



Institut de Physique et Chimie des Matériaux de Strasbourg

From atoms to solids to nanostructures

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Course content

- I. Magnetic moment and magnetic field
- II. No magnetism in classical mechanics
- III. Where does magnetism come from?
- IV. Crystal field, superexchange, double exchange
- V. Free electron model: Spontaneous magnetization
- VI. The local spin density approximation of the DFT
- VI. Beyond the DFT: LDA+U
- VII. Spin-orbit effects: Magnetic anisotropy, XMCD
- VIII. Bibliography



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Magnetic moments

In classical electrodynamics, the vector potential, in the magnetic dipole approximation, is given by:

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{\boldsymbol{\mu} \times \hat{\mathbf{r}}}{r^2}$$

where the magnetic moment $\boldsymbol{\mu}$ is defined as:

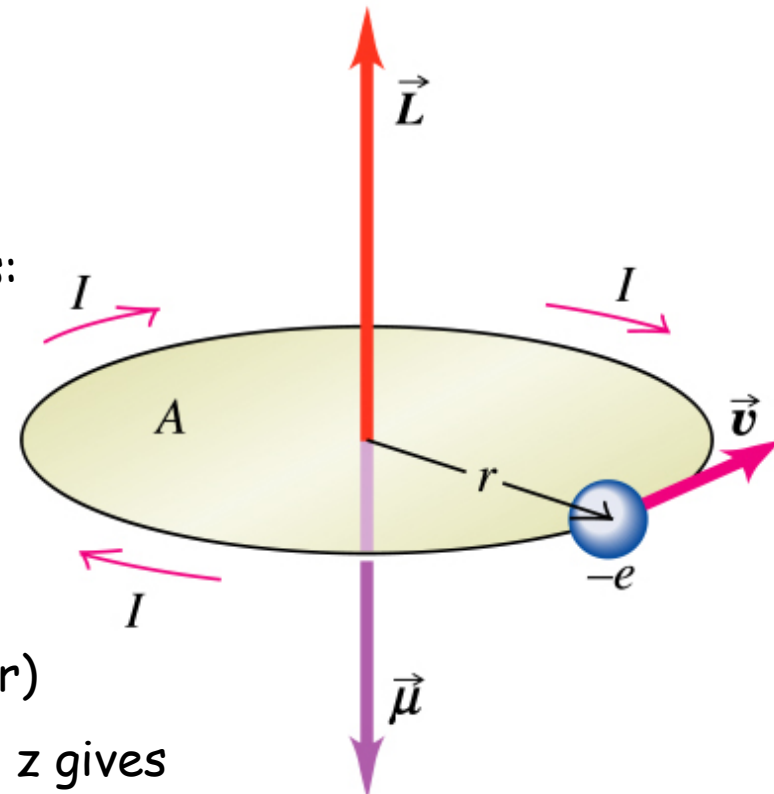
$$\boldsymbol{\mu} = \frac{1}{2} I \oint (\mathbf{r}' \times d\mathbf{l})$$

It is shown that the magnetic moment is proportional to the angular momentum

$$\boldsymbol{\mu} = \gamma \mathbf{L} \quad (\gamma \text{ the gyromagnetic factor})$$

The projection along the quantification axis z gives

$$\mu_z = -g \mu_B m \quad (\mu_B = e\hbar / 2m_e \text{ Bohr magneton})$$



Magnetization and Field

The magnetization M is the magnetic moment per unit volume

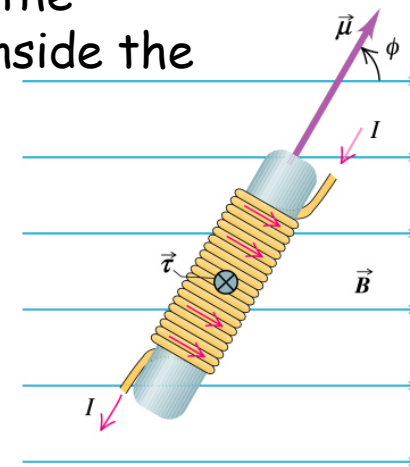
In free space $B = \mu_0 H$ because there is no net magnetization.

Inside a magnet, the relation is more complicated $B = \mu_0 (H + M)$.

For linear materials, the magnetic susceptibility χ is defined as $M = \chi H$.
In this case there is still a linear relationship between B and H
($B = \mu_0 (1 + \chi) H = \mu_0 \mu_r H$).
relative permeability

Example: For a cylinder $B_i = B_a + \mu_0 M$. so that $H = H_a = B_a / \mu_0$
In this case it is the free current (coil) that controls the magnetization and hence controls the magnetic field inside the cylinder.

In other more complex geometry, one has to subtract out the **demagnetizing field** to find H .



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The magnetization is zero in classical mechanics

This is because the application of a **magnetic field** amounts in **changing the kinetic energy** to :

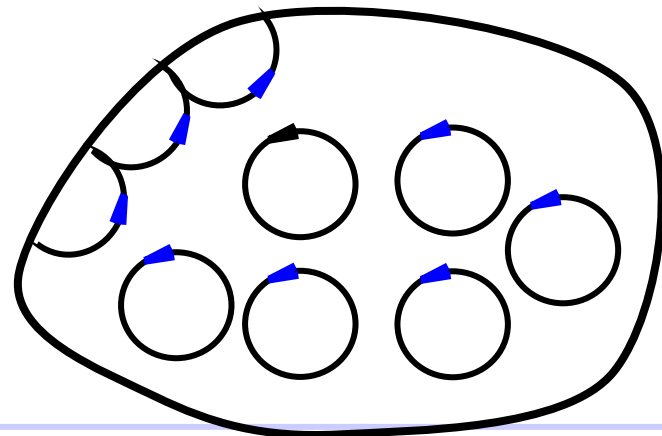
$$W_K = \frac{(\mathbf{p} - e\mathbf{A})^2}{2m}$$

$$Z \sim \int \exp(-\beta E(p_1, \dots, p_N, r_1, \dots, r_N)) d^3 p_1 \dots d^3 p_N d^3 r_1 \dots d^3 r_N$$

Since the integral goes all over the phase space, the effect of a magnetic field is just to shift the momentum zero. The partition function is therefore independent of the magnetic field (**Bohr-van Leeuwen theorem**)

$$M = -\left(\frac{\partial F}{\partial B}\right)_{T,V} = Nk_B T \left(\frac{\partial \ln Z}{\partial B}\right)_{T,V} = 0$$

This can be easily seen in a finite magnetic sample where the orbital current that scatter at the surface cancels out the orbital volume current.



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Two particle system

A single particle wave function: $\Psi(r, t)$ A Two-particle wave function: $\Psi(r_1, r_2, t)$

The time evolution is determined by the non relativistic Schrödinger equation (SE):

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi$$

The Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m} \Delta_1 - \frac{\hbar^2}{2m} \Delta_2 + V(r_1, r_2, t)$$

$$\iint |\Psi(r_1, r_2, t)|^2 d^3r d^3r' = 1$$

For **time-independent potential** the wave function is given by $\Psi(r_1, r_2, t) = \psi(r_1, r_2) e^{-i\frac{Et}{\hbar}}$

where E is the total energy of the system given by

$$H\psi(r_1, r_2) = E\psi(r_1, r_2)$$

BOSONS AND FERMIONS

Symmetrization of the wave function

Distinguishable particles: particle 1 in ψ_1 and particle 2 in ψ_2 . The state of the 2 particles is:

$$\psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2)$$

Indistinguishable particles: In QM all particles are identical. We construct a wave function that is noncommittal as to which particle is in which state:

$$\psi_{\pm}(r_1, r_2) = C [\psi_1(r_1)\psi_2(r_2) \pm \psi_2(r_1)\psi_1(r_2)]$$

QM accommodates 2 kinds of identical particles, for **bosons** we use **+ sign**, for **fermions** the **minus sign**.

Spin statistics Theorem: particles with **integer spin** are **bosons**, and particles with **half-integer** spin are **fermions** (W. Pauli, PR 1940).

Note: This spin statistics Theorem can be proved in relativistic QM. **Pauli exclusion principle (PEP)** is a consequence of this Theorem.

PEP: Two identical fermions can not occupy the same state.



The exchange operator P

The **exchange operator P** interchanges the two particles: $P\psi(r_1, r_2) = \psi(r_2, r_1)$

It is then obvious that $P^2 = 1$ and P and H commute (compatible observables).

We can find a complete set of functions that are simultaneous eigenstates of H and P . The eigenvalues of P are **+1** and **-1**.

$$\psi(r_1, r_2) = \pm\psi(r_2, r_1) \quad + \text{ for bosons and } - \text{ for fermions.}$$

If the system starts in a given symmetrized state, it remains in such state during its evolution.

The wave function of a QM system is required to be symmetric or antisymmetric.



Exchange force

The **expectation value** of the square of the **separation value** of **two bosons** is **reduced** compared to that of distinguishable particles, and that of **two identical fermions** is **increased**. It is like there is an **exchange force** between identical particles.

Proof (one dimension case)

Distinguishable particles: $\psi_D(x_1, x_2) = \psi_1(x_1)\psi_2(x_2)$ and $\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

$$\langle x_1^2 \rangle = \iint x_1^2 |\psi_D(x_1, x_2)|^2 dx_1 dx_2 = \int x_1^2 |\psi_1(x_1)|^2 dx_1 \int |\psi_2(x_2)|^2 dx_2 = \langle x^2 \rangle_1$$

Similarly, $\langle x_2^2 \rangle = \langle x^2 \rangle_2$ and $\langle x_1 x_2 \rangle = \langle x \rangle_1 \langle x \rangle_2$ so that $\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2\langle x \rangle_1 \langle x \rangle_2$

Identical particles: $\psi_{\pm}(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) \pm \psi_2(r_1)\psi_1(r_2)]$

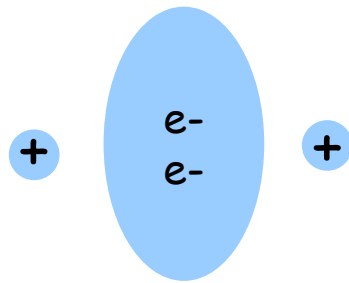
$$\langle x_1^2 \rangle = \frac{1}{2} [\langle x^2 \rangle_1 + \langle x^2 \rangle_2], \quad \langle x_2^2 \rangle = \frac{1}{2} [\langle x^2 \rangle_2 + \langle x^2 \rangle_1], \quad \text{and} \quad \langle x_1 x_2 \rangle = \langle x \rangle_1 \langle x \rangle_2 \pm |\langle x \rangle_{1,2}|^2$$

$$\text{where} \quad \langle x \rangle_{1,2} = \int x \psi_1(x)^* \psi_2(x) dx$$

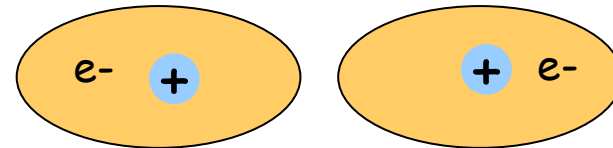
$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2\langle x \rangle_1 \langle x \rangle_2 \mp 2|\langle x \rangle_{1,2}|^2 = \langle (x_1 - x_2)^2 \rangle_D \mp 2|\langle x \rangle_{1,2}|^2$$



Exchange force (continued)



Symmetric configuration produces **attractive exchange force**



Antisymmetric configuration produces at **repulsive exchange force**

The **exchange force** is a **purely geometrical consequence** of the **symmetrization** requirement. It **is not a real force** because **no energy is spent in moving the particles**.

Because electrons are fermions, in molecules it is the antisymmetric configuration that should happen. This is true but one has to take into account the spin of the electrons.

$$\psi_{s_1, s_2}(r_1, r_2) = \psi(r_1, r_2) \chi(s_1, s_2)$$

The spatial part can be symmetric if the spin part is antisymmetric.

Note: In molecules, the bonding state is a singlet (antisymmetric spin state) and the anti-bonding a triplet state (antisymmetric spatial wave function, but symmetric spin function).

Molecules: The hydrogen molecule

It is difficult to get the correct GS of H_2 because of the $e-e$ interaction. Instead, a simple molecular orbital approach captures most of the physics.

Let ψ denote the state of an electron in the molecule, it can be written as a linear combination of the state of the isolated atoms:

$$|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle \quad \text{and assume that } \langle i | j \rangle = \delta_{i,j} \quad \text{for simplification.}$$

The SE for the molecule is : $H |\psi\rangle = E |\psi\rangle$


To solve it we project it into the atomic basis and obtain:

$$\begin{cases} E_0 c_1 + H_{12} c_2 = E c_1 \\ H_{21} c_1 + E_0 c_2 = E c_2 \end{cases} \quad \text{with } E_0 = H_{11} = H_{22} \quad \text{different from the atomic s level.}$$

The fact that the Hamiltonian is hermitian and the s orbital is real implies that $H_{12} = H_{21} = \beta$.

The solutions are: $E_b = E_0 + \beta$ et $E_a = E_0 - \beta$ and the eigenvectors are:

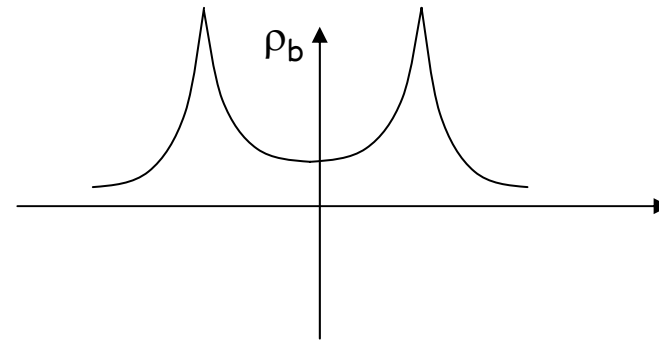
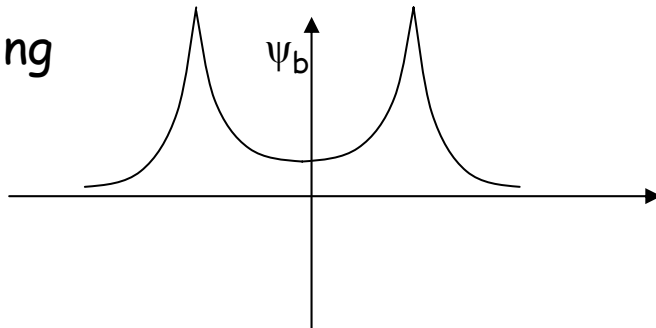
$$|\psi_b\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \quad \text{and} \quad |\psi_a\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

$\beta < 0$  the molecular state $|\psi_b\rangle$ has the lowest energy E_b .
The spin state is therefore antisymmetric and correspond to a **singlet state**.

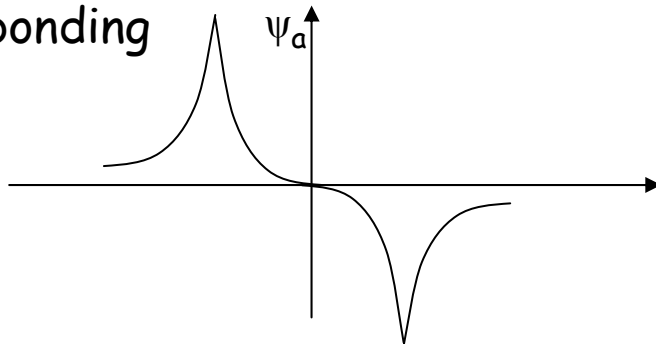


Representation of bonding and antibonding states

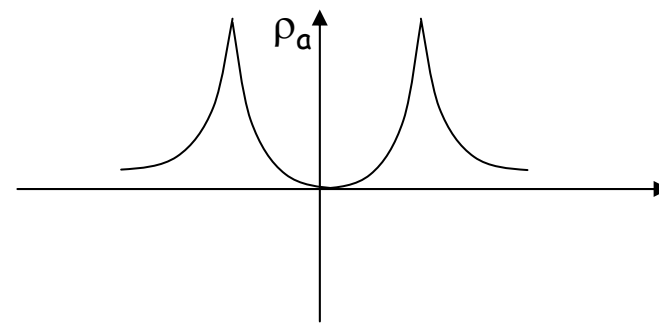
a. Bonding



b. Antibonding



wave function



Charge density

$$\rho_b(r) = 2 |\psi_b(r)|^2 = \rho_1(r) + \rho_2(r) + \rho_{bond}(r) \text{ where } \rho_{bond}(r) = 2\psi_1(r)\psi_2(r)$$

The chemical bond in molecules is a direct consequence of **QM interference** between the wave functions of the constituent atoms. **There is no analogue in classical physics.**



Importance of the off-diagonal Hamiltonian matrix elements H_{12} and H_{21}

We start from the time-dependent SE for the state Ψ :

$$i\hbar \frac{\partial}{\partial t} \Psi(r,t) = H\Psi(r,t) \quad \longrightarrow \quad \begin{cases} i\hbar \frac{dc_1}{dt} = E_0 c_1 + \beta c_2 \\ i\hbar \frac{dc_2}{dt} = \beta c_1 + E_0 c_2 \end{cases}$$

If we set $c_i = A_i e^{-i\omega t}$ and insert them into these coupled equations, we obtain:

$$\omega_b = \frac{E_0 + \beta}{\hbar} \quad \text{and} \quad \omega_a = \frac{E_0 - \beta}{\hbar}$$

and the coefficients c_1 et c_2 are given by

$$\begin{cases} c_1(t) = A_1 e^{-i\frac{\omega_b}{\hbar}t} + A_2 e^{-i\frac{\omega_a}{\hbar}t} \\ c_2(t) = A_1 e^{-i\frac{\omega_b}{\hbar}t} - A_2 e^{-i\frac{\omega_a}{\hbar}t} \end{cases}$$

where A_1 and A_2 are arbitrary constants to be determined by the initial conditions.

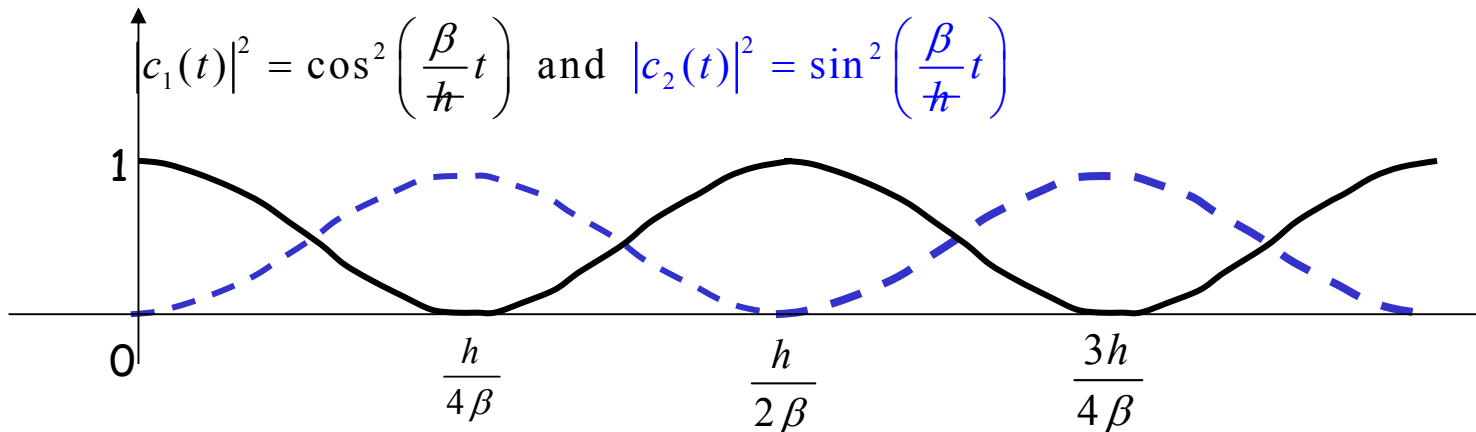
If we know that at $t=0$ s, the molecule is in the state $|1\rangle$ so that $c_1(0)=1$ and $c_2(0)=0$, then $A_1=A_2=1/2$. The coefficients c_1 and c_2 are then given by:

$$c_1(t) = e^{-i\frac{E_0}{\hbar}t} \cos\left(\frac{\beta}{\hbar}t\right) \quad \text{and} \quad c_2(t) = e^{-i\frac{E_0}{\hbar}t} \sin\left(\frac{\beta}{\hbar}t\right)$$

The amplitudes c_1 and c_2 oscillate harmonically with time.



Probabilities $|c_1(t)|^2$ et $|c_2(t)|^2$



The probability starts at 1 and then decreases to 0 in time $h/4\beta$, and returns to one in $h/2\beta$. At the same time the probability that the molecule is in state $|2\rangle$ is exactly out of phase.

The frequency of the molecule passing from state $|1\rangle$ to state $|2\rangle$ and back again to state $|1\rangle$ is $2\beta/h$. An electron in this molecular orbital is vibrating between the two atoms.

The electron tunnel from atom 1 to atom 2 back and forth despite the energy barrier of about 13.6 eV corresponding to the ionization energy.

The probability per unit time that the electron tunnels or "hops" from one atom to the other is $2\beta/h$. For this reason the off-diagonal elements of the Hamiltonian are called hopping integrals.

Heteronuclear diatomic molecule

The problem is similar to that of the H_2 molecule except that the H_{11} is now different from the H_{22} . Let us call them E_1 and E_2 , respectively.

The SE of the molecule's gives:

$$\begin{cases} E_1 c_1 + \beta c_2 = E c_1 \\ \beta c_1 + E_2 c_2 = E c_2 \end{cases}$$

The secular determinant leads to a bonding state (**BS**) and antibonding state (**ABS**) eigenvalues:

$$\begin{cases} E_b = \frac{(E_1 + E_2)}{2} - \sqrt{\Delta^2 + \beta^2} \\ E_a = \frac{(E_1 + E_2)}{2} + \sqrt{\Delta^2 + \beta^2} \end{cases} \quad \text{where} \quad \Delta = \frac{E_1 - E_2}{2}$$

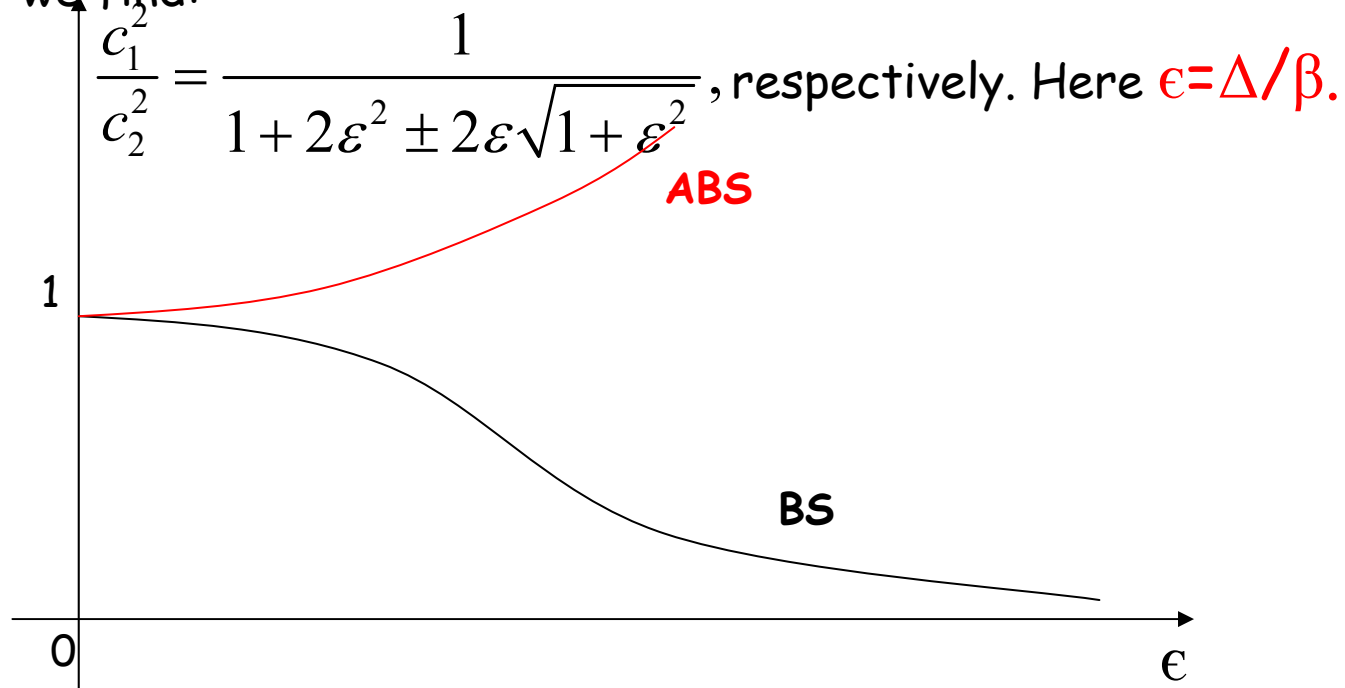
Notice that the difference in the on-site energies E_1 et E_2 is to increase the splitting between the bonding and antibonding states.

In the homonuclear case the charge density associated with each atom in both the **BS** and **ABS** are equal.

For the heteronuclear molecule, the fact that (for example $E_1 > E_2$) results in it being energetically favorable in the **BS** for some **charge density to be transferred from atom 1 to atom 2** and is in **reverse direction for the ABS**.

Heteronuclear diatomic molecule

Indeed if we insert the eigenvalues of **BS** or the **ABS** in the secular equation we find:



As ϵ increases all the charge density is transferred to atom 2 for the BS and all charge is transferred to atom 1 for the ABS.

Conclusion, when Δ is not zero the bond becomes partially ionic because some charge transfer takes place in the molecule. These simple ideas hold also for alloys.

Heisenberg Hamiltonian

The wave functions of the singlet and triplet states are:

$$\psi_S(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) + \psi_2(r_1)\psi_1(r_2)] \chi_S$$

$$\psi_T(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) - \psi_2(r_1)\psi_1(r_2)] \chi_T$$

$$E_S - E_T = 2 \int \psi_1^*(r_1)\psi_2^*(r_2)\hat{H}\psi_1(r_2)\psi_2(r_1)d^3r_1d^3r_2$$

The effective spin Hamiltonian is therefore given by:

$$\hat{H} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\hat{S}_1 \cdot \hat{S}_2 \quad \text{this is because } \langle \hat{S}_1 \cdot \hat{S}_2 \rangle = \begin{cases} \frac{1}{4} & \text{triplet state} \\ -\frac{3}{4} & \text{singlet state} \end{cases}$$

Defining $J = E_S - E_T$, the spin dependent term of the effective Hamiltonian is:

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 \quad J \text{ is the exchange parameter}$$

The generalization to N spins leads to the Heisenberg Hamiltonian

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

Notice if $J > 0$ $E_S > E_T$ and the triplet state is favored (**ferromagnetic coupling**)

if $J < 0$ $E_S < E_T$ and the singlet state is favored (**antiferromagnetic coupling**)



Los Alamos National Laboratory Chemistry Division

Periodic Table of the Elements

1A 1 H hydrogen 1.008	2A 4 Be beryllium 9.012	3A 5 B boron 10.81	4A 6 C carbon 12.01	5A 7 N nitrogen 14.01	6A 8 O oxygen 16.00	7A 9 F fluorine 19.00	8A 2 He helium 4.003						
3 Li lithium 6.941	11 Na sodium 22.99	19 K potassium 39.10	20 Ca calcium 40.08	37 Rb rubidium 85.47	55 Cs cesium 132.9	87 Fr francium (223)							
12 Mg magnesium 24.31	39 Y yttrium 88.91	57 La* lanthanum 138.9	89 Ac~ actinium (227)										
3B 21 Sc scandium 44.96	4B 22 Ti titanium 47.88	5B 23 V vanadium 50.94	6B 24 Cr chromium 52.00	7B 25 Mn manganese 54.94	8B 26 Fe iron 55.85	11B 29 Cu copper 63.55	12B 30 Zn zinc 65.39						
41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4						
73 Ta tantalum 183.9	74 W tungsten 186.2	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 190.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.5						
104 Rf rutherfordium (257)	105 Db dubnium (260)	106 Sg seaborgium (263)	107 Bh bohrium (262)	108 Hs hassium (265)	109 Mt meitnerium (266)	110 Ds darmstadtium (271)	111 Uuu (272)						
114 Uuq (296)	116 Uuh (298)	118 Uuo (?)											
Lanthanide Series* 58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium (147)	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
Actinide Series~ 90 Th thorium 232.0	91 Pa protactinium (231)	92 U uranium (238)	93 Np neptunium (237)	94 Pu plutonium (242)	95 Am americium (243)	96 Cm curium (247)	97 Bk berkelium (247)	98 Cf californium (249)	99 Es einsteinium (254)	100 Fm fermium (253)	101 Md mendelevium (256)	102 No nobelium (254)	103 Lr lawrencium (257)

Hund's rules

Hund's first rule: The state with the highest total spin has the lowest energy, and for the largest multiplicity of S , it has the lowest energy for the largest L value.

Hund's second rule: If a subshell (n,l) is no more than half filled, then the lowest energy level has the total angular momentum $J=|L-S|$; if it is more than half filled, then $J=|L+S|$ has the lowest energy.

The ground state of an atom is then denoted: $2S+1L_J$

S is the total spin momentum, J is the total angular momentum and L is the orbital angular momentum written $S, P, D, F, G, H, I, K, L, M, N$, etc.

Examples:

He	$1s^2$	1S_0	} maximize M_L
O	$1s^2 2s^2 2p^4$	3P_2	
Si	$(Ne)3s^2 3p^2$	3P_0	
Fe	$(Ar)4s^2 3d^6$	5D_4	
Co	$(Ar)4s^2 3d^7$	$^4F_{9/2}$	
Ni	$(Ar)4s^2 3d^8$	3F_4	
Cu	$(Ar)4s^1 3d^{10}$	1S_0	

Magnetic ground states of 4f and 3d ions using Hund's rules

ion	shell	S	L	J	term	μ_{eff}/μ_B	Expt.
Ce ³⁺	4f ¹	1/2	3	5/2	² F _{5/2}	2.54	2.51
Gd ³⁺	4f ⁷	7/2	0	7/2	⁸ S _{7/2}	7.94	7.98
Tb ³⁺	4f ⁸	3	3	6	⁷ F ₆	9.72	9.77
Er ³⁺	4f ¹¹	3/2	6	15/2	⁴ I _{15/2}	9.59	9.5

$$\mu_{\text{eff}} = \mu_B g_J \sqrt{J(J+1)}$$

g_J is the Landé factor

$$\chi = \frac{n \mu_0 \mu_{\text{eff}}}{3k_B T} \quad (\text{Brillouin})$$

$$\mu'_{\text{eff}} = 2\mu_B \sqrt{S(S+1)}$$

ion	shell	S	L	J	term	μ_{eff}/μ_B	μ'_{eff}/μ_B	Expt
Ti ³⁺	3d ¹	1/2	2	3/2	² D _{3/2}	1.55	1.73	1.70
Fe ²⁺	3d ⁶	2	2	4	⁵ D ₄	6.70	4.90	5.36
Fe ³⁺	3d ⁵	5/2	0	5/2	⁶ S _{5/2}	5.92	5.92	5.82
Cu ²⁺	3d ⁹	1/2	2	5/2	² D _{5/2}	3.55	1.73	1.83

3d orbital quenching

because the crystal field splitting is much larger than the SOC.



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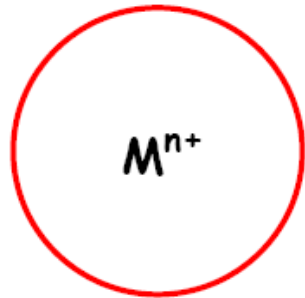
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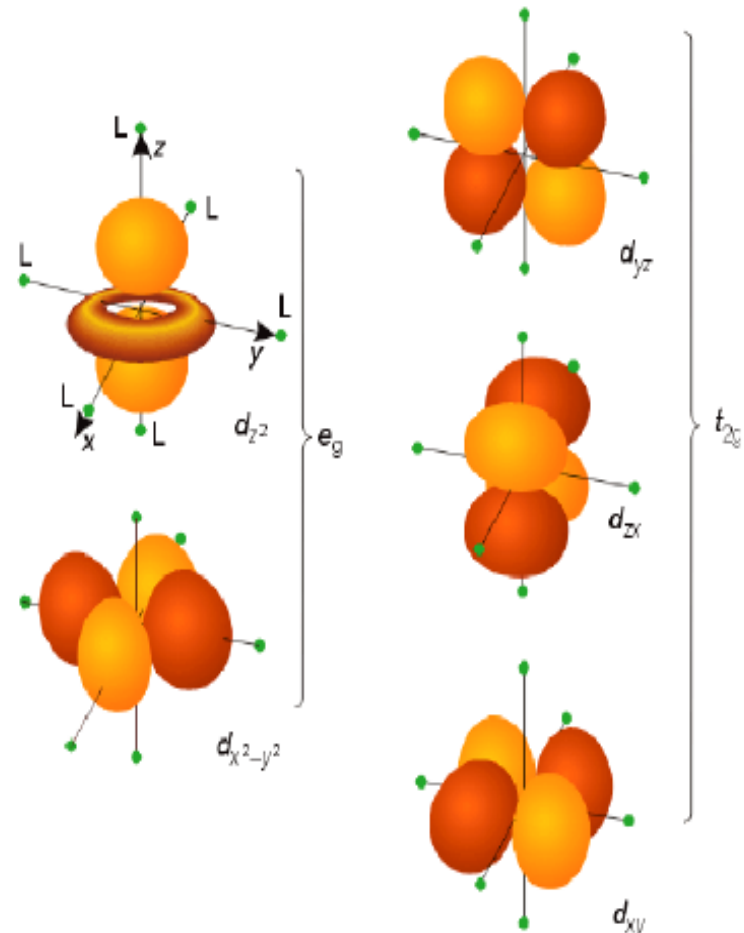
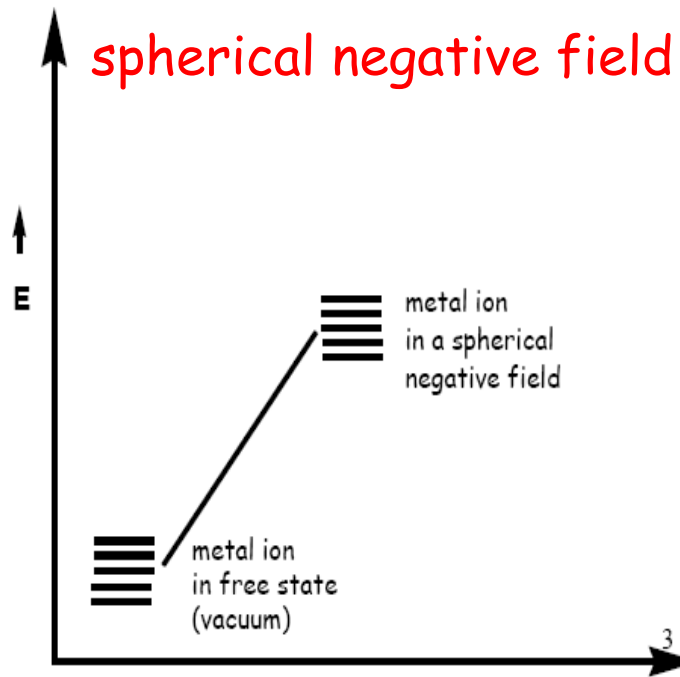
VIII. Bibliography



Crystal field

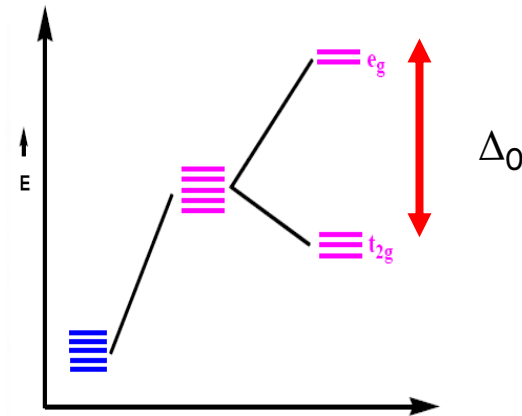
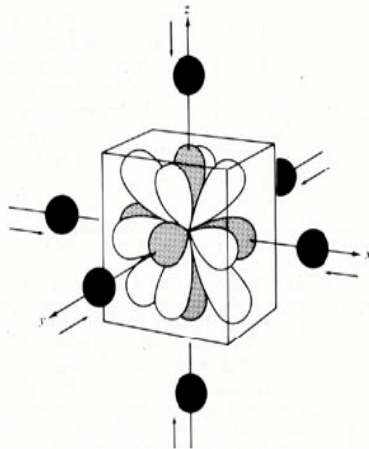


The d orbitals form two types of irreducible representations (e_g and t_{2g}) in cubic O_h symmetry.



Octahedral crystal field

In octahedral field the degeneracy of the d-orbitals is lifted.



The d-orbitals interact differently with the point charges located at $+x$, $-x$, $+y$, $-y$, $+z$ and $-z$

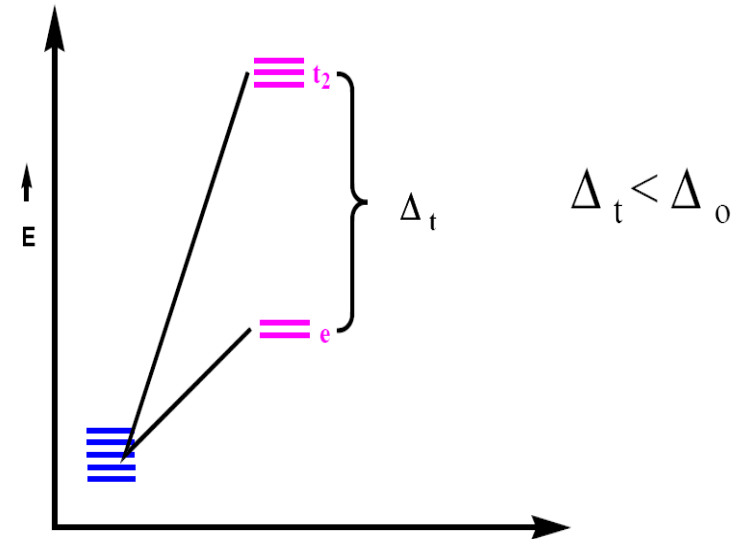
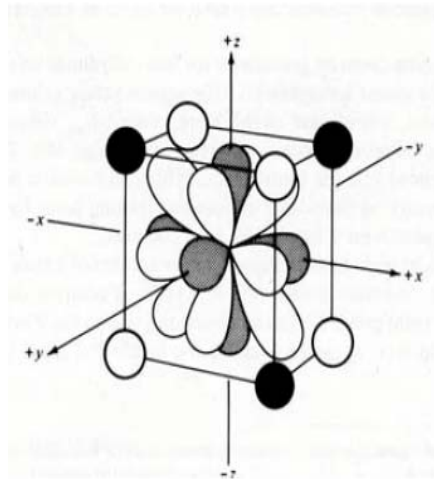
The e_g orbitals will lie along these axes are affected more with the ionic electrostatic interaction and move higher in energy.

Δ_0 depends on:

1. Nature of the ligands
2. The charge on the metal ion
3. The nature of the orbital (3d, 4d, 5d)

If $\Delta_0 < 3 \text{ eV}$: Weak crystal field and if $\Delta_0 > 3 \text{ eV}$ Strong crystal field

Tetrahedral crystal field

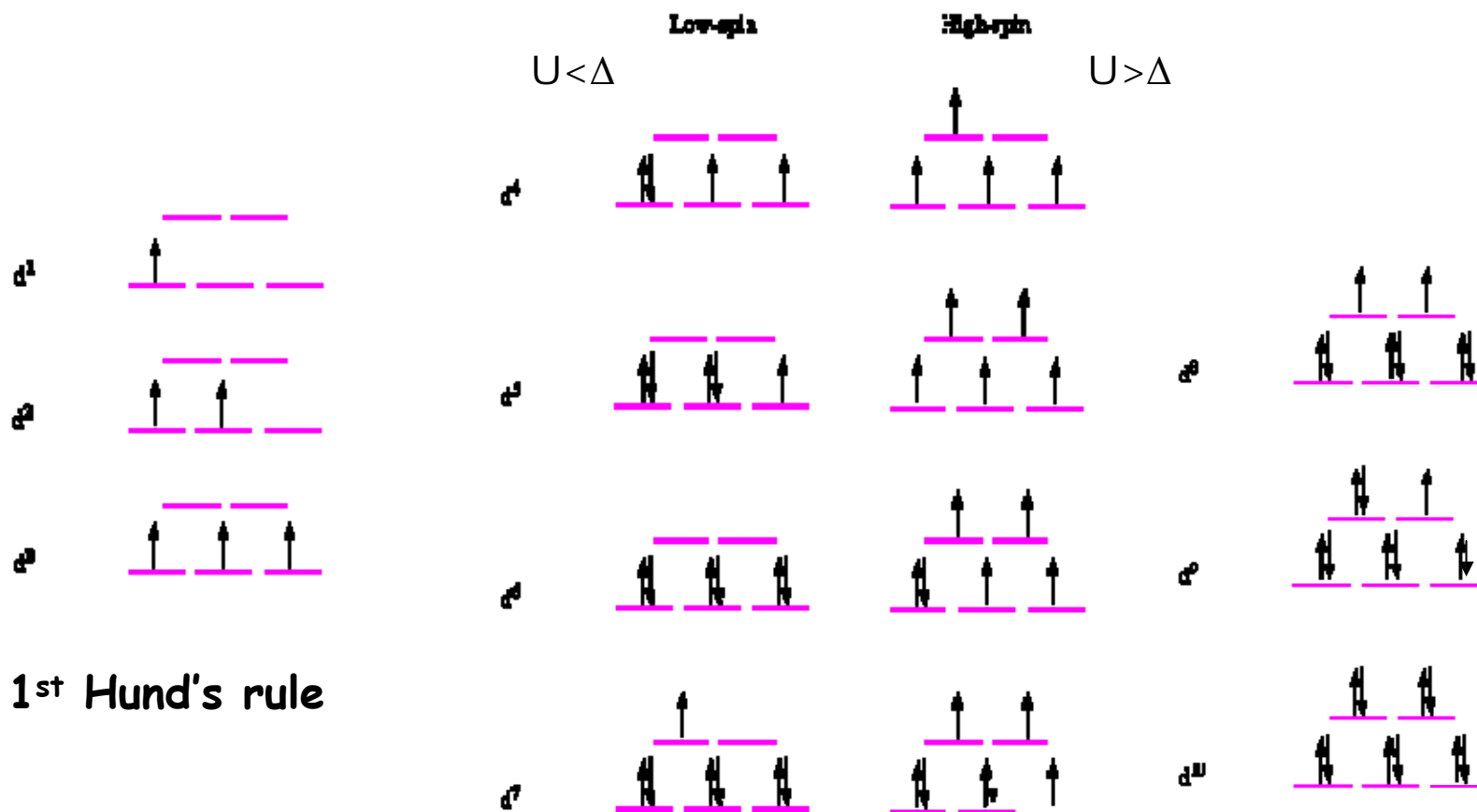


There are only **4 ligands in the tetrahedral complex** and therefore the electrostatic potential is reduced by roughly 2/3 from its octahedron complex value. The tetrahedron crystal field is therefore reduced by $(2/3)^2$:

$$\Delta_t = \frac{4}{9} \Delta_0$$

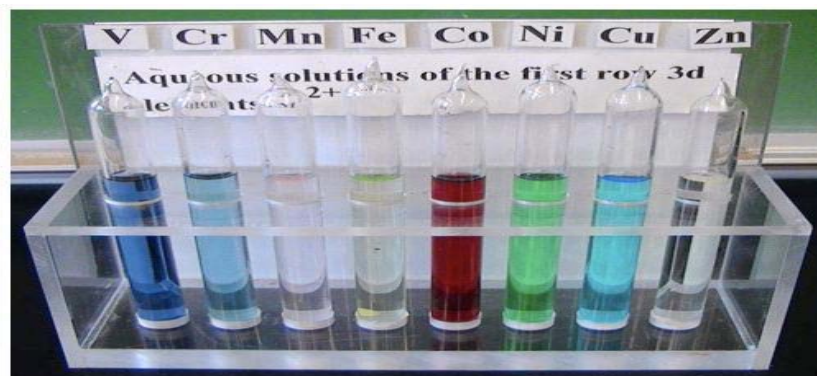
This makes all tetrahedral complexes high spin due to the reduced crystal field splitting compared to the pairing energy (U).

Pairing energy (U) versus e_g-t_{2g} splitting



1st Hund's rule

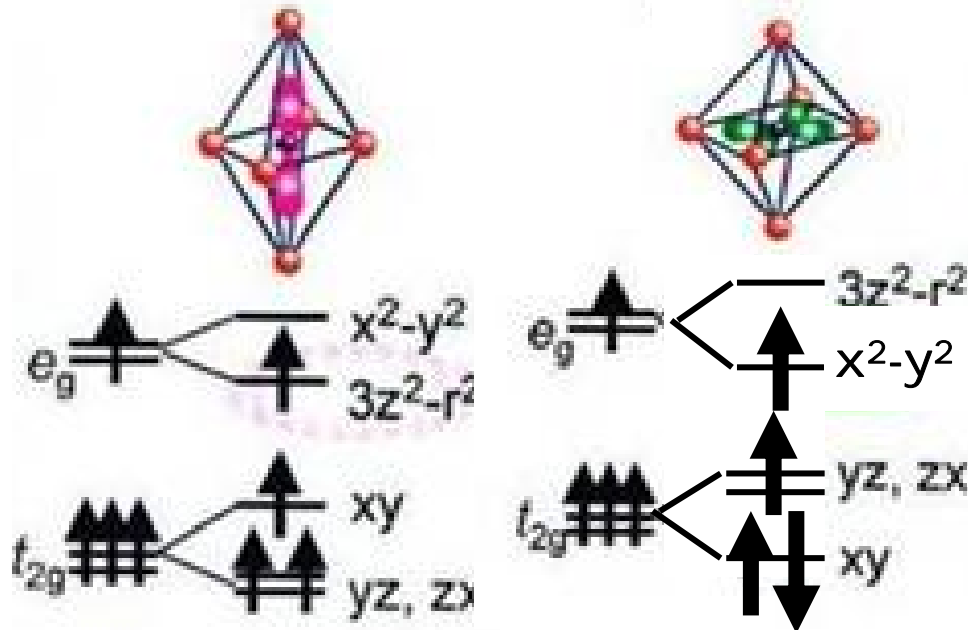
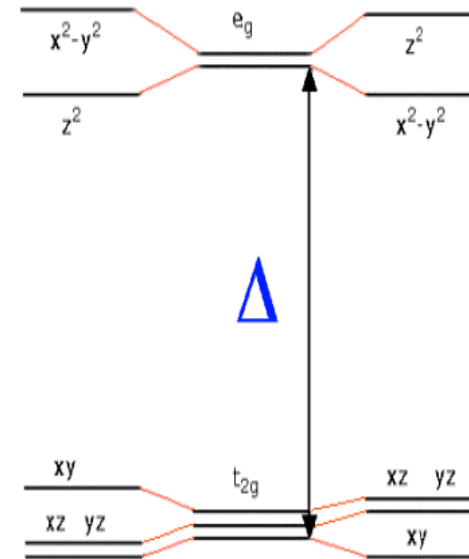
The colors of metallic ions is a consequence of the e_g and t_{2g} energy splitting



Jahn-Teller distortion

Jahn-Teller theorem, 1937:

Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower energy thereby removing the degeneracy.



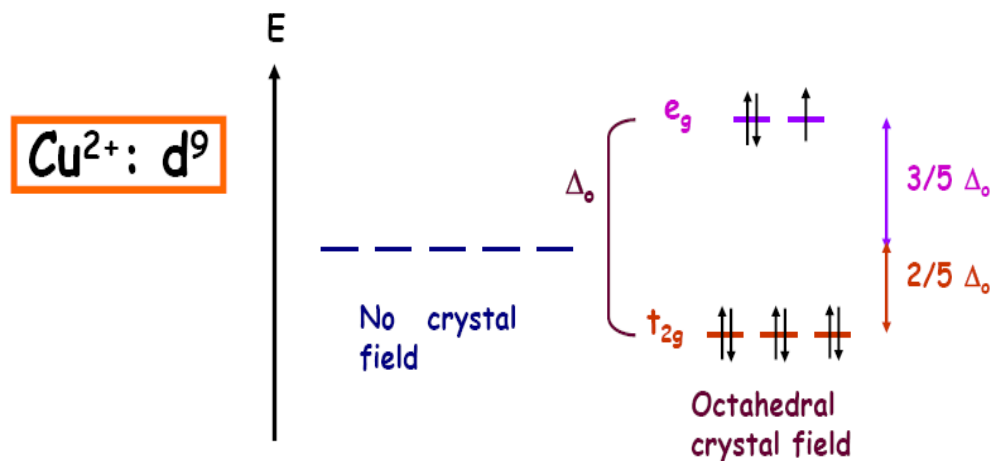
z elongation
2 long and 4 short bonds

z compression
2 short and 4 long bonds

For $(d_Z^2)^1 (d_{x^2-y^2})^0$: ligands along z, -z will be repelled more and bonds elongated
 → The octahedron will be elongated along the z direction.

The opposite happen for $(d_Z^2)^0 (d_{x^2-y^2})^1$ configuration → octahedron compressed along the z direction.

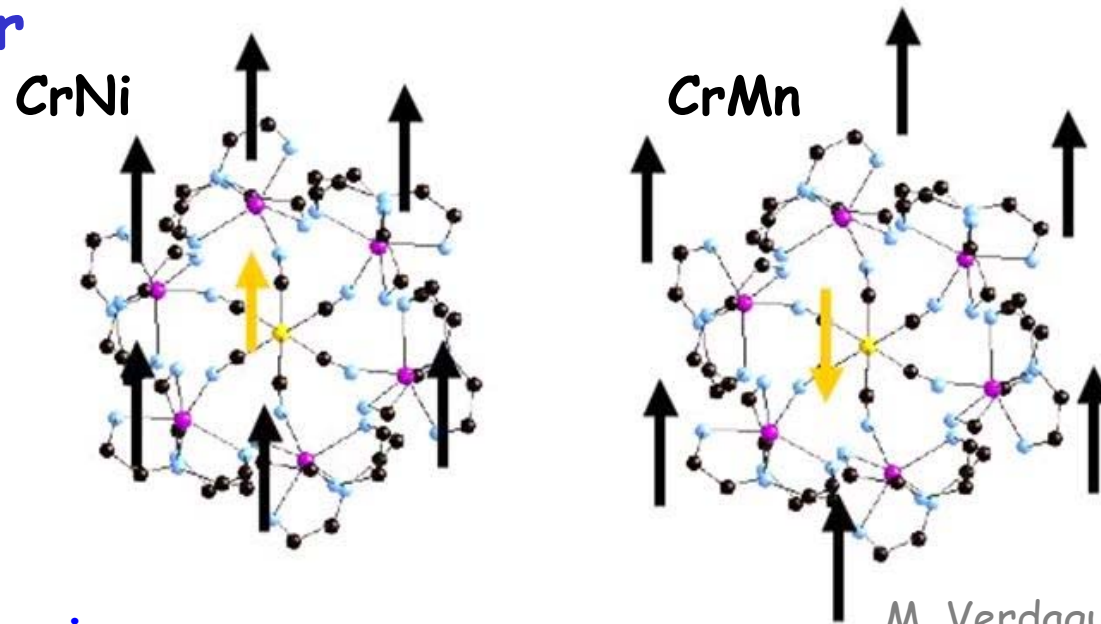
Examples of Jahn-Teller distortions



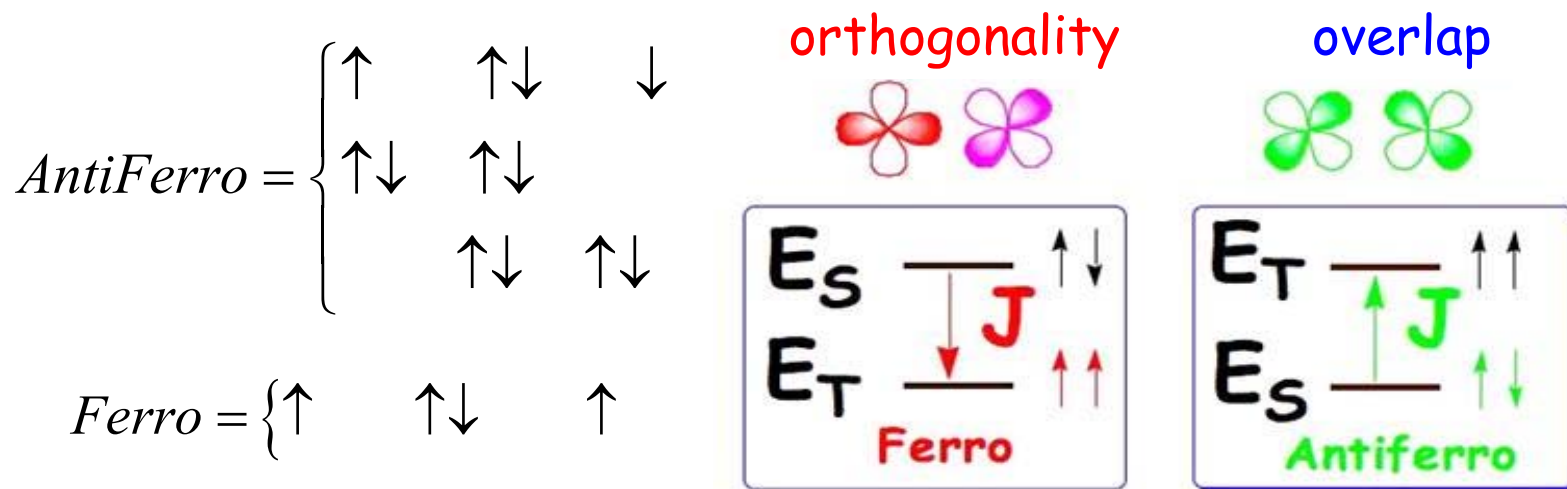
Examples of JT-distorted Cu^{2+} compounds

CuBr_2	4 Br at 240 pm + 2 Br at 318 pm
CuCl_2	4 Cl at 230 pm + 2 Cl at 295 pm
CuF_2	4 F at 193 pm + 2 F at 227 pm
K_2CuF_4	4 F at 191 pm + 2 F at 237 pm
KCuAlF_6	2 F at 188 pm + 4 F at 220 pm

Magnetic order

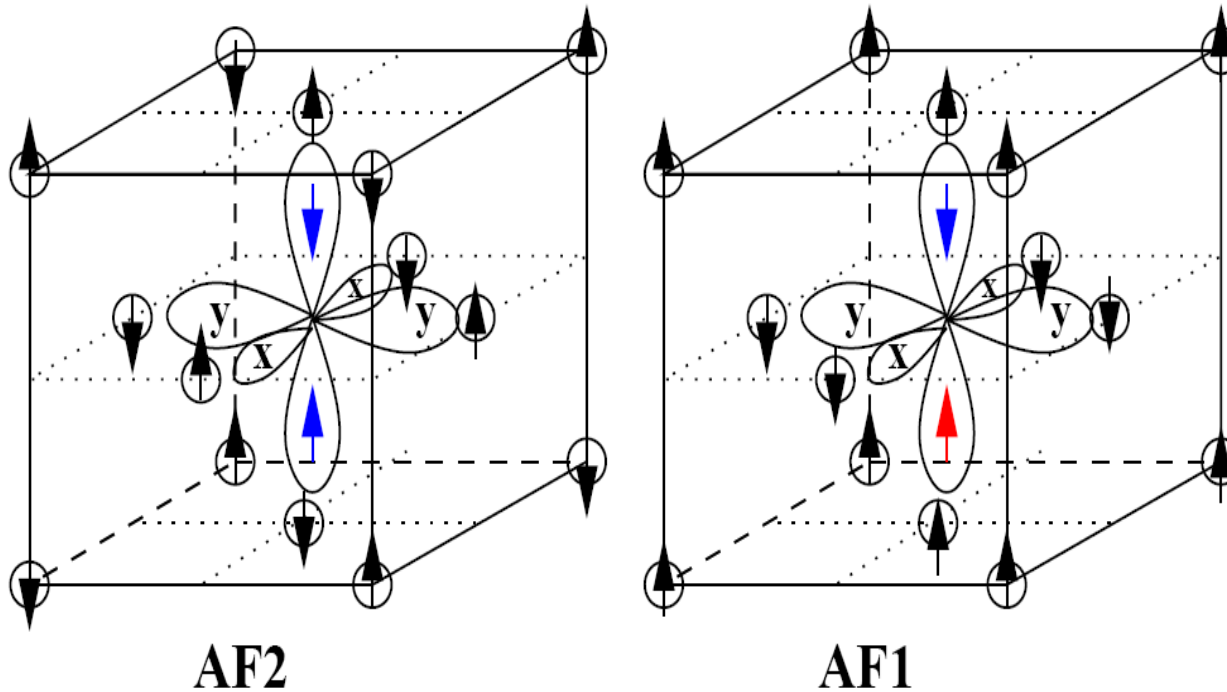


Superexchange mechanism



The superexchange reduces the kinetic energy of electrons and stabilizes the antiferromagnetism

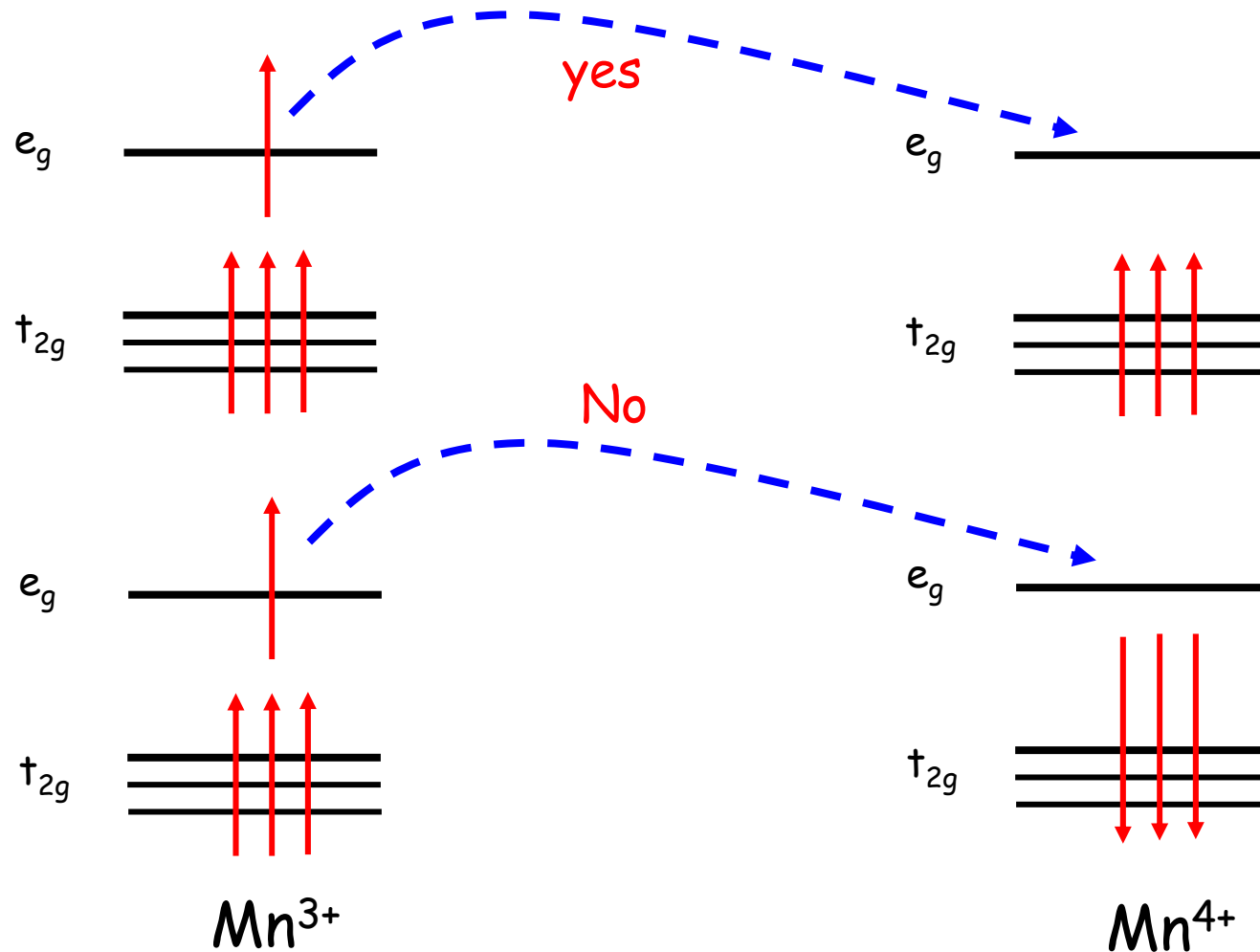
Magnetic order in NiO



The **AF2** structure is energetically the most stable because of the superexchange mediated by the oxygen atoms.

Double exchange

In some mixed valence oxides (example: Mn^{3+} and Mn^{4+} in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$)



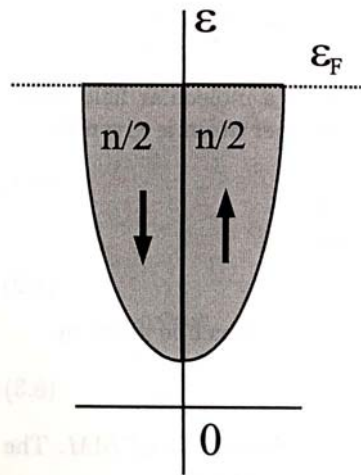
The double exchange mechanism produces ferromagnetic coupling in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$



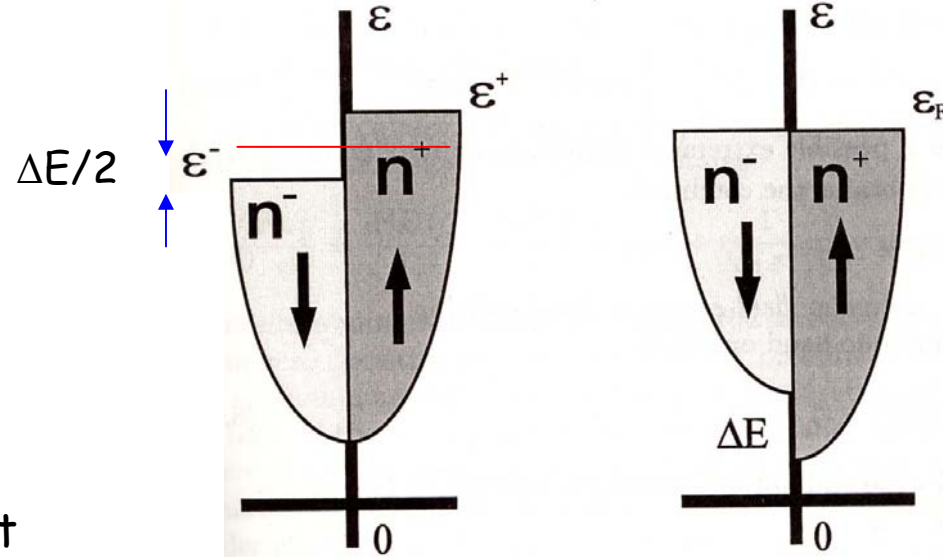
Course content

- I. Magnetic moment and magnetic field
- II. No magnetism in classical mechanics
- III. Where does magnetism come from?
- IV. Crystal field, superexchange, double exchange
- V. Free electron model: Spontaneous magnetization**
- VI. The local spin density approximation of the DFT
- VI. Beyond the DFT: LDA+U
- VII. Spin-orbit effects: Magnetic anisotropy, XMCD
- XIII. Bibliography

Free-electron model: magnetism of metals (Stoner Criterion)



Paramagnetic DOS $g(\epsilon)$ split into **two subbands** for the **2 spin directions**.



Spontaneous spin split DOS and appearance of magnetism.

Question: Can a material save energy by becoming ferromagnetic?

The total kinetic energy cost due to spin split is: $\Delta W_K = \frac{1}{2} g(E_F) (\Delta E)^2$

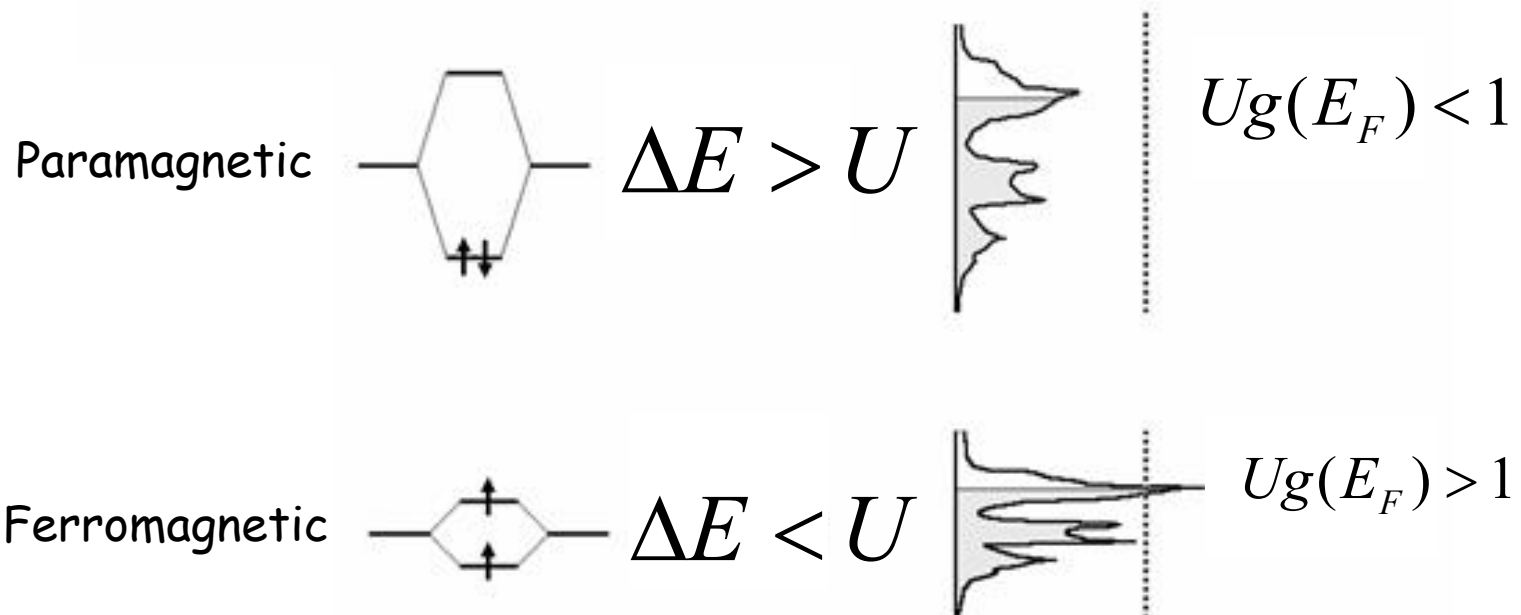
This energy cost is compensated by an energy reduction of the magnetic moment with the molecular field:

$$\Delta W_{MF} = - \int_0^M \mu_0 (\lambda M') dM' = - \frac{1}{2} \mu_0 \lambda M^2 = - \frac{1}{2} \mu_0 \mu_B^2 \lambda (n^+ - n^-)^2 = - \frac{1}{2} U (g(E_F) \Delta E)^2$$

where $U = \mu_0 \mu_B^2 \lambda$

$$\Delta W = \Delta W_K + \Delta W_{MF} = \frac{1}{2} g(E_F) (\Delta E)^2 (1 - U g(E_F)) < 0 \quad \rightarrow \quad U g(E_F) > 1$$

Stoner Criterion (continued)



In the ferromagnetic ground state, the DOS at the Fermi level are split by the exchange splitting ΔE .

If we add the effect of an applied magnetic field then we can determine the magnetic susceptibility

$$\Delta W = \Delta W_K + \Delta W_{MF} = \frac{1}{2} g(E_F) (\Delta E)^2 (1 - Ug(E_F)) - MB = \frac{M^2}{2\mu_B^2 g(E_F)} (1 - Ug(E_F)) - MB$$

The minimization of ΔW with respect to M leads to:

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{\chi_P}{1 - Ug(E_F)} \quad (\text{Stoner enhancement}) \quad \text{where} \quad \chi_P = \mu_0 \mu_B^2 g(E_F)$$

Course content

- I. Magnetic moment and magnetic field
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- VI. The local spin density approximation of the DFT**
- VI. Beyond the DFT: LDA+U
- VII. Spin-orbit effects: Magnetic anisotropy, XMCD
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Nobel lectures by W. Kohn and J. A. Pople

Nobel prize in Chemistry 1998

Walter Kohn

213

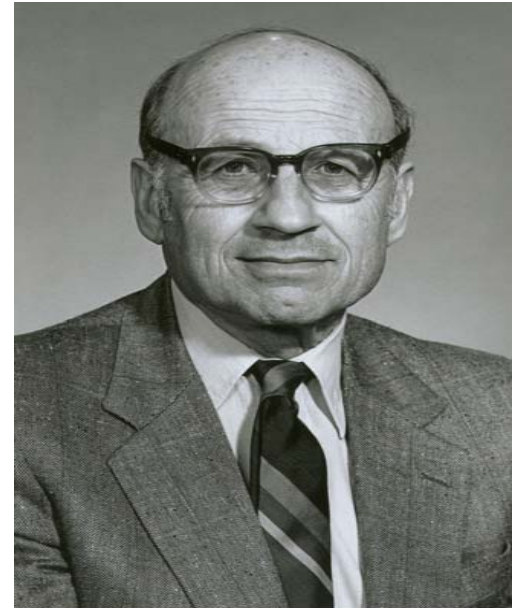
ELECTRONIC STRUCTURE OF MATTER – WAVE FUNCTIONS AND DENSITY FUNCTIONALS

Nobel Lecture, January 28, 1999

by

WALTER KOHN

Department of Physics, University of California, Santa Barbara, CA 93106-
8000, USA



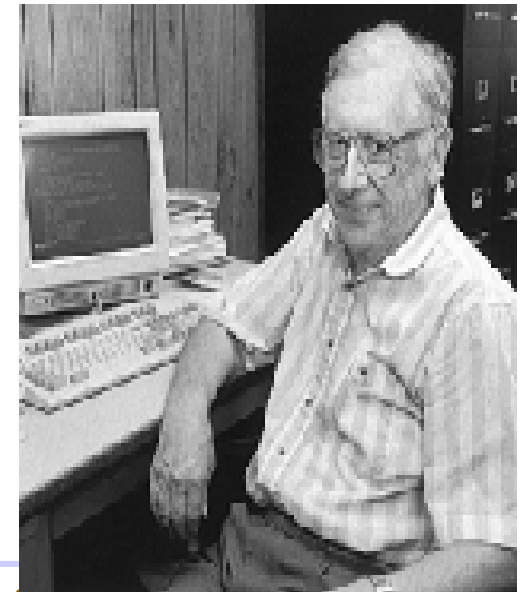
QUANTUM CHEMICAL MODELS

Nobel Lecture, December 8, 1998

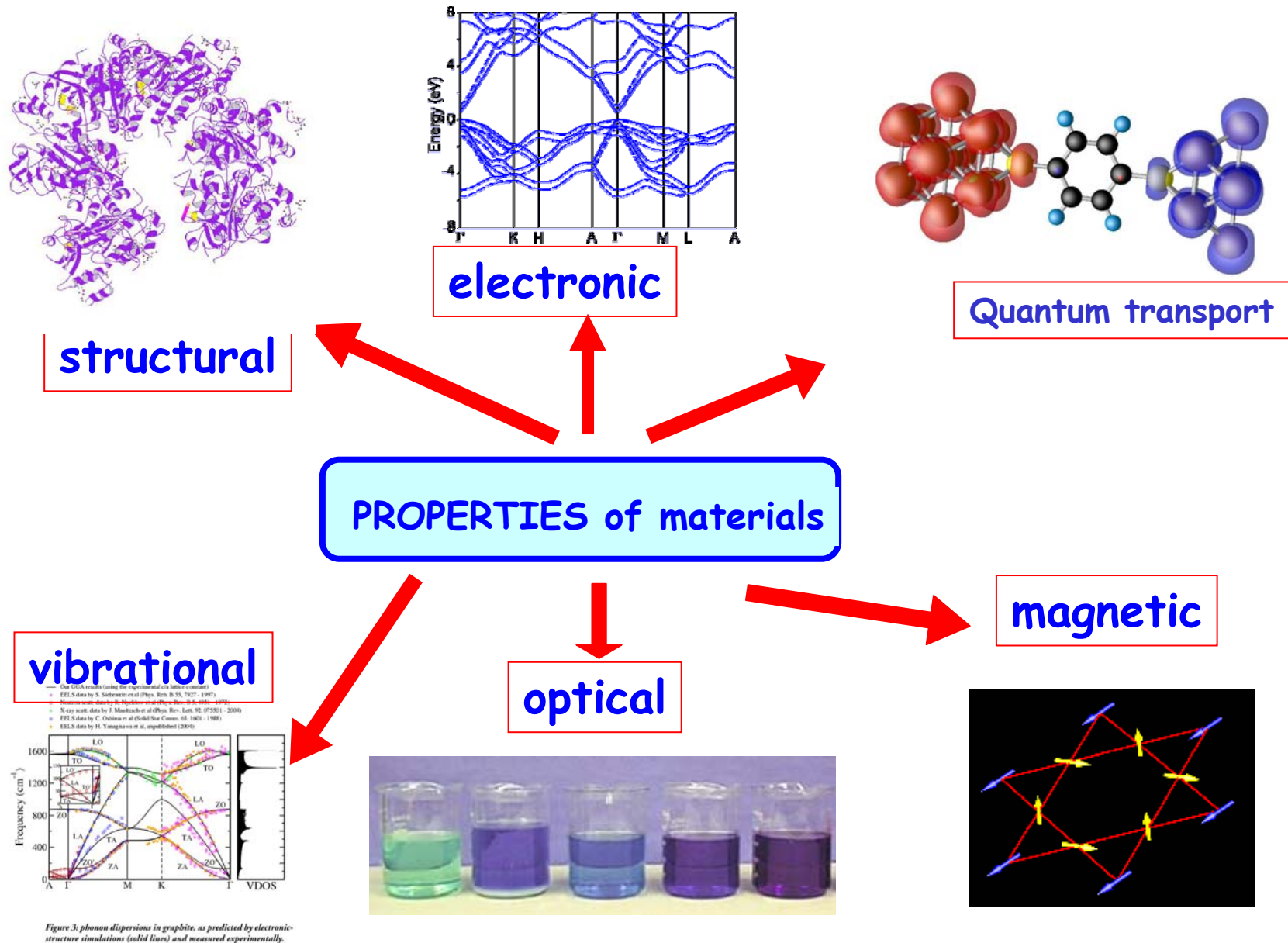
by

JOHN A. POPLÉ

Department of Chemistry, Northwestern University, 2145 Sheridan Road,
Evanston, Illinois 60208, USA



Goal: Describe properties of matter from ab initio methods.



Main approximations:

Born-Oppenheimer

Decouple the movement of the electrons and the nuclei.

Hartree-Fock Approximation

Treatment of the electron – electron interactions.

Density Functional Theory

Treatment of the electron – electron interactions.

Pseudopotentials or all electron potentials

Treatment of the (nuclei + core) – valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

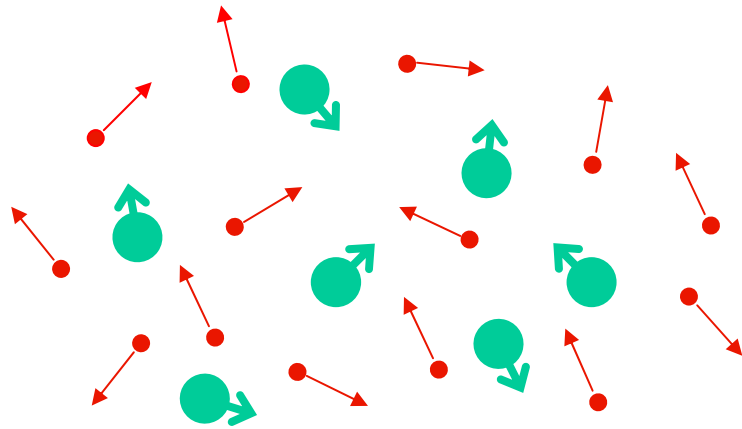
Efficient and self-consistent computations of H and S .

Supercells

Makes the calculation of materials possible (Bloch theorem)

Born-Oppenheimer Approximation

Adiabatic or Born-Oppenheimer approximation decouple the electronic and nuclear degrees of freedom



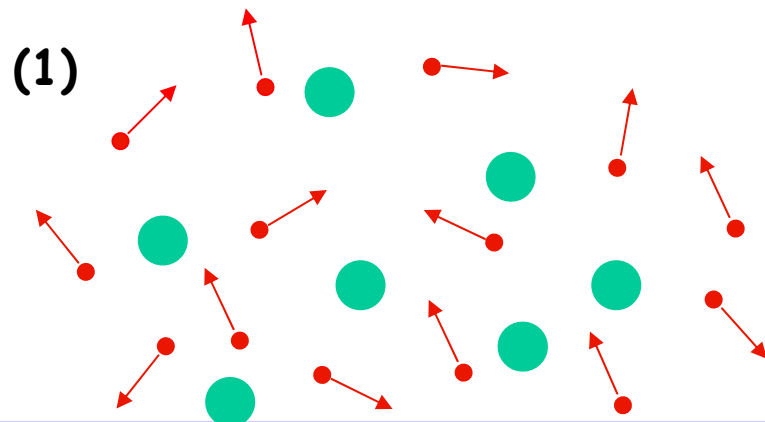
$$M_p \gg M_e$$

⇒ Nuclei much slower than the electrons

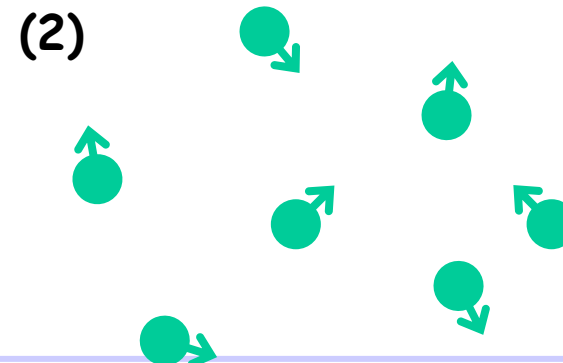
$$v_e \gg v_p$$

Electrons in their ground state for any instantaneous ionic configuration.

Solve electronic equations assuming fixed positions for nuclei



Move the nuclei as classical particles in the potential generated by the e^-



Born-Oppenheimer Approximation

If the nuclear positions are fixed, the wave function can be decoupled

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Fixed potential "external" to e^-

$$\begin{cases} \hat{H}_{\{\vec{R}_\alpha\}}^{el} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\{\vec{R}_\alpha\}}^{ext}(\{\vec{r}_i\}) \\ \hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) = E_n^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) \end{cases}$$

$$\begin{cases} \hat{H} = \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + E_n^{el}(\{\vec{R}_\alpha\}) \\ \text{Classical displacement} \quad \vec{F}_\alpha = -\frac{\partial E_0^{el}(\{\vec{R}_\mu\})}{\partial \vec{R}_\alpha} \end{cases}$$

Density Functional Theory

DFT: primary tool for calculation of electronic structure
in condensed matter

Many electron wave function

Satisfies the many-electron
Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

Contains all information about the
system

3N degrees of freedom for N
electrons

One electron density

All properties of the system can
be considered as unique
functionals of the ground state
density

Integrates out this information

One equation for the density is
simpler than the full many-body
Schrödinger equation

A special role can be assigned to the density of particles in the
ground-state of a quantum many-body system



Density Functional Theory

First theorem of Hohenberg-Kohn:

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

We shall now show that conversely $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant. The proof proceeds by *reductio ad absurdum*. As-

Theorem I: For any system of interacting particles in an external potential, this potential is determined uniquely, except for a constant, by the ground-particle density .



Density Functional Theory

Proof by reductio absurdum:

- i. Let's suppose that we have an exact ground state density $n_0(\mathbf{r})$.
- ii. Let's assume that there is only one wave function for this ground state (nondegenerate state)
- iii. Let's suppose that we have 2 external potentials $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ for this ground state density.

These 2 potentials produce 2 different wave functions ψ and ψ' , and 2 total energies $E_0 = \langle \psi | H | \psi \rangle$ and $E'_0 = \langle \psi' | H' | \psi' \rangle$ respectively.

The variational theorem insures that

$$E_0 = \langle \psi | H | \psi \rangle < \langle \psi' | H | \psi' \rangle = \langle \psi' | H - H' + H' | \psi' \rangle = \int d^3r n_0(\mathbf{r}) (V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})) + E'_0$$

Similarly:

$$E'_0 = \langle \psi' | H' | \psi' \rangle < \langle \psi | H' | \psi \rangle = \langle \psi | H' - H + H | \psi \rangle = - \int d^3r n_0(\mathbf{r}) (V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})) + E_0$$

By adding these 2 equations we obtain:

$$E_0 + E'_0 < E'_0 + E_0$$

The outcome is absurd, so there cannot be two different external potentials that produce the same density for their ground state.



Density Functional Theory

Second theorem of Hohenberg-Kohn:

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

where $F[n]$ is a universal functional, valid for any number of particles¹¹ and *any* external potential. This functional plays a central role in the present paper.

With its aid we define, for a given potential $v(\mathbf{r})$, the energy functional

$$E_v[n] \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]. \quad (10)$$

Clearly, for the correct $n(\mathbf{r})$, $E_v[n]$ equals the ground-state energy E .

Theorem II: A universal functional for the energy $E[n]$ in terms of the density n can be defined, valid for any external potential V_{ext} . For any particular V_{ext} , the exact ground state of the system is the global minimum value of this functional, and the density n that minimizes the functional is the exact ground state density n_0 .



Density Functional Theory

This second theorem can be rewritten as:

For a trial electron density $n'(r) \geq 0$ and $\int d^3r n'(r) = N$, $E_0 \leq E[n']$.

$$E[n] = F_{HK}[n] + \int d^3r n(r) V_{ext}(r)$$

The ground-state total energy calculated from the trial density $n'(r)$ cannot be lower than the exact energy E_0 .

This theorem is easily proved since:

to the density n' corresponds a wave function ψ' and an external potential V'_{ext} , and to n correspond the external potential V_{ext} then:

$$\langle \psi' | H | \psi' \rangle = F_{HK}[n'] + \int d^3r n'(r) V_{ext}(r) = E[n'] \geq E_0[n]$$

This is because there is one to one correspondence between the wave function and the electronic density.

Density Functional Theory

The Kohn-Sham ansatz replaces the many-body problem with an independent-particle problem

All the properties of the system are completely determined given only the ground state density n

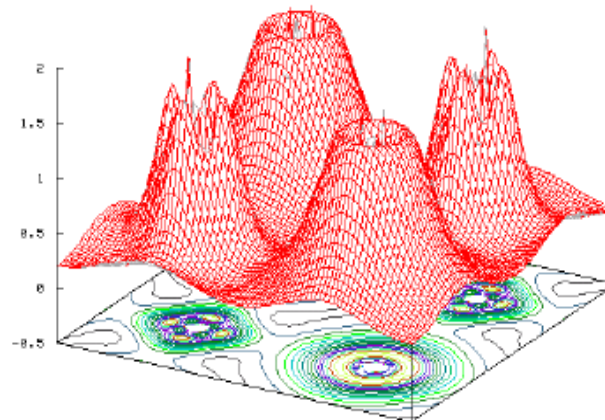
But no prescription to solve the difficult interacting many-body hamiltonian

$$\hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) = E_n^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\})$$

Ground state density of the many-body interacting system

=

Density of an auxiliary non-interacting independent particle system



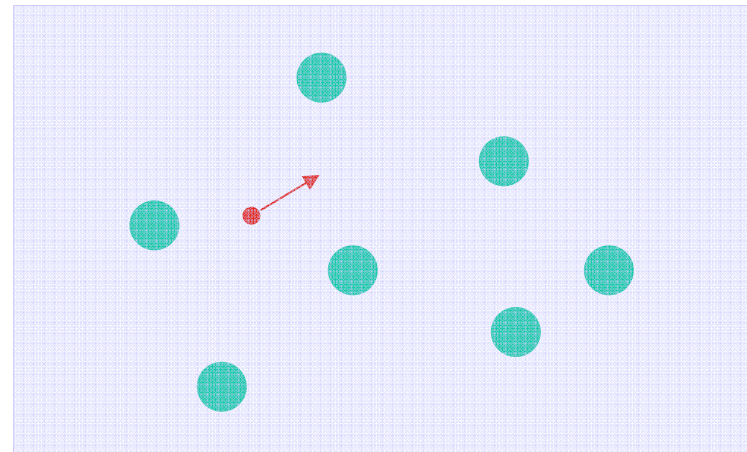
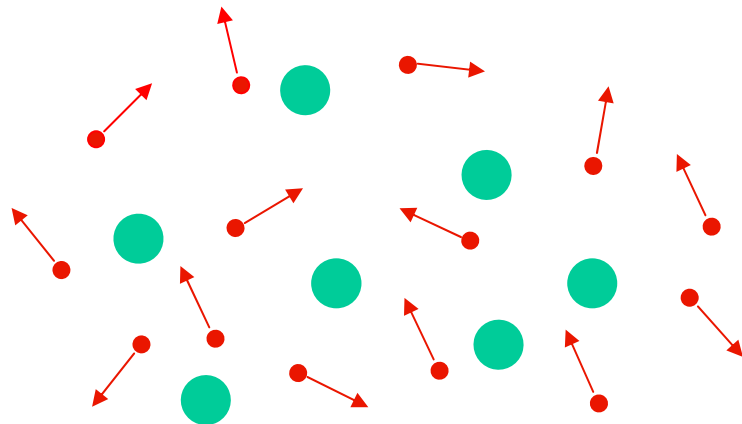
**Kohn-Sham
ansatz**

(never proven in general)

Density Functional Theory

One electron or independent particle model

We assume that each electron moves independently in a potential created by the nuclei and the rest of the electrons.



Actual calculations performed on the auxiliary independent-particle system

$$\hat{H}_{\text{aux}}^{\sigma} = -\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\sigma}(\vec{r})$$

Density Functional Theory

Like the derivation of the **HF** equations, we can use the variational theorem to find out the KS equations. This time we take a variation with respect to the electron density:

$$\delta \left\{ E[n] - \varepsilon \left[\int d^3r n(\mathbf{r}) - N \right] \right\} = 0$$

If we write $n(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r})$ and knowing that $\delta E[n] = \frac{\delta E[n]}{\delta n} \delta n$

We then obtain from the variational theorem the KS SE:

$$\left(\frac{\delta F_{HK}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) \right) \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

If the exact form of the F_{HK} is known then the problem is solved, since the SE will produce a selfconsistent ψ that determines the density, and hence the ground state total energy.

The trick is to use the independent-particle kinetic energy which is given explicitly as a functional of the orbitals:

$$T_s = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \langle \psi_i^{\sigma} | \nabla^2 | \psi_i^{\sigma} \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\nabla \psi_i^{\sigma}|^2$$

Density Functional Theory

Then one has to rewrite the functional as

$$E_{KS}[n] = T_s[n] + \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) + E_{Hartree}[n] + E_{xc}[n]$$

The variational theorem gives then:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

The exchange-correlation energy has to obey certain rules:

1. Like in the HFA, E_{xc} can be written in terms of the exchange-correlation hole n_{xc} :

$$E_{xc}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_{xc}(\mathbf{r}, \mathbf{r}').$$

2. Again, like in the HFA, the exchange-correlation hole has to fulfill the sum rule:

$$\int d\mathbf{r}' n_{xc}(\mathbf{r}, \mathbf{r}') = -1$$

This last sum rule help constrain the search for E_{xc} .



Density Functional Theory

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

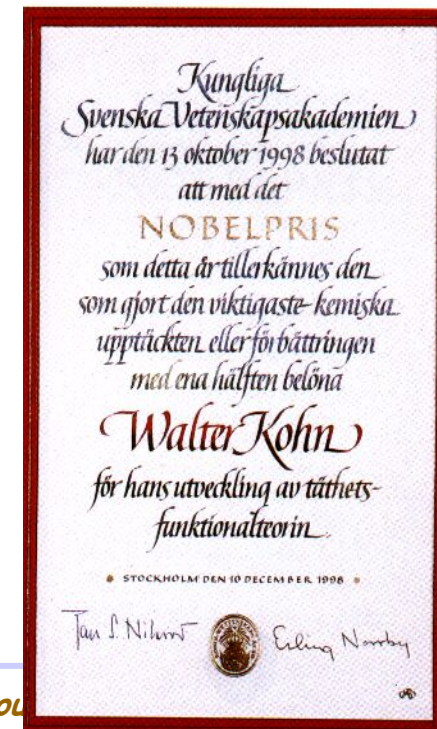
15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course,

Density functional theory is the most widely used method today for electronic structure calculations because of the approach proposed by Kohn and Sham



Density Functional Theory

The general form of E_{XC} : $E_{XC}[n] = \int n(r) \epsilon_{XC}[n, r] d^3 r$

ϵ_{XC} at r depends on the density shape n in the whole space.

Local density approximation (LDA): $E_{XC}[n] = \int n(r) \epsilon_{XC}(n(r)) d^3 r$

ϵ_{XC} at r depends only on the density at r (exact for a homogeneous electron gas).

It is a function of the density and not a functional!

Generalized Gradient Approximation (GGA)

$$E_{XC}[n] = \int n(r) \epsilon_{XC}(n(r), \nabla n(r), \dots) d^3 r$$

ϵ_{XC} at r depends on the density and its gradient at r .

Second generation Gradient Corrected Functionals



Axel Becke
Queens University



John Perdew
Tulane

1983-1992

The success of the LDA is certainly due to the fact that it satisfies the n_{XC} sum rule, and being constructed from a homogeneous electron gas, it depends only on the spherical average of this hole density.

Density Functional Theory

Local spin density approximation

Here the functional is of the density $n(\mathbf{r})$ and the magnetization $m(\mathbf{r})$.
LSDA was first introduced by **Von Barth and Hedin, J. Phys. C 5, 1629 (1972)**.

In the collinear case, we assume that the direction of the magnetization does not depend on the position. We can always use the z-direction for convenience.

The wave function for each spin direction (+ or -) is given by:

$$\phi^{(+)}(\mathbf{r}) = \phi(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad ; \quad \phi^{(-)}(\mathbf{r}) = \phi(\mathbf{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} .$$

The spin-up (+) and down (-) electron densities are given by:

$$n^{(+)}(\mathbf{r}) = \sum_i w_i^{(+)} |\phi_i^{(+)}(\mathbf{r})|^2 \quad \text{and} \quad n^{(-)}(\mathbf{r}) = \sum_i w_i^{(-)} |\phi_i^{(-)}(\mathbf{r})|^2$$

The total charge density and the magnetization are given by:

$$n(\mathbf{r}) = e (n^{(+)}(\mathbf{r}) + n^{(-)}(\mathbf{r})) \quad \text{and} \quad m(\mathbf{r}) = \mu_B (n^{(+)}(\mathbf{r}) - n^{(-)}(\mathbf{r})) .$$

Density Functional Theory

The exchange-correlation per spin is determined by functional derivative:

$$\frac{\delta E_{\text{xc}}[n^{(+)}, n^{(-)}]}{\delta n^{(\pm)}(\vec{r})} = V_{\text{xc}}^{(\pm)}$$

The variational theorem gives the one particle equation for each spin direction:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{Coul}}(\mathbf{r}) + V(\mathbf{r}) + V_{\text{xc}}^{(+)}(\mathbf{r}) \right) \phi_i^{(+)}(\mathbf{r}) = \varepsilon_i^{(+)} \phi_i^{(+)}(\mathbf{r})$$
$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{Coul}}(\mathbf{r}) + V(\mathbf{r}) + V_{\text{xc}}^{(-)}(\mathbf{r}) \right) \phi_i^{(-)}(\mathbf{r}) = \varepsilon_i^{(-)} \phi_i^{(-)}(\mathbf{r})$$

The weights w_i are determined so that the total density of states integrated up to the **Fermi energy** yields the number of valence electrons in the unit cell:

$$N = \int^{E_F} [N^{(+)}(E) + N^{(-)}(E)] dE \quad \text{where} \quad N^{(\pm)}(E) = \sum_i \delta(E - \varepsilon_i^{(\pm)}).$$

Density Functional Theory

The Kohn-Sham equations must be solved self-consistently The potential (input) depends on the density (output)

I. Input: Structure, Atomic species

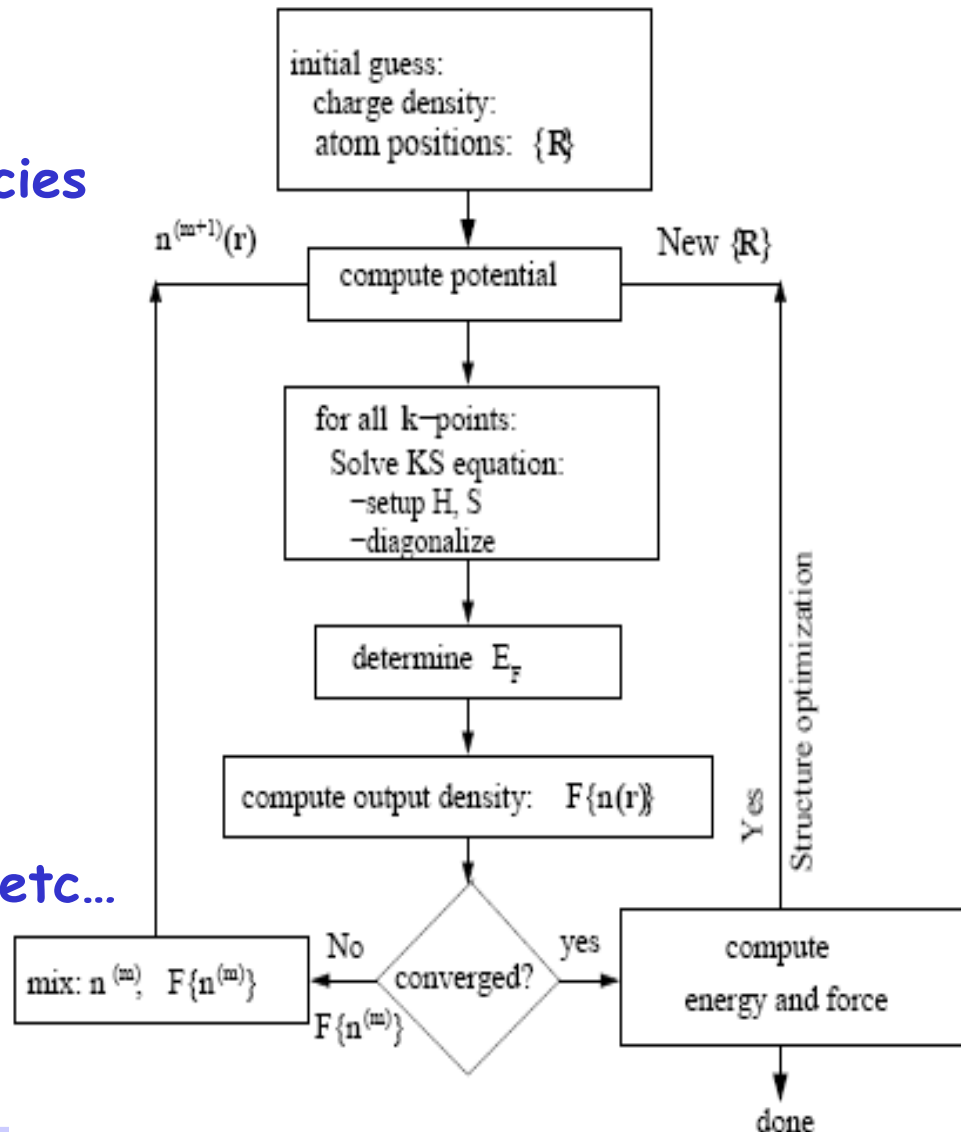
II. Guess for input

III. Compute the potential

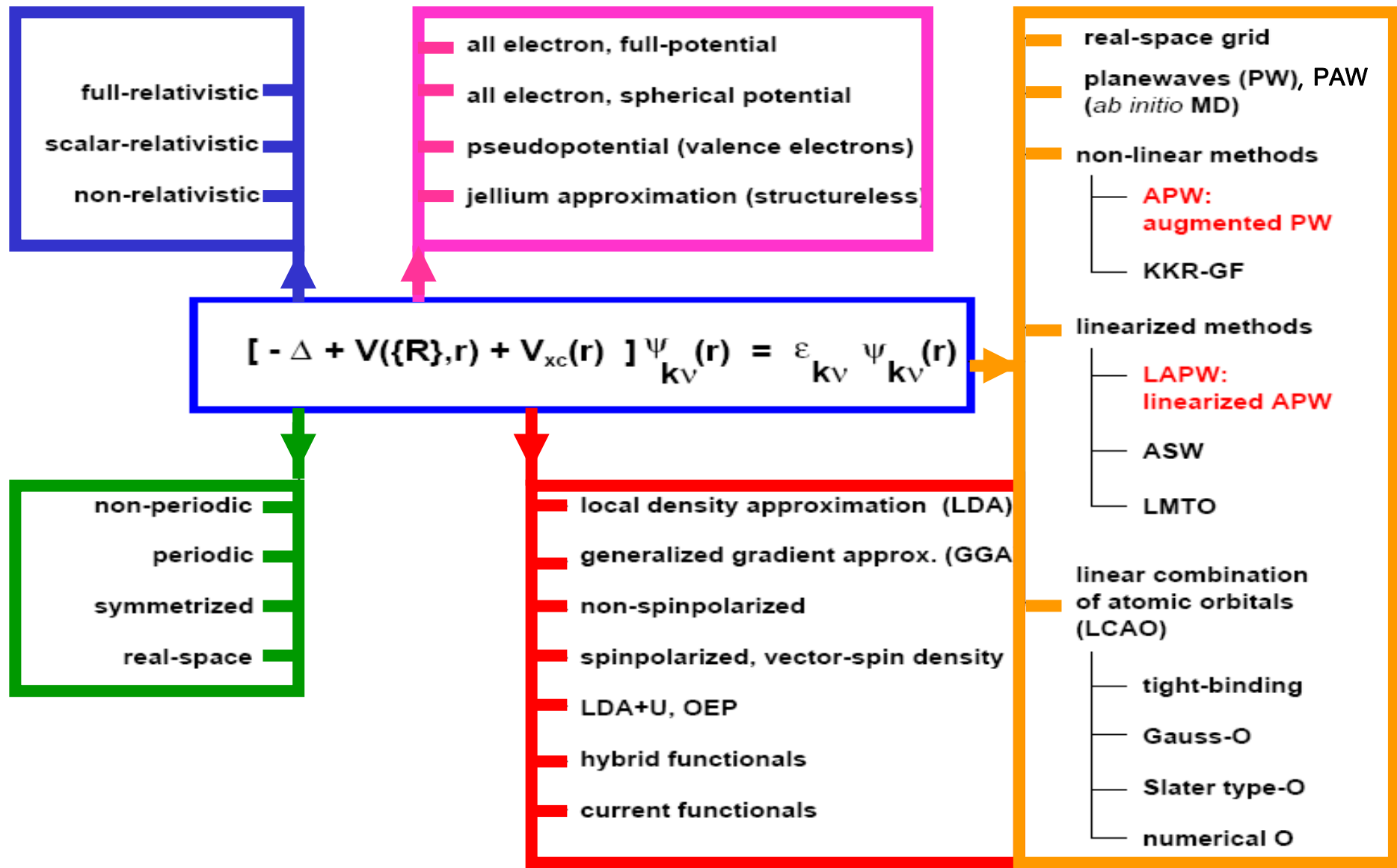
IV. Solve the Ks equations

V. Compute the output density

VI. If selfconsistent:
output the total energy, forces, etc...



Used approximations, basis-sets, potentials, etc

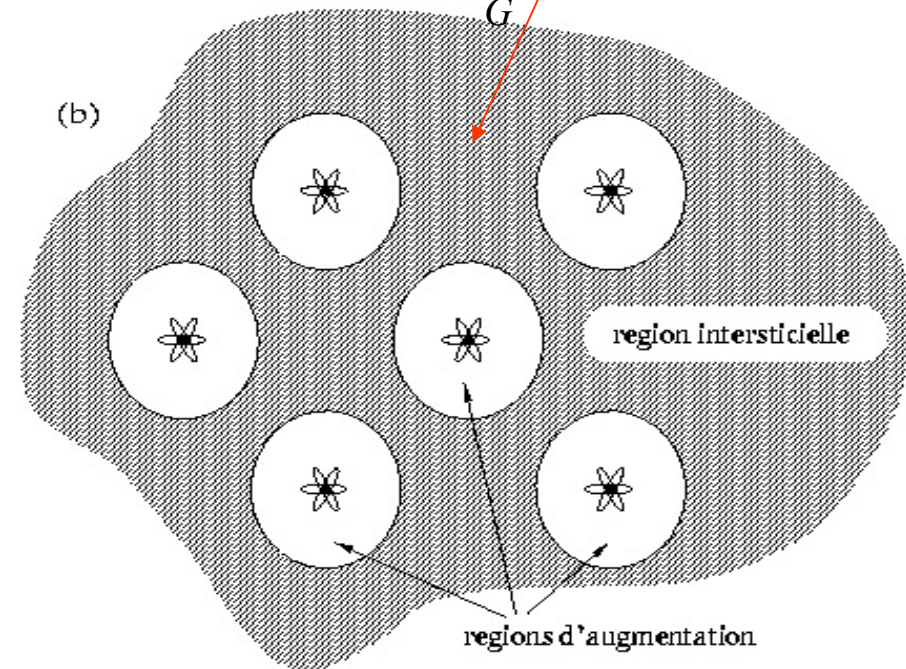
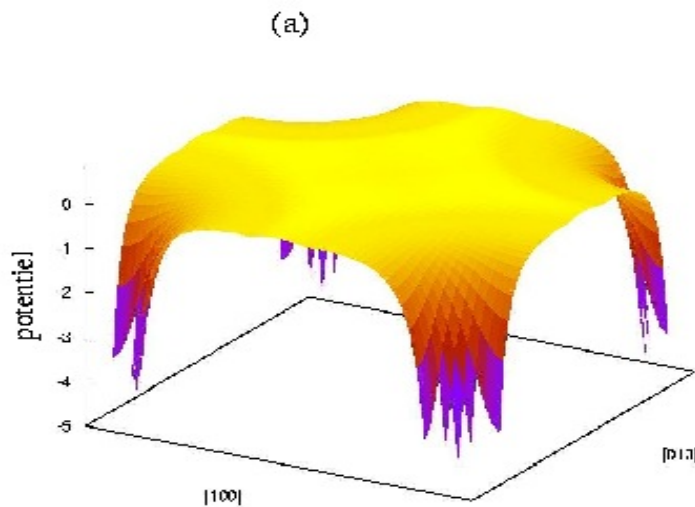


Methods of calculation

(Full-Potential Linear Augmented Plane-Wave method

- LSDA, GGA, or LDA+U
- Different treatment of the muffin-tin spheres and the interstitial region

Plane waves in the interstitial: $\sum_{\vec{G}} C_{n,\vec{k}}^{\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$



Partial waves in the muffin-tin spheres

$$\sum_{lm} \left[A_{lm}^{n,\vec{k}}(\vec{G}) U_l(r) + B_{lm}^{n,\vec{k}}(\vec{G}) \dot{U}_l(r) \right] Y_l^m(\hat{r})$$

Density Functional Theory

Accuracy of the XC functionals in the structural and electronic properties

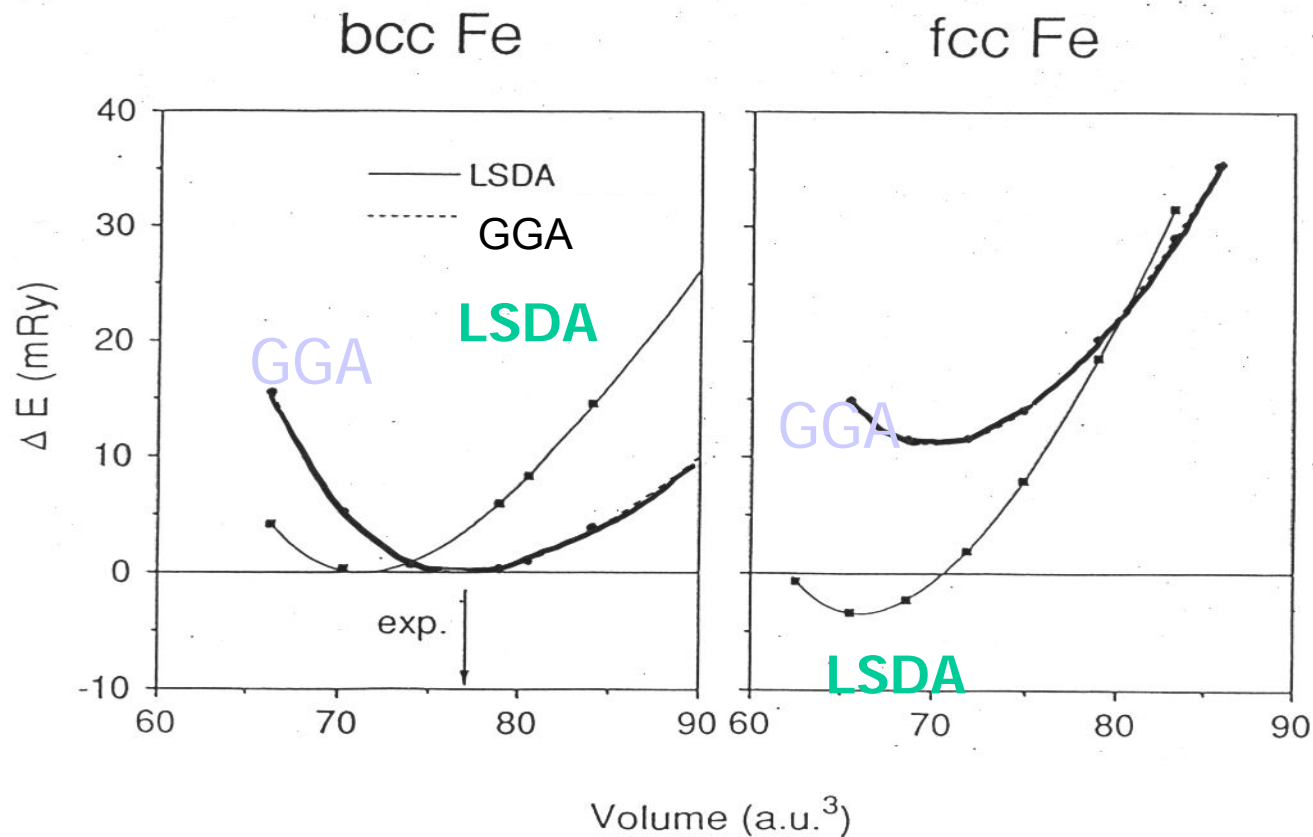
	LDA	GGA
a	-1% , -3%	+1%
B	+10, +40%	-20%, +10%
E_c	+15%	-5%
E_{gap}	-50%	-50%

LDA: simplest approximation but accurate enough (structural properties, ...).

GGA: usually tends to overcompensate LDA results, but not always better.

Density Functional Theory

In some cases, *GGA* is a must: DFT ground state of iron



P. Bagno et al., PRB 40, 1997 (1987)

LSDA

- NM
- fcc

GGA

- FM
- bcc
- Correct lattice constant

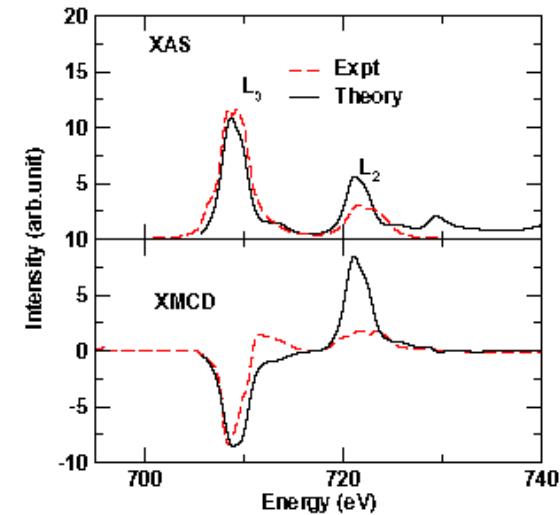
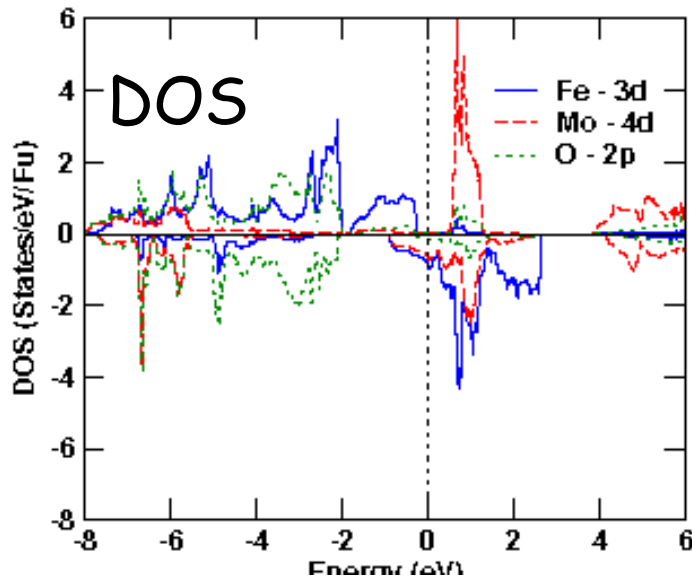
Experiment

- FM
- bcc



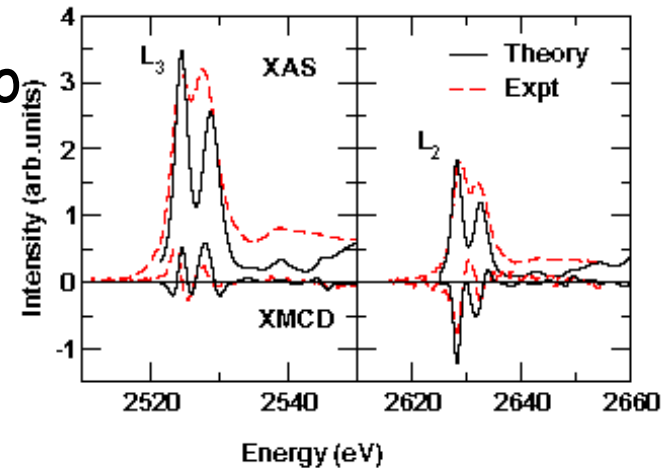
Sr₂FeMoO₆ (SFMO)

SFMO crystallizes in a bct, $a=b=5.55\text{\AA}$ and $c=7.90\text{\AA}$



Spin and orbital moments of Fe and Mo

	Spin			Orbital		
	SC	SR	Expt.	SC	SR	Expt.
Fe	3.72	3.67	3.05 ± 0.2	0.042	0.052	0.02
Mo	-0.29	-0.23	-0.32 ± 0.05	0.020	-0.042	-0.05 ± 0.05



Kanchana et al., PRB 75, 22040(R), 2007

XAS and XMCD at Fe and Mo L_{2,3} edges



Course content

- I. Magnetic moment and magnetic field
- II. No magnetism in classical mechanics
- III. Where does magnetism come from?
- IV. Crystal field, superexchange, double exchange
- V. Free electron model: Spontaneous magnetization
- VI. The local spin density approximation of the DFT
- VI. Beyond the DFT: LDA+U
- VII. Spin-orbit effects: Magnetic anisotropy, XMCD
- VIII. Bibliography**

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