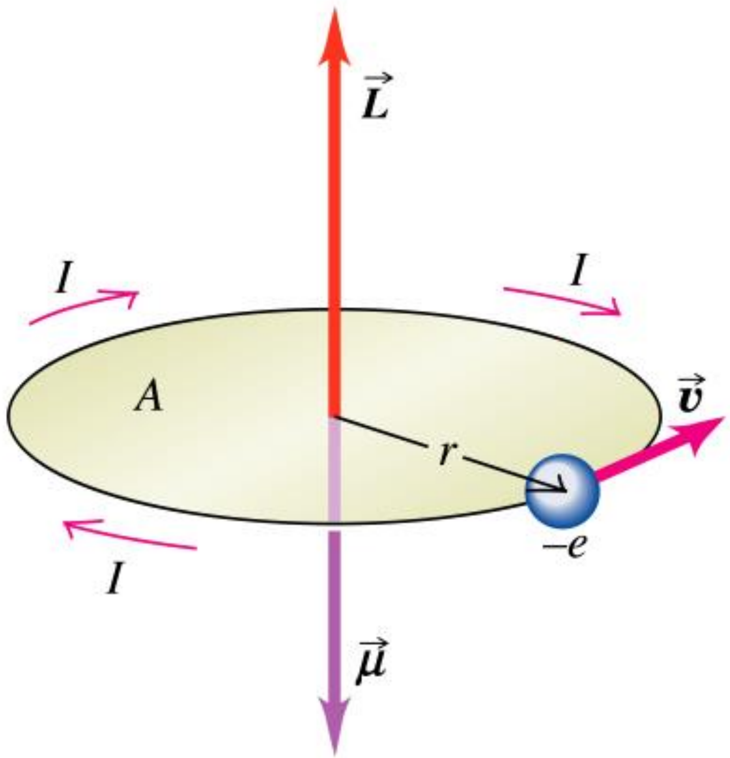
Borh magneton

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:

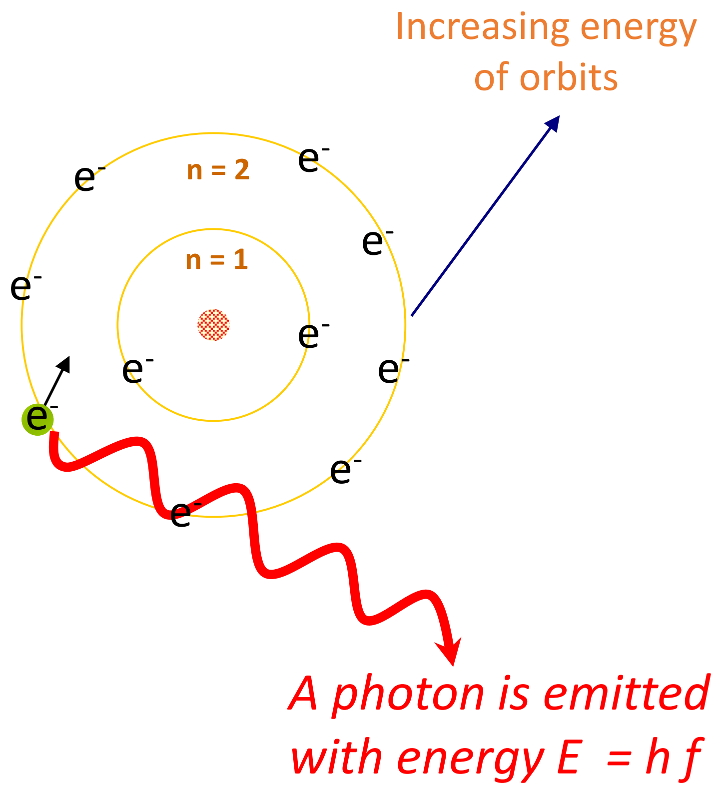
$$|\mu| = iA$$

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 → $E = h\nu$ *Borh-Einstein interpretation*

Borh radius

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

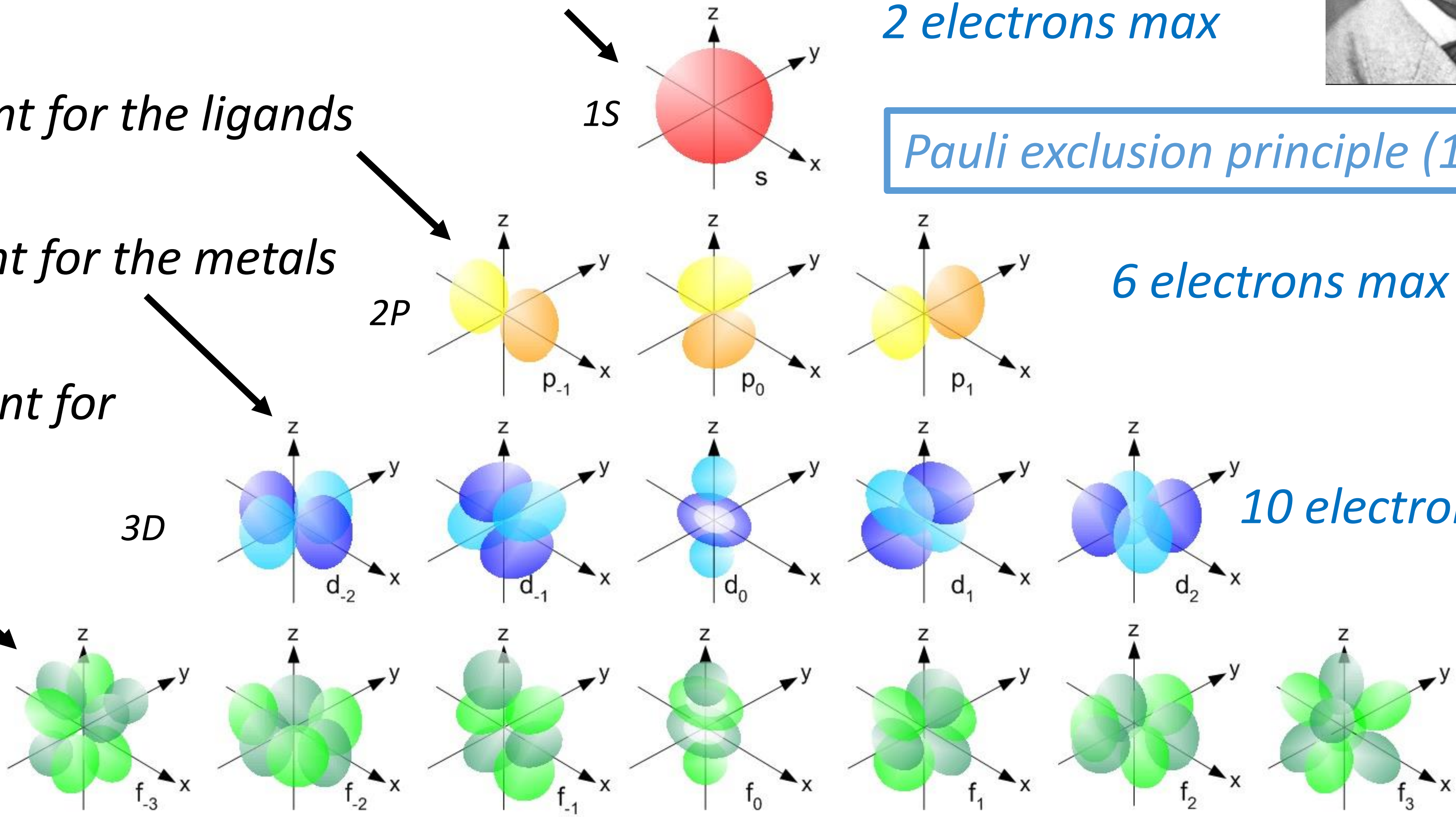
Subshells Schrödinger (1922)

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



2 electrons max

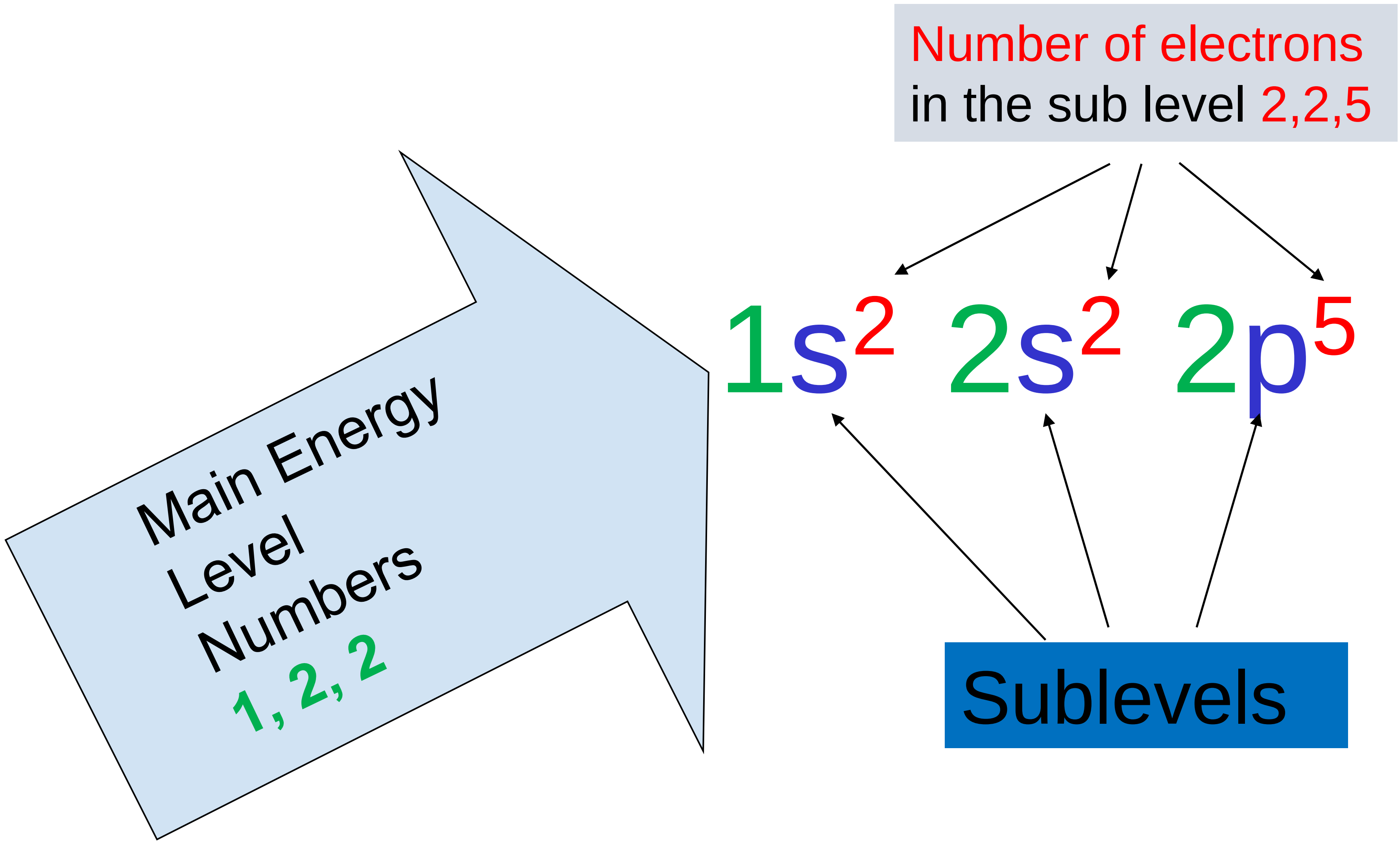
Pauli exclusion principle (1925)

6 electrons max

10 electrons max

14 electrons max

Standard Notation of Fluorine

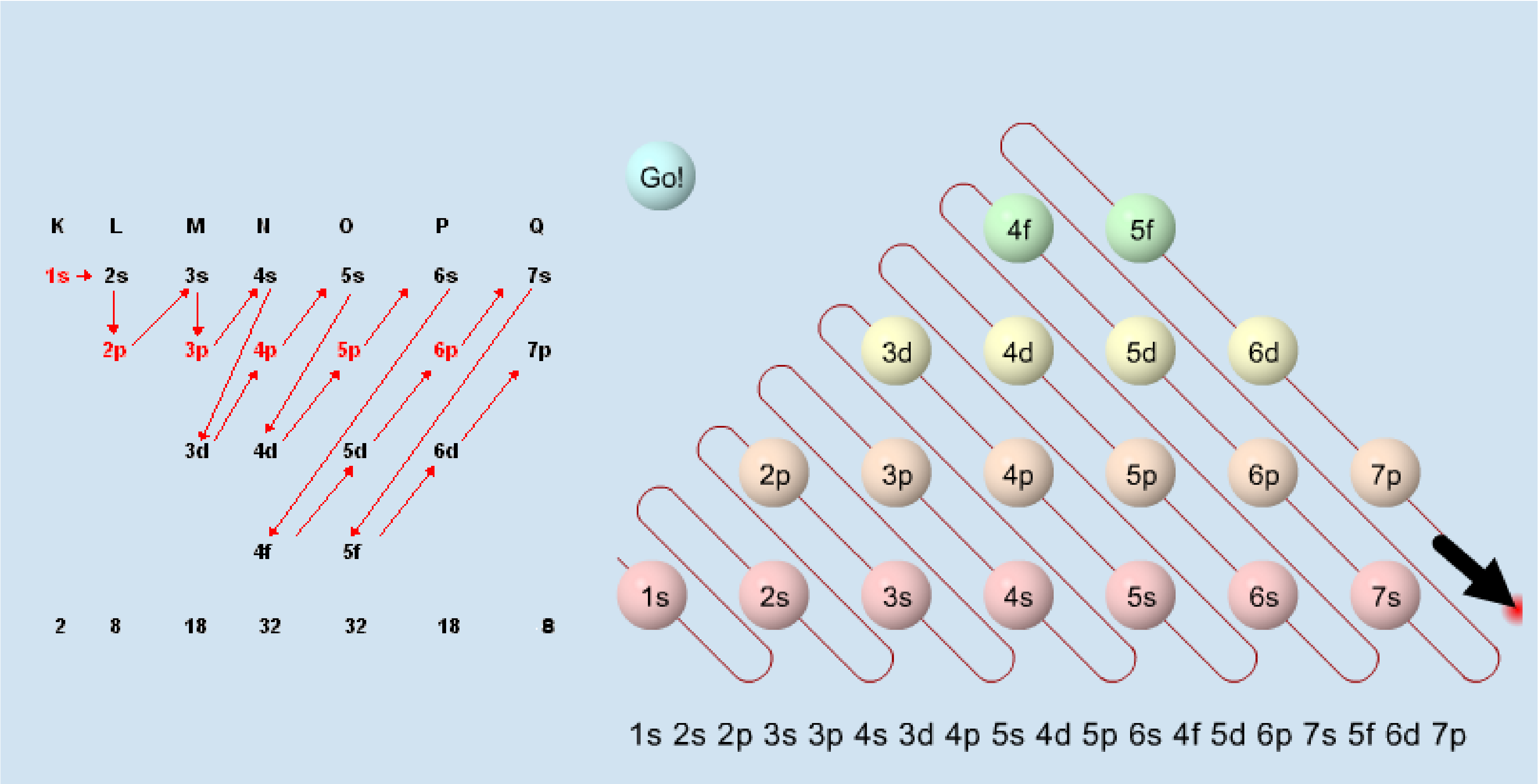


Hund’s rule

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

Element	Partial Orbital Diagram 4s	3d					4p			Unpaired Electrons
Sc	↑↓	↑								1
Ti	↑↓	↑	↑							2
V	↑↓	↑	↑	↑						3
Cr	↑	↑	↑	↑	↑	↑				6
Mn	↑↓	↑	↑	↑	↑	↑				5
Fe	↑↓	↑↓	↑	↑	↑	↑				4
Co	↑↓	↑↓	↑↓	↑	↑	↑				3
Ni	↑↓	↑↓	↑↓	↑↓	↑	↑				2
Cu	↑	↑↓	↑↓	↑↓	↑↓	↑↓				1
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				0

Paramagnetic (Sc, Ti, V)

Antiferromagnetic !!!!
Néel temperature (Cr)

Antiferromagnetic
or paramagnetic !!!!
Néel temperature (Mn)

Ferromagnetic (Fe, Co, Ni)

Diamagnetic (Cu, Zn)

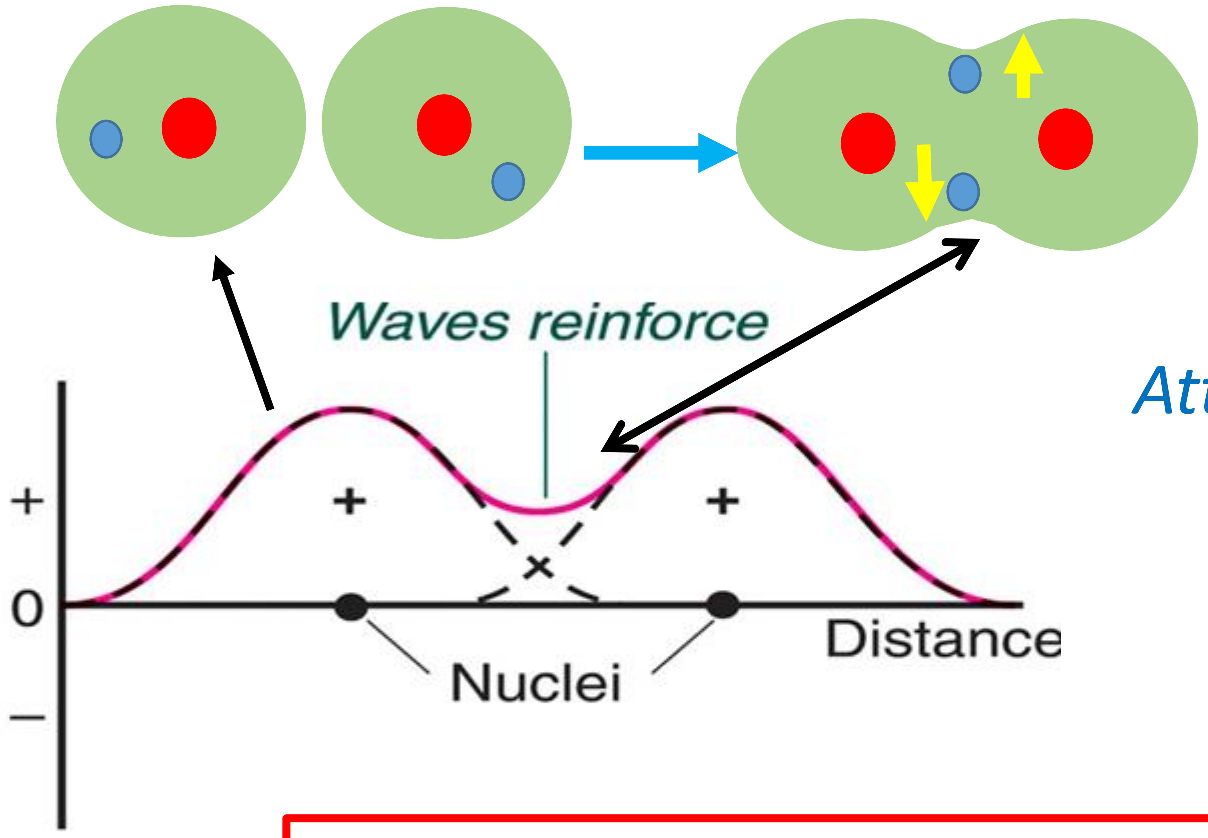
3d ferromagnetism

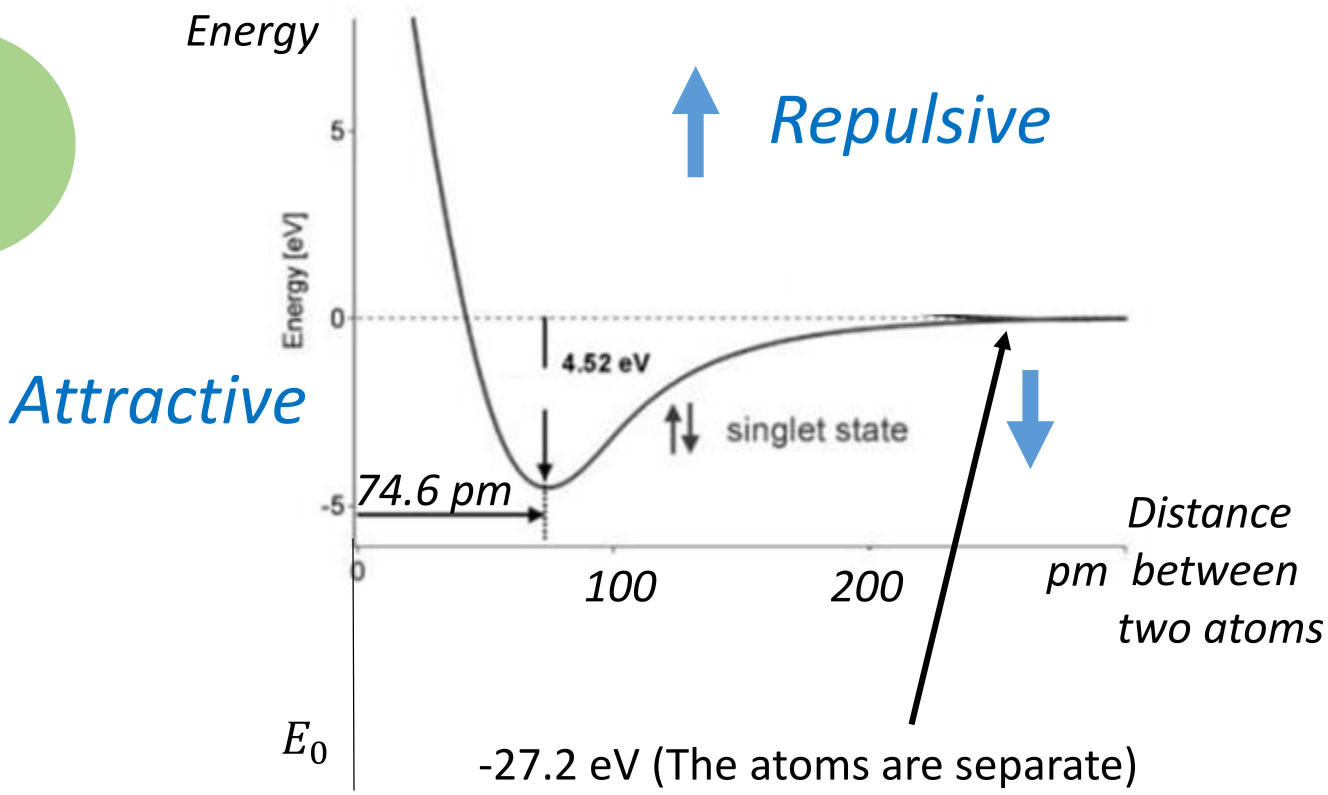
1) *When the sub schell is not full.*
2) *Depend of the distance between the atoms and the radius shell 3d.*
3) *Exchange energy (Heisenberg 1927)*

It is preferable to use the exchange model

Orbital model for H_2

Bonding



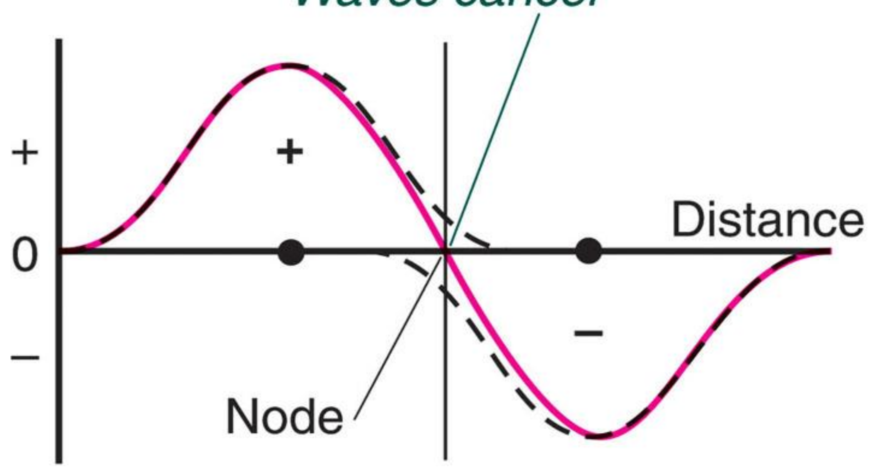


Pauli exclusion principle forbid the same spin orientation.

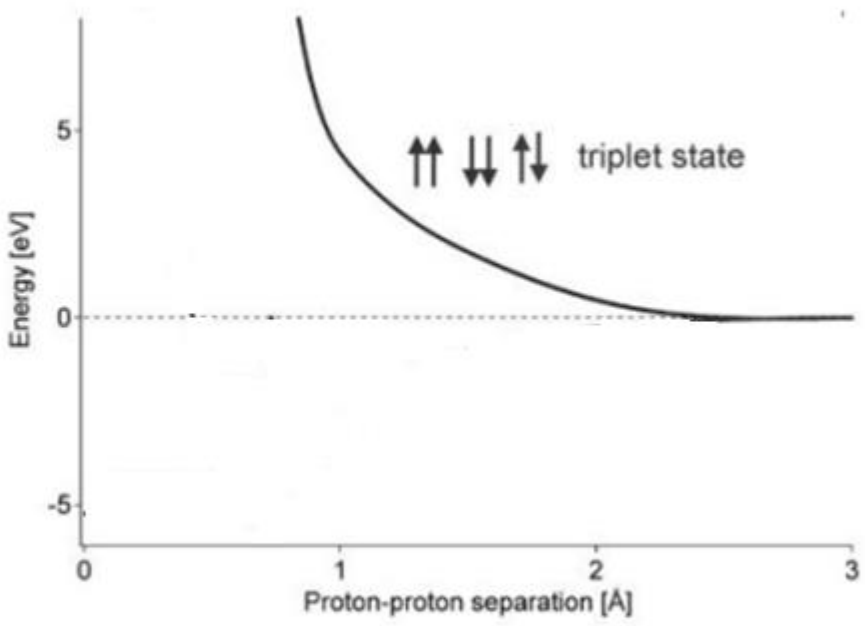
symmetric for the waves, antisymmetric for the spin

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.

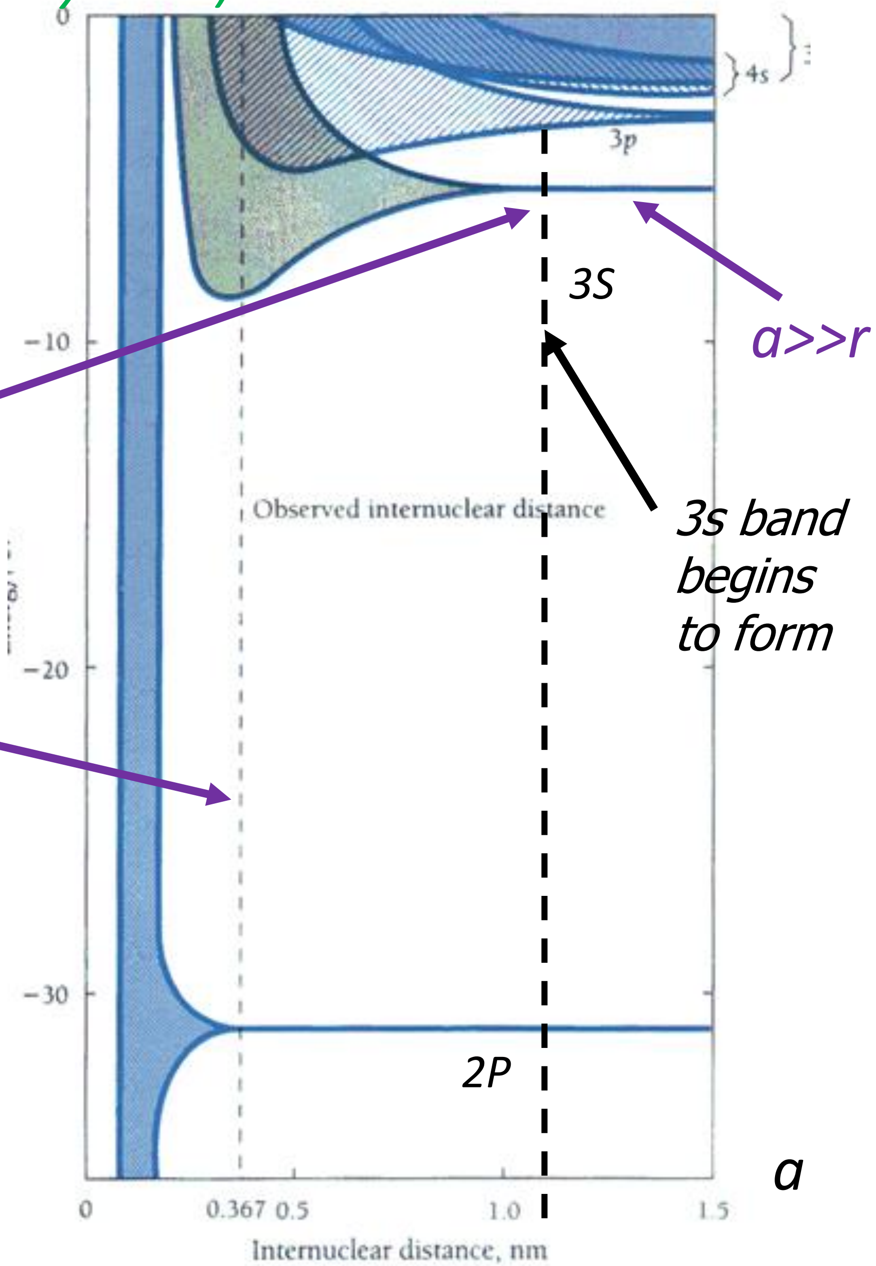
Radius atom Na = 180 pm

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

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

$a \approx 2\,r$

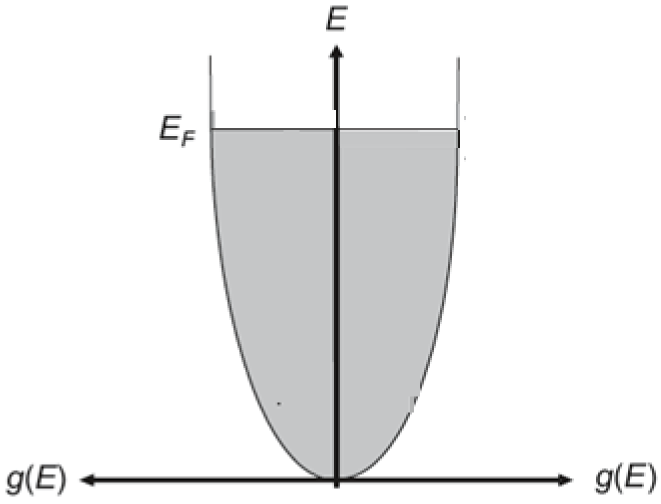
The result is the formation of energy ***bands****, consisting of many states close together but slightly split in energy.*



Internuclear distance nm

Sommerfeld model of free electrons (1928)

1) We are in the non relativist case.
2) We don’t consider the full subshells ΣL_i=0 and ΣS_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.

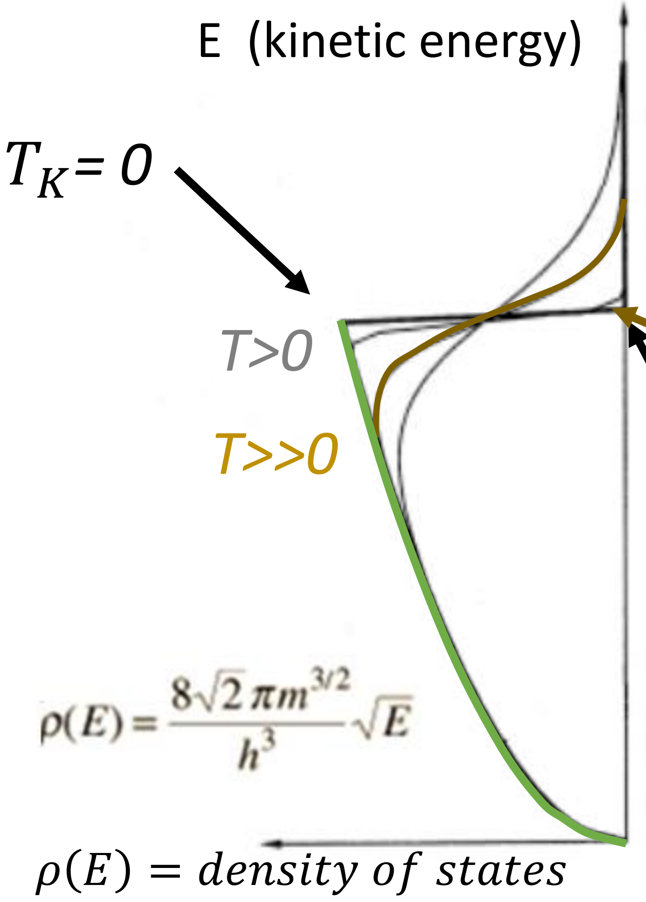
2) If you increase the number of electrons , you must increase their velocity because all the states with a lower energy are busy…

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.

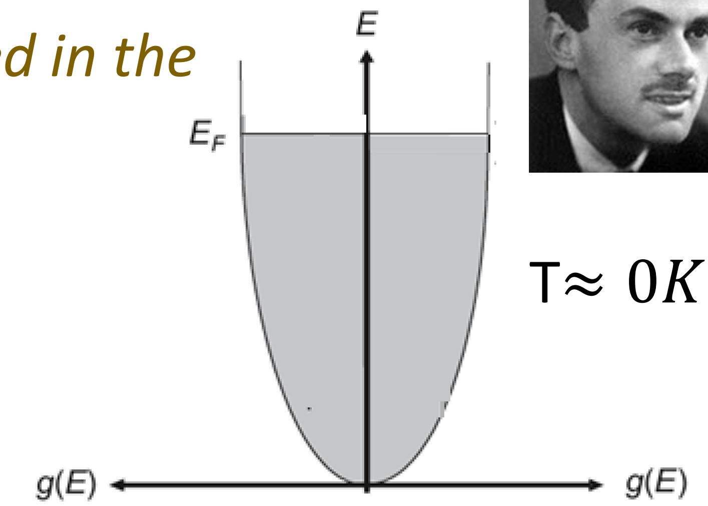
Only the free electrons near the Fermi are sensitive to the temperature (Fermi-Dirac distribution).



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

E_F (Fermi energy)

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



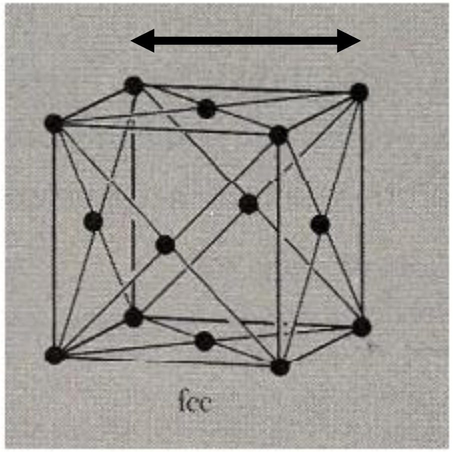
$T \approx 0K$

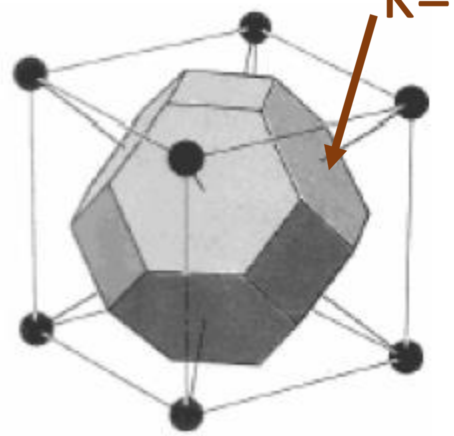
Fermi Parameters for some metals (Sommerfeld model)

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				4.01 10^22
Titanium	10,64×10-6	22	4.506				5.67 10^22
Vanadium	8,32×10-6	23	6.01				7.20 10^22
Chromium	7,23×10-6	24	7.19				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

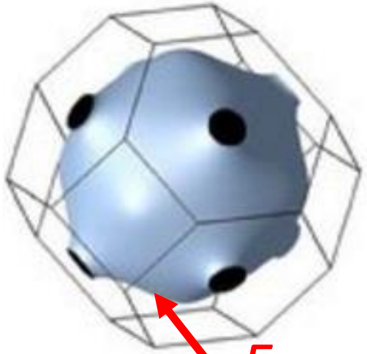
a





fcc BZ

k= $19.6\ 10^9\ m^{-1}$

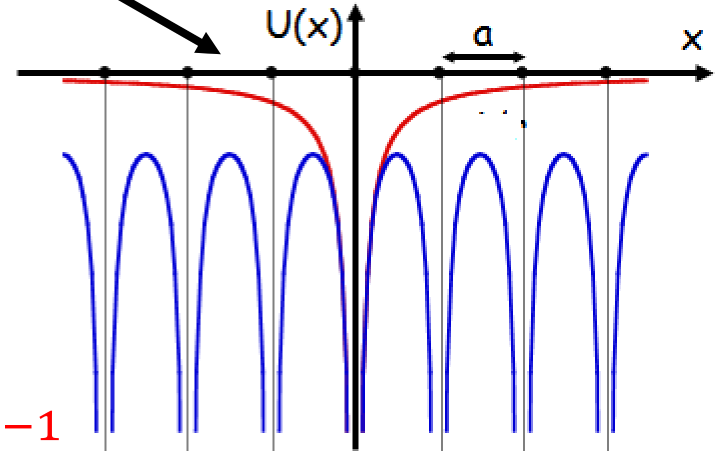


Fermi surface

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

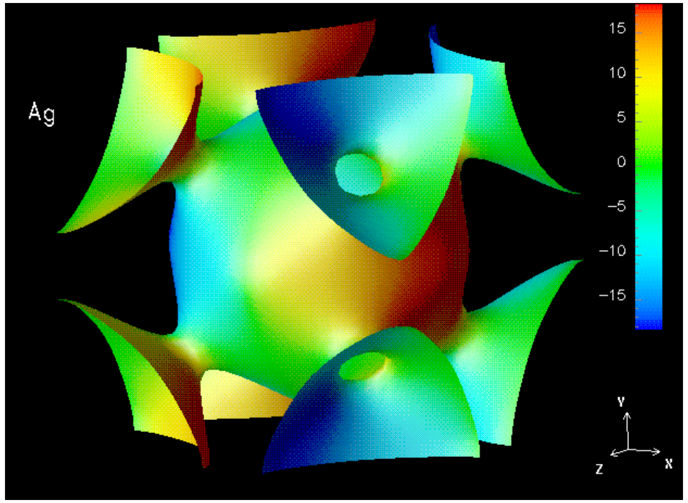
Atomic nucleus

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



Crystalline structure for Ag

The reference for k is the radius of the atom



$p * \lambda = h$

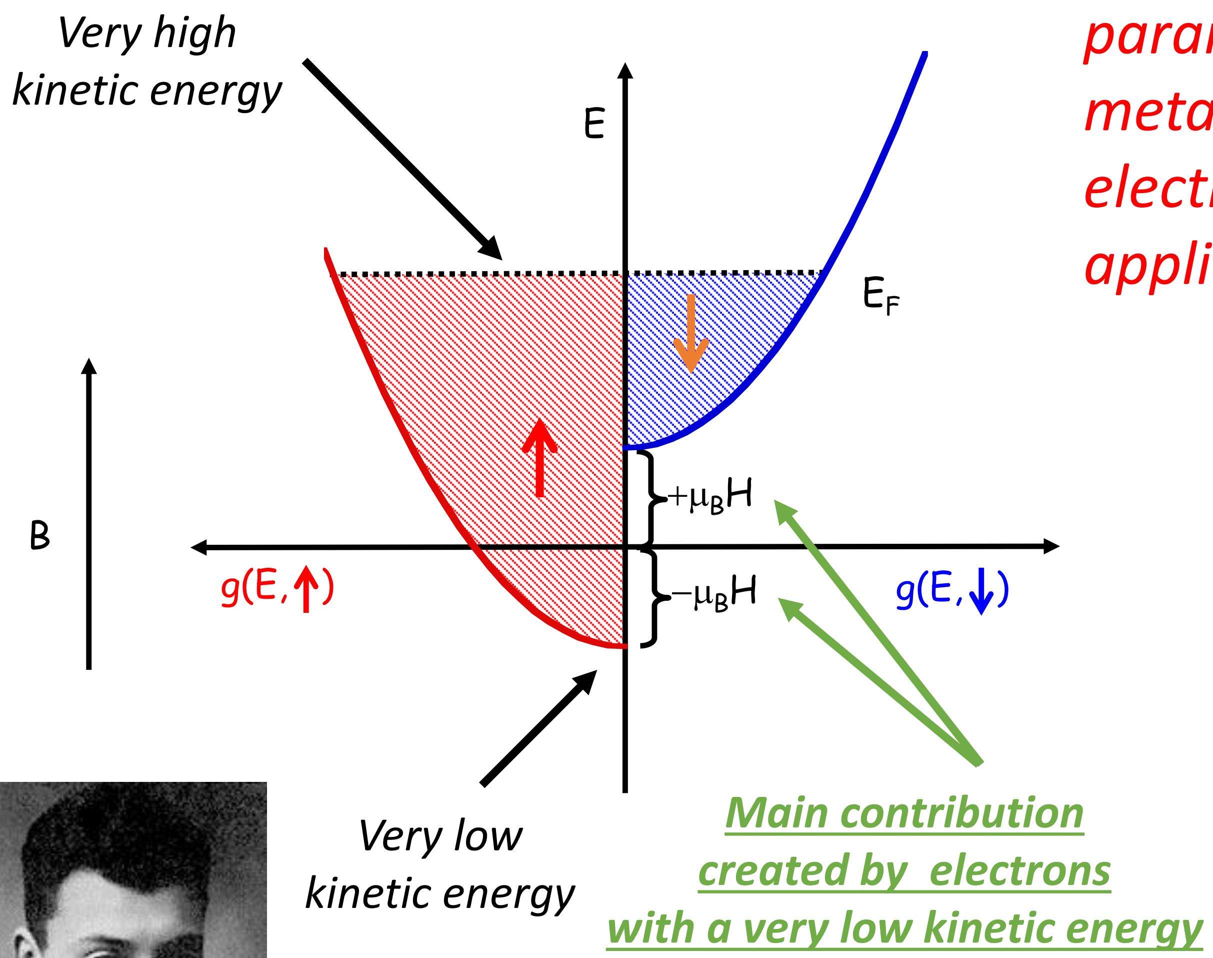
$p = \hbar * k$

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 $T \approx 0K$)

"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 (Standford)



Magnetic Spin – Susceptibility
Low temperature

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

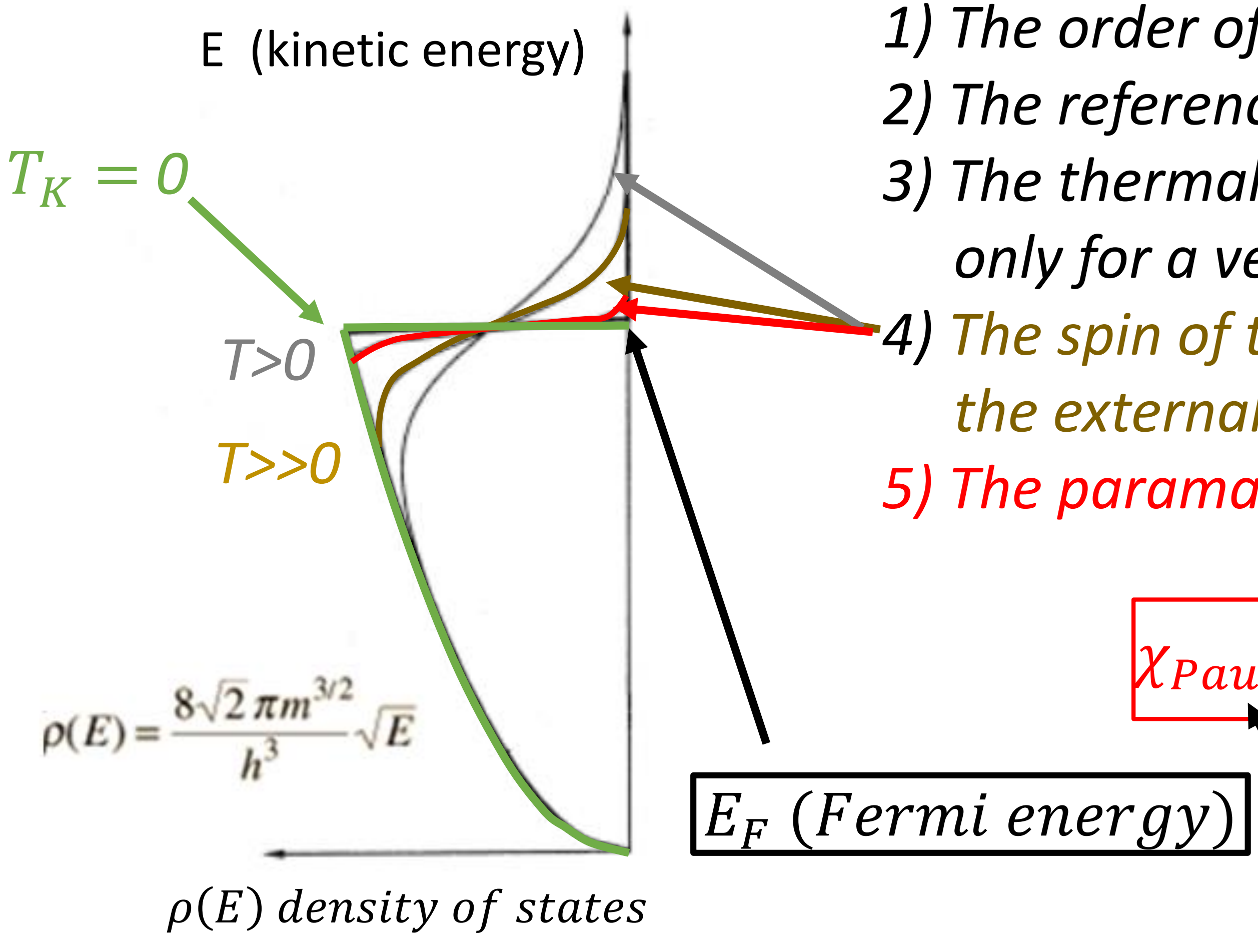
(Pauli Paramagnetism)

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)



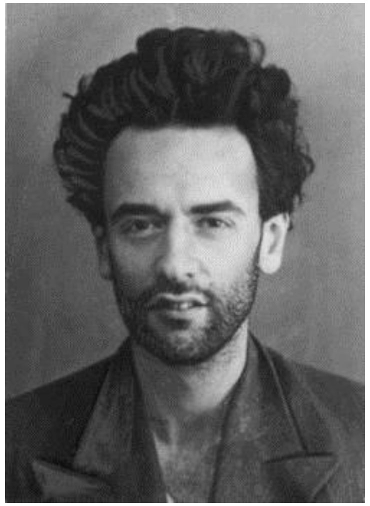
1) The order of the Fermi kinetic energy is high T ≈10 000 K.
2) The reference temperature is ≈ 300K.
3) The thermal energy can increase the kinetic energy only for a very small number of particles.
4) The spin of these particles is oriented in the sense that the external field.
5) The paramagnetism is created by these electrons…

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

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 is principally limited by the energy of Fermi.*
   - B) *The quantification of the energy created by the circular movement of the electrons*

$$E_l = (l + \frac{1}{2})\hbar\omega_c.$$

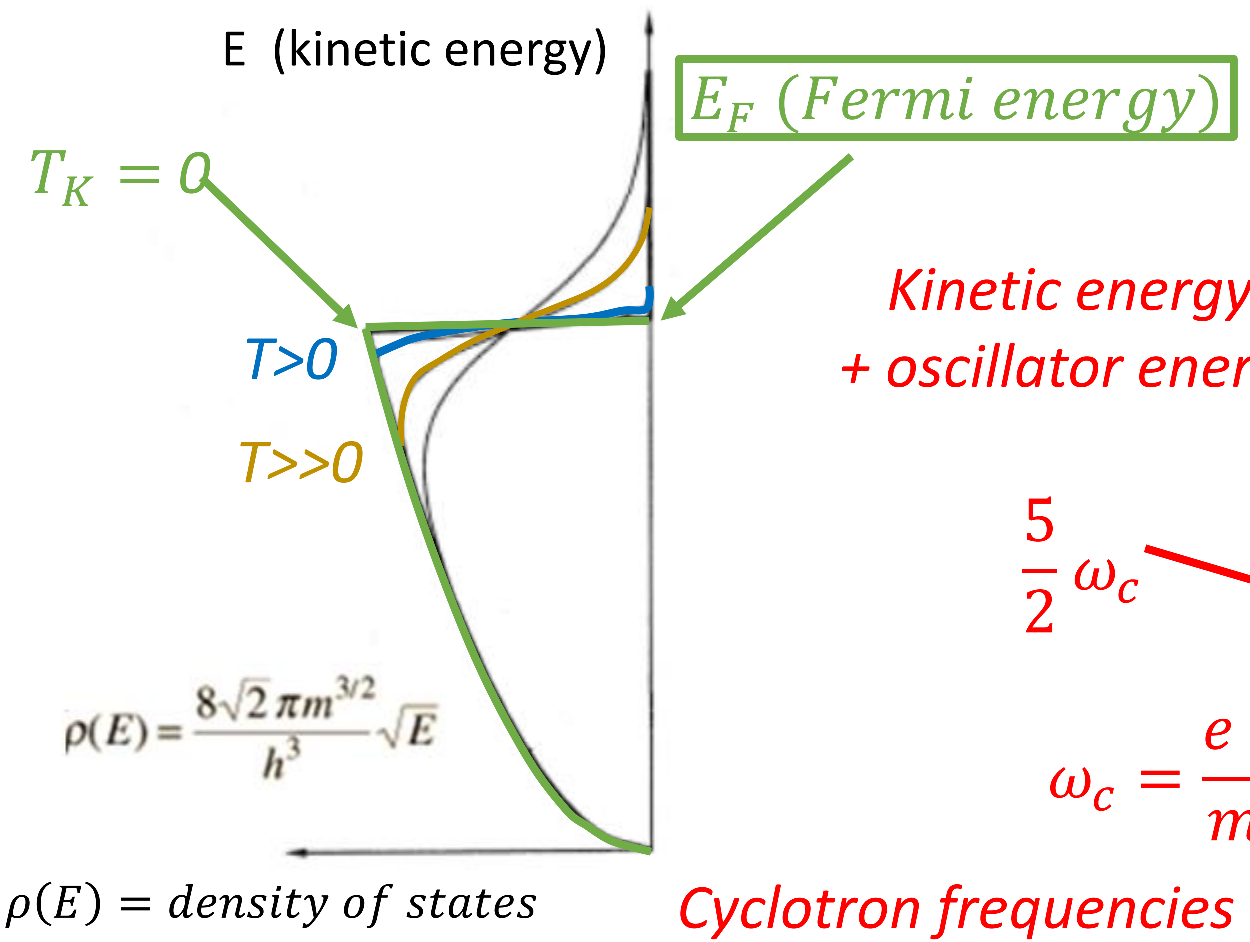
$$M_{Landau} = -\frac{N\mu^2}{2k_B T_F} B$$

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

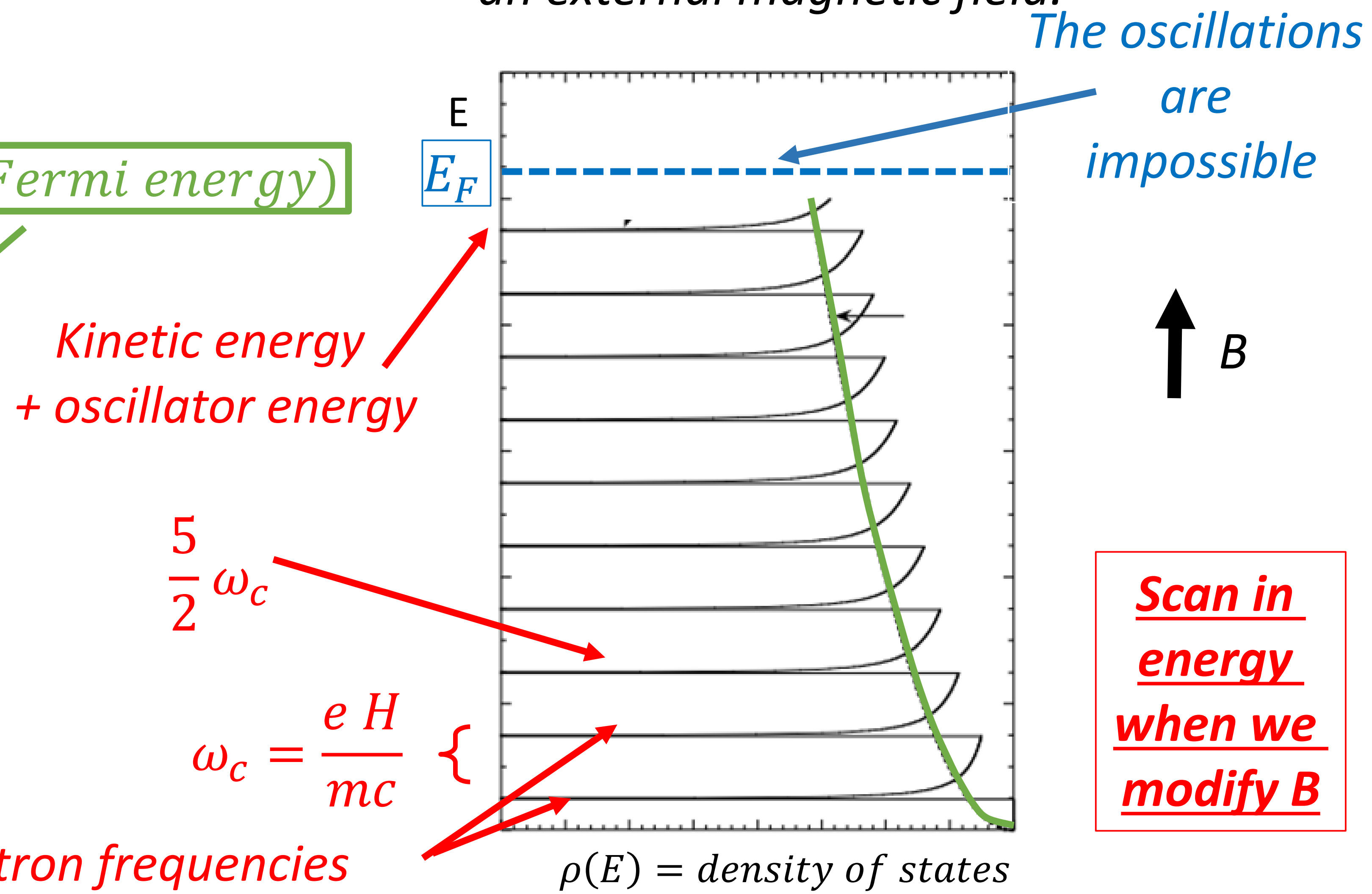
Titanium	Landau diamagnetic susceptibility (χmol)	$-11.1\ 10^{-6}\ cm^3/mol$
Vanadium	Landau diamagnetic susceptibility (χmol)	$-28.6\ 10^{-6}\ cm^3/mol$

Landau diamagnetism $T \approx 0K$

Fermi gas of electrons without an external magnetic field.

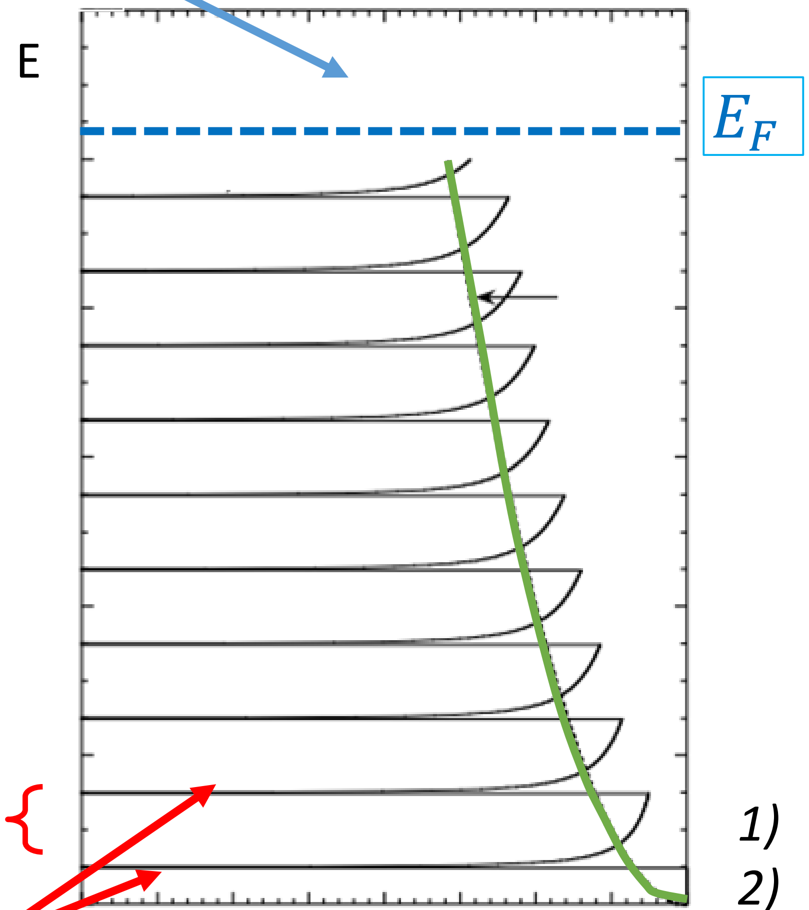


Fermi gas of electrons with an external magnetic field.



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

The oscillations are impossible



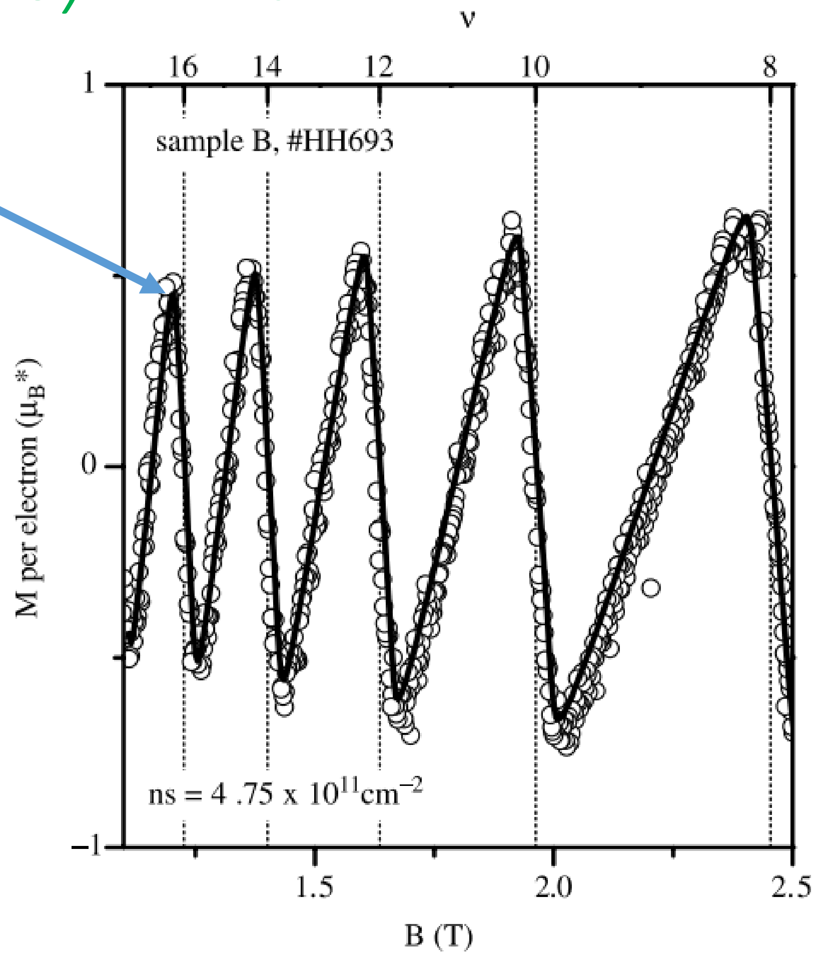
$\rho(E) = desity\ of\ states$

$\omega_c \uparrow if\ H \uparrow$

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

Cyclotron frequencies

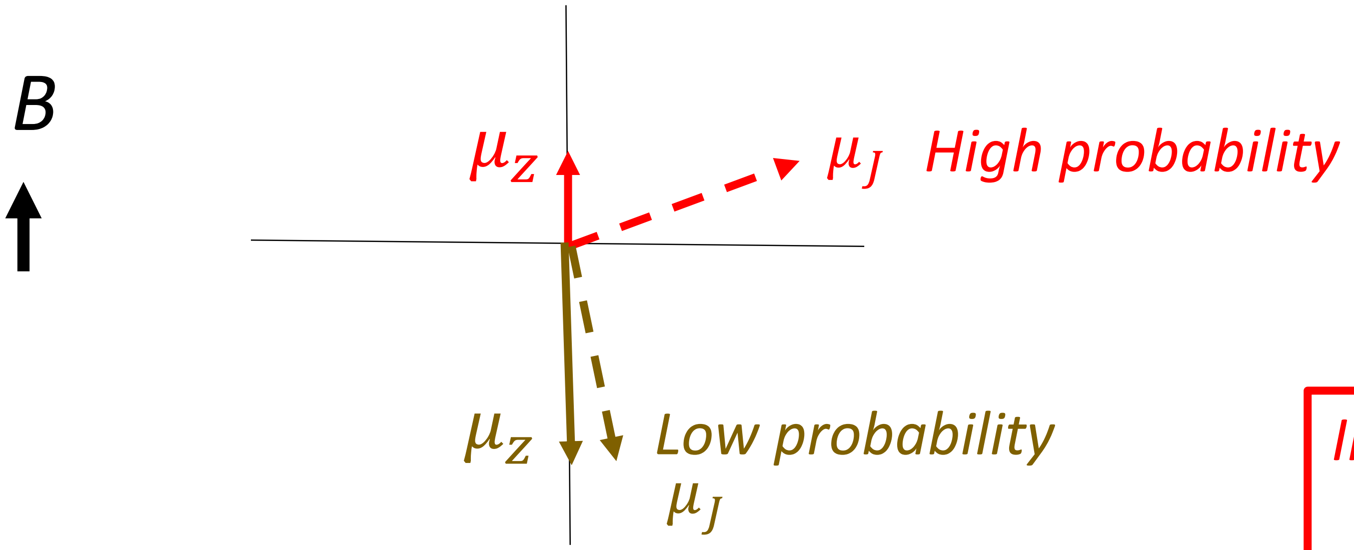
E_F



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.*

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) *The distribution of the magnetic moments obey to the Boltzmann distribution.*
4) *We calculate < total magnetic moment > for one atom and we multiply by N.*
5) *We use the Z axis as reference.*



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

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

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

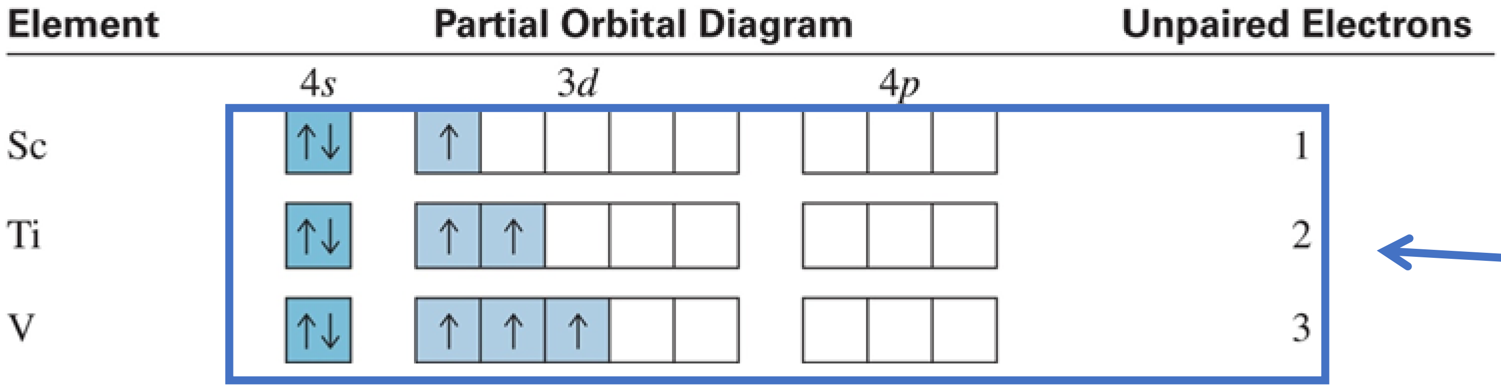
Electrical resistivity	40 ×10^{-8} Ω m (at 20 °C)
Magnetic susceptibility (χmol)	+1.919 10$^{−9}$ m^{3}/mol
Electronegativity	Pauling scale: 1.54

Vanadium

Electrical resistivity	20 ×10^{-8} Ω m (at 20 °C)
Magnetic susceptibility (χmol)	+3.199 10^{-9} m^{3}/mol
Electronegativity	Pauling scale: 1.63

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

$< r^2 > \approx 1$

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

≈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} m³/mol

Zinc

Electrical resistivity	59.0 nΩ·m (at 20 °C)
Electronegativity	Pauling scale: 1.65
Magnetic susceptibility(χ_{mol})	-1.45×10^{-10} m³/mol

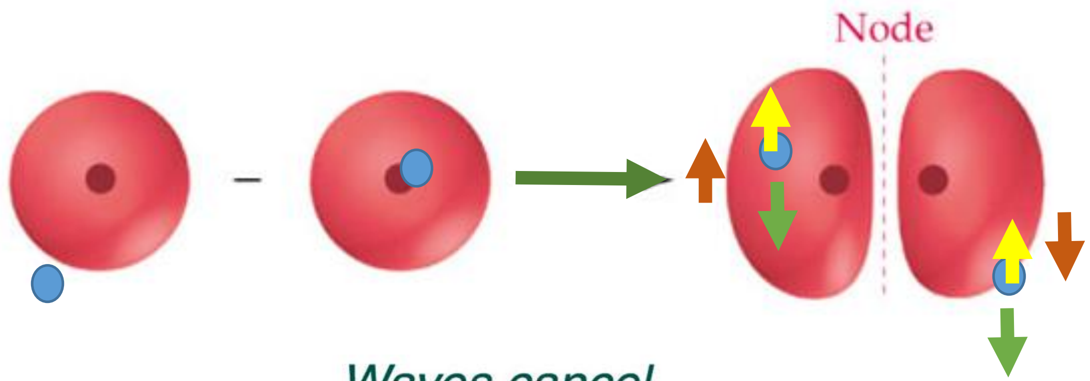
Element	Partial Orbital Diagram 4s	3d	4p	Unpaired Electrons
Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	(empty)	1
Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	(empty)	0

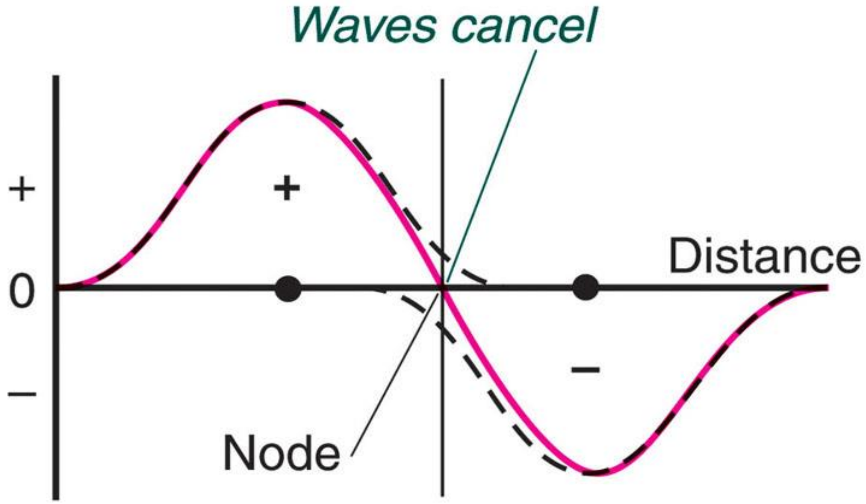
Diamagnetic

http://www.periodictable.com

Ferromagnetism Heisenberg model (1932)

Antibonding

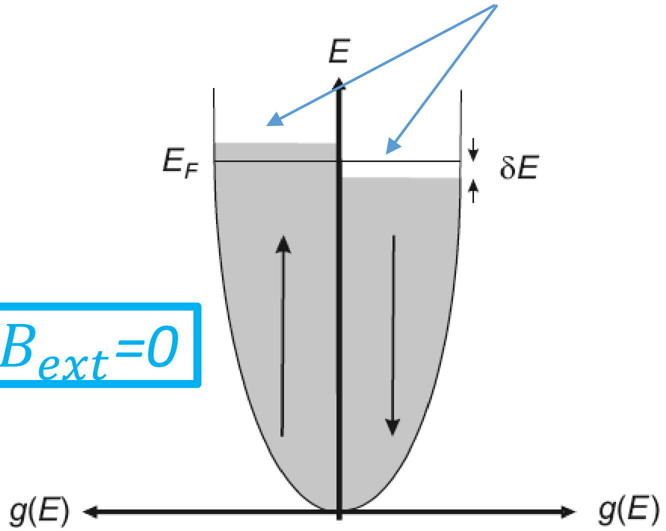




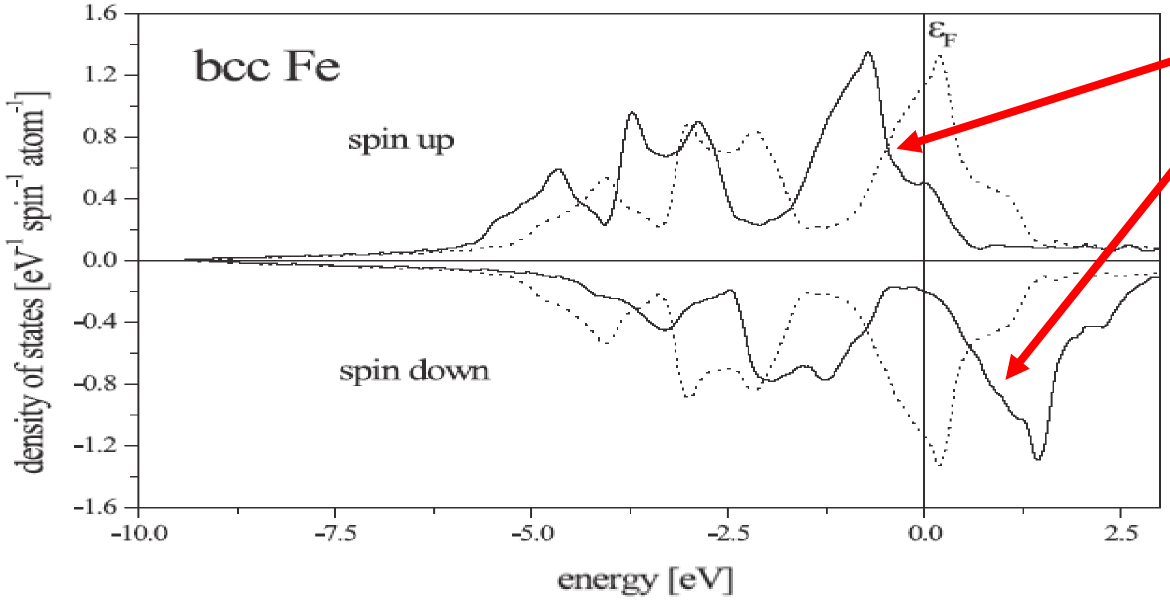
Antibonding
Not stable (Coulomb repulsion between protons)

1) The antibonding create the possibility to align the spin in the same direction.
2) The ferromagnetism is the result between the Coulomb interaction and the Pauli exclusion principle.
3) The spontaneous spin orientation of the others electrons create a mean magnetic field called molecular field by Weiss.
4) The model is anisotropic.
5) The electrons are localized inside the atoms.

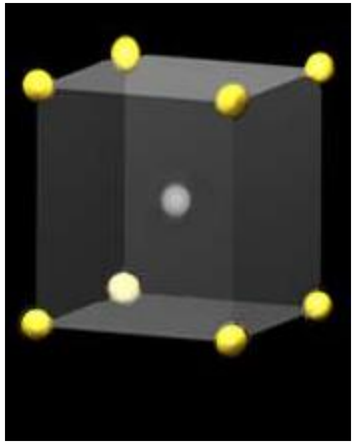
Ferromagnetism Fermi gas (Solid state physics)

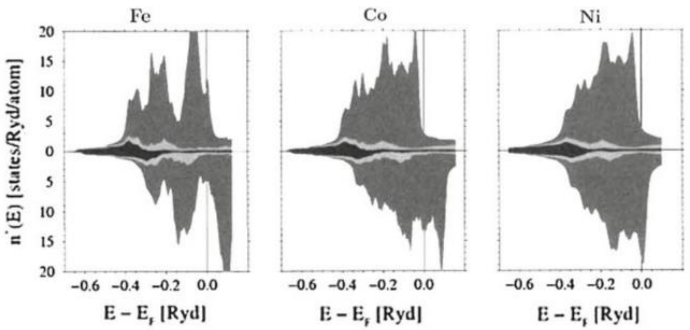


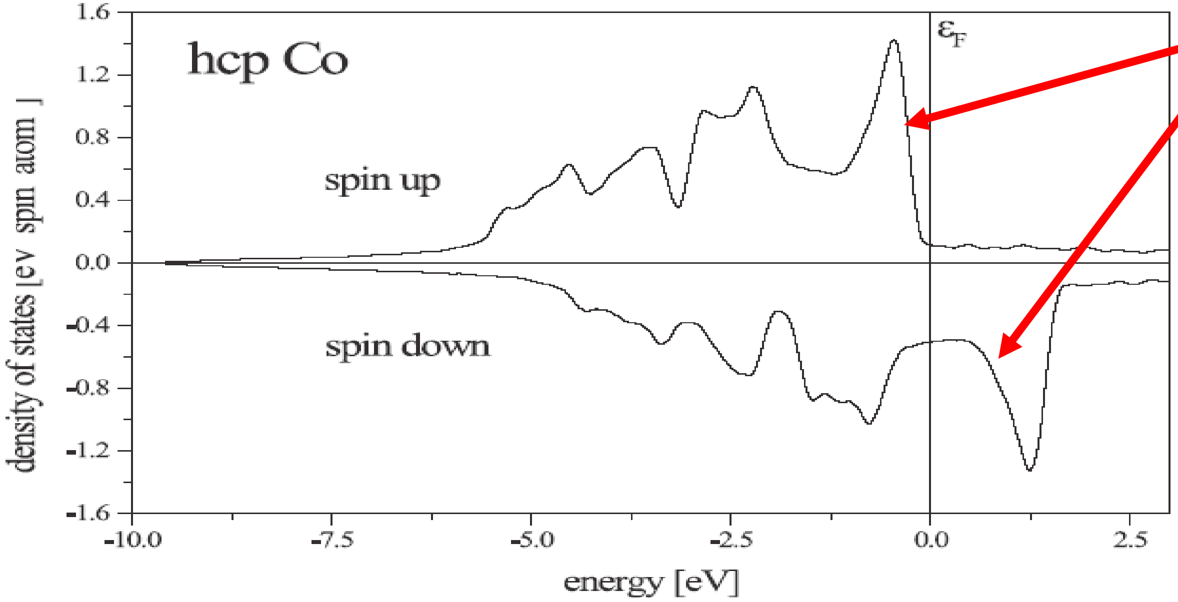
B_{ext}=0



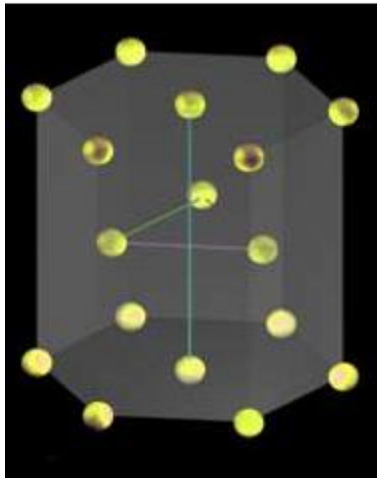
T_K= 300

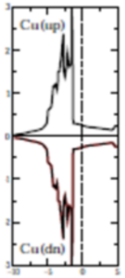






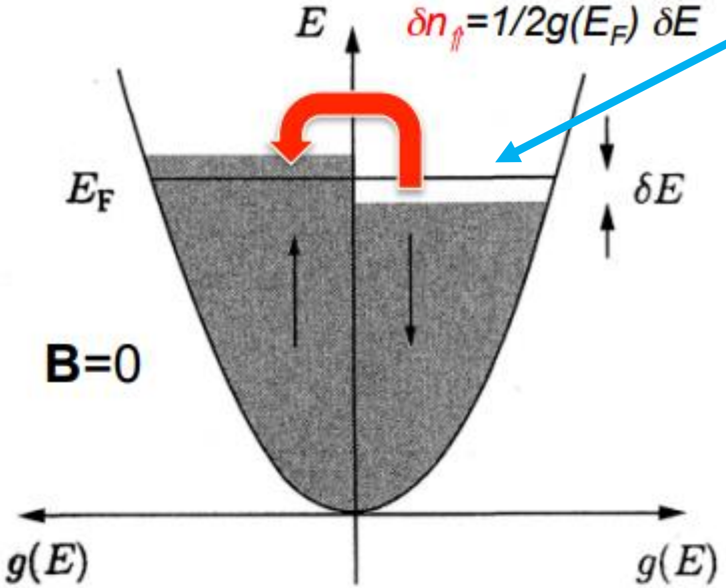
T_K= 300





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.*

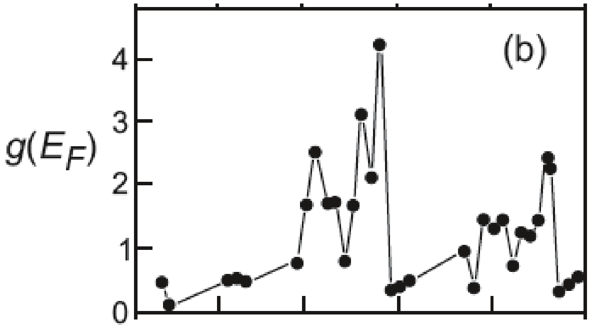
2) $\delta n \downarrow$ *are flip in* $\delta n \uparrow$ *sub-band close* $E_F + \delta E$.
The number of electrons moved is $\delta n_{\Uparrow}$.

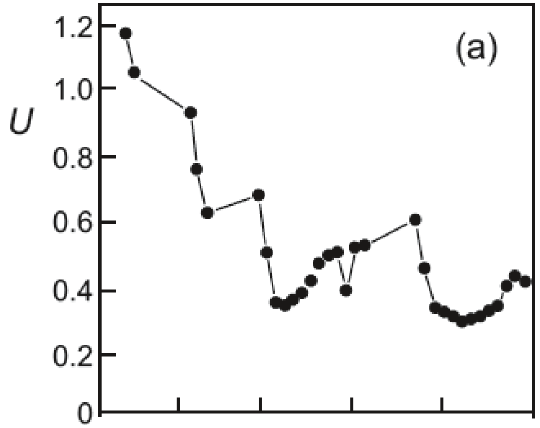
3) *The potential energy* $\Rightarrow \Delta E_{pot} = -\frac{1}{2} U g((E_F)\delta E^2$

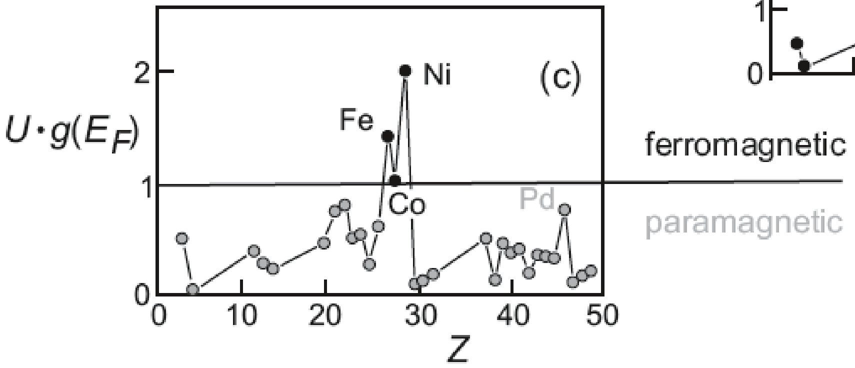
3) *Kinetic energy cost* $\Rightarrow$ $\Delta E_{kin} = \frac{1}{2} g((E_F)\delta E^2$.

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

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

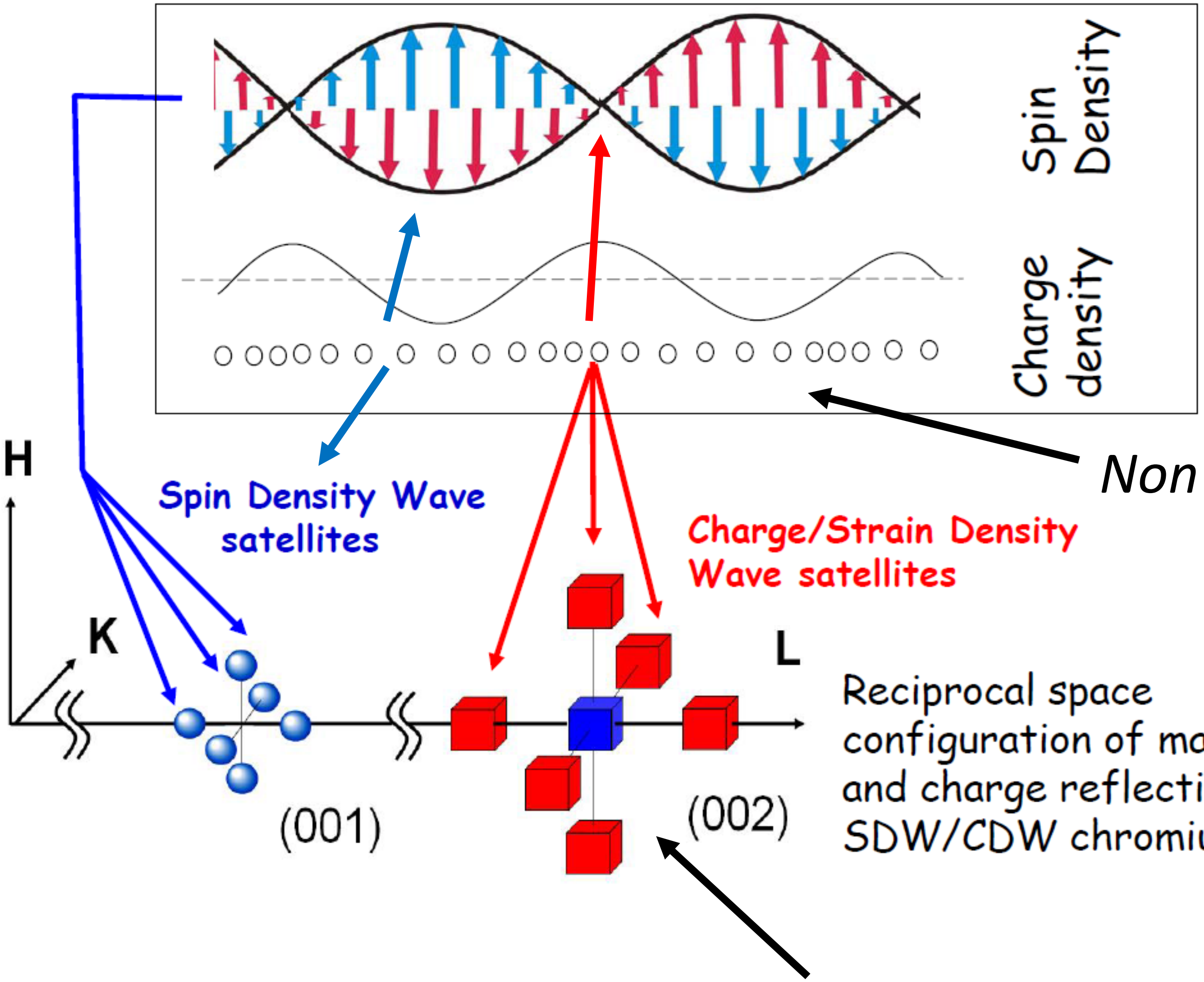


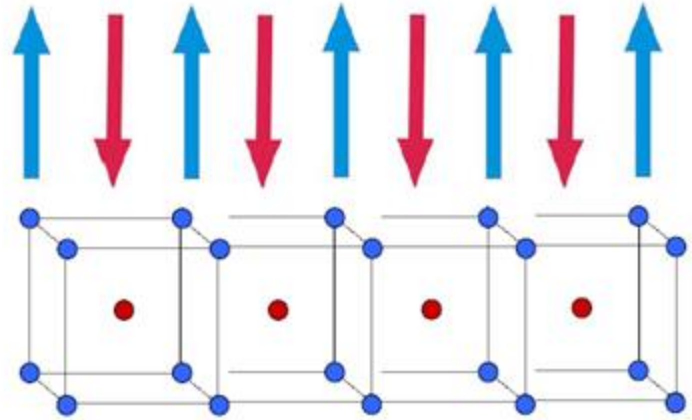




Antiferromagnetism chromium (molecular

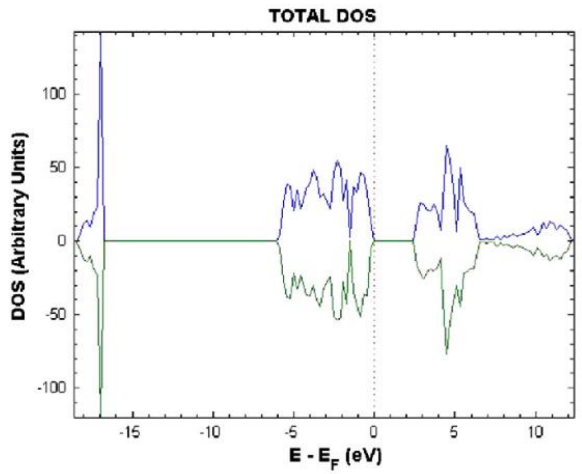
Uniform distance between the atoms.





Non uniform distance between the atoms.

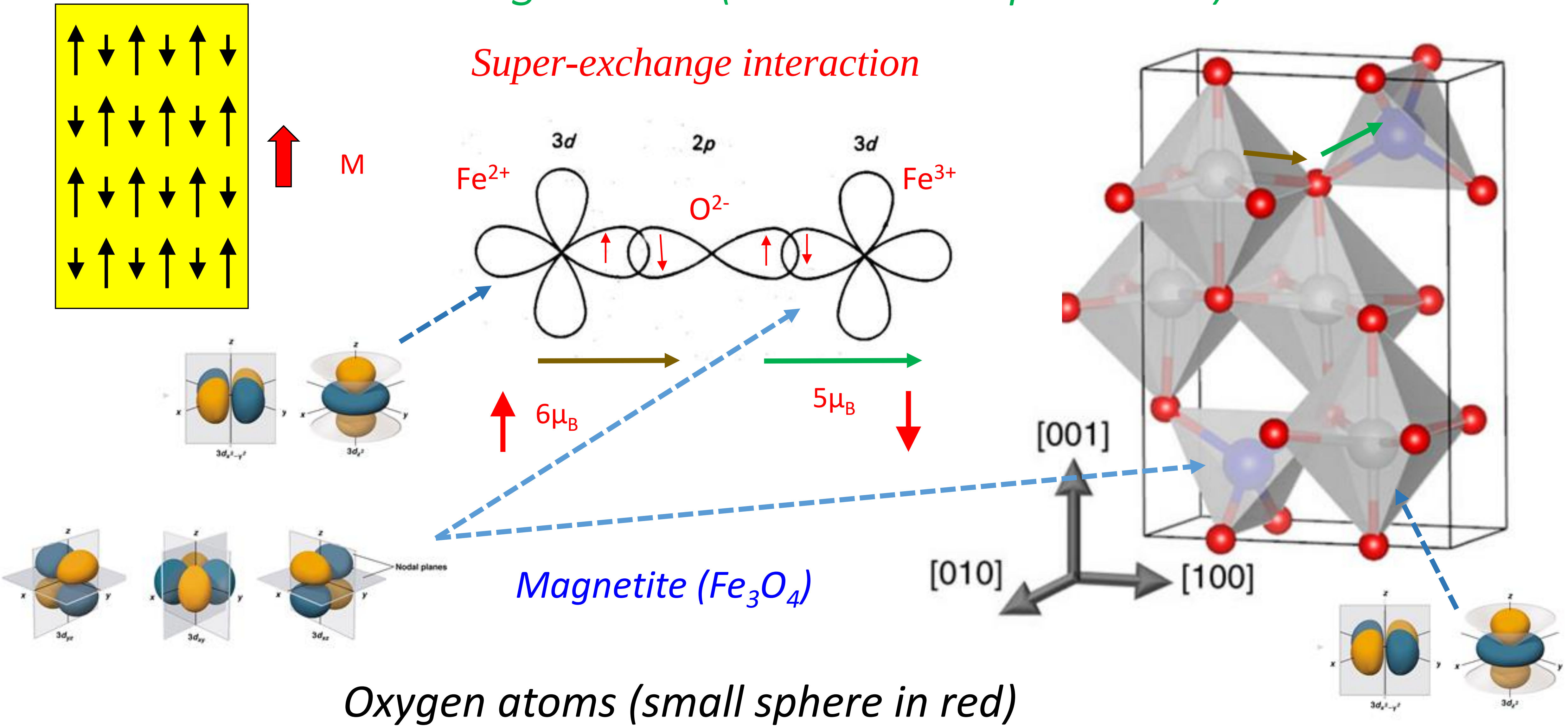
Reciprocal space configuration of magnetic and charge reflection of SDW/CDW chromium



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)



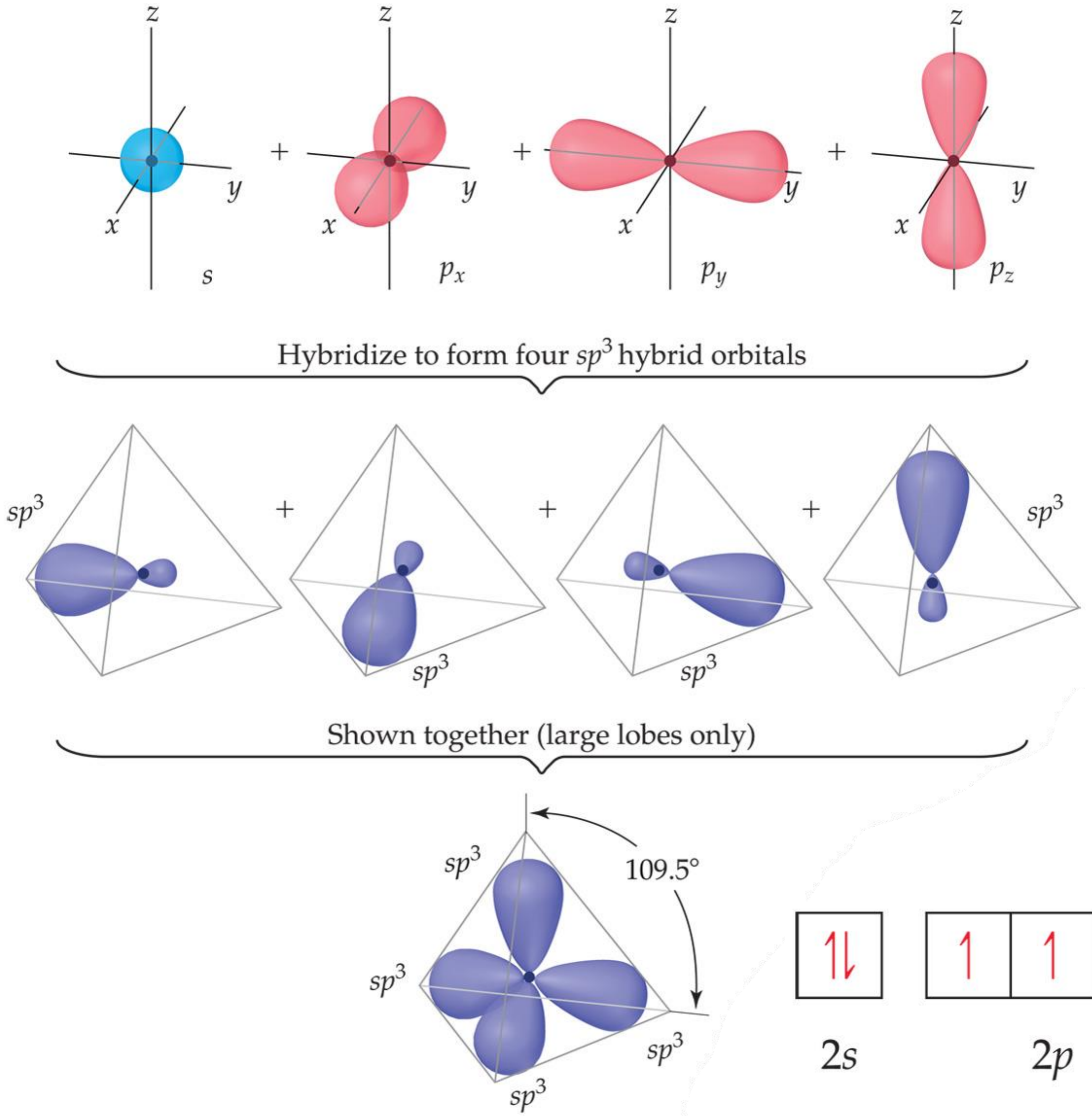
Oxygen atoms (small sphere in red)

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

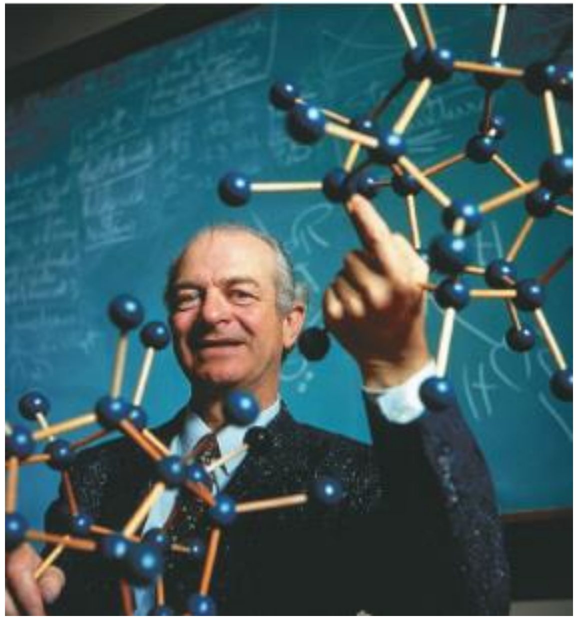
Valence Bond Theory (molecular physic)

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

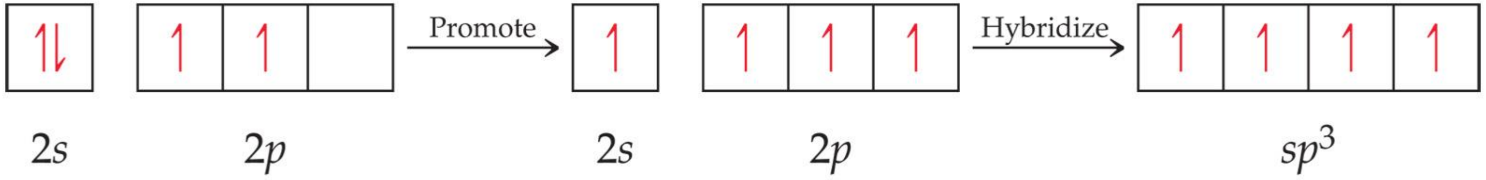
Suitable for the qualitative description of atomic bonding properties.

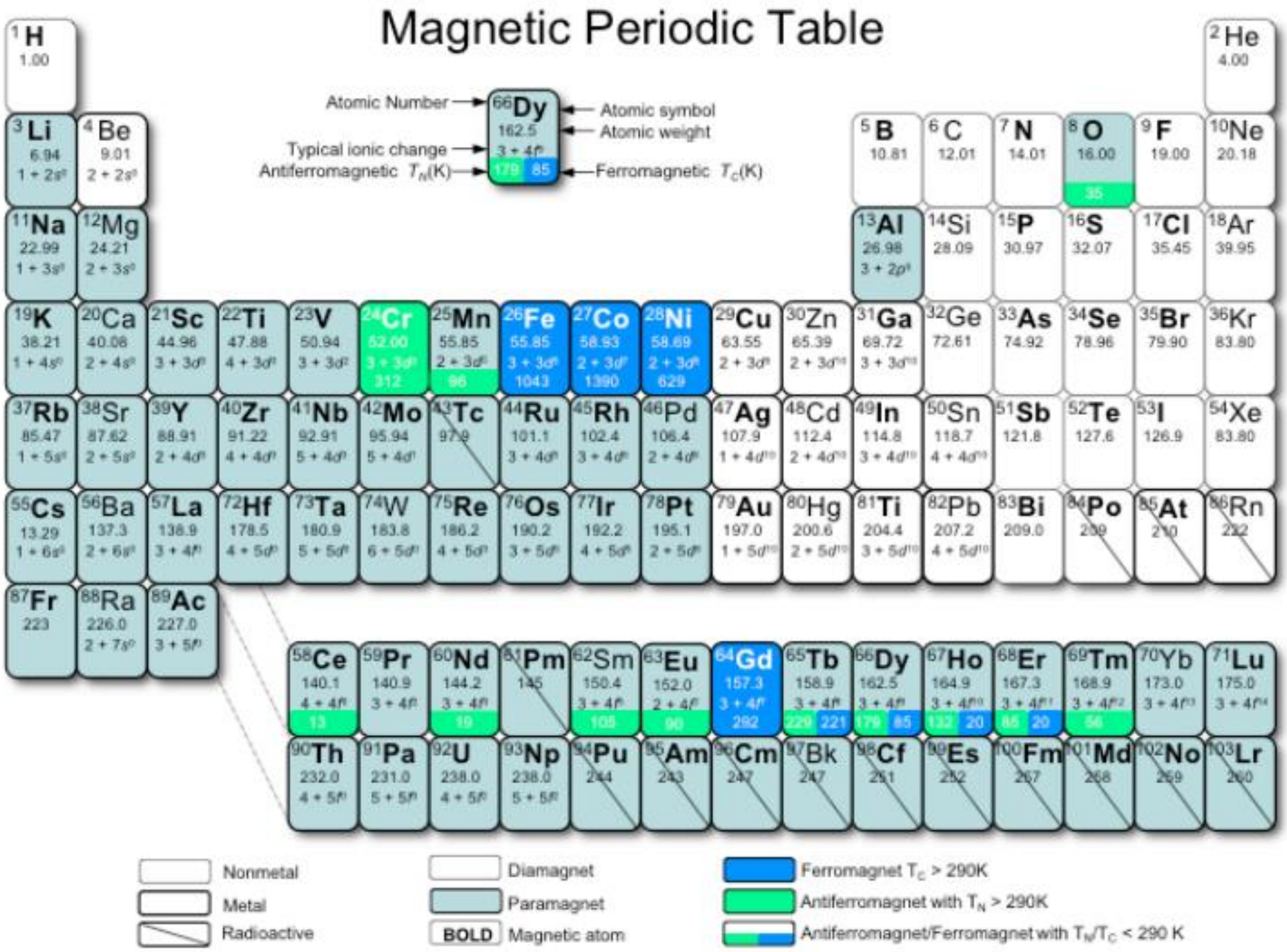


Linus Pauling



Example:
sp^3 orbitals.





Magnetic Periodic Table
Atomic Number
Atomic symbol
Atomic weight
Typical ionic change
Antiferromagnetic T_N(K)
Ferromagnetic T_C(K)
66 Dy 162.5 179 85
1 H 1.00
2 He 4.00
3 Li 6.94
4 Be 9.01
5 B 10.81
6 C 12.01
7 N 14.01
8 O 16.00 35
9 F 19.00
10 Ne 20.18
11 Na 22.99
12 Mg 24.21
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
19 K 38.21
20 Ca 40.08
21 Sc 44.96
22 Ti 47.88
23 V 50.94
24 Cr 52.00 312
25 Mn 55.85 96
26 Fe 55.85 1043
27 Co 58.93 1390
28 Ni 58.69 629
29 Cu 63.55
30 Zn 65.39
31 Ga 69.72
32 Ge 72.61
33 As 74.92
34 Se 78.96
35 Br 79.90
36 Kr 83.80
37 Rb 85.47
38 Sr 87.62
39 Y 88.91
40 Zr 91.22
41 Nb 92.91
42 Mo 95.94
43 Tc 97.9
44 Ru 101.1
45 Rh 102.4
46 Pd 106.4
47 Ag 107.9
48 Cd 112.4
49 In 114.8
50 Sn 118.7
51 Sb 121.8
52 Te 127.6
53 I 126.9
54 Xe 83.80
55 Cs 13.29
56 Ba 137.3
57 La 138.9
72 Hf 178.5
73 Ta 180.9
74 W 183.8
75 Re 186.2
76 Os 190.2
77 Ir 192.2
78 Pt 195.1
79 Au 197.0
80 Hg 200.6
81 Ti 204.4
82 Pb 207.2
83 Bi 209.0
84 Po 209
85 At 210
86 Rn 222
87 Fr 223
88 Ra 226.0
89 Ac 227.0
58 Ce 140.1 13
59 Pr 140.9
60 Nd 144.2 19
61 Pm 145
62 Sm 150.4 105
63 Eu 152.0 90
64 Gd 157.3 292
65 Tb 158.9 229 221
66 Dy 162.5 179 85
67 Ho 164.9 132 20
68 Er 167.3 85 20
69 Tm 168.9 56
70 Yb 173.0
71 Lu 175.0
90 Th 232.0
91 Pa 231.0
92 U 238.0
93 Np 238.0
94 Pu 244
95 Am 243
96 Cm 247
97 Bk 247
98 Cf 251
99 Es 252
100 Fm 257
101 Md 258
102 No 259
103 Lr 260
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 Pnictogens	16 Chalcogens	17 Halogènes	18
1	1 H Hydrogène 1,008	Atomique Sym Nom Masse																2 He Hélium 4,0026
2	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
3	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
4	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
5	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
6	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)
7	87 Fr Francium (223)	88 Ra Radium (226)	89–103	104 Rf Rutherfordiu (267)	105 Db Dubnium (268)	106 Sg Seaborgiur (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 Livermoriur (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)

Légende : 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

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

57 La Lanthane 138,91	58 Ce Cérium 140,12	59 Pr Praséodym 140,91	60 Nd Néodyme 144,24	61 Pm Prométhiur (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 Mendélévu (258)	102 No Nobélium (259)	103 Lr Lawrencium (266)