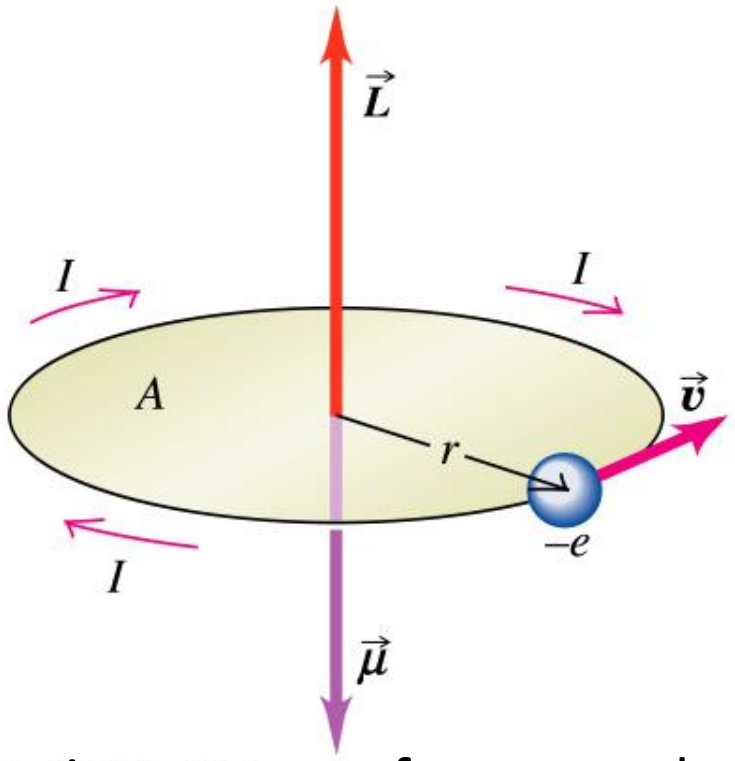
Borh magneton

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



$$i = -\frac{e}{T} = -\frac{e\,v}{2\pi r} \qquad A = \pi r^2$$

$$\mu = -\frac{e\,v}{2\pi}\pi r^2 = -\frac{e\,v\,r\,m_e}{2\,m_e} \qquad \hbar = v\,m_e\,r$$

For the electron:

$$\mu_b = \frac{e\hbar}{2m_e} = 9.274\,10^{-24}\,\frac{J}{T}$$

$$\mu_b = \frac{e\hbar}{2m_e} = 5.788\,10^{-5}\,\frac{eV}{T}$$

Magnetic moment of a current loop:

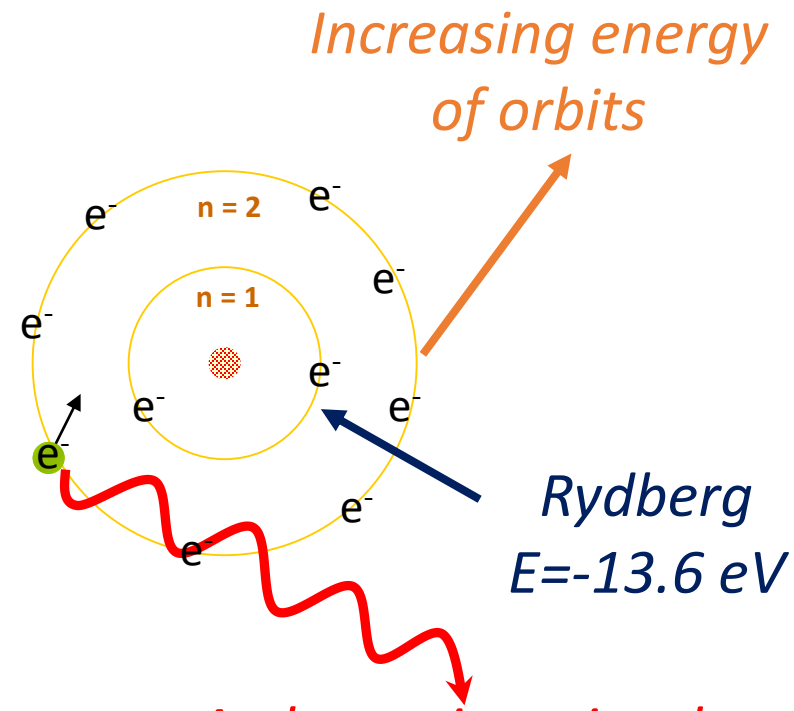
$$|\mu| = iA$$

current — area enclosed by current loop

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

Rutherfod (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 f



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

Photon energy → $E = h\,\nu$ Einstein (1905)

Borh radius

$$a_0 = \frac{\hbar^2}{m_e k e^2} = 52.97\ pm$$

Subshells Schrödinger (1922)

Subshell very important to capture or loss an electron

Subshell very important for the ligands

Subshell very important for the metals

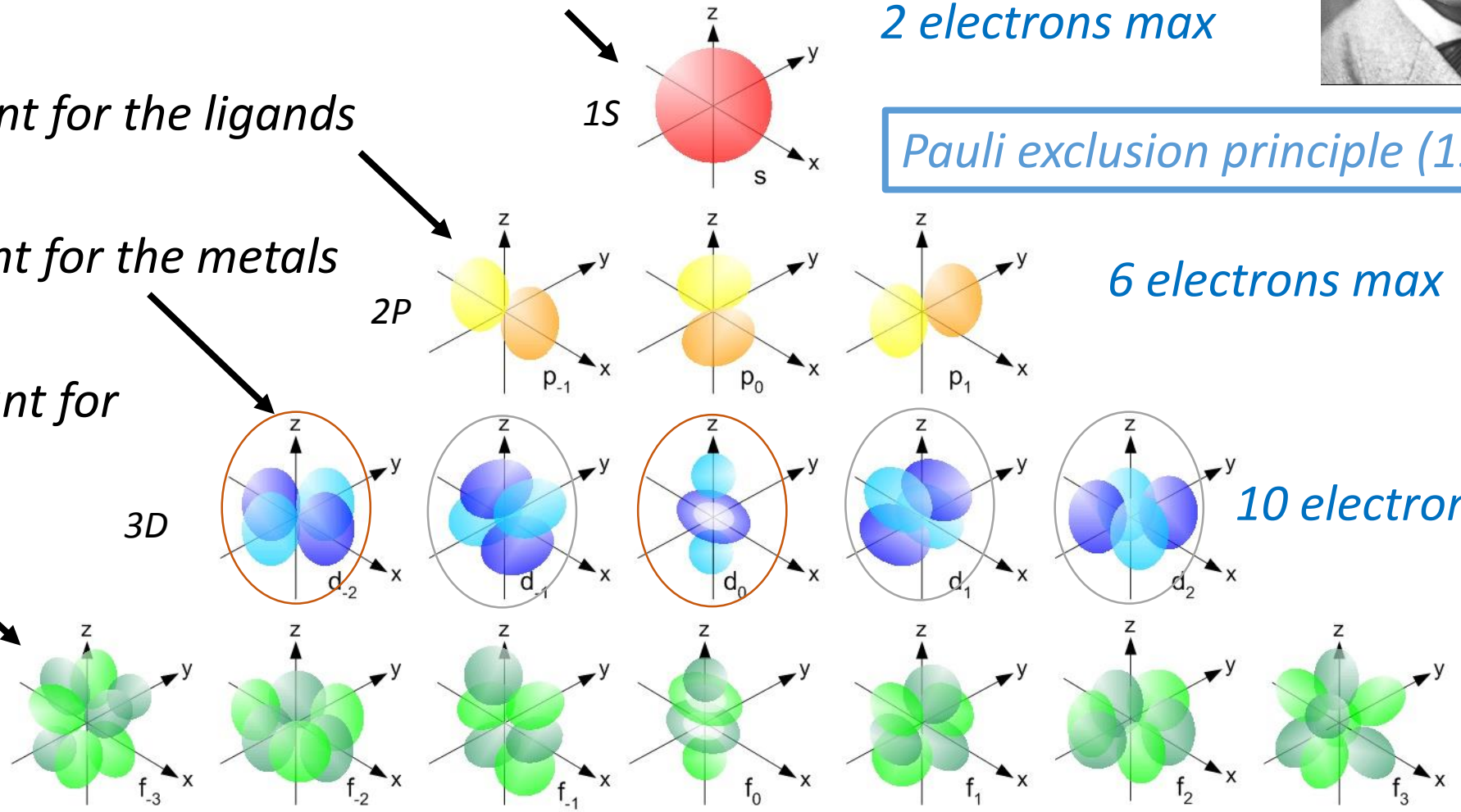
Subshell very important for rare earths

1S — *2 electrons max*

2P — *6 electrons max*

3D — *10 electrons max*

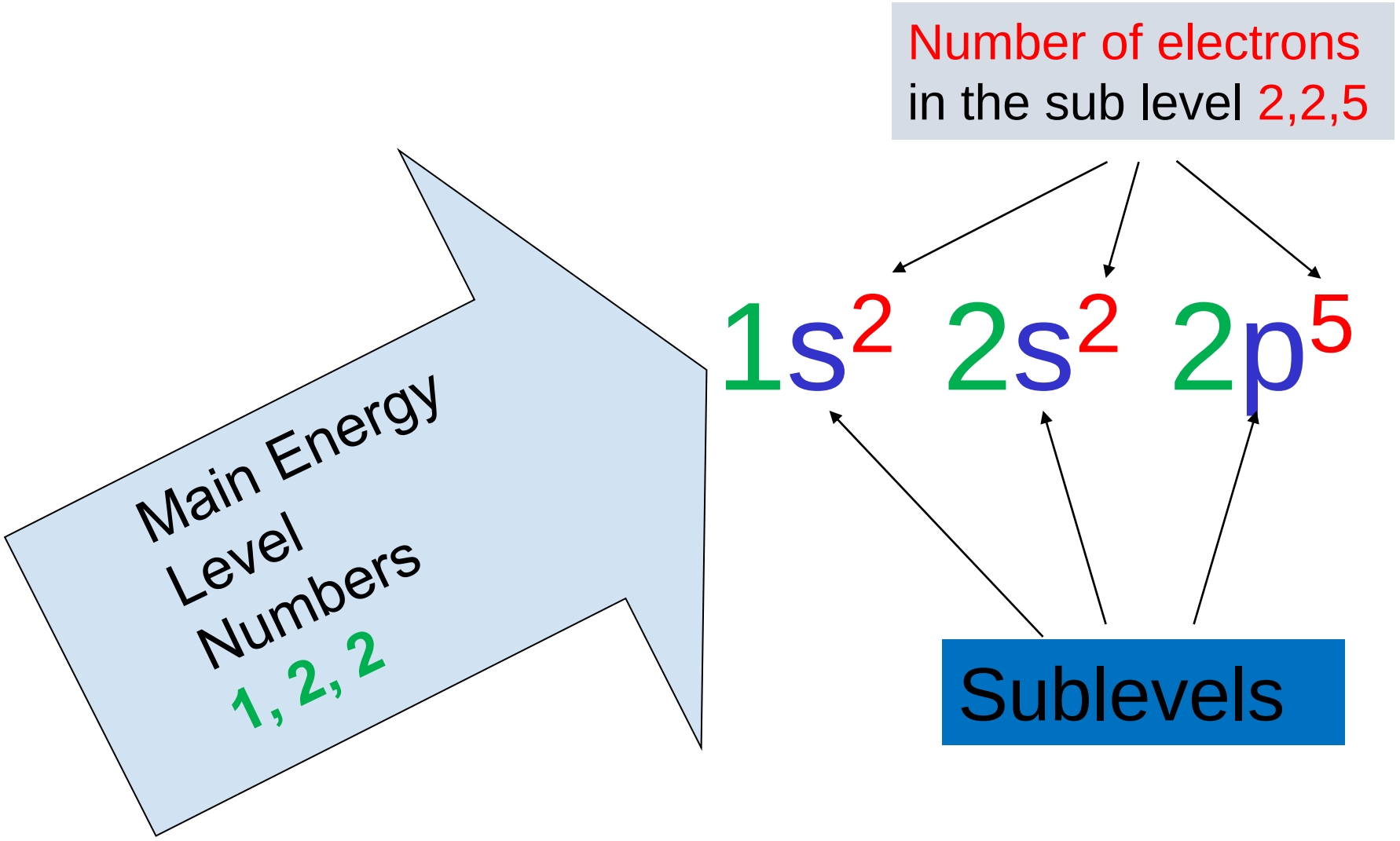
4F — *14 electrons max*



Pauli exclusion principle (1925)

Caution: This presentation is valid for isolated atoms only.

Standard Notation of Fluorine

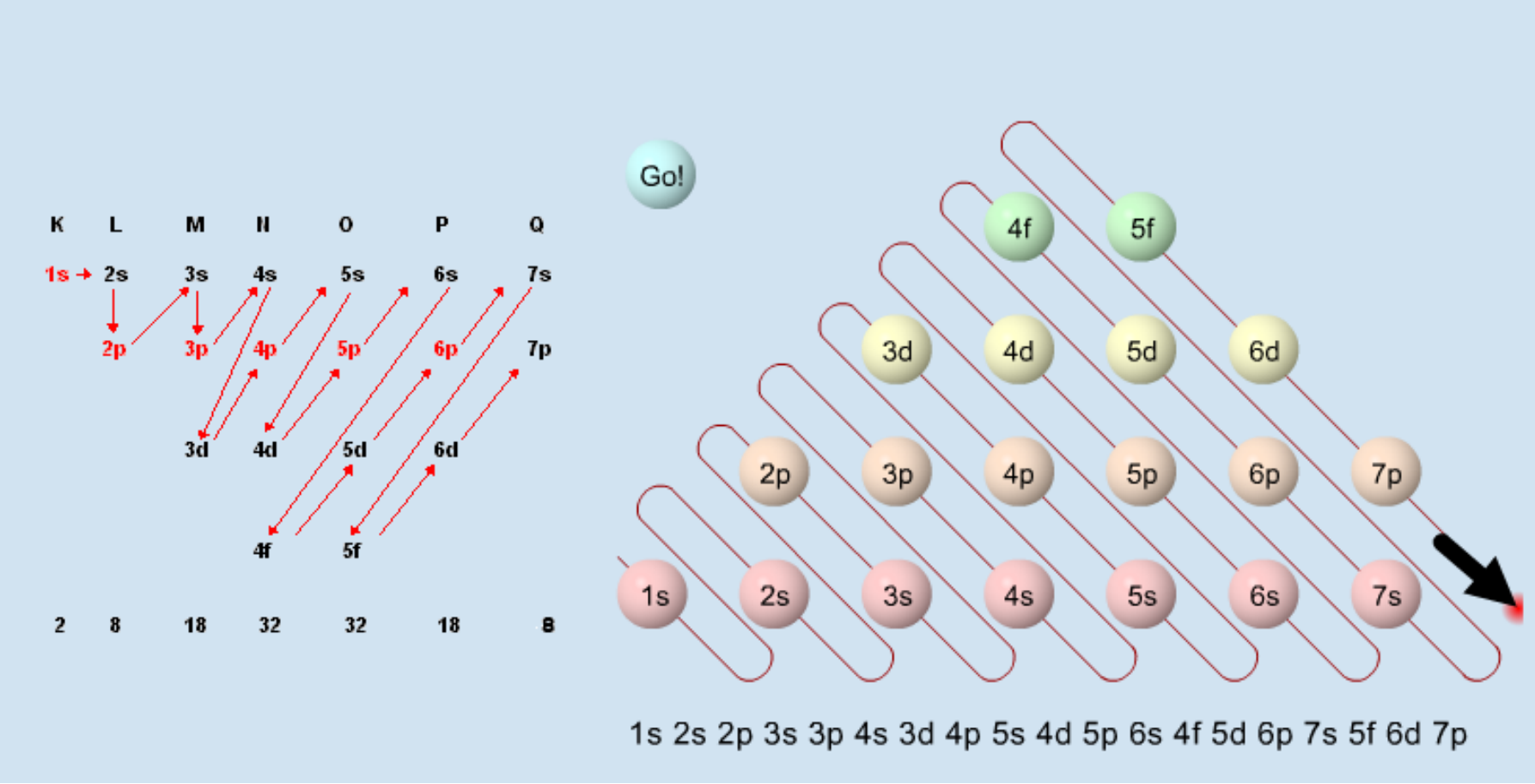


Hund's rule

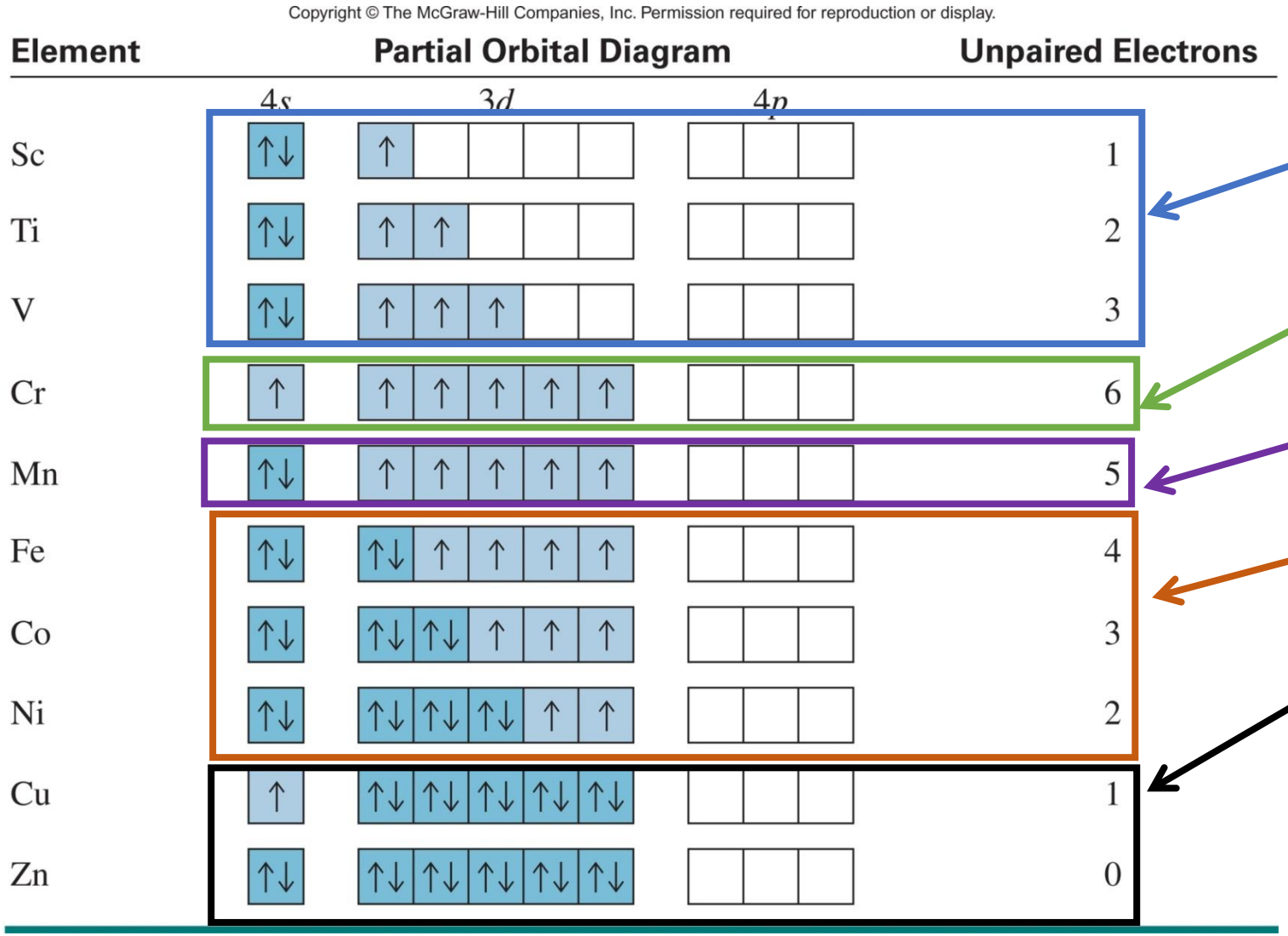
Orbital Filling Order (Diagonal Rule).

It is a semi-empirical law with exceptions case

Minimize the coulomb interaction + Pauli exclusion principle.



Orbital occupancy for the transition metals



Paramagnetic

Antiferromagnetic !!!!
Néel temperature

Antiferromagnetic
Néel temperature

Ferromagnetic

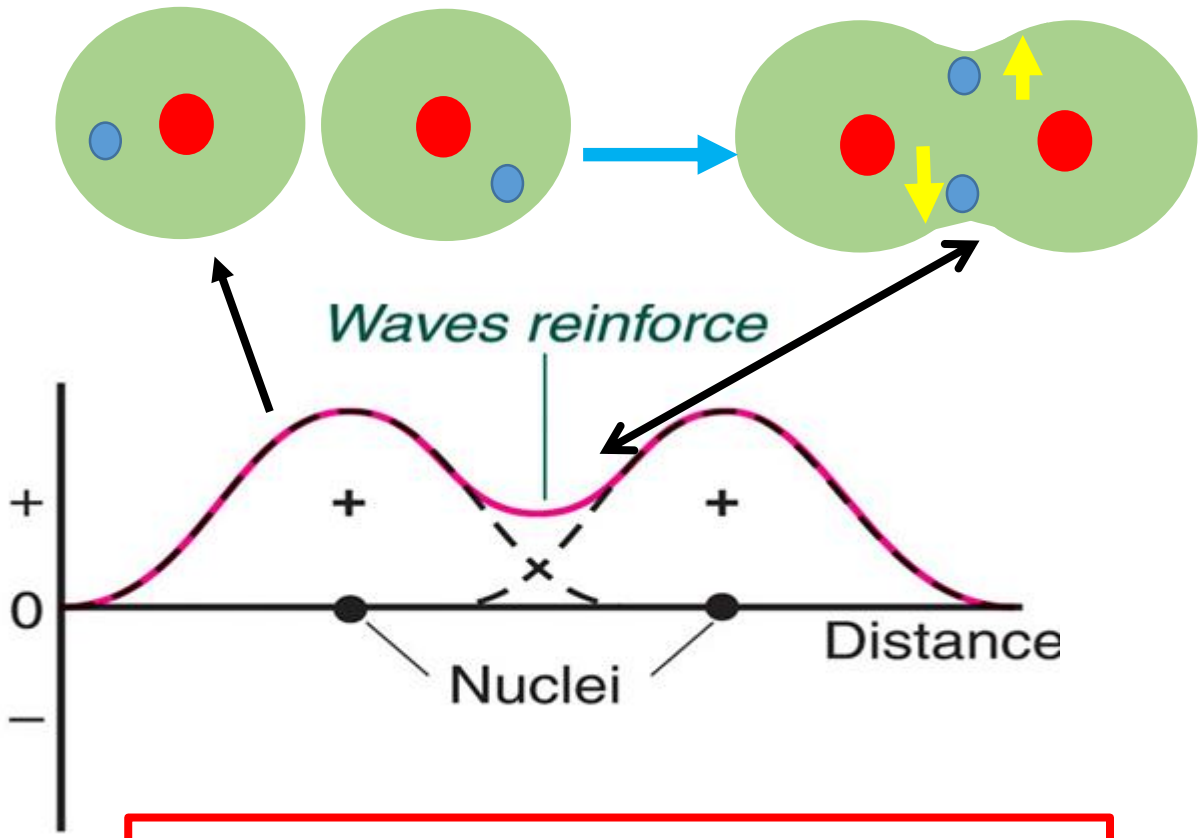
Diamagnetic

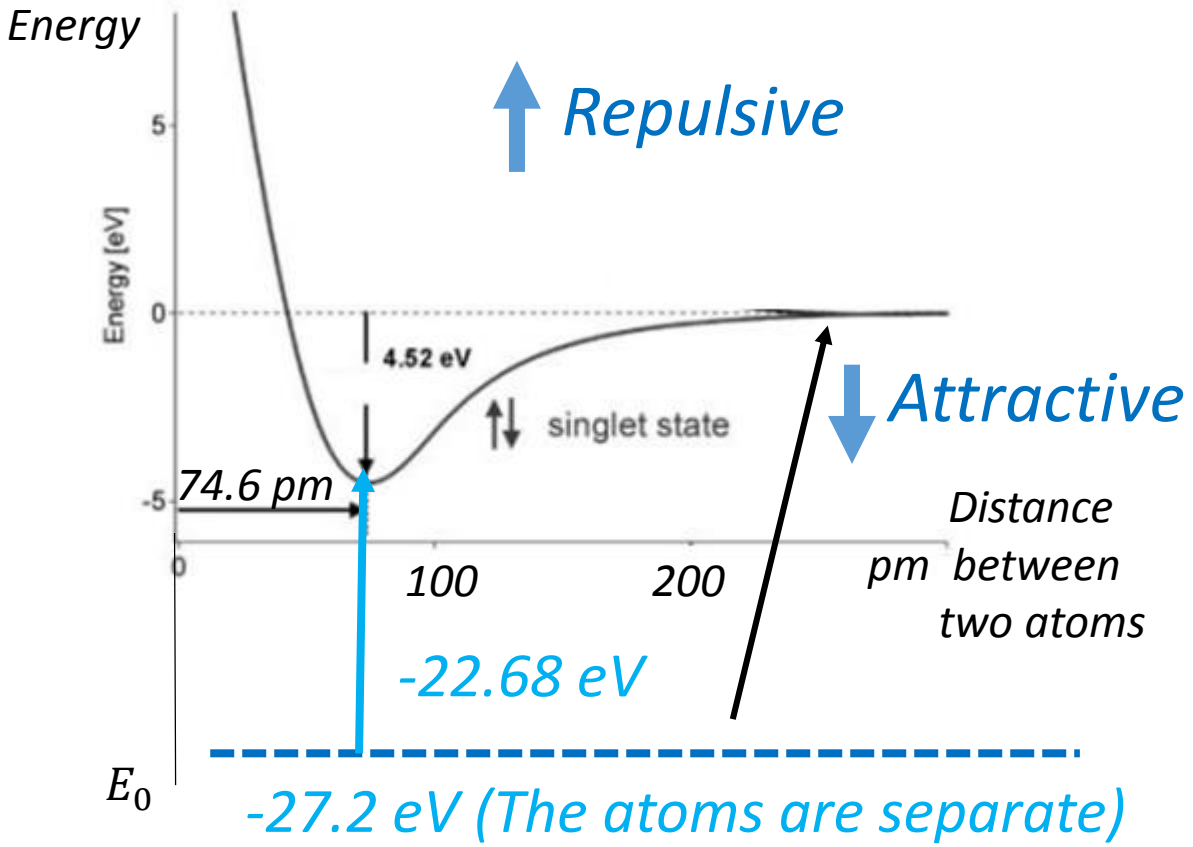
Remark:
the electrons are not linked
inside the subshells of the atoms

Caution: This presentation is valid for isolated atoms only.

Orbital model for H_2

Bonding



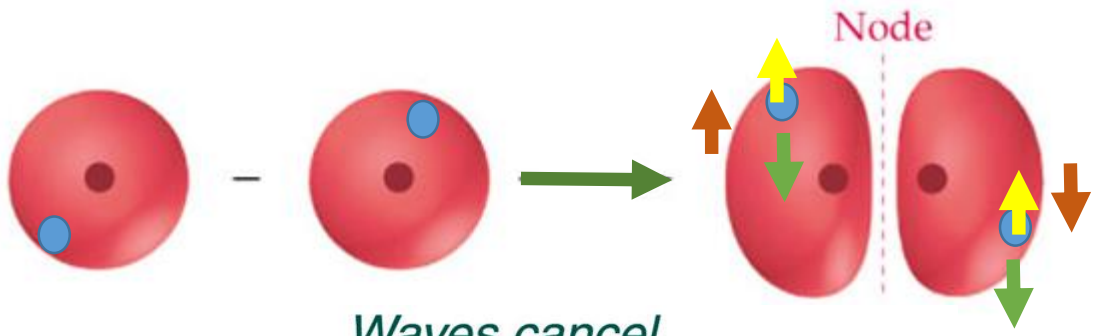


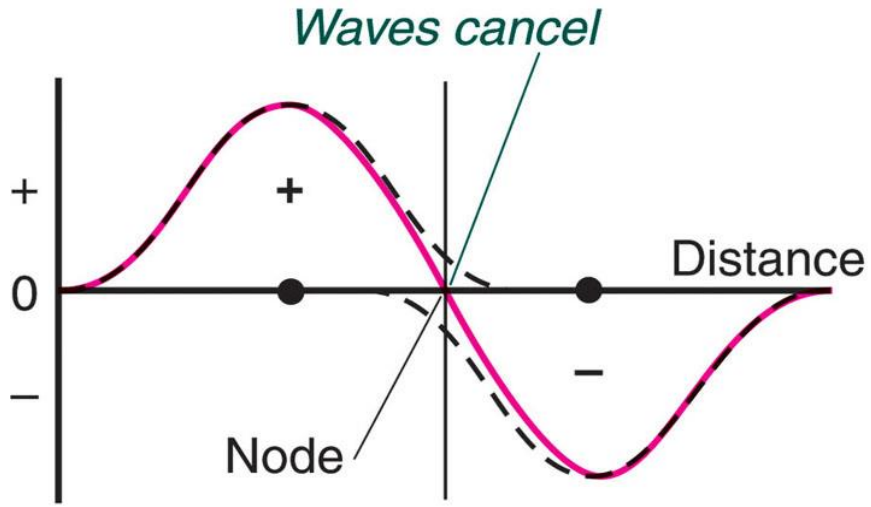
Pauli exclusion principle forbid the same spin orientation.

symmetric for the waves, antisymmetric for the spin

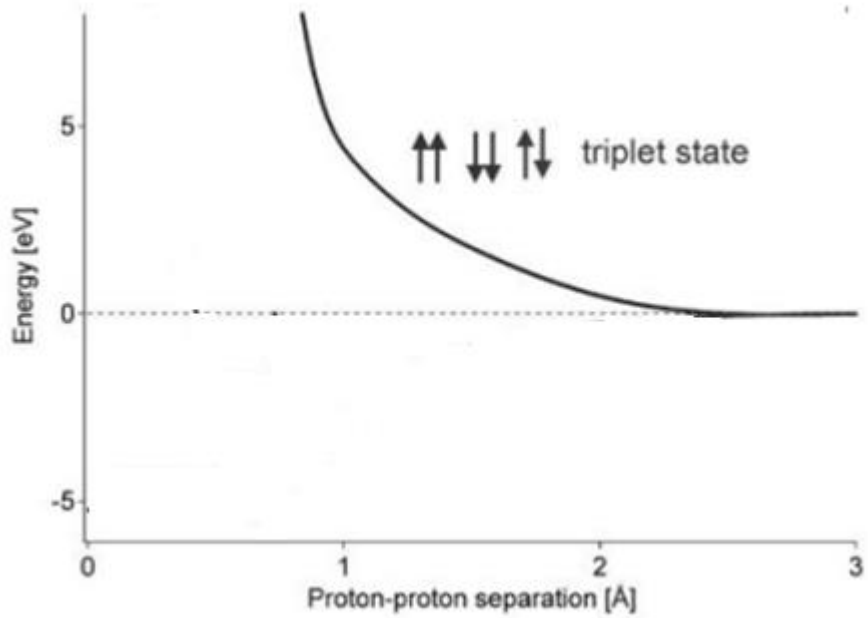
Orbital model for H_2

Antibonding





Antibonding
Not stable (Coulomb repulsion between protons)



Two different orbits 1S allow the same spin orientation.

symmetric for the spin, antisymmetric for the waves

Band theory (Solid state physics)

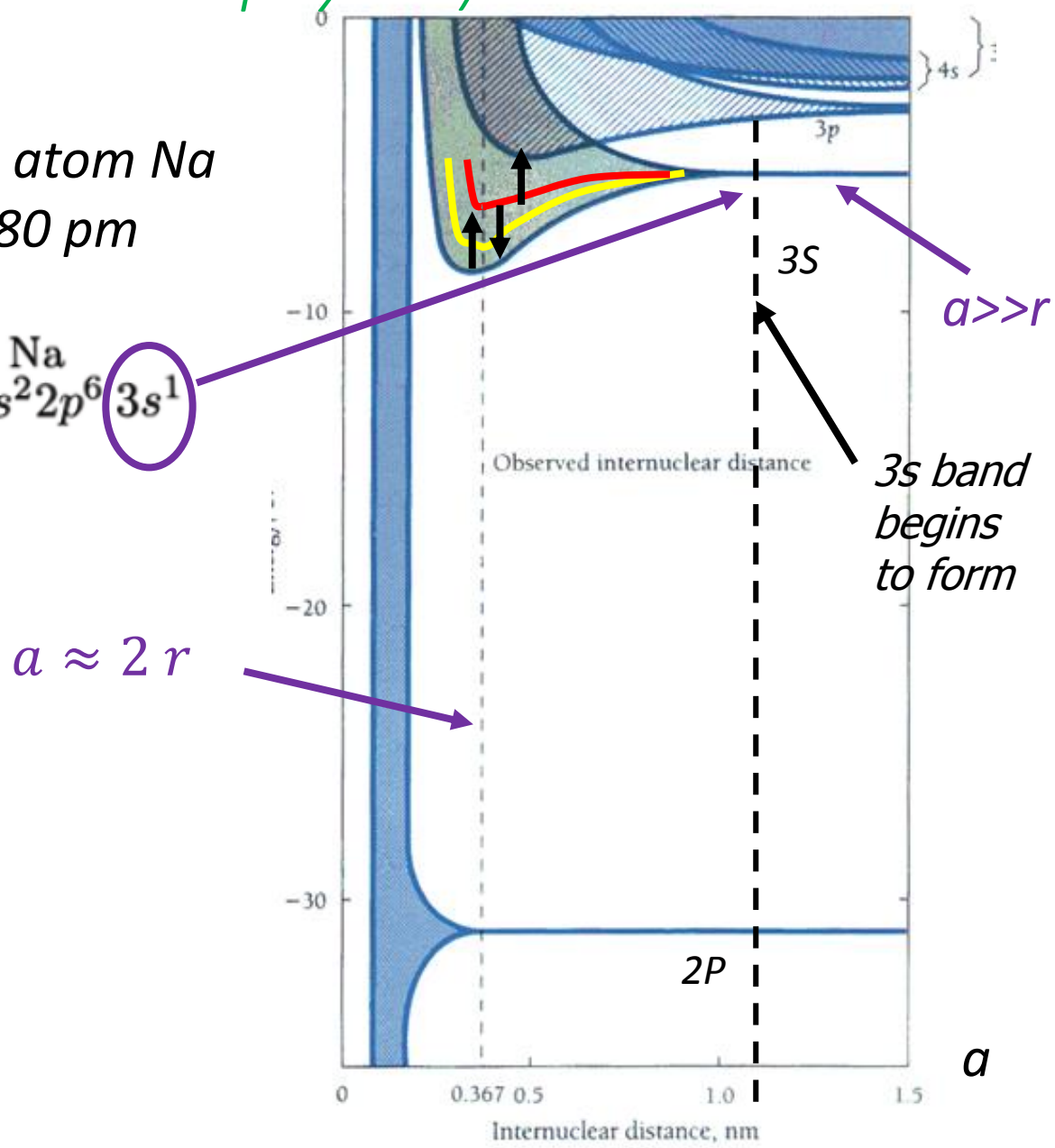
Now let's take a closer look at the energy levels in solid sodium. Remember, the 3s is the outermost occupied level.

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.*

Radius atom Na = 180 pm

Na
$1s^2 2s^2 2p^6 3s^1$



a>>r

3s band begins to form

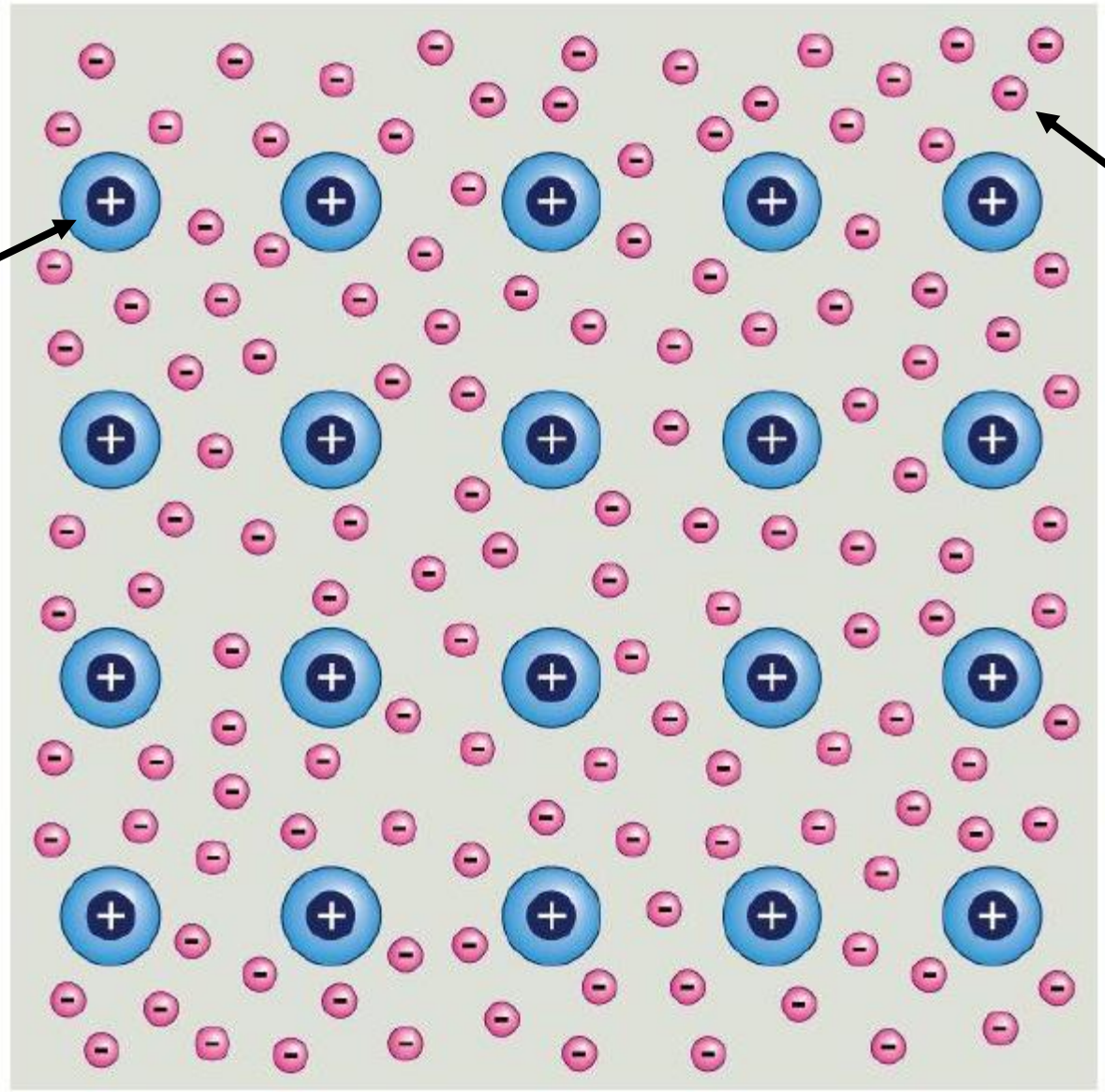
$a \approx 2\,r$

a

Internuclear distance nm

Sommerfeld model of free electrons (1928)

Nucleus
+ all the electrons
with the orbitals full.



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

Sommerfeld model of free electrons (1928)

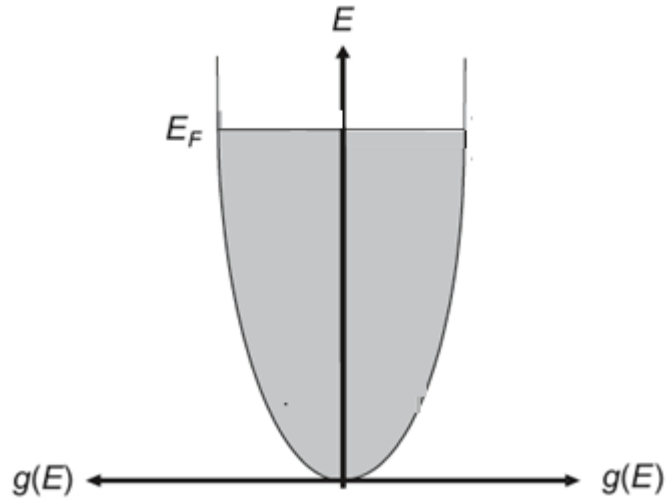
1) We are in the non relativist case.

2) We don't consider the full subshells $\Sigma L_i=0$ *and* $\Sigma S_i=0$ *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)

$$\Delta p * \Delta r \geq \hbar/2$$

1)*The Pauli exclusion principle and the uncertainty principle limit the number of electrons with a low velocity.*

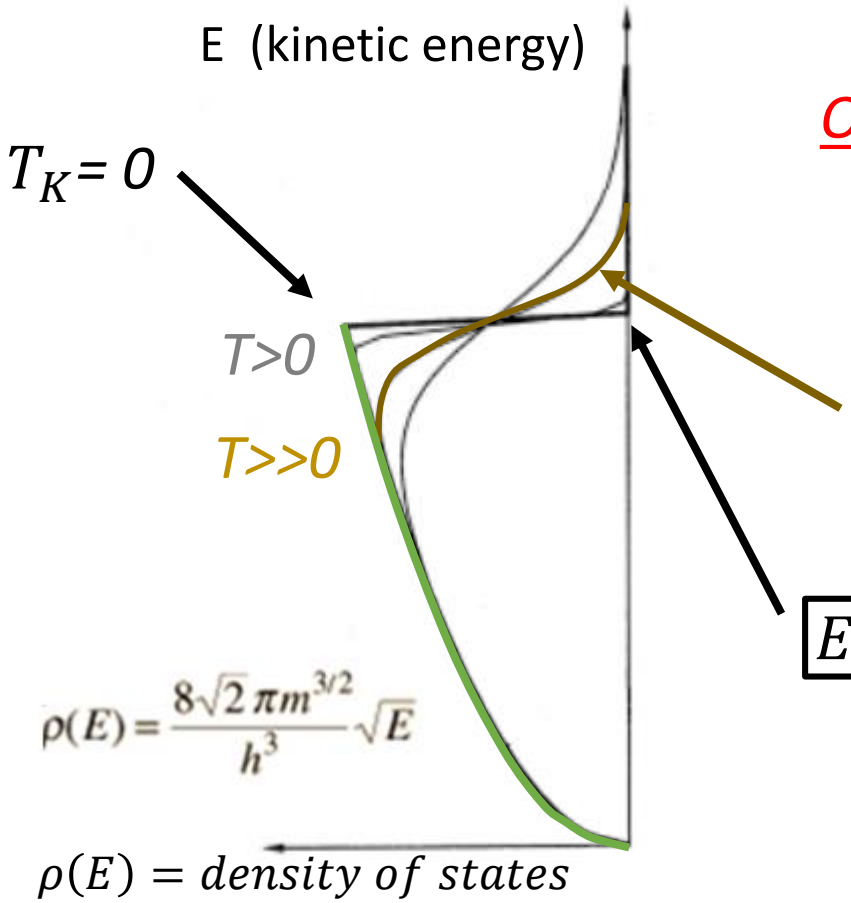
2) If you increase the number of electrons , you must increase their velocity because all the states with a lower energy are busy…

Fermi-Dirac distribution (Sommerfeld model)

- *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.

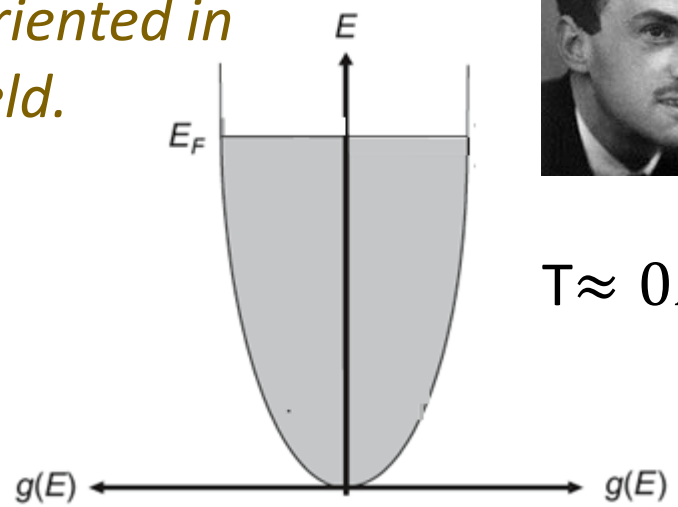
Only the free electrons near the Fermi are sensitive to the temperature (Fermi-Dirac distribution).



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

$E_F\ (Fermi\ energy)$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 \eta_e\right)^{2/3}$$

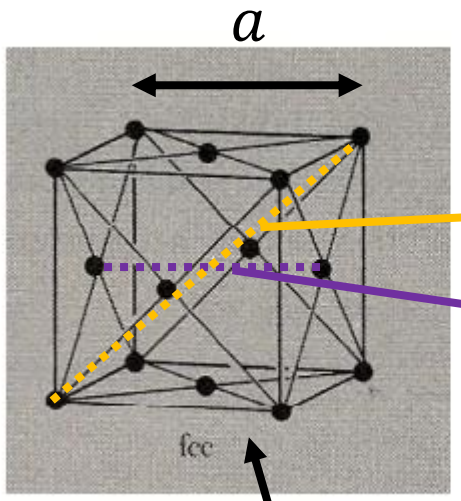


$T \approx 0K$

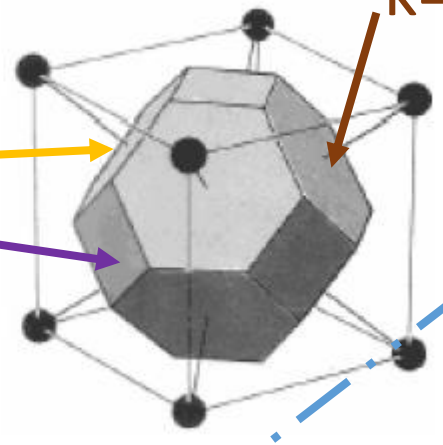
Fermi Parameters for some metals (Sommerfeld model)

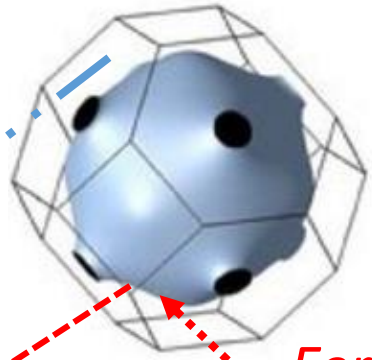
Element	Molar volume	electrons	density	Fermi energy calculated	Fermi temperature	Fermi velocity	electrons cm-3
	m^3/mol		g/cm^3	E_F[eV]	T_F[10^3K]	10^8 cm^{-1}	
Scandium	15,00×10-6	21	2.985	6.6	7.7		4.01 10^22
Titanium	10,64×10-6	22	4.506	8.745	10.15		5.67 10^22
Vanadium	8,32×10-6	23	6.01	10.36	12		7.20 10^22
Chromium	7,23×10-6	24	7.19	11.64	13.51		8.33 10^22
manganese	7,35×10-6	25	7.31	10.9	12.7	1.96	8.19 10^22
Fe	7,09×10−6	26	7.874	11.15	12.94	1.98	8.49 10^22
Co	6,67×10-6	27	8.9	11.7	13.58	2.03	9.01 10^22
Ni	6,59×10-6	28	8.902	11.74	13.62	2.03	9.14 10^22
Cu	7,11×10-6	29	8.96	7.04	8.17	1.57	8.47 10^22
Zn	9,16×10-6	30	7.14	9.47	10.9	1.82	6.57 10^22

Fermi surface for Ag Bloch model 1946



Crystalline structure for Ag



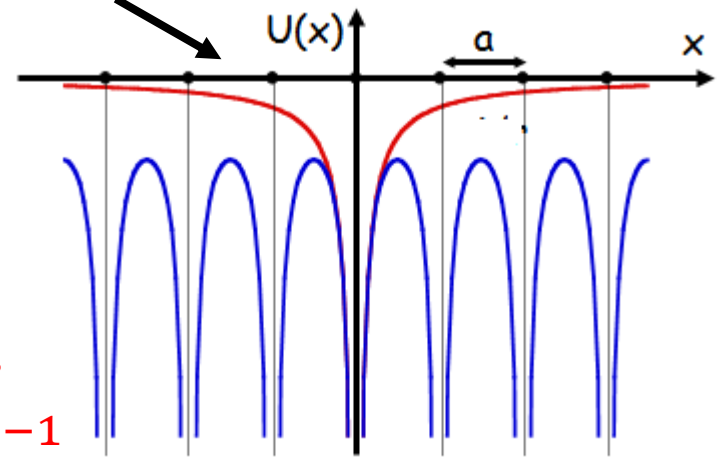


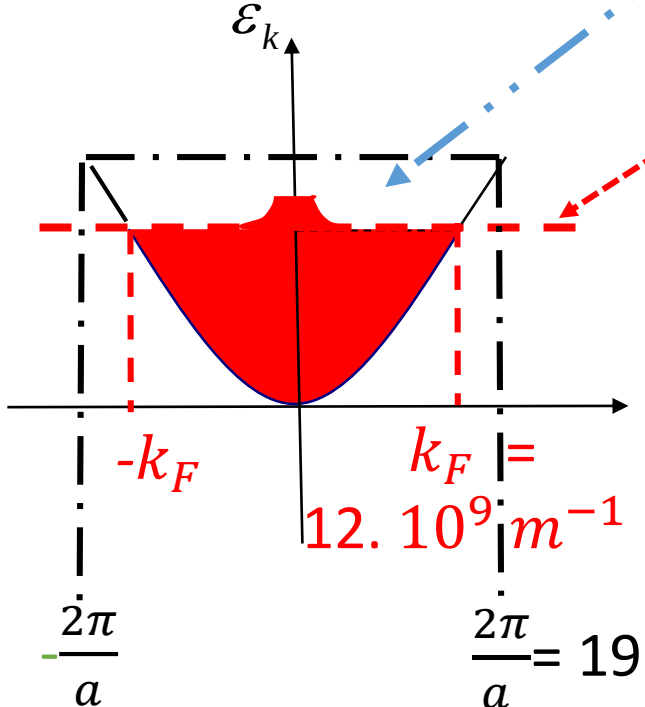
Fermi surface

k_F= 12. $10^9\ m^{-1}$

Atomic nucleus

k= $\frac{4\pi}{a}$ = 39.2 $10^9 m^{-1}$





$p * \lambda = h$

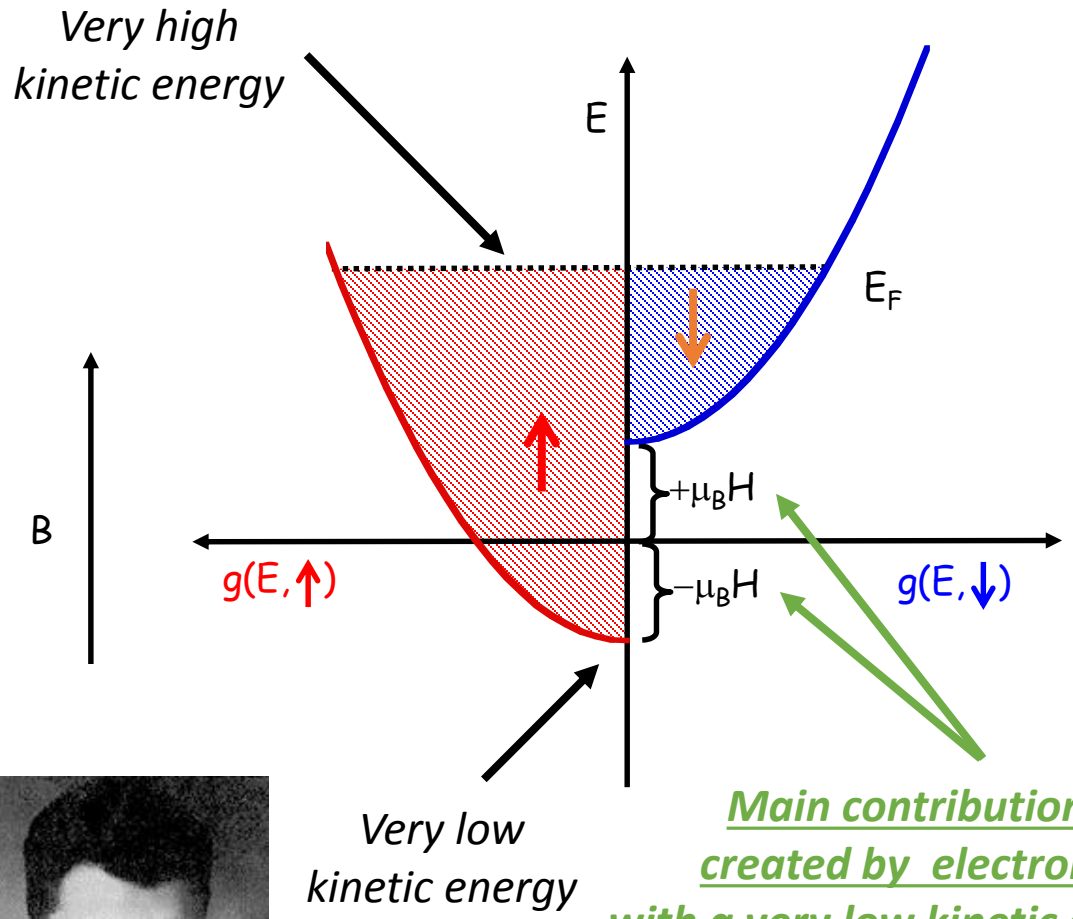
$p = \hbar * k$

$k = 2\ \pi/\lambda$

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

$\frac{p}{\hbar}$ = k< $4\pi/a$

Free Electrons for the metals in a Magnetic Field (Pauli paramagnetism T ≈ 0K)



Main contribution created by electrons with a very low kinetic energy

"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 (Standford)

Magnetic Spin – Susceptibility
Low temperature

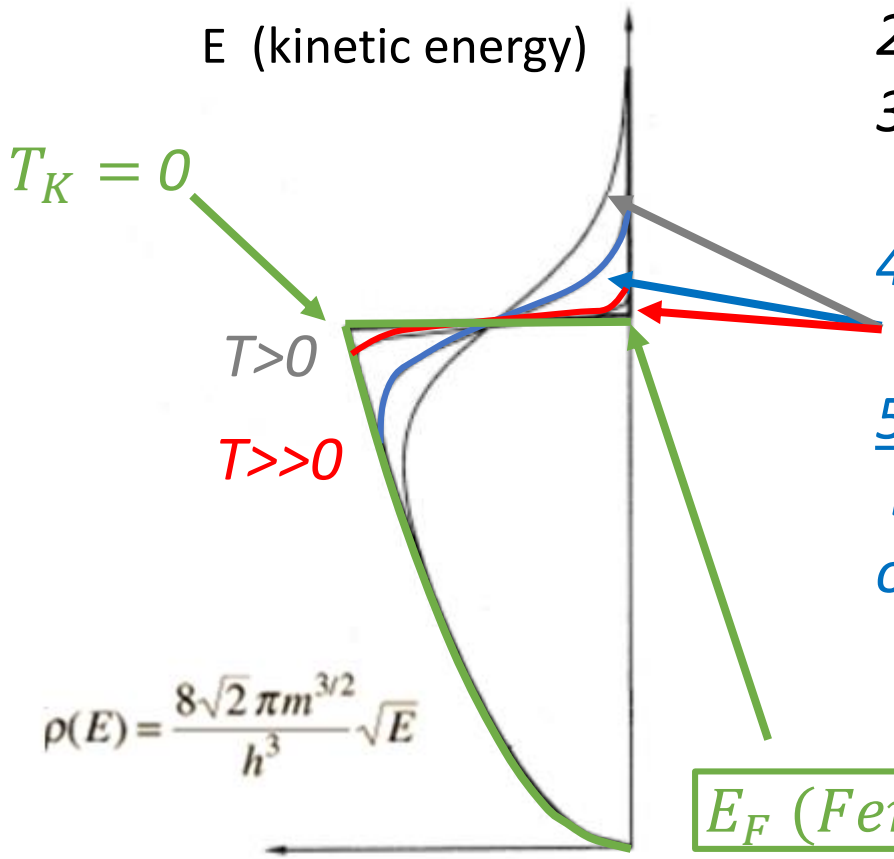
$$\chi_P = \frac{M}{H} = \frac{3\eta_e \mu_0 \mu_B^{\ 2}}{2E_F}$$

(Pauli Paramagnetism)

Titanium	Pauli magnetic susceptibility (χmol)	$33.4\ 10^{-6}\ cm^3/mol$
Vanadium	Pauli magnetic susceptibility (χmol)	$84.2\ 10^{-6}\ cm^3/mol$

Paramagnetism for free electrons.

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



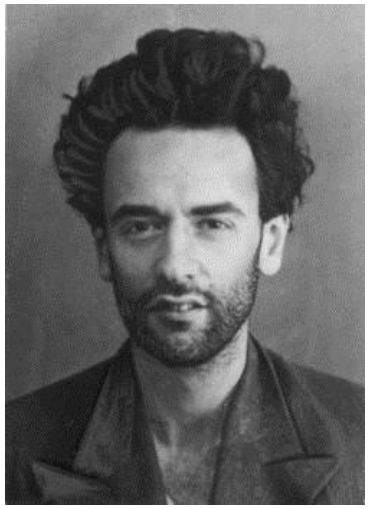
1) The order of the Fermi kinetic energy is high T ≈10 000 K.
2) The reference temperature is ≈ 300K.
3) The thermal energy can increase the kinetic energy only for a very small number of particles.
4) The spin of these particles is oriented in the sense that the external field.
5) The paramagnetism of Curie is created by these electrons.
Do not forget the influence of thermal energy on the spin orientation

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

T≈ 0K

T≈ 300K

Landau diamagnetism (1930) T≈ 0K



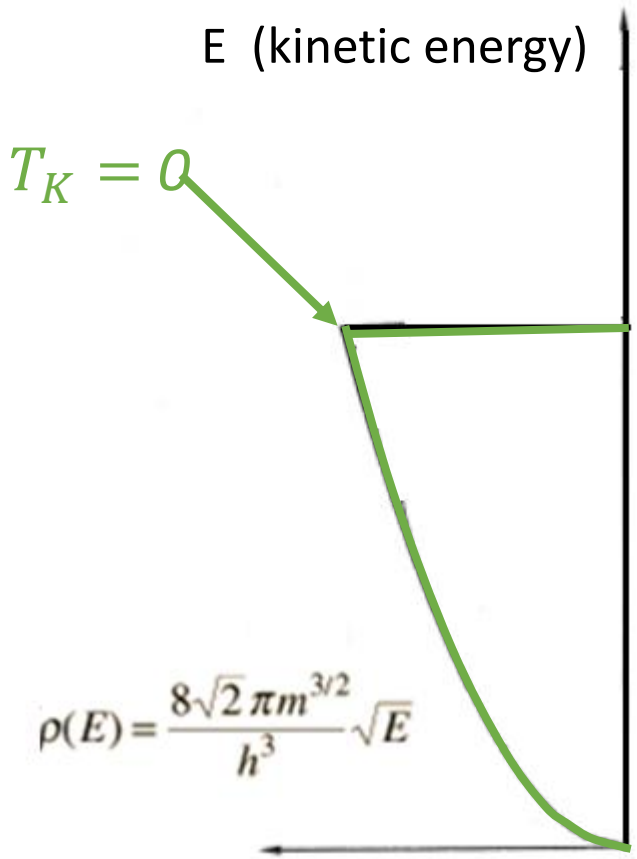
1) A gas of free electrons in a magnetic field.
2) Free electrons move along spiral trajectories.
3) Lenz's law.
4) Diamagnetic effect.
5) The energy of the free electrons depend of
A) The kinetic energy (limited by the energy of Fermi).
B) The quantification of the energy created by the circular movement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

$$\chi_{Landau} = -\frac{\chi_{Pauli}}{3}$$

Titanium	*Landau diamagnetic susceptibility (χmol)*	$-11.1\ 10^{-6}\ cm^3/mol$
Vanadium	*Landau diamagnetic susceptibility (χmol)*	$-28.6\ 10^{-6}\ cm^3/mol$

Landau diamagnetism $T \approx 0K$

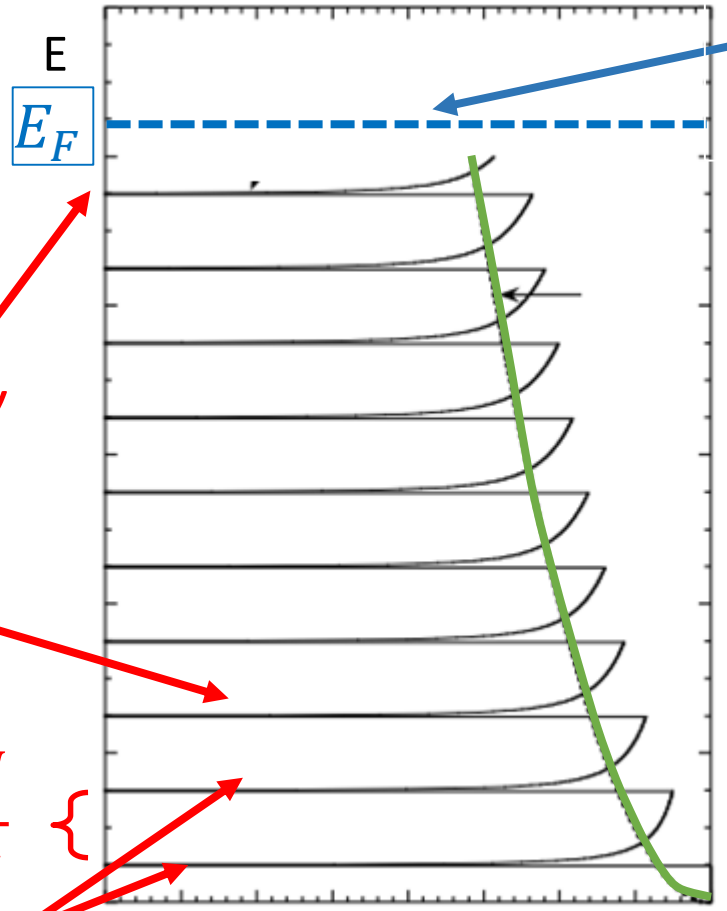
Fermi gas of electrons without an external magnetic field.



$\rho(E) = density\ of\ states$

Fermi gas of electrons with an external magnetic field.

The oscillations are impossible



Kinetic energy + oscillator energy

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

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

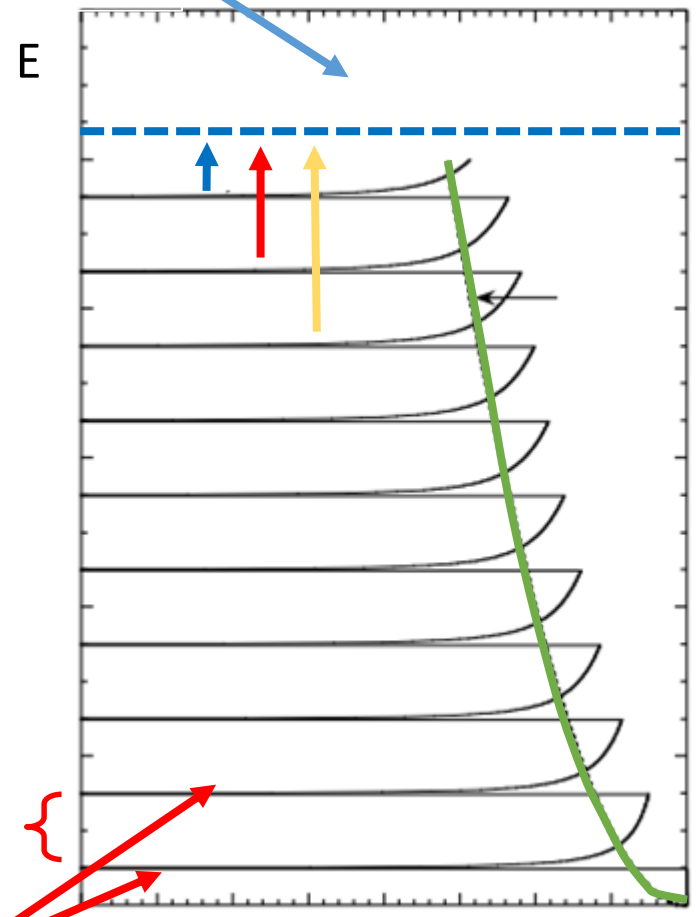
Cyclotron frequencies

$\rho(E) = density\ of\ states$

Scan in energy when we modify B

Haas-van Halphen effect (1930) $T \approx 0K$

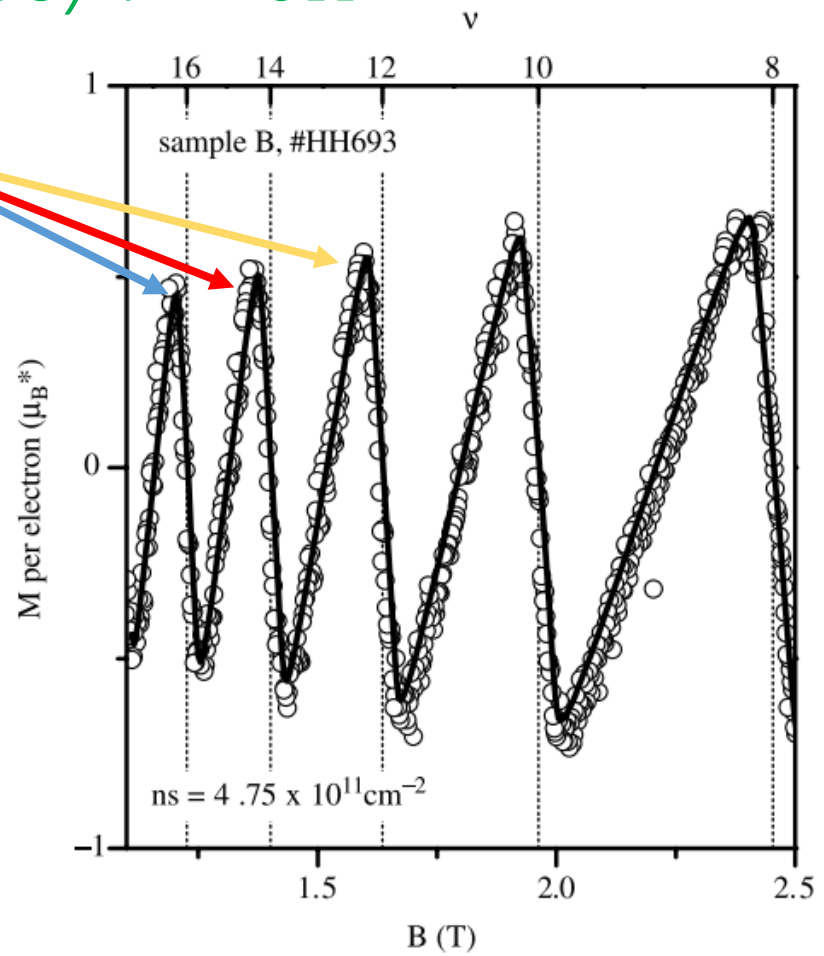
These frequencies are impossible



$\omega_c \uparrow if\ H \uparrow$

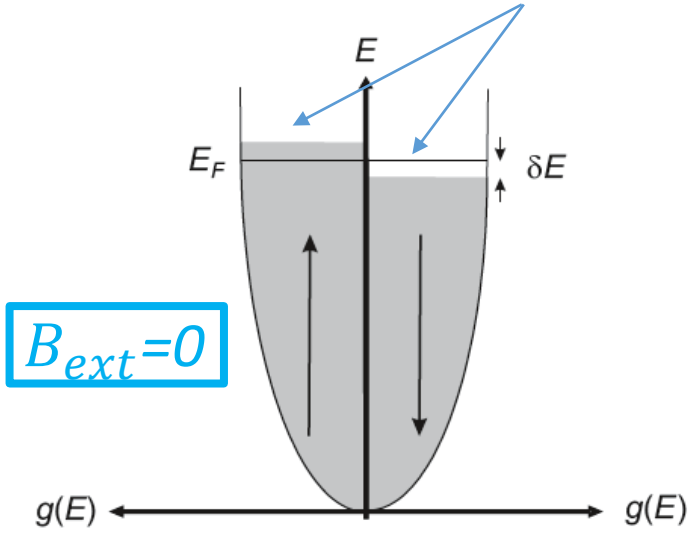
$$\omega_c = \frac{e\,H}{mc}$$

Cyclotron frequencies

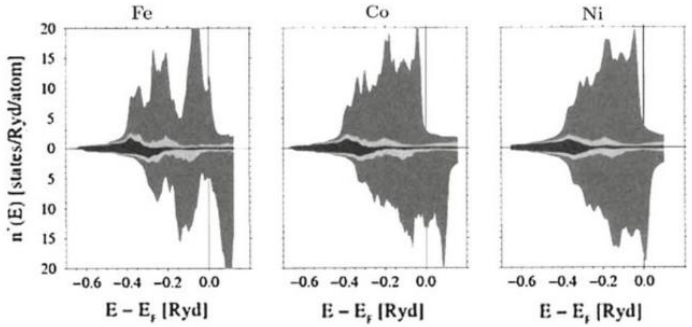


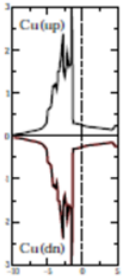
1) *The cyclotron frequencies increase with the magnetic field.*
2) *The diamagnetic field increase with the energy.*
3) *The diamagnetic field stopped with the E_F.*
4) *The diamagnetic field increase again with the next cyclotron frequency.*

Ferromagnetism Fermi gas (Solid state physics)

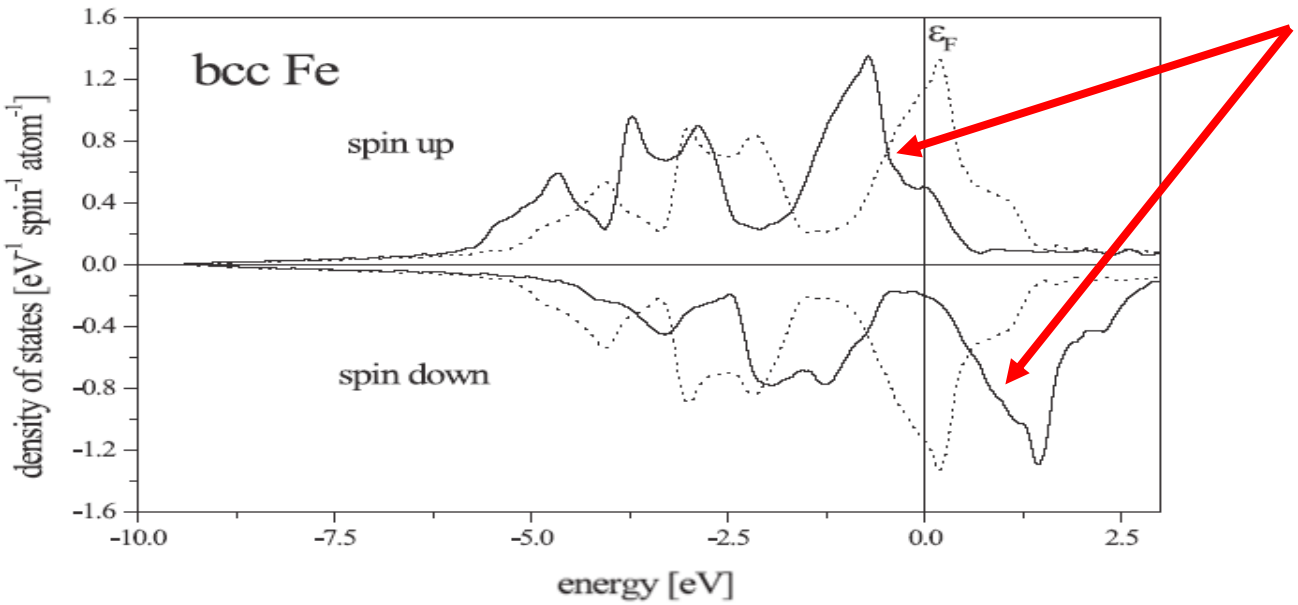


$B_{ext}=0$

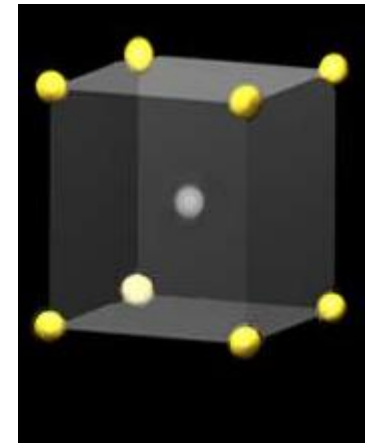


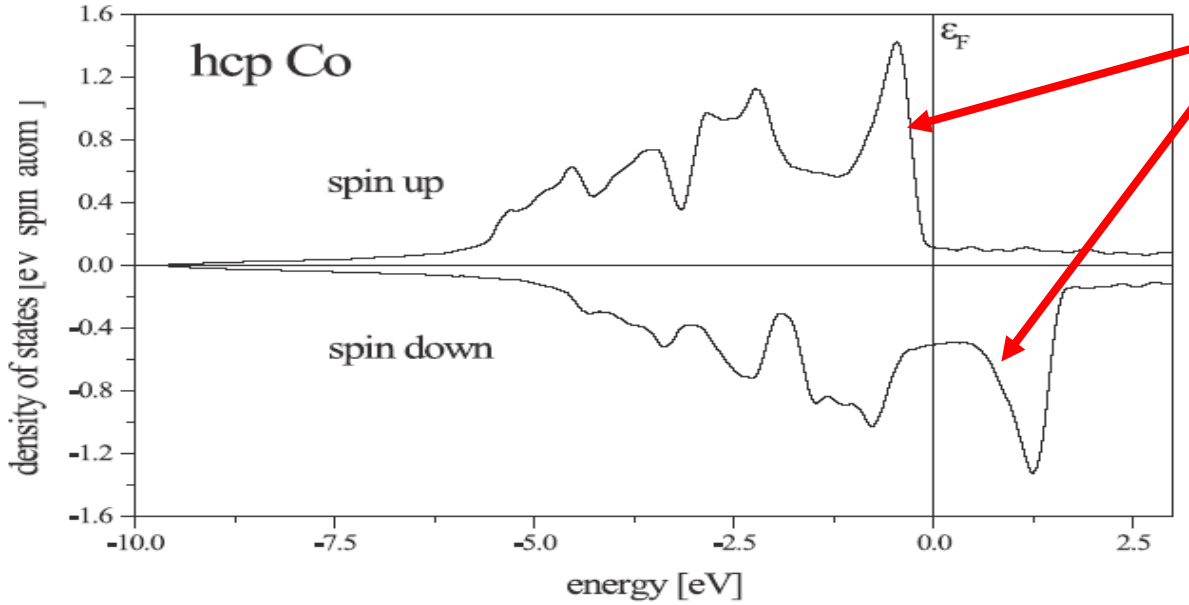


$T_K = 300$

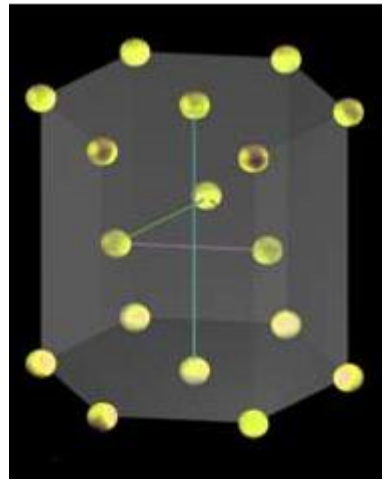


$T_K = 300$

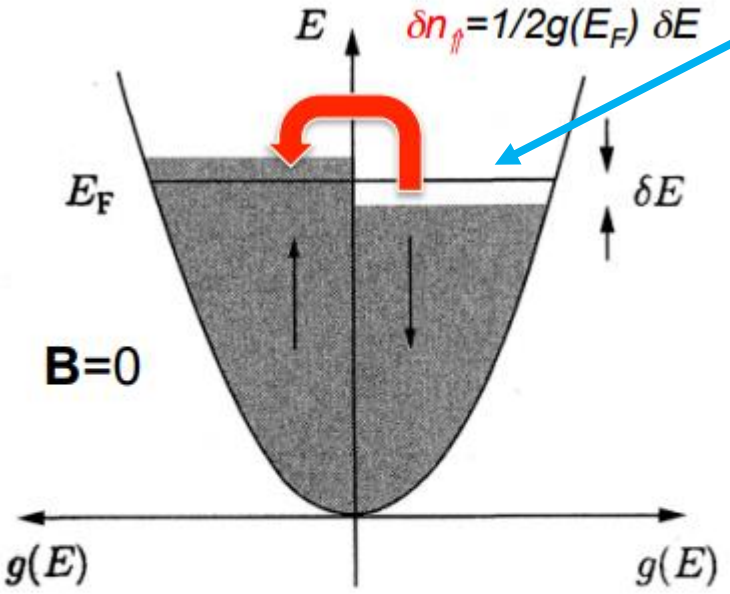




$T_K = 300$



Ferromagnetism Stoner model (1938)



$$n_\uparrow = 1/2(n + g(E_F)\delta E)$$
$$n_\downarrow = 1/2(n - g(E_F)\delta E)$$

1) *The molecular field magnetizes the electron gas due to the Pauli paramagnetism (bootstrapping mechanism) without exeternal magnetic field.*

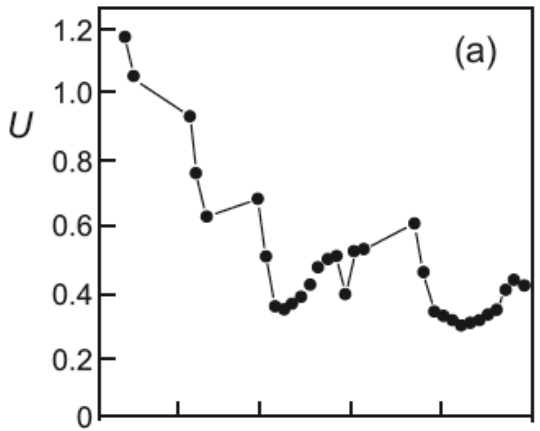
2) $\delta n \downarrow$ *are flip in* $\delta n \uparrow$ *sub-band close* $E_F + \delta E$.
The number of electrons moved is $\delta n_\uparrow$.

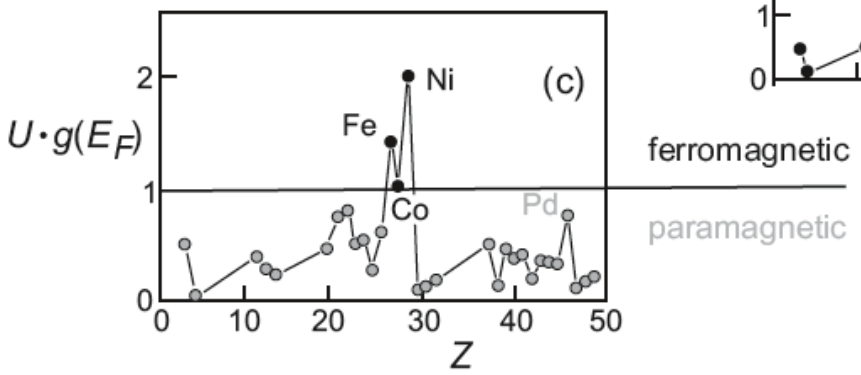
3) *The potential energy* $\Rightarrow \Delta E_{pot} = -\frac{1}{2} U g((E_F)\delta E^2$

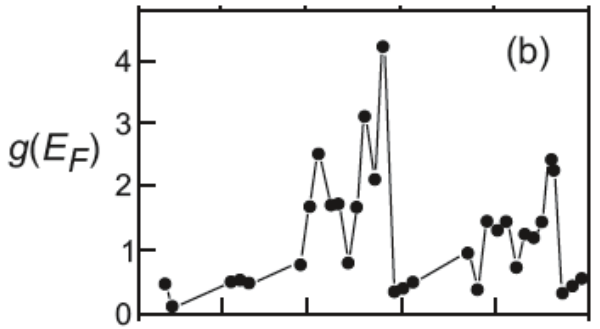
3) *Kinetic energy cost* $\Rightarrow \Delta E_{kin} = \frac{1}{2} g((E_F)\delta E^2$.

4) $\boldsymbol{\Delta E_{kin} + \Delta E_{pot} < 0}$

$U\, g(E_F) \geq 1$ *"Stoner criterion"*





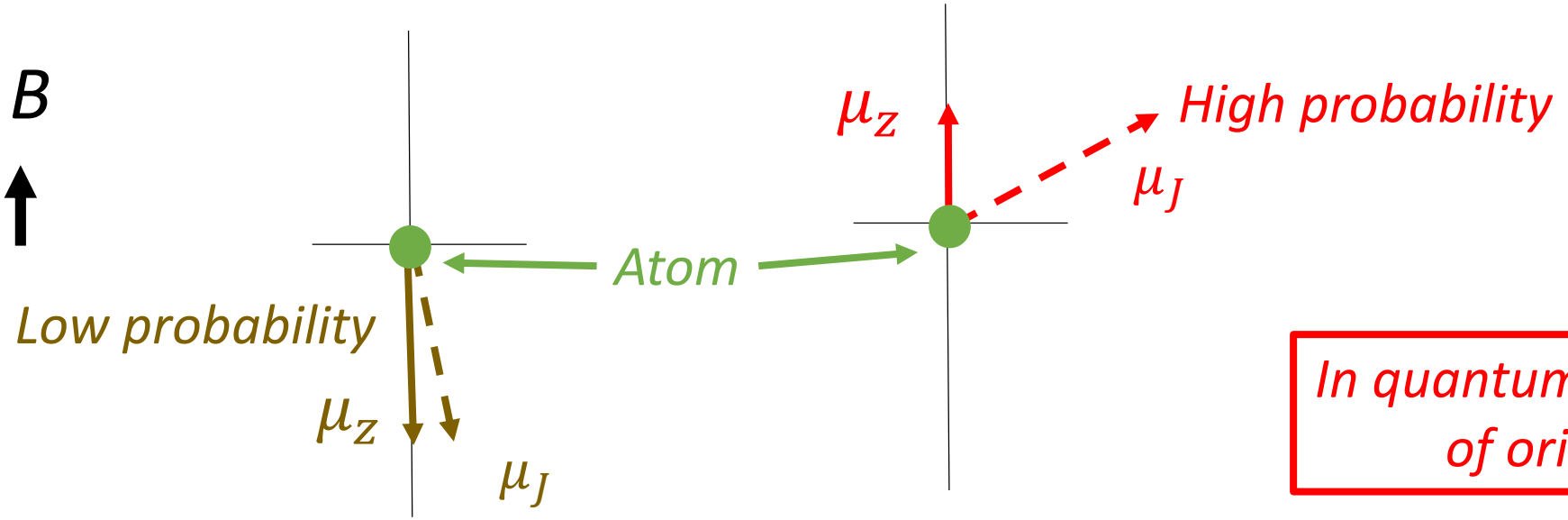


ferromagnetic

paramagnetic

Brillouin-Langevin paramagnetism

1) Each atom is independent.
2) For each atom, the total magnetic moment μ_J(orbitals + spin) is the same for each atom. It is calculate 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 $= \frac{\sum \mu_Z}{Volume}$



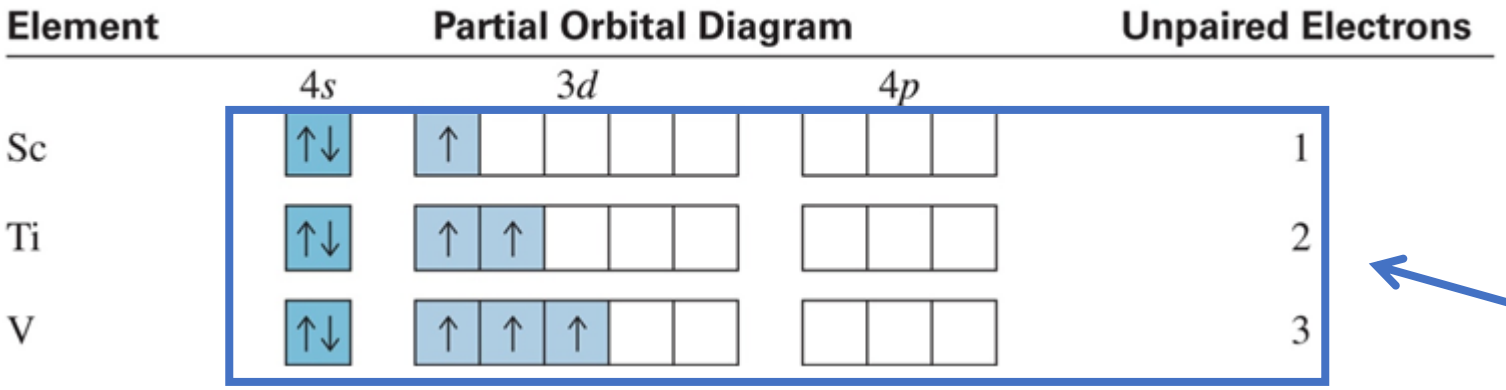
$$\mu_J = g_J \mathrm{J}\, \mu_b$$

$$\mu_z = g_J \mathrm{m}\, \mu_b$$

In quantum mechanics the number of orientations is limited

Paramagnetism

Scandium	Electrical resistivity	55×10^{-8} Ω m (at 20 °C)
	Magnetic susceptibility (χmol)	+ 3.956 10^{-9} m^3/mol
	Electronegativity	Pauling scale: 1.36
Titanium	Electrical resistivity	40 $\times10^{-8}$ Ω m (at 20 °C)
	Magnetic susceptibility (χmol)	+1.919 10^{-9} m^3/mol
	Electronegativity	Pauling scale: 1.54
Vanadium	Electrical resistivity	20 $\times10^{-8}$ Ω m (at 20 °C)
	Magnetic susceptibility (χmol)	+3.199 10^{-9} m^3/mol
	Electronegativity	Pauling scale: 1.63



https://www.gemstonemagnetism.com/uploads/Magnetic_Susceptibilities_of_the_Elements.pdf

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.*

Paramagnetic

http://www.periodictable.com/

Langevin-Larmor diamagnetism

$< r^2 > \approx 1$

$$\chi \approx -0.99\ 10^{-5}\ Z \sum_{i=1}^{Z} \frac{1}{Z} <0 \left[\frac{r_i^2}{a_0^2}\right] 0>$$

$\approx$ Borh radius

Atom radius

1)The number of electrons with the same spin orientation is limited.
2) The external field modify the external orbit.
3) By the law Lenz the electrons create a magnetic field in opposition wit 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	-6.86×10^{-11} m^3/mol

Zinc

Electrical resistivity	59.0 nΩ·m (at 20 °C)
Electronegativity	Pauling scale: 1.65
Magnetic susceptibility(χ_{mol})	-1.45×10^{-10} m^3/mol

Element	Partial Orbital Diagram (4s, 3d, 4p)	Unpaired Electrons
Cu	↑ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	1
Zn	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0

Diamagnetic

http://www.periodictable.com

Van Vleck paramagnetism

*Second order perturbation is **positive***

Van Vleck paramagnetism

Mean value or expected value

Expected value

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

Energy gap

Ground energy level (B=0)

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.*

If the perturbation is sufficiently large, the Van Vleck paramagnetism represent the probability that the expected value of the perturbation modify χ_{dia} *if the perturbation is sufficient to go until a new high energy level .*

Ising model (1925)

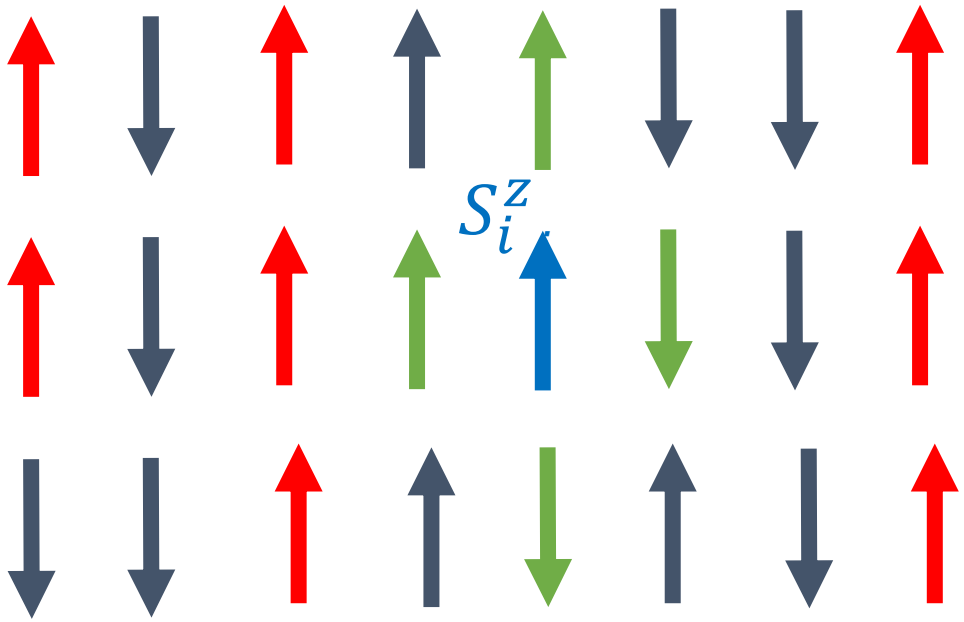
$$H = -\sum_{N>i>i} J_{ij} S_i^z S_j^z - g\mu_B m^z \sum_i S_i^z$$

neighbor-interaction (ferromagnetic or antiferromagnetic coupling)

interaction with the external magnetic field

σ = +1 spin up

σ = -1 spin down



1) Random "perturbation" for blue spin (energy Ω=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 choice 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.

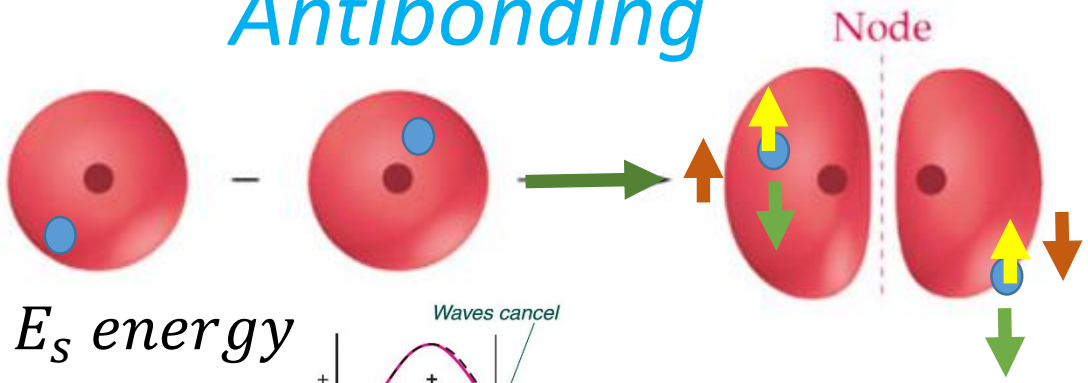
$$\text{Exp}\left(-\frac{H_b - H_a}{k_B T}\right) \geq x$$

configuration Ω

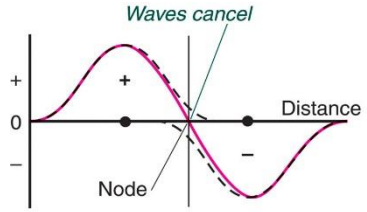
Ferromagnetism exchange interaction (1928)

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

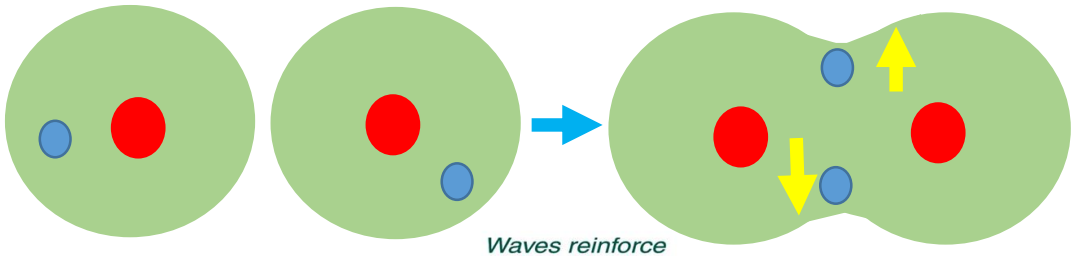
Antibonding



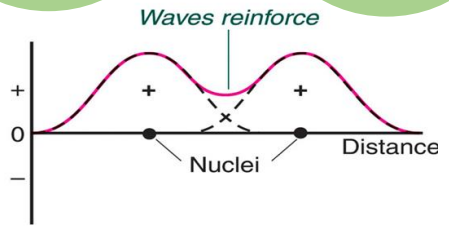
E_s energy



Bonding



E_a energy



$$J = \frac{E_s - E_a}{2}$$

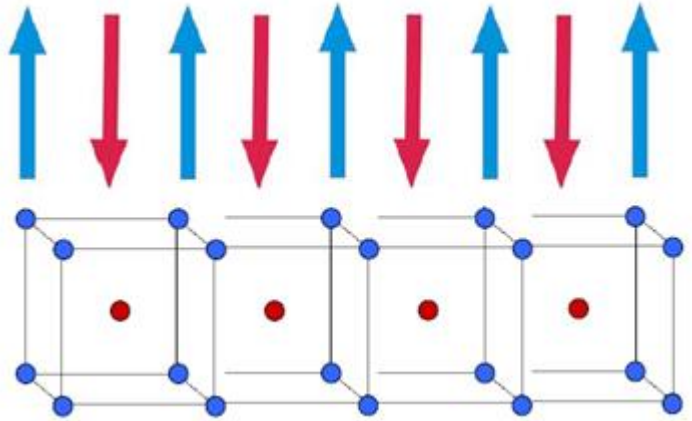
1) *The particles are indistinguishable and a wave function is attached to the particles.*
2) *We have a difference in energy between the bonding and antibonding.*
3) *If the wave function is symmetric the spin function is antisymmetric and reciprocally.*
4) *The fundamental link between the principle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

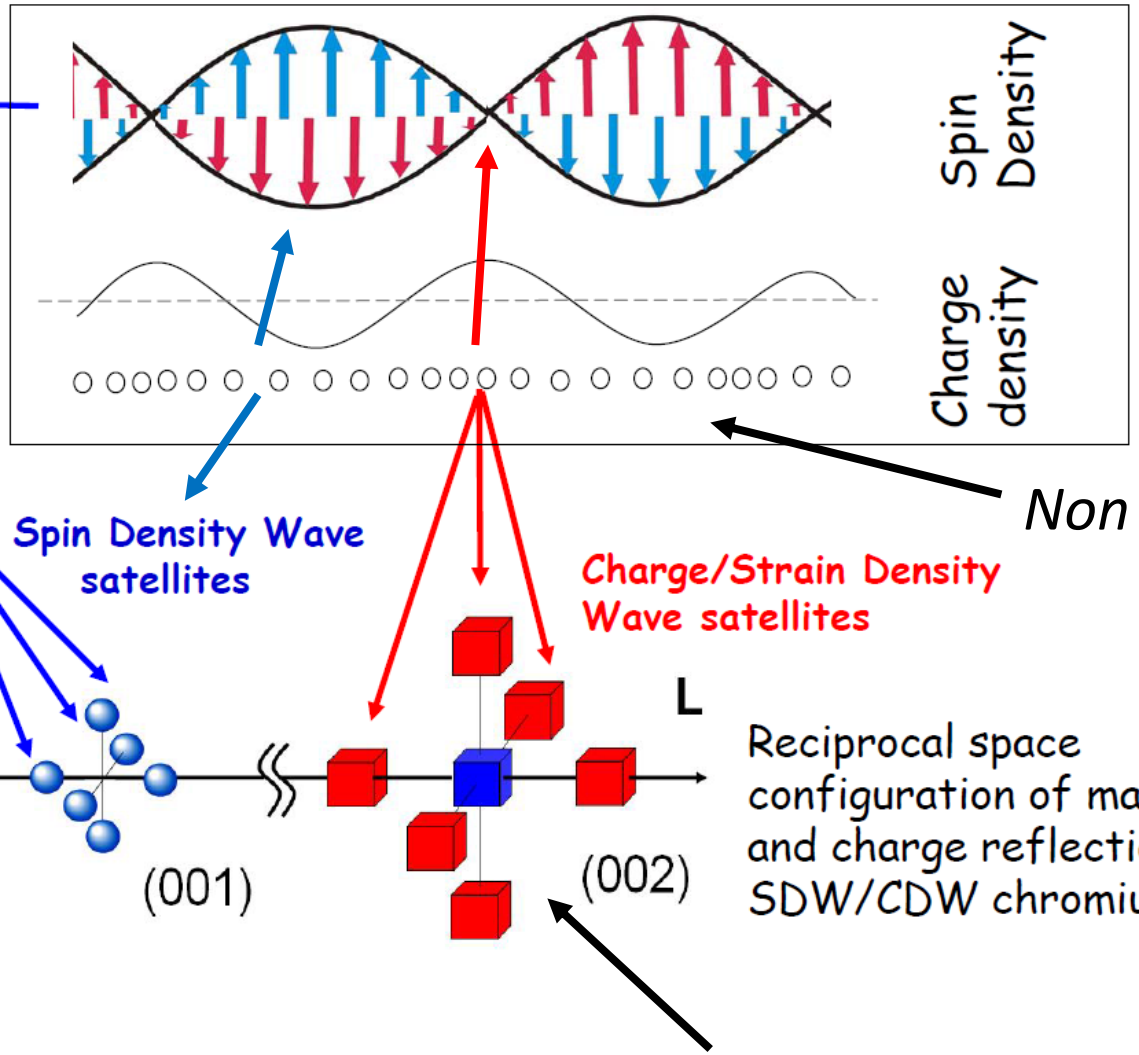
$J > 0$ =>antibonding => ferromagnetsim

$J < 0$ => bonding => antiferromagnetism

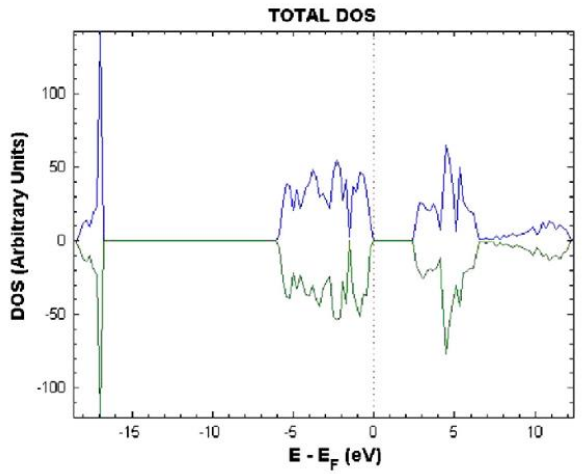
Antiferromagnetism chromium (molecular

Uniform distance between the atoms.





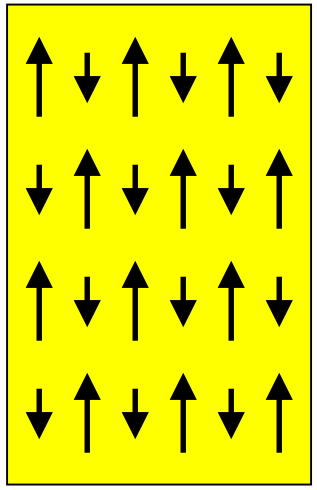
Non uniform distance between the atoms.



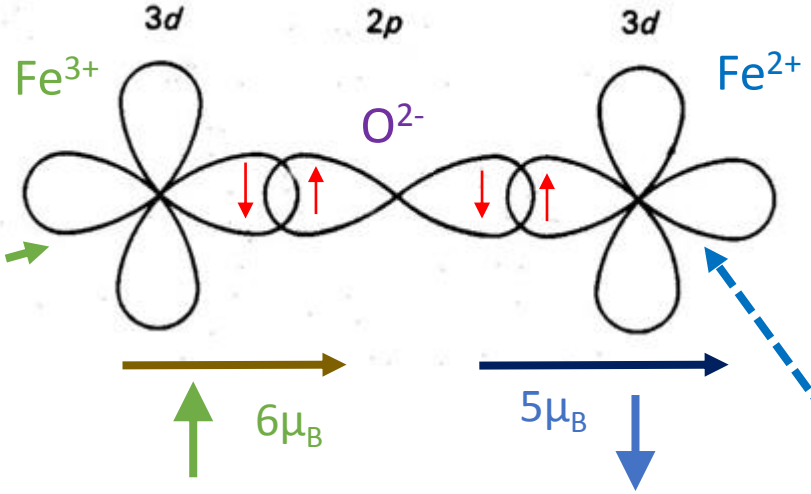
Cr_2O_3

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.

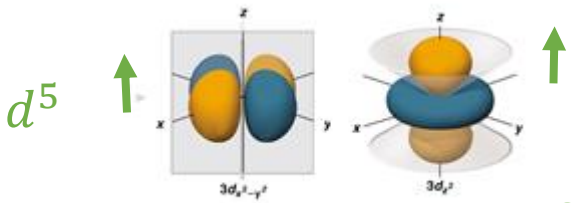
Ferrimagnetism (molecular quantum)



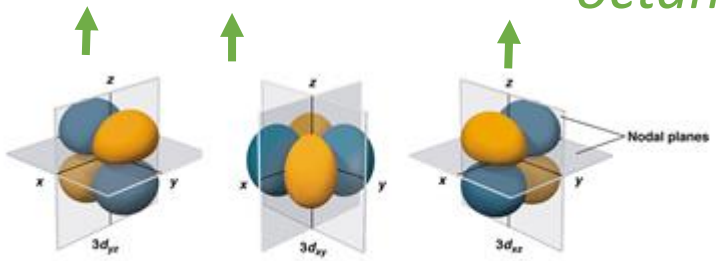
M

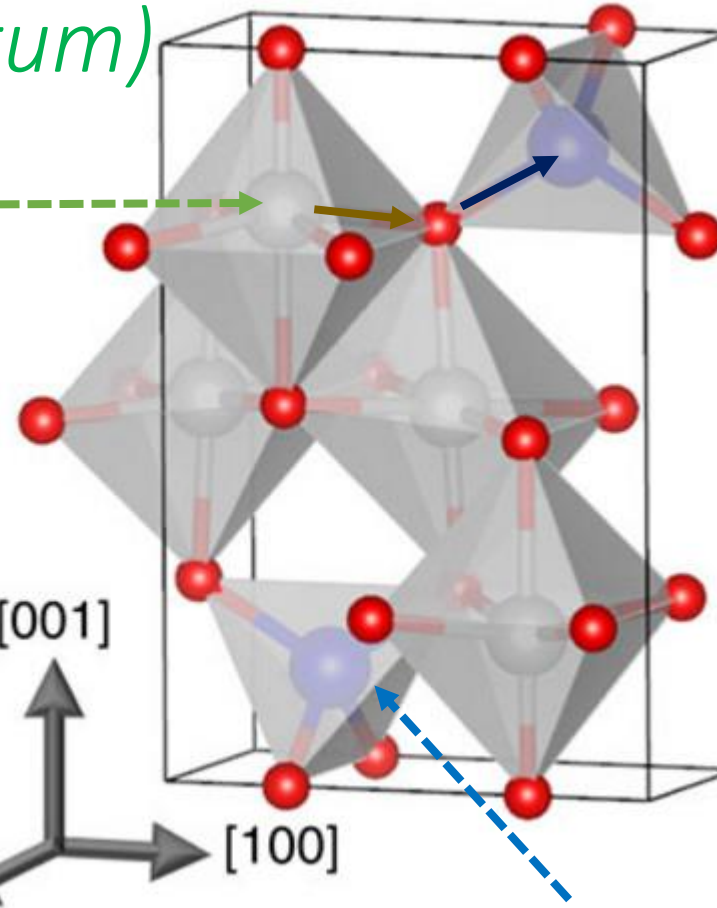


octahedral

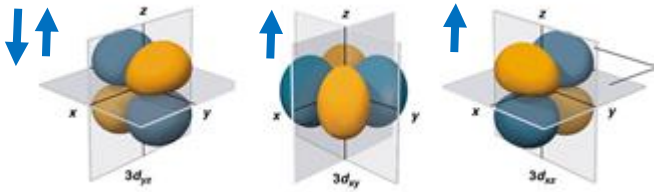


octahedral



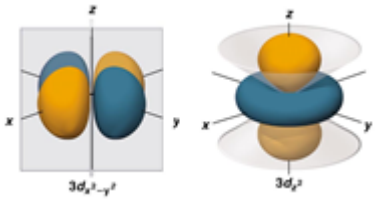


octahedral



Magnetite (Fe_3O_4)

tetrahedral



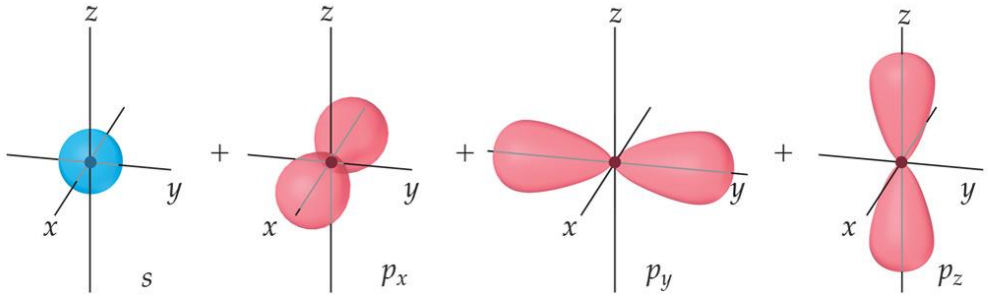
Oxygen atoms (small sphere in red)

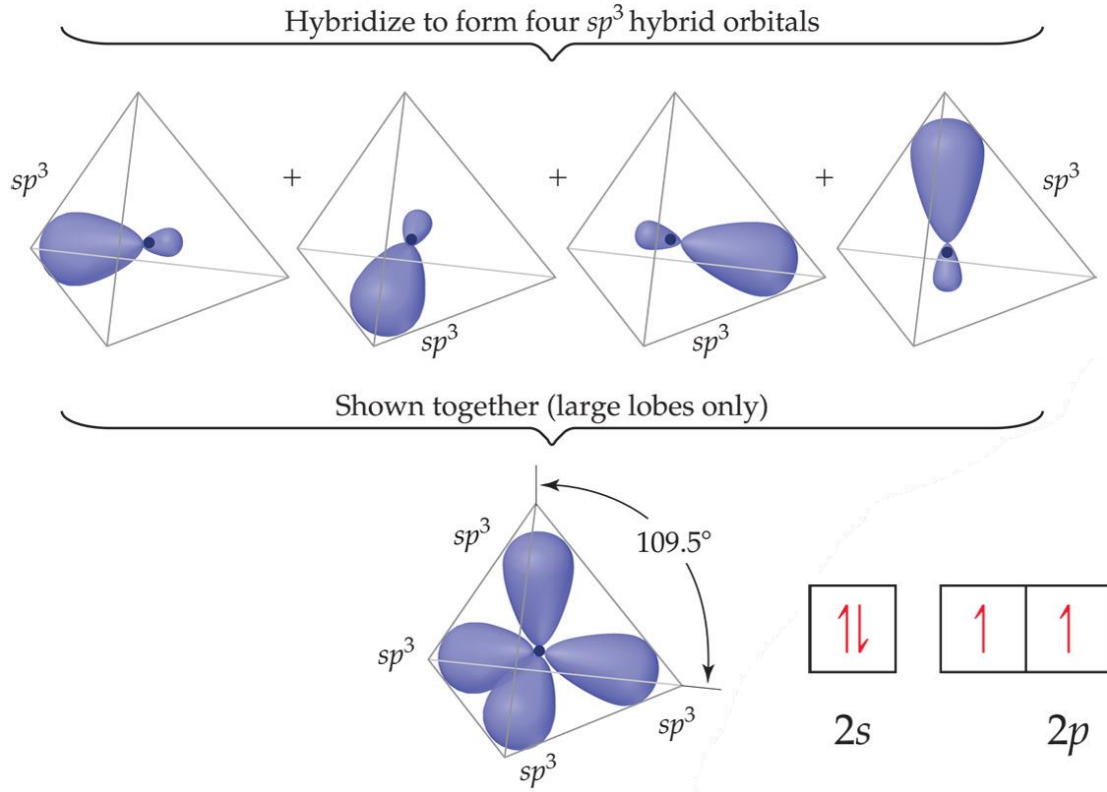
Fe2+ (tetrahedral sphere in blue) , Fe3+ (octahedral sphere grey)

Valence Bond Theory (molecular physic)

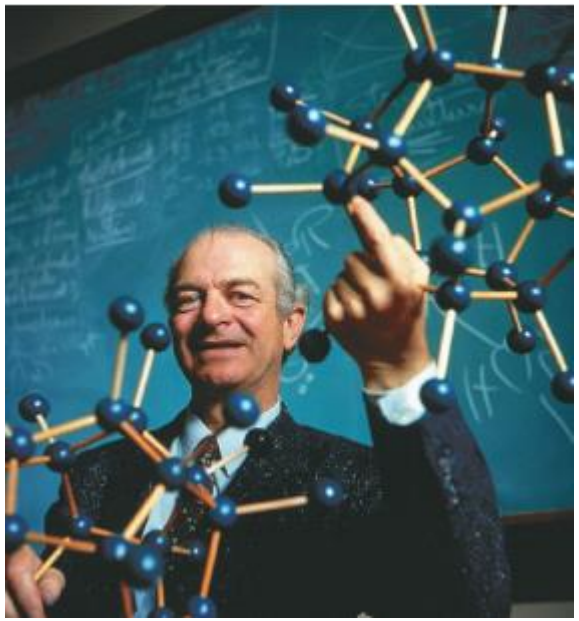
***Hybridisation**: the concept of mixing atomic orbitals to form a new hybrid orbitals*

Suitable for the qualitative description of atomic bonding properties.

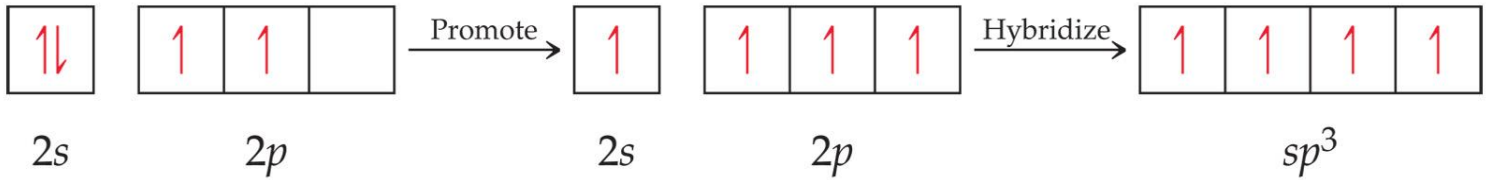


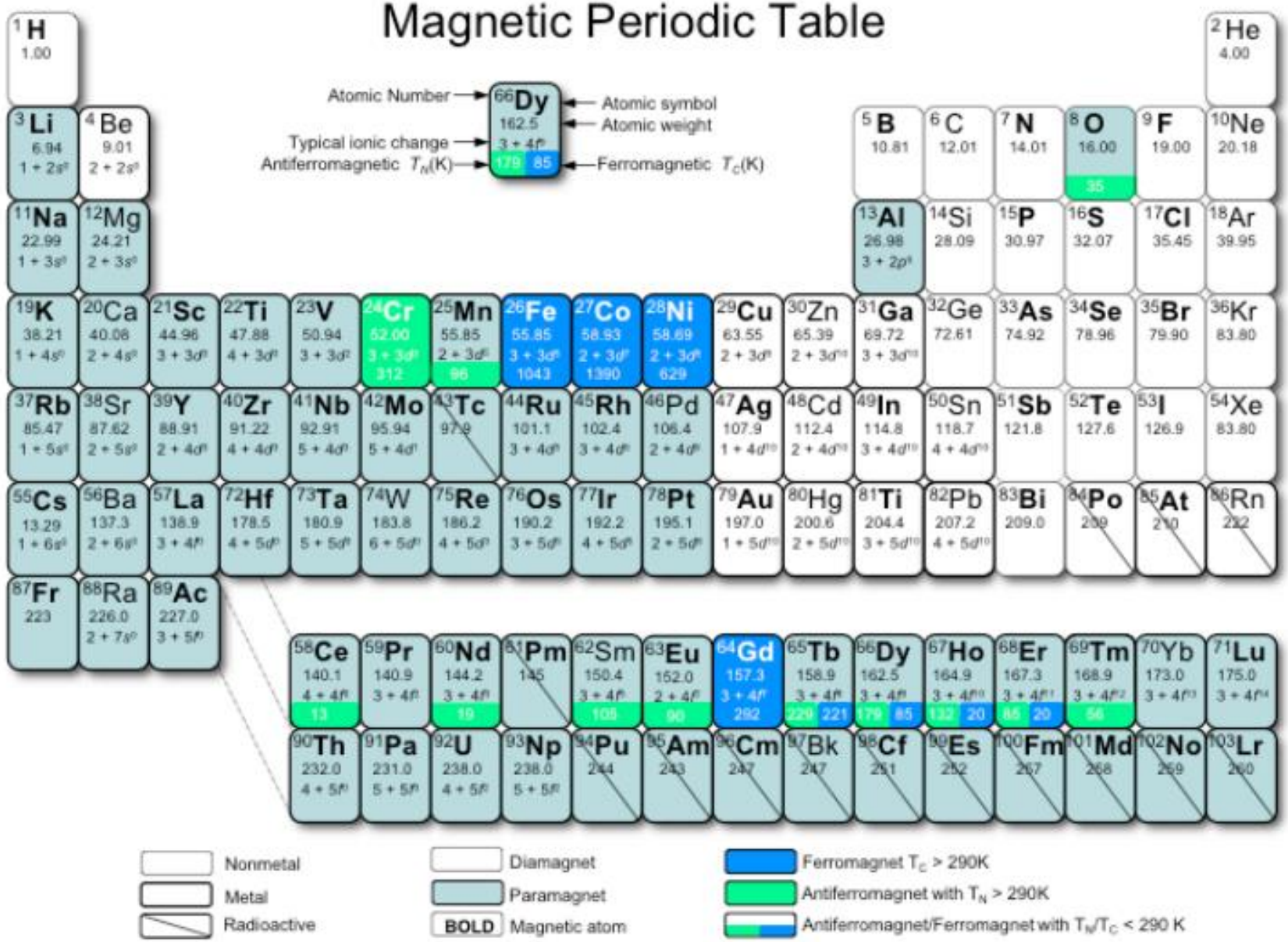


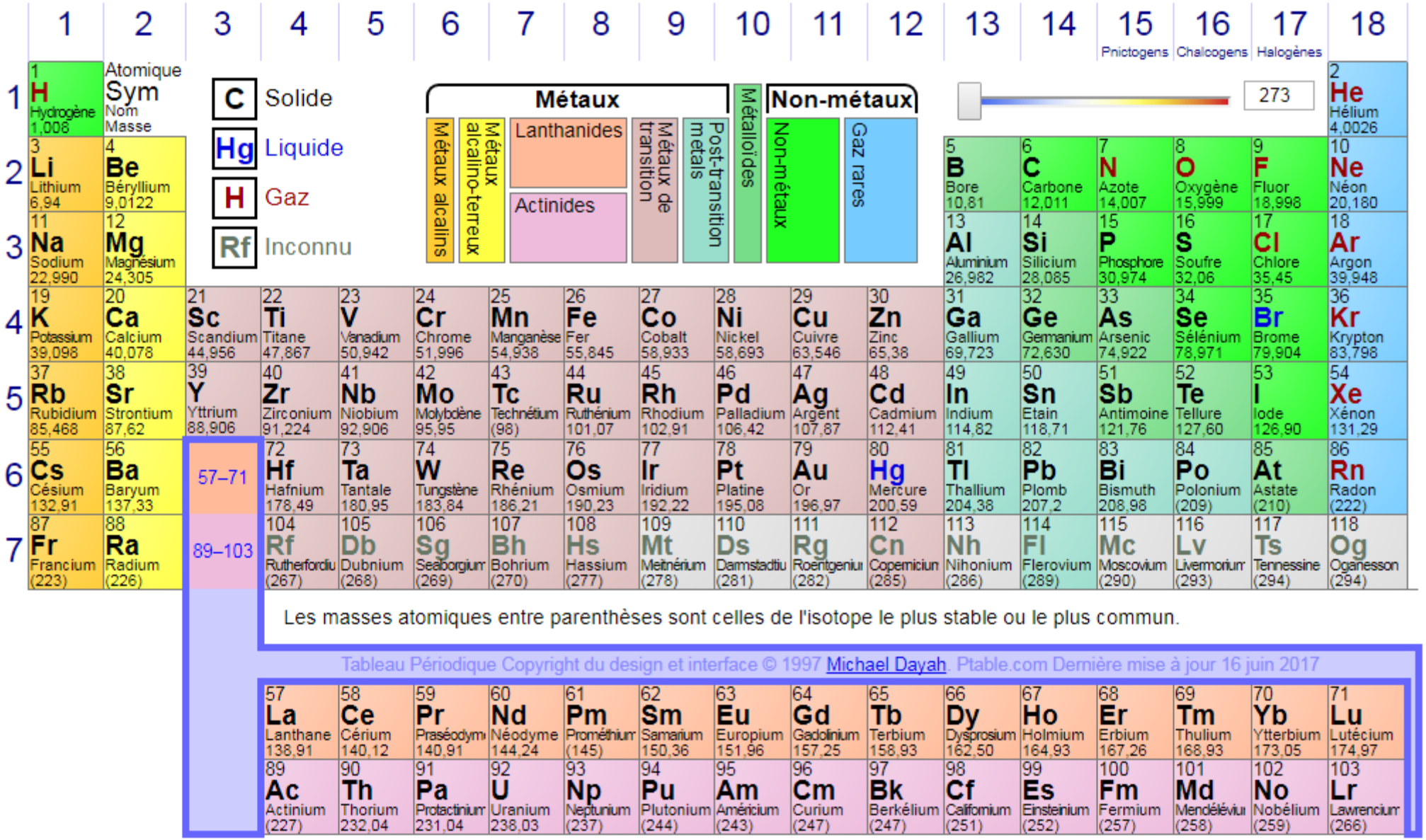
Linus Pauling



Example:
sp^3 orbitals.




Magnetic Periodic Table
Atomic Number
Atomic symbol
Atomic weight
Typical ionic change
Antiferromagnetic T_N(K)
Ferromagnetic T_C(K)
Nonmetal
Metal
Radioactive
Diamagnet
Paramagnet
BOLD Magnetic atom
Ferromagnet T_C > 290K
Antiferromagnet with T_N > 290K
Antiferromagnet/Ferromagnet with T_N/T_C < 290 K


1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Pnictogens
Chalcogens
Halogènes
Atomique
Sym
Nom
Masse
C Solide
Hg Liquide
H Gaz
Rf Inconnu
Métaux
Métaux alcalins
Métaux alcalino-terreux
Lanthanides
Actinides
Métaux de transition
Post-transition metals
Métalloïdes
Non-métaux
Non-métaux
Gaz rares
273
1 H Hydrogène 1,008
2 He Hélium 4,0026
3 Li Lithium 6,94
4 Be Béryllium 9,0122
5 B Bore 10,81
6 C Carbone 12,011
7 N Azote 14,007
8 O Oxygène 15,999
9 F Fluor 18,998
10 Ne Néon 20,180
11 Na Sodium 22,990
12 Mg Magnésium 24,305
13 Al Aluminium 26,982
14 Si Silicium 28,085
15 P Phosphore 30,974
16 S Soufre 32,06
17 Cl Chlore 35,45
18 Ar Argon 39,948
19 K Potassium 39,098
20 Ca Calcium 40,078
21 Sc Scandium 44,956
22 Ti Titane 47,867
23 V Vanadium 50,942
24 Cr Chrome 51,996
25 Mn Manganèse 54,938
26 Fe Fer 55,845
27 Co Cobalt 58,933
28 Ni Nickel 58,693
29 Cu Cuivre 63,546
30 Zn Zinc 65,38
31 Ga Gallium 69,723
32 Ge Germanium 72,630
33 As Arsenic 74,922
34 Se Sélénium 78,971
35 Br Brome 79,904
36 Kr Krypton 83,798
37 Rb Rubidium 85,468
38 Sr Strontium 87,62
39 Y Yttrium 88,906
40 Zr Zirconium 91,224
41 Nb Niobium 92,906
42 Mo Molybdène 95,95
43 Tc Technétium (98)
44 Ru Ruthénium 101,07
45 Rh Rhodium 102,91
46 Pd Palladium 106,42
47 Ag Argent 107,87
48 Cd Cadmium 112,41
49 In Indium 114,82
50 Sn Etain 118,71
51 Sb Antimoine 121,76
52 Te Tellure 127,60
53 I Iode 126,90
54 Xe Xénon 131,29
55 Cs Césium 132,91
56 Ba Baryum 137,33
57–71
72 Hf Hafnium 178,49
73 Ta Tantale 180,95
74 W Tungstène 183,84
75 Re Rhénium 186,21
76 Os Osmium 190,23
77 Ir Iridium 192,22
78 Pt Platine 195,08
79 Au Or 196,97
80 Hg Mercure 200,59
81 Tl Thallium 204,38
82 Pb Plomb 207,2
83 Bi Bismuth 208,98
84 Po Polonium (209)
85 At Astate (210)
86 Rn Radon (222)
87 Fr Francium (223)
88 Ra Radium (226)
89–103
104 Rf Rutherfordiu (267)
105 Db Dubnium (268)
106 Sg Seaborgium (269)
107 Bh Bohrium (270)
108 Hs Hassium (277)
109 Mt Meitnérium (278)
110 Ds Darmstadtiu (281)
111 Rg Roentgeniu (282)
112 Cn Copernicium (285)
113 Nh Nihonium (286)
114 Fl Flerovium (289)
115 Mc Moscovium (290)
116 Lv Livermoriun (293)
117 Ts Tennessine (294)
118 Og Oganesson (294)
Les masses atomiques entre parenthèses sont celles de l'isotope le plus stable ou le plus commun.
Tableau Périodique Copyright du design et interface © 1997 Michael Dayah Ptable.com Dernière mise à jour 16 juin 2017
57 La Lanthane 138,91
58 Ce Cérium 140,12
59 Pr Praséodym 140,91
60 Nd Néodyme 144,24
61 Pm Prométhium (145)
62 Sm Samarium 150,36
63 Eu Europium 151,96
64 Gd Gadolinium 157,25
65 Tb Terbium 158,93
66 Dy Dysprosium 162,50
67 Ho Holmium 164,93
68 Er Erbium 167,26
69 Tm Thulium 168,93
70 Yb Ytterbium 173,05
71 Lu Lutécium 174,97
89 Ac Actinium (227)
90 Th Thorium 232,04
91 Pa Protactinium 231,04
92 U Uranium 238,03
93 Np Neptunium (237)
94 Pu Plutonium (244)
95 Am Américium (243)
96 Cm Curium (247)
97 Bk Berkélium (247)
98 Cf Californium (251)
99 Es Einsteinium (252)
100 Fm Fermium (257)
101 Md Mendélévium (258)
102 No Nobélium (259)
103 Lr Lawrencium (266)