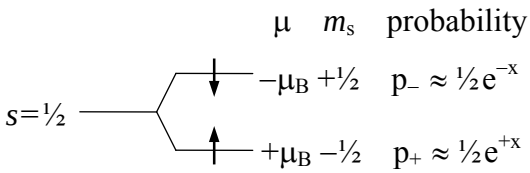
Paramagnetic Susceptibility

A) Bound Electrons in Atoms



Curie Law: $\boxed{\chi \propto 1/T}$

With increasing temperature T the alignment of the magnetic moments in a B field is less effective, due to thermal spin flips. Calculation for an electron (spin ½, negative charge):

Energy of an electron in a magnetic field: $U = m_s \cdot g \cdot \mu_B \cdot B = \pm\mu_B \cdot B$ ($m_s = \pm ½$, g=2)

The probabilities $p_\pm$ are proportional to the Boltzmann factor:

$p_\pm \propto \exp(-U/k_BT) = \exp(\pm\mu_B B/k_BT) = e^{\pm x} \approx 1 \pm x$ with $\boxed{x = \mu_B B/k_BT \ll 1}$

The normalization condition $p_+ + p_- = 1$ gives $\mathbf{p_\pm = e^{\pm x}/(e^{+x}+e^{-x}) \approx ½ \pm ½\, x}$

The magnetization M is obtained by separating the electron density N into opposite spins with magnetic moments $\pm\mu_B$ and probabilities $p_\pm$:

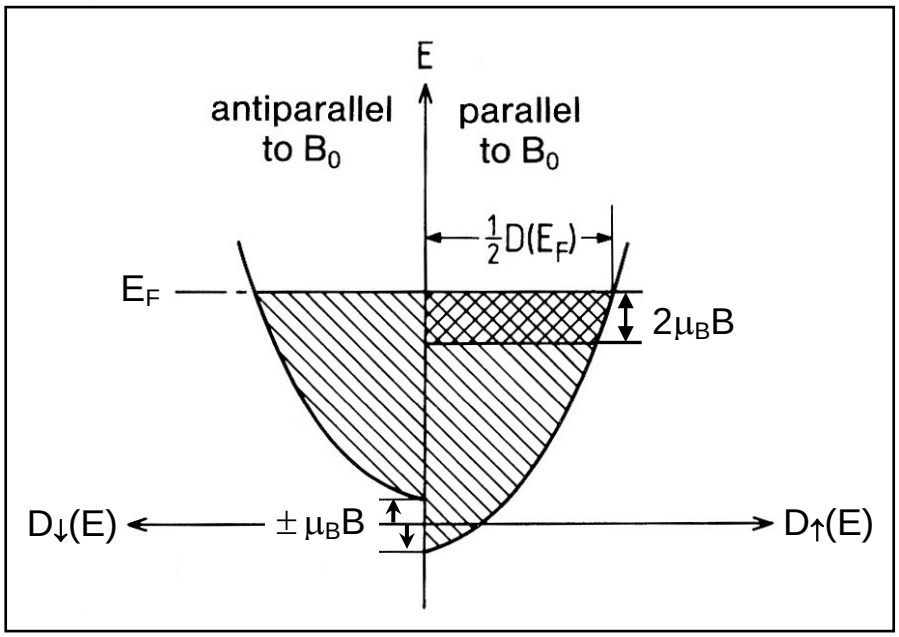
$M = N \cdot (p_+ \cdot \mu_B - p_- \cdot \mu_B) = N \cdot \mu_B \cdot (e^{+x} - e^{-x})/(e^{+x} + e^{-x}) \approx N \cdot \mu_B \cdot x = N \cdot \mu_B \cdot (\mu_B B/k_BT)$

$\chi = \mu_0 \cdot M/B \approx \mu_0 \cdot N \cdot \mu_B^2/k_BT$

The 1/T law originates from $1/k_BT$ in the Boltzmann factor $\exp(-U/k_BT)$.

B) Free Electrons in a Metal

Pauli Paramagnetism: $\boxed{\chi \text{ independent of } T}$, $\boxed{\chi \propto D(E_F)}$, analogous to: $c_V \propto D(E_F)$

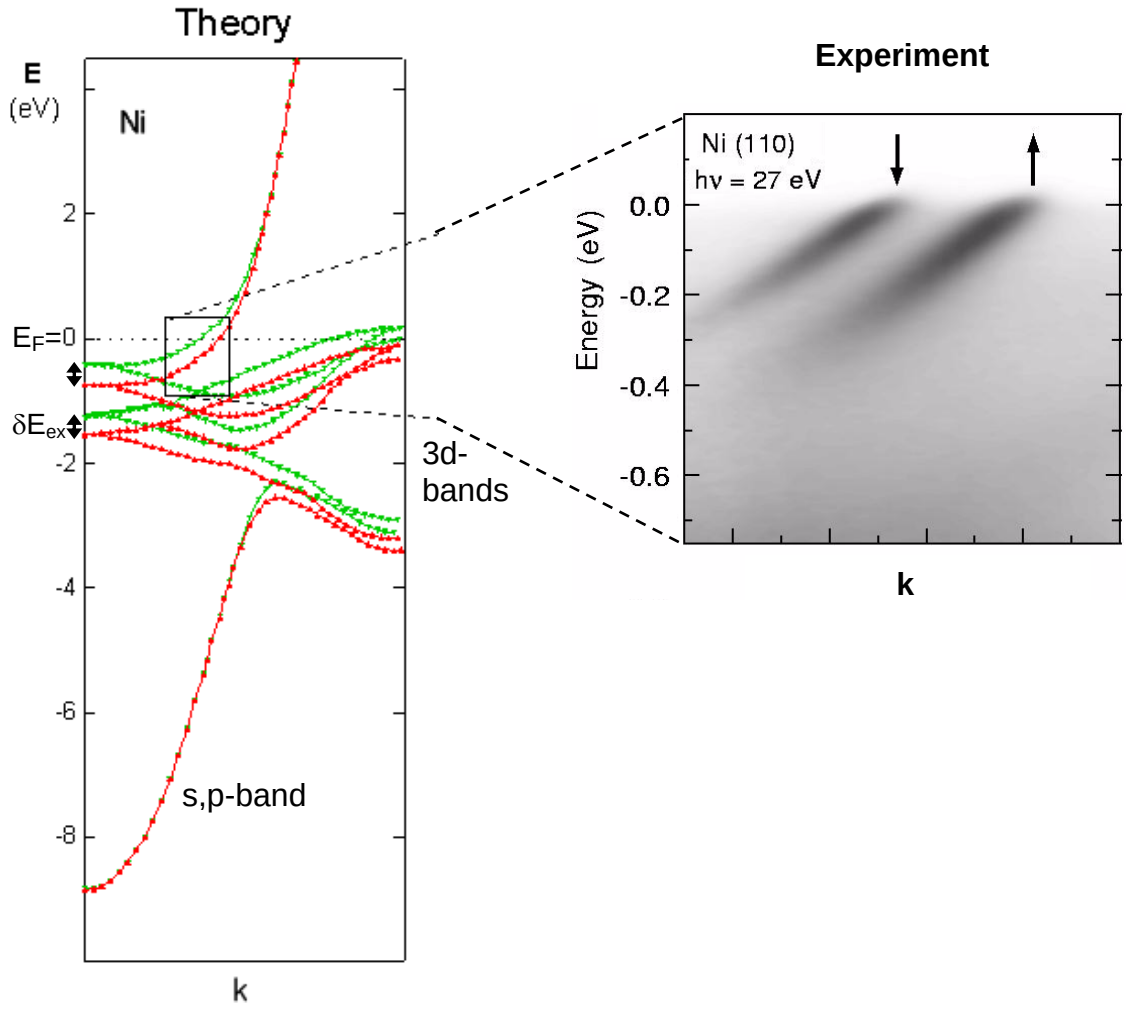


The cross-hatched area corresponds to the excess ↑ spins, i.e. to the induced magnetization M.

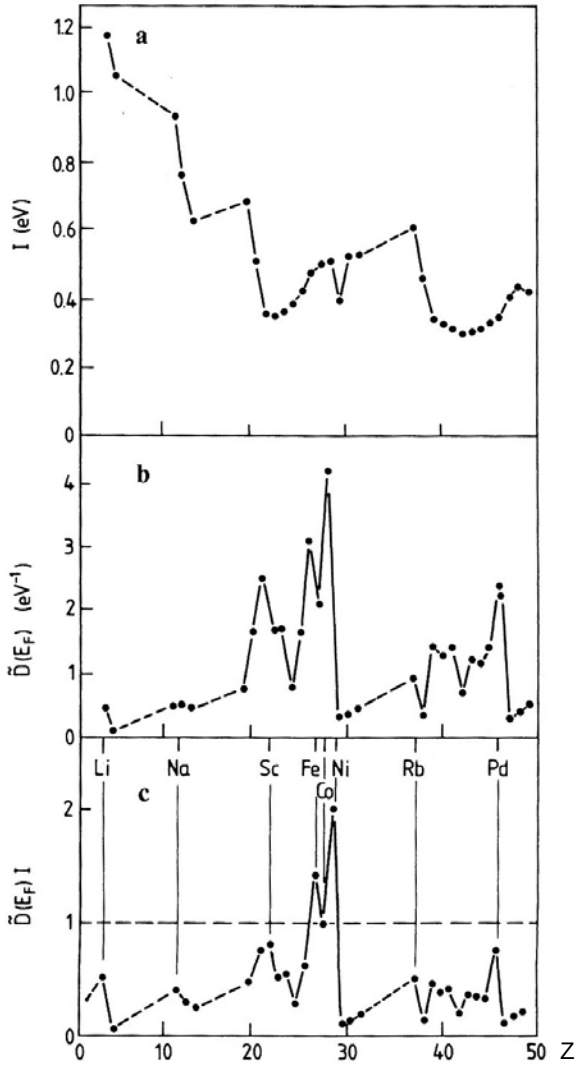
Energy Bands of Ferromagnets

Like the bands of a Pauli paramagnet in **B**-field, the band structure E(**k**) of a ferromagnet can be decomposed into **two sets of bands**, one for majority spin (↑ , "spin up", $\boldsymbol{\mu} \parallel \mathbf{B}$), the other for minority spin (↓ , "spin down", $\boldsymbol{\mu} \parallel -\mathbf{B}$). They are separated by the **magnetic exchange splitting** δE_{ex} , which ranges from 0.3 eV in Ni to 2 eV in Fe. It is orders of magnitude larger than the splitting of paramagnetic bands in a typical **B**-field ($\approx$ 1 Tesla). Magnetism is carried mainly by the flat 3d bands which have a high density of states at E_F . That is necessary for the Stoner criterion for ferromagnetism (see next).

The ferromagnetic bands can be measured by angle-resolved photoemission (Lecture 18), including their ferromagnetic exchange splitting δE_{ex} :



Stoner Criterion for Ferromagnetism: $\boxed{I \cdot \tilde{D}(E_F) > 1}$



I = Exchange integral

$\propto$ Energy reduction per electron

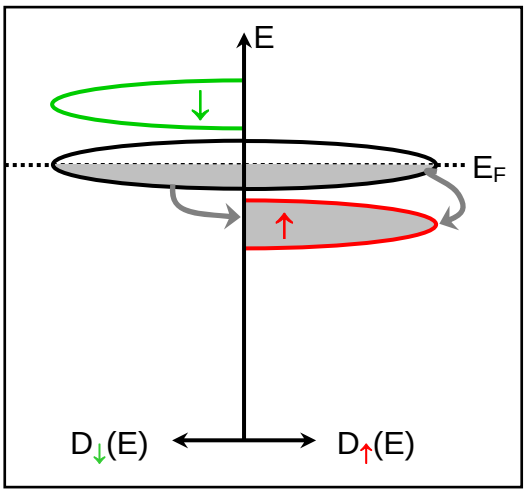
$\tilde{\mathbf{D}}(\mathbf{E_F})$ = Density of states at E_F (per atom, per spin)

$\propto$ Number of electrons reducing their energy

$\mathbf{I \cdot \tilde{D}(E_F)}$

Only Fe, Ni, Co pass the Stoner criterion. These are indeed the only ferromagnets in this range of atomic numbers Z.

Idea behind the Stoner Criterion:

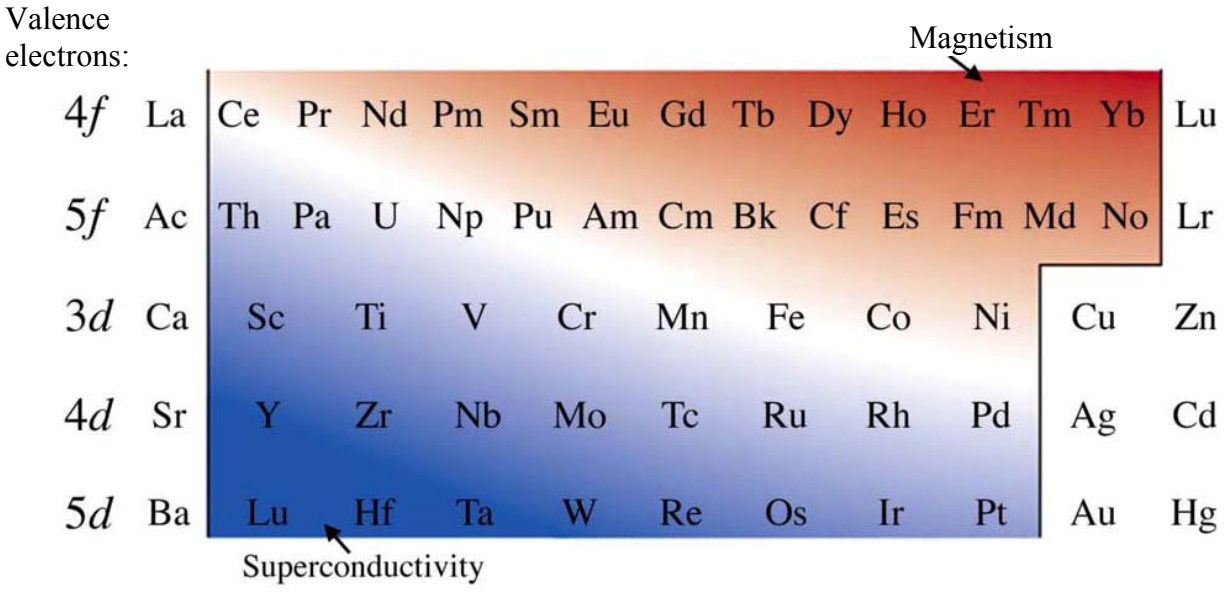


The paramagnetic state has a magnetic moment per atom, for example one electron with spin ½. That corresponds to a half-filled band straddling the Fermi level E_F. For **B**=0 one has equal amounts of spin up and down electrons. The ferromagnetic exchange splitting shifts one band down and the other band up. All the electrons in the gray area end up in the lower band with spin up. That reduces their energy by about half the exchange splitting. We encountered a similar pattern in covalent bonding, i.e., a splitting of two half-filled levels into a completely-filled lower level and an empty upper level.

Competition between Magnetism and Superconductivity

Both magnetism and superconductivity take advantage of a high density of states D(E) at the Fermi level E_F. Electrons just below E_F have the highest possible energy and thus have a tendency to rearrange themselves into energetically more favorable configurations. The principle is rather general: Magnetism and superconductivity both cause a small energy gap at the Fermi level by pushing occupied states down and unoccupied states up. Thereby occupied states lower their energy, while there is nothing lost by pushing unoccupied states up in energy. If $D(E_F)$ is high, many electrons are available to lower their energy via this mechanism. That stabilizes magnetism or superconductivity. In other words, the magnetic ordering temperature T_{Curie}, T_{Neel} or the superconducting transition temperature T_c increases.

Whether **magnetism** or **superconductivity** wins the competition **depends on the localization of the electrons at E_F**. The magnetic exchange interaction is caused by the overlap of atomic wave functions, which decay exponentially over atomic distances. Superconductivity involves the electron-phonon interaction, which extends all the way to the μm range – at least in conventional superconductors. As one moves to the right in the Periodic Table, the attractive nuclear Coulomb potential increases and localizes the electrons, thereby favoring magnetism. When moving from the upper right to the lower left in the rearranged Periodic Table below, the wave functions become less localized and favor superconductivity. Most **high temperature superconductors** contain **Cu^{2+}**, which is **close to the diagonal dividing line**. They are antiferromagnets without doping and become superconductors when doped.



The Magnetic Exchange Interaction

The exchange interaction is responsible for both ferromagnetism and antiferromagnetism. It originates from the **antisymmetry*** of the two-electron wave function with respect to the **exchange** of two electrons **1** and **2** with coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ (compare Lect. 2, p. 5):

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = [\ \psi_a(\mathbf{r}_1)\cdot\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\cdot\psi_b(\mathbf{r}_1)\ ]/\sqrt{2}$$

Spatial wave function for parallel spins (e.g. ferromagnetism)

ψ_a and ψ_b are two different one-electron wave functions. If the two spins are the same, the spatial wave functions have to be different. In other words, **electrons with parallel spins are farther apart**. This is the mathematical version of the Pauli principle ("two electrons with the same spin cannot be at the same place"). Being farther apart **reduces the Coulomb repulsion** between electrons and thus tends to be energetically favorable.

This argument leads to **Hund's 1st rule** (valid for **atoms** with partially-filled shells, mainly d and f electrons): The most stable configuration has **all spins parallel**, i.e. **maximum total spin**. In a **solid**, the electrons do not have enough room to get away from each other, because wave functions become **squeezed** by neighbor atoms. Some of the spins become antiparallel to get closer to each other. Consequently, the **total spin is reduced**. Surfaces are intermediate between atoms and solids, allowing larger total spin than the bulk. That leads to enhanced surface magnetism.

The **exchange energy** is actually part of the electrostatic energy $V \propto 1/|\mathbf{r}_1-\mathbf{r}_2|$ between two electrons, determined via quantum mechanics. The spatial two-electron wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ for parallel spins produces the following expectation value of V:

$$\langle V\rangle = \langle\Psi^*|V|\Psi\rangle = \int \Psi^*(\mathbf{r}_1,\mathbf{r}_2)\cdot V\cdot\Psi(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

$$= +\iint \psi_a^*(\mathbf{r}_1)\,\psi_a(\mathbf{r}_1)\cdot V\cdot\psi_b^*(\mathbf{r}_2)\,\psi_b(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \qquad \textbf{Coulomb energy (+)}$$

$$-\iint \psi_a^*(\mathbf{r}_1)\,\psi_a(\mathbf{r}_2)\cdot V\cdot\psi_b^*(\mathbf{r}_2)\,\psi_b(\mathbf{r}_1)\,d\mathbf{r}_1 d\mathbf{r}_2 \qquad \textbf{Exchange energy (–)}$$

The Coulomb term is repulsive, but the exchange term can be attractive: $\Rightarrow$ parallel spins

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* Electrons are indistinguishable in quantum mechanics. They cannot be "painted red or blue". For fermions (half-integer spin), the sign of the two-particle wave function changes when interchanging the indices 1 and 2. Bosons (integer spin) are also indistinguishable, but their wave function does not change its sign (e.g., photons, phonons).

From Ferromagnetism to Antiferromagnetism

Squeezing of magnetic atoms changes ferromagnetism to antiferromagnetism:

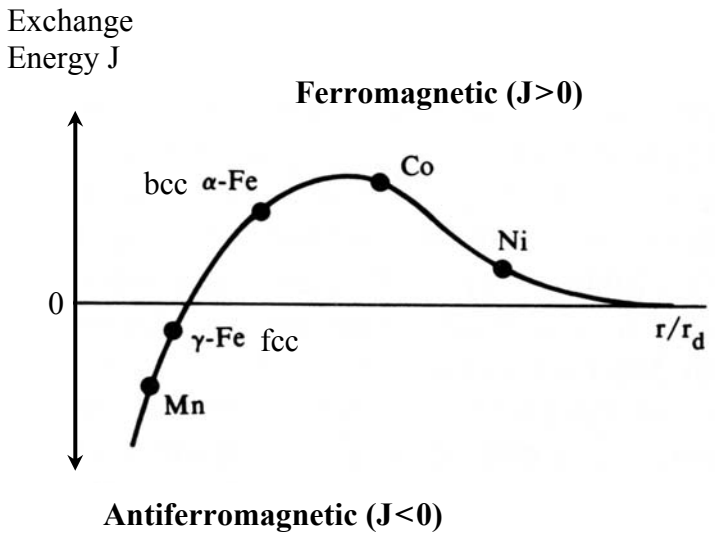
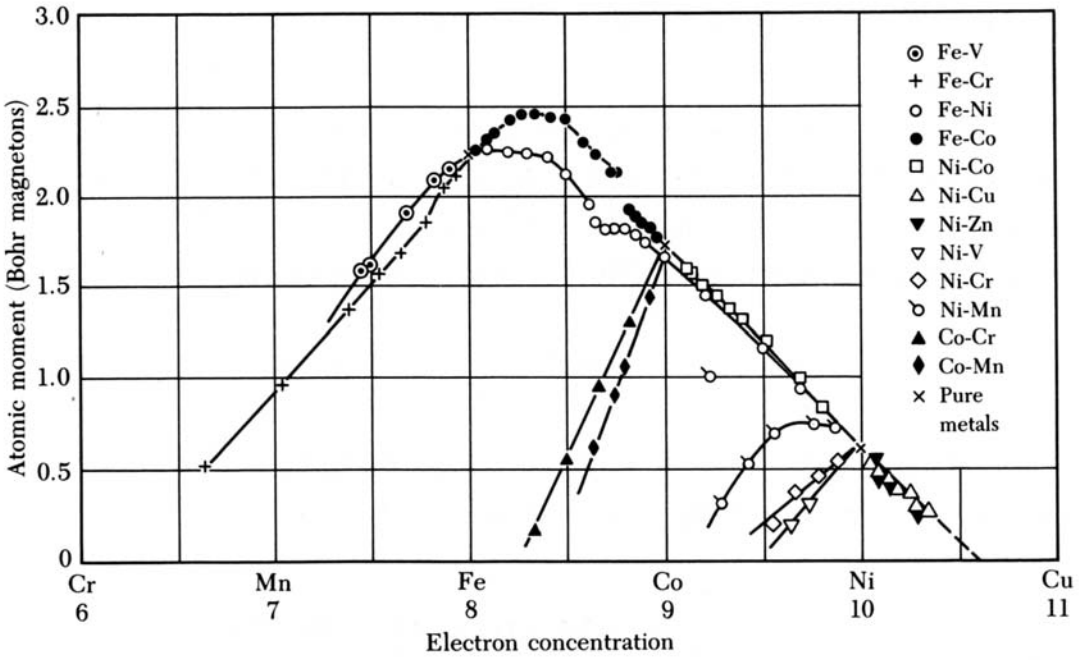


Fig. 15-8 A schematic plot of the exchange constant vs. interatomic distance (r_d is the distance between nearest neighbors). Values for the transition metals are shown.

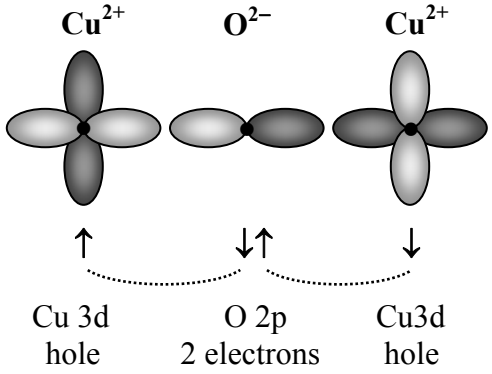
The Slater Curve for the Magnetic Moment (per Atom):



Hund's 1st rule gives up to $5\mu_B$ in a 3d shell (l=2, transition metals), and $7\mu_B$ in a 4f shell (l=3, rare earths): $(2l+1)$ states with different m_l occupied by ↑ spins at half filling.

The exchange interaction comes in many forms. The most common versions are:

1) Exchange between two electrons on the **same atom** (Hund's 1st rule).
2) Exchange between two **adjacent atoms** (ferromagnetism, antiferromagnetism)
3) Superexchange between **second neighbors** via an intermediate atom:



Superexchange via an electron pair of the intermediate oxygen makes the undoped parent compounds of high temperature superconductors antiferromagnetic.

In magnetoelectronics (= spintronics) there are two primary magnetic interactions:

A) **Exchange interaction**: Strong (eV), but short-range (nm)
Quantum: 2-electron Schrödinger equation, $\Psi_{2,1}=-\Psi_{1,2}$
Ferromagnetism, antiferromagnetism

B) **Dipole interaction**: Weak (meV), but long-range (macro)
Classical: Maxwell equations, $U=-\boldsymbol{\mu}\mathbf{B}$
Paramagnetism

These two often counteract each other. For example, the exchange interaction aligns the spins parallel within a bar magnet, but the dipole interaction forces two bar magnets to be antiparallel when putting them side by side (see next lecture).