Magnetic moment of a current loop:

\[ i = -e \frac{v}{T} = -e \frac{v}{2\pi r} \quad A = \pi r^2 \]

\[ \mu = -e \frac{v}{2\pi} \pi r^2 = -e \frac{v r m_e}{2 m_e} \quad \hbar = v m_e r \]

For the electron:

\[ \mu_b = \frac{e \hbar}{2m_e} = 9.274 \times 10^{-24} \frac{J}{T} \]

\[ \mu_b = \frac{e \hbar}{2m_e} = 5.788 \times 10^{-5} \frac{eV}{T} \]

For the electron, the Bohr magneton is the simplest model possible to the smallest possible current to the smallest possible area closed by the current loop.

Orbiting electrons form a current loop which give rise to a magnetic field.

**Borh magneton**
Rutherford (1911)- Borh model of atom (1913)

1) Borh use the classical mechanics.
2) The only permitted orbital are those for with $L_{orb} = n\hbar$.
3) For these orbitals the electrons don’t radiate electromagnetic waves.
4) The energy of the photon is: $E = h\nu$

$$m_e v r = \hbar n$$  Permitted orbitals

Einstein (1905)

Rydberg $E = -13.6\,\text{eV}$

Borh radius

$$a_0 = \frac{\hbar^2}{m_e k e^2} = 52.97\,\text{pm}$$
Subshells Schrödinger (1922)

Subshell very important to capture or loss an electron

Subshell very important for the ligands

Subshell very important for the metals

Subshell very important for rare earths

Pauli exclusion principle (1925)

Caution: This presentation is valid for isolated atoms only.
Standard Notation of Fluorine

Number of electrons in the sub level 2,2,5

Main Energy Level Numbers 1, 2, 2

Sublevels 1s² 2s² 2p⁵
Hund’s rule

Orbital Filling Order (Diagonal Rule).

It is a semi-empirical law with exceptions case

Minimize the coulomb interaction + Pauli exclusion principle.
# Orbital occupancy for the transition metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Partial Orbital Diagram</th>
<th>Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
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<tr>
<td>Ti</td>
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<td></td>
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<tr>
<td>Zn</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

**Caution:** This presentation is valid for isolated atoms only.

**Remark:** the electrons are not linked inside the subshells of the atoms

**Ferromagnetic**

**Diamagnetic**

**Antiferromagnetic !!!!** Néel temperature

**Paramagnetic**

**Antiferromagnetic** Néel temperature
Orbital model for $H_2$

Bonding

Pauli exclusion principle forbid the same spin orientation.

Waves reinforce

Distance between two atoms

Energy

- Repulsive
- Attractive

Distance

74.6 pm

Energy $E_0$

-27.2 eV (The atoms are separate)

-22.68 eV

**symmetric for the waves, antisymmetric for the spin**
Antibonding

Not stable (Coulomb repulsion between protons)

Two different orbits 1S allow the same spin orientation.

symmetric for the spin, antisymmetric for the waves

Orbital model for $H_2$
Now let’s take a closer look at the energy levels in solid sodium. Remember, the 3s is the outermost occupied level.

We reduce the distance between the atoms. The energy differences are very small, but enough so that a large number of electrons can be in close proximity and still satisfy the Pauli exclusion principle.

The result is the formation of energy bands, consisting of many states close together but slightly split in energy.
Nucleus + all the electrons with the orbitals full.

Sommerfeld model of free electrons (1928)

electron gases formed by the electrons of the last two orbital (4S + 3D).
Sommerfeld model of free electrons (1928)

1) We are in the non relativist case.
2) We don’t consider the full subshells $\sum L_i=0$ and $\sum S_i=0$ until the subshell 3p (included). It is a have a positive ion.
3) We consider the itinerant electrons as a gas (the electrons inside the subshell 3d and the last subshell 4s).
4) The itinerant electrons have a kinetic energy only.
5) It is a first approximation.

Heisenberg uncertainty principle (1927)

$$\Delta p \ast \Delta r \geq \frac{\hbar}{2}$$

1) The Pauli exclusion principle and the uncertainty principle limit the number of electrons with a low velocity.
2) If you increase the number of electrons, you must increase their velocity because all the states with a lower energy are busy...
Each state can hold 2 electrons of opposite spin (Pauli’s principle).

Near zero degree Kelvin the free electrons have a kinetic energy.

For a transition metal, the augmentation of temperature is created by the nucleus vibrations. These vibrations obey to a Bose-Einstein distribution.

Only the free electrons near the Fermi are sensitive to the temperature (Fermi-Dirac distribution).

The spin of these particles can be oriented in the sense that the external field.

\[ E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 n_e\right)^{2/3} \]
# Fermi Parameters for some metals (Sommerfeld model)

<table>
<thead>
<tr>
<th>Element</th>
<th>Molar volume</th>
<th>electrons</th>
<th>density</th>
<th>Fermi energy calculated $E_F$ [eV]</th>
<th>Fermi temperature $T_F$ [10$^3$ K]</th>
<th>Fermi velocity 10$^8$ cm$^{-1}$</th>
<th>electrons cm$^{-3}$</th>
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<tr>
<td>Scandium</td>
<td>15,00\times10^{-6}</td>
<td>21</td>
<td>2.985</td>
<td>6.6</td>
<td>7.7</td>
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<tr>
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<td>Vanadium</td>
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<td>10.36</td>
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<tr>
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<td>11.64</td>
<td>13.51</td>
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<td>Manganese</td>
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<td>10.9</td>
<td>12.7</td>
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<td>11.7</td>
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<tr>
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<td>7.04</td>
<td>8.17</td>
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<tr>
<td>Zn</td>
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<td>30</td>
<td>7.14</td>
<td>9.47</td>
<td>10.9</td>
<td>1.82\times10^{22}</td>
<td></td>
</tr>
</tbody>
</table>
Fermi surface for Ag Bloch model 1946

Crystalline structure for Ag

Atomic nucleus

Fermi surface

\[ k_F = 12 \times 10^9 \text{ m}^{-1} \]

\[ k = 19.6 \times 10^9 \text{ m}^{-1} \]

A velocity in a direction isn't possible if the wavelength is already occupied by a distance between two atoms.

\[ \frac{p}{\hbar} = k < \frac{4\pi}{a} \]

\[ k = 2 \pi / \lambda \]

\[ p = \hbar * k \]

\[ p * \lambda = \hbar \]
Free Electrons for the metals in a Magnetic Field (Pauli paramagnetism $T \approx 0K$)

“The difference between paramagnetism and Pauli paramagnetism is that the latter applies to a metal because it describes the tendency of free electrons in an electron gas to align with an applied magnetic field.” Inna Vishik (Stanford)

Magnetic Spin – Susceptibility
Low temperature

$$\chi_p = \frac{M}{H} = \frac{3\eta e\mu_0\mu_B^2}{2E_F}$$

(Pauli Paramagnetism)

Titanium \hspace{1cm} \text{Pauli magnetic susceptibility ($\chi_{mol}$)} \hspace{1cm} 33.4 \times 10^{-6} \text{ cm}^3 / \text{mol}

Vanadium \hspace{1cm} \text{Pauli magnetic susceptibility ($\chi_{mol}$)} \hspace{1cm} 84.2 \times 10^{-6} \text{ cm}^3 / \text{mol}
Paramagnetism for free electrons.

Fermi gas of electrons without an external magnetic field. The electrons are free (no subshell)

1) The order of the Fermi kinetic energy is high $T \approx 10000$ K.
2) The reference temperature is $\approx 300$K.
3) The thermal energy can increase the kinetic energy only for a very small number of particles.
4) The spin of these particles is oriented in the sense that the external field.
5) The paramagnetism of Curie is created by these electrons. Do not forget the influence of thermal energy on the spin orientation

\[ \chi_{\text{Pauli}} \sim \chi_{\text{curie}} \left( \frac{T}{T_F} \right) \sim \chi_{\text{Pauli}} \propto 10^{-2} \]

\[ \rho(E) = \frac{8\sqrt{2} \pi m^{3/2}}{h^3} \sqrt{E} \]

\[ E_F \text{ (Fermi energy)} \]

\[ \rho(E) \text{ density of states} \]
Landau diamagnetism (1930) \( T \approx 0 K \)

1) A gas of free electrons in a magnetic field.
2) Free electrons move along spiral trajectories.
3) Lenz’s law.
4) Diamagnetic effect.
5) The energy of the free electrons depend of
   A) The kinetic energy (limited by the energy of Fermi).
   B) The quantification of the energy created by the circular movement of the electrons

\[
\chi_{Landau} = -\frac{\chi_{Pauli}}{3}
\]

Titanium \hspace{1cm} \textbf{Landau diamagnetic susceptibility (}\chi\text{mol)} \hspace{1cm} -11.1 \times 10^{-6} \text{ cm}^3/\text{mol}

Vanadium \hspace{1cm} \textbf{Landau diamagnetic susceptibility (}\chi\text{mol)} \hspace{1cm} -28.6 \times 10^{-6} \text{ cm}^3/\text{mol}
Landau diamagnetism $T \approx 0K$

Fermi gas of electrons without an external magnetic field.

$E$ (kinetic energy)

$T_K = 0$

$\rho(E) = \text{density of states}$

$\frac{5}{2} \omega_c$

$\omega_c = \frac{e H}{mc}$

Cyclotron frequencies

Fermi gas of electrons with an external magnetic field.

The oscillations are impossible

$E_F$ (Fermi energy)

$E_F = \text{Fermi energy}$

Scan in energy when we modify $B$
Haas-van Halphen effect (1930) \( T \approx 0K \)

1) The cyclotron frequencies increase with the magnetic field.
2) The diamagnetic field increase with the energy.
3) The diamagnetic field stopped with the \( E_F \).
4) The diamagnetic field increase again with the next cyclotron frequency.
Ferromagnetism Fermi gas (Solid state physics)

\[ T_K = 300 \]

\[ B_{ext} = 0 \]
Ferromagnetism Stoner model (1938)

1) The molecular field magnetizes the electron gas due to the Pauli paramagnetism (bootstrapping mechanism) without external magnetic field.
2) \( \delta n \downarrow \) are flip in \( \delta n \uparrow \) sub-band close \( E_F + \delta E \).
   The number of electrons moved is \( \delta n \uparrow \).
3) The potential energy \( \Rightarrow \Delta E_{pot} = - \frac{1}{2} U g(E_F) \delta E^2 \)
4) Kinetic energy cost \( \Rightarrow \Delta E_{kin} = \frac{1}{2} g(E_F) \delta E^2 \).
4) \( \Delta E_{kin} + \Delta E_{pot} < 0 \)

\( U \, g(E_F) \geq 1 \) “Stoner criterion”
Brillouin-Langevin paramagnetism

1) Each atom is independent.
2) For each atom, the total magnetic moment $\mu_J$ (orbitals + spin) is the same for each atom. It is calculated with the quantum mechanics.
3) We use the Z axis as reference.
4) The distribution of the magnetic moments obey to the Boltzmann distribution.
5) We calculate $\sum \mu_Z$.
6) We find the magnetisation $\frac{\sum \mu_Z}{\text{Volume}}$

$$\mu_J = g_J \mu_b$$

$$\mu_z = g_J m \mu_b$$

In quantum mechanics the number of orientations is limited
Paramagnetism

1) The valence electrons are located in the 3d subshell and 4S.
2) The number of electrons with the same spin orientation is limited.

**Remark:**

Electronegativity is a chemical property that describes the tendency of an atom to attract electrons.


http://www.periodictable.com/
Langevin–Larmor diamagnetism

\[
\chi \approx -0.99 \times 10^{-5} Z \sum_{i=1}^{Z} \frac{1}{Z} \langle 0 \left| \frac{r_i^2}{a_0^2} \right| 0 \rangle
\]

\[\approx \text{Borh radius}\]

\[\approx \text{Atom radius}\]

1) The number of electrons with the same spin orientation is limited.
2) The external field modifies the external orbit.
3) By the law Lenz the electrons create a magnetic field in opposition with the external field.
4) The diamagnetism is localized in the atoms.

### Copper
- **Electrical resistivity**: 16.78 nΩ·m (at 20 °C)
- **Electronegativity**: Pauling scale: 1.90
- **Magnetic susceptibility**: \(-6.86 \times 10^{-11}\) m\(^3\)/mol

### Zinc
- **Electrical resistivity**: 59.0 nΩ·m (at 20 °C)
- **Electronegativity**: Pauling scale: 1.65
- **Magnetic susceptibility** (\(\chi_{\text{mol}}\)): \(-1.45 \times 10^{-10}\) m\(^3\)/mol

### Element

<table>
<thead>
<tr>
<th>Element</th>
<th>4s</th>
<th>3d</th>
<th>4p</th>
<th>Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>↑↓</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diamagnetic

http://www.periodictable.com
Van Vleck paramagnetism

1) The diamagnetism exist for all the transition metals.
2) It increase with the number of electrons.
3) It is independent of the temperature
4) First order perturbation, we stay on the ground level
5) Energy level = ground level + perturbation.

\[ \chi_{\text{dia}} \approx -Z \frac{\mu_0 q^2}{6 m_e} \sum_{i=1}^{Z} \langle 0 | r_i^2 | 0 \rangle + Z \frac{\mu_0 q^2}{8 m_e B^2} \sum_{m=1}^{k} \frac{|\langle 0 | r_i^2 | m \rangle|^2}{E_m - E_0} \]

Mean value or expected value

Expected value

Ground energy level (B=0)

If the perturbation is sufficiently large, the Van Vleck paramagnetism represent the probability that the expected value of the perturbation modify \( \chi_{\text{dia}} \) if the perturbation is sufficient to go until a new high energy level.
Ising model (1925)

\[ H = - \sum_{N>i>i} J_{ij} S_i^Z S_j^Z - g \mu_B m^Z \sum_i S_i^Z \]

neighbor-interaction
(ferromagnetic or antiferromagnetic coupling)

interaction with the external magnetic field

\[ \sigma = +1 \text{ spin up} \]
\[ \sigma = -1 \text{ spin down} \]

1) Random “perturbation” for blue spin (energy \( \Omega = H_a \))
2) We consider all the green spin and we calculate the change for \( H = H_b \)
3) If \( H_b < H_a \), we conserve the sense
4) If \( H_b > H_a \), we choose a random number \( x \) between 0 and 1 is drawn and then the spin tilting is performed if the condition is verified and should be as high as possible, then transition is accepted.
5) The system wants to minimize \( F = E - TS \).

\[ \exp \left( -\frac{H_b - H_a}{k_B T} \right) \geq x \]

configuration \( \Omega \)
Ferromagnetism exchange interaction (1928)

1) The particles are indistinguishable and a wave function is attached to the particles.
2) We have a difference in energy between the bonding and antibonding.
3) If the wave function is symmetric the spin function is antisymmetric and reciprocally.
4) The fundamental link between the principle of exclusion of Pauli and electrostatic energy.

\[ \hat{H} = -2 \sum_{<i,j>} J_{ij} \vec{S}_i \cdot \vec{S}_j \]

\[ J = \frac{E_S - E_a}{2} \]

- \( J > 0 \) \( \Rightarrow \) antibonding \( \Rightarrow \) ferromagnetism
- \( J < 0 \) \( \Rightarrow \) bonding \( \Rightarrow \) antiferromagnetism
The span in energy of the band valence increase when the distance between the atoms decrease. The gas of electrons have more space and thus the opposite spin are possible.
Ferrimagnetism (molecular quantum)

Magnetite ($Fe_3O_4$)

Oxygen atoms (small sphere in red)  
$Fe^{2+}$ (tetrahedral sphere in blue), $Fe^{3+}$ (octahedral sphere grey)
Valence Bond Theory (molecular physic)

**Hybridisation**: the concept of mixing atomic orbitals to form a new hybrid orbitals.

Suitable for the qualitative description of atomic bonding properties.

Example: $sp^3$ orbitals.

Linus Pauling
<table>
<thead>
<tr>
<th>Atome</th>
<th>Symbole</th>
<th>État Physique</th>
<th>Complexe Actinides</th>
<th>Métaux de Trans</th>
<th>Métaux de transit</th>
<th>Post-transit</th>
<th>Métaux alcalins</th>
<th>Métaux alcalino-terreux</th>
<th>Non-métaux</th>
<th>Halogènes</th>
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<tbody>
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</tbody>
</table>

Les masses atomiques entre parenthèses sont celles de l'isotope le plus stable ou le plus commun.