Electronic structure calculations for magnetic systems

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1. Hohenberg-Kohn-Sham theory & Local Density Approximation
2. Tight-binding approach and chemical binding in a nutshell
3. Exchange, the root of condensed matter magnetism
4. Binding meets exchange: applications

1. Hohenberg-Kohn-Sham theory & Local Density Approximation

H. Eschrig, *The Fundamentals of Density Functional Theory*, Teubner-Texte zur Physik, Vol. 32, Teubner, Stuttgart 1996, ISBN 3-8154-3030-5.

M. Richter, *Density Functional Theory applied to 4f and 5f Elements and Metallic Compounds*, Handbook of Magnetic Materials (Ed. K.H.J. Buschow), Vol. 13, Elsevier, Amsterdam 2001, pp. 87-228, ISBN 0-444-50666-7.

Our starting point is the non-relativistic Coulomb-Schrödinger Hamiltonian $\hat{H}$ with fixed positions of the nuclei, generating the potential v_{nuc}:

$$\hat{H} = \sum_{i}^{N} \left[-\frac{\Delta_i}{2} + v_{\mathrm{nuc}}(\mathbf{r}_i) + \frac{1}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] = \hat{T} + \hat{V} + \hat{U} \ ,$$

$$(\hat{H} - E_\nu)\psi_\nu(\mathbf{r}_1, \sigma_1; \ldots ; \mathbf{r}_N, \sigma_N) = 0 \ ,$$

with many-particle wave function ψ_ν for N electrons at coordinates $(\mathbf{r}_i, \sigma_i)$. There is no spin-dependent interaction. Where do magnetic states come from?

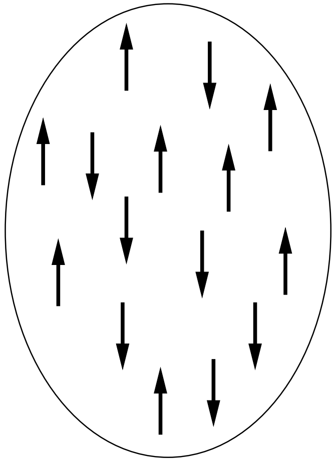
Numerical solutions for ψ_ν can be obtained up to $N \approx 10$. For $N > 100$, the *stationary* states ψ_ν cannot be resolved in general.

Example: an N-particle Ising system with stochastic interaction has 2^{N-1} different levels.

Mean level distance: $\Delta E \approx E_0/2^{N-1}$.

For $N = 100$ and $E_0 = 10$ eV, resolution of a single level needs 10^6 years.

Thus, ψ_ν has no meaning for $N > 100$.



$H = \sum_{j>i}^{100} J_{ij} s_i^z s_j^z$

Exception: the ground state, ψ_0, has a meaning:

(i) it serves as reference for *quasi*-stationary (spin or charge) excitations;

(ii) the ground-state energy $E_0[v_{\rm nuc}[\mathbf{R}_s]]$ allows to determine stable structures with nuclear positions $[\mathbf{R}_s]$.

How can $E_0[v_{\rm nuc}]$ be calculated?

Hohenberg and Kohn [PR **136** (1964) B864]; Levy [PRA **26** (1982) 1200]; Lieb [Int. J. Quant. Chem. **XXIV** (1983) 243]:

$$E_0[v_{\rm nuc}] = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle = \min_{n} \left\{ \int d^3r \; v_{\rm nuc} n + \min_{\psi_n} \langle \psi_n | \hat{T} + \hat{U} | \psi_n \rangle \, \middle| \int d^3r \; n = N \right\} ,$$

where ψ_n are *all* wave functions that generate a density $n(\mathbf{r})$. Definition:

$$\min_{\psi_n} \langle \psi_n | \hat{T} + \hat{U} | \psi_n \rangle =: F[n] =: T_{\rm s}[n] + E_{\rm H}[n] + E_{\rm xc}[n] \; .$$

Here, the exchange-correlation energy $E_{\rm xc}[n]$ contains all contributions which are not included in the other two terms,

(i) the mean-field Hartree energy:

$$E_{\rm H} = \frac{1}{2} \int \int d^3r d^3r' \, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \; ,$$

(ii) the kinetic energy of a model system of non-interacting electrons with density n:

$$T_{\rm s}[n] = \sum_i^N \langle\phi_i| - \Delta/2|\phi_i\rangle \ .$$

The ϕ_i can be obtained from

$$\left[-\frac{\Delta}{2} + v_{\rm nuc}(\mathbf{r}) + v_{\rm H}(\mathbf{r};[n]) + v_{\rm xc}(\mathbf{r};[n])\right]\phi_i = \varepsilon_i\,\phi_i \ ,$$

with $n = \sum_i^N \phi_i\phi_i^*$ and ϕ_i being the N lowest *single-particle* eigenstates in a corresponding *effective* potential,

$$v_{\rm eff} = v_{\rm nuc} + v_{\rm H} + v_{\rm xc} = v_{\rm nuc} + \int d^3r' n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \delta E_{\rm xc}[n]/\delta n \ .$$

Kohn and Sham [PR **140** (1965) A1133].

What does the exchange-correlation potential v_{xc} mean?

(i) Exchange “x”:

$\psi(\mathbf{r}_1, \sigma_1; \ldots; \mathbf{r}_2 = \mathbf{r}_1, \sigma_2 = \sigma_1; \ldots) = 0$

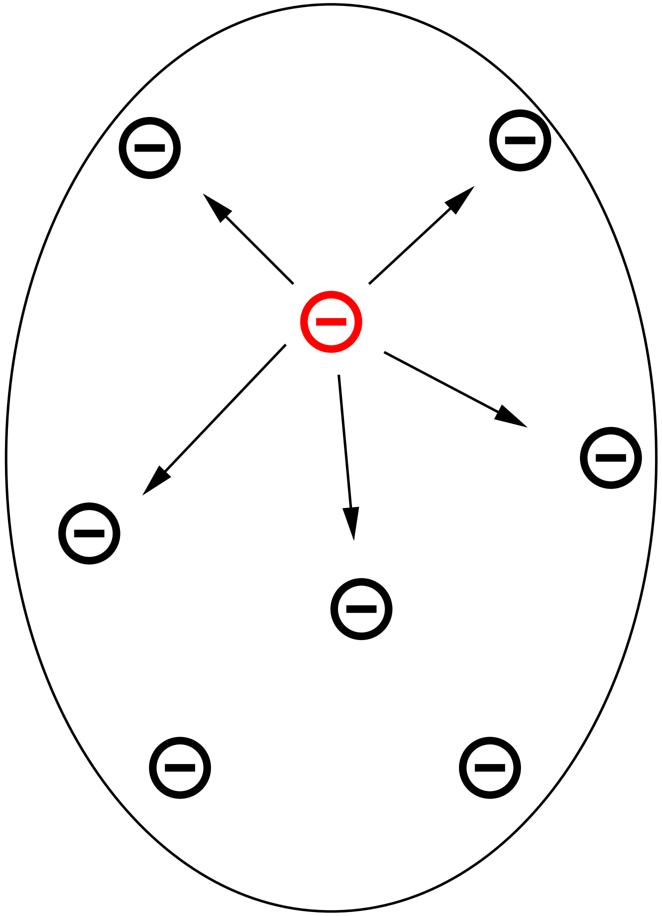
for Fermions;

(ii) Correlation “c”:

$\psi(\mathbf{r}_1, \sigma_1; \ldots; \mathbf{r}_2 = \mathbf{r}_1, \sigma_2; \ldots) <$

$\psi(\mathbf{r}_1, \sigma_1; \ldots; \mathbf{r}_2 \neq \mathbf{r}_1, \sigma_2; \ldots)$

due to Coulomb repulsion.



The total energy is lowered due to the xc-hole around each electron. Thus, v_{xc} is always *attractive*, while v_{H} is repulsive. The xc potential corrects both the mean-field treatment of the Coulomb interaction and the single-particle treatment of the kinetic energy.

Up to this point, the theory is exact. However, v_{xc} is in general not known and has to be approximated. There exists a multitude of different approximations for the xc potential: LDA, GGA, metaGGA, etc.

Most of these approximations do not contain free parameters. However, they should not be called "*ab initio*", since they do *not* solve the general Coulomb-Schrödinger Hamiltonian (this is attempted by quantum chemical methods). Rather, these methods solve a certain model, approximating $\hat{H}$.

For the homogeneous interacting electron gas, $v_{\mathrm{xc}}^{\mathrm{hom}}(n)$ has been obtained numerically by Ceperley and Alder [PRL **45** (1980) 566].

Local Density Approximation (LDA): $v_{\mathrm{xc}}(\mathbf{r};[n]) \approx v_{\mathrm{xc}}^{\mathrm{hom}}(n(\mathbf{r}))$.

Roughly, $v_{\mathrm{xc}}^{\mathrm{hom}} \propto n^{1/3}$ and $E_{\mathrm{xc}}^{\mathrm{hom}} \propto n^{4/3}$. This is similar to what is found for the exchange energy in the Hartree-Fock approximation.

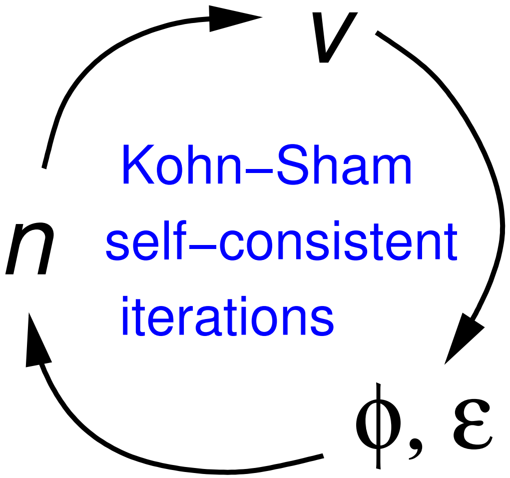
The mostly used parameterization of LDA has been proposed by Perdew and Wang [PRB **45** (1992) 13244]: $v_{\mathrm{xc}}^{\mathrm{PW92}}(n) \approx v_{\mathrm{xc}}^{\mathrm{hom}}(n)$.

Remarks:

LDA, GGA and similar approximations are rather successful in the calculation of structural properties, elasticity, phonons.

The interpretation of Kohn-Sham single-particle energies in terms of charge excitations is justified only in so-called “weakly correlated” materials. This notation is only loosely related with the types of correlations we discussed. What is meant is that charge excitations in such materials are well screened by valence electrons.

A number of codes is available which solve the non-linear integro-differential equations with different methods. They contain typically 10^5 lines of source code and need 10-20 person years development. Total energy deviations between good codes: ≈ 1 meV/atom.



v

Kohn–Sham self–consistent iterations

n

ϕ, ε

2. Tight-binding approach and chemical binding in a nutshell

J. Singleton, *Band Theory and Electronic Properties of Solids*, Oxford Master Series in Condensed Matter Physics, Oxford University Press, Oxford 2006, ISBN 0-19-850644-9.

C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics*, Vol. II, Hermann, Paris 1977, ISBN 0-471-16435-6.

Up to now, nothing has been told about the character of the Kohn-Sham single-particle orbitals ϕ_i. We therefore proceed from the most simple case of atomic orbitals via molecular orbitals to spatially extended Bloch states.

The H_2 molecule, considered in LDA and adiabatic approximation:

$$v_{\mathrm{nuc}}^{\mathrm{H}_2} = -1/|\mathbf{r} - \mathbf{R}_1| - 1/|\mathbf{r} - \mathbf{R}_2| \; ; \quad N = 2.$$

Minimalistic Ansatz for ϕ:

$$\phi = c_1 \varphi_{1s}^{\mathrm{H}}(|\mathbf{r} - \mathbf{R}_1|) + c_2 \varphi_{1s}^{\mathrm{H}}(|\mathbf{r} - \mathbf{R}_2|) =: c_1 \varphi_1 + c_2 \varphi_2$$

$$(-\Delta/2 + v_{\mathrm{eff}}^{\mathrm{H}_2} - \varepsilon)(c_1 \varphi_1 + c_2 \varphi_2) = 0$$

This yields the 2×2 matrix equation

$$\sum_j c_j (-\Delta/2 + v_{\mathrm{eff}}^{\mathrm{H}_2} - \varepsilon)_{ij} = 0$$

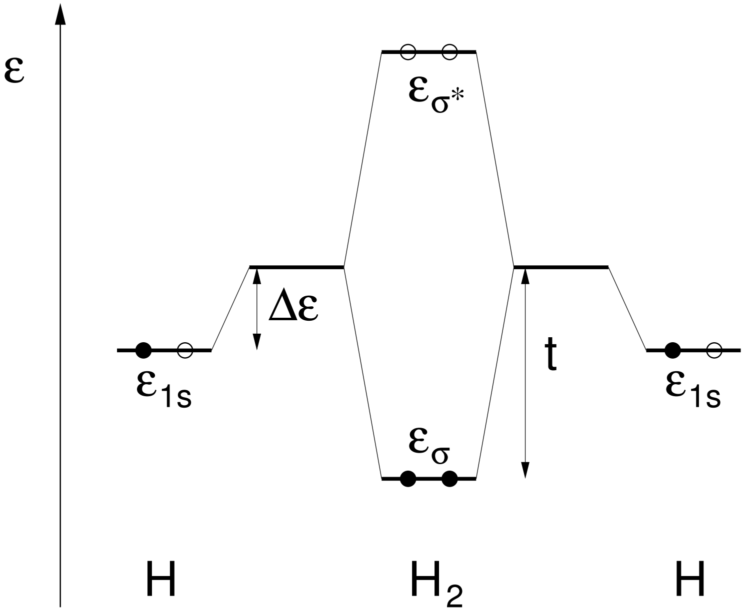
with $(\varphi_i | \hat{A} | \varphi_j) =: A_{ij}$.

Separate the atomic state energy, $\varepsilon^{\mathrm{H}}_{1s}$, from the "crystal field", $\Delta\varepsilon$:

$$(-\Delta/2 + v^{\mathrm{H}_2}_{\mathrm{eff}})_{ii} = (-\Delta/2 + v^{\mathrm{H}}_{\mathrm{eff}})_{ii} + (v^{\mathrm{H}_2}_{\mathrm{eff}} - v^{\mathrm{H}}_{\mathrm{eff}})_{ii} =: \varepsilon^{\mathrm{H}}_{1s} + \Delta\varepsilon \; ; \quad (i \neq j) \; .$$

Tight-binding approximation: $(-\Delta/2 - \varepsilon)_{ij} \approx 0 \; ; \quad (i \neq j)$.

Hopping integral: $t =: (v^{\mathrm{H}_2}_{\mathrm{eff}})_{ij} \; ; \quad (i \neq j)$.



This yields the solutions:

$$\varepsilon^{\mathrm{H}_2}_{\mathrm{bonding}} = \varepsilon^{\mathrm{H}}_{1s} + \Delta\varepsilon - t \; , \quad c_1 = c_2 \; ;$$

$$\varepsilon^{\mathrm{H}_2}_{\mathrm{antibonding}} = \varepsilon^{\mathrm{H}}_{1s} + \Delta\varepsilon + t \; , \quad c_1 = -c_2 \; .$$

Remarks:

v_{eff} needs self-consistent calculations.

As a result, the binding energy (6.6 eV per H_2) is smaller than $2(t - \Delta\varepsilon) = 7.5$ eV.

Toward extended systems: Bloch's theorem.

X-ray diffraction shows that the charge distribution in single crystals is periodic. This means, that also $v_{\mathrm{eff}}^{\mathrm{LDA}}$ is periodic: $v_{\mathrm{eff}}^{\mathrm{LDA}}(\mathbf{r}+\mathbf{R}) = v_{\mathrm{eff}}^{\mathrm{LDA}}(\mathbf{r})$, if $\mathbf{R}$ is a lattice vector.

Then, the Kohn-Sham states can most conviniently be chosen as Bloch states in this periodic potential:

$$\phi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{kR}}\phi_{\mathbf{k}}(\mathbf{r}) \ .$$

The charge density evaluated from this set of states has the same symmetry as the initial potential. Thus, the initial symmetry is always kept in the Kohn-Sham self-consistent cycle. (This does not always hold, if spin-orbit coupling is considered.)

Infinite H-chain: $v_{\rm nuc}(\mathbf{r}) = \sum_m^{\rm integer}(-1/|\mathbf{r}-\mathbf{R}_m|)\ ;\ \ \mathbf{R}_m = m(0,0,a)\ .$

One-band ansatz:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_m^{\rm integer} e^{-i\mathbf{k}\mathbf{R}_m} \varphi_{1s}(|\mathbf{r}-\mathbf{R}_m|) =: \frac{1}{\sqrt{N}} \sum_m^{\rm integer} e^{-ikma} \varphi_m\ .$$

Nearest-neighbor tight-binding:

$$-(v_{\rm eff})_{m,m+1} =: t\ ; \quad (v_{\rm eff})_{m,n} \approx 0\ \ (|m-n|>1)\ ; \quad (-\Delta/2-\varepsilon_k)_{m,n} \approx 0\ \ (m \neq n)$$

provides

$$\varepsilon_k = \varepsilon_{1s} + \Delta\varepsilon - 2t\cos(ka)\ ; \quad \Delta\varepsilon = (v_{\rm eff}^{\rm chain} - v_{\rm eff}^{\rm H})_{00}\ .$$

This dispersion has a period of $2\pi/a$ and a band width of $2t$.

3. Exchange, the root of condensed matter magnetism

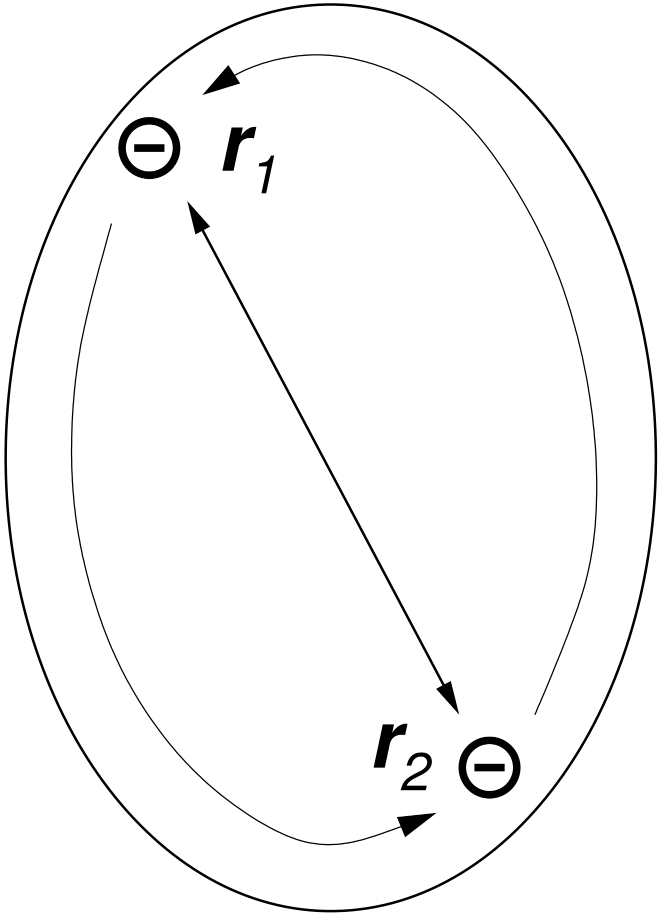
S. Blundell, *Magnetism in Condensed Matter*, Oxford Master Series in Condensed Matter Physics, Oxford University Press, Oxford 2006, ISBN 0-19-850591-4.

J. Kübler, *Theory of Itinerant Electron Magnetism*, International Series of Monographs on Physics, Vol. 106, Oxford Science Publications, Clarendon Press, Oxford 2000, ISBN 0-19-850028-9.

We step back to the case of a free atom and consider an incompletely filled atomic shell with $l \neq 0$.

One electron: trivial case with $s = 1/2$.

Two electrons: Is the ground state a singlet $S = 0$ ($\uparrow\downarrow$) or a triplet $S = 1$ ($\uparrow\uparrow$) ?



Remember, that the two electrons move in a correlated way due to:

(i) (Pauli) exchange (kinematic correlation), $\psi(\mathbf{r}_1, \sigma_1;\ \mathbf{r}_1, \sigma_1) = 0$;

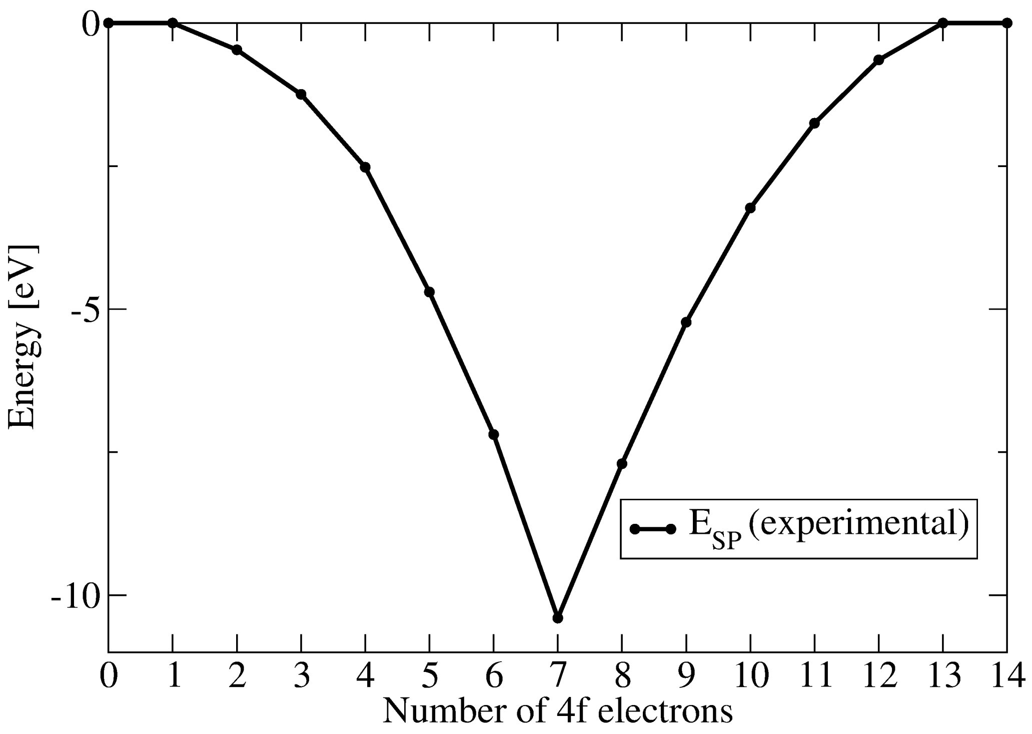
(ii) Coulombic (or, dynamic) correlation, $\psi(\mathbf{r}_1, \sigma_1;\ \mathbf{r}_1, \sigma_2) < \psi(\mathbf{r}_1, \sigma_1;\ \mathbf{r}_2 \neq \mathbf{r}_1, \sigma_2)$.

This correlated movement produces an xc-hole around each electron, which reduces the electron-electron interaction energy.

Thereby, the combined effect of exchange and Coulomb correlation present in the case $\uparrow\uparrow$, $S = 1$, is stronger than the effect of Coulomb correlation alone in the case $\uparrow\downarrow$, $S = 0$.

Thus, the ground state of free atoms is always a state with the largest possible total spin (first Hund rule).

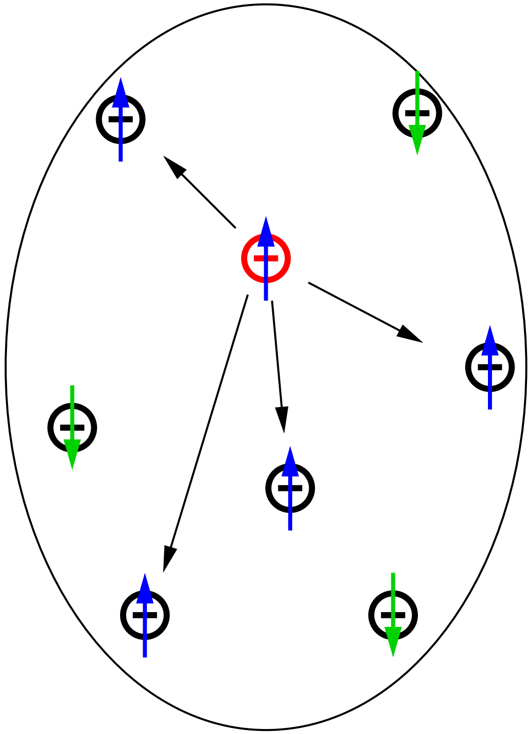
What is the energy scale related to Hund's first rule?



Experimental 4f-E_{SP}: spin polarization energies of lanthanide^{3+}-ions. Data are taken from J. Melsen *et al.* [J. Alloys and Comp. **209** (1994) 15], who evaluated spectroscopic data (energy differences between the ground-state spin multiplet and the gravity center of the configuration).

The two branches meeting at half-filling reflect the electron-hole symmetry. The spin polarization energy is approximately proportional to the number of electron (or hole) pairs. For one electron (or one hole) in the shell, $E_{\mathrm{SP}} = 0$: there is no self-exchange. The energies are comparable with chemical binding energies.

Consider now the other extrem case, the interacting homogeneous electron gas. It should now be allowed to spin-polarize, $n = n^{\uparrow} + n^{\downarrow}$.



Two of the total energy contributions depend on the degree of spin polarization:

$$E_{\mathrm{x}}^{\mathrm{hom}} = -C_x \left[(n^{\uparrow})^{4/3} + (n^{\downarrow})^{4/3} \right] \quad \text{(HF; QMC);}$$

$$T_s^{\mathrm{hom}} = +C_s \left[(n^{\uparrow})^{5/3} + (n^{\downarrow})^{5/3} \right] \quad \text{(Sommerfeld).}$$

Imbalance between $n^{\uparrow}$ and $n^{\downarrow}$ gains exchange energy and costs kinetic energy, both effects arising from the stronger than linear dependence on n.

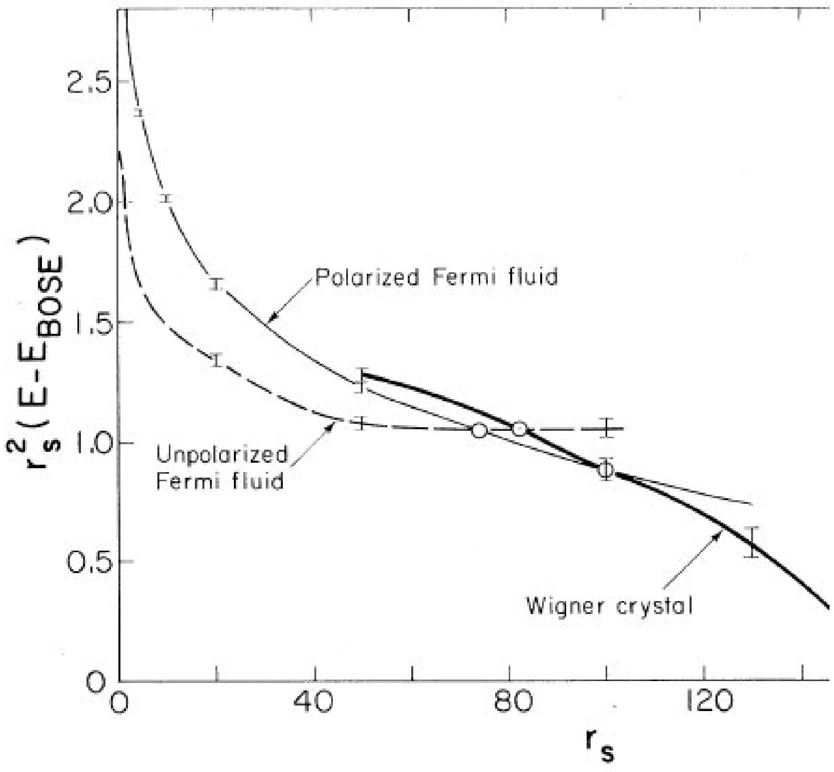
$$n \to 0 : \; E_{\mathrm{x}}/T_s \to \infty \; ; \qquad n \to \infty : \; E_{\mathrm{x}}/T_s \to 0 \; .$$

Thus, spontaneous polarization occurs below a critical value of n.

In free atoms, the kinetic energy is mainly determined by the orbital quantization and does only marginally depend on the spin polarization. Thus, there is no critical n for the first Hund rule. In solids, both situations may be present.

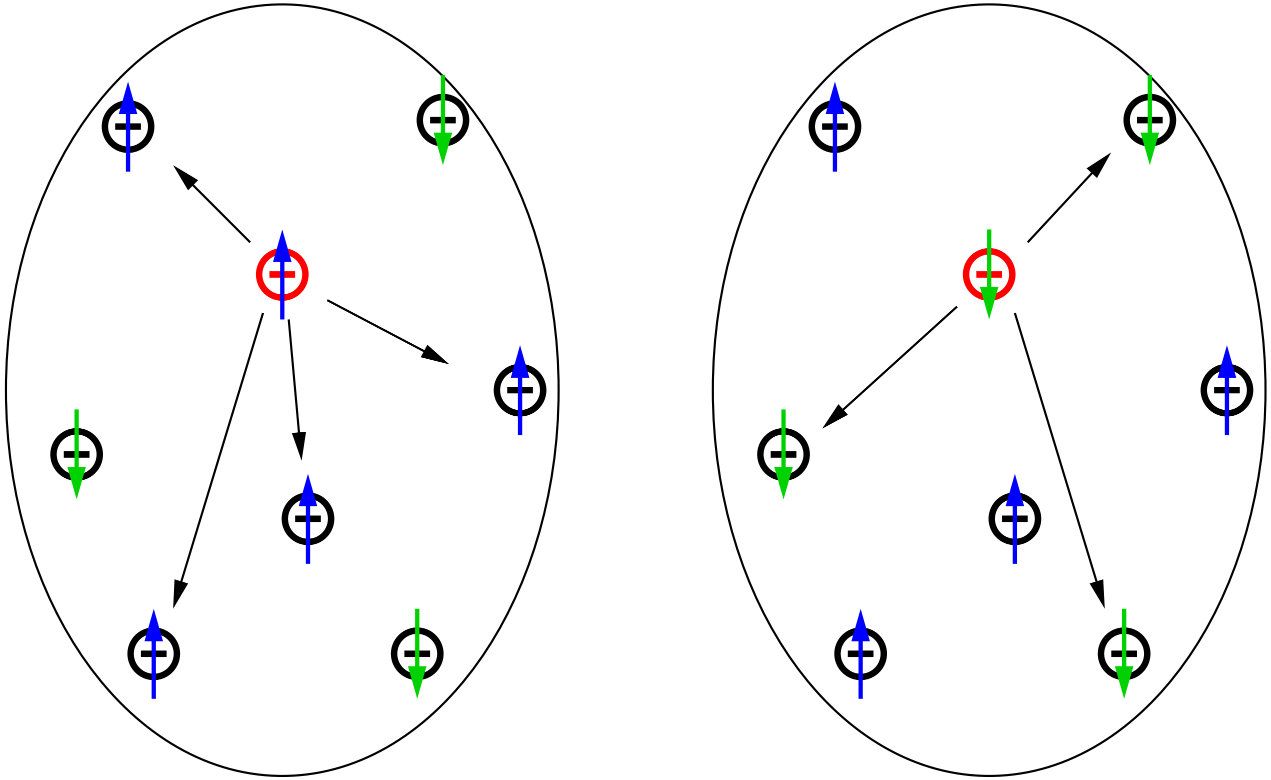
Numerical calculations (Ceperley and Alder [PRL **45** (1980) 566]; about 10.000 quotations) provide a yet more complex picture:

Energy of three possible states of a homogenous electron gas vs. $r_s \propto n^{-1/3}$.



At high densities (small r_s), the unpolarized Fermi liquid is most stable; at intermediate densities, the ground state is a spin polarized Fermi liquid; at low densities, a Wigner crystal with localized electrons is formed. These three states contain a good part of the solid state physics investigated in the past decades. While the transition between unpolarized and polarized states is well described in recent DFT approximations, the localization is still an issue.

Consider now the possibility of spin polarization in a general system. If the densities of spin-up and spin-down electrons, $n^{\uparrow}$ and $n^{\downarrow}$, resp., are different, both species will experience different xc potentials, $v^{\uparrow}_{\mathrm{xc}}$ and $v^{\downarrow}_{\mathrm{xc}}$, since only electrons of the same spin contribute to the respective x-part of these potentials.



The difference between $v_{\mathrm{xc}}^{\uparrow}$ and $v_{\mathrm{xc}}^{\downarrow}$ can be considered as a modern version of the Weiss field. This is the fundamental idea of the spin density functional theory, formulated by von Barth and Hedin [J. Phys. C **5** (1972) 1629].

$$\sum_{\sigma'} \left[\left(-\frac{\Delta}{2} + v_{\mathrm{nuc}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r};[n]) \right) \delta_{\sigma\sigma'} + v_{\mathrm{xc},\sigma\sigma'}(\mathbf{r};[n_{\sigma\sigma'}]) \right] \phi_i^{\sigma'} = \varepsilon_i \phi_i^{\sigma} \ ,$$

$$n_{\sigma\sigma'} = \sum_i^N \phi_i^{\sigma} \phi_i^{\sigma' *} \ ,$$

$$v_{\mathrm{xc},\sigma\sigma'}(\mathbf{r};[n_{\sigma\sigma'}]) = \frac{\delta E_{\mathrm{xc}}[n_{\sigma\sigma'}]}{\delta n_{\sigma\sigma'}} \ ,$$

The matrix notations allow for the consideration of canted spin densities $\mathbf{\Sigma}$ and related canted xc-fields (Weiss fields) $\mathbf{B}_{\mathrm{xc}}$:

$$n_{\sigma\sigma'} = (n \ \delta_{\sigma\sigma'} + \boldsymbol{\sigma} \ \mathbf{\Sigma})/2 \ ; \qquad v_{\mathrm{xc},\sigma\sigma'} = \bar{v}_{\mathrm{xc}} \ \delta_{\sigma\sigma'} + \mu_{\mathrm{B}} \ \boldsymbol{\sigma} \ \mathbf{B}_{\mathrm{xc}} \ .$$

The Local Spin Density Approximation (LSDA) is constructed in complete analogy to the LDA:

$$\bar{v}_{\mathrm{xc}}(\mathbf{r};[n_{\sigma\sigma'}]) \approx v_{\mathrm{xc}}^{\mathrm{hom}}(n(\mathbf{r}),|\boldsymbol{\Sigma}|(\mathbf{r}))\ ;$$

$$\mathbf{B}_{\mathrm{xc}}(\mathbf{r};[n_{\sigma\sigma'}]) \approx \mathbf{B}_{\mathrm{xc}}^{\mathrm{hom}}(n(\mathbf{r}),\boldsymbol{\Sigma}(\mathbf{r}))\ .$$

Again, the numerical data obtained by Ceperley and Alder [PRL **45** (1980) 566] are used in the LSDA parameterization: the same PW92 by Perdew and Wang [PRB **45** (1992) 13244] as in LDA.

The exchange field $\mathbf{B}_{\mathrm{xc}}$ is in many cases much stronger than common magnetic fields. Due to its Coulombic origin, it can reach the order of 10^4 Tesla.

A very useful corollary of LSDA is the LSDA Stoner criterion, see Gunnarsson [J. Phys. F **6** (1976) 587] and Janak [PRB **16** (1977) 255]:

$$D(E_\mathrm{F}) I^\mathrm{LSDA} \geq 1 \; .$$

Here, $D(E_\mathrm{F})$ is the density of states at the Fermi level and I^LSDA is the Stoner parameter in LSDA. This criterion is a sufficient, but not a necessary condition for the instability of the unpolarized state. As before, the instability originates from a competition between gain in xc energy in favor of the polarization and a loss in kinetic energy due to the related band splitting. Without a detailed justification, we note that

$$I^\mathrm{LSDA} = -\frac{1}{D^2(E_\mathrm{F})} \int_\mathrm{ec} d^3r \left(\left. \frac{\partial n(\mathbf{r},\varepsilon)}{\partial \varepsilon} \right|_{\varepsilon = E_\mathrm{F}} \right)^2 \left. \frac{\delta^2 E_\mathrm{xc}}{\delta \Sigma^2} \right|_{\Sigma = 0} \; .$$

The integral runs over the elementary cell and $n(\mathbf{r},\varepsilon)$ denotes the charge density obtained from all states up to the energy ε.

Three further useful implications.

(i) The spin splitting of band states of the magentically active shell, e.g., transition-metal $3d$ states, is proportional to the spin moment M of this shell:

$$\varepsilon^{\downarrow} - \varepsilon^{\uparrow} \approx \frac{1}{\mu_{\mathrm{B}}} I^{\mathrm{LSDA}} M \;, \quad \boldsymbol{M} = -\mu_{\mathrm{B}} \int_{\mathrm{ec}} d^3r \; \mathbf{\Sigma}(\mathbf{r}) \; .$$

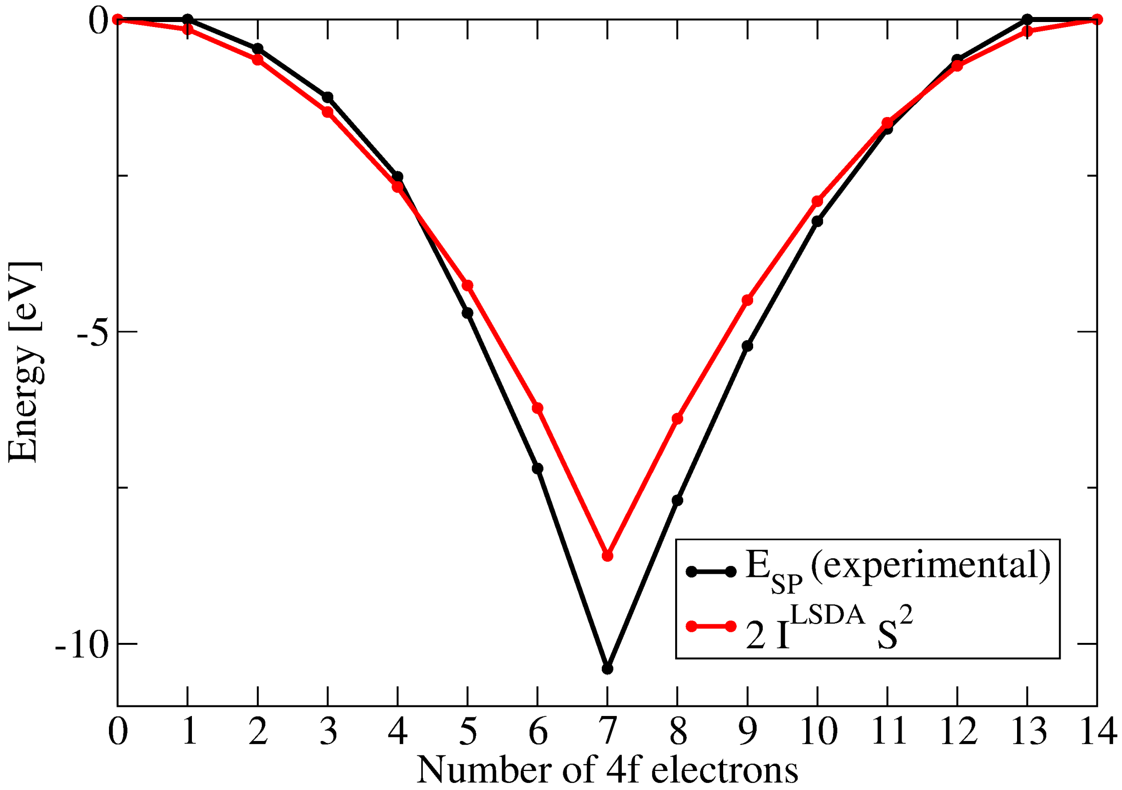
(ii) Exchange-enhanced Pauli susceptibility χ_s:

$$\chi_s = \chi_{\mathrm{P}} / (1 - D(E_{\mathrm{F}}) I^{\mathrm{LSDA}}) \; ,$$

with χ_{P} denoting the Pauli susceptibility $\chi_{\mathrm{P}} = \mu_{\mathrm{B}}^2 \, D(E_{\mathrm{F}})$.

Examples: $\chi_s / \chi_{\mathrm{P}} =$ 1.1 (Cu); 1.9 (Y); $5 \ldots 10$ (Pd).

(iii) The LSDA spin polarization energy is well approximated by $2I^{\mathrm{LSDA}}S^2$. This is approximately I^{LSDA} times half of the number of electron pairs with the same spin.



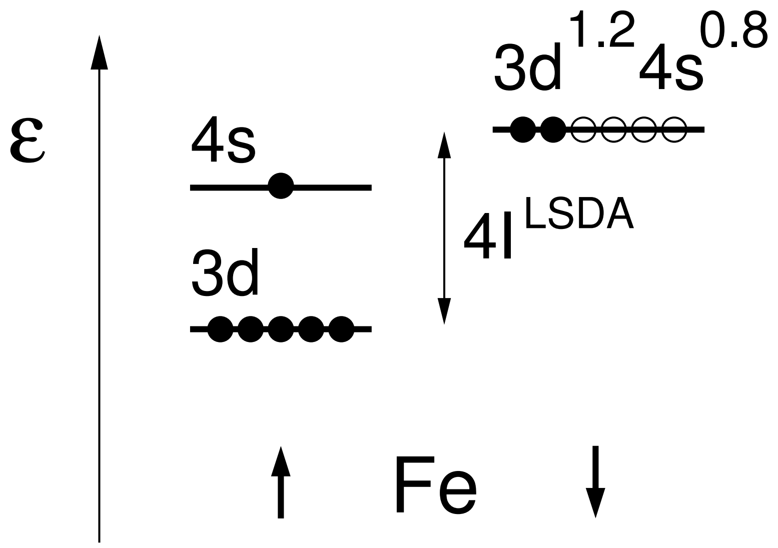
Note the self-interaction error of LSDA for small spin moments.

4. Binding meets exchange: applications

The following calculations were done with the full-potential local orbital code (FPLO). This code uses an optimized set of atom-centered numerical basis functions.

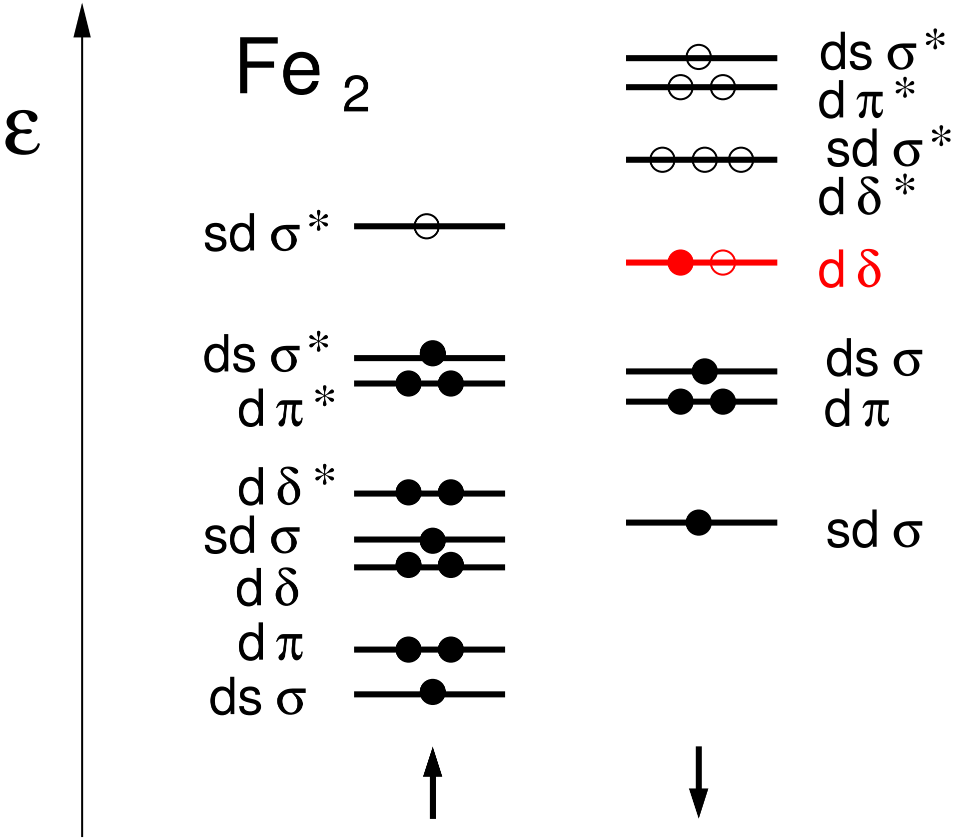
Free iron atom: $S = 2$

The level scheme of a free iron atom is simple, but not trivial. Note the degeneracy of 3d and 4s states in the minority spin channel, which leads to a fractional occupation.

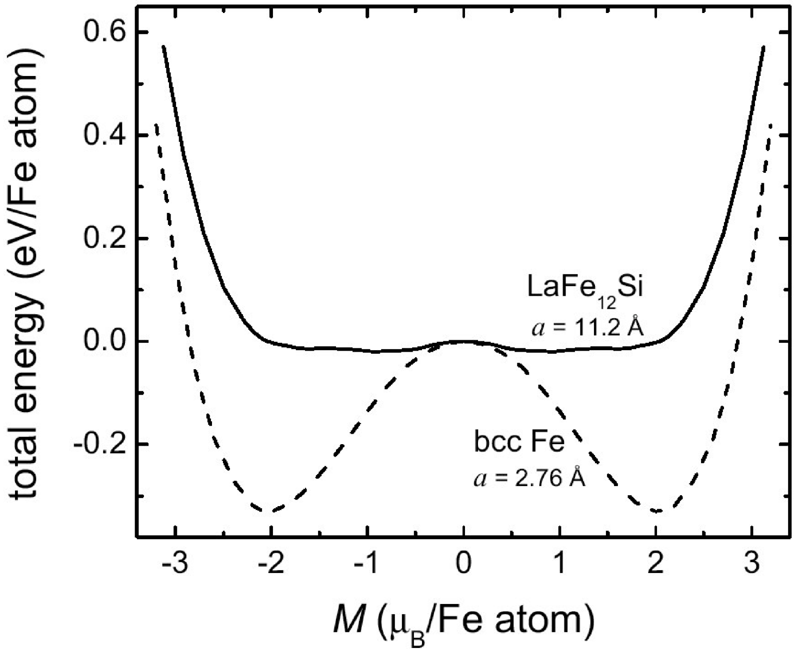


Iron dimer: $S = 3$.

The level scheme of an iron dimer is already much more complicated than that of the atom. The minority-spin $d\delta$ level is only half occupied. If spin-orbit coupling is considered, this level is split and gives rise to a very large magnetic anisotropy. [D. Fritsch *et al.*, J. Comp. Chem. **29** (2008) 2210]

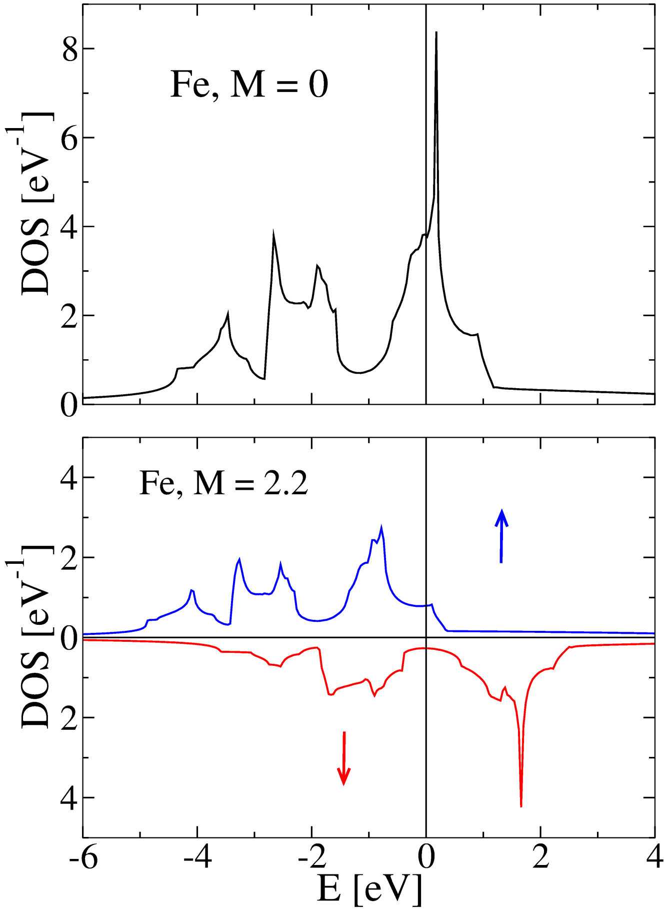


Total energy of LaFe$_{13-x}$Si$_x$ vs. spin moment: Comparison with bcc iron



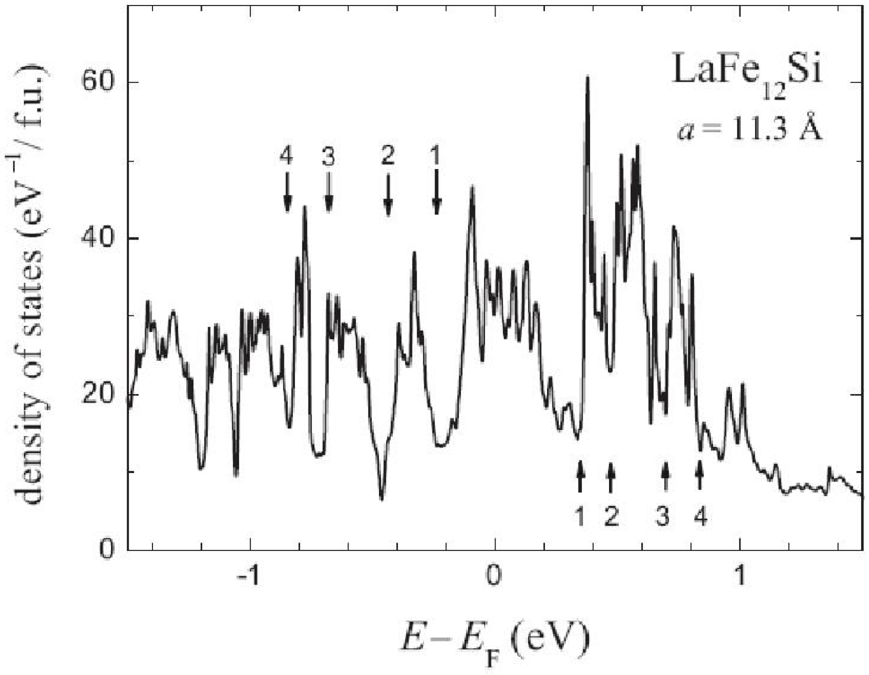
very flat $E(M)$:

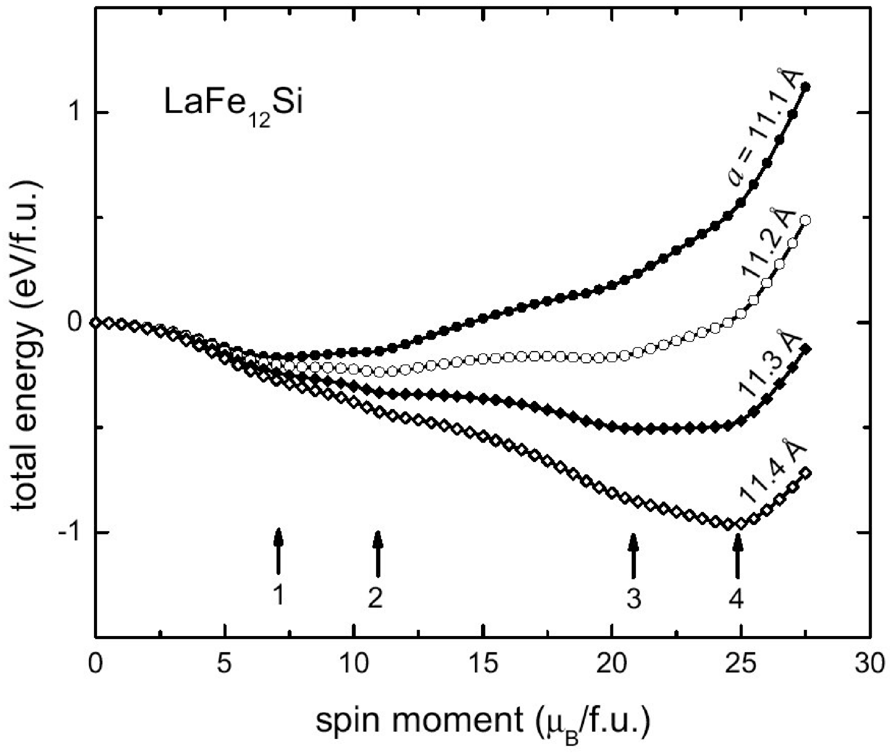
small external fields produce large ΔM and yield a strong magneto-caloric effect.



The ground-state Fermi levels lie in the first DOS-valley below (above) the position in the non-magnetic state.

LaFe$_{12}$Si: Why is $E(M)$ so flat?

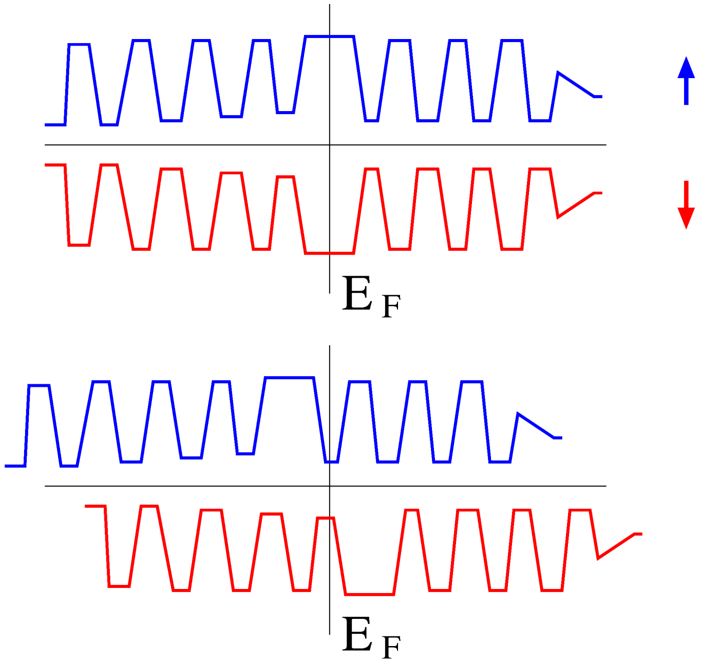




Different from the DOS of bcc Fe, the DOS of LaFe$_{12}$Si has four pairs of minima close to the Fermi level. The Fermi level is approximately in the middle of each pair.

$LaFe_{12}Si$: Why is $E(M)$ so flat?

Model of the DOS:



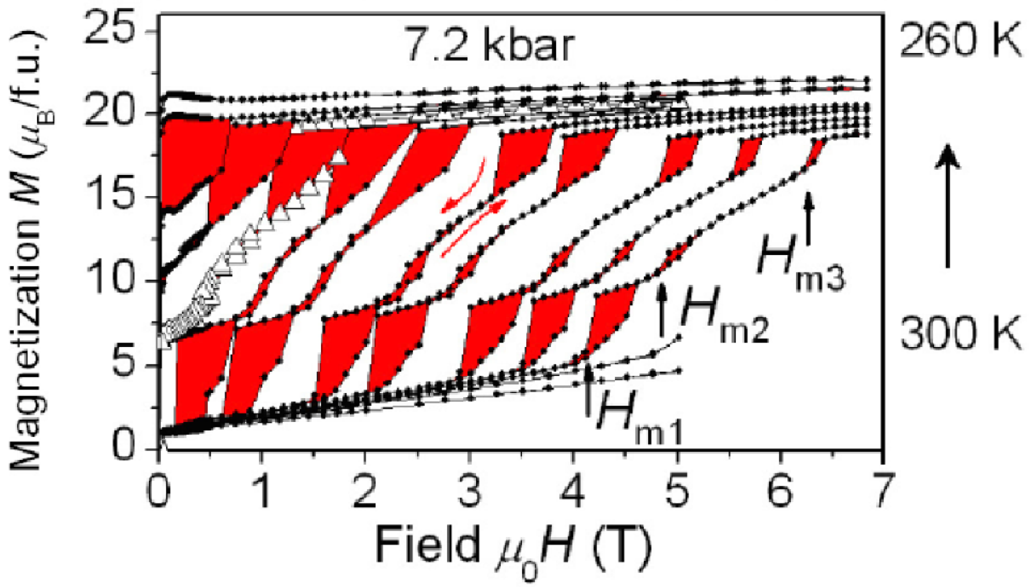
Generalized Stoner criterion:

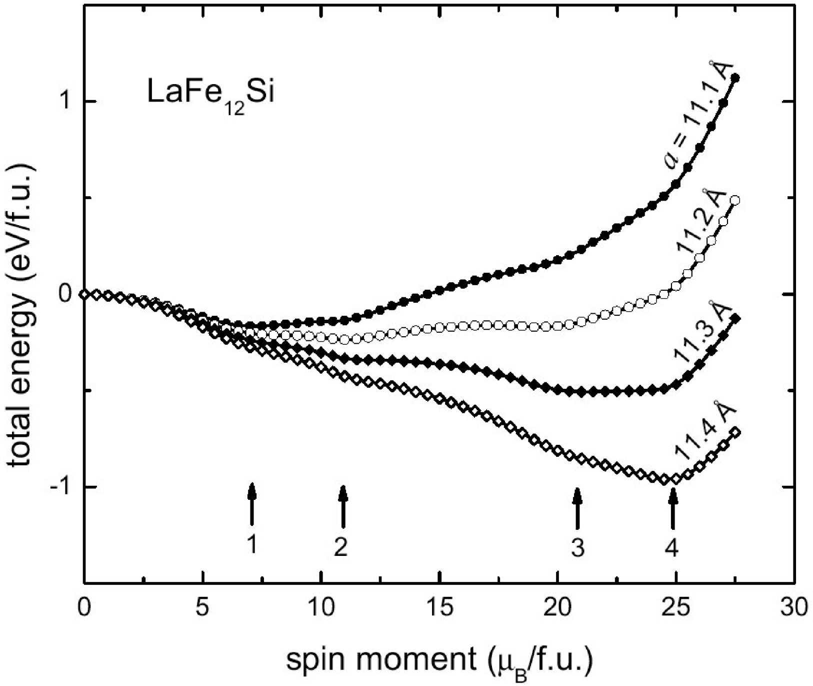
$$4\,I\,(1/D(E_{\mathrm{F}})^{\uparrow} + 1/D(E_{\mathrm{F}})^{\downarrow})^{-1} \;>\; 1$$

If the spin splitting is enhanced, the Fermi level crosses several sequences of minima and maxima. Accordingly, the total energy has wiggles with maxima at those places, where the generalized Stoner criterion is fulfilled.

Kuzmin and Richter, PRB **76** (2007) 092401.

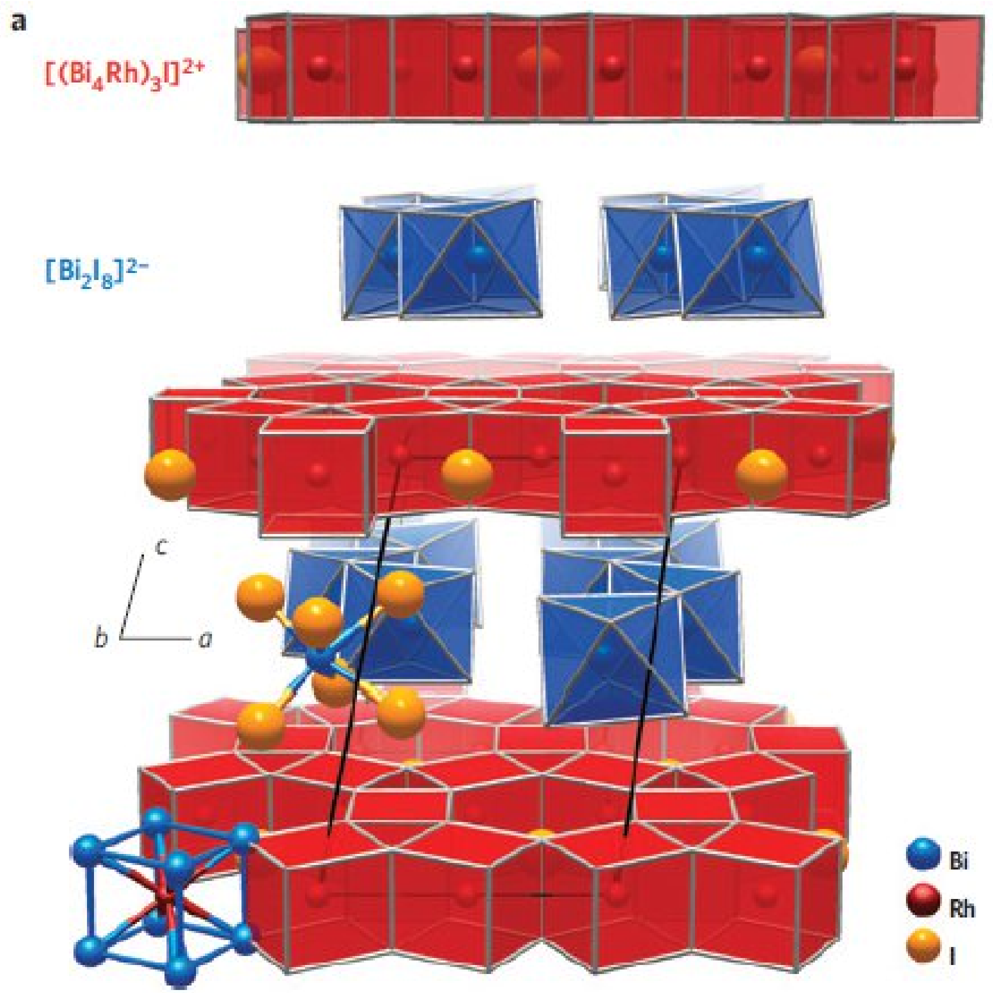
LaFe$_{12}$Si: Experimental confirmation.





A series of up to three metamagnetic transtions observed in La(Fe;Si)$_{13}$H$_x$.
Lyubina *et al.*, PRL **101**, 177203 (2008).

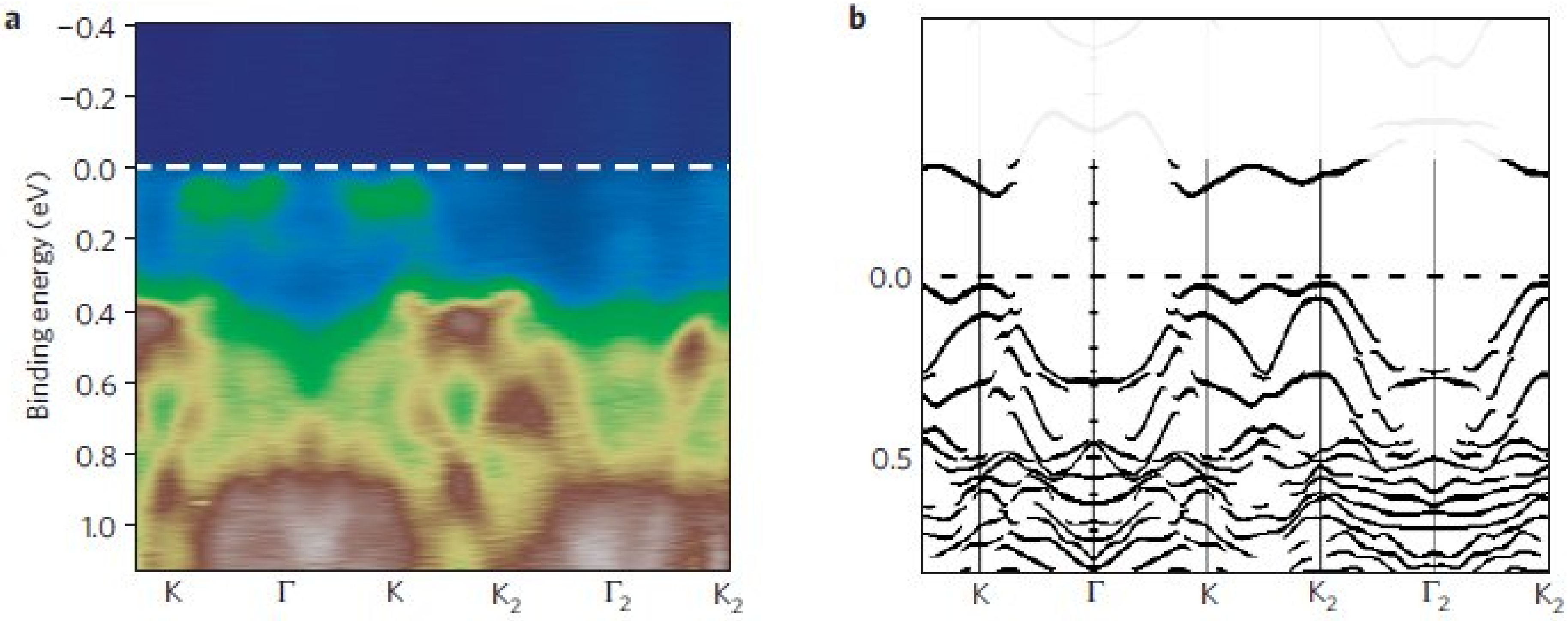
Spin-locked edge currents: a weak 3D topological insulator.



Structure of $Bi_{14}Rh_3I_9$, a layered insulator with a stack of ionic layers, $[(Bi_4Rh)_3I]^{2+}$ and $[Bi_2I_8]^{2-}$.

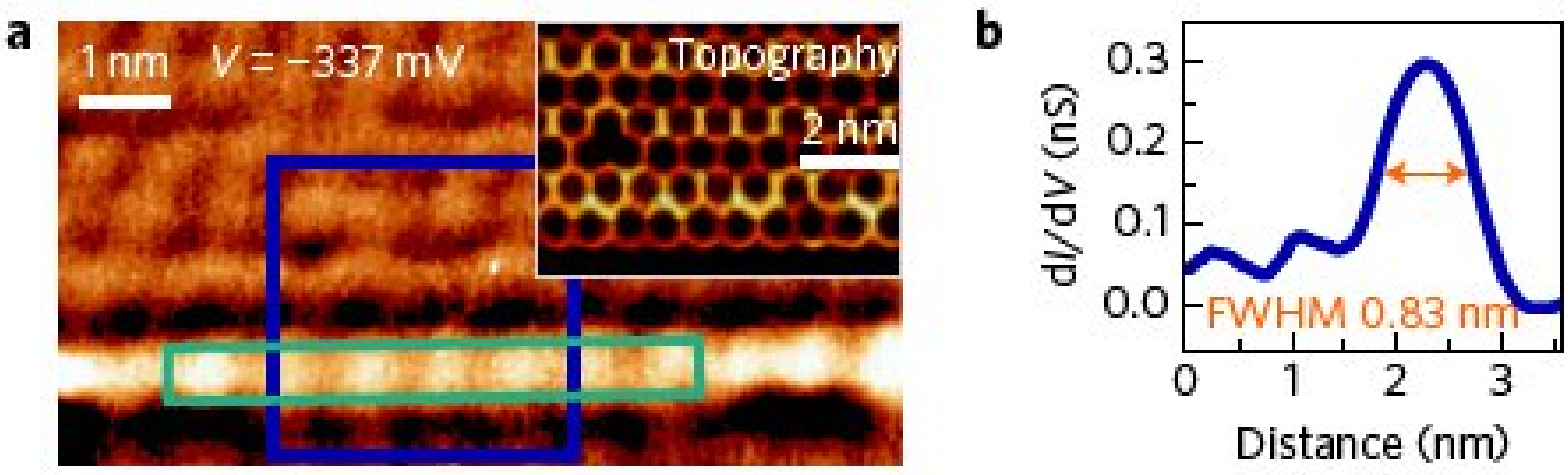
B. Rasche *et al.*, Nature Materials **12** (2013) 422.

Parity analysis of the LDA Bloch states with spin-orbit coupling shows that this material is the first (and, up to now, the only) realization of a weak 3D topological insulator. Comparison between angle-resolved photoemission and LDA band structures to confirm that the Kohn-Sham states make sense.



B. Rasche *et al.*, Nature Materials **12** (2013) 422.

STM observation of the in-gap states at an edge on the cleaved surface of $Bi_{14}Rh_3I_9$. These are the states which are supposed to be spin-locked.



C. Pauly *et al.*, Nature Physics 2015.

Summary

- DFT and SDFT are independent **exact** theories to obtain the ground state energy and related density or spin density of the quantum chemical Hamiltonian.

- LDA and LSDA (or similar) are **model** theories useful for realistic calculations.

- Exchange fields are stronger than the fields produced by electromagnets, as they originate from the Coulomb interaction.

- Quantities accessible to L(S)DA or similar calculations:

densities; band structures; Fermi surfaces; semiclassical transport properties; elastic properties; (magneto)optical properties; chemical binding energies; magnetic anisotropy; model parameters for Heisenberg, Rashba, crystal field models; topological invariants; etc.

- If you aim at evaluating these quantities, be aware of the limitations of the Kohn-Sham states.

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Thank you for your attention!