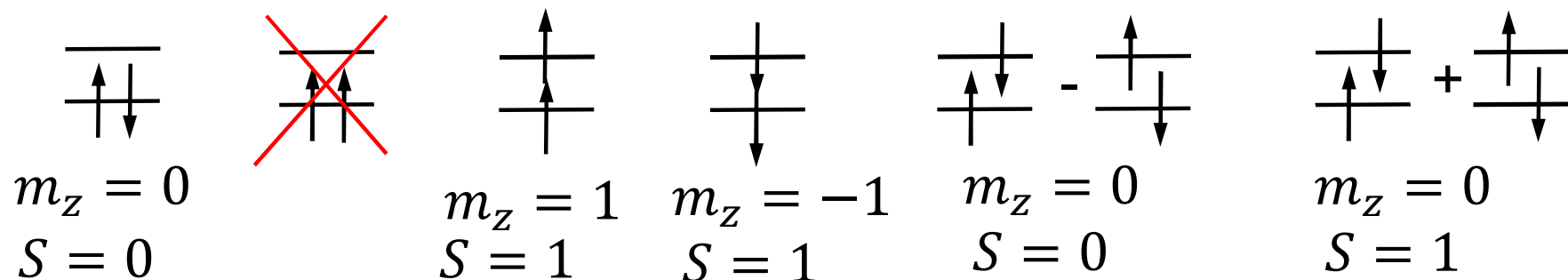
For bcc Fe $z = 8$, $a = 2.49 \text{ \AA} \rightarrow T_c \sim 0.3 \text{ K}$, but in reality it is 1043 K \rightarrow dipole-dipole interaction is not enough!

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

Even if Hamiltonian does not depend on spin (spin-orbit coupling neglected, no magnetic field), the energy of an electronic state depends on the overall spin state because of the Pauli exclusion principle:



What interaction and at what conditions causes spins to align?

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

Let us consider a dimer of atoms with only a single state each. If the atoms are far away then:

$$\Psi_{S=0} \approx \frac{1}{\sqrt{2}} (\Phi_{\alpha\beta} - \Phi_{\beta\alpha}), \quad \Psi_{S=1} \approx \Phi_{\alpha\alpha}$$

$$\Phi_{\alpha\beta} = \frac{1}{\sqrt{2}} \left(\phi_1(\vec{r}_1) \chi^\alpha(1) \phi_2(\vec{r}_2) \chi^\beta(2) - \phi_1(\vec{r}_2) \chi^\alpha(2) \phi_2(\vec{r}_1) \chi^\beta(1) \right)$$

$$\Phi_{\beta\alpha} = \frac{1}{\sqrt{2}} \left(\phi_1(\vec{r}_1) \chi^\beta(1) \phi_2(\vec{r}_2) \chi^\alpha(2) - \phi_1(\vec{r}_2) \chi^\beta(2) \phi_2(\vec{r}_1) \chi^\alpha(1) \right)$$

$$\Phi_{\alpha\alpha} = \frac{1}{\sqrt{2}} \left(\phi_1(\vec{r}_1) \chi^\alpha(1) \phi_2(\vec{r}_2) \chi^\alpha(2) - \phi_1(\vec{r}_2) \chi^\alpha(2) \phi_2(\vec{r}_1) \chi^\alpha(1) \right)$$

$$\Phi_{\alpha\beta} = \begin{array}{c} \uparrow \quad \downarrow \\ | \quad | \\ \phi_1 \quad \phi_2 \end{array} \quad \Phi_{\beta\alpha} = \begin{array}{c} \downarrow \quad \uparrow \\ | \quad | \\ \phi_1 \quad \phi_2 \end{array} \quad \Phi_{\alpha\alpha} = \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \phi_1 \quad \phi_2 \end{array}$$

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

$E_{S=0} \approx \langle \Psi_{S=0} | \hat{H} | \Psi_{S=0} \rangle$, $E_{S=1} = \langle \Psi_{S=1} | \hat{H} | \Psi_{S=1} \rangle$ -- which energy is lower and why?

$$\begin{aligned} E_{S=0} \approx & \frac{1}{2} \left\langle \Phi_{\alpha\beta} - \Phi_{\beta\alpha} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\alpha\beta} - \Phi_{\beta\alpha} \right\rangle = \\ & \frac{1}{2} \left\langle \Phi_{\alpha\beta} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\alpha\beta} \right\rangle + \frac{1}{2} \left\langle \Phi_{\beta\alpha} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\beta\alpha} \right\rangle - \\ & \frac{1}{2} \left\langle \Phi_{\alpha\beta} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\beta\alpha} \right\rangle - \frac{1}{2} \left\langle \Phi_{\beta\alpha} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\alpha\beta} \right\rangle = h_1 + h_2 + \\ & J_{12} + K_{12} \end{aligned}$$

where $h_i = \langle \phi_i | \hat{h} | \phi_i \rangle$, $J_{12} = \int \frac{\phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \phi_1(\vec{r}_1) \phi_2(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$

$$K_{12} = \int \frac{\phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \phi_2(\vec{r}_1) \phi_1(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \text{ (exchange integral)}$$

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

$E_{S=0} \approx \langle \Psi_{S=0} | \hat{H} | \Psi_{S=0} \rangle$, $E_{S=1} = \langle \Psi_{S=1} | \hat{H} | \Psi_{S=1} \rangle$ -- which energy is lower and why?

$$E_{S=1} \approx \left\langle \Phi_{\alpha\alpha} \left| \hat{h} + \frac{1}{r_{12}} \right| \Phi_{\alpha\alpha} \right\rangle = h_1 + h_2 + J_{12} - K_{12}$$

$J_{12} > 0$ (by definition)

$$\frac{1}{|r_{12}|} = \int e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} \frac{4\pi}{k^2} \frac{d\vec{k}}{(2\pi)^3},$$

$$K_{12} = \int \frac{d\vec{k}}{(2\pi)^3} \frac{4\pi}{k^2} \underbrace{\int d\vec{r}_1 \phi_1^*(\vec{r}_1) \phi_2(\vec{r}_1) e^{i\vec{k}\vec{r}_1}}_{I(\vec{k})} \underbrace{\int d\vec{r}_2 \phi_1(\vec{r}_2) \phi_2^*(\vec{r}_2) e^{-i\vec{k}\vec{r}_2}}_{I^*(\vec{k})}$$

$$\Rightarrow K_{12} \geq 0$$

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

$E_{S=0} \approx \langle \Psi_{S=0} | \hat{H} | \Psi_{S=0} \rangle$, $E_{S=1} = \langle \Psi_{S=1} | \hat{H} | \Psi_{S=1} \rangle$ -- which energy is lower and why?

$$E_{S=1} \approx h_1 + h_2 + J_{12} - K_{12}, E_{S=0} \approx h_1 + h_2 + J_{12} + K_{12}$$

$$K_{12} \geq 0 \Rightarrow E_{S=1} \leq E_{S=0}$$

Thus, if there is no hopping from one atom to another, the ferromagnetic state is preferred. For single atom with degenerate levels we obtain Hund's rule:

The total spin of electrons in a partially-filled shell of one ion tends to be maximal.

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

$$E_{S=1} \approx h_1 + h_2 + J_{12} - K_{12}, \quad E_{S=0} \approx h_1 + h_2 + J_{12} + K_{12}$$

Using second quantization, one can show that the Coulomb operator can be split into two parts:

$$\frac{1}{r_{12}} \cong \tilde{H}_C = \frac{1}{2} \sum_{ij} \left\{ \left(J_{ij} - \frac{K_{ij}}{2} \right) n_i n_j - 2K_{ij} \hat{s}_i \hat{s}_j \right\}, \text{ where } n_i, n_j - \text{occupations of orbitals } i \text{ and } j, \hat{s}_i - \text{vector spin operator acting on electron in orbital } i$$

Indeed, for the dimer example ($2\vec{s}_1\vec{s}_2 = (\vec{s}_1 + \vec{s}_2)^2 - \vec{s}_1^2 - \vec{s}_2^2$):

$$\langle \Phi_{\alpha\alpha} | \tilde{H}_C | \Phi_{\alpha\alpha} \rangle = J_{12} - \frac{K_{12}}{2} - K_{12} \left(1(1+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \times 2 \right) = J_{12} - K_{12}$$

$$\langle \Psi_{S=0} | \tilde{H}_C | \Psi_{S=0} \rangle = J_{12} - \frac{K_{12}}{2} - K_{12} \left(0(0+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \times 2 \right) = J_{12} + K_{12}$$

Magnetism

□ Magnetic interactions

Ferromagnetic exchange interaction

Note that $\left(J_{ij} - \frac{K_{ij}}{2}\right) > 0$:

$$\begin{aligned} J_{ij} - \frac{K_{ij}}{2} &> J_{ij} - K_{ij} = \frac{1}{2}(J_{ij} + J_{ji} - K_{ij} - K_{ji}) = \\ &= \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} [\phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2) - \phi_j^*(\vec{r}_1)\phi_i^*(\vec{r}_2)] \times [\phi_i(\vec{r}_1)\phi_j(\vec{r}_2) - \\ &\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)] = \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} |f(\vec{r}_1, \vec{r}_2)|^2 \geq 0 \end{aligned}$$

Thus, the corrected Coulomb interaction is weaker, but always repulsive

Magnetism

□ Magnetic interactions

Kinetic antiferromagnetic exchange interaction

Let us include the possibility for hopping in the dimer model:

$$\begin{aligned}
 \Phi_{\alpha\beta} &= \begin{array}{c} \uparrow \quad \downarrow \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array} & \Phi_{\beta\alpha} &= \begin{array}{c} \downarrow \quad \uparrow \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array} & \Phi_{\alpha\alpha} &= \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array} \\
 \Phi_1 &= \begin{array}{c} \uparrow\downarrow \quad \text{---} \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array} & \Phi_2 &= \begin{array}{c} \text{---} \quad \uparrow\downarrow \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array} & \Phi_{\beta\beta} &= \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline \phi_1 \quad \phi_2 \end{array}
 \end{aligned}$$

The ϕ_1 and ϕ_2 can be chosen as orthonormal Wannier functions, localized on respective atoms

The $\Phi_{\alpha\alpha}$ and $\Phi_{\beta\beta}$ can be omitted, since they do not interact with the other Φ 's through Hamiltonian

Magnetism

□ Magnetic interactions

Kinetic antiferromagnetic exchange interaction

Hamiltonian matrix in the $\{\Phi_1, \Phi_2, \Phi_{\alpha\beta}, \Phi_{\beta\alpha}\}$:

$$\langle \Phi | \hat{H} | \Phi \rangle = \sum_m h_{mm} + \frac{1}{2} \sum_{mn} (\langle mn | mn \rangle - \langle mn | nm \rangle)$$

$$\langle \Phi | \hat{H} | \Phi_i^a \rangle = h_{ia} + \sum_m (\langle im | am \rangle - \langle im | ma \rangle)$$

$$\langle \Phi | \hat{H} | \Phi_{ij}^{ab} \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle \quad (i, j, a, b \text{ denote spin-orbitals})$$

$$\langle \Phi_1 | \hat{H} | \Phi_1 \rangle = 2h_{11} + J_{11}, \quad \langle \Phi_2 | \hat{H} | \Phi_2 \rangle = 2h_{22} + J_{22}$$

$$\langle \Phi_1 | \hat{H} | \Phi_2 \rangle = \langle \Phi_2 | \hat{H} | \Phi_1 \rangle = K_{12}$$

$$\langle \Phi_1 | \hat{H} | \Phi_{\alpha\beta} \rangle = \langle \Phi_{\alpha\beta} | \hat{H} | \Phi_1 \rangle = h_{12} + \langle 11 | 21 \rangle = -\langle \Phi_1 | \hat{H} | \Phi_{\beta\alpha} \rangle$$

$$\langle \Phi_2 | \hat{H} | \Phi_{\alpha\beta} \rangle = \langle \Phi_{\alpha\beta} | \hat{H} | \Phi_2 \rangle = h_{21} + \langle 22 | 12 \rangle = h_{12} + \langle 11 | 21 \rangle = \dots$$

$$\langle \Phi_{\alpha\beta} | \hat{H} | \Phi_{\alpha\beta} \rangle = \langle \Phi_{\beta\alpha} | \hat{H} | \Phi_{\beta\alpha} \rangle = h_{11} + h_{22} + J_{12}$$

$$\langle \Phi_{\alpha\beta} | \hat{H} | \Phi_{\beta\alpha} \rangle = \langle \Phi_{\beta\alpha} | \hat{H} | \Phi_{\alpha\beta} \rangle = -K_{12}$$

Magnetism

□ Magnetic interactions

Kinetic antiferromagnetic exchange interaction

Hamiltonian matrix in the $\{\Phi_1, \Phi_2, \frac{1}{\sqrt{2}}(\Phi_{\alpha\beta} - \Phi_{\beta\alpha}), \frac{1}{\sqrt{2}}(\Phi_{\alpha\beta} + \Phi_{\beta\alpha})\}$:

$$H = \begin{pmatrix} 2h + U & K & \sqrt{2}t & 0 \\ K & 2h + U & \sqrt{2}t & 0 \\ \sqrt{2}t & \sqrt{2}t & 2h + J_{12} + K & 0 \\ 0 & 0 & 0 & 2h + J_{12} - K \end{pmatrix}$$

where $h \equiv h_{11} = h_{22}$

$K \equiv K_{12}$ (direct ferromagnetic exchange),

$U \equiv J_{11} = J_{22}$ (on-site Coulomb repulsion - Hubbard U),

$t \equiv h_{12} + \langle 11|21 \rangle$ (hopping integral)

Let us find eigenvalues of this matrix

Magnetism

□ Magnetic interactions

Kinetic antiferromagnetic exchange interaction

Solutions:

$$E_1 = 2h + J_{12} - K, S = 1$$

$$E_2 = 2h + U - K, S = 0$$

$$E_{3/4} = 2h + K + \frac{1}{2} \left(U + J_{12} \pm \sqrt{(U - J_{12})^2 + 16t^2} \right), S = 0$$

Thus, the system is antiferromagnetic if

$$2h + K + \frac{1}{2} \left(U + J_{12} - \sqrt{(U - J_{12})^2 + 16t^2} \right) < 2h + J_{12} - K$$

$$\sqrt{(U - J_{12})^2 + 16t^2} > 4K - 2J_{12} + U$$

Usually $K \ll U$ and $J_{12} \ll U$, so that

$$\sqrt{(U - J_{12})^2 + 16t^2} \approx U - J_{12} + \frac{8t^2}{U} > 4K - 2J_{12} + U$$

Magnetism

□ Magnetic interactions

Kinetic antiferromagnetic exchange interaction

The system is antiferromagnetic if $J_{12} + \frac{8t^2}{U} > 4K$

If the hopping integrals t are large enough (i.e., the system gains energy due to reduction of the kinetic energy despite larger Coulomb repulsion), the system is antiferromagnetic (spins on adjacent lattice sites tend to be antiparallel)

The mapping to the $-K\vec{s}_1\vec{s}_2$ model for $U \gg |t|$ gives $K \sim -\frac{4t^2}{U}$

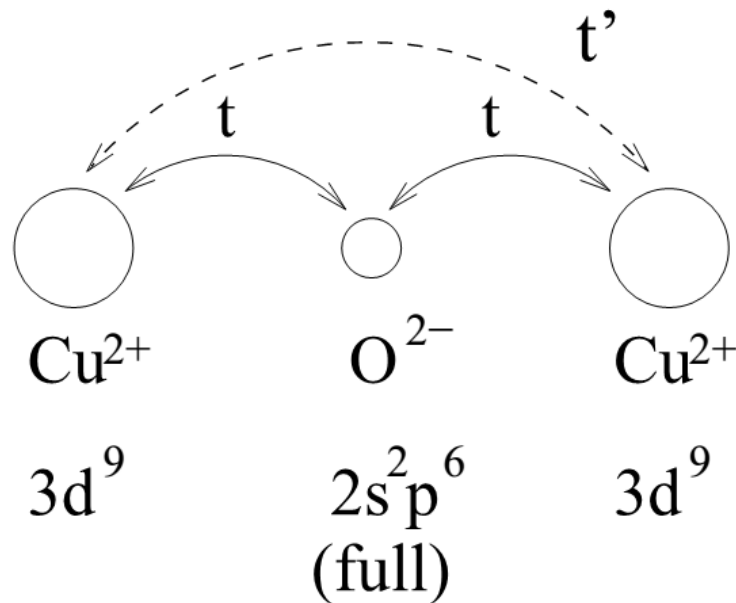
Similar results can be obtained for a lattice of spins, not just a dimer

Magnetism

□ Magnetic interactions

Superexchange

In ionic crystals, magnetic cations are usually separated by non-magnetic anions



Example: cuprates

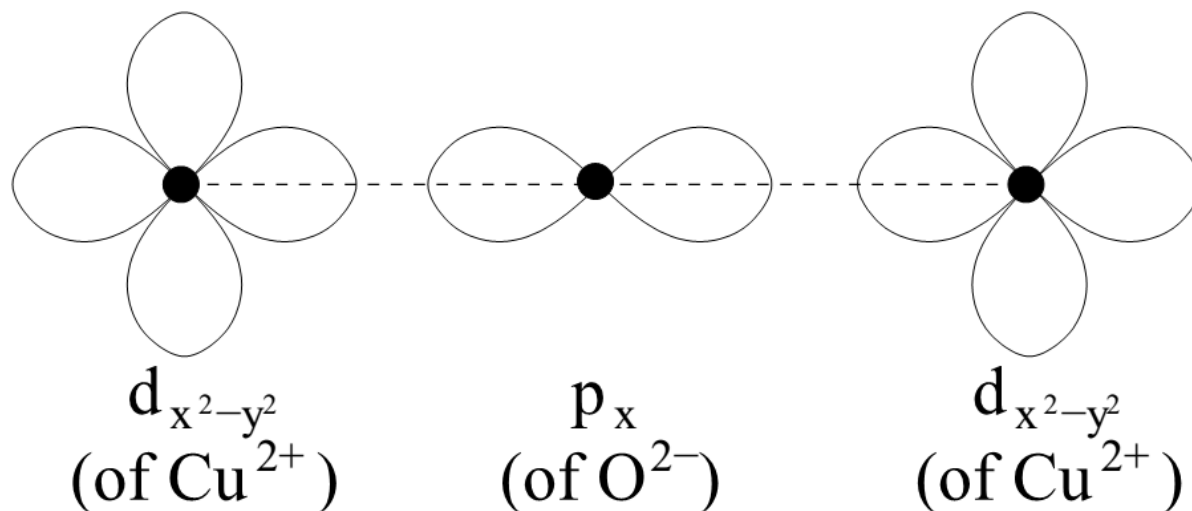
Even though t' is very small, t is relatively large, so that hopping of the hole from Cu to O and then to Cu ($\sim t^4$) results in antiferromagnetic ordering

Magnetism

□ Magnetic interactions

Superexchange does not always lead to antiferromagnetism

There is a strong antiferromagnetic exchange interaction if the half-filled orbitals of two cations overlap with the same empty or filled orbital of the intervening anion:

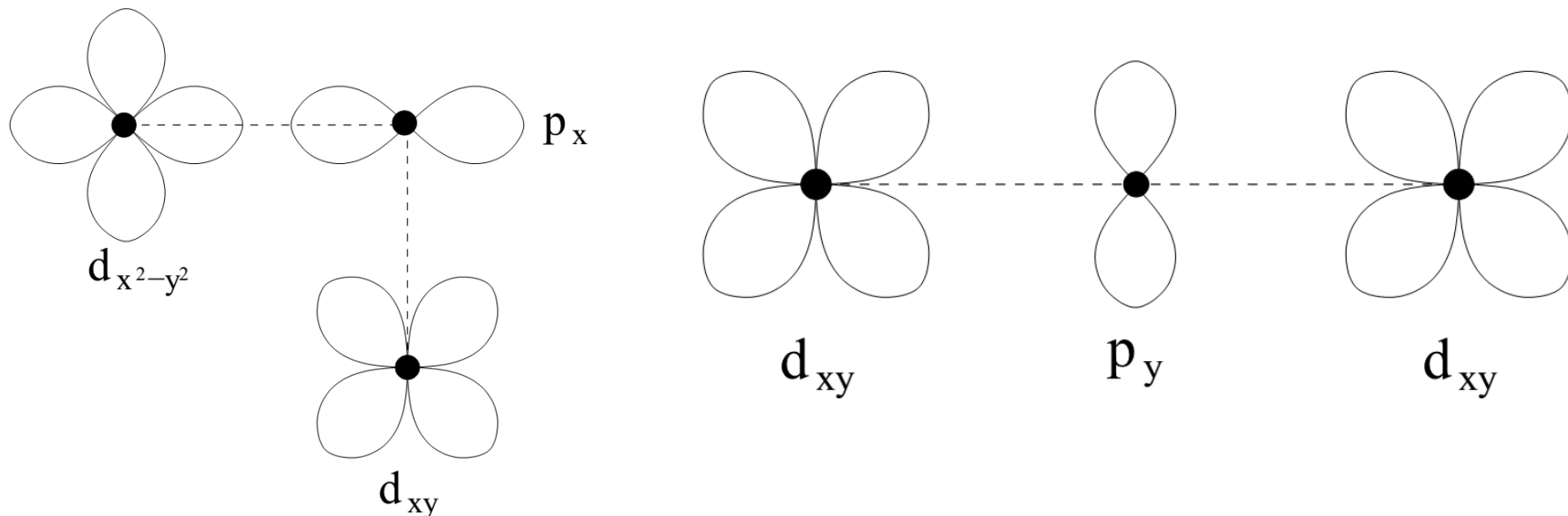


Magnetism

□ Magnetic interactions

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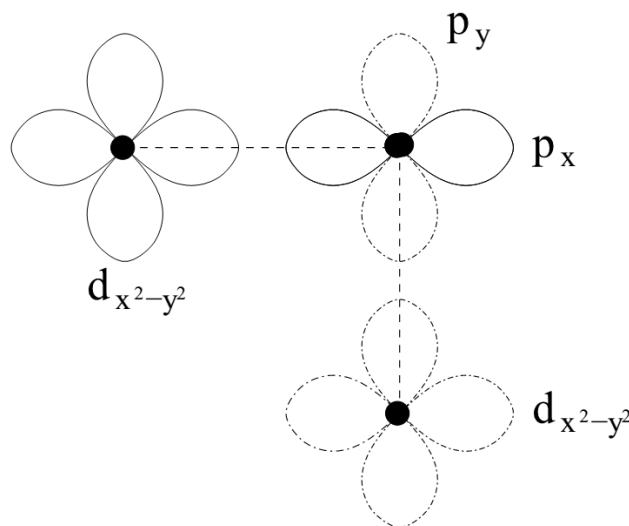


Magnetism

□ Magnetic interactions

Superexchange does not always lead to antiferromagnetism

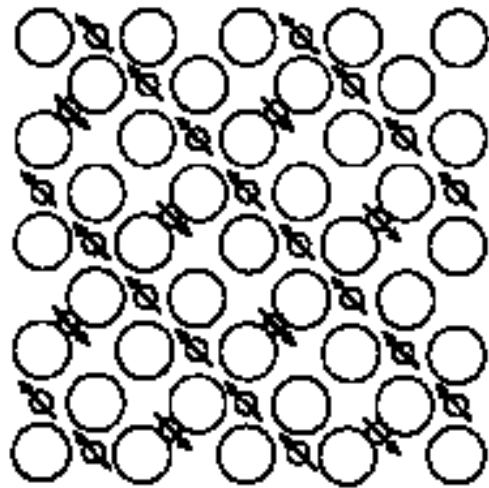
There is a weaker ferromagnetic exchange interaction if the half-filled orbitals of two cations overlap with orthogonal orbitals of the same intervening anion:



Magnetism

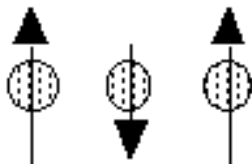
□ Magnetic interactions

Ferrimagnetism



In ferrimagnets, the superexchange causes the antiferromagnetic ordering, and there are two different sites, with different spins, so that the system remains ferromagnetic. Example - magnetite (Fe_3O_4).

Ferrimagnetism



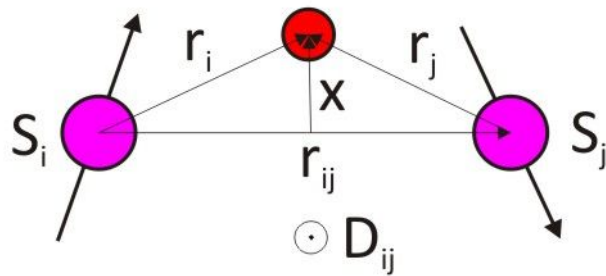
Magnetism

□ Magnetic interactions

Dzyaloshinsky-Moriya interaction

We have neglected other correlation terms. They can give rise to other interactions. One example is the Dzyaloshinsky-Moriya interaction: $\hat{H}_{DM} = \vec{D}_{12}(\vec{S}_1 \times \vec{S}_2)$

If the inversion symmetry is broken, the antiparallel spins will tend to tilt:



Example: multiferroics, become weakly ferromagnetic (magnetism induced electric polarization - lattice energy versus magnetic ordering)

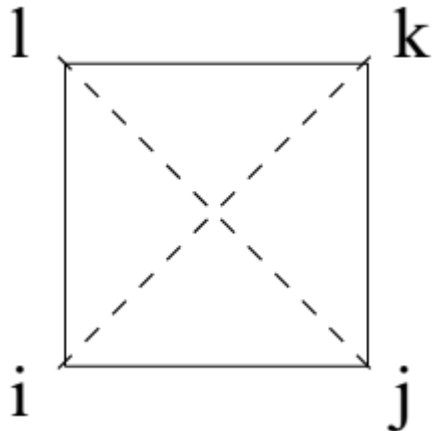
Magnetism

□ Magnetic interactions

Biquadratic and ring exchange interaction

Other higher-order t^4/U^3 interaction terms are biquadratic and ring exchange. They are present in the

Hubbard model on a lattice: $\sim (\vec{S}_i \vec{S}_j)^2$ (biquadratic),
 $\sim (\vec{S}_i \vec{S}_j)(\vec{S}_k \vec{S}_l) + (\vec{S}_i \vec{S}_l)(\vec{S}_k \vec{S}_j) - (\vec{S}_i \vec{S}_k)(\vec{S}_j \vec{S}_l)$ (ring)



Magnetism

□ Heisenberg model

Based on the previous analysis, the system of interacting spins can be modelled with the following Hamiltonian:

$$\hat{H}_H = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j - \mu_0 \mu \sum_i \vec{H}_i \vec{S}_i, \quad J_{ij} = J_{ji}$$

where the last term is the interaction of each spin at site i with the external magnetic field at the same site

The model can be applied to the total angular momenta \vec{J}_i

The model neglects higher-order terms (such as ring exchange), anisotropic couplings ($-\vec{S}_i \mathbf{J}_{ij} \vec{S}_j$), and the Dzyaloshinsky-Moriya interaction

But it can be used to study phase transitions

Magnetism

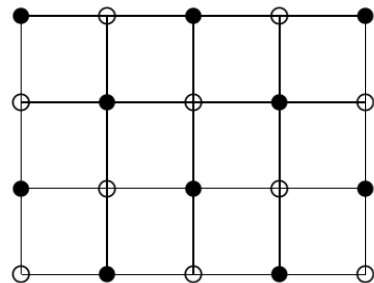
□ Heisenberg model

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$$\hat{H}_H = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j - \mu_0 \mu \sum_i \vec{H}_i \vec{S}_i, \quad J_{ij} = J_{ji}$$

If all interactions are non-negative, a fully polarized state is the ground state (spontaneous symmetry breaking)

If some J_{ij} are negative, no general solution of the Heisenberg model exists. One exclusion is a *bipartite* system:



Marshall's theorem: If all $J_{AB} \leq 0$ and $J_{BA} \leq 0$, and every pair of sites is connected by a non-zero exchange, the system has a non-degenerate antiferromagnetic ground state

Magnetism

□ Ising model

The Ising model considers strongly anisotropic spin-spin interaction:

$$\hat{H}_I = -\sum_{i>j} J_{ij}^{zz} S_i^z S_j^z + g\mu_0\mu_B \sum_i H_i^z S_i^z, \quad J_{ij}^{zz} = J_{ji}^{zz}$$

Usually $J_{ij}^{zz} \neq 0$ only for adjacent i, j

If $\vec{H} = 0$, the model predicts order-disorder phase transition for a lattice of dimension $d \geq 2$ (but not $d = 1$)

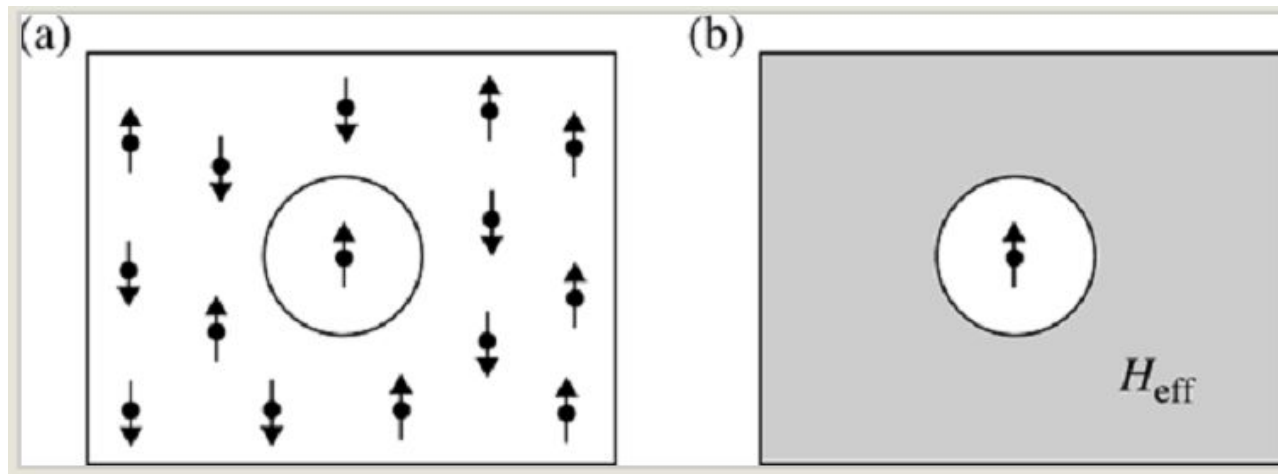
The general solution of the model is complicated (too many configurations, especially for larger d)

The simplest but powerful approximation is mean-field

Magnetism

□ Mean-field approximation

Weiß' mean-field theory



Magnetism

□ Mean-field approximation

Weiß' mean-field theory

$$\hat{H}_H = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j + g\mu_0\mu_B \sum_i \vec{H}_i \vec{S}_i, \quad J_{ij} = J_{ji}$$

$$\vec{S}_i = \langle \vec{S}_i \rangle + (\vec{S}_i - \langle \vec{S}_i \rangle)$$

$$\hat{H}_H = -\frac{1}{2} \sum_{ij} J_{ij} \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle - \frac{1}{2} \sum_{ij} J_{ij} \langle \vec{S}_i \rangle (\vec{S}_j - \langle \vec{S}_j \rangle) - \frac{1}{2} \sum_{ij} J_{ij} (\vec{S}_i - \langle \vec{S}_i \rangle) \langle \vec{S}_j \rangle - \frac{1}{2} \sum_{ij} J_{ij} (\vec{S}_i - \langle \vec{S}_i \rangle) (\vec{S}_j - \langle \vec{S}_j \rangle) + g\mu_0\mu_B \sum_i \vec{H}_i \vec{S}_i$$

$$\hat{H}_H \approx \frac{1}{2} \sum_{ij} J_{ij} \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle - \sum_i (-g\mu_0\mu_B \vec{H}_i + \sum_j J_{ij} \langle \vec{S}_j \rangle) \vec{S}_i \equiv H_{MF}$$

mean-field
Hamiltonian

Just as for a paramagnetic material, we can calculate the dependence of magnetization and susceptibility on temperature

Magnetism

□ Mean-field approximation

Mean-field approximation to Ising model

$$\hat{H}_{MF} = \frac{1}{2} \sum_{ij} J_{ij}^{zz} \langle S_i^z \rangle \langle S_j^z \rangle - \sum_i (-g\mu_0\mu_B H_i^z + \sum_j J_{ij}^{zz} \langle S_j^z \rangle) S_i^z$$

If all spins are equivalent, then $\langle \vec{S}_i \rangle = \langle \vec{S} \rangle$ does not depend on i

$$\hat{H}_{MF} = \left(\frac{1}{2} \sum_{ij} J_{ij}^{zz} \right) \langle S \rangle^2 - \sum_i (-g\mu_0\mu_B H_i^z + (\sum_j J_{ij}^{zz}) \langle S \rangle) S_i^z$$

For simplicity, let us assume that $|\vec{S}| = \frac{1}{2}$, $g = 2$, and \vec{H} is uniform ($H_i^z = H \forall i$). Partition function for N spins $Z = (z)^N$

$$z = \exp\left(-\frac{E_{\uparrow}}{kT}\right) + \exp\left(-\frac{E_{\downarrow}}{kT}\right), \quad E_{\uparrow} = E_0 + \mu_0\mu_B H - \frac{1}{2} J_{MF} \langle S \rangle$$

$$E_{\downarrow} = E_0 - \mu_0\mu_B H + \frac{1}{2} J_{MF} \langle S \rangle, \quad \text{where } E_0 = \frac{\langle S \rangle^2}{2} \sum_{ij} J_{ij}^{zz}, \quad J_{MF} = \sum_j J_{ij}^{zz}$$

Magnetism

□ Mean-field approximation

Mean-field approximation to Ising model

The average spin: $\langle S \rangle = \frac{1}{2} \tanh \left\{ \left(-\mu_0 \mu_B H + \frac{1}{2} J_{MF} \langle S \rangle \right) / kT \right\}$

When $H = 0$, there is a spontaneous magnetization if

$$\frac{J_{MF}}{4kT} > 1 \Rightarrow T_C = \frac{J_{MF}}{4k}, \langle S \rangle = 0 \text{ when } T \geq T_C$$

When $T > T_C$, average spin $\langle S \rangle \rightarrow 0$, so that for small H

$$\langle S \rangle = \frac{1}{2} \tanh \left\{ \left(-\mu_0 \mu_B H + \frac{1}{2} J_{MF} \langle S \rangle \right) / kT \right\} \approx \frac{(-\mu_0 \mu_B H + J_{MF} \langle S \rangle / 2)}{2kT},$$

$$\langle S \rangle \approx -\frac{\mu_0 \mu_B H}{2k} \frac{1}{T - T_C}, M = -N_S g \mu_B \langle S \rangle \approx \frac{N_S g \mu_0 \mu_B^2 H}{2k} \frac{1}{T - T_C}, \text{ and}$$

$$\chi = \left. \frac{dM}{dH} \right|_{H=0} \sim (T - T_C)^{-1} \text{ -- Curie-Weiß law}$$

Magnetism

□ Mean-field approximation

Magnetization of a ferromagnetic (N_S - spin concentration):

$$M = -g\mu_B N_S \langle S \rangle = \frac{1}{2} g\mu_B N_S \tanh \left(\frac{J_{MF} M}{2kT g\mu_B N_S} \right)$$

When $T \rightarrow T_C$, $T < T_C$, then M is small, and

$$M \approx \frac{1}{2} g\mu_B N_S \left(CM - \frac{C^3}{3} M^3 \right), \text{ where } C = \frac{J_{MF}}{2kT g\mu_B N_S}$$

$$M \approx \frac{48k^3 T_C^2 g^2 \mu_B^2 N_S^2}{J_{MF}^3} \sqrt{T_C - T}, \text{ where } T_C = \frac{J_{MF}}{4k}$$

Magnetism from electronic structure

- We have to introduce spin densities

$$n_{\sigma}(\vec{r}) = \sum_i |u_{i,\sigma}(\vec{r})|^2$$

- summing up to the total density

$$n(\vec{r}) = n_{\uparrow}(\vec{r}) + n_{\downarrow}(\vec{r})$$

- They are obtained from the spin-dependent KS equations

$$\left\{ -\frac{1}{2} \nabla^2 + V(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{XC,\sigma}(\vec{r}) - \epsilon_{i,\sigma} \right\} u_{i,\sigma}(\vec{r}) = 0$$

with $V_{XC,\sigma}(\vec{r}) = \frac{\delta E_{XC}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\vec{r})}$

Monte Carlo (random) sampling

Monte Carlo (random) sampling

□ Calculation of integrals numerically

Consider a multidimensional integral: $I[f] = \int_{\Omega} f(\mathbf{X}) d^M X$

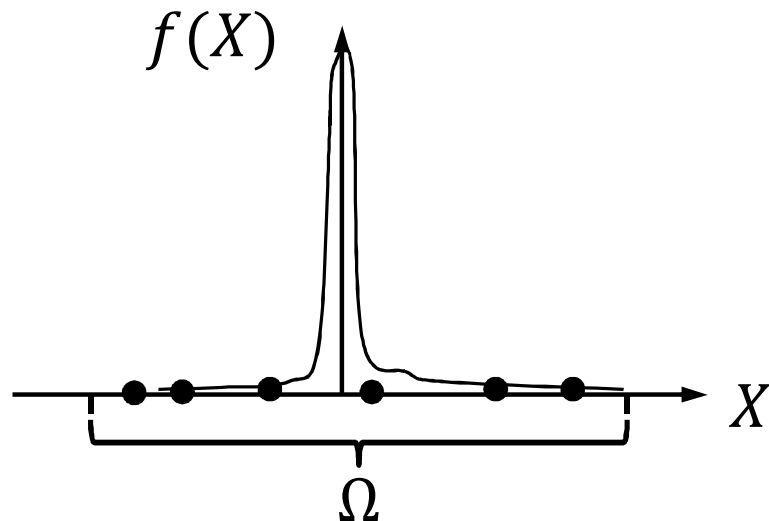
How to calculate it numerically? 1) Choose a regular grid in Ω . However, for a very modest sampling of 10 points per direction, we need to calculate $f(\mathbf{X})$ at 10^M points - not practical for $M > 10$

2) Choose points in Ω randomly - the “curse of dimensions” is alleviated

Is a uniform distribution of the random points a good choice?

Monte Carlo (random) sampling

□ Calculation of integrals numerically



$$I[f] = \int_{\Omega} f(X) d^M X$$

Obviously, in this case uniform sampling is not the best choice: the error in $I[f]$ converges very slowly with number of samples N :

$$\delta I \approx \Omega \sqrt{\frac{\text{Var}(f)}{N}}, \quad \text{Var}(f) = \frac{1}{N-1} \sum_{i=1}^N \left(f(X_i) - \frac{1}{N} \sum_{j=1}^N f(X_j) \right)^2$$

variance

Monte Carlo (random) sampling

□ Importance sampling

Perform a trivial transformation:

$$I[f] = \int_{\Omega} f(\mathbf{X}) d^M X = \int_{\Omega} \frac{f(\mathbf{X})}{w(\mathbf{X})} w(\mathbf{X}) d^M X$$

If $w(\mathbf{X}) \geq 0$, $\int_{\Omega} w(\mathbf{X}) d^M X = 1$, this looks like an expectation value of $f(\mathbf{X})/w(\mathbf{X})$ for \mathbf{X} distributed according to probability density $w(\mathbf{X})$:

$$I[f] \approx \frac{1}{N} \sum_{i=1}^N \frac{f(\mathbf{X}_i)}{w(\mathbf{X}_i)}, \quad w(\mathbf{X}) \rightarrow \mathbf{X}_i$$

This gives freedom to minimize the variance by a proper choice of $w(\mathbf{X})$. In particular, if $w(\mathbf{X}) = C f(\mathbf{X})$, the variance is zero. In practice, $w(\mathbf{X}) \approx C f(\mathbf{X})$ is a very good choice (importance sampling)

Monte Carlo (random) sampling

□ Importance sampling

Perform a trivial transformation:

$$I[f] \approx \frac{1}{N} \sum_{i=1}^N \frac{f(\mathbf{X}_i)}{w(\mathbf{X}_i)}, \quad w(\mathbf{X}) \rightarrow \mathbf{X}_i$$

How to generate $\{\mathbf{X}_i\}$ according to $w(\mathbf{X})$?

Metropolis algorithm: (1) generate a set of \mathbf{X}_i ; (2) choose randomly a displacement $\Delta\mathbf{X}_i$ for each i ; (3) replace \mathbf{X}_i with $\mathbf{X}'_i = \mathbf{X}_i + \Delta\mathbf{X}_i$ with the probability:

$$P_{accept}(\mathbf{X}_i \rightarrow \mathbf{X}'_i) = \min\left(1, \frac{w(\mathbf{X}'_i)}{w(\mathbf{X}_i)}\right)$$

(4) continue until convergence

Metropolis, Rosenbluth, Rosenbluth, Teller, Teller, J. Chem. Phys. 21, 1087 (1953)

Monte Carlo (random) sampling

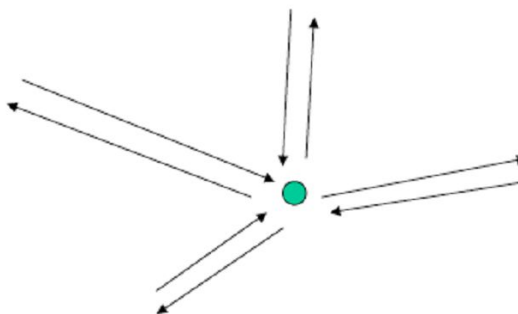
□ Calculation of integrals numerically

$$P_{accept}(X_i \rightarrow X'_i) = \min\left(1, \frac{w(X'_i)}{w(X_i)}\right)$$

This follows from detailed balance in equilibrium:

$$w(X_i)P(X_i \rightarrow X'_i) = w(X'_i)P(X'_i \rightarrow X_i)$$

Detailed balance is sufficient (although not necessary) for equilibrium:


$$\sum_{X'_i} w(X_i)P(X_i \rightarrow X'_i) = \sum_{X'_i} w(X'_i)P(X'_i \rightarrow X_i)$$

Metropolis, Rosenbluth, Rosenbluth, Teller, Teller, J. Chem. Phys. 21, 1087 (1953)

Monte Carlo sampling - applications

□ Computing statistical averages

$$\langle A \rangle = \frac{\int d^{3N}R \int d^{3N}p A(\mathbf{R}, \mathbf{p}) e^{-H(\mathbf{R}, \mathbf{p})/kT}}{\int d^{3N}R \int d^{3N}p e^{-H(\mathbf{R}, \mathbf{p})/kT}}$$

$\frac{e^{-\frac{H(\mathbf{R}, \mathbf{p})}{kT}}}{\int d^{3N}R \int d^{3N}p e^{-H(\mathbf{R}, \mathbf{p})/kT}}$ is a natural choice for $w(\mathbf{X})$ for Monte Carlo integration of thermodynamic averages (easily extendable to ensembles other than canonical; kinetic energy integral can often be taken)

Monte Carlo sampling - applications

□ Electronic structure - variational MC (VMC)

For a trial wavefunction Ψ_T

$$E_T = \frac{\int \Psi_T^* \hat{H} \Psi_T d\vec{r}}{\int \Psi_T^* \Psi_T d\vec{r}} = \frac{\int |\Psi_T|^2 \frac{\hat{H} \Psi_T}{\Psi_T} d\vec{r}}{\int |\Psi_T|^2 d\vec{r}}$$

$E_L(\{\vec{r}\}) = \frac{\hat{H} \Psi_T}{\Psi_T}$ - local energy, should be constant for exact Ψ_T

Monte Carlo sampling - applications

□ Electronic structure - variational MC (VMC)

For a trial wavefunction Ψ_T $E_T = \frac{\int \Psi_T^* \hat{H} \Psi_T d\vec{r}}{\int \Psi_T^* \Psi_T d\vec{r}} = \frac{\int |\Psi_T|^2 \frac{\hat{H} \Psi_T}{\Psi_T} d\vec{r}}{\int |\Psi_T|^2 d\vec{r}}$
 $E_L(\{\vec{r}\}) = \frac{\hat{H} \Psi_T}{\Psi_T}$ - local energy, should be constant for exact Ψ_T

- 1) Choose a form of Ψ_T with parameters (typically $\Psi_T = \Phi_0 \exp(\sum_{i>j} u(r_{ij}))$ - determinant times *Jastrow factor*)
- 2) Calculate the integral using MC, moving electrons one by one ($w(X) \rightarrow |\Psi_T|^2 / \int |\Psi_T|^2 d\vec{r}$, variance in E_L as a criterion for convergence) for a set of parameters
- 3) Find the parameters minimizing the trial energy E_T

Since the integration is done with MC, the form of Ψ_T can be complex (but not too complex)

Monte Carlo sampling - applications

□ Electronic structure - diffusion MC (DMC)

$$\frac{\partial \Psi}{\partial(-it)} = \hat{H}\Psi \Rightarrow \left(\frac{\partial}{\partial \tau} - \frac{1}{2} \sum_i \nabla_i^2 \right) \Psi = -V\Psi \rightarrow (E_T - V)\Psi$$

The formal solution is:

$$\Psi(\{\vec{r}\}, \tau) = \int G(\{\vec{r}\}, \{\vec{r}'\}, \tau) \Psi(\{\vec{r}'\}, 0) d\vec{r}'$$

$G(\{\vec{r}\}, \{\vec{r}'\}, \tau)$ - Green's function, solution of the same equation with initial condition $G(\{\vec{r}\}, \{\vec{r}'\}, 0) = \delta(\{\vec{r}\} - \{\vec{r}'\})$

$$\hat{H}\Psi_i = E_i\Psi_i \Rightarrow G(\{\vec{r}\}, \{\vec{r}'\}, \tau) = \sum_i \Psi_i(\{\vec{r}\}) e^{-\tau E_i} \Psi_i^*(\{\vec{r}'\})$$

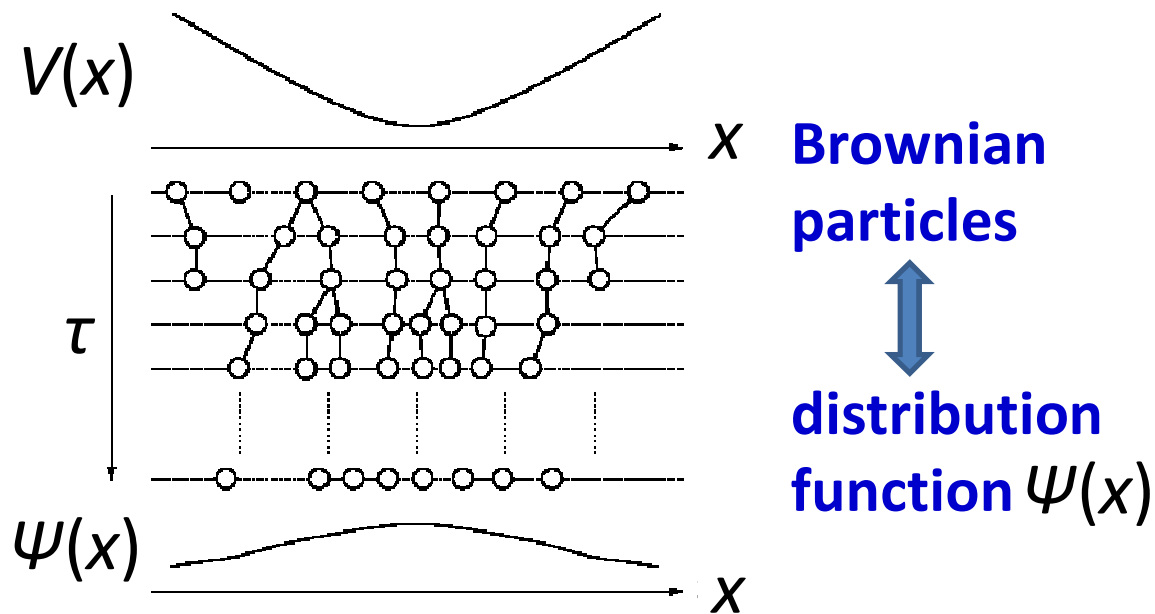


only ground state survives

$$\lim_{\tau \rightarrow \infty} \Psi(\{\vec{r}\}, \tau) = \lim_{\tau \rightarrow \infty} \Psi_0(\{\vec{r}\}) e^{-\tau(E_0 - E_T)} \langle \Psi_0 | \Psi_T \rangle$$

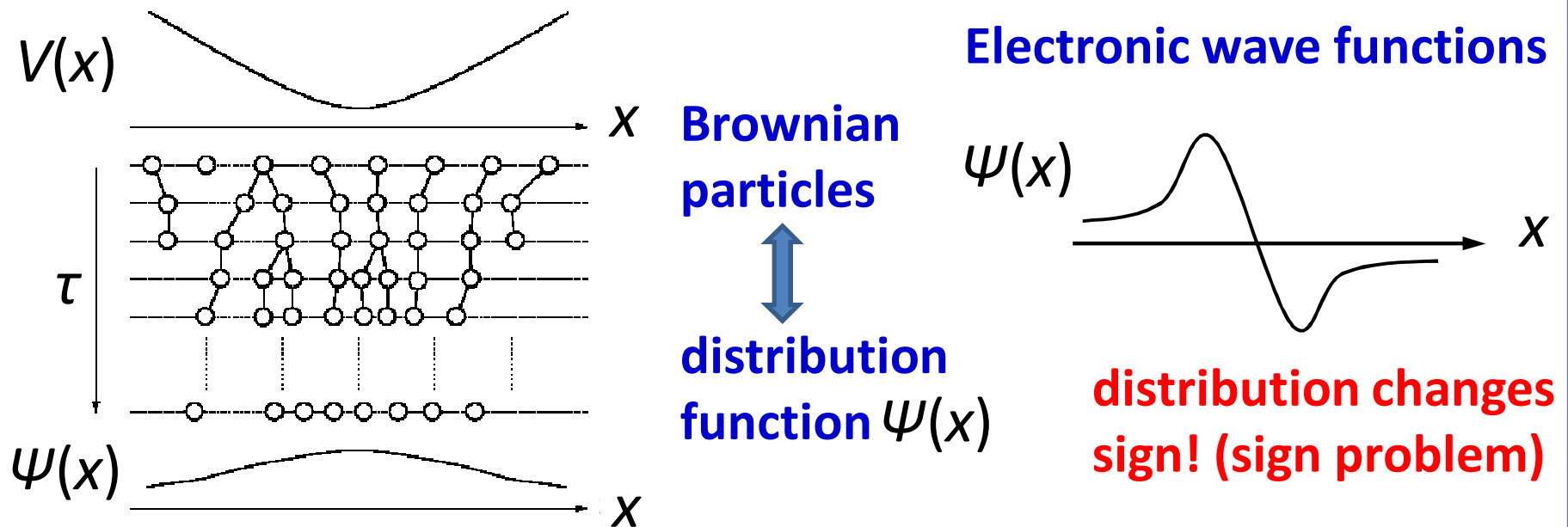
Monte Carlo sampling - applications

□ Electronic structure - diffusion MC (DMC)



Monte Carlo sampling - applications

□ Electronic structure - diffusion MC (DMC)



A possible solution - fixed-node approximation (consider Ψ or $-\Psi$ as distribution function in positive or negative domains) - requires a good approximation for the nodal surface (e.g., from HF)

Monte Carlo sampling - applications

□ Electronic structure - diffusion MC (DMC)

- 1) Choose a trial (guiding) wavefunction (e.g., from VMC)
- 2) Approximate $G(\{\vec{r}\}, \{\vec{r}'\}, \tau)$ (short-time approximations)
- 3) Initialize an ensemble of electronic configurations
- 4) Move electrons one by one with Metropolis acceptance with $w(X) = \frac{|\Psi_T(\{\vec{r}'\})|^2 G(\{\vec{r}'\}, \{\vec{r}\}, \tau)}{|\Psi_T(\{\vec{r}\})|^2 G(\{\vec{r}\}, \{\vec{r}'\}, \tau)}$ (only accept if sign does not change - fixed-node)
- 5) replicate (branch) the current electronic configuration $P \sim \exp(-\tau(E_L - E_T))$ times
- 6) Repeat above 100-1000 times
- 7) Update E_T to the energy of the ensemble; advance τ

Monte Carlo sampling - applications

❑ **Electronic structure - diffusion MC (DMC)**

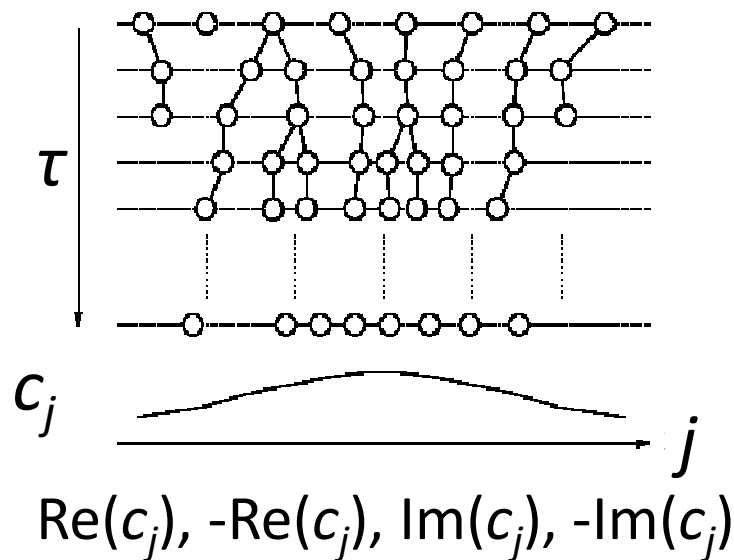
Advantages and disadvantages of DMC:

- + Very accurate for small systems
- + linear scaling implementations were demonstrated, easily parallelizable on many CPUs
- Sign problem (especially solids) → fixed-node approximation (solutions exist, but computationally expensive)
- Computational cost increases as Z^6 in all-electron calculations → need pseudopotentials
- Accurate calculation of energy gradients is difficult

Monte Carlo sampling - applications

❑ Electronic structure - FCIQMC

Walkers – determinants



$$\Psi_0 = \sum_j c_j \Phi_j$$

$$-\frac{dN_i}{d\tau} = (\langle \Phi_i | \hat{H} | \Phi_i \rangle - E_T) N_i + \sum_{j \neq i} \langle \Phi_i | \hat{H} | \Phi_j \rangle N_j$$



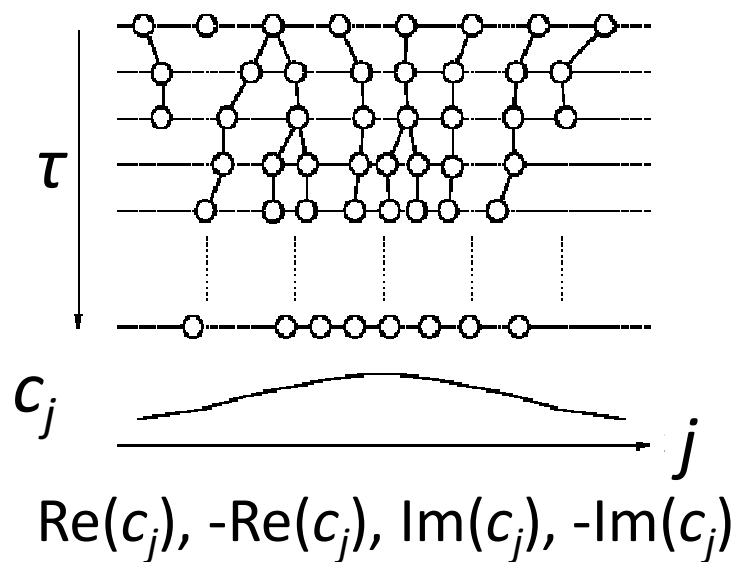
$$E, c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

Each determinant is represented by a number of instances (walkers) that can multiply, die, or spawn another determinant stochastically with probability $\sim H_{ij}$

Monte Carlo sampling - applications

❑ Electronic structure - FCIQMC

Walkers – determinants



$$\Psi_0 = \sum_j c_j \Phi_j$$

$$-\frac{dN_i}{d\tau} = (\langle \Phi_i | \hat{H} | \Phi_i \rangle - E_T) N_i + \sum_{j \neq i} \langle \Phi_i | \hat{H} | \Phi_j \rangle N_j$$

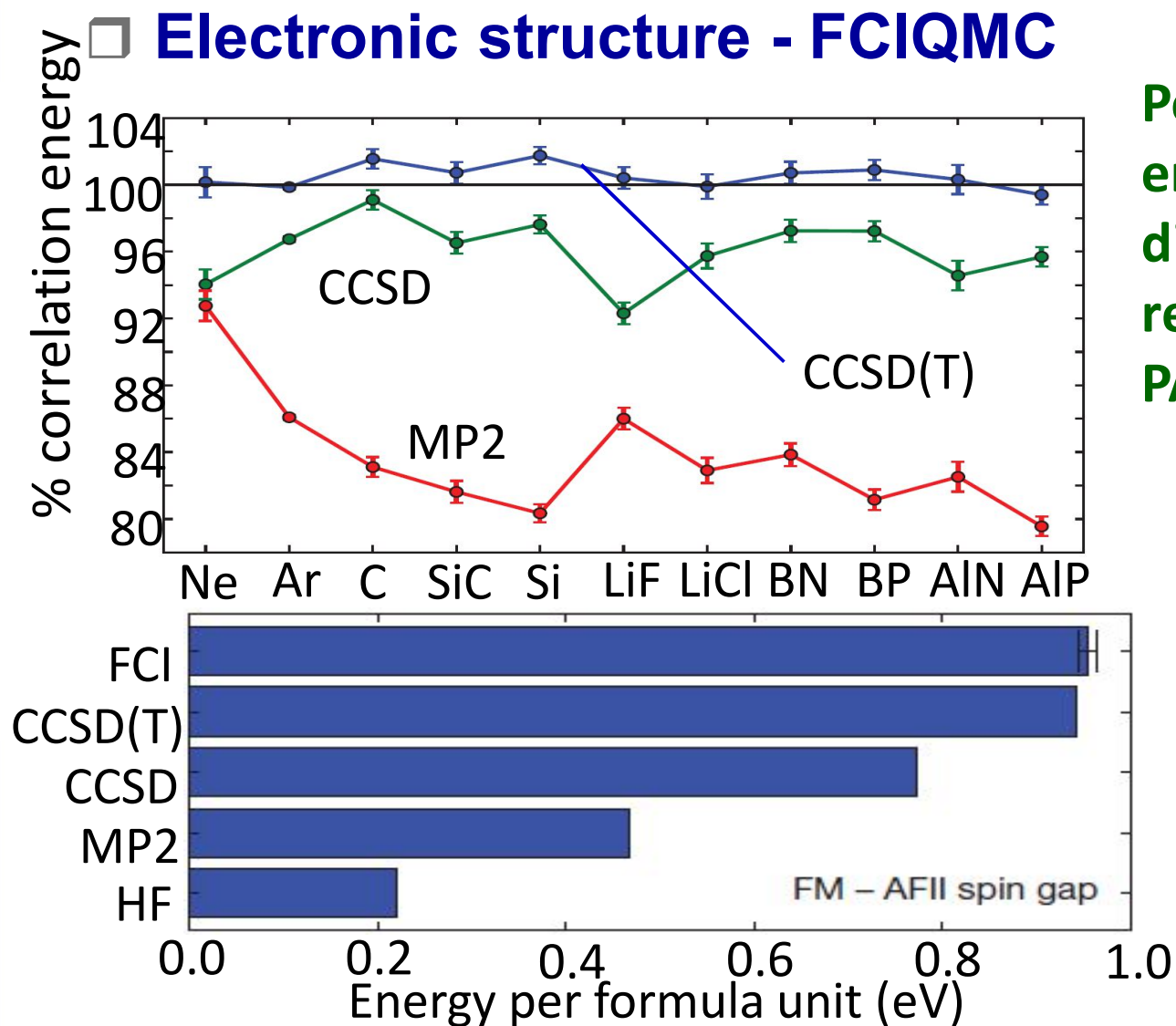


$$E, c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

No sign problem (positive and negative coefficients can be evolved independently)

Timing example: diamond, 4x4x4 k-points – 25,000 CPU hours, ± 20 meV per atom remaining error in correlation energy

Monte Carlo sampling - applications



Percent of correlation energy captured by different methods relative to FCI (VASP, PAW)

Ferromagnetic-antiferromagnetic spin gap in NiO (VASP, PAW)

Booth, Grüneis, Kresse, and Alavi, Nature **493**, 365 (2013)