Magnetism

- How do solids react to an external field?
- What is the cause of spontaneous magnetic ordering?

Magnetic properties

at the end of this lecture you should understand....

- Macroscopic description of magnetism
- Magnetic moments in atoms
- Weak magnetism in solids
- Magnetic ordering

Macroscopic description of magnetism

in vacuum

magnetic induction

magnetic field

$$\mathbf{B} = \mu_0 \mathbf{H}$$

$$\mu_0 = 4\pi 10^{-7}\mathrm{Vs/Am} = 4\pi 10^{-7}\mathrm{T}^2\mathrm{m}^3\mathrm{J}^{-1}$$

in general we have Gauss' law for magnetostatics

$$\oint \mathbf{B} d\mathbf{A} = 0 \qquad div\mathbf{B} = 0$$

Macroscopic description of magnetism

in vacuum

magnetic induction

magnetic field

$$\mathbf{B} = \mu_0 \mathbf{H}$$

$$\mu_0 = 4\pi 10^{-7} \mathrm{Vs/Am} = 4\pi 10^{-7} \mathrm{T^2 m^3 J^{-1}}$$

in matter

magnetization

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mathbf{B}_0 + \mu_0 \mathbf{M}$$

we interpret $\mathbf{B}_0$ as the “external field”

magnetic susceptibility

$$\mu_0 \mathbf{M} = \chi_{\mathrm{m}} \mathbf{B}_0$$

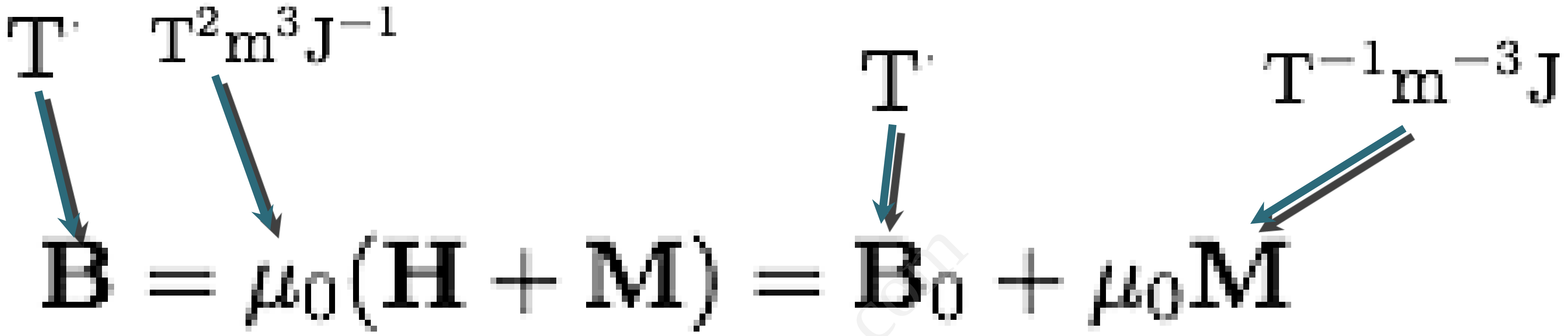
magnetic dipole moment

$$\mathbf{M} = \frac{N}{V} \mu$$

potential energy of one dipole in the external field:

$$U = -\mu \cdot \mathbf{B}_0$$

Units



$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mathbf{B}_0 + \mu_0\mathbf{M}$$

- Both, $\mathbf{B}$ and $\mathbf{B}_0$ are measured in Tesla (T)
- 1 T is a strong field. The magnetic field of the earth is only in the order of 10^{-5} T.

object in homogeneous magnetic field

potential energy of one dipole in the external field:

$$U = -\mu \cdot \mathbf{B}_0$$

so for a macroscopic object that is magnetized by the field

$$\mathbf{M} = \frac{N}{V}\mu$$

$$\mu_0 \mathbf{M} = \chi_{\mathrm{m}} \mathbf{B}_0$$

$$U = -VMB_0 = -V\frac{\chi_{\mathrm{m}}}{\mu_0}B_0^2$$

Note quite because now M depends on the field so

$$dU = -V\mathbf{M}d\mathbf{B}_0$$

$$U = -V\int_0^{B_0} M dB_0' = -V\int_0^{B_0} \frac{\chi_{\mathrm{m}}}{\mu_0} B_0' dB_0' = -V\frac{\chi_{\mathrm{m}}}{2\mu_0}B_0^2$$

Diamagnetism

$$\mu_0 \mathbf{M} = \chi \mathbf{B}_0$$

$$\chi < 0$$

$$U = -VMB_0 = V\frac{|\chi_{\mathrm{m}}|}{2\mu_0}B_0^2$$

- Diamagnetism: negative susceptibility, the magnetization opposes the external field, the potential energy is lowered when moving the magnetized bodies to a lower field strength. A diamagnet opposes both poles of a magnet.

- Diamagnetism is caused by “currents” induced by the external field. According to Lenz’ law, these currents always lead to a field opposing the external field.

Paramagnetism

$$\mu_0 \mathbf{M} = \chi \mathbf{B}_0$$

$$\chi > 0$$

$$U = -VMB_0 = -V\frac{|\chi_{\mathrm{m}}|}{2\mu_0}B_0^2$$

- Paramagnetism: positive susceptibility, the magnetization is parallel to the external field, the potential energy is lowered when moving the magnetized bodies to a higher field strength. A paramagnet is attracted to either pole of an external magnet.

- Paramagnetism is caused by aligning some dipoles, which are already present, with the magnetic field.

for fixed external field

$$U = -VMB_0 = -V\frac{\chi_{\mathrm{m}}}{\mu_0}B_0^2$$

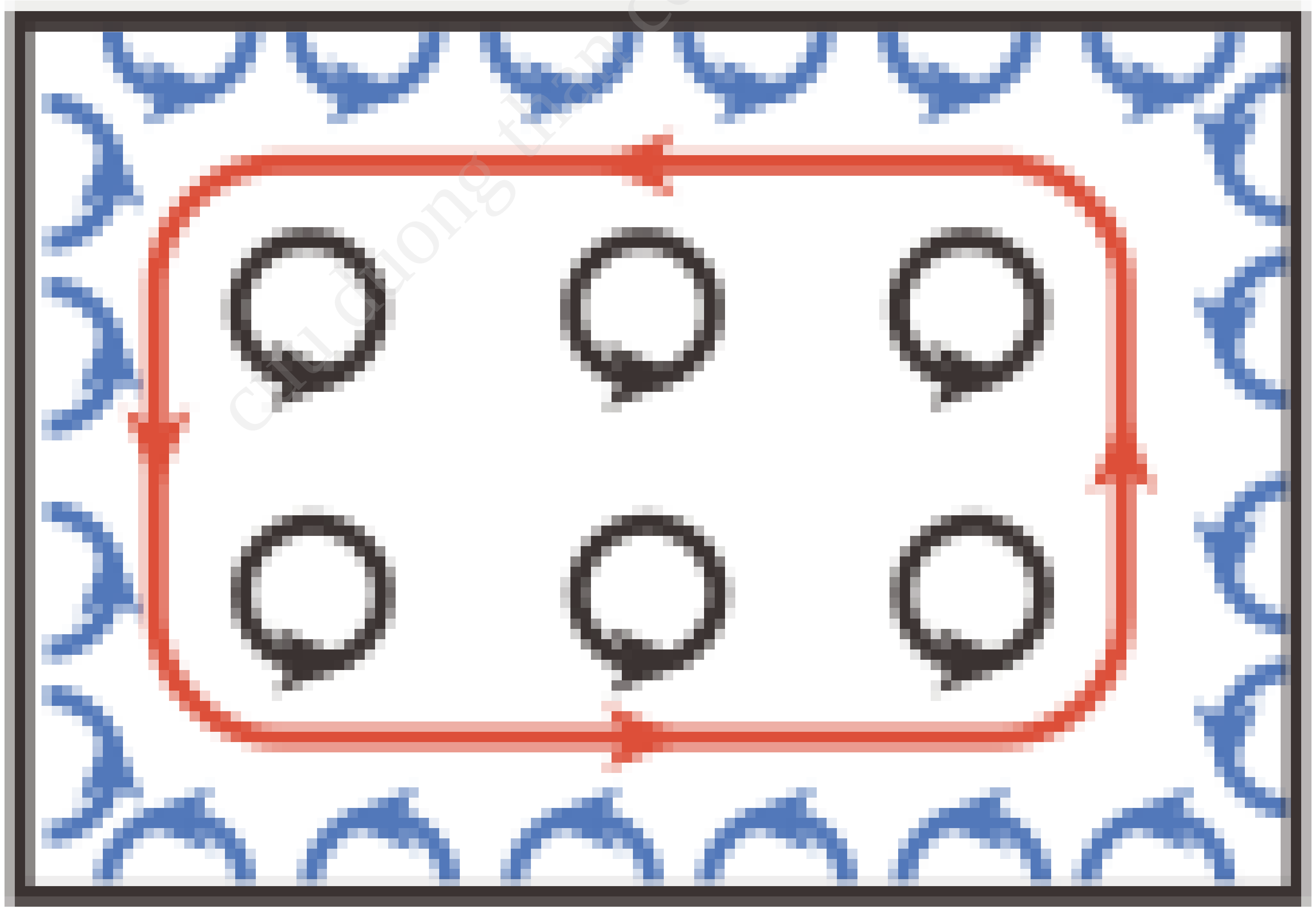
but if the field is turned on from zero

$$U = -V\int_0^{B_0} MdB'_0 = -V\int_0^{B_0}\frac{\chi_{\mathrm{m}}}{\mu_0}B'_0dB'_0 = -V\frac{\chi_{\mathrm{m}}}{2\mu_0}B_0^2$$

- Classical physics does not give diamagnetism or paramagnetism!

$\odot$ B

$$\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$$



The vector potential

scalar potential for static electric field

$$\mathcal{E}(\mathbf{r}) = -\mathrm{grad}\phi(\mathbf{r})$$

scalar potential for B-field?

$$\mathbf{B}(\mathbf{r}) = -\mathrm{grad}\lambda(\mathbf{r})$$

$$\mathbf{j} = \frac{1}{\mu_0}\mathrm{curl}\mathbf{B} - \epsilon_0\frac{\partial\mathcal{E}}{\partial t}$$

No! One can choose

$$\mathbf{B}(\mathbf{r}) = \mathrm{curl}\mathbf{A}(\mathbf{r})$$

$$\mathrm{div}\mathbf{B} = \mathrm{div}\,\mathrm{curl}\mathbf{A} = 0$$

The vector potential

particle in electromagnetic field

change the momentum (operator)

$$\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}$$

change the potential

$$U \rightarrow U + q\phi$$

Quantum Mechanical Description

$$H_{\text{kin}} \rightarrow H'_{\text{kin}}$$

$$\frac{\mathbf{p}^2}{2m_e} \rightarrow \frac{1}{2m_e}(\mathbf{p} + e\mathbf{A})^2$$

constant B field (in z-direction) $\mathbf{B}_0 = (0, 0, B_0)$

$$\mathbf{A} = -\frac{1}{2}\mathbf{r} \times \mathbf{B}_0$$

chosen such that

$$\mathbf{B}_0(\mathbf{r}) = \text{curl}\mathbf{A}(\mathbf{r})$$

$$\frac{\mathbf{p}^2}{2m_e} \rightarrow \frac{1}{2m_e}(\mathbf{p} + e\mathbf{A})^2 = \frac{1}{2m_e}\left(\mathbf{p} - e\frac{\mathbf{r} \times \mathbf{B}_0}{2}\right)^2 = H'_{\text{kin}}$$

Quantum Mechanical Description

$$H'_{\text{kin}} = \frac{1}{2m_e}(\mathbf{p}+e\mathbf{A})^2 = \frac{1}{2m_e}\left(\mathbf{p}-e\frac{\mathbf{r}\times\mathbf{B}_0}{2}\right)^2$$

$$H'_{\text{kin}} = \frac{1}{2m_e}\left(\mathbf{p}^2 + e\mathbf{B}_0\cdot(\mathbf{r}\times\mathbf{p}) + \frac{e^2}{4}(\mathbf{r}\times\mathbf{B}_0)^2\right)$$

because

$$\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = -\mathbf{c}\cdot(\mathbf{b}\times\mathbf{a})$$

use that B only in z direction

$$H'_{\text{kin}} = H_{\text{kin}} + H' = \frac{\mathbf{p}^2}{2m_e} + \underbrace{\frac{e}{2m_e}B_0(\mathbf{r}\times\mathbf{p})_z}_{\text{paramagnetic term}} + \underbrace{\frac{e^2}{8m_e}B_0^2(x^2+y^2)}_{\text{diamagnetic term}}$$

Quantum Mechanical Description

use that B only in z direction

$$H'_{\text{kin}} = H_{\text{kin}} + H' = \frac{\mathbf{p}^2}{2m_e} + \frac{e}{2m_e}B_0(\mathbf{r}\times\mathbf{p})_z + \frac{e^2}{8m_e}B_0^2(x^2+y^2)$$

paramagnetic term

diamagnetic term

Spin is not contained in Schrödinger equation but could be added as

$$g_e m_s \frac{e\hbar}{2m_e}B_0 = g_e m_s \mu_B B_0$$

Quantum Mechanical Description

$$H'_{\text{kin}} = H_{\text{kin}} + H' = \frac{\mathbf{p}^2}{2m_e} + \frac{e}{2m_e}B_0(\mathbf{r}\times\mathbf{p})_z + \frac{e^2}{8m_e}B_0^2(x^2+y^2)$$

$$E' = \frac{e^2}{8m_e}B_0^2\langle\psi|(x^2+y^2)|\psi\rangle$$

magnetic moment

$$\mu = -\frac{\partial E'}{\partial B_0} = -\frac{e^2}{4m_e}B_0\langle\psi|(x^2+y^2)|\psi\rangle$$

$$r_a^2 = x^2+y^2+z^2 \qquad x^2+y^2 = \frac{2}{3}r_a^2$$

very rough estimate for an atom with Z electrons

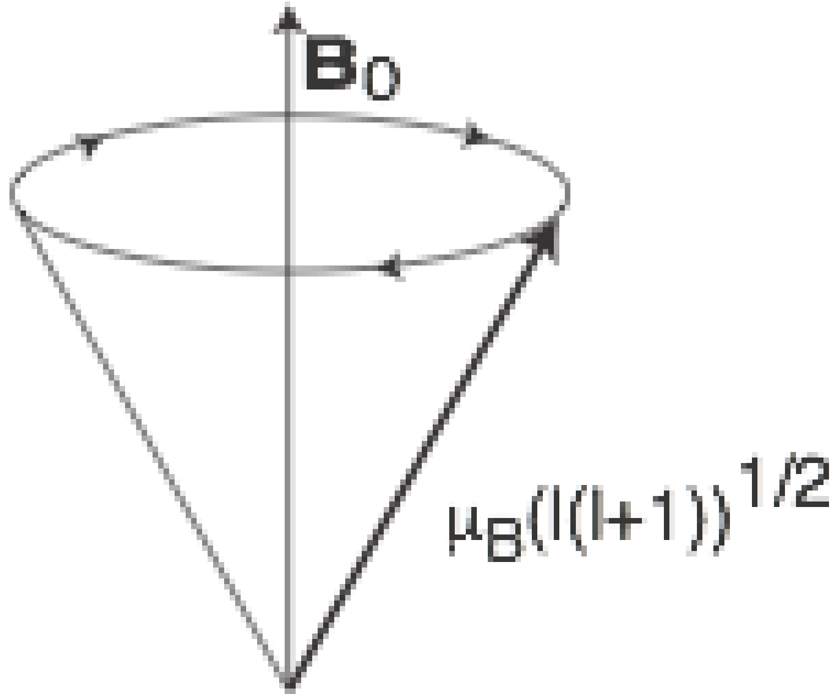
$$\mu = -\frac{Ze^2}{6m_e}r_a^2B_0$$

Proper situation in atoms

- Which magnetic moments are already there? They will lead to paramagnetism.
- Does an external field induce a magnetic moment? This will lead to diamagnetism.

Magnetic moments in atoms

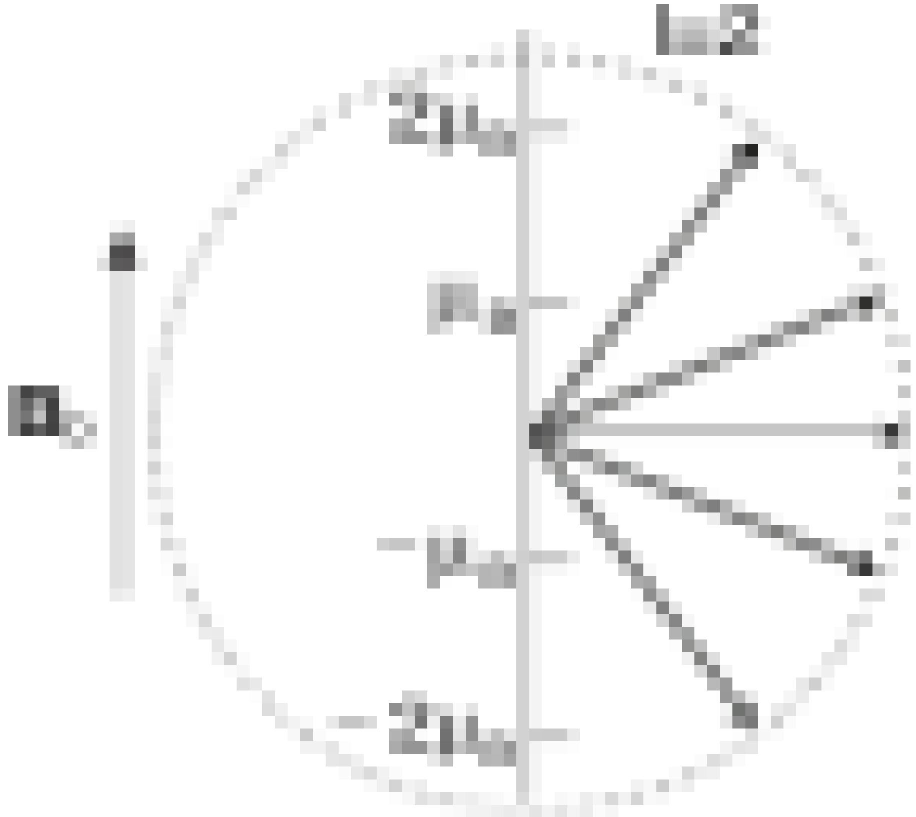
orbital angular momentum
magnetic moment



$$\boldsymbol{\mu} = -\frac{e\hbar}{2m_e}\mathbf{L} = -\mu_B\mathbf{L}$$

component in field direction

$$\mu_L = -\frac{e m_l \hbar}{2m_e} = -m_l\mu_B$$



magnetic moment due to electron spin

$$\boldsymbol{\mu} = -g_e\mu_B\mathbf{S}$$

component in field direction

$$\mu_s = -g_e m_s \mu_B$$

gyromagnetic ratio

$$\mu_B \approx 6 \times 10^{-5}\mathrm{eVT}^{-1}$$

Magnetic moments in atoms

for many electron atoms and a given sub-shell (n,l)

$$S = \sum m_s$$

$$L = \sum m_l$$

so no magnetic moment for closed shells

Non-closed shells have the total angular momentum $\hbar\sqrt{J(J+1)}$

and 2J+1 possibilities of a magnetic moment in field direction

$$\mu_J = -g m_J \mu_B.$$

Landé splitting factor

(1) find J
(2) find the Landé splitting factor g

Magnetic moments in atoms

for many electron atoms and a given sub-shell (n,l)

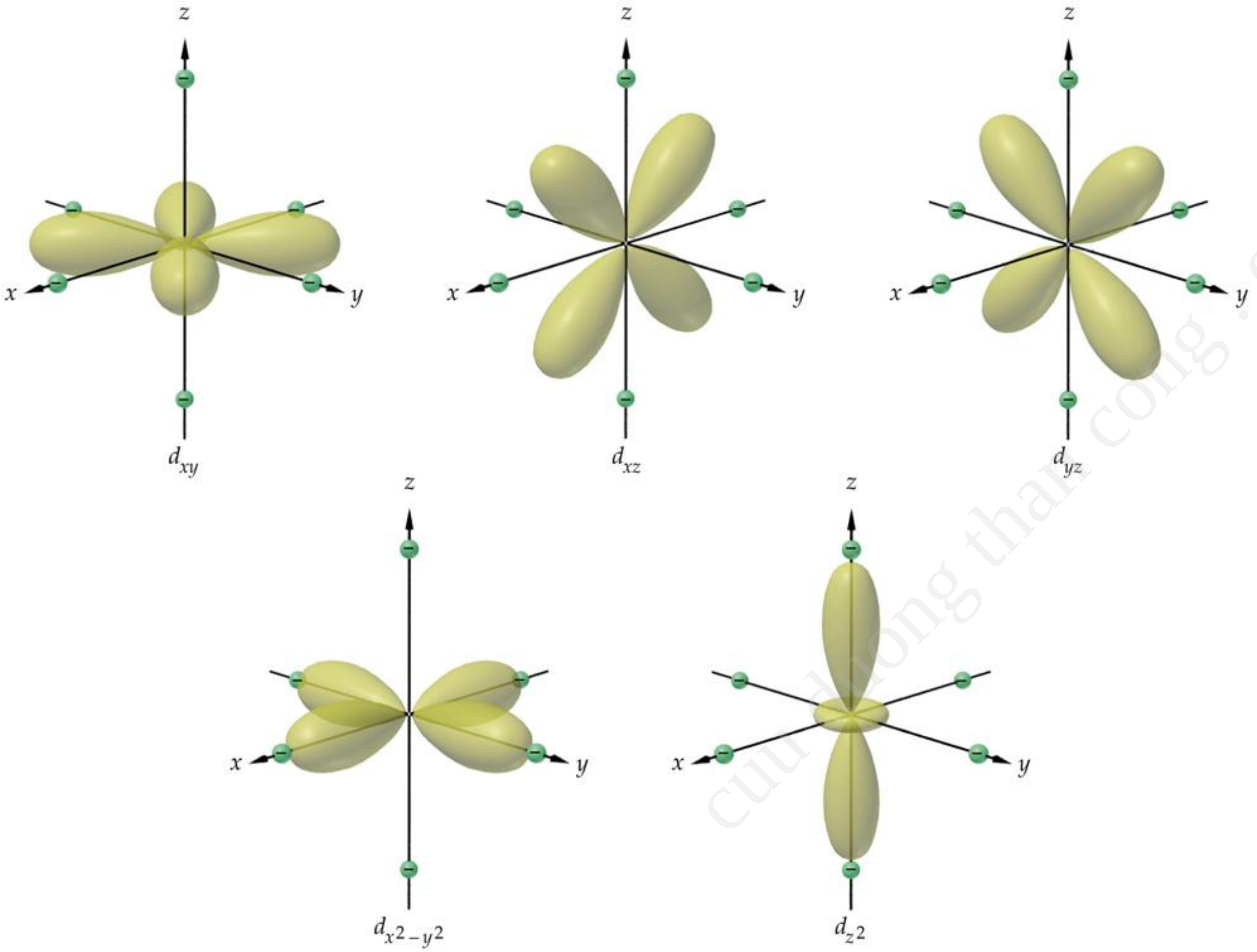
$$S = \sum m_s$$

$$L = \sum m_l$$

for non-closed shells follow Hund's rules

(1) The electrons should occupy the orbitals such that the maximum possible value of the total spin S is realized.

Example: Mn^{2+}



- example Mn^{2+} with 5 d electrons, all in different m_l orbitals (no overlap, smallest repulsion)
- The total spin S has a major influence on the total energy.

Magnetic moments in atoms

for many electron atoms and a given sub-shell (n,l)

$$S = \sum m_s$$

$$L = \sum m_l$$

for non-closed shells follow Hund’s rules

(2) The electrons should occupy the orbitals such that the maximum of L consistent with S is realized.

Magnetic moments in atoms

for many electron atoms and a given sub-shell (n,l)

$$S = \sum m_s$$

$$L = \sum m_l$$

for non-closed shells follow Hund's rules

(3) The total angular momentum J is calculated

- If the sub-shell is less than half-full J=L-S
- If the sub-shell is more than half full J=L+S
- If the sub-shell is half full, L=0 and J=S

Example: Cr^{3+}

$$S = \sum m_s$$

$$L = \sum m_l$$

- Cr^{3+} has three electrons in the 3d sub-shell.
- The first of Hund's rules requires S=3/2.
- The possible m_l values for the 3d shell are -2,-1,0,1,2. Hund's second rule requires to choose the largest possible value of L, i.e. to choose m_l =0,1,2, so L=3.
- Since the sub-band is less than half filled, J=L-S=3-3/2=3/2.

Magnetic moments in atoms

the moment in field direction is

$$\mu_J = -g m_J \mu_B .$$

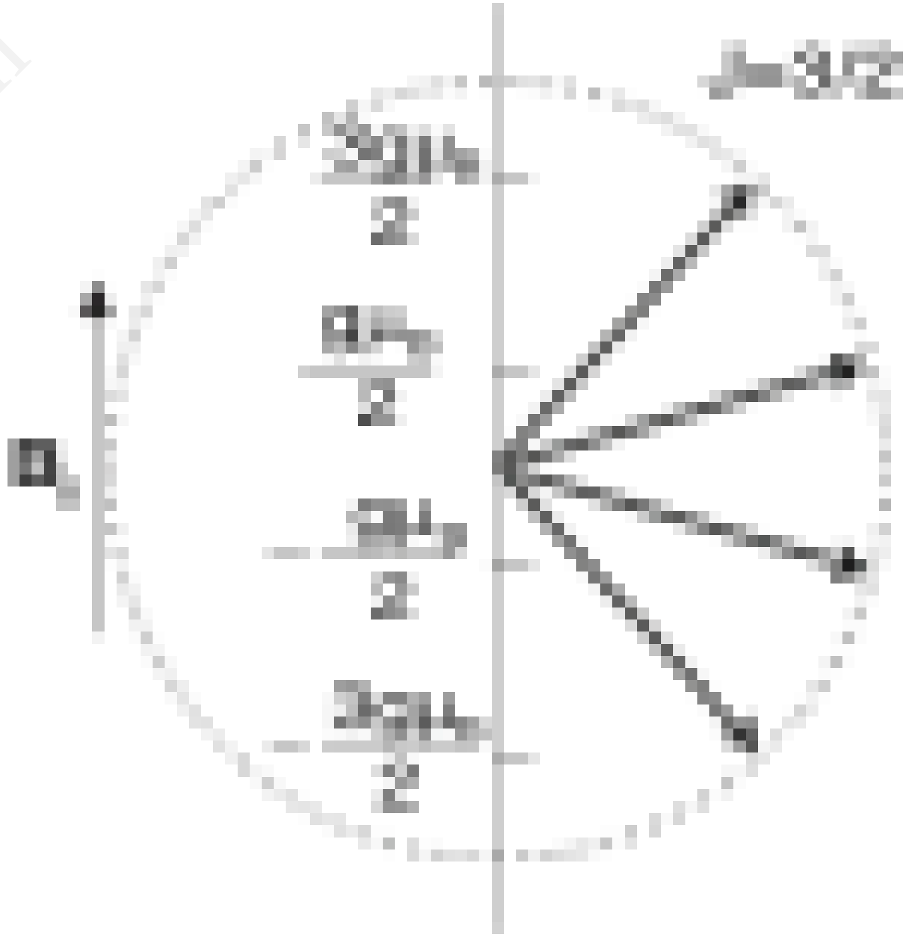
with m_j = -J,-J+1,...J-1,J

and the Landé splitting factor

$$g = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

the highest possible moment in field direction is

$$\mu_J = g \mu_B J$$



Summary atomic magnetism

- Non-filled shells can lead to a permanent magnetic moment described by the total angular momentum *J* and the Landé factor. This magnetic moment gives rise to paramagnetism.
- An external field also gives rise to a diamagnetic response by “inducing a current” in all atomic shells. This gives rise to diamagnetic moment which is always present.
- We have an estimate for the size of both types of magnetic moments.

Weak magnetism in solids

- Atomic diamagnetic contribution is always there.
- The paramagnetic behaviour of non-filled shells is often not present in solid (example: ionic solids)
- The paramagnet behaviour of non-filled shells can be retained if these are inner shells (f- electrons).
- Additional contribution are expected to arise from itinerant electrons in metals.

Diamagnetism from the atoms

$$\boldsymbol{\mu} = -\frac{Ze^2}{6m_e} r_a^2 \mathbf{B}_0$$

$$\mathbf{M} = \boldsymbol{\mu} \frac{N}{V}$$

$$\chi_\mathrm{m} = \mu_0 \frac{\mathbf{M}}{\mathbf{B}_0} = -\frac{\mu_0 Z N e^2}{6 V m_e} r_a^2$$

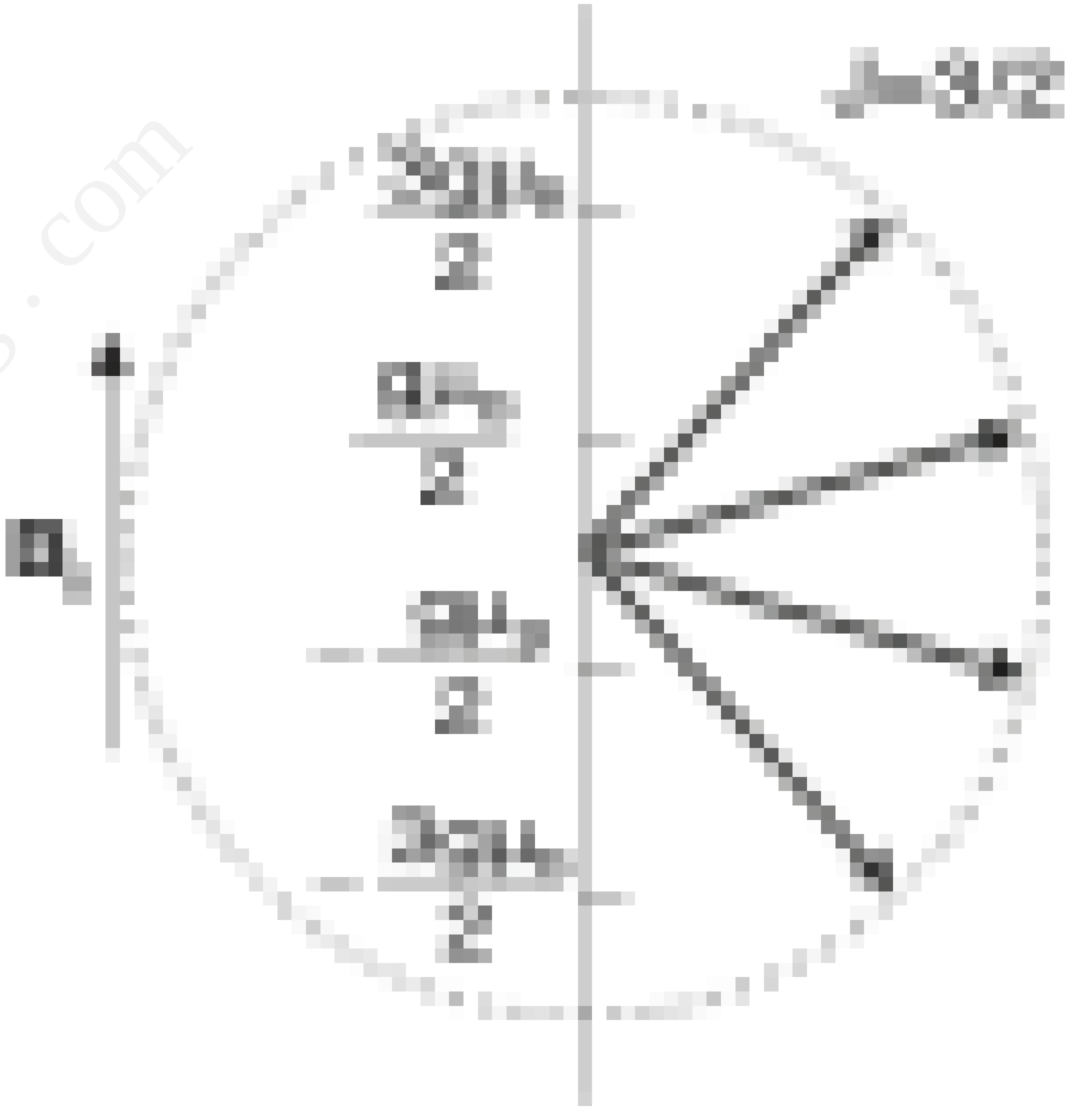
And this is always quite small, 10^{-5} or so.

(Landau) diamagnetism of free electrons

$$\chi_{\mathrm{m}} = -\frac{1}{3V}\mu_B^2\mu_0 g(E_F)\left(\frac{m_e}{m^*}\right)^2$$

Curie paramagnetism

- Treat the localized d and f electrons as if they were atomic magnets.
- This leads to a paramagnetic solid. The paramagnetism is caused by the alignment of existing dipoles to the external field.
- The system consists of <u>distinguishable</u> dipoles with known energy levels.
- Boltzmann statistics can be applied and the effect is temperature-dependent.



Curie paramagnetism

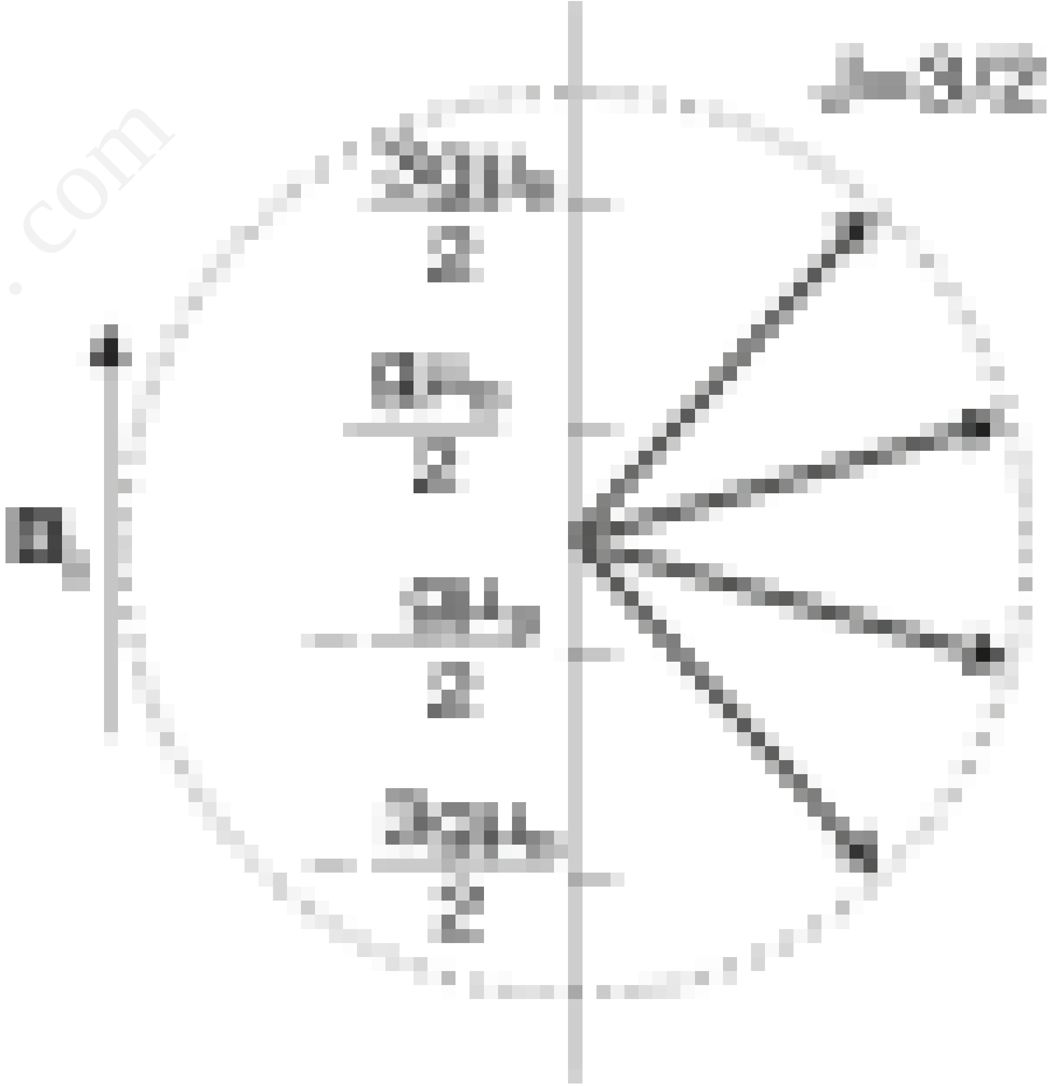
energy levels

$$-g\mu_B m_J B_0$$

partition function

$$Z = \sum_{m_J=-J}^{J} e^{-g\mu_B m_J B_0/k_B T}$$

mean moment in field direction



$$\bar{\mu}_C = \frac{1}{Z} \sum_{m_J=-J}^{J} g\mu_B m_J e^{g\mu_B m_J B_0/k_B T}$$

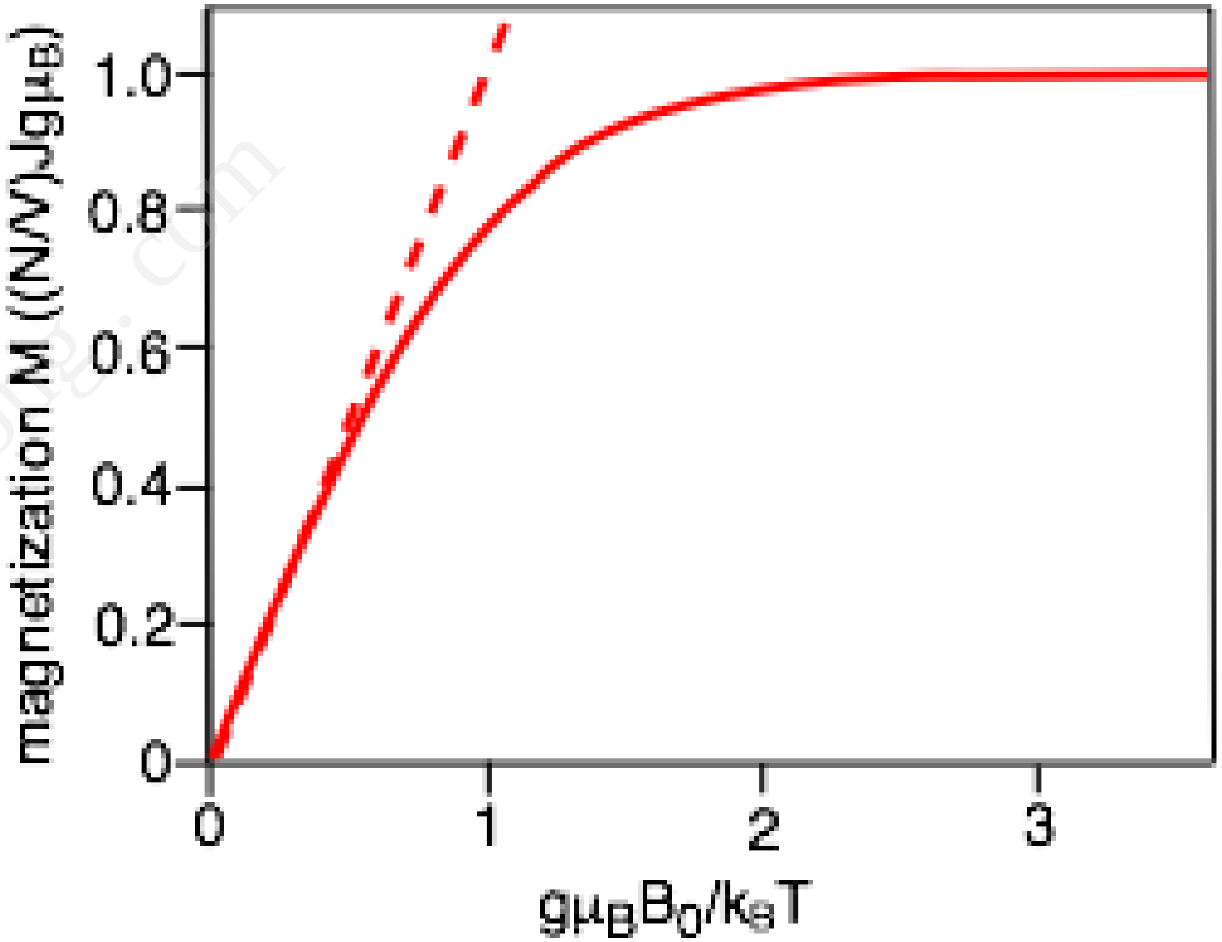
Curie paramagnetism: limiting cases

1. $$g\mu_B B_0 \gg k_B T$$

all moments aligned with field

$$\mathbf{M} = \frac{N}{V} g\mu_B J$$

(independent of field strength)



2. $$g\mu_B B_0 \ll k_B T$$

$$\mathbf{M} = \frac{Ng^2\mu_B^2 J(J+1)}{3Vk_B T}\mathbf{B}_0$$

so that

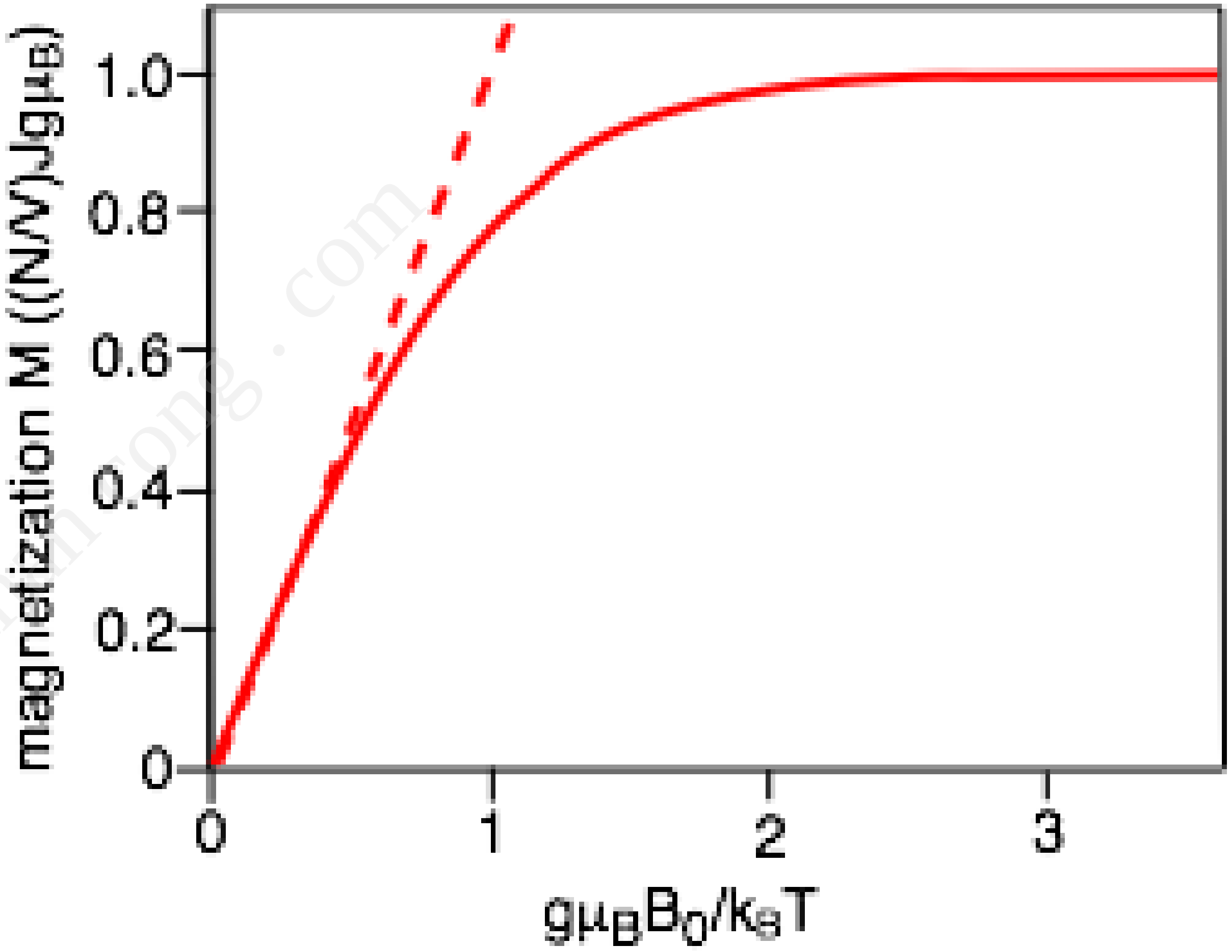
$$\mu_0 \mathbf{M} = \chi_{\mathrm{m}} \mathbf{B}_0$$

Curie's law $\chi_m = \frac{C}{T}$

$$C = \frac{\mu_0 N g^2 \mu_B^2 J(J+1)}{3Vk_B}$$

Curie paramagnetism: limiting cases

- The highest possible magnetization is big.
- But for room temperature, we are in the other regime: the susceptibility is quite small (10^{-3} - 10^{-2} or so).



Curie's law $\chi_m = \frac{C}{T}$

Curie paramagnetism: limitations

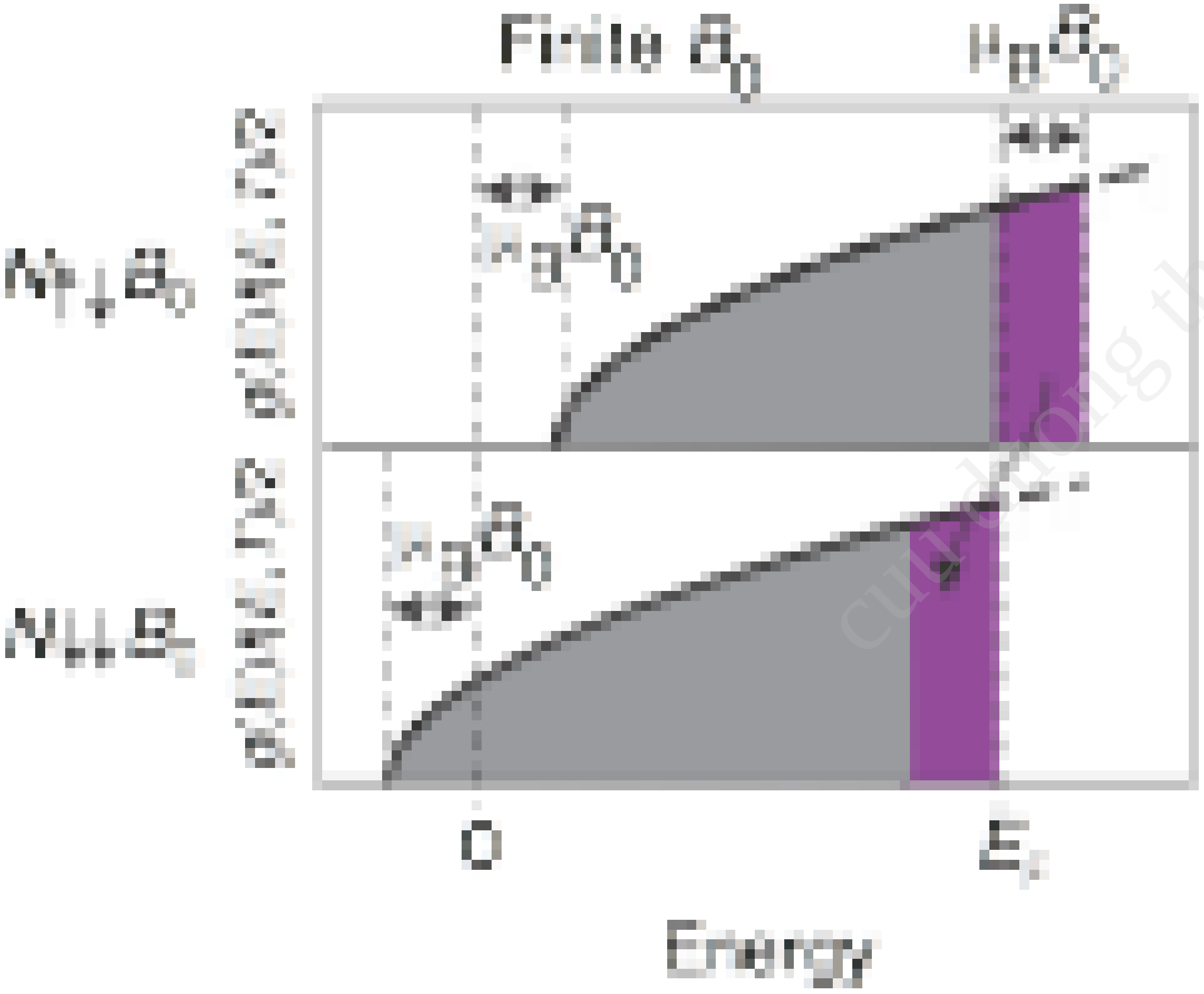
- The Curie constant C is predicted correctly for the *f* transition metals (exercise).
- For the *d* transition metals, the agreement is poor. One often observes a C as if J=S (quenching of orbital angular momentum)
- The reason is that the *d* electrons act as valence electrons / interact strongly with the neighbours and can not be treated like purely atomic levels.

Pauli paramagnetism

- Pauli paramagnetism is associated with the spin of the free electrons.
- Naively, one might expect that all the electrons align their magnetic moment with the external field. This would give rise to strong paramagnetism.
- This is not observed, a puzzling fact for a long time (along with the electrons' heat capacity). You can guess where this is leading....

Pauli paramagnetism

(twice) the coloured area:



$$N_{\downarrow\downarrow B_0} - N_{\downarrow\uparrow B_0} = g(E_F)\mu_B B_0$$

$$M = \frac{1}{V}\left(N_{\downarrow\downarrow B_0} - N_{\downarrow\uparrow B_0}\right)\mu_B$$

$$= \frac{1}{V} g(E_F)\mu_B^2 B_0$$

$$\chi_m = \frac{1}{V}\mu_0 g(E_F)\mu_B^2$$

which is again quite small

Aligning all the moments

paramagnetism of localized ions

$$g\mu_B B_0 \gg k_B T$$

Pauli paramagnetism

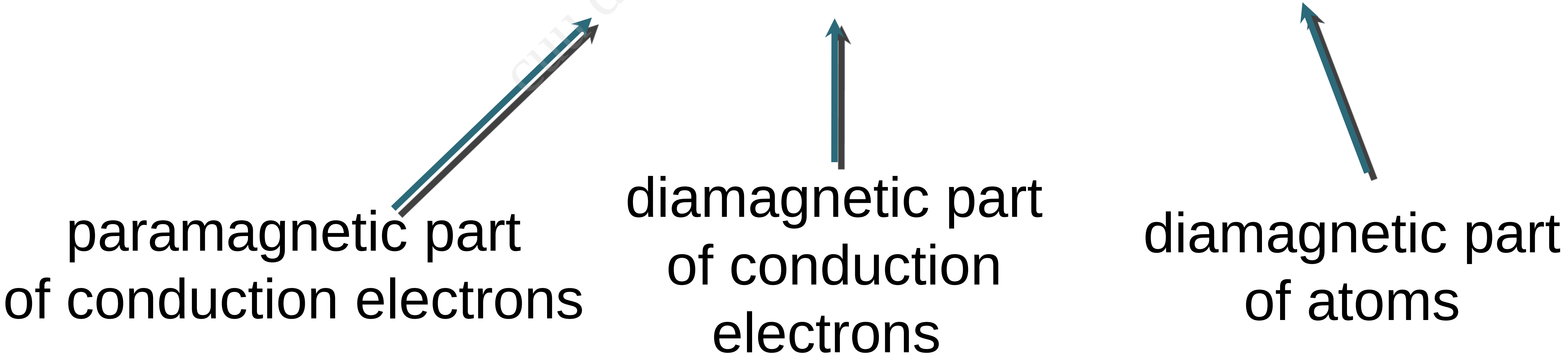
$$\mu_B B_0 > E_F$$

Magnetic response of solids (without Curie pm)

- All solids show very weak diamagnetism, like the atoms.
- Free electron metals show the weak Pauli paramagnetism and Landau diamagnetism.
- The resulting χ is in the order of 10^{-6} to 10^{-5}.

a ‘qualitative equation’ for the total susceptibility is

$$\chi_{\mathrm{m}} = \frac{1}{V}\mu_B^2\mu_0 g(E_F)\left(1-\frac{1}{3}\left(\frac{m_e}{m^*}\right)^2\right) - \frac{N\mu_0 Z e^2}{6Vm_e} r_a^2$$

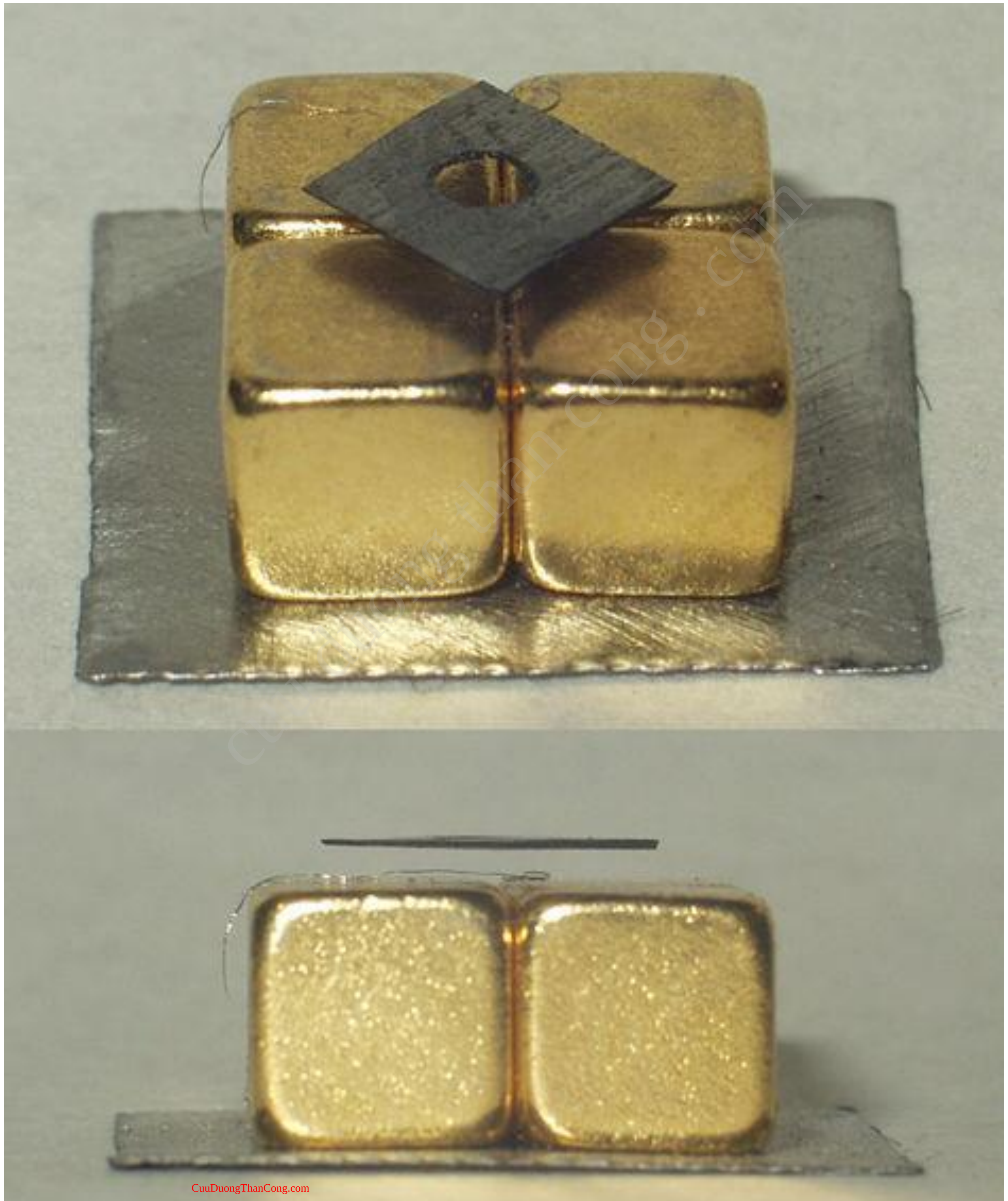


paramagnetic part of conduction electrons

diamagnetic part of conduction electrons

diamagnetic part of atoms

$$\chi_\mathrm{m} = \frac{1}{V}\mu_B^2\mu_0 g(E_F)\left(1-\frac{1}{3}\left(\frac{m_e}{m^*}\right)^2\right) - \frac{N\mu_0 Z e^2}{6Vm_e}r_a^2$$



More fun with diamagnetic levitation

movies

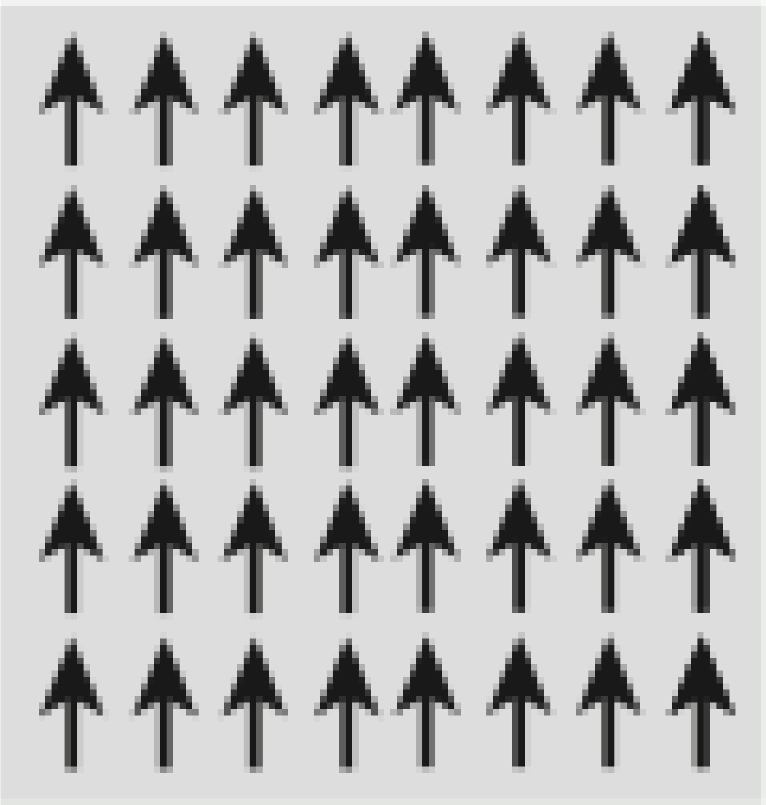
source: High Field Magnet Laboratory, University of Nijmegen

Magnetic ordering

- So far: magnetic response of the solid as a function of applied field (diamagnetic / paramagnetic). Quite weak for most solids at room temperature.
- Now: spontaneous magnetic ordering without any applied field.

Magnetic ordering

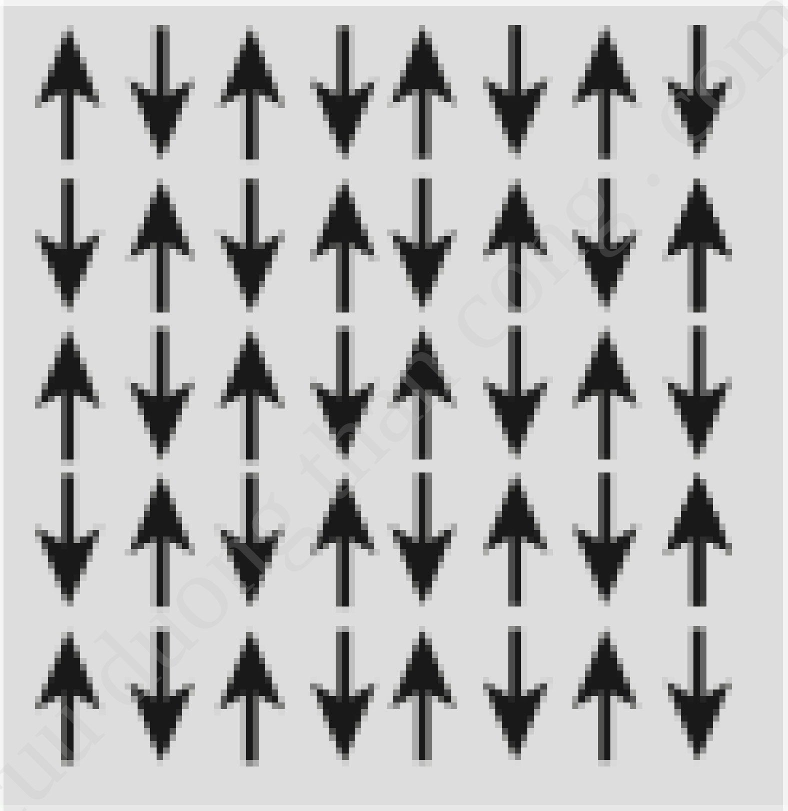
ferromagnetic



M≠0

Fe, Co, Ni...

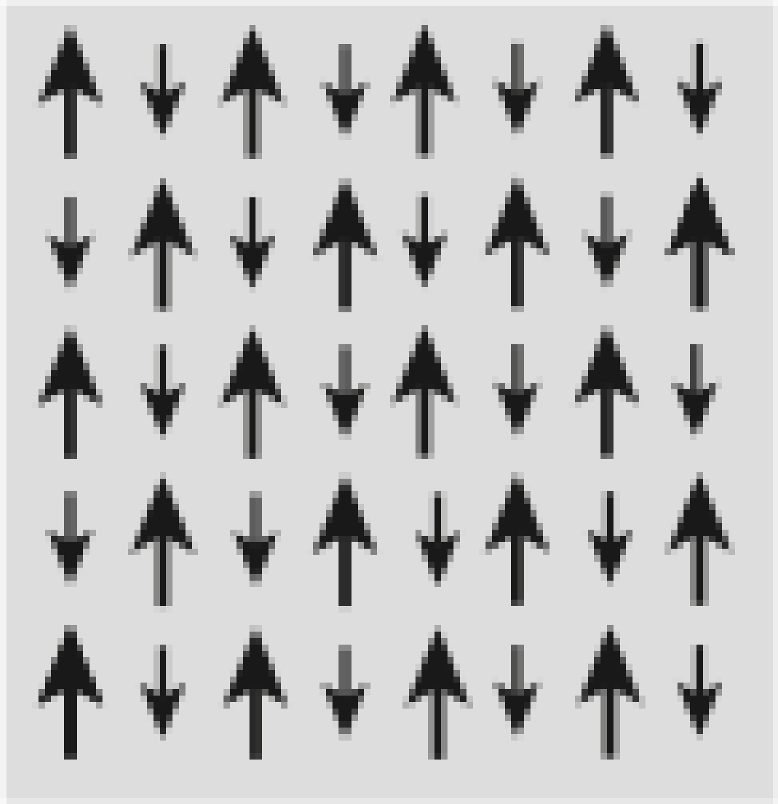
antiferromagnetic



M=0

NiO....

ferrimagnetic



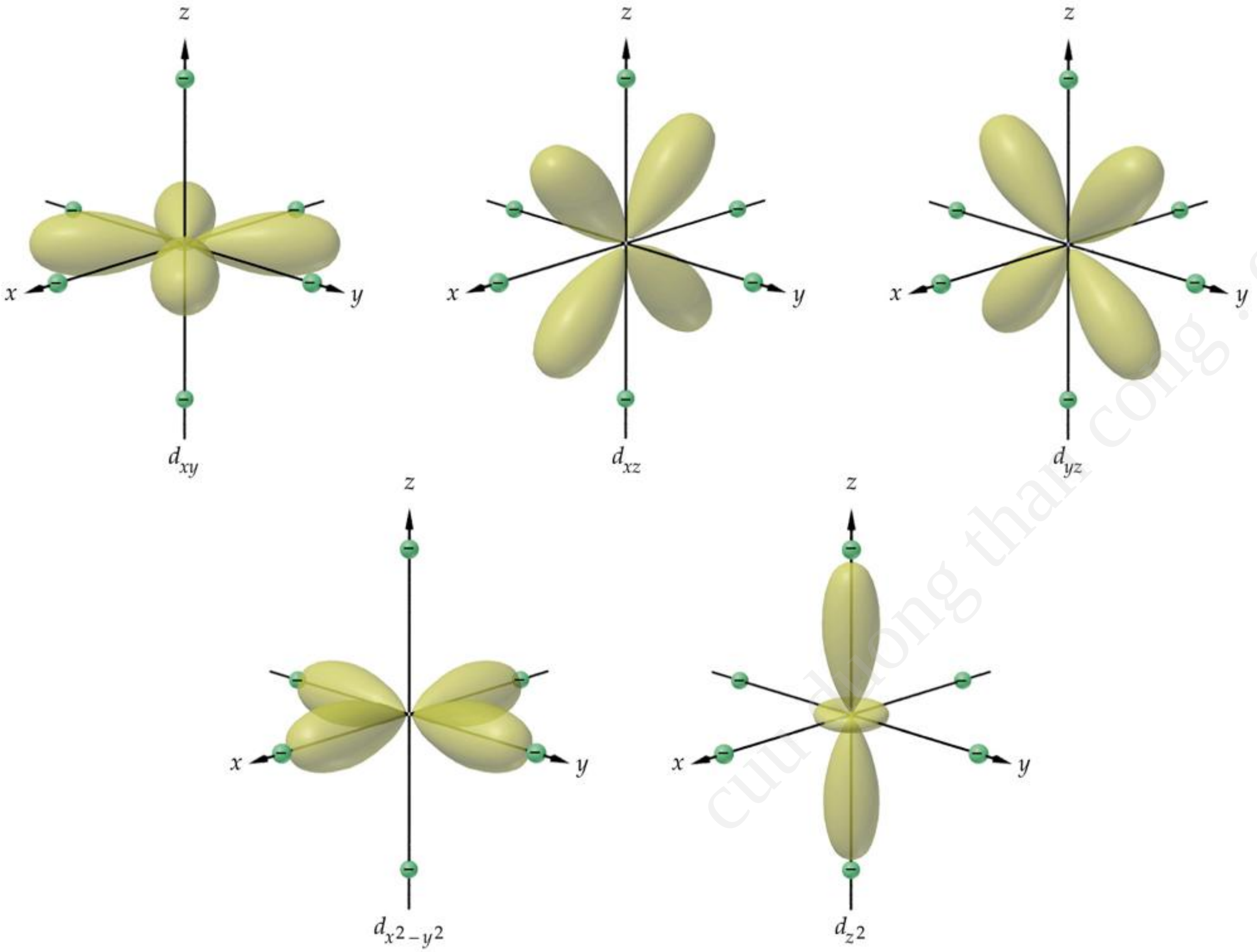
M≠0

Magnetite...

Magnetic ordering: a common misconception

- The magnetic ordering IS NOT caused by the direct magnetic interaction between magnetic moments. This is much too weak (exercise).

Example: Mn^{2+}



- Origin: Coulomb repulsion and Pauli exclusion principle
- example Mn^{2+} with 5 d electrons, all in different m_l orbitals (no overlap, smallest repulsion)
- The total spin S has a major influence on the total energy.

The Hydrogen Molecule: basic “ordering” and the exchange interaction

$$H_A = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|}$$

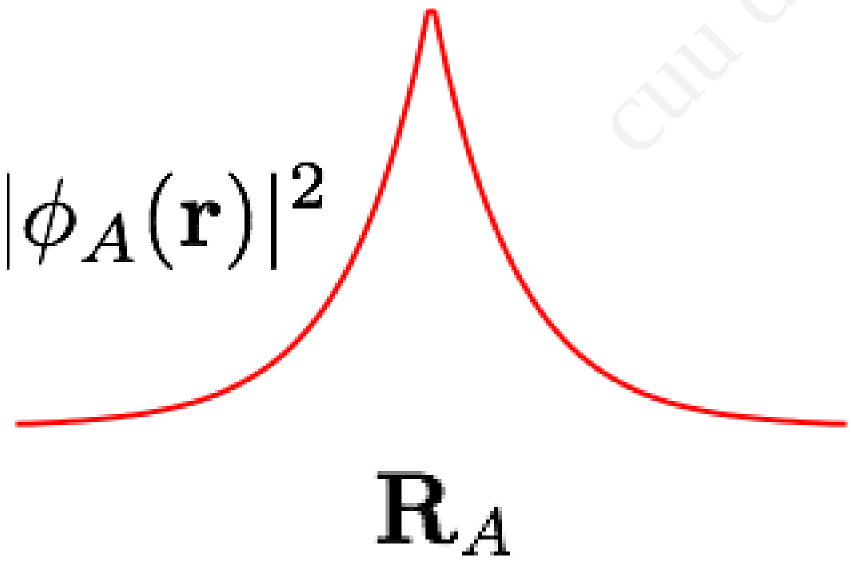
solution

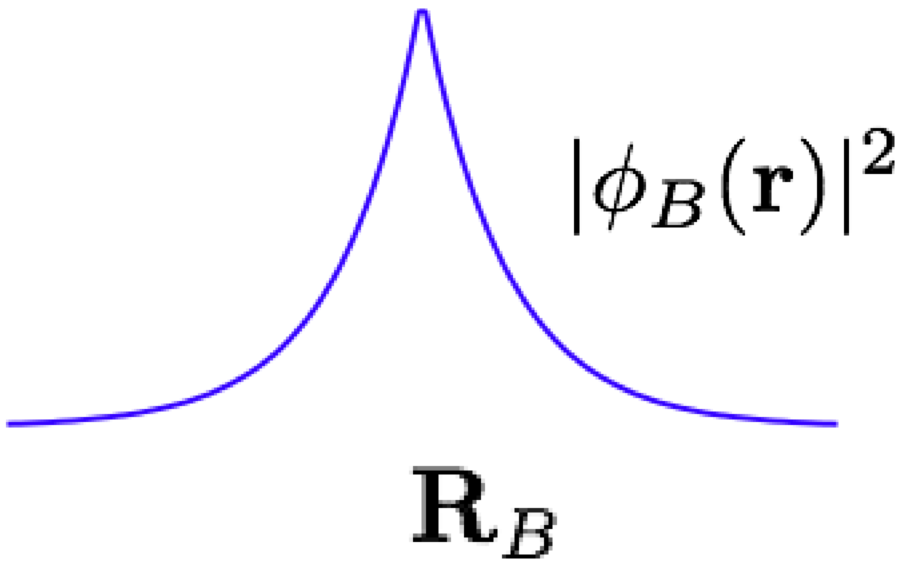
E_A $\phi_A(\mathbf{r}_1)$

$$H_B = -\frac{\hbar^2\nabla_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{R}_B - \mathbf{r}_2|}$$

solution

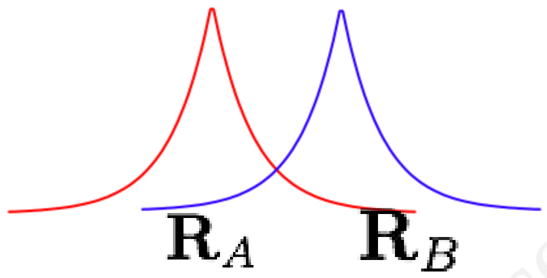
E_B $\phi_B(\mathbf{r}_2)$





The Hydrogen Molecule

$$R = |\mathbf{R}_1 - \mathbf{R}_2|$$



$$H\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$H = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{\hbar^2\nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left\{-\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} + \frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|}\right\}$$

$$H_A = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{R}_A - \mathbf{r}_1|}$$

ground state solution

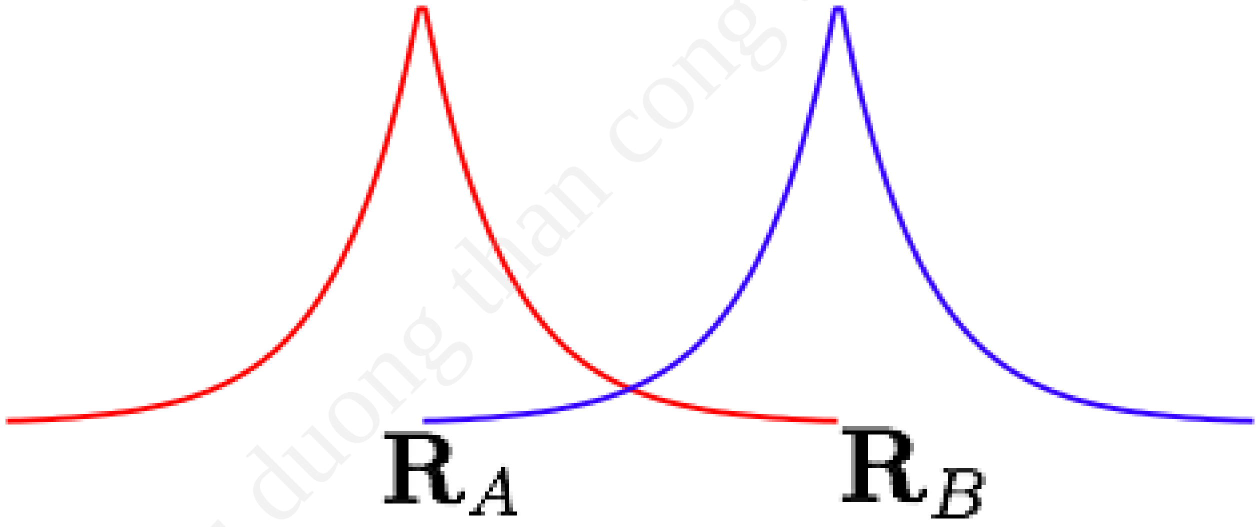
$$E_A \qquad \phi_A(\mathbf{r}_1)$$

$$H_B = -\frac{\hbar^2 \nabla_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|}$$

ground state solution

$$E_B \qquad \phi_B(\mathbf{r}_2)$$

close but no interaction



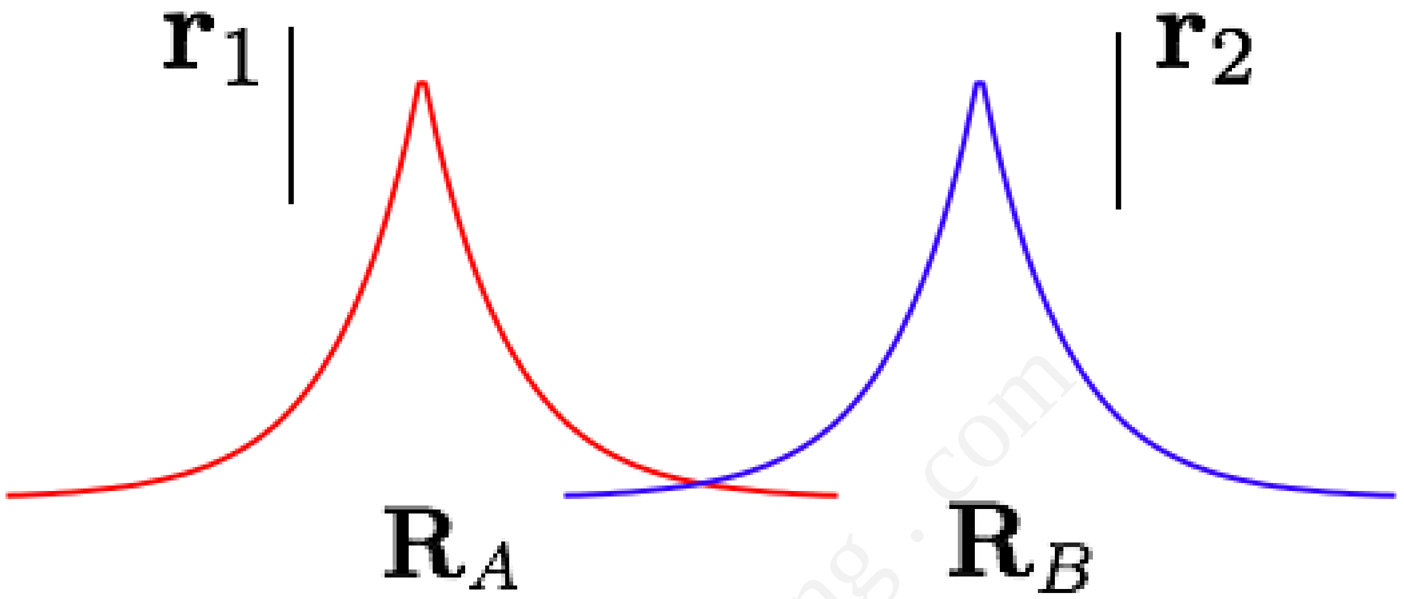
$$H = H_A + H_B$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)$$

$$E = E_A + E_B = 2E_0$$

$$H\Psi(\mathbf{r}_1,\mathbf{r}_2) = (H_A + H_B)\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) = \phi_B(\mathbf{r}_2)E_A\phi_A(\mathbf{r}_1) + \phi_A(\mathbf{r}_1)E_B\phi_B(\mathbf{r}_2) = (E_A + E_B)\Psi(\mathbf{r}_1,\mathbf{r}_2$$

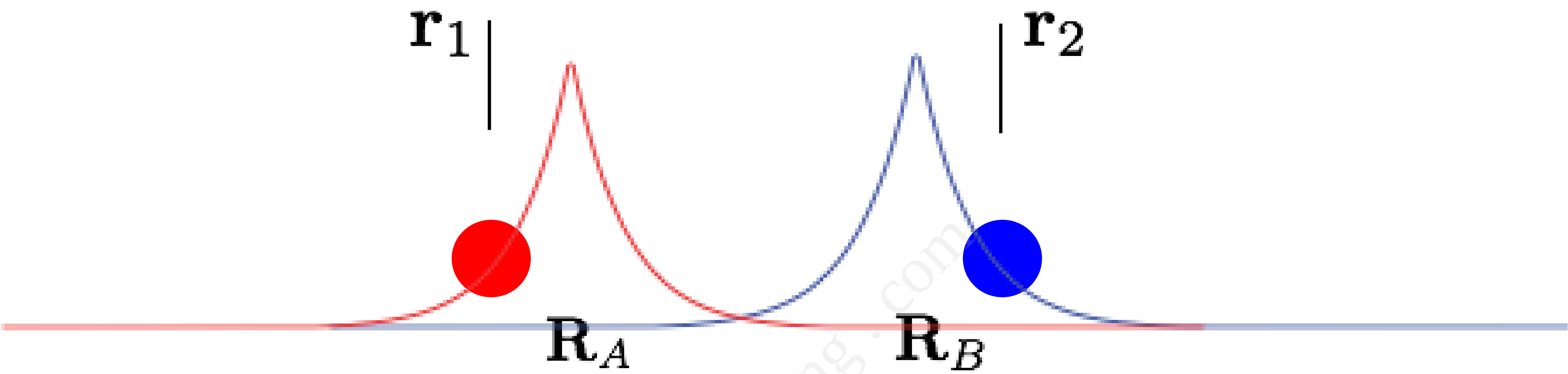
Identical Particles



probability for finding electron of atom A at r_1 and electron of atom B at r_2

$$P_{12} = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = |\phi_A(\mathbf{r}_1)|^2 |\phi_B(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

Identical Particles



probability for finding electron of atom A at r_1 and electron of atom B at r_2

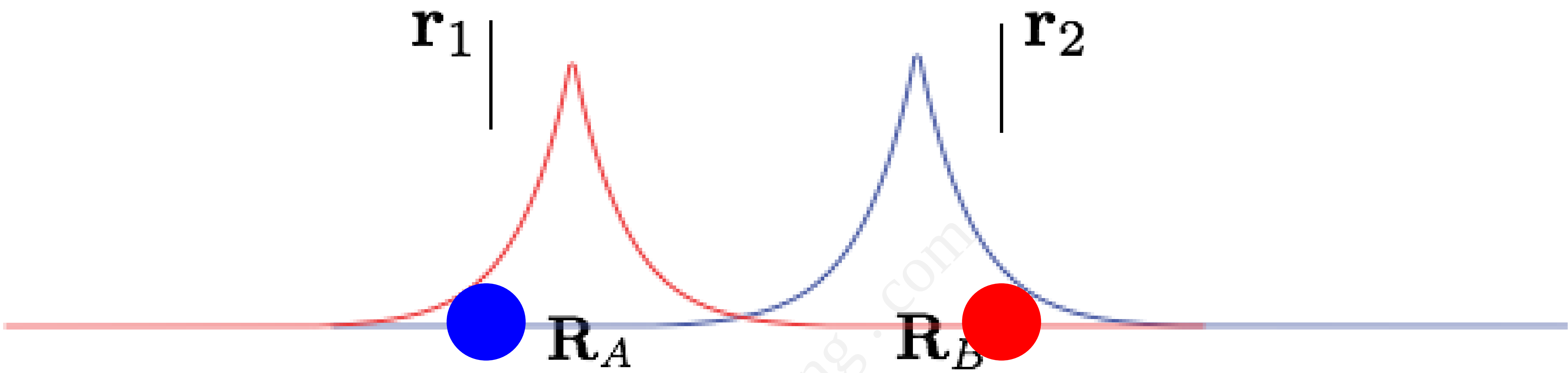
$$P_{12} = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = |\phi_A(\mathbf{r}_1)|^2 |\phi_B(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

probability for finding electron of atom B at r_1 and electron of atom A at r_2

$$P_{21} = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1 = |\phi_A(\mathbf{r}_2)|^2 |\phi_B(\mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1$$

but these are not the same!

Identical Particles



probability for finding electron of atom A at r_1 and electron of atom B at r_2

$$P_{12} = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = |\phi_A(\mathbf{r}_1)|^2 |\phi_B(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

probability for finding electron of atom B at r_1 and electron of atom A at r_2

$$P_{21} = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1 = |\phi_A(\mathbf{r}_2)|^2 |\phi_B(\mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1$$

but these are not the same!

Identical Particles

but we must have

$$P_{12} = P_{21}$$

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

so that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

$$u = e^{i\phi}$$

and we have to get the same upon another exchange

$$u^2 = 1 \qquad u = 1 \quad u = -1$$

Identical Particles

two possible solutions

symmetric (u=1)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

anti-symmetric (u=-1)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) - \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

Identical Particles

Empirical rules for two Fermions

The total wave function for Fermions (including spin) must be anti-symmetric upon particle exchange

The symmetric solution is chosen when the spins are anti-parallel

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)\right)$$

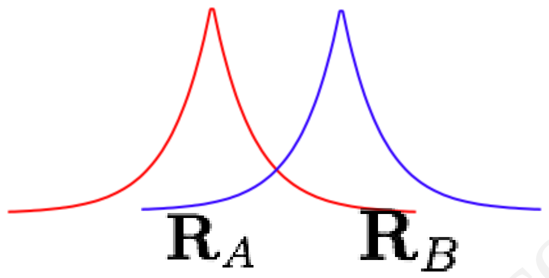
↑↓

The anti-symmetric solution is chosen when the spins are parallel

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) - \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)\right)$$

↑↑

The Hydrogen Molecule: Heitler and London



$$H = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{\hbar^2\nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left\{-\frac{1}{|\mathbf{R}_A-\mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B-\mathbf{r}_2|} + \frac{1}{R} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A-\mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B-\mathbf{r}_1|}\right\}$$

Start by using the atomic wave functions

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \pm \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

with + for spins antiparallel (singlet), S=0, m_s=0

and - for spins parallel (triplet), S=1, m_s=-1,0,1

The Hydrogen Molecule: Heitler and London

$$H = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{\hbar^2\nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left\{-\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} + \frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|}\right\}$$

as trial wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \pm \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

calculate

$$E = \frac{\int \Psi^*(\mathbf{r}_1\mathbf{r}_2) H \Psi(\mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}{\int \Psi^*(\mathbf{r}_1\mathbf{r}_2)\Psi(\mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}$$

The Hydrogen Molecule: Heitler and London

solutions

$$E = 2E_0 + \Delta E$$

with

$$\Delta E_{\uparrow\uparrow} = \frac{C(R) - X(R)}{1 - S(R)}$$

$$\Delta E_{\uparrow\downarrow} = \frac{C(R) + X(R)}{1 + S(R)}$$

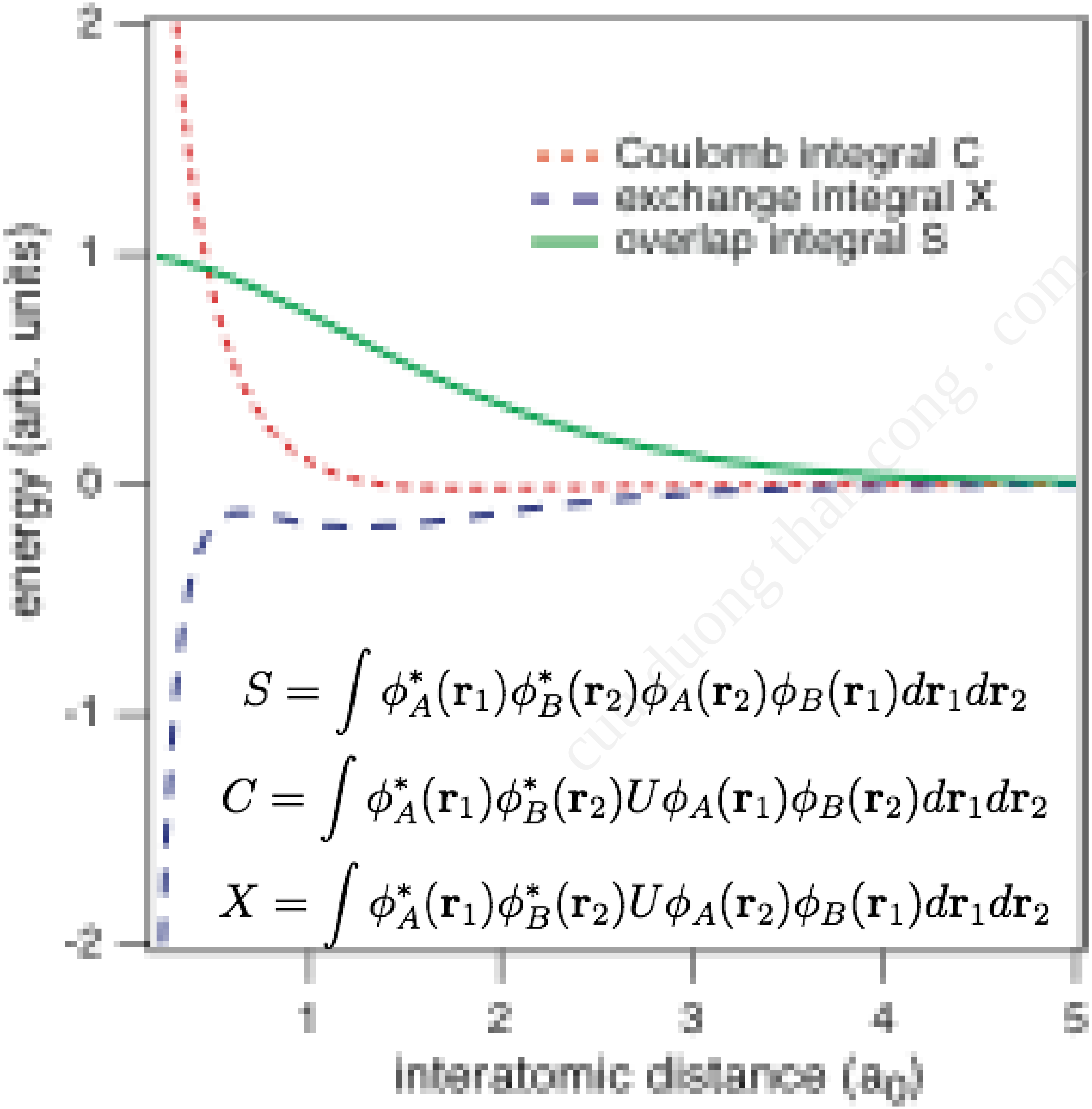
$$S = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2,$$ overlap integral

$$C = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2,$$ Coulomb integral

$$X = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2,$$ exchange integral

$$U = \frac{e^2}{4\pi\epsilon_0}\left\{\frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|}\right\}.$$

The Hydrogen Molecule: Heitler and London



$$S = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2$$

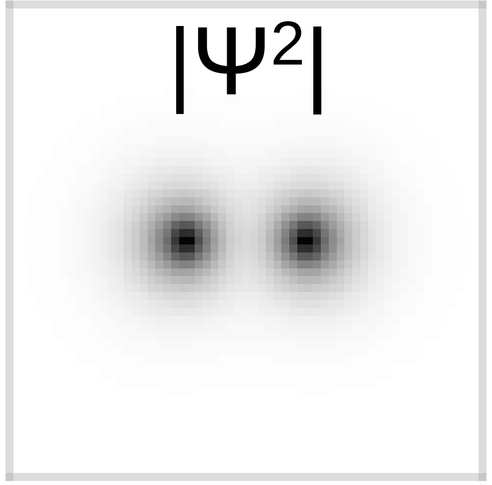
$$C = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

$$X = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2$$

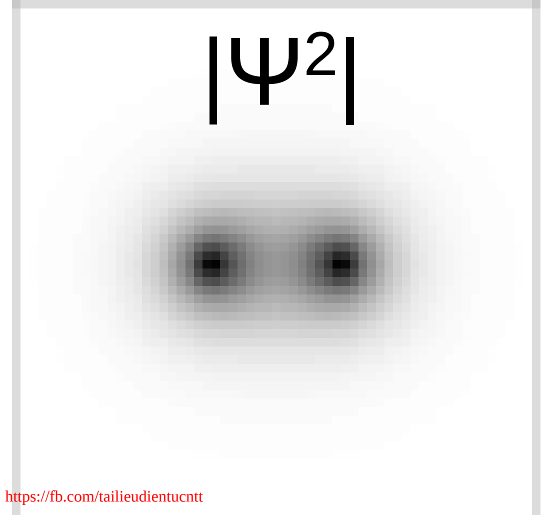
$$E = 2E_0 + \Delta E$$

with

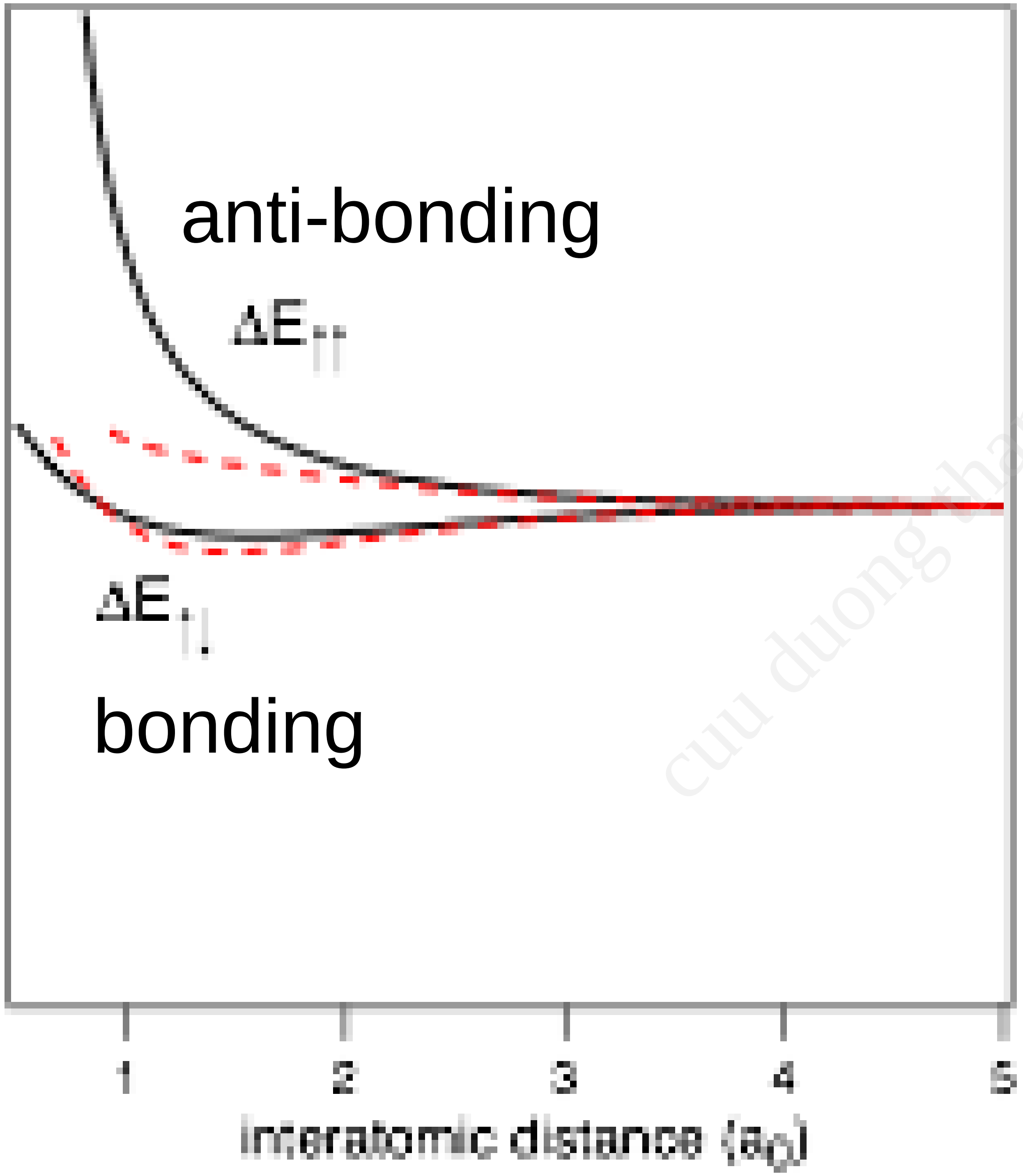
$$\Delta E_{\uparrow\uparrow} = \frac{C(R) - X(R)}{1 - S(R)}$$



$$\Delta E_{\uparrow\downarrow} = \frac{C(R) + X(R)}{1 + S(R)}$$



The Hydrogen Molecule: Heitler and London



$$E = 2E_0 + \Delta E$$

$$\Delta E_{\uparrow\uparrow} = \frac{C(R) - X(R)}{1 - S(R)}$$

$$\Delta E_{\uparrow\downarrow} = \frac{C(R) + X(R)}{1 + S(R)}$$

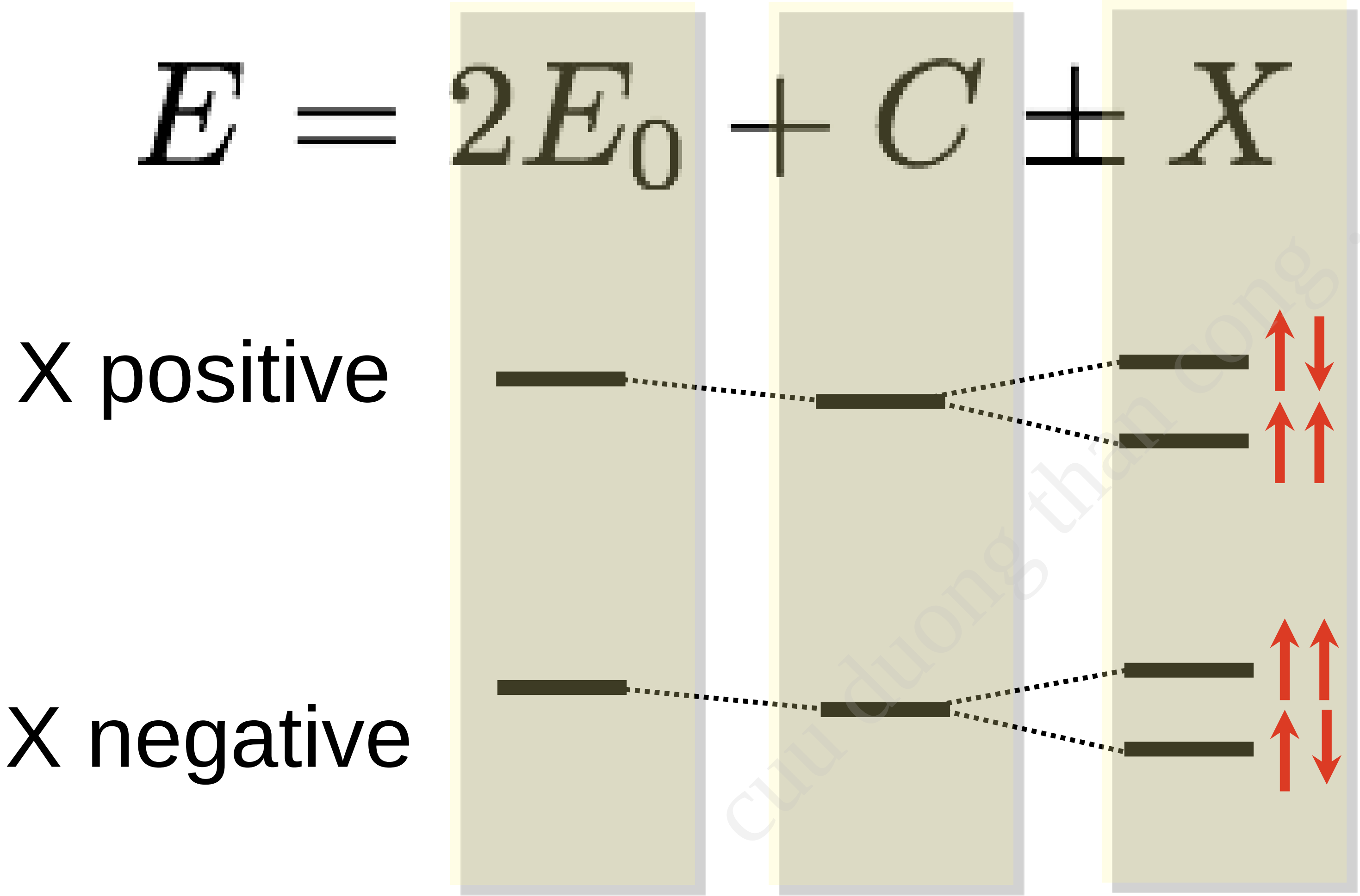
with S(R)=0

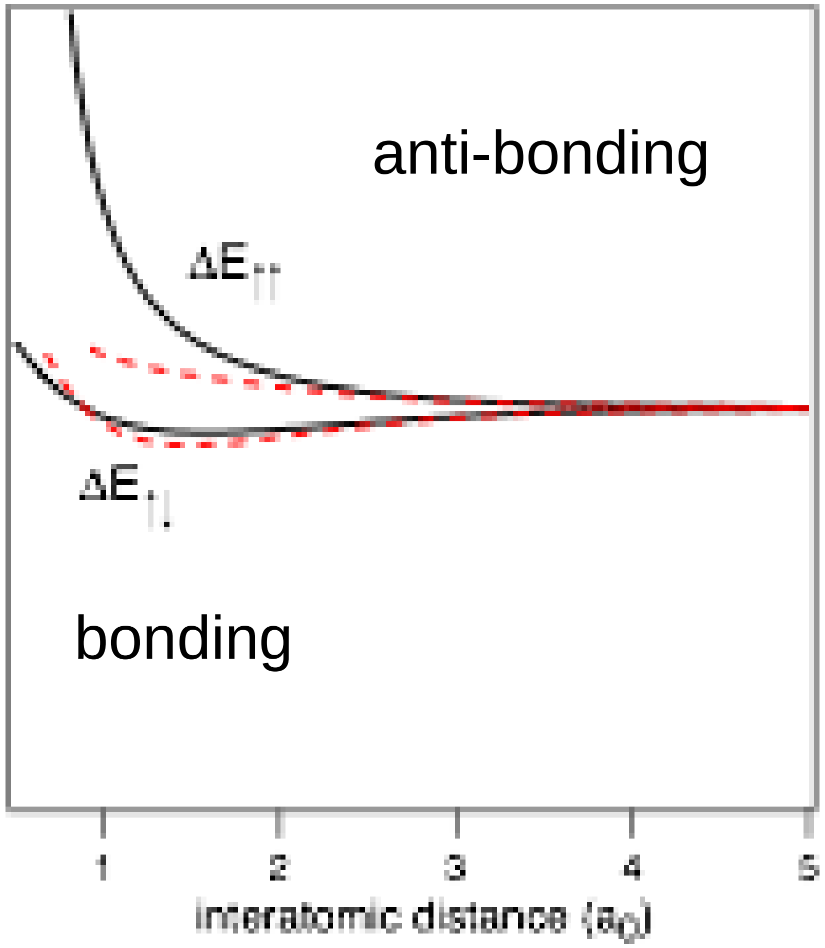
$$E = (2E_0 + C) \pm X$$

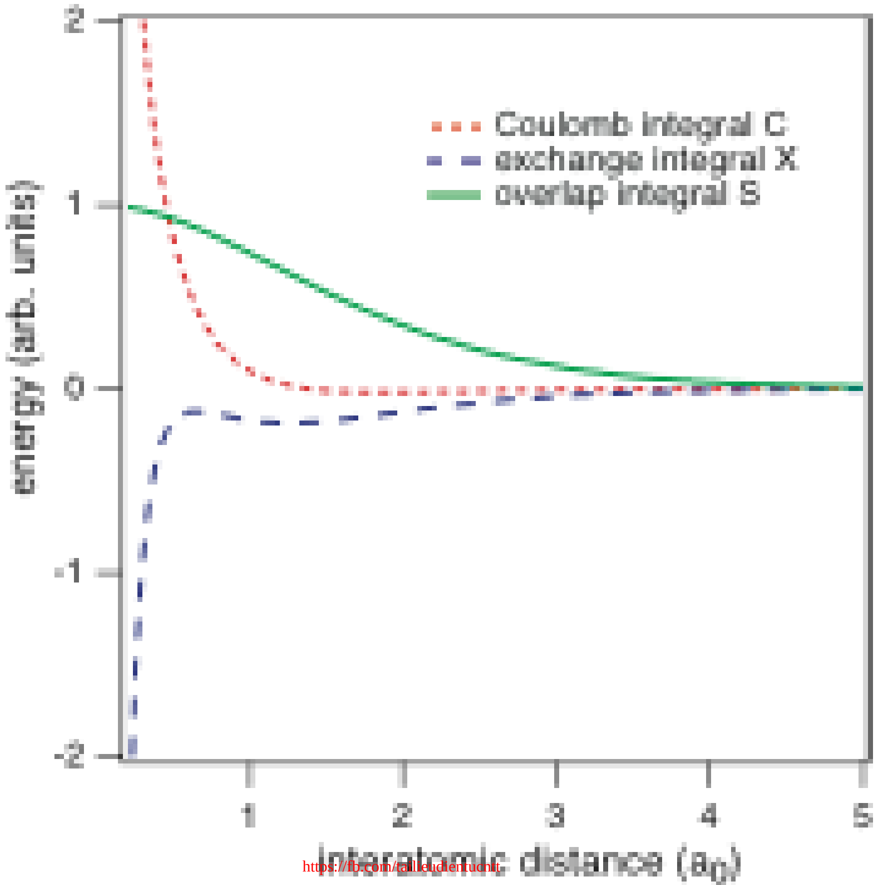
The Hydrogen Molecule: Heitler and London

a “magnetic view”:
(+ for singlet, - for triplet)

$$E = 2E_0 + C \pm X$$







positive exchange?

anti-symmetric

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) - \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

- In an anti-symmetric spacial wave function, the particles are NEVER at the same place. This reduces the Coulomb repulsion.
- This is also true for many electrons.

...but not the whole story

- We also have to consider kinetic energy.
- For instance, a gas of free electrons does not spontaneously magnetise.

Heisenberg model

Hamiltonian for two spins inspired by Heitler-London

$$H = -2X\mathbf{S}_1 \cdot \mathbf{S}_2$$

We want the energy difference between singlet and triplet state to be 2X, like in the H_2 molecule. Is this the case here?

$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ = 0 or 1 (singlet, triplet)

expectation values $\langle \mathbf{S}_1^2 \rangle = \langle \mathbf{S}_2^2 \rangle = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$

$\langle \mathbf{S}^2 \rangle = 1(1+1) = 2$ (triplet)

$\langle \mathbf{S}^2 \rangle = 0(0+1) = 0$ (singlet)

use $\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_1$

$\langle \mathbf{S}_1 \cdot \mathbf{S}_1 \rangle = \frac{1}{4}$ (triplet) $\langle \mathbf{S}_1 \cdot \mathbf{S}_1 \rangle = -\frac{3}{4}$ (singlet)

Heisenberg model

Hamiltonian for two spins inspired by Heitler-London

$$H = -2X\mathbf{S}_1 \cdot \mathbf{S}_2$$

For the entire solid with external field

$$H = -\sum_{i \neq j}\sum X_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + g_e\mu_B\mathbf{B}_0 \cdot \sum_i \mathbf{S}_i$$

Sum only over the (identical) nearest neighbours

$$H = -X\sum_i\sum_{nn}\mathbf{S}_i \cdot \mathbf{S}_{nn} + g_e\mu_B\mathbf{B}_0 \cdot \sum_i \mathbf{S}_i$$

Mean field approximation

$$H = \sum_i \mathbf{S}_i \cdot \left(-\sum_{nn} X\langle\mathbf{S}\rangle + g_e\mu_B\mathbf{B}_0\right) = \sum_i \mathbf{S}_i \cdot (-n_{nn}X\langle\mathbf{S}\rangle + g_e\mu_B\mathbf{B}_0)$$

Heisenberg model

Mean field approximation

$$H = \sum_i \mathbf{S}_i \cdot \left(-\sum_{nn} X \langle \mathbf{S} \rangle + g_e \mu_B \mathbf{B}_0 \right) = \sum_i \mathbf{S}_i \cdot (-n_{nn} X \langle \mathbf{S} \rangle + g_e \mu_B \mathbf{B}_0)$$

The magnetization is

$$\mathbf{M} = -g_e \mu_B \langle \mathbf{S} \rangle \frac{N}{V}$$

$$H = \sum_i \mathbf{S}_i \cdot \left(\frac{n_{nn} X V}{g_e \mu_B N} \mathbf{M} + g_e \mu_B \mathbf{B}_0 \right) = g_e \mu_B \sum_i \mathbf{S}_i \cdot (\mathbf{B}_W + \mathbf{B}_0)$$

with the Weiss field $\mathbf{B}_W = \mathbf{M} \frac{n_{nn} X V}{g_e^2 \mu_B^2 N}$

Heisenberg model

$$H = g_e \mu_B \sum_i \mathbf{S}_i \cdot (\mathbf{B}_W + \mathbf{B}_0)$$

$$\mathbf{B}_W = \mathbf{M} \frac{n_{nn} X V}{g_e^2 \mu_B^2 N}$$

This is like the spins in an “external field” $\mathbf{B}_W + \mathbf{B}_0$

Assume B_0=0 and use the expression from the Curie magnetism for J=1/2

$$\bar{\mu}_C = \frac{1}{Z} \sum_{m_J=-J}^{J} g \mu_B m_J e^{g \mu_B m_J B_0 / k_B T}$$

for the entire solid

with

$$M(T) = \frac{\mu_B N}{V} \frac{e^x - e^{-x}}{e^{-x} + e^x} = M(0) \tanh(x)$$

$$x = g_e |m_s| \mu_B B_W / k_B T$$

$$g_e |m_s| \approx 1$$

$$\frac{M(T)}{M(0)} = \tanh\left(\frac{M(T)}{M(0)} \frac{\Theta_C}{T} \right)$$

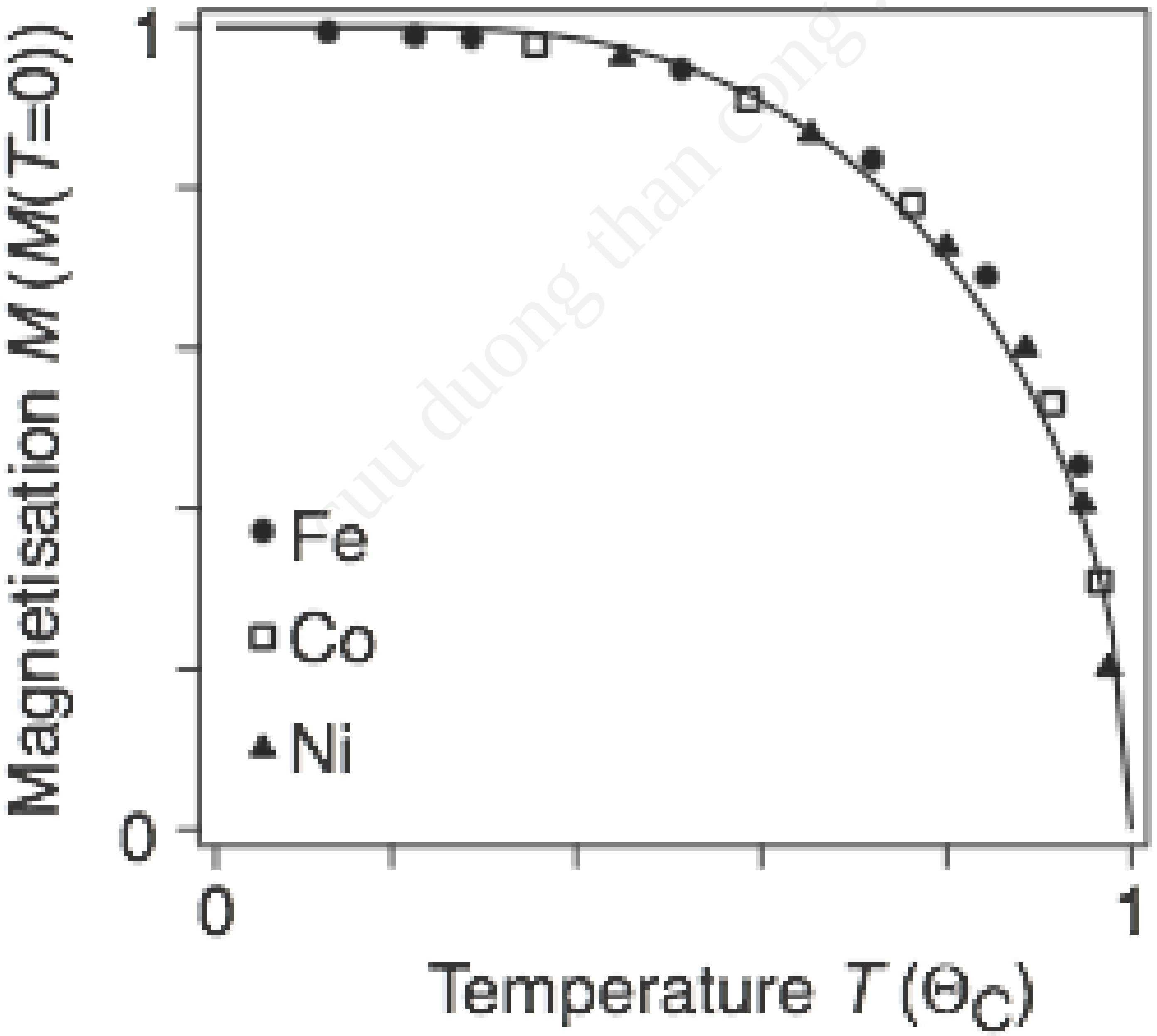
with $\Theta_C = \frac{n_{nn} X}{g_e^2 k_B}$

Heisenberg model

$$\frac{M(T)}{M(0)} = \tanh\left(\frac{M(T)}{M(0)}\frac{\Theta_C}{T}\right)$$

with $\Theta_C = \frac{n_{nn}X}{g_e^2 k_B}$

Curie temperature



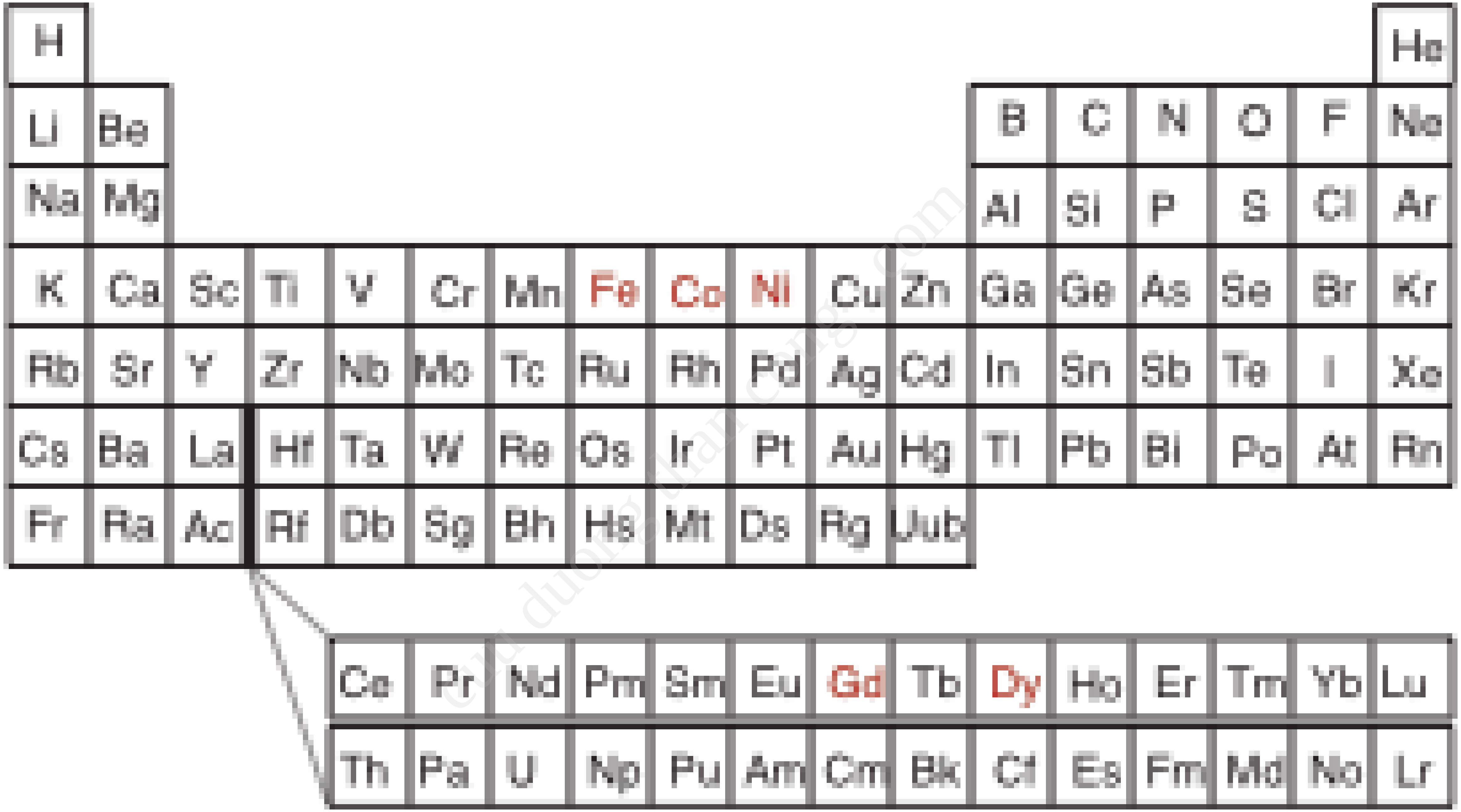
Temperature dependence of permanent magnets: high temperature

- Above the Curie temperature the magnetic moments are still there but the solid behaves like a paramagnet according to the Curie-Weiss law.

$$\chi_m = \frac{C}{T - \Theta_c}$$

Curie temperature

Ferromagnetic elements

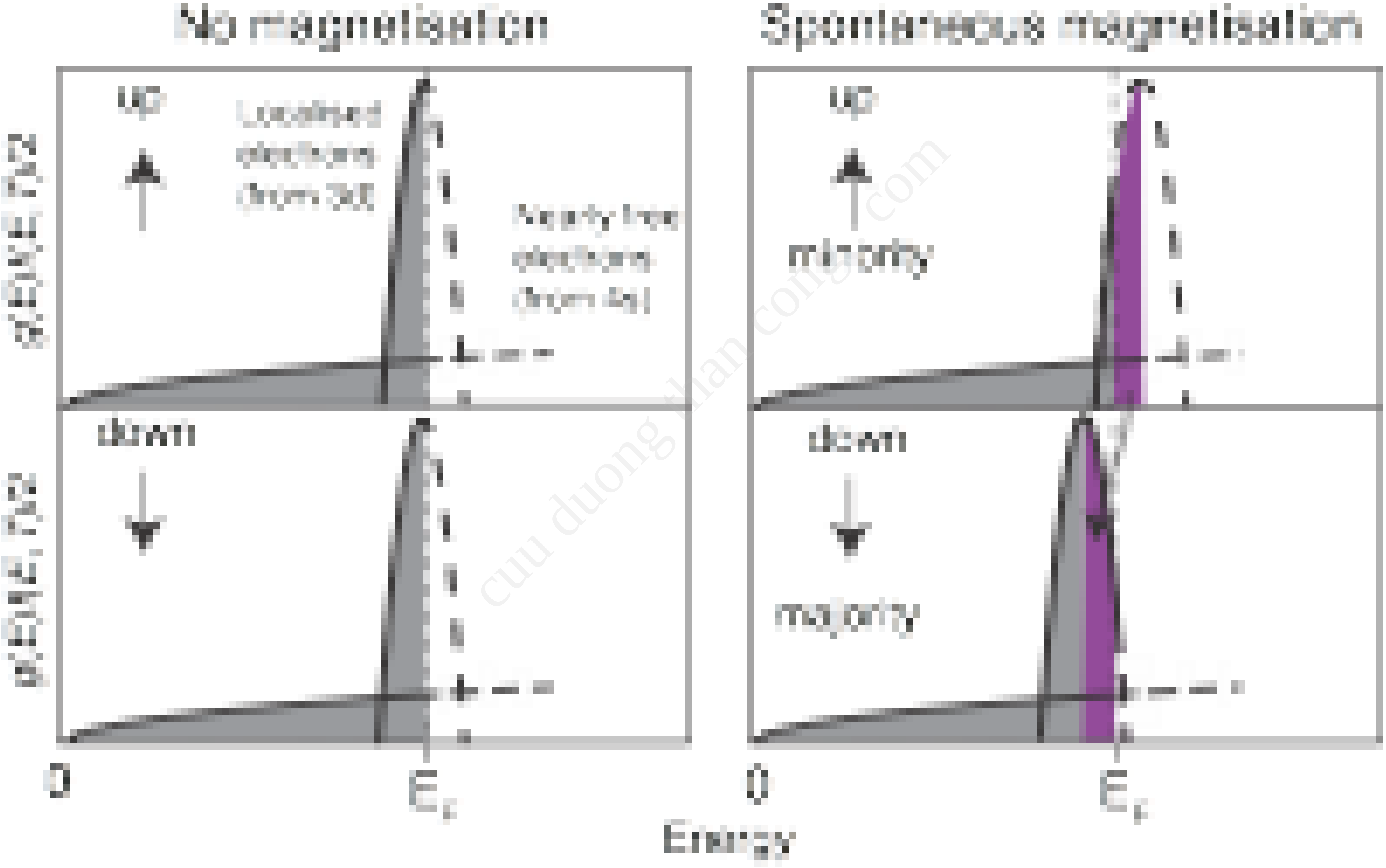


H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	**Fe**	**Co**	**Ni**	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub						
				Ce	Pr	Nd	Pm	Sm	Eu	**Gd**	Tb	**Dy**	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

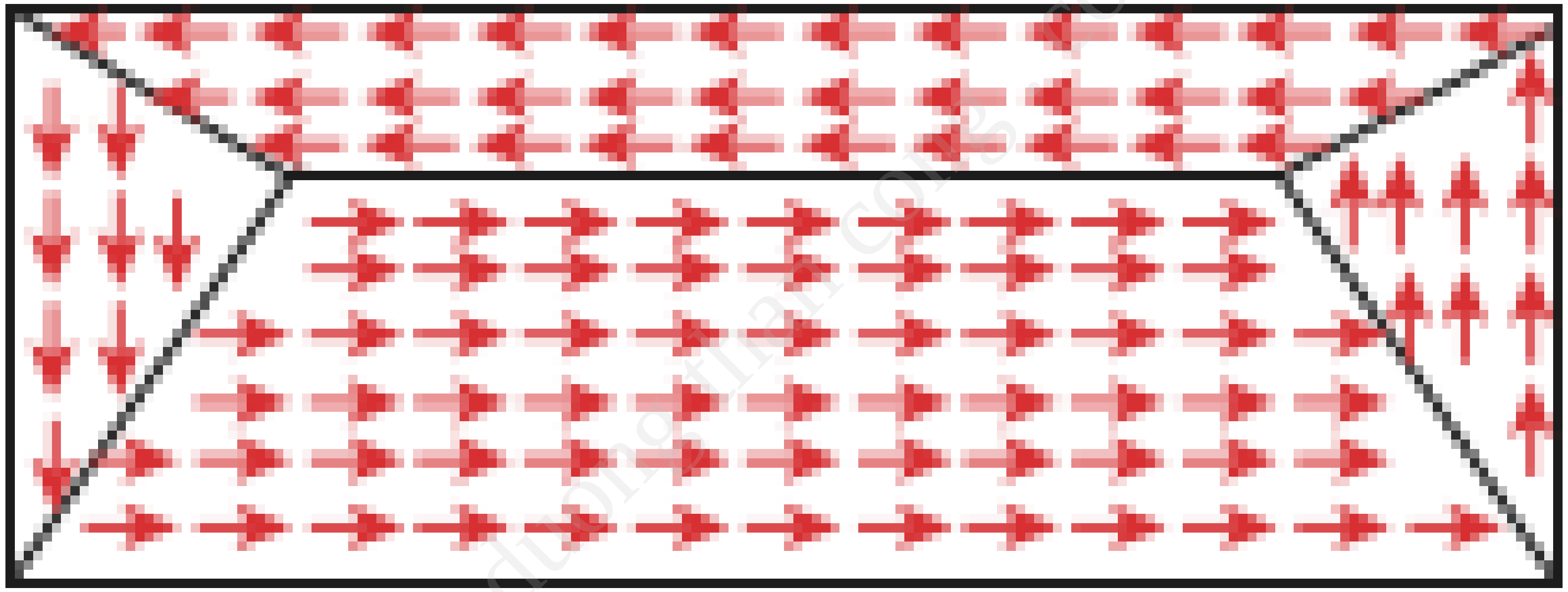
and many alloys are also ferromagnetic

Mostly alignment of spin magnetic moments

Band model of ferromagnetism

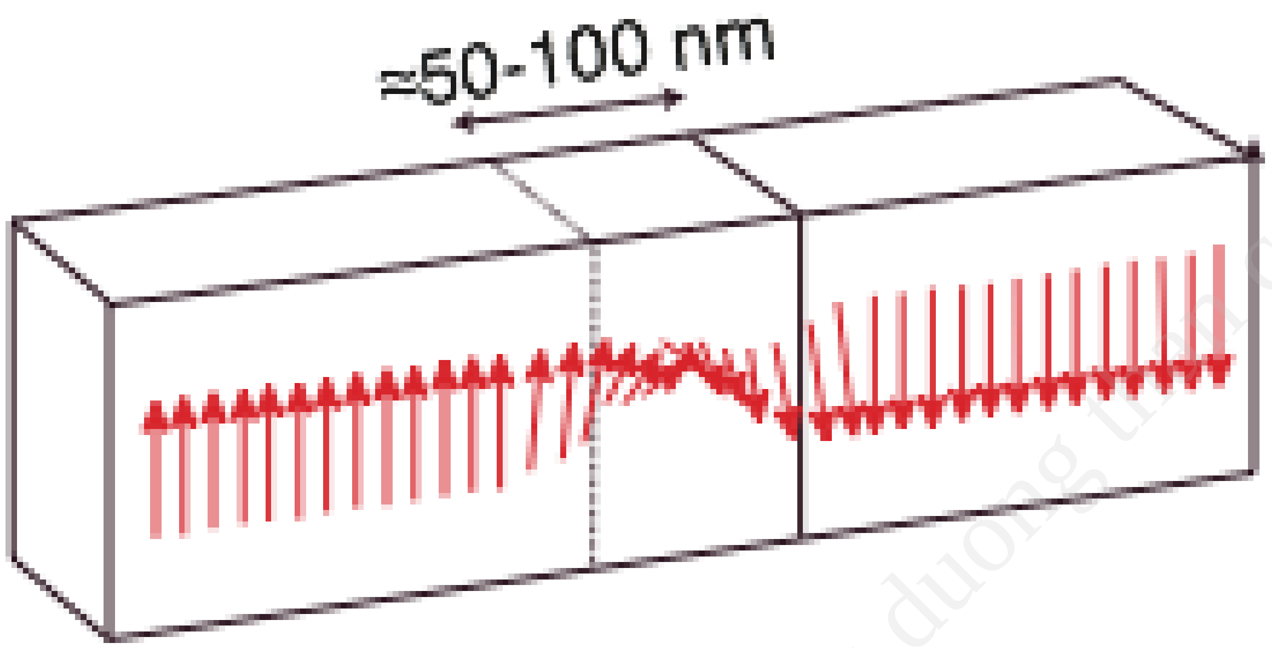


Ferromagnetic domains



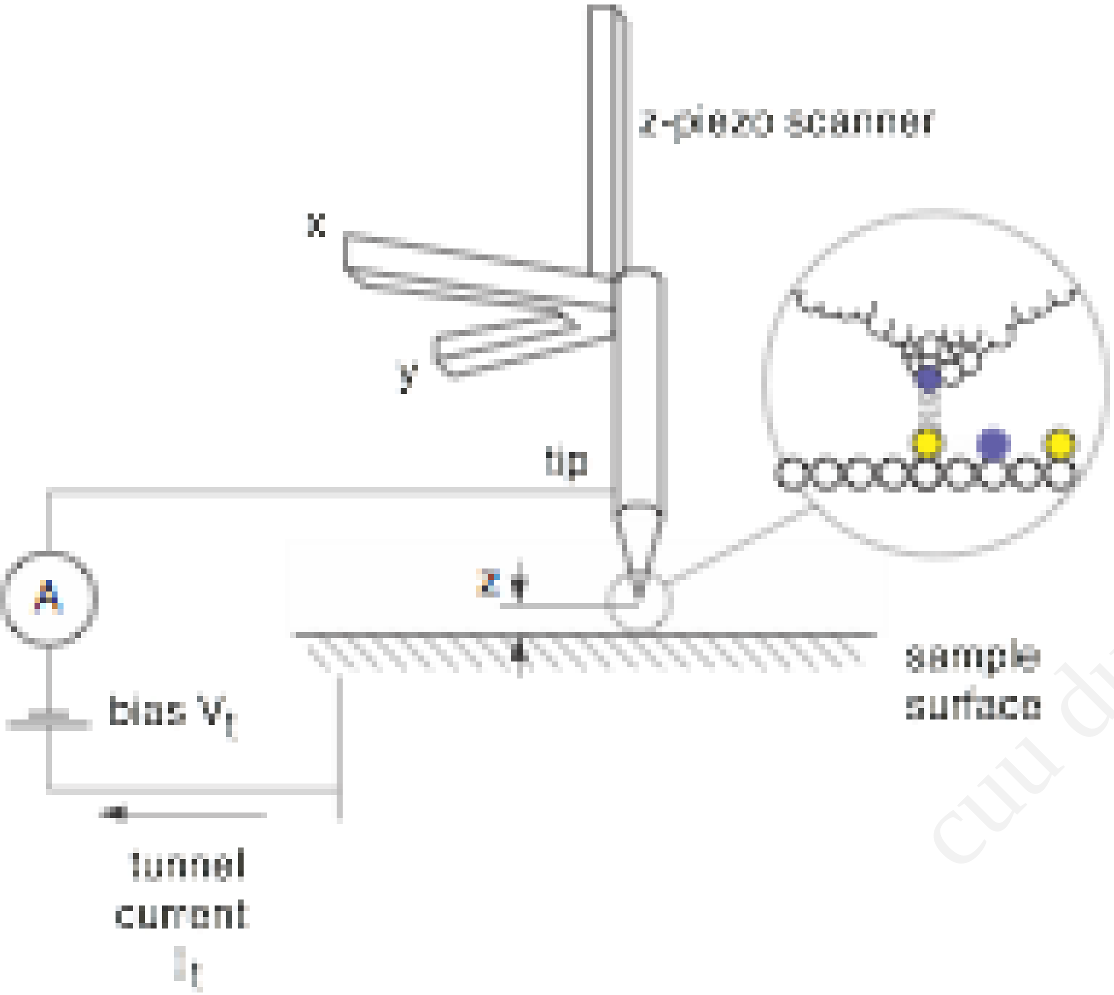
- Suggested by Pierre Weiss (1907)

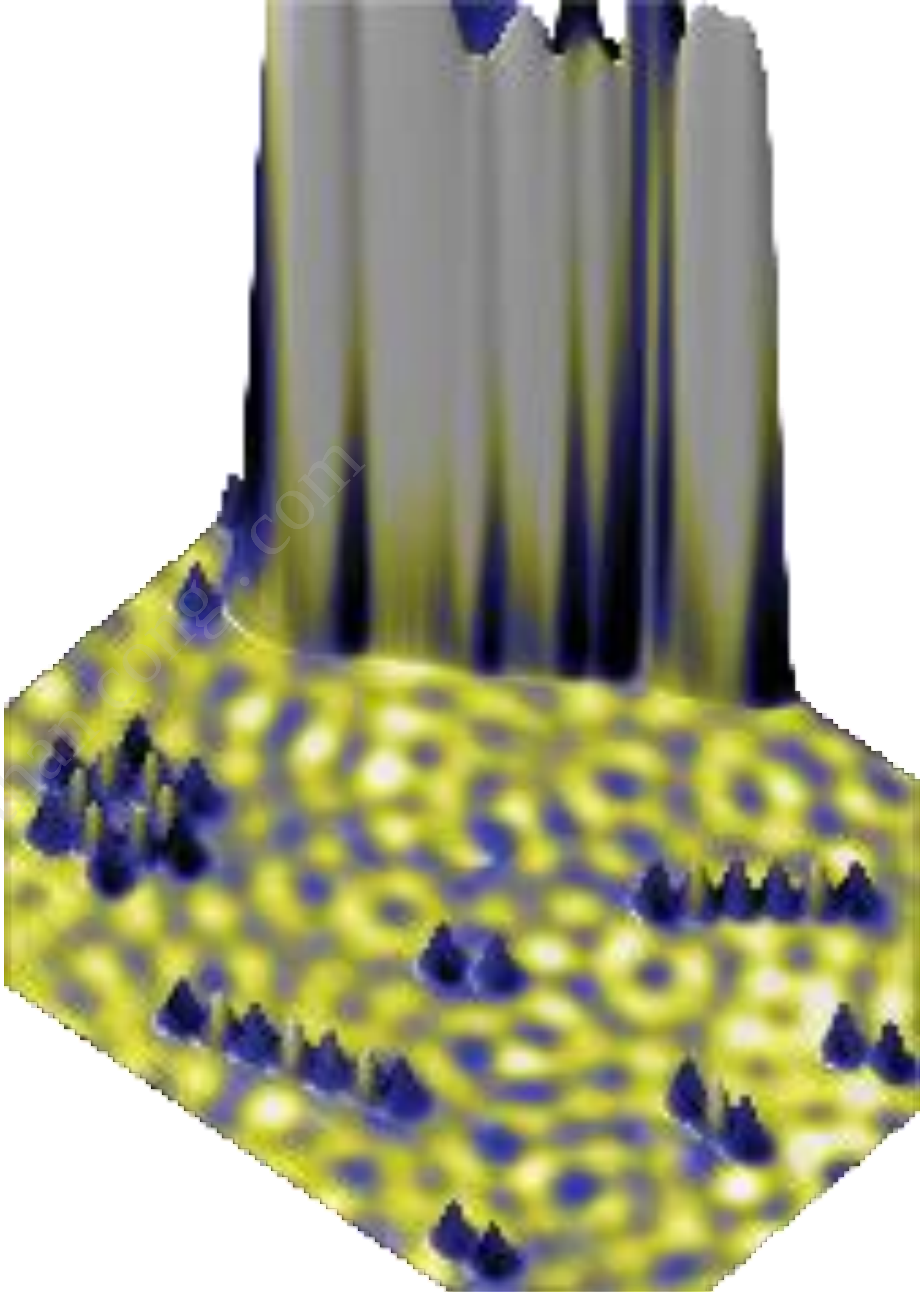
Domain boundaries / Bloch walls



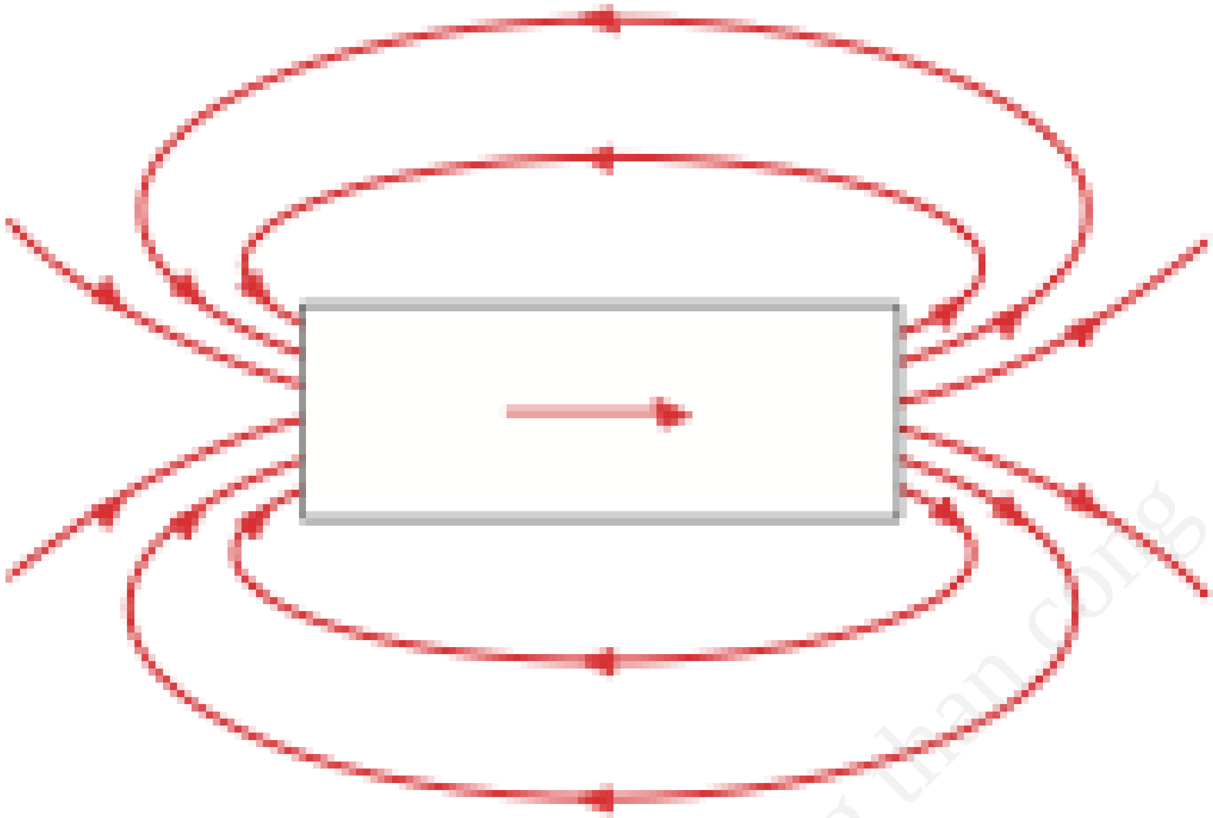
- Imaging domains: Bitter method, magneto-optical effects and magnetic scanning probe techniques

Spin-polarized STM



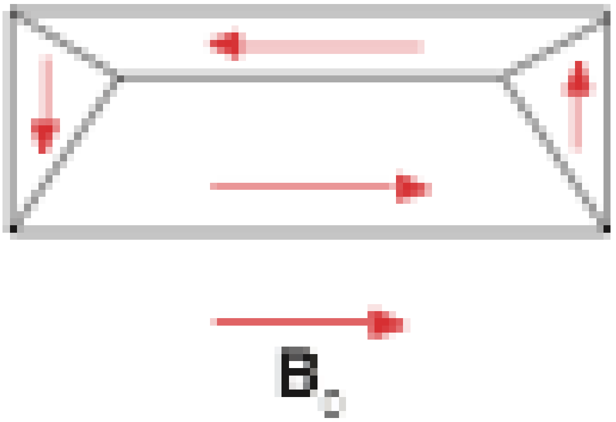


Macroscopic ferromagnetic samples



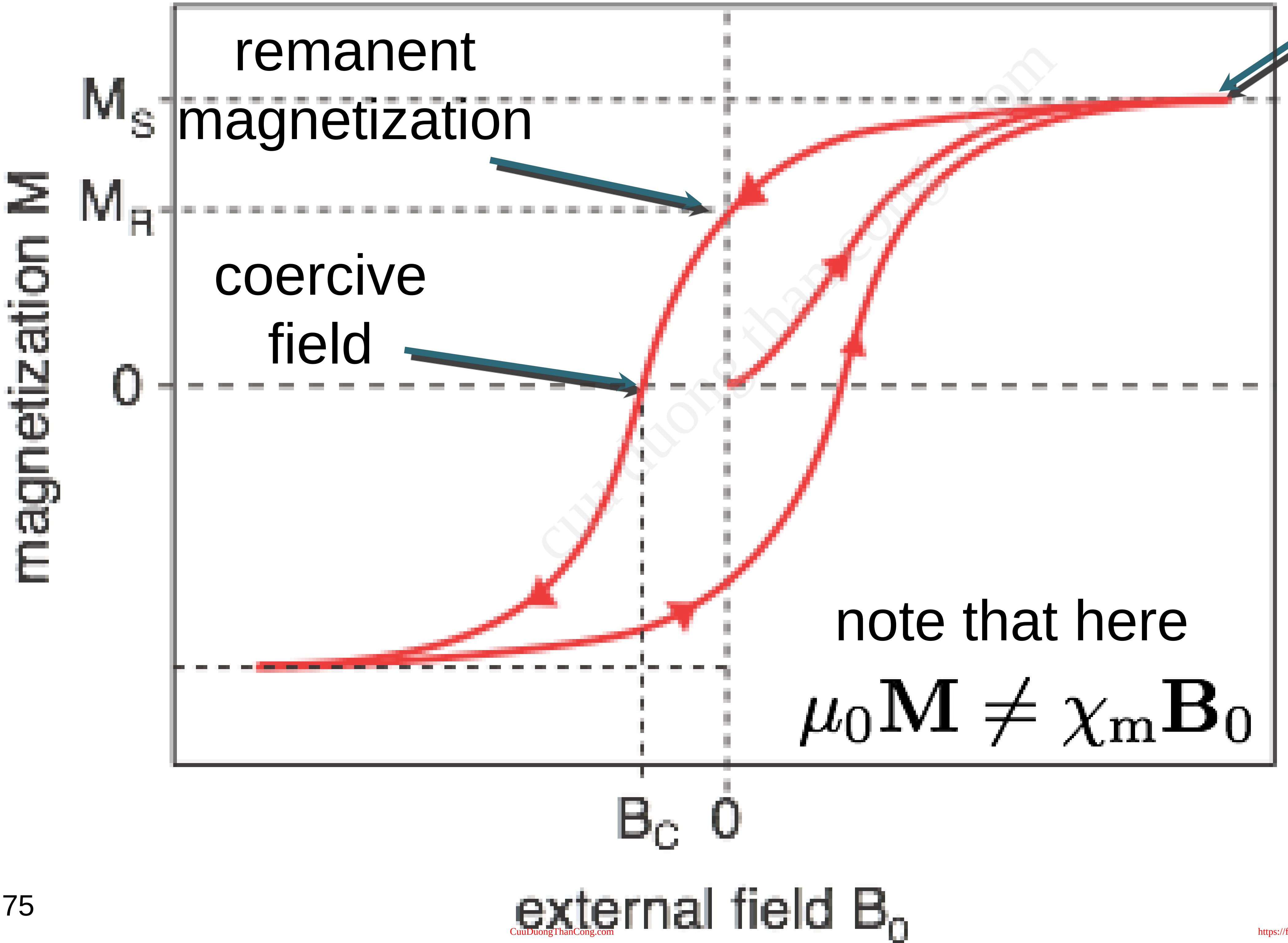
high energy
in external
field

no external
field



field-induced
movement of
domain walls

Hysteresis curve



saturation magnetisation

remanent magnetization

coercive field

note that here

$$\mu_0 \mathbf{M} \neq \chi_{\mathrm{m}} \mathbf{B}_0$$