A. Local Density Approximation

Task: Solve the quantum chemical Hamiltonian for N electrons,

$$\hat{H} = \sum_i^N \left(\hat{t}_i + v_i^{ext}(\underline{r}_i ; \mathbb{R}) \right) + \sum_{i<j}^N v_{ij}(\underline{r}_i, \underline{r}_j) + E^{Coulomb}_{nuclei}(\mathbb{R})$$

Notes: $\mathbb{R}$ ... positions of the nuclei (adiabatic decoupling assumed)

$\underline{r}_i$ ... position of electron i

$\hat{t}_i$ ... kinetic energy operator of electron i

v_i^{ext} ... potential energy in the field of the nuclei

v_{ij} ... electron-electron Coulomb interaction

$\hat{H}\psi = E\psi$; $\psi(\underline{r}_1, s_1 ; \underline{r}_2, s_2 ; \dots ; \underline{r}_N, s_N)$ fermionic wave function

s_i ... spin quantum number of electron i

$\longrightarrow$ <u>no spin dependent interaction</u>

$$\hat{H}\psi = E(\mathbb{R})\,\psi(\mathbb{R})$$

Results: $E_0(\mathbb{R})$ yields the ground state structure $\mathbb{R}_{GS}$, elastic properties and phonons via $\partial E_0/\partial \mathbb{R}$

$E_{i\neq 0}(\mathbb{R})$ yield electronic excitations

Feasibility: The full wave-function equation can be solved for $\boxed{N \leq 10}$

Problems:

- v_i and v_{ij} have singularities on each position of electrons and nuclei
- ψ is anti-symmetric
- We are interested in $N \gg 10$

Do we need the full wave function and excitation spectrum?

Example: random-interaction Ising model with 100 sites,

$$H = \sum_{j>i}^{100} J_{ij} S_i^z S_j^z \quad ; \quad S^z = \pm 1/2 \; ;$$

J_{ij} random in $[0, 1\,eV]$

$$\max_{S_i^z} H = \sum_{j>i}^{100} J_{ij}/4 \approx 4950 \cdot 0.5\,eV/4 \approx 620\,eV$$

$$\min_{S_i^z} H > -620\,eV$$

number of levels: $2^{99} \approx 10^{30}$

mean level distance: $\langle \Delta E \rangle \approx 10^{-27}\,eV \approx 10^{-46}\,J$

measuring time to resolve the mean level distance:

$$\Delta t \approx \hbar / \langle \Delta E \rangle \approx 10^{-34}\,Js \,/\, 10^{-46}\,J \approx \underline{\underline{10^{12}\,s}}$$

It takes 30.000 years to resolve a single level of a system with 100 spins.

So, is there any reasonable quantity that can be calculated?

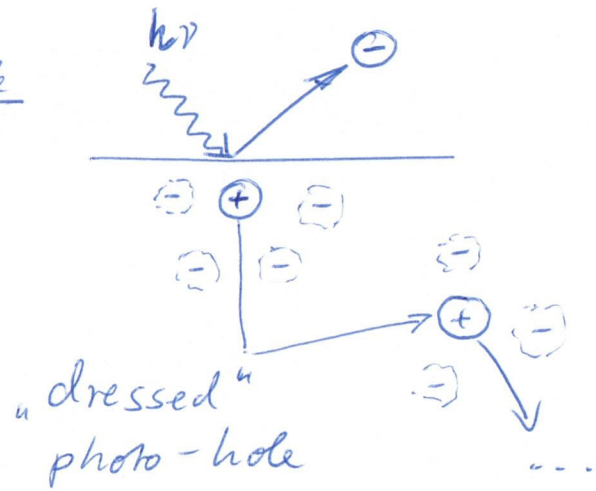
(I) $E_0(\mathbb{R})$ – ground state structure and elastic properties

Q: Can it be evaluated without solving the quantum chemical Hamiltonian?

Yes!
- Hohenberg – Kohn theory (general framework, not considered here)
- Local density approximation (LDA) gives access to the electron density
- Local spin density approximation → spin magnetism
- Relativistic approaches → orbital magnetism

(II) $\varepsilon_i(\mathbb{R})$ – quasi – particle excitations

Q: What is a quasi-particle? Example



- Landau – Theory
- Greens – function techniques
- e.g., dynamical mean field theory (DMFT)

The free electron model (Sommerfeld)

If electrons in a metal can move freely, they screen the Coulomb field of the nuclei and of the other electrons to a large degree.

Ultimate screening would yield:

$$v_i^{ext}(\underline{r}_i; \mathbb{R}) + \sum_{j}^{i<j\leq N} v_{ij}(\underline{r}_i, \underline{r}_j) = \text{const.}$$

$$\left(\sum_i^N \hat{t}_i\right)\Psi = E\Psi$$

factorization of the Slater determinant Ψ:

$$\hat{t}\varphi = \varepsilon\varphi$$

$$\varphi_{\underline{k}s}(\underline{r}) = \frac{1}{\sqrt{V}} e^{i\underline{k}\underline{r}} \; ; \; \varepsilon_{\underline{k}s} = \frac{k^2}{2}$$

(using atomic units)

Periodic boundary conditions:

$$\varphi_{\underline{k}}(\underline{r}) = \varphi_{\underline{k}}\left(\underline{r} + \sum_i^d L_i \underline{e}_i\right)$$

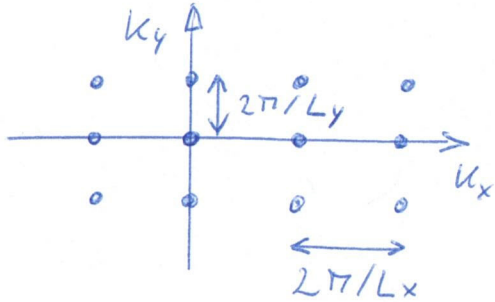
d ... dimension

$\underline{e}_i$ ... unit vector

L_i ... arbitrary integer

$$\Rightarrow \quad k_i L_i = 2\pi m, \quad m \text{ integer}$$

allowed $\underline{k}$-values:



available k-space volume per electron:

$$V^k(d)/N = \underset{\text{spin}}{2^{-1}} \cdot (2\pi)^d / (L_1 \cdot L_2 \cdot \ldots \cdot L_d)$$

electron density:

$$n = N/(L_1 \cdot L_2 \cdot \ldots \cdot L_d) = V^k / 2^{-1} \cdot (2\pi)^d$$

isotropic dispersion, $d=3$:

all states in a sphere with $|k| \leq k_F$ are filled,

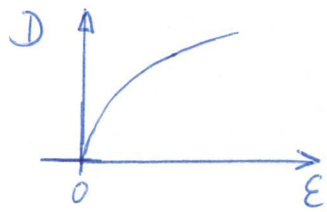
$$V^k = \frac{4}{3}\pi k_F^3 \; ; \quad \underline{k_F = (3\pi^2 n)^{1/3}} \; ; \quad \underline{E^{\text{free electrons}} \sim V n^{5/3}}$$

$$n \sim 10^{23}/\text{cm}^3 \; ; \quad \varepsilon_F = k_F^2/2 \sim 10\,\text{eV} \; ; \quad k_F \sim 0.5\,\text{Å}^{-1}$$

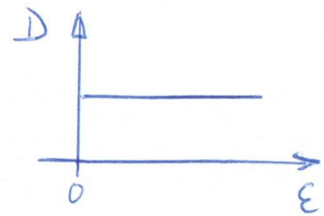
Density of states (DOS) in the free electron model

Let $n(k)$ the density of electrons in states with wave vector smaller than $|k|$:

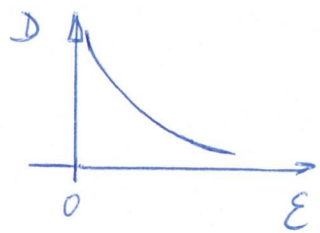
$$D(\varepsilon) := dn(k(\varepsilon)) / d\varepsilon$$



$d = 3$: $\quad D(\varepsilon) \sim \sqrt{\varepsilon}$



$d = 2$: $\quad D(\varepsilon) = \text{const.} \qquad \varepsilon \geq 0$



$d = 1$: $\quad D(\varepsilon) \sim 1/\sqrt{\varepsilon}$

Bloch theorem

Let the screening be incomplete but neglect electron-electron interaction. In a perfect crystal, the potential is periodic and the Schrödinger equation factorizes as in the Sommerfeld model.

$$(\hat{t} + v(\underline{r}))\,\varphi = \varepsilon\,\varphi \quad ; \quad v(\underline{r}) = v(\underline{r} + \underline{R})$$

$\underline{R}$ ... lattice vectors, forming the translation group

$$\Rightarrow \quad \underline{\varphi_{\underline{k}}(\underline{r} + \underline{R}) = e^{i\underline{k}\underline{R}}\,\varphi_{\underline{k}}(\underline{r})}$$

This results, e.g., in a periodic electron density,

$$|\varphi(\underline{r})|^2 = |\varphi(\underline{r} + \underline{R})|^2$$

and thus in a periodic <u>mean</u> electron potential.

Brillouin zones

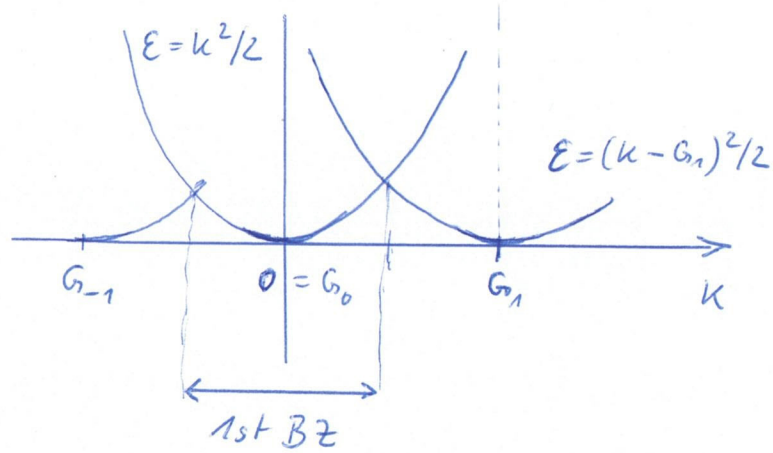
be $\underline{k} = \underline{k}' + \underline{G}$ with $\underline{G}\,\underline{R} = 2\pi m$, m integer

$\underline{G}$ ... lattice vectors of the reciprocal lattice

$$\Rightarrow \quad \varphi_{\underline{k}}(\underline{r}+\underline{R}) = e^{i(\underline{G}+\underline{k}')\underline{R}}\,\varphi_{\underline{k}}(\underline{r})$$

$$= e^{i\underline{k}'\underline{R}}\,\varphi_{\underline{k}}(\underline{r}) = \varphi_{\underline{k}'}(\underline{r}+\underline{R})$$

- $\underline{k}$ and $\underline{k}'$ are equivalent for any $\underline{G}$
- infinite number of replicas of the dispersion relation
- choose $\underline{G}$ such, that $|\underline{k}'| \to$ min.; this defines the first Brillouin zone
- introduce band index, $\underline{k} \to \nu\underline{k}$



Local Density Approximation (LDA)

Replace the electron-electron interaction by a local potential and take the full electron-nucleon interaction; this yields, as before, a periodic local potential:

$$\left(\hat{t} + v^{LDA}(\underline{r})\right) \varphi = \varepsilon \varphi$$

$$v^{LDA} = v^{ext}(\underline{r}) + v^{Hartree}(\underline{r}) + v^{xc}(\underline{r})$$

$$v^{Hartree} = \int d^3r' \; n(\underline{r}')/|\underline{r}-\underline{r}'|$$ ... mean electron potential

$$n(\underline{r}) = \sum_{\varepsilon_{\nu\underline{k}} \leq \varepsilon_F} |\varphi_{\nu\underline{k}}|^2$$

Kohn-Sham equations

$$\boxed{Q: \; v^{xc} = \; ?}$$

Exchange-correlation potential, v^{xc}

exact formulation (Hohenberg & Kohn):

$$v^{xc}(\underline{r}) = \delta E^{xc}[n(\underline{r})] / \delta n(\underline{r})$$

unknown

<u>local</u> potential derived from an unknown exchange-correlation energy functional E^{xc}.

This functional contains all energy contributions due to the correlated motion of the electrons, i.e., <u>beyond</u> the <u>mean-field</u> energy. $E^{xc} < 0$

LDA (Kohn & Sham): $v^{xc,LDA}(\underline{r}) = v^{xc,LDA}(n(\underline{r}))$

local density

<u>Notes:</u>

- LDA is exact for the homogeneous <u>interacting</u> electron gas
- LDA works with astonishing precision for structural and elastic properties of all nonmagnetic systems
- ε cannot be considered, in general, as quasiparticle energies

LDA, practical aspects

$$\left(\hat{t} + v^{LDA}(\underline{r}; n(\underline{r}'))\right)\varphi = \varepsilon\varphi$$

$$n(\underline{r}) = n(\varphi(\underline{r}); \varepsilon)$$

- non-linear system of integro-differential equations
- has to be solved by iteration

$$\begin{tikzcd} & v \arrow[dr] & \\ n \arrow[ur] & & \varphi; \varepsilon \arrow[ll] \end{tikzcd}$$

- modern codes can achieve an absolute precision of the total energy close to 10 meV / atom, a relative precision of about $\frac{1\,\mu eV}{atom}$, i.e. 10^{-11}.

B. The tight binding approximation (TB)

Consider H_2 in LDA and adiabatic approximation.

$$v^{ext}(\underline{r}) = -1/|\underline{r}-\underline{R}_1| - 1/|\underline{r}-\underline{R}_2| \quad ; \quad N=2$$

Ansatz for φ: $\quad \varphi = c_1 \varphi_{1s}^H(|\underline{r}-\underline{R}_1|) + c_2 \varphi_{1s}^H(|\underline{r}-\underline{R}_2|) =: c_1\varphi_1 + c_2\varphi_2$

$$(\hat{t} + v^{LDA} - \varepsilon)(c_1\varphi_1 + c_2\varphi_2) = 0$$

$$0 = c_1(\varphi_1|\hat{t} + v^{LDA} - \varepsilon|\varphi_1) + c_2(\varphi_1|\dots|\varphi_2)$$

$$0 = c_1(\varphi_2|\quad\dots\quad|\varphi_1) + c_2(\varphi_2|\dots|\varphi_2)$$

let $v^{LDA} =: -\dfrac{1}{|\underline{r}-\underline{R}_1|} + \Delta v_1 \equiv -\dfrac{1}{|\underline{r}-\underline{R}_2|} + \Delta v_2$

$$\Rightarrow (\varphi_i|\hat{t} + v^{LDA}|\varphi_i) = \varepsilon_{1s}^H + (\varphi_i|\Delta v_i|\varphi_i) =: \varepsilon_{1s}^H + \Delta \quad ; \quad \Delta < 0$$

<u>TB:</u> $\quad \underline{(\varphi_1|\hat{t} - \varepsilon|\varphi_2) \approx 0}$

<u>Def.:</u> $-(\varphi_1|v^{LDA}|\varphi_2) =: t \;,\; t > 0$

t ... transfer integral, hopping integral

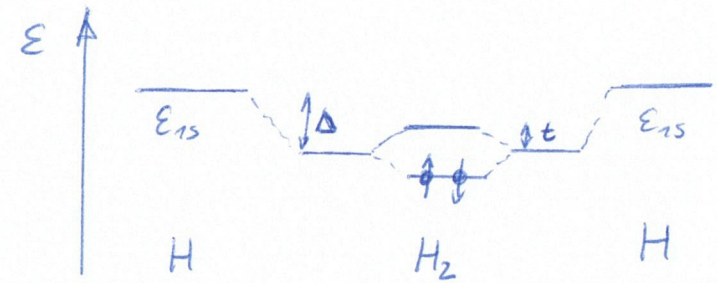
H_2 in TB, continued

simplified secular equations:

$$0 = C_1 (\varepsilon_{1s} + \Delta - \varepsilon) - C_2 t$$
$$0 = -C_1 t + C_2 (\varepsilon_{1s} + \Delta - \varepsilon)$$

$$\Rightarrow (\varepsilon_{1s} + \Delta - \varepsilon)^2 - t^2 = 0$$

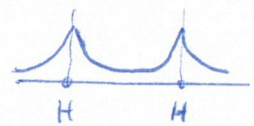
$$\boxed{\varepsilon_{1/2} = \varepsilon_{1s} + \Delta \mp t}$$



schematic!

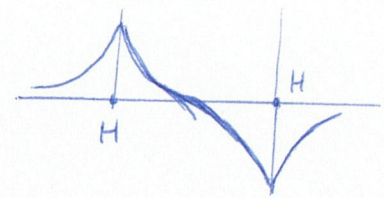
1) bonding solution

$C_1 t - C_2 t = 0$; $C_1 = C_2$



2) antibonding solution

$-C_1 t - C_2 t = 0$; $C_1 = -C_2$



Notes:

- high accuracy needs larger basis set, e.g. 1s 2s 2p 3d
- self-consistent calculation
- $\Delta E^{binding} \neq \Delta \varepsilon$
- virial theorem: $\Delta E^{binding} = \Delta E^{pot.}/2 = -\Delta E^{kin.}$

Infinite H-chain in TB

$$v^{ext}(\underline{r}) = \sum_{m}^{\text{integer}} -1/|\underline{r}-\underline{R}_m| \quad ; \qquad \underline{R}_m = m\,(0,0,a)$$

Ansatz:
$$\varphi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{N}} \sum_{m}^{\text{integer}} e^{-i\underline{k}\underline{R}_m}\, \varphi_{1s}(|\underline{r}-\underline{R}_m|) =: \frac{1}{\sqrt{N}} \sum_m e^{-ikma}\, \varphi_m$$

$(N \to \infty)$

This special choice of C_m fulfills the Bloch theorem.

"One-band TB"

$$(\hat{t} + v - \varepsilon_k)\,\varphi_{\underline{k}} = 0$$

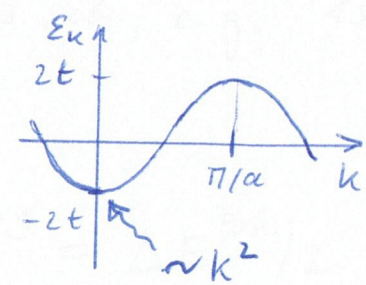
$$\Big(\varphi_0 \,\Big|\, \hat{t} + v - \varepsilon_k \Big| \sum_m e^{-ikma}\varphi_m\Big) = 0 \quad ; \qquad v =: -\frac{1}{|\underline{r}|} + \Delta v_0$$

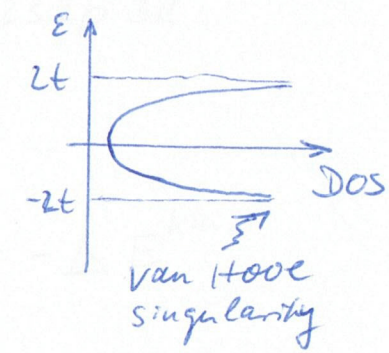
$$\hookrightarrow \quad \varepsilon_{1s} + \Delta - \varepsilon_k + \sum_{m\neq 0} e^{-ikma}\,(\varphi_0|\hat{t}+v-\varepsilon_k|\varphi_m) = 0$$

nearest neighbor TB:
$$(\varphi_0|v|\varphi_1) = (\varphi_1|v|\varphi_0) =: -t \quad ; \quad (\varphi_m|v|\varphi_n) = 0,\ |m-n|>1$$

$$\varepsilon_k = \varepsilon_{1s} + \Delta - t\left(e^{-ik(-a)} + e^{-ika}\right)$$

$$\boxed{\varepsilon_k = \varepsilon_{1s} + \Delta - 2t\cos ka}$$





C. Local spin density approximation (LSDA)

von Barth & Hedin

In the LDA, there is no possibility to describe magnetic properties.

Now, $n(\underline{r}) = n_\uparrow + n_\downarrow$ $\qquad$ $n_{\uparrow(\downarrow)}$ ... majority (minority) spin density

$m(\underline{r}) = -(n_\uparrow - n_\downarrow)\mu_B$ $\qquad$ m ... spin magnetization density

<u>LSDA</u>

$$\left(\hat{t} + v_s^{LSDA}(\underline{r})\right)\varphi_s = \varepsilon_s \varphi_s \; ; \qquad s = \pm 1/2 \text{ or } \uparrow, \downarrow .$$

$$v_s^{LSDA} = v^{ext} + v^{Hartree} + \underbrace{v^{xc,LSDA}}_{\approx v^{xc,LDA}} + 2s\,\mu_B B^{xc,LSDA}$$

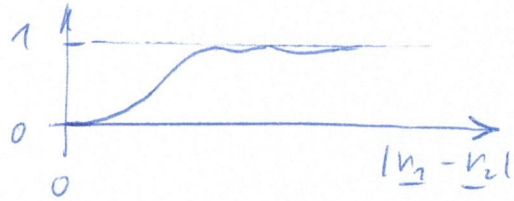
$$\underline{B^{xc,LSDA} \approx -f(n(\underline{r}))\cdot m(\underline{r})/\mu_B}$$

"molecular field" $\qquad (f < 0)$

Origin of the molecular field: Coulomb interaction of particles with antisymmetric wave function.

Origin of the molecular field, continued:

$$\Psi(\underline{r}_1, s_1; \underline{r}_2 = \underline{r}_1, s_2 = s_1) \equiv 0$$



"exchange hole": reduced probability to find electrons with the same spin at small distance.

Energy gain due to exchange in the homogeneous spin polarized electron gas:

$$E^{x,\,hom} \sim -V\left[n_\uparrow^{4/3} + n_\downarrow^{4/3}\right] \qquad \text{(Hartree-Fock result)}$$

Reduction of the Coulomb energy due to correlated motion favours complete polarization. This is opposed by the Sommerfeld single-particle energy (level occupation obeying Fermion statistics),

$$E^{free} \sim +V\left[n_\uparrow^{5/3} + n_\downarrow^{5/3}\right] \qquad \text{(discussed before)}$$

$\Longrightarrow$ $\exists$ critical density, below which the homogeneous system is spontaneously polarized (broken symmetry).

Exchange enhanced Pauli susceptibility and Stoner parameter

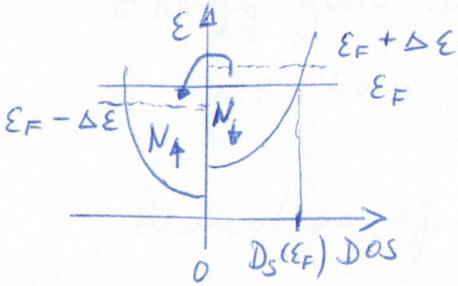
LSDA with a small external field (Zeeman splitting of the spin states):

$$\left(\hat{t} + v^{ext} + v^{Hartree} + v^{xc,LSDA} + 2s\mu_B\left(B^{ext} + B^{xc}\right)\right)\varphi_s = \varepsilon_s \varphi_s \; ; \; B^{ext} < 0$$

assume an unpolarized solution, $m(\underline{r}) \equiv 0$, if $B^{ext} \equiv 0$.

First order perturbation theory for $B^{ext} \neq 0$:

$$\varepsilon_s = \varepsilon\left(B^{ext}=0\right) + 2s\mu_B\left(B^{ext} + \int d^3r\, B^{xc}(\underline{r})\,|\varphi|^2\right) =: \varepsilon + 2s\,\Delta\varepsilon$$



$$\Delta\varepsilon = \mu_B\left(B^{ext} - \int d^3r\, f(n(\underline{r}))\,\frac{m(\underline{r})}{\mu_0}\,|\varphi|^2\right) \quad (<0)$$

$$\int d^3r\, m(\underline{r}) =: M = -(N_\uparrow - N_\downarrow)\mu_B = +2\,\Delta\varepsilon\, D_s(\varepsilon_F)\mu_B$$

$$\hookrightarrow m(\underline{r}) \approx +2\,\Delta\varepsilon\, D_s(\varepsilon_F)\mu_B\,|\varphi_{\varepsilon_F}(\underline{r})|^2$$

$$\Delta\varepsilon = \mu_B\left(B^{ext} - 2\int d^3r\, f\,\Delta\varepsilon\, D_s(\varepsilon_F)\,|\varphi_{\varepsilon_F}(\underline{r})|^4\right) =: \mu_B B^{ext} + \Delta\varepsilon\, D_s(\varepsilon_F)\cdot I$$

$$\Delta\varepsilon = \mu_B B^{ext}/\left(1 - D_s(\varepsilon_F)\, I\right)$$

$$\boxed{I = -\int d^3r\, 2 f(n(\underline{r}))\,|\varphi_{\varepsilon_F}(\underline{r})|^4}$$

$$M = +2\, D_s(\varepsilon_F)\,\mu_B^2 B^{ext}/\left(1 - D_s I\right)$$

LSDA-Stoner parameter,

$$\boxed{\chi = +\frac{\mu_0 M}{B^{ext}} = \frac{\chi_{Pauli}}{1 - D_s(\varepsilon_F) I} \; ; \; \chi_{Pauli} = \mu_0\mu_B^2\, 2 D_s}$$

$I \approx 0.4 \ldots 0.8\,eV$

Notes on the exchange enhanced χ_{Pauli}

Examples:

metal	Cu	Y	Pd
χ / χ_{Pauli}	1.1	1.9	5...10
φ_{ε_F}	4s	4d	3d

Ferromagnets: Fe, Co, Ni $\quad D_s I > 1$, a <u>sufficient condition</u> for a spontaneously broken symmetry!

Cave: $D_s I > 1$ is <u>not a sufficient condition</u> for ferromagnetism to occur; other magnetic or non-magnetic states can be more stable, e.g. a lattice distortion.

$D_s I > 1$ is <u>not a necessary condition</u> for ferromagnets either; local-moment systems like Gd are ferromagnetic without the Stoner criterion being fulfilled.

Pauli paramagnetism vs. atomic diamagnetism

Local-moment paramagnetism is T-dependent and not considered here.

Pauli paramagnetism is almost temperature independent, like diamagnetism. The latter is obtained in first order perturbation theory from $(\underline{B}^{ext} \times \underline{r}_i)^2$ applied to atomic orbitals:

$$\chi_{dia} = -\frac{N_{atoms}}{V} \frac{e^2 \mu_0}{6 m_e} \sum_i^{N/N_{atom}} \langle r_i^2 \rangle ,$$

Lenz's law

r_i ... radii of the atomic orbitals, outer shell with N/N_{atom} electrons is considered only.

$$\chi_{Pauli} = \mu_0 \mu_B^2 D(\varepsilon_F) = \mu_0 \mu_B^2 \frac{m_e}{\hbar} (3\pi^2)^{-2/3} (N/V)^{1/3}$$

... now in full units!
... but still for the homogenous electron gas.

Assuming $V_{atom} = \frac{4\pi}{3} \langle r_i^2 \rangle^{3/2} = V/N_{atoms}$,

$$\boxed{\chi_{Pauli} / \chi_{dia} \approx 1.8 / (N/N_{atom})^{2/3}}$$

N/N_{atom}	χ_{Pauli}/χ_{dia}
10	0.4 (!)
1	1.8
Landau	3

Comments

- d-electrons are not "free" electrons, larger $D(\varepsilon_F)$
- exchange enhancement